Soil Acidity

$$H_2O \leftrightarrow H^+ + OH^-$$

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^{O} C …

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

Therefore when water is pure this dissociation must be equal, and…

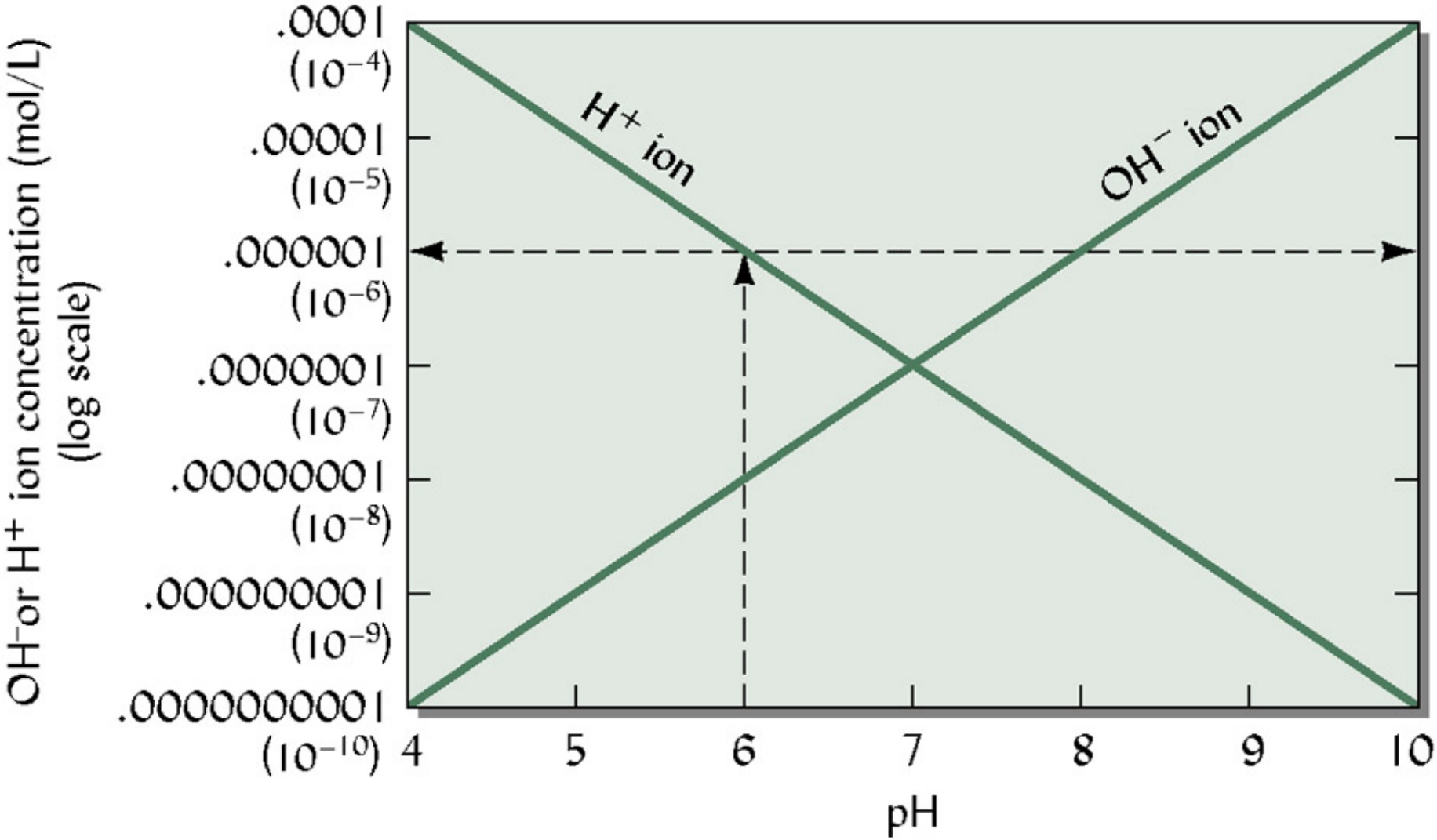
$$[H^+] \times [OH^-] = [10^{-7}] \times [10^{-7}] = 10^{-14}$$

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

An increasing $[H^+]$ will result in … ↓ $[OH^-]$

and

An decreasing $[H^+]$ will result in … ↑ $[OH^-]$


OH⁻ or H⁺ ion concentration (mol/L)
(log scale)
.0001
(10⁻⁴)
.00001
(10⁻⁵)
.000001
(10⁻⁶)
.0000001
(10⁻⁷)
.00000001
(10⁻⁸)
.000000001
(10⁻⁹)
.0000000001
(10⁻¹⁰)
H⁺ ion
OH⁻ ion
4
5
6
7
8
9
10
pH

