

The reaction rate and residual value of particle size fractions of limestone in southern New South Wales

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Abstract. Grain yield is frequently constrained by soil acidity in southern Australia yet limestone crushing plants are few and distant, making the use of limestone costly. The efficient technology of agricultural liming is therefore critical to the continuation of the practice following its adoption during the 1980s. We hypothesise that finer particles are the most effective materials for ameliorating soil acidity even over the longer term, when the residual value of coarser particles might be expected to be greater. Finer particle sizes of limestone, particularly <0.075 mm, initially gave the largest increases in soil pH per tonne of limestone applied. Despite the rapid and large increase in soil pH with finer particles, there was no less residual value in surface soil pH after 7 years or in grain yield in the 7th and 8th growing seasons compared with coarser particles. Most particle size fractions of limestone converged to a similar soil pH_{ca} at 0–10 cm depth after about 6 years but the coarsest particle size fraction (2–5 mm) lagged the other five. Finer particles also resulted in better movement of alkali and Ca into the subsurface soil layers below the depth of incorporation (0–10 cm). The measurement of unreacted limestone in the soil showed that the dissolution of limestone took up to 3 years (1807 mm of rainfall) for the 2.5 t/ha rate and up to 6 years (3592 mm) for the 5 t/ha rate. The rapid increase in soil pH in Year 1, the slow ongoing reaction of limestone over 3–6 years as measured by unreacted limestone, the slow but measurable improvement in subsurface acidity, and the sustained residual value to grain yield over in excess of eight seasons, indicate that the use of finer liming materials should remain a viable practice for growers.

Additional keywords: residual carbonate, soil acidity, soil pH, unreacted limestone.

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Introduction

The commercial viability of liming is influenced by how efficiently (ΔpH of a soil volume/tonne of limestone applied) and how rapidly ($\Delta\text{pH}/\text{time}$) soil acidity is amended by limestone application, and the longevity of the benefits. Further, the longer the benefits of liming persist and the deeper the neutralisation of any subsurface acidity, the greater the chances of liming being commercially viable in broadacre agriculture that is remote from limestone crushing plants.

Limestone is an ameliorant that is characterised by low solubility (0.052 g/L in water at atmospheric CO₂). The low solubility of limestone can be partially compensated for by using a finer particle size of product (i.e. increased exposed surface area) that increases both the apparent reaction rate (Scott *et al.* 1992; Conyers *et al.* 1995) and the likely homogeneity of distribution within the soil volume being amended (Barber 1984; Cregan *et al.* 1989). The field study

of Scott *et al.* (1992) was consistent with two glasshouse studies conducted in the United States (Beacher *et al.* 1952; Meyer and Volk 1952), which also used liming materials that extended to particles finer than 0.25 mm. The results of the three studies were compared by Conyers (2006). Therefore, the empirical field study from New South Wales (Scott *et al.* 1992) has broader application to the assessment of limestone effectiveness in the field. Although there are some recent laboratory incubation studies on particle size effectiveness (Huang *et al.* 2007; Jones and Mallarino 2018), the only other field study on particle size effectiveness and longevity is that of Haby and Leonard (2002) from Texas. Consistent with Scott *et al.* (1992) these authors reported that finer particle sizes of limestone gave a better initial increase in soil pH but also that they gave a better residual effect on soil pH than coarser particles for up to 7 years.

If finer particles react more quickly, there could be a trade-off between speed of reaction and longevity of the liming

effect. There is no evidence for this to date; this apparent lack of greater residual value from coarser particles has been explained by the sparse spacing of particles of coarse liming materials (Barber 1984). The finer particle sizes not only react more quickly but the greater number of particles from a given mass of material enables a greater proportional coverage of the soil volume to which limestone is applied (Cregan *et al.* 1989). However, measuring the rate or efficiency of reaction of limestone with acidic soil simply by measuring soil pH can be problematic. Measurements of pH of recently limed soil at intervals ranging from 5 min up to the standard 1 h indicate that at least part of the reaction is taking place in the test tube rather than having actually occurred in the field soil (data not shown). Therefore, to obtain an unambiguous assessment of the rate of limestone dissolution in the field we measured the unreacted limestone (Whitten 2002) remaining in the soil at 1, 3 and 6 years after limestone application. We also report the trends over 7 years in soil pH_{ca} , Ca_{ex} , in the apparent recovery of limestone, and over eight seasons, in the grain yield at a site in southern NSW (Scott *et al.* 1992). These measures of residual value include lime movement to depth as assessed by soil pH_{ca} and Ca_{ex} ; the latter was used in the estimation of apparent recovery of applied limestone. Finally, we compare the unreacted limestone remaining in the soil with the soil pH_{ca} and Ca_{ex} data to compare the rate of limestone reaction with the rate of soil re-acidification. We hypothesise that finer particles of limestone remain the most effective liming materials despite the apparent potential for better residual values from coarser materials.

Materials and methods

Experimental site

The experiment was located 30 km east of Wagga Wagga in southern New South Wales (35°12'45"S, 147°39'01"E). The soil type was an intergrade between a Yellow Chromosol and a Sodosol (Isbell 1996), Dy 3.41/3.42 (Northcote 1979), Yellow Podsollic/Solodic (Stace *et al.* 1968), Albic Luvisol (FAO-UNESCO 1974), or Aeric Albaqualf (Soil Survey Staff 1975). The mineralogy was dominated by illite > kaolinite > quartz. The surface 10 cm soil had a mean pH (0.01 M CaCl_2 , pH_{ca}) of 4.1, 0.7% organic C, 12% clay and an effective cation exchange capacity of 2.51 cmol/kg. Exchangeable Al occupied 24% of exchange sites. The subsurface 10–20 cm soil had an initial pH_{ca} of 4.0 and 37% exchangeable Al.

Rainfall

Monthly rainfall was obtained from a Bureau of Meteorology station 17 km from the site: Station 072150 (Wagga Wagga Airport), 35.16°S, 147.46°E. Rainfall for each year and between sampling periods are calculated from this data (Table 1).

Experimental design

The experiment was a modified randomised block design with 31 treatments and four replicate blocks. The modification was that the control plots were distributed every sixth plot in a grid across the trial (Scott *et al.* 1992), giving seven control plots per block. Plots were 10 m long by 1.2 m wide. The treatments consisted of the control (unlimed), six particle size segregations (PS 1 to PS6) at three application rates (2.5, 5 and 10 t/ha) and also 12 commercial liming materials at 5 t/ha that are not described here.

