

Relative Toxicities of Inorganic Aluminum Complexes to Barley¹

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ABSTRACT

The inorganic forms of Al in the soil solution that decrease plant growth in acid soils have not been clearly identified. Therefore, we examined the effects of Al and its complexes with F^- and SO_4^{2-} on the root elongation of barley (*Hordeum vulgare*) in nutrient solutions containing 3333 $\mu\text{mol Ca L}^{-1}$ and 6 $\mu\text{mol B L}^{-1}$ at pH 4.5. The anions were chosen because of their presence in the soil solution at levels sufficient to complex Al. The toxicity of 0 to 100 $\mu\text{mol Al L}^{-1}$ was studied in the presence of 0 to 10 $\mu\text{mol F}^- \text{ L}^{-1}$ or 0-3300 $\mu\text{mol SO}_4^{2-} \text{ L}^{-1}$. The elongation of roots of barley seedlings was correlated with Al^{3+} concentrations but not with total soluble Al or Al complexed with F^- and SO_4^{2-} . This could be one of the reasons why measurements of labile Al using complexing agents have not always been successful at distinguishing between Al-toxic and nontoxic soils.

Additional Index Words: pH, Ca, F^- , SO_4^{2-} , nutrient solutions, soil acidity, alfalfa, *Hordeum vulgare* L.

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ALUMINUM TOXICITY is a major factor limiting the growth of plants on acid soils (Foy, 1984). Despite considerable research, the identification of soils containing toxic levels of Al is still limited by our lack of understanding of which forms of soluble Al are responsible for decreased plant growth. The activity of total soluble aluminum, (Al_T), has been shown to be more correlated with root elongation than total soluble Al concentration, $[Al_T]$ (Adams and Lund, 1966; Helyar, 1978). More recent studies with nutrient solutions have indicated that the "free" ion, Al^{3+} , or the labile monomeric forms (i.e., Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$) may be the major toxic species (Pavan and Bingham, 1982; Blamey et al., 1983).

The application of the above work to natural soil conditions has met with partial success when the activity of Al^{3+} , (Al^{3+}), is calculated from the total concentrations of all soluble ions and thermodynamic stability constants (e.g., Pavan et al., 1982; Sheppard and Floate, 1984). However, comparisons have not been so encouraging when toxic Al in soil is estimated by the speed with which it reacts with a complexing reagent (Adams and Hathcock, 1984). This measure of Al (labile Al) is thought to consist of Al^{3+} and monomeric complexes with inorganic anions (James et al., 1983). The cause of such an anomaly could be due to the different toxicities of the inorganic forms of Al in solutions. Sulphate and F^- are both capable of forming soluble complexes with Al at levels found in the soil solution (Ritchie, 1986).

The purpose of this work was to compare the toxic effect of Al^{3+} and its complexes with F^- and SO_4^{2-} .

Initially, we examined the effect of pH, ionic strength, and Ca^{2+} concentration on the elongation of the primary root of seedlings of barley (*Hordeum vulgare* L., cv. Beecher) and alfalfa (*Medicago sativa* L., cv. CUF 101) so that we could develop a suitable bioassay for examining the effects of Al on root growth.

MATERIALS AND METHODS

Germination and Growth of Seedlings

All seeds were sieved and germinated by immersion in an aerated, 200 $\mu\text{mol CaSO}_4 \cdot 2H_2O \text{ L}^{-1}$ solution at $25 \pm 3^\circ\text{C}$. Six seedlings were transplanted to each test solution when the radicles had emerged to approximately 3 mm. The plants were suspended at the surface of the nutrient solution on cheesecloth stretched over a wire mesh template. This ensured that the root tips were always immersed in the solution.

