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Modeling lime reaction in peat-based substrates

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Abstract

Limestone is incorporated into peat-based substrates to neutralize substrate acidity, increase pH buffering capacity, and provide calcium and magnesium. Limestones differ in their rate of pH change, equilibrium pH, and proportion of unreacted “residual” lime. In horticulture, lime reactivity is currently measured empirically in batch tests whereby limestone is incorporated into a batch of substrate and pH change is measured over time. Our objective was to develop a quantitative model to describe reaction of lime over time. The lime reaction model predicts the substrate-pH based on lime acid neutralizing capacity, lime type (calcitic, dolomitic, or hydrated), lime particle size distribution, application concentration, and the non-limed pH and neutralizing requirement (buffering) of the substrate. Residual lime is calculated as the proportion of lime remaining following gradual neutralization of the substrate acidity (by subtraction of reacted lime from total applied lime).

INTRODUCTION

The amount of lime required to neutralize acidity of a soilless container growing medium is currently measured empirically in batch tests, whereby limestone is incorporated into substrates and pH change is measured over time (Argo and Fisher, 2002). In order to develop a quantitative model of lime reaction in horticultural substrates, three “R’s” need to be considered: Reactivity, Residual, and Requirement. **Reactivity**, which describes the magnitude of pH change (ΔpH) over time, is primarily a function of lime particle size, lime chemistry (calcitic (CaCO_3) versus dolomitic ($\text{CaMg}(\text{CO}_3)_2$) versus hydrated ($\text{Ca}(\text{OH})_2$), acid neutralizing value (NV)), and initial substrate-pH. **Residual** lime is the proportion of unreacted lime remaining following neutralization of substrate acidity. Residual lime is the major source of buffering to pH change over time in soilless substrates, which have low cation exchange capacity per unit volume (Argo and Biernbaum, 1996). **Lime Requirement** (g of lime/L of substrate) depends on the amount of acidity that needs to be neutralized in order to raise the substrate pH to a specific level (pH buffering), and is measured in units of ΔpH per milliequivalent of base per unit volume (liters) of substrate.

Our objective was to develop a quantitative model to describe reaction of lime over time. The model predicts the substrate-pH based on lime acid neutralizing capacity, lime type (calcitic, dolomitic, or hydrated), lime particle size distribution, application concentration, and the non-limed pH and neutralizing requirement (pH buffering) of the substrate.

MATERIALS AND METHODS

Reactivity

Figure 1 illustrates how substrate-pH response can differ between liming sources. Rate of pH change decreased in the order from reagent grade calcium carbonate (CaCO_3) to NLS limestone to OldCastle limestone. Substrate-pH was measured in all experiments using the squeeze solution displacement method where moisture level was maintained at 95% container capacity (Rippy and Nelson, 2005). The difference in reaction rate resulted primarily from differences in particle size distribution, and secondarily in NV (Table 1, where NV was determined using the AOAC Official Method 955.01 (Horwitz, 2003)). Reagent grade calcium carbonate was composed entirely of particles that passed a 45 μm (U.S. 325 mesh) screen. In contrast, NLS had a particle size distribution similar to the mean of our survey of limes used in horticultural substrates in the U.S. and Canada, and OldCastle was coarser than the mean particle size distribution of horticultural limes (Table 1). Differences between limes in NV occur because of the low molecular weight of magnesium compared with calcium carbonates – compared with pure CaCO_3 as a standard, dolomitic ($\text{CaMg}(\text{CO}_3)_2$) carbonate limes have a higher NV per gram of lime. In addition, hydrated lime (calcium or magnesium hydroxide), which is commonly used in container media has a lower molecular weight, faster reaction rate, and higher NV than carbonate limes. For four hydrated limes we tested that are used in horticultural substrates in the U.S. and Canada, NV ranged from 117.2% to 162.6% CaCO_3 equivalents. Hydrated limes are chemically manufactured, with very fine particle size.

