

AN ABSTRACT OF THE THESIS OF

Carl A. Makepeace for the degree of Master of Science in Soil Science presented on October 28, 2021

Title: Estimating Lime Requirement for Oregon Soils with Non-Hazardous Soil Test Methods

Abstract approved: _____
Amber D. Moore

Various soil tests are routinely used in the United States to predict soil lime requirement. New non-hazardous methods have recently been proposed for adoption in Oregon, however the accuracy of these methods for Oregon soils has not been established. The objectives of this investigation were: (a) to document and describe the development of lime requirement estimate (LRE) soil tests from 1900 to 2020, (b) to evaluate the accuracy of five non-hazardous LRE methods for Oregon soils, and (c) to evaluate how laboratory modifications to the Sikora LRE method affect the accuracy of lime rate recommendations.

Four historical periods pertaining to the development of LRE methods were identified. From the 1900s to the 1930s, many wet-chemistry methods were proposed but were not adopted by commercial labs due to lack of method accuracy and to the amount of labor required. From the 1930s to the 1970s, the availability of the pH-sensitive glass electrode led to the development of fast and accurate buffer pH methods that are the foundation for methods that are still used today. From the 2000s to 2020, researchers proposed non-hazardous adaptations of buffer methods as

well as the use of other soil test properties. Current research is focused on developing regional calibrations of non-hazardous methods.

Twenty-four Oregon soils were incubated with lime ($0 - 22.4 \text{ Mg ha}^{-1}$) to determine their incubation lime requirement. Candidate LRE methods were correlated to incubation lime requirement to evaluate their accuracy. The Sikora ($r^2 = .90 - .92$), Modified Mehlich ($r^2 = .87 - .89$), and Sikora-2 ($r^2 = .81 - .93$) buffer methods showed potential as non-hazardous alternatives to SMP ($r^2 = .90 - .92$) based on accuracy and precision. Combining clay concentration, KCl-extractable Al, soil organic matter (SOM), extractable Mg, and $\text{pH}_{1.2}$ also effectively predicted LRE with $r^2 = .96 - .97$. The Moore-Sikora buffer method ($r^2 = .89 - .93$) was similarly accurate but showed precision issues due to high replication variability. The Single Addition of $\text{Ca}(\text{OH})_2$ method ($r^2 = .69 - .77$) was not considered to be an accurate predictor of lime requirement for Oregon soils.

Five modifications to the Sikora buffer pH method were evaluated for five Oregon soils. Modifications related to mixing method, measurement in supernatant instead of slurry, and soil:water:buffer ratio were found to significantly increase the Sikora buffer pH value by 0.063, 0.065, and 0.058 units respectively in comparison to the control. Mean Sikora buffer pH decreased by 0.02 – 0.05 units when equilibration time was increased from 0 to 180 min.

The results of these investigations demonstrate the feasibility of adopting at least one non-hazardous method for predicting lime requirement of Oregon soils. They also demonstrate the importance of accounting for method modifications and inter-laboratory variation for the Sikora LRE method. These results are anticipated to be used to help make accurate lime rate recommendations in Oregon.

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Estimating Lime Requirement for Oregon Soils with Non-Hazardous Soil Test Methods

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Carl A. Makepeace

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APPROVED:

Major Professor, Representing Crop and Soil Science

Head of the Department of Crop and Soil Science

Dean of the Graduate School

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**CHAPTER 1: A HISTORICAL REVIEW OF LIME REQUIREMENT ESTIMATION
METHODS**

ABSTRACT

Lime requirement estimation (LRE) methods are essential agronomic soil tests that have undergone considerable development between 1900 and 2020. Four distinct periods of development were identified and examined: (1) Early LRE Testing (1900s-1930s), (2) Buffer pH Method Development (1930s-1970s), (3) Buffer pH Method Improvements (1970s – 1980s), and (4) Non-hazardous Buffer Adaptations, and Alternatives to Buffer Methods (2000s-2020). From the 1930s to 1940s, several titration methods were proposed. The buffer pH methods developed from the 1930s to 1970s were more accurate and more convenient than previous methods. In the 1970s, researchers proposed some adaptations to buffer pH methods such as field calibration and double-buffer methodologies. In 1976, the Resource Conservation and Recovery Act (RCRA) regulated chemical components used in several common buffer pH methods. Most efforts from the 2000s to 2020 focused on replacing the use of regulated hazardous chemicals. Other recent studies have sought to estimate soil lime requirement using soil properties. Current efforts in the field of lime requirement estimation are focused on increasing implementation of non-hazardous methods, as well as the exploration of LRE modeling based on soil properties.

INTRODUCTION

Soil acidity is an important aspect of soil fertility. Excessive soil acidity is associated with multiple phenomena that harm crop growth, including Al and Mn toxicity, reduced availability of nutrients such as P, and reduced supply of N from organic matter decomposition. Soils may become excessively acidic through a combination of different mechanisms, including nitrification of ammonium-based N fertilizers, breakdown of organic matter, and the leaching effect of acidic rainwater. Soil acidity is typically evaluated by measuring pH in an established ratio of soil to distilled water. pH is defined as the negative logarithm of the concentration of H^+

ions. In the context of soil fertility, soil pH is used to indicate the likelihood of crop damage from acidity (Havlin et al., 2014).

Soil acidity can be neutralized by applying crushed limestone (or ‘lime’) to the soil. Agricultural lime products are typically composed of CaCO_3 , which reacts with H^+ ions in the soil, thereby increasing the pH and reducing soil acidity. Lime requirement (LR) is defined as the amount of CaCO_3 needed to raise soil pH to a level adequate for crop growth. Lime requirement is directly related to the amount of acidity in soil, which exists in two primary forms: active and exchangeable acidity. Active acidity is the acidity dissolved in solution and is evaluated by measuring soil pH. Exchangeable acidity is the acidity that is adsorbed to negatively charged soil colloids. Active and exchangeable acidity exist in equilibrium with each other, therefore both must be neutralized in order to raise soil pH. Soils vary in the amount of negatively charged soil colloids that they contain (namely clays and organic matter), so they also vary significantly in their capacity for exchangeable acidity. Soils high in exchangeable acidity, such as soils rich in clay and organic matter, typically require more lime to increase in pH compared to soils low in clay and organic matter (Brady & Weil, 2008). As an example, two soils may have the same soil pH (active acidity), but because of differences in composition, they will require different amounts of lime to reach a target pH.

Soil methods have been developed to provide lime requirement estimates (LREs) to account for differences in exchangeable soil acidity. The purpose of these methods is to accurately estimate the amount of acidity in a soil sample quickly and affordably enough to allow for high throughput testing, a necessity in the agriculture industry. The majority of LRE methods used currently in the United States were developed between 1948 and 1976. Although modern practices are predominantly based on developments from this time period, LRE methodology has

seen numerous relevant developments from 1900 through 2020. As the work to develop new methods continues, it is important to consider the most recent advances, as well as the full history of LRE testing development.

The purpose of this paper is to help guide the next steps in LRE testing innovation by exploring the scientific and technological paradigms that guided the development of methods from their origins in the 1900s to 2020. We have identified four distinct historical periods of LRE method development in the United States:

- (1) **Early LRE testing** (1900s-1930s), a period characterized by the use of wet chemistry techniques to quantify the short-term reaction of soil with alkaline materials.
- (2) **Buffer pH method development** (1930s-1970s), a period during which calibrated buffer solutions were developed that estimated exchangeable acidity and lime requirement through the use of a pH-sensitive glass electrode.
- (3) **Buffer pH method improvements** (1970s – 1980s), a period in which researchers proposed refinements to existing buffer methods in order to improve accuracy.
- (4) **Non-hazardous buffer adaptations, and alternatives to buffer methods** (2000s-2020), a period in which researchers proposed non-hazardous adaptations of buffer methods as well as the use of other soil test properties.

EARLY LRE TESTING: 1900s – 1930s

Lime and other alkaline materials have been used as soil amendments for centuries (Dickson, 1788). By the early 1900s, it was commonly known that agricultural fields could suffer from a condition known as ‘sour soil’, where poor crop yields could be improved by adding lime, but

could not be improved by adding traditional macronutrient fertilizers (Agee, 1919; Veitch, 1906). At this time, agronomists were aware of the acid-base chemistry underlying this phenomenon: that 'sour soil' is really an acidic soil and that this acidity can be neutralized by reacting it with lime. In the context of soil fertility, soil acidity was not conceptualized in terms of pH; the logarithmic pH scale was only introduced in 1909, and a convenient method for measuring pH was not widely available until the 1930s (Belyustin, 2011). Instead, soil acidity was first conceptualized directly in reference to literal lime requirement, and acid soils were treated as containing a discrete, measurable quantity of acidity. Based on this understanding, the LRE methods developed before the 1930s generally consisted of lab-scale proxies for lime application. In these methods, soil is combined with an alkaline material and various approaches are used to measure the degree of reaction.

The first of these methods was the Veitch method, which was developed to estimate lime requirement through the titration of a soil slurry using $\text{Ca}(\text{OH})_2$ as a base and phenolphthalein as an acidity indicator (Veitch, 1902). In the Veitch method, soil, water, and $\text{Ca}(\text{OH})_2$ solution are mixed, after which the slurry is dried and rehydrated to maximize reaction of acidic soil with alkaline $\text{Ca}(\text{OH})_2$. Then, phenolphthalein is added to determine if the amount of base added is sufficient to give a pink reaction, which would indicate if sufficient base has been added to neutralize soil acidity. The entire process is repeated on four to six soil samples using varying levels of $\text{Ca}(\text{OH})_2$ to narrow down the minimum amount needed to produce the pink phenolphthalein reaction.

The Veitch method was a lengthy procedure, requiring at least two days to make one LRE determination. In contrast, Hopkins proposed a quicker method, requiring only one iteration and a shorter equilibration time period (Hopkins et al., 1903). The Hopkins method is based on the

observation that mixing soil with a salt solution produced more acidity than it does when mixed with deionized water. Hopkins correctly inferred that this excess acidity (now referred to as exchangeable acidity) was a significant portion of the soil acidity that needed to be neutralized. By taking exchangeable acidity into account, the Hopkins method may also have been more accurate than the Veitch method, in addition to being faster. In the Hopkins method, soil is first mixed with a 5% NaCl solution. The supernatant is decanted and titrated with a 'strong base' (possibly NaOH) and phenolphthalein to determine the soil's titratable acidity. This measurement is multiplied by a factor of three, to correct for incomplete extraction of the method as determined by Hopkins. This measurement of acidity is then converted to lime requirement on an equivalent basis.

Rather than using titration, the Süchting method estimated lime requirement through the use of a sealed glassware apparatus that is able to quantify the production of CO₂ gas (Lipman, 1910). Since CO₂ is produced by the reaction between acidity and CaCO₃, the Süchting method estimates soil acidity by reacting acid soil with CaCO₃ in the apparatus. As with the Veitch and Hopkins methods, this measurement of acidity is converted directly to lime requirement on an equivalent basis. The Süchting glassware apparatus is significantly more complex than the equipment required by the Veitch and Hopkins method, and includes several parts: a chamber for producing H₂ carrier gas, a chamber for reacting soil with CaCO₃, and a chamber filled with NaOH solution for capturing CO₂.

In contrast to previous methods, the Truog method was an attempt to make lime requirement estimation more convenient, at some cost to accuracy and to the ability to provide quantitative results. The Truog method was developed to estimate lime requirement by observing the degree of color change resulting from a reaction between soil and ZnS (Truog, 1914). In the Truog

method, soil, CaCl_2 , and ZnS are mixed in water, and this mixture is boiled. According to Truog, this process causes exchangeable soil acidity to be liberated in the form of H_2S gas. The H_2S is then estimated by observing the darkening of a lead acetate-impregnated paper that has been placed over the boiling beaker. Darker color on the paper indicates a larger amount of soil acidity and therefore a greater need for lime. Compared to previous methods, the Truog method strikes a different balance in the tradeoff between accuracy and convenience. While much faster and easier than contemporary methods, the Truog method provides a qualitative estimation of lime requirement rather than quantitative. Furthermore, the use of lead posed a significant health risk, a risk that was already well documented at this time (Riva et al., 2012).

In an attempt to make use of more advanced technology, Knight published a dissertation evaluating the feasibility of estimating lime requirement using an H^+ -sensitive platinum electrode (Knight, 1917). Knight's investigations focused on an apparatus in which a platinum plate is immersed in a soil slurry. The voltage between this plate and a reference mercury electrode was measured to estimate H^+ concentration in the soil slurry. In the end, Knight was not able to get consistent results from any approach. He therefore determined that use of the platinum electrode was too delicate and time-consuming to be useful as an LRE method. While Knight found the platinum electrode to be ineffective in 1917, its successor, the glass electrode would become a vital tool for soil acidity testing in the 1940s with the advent of buffer pH methods (Woodruff, 1948).

Legacy of the 1900s – 1930s

The efforts to develop LRE tests from the 1900s to the 1930s were an important first step, in that they were the first attempts to use scientific methods to estimate lime requirement. It was this foundation that allowed researchers from the 1940s to 1970s to develop approaches that are

still relevant today. There is little record of the methods from before the 1940s being widely adopted. This is likely due to two factors: 1) these methods were either time consuming or non-quantitative, and 2) these methods were all uncalibrated to actual lime requirement. All of these methods operated on the assumption that the amount of acidity measured in the laboratory can be directly converted to lime requirement. This is problematic because these methods are based on laboratory reactions that are different from the actual reaction of lime in the field. In particular, these methods involve reactions that last less than a day, while the reaction of lime in the field takes place over many months. Furthermore, the reaction of lime in the field takes place under different biological, physical, and chemical conditions than in the lab. While the acidity estimated by these methods may be correlated to actual lime requirement, they are unlikely to be equal to actual lime requirement on a 1:1 basis. Methods after 1940 recognized that laboratory measurements of soil acidity are imperfectly related to lime requirement and that for a method to be useful, it must be correlated and validated to real-world experimental data.

BUFFER PH METHODS 1930s – 1970s:

There were three key innovations that enabled researchers from the 1930s to the 1970s to improve on previous efforts: (1) the pH-sensitive glass electrode; (2) buffer solutions with linear pH response; and (3) calibration studies linking method results to real-world lime application. In this section, we will explain how these three innovations came together to allow for the development of buffer pH LRE methods that are still used by soil testing laboratories today.

The glass electrode

The pH-sensitive glass electrode became widely available in the 1930s (Belyustin, 2011). Whereas previous LRE methods relied on titration with phenolphthalein as an indicator, the pH

electrode allowed rapid, direct measurement of pH in solutions. This was useful not just for measuring active acidity in a mixture of soil and water, but also as a way to estimate exchangeable acidity through the pH measurement of soil-buffer mixtures. As is explained below, the convenience and accuracy offered by buffer solutions were made possible by the capability of the pH electrode to quickly evaluate pH in a solution.

Buffer solutions

In the 1930s and 1940s, scientists began experimenting with buffer solutions as a way to quickly and accurately estimate lime requirement. Buffer solutions developed for lime requirement testing are formulated to have a linear pH response to added acidity. When a soil sample is mixed with such a buffer, along with an exchange cation, the resulting depression in pH is proportional to the amount of exchange acidity present in the sample. Figure 1.1 illustrates how the Woodruff buffer pH method uses a linear buffer pH response to estimate lime requirement. As an example, a depression in pH from 7.0 to 6.6 indicates that $4 \text{ cmol}_c \text{ H}^+ \text{ L}^{-1}$ have been added to the Woodruff buffer. Other buffer methods differ in their starting pH and the slope of their pH response.

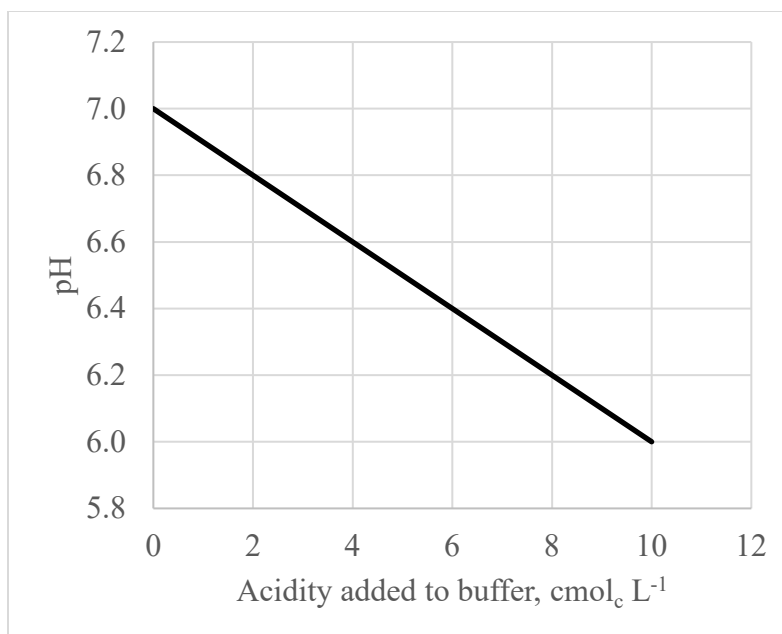


Figure 1.1. Theoretical pH response of the Woodruff buffer to added acidity. Adapted from Woodruff, 1948.

Paired with a pH electrode, the use of buffers allowed lime requirement to be estimated much more quickly than previous methods. In buffer pH methods, soil is mixed with buffer, left to equilibrate for a brief period, and then the pH of the mixture is measured.

