HIGH pH AND SALT AFFECTED SOILS

Assigned Reading: Sparks, Chapter 10.
Additional Reading McBride Chapter 8 (except 8.4c and 8.4d) Lindsay Chapter 6 and Agricultural Salinity Assessment and Management. ASCE. 1990. Chap. 3.

Carbonate Chemistry

Carbonates are Important in the Chemistry of Most High pH Soils
Equilibrium Solubility for the Carbonates of 2+ Metals

• This involves solid--solution--gas phase equilibria.
  —Equilibrium is generally considered to be quite rapid relative to the alumino-silicates and hydrous oxides but slower than for gypsum and other evaporite minerals.

Crystalline forms

— Calcite CaCO₃
— Aragonite CaCO₃
  • A biogenic form slightly more soluble than calcite
— Dolomite CaMg(CO₃)₂
  • Forms very slowly in geological sediments
— Magnesite MgCO₃
  • More soluble than calcite
— Siderite FeCO₃
  • flooded soils
— Rhodochrosite MnCO₃
  • flooded soils - solid solution with siderite
Carbonate species in water

- **CO₂ in water:** \( CO_2 + H_2O = H_2CO_3^* \) (aq)

- **H₂CO₃⁺**
  - Includes both hydrated carbon dioxide molecules and carbonic acid.
  - Hydrated CO₂ is about 400x H₂CO₃⁻.

- Is a function of the partial pressure of CO₂ (Pco₂) only. It is independent of pH.

Carbonate species in water (cont.)

- In ambient air, CO₂ is 0.00035 atm or 0.035%.
- Soil Pco₂ is elevated due to respiration by roots and microbes.
  - 0.003 to 0.2 atm
    - Highest in flooded soils.
      - The rate of movement of CO₂ (or any gas) through water is about 0.00001x that in the air.

- When soils very wet gas exchange with the ambient air is slow
Calculation of $[\text{H}_2\text{CO}_3^*]$ 

\[ \text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^* \quad \log K = -1.46 \]

\[ \log (\text{H}_2\text{CO}_3^*) = -1.46 + \log (\text{P}_{\text{CO}_2}) \]

If $\text{P}_{\text{CO}_2} = .0003 \ \text{atm}$ then

\[ \log (\text{H}_2\text{CO}_3^*) = -5.0 \]

(increases linearly with $\text{P}_{\text{CO}_2}$)

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Basic Equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>log $K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O} + \text{CO}_2 = \text{H}_2\text{CO}_3^*$</td>
<td>-1.46</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$</td>
<td>-6.35</td>
</tr>
<tr>
<td>$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$</td>
<td>-10.33</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^-$ (equation 1 and 2)</td>
<td>-7.81</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{CO}_2 = 2\text{H}^+ + \text{CO}_3^{2-}$ (equations 1,2, and 3)</td>
<td>-18.14</td>
</tr>
<tr>
<td>$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$</td>
<td>-14.00 ($K_w$)</td>
</tr>
<tr>
<td>$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$</td>
<td>-8.48 to -8.35</td>
</tr>
</tbody>
</table>
Equilibrium Equations (cont.)

- For some calculations we need the electroneutrality equation for the CO$_2$/H$_2$O system

\[ [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \quad (8) \]

- For some calculations we need the mass balance equation for carbon:
- \( C_T = [H_2CO_3^+] + [CO_3^{2-}] + [HCO_3^-] \quad (9) \)
  - \( C_T = \) Dissolved Inorganic Carbon (DIC)

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Equilibrium Equations (cont.)

