Chapter 9
Soil Acidity, Alkalinity, and Salinity
Main Objectives:
1. Able to explain why soil pH is an important property of a soil.
2. Understand how soil pH is maintained and altered
3. Understand what causes soil alkalinity
5. Able to fully discuss the issue of salt accumulation in soils
Key Terms and Concepts:
1. Active acidity; exchangeable acidity, residual acidity
2. pH buffering capacity
3. Salinity
4. Alkalinity
5. Acid deposition
1. Soil pH

The pH scale: molar $[\text{H}^+] = 10^{-\text{pH}}$

Soil pH is controlled and influenced by (1) the kind of parent material, the amount and the chemical nature of the precipitation (leaching of base cations), land management practices, the kind of organic input, and the activities of organisms (e.g., roots).

Why does soil pH matter?

Some problems with soil pH being too high?

Some problems with soil pH being too low?
Figure 9.1 The relationship between pH, pOH, and the concentrations of hydrogen and hydroxyl ions in water solution.
Figure 9.2

**pH scale**

- Bleach: 12
- Milk of magnesia: 11
- Antacid tablets: 10
- Sea water: 9
- Baking soda: 8
- Pure water: 7
- Milk: 6
- Natural rain: 5
- Beer: 4
- Coffee: 3
- Vinegar: 2
- Lemon juice: 1
- Battery acid: 0

**Ranges found in soils**

- Sodic soils
- Calcareous soils
- Humid region arable soils
- Forest soils
- Acid sulfate soils
Figure 9.16  Ranges of pH in mineral soils optimal for growth of selected plants.
2. Sources of Hydrogen Ions

1. Carbonic acid
2. Organic acid
3. Oxidation of N, S, Fe, etc.
4. Acid deposition from the air
5. Cation uptake by plants

Figure 9.3
Figure 9.12

The diagram illustrates the processes involved in the formation of acid rain. The reactions shown are:

1. $	ext{SO}_2 + 	ext{Sunlight} \rightarrow 	ext{SO}_3$
2. $2	ext{SO}_2 + 	ext{O}_2 \rightarrow 2	ext{SO}_3$
3. $2	ext{SO}_3 + 	ext{H}_2	ext{O} \rightarrow 2	ext{H}^+ + 2	ext{SO}_4^{2-}$
4. $2	ext{N}_2	ext{O} + 	ext{O}_2 \rightarrow 4	ext{NO}$
5. $4	ext{NO} + 2	ext{O}_2 \rightarrow 4	ext{NO}_2$
6. $2	ext{NO}_2 + 	ext{H}_2	ext{O} \rightarrow 2	ext{HNO}_3$
7. $2	ext{H}^+ + 2	ext{NO}_3^-$

These reactions release sulfuric acid and nitric acid into the atmosphere, contributing to acid rain.
3. Sources of Hydroxide (OH\textsuperscript{-})
Mainly from carbonate and bicarbonate reactions. But base cations like Ca\textsuperscript{2+} and Mg\textsuperscript{2+} are often facilitating the formation of carbonate salts under drier climate. (See equations 9.6-9.10)
4. Production and Consumption of H⁺: a balance?

Table 9.1

| The Main Processes That Produce or Consume Hydrogen Ions (H⁺) in Soil Systems |
|---|---|
| Production of H⁺ ions increases soil acidity, while consumption of H⁺ ions delays acidification and leads to alkalinity. The pH level of a soil reflects the long-term balance between these two types of processes. |

<table>
<thead>
<tr>
<th>Acidifying (H⁺ ion–producing) processes</th>
<th>Alkalinizing (H⁺ ion–consuming) processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of carbonic acid from CO₂</td>
<td>Input of bicarbonates or carbonates</td>
</tr>
<tr>
<td>Acid dissociation such as: RCOOH → RCOO⁻ + H⁺</td>
<td>Anion protonation such as: RCOO⁻ + H⁺ → RCOOH</td>
</tr>
<tr>
<td>Oxidation of N, S, and Fe compounds</td>
<td>Reduction of N, S, and Fe compounds</td>
</tr>
<tr>
<td>Atmospheric H₂SO₄ and HNO₃ deposition</td>
<td>Atmospheric Ca, Mg deposition</td>
</tr>
<tr>
<td>Cation uptake by plants</td>
<td>Anion uptake by plants</td>
</tr>
<tr>
<td>Accumulation of acidic organic matter (e.g., fulvic acids)</td>
<td>Specific (inner sphere) adsorption of anions (especially SO₄^{2⁻})</td>
</tr>
<tr>
<td>Cation precipitation such as: Al³⁺ + 3H₂O → 3H⁺ + Al(OH)₃⁺</td>
<td>Cation weathering from minerals such as: 3H⁺ + Al(OH)₃⁺ → Al³⁺ + 3H₂O</td>
</tr>
<tr>
<td>SiO₂ + 2Al(OH)₃ + Ca²⁺ → CaAl₂SiO₆ + 2H₂O + 2H⁺</td>
<td>CaAl₂SiO₆ + 2H₂O + 2H⁺ → SiO₂ + 2Al(OH)₃ + Ca²⁺</td>
</tr>
<tr>
<td>Deprotonation of pH-dependent charges</td>
<td>Protonation of pH-dependent charges</td>
</tr>
</tbody>
</table>
5. Acidity