$$pH = - \log [H^+]$$

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

$$pOH = - \log [OH^-]$$

So if the $[OH^-] = [10^{-8}]$, the pOH is 8

Finally as the ion concentration maintains a 10^{-14} constant…

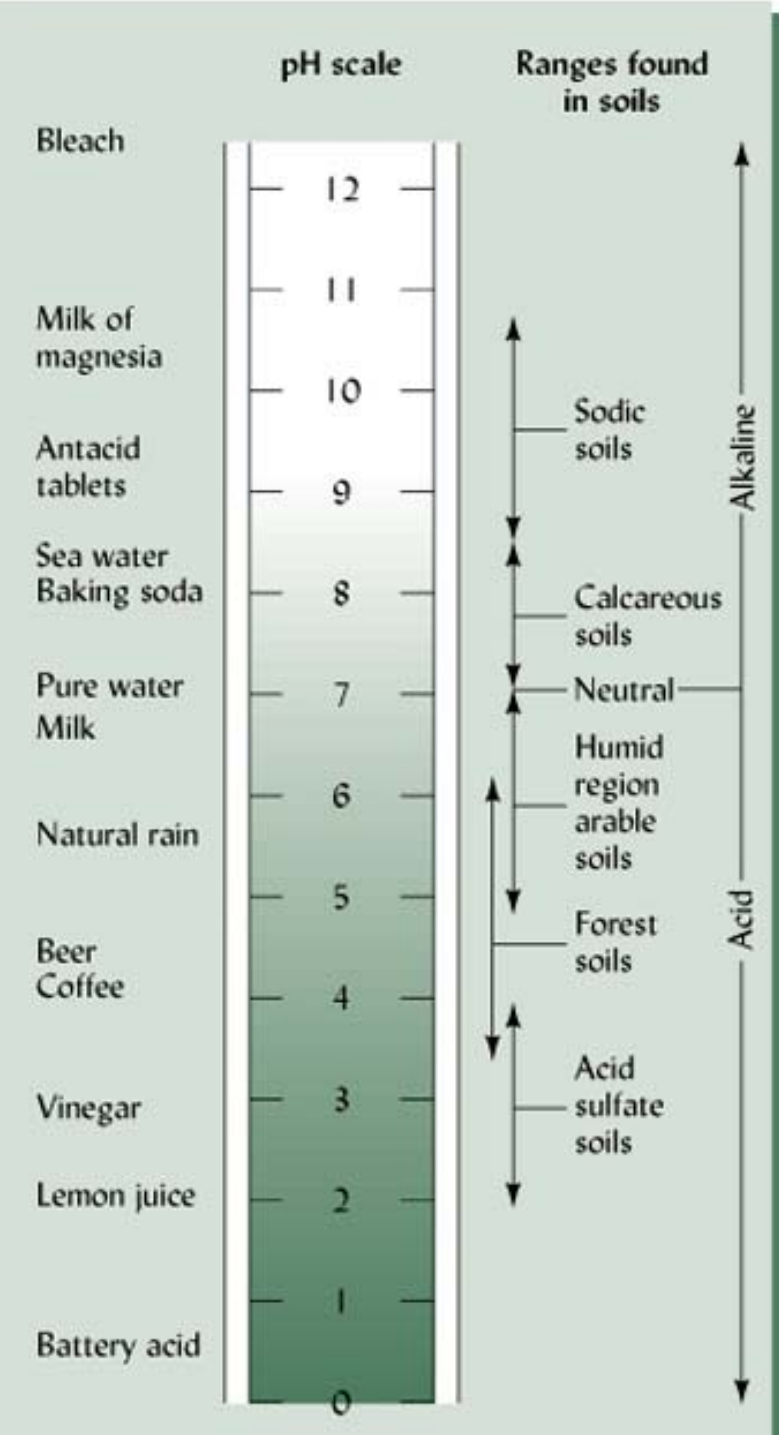
at a pH of 5 → $[H^+] \times [OH^-] = [10^{-5}] \times [10^{-9}] = 10^{-14}$

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



Extremely acid: < than 4.5;
lemon=2.5; vinegar=3.0; stomach acid=2.0; soda=2–4

Very strongly acid: 4.5–5.0;
beer=4.5–5.0; tomatoes=4.5

Strongly acid: 5.1–5.5;
carrots=5.0; asparagus=5.5; boric acid=5.2; cabbage=5.3

Moderately acid: 5.6–6.0;
potatoes=5.6

Slightly acid: 6.1–6.5;
salmon=6.2; cow's milk=6.5

Neutral: 6.6–7.3;
saliva=6.6–7.3; blood=7.3; shrimp=7.0

Slightly alkaline: **7.4–7.8**;
eggs=7.6–7.8

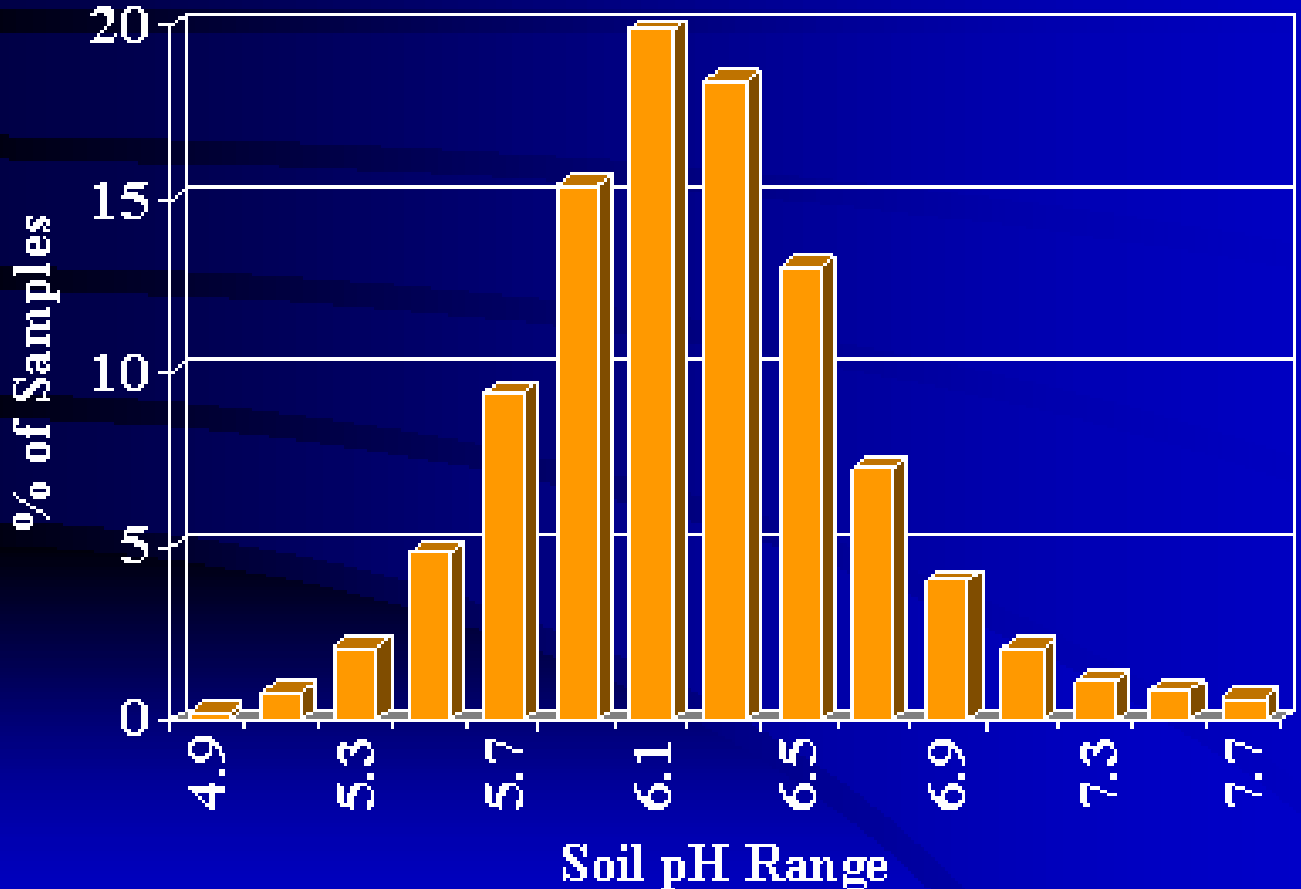
Moderately alkaline: 7.9–8.4;
sea water=8.2; sodium bicarbonate=8.4

