Undiagnosed metal phytotoxicity in soils: Measurement of soil pH micro-variability under Manawatu pastures, and assessment of an alternative means of amelioration.

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Abstract

Although not always recognised as such, the major reason for the recommended application of sufficient lime to achieve a soil pH of 5.5 or more on New Zealand pastures is to ameliorate phytotoxic effects of water soluble cations of aluminium (Al), manganese (Mn) and iron (Fe). However, evidence that increasing numbers of farms have sub-optimum soil pH levels suggests that traditional treatment, *viz.* infrequent heavy applications of agricultural lime, is not considered cost-effective by many farmers, probably due largely to increasing application costs. Application of the carboxylate co-polymer AlpHa® to eliminate phytotoxic levels of Al, Mn and Fe was found to be comparable in effectiveness to typical rates of lime application, but with the advantage of minimal application cost, as the low application rate required (2 L/ha) can be incorporated into fertiliser or (reduced) lime applications. Standard soil testing of commercial farms involves combining 15–20 soil cores from a given paddock to determine the "average" pH. As well as underestimating the mean pH, this method gives no information regarding micro-variability of soil pH in the pasture root zone. Over 25% of the pasture root zone was found to have pH levels 0.3 to 0.6 lower than the true average, the therefore susceptible to metal toxicity. Commercial laboratory testing of individual cores would be uneconomic. The in-field direct measurement of soil (damp) pH using the antimony (Sb) electrode was found to be a very convenient and robust technique for assessing variability. The benefits of more accurate identification of metal toxicity risk coupled with the potential of a more cost-effective method of amelioration are discussed.

Keywords: metal toxicities, Al, Mn, Fe toxicity treatment, alternatives to liming, acid soils under pastures, pH variability in pastures, urine patch pH effects, AlpHa®, carboxylate co-polymers

Introduction

Aluminium (Al) and manganese (Mn) phytotoxicity in New Zealand pastures have been identified as major risks to maximum production (Smith *et al.* 1983; Edmeades *et al.* 1991). Al phytotoxicity increases as soil pH falls below 5.5, while Mn phytotoxicity occurs under reducing/water-logged conditions. The phytotoxic effects of these metals has traditionally been minimised by the infrequent heavy applications of agricultural lime. Over 90% of New Zealand pasture soils have been identified as requiring maintenance lime (During 1984).

Recent studies (Bishop *et al.* 2012) have shown that these phytotoxicities can also be reduced by the low application rates (2 L/ha) of the carboxylate co-polymer AlpHa® (Patent Application NZ597821) in pot and field trials. This product is not to be confused with the poly dicarboxylic acid Avail®, which is promoted as increasing crop yield through reduction in P fixation.

Bishop *et al.* (2012) found a 25% greater increase in ryegrass dry matter (DM) production following the application of 2 L/ha AlpHa® compared to 1000 kg of finely ground limestone in a 6-week pot trial grown in soil with phytotoxic levels of Al (Dannevirke silt loam, pH 4.3, with rhizospheric Al solution concentration of 4.9 mg/L). In a field trial on water-logged pasture (Tokomaru silt loam, pH 5.8 with phytotoxic levels of Mn (0.35% DM) and iron (Fe) (3.7%), as measured in washed grass roots), the application of 2 L/ha of AlpHa® in conjunction with 2 L/ha of sodium silicate solution increased DM production by 241 kg DM/ha over a 30-day period.

To further understand the reasons for these effects, Bishop *et al.* (2013) conducted a glasshouse solution culture growth response trial for ryegrass with solution culture media containing various levels of Al, Mn, Fe and AlpHa®. The base solution culture media was the mixture of "Solution A" (KNO_3 – 530 mg/L, $(NH_4)_2SO_4$ – 100 mg/L, $MgSO_4$ – 370 mg/L, $CaSO_4$ – 1290 mg/L, Na_2SO_4 – 480 mg/L, Na_2SiO_3 – 60 mg/L and NH_4NO_3 – 400 mg/L), "Solution B" (KH_2PO_3 – 200 mg/L, H_3PO_3 – 270 mg/L, $ZnSO_4$ – 220 mg/L, $MnCl_2$ – 70 mg/L, $CuSO_4$ – 40 mg/L, NaMoO4 – 4 mg/L and $CoSO_4$ – 20 mg/L) and Fe solution ($FeSO_4.7H_2O$ – 8340 mg/L) at the rate of 100A:1B:1Fe solution, respectively per litre of purified water. The metal and AlpHa® treatments were then added to the base solution to give total metal concentrations (mg/L solution) of Al 0, 0.1, 0.2, 0.4, 0.8