Total acidity = Active + Exchangeable + Residual

**Active** = H\(^+\) and Al\(^{3+}\) in the soil solution (in water extract)

**Exchangeable** = extracted with un-buffered salt solution (e.g., KCl)

**Residual** = the remaining acidity after water and salt extract, but can be neutralized by limestone (this is the most part of the total acidity (from organic matter and Al\(^{3+}\)).

So, acidity \(\neq\) pH
Figure 9.7  Equilibrium relationship among residual, salt-replaceable (exchangeable), and soil solution (active) acidity in a soil with organic and mineral colloids. Note that the adsorbed (exchangeable) and residual (bound) ions are much more numerous than those in the soil solution, even when only a small portion of the ions associated with the colloids is shown. Most of the bound aluminum is in the form of Al(OH)xy2 ions that are held tightly on the surfaces of the clay or complexed with the humus; relatively few Al(OH)xy2 ions are exchangeable. Remember that the aluminum ions, by hydrolysis, also supply H+ ions in the soil solution. It is obvious that neutralizing only the hydrogen and aluminum ions in the soil solution will be of little consequence. They will be quickly re-placed by ions associated with the colloid. The soil, therefore, demonstrates high buffering capacity.
6. Alkalinity

Mainly caused by the accumulation of CaCO$_3$ and NaCO$_3$ in arid regions or some irrigated land.
7. Buffering of Soil pH
When acidic or basic materials are added, a soil's ability to resist an appreciable change in pH is the buffering capacity of the soil (see the titration curve of Figure 9.6).

The sources of pH buffering:
- Exchangeable cations and anions;
- Organic matter (remember pH dependent charges?)
- Aluminum hydrolysis
- Carbonates dissolution and precipitation

Why is soil pH buffering capacity important?

How to change soil pH purposely?
Add CaCO₃ (Calcium carbonate), organic matter, and/or FeSO₄ (ferrous sulfate).
Figure 9.6 Buffering of soils against changes in pH when acid (H2SO4) or base (CaCO3) is added. A moderately buffered soil (B) and a strongly buffered soil (C) are compared to unbuffered water (A). Most soils are strongly buffered at low pH by the hydrolysis and precipitation of aluminum compounds and at high pH by the precipitation and dissolution of calcium carbonate. Most of the buffering at intermediate pH levels (pH 4.5 to 7.5) is provided by cation exchange and protonation or deprotonation (gain or loss of H+ ions) of pH-dependent exchange sites on clay and humus colloids. The well-buffered soil (C) would have a higher amount of organic matter and/or highly charged clay than the moderately buffered soil (B). [Curves based on data from Magdoff and Bartlett (1985) and Lumbanraja and Evangelou (1991)]
From Miller & Gardiner 2001, page 244
8. Soil pH and Some Environmental Issues

• Acid deposition
• Acidifying chemical fertilizers
• Global change
• Acidic waste or pollutants
• Irrigation
• Draining of wet lands
From: Singer & Munns 1999
Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2000

From: NADP--The National Atmospheric Deposition Program
http://nadp.sws.uiuc.edu/

Sites not pictured:
Alaska 01  5.2
Alaska 03  5.2
Virgin Islands 01  5.0

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2010

Sites not pictured:
Alaska 01  5.2
Alaska 03  5.2
Alaska 06  5.3
Puerto Rico 20  6.0
Virgin Islands 01  5.1
**Table 1.** Topsoil pH changes in major Chinese croplands between the 1980s and 2000s. The soil groups are defined in (13). NS, not significant; pH range is an average (5 to 95 percentile).

