## ACIDIC AND BASIC SOILS - BUFFERING

The interaction among a number of factors including parent material, climate, vegetation and management determine whether a soil has a neutral, acidic or alkaline reaction.   In this section we will examine the chemistry of alkaline, and acidic soils and the unique properties of each soil type. In addition we will examine the ability of a soil to resist change in pH via a number of buffering reactions.

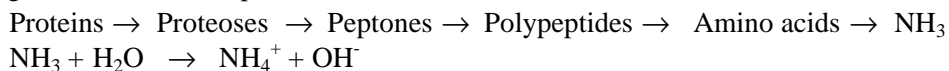**Figure 8.1 A schematic view of soil processes and factors affecting soil pH.**
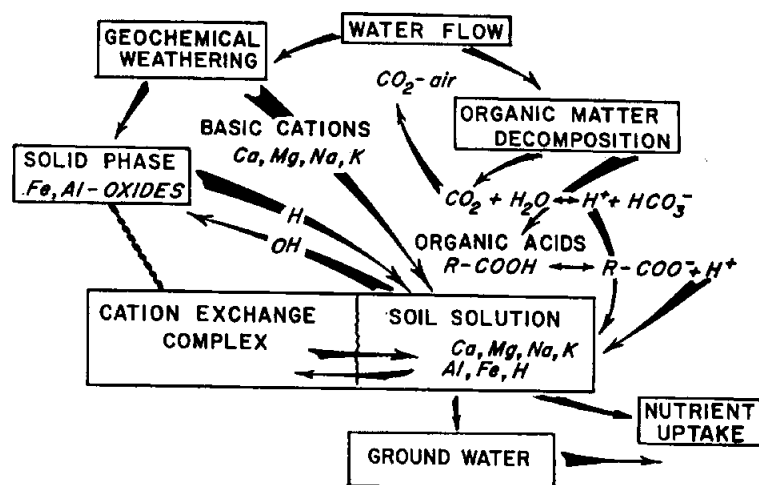
There are a number of processes in soils and sediments which generate or consume proton and therefore affect pH. These processes interact with the local climate, parent material, and organisms over time to determine soil pH. Water flow through the system is an important variable as it removes weathering products and supplies protons for exchange reactions.
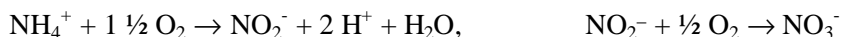
Some of the important processes that either generate or consume protons are list below. Protons that are generated by these processes interact with the soil exchange complex and the solid phase. Thus, primary minerals, clay and organic matter content and percolation are important aspects of soil pH regulation.
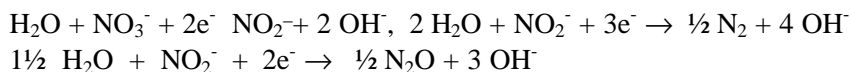
Important processes generating or consuming protons.
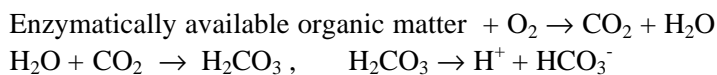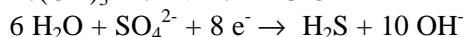
1. Biological breakdown of proteins
$$\text{Proteins} \rightarrow \text{Proteoses} \rightarrow \text{Peptones} \rightarrow \text{Polypeptides} \rightarrow \text{Amino acids} \rightarrow NH_3$$
$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

2. Nitrification
$$NH_4^+ + 1\tfrac{1}{2} O_2 \rightarrow NO_2^- + 2 H^+ + H_2O, \qquad NO_2^- + \tfrac{1}{2} O_2 \rightarrow NO_3^-$$

3. Denitrification
$$H_2O + NO_3^- + 2e^- \ \ NO_2^- + 2 OH^-, \ \ 2 H_2O + NO_2^- + 3e^- \rightarrow \tfrac{1}{2} N_2 + 4 OH^-$$
$$1\tfrac{1}{2} \ H_2O + NO_2^- + 2e^- \rightarrow \tfrac{1}{2} N_2O + 3 OH^-$$

4. Oxidative metabolism
$$\text{Enzymatically available organic matter} + O_2 \rightarrow CO_2 + H_2O$$
$$H_2O + CO_2 \rightarrow H_2CO_3 , \qquad H_2CO_3 \rightarrow H^+ + HCO_3^-$$

5. Other electron acceptors for microbiological respiration.

$$2\ H_2O + MnO_2 + 2e^- \rightarrow Mn^{2+} + 4\ OH^-$$
$$Fe(OH)_3 + e^- \rightarrow Fe^{2+} + 3\ OH^-$$
$$6\ H_2O + SO_4^{2-} + 8\ e^- \rightarrow\ H_2S + 10\ OH^-$$
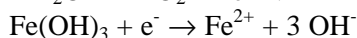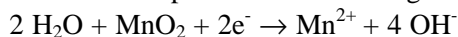
6. Addition of "lime" to an acid soil.

$$H_2O + CO_2 + CaCO_3 \rightarrow Ca^{2+} + 2\ HCO_3^-\ , \qquad 2\ HCO_3^- + 2\ OH^- \rightarrow 2\ CO_2$$

