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Influence of pH, exchangeable aluminium and 0.02*M* $CaCl_2$-extractable aluminium on the growth and nitrogen-fixing activity of white clover (*Trifolium repens*) in some New Zealand soils

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Abstract

The effects of soil acidity on the growth and N_2-fixing activity of white clover in seven acid topsoils and subsoils of New Zealand were investigated using a glasshouse experiment.

The application of phosphate ($Ca(H_2PO_4)_2$) to the soils resulted in very large increases in white clover growth on all soils. The application of phosphate, as well as increasing P supply, also decreased 0.02*M* $CaCl_2$-extractable Al levels, but had little effect on exchangeable Al levels.

Where adequate phosphate was applied, increasing rates of lime ($CaCO_3$) resulted in increased plant growth on most soils. $N_2[C_2H_2]$-fixing activity was increased by the first level of lime for one soil, but generally remained approximately constant or declined slightly at higher rates of lime. Up to the point of maximum yield, white clover top weight was more highly correlated with 0.02*M* $CaCl_2$-extractable soil Al than with exchangeable Al or pH. At pH values greater than 5.5, plant yield declined on some soils, apparently because of Zn deficiency. The data suggest that white clover is unlikely to be affected by Al toxicity at 0.02*M* $CaCl_2$-extractable Al levels of less than about $3.3\,\mu g\,g^{-1}$. However, there were differences between soils in apparent plant tolerance to 0.02*M* $CaCl_2$-extractable Al, which appeared to be caused by differing C levels in the 0.02*M* $CaCl_2$ extracts.

Introduction

Large areas of low fertility hill country in New Zealand have soils which are strongly acid. Pasture legumes tend to perform poorly on these soils, and one possible reason for this is that toxic levels of plant available aluminium (Al) are present. There are also some lowland soils which have high levels of Al, particularly in their subsoils, which may restrict root penetration by sensitive crops.

Al toxicity is a major factor resulting in reduced plant growth in many acid soils (Adams and Pearson, 1967; Foy, 1974). It is well known that the solubility of Al in soils increases sharply below pH 5.5 (Coleman *et al.*, 1958; McCart and Kamprath, 1965). Some of the indices of soil Al which have been used to estimate likely Al toxicity include 1 *M* KCl-extractable Al, dilute $CaCl_2$-extractable Al and soil solution Al. Plant growth has been found to be negatively correlated with all of these indices of soil Al (Adams and Lund, 1966; Hoyt and Nyborg, 1972; Moschler *et al.*, 1960). However, for 1 *M* KCl-extractable Al at least, the minimum level that is toxic for plant growth varies for different soils (Adams and Pearson, 1967).

The aim of this experiment was threefold:

1. To ascertain the extent to which soil acidity/Al toxicity caused reduced white clover growth in the soils being studied.
2. To select an index of soil acidity or Al level

which was closely related to plant growth..

3. To ascertain the level of soil Al/acidity at which decreased plant growth occurred.

Experimental

Soils

Seven strongly acid hill country topsoils and subsoils were collected from the South Island and lower North Island of New Zealand. The soils are all very strongly leached yellow-brown earths. Their classifications according to US Department of Agriculture 'Soil Taxonomy' are given in Table 1. The chemical characteristics of the soils are shown in Table 2. Most analyses were carried out according to the methods of Blakemore *et al.* (1981). pH was measured on air-dried soil, with a soil : water ratio of 1 : 2.5. The method for determining $CaCl_2$-extractable Al and manganese (Mn) was based on that of Hoyt and Nyborg (1972). 10 g of air-dried soil was shaken with 20 ml of $0.02M$ $CaCl_2$ in an end-over-end shaker for 1 h, centrifuged (9000 rpm for 5 minutes) and filtered (Whatman no. 42 filter paper). The resulting solution was analysed using atomic absorption spectroscopy. Soil pH, $1M$ KCl-extractable Al (exch. Al) and $0.02M$ $CaCl_2$-extractable Al ($CaCl_2$-Al) levels were determined at both the beginning and end of the experiment, and $0.02M$ $CaCl_2$-extractable Mn ($CaCl_2$-Mn) was determined at the end of the experiment only ($CaCl_2$-Mn determinations carried out on selected samples from the beginning of the experiment indicated little change in $CaCl_2$-Mn level over the course of the experiment.) The pH, exch. Al and $CaCl_2$-Al data recorded in Table 5 are those from the beginning of the experiment. C levels in $0.02M$ $CaCl_2$ extracts were determined by the methods of Kalembasa and Jenkinson (1973) as used by Jenkinson and Powlson (1976).

