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Effect of soil pH on Al availability in soils and its uptake by the soybean plant (*Glycine max*)

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Abstract

A greenhouse experiment was designed to investigate the effects of soil pH and other soil properties on the availability of Al and its uptake by the soybean plant. Three soils were compared that were developed over three contrasting bedrock types. These soils were (1) a sandy loam over Devonian shale; (2) a sandy loam over granite; and (3) a loamy sand over the Lower Greensand. The natural pH of the soils ranged from 4.2 to $\ll$ 5.5 and each soil was also amended to give two other pH levels using elemental sulphur and/or calcium carbonate. The solubility of the Al in the soils, and hence its availability to the plants, was estimated using extraction with 0.02 M $CaCl_2$ and 0.05 M EDTA prior to determination by ICP-AES. The Al concentrations in the plant materials were similarly determined after acid digestion with concentrated nitric and perchloric acids. In the comparison between two empirical extractants, the best predictor of soil Al available for uptake into the soybean plant was found to be 0.02 M $CaCl_2$. This relationship appears to be linear. The amounts of extractable Al in the soils and the uptake of Al by the soybean plants both increased as the soil pH decreased. These relationships are both non-linear with marked increases in extractability and uptake when the soil pH falls below 4.4. It is concluded that the speciation of Al in the soils changes at this pH value, and that the specie of Al taken up by soybean plants is the Al^{3+} ion, which is the only stable Al ion at a pH of less than 4.4. Soil pH has been identified as the major factor that controls the uptake of Al from soil into the soybean plant.

1. Introduction

The soybean plant (*Glycine max*), economically one of the most important leguminous plant in the world, has been found to contain higher concentrations of Al than other major food plants, up to 210 μg/g (dry weight basis) (Sartain and Kamprath, 1978). Aluminum toxicity to the soybean plant, on the other hand, is believed to be a problem only in acid soils (pH < 5.0) (Foy, 1974). However, the general state of knowledge regarding the biochemistry of Al still contains some important gaps. For example, there is no general agreement as to whether or not Al is an essential element in plant nutrition. An element so abundant would not be expected to be in short supply for any terrestrial species, in any event (Hem, 1969). The solubility of Al is very low over the normal range of soil pH values (5.0–7.0), and only below pH 5 is Al^{3+} the dominant Al species in soil solution. It is for this reason that research into plant availability of Al in soils has almost always been undertaken in acid soils.

Bowie and Thornton (1985) indicated that there is no one value for the "availability" of a given element in a given soil, and indeed the concept of "availability" is difficult to define, and is now regarded rather critically. Even more emphatically, there is no one extrac-

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Table 1
Some properties of the soils used in the pot experiment. Values are given as the mean ± standard deviation

Soil No.	Parent material	Soil series	Soil group	Total Al (μg/g) [a]	Clay (%)	LOI (%) [b]	CEC (meq.100/g) [c]
1	Devonian shale	Bridford complex	Brown earth	54200 ± 1090	13.1	9.2 ± 0.3	31.4 ± 1.5
2	granite	Moreton- Hampstead	Brown earth	61700 ± 1270	13.4	10.0 ± 0.2	25.4 ± 1.5
3	Lower Greensand	Bearsted	Brown earth	4880 ± 113	4.1	3.0 ± 0.1	9.1 ± 0.3

[a] $n = 8$.
[b] Loss on ignition, $n = 5$.
[c] Cation exchange capacity, $n = 6$.

tant solution which can be used to test a soil and which can always define the "availability" of a given ion.

Availability of Al in soils is commonly evaluated by the extraction of a fraction of the total Al by chemical reagents. The selection of extracting solutions has often been based on experimental rather than theoretical considerations. Moreover, the analytical results are influenced by operating conditions such as the soil/solution ratio, extraction time, soil properties, chemical form or matrix of Al present in the soil (Hoyt and Nyborg, 1971; Clark, 1965; Bache, 1974; Little, 1964; Jarvis, 1986). Hoyt and Nyborg (1971, 1972) reported that Al dissolved in dilute $CaCl_2$ solution correlated with the barley yield. Hume et al. (1988) reported that the yield of white clover (*Trifolium repens*) above ground was more highly correlated with 0.02 M $CaCl_2$-extractable soil Al than with exchangeable Al (extracted with 1 M KCl) or with pH. The amounts of Al extracted with dilute $CaCl_2$ did not appear to be related to soil organic matter content, nor to the other soil properties except soil pH (Jarvis, 1986).

