

Chapter 3

Recommended Soil pH and Lime Requirement Tests

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Soil pH is a measure of hydronium ion (H_3O^+ , or more commonly the H^+) activity in the soil solution. Activity is similar to concentration in non-salt-affected soils. Soil pH influences many facets of crop production and soil chemistry, including availabilities of nutrients and toxic substances, activities and nature of microbial populations, and activities of certain pesticides. Soil pH is defined as the negative logarithm (base 10) of the H^+ activity (moles per liter) in the soil solution. As the activity of H^+ in the soil solution increases, the soil pH value decreases. Soils with pH values below pH 7 are referred to as "acid" and those with pH values above pH 7 as "alkaline"; soils at pH 7 are referred to as "neutral."

In most soils the soil pH is buffered by several components of the solid phase, including hydroxyaluminum monomers and polymers, the soil organic matter, and (in alkaline soils) undissolved carbonate compounds. An equilibrium condition exists between these components and the soil solution such that when acid or base is added to the solution, the buffering agents may absorb the addition and/or release acid or base to maintain the initial equilibrium. Thus, a change in soil pH due to the addition of an acid or base is usually much less than predicted by neutralization based only on the quantity of acid or base present in the soil solution (as given by the soil pH). Lime requirement tests for soils, which generate recommendations for effecting relatively long-term changes in soil pH, are designed to evaluate the buffering power of soils. In the Northeast, lime requirement is estimated by several techniques. Most laboratories use a chemical measure of soil buffering, such as a buffer pH (SMP, Adams-Evans), titratable soil acidity, or reactive aluminum, while others measure soil pH and estimate buffer capacity from soil organic matter or texture.

Soil pH Determination

Soil pH is usually determined potentiometrically in a slurry system using an electronic pH meter (McLean, 1982). The proliferation of pH meters in recent years precludes an in-depth discussion of meter operation; specific instructions are provided with individual units. However, several precautions are presented as general considerations for all labs. First, electrodes should be checked and maintained frequently to prevent residue buildup which may affect operation. Rinsing between each soil sample, however, is not usually necessary. Electrodes should be protected in a way which prevents insertion to the very bottom of a slurry vessel which will cause abrasion of the sensing surface, decreasing electrode life and causing inaccurate readings. All meters should be calibrated routinely at two points before operation. One point of calibration should be at pH 7, while the other should be chosen based on the range of soil pH normally encountered by the lab. A lab dealing mainly with acid soils should calibrate across the acid range (second point at pH 4, for example) while a lab dealing with mainly alkaline soils should calibrate across the alkaline range (use second pH buffer at pH 9 or 10).

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Reference and/or combination electrodes for measuring soil pH should be chosen carefully because flow rates at the liquid junction can affect the accuracy of soil pH readings. Labs may wish to use a set of reference soil samples of known pH to evaluate the performance of electrodes. Such samples should be stored and handled under carefully controlled conditions to prevent changes in soil properties over time. The reference soil pH of these samples should be determined using the average reading of several meters. Electrodes that fail to produce pH readings consistent with established values when calibrated with clear buffers can be calibrated successfully using the reference soils themselves, but only if soil storage and handling are well controlled.

Soil pH is normally measured in a soil-water slurry. The presence of soluble salts in a soil sample may affect pH, and for that reason, some analysts prefer to measure it in a mixture of soil and 0.01 M CaCl₂ (Graham, 1959; Schofield and Taylor, 1955). The excess salt in this solution masks the effects of differential soluble salt concentrations in individual samples. Procedures for each method are given below.

Lime Requirement Determination

The lime requirement procedures described below, the SMP (Shoemaker-McLean-Pratt) and Adams-Evans buffer methods, were developed for distinctly different soils. The SMP method was designed for use with soils that have large lime requirements and significant reserves of exchangeable Al (Shoemaker et al., 1961). The Adams-Evans buffer, however, was designed for soils that are coarse-textured, with low cation exchange capacities and organic matter contents, and thus low lime requirements (<2 T/A) (Adams and Evans, 1962). The Mehlich lime buffer was developed for use on soils of the Southeast US (primarily Ultisols), though Mehlich did calibrate the method for many other soil orders, including Histosols, Alfisols, and Inceptisols (Mehlich, 1976).