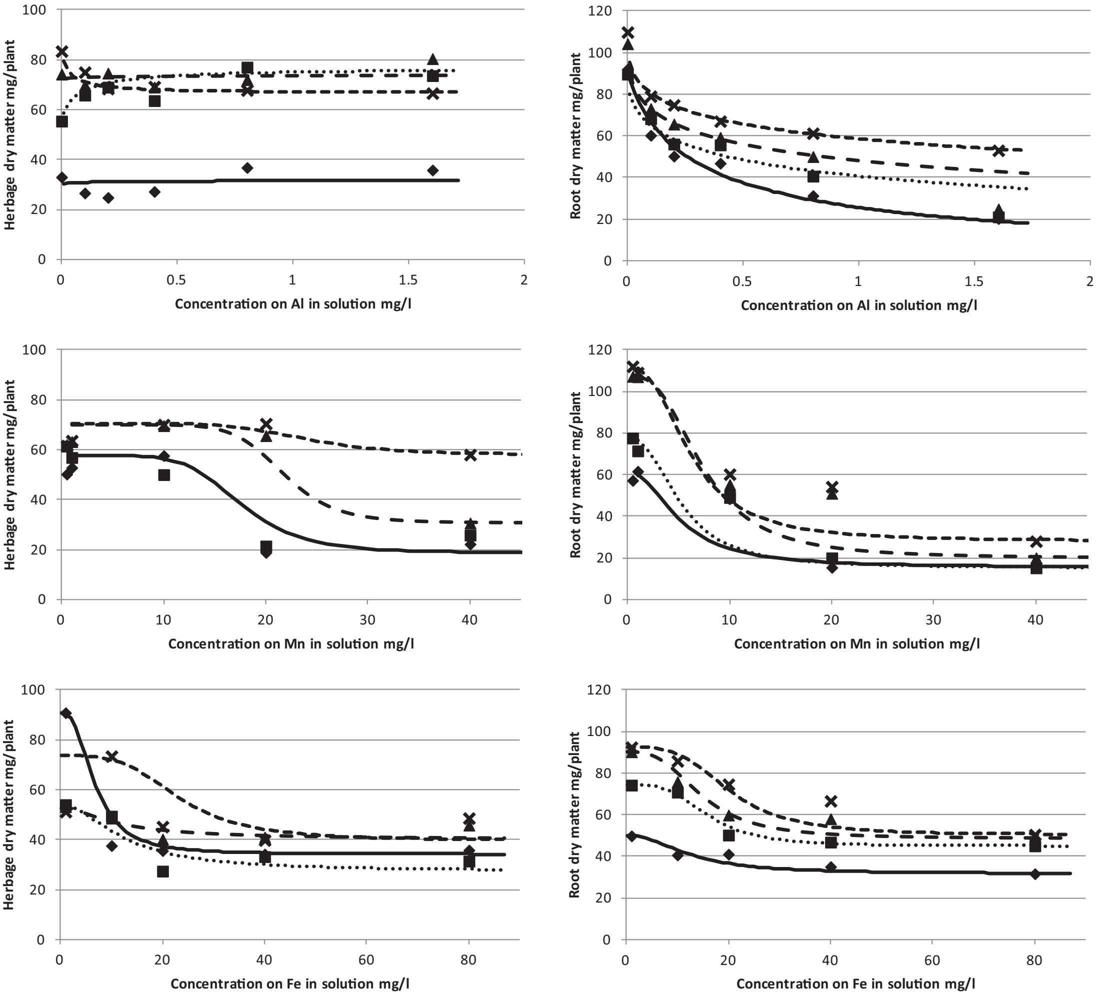

Figure 1 Growth response curves for herbage and roots of annual ryegrass grown in nutrient solutions containing additional Al, Mn and Fe with AlpHa® added at 0(♦), 0.2(■), 2(▲) and 20(×) ul/L. lines are lest squares fitted herbicide dose response (equation 2) for each metal and AlpHa® combination (from Bishop *et al*. 2013).

