

# Effects of brown coal derived materials on pH and electrical conductivity of an acidic vineyard soil

Albert U. Imbufe<sup>1,3</sup>, Antonio F. Patti<sup>1,2</sup>, Aravind Surapaneni<sup>3</sup>, Roy Jackson<sup>1</sup> and J. Angus Webb<sup>4</sup>

<sup>1</sup>Centre for Green Chemistry, School of Chemistry, Monash University, PO Box 23 Clayton campus Victoria, Australia. Email: [Albert.Imbufe@sci.monash.edu.au](mailto:Albert.Imbufe@sci.monash.edu.au)

<sup>2</sup>School of Applied Sciences, Monash University, Churchill, Victoria, Australia.

<sup>3</sup>Primary Industries Research Victoria, Department of Primary Industries (DPI), Tatura Centre, Ferguson Rd, Tatura, Victoria 3616, Australia.

<sup>4</sup>Water Studies Centre, School of Chemistry, Monash University, Clayton Campus, Victoria 3800, Australia

## Abstract

Humic substances derived from brown coal (lignite) are a rich source of acidic carboxylic and phenolic groups which can provide reactive sites for cation exchange, bind and sequester phytotoxic elements, increase pH buffering of soils, and promote the penetration and retention of calcium in the soil as well as improve nutrient transport to plants. Potassium humate (K-humate) is obtained by alkaline extraction of Victorian brown coal and is used commercially as a soil conditioner. Calsulmag (CSM) is an alkaline material rich in calcium and magnesium which is obtained from power station fly ash and used as a substitute for lime. OMNIA Specialities Australia Pty. Ltd supplied samples of these materials. In this paper, the effects of K-humate and K-humate+CSM on selected chemical properties of an acidic vineyard soil were investigated under field conditions. Results indicate statistically significant increases ( $P < 0.001$ ) in soil pH, and electrical conductivity (EC) relative to the control. The K-humate+CSM treatment demonstrated the most beneficial effects.

## Key Words

Humic substances, K-humate, calsulmag, soil acidity.

## Introduction

Soil acidity within the rhizosphere is recognised as a major limiting constraint in crop productivity in Australia. Soils in the vineyard areas of Yarra Valley (south-eastern Victoria) are inherently acidic. Low soil pH is usually associated with an increased phytotoxicity of Al and Mn, and a deficiency of Ca and Mg (Leeper and Uren, 1993). Conventional liming treatment has proved to be largely ineffective in the short term due to the slow vertical movement of surface-applied lime (Pavan *et al.*, 1982; Ritchey, 1996), and costly (Cassel, 1980), particularly within the root-zone (Noble *et al.* 1995, Bruce *et al.* 1988). However, treatment of subsoil acidity with Ca-rich organic materials such as fulvic and humic acids has shown some considerable promise (Van der Watt *et al.* 1991, Noble *et al.* 1995).

Humic acids and their salts which are derived from coal and other natural sources may provide a viable alternative to liming, to ameliorate soil acidity and improve soil structural stability. Research has shown that it is the humic fractions (humic acid, fulvic acid and humin) of the soil organic matter that are responsible for the generic improvement of soil fertility and improved productivity (Kononova, 1966, Fortun *et al.* 1989).

In this study, the potential for using commercially available potassium humates (K-humates) derived from Victorian brown coal to treat soil acidity was assessed under field conditions in an acidic vineyard soil.

## Materials and Methods

### Soils

The acidic vineyard soil used in this study is located at Dixons Creek in the Yarra Valley, in south-eastern Victoria, Australia. The soil has a characteristic fine sandy loam texture in the A horizon and is classified as a Grey Kurosol (Isbell 1996). It displays a strongly acidic ( $\text{pH}_{\text{H}_2\text{O}} < 5.5$ ) B horizon. The soil is typical of the soils of economic importance within the south-eastern agricultural belt of Australia. As it is under continuous mechanised cultivation, structural decline is likely to occur, manifested for example in soil surface crusting, poor aggregation, compaction, and poor water availability to plants. Increasing levels of phytotoxic Al and Mn will also probably occur. Thus, a significant loss in crop productivity is

expected. Standard methods of soil analysis (Rayment and Higginson, 1992) were used to determine the initial soil properties (Table 1).

