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A decade of monitoring at Swiss Long-Term Forest Ecosystem Research (LWF) sites: can we observe trends in atmospheric acid deposition and in soil solution acidity?

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Abstract Trends in atmospheric acid deposition and in soil solution acidity from 1995 or later until 2007 were investigated at several forest sites throughout Switzerland to assess the effects of air pollution abatements on deposition and the response of the soil solution chemistry. Deposition of the major elements was estimated from throughfall and bulk deposition measurements at nine sites of the Swiss Long-Term Forest Ecosystem Research network (LWF) since 1995 or later. Soil solution was measured at seven plots at four soil depths since 1998 or later. Trends in the molar ratio of base cations to aluminum (BC/Al) in soil solutions and in concentrations and fluxes of inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$), sulfate ($\text{SO}_4\text{-S}$), and base cations (BC) were used to detect changes in soil solution chemistry. Acid deposition significantly decreased at three out of the nine study sites due to a decrease in total N deposition. Total $\text{SO}_4\text{-S}$ deposition decreased at the nine sites, but due to the relatively low amount of $\text{SO}_4\text{-S}$ load compared to N deposition, it did not contribute to decrease acid deposition significantly. No trend in total BC deposition was detected. In the soil

solution, no trend in concentrations and fluxes of BC, $\text{SO}_4\text{-S}$, and inorganic N were found at most soil depths at five out of the seven sites. This suggests that the soil solution reacted very little to the changes in atmospheric deposition. A stronger reduction in base cations compared to aluminum was detected at two sites, which might indicate that acidification of the soil solution was proceeding faster at these sites.

Keywords Acid deposition · Acidification · Soil solution · ICP-Forests

Introduction

Acid atmospheric deposition has been shown to affect the chemistry of soils and drainage waters in forest ecosystems and accelerate the acidification of soils (e.g., Binkley et al. 1989). Acidifying emissions, especially of sulfur dioxide (SO_2), have decreased considerably since the mid 1980s across large regions of Europe and North America as a result of air pollution abatements. After a strong reduction between 1985 and the mid 1990s, S emissions declined more slowly (Schöpp et al. 2003). Emissions of oxidized and reduced nitrogen in Europe have been reduced during the last 15–20 years, but they have remained on a high level. The reduction of acid deposition has raised questions about the recovery of surface waters

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and soils from acidification. The data analysis of the ICP-Water Program between 1985 and 1995 showed an increase in alkalinity, which was regarded as a recovery from acidification, in streams and lakes in response to the reduction in sulfate deposition (Stoddard et al. 1999; Evans et al. 2001). Other studies have reported a delay or even no reaction in respect to water acidification, which was attributed to the release of previously stored sulfate from developed soils, coupled to the leaching of aluminum (Al) and base cations (BC; e.g. Alewell et al. 2000a; Prechtel et al. 2001; Armbruster et al. 2003). Chronic high atmospheric input of nitrogen (N) also leads to a net acidification in N-rich forest ecosystem, where inorganic N (mostly NO_3^-), exceeding the plant and microbe demand, is leached below the root zone (Gundersen et al. 2006). The release of the strong acid anions SO_4^{2-} and NO_3^- in the soil solution, balanced by cation leaching, may significantly contribute to the acidification of soils and surface waters (Reuss and Johnson 1986). Several field studies have shown that soil solution acidification was still progressing in the late 1990s, despite reduced deposition (Blaser et al. 1999; Alewell et al. 2000b; Moffat et al. 2002). An increasing net loss of BC from ecosystems due to a combination of high anion leaching and reduction in BC deposition has been reported in several catchments in Europe (Alewell et al. 2001) and North America (Likens et al. 1998; Watmough and Dillon 2004). Depletion of exchangeable base cations in soils has been suggested as a major process preventing the recovery of surface waters despite large reductions in S emissions.

Trend analyses in soil solution collected in forest ecosystems were performed in several countries in Europe in the late 1980s and in the 1990s such as in Belgium (Neirynek et al. 2002), Germany (e.g. Meesenburg et al. 1995; Alewell et al. 2000b; Armbruster et al. 2003), Norway (Kvaalen et al. 2002; Moffat et al. 2002), Sweden (Fölster et al. 2003), and Switzerland (Blaser et al. 1999). Later, the studies of Boxman et al. (2008), Oulehle et al. (2006), and Neirynek et al. (2008) reported long-term trends of the soil solution chemistry until 2005–2007 at single forest plots. Very few studies (e.g. Vanguelova et al. 2010) investigated the response of the soil solution quality to declining acid

deposition after 2000 in different forest ecosystems at a larger spatial scale. However, these data are relevant, not only to show the effects of the measures taken for air quality improvement and to survey the potential ecological risks for forest and aquatic ecosystems at the national or regional level but also to calibrate and validate dynamic soil chemistry models (Reinds et al. 2009a). The models are getting more complex and integrate not only the effects of deposition on soils but also the response to climate change and forest management practices (e.g., ForSafe in Wallman et al. 2005; Belyazid et al. 2006; Reinds et al. 2009b).

The monitoring of Swiss Level II plots in the framework of the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP-Forests; e.g. UNECE 2008) provides useful data to assess the response of soil solution to decreasing acid deposition in Switzerland. The Swiss Long-Term Forest Ecosystem Research LWF was established in 1994, with the aim of gaining a better knowledge of how natural and anthropogenic stresses affect forests in the long term (Cherubini and Innes 2000; Thimonier et al. 2001). Deposition measurements started in 1995 or later at nine sites and soil solution sampling began between 1998 and 2000 at seven sites. To assess the effects of air pollution abatements on acid deposition and the response of the soil solution chemistry, trends in acid deposition and in soil solution acidity until 2007 were investigated in various mature forest stands in different climatic regions of Switzerland. The measurement period corresponds to the phase of slow decline in S emissions and of rather constant N and BC emissions in Switzerland (FOEN 2009). The long-term trends in the ratios of BC to Al in the soil solution (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) were used to characterize soil solution acidification (Blaser et al. 1999; Neirynek et al. 2002; Graf Pannatier et al. 2005). Depletion of exchangeable base cations by acidification might lead to a decrease in base saturation and possibly in a decrease in the BC/Al ratio in the soil solution (Cronan and Grigal 1995). Input and output budget of inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) and

sulfate (SO_4^{2-}) were also analyzed to assess the response of soil solution chemistry to changing deposition (Alewell et al. 2001; Vanguelova et al. 2010). Although precipitation amount and water fluxes have been shown to influence total deposition (e.g. Thimonier et al. 2005) and element fluxes in the soil solution (e.g. Michalzik et al. 2001), very few studies have considered this aspect in their trend analysis.

The three main objectives of this study were (1) to assess the effects of emission abatement on acid deposition at nine forest sites throughout Switzerland, (2) to investigate the response of the soil solution chemistry to acid deposition at seven sites, (3) to check the influence of the variations in precipitation amount and soil water fluxes on the trends of acid deposition and soil solution chemistry. The observation period considered in this study started in 1995 or later until 2007.

Material and methods

Sites

The nine study sites are part of a national forest monitoring network that was set up within the framework of the Swiss Long-Term Forest

Ecosystem Research project LWF. These sites are part of the Level II plots network of ICP-Forests.

The sites are distributed across Switzerland from the Jura Mountains to the southern part of the Alps (Fig. 1). The main characteristics of the study sites, including location, main tree species, and soil type, are given in Tables 1 and 2. Seven main tree species are represented including beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*). The forests were not managed during the whole observation period. The sites cover a broad range of soils, from calcareous soils to podzols. The type of parent material (carbonate or free of carbonate) and the depth of the first appearance of carbonate in the fine earth are presented in Table 2. The chemistry (pH, effective cation exchange capacity, and base saturation) of the soil profiles is provided in Walthert et al. (2003) and summarized in Table 2.

Atmospheric deposition

Atmospheric deposition was monitored at nine sites for a period of 8 to 13 years (starting in 1995 at the earliest and in 2000 at the latest until 2007) using the throughfall method (Table 1). This method relies on the parallel sampling of throughfall and precipitation in an open area close

Fig. 1 Location of study sites with sampling of atmospheric deposition and soil solution



Table 1 Main site characteristics: location, climate, main tree species, maximal leaf area index (LAI_{max}), and sampling period

Region Site	Altitude a.s.l. [m]	Mean annual temperature [°C]	Mean annual precipitation [mm]	Main tree species (max tree age)	LAI _{max} ^a	Deposition	Soil solution
Jura Bettlachstock	1149	6.0	1454	<i>Fagus sylvatica</i> L. (170), <i>Abies alba</i> Mill. (180)	6.5	May 1998–Dec 2007	Aug 1999–Dec 2007
Swiss Plateau Jussy	501	9.7	977	<i>Quercus robur</i> L. (80)	5.8	Mar 1997–Dec 2007	
Lausanne	807	7.6	1210	<i>Fagus sylvatica</i> L. (150–160)	6.9	Nov 1996–Dec 2007	Jan 1999–Dec 2007
Othmarsingen	484	8.6	1045	<i>Fagus sylvatica</i> L. (110–130)	4.6	Oct 1994–Dec 2007	
Vorderwald	480	8.4	1106	<i>Abies alba</i> Mill. (100)	6.1	May 1996–Dec 2007	Aug 1999–Dec 2007
Pre-Alps Schânis	733	7.9	1801	<i>Fagus sylvatica</i> L. (120–140)	5.5	Jul 1998–Dec 2007	Sept 1999–Dec 2007
Beatenberg	1511	4.6	1305	<i>Picea abies</i> (L.) (180–220)	3.5	Aug 1999–Dec 2007	Aug 1999–Dec 2007
Alps Celerina	1871	2.8	1024	<i>Pinus cembra</i> L. (200–240), <i>Larix decidua</i>	1.8	Jul 1999–Dec 2007	Oct 1999–Dec 2007
Southern Alps Novaggio	950	9.7	2022	<i>Quercus cerris</i> L. (60)	4.9	Mar 1996–Dec 2007	Jan 2000–Dec 2007

^aLAI_{max} in Thimonier et al. (2010b)

Table 2 Soil type, parent material, root zone depth and summary of soil pH (CaCl₂), base saturation and texture

