REACTION EQUILIBRATION FROM SINGLE-ADDITION BASE TITRATION AND COMMERCIAL AG LIME EFFICIENCY FOR LIME REQUIREMENT DETERMINATION

by

JOHN S. THOMPSON

(Under the Direction of David E. Kissel)

ABSTRACT

The University of Georgia makes lime recommendations using a single-addition titration procedure. An issue with the procedure is the reaction with soil from $Ca(OH)_2$ addition does not reach equilibrium. The purpose of this research was to i) determine the time $Ca(OH)_2$ treated samples reached pH equilibrium, ii) determine if a relationship exists between lime buffer capacity (LBC) estimated from a 30 min equilibration and the LBC estimated at a time the sample has reached pH equilibrium, and iii) evaluate the efficiency of five ag limes compared to reagent-grade $CaCO_3$ on Georgia soils. All soils used for the titration study reached an equilibrium pH by 84 and 96 hours after $Ca(OH)_2$ addition. The ratio of the equilibrated LBC/30 min LBC could be predicted from the 30 min LBC ($r^2 = 0.83$). The ag lime study showed on average ag lime is 73% as effective as reagent-grade $CaCO_3$ powder.

INDEX WORDS: Lime requirement, titration, ag lime, soil testing, soil acidity, buffer method

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DEDICATION

This thesis is dedicated to my father, Harold Thompson, for his constant support and encouragement throughout, and to my late mother, Virginia Louise Thompson. I know you would be proud.

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INTRODUCTION

The lime requirement (LR) of a soil is defined as the amount of agricultural limestone or other basic material needed to increase the pH of the soil from an unacceptably acidic condition to a value that is considered optimum for the desired use of the soil (Sims, 1996). Soil-lime incubations in the laboratory or soil titrations with a standardized base are recognized as reliable methods to determine soil LR (Evans and Kamprath, 1970; Follett and Follett, 1983; Sims, 1996; Tran and van Lierop, 1981). However, incubations and titrations can be too laborious and time-consuming for routine soil testing (McLean et al., 1966).

Most LR determinations by soil test laboratories are made using buffers because they are quick and relatively reliable (Adams and Evans, 1962; Mehlich, 1976; Shoemaker et al., 1961; Woodruff, 1948; Yuan, 1974). One problem with buffers is that they must be calibrated against soil-lime incubations or titrations (Sims, 1996; Tran and van Lierop, 1981). Also, many buffers contain hazardous chemicals such as paranitrophenol, barium, or hexavalent chromium which present disposal and employee health issues (USEPA, 1980b; USEPA, 1998).

In part because of the environmental and toxicity issues associated with the use of buffers, The University of Georgia Soil, Plant, and Water laboratory (SPW) developed and uses a single-addition titration procedure to determine the LR (Kissel et al., 2007; Liu et al., 2004; 2005). This procedure was possible because the research of Magdoff and Bartlett (1985) and Weaver (2004) showed that the relationship between pH vs. added base was approximately linear between pH 4.5 and 6.5. The procedure as currently used allows an equilibration time of 30 minutes after base addition to determine a soil's H^+ buffering capacity, which is expressed as the lime buffer capacity (LBC). It is recognized that this equilibration time is not adequate for the sample to reach a pH equilibrium after the addition of $Ca(OH)_2$ (Kissel et al., 2007). The lime recommendations made from the LBC to clients are corrected to account for the lack of equilibrium (Kissel et al., 2007). Whereas the lime recommendations are adequate, finding a relationship between the equilibrated LBC and the 30 minute equilibrated LBC may give more accurate LBC values, thus more accurate lime recommendations.

A part of the lime recommendation equation is a 1.5 multiplier. This multiplier is an ag lime efficiency factor used to convert a lime recommendation for pure $CaCO_3$ to less than pure ag lime. This multiplier has also been used with the Adam-Evans (A-E) LR calculation. Adams and Evans (1962), citing unpublished data from their Alabama experiment station as well as published data from Pierre and Worley (1928) and Schollenberger and Salter (1943), recommended use of the 1.5 factor due to ag lime not completely neutralizing soil acidity. Dunn (1943) also suggested an efficiency factor of 1.5 for Washington soils. No research has been done on the efficiency of ag lime sold for use on Georgia soils.

LITERATURE REVIEW

The application of ammoniacal N fertilizer can lead to acidification of soils (Alabi et al., 1986). Toxic elements in soil such as Al and Mn can become available for plant uptake at acid pH values; thus, lime is applied to increase the pH to a level where most toxic elements become unavailable to plants (Follett and Follett, 1983). Whereas the pH of a soil is an intensity factor which may indicate the H^+ concentration in the soil solution, it is not a good index of the total amount of acidity present (McLean, 1978). To apply lime in the correct quantity to achieve a desired pH, the soil lime requirement must be determined. The lime requirement has been defined many different ways. Follett and Follett (1983) described it simply as the amount of lime that must be applied to grow a selected crop. Alabi et al. (1985) defined it as a quantitative measure of the amount of agriculturally important acidity in soils. Sims (1996) defined LR as the amount of agricultural limestone or other basic material needed to increase the pH of the soil from an unacceptably acidic condition to a value that is considered optimum for the desired use of the soil.

Measuring the LR of a soil has been the focus of much research. The most accurate way to determine the lime requirement of a soil is to apply different rates of lime in the field, followed by measurement of soil pH after a suitable incubation time (Sims, 1996). Because the results are not transferrable to other fields and because of high costs, this method is usually not feasible. Because of the problems associated with field-scale LR determinations, soil-lime incubations in the laboratory or soil titrations with a standardized base have been used for comparison

(Evans and Kamprath, 1970; Follett and Follett, 1983; Sims, 1996; Tran and van Lierop, 1981). The incubations and titrations can be too laborious and time-consuming for routine soil testing (McLean et al., 1966). Because of this, soil test laboratories needed quick and reliable methods to accurately predict the LR of a soil. Many different buffer methods have been developed to provide a quick and accurate way to determine the LR of a soil (Adams and Evans, 1962; Brown and Cisco, 1984; Huluka, 2005; Mehlich, 1976; Shoemaker et al., 1961; Woodruff, 1948; Yuan, 1974). A buffer is generally a weak acid mixed with a salt of the same weak acid, thus it can neutralize both acids and bases and can resist changes in pH (McLean, 1978). The reaction, and resulting decrease in pH, between a buffer mixture and an acid soil is an index of the lime requirement because the pH decrease of the buffer is directly proportional to the amount of acidity added (McLean, 1978).

Adams and Evans (A-E) (1962) developed a buffer method for measuring the lime requirement of red-yellow podzolic soils (Ultisols). It was developed to predict the lime requirement of soils with low CEC (1-10 cmol_c/kg) which are generally highly weathered soils dominated by 1:1 clay minerals (Adams and Evans, 1962). These types of soils may be adversely affected by over-liming (Adams and Evans, 1962; Alatas et al., 2005; Follett and Follett, 1983; Sims, 1996). The pH of the buffer solution is 8.0 +/- 0.1. It contains paranitrophenol, boric acid (H_3BO_3), potassium chloride (KCl), potassium hydroxide (KOH), and water (H_2O). Most of the buffering is provided by paranitrophenol with borate contributing some buffering at higher pH values (Adams and Evans, 1962). The LR calculation is based upon a general relationship between soil pH and base unsaturation as well as the ability of the buffer to indicate the amount of exchangeable acidity to be neutralized (van Lierop, 1990). Soil pH is used to estimate the acid saturation of the soil at its current pH by:

$$\text{Soil pH} = 7.79 – 5.55 (H_{sat1}) + 2.27 (H_{sat1})^2$$

Where, H_{sat1} is the base unsaturation (acid saturation) of the soil at its initial pH. Acid saturation of the soil at the desired pH (H_{sat2}) is determined by the same relationship. Because of the fact that each 0.008 mmol of acidity decreases the pH of 20 mL of a 1:1 buffer/water mixture by 0.01 pH units, the A-E buffer solution can then used to estimate the exchangeable acidity of the soil by:

$$\text{Soil H (cmol/L)} = 8 (8.00 – \text{buffer pH})$$

Where, Soil H is the acid saturation of the soil. The desired change in soil acid saturation is then used to calculate the amount of acidity that needs to be neutralized:

$$\text{Acid to be neutralized} + (\text{Soil H}/ H_{sat1}) \text{ x } (H_{sat1} - H_{sat2})$$

The LR is calculated by the following:

$$\text{LR (Mg/ha)} = [8000 (8.00 – \text{buffer pH})/ H_{sat1}] \text{ x } (H_{sat1} - H_{sat2}) \text{ x } 1.5 \text{ x } 2.24$$

Where 1.5 is a “lime factor” to account for agricultural limestone not being as effective at neutralizing soil acidity as reagent grade calcium carbonate and 2.24 is the weight of soil (Mg) of a hectare that is 15 cm deep (Adams and Evans, 1962; Sims, 1996).

The A-E buffer procedure is widely used in the southeastern United States (Adams, 1984). Research has shown that the A-E buffer method is accurate when compared to soil-lime incubations for low CEC soils dominated by 1:1 clay minerals (Adams and Evans, 1962; Alabi et al., 1986; Fox, 1980). However, it does have a tendency to overestimate the LR of low CEC soils. This has been attributed to the high initial pH of the buffer solution (8.0) which may include some pH-dependent acidity in the soil that does not need to be neutralized in order to achieve the target pH (Alabi et al., 1986; Fox, 1980; Tran and van Lierop, 1981). The liming factor of 1.5 has also been attributed to being part of the overestimation problems with the A-E buffer method (van Lierop, 1990). The A-E buffer method can underestimate the LR of soils with high CEC, indicating that it is not well suited for soils with appreciable amounts of 2:1 clay minerals (Follett and Follett, 1983).

Shoemaker et al. (1961) developed a buffer method because certain soil test methods for estimating the LR of Ohio soils were inaccurate. The Shoemaker, McLean, and Pratt single buffer (SMP-SB) is the most widely used buffer and is commonly used throughout the midwestern United States (Follett and Follett, 1983). Shoemaker et al. found that the Woodruff buffer procedure underestimated the LR while the original Mehlich-TEA buffer procedure over estimated the LR on partially limed soils but was accurate for unlimed soils (Shoemaker et al., 1961). The method was developed for use with acidic, high LR soils with < 10% organic matter (Alabi et al., 1986; Follett and Follett, 1983; Sims, 1996; van Lierop, 1990). The buffer contains paranitrophenol, triethanolamine, potassium chromate, calcium acetate, calcium chloride, and is adjusted to a pH of 7.5 with sodium hydroxide (Shoemaker et al., 1961). The SMP buffer has been shown to be very accurate for medium and fine textured, acidic, high LR soils (Follett and Follett, 1983; McLean et al., 1966; Tran and van Lierop, 1981). Because of the buffer's dilute nature it is very sensitive for measuring the acidity of soils (Baker et al., 1977). One peculiarity of the SMP-SB buffer is that it overestimates the LR of low LR soils (McLean, 1982a; McLean et al., 1966; Shoemaker et al., 1961). Brown and Cisco (1984) found the SMP-SB to underestimate the lower LR and overestimate the higher LR soils. Although the calibration of the SMP-SB buffer was not described originally, they apparently used linear regression to relate soil-buffer pH to reference LR values (Tran and van Lierop, 1981). The inaccuracy of the SMP-SB buffer for low LR soils is said to be caused by the calibration method employed by Shoemaker et al. It has been suggested that the relationship is not linear but in fact curvilinear

(Mehlich et al., 1976; Tran and van Lierop, 1981). Research has shown that the curvilinearly modified SMP-SB buffer more accurately estimates the LR of low LR soils while keeping the precision of estimating the LR for high LR soils (Aitken et al., 1990; Tran and van Lierop, 1981).

McLean et al. (1977) later developed an SMP-double buffer (DB) procedure to correct the inaccuracies of the SB. This DB method was developed using the same principles as the Yuan-DB procedure. The SMP-DB method utilizes the original SMP buffer adjusted to pH 7.5. Water is added to the soil samples, which are shaken or stirred for one minute, then allowed to stand for 10 minutes before the pH is measured. Ten mL of SMP buffer adjusted to pH 7.5 is added to the samples. The samples are shaken for 10 minutes and then allowed to stand for 30 minutes before the pH is measured. Fifteen minutes of shaking and 15 minutes of standing are sufficient for use in routine soil testing laboratories. Next, an aliquot of HCl equivalent to the amount required to decrease a 10-mL aliquot of pH 7.5 buffer to 6.0 is added to the sample. The shaking and standing procedure as described previously are repeated (McLean et al., 1977). In addition to the increased accuracy of estimating the LR for low LR soils, another proposed advantage to DB methods is that it measures more accurately the buffering capacity of each soil (van Lierop, 1990). Thus it allows the calculation of LR to any desired pH (Aitken et al., 1990). A disadvantage of the SMP-DB is that it is costlier and more time consuming (van Lierop, 1990). Due to the fact that the SMP-DB was not significantly more precise in predicting the LR of low LR soils over that of the curvilinearly modified SMP-SB, the modified SMP-SB method is considered more advantageous because of its greater simplicity (Tran and van Lierop, 1981).

Mehlich (1976) developed a buffer procedure based on the amount of lime required to neutralize the unbuffered salt-exchangeable acidity found in acid, mineral soils (Mehlich, 1976).

The calibration was based on the neutralization of acidity that was considered harmful to plant growth, not a specific pH. The relationship between total acidity determined with the buffer and the LR determined by incubation was found to be curvilinear (Mehlich, 1976; Tran and van Lierop, 1981). The curvilinear relationship exists because a liming factor was applied to the total acidity determined by the buffer (Mehlich, 1976). The lime factor was needed because the amount of lime needed to neutralize the exchangeable acidity was more than the buffer was suggesting (Mehlich, 1976). The buffer consisted of sodium glycerophosphate, acetic acid, triethanolamine (TEA), ammonium chloride, and barium chloride (Mehlich, 1976). Since exchangeable acidity is essentially neutralized at pH values greater than 5.5, research has shown the Mehlich buffer to be very accurate at predicting the LR to pH 5.5 (Aitken et al., 1990; Tran and van Lierop, 1982). Tran and van Lierop (1982) and Aitken et al. (1990) both found that the Mehlich buffer not only reacted with the unbuffered, salt-exchangeable acidity, but also reacted with other forms of soil acidity.

Yuan (1974; 1976) was the first to introduce a double buffer (DB) method. The method is based on the assumptions that the buffer measures the exact amount of acidity neutralizable by $CaCO_3$ and pH increases are linearly related to the quantities of neutralizable soil acidity (Tran and van Lierop, 1982). The buffer was developed for poorly buffered, sandy soils in Florida. It consists of tris, imidazol, chromate, and pyridine in a 0.2M calcium chloride solution. It was prepared so that the depression in soil buffer pH would be linear so that the LR determination could be calculated easily (Yuan, 1974). The method utilizes two buffers of identical composition, one adjusted to pH 7.0 and one adjusted to pH 6.0. Soil-buffer pH values are determined for both buffer solutions and a relationship (slope) between acidity measured at pH 6.0 and pH 7.0 per pH unit change by the buffers (van Lierop, 1990). Research has shown that the Yuan-DB is precise at predicting the LR to 6.5 but not precise at predicting LR to 5.5 (Aitken et al., 1990; Fox, 1980; McConnell et al., 1991; Tran and van Lierop, 1981). The decrease in precision is not clear, however it may be related to a break in the titration curve's linearity around pH 6.2 (Tran and van Lierop, 1982; Yuan, 1976). As with the SMP-DB method, increased cost and time to perform the procedure prohibit this method from being utilized (van Lierop, 1990).

Woodruff (1948) developed the first widely used buffer method. The buffer consisted of paranitrophenol, calcium acetate, and magnesium oxide adjusted to pH 7.0 with either hydrochloric acid or magnesium oxide. The buffer was formulated so that every 0.1 decrease in pH represented 10 $\text{cmol}_c\ \text{kg}^{-1}$ of neutralizable acidity. The Woodruff buffer has been widely studied. Many researchers have found that the Woodruff buffer is as precise as any of the other buffers and is accurate at low LRs but underestimates high LRs (Alabi et al., 1986; Brown and Cisco, 1984; Fox, 1980; McLean et al., 1966; Tran and van Lierop, 1981). Loynachan (1981) found that it underestimated the LR for high LR soils and overestimated the LR for low LR soils. Tran and van Lierop (1982) suggested that fitting a curvilinear regression equation to the relationship between soil-buffer pH and LR at 6.0 might increase the accuracy of the estimation for high and low LRs. However they found that the curvilinear fitting did not increase the precision of the relationship. Tran and van Lierop (1981) found that the Woodruff buffer used as a single buffer was accurate for soils requiring less than 10 $\text{cmol}_c\ \text{CaCO}_3\ \text{kg}^{-1}$.

When most of the buffers were developed, there was no consideration given to whether any of the chemicals used were hazardous (Sikora and Moore, 2008). In 1976, the U.S. Congress passed the Resource Conservation and Recovery Act (RCRA) to improve waste management (Horinko, 2002). Further refinement occurred in 1980 with the passage of regulations controlling the disposal of chemicals that were considered hazardous due to ignitability, corrosivity, reactivity, or toxicity (USEPA, 1980a). The chemicals used in the buffers that are considered hazardous due to toxicity are *p*-nitrophenol in the A-E buffer, *p*-nitrophenol and chromium in the SMP buffer, and barium in the Mehlich buffer. The chromium in the SMP buffer is present as potassium chromate (K_2CrO_4), which is hexavalent and carcinogenic via inhalation (USEPA, 1998). If a laboratory generates 100 kg or more of the soil and buffer in a one month period, the lab is considered a hazardous waste generator and must follow certain protocols for hazardous waste disposal (USEPA, 1980b). For this reason, there has been much research to find non-hazardous chemicals to replace the hazardous chemicals in these buffer or to find new methods to determine soil LR (Hoskins and Erich, 2008; Huluka, 2005; Kissel et al., 2007; Liu et al., 2004; 2005; Sikora, 2006; Sikora and Moore, 2008).

Paranitrophenol has been shown to be environmentally toxic (Braunbeck et al., 1989; USEPA, 1980a). Because of the toxic nature of paranitrophenol, a modification to the A-E buffer method was developed (Huluka, 2005). Paranitrophenol was replaced by monobasic potassium phosphate (KH_2PO_4) which has a similar buffering capacity but no known toxicity. The linear regression between the buffer pH values and the lime recommendations made by the original A-E buffer solution and that of the modified A-E buffer solution were highly significant ($r^2 = 0.65$). This result allows the use of previously established criteria generated from the original A-E buffer solution to still be used for making lime recommendations (Huluka, 2005).

Another modification to the A-E buffer was done my Sikora and Moore (2008). Although a modified A-E buffer that did not contain *p*-nitrophenol existed, Sikora and Moore (2008) wanted to develop a buffer that mimicked the A-E buffer but with better precision than the Huluka (2005) modification. Three considerations during the development of the Moore-

Sikora (MS) buffer were a) the pK_a of the chemical or chemicals chosen to replace *p*-nitrophenol should be similar, b) the replacement chemical or chemicals should not have side reactions with the soil that would alter the acidity that reacts with the buffer (Woodruff, 1948), and c) the chemical composition of the buffer should inhibit or minimize microbial activity for a good shelf life (Sikora and Moore, 2008). The chemicals chosen to replace *p*-nitrophenol were boric acid, 3-(*N*-morpholino)propanesulfonic acid (MOPS), and 2-(*N*-morpholino)ethanesulfonic acid hydrate (MES). Comparison of the A-E and MS buffers on 222 South Carolina soils and 41 NAPT soils showed a good relationship ($r^2 > 0.98$). The MS buffer, due to a lower soil-buffer pH in some samples, did predict a higher LR than the A-E buffer. This difference was not expected to raise soil pH much above target pH values (Sikora and Moore, 2008).

Like the A-E buffer, the SMP buffer generates hazardous waste because it contains paranitrophenol and potassium chromate (Sikora, 2006; USEPA, 1980a). Sikora (2006) developed a buffer that mimics the SMP buffer yet does not contains paranitrophenol or potassium chromate. He replaced paranitrophenol (pKa = 6.85) and potassium chromate (pKa = 5.81) with imidazole (pKa = 6.95) and 2-(N-morpholino)ethanesulfonic acid monohydrate (MES) (pKa = 6.10), respectively. These chemicals were non-hazardous, had similar pKa values, had a low availability to complex Al, are stable, readily available, and relatively inexpensive. Similar pKa values were important to retain the linear relationship between the buffer's response to soil acidity (Sikora, 2006). The soil-buffer pH with the newly formulated buffer agreed closely with the soil-buffer pH using the SMP buffer for 255 Kentucky soils (r^2 = 0.974) and 87 NAPT (North American Proficiency Testing) soils (r^2 = 0.967). Limestone recommendations made by the two buffers also had good agreement for Kentucky (r^2 = 0.935) and NAPT soils (r^2 = 0.876).

