Lime Requirement by Measurement of the Lime Buffer Capacity

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The University of Georgia Soil, Plant, and Water Lab introduced two new soil test methods for soil pH and lime requirement (LR) on November 1, 2004. The new methods were developed and introduced to eliminate the use of the Adams-Evans Buffer (which contains toxic p-nitrophenol), to increase automation for both pH and lime requirement, and to add stability to the measured values of soil pH within a year and between years. Soil pH is now measured in a 1:1 suspension of soil:0.01 M $CaCl_2$, rather than 1:1 in water. This change was discussed in a previous report to NAPT (Kissel et al., 2004). Briefly, measurement of pH in 0.01 M $CaCl_2$ greatly reduces errors caused by increases in ionic strength from fertilizer and manure or by decreases in ionic strength from rainfall. As noted in the previous report, with no appreciable change in the amount of acid cations, differences in ionic strength from season to season or year to year can change soil pH by more than 0.5 units.

The LR of a soil is the amount of ag lime needed to neutralize the acid cations (H^+ or cations such as Al^{+3} that produce H^+) to a given target pH. In the US, soil-testing laboratories typically use buffer methods such as the Adams-Evans (AE) buffer (Adams and Evans, 1962) used in many Southeastern states, and the SMP buffer that is used widely in the mid-west (Shoemaker et al., 1961). Buffer procedures are calibrated by relating the depression in buffer pH (some calibrations include water pH) to the amount of $CaCO_3$ needed to raise soil pH to the target value. Our procedure is not based on a calibration, but instead it directly measures the soil pH buffering capacity by a single addition titration. This pH buffering capacity is calculated from the rise in pH measured 30-45 minutes after adding an aliquot of $Ca(OH)_2$.

What is the Lime Buffer Capacity?
The Lime Buffer Capacity (LBC) is another way to describe the pH buffering capacity of a soil. Soil pH buffering capacity is a measure of the amount of H^+ in the soil that must be neutralized to raise pH by one unit; or the amount of H^+ that must be added to drop soil pH by one unit. LBC is measured by adding a base such as $Ca(OH)_2$ and calculating its value from the relationship of soil pH vs. OH^- added. For surface soils, the relationship of soil pH vs. OH^- added is generally linear over a pH range of 4.5 to 6.5 (Magdoff and Bartlett, 1985; Weaver et al., 2004; Liu et al., 2004); therefore, buffering capacity can be described quantitatively by the slope of the relationship of pH vs. OH^{-1} added to the soil. Buffering begins to depart from linearity above pH 6.5 and below pH 4 to 4.5. As noted

by both Magdoff and Bartlett (1985) and Weaver et al. (2004), the linear buffering of surface soils is due largely to soil organic matter present in surface soils, long recognized by soil scientists as a source of pH dependent charge in soils. In contrast, the soil pH buffering of subsoils, notably low in organic matter, are often not linear. Coleman and Thomas (1967), citing data of Turner and Nichol (1962a, b), compared titration curves of acid clays (non-linear in the pH range of 4 to 7) and acid peats, which were linear over the same pH range.

For purposes of routine soil testing, a linear relationship between soil pH and added base can be used to develop a practical test for the lime requirement using a single addition titration, as proposed by Liu et al. (2005). From the titration data, the soil pH buffering capacity can be calculated. The LBC is another way to express soil pH buffering capacity of a soil, i.e., the amount of $CaCO_3$ needed to raise soil pH by one unit, expressed as mg $CaCO_3$ kg^{-1} soil pH^{-1} (ppm $CaCO_3$ pH^{-1}). The conversion of soil pH buffering capacity, expressed in units of meq $H^+(kg\ soil)^{-1}(pH)^{-1}$, to units of LBC is described by the equation:

LBC (mg $CaCO_3$ kg^{-1} pH^{-1}) = Soil pH Buffering Capacity (meq $H^+(kg\ soil)^{-1}(pH)^{-1}$) X

50 mg $CaCO_3$ $(meq)^{-1}$ [1]

Calculation of the LBC.

