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An Overview of Atmospheric Deposition Chemistry over the Alps: Present Status and Long-term Trends — Source link

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An overview of atmospheric deposition chemistry over the Alps: present status and long-term trends

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Abstract

Several research programs monitoring atmospheric deposition have been launched in the Alpine countries in the last few decades. This paper uses data from previous and ongoing projects to: (i) investigate geographical variability in wet deposition chemistry over the Alps; (ii) assess temporal trends of the major chemical variables in response to changes in the atmospheric emission of pollutants; (iii) discuss the potential relationship between the status of atmospheric deposition and its effects on forest ecosystems in the alpine and subalpine area, focusing particularly on nitrogen input. We also present results of studies performed at a local level on specific topics such as long-term changes in lead deposition and the role of occult deposition in total nitrogen input. The analysis performed here highlights the marked geographical variability of atmospheric deposition in the Alpine region. Apart from some evidence of geographically limited effects, due to local sources, no obvious gradients were identified in the major ion deposition. The highest ionic loads were recorded in areas in the foothills of the Alps, such as the pre-alpine area in North-Western Italy and the area of Canton Ticino, Switzerland. Trend analysis shows a widespread decrease in the acidity of precipitation in the last 15–20 years as a consequence of the reduced emission of S compounds. On the other hand, nitrate concentrations in rain have not changed so much, and ammonium has decreased significantly only at the Austrian sampling sites. The deposition of N is still well above the estimated critical loads of nutrient N at some forest sites in the alpine and subalpine areas, thus confirming the critical situation of both terrestrial and aquatic ecosystems regarding N inputs. Existing data highlights the importance of continuously monitoring atmospheric deposition chemistry in the Alpine area, taking account of acidifying elements, nutrients and other pollutants such as heavy metals and organic compounds. There is also a need for unifying sampling and analytical methods in order to obtain comparable data from the different regions of the Alps.

Introduction

Water resources play an important role in the alpine and subalpine areas of Europe. Rivers and lakes in the Alps constitute an essential source of water for wide areas of Europe. Discharge from the Alps is of major quantitative importance for many rivers, such as the Rhine, Rhone, Inn and Po.

The Convention for the Protection of the Alps, signed in 1991 by the EU and by the countries which have territory in the Alps (Germany, France, Liechtenstein, Italy, Monaco, Austria, Switzerland and Slovenia) contains an explicit demand for healthy water systems to be preserved or restored. From the chemical point of view, the quality of water resources in the Alps is closely related to atmospheric deposition and hence to the composition of the atmosphere in the areas where the air masses originate. An example is the Po Plain in Northern Italy, one of the most densely populated and industrialised regions in Europe, from which air masses move towards the subalpine and alpine areas, where most of the precipitation occurs (Mosello et al., 2001).

Precipitation is not only a source of water for a number of uses such as drinking, irrigation in agriculture, hydroelectric power plants and industrial processes, but is also a vehicle conveying several chemical compounds to terrestrial and aquatic ecosystems. Both natural and anthropogenic substances can be transported many hundreds of kilometres from source regions before being deposited onto surfaces in dry or wet form. They can affect ecosystems by promoting acidification of soil and water (Reuss & Johnson, 1985; Schindler, 1988), nitrogen enrichment and nutrient imbalances in terrestrial and aquatic ecosystems (Matson et al., 2002; Rabalais, 2002), and eutrophication of N limited water bodies like coastal waters (Paerl & Whitall, 1999).

In remote high-altitude areas of the Alps, rain and snow may be the main source of solutes and nutrients for aquatic ecosystems. A number of studies on high-altitude lakes in the Alps have shown how water chemistry in areas characterised by low-weathering rocks is highly dependent on atmospheric inputs (Psenner, 1989; Marchetto et al., 1995).

Alpine lakes and streams are also increasingly threatened by anthropogenic influences such as the atmospheric deposition of acidifying compounds, organic chemicals and heavy metals. During the winter season, pollutants accumulate in the seasonal snow pack, and are released at high concentrations within a short period, when the snow pack melts in spring. It is well-known that low-volatile pollutants such as PCBs, DDT and their degradation products are transported for long distances around the globe and then accumulate in cold regions of low altitude or at high-altitude sites in the Alps (Grimalt et al., 2001; Carrera et al., 2002).

Dry and wet deposition of pollutants also impacts on forest ecosystems. Investigations on forest decline have been carried out throughout Europe in the last two decades. Acid rain has been identified as one of the major stress factors for forest ecosystems, but it is now recognised that a number of atmospheric pollutants and environmental factors interact to determine forest condition (Kandler & Innes, 1995; Van Leeuwen et al., 2000). Cloud and fog deposition must also be taken into account when evaluating the pollutant fluxes to forest ecosystems. Vegetation may efficiently intercept cloud and fog droplets (Fowler et al., 1991). Cloud droplets usually contain higher concentrations of pollutants than are found in rain and cloud water deposition might be an important input mechanism for pollutants, especially at high elevation sites (Lovett & Kinsman, 1990; Miller et al., 1993).

A further threat to both terrestrial and aquatic ecosystems is the atmospheric input of N compounds in excess of their retention capacity. It is widely known that N can act as a fertiliser for forest ecosystems, enhancing forest growth. On the other hand, high N loads can determine nutrient imbalances, changes in the composition of ground vegetation, and increased sensitivity to other stress factors (de Vries et al., 2000; Van Leeuwen et al., 2000). In areas affected by high N deposition (usually above 10 kg N ha^{-1} y^{-1}) there is increasing evidence of N saturation, a status which is reached when the availability of inorganic N is in excess of the nutritional demand by plants and microorganisms (Aber et al., 1989). Under such conditions, the ecosystem can no longer retain all the incoming N, which is leached below the rooting zone and may reach surface water determining an increase in nitrate concentrations (Dise & Wright, 1995; Wright et al., 2001).

The continental scale of the problems related to acidification and the deposition of air pollutants prompted the establishment of the Convention on Long Range Transboundary Air Pollution (CLRTAP) under the auspices of the United Nations Economic Commission for Europe (UN-ECE) (UN-ECE, 1996a). The Convention came into effect in 1983 and was subsequently extended by eight specific protocols. Most of the CLRTAP agreements were based on the application of the critical load concept (Nillson & Grennfelt, 1988). This approach couples regional scale emission transport and deposition with the sensitivity of ecosystems, and has led to the identification of some key areas where critical loads (CLs) were greatly exceeded by atmospheric inputs.

To tackle environmental problems such as the deposition of air pollutants and its effects on ecosystems, a number of research programs for monitoring atmospheric deposition have been launched in the Alpine countries in the last few decades. Data from previous and ongoing projects were synthesised in this paper with the following aims: (i) to evaluate spatial variations in the chemistry of atmospheric deposition over the Alps; (ii) to assess temporal trends of wet deposition chemistry in relation to changes occurring in the atmospheric emission of pollutants in the last few decades; (iii) to discuss the potential relationship between the status of atmospheric deposition and its effects on ecosystems in the alpine and subalpine area, focusing particularly on nitrogen input. Another objective was to point out the main gaps existing in the research on the ecological role of atmospheric deposition in the Alpine area, with a view to identifying a possible strategy for a common research policy.

Data and methods

Study sites and research programs

Atmospheric deposition data from 51 sampling sites were used in this study (Table 1). They are all located in the alpine and subalpine areas of Italy, Switzerland, Austria and France (Fig. 1) and run by different institutions in the framework of national or international research projects (Table 1). Most of the deposition data are from national networks monitoring the chemistry of atmospheric deposition in the long-term, with particular attention towards acidity and acidifying compounds. Some of these sites are part of the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe (EMEP). In addition, data from national projects focusing on specific topics (e.g. nutrient cycling, heavy metals, occult deposition) were included.

To monitor the atmospheric deposition onto forests, national programmes in many European countries sample bulk and throughfall deposition as part of the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) (UN ECE, 1998), established under the terms of the CLRTAP. This study uses data from stations in the Alps run by the national programmes of the ICP Forests network of Italy, Switzerland and France.

Information on the importance of occult deposition (cloud water interception) was gained by considering data of wet precipitation, cloud water, reactive gases and particulate matter collected at different elevation levels at the Achenkirch site, Austria. Furthermore, lead deposition data collated during two 1-year field campaigns (November 1995 to October 1996, October 1997 to September 1998) at three sites in Salzburg, Austria, are presented. These sites belong to the WADOS network (Kalina et al., 1997, 1999), and are located along a North to South transect (Fig. 1), with NUD (rural site north of the city of Salzburg, 520 m a.s.l.), WER (inneralpine valley, 940 m a.s.l.) and SON (high alpine site in the Hohen Tauern, 3106 m a.s.l.).

For details on sampling site characteristics, research programme, institutions and laboratories involved see the references provided in Table 1.