Calibration of buffer pH methods to lime requirement

Methods from before the 1930s calculated lime requirement based on the assumption that the amount of acidity measured in the laboratory was the same as the amount of acidity needing to be neutralized in the field. This assumption was problematic because laboratory estimates of exchangeable acidity are not generally equal to lime requirement. As an example, with the Shoemaker, McLean and Pratt method, a soil-buffer pH measurement of 6.0 indicates 4.4 cmol_c of acidity per kg of soil, which, if converted on an equivalent basis, corresponds to 2.2 tons of limestone per acre (Shoemaker et al., 1961). However, in a laboratory incubation trial, Shoemaker et al. showed that a soil with a buffer pH of 6.0 needs on average 5.4 tons per acre to

reach a soil pH of 6.8. Therefore, a calibration adjustment was used to connect buffer pH to actual lime requirement data. Since the 1940s, researchers have used calibration studies to ensure that lime requirement estimations are accurate to real-world data.

The Brown method

The Brown method may be the first method to estimate exchangeable acidity by directly measuring the pH of a soil-buffer mixture (Brown, 1943). The buffer used in the Brown method consisted of 1 M NH_4OAc . While the Brown method did not see widespread adoption, it served as a foundation for later buffer pH methods, which improved on the accuracy of this labor-saving innovation.

The key advantage of the Brown method over previously developed LRE methods is speed and convenience. By measuring pH directly in a soil-buffer mixture instead of conducting a titration step, the labor and cost associated with previous methods can be avoided. However, like previous methods, the Brown method was not calibrated against actual lime response. Another limitation is the method's sensitivity to soil acidity. For the Brown method, small changes in buffer pH correspond to large changes in estimated lime requirement, primarily due to the fact that the buffer used in this method is comprised only of NH_4OAc . Small errors in pH measurement can therefore have a large effect on lime requirement recommendations. Later methods used multiple buffer components in order to improve sensitivity and accuracy. These advances, along with the implementation of calibration, allowed the buffer methods that followed to see continued widespread use up to the present.

The Woodruff method

In 1948, Woodruff published a buffer pH method designed to have improved accuracy and sensitivity relative to the Brown method from 1943 (Woodruff, 1948). In practice the Woodruff method is similar to the buffer method proposed by Brown (1943), where soil is thoroughly mixed with a buffer solution and pH is directly measured. Like previous methods, the result of the Woodruff method is converted directly to lime requirement without a calibration adjustment.

The Woodruff method improved on the approach of Brown (1943) in two ways. First, Woodruff incorporated two components into the buffer: para-nitrophenol and acetate. This formulation gave the buffer a wider range and reduced sensitivity to pH measurement error. Secondly, Woodruff used a field trial to validate the accuracy of the method. The field trial consisted of a single site in Missouri which was limed at varying rates. Although this study was limited in scale, it represented the beginning of more rigorous studies used by later methods to connect lime requirement estimation to actual lime requirement.

The Shoemaker, McLean, and Pratt method

The Shoemaker, McLean, and Pratt (SMP) method was designed to improve upon buffer pH techniques developed by Brown (1943) and Woodruff (1948). The specific goal for the SMP method was to develop a buffer formulation with characteristics that allow for greater accuracy, especially on soils with “appreciable” aluminum (Shoemaker et al., 1961). The SMP buffer method is executed similarly to other buffer methods, where pH is measured in a soil-buffer mixture. The SMP method differs from previous buffer methods in a three key ways: its buffering characteristics, its robust calibration, and its use of multiple pH targets.

The SMP method uses four buffer components. These are K_2CrO_4 , para-nitrophenol, triethanolamine, and acetate. The use of these four components gives the SMP buffer a wider pH range than the Woodruff or Brown methods. This allows the method to make finer measurements of acidity that are more resistant to measurement errors than the Woodruff buffer (Shoemaker et al., 1961; Woodruff, 1948).

The SMP method was correlated to the results of a lime incubation trial consisting of 14 Ohio soils, as well as a $Ca(OH)_2$ titration of 101 soils submitted to the Ohio State University testing laboratory (Shoemaker et al., 1961). Buffer pH from the SMP method was regressed with lime requirement from both studies, producing r^2 values of .94 and .86 respectively. These regressions were used to create a model for predicting actual lime requirement directly from buffer pH. This model was encoded into an interpretation table that converts buffer pH to a LRE, which was published with the method (Shoemaker et al., 1961).

It should be noted that the calibration to lime response was performed for three pH targets, 6.0, 6.4, and 6.8. While the Woodruff buffer only indicates lime requirement necessary to reach soil pH 7.0, the authors of the SMP method recognized that one pH target may not be appropriate or economical for a variety of farming situations. This is reflected in the interpretation table, which gives different lime requirement recommendations depending on the target pH.

The SMP method offers various advantages over previous methods, including flexibility of pH targets, and calibration against extensive actual lime requirement data. These features likely explain why the SMP method became widely adopted across many regions of the US, and is still in common use today (NAPT, 2020).

The Adams-Evans method

During the same time period that Shoemaker, McLean, and Pratt were developing a method for estimating lime requirement for the high-aluminum, high lime requirement soils of Ohio, researchers Adams & Evans were developing a method tailored to the characteristics of Alabama soils. The objective of the Adams-Evans method was to create a buffer capable of detecting small differences in lime requirement on Alabama soils with relatively low buffering capacity (Adams & Evans, 1962). The Adams-Evans method has some similarities to the SMP method: it was calibrated using multiple soils and its calibration is presented in a buffer pH interpretation table. The Adams-Evans method also introduced the use of a model that combines soil pH with buffer pH for making LRE recommendations.

Adams & Evans cite the Brown (1943) and Woodruff (1948) methods as being unsuitable for Alabama soils. For these two methods, a change in buffer pH of 0.1 units—commonly the smallest difference that can be consistently measured by a pH electrode—corresponds to approximately 1.1 and 0.5 ton acre⁻¹ respectively. In Alabama, soils with low levels of 2:1 clay and organic matter require small amounts of lime to increase pH, and over-application of lime may cause pH to rise to a level that is damaging to crops. Therefore Adams & Evans designed a buffer pH method that estimated lime requirement in finer gradations of 0.1 to 0.5 ton acre⁻¹ (depending on soil pH). This focus on differentiating fine differences in lime requirement allowed Alabama farmers to apply more economical rates of lime. This feature also lessened the risk of crop damage through over-application of lime. A disadvantage of this approach is that the Adams-Evans method is only able to estimate a maximum lime requirement of 4.5 ton acre⁻¹, while the Brown (1943) and Woodruff (1948) methods can measure a higher range, up to 9 and 10 ton acre⁻¹ respectively.

The Adams-Evans method was calibrated with a laboratory lime incubation of three soils, as well as a study that estimated the acidity of 348 soils using an ammonium acetate extraction method. This calibration was not based on a simple regression between buffer pH and experimental acidity, but rather constructed a linear regression that uses buffer pH and soil pH (in 1:1 water) to predict lime requirement. As an example, for a buffer pH of 7.4, recommended total lime application can range from 0.5 to 2.5 ton acre⁻¹, depending on soil pH. As with the SMP method, LRE determination based on Adams-Evans buffer pH and soil pH is encoded in a table that was published with the method (Adams & Evans, 1962).

The Adams-Evans method is the successful combination of several features: estimation of small differences in lime requirement, rapid buffer pH measurement, and calibration to actual lime requirement. Similar to the SMP method, these characteristics likely explain the adoption of the Adams-Evans method for estimating low pH-buffering soils throughout the southeastern United States (J. T. Sims, 1996a).

The Mehlich buffer pH method

While previous methods were calibrated based on the amount lime needed to reach a target pH, Mehlich sought to develop a buffer pH method that was calibrated to the amount of lime that maximized crop production (Mehlich, 1976). The Mehlich method also used separate calibrations for mineral and organic soils.

To calibrate the Mehlich method, a greenhouse lime trial was conducted. In this trial, the optimum amount of lime was the rate that corresponded to the highest yield, and the optimum rate for each soil was used to calibrate the Mehlich method. The trial was split by soil type: 6 organic soils (> 39% organic matter), which were planted with soybeans, and 4 ultisols planted

with barley. The soils in this study originated from North Carolina, which is also where the trial was conducted. The results of these trials were used to create separate organic and mineral soil calibrations for converting Mehlich buffer pH to a LRE.

A drawback of this approach is the difficulty of developing a comprehensive calibration. Different plants have varying levels of sensitivity to acidity (Havlin et al., 2014). Only barley and soybeans were used for this calibration, limiting its applicability for other plants in other regions. Furthermore, the lack of a full factorial combination between crop and soil type makes the calibration applicable only to the crop-soil type combinations tested. However, these limitations have not prevented successful implementation of the Mehlich method outside of North Carolina in states such as West Virginia and Virginia (Savoy, 2007; J. T. Sims, 1996a).

Legacy of the buffer pH development era

The period from the 1930s to the 1970s saw the adoption of new techniques for estimating lime requirement, including the invention of the glass electrode for pH measurement, the use of buffer solutions for the indirect estimation of exchangeable acidity, and the use of lime-response calibration studies. These innovations allowed methods to be created which were significantly more convenient and accurate than previous ones. Of the buffer methods from this time period, the Woodruff (1948), SMP (1961), Adams-Evans (1962), and Mehlich (1976) methods are all still in use today throughout different regions of the United States (NAPT, 2020). The buffer method developed by Brown (1943) is the only method mentioned that is no longer in use.

Some methods originally used calibration approaches that were not directly connected to real lime application. Specifically, 348 of the 351 soils used for the Adams-Evans method were evaluated by ammonium acetate extraction, instead of by incubation or titration with CaCO_3 or

Ca(OH)₂. Similarly, the use of specific crops in the Mehlich (1976) calibration studies limits the applicability of that calibration for other cropping systems. However, these methods have been implemented and are still used in many different areas, reflecting their underlying utility as agronomic tests (J. T. Sims, 1996a).

All four buffer methods that were adopted from this time period include components that are classified as hazardous under the Resource Conservation and Recovery Act (Woodruff, 1948; Shoemaker et al., 1961; Adams & Evans, 1962; Mehlich, 1976; US EPA, 1980). Table 1.1 summarizes the hazardous components used in each, as well as the components used in non-hazardous adaptations of these methods that were developed later.

Table 1.1. Summary of the hazardous components used in common buffer LRE methods, as well as the non-hazardous components used by later methods to replace them.

Method	Prior Method Adapted	Hazardous Components	Non-Hazardous Substitutes
Woodruff (1948)	-	para-nitrophenol	-
SMP ^a (1961)	-	K ₂ CrO ₄ , para-nitrophenol	-
Sikora (2006)	SMP	-	MES ^b , imidazole
Adams-Evans (1962)	-	para-nitrophenol	-
Huluka (2005)	Adams-Evans	-	KH ₂ PO ₄
Moore-Sikora (2014)	Adams-Evans	-	MES ^b , MOPS ^c
Mehlich (1976)	-	BaCl ₂	-
Hoskins & Ehrich (2008)	Mehlich	-	CaCl ₂

^a Shoemaker, McLean, and Pratt

^b 2-(N-morpholino)ethanesulfonic acid

^c 3-(N-morpholino)propanesulfonic acid

Although these components were not regulated when these methods were designed, they became regulated with the passage of the Resource Conservation and Recovery Act in 1976 (Title 40--Protection of the Environment, 1980). This federal law regulated the disposal of hazardous material, making the use of these methods more costly for laboratories. Fixing this issue became a focus of research in the 2000s. However, in the intervening period, research focused on developing new buffer pH methods that were more accurate than their predecessors.

CONTINUED BUFFER INNOVATION: 1970s – 1980s

Beginning in the 1970s, researchers sought to refine the buffer pH approach by developing methods with improved accuracy. Innovations included the double-buffer approach and the use of field-based lime studies to calibrate buffer pH methods. Both of these innovations to the buffer pH approach will be discussed.

Double buffer pH methods

The double buffer approach was introduced by Yuan in 1974. In this approach, one buffer is divided in two, with each buffer adjusted to two different pre-determined starting pH levels. Soil is added to each buffer and pH is measured, producing two buffer pH values instead of just one as is done for traditional buffer methods described previously. These two data points are interpreted together to produce a LRE, as described in Figure 1.2.

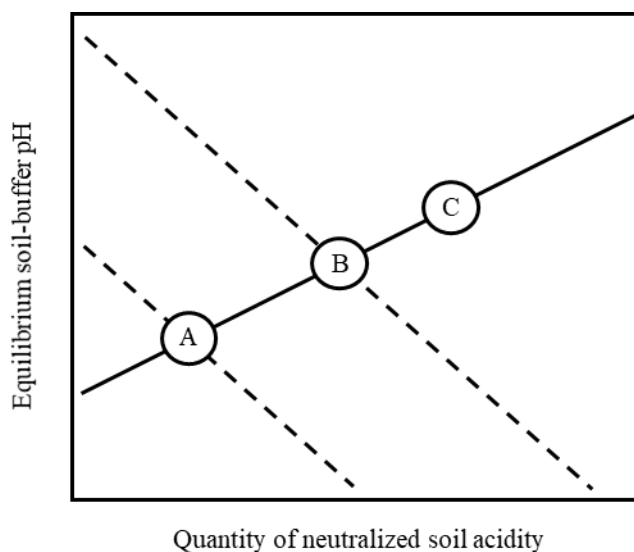


Figure 1.2. A theoretical representation of double-buffer methodology. Dashed lines represent the defined pH response of the two buffers used. Points A and B represent two buffer pH measurements whose coordinates are derived from the defined buffering curves. The solid line represents a linear equation calculated from A and B. C represents a point whose y-value is a target soil pH, and whose x-value, LRE, is interpolated or extrapolated from the solid line relationship.

Yuan (1974) developed the first double buffer pH method, with the goal of estimating the lime requirement of poorly buffered soils with greater accuracy than previous methods. The two buffer solutions used are adjusted to pH 7.0 and 6.0. The method was calibrated using a 7-day laboratory lime incubation of 20 acidic Florida soils, which showed a high level of correlation to lime requirement as estimated by the Yuan method ($r^2 = .996$). There is little record of the Yuan method seeing widespread adoption.

The SMP double-buffer (SMP-DB) method was proposed by McLean et al. in 1978. Using the original SMP buffer formulation, the authors experimented with different starting buffer pH values, as well as varying soil-buffer ratios in order to develop a double-buffer method with higher accuracy than the original single-buffer SMP method. In their study, McLean et al. (1978) calibrated their approach using a $\text{Ca}(\text{OH})_2$ titration of 54 soils from 12 states and demonstrated that the SMP-DB method was slightly more accurate than the single buffer SMP method on these soils with a wide range of characteristics. The results of the $\text{Ca}(\text{OH})_2$ titration trial were strongly correlated with the SMP-DB buffer method (mean $r^2 = .96$). In comparison, this relationship was slightly stronger than that seen with the SMP single-buffer method (mean $r^2 = .95$). McLean et al. stated that this modest improvement in accuracy is unlikely to be worth the added labor that comes from making two buffer pH measurements. This study also evaluated the Yuan method, and found that it correlated to titration lime requirement with slightly lower accuracy ($r^2 = .93$) compared to the SMP and SMP-DB methods.

Similar to other buffer methods previously described, the double buffer methods developed by Yuan (1974) and McLean (1978) use regulated hazardous chemicals: K_2CrO_4 for the Yuan method, and para-nitrophenol and K_2CrO_4 for the SMP-DB method. This disadvantage, combined with the added labor compared to single buffer methods, may explain the lack of widespread adoption of double-buffer methods. Nevertheless, the publication of these methods influenced later LRE methods. The Single Addition of $\text{Ca}(\text{OH})_2$ method (Liu et al., 2005) and the Sikora-2 method (Sikora, 2012) both estimate lime requirement partly by estimating a soil's lime buffering capacity, a concept demonstrated by the double-buffer work of Yuan (1974) and McLean et al. (1978).

Field calibration efforts

The 1970s to the 1980s also saw efforts to improve LRE accuracy through the use of field calibration. Previous buffer pH methods were calibrated using laboratory methods, such as $\text{Ca}(\text{OH})_2$ titration or CaCO_3 incubation. In their 1977 paper, Baker & Chae sought to further improve the accuracy of the SMP method by calibrating it to two lime application field trials in western Washington.

In the first trial, varying rates of lime were applied at seven sites in western Washington, and pH was sampled and evaluated over the following 24 months. The second trial consisted of a simulated field liming trial, in which 16 soils were mixed with varying rates of lime and placed in cardboard cylinders, which were embedded in soil at a single outdoor site. The first trial was used to develop an SMP calibration for estimating LR, and the second trial was used to verify the accuracy of those calibrations, producing r^2 of .97 and .96 for pH targets of 5.4 and 5.8, respectively.

With the exception of the Woodruff method and the Mehlich method, LRE methods up to the 1970s had been calibrated using either laboratory incubation with CaCO_3 or soil slurry titration with $\text{Ca}(\text{OH})_2$, based on the assumption that these methods closely approximated the reaction of lime with soil in the field. The use of these practices is likely due to the significantly reduced cost of laboratory incubation and titration trials compared to field trials. In their study, Baker & Chae compared field lime requirement results with laboratory lime incubation and titration to determine the degree of agreement between those methods. Incubation was shown to overestimate field lime requirement by an average of $0.5 \text{ ton acre}^{-1}$ over seven field sites with a total range in lime requirement of $0 - 10 \text{ ton acre}^{-1}$. In contrast, $\text{Ca}(\text{OH})_2$ titration was shown to underestimate field lime requirement by $0.4 \text{ ton acre}^{-1}$ for the same set of soils. These results are

specific to the soils of western Washington state and it is unclear if they would be the same or different in other regions. The advantage of the field calibration was reinforced by a study finding that Baker & Chae's calibration of the SMP method (1977) was more accurate than the original SMP calibration (1961) in its ability to predict field lime requirement for two western Oregon soils (Doerge & Gardner, 1988). Field lime trials may help improve the accuracy of LRE methods, however they are also significantly more expensive than laboratory trials. Therefore their use could lead to fewer total soils being used in calibration studies.

