Soil Acidity

\[ \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^- \]

This reaction is FAR to the left!
- only 1 in a 10 MILLION water molecules are disassociated

Therefore the ion product of this dissociation is a constant (Kw) and at 25\(^\circ\) C …

\[ [\text{H}^+] \times [\text{OH}^-] = K_w = 10^{-14} \]
Therefore when water is pure this dissociation must be equal, and...

\[ [H^+] \times [OH^-] = [10^{-7}] \times [10^{-7}] = 10^{-14} \]

But if the ion concentration of \( H^+ \) increases or decreases the corresponding \( OH^- \) must decrease or increase, therefore...

An increasing \([H^+]\) will result in \( \downarrow [OH^-] \)

and

An decreasing \([H^+]\) will result in \( \uparrow [OH^-] \)
\[ \text{pH} = - \log [H^+] \]

So if the \([H^+] = [10^{-6}]\), the pH is 6

\[ \text{pOH} = - \log [OH^-] \]

So if the \([OH^-] = [10^{-8}]\), the pOH is 8
Finally as the ion concentration maintains a $10^{-14}$ constant…

**at a pH of 5** → $[H^+] \times [OH^-] = [10^{-5}] \times [10^{-9}] = 10^{-14}$

and the pOH is 9

and

**at a pH of 8** → $[H^+] \times [OH^-] = [10^{-8}] \times [10^{-6}] = 10^{-14}$

and the pOH is 6
### pH Scale

<table>
<thead>
<tr>
<th>pH Value</th>
<th>Description</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 4.5</td>
<td>Extremely acid</td>
<td>lemon=2.5; vinegar=3.0; stomach acid=2.0; soda=2–4</td>
</tr>
<tr>
<td>4.5–5.0</td>
<td>Very strongly acid</td>
<td>beer=4.5–5.0; tomatoes=4.5</td>
</tr>
<tr>
<td>5.1–5.5</td>
<td>Strongly acid</td>
<td>carrots=5.0; asparagus=5.5; boric acid=5.2; cabbage=5.3</td>
</tr>
<tr>
<td>5.6–6.0</td>
<td>Moderately acid</td>
<td>potatoes=5.6</td>
</tr>
<tr>
<td>6.1–6.5</td>
<td>Slightly acid</td>
<td>salmon=6.2; cow's milk=6.5</td>
</tr>
<tr>
<td>6.6–7.3</td>
<td>Neutral</td>
<td>saliva=6.6–7.3; blood=7.3; shrimp=7.0</td>
</tr>
<tr>
<td>7.4–7.8</td>
<td>Slightly alkaline</td>
<td>eggs=7.6–7.8</td>
</tr>
<tr>
<td>7.9–8.4</td>
<td>Moderately alkaline</td>
<td>sea water=8.2; sodium bicarbonate=8.4</td>
</tr>
<tr>
<td>8.5–9.0</td>
<td>Strongly alkaline</td>
<td>borax=9.0</td>
</tr>
<tr>
<td>&gt; 9.1</td>
<td>Very strongly alkaline</td>
<td>milk of magnesia=10.5, ammonia=11.1; lime=12</td>
</tr>
</tbody>
</table>
Soil pH Sample Distribution

Illini FS, Inc.

Mean: 6.1
Median: 6.1

% of Samples

Soil pH Range

Illini FS, Inc.
Mechanism of Acidification:

CATION EXCHANGE

acid $H^+$ is not readily leached out

$H^+ + Ca^{2+}$-colloid $\rightleftharpoons H^+$-colloid + $Ca^{2+}$

displaced "bases" (Ca, Mg, Na, K) are leached out.

Over centuries, "exchange complex" becomes dominated by acid cations
(1) Addition of $\text{H}^+$ ions from acid-forming processes

(2) Exchange of 2 $\text{H}^+$ ions for a $\text{Ca}^{2+}$ ion

(3) Leaching loss of $\text{Ca}$, $\text{Mg}$, $\text{K}$, and $\text{Na}$ along with anions

Anions of acids ($\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{HCO}_3^-$, etc.)
Natural Conditions Favorable to Acidification

- vigorous leaching (high rainfall, good drainage)
- high biological activity
- non-basic parent material (low Ca, Mg, K, Na)  
  e.g. granite, quartz sandstone
So where does the pH (and pOH) come from?