Numerous studies have been performed regarding Al uptake and distribution in plant tissue or in whole plants. The soil factors affecting the amounts of metal absorbed by plants, as summarised by Alloway (1990) and Bowie and Thornton (1985), are those controlling: (1) the concentrations and chemical forms of metal in the soil solution, and (2) the movement of metal from the bulk soil to the root surface. Therefore, elemental speciation in soil solution is a major factor in controlling the availability and uptake of various essential and non-essential elements including Al by plants (Mattigod and Page, 1983). Kubota (1983) indicated that soil pH is a factor that strongly influences the release of mineral elements to plants. Examining Al uptake by multilamellar phospholipid vesicles, maximal Al uptake was strongly dependent on the lipid composition of the liposome and the pH of the suspension medium. Characterized by an Al uptake maximum in the range from pH 4.0 to 5.0, low pH in the suspension medium facilitated Al entry into vesicles composed of dimyristoyl phosphatidylcholine (DMPC) and acidic phosphatidylserine (Haug and Shi, 1991).

The objectives of this study are as follows: (1) to investigate the effects of soil pH on extractable Al in soils and the uptake of Al from soil into soybean plants; (2) to identify Al species associated with the Al available for uptake into soybean plants.

2. Experimental methods

A soybean cultivar Major[1] was grown in a greenhouse at 25°C over a period of two months. Three soil types were collected. Those were a sandy loam over Devonian shale, a sandy loam over granite, and a loamy sand over the Lower Greensand. Some properties of the soils used for the experiments are listed in Table 1.

In order to understand the effect of pH on Al availability, each of the three soils was amended to give two other pH levels. As appropriate, the pH was lowered by adding finely divided elemental sulphur to dry soil, or it was raised using powdered calcium carbonate (Merry et al., 1986). Equilibrium conditions in the amended soil were achieved by leaving the water-saturated soil in the greenhouse for 30 days before planting. Soil pH was monitored periodically during this period, and also at the end of harvesting using a method described by Avery and Bascomb (1974). The ranges

[1] Soybean seeds were produced by Rusrica Semineces, Toulouse, France and supplied by Harlow Agricultural Merchants, Letchmoor Bank, Little Hallingbury, Bishops Stortford, Herts CM22 7PJ, UK.

Table 2
pH of soils at the completion of pot experiment

Treatment [a]	Sulphur	Soil (unamended)	$CaCO_2$
Soil No. 1	4.34 (1.6)	5.38	6.21 (4.0)
2	4.35 (1.6)	5.47	6.26 (4.0)
3		4.21	5.10 (2.0); 6.12 (4.0)

[a] Figures in brackets indicate rate (g/pot) of elemental sulphur and calcium carbonate applied to each pot. The pH is the mean value of the measurements from five pots.

of soil pH in the natural and amended soils at the end of the experiment are shown in Table 2.

The method used to estimate cation exchange capacity has been described by Hesse (1971), in which Na is used as the exchange ion. The procedure of measuring organic matter in soils is that described by Avery and Bascomb (1974), and Ball (1964). Total Al in the soil was estimated using a digestion with a mixture of concentrated acids (HNO_3, $HClO_4$ and HF) (Thompson and Walsh, 1983).

The pot trial was set up with three soil types, each under three pH conditions and each replicated five times, in randomised blocks. This resulted in a total of 45 pots. The variance of the measurements was determined using five replicates of each soil treatment. This then enabled the statistical significance of the difference between results for each soil treatment to be established. Growth of the soybean plants was optimized by applying specially prepared fertilizer to each pot (Armiger et al., 1968). The fertilizer was applied twice, 20 and 50 days after planting. N (80 mg), P (87 mg) and K (110 mg), as NH_4NO_3 and KH_2PO_4, were applied to each pot, which contained 1.6 kg of air-dry soil. The pots were watered with deionized water to keep the soil moisture approximately equal to that found in the field, (i.e. 20–25% w/w). After two months, whole plants were harvested at 5 cm above the soil level to avoid soil contamination (Dong et al., 1993).

The plant materials were rinsed thoroughly with deionised water to reduce surface contamination, dried at 30°C, weighed, then ground prior to chemical analysis. Care was taken at each stage to minimize any Al contamination from either the laboratory procedures used or from the laboratory atmosphere. Soils were also collected from the pots after the plants were harvested. They were dried at 30°C. Representative soil samples for determining "available" Al and soil pH were air-dried, and then disaggregated to pass a 2 mm mesh sieve prior to chemical analysis.

