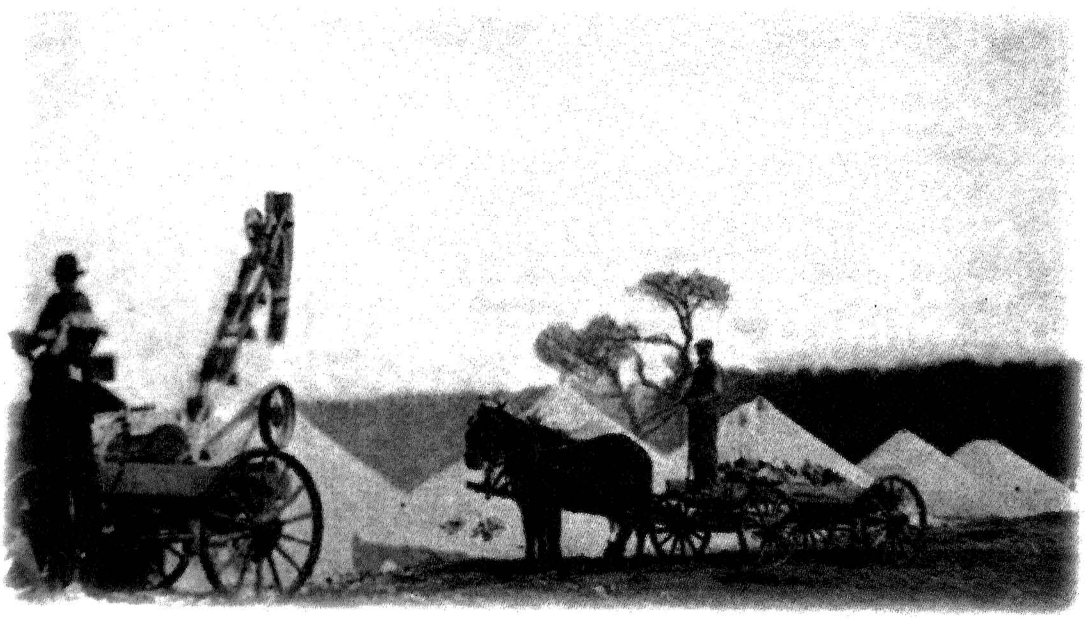
Liming in Missouri
in the 20th Century



J.R. Brown and John Stecker

Agricultural Experiment Station
College of Agriculture, Food and Natural Resources
University of Missouri-Columbia

Special Report 548

February 2003

Liming in Missouri in the 20th Century

J. R. Brown and John Stecker

Preface

Soil acidity research conducted in Missouri was last summarized in 1969 (Fisher, 1969). More than thirty years have passed, which suggested that another summary may be in order. Therefore, a formal proposal was made to review the research conducted since the mid-1960s and publish a summary for distribution to interested parties. The Fertilizer and Liming Materials Advisory Councils established by the Missouri Fertilizer and the Missouri Agricultural Liming Materials Laws (Missouri Revised Statutes, sections 266.336 and 266.543) oversee the implementation of the laws. The Director of the Missouri Agricultural Experiment Station manages the fees collected under the inspection programs for fertilizer and liming materials with the advice of the advisory councils. The councils recommended funding of the proposal in early 2000 and this document is the result.

Research done at the Missouri Agricultural Experiment Station since the mid-1960s included both field projects and graduate student research problems focused mainly in the laboratory. As we started the review, historical questions concerning the derivation of the Missouri liming program arose. Thus, the document expanded over that which may be expected from the statement of objectives in the original request for funding and includes both state of the liming program in Missouri as well as a condensed history.

The authors considered the following target audiences might benefit from material in this paper:

1. Farmers and consultants.
2. University of Missouri research and extension soil scientists and agronomists.
3. Agricultural faculty and students at the universities and colleges of the state.
4. Regional and national soil testing and nutrient management specialists.
5. Missouri Limestone Producers Association and MO-AG Industries Council members.

Acknowledgements

This paper could not have been written without the work done by many research scientists and extension specialists. We have cited much of this work, but likely we have missed some that should have been cited. For those unintentional omissions we apologize.

The Missouri liming program is especially indebted to Dr. Ted R. Fisher, who devoted much of his short career as a MU faculty member to liming issues. Dr. Manjula Nathan, Director of the Columbia-based Soil Testing Laboratory, Associate Dean Michael Chippendale, and Joe Slater, Manager of Missouri Fertilizer/Agricultural Lime Control Services, were particularly helpful by providing access to the soil test files, for support of our proposal, and for procedural information, respectively.

The Director of the Missouri Agricultural Experiment Station provided funding for this paper with the advice of the Advisory Council as established by the Missouri Agricultural Liming Materials Law. The Executive Director of the Missouri Limestone Producers Association, Steve Rudloff, was supportive in getting this paper published.

Matthew Herring, agronomy specialist, University Outreach and Extension, reviewed the manuscript.

Contents

Introduction

A thorough review of liming in Missouri has not been conducted since Dr. Ted Fisher summarized research through 1967 (Fisher, 1969). The Fisher summary provided the data supporting changes in the liming recommendations. More than 30 years have now passed, and it seems appropriate to review the recommendations and utilize research on liming conducted since 1970, which may suggest modifications in the recommendations.

This publication reviews the status of liming and soil acidity at the end of the Twentieth Century. There are several issues involved, which are overlapping, causing organizational problems in putting this publication in readable form. Following a broad overview of soil acidity, there is a condensed discussion of the evolution of liming practices since the formation of the Missouri Agricultural Experiment Station with the addition of research results of liming studies conducted since 1970. A discussion of current laboratory methods, a reevaluation of the current recommendations, and suggestions for changes and further research follow the discussion of the evolution of liming activity in Missouri.

The following are the objectives of this publication.

Objectives

- Provide a condensed history of liming research and practices in Missouri.
- Summarize the methods in use at the end of the Twentieth Century to estimate the need for liming material.
- Summarize research on liming conducted by the Missouri Agricultural Experiment Station between 1967 and 1999 and related issues.
- Recommend improvements in the recommendation program for agricultural liming materials in Missouri.

Soil Acidity

Liming of acid soils is considered by many soil scientists as the first step toward balanced nutrition of cultivated plants. Barber (1984), in a condensed review of the history of liming of agricultural soils, cited references as far back as 200 BC that extol the virtues of lime. Remnant pits from which marl was mined for spreading on crop fields are still present on fields at the Rothamsted Station in the United Kingdom. The first experiments were started at Rothamsted in 1843, so spreading of marl must have started in the previous century or before. In the Western Hemisphere Ruffin (1821) is given credit for drawing attention to the benefits of "calcareous manures."

Acid soils in humid regions have developed through removal of basic cations by leaching with rainfall charged with carbon dioxide. Additionally, crop removal and acidifying fertilizers, especially ammoniacal nitrogen and sulfur containing materials, have increased soil acidity. Removal of produce from agricultural land is also inherently acidifying (Albrecht and Smith, 1952).

Soil acidity adversely affects most arable crops in several ways. Albrecht (1941), for example, showed that acid soils were infertile because of inadequate calcium (Ca). Foy (1984) summarized the physiological effects of hydrogen (H), aluminum (Al) and manganese (Mn) toxicities on plants in acid soils. Deficiencies of calcium, magnesium (Mg) and molybdenum (Mo) resulting from soil acidification significantly decrease plant biomass production (Clark, 1984). In addition to toxicities and deficiencies associated with soil acidity, availability of almost all essential nutrients and activity and species distribution of microbes are influenced by the relative acidity of a soil (VPI, 1953; Coyne, 1999).

Field studies to determine the benefits to plants of reducing soil acidity have been conducted at least since the early 19th Century. Attempts were made to determine the nature of soil acidity and to explain soil acidification. Jenny (1961) likened the course of these studies to a merry-go-round. Illustrating the analogy were alternating emphases of the causal agents responsible for the negative effects of soil acidity on plant growth. The impact of aluminum on plants and its role in soil acidity was of great interest in the early 20th Century (Hartwell and Pembee, 1918). As methods of measuring proton activity in soils improved, the focus shifted to the study of hydrogen in soil acidity. Then in the early 1950s attention was redirected toward aluminum (see, for example, Coleman and Harward, 1953). The role of aluminum in soil acidity has become better understood, however, there are unanswered questions concerning the nature of the interacting factors that affect soil acidity and its impact upon plant growth. One excellent review of soil acidity concepts was written by Bloom (2000).

Magdoff and Bartlett (1985) showed variable buffering of soil to lime additions. They titrated soil samples that had been incubated with calcium carbonate ($CaCO_3$) with strong acid. The pH in the resulting titration curves changed exponentially with applied acid. When these titrations were conducted in 0.01 M $CaCl_2$ (calcium chloride), the plot of pH against quantity of acid was linear between pH 4.5 and 6.5. The soils were highly buffered above and below pH 6.5 and 4.5, respectively. Buffering increased with an increase in cation exchange capacity (CEC).

Soils contain both permanent and variable cation exchange capacities. When the acidity in an acid soil is progressively eliminated by liming, the CEC tends to increase as the impact of the variable charges comes into play (Thomas and Hargrove, 1984). Soil organic matter (SOM) contributes much of the variable CEC in soils through ionization of carboxyl (-COOH) and aromatic hydroxyl (AR-OH) groups. The ionization of these two organic groups is not complete until pH 8 and 11 are reached, respectively. The ionization process contributes to the buffering of both soil pH and active aluminum. In acid soils many –COOH sites are satisfied with Al^{+3} not exchangeable to potassium chloride (KCl) (Bloom et al., 1979, Bertsch and Bloom, 1996).

Hargrove and Thomas (1982) reported that Al-SOM buffers at a higher pH than H-SOM. In general as the soil solution pH rises above 5, the Al-SOM ionizes and the aluminum activity is controlled by the solubility of $Al(OH)_3$. The aluminum in SOM combinations slowly becomes active and is precipitated as gibbsite. In the process as many as three protons may be released by the reaction of active aluminum and water at soil pHs below 7.0 (McLean, 1976). Barium chloride ($BaCl_2$) and triethanolamine (TEA) have been used to determine total titratable acidity (Mehlich, 1948, Thomas, 1982). This procedure measures the total acidity to pH 8.2. It may, however, be more useful to have an estimate of total acidity based at pH 7.0, because most arable crops do best when soils are slightly on the acid side of neutral. The increase in soil pH from 7.0 to 8.0 is slow as suggested, for example, by the work reported by Magdoff and Bartlett (1985). In order to neutralize soil acidity to a target pH, one must account for the slowly released acidity that is non-exchangeable to 1 M KCl. This acidity, variably termed residual, labile, or pH dependent acidity, can be calculated by subtracting the quantity of KCl extractable acidity from the total acidity determined by $BaCl_2$-TEA @ pH 8.2 or a method that measures total acidity at pH 7.0.

It is this residual acidity that is estimated by the various buffer methods used to determine lime requirements by soil testing laboratories. These buffer methods include the original Woodruff method (Woodruff, 1948), the revised Woodruff (Cisco and Brown, 1984), and the SMP method (Shoemaker, McLean, and Pratt, 1961; Watson and Brown, 1998). All these soil test methods are quick test methods, which permit only a short contact time between the buffer solution and the soil sample. It is unlikely that all the residual acidity, as defined in the previous paragraph, can be estimated by quick test methodology. Therein lies the need for calibration (Sims, 1996).

Liming soils with agricultural limestone or other liming materials neutralizes the hydrogen and aluminum ions held on the soil exchange sites to form either neutral (H_2O) or insoluble products

($Al(OH)_2$). This neutralization causes the soil pH to approach 7.0. Excess lime raises the pH above 7.0 often with adverse effects on plant nutrition.

Attempts to calibrate plant response to measures of acidity (pH, KCl extractable, total acidity, $CaCO_3$ incubation titration, percentage base saturation, etc.) have given erratic results (Farina and Channon, 1991 and Blosser and Jenny, 1971 as examples). This failure is especially true with attempts to extrapolate laboratory and greenhouse results to the field and emphasizes the need for field calibration of any quick soil test.

Adding liming materials to acid soil benefits many species of plants, but plants thrive at different ranges of soil acidity, so the target of liming is to provide the proper soil acidity for the plant or plants to be grown (Havlin et al., 1999). Liming an acid soil usually increases the soil content of the essential nutrients calcium and magnesium. Adding calcium and magnesium to acid soil replaces acidity from the exchange complex, which subsequently is neutralized by the basic component of the liming material. Lowering the intensity of soil acidity enhances microbial activity, which tends to increase the availability of nutrients, especially N, P, and S. Alteration of the proton activity in soil solution affects the solubility of most micronutrients. A more complete discussion of soil acidity can be found in soil science texts such as Hassett and Banwart (1992).

History of Liming in Missouri

Liming experiments had been conducted in Midwestern United States by 1903 (McLean and Brown, 1984). A review of Agricultural Experiment Station publications of humid region states from the first decade of the Twentieth Century makes numerous references to research that included liming treatments (Duley and Miller, 1926). Most early field studies were designed in a very systematic manner without replication to determine the factors most limiting crop production. Nitrogen fertilizers were not readily available, so reliance was placed on manure and legume crops as sources of N. Bonemeal was an early P source with acidulated phosphate (ordinary superphosphate) and ground rock phosphate also used. Potassium was applied as "potash" which likely was muriate of potash (KCl). The focus of liming treatments in these early field studies seemed directed toward demonstration of the value of liming rather than the determination of rates of application.

Selected citations of the earlier work on liming in Missouri have been included in chronological order. The 40 years from 1888 through 1927 included numerous demonstration studies scattered across the state. The sophistication of liming research intensified from 1928 through 1946. Research focused on soil chemistry because the Soils Department faculty and graduate students included people such as C. E. Marshall, Hans Jenny, L. D. Baver, and Ellis Graham. In addition, World War II affected both the approach to the science of soil and the management of cropland. Starting in 1947 the increasing availability of manufactured fertilizers changed agriculture forever. Intensive research funded by the fertilizer industry and state and federal governments resulted in hundreds of fertilizer and lime studies including soil test calibration.

Soil testing laboratories were located in almost all Missouri counties by 1950. Extension programs on crop production were generated by interest in fertilizer. However, by 1969 methodology had changed such that the accuracy and precision of the county soil testing labs was questioned. This led to the centralization of soil testing at Portageville and Columbia, where the soil sample volume could support precise analytical tools. From 1970 to the end of the century interest in soil fertility including liming continued. Yield levels increased with improved varieties and the development of hybrids. Also greater precision was desired in recommendations and management of nutrients.

1888–1927

Soil acidity and liming did not seem to be of much concern prior to 1900. In fact, historic Sanborn Field, which was started in 1888, did not have a liming treatment until 1928 (Smith, 1942). Field experiments were started in many of the soil regions of the state in the first decade of the century (Miller and Hutchison, 1910). The experimental sites were located near local train stations, as trains and horses were the common means of transportation at the time.

In most cases, the set of treatments in these early experiments consisted of manure, P, P + K, P + K + manure, and P + K + manure + lime or some variation of these combinations (Miller et al., 1915; Krusekopf, 1938). These treatments were similar to those used in other states such as Illinois (Bauer et al., 1945). Lime was rarely applied in excess of 4,000 pounds per acre. There were no early rate studies with lime due to limitations of material and labor. These early field studies, while unacceptable by late 20th Century research standards, provided information that was the basis for liming and fertility practices recommended to farmers into the middle of the 20th Century.

Early Missouri liming studies were reviewed by Miller (1909) for the American Society of Agronomy. Some yield depressions attributed to lime were observed but with no explanation. Duley and Miller (1926) summarized studies on 14 different fields and stated that "on fields where the combination of all three (phosphate, lime, and manure) of the above materials [were all applied], the yields have usually been outstandingly high."

The lack of a reliable measurement of intensity of acidity in soils was an early limitation to scientific study of soil acidity problems. One early measurement technique was the litmus paper test. Barlow (1916) described in detail how to use litmus paper to estimate the intensity of soil acidity. The litmus paper test, however, was very subjective, and, according to Barlow, the interpretation of the test differed between practitioners.

The Bureau of Chemistry in the United States Department of Agriculture was a major player in developing methodology for estimating acidity in agriculture. For example, the Vietch test for acidity was formulated and was used extensively in some state laboratories (Vietch, 1902). By 1920 there were several methods to estimate the intensity of acidity. These included the use of litmus paper, the Truog test, and the Vietch test (Miller and Krusekopf, 1920).

Although by the 1920s soil testing materials to estimate lime needs were made directly available to farmers, calibration studies that linked liming material to be applied with the results of these soil tests were limited. Miller and Krusekopf (1920) thoroughly covered agricultural liming practices in a Missouri Agricultural Experiment Station bulletin.

Availability of liming material during this period gradually increased, as the need became more apparent. By 1920 commercial limestone quarries were in operation. Also, Missouri extension personnel were providing individuals and groups of farmers with information about the purchase and use of small limestone crushers (Miller and Krusekopf, 1920).

Lime recommendations were based on material such that the majority passed a 10-mesh screen. While it was recognized that some fields needed 5 or more tons of ground limestone, the dominant recommendation for the period was 1 to 2.5 tons per acre. An application of 1 to 1.5 tons per acre every 4 to 6 years was suggested as a reasonable practice (Miller and Krusekopf, 1920). Miller (1924) suggested limestone rates of 1 to 2.5 tons per acre in his soil management textbook.

Thus by 1927 there was widespread knowledge about liming acid soils to benefit the contemporary corn-forage legume based crop rotations. Acceptance of soil testing to estimate lime needs was increasing, yet calibration data for the tests regarding the amount of liming material needed were still lacking.

1928-1946

During this time period, the Soils Department developed expertise in clay mineralogy and ionic chemistry, which led to better understanding of the behavior of soil additives. Concurrently the liming program improved quantitative estimation of lime needs and increased the emphasis on quality of agricultural liming materials.

According to Trotter and Coleman, "Recommendations are uniformly made in terms of limestone ground finely enough so it will all pass through a 10-mesh screen and have a calcium carbonate equivalent of 95% or more." When lime was coarser than 10-mesh, their suggestion was "The recommendation gives the minimum amount to apply. If in doubt apply more" (Trotter and Coleman, 1928). The authors republished their circular with only minor modifications in 1935 (Trotter and Coleman, 1935).

Miller (1936) published guides for quantities of limestone based upon the Comber soil test for acidity, the fertility rating of the soil and the kind of legume crop. The Comber test used an alcoholic solution of potassium thiocyanate (KSCN) (Comber, 1920). The KSCN reacted with soluble iron (Fe^{2+}) forming a red colored complex. Increasing intensity of red color in the filtrate indicated increasing soil acidity. Color charts were available for conversion of color intensity into pounds of limestone per acre.

Although not specifically stated by Miller (1936) and other authors of the period, it was implied that since crop rotations included legumes to supply N for grain crops, lime needed by the legume would automatically satisfy the lime needs of the non-legume crops. The amount of N added to soil by legumes would sustain yields on low fertility land of 25 bushels corn per acre, while medium and high fertility land would produce 35 and 50 bushels per acre, respectively. The Miller recommendations for limestone called for a calcium carbonate equivalent (CCE) of 95% with nearly all material passing a 10-mesh screen. Miller (1936) stated "...the percentage of material which passes a 40-mesh screen represents the percentage of limestone which is active in the soil the first year." Miller's comments were similar to those made by Trotter and Coleman (1935).

Baver and Bruner (1939), in their comprehensive soil testing methods bulletin, included a modification of the Comber approach for estimating lime requirement. They retained the Comber test, but instead of a fertility rating they used 3 categories of exchangeable calcium as determined by an oxalate turbidimetric test using an acid extractant. The quantities of limestone recommended for each Comber-calcium category differed from those used by Miller (1936). No mention was made of limestone quality. Because of the apparent absence of published material, it is assumed that the bulletin by Baver and Bruner served as a basis of lime recommendations up through the end of World War II.

The primary achievement of soil liming research during the period 1928 to 1946 was the improved estimation of the amount of lime to apply. Several extension publications on liming were published up through 1941. As World War II ended in 1945, faculty returned to campus to resume a departmental research program, and an influx of veterans financed by the GI bill provided a sizeable pool of graduate students. Going into 1947, the stage was set for rapid advancement of soil science knowledge and an explosion in agricultural production.

1947-1970

Significant changes occurred in agriculture in general and in the soil fertility programs of the Missouri College of Agriculture from 1947 to 1970. Manufactured fertilizer became readily available after World War II as a result of advancements made in the munitions industry during the war. Cheap nitrogen fertilizer for the first time became readily available. Use of ammonium nitrate and anhydrous ammonia increased almost exponentially after 1947. Both of these nitrogen fertilizers increase soil acidity, which increased the importance for a soil acidity monitoring program. The research and extension faculty of the Soils Department did an excellent job of providing an information stream for Missouri farmers, which resulted in increases in crop production and the use of fertilizers and liming materials.

During World War II, C.M. Woodruff served as an electronics scientist with the War Department. Upon his return to the University of Missouri after the war, he used his experience to construct a simple pH meter, which he called a limemeter. Potentiometers with a glass electrode and a calomel electrode were more accurate and precise in measuring active acidity than the Comber test or other indirect measurements. At the time the potentiometers used to measure soil acidity were fragile and expensive in part because of reliance upon tube electronics. Woodruff used his experience with the electronics of ruggedly built military radar instrumentation to make a rugged and cheap pH meter.

To supplement the limemeter, Woodruff formulated a buffer to estimate the lime requirement of soils. His initial publication reported that the buffer was formulated to have a pH of 7.0 (Woodruff, 1947). When mixed in the correct proportion with acid soil, the calcium and magnesium in the buffer mixture replaced exchangeable acidity from the soil exchange complex, which Woodruff called exchangeable hydrogen. In turn, this exchangeable acidity depressed the pH of the soil/buffer mixture. Woodruff stated that each 0.1 pH unit depression from 7.0 "corresponds to a requirement of 1000 pounds of 10-mesh mill run limestone per acre-plow-depth of soil" (Woodruff, 1947). The following year Woodruff published a refinement, which showed that each 0.1 unit of pH depression of the soil/buffer mix below 7.0 was equivalent to 1 me H per 100 grams of soil (Woodruff, 1948).

During the later part of the 1940s, Ellis Graham developed a set of simple soil tests that enabled each county to have a soil testing lab. Graham (1950) incorporated the Woodruff methodology of estimating the lime requirement of Missouri soils in his circular entitled "Testing Missouri Soils." This circular and the succeeding bulletin used the concept of ionic saturation of the colloidal complex, which subsequently was expanded into the Balanced Soil Saturation method of evaluating the cation balance in soils. Graham made no statements about limestone quantity or quality in his circular.

Later Graham (1959) expanded upon his concept of the balance of cations and salt pH. In theory if the balanced soil saturation concept was followed, a lime requirement could be calculated from the quantity of calcium needed to achieve 75% calcium saturation of the calculated CEC of the soil. Graham included a table to determine the effective calcium per ton of limestone using the CCE and percentage of particles that passed a 40-mesh screen with "proportionate amounts" through 8 and 100-mesh screens. The maximum effective calcium per ton allowed was 400 pounds per ton (Note that if a liming material has 100% CCE there should be 800 pounds of calcium per ton with the effectiveness reduced by particles larger than 100- or 60-mesh). Graham's publications served as resource material for the county lab soil testing program.

The county soil testing laboratories served the county agents (later many became area agronomists) in promoting increased crop yields through balanced fertility programs. The Soils Department provided the county labs with supplies and equipment at cost. Research faculty in the Soils Department developed a statewide program of soil fertility research, including liming studies to calibrate the soil tests for improved interpretation. George Smith, C.M. Woodruff, C.E. Marshall, Ellis Graham, Ted Fisher, and Earl Kroth all contributed to a strong soil fertility research program. Arnold Klemme, Marshall Christy, Alva Preston, and John Falloon (state extension soil fertility specialists) provided interpretive material and technical support during the years when the county labs were most active. The interpretive material enabled the county extension agents and later area agronomists to make recommendations for lime and fertility based upon soil tests run in the local soil testing lab.

Another addition to the soil evaluation program of the Soils Department in 1957 was the introduction of the salt pH measurement (pH_s or pH in a 1:1 soil and 0.01 M $CaCl_2$ suspension). This pH measurement was based on work by Schofield and Taylor (1955). It provided the grower with an estimate of the active acidity in the soil following application of the recommended amount of chemical fertilizer. The application of fertilizers, which are salts, tends to lower the pH of the soil. Both the Woodruff buffer and salt pH remain routine soil tests in the Missouri soil testing program.

Graham (1959) included an interpretive scale for soil pH measured in 0.01 M $CaCl_2$ suspension. This scale is reproduced as follows:

pH_s	**Interpretation**
>7.5	Alkali soil
7.5	Free lime
7.0	100% base saturation
6.5-7.0	Ideal for alfalfa, satisfactory for most crops
6.0-6.5	Ideal for most crops, satisfactory for alfalfa
5.5-6.0	Satisfactory for grasses, small grains and corn
5.0-5.5	Deficient in calcium, should be limed
4.5-5.0	Very deficient in Ca; unsatisfactory for almost all crops

Graham (1959) included the concept of balanced soil saturation in his revised bulletin. Simply stated, addition of liming material and potassium was needed to provide 75% saturation of the CEC with calcium, 10% with magnesium, 2.5 to 5% with potassium and the remaining 10 to 12.5% with acidity. This concept was included in Missouri lime and fertilizer recommendations in part as a teaching tool. Emphasis on the balanced soil saturation concept became minimal after 1968 for two reasons. Research demonstrated that considerable fluctuation in the percentages was possible without affecting crop performance. Further, the concept was expanded into areas of calcareous soils where soluble calcium inflated the CEC, resulting in unneeded recommendations of potassium.

Interpretation guidelines by Christy (1965, 1968) provided information on making lime recommendations for the period from 1961 through 1977. The Woodruff buffer procedure was used to estimate "exchangeable hydrogen" in a soil sample (Graham, 1959). Through 1965 the exchangeable hydrogen amount expressed in milliequivalents (Me or me per 100g) was multiplied by 400 to get an "acidity index." An acidity index of 400 represents the pounds of effective calcium per acre furrow slice of soil (2,000,000 pounds) equivalent to 1 me of exchangeable hydrogen per 100 grams of soil. The lime recommendation was given in pounds of effective calcium needed to neutralize the estimated acidity with 100 added to give a range in the recommended amount of lime. The grower calculated his actual agricultural lime need by dividing the acidity index on the soil test report form by the "effective Calcium Index" of the limestone to be used to get tons of limestone to apply per acre.

During this period recommendations included statements concerning the adequacy of calcium and magnesium as measured by soil tests based on the balanced soil saturation tables. Dolomitic limestone was always recommended when the percentage of magnesium saturation was below 10%. Soluble magnesium was recommended only when the magnesium saturation was below 5% of the CEC.

Significant changes in the soil testing program were started in 1968, which indirectly impacted both soil testing and the interpretation of those tests. The Missouri Cooperative Extension Service decided to start phasing out the county soil testing program and developed a computer program to interpret the soil test results. A regional soil testing lab was installed at the University of Missouri Delta Center in 1968. In 1976 a second regional soil testing lab started operation in Columbia. By 1977 there were only 26 county labs still operating, and these were gradually phased out.

In September 1968 the lime recommendation terminology and calculations were changed (Christy, 1968). The term "neutralizable acidity" was introduced to replace reference to "exchangeable hydrogen." Christy stated "1 ton per acre of standard agricultural limestone is required to supply enough carbonate to offset 1 Me of neutralizable acidity. The value 400 is used below because that figure represents 1 ton of "standard agricultural limestone" in the acidity index tables. Further, lime requirement guidelines for the first time considered pH_s. An attachment to a letter by Alva Preston, Extension Agronomist (Soils), dated August 2, 1968 is summarized below and was incorporated in Christy's material (Christy, 1968).

"1. For pH less than 6.0, multiply neutralizable acidity (Me) by 400."

The value 400 was the effective calcium content in 1 ton of "standard agricultural limestone." The Woodruff buffer had been formulated so that when used with the soil test procedure in theory each 1 Me acidity/100g of soil would depress the buffer pH 0.1 unit.

"2. For pH 6.0 to 6.5, enter 0 except for the following:"

For southern and southwestern soils where forage legumes were to be grown, use the effective calcium (ENM) representing 2 tons of limestone. For other conditions and locations, a maintenance application equivalent to 2 tons of limestone per acre was to be suggested.

"3. For pH 6.5 and above, enter 0."

Note that up to this point, several abbreviations for milliequivalents have been used including Me, me, and meq because of the direct quotations. The current preferred abbreviation is meq (Soil Sci. Soc. Am., 1997).

At this point it seems appropriate to insert some comment on limestone quality, although more detail will be provided in a later section. Prior to World War II, the standard for making lime recommendations was a limestone having nearly 100% passing a 10-mesh screen with a CCE of at least 95% (Trotter and Coleman, 1935). In the 1950s new lime and fertility recommendations adopted a standard limestone that had at least 50% passing a 40-mesh screen and "proportionate amounts through 8 and 100 mesh" and a CCE of 100% (Falloon, 1965). Limestone meeting these qualifications was given an Acidity Index of 400. Falloon (1965) included a table in his publication giving acidity indices for limestones with <100% CCE and/or <50% passing a 40-mesh screen.

The consolidation of the Soils Department and the Field Crops Department into an Agronomy Department under a new chair resulted in, among other activities, a total review of the soil fertility program in Missouri. From about 1968 through 1972 there was considerable activity that makes the time break we have made at 1970 somewhat arbitrary. The 1946-1970 period saw rapid development of the Missouri soil fertility and liming programs. The introduction of calibrated soil tests, the limemeter, increased availability of manufactured fertilizer and the Woodruff buffer all impacted the practice of liming acid soils during the 1947 through 1970 period. Fisher's summary of the liming experiments provided the substance behind the move toward the new liming programs introduced shortly after 1970 (Fisher, 1969).