#### *Treatments and experimental design*

Field plots (1x1 m) previously treated with a range of brown coal derived materials in 1999 (Issa 2002) were used in this follow-up study. Results from that study showed that of all the treatments tested, the 18% K-humate and 18% K-humate+Calsulmag treatments performed better. Therefore, these treatments were reapplied in March 2002 to assess cumulative effects of these materials on soil properties. An additional new treatment viz. 26% K-humate (a newly formulated product of interest) was also applied in March 2002 on new plots at the same vineyard. Control plots from the previous study (Issa 2002) were retained as the controls for this current study. The field trial thus comprised of 4 treatments and 4 replicates (16 plots) in a randomised block design. The treatments were surface applied at same rate in the rows between the vines.

#### *Potassium humate*

The K-humate used in this study is produced by alkaline treatment of Victorian brown coal and is commercially available in Australia (sold as a concentrated liquid soil conditioner). It is available in two concentrations (i) 18% K-humate and (ii) 26% K-humate. These products will be referred to as KH18 and KH26 in this paper, respectively, and the term "K-humate" will be used as a generic word for both 18% K-humate and 26% K-humate.

K-humate contains potassium salts of water-soluble humate (26% w/v) and fulvate (0.7% w/v). It contains 15% (w/w) total organic carbon and 1.6 mmol/g of acid functional groups. The solid-state  $^{13}\text{C}$  CP NMR spectrum of the humate salt isolated from the 26% K-humate preparation is shown in Figure 1. The tallest peak (0-60 ppm) can be assigned to alkyl groups, both straight chain and substituted. Carbonyl-C is observed in the 160-190 ppm region and O-substituted aryl C between 140 and 160 ppm. Resonances in the 100-140 ppm region of the spectrum are mainly due to aromatic-C. The distribution of carbon signals in the K-humate  $^{13}\text{C}$ -NMR spectrum gave the following results: aliphatic-C 44%, aromatic 32%, carbonyl 11%, O-alkyl 9% and the balance from methoxyl and N-alkyl type groups. It should be noted that not all the carbon in such humate samples is observable by  $^{13}\text{C}$  CP NMR and spectra need to be interpreted with caution (Smernik and Oades, 2000).

Figure 2 indicates the proton NMR of a freeze-dried sample of the 18% K-humate, and Figure 3 shows the Carbon-13 Solid State NMR spectra of the acidic vineyard soil (a) and a sample of the soil after treatment with K-humate-18 (b), Issa (2002).

Quantitative total elemental analyses of 26% K-humate gave the following results (% w/v): 4.80% potassium, 0.50% iron, 0.15% nitrogen, 0.15% silicon, 0.10% sulphur, 0.09% sodium, 0.07% chloride, 0.05% calcium, 0.04% phosphorus, and 0.60% total aluminium. This product also contains about 18.7% (w/v) humic acid fraction, 2.7% fulvic acid and zero humin fractions, within limits of experimental error.

#### *Calsulmag (CSM)*

Calsulmag is a coal derived treated fly ash product also available commercially as a light-coloured alkaline powder. It contains 19.5% calcium, 5.1% sulphur, and 7.0% magnesium on dry basis. In this field trial, Calsulmag was used as a lime substitute.

#### *Soil sampling and measurements*

Soil samples at different depths (0-3, 3-6, 6-10, 10-15 and 15-25 cm) were taken twice (i) before the reapplication of old treatments (KH18 and KH18+CSM) and application of new treatment (KH26) to obtain baseline data (March 2002) and, (ii) 7 months after application of treatments (October 2002).

The soil properties measured included electrical conductivity (EC) - 1:5 soil/water extract, and  $\text{pH}_{\text{Ca}}$  using 1:5 soil/0.01M  $\text{CaCl}_2$  extract.

