QUICK FIELD TEST FOR LIME RATES OF PYRITIC DRAIN-SPOIL IN NSW CANELANDS

By

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Abstract

Knowledge of soil texture class and soil pH following peroxide oxidation, both from a survey of low-lying soils from northern NSW cane farms, was integrated with laboratory data on peroxide-oxidised pH and lime requirements to extend the value of an existing field test used to indicate the presence of acid sulfate soils (ASS). The rapid field test now enables prediction of the quantity of agricultural limestone required to neutralise drain spoil containing actual and potential pyritic acidity. The paper describes the data-gathering process and the statistical approach used to develop the lime rate calibration curves. There are supporting data on field and laboratory derived soil pH values before and following oxidation with hydrogen peroxide. The data cover three mill regions and five depths to 1.5 m. A 'look-up' Table to simplify use of the quick field test for lime requirements for three soil texture classes (fine, medium, coarse) is provided, although the great majority of soils to 0.8 m were fine textured. The new application, supported by validation data from 68 samples, is now routinely used in northern NSW as one tool to assist the management of drain spoil in acid sulfate affected areas, both within the sugar industry and externally.

Introduction

The NSW sugar industry attracted criticism in the early to mid-1990s from government and the community over its use and management of acid sulfate soils (ASS). An early catalyst was the complete clearing of suspended sediments from 23 km of the Tweed River estuary in 1987 and the associated death of fish, crustaceans and annelid worms (Easton, 1989). An outraged community in the Tweed, Brunswick, Richmond and Clarence Catchments believed that cane farming was contributing to a severe acid hazard in local waterways and drains. Action was required from canegrowers threatened with the imposition of severe environmental protection requirements by the NSW government.

The New South Wales Sugar Milling Company Ltd and the CRC for Sustainable Sugar Production commenced a project in 1995–96, designed to transform the ASS issue from an environmental problem to a self-regulating, routine land and water management function. A local capability to analyse quantitatively for actual and potential ASS hazard and associated lime requirements was established at the Broadwater Sugar Mill. In addition, qualitative assessments were made for the presence of pyritic materials in segments of soil profiles from over 400 NSW cane farms. While this strategy was appropriate for an interactive scientific study, costs and time associated with the laboratory analysis of ASS were an impediment to making evidence-based decisions on routine drain construction and maintenance. An efficient (cheap, speedy, effective) soil test was needed, ideally one based on an established field test for ASS (Ford and Calvert, 1970; Ahern *et al.*, 1998a) but capable of predicting the lime requirements of exposed pyritic drain spoil. The spoil, brought to the surface when developing and maintaining deep drains in low-lying areas in northern NSW, was known to have exposed sulfidic materials to rapid oxidation, with subsequent release of strong acid.

KEYWORDS: Acid Sulfate Soils, Environment, Lime Requirements, NSW Canelands, Soil Testing, Sustainability.

This paper describes selected soil properties of NSW canelands relevant to the calibration of a rapid ASS field test for predicting the quantity of agricultural limestone required to neutralise pyrite-affected drain spoil. It gives calibration curves and a look-up table for predicting lime requirements for three soil texture classes and includes validation data.

Methods and materials

Soil cores were collected mostly to a depth of 1.5 m, using a 0.1 m diameter Jarret soil auger, from low-lying areas of 446 NSW cane farms. Each profile was laid out (in the presence of the cane grower) onto a halved PVC pipe graduated from 0.2 m down to 1.5 m. Soil texture was recorded for each interval, using the method described by McDonald *et al.* (1990).

Field pH (pH_F) was measured in duplicate at each depth interval (≤ 0.25, 0.25–0.5, 0.5–0.8, 0.8–1.2, 1.2–1.5 m) after mixing ≈ 1 part of moist soil with ≈ 5 parts distilled water. Measurement was effected using a portable pH meter. Subsequently, a small, representative portion of soil from each depth interval was treated with 30% w/v H_2O_2, pre-adjusted to pH 4.5–5.5 with aqueous NaOH. The H_2O_2 was allowed to react for a minimum of 3–4 min, sometimes after warming the mixture to accelerate the reaction (Ahern *et al.*, 1998a). Each oxidised pH value (pH_{FOX}) was measured with the same portable pH meter. An initial soil pH ≤ 4.0 was indicative of the presence of active sulfides (Thomas, 1967; van Breeman, 1982), while a corresponding pH_{FOX} of ≤ 3.0 was indicative of the presence of un-oxidised or incompletely oxidised pyritic minerals. Field data were used only from those profiles subsequently submitted to the laboratory for more detailed analysis (typically one in three).