1971-2000

At the start of the 1971 to 2000 period, the fertility recommendation programs were under review. The introduction of the computer and computer compatible laboratory instrumentation changed the way soil tests were done and interpreted.

Soil testing and recommendations

A gradual change occurred in soil extension activities, which in part might be attributed to the combination of the Soils Department and the Field Crops Department into the Agronomy Department. The state soil extension people were moved to Waters Hall leaving the soil research/teaching faculty in Mumford Hall. A formal Soil Testing and Soil Fertility Committee in the Agronomy Department was charged with the review of all soil fertility programs. This departmental committee continued a high level of activity through the initial tenure of Department Chair R.L. Mitchell and of E.C.A. Runge who followed Dr. Mitchell.

The Fisher (1969) summarization of the results of field lime studies conducted between 1956 and 1963 provided up-to-date calibration data for the Woodruff buffer and salt pH. Fisher summarized the data graphically using relative crop yield within a given site-year as the dependent variable and soil pH_s as the independent variable. Variable soil acidity levels were attained at the initiation of the experiments with the addition of agricultural limestone. Data were analyzed to determine the soil pH_s above which no additional yield increase would be expected. This provided a target pH_s to be attained by application of a "lime requirement" as agricultural limestone.

The review of soil testing and fertilizer and lime recommendations starting in 1969 led to computerization of recommendations. This computerization was finally accomplished in 1971 under the guidance of Dr. Roger Hanson and Marshall Christy.

Prior to the late 1940s, it was assumed that the soil should be near neutral for optimum crop growth. This assumption, in hindsight, likely came from the reliance on crop rotations containing legumes to provide a significant amount of nitrogen for the grain crops to follow. It was understood that one should lime to the needs of the least acid tolerant crop in the crop rotation. By mid-century the use of legumes as the major source of N had declined.

A Missouri liming materials law was passed in 1976 that set standards for agricultural liming materials and included some unique terminology. A discussion of liming material terminology will be included later in this publication. Effective neutralizing material (ENM) was introduced in the new law as the liming material quality designator.

By 1976 the definition of a standard limestone had changed to 50% or more passing a 40-mesh screen with all passing through an 8 and 25% through a 100 mesh screen (Christy, 1976). This change in definition of the standard limestone had been presented earlier by Coleman (1955), but it seemed to take nearly 20 years for it to be used. There are two reasons for pointing out these subtle changes. First, no data based verification for the changes in wording were found, and secondly, it was possible that some limestones were undervalued.

Recommendations were programmed into the University mainframe computer in 1977, and a hard copy was published for use manually (Hanson and Brown, 1977). These recommendations also incorporated the use of Effective Neutralizing Material (ENM) as the liming material quality factor dictated by the state liming law passed in 1976. Calculation of the ENM value of liming materials included an adjustment of the calcium carbonate equivalent (CCE), based upon the fineness assumptions given in the preceding paragraph. In 1985 the liming materials law was modified to include a new fineness factor for calculating the ENM of liming materials. The lime inspection program administered by the provisions of the law started using 8-mesh and 60-mesh screens in addition to the 40-mesh. Weighting was assigned to each particle size based on a review of literature that reported on effectiveness of different particle sizes of liming materials.

The computer program used for converting soil test results to recommendations was rewritten in 1980, particularly to condense the program from a table based interpretation to interpretations based on equations and to base the fertility recommendations, especially P and K, upon research reported by Fisher (1974) (Brown, et al., 1980). A few minor changes have been made in the recommendation program since 1980 (Buchholz, 1992).

The major events affecting the liming program during the 1970-1999 period was the passage of the Missouri liming materials law, especially a data-based-fineness evaluation, and the complete revision of the liming and fertility programs with the appropriate software written for interpretation of soil test results by computers.

Published research

Several field research projects started after the Fisher summary did not have liming as a primary objective, yet liming treatments within the studies provided insight to liming issues. For example, while studying fertility management of forages, Dr. Earl Kroth found that red clover could be successfully grown in established cool season grass fields with acid soils if 2 tons per acre of agricultural limestone were top dressed prior to seeding. Similar results were found by J.R. Brown in his studies on utilization of lime stabilized sludge from milk processing plants in southern Missouri (Brown et al., 1993).

In three studies in the early 1970s, Jim Roth and T.E. (Jake) Fisher evaluated cotton response to lime on three soils that are widespread in the Missouri Bootheel. As the soils varied in texture, CEC, pH_s, lime requirement, and exchangeable magnesium, Roth and Fisher using three distinctly different limestones were able to evaluate several aspects of the current lime recommendations. Table 1 shows the limestone treatments for the different studies (identified by soil series). Because the current limestone recommendations were not in use at the time of study initiation, treatments are given in tons/acre rather than lb ENM/acre.

Table 1. Limestone quantities applied by Roth and Fisher to three sites using cotton as a test crop.

Limestone Source*	Tiptonville	Portageville	Beulah**
		---------------------------- tons/acre ----------------------------	
Jonesboro, IL	0,2,4,8,12	0,2,4,8,12,24	none
Ste. Genevieve, MO (fine)	1,2,4	0.5 banded	2,4,8
Piedmont, MO (dolomitic)	none	none	0,2,4,8,12

*The Jonesboro and Ste. Genevieve limestones were calcitic. The Ste. Genevieve stone was more finely ground than the other two stones.
**Low soil magnesium (62 lb/acre ≈ 3.9% of the CEC).

Jonesboro limestone caused a slight non-significant cotton yield response on the Tiptonville loam soil with 2 tons/acre applied. The lime requirement of this soil (684 lb ENM/acre) with the Jonesboro lime (522 lb ENM/ton) was 1.3 tons per acre. Beginning with a pH_s of 5.3, the Jonesboro limestone increased pH_s linearly with the incremental rates to pH 7.0. Alternatively, the finely ground Ste. Genevieve limestone resulted in the pH_s plateauing at 5.8 with 2 and 4 tons/acre (Roth and Fisher, 1972a). This is consistent with earlier work.

Maximum seed cotton yield (through 8 years) was obtained on the Portageville clay soil with the 4 tons/acre treatment, significantly greater than the 2 ton/acre treatment. This soil with an initial pH_s of 5.8 and CEC of 23 meq/100g had a lime requirement of 748 lb ENM/acre, which translates to 1.4 tons/acre of the Jonesboro lime. So in this case the calculated lime requirement was less than the actual amount of lime that resulted in maximum yield. Maximum pH_s levels on the limestone treated soil occurred 5 to 6 years following application. Previous assumptions suggested that the full effect of lime on soil acidity maximized 4 years following application. Annual banding of the fine Ste. Genevieve limestone (at 500 lb/acre) had no effect on cotton seed yields (Roth and Fisher, 1972b).

Roth and Fisher recognized the low magnesium of the Beulah fine sandy loam (3.9% of the CEC — a minimum of 5% is recommended for row crops and 10% for forages) as an opportunity to evaluate dolomitic limestone relative to cacitic limestone. From the initial soil tests, the estimated lime requirement was 1.4 ton/acre for the Ste. Genevieve limestone (ENM of 788 lb/ton) and 1.7 tons/acre for the dolomitic limestone (ENM of 632 lb/acre). Only the first increment of both applied limestones (2 tons/acre) resulted in significant cotton yield increases. Thus the lime requirement seemed to be validated from the perspective of crop response. However based on a plot of pH_s versus ENM applied, an estimated 8 tons/acre (4728 lb ENM/ acre) of the St. Genevieve limestone would have been required to raise the pH_s to 5.9. Alternatively, 7000 lb ENM/acre of the dolomitic limestone would have been required to reach the same pH_s. Also observed, the finer calcitic limestone increased soil pH_s faster than the dolomitic limestone.

Roth and Fisher's results corroborated some of the limestone recommendations, but also indicated potential inconsistencies or needed refinements in others. On high CEC soils, the calculated lime requirement appeared to be underestimating actual needs. On low CEC soils, the estimated amount of limestone required to reach the target pH_s exceeded the actual amount to which cotton was responsive. There seemed to be no advantage to banding limestone.

During the 1970s and 80s, Dr. Earl Kroth included liming treatments (primarily placement and rate) in several forage studies that also investigated N, P, and K management. In one study there was no crop response to dolomitic limestone on a pH_s 4.0 soil (Kroth and Mattas, 1974). Red clover was successfully seeded into established cool season grass fields that had acid soils provided 2 tons of limestone were topdressed per acre prior to seeding. Similar results were observed in studies of surface applied lime-stabilized sludge in southern Missouri (Brown et al. 1993).

In an extensive study at the Southwest Missouri Research Center, Kroth and Mattas (1981) used five N-P-K topdressing treatments and four liming treatments (unlimed, 8 ton lime/acre plowed down, and top dressing treatments of 3 and 6 ton/acre). This study investigated the interactive effects of the acidifying effect of nitrogen fertilizer with limestone application on crop yields and soil pH and the effect of lime-stone placement (Table 2). The lime treatments were applied in 1972 (plowdown) and 1973 (topdressing), and forage yields were measured from 1974 through 1978. Specifications on the limestone used were not provided, however soil test results indicate that a dolomitic limestone was used. The only quarry in the vicinity of the Southwest Center that would supply such limestone was at Chesapeake, MO. Assuming no change with time of the limestone from the quarry, a 1997 analysis of this limestone (Missouri Agricultural Liming Materials Report, July 1 to December 31, 1997; Missouri Agricultural Experiment Station, 1998) indicated an ENM value of 432 lb/ton and an magnesium content of 2.5%.

Table 2. Lime placement treatments of a study at the Southwest Missouri Research Center.

Treatment	Applied ENM	Applied Mg	Yield*
Tons/acre	------------------lb/acre-------------------		
None	0	0	5,800b
3 top-dress	1296	150	5,820b
6 top-dress	2592	300	6,080b
8 plowed	3456	400	6,620a

*Values followed by the same letter are not significantly different.

Kroth and Mattas (1974) concluded, "Three T/A calcium limestone topdressed on tall-fescue is adequate to provide high quality forage free of weedy plants and grasses that are tolerant of acid soil." The only reference to sward composition was given on page 9 in their bulletin in which the zero lime plots were stated to have large quantities of "blackberry vines, sour dock and weedy grasses." One could challenge Kroth and Mattas' conclusion that 3 tons/acre top-dressed is an adequate lime treatment. The plow-down treatment of the study significantly increased hay yields over the topdress treatments. The long-term economics need to be calculated to determine if the extra expense of treating the plow layer with lime at establishment is justified.

Perhaps a more valuable component of this study was the soil data (Kroth and Mattas, 1981). At the conclusion of the study, they sampled every plot by one-inch increments to a total depth of 6 inches and tested each 1-inch increment. Initial soil test results made on samples randomly collected to a 7 inch depth over the entire study area were as follows:

> OM, 2.6%; pH_s, 4.7; neutralizable acidity, 6.1 meq/100g; Ca, 2025; Mg, 151; and K, 154 lb/acre; and CEC, 12.0 meq/100g.

During the seven-year period of the study, the 160 pounds of N applied each year as ammonium nitrate to all plots would have generated the equivalent of 3.4 me of acidity per 100 grams of soil (Kroth and Mattas, 1981)—each pound of N as ammonium nitrate theoretically will result in formation of acidity equal to 3.6 pounds of $CaCO_3$ (Havlin et al., 1999). This quantity of acidity attributable to the nitrogen was equivalent to over half the quantity of acidity in the soil initially. The 3 tons/acre treatment supplied

Table 3. Effects of limestone treatments on soil properties by 1 inch depth increments 7 years after treatment (Kroth and Mattas, 1981).

	Lime treatment*			
Soil Depth	None	3 T/a TD	6 T/a TD	8 T/a PD
inch		pH_s		
1	4.1	6.4	6.7	5.0
2	4.1	5.9	6.5	5.9
3	4.4	5.8	6.2	6.7
4	4.8	5.7	6.0	6.8
5	4.9	5.7	5.9	6.8
6	5.0	5.5	5.1	6.7
		Mg lb/acre		
1	135	227	202	259
2	75	120	99	203
3	93	98	80	166
4	96	85	80	128
5	91	83	76	107
6	94	83	86	98
		Ca lb/acre		
1	690	3540	4492	1810
2	567	2608	3177	2950
3	1184	2529	2814	3435
4	1654	2507	2721	3555
5	1932	2546	2658	3661
6	2049	2344	2479	3568

*TD = top-dressed; PD = 50% plowed down and 50% applied after plowing and disked in.

sufficient liming material (6 meq/100g) to neutralize the acidity initially in the soil. The pH_s results in Table 3 show that the soil treated with 3 tons/acre still reflected the neutralizing ability of the applied limestone seven years after application. The unlimed plots received the same quantity of N as the limed ones, but the pH_s in the upper three inches of soil dropped well below the initial pH_s of 4.7 (Table 3).

Limestone placement had marked effects on the distribution of the soil acidity neutralization. Despite no mixing with the soil, top-dressed treatments showed neutralization through the full 6 inches sampled. Where the limestone had been mixed with the soil (8 ton/acre plowed down), soil acidity appeared to be neutralized deeper than with the top-dressed treatments, but the acidifying N effect was marked in the upper 2 inches compared to the lower 4 inches of soil. The calcium data in Table 3 further demonstrate the effects of lime placement and N application over time. As Kroth and Mattas pointed out, the top-dressing effects on hay production were marked. This effect was in part due to the movement of calcium downward. Earlier in this paper reference was made to Albrecht's emphasis of the value of calcium added to acid soils as a benefit separate from but complementary to acidity neutralization (Albrecht, 1941).

The Kroth and Mattas work focused on semi-permanent forage production systems. The nature of permanent forage programs dictate that soil amendments such as limestone and fertilizer are surface applied once the forage is established. The use of the moldboard plow declined during last three decades of the 20th Century, and row crop producers shifted to reduced tillage or no-till culture. Therefore lessons learned from forage research may also be applicable to no-till culture.

Alkaline by-products such as kiln dust, lime stabilized sludges (biosolids), lime from clarifiers in sugar plants, and water treatment sludges have become available for land application in some areas. The increased number of potential combinations of liming materials and crop management practices raised several issues.

- How may the alkaline by-products substitute for agricultural limestone?
- Under what conditions can lime suspensions, pelletized lime, and by-products be used to correct soil acidity problems?
- How should no-till and reduced tillage fields be sampled to provide accurate guides to liming material application?
- How may variable rate application of liming materials be done on individual fields?

In addition to these concerns, there remain questions about longevity of lime treatments, ionic ratios (especially calcium and magnesium), impact of lime placement on the soil surface on sub-surface soil over time, and liming for forage establishment. A recent concern is the failure to reach the target pH_s after application of recommended quantities of limestone.

Recent sparse budgets have prevented addressing these questions that were deemed of lower priority than other agricultural production problems. Attempts were made to "bootleg" lime studies in other projects. However, the limited scope of the studies resulted in mixed successes. For example, Brown et al. (1993) found that lime stabilized biosolids were useful as lime sources in forage systems. Application rates based upon percent solids and ENM of the dried solids worked well.

Limited work showed that fluid lime, pelletized lime, and kiln dust products that the Missouri ENM measurement on dry basis worked well. An analysis of each product for other components is highly suggested. For example some kiln dusts have been found to contain sufficient boron to be toxic to sensitive plants. Most of these finely ground or suspended by-products will quickly lower soil acidity but do not maintain a higher pH as does quarry-run limestone which has a range in particle sizes.

Long-term research results on liming in no-till and reduced tillage cropping systems are scarce. The Kroth work demonstrated movement of the liming effect from the soil surface downward as much as 6 inches into the soil. Also Kroth and Mattas showed that when lime had been mixed to plow depth, application of acidifying N fertilizer to the soil surface over several years lowered the pH_s at least 2 inches below the surface. These observations, while on permanent forage fields, suggest that a soil-sampling regimen for pastures, hay fields, no-till fields and fields in other reduced tillage systems should be revised. A monitoring sampling program should consist of two samples from each field or sampling area of a field — a 2 to 3 inch sample and a 6 to 7 inch sample. There remains a need for lime-soil sampling calibration work on non-moldboard plow cropping systems.

Another concern is that of variable rate or precision farming. The authors have not seen sufficient research reports to properly address this concern. There is a limited amount of on-going research, but conclusive recommendations are not available. It is logical that where field variability is anticipated some form of systematic sampling be conducted. Application of lime can then be focused on the portion of the field that requires neutralization of acidity.

Liming recommendations of the 1950 to 1970 period in Missouri were based upon the balanced soil saturation concept incorrectly attributed to Dr. W. A. Albrecht. The concept, useful as a teaching tool in extension, originated in New Jersey. It was unfortunate that the concept useful for humid region soils was used on semi-arid soils. It resulted in applications of fertilizers to balance the ratios resulting from dissolution of calcium from calcareous soils, which inflated the CEC of the soil. This problem was deemed sufficiently important by members of North Central Region Soil Testing and Soil Amendments committees for them to develop a policy statement (Rehm, 1994). Fertility programs should be based on calibrated crop response to target soil test levels, rather than a particular balance between calcium, magnesium, and potassium. The Ca/Mg ratio idea has hung on far too long, as numerous studies have shown that the Ca/Mg ratio in soils can vary widely without detrimental effects upon crop performance. Deficiencies of either magnesium or calcium must be corrected. Toxicities of magnesium have not been documented in field studies, but allusions to poisonous levels of magnesium in soil still persist. Adverse effects of magnesium on rainfall infiltration into the soil profile have been suggested. As with the nutrient aspects of calcium and magnesium, any effect of magnesium on infiltration may well be due to lack of calcium to promote soil aggregation.

Concern about high pH_s levels in limed cropland soils surfaced especially in the 1990s. These conditions arose, in part, because in the early days of liming in Missouri, the quality of applied limestone was not appropriately accounted for in the recommendation procedures. Therefore, at times twice as much limestone was applied as needed for at least two reasons. First, was the mistaken idea that all soils should be limed to near pH 7.0. Second, limestone was evaluated only on the basis of CCE and percentage passing through a 40-mesh screen, and a maximum of 400 lb of effective calcium equivalent (ECE or ENM) per ton was allotted (Falloon, 1966). The consequence of use of a single screen size to estimate effectiveness and allowing at best-half credit for the CCE of the limestone was failure to properly account for the larger particle sizes, which slowly dissolve with time. The result was pH_s values on well-limed fields that exceeded 7.0. Consequently herbicide carryover has adversely affected succeeding crops. The changes in liming material recommendations brought about in the 1970s should avoid excessive increases in pH_s value. By fully crediting the effective calcium equivalent in liming material, the "cushion" of liming material has been removed. Close monitoring of soil acidity will be important with the removal of the "cushion."

Recent technology developments have focused attention, among other things, on patterns of soil acidity. Spacial variability of soil acidity is not new; the effects of dust from lime rock roads has been observed for most of the 20th Century. However, the means are available now to consider the inherent and manmade variability of the soil resource over the field on nutrient availability, herbicide effectiveness, and over-all crop vigor.

The research related to liming since 1970 has been limited. The work directed by Earl Kroth provided data to better account for placement of limestone and should be referred to when studies are designed to calibrate liming of unplowed fields with soil tests. Liming effects persist beyond four years meaning that long-term liming research is needed to provide justification for recommendations. The high CEC soils of the Missouri Bootheel seem to require additional calibration work based on the Roth and Fisher results.

Summaries of graduate student research

Between 1970 and 1999 several soil science graduate students conducted research on liming and soil pH problems. The students' theses are available for loan from Ellis Library on the University of Missouri campus. Short summaries of each student's thesis or dissertation are included in this section. A more comprehensive condensation of each has been included in Appendix D for the reader wishing more detail.

Measurement of soil CEC contains some uncertainty, especially considering its variable nature. Permanent CEC arises from the mineralogy of the clay sized particles, while pH-dependent CEC results from the chemical reactivity of many soil components, especially aluminum compounds and organic matter. In acid soils the measured CEC will usually increase as liming neutralizes the acidity. It is of value in the management of soil fertility to have an idea of the magnitude of the CEC of soil both before and after liming. Thus the estimation of the CEC is of value especially at the pH desired for crop production.

The estimation of a soil's CEC is useful for other purposes. For example, the USDA taxonomic classification of soils requires measurement of the percentage base saturation of selected diagnostic horizons (Soil Survey Staff, 1975). A relatively quick and precise method of CEC measurement is desirable for both plant nutrition and soil classification purposes.

Kenneth Benham — Estimation of exchangeable acidity

Kenneth Benham (1970), for his MS research problem, evaluated techniques to measure exchangeable acidity with reasonable accuracy. It was easier to titrate an acid soil to neutrality with $Ca(OH)_2/CaCl_2$ (standardized @ 0.01 M) solution than it was with the Mehlich $BaCl_2$/triethanolamine procedure (Soil Survey Staff, 1972). Many of the graduate students who followed Benham conducted research on liming related problems and used the $Ca(OH)_2/CaCl_2$ titration as the basic estimation of exchangeable acidity.

James Cisco — Buffer estimation of neutralizable acidity

James Cisco (1981) evaluated three buffer methods for estimation of neutralizable acidity for quick soil testing purposes. These methods were the old Woodruff buffer (Woodruff, 1947), the SMP buffer (Shoemaker et al., 1961) and a modified Woodruff buffer. The modified Woodruff buffer had been developed to replace the older formulation (Brown and Cisco, 1984).

Cisco used the $Ca(OH)_2/CaCl_2$ titration as the reference procedure for the estimation of neutralizable acidity. He used incremental rates of laboratory grade $CaCO_3$ added to acid soil in a greenhouse-pot study with soybean and in a closed-system incubation. Cisco's results supported the adaptation of the modified Woodruff buffer as a basis for estimating neutralizable acidity in farmer soil samples submitted for soil testing.

With the demonstration of a $Ca(OH)_2/CaCl_2$ titration as a useful reference procedure for measuring exchangeable acidity and the Woodruff buffer as the best available estimate of reserve acidity, succeeding graduate students focused on other problems and questions related to liming acid soils. One problem was the often reported failure of lime recommendations to raise the soil pH_s to the target range, especially in southern Missouri. Concurrently, some growers observed stand and germination problems with alfalfa seeded on recently limed fields

A.A. Yusef — Aluminum and lime requirements of southern Missouri soils

Many of the fields where questions about liming arose in southern Missouri were dominated by highly weathered soils developed from bedrock. These soils, mapped as Ultisols and some as Alfisols, have measurable amounts of exchangeable aluminum. Much of the field calibration work on liming practices prior to 1970 had been done on Mollisols and associated Alfisols in northern Missouri. These northern soils have higher amounts of soil organic matter and little exchangeable aluminum relative to the soils of southern Missouri. These facts led A.A. Yusef (1986) to study aluminum chemistry in these soils for his Ph.D. dissertation. His objectives were to characterize the nature of soil acidity and to evaluate alternatives to buffer procedures for estimating neutralizable acidity in southern Missouri soils containing significant quantities of exchangeable aluminum. He conducted pot studies with incremental rates of $CaCO_3$ using alfalfa and soybean as test crops. Like Cisco he incubated soils in a closed system to evaluate acidity changes resulting from incremental lime additions.

Yusef used several methods to estimate acidity. These included the New Woodruff and the SMP buffers to estimate neutralizable acidity. Exchangeable aluminum was extracted with 1 M KCl, 0.5 M $CuCl_2$, and 1 M NH_4Acetate @ pH 4.0. "Total acidity" was estimated using the Benham procedure, ($Ca(OH)_2/CaCl_2$). Yusef concluded that KCl exchangeable acidity may have merit as a basis for calculating lime requirements if the measured quantity of acidity was doubled and KCl extraction is restricted to soils with $pH_s < 4.8$. This conclusion needs field verification. The KCl extraction step would increase a soil testing lab's workload, as the pH_s would have to be determined and then a separate KCl extraction would be required if the $pH_s < 4.8$.

Maximum yields of both soybean and alfalfa were obtained in Yusef's greenhouse studies at pH_s values below the target levels used in the statewide liming program. The quantity of lime calculated to reach the pH_s range of 6.5 to 7.0 instead raised the pH_s only to the 6.0 to 6.5 range. Yusef noted that the soil pH_s increase to added lime was nearly linear from the mid 4s to nearly 6.5, which supported the published work by Magdoff and Bartlett (1985). Based upon the currently used formulas for calculating lime requirements using the Woodruff buffer, Yusef calculated that 16% of the lime requirement was needed to increase pH_s from 5.5 to 6.0, 20% from 6.0 to 6.5, and 29% from 6.5 to 7.0. Therein may lie the explanation for the failure of recommended lime requirement to reach target pH_s range because of the increased quantity of liming material needed to effect a pH change at higher pH values.

David Bennett — Liming forage legumes

Cisco and Yusef pointed out problems in calibration of acidity measures and liming material recommendations using greenhouse and incubation studies. Therefore, David Bennett, for his MS research, studied the adequacy of liming material recommendations for alfalfa, red clover, and lespedeza in a southern Missouri field study. This work was needed to help answer the questions about the failure of recommendations to reach the target acidity ranges. His project included a limestone particle size incubation.

The selected field sites were located in southwestern Gasconade County (Wilson site) and in Phelps County, southeast of Rolla (McWhorter site). Both sites were on Typic Paleudults. The soil used for Bennett's greenhouse and incubation studies was surface soil of a Typic Paleudult from a cleared site in the Mark Twain National Forest southwest of Rolla. The acidity-related measurements made on 0-6 inch soil samples from the three sites are recorded in Table 4.

Table 4. Acidic properties of soils used in the Bennett limestone studies.

Site	pH_s	Neutralizable Acidity	Exchangeable Al
		meq/100g	ppm
Greenhouse	4.8	4.0	24
McWhorter	4.7	4.5	14
Wilson	4.5	7.0	76

Bagged calcitic limestone (Columbia, IL) was used for the major part of the field studies. One treatment was a dolomitic limestone from a stockpile at a Beck quarry near Rolla. One greenhouse treatment was <60 mesh material from the bagged Columbia limestone. Inadequate bagged Columbia limestone was available for the Wilson site when the treatments were applied, so a limestone from Alton, IL (Mississippi limestone) was used instead on the lespedeza block. The limestone characteristics are given in Table 5.

Table 5. Characteristics of limestone used in the Bennett studies.

Limestone	ENM	Ca	Mg
	lb/ton	--------------%--------------	
Columbia	427	38.4	0.4
Columbia <60	782	38.4	0.4
Beck	342	18.8	8.9
Mississippi	448	35.0	0.1

Lime treatments were applied and plowed under in late summer 1988. The treatment quantities were based upon the lime requirement for alfalfa, red clover, and lespedeza for each location using soil test results (Table DB-1, Appendix D; Buchholz, 1983). The target pH_s range was 6.6 to 7.0 for alfalfa and 6.1 to 6.5 for red clover and lespedeza. The spreader could not be calibrated to deliver precise fractional increments of the lime requirements as planned, so the actual fractional application for each treatment was calculated from the amount of liming material spread (Table 6).

Soil samples taken in fall 1989 to a 6 inch depth showed that the treatments failed to reach the target pH_s range and did not show the incremental declines in acidity expected from the quantities of ENM applied (Table DB-7, Appendix D). The 1991 sampling showed the major limestone effects on soil acidity were in the 3-6 and 6-9 inch layers, suggesting that plow depth was nearer 9 inches than 6.67 inches as planned. Table 6, in addition to the fractional increments of the lime requirement calculated after treatment application, contains recalculated incremental treatments adjusted for a plow depth of 9 inches.

Seeding of the forages was completed in spring 1989. Yields only for 1989 were reported in Bennett's thesis, but the study was continued into 1991. Combined and individual yield results were not significantly affected by treatment. Summer moisture stress in 1989 and 1991 caused quite low yields (see Table DB-9 in Appendix D).

The average 1991 pH$_s$ results were plotted against the recalculated fractional lime requirements applied. From this plot the pH$_s$ for each quarter increment was estimated for each of the two sites giving the results in Table 7 (Appendix D, Table DB-7).

These results were surprising since the actual quantity of liming material applied for a given fractional treatment was greater for the more acid Wilson site. The Wilson site originally had 76 ppm KCl extractable aluminum and the McWhorter site had 14 ppm. These results suggest that as time passes after incorporation of lime into soils containing significant exchangeable aluminum, the lime is neutralized faster than would be expected based upon old calibration data. These results also support grower observations that the target pH$_s$ ranges are not reached when recommended lime requirements have been applied. The real puzzle in the Bennett results is why there were no significant yield responses to lime, especially at the Wilson site.

Table 6. Fractional limestone treatments used in Bennett's field studies on liming.

Treatment Number*	Limestone Source	McWhorter Alfalfa	McWhorter Red Clover	McWhorter Lespedeza	Wilson Alfalfa	Wilson Red Clover	Wilson Lespedeza**
		Original fraction of lime requirement***					
1	None	0	0	0	0	0	0
2	Columbia	0.42	0.49	0.49	0.26	0.30	0.48[2]
3	Columbia	0.83	0.98	0.98	0.52	0.60	0.96
4	Columbia	1.25	1.47	1.47	0.79	0.92	1.43
5	Columbia	1.67	1.96	1.96	1.04	1.20	1.91
6	Beck	1.09	1.28	1.28	0.70	0.81	1.27
		Recalculated fraction of lime requirement					
1	None	0	0	0	0	0	0
2	Columbia	0.28	0.33	0.33	0.17	0.20	0.32
3	Columbia	0.55	0.66	0.66	0.35	0.40	0.64
4	Columbia	0.82	0.98	0.98	0.52	0.61	0.95
5	Columbia	1.10	1.30	1.30	0.69	0.80	1.27
6	Beck	0.73	0.83	0.83	0.54	0.54	0.85

*The original quantities of limestone were determined assuming a 6-inch plow depth and quantity of limestone applied. The recalculated fractional applications were based on a 9-inch plow depth.

