Acidification of Soil Solution in a Chestnut Forest Stand in Southern Switzerland: Are There Signs of Recovery?

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In a previous study, a rapid acidification of soil solution was observed between 1987 and 1997 in a cryptopodzolic soil in southern Switzerland despite a reduction in acidic deposition. The molar ratio of base nutrient cations to aluminum (BC/Al) in the soil solution was used to assess acidification. The monitoring of the soil solution chemistry was continued at the same site between 1998 and 2003 to find out how long the delay in reaction to reduced deposition would last and whether the BC/Al ratios would recover. The reevaluation of all data collected during the 16-year observation period showed no clear improvement in the BC/Al ratios, except below the litter layer where the ratios greatly increased after 1998. Initial signs of recovery were also detected in the mineral horizons, the ratios stabilizing in the second part of the observation period. Sulfate concentrations decreased significantly below the litter mat in response to decreased S deposition. BC concentrations markedly declined below the litter layer and in the mineral horizons, which was attributed to the depletion of the BC exchangeable pool as a result of continued acidic deposition.

Introduction

Acid atmospheric deposition has been shown to affect the chemistry of soil and drainage waters in forest ecosystems and to accelerate the acidification of soils (*1*). Rates of acidic deposition, especially of sulfur, declined through the 1980s and 1990s in Europe, mainly because of the reduction of SO_2 emissions following air pollution abatements (*2*). Since 1980, emissions of nitrogen compounds have leveled off and decreased in most European countries, but they are still today on a high level (*2*, *3*). The reduction in acid deposition has raised questions about the recovery of surface waters and soils from acidification. With decreases in acidic deposition, the alkalinity of surface waters has been observed to recover in many streams and lakes throughout Europe (*4*, *5*). In contrast, other studies have reported a significant delay in the recovery of surface waters, which has been attributed to the release of previously stored sulfate from deeply weathered soils, coupled with the leaching of Al and base cations (*6*, *7*). Several field studies have shown that soil acidification is still progressing, especially at greater depths, despite reduced acidic deposition (*8*, *9*). An increasing net loss of base cations from ecosystems because of a combination of continued high anion leaching and significant reduction in base cation deposition has been observed in several catchment areas in Europe (*10*) and in North America (*11*, *12*). Depletion of the BC reserves in soils has been proposed as a major factor preventing the chemical recovery of surface waters despite large reductions in sulfur emissions (*11*, *12*).

The study site, located in canton Ticino in Switzerland, is in the Lake Maggiore catchment area on the border of southern Switzerland and northern Italy. This region receives high deposition rates in nitrogen (up to 40 kg/ha/year) and sulfur (up to 20 kg/ha/year) because of local and long-range emissions from the industrial Po Valley in Italy (*13*, *14*). There is a high level of precipitation (up to 2 m/year), which often comes from the south bringing with it high loads of sulfate and nitrate (*15*). An improvement in the quality of atmospheric deposition in terms of pH level has recently been detected in Switzerland (*14*) and in the Lake Maggiore catchment area (*13*). The chemical composition of the local rivers and lakes appears to be responding to changes in atmospheric deposition with a general decrease in SO_4 concentrations and an increase in pH and alkalinity (*13*).

This improvement in water quality raises questions about whether and how the local soils and soil solution are recovering from acidification. Southern Switzerland with its mainly acidic bedrock is very sensitive to the effects of acidic deposition (*16*). At the study site in Copera, a rapid acidification of soil solution was observed between 1987 and 1997, even though acidic deposition had already fallen below the critical load by 1985 (*17*). These results were based on analyzing the long-term trends in the ratios of base cations (BC) to aluminum in soil solutions (with BC corresponding to the sum of the molar concentrations of Ca^{2+}, Mg^{2+}, and K^{+}, and Al representing the total molar concentration of dissolved aluminum). A decrease in the BC/Al ratios in the soil solution was used as an indicator for soil acidification. Depletion of exchangeable base cations by acidification and leaching processes leads to a larger fraction of exchange sites being occupied by aluminum at the expense of sites occupied by Ca and Mg and ultimately to a decrease in the BC/Al ratio in the soil solution (*18*). The monitoring of the soil solution chemistry allows us to find out how the soil solution chemistry reacts to the declining acidic deposition and how long the delay in recovery is likely to last. The start of a potential recovery from soil solution acidification would be indicated if the trend in the BC/Al ratios reversed. This paper presents the latest soil solution data (6 additional years between 1997 and 2003) at Copera and reevaluates the data from the entire observation period from 1987 to 2003 with new types of data analysis and interpretation.

