Replacing SMP buffer with Sikora Buffer for Determining Lime Requirement of Soil

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Buffer solutions have been developed to react with soil acidity and aid the recommendation of lime requirement. The four most widely used buffers are Woodruff (Woodruff, 1948), Shoemaker-McLean-Pratt (SMP) (Shoemaker et al., 1961), Adams-Evans (Adams and Evans, 1962), and Mehlich (Mehlich, 1976). In the 2004 reports of the North American Proficiency Testing (NAPT) program (Miller and Kotuby-Amacher, 2004), the average number of laboratories reporting values for Woodruff, SMP, Adams-Evans, and Mehlich buffers were 18, 58, 16, and 6, respectively.

The buffers used in soil testing were developed prior to federal laws regulating the disposal of hazardous waste. The Resource Conservation and Recovery Act (RCRA) was passed in 1976 by the U.S. Congress to improve waste management (Horinko, 2002). Hazardous waste management was further refined in 1980 with the passage of regulation controlling the disposal of chemicals considered hazardous due to ignitability, corrosivity, reactivity, or toxicity (USEPA, 1980a). Buffer constituents defined to be hazardous due to toxicity are p-nitrophenol in Adams-Evans, barium in Mehlich, and p-nitrophenol and chromium in SMP. The chromium in the SMP buffer, present as chromate (CrO_4^{2-}), is hexavalent and carcinogenic (USEPA, 1998). Since these buffers contain hazardous chemicals as defined by RCRA, a laboratory discarding 100 kg or more of the soil and buffer in a one month period is considered a hazardous waste generator and has to follow certain protocols for hazardous waste disposal (USEPA, 1980b).

Studies have been conducted to develop alternative methods for making lime recommendations without the use of hazardous chemicals. Vaughn (2004) suggests replacing chromate with citric acid or succinic acid and p-nitrophenol with ethylenediamine or imidazole in the SMP buffer without specifying specific concentrations for the alternative chemicals. Wolf and Beegle (2005) have evaluated the use of a modified Mehlich buffer, with barium replaced by calcium, to replace their routine use of the SMP buffer. Huluka (2005) replaced p-nitrophenol with potassium phosphate in the Adams-Evans buffer. The University of Georgia laboratory has discontinued use of the Adams-Evans buffer and is using direct titration with calcium hydroxide for estimating lime requirement (Liu et al., 2004; Liu et al. 2005).

At the University of Kentucky soil test laboratories, SMP buffer was used for making soil lime recommendations. Replacing SMP buffer with the modified Mehlich buffer (Wolf and Beegle, 2005) was considered as a viable option to eliminate the use of chromate and p-nitrophenol. However, the buffer pH obtained from the modified Mehlich buffer would be different than the value obtained from an SMP buffer which would necessitate lime calibration studies or conversion to SMP buffer pH for making lime recommendations. Rather than using a buffer producing a different buffer pH value than SMP buffer, research was conducted to develop a new buffer that would duplicate the pH value from SMP buffer. This report summarizes data on the Sikora buffer which is free of hazardous constituents on the RCRA list (USEPA, 1980a), duplicates the buffer pH value obtained with the SMP buffer, and is currently being used at the University of Kentucky soil test laboratories. Details on the chemistry and development of the replacement buffer are reported elsewhere (Sikora, 2006).

COMPONENTS OF THE SIKORA BUFFER AND METHODOLOGY IN OBTAINING SOIL-BUFFER PH

For every liter of solution, the following quantities of chemicals are dissolved.
Potassium chloride (KCl, mw=74.55): 149 g
Glacial acetic acid (CH_3COOH, mw=60.05): 5.36 g or 5.11 ml
MES (2-(N-morpholino)ethanesulfonic acid) monohydrate ($C_6H_{13}NO_4S \cdot H_2O$, mw=213.24): 6.70 g
Imidazole ($C_3H_4N_2$, mw=68.08): 0.936 g
Triethanolamine ($(HOCH_2CH_2)_3N$, mw=149.19): 10.38 g or 9.23 ml
Sodium hydroxide (40% NaOH (w/w)): 5 ml