The LBC of a soil is calculated from the slope of the linear relationship between soil pH and the amount of OH^{-1} added to raise pH. We use $Ca(OH)_2$ as the source of OH^-, but we express the $Ca(OH)_2$ as the chemically equivalent amount of $CaCO_3$, as shown in Figure 1. In the case of soil A, the slope of that line is (6-5)/(1250-0) = 1/1250 or 0.0008 pH/ppm $CaCO_3$. The slope unit of 0.0008 pH/ppm $CaCO_3$ describes the fraction of a pH unit increase that results from the addition of one pound equivalent of $CaCO_3$ per million pounds of soil. This unit is not directly useful in common practice, but the inverse of the slope for the graph in Figure 1 (1/slope, i.e., the slope from a graph with soil pH in calcium chloride on the x axis and ppm of pure $CaCO_3$ on the y axis) has units of ppm $CaCO_3$ pH^{-1}, i.e., the ppm of pure $CaCO_3$ needed to raise soil pH by one unit. For soil A, the inverse of the slope takes the value of (1250-0)/(6-5) = 1250 ppm $CaCO_3$ pH^{-1} or 1250 ppm of pure $CaCO_3$ needed to raise soil pH by one unit. This number has important physical meaning since it can be used to calculate lime recommendations or the pH dependent charge in the soil per unit change in pH as described by Eq [1]. Soil pH buffering capacity is typically expressed as the moles of H^+ that must be neutralized per unit weight of soil to raise pH by one unit (cmol (H^+) $(kg\ soil)^{-1}$ pH^{-1}). Conversely, this value is also the amount of H^+ added per unit weight of soil that would drop pH by one unit.
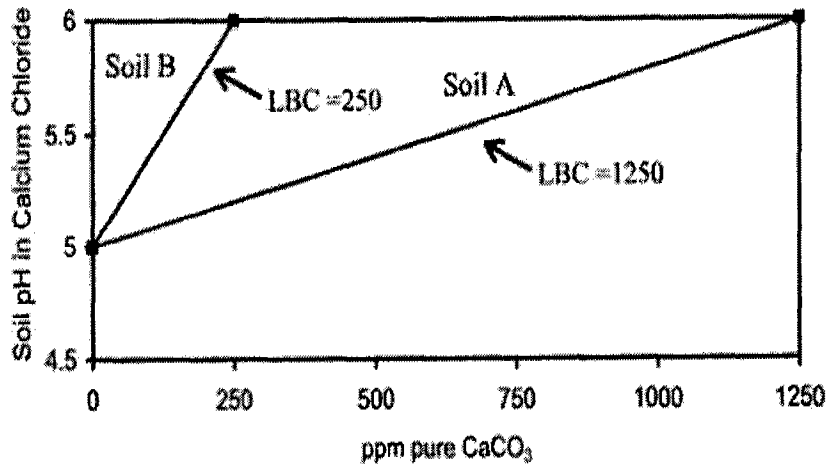
Figure 1. Graph showing a comparison of the Lime Buffer Capacity for two soils.

Calculation of LBC in routine laboratory practice.

The University of Georgia implemented the new titration method on November 1, 2004. In routine laboratory practice, sequentially, we dip soil with a 20 ml scoop, add 20 ml of 0.01 M $CaCl_2$, equilibrate for at least 15 minutes, measure pH (referred to as pH_1) using a specially modified LabFit AS-3000, followed by the addition of $Ca(OH)_2$ while stirring (currently 1.8 ml saturated $Ca(OH)_2$), equilibrate for an additional 30 minutes, and a second measurement of pH (referred to as pH_2). The following equation is used for calculation of the LBC,

$$LBC = [ml \times N \times EW \ CaCO_3]/soil \ weight/(pH_2-pH_1) \qquad [2]$$

where ml is the amount of $Ca(OH)_2$ added, N is the normality of the saturated $Ca(OH)_2$ (0.047 N), EW is the equivalent weight of $CaCO_3$ (50 mg meq^{-1}), the soil weight is adjusted according to soil province based on an average bulk density (BD) (20.7 g for Piedmont and 25.7 g for Coastal Plain), and pH_1 and pH_2 are the measured values of soil pH before and after the addition of $Ca(OH)_2$, respectively. In order for the LBC to be directly expressed as mg $CaCO_3 \ kg^{-1} \ pH^{-1}$, the soil weight for eq. [2] is entered as kg (20.7 g = 0.027 kg).