- These equations can be used to express species in terms of other species e.g. H$_2$CO$_3^+$ and CO$_3^{2-}$ can be expressed in terms of HCO$_3^-$ and H$^+$.
- In soils and natural waters with pH 5.5 - 9.5, HCO$_3^-$ is a very important anion.
- In low pH soils, organic anions and SO$_4^{2-}$ become relatively more important.
- CO$_3^{2-}$ is important only in very alkaline soils.
Activity of dissolved inorganic C species at \( \log P_{\text{CO}_2} = -3.5 \) and \(-2.0\) (Fig 8.2)

\[
\text{CO}_2 \text{ in water with no Carbonate Solids}
\]

- **Alkalinity**

\[
\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] + \text{titratable organic anions}
\]

- Alkalinity is normally determined by titration with acid to pH 4.8 (pH at which all DIC is in the form of \(\text{H}_2\text{CO}_3^-\)).
- In MINTEQ, Alk is given in cmol L\(^{-1}\)
  
  \[
  \text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]
  \]
- In the range of 5.6-9.5 alkalinity is primarily due to \(\text{HCO}_3^-\).
Effect of pH and $P_{CO_2}$ on $[HCO_3^-]$ and $[CO_3^{2-}]$

- From equations 1 & 2 we get equation

\[ \text{H}_2\text{O} + \text{CO}_2 = \text{H}^+ + \text{HCO}_3^- \quad \log K = -7.81 \]

\[ \log (\text{HCO}_3^-) = \text{pH} + \log P_{CO_2} - 7.81 \quad (10) \]

\[ K = \frac{(\text{H}^+)(\text{HCO}_3^-)}{P_{CO_2}} \]

Effect of pH and $P_{CO_2}$ on $[HCO_3^-]$ and $[CO_3^{2-}]$ (cont.)

- On a log $(\text{HCO}_3^-)$ vs. pH plot the slope = +1
- From equations 1, 2, and 3 we get equation 5 (see McBride Fig. 8.2)

\[ \text{H}_2\text{O} + \text{CO}_2 = 2\text{H}^+ + \text{CO}_3^{2-} \quad \log K = -18.14 \]

- From the equilibrium constant expressions
  - $\log (\text{CO}_3^{2-}) = 2\text{pH} + \log P_{CO_2} - 18.14$
  - On a log $(\text{CO}_3^{2-})$ vs. pH plot the slope = +2
**Effect of pH and $P_{CO_2}$ on [HCO$_3^-$] and [CO$_3^{2-}$](cont.)**

Example: pH = 7.0, $P_{CO_2} = 0.0050$ atm

* $\log (HCO_3^-) = 7.0 - 2.3 - 7.81$

$\log (HCO_3^-) = -3.1$

* $\log (CO_3^{2-}) = 2(7.0) - 2.3 - 18.14$

$\log (CO_3^{2-}) = -6.44$

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**Review of Basic Equations**

<table>
<thead>
<tr>
<th>Equation</th>
<th>$\log K$</th>
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<tbody>
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<td>(K$_w$)</td>
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<td>7. $CaCO_3 = Ca^{2+} + CO_3^{2-}$</td>
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Dissolution of Calcite

• Combining eqn. 7 with eqn. 5.
  \[ \text{CaCO}_3 + 2\text{H}^+ = \text{H}_2\text{O} + \text{CO}_2 + \text{Ca}^{2+} \quad \log K = 9.66 \] (11)

• Write the equilibrium constant then take the log of both sides.
  \[
  9.79 = \log \text{Pco}_2 + \log \text{Ca}^{2+} + 2 \text{pH} \quad (12)
  \]
  \[
  \log [\text{Ca}^{2+}] = 9.79 - \log \text{Pco}_2 \cdot 2\text{pH}
  \]

• Fixed [Ca$^{2+}$]
  - e.g. \text{Fix(Ca}^{2+}) at 0.010 M, \text{Pco}_2 = 10^{-3.5}
    * pH = 7.6

pH in Equilibrium with Calcite and No other Acidity or Alkalinity

• Species Ca$^{2+}$, H$_2$CO$_3^*$, HCO$_3^-$, H$^+$, CO$_3^{2-}$, OH$^-$
• Use eqns. 1, 2, 3, 6, 7 plus the charge balance.
• Charge balance

\[
2[\text{Ca}^{2+}] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (13)
\]
ph in Equilibrium with Calcite (cont)