Legacy of the 1970s

The focus of research during this time period was to improve the accuracy of the already successful buffer approach for LRE. The two key approaches to this were the double-buffer method and the use of field trials to calibrate LRE methods. The two papers proposing double-buffer methods did not demonstrate a significant advantage over single-buffer methods. However, the approach that McLean et al. (1978), and Yuan (1974) used to estimate the slope of the soil's pH response to added alkalinity (lime buffer capacity) is an idea that influenced later methods. Similarly, the use of field lime trials by Baker & Chae (1977) and Doerge & Gardner (1988) showed that there may be some disagreement between field lime requirement and laboratory incubation lime requirement. Nevertheless, field liming trials have rarely been employed since, likely due to the cost effectiveness, and higher precision of using laboratory incubation and titration methods.

NON-HAZARDOUS BUFFER ADAPTATIONS, AND ALTERNATIVES TO BUFFER

METHODS: 2000s – 2020

The Resource Conservation and Recovery Act (RCRA) was passed in 1976, and was a key motivation for LRE method innovation starting in the 2000s. The RCRA regulates organizations that produce hazardous waste, including university and private soil testing laboratories. The LRE methods commonly used when the RCRA was passed use hazardous chemicals, including BaCl_2 (Mehlich 1976), para-nitrophenol (Woodruff, 1948; Shoemaker et al., 1961; Adams & Evans, 1962), and K_2CrO_4 (Shoemaker et al., 1961). The growing awareness of the hazards of these chemicals motivated efforts starting in the 2000s to either modify existing buffer LRE methods to use non-hazardous chemicals or create novel non-hazardous alternative LRE methods.

New LRE alternatives to the buffer pH approach

While buffer pH measurement has been the most successful approach to estimating lime requirement, alternative approaches offer the potential for improvements in accuracy and convenience. One alternative is the use of multiple soil test properties such as organic matter or extractable Al concentration to estimate lime requirement, an approach which has been evaluated by various researchers. Using a different approach, the Single Addition of $\text{Ca}(\text{OH})_2$ method (Liu et al., 2005) estimates lime requirement similarly to the methods of the early 1900s, by measuring the reaction of soil with a strong base. While these approaches have not seen the level of adoption of buffer LRE methods, exploring alternatives to buffer pH testing remains an ongoing area of research.

The single addition of Ca(OH)₂ method

The Single Addition of Ca(OH)₂ method is a unique LRE method that combines the strong base addition approach of the 1900s – 1930s with the double buffer approach of the 1970s. In the Ca(OH)₂ method, soil pH is first measured in 1:1 mixture of soil and 0.01 M CaCl₂ (pH_{CaCl₂}). Standardized saturated Ca(OH)₂ solution is then added, and the pH is measured again after 30 minutes of equilibration (Liu et al., 2005). Although this short period of equilibration is not enough to measure the full quantity of acidity in the soil, Liu et al. deemed it to be an acceptable approximation. As with double-buffer methods, these two measurements are used to construct a relationship between pH and added alkalinity for the soil. From this relationship, a lime requirement estimate can be calculated based on a selected target pH. The single addition of Ca(OH)₂ method was validated using a 3-day titration trial of 17 Georgia soils. The method correlated to titration lime requirement with $r^2 = .93$.

Due to its use of two data points, the Ca(OH)₂ method may be more accurate than buffer pH methods for estimating lime requirement. The Ca(OH)₂ method remains largely unevaluated outside of Georgia, so it is unclear if this benefit outweighs the added complexity of the Ca(OH)₂ method. Also, the use of pH_{CaCl₂} could prevent implementation in regions where standard pH recommendations are not based on pH_{CaCl₂}.

LRE modeling using soil properties

Various researchers have proposed LRE models that use multiple soil test properties (Keeney & Corey, 1963; Lemire et al., 2005; McFarland et al., 2020; Miller et al., 2005). These approaches vary in the properties used, as well as their accuracy relative to buffer pH methods, as shown in Table 1.2.

Table 1.2. Summary of the accuracy of soil property LRE models compared to buffer pH methods, for estimating lime requirement. Each study evaluated one or more soil property LRE models as well as one or more buffer pH methods. Correlations shown are between models or buffer pH methods and incubation lime requirement for regional soils. For each study, the buffer pH method with the highest r^2 is shown, except for Lemire et al. 2005, which only evaluated the SMP method.

Reference	Region	Model variables ^a		Buffer pH method	
			r^2		r^2
Keeney & Corey 1963	Wisconsin	SOM, pH	.78	SMP ^b	.90
Lemire et al. 2005	Quebec, Canada	SOM, pH, Fe	.77	SMP	.80
		SOM, pH	.71		
Miller et al. 2005	California	SP, pH _{CaCl2} , Al	.75	Mehlich ^c	.88
McFarland et al. 2020	E. Washington State	SOM, Al	.72	Modified Mehlich ^d	.90
		SOM, pH	.71		

^a SOM = Soil Organic Matter, Fe = Fe oxides extracted by $(\text{NH}_4)_2\text{C}_2\text{O}_4$, SP = saturated paste moisture content, pH_{CaCl2} = pH measured in 1:1 0.01 M CaCl₂, and Al = Al extracted by KCl

^b Shoemaker et al., 1961

^c Mehlich, 1976

^d Hoskins & Erich, 2008

These models were shown to be slightly or significantly less accurate than buffer pH methods. Apart from accuracy, LRE models based on soil properties may also differ from buffer pH methods in terms of cost. Some LRE models may reduce costs by using soil test properties that are already used for other agronomic interpretation. Therefore the soil test properties that are convenient for LRE interpretation will vary according to the soil tests recommended in different regions. For example, the model proposed by Miller et al. (2005) used two procedures that were already recommended in California: saturated paste and pH_{CaCl2}. Other properties may have little use for agronomic interpretation, such as the use of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ -extractable Fe oxides proposed

by Lemire et al. (2005). The use of properties that are not used for routine agronomic testing may increase costs relative to buffer pH methods.

The use of soil organic matter (SOM) presents its own set of challenges. Depending on regional recommendations, monitoring organic matter may not always be conducted as a routine test. SOM may also be measured using different methods, the three main methods being loss on ignition (LOI), combustion, and Walkley-Black. Each of these methods varies in its cost and accuracy (Nelson & Sommer, 1996). Furthermore, the Walkley-Black method creates regulated hazardous waste due to the use of $K_2Cr_2O_7$ (Title 40--Protection of the Environment, 1980). Therefore the utility of using SOM to estimate LR will vary depending on the method used to measure it.

LRE modeling using soil test properties has shown limited success in providing means of lime requirement estimation that is more accurate or more convenient than buffer methods. Nevertheless, it remains an ongoing area of research due to the potential for reducing costs by using existing agronomic soil test properties.

Non-hazardous adaptations of buffer pH methods

Buffer pH methods have been and continue to be popular methods for estimating lime requirement. As of 2005, the four most commonly used buffer pH methods—Woodruff (1948), SMP (1961), Adams-Evans (1962), and Mehlich (1976)—required at least one hazardous component, and produced regulated hazardous waste (NAPT, 2005; Title 40--Protection of the Environment, 1980). Due to their popularity, in the 2000s researchers began to develop non-hazardous adaptations of three of these methods: the SMP, Adams-Evans, and Mehlich methods. These non-hazardous methods were developed by replacing hazardous components with non-

hazardous ones in a way that gave the new methods pH response characteristics very similar to that of their predecessors. Instead of using calibration studies, the researchers who developed these adaptations typically validated their new methods by correlating their buffer pH results to those of the original method. Nevertheless, regional calibration of new methods to incubation or field lime requirement is still recommended for adoption. This lack of regional calibration presents the most significant barrier to widespread adoption of these methods.

Another potential disadvantage of non-hazardous adaptations is that in many cases, the replacement of hazardous components makes the buffer reagent more susceptible to microbial growth. Microbial growth in buffer solutions is a problem, as it can degrade buffer components and affect test results. This problem is shown to affect some methods more than others, and is discussed in detail below. Non-Hazardous Adaptation of the SMP Buffer pH Method: The Sikora Method

In 2006, the Sikora method was developed as a non-hazardous adaptation of the SMP method (Sikora, 2006). As of 2005, the SMP buffer method was the LRE test most commonly used by laboratories participating in the North American Proficiency Testing Program (NAPT, 2005). The widespread use of the SMP method may explain why it was one of the first buffer methods to have a nonhazardous adaptation. This adaptation was accomplished by replacing the hazardous components in SMP (para-nitrophenol and K_2CrO_4) with non-hazardous alternatives, 2-(N-morpholino)ethanesulfonic acid (MES) and imidazole. The Sikora method was correlated to the SMP method using 87 national reference soils, as well as 255 Kentucky soils. These correlations indicated a relationship between the two methods close to 1:1, with r^2 values of .97 for both the Kentucky and NAPT datasets.

While it eliminated the use of hazardous materials, the Sikora method has some disadvantages relative to the SMP method. The first disadvantage is that the Sikora method cannot accurately measure buffer pH below 5.3; in contrast the SMP method can measure buffer pH values down to 4.8. This reduction in pH range effectively diminishes the total range of lime requirement that the Sikora method can measure. Using the original calibration for the SMP method, the Sikora method can measure up to 9.4 ton acre⁻¹ compared to 12.4 ton acre⁻¹ with the SMP method (Shoemaker et al., 1961). Although Sikora noted a concern about microbial growth in the buffer reagent, it was reported that the reagent gave stable results after 150 days of storage, a result which was replicated by Nathan et al. (2012).

In general, follow-up studies have indicated that the Sikora method can be an effective replacement for the SMP method. Three notable studies have used laboratory incubation trials to compare the effectiveness of the Sikora and the SMP methods. Viswakumar et al., (2010) showed the Sikora method to be slightly less accurate than the SMP method for Ohio soils. Santanna et al. (2011) showed equivalent accuracy between the SMP and Sikora methods for soils in Brazil. McFarland et al. (2020) showed higher accuracy for the Sikora method than the SMP method for eastern Washington soils. These mixed results underscore the importance of developing regional calibrations for new LRE methods.

In 2012, Sikora proposed a further modification to the Sikora method. Referred to as ‘Sikora-2’, this method estimates lime requirement by pairing Sikora buffer pH with soil pH measured in a 1:1 mixture with 1 M KCl (pH_{KCl}). The Sikora-2 method is similar to double-buffer methods because it is based on estimating the slope of the soil’s pH response to base addition, also known as lime buffer capacity. The use of pH_{KCl} represents an additional step required for the Sikora-2

method. The Sikora-2 method remains uncalibrated by secondary field or incubation studies, therefore it is still unknown whether it is more accurate than the SMP or Sikora methods.

Non-hazardous adaptations of the Adams-Evans method

Two non-hazardous adaptations of the Adams-Evans method have been developed. Huluka developed the first by replacing para-nitrophenol with KH_2PO_4 (Huluka, 2005). The Huluka method was compared to the original Adams-Evans method using 407 acidic Alabama soils in a direct correlation, producing an r^2 value of .83. Furthermore, the Huluka method recommended on average 0.34 Mg ha^{-1} less than the original Adams-Evans method.

In 2008, Sikora & Moore developed another non-hazardous adaptation of the Adams-Evans method (Sikora & Moore, 2008). These authors determined that the use of KH_2PO_4 in the Huluka method had two potential disadvantages. First, KH_2PO_4 provides a source of P to microbes, potentially accelerating microbial degradation of the buffer. Second, the PO_4^{3-} ion has the potential to interact with soil colloids and metal cations, which could reduce its effectiveness as a buffer (Sikora & Moore, 2008). Therefore Sikora & Moore used 2-(N-morpholino)ethanesulfonic acid (MES) and 3-(N-morpholino)propanesulfonic acid (MOPS) to replace para-nitrophenol, due to their lower potential for interacting with soil components, and the absence of P in both (Sikora & Moore, 2008).

To evaluate their proposed method, Sikora & Moore correlated buffer pH values between the proposed method and the original Adams-Evans method for 222 South Carolina soils and 41 national reference soils. These correlations produced r^2 values of .99 and .98 respectively. The proposed method gave lime requirement estimates that were on average 0.34 Mg ha^{-1} greater than the original Adams-Evans method.

Unfortunately there is little record of incubation or field studies used to calibrate the Moore-Sikora or the Huluka methods. As with the Sikora method, regional calibration studies are recommended to confirm the accuracy of new methods before adoption.

Non-hazardous adaptation of the Mehlich method

In addition to the efforts described above to develop non-hazardous versions of the SMP and Adams-Evans buffers for LRE, Hoskins & Erich (2008) sought to modify the Mehlich method by replacing BaCl_2 with the non-hazardous chemical CaCl_2 . A laboratory incubation study consisting of 7 Maine soils was used to calibrate the new method, which showed correlations with an average r^2 of .94. Hoskins & Erich concluded that the correlation was strong enough to support the potential replacement of the Mehlich buffer with the CaCl_2 -based adaptation. Other researchers developed calibrations for the modified Mehlich buffer in Missouri and Pennsylvania, and showed it to be acceptably accurate in both cases (Nathan et al., 2012; Wolf et al., 2008).

As with the Sikora method (2006), the modified Mehlich formulation does not have the same anti-microbial properties as the original, therefore buffer degradation is a concern. The authors recommend extra labware sanitization, and remaking or checking the buffer every 10 – 14 days, measures that are not necessary with the original formulation. The sensitivity of the modified Mehlich buffer to microbial degradation was confirmed by Nathan et al., who showed that the buffer gave erratic results after 21 days (Nathan et al., 2012). This period is substantially less than the storage period of the Sikora buffer, which is 150 days (Sikora, 2006). Sikora & Moore (2008) note that buffers with low ionic strength and that contain P are more likely to promote microbial growth. The modified Mehlich buffer has lower ionic strength than the Sikora buffer,

as well as more P, which may explain the erratic buffer pH results after 21 days observed by Nathan et al. (Hoskins & Erich, 2008).

CONCLUSION

Lime requirement estimation methods are essential agronomic soil tests in regions where lime is applied to neutralize soil acidity. These methods have undergone considerable innovation between 1900 and 2020. Most significantly, advancements in science and technology enabled the development of buffer pH methods in the 1940s – 1970s, methods which form the basis for most LRE testing today. Another significant development was the passage of the Resource Conservation and Recovery Act in 1976, which drove the development of non-hazardous adaptations of commonly used buffer methods, an area of research that is still ongoing in 2021.

Currently, the most promising opportunities in LRE method research fall into two groups: 1) regional calibration and adoption of non-hazardous LRE methods, and 2) continued exploration of models based on soil properties. Hazardous LRE methods are still used in many regions, despite evidence of the effectiveness of non-hazardous alternatives. Previously developed soil property LRE models have been shown to be less accurate than buffer methods. As soil test technology improves, it will be important to continue to assess the viability of using soil properties as an alternative to buffer methods, for estimation of lime requirement.

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**CHAPTER 2: EVALUATION OF NON-HAZARDOUS LIME REQUIREMENT
ESTIMATION METHODS FOR OREGON SOILS**

ABSTRACT

The Shoemaker, McLean, and Pratt (SMP) buffer pH method has been used historically in Oregon for estimating lime requirement, however, concerns regarding hazardous waste disposal have caused soil testing laboratories to seek out alternative non-hazardous methods. Non-hazardous lime requirement estimation (LRE) methods have been adopted in other regions, but have not been evaluated for Oregon soils. The objective was to compare non-hazardous LRE methods to the SMP method for predicting incubation lime requirement (LR_i) for Oregon soils. Twenty-four soils ($pH \leq 5.5$) from western and eastern Oregon were incubated with seven rates of $CaCO_3$ ranging from 0 to 22.4 Mg ha^{-1} and incubated for 90 d at 19° C . Seven different LRE methods were evaluated and regressed against incubation lime requirement (LR_i) for pH targets of 5.6, 6.0, and 6.4 using linear regression. The Sikora ($r^2 = .90 - .92$), Modified Mehlich ($r^2 = .87 - .89$), and Sikora-2 ($r^2 = .81 - .93$) buffer methods showed potential as non-hazardous alternatives to SMP ($r^2 = .90 - .92$) based on accuracy and precision. Combining clay concentration, KCl-extractable Al, soil organic matter (SOM), extractable Mg, and $pH_{1:2}$ also effectively predicted LRE ($r^2 = .96 - .97$). The Moore-Sikora buffer method ($r^2 = .89 - .93$) was accurate but showed precision issues due to high replication variability. The Single Addition of $Ca(OH)_2$ method ($r^2 = .69 - .77$) was less accurate than other evaluated methods for Oregon soils. We conclude that there are several viable non-hazardous LRE method alternatives to the SMP buffer method for Oregon soils based on accuracy and precision alone, understanding that factors including time and expense required must also be considered by soil testing programs before a specific method can be adopted.

