Soil Acidification in Southern Switzerland between 1987 and 1997: A Case Study Based on the Critical Load Concept

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Southern Switzerland with its mainly acidic bedrock is potentially very sensitive to the effects of atmospheric proton input. In addition, this region suffers from relatively high acid deposition originating from the greater Milan area. The soil solution composition at different depths of a cryptopodzolic soil was monitored over a 10 year period with samples collected fortnightly. On the basis of the concept of critical loads of acidity, the molar ratio of base nutrient cations (BC) to aluminum was used as the parameter to assess acidification. Despite characteristic seasonal short-term variations of BC and Al, which could be attributed qualitatively to specific soil chemical processes, statistically significant trends over the entire observation period were observed. In all horizons a depletion of BC concentrations indicated an impoverishment of the nutrient status of the vegetation. Aluminum decreased in the upper soil, whereas a significant increase was observed at the lowest soil depth. The BC/Al ratio decreased significantly in all mineral soil horizons, indicating rapid soil acidification. Considering the constant decrease of acid deposition at the site during the observation period with values significantly below calculated critical loads, the observed acidification is attributed to a memory effect of the high acid loads between 1965 and 1985.

Introduction

The concept of critical loads was established to evaluate the potential environmental risk of acid deposition, with the effects of pollutants being related to the specific vulnerability of a particular sensitive ecosystem. The critical load of acidity is defined as the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function (1). Depending on the chemical status of a soil, atmospheric input of acidity is neutralized by a number of buffer reactions (2). On the basis of these reactions soil acidification can be established in various ways, e.g., by decreasing pH or base saturation of the soil matrix, by reduced soil microbial activity or plant growth, or by changes in the soil solution chemistry (3). In the context of the critical load concept for forest ecosystems, soil acidification is related indirectly to the effects of altered soil properties on vulnerable plant species (4, 5). In acidic soils, the input of additional acidity is buffered most efficiently by cation exchange reactions and by the release of aluminum from secondary reactive Al phases (6). Because of the strong selectivity of the cation exchanger sites for aluminum species, especially for $\mathrm{Al}^{3+}$, the Al saturation increases with decreasing pH while the nutrient cations in the soil become depleted (7). Some dissolved aluminum species act as phytotoxic agents to most plants. They can inhibit the growth of roots, and change root morphology and functioning. In addition, aluminum has an antagonistic effect on the uptake of Ca and Mg, leading to deficiency symptoms in plants (8).

Due to the large buffer capacities of soils, acidification is a very slow process that may last for decades before becoming evident in the soil matrix (3). In contrast, the chemistry of the soil solution may react more sensitively and rapidly to acidification processes. Hence, the analysis of the soil solution offers a more promising alternative to monitor acidification than the resampling and reanalyzing of solid soil samples. The Ca/Al ratio of the soil solution is a chemical parameter which is often used to characterize the acidity status of a soil and which is closely related to plant growth (9). The BC/Al molar ratio (with BC corresponding to the sum of the molar concentrations of $\mathrm{Ca}^{2+}$, $\mathrm{Mg}^{2+}$, and $\mathrm{K}^{+}$, and Al representing the total molar concentration of dissolved aluminum in the soil solution) is an even more promising parameter for the assessment of the acidification of a soil and the associated ecological risks. A large number of plant species have shown growth reductions at BC/Al $< 1$ (10, 11). It can be expected that both the BC/Al molar ratio and the Ca/Al ratio show seasonal short-term variations (12) related to nutrient uptake. While more base cations are taken up during the growing season, uptake of toxic aluminum is likely to be low throughout the year (8).

In this study, we assessed the acidification of a cryptopodzolic soil in the canton Ticino (southern Switzerland) during a 10 year observation period. We tested the suitability of the BC/Al molar ratio in the soil solution as a monitoring parameter by separating long-term trends from seasonal short-term variations. Finally, we interpreted the observed long-term trends with respect to their ecological significance and compared this interpretation with results from model calculations of critical loads of acidity. According to such calculations, the major part of the canton Ticino with its mainly gneissic bedrock is one of Switzerland’s most sensitive regions with respect to the effects of acid deposition (13).