Region Site	Soil type (FAO 1988)	Parent material	depth (m) of carbonated material ^a	Root zone (m)		pH		Base saturation (%)			Texture range (min-max) ^b			
				0–5 cm	60–80 cm	0–5 cm	60–80 cm	0–5 cm	60–80 cm	BS	min	parent material	Sand %	Clay %
Jura														
Bettlachstock	Rendzic Leptosol	Carbonate hauptrogenstein	0.05	>1.2	6.5	7.7	6.5	7.7	100	100	100	100	9–43	32–56
Swiss Plateau														
Jussy	Eutric Gleysol	Carbonate moraine	0.7	>1.0	4.6	7.6	4.5	7.6	96	100	87	100	19–30	27–46
Lausanne	Dystric Cambisol	Carbonate moraine	3.0	>2.4	3.9	4.0	3.9	7.4	29	7	7	100	51–62	13–17
Othmarsingen	Haplic Acrisol	Carbonate moraine	1.7	>1.9	3.9	4.0	3.9	7.8	59	34	9	100	49–57	12–25
Vordemwald	Dystric Planosol	Carbonate moraine	>4.5	>1.2	3.3	3.9	3.3	>5.0	7	5	4	>80	18–52	16–20
Pre-Alps														
Schänis	Eutric Cambisol	Carbonate conglomerate	1.0	>1.6	5.0	5.4	4.3	7.7	96	99	77	100	15–50	21–41
Beatenberg	Podzol	Non-carbonate sandstone	–	0.55	2.8	4.0	2.8	n.d.	28	5	3	n.d.	78–87	3–9
Alps														
Celerina	Podzol	Non-carbonate moraine	–	>1.0	4.0	4.5	4.0	>4.5	57	46	27	>46	36–50	4–12
Southern Alps														
Novaggio	Dystric Cambisol	Non-carbonate moraine	–	>1.5	3.8	5.0	3.8	>5.0	12	23	9	>34	65–90	2–14

From Walther et al. (2003)

n.d. not determined, – the bedrock was free of carbonate

^aDepth of the first appearance of carbonate in the fine earth

^bTexture of fine earth <2 mm

to the forest stand. Precipitation in the open area was collected with three funnel-type (100 cm² opening) polyethylene collectors (bulk precipitation). At the sites where abundant snowfall could be expected (Bettlachstock, Beatenberg, Schänis, Celerina, Lausanne, and Novaggio), the funnel-type collectors were replaced by a single bucket-type snow collector (30 cm diameter) in winter. Throughfall was sampled with 16 funnel-type collectors systematically distributed into two sets of equal numbers in two 43 × 43 m subplots inside the forest plot. The collectors were replaced by four 30-cm diameter buckets for snow collection during the winter at the sites where abundant snowfall was expected (see above). A detailed description of the sampling design is provided in Thimonier et al. (2005).

Both throughfall and bulk deposition samples were collected every two weeks except during the winter in Celerina and in Bettlachstock (every 4 weeks). Upon arrival of the samples in the laboratory, the samples were pooled and filtered (0.45 μm). Ammonium (NH₄⁺) was determined colorimetrically through automated flow injection analysis. Total dissolved Al, calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺), and sodium (Na⁺) were determined by inductively coupled plasma-atomic emission spectrometry. Nitrate (NO₃⁻), sulfate (SO₄²⁻) and chloride (Cl⁻) were measured by ion chromatography (DX-120, Dionex). The pH of the samples was also measured, but because of the use of different pH electrodes during the observation period and the lack of accuracy in the weak acid range (pH 5–6) revealed from international ring tests, the measurements, and especially trend analysis of pH are not presented in this paper.

Throughfall and bulk deposition fluxes were calculated multiplying precipitation amount and concentrations for each collection interval and were summed over months and calendar years, using time weighting to interpolate at transitions between months.

To estimate the total deposition, we used the canopy budget model developed by Ulrich (1983), synthesized by De Vries et al. (2001). In this model, throughfall fluxes represent total deposition plus or minus canopy exchanges (leaching or uptake). Sodium is assumed to interact little with

the canopy and is used as a tracer for estimating the dry deposition of base cations. Other assumptions in the model include the relative exchange capacities of protons, ammonium, and nitrate. In our calculations, the estimated leaching of weak acids was also taken into account. All equations are given in Thimonier et al. (2005).

Based on the Manual on methodologies and criteria for modeling and mapping critical loads and levels of ICP-Mapping (UNECE 2004), the load of acidity (TDA) was defined as the sum of total deposition of strong acid anions minus non-sea-salt cations plus non-sea-salt chloride:

$$TDA = TDS^* + TDN - TDBC^* + TDCI^* \quad (1)$$

where TDS, TDN, TDBC, TDCI are the total atmospheric deposition of sulfur (S), nitrogen (N), base cations (BC = Ca²⁺ + Mg²⁺ + K⁺) and chloride (Cl⁻) respectively with all terms in kmol_e ha⁻¹ a⁻¹. A factor of 2 and 1 eq mol⁻¹ of deposited S and N respectively was used in Eq. 1. Total deposition denoted with an asterisk was corrected for sea-salt, using sodium as a tracer for sea-salt (UNECE 2004). Since the aim of the Convention on Long-range Transboundary Air Pollution is to reduce anthropogenic emissions of S and N, total deposition derived from sea-salt was not considered in the balance (UNECE 2004). Total deposition was calculated on an annual basis. For trend analysis, it was also calculated at the monthly basis but the assumptions of the canopy budget model might not be valid at that time scale.

Soil solution

Soil solution was analyzed at seven sites for a period of 8–9 years since 1999/2000 until 2007 (Table 1). At each site, it was collected at eight sampling points systematically distributed in one 43 × 43 m subplot where eight of the throughfall collectors were also installed. Soil solution was sampled below the litter Oi layer or in the humus Oe horizon (defined as 0 cm of depth) using zero-tension lysimetry with Plexiglas plates and in the mineral horizons at three depths (15, 50, and 80 cm) using tension lysimetry with ceramic cups (highflow porous ceramic cups, Soil moisture Equipment Cop. Santa Barbara, USA). At the beginning of each sampling period, a vacuum of

500 hPa was applied to the suction cups. The detailed sampling method is described in Graf Pannatier et al. (2004). Soil solution was taken every 2 weeks, together with the precipitation samples. Upon arrival of the samples in the laboratory, the samples were pooled, filtered (0.45 μm) and analyzed for pH. The same elements as those measured in the precipitation samples were determined in the soil solution samples. Only mean pH values were presented in this paper. Trend analysis of pH was not performed for the same reasons as those mentioned for the deposition samples.

The molar BC/Al ratio in the soil solution (with BC corresponding to the sum of Ca^{2+} , Mg^{2+} , and K^{+} , and Al representing the total concentration of dissolved Al) was calculated for each sample.

In addition to soil solution collection, the soil matric potential Ψ was measured every two weeks at five depths (15, 30, 50, 80, and 130 cm) with at least eight tensiometers per depth installed permanently in the soil. The lower limit of the measurable range was -90 kPa. These measurements were used to check the plausibility of results from water balance model (see below).

Modelling of water and element fluxes in soils

CoupModel, a coupled heat and mass transfer model for soil-plant-atmosphere systems (Jansson and Karlberg 2004) was used to simulate daily matric potential and daily water fluxes at the seven sites where soil solution was collected. The meteorological data (air temperature, precipitation, relative humidity, global radiation, and wind speed) came from the weather station installed at the study site. Stand characteristics and soil properties were available in Walthert et al. (2003) and maximal leaf area index (LAI_{max}) in Thimonier et al. (2010b; Table 1). Pedo-transfer functions derived from soil texture, bulk density and organic matter content (Tables 70 and 72 in KA5 2005) were used to estimate the water contents at saturation, field capacity and wilting point. The van Genuchten parameters were fitted to these points by Schramm et al. (2006) and were applied to the soil horizons of the study sites.

Daily element fluxes were calculated by multiplying the concentrations in the soil solution mea-

sured during each 2-week sampling period with the modeled daily water fluxes at each depth. Daily fluxes were cumulated to monthly and yearly fluxes.

Trend analysis

The nonparametric seasonal Mann–Kendall Test (MKT) (Hirsch and Slack 1984) was applied to detect monotonic trends in monthly data. Trend slopes were calculated using Sen's slope estimates, which is the median change between years for all seasonal blocks (Sen 1968). Partial seasonal Mann–Kendall Tests (PMKT) were also applied to find out whether the temporal variations of the studied variables could be explained by fluctuations of precipitation amount or soil water fluxes (Libiseller and Grimvall 2002). Simple Mann–Kendall Tests (without seasonality) were applied to annual fluxes. All Mann–Kendall Tests were computed using the MULTMK/PARTMK program (Libiseller 2004).

Results

Trends in acid atmospheric deposition

Annual precipitation, acid deposition (TDA) and the contributions of total deposition of sulfur (TDS^*), nitrogen (TDN), and base cations (TDBC^*) to the load of acidity during the observation period (since 1995 or later until 2007) are illustrated in Fig. 2. The range of TDA differed between the regions. When considering the mean annual TDA between 2000 and 2007 at all plots, the lowest values were found in Celerina in the Alps (-0.02 $\text{kmol}_c \text{ha}^{-1} \text{a}^{-1}$), the highest in Novaggio in southern Switzerland (1.99 $\text{kmol}_c \text{ha}^{-1} \text{a}^{-1}$), and in Schänis in the Pre-Alps (1.70 $\text{kmol}_c \text{ha}^{-1} \text{a}^{-1}$). Intermediate values were found on the Swiss Plateau (from 0.35 to 1.24 $\text{kmol}_c \text{ha}^{-1} \text{a}^{-1}$ in Othmarsingen, Vordemwald, Lausanne, Jussy), in the Jura (0.91 $\text{kmol}_c \text{ha}^{-1} \text{a}^{-1}$ in Bettlachstock), and in the Pre-Alps (0.56 $\text{kmol}_c \text{ha}^{-1} \text{a}^{-1}$ in Beatenberg).

