

LIME REQUIREMENT DETERMINATION OF ACID ORGANIC SOILS  
USING BUFFER-pH METHODSW. VAN LIEROP<sup>1</sup>*Soil Research Service, 2700 Einstein Street, Ste. Foy, Quebec G1P 3W8. Quebec Ministry of Agriculture, Fisheries and Food contribution no. 323, received 25 Aug. 1982, accepted 14 Jan. 1983.*VAN LIEROP, W. 1983. Lime requirement determination of acid organic soils using buffer-pH methods. *Can. J. Soil Sci.* **63**: 411–423.

The aims of this study were to calibrate and assess the accuracy of seven buffer solutions for determining the lime requirement (LR) of organic soils using buffer-pH methodology. The various buffers were evaluated by comparing the precision of regression equations adjusted to the relationships between the LR rates required to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>; ≈ 5.4 (H<sub>2</sub>O)), as determined by incubation, and soil-buffer pH values. The buffers tested and their initial pH values were as follows: Shoemaker, McLean and Pratt (SMP), pH 7.5; Woodruff, pH 7.0; Yuan, pH 7.0 and 6.0; Mehlich, pH 6.6; 0.1 N Ca(OAc)<sub>2</sub>, pH 5.5; 0.1 N Ba(OAc)<sub>2</sub>, pH 5.5; and 0.1 N NH<sub>4</sub>OAc, pH 5.5.

Results indicate that the liming material had reacted with the CaCO<sub>3</sub> neutralizable acidity of these soils within 2 mo as the pH values of the incubated samples did not change materially from the 2nd to the 8th month of incubation. Furthermore, the pH values of the soils utilized in this study increased linearly with increasing rates of applied CaCO<sub>3</sub>. Incubation lime requirements to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>) by the 34 unlimed and 12 partially limed organic soils utilized in this study to calibrate each buffer varied from about 1 to 28 meq CaCO<sub>3</sub>/100 mL soil (1–28 tonne/ha to a depth of 20 cm). Although, the SMP ( $r = -0.957^{**}$ ) and Woodruff ( $r = -0.943^{**}$ ) buffers were somewhat less precise than the Mehlich ( $r = -0.975$ ), Ba-acetate ( $r = -0.966^{**}$ ), or ammonium acetate ( $r = -0.976^{**}$ ) buffers for determining the full range of LR rates encountered in this study, they were nonetheless as precise as any for determining the LR of organic soils needing less than about 20 meq CaCO<sub>3</sub>/100 mL soil to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>). Regression equations for calculating the LR of organic soils, adjusted for differences in their bulk densities, from soil-buffer pH values are provided in the text.

Key words: SMP, Woodruff, Mehlich, Yuan, acetate buffers

[Détermination des besoins en chaux de sols organiques acides au moyen de solutions tampon.]

Titre abrégé: Détermination des besoins en chaux des sols organiques.

Les buts de cette étude furent de calibrer et d'évaluer l'exactitude de sept solutions tampons pour déterminer le besoin en chaux des sols organiques acides. L'évaluation de ces divers tampons fut réalisée en comparant la précision des équations de régression ajustées aux relations entre le besoin en chaux pour atteindre un pH de 5,0 (0,01 M CaCl<sub>2</sub>; 5,4 (H<sub>2</sub>O), tel qu'indiqué par la méthode d'incubation, et les valeurs du pH des mélanges sols-tampons. Les tampons suivants furent vérifiés

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aux pH initiaux indiqués: Shoemaker, McLean et Pratt (SMP), pH 7,5; Woodruff, pH 7,0; Yuan, pH 7,0 et 6,0; Mehlich, pH 6,6; 0,1 N Ca(OAc)<sub>2</sub>, pH 5,5; 0,1 N Ba(OAc)<sub>2</sub>, pH 5,5; et 0,1 N NH<sub>4</sub>OAc<sub>2</sub>, pH 5,5. Les résultats de cette étude indiquent que la chaux appliquée (CaCO<sub>3</sub>) réagit avec l'acidité du sol neutralisable par le CaCO<sub>3</sub> en moins de deux mois, puisque les valeurs de pH des sols incubés ne changeaient plus de façon importante entre le 2<sup>ième</sup> et le 8<sup>ième</sup> mois. De plus, les pH des sols de cette étude augmentaient linéairement avec des doses croissantes de CaCO<sub>3</sub> ajoutées au sol.

Tel qu'indiqué par la méthode d'incubation, les besoins en chaux pour atteindre un pH de 5,0 (0,01 M CaCl<sub>2</sub>) des 34 sols non chaulés et 12 partiellement chaulés, utilisés pour calibrer chaque tampon, se situaient entre 1–28 meq CaCO<sub>3</sub>/100 mL de sol (1–28 tonne/ha pour une profondeur de 20 cm). A partir de sept tampons essayés, cinq furent calibrés pour déterminer le besoin en chaux des sols organiques. Quoique les tampons SMP ( $r = -0,957^{**}$ ) et Woodruff ( $r = -0,943^{**}$ ) furent quelque peu moins précis que ceux de Mehlich ( $r = -0,975^{**}$ ) ou de l'acétate de barium ( $r = -0,966^{**}$ ) ou d'ammonium ( $r = -0,976^{**}$ ) pour déterminer le besoin en chaux de l'ensemble des sols de cette étude, ces tampons étaient néanmoins aussi précis que les autres pour déterminer le besoin en chaux des sols organiques ayant besoin de moins de 20 meq CaCO<sub>3</sub>/100 mL pour atteindre un pH de 5,0 (0,01 M CaCO<sub>3</sub>). Les besoins en chaux de ces sols, ajustés pour leurs différences en densité apparente peuvent être calculés à partir des valeurs du pH des mélanges sol-tampon au moyen des équations de régression incluses dans le texte.