Liming material

Six particle size segregations of CaCO_3 were derived from a 98% pure calcitic microcrystalline limestone from the Marulan quarry, NSW. The initial six segregations were supplied by Southern Limestone Pty Ltd of Moss Vale, who supply an array of commercial products covering this particle size range. The particle diameter ranges were further narrowed by the use of vibrating seed cleaners modified with appropriate commercial screens. Accurate definition of the final six particle size segregations was obtained by screening each through a nest of British Standard Sieves. A description of both the range and the mean particle size of the six segregations is given (Table 2; see also Scott *et al.* 1992). The particle sizes ranged from a particle diameter 2–5 mm (mean 3 mm) to <0.075 mm (mean 0.005 mm). The water content of the liming materials ranged from 0 to 0.2% and was therefore ignored in calculations. Because of soil sample preparation (ground to pass a 2-mm sieve) the unreacted limestone determination for the coarsest particle size was not conducted. The concern was that unreacted limestone particles may have been discarded along with a small quantity of residual gravel which would not pass the 2-mm sieve after gentle grinding. Liming materials were weighed and hand-spread on the site in April 1986. The limestone was incorporated by rotary hoe to ~10 cm depth. Control plots were also rotary hoed.

Table 1. Monthly rainfall from Meteorological Station 072150 (Wagga Wagga Airport) for the experimental period

| Year | January | February | March | April | May | June | July | August | September | October | November | December | Total |
|------|---------|----------|-------|-------|-------|-------|-------|--------|-----------|---------|----------|----------|-------|
| 1986 | 65.8 | 4.4 | 2.0 | 33.4 | 46.8 | 21.2 | 101.6 | 47.7 | 52.0 | 104.6 | 69.6 | 38.0 | 586.6 |
| 1987 | 16.4 | 50.6 | 12.2 | 22.6 | 49.6 | 94.0 | 60.0 | 35.6 | 29.0 | 23.6 | 28.8 | 23.0 | 445.4 |
| 1988 | 14.6 | 8.0 | 25.6 | 12.4 | 153.8 | 47.2 | 93.2 | 18.0 | 37.4 | 15.8 | 29.4 | 213.4 | 668.8 |
| 1989 | 23.0 | 22.0 | 133.6 | 102.8 | 76.2 | 62.2 | 36.2 | 69.6 | 21.0 | 62.8 | 68.2 | 27.0 | 704.6 |
| 1990 | 41.0 | 69.4 | 7.2 | 97.0 | 95.6 | 24.2 | 76.6 | 64.0 | 46.2 | 50.6 | 9.4 | 18.6 | 599.8 |
| 1991 | 34.8 | 4.2 | 10.4 | 7.4 | 8.0 | 138.8 | 73.0 | 52.2 | 57.8 | 11.2 | 11.8 | 22.8 | 432.4 |
| 1992 | 30.0 | 81.0 | 115.4 | 84.2 | 24.4 | 43.0 | 41.0 | 87.4 | 89.6 | 112.8 | 82.4 | 132.0 | 923.2 |
| 1993 | 20.2 | 14.2 | 88.7 | 9.6 | 32.0 | 28.4 | 130.0 | 27.2 | 121.4 | 90.8 | 96.8 | 58.8 | 718.1 |

Table 2. Particle size segregations of limestone used in the present study

| Particle size | Range | | Mean diameter (mm) |
|---------------|-------------------|------------|--------------------|
| | Mesh ^A | (mm) | |
| PS 1 | 4–8 | 2.0–5.0 | 3.0 |
| PS 2 | 16–30 | 0.5–1.0 | 0.6 |
| PS 3 | 30–60 | 0.25–0.50 | 0.35 |
| PS 4 | 60–100 | 0.15–0.25 | 0.20 |
| PS 5 | 100–200 | 0.075–0.15 | 0.11 |
| PS 6 | <200 | <0.075 | 0.005 |

^ABritish Standard Sieve.

Field measurements

The plots were initially sampled to a 10 cm depth in April 1986 before the application of liming materials. Sampling of all plots subsequently took place in November 1986 (0.5 years after lime application), April of 1987 (1 year), 1989 (3 years), 1992 (6 years) and 1993 (7 years). Soil sampling took place before harrowing and sowing in each year. In Year 3 the soil depth 10–15 cm was also sampled in the nil lime and some high lime rates plots (10 t/ha for the finest particle size only). In Years 6 and 7 soil cores were also taken to 15–20 cm depth for all plots. The plot samples consisted of 10 cores per plot (each plot being 12 m²). Soil samples were air-dried and ground to pass a 2-mm sieve.

Grain yield of wheat (*Triticum aestivum* cv. Millewa in Year 1 to Year 3, and Dollarbird in Years 7 and 8) was determined by mechanical harvesting of the whole plot and Years 1 to 3 have been reported previously (Scott *et al.* 1992; Conyers *et al.* 2003).

Chemical analyses

Soil pH_{Ca} in 0.01 CaCl₂ (pH_{Ca}) was determined after a 1 h end-over-end shake at 5 rpm at 20°C in a 1 : 5, soil : solution extract. Exchangeable cations were determined by a BaCl₂ leach (Vimpany *et al.* 1985) for the first 3 years and by the method of Gillman and Sumpter (1986) for Years 6 and 7, as the latter method uses a controlled duration of extraction (2 h), which might minimise ongoing dissolution of Ca from limestone compared with the leaching procedure.

Unreacted limestone was estimated by the method of Whitten (2002). Briefly, CO₂ evolved by reacting known weights of soil or analytical CaCO₃ with an excess of acid was measured by gas analysis. The acid, 5 M HCl, was made on the day of analysis and contained 30 g/L of FeCl₂·4H₂O to prevent formation of CO₂ from oxidation of organic matter by free Cl₂ that could form in the presence of MnO₂ (Martin and Reeve 1955). The soil or analytical reagent CaCO₃ was placed into a sealed container and the acid was injected via a septum and mixed thoroughly. After the reaction appeared complete (a minimum of 1 h) known volumes of the entrapped headspace were injected into an infrared gas analyser (Analytical Development Co., Herts, UK, Series 225) in a stream of high purity nitrogen gas. Any effect of differences in CO₂ pressure between treatments would also occur in the CaCO₃ standards and therefore be cancelled. Little CO₂ was evolved from unlimed soils, indicating no pedogenic

carbonate and little decomposition of resident organic C, and this quantity was deducted when calculating unreacted limestone for the limed treatments. Recoveries of known weights of CaCO₃ added to soil ranged from 96 to 103% for this method. Detection limits (3 × standard deviation of unlimed soil) averaged 0.024 t/ha of CaCO₃.