Glasshouse experiment

The glasshouse experiment was of factorial design with 2 rates of phosphorus (P) as $Ca(H_2PO_4)_2$ and 4 rates of lime ($CaCO_3$) (Table 3), with 3 replicates. The P1 rates of P were based on P adsorption curves and were sufficient to give 0.2 ppm P in soil solution, a level thought to be sufficient for near maximum white clover growth (Parfitt *et al.*, 1982).

The rates of lime ($CaCO_3$) added (Table 3) were based on curves of soil pH *versus* amount of lime added. The aim was to have evenly spaced pH levels, ranging from natural pH to a maximum of 6, for each soil.

The soils were passed through a 6-mm sieve while in a field moist state. The lime and P were mixed uniformly throughout each of the soils 67 days before sowing. pH and exchangeable Al levels were determined at 10, 20 and 31 days after lime and P addition, and were found to have stabilised by day 10. The soils were packed into 1.4 litre plastic pots. 'Grasslands Huia' white clover (*Trifolium repens* L.) was sown and the plants were thinned to 4 per pot after emergence. After emergence a basal nutrient solution was applied to provide 100 mg K, 50 mg Mg, 107 mg S and 0.103 mg Mo per pot. Pots were inoculated twice with Rhizobium strains 2153 and 2668. Day/night temperatures in the glasshouse were approximately 25/16°C.

The experiment was set out in the glasshouse in three blocks, according to replicate. Within each block the seven soils were located randomly. Treatments were located randomly within soils.

Table 1. Classification of soils according to soil taxonomy

Soil	Soil taxonomy
Katrine silt loam (moderately podzolised variant)	Andic Dystrochrept, fine loamy, mixed, mesic
Kaiuma clay loam	Typic Dystrochrept, clayey, vermiculitic, mesic
Taita hill soil	Typic Haplohumult, clayey, mixed, mesic
Waipori silt loam	Lithic Dystrochrept, loamy, mixed, cryic

Table 2. Soil chemical properties

Soil	Depth (cm)	pH	Olsen P (μg g^{-1})	Total C (%)	Total N (%)	C/N	Cation exchange										Al saturation (%)	0.02*M* $CaCl_2$-extractable		
							CEC (meq %)	bases	BS (%)	Ca (meq %)	Mg	K	Na	Al	Mn	ECEC		Al	Mn (μg g^{-1})	C
Katrine silt loam (moderately podzolised variant)	0–8	4.5	–	7.3	0.51	14	24.2	6.7	28	4.6	1.72	0.27	0.15	5.1	0.16	12.0	43	19.9	18.0	757
	8–20	4.3	1.8	3.3	0.13	25	19.0	1.7	9	1.1	0.40	0.10	0.06	14.3	0.01	16.0	89	71.6	1.9	400
Kaiuma clay loam	0–15	4.8	0.9	4.6	0.23	20	31.2	9.0	29	6.7	1.85	0.17	0.30	10.8	0.28	20.1	54	14.1	25.1	587
	15–40	4.6	0.8	2.7	1.13	21	27.1	3.1	11	2.0	0.61	0.25	0.20	14.0	0.08	17.1	82	40.0	8.3	359
Taita hill soil	0–10	4.6	1.3	3.8	0.18	21	22.7	7.1	31	3.3	2.94	0.36	0.49	6.4	0.06	13.6	47	17.7	8.2	632
	12–30	4.5	1.9	1.6	0.09	18	19.1	2.9	15	1.0	1.33	0.24	0.29	11.4	0.01	14.3	80	55.9	1.8	284
Waipori silt loam	0–10	4.0	–	5.8	0.42	14	23.9	1.9	8	0.7	0.71	0.31	0.14	13.1	0.02	15.0	87	83.8	3.9	1045

Pots were watered up to their water content at a soil matrix potential of – 5 kPa.

The experiment was harvested one replicate at a time 84–92 days after sowing. White clover tops were removed at soil level and dried at 65°C in a forced-draught oven. The soil, complete with roots, from each pot was cut exactly in half vertically. From one half, the roots were washed free, rinsed with distilled water and oven dried at 65°C. The other half was used as a soil sample, after removal of the larger pieces of root.