INTRODUCTION

Lime requirement estimate (LRE) tests are used throughout the United States to determine the lime (CaCO_3) rate needed to raise soil pH to a crop-appropriate target pH. The Shoemaker, McLean and Pratt (SMP) buffer method has been historically recommended for lime requirement estimation in Oregon (Anderson et al., 2013; Sullivan et al., 2013). Buffer pH methods, such as the SMP method, are the predominant approach used to estimate lime requirement in the United States (Sims, 1996). Buffer pH methods estimate lime requirement by measuring pH in a soil-buffer mixture. The buffers used for LRE methods have a consistent pH response to added acidity, therefore soil buffer pH can be correlated to exchangeable acidity and lime requirement. The use of the SMP method is supported by prior research showing a correlation ($r^2 = .74 - .81$) between the SMP method and incubation lime requirement for 45 agricultural soils from the Willamette Valley in Oregon (Peterson, 1971).

The SMP method produces waste that is classified as hazardous under the Resource Conservation and Recovery Act (Shoemaker et al., 1961; US Environmental Protection Agency, 1980). Specifically, the hazardous materials used by the SMP method are para-nitrophenol and K_2CrO_4 . The use of these components for the SMP method causes significant cost to soil test laboratories due to labor and fees associated with segregating and disposing of waste.

Non-hazardous methods have been developed as alternatives to hazardous LRE methods. The Sikora method (2006) was developed to mimic the SMP method (Shoemaker et al., 1961). In this adapted method, Sikora replaced para-nitrophenol and K_2CrO_4 with 2-(N-morpholino)ethanesulfonic acid monohydrate (MES) and imidazole. Similarly, the Moore-Sikora method (Sikora & Moore, 2008) was developed to mimic the Adams-Evans method (1962), and was made non-hazardous by replacing para-nitrophenol with MES and 3-(N-

morpholino)propanesulfonic acid (MOPS). Lastly, Hoskins & Erich (2008) modified the Mehlich buffer method (1976) by replacing hazardous BaCl_2 with CaCl_2 .

Apart from non-hazardous adaptations of buffer methods, there are other non-hazardous LRE methods based on lime buffer capacity. Lime buffer capacity is the response of soil pH to addition of alkaline materials. These methods estimate lime buffer capacity based on soil pH measurements before and after a base addition. Once the lime buffer capacity is estimated, a LRE can be calculated from a selected pH target. Lime buffer capacity methods typically require two separate measurements in order to calculate the lime buffer capacity. One method is the Sikora-2 method (Sikora, 2012). In the Sikora-2 method, lime buffer capacity is calculated based on pH_{KCl} and Sikora buffer pH (Sikora, 2012). Another method is the Single Addition of $\text{Ca}(\text{OH})_2$ method (Liu et al., 2005), in which the lime buffer capacity calculation is based on initial $\text{pH}_{\text{CaCl}_2}$, and $\text{pH}_{\text{CaCl}_2}$ after an addition of $\text{Ca}(\text{OH})_2$.

Regional calibrations are necessary to ensure that LRE methods accurately estimate lime requirement across diverse soil types. Lime requirement estimation methods are typically calibrated against the lime requirement of regional soils, which is usually determined for one or more agronomic pH targets using a laboratory lime incubation trial. Non-hazardous buffer pH methods have been calibrated using lime incubation studies in various regions throughout the United States, and have been shown to be effective alternatives to hazardous methods. Based on correlation to incubation lime requirement, the Sikora method was shown to be accurate for estimating lime requirement in Ohio (Viswakumar et al., 2010), Brazil (Santanna et al., 2011), and Missouri (Nathan et al., 2012), with $r^2 = .40 - .73, .97, \text{ and } .73 - .82$ respectively. Similarly, the Modified Mehlich method was shown to be an accurate LRE method in Maine (Hoskins & Erich, 2008), Missouri (Nathan et al., 2012), and eastern Washington (McFarland et al., 2020),

with $r^2 = .91 - .96$, $.82 - .89$, and $.90$ respectively. The $\text{Ca}(\text{OH})_2$ method was determined to be accurate in Georgia with $r^2 = .93$ (Liu et al., 2005). Other methods, such as Moore-Sikora or Sikora-2 have not been similarly evaluated for U.S. soils. Based on these demonstrations of accuracy in other regions, one or more of these non-hazardous methods may be useful for estimating lime requirement in Oregon. However, at present, none of these methods have been evaluated in Oregon.

The buffer and lime buffer capacity methods described above were all designed for the sole purpose of estimating lime requirement. It has been suggested that existing traditional agronomic soil test properties may also be used to estimate lime requirement. Use of soil properties for LRE has been proposed as a way to reduce costs relative to buffer LRE methods, since the properties used may already be known from other agronomic soil testing. The soil properties approach has also been proposed as a way to improve LRE accuracy over more commonly used buffer methods.

Lime requirement and soil acidity are known to relate to various measurable soil properties. Clay and SOM contribute to negative charge and pH buffering in soil, therefore measurements of these properties are known to relate to lime requirement (Brady & Weil, 2008). Exchangeable Al is a source of acidity in soil, therefore Al may be related to lime requirement (Sims, 1996). Soil pH is a measure of the active acidity of the soil, as such its connection to exchangeable acidity and to lime requirement is variable and dependent on the concentration of pH buffering materials in soil, such as clay and SOM (Sims, 1996). While these individual properties are all related to soil acidity and lime requirement, previously-developed soil property LRE methods have used two or more properties in order to achieve an acceptable level of accuracy (Keeney & Corey, 1963; Lemire et al., 2005; McFarland et al., 2020; Miller et al., 2005).

Soil property LRE methods have been developed and evaluated (based on regression to incubation lime requirement) in various regions of North America, including Wisconsin (Keeney & Corey, 1963), Quebec (Lemire et al., 2005), California (Miller et al., 2005), and eastern Washington State (McFarland et al., 2020). These soil property LRE models may not be effective for Oregon due to differences in soil characteristics. However, the soil properties most commonly used by these methods may indicate properties more likely to be useful for estimating lime requirement in Oregon. For example: soil pH was used in all four studies, SOM was used in three cases (Keeney & Corey, 1963; Lemire et al., 2005; McFarland et al., 2020), and KCl-extractable Al was used in two studies (Miller et al., 2005; McFarland et al., 2020). Overall, the four soil property models developed by Keeney & Corey (1963), Lemire et al. (2005), Miller et al. (2005), and McFarland et al. (2020) were shown to be acceptably accurate for estimating lime requirement in their respective regions, based on r^2 values ranging from .71 to .88. However, each model had slightly lower r^2 values than at least one buffer method evaluated in the same study, indicating that in general, buffer methods were more accurate for estimating lime requirement than methods based on multiple soil test properties (Keeney & Corey, 1963; Lemire et al., 2005; McFarland et al., 2020; Miller et al., 2005). While soil properties have shown promise in other parts of the United States for LRE, this approach has not yet been evaluated for Oregon agricultural soils.

The objectives of this project were: (a) to determine the incubation lime requirement of 24 acid Oregon agricultural soils for pH targets 5.6, 6.0, and 6.4; (b) to compare the accuracy and precision of five non-hazardous LRE methods to the SMP method; and (c) to evaluate soil properties including SOM, clay concentration, KCl-extractable Al, and soil pH for estimating lime requirement.

MATERIALS AND METHODS

Location

Soil samples were collected from 24 agricultural cooperator fields in Oregon. Field sites were distributed between the Willamette Valley (n=20), central Oregon (n=1), and eastern Oregon (n=3). Soil taxonomic classification is given in Table 2.1.

Soil collection

For this study, acidic soils with $\text{pH}_{1:2}$ of 5.5 or less were desired in order to illustrate an effective response to lime additions under acidic soil conditions. Before sampling, multiple locations within a field site were evaluated for pH in the field using a handheld pH meter (FieldScout SoilStik, Spectrum Technologies, Inc., Aurora, IL), in order to identify a location with $\text{pH}_{1:2}$ below 5.6. Soil samples were collected from 0 – 15 cm depth, except for two samples, Nekia-1 and DNF-36 which were sampled from 0 – 7.5 cm depth in order to acquire a sample with sufficiently low pH. Samples were collected from within a 1 m by 1 m area using a sharpshooter shovel. Samples were laid out to dry within eight hours of collection. Samples were air-dried for 7 – 45 d in an open-air shed in Corvallis, OR, from July to September 2019. During this time average daily minimum and maximum temperatures were 12° and 26° C respectively. After air-drying, soil samples were ground with a porcelain mortar and pestle and then sieved to 2 mm.

Table 2.1. Soil taxonomic classification of 24 Oregon agricultural soils included in the lime incubation trial.

Region and soil series	Soil taxonomic subgroup^a
Willamette Valley	
Aloha	Aquic Haploxerepts
Amity	Argiaquic Xeric Argialbolls
Awbrig	Chromic Vertic Albaqualfs
Bashaw	Xeric Endoaquerts
Bellpine	Xeric Haplohumults
Camas	Fluventic Haploxerolls
Concord	Typic Endoaqualfs
Conser	Vertic Argiaquolls
Cornelius	Mollic Fragixeralfs
Cove	Vertic Endoaquolls
Dayton-1	Vertic Albaqualfs
Dayton-2	Vertic Albaqualfs
Jory	Xeric Palehumults
Malabon	Pachic Ultic Argixerolls
Natroy	Xeric Endoaquerts
Nekia-1	Xeric Haplohumults
Nekia-2	Xeric Haplohumults
Salem	Pachic Ultic Argixerolls
Willamette	Pachic Ultic Argixerolls
Woodburn	Aquultic Argixerolls
Eastern Oregon	
Athena	Pachic Haploxerolls
Palouse	Pachic Ultic Haploxerolls
Walla Walla	Typic Haploxerolls
Central Oregon	
DNF-36	Unit 36: Sandy volcanic ash soils ^b

^a Source: Soil Survey Staff, National Resources Conservation Service.

^b The soil sample from central Oregon does not have an assigned soil series; in this paper it will be referred to as 'DNF-36'. Classification from Larsen (1976).

Soil characterization

Three representative subsamples were used for all characterization analyses for each of the 24 soils. Soil pH measurements were performed using an Orion ROSS Sure-Flow pH electrode with an Orion Star A211 Benchtop pH meter (Thermo Fisher Scientific, Waltham, MA). Soil was measured by weight, and water was measured by volume. Soil pH_{1:2} (1:2 soil:water) was evaluated according to Thomas (1996). Soil pH_{1:1} (1:1 soil:water), pH_{CaCl2} (1:1 soil:0.01 M CaCl₂), and pH_{KCl} (1:1 soil:1.0 M KCl) were evaluated according to Sikora & Moore (2014).

Soil KCl-extractable Al was evaluated following procedure S – 15.10 from Gavlak et al. (2005). Soil K, Ca, Mg, and Na were extracted with NH₄OAc following procedure S – 5.10 from Gavlak et al. (2005). Cation exchange capacity at pH 7.0 (CEC) was evaluated following procedure S – 10.10 from Gavlak et al. (2005), replacing 1 M NH₄OAc with 1 M NaOAc in the initial extraction step, and replacing HCl with 1 M NH₄OAc in the final Na displacement step. Base saturation was calculated by dividing the sum of extractable K, Ca, Mg, and Na by CEC. DTPA-extractable Zn, Mn, Cu, and Fe were evaluated following procedure S – 6.12 from Gavlak et al. (2005). Extracted Al, K, Ca, Mg, Na, Zn, Mn, Cu, and Fe and displaced Na were analyzed using inductively-coupled plasma atomic emission spectroscopy (Optima 7300DV, Perkin Elmer, Waltham, MA). Soil organic matter was evaluated using the Walkley-Black method following procedure S – 9.10 from Gavlak et al. (2005). A spectrometer (Aquamate 8000, Thermo Fisher Scientific, Waltham, MA) was used to evaluate Cr³⁺ instead of titration, a modification recommended by Sims & Haby (1971). Sand, silt, and clay concentration were evaluated using the hydrometer method, following procedure S – 14.10 from Gavlak et al. (2005). Soil analysis results are shown in Table 2.2 and Table 2.3.

Table 2.2. Mean soil pH, electrical conductivity (EC), KCl-extractable Al, and DTPA-extractable micronutrient measurement for 24 Oregon soils. Nekia-1 and DNF-36 were sampled from the 0 – 7.5 cm soil depth, while all other soils were sampled from the 0 – 15 cm soil depth.

Region and soil series	pH _{1:2}	pH _{1:1}	pH _{CaCl2}	pH _{KCl}	EC	Al _{KCl}	Mn ^a	Zn ^a	Cu ^a	Fe ^a
Willamette Valley										
Aloha	5.1	5.0	4.3	3.8	0.1	96	34	1.8	0.5	108
Amity	4.9	4.8	4.3	3.8	0.2	57	35	3.4	0.5	146
Awbrig	5.3	5.2	4.3	3.8	0.1	259	168	2.7	3.1	86
Bashaw	5.1	4.8	4.3	3.7	0.2	78	74	3.1	3.3	379
Bellpine	5.3	5.1	4.5	4.0	0.1	107	91	2.5	0.8	110
Camas	5.3	5.1	4.5	3.8	0.2	59	35	2.3	1.1	157
Concord	4.9	4.9	4.1	3.6	0.1	107	61	2.6	1.3	252
Conser	5.0	4.9	4.5	3.9	0.4	29	129	7.2	1.8	218
Cornelius	4.8	4.7	4.3	3.8	0.3	66	69	1.6	0.4	71
Cove	4.9	4.8	4.2	3.7	0.2	67	82	3.1	0.8	137
Dayton-1	5.1	5.0	4.3	3.8	0.1	61	99	4.0	1.1	222
Dayton-2	4.9	4.7	4.2	3.6	0.2	94	114	2.4	1.0	135
Jory	5.4	5.3	4.7	4.3	0.1	22	63	2.7	1.1	145
Malabon	5.5	5.3	4.6	4.0	0.2	18	77	8.7	2.3	222
Natroy	5.2	5.1	4.7	4.1	0.4	6	121	2.8	3.0	208
Nekia-1	5.0	4.9	4.4	4.0	0.2	106	68	3.5	0.8	98
Nekia-2	4.9	4.7	4.3	3.9	0.2	100	99	4.0	1.7	130
Salem	5.0	4.8	4.4	3.7	0.2	75	33	2.8	0.6	96
Willamette	5.1	4.9	4.6	4.1	0.5	12	46	1.8	0.8	107
Woodburn	5.2	5.1	4.4	3.9	0.1	65	52	3.6	1.1	178
Eastern Oregon										
Athena	5.3	5.2	4.7	4.2	0.3	2	61	1.3	1.2	56
Palouse	5.5	5.4	4.6	4.1	0.1	7	86	5.0	1.3	95
Walla Walla	5.3	5.2	4.5	4.0	0.2	10	90	2.3	1.2	79
Central Oregon										
DNF-36	5.5	5.3	4.5	4.0	0.1	55	6	1.5	0.5	123

^a DTPA extractable.

Table 2.3. Mean extractable Ca, K, Mg, and Na, cation exchange capacity (CEC), base saturation (BS), soil texture, and soil organic matter (SOM) for 24 Oregon soils. Nekia-1 and DNF-36 were sampled from the 0 – 7.5 cm soil depth, while all other soils were sampled from the 0 – 15 cm soil depth.

Region and soil series	Ca ^a	K ^a	Mg ^a	Na ^a	CEC	BS	Clay	Sand	SOM
	————— cmol _c kg ⁻¹ —————					%	————— g kg ⁻¹ —————		
Willamette Valley									
Aloha	3.9	0.7	1.0	0.1	16.5	34	205	134	34
Amity	5.3	0.6	0.9	0.1	15.0	46	197	239	40
Awbrig	9.1	0.2	3.1	0.2	32.7	39	426	200	68
Bashaw	13.3	0.4	5.5	0.2	39.0	50	476	124	70
Bellpine	7.8	0.6	0.8	0.1	27.6	34	494	158	90
Camas	9.9	1.2	3.0	0.1	20.5	70	233	377	34
Concord	6.3	0.4	1.2	0.1	17.8	45	193	71	38
Conser	10.8	0.3	3.2	0.2	23.3	63	353	98	54
Cornelius	2.9	0.8	0.6	0.1	13.3	33	178	198	35
Cove	5.6	0.6	0.9	0.1	15.8	46	153	216	44
Dayton-1	4.7	0.2	0.6	0.1	16.1	34	179	77	39
Dayton-2	5.0	0.6	1.1	0.1	15.1	45	175	68	33
Jory	9.4	0.3	0.8	0.1	25.5	42	530	120	94
Malabon	14.2	2.7	3.2	0.1	31.9	64	403	95	67
Natroy	10.1	0.4	2.8	0.3	18.5	74	234	338	36
Nekia-1	6.5	0.4	0.9	0.1	27.7	29	532	126	103
Nekia-2	3.9	0.7	0.7	0.1	22.2	24	435	191	77
Salem	10.1	1.0	1.9	0.1	23.5	56	288	232	38
Willamette	9.2	0.8	1.5	0.1	20.6	56	257	59	41
Woodburn	6.1	0.7	1.4	0.1	18.9	44	213	79	36
Eastern Oregon									
Athena	8.3	1.9	2.9	0.1	17.4	76	177	192	32
Palouse	8.6	0.9	2.9	0.1	20.7	61	204	183	54
Walla Walla	6.0	2.4	2.1	0.1	16.5	64	142	192	34
Central Oregon									
DNF-36	3.2	0.5	1.3	0.1	12.4	41	104	592	59

^a NH₄OAc extractable.

