Lab 8 – Dynamic Soil Systems I: Soil pH and Liming

Objectives:

- To measure soil pH and observe conditions which change pH
- To distinguish between active acidity (soil solution pH) and exchangeable acidity
- To understand the function of CO_2 in determining pH
- To understand liming reactions and the calculation of lime requirements

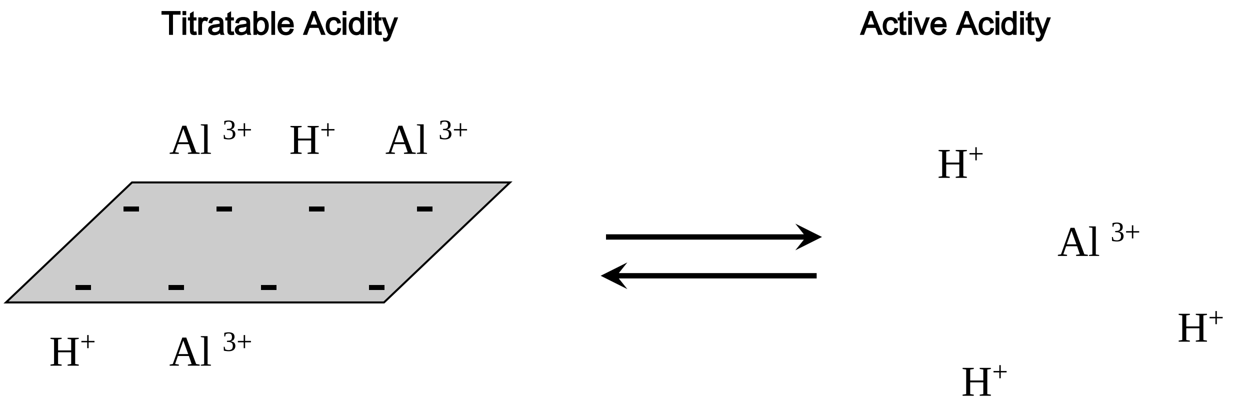
Active and exchangeable acidity

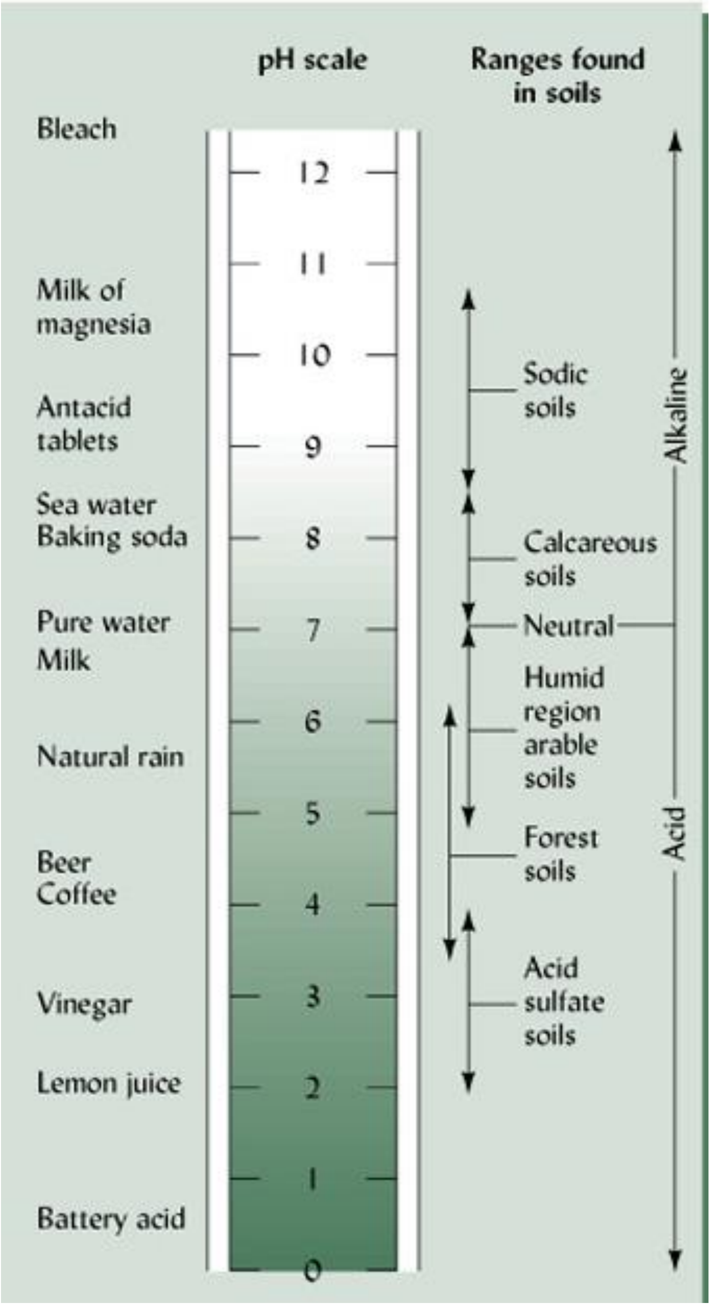
The pH of a soil is a measure of the **hydrogen ion** concentration in the soil solution. pH is a the negative logarithm of H^+ concentration in moles / liter:

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

and is therefore a **solution** measurement which only **reflects** the presence of acid cations adsorbed on soil colloids. A pH scale is shown below along with some reference points.

Hydrogen ion concentration is acidic soils is largely determined by the number of hydrogen ions that disassociate from the cation exchange complex. Dissociation of hydrogen is directly related to the fraction of the exchange complex that is occupied by hydrogen and aluminum ions. pH decreases (or acidity increases) as percentage saturation of H^+ and Al^{3+} increases. Hydrogen ion in soil solution is termed **active acidity** and is the acidity measured by common pH tests. Hydrogen and aluminum ions adsorbed on soil colloids are termed **exchangeable** (*or sometimes reserve*) **acidity**. Exchangeable acidity is much larger than active acidity.





From Brady and Weil, 2002, The Nature and Properties of Soil. 13th Edition

Soil pH and Salt Concentration

Acidic cations on soil colloids will exchange with cations in the soil solution. The amount of exchange is proportional to the concentration of all cations in solution, since equilibrium conditions exist. Consequently, pH of a soil solution decreases as the concentration of neutral salts (eg. NaCl, $CaSO_4$, etc.) increases.

This phenomenon has considerable influence on measurements of pH. Measurements of pH in a soil that has been dried will be lower than those measured in the same soil when wet. Measurements of soil pH in water will be higher in situ. Further fertilizer salts will lower pH measurements.

Several methodologies have been proposed for measuring pH. Measurement in distilled water is common, but its limitations in replicating field conditions must be recognized. Measurement in 0.01 M $CaCl_2$ has advantages in that it replicates "typical" soil solution concentrations at "average moisture contents".

EXERCISE A:

1. Weigh 5 grams of moderately acid soil (Windsor) into three 25 <u>or</u> 50 ml beakers and label them as "water", "$CaCl_2$" and "KCl".
2. Add 10 ml of distilled H_2O to the beaker labeled "water".
3. To the beaker labeled "$CaCl_2$" add 10 ml of distilled H_2O plus two drops of 1 M $CaCl_2$
4. To the beaker labeled "KCl" add 10 ml of distilled H_2O plus two drops of 1 M KCl.
5. Stir each beaker and allow to stand for 15 minutes
6. Measure and record Ph of each using a pH meter.

Distilled H_2O ____________________
0.01 M $CaCl_2$ ____________________
0.01 M KCl ____________________

7. Measure the pH of the same soil using a pH test kit. Compare this pH to the ones recorded using the meter. ____________________ = test kit pH

Explain these results:

Calcium Carbonate Reactions

Soils which contain calcium carbonate are termed **calcareous**. In these soils, the pH is regulated by an equilibrium involving soluble calcium and carbon dioxide. The higher the gas pressure of carbon dioxide, PCO_2, in the soil air, the higher is the concentration of dissolved CO_2 (carbonic acid) in the soil solution.

$$\text{Dissolved } CO_2 \text{ concentration} = (H_2CO_3) = 0.03\, PCO_2$$

Since microbial and plant root metabolism in the soil generates CO_2, the dissolved carbonic acid can be much higher in soil solution than is in water directly exposed to the atmosphere.

The carbonic acid dissociates to bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions in soil solution:

$$H_2CO_3 = H^+ + HCO_3^-$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

However, in soils containing large quantities of calcium, soluble carbonate does not reach high concentrations because it precipitation of calcium carbonate:

$$Ca^{2+} + CO_3^{2-} = CaCO_3$$

And the pH does not attain very alkaline values. It is only in soils containing relatively little calcium, and a great deal of sodium, that soluble carbonates accumulate in the form of $NaHCO_3$ and Na_2CO_3, salts which are very soluble and produce alkaline soil solutions. Such soils are termed **saline** or **sodic** and occur in arid climates of the world.

