

SOIL TESTS FOR ALUMINUM TOXICITY IN THE PRESENCE OF ORGANIC MATTER: LABORATORY DEVELOPMENT AND ASSESSMENT

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ABSTRACT: Al toxicity in plants is related to the activity of Al^{3+} and Al-hydroxy monomers in the soil solution, whereas Al complexed with ligands such as fluoride (F), sulphate (SO_4^{2-}), and oxalate is not toxic. Estimation of toxic Al relies on measurement of "labile" Al after short contact times with colorimetric reagents or cation-exchange resins. However, shifts in equilibrium may result in non-toxic forms of Al reacting with the complexing agent or resin.

A series of laboratory experiments tested the degree to which labile Al is related to Al^{3+} in simplified media and compared methods of estimating labile Al in the presence of organic ligands and in soils. Cation-exchange resins extracted more than the theoretical concentration of Al^{3+} from solutions containing a range of concentrations of OH^- and SO_4^{2-} . More Al was extracted in 15 s by 8-hydroxy-quinoline than by Chelex-100 from solutions of Al-humate at pH 4. In sands which had been spiked with Al and organic matter, the estimation of labile Al varied with both the method of measurement and type of extract. The cations present in commonly used soil-extracting chloride solutions can decrease the proportion of organically complexed Al.

INTRODUCTION

An important criteria for the selection of a soil test is that the extraction method and subsequent analytical determination should extract and measure the concentration of the forms of aluminum (Al) that are correlated with reductions in plant growth. In addition, both steps of the determination should be simple and suitable for routine use. Unfortunately, these two criteria are not necessarily compatible when soil tests are selected for Al toxicity.

With respect to the first criteria, research has indicated that Al toxicity is related to the activity of Al^{3+} and Al-hydroxy monomers in the soil solution, whereas Al complexed with ligands such as fluoride (F), sulphate (SO_4^{2-}) and oxalate is not toxic (1,2,3). Nuclear magnetic resonance (NMR) is the only truly direct method of measuring the concentration of Al^{3+} without disturbing the equilibrium. However, NMR lacks the sensitivity required to measure Al^{3+} at the concentrations thought to be marginally toxic to plants ($< 50 \mu\text{M}$). The next best alternative is to use indirect methods which measure the proportion of Al which reacts with a colour-forming complexing reagent (eg., 8-hydroxyquinoline, pyrocatechol violet) or a cation-exchange resin during a short contact time. These estimates of Al are often referred to as "labile Al" and are considered to be correlated with the concentration Al^{3+} and Al-hydroxy monomers. Their main disadvantage appears to be that they disturb the Al equilibrium in solution and the complexing agent or resin reacts with forms of Al that are not toxic to plants. Nevertheless, they remain one of the only options available and therefore it is necessary to assess whether different analytical methods are capable of estimating a concentration of Al that is correlated with toxic Al.

Recent work has shown the importance of soluble organic ligands in controlling the concentration of Al^{3+} (3,4). However, in order to determine whether an analytical method is capable of distinguishing between organically complexed Al and free Al, it is necessary to have soils in which the extent of such complexing can be established by some independent means. This problem can be

partially overcome by using pure solutions of humic acids (4), but caution should be exercised in extrapolating these results to soil solutions which may contain other cations and anions. Sand-peat mixtures which are less refined than humic acid may provide a link between pure solutions and natural soils. In such mixtures, the organic matter is from a common source and therefore a measure of soluble carbon (C) can be used as an indicator of the amount of organic-complexing ions in solution if one assumes complexing capacity is proportional to the concentration of soluble C. Even though absolute complexing cannot be determined, relative complexing can be estimated from soluble C and from knowledge of pH effects on complexing from pure solution studies. The Al extracted by an analytical method would be expected to be negatively correlated with soluble C as long as there was not too great an excess of either Al or soluble C.

Another problem with estimating toxic Al is the extraction method. Extraction by a large volume of a salt solution is simple and more easily adapted to routine use than extracting the soil solution. However, it is not known if the proportion of complexed Al extracted by salt solutions in the presence of soluble organic ligands is similar to that found in soil solutions. Moore and Ritchie (5) found that Al extracted by salt solutions was not a good indicator of Al^{3+} in soil solutions containing fluoride.

The objectives of our work were twofold. First, we sought to assess the ability of two indirect methods of estimating labile Al, a cation-exchange resin and 8-hydroxyquinoline (8-HQ), to distinguish between uncomplexed Al and Al complexed with soluble organic ligands in pure solutions, sand-peat mixtures, and peaty sands. The second objective was to ascertain if complexed and total Al (Al-tot) extracted by $CaCl_2$ and $LaCl_3$ was correlated with that in the centrifuged soil solution. In order to achieve these objectives, we also had to develop extraction and analytical techniques that were suitable for use with soils.

MATERIALS AND METHODS

Method Development and Forms of Al Extracted by Cation-Exchange Resins:

A column method of removing resin-extractable Al (Al-res) was developed and, in two experiments (A and B), compared with the stirred-suspension method of Campbell et al. (6), which is unsuitable for soil solutions because large volumes are required. The effects of the type of resin, the exchanging cation, and the presence of anions on the amount of Al removed by the column method were also investigated.

The columns consisted of 5 ml Oxford autopipette tips plugged with acid-washed polyester aquarium filter and contained 1g of moist resin. Two 5 mL aliquots of solution were pipetted into the column, which was then allowed to drain under gravity into an acid-washed vial after the first 10 drops of effluent were discarded. This weight of resin was found to be sufficient to remove all the Al from a solution of AlCl_3 at pH 4 with a concentration of Al in excess of that used in the subsequent experiments at similar flow rates. The concentration of Al in the samples was determined before and after contact with the resin.

The resins used were Chelex-100 (50-100 mesh, expts. A-D; 100-200 mesh, expts. E and F; Bio-Rad, California, USA) and Dowex 50W-X8 (20-50 mesh, BDH Chemicals, Poole, Dorset, UK). They were cleaned by suspending the beads in successive solutions of 1 M NaOH and HCl, followed by deionised water. The sequence was repeated several times. The H form of the resin was then converted to the appropriate cationic form by suspension in successive aliquots of a solution of the chloride of Ca (0.0017 M) or Zn (0.1 M) until the solution reached the desired pH.

