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 dépeuplées. 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 dépeuplée 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 dépeuplé 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 mycorhizées 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 Ugolini, 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⁻¹ 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, Ca$^{2+}$ and 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; Schimanisky, 1991), but not, despite a number of conflicting reports, towards a direct inhibition of potassium uptake (Petterson 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 Ca$^{2+}$ and Mg$^{2+}$ but also to iron and important anions such as SO$_4^{2-}$, PO$_4^{3-}$, Cl$^-$ and 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, mycorrhizal fungi Pisolithus tinctorius Coker and Couch and Paxillus involutus Fr 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,
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, Al\(^{3+}\), AlOH\(^{2+}\), Al(OH)\(_2^+\) and Al(OH)\(_4^-\) (due to its polymerisation to 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 AlSO\(_4^+\) must be included here, despite repeated reports about its so-called non-toxicity. This will be discussed below.

The toxicity of 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 Al\(^{3+}\) > AlOH\(^{2+}\) > Al(OH)\(_2^+\). This view is not so far away from the conclusion of Bruce *et al* (1988), for which Al\(^{3+}\) and AlOH\(^{2+}\) are the only toxic inorganic monomeric Al species. Other data suggest conversely that AlOH\(^{2+}\) and Al(OH)\(_2^+\) are much more toxic for soybean than Al\(^{3+}\) (Alva *et al*, 1986a). Polymeric forms of Al occurred in this case and the presence of the very toxic 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 Al\(^{3+}\) but not to the Al-OH mononuclear species. Dicotyledons would be sensitive to Al-OH monomers at least and perhaps also to Al\(^{3+}\). This is not totally convincing, however, since: i) their assumption that H\(^+\) is less toxic than 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 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 Ca\(^{2+}\), 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).

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

<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 Al$^{3+}$ with a good certitude; data are, however, lacking with regards to their sensitivity to AlOH$^{2+}$ and Al(OH)$_2^+$. Although it does not constitute a toxic species per se, the aluminate ion Al(OH)$_4^-$ should be included in the harmful forms of Al, as it is expected to transform easily into the very toxic 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, Al(OH)$_3^-$ does not constitute a toxic species (Alva et al, 1986a; Tanaka et al, 1987).

Strong controversies exist about the toxicity of 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 silvatica 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 AlSO$_4^+$, regarded as the prevailing Al-sulphate ion pair in their experimental conditions. In most of these experiments, however, the SO$_4$/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 AlSO$_4^+$ but a more recently discovered one (approximately Al(SO$_4$)$_2$H$_2$O)$.^2_4$ (Alva et al, 1991). As the latter was found to be non-toxic, there is a great probability that the so-called “non-toxic AlSO$_4^+$” was in fact this new species and that the toxic Al-sulphate ion pair must be identified as AlSO$_4^+$.

The fluoride complexes of Al prevailing in the acid range, namely AlF$_2^+$, AlF$_2^+$, AlF$_3^-$ and, more rarely, AlF$_4^-$, have been proved to be non-toxic (AlOHF$_2^+$, AlOHF$_2^+$ and Al(OH)$_3$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 Al-PO$_4$ and Al-Si complexes remains mostly unknown but White et al (1976) and Alva et al (1986a) demonstrated that adding PO$_4^{3-}$-ions will induce a dramatic formation of non-toxic Al-PO$_4$ polymers, to such a large extent that the residual concentration of Al-PO$_4$ monomers can probably be neglected. Additionally, the non-toxicity of Al-PO$_4$ and 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 “Al$_{13}$” polymer AlO$_4$Al$_{12}$(OH)$_{24}$(H$_2$O)$_{12}^+$. Its toxicity was often considerably higher than that of Al$^{3+}$ (Parker et al, 1989; Shann and Bertsch, 1993). About 1 to 11.5 times less Al as Al$_{13}$ than as 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 Al$_{13}$, suggesting the occurrence of mechanisms other than those
listed above. The $\text{Al}_{13}$ 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 $\text{Al}_{13}$ formation, this presence is very surprising. Additionally, the occurrence of $\text{Al}$(OH)$_4^-$ is believed to be a prerequisite to the formation of $\text{Al}_{13}$ (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 $\text{Al}_{13}$, 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 $\text{Al}_{13}$ 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 $^{27}\text{Al}$ 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 $\text{Al}_{13}$ 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 $\text{Al}_{13}$ 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 $\text{Al}_{13}$ 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: $\text{Ca}^{2+} \approx \text{Mg}^{2+} \approx \text{Sr}^{2+} \gg \text{K}^+ = \text{Na}^+$ (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, Mg2+ was reported to be either more efficient, less efficient or as efficient as Ca2+, 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

45Ca2+, 48Mg2+ and 86Rb+ (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, 46Sc, a trivalent cation which may be complexed by both phosphate 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·kg⁻¹ needles without damage. Additionally and according to McCormick and Borden (1972), Huett and Menary (1980), Wagsatsuma (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·100 g⁻¹. A weaker ionic strength of the extractant was recommended by other authors. Both 0.01 M SrCl₂- and CaCl₂-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⁻¹ 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 ≤ 150 μM·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 μM·l⁻¹ (Schaedle et al, 1989; Sucoff et al, 1990). Higher toxicity thresholds (ranging from 200 to 700 μM·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 μM·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 μM·l⁻¹), which would pertain in this case to the following group (Schier, 1985).