Acetylene reduction assays

Acetylene reduction assays wee carried out 65 to 83 days after sowing. Intact plants in pots were sealed in airtight 5-litre plastic containers. 350 ml of commercial grade acetylene (C_2H_2), which had been bubbled through concentrated H_2SO_4 and distilled water (to remove acetone), was injected into each container. Plants were incubated for 2 hours, starting at approximately 11.30 am. At the end of the 2 hour period three 1 ml gas samples were removed from each incubation container and analysed using a Varian series 1700 gas chromatograph fitted with a flame ionisation detector. Gas samples were passed through a 1 m long, 3 mm internal diameter stainless steel column, packed with Porapak T (80–100 mesh), at a flow rate of 20 ml minute^{-1}. Injector, oven and detector temperatures were 160, 95 and 160°C respectively. Ethylene (C_2H_4) production was calculated by comparison of gas samples with C_2H_4/C_2H_2 gas mixture standards. Assays were scheduled according to 2 partially balanced incomplete block designs to enable estimation of treatment effects free from any day-of-assay effects.

Plant analyses

Plants were analysed for total N using a Kjeldahl method (Blakemore *et al.*, 1981). Levels of other elements were determined using X-ray fluorescence.

Statistical methods

Statistical analysis of results was carried out using the Genstat statistical package. Analysis of

Table 3. Lime and P treatments

Soil	Depth (cm)	Lime added ($gCaCO_3$. $100\,g^{-1}$ dry soil)					P added (μg P. g^{-1} dry soil)	
		L0	L1	L2	L3	L4	P0	P1
Katrine	0–8	0	0.25	0.51	0.76	–	0	290
	8–20	0	0.22	0.46	0.73	–	0	380
Kaiuma	0–15	0	0.26	0.53	0.81	–	0	790
	15–40	0	0.22	0.45	0.67	–	0	860
Taita	0–10	0	0.19	0.37	0.57	–	0	420
	12–30	0	0.27	0.54	0.81	–	0	420
Waipori	0–10	0	0.23	0.48	0.74	1.05	0	260

variance techniques were used to test the significance of differences between soil × treatment means.

Results and discussion

All of the soils in this experiment had a pH < 5.5, the level below which Al solubility begins to increase sharply with decreasing pH (Coleman *et al.*, 1958; McCart and Kamprath, 1965), and aluminium was a major component of the exchange complex of each soil (Table 2). Plant growth is known to be inversely related to percent Al saturation of the effective cation exchange capacity (ECEC) and critical values for Al saturation, below which optimum yield of various legumes is found to occur, range from 0 to 30% (Abruna *et al.*, 1975; de Carvalho *et al.*, 1980; Evans and Kamprath, 1970; Kamprath, 1970). The data cited suggest that all of the soils included in this experiment would have sufficiently high Al levels (Table 2) to impair legume growth.

The effects of lime and P on top and root weights of white clover are presented in Table 4. Corresponding levels of pH, exch. Al, $CaCl_2$-Al and $CaCl_2$-Mn are presented in Table 5.

For all soils there was a very large increase in white clover growth when P was added (Table 4). This was probably because of very low Olsen P levels in the soils to which no P had been added (Table 2). Levels of P in the clover tissue tended to be higher in the P1 than in the P0 treatments (data not presented). With no added P, however, yields did increase (non significantly) with increasing rates of lime, but even at the highest rates of lime yields were relatively low (Table 4). Where P was added, liming significantly increased top growth on 6 of the 7 soils (Table 4). The addition of P, as well as increasing P supply, decreased soil Al levels. P addition had very little effect on exch. Al, but a much greater effect on $CaCl_2$-Al levels (Table 5). With added P, increasing rates of lime also increased root growth in 3 of the soils, but the effect was more variable than that on top weight (Table 4).