Lime incubation

Experimental design

The lime incubation trial was a two-factor factorial design. For the first factor, the 24 Oregon soils were used. For the second factor, six rates of CaCO₃ (ACS grade, 99.7% pure) ranging from 1.15 to 11.50 g kg⁻¹ were used, as well as a control treatment with no CaCO₃ added. Four replications were used in a complete randomized design. With 24 soil types, 7 lime rates, and 4 replications, the trial consisted of 672 experimental units. The actual CaCO₃ rates in g kg⁻¹ and the equivalent rates in Mg ha⁻¹ (based on an assumed bulk density of 1.3 g cm⁻³ at the 0 – 15 cm soil depth) are shown in Table 2.4.

Table 2.4. Actual and equivalent rates of CaCO₃ used in a laboratory lime incubation trial.

Actual CaCO ₃ rate	Equivalent CaCO ₃ rate ^a
g kg ⁻¹	Mg ha ⁻¹
0	0
1.15	2.2
2.30	4.5
4.60	9.0
6.90	13.5
9.20	17.9
11.50	22.4

^a Equivalent CaCO₃ rates are based on an assumed bulk density of 1.3 g cm⁻³ at the 0 – 15 cm soil depth.

Establishing optimal soil moisture content

Water holding capacity was determined for each of the 24 soils, allowing for soil moisture to be adjusted for each soil type to approximately 80 – 90% field capacity throughout the incubation. Field capacity was initially estimated using a pressure plate (1600F1 Pressure Plate Extractor, SoilMoisture, Goleta, CA) set to 0.33 bar (Reynolds & Topp, 2008). As some soils appeared to be excessively wet or dry at 80 – 90% field capacity, some soil moistures were

adjusted slightly to avoid saturation or dryness issues. Based on field capacity determined in this way, acceptable upper and lower limits for soil moisture during incubation were established for each of the 24 soils, based on approximately 80% and 90% of field capacity. These limits, expressed as gravimetric moisture content, are listed in Appendix 2.1. Lower limits ranged from 185 to 366 g kg⁻¹, and upper limits ranged from 208 to 387 g kg⁻¹.

Additionally, samples of each of the 24 soils were oven-dried for 24 h at 105° C to determine air-dry moisture content. Air-dry moisture content was taken into account when adding water for incubation.

Soil preparation

Air-dry soil was weighed into resealable polyethylene plastic bags to give 200 g of oven-dry equivalent soil. Resealable plastic bags had a wall thickness of 0.069 mm, and dimensions of 17.9 by 19.1 cm. Based on a trial-run incubation, the walls were thin enough to allow exchange of CO₂ and moisture. Additionally, Hoskins & Erich (2008) found that lime incubation in sealed plastic bags did not induce anaerobic conditions or prevent sufficient gas exchange.

Calcium carbonate was added to the air-dry soil and mixed by hand in the bags. No CaCO₃ was added to the control experimental units. Deionized water was added to each bag bring it to the upper moisture content limit (approximately 90% of field capacity) as previously determined. Water was mixed with soil by hand in the bags.

Incubation

Bags were sealed, rolled into cylinders, and placed on-end in closed cardboard boxes, with the intention of providing conditions similar to buried soil in the field. Soil bags were incubated in this way for 90 d. During this time, temperature fluctuated from 17 to 21° C for a mean

incubation temperature of 19° C. All bags were weighed every two weeks to determine moisture loss. Deionized water was added to individual bags when moisture content was below its previously determined soil moisture lower limit (approximately 80% of field capacity).

Post-incubation pH analysis

After incubation, samples were air-dried in a forced-air cabinet at 27° C, crushed and sieved to 2 mm, and analyzed for pH_{1:2} as described above. The 24 soils evaluated varied in the shape of their pH_{1:2} response to CaCO₃ rate, therefore linear and 2nd-order polynomial equations were considered for each soil. For each of the 24 soils, the equation type with the lowest corrected Akaike Information Criterion (AICc) was fit to the data using least-square regression, with CaCO₃ rate as the independent variable, and post-incubation pH_{1:2} as the dependent variable. Incubation lime requirement (LR_i) was determined for three pH_{1:2} targets, 5.6, 6.0, and 6.4, for each of the 24 soils. Incubation lime requirement values were interpolated from the regression equations. Statistical analysis was performed in RStudio Version 1.1.463 (R Core Team, 2018). Regression equations were determined using the base R function 'lm'. Interpolation of LR_i was accomplished using the function 'invest' from the R package 'investr' (Greenwell & Schubert Kabban, 2014).

Lime requirement estimation methods

Methods used to estimate lime requirement included SMP, Sikora, Modified Mehlich, Moore-Sikora, Sikora-2, and the Ca(OH)₂ method. The SMP method was analyzed following Gavlak et al. (2005): 5 g of soil were mixed with 5 ml deionized water and 10 ml SMP buffer for 10 min on an end-to-end oscillating shaker set to 180 oscillations per min (opm), followed by buffer pH measurement in the supernatant.

Sikora buffer pH was analyzed following Sikora (2006): 10 g of soil were mixed with 10 ml deionized water and 10 ml Sikora buffer for ten min on an end-to-end oscillating shaker set to 180 rpm, followed by buffer pH measurement in the supernatant.

The Modified Mehlich method was analyzed according to Sikora & Moore (2014): 10 g soil were mixed with 10 ml deionized water and 10 ml Modified Mehlich buffer with a glass rod, and then left to sit for 30 min. The mixture was stirred briefly to resuspend the slurry immediately before buffer pH measurement.

Moore-Sikora buffer pH was analyzed according to Sikora & Moore (2014): 15 g soil were mixed with 15 ml deionized water and 15 ml Moore-Sikora buffer with a glass rod, and then left to sit for 30 min. The mixture was stirred briefly to resuspend the slurry immediately before buffer pH measurement.

The Sikora-2 method was evaluated following Sikora & Moore (2014). In the original protocol for the Sikora-2 method, pH_{KCl} is measured first, and then a modified Sikora buffer is added, followed by mixing and measurement of buffer pH. In this study, pH_{KCl} and Sikora buffer pH were analyzed on separate representative subsamples. Lime requirement estimates were calculated using these measurements with the Sikora-2 equations from Sikora & Moore (2014). Additionally, calculation of LRE using the Sikora-2 method requires a target pH_{KCl} . For the purposes of this calculation, the $\text{pH}_{1:2}$ targets used in this study—5.6, 6.0, and 6.4—were converted to pH_{KCl} using the following equation: $\text{pH}_{\text{KCl}} = 1.088 \cdot \text{pH}_{1:2} - 1.516$, which was derived from Sikora & Moore (2014). Therefore, the pH_{KCl} targets used for calculation were 4.58, 5.01, and 5.45 respectively.

The Single Addition of $\text{Ca}(\text{OH})_2$ method was evaluated following Sikora & Moore (2014): 20 ml 0.01 M CaCl_2 were mixed with 20 g soil and the pH of this mixture was recorded as

$\text{pH}_{\text{CaCl}_2}$. To this mixture 10 ml of saturated, standardized $\text{Ca}(\text{OH})_2$ (0.0220 – 0.0228 M) were added, and the mixture was placed on an end-to-end oscillating shaker at 180 rpm for 5 min. After 25 min of equilibration, the mixture was stirred to resuspend the soil, and pH was measured in the slurry. In order to accurately measure the high pH buffering capacity found in some Oregon soils 10 ml of $\text{Ca}(\text{OH})_2$ was used instead of 2.7 ml as in the original method. This amount was sufficient to increase $\text{pH}_{\text{CaCl}_2}$ by more than 0.3 units but not above $\text{pH}_{\text{CaCl}_2}$ 6.5 for all 24 soils evaluated, as recommended for the $\text{Ca}(\text{OH})_2$ method (Sikora & Moore, 2014). Calculation of estimated lime rate requires a target $\text{pH}_{1:1}$. The $\text{pH}_{1:2}$ targets used in this study were converted to $\text{pH}_{1:1}$ using the following equation: $\text{pH}_{1:1} = 0.99 \cdot \text{pH}_{1:2} - 0.04$, which was derived from Sikora & Moore (2014). Therefore the $\text{pH}_{1:1}$ targets used for calculation were 5.50, 5.90, and 6.30.

Statistical analysis

All statistical analysis was performed in RStudio Version 1.1.463 (R Core Team, 2018). The accuracy of candidate LRE methods was evaluated according to the coefficient of determination determined by linear regressions between candidate methods and LR_i . For the SMP, Sikora, Moore-Sikora, and Modified Mehlich methods, mean buffer pH was regressed with LR_i across the three pH targets of 5.6, 6.0, and 6.4. For the Sikora-2 and $\text{Ca}(\text{OH})_2$ methods, mean calculated LRE was regressed with LR_i across the three pH targets. Linear regression was determined using the base R function ‘lm’ (R Core Team, 2018).

The coefficient of determination was evaluated between soil test properties and LR_i for each pH target. Multiple linear regression models for the three pH targets were determined using a forward stepwise regression process. In this iterative process, candidate soil properties were added sequentially based on maximizing improvement to the AICc of the models. When no other

soil parameter improved AICc, the stepwise process halted. Candidate soil test properties used in this process were: pH_{1:2}; extractable Ca, K, Mg, Na, Mn, Fe, Cu and Zn; sum of extractable Ca, K, Mg, and Na; EC; KCl-extractable Al; SOM concentration; and sand, silt, and clay concentration. Linear and multiple linear regressions were determined using the base R function 'lm'. Stepwise regression was performed using the function 'stepwise' from the R package 'StepReg' (Li et al., 2020).

RESULTS AND DISCUSSION

Incubation lime requirement

As anticipated, soil pH increased with increasing CaCO₃ rate from 0 to 22.4 Mg ha⁻¹ for all 24 evaluated soils (Figure 2.1). The soils generally fell into two groups that differed in buffer capacity. Six highly buffered soils—Awbrig, Bashaw, Bellpine, Jory, Nekia-1, and Nekia-2—appeared to show a linear pH response to CaCO₃ across the evaluated CaCO₃ rates of 0 – 22.4 Mg ha⁻¹. These six soils increased in pH much less than the other 18 soils evaluated, only reaching pH 6.4 – 7.0 at the highest CaCO₃ rate of 22.4 Mg ha⁻¹. The high buffering capacity of these six soils is likely due to high levels of clay and SOM concentration, 426 – 530 g kg⁻¹ and 68 – 103 g kg⁻¹ respectively. In contrast, the remaining 18 soils showed a lower buffering capacity, reaching maximum pH values of 7.3 – 7.8. Furthermore, these 18 soils showed a gradual decrease in positive slope above pH 6.5, and appeared to approach a plateau of pH 7.0 – 7.5. These soils had a lower range of clay and SOM concentration, 104 – 403 g kg⁻¹ and 32 – 67 g kg⁻¹ respectively. Prior lime incubation studies saw similar lime incubation response, with a linear response below pH 6.5, and with decreases in slope above pH 6.5 (McFarland et al., 2020; Peterson, 1971). Apart from the six highly buffered soils (Awbrig, Bashaw, Bellpine, Jory,

Nekia-1, and Nekia-2), soils from the Willamette Valley appeared to respond to CaCO_3 addition similarly to soils from central and eastern Oregon. Appendix 2.2 summarizes the 3rd-order polynomial equations that relate CaCO_3 rate to post-incubation $\text{pH}_{1:2}$, as well as the LR_i values derived from those equations for the three $\text{pH}_{1:2}$ targets used in this study.

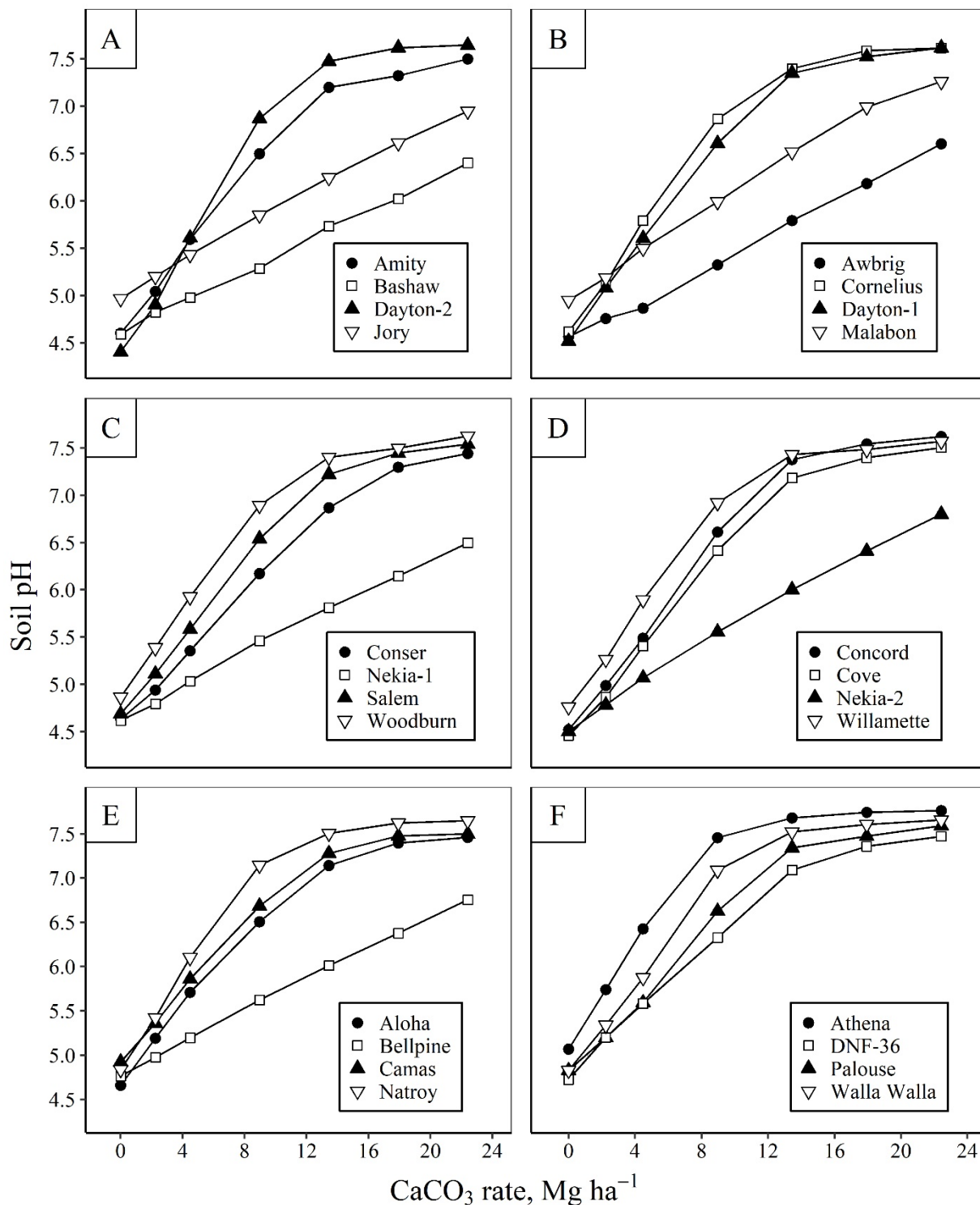


Figure 2.1. Soil pH_{1:2} response to increasing CaCO_3 application rate for 24 Oregon soils following a 90 d lime incubation. Points represent means of four replications; standard deviations ranged from 0.00 to 0.11 pH units. Plots A though E correspond to Willamette Valley soils. Plot F corresponds to central Oregon soils and eastern Oregon soils.

Buffer LRE method evaluation

In their linear regressions to LR_i , buffer pH for the SMP, Sikora, Modified Mehlich, and Moore-Sikora methods had similar r^2 ranging between .87 and .93, as shown in Figure 2.2. Among the four buffer LRE methods evaluated, the SMP and Sikora had the highest r^2 (.90 – .92 for both). Peterson (1971) showed similar results in correlations between SMP buffer pH and LR_i for a range of Willamette Valley soils, with $r^2 = .74 - .81$ across $pH_{1:2}$ targets. Sikora and SMP buffer pH also had similar regression equations, with slopes deviating by less than $0.5 \text{ Mg ha}^{-1} [\Delta \text{ buffer pH}]^{-1}$, and y-intercepts deviating less than 3.7 Mg ha^{-1} . This similarity is consistent with the original intent of the Sikora method (Sikora, 2006) to mimic the SMP method (Shoemaker et al., 1961). In addition to direct regression between Sikora buffer pH and LR_i , models combining Sikora buffer pH and $pH_{1:2}$ were evaluated (data not shown). However, these models did not lead to significant improvements to r^2 .