**The Mississippi limestone was used only on the lespedeza block at the Wilson site.

***The LRs were to increase pH$_s$ to 6.6-7.0 for alfalfa and 6.1-6.5 for red clover and lespedeza.

Table 7. Estimated pH$_s$ for fractions of lime requirements from plots of measured pH$_s$ and applied limestone adjusted to 9-inch plow depth.

		Fractional Lime Requirement				
Site	Species	0	0.25	0.5	0.75	1.00
McWhorter	Alfalfa	5.2	5.8	6.15	6.4	6.55
	Red clover	5.4	5.8	6.1	6.3	6.5
	Lespedeza	5.7	6.05	6.3	6.5	6.7
Wilson	Alfalfa	4.6	5.1	5.6	6.0	*
	Red clover	4.5	4.95	5.3	5.55	*
	Lespedeza**	5.1	5.4	5.65	5.8	5.9

*Based upon calculations the full lime requirement for 9 inches was not applied.

**Columbia limestone used for all except lespedeza at the Wilson site.

Maximum yields of the forage legumes in Bennett's greenhouse study were reached at 0.67 to 1.00 times the calculated lime requirements, which were at a higher fractional lime requirement than obtained by Yusef. The effect on soil pH_s in both studies was similar in that the lime requirement that was to bring the soil to a particular range actually resulted in a pH_s the next range lower (6.0 to 6.5 rather than 6.5 to 7.0). This might be explained by a shorter contact time of the lime treatments with soil in the greenhouse than in the field study. A different soil was used, so the field and greenhouse results should not be directly compared.

In an incubation study Bennett evaluated the relative effectiveness of particle sizes in changing soil acidity. The Beck limestone was sieved into separates using the screen sizes used to estimate of fineness by the Missouri Fertilizer and Lime Control Laboratory (>8, 8-40, 40-60, and <60 mesh). Lime requirements were calculated for each particle size including the bulk quarry run sample. Fractional quantities of the lime requirement were applied to soil in plastic bags. The soil/limestone mixture was then wetted to field capacity and incubated in the dark for 9 months. In 3-month intervals the incubated soil/lime mixture were sampled and pH in water and 0.01 M $CaCl_2$ were measured.

Table 8. The effects of quantities of different limestone particle sizes on pH_s of soils incubated for 9 months.

Material	Fraction of LR*	Incubation time-months 3**	6	9
None		4.5j	4.3h	4.2k
Bulk	0.33	5.8efg	5.4k	5.3h
	0.66	6.0def	5.9hi	5.9f
	1.00	6.2bc	6.5def	6.4de
	1.33	6.5a	6.6cde	6.6cd
	1.66	6.4ab	6.7bcde	6.6bcd
>8 mesh	0.33	4.5j	4.3n	4.2k
	0.66	4.8j	4.6m	4.5j
	1.00	4.6j	4.6m	4.5j
	1.33	5.1I	4.9l	4.9i
	1.66	5.1I	4.9l	4.8i
8-40 mesh	0.33	5.0i	5.0l	4.9i
	0.66	5.5h	5.6jk	5.5h
	1.00	5.7gh	6.0h	5.9f
	1.33	5.9efg	6.3fg	6.2e
	1.66	6.0cde	6.3fg	6.3e
40-60 mesh	0.33	5.7fgh	5.4k	5.5h
	0.66	6.1cd	6.5efg	6.4de
	1.00	6.4ab	6.7abcd	6.7bc
	1.33	6.6a	6.8ab	6.7bc
	1.66	6.5a	6.7bcde	6.7bc
<60 mesh	0.33	5.9defg	5.7b	5.7g
	0.66	6.4ab	6.8a	6.7abc
	1.00	6.5a	6.8a	6.8ab
	1.33	6.6a	6.9a	6.9a
	1.66	6.6a	6.8a	6.9a

*Particle size range and fraction of total lime requirement for alfalfa.

**pH_s values within a column followed by the same letter were not significantly different at the 5% level.

The pH_s of the untreated control samples declined over the 9 month incubation from an initial 4.8 (Table 8). This increase in acidity might have resulted from CO_2 generated by microbial activity. The greatest effect from the >8 mesh material was to maintain the acidity near the initial pH_s 4.8. The data in Table 8 supports the practice of not allowing effectiveness credit for particles >8 mesh. All particle size fractions, except the 8 mesh material, significantly lowered the amount of acidity in the soil (Table 8). The two finer particle size groups (40-60 and <60 mesh) raised the pH_s near the target pH_s (6.6-7.0) within 3 months and reached mid-range by 6 months. The 8-40 mesh material failed to reach the target range even when 1.66 times the lime requirement was applied.

The Bennett studies did not provide useful field yield-response data, due in large part because of severe moisture stress in 2 of the 3 summers of the field study. The McWhorter site would have reached the target pH_s range had the lime requirement been calculated for the actual depth of plowing. The Wilson site had significantly more aluminum (76 vs. 14 ppm) and less organic matter (2.0 vs. 2.3%) than the McWhorter site. The Wilson site when plowed supported a stand of stunted ragweed, while a vigorous stand of tall fescue was plowed under on the McWhorter site. The failure of any treatment on the Wilson site to exceed pH_s 6.0 concurs with farmer observations and likely was due to aluminum reacting with the liming material (Table 7). Unfortunately the site was sold and the project was terminated at the new owner's request.

The particle size results tended to support the weightings used for estimating the effectiveness of the different particle size groups.

Lime particle size serves as a rough index of surface area exposed by a given quantity of liming material. The finer the size of particles the greater is the surface area exposed to soil particles and moisture. That is, both quantity of material applied and particle size determine the reactivity of liming material (Table 8).

Jeffrey Stevens — Dissolution of limestone particles

In a moist acid soil that has been mixed with crushed limestone, soil moisture bathes both the soil and limestone particles. Acidity in soil solution attacks the limestone surface and is neutralized with calcium released from the particle into soil solution. In the past it was not possible to measure the rate and magnitude of these reactions. However the development of microelectrodes has permitted the measurement of the rate of limestone-soil solution interactions with time at selected distances from limestone particles into the soil surrounding the particles.

Jeffrey Stevens conducted an MS study on dissolution of limestone particles in a soil collected from Tucker Prairie that had an initial pH_s of 4.5. Microelectrodes were used to measure acidity changes at selected distances from individual limestone particles. Stevens found that dissolution occurred within 15 minutes, but the effect extended only 1.0 mm from the particles. The pH was always greater at a given distance from a calcitic limestone particle than a dolomitic limestone particle. Small leaching cells were used to simulate up to 4 years of leaching under Missouri rainfall conditions. Stevens observed no significant directional differences due to leaching. He presented a discussion of the possible reasons for this lack of significant difference, focusing upon the tortuocity of soil pores and the relative sizes of pores and limestone particles.

Stevens' work has significance for soil testing operations. In the North Central Region pH measurements include a 1:1 (w:v) soil:suspending-medium mixture and a 30 minute wait before the pH measurements are taken (Brown, 1998). Stevens' data showed that dissolution of limestone occurs within 15 minutes of wetting the soil. If in a soil sample undissolved limestone particles are present, it is likely that the measured pH of the soil suspension would be greater than in the field because of the nature of particle dissolution in suspension. At the plant root level, a growing root in a limed soil will be exposed to a range of active acidity.

The preceding studies made it clear that the chemistry of the acid southern Missouri soils is complex. Proper lime application seems to be highly dependent upon the behavior of soil aluminum and its reactions with liming material. It is also clear from the Yusef and Bennett studies that neutralization of acidity in high aluminum soils requires time in terms of months.

Syed Omar Syed Rastan — Soil aluminum behavior as it affects estimates of lime requirements

With an MS degree from the University of Georgia and with research experience in his native Malaysia on plant responses on soils high in active aluminum, Syed Omar Syed Rastan came to the University of Missouri to study. The objectives of his graduate research were to document changes in soil solution chemistry when highly acid soils are limed, evaluate methods to improve estimates of lime requirements of acid soils, and to conduct a pilot study on the influence of organic soil amendments upon active aluminum.

The surface soils of two southern Missouri Typic Fragiudalts (Captina and Hobson series) were collected as soil material for greenhouse and laboratory studies. Some chemical characteristics of the surface soil samples are given below in Table 9.

Table 9. Chemical characteristics of the surface soil samples for Syed Omar's studies.

	Exchangeable		Cation Exchange Capacity		
Soil	Al	NA[*]	Effective	NH_4Acetate	pH_s
	----------	----------	meq/100g ----------	----------	
Captina	3.3	9.0	4.2	9.9	4.0
Hobson	2.8	9.5	3.6	10.3	3.9

[*] Neutralizable acidity by the Woodruff buffer

A greenhouse study was conducted with alfalfa as a test crop through five harvests. Liming treatments included 0, 0.25, 0.5, 1.0, and 2.0 times the equivalent of the 1 M KCl exchangeable aluminum in each soil and another treatment that was the lime requirement for alfalfa based upon the Woodruff buffer estimate of neutralizable acidity. Note that Yusef (1986) suggested 2 times the 1 M KCl extractable aluminum as an alternative to the Woodruff buffer for estimation of lime requirement for high aluminum soils. The liming material (calcium and magnesium in a 6:1 ratio) and the soil were incubated in a closed system. Soil chemical parameters were measured at 1, 2, 5, and 10 months.

A second greenhouse study used 5 rates of lime as fractions of the KCl exchangeable aluminum (0, 0.5, 1.0, and 2.0 x) with a low C:N residue (alfalfa) and a high C:N residue (wheat straw). Alfalfa, the test crop, was grown through 4 harvests.

In the initial greenhouse study, the two soils were sufficiently acid that alfalfa did not grow without added lime. Alfalfa plants were not productive when grown on soil with lime applied at the 0.25 and 0.5 limed fractions of exchangeable aluminum. Maximum yields were obtained with the Woodruff-buffer-based lime requirement, which were 2.96 and 3.38 times the exchangeable aluminum equivalent for the Captina and Hobson soils, respectively.

Soil analyses made after the second and fourth harvests showed that, in spite of adding lime equivalent to the initial exchangeable aluminum, the active acidity produced a $pH_s < 4.9$ in both soils, but KCl ex-changeable aluminum was significantly lowered (Table 10). The lime requirement based upon the Woodruff buffer decreased the active acidity into the target pH_s range for alfalfa (6.5-7.0).

Table 10. Soil chemical parameters measured after the second and fourth harvests in greenhouse study 1.

			Post Harvest 2		Post Harvest 4	
Soil	Initial Al	Treatment[*]	Al	pH_s	Al	pH_s
			meq/100g		meq/100g	
Captina	3.3	0	1.9	4.1	2.0	4.1
		0.25	1.5	4.2	1.6	4.2
		0.5	1.2	4.4	1.2	4.2
		1.0	0.4	4.6	0.6	4.6
		2.0	0	6.1	0	5.8
		2.96[**]	0	6.9	0	6.2
Hobson	2.8	0	1.5	4.1	1.5	4.1
		0.25	1.1	4.2	1.2	4.2
		0.5	0.8	4.3	0.5	4.3
		1.0	0.3	4.8	0.4	4.7
		2.0	0	5.9	0	5.6
		3.38[**]	0	7.2	0	6.8

[*] Lime equivalent to the fraction of initial KCl exchangeable aluminum.
[**] Lime equivalent to the Woodruff buffer estimate of neutralizable acidity.

Syed's results do not agree with those of Yusef, Cisco, and Bennett. They found the Woodruff-based lime requirement raised soil pH_s only into the 6.0 to 6.5 range, but top yields of forage legumes were obtained at pH_s <6.5. Syed's results suggest that at higher lime rates aluminum may be slowly released from a form unextractable by KCl, based upon the decline of the active acidity even at 2.0 times the exchangeable aluminum and the Woodruff-buffer-based lime requirement.

Assuming that there is some level of non-exchangeable but labile aluminum in acid soils, as has been demonstrated in many studies, there remains the problem of estimating that labile aluminum so a more accurate lime requirement estimate may be made. Syed's evaluation of several extractants suggested that 0.33 M $LaCl_2$ merited further study, as he obtained maximum yields with the Woodruff buffer based lime requirement and $LaCl_2$ extracted no aluminum with that treatment (Table 11). The KCl extraction did not measure labile aluminum, while 0.5 M $CuCl_2$ and KCl plus ammonium citrate over-estimated labile aluminum. Oates and Kamprath (1983) also concluded that $LaCl_2$ was a better extractant than $CuCl_2$, because the $CuCl_2$ tended to over-estimate the organically bound aluminum in soils.

In Syed's second study, alfalfa grew without added lime with the low C:N plant residue on both soils. However, after the second harvest yields declined. Alfalfa could not be established without added lime when the high C:N residue was used. Yields of the greenhouse grown alfalfa continued to increase through 4 harvests only when lime was applied at twice the equivalent KCl exchangeable aluminum (see Appendix D, Table SO-7). The effect of the low C:N residue was temporary. However, further research may be merited to evaluate addition of such residues or organic waste materials with lime to enhance legume establishment when it is not convenient to apply the lime requirement a year ahead of legume establishment.

Syed's incubation which included extraction of soil solution indicated as expected that the concentration of calcium increased with lime, but it also suggested that the calcium activity may become sufficiently large that it would interfere with uptake or soil solution activity of other cations. However his study did not conclusively support the inference that a high concentration of active calcium may explain why some growers in southern Missouri have observed off-color early seedling growth of alfalfa.

Table 11. Extractable aluminum in two differentially limed soils as measured by extraction with four different extractants after 2 alfalfa harvests.

			Extractant***				
Soil	Lime*	pH_s	NA**	KCl	$LaCl_2$	$CuCl_2$	KCl + NH_4Citrate
			meq/100g				
Captina	0	4.1	6.37	1.92	2.27	3.50	3.64
	0.25	4.2	6.00	1.52	1.92	3.07	3.26
	0.50	4.4	5.50	1.19	1.58	2.68	2,93
	1.00	4.8	4.12	0.42	0.89	2.0	2.29
	2.00	6.1	1.75	0.00	0.22	1.43	2.00
	2.96	6.9	0.00	0.00	0.00	1.31	1.93
Hobson	0	4.1	6.75	1.47	1.85	2.59	2.82
	0.25	4.2	6.00	1.09	1.64	2.17	2.64
	0.50	4.3	5.50	0.80	1.28	2.00	2.56
	1.00	4.8	4.12	0.28	0.81	1.58	2.17
	2.00	5.9	1.75	0.00	0.25	1.18	1.90
	3.38	7.2	0.00	0.00	0.00	1.00	1.89

*Fractional equivalent of the initial KCl extractable aluminum.

**Neutralizable acidity using the New Woodruff buffer.

***1 M, 0.33 M, 0.5 M, and 1 M + 0.5 M, respectively.

Current Laboratory Methods and Interpretations

At the end of the 20th Century, two regional laboratories conducted soil testing for the Missouri Extension and Outreach programs at Portageville and Columbia. The two labs operated independently but are coordinated so that the same tests, recommendation program, and billing systems are used.

The methods used by the two regional soil testing labs for estimation of lime requirements were first published in 1977 (Brown et al., 1977; Brown and Rodriguez, 1983). The methods used to measure acidity and estimate liming material needs are unique to the Missouri program and differ from those used in the rest of the North Central Region (Brown, 1998).

Measurement of active acidity

Active soil acidity is estimated using a 1:1 soil/0.01 M $CaCl_2$ (wt/v) suspension. If pH in distilled water is desired (the North Central method) a 1:1 suspension is used with distilled water as the suspending liquid. Evaluation of pH_s is made by a rating system modified from that of Graham (1959).

Rating	Alfalfa	All other Crops
	pH_s range	
Very low	<5.0	<4.5
Low	5.0-5.8	4.5-5.3
Medium	5.8-6.5	5.3-6.0
High	6.5-7.5	6.0-7.5
Very High	>7.5	>7.5

The interpretation of these ratings, quoted from Buchholz (1983, page 27), is "Soils with a pH_s rating of very low or low have a definite need for limestone. These soils may be limiting yield potential due to severe soil acidity. A medium pH_s indicates a need for limestone very soon, but soil acidity is likely not so severe at this time to be causing yield reductions. Soils rated high have a soil pH_s optimum for crop growth and limestone is not needed at this time."

Neutralizable acidity

Neutralizable acidity is estimated with 10 g soil, 10 ml 0.01 M $CaCl_2$, and 10 ml of the *New* Woodruff buffer (Brown and Rodriguez, 1983). C.M. Woodruff changed the recipe for the buffer named for him around 1963. The new recipe increased the quantitative estimate of acidity by including an estimate of reactive aluminum. Unfortunately, Dr. Woodruff did not publish the new recipe. Brown and Cisco (1984) compared the old and New Woodruff buffers and the SMP buffer.

Hanson and Brown first published in 1977 the currently used interpretations of soil test results to provide quantitative lime requirements. As responsibility for the soil fertility extension program passed from Roger Hanson to Daryl Buchholz the format changed but not the substance.

The actual quantity of limestone recommended to a grower is based on the test of his soil. The target pH_s range is primarily fixed by the crop, but also in part, by the soil region. Soils for which alfalfa is planned should be limed to pH_s 6.6-7.0 in the Ozarks, Ozark Borders, and Cherokee Prairies of southern Missouri (soil regions 5, 6, 7, 8) and to pH_s 6.1-6.5 in all other soil regions. The target pH_s for all other forage legumes in regions 5, 6, 7, and 8 is 6.1-6.5. The target pH_s range for forage grasses throughout the state is 5.6-6.0. The reason for the higher pH_s for alfalfa and forage legumes in southern Missouri is to assure sufficient liming material to cause some leaching of calcium over time into the very acid, high exchangeable aluminum subsoils. The data of Kroth and Mattas (1981) showed that downward movement of the liming effect does take place given time. The target pH_s for all row crops throughout the state is 6.1-6.5.

Fisher derived the formulae used for calculating the lime requirement in ENM per acre for the Agronomy Department Soil Test Committee. Three target pH_s ranges are used in the program and the appropriate equations are reproduced below. Note that a multiplier of 400 is found in each equation. The value 400 represents the pounds of equivalent calcium per acre furrow slice (2,000,000 pounds of soil) needed to replace or neutralize 1 me of neutralizable acidity per 100 grams of soil.

pH_s Range 6.6-7.0

$$\text{LR ENM lb/acre} = 400 \text{ x NA}$$

pH_s Range 6.1-6.5

$$\text{LR ENM lb/acre} = 400 \{\text{NA} - [(\text{NA}) \div (41.425 - 10.307\ pH_s + 0.629\ (pH_s)^2)]$$

pH_s Range 6.1-6.5

$$\text{LR ENM lb/acre} = 400 \{\text{NA} - [(\text{NA}) \div (19.109 - 4.802\ pH_s + 0.297\ (pH_s)^2)]$$

Ratings of soil test magnesium and effective nutrient requirements to correct soil magnesium limitations are used when soil test magnesium falls below certain values (Buchholz, 1992).

Neutralizing value of liming material

Any grower requiring lime would take soil test results and recommendations to a liming-material dealer who by law must provide the lb ENM and lb EMg per ton of his agricultural limestone or other liming material. The tonnage of liming material required can be calculated with the following formula:

Tons/acre = lb ENM required per acre ÷ lb ENM per ton of liming material.

Two important measures of the acid neutralizing value of liming material are calcium carbonate equivalent (CCE) and the distribution of particle sizes or fineness of grind. Earlier in this paper it was pointed out that Missouri research demonstrated the value of finer limestone particles. Early evaluation of crushed limestone indicated that to be effective all liming material should pass a 10-mesh screen. As late as the mid-1960s, reference was made to ground limestone recommendations based upon the "percent passing 40 mesh screen (with proportionate amounts through 8 and 100 mesh)" (Falloon, 1966). In 1976 the Missouri legislature passed a Missouri Agricultural Liming Materials Law (Missouri Revised Statutes, 1976). All vendors of liming material sold in Missouri are required by law to provide the buyer quality information based upon CCE and fineness of grind.

The 1976 law raised many questions about the rules written to implement the law. In response to the criticism from vendors and others, J.R. Brown and Daryl Buchholz, MU Agronomy Faculty members and members of the Agronomy Department soil test committee, were asked to respond to the criticism by providing the "agronomic basis" for the various rules. This was done in a report submitted to the Director of the Missouri Agricultural Experiment Station and members of the Liming Materials Advisory Council established by RSMo 266.543 (Brown and Buchholz, 1981). This report was based on a review of published literature in which liming material purity (CCE) and/or particle size were studied.

The calculation of the Effective Neutralizing Material (ENM) for liming material was defined by the 1976 version of the lime law rules by the following formula:

ENM = %CCE/100 x [66.67 + (6.67 x % passing U.S. No. 40 sieve)]

The 1976 version of the rules for implementing the law stated that liming materials should have a minimum CCE of 70% and have a fineness range of 35% to 65% passing a 40-mesh screen. Brown and Buchholz could find no agronomic justification for the minimum CCE of 70% although the intent was to protect the buyer from the sale of impure liming material. The right-hand term of the preceding equation [66.67 + (6.67 + % passing U. S. 40 sieve)] had no sound agronomic basis either. The formula was devised around the maximum and minimum percentages passing a 40-mesh screen as written in the rules used to implement the law. If a liming material had 100% CCE and 65% passing a 40-mesh screen the ENM value would be 500 lb. per ton. The rules were worded so that any material passing the 40-mesh screen beyond 65% could not be used in calculation of ENM.

In the review by Brown and Buchholz the following conclusions were reached which parallels those of W.W. Hinish (1981) in Pennsylvania.

1. Limestone particles coarser than 20-mesh give some effect, but anything coarser than 8-mesh is of no value for agronomic liming material.

2. Maximum crop yields in fineness studies occurred when the liming material was finer than 60-mesh.

3. There was little advantage of grinding finer than 100-mesh.

4. Dolomitic limestone needs to be more finely ground than calcitic stone for equal effectiveness.

5. Thorough incorporation into the soil is needed for most effective neutralization.

Brown and Buchholz presented material that showed that the ENM calculation formula was incorrect, because it did not adequately address the relative effectiveness of different particle sizes. In fact, the formula implies an interaction between CCE and fineness that was not supported by any research-based literature. Finally, no justification for using any maximum ENM for liming material could be found. If a liming material is pure $CaCO_3$ (CCE = 100%), then it, in fact, contains 800 lb ENM per ton not 400. Therefore Brown and Buchholz concluded that the rules that implement the lime law should be changed to consider the relative effectiveness of different particle sizes of liming material in neutralization of soil acidity in a 2 to 4 year time frame.

In 1985 the Missouri Agricultural Liming Materials Law rules were modified. The revised rules specified a minimum CCE of 65% (6 CSR 250.10.020(2)). Fineness of grind was changed to require a minimum of 90% to pass an 8-mesh sieve [RSMo 266.505 (1)]. Much of the field research done in calibrating limestone applications to plant growth indicated that limestone particles larger than 8-mesh have relatively little effect in changing soil acidity in a 3 to 4 year period (Barber, 1984).

Particle size and solubility determine the rate of reaction of liming materials placed in acid soil. Small particle sizes are most effective in neutralizing soil acidity, because the finer particles expose more surface area per weight of material. For example, if one has a 1' x 1' x 1' solid cube of liming material it would have 864 sq. in. of surface area (6 sides times 144 sq. in. per side). Cut that cube into eight solid cubes each 0.5' x 0.5' x 0.5' doubles the exposed surface area of the material. Stevens (1990) showed the dissolution products of limestone move only a short distance, thus the more limestone surface exposed the more effective the material will be in neutralizing soil acidity.

The particle size distribution of liming material in the 1985 and the 1999 versions of the rules is determined by screening a sample through sieve sizes of 8-, 40-, and 60-mesh. After shaking a nest of the sieves, the material held on each is weighed and expressed as a percentage of the weight of the entire sample. These percentages as decimals are multiplied by an effectiveness factor for each particle size group shown below. The cumulative total of these values makes up the term Fineness Factor (73.9% in the example).

Screen size	Effectiveness Factor	Example Quantity	Example Weighting
Held on the 8-mesh sieve	0%	2%	0
Passed the 8-mesh, held on the 40-mesh	25%	14%	3.5%
Passed the 40-mesh, held on the 60-mesh	60%	34%	20.4%
Passed the 60-mesh	100%	50%	50.0%
Total		100%	73.9%

The weightings placed on the particle size groups were based upon published research reports and extension publications, principally from the North Central States of the United States. The particle size weightings were selected to estimate of the effect of particle size on the neutralizing ability of limestone over a 3 to 4 year period after incorporation into the upper 6 inches of soil in crop production fields. A review by Barber (1984) provided much of the availability information and would be a good reference to understand the complexity of providing a broad-based estimate of the neutralizing ability of agricultural limestones.

Many small particles in a volume of soil will be more effective than a few larger particles, but there are some negatives to very finely ground materials. First, the additional grinding to produce very fine particles adds to the cost of the limestone. Also, care must be taken in transporting and spreading dry fine material because wind easily moves finely ground solids, which may result in unequal spreading over the field. Larger particles will help maintain a given pH_s for a longer period of time than the finest particles.

One of the earliest guides to proper liming of acid soils was to mix the liming materials with the soil months ahead of planting an acid intolerant crop to allow acid neutralization to occur. The finer portion of the liming material (<60-mesh) would be expected to fully dissolve in a few weeks when mixed with acid soil. The larger particle sizes would provide staying power; that is, they would continue to dissolve over time to maintain the target level of acidity for 3 to 4 years. Now that minimum tillage is widely used, limestone rates likely need to be reduced and the frequency of application increased. This would be especially true if fertilizers are surface applied and not incorporated to plow depth (6 to 8 inches).

Use of liming materials that completely pass a 60-mesh sieve requires more frequent testing for soil acidity buildup, because there are no large particles of liming material to counteract acidity build up from acidic precipitation, crop removal and fertilization. Increasing the soil pH above 7.0 is undesirable, as nutrient availability and herbicide effectiveness may be adversely affected.

In making recommendations that specify limestone particle sizes, agronomists should recognize that for quarry operator there may be little interest in providing specific sized materials, as aggregate is the product of commercial interest and agricultural limestone is, at best, a sideline and, at worst, a waste product. However, because crop production is an acidifying activity that accelerates the natural tendency of soils to become more acid in humid regions, good liming practices should be based upon proper weighting of both fine (<60-mesh) and coarser (8 to 60-mesh) agricultural limestone particles.

Definitions

We have included in this section definitions that apply to liming acid soils. Some terms may have different meaning when used for other applications. Also, some terms have evolved to a meaning that varies from scientific usage. Refer to any soil fertility text, such as Havlin et al. (1999) and to the Soil Science Society of America glossary (SSSA, 1997) for detailed explanations of terms used in liming and soil acidity modification.

Acid soil — A soil with a pH <7.0

Active acidity — The activity of hydrogen ions in the soil solution. Active acidity is estimated by the pH soil test and is an extremely small quantity compared to exchangeable, reserve (residual) and total acidity in a soil.

Cation exchange capacity (CEC) — The capacity of soil particles to hold cations (positively charged ions). The sum of exchangeable bases and total acidity determined at a specified pH which is 7.0 in Missouri.

Effective neutralizing material (ENM) — The quantity of effective calcium equivalent in a liming material. It is determined by measuring the purity of the liming material, expressed as calcium carbonate equivalent (CCE), and multiplying the CCE by a fineness factor, determined by screening a sample of the liming material. The resulting product is multiplied as a decimal times 800 lb to get pounds of ENM per ton of liming material. The 800 lb is the quantity of calcium per ton in pure $CaCO_3$. Thus, ENM is numerically equivalent to effective calcium equivalent.

Exchangeable acidity — Acidity that is replaced from soil particles by an unbuffered salt solution.

Fineness factor — A calculated numerical value that estimates the effectiveness of a liming material based upon particle size distribution. In Missouri the factor is determined by screening a sample through sieve sizes of 8-, 40-, and 60-mesh. The decimal fraction held on each sieve is multiplied by the effectiveness factor to obtain a fineness value for the sieve size group. The cumulative total of these fineness values makes up the term Fineness Factor. An example is given below.

Screen size	Effectiveness Factor	Quantity Held	Fineness Value
Held on the 8-mesh sieve	0%	0	0
Passed the 8-mesh, held on the 40-mesh	25%	10	2.5
Passed the 40-mesh, held on the 60-mesh	60%	10	6.0
Passed the 60-mesh	100%	80	80.0
Total (Fineness Factor)			88.5

Lime requirement (LR) — the quantity of liming material needed to raise the pH of a volume of soil to some specified value expressed in pounds of effective neutralizing material (ENM) per acre.

Neutralizable acidity (NA) — the quantity of soil acidity estimated by the Woodruff buffer soil test.

Reserve acidity — Acidity held on clays and organic matter that can be neutralized by liming to pH 7.0 or some other target pH (also called residual acidity).

Total acidity — The sum of reserve and exchangeable. For soil testing purposes in Missouri total acidity is estimated by the Woodruff buffer procedure.

Salt pH — The pH measured in a soil-0.01 M $CaCl_2$ suspension (pH_s).

Water pH — The pH of a soil-distilled water suspension (pH_w).

Reevaluation of Missouri Limestone Recommendations Incorporating Recent (1993–1999) Soil Test Results

The current recommendations for correction of adverse soil acidity have been in use for about 30 years. The basis for these recommendations is the empirical relationship between two indices of soil acidity: pH_s and neutralizable acidity as measured by the Woodruff Buffer. The relationship was established from a soil test database of samples analyzed in the early 1970s. A larger more current soil test database is now available from which to examine soil-lime interactions.