**Table 1. Some chemical and physical properties of the acidic vineyard soil investigated.**

Soil Property	Acidic Soil (DeBortoli)
CaCO <sub>3</sub> % (w/w)	< 1
Texture	Very fine sandy loam
Coarse sand (0.20-2.0 mm) % (w/w)	1
Fine sand (0.02-0.20 mm) % (w/w)	40
Silt (0.002-0.020 mm) % (w/w)	29
Clay (< 0.002 mm) % (w/w)	24.5
Mean weight diameter	2.04
pH (H <sub>2</sub> O)	5.8
pH (CaCl <sub>2</sub> )	5.1
EC (dS/m)	0.08
TSS % (w/w) <sup>a</sup>	0.03
Total C % (w/w)	3.1
Total N % (w/w)	0.24
C:N ratio	13
Exchangeable cations (mmol (+)/kg)	
Ca	66 <sup>b</sup>
Mg	30 <sup>b</sup>
Na	2.6 <sup>b</sup>
K	2.5 <sup>b</sup>
Sum of all cations	100
Ca:Mg ratio	2.2
ECaP <sup>c</sup> (%)	65
EMgP <sup>c</sup> (%)	30
ENaP <sup>c</sup> (%)	3
EKP <sup>c</sup> (%)	3

<sup>a</sup> TSS = Total Soluble Salts; calculated from EC ( $EC \times 0.297 = TSS$ ).

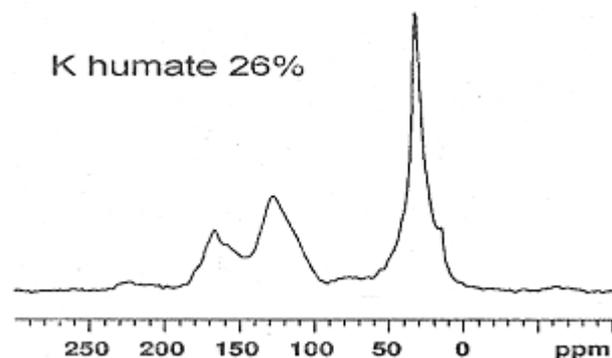
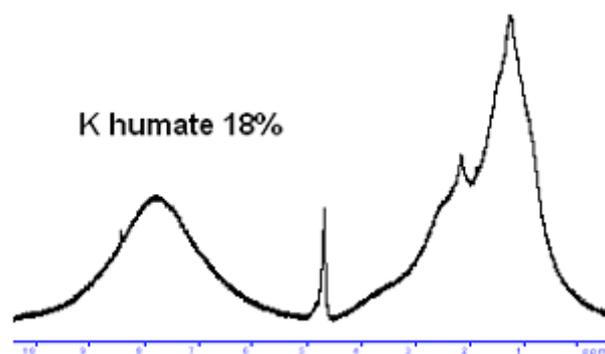
<sup>b</sup> 1 M NH<sub>4</sub>OAc (No wash).

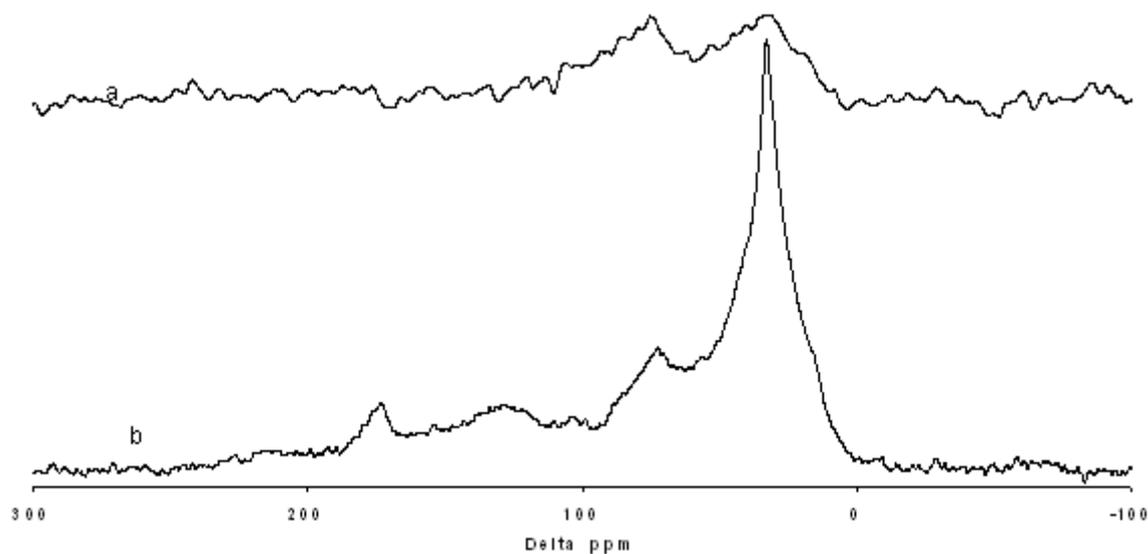
<sup>c</sup> Exchangeable Ca, Mg, Na, and K percentage, respectively.

