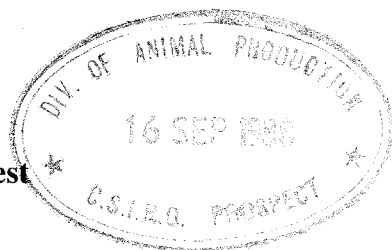


## Effects of Aluminium and Calcium in the Soil Solution of Acid Soils on Root Elongation of *Glycine max* cv. Forrest



R. C. Bruce,<sup>A</sup> L. A. Warrell,<sup>A</sup> D. G. Edwards,<sup>B</sup> and L. C. Bell<sup>B</sup>

<sup>A</sup>Agricultural Chemistry Branch, Department of Primary Industries, Indooroopilly, Qld. 4068.

<sup>B</sup>Department of Agriculture, University of Queensland, St. Lucia, Qld. 4067.

### Abstract

In the course of three experiments, soybean (*Glycine max* (L.) Merr.) cv. Forrest was grown in 21 soils (four surface soils and 17 subsoils) amended with liming materials ( $\text{CaCO}_3$  and  $\text{MgCO}_3$ ) and soluble Ca salts ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ). In most soils, the soluble salts increased concentrations and activities of Al species in solution to levels that restricted root growth, and  $\text{MgCO}_3$  induced a Ca limitation to root growth. Root lengths after three days were related to soil and soil solution attributes.

Suitable diagnostic indices for the prediction of Ca limitations to root growth were either Ca saturation of the effective cation exchange capacity or Ca activity ratio of the soil solution, which was defined as the ratio of the activity of Ca to the sum of the activities of Ca, Mg, Na, and K. Values corresponding to 90% relative root length (RRL) of soybean were 0.05 for the Ca activity ratio and 11% for Ca saturation. Calcium activity and Ca concentration in the soil solution and exchangeable Ca were less useful for this purpose.

Soil Al saturation was not a good predictor of Al toxicity, but soil solution measurements were. The activities of  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$  gave the best associations with RRL, and values corresponding to 90% RRL were  $4 \mu\text{M}$  and  $0.5 \mu\text{M}$  respectively. The results suggested that  $\text{Al}(\text{OH})_3^\circ$ ,  $\text{Al}(\text{OH})_2^+$ , and  $\text{AlSO}_4^+$ , were not toxic species.

Soil solution pH and soil pH measured in water were more sensitive indicators of root growth than soil pH measured in  $0.01 \text{ M CaCl}_2$ .

Using a Ca activity ratio of 0.05 and an  $\text{Al}^{3+}$  activity of  $4 \mu\text{M}$  as diagnostic indices, none of the 20 soils in two experiments were toxic in Al, while 13 (all subsoils) were deficient in Ca. Thus the first limitation on root growth was Ca deficiency and not Al toxicity, in spite of high Al saturations and relatively low pH in these soils. However, Al toxicity could be induced by increasing the ionic strengths of soil solutions.

### Introduction

The understanding of Al toxicity has been advanced by experiments in solution culture in which pH, Al, P, Ca, and ionic strength have been maintained at levels comparable to those of soil solutions. Blamey *et al.* (1983) were able to show that polymeric Al species were not toxic to soybean (*Glycine max*) root growth, but monomeric species, at a sum of activities greater than about  $5 \mu\text{M}$ , were extremely toxic. This finding was supported by Kim (1984), who showed the importance of the sum of activities of monomeric species in limiting growth of subterranean clover (*Trifolium subterraneum*) and in explaining apparent inconsistencies in published data of other workers. Alva *et al.* (1986a) also concluded that the sum of the activities of monomeric Al species was a better index of Al toxicity in nutrient solutions than either total Al concentration or monomeric Al concentration. Relative toxicities of monomeric Al species now need to be clarified. Pavan and Bingham (1982) suggested that  $\text{Al}^{3+}$  was the most toxic species. They measured total Al in solution, assumed that it was present as monomeric species, and used the GEOCHEM model (Sposito and Mattigod 1980) to calculate concentrations and activities of each monomeric species. However, the data of Blamey *et al.* (1983) and Alva *et al.* (1986b), who measured both total Al and monomeric Al in nutrient solutions, suggest that, particularly at P/Al molar ratios  $\geq 2.0$ , a considerable part of the soluble Al

would be present as polymeric species. Since the solutions of Pavan and Bingham (1982) had P/Al molar ratios  $>2$  ( $100 \mu\text{M}$  P and  $37 \mu\text{M}$  Al), their assumption that all Al was monomeric may not be valid, and some uncertainty must surround their conclusions. Recent solution culture experiments of Alva *et al.* (1986b, 1986c, 1987), have shown that sometimes the activity of  $\text{AlOH}^{2+}$ , and sometimes the activity of  $\text{Al}(\text{OH})_2^+$ , gave the best correlation with plant growth parameters. In none of their experiments did  $\text{Al}^{3+}$  activity give the best correlation.

The concepts developed in the relatively simple solution culture system must be extended to soil systems. Little published data are available on the monomeric species present in soil solutions and their importance in Al toxicity. In plant growth experiments where soil solution Al has been measured and activities calculated, it has been assumed that all soluble Al was  $\text{Al}^{3+}$  (Adams and Lund 1966; Adams *et al.* 1967; Brenes and Pearson 1973; Gonzalez-Erico *et al.* 1979; Edmeades *et al.* 1983) or that all soluble Al was monomeric Al (Richburg and Adams 1970; Pavan *et al.* 1982; Adams and Moore 1983). Adams and Hathcock (1984) attempted to measure monomeric Al (using a 15 s reaction with 8-hydroxyquinoline) before applying speciation and activity calculations. They were unable to relate activities of monomeric species (either separately or in combination) to results of their root growth experiments, and concluded that their analytical method was unable to discriminate between toxic (monomeric) and non-toxic (polymeric and organically complexed) Al in soil solution.

The objective of the work described in this paper was to use soil solution composition to bridge the gap between nutrient solution and soil cultures. Experiments were designed to quantify, in terms of a plant growth parameter, the effects of Al toxicity and Ca deficiency on plants grown in soil culture. This growth parameter could then be related to measurements of soil and soil solution Al and Ca to enable the best diagnostic indices and, in the case of Al, the ionic species responsible for toxicity to be identified. Early root elongation of soybean was chosen as the plant parameter. This is sensitive to Al toxicity (Sartain and Kamprath 1978; Blamey *et al.* 1983) and Ca deficiency (Haynes and Robbins 1948; Lund 1970; Ritchey *et al.* 1982), but except for B, is not affected by other cation or P deficiencies or by Mn toxicity, at least in the first few days after radicle emergence (Presley and Leonard 1948; Rios and Pearson 1964).

Three root growth experiments were conducted. Different soils were used in each experiment, and treatments varied slightly between experiments. Altogether, 21 soils were included.

## Materials and Methods

### Root Growth Procedure

Polystyrene containers (225 ml) were filled with air dry soil to within 1 cm of the top. The weight of any one soil was constant but varied between soils in the range 189–279 g. Required amounts of treatment compounds ( $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ) were applied as solids or in solution and mixed throughout the soil. Watering weights were determined on several additional cups of soil, as 90% of the water-holding capacity of a freely drained cup. Experimental cups were then brought to their wet weight, covered, and allowed to equilibrate for four days. During this period, additional water was added if required to replace any evaporative losses that occurred.

Soybean seeds (*Glycine max* cv. Forrest) were inoculated with a peat culture of *Bradyrhizobium japonicum* CB 1809 and germinated in trays containing a moist sand/peat mixture. Germinated seeds with radicles of uniform length (10–15 mm) were selected for planting in cups which had equilibrated for four days. Three germinated seeds were placed in holes made in the soil surface and covered with approximately 10 mm of moist soil. Cup weights were checked daily and water added if necessary. After three days, plants were usually ready for harvesting. This was done by removing the plug of soil from its cup, carefully separating the small plants, rinsing in deionized water, and placing in a vial of water (containing a drop of toluene) for subsequent root length measurement. The soil from all replicate cups of a treatment was bulked and placed in a plastic bag for laboratory extraction of soil solution.

### Soil Solution Extraction and Analysis

Soil solution was extracted from wet soil by a centrifuge method similar to that described by Gillman (1976) using extraction cups made from PVC. Soil was centrifuged at 2000 rpm (RCF about 900) for

45 min. Solution electrical conductivity (EC) and pH were measured immediately on a 5 ml aliquot, which was then retained for sulfate analysis. The remaining solution was filtered through a millipore filter (0.22  $\mu\text{m}$ ) and aliquots taken for Al, Na, K, Ca, and Mg analyses. The following procedures were used: Ca, Mg, Na, and K by inductively coupled plasma emission spectroscopy (ICP); monomeric Al by an 8-hydroxyquinoline method (Turner 1969; Bloom *et al.* 1978); and  $\text{SO}_4$  by an automated distillation procedure similar to that of Keay *et al.* (1972). The Ca activity ratio was calculated as the ratio of the activity of Ca to the sum of the activities of Ca, Mg, Na, and K.

#### Soil Analyses

Soils were air dried (40°C) and ground < 2 mm prior to analysis. Methods of analysis were as described by Bruce and Rayment (1982). Briefly, soil pH was measured in a 1:5 suspension in water and in 0.01 M  $\text{CaCl}_2$ ; EC and Cl were measured in the same extract used for pH in water; exchangeable basic cations were extracted with 1 M  $\text{NH}_4\text{Cl}$  adjusted to pH 7; and exchange acidity and exchangeable Al were extracted with 1 M KCl. Exchange acidity and exchangeable basic cations were summed for the effective cation exchange capacity (ECEC) which was used to calculate cation saturations.

#### Thermodynamic Calculations

Ionic strength ( $I$ ) was calculated from EC of soil solutions using the regression equation of Gillman and Bell (1978). Single-ion activity coefficients were calculated from the Davies equation (Lindsay 1979). An iterative procedure using the equilibrium constants given by Adams (1974) was used to calculate ion pairing with  $\text{SO}_4$  for Ca, Mg, Na, and K. Measured concentrations of these cations were then corrected for ion pairs.

Since measurements of monomeric Al concentration in soil solution were made, a monomeric species model was used in the speciation calculations for Al. The model used was:

$$[\text{Monomeric Al}] = [\text{Al}^{3+}] + [\text{AlOH}^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}(\text{OH})_3^0] + [\text{AlSO}_4^+].$$

The iterative procedure and equilibrium constants given by Lindsay (1979) were used to calculate activities and concentrations of Al species.

#### Experiment 1

Nine acid soils (four surface soils and five subsoils) from the Brisbane region were sampled for this experiment. For each soil, the experimental design included four replicates of the following six treatments arranged in a completely randomized design.

- A. Nil.
- B.  $\text{CaSO}_4$  calculated to increase Ca saturation to 20%.
- C.  $\text{MgCO}_3$  equivalent to  $1.5 \times$  exchangeable Al.
- D.  $\text{MgCO}_3$  equivalent to  $1.5 \times$  exchangeable Al +  $\text{CaSO}_4$  to increase Ca saturation to 20%.
- E.  $\text{MgCO}_3$  equivalent to  $1.5 \times$  exchangeable Al +  $\text{CaSO}_4$  to increase Ca saturation to 40%.
- F.  $\text{CaCO}_3$  equivalent to  $1.5 \times$  exchangeable Al.

