

Review article

# Aluminium toxicity in declining forests: a general overview with a seasonal assessment in a silver fir forest in the Vosges mountains (France)

JP Boudot, T Becquer, D Merlet, J Rouiller

CNRS, Centre de Pédologie Biologique, UPR 6831 associated with the University of Nancy I,  
17, rue Notre-Dame-des-Pauvres, BP 5, 54501 Vandœuvre-lès-Nancy, France

(Received 22 June 1993; accepted 4 September 1993)

**Summary** — A general overview on Al toxicity to plants is given, including the following aspects: symptoms; mechanisms; mitigating environmental factors; and diagnostic possibilities. An Al toxicity index is proposed to replace the classical but poorly performant Ca/Al ratio and is used in a declining fir stand in the Vosges mountains (eastern France). A potential Al toxicity phase was observed in winter only, namely during the vegetation rest phase. As nutrient uptake is expected to be potentially low during this season, this finding suggests that Al toxicity is probably not strongly involved in the local forest decline. However, a low influence may occur with respect to the winter growth of mycorrhized fine roots.

**aluminium toxicity / aluminium speciation / acid rain / forest decline**

**Résumé** — La toxicité de l'aluminium dans les forêts dépérissantes. Connaissances générales et application au cas d'une sapinière vosgienne. Les auteurs passent en revue les principales connaissances portant sur la toxicité de l'aluminium vis-à-vis des végétaux. Un index de toxicité aluminique est proposé en remplacement de l'habituel rapport Ca/Al, très insuffisant. Son application au cas d'une sapinière dépérissante des Vosges permet de mettre en évidence l'existence d'une phase de toxicité aluminique potentielle en hiver. Les besoins en nutriments étant très faibles durant cette saison, cette phase n'a probablement qu'une influence mineure sur l'état dépérissant du peuplement. Un faible impact pourrait néanmoins être envisagé dans l'éventualité où les essences locales présenteraient normalement une croissance optimale de leurs racines fines mycorrhisées en hiver, comme cela a été établi pour une espèce américaine de sapin.

**toxicité aluminique / spéciation de l'aluminium / pluies acides / dépérissement forestier**

## INTRODUCTION

Two of the most striking features of acid soils are their high exchangeable Al content and their low base cation status. Although acid soils have proved to be unsuitable for a number of agricultural species, most of them have till now allowed the development of forest ecosystems. The natural occurrence of soluble, organically complexed Al has been recognized for many years in podzolic soils, where the translocation of organic forms of Al was repeatedly suggested and demonstrated (Kononova, 1961; Duchaufour, 1970; Bartoli *et al*, 1981; Nilsson and Bergkvist, 1983; David and Driscoll, 1984; Dahlgren and Uggolini, 1989; Baur and Feger, 1992; Berggren, 1992). The existence of soluble inorganic Al in acid brown soils, mainly arising from acidification due to biological processes (nitrification, mineralization of organic sulphur), is a more recent observation (Ulrich *et al*, 1980; Van Breemen *et al*, 1987; Nys, 1987; Becquer, 1991; Baur and Feger, 1992; Becquer *et al*, 1992). A number of forest trees have adapted to such chemical environments. Due to atmospheric pollution and related acid deposition, however, Al content in soil solution is now assumed to increase. Moreover, important changes in Al speciation are expected to occur in many acid ecosystems, with possible partial decomplexation of soluble organic Al due to pH decrease. High inputs in nitric, sulphuric and chlorhydric acids are nowadays quantified in a number of ecosystems throughout the world. Whether the vegetation will adapt to such environmental alterations is uncertain. The toxicity of soluble Al was clearly demonstrated for many agricultural species. More recently, it was hypothesized that Al toxicity was also involved in forest decline (Ulrich *et al*, 1980; Hüttermann and Ulrich, 1984).

This paper provides a general overview of Al toxicity to plants. An Al toxicity index will be then proposed and the occurrence of Al toxicity investigated in a declining silver fir (*abies alba* Mill) forest in the Vosges highlands.

## GENERAL OUTLINE OF ALUMINIUM TOXICITY TO PLANTS

Although some plants can accommodate high amounts of Al in their foliage without serious injury (as high as 1 350 mg Al·kg<sup>-1</sup> of dry needles in the case of *Picea abies* (L) Karst (Ogner and Teigen, 1980)), many species are sensitive to soluble Al in soil solutions, which can be highly toxic under certain conditions.

### *Symptoms of Al toxicity*

In a number of crop species, Al toxicity is indicated by a coralloid morphology of the root system, which exhibits scarce root hairs, scarce, short and thick secondary roots and short, swollen, stubby and gnarled primary roots. Root tips may additionally turn brown in the most severe circumstances and, as for tree species, the above-ground organs may wilt and die due to inhibition of water uptake (Foy, 1984; Arp and Strucel, 1989; Grimme and Lindhauer, 1989). In contrast, Ca deficiency leads to short, slender and straight primary roots with brown tips (not swollen).

Coralloid roots due to Al injury are not reported for tree species and specific symptoms cannot be found. Roots are shortened, exhibit a necrotic morphology and turn dark brown. Secondary root formation is restricted and the branching pattern of all the underground system is reduced. Leaves may exhibit a chlorotic appearance and it was demonstrated that

the yellowing of some European conifers was due to magnesium deficiency (Zöttl and Hüttl, 1986; Landmann *et al.*, 1987), the latter being related either to base cation depletion or to Al or Mn toxicity (Hecht-Buchholz *et al.*, 1987; Godbold *et al.*, 1988; Godbold, 1991; Göransson and Eldhuset, 1991; Schlegel *et al.*, 1992). Calcium deficiency has sometimes been reported to also occur in declining stands growing on acid soils, and this may also be related to Al toxicity (Joslin *et al.*, 1988; Shortle and Smith, 1988).

### **Mechanisms involved in Al toxicity**

The main mechanisms that were recognized to operate in the detrimental action of monomeric forms of Al against plants are as follows: i) competition between Al species,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  for the meristematic root absorbing sites acts toward a lowering of Ca and Mg uptake (Asp *et al.*, 1988; Bengtsson *et al.*, 1988; Schröder *et al.*, 1988; Lindberg, 1990; Rengel, 1990; Tan and Keltjens, 1990; Godbold, 1991; Göransson and Eldhuset, 1991; Schimansky, 1991), but not, despite a number of conflicting reports, towards a direct inhibition of potassium uptake (Pettersson and Strid, 1989; Rengel and Robinson, 1990; Horst *et al.*, 1992); ii) inhibition of the meristematic cell division originates mainly from the inhibition of DNA replication and related mitotic activity as a consequence of Al-DNA linkages, and leads to low root growth and efficiency (Matsumoto *et al.*, 1979; Tepper *et al.*, 1989); iii) strong inhibition of cytokinines synthesis and translocation also reinforces the inhibition of the root system development (Pan *et al.*, 1989); iv) alteration of the root membrane structure and functioning (Hecht-Buchholz and Foy, 1981; Foy, 1984), including the blockage of Ca channels (Huang *et al.*, 1992; Rengel and Elliot, 1992); v) low nutrient and water

uptake, in connection to low root elongation and efficiency (Arp and Strucel, 1989; Grimme and Lindhauer, 1989), applies to both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  but also to iron and important anions such as  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  (Foy, 1984; Cambraia *et al.*, 1989); vi) inhibition of important enzymatic systems such as acid phosphatases (Pettersson *et al.*, 1988), ATPases, calmodulin (Haug, 1984), and nitrate reductase (Cambraia *et al.*, 1989); vii) shift from an aerobic metabolism to anaerobic one, with increased activity of the corresponding enzymatic system (Copeland and De Lima, 1992); viii) phosphate precipitation in roots by accumulated Al, with concomitant P deficiency in the above-ground organs (Schaedle *et al.*, 1989; Asp *et al.*, 1991).

### **Mitigating factors for Al toxicity**

The detrimental action of soluble Al to plants can be ameliorated both by biological factors and soil chemical conditions, such as total base cation concentration and the identity of the particular Al species in soil solutions.

### **Biological factors**

It was hypothesized that, in the field, mycorrhizae will protect trees against Al toxicity. A number of conflicting reports, however, have shown that this assertion should not be generalized. Although the mycorrhizal fungi *Pisolithus tinctorius* Coker and Couch and *Paxillus involutus* Fr have been shown to protect at least partly pitch pine (*Pinus rigida* Mill) and Norway spruce, respectively, from Al toxicity (Wilkins and Hodson, 1989; Cumming and Weinstein, 1990; Kasuya *et al.*, 1990; Hentschel *et al.*, 1993), mycorrhizal infection by *Lactarius rufus* (Scop) Fr does not protect Norway spruce (Jentschke *et al.*,

1991). Additionally, Al was found to be toxic for a number of mycorrhizal fungi (Browning and Hutchinson, 1991; Jongbloed and Borst-Pauwels, 1992; Zel *et al*, 1992), so that mycorrhizal infection *per se* may be reduced by Al (Boxman *et al*, 1991). As a consequence, a low density of mycorrhizae was reported in the field in Al-exposed stands (Schlegel *et al*, 1992). No generalisation can be drawn and the hypothesis of the alleviation of Al toxicity by mycorrhizal fungus is far from being verified.

Other biological factors include the so-called strain effect. Both various cultivars of cereals and provenances of Norway spruce were proved to exhibit contrasting Al resistance capacities to Al toxicity, owing to important differences in metabolism and root membranes properties (Geburek *et al*, 1986; Wilkins and Hodson, 1989; Blamey *et al*, 1992).

### Chemical factors

Some inorganic and organic anions alleviate the toxicity of Al by forming soluble complexes (species) of low toxicity or devoid of toxicity. Additionally, some cations act by competing with Al at the root absorbing sites.

#### *Alleviation of Al toxicity by inorganic and organic anionic ligands. Toxic and non-toxic species of aluminium*

Hydroxyls, fluoride, sulphate, phosphate, silica and organic matter are the most important relevant ligands for Al with respect to terrestrial and aquatic ecosystems. Some of the resulting Al species (see table I for a complete list) either are not toxic or have a lower toxicity, and the latter may be partly related to their cationic charge, to their stability in the root environment and to the target organism. Others remain toxic.

Among the monomeric inorganic species of aluminium,  $\text{Al}^{3+}$ ,  $\text{AlOH}^{2+}$ ,  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_4^-$  (due to its polymerisation to  $\text{Al}_{13}$  once absorbed by roots) are currently regarded as toxic. A great controversy exists with respect to their relative toxicity, however, and recent data suggest that  $\text{AlSO}_4^+$  must be included here, despite repeated reports about its so-called non-toxicity. This will be discussed below.

The toxicity of  $\text{Al}^{3+}$  was clearly demonstrated by Parker *et al* (1988a) for wheat. According to Noble *et al* (1988a) and Noble and Summer (1988), the toxicity of mononuclear Al species for soybean decreased in the order  $\text{Al}^{3+} > \text{AlOH}^{2+} > \text{Al}(\text{OH})_2^+$ . This view is not so far away from the conclusion of Bruce *et al* (1988), for which  $\text{Al}^{3+}$  and  $\text{AlOH}^{2+}$  are the only toxic inorganic monomeric Al species. Other data suggest conversely that  $\text{AlOH}^{2+}$  and  $\text{Al}(\text{OH})_2^+$  are much more toxic for soybean than  $\text{Al}^{3+}$  (Alva *et al*, 1986a). Polymeric forms of Al occurred in this case and the presence of the very toxic  $\text{Al}_{13}$  could not be ruled out, invalidating this conclusion as a consequence. According to Kinraide and Parker (1989, 1990) and Kinraide (1991), wheat and possibly a number of monocotyledons would be sensitive to  $\text{Al}^{3+}$  but not to the Al-OH mononuclear species. Dicotyledons would be sensitive to Al-OH monomers at least and perhaps also to  $\text{Al}^{3+}$ . This is not totally convincing, however, since: i) their assumption that  $\text{H}^+$  is less toxic than  $\text{Al}^{3+}$  is clearly an accommodation in contradiction with literature data (Shuman *et al*, 1991), particularly with the repeated observation that a low concentration of Al exerts a beneficial effect on root elongation as a consequence of the replacement of a strong  $\text{H}^+$  toxicity by a lower Al one (Viets, 1944; Fawzy *et al*, 1954; Thornton *et al*, 1986a, 1986b; Keltjens, 1990; Huang and Bachelard, 1993); and ii) the variations of the respective proportions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and Al were not taken into account. What-

**Table I.** Al species and minerals and modified thermodynamic data used for Al speciation by MINEQL+ (others are those of the original database).

