Aluminum speciation in acid forest soil solutions: comparison of different methods
Spéciation de l'aluminium dans la solution de sols forestiers acides: comparaison de différentes méthodes

LUSTER Jörg, PENA-RODRIGUEZ Maria, HEIM Alexander, BLASER Peter

Swiss Federal Institute for Forest, Snow and Landscape Research, CH-8903 Birmensdorf, Switzerland

Introduction

High concentrations of aluminum in the soil solution of acid forest soils can be a major stress for trees (e.g. Marschner, 1989). The toxic effect depends to a great extent on the chemical nature of the Al species present (e.g. Kinraide, 1991). Several methods have been proposed for chemical speciation of Al present in soil solutions (Bloom and Erich, 1996). Probably the most widely used fractionation scheme is the one proposed by Driscoll (1984). Three fractions are determined: acid reactive Al is measured colorimetrically after acidification of the sample to pH 1, mononuclear Al by the same method in the unmodified sample, and ion exchange-labile Al as the difference between mononuclear Al and Al measured after passage of the sample over a strongly acidic cation exchange resin. The method has been automatized using flow injection analysis (FIA) (e.g. Royset, 1987, 1992). A different approach is the determination of complexation-labile Al based on fast reaction with 8-hydroxyquinoline (HQ). Both manual (e.g. Luster et al., 1993) and FIA methods (Clarke et al., 1992) have been described. Recently, Göttlein (1998) has shown that free Al$^{3+}$ concentrations can be measured by means of capillary electrophoresis (CE). Finally, Aluminum bound by dissolved organic matter can be detected by fluorescence spectroscopy (e.g. Luster et al., 1996). The aim of this paper was to compare the results obtained by all these different methods for soil solutions collected from two acid soil profiles typical for two regions of Switzerland. The results are interpreted by comparison with results obtained for synthetic solutions of various model organic ligands which were prepared once by avoiding formation of polynuclear Al species and once by synthesizing polynuclear Al at a defined OH/Al ratio.
Materials and Methods

Soil solutions
Soil solutions were collected in summer 1997 from a haplic alisol located near Ermatingen in north eastern Switzerland (Lüscher et al., 1997; bedrock: boulder marl; vegetation: Norway spruce; elevation: 560 m; mean annual precipitation: 900 mm; mean annual temperature: 8-9 °C) and from a haplic podzol located at Copera in southern Switzerland (bedrock: gneiss; vegetation: European chestnut; elevation: 650 m; slope: 26°; exposure: NW; mean annual precipitation: 1600 mm; mean annual temperature: 10 °C). The latter soil was classified also as cryptopodzolic soil (Blaser et al., 1997).
Solutions from just below the litter horizon were collected by tension-free lysimetry, those from mineral horizons by tension lysimetry using ceramic suction cups (highflow, Soilmoisture Equipment Corp., Santa Barbara, U.S.A.). In the latter case a vacuum of 60 kPa was applied at the beginning of each sampling period of 1 or 2 weeks.
In the collected soil solutions pH was measured immediately by potentiometry. Concentrations of dissolved organic carbon (DOC) were determined with a TOC analyzer (Shimadzu TOC 500) after storing the solutions at -20 °C. Total luminescence spectra were recorded of soil solutions that were diluted or concentrated to a DOC concentration of 10 mg/L and adjusted to pH 4.

Synthetic model solutions
„Polynuclear free“ solutions of catechol (30 µmol/L), oxalate (30 µmol/L) or citrate (20 µmol/L) and Al (20 µmol/L) were prepared by mixing 1mM stock ligand solutions adjusted to pH4 with a 100 µM stock Al solution (pH4, 0.01 M NaCl; from a 1000 mg/L AlCl$_3$ standard solution, Merck Titrisol) and diluting with 0.01 M NaCl adjusted to pH4.
„Polynuclear free“ solutions of Norway spruce litter (DOC = 10 mg/L) and Al (50 µmol/L) were prepared from aqueous litter extracts (2.5 g brown needles collected from the forest floor and dried at 40 °C extracted with doubly deionized water (Millipore MQ) for 16 hours on an end-over-end shaker; pH = 6.5; DOC = 90 mg/L), a 1000 mg/L AlCl$_3$ standard solution (Merck Titrisol) and doubly deionized water. The pH was adjusted to 4 with HCl. Solutions with a defined OH/Al ratio of 3 were prepared following the protocols of Parker and Bertsch (1992). An aliquot of 750 µL of a 1000 mg/L AlCl$_3$ standard solution (Merck Titrisol) was diluted to 50 ml with doubly deionized water. To this solution 50 ml of 525 µM NaOH were added at a rate of 20 ml/Min under stirring. The pH of this solution was measured and 50ml of ligand solution (catechol 90 µmol/L; oxalate 90 µmol/L; citrate 60 µmol/L; spruce litter extract with DOC = 30 mg/L) were adjusted to this pH. The ligand solution was then added to the Al/OH solution at a rate of 20 ml/Min under stirring. The final solution was equilibrated for 4 days at 25 °C. A second set of solutions was prepared by reversing base and ligand addition.