In the Katrine, Kaiuma and Waipori soils, the nature of the response to lime was similar, with increases in white clover growth occurring at lower rates of lime (generally with pH < 5) and reaching a plateau or declining at higher rates. The fact that responses to lime occurred mostly at pH < 5.5 suggests that they were linked to decreasing Al levels, because the solubility of soil Al is very low above this pH level (Coleman *et al.*, 1958; McCart and Kamprath, 1965). In the Taita 0–10 cm soil, however, the growth response to lime was quite different. There was very little growth in any treatment until the latter stages of the experiment when, particularly at the highest rates of lime, the white clover began to grow more rapidly (Table 4). It appeared that a factor other than soil acidity (directly), or lack of P, was limitng white clover growth on this soil. There was no indication as to what this factor might be. Leaf P levels were relatively high (compared to other soils and compared to the standards of McNaught (1970)), as were soil P levels at the P1 rate of P (Olsen P levels were $> 57\,\mu g\,g^{-1}$ in the P1 treatment). This tends to eliminate the possibility that initial lack of a suitable mycorrhizal fungus caused the delay in growth. The clover response to lime on the Taita 12–30 cm horizon soil resembled that on the other soils more closely than that on the Taita 0–10 cm soil.

Table 4. Effects of lime and phosphorus treatments on white clover growth and nitrogen-fixing activity

Soil	Depth (cm)		Treatment									
			P0					P1				
			L0	L1	L2	L3	L4	L0	L1	L2	L3	L4
Katrine	0–8	T[a]	2.35	2.92	3.08	2.52	–	11.29a[b]	13.47b	10.70a	10.55a	–
		R[a]	0.800	1.100	0.907	1.000	–	3.520b	2.880ab	2.773a	2.387a	–
		NF[a]	–	–	–	–	–	40.6b	32.7ab	30.0ab	28.5a	–
	8–20	T	0.013	0.460	0.573	0.503	–	7.92a	9.45b	11.41c	9.34b	–
		R	0.007	0.225	0.304	0.217	–	2.027	2.393	2.460	2.420	–
		NF	–	–	–	–	–	27.0	26.0	26.7	26.9	–
Kaiuma	0–15	T	0.011	0.013	0.015	0.018	–	11.84b	13.20c	13.11c	9.14a	–
		R	0.007	0.013	0.011	0.015	–	2.593	2.507	2.627	2.347	–
		NF	–	–	–	–	–	33.8b	28.2b	31.0b	20.9a	–
	15–40	T	0.009	0.020	0.011	0.016	–	7.18b	7.71b	7.47b	5.58a	–
		R	0.006	0.010	0.008	0.008	–	1.933	1.640	1.987	1.707	–
		NF	–	–	–	–	–	20.2b	21.1b	23.3b	11.9a	–
Taita	0–10	T	0.014a	0.022a	0.048a	0.300b	–	1.58a	1.97a	2.33a	6.24b	–
		R	0.014	0.019	0.037	0.125	–	0.424a	0.560a	0.520a	1.273b	–
		NF	–	–	–	–	–	8.4ab	10.8ab	7.4a	12.8b	–
	12–30	T	0.010	0.016	0.014	0.010	–	2.57a	3.71b	5.80d	4.84c	–
		R	0.011	0.011	0.017	0.012	–	0.713a	0.773a	1.313b	1.473b	–
		NF	–	–	–	–	–	18.5bc	25.0c	13.1ab	9.3a	–
Waipori	0–10	T	0.029a	0.263b	0.370bc	0.427cd	0.533d	3.53a	9.28c	9.27c	9.41c	8.41b
		R	0.263	0.311	0.296	0.333	0.660	1.780a	2.953bc	2.533b	3.053c	3.240c
		NF	–	–	–	–	–	10.7a	25.7b	16.1ab	15.8ab	15.5ab

[a] T = top weight (g), R = root weight (g), NF = nitrogen-fixing activity (μM $C_2H_4.h^{-1}$)

[b] Values followed by different lower case letters differ significantly at the 5% level according to Fisher's least significant difference.

At the P1 level of P, N_2-fixing activity generally remained approximately constant or declined with increasing rates of lime (Table 4). For the Waipori soil, however, there was a significant increase in N_2-fixing activity from the L0 to the L1 rate of lime, which was proportionately similar to the increase in clover growth (Table 4). In several of the soils (Katrine 0–8 cm, Kaiuma 0–15 cm, Kaiuma 15–40 cm, Taita 12–30 cm) N_2-fixing activity declined significantly with increasing rates of lime, particularly at the higher rates of lime. Where N_2-fixing activity delined as yield was increasing, or the rate of decline exceeded the rate of decline in yield with increasing lime rate, this was probably the result of greater N mineralisation (Edmeades *et al.*, 1983) and hence greater uptake of mineral N by the plants, resulting in lower rates of N_2 fixation (Hoglund, 1973). Where the rate of decline in N_2-fixing activity was similar to or less than the rate of decline in plant yield, the decline in N_2-fixing activity was probably a result of reduced plant growth. At the P0 level of P, levels of N_2-fixing activity were very low (data not shown), reflecting poor plant growth (Table 4). There were small increases in N_2-fixing activity at the highest lime rates in the Kaiuma soil, but generally rates of activity were approximately constant over the range of lime rates. Leaf N levels showed no significant response to treatments, and tended to be low over all treatments (McNaught, 1970).