Three soils (6, 7, and 8) had Ca initial saturations in excess of 20%, so treatment D was omitted, and treatment B then received the same rate of  $\text{CaSO}_4$  as treatment E.

#### Experiment 2

In this experiment, 11 acid subsoils from the Gympie-Cooroy district of south-east Queensland were selected. Treatments used in Experiment 1 were modified by omitting treatment E ( $\text{MgCO}_3 + \text{CaSO}_4$  to increase Ca saturation to 40%) and including a  $\text{CaCl}_2$  treatment. This  $\text{CaCl}_2$  treatment was introduced, as it would bring Al into solution, but, because it added no  $\text{SO}_4$ , it would be expected to produce lower  $\text{AlSO}_4^+$  and higher  $\text{Al}^{3+}$  concentrations. There were four replications of the following six treatments arranged in a completely randomized design.

- A. Nil.
- B.  $\text{CaSO}_4$  calculated to increase Ca saturation to 20%.
- C.  $\text{MgCO}_3$  equivalent to  $1.5 \times$  exchangeable Al.
- D.  $\text{MgCO}_3$  equivalent to  $1.5 \times$  exchangeable Al +  $\text{CaSO}_4$  as in treatment B.
- F.  $\text{CaCO}_3$  equivalent to  $1.5 \times$  exchangeable Al.
- G.  $\text{CaCl}_2$  calculated to increase Ca saturation to 20%.

#### Experiment 3

Results from Experiment 2 showed marked differences in root response to  $\text{CaCl}_2$  and  $\text{CaSO}_4$  additions.

Table 1. Analytical data and clay mineralogy for untreated soils used in Experiments 1 (soils 1 to 9), 2 (soils 10 to 20), and 3 (soil 21)

Soil No.	Great Soil Group <sup>B</sup>	pH H <sub>2</sub> O	EC (mS cm <sup>-1</sup> )	ECEC	Ca	Exchangeable cation				Exchange acidity (cmol (p <sup>+</sup> ) kg <sup>-1</sup> )	Saturation		Clay (%)	Mn <sup>C</sup> (mg kg <sup>-1</sup> )	Clay mineralogy <sup>D</sup>	
						Mg	Na	K	Al		Al	Ca			Major	Minor
<i>Experiment 1</i>																
1	YP	5.46	0.012	2.55	0.32	0.91	0.09	0.05	1.08	1.18	42.4	12.6	12	4	K,M	Q,F
2 <sup>A</sup>	YP	5.04	0.035	2.28	0.44	0.71	0.14	0.09	0.72	0.90	31.6	19.3	8	12	K,V	Q,F
3	YP	5.47	0.012	1.41	0.10	0.50	0.11	0.06	0.54	0.64	33.5	6.2	8	3	K,V,Q	F
4	GP	5.57	0.029	3.53	0.24	1.82	0.29	0.02	0.93	1.16	25.2	6.5	19	1	K,V	Q,F
5	YP	5.46	0.030	6.69	0.08	4.30	0.31	0.03	1.70	1.97	25.4	1.2	63	<1	K	Q,F
6 <sup>A</sup>	YP	5.38	0.017	1.93	0.74	0.70	0.06	0.07	0.27	0.36	14.0	38.3	8	5	Q,K	F
7 <sup>A</sup>	YP	5.63	0.027	2.36	0.75	0.81	0.07	0.13	0.50	0.60	21.2	31.8	13	13	Q,K	F,V
8	SH	4.82	0.030	17.2	0.17	2.19	0.22	0.23	12.7	14.4	73.6	1.0	41	<1	K,M	Q,F
9 <sup>A</sup>	YP	5.53	0.034	2.13	0.62	0.91	0.07	0.07	0.39	0.46	18.3	29.1	13	5	K,Q	F
<i>Experiment 2</i>																
10	YP	4.76	0.069	12.4	0.11	0.90	0.20	0.11	10.5	11.1	84.6	0.9	51	<1	K,V	Q,F
11	RP	4.63	0.046	8.48	0.20	0.45	0.15	0.08	7.20	7.60	84.9	2.4	64	<1	K	V,I,Q,F
12	NKB	4.87	0.066	11.7	0.12	1.54	0.38	0.10	8.89	9.51	76.3	1.0	62	<1	I,K,M	F
13	YP	4.59	0.056	6.12	0.48	0.28	0.08	0.04	4.98	5.24	81.4	7.8	59	<1	K,I	M/V,F,He
14	RP	4.78	0.099	7.55	0.34	1.27	0.54	0.07	4.74	5.33	62.8	4.5	77	<1	K,I	He
15	SH	5.10	0.089	7.10	0.89	1.26	0.55	0.11	3.84	4.29	54.1	12.5	45	3	I	K,F,He
16	YP	5.51	0.018	3.51	0.31	1.37	0.08	0.006	1.54	1.69	43.9	8.8	35	2	K,V	I,Q,F,He
17	YP	4.77	0.078	7.93	0.22	1.26	0.26	0.11	5.94	6.08	74.9	2.8	59	<1	K,I,M	F
18	GP	5.45	0.022	3.75	0.12	0.83	0.09	0.03	2.52	2.68	67.2	3.2	23	1	K,M/V	Q,F,He/Go
19	NKB	5.10	0.063	7.67	0.32	3.29	0.37	0.17	3.30	3.52	43.0	4.2	61	1	I,H/K	F,M/V He/Go
20	YP	5.30	0.019	3.63	0.11	1.66	0.15	0.06	1.60	1.65	44.1	3.0	24	<1	K,V	Q,F,Go,Gi
<i>Experiment 3</i>																
21	RP	4.50	0.049	8.85	0.14	0.47	0.16	0.09	7.94	7.99	89.7	1.6	64	<1	K	V,I,Q,F

<sup>A</sup>Surface soils.<sup>B</sup>Stace *et al.* (1968). YP, yellow podzolic; GP, gleyed podzolic; SH, soloth; RP, red podzolic; NKB, non-calcic brown.<sup>C</sup>DTPA-extractable Mn.<sup>D</sup>K, kaolinite; M, smectite; Q, quartz; F, feldspar; V, vermiculite; I, illite; He, hematite; Go, goethite; Gi, gibbsite; M/V, random interstratified material; H/K, halloysite/kaolinite.

In Experiment 3, different rates of these salts (Fig. 1) were used on one acid subsoil to provide a range of soluble Al concentrations and different combinations of  $\text{Al}^{3+}$  and  $\text{AlSO}_4^+$  species in soil solution. The following treatments were used:

- A. Nil.
- H.  $\text{CaCl}_2$  calculated to increase Ca saturation to 7.5%.
- I.  $\text{CaCl}_2$  calculated to increase Ca saturation to 10%.
- J.  $\text{CaCl}_2$  calculated to increase Ca saturation to 15%.
- G.  $\text{CaCl}_2$  calculated to increase Ca saturation to 20%.
- K.  $\text{CaSO}_4$  calculated to increase Ca saturation to 7.5%.
- L.  $\text{CaSO}_4$  calculated to increase Ca saturation to 10%.
- M.  $\text{CaSO}_4$  calculated to increase Ca saturation to 15%.
- B.  $\text{CaSO}_4$  calculated to increase Ca saturation to 20%.
- F.  $\text{CaCO}_3$  equivalent to  $1.5 \times$  exchangeable Al.

To preserve a factorial structure (2 sources of Ca  $\times$  5 rates  $\times$  4 replications), the nil treatment was applied to 8 cups (Li 1964), of which four were randomly designated nil  $\text{CaCl}_2$  treatments and four nil  $\text{CaSO}_4$  treatments. Other treatments were replicated four times.

## Results

### Soil Analyses

Analytical data and Great Soil Groups (Stace *et al.* 1968) for the 21 soils used in Experiments 1, 2, and 3 are given in Table 1. These soils (mostly subsoils) were acid (pH  $\text{H}_2\text{O}$ ) 4.6–5.6), generally low in Ca (Ca saturations 1–38%), and high in Al (Al saturations 14–85%). Kaolinite was commonly the major clay mineral present.

**Table 2. The effect of treatments on properties of soils sampled after harvest**

Values were meaned over soils for Experiments 1 and 2, but represent individual treatments for Experiment 3

Treatment	pH		Cl (mg $\text{kg}^{-1}$ )	ECEC	Exchangeable cations					Exchange acidity ( $\text{cmol (p+) kg}^{-1}$ )	Saturation	
	$\text{H}_2\text{O}^A$	$\text{CaCl}_2$			Ca	Mg	Na	K	Al		Al	Ca
					(cmol (p+) $\text{kg}^{-1}$ )						(%)	
<i>Experiment 1</i>												
A. Nil	5.4	4.32	16	4.45	0.38	1.43	0.15	0.08	2.09	2.41	31.7	16.2
B. $\text{CaSO}_4$	5.0	4.32	14	5.03	0.99	1.41	0.15	0.08	2.07	2.35	28.3	24.0
C. $\text{MgCO}_3$	6.0	4.89	14	5.17	0.37	4.30	0.16	0.09	0.17	0.23	5.9	14.8
D. $\text{MgCO}_3 + \text{CaSO}_4$	5.7	4.99	17	7.14	1.07	5.58	0.18	0.08	0.14	0.19	3.5	16.7
E. $\text{MgCO}_3 + \text{CaSO}_4$	5.6	4.92	14	6.21	1.64	4.10	0.15	0.08	0.16	0.20	5.1	28.8
F. $\text{CaCO}_3$	6.2	5.13	16	5.24	3.52	1.31	0.15	0.08	0.13	0.16	4.5	55.1
<i>Experiment 2</i>												
A. Nil	5.0	3.99	29	7.26	0.29	1.28	0.26	0.09	5.00	5.34	65.2	4.6
B. $\text{CaSO}_4$	4.6	4.01	35	8.01	1.17	1.26	0.25	0.09	4.97	5.23	58.8	15.1
C. $\text{MgCO}_3$	5.8	5.10	28	7.56	0.26	6.70	0.24	0.08	0.24	0.29	3.3	3.9
D. $\text{MgCO}_3 + \text{CaSO}_4$	5.5	5.10	30	8.44	1.18	5.60	0.24	0.08	0.32	0.37	3.9	13.9
F. $\text{CaCO}_3$	6.2	5.64	31	8.53	6.83	1.31	0.25	0.09	0.04	0.06	0.6	76.1
G. $\text{CaCl}_2$	4.4	3.98	313	8.06	1.24	1.26	0.24	0.08	4.94	5.24	58.4	15.5
<i>Experiment 3</i>												
A. Nil	4.5	3.83	30	8.97	0.70	0.47	0.16	0.09	7.99	8.08	89.1	1.9
H. $\text{CaCl}_2$ 7.5%	4.3	3.83	100	9.12	0.36	0.48	0.16	0.10	7.85	8.02	86.1	4.0
I. $\text{CaCl}_2$ 10%	4.1	3.82	170	9.25	0.55	0.46	0.15	0.10	7.95	7.99	86.0	6.0
J. $\text{CaCl}_2$ 15%	4.0	3.81	280	9.55	0.94	0.45	0.15	0.09	7.74	7.92	81.1	9.8
G. $\text{CaCl}_2$ 20%	4.0	3.81	380	9.89	1.32	0.46	0.16	0.10	7.82	7.85	79.1	13.4
K. $\text{CaSO}_4$ 7.5%	4.4	3.81	30	9.27	0.48	0.46	0.20	0.10	8.00	8.03	86.3	5.2
L. $\text{CaSO}_4$ 10%	4.4	3.82	30	9.27	0.50	0.48	0.18	0.10	8.01	8.01	86.4	5.4
M. $\text{CaSO}_4$ 15%	4.3	3.82	30	9.71	0.96	0.47	0.17	0.09	7.95	8.02	81.9	9.9
B. $\text{CaSO}_4$ 20%	4.2	3.82	30	9.88	1.37	0.47	0.15	0.11	7.66	7.78	77.5	13.9
F. $\text{CaCO}_3$	5.7	5.20	30	10.1	9.28	0.34	0.16	0.12	0.15	0.16	1.5	92.3

<sup>A</sup>As pH ( $\text{H}_2\text{O}$ ) was measured to only one decimal place in some treatments, results for all treatments are reported to one decimal place.