Experimental Section

Site Description. The study site is located in Copera, at 650 m above sea level on the NE facing slope of Monte Ceneri, close to Lago Maggiore, southern Switzerland (45° 58’ N; 9° 20’ E). The climate in this area is mild with a mean annual temperature during the observation period of 10.3 °C. December and January are coldest with a monthly mean of 2 °C; hottest are July and August with 17.5 °C. The mean annual precipitation is 1740 mm with relatively dry winters but fairly high precipitation during the rest of the year (Figure 1). Snowfall is rare with about 10 days/year. The vegetation at the sampling site is a mixed hardwood forest dominated by European chestnut (Castanea sativa Mill.). The soil is a cryptopodzolic soil, common on gneiss in the whole region (14).
Soil Chemical Analyses. Soil properties were characterized by taking samples from a profile near the site where the soil solution was collected. The following parameters were measured or calculated for these samples as described elsewhere (14): pH; concentration of exchangeable cations and exchangeable protons; effective cation exchange capacity (CECeff); total carbon contents; sand, silt, and clay contents. The mineralogical composition was determined by X-ray diffractometry after removing soil organic matter. Porosity was calculated from bulk and mineral densities.

Soil Solution. Collection of the soil solution started in late 1986. To avoid artifacts due to equilibration of the system, the samples collected during the first 8 months were discarded. Soil solution was collected directly underneath the litter layer, as well as at 30, 57, and 110 cm depth, corresponding to the (AE)-, Bh(Bs)-, and B(s)C-horizons. The freely draining water below the litter layer (L- and F-horizons) was collected on a 35 x 25 cm² polyethylene plate, connected to a 5 L polyethylene container buried in the soil. The sampling plate was regularly perforated to ensure contact of the litter with the underlying soil. The soil solution at the other depths was collected using ceramic suction cups (highflow porous ceramic cups, Soilmoisture Equipment Corp., Santa Barbara, USA) that were washed repeatedly with 0.1 M HCl and rinsed with distilled water prior to installation. Three of these tension lysimeters were installed at each depth. Sampling of the soil solution usually was performed fortnightly. At the beginning of each sampling interval a tension of 60 kPa was applied. No effort was made to keep this tension constant. The lysimeters were connected to 2 L glass bottles (1 bottle per soil horizon) which were sealed with a rubber stopper. This container was placed in an insulated plastic barrel and buried in the soil to minimize temperature effects. The pH of the soil solution was measured immediately after sampling (pH stick, Gallenkamp, London). Samples were processed further only if the sampling volume was larger than 100 mL. Aliquots of 100–250 mL were transferred into acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃ acid-washed PE bottles and immediately sent to the laboratory where a subsample was acidified to pH 1 with HNO₃.

Acid Deposition. Throughfall chemistry at the study site was measured in 1994 and 1995 with the method described in ref 16 and used to calculate loads of acid deposition by the model approach presented in ref 13. On the basis of these data the development of atmospheric deposition into Swiss forests from 1900 to 2000 (for N compounds see ref 17) was rescaled for the study site (18).

Results

Soil Chemical Data. The pH, exchange characteristics, organic carbon content, texture, and porosity of the soil horizons are listed in Table 1. The pH values increase from 4.0 in the Ah-horizon to 4.9 in the (BC)-horizon, with a sharp increase below the Ah-horizon and only a gradual increase at lower depths. The cation exchange capacity decreases from 108 mequiv/kg in the Ah-horizon to 9 mequiv/kg in the (BC)-horizon with a minor second maximum of 37 mequiv/kg in the Bh-horizon. The base saturation is 28% in the Ah-horizon and between 10 and 13% at all other depths. Another prominent feature is the high organic carbon content in the upper horizons. The texture of the soil is dominated by 50–75% sand with a distinct minimum in the Bh-horizon. The clay content is below 10% throughout the profile. The soil is highly porous. The mineralogical composition of the soil, which developed from a gneissic bedrock, is dominated by primary minerals, mainly quartz and muscovite. Secondary minerals such as kaolinite, vermiculite, and chlorite account for about 30%.

