LABORATORY 7

SOIL REACTION (pH) AND LIME REQUIREMENT

I   Objectives

Gain a better understanding of soil pH and how it is measured. Understand how lime requirement is determined.

II   Introduction

  A   Soil Reaction (pH)

The relative amount of acidity and alkalinity in a soil is referred to as the **soil reaction**. Soil reaction is expressed in pH units, covering a scale from 0 to 14. pH values less than 7.0 indicate soil acidity, the value 7.0 is neutral and values greater than 7.0 indicate soil alkalinity. pH is defined as the negative logarithm of the H^+ activity (concentration, approximately). Soil pH is a measure of the amount of H^+ ions in the soil solution, but it does not measure the amount of H^+ adsorbed onto exchange sites.

Most soils have a pH in the range of 3.5 to 8.5. Soil pH is important inasmuch as it is related to many other soil properties. For example, many of the desirable soil microbes that carry out organic matter decomposition and release of essential plant nutrients are much more active at near neutral pH values. Their activity results in stronger binding of soil aggregates into a stable soil structure, improving conditions for plant growth. Also, the availability of most essential plant nutrients is near optimum and the availability of toxic elements is low in mildly acid to neutral soils. Thus, if we know pH, we have some idea about a host of other soil properties.

However, as important an indicator of the soil biological and chemical environment as it is, soil pH tells us little about the absolute concentration of adsorbed acidic and basic cations. Rather, it is the amount of adsorbed acidic (H^+, Al^{+3} and hydroxy aluminum) and basic (principally, Ca^{+2}, Mg^{+2}, K^+, and Na^+) cations that largely controls soil pH and buffers it with respect to an imposed change.

There is a positive relationship between soil pH and the proportion of cation exchange sites occupied by basic cations. As the fractional saturation of the CEC with basic cations increases, soil pH increases. When the proportion of cation exchange sites occupied by basic cations is expressed as a percentage it is called the **percent base saturation** (**% BS**). Conversely, as base saturation decreases, pH decreases. Unfortunately, the specific relationship between base saturation and pH varies widely from one soil to another depending on mineral and organic matter composition.

The natural tendency is for soils to become depleted of basic cations, enriched in acidic cations and, therefore, acidic. During weathering, basic cations are lost through leaching and are replaced by H^+ and Al^{+3} ions, decreasing the base saturation and pH. A major source of soil acidity is carbonic acid (H_2CO_3) formed by dissolution of CO_2 in the soil solution. The CO_2 is due primarily to biological activity such as organic matter decomposition and root respiration. When H_2CO_3 ionizes, it releases H^+ ions. The H^+ ions replace exchangeable bases in the soil, making it more acidic. Also, this natural tendency toward acidification is exacerbated by crop production. Basic cations are removed in harvest. Also, some fertilizers are acidic and add H^+ ions to solution.

Adsorbed H^+ and Al^{+3} ions are called **reserve** or **potential acidity**. When H^+ ions in the soil solution are neutralized by addition of a base, these are largely replaced by previously adsorbed H^+ or by H^+ produced by hydrolysis of Al^{+3}. Unless a big slug of base is added, little or no detectable increase in pH may occur. Therefore, the pH is said to be **buffered** or resistant to change. In order to raise the pH a unit or more, enough base must be added to replace a substantial fraction of the adsorbed acidity. Clearly, the greater is the amount of adsorbed acidity, the greater is the amount of base needed to increase soil pH. Thus, pH buffering in a soil is directly related to the CEC of the soil. Soils with high CECs are more highly buffered and require more base to bring about a specified pH change.

Soil pH is also buffered against a decrease in pH. If H^+ ion is added to a soil, much will adsorb to the exchange complex, displacing previously adsorbed basic cations. Unless a lot of acid is added, there will only be a small decrease in pH. However, with massive or continued (as in natural weathering) addition of acid, the pH decreases since exchangeable bases are depleted due to cation exchange and leaching.

Calcareous soils contain small particles of calcium carbonate (lime) and have alkaline pHs. To lower the pH of these soils, all of the calcium carbonate must be undergo reaction with acid before the added acid will begin to replace the exchangeable bases and lower the soil pH. As a result it is usually impractical to lower the pH of calcareous soils because their total calcium carbonate content is usually very large.