Because the dissolution of limestone occurs as a surface reaction, the particle size distribution of a liming material directly influences dissolution rate. To evaluate the effect of particle size on soil pH changes in agronomy, a particle size efficiency (PSE) factor can be assigned to each particle size fraction of an agricultural limestone ranging from 0 (unreactive) to 1 (highly reactive) (Barber, 1984; Tisdale and Nelson, 1975). However, because lime sources used in horticulture tend to be finer and faster-reacting than limes used on field soils, PSE from the agronomy literature are too imprecise for a horticultural model.

We quantified new PSE parameters for six lime particle size fractions (>850 (retained on 20 U.S. standard mesh), 850 to 250 (retained on 60 mesh), 250 to 150 (retained on 100 mesh), 150 to 75 (retained 200 mesh), 75 to 45 (retained on 325 mesh), and < 45 μm (passed through 325 mesh)). PSE was calculated from pH responses for separated lime fractions from ten calcitic and dolomitic limes, based on their increase in substrate pH (ΔpH) relative to reagent grade CaCO_3 when mixed in a Canadian sphagnum peat substrate (SunGro Horticulture Inc., Bellevue, Wash.) with long fibers and little dust (Von Post scale 2-3; Puustjarvi and Robertson, 1975) at 22°C and maintained at a moisture level near container capacity, at 5 g CaCO_3 equivalents/L of peat.

PSE increases over time to a maximum of 1, as the lime fraction gradually reacts with the peat acidity. We were interested in simulating pH response, and the response in pH over time shows diminishing returns (Figure 2). We therefore empirically quantified the change in PSE over time using an exponential decay (monomolecular) function (Table 2), where A represents the maximum PSE (equal to 1) and k is a rate parameter. The monomolecular function closely fit the measured PSE data, with a p-value less than 0.001 for all curve fittings, and r^2 greater than 0.98.

Lime sources normally include a range in particle sizes, and the percent by weight of each particle size fraction (PF) describes the distribution. The overall particle size efficiency of a lime source was described by its fineness factor (FF), calculated for time t as the sum of PF and PSE for each of the six particle size fractions described in Table 2:

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$$FF_t = \sum_{i=1}^6 (PF_i \times PSE_{i,t}) \quad [1]$$

The term calcium carbonate equivalence (ECC), calculated as a ratio of neutralizing value compared with CaCO_3 , quantifies the combined effects of particle size distribution and acid neutralizing value (NV) of a limestone on pH response, calculated as:

$$ECC = FF \times NV \quad [2]$$

Factors other than acid neutralizing value and particle size may affect lime reaction rate. For example, Rippey et al. (2004) found large differences in surface area between limes within a given particle size fraction. When we evaluated pH response over time for each of six particle size fractions using three calcitic and seven dolomitic limes, pH varied by less than 0.3 pH units between lime sources of a given type (calcitic or dolomitic) for almost all data points, particularly for the fine particle sizes that predominate in horticultural limes. We consider that error level acceptable, and both particle size distribution and lime chemistry are factors that are easily measured and are standard reported technical specifications for lime sources.

Residual

When a lime is incorporated into a growing medium, a proportion of the lime may remain unreacted. This residual lime fraction is very important because most of the buffering to pH change in container media comes from this unreacted pool of lime (Argo and Biernbaum, 1996). Residual lime arises both because the solubility of limestone decreases as pH increases, and because coarse particles may become coated with organic and mineral precipitates over time, thereby reducing surface reactivity (Warfvinge and Sverdrup, 1989). For example, for the most coarse lime particles (>850 μm), the asymptote for the pH reaction was only 56.3% of the chemically-potential pH response (Table 2), even though the curve was fitted using pH data from up to 77 days after mixing at near ideal conditions. Therefore, coarse lime particles contribute little to initial neutralization of substrate acidity, but contribute more to the residual lime pool compared with fine lime particles. Figure 3 shows that as lime application rate increased, pH increased to a plateau level around 7.5 for CaCO_3 – additional lime remained as unreacted residual. pH response (and therefore the proportion of lime reacted) was less for the NLS and Oldcastle lime sources than CaCO_3 , and consequently the quantity of unreacted residual lime was greater for these two limestones.