• At the pH of the equilibrium system
  – $[H^+], [CO_3^{2-}]$, and $[OH^-] = 0$
  – Thus the charge balance is $2[Ca^{2+}] = [HCO_3^-]$
  – Use eqn. 10 to calculate $[HCO_3^-]$ assuming $a_{HCO_3} = 1$,
    and substitute for $[HCO_3^-]$ using equation 13.
  – Then (14)

\[ 2[Ca^{2+}] = \frac{(10^{-7.81})(P_{CO_2})}{[H^+]} \]

ph in Equilibrium with Calcite (cont)

• Taking the log of both sides
  $\log [Ca^{2+}] = -8.11 + \log P_{co_2} + pH$

• equate to eqn. 12
  $-8.11 + \log P_{co_2} + pH = 9.79 - \log P_{co_2} - 2pH$

  $3 \ pH = 17.90 - 2 \ log P_{co_2}$

• pH is a function of $P_{co_2}$, only.
  – If $P_{co_2} = 10^{-3.5}$, $pH = 8.3$
    • This is often the reference pH for potential CEC.
  – If $P_{co_2} = 10^{-2.5}$, $pH = 7.6$
Equilibrium with Calcite (cont.)

• Calculate the Ca\(^{2+}\) concentration using equation 12 and the HCO\(_3\)^- concentration using equation 10 or the charge balance

  –for Pco\(_2\) = 10\(^{-3.5}\) , [Ca\(^{2+}\)] = 5.0 \times 10^{-4}M
  –for Pco\(_2\) = 10\(^{-2.5}\) , [Ca\(^{2+}\)] = 1.2 \times 10^{-3}M

pH in Equilibrium with Calcite (cont.)

• In most soils 2[Ca\(^{2+}\)] does not equal [HCO\(_3\)^-]
  • If [Ca\(^{2+}\)] = 0.010 M and Pco\(_2\) = 0.005, then 2[Ca\(^{2+}\)] > [HCO\(_3\)^-]
  • From eq. 12, pH = 7.05.
  • From equation 10. [HCO\(_3\)^-] = 1.0 \times 10^{-3} M and anions other than bicarbonate make up most of the anionic charge.
  • In soils with Ca controlled by gypsum [Ca\(^{2+}\)] > 0.01 M.
pH with calcite and added alkalinity

- Soils containing bicarbonate of Na\(^+\) and Mg\(^{2+}\) and 2[Ca\(^{2+}\)] is <[HCO\(_3\)]

- If [HCO\(_3\)] = 0.010 M and P\(_{\text{CO}_2}\) = 0.005
  - From equation 10  pH = 8.05
  - From eqn. 12, and [Ca\(^{2+}\)] = 1.0 \times 10^{-4} M

SWELLING AND DISPERSION OF CHARGED PARTICLES IN SOILS
Charged surfaces

- Charged Surfaces
  - pH dependent
    - hydrous oxides
    - silicate clay edges
    - organic matter

Example: Permanent Charge Clays

- Monovalent cations near charged surfaces

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Wet | Dry
Diffuse double layer thickness (DDL)

• DDL is a function of $C_o$ and $z$ of cation.
  —Example: $10^{-3}$ mol L$^{-1}$ NaCl
    • DDL for smectite $\approx$ 20 nm
  —Increasing salt concentration reduces DDL and hence reduces swelling pressure
    • In Ca$^{2+}$, less than 10 Å
    • Tactoid formation

Diffuse double layer thickness (cont.)

• Swelling of Clays
  —Monovalent cations
    • At low ionic strength platelets are at the maximum distance apart.
    • Divalent and trivalent
      – Tactoid formation
Free swelling of a clay paste

- Soil moisture tension = 0

Free swelling of a clay paste (cont)

<table>
<thead>
<tr>
<th></th>
<th>H⁺</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.20)⁺</td>
<td>10.8</td>
<td>11.1</td>
<td>8.6</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

*Clay has probably decomposed to the Al³⁺-saturated form*
Potential (volts) that causes swelling

Concentration of NaCl between clay platelets with a positive swelling pressure
• Increasing salt concentration reduces DDL thickness and hence reduces swelling pressure

Aggregation of smectites with increasing salt concentration (McBride Fig 8.6)
Effect of NaCl concentration on interlayer swelling (Fig. 8-7)

Flocculation

- High salt concentration
- High charge cations
- With monovalent ions the critical concentration for coagulation (CCC) of smectite clay is high. (0.025-0.150 M)
- With multicharge ions the CCC is low. (0.0005-0.002 M for $M^{2+}$; $1 \times 10^{-5}$ - $1 \times 10^{-4}$ M for $M^{3+}$)
Flocculation (cont.)