Strongly alkaline: 8.5–9.0;
borax=9.0

Very strongly alkaline: > than 9.1;
milk of magnesia=10.5, ammonia=11.1; lime=12

Soil pH Sample Distribution

Illini FS, Inc.



Mean : 6.1

Median : 6.1

Frequency

7/22/97

Illini FS, Inc.

GREEN PLAN

Mechanism of Acidification:

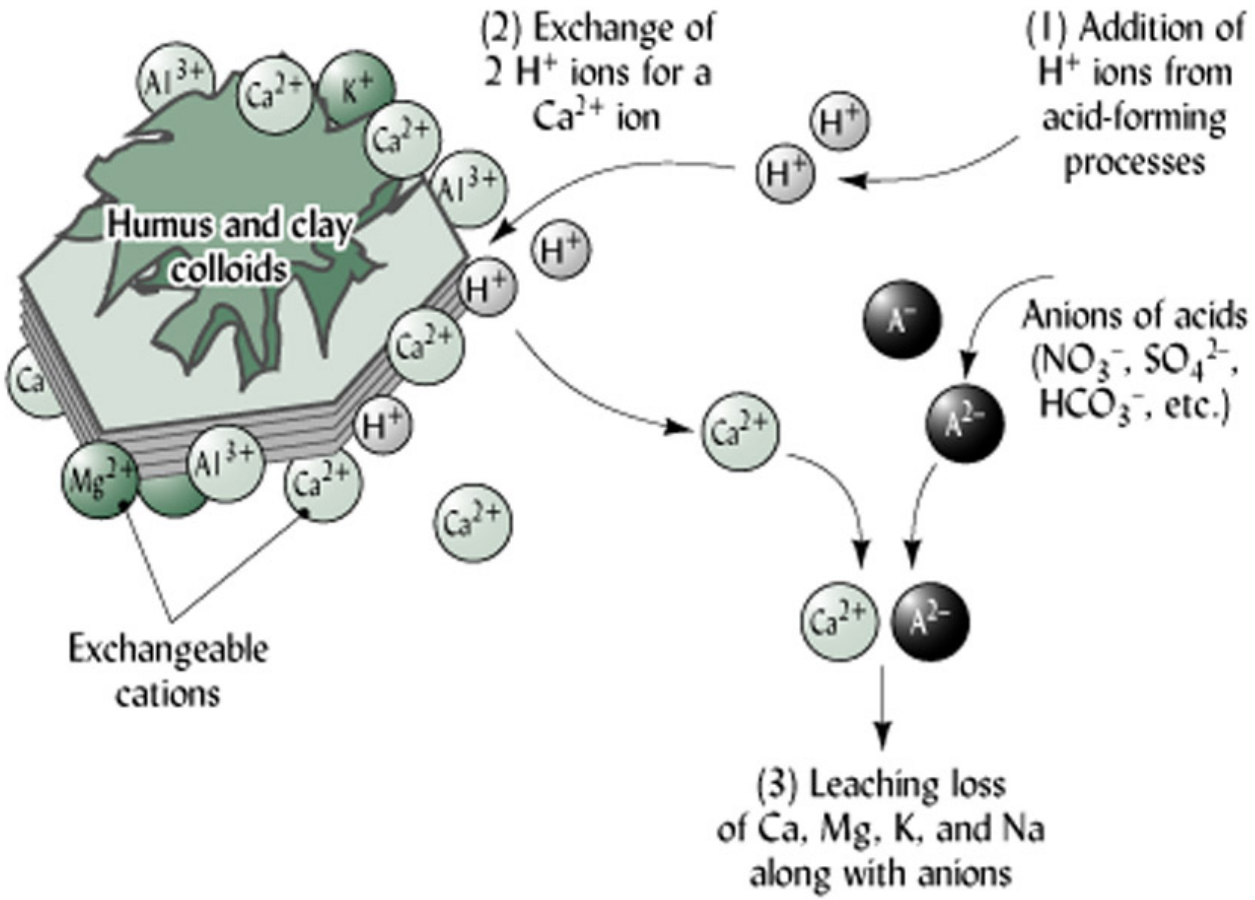
CATION EXCHANGE

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


(2) Exchange of 2 H+ ions for a Ca2+ ion
(1) Addition of H+ ions from acid-forming processes
Humus and clay colloids
Anions of acids (NO3−, SO4 2−, HCO3−, etc.)
Exchangeable cations
(3) Leaching loss of Ca, Mg, K, and Na along with anions