Sampling and analytical methods

Different sampling techniques were used at the sites considered in this paper (Table 1). Wet-only collectors are used at most of the sites (Fig. 1). Because wet-only samplers are usually expensive and need a power source which is not always

Table 1. Main characteristics of the atmospheric deposition sampling sites

Sampling site	Acronym	Region	Country	Typology	Latitude	Longitude	Altitude, m a.s.l.	Precipitation, mm	Collector type	Sampling period	Research program	Run by	Reference for sampling and analytical methods
Pallanza	PAL	Piedmont	I	Pre-alpine small town	45.92	8.57	208	1889	Bulk, wet-only	1975–2002	CNR ISE Project	CNR ISE	Tartari & Mosello (1997)
Domodossola	DOM	Piedmont	I	Pre-alpine small town	46.11	8.29	270	1483	Wet-only	1980–2002			
Graniga	GRA	Piedmont	I	Alpine rural	46.13	8.19	1080	1833	Wet-only	1994–2002			
Devero	DEV	Piedmont	I	Alpine rural	46.32	8.26	1634	1915	Wet-only	1996–2002			
Lunecco	LUN	Piedmont	I	Pre-alpine rural	46.07	8.61	415	2334	Wet-only	1989–2002			
Orta	ORT	Piedmont	I	Pre-alpine rural	45.80	8.40	360	1670	Bulk, wet-only	1984–2002			
Tarvisio	FRI2	Friuli	I	Alpine forest	46.49	13.59	820	1500	Bulk, throughfall, wet-only	1998–2002	CONECOFOR	CNR ISE	Tartari & Mosello (1997)
Val Sessera	PIE1	Piedmont	I	Alpine forest	45.68	8.07	1150	1500	Bulk, throughfall, wet-only	1998–2002			
Passo Lavazè	TRE1	Trentino	I	Alpine forest	46.36	11.50	1800	800	Bulk, throughfall	1998–2002			
Val Masino	LOM1	Lombardy	I	Alpine forest	46.24	9.55	1190	1300	Bulk, throughfall, wet-only	1998–2002	CONECOFOR	CNR IRSA	Balestrini et al. (2002)
Giovetto	LOM2	Lombardy	I	Alpine forest	45.57	10.07	1150	1350	Bulk, throughfall	2000–2003			
Val Penscei	LOM3	Lombardy	I	Alpine forest	45.54	9.30	1250	1500	Bulk, throughfall	2000–2003			
Renon/Ritten	BOL1	South Tyrol	I	Alpine forest	46.58	11.43	1780	970	Bulk, throughfall, wet-only	1998–2002	CONECOFOR	APPA Bolzano	Marchetti et al. (2002)
Beatenberg	BEA	Lower Alps	CH	Subalpine forest	46.72	7.77	1511	1370	Bulk, throughfall	2000–2001	LWF	WSL	Cherubini & Innes (2000), Thimonier et al. (2005)
Schänis	SCH	Lower Alps	CH	Subalpine forest	47.17	9.07	733	2280	Bulk, throughfall	1999–2001			
Celerina	CEL	Alps	CH	Alpine forest	46.50	9.88	1871	957	Bulk, throughfall	1999–2001			
Nationalpark	NAT	Alps	CH	Alpine forest	46.67	10.23	1899	1058	bulk, throughfall	1999–2001			
Chironico	CHI	Southern Alps	CH	Alpine forest	46.45	8.82	1365	1865	Bulk	2001			
Novaggio	NOV	Southern Alps	CH	Subalpine forest	46.02	8.83	950	2092	bulk, throughfall	1997–2001			
Alptal	ALP	Lower Alps	CH	Subalpine forest	47.05	8.72	1160	2088	bulk, throughfall	1997–1998			
Erlenbach/Zwäcken	ERL	Lower Alps	CH	Subalpine rural	47.05	8.72	1210	1990	bulk	1976–2001	HYDRO	WSL/FH	Keller et al. (1989), Klöti et al. (1989)
Locarno	LOC	Canton Ticino	CH	Pre-alpine small town	46.17	8.79	380	1725	wet-only	1988–2002	SAEFL/TI	UPDA-SPAAS	Barbieri & Pozzi (2001)
Lugano	LUG	Canton Ticino	CH	Pre-alpine small town	46.01	8.94	350	1382	Wet-only	1989–2002			
Piotta	PIO	Canton Ticino	CH	Pre-alpine rural	46.51	8.68	1007	1389	Wet-only	1990–2002			
Acquarossa	ACQ	Canton Ticino	CH	Pre-alpine rural	46.41	8.93	575	1267	Wet-only	1990–2002			
Stabio	STA	Canton Ticino	CH	Pre-alpine rural	45.85	8.93	353	1425	Wet-only	1990–2002			

Robiei	ROB	Canton Ticino	CH	Alpine rural	46.44	8.51	1890	2421	Wet-only	1997–2002			
Bré	BRE	Canton Ticino	CH	Pre-alpine small town	46.01	8.99	925	1553	Wet-only	1997–2002			
Dübendorf	DUB	Lowland	CH	Subalpine rural/urban	47.40	8.60	430	1014	Wet-only	1985–2002	NABEL, EMEP	SAEFL	Leutert (2001)
Chaumont	CHA	Jura	CH	Alpine rural	47.05	6.97	1140	1138	Wet-only	1997–2002			
Payerne	PAY	Lowland	CH	Subalpine rural/urban	46.80	6.93	490	780	Wet-only	1985–2002			
Magadino	MAG	South of Alps	CH	Subalpine rural/urban	46.15	8.93	200	2216	Wet-only	2000–2002			
Tänikon	TAN	Lowland	CH	Subalpine rural/urban	47.47	8.90	540	1293	Wet-only	1997–1999			
Rigi-Seebodenalp	RIG	Subalpine	CH	Subalpine rural/urban	47.07	8.45	1030	960	Wet-only	1997–2002			
Reutte	REU	Tyrol	A	Alpine valley, rural	47.49	10.68	930	1458	Wet-only	11/83–09/02	WADOS network	LG-IAC	Kalina & Puxbaum (1995)
Kufstein	KUF	Tyrol	A	Alpine, rural	47.66	12.23	680	1245	Wet-only	11/83–09/02			
Innervillgraten	INN	Tyrol	A	Inneralpine, rural	46.82	12.35	1730	758	Wet-only	08/84–09/02			
Nußdorf/Haunsberg	NUD	Salzburg	A	Prealpine, rural	47.96	13.02	520	1014	Wet-only	10/83–09/02			
Werfenweng	WER	Salzburg	A	Inneralpine, rural	47.42	13.25	940	909	Wet-only	10/83–09/02			
Sonnblick	SON	Salzburg	A	High alpine mountain	47.05	12.96	3106	1628	Wet-only	10/87–09/02			
Naßwald	NAW	Lower Austria	A	Prealpine, small town	47.77	15.71	600	1041	Wet-only	05/88–09/02			
Lunz	LUZ	Lower Austria	A	Prealpine, small town	47.86	15.07	618	1600	Wet-only	04/90–09/02			
Naßfeld	NAF	Carinthia	A	Alpine, forest	46.56	13.28	1530	1959	Wet-only	11/89–09/98			
Masenberg	MAS	Styria	A	Prealpine, forest	47.35	15.88	1137	775	Wet-only	03/90–09/02			
Hochgößnitz	HOC	Styria	A	Prealpine, forest	47.06	15.02	900	756	Wet-only	03/90–09/02			
Grundlsee	GRU	Styria	A	Alpine, forest	47.63	13.80	954	1021	Wet-only	03/90–09/02			
Stolzalpe	STO	Styria	A	Alpine, forest	47.13	14.20	1302	672	Wet-only	12/91–04/97			
F.D. de Voirons	EPC74	Rhône-Alpes	F	Pre-alpine rural	46.22	6.35	1200	1389	Bulk, throughfall	1993–2002	CATAENAT network	ONF	Ulrich *et al.* (2002), ONF (1996)
F.D. de Boscodon	SP05	Provence-Alpes-Côtes d'Azur	F	Alpine forest	44.50	6.46	1360	1007	Bulk, throughfall	1993–2002			
F.D. de Ban	SP25	Franche-Comté	F	Pre-alpine rural	46.97	6.45	1000	1601	Bulk, throughfall, wet-only	1993–2002			
F.D. de Saint-Hugon	SP38	Rhône-Alpes	F	Alpine forest	45.42	6.13	1100	1449	Bulk, throughfall	1993–2002			

CNR ISE Institute of the Ecosystem Study, Verbania Pallanza (I). UPDA-SPAAS Cantonal Agency for Water Protection (CH). SAEFL Swiss Agency for the Environment, Forest and Landscape (CH). CNR IRSA Water Research Institute, Brugherio (I). APPA Agenzia per la Protezione dell'Ambiente, Bolzano (I). WSL Swiss Federal Research Institute for Forest, Snow and Landscape, Birmensdorf (CH). CFO Cantonal Forest Office (CH). LG-IAC Co-Operation between Local Government and Institute for Analytical Chemistry, Vienna University of Technology (A). ONF National Forest Board, Fontainebleau (F). CONECOFOR National Programme for Forest Ecosystem Control. LWF Swiss Long-Term Forest Ecosystem Research. HYDRO WSL-Project Nutrient Balance of Small Subalpine Catchments. FH Forest Hydrology. NABEL National Air Pollution Monitoring Network (CH). EMEP Co-Operative Programme for monitoring and Evaluation of the long-range transmission of air pollutants in Europe. WADOS Austrian wet-only precipitation network. CATANAT Charge Acide Totale d'origine Atmosphérique dans les Écosystèmes Naturels Terrestres.

