

Soil pH and lime management for corn and soybean

by

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CHAPTER 1. GENERAL INTRODUCTION

Soil acidity can affect plant growth directly and indirectly by affecting the plant availability of nutrients, levels of phytotoxic elements, and microbial activity. Soils may become acidic in the long term as a result of several natural processes. In the short term, however, soil acidity develops mainly due to application of N fertilizers or manure, primarily those having high concentrations of ammonium or urea because nitrification releases hydrogen ions (H^+). Soil pH decreases as the acidity increases because pH expresses acidity as the negative logarithm of concentration (activity) of H^+ . Limestone application is the most widely used practice to correct soil pH in agricultural acidic soils. Soil pH should be used to determine whether or not to lime a soil, but soils have a significant (although variable) buffer capacity and it cannot indicate the quantity of reserve acidity that should be neutralized. Direct titration of reserve soil acidity is impractical as a routine test and seldom is used in the U.S., so a buffer test often is used to determine lime requirements. The amount of lime needed to increase pH to a desirable level can be estimated by mixing a buffer of known pH with soil and measuring the resulting pH decrease.

In Iowa, as in many Midwestern states, the Shoemaker-McLean-Pratt (SMP) buffer is used to estimate lime requirement (LR) of soils. Since this methodology uses hazardous chemicals, work has been done to develop alternative methods, such as the modified Mehlich and Sikora methods. Various studies have emphasized the need for regional calibration of buffer pH methods to determine lime needs, and few field studies have compared methods to determine lime requirement including methods that avoid the use of hazardous chemicals. In addition, there is little information in Iowa and the Midwest about what soil parameters are most important to predict soil pH change due to lime application, and therefore lime requirement.

There is renewed interest in soil pH and liming issues in relation to within-field variability because dense grid soil sampling approaches and variable rate technology are being adopted at a rapid rate by producers. Results from samples collected from producers' fields and limited field-scale research have shown very high pH variation within fields and even within soil map units. However, no study of buffer pH methods has included multiple samples from several fields, and there is no published information about within-field variation of pH change due to liming and little about within-field response variation to lime application. Iowa State University recommendations suggest lime applications for grass hay or pastures, corn or soybean, and alfalfa when soil pH is < 6.0, < 6.5, and < 6.9, respectively. However, a pH of 6.0 is considered sufficient for corn and soybean for soil series with free carbonates at a shallow depth. Research to update these recommendations is needed because of changes in production practices and yield levels since the original supporting research was conducted. Also, a few recent field trials confirmed the need for lime in strongly acid soils, but results from other trials, mainly in soils with calcareous subsoil, suggested pH values lower than currently recommended might be sufficient for corn and soybean.

Long-term field studies that evaluate soil pH over time as affected by limestone rate and source are not abundant in literature for the U.S. Because of the expense and intense labor, field experiments to evaluate soil pH changes over time due to lime application and to determine lime requirement are rarely conducted. Instead, most of the information available derives from incubation studies which may not be representative of field situations. In this sense, there is insufficient information coming from field studies concerning reaction time of limestone in the soil and short-term effects on crop yield for different sources and application rates. This information is needed to improve soil pH management and liming recommendations.

The overall objective of this research was to generate information to improve soil pH and lime management for corn-soybean rotations. Two distinct studies were conducted to achieve this general objective; one was based on a strip-trial methodology (Chapter 2 and 3) and the other based on conventional field-plot experiments (Chapter 4). Specific objectives for Chapter 2 were to (1) compare the SMP buffer method, which is currently used in most states of the Corn Belt, Sikora and modified Mehlich buffer methods, and titratable acidity under field conditions and (2) identify soil properties that best explain the variation in soil pH response to lime within and across some typical Iowa corn and soybean fields. Specific objectives for Chapter 3 were to (1) study the variation of soil pH and crop response to lime application within fields, (2) identify optimum soil pH for corn and soybean in some important Iowa soils, and (3) evaluate the effect of subsoil pH on crop response to application of lime. The specific objective for Chapter 4 was to evaluate soil pH and crop response to the application of pure calcium carbonate, calcitic limestone, and dolomitic limestone in four acidic Iowa soils.

DISSERTATION ORGANIZATION

This dissertation is organized in three papers suitable for publication in scientific journals of the American Society of Agronomy. The title of the first paper is “Comparison of methods to determine crop lime requirement under field conditions”. The title of the second paper is “On-farm evaluation of corn and soybean yield and soil pH responses to lime application”. The title of the third paper is “Soil pH change over time as affected by sources and rates of limestone”. Each paper is divided in sections that include an abstract, introduction, materials and methods, results and discussion, conclusion, references, tables, and figures. The papers are preceded by a general introduction and followed by general conclusion section.

CHAPTER 2. COMPARISON OF METHODS TO DETERMINE CROP LIME REQUIREMENT UNDER FIELD CONDITIONS

A paper submitted to the Soil Science Society of America Journal by

Agustín Pagani and Antonio P. Mallarino

ABSTRACT

Little field research evaluated buffer pH methods to estimate lime requirement (LR) such as Sikora and Mehlich that include no hazardous chemicals. This study assessed how Shoemaker-McLean-Pratt (SMP), Sikora, and Mehlich buffers, titratable acidity (TA), and soil properties relate to soil pH change due to liming under on-farm conditions. Experiments were established in 2.54- to 6.42-ha areas of 14 Iowa fields. Replicated treatments were a control and 6.72 Mg ha⁻¹ of effective calcium carbonate equivalent. Soil samples (19 - 48 per site, 15-cm depth) were collected before and 6- to 12-months after liming. Soil pH was 4.60 to 8.05 across all samples. Mean SMP, Sikora, and Mehlich buffer pH values across all samples differed ($P < 0.05$) and were 6.44, 6.38, and 5.78, respectively. Soil pH, organic matter (OM), and clay explained a higher proportion of soil pH change variation due to liming (23, 9, and 6%) than any buffer method or TA (1 to 3%). Sikora and SMP were highly correlated (r^2 0.92), did not differ for most soil series, and current SMP calibrations for LR could be used for Sikora. Sikora needs a different calibration for five soils and Mehlich for all soils, however, because values were lower than for SMP. Soil pH and OM together with SMP, Sikora, or Mehlich explained 28, 37, and 45% of the field pH change variation. Therefore, use of pH and OM together with Sikora or Mehlich buffers would provide the best prediction of LR under conditions like those in this study.

Abbreviations: ANOVA, analysis of variance; CCE, calcium carbonate equivalent; CV, coefficient of variation; DGPS, differential global positioning system; GIS, geographical information system; ECCE, effective calcium carbonate equivalent; LR, lime requirement; SMP, Shomaker-McLean-Pratt; OM, organic matter; TA, titratable acidity.

INTRODUCTION

Soil acidity influences many chemical and biological reactions that control plant nutrient availability and toxicity of some elements, and is a serious limitation for crop production in many regions of the world. Soil pH is used to determine whether or not soil acidity limits crop growth but does not directly estimate lime requirement (LR). Therefore, several analytical methods have been developed to determine LR. These include soil incubation, direct titration, and use of buffer solutions. Whereas long-term soil incubation with CaCO_3 seems an ideal method, it is impractical for use by routine testing laboratories. The usual procedure consists of adding pure, finely divided CaCO_3 to soil in different quantities, to moisten the soil, and allow the reaction to take place at room temperature over a time considered long enough for equilibrium to be attained (several weeks), pH is measured, and LR can be calculated. Therefore, this method has been occasionally used only as a laboratory standard to evaluate the results obtained by more rapid and convenient methods (McLean et al., 1961; Shoemaker et al., 1961; Hoskins and Erich, 2008). Direct titrations also can be used by adding incremental small amounts of $\text{Ca}(\text{OH})_2$ or KOH to a slurry of water and soil, measuring the pH of the slurry after the reaction is complete, and repeating the process until an end point is reached at some pH value (Dunn, 1943). This procedure may require days, and still is not practical

for use in routine soil testing laboratories. The measurement of TA by a short, one-time titration with BaCl_2 -trietanolamine at pH 8.2 also has been used (Bhumbla and McLean, 1965; Dietzel et al., 2009). This method still is laborious and time-consuming for routine analysis, however.

Buffer pH methods have been developed for a quicker assessment of LR. A buffer solution (mixture of a weak acid and its conjugate base) resists pH changes in the solution but gives a linear decrease in pH when the soil's potential acidity reacts with the buffer (Sims, 1996). This decrease in buffer pH estimates the lime required to neutralize the total acidity of the soil to a desired pH (Jones, 2001). A calibration study of buffers is usually done to verify the accuracy of the test (Sims, 1996) and the suitability of the buffer to the range of soil characteristics pertaining to a certain geographical region. In Iowa, as in most Midwestern states, the SMP buffer adjusted to pH 7.5 is used to estimate the LR of soils (Shoemaker et al., 1961; Watson and Brown, 1998). Buffers used in other regions until the late 2010s have been original or modified versions of Woodruff (Woodruff, 1948; Watson and Brown, 1998), Adams-Evans (Adams and Evans, 1962), and Mehlich (Mehlich, 1976) methods.

Most buffer pH methods were developed before federal laws regulated disposal of hazardous waste due to ignitability, corrosivity, reactivity, or toxicity. Chemicals in this category are p-nitrophenol and K_2CrO_4 in the SMP buffer and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in the Mehlich buffer that must be handled and disposed properly. Therefore, work has been done to develop alternative methods for determining lime needs without using hazardous chemicals. Some researchers have tried direct titrations using single additions of $\text{Ca}(\text{OH})_2$ (Liu et al., 2005; Kissel et al., 2007; Thompson et al., 2010). The modified Mehlich buffer was developed by Hoskins and Erich (2008) primarily to overcome the drawbacks of the SMP buffer procedure (i.e., unstable buffer pH readings, rapid electrode

degradation, poor precision of results, and the production of hazardous waste in the laboratory). Barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in the original Mehlich buffer was replaced with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at the same concentration. The disadvantage is that it cannot be stored for more than approximately 3 weeks (Hoskins and Erich, 2008). This relatively short shelf-life is a result of precipitation, and also a potential for fungal growth because this buffer is an excellent medium for microbial growth. Hoskins and Erich (2008) worked with incubations and showed that buffer pH values for the original or modified Mehlich buffer were similar than for the SMP method. Godsey et al. (2007) evaluated the SMP and the modified Mehlich buffers in Kansas soils based on laboratory soil incubations and limestone application at the field. They reported that buffer pH values were significantly lower for the Mehlich buffer, and that with the local calibration this method would predict LR better than the SMP buffer.

Sikora (2006) developed a buffer that mimics the SMP buffer in its buffering capacity and includes no hazardous chemicals. He replaced K_2CrO_4 and p-nitrophenol in the SMP method by 2-(N-morpholino) ethanesulfonic acid monohydrate (MES) and imidazole. The modification makes the measured buffer pH range narrower (i.e., from 5.30 to 7.56) and uses a 1:1:1 ratio of buffer/soil/water as the SMP procedure. The new buffer produced similar buffer pH values as the SMP buffer on 255 Kentucky soils and 87 NAPT soils, and had a shelf life of 150 days (Sikora, 2006).

Several soil properties have been identified as being related to LR. For example, Keeney and Corey (1963) working with incubation experiments in Missouri, correlated LR with various soil properties (OM, pH, SMP buffer pH, Woodruff buffer pH, clay concentration, extractable and exchangeable aluminum). They reported that SMP buffer pH was the best single predictor variable for LR ($r = 0.95$). Their results also showed that both OM and soil pH explained the largest proportion of LR variation across soils

compared to initial soil pH alone. Because of this result, a combined parameter was calculated as the desired target pH minus initial soil pH multiplied by OM. The combined parameter was well correlated ($r = 0.88$) to LR. Because most routine soil testing labs measure pH and OM in soil samples, they proposed that LR could be predicted using an equation they developed based on soil pH, target pH, and OM. They suggested that the estimated LR should be multiplied by a factor of 2 because past experiences demonstrated that it was required to achieve the desired pH under field conditions.

Various studies have emphasized the need for regional calibration of buffer pH methods to determine lime needs (Sims, 1996; Rossel and McBratney, 2001). Moreover, few field studies have compared methods to determine LR including methods that avoid the use of hazardous chemicals. In addition, there is little information in Iowa and the Midwest about what soil parameters are most important to predict soil pH change due to lime application and, therefore, LR. There is renewed interest in soil pH and liming issues in relation to within-field variability because dense grid soil sampling approaches and variable rate technology are being adopted at a rapid rate by producers. Results from samples collected from producers' fields and limited field-scale research have shown very high pH variation within fields and even within soil map units (Peck and Melsted, 1973; Bianchini and Mallarino, 2002; Mallarino and Wittry, 2004). However, no study of buffer pH methods has included multiple samples from each of several fields and there is no published information about within-field variation of pH change due to liming. Several soils of Iowa also are found in neighboring states and some major properties are similar to other soils of temperate regions. Therefore, the objectives of this study were to assess how the Shoemaker-McLean-Pratt (SMP), Sikora, and Mehlich buffer pH methods, titratable acidity (TA), and other soil properties explain soil pH change due to liming under on-farm field conditions.

MATERIALS AND METHODS

Soil samples for this study were collected from the first year of 14 trials established in Iowa farmers' fields planted to corn (*Zea mays* L.) or soybean [*Glycine max* (L.) Merr.]. There were five trials in 2007, five in 2008, and four in 2009. The trials were conducted using a dense soil sampling approach, precision agriculture technologies, and replicated treatments applied to long plots (strips) as was used in previous works with lime (Bianchini and Mallarino, 2002) and other nutrients (Wittry and Mallarino, 2004; Bermudez and Mallarino, 2007; Mallarino and Wittry, 2010). Differential global positioning systems (DGPS) and geographical information systems (GIS) technique were used. Treatments replicated two to five times at each site were no lime or a uniform lime rate. There were two replications only at site 10 that was very narrow. The treatment plots ranged from 15 to 25 m across sites and their lengths (exclusive of at least 30-m borders on each side) varied from 245 to 400 m across sites, but both width and length were similar within a site. The experimental areas (excluding borders) ranged from 2.54 to 6.42 ha. The dominant soil series (Iowa Cooperative Soil Survey, 2001) were typical soils of Iowa and neighboring states where grain crops are planted (Table 1). Soil management practices included no-till, strip-till, and chisel-plow/disk tillage before soybean and only disking before corn (Table 1).

The limestone rate applied to all sites was 6.7 Mg ha^{-1} of effective calcium carbonate equivalent (ECCE) using calibrated custom applicators' equipment. Table 2 provides information about the limestone materials used at each site. The use of ECCE is required in the State of Iowa for analysis of neutralizing power of limestone and quantifies the combined effect of particle size distribution and neutralizing value of limestone (IDALS, 2008). The ECCE is defined as the product of the CaCO_3 equivalent (CCE) and a fineness factor (Table 2). The CCE application rate was the same within a site but ranged from 8.3

to 13.2 Mg ha⁻¹ across sites due to differences in the fineness of limestone from sometimes different quarries used across sites. The limestone application date across sites ranged from fall to spring before planting (Table 2), and was incorporated with the primary or secondary tillage in the fields managed with tillage.

Soil samples were collected before applying lime and after harvest of the first crop (in late October or early November) from a 15-cm depth using a dense grid sampling approach adapted to the experimental layout. Grid lines spacing across the plots and crop rows coincided with the width of a replication (two plots each measuring 15 to 25 m in width depending on the site), and the spacing along the plots was set to 30 to 40 m depending on the site. Therefore, for the initial sampling before lime application, the width of each soil sampling cell was similar within each site but ranged from 0.12 to 0.18 ha across sites. One 12-core composite soil sample was collected from each cell by collecting the cores randomly from a circle approximately 120 to 150 m² in size at the center of each cell. The center of each sampling area was georeferenced with a hand-held DGPS device. In three sites, the samples were collected from the area corresponding to the control plots because lime had to be applied before soil sampling. After crop harvest, the soil samples were collected from limed and not limed grid cells. In this case the width of each cell was defined by each plot border, and the length was the same as for the initial soil sampling cell. The time encompassed between lime application and the post-harvest soil sampling ranged from 6 to 12 months (Table 2). Rainfall amounts between lime application and soil sampling were approximately normal for the regions (Table 3). Rainfall data were obtained from the nearest weather stations, which were located 3 to 25 km from the sites.

Soil samples taken before lime application were analyzed for pH using a 1:1 soil-water ratio, OM by a combustion method (Wang and Anderson, 1998), texture by the

pipette method (Soil Survey Staff, 2004), soil buffer pH by three methods, and TA. Buffer pH was measured by the method currently recommended for the North Central Region (Watson and Brown, 1998), by the method described by Sikora (2006), which hereon will be referred to as Sikora), and the modified Mehlich method as described by Hoskins and Erich (2008), which hereon will be referred to as Mehlich. The soil:water:buffer ratio used was 1:1:1 for the three methods. The buffer solution final pH was 7.5 for SMP, 7.7 for Sikora, and 6.6 for Mehlich. The TA was determined by the BaCl₂-trietanolamine titration method as described by Greweling and Peech (1960). Post-harvest soil samples were analyzed for pH. All analyses were done in duplicate.

Soil pH change due to liming for each initial grid sampling cell was calculated as follows:

pH change = initial pH before liming - post-harvest pH of the limed one-half of each cell.

ArcGIS software (Environmental Systems Research Inst., Redlands, CA) was used to create a database consisting of georeferenced data of all soil measurements. Also, ArcGIS was used to identify soil measurements corresponding to each soil series in each site by overlaying georeferenced data and polygons of digitized, 1:12000-scale soil survey maps (Iowa Cooperative Soil Survey, 2001).

Soil-test results for soil samples with initial pH > 7.00 are shown in tables that show descriptive statistics, but were excluded for study of relationships between soil properties and pH change due to lime application because there is no logical agronomic reason measure LR and increase soil pH above 7.00. Analysis of variance (ANOVA) was conducted to assess differences between buffer pH means by site, across all sites, for each soil series, each of six OM concentration ranges, and each of seven clay concentration ranges. The analysis by soil series was done only for those soils encompassing at least

eight initial sampling cells. The OM and clay ranges were arbitrarily chosen to be meaningful according to values commonly found in Iowa. For these analyses, we assumed a completely randomized design in which treatments were the three buffer pH methods and replications were the sampling cells within each soil (9 to 115) and within each range OM or clay range (17 to 203). We did not perform an analysis by site for each soil series and OM or clay range because of sometimes insufficient reasonable replication and an interest for evaluating methods differences independently of the field. The buffer pH methods means were compared by LSD only when the treatments main effect was significant at $P < 0.05$. Relationships between soil measurements and pH change due to liming were studied by simple and multiple regression analyses using the REG procedure of SAS (SAS Inst., 2010).

RESULTS AND DISCUSSION

Soil Test Results

The soil pH, clay, and OM test results from the initial soil samples showed large differences across sites and sometimes also within the experimental area of each site (Table 4). Soil pH ranged from 4.60 to 8.05 across all samples. The mean pH of each site was at or below 6.5, which is the suggested target pH for corn and soybean in most Iowa soils (Sawyer et al., 2002). Soil pH variability was especially high at Sites 1, 2, 4, 6, 8 and 10, where differences between the maximum and minimum pH ranged from 1.50 to 2.97 pH units. A very high within-field pH variability such as the one observed for Site 4 has been observed before for fields located in that Iowa region (Bianchini and Mallarino, 2002). The site included Canisteo and Okoboji soil series, which have very large variation in pH and calcareous concentration in the surface layers. Clay and OM concentrations variability was higher at Sites 2, 4, 5, 6, 9, 10, and 14, where differences

between the maximum and minimum values ranged from 90 to 200 g kg⁻¹ clay and 13 to 45 g kg⁻¹ OM. Coefficients of variation for pH, OM, and clay within each soil series included in the study (Table 5) ranged from 3 to 9, 5 to 30, and 6 to 23%, respectively. The range of the within-site pH variation across the 14 sites (Table 4) was much larger than the range of pH variation across the soil series (Table 6) but, in contrast, similar comparisons for OM and clay concentrations do not show clear differences. This result is evidence of comparatively larger differences in pH than in OM or texture for these Iowa soil series.

Table 6 summarizes results of soil analyses for buffer pH by three methods, TA, and pH change due to lime application for the entire experimental area of each site. The within site-variation was approximately similar for the buffer pH methods, and the CV ranged from 1 to 6 across sites and buffer methods. The within-site TA variation differed greatly across sites (CV 7 to 44), but there is no previous on-farm research with which our results could be compared with. The range of within-site variation for pH change (CV 25 to 84%) approximately compares to results found for two central Iowa soils by Bianchini and Mallarino (2002). High within-site pH change variation should not be surprising because the effect of lime on soil pH is a complex interaction among the variations in pH, buffer pH, and other soil properties.

The mean soil buffer pH values for SMP and Sikora differed ($P \leq 0.05$) in six of the 14 sites (Sites 8 - 9 and 11 - 14), in which Sikora values always were lower than for SMP (Table 6). The difference between SMP and Sikora for those sites ranged from 0.09 to 0.17 pH units. The Mehlich soil buffer pH values always were much lower than for SMP (by 0.53 to 0.84 pH units) and Sikora (by 0.49 to 0.72 pH units), however. Soil buffer pH means across all sites were 6.44, 6.38, and 5.78 for SMP, Sikora, and Mehlich methods,

respectively, which differed ($P \leq 0.05$) according to ANOVA across all sites (not shown) although the difference between SMP and Sikora was small.