Soil Water Content. From June 1994 to September 1995 volumetric soil water content was assessed by time domain reflectometry (TDR) at different soil depths. Readings usually were taken in time intervals of 2–4 weeks and analyzed as described in ref 15. The TDR measurements were calibrated on soil samples taken to the laboratory by comparing TDR readings with thermogravimetrically determined water contents.
At lower depths this increase was delayed until September in the \( \text{B(Bs)} \)-horizon and until November in the \( \text{B(s)C} \)-horizon. The \( \text{BC}/\text{Al} \) molar ratio (Figure 5C) showed a seasonal variation with low values in spring and highest values in fall. \( \text{BC}/\text{Al} \) molar ratios were lowest in the \( \text{(AE)} \)-horizon and highest in the \( \text{B(s)C} \)-horizon. Several DOC maxima were observed during the same 2 year period (Figure 5D). In both years a peak occurred during winter (December, January) and additional peaks in late spring/early summer.

Long-Term Trends in Soil Solution Chemistry. Mean values and standard deviations of pH, DOC, BC, and Al concentrations, and \( \text{BC}/\text{Al} \) molar ratios calculated for the 10 year period are listed in Table 2. The pH values mainly were between 4 and 5, exhibiting only little variation with depth.

The mean molar concentration of the base cations was between 100 and 300 mmol/L with the highest value below the litter mat and a second maximum in the \( \text{B(Bs)} \)-horizon. In contrast, the mean Al concentration was lowest below the litter layer and more than twice as high (68 mmol/L) in the \( \text{(AE)} \)-horizon. At greater depth it decreased to 40 mmol/L in the \( \text{B(s)C} \)-horizon. The mean \( \text{BC}/\text{Al} \) ratio, calculated from the individual ratios of each sampling event, was 13.5 below the litter layer. It dropped sharply to a minimum value of 2 in the \( \text{(AE)} \)-horizon and increased slightly with depth to 3.5 in the \( \text{B(s)C} \)-horizon. The DOC concentration decreased drastically from 26.9 mg/L below the litter layer to 4.3 mg/L in the \( \text{(AE)} \)-horizon. At greater depths its concentration changed only slightly to 2.6 mg/L.

Figure 6A–D shows the \( \text{BC}/\text{Al} \) molar ratios below the litter layer and in the three mineral soil horizons for the 10 year observation period, together with trend lines as fitted by a linear regression model. The \( \text{BC}/\text{Al} \) values below the litter layer (0 cm) scattered between approximately 2 and 40, and there was a weak trend toward higher values. In the \( \text{(AE)} \)-horizon (30 cm), a clear seasonal short-term fluctuation of

| soil horizon | depth (cm) | \( \text{H}_2\text{O} \) | \( \text{Na} \) | \( \text{K} \) | \( \text{Ca} \) | \( \text{Mg} \) | \( \text{Al} \) | CEC\(_{\text{eff}} \) (mmolc/kg) | BS (%) | C\(_{\text{org}} \) (g/kg) | sand (0.05–2 mm) | silt (2–50 \( \mu \)m) | clay (<2 \( \mu \)m) | porosity (%) |
|-------------|-----------|----------------|-----|-----|-----|-----|-----|----------------|-------|-----------|-------------|-------------|-------------|-------------|---------|
| \( \text{Ah} \) | 0–10      | 4.04          | 0.4 | 7.3 | 16.5| 5.5 | 6.1 | 61.6           | 16.2  | 107.6     | 27.6        | 179         | 59.4        | 31.4        | 9.2     | 75       |
| \( \text{(AE)} \) | 15–25   | 4.67          | 0.1 | 1.0 | 1.9 | 0.5 | 25.2| 2.6            | 31.4  | 31.4      | 11.3        | 110         | 60.8        | 32.8        | 6.4     | 77       |
| \( \text{B(Bs)} \) | 25–35   | 4.60          | 0.2 | 0.9 | 2.3 | 0.5 | 28.7| 4.4            | 36.9  | 10.2      | 12.6        | 38          | 51.1        | 39.6        | 5.3     | 76       |
| \( \text{(B(s)C)} \) | 55–65   | 4.75          | 0.1 | 0.7 | 1.5 | 0.2 | 16.9| 2.7            | 22.1  | 11.2      | 8.5         | 38          | 55.7        | 28.8        | 5.9     | 71       |
| \( \text{B(s)C} \) | 80–90   | 4.80          | 0.1 | 0.9 | 0.9 | 0.1 | 11.5| 1.8            | 15.2  | 12.6      | 11.0        | 16          | 58.6        | 38.5        | 2.9     | 58       |
| \( \text{B(s)C} \) | 100–110 | 4.88          | 0.1 | 0.7 | 0.7 | 0.1 | 8.6 | 1.8            | 11.8  | 12.6      | 11.0        | 16          | 70.6        | 27.7        | 1.7     | 64       |
| \( \text{B(s)C} \) | 120–130 | 4.92          | 0.1 | 0.4 | 0.4 | 0.1 | 6.6 | 1.2            | 9.0   | 13.4      | 8           |             | 76.6        | 21.2        | 2.2     | 62       |