Aluminum speciation
For measuring acid reactive Al, an aliquot of the sample solution was acidified to pH 1 with HCl and equilibrated for at least 1 day. The Al concentration in the acidified solution was
measured using the FIA method of Royset (1987; modified by Royset, 1992) which is based on the colorimetric determination of Al with eriochrome cyanine R buffered at pH 7.5 and in presence of the cationic surfactant cetyltrimethylammonium bromide (ECR-method). Carrier solution was 0.1 M HCl.

Mononuclear Al was measured in the original sample solutions by the same method but using 0.01 M NaCl, pH4 as carrier solution.

Ion exchange-labile Al was obtained as difference between mononuclear Al and ion-exchange-inert Al. The latter was measured in the same way as mononuclear Al but with a column of strongly acidic cation exchanger (Amberlite IR-120, 99% Na/1% H; 350 µl) installed between injection valve and mixing with the first reagent. To keep constant pH conditions in the column effluent it was necessary to wait at least 10 Min. between injections.

Complexation-labile Al was measured in the original sample solutions by using the FIA method of Clarke et al. (1992) which is based on a 2.3s reaction with 8-hydroxyquinoline buffered at pH 5 (HQ-method).

Determination of free Al$^{3+}$ by capillary electrophoresis (CE) followed the method described by Göttlein (1998).

Results and discussion

Soil solution data

The preliminary results discussed in the following are based on two sampling dates for the haplic alisol (at 0 and 95 cm depth one sampling date only) and three sampling dates for the haplic podzol. The soil solution in the AE horizon of the alisol was moderately acidic, and was weakly acidic in the other horizons (Table 1). The podzol soil solutions were weakly acidic throughout the profile. The alisol soil solutions at 0 and 15 cm depth showed high DOC concentrations of more than 4 mmol/L. Only low concentrations were found at greater depth. In contrast, the podzol exhibited high DOC concentrations over 2 mmol/L only just below the litter layer. Concentrations of acid reactive Al (Al$_{AR}$) exhibited a distribution within the profile which was opposite to the one of pH. The molar ratio between Al$_{AR}$ and DOC was below 0.01 at 0 cm in both profiles. At greater depth values around 0.05 were found in the alisol whereas up to 10 times higher ratios were observed for the podzol. This ratio is reflected in the total luminescence spectra of the soil solutions that were set to the same pH and DOC content. In Fig. 1 the spectra of the soil solutions from two different depths of the podzol are shown. The spectrum from the solution collected at 0 cm exhibits a major peak at excitation wavelength 330 nm and emission wavelength 440 nm which can be attributed to simple phenolic substances (Senesi et al. 1991). The spectrum from 57 cm depth is characterized by a shift of the phenolic signal to shorter emission wavelengths and a second intensive signal at 320/380. Such a spectrum is characteristic for Al complexed by simple phenolic substances (Luster et al., 1996). The 0cm spectrum of the alisol is very similar to the 0cm spectrum of the podzol, and the spectra from all other horizons of the alisol and the podzol resemble the 57 cm spectrum of the podzol.
Table 1: pH, dissolved organic carbon (DOC) content, and concentration of acid reactive aluminum (Al$_{AR}$) in soil solutions from two acid soil profiles (n: number of sampling dates)

<table>
<thead>
<tr>
<th>Depth [cm]</th>
<th>Horizon</th>
<th>n</th>
<th>pH</th>
<th>DOC [mmol/L]</th>
<th>Al$_{AR}$ [µmol/L]</th>
<th>Al$_{AR}$/DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td></td>
<td>5.2</td>
<td>5.66</td>
<td>12</td>
<td>0.002</td>
</tr>
<tr>
<td>15</td>
<td>AE</td>
<td>2</td>
<td>4.0 ± 0.1</td>
<td>4.44 ± 0.20</td>
<td>188 ± 18</td>
<td>0.044 ± 0.001</td>
</tr>
<tr>
<td>45</td>
<td>Bt</td>
<td>2</td>
<td>4.7 ± 0.1</td>
<td>0.30 ± 0.01</td>
<td>13 ± 0</td>
<td>0.059</td>
</tr>
<tr>
<td>95</td>
<td>Bt,v</td>
<td>1</td>
<td>5.0</td>
<td>0.15</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td></td>
<td>4.5 ± 0.1</td>
<td>2.53 ± 0.61</td>
<td>22 ± 4</td>
<td>0.009 ± 0.001</td>
</tr>
<tr>
<td>30</td>
<td>A(E)</td>
<td>3</td>
<td>4.5 ± 0.5</td>
<td>0.21 ± 0.05</td>
<td>31 ± 7</td>
<td>0.146 ± 0.028</td>
</tr>
<tr>
<td>57</td>
<td>Bh</td>
<td>3</td>
<td>4.4 ± 0.3</td>
<td>0.10 ± 0.03</td>
<td>38 ± 8</td>
<td>0.430 ± 0.202</td>
</tr>
<tr>
<td>110</td>
<td>Bs,v</td>
<td>3</td>
<td>4.8 ± 0.3</td>
<td>0.05 ± 0.02</td>
<td>24 ± 2</td>
<td>0.507 ± 0.118</td>
</tr>
</tbody>
</table>