#### Statistical analysis

The data were statistically analysed by a partly-nested analysis of variance (Quinn and Keough, 2002).

The treated plots were used as units of repeated sampling (x 4 replicates), and were considered as random factors within the treatments. Time and depth were considered as within-subjects factors.

**Figure 1. Solid-state <sup>13</sup>C CP NMR spectrum of 26% K-humate.****Figure 2. <sup>1</sup>H Liquid NMR Spectrum of Freeze-Dried 18% K-humate dissolved in D<sub>2</sub>O.**



**Figure 3. Solid State  $^{13}\text{C}$  CP/MAS NMR of a) A1 Horizon (0-25 cm) Acidic Vineyard Soil b) Acidic Vineyard Soil + K-humate (Issa, 2002).**

### Results

There were highly significant effects of the treatments on both the EC and pH. This was evidenced by a significant Treatment x Time interaction, Treatment x Depth interaction (for EC only), as well as Treatment x Time x Depth interaction as shown in Table 2. These significant interaction effects are printed in bold typeface in Table 2.

Relative to the control, the Treatment x Time interaction plots showed significant increases in both the soil EC and pH ( $P < 0.001$ ) for all the treatments, with the KH18+CSM treatment demonstrating the highest increases in EC and pH. Figures 4 and 5 are plots of the overall effects of Treatments over time as compared to control for the EC and pH. Baseline in Figures 4 and 5 refers to results from sampling data collected just before treatment application (March 2002) compared with results from samples collected 7 months later (October 2002) from the same plots.

**Table 2 Summary of the partly-nested analysis of variance. Columns show the  $p$ -values for squared root of the (pH) and log(EC) for each effect in the analysis. Appropriate denominator Mean-Square (MS) is shown beneath each effect, along with numerator and denominator degrees of freedom. Significant results at  $P < 0.05$  are shown in bold typeface.**

<b>Term</b>	<b>df</b>	<b>pH</b>	<b>EC</b>
<b>Between Subjects Test</b>			
Treatment	4	< 0.001	< 0.001
Plot (Treatment) MS	15	0.001119	0.000009
<b>Within Subjects Tests</b>			
Time	1	< 0.001	< 0.001
Treatment x Time	4	< 0.001	< 0.001
Plot (Treatment) x Time MS	15	0.000989	0.000004
Depth	4	< 0.001	< 0.001
Treatment x Depth	16	0.380	< 0.001
Plot (Treatment) x Depth MS	60	0.00145	0.000006
Time x Depth	4	0.772	< 0.001
Treatment x Time x Depth	16	< 0.001	< 0.001
Error MS	60	0.000867	0.000007

Figure 6 shows results for EC baseline of the initial sampling prior to treatment, while the results for samples collected after 7 months are indicated in Figure 7. Again, the KH18+CSM treatment

demonstrates the highest increase in EC over the KH18 and KH26 treatments. These significant increases in EC in the treated plots are probably due to the action of K-humate as a chelating agent of cations in the soil, as well as a direct addition of cations from the product itself, which is rich in potassium, magnesium and calcium. Calsumag is also known to be a rich source of these cations, and when used in combination with K-humate will introduce more cations to the soil.

Figures 8 and 9 shows the plots of pH for the Treatment x Depth x Time interaction effects. As with the EC, the pH effects were also significant relative to the control and the baseline, and the trend down the soil profile were consistent with the lowering of pH as the soil depth increases. As shown in Figure 9, the KH18+CSM treatment demonstrated the highest increase in pH relative to the control and baseline (Figure 8), as well as across the various depths and soil profiles downwards.