Mots clés: SMP, Woodruff, Mehlich, Yuan, tampons acetate

A number of studies indicate that maximum crop yields can be obtained on organic soils at lower soil pH levels than usually recommended for similar crops grown on mineral soils (Nygard 1954; Davis and Lucas 1959; Jasmin and Heeney 1962; Reith and Robertson 1971; van Lierop and MacKenzie 1975). These inquiries have, however, also shown that crops attain such yields at different degrees of soil acidity. Nonetheless, results obtained by van Lierop and MacKenzie (1975) and van Lierop et al. (1980) indicate that crop yields remain at a maximum over a fairly wide range of soil pH values.

A wide variety of crops are frequently grown on a given field of organic soil when used for vegetable production. Therefore, an appropriate criterion for liming such fields is to choose a pH level sufficiently high to allow production of the most demanding crop in the sequence, while maintaining these soils as acid as possible to minimize their rate of oxidation, hence subsidence. The lime requirement (LR) of a soil is usually defined as the amount of liming material required by a plow layer of

soil to raise its pH to a specific value. To this end, several buffer-pH methods have been developed and verified for measuring the LR of mineral soils (Woodruff 1948; Shoemaker et al. 1961; Yuan 1974, 1976; Mehlich 1976; McLean et al. 1978; Fox 1980; Tran and van Lierop 1981, 1982).

McLean et al. (1966) mentioned that the SMP buffer (Shoemaker et al. 1961) had also been calibrated for determining the lime requirement (LR) of peat soils and he, presumably, published that calibration in 1973 (McLean 1973). Neither the technique used for achieving that calibration nor any verification seem, however, to have been published since then. More recently, Mehlich (1976) proposed a new LR determination buffer which he also calibrated for organic soils containing more than 20% organic matter; his calibration was, however, not achieved by using incubation LR values as is usually done for reference purposes. The quantities of limestone indicated by the SMP buffer are meant to raise the pH of organic soils to 5.2 (H<sub>2</sub>O). On the other hand, the quantities recommended by the Mehlich buffer

are not meant to achieve any particular soil pH but rather to neutralize that fraction of the soil acidity presumed harmful to plant growth.

A soil pH of 5.2 (H<sub>2</sub>O) seems high enough for achieving maximum crop yields on peat soils according to the results obtained by van Lierop et al. (1980). According to their study, alfalfa attained maximum yield at pH 4.5 (KCl) which is equivalent to about pH 5.2 (H<sub>2</sub>O) according to van Lierop (1981a). Although a soil pH of 5.2 (H<sub>2</sub>O) would permit achieving maximum yields by crops which have a tolerance to acid soil conditions that is greater or equal to that of alfalfa, this norm would not allow any safety margin for growing crops that have a tolerance comparable to that of alfalfa. Such a margin might be of some practical benefit as field pH values fluctuate during a growing season, particularly in soils that contain unreacted carbonate, as indicated by van Lierop and MacKenzie (1977). Consequently growth of the more sensitive crops could be hindered by excessive acidity during part of the growing season if the soil pH should fall below this norm. A soil pH of 5.0 (0.01 M CaCl<sub>2</sub>) which is approximately equivalent to 5.4 (H<sub>2</sub>O) was, therefore, chosen for calibrating the buffers verified in this study.

The quantities of limestone recommended by the SMP buffer method for achieving pH 5.2 (H<sub>2</sub>O) are, however, not adjusted for differences in bulk densities between organic soils, though in the procedure proposed by Mehlich soil samples are scooped instead of weighed and thus the recommended LR values obtained may be more accurate. Laboratory data can, however, only be accurately extrapolated into field recommendation by compensating for differences in BD as indicated by van Lierop (1981b). Accordingly, the accuracy of recommendations can be increased by using a measured instead of an assumed average BD value, as the actual BD of organic soils may vary by several

hundred percent from an average value. The objectives of this study were, therefore, to calibrate and evaluate a number of buffers for determining the LR of organic soils using buffer-pH values to indicate the LR. Furthermore, these calibrations should compensate for differences in BD among organic soils thereby improving the accuracy of field recommendations.

## MATERIALS AND METHODS

To achieve the objectives of this study, seven LR determination buffers were evaluated by comparing the precision of regression equations fitted to relationships between incubation LR and buffer pH values. The magnitude of the standard error of estimate ( $s_{y,x}$ ) and correlation coefficient ( $r$ ) were taken as measures of relative precision of the regression equations in this study. The following buffers were tested at the indicated initial pH values: SMP, pH 7.5 (Shoemaker et al. 1961); Woodruff, pH 7.0 (Woodruff 1948); Yuan, pH 7.0 and 6.0 (Yuan 1974, 1976); Mehlich, pH 6.6 (Mehlich 1976); 0.1 N NH<sub>4</sub>OAc, pH 5.5; 0.1 N Ba(OAc)<sub>2</sub>, pH 5.5; and 0.1 N Ca(OAc)<sub>2</sub>, pH 5.5. The initial pH values of 0.1 N calcium, barium and ammonium acetates were decreased to pH 5.5 with 0.1 N HCl. All buffers were tested by using 1:2 vol/vol soil-buffer ratios. The soil-buffer mixtures were swirled for 30-min at about 130 oscillations per minute before measuring soil-buffer pH values. Both supernatant and suspension pH values were measured in each sample for every buffer tested; these operating modes were examined to select the one which was most closely correlated with the incubation lime requirements of these soils. After obtaining the supernatant pH value, a magnetic stirrer was added to the sample and used to agitate it vigorously while reading the suspension value. The effect of soil water content on soil-buffer pH values was also examined by comparing the average suspension pH values obtained at two soil water contents with a *t*-test. Soil-buffer pH data for this comparison were obtained by using buffers at their usual and twice their usual concentrations at 1:4 and 1:2 soil-buffer ratios, respectively.