Statistical procedures

The soil pH_{Ca}, Ca_{ex}, unreacted limestone, apparent recovery of limestone (using Ca_{ex} plus unreacted limestone) and wheat grain yield data were analysed by ANOVA, generally two-way (particle size by application rate), and by regressions (linear, polynomial and Mitscherlich) of relationships between variables using SigmaPlot 13 (Systat 2014). Least significant differences at *P* < 0.05 or standard errors of the mean are given as appropriate. Standard deviations are also shown as a measure of sampling and subsampling variability for the unreacted limestone data.

Results

Soil pH

Surface soil

At 2.5 t/ha the finest particle size gave the highest pH_{Ca} for the first few years of the trial but by Years 6 and 7, five of the six particle sizes had converged, with only the coarsest material lagging (Fig. 1a). Despite this convergence over time, none of the other particle sizes reached the same pH_{Ca} increase (1.5–2.0 pH) that had been attained by the finest particle sized fraction (<0.075 mm) over the first 3 years. The pH_{Ca} trend in Fig. 1a shows that the rate of re-acidification was greatest for the finest particle size fraction, PS6 (which achieved the highest pH_{Ca}), and exceeded any ongoing reaction rate of limestone. For the coarsest particle size, PS1, the apparent ongoing reaction rate exceeded the acidification rate so pH_{Ca} continued to rise. For the mid-range particle sizes (PS2 to 5, Table 2) there was a near steady-state pH_{Ca}.

At 5 t/ha the finest particle size again achieved the highest pH_{Ca} and convergence of the data was apparent at 7 years (Fig. 1b). At 10 t/ha the increase in pH_{Ca} was ongoing, except possibly for the finest particle size where the trend was ambiguous (Fig. 1c). Again, the mid-range particle sizes converged and the coarsest particle size lagged.

Subsurface soil

In Years 6 and 7 the pH_{Ca} in each subsurface soil layer (below the surface 0–10 cm) was correlated with that in the layer above (Fig. 2). The regression for the 10–15 cm layer as a function of the 0–10 cm layer shows an increase in slope as the latter pH exceeds ~5.5 (Fig. 2a, b). A quadratic regression gave a significantly (*P* < 0.01) improved *r*² over a linear fit for each year (0.913–0.970 for Year 6 and 0.947–0.973 for Year 7). At 15–20 cm the relationship was a simple linear increase as a function of the 10–15 cm pH_{Ca} (Fig. 2c, d), probably because there was little data reaching pH_{Ca} 5.5 at 10–15 cm depth, and this was only provided by the 10 t/ha rate. The availability of data on the time course of pH_{Ca} increase at depth is limited in the present study due to our soil sampling

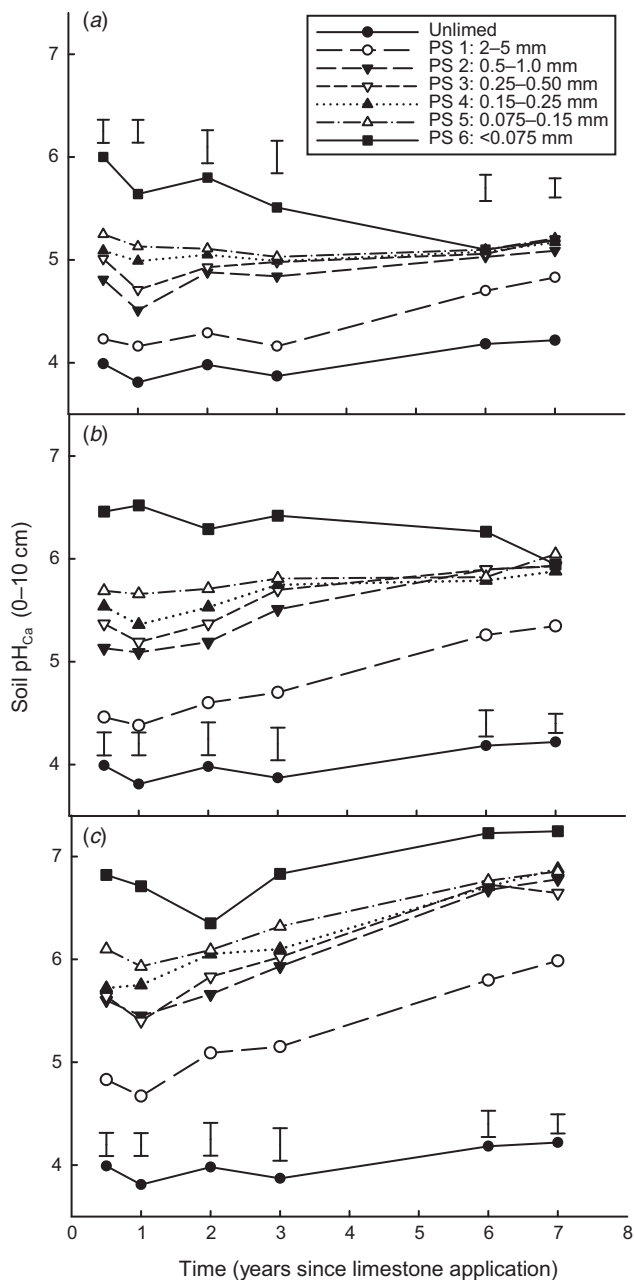


Fig. 1. Time course over 7 years of soil pH_{Ca} (0–10 cm) for six particle sizes of limestone at three application rates: (a) 2.5 t/ha, (b) 5 t/ha, and (c) 10 t/ha. Error bars represent the 5% l.s.d.

below 10 cm developing only gradually through time (Fig. 3). In the range of common application rates (2.5–5 t/ha) the amelioration of the subsurface is slow but significant and the finest particle size was far more effective than the coarsest particle size.

Unreacted limestone

The broad trend was for unreacted limestone to diminish over time as expected, with almost complete reaction of the 2.5 t/ha

rate after 3 years or 1807 mm rainfall (Fig. 4a); of the 5 t/ha rate by 6 years or 3592 mm (Fig. 4b); but with 2 to 4 t/ha of the 10 t/ha rate remaining after 6 years (Fig. 4c). Clearly, even a commonly used rate of limestone application, 2.5 t/ha (Scott *et al.* 2007), did not react fully within 12 months or 594 mm, with ~0.5 t/ha (20% of that applied) remaining in the soil even for the finer particle sizes.