7. Addition of sulfur

$$H_2O + S^o + 1\ \tfrac{1}{2}\ O_2 \rightarrow SO_4^{2-} + 2\ H^+$$
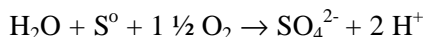
8. Protolysis due to dilution

$$M_{exch} + H_2O\ \rightarrow\ H_{exch} + M^+ + OH^-$$

9. Ion uptake

$$Root + K^+\ \rightarrow\ K(Root) + H^+$$
$$Root + NO_3^-\ \rightarrow\ Root\ (NO_3^-) + OH^-$$
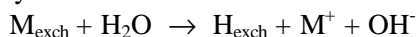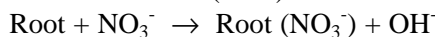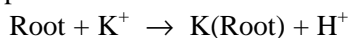
10. Fire - rapid mineralization of soil organics

$$Ca\text{-}O.M.\ \rightarrow\ CO_2\ +\ CaO$$
$$CaO\ + H_2O\ \rightarrow\ Ca^{2+} + 2\ OH^-$$
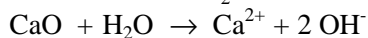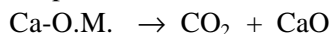
Buffering in Soils

We probably all first encountered the term buffering in chemistry in the study of buffering of pH in aqueous, acid-base systems. A system was "well buffered" if it would accept either some strong acid or strong base without changing pH very much. The concept was often illustrated by observing the behavior of a beaker of water containing a mixture of acetic acid and a salt of its conjugate base, sodium acetate. If these 2 solutes were present in equal concentration, the pH would be approximately 4.5. If some strong acid such as HCl were added to this mixture, the pH would decrease but much less than expected because most of the H+ from the strong acid was "bound" to the acetate (OAc^-) to form neutral, undissociated molecules of acetic acid

$$H^+ + OAc^-\ :\ HOAc$$

A fundamental concept is that only free, unbound H^+ ions affect pH. The small amount of H^+ that stayed as unbound or "free" H^+ was the cause of the observed small decrease in pH. On the other hand, if we add instead some sodium hydroxide to such a beaker, we would note a small pH rise. Again much smaller than expected. This buffering is due to the destruction or inactivation of most of the added hydroxide by the reaction

$$OH^- + HOAc\ :\ OAc\_ + H_2O$$
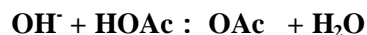
If you will, the OH⁻ ions are bound into neutral H_2O molecules by the H^+ that dissociated from neutral HOAc molecules. If there were no HOAc in solution, all (or almost all) of the OH^- would stay in this form and cause a large pH rise.

In addition to the above classic case of acid_base buffering, the term buffering can be extended to other soil_water phenomena including heat, water, and nutrients. In order for these extensions of the term to be clearly understood we must first define buffering in general terms. Although other terms are sometimes used we will use the words "quantity" and "intensity" to name the variables involved in buffering. In acid_base systems, pH is the intensity (**I**) variable while the quantity (**Q**) variable is either the amount (**C_a**) of strong acid or of strong base (**C_b**) added to the system. Above, we loosely used terms like small change of pH resulting from addition of either acid or base. This can be made more quantitative by using the differential expressions **d(pH)/d(C_a)** or **d(pH)/d(C_b)** which literally indicate the change in pH per unit of added acid or base. Using these mathematical forms, strong or effective buffering by the system results in a small numerical number which is contrary to the intuitive philosophy that bigger is better. This is quickly rectified by using the inverse of these expressions as an index of buffering. In acid_base literature, this parameter (**dC_b/dpH**) or alternatively (**dC_a/dpH**) is given the symbol **$** and has been named the **van Slyke buffering index**. This is a form of the general expression for any type of system: **dQ/dI**. We discussed **Q/I** relationships with respect to cation exchange in Section 6.

The laboratory exercise associated with the above theory is pH buffering. In this exercise, you will be asked so plot titration curves for soils and to graphically calculate the van Slyke buffering index. Note that the buffering index is for solution phase.

In order to appreciate the magnitude of these values and to become familiar with the form of these curves, we will calculate a buffer index curve for an aqueous sample initially **0.1 molar** in strong acid which is neutralized by strong base until the concentration of free OH^- in solution is **0.1 molar**. The pH range for this calculation is from 1 to 13. In the following theory, we will make the simplification that **concentrations of ions are equal to activities so that pH = - log [H^+]**.   If C_b = **the analytical concentration of strong base** (e.g. NaOH) added to water (in dimensions of mol L^{-1}) and if **C_a = the analytical concentration of strong acid** (e.g. HCl) then at any point during the mixing of a specific amount of acid with a specific amount of base the following is true from the principle of electroneutrality:

$$\textbf{(H}^+\textbf{) + C}_b \; = \; \textbf{(OH}^-\textbf{) + C}_a \tag{1}$$

Let **C$_a$ be constant at 0.1 *M*,** Then, since we seek the differential effect of adding increments of acid or base we take the derivative of this expression:

$$d\,[H^+] + d\,C_b \;\; = \;\; \frac{d\,[H^+]}{[H^+]^2}\,K_w \tag{2}$$

where K_w is the protolysis (dissociation) constant for water and is $= 10^{-14}$.