The effects of treatments on soil attributes were consistent across soils, even though the magnitude of the changes depended upon the initial soil properties and the amount of treatment compound applied. Mean data for each experiment illustrate these treatment effects (Table 2). Relative to the nil treatment,  $\text{CaCO}_3$  increased pH and exchangeable Ca and reduced exchangeable Al;  $\text{MgCO}_3$  increased pH and exchangeable Mg and reduced exchangeable Al;  $\text{CaSO}_4$  and  $\text{CaCl}_2$  both decreased pH ( $\text{H}_2\text{O}$ ) and increased exchangeable Ca; the  $\text{MgCO}_3 + \text{CaSO}_4$  treatments increased pH, exchangeable Ca, and Mg, and reduced exchangeable Al. The  $\text{CaSO}_4$  and  $\text{CaCl}_2$  treatments showed that increased electrolyte concentration in soil reduced soil pH measured in 1:5 suspension in water. Soil pH values measured in 0.01 M  $\text{CaCl}_2$  did not show the same decrease because the ionic strength of these suspensions was dominated by 0.01 M  $\text{CaCl}_2$  solution and not by the treatments. In Experiment 3, at similar additions of Ca,  $\text{CaCl}_2$  and  $\text{CaSO}_4$  increased exchangeable Ca by similar amounts, but  $\text{CaCl}_2$  decreased  $\text{pH}(\text{H}_2\text{O})$  more than  $\text{CaSO}_4$ .

**Table 3. The effect of treatments on soil solution properties as shown by mean values over soils for Experiment 1 (9 soils) and Experiment 2 (11 soils) and Experiment 3 (1 soil)**

Cation and sulfate values are concentrations

Treatment	pH	EC ( $\text{mS cm}^{-1}$ )	Al	Ca	Mg ( $\mu\text{M}$ )	Na	K	$\text{SO}_4$	Ca activity ratio
<i>Experiment 1</i>									
A. Nil	5.38	0.204	6.3	61	158	916	104	244	0.044
B. $\text{CaSO}_4$	4.77	0.981	700	1822	2209	2189	287	5831	0.148
B. $\text{CaSO}_4^{\text{A}}$	4.91	0.685	12	724	1372	1919	270	2801	0.128
C. $\text{MgCO}_3$	6.22	0.274	5.0	67	500	900	106	416	0.040
D. $\text{MgCO}_3 + \text{CaSO}_4$	5.73	1.50	2.7	1189	6318	1907	228	8037	0.092
E. $\text{MgCO}_3 + \text{CaSO}_4$	5.49	2.03	3.8	4265	15950	3004	195	19200	0.145
F. $\text{CaCO}_3$	6.46	0.284	3.3	397	205	937	110	375	0.172
<i>Experiment 2</i>									
A. Nil	4.78	0.276	4.9	64	250	1660	54	406	0.029
B. $\text{CaSO}_4$	4.17	1.10	428	1971	1991	3264	175	5628	0.170
B. $\text{CaSO}_4^{\text{B}}$	3.91	1.59	907	3433	2543	4299	155	9060	0.229
B. $\text{CaSO}_4^{\text{C}}$	4.38	0.693	29	753	1531	2401	192	2767	0.120
C. $\text{MgCO}_3$	5.68	0.562	1.0	93	1833	1482	64	1700	0.023
D. $\text{MgCO}_3 + \text{CaSO}_4$	5.31	1.64	4.6	1427	8809	2129	231	10312	0.082
F. $\text{CaCO}_3$	6.43	0.708	0.6	2061	477	1655	46	2417	0.405
G. $\text{CaCl}_2$	3.88	2.58	881	4048	4368	3990	273	188	0.258
G. $\text{CaCl}_2^{\ddagger}$	3.70	3.53	1758	6477	4632	5060	240	219	0.331
G. $\text{CaCl}_2^{\ddagger}$	4.03	1.80	150	2023	4149	3098	301	163	0.197
<i>Experiment 3</i>									
A. Nil	4.31	0.188	6.7	25	60	1064	27	115	0.018
B. $\text{CaSO}_4$ 20%	3.95	0.738	285	1462	534	2007	107	2723	0.271
F. $\text{CaCO}_3$	6.64	0.726	0.1	2969	138	750	38	2531	0.683
G. $\text{CaCl}_2$ 20%	3.61	2.44	1523	4962	1872	2827	220	96	0.420
H. $\text{CaCl}_2$ 7.5%	3.87	0.493	100	278	406	1855	65	60	0.088
I. $\text{CaCl}_2$ 10%	3.72	0.823	300	804	758	2218	95	88	0.170
J. $\text{CaCl}_2$ 15%	3.64	1.70	937	2897	1478	2721	50	87	0.336
K. $\text{CaSO}_4$ 7.5%	4.25	0.220	9.2	76	79	1143	29	202	0.048
L. $\text{CaSO}_4$ 10%	4.14	0.269	20	131	130	1306	34	277	0.068
M. $\text{CaSO}_4$ 15%	4.09	0.466	90	606	283	1642	30	1109	0.188

<sup>A</sup>Mean values for eight soils after omitting soil 8 which had  $\Sigma$  activities of Al monomers of 4149  $\mu\text{M}$ .

<sup>B</sup>Mean values for five soils with high Al concentration (240–2065  $\mu\text{M}$ ) in their  $\text{CaSO}_4$  treatment (10, 11, 12, 15, and 17).

<sup>C</sup>Mean values for six soils with low Al concentration (3.7–41  $\mu\text{M}$ ) in their  $\text{CaSO}_4$  treatment (13, 14, 16, 18, 19, and 20).

### Soil Solution Composition

Treatments had marked effects on soil solution compositions, and these are shown in Table 3 as mean values across soils. The  $\text{CaSO}_4$  treatment for soil 8 (Experiment 1), and the  $\text{CaSO}_4$  and  $\text{CaCl}_2$  treatments for soils 13, 14, 16, 18, 19, and 20 (Experiment 2) produced higher Al concentrations in soil solution than corresponding treatments in other soils. Accordingly, mean values for treatments within experiments are shown in Table 3 for all soils and for the high and low Al groups separately. However, the pattern of treatment effects was generally similar for all soils. In comparison with the nil treatment,  $\text{CaSO}_4$  decreased pH, increased EC, and increased concentrations of Al, Ca, Mg, Na, K, and  $\text{SO}_4$ ;  $\text{MgCO}_3$  decreased Al concentration and increased pH, EC, and concentrations of Mg and  $\text{SO}_4$ ; the ( $\text{MgCO}_3 + \text{CaSO}_4$ ) treatments decreased Al concentration and increased pH, EC and the concentrations of all other attributes;  $\text{CaCl}_2$  decreased pH and  $\text{SO}_4$ , increased EC, and increased concentrations of Al, Ca, Mg, Na, and K. The Ca activity ratio was reduced slightly by  $\text{MgCO}_3$  and increased by all other treatments.

In Experiment 3, the magnitude of the changes brought about by  $\text{CaSO}_4$  and  $\text{CaCl}_2$  increased progressively with increasing rates, but effects of  $\text{CaCl}_2$  were greater than those of  $\text{CaSO}_4$  at equivalent additions of Ca.

The relative amounts (percentages) of each species comprising the  $\Sigma$  activities of Al monomers varied with treatment. Mean values for Experiments 1 and 2 (Table 4) showed that predominant species were  $\text{Al}(\text{OH})_2^+$  in nil treatments,  $\text{Al}(\text{OH})_3^\circ$  in  $\text{CaCO}_3$  treatments,  $\text{AlSO}_4^+$  in  $\text{CaSO}_4$  treatments and  $\text{Al}^{3+}$  in  $\text{CaCl}_2$  treatments. As a group, soils of Experiment 2 were more acid than those of Experiment 1, so the proportions of  $\text{Al}^{3+}$  in nil and  $\text{CaSO}_4$  treatments were higher than those for corresponding treatments of Experiment 1. The preponderance of  $\text{Al}^{3+}$  in  $\text{CaCl}_2$  treatments and  $\text{AlSO}_4^+$  in  $\text{CaSO}_4$  treatments, together with higher ionic strengths (as indicated by EC values) in  $\text{CaCl}_2$  treatments, led to differences between these treatments in the conversion of Al concentrations to  $\Sigma$  activities of monomeric Al species. Concentrations of Al were higher in  $\text{CaCl}_2$  treatments (Table 3), but  $\Sigma$  activities of monomeric Al species were higher in  $\text{CaSO}_4$  treatments (Table 4). This is because activity coefficients for trivalent ions ( $\text{Al}^{3+}$ ) are much smaller than those for monovalent ions ( $\text{AlSO}_4^+$ ), and because all activity coefficients are smaller at higher ionic strengths.

**Table 4. Effects of treatments on the sum of the activities of monomeric Al species and the relative amounts (percentages) of each species in soil solutions**

Treatment	Values are meaned across soils for Experiment 1 (9 soils) and Experiment 2 (11 soils)					
	$\text{Al}^{3+}$	$\text{AlOH}^{2+}$	$\text{Al}(\text{OH})_2^+$	$\text{Al}(\text{OH})_3^\circ$	$\text{AlSO}_4^+$	$\Sigma$ activities Al monomers ( $\mu\text{M}$ )
	Experiment 1					
A. Nil	7.5	6.1	51	33	2.0	5.6
B. $\text{CaSO}_4$	11	6.7	34	8.9	39	469
B. $\text{CaSO}_4^A$	12	7.5	38	10	33	9
F. $\text{CaCO}_3$	0.5	1.0	22	76	0.2	3.2
	Experiment 2					
A. Nil	30	12	37	8.9	12	3.5
B. $\text{CaSO}_4$	24	4.4	5.5	0.3	66	294
B. $\text{CaSO}_4^B$	16	1.4	0.7	<0.1	81	622
B. $\text{CaSO}_4^C$	31	6.9	9.5	0.6	52	20
F. $\text{CaCO}_3$	0.4	0.9	21	77	0.7	0.5
G. $\text{CaCl}_2$	82	6.4	3.4	0.1	7.7	187
G. $\text{CaCl}_2^C$	87	4.2	1.2	<0.1	7.8	349
G. $\text{CaCl}_2^B$	79	8.2	5.2	0.1	7.6	52

<sup>A</sup>Mean values for eight soils after omitting soil 8 which had  $\Sigma$  activities of Al monomers of 4149  $\mu\text{M}$ .