Tolerant species are those which are sensitive to Al concentrations ≥ 800 μM·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. A considerably lower Al threshold has also been reported for *Quercus rubra* (120–280 μM·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 μM·l⁻¹ Al in nutrient solutions when Ca²⁺ = 1 300 μM·l⁻¹ and Mg²⁺ = 300 μM·l⁻¹ but are strongly damaged when these 2 elements reach only 130 and 30 μM·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 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 Ca$^{2+}$ ≤ 1/3 log 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 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 = [2log(Ca$^{2+}$)] − [3log(Al$^{3+}$) + 2log(AOH$^{2+}$) + log {Al(OH)$_2$$^{+}$}]) of Noble et al (1988a, 1988b) and Noble and Sumner (1988) overcomes some of these imperfections. Obviously, it must be completed by taking into account both the beneficial effect of Mg$^{2+}$ and the toxicity of AlSO$_4$$^{+}$, Al(OH)$_4$$^{-}$ and 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 toxicity of Al to wheat, the latter being regarded as insensitive to Al-OH monomers: % root growth inhibition = 100{Al$^{3+}$} / [{Al$^{3+}$} + 1.2 + 2.4{Ca$^{2+}$}$^{1.5}$ + 1.6{Mg$^{2+}$}$^{1.5}$ + 0.011{Na$^{+}$}$^{1.8}$ + 0.011{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 AlSO$_4$$^{+}$ monomers and do not involve the well-demonstrated toxicity of Al$_{13}$. The same remark applies to the Al activity ratio (AER) of Bessho and Bell (1992): AER = 1000 [3{Al$^{3+}$} / (3{Al$^{3+}$} + 2{Ca$^{2+}$} + 2{Mg$^{2+}$} + {K$^{+}$} + {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:

\[
\text{ATI (aluminium toxicity index)} = \frac{[4\{\text{Ca}^{2+}\} + 4\{\text{Mg}^{2+}\} + 0.02\{\text{K}^{+}\} + 0.02\{\text{Na}^{+}\}]}{[9\{\text{Al}^{3+}\} + 4\{\text{AlOH}^{2+}\} + {\text{Al(OH)}_{2}^{+}} + \{\text{AlSO}_{4}^{+}\} + 117-1345\{\text{Al}_{13}\} + 9-103\{\text{Al(OH)}_{4}^{-}\}].
\]

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 Gliricidia triacanthos (> 4.3) and some cereal species (4.8 to > 10) (from Hecht-Buchholz and Schuster, 1987; Soccov 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 Benschooten 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 μM Al·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; Royle 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 La3+ and organic Al was decomplexed by the addition of Fe3+ 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 soluble Al may allow, under certain conditions, the quantitative determination of several categories of Al, including monomeric Al, polymeric Al13 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 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-hydroxiquinoline-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 K₂SO₄ elution, 3 peaks are separated. The first involves the monovalent species that did not undergo dissociation during the chromatographic pathways, which were identified as AlF²⁺ 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 AlF₅⁺ and Al-humic acids₂⁺ complexes. The third involves as a single Al³⁺ species both initial Al³⁺ and all species that undergo dissociation during the chromatographic pathways, namely the Al-OH and Al-SO₄ monomers. Uncharged and probably negatively charged species such as AlF₃⁻ and AlF₄⁻ 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-PO₄ 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-PO₄ 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 AlF₂⁺ towards (AlF₂⁺ + AlF₃⁻). In addition, there is an important but variable decomplexation of organic Al, even with respect to some inner-sphere complexes. Uncharged species such as AlF₃⁻ 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 Al³⁺ in synthetic solutions, natural soil leachates and aqueous soil extracts, by isotachophoresis, without any interferences of Al-sulphate ion-pairs. The
interferences of Al-F, Al-PO₄ 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 NH₄⁺·ha⁻¹·yr⁻¹, 15 kg NO₃⁻·N·ha⁻¹·yr⁻¹, 22 kg SO₄²⁻·S·ha⁻¹·yr⁻¹, 31 kg Cl⁻·ha⁻¹·yr⁻¹ and 0.4 kg free H⁺·ha⁻¹·yr⁻¹ (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 (NH₄⁺), 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 Al₁₃ 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 $\text{Al}_{13}^-$ and $\text{Al(OH)}_4^-$ 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 alkalinisation 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 alkalinisation 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.

![Graphs showing seasonal variations of the ATI, Ca/Al, and Ca/H ratios](image)

**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; Hallbäcken, 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 keq ha\(^{-1}\) 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**


Alva AK, Summer ME, Li YC, Miller WP (1989) Evaluation of three aluminium assay tech-


Bartlett RJ, Riego DC (1972a) Effect of chelation on the toxicity of aluminium. *Plant Soil* 37, 419-423


Berggren D (1989) Speciation of aluminium, cadmium, copper, and lead in humic soil so-


Clarkson DT, Sanderson J (1969) The uptake of a polyvalent cation and its distribution in the
root apices of aillum cepa: traces and autoradiographic studies. Planta 89, 136-154


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


Kelly JM, Schaadle M, Thornton FC, Joslin JD (1990) Sensitivity of tree seedlings to alumin-
Aluminium toxicity in declining forests


Lindberg S (1990) Aluminium interactions with K⁺(⁸⁶Rb⁺) and ⁴⁵Ca²⁺ fluxes in three cultivars of sugar beet (*Beta vulgaris*). *Physiol Plant* 79, 275-282


Rhue RD, Grogan (1977) Screening corn for Al tolerance using different Ca and Mg concentrations. Agron J 69, 755-760

Rost-Siebert K (1983) Aluminium-Toxizität und -Toleranz an Keimpflanzen von Fichte (Picea abies Kart) und Buche (Fagus silvatica L). *Allg Forstzeitschr* 38, 666-689

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


Schecher WD (1989) ALCHEMI 4.1 program. Privately distributed


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


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


Vidal DR, Broyer TC (1962) Effect of high levels of Mg on the Al uptake and growth of 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