The effect of particle size on unreacted limestone was only significant on four out of nine rate by year contrasts (Fig. 4b, c). This was generally due to PS2, the coarsest fraction measured, having the higher values of unreacted limestone as expected. However, PS6 never had the least quantity remaining. None of the differences in unreacted limestone due to particle size occurred at the lower application rate of 2.5 t/ha.

Exchangeable Ca

The increase in Ca_{ex} ($\Delta\text{Ca}_{\text{ex}}$) compared with the unlimed control at Year 1 (limed treatment Ca_{ex} – control Ca_{ex}) made a reasonable proxy for the quantity of limestone reacted (1 – unreacted limestone, UL):

$$\Delta\text{Ca}_{\text{ex}} = 0.80(\pm 0.29) \times (1 - \text{UL}),$$

$$(n = 10, r = 0.694, P = 0.026).$$

The intercept of the regression, $-0.107(\pm 0.675)$, was not significant. The above relationship is based on Table 3 but excluding the 10 t/ha rate as the latter induced a plateau in the relationship, giving a higher r (0.75) but only a 40% apparent recovery. Applied Ca is more mobile in soil than the alkali from limestone (Conyers and Scott 1989) but no subsurface data were collected at this stage of the experiment. The recovery of Ca_{ex} from each soil layer in Year 6 was strongly correlated with the concentration of Ca_{ex} in the layer above:

$$\begin{aligned} \text{Ca}_{\text{ex}}(10-15 \text{ cm}) &= 0.295(0.011) \times \text{Ca}_{\text{ex}}(0-10 \text{ cm}) \\ &- 0.130(0.045), \quad (r = 0.93, n = 100, P < 0.001), \text{ and} \end{aligned}$$

$$\begin{aligned} \text{Ca}_{\text{ex}}(15-20 \text{ cm}) &= 0.655(0.051) \times \text{Ca}_{\text{ex}}(10-15 \text{ cm}) \\ &- 0.157(0.065), \quad (r = 0.79, n = 100, P < 0.001). \end{aligned}$$

Therefore, whether driven by mass flow or diffusion, Ca movement was readily measurable following limestone application under these rainfall conditions (Table 1). The quantities of Ca_{ex} at each depth for each treatment in this study were converted to Ca t/ha as part of the calculation for recovery of applied limestone (Tables 3–5).

Apparent recovery of limestone

In Year 1 the recovery of applied limestone averaged 83% and exceeded 70% on all treatments except for the lowest application rate of the coarsest particle size, despite excess recovery of that fraction at 5 and 10 t/ha (Table 3). Recovery of this treatment remained low over the 6 years. In fact recovery of the 2.5 t/ha rate was significantly low for all particle sizes in Year 1 compared with the other application rates ($P = 0.049$), though the near significant interaction term ($P = 0.06$) and the data in Table 3 suggest that this was probably due dominantly

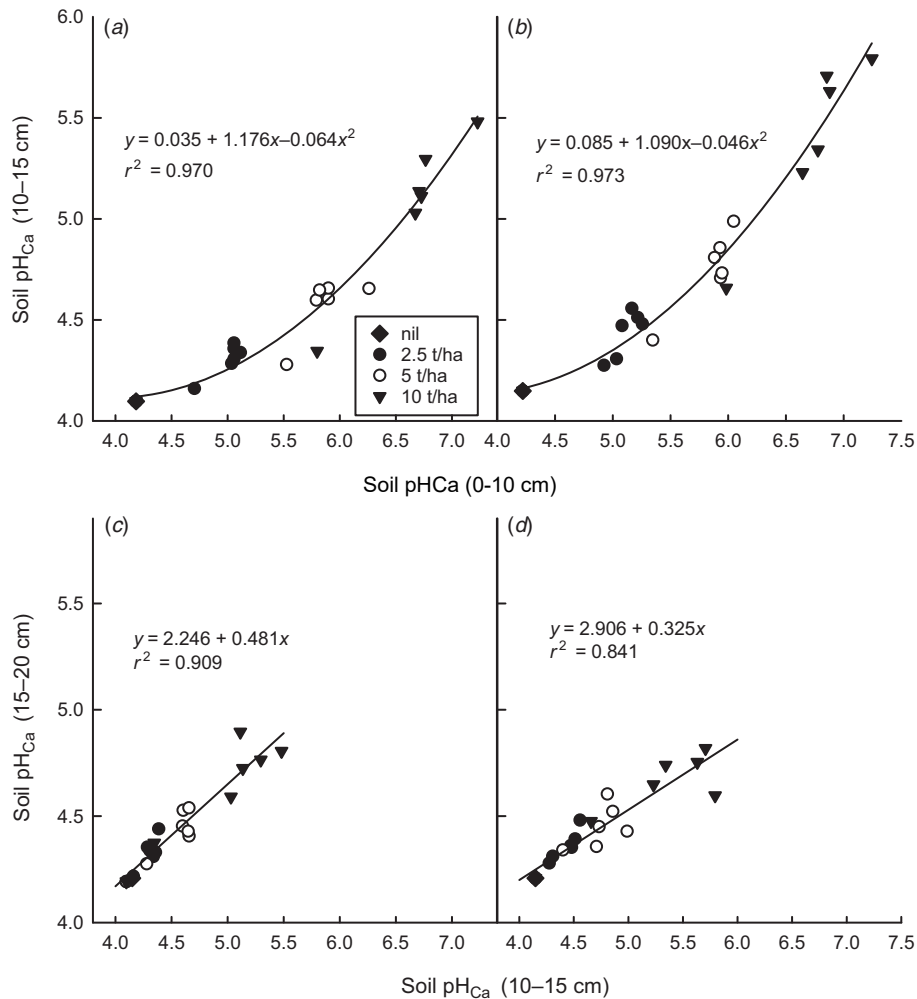


Fig. 2. Dependence of soil pH_{Ca} in subsurface layers on the soil pH_{Ca} above it. (a, c) Year 6; (b, d) Year 7; (a, b) 10–15 cm vs 0–10 cm (c, d) 15–20 vs 10–15 cm.

to the data from the coarsest particle size. In Year 3 the recovery of the coarsest particle size was significantly low across all application rates (Table 4). By Year 6 there was no significant effect of particle size or application rate on recovery of applied limestone (Table 5) with an average recovery of 63%.