<sup>B</sup>Mean values for five soils with high Al concentration in their  $\text{CaSO}_4$  treatment (10, 11, 12, 15, and 17).

<sup>C</sup>Mean values for six soils with low Al concentration in their  $\text{CaSO}_4$  treatment (13, 14, 16, 18, 19, 20).

The effect of  $\text{CaSO}_4$  and  $\text{CaCl}_2$  on the proportions of Al monomers in Experiment 3 is illustrated in Fig. 1. The proportion of  $\text{AlSO}_4^+$  increased markedly with increasing additions of  $\text{CaSO}_4$ , initially by reducing the proportions of Al hydroxide species and then by reducing the proportion of  $\text{Al}^{3+}$ . With increasing  $\text{CaCl}_2$  rates, the proportion of  $\text{Al}^{3+}$  increased at the expense of all other Al species.

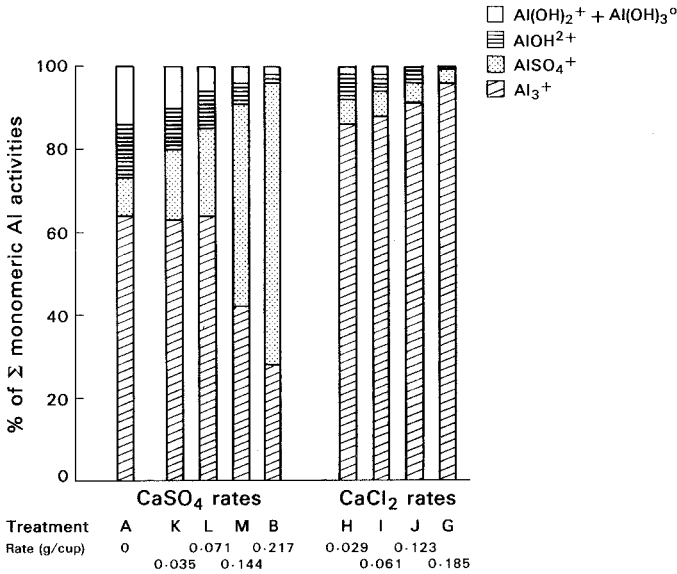


Fig. 1. The effects of rates of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  on the relative amounts (%) of each monomeric Al species in soil solutions of Experiment 3.

### Root Growth

For each soil, the root length of each treatment (means of 12 plants) was expressed as a percentage of the longest root length, which was usually that of the  $\text{CaCO}_3$  treatment, and this is referred to as the relative root length (RRL).

### Experiment 1

In five soils (1, 2, 6, 7 and 9), the nil treatment was not significantly different from the  $\text{CaCO}_3$  treatment (Table 5), indicating neither Ca deficiency nor Al toxicity in unamended soils. The other treatments resulted in reduced RRL in soil 1, but not in the other four soils. The  $(\text{MgCO}_3 + \text{CaSO}_4)$  treatments gave RRL which were not significantly different from those in the  $\text{CaCO}_3$  treatment, except in soil 1.

All four soils with significantly lower RRL in the nil treatment (3, 4, 5, and 8) also had lower RRL in the  $\text{MgCO}_3$  treatment. In three of these soils (3, 4, and 5),  $\text{CaSO}_4$  gave close to maximum RRL, indicating a simple Ca deficiency which was exacerbated by  $\text{MgCO}_3$  but corrected by  $\text{CaSO}_4$ . Because  $\text{MgCO}_3$  and  $\text{CaSO}_4$  treatments both reduced RRL in soil 8, one cannot generalize as to the root growth limitations in this soil solely on the basis of treatment effects. Added  $\text{MgCO}_3$  may have induced Ca deficiency in an Al-toxic nil treatment, or  $\text{CaSO}_4$  may have induced Al toxicity in a Ca-deficient nil treatment. Alternatively, both treatments may have exacerbated conditions in the nil treatment which was already both Al-toxic and Ca-deficient. Whatever the limitations to root growth in soil 8, they were overcome by both  $\text{CaCO}_3$  and  $(\text{MgCO}_3 + \text{CaSO}_4)$  treatments.

### Experiment 2

Only in soil 13 were RRL of nil and  $\text{CaCO}_3$  treatments not significantly different (Table



5); other treatments in this soil resulted in lower RRL. The  $\text{MgCO}_3$  treatment had lower RRL than the  $\text{CaCO}_3$  treatment in all soils except 16, while RRL in the  $\text{CaSO}_4$  treatment was less

**Table 5. Relative root lengths and maximum root lengths of soybean (cv. Forrest) grown for three days in 20 acid soils amended with liming materials and calcium salts (treatments A to G) in Experiments 1 and 2**

Soil No.	Relative root length							Maximum root length (cm)
	A Nil	B $\text{CaSO}_4$	C $\text{MgCO}_3$	D $\text{MgCO}_3$ + $\text{CaSO}_4$	E $\text{MgCO}_3$ + $\text{CaSO}_4$	F $\text{CaCO}_3$	G $\text{CaCl}_2$	
<i>Experiment 1</i>								
1	91.5	85.9 <sup>A</sup>	75.2 <sup>A</sup>	81.3 <sup>A</sup>	86.3 <sup>A</sup>	100		7.75
2	99.2	90.2	92.9	93.1	93.3	100		3.78
3	63.5 <sup>A</sup>	91.9	48.6 <sup>A</sup>	86.9	93.2	100		4.69
4	61.0 <sup>A</sup>	87.2	69.8 <sup>A</sup>	98.0	100	95.4		7.11
5	33.6 <sup>A</sup>	90.1	21.0 <sup>A</sup>	88.9	96.1	100		6.39
6	91.2	95.5	98.6		100	97.4		7.73
7	93.8	91.2	100		97.9	97.5		6.28
8	31.1 <sup>A</sup>	17.0 <sup>A</sup>	17.6 <sup>A</sup>	86.8	100	94.0		5.69
9	93.5	84.8	87.3		87.6	100		9.27
<i>Experiment 2</i>								
10	40.0 <sup>A</sup>	35.8 <sup>A</sup>	16.4 <sup>A</sup>	98.8		100	17.8 <sup>A</sup>	7.06
11	54.9 <sup>A</sup>	41.7 <sup>A</sup>	17.3 <sup>A</sup>	94.7		100	22.2 <sup>A</sup>	6.84
12	48.3 <sup>A</sup>	40.9 <sup>A</sup>	21.0 <sup>A</sup>	98.8		100	30.4 <sup>A</sup>	6.85
13	88.5	79.2 <sup>A</sup>	61.0 <sup>A</sup>	90.3		100	48.4 <sup>A</sup>	6.20
14	64.0 <sup>A</sup>	70.8 <sup>A</sup>	65.0 <sup>A</sup>	88.3		100	59.8 <sup>A</sup>	7.05
15	56.6 <sup>A</sup>	58.0 <sup>A</sup>	56.6 <sup>A</sup>	88.2		100	53.2 <sup>A</sup>	7.60
16	81.6 <sup>A</sup>	82.2 <sup>A</sup>	83.0	100		100	67.3 <sup>A</sup>	9.80
17	66.4 <sup>A</sup>	66.3 <sup>A</sup>	45.7 <sup>A</sup>	92.6		100	47.5 <sup>A</sup>	7.92
18	61.8 <sup>A</sup>	81.0 <sup>A</sup>	52.0 <sup>A</sup>	41.5 <sup>A</sup>		100	64.5 <sup>A</sup>	9.21
19	72.3 <sup>A</sup>	85.1 <sup>A</sup>	34.7 <sup>A</sup>	97.1		100	79.6 <sup>A</sup>	7.50
20	21.3 <sup>A</sup>	76.6 <sup>A</sup>	12.6 <sup>A</sup>	95.2		100	71.1 <sup>A</sup>	9.88

<sup>A</sup>For a given soil, treatment root length was significantly different ( $P < 0.05$ ) from maximum root length.

than that in the  $\text{CaCO}_3$  treatment in all 11 soils. The  $\text{CaSO}_4$  treatment increased RRL over that of the nil treatment in soils 18 and 20, but unlike some soils in Experiment 1, maximum root lengths were not achieved. The  $\text{CaCl}_2$  treatment had lower RRL than the  $\text{CaCO}_3$  treatment in every soil and consistently lower RRL than the corresponding  $\text{CaSO}_4$  treatment. This difference between  $\text{CaCl}_2$  and  $\text{CaSO}_4$  treatments is consistent with the greater ability of  $\text{CaCl}_2$  to decrease pH and increase Al concentration in soil solution (Table 3). For the ( $\text{MgCO}_3$  +  $\text{CaSO}_4$ ) treatment, RRL was not significantly different from that of the  $\text{CaCO}_3$  treatment, except for soil 18 where RRL was similar to that of the  $\text{MgCO}_3$  treatment. Analytical data (not presented) suggest that  $\text{CaSO}_4$  was accidentally omitted from the combined treatment for this soil.

Consideration of the treatment effects on RRL allows only the conclusion that soil 13 is neither Ca-deficient nor Al-toxic. For the remaining 10 soils the situation is similar to that of soil 8 in Experiment 1. When soluble Ca ( $\text{CaSO}_4$  or  $\text{CaCl}_2$ ) and  $\text{MgCO}_3$  treatments both fail to give the same RRL as  $\text{CaCO}_3$ , growth limitations in the unamended soils cannot be identified from root growth in the amended soils. The use of soil solution compositions for this purpose is discussed later.

### Experiment 3

Root growth in the  $\text{CaCO}_3$  treatment (7.3 cm) was much greater than that in the nil treatment

(4.5 cm) or any other treatment (range 2.1–4.9 cm). Root lengths for treatments involving rates of  $\text{CaCl}_2$  and  $\text{CaSO}_4$  are given in Table 6. There was no interaction between rates and sources of Ca, so the main effects can be considered. Root lengths were lower with  $\text{CaCl}_2$

**Table 6. Root lengths (cm) of soybean cv. Forrest grown for 3 days in soil 21 with five rates of Ca as both  $\text{CaCl}_2$  and  $\text{CaSO}_4$  (Experiment 3)**

Source of Ca	Rate <sup>A</sup> :					Mean <sup>B</sup>
	0	1	2	3	4	
$\text{CaCl}_2$		3.86	2.96	2.16	2.10	2.75
$\text{CaSO}_4$		4.93	4.93	4.05	3.44	4.34
Mean <sup>C</sup>	4.49	4.39	3.94	3.10	2.72	

<sup>A</sup>Rate 0 indicates the nil treatment while rates 1 to 4 indicate Ca added to increase Ca saturation of the ECCEC to 7.5, 10, 15, and 20% respectively.

<sup>B</sup>For source means, l.s.d. is 0.45 ( $P < 0.05$ ).

<sup>C</sup>For rate means, l.s.d. is 0.72 ( $P < 0.05$ ).

(2.7 cm) than with  $\text{CaSO}_4$  (4.3 cm), a result which is consistent with that of Experiment 2. As Ca rate increased, root length decreased, but only the two highest rates were significantly less than the nil treatment. At the lower rates, the opposing effects of alleviating Ca deficiency (if present) and inducing or exacerbating Al toxicity would have been operative, and root growth would have depended upon which factor imposed the greater limitation. At higher rates, Ca would have been sufficient, but Al would have been toxic.