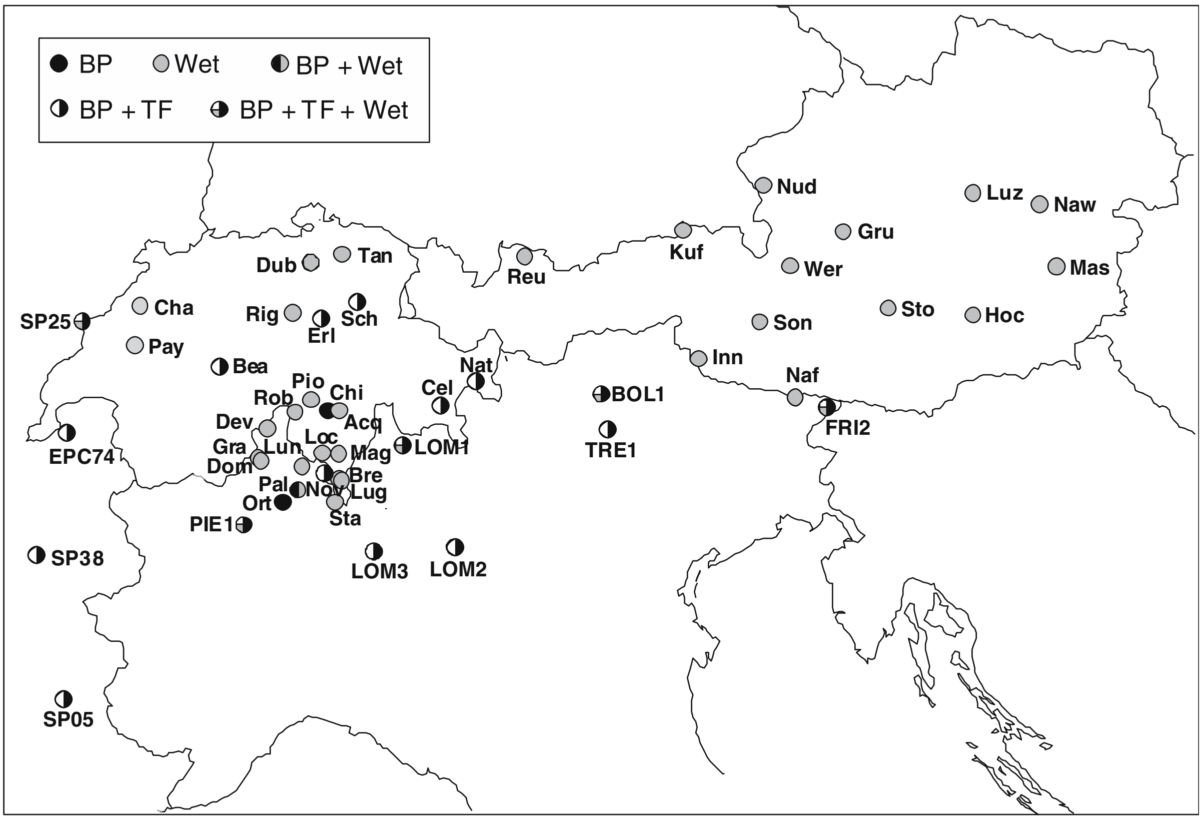

Figure 1. Location of the atmospheric deposition sampling stations in the Alpine area. Acronyms as in Table 1.

available, bulk collectors are often used to collect precipitation samples. The contribution of dry to bulk deposition can vary considerably, according to (i) local gas and aerosol concentrations in the atmosphere, (ii) local dust sources, (iii) turbulence processes and (iv) the collection efficiency of the samplers (Draajiers & Erisman, 1995). The dry deposition in forests is usually substantially higher than that of a bulk sampler, due to the roughness of the canopy, the large foliage surfaces and the physiological and chemical properties of the foliage. In forests, part of the dry deposition and the occult deposition (by fog or clouds) is washed from the foliage during rain events and is collected, together with the wet deposition, as throughfall below the canopy. However, some elements may be taken up (e.g. nitrogen) or leached (e.g. base cations) in the canopy. To take these exchanges into account, we applied a canopy budget model, as described in EC-UN/ECE (2001), to the bulk and throughfall deposition data, to obtain estimates of the total deposition (wet + dry deposition).

Representative measurements for the whole study site are usually obtained by using at least 10 funnels for throughfall within each forest plot, with 2–3 bulk collectors located in the open area. Samples are then mixed to form composite samples of throughfall and bulk precipitation (ICP-Forests, 1994; Thimonier et al., 2005; Mosello et al., 2002a).

During the Achenkirch project (Kalina et al., 1998, 2002), nitrogen concentrations were measured in wet precipitation and in cloud water (ammonium and nitrate) on a daily basis, in the gas phase (ammonia, nitric acid and nitrogen dioxide) and in aerosol (particulate ammonium and particulate nitrate) at biweekly intervals. The total deposition of nitrogen was calculated by combining measured concentrations in wet, dry and occult depositions with the corresponding deposition fluxes. Two multilayer deposition models were used for the calculation of dry and occult deposition (Kalina et al., 1998, 2002).

All the data used here were previously checked and validated in the framework of the different research programs. Moreover, all the laboratories participating in monitoring programs regularly perform analytical quality controls after each set of analyses. These controls are based on the ionic balance and on the comparison between measured and calculated conductivity (Mosello et al., 1998). In most cases the analysis of certified standards and the participation in international intercomparison exercises (e.g. Mosello et al., 1998, 2002b) provided a further check of the analytical quality of the data.

Information on sampling methods employed, and the time period covered by available data at the various sites, is given in Table 1.

Data analysis

Statistical analysis

Statistical analyses were performed with STATISTICA for Windows (StatSoft). All variables were log transformed before analysis. A principal component analysis (PCA) was applied to wet-only chemical data, available for 31 sites, to identify the main factors explaining chemical variability. The main groups of sites according to the rain chemistry were then identified through a Cluster Analysis (Ward's method, Euclidean distance between cases). To minimise the influence of interannual variability, the volume-weighted mean values for a 5-year period (1998–2002) were used in both analyses.

The relation of the chemistry of wet precipitation to geographical attributes (altitude, longitude and latitude) was investigated by means of the Pearson product–moment correlation.

The deposition maps of the major pollutants were created with the Software SURFER (Golden Software), version 7.0. Fluxes were calculated as the product of volume-weighted mean concentrations and precipitation amount at each site. Wet-only data (mean values of the period 1998–2002) were used to assure the comparability of the data collected in different areas.

Differences between deposition collected with bulk open field (BP) samplers and under the crown of vegetation (throughfall, TF) were tested using the non-parametric sign test. Alkalinity was excluded from the analysis because it was not measured at all sites.

Temporal trends in precipitation chemistry were tested with the Seasonal Kendall Test (SKT) (Hirsch et al., 1982) applied to monthly data. Trend analysis was performed with SKT at selected sites for the period 1990–2001 (1993–2001 for three sites in the French Alps). For sites with data series dating back to before 1985, trends were analysed for both periods: 1985–2001 and 1990–2001. SKT is a refinement of the Mann–Kendall Test, a non-parametric method of trend analysis which is robust with regard to non-normality, missing or censored data (Evans et al., 2001). SKT is also robust with respect to seasonality in time series, whereby data are first grouped into either monthly or quarterly mean values (Hirsch et al., 1982). Both methods can detect only monotonic trends within time series (Evans et al., 2001). Trend slopes were calculated according to Sen (1968) as the median of between-year differences in values within each seasonal block.

Critical load and N budget calculation

At all sites CLs were estimated with the steady state mass balance approach (SMB) as described by UN-ECE (1996b). The SMB method is based on the N saturation concept (Aber et al., 1989), i.e. the total deposition of N on the forests must not lead to a situation where the availability of inorganic N is in excess of the total combined plant and microbial nutritional demand. CLs estimates at the Italian sites were calculated at the 1 × 1 km grid cells in which the forest plots were located, with the exception of the sites in Lombardy (LOM1, LOM2, LOM3), where CLs were estimated for grid cells of 50 × 50 km (Posch et al., 1997). For the Swiss sites, the parameters of the SMB approach were set to values specific for each site (Thimonier et al., 2005). For the French sites, CLs were calculated at the 1:1,000,000 scale on the map of French ecosystems (forest, grassland and marshes). Each ecosystem is characterised by a soil type, a bedrock type and a potential vegetation type. To calculate CLs, an ecosystem map was combined with the land use map, as described in Probst et al. (2003).

The inorganic nitrogen fluxes at each plot were calculated using the canopy budget model (Ulrich, 1983; Draaijers & Erisman, 1995) as described in Thimonier et al. (2005). In this model TF fluxes represent total deposition (TD) plus or minus canopy exchanges, which are the result of both canopy leaching and uptake. For Na^+, Cl^- and $SO_4^=$ the canopy exchange is assumed to be negligible (Lindberg & Lovett, 1992). Total deposition of base cations is estimated assuming Na^+ as a tracer having a TD/BP ratio similar to that of Ca^{++}, Mg^{++} and K^+ (Draajiers & Erisman, 1995).

To investigate the factors controlling the biological sequestration and release of N, a mass balance was calculated at the forested site LOM1 (Val Masino catchment) using atmospheric deposition as input and the soil solution (at 50 cm depth) as output. The monitoring plot covers an area of 30 × 30 m within the forested part of the Val Masino catchment (25.2 km^2), where the throughfall samplers are also installed. Suction lysimeters were installed in the rooting zone, corresponding to the B-horizon (30 cm), and in the upper parts of the C horizon (50 cm) (Balestrini et al., 2003).

Results and discussion

Comparison of bulk and wet-only data

Both bulk and wet-only samplers are used at five sites in Northern Italy. At the sampling station of Pallanza bulk and wet-only data have been collected in parallel since 1984 (Table 1). Further data are available for BOL1, FRI2, PIE1 and LOM1, though for a more limited period of time. These data were used to compare the two sampling methods and to evaluate the differences in terms of precipitation volume and chemistry (Table 2). The relative differences (RD) were calculated using all the sample pairs available for each site as follows:

$$RD = (bulk - wet)/bulk * 100$$

where bulk and wet are the volume-weighted mean annual concentrations in bulk and wet-only deposition.

Precipitation amount is always lower in wet-only than in bulk deposition, with RD ranging from 4 to 18%. The greatest difference between bulk and wet-only data was found at the sampling site PIE1, with an RD for conductivity of 25%. However, the data available from PIE1 cover 1 year only (30 events altogether). At the remaining sites the differences were below 20% for all the chemical variables, with the exception of Mg^{++} (RD of 22 and 26% at Pallanza and BOL1, respectively), Cl^- at BOL1 and K^+ at FRI2 (Table 2). Ammonium concentrations were lower in bulk samples than in wet-only samples at PIE1 and LOM1 (Table 2), which might be due to biochemical transformation of ammonium to nitrate in the bulk samplers, constantly open to the atmosphere.

Generally speaking, the differences found between bulk and wet-only data for $SO_4^=$ and NO_3^- were limited. At Pallanza, for which the longest data series are available, differences were below 10% for NH_4^+ and NO_3^- and below 12% for $SO_4^=$.