Soil pH declined slightly over the course of the experiment, and there were corresponding increases in $CaCl_2$-Al levels in some soils (data not shown). The decline in pH was significant at the 5% level in 6 of the 7 soils, with an average decline in pH of 0.27 units. There were significant increases in $CaCl_2$-Al in only 2 of the 7 soils, with increases ranging from -0.10 to 9.30 $\mu g\,g^{-1}$ for the Katrine 8–20 cm soil and from 0.38 to 12.85 $\mu g\,g^{-1}$ for the Waipori soil. It is unlikely that the decreases in pH resulted from increases in ionic strength of the soil solutions (Edmeades *et al.*, 1983), because the quantities of nutrients added (except P, which was added well before the beginning of the experiment) were similar to the quantities taken up by the plants. If the presence of roots of clover dependent on symbiotic N_2 fixation caused the decline in pH (Israel and Jackson, 1978) a greater decline would

Table 5. Effects of lime and phosphorus treatments on soil properties

Soil	Depth (cm)	Property	Treatment									
			P0					P1				
			L0	L1	L2	L3	L4	L0	L1	L2	L3	L4
Katrine	0–8	pH	4.3	4.8	5.3	5.8	–	4.3	4.8	5.3	5.7	–
		Exch. Al (meq. %)	6.3	2.5	0.3	0.09	–	5.5	2.1	0.2	0.2	–
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	22.4	5.4	1.6	0.2	–	15.3	3.5	1.2	0.5	–
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	21.4	7.2	2.6	1.1	–	17.1	8.2	2.4	0.9	–
	8–20	pH	4.2	4.8	5.2	5.6	–	4.3	4.8	5.2	5.6	–
		Exch. Al (meq. %)	14.2	9.3	4.1	0.3	–	13.0	8.9	3.7	0.3	–
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	81.6	12.0	2.5	0.9	–	47.2	7.0	1.7	0.4	–
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	1.9	1.0	0.6	0.3	–	1.1	0.6	0.4	0.2	–
Kaiuma	0–15	pH	5.1	5.4	5.7	6.0	–	5.1	5.4	5.7	6.1	–
		Exch. Al (meq. %)	10.8	5.6	2.1	0.2	–	9.8	4.8	1.8	0.06	–
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	8.4	2.5	1.9	1.3	–	4.9	2.5	1.4	0.7	–
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	15.5	9.1	5.5	2.4	–	11.7	6.7	4.4	2.1	–
	15–40	pH	5.0	5.4	5.8	6.0	–	5.1	5.4	5.7	6.2	–
		Exch. Al (meq. %)	14.6	9.3	4.6	2.1	–	11.4	8.1	4.1	1.4	–
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	33.2	5.6	1.4	0.7	–	10.6	2.3	1.5	1.0	–
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	5.5	3.2	1.8	1.1	–	3.9	2.4	1.6	0.9	–
Taita	0–10	pH	5.0	5.2	5.5	6.0	–	4.9	5.2	5.6	6.1	–
		Exch. Al (meq. %)	6.6	2.6	0.4	0.01	–	5.4	2.1	0.3	0.01	–
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	11.5	3.1	1.2	0.6	–	7.4	2.3	1.5	0.6	–
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	8.1	4.2	2.1	0.9	–	6.9	3.3	1.6	0.9	–
	12–30	pH	4.7	5.2	5.8	6.5	–	4.6	5.2	5.9	6.5	–
		Exch. Al (meq. %)	10.7	5.0	0.6	0.03	–	9.7	4.6	0.6	0.6	–
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	54.9	4.7	0.3	0	–	31.5	2.8	0.3	0	–
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	1.5	0.9	0.5	0.1	–	1.3	0.7	0.3	0.1	–
Waipori	0–10	pH	4.4	4.9	5.1	5.5	6.0	4.4	4.8	5.2	5.5	6.0
		Exch. Al (meq. %)	12.3	8.2	3.5	0.6	0	11.7	7.9	3.5	0.5	0
		0.02*M* $CaCl_2$-Al ($\mu g\, g^{-1}$)	69.8	12.9	3.1	1.1	0.5	49.3	9.7	2.5	0.9	0.4
		0.02*M* $CaCl_2$-Mn ($\mu g\, g^{-1}$)	4.0	2.8	1.8	1.1	0.6	3.0	1.9	1.2	0.8	0.4