Soil samples for laboratory analysis at Broadwater were placed in polythene bags and sealed immediately to minimise contact with the atmosphere. These were kept cool and delivered to the laboratory within 24 h of collection to reduce the possibility of biologically catalysed oxidation of sulfide minerals. Sub-samples were dried for at least 48 h at 80–85°C and coarse material removed manually (especially shell and gravel) prior to mechanical grinding to < 0.5 mm to produce homogenous samples and to encourage more complete peroxide oxidation (Ahern *et al.*, 1998b). The ground samples were analysed according to the nationally endorsed peroxide oxidation combined acidity and sulfate (POCAS) method (Ahern *et al.*, 1998a). Key measurements included the pH of a filtered 1:20 soil/1 M KCl extract (pH_{KCl}) and pH of a filtered 1:20 soil/1 M KCl extract after peroxide oxidation (pH_{OX}). Lime requirements to neutralise actual and potential sulfidic acidity were derived theoretically from POCAS measurements of total potential acidity expressed as equivalent pyrite (S_{TPA}; acid trail) and peroxide S after peroxide oxidation and a HPLC finish for dissolved sulfate (S_P; sulfur trail). Assumptions were that 1% S will, on oxidation, produce 30.6 kg H_2SO_4 for each tonne of soil, equivalent to 624 moles H^+/tonne of soil, requiring 31.2 kg of high purity limestone to neutralise the acidity generated. After inclusion of a 1.5 safety factor for reasons similar to those outlined by Cregan (1980) and Kamprath (1980), the rate rises to 46.8 kg lime/m^3 (equivalent to 46.8 kg lime/tonne of affected soil).

Conventional statistical procedures were used to calculate median, arithmetic mean, standard deviation and ranges of relevant field and laboratory results. Soil pH values were typically converted to hydrogen ion concentrations prior to statistical assessment and subsequently reconverted. In most cases, statistical functions in Microsoft Excel 97 were used. Two-dimensional regressions were performed (Jandel Scientific Software, 1996), with preferred regressions a compromise involving 'goodness-of-fit', the spread of residuals and avoidance of high-order polynomials.

Results and discussion

Regulatory authorities in NSW use 'action levels' of S_{TPA}, S_P or similar (Ahern *et al.*, 1998a) to confirm the presence of ASS. Soil texture affects these action levels. As soil textures were assessed in the field, it was possible for the first time to compile information on soil texture class (aggregated into fine, medium and coarse) by mill region and depth for canelands in northern NSW (Figure 1).

A prominent feature of the frequency distributions for soil texture classes was the dominance of fine textures at all soil depth segments to 0.8 m, and particularly at ≤ 0.25 m and 0.25–0.5 m. In contrast to many Australian soils (Stace *et al.*, 1968), there was an increasing frequency of medium and coarse textured soil profile segments with increasing depth, particularly evident at 0.8–1.2 and 1.2–1.5 m. The presence of medium and coarse textured soil particles at these depths has implications both for chemical ASS hazard assessment and for sub-soil hydrology. The