Experimental Section

Details concerning the Experimental Section and the soil chemical data are given in ref *17*. Only the most relevant information is summarized here.

Site Description. The study site is located at Copera, 650 m above sea level in southern Switzerland (45°58′N; 9°20′E). The climate in this area is mild with a mean annual temperature of 10.3 °C during the observation period. December and January are the coldest months with a monthly mean of 2 °C. The hottest months are July and August (mean 17.5 °C). Canton Ticino is the wettest region of the Alps in terms of total annual precipitation (*19*). Copera records a

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TABLE 1. Mean Values of Soil Solution Parameters, Calculated for the 16-Year Observation Period

soil horizon	sampling depth (cm)	pH[a]	ANC[b] μmolc/L	BC μmol/L	Al μmol/L	BC/Al	DOC mg/ L	NO_3 μmol/L	SO_4 μmol/L
litter layer	0	5.3 ± 0.8	n.d.[c]	266 ± 175	21 ± 17	19.2 ± 13.7	16.6 ± 9.4	238 ± 235	53 ± 38
(AE)	30	4.7 ± 0.2	−92 ± 75	82 ± 56	58 ± 38	1.5 ± 0.7	3.6 ± 2.3	228 ± 198	44 ± 17
$(B_h)B_s$	57	4.8 ± 0.2	−82 ± 65	111 ± 60	48 ± 29	2.4 ± 0.7	2.2 ± 1.8	249 ± 197	53 ± 16
$B_{(s)}C$	110	5.1 ± 0.2	−52 ± 28	82 ± 36	33 ± 14	2.7 ± 1.0	1.9 ± 1.6	154 ± 109	48 ± 12

[a] pH values since November 2000. [b] Mean ANC values between 1997 and 2003. [c] n.d. = not determined.

mean annual precipitation level of 1740 mm with most of the precipitation falling between April and October. Precipitation is concentrated in intense episodes so that the region is also the sunniest of Switzerland (*20*). The winter is dry. The much lower precipitation from November to March is one of the main characteristics of the precipitation regime in Ticino compared to that of the rest of the country (*20*, *21*) and the rest of the European Alps (*19*). Snowfall in the study area is rare with about 10 days/year.

The vegetation at the sampling site is mixed hardwood forest dominated by European chestnut (*Castanea sativa* Mill.). The soil is a cryptopodzolic soil, common on gneiss in the whole region (*22*). A description of the soil chemical data is given in ref *17* and in the Supporting Information.

Soil Solution Chemistry. Soil solution samples were collected fortnightly between 1987 and 2003 below the litter layer (0 cm) and at depths of 30, 57, and 110 cm, corresponding to the (AE) eluvial horizon, $(B_h)B_s$ enrichment horizon, and $B_{(s)}C$ transition horizon to bedrock. Soil solutions below the litter layer were collected by zero-tension lysimetry with a plexiglass plate connected to a polyethylene bottle, and soil solutions in mineral soil horizons were sampled by tension lysimetry using ceramic suction cups (see Supporting Information). The pooled samples were filtered (0.45 μm) in the laboratory and were analyzed for pH, dissolved organic carbon (DOC), and major cations and anions.

The pH was measured with different methods and electrodes over the whole observation period (see Supporting Information). Since there were large pH differences between the different methods, only the pH values measured after 2000 could be used (combined glass electrode Meterlab PHM250 and CDM210 Radiometer). DOC was determined with high-temperature combustion followed by IR detection of CO_2 (Shimadzu TOC500, TOC5000, and TOC-V). Total cation concentrations were analyzed by ICP-AES (ARL 3580, Perkin-Elmer OPTIMA 3000), and the concentrations of major anions were analyzed by ion chromatography (DX-120, Dionex). The reliability of the chemical analyses was assessed by checking the charge balance of the samples and the difference between the calculated and the measured electrical conductivity.

Fractionation of dissolved aluminum was performed monthly in the soil solution samples between August 1997 and May 1998. Total mononuclear Al was measured with the flow injection analysis (FIA) method according to ref *23*. It includes mononuclear inorganic and organic complexes of aluminum. The concentrations of the inorganic mononuclear species (e.g., Al^{3+}) were calculated in the (AE)-horizon (30 cm) and in the $B_{(s)}C$-horizon (110 cm) for the 16-year observation period with a chemical equilibrium model for waters (WHAM 6.0, *24*). The total mononuclear Al concentrations were used as input data in the model (see Supporting Information).