Chromium in the original SMP buffer provided protection against microbial growth, allowing it to be stored for long periods of time. The high ionic strength (1.08 M) due to $CaCl_2$ also provided microbial growth inhibition. Research showed that the new buffer Sikora (2006) formulated could be stored for up to 150 days with no effect of pH measurements. The new buffer's high ionic strength (2.00 M due to KCl) as well as the absence of P in any of the buffer's ingredients is suspected in helping minimize or eliminate any microbial growth when being stored (Sikora, 2006).

Similarly to the A-E and SMP buffers, the Mehlich buffer presents a hazard because it contains $BaCl_2$ (Hoskins, 2005; Hoskins and Erich, 2008; USEPA, 1980a; Wolf et al., 2008). Because routine use of the SMP buffer resulted in problems with electrode reference junction degradation, stability of readings in relation to contact time, and generation of hazardous waste, Hoskins and Erich (2008) sought to improve the method performance and eliminate hazardous waste generation. To address these issues, Hoskins and Erich (2008) chose to evaluate the SMP buffer parallel to the Mehlich buffer. The result of the parallel comparison was a modification to the original Mehlich buffer by replacing the $BaCl_2$ with $CaCl_2$, a non-hazardous compound (Hoskins and Erich, 2008). He found that the modified buffer did not have a significant change in buffering properties or its effectiveness in estimating the LR of Maine soils. The $CaCl_2$ modification allows the respective soil test lab the ability to use the normal waste stream instead of handling as a hazardous waste (Hoskins, 2005; Hoskins and Erich, 2008). The $CaCl_2$ modification did reduce the shelf life of the buffer because $BaCl_2$ had microbicidal properties that helped preserve the buffer (Hoskins and Erich, 2008; Mehlich, 1976).

Wolf et al. (2008) compared the modified Mehlich buffer to the SMP-SB and found that the modified Mehlich buffer was a more accurate predictor of the lime needed to raise the pH to

6.5 ($r^2 = 0.92$) and 7.0 ($r^2 = 0.87$) in comparison to the SMP buffer ($r^2 = 0.87$ and 0.82, respectively) for agriculturally important PA soils. The modified Mehlich buffer also exhibited good relationships between calibrations on soils from different regions (ME, NC, PA and VA; $r^2 \geq 0.92$), suggesting that the LR test would be appropriate for soils with diverse properties (Wolf et al., 2008).

In part because of the environmental and toxicity issues associated with using the A-E buffer, the University of Georgia Soil, Plant, and Water Lab started to study the possibility of direct titration procedure to determine soil LR. Direct titration for LR determination was first studied by Dunn (1943). The procedure proposed by Dunn required incubations for up to 4 days which was deemed too long and time consuming for routine soil test labs. However the 3-day $Ca(OH)_2$ incubation developed by Dunn is a widely accepted reference method for comparing other methods for determining the LR (Alabi et al., 1986; Follett and Follett, 1983; Loynachan, 1981; McConnell et al., 1991). Magdoff and Bartlett (1985) found that titration curves for acid soils were approximately linear. Weaver et al. (2004) found that a linear expression described well the relationship of pH vs. added base between pH 4.5 and 6.5 for some coastal plain soils of Georgia.

Because the relationship between pH and added base was linear between pH 4.5 and 6.5, Liu (2004; 2005) suggested it may be possible to use regression analysis to develop a titration procedure that could be used for routine LR determination by soil test labs. One advantage of a single-addition titration over buffer procedures is that the titration is not based upon a calibration but instead provides data on the rise in pH from a given addition of base. The rise in pH can be used to calculate the pH buffering capacity of the soil. The soil pH buffering capacity, initial pH, and the target pH can then be used to calculate the LR of a soil (Kissel et al., 2007).

One issue that became apparent during the Liu's research was that the initial soil pH taken in deionized (DI) water with no $Ca(OH)_2$ addition was below the y-intercept of the regression. This issue was resolved by measuring the soil pH in 0.01 M $CaCl_2$. By doing this, the soil pH with no $Ca(OH)_2$ addition agreed more closely to that of the y-intercept from the regression analysis, and it stabilized pH readings of low ionic strength soils (Liu et al., 2005; Sumner, 1994).

For the single-addition titration procedure, soil pH buffering capacity was expressed by the term lime buffer capacity (LBC) (Kissel et al., 2007). Soil pH buffering capacity can be expressed as [meq H^+ (kg soil)$^{-1}$] (Murphy and Follett)$^{-1}$. The LBC is related to soil pH buffering capacity as follows:

$$\text{LBC (mg } CaCO_3 \text{ kg}^{-1} \text{ pH}^{-1}) = \text{Soil pH buffering capacity ([[meq } H^+ \text{ (kg soil)}^{-1}] \text{ (Murphy and Follett)}^{-1}] \times 50 \text{ mg } CaCO_3 \text{ (meq)}^{-1}$$

The LBC would have units of mg $CaCO_3$ kg^{-1} pH^{-1} and would be calculated from the following equation:

$$\text{LBC} = (\text{V x N x EW}) \text{ kg}^{-1} (\text{pH}_2\text{-pH}_1)^{-1}$$

Where V is the volume of calcium hydroxide added, N is the normality of calcium hydroxide (0.046 N), and EW is the equivalent weight of calcium carbonate known to react identically to calcium hydroxide for soil pH less than 8 (50 mg meq^{-1}). The weight of soil in equation 1 is expressed in kg, pH_1 is the initial soil pH, and pH_2 is the pH taken 30 minutes after addition of the calcium hydroxide (Kissel et al., 2007).

The LR is determined from the following equation:

$$\text{LR (lbs/ac)} = \text{LBC x (Target pH}_w - \text{Initial pH}_{CaCl}) \text{ x 2 x 1.5 x 1.33}$$

where the target pH_w is the desired final pH of the soil as measured in DI water and initial pH_{CaCl} is the initial pH as measured in 0.01 M $CaCl_2$. The target pH_w is used rather than target pH_{CaCl} because the samples are only equilibrated for 30 minutes which is not enough time to allow the samples to reach equilibrium (Kissel et al., 2007). The value of (target pH_w - initial pH_{CaCl}) is larger than if target pH_{CaCl} was used which compensates for the lower LBC due to the lack of equilibrium. The factor 2 converts LBC units of ppm to lbs/ac furrow slice (1 ac., 6" deep). The factor 1.5 is an efficiency factor converting pure $CaCO_3$ to ag lime which has been used by Auburn University as well as the University of Georgia to compensate for large, poorly reactive lime particles. The factor 1.33 is a depth conversion for 8" furrow depth (8/6 = 1.33) (Kissel et al., 2007).

The 1.5 factor for converting pure $CaCO_3$ to ag lime mentioned above is a carry over from the A-E LR calculation. Adams and Evans (1962), citing unpublished data from their Alabama experiment station as well as published data from Pierre and Worley (1928) and Schollenberger and Salter (1943), suggested the 1.5 factor due to ag lime not completely neutralizing soil acidity.

Limestone is the main liming material used in the U.S. (Barber, 1984). The limestone may either be calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), or a combination of the two (Barber, 1984). Pure dolomite has a calcium carbonate equivalence of 1.08, yet research has shown that is reacts slower than calcite of the same fineness in acid soils (Beacher et al., 1952; Rippy et al., 2007; Schollenberger and Salter, 1943; Thomas and Hargrove, 1984). Dolomitic limestone reacts at a rate twice that of calcitic limestone (Barber, 1984). Rippy et al. (2007) showed that dolomitic limestone reacted 3 to 4 times more slowly than calcitic limestones of the same fineness. Schollenberger and Salter (1943) noted that the difference in reactivity between dolomitic and calcitic limestones was only important over shorter time periods. To get an equal reaction rate, dolomitic limestone particle size should be half of calcitic limestone particle size (Barber, 1984). The reaction of a liming material with acid soil is the dissolution of $CaCO_3$ and then Ca^{2+} binds to the soil exchange complex while H^+ in the soil reacts with the CO_3^- into the soil solution:

$$CaCO_3 \longrightarrow Ca^{2+} + CO_3^- \Longleftrightarrow HCO_3^- + Ca^{2+}\text{-soil}$$

The HCO_3^- then reacts with more H^+ in the soil to produce H_2O and CO_2:

$$HCO_3^- \longrightarrow H_2O + CO_2$$

The degree of fineness to which the limestone is ground plays an important role in the rate of reaction with soils. The finer the material, the quicker it reacts with the soil (Barber, 1984; Beacher et al., 1952; Motto and Melsted, 1960). Meyer and Volk (1952) found that pH values were highest 6 months after application of calcitic limestone of U.S. Standard No. 60 sieve or finer while 50-mesh or finer material needed 12 months to reach it's highest pH. They also found that particles coarser than 20-mesh had little value at neutralizing soil acidity even after 18 months (Meyer and Volk, 1952). Meyer and Volk (1952) also found dolomitic limestone to react slower than calcitic limestone, but if given enough time (>9 months), the soils treated with 50-mesh or finer dolomitic limestone reached a higher pH than those treated with calcitic limestone of equivalent fineness. Barber (1984) suggested that ag limes should be fine enough so that 80% will pass a U.S. Standard No. 8 sieve (2.36 mm opening).

Pierre and Worley (1928) conducted experiments on 77 Alabama soils to find an easy way to determine the LR of soils to bring them to a desired pH value. They established soil titration curves by incubating the soils with $Ba(OH)_2$ for three days. Pot studies on unlimed and limed samples were then performed on all of the soils. The pots prevented any leaching loss and allowed the lime material to react with a known quantity of soil. After 6 months, the pH of the limed and unlimed soils was determined. They calculated the "liming factor" by:

"Liming factor" = mg of lime per 100 g soil to bring to desired pH/mg of base per 100 g soil in soil suspension to bring to desired pH

They found the liming factor to range from 1.27 to 1.77, with an average of 1.43. They suggested, for all practical purposes, to use a liming factor of 1.50 (Pierre and Worley, 1928).

With the need for a simple way to evaluate ag lime on the basis of reactivity and cost, Schollenberger and Salter (1943) generated a lime evaluation chart. To use the chart, you need to know at least one percentage from a sieve analysis, the CCE, % Ca, % Mg, and the moisture content. With this information, you can then plot the point(s) on their lime evaluation chart and get an efficiency factor for that particular lime based on the amount of time needed for the ag lime to neutralize the soil acidity (Schollenberger and Salter, 1943).

While developing titration curves for LR calculation, Dunn (1943) also determined "liming factors" for some Washington soils. Dunn (1943) treated soils with differing amounts of either $CaCO_3$ or $Ca(OH)_2$ with amounts ranging from 0 to 15 tons of $CaCO_3$ or the equivalent in $Ca(OH)_2$ on a per acre basis and incubated them at a normal field moisture content for six months. Soil pH values were determined at 1, 3, and 6 months, with no significant difference in pH at the three incubation times. The pH values had reached equilibrium for both the $CaCO_3$ and $Ca(OH)_2$ treatment within 1 month under laboratory conditions. His calculated liming factors ranged from 0.9 to 1.9, with an average of 1.3 (Dunn, 1943).

An alternative to using an average factor to determine the lime recommendation is to calculate a liming efficiency factor for each liming material, as done by the Kansas State University (KSU) method. KSU uses the SMP buffer to determine the amount effective calcium carbonate (ECC) necessary to raise the soil pH to a desired level (Whitney and Lamond, 1993). The amount of lime needed to achieve a desired pH will vary with depth of incorporation as well as the quality of the lime material. To account for the quality of the ag lime when making a lime recommendation, KSU derived a Fineness Factor (FF). The FF is calculated by the following:

Size of Material	**Percent of Material**		**Effectiveness Factor**	**Effectiveness**
>8 mesh	_______	x	0	0
8-60 mesh	_______	x	0.5	_______
<60 mesh	_______	x	1.0	_______
			Fineness Factor (FF)	_______

To calculate the ECC that the lime would supply, multiply the FF by the CCE of the ag lime. For example, an ag lime has a CCE of 95 percent and an FF of 80 percent. The ECC of that particular ag lime is 76 percent (0.95 x 0.80). If the soil test recommendation suggested applying an ECC of 3,000 lbs/a of ECC, then 3,947 lbs/a would need to be applied to achieve the desired pH (3,000/.76) (Whitney and Lamond, 1993).

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CHAPTER 1

REACTION EQUILIBRATION FROM SINGLE-ADDITION BASE TITRATION FOR LIME REQUIREMENT[1]

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[1] John S. Thompson and David E. Kissel. To be submitted to *Soil Science Society of America Journal*.

Abstract

The current University of Georgia single-addition titration lime requirement (LR) procedure only allows the reaction between soil and $Ca(OH)_2$ to equilibrate for 30 minutes after $Ca(OH)_2$ addition. Lime recommendations are corrected for the lack of equilibrium. The purpose of this study was to i) determine the time $Ca(OH)_2$ treated samples reached pH equilibrium and ii) determine if a relationship exists between lime buffer capacity (LBC) estimated from a 30-min equilibration and the LBC estimated at a time the sample has reached pH equilibrium. Twenty five soils in this study were equilibrated for up to 96 hours. All soils reached an equilibrium pH by 84 and 96 hours after $Ca(OH)_2$ addition. The ratio of the equilibrated LBC/30 min LBC could be predicted from the 30 min LBC ($r^2 = 0.83$). The current titration procedure can be used to predict the equilibrium LBC for calculating more accurate lime recommendations.

Introduction

Much research has been done to develop quick and accurate methods to predict the lime requirement (LR) of a soil. In soil test labs, the LR has typically been determined by the use of buffers. Generally speaking, a buffer is a weak acid mixed with a salt of the same weak acid; thus it can neutralize both acids and bases and can resist pH changes. The reaction and subsequent decrease in pH between a buffer mixture and an acid soil is an index of the LR (McLean, 1978).

Two of the most widely used buffers are the Adams-Evans (A-E) buffer and the Shoemaker, McLean, and Pratt (SMP) buffer. The A-E buffer is widely used in the Southeastern US (Adams, 1984). It was developed for measuring the LR of red-yellow podzolic soils

(Ultisols) which can be adversely affected by over-liming (Adams and Evans, 1962). The LR calculation with the A-E buffer is based upon a general relationship between soil pH and base unsaturation as well as the buffer's ability to indicate the amount of exchangeable acidity to be neutralized (van Lierop, 1990). The A-E buffer works well for highly weathered, low CEC (1-10 $cmol_c/kg$) soils but some research has shown that it can overestimate the LR of low CEC soils and underestimate the LR of high CEC (> 10 $cmol_c/kg$) soils (Alabi et al., 1986; Follett and Follett, 1983; Fox, 1980; Tran and van Lierop, 1981).

The SMP buffer is the most widely used and is commonly used in the Midwestern US (Follett and Follett, 1983). It was developed using acidic, high LR soils with <10% organic matter (Alabi et al., 1986; Follett and Follett, 1983; Shoemaker et al., 1961). If the pH of the soil measured in water is below a user-defined value, buffer solution is added to the samples and the soil:buffer pH is used to determine the LR via a table (Shoemaker et al., 1961). The SMP buffer has been shown to be very accurate when compared to laboratory incubations for medium and fine textured, acidic, high LR soils (Follett and Follett, 1983; McLean et al., 1966; Tran and van Lierop, 1981). However, it does tend to overestimate the LR of low LR soils (McLean, 1982b; McLean et al., 1966; Shoemaker et al., 1961).

A feature both the A-E and SMP buffers share is the use of paranitrophenol (Adams and Evans, 1962; Shoemaker et al., 1961). Paranitrophenol has been shown to be environmentally toxic and as such has to be handled and disposed of properly (Braunbeck et al., 1989). In part because of the toxicity issues, The University of Georgia Soil, Plant, and Water (UGA SPW) laboratory, which utilized the A-E buffer, started to investigate the feasibility of a titration using $Ca(OH)_2$ procedure to determine the LR.

Direct titration for LR determination was first studied by Dunn (1943). The procedure proposed by Dunn required incubations for up to 4 days which was deemed not practical for use in routine soil test labs. However, the 3-day $Ca(OH)_2$ incubation developed by Dunn is a widely accepted reference method for comparing other methods for determining the LR (Alabi et al., 1986; Follett and Follett, 1983; Loynachan, 1981; McConnell et al., 1991). Magdoff and Bartlett (1985) found that titration curves for acid soils were approximately linear. Weaver et al. (2004) found that a linear expression described well the relationship of pH vs. added base between pH 4.5 and 6.5 for some coastal plain soils of Georgia. Liu et al. (2004; 2005) continued Weaver's research which led to the development and implementation of an automated single-addition titration procedure by Kissel et al. (2007) at the UGA SPW laboratory.

Because the relationship between pH and added base was linear between pH 4.5 and 6.5, Liu (2005) suggested it may be possible to use regression analysis to develop a titration procedure that could be used for routine LR determination by soil test labs. One advantage of a single-addition titration over buffer procedures is that the titration is not based upon a calibration but instead provides data on the rise in pH from a given addition of base. The rise in pH can be used to calculate the pH buffering capacity of the soil. The soil pH buffering capacity, initial pH, and the target pH can then be used to calculate the LR of a soil (Kissel et al., 2007).

One issue that became apparent during Liu's research was that the initial soil pH taken in deionized (DI) water without $Ca(OH)_2$ addition was below the y-intercept of the regression. This issue was resolved by measuring the soil pH in 0.01 M $CaCl_2$. By doing this, the soil pH with no $Ca(OH)_2$ addition agreed more closely to that of the regression analysis, and it stabilized pH readings of low ionic strength soils (Liu et al., 2005; Sumner, 1994).

For the single-addition titration procedure, soil pH buffering capacity was expressed by the term lime buffer capacity (LBC) which is the equivalent weight of $CaCO_3$ required to change soil pH one unit per kg of soil (Kissel et al., 2007). The LBC has units of mg $CaCO_3$ kg^{-1} pH^{-1} and can be calculated from the following equation:

$$\text{LBC} = (\text{V x N x EW})\ \text{kg}^{-1}\ (\text{pH}_2\text{-pH}_1)^{-1} \qquad [1.1]$$

Where V is the volume of calcium hydroxide added, N is the normality of calcium hydroxide (0.046 N), and EW is the equivalent weight of calcium carbonate (50 mg meq^{-1}), which is known to react identically to calcium hydroxide for soil pH less than 8. The weight of soil in Eq. [1.1] is expressed in kg, pH_1 is the initial soil pH, and pH_2 is the pH taken 30 minutes after addition of the calcium hydroxide (Kissel et al., 2007).

The LR for a depth of 8" is determined from the following equation:

$$\text{LR (lbs/ac)} = \text{LBC x (Target pH}_\text{w} - \text{Initial pH}_{\text{CaCl2}}) \text{ x 2 x 1.5 x 1.33}, \qquad [1.2]$$

where the target pH_w is the desired final pH of the soil as measured in DI water and initial pH_{CaCl2} is the initial pH as measured in 0.01 M $CaCl_2$. The target pH_w is used rather than target pH_{CaCl2} because the samples are only equilibrated for 30 minutes which is not enough time to allow the samples to reach equilibrium. The value of (target pH_w - initial pH_{CaCl2}) is larger than if target pH_{CaCl2} is used, which compensates for the lower LBC due to the lack of equilibrium. The factor 2 converts LBC units of ppm to lbs/ac furrow slice (1 ac., 6" deep). The factor 1.5 is an efficiency factor converting pure $CaCO_3$ to ag lime. This efficiency factor has been used by Auburn University as well as the University of Georgia to compensate for large, poorly reactive lime particles. The factor 1.33 is a depth conversion for 8" furrow depth (8/6 = 1.33) (Kissel et al., 2007).

The objective of this research was to i) determine the time $Ca(OH)_2$ treated samples reached pH equilibrium and ii) determine if a relationship exists between LBC estimated from a 30-min equilibration and the LBC estimated from pH data in which the sample has reached pH equilibrium with respect to the added base.

