DIRECT TITRATION FOR MEASUREMENT OF SOIL LIME REQUIREMENT AND INDIRECT LIME REQUIREMENT ESTIMATION BY SOIL PROPERTIES

by

MIN LIU

(Under the direction of David E. Kissel, Ph. D)

ABSTRACT

Previous studies about the titration curves of acid soils reported a linear relationship in the approximate range $4.5 < pH(H_2O) < 6.5$. It appears possible to establish the slope of the titration curve with 3 aliquots of $Ca(OH)_2$ and then predict the lime requirements (LRs) to pH 6.5. The objective of this study was to evaluate the possibility of developing a direct titration procedure to measure the LRs of acid soils for routine use in soil testing laboratories. Seventeen soil samples with a wide range of clay and soil organic carbon contents were collected from five of the major land resource areas of Georgia. A 30 minute interval time between additions was found to be relatively short but adequate for the base added to react with the soil acids. A 3-day $Ca(OH)_2$ incubation study revealed that the 3-points prediction from the direct titration with 30 minute interval time between additions estimated approximately 80% of the soil acidity. To simplify the procedure, one dosing of $Ca(OH)_2$ was also tried to establish the titration slope in both water and 0.01 M $CaCl_2$. Although the 2-point titration in water was subject to errors, the two point prediction of the LRs in 0.01 M $CaCl_2$ estimated approximately 83% of the soil acidity. The $CaCO_3$ incubation was found to overestimate the LRs. The LRs were highly correlated with initial pH and total carbon content.

INDEX WORDS: Titration, Lime requirement, Soil testing, Soil acidity

DIRECT TITRATION FOR MEASUREMENT OF SOIL LIME REQUIREMENT AND INDIRECT LIME REQUIREMENT ESTIMATION BY SOIL PROPERTIES

By

MIN LIU

B.S., China Agricultural University, 2001

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2003

DIRECT TITRATION FOR MEASUREMENT OF SOIL LIME REQUIREMENT AND INDIRECT LIME REQUIREMENT ESTIMATION BY SOIL PROPERTIES

by

MIN LIU

Approved:

Major Professor: David E. Kissel

Committee: Miguel Cabrera
Paul Vendrell

Electronic Version Approved:

Maureen Grasso
Dean of the Graduate School
The University of Geogia
August 2003

DEDICATION

This thesis is dedicated to my father, Mr. Dinghong, Liu and to my mother, Mrs. Wanmei, He. God bless you.

ACKNOWLEGEMENTS

I would like to express my special thanks to Dr. David E. Kissel, my major professor, for this guidance, patience and assistance in completion of this degree. The project would not have been successful without his continued support and encouragement. I also thank Dr. Miguel L. Cabrera and Dr. Paul Vendrell for serving as the committee members.

There were many other people who have assisted in different aspects of this project during the past two years. I would thank Dr. Feng Chen, who has been a very good helper and honest friend in many aspects of my foreign life here. Much appreciation is extended to Wick Johnson for his patience on my endless questions and to Kim for her analysis of the soil particle size distribution.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The lime requirement (LR) is the amount of limestone needed to increase the pH of the plow layer of acid soil to a desired level (McLean, 1970). Dunn (1943) studied direct titration to predict the LR of acid soils and focused on the influence of equilibrium time on the reaction between added base and soil acids. He found that four days were needed for pH values to reach equilibrium when 0.022 M $Ca(OH)_2$ solution was added to acid soils. He also discovered that shaking affected the time required for soil pH values to reach equilibrium. He reported that equilibrium was reached within eight hours with shaking as compared to four days for the suspensions without shaking. Finally, he suggested a standard direct titration method for lime requirement by incorporating acid soils with different rates of 0.022 M $Ca(OH)_2$ for four days. The $Ca(OH)_2$ titration method proposed by Dunn (1943) for measuring the LR was widely accepted as a reliable method for estimating the LRs (Follett and Follett, 1980; Alabi et al, 1986; McConell et al., 1990; Owusu-Bennoah et al., 1995). However, Dunn's method was also considered to be a time-consuming procedure and not suitable for routine use in soil testing laboratories. Many studies focused on the titration curve itself. Magdoff and Bartlett (1985) concluded that the relationship between pH and OH^- added is nearly linear within the pH range of most agricultural soils (4.5 to 6.5). Weaver (2002) also reported an approximately linear relationship between pH and base added for a series of Georgia soils.

The Adams-Evans (AE) buffer procedure (Adams and Evans, 1962) for predicting LR is used widely in soil test laboratories in the south-east United States. However, it has been reported to overestimate the LR (Follett and Follett, 1980; Tran and Lierop, 1981; Alabi et al, 1986). Tran and Lierop (1981) also noted the limited range of the AE buffer and its relatively poor precision, as indicated by the relatively low correlation coefficient between estimates of LR from incubation and those using the AE procedure ($r^2 = 0.78^{**}$). Another concern about the AE buffer is the potential toxicity from one of its components, p-nitrophenol. Considering the inaccuracy and environmental concern of the AE buffer procedure, the objectives of these studies were to evaluate the possibility of developing a direct titration procedure to measure the LRs of acid soils for routine use in soil testing laboratories.

Incubation methods with $CaCO_3$ are also considered reliable to determine the lime requirements of acid soils. They are often used as calibrations for buffer methods (Tran and van Lierop, 1981; Loynachan, 1981; Barrow and Cox, 1990). Baker and Chae (1977) reported that the use of room temperature incubation of incremental mixtures of $CaCO_3$ and soil to determine lime requirements overestimates the actual lime requirements determined by field testing. This occurs because soil acidity increases under room temperature incubation. Incubation methods using $CaCO_3$ are subject to some arbitrary influences such as incubation time, moisture content, carbon dioxide levels, and air pollutants (Alabi et. al. 1986).

Indirect LR-determination procedures rely on estimating a LR from soil properties without directly measuring acidity. The indirect LR estimation procedure is advanced for use when buffer-pH values are not available and a LR recommendation is needed. It is fairly accurate and relies on common soil tests. Owusu-Bennoah et. al. (1995) related pH, organic carbon, and clay with $Ca(OH)_2$ incubated LR and found: LR (10^3 kg ha^{-1}) = 4.2 – 1.1pH + 1.7(% organic carbon) + 0.05(% clay), $R^2 = 0.92$.

LITERATURE REVIEW

pH Determination and Measurement

Sorensen(1909) defined pH as the negative logarithm of H^+ concentration. This notation has been maintained; though, H^+ activity has replaced concentration to adapt it to electromotive cell potentials. Soil pH is determined routinely with a glass combined with a calomel reference electrode. It consists of measuring soil-solution electromotive force (emf) and comparing it to defined buffer standard values. Accuracy depends on the differences in the liquid junction-potential error between standards and sample. A soil pH is determined by the activity of H^+ in solution to which are added the influence of several other factors. These are discussed under the following subheadings: A. soil/solution ratios and sample size; B. soluble salts; C. suspension effect; D. carbonic acid; E. drying; and F. seasonal pH fluctuation. Many of those factors are closely interrelated.

A. Soil/Solution Ratios and Sample Size

In early research, soil pH was typically measured at moisture contents approaching those found in the field. However, both Huberty and Haas (1940) and Chapman et al. (1941) found that soil pH varied from about 0.5 to 1.5 pH with changing moisture contents. Water contents greater than those to produce a paste were required to ensure stable and reproducible results (Chapman et al., 1941). The reasons for Chapman et. al.'s observations are the following: 1, moisture content varies with sample texture and OM content; 2, moisture content is often subjective; 3, low moisture contents aggravate junction potential errors; 4, low moisture contents provide unreliable electrode-solution contact; and 5, electrode malfunction and breakage risk are higher when inserting into a paste. Peech (1965a) and McLean (1973) recommended a 1:1 soil/water ratio for determining soil pH. Peech (1965a) also recommended a 20-g soil sample in 20 mL water and concluded that soil pH, measured at a given soil/solution ratio is not affected by sample size. Sixty soils samples were weighed out (Y) and scooped out (X) and then pHs were determined in 1:1 soil/water ratio. pHs were in the range from 3.59 to 8.81(Y), and 3.56 to 8.79 (X) with means of 6.28 and 6.25, respectively ($Y=1.01X+0.05$; $r=0.999^{**}$, significant at $P=0.01$; $s_{y.x}=0.06$), indicating a very close agreement and that weighing was unnecessary for precise pH measurement. Schofield and Taylor (1955) originally recommended that soil pH be measured in 0.01 M $CaCl_2$ with a 1:2 soil/solution ratio. Values are not sensitive to fairly wide changes in soil/solution ratio when measured in 0.01 M $CaCl_2$ (Schofield & Taylor, 1955; Clark 1964; Ryti, 1965; White, 1969). Puri and Asghar (1938) also reported using soil/1 N KCl ratios ranging from 1:2.5 to 1:25 and found little effect on pH of acid soils, but a significant effect on that of calcareous soils. Little, if any, dilution effect was reported between pH measurements made at 1:1 and 1:2 ratios with 0.01 M $CaCl_2$ and 1 N KCl for mineral soils and Histosols by van Lierop and Tran (1979) and van Lierop (1981), respectively. It is unnecessary, therefore, to weigh soil samples for pH determination when using these solutions.

B. Soluble Salts and Lime Potential

The lime potential was defined as being: pH – 1/2p(Ca +Mg). Schofield and Taylor (1955) found that soil pH and ½ p(Ca +Mg) increase in value with dilution but their difference, the lime potential, remains constant over a relatively wide range of ratios and electrolyte concentrations. The increase in pH produced by diluting soils from a 1:1 to a 1:2 soil/solution ratio is not directly related to acid dilution, but is caused by a decrease in H^+ dissociation. The difference in pH between water and 0.01 M $CaCl_2$ measurements is often assumed to be about 0.5 units. Generally, pH differences between water and 0.01 M $CaCl_2$ decrease as salt content of the soil solution increases. The effect of salt level on pH divergence is suggested by lime-potential findings. Ryti (1965) also demonstrated the effect of salt concentration on the disparity between water and 0.01 M $CaCl_2$ pH values. They found an average of 0.83 pH unit difference between measurements in water and 0.01 M $CaCl_2$ for 30 relatively low-salt soils with conductivities ≤ 0.1 dS m^{-1} (1:2 soil:water ratio). In contrast, they found 0.07 pH unit difference for soils with higher conductivities ranging from 0.1 to 8 dS m^{-1}. This emphasizes the role of solution ionic level on the disparity between water and 0.01 M $CaCl_2$ pH values.

C. Suspension effect

Overbeek (1953) developed the theory that attributes junction potential to a Donnan emf generated by an impeded mobility of K^+ relative to Cl^-. Experimental results supporting it were obtained by Coleman et al. (1951) and Bloksma (1957). Peech et al. (1953) indicated that junction potential rarely exceeds 0.25 pH unit. Peech (1965a) suggest that the liquid junction be located in the supernatant after settling of soil particles when measuring pH. However, it takes considerably longer to obtain a clear supernatant than is typically allocated for measuring pH. Maximum pH values due to junction potential of 0.9 and 0.5 pH units were reported for mineral soils by Coleman et al. (1951) and Ryti (1965), respectively. Similarly, a maximum value of 1.1 pH units was observed with acid Histosols by van Lierop and MacKenzie (1977). The magnitude of the suspension effect can vary from being negligible to over a pH unit, and appears to be largely influenced by soil salt content. Coleman et al. (1951) reported that soil pH in 1 N KCl remained unaffected by electrode position in the sample. Clark (1964) reported finding no suspension effect when the salt content was higher than 0.005 M $CaCl_2$.

D. Effect of Carbon Dioxide on Soil pH

The pH of distilled water at equilibrium with carbonic acid at partial pressure of 0.03% CO_2 (pCO_2) in the atmosphere is about 5.72 (Bradfield, 1941). However, a soil atmosphere contains much higher pCO_2 pressures than the air above it. Bradfield (1941) suggested that soils contain from 10 to 100 times more CO_2 than the atmosphere above it, and values as high as 12% CO_2 have been proposed (Simmons, 1939). Higher pCO_2 pressures impose higher soil-solution carbonic and bicarbonic acid contents. In turn, these higher contents lower soil pH and increase the concentration of Ca and Mg in solution (Simmons, 1939; Turner & Clark, 1956). Although pCO_2 changes can affect soil pH significantly, air or oven-drying samples reduces pCO_2 pressures to that in the atmosphere. As the pCO_2 pressure in the atmosphere can be considered constant, drying samples before analysis should eliminate the effect of variable pCO_2 on soil pH.

E. Effect of Drying on Soil pH

Soils are usually dried, crushed, and sieved before analysis. Drying may have effects other than those from loss of CO_2. Baver (1927) reported a decrease between 0 and 0.6 pH by air drying. Bailey (1932) concluded that pH was generally lowered somewhat by air drying. Similarly, Huberty and Haas (1940) and Collins et al. (1970) found that oven drying decreased pH. Bowser and Leat (1958) also observed that pH decreased an average of about 0.4 pH unit with drying, but noted that it increased with a calcareous soil. Average decreases of 0.15 and 0.5 pH unit were reported for drying acid Histosols by Davis and Lawton (1947) and van Lierop and MacKenzie (1977), respectively. This may occur because drying-wetting cycles promote OM mineralization, which in turn would produce a salt effect on soil pH.

F. Seasonal pH Fluctuation

In view of the many factors that affect soil pH during the growing season, it is not surprising that it fluctuates during the year and from year to year. Baver (1927) and Huberty and Haas (1940) noted that pH varied about a unit during the growing season and that variations seemed related to prevailing moisture regime. Bowser and Leat (1958) found that pH varied by as much as 2 units during the growing season on a calcareous soil, and that moisture and pH fluctuations appeared interrelated. Generally, pH gradually increased and decreased during periods of high and low rainfall, respectively (van der Paauw, 1962). Although, fluctuations of field-moist soils may be partially attributable to changes in soil atmosphere pCO_2 pressure during periods of high biological activity, low pH tends to occur during summer months when moisture levels are often lower and presumably aeration is better. Also, most crops are produced during summer following N mineralization, fertilization, and nitrification, all increasing the salt content of the soil solution, which in turn decreases pH.

pH Buffering Capacity

The pH buffering capacity of a soil is defined as its resistance to changes in pH when an acid or a base is added. It can be expressed as the quantity of protons required for changing the soil pH one unit (mmol H^+ kg^{-1} soil pH^{-1}) (Rowell, 1994). Magdoff and Bartlett (1985) found that organic matter is an important determinant of pH buffering in soils. They also reported that soils are very well buffered above pH 7 and below pH 4. Within the pH range of most agricultural soils (4.5 to 6.5) the pH relationship is nearly linear. Aitken, et.al., (1990) also found that the buffering capacity of a soil is governed by organic carbon, clay and exchangeable acidity. There was a better relationship between pH buffering capacity and organic carbon than between pH buffering capacity and clay. This is consistent with the large difference in buffer capacities of clay and organic matter. For example, organic matter may have a buffering capacity >300 times that of kaolinite (Vache, 1988). Laboratory methods for evaluating buffering capacity involve potentiometric titration of a suspended soil sample with either an acid or a base (Magdoff and Bartlett, 1985). Changes in pH after acid or base addition were related to reaction time and soil characteristics (Dunn, 1943). Dunn (1943) recommended the reaction of soil-water suspensions with 0.04 N $Ca(OH)_2$ for three days to reach an equilibrium pH. In most recent work, Schaller and Fischer (1984) reported that between 80 and 100% of the added protons were taken up by the soils within a few seconds, resulting in the neutralization of H^+ and the adsorption on exchange sites of Ca^{2+} and Mg^{2+} released from the lime.

Lime Requirement Determination

The lime requirement (LR) is the amount of limestone ($CaCO_3$) needed to increase the pH of the plow layer of acid soil to a desired level (McLean, 1970). The lime requirement is affected by a soil's pH and its buffering capacity, which is determined by soil texture, type of clay minerals, and the amount of organic matter (Johnson et.al., 1979). Many qualitative and quantitative methods have been used to estimate the lime requirement including $CaCO_3$ incubations, titration techniques, buffer methods, determination of exchangeable aluminum, and indirect lime requirement determination methods. Different rapid LR methods can give widely divergent results (Peech and Michael., 1965). Certain methods are better suited to specific soil conditions (Mehlich, et. al., 1976).

Incubation in the field would be ideal for determining LR, but it is prohibitive due to the high cost and time required. Instead, the $CaCO_3$-moisture-incubation method has been considered as a standard for comparative purposes by some scientists (Kamprath, 1970, McLean, et. al. 1966, Mehlich, A. 1976). Incubation methods are considered to be reliable but also time consuming (Bache, 1988) and long-term incubations are likely to lead to mineral nitrogen accumulations and the associated pH changes (Barrow and Cox, 1990). Barrow and Cox (1990) investigated the effects of time and temperature of incubation on the pH of soils to which acid or alkali had been added. They found that because of the increased rate of reaction at high temperatures, it is possible to produce in a few days at 60˚C effects similar to several months' incubation at 25˚C. Backer and Chae (1977) reported that the use of room temperature incubation of incremental mixtures of $CaCO_3$ and soil tends to overestimate the actual lime requirement. This occurs because soil acidity increases under room temperature incubation.

Measuring the soil pH buffering capacity by titration has been used to determine the lime requirement, to calculate soil acidification rates, and to calibrate lime requirement tests (Aitken and Moody, 1994). Even though the titration method for determining the soil pH buffering capacity is considered reliable and is often used as a calibration for buffer methods, it is not considered a viable option for routine measurement of the lime requirement especially in soil testing laboratories, because of the time required (Follett and Follett, 1980).

Crop yield responses to liming are closely related to exchangeable-Al reductions. So measurement of exchangeable-Al has also been used as a liming criterion. The amount of Al^{3+} on the permanent soil-exchange sites is largely influenced by soil pH (McLean, 1976). Liming to pH 5.5 ensures elimination of Al^{3+} toxicity. The maximum yield of relatively Al-sensitive crops like alfalfa, soybean, and barley is realized when the exchangeable-Al level is lower than 0.1 $cmol_c$ Al^{3+} kg^{-1} of soil (Ragland and Coleman, 1959; Hoyt and Nyborg, 1987). Accordingly, this level was selected as the testing norm. Soils that have a pH $\leq$ 5.5 and contain more than 0.1 $cmol_c$ of 1 N KCl extractable Al kg^{-1} of soil (about 10 μg of Al g^{-1} of soil) are limed to pH 5.5. An alternative approach that relies on calculating the LR levels needed to neutralize exchangeable Al^{3+} was also proposed by Kamprath (1970). He suggested the following equations: LR(a) = Al^{3+}; LR(b) = $1.5Al^{3+}$; LR(c) = $2Al^{3+}$. Where LR(a), LR(b) and LR(c) represent the LR in metric tones of $CaCO_3$ ha^{-1} for crops having most, moderate, and least Al^{3+} tolerance, respectively. The Al^{3+} concentrations in these equations are expressed in $cmol_c$ Al^{3+} L^{-1} of soil. The main advantage that favors using Al^{3+} as a liming criterion is that smaller amounts of liming material are required to precipitate plant-toxic Al^{3+} levels than by liming to higher soil pH values. However, there is very little buffering against further drops in pH when the limed soils become acidified and the pHs drop again to less than 5.5.