The results presented here are consistent with those reported by Draaijers et al. (1998) for several locations in The Netherlands, Germany, Sweden and the UK. On average, their RD were below 20% for $SO_4^=$, NO_3^-, NH_4^+, Na^+ and Cl^-, between 27 and 33% for Ca^{++}, Mg^{++}, and K^+ and slightly negative for H^+. The RD for base cations also showed higher coefficient of variation (20–30%) compared to $SO_4^=$ and NO_3^- (12–13%) (Draaijers et al., 1998).

Table 2. Relative differences (RD) between bulk and wet-only data for the major chemical variables at those sites where both methods were in use

Station	Period	mm	Cond.	H^+	Ca^{++}	Mg^{++}	Na^+	K^+	NH_4^+	$SO_4^=$	NO_3^-	Cl^-
Pallanza	1984–2002	7	7	6	15	22	8	12	3	12	8	11
BOL1	2000–2002	18	13	10	6	26	19	21	16	7	19	22
FRI2	1999–2002	4	7	28	8	20	1	33	7	12	17	12
PIE1	2002	15	25	53	16	26	24	18	−19	15	20	−6
LOM1	1997–2000	9	–	13	20	3	11	16	−15	7	2	1

Because the differences between the two sampling methods according to our knowledge and the literature were not negligible, wet-only and bulk data are discussed separately in the paper. Bulk samples in particular are much more affected by dust from local or urban/industrial sources. For this reason the geographical variability of precipitation chemistry in the Alps is discussed using wet-only data. Bulk precipitation chemistry is discussed together with throughfall data collected at the ICP Forest sites in Italy, France and Switzerland to analyse canopy exchange processes.

Geographical variability of the chemistry of wet deposition in the Alps

The PCA of wet-only data yields two factors which explain 83% of the total variance (Table 3). The first factor (F1) accounts for 48% of the total variance and loads positively on base cations (BC) and Cl^-. The driving variables of F2 (about 35% of the variance) are acidity, $SO_4^=$, NO_3^- and NH_4^+. The first factor is mainly related to the emission sources in Eastern Austria, which determine high concentrations of base cations and chloride; the second is related to the emission of acidifying compounds. This interpretation is confirmed by the relationship between deposition chemistry and geographical attributes reported below.

The Cluster Analysis of rain chemistry identified four main clusters with a linkage distance of 1.5. The first cluster, including 13 sites, is the most heterogeneous, and can be divided into three main subclusters: (i) three sites in Tyrol (KUF, INN, REU) (ii) some stations located at the foot of the Alps in Switzerland and France ($n = 6$) and (iii) three subalpine sites in Italy and Switzerland (MAG, GRA, DOM) plus one site in Eastern Austria (LUZ) (Fig. 2). The second cluster includes three sites in the Styria region, characterised by unusually high concentrations of Ca^{++}, Na^+ and Cl^-, as well as S and N compounds. Nine sites are grouped into cluster 3. They are located at both high and medium altitudes, and are representative of the areas in each region farthest from the deposition of anthropogenic pollutants. This cluster consequently shows the lowest mean concentrations of $SO_4^=$, NH_4^+, NO_3^- and acidity (Table 4). Clusters 4 includes 6 subalpine stations in Piedmont, Northern Italy, which have remarkably high concentrations of ammonium and nitrate, of the same order as those in cluster 2. Clusters 2 and 4 also show the lowest median pH values (Table 4).

Table 3. Results of the PCA of wet-only chemical data (31 sites, volume weighted mean of 1998–2002)

	Factor 1	Factor 2
H^+	−0.1371	0.8787
NH_4	0.2256	0.9076
Ca^{++}	0.9004	0.2966
Mg^{++}	0.8928	0.2113
Na^+	0.9016	0.1227
K^+	0.7344	0.2547
$SO_4^=$	0.5898	0.7533
NO_3^-	0.3897	0.8797
Cl^-	0.8903	0.1299
Explained Var.	4.3221	3.1666
% of total var.	48.0	35.1

The relationships between wet precipitation chemistry and geographical attributes are shown in Table 5. Longitude is well correlated with Ca^{++}, Mg^{++}, Na^+, K^+, and Cl^-, mainly because the sites in the Eastern Alps, especially in Austria, are affected by high concentrations of base cations and chloride in wet precipitation. Base cations are mainly from local emission sources. Chloride may be related both to the chemical industry and, in winter, to the use of salt on roads. Acidity, NH_4^+ and NO_3^- are negatively related to altitude (Table 5). If the high-altitude site SON (3100 m a.s.l.) is excluded from the analysis, a negative significant relationship ($p < 0.01$) between sulphate concentration and altitude also appears.

Deposition chemistry at the different locations is largely influenced by the topography. Altitude, orientation of the valley and exposure to the main wind directions are probably the major factors determining both precipitation amount and deposition chemistry at the study sites. These can be roughly divided into "alpine" stations, located at medium and high altitudes, and "subalpine" stations, situated in lowland areas at the foot of the Alps (both North and South of the mountains). Possible effects of altitude on precipitation chemistry cannot be investigated fully, because we lack data in the altitudinal range between 1800 and 1900 m a.s.l., where most of the stations lie, and the 3100 m a.s.l of the SON station.

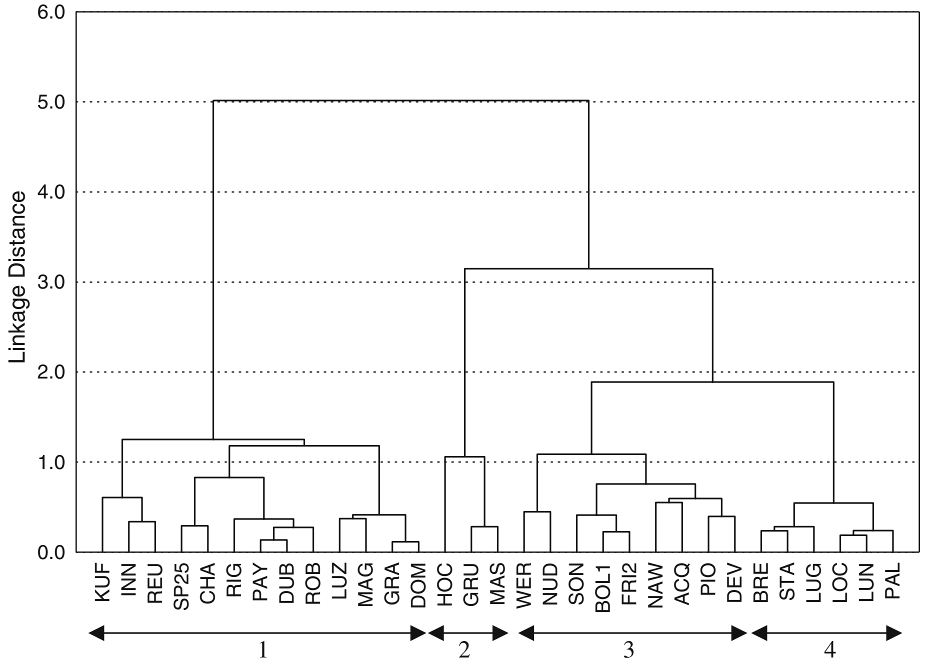

Figure 2. Result of the cluster analysis (Ward's method, Euclidean distance) of wet-only chemical data (volume weighted mean values of 1998–2002). Acronyms as in Table 1.

Geographical variability in atmospheric deposition chemistry in the Alpine area was further evaluated from fluxes of the major inorganic compounds (Fig. 3). The annual precipitation volume ranged from 600 to 800 mm in Eastern Austria (HOC, MAS) and Tyrol (INN, BOL1) to more than 2000 mm in the subalpine and alpine area of Piedmont and Canton Ticino (PAL, GRA, DEV, ROB) (Fig. 3). There, the high amounts are mainly due to orographic precipitation, which occurs when warm, moist air masses from the Mediterranean collide with the southern rim of the Alps, and which falls most intensely in the subalpine area (Mosello et al., 2001).

The highest concentrations of acidity and acidifying compounds (not shown) are recorded in the Styria region, Eastern Austria. As already pointed out, in this area wet deposition is also characterised by very high concentrations of base cations (100–150 μeq l^{-1}) from local emission sources. Concen-

Table 4. Mean chemical values of the main groups of wet-only sites identified by cluster analysis

	Altitude	Precipitation	pH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	NH$_4^+$	SO$_4^=$	NO$_3^-$	Cl$^-$
Cluster 1											
13 sites	884	1552	5.03	16	3	5	2	29	22	24	5
Cluster 2											
3 sites	997	694	4.87	91	11	15	9	48	69	40	43
Cluster 3											
9 sites	1220	1301	5.14	29	7	11	3	25	26	24	10
Cluster 4											
6 sites	439	1965	4.89	34	6	10	3	48	43	40	9

Altitude: m a.s.l. Precipitation: mm. Ionic concentrations: μeq l^{-1}.

Table 5. Pearson product–moment correlations between chemical variables and geographical attributes

	Latitude			Longitude			Altitude		
	r^2	t	p	r^2	t	p	r^2	t	p
H^+	0.010	−0.535	0.597	0.020	0.756	0.456	**0.174**	**−2.431**	**0.022**
NH_4^+	0.092	−1.687	0.103	0.005	−0.367	0.717	**0.316**	**−3.599**	**0.001**
Ca^{++}	0.026	0.863	0.395	**0.218**	**2.794**	**0.009**	0.000	−0.023	0.982
Mg^{++}	0.057	1.305	0.203	**0.347**	**3.858**	**0.001**	0.010	−0.527	0.603
Na^+	0.036	1.019	0.317	**0.285**	**3.339**	**0.002**	0.001	0.167	0.869
K^+	0.112	1.881	0.070	**0.333**	**3.742**	**0.001**	0.000	−0.073	0.942
$SO_4^=$	0.022	−0.795	0.433	0.092	1.681	0.104	0.063	−1.376	0.180
NO_3^-	0.052	−1.238	0.226	0.006	0.419	0.679	**0.341**	−3.803	**0.001**
Cl^-	0.106	1.826	0.078	**0.242**	**2.991**	**0.006**	0.002	0.226	0.822

Significant correlations ($p < 0.05$) are in bold.

trations of ammonium and nitrate are remarkably high (above 50 and 40 μeq l^{-1}, respectively) both in Central-Eastern Austria (Styria and Salzburg) and at the lowland sites in Piedmont and Canton Ticino. This general pattern changes when fluxes are considered instead of concentrations (Fig. 3). The lowest deposition of acidity, $SO_4^=$ and N compounds are recorded at some sites in Tyrol and Salzburg (INN, SON, WER) and in the Eastern Italian Alps (BOL1, FRI2) as well in the western part of the Alpine region (SP25, CHA, PAY). Generally high loads of acidity and of the major pollutants affect the areas of Piedmont and Canton Ticino, where precipitation amount is often above 2000 mm y^{-1}. In particular, at the subalpine sites in this area inorganic N deposition is about 150–200 meq m^{-2} y^{-1}. Previous studies on the chemistry of atmospheric deposition in this area showed the existence of a North–South gradient, with the highest values of acidity, sulphate, nitrate and ammonium deposition in the southern part of the area, close to the Po Valley, where the main sources of pollutants are located (Della Lucia et al., 1996; Mosello et al., 2001).