Table 7 summarizes test results for buffer pH, TA, and pH change due to lime application for each soil series included in the study. The within site-variation was approximately similar for the three buffer pH methods, ranged from 1.4 to 5.1 pH units across methods and soils, and was of approximately similar magnitude to variation observed for the entire experimental area of each site (Table 6). The within-site variation range across soils for TA (CV 7 to 26) and for pH change due to lime application (CV 23 to 61) was lower than for the entire experimental area of each site (Table 6). The Mehlich soil buffer pH values were consistently lower than SMP or Sikora values for all soil series included in the study (0.54 to 0.77 pH units lower than SMP and 0.50 to 0.66 pH units lower than Sikora). The SMP and Sikora buffer pH means differed for only five soil series (Galva, Marcus, Marshall, Nira, and Primghar), for which Sikora values were 0.07 to 0.17 pH units lower. We could not find a reasonable explanation for inconsistent differences between SMP and Sikora across soil series on the basis of known chemical properties of the buffer solutions and measured soil properties. These five soils developed on deep loess (Iowa Cooperative Soil Survey, 2001) but the series Judson, Muscatine, and Sharpsburg also developed on loess and the methods did not differ (other series developed on glacial till).

The difference between SMP and Sikora buffer pH methods found for six of the 14 sites (Table 6) and five soil series (Table 7) is in contrast with no significant differences found for other regions or soils by Sikora (2006) and Peters and Laboski (2007). The buffer pH differences do not seem large, but could result in considerably different estimates of LR and lime application. Assuming buffer pH values of 6.39 and 6.27 (the SMP mean and the mean difference with Sikora across the five soil series), a 15-cm soil

depth, and a 6.5 target soil pH, for example, LR would be 4.0 and 5.0 Mg CCE ha⁻¹, respectively, according to Iowa LR equations for SMP (Sawyer et al., 2002).

Relationships between the Buffer pH Methods

Figure 1 shows relationships between the three buffer pH methods across all soil samples collected from the 14 sites. The buffer pH values for the three methods were linearly related ($P < 0.001$). The r^2 of the relationships was lowest between SMP and Mehlich (0.72), and higher and approximately similar between SMP and Sikora (0.85) and between Sikora and Mehlich (0.87). The intercept and slope coefficients of the regression line between SMP and Sikora did not differ from 0 and 1 ($P > 0.05$), respectively, which would suggest that both methods yield statistically similar results across many samples and fields. This result was also observed for soils of other regions by Sikora (2006) and Peters and Laboski (2007). As we indicated before, however, ANOVA across all sites indicated a small but statistical difference between SMP and Sikora (0.06 pH units less for Sikora). The Mehlich buffer pH method, in agreement with ANOVA across sites, by site, or by soil series resulted in significantly lower values than the SMP and Sikora methods (intercept and slope were lower than 0 and 1, respectively). A large difference between Mehlich and SMP or Sikora was also shown for other soils of the Midwest (Godsey et al., 2007; Peters and Laboski, 2007). The magnitude of the difference varied greatly across states, however, which confirms a need for local calibrations to determine LR as reported by Sims (1996) and Rossel and McBratney (2001).

The Mehlich buffer pH values were lower than SMP and Sikora values for all defined OM ranges (Table 8) and clay ranges (Table 9). The SMP and Sikora buffer pH means were statistically similar ($P > 0.05$) for most OM or clay ranges, but Sikora values were

lower for three OM ranges (30-39, 40-49, and 60-69 g kg⁻¹) and three clay ranges (250-299, 300-349, and 350-400 g kg⁻¹). The inconsistent results as OM increases could be random results because the OM values for the three ranges were not consecutively lower or higher. The results for clay (Table 9) suggest, however, that the differences between SMP and Sikora methods occurred only with high clay concentration. The methods differed for three of the highest clay ranges, and did not differ for the highest range (at $P < 0.05$) probably due to by the considerably fewer numbers of samples and higher variability than for the other high ranges. The absolute magnitudes of the difference between SMP and Sikora methods were 0 to 0.02 pH units for the lowest three clay ranges (similar or higher for Sikora) but 0.07 to 0.15 for the highest four ranges (always lower for Sikora). Previous comparisons of SMP and Sikora did not study this type of relationship with clay concentration or did not show a consistent difference. Consideration of properties of the buffer solutions and known mechanisms for acidity exchange do not indicate an obvious explanation for our result. It is noteworthy that as indicated before for differences between soil series, however, the magnitudes of buffer pH values always were very small and of little agronomic relevance.

Relationship between Titratable Acidity and the Buffer pH Methods

Highly significant correlations ($P < 0.001$) were observed between TA and the three buffer pH methods (Figure 2). More dispersion in the data and lower r^2 were found, than for relationships between the three buffer pH methods (Figure 1). Titratable acidity was better related to SMP and Sikora buffer pH values (r^2 0.53 and 0.59) than to Mehlich buffer pH values (r^2 0.39). These results may reflect the differences between the buffer pH value of the solutions and different reaction kinetics of the different component buffer compounds, but we cannot identify the specific reason. Interestingly, Table 10 indicates

that the relationship between TA and the buffer pH methods consistently improved as the soil OM content increased. We believe that the main reason for such improvement is that the buffer pH and TA values included in each OM class and also their respective ranges progressively increased as the OM level increased. For example, the ranges for SMP and TA were only 6.10 to 6.85 and 2.6 to 5.5 for samples with $< 30 \text{ g kg}^{-1}$ OM but 6.17 to 6.93 and 3.7 to 7.7 for samples with $>70 \text{ g kg}^{-1}$ OM. Others have shown that soils with higher OM and clay concentrations have higher cation exchange capacity and greater potential acidity (Havlin et al., 2005). The relationships between the TA and the buffer methods also tended to increase as the soil clay concentration increased (Table 11), although less consistently than with OM. In a New York State study that included 43 soil series, Dietzel et al. (2009) reported very close association between LR estimated by TA and the buffer pH methods SMP, Sikora, Melhlich, and Mehlich (r^2 0.90, 0.87, and 0.91, respectively).

Relationship between Soil pH Change Due to Liming and Soil Measurements

Significant relationships ($P < 0.001$) were observed between the soil pH change after 6 to 12 months of lime application and initial soil pH and OM or clay concentration across all samples (Figure 3). Significant relationships also were observed between soil pH change and the SMP and Sikora buffer methods or TA, but not between pH change and the Mehlich buffer method (Figure 4). The observed pH change range (-0.40 to 2.60 pH units) reflects the wide range of soil pH responses expected in Iowa, given the soil properties and amount of lime applied. Except for the relationship with initial pH (r^2 0.23) (Figure 3), the r^2 values for the relationships between pH change and all other measurements was very low (Figure 3 and 4). The r^2 of relationship between pH change and OM or clay (r^2 0.06 and 0.09) was higher than for the relationship between pH

change and any of the three buffer pH methods or TA (r^2 0.01 to 0.03) (Figure 3). This result suggests (for the Iowa soils included in this study) the greater importance of soil pH compared with measurements such as OM or clay concentration or buffer pH assumed to be related to the buffer capacity of the soil and LR. Most studies referred to before did not report the relationship between soil pH and buffer pH values or LR. Keeney and Corey (1963) based on an incubation study showed how various soil properties including pH and buffer pH predicted LR, and reported that SMP buffer pH was the best single predictor variable for LR.

Consideration of more than one soil measurement increased the proportion of the variation of pH change due to liming that was accounted for by soil pH, which was the best single variable. Table 12 shows that two-variable equations including initial pH and any other measurement improved by 1 to 19% the proportion of pH change variation explained by soil pH alone. The best two-variable model included soil pH and Mehlich buffer pH (R^2 0.42), and the second best model included soil pH and Sikora buffer pH (R^2 0.34). Three-variable models that included initial pH, clay concentration, and any one buffer pH method or TA resulted in small improvements, but inclusion of OM resulted in larger improvements. The best three-variable model included soil pH, OM, and Mehlich buffer pH (R^2 0.45), and the second best included soil pH, OM, and Sikora buffer pH (R^2 0.36). Study of relationships between the soil measurements and soil pH change across sites using the average values from samples for each soil series showed no improvement and mostly poorer relationships (not shown).

The results of our study under field conditions showed disappointingly low relationship between pH change due to lime application and any of the three buffer pH methods compared, which imply very poor estimates of LR based on these buffer methods. There has been no Iowa study under field conditions that assessed relationships

between buffer pH or TA and pH change due to lime application or LR. Soil incubation studies in the 1960s (J.J. Hanway, Iowa State University, unpublished) indicated higher relationships between the SMP buffer and LR, which were used to develop equations for LR that have been used in Iowa since then. Other research that evaluated buffer pH methods under laboratory incubation conditions has reported better relationships between buffer pH and soil pH change due to liming or LR than in our study. For example, working on Pennsylvania soils under incubation conditions, Wolf et al. (2008) found high associations between LR and SMP or Mehlich buffer pH methods (r^2 0.81 and 0.92, respectively). Dietzel et al. (2009) reported that TA was highly correlated with LR across 18 New York soils. The presence of variable concentrations of exchangeable Al in some of these New York soils might help explain the better performance of TA compared with our study (no measurable exchangeable Al has been reported for the A horizons of Iowa soils). Research with Midwestern soils to evaluate buffer pH methods based on incubated samples also resulted in a better relationship between buffer pH and soil pH change due to liming than in our study (Shoemaker et al., 1961; Bhumbra and McLean, 1965; Jones, 2001; Sikora 2006; Godsey et al., 2007; Hoskins and Erich, 2008). The soils, pH ranges, and pH change due to liming included in our study represent well the vast majority of Iowa soils where corn and soybean are planted. Several samples had pH 4.6 to 5.0, and our experience indicates that lower pH values seldom are found in Iowa agricultural soils. Certainly, our study did not include all Iowa soil series, and did not include soils with OM levels beyond a range of 12 to 92 g kg⁻¹ or clay concentration beyond a range of 90 to 500 g kg⁻¹ because they represent less than 0.1% of area of the state and are seldom found in fields where grain crops are regularly planted (Iowa Cooperative Soil Survey, 2001).

Relatively narrow ranges of OM and clay concentrations in this study (and in Iowa) and the short-term reserve acidity assessed by laboratory buffer pH and TA methods may

explain the little value of these methods at explaining soil pH change due to liming in the field. The results of this study under field conditions and the general lack of similar field studies in the Midwest and other regions of the US suggest a need to validate under field conditions calibrations of equations based on soil properties or buffer pH methods to assess LR. A study conducted in the Midwest (Godsey et al., 2007), compared the LR from 60-d incubations with field-observed lime response and showed that the actual LR in the field was greater than that predicted by the 60-d incubation. It is possible that use of large equipment to apply the lime and different timing of the post-liming sampling date across fields (6 to 12 months) contributed to high variation in pH change, which may have reflected on poor correlation with the soil measurements. The much better relationship found between pH change and initial pH (r^2 0.23) than for any buffer pH method or TA (r^2 0.01 to 0.03), demonstrates that the field methodology used was not the cause of poor performance of these approaches to estimate LR in these soils.

CONCLUSIONS

Mean SMP, Sikora, and Mehlich soil buffer pH values across all sites were 6.44, 6.38, and 5.78, which differed at $P < 0.05$, respectively. The small difference between SMP and Sikora across all samples and sites was explained mainly by also small significant differences in five loess-derived soil series, but no difference was observed for three other loess derived series. The pH change variation due to lime application under field conditions was better explained by pH, OM, and clay (23, 9, and 6%, respectively) than by TA or any buffer pH method (1 to 3%). This result might be explained by relatively narrow ranges of OM and clay concentrations in Iowa and in this study, and also by the short-term reserve acidity assessed by laboratory methods. The SMP and Sikora buffer methods were highly correlated (r 0.92), values did not differ significantly across most

soil series included in the study, and current SMP calibrations for LR could be used for Sikora. For five soil series, however, Sikora would require a different calibration because its values were slightly lower than for SMP. The Mehlich buffer method requires a different calibration for all soils, however, because its values always were much lower and related to pH change across all soils with a different slope compared with SMP or Sikora. Although all buffer methods had similarly poor correlation with soil pH change, an advantage of Sikora and Mehlich is that they include no hazardous chemicals. Soil pH and OM, which are routinely measured in samples collected from agricultural fields, together explained 24% of the soil pH change due to liming. Their consideration together with SMP, Sikora, or Mehlich buffer methods improved the explanation of soil pH change variation to 28, 37, and 45%, Therefore, use of pH and OM together and Sikora or Mehlich buffer methods would provide the best prediction of LR for the soils and conditions similar to those included in this study.

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Table 1. Site location and information for 14 field trials.

Site	Year	County	Crop	Tillage system‡	Soil series †					
					First		Second		Third	
					Series	Classification ¶	Series	Classification	Series	Classification
1	2007	Jasper	Corn	ST	Clarion	T. Hapludoll	-	-	-	-
2	2007	Story	Soybean	CPD	Webster	T. Endoaquoll	Nicollet	A. Hapludoll	Clarion	T. Hapludoll
3	2007	Boone	Corn	CPD	Canisteo	T. Endoaquoll	Nicollet	A. Hapludoll	Clarion	T. Hapludoll
4	2007	Greene	Corn	CPD	Canisteo	T. Endoaquoll	Okoboji	V. Endoaquoll	-	-
5	2007	Boone	Corn	CPD	Talcot	T. Endoaquoll	Dickman	T. Hapludoll	Clarion	T. Hapludoll
6	2008	Cedar	Corn	CPD	Dinsdale	T. Argiudoll	Muscatine	A. Hapludoll	-	-
7	2008	O'Brien	Soybean	CPD	Primghar	A. Hapludoll	Galva	T. Hapludoll	-	-
8	2008	O'Brien	Corn	CPD	Galva	T. Hapludoll	-	-	-	-
9	2008	O'Brien	Corn	CPD	Marcus	T. Haplaquoll	Primghar	A. Hapludoll	Galva	T. Hapludoll
10	2008	Union	Soybean	NT	Sharpsburg	T. Hapludoll	Nira	T. Argiudoll	-	-
11	2009	Ringgold	Soybean	NT	Nira	T. Argiudoll	Sharpsburg	T. Hapludoll	-	-
12	2009	Pottawattamie	Soybean	NT	Marshall	T. Hapludoll	-	-	-	-
13	2009	Pottawattamie	Soybean	CPD	Marshall	T. Hapludoll	-	-	-	-
14	2009	Crawford	Soybean	NT	Marshall	T. Hapludoll	Judson	C. Hapludoll	-	-

† There were at least eight soil sampling areas (grid cells) for most soils, except for Okoboji in Site 4 (six) and Judson in Site 14 (five).

‡ ST, strip till; CPD, chisel-plow/disking; NT, no-till.

¶ A., Aquic; C., Cumulic; T., Typic; V., Vertic.

Table 2. Characteristics of the limestone used in 14 field trials.

Site	CCE†	Ca	Mg	Particle size ‡			FF	ECCE §	Limestone application date
				Mesh 4	Mesh 8	Mesh 60			
----- % -----									
1	94.9	22.4	10.8	100	92	30	56	53	May 18 2007
2	97.3	40.7	0.4	100	100	44	66	64	May 25 2007
3	93.8	37.7	0.5	100	100	38	63	59	Nov 14 2006
4	95.9	39.7	0.3	100	99	59	75	72	Oct 28 2006
5	98.1	40.5	0.4	100	96	38	62	60	Jan 27 2007
6	99.4	21.5	12.2	99	85	36	57	57	May 12 2008
7	98.7	5.4	0.5	100	99	70	81	80	Nov 9 2007
8	98.7	5.4	0.5	100	99	70	81	80	Nov 9 2007
9	98.7	5.4	0.5	100	99	70	81	80	Apr 15 2008
10	89.6	34.7	1.1	100	97	41	64	57	Apr 28 2008
11	70.0	29.7	1.6	100	99	53	72	50	Feb 23 2009
12	66.0	28.3	1.5	100	98	48	68	45	Jan 9 2009
13	66.0	28.3	1.5	100	98	48	68	45	Jan 9 2009
14	101.0	44.9	0.4	98	94	51	69	69	Dec 12 2008

† CaCO₃ equivalent.

‡ Fineness according to State of Iowa limestone analysis regulations (IDALS, 2008), with percentage of material passing sieves with Tyler mesh sizes 4, 8, and 60 (4.75, 2.38, and 0.25 mm, respectively). FF, fineness factor defined as amounts passing sieves with mesh 4, 8, and 60 multiplied by the factors of 0.1, 0.3, and 0.6, respectively.

§ Effective CaCO₃ equivalent as defined in Iowa (IDALS, 2008).

Table 3. Monthly and cumulative precipitation occurring between the lime application date and the post-liming soil sampling date for 14 field trials. †

Site	Month after liming												Cumulative
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th	
	----- mm -----												
1	63	81	195	106	147	5	na ‡	na	na	na	na	na	597
2	52	75	200	48	137	4	na	na	na	na	na	na	516
3	33	68	46	46	82	183	121	76	60	167	41	128	1051
4	35	57	36	55	79	176	152	75	59	333	52	na	1109
5	55	79	176	152	75	59	333	52	139	5	na	na	1125
6	164	241	189	76	125	35	na	na	na	na	na	na	830
7	1	45	13	17	34	61	116	137	87	56	95	99	761
8	1	45	13	17	34	61	116	137	87	56	95	99	761
9	97	161	121	133	47	97	123	na	na	na	na	na	779
10	127	349	230	9	142	120	50	na	na	na	na	na	1027
11	108	104	80	162	149	169	18	154	61	na	na	na	1005
12	20	12	34	76	74	158	148	160	8	121	21	na	832
13	20	12	34	76	74	158	148	160	8	121	21	na	832
14	51	21	13	49	67	60	123	168	131	16	148	25	872

† Data from Iowa Environmental Mesonet, mesonet.agron.iastate.edu/index.phtml; verified 12 Sep. 2011).

‡ na, not applicable because dates were after the soil sampling.

Table 4. Descriptive statistics for initial soil pH, organic matter concentration, and clay concentration for samples collected from 14 field trials.

Site	n †	Descriptive statistics											
		pH				Organic matter concentration				Clay concentration			
		Mean	Min.	Max.	CV ‡	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV
		----- g kg ⁻¹ -----											
1	32	6.05	5.55	7.28	5.8	33	22	44	15	230	169	290	11
2	40	6.01	5.7	7.23	5.2	44	27	72	22	261	202	386	15
3	36	5.23	4.83	5.98	5.6	38	26	52	16	261	192	321	13
4	32	6.47	5.08	8.05	13.2	52	36	78	21	261	189	356	16
5	40	5.04	4.6	5.83	5.5	33	12	47	27	191	91	264	24
6	40	5.51	5.1	6.65	4.8	34	23	41	9	255	208	404	13
7	36	5.52	5.23	5.98	3.3	52	45	57	5	334	293	361	4
8	36	5.87	5.15	6.65	5.2	49	44	60	7	314	276	342	5
9	36	5.71	5.48	6.13	3.3	69	53	92	14	387	335	423	5
10	19	5.58	4.75	6.15	6.9	40	34	47	9	384	351	502	10
11	36	5.7	5.33	6.21	4.3	45	36	50	7	298	249	357	10
12	36	5.26	5.1	5.56	1.8	38	30	41	5	295	250	373	11
13	36	5.36	5.15	5.65	2.3	41	37	44	5	274	243	341	9
14	48	5.29	4.98	5.73	3.4	33	26	48	10	307	277	431	7

† n, number of samples.

‡ CV, coefficient of variation.

Table 5. Descriptive statistics for initial soil pH and organic matter and clay concentrations for soil series included in the study across 14 field trials. †

Soil	Descriptive statistics											
	pH				Organic matter concentration				Clay concentration			
	Mean	Min.	Max.	CV ‡	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV
	----- g kg ⁻¹ -----											
Canisteo	5.72	4.95	6.95	8.6	45	34	66	19	259	189	322	14
Clarion	5.73	4.83	6.70	8.7	34	22	44	15	233	169	304	12
Dickman	4.89	4.65	5.18	4.3	28	14	42	30	165	119	213	20
Dinsdale	5.43	5.10	5.75	3.4	34	29	41	8	252	222	284	8
Galva	5.84	5.15	6.65	5.2	50	44	60	8	320	276	388	8
Marcus	5.78	5.55	6.13	3.4	73	59	92	12	391	335	423	6
Marshall	5.30	4.98	5.73	2.8	37	26	48	12	293	243	431	10
Muscatine	5.66	5.33	5.85	2.7	36	32	38	5	274	208	404	23
Nicollet	5.63	4.85	6.33	6.8	42	26	59	19	260	194	308	12
Nira	5.69	5.33	6.21	4.0	44	34	50	8	308	249	399	12
Primghar	5.58	5.33	5.98	2.8	55	48	66	8	345	293	402	8
Sharpsburg	5.55	4.75	6.18	8.5	40	34	46	9	336	266	397	19
Talcot	5.16	4.90	5.83	5.4	38	26	47	14	206	113	264	19
Webster	6.03	5.75	6.75	5.0	46	27	72	25	271	202	386	18

† Data shown only for soil series for which there were at least eight samples across all sites.

‡ CV, coefficient of variation.