It is possible to analytically measure total alkalinity in the substrate (including carbonates, hydroxides, and other molecules such as phosphate, and ammonia/ammonium that contribute to pH buffering) through acid titration (Richards, 1954; Loeppert et al., 1984). Carbonate sources of alkalinity can also be quantified using a gasometric Chittick apparatus (Dreimanis, 1962). In addition, if the pH buffering of a particular substrate is calculated, residual lime can be calculated by subtracting the proportion of reacted lime from the total lime applied.

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Requirement

Lime requirement for a substrate depends on the initial substrate pH, and the buffering of the substrate to changes in substrate-pH. Substrate buffering (pHB) can be quantified with units of ΔpH per milliequivalent of base per L of substrate ($\Delta\text{pH}\cdot\text{meq}\cdot\text{L}^{-1}$). Titration of peat with $\text{Ca}(\text{OH})_2$ shows an approximately linear pH response with increasing application rate of base up to a pH near 7.0 (Rippy and Nelson, 2005). Because of this linearity, few data points are needed to quantify pHB for any given substrate.

The target pH ($\text{pH}_{\text{target}}$), often around 6.0 for horticulture, can be calculated from the initial substrate pH (pH_{init}), resulting in a required $\Delta\text{pH}_{\text{required}}$:

$$\Delta\text{pH}_{\text{required}} = \text{pH}_{\text{target}} - \text{pH}_{\text{init}} \quad [3]$$

The milliequivalents of base ($\text{meq}_{\text{required}}$) required to achieve a target substrate-pH can be calculated from the substrate buffering and initial substrate pH.

$$\text{meq}_{\text{required}}\cdot\text{L}^{-1} = \Delta\text{pH}_{\text{required}}/\text{pHB} \quad [4]$$

The effective milliequivalents of a particular lime source at a given number of days t after incorporating lime can be calculated from equation 2 in order to convert $\text{meq}\cdot\text{L}^{-1}$ to $\text{g lime}\cdot\text{L}^{-1}$. In addition, the pH response at time t for a given number of grams of applied lime, L^{-1} (C) can be calculated from

$$\text{pH}_t = \text{pH}_{\text{init}} + C\cdot(\text{ECC}_t\cdot\text{meq CaCO}_3/\text{g lime})\cdot\text{pHB} \quad [5]$$

where ECC on day t is calculated using the monomolecular function parameters in Table 2.

The parameters for equations [1] and Table 2 were calibrated using screened particle size fractions of three calcitic limes, and seven dolomitic limes. We then validated the model in two experiments using 29 unscreened calcitic and dolomitic carbonate and hydrated lime sources, including the 10 calibration limes. In one experiment, 1L of peat was blended at 5g of lime (i.e. not corrected for differences in NV between limes). In the second experiment, 5 g/L of CaCO_3 equivalents for each lime, i.e. corrected for NV, was blended with a different peat source, using the same 29 lime sources. The predicted pH on days 7 and 28 are compared with measured media-pH in Fig. 4. The model described the overall pH trend for different lime types, with improved prediction of pH at day 28 compared with day 7.

MODEL APPLICATION AND CONCLUSIONS

We developed a prototype application based on the model for predicting lime requirement for a given lime source and substrate. The inputs are data from a $\text{Ca}(\text{OH})_2$ titration to quantify pH buffering of the substrate, the particle size distribution and chemical characteristics of the lime, and the target pH (assumed to occur at $t=14$ days). Outputs of the model are the contribution of each particle size to pH change, residual, or reactivity; proportion of the lime that is expected to be residual or reacted, and a sensitivity analysis of pH, which includes a monomolecular curve to represent the solubility of CaCO_3 with increasing pH. Further research is needed to validate and expand the scope of the model. Environmental conditions could certainly affect reactivity and need to be incorporated into the model, particularly media temperature and moisture level.

The majority of published lime research has been conducted with field soils over long time periods, typically with limestones that are coarser than those used in peat-based substrates. A quantitative model has potential to improve lime selection, lime incorporation rate, and management

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of residual buffering. The model provides a framework to incorporate other factors that influence substrate-pH over time, for example fertilizer and water alkalinity in simulation of substrate-pH.

