0014-4754/94/070701-03$1.50 + 0.20 © Birkhäuser Verlag Basel, 1994

Plant uptake of aluminium from calcareous soils

G. Tyler

University of Lund, Department of Ecology, Soil Ecology Group, Östra Vallgatan 14, S-223 61 Lund (Sweden)

Received 12 October 1993; accepted 28 January 1994

Abstract. Concentrations of Al in leaf tissue of plants growing on limestone soils (pH ca. 8) are similar to, or do not deviate much from, concentrations in plants growing on acid silicate soils. Aluminium concentrations in the topsoil solution are at least one order of magnitude lower in limestone than in acid silicate soils. Plants seem to absorb Al quite efficiently under moderately alkaline soil conditions. Possible mechanisms for this are discussed.

Key words. Aluminium; aluminate; plant uptake; calcareous soil; limestone; pH.

Considerable interest has been devoted to aluminium in plants under acid conditions, since aluminium toxicity is a well-known problem in plant production on acid soils[1,2]. Growth of wild plants may be inhibited at Al ion concentrations as low as 10–20 μM[3,4]. However, little attention has been paid to the availability and plant uptake from Al from moderately alkaline, e.g. calcareous soils.

Several ionic species of Al occur in soil solutions, their nature, concentrations and proportions being principally a function of pH. At $\mathrm{pH} < 4$, phytotoxic Al^{3+} predominates and may attain high concentrations. At pH 5–6, $Al(OH)_2^+$ is the predominant species, the solubility of which is lower. At pH 7 the concentration of Al is minimal, but as the pH rises above neutrality $Al(OH)_4^-$ appears at low concentrations, and this is the only species of monomeric ionic Al in a solution of pH 8 (ref. 5). The solubility of $Al(OH)_4^-$ increases greatly towards more alkaline soil conditions but its predominance is gradually taken over by $Al(OH)_5^{2-}$ in highly alkaline solutions[6]. Variable ion matrices and concentrations may modify these relationships to some extent.

There are also a number of polymeric (polynuclear) species, which occur or have been calculated to occur in soil or nutrient solutions. A highly toxic Al_{13} species, having a charge of +7, might form in solutions under unstable pH conditions[7]. Aluminium chelates with organic acids, including charged chelates of carboxylic acids[8], are probably little available and not very phytotoxic[9, 10].

Magistad[11] suggested that one reason why strongly alkaline soils ($\mathrm{pH} > 9$) do not support good plant growth is the presence of soluble Al. Agricultural plants may accumulate high foliar concentrations of Al when grown on fly-ash at $\mathrm{pH} > 8.5$ (ref. 12). Jones[13], working with barley grown on fly-ash, demonstrated increased solubility and plant uptake of Al between pH 7 and pH 9. The Al concentration of *Avena sterilis* (shoots and roots) was greater in plants grown at pH 10 than at pH 4.5, which might indicate a preferential absorption in alkaline compared to acid medium[14]. A desert grass grown in hydroponic culture at pH 9.5 produced much less shoot biomass when 1 mM $Al(OH)_4^-$ was added[15]. Little seems to be known about Al uptake and concentrations in wild plants growing on limestone soils, which usually have a soil solution pH around 8. This paper reports some studies where foliar Al concentrations in plants from limestone and granite/gneiss sites are compared. Possible mechanisms of plant uptake of Al from calcareous soils are also discussed.

Materials and methods

Plants. For study 1 vegetation was sampled in mid-August at two acidic sites (grass-heath on podzol and beech forest on dystric cambisol) and one calcareous site (grassland on cretaceous rendzina) in Scania in southern Sweden. Each sample ($n = 5$ site^{-1}) consisted of the above-ground biomass of mixed grasses and herbs (usually 5–10 species) developed on 1 m^2 and cut at ca. 5 cm from the ground. In study 2, young (freshly formed) leaves of 8 plant species were sampled in late May in an Archaen limestone site and an adjacent granite site in southern Sweden; 5 samples per species and site, each composed of leaves from several individuals. In study 3, nine plant species were field-grown at one and the same site in south Sweden for 3 months (June–August). Using rhizomes or plants with roots and shoot biomass cut to ca. 20 mm, these species were then transplanted into one limestone soil and one acid gneiss soil; 5 individuals per species and soil. Leaves formed were sampled at the end of the experiment. In dicots the petioles were included in the analysis, whereas in monocots only the laminas were analyzed. Dry matter yields per plant (total shoot biomass) were also determined.