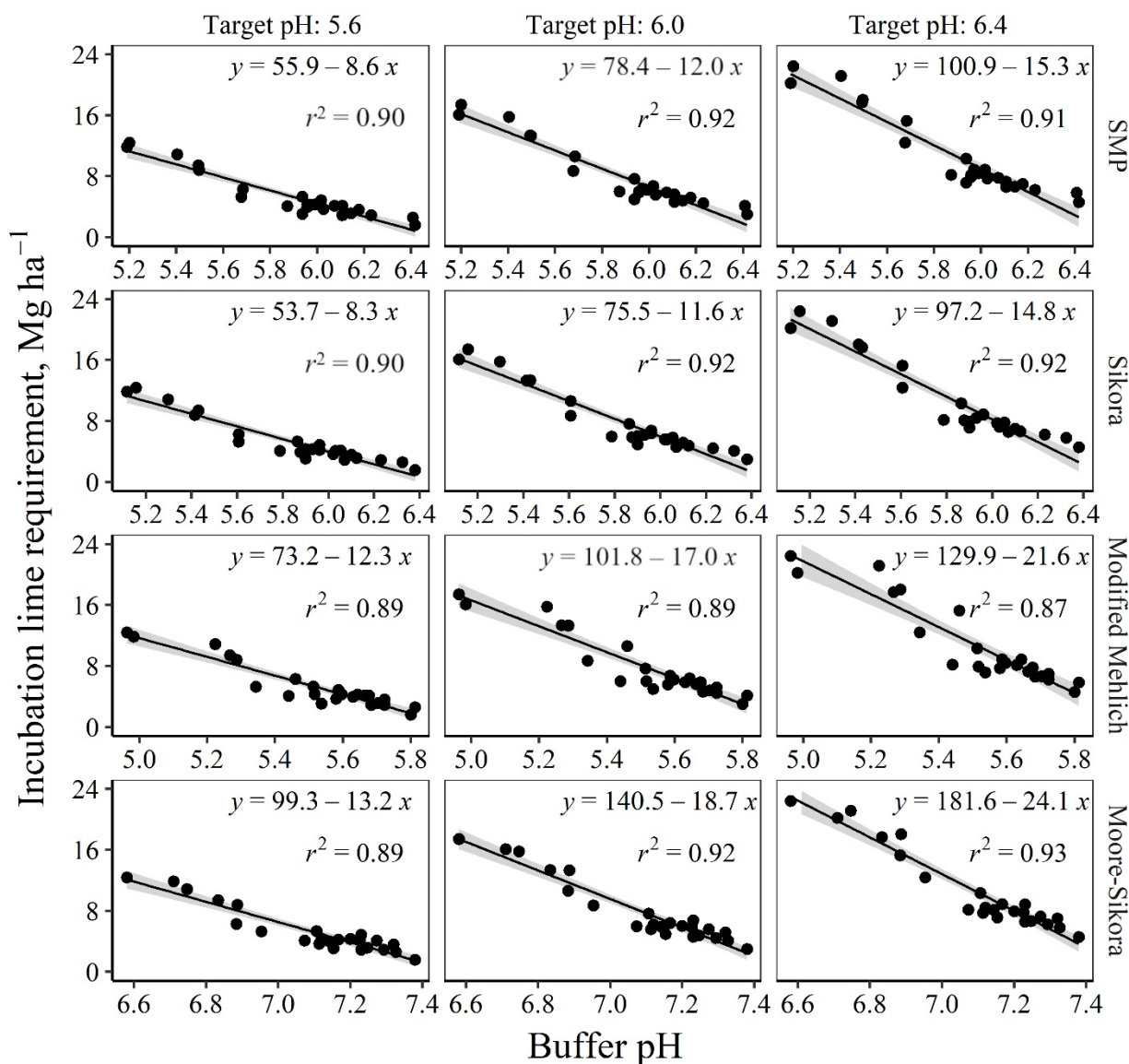


Figure 2.2. Linear regressions between buffer pH methods and incubation lime requirement for 24 Oregon soils. Rows correspond to candidate methods, and columns correspond to calibrations for specific pH targets. Data points represent mean buffer pH. Shaded regions indicate the 95% confidence interval for each regression line.

Buffer pH for the Modified Mehlich and Moore-Sikora methods had r^2 ranges of .87 – .89 and .89 – .93 respectively (Figure 2.2). However, the Moore-Sikora method showed greater replication variability than the other methods evaluated (Figure 2.3). For the Moore-Sikora method, 14 of the 24 soils evaluated had replication SD values above 0.05 buffer pH units. In

contrast, the SMP, Sikora, and Modified Mehlich methods respectively had one, zero, and three soils with SD values above this level. The two soils with the lowest Moore-Sikora buffer pH, Awbrig and Bashaw, also had the highest SD values of 0.14 and 0.13 respectively. These soils are classified as smectitic, and have high levels of clay and SOM (436 – 476 g kg⁻¹ and 68 – 70 g kg⁻¹ respectively). These findings show that replication variability is important to consider in addition to the r^2 value of linear regression.

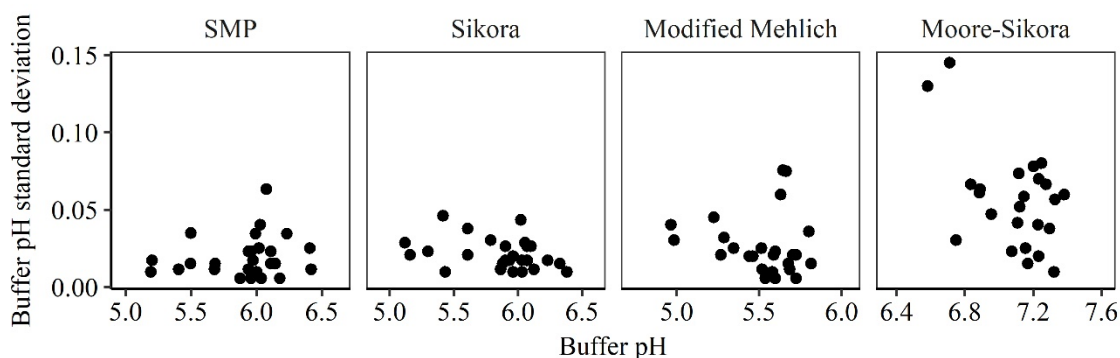


Figure 2.3. Variability in buffer pH test results for 24 Oregon soils.

These results indicate that among the buffer methods evaluated, the SMP, Sikora, and Modified Mehlich methods were the most suitable for predicting lime requirement for Oregon soils. The SMP, Sikora, and Modified Mehlich methods had strong correlations to LR_i ($r^2 = .87 - .92$ overall) in this study, possibly because the Oregon soils used had similar ranges in clay concentration (104 – 530 g kg⁻¹) and SOM concentration (32 – 103 g kg⁻¹) to the regions where those methods were developed. For example, the SMP method was originally developed to predict a range of lime requirement from 2 to 28 Mg ha⁻¹ (Shoemaker et al., 1961). The 14 Ohio soils used to evaluate and calibrate the SMP method had clay concentration of approximately 170 to 370 g kg⁻¹ (Shoemaker, 1959). Similarly, the original Mehlich buffer method (Mehlich, 1976) was developed using 91 North Carolina mineral soils with a range of clay concentration of approximately 100 to 300 g kg⁻¹.

Furthermore, the SMP, Sikora, and Modified Mehlich methods have been determined to be suitable in regions with similar clay and SOM concentration to Oregon soils. Keeney & Corey (1963) determined the SMP method to be suitable for Wisconsin soils. The 26 soils used by Keeney & Corey had a wide range of SOM (14 – 170 g kg⁻¹) and clay concentration (50 – 270 g kg⁻¹). Santanna et al. (2011) also determined the Sikora method to be suitable for Brazilian soils based on a study of 24 soils with ranges of clay concentration from 56 to 601 g kg⁻¹ and SOM concentration from 11 to 82 g kg⁻¹. Nathan et al. (2012) showed the Sikora and the Modified Mehlich methods to be suitable for Missouri based on a study of 30 soils with clay concentration ranging from approximately 150 to 350 g kg⁻¹ and SOM ranging from 13 to 52 g kg⁻¹.

In contrast, the high replication variability of the Moore-Sikora method (with 14 soils having buffer pH SD greater than 0.05 units) indicates that this method would be less suitable as an LRE method for Oregon soils. The high replication variability of the Moore-Sikora method seen in this study may be due to differences in soil type between Oregon soils and the soils used to develop the Adams-Evans method (Adams & Evans, 1962), which the Moore-Sikora method is based on. The Adams-Evans method was originally developed to estimate a narrow range of lime requirement from 0.2 to 10 Mg ha⁻¹, for ‘red-yellow podzolic soils’ in Alabama, soils which have low CEC, low clay concentration, and low SOM (Adams & Evans, 1962; Sikora & Moore, 2014). Since the Moore-Sikora buffer was designed to mimic the Adams-Evans buffer, it is possible that the high replication variability of the Moore-Sikora method was caused by the high clay or SOM concentration in the Oregon soils used in this study. A controlled study would be needed to confirm which characteristics of Oregon soils contribute to high replication variability of the Moore-Sikora method. Furthermore, the Adams-Evans and Moore-Sikora methods are intended to estimate lime requirement only when buffer pH is between 7.0 and 8.0 (Adams &

Evans, 1962; Sikora & Moore, 2008). Seven of the 24 soils in this study were below this range, underscoring the unsuitability of the Moore-Sikora method for Oregon soils.

Lime buffer capacity LRE methods

The $\text{Ca}(\text{OH})_2$ method had weaker regression to LR_i across $\text{pH}_{1.2}$ targets ($r^2 = .69 - .77$, Figure 2.4) than the SMP, Sikora, Moore-Sikora, and Modified Mehlich buffer methods evaluated above. A disproportionate amount of regression deviation came from the six highly buffered soils mentioned previously: Awbrig, Bashaw, Jory, Nekia-1, Nekia-2, and Bellpine. The Awbrig and Bashaw soils were classified as having smectitic mineralogy, and the Jory, Nekia-1, Nekia-2, and Bellpine soils were classified as having mixed mineralogy, implying that they may include smectite or other charged 2:1 clays, among other clay minerals. The 17 soils used by Liu et al. (2005) to develop the $\text{Ca}(\text{OH})_2$ method had similar clay concentration (23 – 507 g kg^{-1}) to Oregon soils, but a smaller range of SOM concentration (7 – 54 g kg^{-1}). Furthermore, only three of the soils used by Liu et al. (2005) were classified as having mixed mineralogy, with the remainder classified as kaolinitic or siliceous. The $\text{Ca}(\text{OH})_2$ method may be more appropriate for soils with predominantly 1:1 kaolinite clays as opposed to 2:1 clays. Controlled studies would be needed to confirm the effect of clay type on $\text{Ca}(\text{OH})_2$ method accuracy.

The Sikora-2 method correlated strongly to LR_i across $\text{pH}_{1.2}$ targets ($r^2 = .81 - .93$, Figure 2.4). However, r^2 values were not higher than those produced by the Sikora (2006) or SMP (Shoemaker et al., 1961) methods in this study.

The LR values predicted by the $\text{Ca}(\text{OH})_2$ and Sikora-2 methods were lower than corresponding LR_i values. Sikora & Moore (2014) note that corrective factors are recommended for both of these methods in order to convert from method-predicted LR to actual LR. A

corrective factor has been developed for the $\text{Ca}(\text{OH})_2$ method using Georgia soils (Sonon & Kissel, 2015), and a corrective factor for Kentucky soils has been developed for the Sikora-2 method (Sikora & Moore, 2014). If the $\text{Ca}(\text{OH})_2$ or Sikora-2 methods were to be used in Oregon, the regression equations shown in Figure 2.4 could be used to recommend similar adjustments.

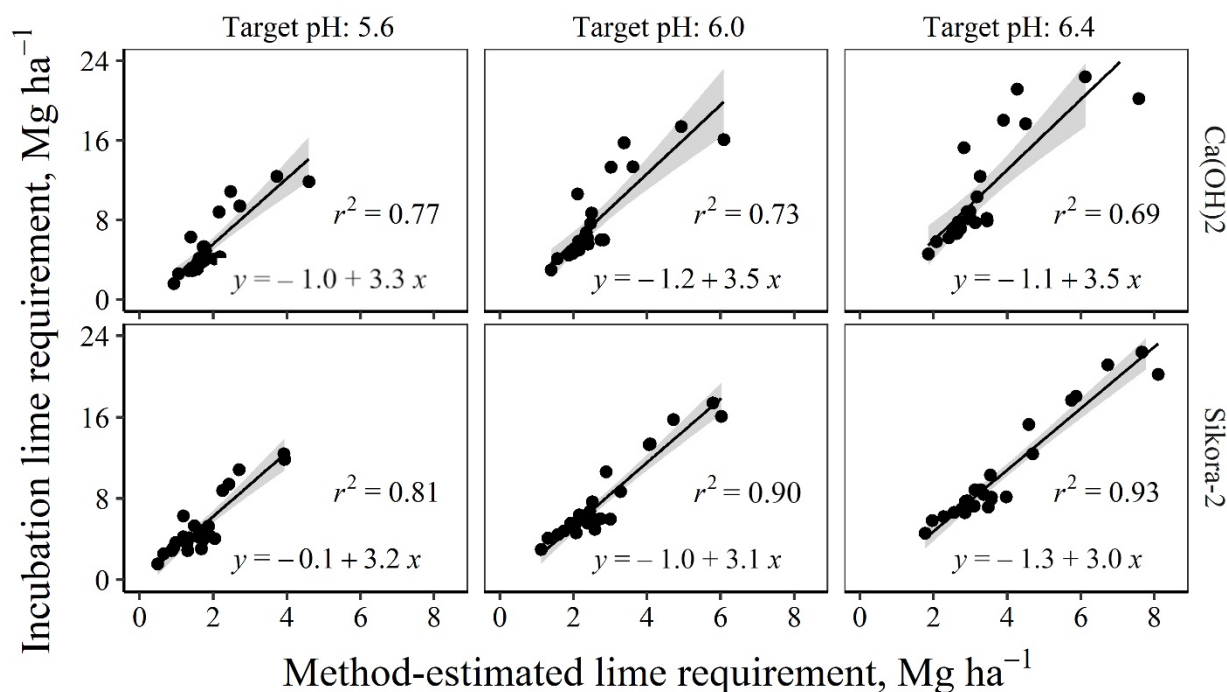


Figure 2.4. Linear regressions between incubation LR and lime buffer capacity methods, for 24 Oregon soils. Shaded regions indicate the 95% confidence interval for each regression line.

LRE modeling with soil properties

The agronomic soil test properties evaluated showed variable correlation with LR_i (Table 2.5). Clay, SOM, and CEC had high correlation with LR_i across $\text{pH}_{1:2}$ targets ($r^2 > .50$). Among the various measures of soil pH ($\text{pH}_{\text{CaCl}_2}$, pH_{KCl} , $\text{pH}_{1:1}$, $\text{pH}_{1:2}$), none correlated significantly to LR_i . The parameter with the strongest correlation to LR_i , clay concentration, had lower r^2 (.64 – .77) than the SMP and Sikora methods ($r^2 = .91 - .93$). For this reason, LRE models combining multiple soil properties were also evaluated.

Table 2.5. Coefficients of determination between soil properties and incubation lime requirement for three pH targets.

Soil test property	Unit	r^2		
		— pH _{1:2} targets —		
		5.6	6.0	6.4
Clay	g kg ⁻¹	.65	.73	.78
SOM ^a	g kg ⁻¹	.61	.71	.76
CEC	cmol _c kg ⁻¹	.61	.64	.66
Silt	g kg ⁻¹	.36	.42	.45
Al ^b	mg kg ⁻¹	.42	.36	.31
Base Saturation	%	.27	.25	.24
Cu ^c	mg kg ⁻¹	.21	.20	.18
Mn ^c	mg kg ⁻¹	.14	.12	.10
Electrical Conductivity	dS m ⁻¹	.09	.10	.09
K ^d	mg kg ⁻¹	.12	.10	.08
Fe ^c	mg kg ⁻¹	.06	.06	.06
Ca ^d	cmol _c kg ⁻¹	.04	.06	.07
pH _{CaCl2}		.08	.04	.02
Mg ^d	cmol _c kg ⁻¹	.05	.04	.04
Na ^d	cmol _c kg ⁻¹	.05	.04	.04
Zn ^c	mg kg ⁻¹	.02	.03	.03
Sum of Ca, K, Na, and Mg ^d	cmol _c kg ⁻¹	.03	.04	.04
Sand	g kg ⁻¹	.02	.02	.02
pH _{1:1}		.03	.01	.01
pH _{KCl}		.03	.01	<0.01
pH _{1:2}		.01	<0.01	<0.01

^a Walkley-Black method.

^b KCl extractable.

^c DTPA extractable.

^d NH₄OAc extractable.

Table 2.6. Multi-parameter linear models for estimating lime requirement for three pH targets. Models were constructed using a forward stepwise regression method with incubation lime requirement as the dependent variable.

pH _{1:2} target	Equation ^a	r ²
5.6	LRE = 0.2 + 0.0181[Clay]	.65
6.0	LRE = 0.3 + 0.0266[Clay]	.73
6.4	LRE = 0.7 + 0.0351[Clay]	.78
5.6	LRE = -0.5 + 0.0150[Clay] + 0.0246[Al]	.83
6.0	LRE = -0.5 + 0.0230[Clay] + 0.0283[Al]	.85
6.4	LRE = -0.2 + 0.0312[Clay] + 0.0309[Al]	.87
5.6	LRE = -1.1 + 0.00808[Clay] + 0.0248[Al] + 0.0491[SOM]	.85
6.0	LRE = -1.5 + 0.0123[Clay] + 0.0286[Al] + 0.0768[SOM]	.89
6.4	LRE = -1.6 + 0.0160[Clay] + 0.0314[Al] + 0.109[SOM]	.91
5.6	LRE = -2.3 + 0.00311[Clay] + 0.0271[Al] + 0.0753[SOM] + 0.582[Mg]	.90
6.0	LRE = -3.0 + 0.00595[Clay] + 0.0315[Al] + 0.110[SOM] + 0.739[Mg]	.93
6.4	LRE = -3.3 + 0.00883[Clay] + 0.0346[Al] + 0.146[SOM] + 0.841[Mg]	.94
5.6	LRE = 18.6 – 0.00308[Clay] + 0.0244[Al] + 0.122[SOM] + 0.975[Mg] – 4.31[pH]	.96
6.0	LRE = 19.6 – 0.000715[Clay] + 0.0285[Al] + 0.160[SOM] + 1.16[Mg] – 4.64[pH]	.96
6.4	LRE = 21.2 + 0.00157[Clay] + 0.0314[Al] + 0.201[SOM] + 1.30[Mg] – 5.05[pH]	.97

^a LRE = Lime requirement estimate in Mg ha⁻¹, Clay = clay concentration (g kg⁻¹), Al = KCl-extractable Al (mg kg⁻¹), SOM = soil organic matter concentration (Walkley-Black method, g kg⁻¹), Mg = NH₄OAc-extractable Mg (cmol_c kg⁻¹), pH = pH_{1:2}

For pH_{1:2} targets 5.6, 6.0, and 6.4, the stepwise regression process produced multi-parameter linear models that used clay concentration, KCl-extractable Al, SOM, Mg, and pH_{1:2} (Table 2.6). As mentioned above, KCl-extractable Al, and SOM have been shown by prior studies to be effective for lime requirement estimation (Keeney & Corey, 1963; Lemire et al., 2005; McFarland et al., 2020; Miller et al., 2005).