The solutions contained only $\leq 1600 \mu\text{mol Ca}^{2+} \text{ L}^{-1}$ and 6 $\mu\text{mol B L}^{-1}$, as well as the experimental treatments. Calcium and B are immobile in plants and are essential for root growth because they maintain the integrity of the root membrane (Haynes and Robbins, 1948). The seed provided an adequate source of all other nutrients over the short time period of the experiment. This prevented complications in the calculation of (Al^{3+}), which may have occurred if nutrients such as $H_2PO_4^-$ had been added. The nutrient solutions were contained in 5-L plastic pots placed in root cooling tanks at $23 \pm 2^\circ\text{C}$. During plant growth, the solutions were aerated continuously and renewed daily to ensure constant levels of the ions present. The treatments were duplicated in all experiments.

Development of Bioassay

The purpose of the bioassay was to study the influence of external factors on Al toxicity and was not designed to monitor internal effects that may influence shoot growth only. The criterion for the development of the procedure was to establish a nutrient solution that contained the minimum nutrients required for adequate seedling growth over short time periods (3 d) but contained a minimum of ions that could affect the response of roots to Al. No effort was made to use normal nutrient solutions or simulate the soil solution because both solutions are too complex to differentiate between the mechanisms under investigation.

Three factorial experiments were designed to study the effect of pH, Al, Ca^{2+} , and ionic strength on primary root elongation of alfalfa and barley (Table 1). These plant species were chosen because of their sensitivity to Al toxicity (Russell, 1973).

Experiment 1 investigated the effect of pH on root elongation of alfalfa and barley seedlings and also the effect of Al at pH 4.0 only. Subsequently, alfalfa was chosen for further studies of the Al-H interaction (Exp. 2), whereas barley was selected to study the Al-Ca interaction (Exp. 3). Where necessary, pH was controlled by the addition of 17.3 mmol HCl L^{-1} or 1.4 mmol $NaHCO_3 \text{ L}^{-1}$. Ionic strength was maintained with $CaCl_2$ and KCl. Aluminum chloride was added to give a range of values of (Al^{3+}) from 0 to 16 $\mu\text{mol L}^{-1}$.

A preliminary experiment indicated that there was no effect of Na^+ or K^+ on root elongation at the levels used. Hence, in the subsequent experiments, F^- and SO_4^{2-} were added as either the Na^+ , K^+ , or Ca^{2+} salts to ensure that

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Table 1. Experiment design and treatment levels for Exp. 1 to 3.

Experiment no.	Plant species	Treatments				Speciation of Al [†]		
		I [‡]	pH	Ca _T [§]	Al _T [§]	(Al ³⁺)	Al(OH) ²⁺ (μmol L ⁻¹)	Al(OH) ₃
1a	Alfalfa	0.01	3.4, 3.7,	3330	0	0	0	0
	Barley		4.0, 4.5 5.0, 5.5					
1b	As above	0.01	4.0	3330	0, 2 10, 50	0, 0.89 4.43, 22.2	0	0
2	Alfalfa	0.005	4.4	1600	0, 18	0, 8	0, 2	0, 0.38
		0.005	4.7	1600	0, 6 11, 22	0, 2 4, 8	0, 1 2, 4	0, 0.38 0.75, 1.5
		0.005	5.0	1600	0, 4 8, 16	0, 1 2, 4	0, 1 2, 4	0, 0.75 1.5, 3
		0.005	5.2	1600	0, 4 8, 16	0, 0.5 1, 2	0, 1 2, 4	0, 1.5 3, 6
3	Barley	0.02	4.5	6667	0, 1.73 3.43, 6.86 13.72, 27.44 54.9	0, 0.5 1.0, 2.0 4, 8 16	0, 0.16 0.33, 0.65 1.3, 2.6 5.2	0, 0.04 0.07, 0.14 0.28, 0.56 1.12
		0.02	4.5	3333		same as above		
		0.01	4.5	3333	0, 1.4, 2.8 5.6, 11.2 22.4, 44.8	same as above		

[†] The corresponding activity of Al species in each treatment.

[‡] Ionic strength, mol L⁻¹.