1. Carbonic Acid (CO$_2$ reaction with H$_2$O)
2. Biological Metabolism
3. Accumulation of OM
4. Oxidation Reactions (S and N)
5. Acid Rain
6. Plant Uptake of Cations
7. Aluminum
8. Parent Material dissolution
1. Carbonic Acid (CO$_2$ rxn with H$_2$O)

pH’s ranging @ 6.5

\[
\text{CH}_2\text{O (s)} + \text{O}_2 (\text{g}) \leftrightarrow \text{CO}_2 (\text{g}) + \text{H}_2\text{O (g)}
\]

With the CO$_2$ reaction with H$_2$O carbonic acid is produced

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+
\]
2. Biological Metabolism

pH’s ranging from ~ 3-5

\[ R-\text{CH}_2\text{OH} + \text{O}_2 + \text{H}_2\text{O} \leftrightarrow R-\text{COOH} \]

(strong organic acid)

\[ R-\text{COOH} \leftrightarrow R-\text{COO}^- + \text{H}^+ \]
3. Accumulation of OM

2 Processes

1. Complexation with Base Cations (Ca, Na, Mg, etc.), thus removing them from the solution via leaching and therefore increasing \([H^+]\)

2. Organic matter has LOTS of hydroxyl groups from which protons can dissociate (acts to buffer high pH’s) and further remove base cations from solution.
4. Oxidation Reactions (S and N)

Sulfuricization

\[
\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} \leftrightarrow \text{FeSO}_4 + 2\text{H}^+ + \text{SO}_4^{2-}
\]

This reaction is associated with soils which have high sulfur contents – eg estuarine dredge materials

and

Nitrification

\[
\text{NH}_4^+ + 2\text{O}_2 \leftrightarrow \text{H}_2\text{O} + 2\text{H}^+ + \text{NO}_3^-
\]

This reaction is associated with soils which have fertilization additions – eg agriculture
ACIDIFICATION AND AGRICULTURE

Agricultural practices accelerate acidification.

1. Intentional

Adding acidifying materials to neutral, alkaline soils (localized).

2. Side-Effects

(a) use of ammonium/ammonium-generating fertilizers (includes organic fertilizers)

$$\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$$

nitrification

(b) removal of cations from soil by harvesting-

\[\text{NH}_4^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+} \rightarrow \text{H}^+\]

(c) $\text{N}_2$ fixation
5. Acid Rain

- solution reaction of nitrogen and sulfur gases, from a variety of natural sources **AND** the combustion of fossil fuels, with atmospheric water.
Unlike carbonic acid (pH @ 6.5) these are strong acids which completely dissociate putting large amounts of protons in the environment.
6. Plant Uptake

1. Maintenance of charge balance
2. Proton pumps
7. Aluminum - paired reaction (1) solubilization and (2) hydrolyzation

(1) H⁺ chemically weather phylosilicate structure releasing Al into soil solution

(2) Al reacts in solution with H₂O to form Al(OH)₃
ACIDITY AND ALUMINUM

As soil becomes acid, Al becomes more soluble:

\[
\text{H}^+ \rightarrow \text{Al}^{3+} \text{ (soluble)}
\]

\[
\text{Al}^{3+} + \text{Ca}^{2+} \rightarrow \text{Al}^{3+} - \text{colloids} + \text{Ca}^{2+} > 20\% \text{ Al on "exchange complex" = TROUBLE!}
\]

Exchangeable H\(^+\) is minor, even in acid soils.
ACIDITY AND OTHER METALS

In strongly acid soils, Mn and Fe reduce to soluble forms:

$\text{Mn}^{(+4)} \text{ oxides} \rightarrow \text{Mn}^{2+} \text{ (soluble)}$
$\text{Fe} \text{ (+3) oxides} \rightarrow \text{Fe}^{2+} \text{ (soluble)}$

These can be toxic to crops
8. Parent Material dissolution

![Bed Rocks of New York](image)
### 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>Alkalining (H(^+) ion-consuming) processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation of carbonic acid from CO(_2)</td>
<td>Input of bicarbonates or carbonates</td>
</tr>
<tr>
<td>Acid dissociation such as:</td>
<td>Anion protonation such as:</td>
</tr>
<tr>
<td>RCOOH (\rightarrow) RCOO(^-) + H(^+)</td>
<td>RCOO(^-) + H(^+) (\rightarrow) 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 H(_2)SO(_4) and HNO(_3) 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 SO(_4^{2-}))</td>
</tr>
<tr>
<td>Cation precipitation such as:</td>
<td>Cation weathering from minerals such as:</td>
</tr>
<tr>
<td>Al(^{3+}) + 3H(_2)O (\rightarrow) 3H(^+) + Al(OH)(_3)(^0)</td>
<td>3H(^+) + Al(OH)(_3)(^0) (\rightarrow) Al(^{3+}) + 3H(_2)O</td>
</tr>
<tr>
<td>SiO(_2) + 2Al(OH)(_3) + Ca(^{2+}) (\rightarrow) CaAl(_2)SiO(_6) + 2H(_2)O + 2H(^+)</td>
<td>CaAl(_2)SiO(_6) + 2H(_2)O + 2H(^+) (\rightarrow) SiO(_2) + 2Al(OH)(_3) + Ca(^{2+})</td>
</tr>
<tr>
<td>Deprotonation of pH-dependent charges</td>
<td>Protonation of pH-dependent charges</td>
</tr>
</tbody>
</table>
What is going on in the environment to produce a specific pH at one “place” and a different pH at another “place”?

What are the consequences of pH?