Natural Conditions Favorable to Acidification

- vigorous leaching (high rainfall, good drainage)
- high biological activitiy
- 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_2O)
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_2O)

pH's ranging @ 6.5

$$CH_2O\ (s) + O_2\ (g) \leftrightarrow CO_2\ (g) + H_2O\ (g)$$

With the CO_2 reaction with H_2O carbonic acid is produced

$$CO_2 + H_2O \leftrightarrow HCO_3^- + \mathbf{H^+}$$

2. Biological Metabolism

pH's ranging from ~ 3-5

$$R\text{-}CH_2OH + O_2 + H_2O \leftrightarrow R\text{-}COOH$$

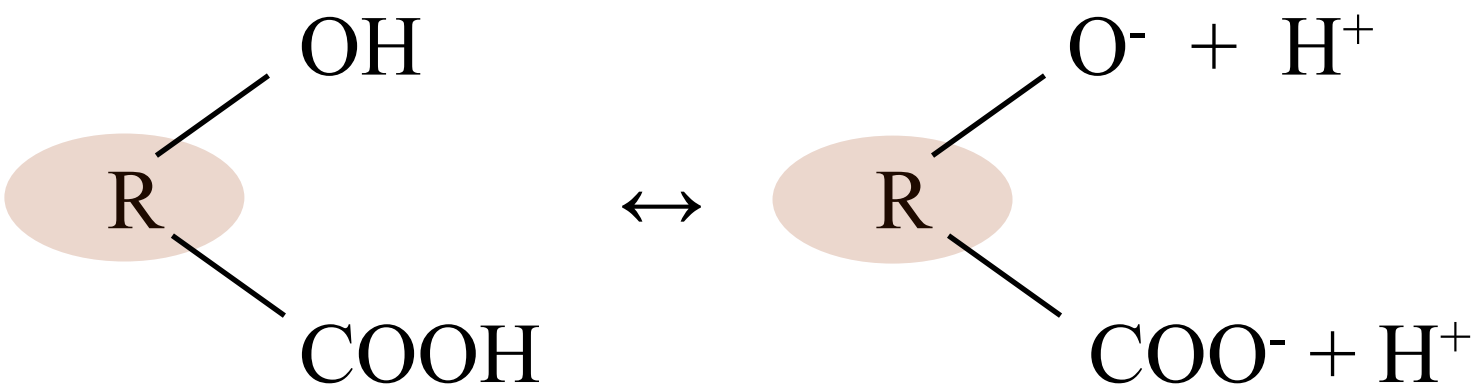
(strong organic acid)

$$R\text{-}COOH \leftrightarrow R\text{-}COO^- + H^+$$

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

$$FeS_2 + 3.5O_2 + H_2O \leftrightarrow FeSO_4 + 2H^+ + SO_4^{2-}$$

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

and

Nitrification

$$NH_4^+ + 2O_2 \leftrightarrow H_2O + 2H^+ + NO_3^-$$

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

ACIDIFICATION AND AGRICULTURE

Agricultural practices accelerate acidification.

1. **Intentional**

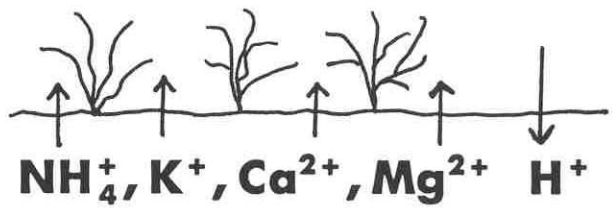
   Adding acidifying materials to neutral, alkaline soils (localized).

2. **Side-Effects**

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

   $$NH_4^+ + 2O_2 \dashrightarrow NO_3^- + 2H^+ + H_2O$$
   nitrification

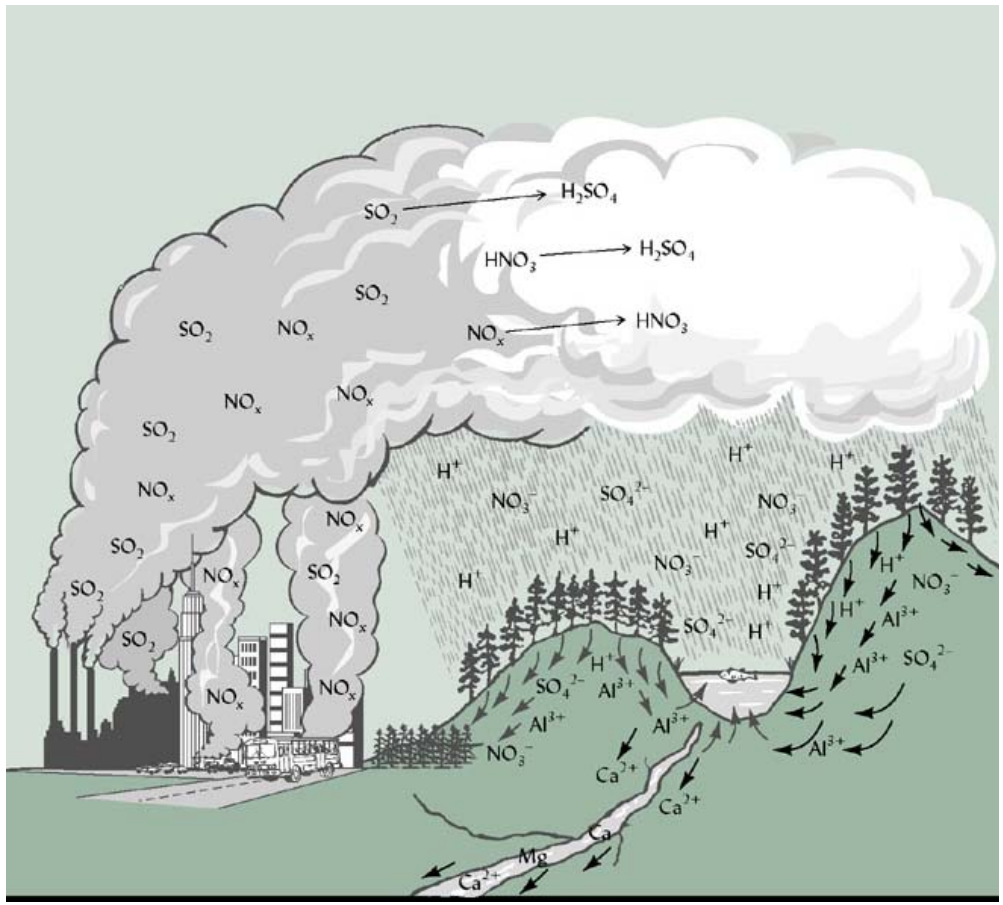
   (b) **removal of cations from soil by harvesting-**