Table 1 Summary of micro-variation in soil pH transects taken between Manawatu and Tokomau Rivers.

Location/Soil classification	(Site No.) Mean pH / Standards deviation		
Manawatu floodplan /Rangitikei silt/ recent fluvial	(1) 5.3/0.83^{a}	(1) 4.9/0.36^{a}	(2) 5.1/0.45^{a}
Opiki Silt/ orthic gley	(3) 6.1/0.44^{g}	(4) 5.9/0.45^{g}	(5) 6.5/0.29^{g}
Tokomaru silt loam/ Perch-gley pallic	(6) 6.2/0.38^{g}	(7) 5.8/0.09^{g}	
Tararua Plateau brown earth	(8) 4.8/0.42^{a}		

^{a} direct soil pH measurement using antimony electrode
^{g} laboratory analysed soil pH in a 1:2 soil to water suspension read using a glass pH electrode
Note: Sites 4–8 were too dry at time of sampling to use Sb electrode and laboratory testing was required.

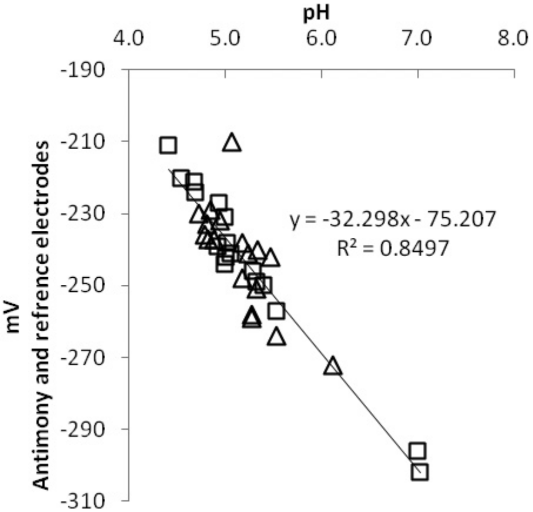

Figure 2 mV response of Sb electrode system to pH in soil water suspension at 1: 2 ratio as measured by H+ selective electrode and meter. Soils used were Manawatu silt (□) and Dannevirke silt (Δ).

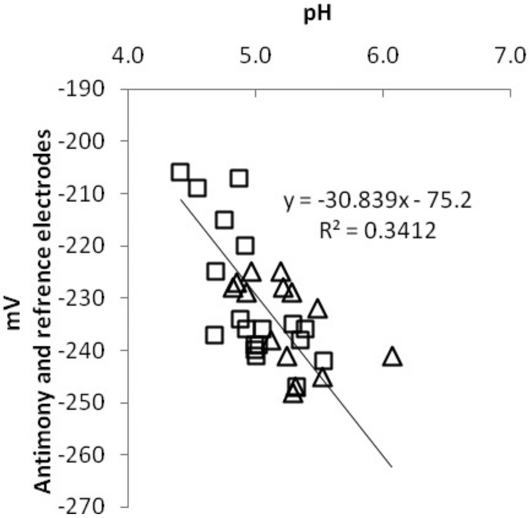

Figure 3 mV response of Sb electrode system on wet soil surface compared to pH in soil water suspension at 1: 2 ratio as measured by H^+ selective electrode meter. Soils used were Manawatu silt (□) and Dannevirke silt (Δ).

and 1.6 ; Mn 0.5, 1, 10, 20 and 40; and for Fe 1, 10, 20, 40, and 80. Each metal treatment was again treated with AlpHa® at the rate of 0.0, 0.2, 2.0 and 20 µl/ml. Therefore each metal level contained four levels of AlpHa® (including the nil rate). The treatments were replicated five times. The containers were arranged in a randomised complete block design (RCBD) in a glasshouse. The glasshouse temperature was maintained at 11±5°C minimum (night) and 30±6°C maximum (day). After 42 days of plant growth the experiment was concluded, and plant shoots and roots from each container were progressively collected. The pH and EC of each treatments solutions were measured periodically.

The results of this solution culture study (Figure 1) show a significant increase in herbage growth from all AlpHa® concentrations from 0.2 to 20 uL/L at Al concentrations from 0 to the highest tested (1.6 mg Al/L). AlpHa® showed a more rate-sensitive effect on herbage growth in the presence of Mn. The two highest concentrations (2 and 20 µL/L) of AlpHa® delayed the onset of Mn phytotoxicity to between 20 and 40 mg Mn/L. AlpHa® offset the effect of iron phytotoxicity on herbage growth only at the highest AlpHa® level and lowest Fe level tested, but positive AlpHa® effects on root growth were found at all concentrations of Fe.