Materials and Methods

Twenty soil samples were collected from three of the major land resource areas (MLRA) in Georgia including five samples from the Ridge and Valley, three from the Atlantic Coast Flatwoods, and 12 samples from the Coastal Plain. Five samples were provided by the North Carolina Department of Agriculture – Agronomic Division Soil Test Lab from samples submitted for analysis. Each of the five samples provided by North Carolina was obtained by combining samples with similar pH, texture, and organic matter. All soils were oven dried (43° C) overnight, ground and sieved (2 mm) to remove any stones or plant matter, and stored in large Ziploc® freezer bags for later analysis. Soil classifications and select soil physical properties are shown in Tables 1.1 and 1.2. Particle size distribution was determined by the pipette method as described by Kilmer and Alexander (1949). The range in pH_{CaCl2} was 3.34 to 5.49. CEC ranged from 2.1 to 76.1 $cmol_c\ kg^{-1}$. Cation exchange capacity (CEC) was determined by the soil survey laboratory method (Soil Survey Staff, 1996). Total carbon and total nitrogen contents of each soil were determined by dry combustion using a LECO CNS-2000 (Kirsten, 1979).

Preliminary Experiments

Because the soils would be submerged in 0.01 M $CaCl_2$ for four days in the main experiments, preliminary studies were carried out to determine if sterilization would minimize or eliminate any change in pH due to submergence. Three sterilization methods were tested: chloroform treatment, sodium azide (NaN_3) treatment, and exposing the soil samples to gamma radiation.

For the chloroform treatment, three drops of chloroform was added to 20 g soil samples that were previously mixed with 20 mL of 0.01M $CaCl_2$ solution and thoroughly mixed with a glass rod. Following the addition of chloroform, 2.4 mL of 0.046 N $Ca(OH)_2$ was added to all samples and soil pH was determined utilizing a LabFit AS-3000 pH analyzer. Three replicates of each soil were used.

Sodium azide (NaN_3) was investigated in two methods. In the first method, solutions were prepared that gave final concentrations of 0.01M $CaCl_2$ alone or 0.01 M $CaCl_2$ plus either 3 mmol or 6 mmol NaN_3 per 20 mL, respectively. Twenty mL of these solutions were added to the soil sample and pH measurements were begun immediately and continued periodically for 48 hours. There was no incubation with NaN_3 solution before pH measurements were started.

For the second NaN_3 method, 20-g soil samples were weighed into 50-mL polyethylene beakers. Four mg (3 mmol) of dry NaN_3 was added to the samples and mixed with a glass rod. The samples were moistened with deionized (DI) water to approximately FC, covered with Parafilm (three small holes allowed for air exchange), and incubated at room temperature for 48 hours. After the incubations were complete, 20 mL of 0.01M $CaCl_2$ was added to each beaker and pH determined periodically for a 76-hour period.

The third procedure for soil sterilization was exposing the soils to gamma irradiation by Cobalt^{60}. Approximately 400 g of soil was placed in a large Ziploc® bag. The bag was placed into the gamma irradiator and administered a dose of 0.3 MGy (3 Mrad). The 0.3 MGy dose rate was suggested by Jackson et al. (1967) to completely sterilize a soil. After irradiation, 20 g samples of each soil were placed into 50-mL polyethylene beakers, 20 mL of 0.01M $CaCl_2$ was added, and pH was determined periodically for 72 hours.

Main Experiment

The objective of the main experiment was to determine the time required for the pH to stabilize from the addition of $Ca(OH)_2$. Because it was not possible in the preliminary experiments to completely stop biological activity, and therefore to stop pH change of untreated flooded soil over a 3- to 4-day period, a check soil was also included. It was assumed in this analysis that the pH change of treated soils due to biological activity alone was the same as for untreated soils over the 96 hours of the experiment. The 25 soils were prepared for pH measurement as follows: 20 g of air dry soil was placed with 20 mL 0.01 M $CaCl_2$ in 50-mL polyethylene beakers, except for high organic matter soils 12 and 13, for which a soil to solution ratio of 1:2 was used. The two treatments for each soil were 1) soil treated with 2.4 mL of 0.046 N $Ca(OH)_2$, and 2) control soil not receiving $Ca(OH)_2$. Each treatment was replicated four times. After the 0.01 M $CaCl_2$ was added, the samples were allowed to equilibrate for 30 minutes, followed by pH measurement on the LabFit AS-3000 pH analyzer (LabFit, Burswood, Western Australia). The samples were stirred during measurement. After the initial pH measurement, the LabFit AS-3000 automatically dispensed 2.4 mL of 0.046 N $Ca(OH)_2$ into the samples and stirred for 20 seconds. Subsequent pH readings were taken at 30 minutes (treated samples only), 2, 4, 8, 12, 24, 36, 48, 60, 72, 84, and 96 hours after the initial pH determination. After each pH determination, the samples were covered with parafilm until the next pH reading.

Calculation of Lime Buffer Capacity

The lime buffer capacity (LBC), expressed as mg CaCO3/kg soil/pH unit, was calculated for each sample using the following equation:

$$LBC = [mL \times N \times EW\ CaCO_3]/\text{soil weight}/(pH_2 - pH_1) \qquad [1.3]$$

for which mL is the volume of $Ca(OH)_2$ added (2.4 mL), N is the normality of the saturated $Ca(OH)_2$ (0.046 N), EW $CaCO_3$ is the equivalent weight of $CaCO_3$ (50 mg meq^{-1}), the soil weight was 0.020 kg, pH_2 was the pH of the calcium hydroxide treated sample at any of the measurement times, and pH_1 was the pH of the control sample at the same time of measurement.

Laboratory Incubations

To validate the LBC values obtained after reaching pH equilibrium, each soil was incubated with the amounts of $Ca(OH)_2$ calculated to raise pH_{CaCl2} to 6.0, according to three different procedures. One procedure was based upon the LBC calculated from the average pH at the 84-hour and 96-hour equilibration time. A second procedure was based upon the power regression equation in which $LBC_{equil} = f(LBC_{30\ min})$. The study included a third treatment, which was an untreated check. There were four replicates of each treatment.

The amounts of dry $Ca(OH)_2$ added to each 20 g soil sample were calculated as follows:

$$\text{mg of } Ca(OH)_2 = LBC \times (\text{target pH} - \text{initial pH}) \times 0.02 \times (74/100) \qquad [1.4]$$

where the LBC was defined above, 0.02 is the weight of soil (kg) and 74 and 100 were the molecular weights of $Ca(OH)_2$ and $CaCO_3$ respectively. After the dry $Ca(OH)_2$ powder was added, the samples were stirred thoroughly with a glass rod. DI water was then added to each sample. Samples were wetted to at least 85% of estimated field capacity (FC). It was not crucial to have an exact water content for the incubations so FC was estimated by filling a tared 10 mL graduated cylinder with soil and lightly packing it. The weight of 10-mL of dry soil was determined. One mL of deionized (DI) water was added to the surface of the soil column and was allowed to infiltrate. The top was covered with Parafilm to prevent evaporation. By 14 hours, the wetting front stopped. Because the 1 g of DI water was contained in the weight of dry soil that had been wetted, FC (g H_2O g dry soil^{-1}) = 1 g/(wd/10) where d is the wet volume and w is the weight of 10 mL dry soil.

The samples for incubation were covered with Parafilm and three small holes were made with a syringe to allow air exchange. The samples were incubated for 5 d at room temperature. On Day 5, enough $CaCl_2$ and DI water was added to bring the samples to 20 mL of 0.01 M $CaCl_2$. The samples were stirred briefly and allowed to equilibrate for 30 minutes. The samples were then placed on the LabFit AS-3000 and pH values were determined.

Statistical Analysis

For the individual soil LBC graphs (Figure 5), the exponential function was fitted to a one-pool exponential model (SAS, 1985). All other statistical analyses were performed using the regression wizard in SigmaPlot (Systat Software, 2004).

Results and Discussion

Preliminary Experiments

Two soils from the Coastal Plain of Georgia with different organic matter contents were used for the preliminary chloroform experiment. Because the pH of the samples not treated with $Ca(OH)_2$ continued to increase during the 48 hour experiment (Fig. 1.1), we concluded that treating samples with 3 drops of chloroform did not stop the possible influence on pH due to microbial activity.

For the NaN_3 experiments, the 3 and 6 mmol NaN_3 solutions did not stop the pH increase that may have been due to microbial activity. The results for Soil 2 are shown in Fig. 1.2. The response for Soil 2 is similar to that for Soils 1 and 3, so only Soil 2 results are shown. The pre-treatment of soil with NaN_3 increased the pH of Soil 2 at time 0 from 4.73 to 5.10 with the 3 mmol NaN_3 solution, and the increase in pH was approximately 0.15 pH units higher at the highest treatment of 6 mmol NaN_3 solution. The increase in pH with time was similar for all treatments, indicating that the NaN_3 was not limiting the rise in pH.

The same three soils used for the NaN_3 solution experiment were used for the NaN_3 incubation experiment. Because all three soils treated with NaN_3 reacted similarly, only results for Soil 2 are shown (Fig. 1.3). Treated samples reacted similarly to samples that did not receive NaN_3, with the NaN_3 treated samples exhibiting a pH increase above that of the untreated samples. As mentioned earlier, this increase was also evident in the samples treated with NaN_3 solution. Sodium azide is a weak base and neutralizes soil acidity (Skipper and Westermann, 1973). The pH increase is caused by the conversion of the non-volatile azide salt to hydrozoic acid, which is highly volatile and represents an explosion hazard (Rozycki and Bartha, 1981).

Exposing the soils to gamma radiation was the final method evaluated for stopping microbial activity in submerged samples. As before, results for all three soils were similar, therefore only results for Soil 2 are shown. Irradiating samples did not suppress the increase in pH over the 72 hours of the experiment (Fig. 1.4). The irradiated sample for Soil 2 had a lower pH than that of the untreated samples. All samples exhibited a pH increase over time, suggesting that the dose of gamma radiation applied did not stop the pH influence, possibly due to microbial activity.

Because the preliminary experiments indicated that it was not possible to stop microbial activity from the pretreatment with either chloroform, NaN_3, or with 0.3 MGy doses of gamma radiation, the decision was made to carry out the main experiment without pre-treatment. Instead, the pH was measured on samples treated with $Ca(OH)_2$ and on samples not treated with $Ca(OH)_2$, which served as controls.

Main Experiment

Individual plots of soil pH versus time and LBC versus time generally show that equilibrium is reached around 84 or 96 hours (Fig. 1.5). This equilibration time is much larger than the 10 to 15 minute equilibration between base additions used by Weaver (2004) or the 30-min equilibration time suggested by Liu et al. (2004) that is currently used for the UGA single-addition titration procedure (but with an adjustment for lack of equilibrium when making lime recommendations). To further evaluate the data, a decision was made to average the 84 and 96-h LBC values because the line fitted by the exponential function generally appeared to be around or between those two data points. We chose not to use the exponential function because in some cases the fit did not appear as good as the mean of the 84 + 96-h LBC values. A plot of the 84 and 96-h avg. LBC versus the 30-min LBC for all of the soils is shown in Fig. 1.6. The spread between the actual LBC and the predicted LBC among the soils with a 30-min LBC >1000 was larger than those soils with a 30-min LBC <1000.

The 84 and 96-h avg. LBC values (considered to be at equilibrium) for each soil were divided by their respective 30-min LBCs to calculate a ratio that might be related to other soil properties or to the 30-min LBC.

$$\mathrm{LBC_{equil}/LBC_{30\ min}\ ratio = 84 + 96\ h\ avg.\ LBC/30\ min\ LBC} \qquad [1.5]$$

If, for example, the LBC ratio is related statistically to the routinely measured 30-min LBC, then it might be used by the SPW laboratory to improve lime recommendations made to clients.

A plot of the LBC ratio data revealed that five soils appeared to be outliers (Fig. 1.7). Soils 1 and 5 from the Ridge and Valley had an LBC ratio of 3.60 and 3.22 respectively, while Soils 6, 7, and 8 from the Atlantic Coast Flatwoods had values of 2.31, 1.79, and 1.47 respectively. All five soils were forest soils, though it is not clear as to why these soils reacted differently. Because those five soils appeared to be outliers, it was decided to remove those five data points from the regression analysis. When these soils were removed, a curvilinear relationship was evident between the LBC ratio and the 30-min. LBC (Fig. 1.7). The equation for the regression line in Figure 7 is $LBC_{equil} = 0.7593 \times 30\ min\ LBC^{0.1939}$ where 30-min LBC is the LBC measured from a 30-min equilibration time.

Laboratory Incubations

Laboratory incubations were carried out to verify the accuracy of the earlier results for determination of an LBC_{equil} value for each soil. For example, the samples in the main experiment were submerged for 96 hours, which could have caused different results than for a well aerated soil. Furthermore the $LBC_{30\ min}$ is proposed as a means to calculate the LBC_{equil}. The lab incubations served two purposes; 1) to evaluate the 84 + 96 h avg. LBC in making lime recommendations and 2) to test the accuracy of the LBC ratio model (Eq. [1.5]) in predicting the amount of ag lime needed to reach a target pH.

The pH (in 0.01 M $CaCl_2$) results from the incubation experiment are shown in Fig. 1.8. For the 30-min LBC model, 68% of the pH values were within 0.25 pH units of the target pH_{CaCl2} (6.0) and 84% were within 0.5 pH units of the target. The 84 + 96-h avg. LBC approach, 52% of the incubated samples were within 0.25 pH units and 88% within 0.5 pH units of the target. Because some pH values were above or below the target pH, it is clear that the LBC_{equil} determined from the 84 + 96 h pH data were subject to some error, possibly due to the samples being submerged for 96 hours. The incubation experiment more closely mimicked conditions in the field because powdered $Ca(OH)_2$ was added to dry soil, mixed, and then wetted to either 85% or 100% FC and left undisturbed for 5 days. Because the incubation experiment was closer to conditions in the field, it was decided to use the incubation data to correct the 84 + 96-h avg.

LBC values from the main experiment. The corrected 84 + 96-h LBC was calculated by the following equation:

$$LBC_{84+96\ \mathrm{corrected}} = 84 + 96\text{ h avg. LBC}/[(\text{Final }84 + 96\text{ h avg. LBC treated pH} - 84 + 96\text{ h Control pH})/(\text{Target pH} - \text{Initial soil pH})], \quad [1.6]$$

where the Final 84 + 96-h avg LBC is the LBC calculated from the main experiment and all other values are pH values from the incubation experiment. The denominator is calculated from the actual rise in pH of the treated samples. Using Soil 14 as an example, the 84 + 96-h LBC from the main experiment was 389, the final treated pH from the incubation was 6.05, the 84 + 96-h control pH from the incubation was 5.14, the target pH was 6.00, and the initial soil pH was 5.03. The calculated denominator for Soil 14 is 0.938, which means that the original 84 + 96-h LBC calculated from the main experiment accounted for 93% of the actual LBC determined from the incubation experiment. Dividing the original LBC of 389 by 0.938 gives the corrected 84 + 96-h LBC of 415. For that particular soil, the main experiment under predicted the LBC from the incubation experiment.

The $LBC_{84+96\ \mathrm{corrected}}$ above was verified by calculating the LBC by the following equation:

$$LBC_{84+96\ \mathrm{corrected}} = [\text{mg of } Ca(OH)_2 \text{ x } (100/74)]/0.02/(pH_2 - pH_1) \quad [1.7]$$

where mg of $Ca(OH)_2$ was the amount used to treat the soil for the incubation, (100/74) converts mg of $Ca(OH)_2$ to mg of $CaCO_3$, 0.02 is the weight of soil in kg, pH_2 is the pH of the $Ca(OH)_2$ treated soil on day 5 of the incubation, and pH_1 is the pH of the control on day 5. Again, taking Soil 14 as an example; 5.59 mg of $Ca(OH)_2$ was added to the soil sample, pH_2 was 6.05, and pH_1 was 5.14. The incubation resulted in an LBC of 415, the same LBC calculated from Eq. [1.6].

The corrected 84 + 96-h LBCs were used again to calculate the LBC ratio. The corrected ratio was calculated as in Eq. [1.5], however the corrected 84 + 96-h avg. LBC was used in the calculation. A plot of the corrected LBC ratio vs. 30-min LBC is shown in Fig. 1.9. Soils with LBC values close to 1,400 and larger did not closely follow the linear regression ($r^2 = 0.22$). Upon closer inspection, three data points with unusually low 84 + 96-h avg. LBCs were influencing the linear regression. Removing those three soils (the three ACF soils) resulted in a much better linear regression ($r^2 = 0.83$), as shown in Fig. 1.10.

The equation for the regression line in Fig. 1.10 is:

$$\text{Corrected LBC ratio} = 1.4745 + 0.0023 * 30 \text{ min LBC} \qquad [1.8]$$

For example, a soil that has a 30-min LBC of 500 will have a corrected LBC ratio of 2.674.

To calculate the LBC_{equil} of a sample from only measuring the $LBC_{30\ min}$, the $LBC_{30\ min}$ is multiplied by the samples corrected LBC ratio, as calculated in Eq. [1.8]. For example, the soil mentioned previously with a 30-min LBC of 500 and a corrected LBC ratio of 2.674 would have a corrected LBC of 1337. The calculation to determine the amount of ag lime recommended would then change to:

$$\text{LR (lbs/ac)} = LBC_{equil} \text{ x } (\text{Target } pH_{CaCl2} - \text{Initial } pH_{CaCl2}) \text{ x } 2 \text{ x } 1.5 \text{ x } 1.33, \qquad [1.9]$$

where LBC_{equil} is the $LBC_{30\ min}$ multiplied by the corrected LBC ratio calculated from equation 1.8, the target pH_{CaCl2} is the desired final pH of the soil as measured in 0.01 M $CaCl_2$, and initial pH_{CaCl} is the initial pH as measured in 0.01 M $CaCl_2$. The factor 2 converts LBC units of ppm to lbs/ac furrow slice (1 ac., 6” deep). The factor 1.5 is an efficiency factor converting pure $CaCO_3$ to ag lime which has been used by Auburn University as well as the University of Georgia to compensate for large, poorly reactive lime particles. The factor 1.33 is a depth conversion for 8” furrow depth (8/6 = 1.33) (Kissel et al., 2007).

Table 1.1 – Selected physical and chemical properties of the soils used.

MLRA	Soil No.	Soil Classification	Initial Soil pH_{CaCl2}	Sand	Silt	Clay	Textural Class
					$g\ kg^{-1}$		
RV	1	Fine-loamy, siliceous, semiactive, thermic Aquic Hapludult	4.91	21.0	56.6	22.4	silt loam
RV	2	Fine-silty, mixed, active, thermic Oxyaquic Dystrudept	5.12	38.7	50.9	10.3	silt loam
RV	3	Fine-loamy, siliceous, semiactive, thermic Fragic Paleudult	4.17	42.8	51.2	6.0	silt loam
RV	4	Fine, mixed, semiactive, thermic Typic Hapludult	4.23	19.9	62.8	17.3	silt loam
RV	5	Fine-loamy, mixed, semiactive, thermic Typic Hapludult	5.49	19.5	66.2	14.3	silt loam
ACF	6	Loamy, siliceous, subactive, thermic Grossarenic Paleudult	3.38	80.3	12.9	6.8	loamy sand
ACF	7	Fine, mixed, semiactive, thermic Typic Albaquult	3.67	65.2	16.2	18.5	sandy loam
ACF	8	Sandy over loamy, siliceous, active, thermic Ultic Alaquod	3.34	92.5	5.9	1.6	sand
NC	9	NC Mixed - mineral	4.98	64.2	27.2	8.6	sandy loam
NC	10	NC Mixed - mineral organic	4.70	61.9	25.2	13.0	sandy loam
NC	11	NC Mixed - mineral organic	4.70	63.4	27.1	9.5	sandy loam
NC	12	NC Mixed - organic	4.60	59.2	28.5	12.3	sandy loam
NC	13	NC Mixed - organic	4.45	56.1	23.7	20.3	sandy clay loam
CP	14	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	5.03	87.5	10.4	2.1	sand
CP	15	Loamy, siliceous, subactive, thermic Arenic Paleudult	3.86	89.4	10.0	0.6	sand
CP	16	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.93	80.8	11.9	7.3	loamy sand
CP	17	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.93	19.3	51.6	29.0	silty clay loam
CP	18	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.88	43.7	38.1	18.2	loam
CP	19	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	5.19	87.9	10.7	1.5	sand
CP	20	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.46	85.3	10.9	3.8	loamy sand
CP	21	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.80	84.4	10.3	5.3	loamy sand
CP	22	Fine, kaolinitic, thermic Typic Kandiudult	5.15	42.7	31.1	26.2	loam
CP	23	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.17	75.1	13.1	11.8	sandy loam
CP	24	Fine-loamy, kaolinitic, thermic Plinthic Kandiudult	4.89	42.7	31.1	26.2	sand
CP	25	Fine-loamy, kaolinitic, thermic Typic Kandiudult	4.68	75.1	13.1	11.8	loamy sand

RV - Ridge & Valley, ACF - Atlantic Coast Flatwoods, NC - North Carolina, CP - Coastal Plain

Table 1.2 – Selected physical and chemical properties of the soils used (cont'd).