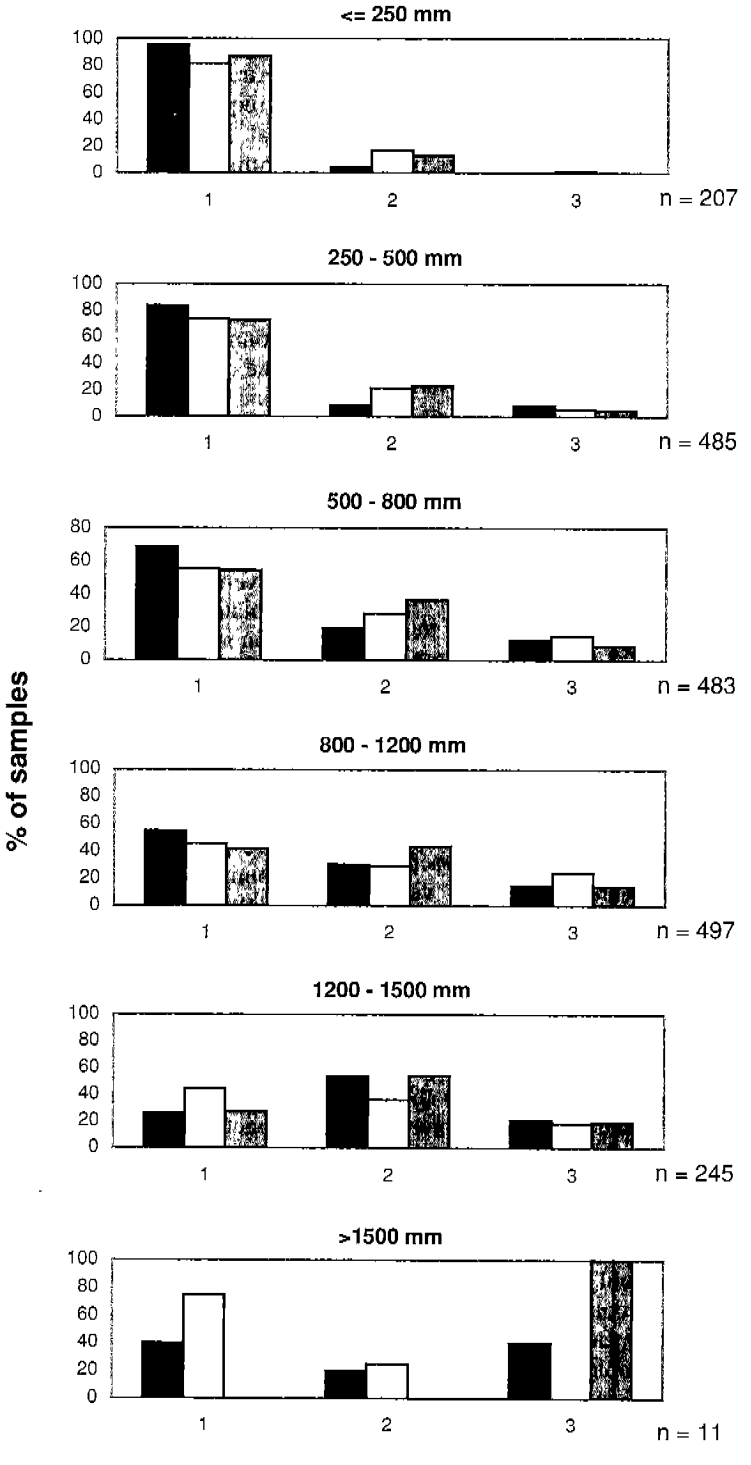

Fig. 1—Frequency distribution percentages of fine, medium and coarse soil texture classes by depth and mill region (C = Condong; B = Broadwater; H = Harwood) in low-lying canelands of northern NSW.

expectation is that medium and coarse textured zones will have greater hydraulic conductivity than fine textured zones.

For the three mill regions and depths to 0.8–1.2 m, the Condong region had the highest percentages of fine soil textures. There were, on average, few meaningful differences in the distribution percentages of soil texture classes below this depth interval.

Application and mixing with finely divided neutralising agents such as agricultural limestone and dolomite is a 'standard' method of treating soil acidity. The same materials are appropriate and recommended (Evangelou, 1995; Bowman, 1996; Gardner *et al.*, 2000) for neutralising actual and potential pyritic acidity. From the pH data presented in Table 1, the need to incorporate neutralising agents into the management of ASS in NSW canelands both initially and following oxidation is certain. Median values, irrespective of whether measured in the field or laboratory were all medium to extremely acidic (Rayment and Bruce, 1984).

The lower pH_{KCl} values relative to corresponding pH_F values are consistent with expectations (White, 1969; Conyers and Davey, 1988) that pH measurements made in water extracts (the field situation) are mostly higher by 0.5–1.0 unit than pH values measured in neutral salt solutions (the laboratory situation). Median pH_{KCl} values were extremely acidic at all depths, while median pH_{OX} values were lower than corresponding pH_{KCl} values, particularly at depths ≥ 0.8 m. It can be inferred from these trends (supported by corresponding field pH data) that there is considerably more potential oxidisable acidity below 0.8 m than in soil-profile segments nearer to the surface. If these soils were to become drain spoil, much limestone would be required to neutralise the actual and potential sulfidic acidity that could be mobilised.

