Simulation of the changes in soil pH of various acidic soils through lime applications

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Abstract: Incorporation of lime in plough-layer soil is widely recommended for the amelioration of acid soils in the southern wheat belt of New South Wales. However, farmers need to estimate how much lime is required to increase the soil pH to a target pH associated with optimum economic returns from the application of lime. This paper reports a function that simulates the rate of dissolution of ground limestone in the LimeIt-3 model. The model initially estimates the amount of $CaCO_3$ reacted in soil in one year. The reaction rate is modelled as a function of soil pH, the annual rainfall, the particle size distribution, the solubility of the limestone source and the soil cation exchangeable capacity at pH 5.4. Changes in soil pH are simulated for six soil types that range from weakly weathered forms of chromosols, dermosols, vertosols and kandosols to highly weathered tenosols and ferrosols. The soil pH changes are simulated for each of the soils, for an annual rainfall of 550 mm and a wheat-canola rotation over 10 years. The results give the amount of lime required to raise the soil pH (0-10 cm) from an initial pH between 4.1 and 4.8 to give a nominated average pH of over 10 years. The lime required ranged between 3.6 t/ha (strongly weathered form of chromosols and kandosols) to 6.2 t/ha (ferrosols). The economically optimum rate of lime for the 10 year rotation varied from 2.0 t/ha (strongly weathered forms of chromosols, dermosols and kandosols) to 5.5 t/ha (kurosols) at \$40/t lime cost landed on farm and \$15/t spread cost.

Keywords: Soil acidification; pH; LimeIt 3; effective cation exchange capacity

1. INTRODUCTION

Application of ground limestone is the most common agronomic approach to management of acidic soils. A number of questions need to be answered for farmers in a decision-making process for lime application. The key question is how much lime is needed to raise the current soil pH to a value high enough to avoid economically significant decreases in crop yield. Because the relationships between crop yield and soil pH differ depending on crop species and varieties, it is hard to answer the question without considering the complexity of the system. Simulation models for calculating the lime requirements are an effective approach. In these models, various methods are used to estimate lime requirement, based on changes in the ECEC (effective cation exchangeable capacity) (Hochman et al., 1989), changes in exchangeable Al (Kamprath, 1970), Al saturation of cation exchange complex (Sanchez, 1976) or soil pH (McLean, 1971).

One of the key functions in modelling lime use is to predict residual value of lime applications, but little information is available. It is expected that the residual value of applied lime is associated with the amount of lime applied, soil characteristics and rainfall. A lime model should involve chemical interactions in dissolution and reaction of lime.

The aims of this paper are to present a method for simulating the rate of lime reaction in LimeIt3 and compare the predicted pH changes in various soil types though application of lime.

2. MATERIAL AND METHODS

Outline of LimeIt 3 model The Lime-it 3 model has been designed to recommend the most profitable lime rate for a nominated rotation over a 10 year period. It is sufficiently general to be applied to the range of climates and acid soils and plant species used for agriculture in Australia. The soil module estimates the amount of OH^- or H^+ that reacts with the soil as the pH increases due to addition of alkali over the pH range from near 3.5

to near 7.4 (assuming an ionic strength of 0.03M). The OH^- or H^+ requirement is estimated from changes in the pH-dependant effective cation exchange capacity (ECEC) and in exchangeable Al^{3+}. The rate of dissolution of ground limestone added as the source of alkali is estimated as a function of the particle size distribution, the source of limestone (calcite, dolomite or soft or 'coraline' limestone), the rainfall, the soil pH and the neutralising value or purity of the limestone. The rate of acid addition to the soil from the biological C and N cycles, is estimated from tabular data on the acidification rates experienced by typical crop, annual pasture or perennial pasture systems. Data are provided for each system across a range of climatic conditions from strongly perennial (ie. high rainfall and moderate seasonal variation in soil moisture supply) to strongly annual (ie. lower rainfall and strongly seasonal variation in soil moisture). The initial estimates of acid addition rates are then adjusted for: i) systems with exceptionally high or low soil N status; ii) application of N fertilizer in forms that are more (NH_4) or less (NO_3) acidifying than the form of N added to the experimental systems used to define the initial estimates of rates of acid addition (organic or N from N_2 fixation or urea fertilizer); iii) removal of organic anions in products not removed in the typical systems; and iv) observed effects of low pH reducing the rate of decline of pH expected from changes in ECEC and Al^{3+} alone (assumed to be a surrogate method of accounting for the weathering of minerals containing cations of strong bases). Movement of the effects of acid or lime addition down the soil profile is modelled as an empirical function of soil pH.