[§] Total concentration in solution, μmol L⁻¹.

the toxicity of Al was related to the effects of F⁻ and SO₄²⁻ only.

Aluminum Toxicity in the Presence of Fluoride

The effect of F⁻ on the toxicity of Al to seedlings of barley was studied by measuring root elongation after 3 d growth in nutrient solutions (Exp. 4). The experiment was an incomplete factorial combination of 25 treatments with four levels of total F⁻ concentrations, [F_T], and 10 levels of total Al concentrations, [Al_T], replicated in a completely random arrangement (Table 2). Aluminum and F⁻ were added to the nutrient solutions as AlCl₃ and NaF, respectively. A Ca concentration of 3333 μmol L⁻¹, an ionic strength of 10 000 μmol L⁻¹ and a pH of 4.5 were used in all treatments. Ionic strength was maintained as in Exp. 1, 2, and 3.

Aluminum Toxicity in the Presence of Sulphate

An incomplete factorial design of 13 treatments was used to study the effect of SO₄²⁻ on the relationship between root elongation and Al toxicity to barley seedlings (Exp. 5). The experimental conditions were the same as for Exp. 4 except that no F⁻ was present and SO₄²⁻ was added either as CaSO₄·2H₂O and/or KAl(SO₄)₂. The treatment levels are given in Table 2.

Calculation of Al Speciation

The solution activities of free Al³⁺ and Ca²⁺ were calculated at each pH and ionic strength, I, from the thermodynamic stability constants given by Lindsay (1979) for the hydrolysis of Al³⁺ to Al(OH)²⁺ and Al(OH)₃ and from activity co-efficients calculated from thermodynamic stability constants for the formation of the species CaSO₄⁰, AlOH²⁺, Al(OH)₂⁺, AlF²⁺, AlF₂⁺, AlF₃⁰, AlSO₄⁺, and Al(SO₄)₂⁻ (Lindsay, 1979).

RESULTS AND DISCUSSION

Development of Bioassay

In Exp. 1, increasing H⁺ ion activity decreased the elongation of the primary root of both alfalfa and bar-

ley (Fig. 1a and b). At pH 4, [Al_T] > 10 μmol L⁻¹ decreased root growth of barley seedling from 29 mm to ≤ 11.3 mm (Fig. 1d). The growth of roots of alfalfa showed little response to Al (Fig. 1c), presumably because root growth had already been reduced to a minimum by the low pH. However, at the higher pH values used in Exp. 2 (pH 4.4–5.2), root elongation of alfalfa seedlings was dependent on both pH and Al activity. In an attempt to combine these effects, root length was expressed as a percentage of root length in the absence of Al at the corresponding pH (i.e., relative root length, RRL) and plotted separately against the activities of Al³⁺, Al(OH)²⁺, and Al(OH)₃.

Regardless of the Al species considered, there was still a wide range of RRL values at a constant activity. For example, RRL varied from 19 to 33% at a constant level of 2 μmol L⁻¹ of Al³⁺ (Fig. 2a) and from 12.6 to 24% at 1 μmol L⁻¹ of Al(OH)²⁺. Plots of root length vs. the individual Al species plus H⁺ activity, (H⁺), could not explain the response adequately either (data not shown). Assuming there is no effect on root elongation of H⁺ at pH 5.2, then the effect of 0.5 μmol (Al³⁺) L⁻¹ at pH 5.2 is approximately equal to the effect of 40 μmol (H⁺) L⁻¹ in the absence of Al (i.e., pH 4.4). Therefore, the depression in root growth caused by 1 μmol (Al³⁺) L⁻¹ was approximately equivalent to the reduction caused by 80 μmol (H⁺) L⁻¹. Similar relationships were estimated for the activities of Al(OH)²⁺ and Al_T. When the combined contribution of Al and H⁺ was expressed in this manner, the response of root elongation to pH and Al was described by a single consistent relationship. This indicates that H⁺ ions affected root growth of alfalfa seedlings in nutrient solutions in an independent but similar manner to Al. Even though the highest correlation was achieved by considering (Al³⁺) alone (Fig. 2b), the relationships with (Al_T) and (Al(OH)₃) were also quite adequate (Table 3). It is difficult to distinguish whether Al³⁺ or a hydrolyzed form is the major