Soil No.	Total C	Total N	C/N	CEC
	mg kg^{-1}			cmol$_c$/kg^{-1}
1	39920	2765	14.4	17.6
2	24860	1714	14.5	12.4
3	21780	995	21.9	6.6
4	21900	1122	19.5	11.4
5	45210	3192	14.2	18.4
6	59190	2345	25.2	18.1
7	22280	1495	14.9	14.7
8	10910	573	19.0	4.5
9	15030	992	15.2	6.6
10	32470	1993	16.3	14.0
11	35720	2122	16.8	14.1
12	118000	5260	22.4	40.5
13	219200	9271	23.6	76.1
14	7066	519	13.6	3.1
15	4899	257	19.1	2.6
16	7544	456	16.5	4.1
17	36340	1905	19.1	22.4
18	27250	1325	20.6	13.8
19	5373	328	16.4	2.4
20	4518	267	16.9	2.2
21	5206	330	15.8	2.9
22	19500	1161	16.8	12.2
23	7678	587	13.1	4.0
24	4170	232	18.0	2.1
25	4443	265	16.8	2.6

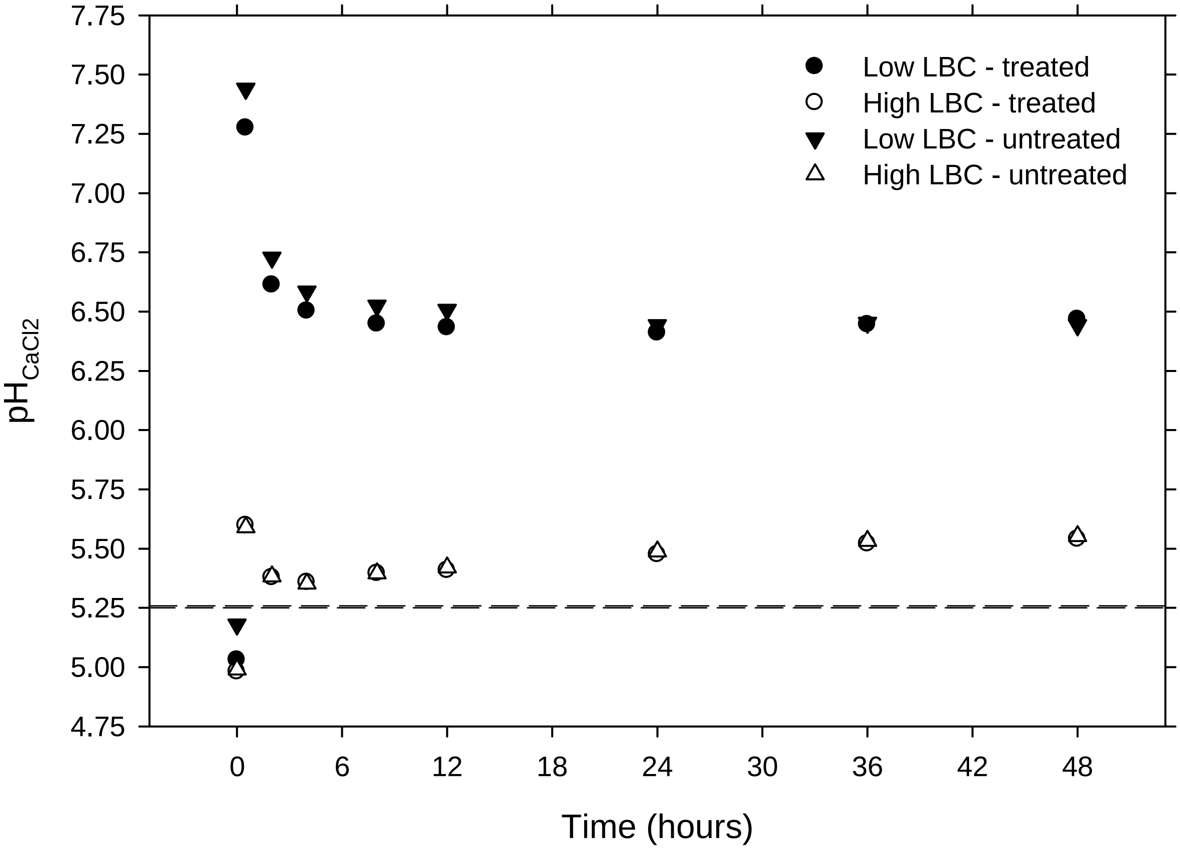

Figure 1.1 – pH of $Ca(OH)_2$ treated samples that were treated and not treated with chloroform.

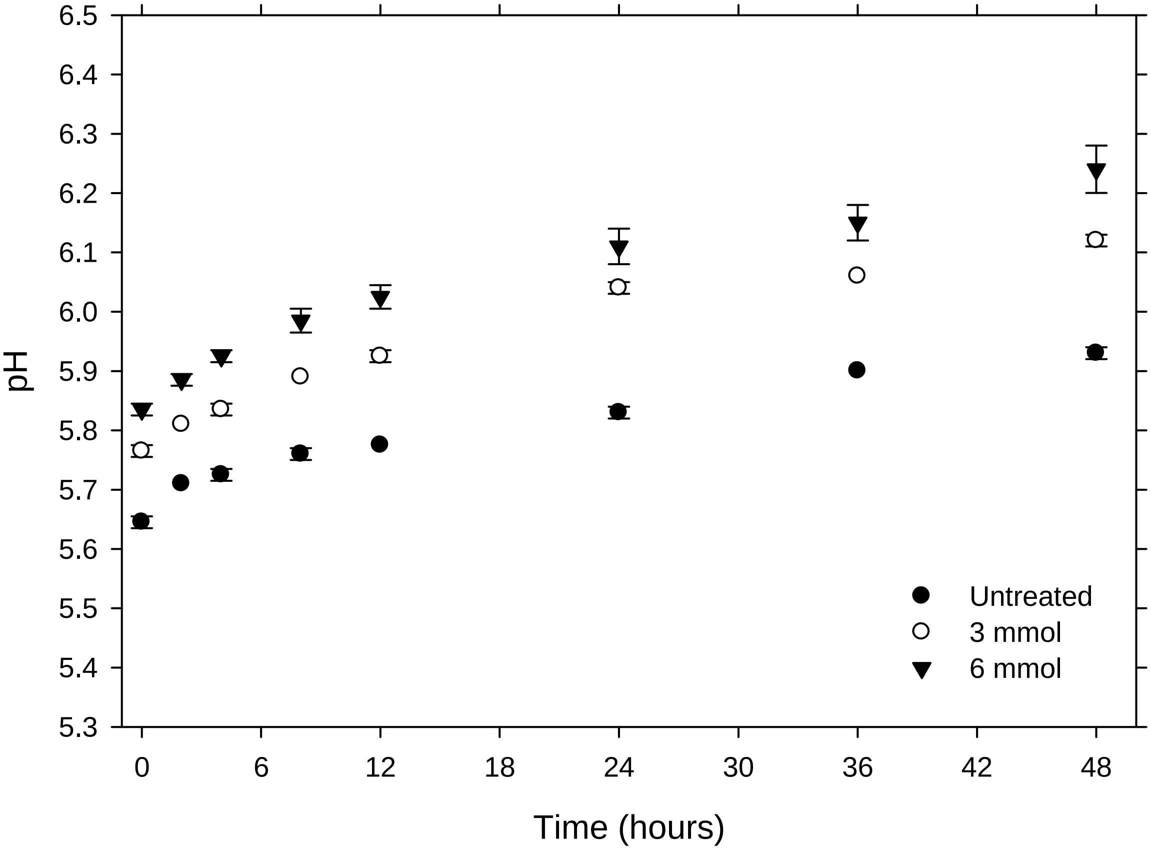

Figure 1.2 – Soil 2 pH when untreated, treated with a 3 mmol NaN_3 solution or treated with a 6 mmol NaN_3 solution. Error bars are one standard deviation.

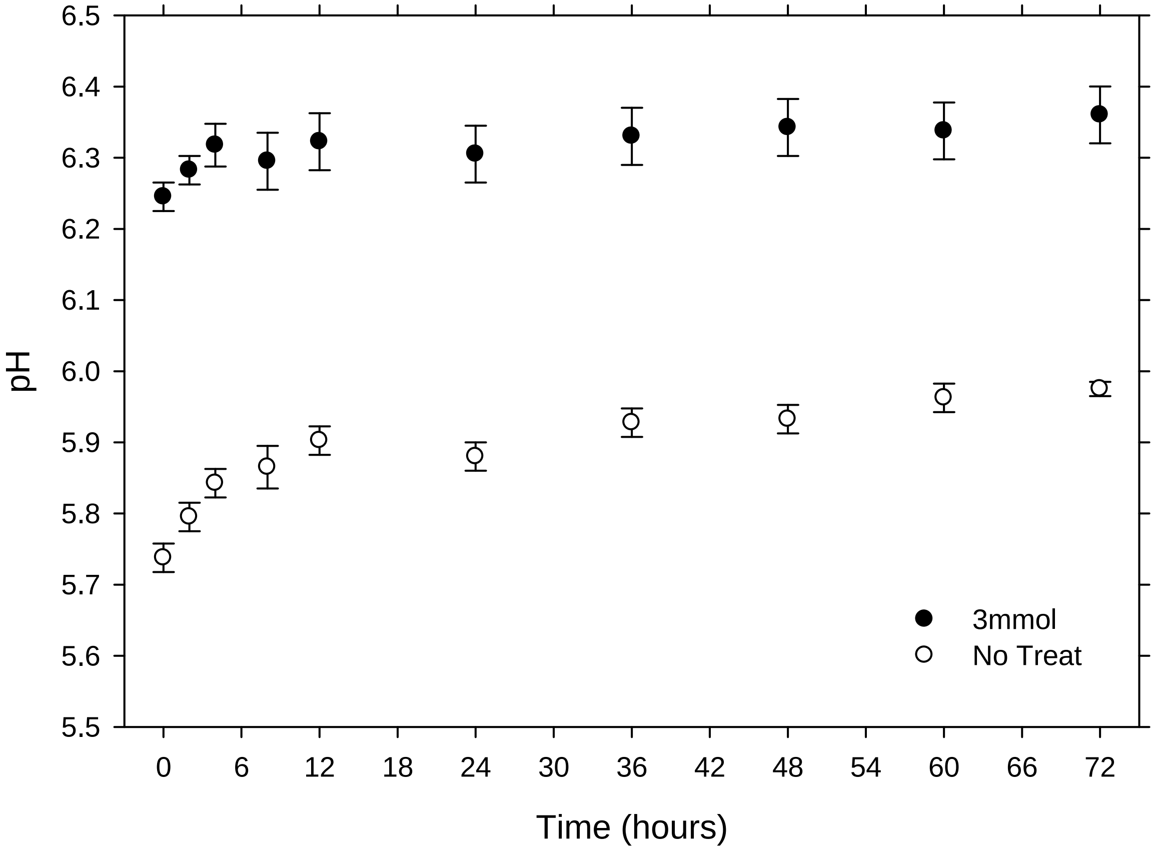

Figure 1.3 – Soil 2 pH in 0.01 M $CaCl_2$ when untreated or incubated with 3 mmol NaN_3 for 48 hours. Error bars are one standard deviation.

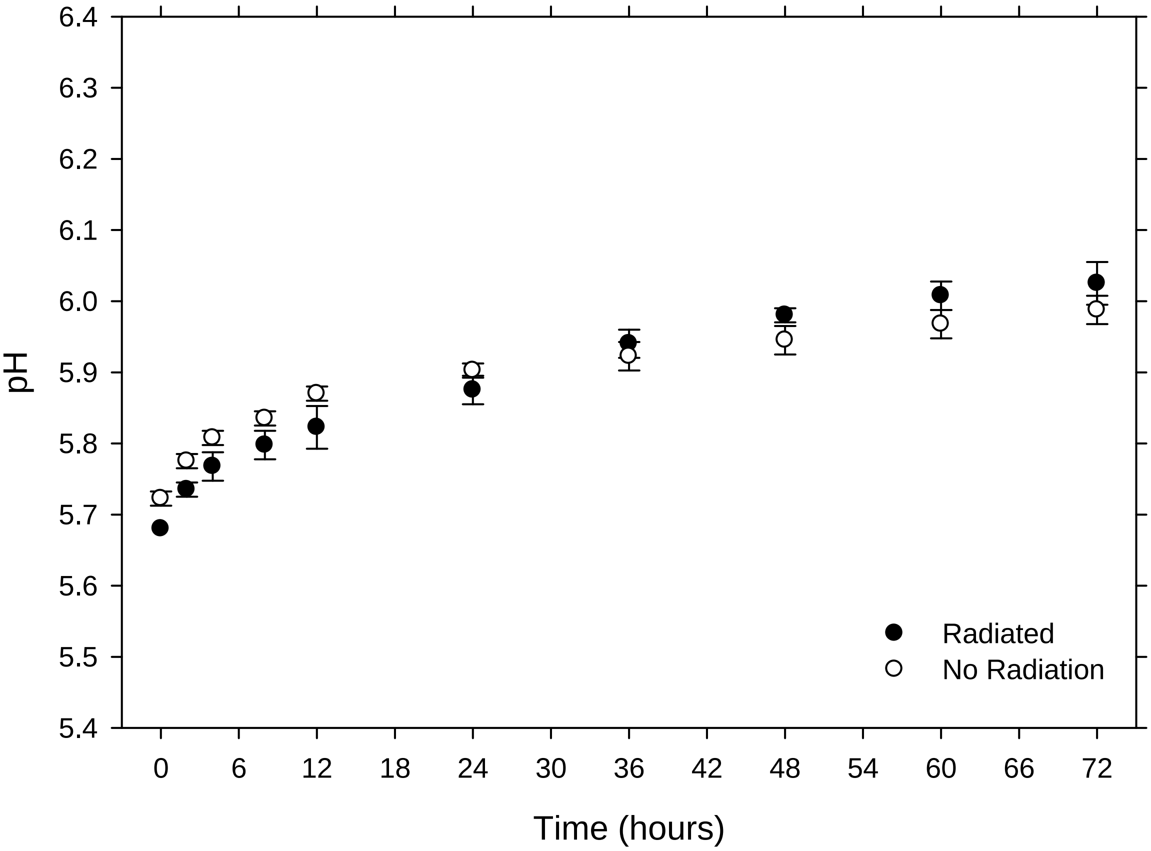

Figure 1.4 – Soil 2 pH in 0.01 M $CaCl_2$ when untreated or treated with 0.3 MGy of gamma radiation. Error bars are one standard deviation.

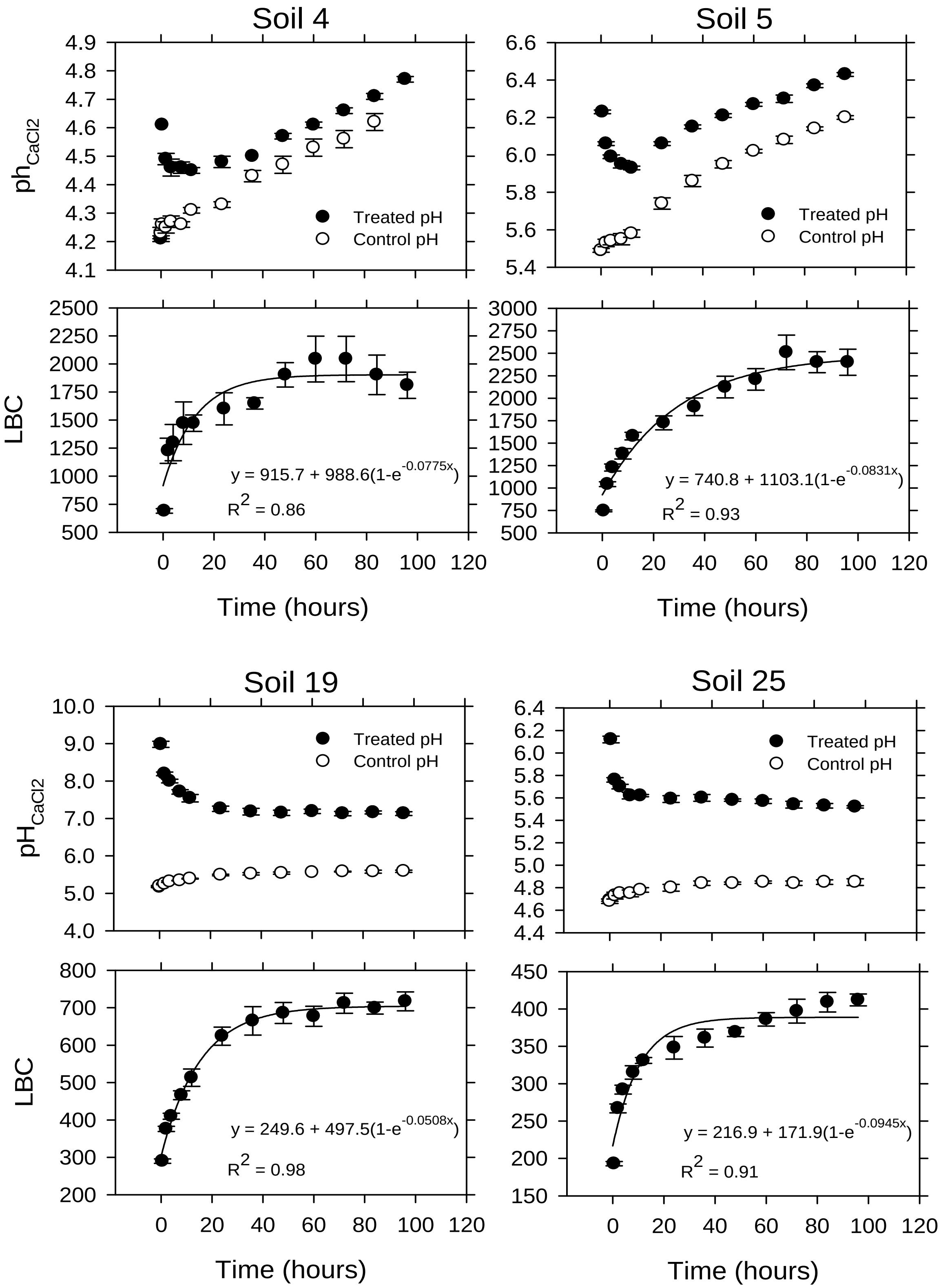

Figure 1.5 – Plots of select soil pH and LBC values with their respective exponential model (solid line). Error bars are one standard deviation.

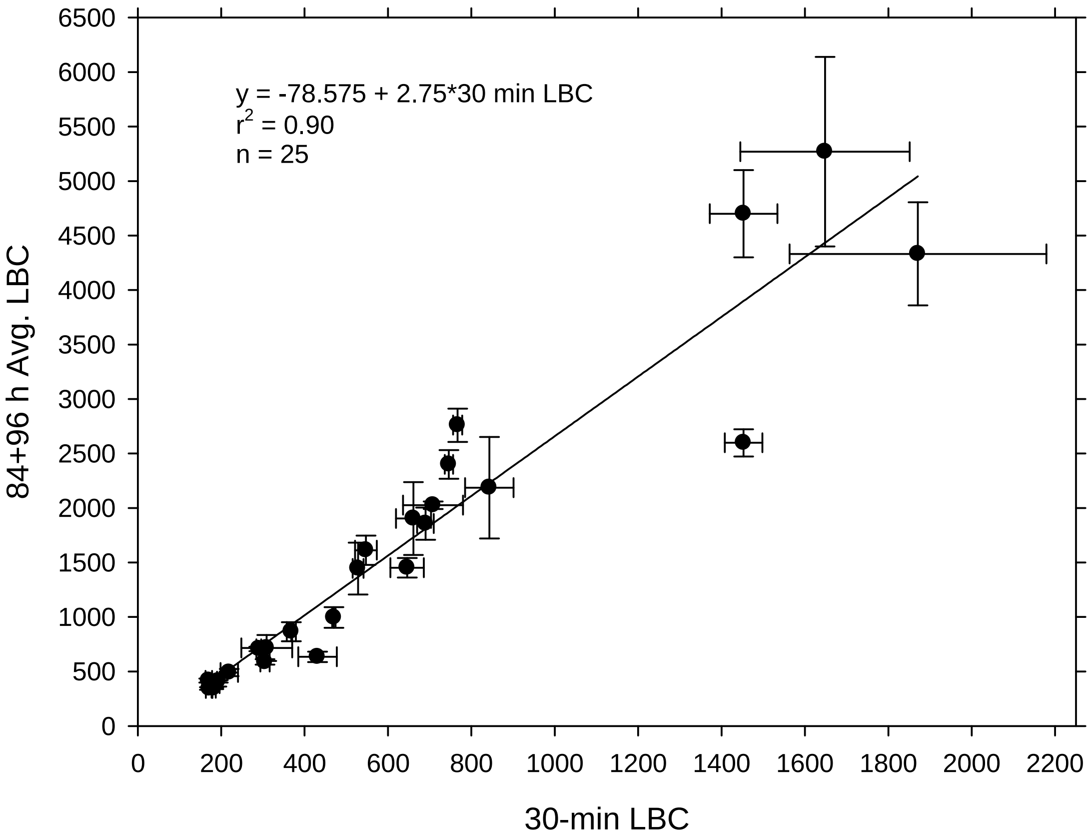

Figure 1.6 – 84-h and 96-h avg. LBC vs. 30-min LBC for the 25 soils. Error bars are one standard deviation.