Experiment A: In experiment A, we studied the effects of time and three concentrations of humic acid (HA; 0, 4, and 20 mg/L) on the removal of Al from a solution at pH 4.5 by two types of resin (Chelex-100 and Dowex 50W-X8), using the column and stirred-suspension methods.

The humic acid was extracted from a peat soil with cold NaOH (7). A stock solution was prepared as described by Ritchie et al. (4) and the pH adjusted to 4.0 by stirring with H-saturated Dowex 50W-X8 resin. Aliquots of 200-1000 μ l of a 500 μ M AlCl_3 stock solution were diluted to 80% of final volume and then sufficient humic acid stock solution was added to give final concentrations of 0, 4, and 20 mg/L HA. The pH of each solution was adjusted using 0.1 M or 0.01 M HCl or KOH and then made up to volume with deionised water acidified to the same pH. Each solution was brought in contact with the two resin types by both the column and stirred-suspension methods. Contact time in the columns was controlled by restricting the flow by attaching hypodermic needles to the tips of the columns. In the stirred-suspension method, subsamples were withdrawn through a filter attached to a syringe at intervals from 1 minute to 7 hours after adding the resin.

Experiment B: In experiment B, solutions containing three concentrations of Al (20, 40, and 80 μ M) and five of HA (0, 50, 100, 200, and 400 mg/L), all at pH 4, were reacted with Chelex-100 in columns and stirred suspensions. The experiment was a complete factorial design except that samples containing 50 mg/L HA and 20 or 80 μ M Al were omitted. The solutions were made as described in the previous experiment. Each solution remained in the stirred suspensions for 60 minutes. In the column technique, the solutions took approximately 5 minutes to flow through the columns under gravity, giving a contact time of 15-20 seconds as calculated from the flow rate and void volume in the resin bed (8). This procedure was used in subsequent experiments.

Experiment C: We studied the effect of 4 pHs (4.0, 4.5, 4.75, and 5.0) and five concentrations of SO_4^{2-} on the removal of Al from solution by two types of resin with two different exchanging cations (Ca/H and Zn/H), using the column method. The resins and solutions were prepared as described previously. Sulphate was added to the solutions by adding aliquots of a 0.5 M K_2SO_4 stock solution sufficient to give final concentrations of 0, 500, 1500, 3000, and 5000 μ M total SO_4^{2-} . The ionic strength was adjusted to 0.015 M in all solutions with KCl.

The speciation of Al in solution was estimated from the total concentrations and pH using the computer program Microql (9) and Qelios (10). The formation of AlOH^+ , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and AlSO_4^+ were considered and the thermodynamic formation constants were taken from Lindsay (11).

Al-Organic Matter Reactions in Solution: Experiment D: The labile Al extracted in 15 s by 8-HQ (12) from the Al-humate solutions prepared in experiment B was compared with the labile Al extracted by the column resin method described above. The 8-HQ method differed from that of James et al. (12) in that separation of the butyl acetate was aided by centrifugation and Al in the butyl acetate was determined by GFAAS.

Al-Organic Matter Reactions in Sand-Peat Mixtures: Experiment E: We measured soluble C, pH, Al-tot, and labile Al (Table 1) in a sand amended with four additions of peat (0.5%-4% w/w) and six concentrations of Al, 0-200 $\mu\text{g/g}$ (Table 1).

The sand was from the C horizon (1-2 m) of a Gavin sand, Uc2.22 (13) from the Bassendean Sand Association described by Bettenay et al. (14). The sand was mixed with peat ("Compeat", Magnet Industries, Western Australia) which had been finely ground, acid-leached, and partially neutralised with KOH, to give sand-peat mixtures that were 0%, 0.5%, 1.0%, 2.0%, and 4.0% w/w peat. Al was added to the soil as AlCl_3 at pH 4 in a volume sufficient to wet the sand-peat mixture to 18% w/w water content and at a concentration to achieve the rates of addition given in Table 2. The mixtures were incubated for 16 h at 60° C and then dried at 60° C for approximately one week and divided into two equal portions. Soil solutions of approximately pH 4 were prepared by wetting the mixtures to 18% w/w moisture content with dilute HCl or KOH solutions containing sufficient H^+/OH^- as estimated from pH buffer curves for each treatment combination. After incubating the mixtures for 16 h, treatments were divided into five subsamples. The soil solution was extracted from one sample by the method of Gillman (15). Three subsamples were shaken with 0.0017 M and 0.01 M CaCl_2 and 0.00083 M LaCl_3 at a soil:liquid ratio of 1:5 for 1 h. The remaining sample was shaken with

TABLE 1: Al Additions ($\mu\text{g/g}$) to Sand-Peat Mixtures (Expt. E) and Peaty Sands (Expt. F).

Al $\mu\text{g/g}$	Peaty Sands (% Org C)				Sand + peat (% w/w)			
	Joel B (0.2)	Gav (0.6)	Joel A (1.2)	Mung (2.2)	0.5	1	2	4
0	x	x	x	x	x	x	x	x
0.1								
1								
2	x		x		x			
4	x			x	x			
8								
10	x	x	x	x	x	x	x	x
15	x							
20	x	x	x	x	x	x	x	x
40		x						
50			x	x	x	x	x	x
100		x	x	x		x	x	x
200		x				x	x	x

TABLE 2. Analyses for Each Type of Extract of the of Sand-Peat Mixtures (Expt. E) and Peaty Sands (Expt. F).

Analysis	Soil Solution	Extracts			
		1:5		1:20	
		CaCl ₂ 0.01M	0.0017 M	LaCl ₃ 0.00083 M	BaCl ₂ 0.1 M
Al-res	x				
Al-HQ	x	x	x	x	
Al-tot	x	x	x	x	x
Org-C	x	x	x	x	x
pH	x	x	x	x	x

0.1 M BaCl₂ at a soil:liquid ratio of 1:20 for 1 h. The soil solution and the four extracts were then centrifuged, filtered (0.45 µm), and analysed for pH, Al-tot, Fe, Ca, and C by ICPES and labile Al-res using Chelex-100 in the Mg/H form and Al-HQ (Table 2).

Al-Organic Matter Reactions in Soils: Experiment F: We measured pH, soluble C, Al-tot, Al-res, and Al-HQ in five soils amended with six rates of Al (0-200 µg/g, Table 2). The soils were four peaty sands, naturally acidic (pH 3.5-4.6 in 1:5 0.01M CaCl₂) with low CEC (4-8 cmolc/kg) and a range of organic C contents (Table 2). They have been described in detail by Bettenay et al. (14) and Smith (16). The preparation of the soils and their subsequent extraction and analysis were the same as in the previous experiment.