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Tables

Table 1. Physical and chemical characteristics of the three lime materials (CaCO₃, and two limestones – NLS and OldCastle) tested in Figure 1, along with the mean and standard deviation for 24 calcitic and dolomitic carbonate lime sources used in horticultural substrates in the U.S. and Canada.

		CaCO ₃	NLS	OldCastle	Mean of 24 horticultural lime samples (± s. dev.)
µm	U.S. mesh				Passing (%)
Screen size	Screen size				
850	20	100	100	98	99.7±0.9
250	60	100	98	73	92.9±17.4
150	100	100	93	55	86.8±21.5
75	200	100	65	23	69.6±22.7
45	325	100	50	< 23	52.2±22.3
Chemical analysis					
	Ca (%)	40	21	22	24.5±7.4
	Mg (%)	0	12	11.5	8.4±4.6
	NV (%)	100	105	104	102.1±4.9

Table 2. The monomolecular function used to empirically quantify the particle size effectiveness (PSE) for six lime particle size fractions over time, with the exponential decay curve $PSE = A(1 - e^{-kt})$. *A* represents the maximum effectiveness between 0 and 1, *k* is a rate parameter, and *t* represents the days after incorporating the lime into peat. *A* was not significantly different from 1 for particles sizes greater than 250 µm.

Particle size fraction (µm)	850-2000	250-850	150-250	150-250	75-150	75-150	45-75	45-75	<45	<45
Lime type ^z	C,D	C,D	C	D	C	D	C	D	C	D
K	0.038	0.085	0.219	0.152	0.513	0.335	1.027	0.693	1.504	1.009
S. err. of K	0.003	0.003	0.009	0.003	0.027	0.011	0.003	0.016	0.059	0.016
A	0.563	0.900	1	1	1	1	1	1	1	1
S. err. of A	0.019	0.007								
Days to 95% reaction	n/a	n/a	13.7	19.7	5.8	8.9	2.9	4.3	2.0	3.0
Days to 50% reaction	58.2	9.5	3.2	4.5	1.4	2.1	0.7	1.0	0.5	0.7
r ² ^y	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.99

^z C = calcitic, and D = dolomitic carbonate limes. For the two most coarse particle size fractions, there was no significant difference between PSE for calcitic and dolomitic limes.

^y The r² is based on correlation between the PSE estimated using the monomolecular function versus the measured PSE. Measured PSE was calculated as ΔpH from the lime fraction/ ΔpH from reagent grade CaCO₃.