Table 6. Descriptive statistics for three buffer pH methods, titratable acidity, and pH change due to lime application for 14 field trials. †

Site	Descriptive statistics																			
	Shoemaker-McLean-Pratt				Sikora				Mehlich				Titratable acidity				pH change due to liming			
	Mean	Min.	Max.	CV ‡	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV
	----- cmol kg ⁻¹ -----																			
1	6.67a	6.38	7.20	2.4	6.74a	6.43	7.28	2.6	6.13b	5.90	6.60	2.2	4.3	1.7	5.9	19.4	0.7	0.0	1.2	46
2	6.52a	6.30	7.08	2.7	6.49a	6.25	7.05	2.5	5.93b	5.75	6.40	2.2	4.2	1.3	6.1	22.1	0.6	0.0	1.5	51
3	6.41a	6.15	6.80	3.0	6.41a	6.15	6.80	2.7	5.79b	5.63	6.08	2.2	4.9	3.0	6.4	16.4	1.3	0.7	2.2	29
4	6.85a	6.10	7.45	5.5	6.84a	6.15	7.45	5.6	6.16b	5.60	6.83	5.7	3.5	0.7	6.0	43.7	0.6	-0.4	1.9	84
5	6.39a	6.05	6.93	3.2	6.39a	6.08	6.83	2.7	5.81b	5.58	6.10	2.2	5.3	2.6	8.1	23.1	1.4	0.7	2.6	26
6	6.50a	6.30	6.98	2.2	6.47a	6.25	6.95	2.1	5.88b	5.73	6.25	1.8	4.5	3.1	5.8	14.4	0.7	0.2	1.3	29
7	6.19a	5.98	6.48	1.8	6.15a	5.98	6.40	1.8	5.66b	5.50	5.88	1.6	6.4	5.4	7.4	7.3	0.7	0.4	1.1	25
8	6.58a	6.30	6.95	2.4	6.44b	6.20	6.85	2.7	5.87c	5.68	6.20	2.3	5.1	3.7	6.5	15.3	0.8	0.2	1.4	37
9	6.32a	6.08	6.63	2.1	6.15b	6.00	6.50	2.0	5.64c	5.50	5.88	1.8	6.6	4.8	7.8	11.9	0.7	-0.1	1.3	54
10	6.40a	5.88	6.78	4.0	6.25a	5.70	6.60	4.0	5.76b	5.35	6.05	3.3	5.4	4.0	7.8	17.9	0.9	0.3	1.5	32
11	6.53a	6.28	6.86	2.2	6.42b	6.20	6.74	2.2	5.76c	5.55	6.05	2.3	4.7	3.2	5.8	13.5	0.7	0.1	2.6	64
12	6.17a	5.93	6.48	2.5	6.03b	5.88	6.30	1.9	5.45c	5.33	5.65	1.5	5.8	4.5	6.9	9.5	0.5	0.2	1.0	32
13	6.25a	6.10	6.78	2.2	6.16b	6.00	6.45	1.9	5.50c	5.35	5.75	1.7	5.5	4.4	6.2	8.4	0.8	0.3	1.3	25
14	6.46a	6.25	6.80	2.1	6.34b	6.20	6.55	1.3	5.62c	5.45	5.75	1.2	4.2	2.9	5.5	16.2	0.7	0.4	1.1	30

† Buffer pH means in a row followed by different letters indicate differences between methods (LSD, $P \leq 0.05$).

‡ CV, coefficient of variation.

Table 7. Descriptive statistics for three buffer pH methods, and titratable acidity for each soil series across 14 field trials. †

Soil	Descriptive statistics																			
	Shoemaker-McLean-Pratt				Sikora				Mehlich				Titratable acidity				pH change due to liming			
	Mean ‡	Min.	Max.	CV§	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV
	----- cmol kg ⁻¹ -----																			
Canisteo	6.59a	6.23	7.10	3.6	6.57a	6.15	7.15	3.7	5.91b	5.63	6.35	3.0	4.3	2.5	6.0	22.2	0.86	-0.40	1.93	61
Clarion	6.55a	6.10	6.95	3.0	6.59a	6.15	7.05	3.3	5.99b	5.60	6.40	3.2	4.6	3.2	6.4	18.1	0.93	0.00	2.20	54
Dickman	6.31a	6.15	6.45	1.8	6.32a	6.15	6.50	1.87	5.77b	5.60	5.90	1.5	4.7	3.4	6.2	16.2	1.48	0.95	2.12	23
Dinsdale	6.45a	6.30	6.65	1.6	6.41a	6.25	6.60	1.5	5.84b	5.73	6.00	1.4	4.6	3.2	5.6	13.9	0.63	0.35	0.90	24
Galva	6.55a	6.23	6.95	2.6	6.41b	6.03	6.85	3.1	5.85c	5.53	6.20	2.6	5.3	3.7	7.8	17.7	0.74	-0.05	1.35	40
Marcus	6.35a	6.18	6.63	2.3	6.18b	6.03	6.50	2.3	5.66c	5.50	5.88	2.1	6.5	4.8	7.7	14.3	0.60	0.00	1.23	56
Marshall	6.30a	5.93	6.80	3.0	6.19b	5.88	6.55	2.7	5.53c	5.33	5.75	2.0	5.1	2.9	6.9	17.7	0.67	0.20	1.25	33
Nicollet	6.44a	6.20	6.80	2.5	6.43a	6.23	6.80	2.3	5.85b	5.68	6.08	1.8	4.6	3.0	6.0	17.6	0.89	0.25	1.95	51
Muscatine	6.62a	6.45	6.98	2.2	6.58a	6.45	6.95	2.12	5.96b	5.85	6.25	1.8	4.2	3.1	4.8	13.9	0.73	0.15	1.28	40
Nira	6.52a	6.30	6.86	2.1	6.39b	6.15	6.70	2.2	5.77c	5.55	6.05	2.2	4.8	3.2	5.8	12.9	0.73	0.11	2.59	56
Primghar	6.23a	6.08	6.48	1.7	6.16b	6.00	6.40	1.7	5.66c	5.50	5.88	1.6	6.4	5.4	7.4	7.1	0.76	0.20	1.33	33
Sharpsburg	6.40a	5.88	6.78	4.7	6.27a	5.70	6.74	5.1	5.74b	5.35	6.05	4.2	5.4	3.4	7.8	25.6	0.63	0.11	1.20	50
Talcot	6.41a	6.05	6.93	3.8	6.40a	6.08	6.83	3.0	5.81b	5.58	6.10	2.5	5.7	3.5	7.7	17.4	1.31	0.73	1.85	25
Webster	6.53a	6.33	6.98	2.8	6.49a	6.28	6.80	2.4	5.92b	5.80	6.20	1.9	4.2	3.1	6.1	21.7	0.69	0.03	1.33	47

† Data shown only for soil series for which there were at least eight samples across all sites.

‡ Buffer pH means in a row followed by different letters indicate differences between methods for each soil series (LSD, $P \leq 0.05$).

§ CV, coefficient of variation.

Table 8. Buffer pH mean and standard deviation for several organic matter ranges before lime application for all soil samples collected across 14 field trials. †

Organic matter range	n §	Buffer pH method					
		SMP ‡		Sikora		Mehlich	
		Mean	SD ¶	Mean	SD	Mean	SD
g kg ⁻¹							
< 30	36	6.60a	0.19	6.56a	0.19	5.92b	0.18
30 - 39	203	6.41a	0.21	6.35b	0.24	5.74c	0.23
40 - 49	163	6.43a	0.21	6.36b	0.22	5.76c	0.19
50 - 59	61	6.35a	0.22	6.27a	0.21	5.74b	0.15
60 - 69	23	6.38a	0.2	6.25b	0.22	5.70c	0.16
> 70	17	6.40a	0.24	6.25a	0.26	5.71b	0.22

† Mean values in a row followed by different letters differ (LSD, $P \leq 0.05$).

‡ SMP, Shoemaker-McLean-Pratt buffer method.

§ n, number of samples.

¶ SD, standard deviation.

Table 9. Buffer pH means and standard deviation for several clay concentration ranges before lime application for all soil samples collected across 14 field trials. †

Clay range g kg ⁻¹	n §	Buffer pH method					
		SMP ‡		Sikora		Mehlich	
		Mean	SD ¶	Mean	SD	Mean	SD
< 150	8	6.43a	0.18	6.45a	0.18	5.85b	0.12
150 - 199	18	6.45a	0.21	6.47a	0.21	5.88b	0.17
200 - 249	106	6.52a	0.21	6.52a	0.21	5.92b	0.18
250 - 299	162	6.42a	0.28	6.35b	0.29	5.73c	0.27
300 - 349	135	6.41a	0.2	6.30b	0.19	5.70c	0.17
350 - 400	47	6.34a	0.19	6.19b	0.19	5.68c	0.16
> 400	11	6.45a	0.25	6.32a	0.26	5.76b	0.22

† Mean values in a row followed by different letters differ (LSD, $P \leq 0.05$).

‡ SMP, Shoemaker-McLean-Pratt buffer method.

§ n, number of samples.

¶ SD, standard deviation.

Table 10. Coefficient of determination (r^2) † and statistical significance of relationships between titratable acidity and three buffer pH methods for different soil organic matter concentration ranges for all samples collected before liming across 14 field trials.

Organic matter range	n §	Buffer pH method					
		SMP ‡		Sikora		Mehlich	
		r^2	$P>F$	r^2	$P>F$	r^2	$P>F$
g kg ⁻¹							
< 30	35	0.08	0.06	0.06	0.09	0.01	0.25
30 - 39	199	0.47	<0.01	0.40	<0.01	0.26	<0.01
40 - 49	155	0.63	<0.01	0.71	<0.01	0.56	<0.01
50 - 59	56	0.67	<0.01	0.83	<0.01	0.74	<0.01
60 - 69	22	0.88	<0.01	0.92	<0.01	0.92	<0.01
> 70	15	0.91	<0.01	0.90	<0.01	0.90	<0.01

† Adjusted for degrees of freedom.

‡ SMP, Shoemaker-McLean-Pratt buffer method.

§ Numbers of samples

Table 11. Coefficient of determination (r^2) † and statistical significance of relationships between titratable acidity and three buffer pH methods for different soil clay concentration ranges for all samples collected before liming across 14 field trials.

Clay range	n §	Buffer pH method					
		SMP ‡		Sikora		Mehlich	
		r^2	$P>F$	r^2	$P>F$	r^2	$P>F$
g kg ⁻¹							
< 150	8	0.29	0.10	0.48	0.02	0.55	0.01
150 - 199	18	0.22	0.03	0.21	0.03	0.14	0.07
200 - 249	97	0.53	<0.01	0.44	<0.01	0.45	<0.01
250 - 299	155	0.59	<0.01	0.61	<0.01	0.46	<0.01
300 - 349	133	0.53	<0.01	0.54	<0.01	0.17	<0.01
350 - 400	45	0.63	<0.01	0.71	<0.01	0.72	<0.01
> 400	11	0.79	<0.01	0.80	<0.01	0.70	<0.01

† Adjusted for degrees of freedom.

‡ SMP, Shoemaker-McLean-Pratt buffer method.

§ Numbers of samples

Table 12. Multiple-regression equations relating soil pH change (dependent variable) due to lime application with initial pH and other soil properties for all samples collected from 14 field trials. †

Equation ‡	$P > F$	R^2 §
3.36 - 0.44pH - 0.002OM	$P < 0.01$	0.24
3.57 - 0.43pH - 0.01Clay	$P < 0.01$	0.27
1.24 - 0.67pH + 0.51SMP	$P < 0.01$	0.27
0.66 - 0.54pH + 0.67Sikora	$P < 0.01$	0.34
-0.51 - 0.88pH + 1.07Mehlich	$P < 0.01$	0.42
3.77 - 0.51pH - 0.03TA	$P < 0.01$	0.24
0.52 - 0.95pH + 0.01OM + 0.98Sikora	$P < 0.01$	0.36
-1.55 - 1.08pH + 0.01OM + 1.39Mehlich	$P < 0.01$	0.45
1.98 - 0.58pH - 0.01Clay + 0.36SMP	$P < 0.01$	0.29
-1.20 - 0.95pH + 0.01Clay + 1.23Mehlich	$P < 0.01$	0.42

† Equations without initial pH are not shown because their highest R^2 (0.16 for OM, clay, TA) was lower than for any equation including pH.

‡ OM, organic matter; SMP, Shoemaker-McLean-Pratt buffer, TA, titratable acidity. Some triple-variable equations and the four-variable equations are not listed because one variable was not significant ($P < 0.05$).

§ Adjusted for degrees of freedom

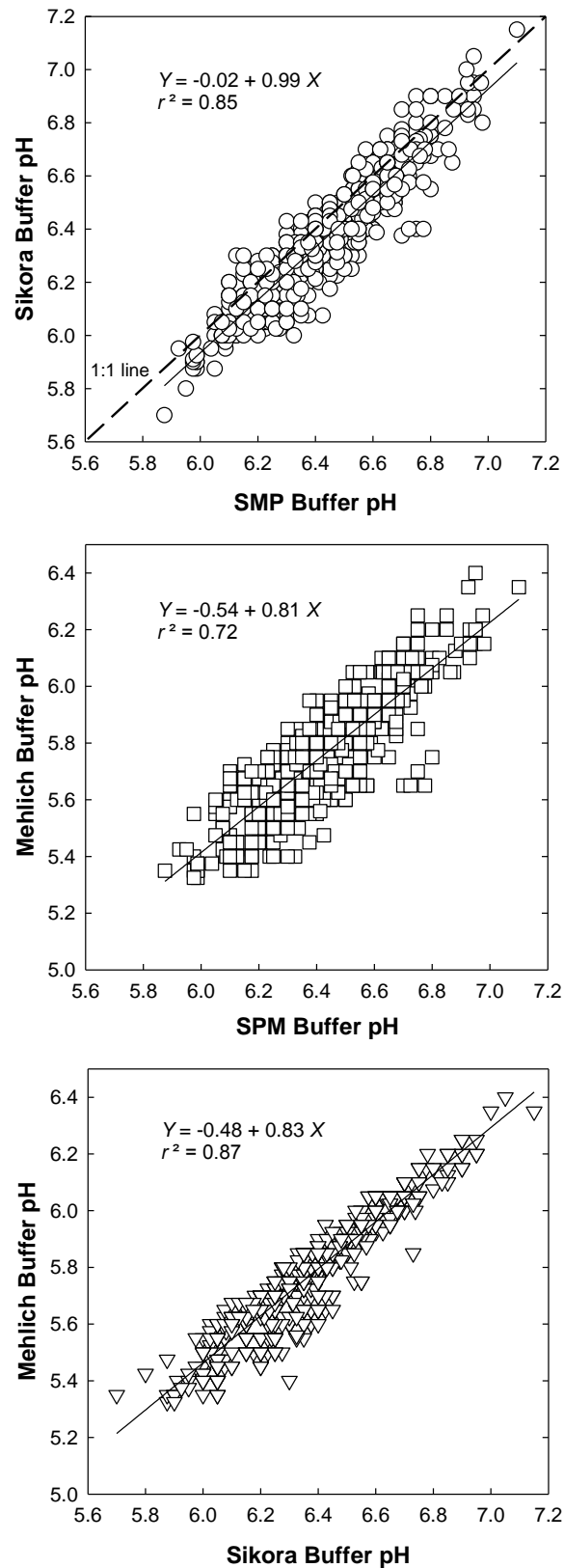


Figure 1. Relationship between buffer pH measured with the Shoemaker-McLean-Pratt (SMP), Sikora, and Mehlich methods for all soil samples collected from 14 field trials before lime application. All relationships were significant ($P \leq 0.001$).

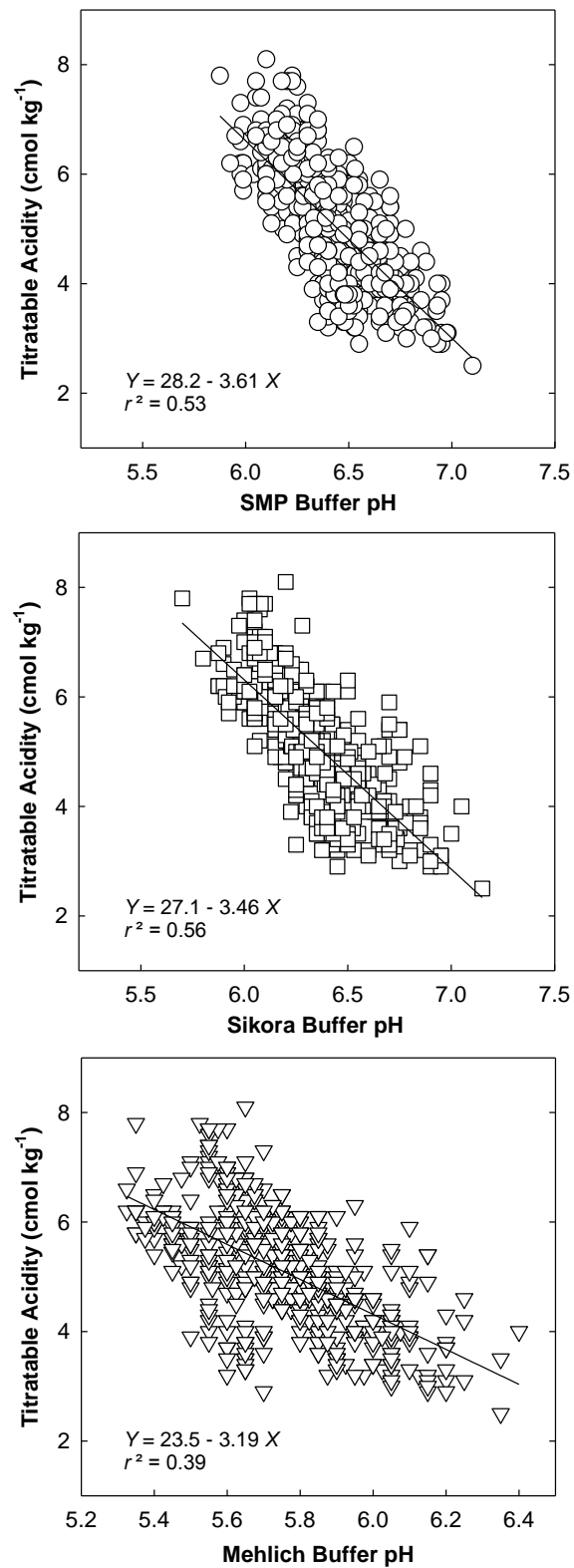


Figure 2. Relationship between titratable acidity and buffer pH measured with the Shoemaker-McLean-Pratt (SMP), Sikora, and Mehlich methods for all soil samples collected from 14 field trials before lime application. All relationships were significant ($P \leq 0.001$).

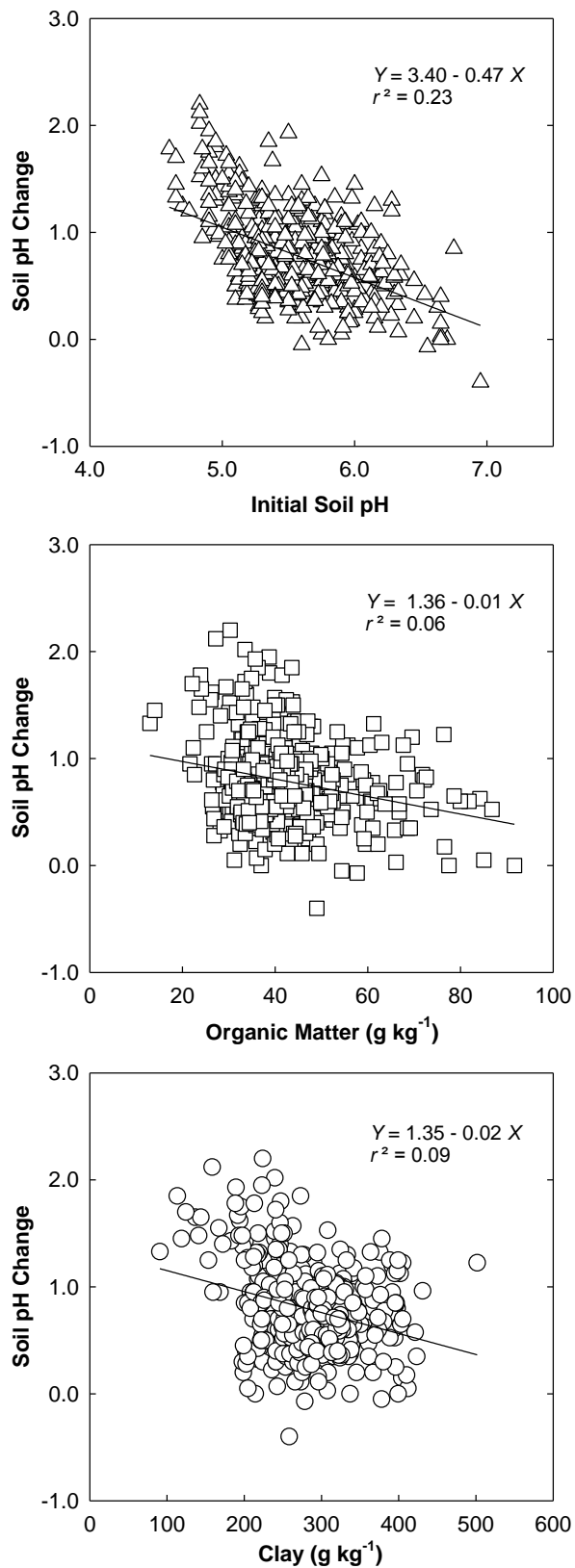


Figure 3. Relationship between soil pH change due to lime application and initial soil pH, organic matter concentration, and clay concentration for soil samples collected from 14 field trials. All relationships were significant ($P \leq 0.001$).