Species	LogK <sup>a</sup>	Source
Al <sup>3+</sup>		
AlOH <sup>2+</sup>	-5	Nordstrom and May (1989)
Al(OH) <sub>2</sub> <sup>+</sup>	-10.1	"
Al(OH) <sub>3</sub> <sup>·</sup>	-16.8	"
Al(OH) <sub>4</sub> <sup>-</sup>	-22.7	"
AlSO <sub>4</sub> <sup>+</sup>	3.5	"
Al(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup>	5	"
AlF <sub>2</sub> <sup>+</sup>	7	"
AlF <sub>2</sub> <sup>+</sup>	12.7	"
AlF <sub>3</sub> <sup>·</sup>	16.8	"
AlF <sub>4</sub> <sup>-</sup>	19.4	"
AlF <sub>5</sub> <sup>2-</sup>	20.6	"
AlPO <sub>4</sub> <sup>·</sup>	16.76	Duffield <i>et al</i> (1991)
AlHPO <sub>4</sub> <sup>+</sup>	19.1	"
AlH <sub>2</sub> PO <sub>4</sub> <sup>2+</sup>	21.83	"
Al <sub>2</sub> PO <sub>4</sub> <sup>3+</sup>	18.87	"
Al <sub>2</sub> (OH) <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	13.85	"
Al <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup>	-7.7	Stumm and Morgan (1981)
AlO <sub>4</sub> Al <sub>12</sub> (OH) <sub>29</sub> <sup>2+</sup>	-131	Bottero <i>et al</i> (1982a) <sup>b</sup>
AlOSi(OH) <sub>3</sub> <sup>2+</sup>	-1.07	Browne and Driscoll (1992)
Al <sub>2</sub> (OH) <sub>2</sub> OSi(OH) <sub>3</sub> <sup>3+</sup>	-5.11	"
Al <sub>2</sub> (OH) <sub>2</sub> (OSi(OH) <sub>3</sub> ) <sub>2</sub> <sup>2+</sup>	-6.72	"
AlFulvate <sup>+</sup>	6.48	Schecher (1989)
AlOHFulvate <sup>·</sup>	1.745	"
AlHPO <sub>4</sub> Fulvate <sup>-</sup>	27.69	Arp and Meyer, 1985
Si <sub>4</sub> O <sub>6</sub> (OH) <sub>6</sub> <sup>2-</sup>	-12.57	Schecher (1989)
FeH <sub>2</sub> PO <sub>4</sub> <sup>2+</sup>	21.35	Stumm and Morgan (1981)
FeHPO <sub>4</sub> <sup>+</sup>	20.65	"
H <sub>2</sub> SiO <sub>4</sub> <sup>2-</sup>	-22.02	Schecher (1989)
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	-9.46	"
HFulvate <sup>-</sup>	6.22	"
H <sub>2</sub> Fulvate <sup>·</sup>	9.59	"
Amorphous Al(OH) <sub>3</sub>	-10.38	MINEQL+ (Schecher and McAvoy, 1992)
Gibbsite	-8.77	"
Imogolite	-12.09	Bourrié <i>et al</i> (1989)
Jurbanite	3.23	MINEQL+ (Schecher and McAvoy, 1992)
Alunite	1.346	"
Amorphous AlPO <sub>4</sub>	19.80	Duffield <i>et al</i> (1991)

<sup>a</sup> Corrected to zero ionic strength and 25°C, when necessary (according to Stumm and Morgan, 1981); <sup>b</sup> charge and logK depending on Al concentration.

ever the reality and according to Rost-Siebert (1983), Hüttermann and Ulrich (1984), Hutchinson *et al* (1986), Thornton *et al* (1987), Asp *et al* (1988) and Nosko and Kershaw (1992), the European spruce (*Picea abies*) and several American spruce appear to be sensitive at least to  $\text{Al}^{3+}$  with a good certitude; data are, however, lacking with regards to their sensitivity to  $\text{AlOH}^{2+}$  and  $\text{Al(OH)}_2^+$ .

Although it does not constitute a toxic species *per se*, the aluminate ion  $\text{Al(OH)}_4^-$  should be included in the harmful forms of Al, as it is expected to transform easily into the very toxic  $\text{Al}_{13}$  polymer within the roots, from which the free space remains in the acid range as long as the external pH was  $< 8.9$  (Kinraide, 1990). Conversely,  $\text{Al(OH)}_3^*$  does not constitute a toxic species (Alva *et al*, 1986a; Tanaka *et al*, 1987).

Strong controversies exist about the toxicity of  $\text{AlSO}_4^+$ . The existence of a toxic species of Al-sulphate was demonstrated by Van Praag *et al* (1985), Alva *et al* (1986b), Joslin and Wolfe (1988) and Tang *et al* (1989), with respect to the European beech (*Fagus sylvatica* L), the American red spruce (*Picea rubens* Sarg), soybean (*Glycine max* (L)) and rice (*Oriza sativa* L). Conversely Pavan and Bingham (1982), Cameron *et al* (1986), Kinraide and Parker (1987a), Tanaka *et al* (1987), Noble *et al* (1988a, 1988b) and Wright *et al* (1989) claimed the non-toxicity of  $\text{AlSO}_4^+$ , regarded as the prevailing Al-sulphate ion pair in their experimental conditions. In most of these experiments, however, the  $\text{SO}_4/\text{Al}$  ratio was high to very high, ranged from 0.1 to 2 700 and was almost always  $> 1$ . As a consequence, the prevailing sulphate ion was not  $\text{AlSO}_4^+$  but a more recently discovered one (approximately  $\text{Al(SO}_4)_2.7^{2.4-}$ ) (Alva *et al*, 1991). As the latter was found to be non-toxic, there is a great probability that the so-called "non-toxic  $\text{AlSO}_4^+$ " was in fact this

new species and that the toxic Al-sulphate ion pair must be identified as  $\text{AlSO}_4^+$ .

The fluoride complexes of Al prevailing in the acid range, namely  $\text{AlF}^{2+}$ ,  $\text{AlF}_2^+$ ,  $\text{AlF}_3^*$  and, more rarely,  $\text{AlF}_4^-$ , have been proved to be non-toxic ( $\text{AlOH}^+$ ,  $\text{AlOH}_2^+$  and  $\text{Al(OH)}_3\text{F}^-$  being neglected due to their short half-life (Nordström and May, 1989)) (Cameron *et al*, 1986; Tanaka *et al*, 1987). Such species do not prevent root growth and do not inhibit Ca or Mg uptake (MacLean *et al*, 1992).

The toxicity of the monomeric  $\text{Al-PO}_4$  and  $\text{Al-Si}$  complexes remains mostly unknown but White *et al* (1976) and Alva *et al* (1986a) demonstrated that adding  $\text{PO}_4^{3-}$  ions will induce a dramatic formation of non-toxic  $\text{Al-PO}_4$  polymers, to such a large extent that the residual concentration of  $\text{Al-PO}_4$  monomers can probably be neglected. Additionally, the non-toxicity of  $\text{Al-PO}_4$  and  $\text{Al-Si}$  species have been proved with respect to *Chlorella pyrenoidosa* (Helliwell *et al*, 1983), so that the same situation can be eventually expected with regards to terrestrial plant species.

Polymeric forms of Al occur in acid solutions above pH 3.5–5.5, depending on the concentration and the ionic strength. The existence of both toxic (Bartlett and Riego, 1972a; Wagatsuma and Ezoe, 1985; Wagatsuma and Kaneko, 1987; Parker *et al*, 1988a) and non-toxic (Blamey *et al*, 1983) Al polymers is now well documented. The former was recently identified as the " $\text{Al}_{13}$ " polymer  $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ . Its toxicity was often considerably higher than that of  $\text{Al}^{3+}$  (Parker *et al*, 1989; Shann and Bertsch, 1993). About 1 to 11.5 times less Al as  $\text{Al}_{13}$  than as  $\text{Al}^{3+}$  (*ie* about 13 to 150 times on a molar basis) was needed to obtain an inhibition of 20% of either soybean or wheat root elongation. Moreover, plant species tolerant to monomeric Al remain highly sensitive to  $\text{Al}_{13}$ , suggesting the occurrence of mechanisms other than those

listed above. The  $Al_{13}$  polymer has been recently reported to occur in soils (Hunter and Ross, 1991), under an adsorbed state in a podzol humus. As chelating organic matter is regarded as an inhibitor of  $Al_{13}$  formation, this presence is very surprising. Additionally, the occurrence of  $Al(OH)_4^-$  is believed to be a prerequisite to the formation of  $Al_{13}$  (Bertsch, 1987) and it is not easily conceivable that podzol humus offers favourable conditions to its formation. Clay surfaces, however, would be highly favourable to Al hydrolysis and polymerisation, even in unsaturated solutions (Tennakoon *et al*, 1986), so that some generalisation of this finding cannot be ruled out. The toxicity of adsorbed  $Al_{13}$ , if any, remains so far unknown but in the event that it equilibrates with soil solution, it would constitute a source of a high toxicity, especially during soil acidification phases (Bertsch, 1989).

The occurrence of  $Al_{13}$  in soil solutions remains undocumented, due in part to the lack of diagnostic tools compatible with natural soil water composition (Al concentration being mostly too low for  $^{27}Al$  NMR studies). That the ferron kinetic analysis procedure can be used successfully in natural soil solutions must be verified in true samples, as many interfering substances are able to darken the expected clarity of kinetic curves (Parker and Bertsch, 1992). The presence of  $Al_{13}$  in natural soil water should be regarded as uncertain for several reasons. Al polymers are allowed to appear only in supersaturated solutions with respect to gibbsite (when the saturation index is calculated without taking the possibility of  $Al_{13}$  formation into account) (Stumm and Morgan, 1981; Bloom and Erich, 1989; Kinraide and Parker, 1989), and this is known to occur in natural soil solutions. Once formed, however, Al polymers are readily adsorbed onto anionic soil organic and inorganic surfaces (Brown and Hem, 1975; Parker *et al*, 1988a; Zelazny

and Jardine, 1989) and would not be allowed to maintain in the aqueous phase other than in minor proportions, if any (Brown and Newman, 1973; Bache and Sharp, 1976). Additionally, sulphate ions are known to restrict  $Al_{13}$  formation and phosphate to precipitate Al polymers (Bartlett and Riego, 1972a; Blamey *et al*, 1983; Alva *et al*, 1986b; Parker *et al*, 1989).

Organic complexes of Al are widespread in acid soils. According to Arp and Ouimet (1986) and Asp and Berggren (1990), plant roots do not absorb Al complexed with colloidal organic acids (at least the largest fulvic and humic acids). Al complexed with non-colloidal organic acids (simple carboxylic acids and perhaps small fulvic acids) are easily absorbed by roots, however, to such an extent that complexation has been reported to enhance Al absorption (Van Praag and Weissen, 1985; Arp and Ouimet, 1986; Arp and Strucel, 1989). Both absorbed and non-absorbed organic complexes of Al are currently referred to as non-toxic (Brogan, 1964; Bartlett and Riego, 1972b; Rost-Siebert, 1983; Van Praag and Weissen, 1985; Van Praag *et al*, 1985; Hue *et al*, 1986; Suhayda and Haug, 1986; Tan and Binger, 1986; Arp and Strucel, 1989; Asp and Berggren, 1990; Suthipradit *et al*, 1990), so that the ability to synthesize and to exude chelating organics can be regarded as a mechanism of Al resistance (Horst *et al*, 1982; Miyasaka *et al*, 1991).