Various buffer methods include: the procedure by Shoemaker, McLean, and Pratt (1961), the Single Buffer Method of Woodruff (1947), the Single-Buffer Method of Mehlich (1976), the New Woodruff Single-Buffer Method (Brown et al., 1977), the Single-Buffer Method of Adams and Evans (1962), the Double-Buffer Method of Yuan (1974), and SMP Double-Buffer Method (McLean et al., 1977). Rapid buffer-pH methods measure a proportion of the acidity. The more accurate methods rely on exhaustive displacement of acidity to measure LR (Peech and Michael, 1965b). Disparity of LR values between various buffer-pH procedures have two principal causes. First, calibration accuracy affects recommendations. Calibration should be adjusted for incomplete measurement of acidity by a buffer. Second, the discrepancy between soil-buffer and target pH affects the amount and proportion of acidity measured. The buffer's initial pH and buffering capacity also influence equilibrium pH and consequently, the amount and proportion of acidity included in a measurement.

The Shoemaker, McLean, and Pratt (SMP) (Shoemaker et al., 1961) single-buffer procedure has been widely adopted and found particularly accurate for soils with high LR and trivalent Al. (Mclean et al., 1966, 1978). The relationship between SMP soil-buffer pH (X) and LR (Y) is not linear but curvilinear (Tran & van Lierop, 1982) ($Y = 4.0X^2 - 54.7X + 188$, $r^2 = 89.4\%^{**}$, $S_{y.x} = 0.89$). Curvilinearity increases with increasing difference between initial buffer and target pH (Tran & van Lierop, 1981a, 1982). The principal reason for curvilinearity is that buffer-pH procedures measure a greater proportion of soil acidity from low than from high LR soils. Superfluous pH-dependent acidity is measured when soil-buffer pH is higher than target pH. The SMP buffer contains p-nitrophenol, potassium chromate, calcium chloride dihydrate, calcium acetate and triethanolamine. It’s buffering capacity is 0.28 ± 0.02 cmol_c HCl/pH from pH 7.50 to 5.50.

Webber et al. (1977) evaluated the Woodruff buffer for determining the LR of Canadian soils to pH 5.5 and 6.0 and found it was as accurate as the SMP (Shoemaker et al., 1961) buffer. Loynachan (1981) compared Woodruff buffer with the SMP buffer and found that the LR values were closely correlated (r = 0.99**). Fox (1980) evaluated the Woodruff procedure and found that it was quite accurate at low values, but that it underestimated at high LR. Brown and Cisco (1984) and Alibi et al. (1986) confirmed the observations of Fox (1980). The woodruff single buffer contains p-nitrophenol, magnesium oxide, and calcium acetate. Its buffering capacity is 0.70 ± 0.02 cmol_c HCl for the pH range from pH 7.0 to 6.0.

Mehlich (1976) calibrated his buffer to determine the amount of lime needed to neutralize permanent (neutral-salt) exchangeable acidity (EA). This is the acidity implied in restricting crop growth on acid mineral soils (Kamprath, 1970; Evans & Kamprath, 1970; Mehlich, 1976). Calibration of this buffer differs from others in that LR recommendations are meant to produce optimum yields rather than achieve a certain pH (Mehlich, 1976). Tran and van Lierop (1982) found the Mehlich buffer to be the most accurate among the procedures tested. The probable reason is that neutral-salt EA tends to predominate in acid soils at pH levels lower than 5.5. This buffer-pH procedure recommends about 50, 59, and 60% of reference values from calcium carbonate incubation to obtain pH 6.5 (McLean et al., 1978; Tran & van Lierop, 1981a; Ssali & Nuwamanya, 1981, respectively). Nonethless, it is particularly well suited for determining the LR for neutralizing acidity harmful to crop productivity and will generally recommend sufficient limestone to achieve a pH slightly above 5.5. This pH is sufficient to eliminate possible Al^{3+} toxicity for only a short time until nitrificaition of N fertilizers acidifies the soil further. The Mehlich buffer contains glacial acetic acid, TEA, ammonium chloride, barium chloride, and sodium glycerophosphate. Its buffering capacity is checked by mixing 20 mL of Mehlich buffer with 10 mL 0.1 N HCl-$AlCl_3$ solution. The pH of the resulting mixture should be 4.1 ± 0.05.

The new Woodruff (NW) buffer was discussed by McLean (1973). The NW buffer is as precise as the original but recommends about 1.6 times higher LR (Brown and Cisco, 1984; Alabi et al., 1986). The NW buffer is more accurate than the original for determining the LR to pH 7.0. (Brown and Cisco, 1984). Regression parameters from Alabi et al. (1986) suggest that the NW-buffer method recommends higher LR values than required to achieve pH 6.5. When comparing results of studies using different methods, an interesting observation is that both studies found that the SMP single-buffer procedure recommended higher values than the NW procedure. The SMP procedure has been shown to overestimate the LR of soils with low LR, according to McLean et al. (1966, 1978) and Tran and van Lierop (1981a, 1982). Since low LR soils were predominantly studied by Brown and Cisco (1984) and Alabi et al. (1986), this suggests that the NW-buffer LR procedure is more accurate for low LR soils.

The Adams and Evans (A-E) method was developed for measuring the LR of Red-Yellow Podzolic soils (Ultisols) that have low LRs and which may be affected by crop yield reduction from overliming (Adams & Evans, 1962). The method was developed because other buffers were not satisfactory for determining the LR of these Low-exchange capacity soils. According to McLean (1982), the A-E buffer is very sensitive and particularly useful for soils with low LRs. It is used by several laboratories in the southern USA (Adams, 1984). Fox (1980) evaluated the A-E method and concluded that it tended to overestimate LR, though these were well correlated with incubation values. Similarly, Tran and van Lierop (1981a) found that that it was suitable essentially for low LR soils, but that it was not as accurate as some for determining higher LR. They also found that the A-E method overestimated the LR, and suggested that high initial buffer pH (pH 8.0) could be responsible. Because of this initial buffer pH, it would include pH-dependent acidity between pH 6.5 and 8.0 that should not be included. More recently, Alabi et al. (1986) confirmed that the A-E method overestimated the LR of coarse-textured soils. The A-E buffer contains p-nitrophenol, H_3BO_3, KCl, and KOH. Each 0.08 milli-equivalent of a strong acid added to 20 mL of the buffered solution results in a pH change of 0.10 unit between pH 7.0 and 8.0.

A Double-buffer LR method was introduced by Yuan (1974). It is said Double-buffer procedures differ from single-buffer procedures in that the former determines the characteristic buffering capacity of the soil to be limed. In the case of single-buffer methods, the amount of acidity or the LR to a target pH is determined from the relationship between soil-buffer pH and incubation values preferably established by regression techniques. On the other hand, double-buffer procedures rely on three fundamental assumptions. The first is that changes in soil pH with additions of base or buffer are linear. Second, the change in soil pH produced by adding buffers is extrapolated to the neutralization of soil acidity by $CaCO_3$. Third, the buffers completely displace and assess the same acidity that is neutralized by limestone (Yuan, 1974). The adoption of the first assumption theoretically allows double-buffer procedures to determine LR values to any selected target pH situated between the current soil pH and about 6.0 to 7.0. The second assumption is usually described as directly measuring the individual buffering capacity of a soil. This measurement relies on extrapolating the amount of acidity displaced by the buffers, as indicated by their change in pH, into a LR. The main advantage claimed in favor of double-buffer procedures is their greater accuracy at low LR values.

The Yuan Double-Buffer Method takes into consideration both the total acidity and buffering capacity of individual acid soils. According to Yuan (1974), the double-buffer procedure measured an average of about 90% of reference values by incubation with $CaCO_3$. McLean et al. (1978) also studied the Yuan-double-buffer procedure and found the measured LR values too low compared with incubation with $CaCO_3$; this finding was confirmed by Tran and van Lierop (1981a, 1982). Apparently, the buffers do not displace all acidity that reacts with $CaCO_3$ when increasing soil pH to the target value. Tran and van Lierop (1981a, 1982) suggested that the accuracy of the Yuan-double-buffer procedure could be improved substantially by incorporating a correction factor to adjust for the incomplete measurement of soil acidity. They found the Yuan-double-buffer procedure was as precise as any for determining the LR to pH 6.5 and 6.0, but slightly less precise for 5.5. The Yuan buffer contains tris(hydroxymethyl)-aminomethane, imidazol, K_2CrO_4, pyridine and calcium chloride. The buffer gave a linear pH reduction of 0.1 unit down to pH 5.4 from pH 7.0 with each increment of 0.1 meq strong acid added to 50 mL of the buffer.

The SMP buffer was adapted by McLean et al. (1977, 1978) to a double-buffer methodology similar to that proposed by Yuan (1974). This approach was selected for improving the accuracy of LR determination for low-buffering capacity soils. McLean et al. (1977, 1978) concluded that double buffer procedures do not measure all the acidity neutralized by $CaCO_3$ either, if we believe in the $CaCO_3$ incubation methods. They therefore, included a proportionality factor into the SMP-double buffer calibration similar to that needed for single-buffer calibrations. This factor which is derived from incubation data using regression techniques corrects for partial acidity displacement.

Indirect LR-determination procedures rely on estimating a LR from soil properties without directly measuring acidity. Joret et al. (1934) proposed the following equation relating soil OM and clay content to LR: LR (mmol(+) kg^{-1}) = 0.11[%clay + (5 × %OM)]. Keeney and Corey (1963) found that clay content or exchangeable Al had a relatively smaller influence on LR. They formulated the following equation relating a desired change in pH and soil OM content to LR: LR (mmol(+) kg^{-1}) = (pH 6.5 – soil pH) × (%OM). Owusu-Bennoah et. al. (1995) related pH, organic carbon, and clay with LR determined by incubation with $Ca(OH)_2$ and found: LR (mmol(+) kg^{-1}) = 4.2 – 1.1pH + 1.7(% organic carbon) + 0.05(% clay), $R^2 = 0.92$.

Incubation Methods

Incubation methods are considered mostly reliable to determine the LRs of soils. They are often used as calibrations for buffer methods (Barrow and Cox, 1990). Adams and Evans (1962) used incubation of acid soils with solid $Ca(OH)_2$ to verify the Adams Evans buffer procedure for Red-Yellow Podzolic soils. Soils were treated with rates of $Ca(OH)_2$ in the laboratory and incubated moist for 4 weeks to obtain titration curves. The amounts of $CaCO_3$ required to change the soil pH to 6.5 according to the titration curves were then compared to the amounts measured by the buffered solution-soil pH method. Baker and Chae (1977) did a $CaCO_3$ incubation for seven Washington acid mineral soils. The $CaCO_3$ and dry soil were thoroughly mixed, placed in plastic beakers, wet to field capacity, and covered with 1-mil polyethylene films secured with rubber bands. The soils were incubated at room temperature (20 to 25 °C) and brought to field capacity periodically by adding distilled H_2O to produce a predetermined weight. Three sets of each treatment were established; one set was terminated after each of 6, 9, and 12 months of incubation. Tran and van Lierop (1981) incubated soils with rates of a chemically pure $CaCO_3$ ground to pass a 400-mesh sieve. The incubation LRs (to achieve pH 6.5) were obtained by graphing the applied liming rates against the ensuing soil pH after incubating soils for 8 weeks. Soil pH was determined six times during the first month of incubation, and it was found to have stabilized within that time. The soils were also air-dried, crushed, mixed, and remoistened 1 month after starting the incubations and kept moist for the remaining month. Loynachan (1981) stored soils at 2 °C in sealed polyethylene bags prior to lime additions. Precipitated $CaCO_3$ smaller than 100 mesh was added to 675 mL of uniformly packed soil at different rates. After the lime-soil mixtures were thoroughly mixed in polyethylene bags, they were subdivided into three equal volumes and placed into 250mL Styrofoam containers. At the end of six weeks, soil from each container was thoroughly mixed, and a subsample was air dried for pH determinations using a 1:1 water to soil ratio. McConnell et. al, (1990) incubated Arkansas soils with standardized $Ca(OH)_2$ solution. Each soil was air dried, ground and passed through a 2-mm mesh sieve. Subsamples of each soil were treated with aliquots of standardized 0.022 M $Ca(OH)_2$ solution similar to the procedure described by Bradfield (1941). The mixtures were equilibrated for three days, and pH was measured. The soil pH was then plotted as a function of the $Ca(OH)_2$ solution additions to obtain a buffer curve, and linear regression was used to find the slope.

Refenrences

Adams, F. 1984. Crop responses to liming in the southern United States. p. 211-266. In F. Adams (ed.) Soil acidity and liming. 2nd ed. Agronomy Monogr. 12. ASA, Madison, WI.

Adams, F., and C.E. Evans. 1962. A rapid method for measuring the lime requirement of Red-Yellow Podzolic soils. Soil Sci. Am. Proc. 26:255-357.

Aitken, R.L., Moody, P.W., and McKinley, P.G. 1990. Lime requirement of acidic queensland soils. Comparison of laboratory methods for predicting lime requirement. Aust. J. Soil Res. 28:703-715.

Alabi, K.E., R.C. Sorensen, D. Knudsen, and G.W. Rehm. 1986. Comparison of several lime requirement methods on coarse textured soils of Northeastern Nebraska. Soil Sci. Soc. Am. J. 50:937-941.

Bache, B.W. 1988. Measurements and mechanisms in acid soils. Commun. Soil Sci. Plant Anal. 19:775-792.

Baker, A.S., and Y.M. Chae. 1977. A laboratory quick test for predicting the lime requirements of acid mineral soils. Tech. Bull. 88, Washington State Univ., 11 p.

Bailey, E.H. 1932. The effect of air drying on the hydrogen ion concentration in the soils of the United States and Canada. USDA Tech. Bull. 291. U.S. Gov. Print. Office, Washington, DC.

Barrow, N.J, and Cox, V.C. 1990. A quick and simple method for determining the titration curve and estimating the lime requirement of soils. Austri. J. Soil Research: 28:685-694.

Baver, L.D. 1927. Factors affecting the hydrogen ion concentration in soils. Soil Sci. 23:399-414.

Bloksma, A.H. 1957. An experimental test of Overbeek's treatment of the suspension effect. J. Colloid Sci. 12:135-143.

Bowser, W.E., and J.N. Leat. 1958. Seasonal pH fluctuations in a Gray Wooded soil. Can. J. Soil Sci. 38:128-133.

Bradfield, R. 1941. Calcium in the soil: 1. Physico-chemical relations. Soil Sci. Soc. Am. Proc.6:8-15.

Brown, J.R., J. Garett, and T.R. Fisher. 1977. Soil testing in Missouri. Univ. of Missouri-Columbia Ext. Div. Ext. Circ. 923.

Brown, J.R., and J.R. Cisco. 1984. An improved Woodruff buffer for estimation of lime requirements. Soil Sci. Soc. Am. J. 48:587-592.

Chapman, H.D., J.H. Axley, and D.S. Curtis. 1941. The determination of pH at soil moisture levels approximating field conditions. Soil Sci. Soc. Am. Proc. (1940) 5:191-200.

Clark, J.S. 1964. An examination of the pH of calcareous soils. Soil Sci. 98:145-151.

Collins, J.B., E.P. Whiteside, and C.E. Cress. 1970. Seasonal variability of pH and lime requirements in several southern Michigan soils when measured in different ways. Soil Sci. Soc. Am. Proc. 34:56-61.

Coleman, N.T., D.E. Williams, T.R. Nielsen, and H. Jenny. 1951. On the validity of interpretations of potentiometrically measured soil pH. Soil Sci. Soc. Am. Proc. (1950) 15:106-110.

Davis, J.F., and K. Lawton. 1947. A comparison of the glass electrode and indicator methods for determining the pH of organic soils and the effect of time, soil-water ratio and air-drying on glass electrode results. J. Am. Soc. Agron. 39:719-723.

Dunn, L.E. 1943. Lime requirement determination of soils by means of titration curves. Soil Sci. 56:341-351.

Evans, C.E. and E.J. Kamprath. 1970. Lime response as related to percent Al Saturation, solution Al, and organic matter content. Soil Sci. Soc. Am. Proc. 34:893-896.

Follett, R.H, and R.F, Follett. 1980. Strengths and weaknesses of soil testing in determining lime requirements for soils. p 40-51. In Proc. Of the Natl. Conf. on Agric. Limestone 16-18 Oct. 1980.

Fox, R.H. 1980. Comparison of several lime requirement methods for agricultural soils in Pennsylvania. Commun. Soil Sci. Plant Anal. 11:57-69.

Hoyt, P.B., and M. Nyborg. 1987. Field calibration of liming responses of four crops using pH, Al, and Mn. Plant Soil 102:21-25.

Huberty, M.R., and A.R.C. Haas. 1940. The pH of soil as affected by soil moisture and other factors. Soil Sci. 49:455-478.

Joret, G., H. Malterre, and M. Cabazan. 1934. L'appréciation des besoins en chaux des sols de limon d'après leur état de saturation en bases échangeables. Ann. Agron. 22:453-479.

Kamprath, E.J. 1970. Exchangeable aluminum as a criterion for liming leached mineral soils. Soil Sci. Soc. Am. Proc. 34:252-254.

Keeney, D.R., and R.B. Corey. 1963. Factors affecting the lime requirement of Wisconsin soils. Soil Sci. Soc. Am. Proc. 27:277-280.

Loynachan, T.E. 1981. Lime requirement methods for cold regions. Soil Sci. Soc. Am. J. 45:77-80.

Magdoff, F.R. and Bartlett, R.J. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. Proc. 49:145-148.

McConnell, J.S., Gilmour, J.T., Baser, R.E., and Frizzell, B.S. 1990. Lime Requirement of acid soils of Arkansas. Arkansas Experiment Station Special Report 150.

McLean, E.O. 1970. Lime requirement of soils-inactive toxic substances or favorable pH range. Soil Sci. Soc. Am. Proc. 34:363-364.

McLean, E.O. 1973. Testing soils for pH and lime requirement. In L.M. Walsh and J.D. Beaton (ed.) Soil testing and plant analysis. SSSA, Madison, WI.

McLean, E.O. 1976. Chemistry of soil aluminum. Commun. Soil Sci. Plant Anal. 7:619-636.

McLean, E.O. 1982. Soil pH and lime requirement. p. 199-224. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agronomy Monogr. 9. ASA and SSSA, Madison, WI.