have been expected in treatments where there was better plant growth, but this was not the case. The soils data discussed in this paper are generally data from thebeginning of the experiment because it was thought that they best represent the conditions under which the plants established and carried out a substantial proportion of their growth. One of the effects of this choice is that the suggested level of $CaCl_2$-Al below which Al toxicity is unlikely, as discussed later in this paper, is a little lower than it would be if based on soils data from the end of the experiment.

Correlations of top growth, root growth and N_2-fixing activity with pH, exch. Al, $CaCl_2$-Al and $CaCl_2$-Mn were not significant when all data were included, or when the complete sets of P0 and P1 data were considered separately. Because interest was centred on soil acidity factors in this experiment, an attempt was made to remove variations in yield due to soil or rate of P, by expressing yields as a proportion of the maximum yield for particular soils and rates of P. In addition, data from beyond the point of maximum yield (except where pH $\leqslant 5.5$) were discarded from the correlations, because it was considered that soil acidity factors were not directly affecting yields here. All data from the Taita 0–10 cm soil were discarded because there appeared to be factors other than soil acidity involved in the yield response on this soil. Correlations based on relative yields from this reduced data are presented in Table 6. These data suggest that, of the soil acidity characteristics measured, $CaCl_2$-Al is the most closely related to plant growth, followed exch. Al and pH.

The mean level of $CaCl_2$-Al at which maximum, or near maximum yield occurred was 3.3 $\mu g\, g^{-1}$ (Tables 4 and 5, Taita 0–10 cm data excluded). Thus the data suggest that if soil $CaCl_2$-Al is below this level, then white clover growth is unlikely to be impaired by Al toxicity. Because of the intervals

Table 6. Correlations of white clover weight with soil acidity characteristics (n = 39)[a].

	pH	Exch. Al	$CaCl_2$-Al	$CaCl_2$-Mn
Relative top weight	0.60*	−0.66**	−0.85**	−0.05
Relative root weight	0.46*	−0.47*	−0.64**	0.002

* and ** indicate correlations significant at the 1% and 0.1% levels respectively.

[a] Correlations are for P0 and P1 pots with soil pH $\leqslant 5.5$ or with rates of lime $\leqslant$ the rate associated with maximum yield for individual soils. The soils data used are those from the beginning of the experiment, except for $CaCl_2$-Mn which was measured at the end of the experiment only.

between $CaCl_2$-Al levels for individual soils, the critical $CaCl_2$-Al level, above which yield depression would be expected, is difficult to estimate and may be a little higher than 3.3 $\mu g\,g^{-1}$. The value of 3.3 $\mu g\,g^{-1}$ agrees well with the findings of Edmeades *et al.* (1983), that Al toxicity for white clover was associated with $CaCl_2$-Al levels > 3.0–5.0 $\mu g\,g^{-1}$. However there was quite a range of $CaCl_2$-Al levels at which maximum yield occurred. In the Waipori soil, yield of tops reached a plateau at 9.7 $\mu g\,g^{-1}$ $CaCl_2$-Al. In contrast, in the Katrine 8–20 cm and Kaiuma 0–15 cm soils, there were significant yield increases as $CaCl_2$-Al decreased from 7.0 to 1.7 $\mu g\,g^{-1}$ and from 4.9 to 2.5 $\mu g\,g^{-1}$ respectively (Tables 4 and 5). In addition there was a yield increase on the Taita 12–30 cm soil as $CaCl_2$-Al was decreased from 2.8 to 0.3 $\mu g\,g^{-1}$. It could be argued here, though, that the response was not entirely a result of decreasing soil Al levels. Hence, it appears that the level of $CaCl_2$-Al which is toxic to white clover is different for different soils, *i.e.* included in the amount of Al extracted by $CaCl_2$ is an amount, that varies from one soil to another, which does not influence plant growth. The differences between soils in this respect may be explained by the reactions of Al with organic matter.