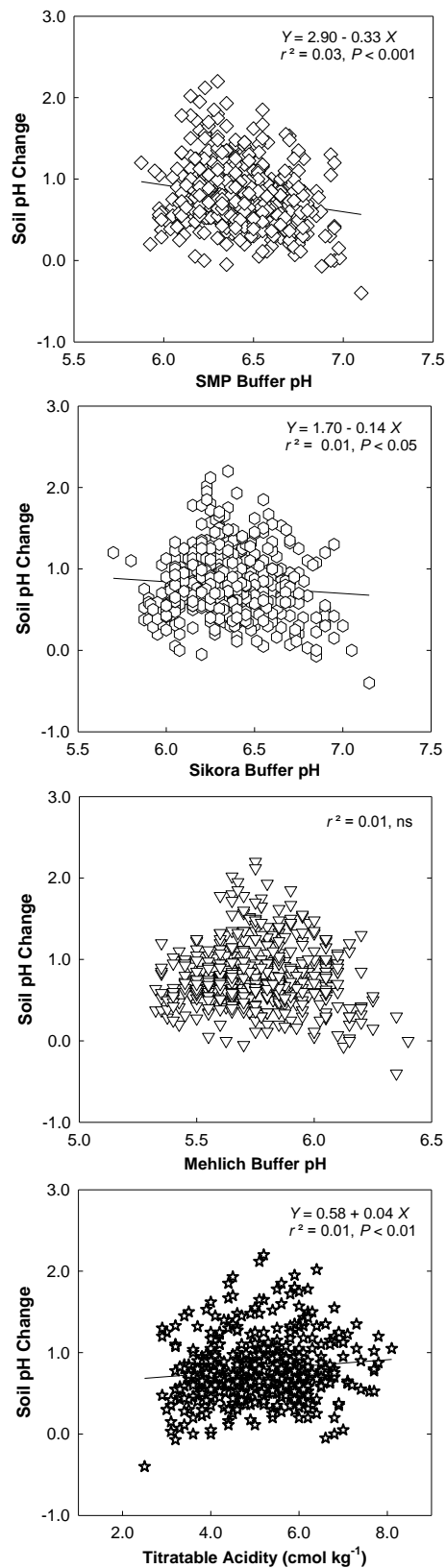


Figure 4. Relationship between soil pH change due to lime application and buffer pH measured with Shoemaker-McLean-Pratt (SMP), Sikora, and Mehlich methods and titratable acidity for soil all samples collected from 14 field trials.

CHAPTER 3. ON-FARM EVALUATION OF CORN AND SOYBEAN YIELD AND SOIL pH RESPONSES TO LIME APPLICATION

A paper to be submitted to the Agronomy Journal by

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ABSTRACT

Soil acidity can be an important yield-limiting factor but little research has focused on within-field variation of soil pH and crop response to lime application. The objectives of this work were to (1) study the variation of soil pH and crop response to lime within fields, (2) identify optimum soil pH for corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] in some important Iowa soils, and (3) evaluate the effect of subsoil pH on crop response to lime. Fourteen replicated strip trials were established from 2007 to 2009 using differential global positioning system (DGPS), dense grid soil sampling (0.07-ha cells), harvest with yield monitors, and geographical information systems (GIS). The trials were evaluated two, three, or four years according to the year of establishment. Treatments replicated 2 to 5 times at each field were a control and application of agricultural lime at 6.72 Mg ha^{-1} of effective calcium carbonate equivalent (ECCE). Soil samples were collected from a 15-cm depth before applying lime and also after each crop harvest. Subsoil (30- to 90-cm depth) samples were collected in 2010 and analyzed for pH. Within-field initial soil pH variation (CV) ranged from low (3.28 %) to very high (13.2 %) across fields. Limestone application significantly increased ($P < 0.05$) soil pH in all sites, and maximum pH values were generally reached during the second year after liming. Crop grain yield was increased due to liming in 12 of 42 site-years. The yield response to lime did not differ between crops. Crop response decreased with increasing

initial soil pH, but was highly affected by subsoil pH. Optimum pH range for corn and soybean was 6.0-6.5 for soil series with subsoil (30 to 90 cm) having pH < 7.0 but was significantly lower (pH 5.0-5.5) for soils with subsoil having a higher pH. Results from this study will provide crop producers with improved criteria for site-specific lime management.

Abbreviations: ANOVA, analysis of variance; DGPS, differential global information system; CCE, calcium carbonate equivalent; ECCE, GIS, geographical information systems; effective calcium carbonate equivalent; LR, lime requirements; OM, organic matter; RCBD, randomized complete block design; SCN, soybean cyst nematodes.

INTRODUCTION

The negative impact of soil acidity on crop productivity is well known. Soil acidity may be created by a removal of bases by harvested crops (Bouman et al., 1995), leaching (Poss et al., 1995), and acid residuals that are left in the soil from N fertilizers (Tarkalson et al., 2006). The value of liming to correct soil acidity and enhance agricultural productivity also has been well documented (Adams, 1984; Ulrich and Sumner, 1991; Black, 1993; Woodard and Bly 2010). However, over-liming of agricultural soils is known to reduce potential soil productivity through a variety of complex, pH-dependent processes ranging from restricted nutrient availability (Marschner, 1995; Olness, 1999), element toxicity (Adams, 1984), and increased disease (Huber and Wilhelm, 1988; Kurtzweil et al., 2002) or weed pressure (Childs et al., 1997). For these reasons it is imperative to correctly define optimum soil pH for crops and lime requirements (LR). Soil pH is used to determine whether or not soil acidity limits crop growth but does not directly estimate LR. Several analytical methods have been developed to determine LR.

These include soil incubation, direct titration, and buffer solutions (McLean et al., 1961; Shoemaker et al., 1961; Hoskins, 2005; Sikora, 2006).

The pH values of agricultural fields vary widely within and across regions. Within-field variability in soil pH and LR also has long been identified to be a common feature of many agricultural fields (Cline 1944; Peck and Melsted, 1973) indicating a high potential for site-specific lime management (Laslett et al., 1987; Tevis et al., 1991; McBratney and Pringle, 1999). Variability patterns sometimes are related to soil map units but not when liming or fertilizer have changed soil test values and created new patterns of variability (Franzen and Peck, 1995). There is renewed interest in soil pH and liming in relation to within-field variability because dense grid soil sampling approaches, global positioning systems (GPS) and variable rate technology are being adopted at a rapid rate by crop producers. Results of samples collected from producers' fields and limited field-scale research have shown very high pH variation within fields and even within soil map units (Peck and Melsted, 1973; Bianchini and Mallarino, 2002; Mallarino and Wittry, 2004).

Research concerning site-specific lime management has increased in recent years. Borgelt et al. (1994) showed that 9 to 12% of an 8.8-ha field would have been overlimed and 37 to 41% of the field underlimed with a uniform application, with the range in percentages corresponding with different methods of lime determination used in their study. Bongiovanni and Lowenberg-DeBoer (2000) simulated corn and soybean yields using soil pH response functions from small-plot data and predicted larger annual returns with site-specific pH management. Pierce and Warncke (2000) applied five lime treatments for corn and soybean to small field plots (4.5 by 30.5 m) located according to interpolated surfaces from soil samples collected from 0.5-, 61-, and 91.5-m cells and found no corn response to lime but a critical pH value of approximately 6.0 below which soybean response to lime was observed. They concluded that grid soil sampling did not

accurately predict soil pH or lime requirements for corn or soybean. Bianchini and Mallarino (2002) suggested that less lime may be needed when using variable-rate application in comparison with fixed rate applications in the whole field.

Few published studies in the U.S. Corn Belt have been conducted to determine optimal soil pH for corn and soybean along with long term lime application effects on soil pH. McLean and Brown's (1984) summary of previous crop responses to soil pH in the Midwest showed that corn frequently did not respond to soil pH in the range of 5 to 6, alfalfa (*Medicago sativa* L.) was strongly affected by this pH range, and soybean showed intermediate in response. Hergert et al. (1997) in Nebraska, reported that corn and soybean grain yields were positively correlated with soil pH before liming (pH ranging between 5.5 and 8.0), but soybean yield was unrelated to soil pH after lime application, indicating that a threshold pH for soybean had been exceeded. Bongiovanni and Lowenberg-DeBoer (2000) in Indiana, explained the relationship between corn and soybean yield and soil pH by a quadratic-plateau function and determined optimum pH range of 6.5-7.5 for both crops.

Iowa State University guidelines for pH and lime management were developed in the 1970s and have been maintained with little or no change since then (Sawyer et al., 2002). These guidelines suggest lime application for corn and soybean when soil pH is < 6.5 for most Iowa soils, but $\text{pH} < 6.0$ is suggested for fields located in soil associations with high-pH (>7.4) subsoil. Bianchini and Mallarino (2002) worked with corn and soybean on two central Iowa fields with soils classified as having high subsoil pH and reported a small yield increase (for corn) in only one of five site years even when surface pH was as low as 5.5. Henning (2007) working on acid soils of south Iowa found very inconsistent and small corn and soybean yield increase to lime application in soils classified as having high-pH subsoil (> 7.3 within a 1-m depth). Similar results for corn in acid soils with

high-pH subsoil were reported by Kassel (2008) in a 4-year study at northwest Iowa. In this study, however, soybean yield was consistently increased by lime application. On the other hand, substantial corn and soybean responses to lime (average of 6 years after liming) were found by Henning (2008) at northeast Iowa in acid soils not classified as having high-pH subsoil.

Research is needed to identify optimal soil pH for corn and soybean and at the same time understand better lime application effects on crop yield and soil pH in relation to within-field pH and soil type variation. There have been significant changes in production practices, cultivars/hybrids, and yield levels since much of the published research and recommendations were developed, and few of those studies addressed the issue of within-field variation in crop response to lime application. Therefore, the objectives of this study were to (1) study the variation of soil pH and crop response to lime within fields, (2) identify optimum soil pH for corn and soybean in some important Iowa soils, and (3) evaluate the effect of subsoil pH on crop response to lime.

MATERIALS AND METHODS

Fourteen replicated, multi-year strip-trials were conducted on Iowa farmers' fields managed with corn and soybean. Five trials established in 2007, five in 2008, and four in 2009, were evaluated for four, three, and two years, respectively. Corn-soybean rotations were used in most fields, with the only exception of one field with continuous corn and two fields where farmers planted corn after corn, which will be identified when appropriate. Experiments were conducted using a dense soil sampling approach and precision agriculture technologies based on replicated treatments applied to long strips as was used in previous work with lime or other nutrients (Bianchini and Mallarino, 2002; Bermudez and Mallarino, 2007; Mallarino and Wittry, 2010). Custom applicators'

equipment, differential GPS (DGPS) and geographical information systems (GIS) software and techniques were used. Treatments replicated two to five times were no lime or a uniform lime rate were arranged as a randomized complete block design at each field. There were two replications only at one site that was too narrow to accommodate more replications. The treatment strip width ranged from 15 to 20 m across fields and their lengths (exclusive of at least 30-m borders on each side) varied from 245 to 400 m across fields. The experimental areas (excluding borders) ranged from 2.54 to 6.42 ha. The dominant soil series according to digitized, 1:12000-scale soil survey maps (ICSS, 2003) were typical soils of Iowa and neighboring states (Table 1). Nine of the fourteen sites had soil associations with high pH ($\text{pH} > 7.4$) subsoils based on Iowa State University recommendations (Sawyer et al., 2002) (Table 2).

The limestone rate applied to all fields was 6.72 Mg ha^{-1} of ECCE. Table 2 provides summary information about the limestone materials used at each site. The use of ECCE is required in the State of Iowa for analysis of neutralizing power of limestone and quantifies the combined effect of particle size distribution and neutralizing value of limestone (IDALS, 2008). The ECCE is defined as the product of the CaCO_3 equivalent (CCE) and a fineness factor (Table 2). The CCE application rate was the same within a field but ranged from 8.29 to 13.22 Mg ha^{-1} across fields due to differences in the fineness of the limestone from sometimes different quarries that were used across fields. Soil management practices included no-till, strip-till, and chisel-plow/disk tillage before soybean and only disking before corn (Table 1). The limestone application time ranged from fall to spring across the sites (Table 1) and was incorporated with the primary or secondary tillage in the fields managed with tillage. Other management practices such as hybrids or varieties, fertilization, and weed and pest control were those used by each farmer and, therefore, they varied across fields. Rainfall in all sites was high enough for

allowing the lime to adequately react with the soil (Table 3). Rainfall data were obtained from the nearest weather stations (Iowa Environmental Mesonet, mesonet.agron.iastate.edu/index.phtml; verified 1 June 2011), which were located 3 to 25 km from the sites.

Soil samples were collected from 0- to 15-cm depth before applying lime using a dense, systematic grid sampling approach adapted to the experimental layout. The sampling depth suggested for lime application in Iowa for corn and soybean is 0- to 15-cm for fields managed with tillage and 5 to 7.5 cm for no-till (Sawyer et al., 2002). Many farmers collect 15-cm samples for no-till, however, because it is the depth recommended for P, K, and other nutrients. For the four no-till fields in this study, we sampled soil from depths of 0- to 7.5- and 7.5- to 15-cm, but used the average pH to estimate pH for the 0- to 15-cm to facilitate comparison across all fields and because studying lime effects on pH with depth was not an objective. Grid lines were spaced 30 to 40 m along strips and 15 to 25 m across the strips (depending on the field). The width of each cell coincided with the width of each replication. One 12-core composite sample was collected from each cell (ranging from 0.12 to 0.18 ha depending on the field) by collecting the soil cores from a circle approximately 120 to 150 m² in size at the center of each cell. At three sites, the initial samples were collected from cells corresponding to the control strips only because lime had to be applied before soil sampling. Soil samples taken before lime application were analyzed for pH using a 1:1 soil-water ratio, for soil organic matter (OM) by a combustion method (Wang and Anderson, 1998). Soil buffer pH was measured with the Shoemaker-McLean-Pratt (SMP) method as recommended for the North Central Region (Watson and Brown, 1998). Post-harvest soil samples from a 0- to 15-cm depth were collected from both limed and not limed soil sampling cells every year after corn or soybean harvest and analyzed for pH to calculate the change from initial pH

due to lime application. In this case the width of each cell was defined by each strip width and the length was the same as for the initial soil sampling cell. Subsoil samples (30- to 90-cm depth) were also collected by soil series in each field in 2010 and analyzed for pH. The post-harvest soil samples were analyzed for pH. All determinations were performed in duplicate. Soil samples were also analyzed for soybean cyst nematodes (SCN) before every soybean crop. Cysts of SCN were extracted from 100 cm³ subsamples of soil using a modified wet-sieving and decanting method (Gerdemann 1955), then eggs were extracted from cysts by crushing the cysts with a motorized rubber stopper (Faghihi and Ferris 2000). The SCN eggs were collected on a 25-um-pore sieve, stained with acid fuchsin (Niblack et al., 1993), and counted with a dissecting microscope. In all cells, the SCN population densities were in the “low” category so severe soybean damage by SCN was not expected.

The initial pH, buffer pH, and OM data were imported into ArcGIS software to calculate descriptive statistics for the entire experimental area of each field and for each soil series. Coordinates for soil series polygons were imported to ArcGIS from digitized, 1:12000 scale Iowa soil survey maps (ICSS, 2003). Initial soil pH values and also pH values from samples collected from cells corresponding to the control treatment were classified into several pH ranges: < 5.00, 5.00-5.49, 5.50-5.99, 6.00-6.49, 6.50-6.99, 7.00-7.49, and ≥ 7.50 for further analysis. Information from the Iowa soil survey maps (ICSS, 2003) and from Iowa State University recommendations for lime (Sawyer et al., 2002) were used to classify each site based on the subsoil pH of the soil association (with subsoil pH ≤ 7.4 that we called “low”, or > 7.4 that we called “high”). Results from our subsoil sampling were used to classify soil series based on actual measured subsoil pH. We called those series having pH ≥ 7.0 at 30- to 90-cm depth “high pH subsoil series” and the others were designated “low pH subsoil series”.

Management practices other than lime application were those used by each farmer, therefore they varied across fields. Potassium and P applications followed recommendations for corn and soybean in Iowa (Sawyer et al., 2002). The farmers also applied N fertilizer at rates that were at least as high as the highest N rates recommended in Iowa (Blackmer et al., 1997), which are 168 kg N ha⁻¹ for corn after soybean and 224 kg N ha⁻¹ for corn after corn. Grain yield was harvested and recorded with combines equipped with impact flow-rate yield monitors and DGPS receivers. The yield monitors used recorded a yield value at 1-s intervals and were calibrated by weighing grain harvested along combine passes outside the experimental areas. Grain moisture was determined by a sensor located in the combine auger. The yield monitor spatial accuracy was checked in several field locations with a hand-held DGPS receiver. The grain yield and moisture records were imported into ArcGIS software for further processing. Data were unaffected by borders because at least 20 m at each strip end were harvested but not used for data collection, and data from at least two crop rows on each side of a strip border were not used. The data were also analyzed for common yield monitor problems such as unexpected combine stops or waterways, and affected data were deleted as outlined in previous studies (Bianchini and Mallarino, 2002; Bermudez and Mallarino, 2007; Mallarino and Wittry, 2010). ArcGIS software was used to calculate means for areas defined by each treatment strip and also for smaller areas defined by each strip and soil series or soil pH ranges present in a field. Corn and soybean yield data were adjusted to 155 and 130 g kg⁻¹ moisture concentration, respectively.

Relative crop yields were calculated for each site and year as the ratio between each cell yield and the average of the two maximum yields of limed cells following the methodology used by Mc Lean and Brown (1984). Crop relative yield response to lime (relative increase over the control) was calculated for each site, year, and initial soil

sampling cell as the difference between the grain yield of the limed portion of each cell and the yield of the adjacent control portion of the cell divided by the yield of the control multiplied by 100. Use of relative yield and relative yield response allowed for combining data from crops, sites, and/or years without significant bias.

Analyses of variance (ANOVA) of treatment effects on grain yield were conducted for each site and year after liming using the MIXED procedure of SAS (SAS Inst., 2010) assuming fixed treatment effects and random block effects. For each strip-trial and year after liming, three ANOVA procedures were conducted according to a RCBD. One procedure assessed treatment effects for the entire experimental area of each field, and data inputs were means of yield monitor points for each strip (4 to 10 numbers for each site, from two treatments and two to five replications). This procedure was performed for the yield data of each year and for the average of all years combining both crops by using relative yields. The second procedure assessed treatment effects on grain yield for each soil series present at each field whose area encompassed at least two replications of the field design. The third procedure assessed treatment effects on grain yield for each pH range (as defined above) present at each field whose area encompassed at least two replications of the field design. The data inputs for the last two approaches were means for areas defined by the width of each strip and each soil series/pH range polygon (one value for each treatment, replication, and soil series/pH range combination). Each line of the input data set for each site and year after liming consisted of codes for treatment, replication, soil series/pH range, and grain yield.

Analyses of variance of lime effects on soil pH over time were conducted for each soil series within each site using data from the initial soil pH before liming and that from limed cells, one, two, three, and four years after the application. The GLM procedure of SAS (SAS Inst., 2010) was used for this analysis, assuming year as treatment (initial,

first, second, third, and fourth) and means were compared by LSD ($P \leq 0.1$). An combined analysis of crop response to lime as related to initial soil pH range across sites was performed combining data from crops, years after liming, and sites using the MIXED procedure of SAS (SAS Inst., 2010). This analysis was conducted across all sites and soils, for soil associations classified as having high or low subsoil pH based on Iowa State University recommendations (Sawyer et al., 2002) and Iowa digitized soil survey maps (ICSS, 2003), and for two groups of subsoil series having measured subsoil pH ≥ 7.0 or <7.0 . Linear regressions for the relationship between relative crop yield response to lime and initial soil pH or soil pH for the unlimed control after the first year were performed using the REG procedure of SAS (SAS Inst., 2010).

RESULTS AND DISCUSSION

Within-Field Initial pH Variation.

Substantial initial soil pH and buffer pH variability within each trial (Table 2) confirmed the value of dense soil sampling, GIS, and DGPS for field-scale on-farm research using replicated strip trials. The pH variability was especially high at Sites 1, 2, 4, 6, 8 and 10 where differences between the maximum and minimum pH were as high as 1.4 to 3.0 pH units. Variability of buffer pH, although lower than for pH, was highest at Sites 1, 4, and 10. Descriptive statistics of soil samples for each soil series at each field in Table 4 also show substantial pH and buffer pH (to a lesser extent than within-fields) variation within soil boundaries of digitized soil survey maps using a scale 1:12000 (ICSS, 2003). The pH and buffer pH CV values ranged from 0.8 to 12.2 and from 0.8 to 5.4%, respectively, across the soil series. Organic matter variation was also high within and across fields (Tables 2 and 4). Study of only average soil pH values for the experimental areas at each field (2.54 - 6.42 ha) would have resulted in a much smaller

range of values and probably misleading conclusions as suggested by Pierce and Warncke (2000). The pH and buffer pH variation observed in most fields was at such level that would result in very different lime application recommendations. In Iowa, pH 6.9 is recommended for alfalfa (*Medicago sativa* L) and pH 6.0 to 6.5 is recommended for corn and soybean depending on the soil association (Sawyer et al., 2002). For example, the variation in pH and buffer pH would have resulted in lime recommendations for corn and soybean ranging from zero (in Site 4) to more than 5 Mg ECCE ha⁻¹ (in Sites 7, 12, and 13). Bianchini and Mallarino (2002) and Mallarino and Wittry (2004) also found very large within-field pH variability in Iowa fields. They also reported evidence of high small (< 10 m) and large-scale variability in those fields and suggested a combination of natural and management causes.

