

Acidity

- What is pH?
- What, then, is the pH of soil?
- Why is pH often called the “master variable” in soils?
- Why is Al^{3+} considered an acid and Ca^{2+} , Mg^{2+} , and K^{+} considered bases (all are Lewis acids)?

Soil Acidity

- “The central problem in soil acidity is the relationship between the total acidity of the system (i.e. the nature and amounts of the proton donors in the solid phase) and the intensity of acidity (i.e. the activity of hydrogen ions in solution).”
 - Byron Bache. 1988. Commun. Soil Sci. Plant Anal. 19:775-796

Soil pH

- One can only take the pH of a solution
- What solution would you use in soils?
- Factors affecting pH measurement:
 - soil:solution ratio
 - type and concentration of solution (water, CaCl_2 , KCl)
 - positions of electrodes in the solution
 - to stir or not to stir
- $\text{pH} - \frac{1}{2} \text{pCa}$ is reasonably constant

Definitions from SSSA glossary

- acidity, active - (no longer used in SSSA publications) The activity of hydrogen ion in the aqueous phase of a soil as a pH value.
- acidity, exchange - (no longer used in SSSA publications) The acidity of a soil that can be neutralized by lime or a solution buffered in the range 7 to 8. See also acidity, total.
- acidity, exchangeable - see acidity, salt-replaceable.
- acidity, free - (no longer used in SSSA publications) The titratable acidity in the aqueous phase of the soil.
- acidity, reserve - see acidity, residual.

More definitions

- acidity, residual - Soil acidity that is neutralized by lime or a buffered salt solution to raise the pH to a specified value (usually 7.0 or 8.0) but which cannot be replaced by an unbuffered salt solution. It can be calculated by subtraction of salt replaceable acidity from total acidity. See also acidity, salt-replaceable and acidity, total.
- acidity, salt-replaceable - The aluminium and hydrogen that can be replaced from an acid soil by an unbuffered salt solution such as KCl or NaCl [usually 1 M KCl].
- acidity, total - The total acidity including residual and exchangeable acidity. Often it is calculated by subtraction of exchangeable bases from the cation exchange capacity determined by ammonium exchange at pH 7.0. It can be determined directly using pH buffer-salt mixtures (e.g. BaCl₂ plus triethanolamine, pH 8.0 or 8.2) and titrating the basicity neutralized after reaction with a soil.

So, what determines the pH of a soil?