   (c) N_2 **fixation**

5. Acid Rain

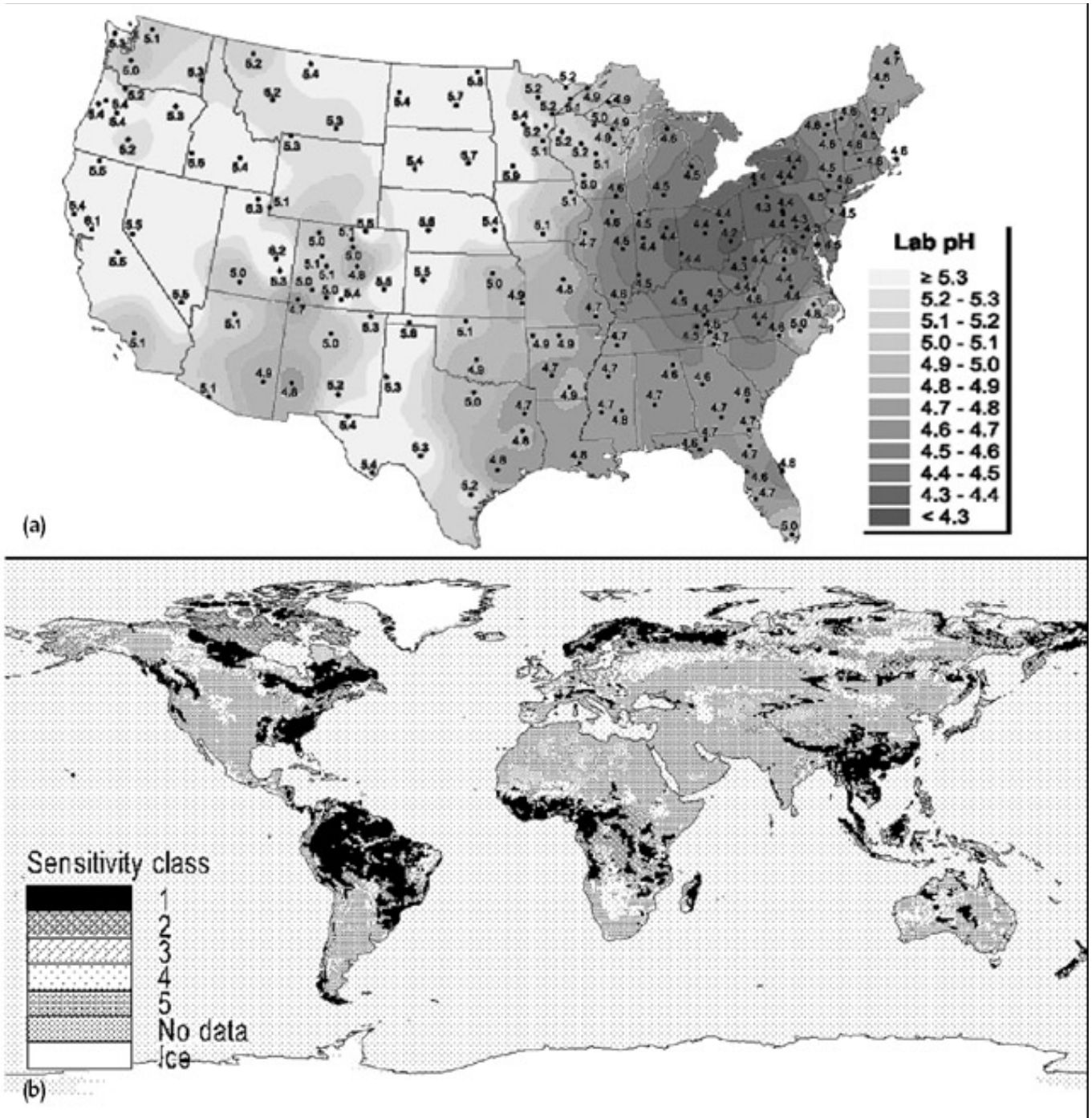
- solution reaction of nitrogen and sulfur gases, from a variety of natural sources **AND** the combustion of fossil fuels, with atmospheric water.



$$H_2SO_4 \leftrightarrow SO_4^{2-} + 2H^+$$

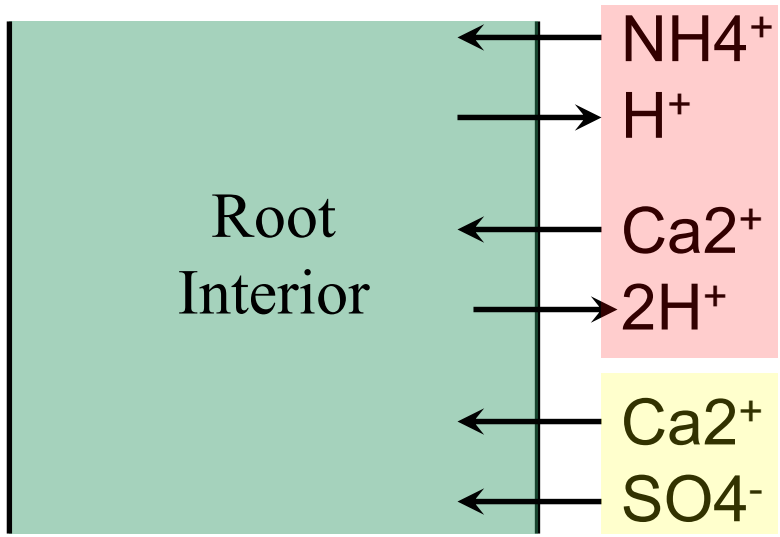
$$HNO_3 \leftrightarrow NO_3^- + H^+$$

Unlike carbonic acid (pH @ 6.5) these are strong acids which completely dissociate putting large amounts of protons in the environment