#### *Alleviation of Al toxicity by competing elements*

Some cations have been proved to mitigate Al toxicity by competing with monomeric Al species and by lowering Al activity. Non-toxic divalent cations are more efficient than monovalent ones so that the following general classification can be put forward:  $Ca^{2+} \approx Mg^{2+} \approx Sr^{2+} \ggg K^+ = Na^+$  (Vidal and Broyer, 1962; Rhue and Gro-

gan, 1977; Alva *et al*, 1986c; Hecht-Buchholz and Schuster, 1987; Hecht-Buchholz *et al*, 1987; Kinraide and Parker, 1987b; Tanaka *et al*, 1987; Rengel and Robinson, 1990; Edmeades *et al*, 1991; Tan *et al*, 1991; Blamey *et al*, 1992). Depending on the studies,  $Mg^{2+}$  was reported to be either more efficient, less efficient or as efficient as  $Ca^{2+}$ , however, and a surprising lack of amelioration of Al toxicity by the latter was even, but rarely, observed. The competing effect of  $K^+$  and  $Na^+$  is about 200 times weaker than that of calcium (Kinraide and Parker, 1987b). Strontium is only a minor element in natural soil solutions and can be neglected in field conditions.

### **Diagnostic tools for the assessment of Al toxicity in soils**

#### **Root elongation**

Root elongation measurement is generally regarded as a better indicator of Al toxicity than either roots or leaf dry weight. These values are currently used to calibrate the detrimental effect of various species of Al in toxicological studies. The use of this criterion in natural forest ecosystems is, however, time consuming and poorly suitable.

#### **Tracer studies**

$^{45}Ca^{2+}$ ,  $^{48}Mg^{2+}$  and  $^{86}Rb^+$  (the latter regarded as a substitute of  $K^+$ ) have been used to assess Al influence on nutrient uptake with a good accuracy (Asp *et al*, 1988; Bengtsson *et al*, 1988; Godbold *et al*, 1988; Petterson and Strid, 1989; Asp and Berggren, 1990; Lindberg, 1990; Schimansky, 1991; Horst *et al*, 1992; Rengel and Elliot, 1992). Due to some common properties with Al,  $^{46}Sc$ , a trivalent cation which may be complexed by both phos-

phate and organic anions and which also forms several pH-dependent hydroxy species, has been used as a substitute of Al in toxicological studies to assess translocation pathways and mechanisms (Clarkson and Sanderson, 1969). As scandium is 10 to 30 times more toxic than Al, this can be validated only in the case of short-term laboratory experiments (Yang *et al*, 1989).

#### **Al content of plant organs**

Neither leaf nor root Al content can be used as a realistic tool for the assessment of Al toxicity. Al content in needles of various *Picea* species from north America and Europe is not related to Al concentration in soil solutions (Joslin and Wolfe, 1988). Moreover, as mentioned above, *Picea abies* can accommodate up to 1 350 mg  $Al \cdot kg^{-1}$  needles without damage. Additionally and according to McCormick and Borden (1972), Huett and Menary (1980), Wagaatsuma (1983) and Schaedle *et al* (1986), a high proportion of root Al originates from non-metabolic processes, accumulates in cortical cells without further significant penetration inside roots (Godbold *et al*, 1988; Schlegel *et al*, 1992) and is not toxic. Only the Al which is related to the meristem area is regarded as directly toxic.

#### **Exchangeable soil Al concentrations**

Saigusa *et al* (1980) stated that Al toxicity appeared when 1 N KCl exchangeable soil Al was in excess of 2 meq $\cdot 100 g^{-1}$ . A weaker ionic strength of the extractant was recommended by other authors. Both 0.01 M  $SrCl_2$ - and  $CaCl_2$ -extractable Al were found to be well correlated with total Al, monomeric Al, fine root Al content (in inorganic soil layers only) (Joslin and Wolfe, 1988; Joslin *et al*, 1988; Conyers *et al*, 1991a, 1991b), response to Al toxicity (Kelly *et al*, 1990) and root growth (Baligar *et*

al, 1992). Although a toxicity threshold was found to be reached for 10 mg extractable Al·kg<sup>-1</sup> soil, it is clear that such procedures address the source of toxic Al more than genuine toxic Al *per se*, the latter being only a part of soluble Al in soil solutions. Therefore, exchangeable Al can constitute at best an indicative value only.

### Aluminium concentrations in soil solutions

Schaedle *et al* (1989) proposed the classification of some important forest trees into 3 groups, according to their sensitivity to soluble Al.

Sensitive species are those which exhibit sensitivity for Al concentrations  $\leq 150 \mu\text{M}\cdot\text{l}^{-1}$ . Root tips turn brown and swollen and elongation is inhibited. Foliar organs are depleted in calcium and magnesium and strong necrosis may occur. As roots and sometimes shoots growing area are destroyed, natural maxima in Al concentrations (Al pulses) affect durably plant development in the field and these species recover only slowly once Al stress has ceased. *Picea abies*, *P. glauca* (Moench) Voss and *Gleditsia triacanthos* L belong here, the latter being sensitive to Al concentrations as low as  $12 \mu\text{M}\cdot\text{l}^{-1}$  (Schaedle *et al*, 1989; Sucoff *et al*, 1990). Higher toxicity thresholds (ranging from 200 to  $700 \mu\text{M}\cdot\text{l}^{-1}$ ) have been reported for *Picea abies*, which could belong to the following group as well (Göransson and Eldhuset, 1991; Van Praag *et al*, 1985).

Intermediate species are those which exhibit sensitivity for Al concentrations ranging from 150 to  $800 \mu\text{M}\cdot\text{l}^{-1}$ . Roots are apparently not damaged and only root and/or shoot growth was affected. As growing points are not destroyed but only inhibited in their functioning, Al pulses affect root development only temporarily and such species recover rapidly once Al stress has

decreased. *Picea rubens*, *P. mariana* (Mill) Britt, *Fagus silvatica* L and *Acer saccharum* Marsch belong to this group. A considerably higher Al threshold has been reported for *Picea rubens* ( $3\,700 \mu\text{M}\cdot\text{l}^{-1}$ ), which would pertain in this case to the following group (Schier, 1985).

Tolerant species are those which are sensitive to Al concentrations  $\geq 800 \mu\text{M}\cdot\text{l}^{-1}$  only. Species such as *Pinus strobus* L, *P. sylvestris* L, *Picea sitchensis* (Borg) Car, *Pseudotsuga douglasii* (Lindley) Car, *Abies balsamea* Mill, *Fagus grandifolia* Ehrh, *Betula pendula* Roth and *Quercus rubra* L pertain to this group (Schaedle *et al*, 1989; Göransson and Eldhuset, 1991). A considerably lower Al threshold has also been reported for *Quercus rubra* ( $120\text{--}280 \mu\text{M}\cdot\text{l}^{-1}$ ) (Kelly *et al*, 1990), which would pertain in this case to one of the previous 2 groups.

It can be noted that important discrepancies occur for several species, due either to uncontrolled strain effects or to ignored nutrient factors. Indeed, a number of species are more tolerant to Al in Ca- and Mg-rich solutions. Roots of *Picea abies* do not show any injury as a consequence of  $1\,700 \mu\text{M}\cdot\text{l}^{-1}$  Al in nutrient solutions when  $\text{Ca}^{2+} = 1\,300 \mu\text{M}\cdot\text{l}^{-1}$  and  $\text{Mg}^{2+} = 300 \mu\text{M}\cdot\text{l}^{-1}$  but are strongly damaged when these 2 elements reach only 130 and  $30 \mu\text{M}\cdot\text{l}^{-1}$ , respectively (Hecht-Buchholz *et al*, 1987). Thus, the concept of a given Al concentration threshold for a given species is probably not appropriate for the majority of plant species.

### Aluminium toxicity index

To overcome some of the previous discrepancies, the calculation of a toxicity index that takes into account all the factors controlling Al toxicity is a useful and promising approach to assess Al toxicity in a given ecosystem.

According to Lund (1970), Rost-Siebert (1983, 1984), Hüttermann and Ulrich (1984), Wolfe and Joslin (1989) and Kelly *et al* (1990), the Ca/Al ratio in soil solutions would be one of the best expressions for assessing Al toxicity, mainly with respect to root development. It would reflect the competing conditions which occur between  $\text{Ca}^{2+}$ , regarded as the most important base cation, and soluble Al at the root absorbing sites. Al toxicity would be a reality for all values of this ratio  $< 1$  or  $2$  in the case of *Picea abies* and *Fagus silvatica*. A strong root mortality would occur for values of this ratio around  $0.2$ . The observation of Bennet *et al* (1987) that *Zea mays* L root cell division was inhibited when  $1/2 \log \text{Ca}^{2+} \leq 1/3 \log \text{Al}^{3+}$  (on a molar basis) reflects a closely allied concept. Obviously, these expressions are imperfect, as they do not include the beneficial effect of important elements such as Mg and do not take into account the non-toxicity of some Al species. Even the data of Rost-Siebert (1983, 1984) and Hüttermann and Ulrich (1984) stretched the very limits of the Ca/Al ratio, which was validated only at  $\text{pH} < 4$  in absence of organic matter. Additionally, ionic activities instead of concentrations should always be used in such studies (Adams and Lund, 1966; Pavan and Bingham, 1982; Pavan *et al*, 1982; Tanaka *et al*, 1987; Thornton *et al*, 1987).

The calcium–aluminium balance (CAB =  $2\log\{\text{Ca}^{2+}\} - [3\log\{\text{Al}^{3+}\} + 2\log\{\text{AlOH}^{2+}\} + \log\{\text{Al}(\text{OH})_2^+\}]$ ) of Noble *et al* (1988a, 1988b) and Noble and Sumner (1988) overcomes some of these imperfections. Obviously, it must be completed by taking into account both the beneficial effect of  $\text{Mg}^{2+}$  and the toxicity of  $\text{AlSO}_4^+$ ,  $\text{Al}(\text{OH})_4^-$  and  $\text{Al}_{13}$  at least. Other imperfections of the CAB were discussed by Grauer and Horst (1991).

Various other approaches have been tried. Kinraide and Parker (1987b) proposed the following expression for the tox-

icity of Al to wheat, the latter being regarded as insensitive to Al-OH monomers:  $\% \text{ root growth inhibition} = 100\{\text{Al}^{3+}\} / [\{\text{Al}^{3+}\} + 1.2 + 2.4\{\text{Ca}^{2+}\}^{1.5} + 1.6\{\text{Mg}^{2+}\}^{1.5} + 0.011\{\text{Na}^+\}^{1.8} + 0.011\{\text{K}^+\}^{1.8}]$ . Blamey *et al* (1992) put forward an even more sophisticated index for dry weight productivity of wheat. These kinds of index are not standardised for other plant species, denied the probable toxicity of Al-OH and  $\text{AlSO}_4^+$  monomers and do not involve the well-demonstrated toxicity of  $\text{Al}_{13}$ . The same remark applies to the Al activity ratio (AER) of Bessho and Bell (1992):  $\text{AER} = 1000 [3\{\text{Al}^{3+}\} / (3\{\text{Al}^{3+}\} + 2\{\text{Ca}^{2+}\} + 2\{\text{Mg}^{2+}\} + \{\text{K}^+\} + \{\text{Na}^+\})]$ .

Given these imperfections, the previous considerations make it tempting to modify the initial Ca/Al ratio and to propose the following formulation as a general expression intended to assess any risk of Al toxicity:

ATI (aluminium toxicity index) =  $[4\{\text{Ca}^{2+}\} + 4\{\text{Mg}^{2+}\} + 0.02\{\text{K}^+\} + 0.02\{\text{Na}^+\}] / [9\{\text{Al}^{3+}\} + 4\{\text{AlOH}^{2+}\} + \{\text{Al}(\text{OH})_2^+\} + \{\text{AlSO}_4^+\} + 117-1345\{\text{Al}_{13}\} + 9-103\{\text{Al}(\text{OH})_4^-\}]$ . In this expression, brackets denote molar activities and each element is weighted by a coefficient intended to reflect its relative beneficial or detrimental effect. This coefficient is based on values produced by Grauer and Horst (1991) and on the relative effect, detailed above, exerted by each of these elements or species. The toxicity threshold may be derived from literature data by recalculating speciation whenever possible, and falls in the range  $0.9$  to  $2$  for *Picea abies* and *Fagus silvatica* (from Rost-Siebert, 1984; Hüttermann and Ulrich, 1984; Neitzke, 1990). It can be either considerably lower for some *Pinus* ( $0.1-0.2$ ) and *Betula* ( $0.006$ ) species (from Truman *et al*, 1983; Göransson and Eldhuset, 1987; Raynal *et al*, 1990), or considerably higher for *Gleditsia triacanthos* ( $> 4.3$ ) and some cereal species ( $4.8$  to  $> 10$ ) (from Hecht-Buchholz and Schuster, 1987; Succoff *et al*, 1990).