Dissolve the KCl in a volume of water that is 75% of the final intended volume. Make sure all the KCl dissolves. Weigh the other components of the buffer and add them to the solution in the order listed making sure each component dissolves before proceeding. Glacial acetic acid, triethanolamine, and sodium hydroxide are added as liquids. The other chemicals are added as solids. Adjust the volume to the final intended volume by adding water. Add drops of 40% NaOH (w/w) or 50% HCl (v/v) to achieve a pH of 7.70 ± 0.01. Allow time for the solution pH to stabilize. Place 50 ml of the buffer in a beaker and measure pH. The pH should be 7.70 ± 0.01. Add 50 ml of water to the buffer, stir, and measure pH. The pH should be 7.53 ± 0.03. Add 5 ml of 0.5 N HCl to the 1:1 dilution of buffer, stir, and measure pH. The pH should be 5.68 ± 0.06.

Soil pH is determined by stirring 10 cm^3 of soil with 10 ml of water using a stir bar, letting the slurry stand for 10 minutes, and measuring pH in the slurry. After determining soil pH, 10 ml of Sikora buffer is added, then the sample is shaken for 10 minutes on a mechanical shaker at more than 180 oscillations per minute, followed by pH measurement of the slurry to obtain a soil-buffer pH.

RESULTS WITH THE SIKORA BUFFER

The soil-buffer pH values with the Sikora and SMP buffers were compared on 255 Kentucky soils and 84 North American Proficiency Testing (NAPT) samples. The Sikora soil-buffer pH measurements were taken as described in the previous section. The SMP soil-buffer pH measurements were determined the same way except 20 ml of buffer was used rather than 10 ml. The soil-buffer pH values were very similar between the Sikora and SMP buffers as indicated by r^2 values of 0.974 for Kentucky soils and 0.967 for NAPT soils and close congregation of the data around the 1:1 lines (Fig. 1). The difference in soil-buffer pH values ranged from -0.25 to 0.25 (SMP soil-buffer pH minus Sikora soil-buffer pH). Only 1 soil had a difference outside of this range. Half of the soils had a pH difference between -0.05 to 0.05.

On July 1, 2005, the Sikora buffer replaced the SMP buffer in routine operation of testing soil at the University of Kentucky laboratories in Lexington and Princeton. Quality control charts for quality control soils used in the laboratories are shown in Fig. 2. The data prior to 182 days are soil-buffer pH values using SMP buffer. Data after 182 days are soil-buffer pH values using the Sikora buffer. The mean, 2 x standard deviation (2s), and 3 x standard deviation (3s) were taken from the SMP soil-buffer pH data prior to 182 days. The Sikora buffer has been performing

equivalent to the SMP buffer since its adoption on July 1 as indicated by the majority of soil buffer pH values lying within the quality control limits of 2s and 3s. The 3s limits are where 99.7% of the data should lie. This range for SMP soil-buffer pH in the quality control samples is approximately ± 0.25 pH units. This standard laboratory error in obtaining the SMP soil-buffer pH is the same range for differences observed in the soil-buffer pH values between SMP buffer and Sikora buffer in Fig. 1. Therefore, the differences in Fig. 1 were most likely due to standard laboratory error.