"Available" Al in soils was extracted with two different reagents, 0.05 M EDTA (Farmer et al., 1980; Jarvis, 1986) and 0.02 M $CaCl_2$ (Bache, 1974; Hoyt and Nyborg, 1971, 1972; Jarvis, 1986). The Al concentration held in the plant materials was determined following a nitric and perchloric acid digestion (Ramsey et al., 1991; Dong, 1993). The Al concentration in all of the extracts was then determined by ICP-AES at 308.2 nm and reported on a dry weight basis. The relevant instrument condition for determination of Al by ICP-AES and the estimate of accuracy and precision have been described previously (Ramsey et al., 1991).

3. Results and discussion

3.1. *Effects of soil amendments on pH*

Amending the soils produced an increased range of pH values as would be expected (from 4.2 to 6.3, see Table 2). Calcium carbonate was applied to all the three soils, which were originally developed over Devonian shale (No. 1), granite (No. 2) and the Lower Greensand (No. 3). For the latter, two levels of calcium carbonate were used. Elemental sulphur was applied to the first two soils, but not to the Lower Greensand (No. 3) soil, because it was already acidic.

The amendment of the soil pH resulted in significant differences in both the concentrations of soil extractable Al and the Al uptake of the plants between the soil treatments, as discussed below. The Al uptake of the soybean plants grown on the soils amended with elemental sulphur was significantly higher than that in the plants grown on either the unamended soils, or the soils amended with calcium carbonate. High concentrations of extractable Al in the soils (extracted with both 0.02 M $CaCl_2$ and 0.05 M EDTA) were also found in the soils which were amended with elemental sulphur. It is possible to suggest that the sulphur itself may affect the uptake of Al, rather than by its effect on soil pH. However, the effect of soil pH on Al uptake also occurred in the Lower Greensand soil (No. 3) with an originally low pH value that was amended only with calcium carbonate, not sulphur. For this soil, a high concentra-

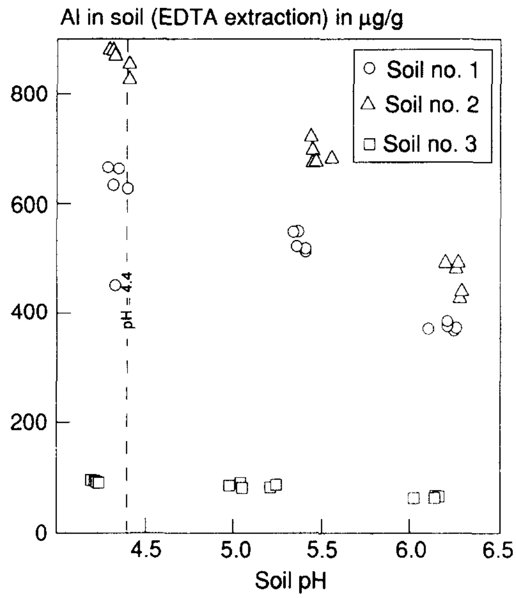


Fig. 1. Relationship between concentrations of extractable Al in soils extracted by 0.05 M EDTA and soil pH.

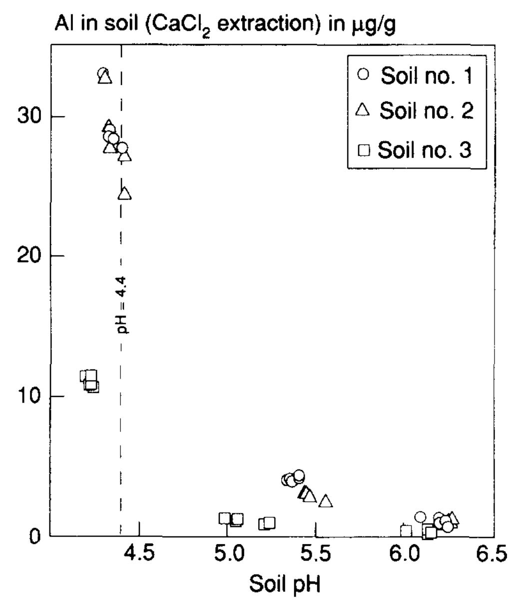


Fig. 2. Relationship between concentrations of extractable Al in soils extracted by 0.02 M $CaCl_2$ and soil pH.

tion of extractable Al and high amounts of Al being taken up by the soybean plant is evident at the low pH values. These results suggest that the increased extractable Al in the soils, and the increased Al uptake by the soybean plant grown in the amended soils, are due to the lowered soil pH rather than to the effect of the sulphur itself.