Since $pH = -\log(H^+) = -\dfrac{\ln(H^+)}{2.3}$; $\quad and \quad \dfrac{d\,[H^+]}{H^+} = \log[H^+]$ $\quad$ then:

$$d\,pH = -\frac{d\,[H^+]}{2.3[H^+]}\,; \quad and \quad d[H^+] = 2.3[H^+]\,d(pH)$$

Substituting and rearranging:

$$\frac{d\,C_b}{d(pH)} \;\; = \;\; 2.3\big([H^+] + [OH^-]\big) \tag{3}$$

For example, at pH 3 when 99% of the original acid has been neutralized, the buffer index is 0.0023. If we solve for the minimum value of $ in the water-strong acid base system, we discover it occurs when $(H^+) =$ (OH^-) or when pH = 7. The numerical value of ?at this point is **4.6*10^{-7} mol L^{-1} pH^{-1} which is the smallest possible buffer index for an aqueous system.**

Many but not all of the surface charge sites (potential or actual, + or −) have weak acid properties including the edges of aluminosilicate clay minerals; surfaces of oxides, oxyhydroxides and hydroxides; as well as functional groups (carboxylate and phenolate) in soil humates and fulvates and thus they account for some of the acid base buffering properties of soil or sediment systems. Other sources of buffering include the dissolution of primary minerals, oxides, or carbonates as well as the precipitation of oxides, hydroxides or carbonates. It is not now possible to measure the contribution of each of these components in a given sample and therefore it is necessary to empirically describe buffering through laboratory observations and graphical techniques. One final note, in order for the van Slyke index for pure or defined aqueous systems to be comparable to the index for a soil, it is necessary to calculate the base or acid added concentrations as if the base or acid were added to the water that is in the soil at the time of pH measurement.

Buffering in soils and sediments can be immediate, short-term and long-term depending upon the particular reactions that are taking place. Immediate reactions are those you have dealt with in chemistry classes. When strong acid is added to strong base, the equilibrium is established nearly instantaneously. The limitation for this system is the rate of reactant diffusion. Cation exchange is also a very rapid process limited only by the access of solution to the reaction sites. If small pores or internal surface is available exchange

reactions may take longer and require a matter of days for equilibration. Some of the biological reactions are also longer-termed.   Nitrification, denitrification, mineralization etc. may take place in hours or days and continue, given the availability of substrate, over prolonged periods.   Weathering of primary minerals is a longer-term reaction which consumes protons for many reactions; however, some secondary and incongruent reaction may be acid producing. For classification purposes, pH ranges over which buffering reactions are important have been tabulated in the following scheme.

Soil Buffering Reactions in Relation to Soil pH

pH range	Important soil buffers
10 - 14	OH^- from water and oxides of Ca, Mg, Na, and K
10 - 6.5	Carbonates *f* (solubility of the carbonate)
All	Mineral weathering
10 - 3	Soil organic matter
4 - up	Exchange reactions
4.2- 2.8	Aluminum oxides and hydroxides
3.8 - 2.4	Iron hydroxides and oxides
< 3	H^+ from water

The short-term buffering of soils is small around neutrality and increases in the alkaline and acid ranges. As might be expected soil buffering depends on several factors:

1.   Clay content and type (texture)
2.   Organic matter content
3.   Oxide components
4.   Carbonate content
5.   Initial pH
6.   Weatherable mineral content

Figure 8.2. Variation in β for the titration of 0.1 and 0.2 M acetic acid in water. Taken from *Biophysical Chemistry by A.G. Marshall, 1978, Wiley and Sons, NY.*
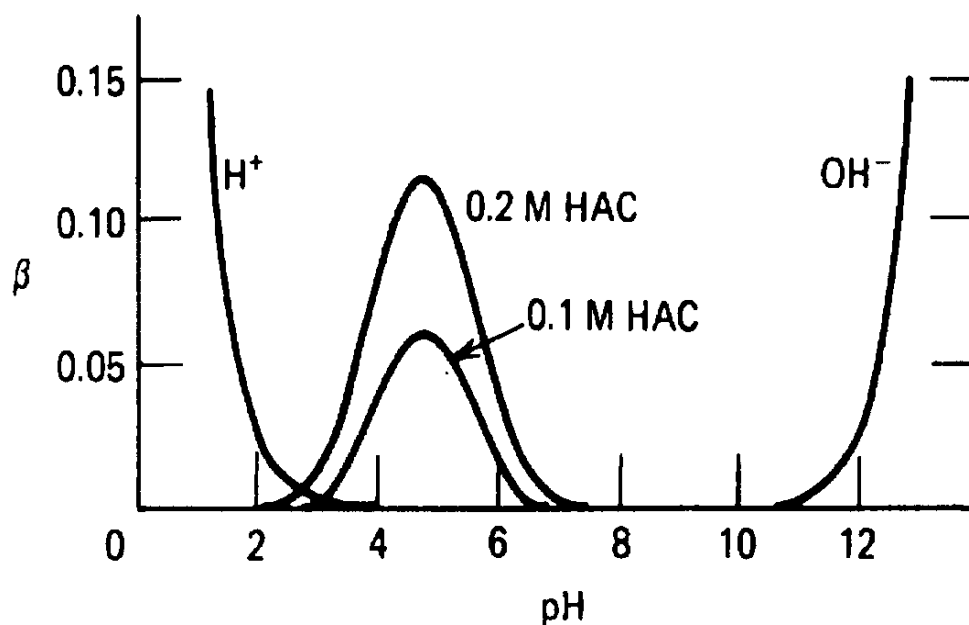