#### *Association of Root Growth with Soil and Soil Solution Properties*

The combined data from Experiments 1, 2, and 3 were used to compare soil and soil solution properties as predictors of Ca deficiency and Al toxicity and to derive diagnostic indices. For Ca, the treatments used were  $\text{MgCO}_3$  (often Ca deficient),  $\text{CaCO}_3$  and  $\text{MgCO}_3 + \text{CaSO}_4$  (both Ca sufficient). All of these treatments were free from Al toxicity. For Al effects,  $\text{CaSO}_4$  and  $\text{CaCl}_2$  treatments (often Al toxic) and  $\text{CaCO}_3$  (not Al toxic) were used. These treatments were free from Ca deficiency.

#### *Calcium*

Three soil solution and two soil attributes were related to soybean RRL. The linear response-and-plateau (LRP) model (Vaughn *et al.* 1973) generally fitted the data better than the Mitscherlich (Snedecor and Cochran 1980), or Cate–Nelson models (Cate and Nelson 1971). Coefficients of determination ( $R^2$ ) for the LRP model, and diagnostic indices, which were taken as the value corresponding to 90% RRL, are given in Table 7.

**Table 7. Coefficients of determination ( $n = 64$ ) for linear response-and-plateau model fitted to describe the relationships between relative root lengths of soybean and soil and soil solution attributes**

Attribute	$R^2$	Diagnostic index <sup>A,B</sup>	Attribute	$R^2$	Diagnostic index <sup>A,B</sup>
Soil			Soil solution		
Exchangeable Ca	0.793	0.45	Ca activity ratio	0.835	0.047
Ca saturation	0.891	11	Ca concentration	0.527	165
			Ca activity	0.607	93

<sup>A</sup>Value corresponding to a relative root length of 90% in the LRP model.

<sup>B</sup>Units: exchangeable Ca,  $\text{cmol}(\text{p}^+) \text{kg}^{-1}$ ; Ca saturation, %; Ca concentration,  $\mu\text{M}$ ; Ca activity,  $\mu\text{M}$ .

The association of Ca activity in soil solution with RRL was better than that of Ca concentration, but neither had high  $R^2$  values. This was due to a wide range of RRL occurring at  $<100 \mu\text{M}$  Ca activity, and at  $<120 \mu\text{M}$  Ca concentration. Responses were rare above these

values. Of the soil solution attributes, Ca activity ratio had the highest  $R^2$  values. Another soil solution attribute which related well to RRL was the Ca activity equivalent ratio ( $R^2 = 0.861$ , data not presented) obtained using the product of ion activity and valence.

Calcium saturation had the higher  $R^2$  of the two soil attributes and is preferred to exchangeable Ca for diagnostic use. The  $R^2$  value for Ca saturation was also higher than that for any of the soil solution attributes.

On the basis of these experiments, either Ca activity ratio of soil solution or Ca saturation of soil is a useful index of Ca deficiency (Fig. 2). Values selected for use in separating Ca-deficient soils from those which are adequately supplied with Ca were 0.05 and 11% respectively.

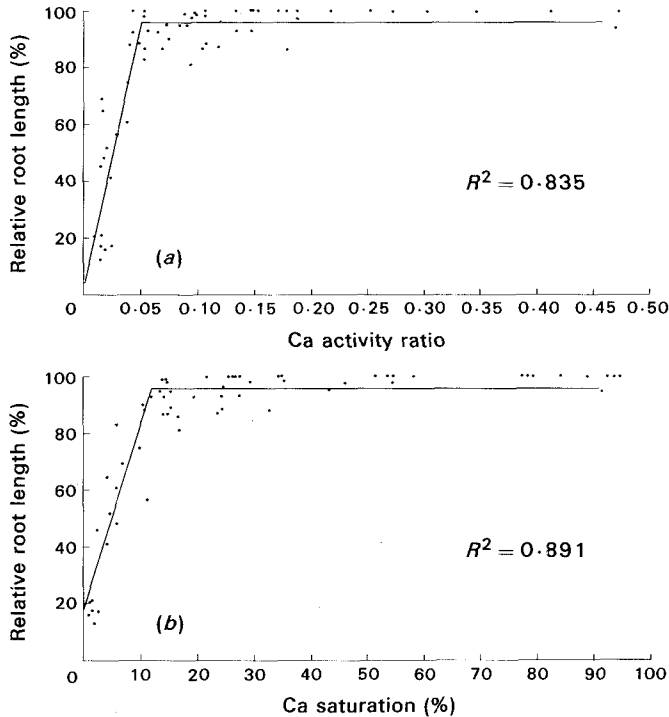


Fig. 2. Data points and linear response-and-plateau models for regression of relative root lengths of soybean on (a) Ca activity ratio, and (b) Ca saturation.

### Aluminium

Mitscherlich equations were fitted to the regressions of RRL on soil solution Al attributes. Coefficients of determination are given in Table 8 for combined data of Experiments 1, 2, and 3, while some of the relationships are plotted in Fig. 3. Regressions were not significant for  $\text{Al}(\text{OH})_3^\circ$ , and  $R^2$  values for  $\text{Al}(\text{OH})_2^+$  were very low. To simplify the graphs in Fig. 3, the cluster of values at 100% RRL from the  $\text{CaCO}_3$  treatments have been omitted, despite their inclusion in regression calculations.

For  $\text{CaCl}_2$  treatments alone, conversion of Al concentrations to  $\Sigma$  activities gave the main improvement in  $R^2$  values (0.949–0.977). Since  $\text{Al}^{3+}$  was the dominant Al species in these soil solutions, there was little increase in  $R^2$  on the omission of  $\text{AlSO}_4^+$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_3^\circ$  from  $\Sigma$  activities (0.977–0.981). The highest  $R^2$  value for a single Al species was 0.980 for  $\text{Al}^{3+}$  activity.

For  $\text{CaSO}_4$  treatments alone, Al concentrations and  $\Sigma$  activities gave similar  $R^2$  values, but there was an increase in  $R^2$  from the omission of  $\text{AlSO}_4^+$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_3^\circ$  from  $\Sigma$  activities (0.824–0.889). The highest  $R^2$  value for a single Al species was 0.915 for  $\text{AlOH}^{2+}$ .

For the combined data, there were successive increases in  $R^2$  when going from concentration to  $\Sigma$  activity and then to  $(\text{Al}^{3+} + \text{AlOH}^{2+})$  (0.861 to 0.881 to 0.914). Individually,  $\text{Al}^{3+}$  and

**Table 8. Coefficients of determination ( $n = 60$ ) for the Mitscherlich model fitted to describe the relationships between relative root lengths of soybean and monomeric Al concentrations and activities of Al species in soil solutions**

Al attribute <sup>A</sup>	$R^2$ value			
	All data	$\text{SO}_4$ treatments	Cl treatments	Diagnostic index <sup>B</sup>
$(\text{Al}^{3+})$	0.910	0.883	0.980	3.6
$(\text{AlOH}^{2+})$	0.930	0.915	0.968	0.5
$(\text{Al}(\text{OH})_2^+)$	0.370	0.399	0.444	0.3
$(\text{AlSO}_4^+)$	0.654	0.783	0.916	0.6
$(\text{Al}^{3+}) + (\text{AlOH}^{2+})$	0.914	0.889	0.981	4.2
$(\text{Al}^{3+}) + (\text{Al}(\text{OH})_2^+) + (\text{AlSO}_4^+)$	0.884	0.832	0.979	6.8
$\Sigma$ activities of monomers	0.881	0.824	0.977	8.5
[monomeric Al]	0.861	0.832	0.949	15

<sup>A</sup>Round brackets indicate activity, and square brackets, concentration.

<sup>B</sup>Value ( $\mu\text{M}$ ) corresponding to RRL of 90% in the regression equation for all data.

$\text{AlOH}^{2+}$  activities gave the highest  $R^2$  values. These two attributes are strongly intercorrelated ( $r = 0.964$ ), so it is not possible to conclude whether they differ in their toxicity to root growth.

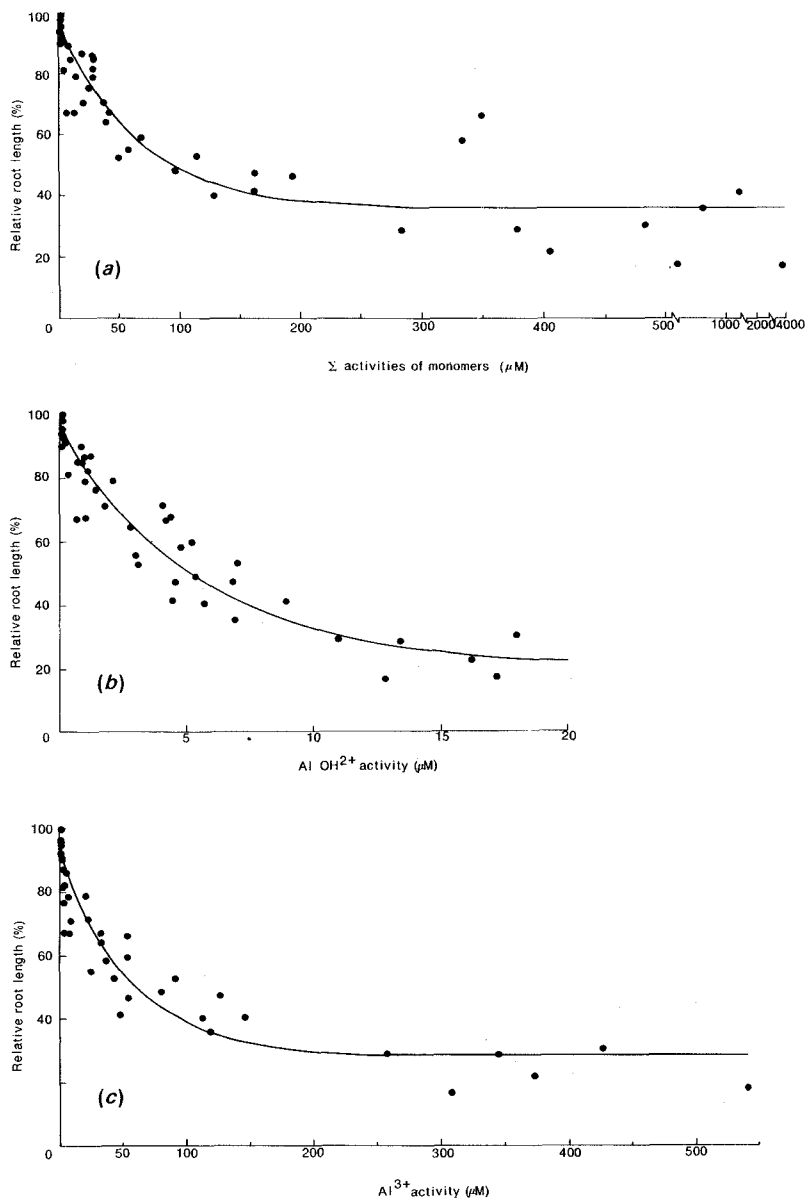
The value of each attribute corresponding to 90% RRL in the regression equations for all data is given in Table 8. Since  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$  activities have the highest  $R^2$  values in Table 8, either of them would be suitable indices for diagnosing Al toxicity. Activities greater than  $4 \mu\text{M}$   $\text{Al}^{3+}$  and  $0.5 \mu\text{M}$   $\text{AlOH}^{2+}$  indicate soils with levels of Al which are toxic to soybean roots.