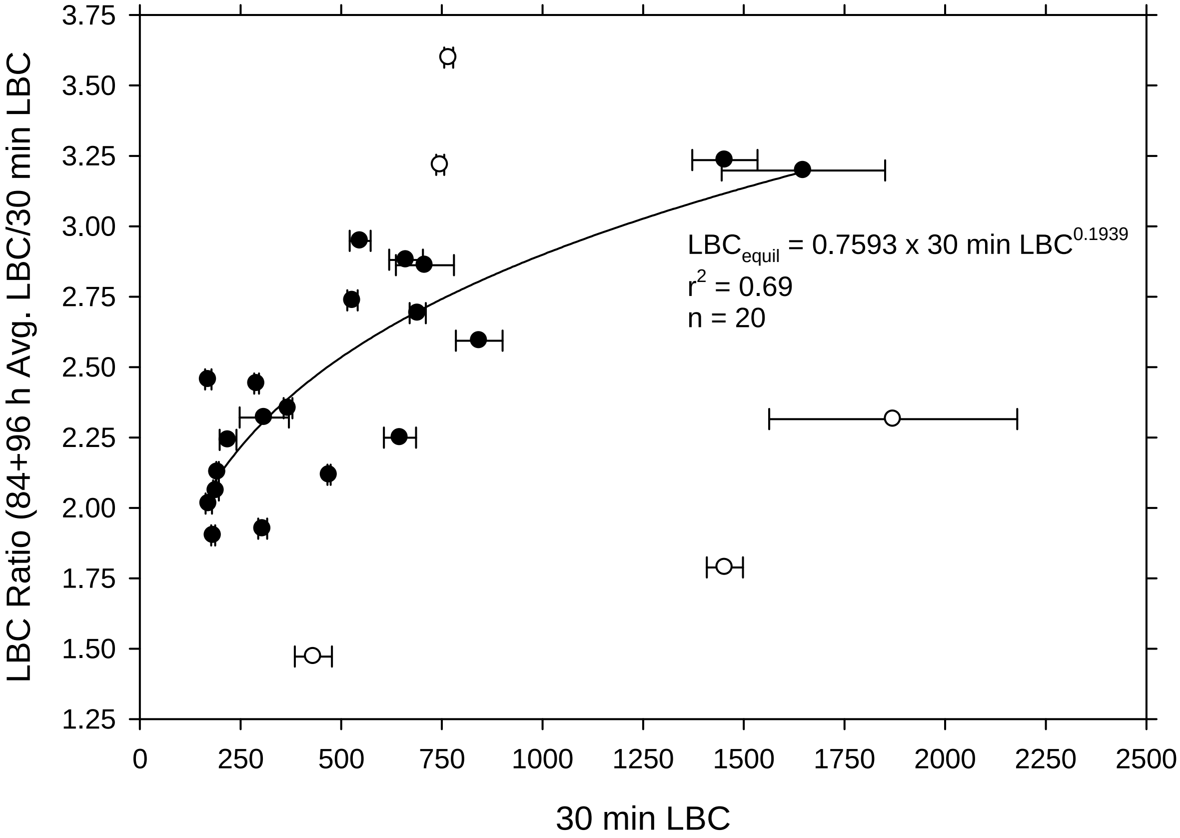

Figure 1.7 – LBC ratio vs. 30 min LBC. Open circle data points are outliers. Power regression excludes outliers. Error bars are one standard deviation.

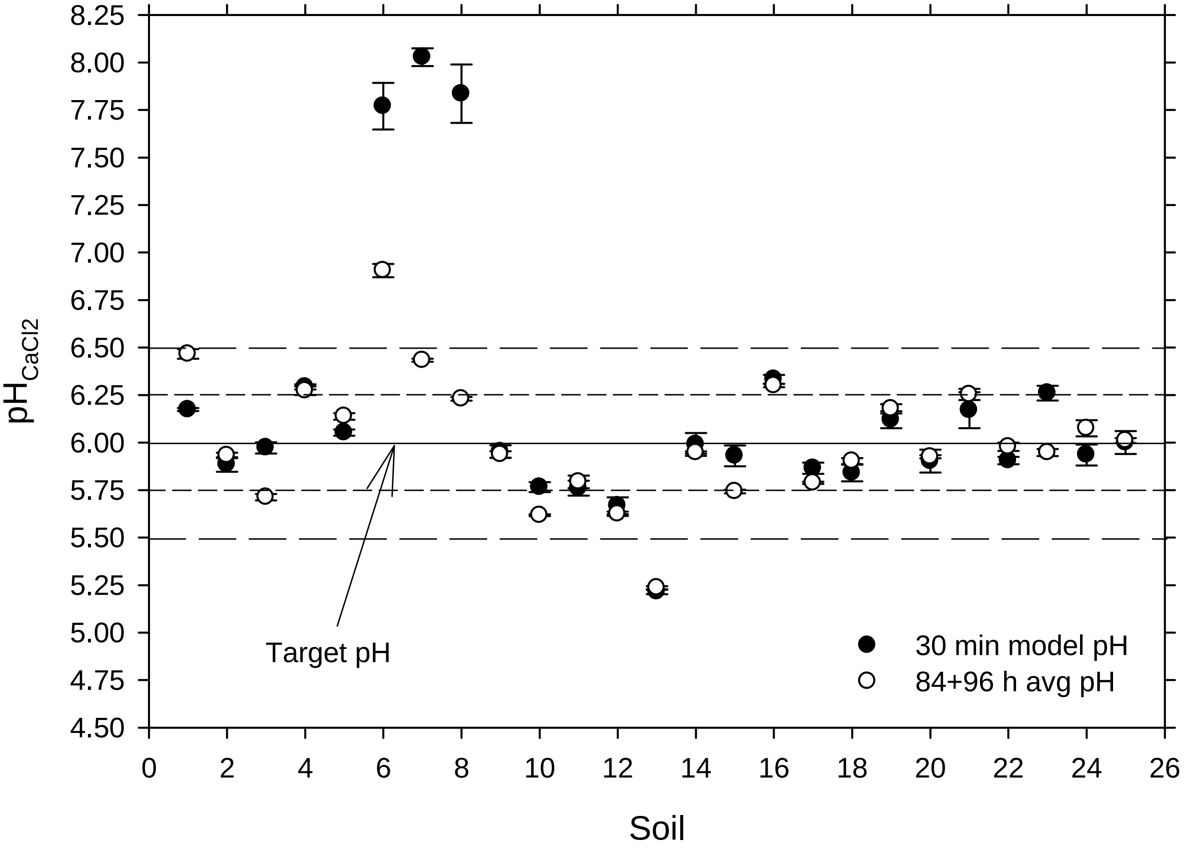

Figure 1.8 – pH results from laboratory incubation for samples treated with the recommended amount of $Ca(OH)_2$ based on the 30 min LBC model or the recommended amount of $Ca(OH)_2$ based on the 84 + 96 h avg. LBC. Error bars are one standard deviation.

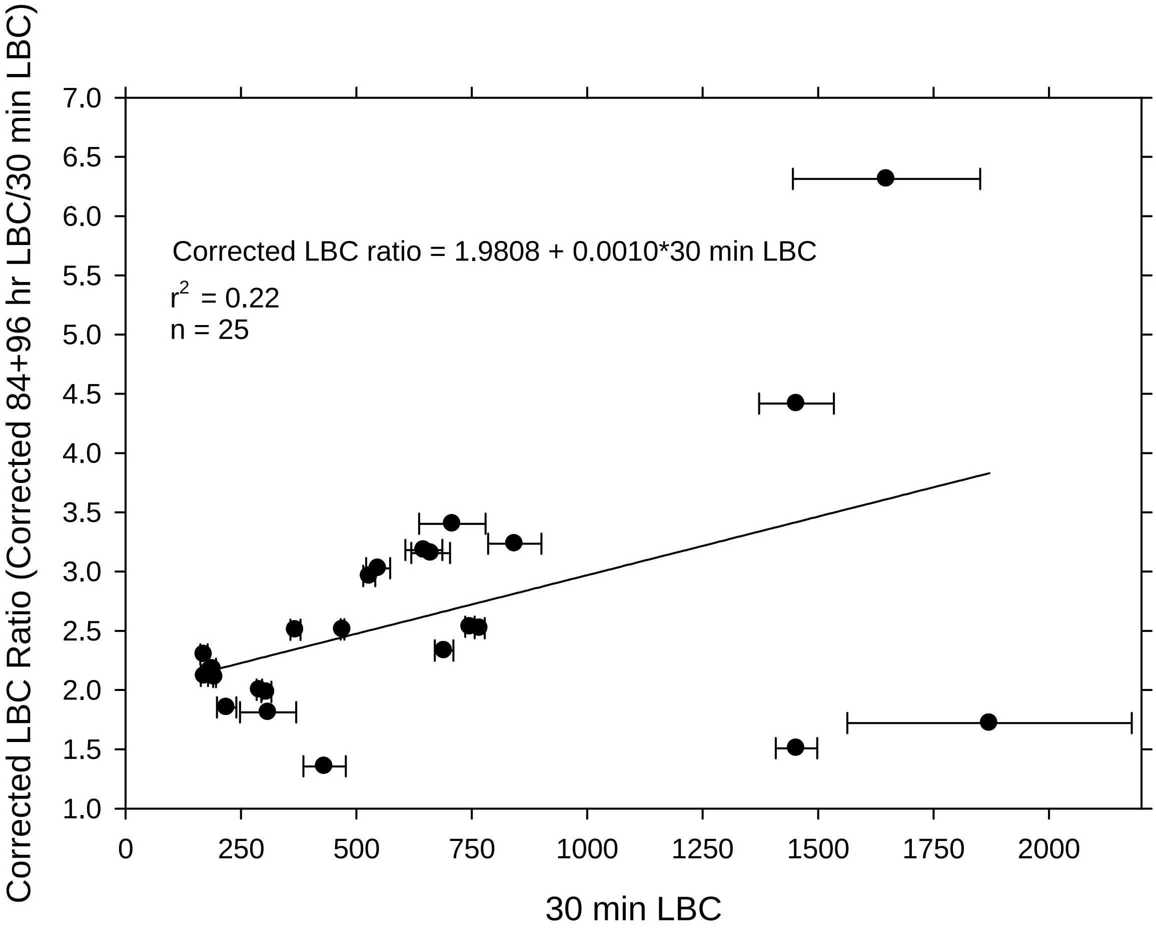

Figure 1.9 – Corrected LBC ratio vs. 30 min LBC for all 25 soils evaluated by linear regression. Error bars are one standard deviation.

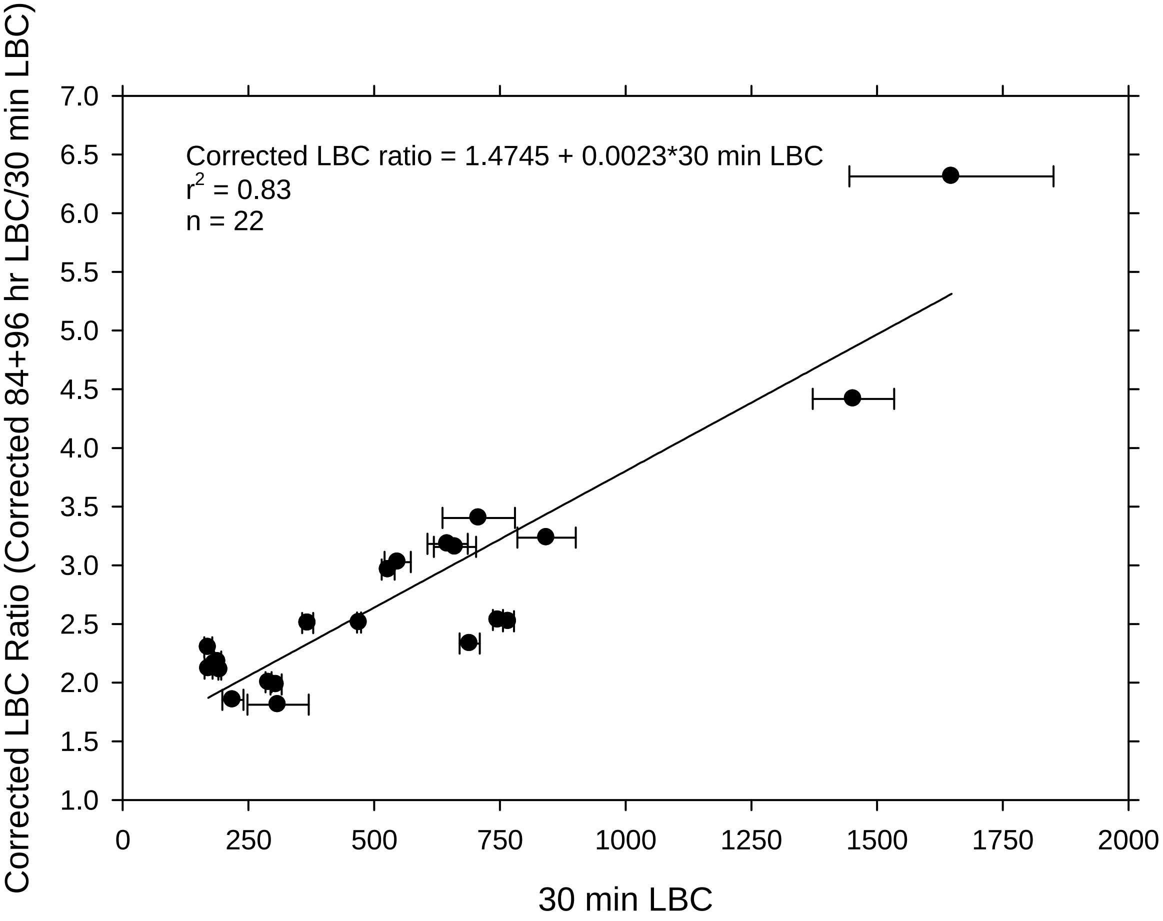

Figure 1.10 – Corrected LBC ratio vs. 30 min LBC (no ACF soils) evaluated by linear regression. Error bars are one standard deviation.

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CHAPTER 2

EFFICIENCY OF COMMERCIAL AGRICULTURAL-GRADE LIMESTONE[2]

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[2] John S. Thompson and David E. Kissel. To be submitted to *Communications in Soil Science and Plant Analysis*.

Abstract

The University of Georgia Soil Testing Laboratory lime recommendation equation includes a multiplier of 1.5 to account for ag lime that is less reactive than reagent-grade $CaCO_3$. Although research has been conducted with ag lime to arrive at this efficiency factor, it has not been conducted using GA soils or with ag limes available in Georgia that may differ in their crystallinity from others tested previously. The efficiency of five ag limes (dolomitic) were compared to reagent-grade $CaCO_3$ powder on two widely different GA soils. The low buffering capacity of one soil resulted in errors with the data for that soil. Results from the high buffering capacity soil yielded multipliers of 1.17, 1.16, 1.48, 1.34, and 1.73 for ag limes 1 through 5, respectively, with an average multiplier of 1.38. For practical purposes, a multiplier of 1.5 is suggested.

Introduction

The lime requirement (LR) calculation for the UGA titration procedure includes a multiplier of 1.5 used to convert a recommendation for pure $CaCO_3$ to less than pure agricultural-grade limestone (ag lime). This multiplier has also been used with the Adam-Evans (A-E) LR calculation. Adams and Evans (1962), citing unpublished data from their Alabama experiment station as well as published data from Pierre and Worley (1928) and Schollenberger and Salter (1943), suggested the 1.5 multiplier because approximately 1.5 times more ag lime than powdered reagent-grade $CaCO_3$ was needed to neutralize a given amount of soil acidity.

Limestone is the main liming material used in the U.S. (Barber, 1984). The limestone may either be calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), or dolomitic limestone (Barber, 1984). Pure dolomite has a calcium carbonate equivalence of 1.08, yet research has shown that it reacts in acid soils more slowly than calcite of the same fineness (Beacher et al., 1952; Rippy et al., 2007; Schollenberger and Salter, 1943; Thomas and Hargrove, 1984). Dolomitic limestone takes twice as long to react with acid soil as does calcitic limestone (Barber, 1984). Rippy et al. (2007) showed that dolomitic limestone reacted 3 to 4 times more slowly than calcitic limestones of the same fineness. Schollenberger and Salter (1943) noted that the difference in reactivity between dolomitic and calcitic limestones was only important over time periods $\leq$ 3 months. To get an equal reaction rate, dolomitic limestone particle size should be half of calcitic limestone particle size (Barber, 1984). The reaction of a liming material with acid soil involves the dissolution of $CaCO_3$, the adsorption of Ca^{2+} to the soil exchange complex, and the reaction of H^+ in the soil with the CO_3^- in the soil solution:

$$CaCO_3 \longrightarrow Ca^{2+} + CO_3^- \Leftrightarrow HCO_3^- + Ca^{2+}\text{-soil}$$

The HCO_3^- then reacts with more H^+ in the soil to produce H_2O and CO_2:

$$HCO_3^- \longrightarrow H_2O + CO_2$$

The degree of fineness to which limestone is ground plays an important role in the rate of reaction with soils. The finer the material, the quicker it reacts with the soil (Barber, 1984; Beacher et al., 1952; Motto and Melsted, 1960). However, because grinding to finer particle sizes requires more energy, it also increases costs, which must be balanced against the faster rate of reaction (Barber, 1984). Meyer and Volk (1952) found that pH values were highest 6 months after application of calcitic limestone of U.S. Standard No. 60 sieve or finer while 50-mesh or finer material needed 12 months to reach its highest pH. They also found that particles coarser than 20-mesh had little value at neutralizing soil acidity, even after 18 months (Meyer and Volk, 1952). Meyer and Volk (1952) also found dolomitic limestone to react slower than calcitic limestone, but if given enough time (>9 months), the soils treated with 50-mesh or finer dolomitic limestone reached a higher pH than those treated with calcitic limestone of equivalent fineness. Barber (1984) suggested that ag limes should be fine enough so that 80% will pass a U.S. Standard No. 8 sieve (2.36-mm opening).

Pierre and Worley (1928) conducted experiments on 77 Alabama soils to find an easy way to determine the LR of soils to bring them to a desired pH value. They established soil titration curves by incubating the soils with $Ba(OH)_2$ for three days. Pot studies on unlimed and limed samples were then performed on all of the soils. The pots prevented any leaching loss and allowed the lime material to react with a known quantity of soil. After 6 months, the pH of the limed and unlimed soils was determined. They calculated the "liming factor" by:

"Liming factor" = meq of lime per 100 g soil for a desired pH/meq of 1.1 N

$Ba(OH)_2$ per 100 g soil for a desired pH

They found the liming factor to range from 1.27 to 1.77, with an average of 1.43. They suggested, for all practical purposes, to use a liming factor of 1.50 (Pierre and Worley, 1928).

In order to evaluate ag lime on the basis of reactivity and cost, Schollenberger and Salter (1943) generated a lime evaluation chart. To use the chart, the percentage passing either a 12, 16, 20, 30, 40, 50, 60, 70, or 100-mesh from a sieve must be known, along with the CCE, % Ca, % Mg, and the moisture content. With this information, an efficiency factor can be selected for any particular lime (Schollenberger and Salter, 1943).

Dunn (1943) determined "liming factors" for some Washington soils. He treated soils with differing amounts of either precipitated $CaCO_3$ or $Ca(OH)_2$ with amounts ranging from 0 to 15 tons $CaCO_3$/acre or the equivalent amount of $Ca(OH)_2$ and incubated them at a normal field moisture content for six months. Soil pH values were determined at 1, 3, and 6 months, with no significant difference in pH at the three incubation times. The pH values had reached equilibrium for both the $CaCO_3$ and $Ca(OH)_2$ treatment within 1 month under laboratory conditions. His calculated liming factors ranged from 0.9 to 1.9, with an average of 1.3 (Dunn, 1943).