It is assumed that the increase in pH buffering capacity (pHBC) as the pH rises above pH 5.4 (ie. the decrease in the slope the curve towards zero as the pH approaches about 7.4) is mainly due to the limitation on the dissolution of lime as the pH increases. At about pH_{Ca} 7.4 the 0.01 M $CaCl_2$ solution becomes saturated with respect to $CaCO_3$, and so will not dissolve.

The subroutine for lime reaction The model estimates the amount of $CaCO_3$ reacted in one year. The rate of reaction (*R*) is a function of soil pH (*pH*), ECEC at pH=5.4 (E_i) and rainfall in the following form

$$R = f(P)\left[\frac{a+bE_i}{1+e^{c+dE_i+e.pH}} - \frac{f}{g+e^{h.pH}}\right] \quad (1)$$

where $R \geq 0.0$. If $R < 0.0$, *R* is assigned a value of 0.0. *f(P)* is a function that accounts for the effect of rainfall on the rate of lime reaction, *a*, *b*, *c*, *d*, e, *f*, *g* and *h* are constants. The pH 5.4 was chosen as the standard pH at which to characterise the ECEC of the soil because it is the ECEC at the point of inflexion of the soil pH buffer curve (Magdoff and Bartlet, 1985). The effect of rainfall, *f(P)* can be defined in a simple hyperbolic equation:

$$f(P) = \frac{qP}{r+P} \quad (2)$$

where *P* is annual rainfall, *q* and *r* are constants.

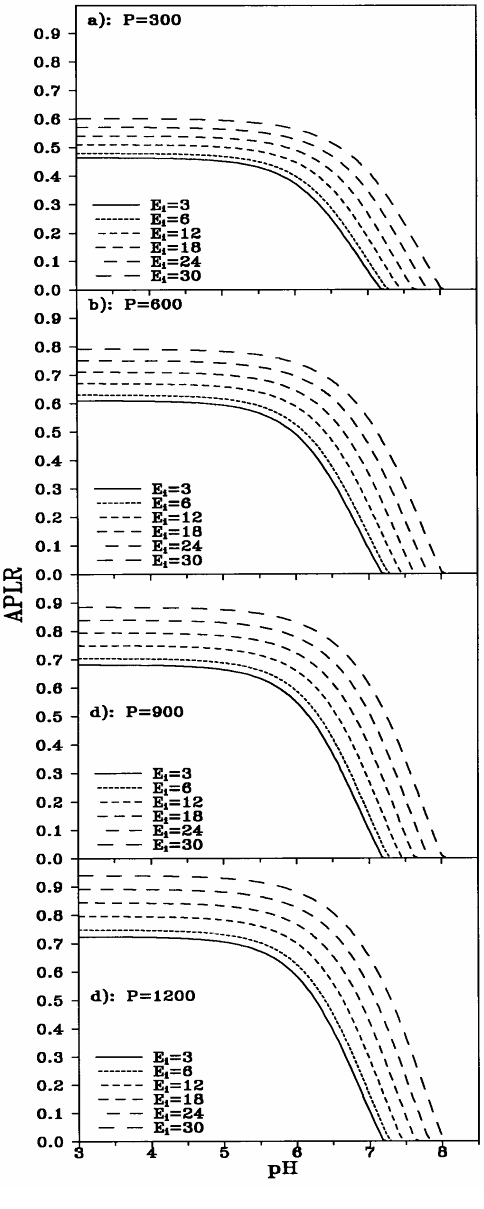

Figure 1. Predicted relationships between the rate of lime reaction and soil pH at various ECEC at pH 5.4 (E_i) and annual rainfall (P).