Because alkalinity was not measured at most of the sites, a comparison cannot be made between the different areas. Alkalinity values available for some sampling stations in Italy and France range between 7 and 22 μeq l^{-1} and 17–45 meq m^{-2} y^{-1} as volume-weighted mean concentrations and fluxes, respectively. A recent analysis of the data collected at the subalpine site of Pallanza, Piedmont, showed a high interannual variability of alkalinity deposition. Annual deposition is almost entirely due to a few Saharan dust events of varying frequency, ranging from 0 to 8 events per year (Rogora et al., 2004).

Bulk and throughfall deposition at forested sites in the Alps

Deposition collected with bulk open field (BP) samplers and under the crown of vegetation (TF) was compared at 16 forested sites (Table 6). Differences were significant ($p < 0.001$) across the entire dataset for all variables with the exception of pH and ammonium. Not surprisingly, BC concentrations were higher in TF than BP in more than 95% of the cases. The corresponding values were 93 and 95% for sulphate and chloride. The increase of ion concentrations in TF samples most likely reflects both dry deposition wash off and foliar leaching, i.e. the process by which nutrients entering the plant by root uptake are incorporated into the foliage and leach into throughfall during a rain event (Erisman et al., 1994).

A different pattern was found for N compounds. In 25% of the cases nitrate concentrations in BP samples were higher than in TF. This mainly occurred at the sites with the lowest range of nitrate concentrations (10–20 μeq l^{-1} in bulk samples), such as the sampling sites in the French Alps (Table 6). The data of ammonium concentrations were almost equally spread around the 1:1 line in the plot comparing BP and TF data. This may indicate that the uptake of ammonia by the tree canopy is on average similar to the dry deposition of ammonium onto forests.

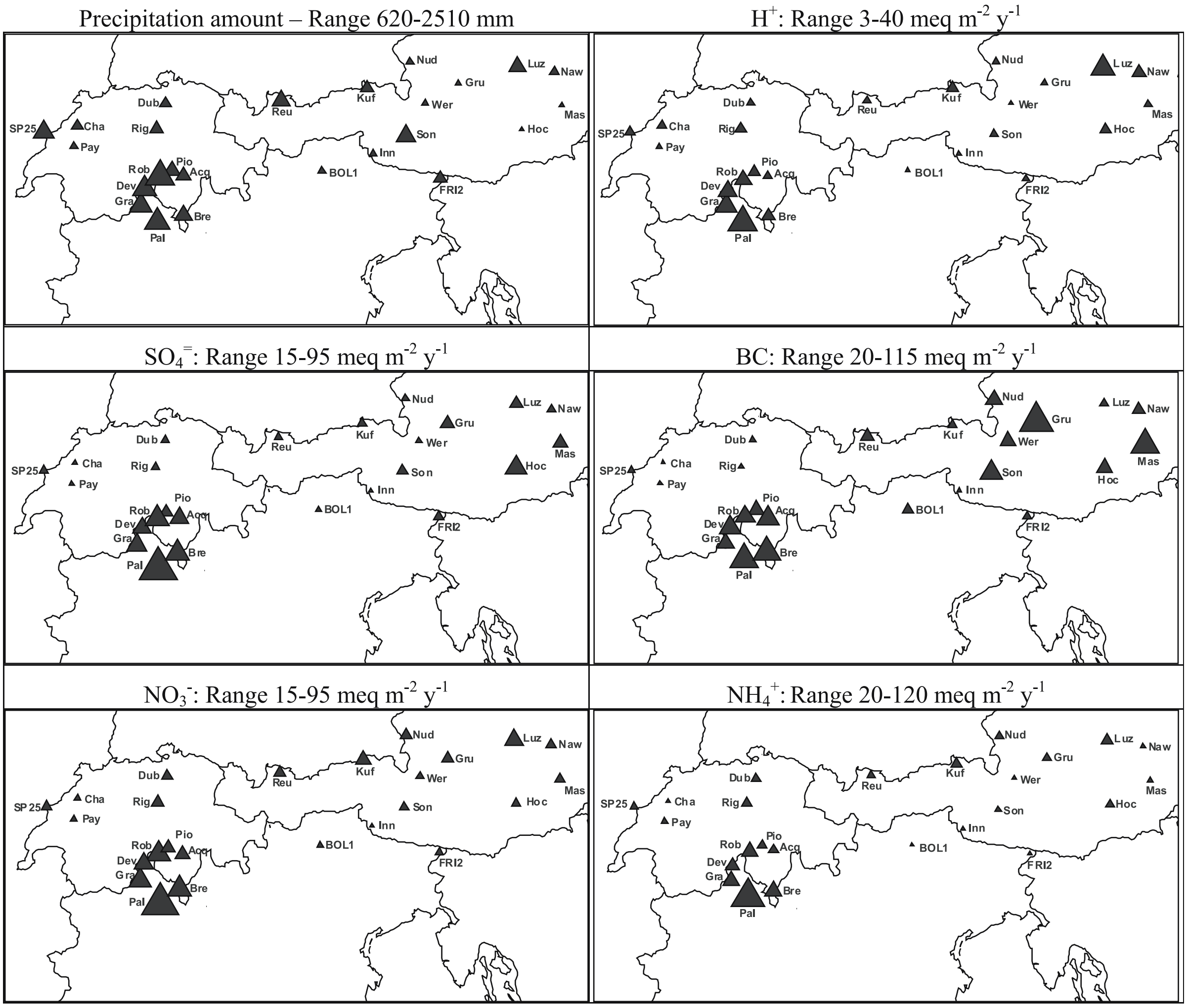

Figure 3. Precipitation amount and fluxes of H^+, $SO_4^=$, BC (base cations = Ca^{++} + Mg^{++} + Na^+ + K^+), NO_3^- and NH_4^+ at wet-only sampling sites (volume weighted mean of 1998–2002). Triangles are proportionally scaled to deposition values. Acronyms as in Table 1.

The study sites in France are those characterised by the highest ratios between TF and BP. Ionic enrichment was particularly high in the case of Mg^{++} (2.5–13.4), K^+ (18.4–26.2) and Cl^- (1.6–2.3).

To explain the pattern of ionic fluxes through the canopy, the different types of vegetation at the sampling sites were also considered (Table 1), but no clear relationship emerged from the data available.

Throughfall deposition can be used as a measure of the actual load of ionic compounds to the soil in forested areas. This information is of major importance for the Alpine region, where much of the territory is covered by forest. The highest load of acidity and acidifying compounds were recorded in the subalpine stations PIE1, SCH and NOV (Table 6). The high deposition rates at PIE 1 and NOV are related to the high level of emissions from the industrialised and densely populated area of the Po Plain, and the relatively high amount of precipitation (Della Lucia et al., 1996). The high deposition rates at SCH, which clearly exceeded the depositions measured on the two other plots

Table 6. Bulk (BP) and throughfall (TF) deposition (meq m^{-2} y^{-1}) at forested sites

Site	Precipitation amount, mm	H^+		NH_4^+		Ca^{++}		Mg^{++}		Na^+		K^+		$SO_4^=$		NO_3^-		Cl^-	
		BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF	BP	TF
EPC 74	1006	9	8	28	25	27	54	1	12	7	12	1	30	29	31	26	49	8	20
SP05	639	1	0	20	6	75	78	8	19	7	7	3	79	23	25	16	5	10	16
SP25	1588	9	8	38	28	36	65	2	15	17	30	2	43	36	44	33	49	17	40
SP38	1201	10	3	32	16	36	44	1	12	7	7	2	60	33	38	29	16	9	18
BEA	1154	4	7	29	26	32	42	4	9	9	11	4	20	22	20	27	41	8	12
SCH	1851	9	4	72	75	45	103	8	31	17	20	9	62	46	50	62	78	15	24
CEL	899	5	5	15	10	32	32	4	8	9	10	3	11	17	18	17	16	8	8
NAT	991	4	4	15	11	30	33	6	11	6	6	3	7	17	16	18	18	8	6
NOV	2009	23	17	105	87	72	100	12	34	26	30	7	67	91	92	96	119	23	28
LOM1	1711	18	3	55	19	86	46	12	13	17	10	6	34	66	32	51	28	17	11
LOM2	1136	5	3	59	61	75	106	12	31	18	19	5	56	55	59	46	92	16	27
LOM3	1551	2	2	74	80	126	142	25	43	23	24	4	25	66	73	64	90	20	27
FRI2	1277	18	8	32	34	30	58	9	25	15	19	5	33	44	48	37	56	13	21
BOL1	907	6	4	32	19	29	33	10	25	13	44	4	31	30	32	30	33	13	18
TRE1	1035	1	3	29	18	54	47	22	22	18	21	9	30	35	32	25	25	17	19
PIE1	1711	22	12	61	54	66	70	12	17	17	18	6	31	73	74	69	74	15	19

Volume weighted mean annual values of 2000–2001.

located in the Lower Swiss Alps (ALP, BEA), are most likely related to the agricultural activities (livestock farming) carried out in the plain and to the geographic situation of the plot, which is located on the northern flank of the Alps, where an orographic barrier effect occurs (Thimonier et al., 2005).