Table 2. Experiment design and treatment levels ($\mu\text{mol dm}^{-3}$) for Exp. 4 and 5. Ionic strength = 0.01 mol L^{-1} , pH = 4.5, $[\text{Ca}_T] = 3333 \mu\text{mol L}^{-1}$.

Complexing anion	[C _T] [†]	× [Al _T]	Speciation of Al [‡]			
			[Al _T ³⁺]	Al(OH) ²⁺	Al(OH) ₂ ⁺	Al-C [§]
Experiment 4						
F	0	0, 2, 4, 6, 8, 100	0, 1.61, 3.23, 4.84, 6.45, 80.6	0, 0.35, 0.7, 1.05, 1.4, 17.7	0, 0.056, 0.11, 0.17, 0.22, 2.82	0
	2.5	0, 2, 4, 6, 8, 10	0, 0.34, 1.50, 2.99, 4.55, 6.14	0, 0.075, 0.33, 0.66, 1.0, 1.35	0, 0.012, 0.052, 0.104, 0.16, 0.21	0, 1.57, 2.12, 2.25, 2.29, 2.30
	5	0, 4, 6, 8, 10, 12	0, 0.54, 1.53, 2.89, 4.37, 5.92	0, 0.11, 0.33, 0.63, 0.95, 1.29	0, 0.017, 0.052, 0.1, 0.15, 0.21	0, 3.33, 4.10, 4.38, 4.52, 4.58
	10	0, 4, 8, 10, 12, 14, 16	0, 0.07, 0.82, 1.69, 2.85, 4.20, 5.63	0, 0.015, 0.18, 0.38, 0.62, 0.91, 1.22	0, 0.0023, 0.029, 0.06, 0.099, 0.145, 0.194	0, 3.91, 6.97, 7.87, 8.43, 8.75, 9.00
Experiment 5						
SO ₄	0	0, 1.26, 3.14, 12.55	0, 1, 2.5, 10	0, 0.22, 0.55, 2.2	0, 0.035, 0.09, 0.35	0
	1000	0, 4.42, 17.68	0, 2.5, 10	0, 0.55, 2.2	0, 0.09, 0.35	0, 1.28, 5.13
	2100	0, 5.77, 23.05	0, 2.5, 10	same as above		0, 2.63, 10.5
	3300	0, 7.17, 28.65	0, 2.5, 10	same as above		0, 4.03, 16.1

† Total concentration of complexing ion.

‡ The corresponding concentration of Al species in each treatment, $\mu\text{mol L}^{-1}$.

§ ($\text{AlF}^{2+} + \text{AlF}_2^+ + \text{AlF}_3$) in Exp. 4 and ($\text{AlSO}_4 + \text{Al}(\text{SO}_4)_2^-$) in Exp. 5.

toxic species because they all vary in the same proportion when Al_T is altered at a constant pH.

At a constant Ca_T of $3333 \mu\text{mol L}^{-1}$, there was a negligible difference in the effect of (Al^{3+}) on root growth of barley seedlings at ionic strengths of 10 000 and 20 000 $\mu\text{mol L}^{-1}$ (Fig. 3a). However, at a constant ionic strength of 20 000 $\mu\text{mol L}^{-1}$ and (Al^{3+}) $< 8 \mu\text{mol L}^{-1}$, root growth was greater at $\text{Ca}_T = 6667 \mu\text{mol L}^{-1}$ than at $3333 \mu\text{mol L}^{-1}$ (Fig. 3a). Therefore, the effect of Al was mitigated by Ca in the ($\text{Al}^{3+}/(\text{Ca}^{2+})$) range of 3.4×10^{-4} to 8.0×10^{-3} . Other studies have also shown that Ca^{2+} can alleviate effects of Al on root growth of cotton (*Gossypium hirsutum* L.) (Adams and Lund, 1966) and soybeans [*Glycine max* (L.) Merr.] (Lund, 1970).