Soil pH Response to Lime in Field Areas with Different Soil Series.

Table 4 shows the limestone application effect on soil pH for each soil series at each site for all years included in the study. The average limestone effect on soil pH for each field is not shown, because such averages would be of little relevance given the high within-field variation in initial soil pH, buffer pH, and soils in most fields. Limestone application significantly ($P < 0.1$) increased soil pH in most soil series regardless of their initial pH (Table 4). Soil pH increases ranged from 0.04 to 1.98, from 0.15 to 2.50, from 0.42 to 2.09, and from -0.23 to 1.73 pH units for the first, second, third, and fourth year after liming, respectively. The negative value in the fourth year corresponds to the Okoboji series whose initial pH was 7.14 and is classified as calcareous, in which little or no soil pH increase due to liming was expected. Maximum pH was reached during the second year after liming for several fields, which suggests that at least for some Iowa soils and limestone sources, one year is not enough time for the lime to fully react with

the soil. The maximum pH was reached after one year of liming for the Marshall and Judson series, where the maximum pH attained in these soils was below 6.2 in contrast to the higher maximum pH observed for the rest of the soil series (Table 4). No particular property of these two soil series (Table 4), the limestone applied to those fields (Table 1) or rainfall (Table 3) allow for a reasonable explanation of this result. Woodard and Bly (2010) reported that soil pH kept increasing to a 0- to 15-cm depth several years after the lime application until pH 7.5 in soils from the Great Plains. Haby et al. (1978) compared the reaction time of two limestones in a Texas field study and reported maximum pH attained (pH between 6.5 and 7.3) approximately 7 months after the application.

Soil pH tended to decrease the third year after liming in several soils, although the decrease started in the second year in the Marshall and Judson series (Table 4). This decrease is probably associated with a slow release of reserve acidity emerging from slow-reacting portions of the buffer capacity and/or the acidifying effect ammonium N-fertilizer applied by farmers to the corn (Mahler and Harder, 1984; Tarkalson et al., 2006). Relatively low buffer pH values for these soils would support that explanation (Table 4).

Site-Average Grain Yield Responses to Lime Application.

Table 5 shows the grain yield responses to lime application across the entire length of the strips at each site. Study of these responses is relevant to demonstrate how use of these strip averages (which would be similar to data obtained by using the traditional weigh wagons) may provide misleading results concerning potential crop responses to lime in many fields. Lime application increased ($P < 0.1$) crop grain yield in two sites during the first year after liming, in eight sites during the second year, in two sites during the third year, and no yield increase was observed in the fourth year of the lime

application. Average corn response for the responsive sites ranged from 302 to 1226, 158 to 532, and 161 to 414 kg ha⁻¹ in the first, second, and third year after liming, respectively. Significant soybean yield increase due to liming was only observed in the second year of the lime application, and ranged from 112 to 364 kg ha⁻¹. An apparent soybean yield decrease ($P < 0.1$) due to liming was also observed in Sites 12 and 13 in the first year after liming, although the magnitude of the yield decrease was smaller than 250 kg ha⁻¹. This result is surprising since the average soil pH at those two locations was low (Table 2), and a yield increase was expected. Analysis of results across both crops and years through relative yields (not shown) indicated a crop yield increase from lime application ($P < 0.1$) at Sites 5, 6, 7, 8, and 11, where on average, the crop productivity was increased by 9, 8, 3, 1, and 5 % over the control, respectively. These sites were not always the ones with more acidic initial pH (only Site 5 was). Such an inconsistent relationship between site-average yield response to lime and average initial pH can be due to complex site and environmental effects, but are most likely due to high within-field variation in both soil pH (Table 2 and 4) and crop response to lime. This result suggests a relative low value of average analyses along the strips for each trial, which also was suggested by Pierce and Warncke (2000) and Bianchini and Mallarino (2002).

Yield Response to Lime in Field Areas with Different Soil Series.

Significant crop yield increases ($P < 0.1$) due to liming were found for several soil series present in the fields (Table 6). Because of imposed replication requirements, analysis of yield responses for field areas with different soil series was done for two to four soil series at Sites 2-7, 9, 10, and 14. At Site 2, crop response to lime ($P < 0.1$) was found in the first three years for the Nicollet series but no response was observed for the other series. This result suggests the Nicollet series as a consistently responsive one,

although its initial pH and buffer pH were not among the lowest (Table 4). At Site 3, crop yield was increased ($P < 0.1$) due to liming in the first and third year for the Clarion series but only in the fourth year for the Canisteo and Nicollet series, although response was expected in all soils based on their low initial pH (Table 4). Site 5 and 7 showed high inconsistency of crop response to lime since responses were observed in different series and years without a clear pattern, a result that is unexpected considering the low soil pH of all soils in these sites (especially Site 5). At Site 9, although crop response to lime was expected in all series, it was only found ($P < 0.1$) in the first two years for the series Primghar and in the third year for the series Marcus. The rest of the sites showed either no response for any soil series (Site 4 and 14) or crop response for two series (Site 10).

The fact that there was no response to lime for some soil series and years should not be surprising. An inconsistent response to lime over time for a soil series within a field shows how site and environmental factors affect crop response to any input even when a response should be likely. Bianchini and Mallarino (2002), Vetch and Randall (2006), and Henning (2007) working on acid soils of Iowa or south-central Minnesota found very inconsistent and small corn and soybean yield increase to lime application in soils classified as having high-pH subsoil (> 7.3 within a 1-m depth). For example, Bianchini and Mallarino (2002) worked on fields having mainly Clarion, Nicollet, and Webster soils (which dominate from central Iowa to south-central Minnesota) and observed a small response in only one of five site-years, even for surface soil pH as low as 5.4. Moreover, based on results of older and unpublished research, Iowa State University liming guidelines have recommended since the early 1970s a lower optimum pH for corn and soybean grown in these soils.

Yield Response to Lime in Field Areas with Different Initial Soil pH.

Study of relationships across sites between relative crop yield response to lime and initial soil pH or soil pH for the unlimed control after the first year were not correlated for each crop or across both crops. Therefore, we studied the crop response to lime for several pH ranges that were reasonable from an agronomic and lime management perspectives.

As expected, grain yield increases ($P < 0.1$) due to lime application were more frequently found in field areas with lower pH (Table 7). Data in this table for each site-year show that yield increases due to lime often were observed below pH 6.5 and seldom for higher pH as literature has shown for corn and soybean (Bongiovanni and Lowenberg-DeBoer, 2000; Pierce and Warncke, 2000). The lack of a significant crop response in some field areas with pH as low as 5 (and even occasional small yield decreases) shows again the impacts of site and environmental factors on crop response even in soils where a response is likely. Analysis of variance showed no average difference between corn and soybean response to lime for any pH range, and no significant interaction between crop and pH range (data not shown). This result is in contrast to the general belief that soybean is a more lime responsive crop than corn, and does not agree with studies in other states (McLean and Browns, 1984; Pierce and Warncke, 2000). However, a similar response for both crops or inconsistent differences, have been observed in Iowa and the western Corn Belt (Bianchini and Mallarino, 2002; Vetch and Randall, 2006; Henning, 2007).

Data in Figure 1 show summarized relative yield responses to lime application across crops and site-years. There was a large relative yield increase for the lowest pH range (< 5.00) and a smaller increase for the second-lowest range (5.00-5.49). There were apparent responses of similar magnitude to that observed for the second-lowest pH range for other pH ranges, but did not reach significance ($P > 0.1$). These results are useful to make a

general characterization of the corn and soybean response to lime in representative Iowa soils but ignore the influence of high pH subsoil at decreasing the magnitude of crop response to lime and/or the optimum pH indicated above. Therefore, Figure 2 summarizes crop responses for the different pH ranges according to soil associations having low- or high-pH subsoil according to current Iowa State University liming guidelines (Sawyer et al., 2002). Relative yield response to lime decreased as the original soil pH increased for soils with high- or low-pH subsoil. For low-pH subsoil associations, however, the crop response was greater (higher than 10% for pH range <5.0), more consistent, and significantly different from 0 for the pH range <5.0 until the pH range 6.0-6.4, in agreement with current Iowa State University recommendations. For high-pH subsoil associations, however, the crop response to lime was observed from the pH range <5.0 until only the pH range 5.5-5.9, which clearly indicates a need for a lower pH than for soils with low subsoil pH. This effect of subsoil pH on decreasing crop response to lime has not been explained by previous research, and it is quite hard to explain with the methods used in this study. Acidic surface soils would generate unbalanced conditions for plant growth (nutrient availability or element toxicity) regardless of the subsoil pH, especially if the high-pH subsoil is deep in the soil profile.

Figure 3 shows summarized crop yield responses for the different pH ranges according to measured subsoil pH (30-90 cm). No significant response to lime was found for any pH range for soil series with measured subsoil pH ≥ 7 , which is in contrast to results in Figure 2 and in agreement with results reported by Bianchini and Mallarino (2002). No site-year included surface with pH < 5.0 and subsoil > 7.0 (the reason there is no bar for this range in Figure 3), but there were several instances with surface pH 5.0-5.49 and high-pH subsoil. For soil series having subsoil pH <7, however, there were significant yield increases due to lime application for acid pH ranges until the pH range

6.0-6.4 These results confirm that the optimal pH range for corn and soybean would be between pH 6.0 to 6.5 for soil series with low-pH subsoil but would be lower for soils with high-pH subsoil.

Study of crop responses according to measured available soil P and K, Ca, Ca plus Mg, cation exchange capacity of the surface (not shown), or OM (Table 4) did not show obvious explanations for the lower optimum pH with high pH subsoil. Given the methods used in the study, we can only speculate about reasons. Soil acidity influences crop growth through multiple and sometimes difficult to identify factors, which include direct effects of high H^+ or toxic elements with strongly acid pH, availability of nutrients, and (for legumes) effects on N fixation. The consistent observed results, which confirm scarce observations in mainly Iowa and Minnesota (Bianchini and Mallarino, 2002; Vetch and Randall, 2006); Henning, 2007), suggest that no matter the reason, corn and soybean have some unknown physiological mechanism by which potentially detrimental effects of acidity in the surface is offset by high-pH subsoil.

CONCLUSIONS

Large within-field soil pH variability suggests that site-specific lime management is necessary for most Iowa soils. Limestone application significantly increased soil pH in all sites, and maximum pH values were generally reached during the second year after liming. Corn and soybean show similar yield response to lime application. Optimum pH range for corn and soybean would be 6.0-6.5 for soils with low-pH subsoil, but significantly lower (5.0 to 5.5) for soils having high pH subsoil according to measured subsoil pH values. The methods used in the study did not allow for a supported explanation for this result. Results from this study will provide crop producers with improved criteria for site-specific lime management.

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Table 1. Field locations and predominant characteristics for 14 experiments.

Site	Year	County	Tillage system [†]	Dominant soils				Soil association	n [¶]	pH (Range)	Mean SMP buffer pH (Range)	Mean OM# (Range)
				Principal		Secondary						
				Series	Classification [‡]	Series	Classification					
1	2007	Jasper	ST	Clarion	T. Hapludolls	-	-	Clarion-Lester	32	6.0 (5.6-7.3)	6.7 (6.4-7.2)	33 (22-44)
2	2007	Story	CPD	Webster	T. Endoaquoll	Nicollet	A. Hapludoll	Clarion-Webster-Nicollet§	40	6.0 (5.7-7.2)	6.5 (6.3-7.1)	44 (27-72)
3	2007	Boone	CPD	Canisteo	T. Endoaquoll	Nicollet	A. Hapludoll	Canisteo-Clarion-Nicollet§	36	5.2 (4.8-6.0)	6.4 (6.1-6.8)	38 (26-52)
4	2007	Greene	CPD	Canisteo	T. Endoaquoll	Okoboji	V. Endoaquoll	Canisteo-Webster-Nicollet§	32	6.5 (5.1-8.1)	6.8 (6.1-7.4)	52 (36-78)
5	2007	Boone	CPD	Talcot	T. Endoaquoll	Dickman	T. Hapludoll	Coland-Talcot-Wadena	40	5.0 (4.6-5.8)	6.4 (6.1-6.9)	33 (12-47)
6	2008	Cedar	CPD	Dinsdale	T. Argiudoll	Muscatine	A. Hapludoll	Tama-Downs-Muscatine	40	5.5 (5.2-6.7)	6.5 (6.3-7.0)	34 (23-38)
7	2008	O'Brien	CPD	Primghar	A. Hapludoll	Galva	T. Hapludoll	Galva-Primghar§	36	5.5 (5.2-6.0)	6.2 (6.0-6.5)	52 (45-57)
8	2008	O'Brien	CPD	Galva	T. Hapludoll	-	-	Galva-Primghar§	36	5.9 (5.2-6.7)	6.6 (6.3-6.9)	49 (45-60)
9	2008	O'Brien	CPD	Marcus	T. Haplaquoll	Primghar	A. Hapludoll	Sac-Galva-Primghar§	36	5.7 (5.5-6.1)	6.3 (6.1-6.6)	69 (53-92)
10	2008	Union	NT	Sharpsburg	T. Hapludoll	Clarinda	T. Argiudoll	Sharpsburg-Shelby-Nira	19	5.6 (4.8-6.2)	6.4 (5.9-6.8)	40 (34-47)
11	2009	Ringgold	NT	Nira	T. Argiudoll	-	-	Nira-Sharpsburg-Shelby	36	5.7 (5.3-6.2)	6.5 (6.3-6.9)	45 (29-57)
12	2009	Pottawattamie	NT	Marshall	T. Hapludoll	-	-	Monona-Ida§	36	5.2 (5.1-5.6)	6.2 (5.9-6.5)	38 (34-45)
13	2009	Pottawattamie	CPD	Marshall	T. Hapludoll	-	-	Monona-Ida§	36	5.4 (5.2-5.6)	6.2 (6.1-6.8)	41 (37-45)
14	2009	Crawford	NT	Marshall	T. Hapludoll	Judson	C. Hapludolls	Marshall§	48	5.3 (5.1-5.8)	6.4 (6.2-6.8)	40 (32-50)

[†] ST, strip till, CPD, chisel-plow/disking, and NT, no-till.

[‡] T., Typic; A., Aquic; V., Vertic; C., Cumulic. OM, organic matter.

§ Soil associations with high pH (pH>7.4) subsoil.

¶ n, number of samples (grid cells).

OM, organic matter.

Table 2. Characteristics of the lime materials used in 14 strip trials.

Site	CCE†	Ca	Mg	Particle size ‡				ECCE§	Application date
				Mesh 4	Mesh 8	Mesh 60	FF		
----- % -----									
1	94.9	22.4	10.8	100	92	30	56	53	May 18 2007
2	97.3	40.7	0.4	100	100	44	66	64	May 25 2007
3	93.8	37.7	0.5	100	100	38	63	59	Nov 14 2006
4	95.9	39.7	0.3	100	99	59	75	72	Oct 28 2006
5	98.1	40.5	0.4	100	96	38	62	60	Jan 27 2007
6	99.4	21.5	12.2	99	85	36	57	57	May 12 2008
7	98.7	5.4	0.5	100	99	70	81	80	Nov 9 2007
8	98.7	5.4	0.5	100	99	70	81	80	Nov 9 2007
9	98.7	5.4	0.5	100	99	70	81	80	Apr 15 2008
10	89.6	34.7	1.1	100	97	41	64	57	Apr 28 2008
11	70.0	29.7	1.6	100	99	53	72	50	Dec 12 2008
12	66.0	28.3	1.5	100	98	48	68	45	Jan 9 2009
13	66.0	28.3	1.5	100	98	48	68	45	Jan 9 2009
14	101.0	44.9	0.4	98	94	51	69	69	Feb 23 2009

† CaCO₃ equivalent.

‡ Fineness according to State of Iowa limestone analysis regulations (IDALS, 2008).

Percentage of material passing sieves with Tyler mesh 4, 8, and 60 (4.75, 2.38, and 0.25 mm, respectively). FF, fineness factor defined as amounts passing sieves with mesh 4, 8, and 60 multiplied by the factors of 0.1, 0.3, and 0.6, respectively.

§ Effective CaCO₃ equivalent as defined in Iowa (IDALS, 2008).

Table 3. Monthly precipitations within one year after lime application for 14 experiments.

Site	Month after liming											
	1st	2nd	3 rd	4 th	5 th	6 th	7 th	8 th	9 th	10 th	11 th	12 th
----- mm -----												
1	63	81	195	106	147	5	66	13	54	22	181	125
2	52	75	200	48	137	4	49	9	18	71	130	216
3	33	68	46	46	82	183	121	76	60	167	41	128
4	35	57	36	55	79	176	152	75	59	333	52	139
5	55	79	176	152	75	59	333	52	139	5	52	17
6	164	241	189	76	125	35	45	62	24	31	81	81
7	1	45	13	17	34	61	116	137	87	56	95	99
8	1	45	13	17	34	61	116	137	87	56	95	99
9	97	161	121	133	47	97	123	20	22	15	21	15
10	127	349	230	9	142	120	50	35	12	21	108	104
11	108	104	80	162	149	169	18	154	61	68	19	24
12	20	12	34	76	74	158	148	160	8	121	21	76
13	20	12	34	76	74	158	148	160	8	121	21	76
14	51	21	13	49	67	60	123	168	131	16	148	25

Table 4. Continuation.

Site	Soil series	n§	Initial soil pH				Initial buffer pH				Organic matter				pH after liming				
			Mean	Min.	Max.	CV	Mean	Min.	Max.	CV	Mean	Min.	Max.	CV	1st year	2nd year	3rd year	4th year	
			----- g kg ⁻¹ -----																
9	Galva	4	5.57c	5.48	5.70	1.8	6.29	6.23	6.35	0.8	58	54	60	4	6.16b	6.60a	6.41ab		
	Marcus	23	5.78c	5.55	6.13	3.4	6.35	6.18	6.63	2.3	73	59	92	12	6.38b	6.67a	6.46b		
	Primghar	8	5.60c	5.50	5.68	1.2	6.25	6.08	6.35	1.3	61	53	66	6	6.50ab	6.65a	6.29b		
10	Clarinda	4	5.82c	5.60	6.13	3.8	6.56	6.45	6.73	1.9	42	38	47	9	6.91b	7.29a	6.71b		
	Nira	6	5.67c	5.45	6.15	4.6	6.45	6.33	6.73	2.3	39	34	45	10	6.58ab	6.96a	6.28b		
	Sharpsburgh	7	5.50c	4.75	6.13	8.5	6.37	5.88	6.78	4.9	39	34	43	8	6.21b	6.95a	6.08b		
11	Nira	31	5.68b	5.33	6.21	3.8	6.52	6.3	6.86	2.0	45	36	50	6	6.39a	6.39a			
12	Marshall	36	5.26c	5.10	5.56	1.8	6.17	5.93	6.48	2.5	38	30	41	5	5.80a	5.46b			
13	Marshall	36	5.36c	5.15	5.65	2.3	6.25	6.1	6.78	2.2	41	37	44	5	6.18a	5.73b			
14	Judson	5	5.33c	5.23	5.48	1.8	6.51	6.38	6.75	2.3	31	29	35	7	6.04a	5.48b			
	Marshall	42	5.28c	4.98	5.73	3.6	6.45	6.25	6.8	2.1	33	26	48	10	5.94a	5.49b			

† Within each site-soil, different letters indicate significant pH differences ($P < 0.05$).

‡ No pH data are available for the fourth year after liming in Sites 6-14 and for the third year after liming for Sites 11-14.

§ n, number of samples (grid cells).

Table 5. Crop grain yield response to lime during four, three, and two years in 14 strip trials. †

Site	n‡	First year				Second year				Third year				Fourth year				All years#
		Crop	App.¶ -- Mg ha ⁻¹ --	Con.¶	Stat.¶ <i>P</i> > <i>F</i>	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.	Crop	App.	Cont.	Stat.	Stat.
1	4	C	12.87	12.90	0.96	C	10.60	10.37	0.05	C	12.81	12.58	0.15	C	10.78	10.52	0.87	0.74
2	4	S	4.09	4.02	0.12	C	13.65	13.49	0.61	C	11.18	10.86	0.51	S	4.44	4.38	0.17	0.44
3	4	C	12.83	12.53	0.09	S	3.84	3.63	0.30	C	14.79	14.56	0.37	C	12.44	11.45	0.54	0.84
4	4	C	12.38	12.42	0.60	C	11.68	11.19	0.01	S	3.81	3.83	0.81	C	13.89	14.22	0.41	0.20
5	5	C	13.18	11.95	0.02	S	3.47	3.27	0.16	C	12.16	11.23	0.01	S	3.58	3.46	0.29	0.03
6	5	C	14.72	13.52	0.18	S	3.97	3.77	0.05	C	11.29	10.87	0.05					<0.01
7	4	S	4.46	4.35	0.12	C	14.12	13.75	0.01	S	4.12	3.96	0.25					<0.01
8	4	C	14.8	14.61	0.31	S	4.15	3.97	0.09	C	13.51	13.44	0.51					0.08
9	4	C	12.68	12.37	0.16	S	4.21	4.00	0.06	C	14.55	14.31	0.20					0.23
10	2	S	3.21	2.77	0.48	C	11.39	11.28	0.65	S	3.63	3.57	0.62					0.12
11	4	S	2.86	2.70	0.10	C	9.44	9.26	0.12									<0.01
12	4	S	3.81	4.02	<0.01	C	12.88	12.63	0.09									0.21
13	4	S	3.74	3.80	0.04	C	13.33	12.79	0.05									0.21
14	4	S	3.65	3.59	0.55	C	11.6	11.40	0.15									0.38

† No yield data is available for the fourth year after liming in Sites 6-14 and for the third year after liming for Sites 11-14.