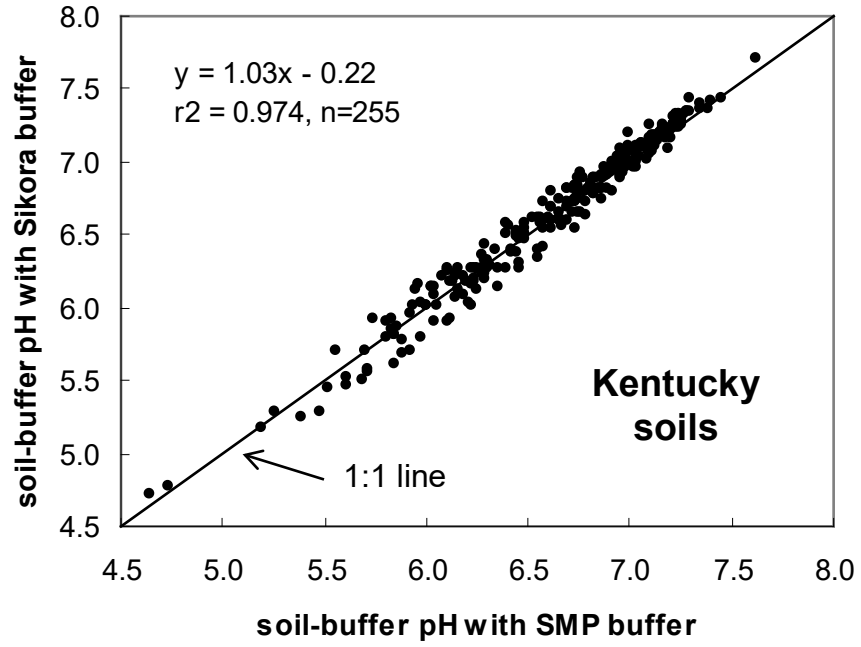
Since the buffer pH obtained with the Sikora buffer is the same as the pH from the SMP buffer, lime recommendations from the buffers would be expected to be the same. Lime recommendations from the University of Kentucky soil test laboratories are based on interpretation of both water pH and buffer pH (University of Kentucky, 2004) and adding lime to achieve a target water pH of 6.4 for most crops. Lime recommendations are based on a statewide average lime quality of 67% relative neutralizing value. Out of the 255 Kentucky soils and 87 NAPT soils in Fig. 1, 144 Kentucky soils and 31 NAPT soils required lime according to University of Kentucky recommendations. About 70% of the soils requiring lime had no difference in lime recommendation between the SMP and Sikora buffer (Fig. 3). About 25% of the soils had a difference of 1 ton/acre in lime recommendation between the two buffers.

CHEMICAL DIFFERENCES BETWEEN THE SIKORA AND SMP BUFFERS

Besides the obvious difference between the Sikora and SMP buffer being a different mix of chemicals, there are other differences which include:
1) Volume of buffers used in the test
2) Different initial pH values of the buffers
3) Soil-buffer pH range suitable for use
4) Different background salts and ionic strength levels

Ten ml of Sikora buffer is added to 10 cm^3 soil and 10 ml of water. Twenty ml of SMP buffer is added to the same quantity of soil and water. In developing the new buffer, ensuring the same volume of buffer was used in the test was not deemed important. The important result was to ensure the soil-buffer pH value was the same using the replacement buffer as it would be using the SMP buffer. To minimize the volume of solution a laboratory would have to handle, the replacement buffer was designed to work with 10 ml added to 10 cm^3 soil. Therefore, the active ingredients to neutralize soil acidity were designed to be twice as strong in the replacement buffer compared to the SMP buffer.

The pH of the Sikora buffer is adjusted to 7.70. The pH of the SMP buffer is adjusted to 7.50. The initial pH of the buffers before adding it to a soil-water slurry changes a little bit due to dilution of the buffer with the water. The pH of 20 ml of SMP buffer diluted with 10 ml of water is 7.57 ± 0.02. The replacement buffer was designed to have the same pH when 10 ml of the buffer was diluted with 10 ml of water. The pH of 10 ml of Sikora buffer diluted with 10 ml of water is 7.53 ± 0.03. The initial pH values of the buffers diluted with water in the soil water slurry were the critical values to make sure were equal since it is the diluted buffer that reacts with soil acidity. For some unknown reason, the Sikora buffer pH decreases upon dilution and the SMP buffer pH increases upon dilution.