BC/Al ratios were calculated by dividing the sum of the molar concentrations of Ca^{2+}, Mg^{2+}, and K^+ by the total molar concentrations of dissolved aluminum in the soil solution. The acid neutralization capacity (ANC) was calculated in the mineral horizons to determine solution acidity and to quantify acidity transfer into deeper horizons. The ANC was calculated according to ref *25* and ref *26*:

$$[\mathrm{ANC}] = 2[\mathrm{Ca}^{2+}] + 2[\mathrm{Mg}^{2+}] + [\mathrm{K}^+] + [\mathrm{Na}^+] - 2[\mathrm{SO_4}^{2-}] - [\mathrm{NO_3}^-] - [\mathrm{Cl}^-]$$

where [x] are molar concentrations. Positive ANC values indicate the presence of HCO_3^- or OH^-, and negative ANC values indicate the presence of H^+, Al, and Fe cations and therefore a transfer of acidity with the soil solution (*26*). Only the mean ANC values between 1997 and 2003 are presented in this paper. The bad quality of the Na analyses between 1987 and 1991 did not allow us to calculate reliable ANC values. In addition, a light thinning of the forest in winter 1991/92 caused a marked decrease in ANC values between 1993 and 1996 (data not shown). Since the trend of the ANC values between 1992 and 2003 would have been biased by this disturbance, we only considered the values at the end of the observation period.

Statistical Methods. The long-term changes in the element concentrations and in BC/Al ratios over time were analyzed using linear regression models. In addition, smoothing curves were fitted to the BC/Al ratios with the distance-weighted least-squares method since it is a sensitive method for revealing nonapparent patterns in data with considerable scattering of data (*27*). This method filters out the noise and converts the data into a smooth curve that is relatively unbiased by outliers. To detect a potential recovery or stabilization of the BC/Al ratios over time, seasonal and cyclic fluctuations were removed by calculating a moving average with a time window longer than the cyclic fluctuations (*28*).

Fluxes of Soil Water and Dissolved Elements. Soil water fluxes were estimated with WATBAL, a monthly soil−water balance model (*29*). Input data are precipitation, air temperature, cloud cover, and aspect. Meteorological data were measured at the study site or were derived from a nearby station (Bellinzona, MeteoSwiss). The model also requires the soil moisture at field capacity and at permanent wilting point. They were derived from transfer functions on the basis of soil texture, bulk density, and organic matter content (*30*). Modeled soil moistures were optimized using the measurements of the volumetric soil−water content performed at the site between 1994 and 1995 at different depths (*17*). Monthly element fluxes were obtained by multiplying the mean monthly concentrations by the monthly water fluxes. Annual fluxes were obtained by summing up the monthly fluxes.

Results

Variations in Soil Solution Chemistry with Depth. Table 1 shows the means and the standard deviations of BC/Al molar ratios and concentrations of Al, BC, DOC, and major anions calculated for the 16 years of observation (1988−2003). The mean concentrations of the base cations were the highest below the litter layer and decreased in the (AE)- and the $B_{(s)}C$-horizons. In contrast, the total Al concentrations were the lowest below the litter mat and the highest in the (AE)-horizon (30 cm). They decreased with depth in the $B_{(s)}C$-

TABLE 2. Mean Al^{3+} Concentrations in the (AE)- and $B_{(s)}C$-horizons and Coefficients for Linear Regression of Al^{3+} Calculated with WHAM 6.0 vs Time ($y = a + bx$) over the 16-Year Observation Period[a]

sampling depth	Al^{3+} ± stand. dev. μmol/L	a	b	Pr(>|*t*|)
30 cm (AE)	24.8 ± 22.6	38	−1.49	0.0362
110 cm $B_{(s)}C$	9.6 ± 6.0	9	0.05	0.7694

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

horizon. The mean Al^{3+} concentrations reached 25 μmol/L in the (AE)-horizon and decreased to 9.6 μmol/L in the $B_{(s)}C$ horizon (Table 2). The mean BC/Al ratios were the highest below the litter layer and declined to 1.5 in the (AE)-horizon (30 cm). They increased with depth to 2.7 in the $B_{(s)}C$-horizon (110 cm).