A calomel reference electrode with a ground-glass sleeve junction instead of the more common fiber junction was used with a glass electrode to determine soil pH; this combination

was found to give relatively faster stable readings with excellent long-term reliability. The pH meter was calibrated with the usual buffer standards (7.0 and 4.0) to ensure that the system was working properly. After this initial verification, the pH meter was adjusted to the initial pH of the LR buffer using an aliquot of that buffer. Thereafter, the buffer was used to verify and adjust the calibration of the pH meter periodically during its use.

Volumetric soil samples were utilized in this study. These were obtained by pressing soils by hand, using thumb and forefinger, until no more soil could be compacted into a 17-mL cup as described for the reconstituted BD method by van Lierop (1981b). The exact size of the cup is, however, not important, any size between about 15 and 20 mL should be adequate as long as twice its volume of buffer is used. This procedure was chosen to simulate the original BD of field moist soil samples.

Thirty-four organic soils were used in this study and represent a typical spread in histic materials found in Quebec. The soils had the following range in soil properties: pH(0.01 M CaCl<sub>2</sub>), 2.64–4.46; BD, 0.17–0.40 g/mL; ash contents 3.5–47%; and Kaila pyrophosphate index values, 93–704. The procedures used to obtain the pH, BD and pyrophosphate data were described by van Lierop (1981a,b) and Schnitzer and Desjardins (1965), respectively. The ash contents were obtained by igniting dried soil samples (105°C) in a muffle furnace at 375°C for 16 h (Ball 1964).

Incubation LR values to attain pH 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) were used to calibrate the various buffers tested. These quantities were obtained graphically from the relationships between the quantities of added CaCO<sub>3</sub> and the ensuing soil pH measured 2, 4, 6 and 8 mo later. The CaCO<sub>3</sub> (<400 mesh) was added to soil samples suspended in four volumes (1:4 vol/vol) of 0.01 M CaCl<sub>2</sub>: water was added to these mixtures as required to approximately maintain this ratio. As fairly acid soils were sampled, they contained an insufficient number of low LR soils for calibrating the full range of buffer-pH values. Accordingly, after completion of the incubation period, from 12–15 partially limed samples were chosen at random for each buffer to provide a greater range in lime requirements. To remove the CaCl<sub>2</sub> from the incubated samples, they were transferred to a Buchner funnel and leached with about 500 mL

of distilled water. The LR rates are expressed in meq CaCO<sub>3</sub>/100 mL soil; these are identical in magnitude to tonnes CaCO<sub>3</sub>/ha to a depth of 20 cm or tonnes CaCO<sub>3</sub>/2.0 × 10<sup>6</sup> L of soil.

## RESULTS AND DISCUSSION

The quantities of CaCO<sub>3</sub> required by the unlimed organic soils of this study to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>; ≈ 5.4 (H<sub>2</sub>O)) ranged from 4.7 to 28.3 meq/100 mL (4.7 to 28.3 tonnes CaCO<sub>3</sub>/ha to a depth of 20 cm). The pH values of all the soils tested increased linearly with increasing rates of applied CaCO<sub>3</sub> (Fig. 1). Furthermore, soil pH did not change materially between the second and eighth month of incubation. Two important practical applications can be derived from the linear relationships between the quantities of added CaCO<sub>3</sub> and ensuing soil pH. These are as follows: (i) the LR to achieve any other soil pH level can easily be calculated from the information given to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>), and (ii) that field data of a recent liming application can be used to calculate the LR to achieve a desired soil pH level.

### SMP Buffer

The pH values of the soil-buffer mixtures for the SMP buffer (Shoemaker et al. 1961)

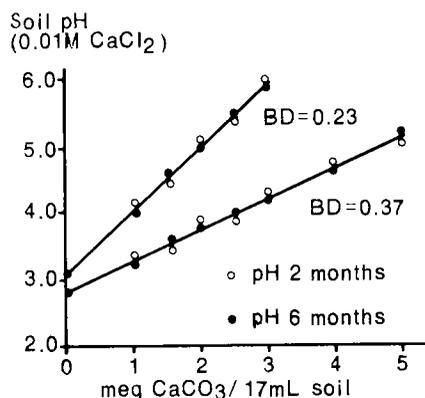


Fig. 1. Representative soil-CaCO<sub>3</sub> incubation graphs for two organic soils of different bulk densities indicating the linear relationship between soil pH and CaCO<sub>3</sub> additions.

and the soils of this study varied from about 3.8 to 6.0 (Fig. 2). The standard error of estimate ( $s_{y,x}$ ) was, however, larger for this buffer than most of the others tested. Nonetheless, as can be seen from the graph, the larger error ( $s_{y,x}$ ) was caused by the high LR soils, as the regression fit for soils requiring less than 20 meq  $\text{CaCO}_3/100$  mL was as good for this buffer as any tested.