3.2. The effect of soil pH on extractable Al in soils

The average concentrations of "available" Al in the soils of each soil treatment extracted by 0.05 M EDTA ranged from 66.1 to 867.6 $\mu g/g$ (Fig. 1) and that extracted by 0.02 M $CaCl_2$ ranged from 0.19 to 29.84 $\mu g/g$ (Fig. 2). The concentrations of the extractable Al in the soils extracted by both 0.02 M $CaCl_2$ and 0.05 M EDTA were the function of soil pH. Generally, both concentrations increased with decreasing soil pH (Figs. 1 and 2). However, the amount of extractable Al in the soils extracted with 0.02 M $CaCl_2$ was much less than that extracted with 0.05 M EDTA, by more than a factor of ten. This was probably because organic complex of Al in soils could be released by EDTA but not by dilute $CaCl_2$ (Jarvis, 1986; Farmer et al., 1980).

The concentration of extractable Al in the soils extracted with 0.02 M $CaCl_2$ increased markedly when the soil pH fell below a value of around 4.4. This statistically significant increase was also found in the relationship between the soil pH and the concentration ratio of 0.02 M $CaCl_2$ extractable Al to total Al in the soils (Fig. 3). It seems probable that these trends reflect changes in the speciation of the Al in the soils at this pH value. It would seem a reasonable hypothesis that the species of Al extracted by 0.02 M $CaCl_2$ was dominantly the Al^{3+} ion, which is the most stable form of

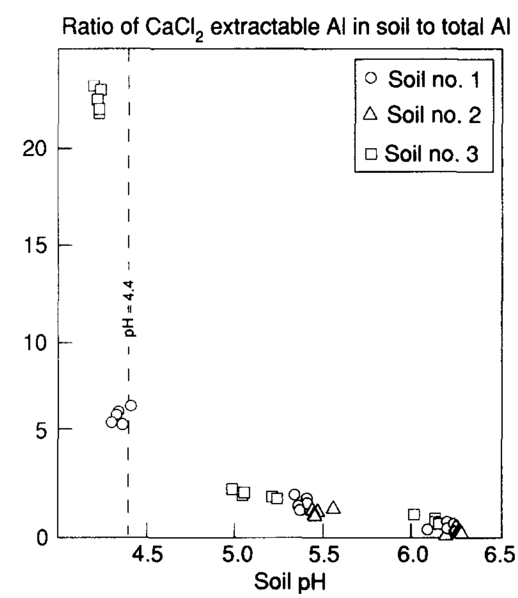


Fig. 3. Relationship between soil pH and the concentration ratio of 0.02 M $CaCl_2$ extractable Al to total Al in soils.

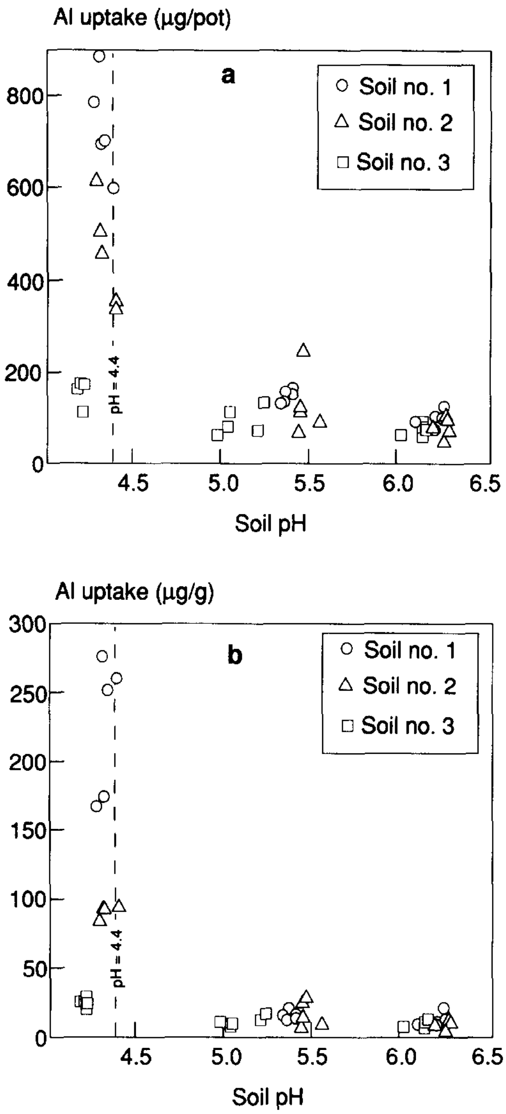


Fig. 4. Relationship between uptake of Al by soybean plants and soil pH. (a) when expressed as absolute weight of Al in the plant (μg/pot); (b) when expressed as concentration of Al in the plant (μg/g).