Nitrate was the major anion at all depths. Concentrations of nitrate were similar below the litter layer, in the (AE)- and $(B_h)B_s$-horizons and declined in the $B_{(s)}C$-horizon (110 cm). Concentrations of sulfate were about 3−5 times smaller than those of nitrate. They showed little variations with depth. The mean pH in the soil solution (2000−2003) was 5.3 below the litter layer and varied between 4.7 and 5.1 in the underlying horizons (Table 1). The DOC concentration was the highest below the litter layer and decreased sharply with depth. The mean ANC values, calculated for the period 1997−2003, increased with depth in the mineral horizons. They were all negative, indicating a transfer of acidity to greater depths.

Temporal Trends in Soil Solution Chemistry. Table 3 lists the coefficients of the linear regressions for the time dependence of the BC/Al ratios, the electrical conductivity, and the concentrations of base cations, aluminum, nitrate, and sulfate calculated for the 16-year observation period. The electrical conductivity and the concentrations of cations and anions decreased significantly at all depths, except for the total Al and sulfate concentrations that showed no significant trend in the B-horizons (depths of 57 and 110 cm). Like total Al, the free Al^{3+} decreased over time in the (AE)-horizon (30 cm) but remained stable in the $B_{(s)}C$-horizon (Table 2). Nitrate tended to decrease in both B-horizons but the trends were not significant. The BC concentrations decreased proportionally more than the Al concentrations in the mineral horizons, resulting in a decrease in the BC/Al ratios. In contrast, the BC/Al ratios increased below the litter mat because of a relatively marked decrease in Al concentrations. The linear regressions of the BC/Al ratios below the litter layer and in the mineral soil horizons are illustrated in Figure 1.

The smoothing curves fitted to the molar BC/Al ratios using the distance-weighted least squares procedure (Figure 1) show that the molar BC/Al ratios did not decrease continuously over time but fluctuated. Periods of decrease in the BC/Al ratios alternated with periods of increase. The cyclic fluctuations are of different lengths and may last up to 5 years. They last longer than the seasonal variations already identified in ref *17*.

To detect a potential stabilization or a recovery of the BC/Al ratios over time, moving averages were calculated. A large time window of 6 years was chosen to filter out the seasonal and the cyclic components of the data. The cyclic fluctuations were identified with the distance-weighted least-squares method. The 6-year mean BC/Al ratios in the mineral horizons decreased rapidly until the period 1993−1999 (Figure 2). Afterward, the ratios remained stable in the (AE)-horizon and decreased slowly in the $B_{(s)}C$ horizon. In contrast, the mean BC/Al ratios below the litter layer were stable until the period 1993−1999 and rapidly increased afterward.

Estimate of Element Fluxes. Detecting changes in element soil pools over time is difficult to do directly from soil analysis given the spatial heterogeneity, differences in sampling techniques, and the slow rate of change in these pools. Calculating element fluxes in the deepest sampled horizon may involve large errors since assumptions have to be made concerning the water flow path. It is, nevertheless, useful in combination with atmospheric deposition to estimate whether the forest ecosystem is releasing or accumulating elements. Annual fluxes of base cations, aluminum, nitrate, and sulfate were estimated below the litter layer and in the $B_{(s)}C$-horizon (110 cm) (Figure 3). Linear regressions were calculated to identify any long-term trends in the fluxes. The drought year in 2003 was not considered to avoid a bias in the calculation of the linear regressions. Fluxes of base cations below the litter layer ranged between 20 and 140 kg/ha/year and tended to decrease over time. In contrast, they remained quite stable in the $B_{(s)}C$-horizon. Aluminum and sulfate fluxes markedly decreased below the litter layer, while they increased in the $B_{(s)}C$-horizon. Sulfate fluxes below the litter layer were about 20 kg/ha/year in the early 1990s and decreased to 10 kg/ha/year within a period of 10 years. The fluxes of sulfate below the litter layer exceeded the sulfate release from the $B_{(s)}C$-horizon between 1988 and 1996 but became smaller between 1999 and 2002. Nitrate fluxes below the litter layer tended to decrease over time, while in the $B_{(s)}C$-horizon they remained quite stable.