Figure 1 illustrates the rate of reaction of lime for various soil types and the effects of rainfall. Limited data sets were available for fitting the coefficients *q* and *r* . They have been chosen to predict the observed data which is dominantly in the rainfall range 500 to 700 mm per annum. Estimates of the rates of dissolution of lime outside this range were chosen to constrain the coefficients. Formal fitting will be used as data across a wider rainfall range becomes available.

In the current model, soil is characterised by ECEC at pH 5.4, which is calculated, given knowledge of the pH and ECEC of an acid soil, by

$$E_i = E + \frac{(E+0.96)(5.40-pH)}{pH-2.04} \qquad (3)$$

It is assumed that all ECEC at pH 2.04 are equal to 0.96. The apparent proportion of lime reacted (APLR) increases with higher E_i and higher rainfall (Figure 1).

There are two distinct features in the current model. As it is a logistic equation, at a wide range of low pH the APLR holds constant. The APLR declined at pH > 5.5 for soils which have $E_i < 3.0$ cmol kg^{-1} and at pH > 6.5 for the soils with $E_i > 20.0$ cmol kg^{-1} soil.

At a high soil pH the $CaCO_3$ is saturated, so the rate of lime reaction equals zero. The $CaCO_3$ saturation pH is normally around 7.4, though this will vary with soil type. The negative term in Equation (1) allows the equation to turn sharply as zero APLR is approached. The early version of the equation without the negative term predicted non-zero rate of reaction at pH above 8.0, which is considered to be unrealistic. In the current model, as the pH increases, the APLR decreases towards zero at pH around 7.0 to 8.0.

Soil types The six soil types used are listed in Table 1. The initial soil pH and ECEC at pH 5.4 is listed in Table 2.

Table 1. Description of soil types

Soil Code	Soil description
1	Weakly weathered forms of chromosols, dermosols, vertosols, and kandosols
2	Strongly weathered forms of chromosols, dermosols and kandosols
3	Sodosols
4	Kurosols
5	Tenosols (highly weathered soils high in SiO_2)
6	Ferrosols (highly weathered soils high in Al and Fe oxides)

Table 2. Key chemical properties of the 6 soils

Soil Code	Initial pH	E_i (cmol /kg)
1	4.17	8.84
2	4.53	4.66
3	4.09	5.10
4	4.10	5.67
5	4.04	5.16
6	4.80	12.85

3. RESULTS AND DISCUSSION

Model development Figure 2 shows the observed apparent proportion of lime reacted (APLR) in 18 acid soils in a pot experiment. Helyar et al. (1995) fitted the data to a modified hyperbolic equation. Due to the nature of hyperbolic equations, the APLR decreased over the whole pH range. However, theoretically, there exists a wide range of low pH which may give a constant APLR. Subsequently, a logistic function (Eq. 1) is used for this study. Further modification of the logistic equation aims to give a sharp asymptote near zero at high pH, instead of a slow approach to a zero value at an indefinite pH. In addition, the current equations include effects of rainfall and ECEC.

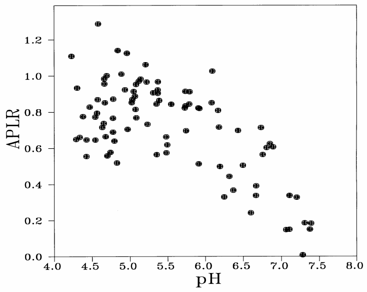

Figure 2. The apparent proportion of lime reacted (APLR) of 18 acid soils

Equation (1) was fitted to pot data for 18 acid soils. The parameters for equation (1) are listed in Table 2. The parameters for the equations (Table 3) account for 61% of the variation in measured data, suggesting a large proportion of variance cannot be explained by the model. In the comparison between the estimated reaction rates and the measured lime reaction rates, the intercept is significantly different from zero (Figure 3). The unexplained variation may, however, be associated with a peculiarity of the pot experiment.