Calculation of the Lime Requirement.
To calculate the agricultural (ag) lime recommendation in pounds of ag lime per acre, the following equation is used:

$$Lbs \ ag \ lime \ per \ acre = LBC \times (target \ pH_W - pH_{CaCl2}) \times 2 \times 1.5 \times (soil \ depth/6) \quad [3]$$

In this equation, the factor 2 converts LBC units of ppm pure $CaCO_3$ to parts per two million (pp2m) pure $CaCO_3$ or lbs of pure $CaCO_3$ per acre 6-inch depth of soil (assumes BD = 1.5 g cm^{-3}). The factor of 1.5 converts pure $CaCO_3$ to ag lime. The factor 1.5 has been used previously by both Auburn University and the University of Georgia to compensate for poorly reactive large particles and $CaCO_3$ equivalents less than 100% of ag lime. The depth conversion is for depths other than 6 inches. We typically use a depth of 8 inches for agronomic crops (8/6 = 1.33 in Eq. [3]), thereby resulting in the equation

$$\text{Lbs ag lime per acre} = \text{LBC X (target } pH_W - pH_{CaCl2}) \text{ X 4} \qquad [4]$$

The target pH_W is the target pH in water and pH_{CaCl2} is the pH measured in 0.01 M $CaCl_2$ before the addition of $Ca(OH)_2$. The target pH_W is used rather than target pH_{CaCl2} because, as noted by Liu et al., 2005, the 30-minute equilibration time for the $Ca(OH)_2$ is not sufficient to reach a final equilibrium pH with the soil acidity, even though the samples are very near equilibrium. Since target pH_W is greater than a target pH_{CaCl2}, the value of (target $pH_W - pH_{CaCl2}$) is larger than (target $pH_{CaCl2} - pH_{CaCl2}$) and makes up for a slightly smaller value of LBC due to lack of complete equilibrium. It also results in a pH somewhat above the target pH following lime application, as will be noted below.

Accuracy of the New Test (UGA Method).
The accuracy of the lime recommendations using the new test was evaluated in two ways: (1) by comparing recommendations developed from the new test with recommendations from the Adams-Evans procedure, which was used by our laboratory for many years, and (2) by comparing the recommendations from the two tests for their ability to raise pH_W to the target value. In order to avoid any errors due to differences in soil weight, all samples were weighed for the comparison.

