EXPERIENCE WITH USING THE SIKORA-2 SOIL/BUFFER pH METHOD IN THE GREAT PLAINS

F. F. Vocasek and S.A. Harrold,
ServiTech Laboratories, Dodge City KS
fred.vocasek@servitech.com Phone: (620) 227-7123

ABSTRACT

The extent of acidic soils in the Great Plains continues to increase from long-term cropping and fertilizer nitrogen use. Acidic soils developed initially in dryland fields and/or in areas dominated by sandy soils, but are now relatively common in irrigated systems and finer-textured soils. Soil pH is typically determined a 1:1 soil:water slurry (pH_w) and exchangeable acidity determined by a buffer pH, which then is used to calculate lime requirements. The widely used SMP buffer contains hazardous materials, so soil test laboratories have largely replaced it with the Sikora-1 buffer (Sikora, 2006). The Sikora-1 buffer closely mimicked the SMP buffer, so recalibration was not considered necessary.

Determining soil pH and identifying effective lime in sandy or poorly buffered soils is a challenge for ServiTech and other soil testing laboratories. Clients were frequently frustrated with test results having a low soil pH with a zero lime rate. Alternative methods, like the modified Woodruff or Adams-Evans buffers help to "improve" lime recommendations. These methods were developed and calibrated for the poorly buffered soils of the southeast U.S., but were not calibrated for the Great Plains. These buffer solutions also contain hazardous compounds.

Sikora (2012) developed a method to measure the soil pH in a 1*M* KCl solution followed by measuring pH in the modified Sikora-2 buffer. This method provides a two-point lime response curve to account for the individual buffering capacity of each soil sample. ServiTech adopted the Sikora-2 method in 2012 as an alternative to pH_w and Sikora-1 buffer. The Sikora-2 method has been well accepted by soil testing clients since then. They have more confidence in the results they receive from samples collected from sandy, poorly buffered soils. Drought conditions often resulted in depressed soil pH values which differed from the long-term soil test history. During the current drought cycles, we have found significantly fewer concerns about drought-depressed soil pH results because of the increased use of the Sikora-2 method.

INTRODUCTION

Soil pH is a routine measurement conducted by soil testing laboratories – public and commercial. Soil pH is determined electrometrically in a soil slurry of a specified soil:deionized-water ratio, like 1:1 or 1:2.5 ("water pH", "pH_w") or with 0.01*M* $CaCl_2$ or 1*M* KCl ("salt pH"). Adding the electrolyte increases the ionic strength for pH measurement and avoids variable pH of a soil:water slurry due to varying background salt levels in different soils (Sikora, 2014a).

Soil acidity has increased across the Great Plains following decades of increasing yield potential with subsequent increases in use and rates of ammoniumand urea-based fertilizers. The nitrification process releases hydrogen ions (H^+) that accumulate in the soil solution, and replace basic cations and continue to drive a decline of soil pH. There are substantial areas of the Great Plains that are occupied by sandy soils (Entisols), notably the Nebraska Sandhills, the Arkansas River valley in Colorado and Kansas, and numerous river valleys in other Great Plains states. Some areas of sandy soils have been under production for 100 years or more and have only recently developed obvious acidity symptoms (Green, 2016). Other areas of sandy soils were developed for crop production with the introduction of center pivot irrigation systems. Sandy, poorly buffered soils pose an increased threat to develop acidity problems, but ServiTech clients with sandy soils often became frustrated with the lime rates determined using pH_w and a single buffer. The buffer pH often indicated a “zero” lime rate for soils with a moderately or strongly acidic pH_w value.

The SMP buffer has been used extensively in the North Central and Western Regions, but was formulated with potentially hazardous materials that require special handling. It may not be accurate for soils with low lime requirements, sandy soils, or soils with certain clay fractions (Peters, 2013). Sikora (2006) developed a modification, Sikora-1, using non-hazardous materials that mimicked the SMP.

Other methods have been used to determine the lower lime rates, required by sandy or poorly buffered soils. They include the modified Woodruff (“Woodruff-2”) and the Adams-Evans buffers, but both of solutions contain hazardous materials. Double-buffer methods (SMP, Yuan, etc.) are another approach to improve accuracy. These two-point methods require a second buffer pH measurement to develop an individual titration curve for each soil sample (Sikora, 2012).

Sikora (2012) introduced the Sikora-2 double-buffer method. Soil pH is measured in a 1*M* KCl solution (pH_{KCl}). The Sikora-2 buffer differs from the Sikora-1 buffer only in the potassium chloride concentration. The final concentration of the initial soil slurry plus the buffer solution is 2*M* KCl for both.