Before assessing Al toxicity, it must be ensured that a minimum amount of Ca is present so as to prevent absolute Ca deficiencies. The minimum Ca requirement is known to be pH-dependent, and Ulrich *et al* (1984) claimed that Ca deficiency occurs for values of the Ca/H molar ratio in soil solutions  $< 0.1$  for conifers such as *Picea abies*, and  $< 1$  for more demanding species such as *Fagus silvatica*.

It goes without saying that it would be highly desirable to take into account any strain effect, as this has proved to be important at least in cereals and *Picea abies* (Geburek *et al*, 1986; Wilkins and Hodson, 1989; Blamey *et al*, 1992).

## OPERATIONAL PROCEDURES FOR ALUMINIUM SPECIATION

The calculation of any valid toxicity index requires the determination of Al speciation. Many procedures have been attempted but operational artifacts have often been reported. The most advanced techniques will be listed below.

### *The Driscoll procedure*

The most widespread procedure of Al speciation is that of Driscoll (1984), which may be accompanied by some minor operational changes (Berggren, 1989; McAvoy *et al*, 1992). This method is founded: i) on the use of a strong cationic exchange resin, set to sample pH and ionic strength, to separate organically complexed Al from inorganic Al; and ii) on a rapid extraction (15 s) of both inorganic and organic monomeric Al by 8-hydroxyquinoline (= oxine) at pH 8.3. With respect to the resin step, inorganic Al is assumed to be fixed by the resin, while organic Al passes through quantitatively. Variable decomplexation of organic

Al complexes has been repeatedly reported, however, ranging from about 0 to 34%, depending mainly on the Al/C ratio of the water sample (Backes and Tipping, 1987; Berggren, 1989; Dahlgren and Ugolini, 1989; Kerven *et al*, 1989a; Van Benschoten and Edzwald, 1990). Decomplexation was negligible at low Al/C ratios, as is the case in podzol solutions, increased progressively once the Al/C ratio exceeded 300–500  $\mu\text{M Al}\cdot\text{g}^{-1}$  organic matter and could reach 25% of initial organic Al for values of this ratio around 1 000. In Al-rich acid brown soils, this ratio ranges from 3 000 to 12 000 and the resin method obviously cannot be used. Moreover, uncharged or negatively charged monomeric and polymeric colloidal inorganic species cannot be fixed by the resin and were recovered as organic Al (Lydersen *et al*, 1990; Alvarez *et al*, 1992). The same imperfections were observed with chelating resins (Campbell *et al*, 1983; Hodges, 1987; Kerven *et al*, 1989a). Additionally, it was shown that the oxine extraction failed to recover quantitatively organic Al (Lalande and Hendershot, 1986; Royset and Sullivan, 1986) and the cumulative effect of all these imperfections will result in strong uncertainties with respect to the reliability of the results.

### *Colorimetric procedures*

The oxine rapid extraction procedure (15 s) can be performed both at pH 8.3 (Lazerte, 1984) and pH 5 (James *et al*, 1983; Clarke *et al*, 1992). The pH 8.3 extraction was at the time assumed to provide a good estimation of both inorganic and organic monomeric Al species. Organic Al, however, is not quantitatively recovered and strong interferences (eg, Cu, Mn, Fe, Zn) occur. The pH 5 extraction does not significantly extract the Al-F complexes but organic Al is partly extracted in variable

proportions, the latter ranging from 26 to 55%, depending on the C/Al ratio (Lalande and Hendershot, 1986; Kerven *et al*, 1989a; Whitten *et al*, 1992). Mn does not significantly interfere, interference by Fe can be corrected, but that of Cu cannot be eliminated. A recent improvement of the procedure by Clarke *et al* (1992) seems to suppress the partial extraction of organic Al and limits strongly the main interferences. This improvement will deserve great attention in the future.

Eriochrome cyanine reagent (McLean, 1965) allows the measurement of inorganic monomeric Al and unfortunately of variable proportions (75 to 95%) of organic Al (Adams and Moore, 1983; Kerven *et al*, 1989a). The use of the aluminon reagent has been attempted as an alternative but it was not very reliable (Wright *et al*, 1987; Alva *et al*, 1989; Kerven *et al*, 1989b). None of these reagents are a good substitute to the oxine reagent.

The use of pyrocatechol violet (PCV) leads to similar results to the oxine rapid extraction at pH 8.3 and suffers comparable imperfections (Whitten *et al*, 1992). Nevertheless, Achilli *et al* (1991) used this reagent with success to perform an organic complexation of all the monomeric Al species and subsequently to measure polymeric Al after separation by a cationic resin procedure. On the other hand, Menzies *et al* (1992) proposed a modified PCV method in order to distinguish between soluble and suspended Al. The latter was flocculated with  $\text{La}^{3+}$  and organic Al was decomplexed by the addition of  $\text{Fe}^{3+}$  before colorimetry. Although the behaviour of polymeric Al was not investigated, this method seems to be very useful, in addition to those addressing inorganic Al monomers.

The analysis of the colorimetric reaction kinetic of the ferron reagent (8-hydroxy-7-iodo-5-quinoline-sulphonic acid) with solu-

ble Al may allow, under certain conditions, the quantitative determination of several categories of Al, including monomeric Al, polymeric  $\text{Al}_{13}$  and colloidal, non-reactive Al (Jardine and Zelazny, 1986, 1987a, 1987b; Parker *et al*, 1988b; Parker and Bertsch, 1992). Strong interferences with Mn strongly limit, however, the application of the method to natural solutions. Additionally, organic, phosphate and fluoride anions tend to make the kinetics obscure and poorly interpretable at anions/Al ratio fairly relevant to surface and soil water composition.

### **Fluoride-selective electrode procedures**

The measurement of both free  $\text{F}^-$  and total F by fluoride-selective electrode would allow theoretically the calculation of Al speciation. The reliability of the method depends on the F/Al ratio, the pH and the organic carbon content of the solutions (Driscoll, 1984; LaZerte, 1984; Hodges, 1987; Munns *et al*, 1992). Small F determination errors lead to small errors in Al speciation at pH 4 but to very high errors at pH 5.5. A low sensitivity was observed for high values of the Al/F ratio. As a consequence, poor reliability would be expected in many natural waters.

Alternatively, Ares (1986a, 1986b) developed a procedure based on the interpretation of the reaction kinetics of added F with soluble Al species. The limits of this method have been poorly investigated.

### **Procedures using fluorescence**

Browne *et al* (1990) developed a procedure using 2,3,4,5,7-pentahydroxy-flavone (morin) as a fluorescing chelating reagent for Al; the fluorescence measurement allowed the calculation of initial Al speciation. Interferences due to naturally fluorescing organic matter cannot always be

corrected and this method cannot apply to carbon-rich soil solution. Additionally, a number of cations tend to lower the yield of the reaction so that each sample should have its own blank. This is poorly compatible with series analysis.

Shotyk and Sposito (1990) emphasized that the fluorescence quenching of organically complexed Al may be used for a quantitative determination of organic Al in simple aqueous solutions. Interfering elements remain unstudied and this method is in need of further developments before it is suitable for natural water, if ever.

### ***Al speciation using ion chromatography***

Al speciation was recently attempted by ion chromatography coupled with post-column reaction with either tiron, pyrocatechol violet or 8-hydroxyquinoline-5-sulphonate, and either UV or fluorescence detection (Anderson and Bertsch, 1988; Bertsch and Anderson, 1989; Willett, 1989; Gibson and Willett, 1991; Jones, 1991; Whitten *et al.*, 1992). Fluorescence detection is suitable for very low Al concentrations (as low as 35 nM), UV detection to higher ones. Tiron would be preferred to pyrocatechol violet due to the inability of the latter to reveal some organically complexed Al. Either guard columns or separation columns have been used. When the guard columns are coupled with a 0.08–0.1 M  $K_2SO_4$  elution, 3 peaks are separated. The first involves the monovalent species that did not undergo dissociation during the chromatographic pathways, which were identified as  $AlF_2^+$  and at least the inner sphere organic complexes of Al. The second involves the divalent species that were not dissociated during the chromatographic pathways, *ie*  $AlF_2^+$  and Al-humic acids<sub>2</sub><sup>+</sup> complexes. The third involves as a single  $Al^{3+}$  species

both initial  $Al^{3+}$  and all species that undergo dissociation during the chromatographic pathways, namely the Al-OH and Al-SO<sub>4</sub> monomers. Uncharged and probably negatively charged species such as  $AlF_3^*$  and  $AlF_4^-$  are eluted in the dead volume or in the eluent front and cannot be recovered in a defined chromatographic peak. The behaviour of outersphere organic complexes of Al and the Al-PO<sub>4</sub> and Al-Si monomers along the chromatographic pathways remains unknown, but data reported by Whitten *et al.* (1992) suggest strongly that natural organic Al undergoes little decomplexation, if any. Whether or not Al, Al-PO<sub>4</sub> and Al-Si polymers are eluted or fixed by the resin is unknown. The main interest of this method resides in the fact that the calculation of every monomeric species involved in the third peak by equilibrium calculation provides a fairly good basis for the evaluation of Al toxicity. The use of the separation columns appears to be compatible with natural water samples only at medium to low F/Al ratios. For the values of this ratio higher than 1.5 there is a strong redistribution of  $AlF_2^+$  towards ( $AlF_2^+ + AlF_3^*$ ). In addition, there is an important but variable decomplexation of organic Al, even with respect to some inner-sphere complexes. Uncharged species such as  $AlF_3^*$  can be recovered in one peak, however, and polymeric Al is fixed on the column, perhaps providing a useful tool for the quantitative determination of polymeric Al. The latter would equal unrecovered Al if all organic Al can react with Tiron.

### ***Al speciation using electric methods***

Schmid *et al.* (1989) obtained a reliable quantification of  $Al^{3+}$  in synthetic solutions, natural soil leachates and aqueous soil extracts, by isotachopheresis, without any interferences of Al-sulphate ion-pairs. The

interferences of Al-F, Al-PO<sub>4</sub> and Al-Si complexes, which are widespread in acid soils, were not investigated. As a consequence, this method requires additional studies before it can be applied to natural soil and surface waters.

### ***Al speciation using chemical equilibrium programs***

The distribution of the various species of Al can be predicted by chemical equilibrium models, providing their equilibrium constants are known. Sophisticated programs such as MINEQL+ (Schecher and McAvoy, 1992) and GEOCHEM-PC (Parker *et al*, 1992) are now available for personal microcomputers under the DOS operating system. The former is characterised as being user-friendly and the database can be easily updated. Temperature values can be specified and a number of species and minerals can be added. Both organic and polymeric Al can be consequently computed with reasonable assumptions.

### **APPLICATION: A CASE STUDY IN A DECLINING SILVER FIR FOREST IN THE VOSGES MOUNTAINS (NORTH-EASTERN FRANCE)**

To illustrate the previous considerations, we will briefly report hereafter some data from a study performed in a declining silver fir (*Abies alba*) forest, located in the Mortagne watershed between St-Dié and Rambervillers (Haut-Jacques pass, E 6° 51' – N 48° 17'). The stand has developed on an acid brown soil derived from the weathering of a triassic silty sandstone. The main analytical features of the soil are given elsewhere (Becquer, 1991). Atmospheric inputs were found to be moderate

and reached about 1.4 kg NH<sub>4</sub>-N·ha<sup>-1</sup>·yr<sup>-1</sup>, 15 kg NO<sub>3</sub>-N·ha<sup>-1</sup>·yr<sup>-1</sup>, 22 kg SO<sub>4</sub>-S·ha<sup>-1</sup>·yr<sup>-1</sup>, 31 kg Cl·ha<sup>-1</sup>·yr<sup>-1</sup> and 0.4 kg free H<sup>+</sup>·ha<sup>-1</sup>·yr<sup>-1</sup> (Becquer, 1991). Fluoride inputs occurred very rarely.