Chemical Analyses: Al-tot and Al in solutions which had been in contact with ion exchange resin were measured by graphite furnace atomic absorption spectrophotometry (GFAAS) or inductively coupled plasma emission spectrophotometry (ICPES). The pH was determined with a combination electrode using a Beckman Ø 71 or an Orion EA940 pH meter.

RESULTS

Experiment A: In solutions containing 5 µM Al at pH 4.5, stirred suspensions of both Chelex-100 and Dowex 50W-X8 removed most of the Al from solutions with no humic acid within 60 minutes (Figure 1a, b). However, in the presence of 20 mg/L HA (Al:COO⁻ mole ratio 1:4), uptake of Al by the resins continued for at least 7 hours (Figure 1c). The rate of uptake by the Chelex-100 resin diminished from approximately 1 µM/h in the first hour to an average of approximately 0.1 µM/h for the last 4 hours. In the case of Dowex 50W-X8, the rate of uptake was approximately 0.5 µM/h for the first hour and an average of approximately 0.02 µM/h for the last 4 hours.

Chelex-100 removed more Al from solution than did Dowex 50W-X8 when humic acid was present. For example, after 60 min Chelex-100 removed 21% of

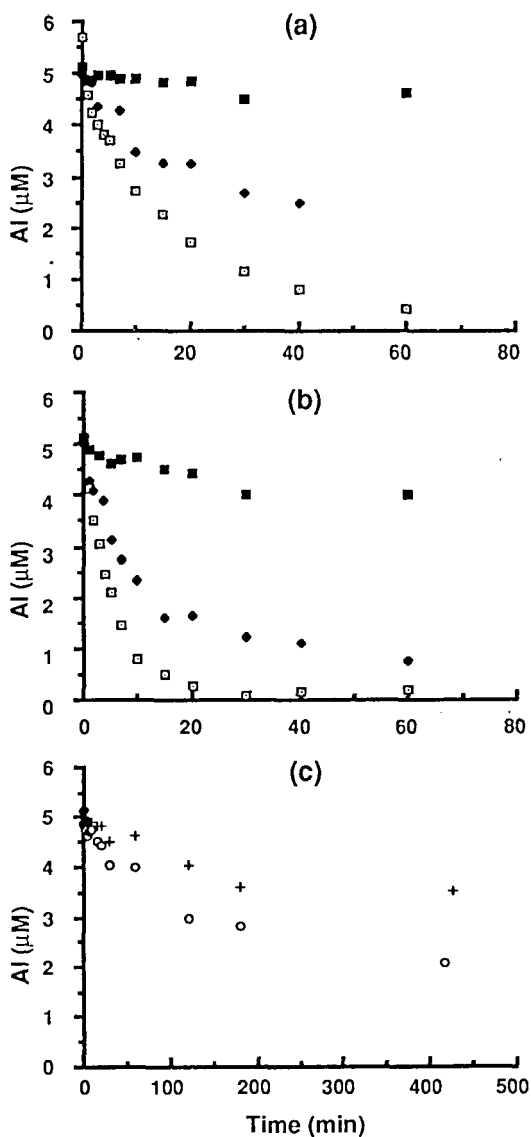


Figure 1. Removal of Al by stirred suspensions of (a) Dowex 50W-X8 and (b) Chelex-100 from a solution of 5 μM Al with 0 HA (□), 4 mg HA/L (◆) and 20 mg HA/L (■) at intervals up to 60 minutes, and (c) over approximately 7 hours from the 20 mg HA/L solution by Dowex 50W-X8 (+) and Chelex-100 (○).

total soluble aluminum in the presence of 20 mg/L HA, whereas the Dowex resin removed only 10% of the Al.

When the same solution of Al and humic acid as used in stirred suspensions of resin was passed through the columns of the resin, the proportion of Al removed (from 5 μM Al, 20 mg/L HA) by Chelex-100 at 3 s and Dowex 50W-X8 at 5-13 s (Figure 2) was similar to that removed by the stirred suspensions of Chelex and Dowex, respectively, at 60 minutes. As the contact time was increased, a greater proportion of Al was removed from solution.

Experiment B: Al removed by Chelex-100 was the same in columns with a contact time of 15-20 s as in a stirred suspension after 60 min (Figure 3).

Experiment C: Al removed by both Chelex and Dowex in the Ca/H form was independent of pH between 4.0 and 5.0, whereas the theoretical estimate of the concentration of Al^{3+} decreased fivefold (Figure 4a). Similarly, the Al removed by both resins did not vary as the total sulphate concentration was increased from 0-5000 μM , even though the theoretical estimate of $[\text{Al}^{3+}]$ decreased from 46 to 20 μM and $[\text{AlSO}_4^+]$ increased from 0-30 μM (Figure 4b). Similar results were obtained when the Zn/H form of the resins was used.

Al-Organic Matter Reactions in Solution: Experiment D: In the comparison between methods of fractionating Al in synthetic solutions of Al and humic acid at pH 4, there was a reasonably good correlation between Al-HQ and Al-res using Ca/H Chelex-100 in the column method ($r^2 = 0.92$). The ratio of Al-HQ:Al-tot was greater than the ratio of Al-res:Al-tot, and the difference between these methods of estimating labile Al increased as the ratio of Al (μM):C (mg/L) increased (Figure 5).

Al-Organic Matter Reactions in Sand-Peat Mixtures: Experiment E: In the soil solution, soluble C decreased exponentially as the additions of Al increased and increased with the percentage of peat present (Figure 6a). Total soluble Al remained approximately the same (0.5% peat) or increased slightly (1%-4% peat) as Al added to each mixture increased. The only exception was a sharp increase in the concentration of Al observed with the addition of 200 $\mu\text{g/g}$ Al to the 1%

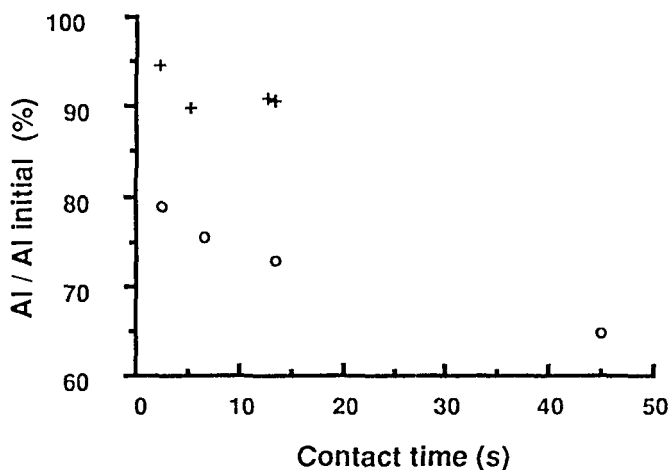


Figure 2. The effect of contact time on the proportion of Al removed from a solution of 5 μM AlCl_3 at pH 4.5 by Dowex 50W-X8 (+) and Chelex-100 (o) in columns.