McLean, E.O., D.J. Eckert, G.Y. Reddy, and J.F. Trierweiler. 1978. An improved SMP soil lime requirement method incorporating double-buffer and quick-test features. Soil Sci. Soc. Am. J. 42:311-316.

McLean, E.O., J.F. Trierweiler, and D.J. Eckert. 1977. Improved SMP buffer method for determining lime requirement of acid soils. Commun. Soil Sci. Plant Anal. 8:667-675.

Mclean, E.O., S.W. Dumford, and F. Cronel. 1966. A comparison of several methods of determining lime requirements of soils. Soil Sci. Soc. Am. Proc. 30:26-30.

Mehlich, A. 1976. New buffer pH method for rapid estimation of exchangeable acidity and lime requirements of soils. Commun. Soil Sci. Plant Anal. 7:253-263.

Mehlich, A., S.S. Bowling, and A.L. Hatfield. 1976. Buffer pH acidity in relation to nature of soil acidity and expression of lime requirement. Commun. Soil Sci. Plant Anal. 7(3):253-263.

Overbeek. J.Th.G. 1953. Donnan-E.M.F. and suspension effect. J. Colloid Sci. 8:593-605.

Owusu-Bennoah, E., Acquaye, D. K., Mahamah, T. 1995. Comparative study of selected lime requirement methods for some acid Ghanaian soils. Commun. soil Sci. Plant Anal., 26(7&8):937-950.

Peech, M., R.A. Olsen, and G.H. Bolt. 1953.The significance of potentiometric measurements involving liquid junction in clay and soil. Soil Sci. Soc. Am. Proc. (1950) 15:112-114.

Peech, M. 1965a. Hydrogen-ion activity. p. 914-926. In C.A. Black et al. (ed.) Methods of soil analysis. Part 2. Agronomy Monogr. 9. ASA, Madison, WI.

Peech, M. 1965b. Lime requirement. p. 927-932. In C.A. Black et al. (ed.) Methods of soil analysis. Part 2. Agronomy Monogr. 9. ASA, Madison, WI.

Rowell, D.L. 1994. Soil science: methods and applications. Longman Scientific and Technical, Harlow.

Puri, A.N., and A.G. Asghar. 1938. Influence of salts and soil water ratio on pH value of soils. Soil Sci. 46: 249-257.

Ragland, J.L., and N.T. Coleman. 1959. The effect of aluminum and calcium on root growth. Soil Sci. Soc. Am. Proc. 23:355-357.

Ryti, R. 1965. On the determination of soil pH. Maataloustiet. Aikak. 37:51-60.

Schaller, G. and Fischer, W.R. 1984. Kurzgristige pH-pufferung von Böden. A. Pflanzenernaehr.Bodenk. 148:471-480.

Schofield, R.K., and A.W. Taylor. 1955. The measurement of soil pH. Soil Sci. Soc. Am. Proc. 19: 164-167.

Shoemaker, H.E., E.O. McLean, and P.F. Pratt. 1961. Buffer methods for determining the lime requirement of soils with appreciable amounts of extractable aluminum. Soil Sci. Soc. Am. Proc. 25:274-277.

Simmons, C.F. 1939. The effect of carbon dioxide pressure on the equilibrium of the system hydrogen colloidal clay-H_2O-$CaCO_3$. J. Am. Soc. Agron. 31:638-648.

Singh, S.S. 1972. The effect of temperature on the ion activity product $(Al)(OH)_3$ and its relation to lime potential and degree of base saturation. Soil Sci. Soc. Am. Proc. 36:47-50.

Sorensen, S.P.L. 1909. Enzyme studies: II. The measurement and importance of the hydrogen ion concentration in enzyme reaction. C.R. Trav. Lab. Carlsberg 8:1.

Ssali, H., and J. K. Nuwamanya. 1981. Buffer pH methods for estimation of lime requirement of tropical acid soils. Commun. Soil Sci. Plant Anal. 12:643-659.

Tran, T. S., and W. van Lierop. 1981. Evaluation and improvement of buffer-pH lime requirement methods. Soil Sci. 131:178-188.

Tran, T. S., and W. van Lierop. 1982. Lime requirement determination for attaining pH 5.5 and 6.0 of coarse textured soils using buffer-pH methods. Soil Sci. Soc. Am. J. 46:1008-1014.

Turner, R.C., and J.S. Clark. 1956. The pH of calcareous soils. Soil Sci. 82:337-341.

van der Paauw, E. 1962. Periodic fluctuations of soil fertility, crop yields, and responses to fertilization as affected by alternating periods of low and high rainfall. Plant Soil 17:155-182.

van Lierop, W. 1981. Conversion of organic soil pH values measured in water, 0.01 M $CaCl_2$, or 1 N KCl. Can. J. Soil Sci. 61:577-579.

van Lierop, W., and A.F. Mackenzie. 1977. Soil pH measurement and its application to organic soils. Can. J. Soil Sci. 57:55-64.

van Lierop, W., and T.S. Tran. 1979. L'acidité et le besoin en chaux: 1. Mesure du pH de sol. Agriculture 36:9-12.

Weaver, A.R. 2002. Characterizing soil acidity in coastal plain soils. Ph.D Dissertation. University of Georgia.

Webber, M.D., P.B. Hoyt, M. Nyborg, and D. Corneau. 1977. A comparison of lime requirement methods for acid Canadian soils. Can. J. Soil Sci. 57:361-370.

White, R.E. 1969. On the measurement of soil pH. J. Austr. Inst. Agric. Sci. 35:3-14.

Woodruff, C.M. 1947. Determination of exchangeable hydrogen and lime requirement of the soil by means of the glass electrode and a buffered solution. Soil Sci. Soc. Am. Proc.12:141-142.

Yuan, T.L. 1974. A double buffer method for the determination of lime requirement of acid soils. Soil Sci. Soc. Am. J. 38:437-440.

CHAPTER 1

DIRECT TITRATION FOR MEASUREMENT OF SOIL LIME REQUIREMENT

Abstract

Previous studies about the titration curves of acid soils reported a linear relationship in the approximate range $4.5 < pH(H_2O) < 6.5$. It appears possible to establish the slope of the titration line by adding three consecutive aliquots of $Ca(OH)_2$, measuring pH, and then predict the lime requirements (LRs) by extrapolation to pH 6.5. The objective of this study was to evaluate the possibility of developing a direct titration procedure to measure the LRs of acid soils for routine use in soil testing laboratories. Seventeen soil samples with a wide range of clay and soil organic carbon (C) contents were collected from five of the major land resource areas of Georgia. A 30 minute interval time between additions gave greater LRs than 15 minute equilibration, but the same as 45 minute equilibration. Thirty minute equilibration was therefore considered the adequate for the base to react with the soil acids. Incubation of the soils with $Ca(OH)_2$ for three days revealed that the 3-points prediction from the direct titration with 30 minute interval time between additions estimated approximately 80% of the soil acidity determined by the 3-day incubation.

Key words: Titration, Lime requirement, Soil testing, Soil acidity.

Introduction

Dunn (1943) studied direct titration to predict the lime requirement of acid soils and focused on the influence of equilibrium time on the reaction between added base and soil acids. He found that 4 days were needed for pH values to reach equilibrium when 0.022 M $Ca(OH)_2$ solution was added to acid soils. He also discovered that shaking affected the time required for soil pH values to reach equilibrium. He reported that equilibrium was reached within 8 hours with shaking as compared to 4 days for the suspensions without shaking. Finally, he suggested a standard direct titration method for lime requirement by incorporating acid soils with different rates of 0.022 M $Ca(OH)_2$ for 4 days. The $Ca(OH)_2$ titration method suggested by Dunn (1943) for measuring the lime requirement was widely accepted as a reliable standard for evaluating buffer methods that were developed for estimating the lime requirement (Follett and Follett, 1980; Alabi et al, 1986; McConell et al., 1990; Owusu-Bennoah et al., 1995). However, Dunn’s method was also considered to be a time-consuming procedure and not suitable for routine use in soil testing laboratories. Many studies focused on the titration curve itself. Magdoff and Bartlett (1985) concluded that the relationship between pH and OH^- added is nearly linear within the pH range of most agricultural soils (4.5 to 6.5). Weaver (2002) also reported an approximately linear relationship between pH and base added for a series of Georgia soils.

The Adams-Evans (AE) buffer procedure (Adams and Evans, 1962) for predicting the lime requirement (LR) is used widely in soil testing laboratories in the south-east United States. However, it has been reported to overestimate the LR (Follett and Follett, 1980; Tran and Lierop, 1981; Alabi et al, 1986). Tran and Lierop (1981) also noted that the the

AE buffer had a limited range and relatively poor precision, indicated by the significantly lower correlation coefficient between estimates of LR from incubation and LR values using the AE procedure ($r^2 = 0.78$). Another concern about the AE buffer is the potential toxicity from one of its components, p-nitrophenol. Considering the inaccuracy and environmental concern of the AE buffer procedure, the objective of this study was to evaluate the possibility of developing a direct titration procedure to measure the LRs of acid soils for routine use in soil testing laboratories

Materials and Methods

Seventeen soil samples with a wide range of clay and soil organic carbon (C) contents were collected in January of 2002 from five of the major land resource areas of Georgia as shown in Figure 1.1. The soils were oven-dried at a temperature of 35˚C, crushed, then sieved (2-mm) to remove small rocks and non-decayed crop residue, which consisted of less than 1% of the soil by weight. Then the soils were stored in the sealed Ziploc® bags until analyzed. A subsample of each soil was analyzed for C and N with a Leco CNS 2000 Analyzer. Four of the soil samples contained more than 30% clay and five had clay contents in the range from 10 to 20%. Eight contained less than 10% clay. Three of the soil samples contained more than 2.0% total C and eight soil samples contained in the range from 1.0 to 2.0% total C. The others had less than 1.0% total C (Table 1.1).

Saturated $Ca(OH)_2$ solution, 0.022 M, was used as the standard base to titrate the soils. In a 12 L Nalgen carboy 50 g of powdered reagent grade $Ca(OH)_2$ was added to 10 L of deionized water, stirred with a glass rod, and then allowed to settle for 4 days. The carboy was fitted with an ascarite trap to prevent carbon dioxide from reacting with the $Ca(OH)_2$.

A Multi-task® version 2.0 digital titrator by Visco Alpha was used to titrate the soil samples. Through programming the software associated with the titrator, the number of aliquots, the interval time between two aliquots, and the stirring speed during titration can be adjusted. A Titronic® Universal Poiston Burette was used to accurately add the $Ca(OH)_2$ solution. A SCHOTT® in the Lab electrode with a colomel reference was used to determine the pHs. The pH meter was calibrated with standard pH 4.00 and 7.00 buffer before each titration. The stirrer was designed to fit the 120 mL polypropylene beaker so that all soil particles were well mixed throughout the titration.

Time Interval Study

Based on Schaller and Fischer (1984)'s report that between 80 and 100% of the added protons were taken up by the soils within a few seconds, interval times of 15, 30 and 45 minutes were chosen between additions of 0.022 M $Ca(OH)_2$. Since titration curves are nearly linear within the pH range of most agricultural surface soils (4.5 to 6.5), three aliquots of base were used to develop the slopes of the titration curves for each soil. Titrations were carried out in a 1:1 soil/water ratio with 30 mL of deionized water added to 30 g of soil. The soil pH was measured while being stirred. One mL of 0.022 M $Ca(OH)_2$ per addition was used for less buffered soil samples No.1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 14, which generally had lime requirements of less than 3360 kg ha^{-1}. Three mL of 0.022 M $Ca(OH)_2$ per addition was used for soil samples No.12, 13, 15, 16, 17 with generally higher lime requirements (more than 3360 kg ha^{-1}). For each titration, a linear regression equation was fitted to the relationship between base added (abscissa) and the soil pH (ordinate). The lime requirements were then calculated based on the slopes of the linear regression equations and the pH difference between initial pH (y intercept) and pH 6.5 as shown by equation (1)

$$\text{LR} = (6.5 - \text{intercept})/\text{slope} \qquad (1)$$

The lime requirements from the three interval times were compared to each other using Paired T-test analysis in SAS software.

Full Titration Curves

The buffer curves of each soil sample were established by titrating 30 grams of soil in water (1:1 soil/water ratio) with either one mL (generally low LR soils) or three mL (generally high LR soils) of 0.022 M $Ca(OH)_2$ per addition. Thirty minutes were chosen as the interval time between additions. The soil suspension was continuously stirred during the titration and the pH was measured while being stirred at the end of each interval time. For electrode safety and accuracy, the pH electrode was stored in the standard 7.00 buffer during each interval time. Each buffer curve was expressed on the basis of kg $CaCO_3$ ha^{-1} (pp2m × 1.12).

$Ca(OH)_2$ Incubation Study

Each soil sample was also incubated for 4 days with 0.022 M $Ca(OH)_2$ solution by adding 30 mL of deionized water to 30 g of each soil in a 120-mL polypropylene beaker. After thoroughly mixing for 30 minutes by stirring with a glass rod, the initial pH of each sample was measured while stirring at the same speed as that in the titration. Then three rates of 0.022 M $Ca(OH)_2$ solution were added to each soil equivalent to 0.5, 1 and 1.5 times the LR to pH 6.5 based on the full titration results. Three drops of chloroform were added to depress microbial activity. The samples were then covered with PARAFILM®

to reduce evaporation. A 10-mm slit was cut on the film for air exchange. A glass stir-rod was inserted through the opening for mixing the soil periodically. The soil samples were incubated for 4 days at room temperature (approximately 23 ^{o} C). The pH was measured at 24, 48, 72, and 96 hours while being stirred. Approximately half of the soil treatments were duplicated to determine the precision of results. The relationship of soil pHs versus $CaCO_3$ added was fitted for each soil by non-linear regression using Table Curve 2D, and the $Ca(OH)_2$ incubation lime requirement to pH 6.5 was calculated from this equation generated by Table Curve 2D.

Adams Evans Buffer Procedure

The Adams Evans buffer procedure was used to predict the lime requirement of each soil sample. Twenty mL of deionized water was added to 20 g of each soil. After sitting 40 minutes, the water pH was measured while stirred. Then, 20 mL of Adams Evans buffer was added to each soil suspension. The soil suspensions were shaken for 10 minutes at 200 oscillations min^{-1} and then allowed to stand for 0.5 h. The buffer pH was then measured while stirred. The AE procedure was duplicated for each soil and the mean value was used in the analysis.

Results and Discussion

Plots of soil pH as a function of $Ca(OH)_2$ added (expressed as equivalent amount of kg $CaCO_3$ ha^{-1}) were generally linear. These results were similar to those reported by Magdoff and Bartlett (1985), and Weaver (2002). The first three aliquots of base were arbitrarily selected to determine the slope of the titration line by using linear regression, as shown in Figure 1.2. The lime requirement to pH 6.5 can be calculated based on the slope and the intercept using equation (1).

The initial pH in some cases was lower than the “y” intercept from the linear regression line, so only the first three data points from dosing aliquots were used for the regression analysis, not including the initial pH point. The main objective of this research was to determine the equilibration time needed between two additions of $Ca(OH)_2$ to reach an equilibrium pH. Three interval times of 15, 30 and 45 minutes between additions were tested. The LRs calculated with equation (1) for the three levels of interval times are given in table 1.2. The mean values of LRs with 15, 30 and 45 minute interval time were 2093, 2591, and 2539 kg ha^{-1} respectively. PROC Paired T-test analysis in SAS showed the 45 minutes LR values and the 30 minutes LR values were not significantly different from each other with a P-value of 0.5958. However, there was a significant difference between the 15 minutes LR values and the 30 minutes LR values (P-value = 0.0062). The results indicate that 30 minutes interval time between two additions of base was adequate for $Ca(OH)_2$ to reach an equilibrium pH.

Using a few titration data points to establish the slope of the linear equation could make possible a rapid titration procedure for routine laboratory use. The linear equation could then be extrapolated to a target pH (6.5) to estimate the lime requirement.

To check the accuracy of this procedure, each soil sample was titrated to pH 7.0 with an interval time of 30 minutes between two additions. The entire titration curve of each soil sample was established by graphing $Ca(OH)_2$ added (expressed as the equivalent $CaCO_3$) as the abscissa and soil pH as the ordinate. The LRs directly read from their titration curves at pH 6.5 were compared with those predicted from the 3 addition method (table

1.3). Proc Paired T-test analysis in SAS showed the titration curve LR values and the LR values from the linear regression and equation (1) were not significantly different with P-value of 0.4729. The results indicate that the use of 3 data points and their linear regression on extrapolation to pH 6.5 worked well for the soils in this experiment.

The 4-day incubation with saturated $Ca(OH)_2$ solution is an accepted reference method to predict the LR of acid soils for comparison with the LRs using buffer methods (Follett and Follett, 1980; Alabi et al, 1986; McConell et al., 1990; Owusu-Bennoah et al., 1995). The 4-day $Ca(OH)_2$ equilibrium was selected as a standard to test the validity of titrations with 30 minute interval time between additions. For each soil titrated, the buffering curve was established again by adding three levels of $Ca(OH)_2$ solution equal to 0.5, 1 and 1.5 times the titration LR values to pH 6.5 with 30 minutes interval time. The change in soil pH of each soil sample treated with 1 LR level is shown in table 1.4. With perfect agreement between the two methods, the equilibrium pH values would be 6.5. For most soil samples, the soil pH continuously decreased from the first day to the third day, although the average pH was about the same on day 2 and 3. Soil pH then increased from the third day to the fourth day. The soil pHs went down in the first three days probably because the base-exchange reactions reached their equilibrium gradually in two-three days. The results are consistent with observations by Dunn (1943), who also found that equilibrium was reached in 3 days of incubating acid soils with standard $Ca(OH)_2$ solution. The soil pH went up from the third day to the fourth day for most of the soil samples, possibly because of the reduction of Fe and Mn minerals (2) and ammonification reactions (3), since the soil samples were kept in reduced conditions.

$$Mn(OH)_2 + 2H^+ \rightarrow Mn^{2+} + 2H_2O \qquad (2)$$

$R\text{-}NH_2 + H^+ \rightarrow NH_4^+$ (3)

Soil pH values from the incubation on day 3 were compared with the target pH of 6.5 (table 4). Soil sample No.13 had the lowest soil pH value of 6.01 and sample No.9 had the highest value of 6.63. The average pH value of the 17 soil samples was 6.36. Based on this result, it appears that the direct titration with 30 minute interval time between additions neutralized a majority of the total soil acidity. A relationship between the predicted LR values from the first 3 aliquots of $Ca(OH)_2$ with interval time of 30 minutes (Y, kg ha^{-1}) and the 3-day incubation LR values (X, kg ha^{-1}) was established to generate a liming factor for the direct titration procedure with 30 minutes interval time between two additions (figure 1.3). The linear regression equation was generated under 99.9% confidence interval: $Y = 0.8013\ X$, $r^2 = 0.9637$***, which indicates that the titration with 30 minutes interval time predicted 80% of the lime requirement measured by the 3-day equilibration. The slow release of H^+ from the soil complex was possibly responsible for the missing 20% of the acidity, which occurred for 2-3 days after $Ca(OH)_2$ was added.