Computing advancements since 1970 have vastly improved the ability to include more complex factors in recommendation calculations. Our improved understanding of soil-plant interrelationships as pertaining to liming and changes in cropping practices may also effect a need for revised recommendations. As a review of the basis of lime recommendations used by the Soil Testing Laboratory, this section has three objectives: 1) review the development of current recommendations, 2) compare the relationship between NA and pH_s as used in the current recommendations to that of a current data-base, and 3) consider potential changes that could update or improve lime recommendations. Questions to be evaluated include: 1) Should lime recommendations be based on percentage base saturation rather than pH_s and NA? 2) Should the "needed ENM" calculation be a function of pH_s, NA, and CEC? 3) Should Soil Regions continue to be included in the lime recommendation? 4) May a measure of extractable aluminum as it relates to NA improve recommendations for low pH_s soils (for example $pH_s < 4.8$)?

Development of current lime recommendations

The current algorithm of lime recommendations by the University of Missouri Soil Testing Lab was developed by T. R. Fisher in 1972. The *Soil Test Interpretations and Recommendations Handbook* (Buchholz, 1992) shows the algorithm as presently used. Fisher did not publish a detailed description of the development of his equations. However, in a letter to the Agronomy Department Soil Testing Committee dated July 20, 1972, he provided a brief description of three equations (Equations 1, 2, 3) that relate NA to pHs for the purpose of making lime recommendations. Each of equations 1, 2, and 3 assumes a different relationship between NA and pH_s. Fisher's letter and a description of his methods were published by J. R. Brown in Agronomy Miscellaneous Publication 84-03 (Brown, 1984). Included were tables that compared lime requirements calculated from the different equations at various pH_s and NA values. As a basis for his recommendation equations, Fisher used a database of about 30,000 soil samples analyzed by extension soil testing laboratories during 1970 and 1971.

Equation 1 was based on a linear relationship between pH_s and NA even though the actual relationship was curvilinear. Equation 1 consistently underestimated lime requirements on low pH_s soils.

$$ENM = 400 * \left(NA - \frac{NA}{14 - 2 * pH_s} \right) \qquad \text{Equation 1}$$

Equation 2 was based on the assumption that on average NA occupied 6% of the soil's CEC with a pH_s of 6.5 (Equation 2a) and 13.5% with a pH_s of 6.0 (Equation 2b). The assumptions were not accurate across all CEC groups (see Figure 1), and as a result some soils would not be given a lime requirement despite having a pH_s value less than optimum for plant growth.

$$ENM = 400 * [NA - (0.06 * CEC)] \qquad \text{Equation 2a}$$

$$ENM = 400 * [NA - (0.13 * CEC)] \qquad \text{Equation 2b}$$

Equation 3 is similar to Equation 1, but it was based on a quadratic relationship between NA and pH_s. Fisher's database (Figure 2A) and that of the 1990's database (Figure 2B) show this to be an accurate assumption. The constants a, b, and c in Equation 3 are obtained from the quadratic equations fitted to the curves in Figure 2A. The presently used lime recommendation equations are variations of Equation 3.

$$ENM = 400 * \left[NA - \frac{NA}{a - b * \left(pH_S\right) + c * \left(pH_S\right)^2} \right] \qquad \text{Equation 3}$$

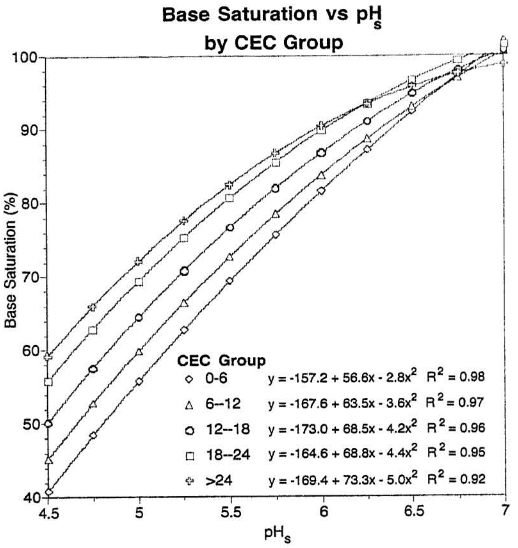


Figure 1. Percent soil base saturation versus pH_s

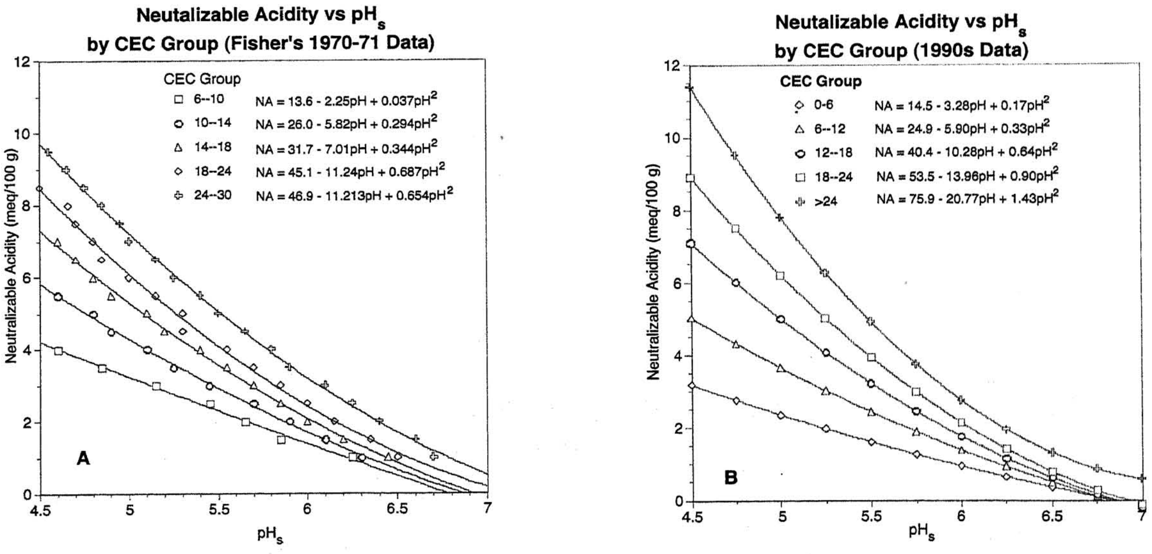


Figure 2. NA versus pH_S as varied by CEC group for A) 1970-1971 and B) 1993-1999 data sets.

Fisher's development of Equation 3 began with a mathematical description of a portion of the NA versus pH_s curve (Equation 4). A graphical example is given in Figure 3. The objective was to describe the portion of the curve (an amount of NA) from NA_o (NA observed) to NA_d (NA desired) and from the observed pH (pH_o) to the desired pH (pH_d). If NA = 0 then $pH_d = pH_v = pH_s$ 7.0.

$$\frac{dNA_o}{dpH_o} = C\left(pH_v - pH_o\right) \qquad \text{Equation 4}$$

where C is a constant

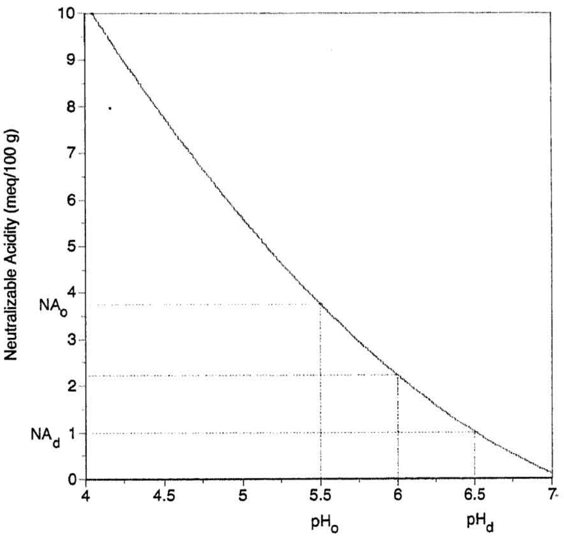


Figure 3. Graphical representation of the calculation of lime requirement (NA) from a NA versus pH_s curve. NA_o is the observed NA, NA_d is the NA at the desired pH_s, pH_o is the observed pH_s and pH_d is the desired pH_s.

Following integration, substitution and rearrangement, Equation 5 is obtained (see Brown, 1984 or Appendix A of this document for a complete description). The denominator in Equation 5 is a quadratic equation, which describes the NA versus pH_s curve. Fisher then could substitute coefficients from NA versus pH_s curves obtained from soil test data into Equation 5 (coefficients l, m, and n).

$$NA_d = \frac{NA_o}{l - m * pH_o + n * pH_o^2} \qquad \text{Equation 5}$$

The amount of NA to neutralize (NA_l) is represented in Equation 6.

$$NA_l = NA_o - NA_d \qquad \text{Equation 6}$$

The final step was to convert the equation into units of effective neutralizing material (ENM), which resulted in Equation 3. In the final algorithm, there were three variations of Equation 3 (Equations 7, 8 and 9), each of which was based on a different target pH_s (6.0, 6.5, and >6.5). With a target pH_s greater than 6.5, the quadratic part of Equation 3 drops out resulting in Equation 7.

$$ENM = (400) * (NA) \qquad \text{Equation 7—for a target } pH_s > 6.5$$

$$ENM = 400 * \left[NA - \frac{NA}{41.425 - 10.307 * (pH_s) + 0.629 * (pH_s)^2} \right]$$ Equation 8—for a target pH_s of 6.5

$$ENM = 400 * \left[NA - \frac{NA}{19.109 - 4.802 * (pH_s) + 0.297 * (pH_s)^2} \right]$$ Equation 9—for a target pH_s of 6.0

The precise dataset used by Fisher is now unavailable, so we are unable to recalculate precisely the coefficients in his recommendation equations (Equations 1, 2 and 3). Yet among the family of CEC group curves in Figure 2A, the coefficients from the 18-24 CEC group essentially match those in Equation 8. The 12-18 CEC group of the 1990's data set resulted in similar coefficients. For a target pH_s of 6.0 (Equation 9), integration of a smaller area of the NA vs pH_s curve results in smaller coefficients.

Evaluation of prospective changes to lime recommendation algorithm

Following the preceding review of data and the methods used to develop the current lime requirement recommendations, it is appropriate to review potential changes that would update or improve recommendations. Some considerations are issues that were originally considered by Fisher, but perhaps were not implemented because of limited computing capabilities. It is not our intent to promote one method over another; rather we want to review the legitimate alternatives to the presently used algorithm.

Use of Percent Base Saturation

Fisher originally explored the possibility of using average percent saturation of the soil exchange complex with NA as a means of making lime recommendations (see Equation 2). His objection to this approach was that occasionally no lime recommendation would be given for samples with pH_s values less than 5.6 or 6.1. As evident in Figure 1, there is a good relationship between base saturation and pH_s. At a target pH_s of 6.5, there is a small range (about 5%) in the percent base saturation across CEC groups. For the 12 to 18 CEC group, the percent base saturation is 95%. Similarly, there is a good relationship between NA and percent base saturation (R^2 between 0.93 to 0.98 across CEC groups). Thus it would be feasible to substitute a measure of base saturation for NA and use the current algorithm to calculate lime requirement. As Fisher noted, there would still be the problem of some soils not receiving a lime recommendation despite the observed pH_s being less than the target pH_s.

Varying Recommendations by CEC Group

The relationship between NA and pH_s is not the same across all soils as shown in Figure 2. As cation exchange capacity increases, it tends to buffer the release of protons from the exchange complex of the soil. The CEC groupings used in Figure 2 illustrate the differences in NA as related to CEC groups, which suggests that CEC may be included in equations used to calculate lime requirements.

In trying to follow Fisher's development of equations 8 and 9, he apparently used coefficients from the 18-24 meq/100 g curve to represent an average of the NA vs pH_s relationship. Using both the 1970's (Table 12) and 1990's databases (Table 13), we attempted to contrast lime requirements that result from Fisher's equations as varied by CEC group. Although the NA groups do not perfectly overlap between the two datasets, this exercise provides an opportunity to analyze the contribution that grouping soils by CEC would make toward improving lime recommendations.

In Tables 12 and 13, lime recommendations were calculated by substituting coefficients generated from curves in Figure 2 into Equation 8. Table 12 was generated from Fisher's 1970 and 1971 dataset (see Figure 2A), and Table 13 from the 1993 to 1999 data set (see Figure 2B). Each pH_s range reflects an appropriate range in NA for the CEC group. For each CEC group, the Curve Coefficient column was generated using coefficients taken from the quadratic equations that describe the curves (in Figure 2). The second column was generated using Equation 8, which remember represents an average CEC (18-24 meq/100g). In Table 12 there is no 18-24 CEC group for comparison, because this is the CEC group on which it is assumed that Fisher based Equation 8. The coefficients are essentially identical.

Table 12. Lime recommendations using coefficients from curves generated by 1970-1971 data set CEC groups that were substituted into Equation 8.

CEC Groups												
		6-10			10-14			14-18			24-30	
NA	pHs	Curve Coeff[†]	Avg Coeff[‡]	pHs	pHs	Curve Coeff	pHs	Curve Coeff	Avg Coeff	pHs	Curve Coeff	Avg Coeff
		lb ENM/acre			lb ENM/acre			lb ENM/acre			lb ENM/acre	
1.0	6.25	0	146	6.30	13	125	6.45	0	41	6.70	0	0
1.5	5.85	245	374	6.10	191	293	6.20	195	247	6.60	166	0
2.0	5.65	411	555	5.90	385	481	6.00	408	441	6.40	384	146
2.5	5.45	588	746	5.70	584	679	5.85	597	623	6.25	577	366
3.0	5.15	798	961	5.45	805	895	5.70	791	814	6.10	777	587
3.5	4.85	1005	1175	5.25	1008	1099	5.55	989	1011	5.90	1001	842
4.0	4.60	1202	1381	5.10	1199	1293	5.40	1189	1211	5.80	1186	1029
4.5	4.30	1409	1594	4.90	1406	1501	5.20	1406	1428	5.65	1393	1249
5.0	4.10	1599	1795	4.80	1589	1690	5.10	1593	1617	5.50	1601	1469
5.5				4.60	1798	1900	4.90	1809	1835	5.40	1794	1665
6.0				4.45	1996	2101	4.80	1999	2028	5.25	2004	1884
6.5				4.25	2206	2311	4.70	2192	2222	5.15	2200	2083
7.0				4.15	2396	2505	4.60	2385	2418	5.00	2410	2301
7.5							4.45	2591	2626	4.95	2596	2484
8.0							4.30	2796	2834	4.85	2795	2686
8.5							4.20	2992	3032	4.75	2995	2889
9.0							4.00	3208	3249	4.65	3196	3093
9.5										4.55	3397	3297
10.0										4.45	3598	3501
Average Difference[#]			163			100			31			-131

[†]Curve coefficients used from curves shown in Figure 2A and substituted into Equation 8.
[‡]Average coefficients used by Fisher in Equation 8—approximately that of the CEC group 18-24.
[#]Average ENM difference between the Curve Coefficients and the Average Coefficients (Fisher's 18-24 CEC Group) across all pH_s values.

Because of the similarity of curve slopes, there is little difference in ENM recommendations between CEC groups. For CEC groups with values less than the presumed 18-24 meq/100 g in Fisher's Equation 8, lime requirements (Curve Coefficient column) are slightly less than recommended by Equation 8 (Avg. Coefficient column). At greater CEC values, lime requirements of the CEC groups are slightly greater than that of the average. The greatest discrepancies between CEC group recommendations and the average CEC recommendation are with the low CEC groups. The curve of the 6-10 CEC group deviates from the other CEC groups by being more linear (small value for the squared term). However, because of the relatively small NA values that are associated with the low CEC soils, ENM recommendations differ only slightly. A direct comparison of CEC-group curves between the two datasets is not possible, because the data were not identically grouped. However there appears to have been little change. An exception is the largest CEC group. The curve for the >24 group (1990s data set) is more strongly curvilinear than the 24-30 group (1970s data set). This may be due to improved precision of lab techniques. The 1970s' dataset consisted of significant numbers of samples that were run in county labs, while

Table 13. Lime recommendations using coefficients from curves generated by the 1993-1999 dataset CEC groups that were substituted into Equation 8.

	CEC Groups														
	0-6			6-12			12-18			18-24			>24		
NA	pH_s	Curve Coeff[†]	Avg Coeff[‡]	pH_s	Curve Coeff	Avg Coeff	pH_s	Curve Coeff	Avg Coeff	pH_s	Curve Coeff	Avg Coeff	pH_s	Curve Coeff	Avg Coeff
		lb ENM/acre			lb ENM/acre			lb ENM/acre			lb ENM/acre			lb ENM/acre	
1.0	6.25	0	146	6.30	0	125	6.45	0	41	6.50	0	2	6.70	0	0
1.5	5.85	69	374	6.10	96	293	6.20	126	247	6.35	76	152	6.60	59	0
2.0	5.65	226	555	5.90	293	481	6.00	345	441	6.15	326	362	6.40	282	146
2.5	5.45	402	746	5.70	498	679	5.85	538	623	6.00	533	551	6.25	486	366
3.0	5.15	633	961	5.45	729	895	5.70	738	814	5.85	744	748	6.10	703	587
3.5	4.85	860	1175	5.25	937	1099	5.55	942	1011	5.70	958	950	5.90	953	842
4.0	4.60	1068	1381	5.10	1128	1293	5.40	1149	1211	5.55	1173	1155	5.80	1148	1029
4.5	4.30	1291	1594	4.90	1340	1501	5.20	1376	1428	5.40	1387	1362	5.65	1371	1249
5.0	4.10	1488	1795	4.80	1522	1690	5.10	1567	1617	5.20	1619	1587	5.50	1594	1469
5.5				4.60	1736	1900	4.90	1792	1835	5.10	1815	1779	5.40	1796	1665
6.0				4.45	1937	2101	4.80	1986	2028	4.90	2042	2002	5.25	2017	1884
6.5				4.25	2151	2311	4.70	2182	2222	4.80	2240	2196	5.15	2221	2083
7.0				4.15	2341	2505	4.60	2379	2418	4.70	2440	2393	5.00	2441	2301
7.5							4.45	2591	2626	4.60	2640	2590	4.95	2631	2484
8.0							4.30	2801	2834	4.45	2852	2801	4.85	2836	2686
8.5							4.20	3001	3032	4.30	3064	3011	4.75	3042	2889
9.0							4.00	3222	3249	4.20	3265	3210	4.65	3248	3093
9.5													4.55	3455	3297
10.0													4.45	3661	3501
Average Difference[#]			299			167			55			-19			-125

[†] Curve coefficients used from curves shown in Figure 2A and substituted into Equation 8.

[‡] Average coefficients used by Fisher in Equation 8—approximately that of the CEC group 18-24.

[#] Average ENM difference between the Curve Coefficients and the Average Coefficients (Fisher's 18-24 CEC Group) across all pH_s values.

the 1990s data came from only two labs (Columbia and Portageville). With the elimination of the county labs, potentially more NA would have been measured on low pH_s soils. Subsequently, a greater curvilinearity resulted in the 1990's dataset curves. Nevertheless, lime recommendations generated from the 1970s' and 1990s' datasets were relatively similar. The small differences due to CEC are not large enough to justify the inclusion of CEC groups in the algorithm.

Varying Recommendations by Soil Region

Soils across Missouri vary considerably with respect to weathering and parent material (see Appendix B), and these differences affect the nature of reserve acidity. In general, weathering of soils in the state increases to the south and east from the northwest corner of the state. Soil regions were established in the recommendation algorithm in order to provide region-specific lime recommendations. Present recommendations vary only by the target pH_s for forage legumes in the Cherokee Prairie, Ozark and Ozark Border regions (Soil Regions 6, 7, and 8).

Each NA versus pH_s curve for any CEC group shown in Figure 2 could be considered an average, comprising a group of curves that result from individual soil regions. An example of a family of curves by soil region for two CEC groups is shown in Figure 4. At lower pH_s values and the larger CEC groups, the NA values of some soil regions diverge from the "pack" of curves of other soil regions. In particular, curves of Soil Regions 6 and 7 lie above those of other soil regions. For Soil Regions 6 (Ozarks) and 7 (Ozark Border), the greater NA per pH_s may be a consequence of increased activity of soil aluminum. As was observed with the different CEC groups, the similarity of curve slopes as varied by soil region would result in little difference in ENM recommendations.

Is There a Need for a Measure of Extractable Aluminum?

The activity of soil aluminum increases appreciably at pH_s values of 4.5 or lower. At such low pH_s values, aluminum activity in soil solution becomes toxic to plant growth. In Missouri the problem of low pH_s and toxic aluminum is mostly isolated to the highly weathered Ozark soils. Even when the surface soil acidity is reduced by application of liming materials, the subsoils remain highly acidic. The present lime recommendations account for the acid subsoils by increasing the amount of lime recommended for legumes. The increase in lime requirement results from an increase in the desired pH_s. The hoped-for-effect is that the greater amount of lime will neutralize some of the subsoil acidity. The effectiveness and efficiency of such an increased lime application toward alleviating aluminum toxicity can not be quantified, but Kroth and Mattas (1981) showed that the liming effect will move downward given time.

It must be remembered that the NA measurement is an index of reserve acidity, and may not accurately represent acidity that results from soil aluminum. A measurement of extractable aluminum may indicate the potential for additional reserve acidity. Yusef (1986) and Syed Rastan (1995) both showed that neither KCl extractable aluminum nor two times that amount of aluminum was a satisfactory estimate of lime requirement. Syed Rastan (1995) had promising results from aluminum extracted with 0.33 M $LaCl_2$. As with any index such as the laboratory measurement of NA, field calibration is necessary to determine the actual effectiveness of the limestone amount recommended by the NA measurement.

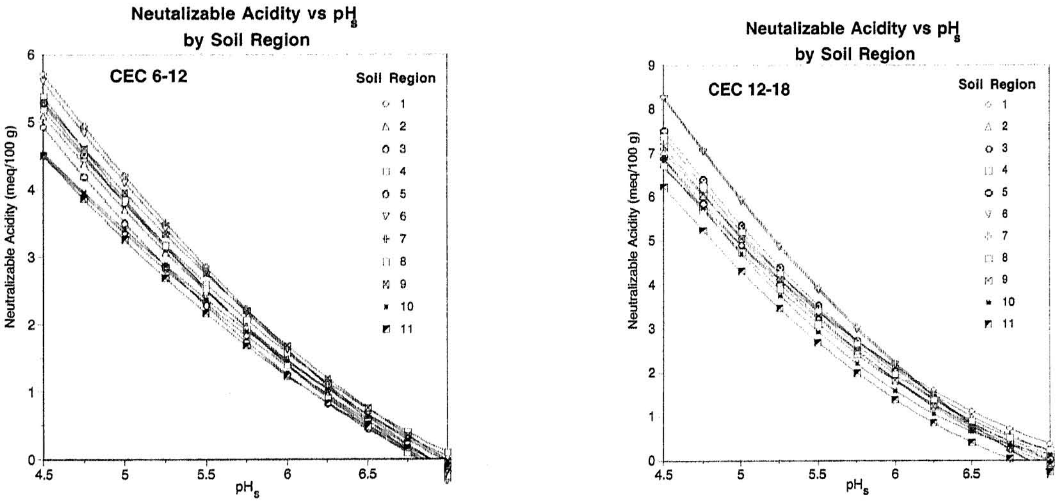


Figure 4. Soil Region effect on NA vs pH_s curves for a) 6-12 CEC and b) 12-18 CEC. 1993 to 1999 data set.

Summary and recommendations

The current lime recommendation algorithm used by the University of Missouri Soil Testing Laboratory has not changed in 30 years since implementation. The essence of the algorithm is that NA and pH_s are measured in the laboratory, and then an empirical relationship between the two is used as the basis for determining the amount of limestone to apply. The algorithm is not varied by soil CEC. Soil test results collected from 1993 to 1999 indicated that the relationship between NA and pH_s is essentially unchanged relative to the data set used in 1972 when the current algorithm was developed. The algorithm was developed such that differences in the NA versus pH_s relationship due to CEC or Soil Region do not dramatically affect limestone recommendations. Thus we do not propose the inclusion of CEC in a new algorithm. We feel that the work by Kroth and Mattas (1981) justify retaining the separate recommendation for legumes grown in Soil Regions 6, 7, and 8.

With each curve of NA versus pH_s examined, there was a considerable scatter of data points around the fitted curve. Identifying the sources of such scatter may lead to modifications in the algorithm that improve recommendations. Some soils may be more buffered against limestone applications. That is, the NA versus pH curve for some soils may have a greater slope or greater curvilinearity than expressed by the recommendation equations. Similarly, different liming materials may vary in their neutralization of soil acidity to a target pH. For example some liming materials may be somewhat self-buffered through reduced dissolution. Some soils may also have large amounts of extractable aluminum, and the NA measurement may not accurately express all of the reserve acidity.

This review of the basis of liming recommendations and its historical background provide the necessary information to answer the questions posed at the start of this section of the paper.

1. Should lime recommendations be based on percentage base saturation rather than pH_s and NA?

   No. Percentage base saturation is calculated from the sum of the milliequivalents of basic cations divided by the CEC. The estimate of basic cations in the soil comes from the soil tests for potassium, calcium, and magnesium, all extracted with 1 M ammonium acetate. The estimate of NA, which is obtained using the Woodruff buffer, is necessary to get the CEC. Thus, no test would be eliminated by using the percentage base saturation method for making recommendations. As yet, there is no quick test method to substitute for the Woodruff buffer as a measure of NA unless there was a significant increase in turn-around time for soil testing.

2. Should the "needed ENM" calculation include CEC in addition to pH_s and NA?

   Probably not. The review using the 1993-1999 data set showed minimal ENM differences (fractional ton of limestone) in recommendations when CEC was included in the algorithm between the current algorithm and the algorithm including CEC. If however, improved precision in calculated quantities is desired, then computing capabilities make this a simple change.

3. Should soil regions continue to be included in lime recommendations?

   A qualified yes. The review using the 1993-1999 dataset suggests using the soil regions added little to the value of the lime recommendations. However, the ultisols of the highly weathered Ozark region have profound effects on rooting depths due to high levels of aluminum. For this reason it seems desirable to continue to use a separate algorithm for soil regions 6 and 7. The curves in Figure 4 showed that Region 7 was somewhat different from the other regions. Historical data have been presented that showed downward movement of the liming effect with time on highly acid soils.

4. May a measure of extractable aluminum as it relates to NA improve recommendations for low pH_s soils?

   Not at this time. Research by Yusef and Syed presented in this paper is not adequate to support inclusion of an extractable aluminum soil test on low pH_s soils. There were no field data on which to base recommendations, even though both former students showed that such a test is feasible. Syed's work suggested that 0.33 M $LaCl_2$ had potential for a test, but requires field calibration; greenhouse results are inadequate for calibration. Addition of an aluminum test to the soil testing program would increase the turn-around time for results and require some laboratory improvements to be able to analyze for aluminum.

No-tillage culture of crops was virtually unknown when the present limestone recommendations were developed. The assumption of the present recommendations is that all liming material is evenly distributed throughout the depth of tillage. Thus a target pH should be achieved uniformly in the tillage depth. As all row crops have a target pH_s of 6.1 to 6.5, application of lime only to the soil surface will likely violate the assumption of reaching a target pH_s with the recommended amount of lime. The NA versus pH_s curves show soil, particularly high CEC soils, to be more buffered at pH_s near or above 6.5. So it seems likely that no-till lime recommendations would require modification.

The average relationship between NA versus pH_s (across all soils) seems to be well defined and provides a good basis for making limestone recommendations. Future directions for liming research should evaluate the impact of extractable aluminum, examine the effects of different liming materials and the response of different soils to effect changes in pH_s. The principles of recommending lime based on laboratory measurement of NA and pH_s seem well based. However, further field calibration of these indices remains ever necessary.

Evaluation of Existing Laboratory Procedures and Suggestions for Improvements in the Limestone Recommendation Programs

As the authors compiled this document, several concerns arose about the management of acid agricultural soils. Mankind has recognized the benefits of liming for centuries as was pointed out in the section on history of liming. Yet today it seems that agricultural producers and researchers have relegated liming to a lessor status than other aspects of crop management.

In this era of precision in agriculture, improving the precision of liming has been difficult. Recommendations for lime based upon quick soil tests often do not lower the soil acidity to the desired levels. Further, liming does not always increase crop yields. There are several reasons for these inconsistencies. First, the quasi-quantitative estimation of the need for liming material seems to under-estimate the amount of soil acidity needing neutralization. Second, assumptions about the ideal soil acidity levels for each crop species (and perhaps variety) may over generalize the actual situation. Third, it is incorrect to assume the ENM measure of reactivity of individual liming materials can be uniformly applied regardless of the physical and chemical properties of individual liming materials. Fourth, recommendations need to be recalibrated for reduced tillage systems, because liming material often is not mixed with the "plow layer" of soil but is placed on the soil surface and mixed only superficially.

The recommendations for liming material in Missouri are based upon the estimate of neutralizable acidity using the Woodruff buffer and an estimate of active acidity in a suspension of soil and 0.01 M $CaCl_2$. Both measurements are made after about 30 minutes of soil/solution contract. While this may be adequate for the measurement of active acidity, the contact time may be insufficient to get a true measure of the labile acidity needing neutralization for optimum growing conditions. The graduate student research summarized herein was inconsistent in finding an optimum measurement of the need for liming material, although 0.33 M $LaCl_2$ extraction of aluminum has possibilities. Any quick test that appears to be improved over existing procedures must be calibrated to field response of crops under field conditions over a period of time. Based upon the experience with the studies reported in this paper, that time period should be a minimum of 10 years. Our experience suggests that no source of funding is available that will support the needed fieldwork for extended time periods. The 1993-1999 data base showed that Soil Regions 6 and 7 have many acres of very acid soil, yet because of the dominant grass-forage-based agriculture of those regions, profit margins are so narrow that financial support of liming research is not considered cost effective.