‡ n, number of strips.

§ C, corn; S, soybean.

¶ App., Applied; Con., Control; Stat., Statistics.

Based on averaged relative yields across crops and years.

Table 6. Crop grain yield response to lime one, two, three, and four years after application for areas of 14 fields with different soil series. † ‡ §

Site	Soil series	n¶	First year				Second year				Third year				Fourth year			
			Crop#	App.#	Con.#	Stat.#	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.
			-- Mg ha ⁻¹ --				-- Mg ha ⁻¹ --				-- Mg ha ⁻¹ --				-- Mg ha ⁻¹ --			
			<i>P > F</i>				<i>P > F</i>				<i>P > F</i>				<i>P > F</i>			
2	Clarion	7	S	3.99	4.04	0.42	C	13.87	13.55	0.38	C	11.21	11.41	0.49	S	4.44	4.36	0.32
	Nicollet	14		4.16	4.02	0.03		13.85	13.46	0.03		11.44	10.76	0.02		4.41	4.37	0.46
	Webster	17		4.08	4.02	0.33		13.45	13.49	0.91		11.04	10.71	0.38		4.5	4.41	0.24
3	Canisteo	13	C	12.77	12.86	0.75	S	4.05	4.01	0.72	C	14.82	14.77	0.69	C	12.45	11.24	0.03
	Clarion	9		13.27	12.61	0.07		3.66	3.29	0.1		14.79	14.17	<0.01		12.8	12.22	0.3
	Nicollet	12		12.67	12	0.29		3.79	3.63	0.44		14.68	14.58	0.52		12.08	11.01	0.06
4	Canisteo	25	C	12.44	12.45	0.93	C	12.11	11.63	0.25	S	3.82	3.84	0.83	C	14.15	14.4	0.22
	Okobojo	5		11.99	12.23	0.33		10.54	9.99	0.43		3.75	3.76			12.68	13.34	0.45
5	Clarion	3	C	12.81	12.39	0.29	S	3.57	2.83	<0.01	C	11.72	10.93		S	3.14	3.4	0.03
	Dickman	9		12.64	11.09	0.09		3.27	2.95	0.11		12.09	11.29	<0.01		3.67	3.63	
	Ridgeport	2						2.44	2.15	0.05		9.42	9.35	0.89		3.23	2.98	0.11
	Talcot	17	C	13.72	12.66	0.18	S	3.66	3.59	0.2	C	12.42	11.26	<0.01	S	3.58	3.39	0.09
6	Dinsdale	21	C	15.94	14.04	0.11	S	4.09	3.81	0.03	C	11.73	11.44	0.51				
	Muscatine	9		11.63	12.56	0.69		3.62	3.64	0.93		10.56	9.9	0.56				

† Within each site-soil, different letters indicate significant differences ($P < 0.05$).

‡ No yield data are available for the fourth year after liming in Sites 6-14 and for the third year after liming for Sites 11-14.

§ No statistics were calculated for some soils because of insufficient degrees of freedom due to missing values or outliers removal.

¶ n, number of samples (grid cells).

C, corn; S, soybean; App., Applied; Con., Control; Stat., Statistics.

Table 6. Continuation.

Site	Soil series	n¶	First year				Second year				Third year				Fourth year			
			Crop#	App.#	Con.#	Stat.#	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.
				-- Mg ha ⁻¹ --		<i>P</i> > <i>F</i>		-- Mg ha ⁻¹ --		<i>P</i> > <i>F</i>		-- Mg ha ⁻¹ --		<i>P</i> > <i>F</i>		-- Mg ha ⁻¹ --		<i>P</i> > <i>F</i>
7	GalvaSTR	11	S	4.47	4.31	0.02	C	14.06	13.69	0.05	S	4.08	4.03	0.44				
	Primghar	18		4.44	4.39	0.63		14.15	13.74	<0.01		4.19	3.95	0.05				
9	Galva	4	C	12.52	12.13		S	4.03	3.59		C	14.76	14.48					
	Marcus	23		12.63	12.47	0.34		4.24	4.17	0.24		14.49	14.26	0.08				
	Primghar	8		12.93	12.28	0.05		4.19	3.85	0.09		14.71	14.33	0.11				
10	Clarinda	4	S	2.24	2.44		C	9.22	8.65		S	3.53	3.56					
	Nira	6		3.25	2.09	0.05		11.42	11.66			3.38	3.27	0.64				
	Sharpsburgh	7		3.65	3.44			12.55	12.24	<0.01		3.91	3.85	0.68				
14	Judson	5	S	3.75	3.44	0.18	C	11.34	10.93									
	Marshall	42		3.64	3.61	0.47		11.64	11.47	0.39								

† Within each site-soil, different letters indicate significant differences (*P* < 0.05).

‡ No yield data are available for the fourth year after liming in Sites 6-14 and for the third year after liming for Sites 11-14.

§ No statistics were calculated for some soils because of insufficient degrees of freedom due to missing values or outliers removal.

¶ n, number of samples (grid cells).

C, corn; S, soybean; App., Applied; Con., Control; Stat., Statistics.

Table 7. Crop grain yield response to lime one, two, three, and four years after application for areas of 14 fields with different soil pH ranges.

† ‡ §

Site	pH range	n¶	First year				Second year				Third year				Fourth year			
			Crop#	App. # -- Mg ha ⁻¹ --	Con. #	Stat. # <i>P</i> > <i>F</i>	Crop	App.	Con.	Stat.	App.	Con.	Stat.	Crop	App.	Con.	Stat.	
1	5.50-5.99	17	C	13.29	12.97	<0.01	C	10.88	10.49	0.03	C	13.02	12.92	0.74	C	11.13	10.56	0.39
	6.00-6.49	12		12.35	12.83	0.02		10.37	10.44	0.66		12.75	12.43	0.63		10.39	10.49	0.85
	6.50-6.99	2		12.39	12.65	0.79		9.81	9.20			12.48	11.67					
2	5.50-5.99	30	S	4.05	3.99	0.13	C	13.8	13.56	0.05	C	11.36	10.84	0.02	S	4.45	4.38	0.13
	6.00-6.49	7		4.19	4.06	0.05		13.72	13.75	0.94		11.00	10.87	0.77		4.43	4.35	0.14
3	<5.00	9	C	13.20	12.96	0.51	S	3.83	3.58	0.11	C	14.82	14.26	<0.01	C	12.87	11.86	0.03
	5.00-5.49	21		12.83	12.66	0.65		3.90	3.75	0.37		14.80	14.67	0.27		12.45	11.57	
	5.50-5.99	6		12.37	11.76			3.67	3.33	0.31		14.72	14.65			12.14	10.99	0.05
4	5.00-5.49	3	C	12.58	12.46		C	12.63	12.75		S	3.94	3.95	0.92	C			
	5.50-5.99	10		12.63	12.59	0.83		12.97	11.58	0.01		3.94	3.88			14.42	14.76	0.16
	6.00-6.49	5		12.16	12.16			11.22	11.58	0.79		3.46	3.75	0.29		13.77	14.48	0.19
	6.50-6.99	5		12.14	12.17	0.86		9.96	9.57			3.89	3.67	0.21		14.46	13.6	0.49
	7.00-7.49	5		12.50	12.76	0.31		11.11	11.69	0.37		3.77	3.94	0.18		13.88	13.95	
	>=7.50	5		12.01	12.18	0.43		10.56	10.17	0.27		3.75	3.73	0.89		12.52	13.62	0.15
5	<5.00	19	C	11.42	10.18	0.28	S	3.26	2.96	0.03	C	11.83	10.72	<0.01	S	3.56	3.40	0.20
	5.00-5.49	17		14.74	13.41	0.03		3.63	3.54	0.37		12.47	11.85	0.01		3.62	3.64	0.83
	5.50-5.99	4		14.14	13.25	0.63		3.66	3.64	0.92		12.30	11.21	0.01		3.56	3.08	0.05
6	5.00-5.49	13	C	16.06	14.49	0.12	S	4.15	3.79	<0.01	C	11.44	11.24	0.65				
	5.50-5.99	6		12.04	11.33	0.60		3.53	3.72	0.49		10.92	9.98	0.38				

† Within each site-soil, different letters indicate significant differences (*P* < 0.05).

‡ No yield data are available for the fourth year after liming in Sites 6-14 and for the third year after liming for Sites 11-14.

§ No statistics were calculated for some soils because of insufficient degrees of freedom due to missing values or outliers removal.

¶ n, number of samples (grid cells).

C, corn; S, soybean; App., Applied; Con., Control; Stat., Statistics.

Table 7. Continuation.

Site	pH range	n¶	First year				Second year				Third year				Fourth year			
			Crop#	App. # -- Mg ha ⁻¹ --	Con. #	Stat. # <i>P</i> > <i>F</i>	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.	Crop	App.	Con.	Stat.
7	5.00-5.49	11	S	4.44	4.29		C	14	13.67	<0.01	S	4.23	4.06	0.05				
	5.50-5.99	9		4.49	4.42	<0.01		14.32	13.86	<0.01		3.92	3.85	0.24				
8	5.00-5.49	2	C	14.56	14.99	0.29	S	4.12	3.89	<0.01	C	13.6	13.31	<0.01				
	5.50-5.99	11		14.79	14.60	<0.01		4.14	3.94	<0.01		13.54	13.45	0.22				
	6.00-6.49	7		14.87	14.40	0.16		4.16	4.16	0.44		13.4	13.51					
9	5.00-5.49	2	C	12.78	12.68	<0.01	S	4.12	3.74	<0.01	C	14.67	14.37	<0.01				
	5.50-5.99	17		12.71	12.34	0.02		4.24	4.00	0.03		14.52	14.31	0.06				
	6.00-6.49	2		12.36	12.48	0.43		4.15	4.15			14.62	14.3	0.32				
10	<5.00	2	S	3.69	3.87	<0.01	C	12.55	12.02	0.24	S	3.85	3.72	0.22				
	5.00-5.49	2		3.25	2.13							3.47	3.58					
	5.50-5.99	4		3.25	3.00	0.69						3.66	3.70	0.88				
	6.00-6.49	3		2.82	2.19	0.22		9.22	8.65			3.25	3.15					
11	5.00-5.49	5	S	2.81	2.65		C	10.27	10.34	0.72								
	5.50-5.99	12		2.91	2.72	0.03		9.45	8.90									
	6.00-6.49	3		2.76	2.73			8.03	9.65									
12	5.00-5.49	19	S	3.81	4.01	<0.01	C	12.88	12.63	<0.01								
13	5.00-5.49	18	S	3.77	3.81	0.20	C	13.31	12.8	<0.01								
14	5.00-5.49	20	S	3.69	3.59	0.08	C	11.67	11.4	0.04								
	5.50-5.99	3		3.46	3.45	0.86		11.11	11.43									

† Within each site-soil, different letters indicate significant differences ($P < 0.05$).

‡ No yield data are available for the fourth year after liming in Sites 6-14 and for the third year after liming for Sites 11-14.

§ No statistics were calculated for some soils because of insufficient degrees of freedom due to missing values or outliers removal.

¶ n, number of samples (grid cells).

C, corn; S, soybean; App., Applied; Con., Control; Stat., Statistics.

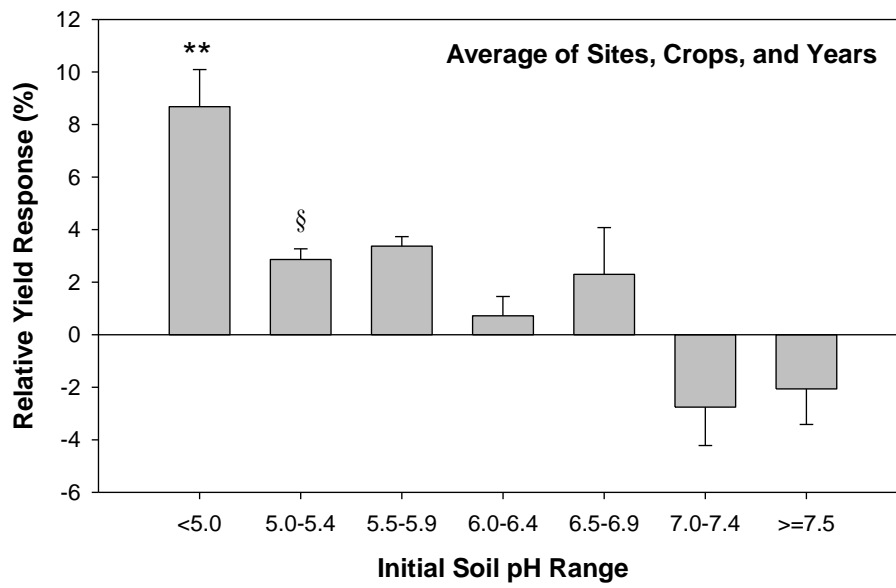


Figure 1. Relative crop response to lime for several initial surface soil pH ranges. Lines represent standard errors, and ** and § represent a significant difference from 0 at $P < 0.01$ and 0.1, respectively.

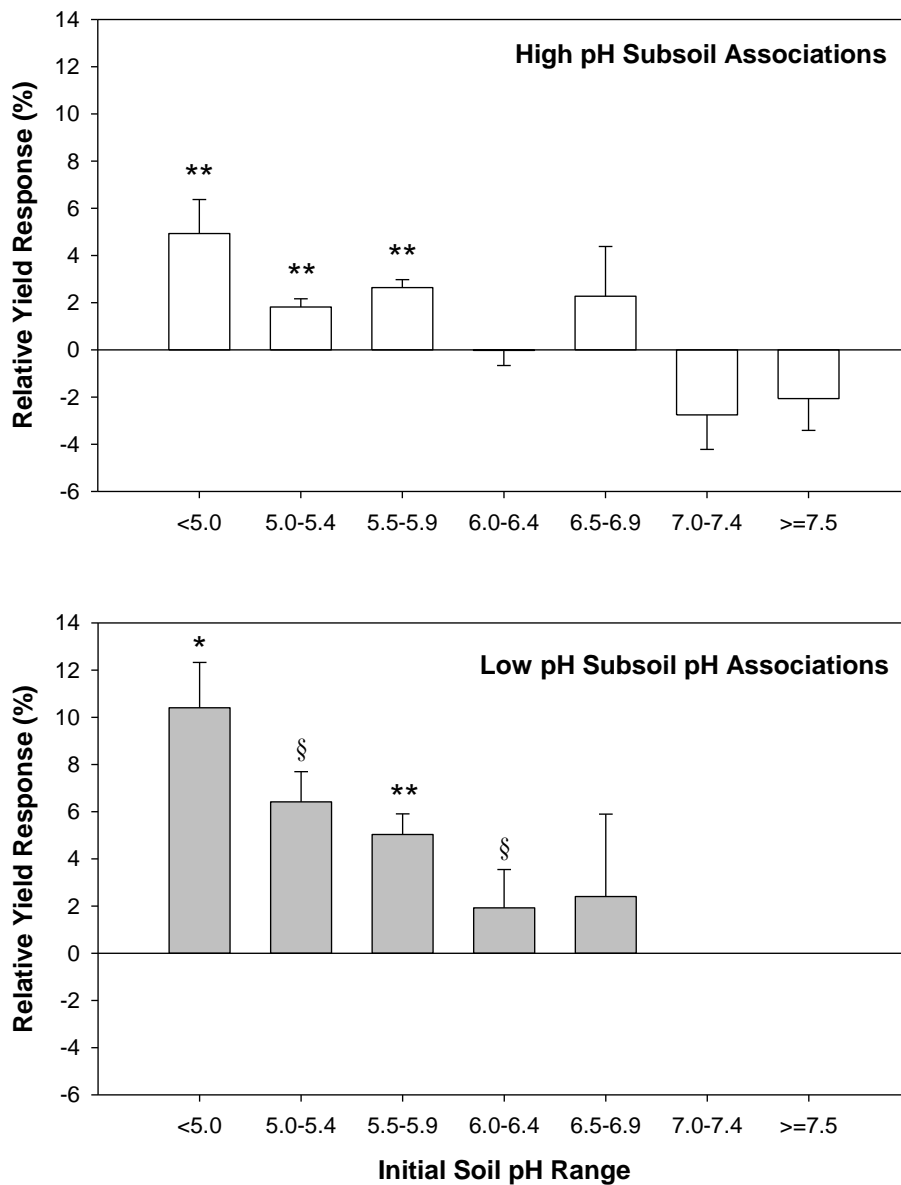


Figure 2. Relative crop response to lime for several initial soil pH ranges for high and low pH subsoil associations, according to Iowa State University recommendations (Sawyer et al., 2002). Averages of crops, years, and sites. Lines represent standard errors, and **, *, and § represent a significant difference from 0 at $P < 0.01$, 0.05, and 0.1, respectively.

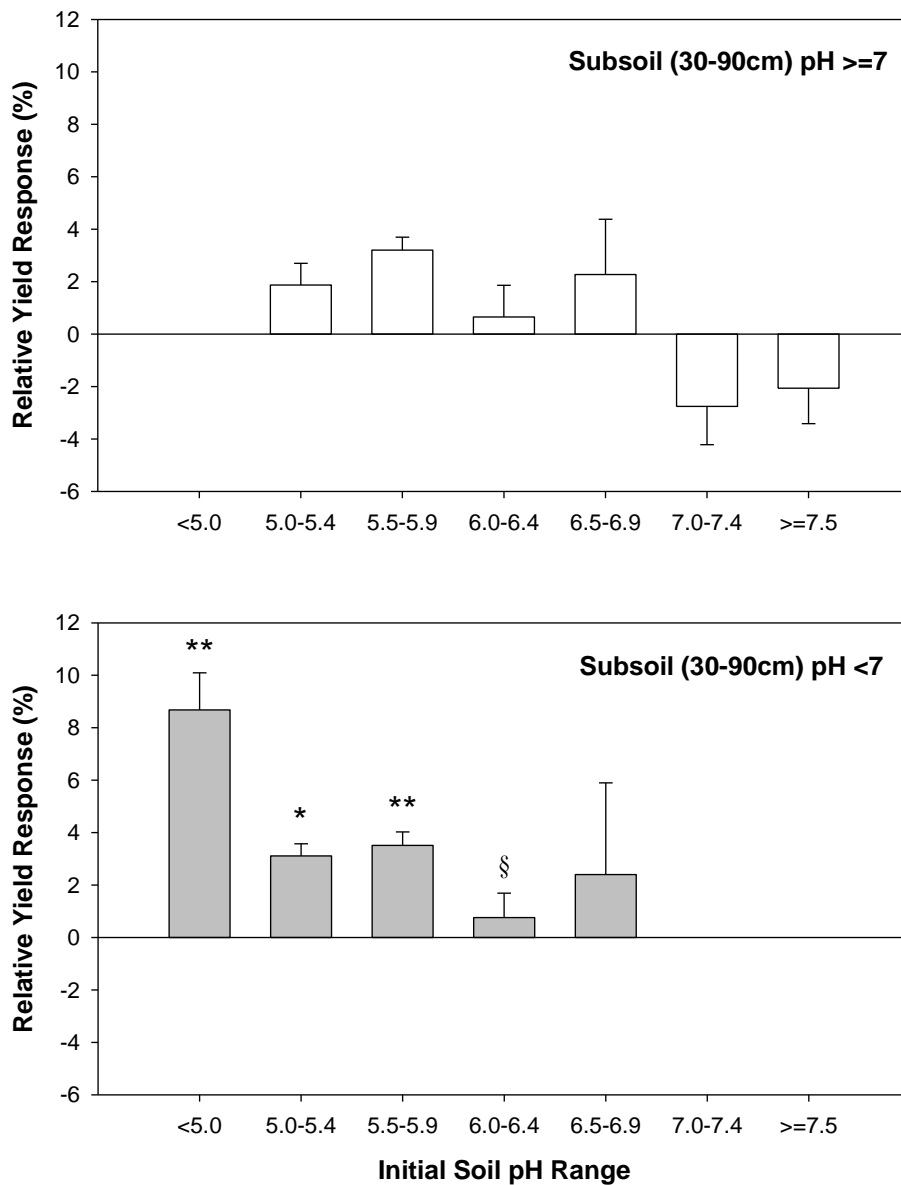


Figure 3. Relative crop response to lime for several initial soil pH ranges for subsoil (30-90cm) series with pH lower or equal/higher than 7 (according to measured values). Averages of crops, years, and sites. Lines represent standard errors, and **, *, and § represent a significant difference from 0 at $P < 0.01$, 0.05, and 0.1, respectively.