Figures

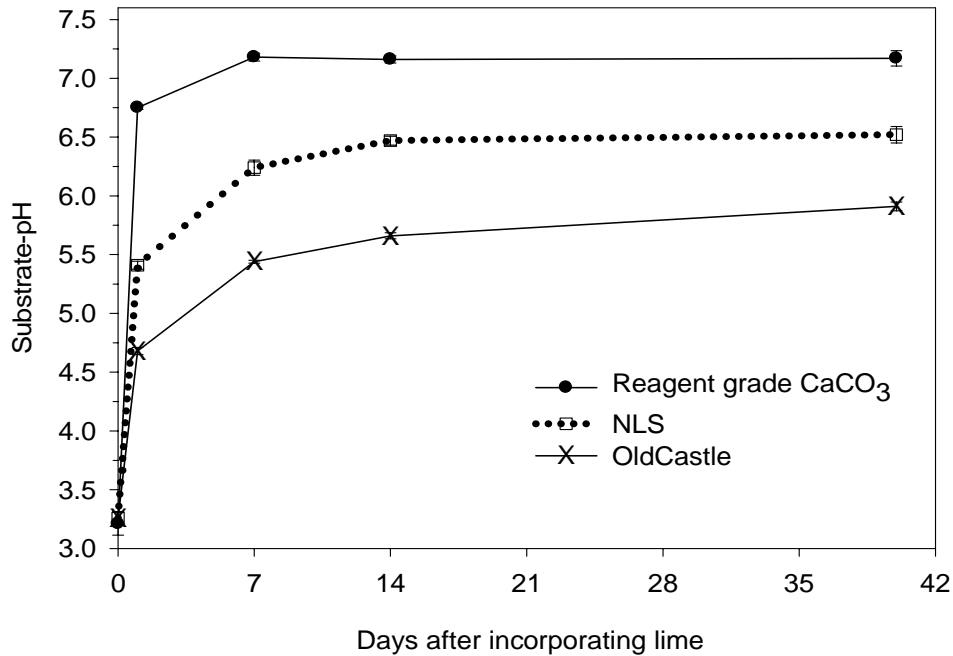


Figure 1. pH response for three liming sources blended into peat at 6 grams of lime per liter of substrate. NLS and OldCastle are two lime sources used in horticultural substrates. The substrate temperature was maintained at 22°C, and substrate moisture was 0.3L deionized water/L of substrate. Symbols represent the average response for 3 media-samples ± one standard error.

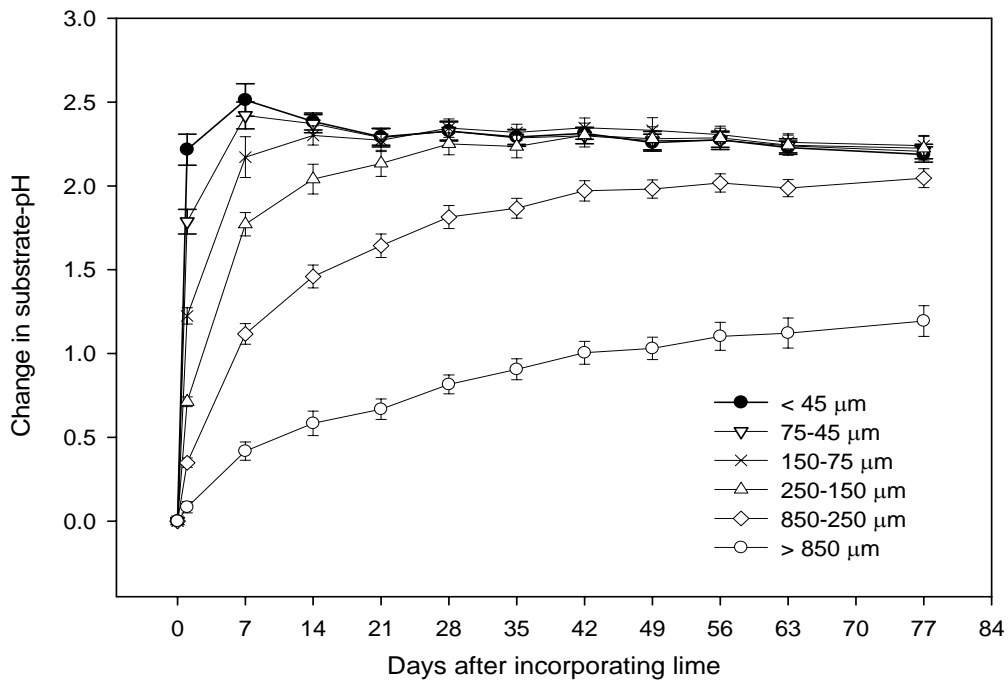


Figure 2. Mean change in substrate-pH for six particle size fractions averaged over ten calcitic and dolomitic limes. Symbols represent the average response for 30 media samples ± 95% confidence error.