The main contributor to acid deposition (TDA) during the observation period was nitrogen deposition (TDN). Mann–Kendall Tests on annual TDA indicated significant decreasing trends ($p < 0.05$) at three sites on the Swiss Plateau (Othmarsingen,

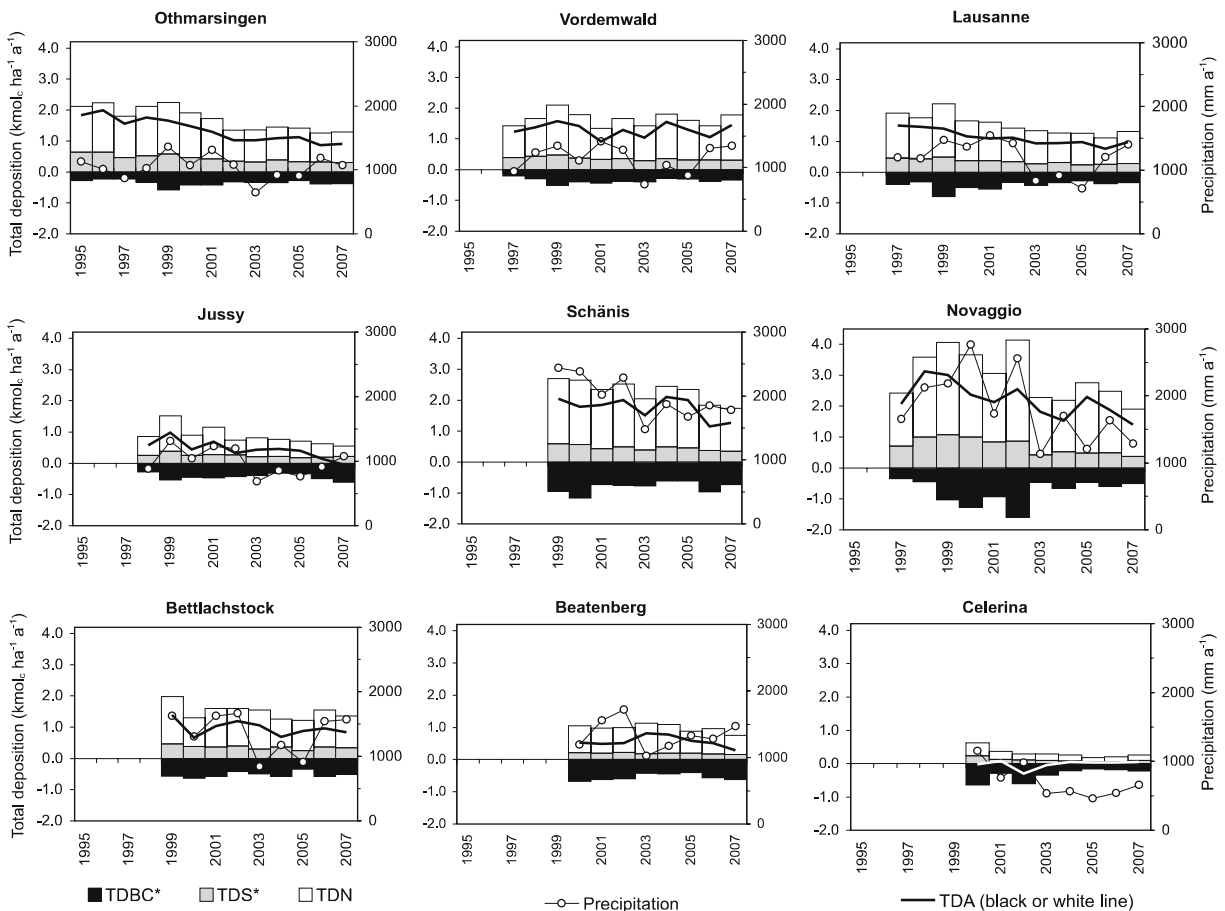


Fig. 2 Annual total acid deposition (TDA), total deposition of sulfur (TDS*), nitrogen (TDN), and base cations (TDBC*) with * denoting correction for sea-salt, and pre-

cipitation in open area (mm a^{-1}) at the 9 sites since 1995 or later until 2007. See Eq. 1 in text for the calculation of TDA

Lausanne, Jussy) and in Novaggio in southern Switzerland (Table 3). The Sen's slopes were quite similar at the three sites on the Swiss Plateau ($-0.07 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$) and higher in Novaggio ($-0.14 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$). The decrease in annual TDA was mainly due to a significant decrease in TDN of ca $0.06 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$. In Novaggio, it was mainly caused by the decline in TDS* (Table 3); TDN also tended to decline (Fig. 2) but the decrease was not significant. TDS* decreased significantly at the nine plots, but due to the relatively low amount of TDS* compared to TDN (on average 30%), it did not contribute to decrease TDA significantly (except in Novaggio). Variations of TDBC* during the observation period were large, with higher values between 1999 and 2002 at all plots. This explains the significant

decreasing trend of TDBC* in Celerina (Table 3) where deposition measurements started in 2000 (Fig. 2). TDCI* was close to zero at all plots (95th percentile = $0.032 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$) and therefore no trend analysis was performed. Partial Mann-Kendall Tests calculated on annual total deposition (Table 3) indicated that variations in precipitation amount were not responsible ($p < 0.05$) for the trends in TDA, TDN, and TDS*, except in Schänis (TDS* and TDN) and in Novaggio (TDA).

Seasonal Mann-Kendall tests were also performed with the monthly values of TDA, TDS*, TDN, and TDBC*. The Sen's slopes calculated with monthly values over the whole observation period were similar or slightly smaller than those computed with annual values (Table 3). Similarly to the findings of Staelens et al. (2008), these

Table 3 Annual trend indicated by Sen’s slope for $p < 0.05$ in precipitation amount (mm a^{-1}) and in total deposition ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$) of acidity (TDA), sulfur (TDS*), and base cations (TDBC*) with * denoting correction for sea-salt

	Number of years	Number of months	Precipitation		
			Starting value (mm a^{-1})	Annual Sen (mm a^{-1})	Monthly Sen (mm a^{-1})
Jura					
Bettlachstock 1999–2007	9	108	1625	–	–
Swiss Plateau					
Jussy 1998–2007	10	120	885	–	–
Lausanne 1997–2007	11	132	1197	–	–
Othmarsingen 1995–2007	13	156	1127	–	–
Vordemwald 1997–2007	11	132	941	–	–
Pre-Alps					
Schänis 1999–2007	9	108	2441	* –84	–
Beatenberg 2000–2007	8	96	1196	–	–
Alps					
Celerina 2000–2007	8	96	1152	–	* –28
Southern Alps					
Novaggio 1997–2007	11	132	1654	–	–
TDA					
			Starting value ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	Annual Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	Monthly Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)
			PMKT	PMKT	PMKT
Jura					
Bettlachstock 1999–2007	1.45	–	–	–	–
Swiss Plateau					
Jussy 1998–2007	0.61	** –0.070	*	* –0.046	*
Lausanne 1997–2007	1.55	** –0.070	**	** –0.070	**
Othmarsingen 1995–2007	1.86	*** –0.095	***	*** –0.095	***
Vordemwald 1997–2007	1.28	–	–	–	–
Pre-Alps					
Schänis 1999–2007	2.09	–	–	–	–
Beatenberg 2000–2007	0.53	–	–	–	–
Alps					
Celerina 2000–2007	0.00	–	–	–	–
Southern Alps					
Novaggio 1997–2007	2.07	* –0.140	–	** –0.132	*
TDS*					
			Starting value ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	Annual Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	Monthly Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)
			PMKT	PMKT	PMKT
Jura					
Bettlachstock 1999–2007	0.44	* –0.013	**	* –0.015	*
Swiss Plateau					
Jussy 1998–2007	0.23	* –0.011	*	* –0.014	*
Lausanne 1997–2007	0.44	** –0.022	***	** –0.025	**
Othmarsingen 1995–2007	0.62	*** –0.028	***	** –0.020	***
Vordemwald 1997–2007	0.38	** –0.013	**	* –0.012	**
Pre-Alps					
Schänis 1999–2007	0.56	** –0.028	–	* –0.011	–
Beatenberg 2000–2007	0.20	* –0.006	*	* –0.008	*
Alps					
Celerina 2000–2007	0.21	* –0.013	*	** –0.010	–
Southern Alps					
Novaggio 1997–2007	0.71	* –0.067	**	** –0.053	*

Table 3 (continued)

	TDN				
	Starting value ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	Annual Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	PMKT	Monthly Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	PMKT
Jura					
Bettlachstock 1999–2007	1.50	–	–	–	–
Swiss Plateau					
Jussy 1998–2007	0.61	** –0.057	**	* –0.045	*
Lausanne 1997–2007	1.45	*** –0.061	***	** –0.064	**
Othmarsingen 1995–2007	1.48	** –0.057	**	** –0.057	**
Vordemwald 1997–2007	1.04	–	–	–	–
Pre-Alps					
Schänis 1999–2007	2.10	** –0.076	–	** –0.057	*
Beatenberg 2000–2007	0.83	–	–	–	–
Alps					
Celerina 2000–2007	0.40	* –0.020	–	* –0.015	–
Southern Alps					
Novaggio 1997–2007	1.71	–	–	–	–
	TDBC*				
	Starting value ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	Annual Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	PMKT	Monthly Sen ($\text{kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$)	PMKT
Jura					
Bettlachstock 1999–2007	0.48	–	–	* –0.024	*
Swiss Plateau					
Jussy 1998–2007	0.23	–	–	–	–
Lausanne 1997–2007	0.34	–	–	–	–
Othmarsingen 1995–2007	0.24	–	–	–	–
Vordemwald 1997–2007	0.14	–	–	–	–
Pre-Alps					
Schänis 1999–2007	0.57	–	–	* –0.037	–
Beatenberg 2000–2007	0.50	–	*	–	*
Alps					
Celerina 2000–2007	0.61	* 0.055	–	* –0.021	–
Southern Alps					
Novaggio 1997–2007	0.33	–	–	–	–

The trends were computed with the Mann–Kendall Test with annual and monthly values. Starting value: sum or mean of the first year of measurement

n number of months used in the MKT, PMKT is the partial MKT performed with precipitation as explanatory variable, – not significant ($p < 0.05$)

*** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$) is given for each variable to the left of the Sen's slope and for each PMKT to the right of the Sen's slope

results suggest that the canopy budget model can be applied on a monthly basis, provided reliable chemical analyses and data quality checking.

