FIGURE 3–9 The expected range of ion concentrations found in well-aerated soils, waterlogged soils, and the ocean. Note the large range of $H^+$ and $Al^{3+}$ concentrations in well-aerated soils. Also note the large increase in $Fe^{2+}$, $Mn^{2+}$, and $NH_4^+$ concentrations (denoted by the arrows) when a well-aerated soil becomes waterlogged. Some metals ($Al$, $Fe$, $Cu$, $Zn$ . . . ) normally occur in solution, mainly in complexed forms.
Soil pH: Review of Concepts

- **Acid**: substance that can donate a proton
- **Base**: substance that can accept a proton

\[ HA \rightleftharpoons H^+ + A^- \]

- \( HA \) and \( A^- \) are called conjugate acid-base pairs.
- The strength of acid-base pairs is evaluated through dissociation constants.

\[ HA + H_2O \rightleftharpoons H_3O^+ + A^- \]

\[ K_{HA} = \frac{[H_3O^+][A^-]}{HA} \]
### Dissociation Constant for Weak Acids

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula of Acid</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>$\text{H}_2\text{CO}_3$, $\text{HCO}_3^-$</td>
<td>6.3, 10.33</td>
</tr>
<tr>
<td>P</td>
<td>$\text{H}_3\text{PO}_4$, $\text{H}_2\text{PO}_4^-$, $\text{HPO}_4^{2-}$</td>
<td>2.23, 7.2, 12.3</td>
</tr>
<tr>
<td>S</td>
<td>$\text{HSO}_4^-$, $\text{H}_2\text{S}$, $\text{HS}^-$</td>
<td>2.0, 7.0, 12.9</td>
</tr>
<tr>
<td>N</td>
<td>$\text{NH}_4^+$</td>
<td>9.2</td>
</tr>
<tr>
<td>B</td>
<td>$\text{H}_2\text{BO}_3$</td>
<td>9.2</td>
</tr>
<tr>
<td>Si</td>
<td>$\text{H}_4\text{SiO}_4$</td>
<td>9.5</td>
</tr>
<tr>
<td>O</td>
<td>$\text{H}_2\text{O}$</td>
<td>14.0</td>
</tr>
</tbody>
</table>
Definition of pH

• General definition:

\[ H_2O \leftrightarrow H^+ + OH^- \]
\[ 10^{-14} = [H^+][OH^-] \]
\[ -14 = \log[H^+] + \log[OH^-] \]
\[ 14 = pH + pOH \]
\[ pH = -\log[H^+] \]

Where \( p \) refers to the negative logarithm. NOTE that a low pH implies a greater concentration of \( H^+ \) than a high pH.
Figure 9.11 Relationships existing in mineral soils between pH and the availability of plant nutrients. The relationship with activity of certain microorganisms is also indicated. The width of the bands indicates the relative microbial activity or nutrient availability. The jagged lines between the P band and the bands for Ca, Al, and Fe represent the effect of these metals in restraining the availability of P. When the correlations are considered as a whole, a pH range of about 5.5 to perhaps 7.0 seems to be best to promote the availability of plant nutrients. In short, if the soil pH is suitably adjusted for phosphorus, the other plant nutrients, if present in adequate amounts, will be satisfactorily available in most cases.
Conceptual Model of Soil H⁺ Budget

**Atmospheric pool: H⁺ acid substances**

**Output of acid gases: N₂, NH₃, NOₓ, CH₄,…**

**H⁺ Sources**
- Oxidation reactions
- Mineralization of cations
- Cation uptake
- Reverse weathering
- Dissociation of CO₂ and organic acids

**H⁺ Sinks**
- Reduction reactions
- Mineralization of anions
- Anion uptake
- Weathering of oxygen-rich metals
- Association of CO₂ and organic acids

**Living + dead biomass**

- Export of H⁺ in the percolation water

**Wet Deposition:** H⁺, NH₄⁺

**Dry Deposition:** CO₂, NH₃, NOₓ, SO₄²⁻,…

SEE EXAMPLES IN TABLE 9.1
The Role of CO$_2$ in Soils

promoted by heat, water loss, and acidity

promoted by cold, alkalinity and Ca$^{2+}$

CO$_2$ → carbon dioxide

H$_2$O → H$_2$CO$_3$ → carbonic acid

H$^+$ → HCO$_3^-$ → bicarbonate

H$^+$ → CO$_3^{2-}$ → carbonate

Ca$^{2+}$ → CaCO$_3$ → calcite

(B)

air

rain, acid soils, and water

alkaline soils and waters, ocean and sediments
**Respiration** (roots and microorganisms):