Soil exchangeable Al and Al saturation cannot be related to RRL in the  $\text{CaCl}_2$  and  $\text{CaSO}_4$  treatments, because these soluble salt additions increase ionic strength and soil solution Al (Table 3), without any appreciable change in exchangeable Al and Al saturation (Table 2). It is possible to have a range of RRL values at the one Al saturation by manipulating ionic strength. Further,  $\text{CaCl}_2$  and  $\text{CaSO}_4$  rates are confounded with Al saturation since they were based upon Ca saturation (see Methods), which is inversely related to Al saturation in these soils. Thus, only the nil treatments can be used to relate RRL to soil Al saturation. A further proviso is that only soils which are not deficient in Ca can be used. There were six soils where the nil and  $\text{CaCO}_3$  treatments were not significantly different (soils, 1, 2, 6, 7, 9, and 13), an indication that they were neither Ca-deficient nor Al-toxic. The RRL of their nil treatments ranged from 88.5 to 99.2% and their Al saturations ranged from 14.0 to 81.4%, suggesting that this attribute is not a good predictor of Al toxicity. Diagnosis of Al toxicity can be done satisfactorily only with soil solution activity measurements.

### pH

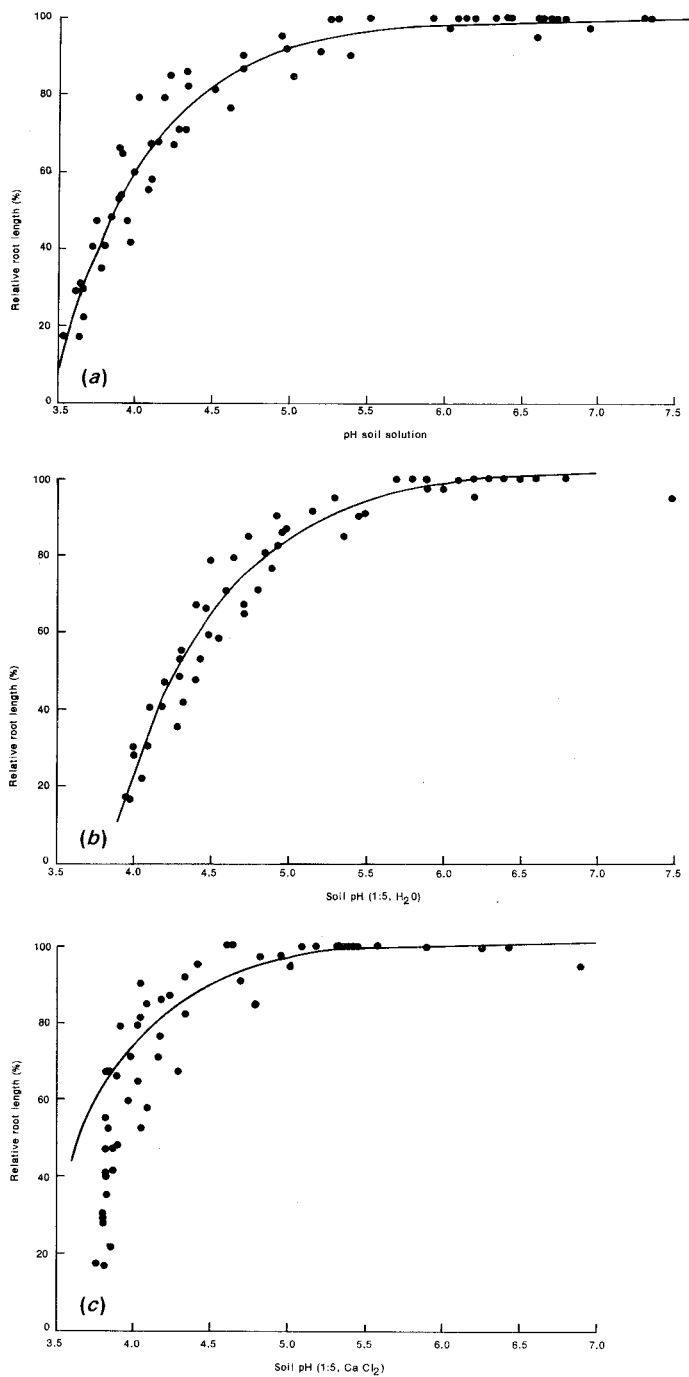
Mitscherlich equations were used for regressions of RRL on pH measurements (Fig. 4) using data from  $\text{CaSO}_4$ ,  $\text{CaCl}_2$ , and  $\text{CaCO}_3$  treatments. Both pH ( $\text{H}_2\text{O}$ ) and soil solution pH gave high  $R^2$  values (0.952 and 0.943 respectively), and 90% RRL corresponded to pH values of 5.25 and 4.85 respectively. Data points fit both curves well, even at the lowest pH values recorded. It is considered that pH *per se* is not a major limitation on root growth under the experimental conditions, and that the relationship of RRL with pH follows from the association of  $\text{Al}^{3+}$  and pH. In experiments at the University of Queensland, Suthipradit (personal communication) has shown that soybean roots tolerate low pH. She studied the growth of soybean in dilute culture solutions at a range of pH values. Five days after transplanting, yields of plant tops did not differ between pH treatments in the range 3.5–5.5, while root weights at pH 3.75, 4.0, 4.5, and 5.5 were not significantly different. At pH 3.5 root weights were slightly reduced, but were significantly different only from those at pH 5.5.

Using the Mitscherlich model, RRL did not relate to pH (CaCl<sub>2</sub>) ( $R^2 = 0.703$ ) as well as to the other pH measurements. The range of pH (CaCl<sub>2</sub>) values over which RRL increased to 90% was much narrower than for pH (H<sub>2</sub>O) and soil solution pH (Fig. 4). This narrow



**Fig. 3.** Data points and fitted Mitscherlich curves for regressions of relative root lengths of soybean on (a)  $\Sigma$  activities of monomers, (b)  $\text{Al}(\text{OH})_2^+$  activity, and (c)  $\text{Al}^{3+}$  activity. (a)  $Y = 35.6 + 62.0 e^{-0.0154X}$  ( $R^2 = 0.881$ ). (b)  $Y = 20.3 + 77.0 e^{-0.1813X}$  ( $R^2 = 0.930$ ). (c)  $Y = 28.4 + 65.8 e^{-0.0184X}$  ( $R^2 = 0.910$ ).

range made pH (CaCl<sub>2</sub>) a less sensitive indicator of root growth. This conclusion would hold even if the pH (CaCl<sub>2</sub>) data were described better by another mathematical model, but use of another model would not allow comparisons with the other two pH measurements.



**Fig. 4.** Data points and fitted Mitscherlich curves for regressions of relative root lengths of soybean on (a) pH of soil solution, (b) pH of soil suspensions (1:5) in water, and (c) pH of soil suspensions (1:5) in 0.01 M  $\text{CaCl}_2$ .  
 (a)  $Y = 99.8 - 29300 e^{-1.65X}$  ( $R^2 = 0.943$ ).  
 (b)  $Y = 102.7 - 30300 e^{-1.48X}$  ( $R^2 = 0.952$ ).  
 (c)  $Y = 101 - 38900 e^{-1.82X}$  ( $R^2 = 0.703$ ).

Results suggest that soil solution pH and  $\text{pH}(\text{H}_2\text{O})$  could both have value in diagnosing the possible incidence of Al toxicity, but they are not necessarily specific measures of Al.

### Discussion

These root growth experiments illustrate the difficulties in the interpretation of plant growth response to soil amendments when the amendments affect more than one soil property capable of influencing plant growth. For example,  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ , and  $\text{MgCO}_3$  all affect both Ca and Al concentrations in soil solution. Adams and Moore (1983) and Adams and Hathcock (1984) tried to overcome these difficulties by using the pattern of responses obtained to  $\text{Ca}(\text{OH})_2$ ,  $\text{CaSO}_4$  and MgO. They recognized different patterns of response for each of Ca deficiency, Al toxicity and the combination of the two. If root growth was enhanced equally by  $\text{CaSO}_4$  and  $\text{Ca}(\text{OH})_2$ , but decreased by MgO, Ca deficiency was indicated; if root growth was enhanced equally by  $\text{Ca}(\text{OH})_2$  and MgO but decreased or unaffected by  $\text{CaSO}_4$ , Al toxicity was indicated; if root growth was enhanced by MgO and  $\text{CaSO}_4$  but enhanced even more by  $\text{Ca}(\text{OH})_2$ , a combination of Ca deficiency and Al toxicity was indicated. However, their results did not include the pattern, which was so common in Experiments 1 and 2, where  $\text{CaCO}_3$  increased growth, soluble Ca ( $\text{CaSO}_4$  or  $\text{CaCl}_2$ ) decreased or did not increase growth, and  $\text{MgCO}_3$  reduced or did not increase growth. As mentioned previously, no general conclusions about growth limitations can be drawn when this pattern occurs. Another important point which arises in the situation where amendments affect more than one soil property is that growth on amended soil should not be related to the chemical composition of unamended soil or its soil solution. For example, if  $\text{MgCO}_3$  induced Ca deficiency in a soil which was not Ca deficient, it would be erroneous to conclude that the depression by  $\text{MgCO}_3$  indicated that the unamended soil was deficient, and that the chemical composition of the unamended soil was indicative of Ca deficiency. In this case, only the composition of the soil amended with  $\text{MgCO}_3$  would actually be indicative of Ca deficiency. The same reasoning applies when Al toxicity is induced by  $\text{CaSO}_4$ . Only the composition of the soil receiving  $\text{CaSO}_4$  is indicative

**Table 9. Selected analytical data for soils and soil solutions of nil treatments of Experiments 1 and 2 together with relative root lengths**