High deposition of N compounds also affected the two forested sites LOM2 and LOM3, owing to their location close to the major pollutant sources in the Po Plain in Italy. Both of these sites are also characterised by high fluxes of BC and alkalinity which almost totally neutralise atmospheric acidity. The French plots do not show a univocal pattern: the two northern sites SP25 and EPC74 were affected by fairly high N deposition, while at SP05 the acidity flux was totally neutralised by a large deposition of alkalinity (Table 6).

Comparison of N deposition with CLs at forest sites
Total fluxes of inorganic N calculated by the canopy budget model were compared with CLs of nutrient N at the forest sites in the Alps (Fig. 4).

Deposition values are remarkably high and exceed the CLs at the forest sites in North-Western Italy (LOM2, LOM3, PIE1) and at SCH and NOV, the Swiss sites located respectively at the Northern and Southern foot of the Alpine rim. At other sites CLs are slightly exceeded (BEA, FRI2, EPC74) or not yet exceeded, even though deposition values are in some cases close to critical limits. Only at the highest sites, CEL and NAT, which are located in inner alpine valleys far from pollution sources, are deposition values still far from CLs (Fig. 4).

When comparing deposition and CLs, it should be remembered that there is a sizeable uncertainty associated to CL calculation (Thimonier et al., 2005; de Vries et al., 2003). Furthermore, the inorganic N deposition considered here is an underestimate of the total N (TN) deposition affecting forest soils. The contribution of organic N to TN deposition proved to be from 20 to 40% at forest sites in Italy. For the Swiss sites a preliminary evaluation of 2 years' measurements indicates that the TN fluxes in throughfall are 10–25% higher than the inorganic N fluxes (Thimonier et al., 2005). However, the dry deposition value of organic N on forests is not well known and some of the organic N found in throughfall

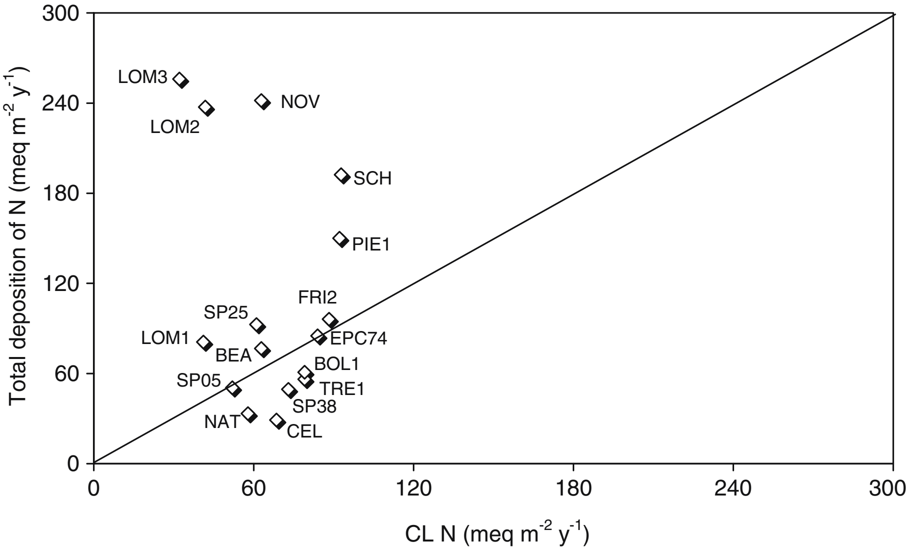

Figure 4. Total deposition of N estimated with the canopy budget model (volume weighted mean of 2000–2001) at some forest sites vs. critical load (CL) of nutrient N at each site. Acronyms as in Table 1.

may have been released by tree leaves in the canopy (internal cycle) and thus does not belong to the atmospheric deposition.

The complexity of the forest ecosystem and the fact that many of the processes taking place in soil and vegetation are not completely understood make it difficult to forecast the effects of over-fertilisation by N inputs. Although the data presented here are available for a limited number of sites only, they nevertheless highlight the critical situation of forested areas on the slopes of the Alps with regard to atmospheric N input, especially for the areas in the vicinity of urban centres.

The role of nitrogen: an example of input/output budget in a forest catchment in Northern Italy

A nitrogen mass balance was estimated at the forest site LOM1 over a 3-year period (1999–2001) (Fig. 5). This site is relatively far (150 km) from the industrialised area of Milan, and not directly subjected to human pressures. Climatic and geopedological features, such as abundant precipitation, siliceous substrata and very acid soils, increase the sensitivity of this forest ecosystem to the impacts of N deposition.

The inorganic N compounds are retained almost completely in the soil solution, with a retention efficiency of 97% for NH_4^+ and 95% for NO_3^- (Fig. 5). The uptake of NH_4^+ by the canopies reduces its atmospheric input by more than 45% even before its deposition on the soil. Fixing in the cation exchange complex or in clay minerals, and root and microbial uptake, further decrease the flux of NH_4^+ in the soil. Biological uptake is the major process affecting the high retention of NO_3^- in the rooting zone and below it.

The measured output flux of 0.3 kg ha^{-1} y^{-1} as nitric N is smaller than the value reported in literature for N limited forest of 1 kg ha^{-1} y^{-1} (Gundersen & Rasmussen, 1990). The lower

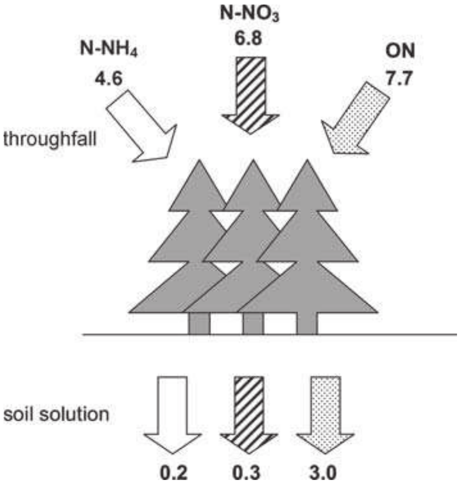

Figure 5. Results of the nitrogen mass balance at the forested site LOM1, Val Masino, Northern Italy. Units: kg ha^{-1} y^{-1}.

retention observed for organic N (61%) reduces the total N yield to 82%. These findings suggest that coniferous forest at the study site is still limited by N despite the relatively high N fluxes: 17 and 19 kg ha^{-1} y^{-1} for bulk deposition and throughfall, respectively. Such loads exceed the nutrient CLs by more than 12 kg ha^{-1} y^{-1}.

Besides the atmospheric inputs, a number of factors may affect the extent of N leaching, including stand age, nutrient soil status, water availability and climate. Results from several N addition experiments carried out throughout Europe and the US indicated high retention efficiency (about 70%) at some sites subjected to inputs of more than 25 kg ha^{-1} y^{-1} (Kahl et al., 1993; Wright & Rasmussen, 1998). Data from the NITREX project showed a significant correlation between N leaching and an index of the "nitrogen status" based on N concentration in foliage and litter, soil N transformation rates and forest floor characteristics. On the other hand, the correlation with N deposition was not significant (Gundersen et al., 1998). The nitrification rate in the soil was well correlated with the N leaching and the C/N ratio of the forest floor. C/N ratios of 25–27, embracing the value measured in the soil of the study area (26.2), were indicated as the crucial limit above which soils are unable to nitrify (Gundersen & Rasmussen, 1990). Aber et al. (1998) identified mycorrhizal assimilation as the dominant biological process able to explain the immobilisation of N in the soil without biomass production. A shift in the dominant soil community from fungal (mycorrhizal) to bacterial could be a key process in the shift of an ecosystem toward a saturation condition.

Another important factor likely to affect the ecosystem's response to the alteration of N cycling is land use history (Tamm, 1991; Aber et al., 1998). The high export of N due to agricultural conversion, fire, or harvesting could increase the limiting function of nitrogen and the amount of N deposition required to promote N saturation. Dendrochronological surveys carried out in the Val Masino area provided some useful information on the history of the tree community, revealing the occurrence of an alteration event corresponding to the removal of a large portion of the forest during the early fifties (Azienda Regionale delle Foreste, 1998).

Further investigations in Val Masino showed relatively high nitrate concentrations in surface waters. According to the approach of Traeen and Stoddard (1995), these data pointed to a surplus of nitrogen bioavailability in the terrestrial ecosystem (Balestrini et al., 2003). The mass balance estimated considering the waters of the River Masino as output revealed that only 50% of inorganic N is retained (Balestrini et al., 2002). The Val Masino catchment is characterised by steep rocky slopes, heterogeneous soil structure, low percentage of soil cover, and low percentage of forested area. These features do not favour the exchange between water nutrients and biological community and consequently militate against an efficient retention of nitrogen. On the other hand, it is clear that the tree vegetation has an important role in removing the atmospheric input of N, and consequently in protecting the quality of surface and ground waters.

Long-term changes in the chemistry of atmospheric deposition

Major ions

Temporal trends in pH values and in the concentrations of sulphate, nitrate, ammonium and base cations were tested at 18 sites for which monthly data were available. Because our aim was to detect trends in response to long-term changes in atmospheric pollution, we excluded a few sites in Austria (HOC, GRU, MAS) sporadically subject to high emission of pollutants at a local level.

The level of significance and the trend slopes are shown in Table 7. An overall decrease of acidity was detected at the study sites, with the exception of the Austrian stations LUZ and of the French site SP38, where trends of pH values were not significant. Trend slopes range between 0.01 and 0.06 pH units per year. At the Swiss site PAY, and at REU, in Tyrol, the pH trend was more significant in the 15-year period than in the last decade, indicating a sharp increase in the late 80s followed by a slight increase in the 90s. The positive pH trends are mainly due to the general decrease in sulphate concentrations, as shown by the significant negative trend of this variable at all sites (Table 7).

