

Thirty Years of Chemical Changes in Alpine Acid-Sensitive Lakes in the Alps

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Received: 20 May 2013 / Accepted: 10 September 2013 / Published online: 28 September 2013
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Abstract The subalpine and alpine areas in North-Western Italy and Southern Switzerland (Canton Ticino) receive high deposition of atmospheric pollutants transported from emission sources in the Po Valley. Long-term studies on high-altitude lakes in these areas indicate widespread recovery from acidification, even though most of them are still substantially affected, especially by deposition of nitrogen compounds. We analysed long-term trends of the major chemical compounds in a sample ($n=41$) of high-altitude lakes, both at the site and regional levels, with the aim to assess the response of water chemistry to changes in atmospheric deposition and climate. These lakes have been studied since the early 1980s in the context of research programmes on acidification and atmospheric pollution. The significant decrease of sulfate and acidity in atmospheric deposition led to acidification recovery in the majority of the lakes. However, some lakes are still acidic or show a high sensitivity to acidification. This sensitivity is particularly evident at the snowmelt, when alkalinity is still fully

depleted in some lakes. At present, nitrate is the dominant acidifying agent in the studied lakes, due to the high input of nitrogen compounds from atmospheric deposition. Our study also demonstrated that climatic factors interact with atmospheric deposition affecting the long-term changes in lake water.

Keywords Mountain lakes · Atmospheric deposition · Recovery · Nitrogen · Climate change

1 Introduction

Mountain lakes are often considered as pristine, unpolluted ecosystems, due to their remote location. Despite that, starting in the 1980s, they were identified as being affected by air pollutants from emission sources in the lowlands. Mountain lakes proved to be useful early-warning indicators of changes in climate and in the chemical composition of the atmosphere. As a consequence, they became the focus of several research projects on surface water acidification due to sulfur (S) and nitrogen (N) deposition (Battarbee et al. 2009; Curtis et al. 2005; Camarero et al. 2009).

In the last 20–25 years, sulfate deposition has decreased sharply across Europe, leading to a widespread recovery from acidification of sensitive freshwater ecosystems (Evans et al. 2001; Skjelkvale et al. 2005). However, reduction in N deposition has been less marked and has not affected all countries to the same extent (Fagerli and Aas 2008; Fowler et al. 2007; Vuorenmaa 2004).

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Since the earliest studies on acidification of surface waters, loss of alkalinity has been identified as a simple, 'early warning' indicator of the first stage of acidification in lakes and rivers (e.g. Henriksen 1979). Alkalinity, or alternatively acid-neutralising capacity (ANC), has been widely used as an index of the acidification status, and of acid sensitivity, of surface waters (Waller et al. 2012). The U.S. EPA (2009), for instance, suggested five classes of ANC representing various levels of concern for surface waters in relation to effect on the biota: acute ($\text{ANC} < 0 \mu\text{eq L}^{-1}$); severe ($\text{ANC} 0\text{--}20 \mu\text{eq L}^{-1}$); elevated ($20\text{--}50 \mu\text{eq L}^{-1}$); moderate ($50\text{--}100 \mu\text{eq L}^{-1}$) and low ($>100 \mu\text{eq L}^{-1}$). In Europe, the value of $20 \mu\text{eq L}^{-1}$ has been identified as the minimum level required for ecosystem protection under UNECE protocols. However, proposed critical limits vary depending on the target group of organisms. Furthermore, even when considering the same target (e.g. macroinvertebrates), critical limits may vary, depending on the typical fauna of sensitive species and their adaptations to native water chemistry. In the high Alps, for instance, an ANC limit of $30 \mu\text{eq L}^{-1}$ has been suggested (Raddum and Skjelkvåle 2001).

Beside changes in average levels of key variables or indicators, short-term changes must be considered to evaluate episodic acidification, i.e. any short-term declines in alkalinity, which may occur through natural (dilution of alkalinity or pulses of organic acids) or anthropogenic (pulses of N or S) processes (Lepori et al. 2003a).

The subalpine and alpine areas of North-Western Italy and Southern Switzerland (Ticino region), in the Central Alps, have been affected by a substantial reduction in sulfate deposition, which has almost halved since the 1980s. However, deposition of oxidised and reduced nitrogen has not changed to the same extent, showing a slight tendency to decrease only in the most recent period (Rogora et al. 2012). High-altitude lakes in these areas have been studied since the 1980s to evaluate the extent of acidification; indeed, surface waters in this region, mainly characterised by crystalline bedrocks, proved to be highly sensitive to acidification (Marchetto et al. 1994a). Subsequently, a monitoring programme on a limited number of lakes was established, to assess the response of lake chemistry and biology to changing deposition patterns (Rogora et al. 2003; Steingruber and Colombo 2010a).