Soil No.	RRL (%)	Ca act. ratio	Ca saturation (%)	Ca concn ( $\mu\text{M}$ )	( $\text{Al}^{3+}$ ) ( $\mu\text{M}$ )	( $\text{AlOH}^{2+}$ ) ( $\mu\text{M}$ )	$\text{pH}_{\text{SS}}$	$\text{pH}(\text{H}_2\text{O})$
1	91.5	0.060	12.6	50	<0.1	<0.1	5.66	5.46
2	99.2	0.055	19.3	130	3.9	1.8 <sup>B</sup>	4.69 <sup>B</sup>	5.04 <sup>B</sup>
3	63.5 <sup>A</sup>	0.010 <sup>B</sup>	6.2 <sup>B</sup>	11	<0.1	<0.1	5.38	5.47
4	61.0 <sup>A</sup>	0.018 <sup>B</sup>	6.5 <sup>B</sup>	60	0.1	0.2	5.12	5.57
5	33.6 <sup>A</sup>	0.015 <sup>B</sup>	1.2 <sup>B</sup>	8	<0.1	<0.1	5.97	5.46
6	91.2	0.095	38.3	110	<0.1	0.2	5.67	5.38
7	93.8	0.057	31.8	58	0.1	0.3	5.55	5.63
8	31.1 <sup>A</sup>	0.030 <sup>B</sup>	1.0 <sup>B</sup>	56	0.4	0.2	4.84 <sup>B</sup>	4.82 <sup>B</sup>
9	93.5	0.058	29.1	62	0.1	0.4	5.53	5.53
10	40.0 <sup>A</sup>	0.017 <sup>B</sup>	0.9 <sup>B</sup>	17	1.3	0.4	4.53 <sup>B</sup>	4.76 <sup>B</sup>
11	54.9 <sup>A</sup>	0.019 <sup>B</sup>	2.4 <sup>B</sup>	33	2.5	0.9 <sup>B</sup>	4.56 <sup>B</sup>	4.63 <sup>B</sup>
12	48.3 <sup>A</sup>	0.022 <sup>B</sup>	1.0 <sup>B</sup>	47	<0.1	0.1	4.70 <sup>B</sup>	4.87 <sup>B</sup>
13	88.5	0.082	7.8 <sup>B</sup>	62	0.9	0.3	4.58 <sup>B</sup>	4.59 <sup>B</sup>
14	64.0 <sup>A</sup>	0.016 <sup>B</sup>	4.5 <sup>B</sup>	86	3.9	1.0 <sup>B</sup>	4.43 <sup>B</sup>	4.78 <sup>B</sup>
15	56.6 <sup>A</sup>	0.031 <sup>B</sup>	12.5	252	2.4	0.8 <sup>B</sup>	4.56 <sup>B</sup>	5.10 <sup>B</sup>
16	81.6 <sup>A</sup>	0.054	8.8 <sup>B</sup>	31	<0.1	<0.1	5.03	5.51
17	66.4 <sup>A</sup>	0.016 <sup>B</sup>	2.8 <sup>B</sup>	54	1.6	0.4	4.40 <sup>B</sup>	4.77 <sup>B</sup>
18	61.8 <sup>A</sup>	0.015 <sup>B</sup>	3.2 <sup>B</sup>	10	0.1	<0.1	4.97	5.45
19	72.3 <sup>A</sup>	0.022 <sup>B</sup>	4.2 <sup>B</sup>	61	0.4	0.4	5.01	5.10 <sup>B</sup>
20	21.3 <sup>A</sup>	0.020 <sup>B</sup>	3.0 <sup>B</sup>	47	0.1	0.2	5.68	5.30

<sup>A</sup>Indicates root length significantly different ( $P < 0.05$ ) from maximum root length.

<sup>B</sup>Values for which interpretative indices (0.05 Ca activity ratio; 11% Ca saturation;  $4 \mu\text{M Al}^{3+}$  activity;  $0.5 \mu\text{M AlOH}^{2+}$  activity;  $\text{pH}_{\text{SS}}$  4.85;  $\text{pH}(\text{H}_2\text{O})$  5.25) indicate a limitation to growth.

of Al toxicity. The interpretative approach used in this study was to derive diagnostic indices from the root growth and chemical composition data for amended soils and to apply them to the unamended soils.

#### *Diagnostic Indices for Calcium*

Either Ca activity ratio in soil solution or Ca saturation of the ECEC were suitable diagnostic indices for the prediction of Ca limitations to root growth. When these indices were applied to the data for the nil treatments of Experiments 1 and 2 (Table 9), 13 soils were rated Ca-deficient on the basis of their Ca activity ratio ( $<0.05$ ), and 14 were rated Ca-deficient on the basis of their Ca saturation ( $<11\%$ ). Calcium activity ratio correctly identified all six soils which were not Ca-deficient (their nil and  $\text{CaCO}_3$  treatments were not different), while Ca saturation correctly identified five of them, missing only soil 13. There was one soil in Experiment 1 (soil 8) and 10 soils in Experiment 2 (all except soil 13) for which the limitations to root growth were uncertain. Of these soils, all but soil 16 were Ca-deficient according to their Ca activity ratio, and all but soil 15 were Ca-deficient according to their Ca saturation. The data in Table 9 also reinforce the finding that Ca concentration in soil solution was poorly related to RRL (Table 7). Based on a diagnostic index of  $165 \mu\text{M}$  (Table 7), Ca concentration failed to identify any of the six soils which were not Ca-deficient. These soils had Ca concentrations ranging from 50 to  $130 \mu\text{M}$ . In addition, five of the soils (4, 8, 14, 17, and 19), which Ca activity ratio and Ca saturation rated as Ca-deficient, had Ca concentrations  $>50 \mu\text{M}$ , overlapping the range of values for Ca-sufficient soils.

The finding that Ca activity ratio in soil solution was more suitable than Ca activity or Ca concentration is in agreement with the work of Howard and Adams (1965), Adams (1966), and Bennett and Adams (1970), but differs from Adams and Moore (1983), who suggested that the ratio had no advantage over Ca activity alone in soil solutions of low ionic strength. The critical ratio of 0.05 derived here for soybean roots is much lower than those suggested for other crops, which have been 0.10–0.15. A reason for this difference, apart from the different test plant, is that other authors have neglected Na activity in soil solution. Since the activity of Na is relatively high (Table 3), its inclusion markedly decreases the activity ratio, as shown in Table 10 for soils of Experiment 1. Only the ratio which included Na separated deficient

**Table 10. Calcium activity ratios for soil solutions of Experiment 1, calculated with and without the inclusion of sodium and potassium in the sum of cation activities**

Soil	Ca activity ratio		
	Ca:(Ca + Mg)	Ca:(Ca + Mg + K)	Ca:(Ca + Mg + K + Na)
6	0.374	0.261	0.096
1	0.313	0.307	0.060
9	0.265	0.155	0.058
7	0.282	0.133	0.057
2	0.288	0.171	0.055
8 <sup>A</sup>	0.284	0.175	0.031
4 <sup>B</sup>	0.175	0.139	0.018
5 <sup>B</sup>	0.258	0.176	0.015
3 <sup>B</sup>	0.184	0.093	0.010

<sup>A</sup>Ca status uncertain in Experiment 1, but Ca activity ratio and Ca saturation indicate deficiency.

<sup>B</sup>Ca deficient in Experiment 1.

from sufficient soils. When Na was omitted from the ratio, values for three of the Ca-sufficient soils fell within the range of values for Ca-deficient soils. When both Na and K were omitted from the ratio, values for two Ca-sufficient soils fell within the range of values for Ca-deficient soils. The failure of Adams and Moore (1983) and Adams and Hathcock (1984) to measure Na in soil solution and to take it into account in calculating their Ca activity ratios in soil solution may explain their inability to separate Ca-deficient from Ca-sufficient soils.



The diagnostic use of Ca saturation has not always been successful (Foy 1974; Adams and Hathcock 1984). This may be due in part to the use of CEC measurements made at pH values higher than soil pH, as shown by Howard and Adams (1965). Their limiting values, based on ECEC, below which cotton root penetration in Norfolk and Dickson soils was restricted, were 12 and 13%. These are similar to the 11% Ca saturation corresponding to 90% RRL (Table 7), which was used to separate Ca-deficient (0.9–8.8% Ca saturation) from Ca adequate soils (12.5–38.3% Ca saturation) in the nil treatments of Experiments 1 and 2 (Table 9).

Whether Ca activity ratio is a more reliable indicator of Ca deficiency than Ca saturation cannot be decided here. Since the soil solution is the environment in which plant roots grow, and since mass flow appears to be the major mechanism by which Ca is transported to the root (Barber *et al.* 1963; Oliver and Barber 1966), it is probable that Ca activity ratio will prove the better indicator of Ca deficiency.

#### *Diagnostic Indices for Aluminium*

Soil solution Al measurements proved to be more reliable than soil measurements for the prediction of Al limitations on root growth. The conclusion that Al saturation was not a good predictor of Al toxicity is consistent with that of Adams (1984) and Kamprath (1984).

The present experiments provide further confirmation of results from solution culture experiments that activities are more relevant than concentrations (Alva *et al.* 1986a), and that Al is toxic at low activities. The results suggest that  $\text{Al}(\text{OH})_3^\circ$ ,  $\text{Al}(\text{OH})_2^+$ , and  $\text{AlSO}_4^+$  are not toxic species. The only comparable published data for soil solutions are those of Adams and Hathcock (1984), but they failed to obtain a relationship between cotton root growth and the activities of any Al species. Results from solution culture are inconsistent, but there is agreement with Pavan and Bingham (1982), who found that  $\text{AlSO}_4^+$  was not correlated with root growth of coffee seedlings, and with Alva *et al.* (1986c) who found that  $\text{Al}(\text{OH})_3^\circ$  was not correlated with soybean root growth and that  $\text{AlSO}_4^+$  and  $\text{Al}(\text{OH})_2^+$  gave lower coefficients of determination than  $\text{AlOH}^{2+}$ . However, in other experiments,  $\text{Al}(\text{OH})_2^+$  has given the best correlations with RRL (Alva *et al.* 1986b, 1987).

It has not been possible, in these experiments, to decide the relative toxicities of  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$ , since they were closely correlated and the activity of either species adequately described soybean root growth (Table 8). In Table 9,  $\text{Al}^{3+}$  activity identified all six of the nil treatments which were neither Ca deficient nor Al toxic (soils without a letter A on their RRL), while  $\text{AlOH}^{2+}$  activity identified five. The soil rated incorrectly was a surface soil (2). For the remaining 14 soils, none were rated Al-toxic on the basis of their  $\text{Al}^{3+}$  activity, but three were Al-toxic on the basis of their  $\text{AlOH}^{2+}$  activity. These three soils (11, 14, and 15) were Ca-deficient, and it cannot be resolved conclusively whether they were also Al-toxic. They had  $\text{Al}^{3+}$  activities in the range 2.4–3.9, suggesting marginal Al toxicity, but they also fit the regression of RRL on Ca activity ratio, which suggests no major Al limitation. These are grounds for slightly favouring  $\text{Al}^{3+}$  activity over  $\text{AlOH}^{2+}$  activity for diagnostic use.

Most work which has successfully established toxicity thresholds of Al in soil solution has assumed that the total Al in solution was present as  $\text{Al}^{3+}$ . Accordingly, threshold values from 4 to 15  $\mu\text{M}$   $\text{Al}^{3+}$  activity in surface soils (Brenes and Pearson 1973; Edmeades *et al.* 1983) and from <1 to 9  $\mu\text{M}$   $\text{Al}^{3+}$  activity in subsoils (Adams and Lund 1966; Adams *et al.* 1967; Adams and Pearson 1970) have been reported. Richburg and Adams (1970) and Pavan *et al.* (1982) allowed for monomeric hydrolysis of soluble Al (assuming all soluble Al was monomeric Al) and derived toxicity thresholds of <2, and 4.2  $\mu\text{M}$   $\text{Al}^{3+}$  activity respectively. All of the values quoted above are of the same order as the 4  $\mu\text{M}$   $\text{Al}^{3+}$  activity derived as a toxicity threshold for soybean roots in these experiments. No toxicity thresholds of  $\text{AlOH}^{2+}$  could be found in the literature for soil solutions or nutrient solutions, but in the data of Alva *et al.* (1986b) a 10% reduction in soybean root growth occurred at about 0.4  $\mu\text{M}$   $\text{AlOH}^{2+}$  activity. This is similar to the value of 0.5  $\mu\text{M}$  derived here.

McLean (1982) regarded soil pH as both a symptom of the soil's condition and a cause of the many reactions that occur in soils. From the narrower point of view of diagnosis of

Al toxicity, pH can indicate whether exchangeable Al or Al saturation may be high and whether Al toxicity (toxic soil solution Al) is possible. It cannot be an absolute indicator of Al toxicity in all soils, as H<sup>+</sup> ions can come from sources other than the hydrolysis of Al ions. A measure of soil solution Al<sup>3+</sup> activity would then be a more absolute index of Al toxicity than pH.