- For pH dependent charge minerals
  - Flocculation at high CCC values or at pHnc
- Divalent and higher charge ions that form surface complexes which neutralize charge and can produce cation bridges with organic matter.
  - This causes flocculation even at low concentrations (low CCC)

Effect of pH on dispersion of iron oxide

![Graph showing the effect of pH on the degree of dispersion of iron oxide and layer silicates]
SODICITY AND SALINITY IN ARID REGION SOILS

Definitions

• Saline soil = high salts

• Sodic soil = high Na
Extent of Agricultural Salt Problems

• United States
  — About 30% of the land has a moderate to severe potential for saline-sodic problems.
  — Western states have a high potential for problems with salinity/sodicity.
  — Example: California:
    • 1,720,000 ha are saline or sodic
    • 1,100,000 ha have a water table at a depth of 1.5 m or less.
    • 1,400,000 ha have problems with water quality.

Measures of salinity and alkalinity (connect to water quality)

• Residual Sodium Carbonate (RSC)
  — Measure excess alkalinity in irrigation water
    \[ \text{RSC} = [\text{HCO}_3^- + \text{CO}_3^{2-}] - [\text{Ca}^{2+} + \text{Mg}^{2+}] \]
    • RSC = the acidity (mmoles, L\(^{-1}\)) that is needed to neutralize the solution alkalinity in excess of the alkalinity associated with Ca and Mg.
    • Titrate to pH = 4.8
  — Any excess of \text{CO}_3^{2-} or \text{HCO}_3^- not precipitated by Mg or Ca during evaporation in soils is alkalinity hazard and can result in high pH values soil
<table>
<thead>
<tr>
<th>RSC &gt; 2.5 (mmole L⁻¹)</th>
<th>Hazardous</th>
</tr>
</thead>
<tbody>
<tr>
<td>RSC = 1.25 - 2.5</td>
<td>Potentially</td>
</tr>
<tr>
<td>hazardous</td>
<td></td>
</tr>
<tr>
<td>RSC &lt; 1.25</td>
<td>Generally safe</td>
</tr>
</tbody>
</table>

**Salinity Hazard**

- **Electrical Conductivity (EC)**
  - **Principles**
    - Conductivity is the ease with which an electric current is carried through a solution
    - Conductivity is proportional to the quantity of ions (quantity of ionic charge) in solution.
  - **Electrical conductance**
    - Reciprocal of electrical resistance
    - ohms (ohms⁻¹), mho
    - Now defined as Siemen (1 Siemen = 1 mho)
**Electrical conductivity (EC)**

- EC = Conductance(Siemens) x distance (cm) ÷ area (cm²)

- Units: S/cm = mho cm⁻¹.
  - mho cm⁻¹ is too large for soil solutions
  - Use mmho cm⁻¹ = mS cm⁻¹ = dS m⁻¹
  - Soil scientist generally use dS m⁻¹
  - McBride uses mS cm⁻¹

**EC of saturated soil paste**

- In the US soil salinity is usually determined by EC of saturated paste extracts.
  - Distilled water is added to dried soil until it is at the saturation limit,
  - Then EC is measured on the extracted solution.
EC of saturated soil paste (cont.)

- Plants vary in response to salt
  - EC values over 2 dS m\(^{-1}\) (m mho cm\(^{-1}\)) suggests potential for problems
  - Value > 4 means that only tolerant plants will survive.
- 1:1 Soil extracts are also used.
  - Different interpretations are needed.