Clay concentration has been used in some cases to estimate lime requirement. According to Follett & Follett (1983) regional laboratories from NJ, TX, MD, CT, and DE reported using soil texture class in conjunction with soil pH or SOM and soil pH to make lime rate recommendations. In published work, clay concentration has not been shown to be among the soil properties most useful for LRE. Keeney & Corey (1963) found clay concentration correlated to incubation lime requirement of Wisconsin soils with $r^2 = .04$, and did not find clay concentration to be a useful parameter when combined with other soil properties. Lemire et al. (2005), Miller et al. (2005), and McFarland et al. (2020) evaluated clay concentration alongside other soil properties for lime requirement estimation, but did not include clay concentration in any of their proposed models, presumably due to lack of a strong statistical relationship to incubation lime requirement among the soils evaluated. McFarland et al. (2020) evaluated soils with a narrow range of clay concentration (110 – 190 g kg⁻¹), which could explain a poor correlation to incubation lime requirement. However, Miller et al. (2005) and Lemire et al. (2005) had clay concentration ranges (40 – 610 g kg⁻¹ and 40 – 530 g kg⁻¹ respectively) similar to the ones in this study (104 – 530 g kg⁻¹), and also did not find compelling reasons to recommend the use of clay concentration for lime requirement estimation. The strong relationship between clay concentration and LR_i seen in this study ($r^2 = .65 - .78$) may be attributable to a greater prevalence of negatively charged 2:1 clays in Oregon soils compared to the soils used by Miller

et al. (2005) and Lemire et al. (2005). However those authors did not list mineralogy classifications for the soils they used, therefore a clear cause for the difference between this study and prior work cannot be established. At the very least, the fact that the findings of this study contrasted with other soil property LRE work indicates that the usefulness of clay concentration for predicting lime requirement may vary significantly by region.

A relationship between extractable Mg and lime requirement has not been documented. Sims (1996) reported that some unidentified laboratories estimate lime requirement in part using Ca+Mg saturation of CEC. A potential explanation for the result seen in this study may be that extractable Mg is serving as an indirect indication of mineralogy, as 2:1 clay minerals such as smectite, illite, vermiculite, and chlorite contain Mg, while kaolinite does not (Brady & Weil, 2008).

This study focused primarily on evaluating the accuracy of LRE methods relative to incubation lime requirement. Baker & Chae (1977) and Doerge & Gardner (1988) have shown that some differences may exist between incubation lime requirement and field lime requirement. For this reason, a follow-up study based on field lime requirement could be used to develop LRE method calibrations with even higher accuracy than ones produced by this study. Furthermore, the inclusion of other Oregon soil types including histosols, andisols, and sandy-textured soils in future studies can help to determine if alternative equations are needed to estimate lime requirement on these less common but still important soil types.

CONCLUSION

Several non-hazardous LRE methods have recently replaced hazardous methods in regions throughout the United States. However, none of these non-hazardous methods have previously

been evaluated to replace the hazardous SMP method in Oregon. A laboratory lime incubation trial was conducted to determine the LR_i of 24 Oregon soils. Six non-hazardous LRE methods were regressed to LR_i for three $pH_{1:2}$ targets of 5.6, 6.0, and 6.4 to determine their accuracy. The SMP method had $r^2 = .90 - .92$ across $pH_{1:2}$ targets. The Sikora, Modified Mehlich, and Moore-Sikora methods showed comparable accuracy to the SMP method, with r^2 values of $.90 - .92$, $.87 - .89$, and $.89 - .93$ respectively. However, the Moore-Sikora method was also found to have poor precision, with 14 of 24 soils having buffer pH SD higher than 0.05 Mg ha^{-1} for replicated measurements. The Sikora-2 method had slightly lower accuracy than the SMP method, with $r^2 = .81 - .93$. The Ca(OH)_2 method was less accurate than the SMP method, with $r^2 = .69 - .77$. The use of soil properties for estimating lime requirement was also explored. Among the soil properties evaluated in this study, clay concentration showed the strongest correlation to incubation lime requirement, with r^2 values of $.65 - .78$. A series of multi-parameter linear equations were developed using stepwise regression. This process produced equations for estimating lime requirement that used clay concentration, KCl-extractable Al, SOM, NH_4OAc -extractable Mg, and $pH_{1:2}$ (with $r^2 = .96 - .97$ across targets). Overall, these results indicate that multiple non-hazardous LRE methods could replace the hazardous SMP method for Oregon soils.

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**CHAPTER 3: QUANTIFYING THE EFFECTS OF MODIFICATIONS TO THE
SIKORA BUFFER PH METHOD FOR OREGON SOILS**

ABSTRACT

The Sikora buffer pH method is a non-hazardous alternative to the SMP method for estimating lime requirement (LRE) for Oregon soils. Commercial soil testing laboratories may implement method modifications in order to streamline the method for large-scale testing, however, the potential effects of these modifications on buffer pH results are currently unknown. Modifications that artificially increase buffer pH are of particular concern, as they could result in under-application of lime and crop damage. The goal of this project was to evaluate and quantify five Sikora buffer pH method modifications for five Oregon agricultural soils. The five soil series evaluated did not show a significant interaction effect with method modifications. Modifications related to mixing method, measurement in supernatant instead of slurry, and soil:water:buffer ratio were found to significantly increase Sikora buffer pH results by 0.063, 0.065, and 0.058 units respectively in comparison to the control. Mean Sikora buffer pH decreased by 0.02 – 0.05 units when equilibration time was increased from 0 to 180 min. Our findings show how even minor modifications can alter Sikora buffer pH results, illustrating the importance of avoiding deviations from the original method. Additionally, comparing results among labs may help minimize over- or under-recommending of lime to agricultural fields.

INTRODUCTION

The Sikora buffer pH method is a soil test method used to estimate the amount of lime (CaCO_3) needed to raise soil pH to a desired target (Sikora, 2006). In the Sikora method, a soil sample is mixed with deionized water and the Sikora buffer, and the measured pH of this mixture is recorded as buffer pH. Using an appropriate regional calibration, a buffer pH measurement can be converted to a lime rate recommendation. Sikora buffer pH is highly correlated to incubation lime requirement for Oregon soils for pH targets ranging from 5.6 to 6.4 ($r^2 = .90 - .92$; see

Chapter 2). However, implementation of the Sikora method may not be completely uniform across soil testing laboratories. For example, the original publication of the Sikora method (2006) differs from the procedure published by Sikora & Moore (2014) in the amount of time that is recommended to wait between mixing and buffer pH measurement. Other modifications of the method may be desired in order to streamline the Sikora method and reduce labor and equipment costs. Specific aspects of the Sikora method that may be modified include equilibrium timing, the method used to shake samples, stirring the slurry immediately prior to pH measurement, and the type of electrode used.

Following the procedure published by Sikora (2006), buffer pH measurement should be made immediately after completion of shaking, while in the procedure published by Sikora & Moore (2014), measurement should be made exactly 30 min after completion of shaking. In either case, a specific timing requirement would theoretically make processing samples in batches more difficult, because samples within a batch may vary in the amount of time they equilibrate with Sikora buffer. Research by Baker & Chae (1977) indicates that SMP buffer pH can decrease 0.2 units over 360 min of equilibration time between soil and buffer. These findings suggest that equilibrium timing should be evaluated for the Sikora method to determine if extended wait periods between mixing and pH measurement significantly alter Sikora buffer pH.

The Sikora method requires mixing on an end-to-end shaker table (Sikora, 2006; Sikora & Moore, 2014). Soil testing laboratories use a variety of mixing methods, including end-to-end and orbital shaker tables. Differences in shaking could affect the speed of reaction between soil acidity and the Sikora buffer, thereby changing the buffer pH at the time of measurement. For this reason the effect of mixing method should be evaluated.

The Sikora method requires buffer pH measurement in the soil slurry (Sikora, 2006; Sikora & Moore, 2014). Soil testing laboratories will often place the pH electrode in the buffer-soil solution supernatant to remove the additional step of re-mixing immediately before measurement. Prior research suggests that soil pH measurement can change depending on whether the slurry is mixed immediately prior to pH measurement, or if pH measurement is made in the supernatant. Coleman et al. (1951) showed soil pH measurements to be on average 0.28 units higher in the supernatant than in the suspended slurry, for 12 soils with a range of characteristics. Conversely, Sumner (1994) showed that soil pH measurements made with the reference junction in the supernatant were approximately 0.2 units lower compared to measurements made with the reference junction in the sediment. Given these results, it appears that buffer pH could be increased or decreased by measuring in the supernatant, relative to measurement in slurry. However, any effect of supernatant measurement on buffer pH is unknown at this time.

In the Sikora method, soil is mixed with water on a 1:1 basis, prior to addition of Sikora buffer. In Oregon, soil pH recommendations are based on $pH_{1:2}$ (1:2 soil:water; Hart et al., 2013). Therefore evaluation of $pH_{1:2}$ and Sikora buffer pH require two soil test procedures, and more total time and labor than a single procedure that integrates $pH_{1:1}$ with the Sikora method. Soil $pH_{1:2}$ evaluation could be integrated with the Sikora method by increasing the amount of water added to soil before Sikora buffer is added. This modification could reduce labor but it could also cause a change in measured buffer pH. In comparing median soil pH values for 134 samples in the North American Proficiency Testing program, Sikora & Moore (2014) showed $pH_{1:2}$ values to be approximately 0.1 units higher than $pH_{1:1}$ values on average. It is unclear if altering the soil:water:buffer ratio would have a similar effect on buffer pH.

The Sikora (2006) method does not require a specific style of pH electrode, however multiple styles exist. Some soil testing laboratories use a pH electrode that has a reference junction that extends around the circumference of the electrode. Other soil testing laboratories are noted to use pH electrodes with a reference junction that is a single point on the side of the electrode. Sumner (1994) showed that pH measurement is dependent on the electrical connection between the reference junction and the exterior of the H⁺-sensitive bulb. For this reason, altering the shape of the reference junction could influence this connection, thereby altering buffer pH measurement.

The goal of this project was to evaluate and quantify Sikora buffer pH method modifications for five Oregon agricultural soils. Modifications included extended equilibration time ranging from 0 to 180 min, slurry vs. supernatant measurement, end-to-end vs. orbital mixing, 1:1:1 vs. 1:2:1 soil:water:buffer ratio, and single point vs. circular reference junction styles of pH electrode.

MATERIALS AND METHODS

Soil collection and characterization

Five acid soils with a range of characteristics were selected from different regions of Oregon for this study. Three soils, Bashaw, Nekia-1, and Woodburn, are from the Willamette Valley in Oregon. Athena is from eastern Oregon. The soil labelled DNF-36 is from central Oregon. Soils had pH_{1:2} of 5.5 or less, in order to cover the range of Oregon soils most likely to need lime application. Samples were collected from within a 1-meter area using a sharpshooter shovel. Bashaw, Woodburn, and Athena were collected from 0 – 15 cm soil depth. Nekia-1 and DNF-36 were collected from 0 – 7.5 cm soil depth in order to ensure soil pH_{1:2} below 5.5.

Soil pH_{1:2} (1:2 soil:water) was evaluated according to Thomas (1996). Soil KCl-extractable Al was evaluated following procedure S – 15.10 from Gavlak et al. (2005). Cation exchange capacity at pH 7.0 (CEC) was evaluated following procedure S – 10.10 from Gavlak et al. (2005), replacing 1 M NH₄OAc with 1 M NaOAc in the initial extraction step, and replacing HCl with 1 M NH₄OAc in the final Na displacement step. Soil K, Ca, Mg, and Na were extracted with NH₄OAc following procedure S – 5.10 from Gavlak et al. (2005). Base saturation was calculated by dividing the sum of extractable K, Ca, Mg, and Na by CEC. Extracted Al, K, Ca, Mg, Na, and displaced Na were analyzed using inductively-coupled plasma atomic emission spectroscopy (Optima 7300DV, Perkin Elmer, Waltham, MA). Sand, silt, and clay concentration were evaluated using the hydrometer method, following procedure S – 14.10 from Gavlak et al. (2005). Soil organic matter was evaluated using the Walkley-Black method following procedure S – 9.10 from Gavlak et al. (2005). A spectrometer (Aquamate 8000, Thermo Fisher Scientific, Waltham, MA) was used to evaluate Cr³⁺ instead of titration, a modification recommended by Sims & Haby (1971). Characterization and taxonomic classification are shown in Table 3.1.

Table 3.1. Taxonomic classification, and mean pH_{1:2}, KCl-extractable Al, CEC, base saturation (BS), and clay and SOM concentration for five Oregon agricultural soils. Nekia-1 and DNF-36 were sampled from the 0 – 7.5 cm soil depth, while all other soils were sampled from the 0 – 15 cm soil depth.

Region and soil series	Classification	pH _{1:2}	Al _{KCl} mg kg ⁻¹	CEC cmol _c kg ⁻¹	BS %	Clay — g kg ⁻¹ —	SOM
Willamette Valley							
Bashaw	Xeric Endoaquerts	5.1	78	39.0	50	476	70
Nekia-1	Xeric Haplohumults	5.0	106	27.7	29	532	103
Woodburn	Aquultic Argixerolls	5.2	65	18.9	44	210	36
Eastern Oregon							
Athena	Pachic Haploxerolls	5.3	2	17.4	76	177	32
Central Oregon							
DNF-36	Unit 36: Sandy volcanic ash soils ^a	5.5	55	12.4	41	104	59

^a Source: Soil Survey Staff, National Resources Conservation Service.

^b The soil sample from central Oregon does not have an assigned soil series; in this paper it will be referred to as ‘DNF-36’. Classification from Larsen (1976).

Modifications to the Sikora method

Method modifications were divided into three trials. Trial 1 evaluated circular mixing and single point reference junction (SPRJ) pH electrode treatments. Trial 2 evaluated the measurement in supernatant and 1:2:1 soil:water:buffer ratio treatments. Trial 3 evaluated the effect of additional equilibration time.

Trial 1 had two factors, organized in a split-plot randomized complete block design. The main plot factor consisted of three method modification treatments: a control treatment, a circular mixing treatment, and a SPRJ pH electrode treatment. The subplot factor consisted of the five soil types. Three full blocks were evaluated across three days. With three treatments, five soil types, and three blocks, there were 45 experimental units. A split plot randomized complete block design was used because these modification treatments required separate equipment, which

prevented complete randomization between modifications. The supernatant and 1:2:1 soil:water:buffer ratio treatments could be randomized together more easily, therefore they were analyzed separately in a complete randomized design in Trial 2.

Control: The control method was the Sikora buffer pH method as described in Sikora & Moore (2014): 10 g of soil were combined with 10 ml of deionized water in a 50 ml centrifuge tube, and allowed to sit for 15 min, followed by addition of 10 ml of Sikora buffer. This mixture was capped, and mixed on an end-to-end oscillating shaker for 10 min at 180 oscillations per min (opm). This mixture sat for an equilibration time of 30 min. The capped tube was briefly inverted several times to form a slurry, the cap was removed and buffer pH was measured in the soil suspension. Buffer pH was measured using an Orion ROSS Sure-Flow pH electrode with an Orion Star A211 Benchtop pH meter (Thermo Fisher Scientific, Waltham, MA). This pH electrode has a circular reference junction that extends around the circumference of the glass electrode. Samples were processed sequentially, instead of in batches, to maintain established shaking and equilibration time periods for all samples.

Circular mixing: Samples were mixed in polypropylene medicine vials (6.3 cm in height with 4.2 cm diameter at the base and 4.6 cm diameter at the top), instead of 50 ml centrifuge tubes. Maintaining the 1:1:1 soil:water:buffer ratio, quantities of soil, water, and buffer were increased to 15 g, 15 ml, and 15 ml respectively, in order to ensure sufficient depth of slurry for complete immersion of the pH electrode. After addition of the Sikora buffer, vials were placed upright and uncapped on an orbital shaker that oscillated at a rate of 200 opm, with an orbital diameter of 1.9 cm, instead of the end-to-end shaker used in the control treatment.

SPRJ pH electrode: Buffer pH was evaluated using a HI-1131B pH electrode with an HI 5522 pH meter (Hanna Instruments, Woonsocket, RI). This alternate pH electrode had a single-

point reference junction, in contrast to the circular reference junction electrode used for the control.

Trial 2 had two factors, organized in a complete randomized design. The first factor consisted of a control treatment, measurement in supernatant, and use of 1:2:1 soil:water:buffer ratio. The second factor consisted of the five soil types. Three replications were used. With three treatments, five soil types, and three replications, there were 45 experimental units. The control treatment was evaluated as in Trial 1.