Bishop *et al.* (2013) also presented preliminary evidence that the extent of Al phytoxicity in grazed pasture is poorly represented by current commercial soil sampling procedures, which combine a number of soil cores from a paddock to give an average soil pH. As well as giving rise to an artificially high average pH compared to the average of individually tested soil cores, possibly as a result of biological processes (Carran & Theobald 1995), the measurement of pH in this manner gives no indication of pH variability. A major cause of this variability is short- and long-term pH changes in urine patches. Normal commercial soil testing procedure intentionally avoids both obvious urine patches or very poorly growing areas, which also leads to underestimation of soil pH variability. The testing of individual soil cores and the statistical analysis of the pH frequency distribution at one site demonstrated that a considerable percentage of the soil in the pasture root zone was suffering from phytotoxic pH levels, even though the soil pH as measured by the standard test was 5.5 (Bishop *et al.* 2013).

Objectives of this study

In the wider field study reported here, the investigation of micro-variability in soil pH under grazed pasture was extended to nine sites on a traverse of soils from the eastern banks of the Manawatu river to the plateau area (elevation 400 m) in the Tararura ranges to the east near Tokomaru, allowing stronger conclusions to be drawn regarding both the extent and amelioration of metal phytotoxicity.

As the second part of this study, the accuracy and convenience of pH measurement using the traditional glass electrode measurement of a soil-water suspension was compared to the use of an antimony (Sb) electrode mV response, after calibration of the latter with directly-measured pH. This was conducted because of two significant practical advantages of the Sb electrode, especially in multi-measurement

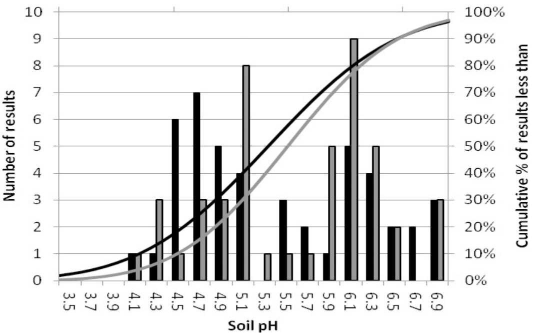

Figure 4 Frequency distribution (columns) and cumulative distribution curves (lines) for 43 soil pH measurements on a 1.5 m transect of grazed pasture on Rangitikei silt with samples every 15 cm to a depth of 20 cm in 5 cm sections, using a direct soil contact Sb electrode (black columns and line) and soil water suspension (1:2) using glass electrode (grey columns and line). Mean pH values were 5.32 for Sb electrode and 5.49 for the glass electrode systems, with standard deviations of 0.83 and 0.75 respectively.

field work: (i) it is far more robust in the field, and (ii) it can be used to test the damp soil surface directly if required, as well as suspensions (Conkling & Blanchar 1988; Adamchuk *et al.* 2007; Schirrmann *et al.* 2011).

Finally, the potential for the use of AlpHa® as a full or partial alternative to lime application for the amelioration of metal toxicity is discussed.

Methodology

Soil traverse

The traverse of the eastern Manawatu flood plains near sea level over the Tokomaru silt terrace to the elevated plateau at 400 m above sea level crosses a spectrum of soil types from the raw/recent Rangitikei silts along the river banks through the orthic gley silts of Opiki, the pallic perched gley soil of the Tokomaru loess deposit, up to the highly weathered brown/allophanic soils of the Tararua ranges. Sampling sites were selected from grazed dairy farms on these main soil types and were sampled prior to grazing.

Sampling of micro-variability

Eleven soil cores were taken from each site spaced every 150 mm over a 1.5 m transect starting at a residual urine patch and radiating outward. The soil cores were sectioned into 5 cm intervals over a depth to 20 cm; this depth was chosen to be able to determine whether pH micro-variability itself changed with depth. The soil pH of the individual soil core sections was analysed in water suspension at a 1:2 fresh soil to water ratio and left for 16 hrs prior to remixing and settling for 30 min prior to reading with a glass pH electrode. The pH was also measured in the field using a surface contact Sb pH selective electrode for comparison between the two methods.