Throughfall fluxes of inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$), S ($\text{SO}_4\text{-S}$), and base cations (Ca, Mg, K) without any sea-salt correction showed similar trends as those found in total deposition (Table 4). The seasonal Mann–Kendall tests performed on

the monthly values indicate that throughfall S fluxes decreased at all plots at rates ranging between -0.009 and $-0.059 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$, which corresponds to the same range of rates determined with TDS* (Table 3). Similarly to TDN, inorganic N fluxes in throughfall also significantly decreased in Othmarsingen, Lausanne, Schänis and Celerina but not in Jussy. The rates varied

between -0.014 and -0.039 $\text{kmol}_c \text{ N ha}^{-1} \text{ a}^{-1}$. The partial Mann–Kendall indicated that variations in precipitation amount were not responsible ($p < 0.05$) for the trends in S and N fluxes in throughfall, except in Schänis and Celerina.

Trends in soil solution chemistry

Element concentrations (e.g. $\text{NO}_3^- \text{N}$, BC or $\text{SO}_4^- \text{S}$) and BC/Al ratios strongly decreased at some plots (e.g. Beatenberg, Novaggio) during the first year of measurement (Fig. 3 and Table 5). This might have been caused by the soil disturbance during the installation of lysimeters, resulting in higher mineralization rates as it was reported in Moffat et al. (2002). For this reason, trends were calculated with and without the first year of measurement. The comparison of the seasonal Mann–Kendall Tests calculated with and without the first year of measurements (Tables 5 and 6) indicates that several significant trends (e.g. in Novaggio, Beatenberg, Celerina, Schänis) were

not significant anymore when the first year of measurements was removed. Based on these results, we only considered the trends calculated without the first year of measurements.

The seasonal Mann–Kendall tests computed with monthly values of BC/Al ratios indicated that no significant trend in BC/Al ratios could be found in Lausanne, Celerina and Novaggio at any soil depths (Table 5). Figure 3 also shows that despite the large seasonal variations at these sites, BC/Al remained stable on average at a depth of 15 and 80 cm. Significant decreases in BC/Al were found at two sites only, in Beatenberg at a depth of 15 cm and in Vordemwald at a depth of 15 and 50 cm (Table 5). The decrease in BC/Al in Beatenberg was due to a decline in base cation concentrations, while in Vordemwald, BC decreased stronger than Al (Table 5). The rate of decrease was slow in Vordemwald (-0.05 BC/Al a^{-1}) and represented an annual decrease of 1% to 4%. In Beatenberg, the decrease was proportionally faster (-7% yearly) at a depth of 15 cm.

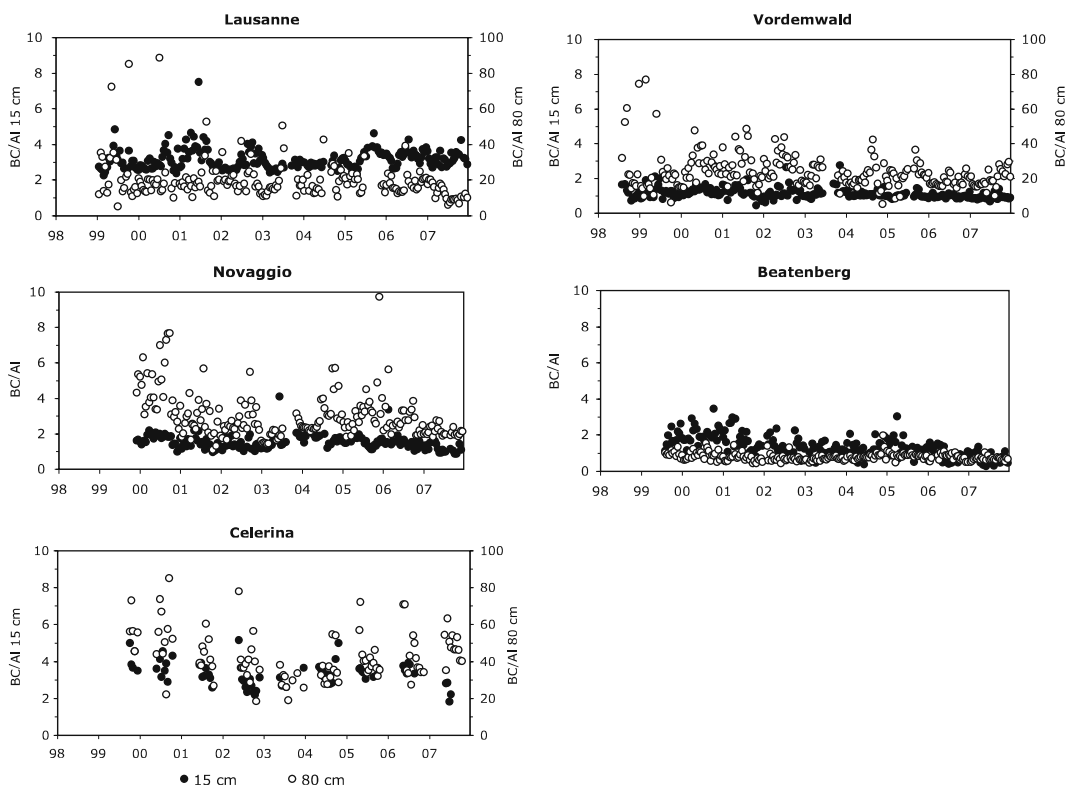


Fig. 3 Molar BC/Al ratio in the soil solution at a depth of 15 and 80 cm at the five sites with acid soil solution ($\text{pH} < 5.5$)

Table 5 Annual trend indicated by Sen's slope for $p < 0.05$ in water fluxes (mm a^{-1}) and concentrations ($\mu\text{mol l}^{-1} \text{a}^{-1}$) of aluminum (Al), base cations (BC), inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$), sulfate ($\text{SO}_4\text{-S}$) and molar BC/Al ratios in soil solution at four soil depths

	Depth (cm)	pH	Water flux			Number of months with chemical data	Al		BC	
			Mean during observation period	Starting value (mm a^{-1})	Number of months		Sen (mm a^{-1})	Starting value ($\mu\text{mol l}^{-1}$)	Sen ($\mu\text{mol l}^{-1} \text{a}^{-1}$)	PMKT ($\mu\text{mol l}^{-1} \text{a}^{-1}$)
Jura										
Bettlachstock										
Aug 1999–Dec 2007										
	0	6.2	931	101	67	<d.l.	<d.l.	469	-	-
	15	8.1	962	101	87	<d.l.	<d.l.	1524	-	-
	50	8.2	794	101	73	<d.l.	<d.l.	1583	-	-
	80	8.2	734	101	77	<d.l.	<d.l.	1668	-	-
Aug 2000–Dec 2007										
	0	6.6	1013	89	60	<d.l.	<d.l.	516	-	-
	15	8.3	1056	89	75	<d.l.	<d.l.	1530	-	-
	50	8.4	865	89	62	<d.l.	<d.l.	1469	-	-
	80	8.4	810	89	65	<d.l.	<d.l.	1536	-	-
Swiss Plateau										
Lausanne										
Jan 1999–Dec 2007										
	0	5.6	1034	108	105	3.80	-	311	-	-
	15	4.2	1002	108	106	60.6	-	177	-	-
	50	4.6	882	108	96	22.7	-	131	-	-
	80	5.4	819	108	101	7.80	-	146	-	* -5.2
Jan 2000–Dec 2007										
	0	5.1	943	96	93	4.06	-	253	-	-
	15	4.4	924	96	94	53.1	-	156	-	-
	50	4.8	817	96	84	29.7	-	128	-	-
	80	5.5	767	96	89	8.67	-	151	-	-
Vordemwald										
Aug 1998–Dec 2007										
	0	4.5	818	113	107	31.8	* -1.6	98.4	* -5.5	**
	15	4.4	789	113	110	30.9	*** -1.1	36.5	** -1.9	***
	50	4.5	598	113	110	19.3	** -0.46	59.8	** -2.4	**
	80	5.1	572	113	109	4.55	-	103	*** -3.0	***
Aug 1999–Dec 2007										
	0	4.3	1102	101	95	36.7	* -1.2	90.7	n.s.	*
	15	4.5	1073	101	98	26.1	** -0.91	31.6	** -2.0	**
	50	4.6	909	101	98	20.0	** -0.55	57.4	** -2.4	**
	80	5.2	869	101	97	4.47	-	94.2	** -2.5	**
Pre-Alps										
Schänis										
Sept 1999–Dec 2007										
	0	6.9	2001	100	95	<d.l.	<d.l.	310	-	-
	15	7.5	1965	100	93	<d.l.	<d.l.	450	** -15.3	*
	50	7.7	1895	100	93	<d.l.	<d.l.	534	** -15.3	*
	80	7.9	1837	100	92	<d.l.	<d.l.	676	-	-

Table 5 (continued)