Grain yield

Grain yield correlated strongly with soil pH_{Ca} at 0–10 cm depth (Fig. 5), with model fits to the treatment mean data in seasons seven and eight respectively of $r^2 = 0.54$ and 0.59 for Mitscherlich models, and 0.91 and 0.92 for quadratic polynomials. The latter are shown as solid lines on Fig. 5a, b. Note the convergence of the plot yield data as pH_{Ca} falls, indicating that acidity became the dominant yield limiting factor. As pH_{Ca} approached 4.0 grain yield approached zero despite good growing season rainfall. Conversely, yield potential was ~4 t/ha in the absence of the acidity constraint in the surface soil. Note that both soil pH_{Ca} and grain yield vary among replicates, so the scatter in plot

data compared with the mean is in both x (soil pH_{Ca}) and y (grain yield) directions.

Discussion

Surface and subsurface soil pH

Over the three application rates, particle size determined the effectiveness of the liming material in increasing soil pH_{Ca} in the early years. Even at 5 and 10 t/ha, the value of fineness was apparent and this higher effectiveness came at no longer-term disadvantage, in agreement with Haby and Leonard (2002). The argument that coarser particles should have a greater residual value might be true beyond 7 years but it would come at the twin costs of lower effectiveness for the first few years and of less homogenous distribution of a given mass of limestone through the soil. Further, the reaction rate of coarse particles has to match the underlying re-acidification rate or the soil will undergo net acidification, even while containing those more widely spaced particles of coarse limestone.

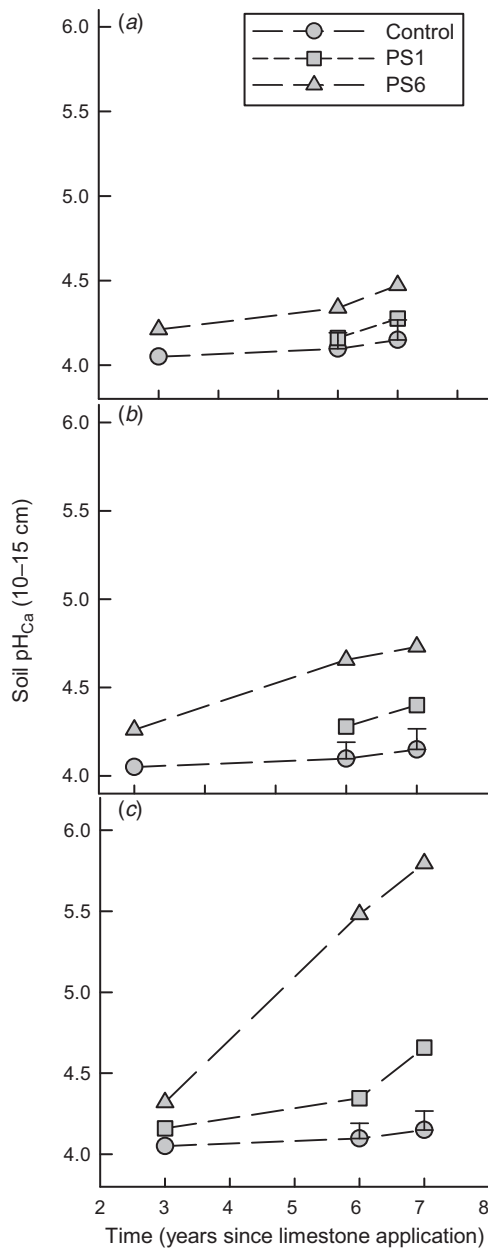


Fig. 3. The time course of soil pH_{Ca} at 10–15 cm depth for the coarsest and finest particle sizes of limestone at three application rates: (a) 2.5 t/ha, (b) 5 t/ha, and (c) 10 t/ha. Error bars represent the 5% l.s.d. in Years 6 and Year 7 and are placed on the unlimed mean values.

In regard to subsurface soil amelioration, Whitten (2002) also reported that pH_{Ca} at 10–20 cm was correlated with pH_{Ca} at 0–10 cm for Western Australian soils, especially if the latter was >5.9. Similarly, greater pH_{Ca} increases in the subsurface soil were reported for finer liming materials (Whitten 2002).

Exchangeable Ca and apparent recovery of limestone

Subsurface Ca_{ex} would need to be measured if ΔCa_{ex} were to be used as an index of limestone reaction for the 10 t/ha rates in

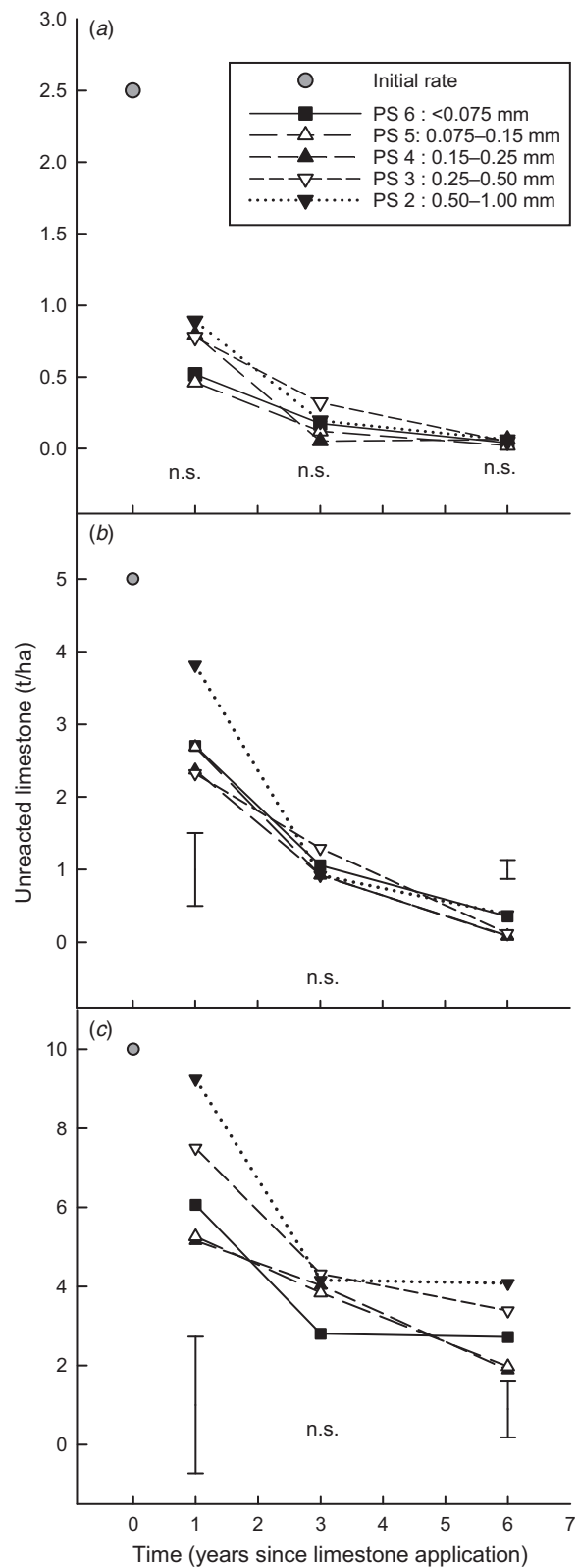


Fig. 4. The time course over 6 years of unreacted limestone in the soil for five particle size fractions at three application rates: (a) 2.5 t/ha, (b) 5 t/ha, and (c) 10 t/ha. Significance levels are shown below each set of lines as 5% l.s.d. or n.s.