This buffer is probably the most widely used and among the most accurate for determining the LR of acid mineral soils (McLean et al. 1978; Fox 1980; Tran and van Lierop 1981, 1982), but it is usually calibrated for pH values ranging from 4.8 to 6.7. The calibration published by

McLean (1973) for determining the LR of organic soils with the SMP buffer also covered that range. Results of the present study indicate, however, that the effective range of this buffer can be extended to the calibrated range. This assertion was confirmed by the fact that the linearity of this buffer was greater than most of the others tested, as indicated by the titration curve, for the buffer-pH range calibrated in this study (Fig. 3). The buffering capacity of the SMP buffer was the lowest of the buffers tested. For this reason the SMP buffer exhibited a greater sensitivity to change in pH for a given soil LR (Table 1). This additional sensitivity could be advantageous when using a pH-meter which lacked this quality. In such cases greater accuracy

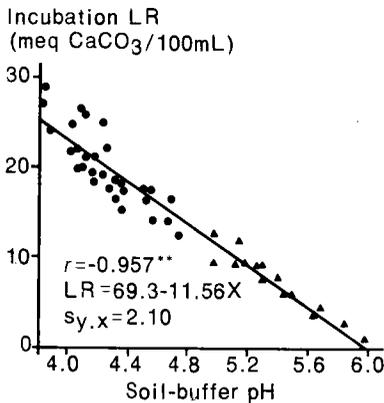


Fig. 2. Relationship between the incubation lime requirement for achieving a soil pH of 5.0 (0.01 M  $\text{CaCl}_2$ ) or 5.4 ( $\text{H}_2\text{O}$ ) and soil-buffer pH values for the SMP buffer ( $\bullet$  = unlimed,  $\blacktriangle$  = partially limed soils).

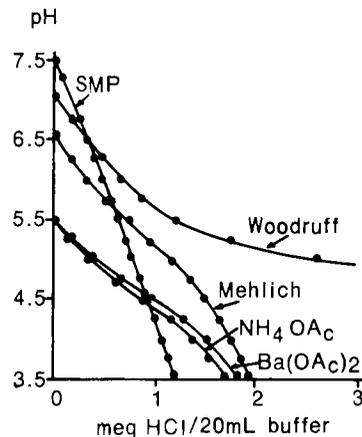


Fig. 3. Titration curves of the five lime requirement determination buffers calibrated for use in organic soils.

Table 1. Regression equations and information for calculating the lime requirement ( $\hat{Y}$ ) of organic soils to achieve a pH of 5.0 (0.01 M  $\text{CaCl}_2$  or 5.4 ( $\text{H}_2\text{O}$ )) with the calibrated buffers

Buffer	Equation	Calibrated range (soil-buffer pH)	$r$	$S_{y,x}$
SMP	$\hat{Y}^\dagger = 69.3 - 11.56X$	3.9–6.0	-0.957**	2.10
Woodruff	$\hat{Y} = 143.14 - 23.6X$	5.0–6.1	-0.943**	2.45
Mehlich	$\hat{Y} = 103.9 - 17.43X$	4.4–6.0	-0.975**	1.64
$\text{Ba}(\text{OAc})_2$	$\hat{Y} = 147.3 - 27.78X$	4.3–5.3	-0.966**	1.90
$\text{NH}_4\text{OAc}$	$\hat{Y} = 206.67 - 38.71X$	4.6–5.4	-0.976**	1.66

$\dagger$ Lime requirements are in meq  $\text{CaCO}_3/100$  mL soil; rates are equivalent in magnitude to tonnes  $\text{CaCO}_3/\text{ha}$  for a plow layer depth of 20 cm.

could perhaps be achieved by using this type of buffer, though the additional sensitivity was not an important advantage in this study as the precision of this buffer was not better than most of the others tested.

A comparison of the calibration for the SMP buffer derived from the data of this study to obtain a soil pH equivalent to 5.4 (H<sub>2</sub>O) with that published by McLean (1973) for attaining pH 5.2 (H<sub>2</sub>O) revealed that McLean's calibration recommended insufficient and superfluous quantities of limestone for organic soils when soil-buffer pH values were lower or higher than about 5.4, respectively (Fig. 4). In fact, by using the calibration suggested by McLean (1973), soils would continue to be limed far beyond pH 5.4 (H<sub>2</sub>O). Although McLean (1973) prescribed that soils be weighed instead of scooped for measuring their LR, this dissimilarity in procedure cannot explain the differences obtained between the calibrations, as using his procedure for dried and ground organic soils would have increased their LR, because drying increases the BD of these soils (van

Lierop 1981b). In any event, McLean (1973) did not describe the procedure used for calibrating this buffer for determining the LR of organic soils and, consequently, it is very difficult to speculate about the dissimilarity between the two calibrations. Nonetheless this difference is probably not related to soil characteristics as such buffers merely react with a calibrated portion of the CaCO<sub>3</sub>-neutralizable soil acidity. This conclusion is confirmed by the similarities between the SMP buffer calibration obtained by Shoemaker et al. (1961), McLean et al. (1978), Tran and van Lierop (1981, 1982) for determining the LR of acid mineral soils.

As with the other buffers reported in this study, soil-buffer pH values should be measured in a suspension as the correlation coefficient calculated between the incubation LR and soil-buffer pH values decreased from 0.957\*\* to 0.793\*\* for data measured in suspensions and supernatants, respectively. Furthermore, soil water contents do not affect soil-buffer pH values. This was verified by practically identical suspension soil-buffer pH values obtained (means 4.61 vs. 4.58,  $r = 0.983^{**}$ ) with the SMP buffer utilized at its usual and twice its usual concentration at 1:4 and 1:2 vol/vol soil-buffer ratios, respectively. The LR rates required by organic soils to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) can be readily calculated from the soil-SMP buffer pH values by using the regression equation provided in Fig. 2 or Table 1 or they can be obtained directly from Table 2.