Figure 8.3. Titration of a solution containing 0.1 M strong acid, and 0.1 M of weak acid one with a pK = 5.0, and a second weak acid with a pK = 9.0. from Kolthoff and Elvins (1959). Treatise on Analytical Chemistry Part I. Theory and Practice. Interscience Publishers, Inc. NY.
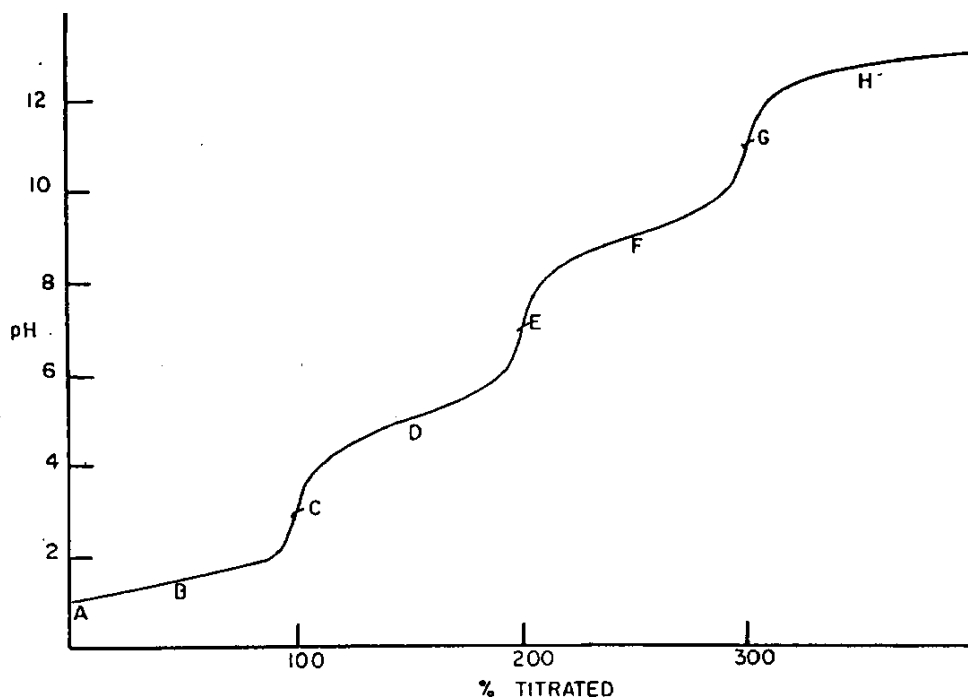
Figure 8.4. The buffering index ($) for the titration in Figure 7.3 *from Kolthoff and Elvins (1959). Treatise on Analytical Chemistry Part I. Theory and Practice. Interscience Publishers, Inc. NY.*
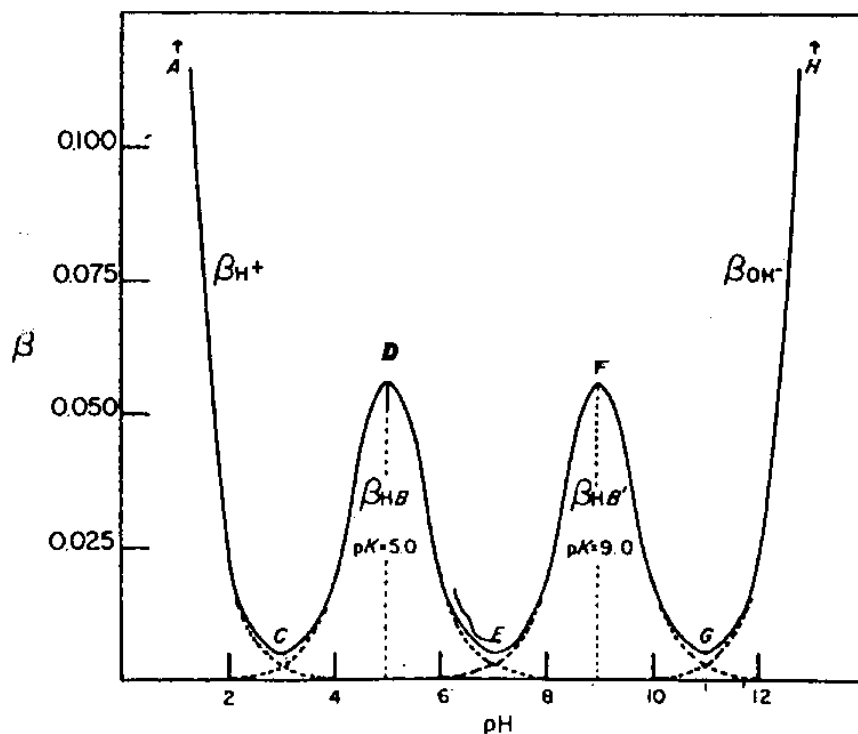