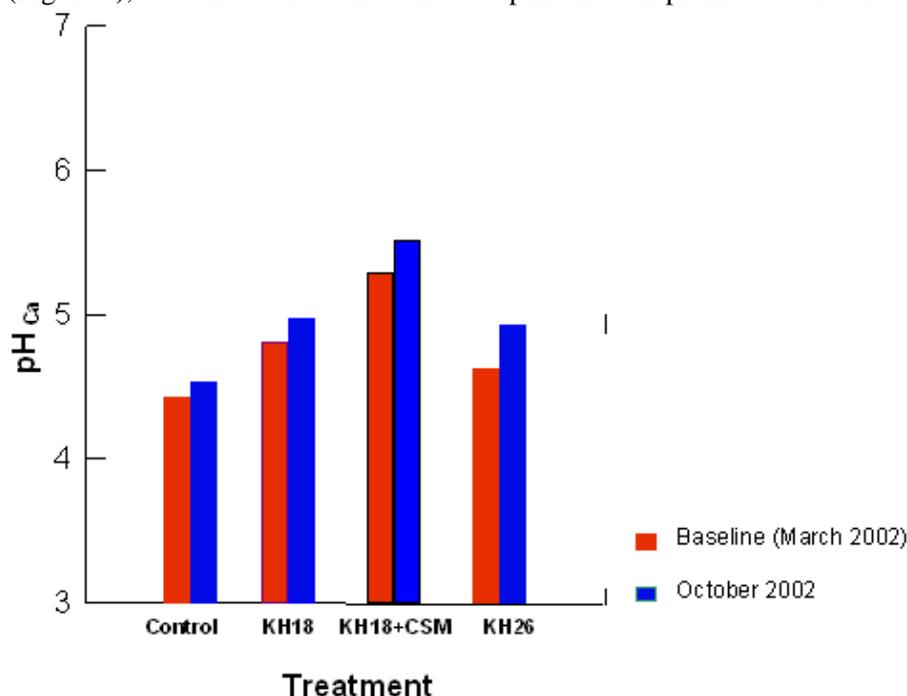


Figure 4. Effects of Treatment over Time for pH<sub>Ca</sub>. Error bar to the top right of graph is 1.0 standard deviation as calculated from the appropriate error mean square - Plot (Treatment x Time).

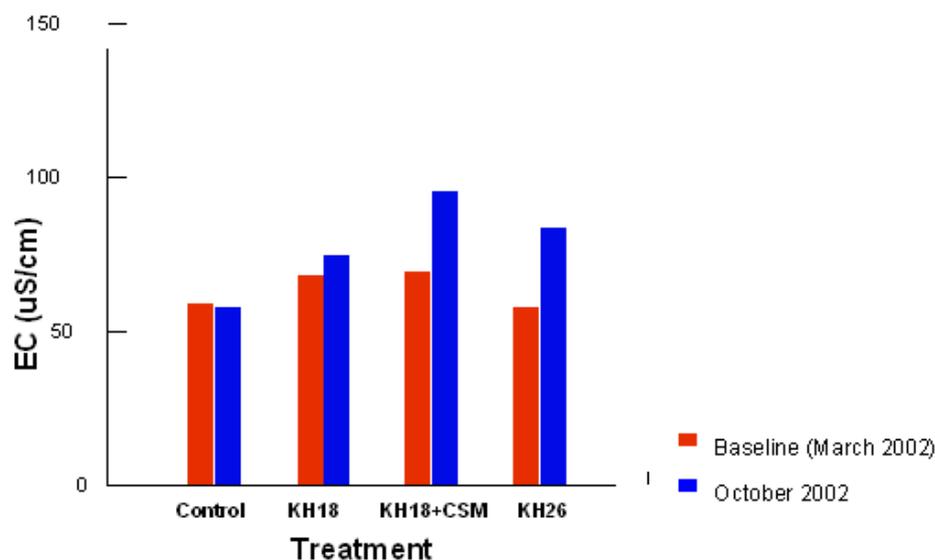


Figure 5. Effects of Treatment over Time for EC (µS/cm). The pooled standard deviation calculated the appropriate error mean square - Plot (Treatment x Time); magnitude is too small (0.181 µS cm<sup>-1</sup>) to show up on the graph.