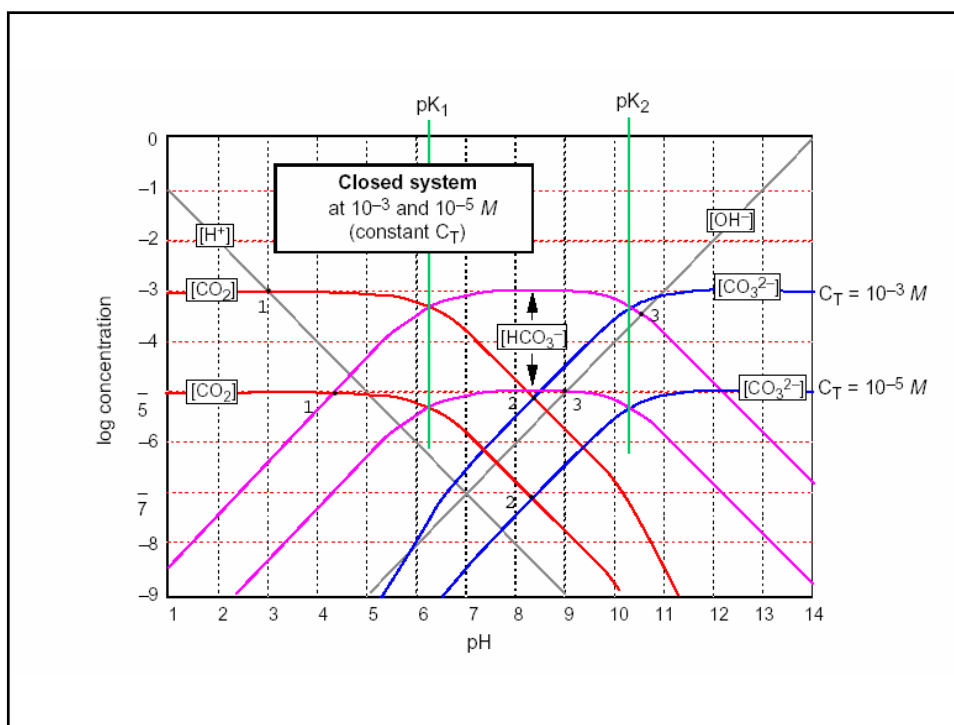
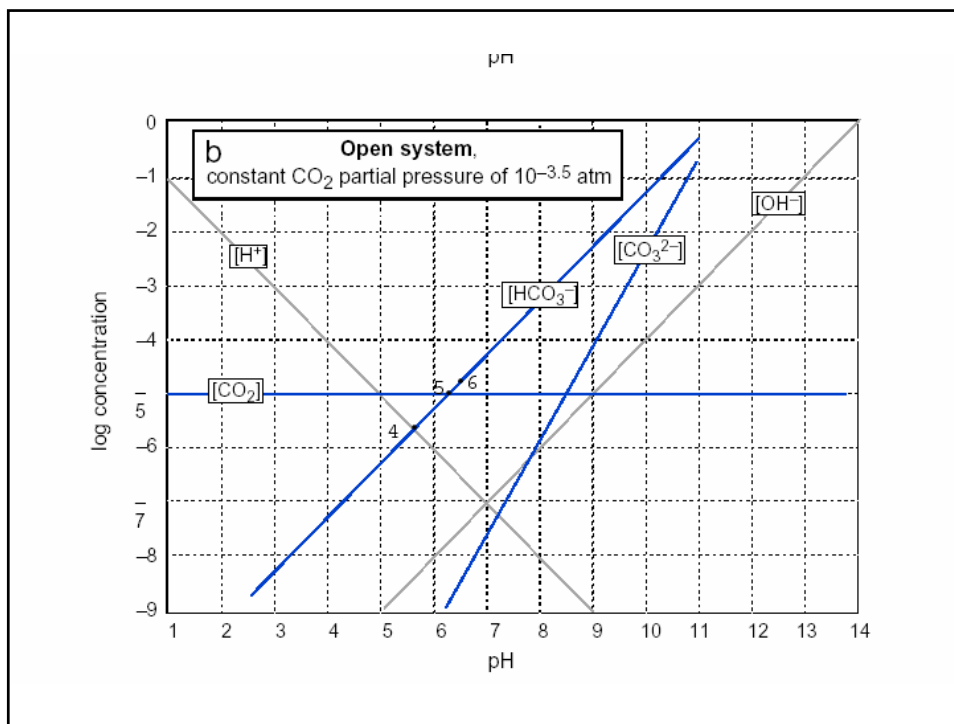
- Dissociation of proton donors (carboxyl groups, phenolic groups, oxides). [These donors were part of the "residual activity".]
- Distribution of proton between surface and solution. [How much of the "salt-replaceable" is in solution.]
- Protons generated by the hydrolysis of displaced Al³⁺.
- "Base saturation" can explain the pH in acid, organic soils if Al is considered a base and the CEC_e is used.
- But it does not do such a good job in mineral soils in the pH range 5.5 to 7. Although, it works OK if the CEC measurement includes the residual activity.