Grand median lime requirements derived from S_{TPA} and S_P, when averaged across all samples and depths (both ASS positive and non-ASS included) were highest in the Condong mill region (grand medians of 14.2 and 12 kg lime/m^3, respectively). These contrast with rates of 6.8 and 6.5 kg lime/m^3 for Broadwater and 3.6 and 5.6 kg lime/m^3 for Harwood. There was little difference in grand median lime requirements for fine and medium textured soils by either trail (8.3 and 8.4 kg lime/m^3 for the acid trail and 7.7 and 9.2 kg lime/m^3 for the S trail) when considered by soil texture class. Corresponding grand median lime requirements for coarse textured soils were 3.0 and 3.3 kg lime/m^3. The linear regression describing the overall relationship between lime requirement (kg lime/m^3) for ASS in NSW canelands derived from the sulfur trail (X) and the acid trail (Y) of the POCAS method (all mill regions, depths and soil texture classes pooled together) was $Y = 3.91 + 1.02X$ (adjusted $r^2 = 0.75$; $n = 1344$). Accordingly, predicted lime rates will be slightly higher on average when the acid trail is used, which is probably good insurance from an environment protection viewpoint.

In the search for a field-derived surrogate for predicting lime requirements from the acid trail of POCAS, a five-point rating for vigour of reaction of the field-performed peroxide oxidation test was dismissed due to poor correlation coefficients. There was encouragement to examine pH_{FOX} because of highly significant predictive relationships between pH_{OX} and lime requirements derived from S_{TPA} for three soil texture classes (Table 2a). Regression equations and goodness-of-fit for corresponding relationships for pH_{FOX} and lime requirements are summarised in Table 2b. The percent variance explained was much lower in all cases, almost certainly because of incomplete peroxide oxidation in the field.

Table 1—Field measured and laboratory measured median soil pH levels (weighted across the three mill regions in Northern NSW) for five depths.

	Depth (m)				
	<0.25	0.25–0.5	0.5–0.8	0.8–1.2	1.2–1.5
Field measured					
Initial (pH_F)	4.8	5.1	5.2	5.8	5.8
Oxidised (pH_{FOX})	3.3	3.6	3.4	3.0	2.0
Laboratory measured					
Initial (pH_{KCl})	4.2	4.3	4.3	4.3	4.4
Oxidised (pH_{OX})	3.9	4.0	3.8	3.5	2.4

Table 2—Regression equations for relationships for three soil texture classes between (a) pH_{OX} and lime requirements (Y; kg/m^3) derived from S_{TPA}, and (b) pH_{FOX} and lime requirements (Y; kg/m^3) derived from S_{TPA}, each for three soil texture classes. All relationships were restricted to soil segments ≤ 1.5 m.

(a)

Soil texture class	Regression equation	r^2	n
Fine	$Y = 244.836\ pH_{OX}^{-2.422}$	0.72	796
Medium	$Y = 220.340\ pH_{OX}^{-2.659}$	0.75	378
Coarse	$Y = 355.584\ pH_{OX}^{-4.055}$	0.77	161

(b)

Fine	$Y = 53.865\ pH_{FOX}^{-1.303}$	0.32	796
Medium	$Y = 38.415\ pH_{FOX}^{-0.877}$	0.20	378
Coarse	$Y = 18.626\ pH_{FOX}^{-1\ 259}$	0.42	161

It was recognised that significant linear relationships between pH_{OX} and pH_{FOX} for NSW canelands (Figure 2), along the lines established for field and laboratory pH values of soils from the lower Burdekin Irrigation Area (Baker *et al.*, 1983), could be used to substitute for the pH_{FOX} term in relationships described in Table 2b. This was done to adjust predicted limestone rates so they more closely harmonised with those derived from laboratory measurements alone. The predictive relationships between derived values for pH_{FOX} and lime requirements of drain spoil for the three soil texture classes (results from mill regions and soil depths combined) are shown graphically in Figure 2. Data points from 68 additional field and laboratory-analysed samples used to validate the new field test for lime requirements of drain spoil are included. A 'look-up' Table for lime requirements (kg/m^3) by soil texture class and pH_{FOX} ensures the field test is easy to use (Table 3).