The plant materials were not washed before analysis. Vigorous shaking of freshly sampled leaves for 5 min with distilled water had only a marginal effect on the Al concentrations. Three species were tested: *Vincetoxicum* *hirundinaria*, *Geranium sanguineum* and *Quercus robur* ($n = 5$ of each) from the same sites as in study 2. 90 (SE 16)%, 91 (SE 10)% and 95 (SE 5)%, respectively, of the Al of unwashed samples was recovered in the washed subsamples.

All materials were dried for 1 week at 85 °C and (in the case of the bulky materials of study 1) ground in a stainless-steel mill (giving no Al contamination, according to tests on reference material). Subsamples of 1–2 g composed of whole (study 2–3) or ground (study 1) tissue were digested with 15–25 ml concentrated HNO_3 for total destruction of organic matter, excess acid was evaporated to 2 ml and the residue made up to 50 ml. Al was determined by flame AAS using a N_2O/acetylene flame.

Soil solutions. Topsoil (0–10 cm) from the limestone and the granite sites of study 2 were sampled from July to September. Soil solutions were obtained by high-speed centrifugation (12,000 rpm) of the freshly sampled and sieved (mesh size 6 mm) soils at field moisture (no water added), followed by ultrafiltration (Acrodisc, 0.2 μm). Organic C and HCO_3^- were determined by IR-technique (Shimadzu TOC-500), total Al by AAS, and 'quick reacting' Al (Al_r, essentially free ionic Al) by flow injection analysis according to Clarke et al.[16]. pH was determined electrometrically in aliquots prior to ultrafiltration.

In study 1, the 5 cm humus layer was sampled for electrometric determination of $pH(H_2O)$ in unfiltered solutions obtained by shaking 10 g of sieved soil at field moisture with 50 ml H_2O for 2 h.

Statistical treatment. Differences between means of Al concentrations in plants of different sites were examined using Tukey's test according to Zar[17], p. 186.

Results

The Al concentration of plant biomass from calcareous grassland was higher than for grass-heath on podzol, and similar to the concentration of biomass from beech forest on dystric cambisol (study 1; table 1). There were no species common to the three ecosystems, but the acid grass-heath and the calcareous grassland were both dominated by graminids.

Table 1. Aluminium concentrations (μmol g^{-1} dry weight) in the shoot biomass (grasses + herbs) from three vegetation/soil types in Scania, south Sweden, and $pH(H_2O)$ of the topsoil humus layer (0–5 cm).

Vegetation type:	Grass-heath	Beech forest	Grassland
Soil type:	Podzol	Dystric cambisol	Cretaceous calcisol
$pH(H_2O)$	4.2 ± 0.1a	4.7 ± 0.0b	8.1 ± 0.1c
Al in biomass μmol g^{-1}	3.2 ± 0.3a	4.9 ± 0.2b	4.7 ± 0.3b

Means ($n = 5$) ± SE with different letters differ ($p < 0.05$).

Table 2. Aluminium concentrations in young leaves of plants from a limestone site (topsoil $pH(H_2O)$ 7.8–8.3) and a granite site (topsoil $pH(H_2O)$ 4.1–4.9) in southeast Sweden.

Sites	Limestone	Granite
	Al, μmol g^{-1} dry weight	
Corylus avellana L.	2.07 ± 0.05b	3.33 ± 0.16a
Vincetoxicum hirundinaria Med.	1.15 ± 0.05	1.11 ± 0.05
Geranium sanguineum L.	1.48 ± 0.26	1.47 ± 0.20
Origanum vulgare L.	1.74 ± 0.08	1.78 ± 0.13
Polygonatum odoratum (Mill.) Druce	0.93 ± 0.04	1.18 ± 0.23
Prunus avium L.	1.48 ± 0.12b	1.96 ± 0.22a
Quercus robur L.	1.00 ± 0.07	1.29 ± 0.25
Rosa canina L.	1.15 ± 0.10	1.37 ± 0.12

Means ($n = 5$) ± SE with different letters differ ($p < 0.05$).