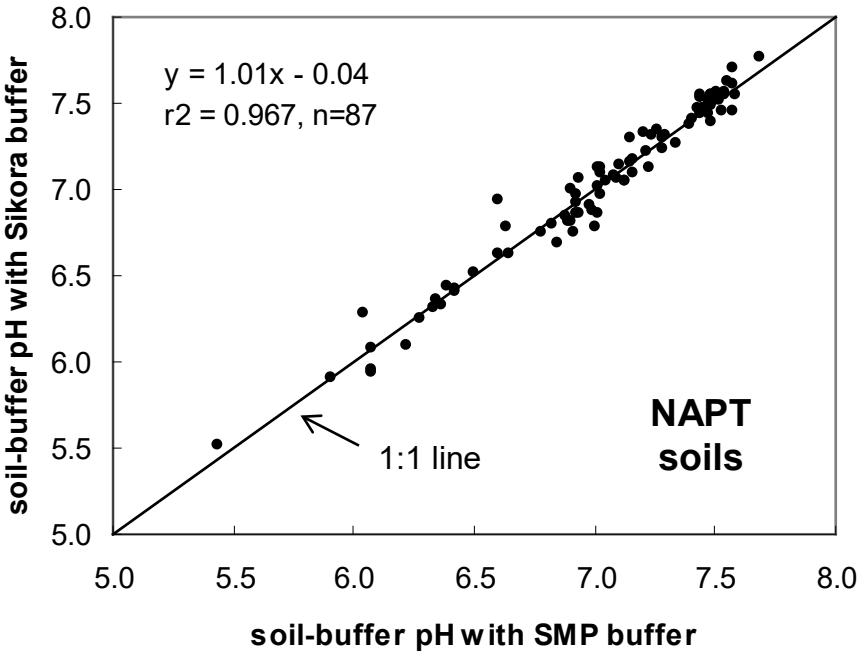
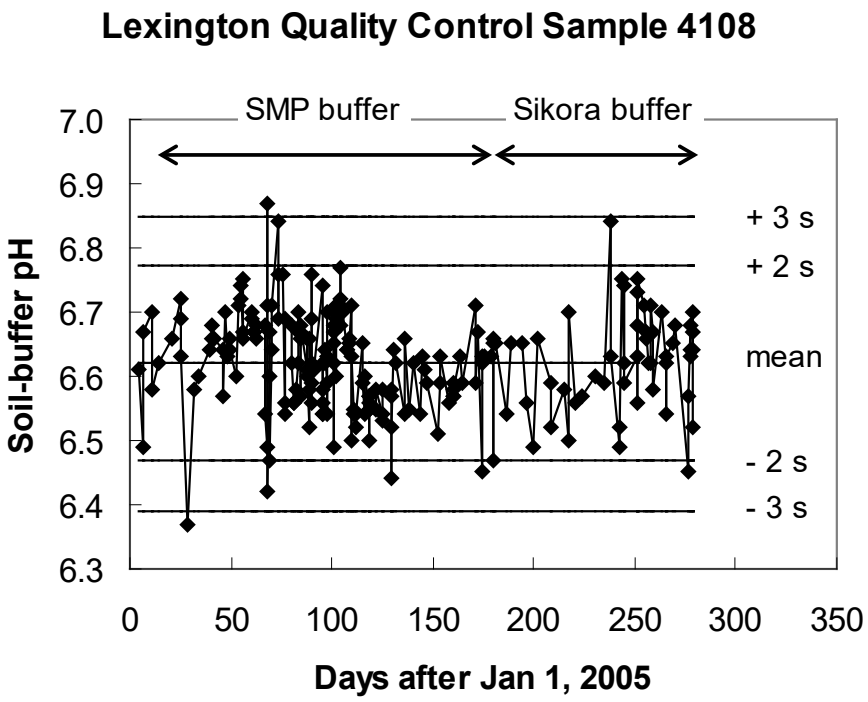


Figure 1. Comparison between soil-buffer pH with the Sikora buffer and soil-buffer pH with the SMP buffer for 255 Kentucky soils and 87 NAPT soils.