The 3-day $Ca(OH)_2$ incubation was also used as the standard for comparison with the LR values from the Adams Evans procedure (AE). The relationship between the AE LR values and the LRs values from $Ca(OH)_2$ equilibrium for all 17 soils is shown in figure 1.4. This regression resulted in the linear relationship:

$$LR\ (AE) = 0.6122LR\ (Ca(OH)_2) + 979,\ r^2 = 0.9334^{**}.$$

Notice the “y” intercept of the relationship was quite high with a value of 979, which indicated that the AE method would overestimate the LRs for soils with low LRs. To make this clear, the seven soils with low LRs (< 1500 kg ha^{-1}) was selected to redo the regression. The regression generated for the seven soils with low LRs as shown in figure 1.4 was:

$$LR\ (AE) = 1.7906LR\ (Ca(OH)_2),\ r^2 = 0.8279^{***}.$$

In this case, the slope of the relationship had increased to 1.79, indicating again that the AE buffer gave values that were considerably larger than those for the $Ca(OH)_2$ incubation. The relationship for the remaining soils with high and medium LR also shown in figure 1.4 was:

$$LR\ (AE) = 0.5985LR\ (Ca(OH)_2) + 1061,\ r^2 = 0.9337^{**}.$$

In this case the y intercept was still quite large at 1061 kg ha^{-1}. Because of this, the soils were grouped further by medium (between 1500 and 4500 kg ha^{-1}) and high LR (> 4500 kg ha^{-1}) levels. When only the six soils with the medium LRs were kept in the analysis, the linear regression resulted in the relationship shown in figure 1.5:

$$LR\ (AE) = 1.0420LR\ (Ca(OH)_2),\ r^2 = 0.9309^{***}.$$

In this case, the slope of the relationship was quite close to one, indicating that the AE buffer gave values that were consistent with those for the $Ca(OH)_2$ incubation. For the four soils with high LRs, the linear regression equation as shown in figure 1.5 was:

$$LR\ (AE) = 0.6841LR\ (Ca(OH)_2),\ r^2 = 0.9941^{***}.$$

This equation indicated that the AE method estimated, on average, 68% of those by the 3-day $Ca(OH)_2$ incubation.

Conclusions

Plots of soil pH as a function of $Ca(OH)_2$ added (expressed as equivalent amount of kg $CaCO_3$ ha^{-1}) were generally linear. A 30 minute interval time between additions of

$Ca(OH)_2$ was adequate for the added base to react with the soil acids. The first 3-points predicted, on average, 80% of the soil acidity measured by the 3-day $Ca(OH)_2$ incubation, which was considered the standard method for determining the lime requirement of acid soils. The AE procedure gave a higher estimate than $Ca(OH)_2$ incubation for those soils with a low LR, but for soils with LR > 4500 kg ha^{-1}, AE gave lower LRs, when compared with the 3-day $Ca(OH)_2$ incubation.

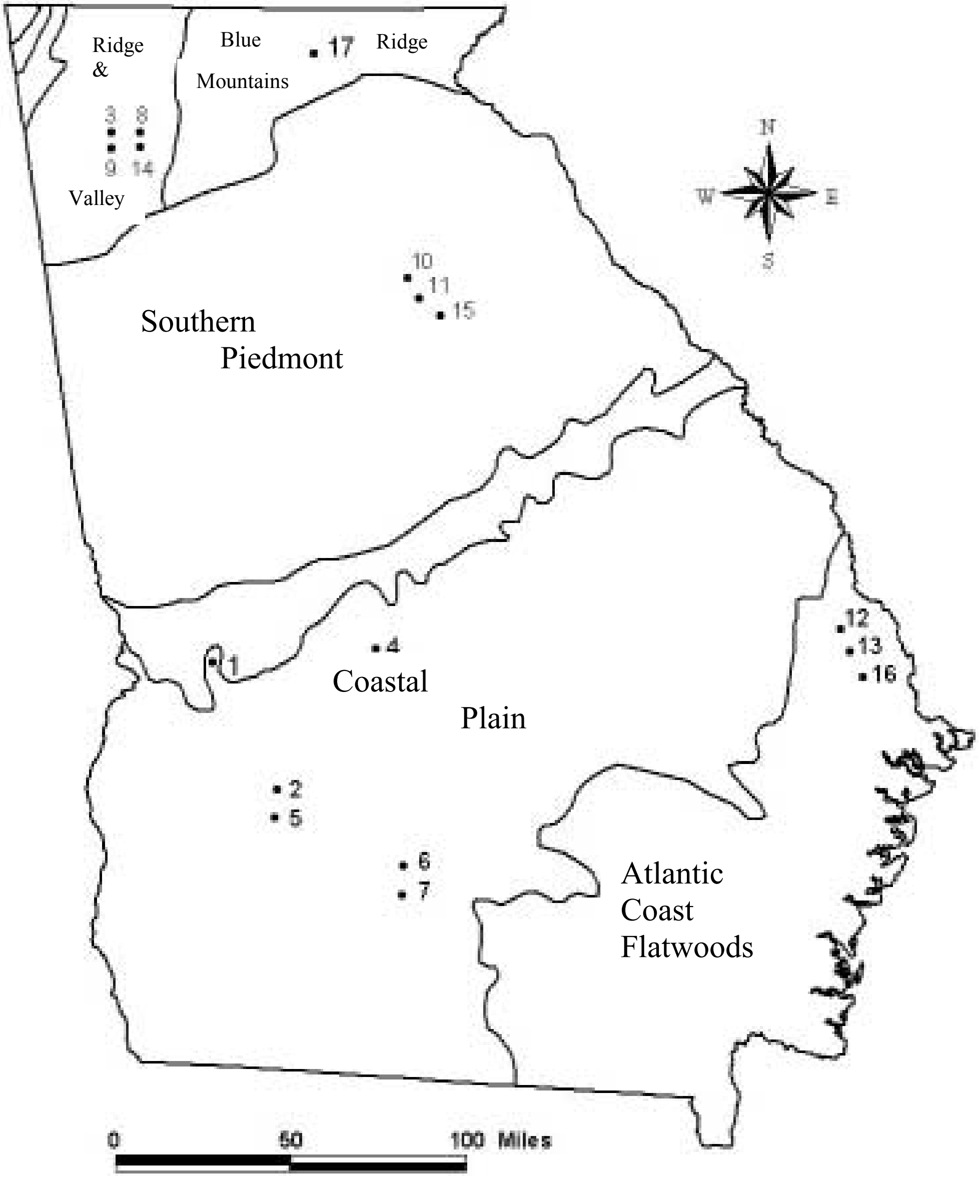


Fig. 1.1 Location of Georgia soils selected for lime requirement study.

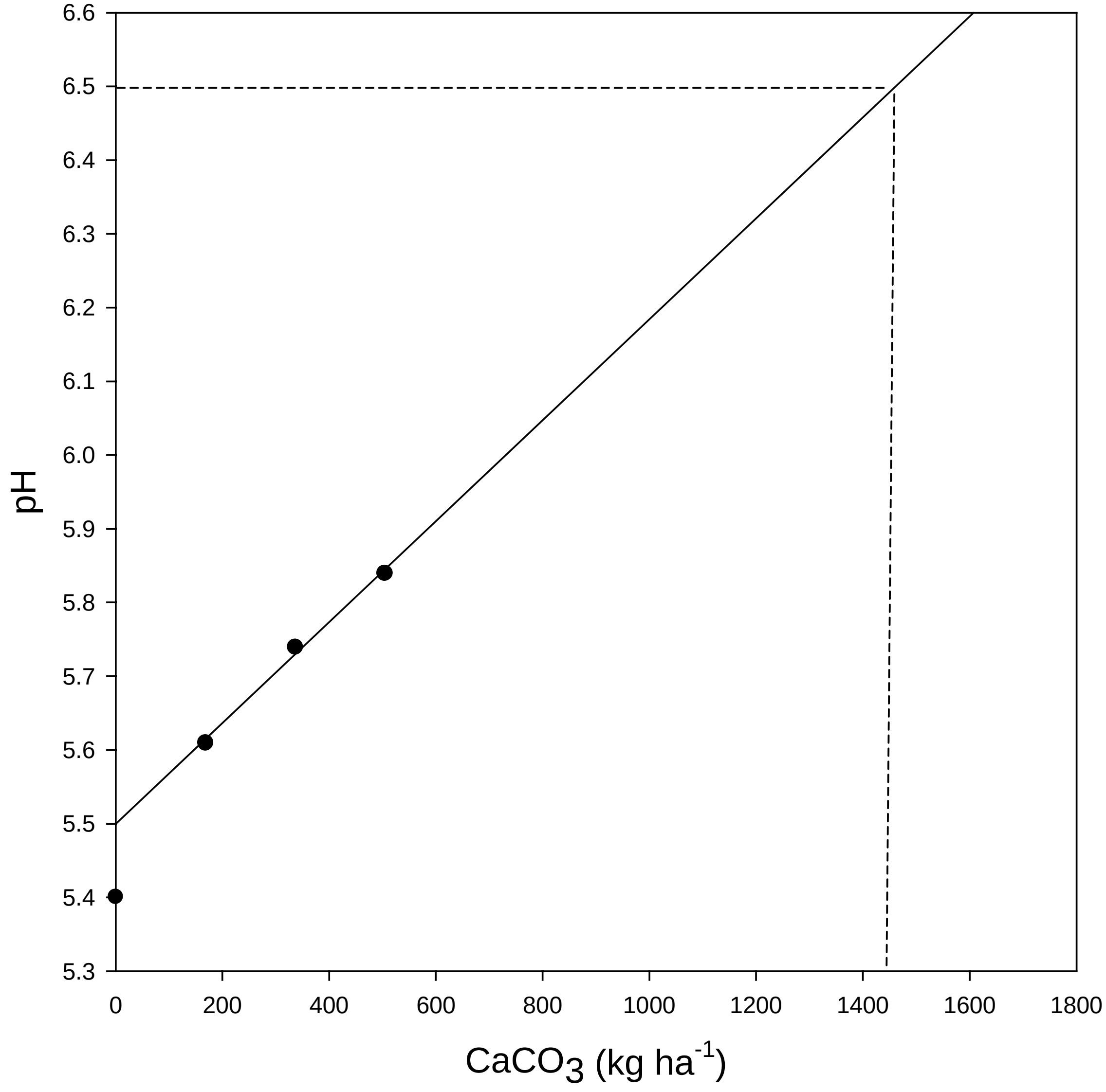


Fig. 1.2 Example of LR Prediction from 3 aliquots of $Ca(OH)_2$ with an interval time of 30 minutes between two additions, for soil No. 9.

Table 1.1 Selected physical and chemical properties of acid soils used.

Soil no.	MLRA	Initial soil pH_w(1:1)	Sand	Clay	Silt	Total N	Total C	C/N
			--------------	%	-------------	---- mg kg^{-1}----		
1	CP	5.4	64.8	20.4	14.8	501	5199	10.4
2	CP	4.95	69	21.2	9.8	490	5087	10.4
3	RV	5.8	39	20.1	40.9	1206	13308	11.0
4	CP	4.29	68.6	8	23.4	789	9244	11.7
5	CP	5.41	82.7	5.5	11.9	459	8985	19.6
6	CP	5.24	86	2.3	11.7	359	6371	17.7
7	CP	4.09	88.7	4.4	6.9	190	4215	22.2
8	RV	5.78	13.2	43.5	43.2	1311	11443	8.7
9	RV	5.47	9.4	33.5	57.1	1053	9193	8.7
10	SP	4.68	70.5	8.9	20.6	1135	16698	14.7
11	SP	4.32	32.8	50.7	16.4	1097	12497	11.4
12	ACF	4.02	88.3	2.1	9.5	472	10479	22.2
13	ACF	4.42	33.2	22.1	44.7	1513	31805	21.0
14	RV	4.95	8.2	43.2	48.6	1274	13923	10.9
15	SP	4.2	64.8	9.3	25.9	810	14327	17.7
16	ACF	4.41	87.9	2.5	9.7	724	20448	28.2
17	BRM	4.42	31.2	10.7	58.1	2072	26959	13.0

MLRA = Major Land Resource Area
CP = Coastal Plain
RV = Ridge & Valley
SP = Southern Piedmont
ACF = Atlantic Coast Flatwoods
BRM = Blue Ridge Mountain

Table 1.2 Comparison of the predicted titration LR values (kg ha^{-1}) among three levels of interval time between two additions of base.

	Interval time		
Soil no.	15 min	30 min	45 min
	----------------- LR (kg ha^{-1}) ------------------		
1	370	426	526
2	504	689	784
3	717	1120	840
4	1366	1669	1736
5	258	420	470
6	558	529	605
7	848	986	1068
8	1019	1176	974
9	1154	1434	1445
10	1075	1523	1159
11	2688	3696	3718
12	3801	4362	4682
13	8820	11583	10528
14	3734	3957	3164
15	2332	2520	3024
16	2755	3611	3718
17	3578	4340	4715
Average	2093	2591	2539

min ----- minutes; LR ----- lime requirement

Table 1.3 Comparison of the LR values (kg ha^{-1}) between titration curve and prediction of its first 3 aliquots of base.

Soil no.	LR from TC	LR predicted from first 3 aliquots
	----------------- LR (kg ha^{-1})	------------------
1	403	403
2	750	706
3	1008	993
4	2100	1867
5	426	437
6	571	552
7	1288	1042
8	1344	1210
9	1764	2251
10	1792	1624
11	3987	4906
12	4704	4239
13	11536	11648
14	3270	3338
15	3024	2654
16	4435	4032
17	5298	4715
Average	2806	2742

LR----- lime requirement; TC----- titration curve

Table 1.4 The soil pH change during the 4-day incubation with standard $Ca(OH)_2$ solution.

	Incubation time			
Soil no.	24 h	48 h	72 h	96 h
	------------------------------ pH	--------------------------------		
1	6.49	6.46	6.49	6.55
2	6.48	6.42	6.46	6.58
3	6.5	6.52	6.58	6.65
4	6.42	6.32	6.32	6.35
5	6.55	6.52	6.57	6.77
6	6.3	6.25	6.34	6.45
7	6.36	6.25	6.22	6.19
8	6.44	6.44	6.59	6.72
9	6.8	6.66	6.63	6.78
10	6.32	6.22	6.21	6.69
11	6.52	6.25	6.19	6.21
12	6.6	6.42	6.32	6.3
13	6.42	6.11	6.01	5.99
14	6.7	6.42	6.44	6.45
15	6.45	6.31	6.33	6.39
16	6.22	6.11	6.1	6.1
17	6.49	6.33	6.38	6.42
Average	6.47	6.35	6.36	6.45

h ----- hour

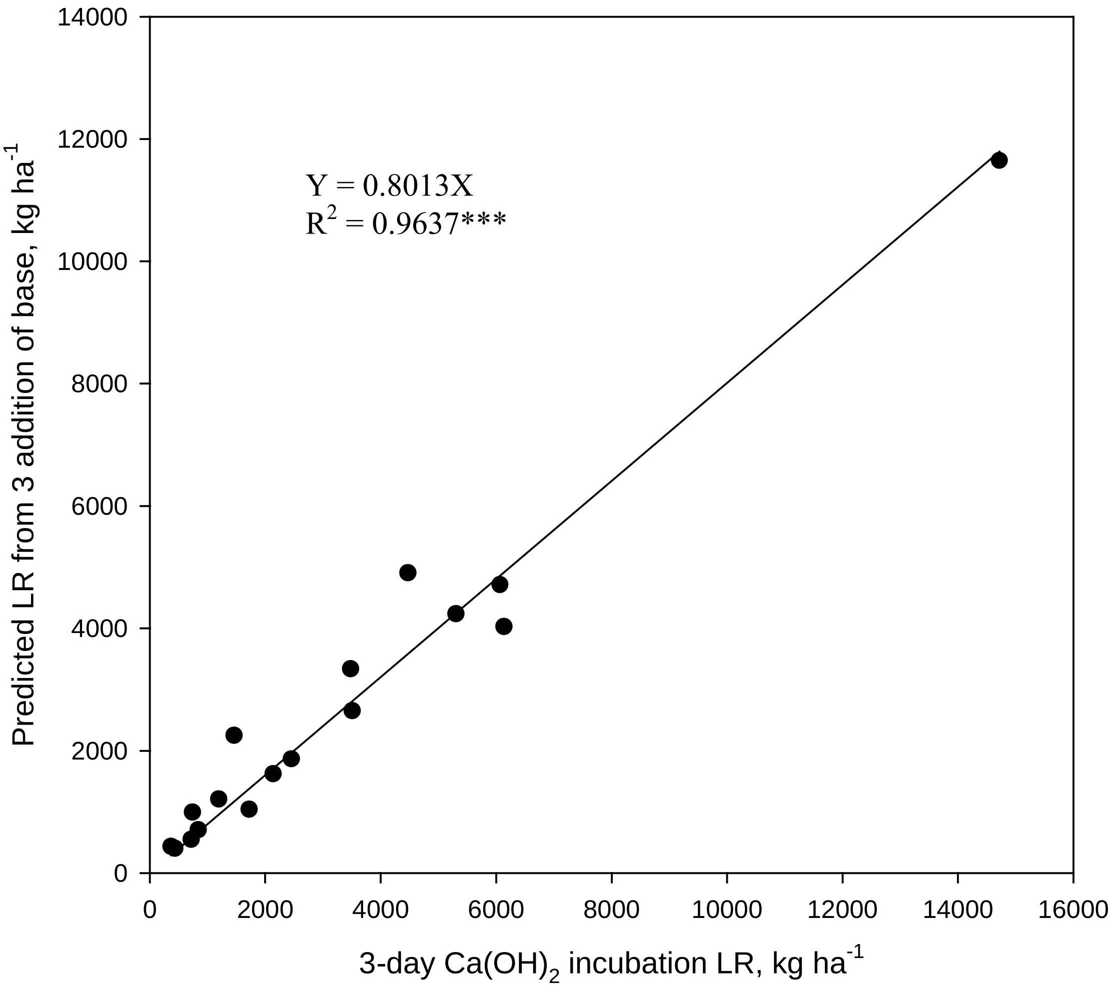


Fig. 1.3 Relationship between $Ca(OH)_2$ incubation LR values and predicted LR values from the first 3 aliquots of $Ca(OH)_2$.