Depth (cm)	pH	Water flux		Number of months	Sen (mm a ⁻¹)	Number of months with chemical data	Al		BC		
		Starting value (mm a ⁻¹)	Sen (mm a ⁻¹)				Starting value (μmol l ⁻¹)	Sen (μmol l ⁻¹)	Starting value (μmol l ⁻¹)	Sen (μmol l ⁻¹)	
Sept 2000–Dec 2007											
0	7.0	1648	-	88	-	83	<d.l.	285	-	-	-
15	7.6	1654	-	88	-	81	<d.l.	469	* -17.1	-	*
50	7.9	1588	-	88	-	81	<d.l.	521	* -16.1	-	*
80	8.0	1533	-	88	-	80	<d.l.	643	-	-	-
Beatenberg											
Aug 1999–Dec 2007											
0	4.4	758	-	101	-	88	2.00	146	* -7.4	-	*
15	3.8	800	-	101	-	101	16.9	31.4	** -2.6	-	**
50	4.1	747	-	101	-	101	35.5	28.4	-	-	-
80	4.2	721	-	101	-	100	36.1	33.9	* 0.84	-	-
Aug 2000–Dec 2007											
0	4.2	1075	-	89	-	78	2.00	110	-	-	-
15	3.8	1061	-	89	-	89	16.4	33.7	* -2.9	-	**
50	4.1	1043	-	89	-	89	37.1	28.4	-	-	-
80	4.3	1037	-	89	-	88	40.0	33.2	-	-	-
Alps											
Celerina											
Oct 1999–Dec 2007											
0	5.2	466	-	99	* -22.5	52	9.54	160	* 1.2	-	-
15	5.1	546	-	99	* -33.0	46	21.6	78.5	-	-	-
50	6.3	508	-	99	* -29.5	52	2.86	55.9	* -2.2	-	-
80	6.5	500	-	99	* -26.0	53	1.35	70.0	-	-	-
Oct 2000–Dec 2007											
0	5.0	989	-	87	-	47	9.55	134	* 1.2	-	-
15	5.2	981	-	87	-	39	19.0	64.9	-	-	-
50	6.4	917	-	87	-	44	3.33	49.7	-0.18	-	-
80	6.7	891	-	87	-	45	1.41	63.6	-	-	-
Southern Alps											
Novaggio											
Jan 2000–Dec 2007											
0	5.3	2368	-	96	-	93	4.62	176	* 0.83	-	-
15	4.5	2365	-	96	-	94	33.8	59.2	-	-	-
50	4.8	2263	-	96	-	93	14.4	37.1	-	-	-
80	5.0	2232	-	96	-	93	9.31	40.1	-	-	-
Jan 2001–Dec 2007											
0	4.9	1489	-	84	-	83	4.22	211	-	-	-
15	4.6	1500	-	84	-	82	26.6	38.5	-	-	-
50	4.8	1428	-	84	-	81	13.2	21.7	-	-	-
80	4.9	1397	-	84	-	81	10.0	26.2	-	-	-

Table 5 (continued)

Jura	Depth (cm)	BC/Al		NO ₃ -N + NH ₄ -N		SO ₄ -S		PMKT
		Starting value (mol l ⁻¹ /mol l ⁻¹)	Sen (mol l ⁻¹ /mol l ⁻¹)	Starting value (μmol l ⁻¹)	Sen (μmol l ⁻¹ a ⁻¹)	Starting value (μmol l ⁻¹)	Sen (μmol l ⁻¹ a ⁻¹)	
Betlachstock Aug 1999–Dec 2007	0	n.d.	–	368	–	73.0	–	–
	15	n.d.	–	101	–	70.8	–	–
	50	n.d.	–	100	–	46.3	–	–
	80	n.d.	–	66.7	–	41.6	–	–
Aug 2000–Dec 2007	0	n.d.	–	446	–	53.9	–	–
	15	n.d.	–	54.9	–	41.6	–	–
	50	n.d.	–	37.0	–	32.9	–	–
	80	n.d.	–	15.9	–	32.6	–	–
Swiss Plateau Lausanne Jan 1999–Dec 2007	0	99.5	–	330	–	28.4	–	–
	15	3.26	–	453	–	47.0	–	–
	50	7.20	–	263	–	58.7	–	–
	80	24.7	–	213	–	66.3	–	–
Jan 2000–Dec 2007	0	65.3	–	332	–	28.1	–	–
	15	3.03	–	382	–	44.5	–	–
	50	4.90	–	277	–	56.5	–	–
	80	20.5	–	243	–	62.9	–	–
Vordemwald Aug 1998–Dec 2007	0	3.41	–	127	–	29.9	–	–
	15	1.23	* –0.05	39.5	* –1.5	68.0	** –3.1	**
	50	3.58	* –0.04	4.61	** –0.27	125	*** –3.5	***
	80	28.3	–	6.97	** –0.46	129	*** –3.0	***
Aug 1999–Dec 2007	0	2.69	–	99.3	–	32.9	–	–
	15	1.22	* –0.04	21.1	* –1.5	61.1	** –2.6	**
	50	2.91	* –0.06	5.39	** –0.26	119	*** –3.4	***
	80	24.1	–	5.43	** –0.33	123	** –2.9	**
Pre-Alps Schânis Sept 1999–Dec 2007	0	n.d.	–	133	–	21.8	* –0.46	*
	15	n.d.	–	91.6	–	21.4	–	–
	50	n.d.	–	123	–	25.5	** –0.94	**
	80	n.d.	–	126	–	25.7	** –0.72	*

Table 5 (continued)

Depth (cm)	BC/Al		NO ₃ -N + NH ₄ -N		SO ₄ -S		PMKT
	Starting value (mol l ⁻¹ /mol l ⁻¹)	Sen (mol l ⁻¹ /mol l ⁻¹)	Starting value (μmol l ⁻¹)	Sen (μmol l ⁻¹ a ⁻¹)	Starting value (μmol l ⁻¹)	Sen (μmol l ⁻¹ a ⁻¹)	
Sept 2000–Dec 2007							
0	n.d.		114	–	18.1	–	*
15	n.d.		99.0	–	20.7	–	–
50	n.d.		66.4	–	19.8	*–0.69	*
80	n.d.		72.6	–	20.7	*–0.44	–
Beatenberg Aug 1999–Dec 2007							
0	71.6	*–3.7	115.4	–	14.0	*–0.61	*
15	1.90	**–0.15	8.00	–	8.60	**–0.61	**
50	0.80	–	5.37	*–0.32	13.8	**–0.57	**
80	0.94	–	3.16	–	19.2	*0.59	*
Aug 2000–Dec 2007							
0	62.4	–	41.3	–	7.8	–	–
15	2.08	*–0.15	5.51	–	5.2	**–0.60	**
50	0.77	–	3.10	*–0.14	10.7	*–0.43	*
80	0.83	–	2.02	–	16.7	*0.80	*
Alps Celerina Oct 1999–Dec 2007							
0	23.4	–	19.7	*–0.15	10.2	–	–
15	3.75	–	< d.l.	–	18.7	–	–
50	21.6	–	< d.l.	–	23.2	*–0.80	–
80	56.2	–	< d.l.	–	25.2	**–0.87	*
Oct 2000–Dec 2007							
0	18.0	–	8.80	–	12.4	–	–
15	3.44	–	< d.l.	–	8.90	–	–
50	15.1	–	< d.l.	–	19.3	–	–
80	45.9	–	< d.l.	–	23.4	*–0.68	–
Southern Alps Novaggio Jan 2000–Dec 2007							
0	39.5	*–2.86	246	–	38.9	–	–
15	1.72	–	74.5	–	31.3	*–1.14	–
50	2.62	–	33.1	–	40.7	*–0.88	–
80	4.55	–	21.9	–	47.0	*–1.46	–
Jan 2001–Dec 2007							
0	46.4	–	192	–	32.1	–	–
15	1.47	–	40	–	27.8	–	–
50	1.65	–	16.8	–	32.4	–	–
80	2.71	–	13	–	41.3	–	–

The trends were computed with seasonal Mann–Kendall Test. Starting value: sum or mean of the first year of measurement
n number of months used in the MKT, PMKT is the partial MKT performed with water fluxes as explanatory variable, – not significant ($p < 0.05$), < d.l. below detection limit, n.d. not determined
 *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$ is given for each variable to the left of the Sen's slope and for each PMKT to the right of the Sen's slope

Table 6 Annual trend indicated by Sen's slope for $p < 0.05$ in water fluxes (mm a^{-1}) and fluxes ($\text{kmolc ha}^{-1} \text{a}^{-1}$) of aluminum (Al), base cations (BC), inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) and sulfate ($\text{SO}_4\text{-S}$) in soil solution at four soil depths

	Depth (cm)	Number of months	Water flux			Al ³⁺			BC		
			Starting value (mm a^{-1})	Sen (mm a^{-1})	PMKT (mm a^{-1})	Starting value ($\text{kmolc ha}^{-1} \text{a}^{-1}$)	Sen ($\text{kmolc ha}^{-1} \text{a}^{-1}$)	PMKT ($\text{kmolc ha}^{-1} \text{a}^{-1}$)	Starting value ($\text{kmolc ha}^{-1} \text{a}^{-1}$)	Sen ($\text{kmolc ha}^{-1} \text{a}^{-1}$)	PMKT ($\text{kmolc ha}^{-1} \text{a}^{-1}$)
Jura											
Bettlachstock											
1999–2007	0	101	931	–	–	n.d.	–	–	–	–	–
	15	101	962	–	–	n.d.	–	–	–	–	–
	50	101	794	–	–	n.d.	–	–	–	–	–
	80	101	734	–	–	n.d.	–	–	–	–	*
2000–2007											
	0	89	1013	–	–	n.d.	–	–	–	–	–
	15	89	1056	–	–	n.d.	–	–	–	–	–
	50	89	865	–	–	n.d.	–	–	–	–	–
	80	89	810	–	–	n.d.	–	–	–	–	–
Swiss Plateau											
Lausanne											
1999–2007	0	108	1034	–	–	0.09	–	–	–	–	–
	15	108	1002	–	–	1.79	–	–	–	–	–
	50	108	882	–	–	0.56	–	–	–	–	–
	80	108	819	–	–	0.18	–	–	–	–	*
2000–2007											
	0	96	943	–	–	0.10	–	–	–	–	–
	15	96	924	–	–	1.32	–	–	–	–	–
	50	96	817	–	–	0.60	–	–	–	–	–
	80	96	767	–	–	0.21	–	–	–	–	–
Vordemwald											
1998–2007	0	113	818	–	–	1.04	–	–	–	–	**
	15	113	789	–	–	0.97	–	*	–	–	**
	50	113	598	–	–	0.52	–	–	–	–	*
	80	113	572	–	–	0.12	–	–	–	–	**
1999–2007											
	0	101	1102	–	–	0.89	–	–	–	–	**
	15	101	1073	–	–	0.63	–	*	–	–	*
	50	101	909	–	–	0.37	–	*	–	–	*
	80	101	869	–	–	0.09	–	–	–	–	*
Pre-Alps											
Schänis											
1999–2007	0	100	2001	–	–	n.d.	–	–	–	–	–
	15	100	1965	–	–	n.d.	–	–	–	–	–
	50	100	1895	–	–	n.d.	–	–	–	–	*
	80	100	1837	–	–	n.d.	–	–	–	–	–