It is known that Al forms complexes with soil organic matter (Schnitzer and Skinner, 1964), that C-bound Al is less toxic to plants than non organically-bound forms (Bartlett and Riego, 1972), and that the level of soil organic matter can influence critical exch. Al levels for plant growth (Kapland and Estes, 1985). Therefore, in an attempt to explain the apparent differences in plant tolerance to $CaCl_2$-Al between soils in this experiment, the C contents of 0.02*M* $CaCl_2$ extracts from these soils were measured. The presence of C-bound Al could explain why plants have apparent tolerance to comparatively high levels of extractable Al in soils such as the Waipori 0–10 cm. C levels in the $CaCl_2$ extracts were highest for the Waipori soil, 37% higher than for the Katrine 0–8 cm soil, which had second highest C levels (Table 2) and second highest apparent plant tolerance to $CaCl_2$-Al (Tables 4 and 5). The results suggest that a proportion of the soluble Al forms complexes with organic matter and that the C-bound Al is less harmful to plants than the non organically bound forms. To eliminate differences in apparent plant tolerance to extractable Al between soils, it may be necessary to measure C-bound Al in addition to total Al levels.

In the Katrine and Kaiuma topsoils, levels of $CaCl_2$-Mn appeared to be relatively high, and Mn levels in white clover were higher at low rates of lime. However the maximum Mn concentrations in white clover tops in this experiment (394 $\mu g\,g^{-1}$) were well below the threshold toxicity levels of 570 $\mu g\,g^{-1}$ and 650 $\mu g\,g^{-1}$ reported by Smith *et al.* (1983) and Andrew and Hegarty (1969) respectively, suggesting that high soil Mn levels are not limiting white clover yields on these soils.

The decline in top weight of white clover at high rates of lime application and at the P1 level of P (Table 4), was probably caused by Zn deficiency. Zn levels in the white clover tops declined with increasing rates of lime application for all soils (data not shown). For the Katrine 8–20 cm, Kaiuma 0–15 cm, Kaiuma 15–40 cm and Taita 12–30 cm soils, leaf Zn levels were below the mean critical levels of McNaught (1970) at the highest rates of lime. This is consistent with findings that Zn availability from soil often decreases with increasing soil pH (Mengel and Kirkby, 1982). There was no consistent trend in leaf Al levels which would indicate that reductions in top growth at the highest pH levels (Table 4) were the result of Al toxicity caused by solubilized Al-organic matter complexes, according to the mechanism of Hargrove (1986).

Leaf Al levels (data not presented) tended to decline with increasing rate of lime in some soils (namely Katrine 8–20 cm, and Kaiuma 0–15 and 15–40 cm) but not in others. Root Al levels were thought to be unreliable because there was some possible soil contamination in the samples. Leaf Ca levels tended to increase with increasing rate of lime. However, even at the low rates of lime, leaf Ca levels were well in excess of the critical range of McNaught (1970), indicating that plants were not suffering from Ca deficiency. Leaf and root P levels showed no clear trend with lime rates, and in some cases leaf levels were slightly low (McNaught, 1970) even in the P1 treatment. High Al levels can result in reduced plant uptake of Ca (Johnson and Jackson, 1964) and P (Foy and Brown, 1963; Foy and Brown, 1964). However, there is no evidence that high Al levels were having such effects in this experiment.

Conclusions

Low levels of soil P severely limited white clover growth on all soils in this experiment. Application of phosphate, in addition to raising soil P levels, also reduced $0.02M$ $CaCl_2$-extractable Al levels. Under conditions of adequate P supply, however, white clover still gave growth responses to lime on most soils. Soil Al appeared to be the main factor associated with decreased white clover growth at pH < 5.5, and yields were more closely related to $0.02M$ $CaCl_2$-extractable Al than to $1M$ KCl-extractable Al or pH. Differences between soils in apparent plant tolerance to $0.02M$ $CaCl_2$-extractable Al appeared to be caused by different C levels in their $0.02M$ $CaCl_2$ extracts. The data from this experiment indicate that $0.02M$ $CaCl_2$-extractable soil Al levels below about $3.3\,\mu g\,g^{-1}$ will not cause reduced white clover growth, and conversely that levels higher than this may be toxic.

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