Discussion

Effects of Deposition on Soil Solution Chemistry. According to a simple mechanistic soil chemistry model assuming weathering and nutrient cycle in steady state, changes in deposition would be reflected in corresponding changes in soil solution concentrations and element fluxes in the soil (*31*). The decrease in sulfate concentrations below the litter layer (Table 3) can probably be attributed to the overall decline in sulfur deposition recorded in the region (published deposition data compiled in Table 4). The estimate of sulfate fluxes from the litter layer and the trends over time are comparable to S deposition in the region (*7*, *13*, *32*−*34*), suggesting that the soil water chemistry in the upper horizon responded rather quickly to the decrease in the S atmospheric deposition. The presence of organic ligands in the forest floor leachates might have inhibited sulfate retention in the litter mat (*35*). The estimated nitrate fluxes below the litter mat declined by about 12 kg/ha between 1988 and 2001 (Table 4). In contrast, nitrogen deposition in the region was fairly constant during the observation period (*13*, *32*). At the study site, it was moderate (18 kg/ha in 1995 in ref *33*) considering the range of N deposition in the southern part of Ticino (24−42 kg/ha/year in ref *32*, *34*). The decrease in nitrate concentrations, therefore, cannot be explained by a decline in N deposition.

The decrease in BC concentrations below the litter layer (−30 kg/ha in 16 years) could be due to a decline in BC deposition. The trend of BC deposition in Switzerland is subject to controversy because data are very scarce. The peak of dust deposition in the 1960s was estimated to be about 10% larger than deposition in the 1990s (*36*). During the observation period, deposition of base cations varied greatly in the region between 7 and 26 kg/ha/year (*14*, *15*, *32*, *34*). This variation is very likely due to episodic Saharan dust storms (*13*) and changing levels of dust originating from arable land, roads, or industrial activities. At the study site, a BC deposition of 25 kg/ha was measured in 1995 (*33*). The BC deposition is thus smaller than the change in BC fluxes observed below the litter layer during the 16-years of observation (Table 4), indicating that a possible decline in

TABLE 3. Coefficients for Linear Regression of Soil Solution Parameters vs Time, $y = a + bx$, over the 16-Year Observation Period[a]

sampling depth (cm)	BC a (μmol/ L)	BC b (μmol/ L/y)	BC Pr(>|t|)	Al a (μmol/L)	Al b (μmol/ L/y)	Al Pr(>|t|)	BC/Al a (μmol/ L)	BC/Al b (μmol/ L/y)	BC/Al Pr(>|t|)
0 litter	381	−13.99	≤0.0001	40	−2.26	≤0.0001	6.81	1.47	0.0018
30 (AE)	151	−7.90	0.0001	84	−2.99	0.0181	2.16	−0.08	0.0019
57 $(B_h)B_s$	171	−6.99	0.0012	63	−1.74	0.1321	3.13	−0.08	0.0005
110 $B_{(s)}C$	121	−4.48	0.0005	33	−0.04	0.9476	3.89	−0.14	≤0.0001

sampling depth (cm)	NO_3 a (μmol/ L)	NO_3 b (μmol/ L/y)	NO_3 Pr(>|t|)	SO_4 a (μmol/ L)	SO_4 b (μmol/ L/y)	SO_4 Pr(>|t|)	EC a (μS/cm)	EC b (μS/cm/y)	EC Pr(>|t|)
0 litter	325	−10.35	0.0139	85	−3.79	≤0.0001	94	−2.64	0.0185
30 (AE)	349	−14.75	0.0347	66	−2.49	0.0002	74	−2.80	0.0040
57 $(B_h)B_s$	344	−11.73	0.1477	63	−1.16	0.1234	73	−2.16	0.0234
110 $B_{(s)}C$	223	−8.22	0.0750	47	−0.09	0.8514	53	−1.49	0.0037