Figure 8.5. The buffering index ($) for a mixture of weak acids with pK's of 3, 5, 7, 9 and 11 to give a well buffered solution over the entire pH range. An example of a universal buffer. *From Kolthoff and Elvins (1959). Treatise on Analytical Chemistry Part I. Theory and Practice. Interscience Publishers, Inc. NY.*
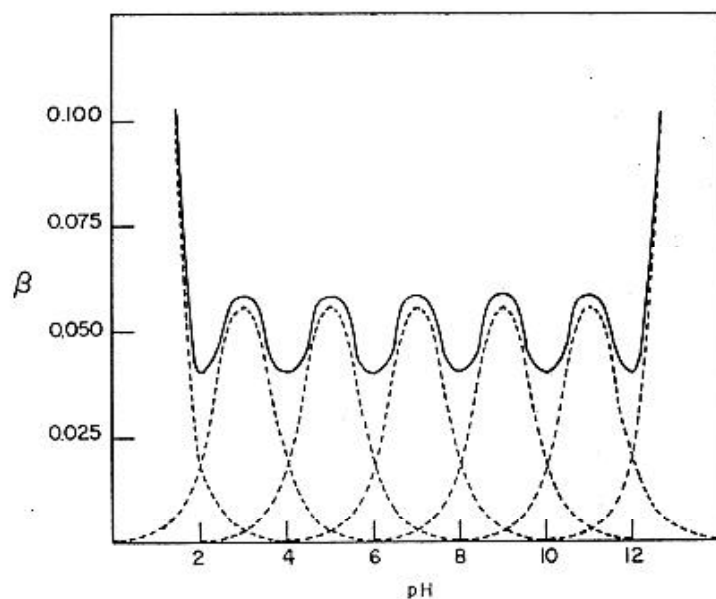
Figure 8.6. The titration curve for Los Osos Clay Loam. The data was generated by mixing either $Ca(OH)_2$ or H_2SO_4 with soil and equilibrating.
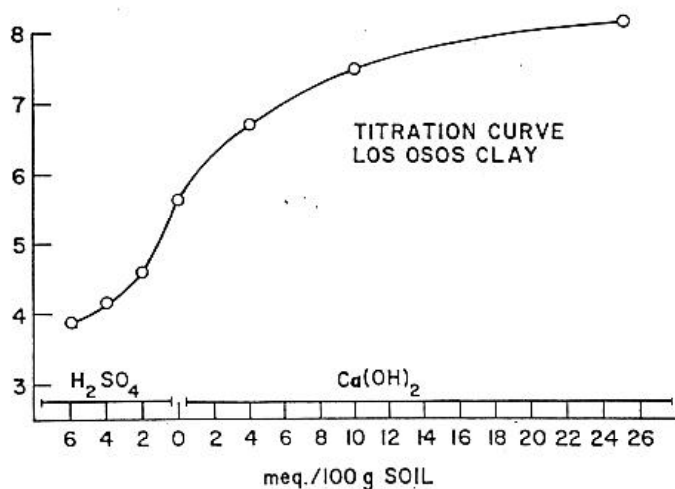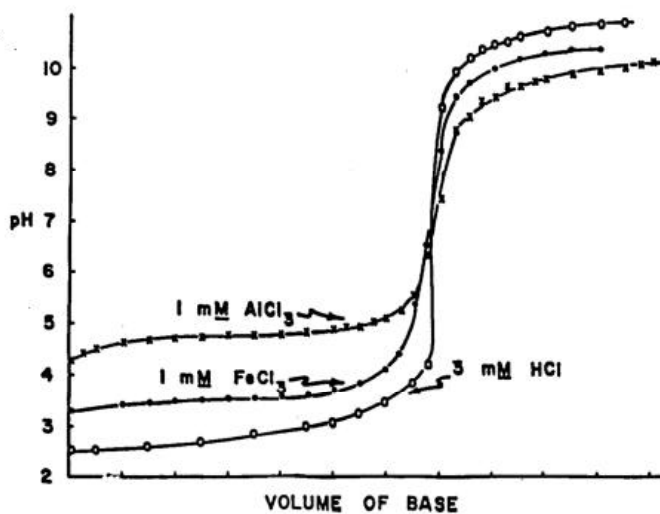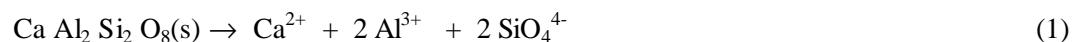

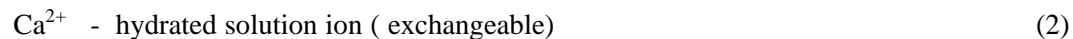***Figure 8.7 Titration curves derived from the addition of NaOH to solutions of 1 mM AlCl₃, FeCl and 3 mM HCl.***

A sampling of mineral weathering reactions which generate or consume protons.

ANORTHITE

   (HYPOTHETICAL - congruent dissolution reaction)

$$Ca\ Al_2\ Si_2\ O_8(s) \rightarrow Ca^{2+} + 2\ Al^{3+} + 2\ SiO_4^{4-} \tag{1}$$

Fate of dissolution products

$$Ca^{2+} \text{ - hydrated solution ion (exchangeable)} \tag{2}$$

$$2\ Al^{3+} + 6\ H_2O \rightarrow 2\ Al(OH)_3(s) + 6\ H^+ \tag{3}$$

$$2\ SiO_4^{4-} + 8\ H_2O \rightarrow 2\ H_4\ SiO_4 + 8\ OH^- \tag{4}$$

$$2\ OH^- + 2\ CO_2 \rightarrow 2\ HCO_3^- \tag{5}$$

Other reactions giving rise to incongruency

$$2\ Al^{3+} + 2\ H_4SiO_4 + H_2O \rightarrow Al_2SiO_5(OH)_4(s) + 6\ H^+ \tag{6}$$

$$2\ H_4SiO_4 \rightarrow 2\ SiO_2(s) + 4\ H_2O \tag{7}$$
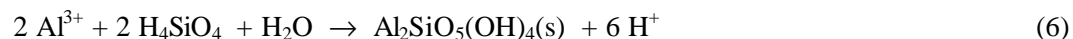
Net Soluble Products

$$Ca^{2+} + 2\ HCO_3^- \tag{8}$$

FAYALITE

   Congruent dissolution reaction

$$Fe_2SiO_4 + 4\ H_2O \rightarrow 2\ Fe^{2+} + H_4SiO_4 + 4\ OH^- \tag{9}$$
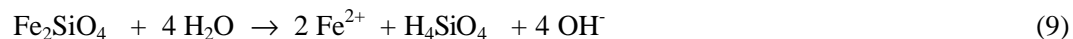
Reaction giving rise to incongruency

$$2\ Fe^{2+} + 0.5\ O_2 + 5\ H_2O \rightarrow 2\ Fe(OH)_3(s) + 4\ H^+ \tag{10}$$

PYRITE

$$FeS_2\ (s) + 3.75\ O_2 + 3.5\ H_2O \rightarrow Fe(OH)_3(s) + 4\ H^+ + 2\ SO_4^{2-} \tag{11}$$
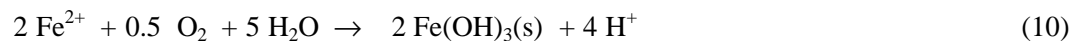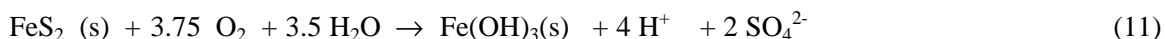
   The net result of weathering and buffering reactions in concert with the attendant climate produce either acid or basic soils. In each of these soil types there are unique reactions.