Table 3. Apparent recovery of applied limestone 1 year after liming
n.s., not significant

| Particle size | Application rate (t/ha) | Unreacted lime (t/ha) | ΔCa 0–10 cm (t/ha) | Sum (t/ha) | Recovered (%) |
|---------------|-------------------------|-----------------------|----------------------------------|------------|---------------|
| PS 2 | 2.5 | 0.89 | 0.81 | 1.70 | 68 |
| | 5 | 3.82 | 1.45 | 5.27 | 105 |
| | 10 | 9.25 | 1.84 | 11.09 | 111 |
| PS 3 | 2.5 | 0.78 | 1.17 | 1.95 | 78 |
| | 5 | 2.32 | 1.69 | 4.01 | 80 |
| | 10 | 7.98 | 1.92 | 9.42 | 94 |
| PS 4 | 2.5 | 0.79 | 1.51 | 2.30 | 92 |
| | 5 | 2.37 | 2.06 | 4.43 | 89 |
| | 10 | 5.16 | 2.60 | 7.76 | 78 |
| PS 5 | 2.5 | 0.46 | 1.49 | 1.95 | 78 |
| | 5 | 2.69 | 2.14 | 4.83 | 97 |
| | 10 | 5.26 | 2.64 | 7.90 | 79 |
| PS 6 | 2.5 | 0.52 | 1.59 | 2.11 | 84 |
| | 5 | 2.70 | 2.99 | 5.69 | 114 |
| | 10 | 6.06 | 3.46 | 9.52 | 95 |
| 5% l.s.d. | rate | | | | 10.0 |
| 5% l.s.d. | size | | | | n.s. |

Table 4. Apparent recovery of applied limestone 3 years after liming
n.d., not determined; n.s., not significant

| Particle size | Application rate (t/ha) | Unreacted lime (t/ha) | ΔCa 0–10 cm (t/ha) | ΔCa 10–15 cm (t/ha) | Sum (t/ha) ^A | Recovered (%) ^A |
|---------------|-------------------------|-----------------------|----------------------------------|-----------------------------------|-------------------------|----------------------------|
| PS 2 | 2.5 | 0.19 | 1.22 | n.d. | (1.42) | (57) |
| | 5 | 0.92 | 1.89 | n.d. | (2.81) | (56) |
| | 10 | 4.16 | 2.39 | 0.19 | 6.74 | 67 |
| PS 3 | 2.5 | 0.32 | 1.49 | n.d. | (1.81) | (72) |
| | 5 | 1.29 | 2.28 | n.d. | (3.57) | (71) |
| | 10 | 4.32 | 2.75 | 0.23 | 7.30 | 73 |
| PS 4 | 2.5 | 0.05 | 1.43 | n.d. | (1.48) | (59) |
| | 5 | 0.92 | 2.43 | n.d. | (3.35) | (67) |
| | 10 | 4.02 | 2.94 | 0.21 | 7.17 | 72 |
| PS 5 | 2.5 | 0.12 | 1.38 | n.d. | (1.50) | (60) |
| | 5 | 0.92 | 2.29 | n.d. | (3.21) | (64) |
| | 10 | 3.84 | 3.07 | 0.18 | 7.09 | 71 |
| PS 6 | 2.5 | 0.17 | 1.68 | 0.07 | 1.93 | 77 |
| | 5 | 1.06 | 2.68 | 0.09 | 3.83 | 77 |
| | 10 | 2.80 | 3.78 | 0.11 | 6.69 | 67 |
| 5% l.s.d. | rate | – | – | – | – | n.s. |
| 5% l.s.d. | size | – | – | – | – | 7.8 |

^AValues in parentheses indicate that the sum and recovery values were determined without 10–15 cm depth.

Year 1 and for all application rates and particle sizes in the years following. However, the quantities of measured Ca_{ex} decreased with depth, suggesting that any loss of Ca beyond our sampling depth of 20 cm in Year 6 was small. Mass balance of applied Ca in limestone has proved challenging (Whitten *et al.* 2000) as it involves numerous potential pools into which the Ca can move.

Reported apparent recoveries in Western Australia ranged from <10 to >90% over 19 budgets at 2–15 years post liming

(Whitten *et al.* 2000), indicating that our understanding of limestone reaction processes and the fate of Ca and alkali could be improved. The bulk density of the surface soil was measured at 1.3 g/cm³ across the present experimental site. However, this probably varied from plot to plot. Further, the bulk density below 10 cm was not measured but assumed to equal that of the surface soil as it was still within the A horizon. Hence bulk density could be a source of error in this recovery calculation. Further, dust loss from the soil surface after

Table 5. Apparent recovery of applied limestone 6 years after liming
n.s., not significant

| Particle size | Application rate (t/ha) | Unreacted lime (t/ha) | ΔCa 0–10 cm (t/ha) | ΔCa 10–15 cm (t/ha) | ΔCa 15–20 cm (t/ha) | Sum (t/ha) | Recovered (%) |
|---------------|-------------------------|-----------------------|----------------------------------|-----------------------------------|-----------------------------------|------------|---------------|
| PS 2 | 2.5 | 0.06 | 1.10 | 0.18 | 0.11 | 1.45 | 58 |
| | 5 | 0.38 | 2.19 | 0.42 | 0.35 | 3.35 | 67 |
| | 10 | 4.08 | 3.46 | 0.49 | 0.19 | 8.21 | 82 |
| PS 3 | 2.5 | 0.05 | 1.21 | 0.16 | 0.08 | 1.52 | 61 |
| | 5 | 0.12 | 2.24 | 0.31 | 0.11 | 2.78 | 56 |
| | 10 | 3.39 | 2.77 | 0.50 | 0.39 | 6.99 | 70 |
| PS 4 | 2.5 | 0.06 | 1.41 | 0.20 | 0.11 | 1.80 | 72 |
| | 5 | 0.08 | 2.38 | 0.36 | 0.21 | 3.05 | 61 |
| | 10 | 1.89 | 3.69 | 0.54 | 0.24 | 6.35 | 64 |
| PS 5 | 2.5 | 0.02 | 1.23 | 0.19 | 0.09 | 1.54 | 62 |
| | 5 | 0.09 | 1.71 | 0.29 | 0.16 | 2.22 | 44 |
| | 10 | 1.97 | 3.64 | 0.58 | 0.33 | 6.49 | 65 |
| PS 6 | 2.5 | 0.03 | 1.26 | 0.16 | 0.08 | 1.53 | 61 |
| | 5 | 0.35 | 2.68 | 0.30 | 0.16 | 3.48 | 70 |
| | 10 | 2.72 | 4.02 | 0.55 | 0.36 | 7.62 | 76 |
| 5% l.s.d. | rate | – | – | – | – | – | n.s. |
| 5% l.s.d. | size | – | – | – | – | – | n.s. |

