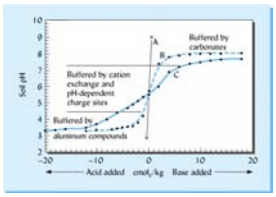
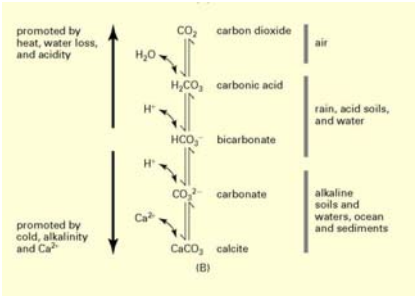


Figure 9.5 Buffering of soils against changes in pH when acid (H_2SO_4) or base ($CaCO_3$) is added. A moderately buffered soil (B) and a strongly buffered soil (C) are compared to unbuffered water (A). Most soils are strongly buffered at low pH by the hydrolysis and precipitation of aluminum compounds 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)]

The Role of CO_2 in Soils



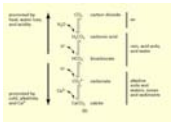
Henry's Law

$$CO_2(sol.) = k\,P[CO_2(gas)]$$

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 CO_2-H_2O System



$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \qquad \log K = -1.46$$

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \qquad \log K = -6.35$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \qquad \log K = -10.33$$

$$CO_3^{2-} + Ca^{2+} \Leftrightarrow CaCO_3$$

$$CO_2 + H_2O + Ca^{2+} \Leftrightarrow CaCO_3 + 2H^+$$

The pH of the CO_2-H_2O System

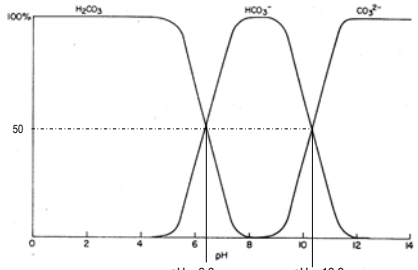


Fig. 3.4 Distribution of aqueous CO_2 species with pH.

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

Aluminum as an Acidic Cation

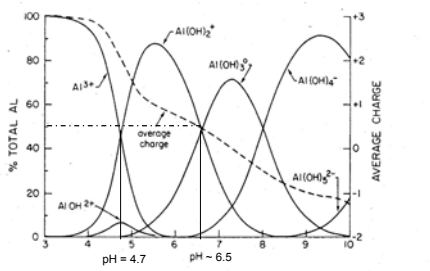


Fig. 8.2 Relative distribution and average charge of the soluble aluminum species

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

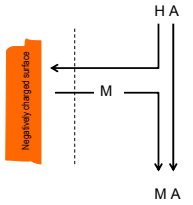
Dissociation Constant for Weak Acids

Element	Formula of Acid	pK_a
C	H_2CO_3	6.3
	HCO_3^-	10.33
P	H_3PO_4	2.23
	$H_2PO_4^-$	7.2
	HPO_4^{2-}	12.3
S	HSO_4^-	2.0
	H_2S	7.0
	HS^-	12.9
N	NH_4^+	9.2
B	H_3BO_3	9.2
Si	H_4SiO_4	9.5
O	H_2O	14.0

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):

Organic molecule from photosynthesis →

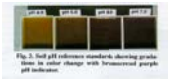
$$CH_2O + O_2 \Leftrightarrow CO_2 + H_2O$$
$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$
$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$$

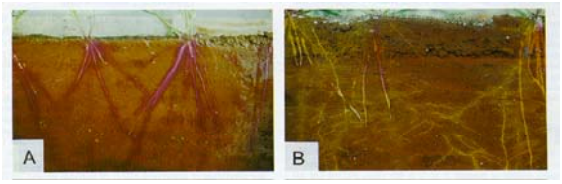
Oxygen is needed to carry out this reaction (*aerobic systems*). In the absence of O_2 other reactions take place.

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





NO_3^- NH_4^+

Source: Heckman, JR and JE Strick. 1996. Teaching Plant-Soil Relationships with Color Images of Rhizosphere pH. J. Nat. Resour. Life Sci. Educ. 25: 13-17.

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+})