An alternative to using an average factor to determine the lime recommendation is to calculate a liming efficiency factor for each liming material, as done by the Kansas State University (KSU) method. KSU uses the SMP buffer to determine the amount of effective calcium carbonate (ECC) necessary to raise the soil pH to a desired level (Whitney and Lamond, 1993). The amount of lime needed to achieve a desired pH will vary with depth of incorporation as well as the quality of the lime material. To account for the quality of the ag lime when making a lime recommendation, KSU derived a Fineness Factor (FF). The FF is calculated by the following:

Size of Material	**Percent of Material**		**Effectiveness Factor**	**Effectiveness**
>8 mesh	_______	x	0	0
8-60 mesh	_______	x	0.5	_______
<60 mesh	_______	x	1.0	_______
			Fineness Factor (FF)	_______

To calculate the ECC that the lime would supply, multiply the FF by the CCE of the ag lime. For example, if an ag lime has a CCE of 95 percent and an FF of 80 percent, the ECC of that particular ag lime is 76 percent (0.95 x 0.80). If the soil test recommendation suggested applying an ECC of 3,000 lbs/a, then 3,947 lbs/a would need to be applied to achieve the desired pH (3,000/0.76) (Whitney and Lamond, 1993). The objective of this research was to investigate the efficiency of five commercial ag limes widely used in Georgia when compared to reagent-grade $CaCO_3$.

Materials and Methods

To evaluate the efficiency of five widely used ag limes in Georgia, two soil samples with differing amounts of organic matter (OM) were selected from the Coastal Plain of Georgia. The soil samples were dried in an oven (43° C) overnight, then crushed and sieved (2 mm) to remove any stones or plant material, and stored in a plastic bag until needed.

In order to determine the correct amount of ag lime to be added to each soil sample, the lime requirement (LR) was determined using the single-addition titration procedure currently used by the University of Georgia Soil, Plant, and Water (SPW) Laboratory (Kissel et al., 2007). With this procedure, the buffering capacity of the soil is determined by measuring the soil pH in 0.01 M calcium chloride (pH_{CaCl2}) and a second pH_{CaCl2} reading following a single addition of calcium hydroxide ($Ca(OH)_2$). The soil pH_{CaCl2} buffering capacity is expressed as lime buffer capacity (LBC), with units of mg $CaCO_3$ kg^{-1} pH^{-1}. The LBC is calculated using the following equation:

$$LBC = (V \text{ x } N \text{ x } EW)\ kg^{-1}\ (pH_2 - pH_1)^{-1}, \qquad [2.1]$$

where V is the volume of calcium hydroxide added, N is the normality of calcium hydroxide, and EW is the equivalent weight of calcium carbonate, known to react identically to calcium hydroxide for soil pH less than 8. The weight of soil in Eq. [2.1] is expressed in kg, pH_1 is the initial soil pH_{CaCl2}, and pH_2 is the pH_{CaCl2} taken 30 minutes after addition of the calcium hydroxide (Kissel et al., 2007).

To do this procedure, 20 g of soil and 20 mL of 0.01 M $CaCl_2$ were placed into a 50 mL polyethylene beaker and allowed to equilibrate for 30 minutes. Soil pH_{CaCl2} was determined with a Labfit AS-3000 pH analyzer (LabFit, Burswood, Western Australia). After the initial pH_{CaCl2} was taken on each sample, 2.4 mL of 0.046 N $Ca(OH)_2$ was added while the samples were stirred. The samples were allowed to equilibrate for 30 minutes and then the second pH_{CaCl2} reading was performed (Kissel et al., 2007). Duplicate samples for each soil were evaluated and the average LBC was used to calculate the LR using the following equation:

$$\text{LR (lbs/ac)} = \text{LBC} \times (\text{Target pH} - \text{Initial pH}) \times 2 \times 1.5 \times 1.33 \qquad [2.2]$$

where the target pH is the desired final pH_{CaCl2} of the soil, 2 converts LBC units of ppm to lbs/ac furrow slice (1 ac., 6" deep), 1.5 is an efficiency factor converting pure $CaCO_3$ to ag lime, and 1.33 is a depth conversion for 8" furrow depth (8/6 = 1.33).

Incubation Studies

Each soil was treated as follows: an untreated control, powdered reagent-grade $CaCO_3$ additions to raise the pH to 5.3, 5.6, 5.9, 6.2, and 6.5 respectively in 0.01 M $CaCl_2$ solution, and an estimated amount of each commercial ag lime calculated from equation 2.2 to reach a desired pH in 0.01 M $CaCl_2$ solution of 5.4 and 5.9. The reagent-grade $CaCO_3$ treatments served as a standard curve for the commercial ag lime treatments. There were 4 replicates of each treatment.

Each experimental unit consisted of 320 g of dry soil placed in a one quart screw top container. The appropriate weights of reagent-grade $CaCO_3$ and ag limes were added and stirred thoroughly with a glass rod. Deionized (DI) water was then added to bring each sample to field capacity (FC) for the low LBC soil and 80% FC for the high LBC soil. Preliminary studies showed the high LBC formed large clods and did not mix well when wetted to 100% FC. The samples were stirred again until uniformly mixed. A lid with three holes drilled in it was secured to each container. Cotton was placed in two of the holes to minimize water loss. The glass rod was placed in the third hole and wrapped with Parafilm to minimize water loss. Soil moisture was measured throughout the experiment by regular weighing of the samples and adding DI water when needed.

Soil pH_{CaCl2} was determined in all treatments at 1, 3, 6, 9, and 12 months. An amount of soil equivalent to 20 g air dry soil was placed in a 3 oz. Dixie cup, along with DI water plus enough 1 M $CaCl_2$ to make 20 mL of 0.01 M $CaCl_2$. The samples were equilibrated for 30 minutes and pH_{CaCL2} was determined using a Labfit AS-3000 pH analyzer.

Both NH_4^+ and NO_3^- were also determined at 1, 3, 6, 9, and 12 months. Soil equivalent to 5 g air dry was mixed with enough 1 M KCl to give 20 mL extraction solution. The samples were shaken for 30 minutes at 250 oscillations min^{-1}, filtered through Whatman no. 42 filter paper, the extracts placed into clean scintillation vials and stored at 4°C until analyzed.

Nitrate-N was analyzed with the Griess-Ilosvay technique after reduction of NO_3^- to NO_2^- through a Cd column (Keeney and Nelson, 1982) and then measured using a Flow Solution 3000 autoanalyer (Perstop Analytical, Inc., Wilsonville, OR). Ammonium was analyzed using the automated phenate colorimetric procedure (USEPA, 1983) and then measured using a Flow Solution 3000 autoanalyer (Perstop Analytical, Inc., Wilsonville, OR). Particle size distribution was determined by the pipette method as described by Kilmer and Alexander (1949).

Results and Discussion

The Georgia Liming Materials Act of 1996 sets the standards that all agricultural limes must meet. For solid liming materials, particle size must be such that 90% will pass through a 10-mesh sieve, 50% through a 50-mesh sieve, and 25% through a 100-mesh sieve. A solid liming material must contain a minimum of 6% Mg to be considered dolomitic. Also, solid liming materials must have a CCE $\geq$ 85% and contain less than 15% moisture. The properties of the five liming materials used for this study are shown Table 2.1.

The low LBC and high LBC soils had LBC values of 200 and 700 mg $CaCO_3$/kg/pH, respectively. The initial pH_{CaCl2} for the low LBC soil was 5.11 and 4.98 for the high LBC soil. The low LBC soil was classified as a sand from the particle size distribution of 88.9% sand, 1.9% clay, and 9.2% silt. The high LBC soil was classified as sandy loam with 55.1% sand, 14.1% clay, and 30.8% silt.

The pH results for the low LBC and high LBC control soils are shown in Fig. 2.1. Both soils exhibited an overall increase in pH over the 12 months. The low LBC control had a significant increase in pH during the experiment, reaching a high of 6.92 at Month 9. The increase in pH was surprising due to an increase in nitrification (acid-producing process) and a decrease in ammonification (acid-consuming process) over the 12 months (Fig. 2.2). Research has shown that a rapid flush of ammonification follows the re-wetting of air-dried soils (Cabrera, 1993; Haynes and Swift, 1989; Stanford and Smith, 1972). Because there were no initial NH_4-N and NO_3-N measurements taken on the two soils, it is unknown whether there was a flush of ammonification from Day 0 to Month 1 that contributed to the rapid pH increase over that time period. Reduction of Fe or Mn (acid-consuming process) should not have been a factor because the soils were wetted to FC and holes in the lid of the containers allowed for air exchange. Some other reaction(s) besides nitrification, ammonification, or reduction of Fe and Mn may have influenced the pH increase.

The high LBC control soil exhibited a smaller pH increase over time compared to the low LBC soil (Fig. 2.1). Similarly to the low LBC soil, pH increased whereas nitrification increased (Fig. 2.2). The buffering capacity of the high LBC soil was more than three times that of the low LBC soil, which helped reduce the pH increase. The high LBC soil was wetted to 85% FC due to it forming clods when wetted to FC. Again, reduction of Fe or Mn should not have been an issue due to the moisture content and the holes in the container to allow air exchange.

Soil pH of the low LBC soil treated with reagent-grade $CaCO_3$ powder is shown in Fig. 2.3. All target pH values were surpassed by Month 3, possibly due to the same processes that raised pH_{CaCl2} of the control soil. Ammonium-N decreased from Month 1 to Month 6 whereas NO_3-N increased during that same time period (Fig. 2.4).

Soil pH of the high LBC soil treated with reagent-grade $CaCO_3$ are shown in Fig. 2.5. The sample with a target pH of 5.3 surpassed its target. With the exception of the target pH of 5.6 which reached its target pH (5.66 at 3 months), all other treatments to the high LBC soil resulted in the pH values not reaching their targets. Ammonium-N and NO_3-N for the high LBC soil treated with reagent-grade $CaCO_3$ are shown in Fig. 2.6. Whereas the low LBC soil NO_3-N started to decrease after Month 6, the high LBC soil NO_3-N continued to increase through Month 12. Ammonium-N production in the high LBC soil was similar to the NH_4-N production in the low LBC soil.

Fig. 2.7 and 2.8 shows the pH results for the commercial ag lime treatments. All five ag limes resulted in pH values greater than 6.5 for the low LBC soil, partially because of the 1.5 multiplier used in the LR equation (equation 2.2). One reason the UGA single-addition titration procedure works is that the relationship between pH increase and amount of base added is linear from 4.5 to 6.5 (Kissel et al., 2007; Liu et al., 2004; Liu et al., 2005). Above pH 6.5, the relationship becomes curvilinear. Because of this, it was decided to not evaluate the data from the low LBC soil due to large errors in the data.

The pH results from the high LBC soil treated with ag lime resulted in much better data. Ag limes 1 and 2 were close to both the 5.4 and 5.9 target pH values. Ag limes 3, 4, and 5 were close to the target pH 5.4, but did not reach the 5.9 target pH even with the 1.5 factor in the LR equation (equation 2.2). The results from the experiment in Chapter 1 have shown that the LBC values used for this experiment were underestimated; however, when this experiment was started, the results from Chapter 1 were not available. The results from that experiment may have resulted in a more accurate LR determination for the high LBC soil.

Because the pH of the control samples increased over time, the data were evaluated further by subtracting the control pH values from the treated pH values (ΔpH). This approach assumes that any reactions other than lime that affect pH are occurring simultaneously and at the same rate in both the control samples and the treated samples. It was also decided to concentrate on the target pH 5.9 data because this target pH was used for both the reagent-grade $CaCO_3$ powder treatment and the ag lime treatments. The ΔpH value determined showed how much the pH increased from the lime treatment, not from other reactions taking place in the soil that affect pH.

The ΔpH data for the reagent-grade $CaCO_3$ powder and the five ag lime treatments are shown in Fig. 2.9 and 2.10 respectively. Each treatment resulted in a similar pH increase, and when the average of the 6, 9, and 12 month ΔpH values were plotted against the amount of $CaCO_3$ powder added, the resulting relationship was linear (Fig. 2.11).

Because the 1.5 multiplier was used in the LR equation (equation 2.2) for calculating the amount of ag lime needed whereas the proper amount of reagent-grade $CaCO_3$ powder was used for the reference samples, the ΔpH for the ag lime treatments was altered so that a comparison between the ag lime and the reagent-grade $CaCO_3$ powder could be made directly. The 1.5 multiplier assumes the commercial ag limes are 2/3 (0.667%) as effective as reagent-grade $CaCO_3$ powder. The conversion is accomplished by the following equation:

ΔpH_y x 0.667 = $\Delta pH_{ag\ lime}$ or [2.3]

$\Delta pH_y / 1.5 = \Delta pH_{ag\ lime}$ [2.4]

where ΔpH_y is the ΔpH determined from the experiment. The multiplier of the ag lime is then determined by:

$\text{Multiplier}_{Ag\ Lime} = \Delta pH_{CaCO3} / \Delta pH_{ag\ lime}$ [2.5]

For example, Lime 1 had an average 6-12 month ΔpH of 0.483 and the average 6-12 month ΔpH (target 5.9) of the reagent-grade $CaCO_3$ powder was 0.340.

0.483 / 1.5 = 0.322

0.340 / 0.322 = 1.06

The $\text{Multiplier}_{Ag\ Lime}$ for Lime 1 is 1.056 which means that is nearly as reactive as reagent-grade $CaCO_3$ powder. The $\text{Multiplier}_{Ag\ Lime}$ for Limes 2-5 were 1.04, 1.33, 1.21, and 1.56, respectively.

It should be noted that the state lime law allows 10% of the particles to be larger than 10-mesh. This size fraction was removed from all five ag limes. Therefore, if one allowed each of the commercial ag limes to contain 10% >10-mesh, the true efficiency of all the ag limes should be divided by 0.9, resulting in multipliers of 1.17, 1.16, 1.48, 1.34, and 1.73 for ag limes 1 through 5, respectively. The mean of these values is 1.38, not too different from the 1.5 multiplier used presently by several laboratories.

Table 2.1 – Properties of the five liming materials used.

Lime Material	CCE	% Ca	% Mg	10-mesh (% pass)	50-mesh (% pass)	100-mesh (% pass)	Moisture (%)
1	101.51	25.07	9.60	100.00	96.31	87.53	0.22
2	96.97	22.63	11.58	100.00	89.08	73.64	0.31
3	99.89	23.29	14.19	100.00	66.11	48.47	0.00
4	94.30	20.57	10.77	100.00	86.42	62.18	0.11
5	96.10	25.78	7.94	99.58	65.87	59.52	0.21

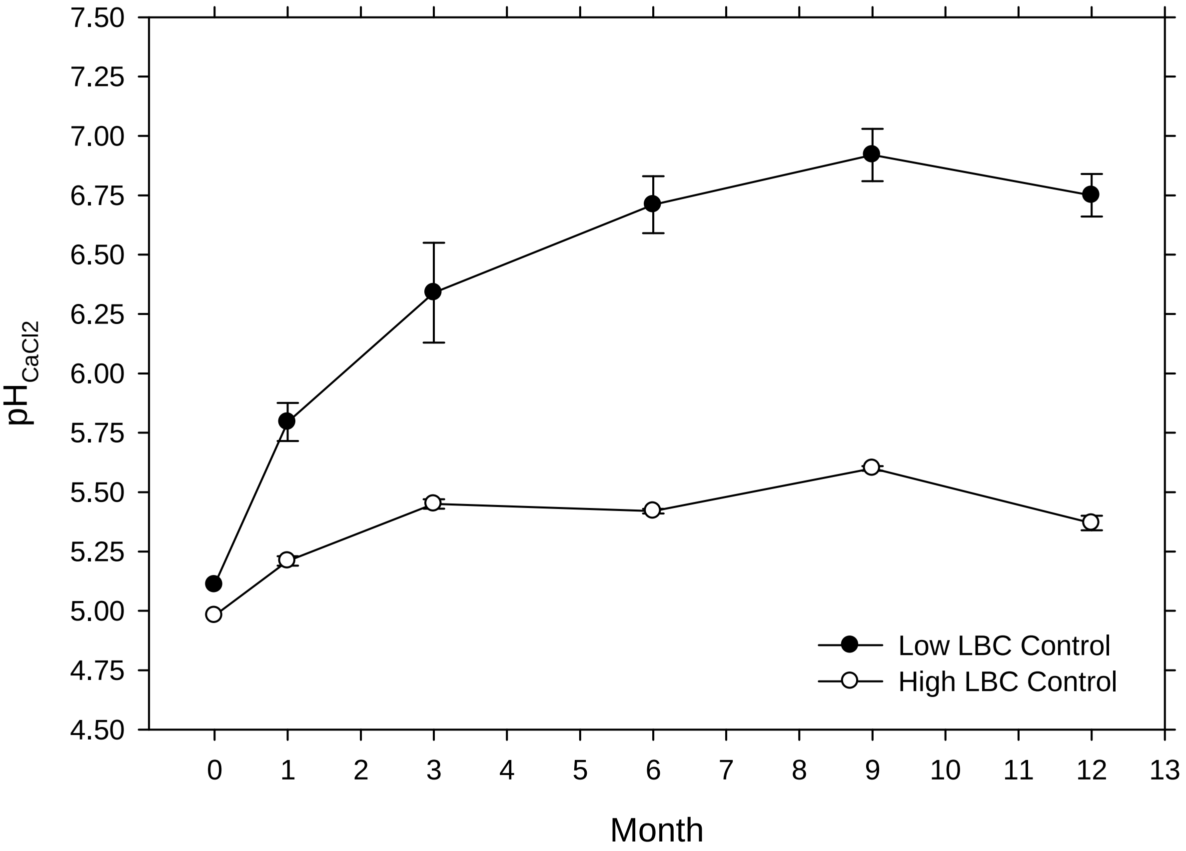

Figure 2.1 – pH in 0.01 M $CaCl_2$ of control (no treatment) samples. Error bars are one standard deviation.

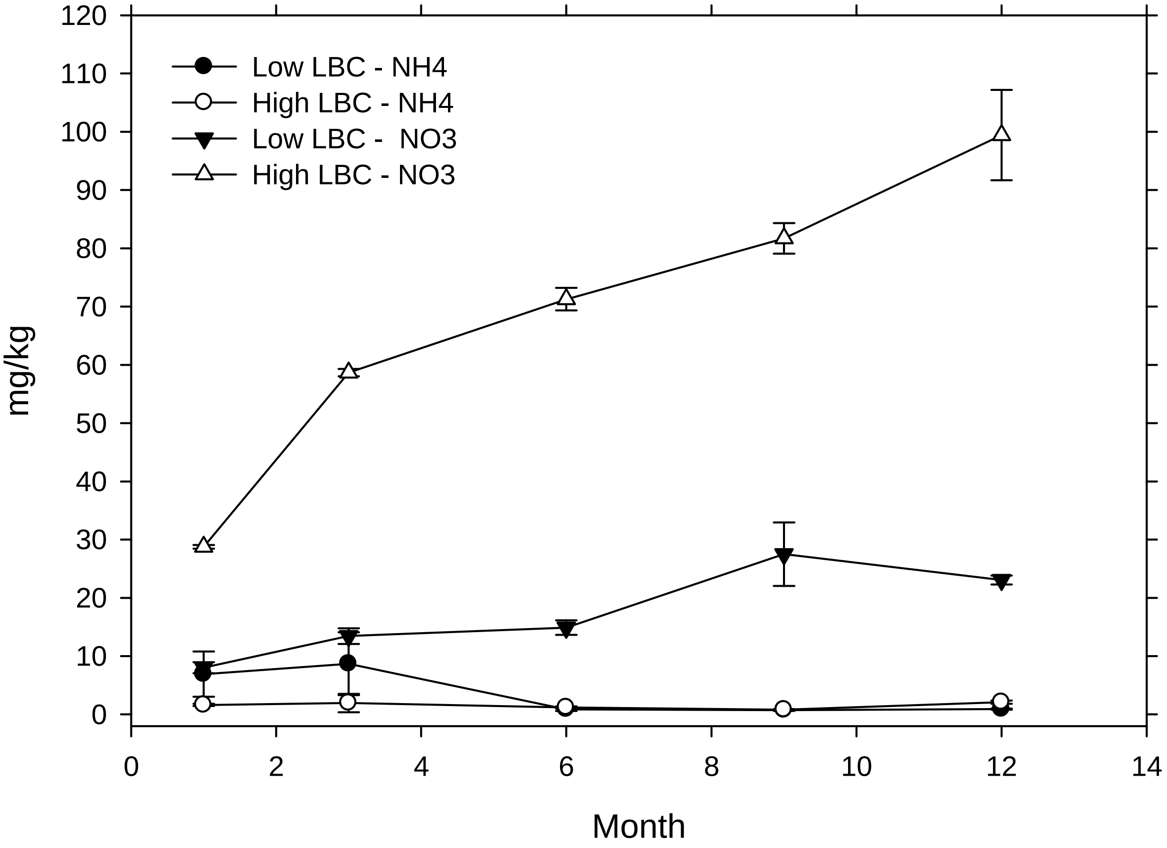

Figure 2.2 – Ammonium-N and NO_3-N in the low LBC and high LBC Controls. Error bars are one standard deviation.