Lab pH
≥ 5.3
5.2 - 5.3
5.1 - 5.2
5.0 - 5.1
4.9 - 5.0
4.8 - 4.9
4.7 - 4.8
4.6 - 4.7
4.5 - 4.6
4.4 - 4.5
4.3 - 4.4
< 4.3
(a)
Sensitivity class
1
2
3
4
5
No data
Ice
(b)

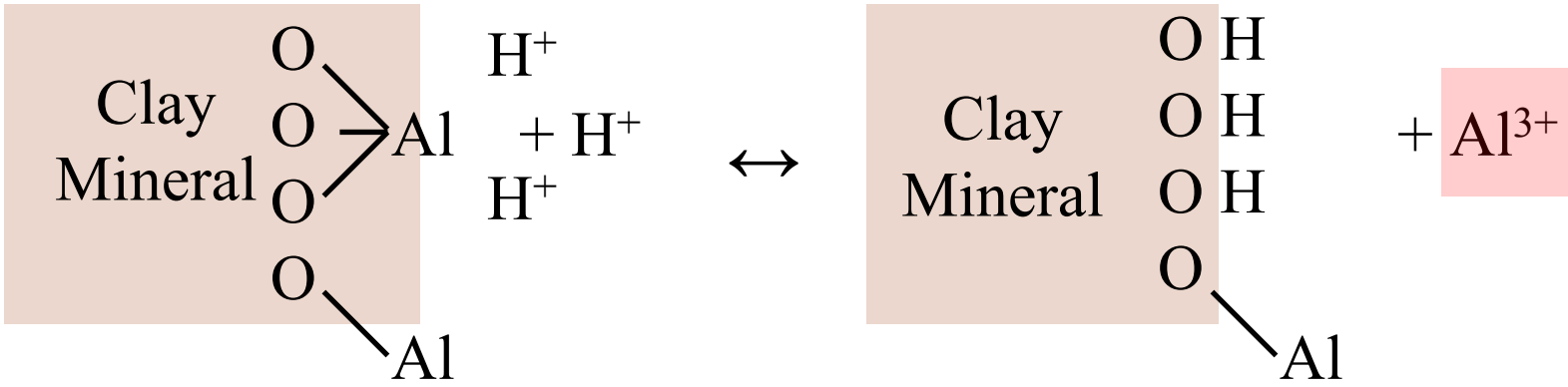
6. Plant Uptake

1. Maintenance of charge balance
2. Proton pumps

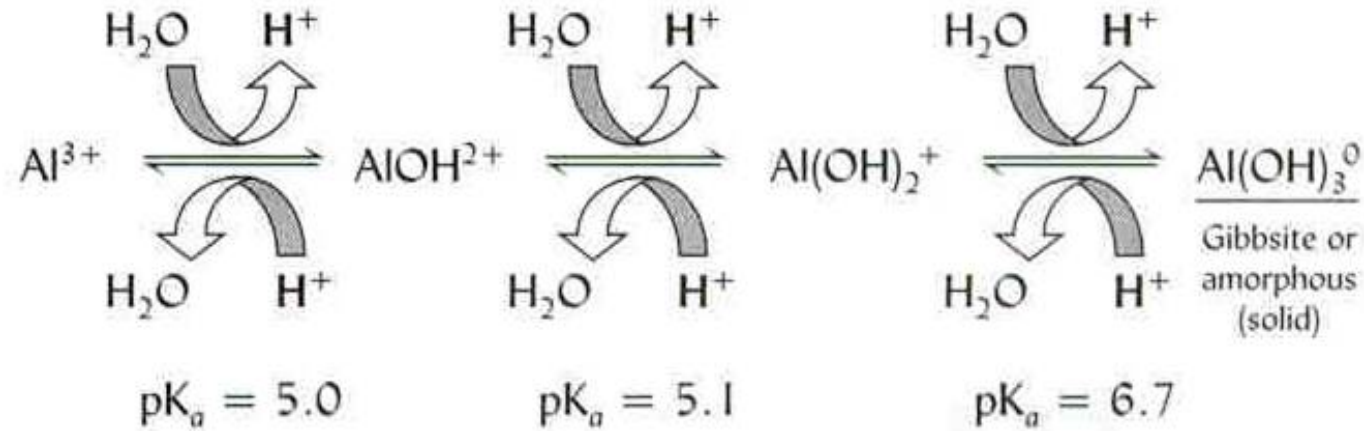


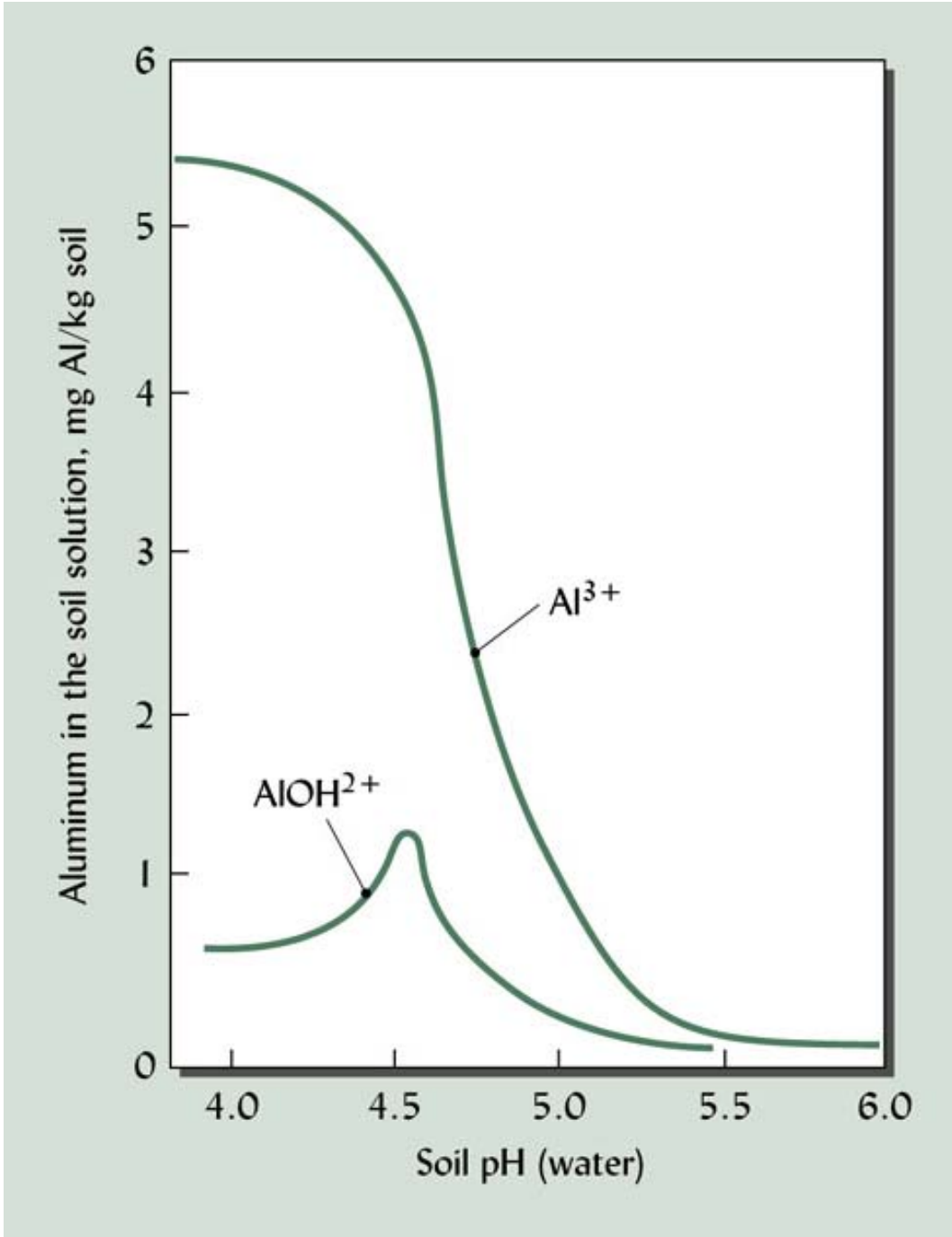
7. Aluminum - paired reaction (1) solubilization and (2) hydrolyzation

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