CHAPTER 4. SOIL pH CHANGE OVER TIME AS AFFECTED BY SOURCES AND RATES OF LIMESTONE

A paper to be submitted to the Soil Science Society of America Journal by

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ABSTRACT

Research has addressed effects of lime application on soil pH, but uncertainty still exists concerning the pH change over time after applying different limestone sources and rates. The objectives of this study were to (1) evaluate the rate of soil pH increase from application of pure CaCO₃, calcitic limestone, and dolomitic limestone; and (2) evaluate the short-term crop response (2 years) to the application of these lime sources. Four replicated field plot trials were established in Iowa acid soils (Typic Hapludolls of pH 5.4 to 5.7) in spring 2009. The amendments were incorporated into the soil by disking. Soybean [*Glycine max* (L.) Merr.] was the first crop and corn (*Zea mays* L.) was planted the second year. Application rates were 0, 4.5, 9, 13.5, and 22.5 Mg ha⁻¹ calcium carbonate equivalent (CCE). Soil samples were collected from a 0- to 15-cm depth at eight sampling dates (SD) during a period of 16 months following lime application and also from a 15- to 30-cm depth before liming and at the sixth SD. The soil pH increase over time for the three lime sources was curvilinear with decreasing increments to a plateau maximum (pH between 6.2 and 7.3 depending on the source) that was reached about 100 days after liming. However, the early pH increases and maximum pH reached were greater for pure CaCO₃ than for the calcitic and dolomitic limestones. Crop yield responses were observed at three sites. There was a yield difference among lime sources

only at one site, where corn yield was higher for CaCO₃, intermediate for the calcitic limestone, and lowest for the dolomitic limestone. Results showed that the time of limestone reaction in the soil was faster than usually assumed for limestone with the composition and fineness sources used in the study and demonstrated that a coarse particle size limits the rate of pH increase but also the maximum pH increase achieved over time.

Abbreviations: ANOVA, analyses of variance; CCE, calcium carbonate equivalent; CEC, exchange capacity; ECCE, effective calcium carbonate equivalence; FF, fineness factor; LR, lime requirement; PSE, particle size efficiency; SD, Sampling date; SMP, Shomaker-McLean-Pratt.

INTRODUCTION

Maintaining adequate soil pH levels is important for crop production because it ensures conditions conducive to optimal plant growth by reducing excessive and potentially toxic concentrations of elements such as aluminum (Al) and manganese (Mn), increasing the availability of several plant nutrients, and enhancing microbial activity (McLean 1982; Sims 1996). However, overliming may cause many nutrient deficiencies such as Zn deficiency in corn (Boswell et al., 1989) and Mn (Parker et al., 1981) or iron (Rogovska et al., 2007) deficiency in soybean. Agricultural limestone is commonly used in the U.S. Corn Belt to maintain optimum soil pH for corn and soybean. The effectiveness of a lime material for neutralizing acidity of substrates depends on its neutralizing capacity, fineness, chemical composition, and mineralogy (Barber, 1984; Thomas and Hargrove, 1984).

Pure and finely ground CaCO_3 is the standard against which other liming materials are measured, and its neutralizing value is considered to be 100%. The calcium carbonate equivalent (CCE) is defined as the acid-neutralizing capacity of a liming material expressed as a weight percentage of CaCO_3 (Havlin et al., 2005). Limestone containing 70–100% CaCO_3 is normally labeled as “calcitic” and that containing 20–50% MgCO_3 is considered as “dolomitic”. Haby et al. (1979) found that calcitic limestone neutralized soil acidity more rapidly than did dolomitic. Lindsay (1979) indicated that calcitic limestone is about threefold more soluble than dolomitic limestone under equivalent conditions of material purity, pH, and partial pressure of CO_2 . An experiment conducted by Rippy et al. (2007) showed very large variation in reaction times among dolomitic limestone sources for any given particle-size fraction (23-, 17-, and 13-fold differences within coarse, medium, and fine fractions, respectively). However, there was very little or no variation among the calcitic limestones (2-fold for coarse particles and none for midsize and fine particles).

Because the dissolution of limestone occurs as a surface reaction, the particle size distribution of a liming material directly influences the dissolution rate and its effectiveness in neutralizing soil acidity. Also, smaller particles and increased surface area allow limestone to react with a larger soil volume, to be more reactive with soil, and thus raise pH in a shorter time. A single agricultural limestone source includes a range in particle sizes, and the percent by weight of each particle size fraction describes the distribution. A particle size efficiency (PSE) factor can be assigned to each particle size fraction of an agricultural limestone (Meyer and Volk, 1952; Motto and Melsted, 1960; Murphy and Follett, 1978). The overall PSE (ranging from 0 to 1) of a lime source can be described by its fineness factor (FF). The term “effective calcium carbonate

equivalence'' (ECCE), calculated as a ratio of neutralizing value compared with CaCO_3 , quantifies the combined effects of particle size distribution (or FF) and acid neutralizing value (or CCE) (IDALS, 2008).

Long-term field studies that evaluate soil pH over time as affected by limestone rate and source are not abundant in literature for the U.S. Corn Belt. Because of the expense and intense labor, field experiments to evaluate soil pH changes over time due to lime application and or to determine lime requirement (LR) are rarely conducted. Instead, most of the information available derives from incubation studies (Follett and Follett, 1980; Alabi et al., 1986; McConnell et al., 1990; Owusu-Bennoah et al., 1995) which may not be representative of field situations. Haby et al. (1978) compared the reaction time of calcitic and dolomitic limestones in a Texas field study and reported higher neutralization capacity by calcitic limestone in relation to dolomitic. In this study, maximum pH (pH between 6.5 and 7.3) was attained approximately 7 month after the application. In South Dakota, Woodard and Bly (2010) measured soil pH change and crop yield response due to two sources of lime (a 90% CCE limestone and a very fine, loose CaCO_3 material with 92% CCE) at various depth increments in an 8-year field study. They reported that maximum pH at 0-15 cm depth was achieved between two and three years after the initial lime application when limestone was incorporated by tillage and they measured corn and soybean yield increases for all liming materials. Research in Northeast Iowa (Voss, 1991) reported that maximum pH (between 7 and 7.5) was reached as late as 7 years after liming, especially at the highest application rates (8 to 32 Mg ECCE ha^{-1}) in a loam soil. This author also reported faster lime reaction rates in Northwest Iowa in a silty clay loam soil, where maximum pH (5.6 and 7) were reached 2 years after the applications for rates ranging from 0.5 to 6 Mg ECCE ha^{-1}). Another study from Northwest Iowa suggested that

maximum pH (between 6 and 6.9 being higher as the rate increased) was reached 3-4 years after the application of aglime and finely ground eggshells with rates between 0.5 and 8 Mg ECCE ha⁻¹ (Kassel, 2008).

The reviewed information indicates that there is insufficient and often conflicting information concerning reaction time of limestone for increasing soil pH and effects on crop yield for different sources and application rates. Therefore, the objectives of this study were to (1) evaluate the rate of soil pH increase from application of pure CaCO₃, calcitic limestone, and dolomitic limestone; and (2) evaluate the short-term crop response (2 years) to the application of these lime sources in four acidic Iowa soils.

MATERIALS AND METHODS

Four trials were established in four acidic Iowa soils in spring 2009 (Table 1). Treatments, replicated three times, were the factorial combinations of three lime sources and five application rates arranged in a completely randomized design. Plots were 4 m² separated by alleys of 40 cm to avoid contamination. The sources were pure (970 g kg⁻¹) finely ground CaCO₃, a calcitic limestone, and a limestone with 80.7 g kg⁻¹ Mg, which hereon will be referred to as dolomitic limestone. Table 2 summarizes characteristics of the lime sources used. Application rates were based on CCE: 0, 4.5, 9, 13.5, and 22.4 Mg ha⁻¹. The effective calcium carbonate equivalent (ECCE) as measured in Iowa (IDALS, 2008) was 54, 39, and 98 % for the calcitic limestone, dolomitic limestone, and CaCO₃, respectively. Therefore, application rates based on ECCE were 0, 4.39, 8.79, 13.18, and 21.97 Mg ha⁻¹ for the CaCO₃, 0, 2.42, 4.84, 7.26, and 12.11 Mg ha⁻¹ for the calcitic limestone, and 0, 1.75, 3.50, 5.25, and 8.74 Mg ha⁻¹ for the dolomitic limestone. We based application rates on CCE because there are no widely accepted standards across

states to consider particle size for limetone application. The lime sources were incorporated into the soil by disking to a 10-15 cm depth. The dominant soil series according to digitized, 1:12000-scale soil survey maps (Iowa Cooperative Soil Survey, 2001) were typical soils of Iowa and neighboring states (Table 1).

An initial per-plot soil sampling was performed before applying lime to 0- to 15-cm depth, and three soil samples per trial were randomly collected to 15- to 30-cm depth. Measurements of soil pH (1:1 soil-water ratio), and SMP buffer pH (Shoemaker et al., 1961) were performed. Soil organic matter was measured by a combustion method (Wang and Anderson, 1998), available P by the Bray-P₁ test (Frank et al., 1998), and extractable cations (K, Ca, Mg, and Na) with the ammonium-acetate method (Watson and Brown, 1998) with determination by inductively coupled plasma spectrometry. Soil-test results for the initial soil samples and other characteristics of the four trials are summarized in Table 1. After liming, soil samples were collected seven times during a period of 16 months to a 0- to 15-cm depth and analyzed for pH (Table 3). A 15- to 30-cm sampling was also taken and analyzed for pH at the SD 6 in order to study lime movement soil pH impact.

Soybean was planted in 2009 in all sites 3 to 4 weeks after lime application, and corn was planted in 2010. Management practices such as hybrids or varieties, plant population, row spacing, and weed and pest control were those recommended for each zone. The soils tested optimum or higher in P and K, but annual broadcast applications of these nutrients were made (as triple-superphosphate (0-46-0 N-P-K), and potassium chloride (0-0-52 N-P-K), respectively) to avoid any deficiency. To avoid N fertilizer effects on soil pH, the N source used for corn was KNO₃ fertilizer at a rate of 200 kg N ha⁻¹. Grain was hand-

harvested from the three central rows of each plot and grain yield was expressed to 155 and 130 g kg⁻¹ for corn and soybean, respectively.

The soil pH response to lime for each source at each site was described by fitting linear and exponential (with rise to a maximum) models using linear and nonlinear fitting procedures in SigmaPlot 11.0 (Systat Software Inc., 2008. 225 W. Washington St., Suite 425, Chicago, IL 60606). We chose the exponential model to describe the response only when the residual sums of squares were significantly smaller ($P < 0.1$) than for the linear model. Within each experiment, analyses of variance (ANOVA) for grain yield and subsoil pH were made using the GLM procedure of SAS assuming fixed treatment effects (SAS Inst., 2010). Yield and subsoil pH were compared by LSD when main effect of source or rate or their interaction were significant ($P \leq 0.1$).

RESULTS AND DISCUSSION

Soil pH Increase over Time

Precipitation at all sites was abundant enough for allowing the lime to appropriately react with the soil (Table 4). In agreement with average Iowa rainfall patterns, rainfall was generally more abundant in the spring, which should have facilitated a rapid lime reaction and early soil pH increase. The Northwest region of the Iowa is normally drier than the rest of the state and precipitation was indeed lower at the Northwest site.

The soil pH increase over time for the three lime sources was curvilinear with decreasing increments to a maximum that was reached approximately 100 days after liming (Figure 1). The equations, significance, and r^2 for each limestone rate, source, and experiment are presented in Table 5. The early pH increases and the maximum pH reached were greater for CaCO₃ than for either other limestone source. The maximum

pHs reached with the CaCO_3 (curve plateau) were 7.17, 7.14, 7.04, and 7.25 for the Southwest, Northeast, Northwest, and Central experiments, respectively.

Higher purity and smaller particle size of CaCO_3 with respect to both other limestones explain the earliest and faster pH increase with CaCO_3 (Barber, 1984; Havlin et al., 2005). The reaction rate (pH increase) and maximum pH attained were higher for the calcitic limestone than for the dolomitic source as suggested by Haby et al. (1978). Two factors would explain this result, first, the dolomitic limestone used had more materials coarse materials than the calcitic limestone (Table 2), and secondly, there is lower solubility and slower reaction in soil of MgCO_3 compared to CaCO_3 (Thomas and Hargrove, 1984; Stevens and Blanchar 1992). In a review of previous literature, Barber (1984) concluded that for an equal reaction time, dolomitic limestones need to average about half the diameter of calcitic limestones to result in a similar pH increase. In a recent study, Rippy et al. (2007) also showed a slower reaction rate of dolomitic limestone in relation to calcitic limestone. The fit of equations describing the pH change over time for each lime source generally were good (r^2 was between 0.65 to 0.99 across all rates, sources, and sites), but there was significant unexplained variation over time even for the control treatment that received no lime. We believe that in addition of an expected degree of experimental error (due to material application, sampling, or analysis), this variation reflects expected pH variation over time. In general, pH in soil samples collected during dry periods is lower compared with humid periods due to increased salt level or increased ionic strength of the soil solution (Schofield and Taylor, 1955). Rainfall removes this salt by leaching, and the measured pH increases (Puri and Asghar, 1938). However, we observed a significant but weak linear relationship between pH variation of the controls

plots over time and measured rainfall only at two of the sites (r^2 0.36 and 0.69), probably because of the low salt concentration of the soils in the study (which was not measured).

Soil pH Increase as Related to Lime Rate

Results of soil pH increase as a function of lime application rate for SD 3, which was the SD at which 95 to 100% of the maximum plateau pH was reached in all experiments, are presented in Figure 2. The relationship between soil pH increase and lime rate for the three sources was curvilinear with decreasing increments (Figure 2). A maximum, however, was only reached by the CaCO_3 at the Northeast and Central experiment (between pH 7 and 7.3), whereas pH kept slightly increasing for the other sources. Regardless of the application rate, CaCO_3 showed a higher neutralization capacity than the calcitic limestone, which was higher than for the dolomitic limestone. Because the application rates were based on similar amounts of CCE for the three lime sources, the results suggest that the coarser particle size of the limestones (especially the dolomitic limestone) explains a lower neutralizing capacity than for pure finely ground CaCO_3 .

The limestone application rate needed to maximize soil pH was lowest for pure CaCO_3 , intermediate for calcitic limestone, and highest for dolomitic limestone (Figure 2). The rate of pH increased per unit of CCE application rate between the initial soil pH and pH 6.5 was near linear for all lime sources. The only exception was the dolomitic limestone at the Northwest experiment, for which pH 6.5 was not reached even at the highest rate. Weaver et al. (2004) also found that a linear expression described well the relationship of pH vs. added base between pH 4.5 and 6.5 for some Coastal Plain soils of Georgia. Liu et al. (2004) found the same result for soils from a wider geographic area. Using equations from Figure 2 and assuming a target pH of 6.5, which is the pH

recommended in Iowa for corn and soybean (Sawyer et al., 2002), LR for the CaCO₃, calcitic, and dolomitic materials were 4.5, 10.3, and 17.7 for the Southwest; 2.5, 6.7, and 9.2 for the Northeast; 6.8, 13.4, and >20 for the Northwest; and 1.4, 4.9, and 9.8 Mg CCE ha⁻¹ for the Central experiment, respectively. These calculated LR were related to the maximum pH attained (Figure 2), being lower as maximum pH was higher (as occurred with the CaCO₃) and higher as maximum pH was lower (as observed with the dolomitic limestone).

Subsoil pH as Related to Lime Rate and Source

Significant lime source effects on subsurface pH (15-30 cm) were observed in the Southwest and Northeast sites, where the subsoil pH increases were largest for CaCO₃, intermediate for the calcitic limestone, and smallest for the dolomitic limestone (Table 6). There was no average rate effect at any site, although a rate by source interaction ($P < 0.1$) in the Southwest site, indicating that subsoil pH increased as the rate increased only for CaCO₃ (Table 6). Cumulative rainfall from the lime application date to the sampling date at which subsoil pH was measured should have been high enough (more than 750 mm) to allow the lime to move down through the soil (Table 4), so this factor would not explain the source differences at two fields. The better performance of the CaCO₃ at increasing subsoil pH in relation to the limestones at the Southwest and Northwest sites may be related to its finer particle size which may allow faster dissolution and migration through the soil in comparison with the limestones (especially the dolomitic one). We cannot find a reasonable explanation for the usual lack of a rate effect, with the only exception of one source at one site. Research in Kentucky by Blevins et al. (1978) suggested that surface application of lime without incorporation is an efficient way to

overcome soil acidity caused by N fertilization of no-till corn in moderately well-drained and well-drained silt loam soils with annual precipitation of 1150 mm. In that study, movement of lime was observed to a depth of 30 cm five years after liming, when limestone was applied at a rate of three times the LR (10 Mg ha^{-1}) and the depth of limestone movement was strongly correlated with the lime application rate. On the other hand, for South Dakota soils, Woodard and Bly (2010) determined small and inconsistent soil pH increases at the 15 to 30 cm depth even after four years of limestone application (without incorporation and incorporated to a 10 cm depth). In their study, very little liming materials (as carbonate or bicarbonate ion) migrated to these depths for either tillage treatment and they stated that rainfall less than normal during the period of the study may influence the extent to which the neutralization reactions of added limestone would progress to completion.

Crop Grain Yield

Limestone application increased soybean grain yield at the Southwest ($P < 0.06$), Northeast ($P < 0.04$), and Central ($P < 0.08$) sites; and corn grain yield at the Northeast ($P < 0.01$) and Central ($P < 0.05$) sites (Table 5). There was a significant lime source difference only for corn ($P < 0.04$) at the Northeast Site, where higher yields were obtained with the CaCO_3 and were followed by the calcitic limestone (Table 5). There was no source by rate interaction effect at any site. Maximum statistical significant response (yield for highest yielding treatment minus control yield) across rates and sources for the responsive sites were 0.57, 0.67, and 0.51 Mg ha^{-1} at the Southwest, Northeast, and Central sites, respectively for soybean; and 3.36 and 2.07 Mg ha^{-1} at the Northeast and Central sites, respectively for corn. Crop response to lime was expected at

all sites based on initial low soil pH values, which ranged from 5.39 to 5.71 in the top 15-cm depth. The initial surface pH of all experiments were below the optimum pH (pH 6.5) suggested for corn and soybean in non-high pH subsoil associations (as the ones in our study) by current Iowa State University recommendations (Sawyer et al., 2002) and other states of the Corn Belt (Bongiovanni and Lowenberg-DeBoer, 2000). In partial agreement with our results, Kassel et al. (2000) reported significant soybean response to lime application in acid soils (pH 5.6) of Northwest Iowa, but they did not observe yield response for corn. It should be noted that this study was conducted only in four sites but under well controlled conditions in terms of spatial variability of soil pH and crop yield (because of the small size of the plots). Studies at more sites are needed to make generalizations about crop response to lime according to soil pH.

CONCLUSIONS

Lime application produced variable pH increase rates and maximum values depending on the source. For all sources, rates, and experiments, pH reached a maximum value approximately 100 days after lime application that remained constant until the end of the 16-month evaluation period. The finely ground pure CaCO_3 produced the highest and earliest soil pH increase, followed by the calcitic limestone and last by the dolomitic limestone. Moreover, the dolomitic limestone reached a maximum plateau pH even for the highest application rate that was lower than for the other two sources, presumably due to a coarser particle size and higher Mg concentration. Although acid soils were selected for this study, significant corn or soybean yield increases were observed in three of the sites. There was a yield difference among lime sources only at the second year of one site, where corn yield was higher for CaCO_3 , intermediate for the calcitic limestone, and

lowest for the dolomitic limestone. Overall, results showed that the time of limestone reaction in the soil was faster than usually assumed for limestone with the composition and fineness sources used in the study and demonstrated that a coarse particle size limits the rate of pH increase but also the maximum pH increase achieved over time

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Table 1. Field locations and soil properties for four experiments.†

	Southwest	Northeast	Northwest	Central
Lime application date	2 Apr 2009	3 Apr 09	11 Apr 2009	17 Apr 2009
Soil classification	Fine-silty, mixed, mesic Typic Hapludolls	Fine-loamy, mixed, superactive, mesic Typic Hapludoll	Fine-silty, mixed, mesic Typic Hapludolls	Fine-loamy, mixed, superactive, mesic Typic Hapludolls
Soil series	Marshall	Kenyon	Galva	Clarion
pH	5.51 (5.20-6.00) ‡	5.39 (5.20-5.55)	5.51 (5.35-5.65)	5.71 (5.50-6.05)
SMP BpH§	6.50 (6.25-6.80)	6.67 (6.57-6.82)	6.32 (6.17-6.60)	6.59 (6.40-6.92)
Organic matter (g kg ⁻¹)	38.7 (35.2-43.8)	27.7 (2.50-30.3)	50.2 (47.6-52.5)	41.7 (37.7-51.3)
P (mg kg ⁻¹)	20 (15-34)	45 (29-62)	22 (15-32)	11 (7-19)
K (mg kg ⁻¹)	243 (176-389)	175 (140-207)	244 (225-271)	221 (122-375)
Ca (mg kg ⁻¹)	2013 (1720-2574)	1458 (1152-1746)	2345 (2140-2612)	3134 (1800-7005)
Mg (mg kg ⁻¹)	327 (288-397)	205 (169-243)	572 (517-631)	462 (334-669)
Na (mg kg ⁻¹)	19 (3-57)	23 (8-52)	36 (29-63)	28 (11-48)
Soil clay concentration (%)	27-35¶	18-26	34-39	18-24

† All soil measurements were performed at 0-15 cm depth

‡ Values between parenthesis indicate minimum and maximum

§ SMP BpH, Shoemaker-McLean-Pratt buffer pH.