Figure 1a illustrates lime rates based on the one-point buffer pH value. The NCR13 calibration is used with the Sikora-1 buffer. No recommendations are made above a Sikora-1 buffer value of 6.8, where lime rates are less than 1 ton/acre. This is a situation where the acid-soil/no-lime anxiety can occur.

Figure 1b illustrates a two-point calibration using the pH_{KCl} and the Sikora-2 buffer pH values. The method uses the measured soil pH_{KCl} to adjust the lime rate that is initially determined by the buffer pH value. This provides a calibration curve for the individual sample. When lime is recommended, the rates are progressively higher as the measured soil pH_{KCl} decreases. The argument can be made to use the pH_w to adjust the lime rate calculated from the single-point Sikora-1 or Woodruff-2 calibration. Sikora (2012) points out that this approach may be misleading. The buffer solution of these two methods have a high ionic strength while the pH_w solution (i.e., soil and deionized water) has a much lower ionic strength. The Sikora-2 method measures both the soil pH and the buffer pH in solutions of the same ionic strength resulting from including potassium chloride in the respective solutions. The advantage is that only two solutions are required for the determination. The other double-buffer methods require a soil pH determination plus two buffer pH determinations.

MATERIALS AND METHODS

A group of 180 diverse soil samples was selected randomly from those submitted to ServiTech Laboratories during September and October 2011 (see Table 1). Summation CEC was used as an indicator of general soil texture. Samples came primarily from Kansas, Nebraska, Oklahoma, Texas, and Colorado.

Soil pH_w, pH_{KCl}, and buffer pH (Sikora-1, Sikora-2, and Woodruff-2) were determined electrometrically. Soluble salts were determined in a 1:1 soil:water slurry. Summation cation exchange capacity (CEC) was calculated from Mehlich-3 extractable cations. Lime rates as “tons of effective calcium carbonate per acre (ton ECC/ac)” for a target soil pH_w of 6.5 at an 8-inch depth were calculated using the respective buffer pH results using equations shown in Table 2.

Table 1. Study population characteristics.	**Mean**	**Standard Deviation**	**Median**	**Minimum**	**Maximum**
1:1 pH_w	5.34	0.70	5.2	3.3	7.4
1:1 pH_{KCl}	4.43	0.72	4.3	2.7	6.6
Meh3 CEC_{sum}, meq/100g	9.5	6.1	8	1	33
1: 1 Soluble salts,	0.26	0.21	0.21	0.05	1.57
Buffer pH					
Sikora-1	6.70	0.37	6.7	5.4	7.4
Sikora-2	6.75	0.37	6.8	5.4	7.4
Woodruff-2	6.52	0.29	6.6	5.4	7.0

RESULTS AND DISCUSSION

Soil pH

Soil pH_w was well correlated with pH_{KCl} (Figure 2, $r^2 = 0.91$). A comparison by Sikora (2014) of 240 Kentucky soils had the relationship in Equation 1. The relationship obtained from the ServiTech study population of 180 samples (Equation 2) was very similar. This suggested to us that there was a robust relationship for pH_{KCl} across a wide range of soils.

[1] $pH_w = (0.91 \times pH_{KCl}) + 1.34$ $r^2 = 0.98$

[2] $pH_w = (0.93 \text{ x } pH_{KCl}) +1.21$ $r^2 = 0.91$

ServiTech, like the University of Kentucky, does not report the pH_{KCl} to clients. The pH_{KCl} value is converted to a pH_w “equivalent” value listed on the ServiTech soil test report as “1:1 (c) Water-Soil”, the “(c)” designating a calculated value. This conversion helps avoid confusion by clients when trying to compare current soil pH results to their historic results, to other laboratory results, or various references. Additionally, we frequently must respond to customers who ask “Why are there two pH values on my soil test?”, referring to the soil pH and buffer pH values. Reporting a third pH_{KCl} value would add significantly to their confusion and not lend to understanding the impact of soil acidity.

Lime requirements (LRs)

Relationships between various LRs are shown in Figures 3a, 3b, and 3c. The regression relationship and a 1:1 relationship are shown with dashed lines; the regression line being thicker and more bold than the 1:1 line. SMP lime requirements less than 2 tons/ac may be inaccurate (Peters, 2013), so the Sikora-1 lime rates from 0 to 2 tons/ac are highlighted with a horizontal arrow. Since Sikora buffer pH values mimic the SMP values, we assume the same inaccuracy may apply.