EXERCISE B:

1. Fill a test tube about ½ full of **tap** water.
2. Add 5 drops of pH indicator solution and agitate. Note color and estimate pH from color chart. pH = ____________________.
3. Now blow air in the water with a straw. Note color and estimate pH. pH = ________.
4. Finally blow pure CO_2 gas from a tank into the water. Note color and estimate pH.
   pH = ____________________.
5. Explain results by writing the relevant chemical reaction.

EXERCISE C:

1. Put 5 ml of saturated $Ca(OH)_2$ into a test tube.
2. Using a straw, blow air into this solution of $Ca(OH)_2$ until a precipitate forms.
3. Pass more CO_2 into the suspension by using CO_2 from a tank until the precipitate disappears.

1. What is the chemical reaction for the dissolution of CO_2 into water?

2. What is the chemical reaction for the formation of the precipitate that formed (in step two above) when air was blown in the $Ca(OH)_2$ solution by mouth?

3. What was the chemical reaction for the subsequent disappearance of the precipitate when CO_2 was blown into water from the tank (step three above)?

EXERCISE D:

1. Add a few drops (3 or 4) of HCl from the dropper to a little of each soil (Windsor, Hudson and Ontario) in a small beaker. Which soil is calcareous?
2. Weigh 10 grams of the calcareous soil into a 50 ml beaker.
3. Add 20 ml of water, stir until mixed and allow to sit for 10 minutes.
4. Measure pH with a pH meter and record pH.

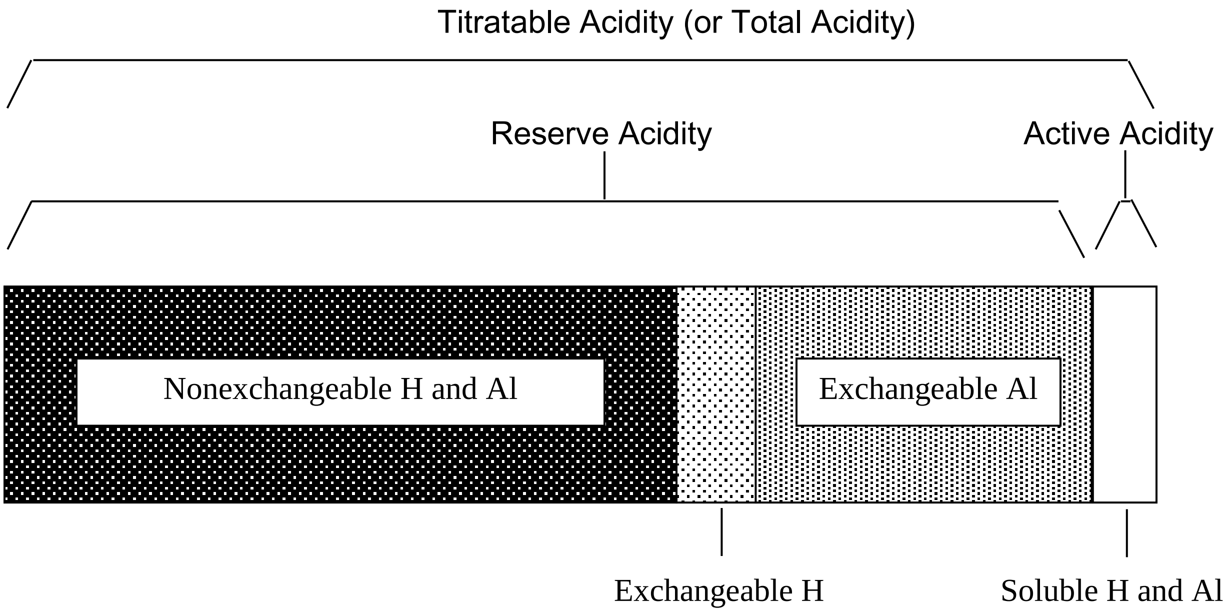
pH = ____________________.

5. Bubble CO_2 (from gas cylinder) into the suspension for a few minutes. Again measure and record the pH. pH = ____________________.

What is the chemical equation that explains this reaction?

Liming

The lime requirement of a soil is the quantity of alkali that must be added to that soil to bring the pH to a desirable value for optimum plant growth (usually 6-7). The exchangeable acidity of soils, which is the quantity of H^+ and Al^{3+} cations that can be exchanged into solution by a neutral salt, generally underestimates lime requirements because not all of the acid content of soils can be exchanged by salts into solution. [The relationships among the various forms of acidity are depicted below.]