Accumulation of salts in irrigated soils (Fig. 8-22)
**Use of Ion Exchange Theory to predict the long-term effect of irrigation water on soils**

- Vanselow equation
  - Vanselow selectivity coefficient is used in California and by some investigators outside of CA.
  - Most use Gapon
- Gapon equation
  \[ \text{Ca}_{1/2}X + 2\text{Na}^+ = 2\text{NaX} + 1/2\text{Ca} \]

---

**Gapon Equation**

- Mg\(^{2+}\) and Ca\(^{2+}\) are considered as one ion
  \[ K_G = \frac{N_{\text{Na}}[[\text{Ca}^{2+}] + [\text{Mg}^{2+}]]^{1/2}}{N_{\text{Ca+Mg}}[\text{Na}^+]} \]

- \( K = 0.015 \) if solution concentrations are in mmol L\(^{-1}\)
Gapon Equation (cont.)

- With long-term addition of irrigation water the soil will be in equilibrium with the water.
- Can predict the equilibrium $N_{Na\#}$ (charge fraction of Na on the soil particles)
- With high Na on the exchange sites the soil particles can disperse.

\[
\frac{N_{Na}}{N_{Ca+Mg}} = K_G \frac{[Na^+]}{[[Ca^{2+}]+[Mg^{2+}]]^{\frac{1}{2}}}
\]

\[
\frac{N_{Na}}{N_{Ca+Mg}} = \frac{E_{NaX}}{CEC - NaX} = K_G \cdot SAR
\]
**SAR: Sodium Adsorption Ratio**

- An irrigation water term

\[
\text{SAR} = \frac{[\text{Na}^+]}{[[\text{Ca}^{2+}] + [\text{Mg}^{2+}]]^{1/2}}
\]

---

**Exchangeable Sodium Ratio (ESR)**

- ESR: Exchangeable Sodium Ratio (a soil term)

\[
\frac{N_{\text{Na}}}{N_{\text{Ca+Mg}}} = \text{ESR}
\]

\[
\text{ESR} = K_G(\text{SAR})
\]
Exchangeable Sodium Percentage (ESP) (a soil term)

- ESR is the equilibrium fraction of Na on exchange sites expressed as a percentage.

\[
\text{ESP} = \frac{\text{ENaX}}{\text{CEC}} \times 100
\]

\[
\frac{\text{ESP}}{100 - \text{ESP}} = \text{ESR} = K_c \text{SAR}
\]

Soil structure stability

- Role of salinity and sodicity in swelling and dispersion
  - Clay swelling enables individual platelets to separate and form a stable dispersion
- This swelling can be suppressed by high salt concentration
- Multivalent exchange cations, Ca, Mg, Al, counteract swelling by forming electrostatic bridges between adjacent platelets (platelets stack), "quasi-crystals"
Soil structure stability (cont.)

- The Na/(Ca+Mg) ratio controls particle size, arrangement, and dispersibility.

- As ESP increases, soil aggregate structure deteriorates. This causes reduced permeability and drainage, poor aeration, surface crusting and shrink-swell under cycles of wetting and drying.

Traditional Classification of Salinity and Sodicity

<table>
<thead>
<tr>
<th>ESP%</th>
<th>pH &gt; 9</th>
<th>Sodic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Poor</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dispersed</td>
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</table>

15%

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<thead>
<tr>
<th>pH &lt; 8.5</th>
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</tr>
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<tbody>
<tr>
<td>Saline-sodic</td>
<td>Fair-good</td>
</tr>
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NORMAL

4 dSm⁻¹
Brief Summary

- The chemistry of dissolved inorganic carbon (DIC) is important in soils.
- Alkalinity in most soils is mostly bicarbonate.
- High pH soils generally contain calcite
  —Calcite buffers the pH in high pH soils.
- Soil clays and OM can disperse in Na⁺, Li⁺, and K⁺.
  —The dispersion is the result of the surface potential and the double layer effects

Brief Summary (cont.)

- Double layer thickness decreases at high salt concentrations.
- Smectites form tactoids in divalent salts and easily flocculate.
- The effects of long-term of irrigation water application on Na⁺ saturation in soils can be predicted by the Gapon ion exchange equation
- Salinity is measured by EC.
- The EC of soil pastes or 1:1 suspensions is used to predict salinity hazard in soils.