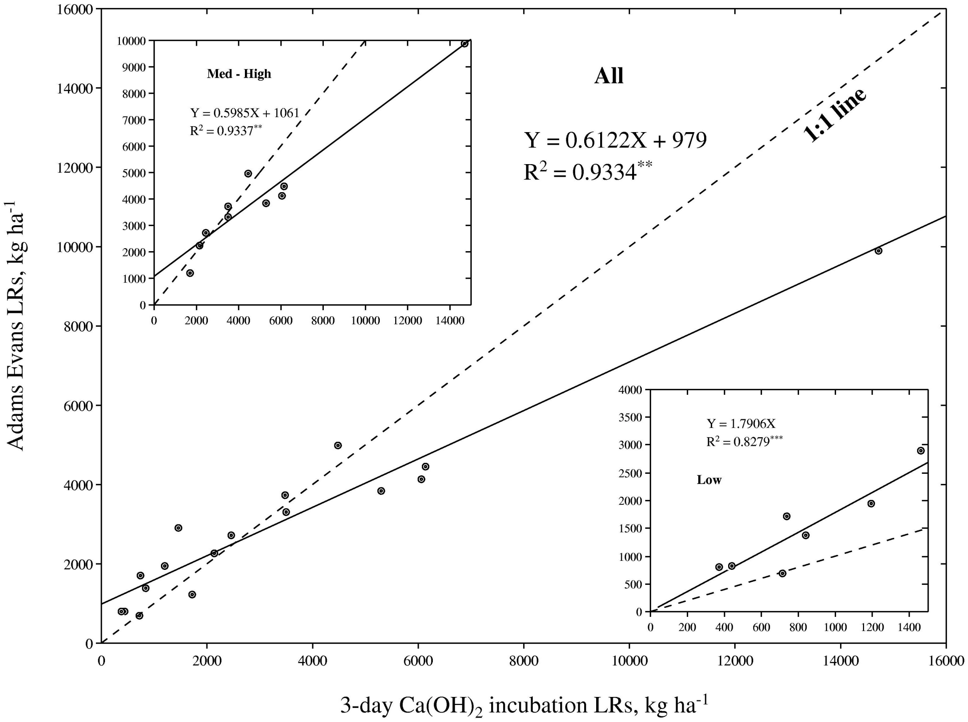


Fig. 1.4 Comparison of the lime requirements between the Adams Evans procedure and the 3-day Ca(OH)$_2$ incubations (M-H and L).

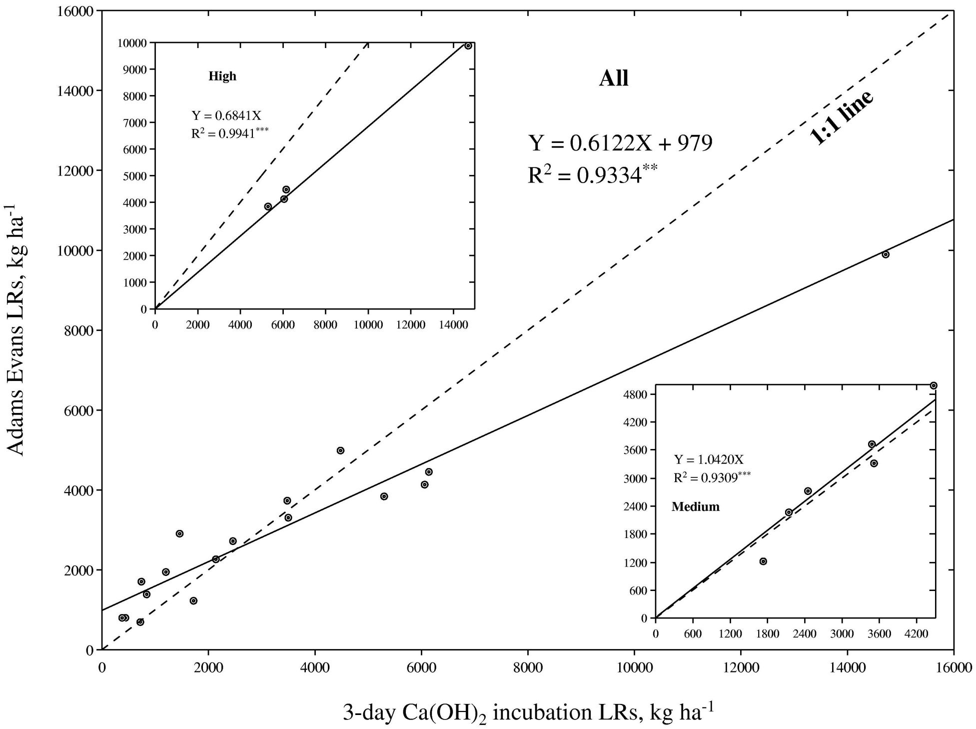


Fig. 1.5 Comparison of the lime requirements between the Adams Evans procedure and the 3-day $Ca(OH)_2$ incubations (M and H).

References

Adams, F., and C.E. Evans. 1962. A rapid method for measuring the lime requirement of Red-Yellow Podzolic soils. Soil Sci. Am. Proc. 26:255-357.

Alabi, K.E., R.C. Sorensen, D. Knudsen, and G.W. Rehm. 1986. Comparison of several lime requirement methods on coarse textured soils of Northeastern Nebraska. Soil Sci. Soc. Am. J. 50:937-941.

Dunn, L.E. 1943. Lime requirement determination of soils by means of titration curves. Soil Sci. 56:341-351.

Follett, R.H, and R.F, Follett. 1980. Strengths and weaknesses of soil testing in determining lime requirements for soils. p 40-51. In Proc. Of the Natl. Conf. on Agric. Limestone 16-18 Oct. 1980

Magdoff, F.R. and Bartlett, R.J. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. Proc. 49:145-148.

McConnell, J.S., Gilmour, J.T., Baser, R.E., and Frizzell, B.S. 1990. Lime Requirement of acid soils of Arkansas. Arkansas Experiment Station Special Report 150.

Owusu-Bennoah, E., Acquaye, D. K., Mahamah, T. 1995. Comparative study of selected lime requirement methods for some acid Ghanaian soils. Commun. Soil Sci. Plant Anal., 26(7&8):937-950.

SAS Institute. 1985. SAS user’s guide: Statistics. Version 6 ed. SAS Institute, Inc., Carg, NC.

Schaller, G. and Fischer, W.R. 1984. Kurzgristige pH-pufferung von Böden. A. Pflanzenernaehr.Bodenk. 148:471-480.

Tran, T. S., and W. van Lierop. 1981. Evaluation and improvement of buffer-pH lime requirement methods. Soil Sci. 131:178-188.

Weaver, A.R. 2002. Characterizing soil acidity in coastal plain soils. Ph.D Dissertation. University of Georgia.

CHAPTER 2

INTERPRETATION OF TITRATION CURVES

Abstract

The three point prediction procedure in the direct titration described in chapter 1 will probably not be accepted for routine laboratory use because it is still too time consuming compared with buffer methods. An alternative approach is to evaluate the accuracy of a simplified titration procedure based on an initial pH reading and a second reading following the addition of one dose of $Ca(OH)_2$. Since this method relies heavily on the accuracy of the initial pH measurement and since the soil salt content has a great effect on the measured pH value, it might be appropriate to make the pH measurements in 0.01 M $CaCl_{2.}$

Seventeen soils were titrated with $Ca(OH)_2$ in both water and 0.01 M $CaCl_2$ with a 30 minute interval time between additions. The 3-day incubation with $Ca(OH)_2$, which is a widely accepted reference method, was also carried out to determine the lime requirement. The data indicated that there was no significant difference between slopes regressed from all data points to pH 6.5 in the 0.01 M $CaCl_2$ titration and the slopes regressed from all data points except the first point in the water titration. The slopes from the first two data points of the titration in the 0.01 M $CaCl_2$ were not significantly different from the slopes regressed by all data points to pH 6.5. However, the slopes from the first two data points of the titration in water were frequently in error for estimation of the slopes regressed by all data points to pH 6.5. Therefore, the first two data points in the 0.01 M $CaCl_2$ titration were considered reliable values for estimating the slope. Both the initial pH in water and in 0.01 M $CaCl_2$ were used to calculate the lime requirement with the two point slope in 0.01 M $CaCl_2$. The results showed that the lime requirement prediction calculated from the initial pH in 0.01 M $CaCl_2$ and the two point slope in 0.01 M $CaCl_2$ gave better estimation of the lime requirement than the initial water pH when compared with 3-day $Ca(OH)_2$ incubation method.

Key words: Titration, Lime requirement, Soil acidity, $CaCl_2$.

Introduction

In the first chapter, we concluded that a 30 minute interval time between additions of $Ca(OH)_2$ was adequate to neutralize most of the acidity in the 17 soils. We also found that the titration curves gave a linear relationship between pH and lime added from pH 4.5 to 6.5 , as noted previously by Magdoff and Bartlett (1985) and Weaver (2002). Based on those results, a direct titration procedure was proposed in which the first three doses of $Ca(OH)_2$ are used to establish the slope of the linear equation. The linear equation is then extrapolated to the target pH (say 6 or 6.5) to estimate the lime requirement. The 3-day incubation with $Ca(OH)_2$ (Dunn,1943), which is a widely accepted reference method (Follett and Follett, 1980; Alabi et al, 1986; McConell et al., 1990; Owusu-Bennoah et al., 1995), showed that the three point prediction procedure estimated about 80 percent of the lime requirement. However, this three point prediction procedure will probably not be accepted for routine laboratory use because it is too time consuming, requiring three additions of $Ca(OH)_2$ and the measurement of four pH values. Buffer methods for determination of the lime requirement are less labor intensive and require less time.

If the slope of the titration curve could be determined with sufficient accuracy from two pH readings and one addition of $Ca(OH)_2$, then it might be possible to adapt such a procedure to routine determination of the lime requirement in the soil testing laboratory. This would require that the slope be established from the initial pH measurement and the pH following one addition of $Ca(OH)_2$. It is obvious that this method relies heavily on the accuracy of the initial pH measurement. Since the soil salt content has a great effect on pH measurement (Schofield and Taylor, 1955; Ryti, 1965), it might be appropriate to make the pH measurements in 0.01 M $CaCl_2$. The objective of this study was to evaluate the accuracy of a simple titration procedure based on an initial pH reading and a second reading following the addition of one dose of $Ca(OH)_2$.

Materials and Methods

Seventeen soil samples with a wide range of clay and soil organic carbon (C) contents were collected from five of the major land resource areas of Georgia. The soils were oven-dried at a temperature of 35 °C, crushed, then sieved (2-mm) to remove small rocks and non-decayed crop residue, which consisted of less than 1% of the soil by weight. Then the soils were stored in sealed Ziploc® bags until analyzed. A subsample of each soil was analyzed for C and N with a Leco CNS 2000 Analyzer. Four of the soil samples contained more than 30% clay and five had clay contents in the range from 10 to 20%. Eight contained less than 10% clay. Three of the soil samples contained more than 2.0%

total C and eight soil samples contained in the range from 1.0 to 2.0% total C. The others had less than 1.0% total C (Table 2.1).

Saturated $Ca(OH)_2$ solution, 0.022 M, was used as the standard base to titrate the selected acid soils. It was made by adding 50 grams of reagent grade $Ca(OH)_2$ powder into 10 L of distilled water in a Nalgene HDPE jerrican container, mixing well by stirring with a glass rod, then allowing it to settle for 4 days. A rubber stopper with an ascarite trap prevented carbon dioxide from reacting with the $Ca(OH)_2$.

A Multi-task® version 2.0 digital titrator by Visco Alpha was used to titrate the soil samples. Through programming the software associated with the titrator, the number of aliquots, the interval time between two aliquots, and the stirring speed during titration can be adjusted. A Titronic® Universal Poiston Burette was used to accurately add $Ca(OH)_2$. A SCHOTT® in the Lab electrode was used to determine the pHs. The pH meter was calibrated with standard pH 4.00 and 7.00 before each titration. The stirrer was designed to fit the 120-cc polypropylene beaker so that all soil particles were well mixed throughout the titration.

The buffer curves of each soil sample were established by titrating 30 grams of soil suspension in deionized water (1:1 soil/water ratio) with either 1 mL (generally low LR soils) or 3 mL (generally high LR soils) of 0.022 M $Ca(OH)_2$ per addition. The soil suspension was continuously stirred during the titration and the pH was measured while being stirred at the end of each interval time, which for this study was 30 minutes. In order to reduce abrasion to the grass electrode and to improve the accuracy, the pH electrode was stored in the standard 7.00 buffer during the interval time. Based on the amount of $Ca(OH)_2$ used, the equivalent amount of calcium carbonate ($CaCO_3$) was calculated to develop each buffer curve. The buffer curve of each soil sample in 0.01 M $CaCl_2$ solution was also established per the method described above.

Each soil sample was also incubated for 4 days with 0.022 M $Ca(OH)_2$ solution by adding 30 mL of distilled water to 30 gram of each soil in a 120-mL polypropylene beaker. After thoroughly mixing for 30 minutes by stirring with a glass rod, the initial pH of each sample was measured while stirring at the same speed as that in the titration. Then four rates of 0.022 M $Ca(OH)_2$ solution were added to each soil equivalent to 0, 0.5, 1 and 1.5 times the LR to pH 6.5 based on the full titration results. Three drops of chloroform were added to depress microbial activity. The samples were then covered with PARAFILM® to reduce evaporation. A 10-mm slit was cut on the film for air exchange. A glass stir-rod was inserted through the opening for mixing the soil periodically. The soil samples were incubated for 4 days at room temperature (approximately 23 ^{o}C). The pH was measured at 24, 48, 72, and 96 hours while being stirred. Approximately half of the soil treatments were duplicated to determine the precision of results. The relationship of soil pHs VS $CaCO_3$ added was fitted for each soil by non-linear regression using Table Curve 2D. And the $Ca(OH)_2$ incubation lime requirement to pH 6.5 was calculated from this equation.

Results and Discussion

The titration curves of 5 soils in both water and 0.01 M $CaCl_2$ are shown in figure 2.1. A titration curve was randomly selected from each of the five major land resources areas in Georgia. Soil No.3 came from the Ridge and Valley, No.5 from the Coastal Plain, No.10 from the Atlanta Piedmont, No.16 from the Atlantic Coast Flatwoods, and No.17

from the Blue Ridge Mountains. The titration curves of the other 12 soils are shown in appendix figure 1. Soil pHs in 0.01 M $CaCl_2$ were depressed at all levels of $Ca(OH)_2$ addition in all soils. The initial soil pH in 0.01 M $CaCl_2$ was depressed from 0.17 to 0.81 pH units when compared to the corresponding pH in water.

In the titrations carried out in water, the initial pH before $Ca(OH)_2$ addition was lower than the y intercept in some soils. In these cases, the use of two points (0 and 3 mL) to establish the slopes would result in high slope values ($\Delta pH/\Delta CaCO_3$) and when the linear equation is extrapolated to the target pH, it would therefore underestimate the lime requirement. In comparison, the initial pH in 0.01 M $CaCl_2$ was more nearly equal to the y intercept (figure 2.1 and appendix figure 1). A comparison of slopes from the fitted linear regression for water titrations and 0.01 M $CaCl_2$ titrations is shown in figure 2.2. The water titration slopes were regressed using all data points to pH 6.5 without the initial pH point because, as noted above, it was sometimes below the y intercept. The 0.01 $CaCl_2$ titration slopes were regressed by using all data points to pH 6.5. The fitted linear equation of slope values by the two titrations was:

$$Y = 0.9806X,\ r^2 = 0.9434.$$

The Paired T Test using STATISTIX 7.0 was also carried out to determine differences in the two set of slopes. The alternative hypothesis was that they were not equal and the resulting P value was 0.2126, which meant that they were statistically equivalent to each other.

To establish the accuracy of determining the slope from a two point titration curve, we first compared the slopes determined from two points (0 and 3 mL) in water with those obtained by regressing all data points (except 0) to pH 6.5 (figure 2.3). The fitted linear equation was:

$$Y = 1.3911X,\ r^2 = 0.8550.$$

The equation indicated that the straight line determined from two data points (0 and 3 mL $Ca(OH)_2$) gave slopes on average of 1.39 times those from using multiple data points for the regression. A similar comparison was made for those titrations done in 0.01 M $CaCl_2$. When slopes determined from regression of all data points to pH 6.5 were compared with those determined from only two points (0 and 3 mL), the agreement was better, as shown in figure 2.4. The comparison of slope values of the 17 soils gave the following result:

$$Y = 1.1093X,\ r^2 = 0.8744.$$

In this case, the slopes using two points from the titration in 0.01 M $CaCl_2$ were 11% larger on average than those from regression of all data points to pH 6.5. This close agreement was due primarily to the fact that the pH at 0 addition in 0.01 M $CaCl_2$ differed little from the y intercept from the regression analysis.

As noted above, the slopes determined from the water titration and the slopes determined from the 0.01 M $CaCl_2$ titration were not significantly different when all data points were used except 0 for those in water. We also found from figure 2.4 that the two point (0 and 3 mL) prediction of slopes in 0.01 M $CaCl_2$ titration were close to those regressed using all data points to pH 6.5. Since we showed earlier that slopes from 2 data points in water were frequently in error, it will be necessary to do the two point titrations in 0.01 M $CaCl_2$ to assure accuracy. It is less clear, however, what initial pH should be used for the LR calculations. Either water pH or pH in 0.01 M $CaCl_2$ could be used. In order to determine the best choice, we calculated the LR using both, but using the 2 point slope determined in 0.01 M $CaCl_2$. We compared these LRs to the LRs considered to be the standard, ie, the LRs from the 3-day incubation with $Ca(OH)_2$. The first comparison using water pH is shown in figure 2.5. The fitted linear relationship was:

$$Y = 0.6879X,\ r^2 = 0.8983.$$

The comparison between the LRs prediction by using the initial pH in 0.01 M $CaCl_2$ and the LRs from 3-day $Ca(OH)_2$ incubation is shown in figure 2.6. The fitted linear equation was:

$$Y = 0.8792X,\ r^2 = 0.9317.$$

If the three soils from Atlantic Coast Flatwoods were not included in the regression, the fitted linear relationship was:

$$Y = 1.0380X,\ r^2 = 0.9272.$$

It is obvious that two data point predictions from the initial pH in 0.01 M $CaCl_2$ gave better estimates of the lime requirements than those from the initial pH in water.