A consistent relationship between Al and root length was observed when (Al^{3+}) was expressed as a ratio with (Ca^{2+}) (Fig. 3b). A logarithm-logarithm transformation of the data was linear ($\log y = 1.456 - 0.346 \log x$; $r^2 = -0.947$) between ($\text{Al}^{3+}/(\text{Ca}^{2+})$) ratios of 3.4×10^{-4} and 8.0×10^{-3} . Outside this range, Al toxicity was independent of Ca concentration.

In experiments investigating Al toxicity, the experimental conditions must be selected so that the H^+ effect is minimized and the (Ca^{2+}) effect is constant. Therefore, the following conditions were selected for the bioassays used to study the Al toxicity in the presence of SO_4^{2-} and F^- ions.

An ionic strength of 10 000 $\mu\text{mol L}^{-1}$ and a $[\text{Ca}_T]$ of $3333 \mu\text{mol L}^{-1}$ were considered representative of levels found in soil solutions. A pH of 4.5 was selected as the highest pH that could be used before hydrolysis and precipitation of Al decreased (Al^{3+}) to negligible levels while still minimizing the H^+ effect on root growth. Barley was chosen as the indicator plant because at pH 4.5 it was less sensitive to H^+ effects than alfalfa. Root growth of barley at pH 4.5 was 79% of the average growth at pHs 5.0 and 5.5, whereas root elongation of alfalfa was only 63% of the average growth at higher pHs.

Table 3. Variance accounted for by linear regression of the log transformation of root length on $[\text{Al} + \text{H}]$ activity.

y	x	Variance
Root length	$(\text{Al}^{3+}) + \text{H}/80$	0.972
	$(\text{Al}(\text{OH})^{2+}) + \text{H}/40$	0.910
	$(\text{Al}(\text{OH})_2^+) + \text{H}/27$	0.632
	$(\text{Al}_T) + \text{H}/13$	0.914

Aluminum Toxicity in the Presence of Fluoride and Sulphate

Increasing the concentration of SO_4^{2-} and F^- in solution increased the elongation of roots of barley seedlings in the presence of Al but not in its absence (Fig. 4a and 5a). For both SO_4^{2-} and F^- , root length was not correlated with Al_T (Fig. 4a and 5a), Al-F or Al- SO_4 complexes, but was closely correlated with the concentration of Al^{3+} (Fig. 4b and 5b). In these experiments Al^{3+} may be expressed as a concentration or an activity because ionic strength was constant. Thus, Al complexed with SO_4^{2-} and F^- does not appear to be toxic to root elongation. There are insufficient data points in Fig. 5 to establish whether the response of barley to Al in the presence of SO_4^{2-} is of a similar shape to that in the presence of F^- (Fig. 4b). However, the points in Fig. 5b fall on the same response curve as the data from the F^- experiment if they are plotted on the same axes. The detoxifying effect of F^- and SO_4^{2-} could be one of the reasons why measurements of labile Al using complexing agents have not always been successful at distinguishing between Al toxic and nontoxic soils.

Fluoride forms complexes with Al very readily and therefore was more effective in reducing the toxic effect of Al when compared with SO_4^{2-} at equal concentrations. Under the conditions of the experiment, $>90\%$ of the total F^- present was complexed with Al, whereas $<0.5\%$ of total SO_4^{2-} was forming ion pairs with Al. Therefore, the ability of these two anions to reduce Al toxicity in soils will depend on their concentration in the soil solution.