Research may improve the laboratory portion of the program. The assumption that 1 milliequivalent of acidity per 100 grams of soil will depress the Woodruff buffer pH by 0.1 unit needs to be reevaluated using very acid soils and aluminum solutions. Further, it might be helpful to manipulate the standing time for the soil-buffer mixture in an attempt to better estimate the reserve or labile acidity due to slow release of bound aluminum.

In addition to questions concerning exactly what the Woodruff buffer does and does not measure, Missouri research suggests that the three target pH_s ranges may be too high. Likely these ranges have a built in "cushion" based on the assumption that growers will not monitor soil acidity sufficiently to detect a gradual drop in pH_s. In addition, these targets may need reevaluation for specific crops. The research upon which the targets are based is, in most cases, older than 25 years. Field work reported by Fisher (1969), Roth and Fisher (1972a, 1972b, 1973) and Bennett (1990) indicated that optimum response to liming treatments in the field is not as predictable as theory suggests.

Our summary of research also suggests that liming materials differ in their reactivity in acid soil. The liming materials used for agriculture lime come from different geologic strata. Geologists characterize the different limestone strata by crystalline structure and physical properties, which in part, would explain differences in dissolution rates and reactivity. We were unable to find any Missouri work that had been designed to determine if dissolution differences affected crop response to lime. Stevens (1990) showed that dolomitic limestone was less effective in neutralizing soil acidity than calcitic stone. Further, some unreported work suggested that certain dolomitic stones will raise the pH only to the mid 6.0s. As we pointed out earlier in the paper, the effectiveness of the different particle size groups needs to be reevaluated, as the 8-40 and 40-60 mesh sizes may be undervalued.

The acceptance of reduced tillage practices makes the lime calibration work done with moldboard plow primary tillage questionable for use in making liming material applications. Unincorporated lime applied to the soil surface results in a greater concentration of the liming material than if thoroughly mixed with the "plow layer." Thus the lime requirement perhaps should be less. Stevens showed that the impact of dissolution of limestone extends only a short distance from the particle and occurs in a very short time. Kroth and Mattas found that surface application of limestone in relatively small quantities was adequate for establishment of clover stands in fescue sod. The timing of lime application affects seedling establishment. Unless time is allowed for reaction of the limestone dissolution products with acid soil, local build up of calcium may adversely affect seedlings, especially alfalfa (Syed, 1995).

The recent emphasis on precision farming for row crops, while focusing on the major nutrients (N, P, K), also considers banding of lime, variable rate application over the field, and frequent application of finely ground or pelletized liming material. Over application of liming material, especially finely ground material, may excessively increase pH_s and interfere with the reactivity of pesticides. There is a limited amount of ongoing research on these later topics, which is not ready to be reported. It is likely that the studies should be expanded, especially to measure the long-term effects of precision and variable rate production practices.

References

Adams, F. 1984. Crop response to lime in the southern United States. Chapter 5. *In* F. Adams. Soil acidity and liming, 2nd ed. Agronomy Monograph 12. American Society of Agronomy. Madison, WI.

Albrecht, W.A. 1941. Drilling limestone for legumes. Missouri Agricultural Experiment Station Bulletin 429.

Albrecht, W.A. and G.E. Smith. 1952. Soil acidity as calcium (fertility) deficiency. Missouri Agricultural Experiment Station Research Bulletin 539.

Allgood, F.P. and L.D. Persinger. 1979. Missouri general soil map and soil association description. USDA SCS Missouri State Office, Columbia, MO.

Barber, S.A. 1984. Liming materials and practices. Chapter 4. *In* F. Adams. Soil acidity and liming, 2nd ed. Agronomy Monograph 12. American Society of Agronomy, Madison, WI.

Barlow, J.T. 1916. Soil acidity and the litmus paper method for its determination. Jour. Amer. Soc. Agronomy 8:23-30.

Bauer, F.C., A.L. Lang, C.J. Badger, L.B. Miller, C.H. Farnham, P.E. Johnson, L.F. Marriott, and M.H. Nelson. 1945. Effects of soil treatment on soil productivity. Illinois Agricultural Experiment Station Bulletin 516.

Baver, L.D. and F.H. Bruner. 1939. Rapid tests for estimating the fertility needs of Missouri soils. Missouri Agricultural Experiment Station Bulletin 404.

Benham, K.E. 1970. Salt pH and base saturation of some Missouri soils. Unpublished MS thesis, Library, University of Missouri, Columbia, MO.

Bennett, D.R. 1990. Agronomic response of three forage legumes to agricultural limestone. Unpublished MS thesis. Library, University of Missouri, Columbia, MO.

Bertsch, P.M. and P.L. Bloom 1996. Aluminum. p. 517-549. *In* D.L. Sparks (ed.). Methods of soil analysis 3. Chemical methods. Soil Science Society of America. Madison, WI.

Black, C.A. 1967. Soil-plant relationships. 2nd ed. John Wiley and Sons, Inc. New York, N. Y.

Bloom, P.R. 2000. Soil pH and pH buffering. Chapter 10. *In* M.E. Sumner (ed.). Handbook of soil science. CRC Press, Boca Raton, FL.

Bloom, P.M., M.B. McBride, and R.M. Weaver. 1979. Aluminum soil organic matter in acid soils: Salt extractable aluminum. Soil Sci. Soc. Am. J. 43:83-85.

Blosser, D.L. and H.Jenny. 1971. Correlations of soil pH and percent base saturation as influenced by soil-forming factors. Soil Sci. Soc. Am. Proc. 35:1017-1018.

Brown, J.R. 1984. A discussion of problems in making lime requirement estimations. Agronomy Department Misc. Publ. 84-03, University of Missouri-Columbia.

Brown, J.R. (ed.). 1998. Recommended chemical soil test procedures for the North Central Region. North Central Regional Research Publication No. 221 (Revised). Missouri Agricultural Experiment Station Special Bulletin 1001.

Brown, J.R. 1981. Laboratory manual of chemical methods of evaluating the nutrient status of soils. Agronomy Department Misc. Publ. 81-04, University of Missouri-Columbia.

Brown, J.R., W. Bough, and C. Hoenshell. 1993. Using food processing waste on fields. Missouri Cooperative Extension Service publication G9332, University of Missouri, Columbia, MO 65211.

Brown, J.R. and D. Buchholz. 1981. Limestone effectiveness factors. Unpublished Report, Agronomy Department, University of Missouri, Columbia.

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.

Brown, J.R., J. Garrett, and T.R. Fisher. 1977. Soil testing in Missouri. Missouri Extension Circular 923.

Brown, J.R., R.G. Hanson, and D.D. Buchholz. 1980. Interpretation of Missouri soil test results. University of Missouri Agronomy Department Misc. Publication. 80-04 (mimeo).

Brown, J.R. and R.R. Rodriguez. 1983. Soil testing, a guide for conducting soil tests in Missouri. Missouri Cooperative Extension Service Extension Circular 923 (revised).

Buchholz, D.D. 1983. Soil test interpretations and recommendations handbook. Unpublished Handbook, Department of Agronomy, College of Agriculture, University of Missouri, Columbia, MO.

Buchholz, D.D. 1992. Soil test interpretations and recommendations handbook (Revised). Unpublished Handbook, Department of Agronomy, College of Agriculture, University of Missouri, Columbia, MO.

Christy, C.M. 1965. General instructions for interpretation of soil tests. Mimeo. University of Missouri, Soils Extension Program.

Christy, C.M. 1968. General instructions for interpretation of soil tests. Mimeo. University of Missouri, Agronomy Extension Program.

Christy, C.M. 1972, Soil testing. Mimeo, Agronomy Extension, University of Missouri- Columbia.

Christy, C.M. 1976. Liming Missouri soils-guided by soil tests. University of Missouri-Columbia Extension Division Science and Technology Guide 9101.

Cisco, J.R. 1981. Estimating the lime requirements of Missouri soils. Unpublished MS thesis, Library, University of Missouri, Columbia, MO.

Clark, R.B. 1984. Physiological aspects of calcium, magnesium, and molybdenum deficiencies in plants. Chapter 3 *In* F. Adams. Soil acidity and liming, 2nd ed. Agronomy Monograph 12. American Society of Agronomy. Madison, WI.

Coleman, N.T. and M.E. Harward. 1953. The heats of neutralization of acid clays and cation exchange resins. J. Amer. Chem. Soc.75:6045-6046.

Coleman, N.T., S.B. Weed, and R. J. McCracken. 1959. Cation-exchange capacity and exchangeable cations in Piedmont soils of North Carolina. Soil Sci. Soc. Am. Proc. 23:146-149.

Coleman, O.T. 1955. Lime your soil for better crops. University of Missouri Agricultural Extension Service Circular 651 (revision 1/1957).

Comber, N.M. 1920. A qualitative test for sour soils. Jour. Agr. Sci. 20:10:420-424.

Council on Soil Testing and Plant Analysis. 1980. Handbook on reference methods for soil testing (revised edition). The Council on Soil Testing and Plant Analysis, Athens, GA.

Coyne, M. 1999. Soil microbiology: An exploratory approach. Delmar Publishers, Albany, NY.

Duley, F.L. and M.F. Miller.1926. The soil experiment fields of Missouri. Missouri Agricultural. Experiment. Station Bulletin 238.

Falloon, J. 1966. Know your lime. University Of Missouri Extension Circular 61.

Farina, M.P.W. and P. Channon. 1991. A field comparison of lime requirement indices for maize. p. 465-473. *In* R.J. Wright, V.G. Baligar and R.P. Murrmann, (eds.). Proceedings of the second international symposium on plant-soil interactions at low pH. Kluwer Academic Publishers. Dordrecht, The Netherlands.

Fisher, T.R. 1969 Crop yields in relation to soil pH as modified by liming acid soils. Missouri Agricultural Experiment Station Research Bulletin 947.

Fisher, T.R. 1974. Some considerations for interpretation of soil tests for phosphorus and potassium. Missouri Agricultural Experiment Station Research Bulletin 1007.

Foy, C.D. 1984. Physiological effects of hydrogen, aluminum, and manganese toxicities in acid soil. Chapter 2. *In* F. Adams. Soil acidity and liming. 2nd ed. Agronomy Monograph 12. American Society of Agronomy. Madison, WI.

Gamble, E.E. and M.J. Mausbach. 1982. Summary report, Missouri Ozark soils-a geomorphic study. Soil Staff, NSSL, and MNTC, Soil Conservation Service, USDA, Lincoln, NE.

Graham, E.R. 1959. An explanation of theory and methods of soil testing. Missouri Agricultural Experiment Station Bulletin 734, Columbia, MO

Graham, E.R. 1950. Testing Missouri soils. Missouri Agricultural Experiment Station Circular 345. Columbia, MO.

Hanson, R. and J.R. Brown. 1977. Handbook: Missouri computerized soil test recommendations, Interim revision. Mimeo, Department of Agronomy, College of Agriculture, University of Missouri, Columbia, MO.

Hartwell, B.L. and F.R. Pembee. 1918. Aluminum as a factor influencing the effect of acid soils on different crops. Jour. Amer. Soc. Agronomy 10:45-47.

Hassett, J.J. and W.A. Banwart. 1992. Soils and their environment. Prentice Hall, Englewood Cliffs, NJ.

Havlin, J.L., J.D. Beaton, S.L. Tisdale and W.L. Nelson. 1999. Soil fertility and fertilizers: An introduction to nutrient management. 6th ed. Prentice-Hall, Upper Saddle River, NJ.

Hinnish, W. W. 1981. The importance of aglime fineness. Limestone 18:72:29, 2,3.

Jenny, H. 1961. Reflections on the soil acidity merry-go-round. Soil Sci. Soc. Am. Proc. 25:428-432.

Juo, A.S.R., and E.J. Kamprath. 1979. Copper chloride as an extractant for estimating the potentially reactive aluminum pool in acid soils. Soil Sci. Soc. Am. J. 43:35-38.

Kamprath, E.J. 1984. Crop response to lime on soil in the tropics. Chapter 9. *In* F. Adams. Soil acidity and liming, 2nd ed.. Agronomy Monograph 12. American Society of Agronomy, Madison, WI.

Kroth, E.M. and R. Mattas. 1981. Effect of top-dressed limestone, nitrogen, phosphorus, and potassium on yield and mineral content of tall fescue forage and soil test values. Missouri Agricultural Experiment Station Research Bulletin 1040.

Kroth, E.M. and R. Mattas. 1974. Yields and soil test values resulting from topdressing forage crops. Missouri Agricultural Experiment Station Research Bulletin 1005.

Krusekopf, H.H. 1938. Soil fertility investigations: Brown limestone land of southwestern Missouri. Missouri Agricultural Experiment Station Bulletin 395.

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

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

McLean, E.O. and J.R. Brown. 1984. Crop response to lime in the Midwestern USA. Chapter 6. *In* F. Adams. Soil acidity and liming, 2nd ed. Agronomy Monograph 12. American Society of Agronomy, Madison, WI.

McLean, E.O. M.R. Heddleson, R.J. Bartlett, and N. Halowaychuk. 1958. Aluminum in soils: I. Extraction methods and magnitudes in clays and Ohio soils. Soil Sci. Soc. Am. Proc. 22:382-387.

Mehlich, A. 1948. Determination of cation and anion exchange properties of soils. Soil Sci. 65:429-445.

Miller, M.F. 1909. Some results with lime on Missouri soils. Jour. Amer. Soc. Agronomy. 1:228-233.

Miller, M.F. 1936. Testing soils for acidity by the modified Comber method. University of Missouri Agricultural Extension Service Circular 339.

Miller, M.F., C.B. Hutchinson and R.R. Hedelson. 1915. Soil experiments on the Gray Prairie soils of southwest Missouri. Missouri Agricultural Experiment Station Bulletin 130.

Miller, M.F. and H.H. Krusekopf. 1920. Agricultural lime. Missouri Agricultural Experiment Station Bulletin.171.

Missouri Agricultural Experiment Station. 1998. Missouri agricultural liming materials report, July 1 to December 31, 1997. Fertilizer Control Division, Missouri Agricultural Experiment Station, Columbia, MO.

Missouri Revised Statutes, 1976 (Revised, 1999). Missouri agricultural liming materials law, Sections 266.500-266.550, Missouri State Legislature, Jefferson City, MO (Rules: 6 CSR 250-1020 and 6 CSR 250-10.010-6 CSR 250-10.050.

Oates, K.M. and E.Kamprath.1983. Soil acidity and liming. II. Evaluation using aluminum extracted by various chloride salts for determining lime requirements. Soil Sci. Soc. Am. J. 47:690-692.

Peech, M. 1963. Exchange acidity. *In* C.A. Black et al. (ed.) Methods of soil analysis, Part 2. Agronomy 9:905-913. American Society of Agronomy Inc., Madison, WI.

Rehm, G. 1994. Soil cation ratios for crop production. North Central Regional Publication 533. Minnesota Extension Service, University of Minnesota, St. Paul, MN 55108-6069

Roth, J.A. and T.E. Fisher. 1972a. Limestone and nitrogen application influence on cotton yields and soil tests in Portageville clay soil in southeast Missouri. Missouri Agricultural Experiment Station Research Bulletin 986.

Roth, J.A. and T.E. Fisher. 1972b. Limestone and nitrogen application influence on cotton yields and soil tests in a Tiptonville silt loam soil in southeast Missouri. Missouri Agricultural Experiment Station Research Bulletin 1002.

Roth, J.A. and T.E. Fisher. 1973. Limestone and nitrogen application influence on cotton yields and soil tests in Beulah fine sandy loam in southeast Missouri. Missouri Agricultural Experiment Station Research Bulletin 1002.

Ruffin, E, 1821. On the composition of soils, and their improvement by calcareous manures. Am. Farmer 3:313-320 (From Barber, 1984).

Schnitzer, M. and U.C. Gupta. 1965. Determination of acidity in soil organic matter. Soil Sci. Soc. Am. Proc. 29:274-

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

Scrivner, C.L., J.C. Baker, and D.R. Brees. 1963. Combined daily climatic data and dilute solution chemistry in studies of profile formation. Soil Sci. 115:213-223.

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

Sims, J.T. 1996. Lime requirement. Chapter 17. *In* D.L.Sparks et al., eds. Methods of soil analysis, Part 3. Soil Sci. Soc. Am. Book Ser. 5, Soil Science Society of America and American Society of Agronomy, Madison, WI.

Smith, G.E. 1942. Sanborn Field, Fifty years of field experiments with crop rotations, manure, and fertilizers. Missouri Agricultural Experiment Station Bulletin 458.

Snedecor, G.W. and W.G. Cochran. 1980. Statistical methods. 7th ed. The Iowa State Press. Ames, IA.

Soil Science Society of America. 1997. Glossary of soil science terms-1996. Soil Science Society of America, Madison, WI, 53711.

Soil Survey Staff. 1972. Soil survey laboratory methods and procedures for collecting soil samples. USDA Soil Survey Investigations Report No. 1.

Soil Survey Staff. 1975. Soil taxonomy. USDA Agricultural Handbook 436. Government Printing Office, Washington, DC.

Stevens, J.J. 1990. Limestone dissolution and pH gradients in soil. Unpublished MS Thesis. Library, University of Missouri, Columbia, MO.

Syed Rastan, Syed Omar. 1995. Application of lime and crop residues to ameliorate phytotoxic aluminum in two acid Missouri soils. Unpublished Doctoral Dissertation, Library, University of Missouri, Columbia, MO.

Thomas, G.W. 1982. Exchangeable cations. Chapter 9. *In* A.L. Page (ed.). Methods of Soil Analysis, Part 2, Second edition. American Society of Agronomy, Madison, WI.

Thomas, G.W. and W.L. Hargrove. 1984. The chemistry of soil acidity. Chapter 1. *In* F. Adams. Soil acidity and liming, 2nd ed. Agronomy Monograph 12. American Society of Agronomy, Madison, WI.

Trotter, I.P. and O.T. Coleman. 1928. How to use agricultural limestone. Missouri Agricultural Extension Service Circular 208.

Trotter, I.P. and O.T. Coleman. 1935. Using limestone on Missouri soils. University of Missouri Agricultural Extension Service Circular 322.

VPI. 1953. How soil reaction affects the supply of plant nutrients. VA Polytechnic Institute Agricultural Extenuation Service Bull 136 (Revision of Pettinger, N. A. 1935. A useful chart for teaching the relation to soil reaction to the availability of plant nutrients in crops. VPI Agricultural Extenuation Service Bull 136.).

Watson, M.E. and J.R. Brown. 1998. pH and lime requirement. Chapter 4. *In* J.R. Brown (ed.). Recommended chemical soil test procedures for the North Central Region, NCR Research Publication 221 (Revised). Missouri Agricultural Experiment Station Special Bulletin 1001.

Woodruff, C.M. 1947. Determination of the 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.

Woodruff, C.M. 1948.Testing soils for lime requirement by means of a buffered solution and the glass electrode. Soil Science 66:53-63.

Yusef, A.A. 1986. Estimation of lime requirements of selected southern Missouri soils. Unpublished Doctoral Dissertation. Library, University of Missouri, Columbia, MO.

Appendix A

Development of the Lime Requirement Equations by T. R. Fisher

In 1972 Dr. T.R. Fisher developed a system to interpret the Woodruff Buffer pH to calculate recommended amounts of limestone that would alleviate deleterious soil acidity to crops. A basic assumption was that soil acidity should be reduced to a level that resulted in an optimum pH. Related to this is the fact that a soil's pH_s is related to its base saturation, or conversely its base unsaturation. The Woodruff Buffer pH estimates a soil's base unsaturation, which is reported as neutralizable acidity (NA). As a soil's CEC increases so must the quantity of neutralizable acidity to maintain a given pH_s. Thus for any given CEC, the pH_s and NA are related and can be expressed mathematically. In the following discussion several subscripts will be used with the pH symbol. All subsequent references to pH infer a pH measured in 0.01 M $CaCl_2$—the standard method of pH measurement used by the University of Missouri Soil Testing Laboratory.

The quantity of NA to be neutralized is the difference between NA in the soil initially (NA_o at an initial pH, pH_o) and the NA in the soil at the target pH (NA_d). A target pH is defined as specific desired pH less than or equal to 7.0.

For a curve that describes NA versus pH, the change in NA relative to a change in pH is described as

$$\frac{dNA_o}{dpH_o} = C(pH_v - pH_o)$$

where NA_o is the observed NA, pH_o is the observed pH, and pH_v is the pH where NA = 0. The integral of this expression is

$$\int dNA_o = C\int (pH_v - pH_o)dpH_o$$

Upon integration ($0 < NA < NA_o$ and $pH_v < pH < pH_o$)

$$NA_o = \frac{c}{2}(pH_v - pH_o)^2 + Ci$$

when $pH_o = pH_v$, NA = 0, therefore the integration constant Ci = 0 and

$$NA_o = \frac{c}{2}(pH_v - pH_o)^2$$

If we define a target pH as pH_d (desired pH), then when $pH_o = pH_d$, $NA_o = NA_d$. Thus

$$NA_d = \frac{c}{2}(pH_v - pH_d)^2$$

Upon rearrangement

$$\frac{c}{2} = \frac{NA_d}{(pH_v - pH_d)^2}$$ and

$$NA_o = NA_d \frac{(pH_v - pH_o)^2}{(pH_v - pH_d)^2} \quad \text{or}$$

$$NA_d = NA_o \frac{(pH_v - pH_d)^2}{(pH_v - pH_o)^2}$$

Upon inversion the expression becomes

$$\frac{1}{NA_d} = \frac{1}{NA_o} \frac{(pH_v - pH_o)^2}{(pH_v - pH_d)^2}$$

Expansion of the numerator gives

$$\frac{1}{NA_d} = \frac{1}{NA_o} * \frac{pH_v^2}{(pH_v - pH_d)^2} - \frac{1}{NA_o} * \frac{2pH_v pH_o}{(pH_v - pH_d)^2} + \frac{1}{NA_o} * \frac{pH_o^2}{(pH_v - pH_d)^2}$$

If we define coefficients l, m, and n as

$$l = \frac{pH_v^2}{(pH_v - pH_d)^2}, \quad m = \frac{2pH_v}{(pH_v - pH_d)^2}, \text{ and } n = \frac{1}{(pH_v - pH_d)^2}$$

then

$$\frac{1}{NA_d} = l * \frac{1}{NA_o} - m * pH_o \frac{1}{NA_o} + n * pH_o^2 \frac{1}{NA_o}$$

which results in

$$NA_d = \frac{NA_o}{l - m * pH_o + n * pH_o^2}$$

In this form pH is related to NA as a second-degree polynomial, and coefficients from empirically derived curves can be substituted for the coefficients l, m, and n.

NA_d was defined as the amount of NA to remain in the soil at the target pH. The amount of NA to be neutralized (NA_l) by liming is

$$NA_l = NA_o - NA_d$$

Substitution results in

$$NA_l = NA_o - \frac{NA_o}{l - m * pH_o + n * pH_o^2}$$

To report NA_l in units of lime the conversion factor of 400 pounds of ENM per unit of NA is used. The equation then becomes

$$lb\ ENM\ /\ acre = 400\left(NA_o - \frac{NA_o}{l - m * pH_o + n * pH_o^{\ 2}} \right)$$

If the target pH is greater than 6.5 then NA_d is effectively equal to zero. The quadratic portion of the curve drops out, which results in

$$lb\ ENM\ /\ acre = 400 * NA_o$$

This equation is one of the three that Fisher developed. Substitution of coefficients from curves resulted in the other two curves for different target pH ranges.

For a target pH = 5.5 to 6.0

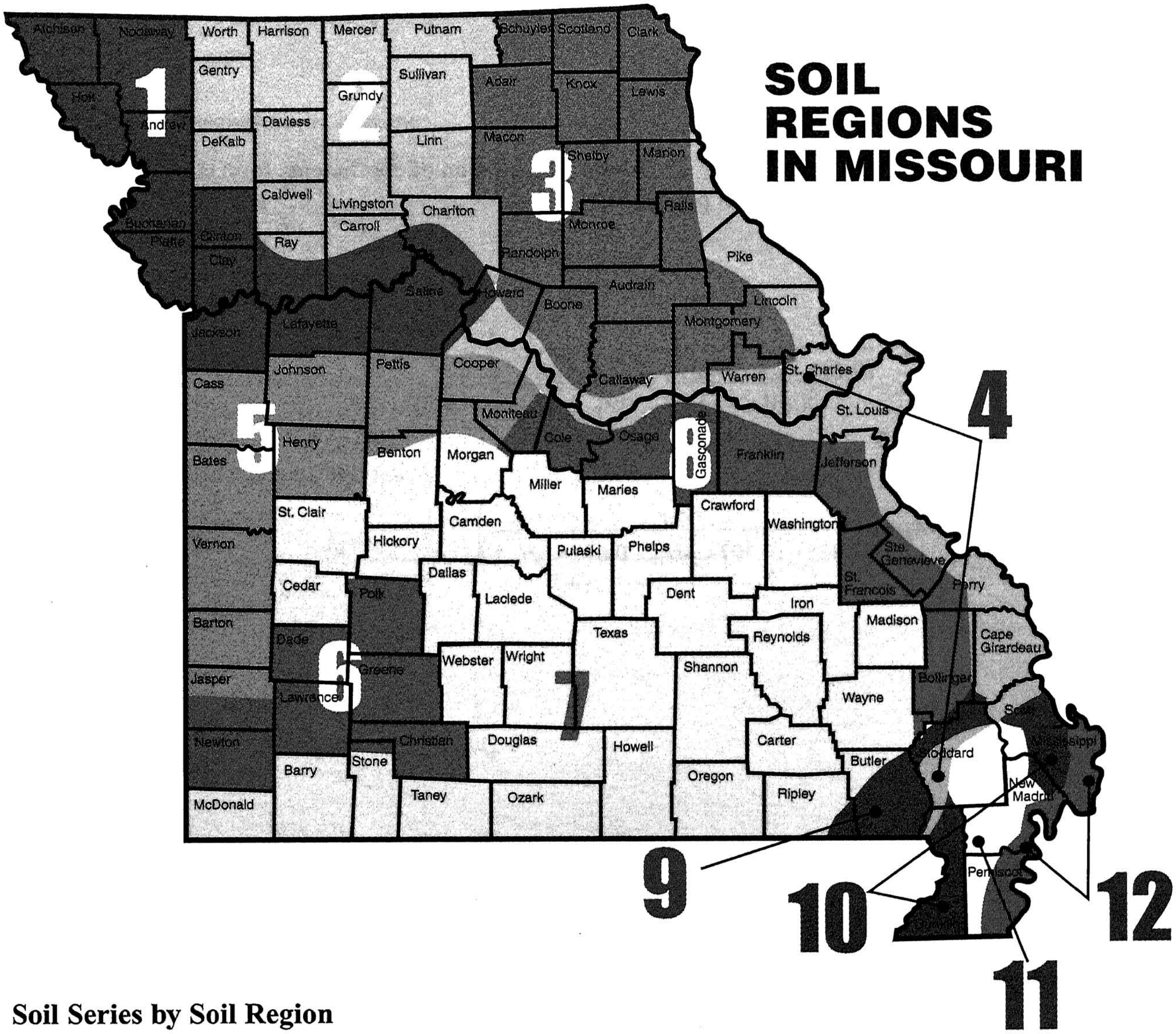
$$lb\ ENM\ /\ acre = 400\left(NA_o - \frac{NA_o}{19.109 - 4.802 * pH_o + 0.297 * pH_o^{\ 2}} \right)$$

For a target pH = 6.0 to 6.5

$$lb\ ENM\ /\ acre = 400\left(NA_o - \frac{NA_o}{41.425 - 10.307 * pH_o + 0.629 * pH_o^{\ 2}} \right)$$

Appendix B

Map of Soil Regions in the State



Soil Series by Soil Region

Region 1: Knox, Marshall (Mollic Hapludalf, Typic Hapludoll)
Region 2: Grundy, Shelby (Aquertic Argiudoll, Typic Argiudoll)
Region 3: Putnam, Mexico, Lindley (Vertic Albaqualf, Vertic Epiaqualf, Typic Hapludalf)
Region 4: Menfro, Winfield (Typic Hapludalf, Oxyaquic Hapludalf)
Region 5: Parsons, Cherokee, Bates (Mollic Albaqualf, Typic Albaqualf, Typic Argiudoll)
Region 6: Baxter, Craig (Typic Paleudalf, Mollic Paleudalf)
Region 7: Clarksville, Lebanon (Typic Paleudult, Typic Fragiudult)
Region 8: Union (Oxyaquic Fragiudalf)
Region 9: Waverly (Typic Fluvaqent)
Region 10: Dexter (Ultic Hapludalf)
Region 11: Sharkey (Chromic Eqiaquert)
Region 12: Sarpy (Typic Udipsamment)

Appendix C

Notes from early Twentieth Century Missouri research and extension reports

Albrecht, W.A. 1941. Drilling limestone for legumes. Missouri Agricultural Experiment Station Bulletin 429.

> Comment: Emphasizes the value of calcium in quantities smaller than that needed to eliminate soil acidity.

Barlow, J.T. 1916. Soil acidity and the litmus paper method for its determination. Jour. Amer. Soc. Agronomy 8:23-30.

Comment: Theory assumed that soil acidity was the result of organic acids, although leaching studies did not support that concept. This was the theory of Hopkins, Petit, Knox, etc.