### Woodruff Buffer

The pH values of the soil-buffer mixtures for the Woodruff buffer (Woodruff 1948) and the soils of this study varied from about 5.1 to 6.1 (Fig. 5). Woodruff calibrated this buffer for measuring the LR of mineral soils so that for every 0.1 pH unit decrease in pH of the soil-buffer mixture, for values situated between pH 7.0 and 6.0, a furrow slice of soil ( $\approx 17$  cm depth)

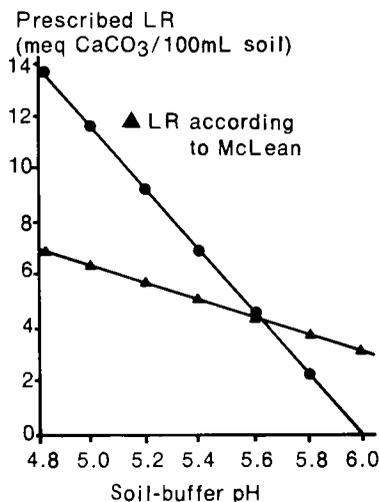


Fig. 4. Comparison of the lime requirement rates prescribed by the SMP buffer using the calibration derived in this study and that published by McLean (1973).

Table 2. Relationship between soil-buffer pH values and the lime requirements† of organic soils for achieving a pH of 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) for the various calibrated buffers

Soil-buffer pH	SMP	Woodruff	Mehlich	Ba(OAc) <sub>2</sub>	NH <sub>4</sub> OAc
6.1	0.0†	0.0	0.0	0.0	0.0
6.0	0.0	1.5	0.0	0.0	0.0
5.9	1.1	3.9	1.1	0.0	0.0
5.8	2.2	6.3	2.8	0.0	0.0
5.7	3.4	8.6	4.5	0.0	0.0
5.6	4.6	11.0	6.3	0.0	0.0
5.5	5.7	13.3	8.0	0.0	0.0
5.4	6.9	15.7	9.8	0.0	0.0
5.3	8.0	18.1	11.5	0.0	1.5
5.2	9.2	20.4	13.3	2.8	5.4
5.1	10.3	22.8	15.0	5.6	9.3
5.0	11.5	25.1	16.7	8.4	13.1
4.9	12.7		18.5	11.2	17.0
4.8	13.8		20.2	14.0	21.0
4.7	15.0		22.0	16.7	24.7
4.6	16.1		23.7	19.5	28.6
4.5	17.3		25.5	22.3	
4.4	18.4		27.2	25.0	
4.3	19.6			27.8	
4.2	20.7				
4.1	21.9				
4.0	23.0				
3.9	24.2				

†Rates are expressed in meq of CaCO<sub>3</sub>/100 mL soil and are equivalent to tonnes of CaCO<sub>3</sub>/ha to a depth of 20 cm.

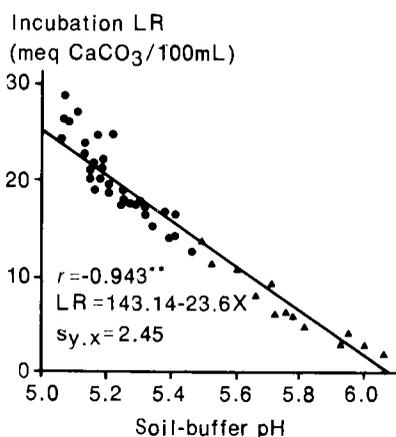


Fig. 5. Relationship between the incubation lime requirement for achieving a soil pH of 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) and soil-buffer pH values for the Woodruff buffer (● = unlimed, ▲ = partially limed soils).

would need 1000 lbs CaCO<sub>3</sub>/acre to achieve pH ≈ 6.5. Furthermore, the Woodruff buffer is probably the first widely used buffer for determining the LR of mineral soils using buffer-pH methodology. Although the precision of this buffer has been corroborated over the years, it has frequently been accused of lacking accuracy (McLean et al. 1966; Webber et al. 1977; Fox 1980). The likely reason for this shortcoming is that the calibration of this buffer was not derived by using incubation LR values for reference purposes as pointed out by Tran and van Lierop (1981). In any event, a different portion of the buffer titration curve was calibrated in this experiment than used by Woodruff: i.e. 6.1–5.1 instead of 7.0–6.0 by Woodruff for mineral soils. The buffer zone calibrated in this study was substantially less linear and more strongly buffered than that proposed for mineral soils by Woodruff. The linearity of a buffer, however, seemed not to

be of overriding importance as the more precise  $\text{NH}_4\text{OAc}$  buffer had a linearity and buffering capacity comparable to that of the Woodruff buffer.

The standard error of estimate ( $s_{y,x}$ ) for the relationship between the incubation LR to attain pH 5.0 (0.01 M  $\text{CaCl}_2$ ) or 5.4 ( $\text{H}_2\text{O}$ ) and the soil-buffer pH values was greater for the Woodruff than the other buffers. However, as can be verified from the graph and found for the SMP buffer, the regression fit for soils requiring less than 20 meq  $\text{CaCO}_3/100$  mL was as good for the Woodruff buffer as any tested. The sensitivity of the Woodruff buffer, though lower than that of the SMP buffer, was comparable to some of the more precise buffers tested; the sensitivity is, therefore, not a primary contributing factor for achieving high precision LR measurements.

A curvilinear equation probably would have provided a better regression fit for the relationship between incubation LR and soil-buffer pH values. This greater precision would, however, not be of any practical importance as it would only apply to soils requiring more than 20 meq  $\text{CaCO}_3/100$  mL (20 tonnes  $\text{CaCO}_3/\text{ha}$ ). On such soils it would probably be better to make several smaller limestone applications as this would result in a more homogeneous dispersion of the liming material throughout the plow layer of soil and thus avoid localized overliming.