Table 6 (continued)

	Depth (cm)	Number of months	Water flux		Al ³⁺		BC		PMKT	
			Starting value (mm a ⁻¹)	Sen (mm a ⁻¹)	Starting value (kmolc ha ⁻¹ a ⁻¹)	Sen (kmolc ha ⁻¹ a ⁻¹)	Starting value (kmolc ha ⁻¹ a ⁻¹)	Sen (kmolc ha ⁻¹ a ⁻¹)		
2000–2007	0	88	1648	–	n.d.	–	2.89	–	–	
	15	88	1654	–	n.d.	–	5.37	–	–	
	50	88	1588	–	n.d.	–	5.69	–	*	
	80	88	1533	–	n.d.	–	6.97	–	–	
Beatenberg 1999–2007	0	101	758	–	0.05	–	0.77	*	–0.048	
	15	101	800	–	0.41	–	0.25	**	–0.024	
	50	101	747	–	0.79	–	0.22	*	–0.016	
	80	101	721	–	0.79	–	0.24	–	–	
2000–2007	0	89	1075	–	0.05	–	0.78	–	–	
	15	89	1061	–	0.45	–	0.32	*	–0.024	
	50	89	1043	–	1.18	–	0.32	*	–0.015	
	80	89	1037	–	1.22	–	0.35	–	–	
Alps Celerina 1999–2007	0	99	466	* –22.5	0.15	–	0.50	–	–	
	15	99	546	* –33.0	0.35	* –0.018	0.32	*	–0.017	
	50	99	508	* –29.5	0.05	* –0.003	0.21	*	–0.011	
	80	99	500	* –26.0	0.02	–	0.25	*	–0.014	
	0	87	989	–	0.33	–	1.17	–	–	
	15	87	981	–	0.62	–	0.53	–	–	
	50	87	917	–	0.09	–	0.32	–	–	
	80	87	891	–	0.04	–	0.39	–	–	
	Southern Alps Novaggio 2000–2007	0	96	2368	–	0.22	–	2.02	–	–
		15	96	2365	–	2.33	–	1.03	*	–0.067
		50	96	2263	–	1.01	* –0.040	0.70	*	–0.046
		80	96	2232	–	0.66	–	0.73	–	–
0		84	1489	–	0.16	–	1.46	–	–	
15		84	1500	–	1.24	–	0.52	–	–	
2001–2007	50	84	1428	–	0.57	–	0.34	–	–	
	80	84	1397	–	0.43	–	0.38	–	–	

Table 6 (continued)

	Depth (cm)	NO ₃ -N + NH ₄ -N		SO ₄ S	
		Starting value (kmol _c ha ⁻¹ a ⁻¹)	Sen (kmol _c ha ⁻¹ a ⁻¹)	Starting value (kmol _c ha ⁻¹ a ⁻¹)	Sen (kmol _c ha ⁻¹ a ⁻¹)
Jura Betlachstock 1999–2007	0	2.94	–	0.87	* –0.044
	15	0.97	–	1.36	–
	50	0.65	* –0.036	0.71	–
	80	0.36	* –0.015	0.60	–
	0	3.37	–	0.85	* –0.036
	15	0.69	–	0.84	–
	50	0.42	–	0.60	–
	80	0.20	–	0.53	–
Swiss Plateau Lausanne 1999–2007	0	2.41	–	0.45	–
	15	4.55	–	0.91	–
	50	2.29	–	1.03	–
	80	1.68	–	1.10	–
	0	1.91	–	0.40	–
	15	2.92	–	0.86	–
	50	1.85	–	0.94	–
	80	1.65	–	0.99	–
Vorderwald 1998–2007	0	1.32	–	0.69	–
	15	0.50	* –0.013	1.42	–
	50	0.05	** –0.002	2.27	–
	80	0.07	* –0.004	2.23	–
	0	0.59	–	0.54	–
	15	0.17	–	0.94	–
	50	0.03	* –0.001	1.43	–
	80	0.03	–	1.42	–
Pre-Alps Schänis 1999–2007	0	2.02	–	0.69	–
	15	1.63	–	0.85	–
	50	1.89	–	0.94	* –0.050
	80	2.15	–	0.93	* –0.053
	0	–	–	–	–
	15	–	–	–	–
	50	–	–	–	–
	80	–	–	–	–

Table 6 (continued)

	Depth (cm)	NO ₃ -N + NH ₄ -N		SO ₄ -S	
		Starting value (kmol _c ha ⁻¹ a ⁻¹)	Sen (kmol _c ha ⁻¹ a ⁻¹)	Starting value (kmol _c ha ⁻¹ a ⁻¹)	Sen (kmol _c ha ⁻¹ a ⁻¹)
2000–2007	0	1.42	–	0.49	–
	15	1.32	–	0.64	–
	50	0.85	–	0.61	*
	80	1.01	–	0.63	–
Beatenberg 1999–2007	0	0.67	–	0.18	* –0.011
	15	0.07	–	0.14	** –0.007
	50	0.05	** –0.002	0.21	* –0.013
	80	0.04	–	0.28	–
2000–2007	0	0.32	–	0.13	–
	15	0.06	–	0.08	* –0.005
	50	0.04	* –0.002	0.20	* –0.012
	80	0.04	–	0.34	–
Alps Celerina 1999–2007	0	0.06	* –0.003	0.07	* –0.006
	15	n.d.	–	0.17	* –0.008
	50	n.d.	–	0.21	–
	80	n.d.	–	0.24	* –0.014
2000–2007	0	0.11	–	0.22	* –0.006
	15	n.d.	–	0.23	* –0.004
	50	n.d.	–	0.33	–
	80	n.d.	–	0.39	–
Southern Alps Novaggio 2000–2007	0	2.84	–	1.07	* –0.071
	15	1.29	–	1.48	–
	50	0.67	–	1.79	–
	80	0.44	–	2.12	–
2001–2007	0	1.85	–	0.84	–
	15	0.64	–	0.83	–
	50	0.25	–	0.92	–
	80	0.19	–	1.16	–

The trends were computed with seasonal Mann–Kendall Test. Starting value: sum or mean of the first year of measurement

n: number of months used in the MKT, PMKT is the partial MKT performed with water fluxes as explanatory variable, – not significant ($p < 0.05$), < *d.l.*: below detection limit, *n.d.*: not determined

*** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$ is given for each variable to the left of the Sen's slope and for each PMKT to the right of the Sen's slope

Significant decreasing trends in $\text{SO}_4\text{-S}$ concentrations were found at four sites (Beatenberg, Celerina, Schänis, and Vordemwald) at different soil depths. The trend found in Celerina was not significant anymore when the water flux was included as explanatory variable in the PMKT, suggesting that the decline was mainly caused by a dilution effect. Inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$) declined mostly in Vordemwald in the mineral horizons (15, 50, and 80 cm) and also in Beatenberg, but only at a depth of 50 cm. Element concentrations at the different soil depths remained stable in Lausanne and in Bettlachstock (Table 5).

Similarly to the trends in $\text{SO}_4\text{-S}$ concentrations, $\text{SO}_4\text{-S}$ fluxes significantly decreased in Beatenberg, Celerina, Schänis, Vordemwald, and Bettlachstock at different soil depths (Table 6). In Celerina, the PMKT indicated that the trends at the different soil depths were not significant anymore when the water fluxes were included in the test, suggesting that the variations of $\text{SO}_4\text{-S}$ fluxes were mainly caused by changes in water fluxes. $\text{SO}_4\text{-S}$ fluxes

leaving the root zone (80 cm) did not show any significant trend at any site except in Vordemwald where $\text{SO}_4\text{-S}$ decreased in the PMKT. Significant decreases in inorganic N fluxes were found in Vordemwald and in Beatenberg but the fluxes were very low ($<1 \text{ kg ha}^{-1} \text{ a}^{-1}$) due to the low N concentrations. BC fluxes decreased significantly in Beatenberg and in Vordemwald.

Mean $\text{SO}_4\text{-S}$ fluxes increased with soil depth at the seven sites (Table 6). Output $\text{SO}_4\text{-S}$ fluxes from the root zone (80 cm) exceeded throughfall input in Lausanne, Vordemwald and Novaggio or were similar in Schänis, Bettlachstock, Beatenberg, and Celerina. There was no significant trend in the difference between input and output (data not shown).

The output of inorganic N varied greatly from site to site. In Vordemwald, Beatenberg and Celerina, the output fluxes were negligible ($<1 \text{ kg ha}^{-1} \text{ a}^{-1}$), small ($2\text{--}6 \text{ kg ha}^{-1} \text{ a}^{-1}$) in Novaggio and Bettlachstock, and large ($>10 \text{ kg ha}^{-1} \text{ a}^{-1}$) in Schänis and Lausanne (Fig. 4).