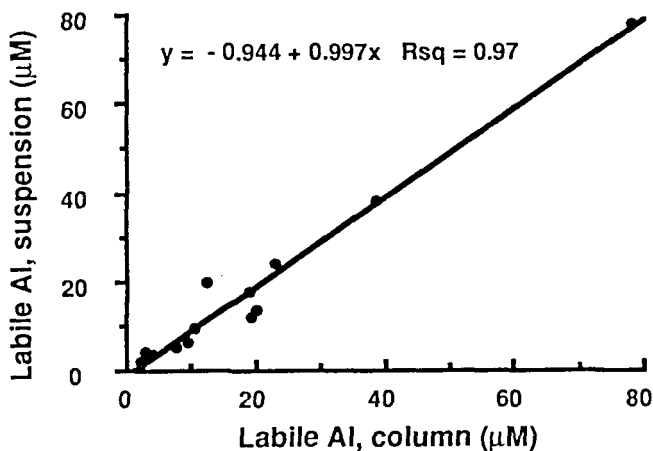


Figure 3. The relationship between Al removed from solutions of AlCl_3 at pH 4 by Chelex-100 with a contact time of 60 minutes in a stirred suspension and 15-20 seconds in columns.

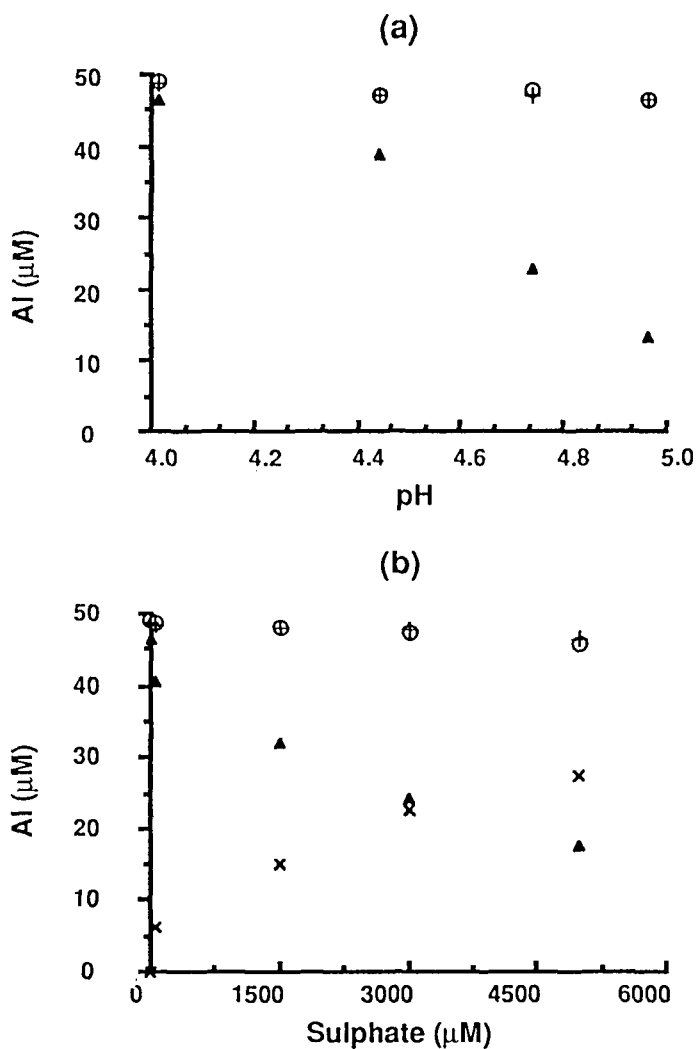


Figure 4. Labile Al (μM) by Chelex-100 (\circ) and Dowex 50W-X8 (+) in columns and calculated concentrations (μM) of Al^{3+} (\blacktriangle) and AlSO_4^+ (\times) plotted against (a) pH and (b) concentration of sulphate.