| a CEC: effective cation exchange capacity; BS: base saturation. |
the BC/Al molar ratio was present with some minimum values below 1 toward the end of the observation period. Despite significantly higher ratios from 1991 to 1993, there was a weak long-term trend toward lower values. In the B₈(B₅)-horizon (57 cm) the BC/Al molar ratios showed a similar seasonal variation, but over the 10 year observation period, there was a strong trend for a decrease from about 3.5 to 2. The same pattern appeared in the B₈(C-horizon at 110 cm depth. Although the mean BC/Al value was higher than that in the B₈(B₅)-horizon, the greatest annual decline was observed in the B₈(C-horizon, amounting to more than 0.2/year. Some values below 1 were reached in winter 1996.

Table 3 lists the regression coefficients for the time dependence of the concentrations of K, Ca, Mg, Al, and BC and the BC/Al ratio in the soil solution, calculated for the entire observation period. Below the litter layer (0 cm), K and Ca contributed most to the BC. Although the change of the BC/Al values was small and insignificant, the concentrations of the individual cations decreased significantly during the observation period. The relative decrease was 5% per year for all cations. In the (AE)-horizon (30 cm) Ca was the most prominent of the base cations, followed by Mg and K. The highest aluminum concentration was found in this horizon, reaching the concentration of Ca. As below the litter layer, the concentrations of all cations decreased significantly between 1987 and 1997. All the base nutrient cations, particularly calcium, decreased also in the B₈(B₅)-horizon (57 cm). However, the Al concentration increased slightly at this soil depth and was mainly responsible for the lowering of BC/Al. A similar pattern appeared in the B₈(C-horizon (110 cm) where the mean annual increase of the Al concentration amounted to 2 μmol/L/year and the annual decrease of BC/Al was highest.

In addition, a quadratic regression model \( y = a + bx + cx^2 \) for the BC/Al values in the B₈(B₅)- and B₈(C-horizons was fitted. Only in these horizons, the residuals of the BC/Al ratios are approximately normally distributed and thus permit a correct statistical interpretation of the computed 0.95 confidential intervals for the regression coefficients. For the B₈(B₅)-horizon the model parameters b and c are \(-0.479 \pm 0.059\) and \(0.0338 \pm 0.0055\), respectively, and for the B₈(C-horizon they are \(0.398 \pm 0.116\) and \(0.0160 \pm 0.0108\), respectively. The corresponding trend lines are depicted in panels C and D of Figure 6, respectively.

**Deposition.** In 1994 and 1995 an acid load of 144 kmol/km²/year was measured at the study site. On the basis of these data and the general development of atmospheric deposition into Swiss forests it can be estimated that the acid load at the site was maximum between 1973 and 1980 at a rate of about 330 kmol/km²/year, then decreased, first rapidly, to about 230 kmol/km²/year in 1984 and more slowly to about 130 kmol/km²/year in 1997. Base cation input by atmospheric deposition amounted to about 100 kmol/km²/year during the entire observation period.