The SMP, Adams-Evans, and Mehlich buffers all contain hazardous reagents. All waste materials from these procedures require segregation and special handling (USEPA, 1980). All three buffers have been modified by substituting non-regulated reagents for the original constituents. All three modifications correlated very well with the original buffer and in most cases resulted in no significant changes in analytical results. No changes in calibration were necessary for any of the modified methods (Huluka, 2005; Sikora, 2006; Hoskins, 2005).

The original SMP buffer or its modification (Sikora buffer) is the most commonly used method in the US and is used by (CT, MA) in the northeast. The Adams-Evans is commonly used in the mid-Atlantic and coastal plains states (DE, NJ). The Modified Mehlich buffer is currently in use in ME and PA.

It is critical that the correct buffer method be used for lime requirement as, for example, the SMP has been shown in several studies to be inaccurate in poorly buffered, sandy soils, in soils with organic matter contents greater than 10%, or in soils with a predominance of kaolinite and Al and Fe oxides in their clay fractions (McLean, 1966). Several excellent, comprehensive

reviews of the methods used to estimate lime requirement for soils are available (McLean, 1982, Sims, 1996; van Lierop, 1991) and should be consulted before selecting or changing a lime requirement procedure.

Soil pH Procedures

Equipment:

1. pH meter with appropriate electrode(s).
2. Electronic balance or standard, 5 cm³ stainless steel scoop.
3. Pipettes or automatic dispensers.
4. 3 oz paper cups or equivalent.

Reagents:

1. Distilled or deionized water.
2. 0.01M CaCl₂: Completely dissolve 1.47g CaCl₂·2H₂O in 1 L of distilled or deionized water.
3. 1.0M CaCl₂: Completely dissolve 14.7g CaCl₂·2H₂O in 100 mL of distilled or deionized water.
4. Standard buffer solutions for calibrating pH meter, usually pH 4.0 and pH 7.0.

Procedure:

1. Calibrate the pH meter over the appropriate range using the standard buffers.
2. Scoop 5 cm³ (or weigh 5 g) of sieved, air-dried soil into a paper cup. See Chapter 2 for details on soil sample preparation and scooping technique.
3. Add 5 mL distilled or deionized water to the sample.
4. Stir vigorously for 15 seconds and let stand for 30 minutes.
5. Place electrodes in the slurry, swirl carefully, and read the pH immediately. Ensure that the electrode tips are in the slurry and not in the overlying solution.
6. For the CaCl₂ pH measurement, add 1 drop of 1.0M CaCl₂ solution to the previous sample. Alternatively, prepare a sample as was done in steps 2 and 3, using 0.01M CaCl₂ instead of water. Stir vigorously and let stand for 30 minutes, stirring occasionally. Read the pH as in step 5.
7. Save the water pH soil sample for use in the lime requirement determination procedures described below.

Lime Requirement Procedures

Equipment:

1. pH meter with appropriate electrode(s).
2. Electronic balance or standard, 5 cm³ stainless steel scoop.
3. Automatic dispensers capable of delivering up to 50 mL.
4. 3 oz paper cups or equivalent.
5. Mechanical shaker.

SMP Buffer Method

Reagent: SMP Buffer (bulk preparation):

1. Weigh into an 18 L bottle: 32.4 g of para-nitrophenol, 54.0 g of K₂CrO₄ and 955.8 g CaCl₂·2H₂O. Add 9 L distilled water, shaking vigorously during addition.
2. Weigh 36.0 g of Ca(OAc)₂ into a large container and dissolve in 5 L of distilled water.
3. Combine the two solutions, shaking during mixing and every 15 to 20 minutes for two to three hours.
4. Add 45 mL triethanolamine, shaking during addition and periodically thereafter until completely dissolved (may take up to 8 hours).
5. Dilute to 18 L with distilled water, adjust to pH 7.50 using 15% NaOH, and filter.
6. Store in a container with the air inlet protected by drierite and ascarite to prevent contamination by water vapor and carbon dioxide. Avoid excessive agitation of the solution after pH adjustment.