Requirements are well correlated (r^2 = 0.89 and 0.94) and can be described using polynomial equations. Sikora-2 lime rates tended to exceed Sikora-1 rates when Sikora-1 rates were less than 2 tons, but rates were lower above 2 tons. Figure 3b shows the Sikora-1 and Woodruff-2 relationship to be nearly linear. A significant difference occurs when Sikora-1 lime rates are zero, while a number of the Woodruff-2 rates for the same samples ranged from 0 to 1.5 tons/ac. The Sikora-2 and Woodruff-2 lime rates are highly correlated, also defined by a polynomial relationship (Figure 3c). Rates do not differ greatly when less than 2 tons per acre. Woodruff-2 requirements are about 1.5X to 2.0X the Sikora-2 requirements at Sikora-2 rates above 2 tons per acre

Customer perception

For many of our clients, the correlation of the buffer pH methods was of significantly less importance than the practical impact on lime requirements, especially those for sandy soils. Clients could be frustrated when the pH_w indicated an acidic soil and the lime recommendation based on the Sikora-1 buffer pH value and the NCR-13 calculation would yield a “zero” result. They were concerned that the lime requirement result based on the buffer pH was not properly addressing potential soil acidity problems. Using the Sikora-2 method has greatly reduced the acid-soil/no-lime anxiety.

This is illustrated in Figure 4. The charts show the frequency of samples with “zero” lime recommended for each buffer pH method. Fifty (50) of the 180 samples in the Sikora-1 study population had no lime recommended. Six (6) Sikora-1 samples had a pH_w of 7.0 or greater, so no lime would have been recommended. However, 21 of the samples (12% of the study population) had a pH_w of 5.5 or less, so would be considered moderately to strongly acidic. Only three samples analyzed with Woodruff-2 buffer had a zero lime rate; two of them had pH_w of 7.0 or more. Thus, only one of the 180 samples below pH_w 7.0 needed lime. The original Woodruff buffer was thought to underestimate lime requirements compared to the SMP buffer and was modified to better reflect exchangeable aluminum (Brown, 1984). The client perception existed that the Woodruff-2 could be overapplying lime in some cases. Seventeen (17) of the Sikora-2 samples did not have lime recommended, but again, six of them had a soil pH exceeding 7.0.

Severe drought periods frequently cause soluble salt levels to increase by 0.3 to 0.4 mmho/cm. We have observed pH_w of 0.4 to 0.5 units lower due to this additional electrolyte impact during pH measurement, creating a sort of “ephemeral” acidity during drought cycles. Clients in the Texas Panhandle noted pH_w depressions of 0.6 to 0.7 units during the record-setting 2011 drought. Since then, using the 1*M* KCl solution has helped assure clients that they are getting the “right” soil pH value.

Experiences with the Sikora-2 method

From an operations standpoint, an important advantage was eliminating the need to maintain stocks of the Woodruff-2 buffer and to capture and store the spent buffer solution as a hazardous material. Another advantage is that the overall reagent requirements for Sikora-1 and Sikora-2 solutions are virtually identical, so no additional chemical expense had to be incurred. One disadvantage is soluble salt determination. The deionized water extract could allow us to measure conductivity and pH simultaneously. Conductivity has to be determined separately when the 1*M* KCl solution is used for pH_{KCl} determination.

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Table 2. Lime requirement calculations

Source	Method	Calculation
NCR-13[*]	Sikora-1	LR = 39.4 - (BpH x 5.69)
Woodruff[**]	Woodruff-2	LR = (7.0 - BpH) x 5
SERA6[***]	Sikora-2	LR = (target pH_{KCl} – pH_{KCl}) × (BpH – 7.55) ÷ [(BpH – pH_{KCl}) × (-0.364)] × 10 ÷ (g soil)

LR = lime requirement, tons ECC/acre; BpH = buffer pH

[*] *derived from Table 2, page 4.6, Peters, et.al., 2013.*

[**] *derived from page 4.5, Peters, et.al., 2013.*

[***] *simplified equation; detailed equation in pages 66-68, Sikora, 2014b*

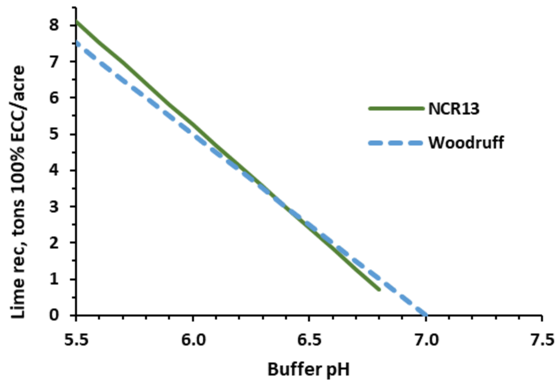

Figure 1a. Lime requirements using one-point buffer calibration methods.