- Organic molecule from photosynthesis: $CH_2O + O_2 \leftrightarrow CO_2 + H_2O$
- $CO_2 + H_2O \leftrightarrow H_2CO_3$
- $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

Oxygen is needed to carry out this reaction (**aerobic systems**). In the absence of $O_2$, other reactions take place.
The CO$_2$-H$_2$O System

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \quad \log K_a = -1.46 \]

\[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad \log K_a = -6.35 \]

\[ \text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+ \quad \log K_a = -10.33 \]

\[ \text{CO}_3^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3 \]

\[ \text{CO}_2 + \text{H}_2\text{O} + \text{Ca}^{2+} \rightleftharpoons \text{CaCO}_3 + 2\text{H}^+ \]
The pH of the CO$_2$-H$_2$O System

Fig. 3.4  Distribution of aqueous CO$_2$ species with pH.

Source: Bohn, McNeal, and O'Connor. 1985. Soil Chemistry
Henry’s Law

\[ CO_2(\text{sol.}) = k \ P[CO_2(\text{gas})] \]

A moderate pressure of CO\(_2\)(g) above the beverage in a soft-drink bottle (right) keeps a significant quantity of the gas dissolved in the water. When the bottle is opened (left), this pressure is released and dissolved CO\(_2\)(g) escapes, causing the familiar fizzing.

Source: Hill and Petrucci (1999). General Chemistry
The Soil System

- The soil is a mix of acid-base pairs with different affinity for the H⁺. Consider addition of a strong acid to a calcareous clayey soil:

\[ CaCO_3(s) + H^+ + A^- \rightarrow Ca^{2+} + HCO_3^- + A^- \]

\[ Clay\_Ca^{2+} + 2H^+ \rightleftharpoons Clay\_2H^+ + Ca^{2+} \]

Soil is a buffered system
Figure 9.5 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)]
Aluminum as an Acidic Cation

Source: Bohn, McNeal, and O'Connor. 1985. Soil Chemistry

Fig. 8.2 Relative distribution and average charge of the soluble aluminum species

Source: Bohn, McNeal, and O'Connor. 1985. Soil Chemistry
Figure 9.6 Equilibrium relationship among residual, salt-replaceable (ex-changeable), and soil solution (active) acidity in a soil with organic and mineral colloids. Note that the adsorbed (ex-changeable) 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.
Relative Size of Acidity Pools

- Consider a soil containing 10% of montmorillonite clay
- Assume a formula for montmorillonite clay (1,118 g):

\[ KAl_7Si_{11}O_{30} (OH)_6 \]

- One kilogram of soil contains 100 g of montmorillonite clay, or 0.63 moles of Al and 0.54 moles of H.
- Number of mol\(_c\) contained in 1 kg of soil:

\[(0.63 \times 3) + 0.54 \times 1 = 2.43\ \text{mol}_c/\text{kg} \text{ or } 243\ \text{cmol}_c/\text{kg}\]

- Using information in Table 8.5: soils in a cool, humid region have a C.E.C. of about 20 cmolc/kg, of which ~ 30% are exchangeable H\(^+\) and Al\(^{3+}\). Number of exchangeable cmol\(_c\) contained in 1 kg of soil

\[20\ \text{cmol}_c/\text{kg} \times 0.3 = 6\ \text{cmol}_c/\text{kg}\]
Relative Size of Acidity Pools

• According to Table 8.5 a soil with ~30% exchangeable $H^+$ and $Al^{3+}$ has a pH of about 5. Number of mol$_c$ of $H^+$ in a solution with pH = 5:

$$mol_c \text{ of } H^+ = \text{mol of } H^+ = 10^{-5} \text{ or } 0.00001 \text{ mol}_c/L$$

• Expressing the result in cmol$_c$/L:

$$0.00001 \text{ mol}_c/L = 0.001 \text{ cmol}_c/L$$

<table>
<thead>
<tr>
<th>Acidity Type</th>
<th>cmol$_c$ of $H^+$ and $Al^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual</td>
<td>243</td>
</tr>
<tr>
<td>Exchangeable</td>
<td>6</td>
</tr>
<tr>
<td>Active</td>
<td>$\sim0.001$</td>
</tr>
</tbody>
</table>
Acidifying Processes

- **Leaching** of basic cations ($Ca^{2+}$, $Mg^{2+}$, $K^+$):

\[
Soil\_Ca^{2+} + 2H^+ \Leftrightarrow Soil\_2H^+ + Ca^{2+}
\]