**Discussion**

**Soil Water Content.** The soil water content in the mineral soil could be shown to be fairly constant during the entire observation period. There are mainly two exceptions. Small collection volumes in fall 1989 can be attributed to an exceptionally dry summer. Relatively large collection volumes in 1992 are likely due to light thinning of the forest during winter 1991/1992 which led to increased throughfall and less evapotranspiration. The large water retention capacity of the sandy/silty soil is very likely due to the relatively high organic carbon content to great depth. Because of the constant soil water content, dilution/concentration effects on seasonal variations and long-term trends in soil solution chemistry can be considered negligible. To illustrate this, Al and BC concentrations at 57 cm depth were plotted together with the concentrations normalized to a collection volume of 1 L (Figure 4C). The picture with respect to seasonal variation is the same. In contrast, the large variation in volume of solution collected just below the litter layer very likely is an important factor for the scattering of chemical parameters at this depth.

**Soil Solution pH.** The first thought in an acidification study would be to evaluate pH data. However, the extent to which the measurements represent the true pH value of the soil solution cannot be estimated to a satisfying degree for two reasons. First, a pH increase caused by CO₂ degassing during the collection with tension lysimeters cannot be excluded. Such an effect is well known (19) but might be negligible at low pH and low CO₂ concentration (20). Soil CO₂ concentrations, however, were not measured in our case. Second, in the last observation year pH was assessed with both the Gallenkamp pH stick, which had been used throughout the entire observation period, and a reference electrode specially constructed for measuring solutions of low conductivity (glass electrode with a bridge of low ionic strength, Metrohm). Values differed between 0 and 1 pH unit without obvious dependence on solution composition, with the reference electrode readings generally being higher. Because of the shortcomings of the pH measurements, the pH data presented in Table 1 just serves to give an idea about the magnitude of variation with depth and over time. The pH data is not used, however, to evaluate seasonal and long-term trends during the observation period. Therefore, for
this purpose, the focus is on the parameters based on total cation concentrations that could be measured much more reliably.

**Seasonal Variation of Soil Solution Chemistry.** Processes affecting the BC concentrations in the soil solution are (i) release by decomposition of organic matter, primarily plant litter, (ii) uptake by living organisms, (iii) leaching losses to groundwater, (iv) cation exchange reactions with the soil, (v) cation release during chemical weathering of rocks and minerals, and (vi) atmospheric deposition. Compared to a base cation input by litter fall of about 600 kmol/km²/year (18), the atmospheric deposition of base cations in the study area was fairly low and the weathering release of cations is slow (about 25 kmol/km²/year) (13). Roughly 90% of the CEC_{eff} in the mineral horizons is occupied by aluminum due to the high selectivity of the cation exchanger for Al^3+. Therefore, the exchange reactions of base cations with the soil matrix are suppressed. The most significant processes governing the BC concentration in the soil solution in the time span under consideration are therefore cation release during decomposition of litter and soil organic matter and nutrient uptake by the vegetation. Litter decomposition is

### TABLE 2. Mean Values of Soil Solution Parameters, Calculated for the 10 Year Observation Period

<table>
<thead>
<tr>
<th>Soil horizon</th>
<th>Sampling depth (cm)</th>
<th>pH mean</th>
<th>std dev</th>
<th>BC (μmol/L) mean</th>
<th>std dev</th>
<th>Al (μmol/L) mean</th>
<th>std dev</th>
<th>BC/Al mean</th>
<th>std dev</th>
<th>DOC (mg/L) mean</th>
<th>std dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litter layer</td>
<td>0</td>
<td>4.3</td>
<td>0.5</td>
<td>303</td>
<td>189</td>
<td>28</td>
<td>18</td>
<td>13.5</td>
<td>8.6</td>
<td>26.9</td>
<td>10.4</td>
</tr>
<tr>
<td>(AE)</td>
<td>30</td>
<td>4.1</td>
<td>0.4</td>
<td>118</td>
<td>55</td>
<td>66</td>
<td>38</td>
<td>2.0</td>
<td>0.8</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>(B_h)B_s</td>
<td>57</td>
<td>4.2</td>
<td>0.4</td>
<td>147</td>
<td>62</td>
<td>57</td>
<td>32</td>
<td>2.8</td>
<td>0.8</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>B_{0/C}</td>
<td>110</td>
<td>4.4</td>
<td>0.4</td>
<td>109</td>
<td>37</td>
<td>36</td>
<td>21</td>
<td>3.5</td>
<td>1.4</td>
<td>2.6</td>
<td>2.2</td>
</tr>
</tbody>
</table>

*a DOC: without the most extreme low and high values.