ACID SOILS - Acid soils are distinguished by a lack of easily soluble salts and an acidic reaction. The low salt content results in low ionic strengths in the solutions (E.C. values commonly ≤ 1.0). In acid soils the pH dependent exchange sites becomes increasingly occupied with hydrogen (nonexchangeable) and the CEC decreases. At the permanent sites Ca, Mg, Na, and K are reduced as the solution concentration of these ions decreases and the concentration of Al increases. Despite the fact that extractable H^+ and Al can be high, there is very little exchangeable H^+ on exchange sites in acid soils a fact not well appreciated.

EXCHANGEABLE HYDROGEN AND ALUMINUM

1. Concepts of acidity in soils and sediments are related to bound protons, to exchangeable hydrogen and to exchangeable aluminum.

> a. Protons bound by covalent as well as electrostatic forces at uncharged surface sites are not exchange ions. They may **dissociate** from the site and create a negatively charged spot or exchange site because the pH of the bathing solution rises or because the ionic strength of the bathing solution rises, also fostering dissociation. But in neither case should the **mechanism** be called exchange.

> b. Exchangeable hydrogen is properly defined as hydrated protons in the **vicinity** of negatively charged surface sites held only by electrostatic forces.

> c. Exchangeable aluminum can be displaced by salt solutions such as 1 *M* KC1. Dr. N.T. Coleman carefully examined the stoichiometry of exchange experiments and concluded that the dominant Al species was monomeric, hydrated Al^{3+}. From consideration of aluminum solubility, significant amounts of aluminum in solution and in exchange will be found only below pH 6. This is still a pH value where we might expect some $AlOH^{2+}$. However, as will be shown below and from experimental evidence, it is likely that pH in the vicinity of the exchanger is lower than in the bulk solution and thus Al^{3+} may be more important on the exchanger than in solution. The remaining question is about polymeric aluminum. Why was it not detected in significant amounts? A probable answer is that this species is stabilized at clay mineral surfaces by electrostatic binding, by van der Waal's forces and by hydrogen bonding. Similar arguments are invoked to explain the stabilization of higher molecular weight organic cations such as the herbicide paraquat or methylene blue. Thus, the small, by comparison, potassium ion, does not displace the large polymeric aluminum cation.

2. If we define exchangeable hydrogen to be only hydrated protons or hydronium ions, then we need to ask about relative amounts of this exchangeable hydrogen in soils as a function of pH. Experiments of this kind are difficult to perform particularly with aluminosilicate clay minerals, because as pH decreases, some octahedral

aluminum in the mineral comes into solution. Thus, an "acid" clay soon becomes an "acid_aluminum" clay showing mixed properties. Gilbert and Laudelot (Soil Science 100:157) have done such experiments. They concluded that hydronium has nearly the same affinity for clays as sodium. In fact the average selectivity coefficient they report was K= 0.5, which shows that this clay had a slight preference for sodium.

Recognizing that divalent calcium and magnesium are likely to be dominant ions in solution in such soil or fresh water systems, we now ask for an estimate of exchangeable hydrogen percentage (**EHP**) in such a system.

a. Assumptions:

1. $K_{Ca}^{Mg} = 1$ Therefore, $(Ca^{2+}) + (Mg^{2+}) = [\ M\ ]$

2. $K_H^M = 1 = \dfrac{(\bar{M})(H^+)^2}{(\bar{H}^+)^2 \, (M^{2+})}$

3.   Soil or sediment is saturated at $\theta = 0.38$. Therefore, 1 L of water is contained in 2632 g of dry soil.

4.   Soil exchange capacity is 19 cmoles (+) kg^{-1} soil = 50.0 cmoles (+) / 2.632 kg soil.

5.   Assume half of the soil water is in the "exchange phase"; the other half contains salts and is the "solution phase". Therefore "normality" of the exchange phase is:

$$\left(\frac{0.5 \, moles(+)}{0.5 \, L} \right) = 1 \, mole \, (+) \, L^{-1} = [\bar{H}^+] + 2[\bar{M}]$$

6.   Select a low solution phase composition of $(M^{2+}) = 10^{-3}$ mol L^{-1}

7.   Select a pH of 5 so that $(H^+) = 10^{-5}$ mol L^{-1}

8.   Substituting from (5), (6, and (7) into (2)

$$K = 1 = \left(\frac{\left(\dfrac{1 - [\bar{H}^+]}{2} \right)(10^{-5})^2}{[H^+]^2 (10^{-3})} \right)$$

$$[\bar{H}^+] = 2.2 * 10^{-4} \, mol(+) L^{-1} = 0.00022 \, mol(+) L^{-1}$$

Since the exchange concentration is l mol (+) L^{-1}, the EHP = 0.022 %.

9.0   Note that the above simplified model shows the pH in the exchange phase to be 3.66 versus

5.0 in solution phase. For a further elaboration, see Stumm and Morgan, p. 463.

10. If the same model is used, but if solution pH is chosen to be pH 3, EHP = 2.2 %. We must

conclude that in soils and sediments having a normal pH (e.g. greater than pH 4)

exchangeable hydrogen is **never** a significant proportion of the exchange capacity.