Fig. 1: total luminescence spectra of soil solutions from two different depths of a Haplic Podzol; spectra were recorded at DOC = 10 mg/L and pH 4
Mononuclear Al was significantly smaller than acid reactive Al in soil solutions collected at 0 cm in both profiles, at 45 cm in the alisol and at 57 and 110 cm in the podzol (Fig. 2, 3). At 15 and 95 cm depth in the alisol mononuclear Al was equal to acid reactive Al (Fig. 2). However, at 95 cm this finding is based on one sampling date only. At 30 cm in the podzol, concentrations of mononuclear Al varied between 50 and 100%.

In both profiles, ion exchange-labile Al equalled mononuclear Al except for the horizons with a DOC content higher than 2 mmol/L where it was significantly lower (Fig. 2, 3).
This is in good agreement with Driscoll (1984) who attributed the ion exchange inert Al to organically bound mononuclear Al species. Complexation-labile Al was found to be significantly smaller than ion-exchange labile Al in soil solutions from all mineral horizons. At 0 cm, however, the opposite was observed (Fig. 2, 3). With capillary electrophoresis we were able to measure free Al$^{3+}$ at concentrations above 5 µmol/L. Concentrations below this value were found for all soil solutions except for those from 15 cm in the alisol and 30 and 57 cm in the podzol. In the latter horizons, free Al$^{3+}$ was smaller than ion exchange-labile in all cases (Fig. 2, 3). For a comparison of free Al$^{3+}$ with complexation-labile Al the data base is too small.

**Synthetic solutions**

For the synthetic solutions only acid reactive, mononuclear and ion exchange-labile Al data are available. Acid reactive Al corresponded to added Al in all cases as expected (data not shown). Mononuclear Al was equal to acid reactive Al for all „polynuclear-free“ samples except for the one with spruce litter extract (Fig. 4). The latter represents a mixture including ligands with very high molecular weight. The fraction of ion exchange-labile Al in the „polynuclear-free“ samples was strongly dependent on the organic ligand. Ion-exchange inertness of the organic complexes increased in the order catechol < oxalate < spruce litter < citrate.
For the solutions with OH/Al = 3 a strong dependence of the mononuclear and ion exchange-labile Al fractions was found on the sequence of base and ligand addition. In all cases, smaller percentages were found for addition of base first (Fig. 4). However, with the exception of catechol, both fractions were smaller than acid reactive Al also for addition of ligand first. The order of magnitude of the differences between ion exchange-labile and mononuclear fractions observed for the „polynuclear-free“ solutions was preserved in the „polynuclear“ solutions except for oxalate.

Fig. 4: mononuclear and ion exchange labile Al in solutions of various organic ligands prepared in different ways (see text)
Conclusions

Preliminary results for soil solutions collected at different depths of two acid soil profiles and comparison with data for synthetic ligand solutions lead to the following conclusions:
In solutions collected from directly below the litter layer of both profiles and at 15 cm depth in the haplic alisol, Al is bound mainly to organic ligands. The complexes are formed either with low-molecular weight organic ligands and are measured partly as ion exchange-inert mononuclear Al, or with high-molecular weight ligands. The latter complexes are found in the difference between acid reactive and mononuclear Al.
At greater depth, in both profiles, Al is of mostly inorganic nature with unsystematically varying polynuclear fractions. However, fluorescence spectroscopy suggests a small contribution of organically bound Al. In contrast to the mononuclear organic Al fraction at 0cm, the inorganic mononuclear fraction at greater depth is almost completely ion exchange-labil but complexation-labile to only a small extent.

References

Luster, J., Fry, I.V., Lloyd, T., and Sposito, G. 1996. Multi-wavelength molecular fluorescence spectrometry for quantitative characterization of copper(II) and


Keywords: aluminum speciation, capillary electrophoresis, eriochrome cyanine R method, fluorescence spectroscopy, 8-hydroxyquinoline method, soil solution

Mots clés : spéciation d’aluminium, électrophorèse capillaire, méthode eriochrome cyanine R, spectroscopie de fluorescence, méthode hydroxyquinoline, solution du sol