<table>
<thead>
<tr>
<th>Soil group</th>
<th>Sample number</th>
<th>pH value</th>
<th>1980s</th>
<th>Cereal crop systems*</th>
<th>2000s</th>
<th>Cash crop systems†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sample number</td>
<td>pH value</td>
<td>pH change</td>
<td>Sample number</td>
</tr>
<tr>
<td>I</td>
<td>301</td>
<td>5.37</td>
<td>(4.40–6.60)</td>
<td>505</td>
<td>5.14</td>
<td>–0.23‡</td>
</tr>
<tr>
<td>II</td>
<td>1157</td>
<td>6.33</td>
<td>(5.00–8.04)</td>
<td>1101</td>
<td>6.20</td>
<td>–0.13‡</td>
</tr>
<tr>
<td>III</td>
<td>297</td>
<td>6.42</td>
<td>(4.50–8.30)</td>
<td>211</td>
<td>5.66</td>
<td>–0.76‡</td>
</tr>
<tr>
<td>IV</td>
<td>562</td>
<td>6.32</td>
<td>(5.10–7.89)</td>
<td>537</td>
<td>6.00</td>
<td>–0.32‡</td>
</tr>
<tr>
<td>V</td>
<td>995</td>
<td>7.96</td>
<td>(6.39–8.80)</td>
<td>850</td>
<td>7.69</td>
<td>–0.27‡</td>
</tr>
<tr>
<td>VI</td>
<td>493</td>
<td>8.16</td>
<td>(7.10–8.80)</td>
<td>250</td>
<td>8.16</td>
<td>–0.00 (ns)</td>
</tr>
</tbody>
</table>

*Cereal/fiber crops (such as rice, wheat, maize, and cotton). †High-input cash crops (such as vegetables, fruit trees, and tea). ‡P < 0.001.
Acidifying from N-fertilization: \( \text{NH}_4^+ + \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}^+ \)

Fig. 3. \( \text{H}^+ \) production budget of main factors in four typical Chinese cropping systems. W-M, wheat-maize; R-W, rice-wheat; R-R, rice-rice; and G-V, greenhouse vegetables. N cycling, S uptake, and P uptake denote the H produced by N cycling and S and P uptake processes. BCs uptake indicates H released by BCs uptake. Net H production is the algebraic sum of H resulting from N cycling and P, S, and BCs uptake. Data are means ± SD. (From: J H Guo et al. 2010, Science 327:1008)
9. Salt Accumulation and Soil Salinity

A significant portion of the world’s land area is affected by high salinity in the topsoil (~320 million hectares, ~2% of land area).

**Where did those salts come from?**
Answer: Parent materials, and secondary deposition/accumulation.

What are the key processes responsible for salt accumulation? (1) evaporation to precipitation ratio; (2) terminal lake effect; (3) saline seepage; (4) change of water table and other hydrological regimes. All are related to water and water movement.

How can irrigation cause salinity problem?
Use irrigation water with high salt content;
Altered hydrology

If you know what causes soil salinity problem, you should know what to do to reduce soil salt content. Right?
Tolerated only by halophytes (but generally unsuitable for crop plants)
Where did those salts come from?
Figure 9.22

Where did those salts come from?
Figure 9.29 Evapotranspiration and salt balance together ensure that the drainage water from irrigated fields is much saltier than the irrigation water applied. In this example, the irrigation water contains 250 mg salts per liter. Some 75% of the applied water is lost to the atmosphere by evapotranspiration. About 25% of the water applied is used for drainage, which is necessary to maintain the salt balance (prevent the buildup of salts) in the field. The added salts are leached away with the drainage water, which then contains the same amount of salt as was added, but in only 25% of the added amount of water. The concentration of salt in the drainage water is thereby four times as great (1000 mg/L) as in the irrigation water. Disposal and/or reuse of the highly saline drainage water present challenges for any irrigation project. (Diagram courtesy of R. Weil)
From: Singer & Munns 1999
Figure 9.25

The diagram illustrates the relationship between electrical conductivity (dS/m) and sodium adsorption ratio (SAR) for different classes of plants showing reduction in growth. The x-axis represents the SAR, while the y-axis shows the electrical conductivity. The diagram categorizes soil types based on pH and sodium percentage:

- **Saline soils** (pH < 8.5)
- **Saline-sodic soils** (soil pH generally < 8.5)
- **Normal soils** (pH < 8.5)
- **Sodic soils** (soil pH > 8.5)

The classes of plants are indicated by vertical lines:

- **Sensitive**
- **Moderately sensitive**
- **Moderately tolerant**
- **Tolerant**
- **Halophytes**

The limit of survival for most plants is indicated by the dashed line connect the different soil and plant classes.
Follow-up Questions:

1. **Does** burning of vegetation affect soil pH temporarily? Explain why?

2. **Why** does the balance between precipitation and evapotranspiration tend to affect soil pH?

3. **Why** does the soil pH under coniferous trees tend to be lower than under broadleaf trees?

4. **What** can you do if you want to increase the pH buffering capacity of a sandy garden soil with a current pH value of 7?

5. **If** the concentration of CO₂ in the atmosphere will increase to 2,000 ppm from the current concentration of 400 ppm because of accelerated fossil fuel combustion, will this change of CO₂ concentration alter soil pH too? Why or why not?

6. **If** a farmer, before irrigating a newly cultivated farmland, want to know whether or not irrigation will increase the salinity of the soil, what would the farmer do to find out?