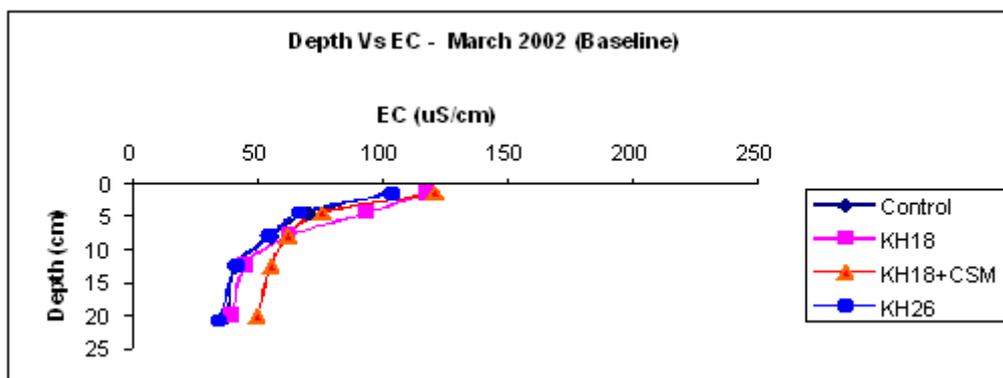


Figure 6. Baseline initial EC results (sampled prior to treatment application).

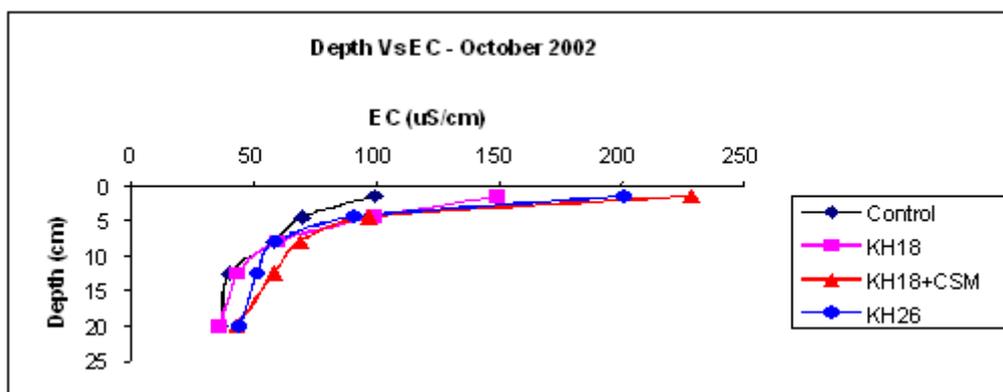


Figure 7. EC results 7 months after treatment application.

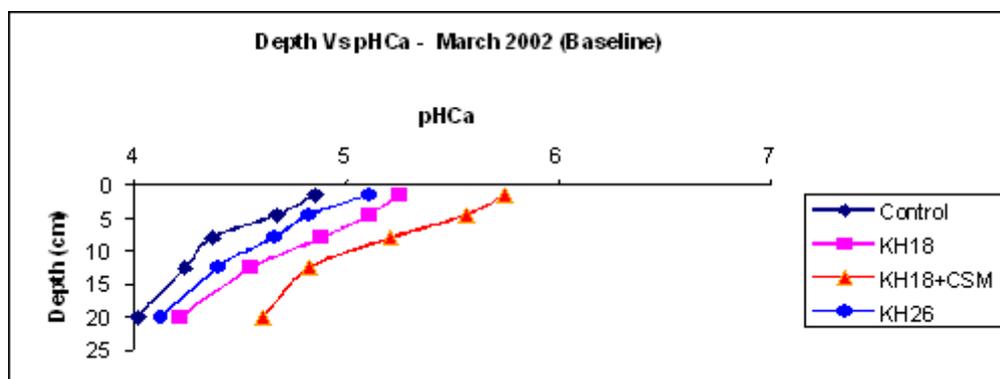


Figure 8. Baseline initial pH results (sampled prior to treatment application).