The high-altitude lakes in this region are indeed affected by long-range transport of pollutants from the plain of the River Po, in Italy, one of the most urbanised and industrialised areas of Europe (Rogora et al. 2006).

Previous studies showed that calcite and silicate weathering in alpine lake catchments is the dominant factor influencing their water chemistry (Marchetto et al. 1995). In response to decreasing acid deposition, lakes in the study area showed signs of recovery from acidification since the mid 1990s (Rogora et al. 2003; Steingruber and Colombo 2010a). Nevertheless, pH and alkalinity remained low in several lakes, and biological recovery has been limited to recolonization by a few acid-sensitive species (Marchetto et al. 2004; Steingruber et al. 2011).

In this paper, we assessed the main chemical changes occurred in a group of lakes, representative of various levels of sensitivity to acidification, over a 30-year period. Both long-term trends and seasonal or short-term variations were considered. The main drivers of changes in lake chemistry were analysed, considering both atmospheric deposition and climatic data available for the lake area. We aimed to assess (1) the response of alpine lakes to declining acid deposition, in terms of long-term changes in key drivers of surface water acidification and acidity status, and (2) which main drivers caused the chemical changes in the lakes, both in short- and long-term perspectives.

2 Study Area and Methods

2.1 Site Description

Forty-one high-altitude lakes, 20 located in the Canton Ticino, Switzerland, and 21 in the Ossola Valley, in Piedmont, Italy, were considered (Fig. 1, Table 1). These lakes have been monitored since the 1980s in the context of research projects on the effects of transboundary air pollution and climate change on mountain lakes (e.g. AL:PE1, AL:PE2, MOLAR, EMERGE; for a synthesis, see Battarbee et al. 2009). Some of the lakes are also included in the UNECE International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP WATERS; Skjelkvåle et al. 2005).

The studied lakes are all located above the tree line, at altitudes ranging between 1,700 and 2,800 m a.s.l. They are located in remote areas far from any local pollution sources. They are characterised by a long period of ice cover, usually from November to mid-June or July. Wet deposition in the lake area is mainly determined by warm, humid air masses originating from the Mediterranean Sea. Average precipitation in this area is approximately