application and cultivation remains unquantified. Only three recovery values exceeded 100% so the error tends to be associated with a net loss of the applied limestone rather than randomly distributed error. Whitten *et al.* (2000) highlighted erosion by wind and water as a possible source of loss of limestone or lime effects from at least two sites. The biggest error seemed to occur with the coarsest particle size in our study and this could be associated with our routine 2-mm sieving of the soil samples, hence PS 1 from the original study was not analysed. Finally, it is clear from the two regressions given concerning Ca movement below the application depth that we should have measured Ca_{ex} to greater depth from the outset of the experiment, as this appears to be an obvious source of apparent Ca loss at least in the early years. The quantities of Ca at 15–20 cm depth in Year 6 were small suggesting limited further movement to depth; however, net Ca uptake by crops was not measured. We therefore suggest that to improve estimates of the apparent recovery of limestone: that the bulk density of all soil layers be measured in future work, that an attempt be made to estimate wind loss of fine limestone, that soil samples not be sieved through a 2-mm sieve unless the sample is first put through a jaw crusher so as to include the coarse fraction of limestone (or to quantify the limestone in that discarded coarse fraction), that soil samples be collected below the depth of application from the first sampling, and that net Ca uptake by crops should be measured. If single superphosphate is used, the input of Ca should be accounted for.

Grain yield

The pattern of grain yield response corresponds with that described by Scott *et al.* (1992) for the first 3 years of the trial but these favourable latter two seasons of 1992 and 1993 (Table 1) produced double the absolute yield (as opposed to relative yield). Good seasons such as these latter two clearly improve the biological residual value of the single application

of limestone seven and eight seasons after application. Grain yields in the eighth season after limestone application remained well above the unlimed controls (Fig. 5). The relatively high surface soil pH_{ca} and the gradual movement of alkali and Ca into the 10–20 cm soil depth ensured an improvement in soil chemical conditions over the eight seasons. The residual value of liming at this site is likely to have extended well beyond these eight seasons, consistent with the report of Conyers *et al.* (2003) where yield benefits on five experiments at three locations exceeded 8–12 years. The rapid amelioration of surface acidity and gradual amelioration of subsurface acidity by the finer particle sizes of limestone together with the ongoing maintenance of grain yield ensures the commercial viability of liming in this environment.

General

The rate of reaction of limestone with acidic soil tends to be inferred from the change in soil pH (any method) and change in Ca_{ex} (Conyers *et al.* 2003). The weaknesses of these approaches are that change in pH depends on the concurrent competing processes of limestone reaction and ongoing soil acidification, and the change in Ca_{ex} is influenced by plant uptake and by the application of some phosphatic fertilisers as well as by any leaching beyond sampling depth. In Fig. 1a for example, from 2 years after liming with the finest particle size there is net acidification while from 3 years the coarsest particle size was showing a net increase in pH_{ca} . After 6 years, five of the six particle sizes had converged. The best way to disentangle the two processes influencing net pH change is with the unreacted limestone data. Unfortunately, we have no data for the coarsest material because it was largely sieved from the soil. However the unreacted limestone data from the five particle sizes available indicate that there was ongoing reaction at the 2.5 t/ha rate up to 3 years (1807 mm cumulative rainfall) post application; up to 6 years (3592 mm) at the 5 t/ha rate and in

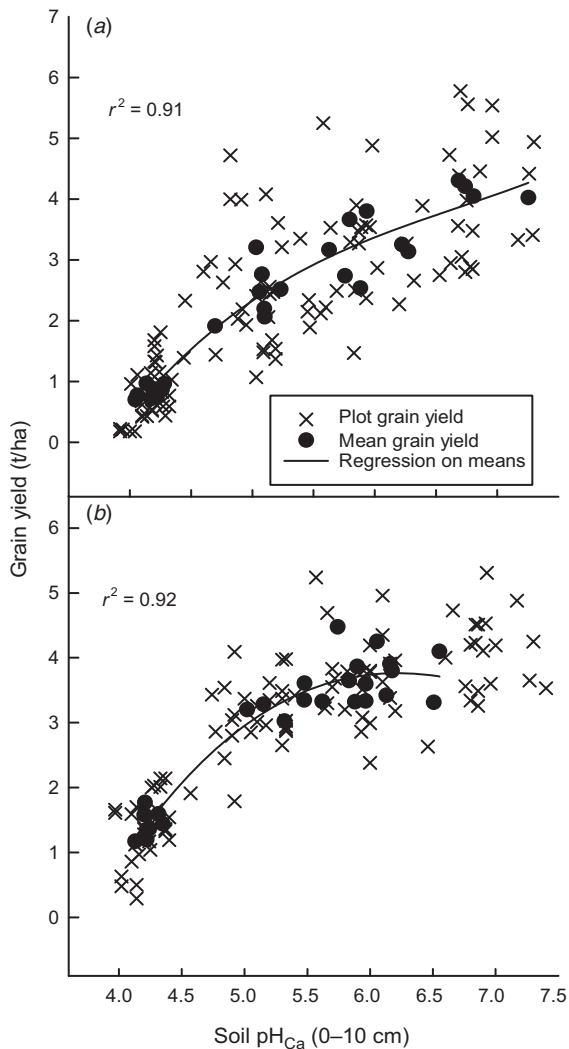


Fig. 5. The influence of surface soil pH_{Ca} (0–10 cm) on the grain yield of Dollarbird wheat in (a) season 7 and (b) season 8. Treatment means are shown as filled circles, and the individual plot yields are shown as crosses. Plotted regression lines are based on the means.

excess of 6 years for the 10 t/ha rate. The decrease in soil pH at 2.5 t/ha for the finest particle size after about 2 years is consistent with the loss of unreacted limestone from the soil. Hence the soil acidification rate dominates the now smaller limestone reaction rate and the soil pH_{Ca} falls. However, there is no statistical difference between particle sizes in the unreacted limestone for any year at this 2.5 t/ha rate.