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

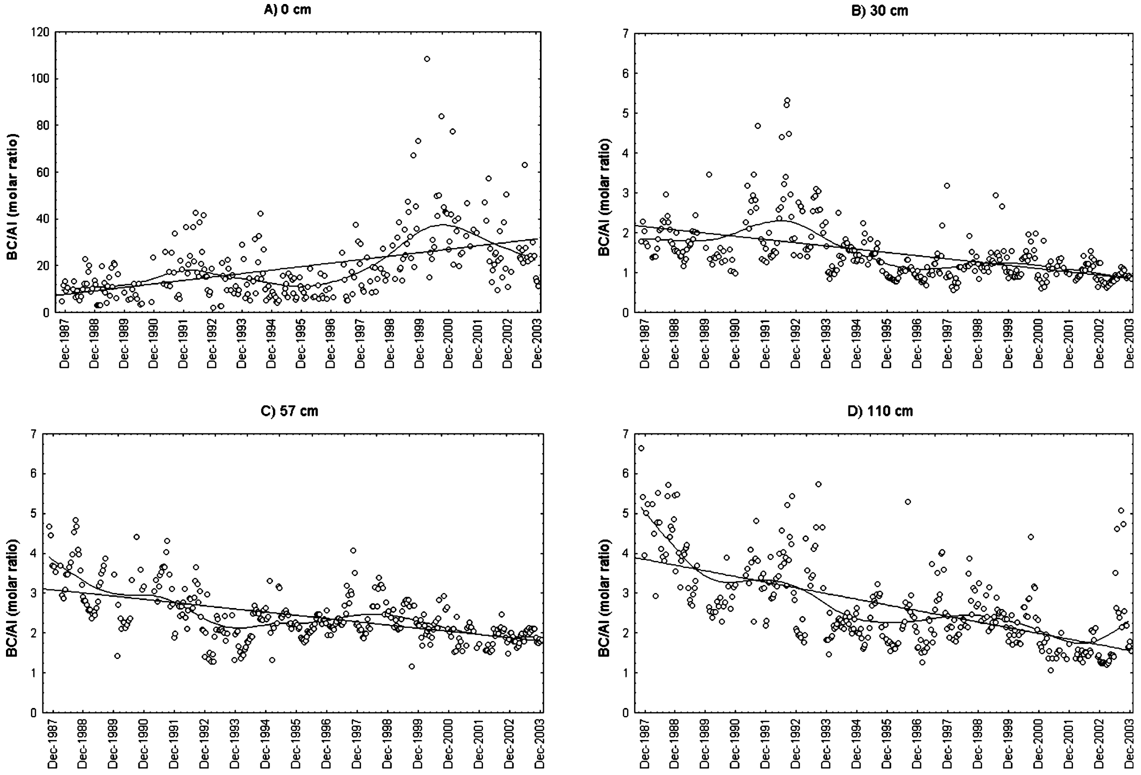

FIGURE 1. Molar BC/Al ratio in the soil solution between 1988 and 2003 at sampling depths of (A) 0 cm, (B) 30 cm, (C) 57 cm, and (D) 110 cm, with linear regressions (coefficient b in Table 3) and fitting of data obtained with the distance-weighted least squares smoothing procedure (stiffness = 0.1).

BC deposition of 10% since the 1960s cannot entirely explain the drop in BC fluxes below the litter layer.

Since the changes in concentrations and fluxes of nitrate and base cations cannot be related to changes in deposition, the assumption of a nutrient cycle in steady state might not be valid at the study site. The chemical composition of the soil water collected below the litter layer represents an integrating value reflecting not only changes in deposition but also changes in litter quality and amount of litter fall. The return of base cations and nitrogen by litterfall (126 kg/ha/year and 93 kg/ha/year, respectively) was large, about 5 times the input from deposition (*33*). An impoverishment in the nutrient status of the vegetation or a reduction in litterfall would have a considerable influence on the chemistry of the soil solution below the litter layer. The sharp decline in BC concentrations in the soil solution below the litter mat and in the underlying mineral horizons (Table 3) might therefore indicate that the pool of exchangeable base cations had decreased and that fewer base cations were available in solutions for tree nutrition. Large losses of base cations from the soil exchangeable pools because of acid deposition have been recorded in North America (*11*, *12*) and in Europe (*31*, *37*, *38*).

Long-Term Trends of Soil Solution Chemistry in the Mineral Horizons. The decline in ionic strength of the soil solution was reflected by a decrease in electrical conductivity during the 16-year observation period (Table 3). The decline in BC/Al ratios was mainly due to a strong decrease in base cation concentrations and may indicate a deterioration of the base saturation status. Despite the ionic strength of the soil solution declining, the increasing contribution of Al to the total cation charge and the decline in the BC/Al ratios

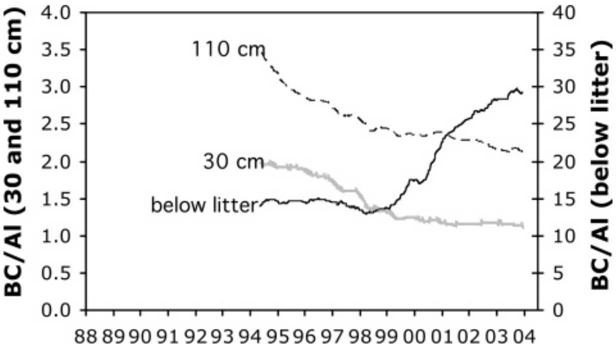

FIGURE 2. Moving average of BC/Al ratios with a time window of 6 years at 0 cm below the litter mat (thick solid line) and at depths of 30 cm in the (AE)-horizon (gray line) and of 110 cm in the $B_{(s)}C$-horizon (dashed line).