The LR rates required by organic soils to achieve pH 5.0 (0.01 M  $\text{CaCl}_2$ ) or 5.4 ( $\text{H}_2\text{O}$ ) can be readily calculated from the soil-Woodruff buffer pH values by using the regression equation provided in Fig. 5 or Table 1 or they can be obtained directly from Table 2. As with the other buffers in this study, soil-buffer pH values should be determined in suspensions as the correlation coefficient calculated between the incubation LR and soil buffer pH values decreased from 0.943\*\* to 0.813\*\* for data obtained in suspensions and supernatants, respectively. Furthermore, soil water con-

tents did not affect soil-buffer pH values. This was verified by the practically identical suspension soil-buffer pH values (means 5.38 vs. 5.35,  $r = 0.993^{**}$ ) of the Woodruff buffer utilized at its usual and twice its usual concentration at 1:4 and 1:2 vol/vol soil-buffer ratios, respectively.

### Mehlich Buffer

The pH values of the soil-buffer mixtures for the Mehlich buffer (Mehlich 1976) and the soils of this study varied from about 4.1 to 5.9 (Fig. 6). The sensitivity of this buffer, as indicated by the size of the decrease in soil-buffer pH for a given LR, was intermediate between that of the SMP and the other buffers reported in Table 1. The slope of the titration curve for the calibrated range showed that the buffering capacity of this buffer was also intermediate between the SMP and the others as shown in Fig. 3. Compared to the SMP or the Woodruff, the Mehlich buffer was, however, more precise for determining the full range of LR values encountered in this study. Mehlich calibrated this buffer to measure the LR of organic soils (soils which had organic matter contents in ex-

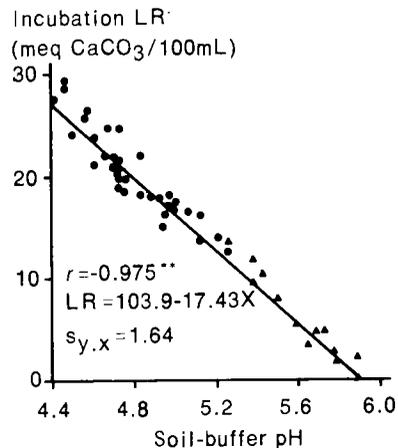


Fig. 6. Incubation lime requirement for achieving a soil pH 5.0 (0.01 M  $\text{CaCl}_2$ ) or 5.4 ( $\text{H}_2\text{O}$ ) as related to soil-buffer pH values for the Mehlich buffer (● = unlimed, ▲ = partially limed soils).

cess of 20%) for soil-buffer values ranging from 3.9 to 5.4 (lime requirements ranging from 0–12.8 tonnes/ha vs. 0–27 tonnes/ha in this study).

The main differences in the procedures used to derive the original calibration and that obtained in this study are as follows: (i) only half the quantity of buffer solution was used in the original, (ii) the reference LR values were calculated from soil cation exchange properties instead of, as more commonly done, incubation LR values, and (iii) 60-min of soil buffer equilibrium times vs. 30-min in this study. The rates of liming material prescribed by this buffer, according to the original calibration, were not intended to achieve any particular soil pH but rather to neutralize that portion of the soil acidity presumed harmful to plant growth. Effectively, this was achieved by reducing the concentration of exchangeable acidity in soils to a level that had been shown by previous liming experiments to allow maximum crop yields.

Despite the differences between the procedures followed by Mehlich and this study, the limestone rates prescribed by both calibrations were compared for the soil-buffer values calibrated in this study. However, as twice as much buffer solution was used in this study than by Mehlich, which should consequently lead to only half the soil-buffer pH decrease, the AC values calculated according to the equation proposed by Mehlich were corrected by multiplying them by two: i.e.  $(6.6\text{-BpH}) \times 8$  instead of  $(6.6\text{-BpH}) \times 4$ . Accordingly, the LR rates calculated with the regression equation derived from the data of this study (included in Fig. 6) were contrasted with those calculated with the system of equations proposed by Mehlich, using corrected AC values, for soil-buffer pH values ranging from 4.8 to 6.0 (Fig. 7). This comparison revealed that both calibrations prescribed practically identical quantities of limestone, but at the lower lime requirements the Mehlich calibration prescribed slightly higher rates.

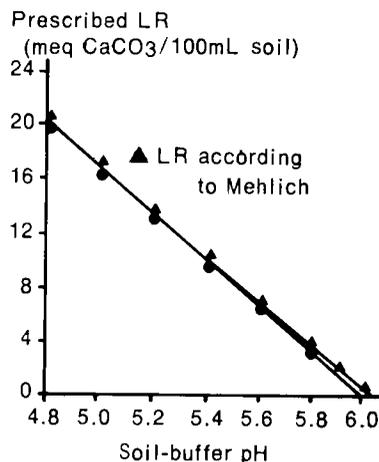


Fig. 7. Comparison of the lime requirement rates prescribed by the Mehlich buffer with the calibration derived in this study and that proposed by Mehlich.

The surprising similarity between these two calibrations revealed several important facts. Firstly, that the calibrations derived in these two independent studies are applicable to a wider range of soils than used in either study. Secondly, that the more rapid (1/2-h) soil-buffer equilibrium time can be substituted for the longer (1-h) period used in the original calibration without sacrificing precision. Lastly, that the original calibration unintentionally prescribes quantities of limestone that tend to raise the pH of soils to the same level. Similarly, Tran and van Lierop (1982) found that the Mehlich buffer tended to prescribe the lime requirements necessary to achieve a pH of about 5.5 (H<sub>2</sub>O) of acid mineral soils.