Unfortunately, the term “exchangeable acidity” is used ambiguously in many soil textbooks and soil analysis laboratories, sometimes referring to the acidity measured by base titration of the soil.

Truly Exchangeable soil acidity is usually much lower than the lime requirement, as the diagram above illustrates.

EXERCISE E:

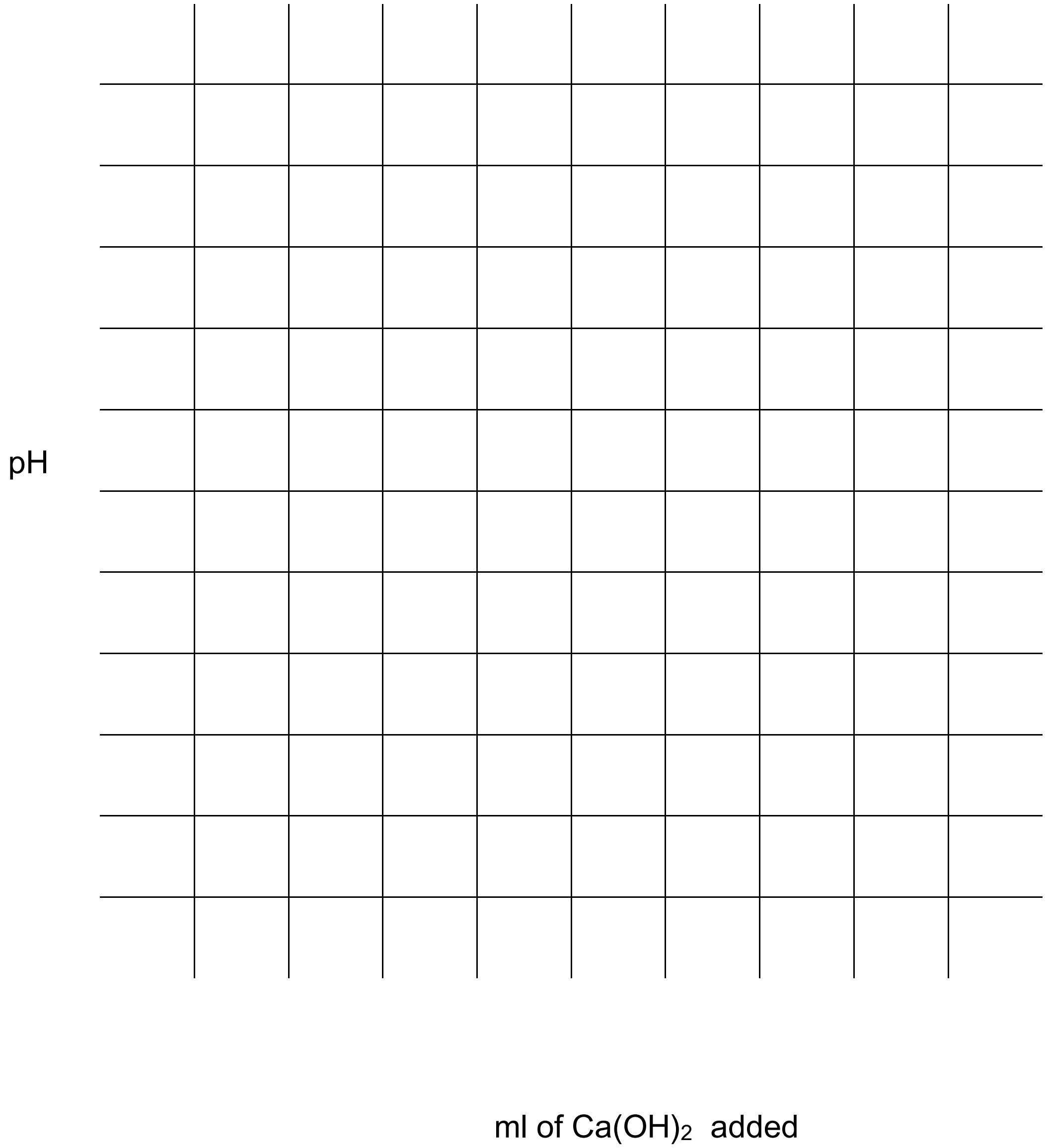
1. Place a 2 gram sample of Windsor soil in each of five 125 ml Erlenmeyer flasks. Label the flasks 0, 1, 3, 5 and 8.