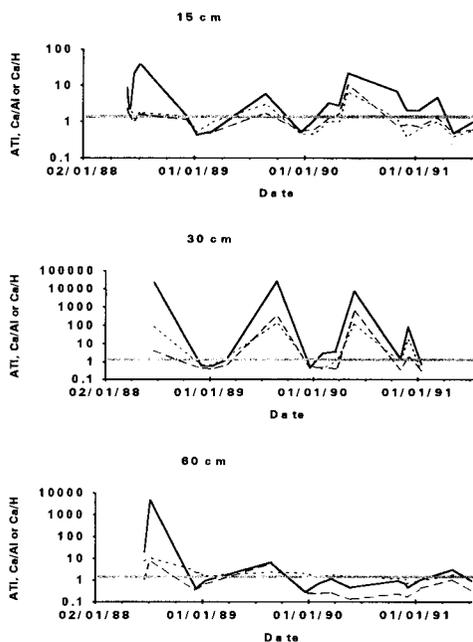
Leaching soil waters were continuously collected during 3 yr at depths of 15, 30 and 60 cm with zero tension Polyethylene-plate-lysimeters, with the sampling frequency being determined by precipitations events. The determination of their chemical composition was performed by colorimetry (NH<sub>4</sub><sup>+</sup>), ion chromatography (inorganic anions), flame-emission spectrophotometry (total K and Na) and inductively coupled plasma emission spectrometry (total Al, Ca, Fe, Mg, Mn and Si). Organic carbon content was determined with a Carlo Erba analyser, and the pH was measured with a pH meter connected to a combined glass electrode. All these data allowed the calculation of Al speciation with the MINEQL+ program, of which the database has been previously updated both by introducing new Al species and mineral and using revised equilibrium constants (table I). The organic matter ("fulvate") molar concentration was derived from the carbon concentration by assuming that only 13% of the total C pertained to complexing functional groups (mean of potentiometric titration data) and that each organic molecule held 2 of these functional groups (diprotic model). Ionic activities were calculated using the extended Debye-Hückel equation, the *a* values (ion-size parameter) being mostly those listed by Truesdell and Jones (1974) and Ritsema (1993), to which we added that of 12.6 for the Al<sub>13</sub> polymer (Bottero *et al*, 1982b). According to the previous considerations, the aluminium toxicity index (ATI) listed above and both the Ca/Al and the Ca/H ratios were calculated on a seasonal basis.

Figure 1 shows the seasonal variations of the ATI and those of both the Ca/Al and the Ca/H ratios. With respect to the cal-

cium status, it must be emphasized that the Ca/H ratio was always  $> 0.1$  and ranged from 0.3 to 142. Values in the range 0.3–1 occurred mainly during autumn and winter. Minimal calcium requirement can be satisfied throughout the year, thus, for coniferous trees at least. As a consequence, the aluminium toxicity hypothesis warrants consideration. With respect to the ATI, we must emphasize the absence of both  $Al_{13}$  and  $Al(OH)_4^-$  in the soil solutions studied. Therefore, the toxicity index was not influenced by species with very strong weighting coefficients. It can be observed that the ATI was affected by strong seasonal variations, with values  $< 1.5$  during autumn and winter only, emphasizing the occurrence of an Al toxicity context during the rest phase of the vegetation and also its spring disappearance. Some

exceptions to this seasonal pattern originated from occasional fluoride inputs derived from atmospheric pollution and concomitant formation of non-toxic Al-F complexes. The values of the Ca/Al ratio followed the same seasonal pattern as those of the ATI, but were often considerably lower, particularly in the upper horizons, where values close to the Al toxicity threshold or below also occurred during spring and summer. As the ATI excludes the non-toxic species of Al and takes into account the beneficial effect of Mg, it is beyond any doubt that it is more reliable than the Ca/Al ratio and that the latter overestimates Al toxicity in waters rich in fluoride and organic matter.

Whether the seasonal phases of Al toxicity indicated by the ATI reflected natural processes or anthropic pollution was investigated in a companion study (Becquer *et al*, 1990, 1992). Seasonal protons budgets were found to be mainly under the dependence of nitrate flux. Despite the poor condition of the stand studied, a total uptake of nitrate was observed along the whole growth period of the vegetation, whether these ions originated from natural nitrification or from atmospheric inputs, resulting in a net alkalisation phase. During autumn and winter, conversely, atmospheric inputs increased and nitrification continued at a rather high rate. Nitrate uptake was very low during this period, however, producing a net acidification phase. We observe here that at the acidification period corresponds both a potential Al toxicity phase and a context of low Ca availability. These poor conditions disappeared during the alkalisation phase. Although atmospheric inputs were higher in winter than during summer, the acidification/potential Al toxicity phases were obviously more related to the seasonal vegetation rest phase than to the atmospheric inputs *per se*. The latter must be regarded as a minor component of Al toxicity, the main component



**Fig 1.** Seasonal variations of the ATI (—), the Ca/Al ratio (---) and the Ca/H ratio (.....) in the leaching soil waters collected at depths of 15, 30 and 60 cm. The horizontal straight line depicts the toxicity threshold.

resting in the intrinsic ecosystem properties and functioning. This point of view is not so far from that of Baur and Feger (1992), for whom natural soil processes have a greater influence than acid deposition upon Al mobilisation in forested ecosystems with low to moderate acid loads. The fact that even low winter acid loads may have cumulative effects on mobilisation of base cations from the soil should not be overlooked, however, as this could be regarded as responsible for the poor base status of many acid soils (Falkengren-Grerup and Eriksson, 1990; Hallbäck, 1992; Joslin *et al*, 1992).

As it occurred during the vegetation rest phase, the influence of such a winter Al toxicity context on forest decline can be questioned. Nutrient uptake during winter may be regarded as potentially low, and the impact of the toxic Al species on tree nutrition would be negligible during this season. Vogt *et al* (1980), however, have shown that the development of the mycorrhized fine roots of *Abies amabilis* Dougl occurred mainly during winter. In the present study it can be hypothesized, therefore, that such a process may be restricted during winter. A better understanding of tree root dynamics is needed to answer this question.

## CONCLUSION

By inhibiting Ca and Mg uptake, the toxic species of Al can be theoretically regarded as constituting a factor contributing to forest decline. Alone or in conjunction with other environmental factors, they could be involved in the discoloration of conifers on acid soils. Neither total Al concentrations (or activities) nor too simple indexes, such as the widely used Ca/Al ratio, can account satisfactorily for the influence of soluble Al. The calculation of a suitable toxicity index involving only the toxic Al species

and all the beneficial cations is a prerequisite to any assessment of Al toxicity. The application of these considerations allowed us to observe a winter seasonal occurrence of a potential Al toxicity phase in a declining silver fir forest from the Vosges highlands receiving moderate acid loads ( $3.78 \text{ keq}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ ). By contrast, the use of the Ca/Al ratio would erroneously suggest the occurrence of Al toxicity during a large part of the year, particularly in the surface soil horizon. Nutrient uptake during winter being potentially low, it seems doubtful that the observed winter Al toxicity context indicated by the ATI may constitute a decisive factor for the declining condition of the stand studied. No generalisation can be drawn with respect to other forests.

## REFERENCES

- Achilli M, Ciceri G, Ferraroli R, Culivicchi G, Pierri S (1991) Aluminium speciation in aqueous solutions. *Water Air Soil Pollut* 57-58, 139-148
- Adams F, Lund ZF (1966) Effect of chemical activity of soil solution aluminium on cotton root penetration of acid subsoils. *Soil Sci* 101 (3), 193-198
- Adams F, Moore BL (1983) Chemical factors affecting root growth in subsoil horizons of coastal plain soils. *Soil Sci Soc Am J* 47, 99-102
- Alva AK, Edwards DG, Asher CJ, Blamer FPC (1986a) Effects of phosphorus/aluminium molar ratio and calcium concentration on plant response to Al toxicity. *Soil Sci Soc Am J* 50, 133-137
- Alva AK, Edwards DG, Asher CJ, Blamey FPC (1986b) Relationships between root length of soybean and calculated activities of aluminium monomers in nutrient solution. *Soil Sci Soc Am J* 50, 959-962
- Alva AK, Asher CJ, Edwards DG (1986c) The role of calcium in alleviating aluminium toxicity. *Aust J Agric Res* 37, 375-382
- Alva AK, Sumner ME, Li YC, Miller WP (1989) Evaluation of three aluminium assay tech-

- niques for excluding aluminium complexed with fluoride or sulfate. *Soil Sci Soc Am J* 53, 38-44
- Alva AK, Kerven GL, Edwards DG, Asher CJ (1991) Reduction in toxic aluminium to plants by sulphate complexation. *Soil Sci* 152 (5), 351-359
- Alvarez E, Martinez A, Calvo R (1992) Geochemical aspects of aluminium in forest soils in Galicia (NW Spain). *Biogeochemistry* 16, 167-180
- Anderson MA, Bertsch PM (1988) Dynamics of aluminium complexation in multiple ligand systems. *Soil Sci Soc Am J* 52, 1597-1602
- Ares J (1986a) Identification of aluminium species in acid forest soil solutions on the basis of Al:F reaction kinetics: 1. Reaction paths in pure solutions. *Soil Sci* 141 (6), 399-407
- Ares J (1986b) Identification of aluminium species in acid forest soil solutions on the basis of Al:F reaction kinetics: 2. An example at the Solling area. *Soil Sci* 142 (1), 13-19
- Arp PA, Meyer WL (1985) Formation constants for selected organo-metal ( $Al^{3+}$ ,  $Fe^{3+}$ )-phosphate complexes. *Can J Chem* 63, 3357-3366
- Arp PA, Ouimet R (1986) Uptake of Al, Ca and P in black spruce seedlings: effect of organic versus inorganic Al in nutrient solutions. *Water Air Soil Pollut* 31, 367-375
- Arp PA, Strucel I (1989) Water uptake by black spruce seedlings from rooting media (solution, sand, peat) treated with inorganic and oxalated aluminium. *Water Air Soil Pollut* 44, 57-70
- Asp H, Berggren D (1990) Phosphate and calcium uptake in beech (*Fagus sylvatica*) in the presence of aluminium and natural fulvic acid. *Physiol Plant* 80, 307-314
- Asp H, Bengtsson B, Jensen P (1988) Growth and cation uptake in spruce (*Picea abies* Karst) grown in sand culture with various aluminium contents. *Plant Soil* 111, 127-133
- Asp H, Bengtsson B, Jensen P (1991) Influence of aluminium on phosphorus and calcium localization in roots of beech (*Fagus sylvatica*). *Physiol Plant* 83, 41-46
- Bache BW, Sharp GS (1976) Soluble polymeric hydroxy-aluminium ions in acid soils. *J Soil Sci* 27, 167-174
- Backes CA, Tipping E (1987) An evaluation of the use of cation-exchange resin for the de-termination of organically-complexed Al in natural acid water. *Int J Environ Anal Chem* 30, 135-143
- Baligar VC, Wright RJ, Ritchey KD (1992) Soil acidity effects on wheat seedling root growth. *J Plant Nutr* 15, 845-856
- Bartlett RJ, Riego DC (1972a) Effect of chelation on the toxicity of aluminium. *Plant Soil* 37, 419-423
- Bartlett RJ, Riego DC (1972b) Toxicity of hydroxy aluminium in relation to pH and phosphorus. *Soil Sci* 114, 194-200
- Bartoli F, Jeanroy E, Vedy JC (1981) Transfert et redistribution du silicium, de l'aluminium et du fer dans les podzols : rôle des composés organiques et des supports minéraux. In : *Migration organo-minérales dans les sols tempérés*. Coll Int CNRS 303 Nancy (1979), 281-289
- Baur S, Feger KH (1992) Importance of natural soil processes relative to atmospheric deposition in the mobility of aluminium in forested watersheds of the Black Forest. *Environ Pollut* 77, 99-105
- Becquer T (1991) Production endogène de protons par les cycles de l'azote et du soufre dans 2 sapinières vosgiennes : bilans saisonniers et incidence sur la toxicité de l'aluminium. Thèse de doctorat de l'Université de Nancy I
- Becquer T, Merlet D, Boudot JP, Rouiller J, Gras F (1990) Nitrification and nitrate uptake: leaching balance in a declined forest ecosystem from eastern France. *Plant Soil* 125, 95-107
- Becquer T, Boudot JP, Merlet D, Rouiller J (1992) Incidence des cycles de l'azote et du soufre sur le bilan de protons d'un écosystème forestier déperissant. Relation avec la toxicité aluminique. *C R Acad Sci Paris Serie II* 314 (5), 527-532
- Bennet RJ, Breen CM, Fey MV (1987) The effect of aluminium on root cap function and root development in *Zea mays* L. *Environ Exp Bot* 27, 91-104
- Bengtsson B, Asp A, Jensen P, Berggren (1988) Influence of aluminium on phosphate and calcium uptake in beech (*Fagus sylvatica*) grown in nutrient solution and soil solution. *Physiol Plant* 74, 299-305
- Berggren D (1989) Speciation of aluminium, cadmium, copper, and lead in humic soil so-