The LR rates required by organic soils to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) can be easily calculated from the soil-Mehlich buffer pH values by using the regression equation provided in Fig. 6 or Table 1 or they can be obtained directly from Table 2. As with the other calibrated buffers, soil-buffer pH values should be measured in suspensions. This was indicated by a lower correlation coefficient for the relationship between the incubation LR

and soil-buffer pH values measured in supernatants ( $r = -0.823^{**}$ ) instead of suspensions ( $r = -0.975^{**}$ ). Furthermore, soil water contents did not materially affect soil-buffer pH as found with the other buffers tested. This was indicated by the practically identical suspension pH values (means 5.03 vs. 5.01,  $r = 0.994^{**}$ ) for the Mehlich buffer utilized as its usual and twice its usual concentration at 1:4 and 1:2 vol/vol soil-buffer ratios, respectively.

### Yuan Buffer

The range in soil-buffer pH values observed with the Yuan buffer (Yuan 1974, 1976) and the soils of this study varied from 4.36 to 5.75 and 3.67 and 5.18 with initial buffer pH values at 7.0 and 6.0, respectively. No calibration is offered for determining the LR of organic soils with this buffer as it was significantly less precise than most of the others tested. This lower precision was indicated by the smaller correlation coefficients for the relationships between the incubation LR of the unlimed soils of this study and the soil-buffer pH values for both initial buffer pHs 7.0 ( $r = -0.751^{**}$ ) and 6.0 ( $r = -0.764^{**}$ ). Although Yuan proposed that his buffer be used in an innovative double-buffer procedure, and that his methodology was adapted by McLean et al. (1978) for the SMP buffer, this buffer, at either initial buffer pH values, was shown by Tran and van Lierop (1982) to work very well as a single buffer method for measuring the LR of mineral soils to achieve pH 5.5 or 6.0. It was thought that the probable reason for the lower precision of this buffer in the present study, when used at the 1:2 vol/vol soil buffer ratio, was caused by the location of the soil-buffer pH values on a very curvilinear portion of the titration curve. For example, the shape of the titration curve for this buffer is fairly linear between pH 7.0 and 5.0, but it is strongly curvilinear between pH 5.0 and 4.0, while it is fairly linear again between pH 4.0 and 3.0.

The buffering capacity of this buffer is, however, about eight times greater (0.4 meq HCl/ $\Delta$  pH for 20 mL buffer) between pH 7.0 and 5.0 than between pH 4.0 and 3.0 (0.05 meq HCl/ $\Delta$  pH). Therefore, the Yuan buffer was also tried at 1:5 vol/vol soil-buffer ratios to raise the soil-buffer pH values in a more linear working range. With the wider soil-buffer ratios, the pH values varied from 5.61 to 6.43 and from 5.2 to 5.8 for data obtained with initial buffer pHs of 7.0 and 6.0, respectively. Unfortunately, the correlation coefficients for the relationships between the incubation LR and soil-buffer pH values decreased to  $-0.37^*$  and  $-0.43^{**}$  for these corresponding initial buffer pH values. Possibly this buffer could be calibrated by selecting a more suitable soil-buffer ratio, however, no exact reasons can be offered for its failure in this study.

### Calcium-acetate Buffer

The pH values of the soil-buffer mixtures for the Ca(OAc)<sub>2</sub> buffer, adjusted initially to pH 5.5, and the soils of this study varied from 4.49 to 4.87. As for the Yuan buffer, no calibration is offered for this buffer for determining the LR of organic soils because the relationship between the incubation LR and the soil-buffer pH values for the unlimed soils of this study was less precise ( $r = -0.722^{**}$ ) for this buffer than those calibrated in this study. The probable reason for this lower precision may be that calcium reacts preferentially with carboxylic exchange groups in organic soils as indicated by Schnitzer and Desjardins (1965). This conclusion was confirmed by adding 1 vol of 0.01 M CaCl<sub>2</sub> to barium- and ammonium-acetate soil-buffer mixtures. The effect of the CaCl<sub>2</sub> was to reduce the correlation coefficients between the incubation LR and soil-buffer pH values for the unlimed samples from  $-0.905^{**}$  and  $-0.923^{**}$  to  $-0.83^{**}$  and  $-0.52^{**}$  for the Ba(OAc)<sub>2</sub> and NH<sub>4</sub>OAc buffers, respectively.

### Barium-acetate Buffer

The range in soil-buffer pH values observed with the 0.1 N Ba(OAc)<sub>2</sub> buffer, adjusted initially to pH 5.5, and the soils of this study varied from about pH 4.4 to 5.2 (Fig. 8). The sensitivity, or the change in pH of the soil-buffer mixture for a given LR, was comparable for this and the Woodruff buffer. Furthermore, the precision of this buffer was intermediate between, on one hand, the SMP and Woodruff buffer, and on the other, the Mehlich and NH<sub>4</sub>OAc buffer. The main advantage, in addition to its good precision, for using this or the NH<sub>4</sub>OAc buffer is their simplicity and ease of preparation compared to the other calibrated buffers. The Ba(OAc)<sub>2</sub> buffer may, however, be somewhat more resistant to microbiological decay than the NH<sub>4</sub>OAc.