$RCOOH + KNO3 \rightarrow RCOOK + HNO3$

Place 25 g soil in a dish. Add distilled water to give a thick paste. Lay 2 strips of blue litmus paper on a clean square glass plate 4 to 5 inches on each side. Place the "mud" on the litmus paper and force down with the palm of the hand. Turn the plate over and observe the color change of the paper to a standard color. The results differ between people.

Baver, L.D. and F.H. Bruner. 1939. Rapid soil tests for estimating the fertility needs of Missouri soils. Missouri Agricultural Experiment Station Bulletin 404.

Comment: Lime requirements were calculated from tables based upon the Comber test and the amount of 0.3 N HCl soluble calcium. calcium described as low, medium and high with the numerical ranges low $\leq$3000, medium = 3000 to 6000, high = 6000 to 7000, and very high $\geq$7000 pounds per acre. Detailed methodology of other soil tests.

Coleman, O.T. 1936 Home grinding limestone. Missouri Agricultural Extension Circular 352

Comment: General discussion of on-farm limestone crushing.

Coleman, O.T. 1955. Lime your soil for better crops. Missouri Agricultural Extension Circular 651.

Comment: A general liming promotion circular.

Duley, F.L. and M.F. Miller.1926. The soils experiment fields of Missouri. Missouri Agricultural Experiment Station Bulletin 238.

Comment: Summary of work on outlying fields, some of which were started in 1905 following the pattern used in Illinois with modifications. That is, the same treatments were used at nearly all locations. "Lime has been of great value on certain soil types in growing the clovers and alfalfa." Rock phosphate did not give the results like bonemeal and acid phosphate. Manure was of such benefit that the recommendation was to use crop rotations and have a livestock enterprise. So most of the grain was fed on the farm.

Hartwell, B.L. and F.R. Pembee. 1918. Aluminum as a factor influencing the effect of acid soils on different crops. Jour. Amer. Soc. Agronomy 10:45-47.

Comment: Barley was more sensitive to soil acidity in a Delaware location than rye. The effect was attributed to aluminum.

Kroth, E.M. and R. Mattas. 1981. Effect of top-dressed limestone, nitrogen, phosphorus and potassium of yield and mineral content of tall fescue forage and soil test values. Missouri Agricultural Experiment Station Research Bulletin 1040.

Comment: Three top-dressed rates of lime and 1 rate (recommended) mixed with the top 7 inches of soil. Soil test data 3 and 7 years after application.

Krusekopf, H.H. 1938. Soil fertility investigations on Brown limestone land of southwestern Missouri. Missouri Missouri Agricultural Experiment Station. Bulletin 395.

Comment: 1921-1931 results from the Newtonia Field (northeast Newton Co.) Treatments: none, P, P+lime, P+lime+potash, N+P+K+lime, Manure, manure+P, manure+P+lime, Manure+lime+rockP. C_SB_Wh_Cl rotation. Manure+lime+superP gave the greatest yields of all crops over the 11 year period. N at only 40 lb to corn and wheat.

Miller, M.F. 1909. Some results with lime on Missouri soils. Jour. of the Amer. Soc. Agronomy. 1:228-233.

Comment: A report on the early liming results of the outlying experiments. Yield depressions were observed, but there was no obvious explanation.

Miller, M.F. 1936. Testing soils for acidity by the modified Comber method. Missouri Agricultural Extension Circular 339.

Comment: Interpretation of the colors from the Comber test. No recipe.

Miller, M.F. and F.L. Duley.1917. Soil experiments on the Ozark upland. Missouri Agricultural Experiment Station Bulletin 148.

Comment: Location 1 mile west of St. James. Introduction refers to soil analysis but does not elaborate. N, P, K, lime need in top 7 inches=2340, 1320, 21480 and 4800 ("rich soil"=6000, 2000, 30000 and 0) Treatments: manure, manure+rock P, legumes+lime+bonemeal+potash, none, legumes+lime+ bonemeal, legumes+lime, legumes. 1911-1916 1000 lb rock P, 2 tons lime, 8 tons manure. Lime paid especially well for legume establishment.

Miller, M.F. and R.R. Hudelson. 1914. Soil investigations- Jasper County Experiment Field. Missouri Agricultural Experiment Station Bulletin 119.

Comment: Site 2.5 miles south of Carthage. Data 1909 to 1913. The acid soil required "2400 pounds of ground limestone to sweeten the surface seven inches of an acre." Treatments: cowpeas (CP), CP+Lime, CP+Lime+Bonemeal (B), CP+Lime+B+K, None, Manure, manure+rock phosphate, manure+rock phosphate+Lime. Manure increased corn yield 10 Bu/a but did not affect wheat yields. Lime and P most beneficial. Soil "so low in organic matter that grain crops should never be continuously grown upon it."

Miller, M.F. and C.B. Hutchison. 1910. Soil experiments on the prairie silt loam of Southwest Missouri. Missouri Agricultural Experiment Station Bulletin 84.

Work done on a farm southeast of Lamar. Treatments: N+P, None, N+K, P+K, N+P+K, N+P+K in hill, N+P+K+Lime. There were other treatments in other experiments, but these were the basic treatments. After the first year, cowpeas were added to the rotation to provide for N. Blood meal (50 lb/acre) was the N source the first year. P = 150 lb fine bone meal, K = 50 lb muriate of potash, Lime = 2000 lb/acre ground limestone before corn each rotation cycle. Experiments suggest the order of deficiency = N>P>lime>K.

Miller, M.F. and C.B. Hutchison. 1910. Soil experiments on the rolling limestone upland of southwest Missouri. Missouri Agricultural Experiment Station. Bulletin 86.

Location selected in 1905 was on a farm 3.5 miles south of Billings. Cowpeas used as a catch crop. Treatments: None, cowpeas (CP), CP+lime, CP+lime+P, CP+lime+P+K. Summary gave recommendations for owned and rented land treatments. 2,000 to 4,000 lb of ground limestone per acre once in a 4 to 5 year rotation. (Area of coverage includes what is now recognized as a low magnesium limestone area.).

Miller, M.F., C.B. Hutchison, and R.R. Hudelson. 1915. Soil experiments on the Gray Prairie soils of southwest Missouri. Missouri Agricultural Experiment Station Bull. 130.

Comment: A complete coverage of the subject including soil tests and lime quality over the state.

Miller, M.F., C.B. Hutchinson, and R.R. Hudelson. 1915. Soil experiments on the level prairies of northeast Missouri. Missouri Agricultural Experiment Station Bull. 126.

Comment: Putnam silt loam. 3 locations: 2.5 miles northeast of Monroe City 1905-1908; 0.25 mile north of the High Hill railroad station 1907-; 1 mile southwest of Bowling Green. 1907. Treatments: cowpeas (CP), CP+Lime, CP+Lime+Bonemeal (B), CP+Lime+B+K, None, Manure, manure+rock phosphate, manure+rock phosphate+Lime. Cowpeas worked only at High Hill. Rock phosphate a long-term treatment. Manure should be carefully returned to the land. Bone meal is productive.

Miller, M.F., C.B. Hutchinson, and R.R. Hudelson. 1915. Soil experiments on the rolling glacial land of north Missouri. Missouri Agricultural Experiment Station Bull. 128.

Comment: Site was 1 mile north of Laclede, classified as Shelby loam. Treatments: Legume, Legume+bonemeal, Legume+bonemeal+lime, Legume+bonemeal+lime+potash, None, Manure, manure+rock phosphate, manure+rock phosphate+legume. Order of response: available P>potash>lime.

Miller, M.F. and H.H. Krusekopf. 1920. Agricultural lime. Missouri Agricultural Experiment Station Bulletin 171.

Trotter, I.P. and O.T. Coleman. 1928. How to use agricultural limestone. Missouri Agricultural Extension Circular 208.

Comment: General use is described based on soil test. The test use is not stated. Directions include the statement "use at least as much lime as the test calls for." Recommendation is based upon 10-mesh grind.

Appendix D

Details from graduate student theses and dissertations

Appendix D contains extended summaries of several thesis and dissertations submitted by soil science graduate students as partial completion of an advanced degree. Several of these theses were not published beyond the requirements for a bound thesis. Therefore, the authors of this document on Liming in Missouri decided to include the following summaries.

Exchangeable Acidity, Salt pH, and Base Saturation of Some Missouri Soils

K.E. Benham, MS Thesis-1970
C.L. Scrivner, advisor

Benham (1970) tested methods for estimating exchangeable acidity to use in calculating percentage base saturation as an aid to classification of upland soils. In his literature review, he cited several references for measuring cation exchange capacity and acidity in soils going back to the early 1900s. One of Benham's objectives was to determine the pH at which the CEC should be determined for use in classification.

Benham selected a group of soil series differing in parent material and native vegetation including 4 Mollisols and 12 Alfisols. With some duplication of series he had a total of 23 different sites. The solum of the soil at each site was sampled by diagnostic horizon. Exchangeable acidity was measured by titration with a standardized solution of $CaOH_2$ and $CaCl_2$ (0.04 N in base and 0.02 N in Cl), the New Woodruff buffer (Brown and Rodriguez, 1983) and the $BaCl_2$/TEA method of Mehlich as outlined by Peech (1965).

Titration curves of samples from diagnostic surface soil horizons differed from those of the subsurface horizons. Benham suggested that the differences might be due to eluviation-illuviation of clay during soil formation and/or to organic matter in the surface soil. No organic matter data were provided.

Benham stated "... the $Ca(OH)_2/CaCl_2$ method provides a reliable and accurate way to measure exchangeable acidity in all horizons of mineral soils." The results compared favorably with measures of exchangeable acidity by the $BaCl_2$–TEA method.

Benham did not succeed in his attempt to develop a family of curves for the set of soils that would relate pH in 0.01 M $CaCl_2$ to percentage base saturation as an aid in soil classification. The amount of scatter was too large for reasonable predictability. Since pH is an intensity value and percentage base saturation is a capacity factor that integrates amounts of three or more cations, such a negative result is not surprising.

Benham also estimated acidity using the New Woodruff buffer and compared those results with the $Ca(OH)_2/CaCl_2$ determinations of acidity. He reported the following results of that comparison:

Samples	Number of Samples	r^2	Slope
A horizons	44	0.690	0.893
B & C horizons	101	0.811	1.400
Combined	145	0.800	1.419

These results indicate the New Woodruff buffer underestimated acidity measured by the titration method. This inconsistency raises the question of validity of using the neutralizable acidity measured by the New Woodruff buffer with the soil test estimates of exchangeable calcium, magnesium, and potassium to calculate a cation exchange capacity (CEC) (Brown and Rodriguez, 1983). However, the quick test measures have been calibrated in field studies to arrive at recommendations of liming material and fertilizer. These relationships emphasize that soil test results are estimates in contrast to the results from analytical procedures used to more accurately measure soil components.

In conclusion, Benham's results showed that the $Ca(OH)_2/CaCl_2$ titration measurement of soil acidity was reasonably accurate when compared to the $BaCl_2$/TEA method of Mehlich. Further, he showed that salt pH was a poor indicator of percentage base saturation.

Estimating the Lime Requirements of Missouri Soils

J.R. Cisco MS Thesis-1981
J.R. Brown, Advisor

J.R. Cisco (1981) evaluated different buffer methods for estimating total (neutralizable) acidity in acid Missouri soils for his thesis problem. Woodruff (1948) developed a buffer solution for estimating lime requirements that was put into practice in the Missouri soil testing program and was adopted by other states. Shoemaker, et al. (1961) proposed a new buffer to use in the North Central states, because research had shown that the Woodruff buffer did not properly account for acidity that arose from exchangeable aluminum. This buffer, termed the SMP, was adapted by the soil testing programs in most of the North Central states. Woodruff reformulated his original buffer, which replaced the original Woodruff buffer in the Missouri soil testing program in 1963. Woodruff never formally published the recipe for his revised buffer, which caused confusion among soil testing professionals.

Cisco obtained 75 samples of acid soil submitted to the two laboratories in the Missouri soil testing program. These samples were from 34 of the 114 counties in the state. The neutralizable acidity in these samples was estimated using the 3 buffers to obtain some idea of anomalies that might arise from soils of different histories. Cisco more extensively studied bulk samples collected from sites in Harrison, Marion, Callaway, Henry, Crawford, and Dent counties. The 14 samples of about 40 kg each were air dried, and crushed to pass a 4-mesh screen. Subsamples for laboratory work were processed through a 10-mesh screen.

Neutralizable acidity was measured using the three soil testing buffer procedures (Graham, 1959; Brown et al., 1977; Shoemaker et al., 1961) and titrated with a mixed solution of $Ca(OH)_2$ and $CaCl_2$ (Benham, 1970). In addition, 2.5 kg quantities of each soil were treated with different rates of laboratory grade $CaCO_3$. After two cycles of wetting to field capacity and drying, the treated samples were potted and soybeans grown for 45 days. Following the first crop soil in each pot was air dried, crushed and then repotted for a second soybean crop. Soil samples (100 grams) for analysis (see table below) were taken prior to planting the first crop and after each of the two crops.

Measurement	Method	Reference
Exchangeable Al	1 M KCl	McLean (1965)
Exchangeable Al	Ammonium Acetate @ pH 4.8	McLean (1968)
pH	0.01 M $CaCl_2$	Brown et al. (1977)
Acidity	$Ca(OH)_2/CaCl_2$	Benham (1970)

Based on Benham's work (Benham, 1970), the $Ca(OH)_2/CaCl_2$ titration was considered as the reference measurement of neutralizable acidity, as it most nearly estimated true neutralizable acidity in each soil. While the differences between the means of SMP, New Woodruff, and $Ca(OH)_2/CaCl_2$ were not statistically significantly different, a trend was indicated (Table C-1). The old Woodruff buffer underestimated neutralizable acidity, as suggested by Shoemaker et al. (1961). The results of the New Woodruff procedure best paralleled the results of the $Ca(OH)_2/CaCl_2$ titration. The intercept in the SMP regression equation showed the SMP method overestimates neutralizable acidity in slightly acid soils.

The other portion of Cisco's work focused on the growth response to lime of two crops of soybean grown in the greenhouse on the 14 acid soils. These soils ranged in pH in 0.01 M $CaCl_2$ from 3.85 to 5.60 (pH 4.37 to 6.00 in distilled water). Only three of the soils had more than 0.5 cmol/100g of aluminum extractable in 1 M KCl.

Table C-1. Comparisons of estimates of lime requirements of 75 farmer samples regressed against the lime requirement calculated using $Ca(OH)_2/CaCl_2$ determinations of neutralizable acidity.

Method	Mean* NA cmol/kg	Regression equation**	R^2
SMP	6.67a	$y = 1.67x - 3.23$	0.91
New Woodruff	6.25a	$y = 1.16x - 0.63$	0.94
$CaCO_3$	5.94a	$y = 0.95x - 0.87$	0.91
Old Woodruff	3.86b	$y = 0.65x - 0.02$	0.95

*Means of NA (Neutralizable Acidity) followed by the same letter are not significantly different at the 5% level.

**y = buffer method and $x = Ca(OH)_2/CaCl_2$.

Based in part upon Fisher's summary of liming in Missouri (Fisher, 1969), a lime requirement target of $pH_s = 6.5$ was selected to evaluate the results. Estimates of lime requirements of each of the 3 buffers were plotted against the incremental amounts of pure $CaCO_3$ added to the soil, which was then incubated and sampled after 2 crops of soybean with soil mixing between crops.

Table C-2. Comparisons of estimates of $CaCO_3$ lime requirements of greenhouse soils and requirements calculated using different determinations of neutralizable acidity.

Method	Regression equation*	R^2
SMP	$y = 1.99x - 7.12$	0.83
New Woodruff	$y = 1.16x - 1.72$	0.88
$Ca(OH)_2/CaCl_2$	$y = 0.95x - 0.87$	0.91
Old Woodruff	$y = 0.75x - 1.35$	0.87

*Each method regressed against the $CaCO_3$ incubation where y = buffer results and $x = CaCO_3$ incubation results.

The plot between lime requirements estimated by the SMP buffer and the $CaCO_3$ incubation had a much different slope and the smallest R^2 relative to the other buffers. Since the basic calibration of the SMP was based upon a 17 month incubation with $CaCO_3$ and pH was measured in distilled water, one would expect the SMP to be different (Shoemaker, et al., 1961). The New Woodruff buffer was the better predictor of lime requirement in Missouri (Brown and Cisco, 1984).

Soil aluminum was measured after each harvest to determine the treatments' effect on plant growth. Yield results were inconclusive in determining the nature of the soybean response to lime. The 3 soils with measurable initial aluminum were the only soils that resulted in 25% or more yield increase to the first increment of $CaCO_3$. There were insufficient data to define a target pH_s from the study. On most of the soils, vegetative growth declined on pots treated with sufficient $CaCO_3$ to raise the pH_s above 7.0. In fact, Cisco fitted a parabola to a plot of yield results from pots that responded to liming, which maximized at pH_s 5.88. Work reported later in this document by Syed-Rastan (1995) suggested that in closed systems, such as greenhouse pots, liming may raise the soil solution calcium activity above saturation and cause a condition that might be called calcium toxicity, which restricted vegetative production.

Liming had no effect on plant aluminum (Table C-3). This result was not surprising based upon several references cited by Cisco and the fact that only 1 soil had a large amount of KCl extractable aluminum (7.1 cmol/100g). Even on that soil the large lime treatments did not consistently reduce plant aluminum concentrations, although plants grown on that soil without any lime had more that twice the aluminum concentrations than plants grown on the other untreated soils.

Table C-3. Mean Al, Fe, and Mn concentrations in soybean averaged across 14 soils.

$CaCO_3$	Al*	Fe*	Mn*
Tons/acre	-----------------	ppm	-----------------
0	93a	81a	236a
2.23	91a	85a	111b
4.46	90a	80a	78c
6.70	93a	73a	72c
8.93	99a	77a	77c
11.16	99a	77a	77c

*Concentrations in a given column followed by the same letter are not significantly different.

There were no significant main effects (lime rate or soil) nor interactions on Fe concentration in soybean vegetative material (Table C-3). In contrast, both main effects and their interaction significantly affected the manganese concentrations. Manganese concentrations were much less on all soils with the lowest two rates of lime. The lime by soil interaction was significant at the 5% level, because the manganese concentrations did not decline with lime rates beyond the first two on all soils. Ozarks soils resulted in the greatest soybean-tissue manganese concentrations as shown below:

Soil Region†	Mn††
	ppm
Ozarks	213a
Central Claypan Area	94b
Cherokee Prairies	67b
Deep Loess and Drift	46b

†Based upon Allgood and Persinger (1979).
††Means across all soils and rates of lime within each region.
Concentrations followed by the same letter are not significantly different at the 5% level.

Cisco titrated both Woodruff buffers and the SMP buffer with incremental additions of 0.05 M HCl and 0.05 M acetic acid. Both Woodruff buffers were formulated with an initial pH of 7.0. In theory when the designed soil:0.01 M $CaCl_2$:New Woodruff buffer ratio of 10 g:10 ml:10 ml was used, each depression in the buffer pH-soil mixture of 0.1 unit represented 1 cmol acidity/kg (Note the appropriate ratio of the old Woodruff buffer was 5 g:5 ml:10 ml). The appropriate buffer/diluent mixture was titrated with standard HCl and the resulting pH measured to evaluate the response of the buffers to acidity. This titration assumed that once the exchangeable acidity was in solution, the activity of the acidity is at equilibrium with any remaining reserve acidity held by the soil particles.

Cisco also used a titration procedure in which increments of all 14 acid soils were added to 30 ml of each buffer and the decline in buffer pH was measured. The total acidity of each increment of soil was based upon the estimation of total acidity using the 7 month incubation of soil and increments of $CaCO_3$ conducted in the greenhouse.

Direct titration of the buffers with 0.05 M HCl caused a faster decline in buffer pH than did titration with acid soil. About 0.3 me of strong acid caused the same decline as 1.0 me of estimated total acidity in soil. The point of this work was that the buffer decline due to a given amount of acidity can not be estimated using only strong acid. The interaction of acid soil and the buffer to cause a decline in the buffer pH is unique to soil systems. Therefore the use of buffers to estimate neutralizable acidity requires calibration to the soils of a given region. Sims (1996) stated "...the suitability of a lime requirement test must be verified by comprehensive *calibration* studies that reflect the intended use of the soil and the variation in soil properties expected in the geographic area where the test will be used."

In summary, Cisco's thesis work supported the use of the New Woodruff buffer for estimation of lime requirements of Missouri soils. The Missouri soil testing procedures (Brown and Cisco, 1984 and Brown and Rodriguez, 1983) should be followed, because the New Woodruff buffer estimation of neutralizable acidity has been calibrated to the range of Missouri soils while the SMP has not. In addition, Cisco showed that SMP tends to be more inaccurate for soils with both low and quite high amounts of neutralizable acidity. Cisco's data showed that if the buffer pH drops below 6.0, the quantity of soil should be reduced as directed by Brown and Rodriguez (1983).

Estimation of Lime Requirements of Selected Missouri Soils

A.A. Yusef Ph.D. Dissertation-1986
J.R. Brown, Advisor

When Abdugiali Ali Yusef's arrived from Libya to work towards a Ph.D., there was some discussion regarding the validity of using the New Woodruff buffer procedure for estimating lime requirements for the Alfisols and Ultisols of southern Missouri. The concern was that the buffer estimate was not correctly accounting for acidity arising from active aluminum in the very acid soils. Yusef's dissertation study attempted to address these concerns. The objectives of Yusef's dissertation were "...to (i) characterize the nature of the acidity in selected Missouri soils and (ii) develop an improved method of estimating lime requirement of these acid soils" (Yusef, 1984).

In cooperation with extension agronomists in southern Missouri and with USDA/NRCS personnel, surface soils from six locations were selected. At each location bulk soil was taken from the A_1 or the A_p horizon. The surface organic layer was removed from the forested sites before sample collection. Two of the locations were farmer fields; three were forested in the area studied by Gamble and Mausbach (1982); and one was a forested portion of the University of Missouri's Wurdack Farm near Cook Station, MO. Location information is given in Table Y-1.

Table Y-1. Location information about the six soils used in the Yusef study.

Location*	County	Vegetation	Classification*
Alton	Oregon	Pasture	Clarksville series
Howell	Howell	Fallow	undetermined
003	Laclede	Hardwood forest	SND**, Loamy-skeletal over clayey siliceous, mesic Typic Paleudalf
005	Laclede	Hardwood forest	Doniphan series, Clayey, mixed, mesic Typic Paleudult
006	Laclede	Open conifer forest	Wilderness series, Loamy-skeletal, siliceous, mesic Typic Fragiudalf
Wurdack	Crawford	Hardwood forest	SND, site appeared to be a Coulstone Clarksville integrade

*The numbered locations were from the NRCS(SCS) study sites (Gamble and Mausbach, 1982).
**SND = series not defined. The Howell location was similar to the 003 and 005 locations, except it had been cleared.

The air-dried soils were crushed to pass a 0.5-mm screen and mixed. A random subsample was taken to obtain quick-test information as a guide to developing a lime treatment plan (Table Y-2). Greenhouse studies were conducted on variably limed soil using both alfalfa (*Medicago sativa* L.) and soybean (*Glycine max* L) as test crops on all six soils. All soils were brought to the recommended levels of P and K in bulk (Buchholz, 1983). The bulk samples of the soils were thoroughly mixed after the appropriate treatments were added and were divided into 2.5 kg quantities. Each 2.5 kg of soil was treated with one of the selected incremental quantities of $CaCO_3$, mixed, and placed in a plastic lined No. 10 metal can. A watering tube was placed vertically in each pot to facilitate watering.

The incremental liming rates were calculated as equivalent fractions of the neutralizable acidity (NA) estimated by the New Woodruff buffer quick test method (Brown and Rodriguez, 1983). The rates were 0, 0.125, 0.25, 0.5, 1.0, 1.5, and 2.0 times the cmol(+) of NA per kilogram of soil. Laboratory grade

$CaCO_3$ was used. It was assumed that CCE and fineness of grind were not factors with laboratory grade $CaCO_3$, and that if all the NA in each soil was neutralized (1.0 x NA) the resulting pH would be 7.0.

Table Y-2. Chemical parameters of the six soils used in the Yusef study.

				P		Exchangeable					NH_4Ac
Location	pH_w	pH_s	OM	P1	P2	NA	Ca	Mg	K	CEC	CEC
			%	mg/g		cmol(+)/kg					
Alton	5.2	4.5	2.4	8.5	2.3	7.00	1.8	0.3	0.2	9.1	7.8
Howell	5.4	4.8	1.7	5.5	1.4	4.00	2.0	0.4	0.2	6.6	5.8
003	5.4	4.7	2.8	5.0	1.3	4.66	2.5	0.6	0.3	8.1	8.1
005	4.9	4.4	3.0	4.5	8.5	5.43	1.4	0.4	0.2	7.3	7.3
006	5.0	4.2	2.3	3.5	6.5	6.12	1.4	0.7	0.2	8.4	8.6
Wurdack	4.8	4.1	2.4	-	7.0	7.20	0.8	0.3	0.3	8.6	7.4

Methods: Brown and Rodriguez (1983); P extracted by Bray and Kurtz extractants: P1 = 0.025 M HCl with 0.03 M NH_4F; P2 = 0.1 M HCl with 0.03 M NH_4F; NA = neutralizable acidity by the New Woodruff buffer. The "exchangeable CEC" is a summation of the exchangeable cations determined in the soil testing process. The NH_4Acetate CEC was determined by distillation of NH_3 following leaching with 1 M NH_4Acetate @ pH 7.0 and methanol with magnesium from MgO as the replacing cation.

The potted soil was brought to field capacity; plastic bag liners were closed; and the pots were incubated for 2 weeks. After this preliminary incubation, the bags were opened and the surface soil allowed to dry. Alfalfa and soybean seeds were planted, the soil moistened, and the stands thinned after germination. Two cuttings of alfalfa were taken, one 60 days after seeding and another 25 days after the first. A soybean vegetative harvest was taken 55 days after seeding. From the time of initial watering, the soils used for alfalfa remained moist for 99 days and the soils for soybeans 69 days. After the last harvests pots were allowed to air dry, after which the soil was removed, mixed, and sampled from each pot.

Table Y-3. Methods applied to subsamples of the initial soils and to soils used in the greenhouse and incubation portions of the studies on lime relationships.

		Soil		
Method	Measurement	Initial	Greenhouse	Incubation
pH_w	Active Acidity	√	√	√
pH_s	Active Acidity	√	√	√
Woodruff buffer	Total acidity	√	√	√
SMP buffer	Total acidity	√	√	√
KCl	Al	√	√	√
$CuCl_2$	Al	√	√	√
1 M NH_4Acetate, pH 4.0	Al	√		
$CaOH_2/CaCl_2$	Total acidity	√		
1 M CaAcetate, pH 4.0	Total acidity	√		
1 M NH_4Acetate, pH 7.0	CEC, Ca, Mg, K	√		

A laboratory incubation study on all six soils was conducted using incremental rates of $CaCO_3$. After treatments were applied, the soil was brought to field capacity, placed into closed plastic bags, and incubated for successive 30-day increments. At the end of each 30-day period, the bags were opened and allowed to air dry. After mixing each bag was subsampled, the soil brought to field capacity, and incubated for another 30 days. At the end of the incubation experiment, the subsamples were tested for pH_w, pH_s, neutralizable acidity (Woodruff buffer), and SMP lime requirement. Several different extractants and measurements were used to characterize the effects of treatments and are summarized in Table Y-3.

Maximum dry matter yields were achieved at different fractional lime requirements for the different soils, suggesting different target pH_s (Table Y-4). Also yields were depressed at the higher rates of $CaCO_3$. However, the very low alfalfa yields make these data questionable. The lsd is not the most appropriate means test to use on the data, but no other is now available, since Yusef did not leave an accessible set of results other than the limited summary data in his dissertation. Assuming that the lsd calculated for the soybean yields in response to lime has some validity, Yusef's data would suggest that half the lime requirement was nearly adequate for the soils used in the soybean study. This result has been observed in other greenhouse studies with lime (Cisco, 1981; Syed Rastan, 1995).

Table Y-4. Average yield of soybean and alfalfa in response to $CaCO_3$ added to six different soils (3 replications).

		Fraction of lime recommendation (LR)				
Crop	Soil	0	0.25	0.5	1.0	2.0
		grams per pot				
Soybean	Alton	4.6	4.7	6.1	3.5	3.3
	Howell	5.8	6.1	6.6	6.8	5.8
	003	6.4	6.5	7.5	6.6	5.4
	005	5.9	6.9	7.2	6.5	4.6
	006	4.7	6.4	5.7	4.8	3.0
	Wurdack	3.1	5.4	4.8	3.8	3.7
	Mean	5.1	6.0	6.3	5.3	4.3
	$Lsd_{0.05}$ LR = 0.75g; soil = 0.82; LR x soil = 1.83					
Alfalfa	Alton	0.23	1.60	0.50	0.44	0.22
	Howell	1.34	1.69	2.02	1.80	1.60
	003	1.95	3.86	2.72	1.66	1.69
	005	1.44	3.68	2.96	1.36	1.15
	006	0.32	1.27	0.58	0	0
	Wurdack	0.22	2.49	1.94	1.15	1.1
	Mean	0.92	2.49	1.77	1.07	0.98
	$Lsd_{0.05}$ LR = NS; soil = NS; LR x soil = 0.72g					

Yields were less at the full lime requirement than at lower rates, which was puzzling at the time Yusef completed his work. Since then, we think that the negative effect on yield may be due to excess calcium in the soil solution that could be obtained under certain circumstances, especially closed systems such as greenhouse pots and incubation bags.