Nitrate concentrations did not show a uniform pattern, owing to the lack of a general decrease in

Table 7. Results of the trend analysis performed on monthly data for selected sites

Site	Country	pH				$SO_4^=$				NO_3^-				NH_4^+				BC			
		1985–2002		1990–2002		1985–2002		1990–2002		1985–2002		1990–2002		1985–2002		1990–2002		1985–2002		1990–2002	
		p	B	*p*	B	*p*	B	*p*	B	*p*	B	*p*	B	*p*	B	*p*	B	*p*	B	*p*	B
PAL	I	***	*0.03*	***	*0.04*	***	−2.30	***	−1.99	n.s.	−0.14	n.s.	−0.24	n.s.	0.11	n.s.	0.02	n.s.	−0.35	n.s.	0.37
DOM	I			***	*0.05*			***	−1.52			n.s.	−0.44			n.s.	0.11			n.s.	−0.06
LUN	I			***	*0.04*			***	−1.60			n.s.	−0.30			n.s.	−0.06			n.s.	−0.12
ORT	I			***	*0.05*			***	−2.77			*	−0.86			n.s.	−0.88			n.s.	0.08
PIO	CH			***	*0.06*			***	−1.44			n.s.	−0.53			n.s.	0.08			**	−1.46
PAY	CH	***	*0.03*	*	*0.02*	***	−2.10	***	−1.84	***	−0.61	***	−0.86	***	−0.92	***	−1.19	**	−0.57	*	−0.74
SP25 (since 1993)	F			*	*0.03*			***	−1.25			n.s.	−0.36			n.s.	−0.71			*	−1.42
SP05 (since 1993)	F			*	*0.04*			**	−1.20			n.s.	−0.24			n.s.	−0.48			n.s.	−1.15
SP38 (since 1993)	F			n.s.	0.03			***	−1.56			n.s.	−0.33			**	−1.19			*	−1.39
REU	A	***	*0.04*	*	*0.01*	***	−0.90	***	−1.09	n.s.	−0.16	n.s.	−0.25	*	−0.31	***	−1.18	***	−2.20	***	−1.94
KUF	A	***	*0.05*	***	*0.04*	***	−1.22	***	−1.17	n.s.	−0.07	n.s.	−0.24	**	−0.51	***	−1.37	**	−0.57	n.s.	−0.35
INN	A	***	*0.05*	***	*0.05*	***	−1.00	***	−1.04	n.s.	−0.12	**	−0.53	*	−0.43	***	−0.71	n.s.	−0.24	n.s.	−0.30
NUD	A	***	*0.05*	***	*0.05*	***	−1.87	***	−2.02	*	−0.38	*	−0.55	***	−1.10	***	−2.84	n.s.	0.14	n.s.	−0.36
WER	A	***	*0.05*	***	*0.04*	***	−1.02	*	−0.56	n.s.	0.05	n.s.	0.05	*	−0.31	***	−1.43	n.s.	−0.42	n.s.	1.06
SON	A			***	*0.05*			*	−0.46			n.s.	−0.16			***	−0.45			**	*1.30*
NAW	A			*	*0.02*			***	−1.85			n.s.	0.01			**	−0.90			**	−1.66
LUZ	A			n.s.	0.01			***	−2.52			n.s.	−0.43			n.s.	−0.06			***	−1.56

p: probability level. *$p < 0.05$; ** $p < 0.01$; ***$p < 0.001$; n.s. not significant. BC: base cations. B: trend slope. Units: pH: pH units y^{-1}; $SO_4^=$, NH_4^+, NO_3^- and BC: μeq l^{-1} y^{-1}.

atmospheric emission of NO_x in Europe. Nitrate significantly decreased at PAY (−0.6 μeq l^{-1} y^{-1} since 1985); a negative trend was also recorded at ORT, in Northern Italy, and at the Austrian sites INN and NUD (Table 6). Ammonium concentrations showed a general decrease, with significant trend at PAY, SP38 and at most of the sites in Austria. Trend slopes and significance are generally higher in the latter part of the record (1990–2001), with slopes ranging between −0.5 and −2.8 μeq l^{-1} y^{-1} (Table 6). No significant trends of ammonium concentrations were found for sites in Piedmont (PAL, DOM, LUN, ORT) and Canton Ticino (PIO), where ammonium deposition was remarkably high. The oxidation of ammonium to nitrate is a major source of potential acidity to surface water (Schuurkes, 1986). Long-term monitoring of atmospheric deposition chemistry in these areas showed that the relative contribution of sulphuric acid to potential acidity has dropped in the last 10–15 years, while nitric acid and the protons produced by ammonium transformation account for more than 60% of total potential acidity (Barbieri et al., 2003).

Base cations showed a somewhat variable response: a significant decrease was detected at PAY, Switzerland, at the French sites SP25 and SP38, at the Tyrolean sites REU and KUF, and at NAW and LUZ in Lower Austria. A highly significant positive trend was found at the high altitude site SON, because of a sharp increase in base cation concentrations in the last few years. As an example, the volume-weighted mean concentrations of calcium has risen from 20 μeq l^{-1} in 1988–1990 to about 40 μeq l^{-1} in the last 3 years. This pattern could be related to the strong dust events which occurred in 2000–2002, affecting rain chemistry at some monitoring sites in the alpine and subalpine area (Rogora et al., 2004).

According to the EMEP Programme, sulphur emissions were reduced by 50–60% in Europe in the period from 1980 to 1995 as a result of international negotiations such as the First S Protocol, signed in 1985, and the Second S Protocol, signed in 1994. The response of sulphate concentration in atmospheric deposition affecting the Alpine area to changes in emissions resulting from this targeted abatement policy was clear. According to the simulation by the RAINS model (Alcamo et al., 1990) the decline of S deposition occurring since the 1980s in the Alps was smaller than in other areas in Europe. Nevertheless, the decline is predicted to continue in the next years in response to the Protocols and to other EU Directives (Ferrier et al., 2001).

Data from EMEP and other long-term monitoring programs also showed that base cation deposition, which may partly neutralise deposited acidity, is constant or declining throughout Europe (e.g. Hedin et al., 1994). This decline may offset some of the benefits of S and N emission cuts. This might be the case for the French Alps and sites such as REU, PAY, LUZ and NAW, where despite a sharp decrease in sulphate concentrations, the base cation decline partly offsets changes in acidity.

Nitrogen has also been the subject of negotiations: with the First N Protocol, signed in 1988, the signatory countries committed themselves to stabilise emission of NO_x by the year 1994 relative to 1987 levels (Ferrier et al., 2001). The most recent agreement, the Gothenburg Protocol, was signed in 1999 and set emission ceilings to be achieved by 2010 (UN-ECE, 1999). When the Protocol is fully implemented, NO_x and NH_3 emissions in Europe will be reduced by at least 41 and 17% respectively compared to the 1990 levels (Ferrier et al., 2001). Measured data from monitoring sites in the Alps showed a slight decrease of NO_3^- concentrations, statistically significant only at a few sites, and a more widespread decline of NH_4^+. Nonetheless concentrations of N compounds are still high, and especially in the foothills of the Alps the high amounts of precipitation determine huge deposition fluxes of N.

Heavy metals: wet deposition of lead at selected sites in Austria

The long-term variation in the wet deposition of lead was evaluated using data from three sites in Salzburg, Austria (Fig. 6). Lead was analysed in samples from these sites, located on a North to South transect, with the aim of describing spatial and temporal variations of atmospheric lead deposition (Kalina et al., 1997, 1999).

Deposition values decreased from 4.3 to 0.7 μg l^{-1} at NUD (1984–2000), from 3.6 to 0.5 μg l^{-1} at WER (1984–2000) and from 5.0 to 0.5 μg l^{-1} at SON (1988–2000) (Fig. 6). The decrease in the deposition of lead by wet precipitation is well correlated with the stepwise reduction of lead

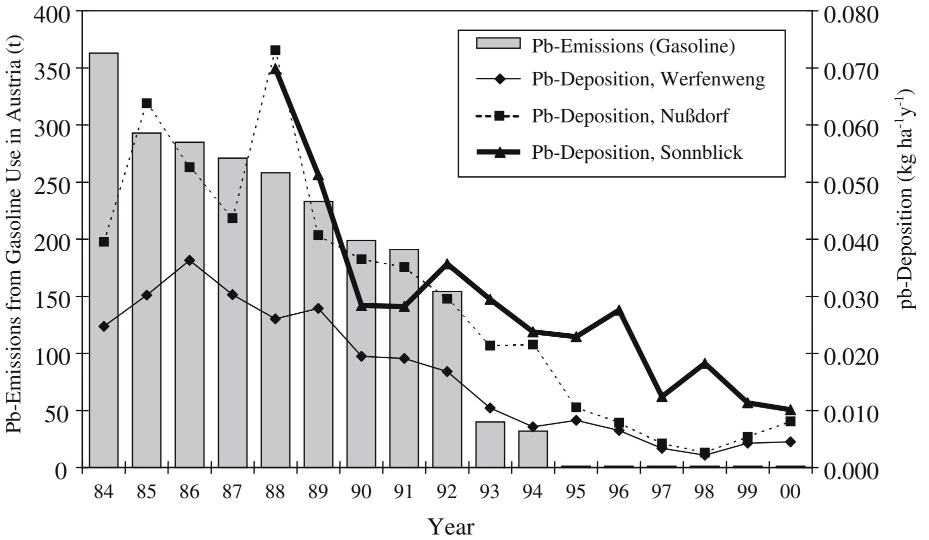

Figure 6. Lead deposition at three sites in Austria compared to lead emissions from gasoline in the period 1984–2000.

emissions deriving from the combustion of leaded gasoline (Fig. 6), which started in the early 1970s and was followed by a ban on lead additives in the mid 1990s. Correlation coefficients for the three sampling sites range from 0.82 to 0.94, the observed decrease was 85–90% between 1988 and 2000.