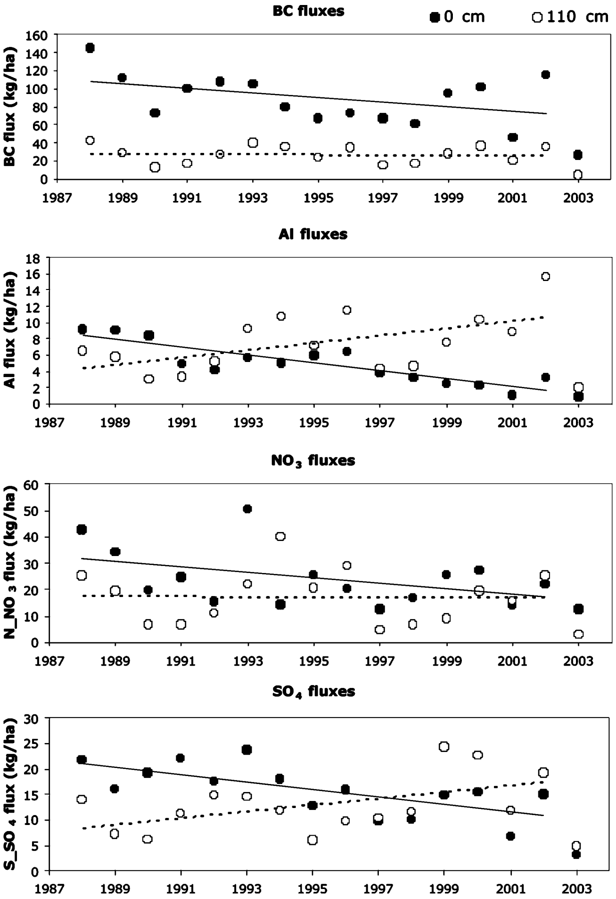

FIGURE 3. Estimate of element fluxes between 1988 and 2003 and linear regressions below the litter mat (●) and at a depth of 110 cm in the $B_{(s)}C$-horizon (○).

in the B-horizons might indicate a further decrease in the base saturation at the cation exchange sites (*26*). In contrast to the marked decrease in base cation concentrations at all depths, the total Al concentrations decreased significantly below the litter layer and in the (AE)-horizon (30 cm) but remained stable in the $B_{(s)}C$ horizon (Table 3). The decline in Al concentrations in the upper layers may be explained by a decrease in proton buffer capacity because of the depletion of reactive Al in the system. The acidity is then transferred to the $B_{(s)}C$ horizon. The soluble Al concentrations indicate that the reactive Al pool in this horizon is still large. A study performed with soil samples collected in Copera showed that the reactive pool in the (AE)-horizon consisted of organically bound Al, and in the $B_{(s)}C$-horizon it consisted of amorphous Al hydroxides and silicates (*39*).

TABLE 4. N, S, and BC Fluxes (kg/ha/year) in Atmospheric Deposition in Copera (1995) and in the Region (1988−2001), in Litterfall (Data from Literature) and Flux Estimates in the Soil Solution below the Litter Layer (0 cm) and in the $B_{(s)}C$-Horizon at 110 cm of Depth (Leaching)

area		references	N	S	BC
		Deposition			
region	1988−1993	*7, 13, 15*	30−42	30−32	24
region	1993−1998	*7, 13, 32*	30−39	15−20	10[a]
Copera	1995	*33*	18	17	25
region	1997−2001	*34*	24-42	11−17	7−26
		Litterfall			
Copera	1995	*33*	93		126
		Below Litter (0 cm)			
Copera	1988−1993		31	20	107
Copera	1993−1998		23	15	75
Copera	1997−2001		19	11	74
		Leaching (110 cm)			
Copera	1988−1993		15	11	28
Copera	1993−1998		23	10	30
Copera	1997−2001		11	16	23

[a] Only wet BC deposition.