Validation of Sb electrode for measurement of soil pH

The Sb electrode mV response to soil pH (as determined by 1:2 soil:water suspension using a glass electrode) was determined by the analysis of two soils types: 18 samples of Manawatu silt, pH range 4.47 to 6.93, and 18 samples of Dannevirke silt, pH range 4.78 to 6.11. The soil sample (10 g) was first placed in a small (35 ml) cup and pressed to form a flat surface. The soil moisture was then increased to saturation point with deionised water and allowed to rest for 30 min prior to direct reading with the Sb electrode, which was pressed into the damp soil surface. Following this direct soil measurement, additional deionised water was added to give a 1:2 soil to water suspension which was mixed and allowed to settle. The suspension pH was measured with glass and Sb electrodes 30 min and 16 hr post-mixing. This allowed pH calibration curves for suspension and moist soil samples to be obtained for the Sb electrode system.

Comparison of Sb electrode soil pH measurements in the field with laboratory soil-water suspension with glass electrode was carried out over a short 1.5 m traverse involving 43 samples from under a grazed Rangitikei silt pasture. Results were compared as population mean, standard deviation and frequency distribution.

The pH frequency distribution for all individual sites was used to determine mean soil pH and variability represented by the standard deviation (SD).

Results and Discussion

Laboratory assessment of pH by Sb electrode in field and soil-water suspension

The mV output of the Sb electrode was strongly correlated with soil pH as measured using the standard method, the response being -32.29 mV per pH unit between pH 4 and pH 7 for soil suspension samples, showing both techniques to have similar accuracy (Figure 2). The Sb electrode is more suitable for field use and direct soil contact compared to the fragile glass membrane electrode which is easily damaged.

The mV response of the Sb electrode of -30.83 mV per pH unit on the wet soil surface was similar to but far more variable than the relationship found in the soil suspensions (Figure 3). This variability reflects the ability of the Sb electrode to respond to localised effects within the sample, whereas soil-water suspensions are homogenised.

The wider variation in soil pH found by the Sb electrode/damp soil system compared to the glass electrode/soil-water suspension system is shown in Figure 4, which shows cumulative distribution frequency (CDF) curves for populations of 43 pH results from a short transect of 1.5 m on a dairy grazed pasture on Rangitikei silt.

The differences in mean soil pH and overall distribution of soil pH results are small and not significantly different, with means and (SDs) of 5.32 (0.83) and 5.49 (0.75) for the Sb and glass electrodes respectively, but the ability of the Sb electrode to accurately measure even smaller micro-sites appears to have been responsible for 46% of its results being found to have a pH of less than 5.1 compared to only 28% for the glass electrode. Note the obvious presence to two data populations at this site (discussed in the next section).

Interpretation of micro-variability of soil pH in a traverse of Manawatu soils

Soil pH measurements from nine short transects on grazed pasture located on the three main soil types encountered on the eastern side of the Manawatu river to the Tararua ranges showed a high degree of soil pH variability within very short distances. Most sites had statistically normal distributions of pH, with standard deviations of 0.36 to 0.45 (Table 1). This distribution of results indicates that as much as 25% of the soil may be 0.3 pH units or more lower than the mean value obtained from bulked soil samples.

The lowest mean soil pH values were found at the two extremes of the soil type, *viz* the recent Rangitikei silt with low CEC and buffering capacity (sites 1–3), and the highly weathered brown/allophanic soils of the hill country plateau (site 9). Site 1 on the Rangitikei silt shows the largest micro-variation in soil pH with a bimodal distribution; examination of the data and frequency distribution (Figure 4) shows this to be due to clusters of soil pH values at 4.5–4.7 and 6.1–6.3, probably representing aged and relatively recent urine depositions respectively. Site 9, on a plateau at 400 m elevation in the Tararua ranges, is an acidic highly weathered brown/allophanic soil with a pH of only 4.8, and is therefore also very susceptible to Al toxicity.

The gley soil sites (sites 4–8) with their imperfect drainage show good resistance to acidification from pastoral farming, and when cultivated and re-sown (site 6) show little variation in soil pH, as does a site recently converted to pasture from fallow (site 8). However, gley soils which become waterlogged over winter have the potential to develop phytotoxic levels of soluble Mn and Fe due to anaerobic-induced reductions in oxidation states to their water-soluble cations.