### TABLE 3. Coefficients for Linear Regression of Soil Solution Parameters vs Time, y = a + bx, over the 10 Year Observation Period

<table>
<thead>
<tr>
<th>Sampling depth (cm)</th>
<th>Regression coefficients for time dependence of pH</th>
<th>Regression coefficients for time dependence of BC</th>
<th>Regression coefficients for time dependence of Al</th>
<th>Regression coefficients for time dependence of Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (μmol/L)</td>
<td>b (μmol/L/y)</td>
<td>Pr(&gt;</td>
<td>t</td>
</tr>
<tr>
<td>0</td>
<td>166.0</td>
<td>-8.78</td>
<td>0.0001</td>
<td>168</td>
</tr>
<tr>
<td>30</td>
<td>30.5</td>
<td>-2.39</td>
<td>0.0001</td>
<td>83</td>
</tr>
<tr>
<td>57</td>
<td>15.1</td>
<td>-0.23</td>
<td>0.2642</td>
<td>112</td>
</tr>
<tr>
<td>110</td>
<td>9.6</td>
<td>-0.35</td>
<td>0.0070</td>
<td>82</td>
</tr>
</tbody>
</table>

*a The coefficient “a” corresponds to the value at the beginning of the observation period; “Pr(>|t|)” is a measure for the probability that “b” is equal to 0.

**FIGURE 6.** Molar BC/Al ratios in the soil solution plotted for the entire 10 year observation period at a sampling depth of (A) 0, (B) 30, (C) 57, and (D) 110 cm. Solid lines represent linear regressions as characterized in Table 3 or quadratic regression as characterized in the text.
responsible for the highest mean BC concentrations below the litter mat (Table 2). The relatively uniform mean BC values at greater depths with only a minor peak in the B$_4$(B$_5$-)horizon may be explained by the high porosity of the soil together with the high precipitation and the limited cation exchange. High BC concentrations (Figure 5A) in the (AE)-horizon during the winter months suggest that despite the relatively dry climate nutrients are leached from the litter layer. In a study performed in the same area (21), it was found that 40–50% of K, 5–20% of Mg, and 3–7% of Ca were leached from litter bags located in the litter layer during a 4 week period in November/December. The sharp drop in concentrations in early March may be caused simultaneously by more intense leaching due to high spring precipitation and by plant nutrient uptake. The delay of the concentration maxima in the soil solution with increasing depth may indicate that leaching is the dominant process.