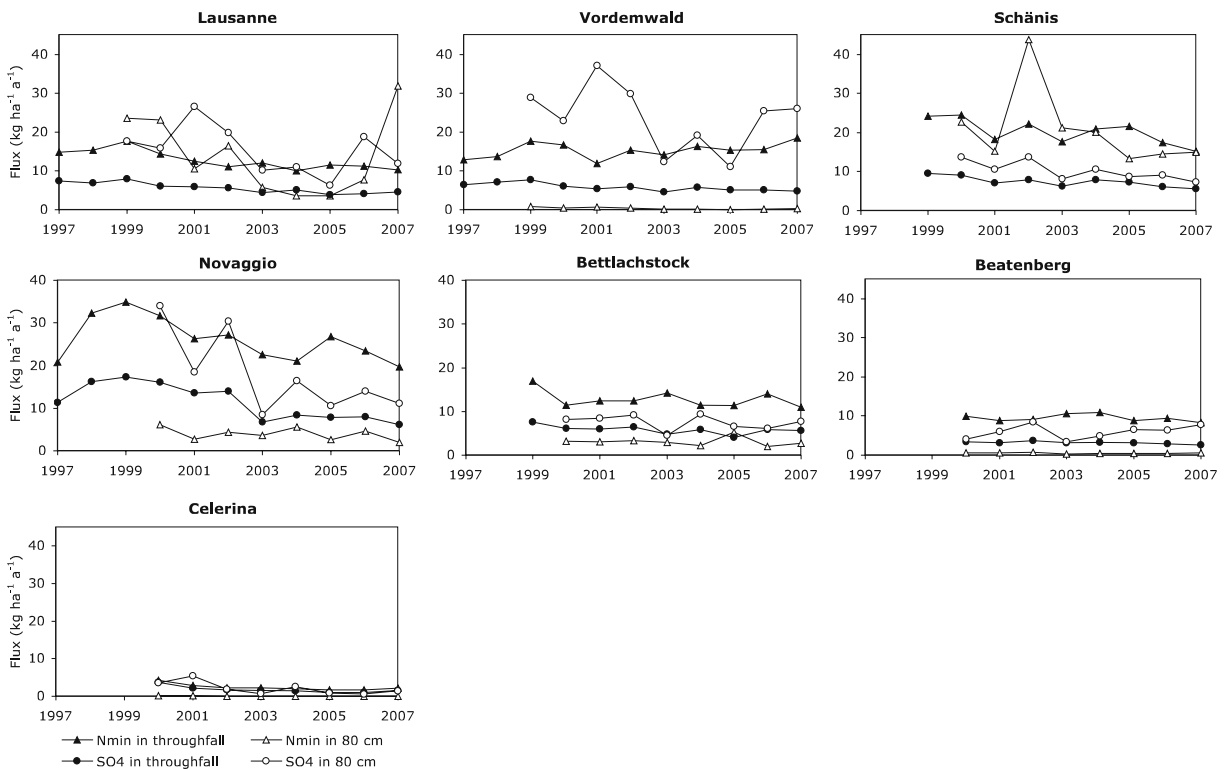


Fig. 4 Annual inorganic N and $\text{SO}_4\text{-S}$ fluxes ($\text{kg ha}^{-1} \text{ a}^{-1}$) in throughfall and in soil solution at a depth of 80 cm

The output fluxes were generally much lower than the input throughfall fluxes except in Lausanne and Schänis (Fig. 4). At these two sites, the difference between input and output varied considerably with time. The N release from the soil was in some years much larger than the input (e.g., 2007 in Lausanne, 2002 in Schänis), while in other years, it was much smaller (e.g., 2003–2005 in Lausanne). The large annual N flux in 2007 in Lausanne was due to high concentrations of $\text{NO}_3\text{-N}$ in July and August combined with large water fluxes. Similarly in Schänis, large $\text{NO}_3\text{-N}$ concentrations coupled to large water fluxes in the fall 2002 resulted in large annual N output. In Celerina, both input and output fluxes were low ($\leq 4 \text{ kg ha}^{-1} \text{ a}^{-1}$).

Discussion

Atmospheric acid deposition

The relatively high deposition loads of acidity (TDA) at Novaggio and Schänis are typical for areas at the foothills of mountain ranges in the proximity of industrialized or agricultural areas such as the Italian Po Plain and the Swiss Plateau (Waldner et al. 2007). These exposed areas are subjected to air pollutants as the plain regions but receive higher precipitation, resulting in higher acid deposition rates. In contrast, the load of acidity was low in Celerina, since it is located in an intra-alpine plain, remote from pollutant sources. The regional distribution of atmospheric S and N deposition at the study sites was already discussed in Thimonier et al. (2005) and Waldner et al. (2007). The highest loads found at the study sites (Novaggio and Schänis) were at the beginning of the observation period in the same range (Table 3) as those found in 1997 in the western and central part of Europe at the monitoring sites of ICP-Forests (Table 4 in De Vries et al. 2003). The atmospheric inputs of acidity estimated at the Swiss sites ($0\text{--}2 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$) were in the lower range of those ($0.2\text{--}4 \text{ kmol}_c \text{ ha}^{-1} \text{ a}^{-1}$) determined by De Vries et al. (2003).

A significant decrease in acid deposition (TDA) was found at only three out of nine study sites (Othmarsingen, Lausanne and Jussy). The

decline (about $-0.7 \text{ kmol}_c \text{ ha}^{-1}$ from 1998 to 2007) mainly resulted from a significant decrease in total N deposition (about $-0.55 \text{ kmol}_c \text{ ha}^{-1}$ or $-7.7 \text{ kg N ha}^{-1}$ from 1998 to 2007). A strong decrease in acid deposition was also found in Novaggio, but it was likely related to the variations in precipitation amount. At the five other sites, no decline in TDA could be found although total S deposition (TDS^*) significantly decreased. Since there was no trend in TDBC at most plots and TDN was larger than TDS^* , trends in acid deposition depended mainly on the development of N deposition. De Vries et al. (2003) also emphasized that N deposition in 1997 was higher than S deposition at a European wide scale. The S emissions and thereby S deposition had continuously declined over large parts of Europe since the mid-1990s, whereas NH_3 emissions mostly stayed constant or even increased. In Switzerland also, while S emission has continued to decrease after 1995, emission of nitrogen oxides and ammonia diminished in a less extent (FOEN 2009). This corresponds to the trends determined in our study. In a ten-year period (1998–2007), TDS^* decreased by $0.53 \text{ kmol}_c \text{ ha}^{-1}$ (7.4 kg ha^{-1}) in Novaggio in Southern Switzerland, between 0.14 and $0.25 \text{ kmol}_c \text{ ha}^{-1}$ ($2.0\text{--}3.5 \text{ kg ha}^{-1}$) on the Swiss Plateau, and $0.1 \text{ kmol}_c \text{ ha}^{-1}$ (1.4 kg ha^{-1}) at sites located in mountainous areas, remote from pollution sources (Beatenberg and Celerina). The different development of S and N deposition was also reported at two stations (Payerne and Dübendorf) of the Swiss National Air Pollution Monitoring Network (NABEL) where wet deposition has been measured since 1985 (FOEN 2009). The $\text{SO}_4\text{-S}$ load at the NABEL stations decreased from 8 to $2 \text{ kg S ha}^{-1} \text{ a}^{-1}$ with a strong decline between 1985 and 1997 and a slower one until 2008. In contrast to the decreasing trends in S deposition, wet deposition of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and base cations remained stable (FOEN 2009). Similarly, wet deposition of nitrogen at the Lägern near Zürich on the Swiss Plateau was about $9 \text{ kg ha}^{-1} \text{ a}^{-1}$ in the late 1980s (Klöti et al. 1989) and decreased only to $7 \text{ kg ha}^{-1} \text{ a}^{-1}$ in 2001 (Burkard et al. 2003). Measurements of wet deposition at 17 monitoring sites across the Alps in Italy, Austria, France, and Switzerland also showed a significant reduction of sulfate

concentrations at all sites, a slight decrease in nitrate, statistically significant only at a few sites, and a more widespread decline of ammonium (Rogora et al. 2006). In northern and central Europe, De Vries et al. (2003) also showed the larger decrease in S deposition compare to N at 53 plots from a comparison of annual N/S ratios in bulk deposition and throughfall in the early 1980s (Ivens 1990) and in the 1990s (Erisman and De Vries 1999). This illustrates the rather constant load of nitrogen for the last 20 years compared to the substantial decrease in $\text{SO}_4\text{-S}$, which caused N to be a dominating factor in the acidic input in large parts of Europe.

Because of the large numbers of tests in Tables 3 and 4 (about 100 tests), it is likely that five tests show a significance at $p < 0.05$ just by chance (type I error). However, the majority of the trends presented in both tables have lower p values (e.g. $p < 0.01$ or $p < 0.001$), which indicates that the trends are effective and not due to chance. Furthermore, significance levels of the negative trends found for S, N, and acid deposition seem to be related to the start of the measurement period. The earlier the time series started, the higher is the significance level. This is in line with the fact that the reduction of N and S emissions mainly occurred in the decade 1990 to 2000.

Trends in deposition might be caused by variations in precipitation amount and not by changes in emissions. Thimonier et al. (2005) showed that annual N and $\text{SO}_4\text{-S}$ deposition at the study sites positively correlated with the annual precipitation amounts at the regional level (plot-to-plot variation), as well as at the plot level (year-to-year variation for each plot). For this reason, the partial Mann–Kendall test (PMKT) represents a relevant test to detect the influence of precipitation variation on deposition trends (Libiseller and Grimvall 2002). The PMKT indicated that the N and $\text{SO}_4\text{-S}$ deposition trends in Schänis were probably caused by variations in precipitation amount, even though no significant trend ($p < 0.05$) was found in precipitation (Tables 3 and 4). These findings suggest that the observation period should be long enough (>10 years) to detect changes not caused by the precipitation amount, in particular at sites with high precipitation amount and large variability in precipitation.

The reductions in annual total deposition and throughfall chemistry presented in Tables 3 and 4 ranged on average between -30% and -50% of the values measured during the first year of observation. The changes were larger than the accuracy of $\pm 30\%$ recommended by the manual on deposition of ICP-Forests (UNECE 2009). However, some significant trends like the decrease in Mg and K in throughfall in Othmarsingen were smaller (-16% and -13% , respectively), showing the high accuracy of the throughfall analysis.