- lutions. A comparison of the ion exchange column procedure and equilibrium dialysis. *Int J Environ Anal Chem* 35, 1-15
- Berggren D (1992) Speciation and mobilization of aluminium and cadmium in podzols and cambisols of S Sweden. *Water Air Soil Pollut* 62, 125-156
- Bertsch PM (1987) Conditions for Al<sub>13</sub> polymer formation in partially neutralized aluminium solutions. *Soil Sci Soc Am J* 51, 825-828
- Bertsch PM (1989) Aqueous polynuclear aluminium species. In: *The Environmental Chemistry of Aluminium* (G Sposito, ed). CRC Press, Boca Baton, Florida, 87-115
- Bertsch PM, Anderson MA (1989) Speciation of aluminium in aqueous solutions using ion chromatography. *Anal Chem* 61 (6), 535-539
- Bessho T, Bell LC (1992) Soil solid and solution phase changes and mung bean response during amelioration of aluminium toxicity with organic matter. *Plant Soil* 140, 183-196
- Blamey FPC, Edwards DG, Asher CJ (1983) Effects of aluminium, OH:Al and P:Al molar ratios, and ionic strength on soybean root elongation in solution culture. *Soil Sci* 136, 197-207
- Blamey FPC, Edmeades DC, Wheeler DM (1992) Empirical models to approximate calcium and magnesium ameliorative effects and genetic differences in aluminium tolerance in wheat. *Plant Soil* 144, 281-287
- Bloom PR, Erich MS (1989) The quantitation of aqueous aluminium. In: *The Environmental Chemistry of Aluminium* (G Sposito, ed). CRC Press, Boca Raton, Florida, 1-27
- Bottero JY, Marchal JP, Poirier JE, Cases JM, Fiessinger F (1982a) Étude, par RMN de l'Aluminium-27, des solutions diluées de chlorure d'aluminium partiellement neutralisées. *Bull Soc Chim Fr* 11-12, I-439-I-444
- Bottero JY, Tchoubar D, Cases JM, Fiessinger F (1982b) Investigation of the hydrolysis of aqueous solutions of aluminium chloride. 2. Nature and structure by small-angle X-ray scattering. *J Phys Chem* 86, 3667-3670
- Bourrié G, Grimaldi C, Régeard A (1989) Monomeric versus mixed monomeric-polymeric models for aqueous aluminium species: constraints from low-temperature natural waters in equilibrium with gibbsite under temperate and tropical climate. *Chem Geol* 76, 403-417
- Boxman AW, Krabbendam H, Bellemakers MJS, Reolofs JGM (1991) Effects of ammonium and aluminium on the development and nutrition of *Pinus nigra* in hydroculture. *Environ Pollut* 73, 119-136
- Brogan JC (1964) The effect of humic acid on aluminium toxicity. In: *Trans 8th Int Congress Soil Sci*, Bucarest, 3, 227-234
- Brown DW, Hem JD (1975) Chemistry of aluminium in natural water. Reactions of aqueous aluminium species at mineral surfaces. *US Geol Survey Water-Supply*, Paper 1827-F
- Brown G, Newman ACD (1973) The reaction of soluble aluminium with montmorillonite. *J Soil Sci* 24, 339-354
- Browne BA, Driscoll CT, McColl JC (1990) Aluminium speciation using morin: II. Principles and procedures. *J Environ Qual* 19 (1), 73-82
- Browne BA, Driscoll CT (1992) Soluble aluminium silicates: stoichiometry, stability, and implications for environmental geochemistry. *Science* 256, 1667-1670
- Browning MHR, Hutchinson TC (1991) The effects of aluminium and calcium on the growth and nutrition of selected ectomycorrhizal fungi of jack pine. *Can J Bot* 69, 1691-1699
- Bruce RC, Warrell LA, Edwards DG, Bell LC (1988) Effects of aluminium and calcium in the soil solution of acid soils on root elongation of Glycine max cv Forrest. *Aust J Agric Res* 38, 319-338
- Cambraia J, Pimenta JA, Esteveao MM, Sant'Anna R (1989) Aluminium effects on nitrate uptake and reduction in sorghum. *J Plant Nutr* 12 (12), 1435-1445
- Cameron RS, Ritchie GSP, Robson AD (1986) Relative toxicities of inorganic aluminium complexes to barley. *Soil Sci Soc Am J* 50, 1231-1236
- Campbell GC, Bisson M, Bougie R, Tessier A, Villeneuve JP (1983) Speciation of aluminium in acidic freshwaters. *Anal Chem* 55, 2246-2252
- Clarke N, Danielsson LG, Sparén A (1977) The determination of quickly reacting aluminium in natural waters by kinetic discrimination in a flow system. *Int J Environ Anal Chem* 48, 77-100
- Clarkson DT, Sanderson J (1969) The uptake of a polyvalent cation and its distribution in the

- root apices of allium cepa: traces and autoradiographic studies. *Planta* 89, 136-154
- Conyers MK, Poile GJ, Cullis BR (1991a) Lime responses by barley as related to available soil aluminium and manganese. *Aust J Agric Res* 42, 379-390
- Conyers MK, Munns DN, Helyar KR, Poile GJ (1991b) The use of cation activity ratios to estimate the intensity of soil acidity. *J Soil Sci* 42, 599-606
- Copeland L, De Lima ML (1992) The effect of aluminium on enzyme activities in wheat roots. *J Plant Physiol* 140, 641-645
- Cumming JR, Weinstein LH (1990) Aluminium-mycorrhizal interactions in the physiology of pitch pine seedlings. *Plant Soil* 125, 7-18
- Dahlgren RA, Ugolini F (1989) Aluminium fractionation of soil solutions from unperturbed and tephra-treated spodosols, Cascade Range, Washington, USA. *Soil Sci Soc Am J* 53, 559-566
- David MB, Driscoll CT (1984) Aluminium speciation and equilibria in soil solutions of a haplorthod in the Adirondack mountains (New York, USA). *Geoderma* 33, 297-318
- Driscoll CT (1984) A procedure for the fractionation of aqueous aluminium in dilute acidic waters. *Int J Environ Anal Chem* 16, 267-283
- Duchaufour P (1970) *Précis de Pédologie*. Masson, Paris, 3rd ed
- Duffield JR, Edwards K, Evans DA, Morrish DM, Vobe RA, Williams DR (1991) Low molecular mass aluminium complex speciation in biofluids. *J Coord Chem* 23, 277-290
- Edmeades DC, Wheeler DM, Blamey FPC, Christie RA (1991) Calcium and magnesium amelioration of aluminium toxicity in Al-sensitive and Al-tolerant wheat. In: *Plant-soil Interactions at Low pH* (RJ Wright *et al*, eds). Kluwer Acad Publ, 755-761
- Falkengren-Grerup U, Eriksson H (1990) Changes in soil, vegetation and forest yield between 1947 and 1988 in beech and oak sites of southern Sweden. *Forest Ecol Manag* 38, 37-53
- Fawzy H, Overstreet RL, Jacobson L (1954) The influence of hydrogen ion concentrations on the cation absorption by barley roots. *Plant Physiol* 29, 234-237
- Foy CD (1984) Physiological effects of hydrogen, aluminium, and manganese toxicities in acid soil. In: *Soil Acidity and Liming, 2nd edn* (F Adams, ed). Agronomy Monograph N° 12, ASA-CSSA-SSSA, WI 53711, USA, 57-97
- Geburek T, Scholz F, Bergmann F (1986) Variation in aluminium sensitivity among *Picea abies* (L) Karst seedlings and genetic differences between their mother trees as studied by isozyme-gene-markers. *Angew Botanik* 60, 451-460
- Gibson JAE, Willet IR (1991) The application of fluorescence detection to the determination and speciation of aluminium in soil solutions by ion chromatography. *Commun Soil Sci Plant Anal* 22 (13-14), 1303-1313
- Godbold DL (1991) Aluminium decreases root growth and calcium and magnesium uptake in *Picea abies* seedlings. In: *Plant-soil Interactions at Low pH* (RJ Wright *et al*, eds). Kluwer Acad Publ, 747-753
- Godbold DL, Fritz E, Hüttermann A (1988) Aluminium toxicity and forest decline. *Proc Natl Acad Sci USA* 85, 3888-3892
- Göransson A, Eldhuset TD (1987) Effects of aluminium on growth and nutrient uptake of *Betula pendula* seedlings. *Physiol Plant* 69, 193-199
- Göransson A, Eldhuset TD (1991) Effects of aluminium on growth and nutrient uptake of small *Picea abies* and *Pinus sylvestris* plants. *Trees* 5, 136-142
- Grimme H, Lindhauer MG (1989) The effect of Al and Mg on the transpiration rate of young maize plants. *Z Pflanzenernähr Bodenk* 151, 453-454
- Grauer UE, Horst W (1991) Comments on the Calcium-Aluminium Balance (CAB). *Soil Sci Soc Am J* 55, 897-898
- Hallbäck L (1992) Long-term changes of base cation pools in soil and biomass in a beech and a spruce forest of southern Sweden. *Z Pflanzenernähr Bodenkol* 155, 51-60
- Haug A (1984) Molecular aspects of aluminium toxicity. *CRC Crit Rev Plant Sci* 2, 345-373
- Hecht-Buchholz C, Foy CD (1981) Effect of aluminium toxicity on root morphology of barley. In: *Structure and Function of Plant Roots* (R Brouwer *et al*, eds). Martinus Nijhoff/Dr W Junk Publishers, The Hague, 343-345
- Hecht-Buchholz C, Schuster J (1987) Responses of Al-tolerant Dayton and Al-sensitive Kearney barley cultivars to calcium