B   Liming and Lime Requirement

Lime is added to increase the base saturation and raise pH of an acid soil. When soil is amended with lime, H^+ ions are neutralized, Al^{+3} ions are precipitated into non-toxic forms, Ca^{2+} and Mg^{2+} from the lime increase the % BS, the pH rises and crop growth increases. The optimum pH for plant growth varies with different crops.

In determining how much lime to add, soil pH is first measured to determine if it is below the optimum pH range for the crop to be grown and, if so, lime is added to raise the pH into the optimum range. The amount of $CaCO_3$ that must be added to raise the soil pH from its current value to the desired value is called the **lime requirement**.

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But exactly how much lime is needed? Methods used to determine lime requirement vary from state to state. In Louisiana, the **soil-lime incubation method** is used. Increments of base are added to samples of soil, then the pH is measured after the added base has reacted with soil acidity. A plot of the results gives the relationship between amount of base added and resulting pH. The amount of base required to achieve the target pH is determined from this plot.

Added base is expressed in milliequivalents (meq), where meq = mL x $\underline{N}$ (mL of added base x normality of base). Since the mass of soil incubated with base is known, the required meq of base / kg of soil is easily determined. Scale-up to kg of lime per ha (or lbs per ac) is straightforward.

In units of kg / ha

kg lime / ha = 2 (milliequivalent weight) (meq base / kg)

In units of lbs / ac

lbs lime / ac = 2 (milliequivalent weight) (meq base / kg)

These identical conversions are based on the assumption that the mass of a hectare furrow slice (depth 15 cm) is 2 million kg and that the weight of an acre furrow slice (depth 6 inches) is 2 million lbs.

There are three types of **lime materials** –oxides, hydroxides, or carbonates of calcium or calcium and magnesium. Respective examples are CaO, $Ca(OH)_2$ and $CaCO_3$. The carbonates are the most widely used lime materials. These are mined, crushed and ground finely enough react fairly quickly (need high surface area for rapid dissolution before any appreciable neutralization can occur). Oxides are produced by heating carbonates, thereby driving off CO_2. Hydroxides are hydrated oxides. The oxides and hydroxides are more soluble and react faster but are more expensive.

All lime materials react with H_2O or CO_2 in the soil to form $Ca(HCO_3)_2$. The bicarbonate (HCO_3^-) then reacts with H^+ to form H_2CO_3, which decomposes to CO_2 and H_2O. The CO_2 escapes to the atmosphere and neutralized H^+ is left behind as water. The pH increases, as does % BS when Ca^{2+} from the lime is adsorbed onto the exchange complex.

A somewhat confusing term applied to lime materials is **CaCO₃ equivalent**. This is a rating, relative to pure $CaCO_3$, of how much soil acidity an equal mass of another lime material can neutralize. Pure $CaCO_3$ is assigned a $CaCO_3$ equivalent of 100. Let's see how it works using CaO as an example. Since the equivalent weight of CaO is 28 g / mole compared with 50 g / mole for $CaCO_3$, any given mass of CaO can neutralize 50 / 28 times as much acidity as can an equal mass of $CaCO_3$. Thus, the $CaCO_3$ equivalent of pure CaO is 179. Purity as well as equivalent weight determines the $CaCO_3$ equivalent of a lime material. For example, $CaCO_3$ that is mixed with an equal mass of non-lime material has a $CaCO_3$ equivalent of 50.

III   Procedures

A   Soil Reaction (pH)

Test for Soil Alkalinity

1.   Put about a gram each of Norwood silt loam, Sacul Bt and Darley sandy loam in separate porcelain dishes.

2.   Add a few drops of dilute HCl to each soil and watch for an effervescence of CO_2, which indicates that the soil is alkaline due to the presence of $CaCO_3$. Record results.

Measure Soil pH

1.   Weigh three 10 g samples of each of the above soils into small wax-coated cups.

2.   Add 10 ml of distilled water to one sample of each soil and stir with a glass rod.

3.   Add 10 ml of 0.05 N NaOH to the second sample and stir.

4.   Add 10 ml of 0.05 N HCl to the third sample and stir.

5.   Let the soils equilibrate for 10 minutes, then measure the soil pH using the pH meter. Stir the solution again before taking the reading. Record results (Table 1).