(2) Al reacts in solution with H_2O to form $Al(OH)_3$




Aluminum in the soil solution, mg Al/kg soil
6
5
4
3
2
1
0
4.0
4.5
5.0
5.5
6.0
Soil pH (water)
Al^{3+}
$AlOH^{2+}$

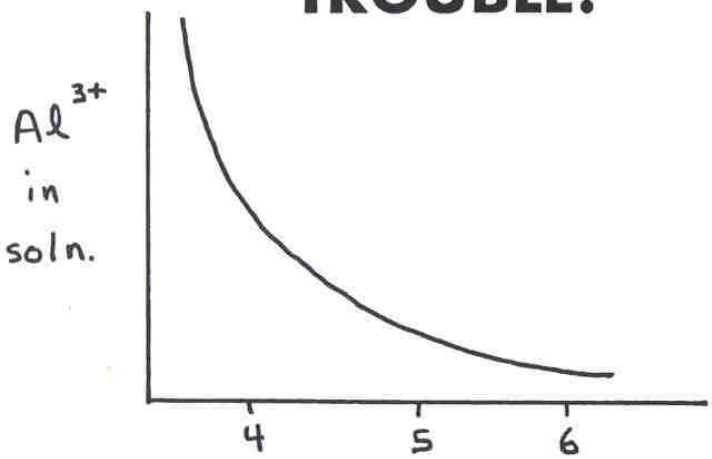
ACIDITY AND ALUMINUM

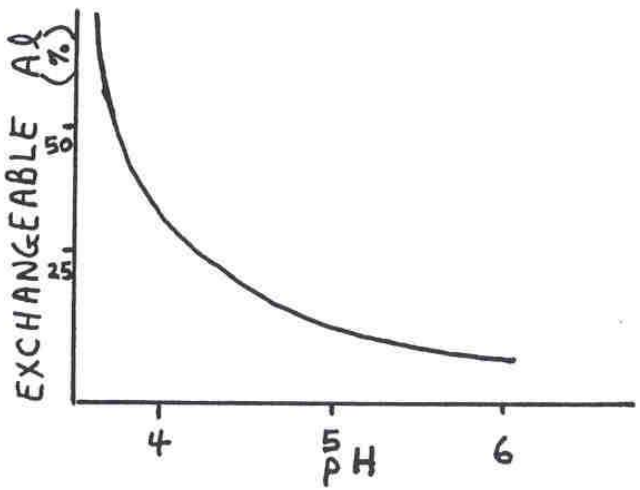
As soil becomes acid, Al becomes more soluble:

$$\text{ALUMINOSILICATES} \xrightarrow{H^+} Al^{3+}\ \text{(soluble)}$$

$$Al^{3+} + Ca^{2+}\text{-colloids} \rightleftharpoons Al^{3+}\text{-colloids} + Ca^{2+}$$

> 20% Al on "exchange complex" = TROUBLE!