- and magnesium during Al stress. *Plant Soil* 99, 47-61
- Hecht-Buchholz C, Jorns CA, Keil P (1987) Effect of excess aluminium and manganese on Norway spruce seedlings as related to magnesium nutrition. *J Plant Nutr* 10 (9-16), 1103-1110
- Helliwell S, Batley GE, Florence TM, Lumsden BG (1983) Speciation and toxicity of aluminium in a model freshwater. *Environ Technol Lett* 4, 141-144
- Hentschel E, Godbold DS, Marschner P, Schlegel H, Jentschke G (1993) The effect of *Paxillus involutus* Fr on aluminium sensitivity of Norway spruce seedlings. *Tree Physiol* 12, 379-390
- Hodges SC (1987) Aluminium speciation: a comparison of five methods. *Soil Sci Soc Am J* 51, 57-64
- Horst WJ, Wagner A, Marschner H (1982) Mucilage protects root meristems from aluminium injury. *Z Pflanzenphysiol* 105, 435-444
- Horst WJ, Asher CJ, Cakmak I, Szulkiewicz P, Wissemeyer AH (1992) Short-term responses of soybean roots to aluminium. *J Plant Physiol* 140, 174-178
- Huang J, Bachelard EP (1993) Effects of aluminium on growth and cation uptake in seedlings of *Eucalyptus mannifera* and *Pinus radiata*. *Plant Soil* 149, 121-127
- Huang JW, Shaff JE, Grunes DL, Kochian LV (1992) Aluminium effects on calcium fluxes at the root apex of aluminium-tolerant and aluminium-sensitive wheat cultivars. *Plant Physiol* 98, 230-237
- Hue NV, Craddock GR, Adams F (1986) Effect of organic acids on aluminium toxicity in subsoils. *Soil Sci Soc Am J* 50, 28-34
- Huett DO, Menary RC (1980) Aluminium distribution in freeze-dried roots of cabbage, lettuce and kikuyu grass by energy-dispersive X-ray analysis. *Aust J Plant Physiol* 7, 101-111
- Hunter D, Ross DS (1991) Evidence for a phytotoxic hydroxy-aluminium polymer in organic soil horizons. *Science* 251 (4997), 1056-1058
- Hutchinson TC, Bozic L, Munoz-Vega G (1986) Response of five species of conifer seedlings to aluminium stress. *Water Air Soil Pollut* 31, 283-294
- Hüttermann A, Ulrich B (1984) Solid phase-solution-root interactions in soils subjected to acid deposition. *Phil Trans R Soc London B* 305, 353-368
- James BR, Clark CJ, Riha SJ (1983) An 8-hydroxyquinoline method for labile and total aluminium in soil extracts. *Soil Sci Soc Am Proc* 47, 893-897
- Jardine PM, Zelazny LW (1986) Mononuclear and polynuclear aluminium speciation through differential kinetic reactions with ferron. *Soil Sci Soc Am J* 50, 895-900
- Jardine PM, Zelazny LW (1987a) Influence of organic anions on the speciation of mononuclear and polynuclear aluminium by ferron. *Soil Sci Soc Am J* 51, 885-889
- Jardine PM, Zelazny LW (1987b) Influence of inorganic anions on the speciation of mononuclear and polynuclear aluminium by ferron. *Soil Sci Soc Am J* 51, 889-892
- Jentschke G, Godbold DL, Hüttermann A (1991) Culture of mycorrhizal tree seedlings under controlled conditions: effects of nitrogen and aluminium. *Physiol Plant* 81, 408-416
- Jones P (1991) The investigation of aluminium speciation in natural and potable waters using short-column ion chromatography. *Int J Environ Anal Chem* 44 (1), 1-10
- Jongbloed RH, Borst-Pauwells GWFH (1992) Effects of aluminium and pH on growth and potassium uptake by three ectomycorrhizal fungi in liquid culture. *Plant Soil* 140, 157-165
- Joslin JD, Wolfe MH (1988) Responses of red spruce seedling to changes in soil aluminium in six amended forest soil horizons. *Can J For Res* 18 (12), 1614-1623
- Joslin JD, Kelly JM, Wolfe MH, Rustad LE (1988) Elemental patterns in roots and foliage of mature spruce across a gradient of soil aluminium. *Water Air Soil Pollut* 40, 375-390
- Joslin JD, Kelly JM, Van Migroet H (1992) Soil chemistry and nutrition of north American spruce-fir stands: evidence for recent change. *J Environ Qual* 21, 12-30
- Kasuya MCM, Muchovej RMC, Muchovej JJ (1990) Influence of aluminium on *in vitro* formation of *Pinus caribaea* mycorrhizae. *Plant Soil* 124, 73-77
- Kelly JM, Schaedle M, Thornton FC, Joslin JD (1990) Sensitivity of tree seedlings to alumin-

- ium: II. Red oak, sugar maple, and European beech. *J Environ Qual* 19 (2), 172-179
- Keltjens WG (1990) Effects of aluminium on growth and nutrient status of Douglas-fir seedlings grown in culture solution. *Tree Physiol* 6, 165-175
- Kerven GL, Edwards DG, Asher CJ, Hallman PS, Kokot S (1989a) Aluminium determination in soil solution. I. Evaluation of existing colorimetric and separation methods for the determination of inorganic monomeric aluminium in the presence of organic acid ligands. *Aust J Soil Res* 27, 79-90
- Kerven GL, Edwards DG, Asher CJ, Hallman PS, Kokot S (1989b) Aluminium determination in soil solution. II. Short-term colorimetric procedures for the measurement of inorganic monomeric aluminium in the presence of organic acid ligands. *Aust J Soil Res* 27, 91-102
- Kinraide TB (1990) Assessing the rhizotoxicity of the aluminate ion,  $\text{Al}(\text{OH})_4^-$ . *Plant Physiol* 94, 1620-1625
- Kinraide TB (1991) Identity of the rhizotoxic aluminium species. *Plant Soil* 134, 167-178
- Kinraide TB, Parker DR (1987a) Non-phytotoxicity of the aluminium sulfate ion,  $\text{AlSO}_4^+$ . *Physiol Plant* 71, 207-212
- Kinraide TB, Parker DR (1987b) Cation amelioration of aluminium toxicity in wheat. *Plant Physiol* 83, 546-551
- Kinraide TB, Parker DR (1989) Assessing the phytotoxicity of mononuclear hydroxy-aluminium. *Plant Cell Environ* 12, 479-487
- Kinraide TB, Parker DR (1990) Apparent phytotoxicity of mononuclear hydroxy-aluminium to four dicotyledonous species. *Physiol Plant* 79, 283-288
- Knononova MM (1961) *Soil Organic Matter. Its Nature, its Role in Soil Formation and in Soil Fertility*. Pergamon press
- Lalande H, Hendershot WH (1986) Aluminium speciation in some synthetic systems: comparison of the fast-oxine, pH 5 extraction and dialysis methods. *Can J Fish Aquat Sci* 43, 231-234
- Landmann G, Bonneau M, Adrian M (1987) Le dépérissement du sapin pectiné et de l'épicéa commun dans le massif vosgien est-il en relation avec l'état nutritionnel des peuplements ? *Rev For Fr* 39, 5-11
- LaZerte BD (1984) Forms of aqueous aluminium in acidified catchments of central Ontario: a methodological analysis. *Can J Fish Aquat Sci* 41, 766-776
- Lindberg S (1990) Aluminium interactions with  $\text{K}^+$  ( $^{86}\text{Rb}^+$ ) and  $^{45}\text{Ca}^{2+}$  fluxes in three cultivars of sugar beet (*Beta vulgaris*). *Physiol Plant* 79, 275-282
- Lund ZF (1970) The effect of calcium and its relation to several cations in soybean root growth. *Soil Sci Soc Am Proc* 34, 456-459
- Lydersen E, Salbu B, Poleo ABS, Muniz IP (1990) The influences of temperature on aqueous aluminium chemistry. *Water Air Soil Pollut* 51, 203-215
- MacLean DC, Hansen KS, Schneider RE (1992) Amelioration of aluminium toxicity in wheat by fluoride. *New Phytol* 121, 81-88
- Matsumoto H, Morimura S, Hirasawa F (1979) Localization of absorbed aluminium in plant tissues and its toxicity studies in the inhibition of pea root elongation. In: *Mineral Nutrition of Plants* (K Kudrev et al, eds). *Proc 1st Int Symp on Plant Nutrition*, Varna, Bulgaria, Vol 1. Bulg Acad Sci, Inst Plant Physiol, Sofia, 171-194
- McAvoy DC, Santore RC, Shosa JD, Driscoll CT (1992) Comparison between pyrocatechol violet and 8-hydroxyquinoline procedures for determining aluminium fractions. *Soil Sci Soc Am J* 56, 449-455
- McCormick LH, Borden FY (1972) Phosphate fixation by aluminium in plant roots. *Soil Sci Soc Am Proc* 39, 799-802
- McLean EO (1965) Aluminium. In: *Methods of Soil Analysis*, part 2 (CA Black, ed). American Society of Agronomy, Vol 9, Madison, WI, 978-998
- Menzies NW, Kerven GL, Bell, Edwards DG (1992) Determination of total soluble aluminium in soil solution using pyrocatechol violet, lanthanum and iron to discriminate against micro-particulates and organic ligands. *Commun Soil Sci Plant Anal* 23, 2525-2545
- Miyasaka SC, Buta JG, Howell RK, Foy CD (1991) Mechanism of aluminium tolerance in snapbeans. Root exudation of citric acid. *Plant Physiol* 96, 737-743
- Munns DN, Helyard KR, Conyers M (1992) Determination of aluminium activity from measurements of fluoride in acid soil solutions. *J Soil Sci* 43, 441-446

- Neitzke M (1990) Stickstoffernährung und Al-toxizität bei Buchenjüngspflanzen. I. Entwicklung von Buchenjüngspflanzen in Abhängigkeit von der Form der Stickstoffernährung und dem Aluminiumgehalt der Nährlösung. *Z Pflanzenernähr Bodenkd* 153, 229-234
- Nilsson SI, Bergkvist B (1983) Aluminium chemistry and acidification processes in a shallow podzol on the Swedish westcoast. *Water Air Soil Pollut* 20, 311-329
- Noble AD, Summer ME (1988) Calcium and Al interactions and soybean growth in nutrient solutions. *Commun Soil Sci Plant Anal* 19, 1119-1131
- Noble AD, Fey MV, Summer ME (1988a) Calcium-aluminium balance and the growth of soybean roots in nutrient solutions. *Soil Sci Soc Am J* 52, 1651-1656
- Noble AD, Sumner ME, Alva AK (1988b) The pH dependency of aluminium phytotoxicity alleviation by calcium sulfate. *Soil Sci Soc Am J* 52, 1398-1402
- Nordstrom DK, May HM (1989) Aqueous equilibrium data for mononuclear aluminium species. In: *The Environmental Chemistry of Aluminium* (G Sposito, ed). CRC Press, Boca Raton, Florida, 29-55
- Nosko P, Kershaw A (1992) The influence of pH on the toxicity of a low concentration of aluminium to white spruce seedlings. *Can J Bot* 70, 1488-1492
- Nys C (1987) Fonctionnement du sol d'un écosystème forestier : Étude des modifications dues à la substitution d'une plantation d'épicéas commun (*Picea abies*) à une forêt feuillue mélangée des Ardennes. Thèse de doctorat de l'Université de Nancy I
- Ogner G, Teigen O (1980) Effects of acid irrigation and liming on two clones of Norway spruce. *Plant Soil* 57, 305-321
- Pan WL, Hopkins AG, Jackson WA (1989) Aluminium inhibition of shoot lateral branches of glycine max and reversal by exogenous cytokinin. *Plant Soil* 120, 1-9
- Parker DR, Bertsch PM (1992) Identification and quantification of the "Al<sub>13</sub>" tridecameric polycation using ferron. *Environ Sci Technol* 26 (5), 908-914
- Parker DR, Kinraide TB, Zelazny LW (1988a) Aluminium speciation and phytotoxicity in dilute hydroxy-aluminium solutions. *Soil Sci Soc Am J* 52, 438-444
- Parker DR, Zelazny LW, Kinraide TB (1988b) Comparison of three spectrophotometric methods for differentiating mono- and polynuclear hydroxy-aluminium complexes. *Soil Sci Soc Am J* 53, 789-796
- Parker DR, Kinraide TB, Zelazny LW (1989) On the phytotoxicity of polynuclear hydroxy-aluminium species. *Soil Sci Soc Am J* 53, 789-796
- Parker DR, Norvell WA, Chaney RL (1992) GEOCHEM-PC: A chemical speciation program for IBM and compatible personal computers. In: *Soil Chemical Equilibrium and Reaction Models* (RH Loeppert *et al*, ed). ASA-SSSA, Madison, WI (in press)
- Pavan MA, Bingham FT (1982) Toxicity of aluminium to coffee seedlings grown in nutrient solution. *Soil Sci Soc Am J* 46, 993-997
- Pavan MA, Bingham FT, Pratt PF (1982) Toxicity of aluminium to coffee in ultisols and oxisols amended with CaCO<sub>3</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O ent solution. *Soil Sci Soc Am J* 46, 1201-1207
- Petterson S, Strid H (1989) Effects of aluminium on growth and kinetics of K<sup>+</sup>(<sup>86</sup>Rb) uptake in two cultivars of wheat (*Triticum aestivum*) with different sensitivity to aluminium. *Physiol Plant* 76, 255-261
- Petterson A, Hällbom L, Bergman B (1988) Aluminium effects on uptake and metabolism of phosphorus by the cyanobacterium *Anabaena cylindrica*. *Plant Physiol* 86, 112-116
- Raynal DJ, Joslin JD, Thornton FC, Schaedle M, Henderson GS (1990) Sensitivity of tree seedlings to aluminium: III. Red spruce and loblolly pine. *J Environ Qual* 19, 180-187
- Rengel Z (1990) Competitive Al<sup>3+</sup> inhibition of net Mg<sup>2+</sup> uptake by intact *Lolium multiflorum* roots. II. Plant age effects. *Plant Physiol* 93, 1261-1267
- Rengel Z, Robinson DL (1990) Temperature and magnesium effects on aluminium toxicity in annual ryegrass (*Lolium multiflorum*). In: *Plant Nutrition Physiology and Applications* (ML Van Beusichem, ed). Kluwer Acad Publ, 413-417
- Rengel Z, Elliot DC (1992) Mechanism of aluminium inhibition of net <sup>45</sup>Ca<sup>2+</sup> uptake by *Amaranthus* protoplasts. *Plant Physiol* 98, 632-638
- Rhue RD, Grogan (1977) Screening corn for Al tolerance using different Ca and Mg concentrations. *Agron J* 69, 755-760