- **M**: $Ca^{2+}$; $Mg^{2+}$; $K^+$; $Na^+$
- **A**: $NO_3^-$; $SO_4^{2-}$; $Cl^-$; $H_2PO_4^-$
- **HA**: Acids produced by microorganisms (carbonic and sulfuric acids and organic acids), human activities (fertilizers, acid rain).
Acidifying Processes

- **Respiration** (roots and microorganisms):

  \[ \text{Organic molecule from photosynthesis} \rightarrow \text{CH}_2\text{O} + \text{O}_2 \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} \]
  \[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \]
  \[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]

  Oxygen is needed to carry out this reaction (aerobic systems). In the absence of O\(_2\), other reactions take place.
pE-pH Diagram for Soils

pE = - log (e^-)
pE = 0.0169 Eh (mvolt)

FIG. 6.1 A pE–pH diagram showing the domain accessible to microorganisms (dashed perimeter) and that observed in soils (shaded area, with experimental data shown as points). [Based on data compiled by L. G. M. Baas Becking, I. R. Kaplan, and D. Moore, Limits of the natural environment in terms of pH and oxidation–reduction potential, J. Geol. 68:243–284 (1960).]

FIG. 8.—Suggested stability fields of various soil types.

## Sequence of Redox Reactions

<table>
<thead>
<tr>
<th>Reduction half-reaction</th>
<th>Range of $pE_{init}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}O_2(g) + H^+(aq) + e^-(aq) = \frac{1}{2}H_2O(l)$</td>
<td>5.0–11.0</td>
</tr>
<tr>
<td>$\frac{1}{2}NO_2^-(aq) + H^+(aq) + e^-(aq) = \frac{1}{2}NO_2^-(aq) + \frac{1}{2}H_2O(l)$</td>
<td>3.4–8.5</td>
</tr>
<tr>
<td>$\frac{1}{2}NO_3^-(aq) + \frac{3}{2}H^+(aq) + e^-(aq) = \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l)$</td>
<td>3.4–6.8</td>
</tr>
<tr>
<td>$\frac{1}{8}NO_3^-(aq) + \frac{1}{2}H^+(aq) + e^-(aq) = \frac{1}{8}NH_4^+(aq) + \frac{3}{8}H_2O(l)$</td>
<td>1.7–5.0</td>
</tr>
<tr>
<td>$\frac{1}{2}MnO_2(s) + 2H^+(aq) + e^-(aq) = \frac{1}{2}Mn^{2+}(aq) + H_2O(l)$</td>
<td>$-2.5–0.0$</td>
</tr>
<tr>
<td>$Fe(OH)_3(s) + 2H^+(aq) + e^-(aq) = Fe^{2+}(aq) + 3H_2O(l)$</td>
<td>$-2.5–0.0$</td>
</tr>
<tr>
<td>$FeOOH(s) + 2H^+(aq) + e^-(aq) = Fe^{2+}(aq) + 2H_2O(l)$</td>
<td>$-2.5–0.0$</td>
</tr>
<tr>
<td>$\frac{1}{2}SO_4^{2-}(aq) + \frac{1}{2}H^+(aq) + e^-(aq) = \frac{1}{2}HS^-(aq) + \frac{1}{2}H_2O(l)$</td>
<td>$-2.5–0.0$</td>
</tr>
<tr>
<td>$\frac{1}{2}SO_4^{2-}(aq) + \frac{3}{2}H^+(aq) + e^-(aq) = \frac{1}{2}S_2O_3^-(aq) + \frac{5}{2}H_2O(l)$</td>
<td>$-2.5–0.0$</td>
</tr>
<tr>
<td>$\frac{1}{2}SO_4^{2-}(aq) + \frac{3}{2}H^+(aq) + e^-(aq) = \frac{1}{2}H_2S(aq) + \frac{1}{2}H_2O(l)$</td>
<td>$-2.5–0.0$</td>
</tr>
</tbody>
</table>

**Source:** Sposito, G. 1989. The Chemistry of Soils.
Flooded Soils

FIG. 6.3 Relative changes in $O_2$, $NO_3^-$, Mn(IV), and Mn(III) solid phases, and Fe(II) content of a soil with time elapsed after flooding. Changes in pE are also shown and labeled on the right side. [Data from F. T. Turner and W. H. Patrick, Chemical changes in waterlogged soils as a result of oxygen depletion, Trans. IX Congress, Int. Soil Sci. Soc. (Adelaide, Australia) 4:53–65 (1968).]