Exchangeable H^+ is <u>minor</u>, even in acid soils.

ACIDITY AND OTHER METALS

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

Mn(+4) oxides ---> Mn^{2+} (soluble)
Fe (+3) oxides ---> Fe^{2+} (soluble)

These can be toxic to crops

8. Parent Material dissolution

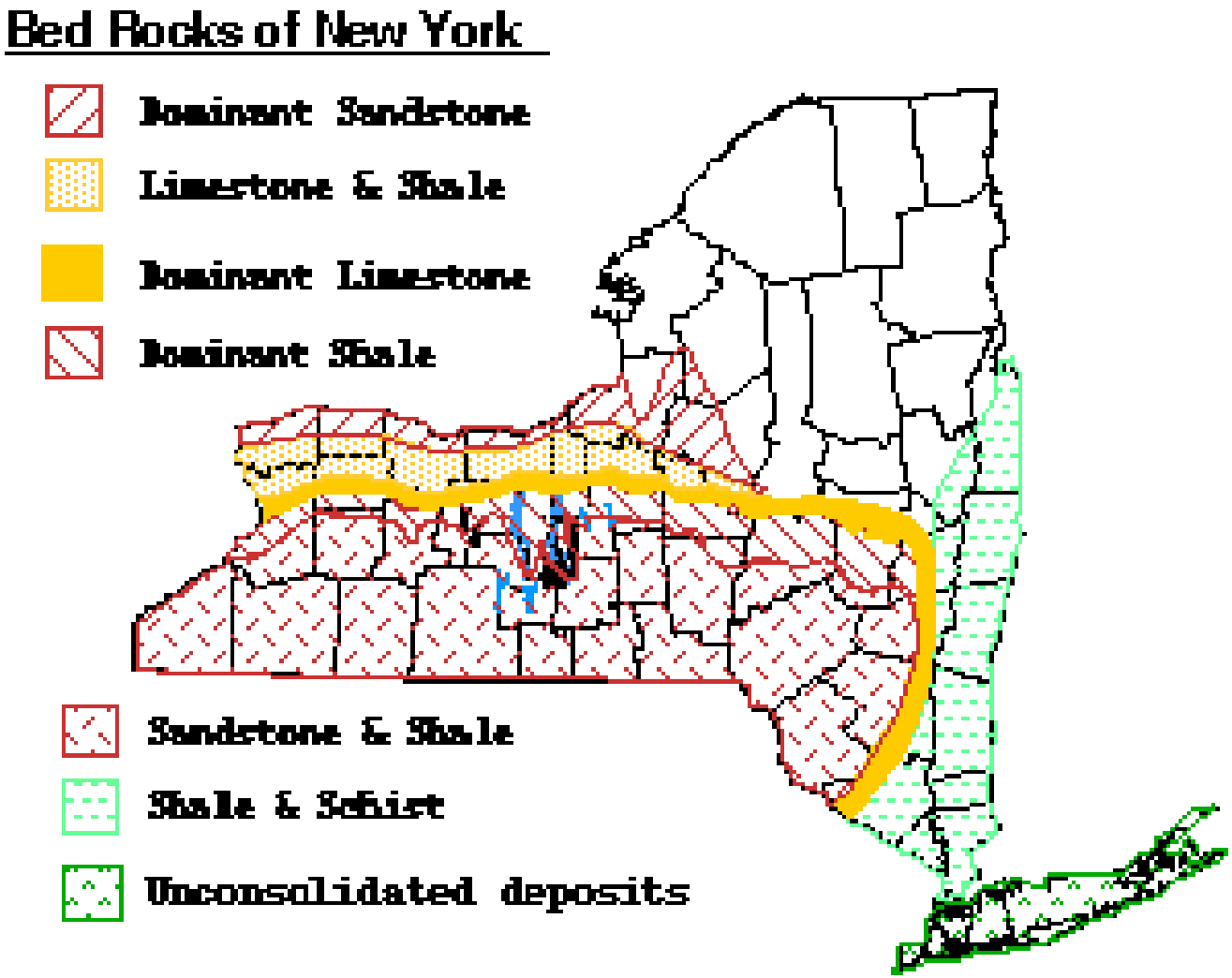


TABLE 9.1 The Main Processes that Produce or Consume Hydrogen Ions (H^+) in Soil Systems

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.

Acidifying (H^+ ion–producing) processes	*Alkalinizing (H^+ ion–consuming) processes*
Formation of carbonic acid from CO_2	Input of bicarbonates or carbonates
Acid dissociation such as: $RCOOH \rightarrow RCOO^- + H^+$	Anion protonation such as: $RCOO^- + H^+ \rightarrow RCOOH$
Oxidation of N, S, and Fe compounds	Reduction of N, S, and Fe compounds
Atmospheric H_2SO_4 and HNO_3 deposition	Atmospheric Ca, Mg deposition
Cation uptake by plants	Anion uptake by plants
Accumulation of acidic organic matter (e.g. fulvic acids)	Specific (inner sphere) adsorption of anions (especially SO_4^{2-})
Cation precipitation such as: $Al^{3+} + 3H_2O \rightarrow 3H^+ + Al(OH)_3^0$ $SiO_2 + 2Al(OH)_3 + Ca^{2+} \rightarrow CaAl_2SiO_6 + 2H_2O + 2H^+$	Cation weathering from minerals such as: $3H^+ + Al(OH)_3^0 \rightarrow Al^{3+} + 3H_2O$ $CaAl_2SiO_6 + 2H_2O + 2H^+ \rightarrow SiO_2 + 2Al(OH)_3 + Ca^{2+}$
Deprotonation of pH-dependent charges	Protonation of pH-dependent charges

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?