- Ritsemá CJ (1993) Estimation of activity coefficients of individual ions in solutions with ionic strengths up to 0.3 mol dm<sup>-3</sup>. *J Soil Sci* 44, 307-315
- Rost-Siebert K (1983) Aluminium-Toxizität und -Toleranz an Keimpflanzen von Fichte (*Picea abies* Kart) und Buche (*Fagus silvatica* L). *Allg Forstzeitschr* 38, 686-689
- Rost-Siebert K (1984) Aluminium toxicity in seedlings of Norway spruce (*Picea abies* Karst) and beech (*Fagus silvatica* L). In: *Aluminium Toxicity in Trees* (F Anderson and JM Kelly, eds). Swedish University of Agricultural Sciences, Uppsala, Sweden, 49-68
- Royset O, Sullivan TJ (1986) Effect of dissolved humic compounds on the determination of aqueous aluminium by three spectrophotometric methods. *Int J Environ Anal Chem* 27, 305-314
- Saigusa M, Shoji S, Takahashi T (1980) Plant root growth in acid andosols from northeastern Japan: 2. Exchange acidity Y1 as a realistic measure of aluminium toxicity potential. *Soil Sci* 130 (5), 242-250
- Schaedle M, Thornton FC, Raynal DJ (1986) Non-metabolic binding of aluminium to roots of loblolly pine and honeylocust. *J Plant Nutr* 9 (9), 1227-1238
- Schaedle M, Thornton FC, Raynal DJ, Tepper HB (1989) Response of tree seedlings to aluminium. *Tree Physiol* 5, 337-356
- Schecher WD (1989) ALCHEMI 4.1 program. Privately distributed
- Schecher WD, McAvoy D (1992) MINEQL+: A software environment for chemical equilibrium modeling. *Comput Environ Systems* 16, 65-76
- Schier GA (1985) Response of red spruce and balsam fir seedlings to aluminium toxicity in nutrient solutions. *Can J For Res* 15, 29-33
- Schimansky C (1991) Einfluss von Aluminium und Protonen auf die Aufnahme und den Transport von Magnesium (<sup>28</sup>Mg) bei Gerste (*Hordeum vulgare* L). *Z Pflanzenernähr Bodenk* 154, 195-198
- Schlegel H, Amundson RG, Hüttermann A (1992) Element distribution in red spruce (*Picea rubens*) fine roots; evidence for aluminium toxicity at Whiteface Mountain. *Can J For Res* 22, 1132-1138
- Schmid S, Kördel W, Klöppel H, Klein W (1989) Differentiation of Al<sup>3+</sup> and Al species in environmental samples by isotachopheresis. *J Chrom* 470, 289-297
- Schröder WH, Bauch J, Endeward R (1988) Microbeam analysis of Ca exchange and uptake in the fine roots of spruce: influence of pH and aluminium. *Trees* 2, 96-103
- Shann JR, Bertsch PM (1993) Differential cultivar response to polynuclear hydroxo-aluminium complexes. *Soil Sci Soc Am J* 57, 116-120
- Shortle WC, Smith KT (1988) Aluminium-induced calcium deficiency syndrome in declining red spruce. *Science* 240, 1017-1018
- Shotyk W, Sposito G (1990) Ligand concentration effect on aluminium complexation by a chesnut leaf litter extract. *Soil Sci Soc Am J* 54, 933-935
- Shuman LM, Wilson DO, Ramseur EL (1991) Testing aluminium-chelate equilibria models using *Sorghum* root growth as a bioassay for aluminium. *Water Air Soil Pollut* 57-58, 149-158
- Stumm W, Morgan JJ (1981) Aquatic chemistry, 2nd ed John Wiley and sons, New York, 780 p
- Suocff E, Thornton FC, Joslin JD (1990) Sensitivity of tree seedlings to aluminium. I. Honeylocust. *J Environ Qual* 19 (2), 163-171
- Suhayda CG, Haug A (1986) Organic acids reduce aluminium toxicity in maize root membranes. *Physiol Plant* 68, 189-195
- Suthipradit S, Edwards DG, Asher CJ (1990) Effects of aluminium on tap-root elongation of soybean (*Glycine max*), cowpea (*Vigna unguiculata*) and green gram (*Vigna radiata*) grown in the presence of organic acids. *Plant Soil* 124, 233-237
- Tan K, Keltjens WG (1990) Effects of aluminium on growth, nutrient uptake, proton efflux and phosphorus assimilation of aluminium-tolerant and -sensitive sorghum (*Sorghum bicolor*) genotypes. In: *Plant Nutrition Physiology and Applications* (ML Van Beusichem, ed) Kluwer Acad Publ, 397-401
- Tan K, Keltjens WG, Findenegg GR (1991) Role of magnesium in combination with liming in alleviating acid-soil stress with the aluminium-sensitive *Sorghum* genotype CV323. *Plant Soil* 136, 65-71
- Tan KH, Binger A (1986) Effect of humic acid on aluminium toxicity in corn plants. *Soil Sci* 141, 20-25

- Tanaka A, Tadano T, Yamamoto K, Kanamura N (1987) Comparison of toxicity to plants among  $Al^{3+}$ ,  $AlSO_4^+$  and Al-F complex ions. *Soil Sci Plant Nutr* 33, 43-55
- Tang VH, Nga TT, Laudelou H (1989) Effect of aluminium on the mineral nutrition of rice. *Plant Soil* 114, 173-185
- Tennakoon DBT, Thomas JM, Jones W, Carpenter TA, Ramadas S (1986) Characterization of clays and clay organic systems cation diffusion and dehydroxylation. *J Chem Soc Faraday Trans* 82, 545-562
- Tepper HB, Yang CS, Schaedle M (1989) Effect of aluminium on growth of root tips of honeylocust and loblolly pine. *Environ Exp Bot* 29 (2), 165-173
- Thornton FC, Schaedle M, Raynal DJ (1986a) Effect of aluminium on the growth of sugar maple in solution culture. *Can J For Res* 16, 892-896
- Thornton FC, Schaedle M, Raynal DJ, Zipperer C (1986b) Effects of aluminium on honeylocust (*Gleditsia triacanthos* L) seedlings in solution culture. *J Exp Bot* 37, 775-785
- Thornton FC, Schaedle M, Raynal DJ (1987) Effects of aluminium on red spruce seedlings in solution culture. *Environ Exp Bot* 27, 489-498
- Truesdell AH, Jones BF (1974) Wateq, a computer program for calculating chemical equilibria of natural waters. *J Res US Geol Survey* 2 (2), 233-248
- Truman R, Humphreys FR, Lambert MJ (1983) Prediction of site index for *Pinus radiata* at Mullions Range State Forest, NSW. *Aust J For Res* 13, 207-215
- Ulrich B, Mayer R, Khanna PK (1980) Chemical changes due to acid precipitation in a loess-derived soil in central Europe. *Soil Sci* 130, 193-199
- Ulrich B, Meiwes KJ, König N, Khanna PK (1984) Criteria proposed for the evaluation of risks caused by soil acidity. In: *Aluminium Toxicity in Trees* (F Anderson, JM Kelly, eds). Swedish Univ Agric Sciences, Uppsala, Sweden, 69-70
- Van Benschoten JE, Edzwald JK (1990) Measuring aluminium during water treatment: methodology and application. *J Am Water Works Assoc* 82 (5), 71-78
- Van Breemen N, Mulder J, Van Grinsven JJM (1987) Impact of acid atmospheric deposition on woodland soils in the Netherlands. II. Nitrogen transformations. *Soil Sci Soc Am J* 51, 1634-1640
- Van Praag HJ, Weissen F (1985) Aluminium effects on spruce and beech seedlings. I. Preliminary observations on plant and soil. *Plant Soil* 83, 331-338
- Van Praag HJ, Weissen F, Sougnez-Rémy S, Carletti G (1985) Aluminium effects on spruce and beech seedlings. II. Statistical analysis of sand culture experiments. *Plant Soil* 83, 339-356
- Vidal DR, Broyer TC (1962) Effect of high levels of Mg on the Al uptake and growth of maize in nutrient solutions. *An Edafol Agrobiol* 21, 13-30
- Viets FG (1944) Calcium and other polyvalent cations as accelerators of ion accumulation in excised barley roots. *Plant Physiol* 19, 446-480
- Vogt KA, Edmonds RK, Grier CC, Piper S (1980) Seasonal changes in mycorrhizal and fibrous-textured root biomass in 23- and 180-year-old Pacific silver fir stands in western Washington. *Can J For Res* 10, 523-529
- Wagatsuma T (1983) Effect of non-metabolic conditions on the uptake of aluminium by plant roots. *Soil Sci Plant Nutr* 29, 323-333
- Wagatsuma T, Ezoë Y (1985) Effect of pH on ionic species of aluminium in medium and on aluminium toxicity under solution culture. *Soil Sci Plant Nutr* 31, 547-561
- Wagatsuma T, Kaneko M (1987) High toxicity of hydroxy-aluminium polymer ions to plant roots. *Soil Sci Plant Nutr* 33, 57-67
- White RE, Tiffin LO, Taylor AW (1976) The existence of polymeric complexes in dilute solutions of aluminium and orthophosphate. *Plant Soil* 45, 521-529
- Whitten MG, Ritchie GSP, Willet IR (1992) Forms of soluble aluminium in acidic topsoils estimated by ion chromatography and 8-hydroxyquinoline and their correlation with growth of subterranean clover. *J Soil Sci* 43, 283-293
- Wilkins DA, Hodson MJ (1989) The effects of aluminium and *Paxillus involutus* Fr on the growth of Norway spruce [*Picea abies* (L) Karst]. *New Phytol* 113, 225-232
- Willet IR (1989) Direct determination of aluminium and its cationic fluoro-complexes by ion chromatography. *Soil Sci Soc Am J* 53, 1385-1391

- Wolfe MH, Joslin JD (1989) Honeylocust (*Gleditsia triacanthos* L.) root response to aluminium and calcium. *Plant Soil* 119, 181-185
- Wright RJ, Baligar VC, Wright SF (1987) Estimation of phytotoxic aluminium in soil solution using three spectrophotometric methods. *Soil Sci* 144, 224-232
- Wright RJ, Baligar VC, Ritchey KD, Wright SF (1989) Influence of soil solution aluminium on root elongation of wheat seedlings. *Plant Soil* 113, 294-298
- Yang CS, Schaedle M, Tepper HB (1989) Phytotoxicity of scandium in solution culture of loblolly pine (*Pinus taeda* L.) and honey locust (*Gleditsia triacanthos* L.). *Environ Ex Bo* 29 (2), 155-164
- Zel J, Blatnik A, Gogala N (1992) *In vitro* aluminium effects on ectomycorrhizal fungi. *Water Air Soil Pollut* 63, 145-153
- Zelazny LW, Jardine PM (1989) Surface reaction of aqueous aluminium. In: *The Environmental Chemistry of Aluminium* (G Sposito, ed). CRC Press, Boca Raton, Florida, 147-184
- Zöttl HW, Hüttl RF (1986) Nutrient supply and forest decline in southwest Germany. *Water Air Soil Pollut* 31, 449-462