Regression equations were fitted to each data set which included estimates of neutralizable acidity using the initial soil analyses and the New Woodruff and SMP buffers. Using the initial soil tests Yusef calculated the percentage base saturation on each soil and then calculated the percentage base saturation at pH_s 6.5 and pH_s 6.0. He assumed stoichiometric reactions from adding $CaCO_3$ to the acid soils and that no neutralizable acidity would remain at pH_s 7.0 (100% saturated). Yusef also estimated lime requirement at pH 6.5 using acidity extractable by molar calcium acetate at pH 7.0 and $CuCl_2$ extractable acidity. In addition to these different estimates of neutralizable acidity at different target pH levels, he used data generated by titrating each incrementally-limed acid soil with $Ca(OH)_2$ solution and measuring pH_s following the growth of soybeans and alfalfa. The data were compared by calculating the lime requirement to raise each soil from the initial pH_s to target pH levels of 6.0, 6.5, and 7.0. These specific pH_s values are at the upper end of the recommended target ranges for crops in Missouri (6.6 to 7.0. 6.1 to 6.5, and 5.6 to 6.0) (Buchholz, 1983).

Examples of Yusef's evaluation of the methods to estimate lime requirements are given in Table Y-5. The most striking observation is that lime requirements estimated from the post cropping measures based upon the incremental carbonate treatments show nearly 3 cmol(+)/kg greater lime requirements than those based upon the calcium hydroxide titration. All the estimates given in the table other than the carbonate are based upon the uncropped soils. It is probable that carbon dioxide from the roots in the soil as a normal result of respiration was responsible for development of acidity. Excretion of protons from active roots may have occurred due to biological nitrogen fixation in the nodules of soybean and alfalfa.

Table Y-5. Estimated lime requirements (LR) to reach alternative target pH values for three acid soils using different estimation methods given in cmol(+)/kg.

Soil	Alton		005		Wurdack	
Target pH_s	LR	Method*	LR	Method*	LR	Method*
	cmol(+)/kg		cmol(+)/kg		cmol(+)/kg	
7.0	8.87	CO	8.85	CO	9.78	CO
	7.87	SMP	5.79	OH	7.70	SMP
	7.00	W	5.69	SMP	7.20	W
	6.50	OH	5.43	W	7.04	OH
6.5	6.68	SMP	6.01	CO	7.29	CO
	6.23	CO	6.00	BS	6.58	SMP
	6.12	W	5.18	Acetate	6.46	W
	5.60	Acetate	4.85	W	6.30	BS
	5.40	BS	4.78	SMP	5.65	Acetate
	4.50	OH	4.18	OH	5.40	OH
6.0	5.49	SMP	4.60	BS	5.57	W
	5.00	W	4.20	CO	5.45	CO
	4.97	CO	4.13	W	5.33	SMP
	4.58	Cu	4.10	Cu	5.10	BS
	4.30	BS	3.92	SMP	4.56	Cu
	3.35	OH	2.98	OH	4.10	OH

*CO = $CaCO_3$ incubation, W = New Woodruff buffer, SMP= Shoemaker-McLean-Pratt buffer, OH = titration with $Ca(OH)_2/CaCl_2$ solution, BS = percentage base saturation, Acetate = Acidity estimated with calcium acetate at pH 7.0, Cu = acidity extracted with $CuCl_2$.

The $Ca(OH)_2$ titration data and the pH_s measurements made after incubation with $CaCO_3$ were fitted to a quadratic expression with pH_s the dependent variable and quantity of base as the independent variable. Regression statistics showed a very good fit, however, examination of the data suggested that the fit was linear from pH_s in the mid 4s to nearly 6.5. Above that pH it then became exponential, as observed by Magdoff and Bartlett (1985) (data not shown). Yusef calculated the percentage of the total lime requirement needed to reach target pH_s 7.0 from starting pH_s values of 5.5 (target pH_s range of 5.5-6.0), 6.0 (target pH_s range of 6.0-6.5), and 6.5 (target pH_s range of 6.5-7.0). For the six soils the average percentage lime requirement for each 0.5 pH_s increment was 16%, 20%, and 29%, respectively. This observation may explain field observations that lime requirements based upon quick test methods do not meet target pH levels in the field. Quick tests are unable to accurately measure the slowly released acidity (pH dependent acidity) encountered in the pH 6.0 to 7.0 range (Sims, 1996). Black (1967) attributed the characterstic acidity in the linear range—noted later by Magdoff and Bartlett (1985)—to weak and very weak acid components of the soil. In the vicinity of pH 6.5, the source of pH dependent acidity is very, very weak acids, characterized by organic phenolic groups and hydroxy aluminum polymers. Because the ionization rate of these two soil components is slow, this acidity is not measured by the quick test methods used in lime requirement determinations.

One of Yusef's objectives was to develop an alternative method of estimation of lime requirement that is more useful for low organic matter, highly weathered soils of the Ozark region of Missouri. Extractants proposed for areas dominated by Ultisols and Oxisols were selected. These aluminum extractants were 1 M KCl (Coleman et al., 1959), 0.5 M $CuCl_2$ (Juo and Kamprath, 1979) and 1 M NH_4Acetate @ pH 4.8 (McLean et al, 1958) (Table Y-6).

Soil aluminum extracted with 1 M KCl is considered exchangeable. According to Kamprath (1984) the resulting acidity is dominantly due to Al^{3+}. However, a multiplier is often used in addition to the factor to convert exchangeable aluminum into equivalent amounts of limestone or $CaCO_3$ per unit area. The need for the multiplier is a result of pH dependent acidity, which likely becomes active with time as the added lime neutralizes more active acidity.

The uncertainty implied by the use of a factor caused Thomas and Hargrove (1984) to state, "However, salt-exchangeable Al^{3+} is scarce in surface soils, even acid ones, and too much reliance should not be put on an ion exchange treatment that may have limited applicability." Yet these authors went on to suggest that since lime application to field soils is not exact, the use of KCl extractable aluminum as a basis for lime requirements might be useful. The use of some measure of soil aluminum for lime requirement estimation will be expanded upon later in this summary.

Yusef suggested in his dissertation that the KCl extractable aluminum might be a useful estimate of lime requirements if multiplied by 2. This calculation has been included in Table Y-6. The resulting average lime requirement is about 1.5 cmol(+)/kg less than the lime requirement of the Woodruff buffer estimate. As an alternative to the Woodruff buffer estimate of lime requirement on acid low organic matter soils of the Ozark portion of Missouri (soil regions 6 and 7; Buchholz, 1983), it is suggested that KCl extractable aluminum be used only on soils with pH_s <4.8.

Table Y-6. Measurements of soil aluminum by different extractants.

Soil	Exchangeable* Al	Extractable Al by CuCl$_2$	Extractable Al by NH$_4$Acetate	NA**	Exchangeable Al x 2
	----------	----------	cmol(+)/kg	----------	----------
Alton	2.20	4.58	3.10	7.0	4.4
Howell	1.70	3.36	1.95	4.0	3.4
003	1.67	3.50	2.60	4.7	3.3
005	2.25	4.10	2.55	5.4	4.5
006	2.50	4.70	3.55	6.1	5.0
Wurdack	2.40	4.56	4.20	7.2	4.8

*Exchanging reagent = M KCl. **NA = neutralizable acidity by the New Woodruff buffer.

It seems logical that the impact of exchangeable aluminum and/or acidity upon the pH measurement depends not only on quantity but upon the nature of the exchange complex. Cation exchange capacity along with the quantity of exchangeable bases held on the soil exchange complex will affect the relationship between active acidity (pH) and total acidity. Yusef measured the CEC of the six soils using different techniques suggested by others.

Effective CEC is that exchange capacity measured with an unbuffered salt (1 M KCl) at near the pH of the unammended soil (Coleman et al., 1959). In his calculations Yusef used the exchangeable bases measured in the 1 M NH_4 acetate @ pH 7.0 extract of unammended soils (except in those instances where he made calculations using the incrementally limed soils). The NH_4 acetate CEC was that measured by saturation with ammonium from NH_4 acetate @ pH 7.0m followed by distillation of the retained ammonium with magnesium as the replacing cation (Brown, 1981).

Yusef also measured the acidity replaced by M calcium acetate @ pH 7.0. He used this quantity of acidity plus the NH_4 acetate exchangeable bases to calculate an estimate of CEC. In a questionable practice, he also plotted the pH of the soils used in the greenhouse studies as a function of added $CaCO_3$ to estimate a quantity at pH 7.0 that he called total acidity. This quantity of acidity was added to NH_4 acetate exchangeable bases to obtain an estimated CEC. As pointed out elsewhere, acidity may have been generated while the soybean and alfalfa plants were growing, which would have inflated the CEC over that of unammended soil. The values obtained from these measures of CEC are given in Table Y-7 except for the CEC values calculated on the limed soils at the end of the greenhouse studies .

Table Y-7. Estimated cation exchange capacities of soils used in the Yusef studies.

	CEC Measurement*				
Soil	Effective	NH_4 Acetate	Ca Acetate	WB	pH dep.
	cmol(+)/kg				
Alton	4.3	7.8	7.7	9.1	3.5
Howell	4.3	5.8	5.9	6.6	1.5
003	5.0	8.1	8.0	8.0	3.1
005	4.3	7.3	7.1	7.5	3.0
006	4.7	8.6	7.9	8.3	3.9
Wurdack	3.7	7.4	6.9	8.5	3.0

*Methods –see text. WB = New Woodruff buffer, pH dep. = pH dependent.

The Missouri Soil Testing laboratories calculate an estimated CEC by summing extractable bases and acidity estimated by the New Woodruff buffer procedure (WB-CEC in Table Y-7). Compared to other measurements of CEC of the soils used in this study, the WB-CEC seems elevated (Table Y-7). This higher value using the Woodruff buffer might explain, at least in part, the yield maxima observed at pH values less than 7.0.

In Yusef's pot studies, among the soils the pH_s varied some at which yield was maximized (5.4 to 6.5 for alfalfa and 4.8 to 6.0 for soybean). Yusef gave several citations of greenhouse pot studies that gave maximum yields in the same pH ranges. These kinds of results suggest that when the plant roots develop in uniform soil material that has been supplied with adequate fertility and water, growth will maximize at a lower level of active acidity than in the field where conditions are more variable. It may be that Albrecht's theory that calcium supply to the root is the key to good growth. In humid region fields calcium, activity especially below the surface soil (A_p horizon) may limit root growth which would not be the case in pot studies.

This latter point about making comparisons should also apply to comparisons of results from incubation and field responses to liming of acid soil and should be considered when evaluating Yusef's conclusions. For example, Yusef stated (p. 113), "The lime requirement estimated by quick test methods to a target pH_s 7.0 were in agreement with the lime requirement estimated by $CaCO_3$ incubation to pH 6.5." The lime requirements estimated using the Woodruff buffer that are used in the current recommendation program were verified using the Fisher (1969) summaries of field-liming studies conducted through 1967 by workers of the Missouri Agricultural Experiment Station. In the Yusef's incubations, he did not account for either the oxidation of ammonium and sulfur compounds released by mineralization or the effect of microbial respiration during incubation, all of which are acidifying. Further, the quick test method is based upon a short 30 minute soil/buffer contact time, which would fail to estimate slowly available acidity that a longer incubation time would measure. Lack of sufficient contact time between the soil sample and the quick test buffer may explain why lime requirements have not been observed to lower soil acidity to the desired target pH. Another explanation, of course, is that the grower may sample the soil the year following application of liming material and find the target pH was not reached. In this case, the grower expected results that would not be possible based upon the findings of J.J. Stevens (see the following section).

Limestone Dissolution and pH Gradients in Soil

J.J. Stevens MS Thesis-1990
R.W. Blanchar, Advisor

The rate of dissolution of individual limestone particles when mixed with acid soil and the resulting affected soil volume determines the effectiveness of the liming material in lowering the quantity of total acidity. Over the years many attempts have been made to quantify both the rate and pattern of dissolution, but the precision of early work was limited by equipment. The development of reliable microelectrodes has improved the accuracy and precision of measurements of soil pH surrounding limestone particles. Jeffrey Stevens utilized microelectrodes in his MS thesis research to study the rate and pattern of limestone particle dissolution (Stevens, 1990).

Stevens' research had three phases. He characterized 7 calcitic (0% Mg) and 6 dolomitic limestones (10.3 to 12.6% Mg) selected from samples submitted between January and June 1988 to the Missouri Fertilizer and Liming Materials Control Service. The second part of the study measured those soil characteristics that might affect the dissolution pattern of limestone particles. Third, the reactivity of one calcitic and one dolomitic limestone was studied after they were mixed with acid soil.

Stevens did not identify the limestones that he used other than by laboratory number and the town nearest the location sampled by the Control Service inspectors. Those towns were Savannah, Kahoka, Hannibal, Kingdom City, Sedalia, Rolla, Mt. Vernon, Springfield, Marshfield, Hollister, Piedmont, and Patterson. The calcitic stone selected for intensive study was from Kahoka and the dolomitic stone was from Patterson. The geologic stratum that each stone represented was not identified. There were no limestones included that contained between 0 and 10% magnesium.

There were few differences in particle size distribution of the limestones with the exception of the dolomitic stones from Piedmont and Patterson, MO. These two limestones had much lower percentages of material in the 8- to 40-mesh size range and much greater percentages of material in the 40- to 60-mesh size range than all other samples. This size distribution caused these two stones to have greater ENM per ton that the other stones. The CCEs of the <60-mesh material in the two stones Stevens used for detailed study were slightly lower than the CCEs of the coarser size fractions, but not by much.

Stevens used a surface soil from Tucker Prairie, west of Kingdom City in Callaway County for his studies. The soil would be mapped as Mexico (fine, smectitic, mesic, Aeric Vertic Epiaqualf). The site had never been plowed, and cover was native prairie vegetation. The surface soil was silt loam and X-ray diffraction patterns indicated the presence of kaolinite and illitic-type clays in addition to smectite. The soil had a pH in water of 5.0 and in 0.01 M $CaCl_2$ of 4.5. The CEC was 21.1 cmol(+)/kg using the $BaCl_2$ measure of acidity (Thomas, 1982) and 17.3 cmol(+)/kg using 1 M NH_4Acetate @ pH 7—used by the Missouri Soil Characterization Laboratory. The organic carbon percentage was 3.02%.

Stevens studied dissolution of three different sizes of limestone particles (2>x>1 mm, 1>x>0.5 mm, and 0.5>x>0.25 mm) under both a static system and a leaching system. Soil was placed in Plexiglas cylinders (internal dimensions were 3 cm high and 5 cm in diameter) and packed to a bulk density of 1.2 Mg/m^3. A single limestone particle was placed on the soil surface in the center of each cylinder and pushed below the surface with a fine tipped weighing spatula. The soil was wetted to field capacity and pH was measured with a calibrated microelectrode at distances of 0, 0.1, 0.2, 0.4, 0.8, and 1.6 mm at 15 and 30 minutes and 1, 2, and 4 hours. Measurements at 2 and 4 days were made at distances of 0. 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mm from the individual limestone particles.

In the static system, changes in pH of the soil surrounding the individual limestone particles occurred within 15 minutes of wetting the soil, and the effect extended to 1.0 mm from the limestone particle surface. There was little change either in the magnitude of pH change or the distance of pH change over 4 days of measurements. There was little difference between calcitic and dolomitic limestones, except the pH attained near the particle surface was slightly less with the dolomitic material.

Leaching studies were conducted in Tempe cells. These cells were modified for entry of a leaching solution of 0.005 M $CaCl_2$.and removal of leachate under slight pressure. The internal cylinder of the cells holding the treated soil was 3 cm high and 5 cm in diameter. An amount of limestone to bring the soil in each Tempe cell cylinder to pH 7.0 was determined based upon CCE of the limestone and the $Ca(OH)_2$ titration curve of the soil. The appropriate amount of limestone was mixed with the soil in each cylinder. Three sets of leaching were done as follows:

Leaching Number	Mesh	Limestone Dimensions	Leaching Conditions	Estimated Field Time
1	60	$0.5\text{ mm} \geq x \geq 0.25\text{ mm}$	Continuous	1 year
		$0.5\text{ mm} \geq x \geq 0.25\text{ mm}$	Discontinuous	1 year
2	18	$2\text{ mm} \geq x \geq 1\text{ mm}$	Continuous	4 years
3	35	$1\text{ mm} \geq x \geq 0.5\text{ mm}$	Continuous	4 years
4	60	$0.5\text{ mm} \geq x \geq 0.25\text{ mm}$	Continuous	1, 4, 8 years

The amount of solution to be leached through each cell was calculated using a formula—developed by Scrivner et al. (1973) for Missouri soils—which estimates the amount of percolation that would pass a given soil depth based on annual precipitation data. A 9 to 12 cm depth was chosen to calculate the amount of leaching solution. The flow rate was 0.7 ml per minute. Both limestones were used in the leaching studies. When the results of leaching number 1 was studied, there was little difference between the continuous and discontinuous leaching, so all other leachings were done continuously.

Unreacted carbonate following leaching in studies 1, 2, and 3 was measured by reacting the cell contents with strong acid and collecting the evolved carbon dioxide. In addition to measuring unreacted carbonate following the leaching periods in study 4, pH gradients were measured above, below, and to the side of the limestone particles with microelectrodes.

The reactivity of the different particle sizes of limestone in a simulated 4 year leaching increased as particle size decreased and was significantly different between the calcitic and dolomitic limestones. The appropriate equations from Stevens' thesis are:

Calcitic $\%\ \text{reacted} = 10.33 - 53.44\ (\log_{10}(d))$ $R = 0.986$

Dolomitic $\%\ \text{reacted} = 3.765 - 58\ (\log_{10}(d))$ $R = 0.998.$

d = mean diameter

Measurement of pH gradients after various leaching regimes failed to demonstrate differences in pH at a given distance above and below the limestone particles and perpendicular to the assumed direction of solution flow. In trying to rationalize this finding, Stevens discussed the complexity of measuring small differences in a complex system like soil. Figure 5 in his thesis is the basis of his arguments about measuring soil pH with microelectrodes. Spatially, a particle of limestone passing a 35-mesh sieve ($d = 0.50$ mm) and held on a 60-mesh sieve ($d = 0.25$ mm) approximates the size of micro-aggregates of soil material that has passed a 2 mm sieve. A 2 mm sieve (10-mesh) is used in most soil testing labs to prepare soil samples for testing. The matrix of soil with a limestone particle fills a volume that has about 50% pore space and 50% solid. The pore spaces may be capillary in size but are tortuous in nature, which affects the movement of reaction products, following dissolution, from the limestone particle surface and counteracts the tendency, in Stevens' study, for leaching. (Note that flow rates used by Stevens were less that 1 ml per minute.) Couple this observation with the fact that there were many limestone particles in the leaching cylinders. Stevens calculated the number of calcitic limestone particles added to each Tempe cell in the leaching study. The cell volume was 67.5 cm^3 and 350 mg of calcitic stone was mixed with the soil. The resulting ideal distribution of particles was calculated for 3 particle sizes with the following results:

Particle Size	Number of Particles	Distance between Particles
mesh		mm
18	87	11.4
35	700	5.69
60	5600	2.85.

Most of the data showed that, at most, the effect of dissolution extended 1 mm from the particle surface. Even though Stevens' calculations only approximate actual field results, one can not help but recognize that when the pH of a limed soil is determined by usual soil testing methods (1:1 soil:solution) with separate glass and calomel electrodes or combination electrodes, the electrode surfaces may contact the dissolution fields of more than one limestone particle. Stevens showed that dissolution from the surface of a limestone particle occurs in less than 15 minutes. The mixing of the soil and suspending solution during the 30 minutes recommended in most soil testing labs for pH measurements allows time for considerable dissolution as limestone particles in a limed soil move around in the suspension. There is good reason for requesting the liming history on any soil sample submitted for testing to aid in evaluating the soil test results.

Since Stevens' data showed that dissolution from a limestone particle affected the pH no more than about 1 mm distance from the particle surface, one should be able to visualize the variability in acidity over short distances. With time however, the bulk soil pH rises, as measured in soil testing programs.

Stevens' results can be extrapolated to common techniques of calibration work in short term studies. Examples are the studies by Yusef (1988), Cisco (1981), and Syed-Omar (1995). Given the nature of quick test estimates of lime requirements, it is important to relate the estimates to target pH values as discussed above. Such field calibration takes many years, which graduate students do not have. Reliance is placed upon calibration in the greenhouse. In those studies reagent grade carbonates are thoroughly mixed with the soil. The carbonates are <100 mesh in size, which given the 1 mm dissolution distance found by Stevens, suggests that the entire soil mass in a pot study would be under the influence of dissolution of the added carbonates. In the field, however, this would not be the case. Thus calibration in the field is required to properly develop lime recommendation algorithms.

Finally, the Stevens data showed that within 1.6 mm of limestone particle surfaces, the pH was always higher with calcitic stone than with dolomitic stone.

The Stevens studies on the whole reinforced several concepts about liming acid soils. Calcitic stone dissolves quicker than dolomitic and tends to raise the bulk soil pH to a higher level than dolomitic stone given equivalent effectiveness estimates (CCE and fineness). Stevens did show that initial effects of dissolution near particle surfaces occur within 15 minutes, but the soil volume affected is limited (1 to 1.6 mm from the lime particle surface). The results support the contention that an effective liming material for agronomic applications must include fines (<60-mesh) and coarser material (between 8- and 40-mesh) for quick immediate action and maintenance of a desirable pH_s for several years.

Agronomic Response of Three Forage Legumes to Agricultural Limestones

D.R. Bennett, MS Thesis-1990
J.R. Brown and J.C. Henning, Advisors

Field verification of the greenhouse observations made by Cisco (1981) and Yusef (1986) was considered a knowledge gap. David Bennett (Bennett, 1990) conducted a three-phase study from 1988 through 1990 to start to fill this knowledge gap. He conducted trials at two southern Missouri sites using alfalfa, red clover, and lespedeza with 6 liming material treatments, which were fractions of the calculated LR.

The Bennett sites were identified as the McWhorter and the Wilson sites, named for the owners of the properties at the initiation of the studies. The McWhorter site, southeast of Rolla in Phelps County, was in a mixed cool-season grass sward harvested for hay, and the Wilson site in southern Gasconade County, was an overgrazed pasture dominated by ragweed with very little evidence of desirable forage species. Deep core samples and observable properties would suggest that both sites were Typic Paleudults. The owners did not provide any past management history. A third soil used in the incubation and greenhouse phases was from the surface horizon of a site in permanent pasture in the Mark Twain National Forest near Rolla, MO. The site had been mapped as a loamy-skeletal, siliceous, mesic Typic Paleudult in the Hudson-Coulstone-Clarksville association.

The field sites were laid out in three blocks one for each of 3 forage legume species. Each block was subdivided into 24 plots (each 8' x 21'), which were sampled to a 6" depth for prior to plowing in late summer of 1988. The soil for the greenhouse and incubation studies was collected in plastic lined metal garbage cans. The bulk soil material was air dried, and screened through a 0.25 inch mesh screen. The screened soil was subsampled for testing (Table DB-1).

Table DB-1. Initial soil test results for soils used in the forage legume study*.

Soil	pH_s	NA	OM	P	Ca	Mg	K	CEC	Al
		meq/100g	%	----------------	ppm	-------------		meq/100g	ppm
Greenhouse	4.8	4.0	2.2	10	410	78	131	7.0	24
McWhorter	4.7	4.5	2.3	1	480	218	66	8.9	13
Wilson	4.5	7.0	2.0	1	700	237	76	12.7	76

*Missouri soil test procedures according to Brown and Rodriguez (1983). P = Bray-Kurtz P1. Al = extractable aluminum by 1 M KCl.

In all cases the bulk soil and the soil at the two field sites were given corrective build-up P and K treatments based on soil tests (Table DB-1) and Missouri fertilizer recommendations (Buchholz, 1983). The soil and corrective fertilizers for the greenhouse and incubation studies were mixed thoroughly before subdivision for the addition of individual limestone treatments. Fertilizer materials for the field study were 0-46-0 and 0-0-60. The nutrient carriers for the greenhouse and incubation studies were laboratory grade monocalcium phosphate, potassium sulfate and magnesium chloride (15 ppm magnesium added).

The limestone carriers differed between studies. The sources of the limestones were the Beck Quarries near Rolla, MO and bagged limestone from Columbia, IL. Insufficient "Columbia" limestone was available for the entire Wilson site so a bagged limestone with the trade name "Mississippi", which originated near Alton, IL, was used for the lespedeza block. Only the Beck limestone was used in the incubation study. All limestone treatments were made using an effective neutralizing material value

(ENM) of the limestone determined in the MU soil fertility research laboratory (ENM = ECE (effective calcium equivalent))(Table DB-2).

Table DB-2. Characteristics of the limestones used in the Bennett studies.

Limestone	Fineness	CCE	ENM	Ca	Mg	Use
	-------- % --------		lb/ton	-------- % --------		
Beck	51.86	82.6	342	18.8	8.9	All
Columbia	54.65	97.7	427	38.4	0.4	Field, GH*
Columbia <60 mesh	100.0	97.7	782	38.4	0.4	Field, GH*
Mississippi	58.47	95.7	448	35.0	0.1	Wilson

*GH = greenhouse.

In the incubation study, samples of the Beck limestone were screened through 8-, 40-, and 60-mesh screens, as used in the Missouri Agricultural Experiment Station Laboratory to determine the fineness grades. Including the unscreened bulk limestone, there were 5 particle size treatments. Bennett selected treatments that were fractions of the calculated lime requirement using the estimate for alfalfa lime requirements in southern Missouri (Buchholz, 1983) and the ENM for the bulk Beck limestone. The estimated lime requirement was 1,600 lb ENM/acre. Table DB-3 gives the actual quantities of ENM applied for the fractional applications. The calculated ENM data for each fraction are also provided in Table DB-3 with the >8-mesh material having no ENM value. The soil-treatment mixtures were incubated in plastic bags at field capacity for 9 months. Samples for measurement of soil acidity were taken each 3 months.

Table DB-3. Equivalent quantities of Beck limestone applied as different particle size fractions based upon a lime requirement of 1,600 lb ENM/acre.

Particle Size	ENM of Particle Size	Fraction of Beck Lime Requirement				
		0.33	0.66	1.00	1.33	1.66
Mesh	lb/ton	---------------------- tons ENM/acre ----------------------				
Beck	342	1.54	3.08	4.68	6.22	7.76
>8	0	0	0	0	0	0
8-40	165	0.74	1.48	2.25	3.00	3.74
40-60	396	1.78	3.57	5.41	7.20	8.98
<60	661	2.98	5.95	9.02	12.02	15.00

Plastic lined pots containing 3 kg of treated soil and a subsurface watering tube were used in the greenhouse study. Pre-germinated Pioneer 532 alfalfa, Redland II red clover, and Korean lespedeza plants were transplanted into pots. Alfalfa and red clover were harvested 3 times at monthly intervals. Lespedeza, which grew more slowly than the other species, was harvested twice.

The target pH_s for red clover and lespedeza is 5.6 to 6.0 in the Missouri program for northern Missouri. The fractional lime increment of 1.00 reached that range (Table DB-4). However, the target for southern Missouri is pH_s 6.1 to 6.5, which was not reached. A similar result was obtained for alfalfa in that the pH_s achieved with the fractional application of 1.00 was in the target range for northern Missouri (pH_s 6.1 to 6.5) not that for southern Missouri (pH_s 6.6 to 7.0). This is not the first time these kinds of results have been observed, as has been pointed out elsewhere in this paper.

The yields for all species approached a maximum at either 0.67 or 1.00 fraction of the calculated "lime requirement." This suggests, based upon the effect of the treatments on soil acidity, that the target pH_s ranges for southern Missouri may not need to be greater than those for northern Missouri. The southern Missouri recommendations being used in the last quarter century were purposely made higher than those for northern Missouri to account for the very acid subsoils found in southern Missouri. For example, the pH$_s$ in the subsoil of the Wilson site used in Bennett's field study was 4.3 in the 8 to 12 inch depth increment and dropped to 4.1 for the next 12 to 16" depth. Active aluminum in the soil solution reaches levels toxic to plant roots at these pH$_s$ levels. Rarely is subsoil acidity in northern Missouri soils sufficient to result in appreciable active aluminum.

Table DB-4. Results from a greenhouse study of incremental quantities of limestone using 3 legume forage species*.

Species	Treatment	Limestone	Fractional LR	Total Yield	pH$_s$	Extractable Aluminum
Number				grams/pot		ppm
Alfalfa	1	Columbia	0	5.2d	4.5f	46a
	2	Columbia	0.33	9.1c	5.1e	6b
	3	Columbia	0.67	15.2a	5.6d	0c
	4	Columbia	1.00	13.8b	6.1b	1bc
	5	Col.<60 mesh	1.22	15.2a	6.3a	2bc
	6	Beck	0.88	13.5b	5.9c	2bc
Red Clover	1	Columbia	0	6.1d	4.4e	38a
	2	Columbia	0.34	9.3c	4.8d	11b
	3	Columbia	0.67	12.8b	5.3c	3c
	4	Columbia	1.00	17.3a	5.7b	3c
	5	Col.<60 mesh	1.22	18.2a	5.9a	2c
	6	Beck	0.89	16.2a	5.4c	2c
Lespedeza	1	Columbia	0	5.0b	4.4f	50a
	2	Columbia	0.34	10.5a	5.0e	7b
	3	Columbia	0.67	11.9a	5.6d	3c
	4	Columbia	1.00	11.5a	5.9b	2b
	5	Col.<60 mesh	1.22	11.1a	6.1a	2b
	6	Beck	0.89	11.8a	5.8c	2b

*Comparisons within columns by species with Fisher's Protected LSD test at alpha = 0.05 (Snedecor and Cochran, 1980).