Al and the dominant ion at pH of less than 4.4 (for [Al^{3+}] at 10^{-6} M) (Brookins, 1988; Rosseland et al., 1990).

The amounts of extractable Al in different soil types with similar pH were found to be markedly different. This may be due in part to other soil factors including Al mineralogy.

3.3. The effect of soil pH on the Al taken up by the soybean plant

The variations found for Al uptake between soil treatments are significantly greater than random variations. The average uptake of Al by the whole plant (total uptake) ranged from 79.4 to 748.8 μg/pot or 10.6 to 213.9 $\mu g/g$ (Fig. 4). The Al uptake increased markedly with decreasing soil pH for all three soil types. The correlation coefficient between soil pH and the Al uptake by the soybean plants is statistically significant at $p = 0.001$ (Table 3). However, there is a marked increase of the uptake when soil pH falls below 4.4 (Fig. 4). Comparison of this trend with the relationship between soil pH and extractable Al in the soils extracted by 0.02 M $CaCl_2$, suggests that the species of Al taken up by the soybean plant was dominantly the Al^{3+} ion. This is in agreement with the results reported by Pavan and Bingham (1982). They found that coffee seedling growth and leaf Al concentrations were closely related to $Al^{3+} \cdot 6\,H_2O$ activities in nutrient solution. Moore et al. (1990) found that Al^{3+} activities in solution were negatively correlated with rice growth rates in the growth-chamber study, and also with the yields of rice from the field study.

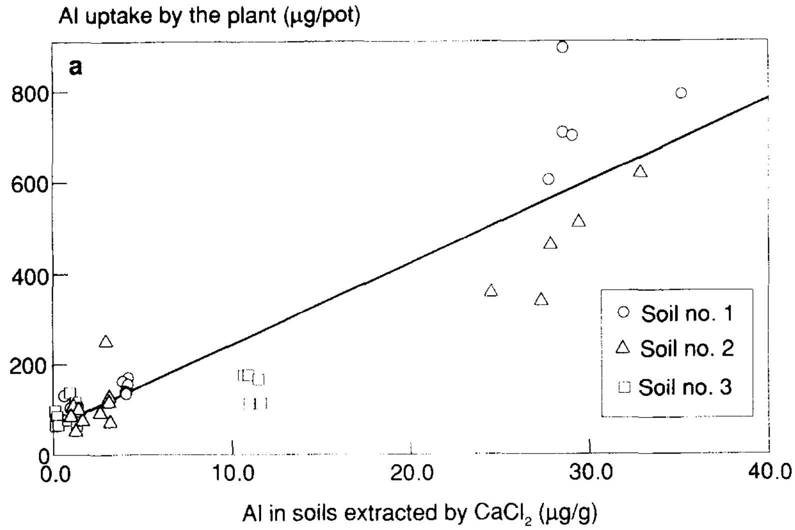
3.4. Relationship between extractable Al in the soils and the uptake of Al by the soybean plant

The uptake of Al by the soybean plant is predicted by both the concentrations of Al in the soils extracted by 0.02 M $CaCl_2$ and that extracted by 0.05 M EDTA with a stronger relationship to the former reagent (Table 3). A similar situation has been reported for alfalfa plant by Hoyt and Nyborg (1971, 1972).