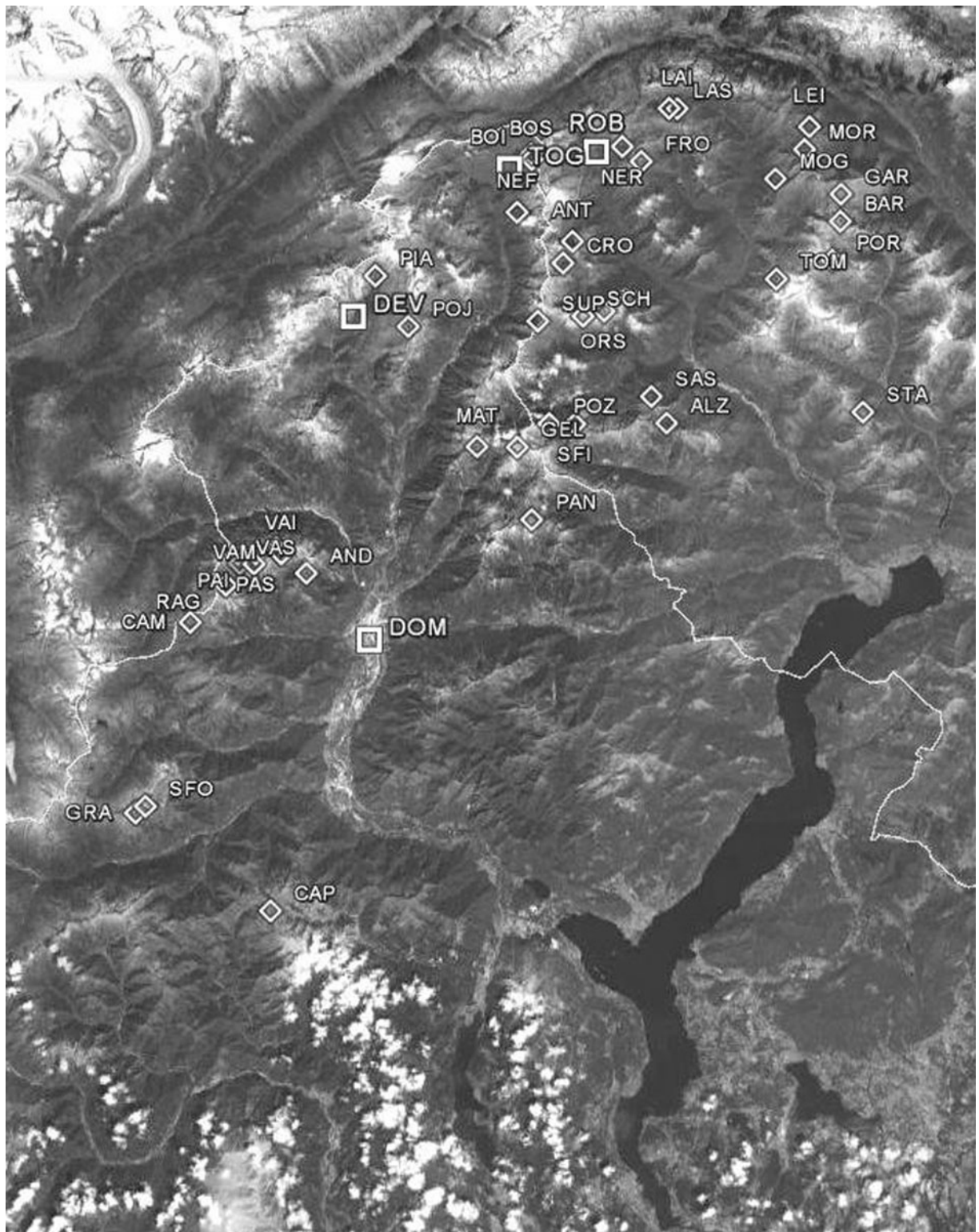


Fig. 1 Map of the study area with the location of the lakes (*white diamonds*), atmospheric deposition sampling sites (DEV, ROB, DOM) and meteorological stations (ROB, TOG) (*white square*). For the acronyms, see Tables 1 and 2

Table 1 Main geographic, morphometric and land cover characteristics of the high-altitude lakes considered in this study

Lake	Acronym	Cluster	Latitude N	Longitude E	Altitude	Lake area	Catchment area	Catchment cover (%)	Rocks	Brushes and meadows	Water (glaciers)
					m a.s.l.	ha	ha		Acidic	Carb.	
Starlaresc da Sgiöf	STA	B	46°16'26"	08°46'25"	1,875	1.1	23	32	64	-	4
Tomè	TOM	B	46°21'47"	08°41'23"	1,692	5.8	294	9	86	-	2
Porchieitisc	POR	C	46°22'33"	08°44'39"	2,190	1.5	43	5	92	-	3
Barone	BAR	B	46°24'07"	08°45'06"	2,391	6.6	51	4	83	-	13
Gardiscio	GAR	B	46°45'22"	08°45'22"	2,580	1.1	12	7	84	-	9
Leit	LEI	C	46°27'55"	08°43'17"	2,260	2.7	52	13	80	-	7
Morghirolo	MOR	C	46°27'03"	08°43'00"	2,264	11.9	166	7	81	-	7 (5)
Mognola	MOG	C	46°25'49"	08°41'19"	2,003	5.4	197	5	92	-	3
Laghetto Inferiore	LAI	B	46°28'34"	08°35'34"	2,074	5.6	182	7	84	-	7
Laghetto Superiore	LAS	B	46°28'34"	08°35'05"	2,128	8.3	125	6	88	-	7
Nero	NER	C	46°26'58"	08°32'22"	2,387	12.7	72	9	73	-	17
Froda	FRO	C	46°26'24"	08°33'29"	2,363	2	67	4	93	-	3
Antabia	ANT	C	46°23'08"	08°29'32"	2,189	6.8	82	2	90	-	9
Crosa	CRO	B	46°22'16"	08°28'60"	2,153	16.9	194	2	90	-	9
Orsalia	ORS	B	46°20'23"	08°31'24"	2,143	2.6	41	7	87	-	6
Schwarzsee	SCH	C	46°20'10"	08°30'11"	2,315	0.3	24	8	90	-	2
Pozzöi	POZ	B	46°15'52"	08°28'17"	1,955	1.1	33	26	67	-	4
Sfille	SFI	B	46°15'52"	08°29'46"	1,909	2.8	63	21	74	-	5
Sascöla	SAS	B	46°17'01"	08°34'11"	1,740	3.2	90	40	54	2	4
Alzasca	ALZ	C	46°15'58"	08°35'05"	1,855	10.4	110	53	38	-	9
Capezzone	CAP	A	45°56'26"	08°12'36"	2,100	0.9	32	29	68	1	3
Grande	GRA	B	46°00'15"	08°04'44"	2,269	0.8	90	2	98	-	1
Sfondato	SFO	B	46°00'30"	08°05'20"	2,422	0.5	20	-	97	-	3
Paione Inferiore	PAI	C	46°10'09"	08°11'24"	2,002	0.9	126	8	90	-	2
Paione Superiore	PAS	B	46°10'26"	08°11'27"	2,269	0.7	50	5	93	-	2
Campo	CAM	A	46°07'46"	08°07'50"	2,290	0.8	71	2	95	2	1
Agro	AGR	C	46°10'13"	08°10'37"	2,041	0.5	60	2	97	-	1
Ragozza	RAG	A	46°09'17"	08°09'46"	2,002	1.3	73	9	90	-	1
Andromia	AND	C	46°09'55"	08°14'22"	1,895	2.9	79	46	50	-	4
Variola Superiore	VAS	C	46°10'48"	08°12'42"	2,190	0.9	58	6	92	-	3