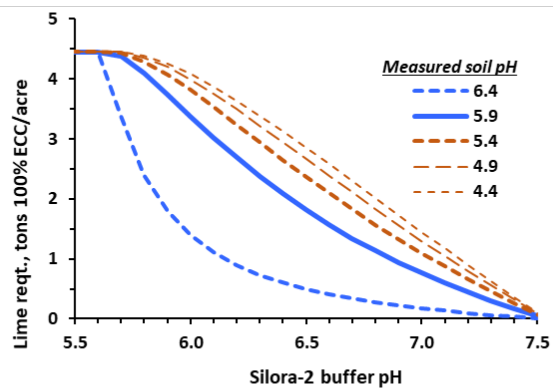

Figure 1b. Lime requirements using two-point buffer calibration method.

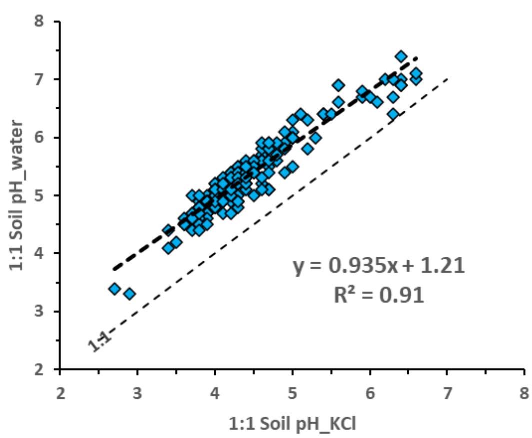

Figure 2. Relationship between soil pH determined with 1*M* KCl or water soil pH.

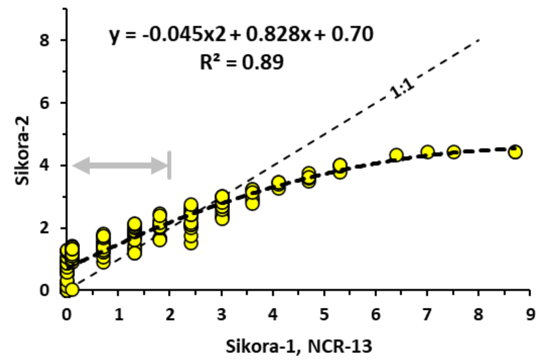

Figure 3a. Lime requirement comparison, Sikora-1 v. Sikora-2, tons ECC lime/acre.

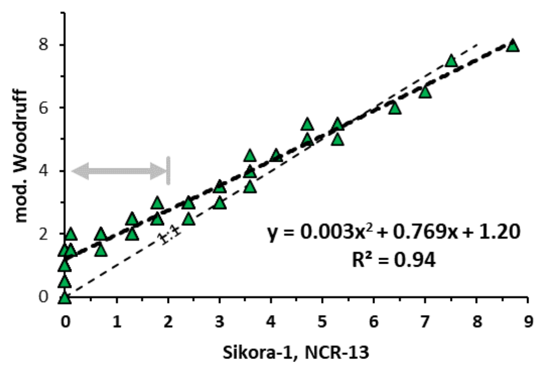

Figure 3b. Lime requirement comparison, Sikora-1 v. Woodruff-2, tons ECC lime/acre.

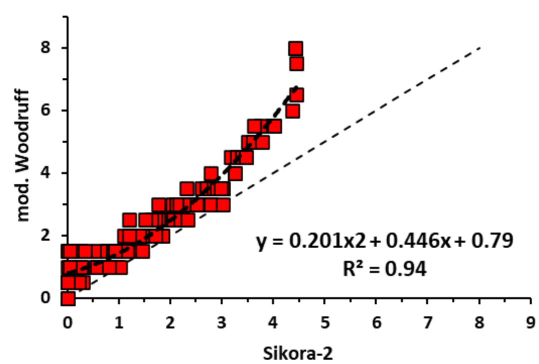

Figure 3c. Lime requirement comparison, Sikkora-2 v. Woodruff-2, tons ECC lime/acre.

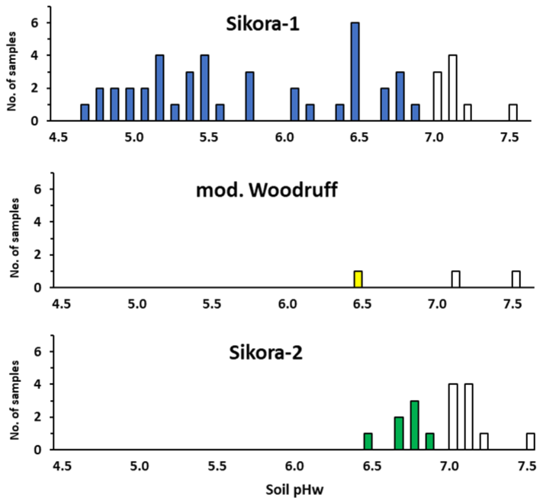

Figure 4. Frequency of "zero" lime requirements by soil pH_w for three buffer methods.