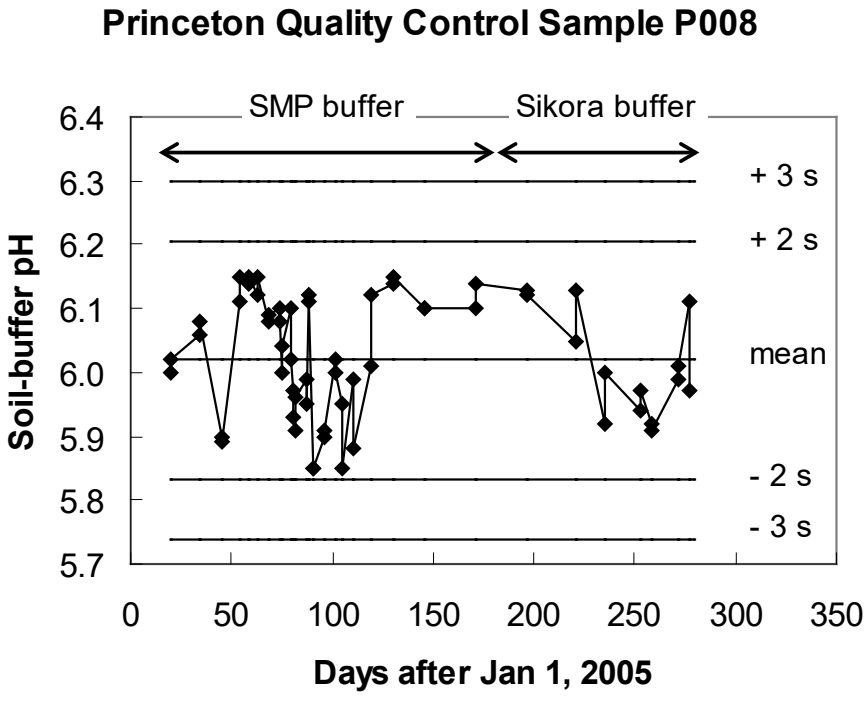
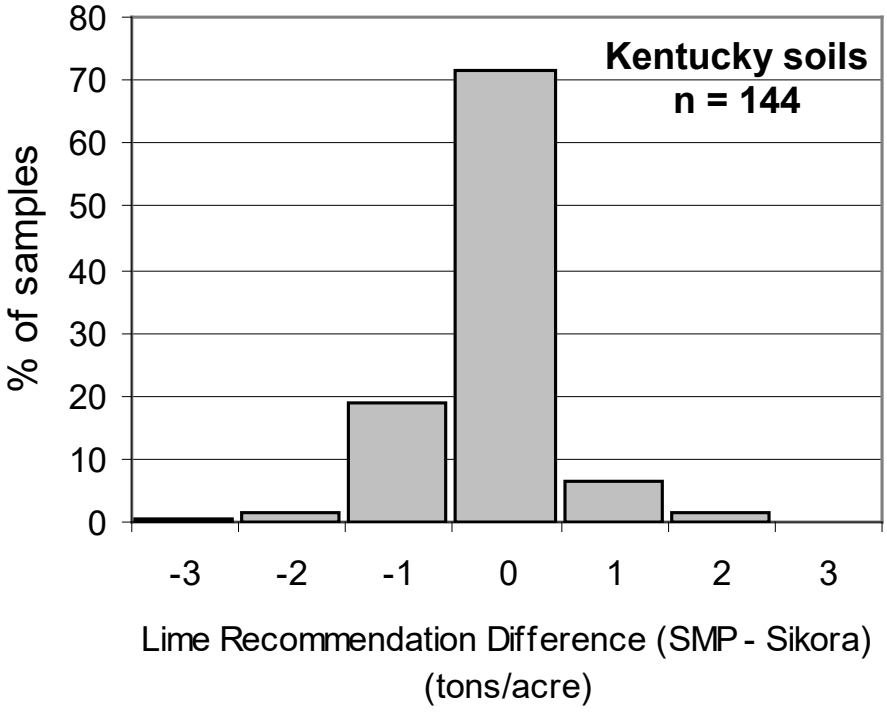


Figure 2. Quality control charts for soil-buffer pH for samples used in the Lexington and Princeton laboratories. The Sikora buffer has been used since July 1, 2005 (182 days). The mean, ±2s, and ±3s are statistics developed from the SMP buffer data prior to 182 days.