The LR rates required by organic soils to achieve pH 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) can be readily calculated from the soil-Ba(OAc)<sub>2</sub> buffer pH values by using the regression equation provided in Fig. 8 or Table 1 or they can be obtained directly from Table 2. As with the other buffers

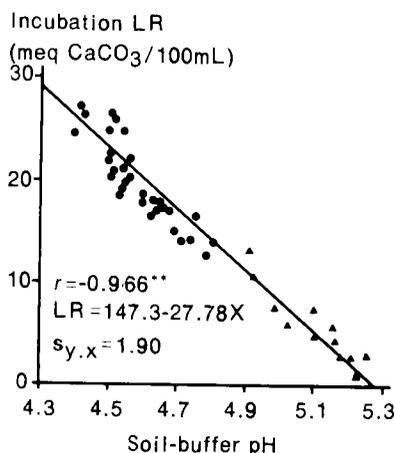


Fig. 8. Relationship between the incubation lime requirement for achieving a soil pH of 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) and soil-buffer pH values for the 0.1 N Ba(OAc)<sub>2</sub> buffer adjusted initially to pH 5.5 (• = unlimed, ▲ = partially limed soils).

calibrated in this study suspension soil-buffer pH values, which were not affected by soil water contents, should be used to calculate the LR rates for organic soils. The precision of this buffer was similarly affected by the mode of pH measurement and the soil water content as reported for some of the others.

### Ammonium-acetate Buffer

The pH values of the soil-buffer mixtures for the 0.1 N NH<sub>4</sub>OAc buffer, adjusted initially to pH 5.5, and the soils of this study varied from about 4.65 to 5.35 (Fig. 9). Although it was the least sensitive buffer tested, as indicated by the size of soil-buffer pH change for a given LR, the NH<sub>4</sub>OAc and the Mehlich buffers were the most precise buffers calibrated. In addition to its unexcelled precision, the main advantages to using this buffer, over the others tested, are its low cost and ease of preparation. It should, however, probably be pointed out that this buffer can be readily contaminated by microbiological growth and should therefore be treated accordingly. Probably the best way to avoid possible contamination is by not preparing more buffer than required for every 4 or 5

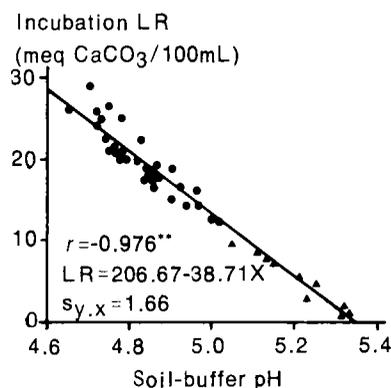


Fig. 9. Connection between the incubation lime requirement for achieving a soil pH of 5.0 (0.01 M CaCl<sub>2</sub>) or 5.4 (H<sub>2</sub>O) and soil-buffer pH values for the 0.1 N NH<sub>4</sub>OAc buffer adjusted initially to pH 5.5 (• = unlimed, ▲ = partially limed soils).

days of operation and store the unnecessary portion in a refrigerator. Though it can be prepared so easily by simply titrating the required volume of 0.1 N  $\text{NH}_4\text{OAc}$  to pH 5.5 with 0.1 N HCl that it is probably just as simple to make it fresh daily.

The rates of LR necessary by organic soils to achieve pH 5.0 (0.01 M  $\text{CaCl}_2$ ) or 5.4 ( $\text{H}_2\text{O}$ ) can be readily calculated from the soil- $\text{NH}_4\text{OAc}$  buffer pH values by using the regression equation provided in Fig. 9 or Table 1 or they can be obtained directly from Table 2. As with the other buffers calibrated in this study, suspension soil-buffer pH values, which were not affected by soil water contents, should be used to calculate the LR rates for organic soils. The precision of this buffer was similarly affected by the mode of pH measurement and the soil water content as reported for some of the others.

### CONCLUSIONS

The calibrations derived in this study revealed that the SMP and Woodruff buffers were somewhat less precise than the Mehlich,  $\text{Ba}(\text{OAc})_2$  or  $\text{NH}_4\text{OAc}$  buffers for determining the LR of organic soils needing more than about 20 meq  $\text{CaCO}_3/100$  mL (20 tonnes/ha to a depth of 20 cm) to achieve pH 5.0 (0.01 M  $\text{CaCl}_2$ ). Nonetheless, the SMP and Woodruff were as precise as the other calibrated buffers for determining the LR of soils needing lower rates of liming material to achieve this pH level. Frequently, liming rates determined from calibrations such as given in this study are multiplied by about 1.4 to compensate for differences between finely ground pure  $\text{CaCO}_3$ , used for calibrating the buffer, and commercial limestone used for liming fields (Woodruff 1948; Shoemaker et al. 1961). A commercial limestone is usually less finely ground than the  $\text{CaCO}_3$  used in this study, and its neutralizing power may vary from about 85 to 105%  $\text{CaCO}_3$  equivalent. As no accurate means seem to be available at present for correcting for differences between reactiv-

ity of available commercial limestone and pure  $\text{CaCO}_3$  as used in this study, it is probably more prudent not to apply any correction factor unless the prescribed rate is less than about 6 tonne/ha. For larger prescribed rates it may be wiser to fractionate these into two or more smaller applications of around 4–8 tonne/ha instead of a single large addition. This approach will result in a more homogeneous dispersion of the liming material in the plow layer and will, thereby, also minimize the risk of yield reductions caused by over-limed zones. The choice of buffer for determining the LR of organic soils is not very important. Probably, if one of these calibrated buffers is already in use for determining the LR of mineral soils, it may be advantageous to merely use the same buffer with the procedure described in this study and the appropriate calibration to determine the LR of organic soils. If a buffer has to be prepared for determining the LR of these soils, however, it would be much simpler to use either the  $\text{Ba}(\text{OAc})_2$  or  $\text{NH}_4\text{OAc}$  buffer.

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