Conclusions

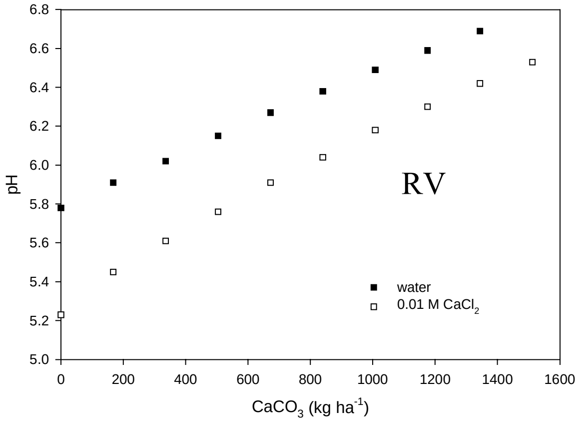
The slopes determined from the water titrations and the slopes determined from the 0.01 M $CaCl_2$ titrations were not significantly different when all data points were used except 0 for those in water. The two data point slope from the titration in 0.01 M $CaCl_2$ gave a better estimate of slopes determined from all data points than the two data point slope from titrations in water. Both water pH and pH in the 0.01 M $CaCl_2$ were used to calculate the LRs with the two point slope in the 0.01 M $CaCl_2$ titration. When both of the LRs were compared to the LRs considered to be the standard, ie, the 3-day $Ca(OH)_2$ incubation method, the LRs calculated from the pH in the 0.01 M $CaCl_2$ had a better relationship with a linear equation of $Y = 0.8792X$, $r^2 = 0.9317$. Therefore, the simple titration procedure in the 0.01 M $CaCl_2$ was recommended for the routine laboratory use based on an initial pH reading and second reading following the addition of one dose of $Ca(OH)_2$.

Table 2.1 Selected physical and chemical properties of acid soils used.

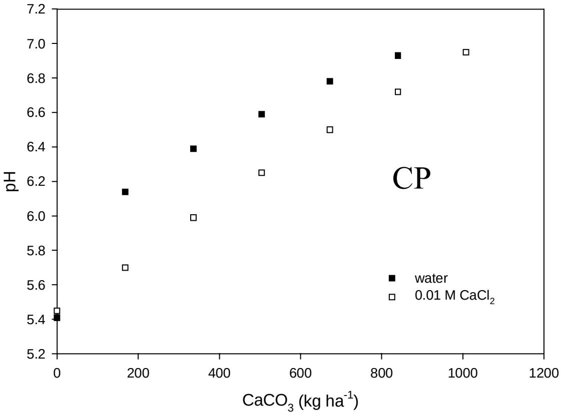
Soil no.	MLRA	Initial soil pH_w(1:1)	Sand	Clay	Silt	Total N	Total C	C/N
			-------------- %	-------------		---- mg kg^{-1}----		
1	CP	5.4	64.8	20.4	14.8	501	5199	10.4
2	CP	4.95	69	21.2	9.8	490	5087	10.4
3	RV	5.8	39	20.1	40.9	1206	13308	11.0
4	CP	4.29	68.6	8	23.4	789	9244	11.7
5	CP	5.41	82.7	5.5	11.9	459	8985	19.6
6	CP	5.24	86	2.3	11.7	359	6371	17.7
7	CP	4.09	88.7	4.4	6.9	190	4215	22.2
8	RV	5.78	13.2	43.5	43.2	1311	11443	8.7
9	RV	5.47	9.4	33.5	57.1	1053	9193	8.7
10	SP	4.68	70.5	8.9	20.6	1135	16698	14.7
11	SP	4.32	32.8	50.7	16.4	1097	12497	11.4
12	ACF	4.02	88.3	2.1	9.5	472	10479	22.2
13	ACF	4.42	33.2	22.1	44.7	1513	31805	21.0
14	RV	4.95	8.2	43.2	48.6	1274	13923	10.9
15	SP	4.2	64.8	9.3	25.9	810	14327	17.7
16	ACF	4.41	87.9	2.5	9.7	724	20448	28.2
17	BRM	4.42	31.2	10.7	58.1	2072	26959	13.0

MLRA = Major Land Resource Area
CP = Coastal Plain
RV = Ridge & Valley
SP = Southern Piedmont
ACF = Atlantic Coast Flatwoods
BRM = Blue Ridge Mountain

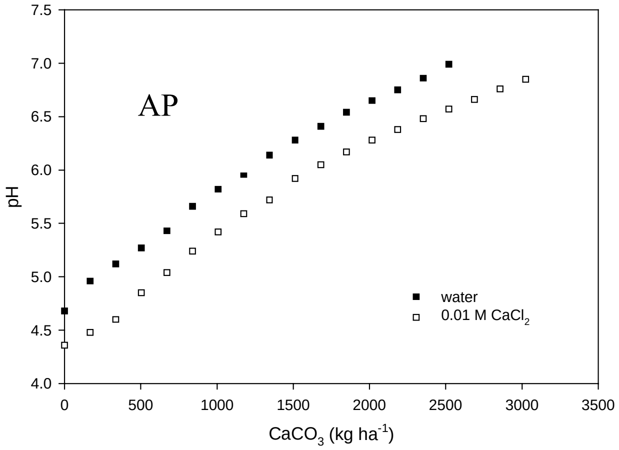
Titration curves for soil No.3 in both water and 0.01 M $CaCl_2$



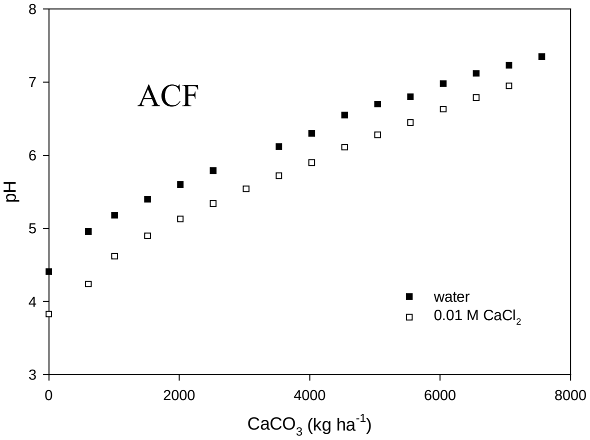
Titration curves for soil No.5 in both water and 0.01 M $CaCl_2$



Titration curves for soil No.10 in both water and 0.01 M $CaCl_2$



Titraiton curves for soil No.16 in both water and 0.01 M $CaCl_2$



Titration curves for soil No.17 in both water and 0.01 M $CaCl_2$

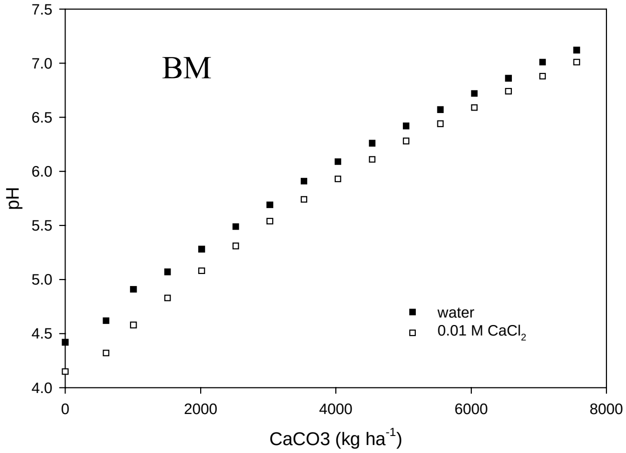


Fig. 2.1 Titration curves for 5 soils in water and in 0.01 M $CaCl_2$.

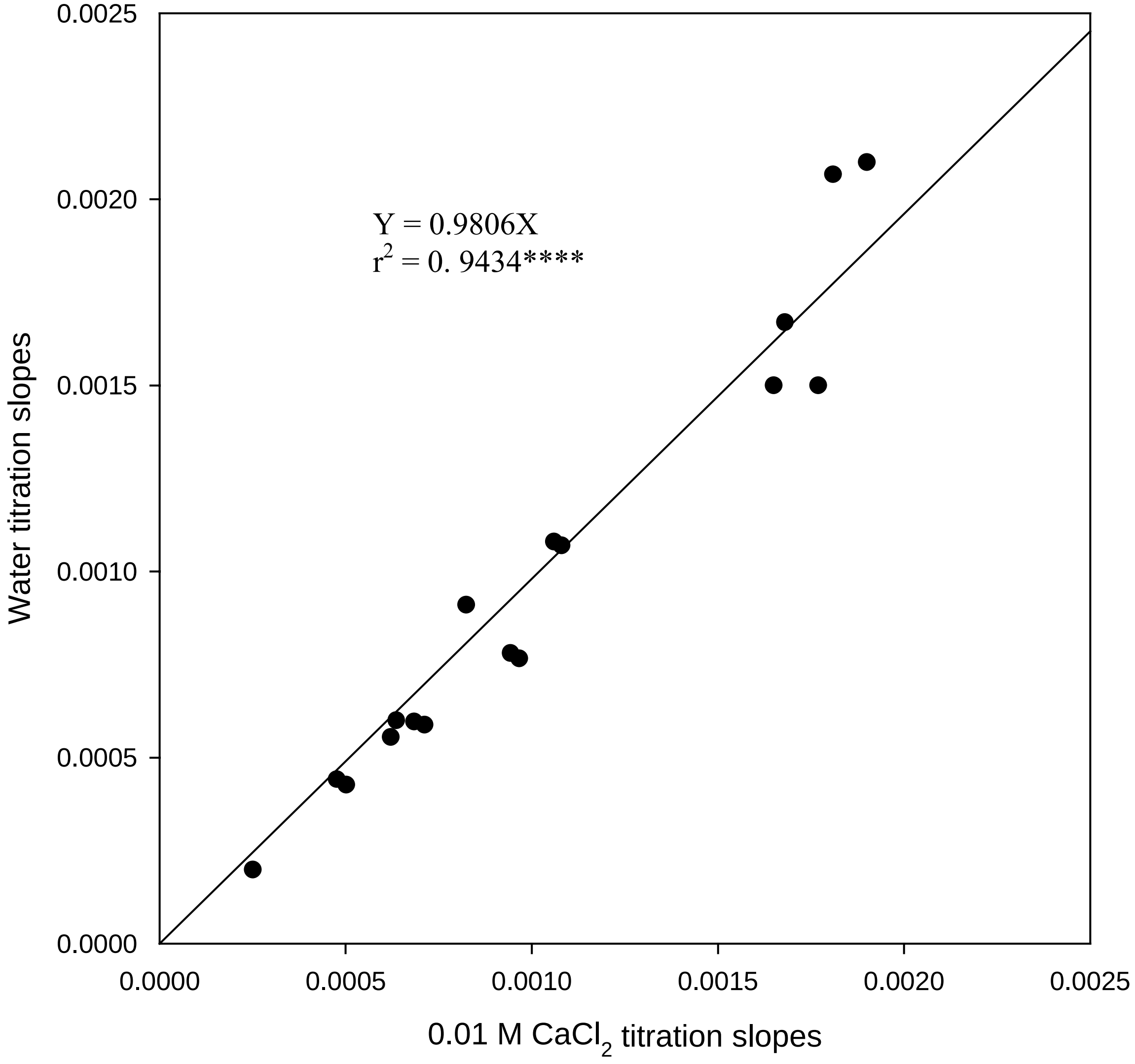


Fig. 2.2 Slope comparison between water titration and 0.01 M $CaCl_2$ titration.

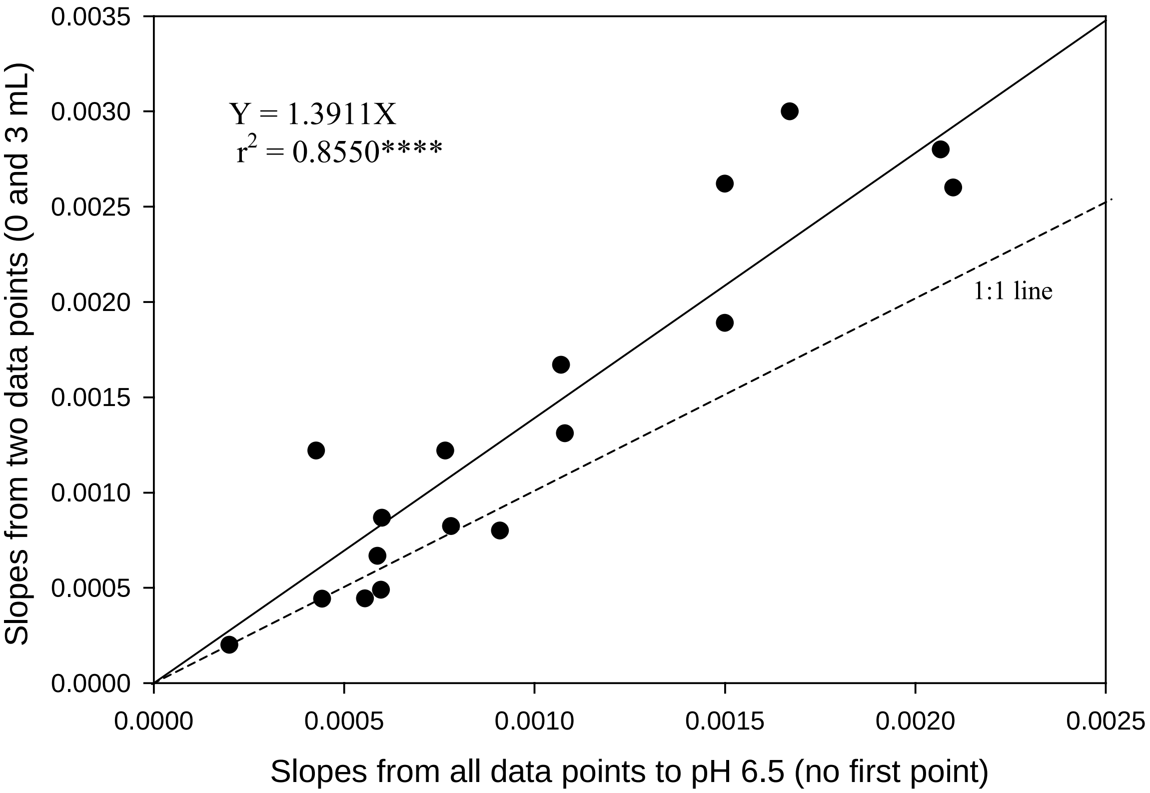


Fig. 2.3 Slope comparison between data points to pH 6.5 (no first point) and two points (0 and 3 mL) in water titration.

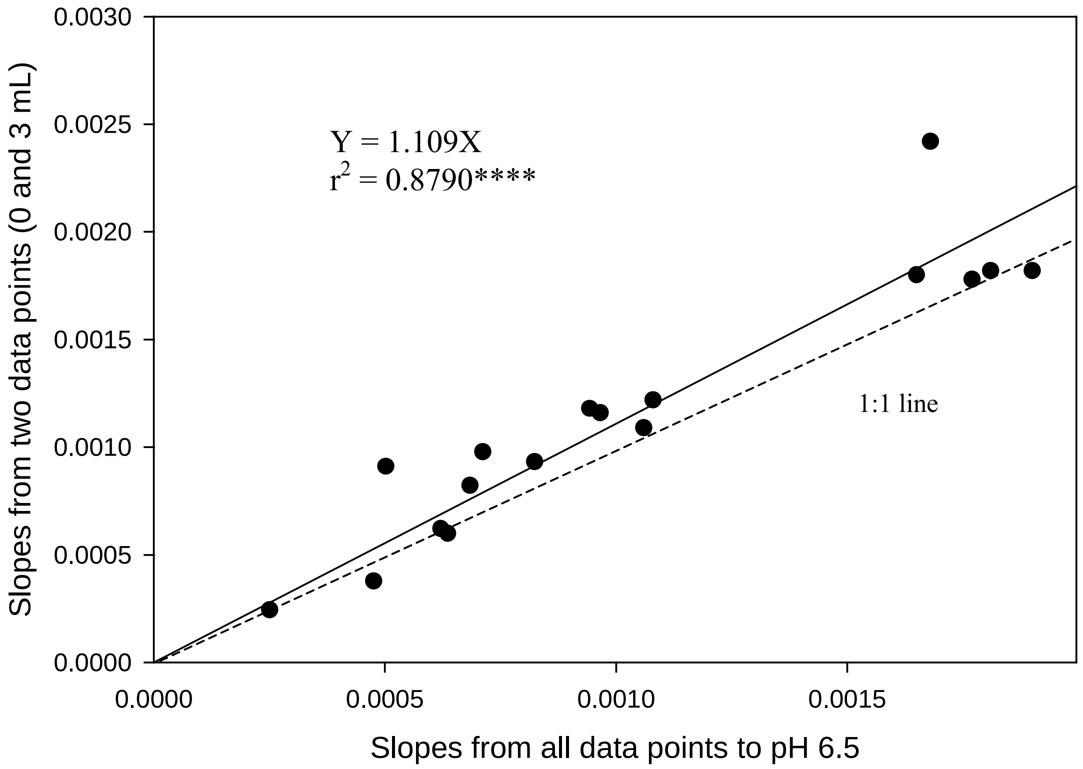


Fig. 2.4 Comparison of titration slopes in 0.01 M $CaCl_2$ determined by regression of all data points vs slopes calculated from two points (0, 3 mL $Ca(OH)_2$)

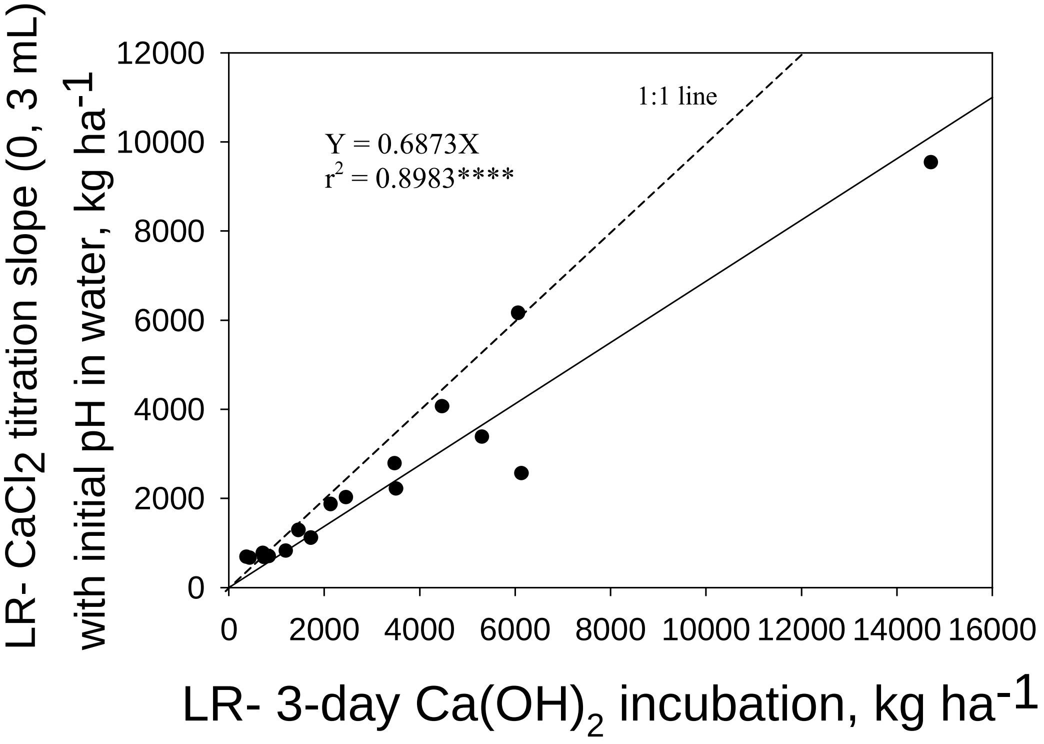


Fig. 2.5 LR comparison between readings on water titration curves and calculations from $CaCl_2$ titration slope (0 and 3 mL) with initial pH in water.