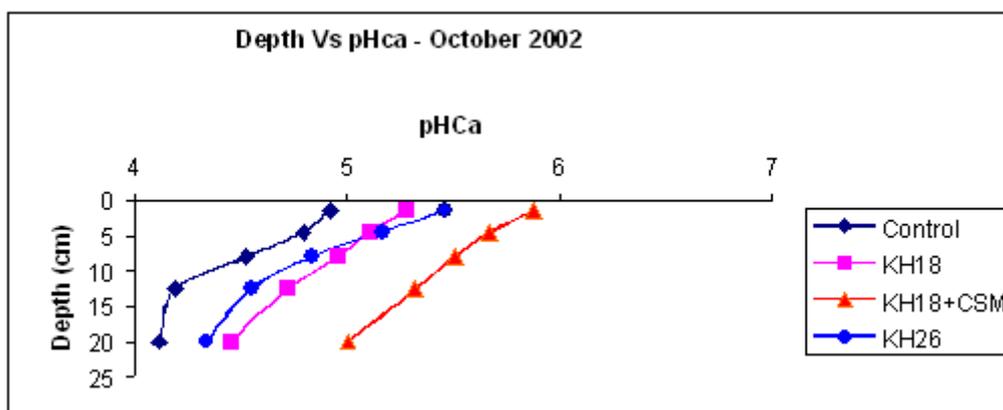


Figure 9. pH results 7 months after treatment application.

## Conclusion

Results from this field trial showed that commercial coal derived K-humate (18% K-humate and 26% K-humate) and Casulmag products are effective for use in ameliorating soil acidity, and for increasing the level of beneficial cations such as potassium, magnesium, and calcium in the soil.

## Acknowledgment

We thank Mr David Robertson (Department of Primary Industries, Tatura) for his valued and timely assistance with formatting the graphs.

## References

- Bruce RC, Warrell LA, Edwards DG, Bell LC (1988) Effects of aluminium and calcium in the soil solution of acid soils on root elongation of Glycine max cv. Forrest. *Australian Journal of Agricultural Research*. **39** (3), 319-338.
- Cassel DK (1980) Effects of ploughing depth and deep incorporation of lime and phosphorus upon physical and chemical properties of two coastal plain soils after 15 years. *Soil Science Society of America Journal*. **41** (1), 89-95.
- Fortun C, Fortun A, Almendros G (1989) The Effect of Organic Materials and their Humified fractions on the Formation and Stabilization of Soil Aggregates. *The Science of the Total Environment*, **81/82**, 561-568.
- Issa J (2002) Coal derived products as soil improvers. *PhD Thesis*, School of Chemistry, Monash University, Clayton, Victoria Australia.
- Isbell RF (1996) *Australian Soil and Land Survey Handbook: The Australian Soil*. (CSIRO Publishing, Collingwood, Victoria).
- Kononova MM (1966) *Soil Organic Matter. Its Role in Soil Formation and in Soil Fertility*. Pergamon Press, Oxford.
- Leeper GW, Uren NC (1993) *Soil science: an introduction*. 5<sup>th</sup> Edition, Melbourne University Press: Carlton.
- Noble AD, Randall PJ, James TR (1995) Evaluation of two coal-derived organic products in ameliorating surface and subsurface soil acidity. *European Journal of Soil Science*. **46**, 65.
- Pavan MA (1982) Toxic effects of aluminium on coffee seedlings in relation to calcium nutrition. *Revista Brasileira de ciencia do Solo*. **6** (3), 209-213.
- Quinn, GP and Keough, MJ (2002). *Experimental Design and Analysis for Biologists*. Cambridge University Press, Cambridge.
- Rayment GE and Higginson FR (1992) *Australian Laboratory Handbook of Soil and Water Chemical Methods*. (Inkata Press : Melbourne) Melbourne. Sydney.
- Ritchey KD (1996) Calcium sulfate or coal combustion byproduct spread on soil surface to reduce evaporation, mitigate subsoil acidity and improve plant growth. *Plant and Soil*. **182** (2), 209-219.
- Smernik RJ, Oades JM (2000) The use of spin counting for determining quantitation in solid state <sup>13</sup>C NMR spectra of natural organic matter, 1. Model systems and the effects of paramagnetic impurities, *Geoderma*, **96**, 101-129.
- Van der Watt HV, Barnard RO, Cronje IJ, Dekker J, Croft GJB, Van der Walt MM (1991) Amelioration of subsoil acidity by application of a coal-derived calcium fulvate to the soil surface. *Nature*, **350**, 146-148.