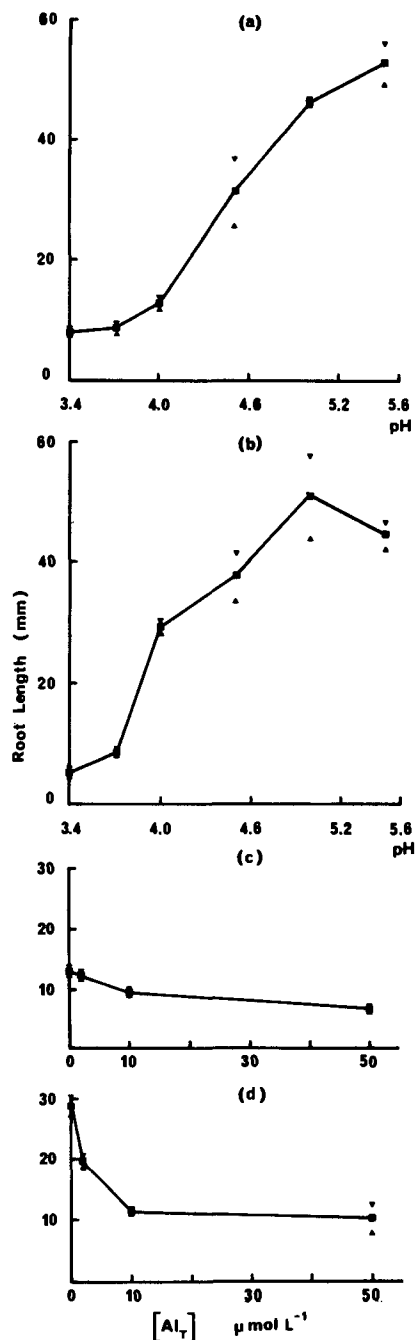


Fig. 1. The effect of pH [(a) and (b)] and $[Al]$ at pH 4 [(c) and (d)] on the root length of alfalfa [(a) and (c)] and barley [(b) and (d)].

The average level of F^- in soil solutions appears to be about $10 \mu\text{M}$ (Larsen and Widdowson, 1971; David and Driscoll, 1984) even though total F^- levels in a soil may be as high as $300 \mu\text{g g}^{-1}$ (Adriano and Doner, 1982). The low levels of soluble F^- suggest that it will only be important in reducing Al toxicity in soils which contain soluble Al levels that are marginally toxic. Even though soluble SO_4^{2-} levels are much higher than F^- in acid soils ($100\text{--}1000 \mu\text{mol L}^{-1}$), SO_4^{2-} will be less effective at reducing Al toxicity because of its low complexing capacity (Ritchie, 1986).

There is also evidence that Al complexed with phosphate and organic ligands is not toxic to plants (Bar-