It is important to label the flask as they can easily be confused

2. Add 50 ml of 1 M KCl to each.
3. Add 1 ml of 0.02 N $Ca(OH)_2$ from the pipette to the flask labeled “1”. Similarly add 3 ml, 5ml and 8 ml to the flasks labeled “3”, “5” and “8”. The “0” flask receives no $Ca(OH)_2$.
4. Mix by swirling and set aside for 10 minutes – swirl occasionally during this period.
5. After 10 minutes, measure pH of each using a pH meter.
6. Label Titrations Acidity Curve below.
7. Plot pH vs. ml of $Ca(OH)_2$ onto Titrations Acidity Curve below.
8. Extrapolate curve to pH 7 and measure the ml. of $Ca(OH)_2$ needed to raise the ph to 7.

9. Calculate Titratable acidity – the number of millimoles of H^+ and Al^{3+} per unit weight of soil that were neutralized by $Ca(OH)_2$ in changing the soil pH from its original value to pH 7.

Titrations Acidity Curve



$$\text{Titratable acidity} = (\text{ml } Ca(OH)_2 \text{ solution to reach pH 7}) \times 0.02 \text{ mmol } OH^{-}/\text{ml} \times \frac{100 \text{ g soil}}{2 \text{ g soil}}$$

= ___________________ mmole (p^{+})/100 g **or** cmole/kg

The titratable acidity is sometimes called the “exchangeable acidity”, although part of this acidity is difficult to exchange. The actual exchangeable acidity will be measured in a later exercise.

Lime Requirement

Application of appropriate quantities of lime to acidic soil has the following results:

- Decreases hydrogen ion concentration
- Decreases solubility of iron, aluminum, manganese and some other trace elements
- Increased availability of phosphates and molybdates
- Increases exchangeable calcium and magnesium

The indirect effects of lime; increased nutrient availability and decreased toxicity of aluminum and manganese are more important for plant growth than direct effects of pH. However, if incorrect quantities of lime are applied, deleterious effects result, e.g. overliming decreases solubility and availability of many trace elements. Soils are usually limed to pH values somewhat less than 7 to avoid overliming.

Calcium carbonate is the most common liming material although oxides and hydroxides of calcium and magnesium compounds are also used. The chemistry in the soil of all sources of lime are similar, eg:

$$CaCO_3 + 2\ H_+ \leftrightarrow H_2CO_3 + Ca^{2+} \leftrightarrow CO_2 + H_2O + Ca_{2+}$$

Neutralization and cation exchange proceed simultaneously. Excess Ca^{2+} displaces exchangeable H^+ and H^+ is neutralized by CO_3^{2-}. The **lime requirement** is equivalent to the amount of basic material required to neutralize most of the available acid cations, H^+ and Al^{3+}, in the soil. Consequently, one can directly determine lime requirement by determining **titratable acidity** to be neutralized to reach the desired pH.

Titratable acidity at pH 7 can be used to determine lime requirement. The volume of base required to change pH from the original value to the desired pH is read from the graph in **EXERCISE E**. The amount of lime ($CaCO_3$) equal in neutralizing capacity to the volume of added $Ca(OH)_2$ is the lime requirement. Calculated as follows:

$$\frac{\text{CaCO}_3\text{ requirement}}{\text{g soil}} = \frac{\text{mmoles H}^+\text{ neutralized}}{\text{g soil}}$$

$$= \text{milliequivalents (meq) Ca(OH)}_2\text{ added to raise 1 g soil to pH 7.}$$

$$= \text{ml Ca(OH)}_2\text{ added} \times \frac{0.02\text{ Ca(OH)}_2\text{ meq}}{\text{ml}} \times \frac{50\text{ mg CaCO}_3}{\text{meq}} \times \frac{1}{2\text{ g soil}}$$

$$= \underline{\hspace{3cm}}\text{ mg CaCO}_3\text{/g soil}$$

EXERCISE F:

1. Calculate the requirements per g soil for the soil used in Exercise E. (show your work on back)

   Lime requirement _________________________ / g soil

Lime requirement is usually expresses in kg or metric tons per hectare. There are approximately 2 x 10^6 kg of soil in the plow layer of one hectare.

$$\text{Lime requirement}\left[\frac{\text{kg CaCO}_3}{\text{hectare}}\right] = \frac{\text{mg CaCO}_3}{\text{g soil}} \times \frac{10^3\text{ g soil}}{\text{kg soil}} \times \frac{2 \times 10^6\text{ kg soil}}{\text{hectare}} \times \frac{1\text{ kg CaCO}_3}{10^6\text{ mg CaCO}_3}$$

2. Show your calculations and answer to determining the lime requirement to raise the pH to 7 for a hectare of the soil used in EXERCISE E.