Implications of pH micro-variability for the use of lime and AlpHa®

In this study, four out of the nine sites sampled had low soil pH levels of 5.3 or less. These, combined with micro-variations between 0.36 to 0.83 make them highly susceptible to Al toxicity. Also, gley soils which become waterlogged over the winter have the potential to develop phytotoxic levels of Mn and Fe. This strongly supports earlier suggestions that the frequency and severity of metal toxicity in New Zealand pastures may be considerably underestimated (Bishop *et al.* 2012; 2013).

Standard mixed-core commercial soil testing procedures give no information regarding micro-variability in pH, and moreover produce an artificially high average test result. Measurement of the distribution of soil pH in this study demonstrated that 25% of the pasture root zone may have soil pH levels 0.3 to 0.6 pH units less than the true average. Therefore many paddocks and farms deemed to be safe (pH>5.6) from Al phytotoxicity may have significant areas with low soil pH, reducing overall pasture yield.

Amelioration of metal toxicity has traditionally been undertaken by the infrequent (every 3–5 years) spreading of heavy (1–2 tonnes/ha) applications of lime. The existence of below-optimum soil pH values on increasing numbers of farms, hill country farms in particular, indicates that with increasing material, transport and aerial spreading costs and relatively static farm incomes, the use of lime for this purpose is being seen by fewer farmers as a cost-effective strategy. In the authors' view, more frequent applications of smaller applications of somewhat finer lime may be more effective in treating toxicities than generally accepted, because frequent application of lime is more likely to prevent the development of the very low soil pH levels in aged urine. However, frequent application would add considerably to total application costs, even with the reduction in the total quantity of lime being applied over time.

The use of lime to elevate the mean soil pH to the point where very little of the soil volume had potentially toxic pH levels runs the real risk of inducing deficiencies of some nutrients, including P, trace elements such as zinc (Zn) and copper (Cu), and also molybdenum (Mo) toxicities, by producing excessively high pH levels at micro-sites which already had adequate pH levels.

Application of the carboxylate co-polymer AlpHa® has been shown to stimulate grass growth and alleviate metal phytotoxicity in ryegrass, at application rates of only 2 L/ha (approximately 1kg/ha of active ingredient), either sprayer-applied or coated onto fertiliser (Bishop *et al.* 2013). Effectiveness at such low application rates is explained by the mode of action of binding toxic soluble metal cations. Critical phytotoxic soil solution concentrations for Al, Mn and Fe are only 0.1, 20 and 10 mg/L respectively. Once reduced, return to these levels is quite slow. This, combined with the estimated 60-day half-life of AlpHa®, suggests that annual applications of AlpHa® should be adequate. At an estimated cost of \$30/ha (2 L/ha) and current farm incomes, AlpHa® may therefore be cost-effective for the farmer, especially if mixed with planned applications of fertiliser or (reduced amounts of) lime to avoid any additional application costs. While treatment of low pH micro-sites such as old urine patches only would be ideal, and indeed may become possible with new technology (Bates & Quin 2013), full-paddock application of AlpHa®, is very unlikely to represent any environmental risk.

Conclusions

Testing of a traverse of Manawatu dairy farms has clearly demonstrated that the proportion of soil in the root zone with pH levels sufficiently low to produce phytotoxic levels of heavy metals is considerably greater than previously assumed, with 25% or more of the soil volume having pH levels 0.3 to 0.6 below the true mean. Toxicity is of course more likely in soils with lower mean pH, but even paddocks with commercially tested "safe" pH levels of 5.6 or more may be suffering from significant metal toxicity-induced limitations on pasture production.

The antimony (Sb) electrode was found to be a more practical tool for measurement of micro-variability of soil pH in the field, particularly as it can measure surface pH of damp soil *in situ*.

Given that increasing numbers of farmers are not viewing traditional heavy, infrequent applications of agricultural lime as cost-effective, the finding in preliminary trials that low application rates (2 L/ha) of the carboxylate co-polymer AlpHa® successfully treat metal toxicity warrants its assessment in a wider range of New Zealand soils.

As more data comes to hand, farmers may well benefit from the production of a "Metal Toxicity Control Guide", which includes instructions to farmers regarding their use of the Sb electrode for direct soil contact pH variability assessment, and product options for the amelioration of metal toxicities.

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