Soil solution

The most striking finding from the trend analysis of element concentrations and BC/Al ratios in the soil solution at the seven sites was the very small number of significant trends determined with the seasonal Mann–Kendall Test. This suggests that the soil solution was relatively little influenced by the recent changes in throughfall deposition or that the trends were too small to be detected. At the sites where the soil has a large capacity to neutralize acid deposition (Bettlachstock and Schänis), it is clear that no substantial changes were expected in the soil solution chemistry. Only the $\text{SO}_4\text{-S}$ fluxes below the litter layer responded to the decrease in $\text{SO}_4\text{-S}$ throughfall in Bettlachstock (Table 6). At sites located far from pollution sources like in Celerina and in Beatenberg, it can be also expected that the soil solution chemistry did not change much. Indeed BC/Al concentrations and fluxes in the soil solution in Celerina remained stable during the observation period (1999–2007), suggesting that acidification was very slow and not detectable within an 8-year period. The trends of element concentrations and fluxes detected by the seasonal Mann–Kendall Tests were mostly due to variations in precipitation amount (Tables 5 and 6). In Beatenberg, the decline in $\text{SO}_4\text{-S}$ concentrations and fluxes detected in the soil solution might have been caused by the decrease in S in throughfall. Similarly, the decrease in BC in the soil solution might result from the reduction in BC from throughfall during the observation period (Table 4). Since the BC concentrations in the soil solution between 15 and 80 cm of depth were in the same order of magnitude as those measured in throughfall,

the concentrations in the soil solution might have reacted very fast to variations in throughfall input. On the other hand, the upper soil in Beatenberg is characterized by a thick organic (Oe + Oa) horizon of 15 cm where the mineralization of the organic matter likely controls BC concentrations in the soil solution. Variations in meteorological conditions (soil temperature, precipitation) might, therefore, explain the decrease in BC concentrations. Changes in BC input from the early stage decomposition of the spruce litter seem unlikely. Based on a mean annual BC input of $7 \text{ kg ha}^{-1} \text{ a}^{-1}$ from litterfall (data not shown) and a decay constant k of 0.437 a^{-1} (Heim and Frey 2004) in Beatenberg, the estimated annual input of BC from litter decomposition would be quite small ($3 \text{ kg BC ha}^{-1} \text{ a}^{-1}$) compared to the throughfall input ($10\text{--}17 \text{ kg BC ha}^{-1} \text{ a}^{-1}$).

Acidification of soil solution was mainly expected in acid soils developed from acid substrate having received substantial atmospheric inputs of acidic compounds for decades like in Novaggio (Blaser et al. 1999). However, the seasonal Mann–Kendall test on BC/Al ratios between 2000 and 2007 did not indicate any significant trend in Novaggio, suggesting that acidification was very slow and not detectable within an 8-year period. This is in agreement with the observations at another site (Copera) in southern Switzerland between 1987 and 2003 where a marked decrease in BC/Al was reported until the end of the 1990s (Blaser et al. 1999), followed by a stabilization of the ratios (Graf Pannatier et al. 2005). These findings suggest that acidification of soil solution slowed down at the end of the 1990s, probably due to the substantial reduction in S emissions between 1985 and 1995. Concentrations and fluxes of nitrogen ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$), $\text{SO}_4\text{-S}$ and base cations (Tables 5 and 6) remained stable in Novaggio, indicating that the system was stable during the observation period. The negative trends in $\text{SO}_4\text{-S}$ concentration at different soils depths between 2000 and 2007 (Table 5) was probably not meaningful for the site, since it disappeared when the first year of measurement was removed. In addition, since variations in precipitation and water fluxes influenced concentrations and fluxes in the soil solution as indicated by the partial Mann–Kendall Tests, a longer time series would

be necessary to detect changes not related to water fluxes. The increase in Al concentration observed below the litter layer (0 cm) probably resulted from the deposition of eroded mineral material or directly from the erosion of the litter layer. The site is located on a steep slope (68%) in a region characterized by intense precipitation, which sporadically leads to erosion of soil surface.

No trend in soil solution chemistry could be found in Lausanne, although acid deposition (TDA) and input in throughfall (N and $\text{SO}_4\text{-S}$) declined. The lack of reaction was probably due to active internal soil processes (e.g. fast decomposition of litter) that masked the changes in atmospheric deposition at the time scale of the observation period (9 years). In addition, the BC, Al, and NO_3 concentrations in the soil solution in Lausanne were characterized by a high variability, exceeding the variations in atmospheric deposition. In contrast to Lausanne, element concentrations and BC/Al ratios in Vordemwald significantly decreased, while acid deposition remained constant. While the decrease in base cations, nitrate, and sulfate in the soil solution would indicate a recovery because of the resulting increase in the acid neutralizing capacity (data not shown, Fölster et al. 2003), the preferential loss of base cations compared to Al suggests that the acidification of soil solution was proceeding quite fast in Vordemwald. This is in agreement with the observations of Boxman et al. (2008) in a Scots pine forest in the Netherlands. Although these authors found a decreasing leaching of nitrate and sulfate at a soil depth of 90 cm due to the reduction in nitrogen and sulfur deposition, they also reported a continuing acidification marked by a pH decrease in the upper soil. The reasons for the decline in concentrations and the stronger decrease in base cations compared to Al in Vordemwald are not completely clear. Aggradation and accumulation of nutrients (e.g. BC, N) in the humus layer (Oe horizon) in this vigorous growing stand (mean age of 100 years for *Abies alba*) might explain the decrease in BC and N concentrations, but no observations could confirm this hypothesis. Like in Beatenberg, the fact that Al concentrations decreased less than BC was probably due to the high proportion of exchangeable Al cations in these low base

saturation soils (Table 2). Speciation of dissolved aluminum into mononuclear inorganic and organic Al species could give some insight into possible changes in the fractions of Al species with time. Aluminum was fractionated at the beginning of the monitoring period only. It showed that Al was partly complexed to dissolved organic matter in Vordemwald and Beatenberg (Graf Pannatier et al. 2004). The modeling of Al species during the whole observation period with a chemical equilibrium model for waters could provide us some indications about possible changes in Al species with time.

The increasing $\text{SO}_4\text{-S}$ fluxes with soil depth in Vordemwald (Table 6) and the large release of $\text{SO}_4\text{-S}$ below the root zone ($24 \text{ kg ha}^{-1} \text{ a}^{-1}$ on average) compared to the throughfall input ($6 \text{ kg ha}^{-1} \text{ a}^{-1}$ on average) indicate an internal source of sulfate, particularly at 50 and 80 cm of depth. As stated in e.g. Prechtel et al. (2001) and in the review of Sokolova and Alekseeva (2008), the net release of sulfate might be caused by four major processes (1) desorption of sulfate, (2) oxidation of reduced S species, (3) excess mineralization of organically bound S, and (4) weathering of S-containing minerals. A mineralogical study of the soil profile in Vordemwald showed that the soil fraction between $63 \mu\text{m}$ and 2 mm contained up to 9% hydroxides (data not shown). Desorption of sulfate from Al and Fe hydroxides, stored during earlier periods of higher S deposition, might have occurred. This process was reported in many studies in Europe and was shown to retard recovery of water acidification in response to the declining sulfate deposition (e.g. Alewell et al. 2000a). Reduction and oxidation of stored sulfur in the temporarily waterlogged soil in Vordemwald might have occurred, but no relationship could be found between sulfate fluxes and matric potential data (data not shown).

Input–output budget

The input–output budget showed that the decrease in $\text{SO}_4\text{-S}$ throughfall was not reflected in the output at 80 cm of depth at most plots (Table 6 and Fig. 4). This lack of response was often reported in studies throughout Europe and was assigned to desorption of previously stored sulfate

(e.g., Alewell et al. 2000b; Neiryneck et al. 2002; Fölster et al. 2003). It is clear from our data that the soil represented a source of sulfate with $\text{SO}_4\text{-S}$ output exceeding input at all plots. Sites located in regions with a long history of S deposition such as on the Swiss Plateau (Lausanne, Vordemwald) and in Southern Switzerland (Novaggio) showed output much larger than input, suggesting that a large amount of S was stored in the soil.

The N budget differed at the seven study sites. Thimonier et al. (2010a) showed that the C/N ratio of the soil organic layer, the humus type (e.g. mull, moder) and the pool of organic carbon in the soil played a critical role for nitrate leaching at these sites. The importance of the N status of the soil is illustrated in Schänis and Novaggio, both sites having received large N deposition ($>25 \text{ kg ha}^{-1} \text{ a}^{-1}$). Little nitrate leaching ($4 \text{ kg ha}^{-1} \text{ a}^{-1}$ on average between 2000 and 2007) was recorded at Novaggio, characterized by a C/N ratio of 24 in the organic layer, a moder humus type, and large organic C stock. In contrast, the mull-type forest floor in Schänis with a C/N ratio of 11 in the upper 5 cm of the mineral horizon was prone to large nitrate leaching ($21 \text{ kg ha}^{-1} \text{ a}^{-1}$ on average between 2000 and 2007). However, the differences between the annual N output fluxes were substantial between the years in Schänis and Lausanne (Fig. 4). During the period 2003–2005, the annual N, S, and BC output fluxes in Lausanne were lower than the fluxes in the other years because of lower precipitation amount. The concern of increased risk of soil acidification in forest soils after extended periods of summer drought like in summer 2003 (Lamersdorf et al. 1998) was not confirmed by our data. The dry years in Lausanne did not affect the long-term trend of BC/Al ratios at a depth of 15 cm (Fig. 3). In contrast, the large N output in the wet year 2007, coupled to a large BC loss, resulted in an increase in acidification as evidenced by the consistent decrease in BC/Al ratios at a depth of 80 cm (Fig. 3).

Conclusions

The trend analysis of atmospheric deposition (from 1995 or later until 2007) at nine sites and soil solution (from 1999 or 2000 until 2007) at

seven sites throughout Switzerland showed the following results:

- Reduction of total S deposition (TDS*) was observed at the nine sites; in a 10-year period, the decline in TDS* ranged between 1.4 to 7.4 kg ha⁻¹, which corresponds to a decrease of 30–50% at most plots. However, acid deposition (TDA) decreased at three sites only on the Swiss Plateau, mainly due to a decrease in TDN. TDBC* remained mostly stable. The partial Mann–Kendall Tests indicated that trends in deposition might result from variations in precipitation, especially at sites with high precipitation amount and large variability in precipitation like in Novaggio and in Schänis.
- The soil solution reacted very little to the changes in atmospheric deposition. At five out of the seven study sites, the concentrations and fluxes of BC, SO₄-S, and inorganic N remained stable at most soil depths during the observation period. Even in acid soils like in Novaggio that received substantial atmospheric inputs of acidic compounds for decades, the BC/Al ratios remained stable, suggesting that acidification was proceeding very slowly (not detectable at this time scale). A stronger reduction in base cations compared to aluminum was detected at two sites, which might indicate that acidification of the soil solution was proceeding faster at these sites.
- The decrease in element concentrations and fluxes in the soil solution in Vordemwald, which could mean a slowing down of acidification since less BC are lost from the soil, was actually coupled to a decrease in BC/Al, suggesting that acidification was actually proceeding rapidly at the site.

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