It follows from the effect of ionic strength on soluble Al that the pH measurement employed must also be sensitive to ionic strength. Data in Table 2 show that CaCl<sub>2</sub> and CaSO<sub>4</sub> treatments had pH(H<sub>2</sub>O) and soil solution pH values less than those of the nil treatments, but this was not the case with pH(CaCl<sub>2</sub>). This latter measurement was made in 0.01 M CaCl<sub>2</sub>, which removed the effect of differences in ionic strength between soils, and resulted in similar pH (CaCl<sub>2</sub>) values for nil, CaCl<sub>2</sub>, and CaSO<sub>4</sub> treatments. It provides a measure of soil pH at a constant, high ionic strength (30 mM), but does not measure the inherent soil pH of soils of lower ionic strength.

Using a Ca activity ratio of 0.05 and Al<sup>3+</sup> activity of 4 μM as diagnostic indices, none of the 20 unamended soils in Experiments 1 and 2 were toxic in Al, while 13 (all subsoils) were deficient in Ca (Table 9). Thus the first limitation on root growth was Ca deficiency and not Al toxicity, in spite of high Al saturations and relatively low pH in the soils.

### Acknowledgments

We are grateful to Miss Helen Murphy and Mrs Helen Dunn for assistance with these experiments, and to Mr I. J. Bruce for help with the Mitscherlich equations.

### References

- Adams, F. (1966). Calcium deficiency as a causal agent of ammonium phosphate injury to cotton seedlings. *Soil Sci. Soc. Am. Proc.* **30**, 485–8.
- Adams, F. (1974). Soil solution. In 'The Plant Root and its Environment'. (Ed. E. W. Carson.) pp. 441–81. (University Press of Virginia: Charlottesville.)
- Adams, F. (1984). Crop response to lime in the southern United States. In 'Soil Acidity and Liming'. (Ed. F. Adams.) pp. 211–66. 2nd Edn, Agronomy No. 12. (Am. Soc. Agron.: Madison, Wisc.)
- Adams, F., and Hathcock, P. J. (1984). Aluminum toxicity and calcium deficiency in acid subsoil horizons of two Coastal Plains soil series. *Soil Sci. Soc. Am. J.* **48**, 1305–9.
- Adams, F., and Lund, Z. F. (1966). Effect of chemical activity of soil solution aluminium on cotton root penetration of acid subsoils. *Soil Sci.* **101**, 193–8.
- Adams, F., and Moore, B. L. (1983). Chemical factors affecting root growth in subsoil horizons of Coastal Plain soils. *Soil Sci. Soc. Am. J.* **47**, 99–102.
- Adams, F., and Pearson, R. W. (1970). Differential response of cotton and peanuts to subsoil acidity. *Agron. J.* **62**, 9–12.
- Adams, F., Pearson, R. W., and Doss, B. D. (1967). Relative effects of acid subsoils on cotton yields in field experiments and on cotton roots in growth-chamber experiments. *Agron. J.* **59**, 453–6.
- Alva, A. K., Blamey, F. P. C., Edwards, D. G., and Asher, C. J. (1986a). An evaluation of aluminum indices to predict aluminum toxicity to plants grown in nutrient solutions. *Commun. Soil Sci. Plant Anal.* **17**, 1271–80.
- Alva, A. K., Edwards, D. G., Asher, C. J., and Blamey, F. P. C. (1986b). Effects of phosphorus/aluminum molar ratio and calcium concentration on plant response to aluminum toxicity. *Soil Sci. Soc. Am. J.* **50**, 133–7.
- Alva, A. K., Edwards, D. G., Asher, C. J., and Blamey, F. P. C. (1986c). Relationships between root length of soybean and calculated activities of aluminum monomers in nutrient solution. *Soil Sci. Soc. Am. J.* **50**, 959–62.
- Alva, A. K., Edwards, D. G., Asher, C. J., and Suthipradit, S. (1987). Effects of acid soil infertility factors on growth and nodulation of soybean. *Agron. J.* **79**, 302–6.
- Barber, S. A., Walker, J. M., and Vasey, E. H. (1963). Mechanisms for the movement of plant nutrients from the soil and fertilizer to the plant root. *J. Agric. Food Chem.* **11**, 204–7.
- Bennett, A. C., and Adams, F. (1970). Calcium deficiency and ammonia toxicity as separate causal factors of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>-injury to seedlings. *Soil Sci. Soc. Am. Proc.* **34**, 255–9.
- Blamey, F. P. C., Edwards, D. G., and Asher, C. J. (1983). Effects of aluminum, OH:Al and P:Al molar ratios, and ionic strength on soybean root elongation in solution culture. *Soil Sci.* **136**, 197–207.

- Bloom, P. R., Weaver, R. M., and McBride, M. B. (1978). The spectrophotometric and fluorometric determination of aluminum with 8-hydroxyquinoline and butyl acetate extraction. *Soil Sci. Soc. Am. J.* **42**, 713-16.
- Brenes, E., and Pearson, R. W. (1973). Root responses of three Gramineae species to soil acidity in a Oxisol and an Ultisol. *Soil Sci.* **116**, 295-302.
- Bruce, R. C., and Rayment, G. E. (1982). Analytical methods and interpretations used by the Agricultural Chemistry Branch for soil and land use surveys. Qld. Dep. Prim. Ind. Bull: QB82004.
- Cate, R. B. (Jr), and Nelson, L. A. (1971). A simple statistical procedure for partitioning soil test correlation data into two classes. *Soil Sci. Soc. Am. Proc.* **35**, 658-60.
- Edmeades, D. C., Smart, C. E, and Wheeler, D. M. (1983). Aluminium toxicity in New Zealand soils: preliminary results on the development of diagnostic criteria. *N.Z. J. Agric. Res.* **26**, 493-501.
- Foy, C. D. (1974). Effects of soil calcium availability on plant growth. In 'The Plant Root and its Environment'. (Ed. E. W. Carson.) pp. 565-600. (University Press of Virginia: Charlottesville.)
- Gillman, G. P. (1976). A centrifuge method for obtaining soil solution. CSIRO Aust. Div. Soils. Divl. Rep. No. 16.
- Gillman, G. P., and Bell, L. C. (1978). Soil solution studies on weathered soils from tropical North Queensland. *Aust. J. Soil Res.* **16**, 67-77.
- Gonzalez-Erico, E., Kamprath, E. J., Naderman, G. C., and Soares, W. V. (1979). Effect of depth of lime incorporation on the growth of corn on an Oxisol of central Brazil. *Soil Sci. Soc. Am. J.* **43**, 1155-8.
- Haynes, J. L., and Robbins, W. R. (1948). Calcium and boron as essential factors in the root environment. *J. Am. Soc. Proc.* **29**, 795-803.
- Howard, D. D., and Adams, F. (1965). Calcium requirement for penetration of subsoils by primary cotton roots. *Soil Sci. Soc. Am. Agron.* **40**, 558-61.
- Kamprath, E. J. (1984). Crop response to lime on soils in the tropics. In 'Soil Acidity and Liming'. (Ed. F. Adams.) pp. 349-68. 2nd Edn., Agronomy No. 12. (Am. Soc. Agron.: Madison, Wisc.)
- Keay, J., Menage, P. M. A., and Dean, G. A. (1972). Automated method for the micro-determination of sulphur. *Analyst* **97**, 897-902.
- Kim, M-K. (1984). Effects of pH and aluminium on nodulation and growth of *Trifolium subterraneum* cultivars. Ph.D. Thesis, University of Queensland.
- Li, C. C. (1964). 'Introduction to Experimental Statistics' (McGraw Hill: New York.)
- Lindsay, W. L. (1979). 'Chemical Equilibria in Soils'. (John Wiley and Sons: New York.)
- Lund, Z. F. (1970). The effect of calcium and its relation to several cations in soybean root growth. *Soil Sci. Soc. Am. Proc.* **34**, 456-9.
- McLean, E. O. (1982). Soil pH and lime requirement. In 'Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties'. (Eds A. L. Page, R. H. Miller and D. R. Keeney.) pp. 199-224. 2nd Edn., Agronomy No. 9 (Am. Soc. Agron.: Madison, Wisc.)
- Oliver, S., and Barber, S. A. (1966). An evaluation of the mechanisms governing the supply of Ca, Mg, K and Na to soybean roots (*Glycine max*). *Soil Sci. Soc. Am. Proc.* **30**, 82-6.
- Pavan, M. A., and Bingham, F. T. (1982). Toxicity of aluminum to coffee seedlings grown in nutrient solution. *Soil Sci. Soc. Am. J.* **46**, 993-7.
- Pavan, M. A., Bingham, F. T., and Pratt, P. F. (1982). Toxicity of aluminum to coffee in Ultisols and Oxisols amended with CaCO<sub>3</sub>, MgCO<sub>3</sub>, and CaSO<sub>4</sub>.2H<sub>2</sub>O. *Soil Sci. Soc. Am. J.* **46**, 1201-7.
- Presley, J. T., and Leonard, O. A. (1948). The effect of calcium and other ions on the early development of the radicle of cotton seedlings. *Plant Physiol.* **23**, 516-25.
- Richburg, J. S., and Adams, F. (1970). Solubility and hydrolysis of aluminum in soil solutions and saturated paste extracts. *Soil Sci. Soc. Am. Proc.* **34**, 728-34.
- Rios, M. A., and Pearson, R. W. (1964). The effect of some chemical environmental factors on cotton root behaviour. *Soil Sci. Soc. Am. Proc.* **28**, 232-5.
- Ritchey, K. D., Silva, J. E., and Costa, U. F. (1982). Calcium deficiency in clayey B horizons of savannah Oxisols. *Soil Sci.* **133**, 378-82.
- Sartain, J. B., and Kamprath, E. J. (1978). Aluminum tolerance of soybean cultivars based on root elongation in solution culture compared with growth in acid soils. *Agron. J.* **70**, 17-20.
- Snedecor, G. W., and Cochran, W. G. (1980). 'Statistical Methods' 7th Edn. (The Iowa State University Press: Ames, Iowa.)
- Sposito, G., and Mattigod, S. V. (1980). GEOCHEM: A computer program for the calculation of chemical equilibria in soil solution and other natural water systems. Kearney Foundation of Soil Sci., Univ. of California, Riverside.
- Stace, H. C. T., Hubble, G. D., Brewer, R., Northcote, K. H., Sleeman, J. R., Mulcahy, M. J., and Hallsworth, E. G. (1968). 'A Handbook of Australian Soils'. (Rellim: Glenside, S.A.)

- Turner, R. C. (1969). Three forms of aluminum in aqueous systems determined by 8-hydroxy-quinolate extraction methods. *Can. J. Chem.* **47**, 2521-7.
- Waugh, D. L., Cate, R. B. (Jr), and Nelson, L. A. (1973). Discontinuous models for rapid correlation, interpretation, and utilization of soil analysis and fertilizer response data. *Int. Soil. Fert. Eval. Impr. Prog., Tech. Bull. No. 7.* (North Carolina State University: Raleigh, North Carolina.)

Manuscript received 31 August 1987, accepted 8 December 1987