Table 3. Parameters determined for the constants in Equations 1 and 2.

Constants in Eqs (1) and (2)	Estimated Parameters
A	0.728
B	0.829×10^{-2}
C	-16.025
D	2.401
E	-0.089
F	0.279×10^{-6}
G	0.588×10^{-6}
H	-1.642
Q	1.182
R	275.000

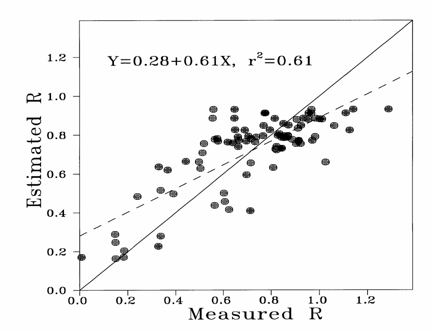

Figure 3. Comparison between measured apparent proportion lime reacted and estimated apparent proportion lime reacted by Equation (1).

The amount of water involved in the processes of lime dissolution is a primary factor determining the rate of lime reaction. In undrained pot experiments, water supply is based on water consumption by the plants, which in turn depends on the plant growth. On the other hand, plant growth is largely affected by soil pH. Thus, on the low soil pH treatment i.e. lower rate of lime application, the water consumption is small due to a low rate of growth. Water use will consequently affect the rate of reaction. The variation may be the amount of water passed through the pot and its interaction with other factors. As it is not possible to separate out the water effect in a pot experiment, the water consumption may be one of the factors contributing to the unexplained variation. In the field however, rainfall dominates the soil water flux rather than the plant growth rate. Therefore fitting the water flux effect from the pot experiment would not be expected to produce a model fully applicable in field conditions.

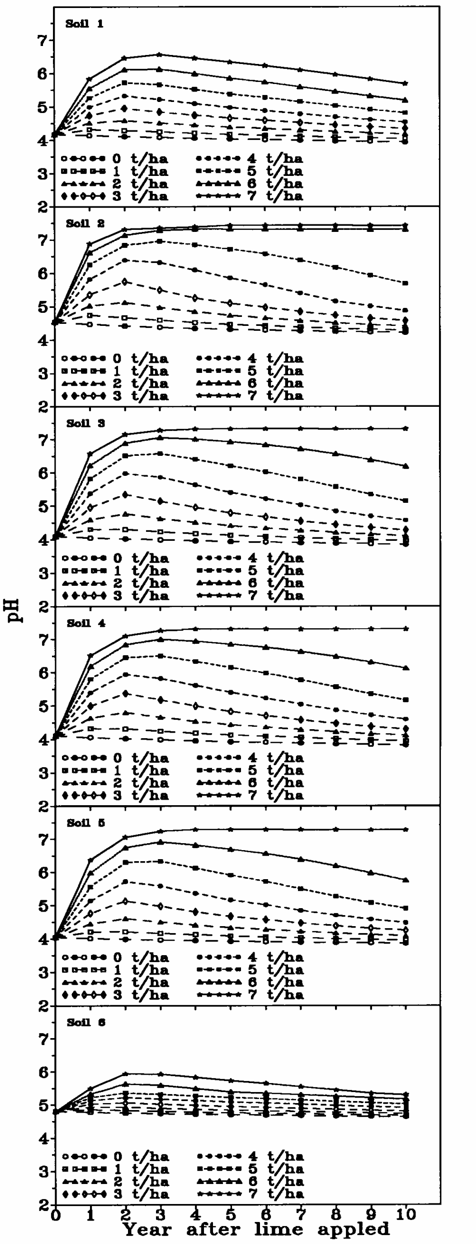

Figure 4: Simulation of soil pH changes in various soil types with the application of various amounts of ground limestone for 10 years after the lime applied. Annual rainfall = 550 mm. Crop was a 10 year canola/wheat rotation. Ammonium nitrate was applied at the rate of 55 kg N ha^{-1}. The N fertility status was high enough to support 90-100% potential yield.