11.   Although the above statement is true, hydronium in exchange phase still has importance. First, it clearly

leads to lower pH in the aqueous part of the exchange phase. Second, if it is displaced to solution

phase, it does significantly affect acidity in solution phase. To illustrate, assume the system shown in

(8) above where $2.2 * 10^{-4}$ mol H^+ L^{-1} was the calculated concentration in 500 mL of exchange water.

The quantity of (H_3O^+) in solution phase is $10^{-6} * 0.5$ L $= 5 * 10^{-6}$ moles H^+. The quantity of H_3O^+ in

the exchange phase is $2.2 * 10^{-4}$ mol L^{-1} x 0.5 L $= 1.1$ x 10^{-4} moles H^+. If the salt content of the solution

phase is greatly increased so that the exchangeable H_3O^+ is displaced by mass action to the solution

phase the (H^+) becomes:

$$\left(\frac{1.1*10^{-4} + 5*10^{-6}}{0.5\,L}\right) \;=\; 2.3*10^{-4} \; mol \; H^+\,L^{-1}$$

If ionic strength and activity coefficients are ignored, the pH would be 3.64.

Note that the above assumes that the only buffer in the solution phase is water and that the anion of the
electrolyte is nitrate, chloride or some other component of a strong acid. Even though the quantity of
exchangeable hydronium is a small proportion of the total exchangeable ions, its displacement to solution
phase may cause a significant pH drop in solution phase.

12.   Some procedures purport to measure "exchange acidity". Although there are many variations, a common
procedure is to titrate 1 *M* KCl extracts of a soil with a standardized NaOH solution. Some of the OH^- will
neutralize H_3O^+ displaced as shown above and that is truly exchange acidity.

However, some of the hydronium being titrated came from the dissociation of bound protons (RH) by an ionic
strength effect.

$$RH = R^- + H^+$$

Note that the above appears to be an exchange reaction because the final state is an increase in exchange
capacity.

In addition, exchangeable aluminum displaced to solution phase will also be titrated by OH⁻ and appear as acidity through the reaction:

$$Al^{3+} + 3\ OH^- \ = \ Al(OH)_{3(s)}$$
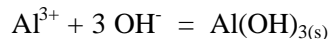
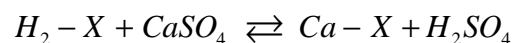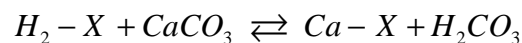Thus, such procedures measure more than "exchangeable hydrogen".

BASE SATURATION - ?

The term base saturation is a very unfortunate one. In a chemical sense Ca, Mg, K, and Na are not bases but the cations associated with many basic (OH) containing solutions. Thus NaOH is a base, not because of Na, but because OH is a strong base. In fact we have seen that in calcareous soils, Ca acts as an acid. None-the-less the term base saturation has persisted in the soils literature and is even used in the classification of soils.

$$Base\ Saturation\quad = \quad \frac{\sum Exchangeable\ Ca,\ Mg,\ Na,\ K}{CEC_{at\ pH\ 7\ or\ 8.2}}$$

Since the denominator is a function of pH (pH dependent charge) and ionic strength, measuring CEC at pH 7 or 8.2 for acid soils with field pH values of 3.5 to 5.5 is an artificial measurement and is misleading. Acid saturation is 1-B.S., and the implied acid saturation at low pH is far too large. To over come this objection, reporting of effective CEC (CEC_e) is becoming more common. That is the CEC of the sample at field pH values. Another approach is to sum the extractable cations including Al and other acid cations.

Lime requirement. Liming or the addition of $CaCO_3$ containing material to acid soils is a common practice designed to improve the fertility of acid soils. Liming accomplished several things simultaneously which generally improves plant growth. From a chemistry perspective, it increases pH, increases Ca (and Mg for dolomitic lime) status, while lowering the availability and toxicity of Al and Mn. As with base saturation, it must be appreciated that Ca is not the active agent increasing pH. The alkalinity is added by the carbonate and bicarbonate ions associated with lime. To illustrate this point consider the parallel reactions of $CaSO_4$ and $CaCO_3$ added to a soil with hypothetical exchangeable H^+. The reactions are as shown below:

$$H_2 - X + CaCO_3 \rightleftarrows Ca - X + H_2CO_3$$

$$H_2CO_3 \rightleftarrows CO_2 \ + \ H_2O$$

$$H_2 - X + CaSO_4 \rightleftarrows Ca - X + H_2SO_4$$
$$H_2SO_4 \rightleftarrows SO_4^{2-} \ + \ 2H^+$$

Since gypsum actually acidifies a system with "exchangeable acidity", while lime causes a rise in pH, one must attribute the change to the anion and not the cation. Actually the cation is acidifying by displacing any acid producing cations into solution, and by deprotonating sites ionic strength increases.

Regardless of the mechanism involved in pH increases, the buffering capacity of a soil directly relates to the amount of lime necessary to raise the pH to an acceptable level. Page 222-223 in *Bohn et al.* describes the measurement of lime requirements.

Saline and Alkali soils

Alkaline reactions and relatively high ionic strengths typify soils of arid regions where soluble and sparingly soluble salt accumulate. We have already examined the chemistry of calcium carbonate and the implications associated with carbonate accumulations in soils. In this section we will extend the discussion of carbonates to systems impacted by other soluble salts.