¶ According to the Iowa Cooperative Soil Survey (2001).

Table 2. Characteristics of the lime materials used in four experiments.

Lime type	CCE†	Ca	Mg	Passing 4‡	Passing 8	Passing 60	ECCE§
	----- g kg ⁻¹ -----			----- % -----			
Calcitic	890	406	2.3	99	95	38	54
Dolomitic	690	203	80.7	96	74	42	39
CaCO ₃	990	274	3.8	100	100	99	98

† CCE, CaCO₃ equivalent.

‡ Passing 4, 8, and 60; percentage of the material passing through 4.75, 2.36, and 0.25-mm screens, respectively.

§ Effective CaCO₃ equivalent as defined in Iowa (IDALS, 2008).

Table 3. Soil sampling dates in the four experiments.

Sampling date	Location			
	Southwest	Northeast	Northwest	Central
Initial†	2-Apr-09	3-Apr-09	11-Apr-09	17-Apr-09
1	4-May-09	5-May-09	11-May-09	15-May-09
2	1-Jun-09	2-Jun-09	11-Jun-09	12-Jun-09
3	15-Jul-09	17-Jul-09	23-Jul-09	30-Jul-09
4	15-Sep-09	17-Sep-09	24-Sep-09	27-Sep-09
5	16-Nov-09	17-Nov-09	20-Nov-09	26-Nov-09
6	29-Mar-10	1-Apr-10	30-Mar-10	31-Mar-10
7	16-Sep-10	17-Sep-10	17-Sep-10	20-Sep-10

† Performed the day of lime application.

Table 4. Monthly rainfall occurring within twelve months after lime application for four experiments.

Location	Month											
	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
	mm											
Southwest	115	80	192	185	143	6	158	24	89	31	23	46
Northeast	100	223	77	99	53	51	201	14	70	23	31	34
Northwest	35	40	108	112	56	34	185	39	42	29	22	53
Central	116	102	104	70	123	24	186	34	50	28	19	55

Table 5. Coefficients, significance, and r^2 of equations in Figure 1 that described the relationships (exponential rise to maximum model) between soil pH and days after the lime application for five lime rates, three lime sources, and four experiments.

Site	Lime rate †	Lime source and equation coefficients and statistics														
		CaCO ₃					Calcitic					Dolomitic				
		y0	a	b	P	r ²	y0	a	b	P	r ²	y0	a	b	P	r ²
	Mg ha ⁻¹															
Southwest	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	4.5	5.48	1.03	0.02	<0.01	0.91	5.47	0.98	0.02	<0.01	0.96	5.41	0.60	0.02	<0.01	0.90
	9	5.58	1.36	0.06	<0.01	0.93	5.49	1.06	0.03	<0.01	0.91	5.56	0.62	0.04	<0.01	0.87
	13.5	5.57	1.40	0.12	<0.01	0.92	5.52	1.13	0.05	<0.01	0.91	5.58	0.67	0.05	0.03	0.77
	22.5	5.47	1.70	0.06	<0.01	0.95	5.63	1.21	0.03	0.04	0.74	5.48	1.10	0.03	<0.01	0.95
Northeast	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	4.5	5.43	1.11	0.10	<0.01	0.85	5.43	0.88	0.05	<0.01	0.91	5.42	0.72	0.03	<0.01	0.96
	9	5.40	1.55	0.08	<0.01	0.95	5.44	1.17	0.03	<0.01	0.90	5.32	0.89	0.04	<0.01	0.92
	13.5	5.36	1.68	0.10	<0.01	0.96	5.40	1.23	0.05	<0.01	0.96	5.44	0.98	0.04	<0.01	0.96
	22.5	5.33	1.80	0.21	<0.01	0.99	5.37	1.60	0.07	<0.01	0.96	5.39	1.07	0.07	<0.01	0.98
Northwest	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	4.5	5.50	0.93	0.08	0.01	0.83	5.54	0.47	0.03	<0.01	0.87	5.5	0.34	0.06	0.07	0.65
	9	5.54	1.16	0.06	<0.01	0.92	5.49	0.90	0.04	<0.01	0.91	5.5	0.59	0.06	<0.01	0.94
	13.5	5.55	1.24	0.09	<0.01	0.91	5.49	1.09	0.05	<0.01	0.91	5.48	0.74	0.06	<0.01	0.93
	22.5	5.50	1.54	0.12	<0.01	0.95	5.50	1.10	0.14	<0.01	0.90	5.51	0.91	0.04	<0.01	0.96
Central	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	4.5	5.77	1.05	0.06	<0.01	0.95	5.69	0.68	0.05	<0.01	0.89	5.6	0.65	0.03	<0.01	0.92
	9	5.70	1.32	0.06	<0.01	0.94	5.71	0.99	0.03	<0.01	0.98	5.76	0.69	0.16	0.01	0.84
	13.5	5.75	1.43	0.11	<0.01	0.98	5.64	1.21	0.05	<0.01	0.93	5.76	0.75	0.05	<0.01	0.94
	22.5	5.70	1.55	0.14	<0.01	0.96	5.68	1.25	0.09	<0.01	0.94	5.76	1.00	0.04	<0.01	0.98

† Lime rate, CaCO₃ equivalent ha⁻¹.

Table 6. Soil pH at the 15- to- 30-cm depth at the sixth sampling date† as a function of the rate and source of limestone applied in the four experiments.

Site	Rate§ Mg ha ⁻¹	Source‡		
		CaCO ₃	Calcitic	Dolomitic
		----- pH -----		
Southwest	0	5.79	5.50	5.49
	2	5.65	5.85	5.39
	4	6.50	5.52	5.60
	6	5.66	5.98	6.04
	10	6.16	6.02	5.54
	Mean	5.95a	5.77ab	5.61b
			----- pH -----	
Northeast	0	5.53	5.73	5.70
	2	6.28	5.71	5.73
	4	5.81	5.81	5.58
	6	5.92	5.73	5.58
	10	6.03	6.01	5.73
	Mean	5.91a	5.80ab	5.67b
			----- pH -----	
Northwest	0	5.63	5.51	5.58
	2	5.54	5.84	5.61
	4	5.69	5.67	5.55
	6	5.74	5.83	5.70
	10	5.55	5.69	5.58
	Mean	5.63	5.71	5.60
			----- pH -----	
Central	0	5.93	5.93	5.87
	2	5.90	5.75	5.93
	4	5.85	5.89	5.93
	6	6.09	5.78	6.16
	10	5.92	5.89	6.08
	Mean	5.94	5.85	5.99

† Dates were 29-Mar-10, 1-Apr-10, 30-Apr-10, and 31-Mar-10 for the Southwest, Northeast, Northwest, and Central sites, respectively.

‡ Within a site, different letters indicate significant average pH differences due to source (LSD, $P \leq 0.1$).

§ Rate was not significant and there was source x rate interaction in the Southwest Site.

Table 7. Grain yield for soybean and corn as a function of the rate and source of limestone applied in four experiments.

Site	Rate†	Crop/Source‡							
		Soybean				Corn			
		CaCO ₃	Calcitic	Dolomitic	Means	CaCO ₃	Calcitic	Dolomitic	Means
----- Mg ha ⁻¹ -----				----- Mg ha ⁻¹ -----					
Southwest	0	4.46	4.19	4.05	4.23b	14.47	13.22	14.35	14.01
	2	4.33	4.60	4.55	4.49ab	13.24	14.07	13.15	13.49
	4	4.23	4.61	4.48	4.44ab	13.71	14.46	14.23	14.13
	6	4.26	4.72	4.60	4.53ab	14.41	14.29	13.85	14.18
	10	4.55	4.81	4.63	4.66a	14.27	14.41	14.44	14.37
Northeast	0	3.65	3.67	3.72	3.68b	10.00	9.24	9.52	9.59b
	2	3.88	3.94	3.93	3.92ab	11.19	10.10	10.07	10.45b
	4	4.07	3.89	3.98	3.98a	12.26	11.32	11.41	11.66a
	6	4.33	4.11	3.79	4.08a	12.94	12.44	10.30	11.89a
	10	4.34	3.62	4.19	4.05a	12.51	11.44	11.71	11.89a
Northwest	0	4.03	4.12	3.95	4.03	13.73	13.51	13.38	13.54
	2	4.31	4.14	4.10	4.18	13.49	11.98	12.96	12.81
	4	4.14	4.03	4.09	4.09	14.30	13.75	13.84	13.96
	6	4.00	4.03	4.09	4.04	11.91	12.49	13.31	12.57
	10	4.10	4.11	4.05	4.09	13.14	13.79	14.27	13.73
Central	0	3.01	3.16	2.9	3.02b	10.72	10.24	10.25	10.40b
	2	2.90	3.35	3.53	3.26ab	11.11	11.56	11.39	11.35ab
	4	3.45	3.47	3.24	3.39a	11.60	12.31	12.48	12.13a
	6	3.45	3.42	3.22	3.363a	12.41	12.05	11.75	12.07a
	10	3.50	3.37	3.23	3.37a	11.50	12.31	12.06	11.96a

† Within site and crop, different letters indicate significant average yield differences due to rate (LSD, $P \leq 0.05$).

‡ Source was only significant for corn in the Northeast site and there was no source x rate interaction.

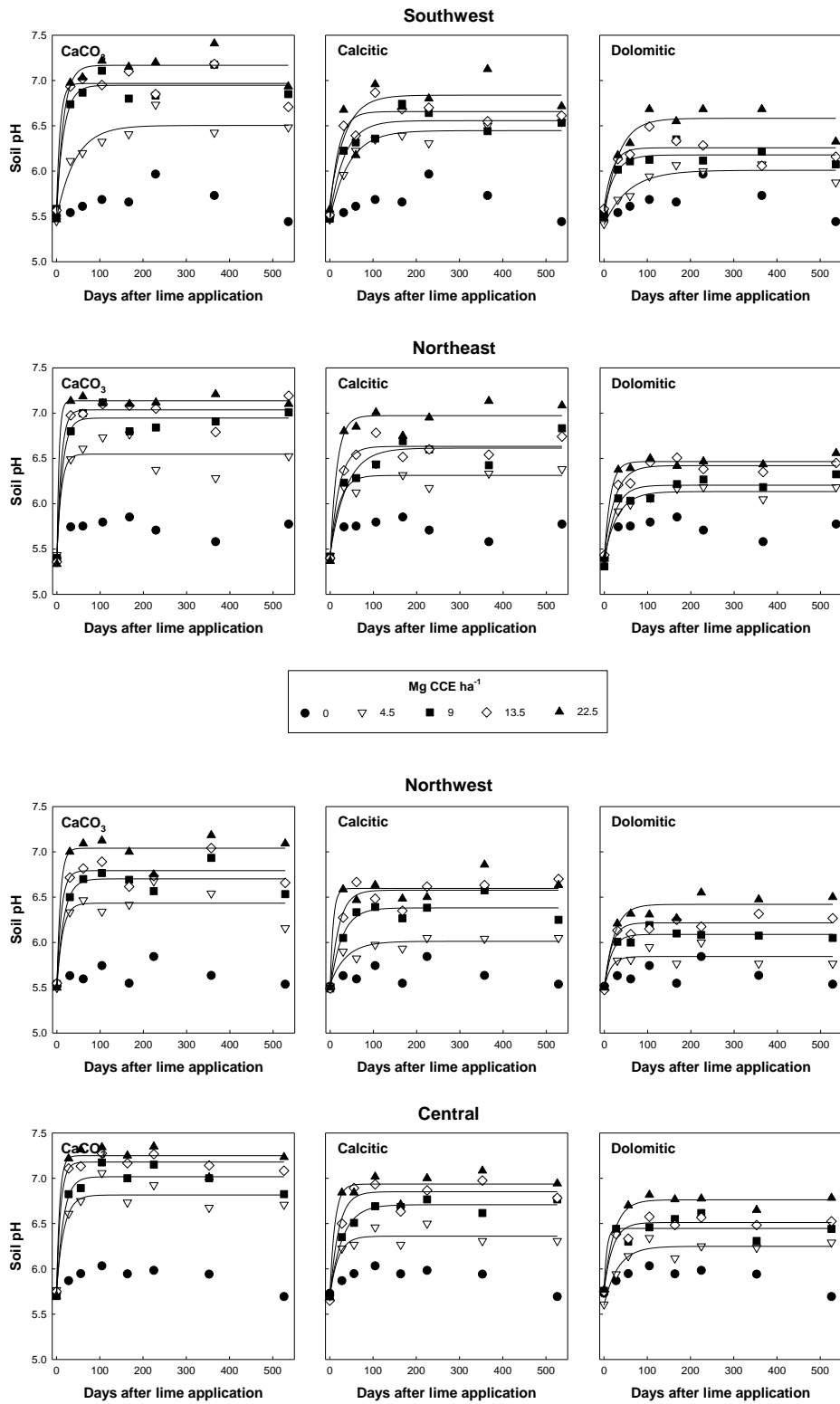


Figure 1. Soil pH as a function of time for different rates and sources of lime for four experiments.

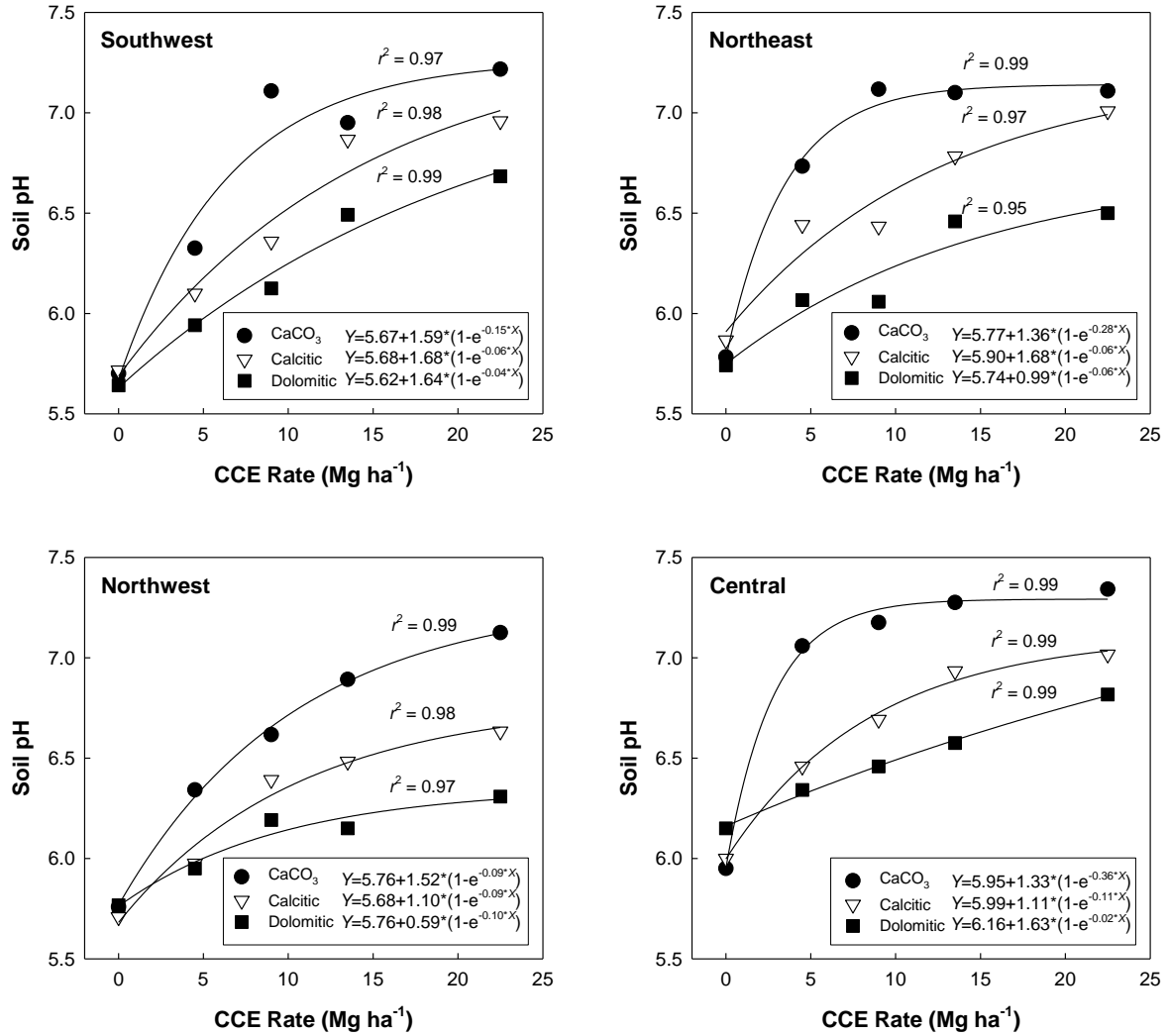


Figure 2. Soil pH as a function of calcium carbonate equivalent (CCE) application rate for different lime sources at the third sampling date (100 days after liming) for four experiments. All relationships were significant ($P \leq 0.01$).

CHAPTER 5. GENERAL CONCLUSIONS

The overall goal of this research was to gain knowledge to improve pH and lime application management for corn and soybean. Specific objectives were to compare methods to determine lime requirements for crops, study the within-field variation of soil pH and other soil properties in combination with crop response to lime, and determine/confirm optimum pH for corn and soybean in Iowa soils. Also, intensively study soil pH over time for different sources of lime and short term crop response to lime. Two sets of distinct experiments were conducted to achieve these general objectives. One set involved on-farm strip-trials (Chapter 2 and 3) that were established in 14 fields from 2007 until 2009 to evaluate the effects of two rates of limestone (zero and 6.72 Mg ha^{-1} of effective calcium carbonate equivalent) on soil pH and crop yield. These trials were evaluated from two to four years using precision agriculture technologies. The other set of experiments involved conventional small-plot trials (Chapter 4) established in 2009 to evaluate the effect of three lime sources and various application rates on soil pH change over time and crop yield, which were evaluated for two years. The experiments encompassed typical Iowa corn-soybean production fields and several important soil series.

Results from the strip-trials suggested that site-specific lime management is necessary for most Iowa soils due to large within-field variability of soil pH and other soil properties that affect the measurement of soil reserve acidity and both, the soil pH and crop response to lime application. The observed within-field variation in pH and buffer pH (which can be assessed by sampling methods used in production agriculture) showed that in most experimental areas (2.5 to 6.4 ha) the amount of lime to be applied would range from none to $8\text{-}10 \text{ Mg ha}^{-1}$ of calcium carbonate equivalent. Undoubtedly, at least this range would be found in commonly

larger production fields. Results also showed that the Shoemaker-McLean-Pratt (SMP), Sikora, and Mehlich buffer pH methods to estimate reserve acidity and lime requirement were highly correlated and would be similarly effective at estimating lime requirement for soils similar to those used in the study. Because the SMP and Sikora buffer pH values were statistically the same for most soils, current calibrations and lime requirement equations for the SMP method can also be used for the Sikora method. An advantage of the Sikora buffer method over the SMP method is, however, that it does not include hazardous chemicals. Use of the Mehlich buffer requires a different calibration concerning interpretation of results for lime recommendations. The relationship between the buffer pH methods and a routine method to determine titratable acidity that is used in many other countries was high in general, but strongly related to soil organic matter concentration, being better as organic matter increased. Initial soil pH was by far the variable best correlated with pH change due to lime application. Multiple regressions including pH and other variables performed significantly better than pH alone. Limestone application significantly increased soil pH in all sites, and maximum pH values were generally reached during the second year after liming. Corn and soybean showed similar yield response to lime application, which is in contrast with the common belief that soybean needs a higher pH but in agreement with current recommendations in Iowa. The results showed that the optimum pH range for corn and soybean was 6.0-6.5 for soils with low-pH subsoil, but was significantly lower (5.0 to 5.5) for soils having high pH subsoil according to measured subsoil pH values. Current recommendations suggest a lower optimum pH for both crops in soils that have high-pH subsoil (6.0), but the results indicate that this pH can be even lower.

Results from the small plots study suggested that lime application produced variable pH increase rates and maximum values that depended on the lime source. For all sources, rates, and experiments, pH reached a maximum value approximately 100 days after lime application that remained constant until the end of the 16-month evaluation period. Finely ground pure CaCO_3 produced the highest and earliest soil pH increase, followed by calcitic limestone, and last by dolomitic limestone. Moreover, the dolomitic limestone reached a maximum plateau pH even for the highest application rate that was lower than for the other two sources, presumably due to a coarser particle size and higher Mg carbonate concentration. Although acid soils were selected for this study, significant corn or soybean yield increases were observed in three of the four sites. Results showed that the time of limestone reaction in the soil was faster than usually assumed for limestone with the composition and fineness sources used in the study, and demonstrated that a coarse particle size limits the rate of pH increase but also the maximum pH increase achieved over time.

Overall, the results from this study advanced scientific knowledge concerning spatial variation of soil properties that influence lime requirement and crop response to lime, determined more accurate optimal pH for corn and soybean production, and provided estimates of the time needed to increase pH of Iowa acid soils to desired targets using several lime sources. In addition, the results will provide crop producers with improved criteria for site-specific lime management and better knowledge about lime reaction rate in Iowa soils.

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