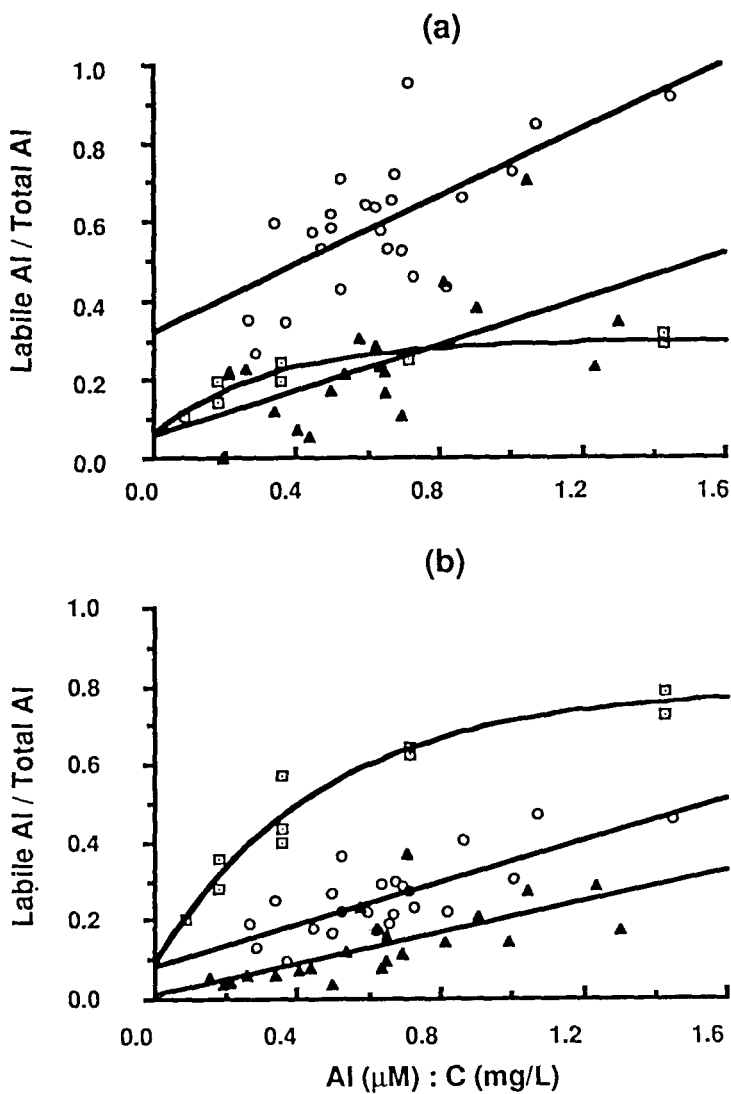


Figure 5. Labile Al (μM) as a proportion of total Al (μM) plotted against the ratio of Al (μM): organic C (mg/L) for (a) Chelex-100 and (b) 8-Hydroxyquinoline in humic acid solutions (\square), sand-peat mixtures (\blacktriangle), and peaty sands (\circ) at $\text{pH } 4.0 \pm 0.1$ with a range of Al additions.

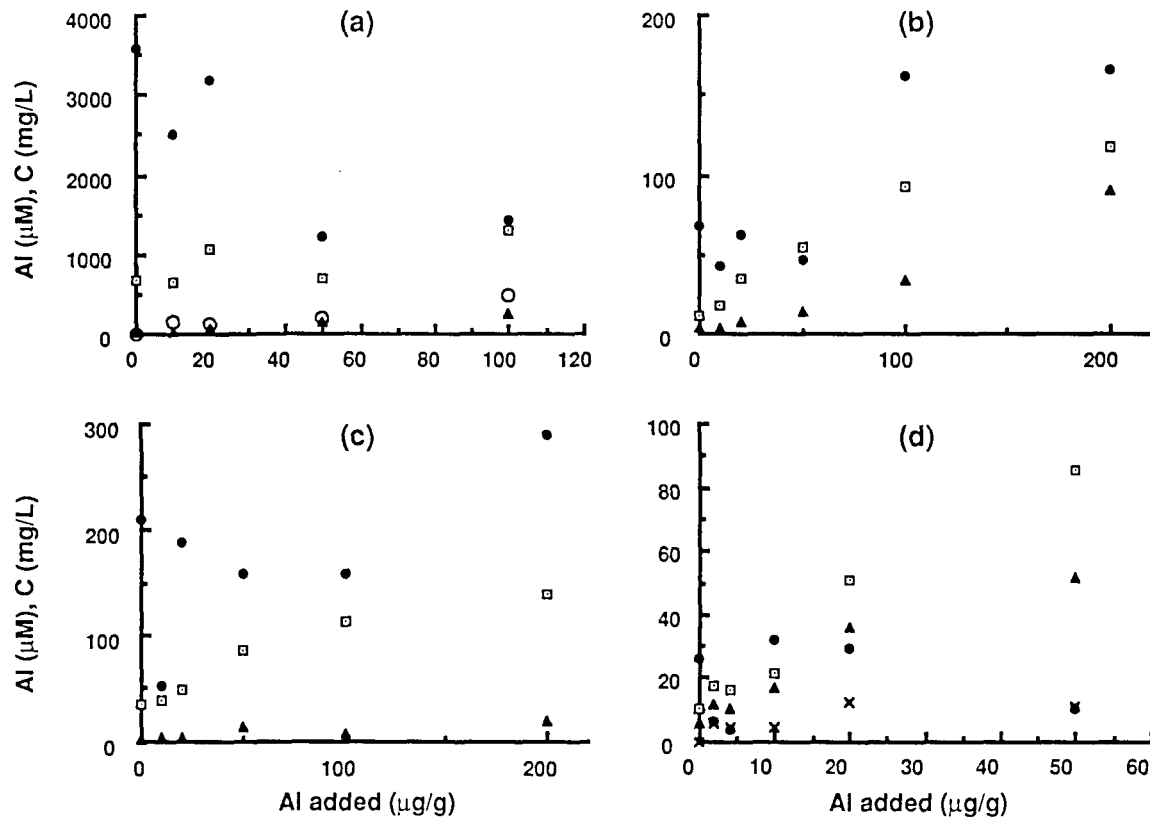


Figure 6. The effect of added Al (μg on the concentration of Al (μM) and C (mg/L) in sand-peat mixtures: soil solution, 2% peat (a), 1:5 0.01 M CaCl₂, 2% peat (b), 1:5 0.0017 M CaCl₂, 4% peat (c) and 1.5 0.00083 M LaCl₃ and 1:20 0.1 M BaCl₂, 0.5 % peat (d). Symbols are Al-tot (□), Al-res (○), Al-HQ (▲), Al-tot in BaCl₂ (×), and organic C (•).

peat mixture, which coincided with an unexpected decrease in pH. Al-HQ was < 10% of Al-tot and tended to remain constant as total Al added to the sand-peat mixtures increased. Al-res was slightly greater than Al-HQ and remained constant (0.5% peat) or increased with Al added (1%-4% peat). The proportion of Al that was labile increased linearly with the ratio Al (μM):C (mg/L) (Figure 5).

In the CaCl_2 extracts, soluble C in the sand-peat mixtures with 0.5% peat and both Al-tot and Al-HQ in all the mixtures followed similar trends to the values found in the soil solution. At higher percentages of peat additions, however, soluble C varied inconsistently at the higher additions of Al (Figure 6b, c). Soluble C tended to be lower in the presence of small additions of Al than in the presence of large amounts of Al.

In the LaCl_3 extracts, both Al-tot and Al-HQ increased with Al added to the sand-peat mixtures, but Al-tot increased at a greater rate than did Al-HQ (Figure 6d). Soluble C did not show any consistent trends with Al added. Al-tot in the BaCl_2 extracts increased slightly with Al added at the 0.5% peat addition (Figure 6d).

The concentration of Al-tot in the soil solution of the sand-peat mixtures was reasonably well correlated ($r^2 > 0.70$) with total Al in the 0.017 and 0.01 M CaCl_2 extracts but not with Al-tot extracted by La and BaCl_2 (Table 2). It was also well correlated with Al-res, and Al-HQ in the 0.017 and 0.01 M CaCl_2 and LaCl_3 extracts (Table 2).