ESP & SAR. SAR was covered in the exchange section. Note that SAR was developed and is applicable to arid regions soils where there is an appreciable amount of soluble and exchangeable Na and smectitic clays. Saturation of the exchange complex with Na is an important factor in the physical behavior of arid soils. One interesting feature of the exchange process, is the apparent change in selectivity for Na as solution ionic strength changes

Exchange Composition During Desiccation of Solution Phase. We have covered desiccation of soil solutions in the exchange section. Note that the idea of desiccation is most relevant for arid region soils where moisture content varies seasonally with rainfall and more frequently with irrigation.

Carbonate and bicarbonate hazard - If the carbonate and bicarbonate values of waters exceeds the level of Ca and Mg, then the divalent ions and especially Ca will precipitate leaving the soluble carbonates Na and K in solution. Since Na is a much more abundant soluble salt in most soils, this is tantamount to saying that Na hazard is high in solutions with "excess" carbonates.

As we learned in the carbonate section, pH will be limited by the solubility of the most soluble carbonate. If Na or K carbonates are present, then pH can exceed the limits imposed by $CaCO_3$. Therefore, pH values in excess of 8.0 or so imply the present of Na, Mg, or K carbonates.

Dispersion and Na Effected Soils - In the discussion of double layer theory we found that ions are "loosely" associated with the negative sites on soil colloids. This swarm of ions (counter ions) distributed away from the colloid surface dictates that an electric field also extends away from the surface and therefore, the negative fields of soil colloids can interact. Since, the fields of

most soil colloids are negative, there is a repulsion between two negatively charged colloids. These electrostatic effects are "long range" interactions and are always repulsive. At shorter range there are attractive forces which cause colloids to aggregate or flocculate. A balance between these attractive and repulsive forces determines whether or not colloids flocculate. The short range forces are more or less independent of the solution phase, while the long range forces depend on ionic strength and the nature of the cation

Hydrolysis of Na - Colloids Sodium saturated colloids are subject to hydrolysis and this reactions can increase solution pH to values as high as 9. Hydrolysis is important only when the ionic strength of the solution is lowered by dilution with rain water or irrigation water.

Reclamation of Saline and Alkaline Soils.

Reclaiming soils with excess salts and high pH depends on several factors. We will not dwell on the process, but only point out a few salient features from a soil chemistry perspective. Soils affected by salt and high pH are group into saline, alkali, and saline alkali as well as normal. The distinction among these categories is pH, electrical conductivity (E.C.), and exchangeable Na percentage. As we know from laboratory, the measurement of pH and E.C. is quite easy, rapid and imparts quite a bit of information about the soil chemistry in these systems. Information on exchangeable Na percentage is more difficult to get and is the reason that SAR is used to estimate ESP.

Soils are classified as follows:

Saline = E.C. > 4 and ESP < 15

Saline Sodic (Alkali) = E.C. > 4 and ESP > 15%; generally, pH < 8.5.

Sodic (Alkali) = E.C. < 4, and ESP > 15 %; 8.5 < soil pH < 10.0

Nonsaline, non sodic = E.C. <4, ESP < 15% and pH generally < 8.5.

In order to reclaim saline and saline-sodic soils there are several options.

Saline Soils. It is necessary to leach the excess salts from the soil profile or to remove sufficient salts from the rooting zone to allow for plant growth. Leaching with low ionic strength water can result in deflocculation of the soils and restrict infiltration and drainage. Since these soils are probably in poorly drained landscapes,

methods to remove the drainage waters are often necessary. A source of "good" water for leaching is often problematic.

Sodic Soils. Reclamation of sodic soils requires a reduction in exchangeable Na levels. The high Na-Ex levels in these soils along with low salt levels generally, means poor physical properties. Therefore, a source of Ca is usually needed to replace the exchangeable Na. Gypsum is a common amendment applied to sodic soils. It functions to provide a source of soluble Ca for exchange with Na and increases the ionic strength. Increased ionic strength and soluble Ca levels help flocculate soil particles and improve water movement into and through the soil.

If the soil contains lime, applications of elemental sulfur (S^o) is another option. As the sulfur is oxidized to sulfuric acid, the protons dissolve $CaCO_3$ consuming the proton and the end product is gypsum. A reduction in pH will also help to flocculate the soil as this pH reduction will lower soil CEC. Remember from the carbonate section that the addition of gypsum to a $CaCO_3$ system will reduce the pH.

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Review Questions

1. What is the general definition of a buffer?

2. What are the sources and sinks for H^+ and OH^- in soils?

3. Soils can be considered to be environmental buffers. In what ways do soils buffer?

4. Interlayer Al does not seem to be observed in very acid and very basic soils. What are some possible explanations for this observation?

5. pH and soil Eh are "master variables" in soil systems. What does this mean?

6. Soils are normally found to have pH values between 4 and 9. Why.

7. What is beta in relation to soil buffering?

8. What are the maximum and minimum values for $ in a water system?

9. How does $ relate to concentration and pK of weak acids?

10. What is the general form of the soil solution volume vs concentration curve (desiccation curve) for soil salts? What processes will modify the shape of this curve?

11. As a soil solution is diluted, the higher valent ion is preferred by the solid phase. What predicts this result? How does this relate to alkaline soils?

12. Why is H^+ seldom if ever a significant fraction of the exchange complex, even in very acid soils?

13. Even though Na ion is not strongly preferred by soil solids, it often becomes a significant exchangeable component in arid soils. What would explain this apparent anomalous behavior?

14. What components affect buffering in different soil pH regions?

15. What soil characteristics affect buffering?

16. What is bases saturation? What is abhorrent about the term?

17. When does Ca^{2+} act as an acid in soil, systems?

18. Why is there confusion about the place of H^+ in the replacement series?

19. Does weathering of minerals generate alkalinity?

20. What is congruent and incongruent weathering?

21. Show that hydrolysis can generate both acidity and alkalinity?