Soil Acids

- Is there exchangeable H^+ ?
- Aluminium (British spelling) as an acid and as a base
- Sources of acidity
 - CO_2 production
 - organic acid production
 - oxidation of reduced S
 - nitrification (and therefore NH_4^+ fertilizers)
 - plant ammonium uptake

Carbonate equilibria

- CO_2 will dissolve into water and produce carbonic acid.
- At atmospheric concentrations (0.0003 atm), the resulting pH of "pure" water will be 5.7.
- In an active soil, the P_{CO_2} can range from 0.01 to as high as 0.1 atm.
- The resulting pH would be 4.91 and 4.41
- When this solution comes back into equilibrium with the atmosphere, the pH will rise.



Carbonate in a Ca system

- In high-pH soils, an excess of Ca and CO_3 will result in the formation of CaCO_3 .
- Under atmospheric concentrations of CO_2 , the soil pH will be 8.30.
- The pH will not become higher because CaCO_3 will precipitate.
- In sodic soil (high Na), the pH can be higher because Na_2CO_3 is more soluble.

Soil Buffering

- Carbonate
 - in Ca-soils above ~pH 7
 - attempts to further raise the pH lead to CaCO_3
- Organic matter
 - throughout the entire pH range but most important in mineral soils between pH ~4 and 7.
 - Carboxylic and phenolic groups.
- Aluminosilicate
 - below pH 4.5 in mineral soils.
 - attempts to further lower the pH lead to mineral dissolution.

Acidity in organic soils

- Mineral soils will not “naturally” reach a pH less than about 4.0.
- Weathering of the minerals is able to consume any acidity generated.
- Organic soils do not have the buffering supplied by these minerals.
- Therefore, they can reach a pH of 3.0 or less by continued leaching of “base” cations and generation of organic acids during decomposition.

Al Chemistry

- Equilibrium concentration predictions for Al species in simple solutions (i.e. AlCl_3 mixed with NaOH) do not always hold true.
- Numerous ligands complicate solution Al chemistry in soils: F , PO_4 , SiO_4 , and a host of organics.
- Numerous solid phases further complicate the picture.
- “Metastable” phases really complicate things.
- Exchangeable Al (found in soils below pH 5.5) probably controls the concentration of Al^{3+} in solution.
- But many other, sometimes slower, reactions occur.

Aqueous Al species

98 *The Environmental Chemistry of Aluminum*

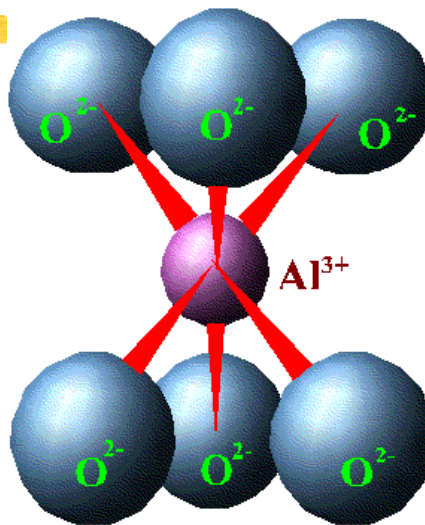
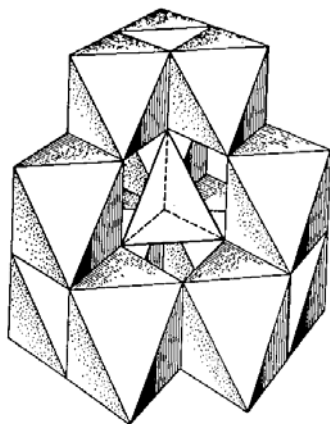


FIGURE 4. Representation of the $[\text{Al}_6\text{O}_{12}(\text{OH})_6(\text{H}_2\text{O})_6]^{3+}$ polynuclear species, demonstrating the tetrahedrally coordinated aluminum at the center of the cage-like structure comprising 12 octahedrally coordinated aluminum atoms joined by common edges. (From Bates, C. F. and Mesmer, R. E., *The Hydrolysis of Cations*, John Wiley & Sons, New York, 1976.)