A more direct comparison between a calcareous and an acid site is possible in study 2, where only species common to both sites and leaves of similar sizes were selected (table 2). Recently formed early-summer leaves were generally lower in Al than the late-summer biomass of study 1. In most species no difference ($p > 0.05$) between the sites was detected; exceptions were leaves of *Corylus avellana* and *Prunus avium*, which had somewhat higher Al concentrations in the granite than in the limestone site. Total Al concentration of the soil solution was more than one order of magnitude higher and Al_r six times higher in the granite site (table 3), a difference which apparently had little influence on plant uptake. Soil solution concentrations of organic (mainly humic) acids, important chelators of Al, were almost similar in the two soils studied, whereas the limestone soil solution was probably oversaturated in HCO_3^-, as shown elsewhere[18].

Greater differences among Al concentrations were measured in mature leaves of field-grown plants developed from transplants to a limestone and a gneiss soil (table 4). Foliar concentrations were generally higher than those measured in the previous studies. Several of the plants had higher Al concentrations when grown in the limestone than in the gneiss soil; in only two species was the opposite found. No consistent difference in the foliar Al concentration of plants grown on the two soils was found, nor did any clear relationship exist between

Table 3. Chemical properties of ultrafiltered (0.2 μm) topsoil (0–10 cm) solutions obtained by centrifugation (12,000 rpm) of soil at field moisture, freshly sampled from a limestone ($n = 11$) and a granite ($n = 18$) site in southeast Sweden; July–September, 1992.

Site		Limestone	Granite
pH		7.8–8.3	4.1–4.9
Organic C,	mM	4.3 ± 0.6	5.0 ± 0.4
HCO_3^-	mM	2.9 ± 0.3	0.0
Al_t	μM	2.2 ± 0.2	35 ± 4
Al_r	μM	1.8 ± 0.2	11 ± 2

Al_t: total Al; Al_r: 'quickly reacting' Al. Means ± SE.

Table 4. Aluminium concentrations in mature leaves and dry matter yields of plants grown under field conditions in a limestone soil ($pH(H_2O) = 8$) and a gneiss soil ($pH(H_2O) = 4.5$). Means ($n = 5$) ± SE of Al concentrations with different letters differ ($p < 0.05$). Differences between yields are significant ($p < 0.05$) except in *Origanum vulgare* and *Hieracium umbellatum*.

Soil origin	Al, $\mu mol\ g^{-1}$ dry weight Limestone	Gneiss	Yield $plant^{-1}$ g Limestone	Gneiss
Agrostis canina L.	2.8 ± 0.5	2.0 ± 0.4	0.96 ± 0.10	1.24 ± 0.04
Artemisia campestris L.	4.6 ± 0.6b	7.8 ± 0.5a	0.48 ± 0.03	0.37 ± 0.01
Carex digitata L.	8.1 ± 1.0a	4.0 ± 0.6b	0.82 ± 0.03	0.59 ± 0.04
Hieracium umbellatum L.	33.0 ± 4.3a	15.7 ± 2.8b	0.52 ± 0.07	0.57 ± 0.08
Melica ciliata L.	3.3 ± 0.4	3.6 ± 0.5	0.77 ± 0.01	0.44 ± 0.08
Origanum vulgare L.	22.2 ± 4.1a	12.6 ± 3.2b	1.21 ± 0.30	1.05 ± 0.16
Rumex acetosella L.	17.0 ± 4.3	12.1 ± 3.6	0.45 ± 0.02	0.89 ± 0.02
Viola hirta L.	15.1 ± 3.5a	7.4 ± 2.4b	0.16 ± 0.02	0.09 ± 0.02
Lychnis viscaria L.	4.8 ± 0.7b	9.5 ± 0.9a	0.61 ± 0.02	1.06 ± 0.04

dry matter yields of the plants and their foliar Al concentrations.