Simulation of changes in pH LimeIt 3 has been validated against field observations at four sites. Good agreement between observed and simulated pH changes was obtained (data not shown).

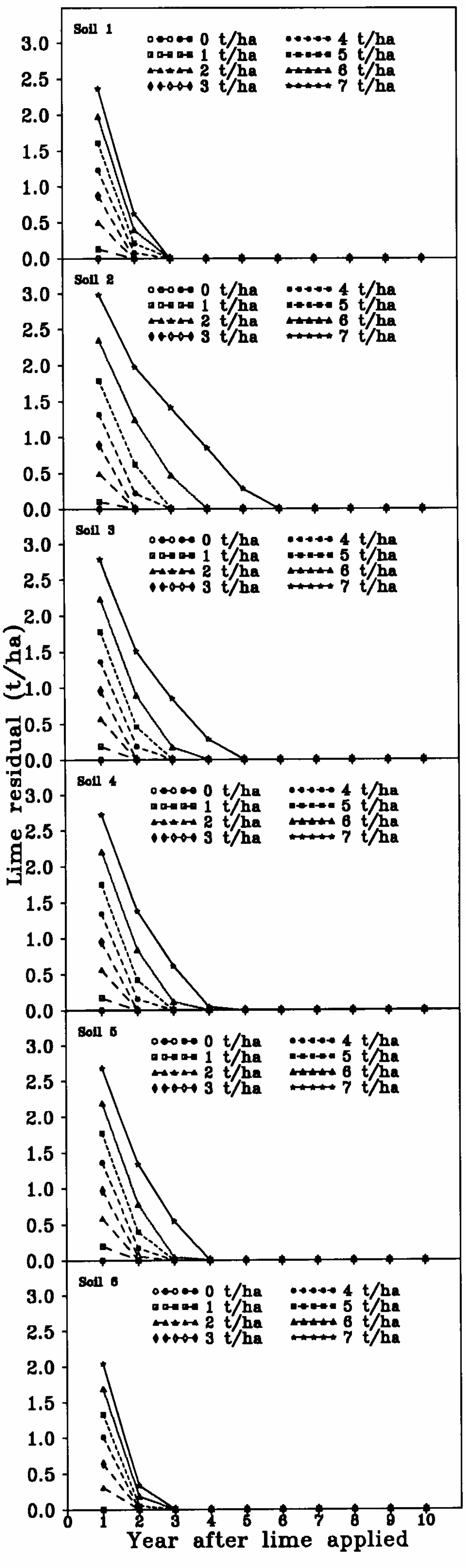

Figure 5. Simulation of lime residual in top layer soil (0-10) after lime application.

LimeIt 3 simulates an increase in soil pH as the rate of lime application increases (Figure 4). The highest soil pH is obtained at 2 or 3 years after lime application. After the peak soil pH is reached, soil pH declines in the following years. This is because soil acidity is induced during crop growth. For un-limed soil, the rate of acidification is very slow and it was estimated that the time required for a decrease of one unit of pH to occur may range from about 50 to well over 100 years depending on the soil type (Williams, 1981). When pH rises to a high value through application of lime, i.e. over 7.0, the decline in pH is very fast due to a high rate of movement down to the lower soil profile. For example, for a Kurosol soil (soil 4) applying 4 t/ha lime raised soil pH from an initial pH 4.1 to 6.0 at year 2 after lime application. The soil pH declined to 5.0 at year 7 after lime application. This means that it will take only 5 years for a decrease of one unit of pH.

The maximum pH 7.4 is reached on soils 2, 3, 4, and 5 at a liming rate of 7 t/ha, while soils 1 and 6 achieved a pH 6.5 and pH 6.0 at two years after lime application, respectively. Soil 6, a highly weathered soil with high Al and Fe oxides, has a high pH buffer capacity due to a high ECEC.