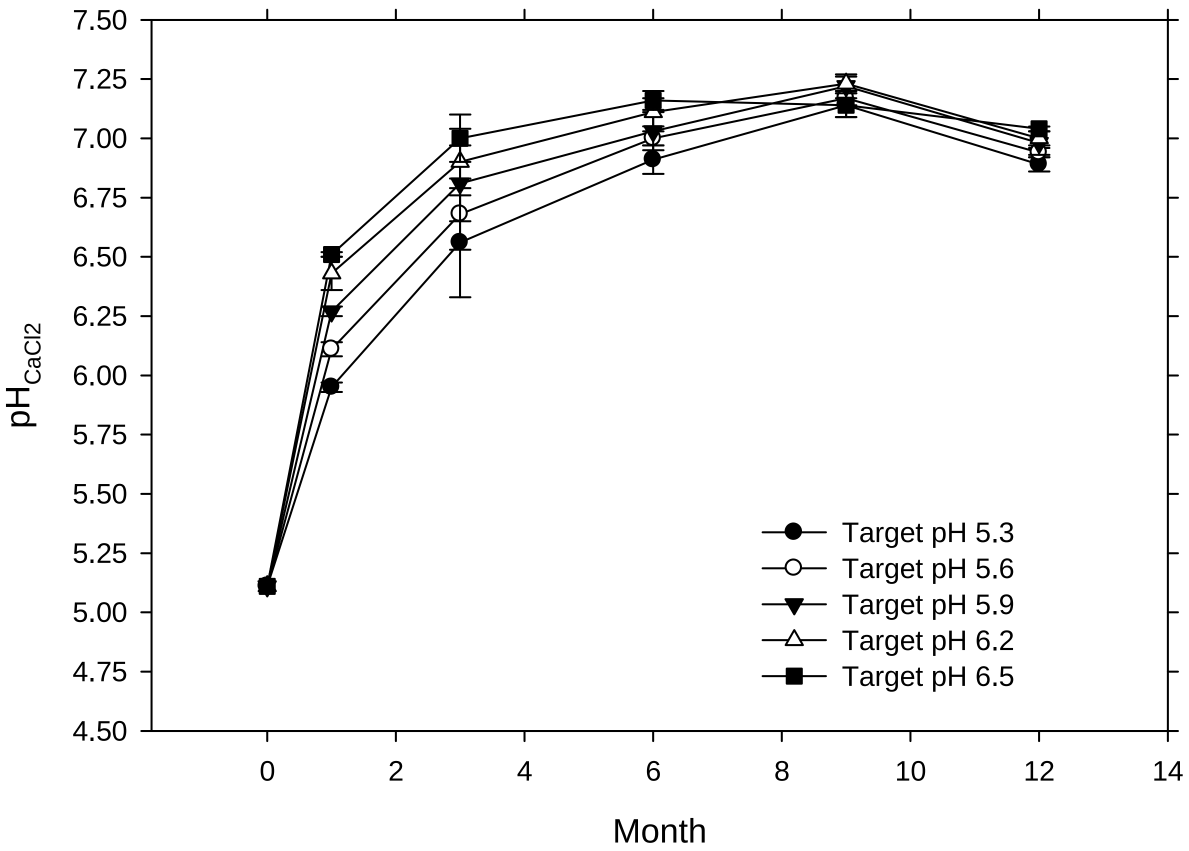

Figure 2.3 – pH results for the low LBC soil treated with increasing amounts of reagent-grade $CaCO_3$ powder. Error bars are one standard deviation.

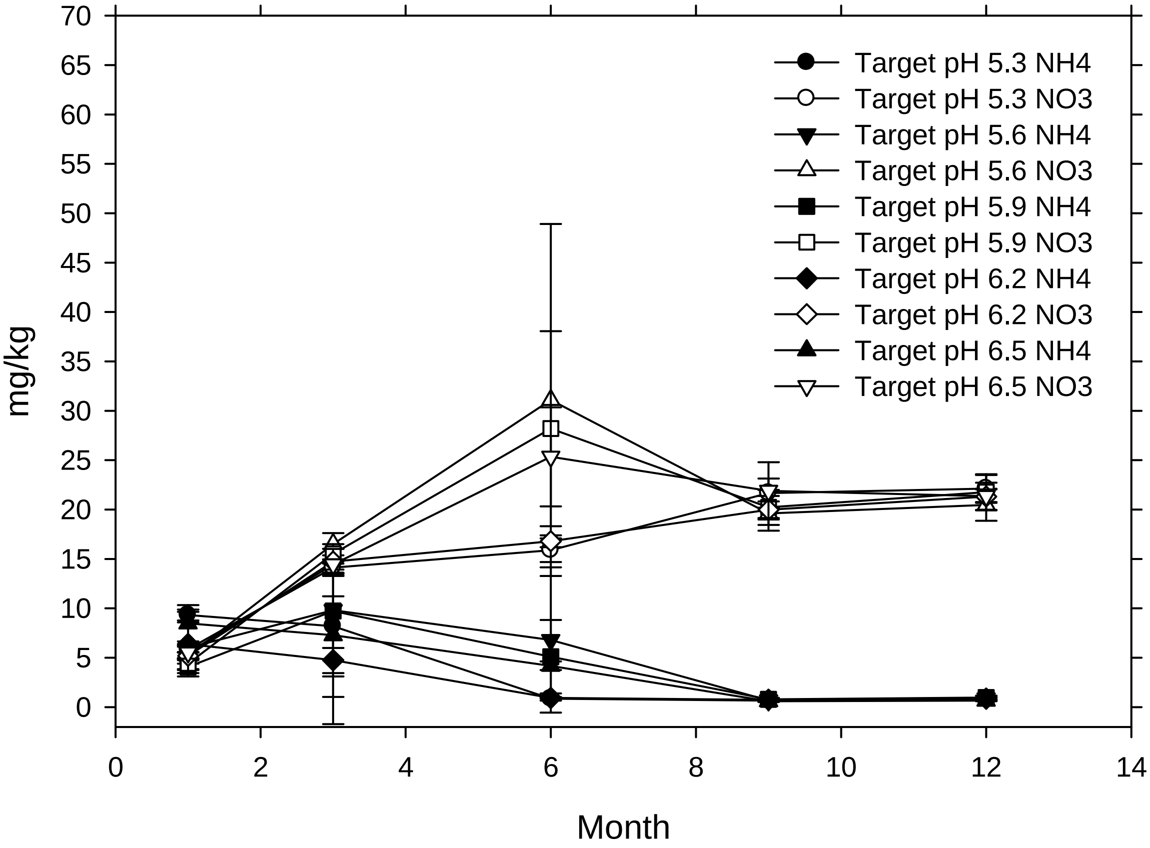

Figure 2.4 – Ammonium-N and Nitrate-N for the low LBC soil treated with increasing amounts of reagent-grade $CaCO_3$ powder. Error bars are one standard deviation.

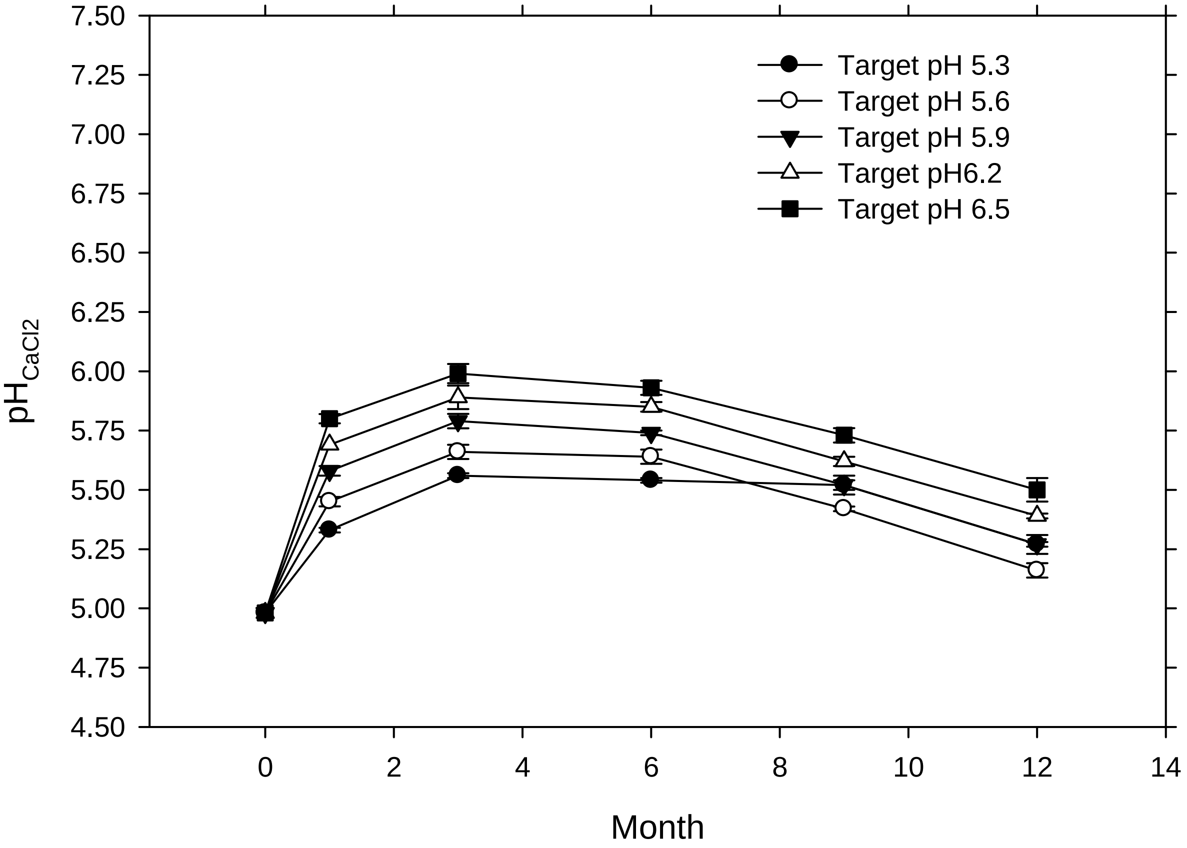

Figure 2.5 - pH results for the high LBC soil treated with increasing amounts of reagent-grade $CaCO_3$ powder. Error bars are one standard deviation.

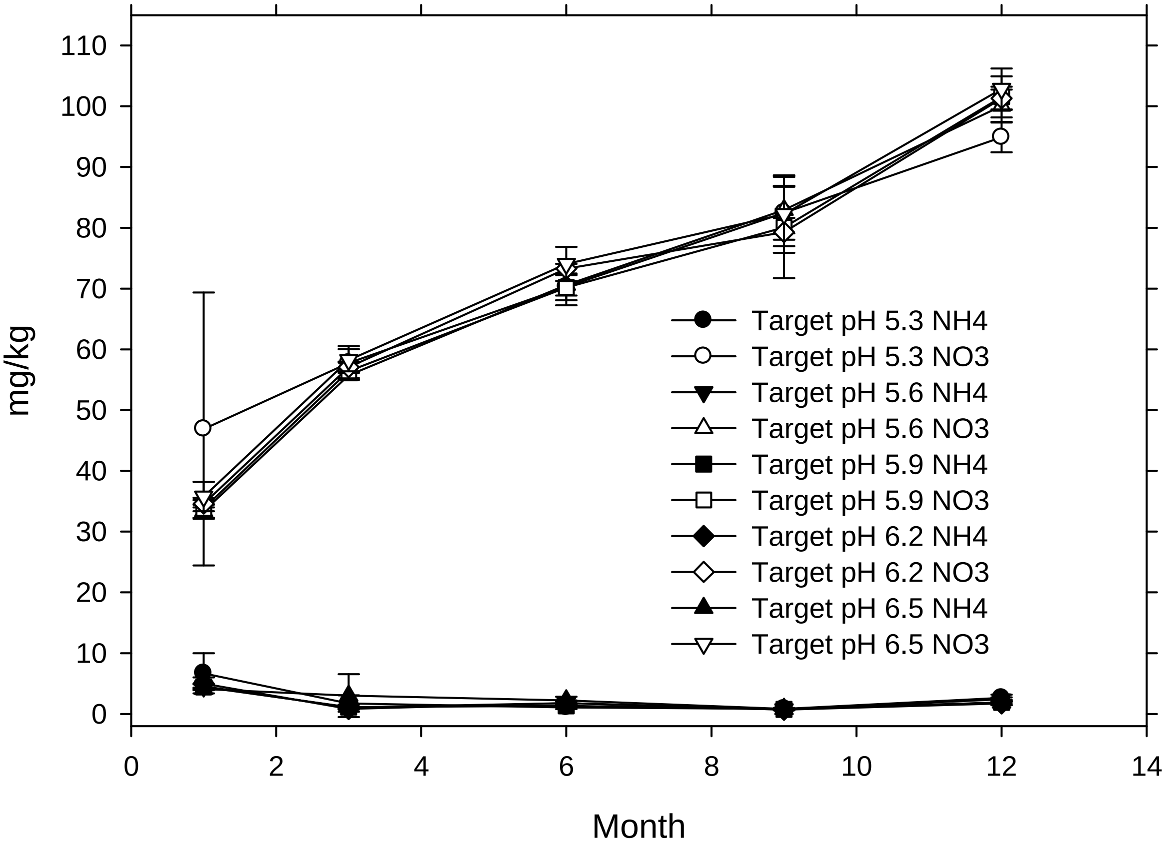

Figure 2.6 - Ammonium-N and Nitrate-N for the high LBC soil treated with increasing amounts of reagent-grade $CaCO_3$ powder. Error bars are one standard deviation.

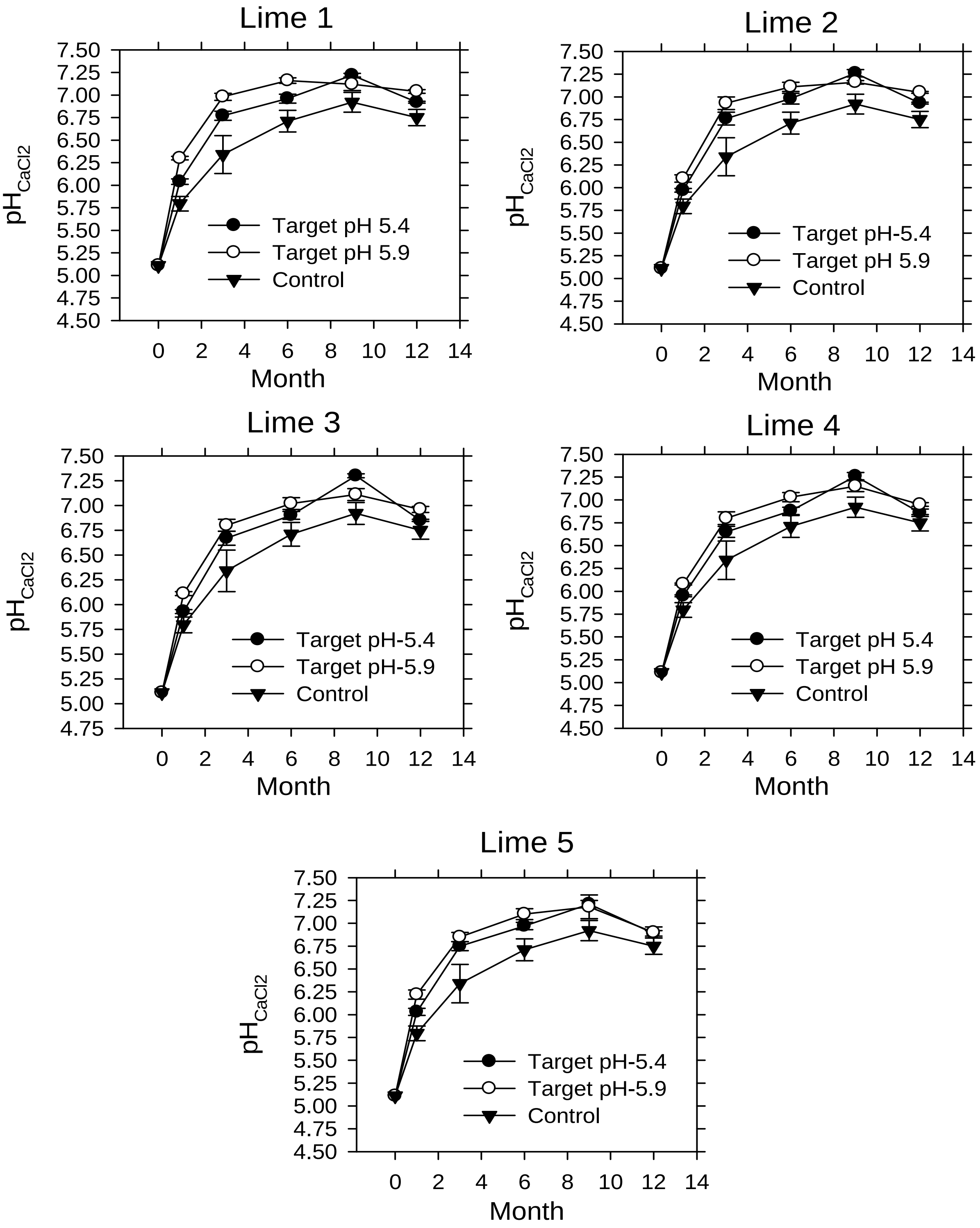

Figure 2.7 – pH results for the low LBC soil treated with five commercial ag limes. Error bars are one standard deviation.

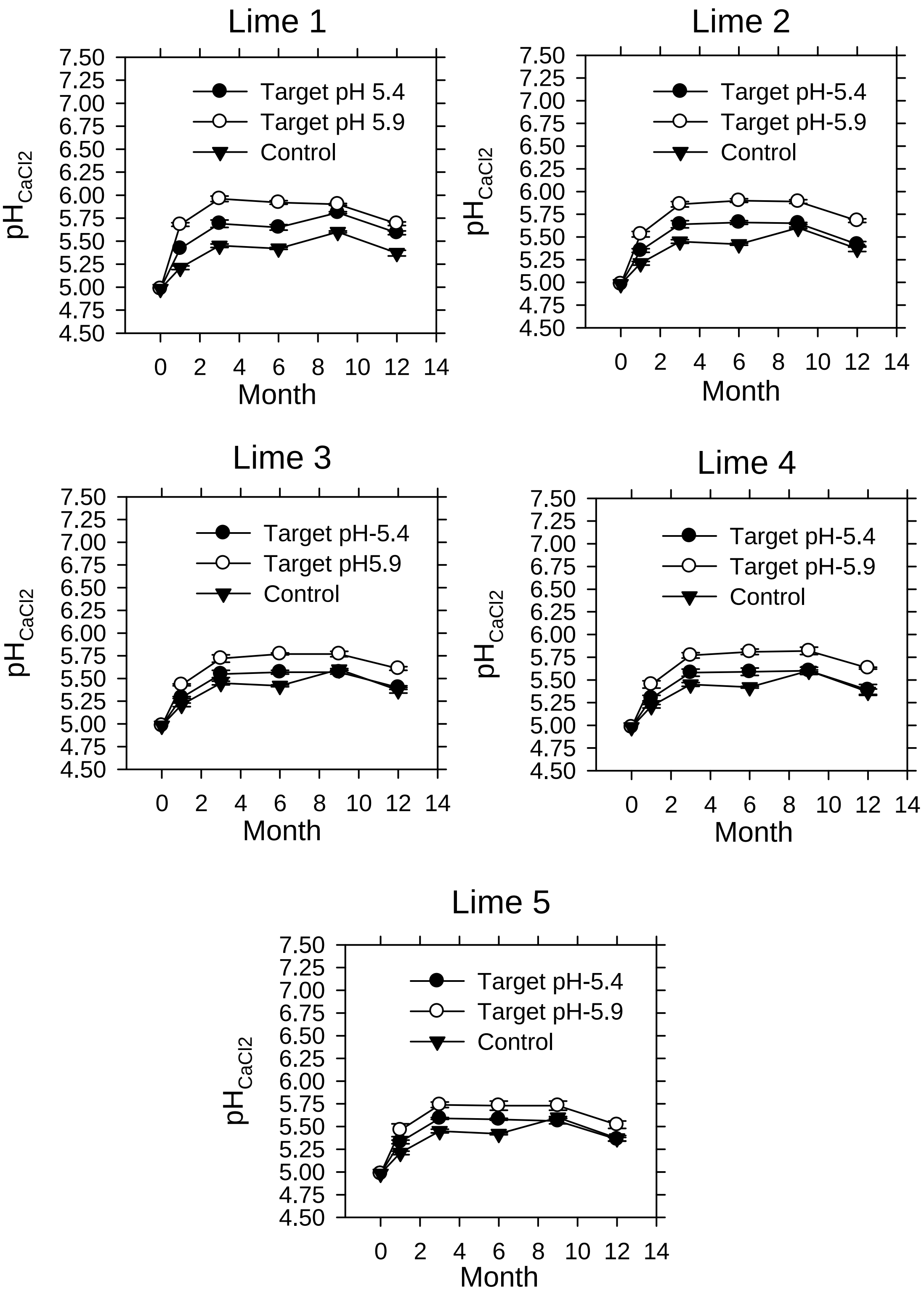

Figure 2.8 – pH results for the high LBC soil treated with five commercial ag limes. Error bars are one standard deviation.