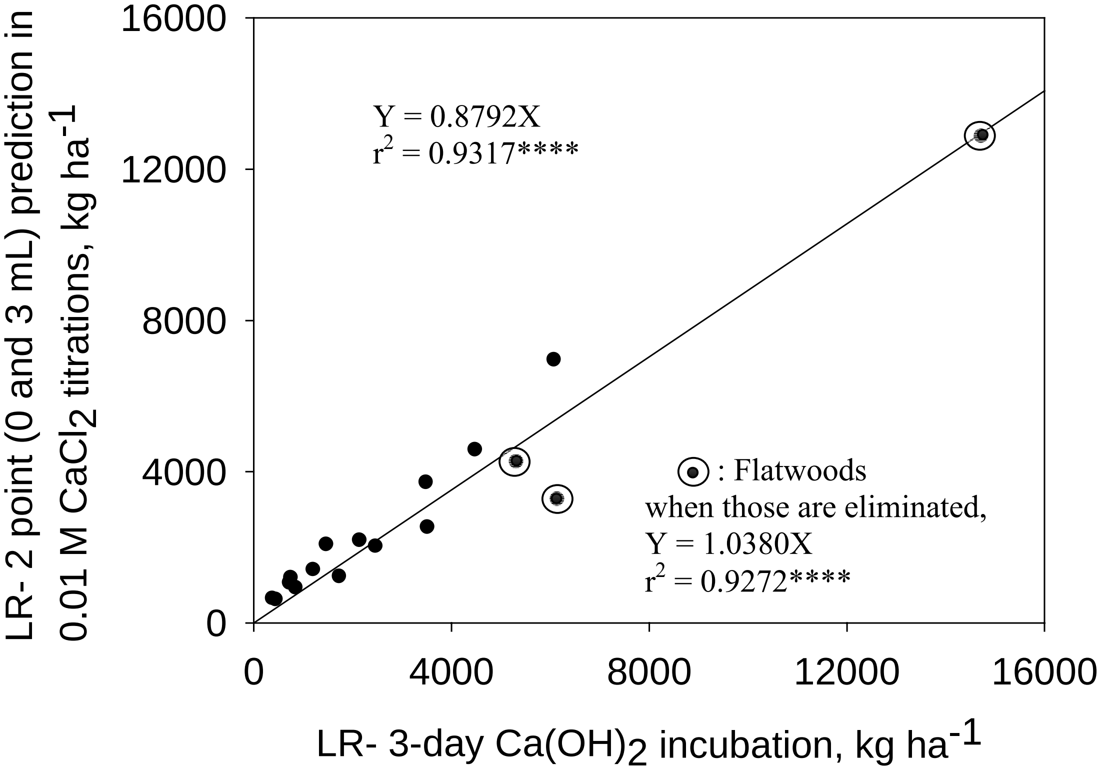


Fig. 2.6 LR comparison between 2 point prediction in 0.01 M $CaCl_2$ titrations and 3-day $Ca(OH)_2$ incubation

References

Alabi, K.E., R.C. Sorensen, D. Knudsen, and G.W. Rehm. 1986. Comparison of several lime requirement methods on coarse textured soils of Northeastern Nebraska. Soil Sci. Soc. Am. J. 50:937-941.

Dunn, L.E. 1943. Lime requirement determination of soils by means of titration curves. Soil Sci. 56:341-351.

Follett, R.H, and R.F, Follett. 1980. Strengths and weaknesses of soil testing in determining lime requirements for soils. p 40-51. In Proc. Of the Natl. Conf. on Agric. Limestone 16-18 Oct. 1980

Magdoff, F.R. and Bartlett, R.J. 1985. Soil pH buffering revisited. Soil Sci. Soc. Am. Proc. 49:145-148.

McConnell, J.S., Gilmour, J.T., Baser, R.E., and Frizzell, B.S. 1990. Lime Requirement of acid soils of Arkansas. Arkansas Experiment Station Special Report 150.

Owusu-Bennoah, E., Acquaye, D. K., Mahamah, T. 1995. Comparative study of selected lime requirement methods for some acid Ghanaian soils. Commun. soil Sci. Plant Anal., 26(7&8):937-950.

Ryti, R. 1965. On the determination of soil pH. Maataloustiet. Aikak. 37:51-60.

Schofield, R.K., and A.W. Taylor. 1955. The measurement of soil pH. Soil Sci. Soc. Am. Proc. 19: 164-167.

STATISTIX 7.0. 1985. STATISTIX for windows, 96 Analytical Software.

Weaver, A.R. 2002. Characterizing soil acidity in coastal plain soils. Dissertation for pH.D. University of Georgia.

CHAPTER 3

$CaCO_3$ INCUBATION METHODS REVISITED AND AN INDIRECT LIME REQUIREMENT

ESTIMATION BY SOIL PROPERTIES

Abstract

$CaCO_3$ incubation methods are considered mostly reliable to determine the lime requirements (LRs) of acid soils, although some studies have reported that the use of room temperature incubation would overestimate the actual LRs determined by field testing. One of the objectives of this study is to reveal the possible reasons for the newly generated acidity during the incubation. Another objective is to explore the possibility of estimating the LR from soil properties. This indirect LR estimation by soil properties is advanced for use when the required soil properties are already known.

Seventeen soils were incubated with $CaCO_3$ for two months at approximately 80% field capacity under room temperature (23˚C ± 2˚C). NH^+_4-N and NO^-_3-N were analyzed at day 60 of the incubation. All soils were also incubated with $Ca(OH)_2$ for 3 days. Soil pH was lower following the 60-day $CaCO_3$ incubation when compared to the 3-day incubation with $Ca(OH)_2$. The analysis of N transformations indicated that positive values of H^+ was generated after two months $CaCO_3$ incubation in 14 cases out of 17 soils. The initial pH and total C were found to be the significant factors for the estimation

of the LR. The generated linear equation was: LR (10^3 kg ha^{-1}) = 1.8043*(6.50 – initial pH) + 3.5273TC (%) – 4.3292; $r^2 = 0.8003$.

Key words: $CaCO_3$ incubation, $Ca(OH)_2$ incubation, total carbon, initial pH.

Introduction

The LR is the amount of limestone needed to increase the pH of the plow layer of acid soil to a desired level (McLean, 1970). $CaCO_3$ incubation methods are considered reliable to determine the LRs of acid soils, and they are often used to calibrate buffer methods (Tran and van Lierop, 1981; Loynachan, 1981; Barrow and Cox, 1990). Baker and Chae (1977) reported that the use of room temperature incubation of incremental mixtures of $CaCO_3$ and soil to determine LRs overestimated the actual LRs determined by field testing. This occurs because soil acidity increases under room temperature incubation. $CaCO_3$ incubation methods are subject to some arbitrary influences such as incubation time, moisture content, carbon dioxide levels, and air pollutants (Alabi et. al. 1986). $Ca(OH)_2$ solution incubation methods are also often used as the reference method to verify other LR predictions (Bradfield, 1941; Dunn, 1943; McConnell et. al, 1990).

The $CaCO_3$ incubation method for estimation of the LR relies on the acid-base reaction. However, indirect LR-estimation from soil properties may also be useful in some cases without directly measuring soil acidity. The indirect LR estimation procedure is advanced for use when buffer-pH values are not available and a LR recommendation is required. It is fairly accurate and relies on common soil tests.

The purposes of this study were:

1. Discover possible reasons that $CaCO_3$ incubation overestimates the LRs.

2. Relate the LRs to soil properties and establish a relationship between the LRs and significant soil properties for Georgia soils.

Materials and Methods

Seventeen soil samples with a wide range of clay and soil organic carbon (C) contents were collected from five of the major land resource areas of Georgia. The soils were oven-dried at a temperature of 35 °C, crushed, then sieved (2-mm) to remove small rocks and non-decayed crop residue, which consisted of less than 1% of the soil by weight. Then the soils were stored in the sealed Ziploc® bags until analyzed. A sub sample of each soil was analyzed for C and N with a Leco CNS 2000 Analyzer for Carbon and Nitrogen. Four of the soil samples contained more than 30% clay and five had clay contents in the range from 10 to 20%. Eight contained less than 10% clay. Three of the soil samples contained more than 2.0% total C and eight soil samples contained in the range from 1.0 to 2.0% total C. The others had less than 1.0% total C (Table 3.1).

The field capacity (FC) of each soil was measured using a 20 mL graduate cylinder. The weight (w) of ten mL of soil was measured in the cylinder. Two grams of distilled water was added into the cylinder. Water was allowed to infiltrate and the volume equivalent to the wetting depth (d) was recorded. Parafilm was placed on the cylinder to prevent evaporation during water infiltration. The field capacity (g water g^{-1} soil) was then calculated by the equation: $FC = 2\ g * 10\ cm / (d * w)$. Each soil was titrated with 0.022 M $Ca(OH)_2$ to establish the full titration curve per the method described in chapter 1.The equivalent amount of pure $CaCO_3$ powder was calculated that would be sufficient to bring the soil pH up to 6.5 based on the titration curve.

The appropriate amount of reagent grade $CaCO_3$ powder needed to raise the initial pH to 6.5 was thoroughly mixed with an 80 gram sample of each soil. Treatments consisted of the 17 soils, each receiving $CaCO_3$ or remaining untreated. Each treatment was replicated three times, resulting in a total of 102 samples for incubation. Enough water was added to each soil sample to bring it to approximately 80% of field capacity. The samples were incubated in 500 mL polyethylene containers with lids. Five-2 mm openings were drilled through each lid for air exchange. A glass stir-rod was inserted through one opening of each container to mix the soil. The soils were incubated for 60 days at room temperature (23˚C ± 2˚C), and were moistened every five days to keep the water content at about 80% of field capacity. At days 30 and 60, 30 g sub samples were taken from each container for the measurement of soil pH. The soil pH was measured at a 1:1 soil/water ratio in a 150-mL beaker.

On day 60 after the pH was measured, 120 mL of 1 M KCl was added to each soil suspension, and transferred into a 250-mL flask. They were then stoppered and shaken at a speed of 200 oscillation min^{-1} for half an hour. They were than allowed to stand for several minutes and then filtered through a Whatman #42 filter paper. The filtrates were frozen at -4 ˚C until analyzed. Nitrate-N was analyzed with the Griess- Ilosvay technique after reduction of NO_3^- to NO_2^- with a Cd column (Keeney and Nelson, 1982) using an OI Analytical Flow Solution 3000 (College Station, TX). Ammonium was analyzed using the automated phenate colorimetric procedure EPA-600/4-79-020, "Nitrogen, Ammonia" Method 350.1 (EPA, March 1984).

Each soil sample was also incubated for 4 days with 0.022 M $Ca(OH)_2$ solution by adding 30 mL of distilled water to 30 gram of each soil in a 120-mL polypropylene beaker. After thoroughly mixing for 30 minutes by stirring with a glass rod, the initial pH of each sample was measured while stirring. Then four rates of 0.022 M $Ca(OH)_2$ solution were added to each soil equivalent to 0, 0.5, 1 and 1.5 times the LR to pH 6.5 based on the full titration results, which were described in chapter 1. Three drops of chloroform were added to depress microbial activity. The samples were then covered with PARAFILM® to reduce evaporation. A 10-mm slit was cut on the film for air exchange. A glass stir-rod was inserted through the opening for mixing the soil periodically. The soil samples were incubated for 4 days at room temperature (approximately 23 °C). The pH was measured at 24, 48, 72, and 96 hours while being stirred. Approximately half of the soil treatments were duplicated to determine the precision of results. The relationship of soil pHs vs equivalent $CaCO_3$ added was fitted for each soil by non-linear regression using Table Curve 2D. Then, the $Ca(OH)_2$ incubation lime requirement to pH 6.5 was calculated with a resulting equation for each soil.

Pearson correlation coefficients (R^2), with two tailed levels of significance, were calculated to identify the relationships between the lime requirement and physicochemical soil properties. The lime requirement was calculated from the 3-day $Ca(OH)_2$ incubation. The procedure adopted was the PROC CORR of the statistical package SAS (SAS Institute, 1985).The tested soil properties included ΔpH (6.5 - initial pH), sand content, clay content, silt content, total N content, and total C content. The procedure PROC GLM of SAS (SAS Institute, 1985) was then conducted to test linear regression between LRs and the soil properties with high R^2 (larger than 0.5) and low P-value (less than 0.05).

Results and Discussion

Soil pHs following the 30 and 60 day $CaCO_3$ incubation and the 3-day $Ca(OH)_2$ incubation are shown in table 2. If no other reactions affected the soil pH except neutralization of the soil acidity, the soil pH value should be 6.50. In the 3-day incubation with $Ca(OH)_2$ the 17 soils had an average pH of 6.36 on day 3. Soil No.9 from the Ridge and Valley had the highest pH of 6.63 and soil No.13 from the Atlantic Coast Flatwoods had the lowest value of 6.01. In the $CaCO_3$ incubation, the average soil pH for the 17 soils on day 30 was 5.98. Only soil No.17 from Blue Ridge Mountains exceeded pH 6.5, with a pH of 6.60. Soil No.12 had a soil pH value 6.46. Most of the others had values of around 6.0. The soil pH values decreased for all 17 soils on day 60 and the average value had decreased to 5.67. In the $CaCO_3$ incubation check soils, 13 of 17 soil pH values on day 30 had increased an average of 0.40 pH unit from their initial pHs. This increase probably occurred because of hydrogen consuming reactions like ammonification that dominated during the first month of incubation, consuming hydrogen ions and raising soil pH. The check soil pH values on day 60 dropped from the values on day 30 in almost all cases except for soil No.17 decreasing an average of 0.21 pH unit. Seven check soils had pH values lower than their initial pH values following 60 days of incubation.

In both incubated and check soils, the soil pH values were lower on day 60 than on day 30. This was probably due to hydrogen ion producing processes like nitrification that dominated between 30 and 60 days of incubation. The average pH value for the 3-day $Ca(OH)_2$ incubation was 6.36 compared to 5.98 on day 30 of the $CaCO_3$ incubation. Although it appears that both $CaCO_3$ and $Ca(OH)_2$ incubation did not raise the soil pH to the target value of 6.50, the $CaCO_3$ incubation method may overestimate the lime requirement of soils if we considered the 3-day $Ca(OH)_2$ incubation as the reference method. The N transformations during the $CaCO_3$ incubation were positive evidence for this conclusion (table 3.3).

The first step in the decomposition of organic N is described by the ammonification process, which is an alkali-producing reaction:

$R^1\text{-}CH(NH_2)\text{-}R + 1/2O_2 + H_2O \rightarrow R^1\text{-}CO\text{-}R + NH_4^+ + OH^-$ (1)

where $R^1$and R represent organic groups (Conyers et al. 1995).

Ammonium ions may be used as an energy source by the chemoautotrophic bacteria nitrosomonas and be transformed to NO_2^- as shown in equation (2). Then, nitrobacter oxides NO_2^- further to NO_3^- as shown in equation (3) (Conyers et al. 1995).

$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + H_2O + 2H^+$ (2)

$NO_2^- + 1/2O_2 \rightarrow NO_3^-$ (3)

The concentration of NH_4^+-N and NO_3^- -N in the $CaCO_3$ incubated soils and check soils at day 60 are shown in table 3.3. The net H^+ produced from the N transformations, calculated using equation (1) and (2), are also listed. In the check soils, 12 of the 17 soils gave the positive values of net H^+ produced. Of the 17 $CaCO_3$ treated soils, 14 had positive values of H^+ produced. In those cases with positive H^+ values, a certain amount of soil acidity during laboratory incubation of the soils had been generated. These results were consistent with the conclusion of Baker and Chae (1977) for seven western Washington soils. In cases with positive values of H^+ produced, the net result will be to lower soil pH for two reasons. First, the production of H^+ in the soil will reduce pH because the H^+ will react with the pH dependent charge (primarily soil organic matter), and the corresponding drop in pH from H^+ addition will also reduce soil CEC, thereby increasing the salt content of the soil solution as some exchangeable cations are forced into the soil solution from the reduction in CEC. The pH will be depressed further because of the increased salt contents. The five cases of negative values of H^+ in the check soils and three in the $CaCO_3$ incubation soils may be explained by other alkali-producing reactions during the incubation process. According to Conyers et al. (1995)'s study, the alkali-producing reactions may include ammonification, reduction of Mn-oxides, oxidation of organic anions and SO_4^- adsorption. It was very likely that in our study the reduction of Mn-oxides may be primarily responsible for the increase in pH because the incubation was carried out in slightly reduced conditions since the soils were moistened to about 80% field capacity.

The correlation coefficients (with $P<0.1$) are presented in Table 3.4. The lime requirement showed significant ($P < 0.05$) positive linear relationships with ΔpH (6.50 – initial pH) and total carbon content. And there was no significant relationship found between the lime requirement and the clay content. Table 3.5 shows the GLM statistical analysis for the linear model between the lime requirement and both ΔpH and total carbon content. Both of the ΔpH and total carbon content were significant factors for the lime requirements at the P level of 0.05. The GLM parameters for the linear model were shown in Table 3.6. The linear relationship generated was:

$$\text{LR } (10^3 \text{ kg ha}^{-1}) = 1.8043*(6.50 - \text{initial pH}) + 3.5273\text{TC } (\%) - 4.3292; \; r^2 = 0.8003.$$

This equation can be used in the cases in which the initial pH and total carbon content were already known.

Table 3.1 Selected physical and chemical properties of acid soils used.

Soil no.	MLRA	Initial soil $pH_w(1:1)$	Sand	Clay	Silt	Total N	Total C	C/N
			--------------	%	-------------	---- mg kg^{-1}----		
1	CP	5.4	64.8	20.4	14.8	501	5199	10.4
2	CP	4.95	69	21.2	9.8	490	5087	10.4
3	RV	5.8	39	20.1	40.9	1206	13308	11.0
4	CP	4.29	68.6	8	23.4	789	9244	11.7
5	CP	5.41	82.7	5.5	11.9	459	8985	19.6
6	CP	5.24	86	2.3	11.7	359	6371	17.7
7	CP	4.09	88.7	4.4	6.9	190	4215	22.2
8	RV	5.78	13.2	43.5	43.2	1311	11443	8.7
9	RV	5.47	9.4	33.5	57.1	1053	9193	8.7
10	SP	4.68	70.5	8.9	20.6	1135	16698	14.7
11	SP	4.32	32.8	50.7	16.4	1097	12497	11.4
12	ACF	4.02	88.3	2.1	9.5	472	10479	22.2
13	ACF	4.42	33.2	22.1	44.7	1513	31805	21.0
14	RV	4.95	8.2	43.2	48.6	1274	13923	10.9
15	SP	4.2	64.8	9.3	25.9	810	14327	17.7
16	ACF	4.41	87.9	2.5	9.7	724	20448	28.2
17	BRM	4.42	31.2	10.7	58.1	2072	26959	13.0

MLRA = Major Land Resource Area
CP = Coastal Plain
RV = Ridge & Valley
SP = Southern Piedmont
ACF = Atlantic Coast Flatwoods
BRM = Blue Ridge Mountain

Table 3.2 Soil pH comparison between $CaCO_3$ incubation and $Ca(OH)_2$ incubation.