For the 7 t/ha rate of lime application, soils 2, 3, 4 and 5 can maintain a high pH for 10 years after lime application. There are some slight decreases in pH at the high rate of lime application, but the decrease rate is not great in comparison with the decreases of moderate rates at lime application.

Simulation of lime residual at top soil layer

After lime application, the reaction of lime will begin as soon as the soil becomes moist. There are many factors that affect the rate of lime reaction. The present soil pH, soil moisture and physical and chemical properties of the soil are the major ones.

LimeIt 3 simulates the process of lime reaction and calculates lime remaining in the soil. Figure 5 shows the lime residual in the top layer (0-10 cm). The amount of lime remaining at year 1 after lime applied is 2 – 3 t/ha at the rate of 7 t/ha lime application, while there are only 0.1-0.2 t/ha lime remaining un-reacted at rate of 1 t/ha lime applied. At the rate of 1-7 t/ha, a complete lime reaction required 3 – 6 years. Soils 1 and 6 required the shortest time for complete reaction, while soil 2 required the longest time for the reaction of all lime.

Soil 6 has the highest ECEC value at pH 5.395 (E_i), while soil 2 has lowest E_i among the six soil groups (Table 2). Equation (1) predicted a higher reaction rate for a higher E_i (Figure 1). This explains the difference in lime residual for different soil types in the top soil layer (Figure 5).

Simulation of profitable lime application rate
The following parameters were used in LimeIt3 to simulate the most profitable lime application:

- 10 years of canola-wheat rotation;
- Wheat/canola yields without lime are 2.0/1.5 for soils 1, 3, 4, 5 and 6; 2.5/2.0 for soil 2 and 3.0/2.5 for soil 6;
- The farm enterprise budget was obtained from NSW Agriculture internet. Wheat budget: Grazing and grain in southern zone – east and the canola budget: Canola after cereal in southern zone – east;
- Lime spreading cost $15/t;
- Long term inflation rate for prices paid 2% per year;
- Long term inflation rate for price received 2% per year;
- Discount rate 7% per year.

Table 4 shows that the lime rate for a 10-year mean pH 5.4 ($LR_{5.4}$) ranged from 3.6 t/ha for soil 2 to 6.2 t/ha for soil 6. The most profitable rate of lime application depends on soil types and lime cost landed on farm. At $40/t lime cost landed on farm, the profitable lime rate ranges from 2.0 to 5.5 t/ha; while at $65/t lime cost landed on farm, the profitable lime rate is 0 to 5 t/ha. At a higher price of lime landed on farm, it is not profitable to apply lime to soil 2 and soil 6, but soil pH will decrease from current pH 4.53 and 4.80 to 4.22 and 4.38, respectively. Note that the residual value (negative or positive) of changes in pH at the end of 10 years is not considered in LimeIt 3.

Table 4. Profitable rate of lime application.

Soil Code	$LR_{5.4}$ (t/ha)	Lime cost landed on farm			
		$40.0/t		$65.0/t	
		LR (t/ha)	10 yr pH_{10}	LR (t/ha)	10 yr pH
1	5.4	2.5	4.50	1.5	4.27
2	3.6	2.0	4.73	0.0	4.39
3	4.2	4.5	5.57	4.0	5.26
4	4.3	5.5	6.24	5.0	5.91
5	4.6	4.0	5.06	3.0	4.63
6	6.2	3.5	5.01	0.0	4.63

4. CONCLUSIONS

The LimeIt 3 model has been designed to simulate the effect of rate of lime application and the most profitable lime rate for a nominated rotation over 10 years. The key process featured in this paper is simulation of the lime reaction. The approach using ECEC at pH 5.4 to represent soil characteristics in the model is simplistic, but illustrates the importance of the effect that the CEC has on the reaction of lime. The model also incorporated the soil pH and annual rainfall in the subroutine for simulating the lime reaction. By testing the LimeIt 3 model against data from the field experiments, good agreement of soil pH changes between the observed and simulated data was obtained, indicating the subroutine presented in this paper is a reasonable approach in simulating the lime reaction and soil pH changes.

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