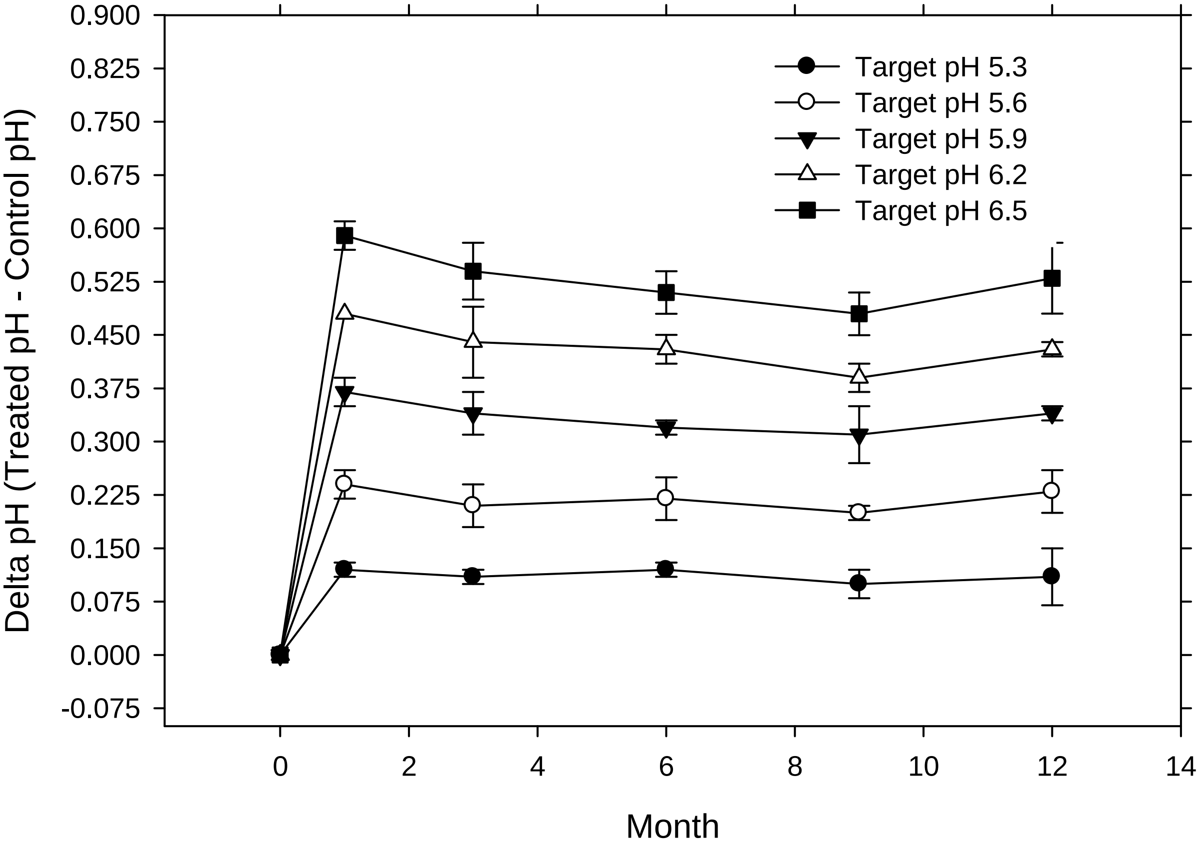

Figure 2.9 – ΔpH vs. Time for the reagent-grade $CaCO_3$ powder treated high LBC soil. Error bars are one standard deviation.

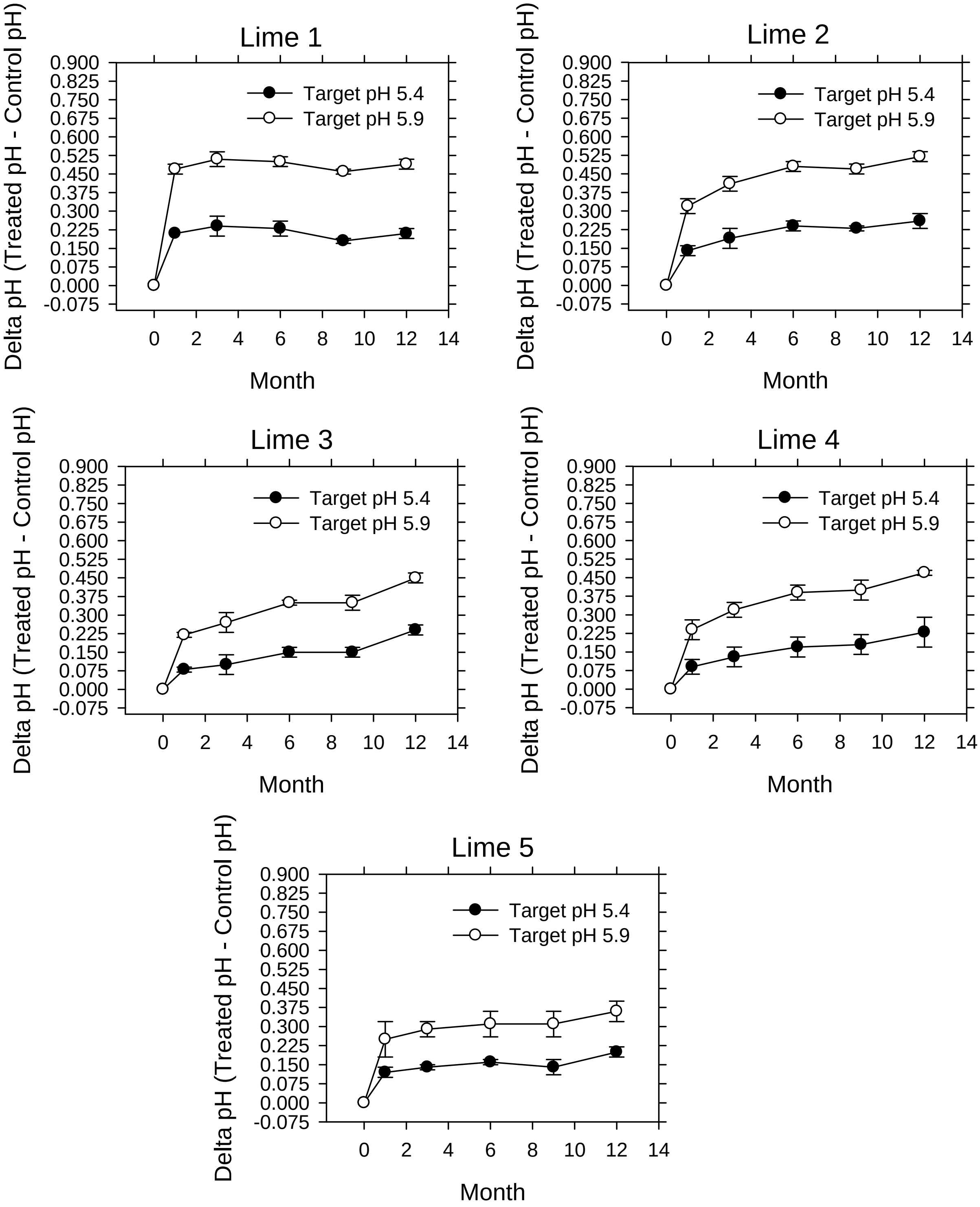

Figure 2.10 - ΔpH vs. Time for the ag lime treated high LBC soil. Error bars are one standard deviation.

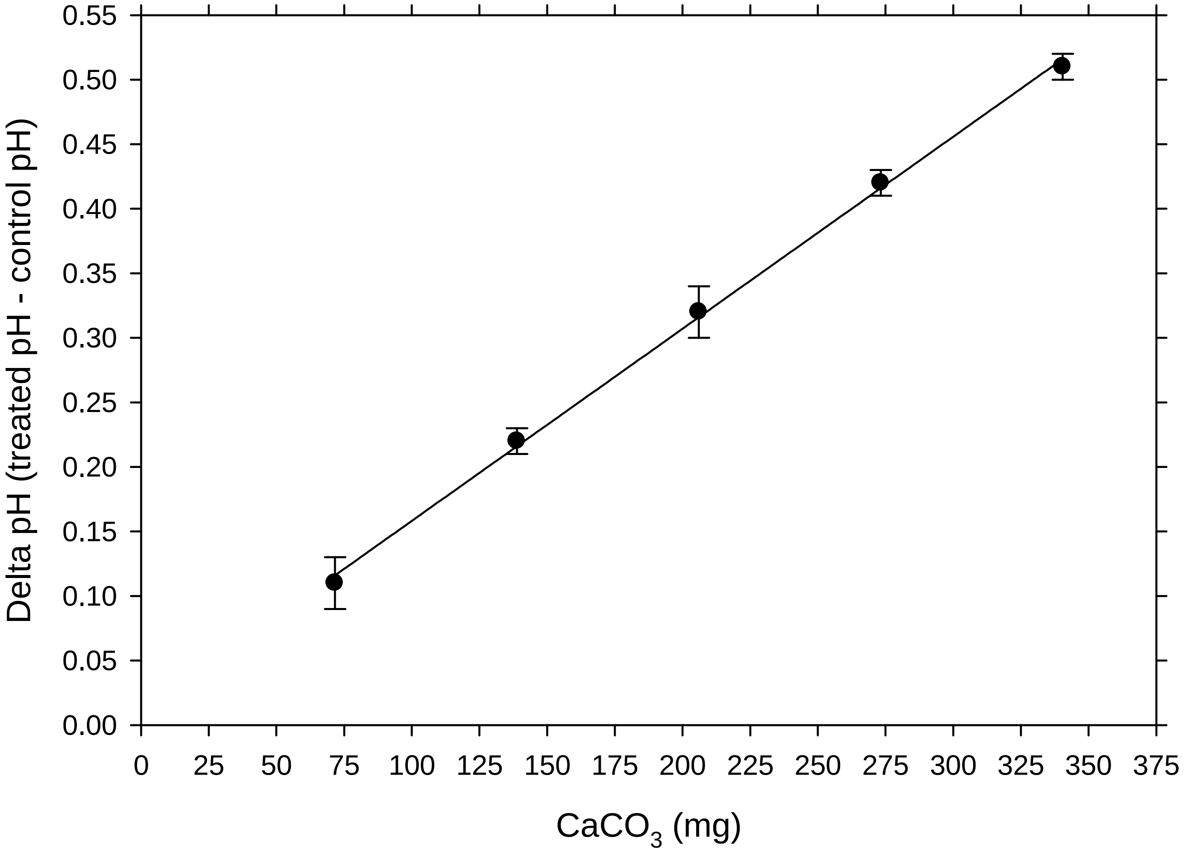

Figure 2.11 – Average ΔpH for Months 6-12 vs. amount of reagent-grade $CaCO_3$ powder added to the high LBC soil. Error bars are one standard deviation.

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CHAPTER 3

CONCLUSIONS

The University of Georgia uses a single-addition titration procedure to estimate soil lime requirement (LR). The lime buffer capacity (LBC) is calculated from the rise in pH after $Ca(OH)_2$ addition to the soil. With the current procedure, the reaction between soil and $Ca(OH)_2$ is not at equilibrium when the pH measurement is taken 30 minutes after $Ca(OH)_2$ addition. Therefore, the ag lime recommendation made to clients is corrected for the lack of reaction equilibrium. The ratio of the mean of 84 and 96hour LBC/30 minute LBC could be predicted with the equation 1.4744 + 0.0024*30 min LBC ($r^2 = 0.83$). This relationship allows the current titration procedure with 30 minute equilibration time to be used to predict the equilibrium LBC, which in turn is used to calculate more accurate lime recommendations.

Also, the lime recommendation equation (Eq. [2.2]) includes a multiplier of 1.5 to account for ag lime that is less reactive than reagent-grade $CaCO_3$ due to impurities and the presence of large poorly reactive particles. Although research has been conducted with ag lime to arrive at this efficiency factor, it has not been conducted using GA soils or with ag limes available in Georgia that may differ in their crystallinity from others tested previously. Low buffering capacity of one soil resulted in errors with the data for that soil. Results from the high buffering capacity soil yielded multipliers of 1.17, 1.16, 1.48, 1.34, and 1.73 for ag limes 1 through 5, respectively, with an average multiplier of 1.38, nearly the same as the multiplier presently used. For practical purposes, a multiplier of 1.5 will ensure that sufficient ag lime is recommended to neutralize the acidity measured by a soil test.

APPENDICES

Appendix A: Average pH data for low LBC soil used in lime efficiency study.

Treatment	Target pH	Month 0	1	3	6	9	12
Control		5.11	5.80	6.34	6.71	6.92	6.75
$CaCO_3$	5.30	5.11	5.95	6.56	6.91	7.14	6.89
(reagent-grade)	5.60	5.11	6.11	6.68	7.00	7.17	6.94
	5.90	5.11	6.27	6.81	7.03	7.22	6.98
	6.20	5.11	6.43	6.90	7.11	7.23	7.00
	6.50	5.11	6.51	7.00	7.16	7.14	7.04
Lime 1	5.40	5.11	6.04	6.77	6.96	7.22	6.92
	5.90	5.11	6.30	6.98	7.16	7.12	7.04
Lime 2	5.40	5.11	5.97	6.76	6.98	7.26	6.93
	5.90	5.11	6.10	6.93	7.11	7.16	7.05
Lime 3	5.40	5.11	5.93	6.67	6.90	7.30	6.85
	5.90	5.11	6.11	6.80	7.02	7.11	6.96
Lime 4	5.40	5.11	5.95	6.65	6.88	7.26	6.86
	5.90	5.11	6.08	6.80	7.03	7.15	6.95
Lime 5	5.40	5.11	6.03	6.75	6.97	7.21	6.89
	5.90	5.11	6.22	6.85	7.10	7.18	6.90

Appendix B: Average pH data for high LBC soil used in lime efficiency study.

Treatment	Target pH	Month 0	1	3	6	9	12
Control		4.98	5.21	5.45	5.42	5.42	5.16
$CaCO_3$	5.30	4.98	5.33	5.56	5.54	5.52	5.27
(reagent-grade)	5.60	4.98	5.45	5.66	5.64	5.62	5.39
	5.90	4.98	5.58	5.79	5.74	5.73	5.50
	6.20	4.98	5.69	5.89	5.85	5.81	5.59
	6.50	4.98	5.8	5.99	5.93	5.90	5.69
Lime 1	5.40	4.98	5.42	5.69	5.65	5.60	5.37
	5.90	4.98	5.68	5.96	5.92	5.88	5.65
Lime 2	5.40	4.98	5.35	5.64	5.66	5.65	5.42
	5.90	4.98	5.53	5.86	5.90	5.89	5.68
Lime 3	5.40	4.98	5.29	5.55	5.57	5.57	5.40
	5.90	4.98	5.43	5.72	5.77	5.77	5.61
Lime 4	5.40	4.98	5.3	5.58	5.59	5.60	5.39
	5.90	4.98	5.45	5.77	5.81	5.82	5.63
Lime 5	5.40	4.98	5.33	5.59	5.58	5.56	5.36
	5.90	4.98	5.46	5.74	5.73	5.73	5.52

Appendix C: Average NH_4-N and NO_3-N data for low LBC soil used in lime efficiency study.

		Month									
		1		3		6		9		12	
		mg kg^{-1}									
Treatment	Target pH	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3
Control		6.92	8.03	8.70	13.45	0.87	14.90	0.72	27.51	0.91	23.08
$CaCO_3$	5.30	9.32	5.87	8.20	14.12	0.84	15.89	0.67	21.66	0.82	22.13
(reagent-grade)	5.60	6.01	5.17	9.81	16.50	6.80	31.09	0.68	19.62	0.86	20.48
	5.90	4.07	4.41	9.74	15.52	5.11	28.19	0.78	20.22	0.97	21.77
	6.20	6.39	5.20	4.75	14.74	0.93	16.79	0.75	19.98	0.88	21.32
	6.50	8.49	5.51	7.29	14.45	4.19	25.34	0.60	21.89	0.66	21.35
Lime 1	5.40	2.63	7.93	6.97	13.64	1.40	17.48	0.71	18.24	0.68	21.94
	5.90	4.66	8.52	11.33	14.81	1.88	18.54	0.54	19.97	0.75	22.23
Lime 2	5.40	2.34	8.21	7.72	13.48	1.76	19.09	0.46	21.13	0.86	22.68
	5.90	7.39	8.22	4.15	14.51	1.11	18.61	0.47	21.79	0.86	22.94
Lime 3	5.40	6.71	8.92	15.13	13.32	3.85	16.05	0.58	21.06	1.35	21.81
	5.90	5.67	7.51	11.63	14.95	1.51	17.41	0.63	21.54	1.26	23.64
Lime 4	5.40	3.88	7.85	9.19	13.89	1.44	17.39	0.58	22.18	1.19	24.10
	5.90	2.94	7.84	4.73	14.43	0.87	16.74	0.61	22.60	1.30	25.43
Lime 5	5.40	2.26	9.09	12.76	14.89	1.29	16.71	0.63	23.22	1.13	23.23
	5.90	5.57	8.56	6.37	14.90	0.84	16.88	0.65	24.69	0.92	24.84

Appendix D: Average NH_4-N and NO_3-N data for high LBC soil used in lime efficiency study.

		Month									
		1		3		6		9		12	
		mg kg^{-1}									
Treatment	Target pH	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3
Control		1.62	28.76	1.96	58.68	1.18	71.26	0.81	81.72	2.11	99.43
$CaCO_3$ (reagent-grade)	5.30	6.66	46.88	1.72	57.74	1.05	70.28	0.81	82.47	2.63	94.88
	5.60	4.55	33.35	1.07	55.73	1.76	70.58	0.75	82.92	2.40	100.09
	5.90	4.44	33.83	1.13	56.42	1.31	70.15	0.76	80.04	1.88	101.55
	6.20	4.98	34.59	0.81	57.05	1.77	73.28	0.70	79.29	1.73	101.31
	6.50	4.11	35.77	3.01	58.21	2.24	74.05	0.83	82.26	1.86	102.84
Lime 1	5.40	7.55	29.01	1.08	53.47	1.28	70.96	0.78	76.94	1.35	95.21
	5.90	1.75	29.21	3.35	58.11	1.26	71.38	0.80	77.83	1.37	98.40
Lime 2	5.40	3.56	27.56	3.04	57.19	1.78	70.46	0.86	83.01	1.88	97.29
	5.90	2.89	27.57	0.81	53.11	1.64	67.54	0.81	83.93	1.95	101.89
Lime 3	5.40	1.80	29.89	3.31	56.84	1.31	70.78	0.81	82.31	2.49	103.22
	5.90	3.03	28.23	1.16	55.44	1.17	71.51	0.76	78.48	2.06	100.06
Lime 4	5.40	3.09	28.74	7.13	53.15	1.37	70.29	0.64	78.46	1.88	105.70
	5.90	2.53	29.32	0.92	55.72	1.19	71.07	0.78	80.84	1.73	100.05
Lime 5	5.40	3.60	28.74	3.84	56.53	1.04	72.61	0.94	85.83	1.77	105.38
	5.90	3.47	29.05	1.07	55.11	0.86	72.73	0.87	83.52	1.87	107.11