The highest deposition loads for lead in Salzburg are observed at SON, with values between 0.070 and 0.010 kg ha^{-1} y^{-1} (1988–2000) caused by the high amount of precipitation, with up to 2200 mm y^{-1} compared to 1000–1300 mm y^{-1} at the other two sites. Thus the sensitive ecosystems at high altitude sites are exposed to higher deposition loads than any other site in the Alpine region.

Under Austrian law lead deposition must not exceed 2.5 kg ha^{-1} y^{-1} for forest ecosystems. The data presented show that the legal limit was respected in every year of observation at all the Salzburg sampling sites.

Importance of the occult impact on total deposition

The Achenkirch sampling site reveals a west to east profile from Christlumkopf (mountain top, 1758 m a.s.l.) through Christlumalm (mountain slope with alpine pasture, 1280 m a.s.l.) to Talboden (valley bottom, vicinity of the Achenkirch village, 930 m a.s.l.) (Fig. 7). The Mühleggerköpfl sampling site (about 10 km north of Talboden, 920 m a.s.l.) replaced Talboden in 1997/98 to avoid the influence of the village, especially as regards local nitrogen emissions (NH_3-farming, NO_x-traffic). Figure 7 shows the resulting deposition loads for nitrogen at the operated sites.

CLs of nitrogen for coniferous forests were exceeded significantly in near-source regions represented by intensely used agricultural areas (Talboden) and at forest areas at high elevations (Christlumkopf). The contribution of cloud water interception to total nitrogen deposition was estimated to be about 20% at the higher altitude sites (Christlumkopf and Christlumalm) and just about 1% at the sites located on the valley floor (Talboden and Mühleggerköpfl). This significant difference can be explained by the occurrence of two main types of fog/cloud in the Achenkirch area: (a) Radiation fog with low cloud frequency (~2% per year) at the ground stations and (b) frontal cloud systems with higher cloud frequency (~12% per year) at higher altitudes.

Forest ecosystems in alpine regions are typically exposed to higher ionic concentrations through cloud water than through wet or dry precipitation (Kalina & Puxbaum, 1994; Kalina et al., 1998). Estimates of occult deposition in the Whiteface Mountains, USA, showed that cloud water can contribute up to 60% of the total deposition fluxes, especially at high altitude sites (Miller et al., 1993). Compared to this value, a

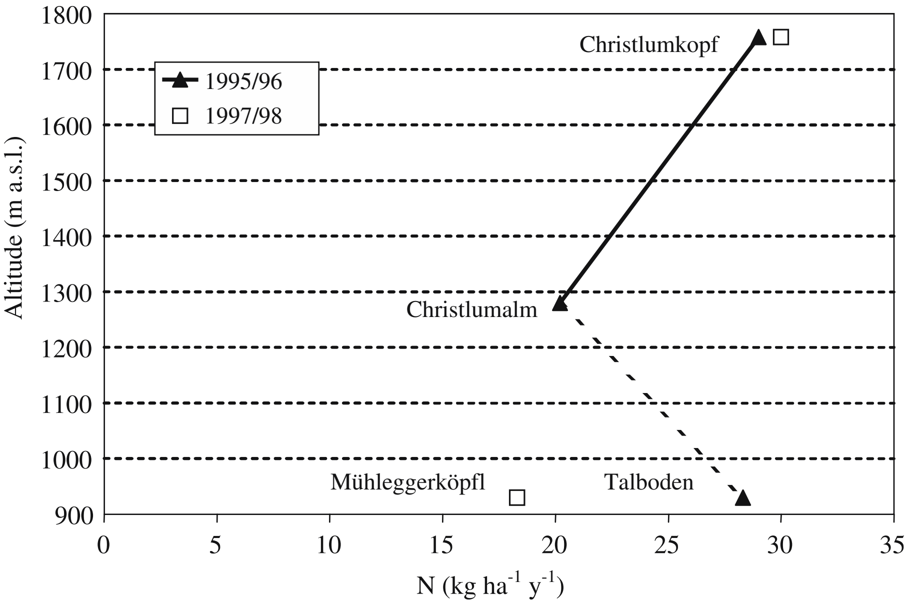

Figure 7. Deposition loads of nitrogen at selected sites in Austria resulting from multilayer deposition models.

20% contribution at high alpine sites in Europe seems rather low, but can be explained by (a) higher wet precipitation in Achenkirch (1900–2300 mm at Christlumkopf vs. 1400 mm at Whiteface), (b) a higher liquid water content of the clouds at Whiteface (0.44 g m^{-3} vs. 0.12 g m^{-3} at Christlumkopf) and (c) higher cloud frequency at Whiteface (28% vs. 12% at Christlumkopf).

These results on the contribution of occult deposition to total deposition in an Alpine area were supported by findings for the locations Hoher Peißenberg (980 m a.s.l., about 30 km north of Garmisch-Partenkirchen, Germany) (Pahl et al., 1994) and Aubure (1146 m a.s.l., Vosges Mountains, France) (Herckes et al., 2001) and highlight the importance of taking occult deposition into account in assessing whether the CLs are exceeded, especially for mountainous ecosystems close to the timber line.

Conclusions

The analysis performed here highlights the marked geographical variability of atmospheric deposition in the Alpine region, mainly due to the topographical complexity of the area. The Alpine area is characterised by a high variability in emission sources. There is some evidence of geographically limited effects, deriving from local sources, such as in the Styria region, Austria. But in general no obvious gradients were identified in the major ion concentrations, nor clear relationships between precipitation chemistry and the geographical attributes of the sampling sites. The highest ionic loads are recorded in areas in the foothills of the Alps, such as the pre-alpine area in North-Western Italy and the area of Canton Ticino, Switzerland. High deposition values in these areas, particularly of N compounds, usually result from the combined effect of high amounts of precipitation and high concentrations of pollutants, transported with air masses from industrialised and urbanised regions and intensive agriculture on the plains bordering the Alpine rim (e.g. Po Plain, Swiss Central Plain). In particular some subalpine sites in Northern Italy with long-term data are exposed to N deposition which is among the highest in Europe (Rogora et al., 2001).

The long-term changes in the chemistry of atmospheric deposition in the Alps fit well with those reported for different regions of Europe (e.g. Evans et al., 2001; Marquardt et al., 2001; Avila & Rodà, 2002), i.e. the acidity of precipitation has been decreasing in the last 15–20 years as a consequence of the reduced emission of sulphur compounds. On the other hand, despite the fact that NO_x emissions are decreasing slightly in most European countries (Tarrason & Schaug, 2000), N deposition, both as oxidised and reduced N, has not changed significantly at most European sites (Evans et al., 2001; Wright et al., 2001). The lack of trends in N deposition in the Alpine area too is confirmed by an examination of the data from the study sites included in this paper.

The deposition of N is still well above the estimated CLs of nutrient N at some forest sites in the alpine and subalpine areas of Italy and Switzerland, thus confirming that important terrestrial ecosystems in these regions of the Alps are in a critical situation regarding N inputs. The example of the alpine catchment of Val Masino in Northern Italy highlights the need for studies to be performed at both plot and catchment scales, for example to assess the impact of stand history on nitrogen retention and leaching. Furthermore, the peculiarity of eco-regions like the Alps requires "ad hoc" investigations for a better understanding of complex environmental phenomena, such as the N saturation of terrestrial ecosystems. For example, the biological community above the tree line might represent a key component of the Alpine ecosystem which is often not considered in N cycling studies.

The high nitrogen load in the Alps is also reflected in the relatively high nitrate concentrations in alpine lakes and streams, and in the large subalpine lakes, north and south of the Alps. Evidence of this impact came from long-term data series from Lake Maggiore and the other deep Italian lakes, which showed a marked increase of nitrate in the last few decades, mainly related to the atmospheric input of N (Mosello et al., 2001).

Industrialisation and anthropogenic emissions have changed the major ion concentrations in precipitation, as well as the biogeochemical cycling of trace elements. It is of major importance to monitor lead and other heavy metals in precipitation because of their well known negative effects on human health. The long-term data of lead content in atmospheric deposition at some Austrian sites showed a decrease which was well correlated with the sharp reduction of emissions from leaded gasoline. Unfortunately, at present there is a lack of long-term observation projects focusing on trace metals in wet deposition in the Alpine regions.

Furthermore, while wet deposition has been investigated at several sites in the Alps, and the results widely reported in the literature, not many studies have been performed on fog/cloud deposition. Available data from study sites in Austria showed how fog and cloud water interception can substantially contribute to total deposition fluxes of pollutants, especially on forest ecosystems (Kalina et al., 1998, 2002). This contribution cannot be neglected when dealing with CLs and exceedances in alpine ecosystems. Studies on the impact of occult deposition at different locations (e.g. covering a geographical gradient, or characterised by different types of vegetation) will be of major importance in future research programmes.

The data analysed in this paper were produced within the framework of national projects not co-ordinated with one another, or within the ICP Forests programme. Samples were collated and analysed using different methodologies. Some information on variables other than the major ions and on specific processes such as occult deposition is available, but at a site-specific level only. Accordingly, we should be cautious about extrapolating the results to a wider spatial scale, and remember the extreme spatial variability of the processes involved in the transport and deposition of pollutants across the Alps.

Despite these limitations, the data set used in this paper proved to be suitable for a general characterisation of the deposition pattern of the major ions and other compounds across the Alps. While continuous monitoring both of acidifying compounds and other pollutants such as heavy metals and organics will be essential in the near future, an effort should also be made to co-ordinate the different monitoring programmes already existing at a national level. Research programs aimed at tackling problems such as the effects of pollutant deposition on surface waters and Alpine ecosystems in general will necessarily require harmonisation of sampling procedures and analytical methods and an integrated elaboration of the data. To this end it would be extremely useful to create an "ad hoc" working group in the framework of the ICP Forests programme, which already sees the participation of all the Alpine countries, to make a specific elaboration of the data collected in the Alps.

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