The concentration of Al-HQ in the soil solution was not well correlated with Al-res in the soil solution or Al-HQ in the chloride extracts (Table 2). It was, however, well correlated with Al-tot extracted by BaCl_2 and LaCl_3 . In contrast, Al-res was well correlated with Al-HQ in the CaCl_2 and LaCl_3 extracts (Table 2) and was also well correlated with Al-tot extracted by LaCl_3 and 0.01 M CaCl_2 .

Al-Organic Matter Reactions in Soils: Experiment F: Even though the soils were all sandy by texture, the variation in Al, pH, and C in their soil solutions and the extracts was not always similar.

The pH remained at 4.0 ± 0.1 (Figure 7) except for Joel A, in which the pH

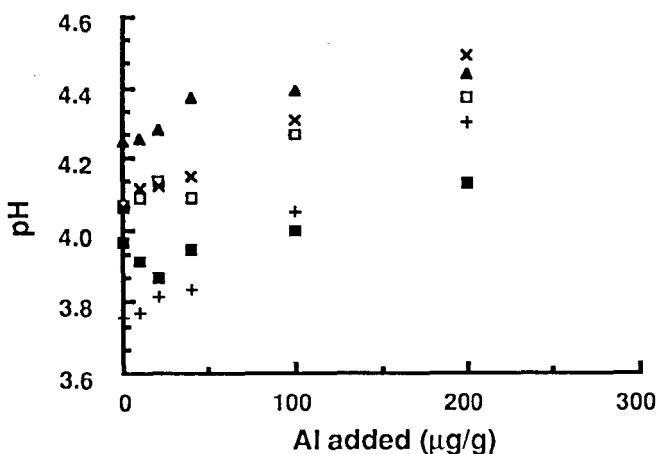


Figure 7. pH in the soil solution (■), 1:5 0.0017 M CaCl₂ (▲), 1:5 0.01 M CaCl₂ (□), 1:5 0.00083M LaCl₃, and 1:20 0.1M BaCl₂ (×) of Gavin peaty sand as affected by the addition of Al (μg/g).

decreased to 3.85 at the highest Al addition. Al-tot, Al-res, and Al-HQ in the soil solution all increased linearly as the added Al increased (Figure 8a), except for the Mungite soil in which they decreased initially and then became constant. The resin extracted a greater proportion of Al-tot than did the 8-HQ, and the proportion increased as the ratio Al (μM):C (mg/L) increased (Figure 5). Soluble C tended to remain constant (Figure 8a) in all the soils or increase slightly (Joel B). In the CaCl₂, LaCl₃, and BaCl₃ extracts, Al-tot increased very slightly and Al-HQ did not change much as added Al increased (Figure 8b-d). Soluble C remained constant except at the highest Al addition when there was a large increase in the Gavin, Joel A (LaCl₃ only), Joel B (0.01 M CaCl₂ only), and Mungite (0.01 M CaCl₂ and LaCl₃ only) soils. The pH values of the extracts were all higher (except for the LaCl₃ extracts for soils other than Joel A with Al added < 50 μg/g) than

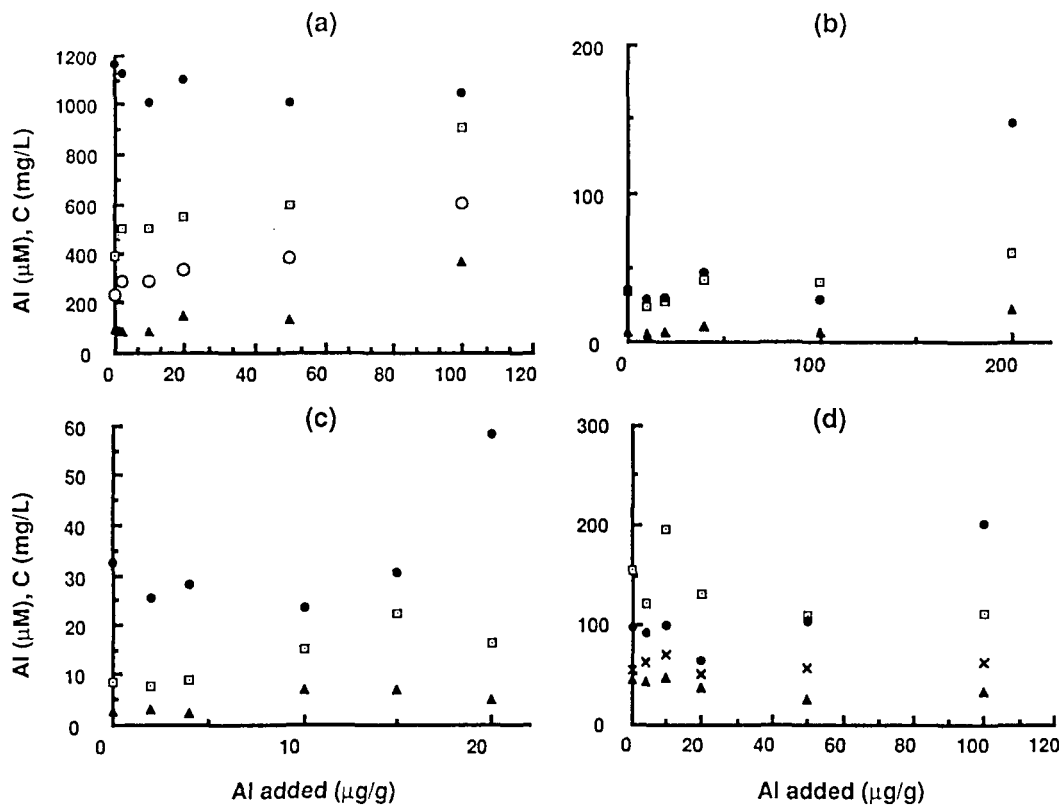


Figure 8. The effect of added Al on the concentration of Al (μM) and C (mg/L) in peaty sands: soil solution, Joel A (a), 1:5 0.0017 M CaCl₂, Gavin (b), 1:5 0.01 M CaCl₂, Joel B (c) and 1:5 0.00083 M LaCl₃ and 1:20 0.1 M BaCl₂ (d). Symbols are Al-tot (□), Al-res (○), Al-HQ (▲), Al-tot in BaCl₂ (×), and organic C (•).

that of the soil solution and increased approximately 0.1 - 0.45 units as added Al increased (Figure 7). For the Joel B soil, there was a large increase in pH (0.5 - 0.7 units) at the highest Al addition.