B   Lime Requirement for an Acid Soil

1.   Weigh 10 g of Darley soil into each of 4 waxed cups.

2.   Add either 0, 4, 8, or 12 mL of 0.05 N NaOH to each of the four cups.

3.   Add either 12, 8, 4, or 0 mLof distilled H_2O to each of the 4 cups so that the total volume of liquid is 12 mL in each cup.

4.   Stir the soil samples and let react for one hour with occasional stirring. *For greater accuracy the pH readings should be taken after about 8 h.*

5.   Measure the pH of the soil in each cup and record (Table 2).

IV Worksheet and Questions

A Soil Reaction (pH)

Soil Alkalinity

1. Which soil showed CO_2 effervescence when HCl was added?

2. Write a chemical reaction showing how the CO_2 was produced.

3. When the acid (HCl) was added to the soil containing lime ($CaCO_3$), CO_2 was produced. If lime is added to an acid soil, is CO_2 produced?
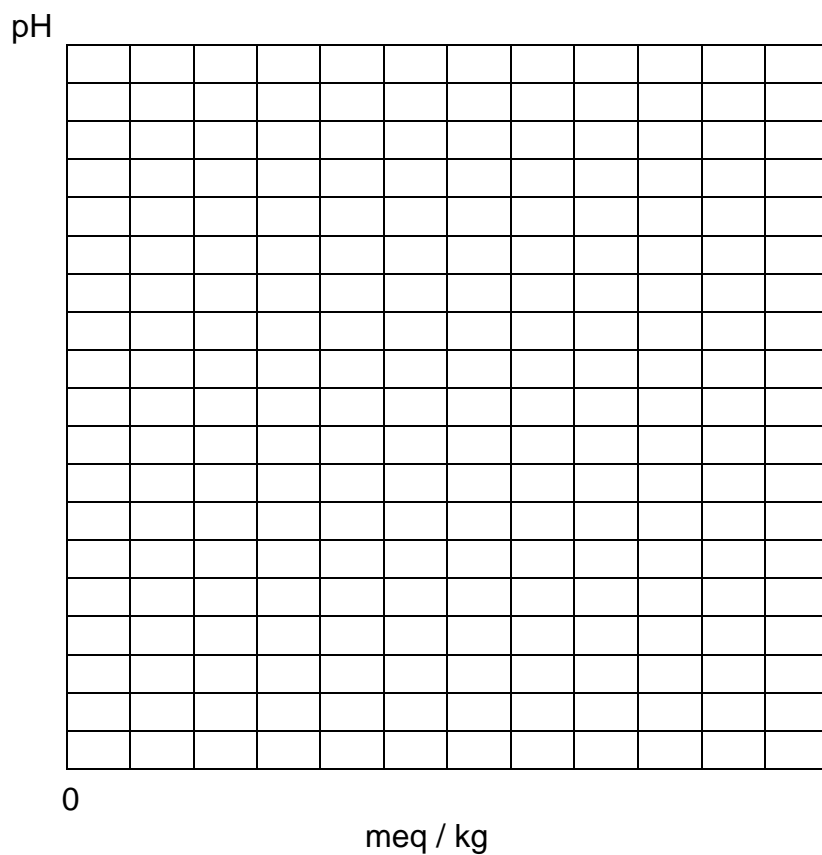
Soil pH

Soil	pH in d-water	pH in 0.05 N NaOH	pH in 0.05 N HCl
Norwood			
Sacul			
Darley			

1. Which of the acid soils is more highly buffered?

2. Explain why the same amount of base or acid caused a different pH change in two acid soils

3. Why didn't the acid lower the pH of the calcareous soil?

B   Lime Requirement of an Acid Soil

mL NaOH added	meq added	meq / kg	Equilibrium pH
0.0			
4.0			
8.0			
12.0			

1.   Graph soil pH and meq of base added.

pH

meq / kg

2.   To raise the soil pH to 6.4, how many meq of base / kg would be needed?

3.   Calculate the lime requirement in lbs / ac to raise the soil pH to 6.4 by applying

CaCO₃	CaO	Ca(OH)₂	90 % pure CaCO₃

4.   Which of the above liming materials has the highest neutralizing power?   The lowest?

5.   Calculate the $CaCO_3$ equivalent of CaO.

6.   Why does lime particle size affect the rate at which soil acidity is neutralized?

7.   Write a chemical reaction showing the neutralization of soil acidity by adding $CaCO_3$ to the soil.