In contrast to the fast response of SO_4 concentrations below the litter mat to the decline in S deposition, sulfate concentrations remained on average stable in the $B_{(s)}C$-horizon (110-cm depth). The SO_4 concentrations at the end of the observation period were higher than the concentrations in the above-lying layers, indicating an internal source of SO_4 in the $B_{(s)}C$-horizon (Table 3). Possible sulfate sources include weathering of S-bearing minerals, net mineralization of organic S, desorption of previously adsorbed inorganic SO_4, and reoxidation of previously reduced and stored S (*10*, *40*). At the study site, desorption of SO_4 from sesquioxides in the spodic horizon, stored during earlier periods of higher deposition, might occur. The spodic horizon at the study site is characterized by a strong interaction of soil organic matter with pedogenic Fe- and Al-oxides or clay minerals (*22*). Mineralization of organic S probably plays a minor role, since the soil organic matter in this soil is biologically very stable (*22*). Dissolution of $AlOHSO_4$ compounds probably did not control the SO_4 release since the sulfate concentrations were negatively correlated to the aluminum concentrations ($r = -0.66$, $n = 283$, data not shown). With the decrease in S deposition, the soil at the study site might have changed from a net retention to a net loss of sulfate by the end of the observation period. Between 1998 and 2003, the release of sulfate from the $B_{(s)}C$-horizon tended to be greater than the fluxes from the litter mat or from S deposition (Table 4).

Ecological Risks Related to Soil Solution Acidification. In most critical load models in Europe, the BC/Al ratio is used as an indicator to assess the ecological risk to plants associated with soil solution acidification (*41*). It is assumed that BC/Al ratios ≤ 1 might cause adverse effects on the tree roots (*41*). In this context, the low BC/Al ratios in the root zone (AE-horizon), reaching 1.3 at the end of the observation period (Figure 1), suggest that the risk of adverse impacts on roots is high (*41*). The situation might stabilize, since the BC/Al ratios remained on average constant during the late 1990s (Figure 2). In addition, the ecological risk to tree roots became smaller in the (AE)-horizon, since the concentrations of Al^{3+}, one of the most toxic forms of Al species (*42*), decreased over time, and, after 1996, were always smaller than the critical value of 200 $\mu mol_c/L$ (*43*) (data not shown). In the $B_{(s)}C$-horizon, the risk related to Al^{3+} seems to be limited, since the concentrations are much smaller than the critical values (Table 2). Assuming that the base cation input (sum of deposition and litterfall) continues to decline at the same rate as it did previously (Table 3) and that the reactive pool of Al in the $B_{(s)}$C-horizon is not exhausted, the BC/Al ratios will continue to decrease in this horizon and will very soon reach the critical value of 1.

Stabilization of BC/Al Ratios. It was not possible to demonstrate that the BC/Al ratios in the root zone had completely recovered in response to declining acidic deposition in the study area. Soil solution continued to acidify in the mineral soil horizons, like in many sites in Europe (*8*, *26*, *44*, *45*). However, the trends of the 6-year moving averages of the BC/Al ratios in Copera (Figure 2) might be seen as signs that the ratios are starting to recover and that the acidification rate is slowing down, first in the upper layers and then in the underlying layers. These signs include the large increase in the BC/Al ratios below the litter layer, the stabilization of the BC/Al ratios in the (AE)-horizon, and the slower decrease in the BC/Al ratios in the $B_{(s)}$C-horizon after the period 1993−1999. At several forest sites in Europe, the reduction in acid inputs resulted in a recovery of soil solution from acidification, as indicated by increasing ANC values, BC/Al ratios, or pH values (*9*, *46*, *47*). The extent and rapidity of recovery of forest soils and streamwater depends on several factors including the degree to which deposition alkalinity has increased (*26*, *31*). At the study site, the observed recovery of BC/Al ratios, especially the strong increase in ratios below the litter layer because of a decline in Al, might reflect the increase in the deposition alkalinity observed in the Lake Maggiore catchment since the 1990s (*13*, *34*, *48*). Reversing the decreasing trend of BC/Al ratios in the mineral horizons requires an input of BC through deposition and weathering that is larger than the loss of BC through leaching. Reducing the deposition of acidifying compounds would help to improve the soil water quality by diminishing cation leaching.

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Supporting Information Available

More detailed descriptions about the site and the methods used for the chemical analysis of the soil solution samples (replicates, pH, fractionation of Al). This material is available free of charge via the Internet at http://pubs.acs.org.

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