Al-tot in the soil solution was correlated ($r^2 > 0.70$) with Al-tot in the 0.01 M CaCl_2 , LaCl_3 , and BaCl_2 extracts and with Al-HQ in both CaCl_2 extracts (Table 3). It was also correlated with Al-res but not Al-HQ in the soil solution. The latter was well correlated ($r^2 = 0.86$) with only one other measure of labile Al (Al-HQ in 0.01 M CaCl_2) and was also correlated with Al-tot in 0.01 M CaCl_2 and LaCl_3 .

DISCUSSION

The forms of aluminum extracted by the resin and by 8-HQ were not the same in either the humic acid or the soil solutions. In addition, the concentration of Al in the different forms did not change in a similar manner when Al or peat was added to the soils or to the sand-peat mixtures. Labile Al in the extracts was not well correlated with labile Al in the soil solution, possibly because the cation of the extracting solutions precipitated soluble C under certain circumstances. Therefore, no uniform relationship was observed between Al-HQ in the soil solution and that in any of the extracts. In contrast, Al-tot in the soil solution was correlated with Al-tot in the extracts, but this measure of Al is not necessarily related to plant growth.

Method Development: Columns of Ca/H saturated Chelex-100 could be substituted for the more time-consuming and cumbersome stirred-suspension method of estimating rapidly labile Al, provided a contact time of < 20 s could be attained.

Similar results were achieved with the Zn/H form of the resins, indicating that selective blocking of uptake of $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{SO}_4)^+$ by the resin is not possible. This may be because these monomeric species occur between Al^{3+} and Zn^{2+} in the series of relative affinities for Chelex-100, $\text{Cu}^{2+} \gg \text{Pb}^{2+} > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Ag}^+ > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} \gg \text{Na}^+$ (17) or the equilibria $\text{Al}^{3+} = \text{Al}(\text{I})^{(3-n)+}$, where I = inorganic ligand of valence -n, shifts rapidly

TABLE 3. Correlation Matrix (r^2) for Al-tot and Labile Al in Different Types of Extracts for Sand-Peat Mixtures (1st row) and Peaty Sands (2nd row).

		Total					8-HQ				Resin	
		S	C ₁	C ₂	L	B	S	C ₁	C ₂	L	S	
Total	S	-										
	C ₁	0.75 <	-									
	C ₂	0.84 0.76	0.89 0.86	-								
	L	0.69 0.73	0.77 0.80	0.90 0.88	-							
	B	0.64 0.74	0.81 0.80	0.87 0.82	0.88 0.86	-						
8-HQ	S	0.64 <	< <	< 0.72	0.73 0.73	0.89 <	-					
	C ₁	0.84 0.85	< <	0.75 0.73	0.74 <	< <	< <	-				
	C ₂	0.84 0.77	0.69 0.69	0.86 0.88	0.88 0.84	0.70 0.76	< 0.86	0.95 0.80	-			
	L	0.75 <	< <	0.72 <	0.78 <	< <	< 0.65	0.97 <	0.95 <	-		
Resin	S	0.87 0.76	0.68 <	0.83 0.67	0.81 0.77	0.64 0.65	< <	0.97 <	0.98 0.73	0.93 <	-	

S = Soil Solution
 B = 1:10 0.1 M BaCl₂
 C₁ = 1:5 0.0017 M CaCl₂
 C₂ = 1:5 0.01 M CaCl₂
 L = 1:5 0.00083 M LaCl₃
 < = r^2 less than 0.64

to the left as the Al^{3+} is removed from solution.

Forms of Al Extracted by Resins: The fraction of total aluminum removed by both exchange resins was greater than that attributable to Al^{3+} and included Al which would have been in the form of both inorganic and organic (humate) complexes before the resin was added. In experiments A and C most of the Al in solution was taken up by the resins very quickly even though hydroxy and sulphate complexes of Al were present. Campbell et al. (6) found that inorganic complexing of Al by OH^- and F^- had little effect on the proportion of Al removed from solution by Chelex-100.

Removal of Al by the resins from Al-humate solutions (experiments A and B) was much slower than from solutions containing only inorganic ligands. This suggests that dissociation of Al-humate occurred before uptake by the resin and that resins can compete with soluble ligands that have a high affinity for Al as long as the complex dissociates very readily. Campbell et al. (6) found that Chelex-100 removed 10% of total soluble Al in the presence of 20 mg/L HA at pH 5.0. This slightly smaller proportion in comparison with our results could be due to the higher pH used in their work increasing the complexing capacity of the humic acids compared with that at pH 4.5 used in our work. For example, Ritchie et al. (4) found that humate could compete more effectively with fluoride for Al at pH 6 than at pH 4.

There seems little scope for using cation-exchange resins in this manner to predict the phytotoxicity of Al in the presence of sufficiently high concentrations of inorganic ligands such as F^- and SO_4^{2-} , which have been shown to reduce Al toxicity in barley seedlings (2).

Comparison of Al Removed from Humic Acid Solutions by Chelex-100 Resin and 8-Hydroxyquinoline: 8-HQ extracted a greater proportion of Al-tot than did Chelex-100 from the Al-humate solutions (experiment D). As the ratio of mole of Al:HA increased, the ability of both methods to extract Al decreased (Figure 5), possibly because Al-humate polymers and/or colloids had formed and thus decreased the proportion of rapidly labile Al.

Exclusion of large molecules from the pores of the Chelex-100 (18) and the ability of 8-HQ to mix more intimately than Chelex-100 with polymers and fine colloids could account for the large difference between these two methods at high Al:HA ratios. This could be relevant to (centrifuged) soil solutions, even when they are filtered through 0.45 μm for analysis, and therefore choice of method of measuring rapidly labile Al may be important in attempting to measure phytotoxic Al in the presence of organic ligands over a range of Al:organic ligand ratios.