Procedure:

1. Add 10 mL of SMP buffer to the soil-water slurry used for pH determination.
2. Place in a mechanical shaker, close tightly, shake at 250 excursions/min for 10 minutes, and let sit for 20 minutes. (15 minutes shaking and 15 minutes standing is also acceptable.)
3. Swirl, insert electrodes, and read the pH. Read to the nearest 0.01 pH unit.
4. Determine lime requirement from soil-buffer pH and calibration data for local soils.

Adams-Evans Buffer Method

Reagent:

1. Dissolve 74 g of KCl in 500 mL of distilled water in a 1 L volumetric flask.
2. Add 10.5 g of KOH and stir to bring into solution.
3. Add 20 g of para-nitrophenol and stir again. Breaking up the large crystals of para-nitrophenol before adding facilitates dissolution.
4. Add 15 g of H₃BO₃ and stir, with heating if necessary, to dissolve.
5. Cool and dilute to a final volume of 1 L.
6. Adjust pH to 8.0 with either KOH or HCl.
7. Alternatively: Bulk solutions of Adams-Evans buffer can be prepared by use of appropriate weights and volumes of the above reagents, or are available commercially (e.g., Columbus Chemical Industries, Inc. catalog #61296-292). pH adjustment will still be required for commercially obtained solutions.

Procedure:

1. Use the soil sample previously prepared for a water pH measurement.
2. Add, in a fume hood, using an automatic dispenser, 10 mL of the Adams-Evans buffer solution to the sample from step 1.
3. Stir thoroughly with a glass rod, allow to equilibrate for 15 minutes and stir again.
4. Let stand another 15 minutes.
5. Prepare a diluted solution of the Adams-Evans buffer by adding 10 mL of distilled water to the Adams-Evans buffer solution.
6. Check pH of diluted Adams-Evans solution. It should read pH 8.00 +/- 0.10. Adjust pH meter to 8.00.
7. Insert electrodes into soil-buffer slurry and read pH to nearest 0.05 pH units.
8. Use the soil-buffer pH and calibration data from local soils to determine lime requirement.

Modified Mehlich Buffer Method

Reagent:

1. Add 1 L distilled water to a 2 L bottle
2. In an operating hood, add 4 ml glacial acetic acid
3. Place flask on a magnetic stirrer and add:
 - a. 20 ml 50 % Triethanolamine (50 % dilution aids dispensing)
 - b. 36 g Sodium Glycerophosphate
 - c. 84 g Ammonium Chloride
 - d. 24 g Calcium Chloride
4. Stir until completely dissolved and bring to 2 L volume.
5. Add 5 ml distilled water to 5 ml buffer. Diluted (1:1) buffer pH should be 6.60 +/- 0.04. Adjust undiluted buffer with 50 % acetic acid or 50 % triethanolamine if necessary. Check buffer pH before first use each day.

***NOTE:** Modified Mehlich buffer has no preservative content to inhibit microbial growth. Solution should ideally be made fresh each week and stored in a sealed container. Sterilize storage containers and dispensers with sodium hypochlorite bleach or 95 % ethanol between uses.*

Procedure:

1. Add 5 ml MM buffer solution to the soil-water slurry used for pH determination.
2. Stir thoroughly with a rod or mechanical stirrer. Allow to equilibrate for 15 minutes.
3. Stir thoroughly at 15 minutes and allow to stand for another 15 minutes.
4. After 30 minutes contact time, stir and insert electrodes. Read pH to nearest 0.01 units with soil still in suspension.
5. Use buffer pH reading and local calibration data to calculate lime requirement.

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