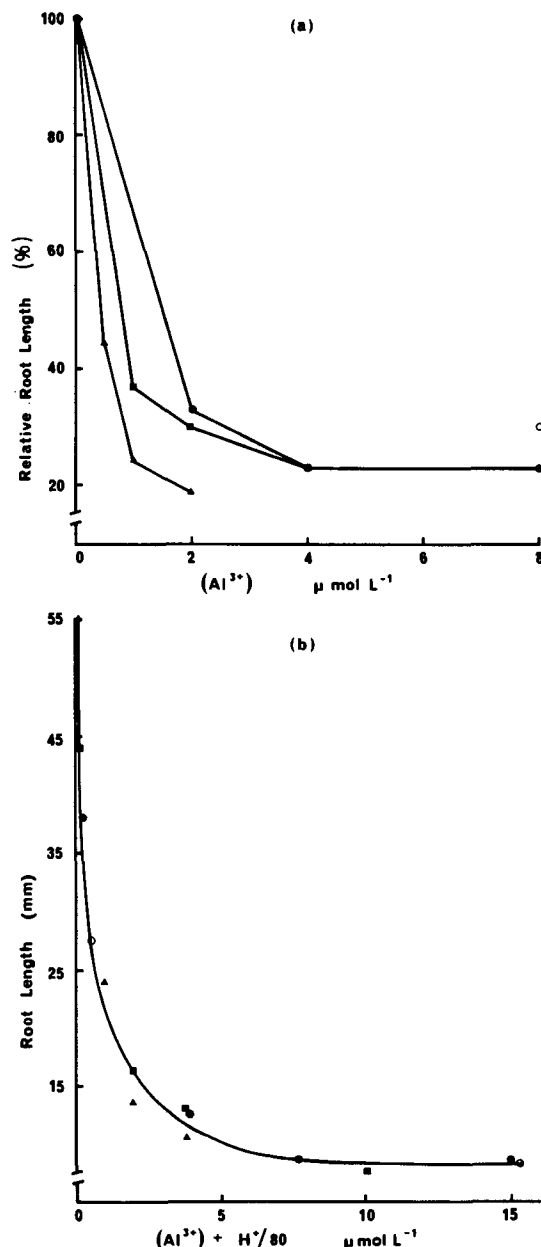


Fig. 2. The variation in relative root length of alfalfa with (a) $[Al^{3+}]$ and (b) $[Al^{3+}] + [H^+/80]$ at pH 4.4 (○) 4.7 (●), 5.0 (■), and 5.2 (▲).

tlett and Riego, 1972; Blamey et al., 1983; Hue et al., 1986). The phosphate complex appears to be polymeric and did not react with a complexing reagent during the short time period that is used to assess labile Al (Blamey et al., 1983). The behavior of Al-organic complexes is less clear. Turner and Sulaiman (1971) and Hoyt and Turner (1975) found that complexing agents (aluminon and hydroxyquinoline) reacted very quickly (<1 min) with salicylate and citrate complexes of Al. On the other hand, complexes with larger organic ligands (e.g., humic or fulvic acids) may not be so reactive (James et al., 1983).

All anions discussed could be responsible for our inability to distinguish between Al toxic and nontoxic soils. However, we have yet to establish their impor-