Labile Al in Humic Acid Solutions and the Soil Solution of Peaty Sands and Peat-Sand Mixtures: In soil solutions of peaty sand the proportion of Al extracted by Chelex-100 was greater than that extracted by 8-HQ (Figure 8a) but was approximately the same in the sand-peat mixture with a similar organic C content (Figure 6a). This contrasts with the humic acid solutions in which Al-HQ was greater than Al-res (Figure 5). A comparison of the proportions of Al extracted by each method plotted against the ratio of Al (μM) : C (mg/L) in the humic acid and soil solutions indicated that Chelex-100 extracted a greater proportion of Al from the soil solutions of peaty sands than from humic acid and the soil solutions of sand-peat mixtures, while 8-HQ extracted more Al from humic acid solutions than from both types of soil solution (Figure 5). Both Chelex-100 and 8-HQ extracted more labile Al from the peaty sands than from the sand-peat mixture.

The interaction between the method of measuring labile Al and the source of organic matter is not explained by this experiment. Some possible explanations can be eliminated. The difference in mesh size and form of Chelex-100 used (Ca/H form, 50-100 mesh for HA; Mg/H form, 100-200 mesh for soil solution) could explain the difference between peaty sands and humic acid. However, the greater proportion of Al extracted from solutions containing humic acid by the larger diameter resin (experiment A) compared with that taken up by the smaller diameter resin used by Campbell et al. (6) indicates that some factors other than size of resin particle are controlling the amount of Al which can exchange with Chelex-100 at any particular pH.

The higher proportion of Al-res at any particular Al (μM):C (mg/L) ratio in the soil solution of the peaty sands compared with that in the sand-peat mixtures or the humic acid solutions (Figure 5a) may be due to a higher proportion of Al complexes in the peaty sands with molecular weights low enough to exchange more readily than Al-humate with Chelex-100. The acid-leaching process may have removed most of the low molecular weight ligands from the peat, so that Al-humate and Al-fulvate, which exchange at similar rates with Chelex-100 (6), were the predominant forms of organically complexed Al in the sand-peat mixtures. Although Hodges (19) reported that in solutions containing Al (8-80 μM) and citrate (1mM) at pH 4.2, Al passed through columns of Rexyn 101, his results are inconclusive because the columns were reused without removing Al accumulated from previous samples. This work has shown that Al complexed with small organic ligands may be taken up by Chelex-100 as completely as is Al which is complexed with OH^- or F^- (6) and OH^- or SO_4^{2-} .

The increasing proportion of Al-HQ at any Al (μM):C (mg/L) ratio in the soil solutions of sand-peat mixtures, peaty sands, and the humic acid solutions, respectively (Figure 5b), corresponds with a decrease in Al and C concentrations (data not shown). This inverse relationship between the concentrations of Al and C and the proportion of Al-HQ but not Al-res at a constant Al (μM):C (mg/L) ratio suggests that the organic ligands are interfering with the 8-HQ assay in a way which is independent of the proportion of Al complexed with the ligands. This could occur if the organic ligands interfered with the formation of the Al-HQ complex and/or decreased the extraction of Al-HQ into the butyl acetate when the reaction is quenched. Controls for colour interference in the spectrophotometric determination of Al-HQ indicated that no soil organic matter or humic acid was extracted into the butyl acetate when 8-HQ was omitted from the assay solution.

Aluminum-Organic Matter Reactions in Sand-Peat Mixtures: At a constant pH, Al-tot in the soil solution of the sand-peat mixtures was a function of soluble organic matter, whereas Al-tot in the salt extracts was also controlled by the presence of the salt cation. Ritchie et al. (20) found that calcium could precipitate

humic acid by electrostatic attraction at molc of calcium:humate < 1, whereas Al precipitated humic acid by complexing at molc of Al: humate > 1.

At a constant pH and high peat additions (> 1%), Al-tot in CaCl₂, BaCl₂, and LaCl₃ extracts are not good indicators of Al-organic matter complexing in the soil solution because the cation of the salt solution can cause soluble organic matter to precipitate and hence change the extent of complexing between Al and organic ligands. Al-HQ in the soil solution was not well correlated with Al-HQ in the CaCl₂ and LaCl₃ solutions, whereas Al-res was linearly related with Al-HQ in the salt extracts.

The poor correlation between Al-HQ in the soil solutions and that in the 1:5 extracts may be due to overestimation of organically complexed Al in the soil solutions with high concentrations of Al and organic C (because of possible interference as outlined above) and underestimation of organically complexed Al in the 1:5 extracts where the equilibrium has been disturbed by the extracting cation.

The good correlation between Al-res and Al-HQ in the extracts suggests that both these methods underestimate the proportion of Al which is organically complexed. Nevertheless, Al-HQ in the soil solution may still be a better estimation of toxic Al than ion exchange resin, provided the concentration of potentially interfering organic compounds is low.

Al-Organic Matter Reactions in Soils: The concentration of Al in solution was affected by pH, the presence of Ca, and adsorption of Al. The amount of Al in 1:5 extracts in salt solutions was only proportional to that in the soil solution when Ca did not precipitate organic ligands or when the pH of the extract changed in a similar manner to that in the soil solution.

The addition of Al to the Gavin soil caused a marked increase in Al in the soil solution even though pH and soluble C remained reasonably constant. The increase in Al concentration was presumably because of a lack of adsorption sites. In the CaCl₂ extracts, there was little change in Al-tot or Al-HQ with Al addition and soluble C increased only at the highest Al addition, possibly because Ca was

precipitating soluble organic matter until the Al concentration was high enough to compete with the Ca to form a soluble organic complex.

In the two Joel soils, the variation of Al-tot, Al-HQ, and C with addition of Al was fairly similar in the soil solution and the CaCl₂ extracts. Soluble C was much higher than in the Gavin soil and hence there was probably insufficient Ca to cause precipitation of soluble organic matter.

The major factor controlling soluble Al in the soil solution of the Mungite soil appeared to be pH. In the CaCl₂ extracts, however, the effect of pH may have been decreased by the presence of Ca. Even though the pH in the extracts increased with Al added, Al-tot did not decrease as much as could be expected from the pH change. This may have been due to precipitation of organic matter by Ca at the lower additions of Al limiting the formation of organic Al complexes. As more Al was added, it was able to successfully compete with the Ca to form a soluble complex with organic ligands and hence the Al concentration did not decrease as much as may be expected from the concurrent drop in pH.

CONCLUSION

Aluminum that reacts with 8-HQ and with resins includes forms that are thought not to be toxic to plants. The forms of Al extracted by large volumes of salt solutions are not necessarily equivalent to the forms in the soil solution because the extracting cation may cause precipitation of a ligand with which some of the Al would have been complexed and hence would become non-toxic. The concentration and form of Al after it has been added to soils is controlled by pH, adsorption, and precipitation.

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