Dissolved aluminum in the soil solution in the (AE)-horizon is released primarily from aluminum that is complexed by organic matter and at greater depth from amorphous Al hydroxides and silicates (22). Its concentration is controlled by the pH of the soil solution and by the concentration of dissolved organic ligands with strong complexing properties. Hence, the decrease in the average Al concentrations in the mineral soil with increasing depth (Table 2) can be explained mainly by increasing pH and decreasing DOC concentrations. The similarity of the seasonal short-term dynamics of the Al concentrations in the soil solution at all three mineral soil depths (Figure 5B) with the pattern of BC is surprising given the fact that aluminum uptake by living organisms in most cases is much lower than the uptake of base nutrient cations. Assuming Al uptake by the vegetation is negligible, the annual variation of the Al concentration is governed mainly by pH and/or the concentration of organic ligands. Unfortunately the influence of pH cannot be evaluated directly due to the uncertainties involved in its measurement. However, it is well known that nutrient uptake by plants leads to a cation deficit in the soil which is balanced by a corresponding release of protons (23). One would therefore expect lower pH values and, as a consequence, elevated Al concentrations during the growing season. Since we have observed the opposite, we conclude that seasonal variation of Al is mainly governed by organic substances with complexing properties. The concentration and properties of organic ligands in the soil solution are controlled by the quality and quantity of litter and by any factor affecting the microbial activity, primarily temperature and precipitation regimes (24, 25). Chestnut litter, which dominates at the study site, is a source of DOC with excellent complexing properties (26). In winter, microbial activity can be inhibited. Hence, biodegradation of DOC remains incomplete, and the formation of metal–organic complexes is favored. Complex formation with Al or Fe makes DOC even more stable against microbial attack (27). Therefore, such compounds persist in the soil solution and become subject to leaching. An intensive formation of Al–organic complexes by DOC leachates from fresh litter together with only moderate translocation may explain the increase of the Al concentration in the (AE)-horizon during the relatively dry winter period. At the beginning of spring with considerably higher precipitation, the Al complexes are leached from the (AE)-horizon to greater depths. The increase of the Al concentration in the (AE)-horizon beginning in July followed by a later and less intense increase at greater soil depths can be explained by the continuous formation of Al–organic complexes resulting from the supply of fresh litter between July and October. In July, chestnut trees produce a considerable quantity of blossom litter. In a nearby stand, this litter amounted to 615 ± 555 kg/ha/year, corresponding to about 15% of the total leaf litter (18).

**Long-Term Trends in Soil Solution Chemistry.** The decrease of BC concentrations over the past 10 years in all horizons indicates that within this decade the nutrient status of the vegetation has become impoverished or that the supply of litter has decreased. The decrease of BC/Al ratios in all mineral horizons is indicative of a rapid acidification of the soil which points to a significant contribution of proton input by acid deposition. The weak decline in the (AE)-horizon has been due to a slow decrease of total dissolved Al and a faster decrease of base cations during the past 10 years (Table 3). However, the concentration of total dissolved Al is still highest in this horizon (Table 2), and reactive aluminum at the soil matrix is largely bound to organic matter (22). In soil horizons in which the Al concentration is controlled by complexation reactions to organic matter, Al solubility decreases with decreasing reactive Al in the system (28). Thus, continuous leaching of Al from the upper soil may lead to a decrease in proton buffer capacity and in dissolved Al concentrations. As a consequence, an increased amount of protons are buffered deeper in the soil by mainly inorganic amorphous Al phases (22), leading to increasing Al concentrations. Such a behavior is observed in the studied soil profile as shown in Table 3.

The elevated BC/Al molar ratios between 1991 and 1994, primarily in the (AE)-horizon, were caused most likely by the light thinning of the forest at the study site in winter 1991/92. On one hand the thinning of a forest can lead to reduced cation uptake and, on the other hand, to more daylight penetrating the canopy, causing elevated temperatures in the litter layer and thus favoring microbial activity and the release of base cations.

Toward the end of the observation period, the BC/Al ratio fell several times below the critical value of 1 in the (AE)- and B$_4$(B$_5$)-horizons. In terms of the critical load concept, this implies exceedence of the critical load of acidity. Using the steady-state models SM B (steady-state mass balance method, e.g., ref 4) and PROFILE (29), calculated critical loads of acidity resulted in 220 kmol/km$^2$/year and 250 kmol/km$^2$/year, respectively (18). On the basis of these calculations and considering the estimated development of acid deposition at the study site, the critical load was exceeded approximately between 1965 and 1985. Since then, i.e., during the entire observation period, acid deposition has been significantly lowered. This indicates that high acid deposition over a longer period can induce soil acidification processes that can continue for decades after deposition falls below critical values. With respect to the further development at the study site, it is emphasized that the linear fittings of the actual BC/Al data (Figure 6, Table 3) with their negative implications should not be extrapolated to the future. This is illustrated by the possibility of fitting the data for the two lowest sampling depths equally well by a quadratic model (Figure 6C,D), which implies a stabilization or even a slight recovery for the past few years. Therefore, only continued measurements will answer the question of whether soil acidification is increasing further.

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