The ag lime recommendations to a target pH_W of 6.0 from both tests are compared in Figure 2. For this comparison, a total of 531 soils were selected from soils submitted to the UGA Soil Plant Water Laboratory during the first seven months of 2004 by selecting sample sets as time permitted. The recommendations (lbs of ag lime per acre) from the new method were regressed against the recommendations from the AE procedure. Results from the regression analysis were given in two ways. First, the linear regression equation with a y-intercept had a value of 484 lbs ag lime per acre. As determined from analysis of the regression equation, the lime recommendation at which both tests gave the same recommendation was 1860 lbs ag lime per acre. For recommended values less than 1860 lbs ag lime per acre, the new titration procedure recommended more lime than the AE procedure, whereas at higher values for the lime recommendation, the new test recommended less lime. The regression with y-intercept set to zero better indicated the degree of reduced recommendations from the new method. The slope of this regression was 0.89, which indicates that the ag lime recommendations at values above 1860 were on average about 11% lower than those by the AE procedure.
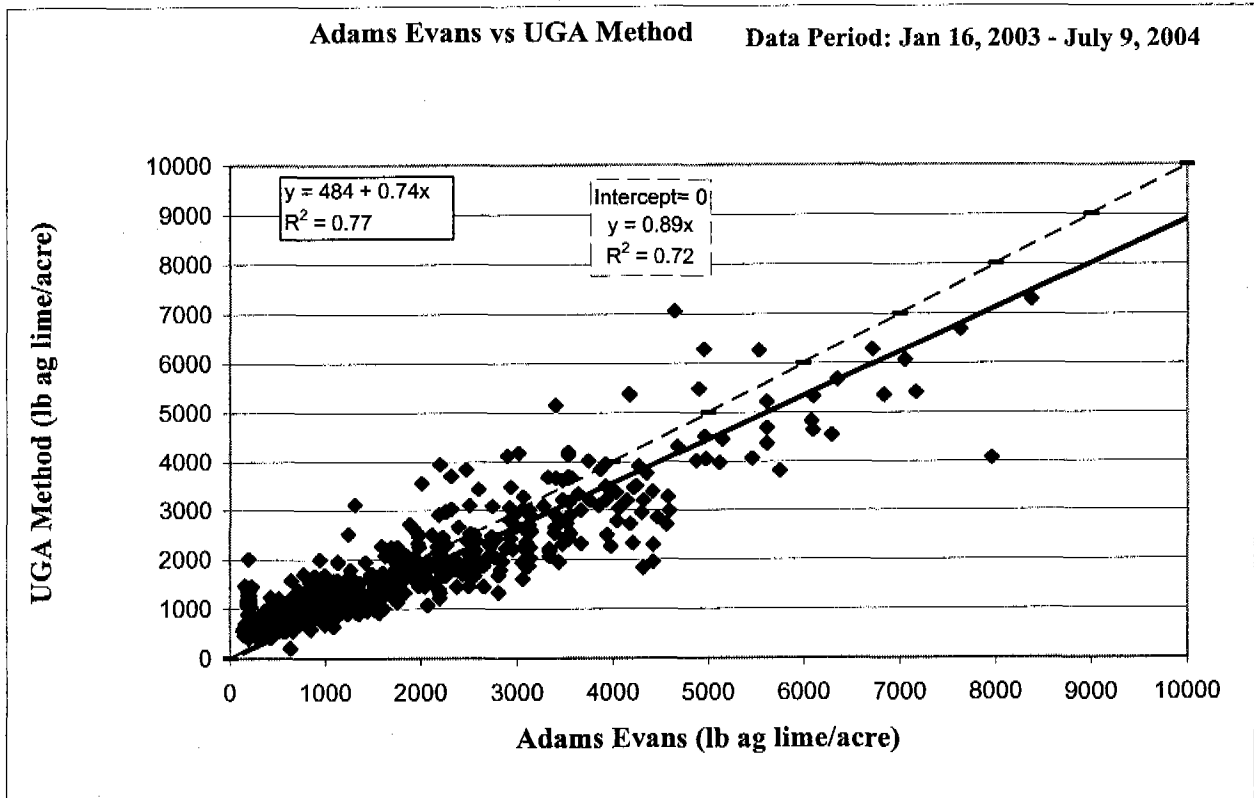
Figure 2. A comparison of ag lime recommendations for 531 Georgia soils by the UGA titration method vs. ag lime recommendations by the Adams-Evans buffer procedure, both to target pH_W of 6.0.