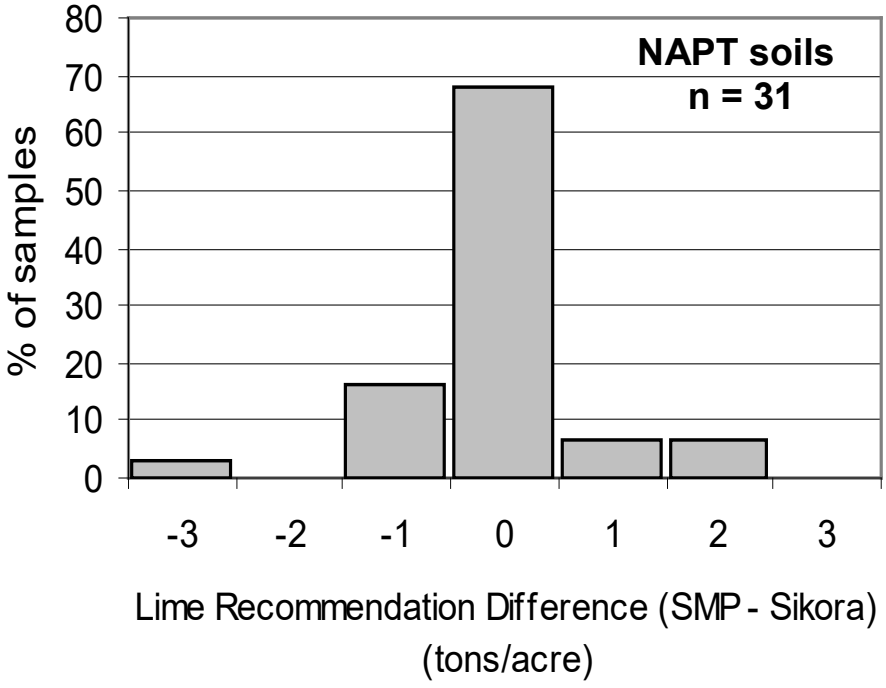


Figure 3. Histograms of the differences in lime recommendations using the Sikora buffer compared to the SMP buffer for the soils in Fig. 1 requiring lime.

The SMP buffer can be utilized with soil-buffer pH levels as low as 4.00 because the buffers reaction with acidity is linear down to that pH level. The Sikora buffer mimics the SMP buffer linearity only down to soil-buffer pH of 5.30. Most soils have soil-buffer pH levels above 5.30. Vaughn (2004) from MDS Harris Laboratories report SMP soil-buffer pH values from 6.40 to 7.20 in soils analyzed all over the world. Soils from the NAPT program from the third quarter of 1999 through 2004 had a range in SMP soil-buffer pH from 5.52 to 7.74 (Miller and Kotuby-Amacher, 2004). In fifteen years of soil test data at the University of Kentucky, 99.9% of SMP soil-buffer pH values were above 5.30. In the extreme case of a very acidic soil with a soil-buffer pH less than 5.30, the Sikora buffer will not mimic the SMP buffer.

The SMP buffer has an ionic strength of 1.08 M due to $CaCl_2$. The Sikora buffer has an ionic strength of 2 M due to KCl. The use of Ca in the replacement buffer was avoided to minimize the possibility of precipitates forming upon storing the buffer. Calcium salts are generally less soluble than potassium salts. The higher ionic strength was utilized in the replacement buffer to maximize the potential of releasing exchangeable acidity from the soil and to act as a microbicide during buffer storage. The higher ionic strength makes it difficult for microorganisms to grow in the solution. The buffer has been stored up to 150 days without any observable microbial growth or affect on soil-buffer pH. The effect of the higher ionic strength had to be capitalized upon because chromium, which acted as an effective microbicide in the SMP buffer, was removed in the Sikora buffer.

COST DIFFERENCES BETWEEN THE SIKORA AND SMP BUFFERS

The cost of the chemicals in the Sikora buffer is greater than the cost of chemicals in the SMP buffer (Table 1). The Sikora buffer costs about 6 cents a sample. The SMP buffer costs about 3 cents a sample. The $CaCl_2$.H2O is the largest contributor to cost of chemicals in the SMP buffer at 56% of total cost. The high cost of $CaCl_2.H_2O$ is due to the large quantity of the chemical needed in the buffer. The MES monohydrate in the Sikora buffer is not used in very large amounts. However, its expense at $426 per kg results in it contributing to half of the chemical cost of the buffer.