Measurement in supernatant: Buffer pH was measured in the supernatant, instead of inverting to resuspend the slurry immediately before measurement.

1:2:1 soil:water:buffer ratio: In the first step, 20 ml of deionized water were mixed with soil instead of 10 ml, giving the final mixture a soil:water:buffer ratio of 1:2:1, instead of 1:1:1, as in the control.

Trial 3 evaluated the effect of additional equilibration time in a randomized complete block design, with repeated measures. Buffer pH was evaluated as described in the supernatant treatment described above, with buffer pH measured repeatedly in the same vials at 0, 15, 30, 60, 120, and 180 min after removing from the shaker. The vials were lightly swirled before each measurement in order to agitate the supernatant. With five soil types, three replications, and six repeated measurements, there were 90 measurements in this experiment.

Statistical analysis

The significance of effects for Trial 1 and Trial 2 were evaluated using SAS statistical software version 9.4, using the PROC GLM procedure (SAS Institute, 2016). For Trial 1, the significance of blocking, method modification, soil type, and modification-soil type interaction

were evaluated with a split-plot analysis of variance with method modification as a main plot effect and soil type as a sub-plot effect. For Trial 2, the significance of method modification, soil type, and their interaction were evaluated as main effects in an analysis of variance. For Trial 1 and Trial 2, the significance of comparisons between method modifications and control were evaluated by applying contrast statements in PROC GLM.

RESULTS

Trial 1 and Trial 2: Treatment effects of mixing, electrode Type, soil:water ratio, and measurement in supernatant

Sikora buffer pH means for qualitative modifications are shown in Table 3.2. Summaries of the analyses of variance are shown in Table 3.3. Method modification and soil type had significant effects on Sikora buffer pH at the .05 significance level, however these factors did not show significant interaction. These soils varied considerably in clay and SOM concentration (Table 3.1). Due to a lack of interaction between method modifications and soil type, further discussion will focus on the main effects of the qualitative Sikora method modifications.

Table 3.2. Sikora buffer pH response to various method modifications for five Oregon agricultural soils. Reported values are means of three measurements.

Trials and method modifications	Sikora buffer pH				
	Bashaw	Nekia	Woodburn	Athena	DNF-36
Trial 1					
Control ^a	5.10	5.28	5.98	6.32	5.92
Circular mixing	5.14	5.36	6.04	6.37	6.01
SPRJ ^b pH electrode	5.12	5.30	6.02	6.34	5.95
Trial 2					
Control ^a	5.04	5.21	5.98	6.31	5.86
Measurement in supernatant	5.12	5.29	6.02	6.35	5.95
1:2:1 soil:water:buffer ratio	5.14	5.29	6.01	6.34	5.91

^a The control treatment is defined as: (1) 40 min of equilibration between soil, water, and buffer, (2) end-to-end shaking in a sealed 50 ml centrifuge tube, (3) buffer pH measurement using a circular reference junction pH electrode, (4) buffer pH measurement in suspended slurry, and (5) soil:water:buffer ratio of 1:1:1.

^b SPRJ, single point reference junction

Table 3.3. Analysis of variance summaries of two trials evaluating the effect of modifications to the Sikora buffer pH method.

Source of variation	p-value	
	Trial 1 ^a	Trial 2 ^b
Method modification (M)	< .0001	< .0001
Soil type (S)	< .0001	< .0001
M × S	.633 NS [†]	.071 NS [†]

^a Treatments included: Control, circular mixing, and single point reference junction pH electrode

^b Treatments included: Control, measurement in supernatant, and 1:2:1 soil:water:buffer ratio.

[†] NS, nonsignificant at the .05 probability level

Modification effects that vary more than 0.05 buffer pH units from the control are of particular concern. Lime recommendations for Oregon based on the Sikora method will likely be interpreted in 0.1 buffer pH unit increments, as is currently done for the SMP method in Oregon (Anderson et al., 2013). A difference of 0.1 Sikora buffer pH units alters lime recommendations by 0.8, 1.1, and 1.5 Mg/ha (or 0.4, 0.5, and 0.7 ton/acre) for pH targets 5.6, 6.0, and 6.4, respectively (See Figure 2.2 in Ch. 2). While an over-application of lime at these quantities would cause little concern for crop production, an under-application of lime at this level could

prevent growers from controlling soil acidity. This could stunt plant growth, produce sub-optimal yields, and compromise crop quality (Hart et al., 2013). A difference of 0.05 units or greater is likely to cause the rounded buffer pH to change by 0.1 units, therefore method modifications that have significant effects greater than 0.05 buffer pH units will be targeted for discussion.

Table 3.4. Contrasts evaluating the effect of modifications to the Sikora buffer pH method.

Contrasts	Buffer pH mean difference	p-value
	buffer pH units	
Control ^a vs. Circular mixing	0.063	<.0001
Control vs. SPRJ ^b pH electrode	0.024	.0592†
Control vs. Measurement in supernatant	0.065	<.0001
Control vs. 1:2:1 soil:water:buffer ratio	0.058	<.0001

^a The control treatment is defined as: (1) 30 min of equilibration between soil, water, and buffer, (2) end-to-end shaking in a sealed 50 ml centrifuge tube, (3) buffer pH measurement using a circular reference junction pH electrode, (4) buffer pH measurement in suspended slurry, and (5) overall soil:water:buffer ratio of 1:1:1.

^b SPRJ, single point reference junction

† NS, nonsignificant at the .05 probability level

The circular mixing, measurement in supernatant, and 1:2:1 soil:water:buffer ratio method modifications showed a significant difference in buffer pH value ($p < .05$) from the control treatment, as indicated by the contrasts in Table 3.4. The SPRJ pH electrode treatment was not significantly different from the control.

The lack of a significant effect from the SPRJ electrode treatment indicates that this difference in pH electrode design is not expected to have an impact on Sikora buffer pH results. Only two electrodes were evaluated, therefore, it may be desirable to evaluate differences between other electrode types and models.

The circular mixing and 1:2:1 soil:water:buffer ratio modifications significantly increased mean buffer pH across soil types by 0.063 and 0.058 buffer pH units, respectively, in comparison

to the control treatment (table 3.4). As these modifications could increase buffer pH by up to 0.1 buffer pH units, lime recommendations could be artificially decreased by 0.8 – 1.5 Mg ha⁻¹, depending on the pH target. Artificially decreasing lime rate recommendations in this way could cause soil pH to be lower than the desired target pH, which is a significant agronomic concern, as noted above.

The supernatant modification significantly increased mean buffer pH across soil types by 0.065 units in comparison to the control treatment (Table 3.4). The Oregon calibration for the Sikora method established in Ch. 2 is based on buffer pH measurement in the supernatant. For this reason, buffer pH measurements made in the supernatant will produce lime rate recommendations that are accurate for Oregon soils. It is not anticipated that laboratories will prefer to measure buffer pH in the slurry vs. the supernatant, nevertheless these results show that this modification can have a significant effect on buffer pH results. Relative to the Sikora method used in Ch. 2, measurement in the slurry would artificially lower buffer pH, and potentially cause lime recommendations to be 0.8 – 1.5 Mg ha⁻¹ higher, depending on the pH target.

Soil-buffer equilibration time

Increasing equilibration time from 0 to 180 min decreased buffer pH by 0.02 – 0.05 units across the five soils evaluated (Table 3.5). The Sikora buffer pH calibration recently developed for Oregon (see Ch. 2) is based on a target equilibration time of 15 min. Relative to 15 min of equilibration time, measuring at 0 min of equilibration resulted in an increase in buffer pH of 0.00 – 0.03 units, and measuring at 180 min of equilibration time resulted in a decrease of 0.01 – 0.03 units. All these differences are less than 0.05 buffer pH units, therefore measuring buffer pH within 0 – 180 min is not expected to substantially affect the accuracy of Oregon lime requirement recommendations.

Table 3.5. Sikora buffer pH of five Oregon soils, measured at six equilibration time intervals from 0 to 180 min. Each reported mean (\bar{x}) and SD value was calculated from three measurements.

Region and soil series	Minutes of equilibration											
	0		15		30		60		120		180	
	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD	\bar{x}	SD
Willamette Valley												
Bashaw	5.21	(0.012)	5.20	(0.000)	5.20	(0.006)	5.20	(0.006)	5.19	(0.006)	5.18	(0.010)
Nekia-1	5.41	(0.026)	5.40	(0.012)	5.40	(0.015)	5.40	(0.006)	5.39	(0.010)	5.39	(0.010)
Woodburn	6.12	(0.006)	6.09	(0.010)	6.08	(0.006)	6.07	(0.006)	6.07	(0.006)	6.07	(0.006)
Eastern Oregon												
Athena	6.40	(0.012)	6.40	(0.006)	6.40	(0.006)	6.39	(0.000)	6.39	(0.006)	6.38	(0.010)
Central Oregon												
DNF-36	6.02	(0.017)	6.01	(0.010)	6.00	(0.006)	6.00	(0.017)	5.99	(0.021)	5.98	(0.020)

DISCUSSION

Interpretation of LRE soil test methods is somewhat unique compared to most other agronomic soil tests, due to the incremental nature of lime rate recommendations. Generally, many fertilizer recommendations are based on whether a soil test result falls into one of a few broad categories such as ‘severely deficient’, ‘moderately deficient’, and ‘sufficient’ (Havlin et al., 2014). In comparison, lime recommendations can change incrementally based on small differences in a test result—0.1 buffer pH units is the resolution typically used to make LRE recommendations for buffer methods (Gavlak et al., 2005). For this reason, special consideration should be given to factors affecting the accuracy of LRE methods such as the Sikora method to ensure accurate lime recommendations.

The results of this study show that minor modifications to the Sikora buffer can have a significant effect on buffer pH results and recommended lime rate. These results suggest two possible paths for maximizing the accuracy of Oregon lime rate recommendations using the Sikora method. First, Sikora buffer pH can be evaluated using the original procedure used to develop the Oregon regional calibration (See Ch. 2). Alternatively, if a modified Sikora procedure is to be used for Oregon, the modified procedure could be evaluated against the original procedure used to develop the Oregon calibration. Such an evaluation should be made using a set of Oregon soils with a wide range of characteristics, similar to the set used for this study. Since all of the modifications evaluated in this study showed uniform effects across Oregon soils with a wide range of characteristics, modified Sikora procedures are expected to show a similarly uniform effect across soil types. If this is the case, a factor may be developed to adjust a modified procedure’s results for interpretation, thereby minimizing the risk of under- or over-application of lime.

Furthermore, comparing Sikora buffer pH results between laboratories that serve Oregon may also be beneficial, regardless of whether modifications are used. This comparison could help account for other sources of error that may occur between laboratories even if the same Sikora procedure is followed.

Most of the other LRE methods used in the United States involve measuring pH resulting from the equilibration between exchangeable soil acidity and an alkaline buffer. For this reason, other LRE buffer methods may be affected by method modifications in similar ways to the Sikora method, therefore other regions may also benefit from comparing buffer pH results among laboratories, using soils representative of their region. Additionally, these results show the usefulness of proficiency testing for maintaining lime rate recommendation accuracy.

CONCLUSION

Five modifications to the Sikora method were evaluated for Oregon soils. Four of the five modifications evaluated were found to have a significant effect on buffer pH, and the effects of these modifications were shown to be uniform across soil type. Circular mixing and using a 1:2:1 soil:water:buffer ratio were shown to cause average increases in buffer pH of 0.063 and 0.058 units, respectively. These increases could cause decreases in lime requirement of 0.8 – 1.5 Mg ha⁻¹ depending on pH target. These effects were of particular concern because they could result in crop damage from under-application of lime and below-target soil pH. Measurement in supernatant compared to measurement in soil slurry was also found to cause an average increase of 0.065 buffer pH units. For Oregon, this was considered less of a concern since the Sikora procedure used to establish an LRE calibration for Oregon soils was performed with measurement in supernatant. Use of a SPRJ pH electrode instead of a circular reference junction pH electrode was not found to have a significant effect. Sikora buffer pH was found to decrease

with increasing equilibration time (across 0 – 180 min), with the decrease ranging from 0.02 to 0.05 units.

While these results indicate that some modifications of the Sikora method can have a significant effect on lime rate recommendations, they do not indicate that all modifications must be avoided. Rather, they indicate that method modifications should be avoided whenever possible. When modifications are unavoidable, their effects should be measured and accounted for in order to ensure the accuracy of lime rate recommendations.

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APPENDICES

Appendix 2.1. Soil moisture target levels used for lime incubation of 24 Oregon soils. Moisture targets were adjusted to approximately 80% and 90% of field capacity, which is also listed.

Soil series	Moisture content		
	Lower limit	Upper limit	Field capacity
	g H ₂ O [kg oven-dry soil] ⁻¹		
Aloha	218	245	273
Amit	185	208	231
Athena	203	228	253
Awbrig	315	334	371
Bashaw	366	387	430
Bellpine	311	328	346
Camas	204	215	227
Concord	251	282	313
Conser	297	334	371
Cornelius	207	219	244
Cove	207	233	259
Dayton-1	261	278	348
Dayton-2	248	278	309
DNF-36	231	243	231
Jory	308	325	342
Malabon	323	341	359
Natroy	219	232	258
Nekia-1	333	352	371
Nekia-2	290	307	341
Palouse	228	257	285
Salem	220	232	244
Walla Walla	213	240	267
Willamette	253	269	316
Woodburn	221	235	277

Appendix 2.2. Third-order polynomial equations used to estimate CaCO₃ rates needed to reach three pH targets in a 90 d soil incubation. Incubation lime requirement values were determined by interpolating on these equations for selected pH targets.

Soil Identifier	Equation ^a	r ²	Incubation Lime Requirement				
			pH targets				
			5.6	6.0	6.4	6.8 ^b	7.2 ^b
Mg ha ⁻¹							
Aloha	$y = 4.64 + 0.268x - 0.00634x^2$.998	3.9	5.9	8.1	10.8	14.6
Amity	$y = 4.53 + 0.278x - 0.00651x^2$.995	4.3	6.2	8.4	11.0	14.7
Awbrig	$y = 4.54 + 0.0856x + 0.000315x^2$.997	11.9	16.1	20.2	- ^c	-
Bashaw	$y = 4.61 + 0.0797x$.995	12.4	17.4	22.4	-	-
Bellpine	$y = 4.76 + 0.0993x - 0.000477x^2$.999	8.8	13.3	18.1	-	-
Camas	$y = 4.86 + 0.261x - 0.00636x^2$.996	3.1	5.0	7.1	9.8	13.3
Concord	$y = 4.40 + 0.312x - 0.00745x^2$.992	4.3	6.0	7.9	10.2	13.1
Conser	$y = 4.53 + 0.223x - 0.00403x^2$.994	5.3	7.7	10.3	13.5	17.6
Cornelius	$y = 4.55 + 0.323x - 0.00837x^2$.996	3.6	5.2	7.0	9.1	11.8
Cove	$y = 4.34 + 0.292x - 0.00669x^2$.994	4.9	6.7	8.9	11.4	14.9
Dayton-1	$y = 4.46 + 0.307x - 0.00740x^2$.997	4.1	5.9	7.8	10.1	13.0
Dayton-2	$y = 4.28 + 0.360x - 0.00940x^2$.993	4.1	5.6	7.3	9.2	11.7
Jory	$y = 4.97 + 0.105x - 0.000755x^2$.999	6.3	10.6	15.3	20.4	-
Malabon	$y = 4.92 + 0.136x - 0.00134x^2$.997	5.3	8.7	12.4	16.5	21.2
Natroy	$y = 4.82 + 0.323x - 0.00891x^2$.993	2.6	4.1	5.8	7.8	10.3
Nekia-1	$y = 4.61 + 0.0987x - 0.000656x^2$.998	10.9	15.8	21.2	-	-
Nekia-2	$y = 4.51 + 0.126x - 0.00107x^2$.999	9.4	13.4	17.7	22.5	-
Salem	$y = 4.59 + 0.272x - 0.00623x^2$.994	4.1	6.0	8.2	10.8	14.2
Willamette	$y = 4.70 + 0.310x - 0.00823x^2$.993	3.2	4.8	6.6	8.8	11.7

Appendix 2.2 continued

Soil Identifier	Equation ^a	r ²	Incubation Lime Requirement				
			pH targets				
			5.6	6.0	6.4	6.8	7.2
			Mg ha ⁻¹				
Woodburn	$y = 4.83 + 0.286x - 0.00729x^2$.995	2.9	4.6	6.6	8.9	11.9
Athena	$y = 5.11 + 0.325x - 0.00944x^2$.987	1.6	3.0	4.6	6.4	8.6
Palouse	$y = 4.69 + 0.268x - 0.00617x^2$.989	3.7	5.6	7.7	10.3	13.6
Walla Walla	$y = 4.74 + 0.319x - 0.00855x^2$.990	2.9	4.5	6.2	8.3	10.8
DNF-36	$y = 4.68 + 0.238x - 0.00499x^2$.996	4.2	6.4	8.9	11.9	15.9

^a $y = \text{pH}_{1:2}$ after 90 d lime incubation, $x = \text{CaCO}_3$ added, Mg ha^{-1} equivalent

^b $\text{pH}_{1:2}$ targets 6.8 and 7.2 were not used in Ch. 2 to evaluate the accuracy of LRE methods

^c Incubation lime requirement was not calculated for pH targets 6.8 and 7.2 for some soils, due to the fact that these soils did not reach those pH levels across the lime rates applied in this study (0 – 22.4 Mg ha^{-1}).