The second method to determine the accuracy of the new test was to incubate soil samples (submitted to the UGA lab by clients) with calcium hydroxide equivalent to the amount of ag lime recommended using both procedures. During January to July, 2004, soil samples were selected for incubation at several times when work-loads were low. Client's samples were analyzed using both the AE and the titration procedures. Samples that gave the most widely different lime recommendations to a target pH_W of 6.0 by the two procedures were selected for incubation. We applied the chemically equivalent amount of $Ca(OH)_2$ with an amount of deionized water to make a 1:1 soil:water ratio, and then incubated the samples for three days, according to the procedure of Dunn (1943). At the end of the three-day incubation, pH_W of the soil-water mixture was measured. Results from one of the first incubations carried out during early January 2004 are shown in Table 1. Some soil samples selected had greater ag lime recommendations using the AE procedure, whereas others had greater recommendations using the UGA titration procedure. Recommendations from the AE procedure ranged from 161 to 5042 lb ag lime per acre, whereas the recommendations from the UGA titration procedure ranged from 814 to 3154 lb ag lime per acre. The slightly lower average ag lime recommendations by titration (1689 lb ag lime per acre) than for the AE (1900) is in agreement with the results

in Figure 2, which in general showed slightly lower recommendations using the UGA titration method.

Table 1. Initial soil pH in deionized water and in 0.01 M calcium chloride, and Ag lime recommended by the UGA titration method and Adams Evans (AE), and the pH in water following a three day incubation with the amount of calcium hydroxide recommended to a target pH$_W$ of 6.0 by the two methods. Values in parenthesis are standard deviations from the mean.

Soil #	Initial pH$_W$	Initial pH$_{CaCl2}$	AE lb ag lime/a	pH AE	UGA lb ag lime/a	pH Titration
1	4.90	4.71	4179	6.61	2851	6.32
2	4.60	4.50	5042	6.65	3154	6.18
3	5.50	4.61	735	5.99	1309	6.31
4	5.80	5.11	466	6.32	1056	6.43
5	5.90	5.10	161	6.22	884	6.45
6	5.50	4.82	1958	6.16	1883	6.11
7	5.40	5.13	937	6.48	814	6.37
8	5.30	4.76	1720	6.40	1562	6.20
Avg.	5.36	4.84	1900	6.35(0.23)	1689	6.30 (0.12)

When pH$_W$ (1:1, water:soil) was determined following the three day incubation, the average pH$_W$ from the AE recommendations was 6.35 and ranged from 5.99 to 6.61, whereas, the pH following incubation of lime recommended by the UGA titration method averaged 6.30 and ranged from 6.11 to 6.45. The standard deviation of pH$_W$ following incubation of the AE recommendation was 0.23, whereas the standard deviation of pH following the titration recommendation was 0.12, indicating that the titration procedure was more precise. In subsequent incubations, we found results similar to those shown in Table 1, with slightly lower incubation pH$_W$ and lower standard deviations following recommendations from the titration method vs those from the AE procedure. For those samples with pH$_w$ only slightly below the target pH of 6 (for example, samples 4 and 5), the titration procedure recommends considerably more lime than the AE procedure. This recommendation is higher than it should be. More than likely, the AE procedure gives the more correct result for such samples based on the lower pH of the incubation for the AE recommendation (pH of 6.32 and 6.22 respectively for samples 4 and 5 vs 6.43 and 6.45 for the recommendations by titration). Since UGA does not recommend less than 1000 lb per acre, such inaccuracies are not a problem.

We assumed there were some samples with a relatively high soil solution ionic strength, because of small differences in pH$_W$ and pH$_{CaCl2}$. Those samples (soils #1 and #2) gave erroneously high results for LR by the AE procedure based on pH$_W$ values following incubation of 6.61 and 6.65 respectively. The differences in pH$_W$ and pH$_{CaCl2}$ for samples 1 and 2 were 0.19 and 0.10, respectively, whereas the differences for the remaining samples averaged 0.65 pH units. Of the recommendations for the eight samples, only samples 1 and 2 gave considerably higher recommendations by the AE procedure. Since

the AE procedure uses both pH_W and buffer pH in calculating a lime recommendation, a pH_W that is substantially reduced because of high ionic strength will result in a higher than normal lime recommendation. We found similar results in other incubations for samples with $pH_W - pH_{CaCl2} < 0.25$ that will not be presented here. Apparently, the original calibration by Adams and Evans (1962) was based on soil samples that were, on average, relatively low in soil solution ionic strength.