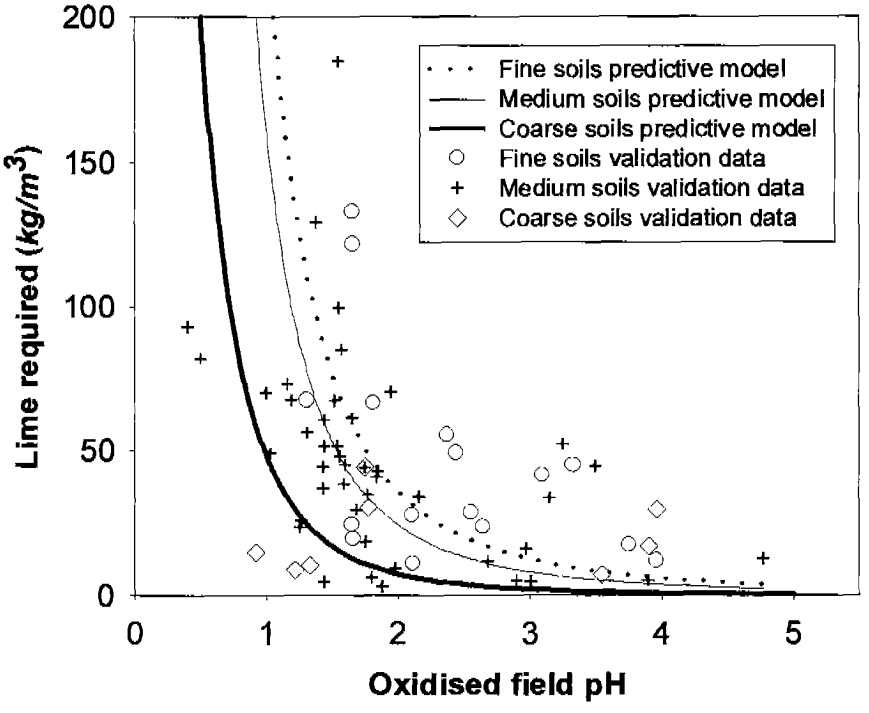

Fig. 2—Lime requirement models for fine, medium and coarse textured soils derived to relate pH_{FOX} values with lime requirements to neutralise actual and potential acidity typically associated with ASS, together with plots of validation samples used to test the models. Linear relationships between pH_{OX} and pH_{FOX} used to substitute pH_{OX} with pH_{FOX} in the original predictions between pH_{OX} and lime requirements given in Table 2 were as follows:

Fine texture: $pH_{FOX} = 0.146 + 0.838\ pH_{OX}$; $r^2 = 0.50$; $n = 796$
Medium texture: $pH_{FOX} = 0.039 + 0.855\ pH_{OX}$; $r^2 = 0.65$; $n = 378$
Coarse texture $pH_{FOX} = -0.675 + 1.025\ pH_{OX}$; $r^2 = 0.63$; $n = 161$

Table 3—'Look-up' Table for lime requirements of drain spoil associated with ASS, based of relationships derived for northern NSW canelands from pH_{FOX}.

pH_{FOX}	Lime required (kg/m^3) by soil texture class		
	Fine	Medium	Coarse
1.0	235	165	50
1.5	77	53	17
2.0	36	24	7
2.5	20	13	4
3.0	13	8	2
3.5	9	5	2
4.0	6	4	1

The validation samples suggest the relationships are sufficiently robust for the purpose. The 1.5 safety factor incorporated into the lime-rate recommendations, use of the acid trail from POCAS, and the reality that all of the potential acidity present in the drain spoil will take time to fully oxidise all combine to provide end users with an adequate margin of protection against recommending insufficient limestone. A further recommendation is to double-check around 5% to 10% of samples in an ASS testing laboratory until local confidence in using the field test is achieved. For example, suitability of the test for use on ASS-affected drain spoils in Qld canelands has still to be confirmed, although success is confidently expected.

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