Soil no.	Initial soil pH_w(1:1)	$CaCO_3$ incubation		check		$Ca(OH)_2$ incubation
		day 30	day 60	day 30	day 60	day 3
1	5.4	6.25	6.07	5.84	5.70	6.49
2	4.95	6.02	5.91	5.49	5.32	6.46
3	5.8	5.92	5.73	5.52	5.40	6.58
4	4.29	5.37	5.02	4.71	4.52	6.32
5	5.41	6.00	5.78	5.84	5.50	6.57
6	5.24	5.80	5.56	5.22	5.06	6.34
7	4.09	5.68	5.55	4.35	4.05	6.22
8	5.78	6.00	5.85	5.52	5.40	6.59
9	5.47	5.72	5.46	5.00	4.69	6.63
10	4.68	5.70	5.30	5.29	4.50	6.21
11	4.32	6.17	5.94	4.69	4.45	6.19
12	4.02	6.46	5.79	4.33	4.32	6.32
13	4.42	5.94	5.80	4.48	4.43	6.01
14	4.95	6.01	5.41	5.11	4.96	6.44
15	4.2	6.03	5.38	4.49	4.01	6.33
16	4.41	6.07	5.53	4.91	4.82	6.10
17	4.42	6.60	6.24	5.26	5.38	6.38
Average	4.81	5.98	5.67	5.06	4.85	6.36

Table 3.3 Net H^+ produced from N transformations in incubated soils at day 60.

Soil	Original soils		CaCO$_3$ incubation			check		
no.	NO_3^+-N	NH_4^+-N	NO_3^+-N	NH_4^+-N	Net H^+	NO_3^+-N	NH_4^+-N	Net H^+ µg g^{-1}
1	7.66	4.03	15	3.97	0.5283	15.82	3.15	0.6456
2	7.29	3.53	13.46	3.15	0.4678	12.56	2.8	0.4279
3	5.87	8.5	33.82	5.74	2.1930	35.97	5.99	2.329
4	34.14	28.91	36.75	3.72	1.9853	36.87	14.55	1.2208
5	1.2	6.57	21.46	2.68	1.725	22.66	2.8	1.8018
6	9.72	3.99	21.05	1.97	0.9532	22.02	2.15	1.01
7	1.82	2.28	6.6	2.03	0.3583	5.11	2.07	0.2496
8	14.62	4.92	29.25	3.25	1.1639	29.31	2.59	1.2153
9	1.82	5.04	18.87	2.58	1.3933	20.01	2.35	1.4917
10	8.28	8.59	29.99	2.34	1.9969	30.43	3.98	1.9115
11	2.56	7.97	14.88	27.21	-0.4938	14.86	6.79	0.9626
12	1.03	6.76	19.47	2.66	1.6099	1.53	25.38	-1.2943
13	1.86	9.4	1.71	51.85	-3.0434	1.26	46.36	-2.6834
14	1.59	12.99	30.1	9.97	2.2523	7.05	52.1	-2.4057
15	5.46	7.45	34.36	2.43	2.4222	23.25	2.54	1.6208
16	1.57	7.16	18.38	2.67	1.5217	2.94	28.35	-1.4159
17	2.03	19	19.39	101.1	-4.6239	1.46	138.4	-8.5692

H^+ (mol) produced from nitrification = $2*(NO_3^+\text{-}N_{incubation} - NO_3^+\text{-}N_{original})$ (mol)

H^+ (mol) consumed from ammonification = $(NO_3^+\text{-}N + NH_4^+\text{-}N)_{incubation}$ (mol)
- $(NO_3^+\text{-}N + NH_4^+\text{-}N)_{original}$ (mol)

Net H^+ (mol) = H^+ (mol) produced - H^+ (mol) consumed
Net H^+ (µg g^{-1}) = Net H^+ (mol) * 1 g mol^{-1} g^{-1} soil

Table 3.4 Pearson correlation coefficients among physicochemical properties of 17 soils and lime requirements (LR).

Soil property	ΔpH	sand	clay	silt	TN	TC
LR	0.526**	---	---	---	0.471*	0.845****

two tailed levels of significance: --- P ≥ 0.1; * P < 0.1; ** P < 0.05; *** P < 0.001; **** P < 0.0001

ΔpH = 6.5 - initial pH; TN = total N; TC = total Carbon; LR = lime requirement

Table 3.5 GLM Table for the linear model of lime requirement (10^3 kg ha^{-1}) relating to ΔpH and total carbon content (%).

Source	df	Type III SS	MS	F	Pr > F
ΔpH	1	17.289	17.289	6.06	0.0274
TC	1	104.752	104.752	36.73	< .0001
Error	14	39.929	2.852		
Total	16	161.97			

ΔpH = 6.50 – initial pH; TC = total carbon content

Table 3.6 GLM Parameter table for the linear model of lime requirement (10^3 kg ha^{-1}) relating to ΔpH and total carbon content (%).

Parameter	Estimate	Standard Error	t value	Pr > | t |
Intercept	-4.3292	1.3127	-3.30	0.0053
ΔpH	1.8043	0.7328	2.46	0.0274
TC	3.5273	0.5820	6.06	< .0001

ΔpH = 6.50 – initial pH; TC = total carbon content

References

Alabi, K.E., R.C. Sorensen, D. Knudsen, and G.W. Rehm. 1986. Comparison of several lime requirement methods on coarse textured soils of Northeastern Nebraska. Soil Sci. Soc. Am. J. 50:937-941.

Backer, A.S., and Y.M. Chae. 1977. A laboratory quick test for predicting the lime requirements of acid mineral soils. Tech. Bull. 88, Washington State Univ., 11 p.

Barrow, N.J, and Cox, V.C. 1990. A quick and simple method for determining the titration curve and estimating the lime requirement of soils. Austra. J. Soil Research: 28:685-694.

Bradfield, R. 1941. Calcium in the soil: 1. Physico-chemical relations. Soil Sci. Soc. Am. Proc.6:8-15.

Conyers, M. K., N. C. Uren and K. R. Helyar. 1995. Causes of changes in pH in acidic mineral soils. Soil Biol. Biochem. 27:1383-1392.

Dunn, L.E. 1943. Lime requirement determination of soils by means of titration curves. Soil Sci. 56:341-351.

EPA. March, 1984. Methods for chemical analysis of water and wastes. EPA-600/4-79-020. "Nitrogen, Ammonia" Methid 350.1 (Colorimetric, Automated Phenate) Storet No. Total 00610, Dissolved 00608.

Keeney, D.R., and D.W. Nelson. 1982. Nitrogen-Inorganic forms. p. 634-698. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. Chemical and microbiological properties. 2nd ed. Agron. Monogr.9. ASA and SSSA, Madison, WI.

Loynachan, T.E. 1981. Lime requirement methods for cold regions. Soil Sci. Soc. Am. J. 45:77-80.

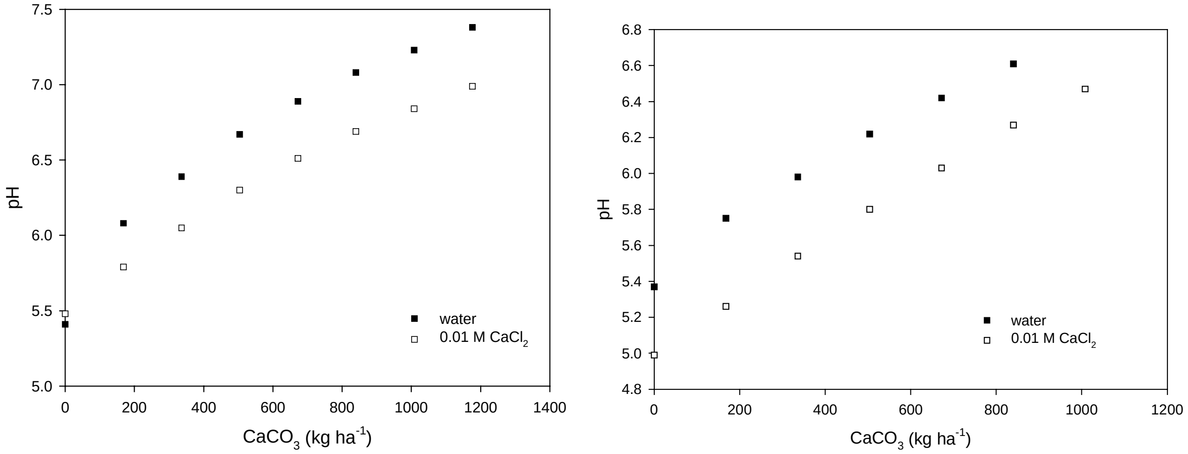
McConnell, J.S., Gilmour, J.T., Baser, R.E., and Frizzell, B.S. 1990. Lime Requirement of acid soils of Arkansas. Arkansas Experiment Station Special Report 150.

McLean, E.O. 1970. Lime requirement of soils-inactive toxic substances or favorable pH range. Soil Sci. Soc. Am. Proc. 34:363-364.

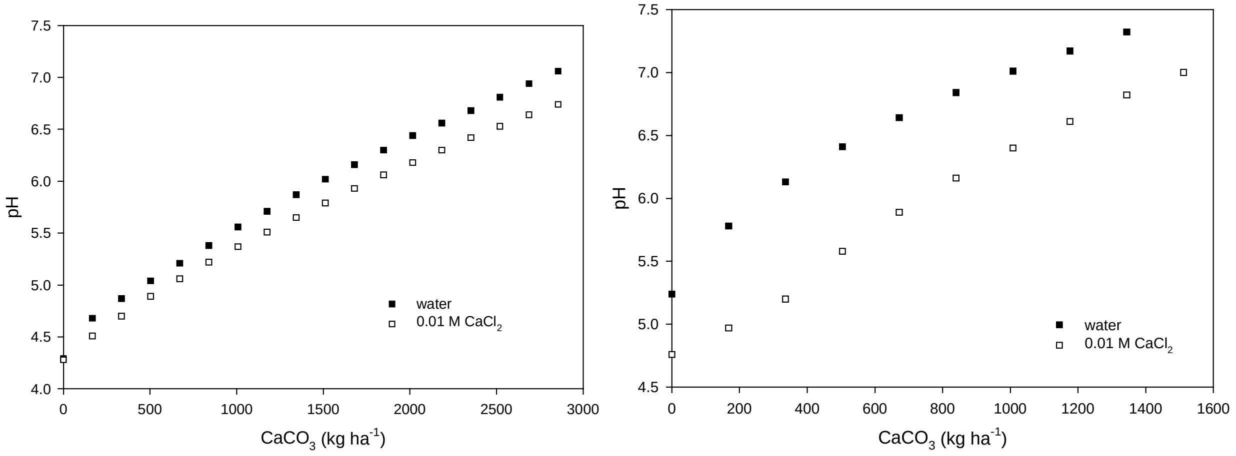
SAS Institute. 1985. SAS user’s guide: Statistics. Version 6 ed. SAS Institute, Inc., Carg, NC.

Tran, T. S., and W. van Lierop. 1981. Evaluation and improvement of buffer-pH lime requirement methods. Soil Sci. 131:178-188.

APPENDIX Fig. 1 Titration curves for twelve soils in water and 0.01 M CaCl$_2$.

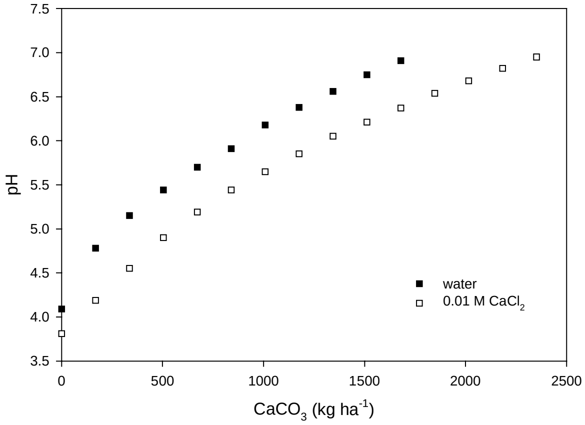

Titration curves for soil No.1 in both water and 0.01 M CaCl$_2$

Titration curves for soil No.2 in both water and 0.01 M CaCl$_2$

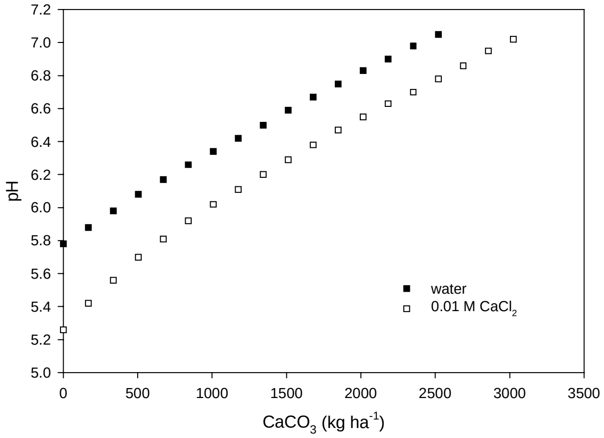

Titration curves for soil No.4 in both water and 0.01 M CaCl$_2$

Titration curves for soil No.6 in both water and 0.01 M CaCl$_2$

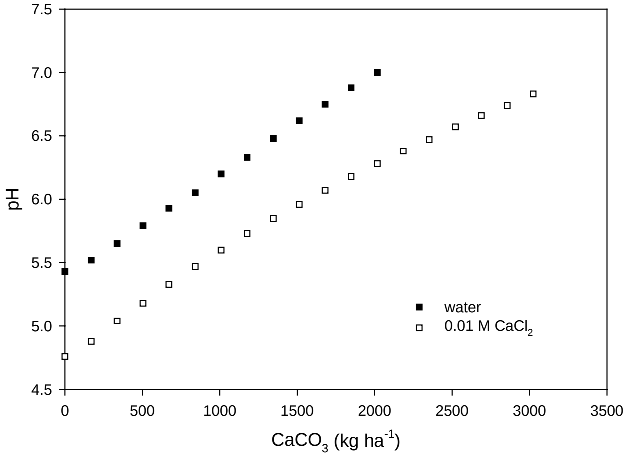
Titration curves for soil No.7 in both water and 0.01 M $CaCl_2$



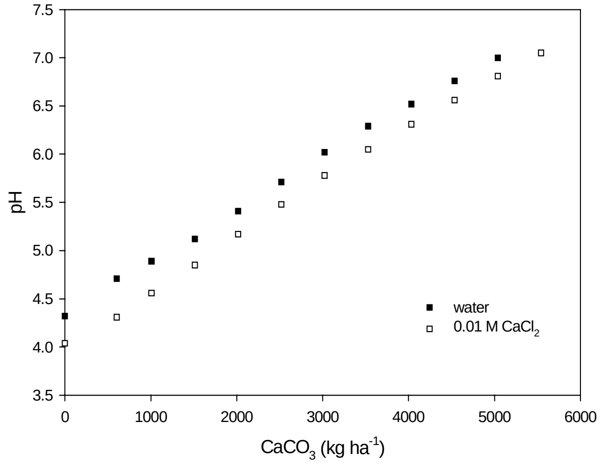
Titration curves for soil No.8 in both water and 0.01 M $CaCl_2$



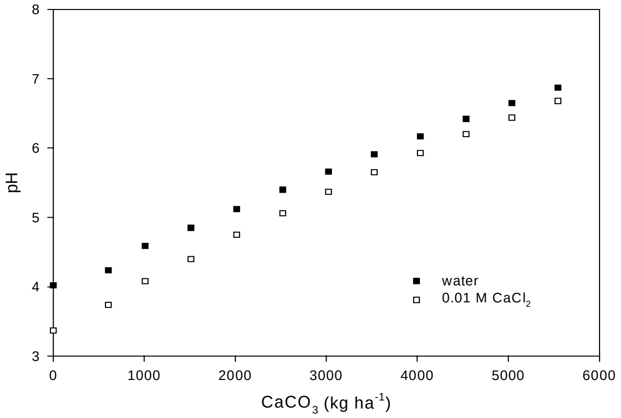
Titration curves for soil No.9 in both water and 0.01 M $CaCl_2$



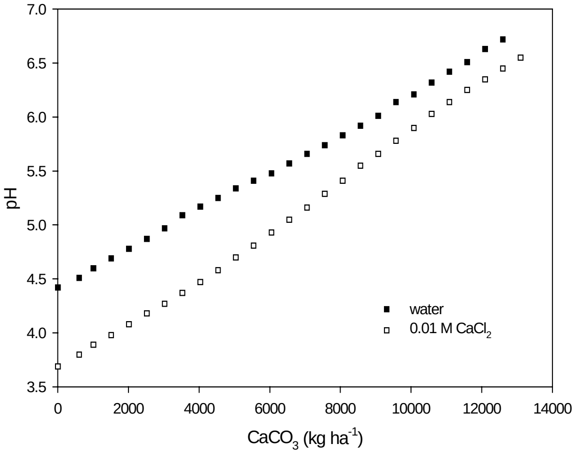
Titration curves for soil No.11 in both water and 0.01 M $CaCl_2$



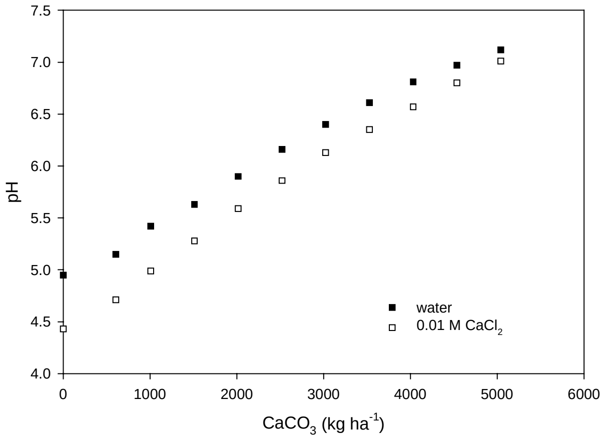
Titration curves for soil No.12 in both water and 0.01 M $CaCl_2$



Titration curves for soil No.13 in both water and 0.01 M $CaCl_2$



Titration curves for soil No.14 in both water and 0.01 M $CaCl_2$



Titration curves for soil No.15 in both water and 0.01 M $CaCl_2$