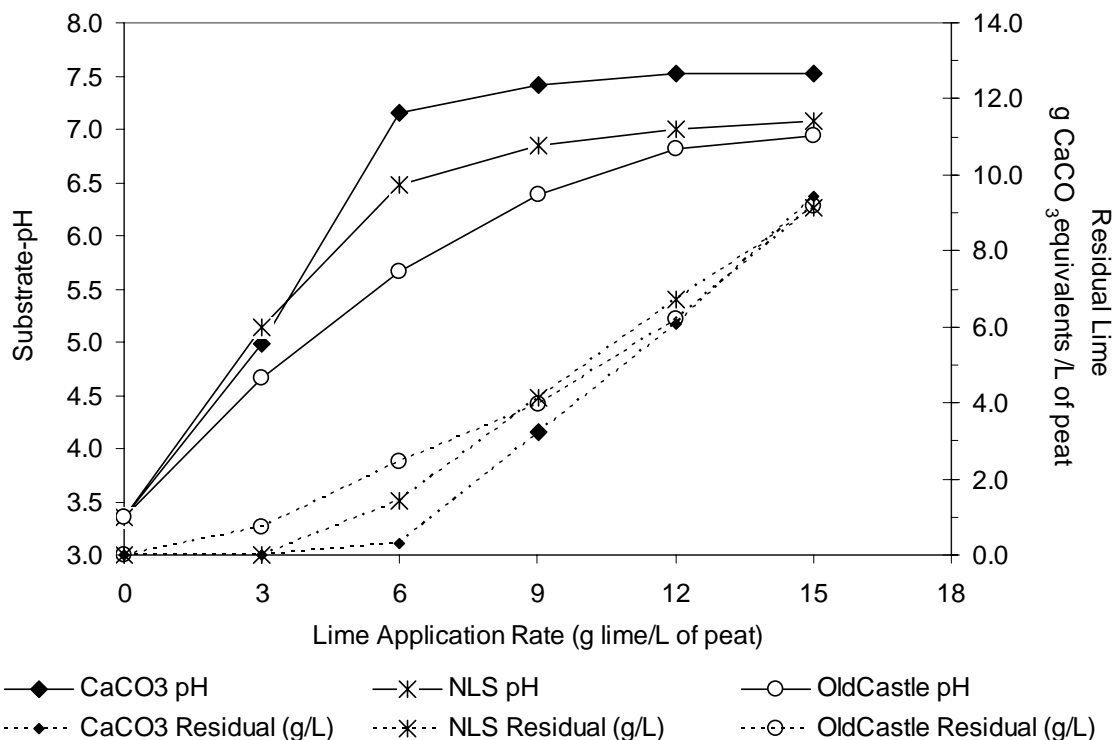


Figure 3. pH response (left vertical axis) and residual lime (right axis) for three lime types with increasing lime application rates, 14 days after incorporating the lime into a peat substrate. Residual lime (g CaCO₃ equivalents per liter of substrate) was measured using gasometric analysis (Dreimanis, 1962).

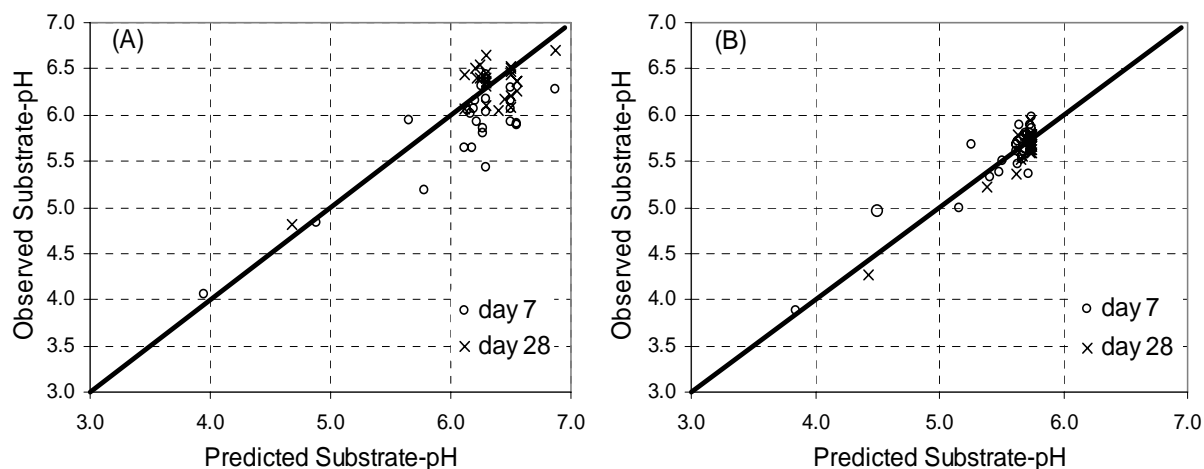


Figure 4. Validation of the pH model, with two experiments and 29 unscreened lime sources applied to peat, with different peat sources in each experiment. In experiment 1 (A), 1L of peat was blended at 5g of lime. In the second experiment (B), 1L of peat was blended at 5 g CaCO₃ equivalents for each lime.