There is an increased cost in chemicals on using the Sikora buffer, but there are also savings associated with its use. The two laboratories at the University of Kentucky test about 50,000 samples a year. With the extra 3 cents per sample cost using the Sikora buffer, this results in an additional cost of $1500 per year for buffer chemicals. However, the University is saving money in hazardous waste disposal. Hazardous waste disposal costs the University about 30 cents a pound. This equates to approximately 3 cents per sample or $1500 per year. Therefore, the monetary savings in not handling a hazardous waste is about the same as the extra cost of buffer chemicals. The savings in not handling a hazardous waste may vary in other locations. If disposal costs are greater than 30 cents a pound, there would be a net savings upon using the Sikora buffer. Another slight savings is associated with a technician's time to properly transfer the remains of the soil and buffer to a hazardous waste container. In our laboratory, a vacuum pump was used to individually pump soil and buffer from each SMP buffer soil test into a hazardous waste drum rather than dumping the remains down a sink. Eliminating this step saved about one-tenth of a technician's time in the lab.

Table 1. Cost of SMP and Sikora buffers required for each soil test based on cost of individual chemical components.

Chemical	Quantity needed for 1 L	Quantity [a]	Catalog price for chemical [b]	Chemical company [c]	Cost for one soil test ($) [d]	% of total cost
SMP Buffer						
$CaCl_2 \cdot 2H_2O$	53.1 g	50 kg	$14.39/kg	EMD	0.015	56
$Ca(acetate)_2$	2 g	1 kg	$ 78.40/kg	Alfa Aesar	0.003	11
K_2CrO_4	3 g	0.5 kg	$ 79.80/kg	Lancaster	0.005	18
p-nitrophenol	1.8 g	1 kg	$ 25.20/kg	Alfa Aesar	0.001	4
Triethanolamine	2.5 ml	5 L	$ 67.74/L	EMD	0.003	11
				Total =	**0.027**	
Sikora Buffer						
KCl	149 g	50 kg	$ 14.14/kg	EMD	0.021	36
Acetic acid	5.11 ml	2.5 L	$ 12.92/L	Lancaster	0.001	2
MES monohydrate [e]	6.70 g	0.5 kg	$ 426.00/kg	Alfa Aesar	0.029	50
Imidazole	0.936 g	0.5 kg	$ 83.40/kg	Alfa Aesar	0.001	2
Triethanolamine	9.23 ml	5 L	$ 67.74/L	EMD	0.006	10
NaOH (40% w/w)	5 ml	4 L	$ 8.72/L	VWR	<0.001	<1
				Total =	**0.058**	

[a] Quantity of chemicals based on availability and approximate proportion needed for each buffer
[b] Prices represent lowest cost available for the chemicals at the designated quantity
[c] EMD, Alfa Aesar, Lancaster Synthesis, and VWR prices from VWR International Research, Organic and Lab Chemicals 2005/2007 catalog.
[d] Cost based on 20 ml of SMP buffer used per test and 10 ml of Sikora buffer used per test.
[e] MES = (2-(N-morpholino)ethanesulfonic acid

SUMMARY

A new buffer has been developed without RCRA defined hazardous chemicals that can replace SMP buffer in determining lime requirement of soil. The new Sikora buffer mimics SMP buffer in that it produces the same soil-buffer pH as obtained with SMP buffer within laboratory error. Because of the similarity in the laboratory soil-buffer pH values, lime recommendations from the two buffers are similar.

The recipe for the Sikora buffer has been provided with a description of the chemical differences between SMP and Sikora buffers. The differences involve volume of buffers used in a test, initial pH values of the buffer, suitable pH range for use, and background salts. The cost of the chemicals in the Sikora buffer are about 3 cents more per sample than the cost of chemicals in the SMP buffer. This increase in cost is offset by eliminating the expense of disposing the SMP buffer as a hazardous waste.

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