Table 3
Correlation coefficients between Al in soybean plants and soil geochemical factors for the results between the soil treatments in the pot experiment ($n = 45$)

	Al uptake by plant	
	(μg/g)	(μg/pot)
Soil pH	-0.58^{***}	-0.65^{***}
Al in soil extracted by $CaCl_2$	0.83^{***}	0.92^{***}
Al in soil extracted by EDTA	0.43^{**}	0.53^{***}

** and ***: r values statistically significant at $p = 0.01$ and 0.001, respectively.



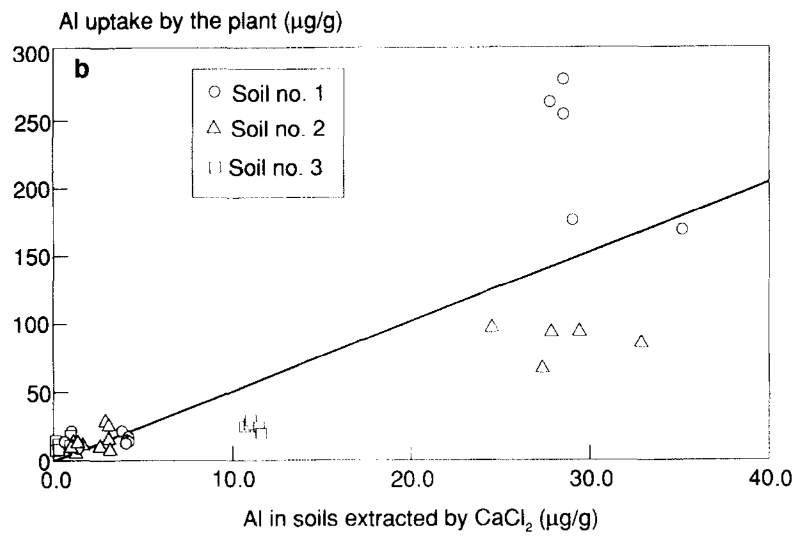


Fig. 5. The uptake of Al by the soybean plant predicted by the concentrations of extractable Al in the soils. (a) the uptake of Al by the plant expressed as absolute weight of Al (μg/pot); (b) the uptake of Al by the plant expressed as the concentration of Al in the plant (μg/g).

The relationship between the amounts of Al taken up by the soybean plant and the concentration of Al extracted from the soils by 0.02 M $CaCl_2$ was found irrespective of whether the measured uptake was expressed as absolute weight of Al (μg) or as the concentration of Al in the plant (μg/g).

If the Al uptake by the plant is expressed as the absolute weight of Al in the plant, the correlation coefficient is significant ($r=0.92$, $p=0.001$). In this case the relationship is shown in Fig. 5a and the equation obtained from regression for this relationship is given below:

$$[\mathrm{Al}]_{\mathrm{plant}\ (\mu\mathrm{g/pot})} = 62.00^{***} + 17.88^{***}[\mathrm{Al}]_{\mathrm{soil}\ (\mathrm{CaCl_2})}$$

(*** coefficient statistically significant at $p=0.001$).

When the Al uptake by the plant was expressed as the concentration of Al in the plant, this relationship also appears to be linear (Fig. 5b), with a correlation coefficient of 0.83 ($p=0.001$). The equations for this relationship are:

$$[Al]_{plant\ (\mu g/g)} = 5.07^{***}[Al]_{soil\ (CaCl_2)}$$

(*** coefficient statistically significant at $p=0.001$).

These results suggest that the amount of Al in the soils extracted by 0.02 M $CaCl_2$ may be regarded as "plant-available" Al.

4. Conclusions

In the comparison between two empirical extractions, the uptake of Al by the soybean plants was best predicted by the amount of Al in the soils extracted by 0.02 M $CaCl_2$, rather than by 0.05 M EDTA. The relationship between the Al uptake and the 0.02 M $CaCl_2$ extractable Al in soils appears to be linear. It does not vary significantly whether the Al uptake is expressed as absolute weight of Al (μg) or as the concentration of Al in the plant (μg/g). Therefore, the amount of Al in soils extracted by 0.02 M $CaCl_2$ may be regarded as the best estimate of "plant-available" Al.

The concentration of Al in the soils extracted by 0.02 M $CaCl_2$ always increased with decreasing soil pH. This is a non-linear relationship with a sharp increase when the soil pH falls below approximately 4.4. This is likely to reflect that the speciation of Al in the soil changes, and the concentration of the specie or species of Al available to be taken up by the soybean plant increases sharply at that pH value.

The uptake of Al by soybean plants also increased as the soil pH decreased. This is also a non-linear relationship with a marked increase at a pH less than approximately 4.4. This suggests that the dominant species of Al in the soils available for uptake into the plant is the Al^{3+} ion, which is the most stable Al species at a pH of less than 4.4, as indicated from thermodynamic data.

Soil pH has been identified as a major factor controlling the uptake of Al from soil into the soybean plant.

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