Analysis precision and other considerations.
For purposes of quality control, we presently duplicate the sample analysis for positions 10 and 20 in each tray of 36 samples. In order to determine the precision of the analyses with the new method, we compared the agreement between the duplicate analyses for the time period of March 16 to May 16, 2005, a time during which 286 duplicates were run. Our measurement of precision was to determine the absolute value of the difference between duplicates and then to calculate the mean and standard deviation of the differences. The mean difference between duplicates was 0.04 pH units, with a standard deviation of 0.03 pH units. For comparison, the mean difference between duplicates for 175 samples run by water pH during March 16 to May 16, 2004 was 0.10 pH units with a standard deviation of 0.07. So, pH in 0.01 M $CaCl_2$ improved precision for us. For measurement of pH_2 (the pH measurement taken after the addition of calcium hydroxide), the mean difference in 2005 of the 286 duplicates was 0.07, with a standard deviation of 0.058.

The saturated calcium hydroxide must be carefully prepared and protected from carbon dioxide since their reaction will produce calcium carbonate. We have found the final normality of saturated calcium hydroxide to vary from 0.044 to 0.047 N depending on the batch and its exposure to carbon dioxide during preparation. Therefore, the normality of each batch should be checked prior to use. It generally takes about 6 weeks for each 20-liter batch to reach its maximum concentration. We always have several batches prepared and ready to put on the instrument when needed. The procedure for preparing saturated calcium hydroxide is available from the Soil, Plant, and Water Lab at UGA upon request (soiltest@uga.edu).

Instrument performance.
A specially modified LabFit pH Analyzer with burette pump and Quad Stirrer Dual pH Probes (model AS-3010) has been used to implement the titration procedure. We have worked closely with LabFit to modify both the hardware and software to implement the procedure. Although there are a few minor changes still being implemented with the software, it functions well and we have analyzed approximately 55,000 samples with two instruments since the new procedure was implemented November 1, 2005. There are a few "lessons learned", listed below.

First, we learned that the stirrers at the positions where calcium hydroxide is being added must turn with sufficient speed to move all the soil during the addition of calcium hydroxide so that all soil is able to react with the added calcium hydroxide. Second, there is a slow buildup of a calcium carbonate film in the burette barrel as the burette pump piston goes up and down. If not removed periodically, these calcium carbonate crystals

increase in size and can scratch the glass, causing air to enter between the piston and the barrel of the burette. We now do routine maintenance by removing the barrel weekly and soaking it in 1 Molar hydrochloric acid at least overnight. A third lesson is to place the burette pump on the lab bench at the same level as the instrument so as to minimize the work the burette pump must do in lifting calcium hydroxide to fill the delivery tubes. Placing the pump above the instrument caused small air bubbles to enter into delivery tube fittings, resulting in errors in delivery of the correct volume of calcium hydroxide for some samples.

Summary.

In summary, the new pH and titration method for LR were developed to find solutions to the following problems. First, we sought to eliminate the use of a soil pH buffer that contained hazardous p-nitrophenol. Second, we wished to employ new methodology that allowed the full automation of soil pH and the LR determination. Finally, we wished to eliminate the seasonal variation in soil pH induced by differences in ionic strength of soils that occur routinely between years and within a year due to weather and soil management. We have found the UGA automated titration procedure to be sufficiently accurate for determination of the LR of Georgia soils. Most soils in Georgia are poorly buffered although we have found the procedure to also work very well with samples with LBCs five to ten times those of the average Coastal Plain soil from South Georgia. After using the procedure routinely since November 1, 2004, we are very satisfied with the new method. Although not discussed at length in this paper, the method depends on the determination of pH in 0.01 M $CaCl_2$, which in itself has required a great deal of education for clients. We are very happy with that change as well, with excellent duplication of pH results (as noted above) and so far no unexplainable shifts in pH due to climatic conditions, which did occur with water pH, and which was the inspiring motivation for measuring pH in 0.01 M $CaCl_2$.

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