Root Uptake of Cations (M)

• Roots also uptake anions, but in less amounts.

• Uptake of anions result in the release of OH\(^-\) and/or HCO\(_3^-\) (soil pH rises).
The Influence of N Fertilizer


\[ \text{NO}_3^- \quad \text{NH}_4^+ \]
Map of Soil pH Near Roots


Figure 4. pH map showing the changes in rhizosphere pH along the root system of P-starved oilseed rape as obtained by videodensitometry of bromocresol purple (dye indicator) incorporated in an agar gel. The dark areas indicate acidification occurring behind the apices of both primary and secondary roots while light areas indicate alkalization occurring along basal parts of the primary root (adapted from Ruiz (1992) and Jaillard and Hinsinger (1993) with permission from Editions Techniques).
Conceptual Model of Soil H⁺ Budget

Atmospheric pool: H⁺ acid substances

Wet Deposition: H⁺, NH₄⁺

Dry Deposition: CO₂, NH₃, NOₓ, SO₄²⁻, ...

Output of acid gases: N₂, NH₃, NOₓ, CH₄, ...

H⁺ Sources

Oxidation reactions
Mineralization of cations
Cation uptake
Reverse weathering
Dissociation of CO₂ and organic acids

H⁺ Sinks

Reduction reactions
Mineralization of anions
Anion uptake
Weathering of oxygen-rich metals
Association of CO₂ and organic acids

SEE EXAMPLES IN TABLE 9.1

Export of H⁺ in the percolation water

Living + dead biomass
## Chemical Composition of Rainfall

<table>
<thead>
<tr>
<th>Ion</th>
<th>Continental Rain&lt;sup&gt;1&lt;/sup&gt;</th>
<th>New Jersey&lt;sup&gt;2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>kg/ha</td>
</tr>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.1-3</td>
<td>0.10±0.05</td>
</tr>
<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.05-0.5</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.1-0.3</td>
<td>0.02±0.01</td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.2-1</td>
<td>0.19±0.06</td>
</tr>
<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.1-0.5</td>
<td>0.23±0.04</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.4-1.3</td>
<td>1.42±0.21</td>
</tr>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>1-3</td>
<td>2.11±0.42</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.2-2</td>
<td>0.36±0.01</td>
</tr>
<tr>
<td>pH</td>
<td>4-6</td>
<td>4.37±0.09</td>
</tr>
</tbody>
</table>

Global Acid Deposition

Figure 3.18. World areas with present or future acid deposition problems. (a) Areas, circled by solid lines, that presently have a problem with anthropogenic acid (sulfur and nitrogen) emissions due to sensitive soils and (b) potential problem areas (circled by dashed lines)—areas with sensitive soils that have or are expected to have rapidly growing acid emissions. (Source: Adapted from Rodhe 1989.)

Chemical Composition of Precipitation and Soil Water

Table 1: Average chemical composition of precipitation and soil water in weathered sandy dolomite near State College, Pennsylvania. Chemical concentrations are in mg/L (from Sears, 1976)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Precipitation</th>
<th>Soil water at 1m depth</th>
<th>Soil water at 3m depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>1.2</td>
<td>3.3</td>
<td>108</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.4</td>
<td>0.8</td>
<td>7.3</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.5</td>
<td>6.9</td>
<td>21</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.0</td>
<td>1.8</td>
<td>5</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.0</td>
<td>1.9</td>
<td>144</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>3.6</td>
<td>2.9</td>
<td>17</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.4</td>
<td>24</td>
<td>53</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>1.0</td>
<td>4.8</td>
<td>55</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0</td>
<td>45</td>
<td>95</td>
</tr>
<tr>
<td>pH</td>
<td>4.5</td>
<td>5.9</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Chemical Composition: Rain and Rivers

Figure 5.3. Comparison of dissolved composition of North American natural and polluted river water (data from Meybeck 1979) with U.S. rainwater (concentrations in mg/l). Rainwater concentrations are multiplied by 2.6 to correct for evaporation from the continents (see text).

Lowering Soil pH

• Add oxidizable compounds:
  – Sulfur, biologically oxidizes to sulfuric acid
  – Aluminum sulfate, which splits $H_2O$ to produce $H^+$.
  – Organic matter.
Raising Soil pH

- Add Limestone: carbonates of Ca$^{2+}$, Mg$^{2+}$
- Burned/Quick lime (oxides of Ca$^{2+}$, Mg$^{2+}$)
- Hydrated lime (hydroxides of Ca$^{2+}$, Mg$^{2+}$)