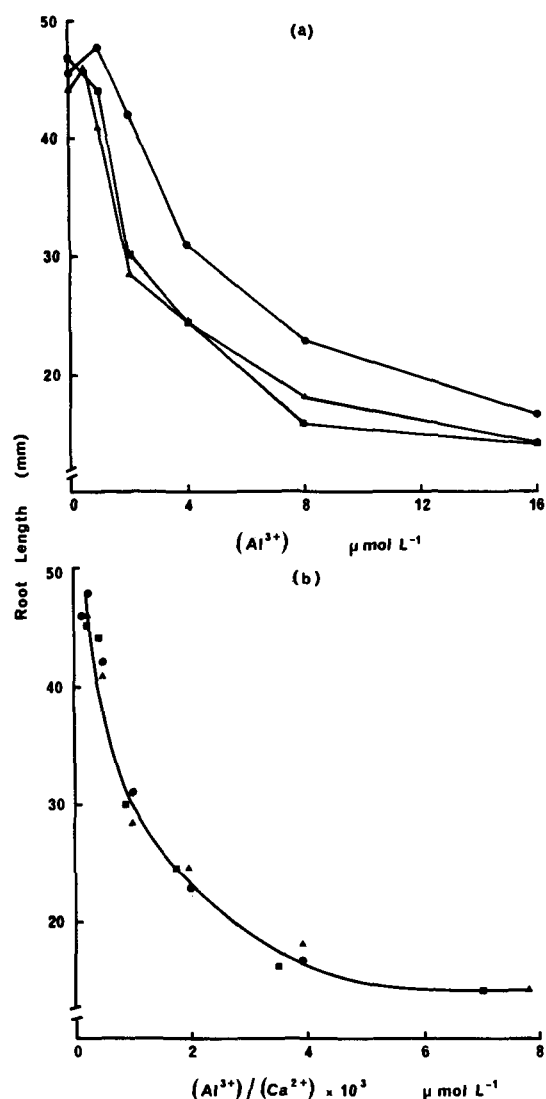


Fig. 3. The variation in root length of barley with (a) $[Al^{3+}]$ and (b) $[Al^{3+}]/[Ca^{2+}]$ at $I = 20000 \mu mol L^{-1}$, $[Ca] = 6667 \mu mol L^{-1}$ (●) and $[Ca] = 3333 \mu mol L^{-1}$ (▲), and $I = 10000 \mu mol L^{-1}$ and $[Ca] = 3333 \mu mol L^{-1}$ (■).

tance relative to each other and to other factors that may influence Al toxicity. Equally, the specificity of methods used to measure labile Al requires further clarification.

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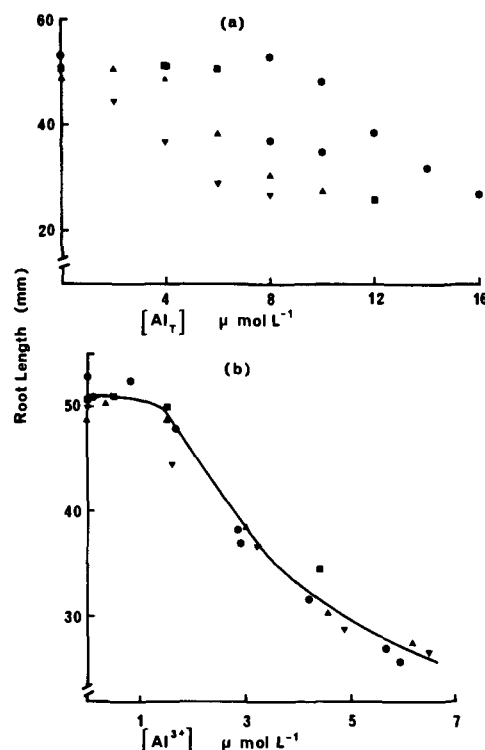


Fig. 4. The variation in root length of barley with (a) $[Al_T]$ and (b) $[Al^{3+}]$ in the presence of 0 (▼), 2.5 (▲), 5 (■), and 10 (●) $\mu mol L^{-1}$.

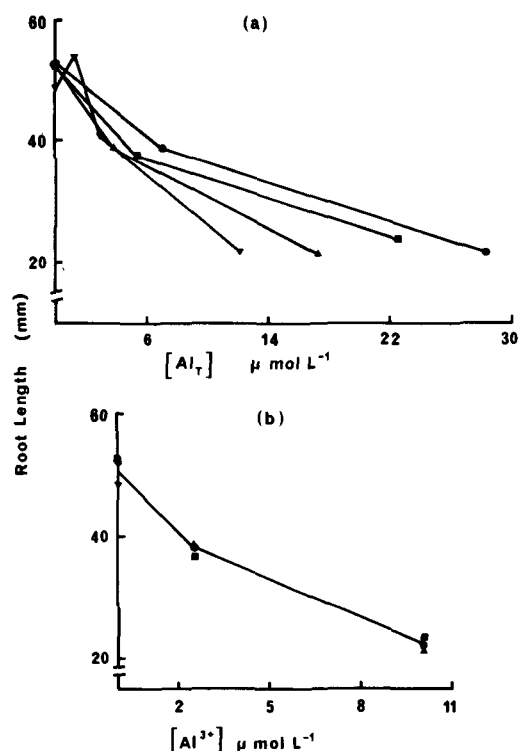


Fig. 5. The variation in root length of barley with (a) $[Al_T]$ and (b) $[Al^{3+}]$ in the presence of 0 (▼), 1000 (▲), 2100 (■), and 3300 (●) $\mu mol SO_4^{2-} L^{-1}$.

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