The conclusion that there is no difference between particle sizes in Fig. 4 is due to the size of the error bars. Yet the laboratory error for the unreacted limestone method is at least an order of magnitude smaller than the difference between the treatments (Whitten 2002). The solution to this problem is not a simple kinetic one as implied by the changes in soil pH_{Ca} and unreacted limestone over time. The application rates of 2.5, 5 and 10 t/ha to 1300 tonne of soil (bulk density of 1.3 g/cm³ to 10 cm depth) represent 0.2, 0.4 and 0.8% of the soil mass to

Table 6. The standard deviation for the four replicates of unreacted limestone measurement 1 year after limestone application

| Particle size | Application rate (t/ha) | | |
|---------------|-------------------------|-------|-------|
| | 2.5 | 5 | 10 |
| PS 2 | 0.353 | 0.863 | 3.469 |
| PS 3 | 0.222 | 0.344 | 0.480 |
| PS 4 | 0.329 | 0.541 | 1.781 |
| PS 5 | 0.188 | 0.393 | 0.614 |
| PS 6 | 0.054 | 1.004 | 1.625 |

Table 7. The reaction of limestone particles <0.075 mm as dependent on time and cumulative rainfall

| Limestone application rate (t/ha) | Limestone reacted (t/ha) and percentage of applied (%) | | |
|-----------------------------------|--|--------------------|--------------------|
| | Cumulative rainfall and year | | |
| | 594 mm at 1 year | 1806 mm at 3 years | 3592 mm at 6 years |
| 2.5 | 1.89 (79) | 2.32 (93) | 2.46 (98) |
| 5 | 2.30 (46) | 3.94 (79) | 4.65 (93) |
| 10 | 3.94 (39) | 7.20 (72) | 7.28 (73) |

which they applied. Given this small relative mass ratio, the increase in soil pH_{Ca} depends on both the quantity of limestone reacted and on the proportion of that soil mass that has been in contact with the applied limestone. For coarser particles, a smaller surface area is exposed and the spacing between particles is larger than for finer particles, which offer both a larger total surface area and a more even distribution through the soil (Barber 1984). The limestone mass is dispersed through the soil in a greater number of particles as fineness increases (tables 13 and 14 in Cregan *et al.* 1989). The value of fine particles then, is not just rate of reaction but in homogeneity of distribution through the soil mass, manifest here as sampling and subsampling error. The standard deviations for the different particle sizes are shown in Table 6, indicating that sampling plus subsampling error tends to be greatest with the coarsest liming fraction. It is likely that the error in soil sampling for unreacted limestone will always be large for coarse liming materials and so intensive soil sampling and sample preparation will be needed before laboratory analyses.

The initial rate of reaction of limestone with soil acidity is rapid (Fig. 4), followed by a slowing phase reminiscent of exponential decay but which is due to the increasing soil pH_{Ca} . Table 15 of Cregan *et al.* (1989) shows that the solubility of CaCO_3 is pH dependent, ranging from 0.89 g/L at aqueous pH 3.95 down to 0.013 g/L at pH 7. It was calculated by Cregan *et al.* (1989) that it would therefore take from 300 to 19 200 mm of rainfall to dissolve 2.5 t/ha of limestone (note the unit in table 15 should be 'm' not 'mm'). In this field experiment the soil pH_{Ca} increased from near 4 to near 7, varying with the limestone rate applied and the particle size range, implying that the solubility of CaCO_3 in this experiment would have decreased as the soil pH_{Ca} increased. Table 7 shows the absolute quantity of reacted limestone for PS 6 as a

function of the cumulative rainfall, together with the % of applied limestone reacted. The finest particle size is used as it would be least constrained in its dissolution by its large surface area. As noted previously with Fig. 4, the faster initial reaction slows in time (Table 7). At higher application rates of limestone, the greater is the absolute quantity of limestone dissolved per unit time or rainfall. However, the percentage of the limestone dissolved decreased as the application rate increased. If we use 90–95% reaction as a threshold for the complete reaction, given the high relative errors in measuring low quantities of limestone in soil, then 2.5 t/ha was dissolved after ~1806 mm and 5 t/ha was dissolved after 3592 mm of rainfall. That is, 722 and 718 mm/tonne of limestone were required to drive the reaction to near completion. We conclude that this data is consistent with the known pH-dependent solubility of CaCO_3 in water and that therefore the rate of limestone reaction will be driven by the quantity of rainfall and the change in soil pH_{Ca} over the period of reaction.

The varying rate of reaction of the limestone at different application rates highlights the difficulty in estimating field pH Buffering Capacity. Although the 2.5 t/ha limestone rate had reacted by ~3 years, there was still a lot of unreacted limestone remaining at the 5 t/ha rate. By the time that the 5 t/ha rate had reacted, the pH_{Ca} of the 2.5 t/ha rate had fallen due to re-acidification. We conclude that field pH Buffering Capacity would therefore be best estimated with fine liming materials and at lower rates of application than used here, and at 1–3 years after application when most limestone has reacted but re-acidification was minor. The linear portion of the titration curve is recommended as it is likely to have minimal unreacted limestone. Hence estimating the limestone reaction rate with increase in soil pH alone can produce ambiguous results. Similarly, estimating the soil acidification rate while limestone is still reacting in the soil would lead to underestimates. Provided that soil sampling and sample grinding are appropriate, we recommend the use of measurement of unreacted limestone (Barber 1984; Whitten 2002) as an unambiguous measure of the time course of limestone reaction in acidic soils.

Conclusion

We conclude that soil pH_{Ca} over 3–6 years is influenced by both the ongoing dissolution of limestone and by reacidification processes. Measurement of unreacted limestone is the only unambiguous way to determine the true reaction rate of limestone. The long-term benefits from liming include increases in soil pH_{Ca} and Ca_{ex} below the layer of application. The sustained increases in surface soil pH_{Ca} and the gradual improvement in subsurface conditions give rise to sustained improvements in grain yield for at least eight seasons. Consistent with our hypothesis, finer particle sizes of limestone are the most effective means of achieving these benefits and did not give way to lesser residual value compared with coarser limestone over the 8 years.

Conflicts of interest

The authors declare no conflicts of interest.

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