A substantial uptake of Al from limestone soil has also been measured in greenhouse experiments designed for other purposes[19]. The foliar Al concentration of *Jasione montana* L. grown from seeds in an Archaean marble soil (pH 8; $CaHPO_4$ added to facilitate normal development) was 6.1 (SE = 0.2) $\mu mol\ g^{-1}$ (dry weight). Freshly formed leaves of *Carex pilulifera* L., *Holcus mollis* L. and *Veronica officinalis* L., grown from rhizomes in the greenhouse in an Ordovician limestone soil, contained 2.5 (SE = 0.1), 4.5 (SE = 0.1), and 11.3 (SE = 1.2) μmol Al g^{-1} (dry weight), which was similar to or more (*V. officialis*) than in plants of the acid field sites from where they originated.

Discussion

The study shows that Al concentrations in leaf tissue of plants growing on limestone soils, pH ca. 8, are similar to or do not deviate much from Al concentrations of plants growing on acid silicate soils.

If soil solution is the immediate source of Al in limestone plants, the amounts available would be expected to be really low, since soil solution concentration usually does not exceed ca. 2 $\mu mol\ L^{-1}$. However, mobilization rates from solid Al species are unknown. At pH 8, non-chelated monomeric Al presumably exists almost exclusively as $Al(OH)_4^-$ which, directly or indirectly, has to be taken up by plants to account for the tissue concentrations measured. A passive root uptake of $Al(OH)_4^-$ might be possible only when the exterior (soil solution) concentration exceeds the interior (intracellular) one, because living cells are negatively charged. This would imply an immobilization of Al in the roots or a rapid translocation in the plant.

As $Al(OH)_4^-$ has some structural similarity to $H_2PO_4^-$/HPO_4^{2-}, there is a possibility that it may be taken up by the same mechanisms as phosphate. However, the pH lability of the Al species and the root surface acidity of plants, which has also been measured or indicated in slightly or moderately alkaline media[13,15], make it far from evident that Al is actually taken up as the $Al(OH)_4^-$ species. One may argue that $Al(OH)_4^-$ may be transformed via uncharged $Al(OH)_3$ to cationic Al species prior to uptake. Immobilization as $Al(OH)_3$ at $pH < 7$ might be counteracted by the production of protons or soluble Al chelators. Transformation kinetics and the nature of possible carrier compounds probably decide which chemical form(s) really enters the plant. Kinraide[5] postulated the formation from $Al(OH)_4^-$ of a polymeric Al_{13} species in the acidic free space of roots in moderately alkaline medium. Research will have to show whether polymeric Al species really contribute to the Al uptake of plants growing on calcareous soils.

1 Foy, C. D., Chaney, R. L., and White, M. C., A. Rev. Pl. Physiol. *29* (1978) 511.
2 Andersson, M., Wat., Air, Soil Pollut. *39* (1988) 439.
3 Andersson, M., Envir. expl Bot. *32* (1992) 497.
4 Andersson, M. E., and Brunet, J., Pl. Soil *153* (1993) 243.
5 Kinraide, T., Pl. Physiol. *93* (1990) 1620.
6 Marion, G. M., Hendricks, D. M., Dutt, G. R., and Fuller, W. H., Soil Sci. *121* (1976) 76.
7 Kinraide, T. B., Pl. Soil *134* (1991) 167.
8 Cotton, F. A., and Wilkinson, G., Advanced Inorganic Chemistry. 5th ed. John Wiley & Sons, New York 1988.
9 Bartlett, R. J., and Riego, D. C., Pl. Soil *37* (1972) 419.
10 Hue, N. V., Craddock, G. R., and Adams, F., Soil. Sci. Soc. Am. J. *50* (1986) 28.
11 Magistad, O. C., Soil Sci. *20* (1925) 181.
12 Rees, W. J., and Sidrak, G. H., Pl. Soil *8* (1956) 141.
13 Jones, L. H., Pl. Soil *13* (1961) 297.
14 Zavas, T., Symeonidis, L., and Karataglis, S., J. Agron. Crop Sci. *167* (1991) 277.
15 Fuller, R. D., and Richardson, C. J., Envir. toxic. Chem. *5* (1986) 905.
16 Clarke, N., Danielsson, L.-G., and Sparén, A., J. envir. analyt. Chem. *48* (1992) 77.
17 Zar, G., Biostatistical Analysis. 2nd ed., Prentice-Hall, Englewood-Cliffs 1984.
18 Tyler, G., Ann. Bot. *71* (1993) 295.
19 Tyler, G., Ann. Bot. *73* (1994) 327.