The initial pH$_s$ of the greenhouse soil was 4.8 with some extractable aluminum, but the first increment of limestone dropped the aluminum to quite low levels. Bennett's thesis contains the plant analysis results of his plants. There were mixed effects from the liming treatments on plant aluminum. In 5 out of the 9 species-harvest combinations, the first increment of limestone significantly decreased aluminum concentration in the harvested material. The data were erratic, and there was no evidence to explain the departure from the usual finding, that plant aluminum also declines as extractable soil aluminum and acidity in soil decline due to liming.

The pH$_s$ data after 6 months of incubation are given in Table DB-5 as representative results. Incubation lowered pH$_s$ from the initial 4.8 to 4.3. In the fineness factor calculation, the >8 mesh particle size is given a value of 0, but that particle size did at least offset the acidification that occurred during incubation. The bulk treatment (quarry-run limestone) raised the pH$_s$ to the upper limit of the alfalfa target range for northern Missouri, as it did in the greenhouse. The data in Table DB-5 suggest that the neutralizing value of the 8-40 and 40-60 mesh fractions are underestimated in the current fineness factor evaluation, at 25% and 60%, respectively. Under the conditions of the Bennett incubation, these values would be closer to 40% and 80%, respectively. However, incubation results in a closed system should not be extrapolated to the field without repeating the study under field conditions.

Soil samples from the field study sites taken in 1988 were only 0-6" samples and the soil test results were used to determine the corrective treatments for P, K and limestone (see Table DB-1 for test results).

Table DB-5. The effects of limestone particle size fractions applied at increments of the calculated lime requirement on the active acidity of an acid soil after 6 months of incubation.

Particle Size	Fraction of Lime Requirement					
	0	0.33	0.66	1.00	1.33	1.66
Mesh	pH$_s$					
Bulk	4.3n	5.4k	5.9hi	6.5efg	6.6cde	6.7bcde
>8	4.3n	4.3n	4.6m	4.6m	4.9l	4.9l
8-40	4.3n	5.0l	5.6jk	6.0h	6.3fg	6.3fg
40-60	4.3n	5.4k	6.5efg	6.7bcde	6.8a	6.7bcde
<60	4.3n	5.7j	6.8a	6.8a	6.9a	6.8a

Bennett used fractional increments of the calculated lime requirement similar to those used in the greenhouse and incubation studies. Due to on-site calibration problems of the limestone spreader, some deviation from intentions resulted (Table DB-6). The treatments were applied prior to plowing in the fall of 1988. Seedbed preparation and seeding at both sites was done in spring 1989.

Table DB-6. Limestone treatments used in liming field studies.

	Treatment	Limestone	Species		
Site	Number	Source	Alfalfa	Red Clover	Lespedeza
			Fraction of LR*		
McWhorter	1	none	0	0	0
	2	Columbia	0.42	0.49	0.49
	3	Columbia	0.83	0.98	0.98
	4	Columbia	1.25	1.47	1.47
	5	Columbia	1.67	1.96	1.96
	6	Beck	1.09	1.28	1.28
Wilson	1	none	0	0	0
	2	Columbia	0.26	0.30	0.48**
	3	Columbia	0.52	0.60	0.96
	4	Columbia	0.79	0.92	1.43
	5	Columbia	1.04	1.20	1.91
	6	Beck	0.70	0.81	1.27

*The LRs were to increase pH$_s$ to 6.6-70 for alfalfa and 6.1-6.5 for red clover and lespedeza.
**The Mississippi limestone was used only on the lespedeza block at the Wilson site.

Bennett's field study was cut short due to the time constraint of his appointment so only the data from the establishment year were included in his thesis. The study was, however, continued through 1991. Yields from 1989, the establishment year, and 1989 soil acidity test results are summarized in Table DB-7. The limestone treatments did not have any statistically significant effects upon forage yields. Dry weather was partly responsible for the low yields and likely for limited response to treatments.

Fall 1989 soil samples taken to a 6 inch depth showed only very modest increases in pH$_s$ and decreases in neutralizable acidity attributable to treatment (Table 14 in Bennett's thesis). There are at least 2 reasons for the apparent lack of response to lime. Logistics in getting the study started in time to have data for Bennett's thesis resulted in the decision to apply all the treatments on the unplowed soil and then plow them under with no mixing with soil before plowing. As a result placement of the treatments was a result of how the plow turned over the soil. As will be shown later, plowing was deeper than 6 inches and the 6" sampling did not probe into the full treated layer of soil.

The pH_s results showed that acidity was lowered by liming but not in the amount expected. Liming did significantly lower the extractable aluminum in the soil at the McWhorter site. However, this was not the case at the Wilson site. The Wilson site initially had 5 to 6 times more extractable aluminum than the McWhorter site (Table DB-1). Liming significantly lowered aluminum on 2 blocks at the Wilson site but did not on the lespedeza block. This block received a different kind of limestone than the alfalfa and red clover blocks. There is no explanation for the different effects on aluminum, as both limestones had nearly the same ENM values.

Table DB-7. Soil acidity measures and forage yields as affected by limestone treatments in the stand establishment year (1989)*.

		Site					
		McWhorter			Wilson		
Species	Treatment	pH_s	Al^*	Yield	pH_s	Al^1	Yield
			ppm	tons/acre		ppm	tons/acre
Alfalfa	1	4.9c	13a	1.51	4.6c	113a	0.98
	2	5.0bc	8b	1.57	4.7c	73ab	0.79
	3	5.4a	5b	1.56	5.3ab	34b	1.02
	4	5.5a	2b	1.78	5.3ab	24b	1.07
	5	5.3ab	5b	1.59	5.4a	23b	1.00
	6	5.3ab	4b	1.83	5.0bc	54b	1.17
Red Clover	1	4.9b	15a	1.92	4.3b	178a	1.01
	2	5.2ab	6b	2.21	4.7a	86b	0.98
	3	5.3ab	6b	2.15	4.7a	97b	1.24
	4	5.4a	4b	2.31	4.7a	98b	1.00
	5	5.5a	5b	2.28	4.9a	85b	1.08
	6	5.2ab	6b	2.06	4.6ab	95b	1.15
Lespedeza	1	5.1c	11a	1.83	5.0c	37	1.24
	2	5.2ab	6b	2.21	5.5b	18	1.08
	3	5.5ab	5b	1.59	5.6b	9	1.10
	4	5.7a	0b	1.98	5.6b	17	1.11
	5	5.6ab	2b	1.97	5.9a	12	1.07
	6	5.3bc	3b	1.78	5.2c	44	1.15

*Comparisons within cells with Fisher's protected LSD test at alpha = 0.05. Yields are means of two harvests, except only one harvest was taken of lespedeza at the Wilson site.

In Fall 1991 all plots at both sites were sampled by 3 inch increments down to 12 inches to document the placement of limestone from plowing prior to forage establishment. This sampling pointed out that the lime treatments based upon a lime requirement which had been calculated for alfalfa in southern Missouri (target pH_s range = 6.6 to 7.0) and a plow depth of 6.67 inches affected the soil to a depth of 9 inches (Table DB-8). Thus if pH_s has any value in detecting the effects of treatments, the fractional lime requirement treatments as set up by Bennett (Table DB-6) need to be adjusted for depth of treatment. This was done by multiplying each of the values in Table DB-6 by 0.75 (rounded 6.67"/9").

Table DB-8. Effects of limestone applied in 1989 upon soil pH_s in samples taken in Fall 1991.

			Treatment[*]					
Site	Block	Depth	1	2	3	4	5	6
		inches						
McWhorter	Alfalfa	0-3	5.2	5.6	5.7	6.0	6.6	5.7
		3-6	5.3	6.2	6.3	6.6	6.7	6.1
		6-9	5.2	6.4	6.5	6.4	6.6	6.0
		9-12	4.7	4.8	5.2	4.8	4.8	4.6
	Red Clover	0-3	5.3	5.7	5.6	6.1	6.2	6.3
		3-6	5.5	6.1	6.2	6.7	6.8	6.4
		6-9	5.5	6.0	6.2	6.7	6.6	6.1
		9-12	4.6	4.8	4.6	5.0	4.9	4.8
	Lespedeza	0-3	5.8	6.1	6.4	6.4	6.6	6.1
		3-6	6.0	6.7	6.6	6.9	7.0	6.6
		6-9	5.4	5.8	6.2	6.5	7.0	6.3
		9-12	4.7	4.7	4.8	4.8	5.0	4.8
Wilson	Alfalfa	0-3	4.7	4.7	5.0	5.6	5.2	5.0
		3-6	4.8	5.2	5.7	6.2	6.3	5.9
		6-9	4.2	4.4	4.5	5.0	5.0	4.6
		9-12	4.0	4.0	4.1	4.2	4.2	4.1
	Red clover	0-3	4.5	4.6	5.2	4.8	5.3	4.8
		3-6	4.6	5.4	5.7	5.6	6.3	5.5
		6-9	4.3	4.5	4.8	4.5	4.5	4.4
		9-12	4.0	4.0	4.0	4.1	4.2	4.0
	Lespedeza	0-3	5.3	5.5	5.8	5.6	6.0	5.4
		3-6	5.4	6.2	6.1	6.3	6.6	6.1
		6-9	4.6	4.8	5.0	4.8	5.5	4.9
		9-12	4.1	4.2	4.2	4.2	4.2	4.2

[*] See Table DB-6 for more detail on the treatments.

The recalculation of the fraction of the lime requirement applied compared to the mean of the pH_s of the 0 to 9 inch layer of each of the cells in Table DB-8 shows the following:

1. At the McWhorter site slightly more than the full lime requirement was needed to get the mean soil pH_s into the target range 30 months after application.

2. At the Wilson site none of the treatments was at full lime requirement after adjustment for depth, and this was reflected by the pH_s values on the alfalfa and red clover blocks, which received the same limestone as the McWhorter site.

3. The Beck limestone at both sites and the Mississippi limestone on the Wilson lespedeza block did not affect the soil as did the Columbia limestone. The neutralizing value of the Beck limestone was slightly over estimated and that of the Mississippi limestone under estimated.

Based upon the soil data after recalculation of the treatments, it appears that the lime requirement was underestimated. Further the soil data suggest that there were distinct differences between the three limestones in their effects on neutralization of soil acidity. These differences may have been due to their mineralogical characteristics, making them differ in reactivity to soil acidity. Stephens' results, however, suggested that in the lab there was no difference between calcitic and dolomitic limestones. In the Bennett study the Beck dolomitic limestone did not react as would be expected from the ENM value. Thus, a single calculation method for limestone needed to correct a soil acidity problem should be expected to have variable effects on soil acidity due to differences in stone and soil parameters. However, due to differences in the reactivity with soil acidity between various liming materials, the recommendation system in place at the start of 2000 may be as good as can be obtained.

The analysis of the yield data from 1990 and 1991 would suggest that there were factors other than calculated lime requirement and the ENM values of the limestones affecting the outcome of the study. Dry weather adversely affected the yields. The region of the study consists of soils with limited rooting depths due to strongly acidic subsurface horizons preventing access of roots to stored soil moisture. Table DB-9 shows a significant but inconsistent response to liming especially at the more acidic Wilson site. Lespedeza failed and attempts to reseed also failed. The 1991 red clover yields were affected by the biennial nature of the species. Reseeding in 1991 was only partially effective. The Wilson site was terminated in mid-1991 at the new land owner's request, and the McWhorter site was terminated at the end of 1991.

Table DB-9. The effects of lime treatments upon annual forage legume yields — 1990 and 1991.

a. Yields

Site	Year	Species	Treatment						Statistics*
			1	2	3	4	5	6	
			------------------------- tons/acre					--------------------------	
McWhorter	1990	Alfalfa	4.4	4.6	4.8	4.9	5.2	4.8	NS
	1991		2.6	2.8	2.9	3.1	2.8	2.9	NS
Wilson	1990	Alfalfa	2.1	3.0	3.0	3.5	3.3	3.2	lsd$_{0.05}$ = 0.18
	1991		1.4	1,4	1.8	1.7	1.6	1.7	NS
McWhorter	1990	Red Clover	5.0	5.2	5.1	4.9	5.2	5.1	NS
	1991		2.6	2.4	2.3	2.4	2.4	2.4	NS
Wilson	1990	Red Clover	4.4	4.7	4.6	4.7	4.5	4.5	NS
	1991					lost			

*Results of general analysis of variance. Analysis of data by fitting to linear and quadratic expressions by regression gave the following significant results (T = treatments as fraction of LR).

b. Model: Yield = f(lime treatments x T)

Site	Year	Species	Model	Equation	Significance
McWhorter	1990	Alfalfa	Linear	Total Y = 4.23 + 0.18075T	10%
Wilson	1990	Alfalfa	Linear	Total Y = 2.13 + 0.294T	<1%
Wilson	1991	Alfalfa	Linear	Total Y = 1.36 + 0.079T	<10%
Wilson	1990	Alfalfa	Quadratic	Total Y = 1.2815 + 1.0204T + $0.121T^2$	<5%
Wilson	1990	Red Clover	Quadratic	Total Y = 4.118 + 0.362T + $0.0585T^2$	<10%

The harvested forages in 1990 were analyzed for N, P, K, Ca, and Mg. The Beck limestone treatment consistently increased magnesium in both alfalfa and red clover, but the absence of significant yield response suggests that magnesium was not limiting on the calcitic limestone treatments.

Based upon the Bennett work, the methods of estimating lime requirements in place since the 1970s are still effective. Changes in the forage recommendations would require several field calibration sites; the expense of these studies likely could not be justified.

Application Of Lime And Crop Residues To Ameliorate Phytotoxic Aluminum In Two Acid Missouri Soils

Syed Omar Syed Rastan, Ph.D. Dissertation-1995
J.R. Brown and R.J. Miles, Advisors

In spite of the work done by the students reported in preceding sections of this paper, there remained several uncertainties about the chemistry of limestone amendments to acid soils. Syed Omar Syed Rastan contacted us concerning a Ph.D. program with emphasis on the chemistry of acid soils. He had experience in Malaysia and in Georgia (USA) with highly acid soils containing toxic levels of active aluminum.

Syed conducted four different studies designed to reach the following objectives:

- Evaluate the merits of the Woodruff buffer and several different extractants of extractable aluminum for estimating lime requirements for highly acid soils.
- Measure the changes in soil solution chemistry in lime amended highly acid soils,
- Document the effects of organic soil amendments upon toxicity of soil aluminum to alfalfa.

Yusef (1986) suggested that extractable aluminum in highly acid soils may be useful as a basis for the estimation of lime requirement of such soils. Syed Omar (1995) tested Yusef's suggestion on two highly acid soils from southern Missouri. One soil, from a second growth timbered site, was classified as Captina (fine-silty, mixed, mesic Typic Fragiudult). The second soil, from a farm woodlot, was classified as Hobson (fine-loamy, mixed, mesic Typic Fragiudalf). The A1 horizon was collected after removal of surface organic material. Chemical characteristics of these two soils are summarized in Table SO-1.

Table SO-1. Chemical characteristics of two soils from the Ozark region of Missouri.

	Columns										
	1	2	3	4	5	6	7	8	8	10	11
Soil	Ca	Mg	K	Al	ECEC[*]	NA[**]	CEC[***]	pH_w	pH_s	OM	P-1
	------------------------------ meq/100g ------------------------------									%	mg/kg
Captina	0.51	0.23	0.17	3.34	4.25	9.0	9.91	4.7	4.0	1.9	7
Hobson	0.38	0.28	0.17	2.81	3.64	9.5	10.33	4.7	3.9	1.8	7

[*] Sum of columns 1, 2, 3, and 4.

[**] Neutralizable acidity using the New Woodruff buffer.

[***] Sum of columns 1, 2, 3, and 6.

The results are based upon routine soil testing methods and aluminum extractable with 1 M KCl.

Study 1 was a greenhouse pot study using both soils and alfalfa as a test crop. Corrective treatments of P, K, B, and S were added to both soils based upon recommendations for establishment and production of alfalfa in Region 7 (central Ozarks) of Missouri (Buchholz, 1983). These corrective treatments were thoroughly mixed in bulk quantities of the two soils. Lime treatments were based upon fractions of the extractable aluminum plus a full lime requirement as estimated using the New Woodruff Buffer. The liming material was analytical grade $CaCO_3$ and $MgCO_3$ mixed in a 6:1 Ca:Mg ratio (Table SO-2). The alfalfa test crop was harvested 5 times at 10% bloom in 30-day intervals. Soil in each pot was sampled for measurement of 1 M KCl extractable aluminum, pH_w, and pH_s after the second and fourth harvests.

Table SO-2. Liming treatments applied to two highly acid soils for a greenhouse study with alfalfa as the test crop.

		Fraction of extractable Al					Woodruff	
Soil	Units	0	0.25	0.50	1.0	2.0	2.7*	3.4*
Captina	meq/100g	0	0.84	1.67	3.04	6.68	9.0	na
Captina	% of WB*	0	9.2	18.50	37.00	74	100	na
Hobson	meq/100g	0	0.70	1.40	2.81	5.62	na	9.5
Hobson	% of WB*	0	7.4	14.70	30.00	59	na	100

*Calculated as an equivalent fraction of the 1 M KCl extractable aluminum. WB = Woodruff buffer.

Alfalfa did not persist without lime (Table SO-3). Lime applied at amounts equivalent to 25 and 50% of the extractable aluminum was unable to sustain even modest yields through five harvests. Lime applied at an amount equivalent to the amount of extractable aluminum was insufficient to maximize yields. In contrast to Yusef's results, application of lime at twice the equivalent amount of extractable aluminum was inadequate to maximize yield. However extractable aluminum was lowered to near zero by a lime equivalent to 2 x KCl extractable aluminum (Table SO-4). Lime, applied at less than 50% extractable aluminum, reduced extractable aluminum in the soils.

Table SO-3. Alfalfa dry matter produced in a greenhouse study in response to differential lime rates (means of 4 replications).

			Harvest .					
Soil	Treatment	Fraction of Extractable Al	1	2	3	4	5	Roots
			grams/pot					
Captina	1	0	0.10	0.03	0	0	0	0
	2	0.25	0.62	1.32	0.64	0.18	0.11	0.60
	3	0.50	1.91	2.47	1.06	0.55	0.65	2.23
	4	1.00	3.78	3.91	3.48	5.12	5.03	6.95
	5	2.00	3.47	5.35	5.98	9.38	9.77	11.12
	6	2.96	2.10	6.66	6.60	9.56	10.88	11.00
Hobson	1	0	0	0	0	0	0	0
	2	0.25	0.72	0.52	0.39	0.32	0.19	0.28
	3	0.50	2.01	2.13	1.08	0.69	0.66	1.38
	4	1.00	3.48	4.18	3.25	4.53	5.81	6.26
	5	2.00	4.48	6.06	5.44	8.40	9.49	10.92
	6	3.38	3.70	5.48	6.68	8.71	10.11	9.25

A separate laboratory incubation study on the Captina and Hobson soil material used for the greenhouse helped explain the alfalfa yield responses over successive harvests. Aluminum activity in the soils increased with time (Table SO-5), and in the soils receiving the two largest lime treatments it was zero throughout the length of the incubation. The alfalfa yield data more or less reflected the changes in pH_s and aluminum activity in extracted soil solution.

The pH_s of the soils receiving the most lime declined measurably in the 60 days between the second and fourth harvests. Only those pots that received the equivalent of the Missouri lime recommendation based on the Woodruff buffer maintained a pH_s in excess of 6.0 after four harvests. These greenhouse results suggest that application of lime at twice the equivalent of extractable aluminum is inadequate for sustaining alfalfa yields over time.

Table SO-4 Effects of incremental lime treatments on soil acidity measurements in a greenhouse study.

			Post-harvest 2		Post-harvest 4	
Soil	Treatment	Fraction of Extractable Al	Al	pH_s	Al	pH_s
			meq/100 g			
Captina	1	0	1.92	4.10	1.96	4.10
	2	0.25	1.52	4.23	1.60	4.15
	3	0.50	1.19	4.35	1.22	4.20
	4	1.00	0.44	4.62	0.59	4.62
	5	2.00	0.01	6.09	0	5.77
	6	2.96	0	6.91	0	6.24
Hobson	1	0	1.47	4.12	1.52	4.14
	2	0.25	1.08	4.24	1.21	4.16
	3	0.50	0.80	4.33	0.52	4.32
	4	1.00	0.29	4.78	0.41	4.67
	5	2.00	0.01	5.89	0.01	5.60
	6	3.38	0	7.24	0	6.81

Table SO-5. Effects of differential liming of two highly acid soils on aluminum activity in extracted soil solution over 10 months of incubation.

			Months of incubation			
Soil	Treatment	Lime*	1	2	5	10
			µM			
Captina	1	0	14	8	11	119
	2	0.25	7	5	27	74
	3	0.50	4	2	45	54
	4	1.00	1	5	8	8
	5	2.00	0	0	0	0
	6	2.96	0	0	0	0
Hobson	1	0	7	3	29	55
	2	0.25	3	3	25	47
	3	0.50	2	3	20	33
	4	1.00	0	3	5	7
	5	2.00	0	0	0	0
	6	3.38	0	0	0	0

*Fractional equivalent of the initial KCl extractable aluminum (see Table SO-2).

Another of Syed Omar's objectives was to evaluate different extractants of aluminum to determine if one might prove best as a basis for lime requirement estimates. Aluminum extracted from differently limed soil by extractants following the second greenhouse harvest is shown in Table SO-6. Syed Omar concluded that $LaCl_2$ was the superior extractant, because both alfalfa yields and soil pH_s were highly correlated with $LaCl_2$ extractable aluminum. The $CuCl_2$ and ammonium citrate extractants extracted aluminum even though the pH_s was at or over 6.9. The question remaining was whether there was an advantage to using extractable aluminum as a basis for estimating lime requirements.

A second greenhouse study was conducted to investigate the addition of plant material and lime upon alfalfa growth. Lime was applied at 0, 0.5, 1 and 2 times the 1 M KCl extractable aluminum (me per 100 g). The plant material treatments were alfalfa and wheat straw ground to pass a 2 mm screen and incorporated into the soils at a rate of 1% (w/w). There was insufficient soil for a true check. The greenhouse study was a 2 x 4 factorial with four replications on each soil. In other respects this second greenhouse experiment was identical to the first.

Table SO-6. Aluminum extracted with four different extractants from two differentially limed soils following 2 harvests.

				Extractant***			
Soil	Lime*	pH_s	NA**	KCl	$LaCl_2$	$CuCl_2$	KCl + NH_4Citrate
				------------------- meq/100 g -------------------			
Captina	0	4.1	6.37	1.92	2.27	3.50	3.64
	0.25	4.2	6.00	1.52	1.92	3.07	3.26
	0.50	4.4	5.50	1.19	1.58	2.68	2,93
	1.00	4.8	4.12	0.42	0.89	2.0	2.29
	2.00	6.1	1.75	0.00	0.22	1.43	2.00
	2.96	6.9	0.00	0.00	0.00	1.31	1.93
Hobson	0	4.1	6.75	1.47	1.85	2.59	2.82
	0.25	4.2	6.00	1.09	1.64	2.17	2.64
	0.50	4.3	5.50	0.80	1.28	2.00	2.56
	1.00	4.8	4.12	0.28	0.81	1.58	2.17
	2.00	5.9	1.75	0.00	0.25	1.18	1.90
	3.38	7.2	0.00	0.00	0.00	1.00	1.89

*Fractional equivalent of the initial KCl extractable aluminum (see Table SO-2).
**Neutralizable acidity using the New Woodruff buffer.
***1 M, 0.33 M, 0.5 M, and 1 M + 0.5 M, respectively.

Dry matter yields showed major interactions between lime and residue treatments (Table SO-7). Alfalfa established well in the unlimed pots that received alfalfa residue. Data in the thesis suggested that mineralization of the low C:N residue resulted in a short-term buildup of ammonium that reduced the toxic effects of active aluminum. Simple organic acids were shown to be present. Calculation of aluminum speciation using GEOCHEM supported the reduction in active aluminum. The beneficial effect of the alfalfa residue lasted only through the second harvest (Table SO-7). Straw addition to the soil did not offset the toxic effects of the unlimed soils.

The lack of a true non-residue treatment weakens conclusions but in greenhouse study 1alfalfa in untreated, unamended soil failed to establish (Table SO-3). The beneficial effects of the alfalfa residues on yields from limed pots lasted longer than with the straw; an effect likely due to the C:N ratio of the plant residues (Table SO-8).

After 4 harvests the lime treatments persisted in reducing extractable soil aluminum, and lime applied at twice the initial equivalent quantity of extractable aluminum kept measurable extractable aluminum from reappearing (SO-9). However, while the lime treatments reduced the aluminum concentration in the harvested alfalfa, aluminum was taken up on all treatments (Table SO-10). Obviously plants are able to take up aluminum even when there was no KCl extractable aluminum. This aluminum in excess of 1 M KCl extractable aluminum reflects slowly available aluminum that over time continues to react with remaining liming material in limed soils. This activity accentuates the need for periodic retesting of limed soils.

Table SO-7. Effects of lime and plant residues on dry matter yields of greenhouse grown alfalfa[*].

			Harvest			
Soil	Residue	Lime[**]	1	2	3	4
			grams/pot			
Captina	Alfalfa	0	2.78	7.28	4.07	0.45
		0.5	4.27	11.66	8.01	2.52
		1.0	2.36	11.75	10.22	8.33
		2.0	1.53	15.22	14.76	21.72
	Straw	0	0.4	0	0	0
		0.5	1.39	2.54	1.72	1.66
		1.0	2.03	3.86	5.10	11.29
		2.0	0.86	4.15	8.22	19.47
Hobson	Alfalfa	0	4.26	10.76	1.77	1.65
		0.5	3.35	9.30	7.30	3.45
		1.0	3.88	13.54	7.78	10.39
		2.0	3.80	14.39	13.39	20.65
	Straw	0	0.05	0	0	0
		0.5	1.75	3.04	2.83	1.51
		1.0	2.94	7.50	9.40	7.48
		2.0	2.50	9.05	12.58	18.09

[*] Means of 4 replications.

[**] Expressed as a fraction of the equivalent KCl extractable aluminum at pre-treatment.

Table SO-8. Composition of plant residues used as soil amendments in greenhouse study 2.

Residue	N	P	K	Ca	Mg	C/N
	%					
Alfalfa	3.40	0.30	3.08	1.77	0.15	12.4
Straw	0.60	0.11	0.62	0.17	0.03	72.5

Table SO-9. Effect of lime and organic residues on soil acidity and KCl extractable aluminum after the fourth harvest (165 days after initial wetting).

		pHs			Al		
Soil	Lime[*]	Alfalfa	Straw	None	Alfalfa	Straw	None
		meq/100g					
Captina	0	4.1	4.1	4.1	1.41	1.50	1.95
	0.5	4.3	4.3	4.3	0.86	1.21	1.22
	1.0	4.8	4.5	4.6	0.32	0.74	0.59
	2.0	5.9	5.7	5.8	0.00	0.00	0.00
	$HSD_{0.05}$[**]	0.3	0.3	0.2	0.27	0.32	0.17
Hobson	0	4.2	4.0	4.0	0.79	1.26	1.52
	0.5	4.4	4.2	4.3	0.55	0.70	0.92
	1.0	4.9	4.5	4.7	0.19	0.47	0.41
	2.0	5.5	5.3	5.6	0.00	0.00	0.00
	$HSD_{0.05}$[**]	0.3	0.2	0.2	0.14	0.15	0.18

[*] Expressed as a fraction of the equivalent KCl extractable aluminum at pre-treatment.

[**] Tukey's test.

After 4 alfalfa harvests, exchangeable calcium and magnesium in the potted soils failed to show recovery of calcium and magnesium added in the treatments (Table SO-11). This lack of recovery suggests that undissolved limestone remained in the soils at the end of the experiment.

Syed Omar concluded that KCl extractable aluminum could serve as a basis for estimating lime requirements on highly acid soils, but doubling the calculated lime equivalent to account for extractable aluminum, as suggested by Yusef, was inferior to lime requirement using the Woodruff buffer. Syed-Omar's results indicated that extractable aluminum using 0.33 M $LaCl_3$ might be a better choice, but he had insufficient data to provide a basis for adaptation. Syed Omar also included some data that perhaps explained observations in the field that poor growth of young alfalfa stands established on recently limed soils may be due to induced nutrient deficiencies.

Table SO-10. Effects of lime and organic residues upon the concentration of aluminum in alfalfa tissue from the fourth harvest on a Hobson soil.

Lime[*]	Alfalfa	Straw	None
	----------------	mg Al/kg	----------------
0	64	ND[**]	106
0.5	46	86	73
1.0	36	42	73
2.0	25	23	71
$HSD_{0.05}$[***]	13	26	22

[*] Expressed as a fraction of the equivalent KCl extractable aluminum at pre-treatment.
[**] No plant material available for analysis.
[***] Tukey's test.

Table SO-11. Ammonium acetate exchangeable cations in the Hobson soil after the fourth harvest of alfalfa grown in the greenhouse.

Lime[*]	No residue			Alfalfa			Straw		
	Ca	Mg	Ca+Mg	Ca	Mg	Ca+Mg	Ca	Mg	Ca+Mg
					meq/100g				
0	0.93	0.42	1.35	1.74	0.56	2.30	1.09	0.48	1.57
0.5	1.98	0.56	1.54	2.56	0.63	3.19	2.04	0.62	2.66
1.0	2.76	0.69	3.45	3.51	0.79	4.30	2.93	0.75	3.68
2.0	4.45	0.90	5.35	4.84	0.64	5.48	4.42	0.90	5.32
$HSD_{0.05}$[**]	0.70	0.08		0.39	0.13		0.52	0.17	

[*] Expressed as a fraction of the equivalent KCl extractable aluminum at pre-treatment.
[**] Tukey's test.

Index

College of
Agriculture
Food and
Natural
Resources

Missouri Agricultural Experiment Station

SR 548

New 2/03/500