Table 1 (continued)

Lake	Acronym	Cluster	Latitude N	Longitude E	Altitude	Lake area	Catchment area	Catchment cover (%)		
Variola Medio	VAM	C	46°10'35"	08°12'55"	2,130	0.7	84	89	8	3
Variola Inferiore	VAI	C	46°10'30"	08°13'02"	2,117	0.3	86	89	8	3
Pian Boglio	PIA	A	46°21'40"	08°18'11"	1,983	5.4	783	70	10	1 (3)
Pojala	POJ	A	46°19'46"	08°20'05"	2,305	5.7	107	68	—	5
Boden Inferiore	BOI	A	46°26'30"	08°27'01"	2,342	5.9	91	79	2	15
Boden Superiore	BOS	A	46°26'23"	08°27'04"	2,348	2.8	30	84	—	7
Nero di Formazza	NEF	A	46°25'03"	08°26'50"	2,428	6.1	104	63	1	4
Superiore	SUP	A	46°20'06"	08°27'32"	2,254	5.8	56	85	2	3
Gelato	GEL	B	46°15'01"	08°26'30"	2,418	0.8	15	93	—	7
Matogno	MAT	A	46°15'03"	08°24'05"	2,087	3	136	19	10	2
Panelatte	PAN	C	46°12'10"	08°27'29"	2,063	0.6	12	52	—	42

Rocks are all acidic; if present, the percent of carbonatic rocks is reported. Percent of glaciers in the catchment is also shown

1,650 mm but interannual variability is very high (from 1,000 to 2,800 mm year⁻¹).

The lakes are small (0.3–16.9 ha), with a high watershed to lake area ratio. The watersheds consist mainly of bare rocks, with vegetation generally confined to small areas of alpine meadow; in most cases, soils are absent or very thin. All the watersheds are dominated by acidic rocks (ortho- and paragneiss), although marbles, amphibolites and serpentines are also locally present. In a few cases, carbonatic rocks are also present, even if in very small amounts (Table 1). As a consequence of this variable lithological composition, the studied lakes represent different levels of sensitivity to acidification. The lakes can be also considered representative of the entire lake population in the study region (Catalan et al. 2009).

In order to assess the possible role of atmospheric deposition on the long-term changes in lake chemistry, precipitation chemistry data collected on three sites were considered: the Alpine stations Alpe Devero and Robiei, and the subalpine station of Domodossola, located at the beginning of the Ossola Valley (Fig. 1, Table 2).

Meteorological data, namely temperature, precipitation and snow cover, were also considered to assess their possible connection with lake chemical changes. At Robiei, a surface weather station of the Federal Office of Meteorology and Climatology (MeteoSwiss) exists. The meteorological data collected at the station of Toggia, located in the upper part of the Ossola valley and run by the National Electric Power Agency were also considered (Fig. 1, Table 2).

2.2 Sampling and Analyses

In this study, only the sample representative of surface waters, measured at about 1 m below the surface or at the outlet, was considered. All the samples of the lakes in Italy were analysed for the main chemical variables at the laboratory of CNR Institute of Ecosystem Study (CNR ISE), while the samples taken from the Swiss lakes were analysed by the section of water, air and soil protection of the Department of the Territory of Canton Ticino. The following variables were considered: pH, conductivity, alkalinity, major anions (sulfate, nitrate, chloride) and cations (calcium, magnesium, sodium and potassium), ammonium, reactive and total phosphorus, total nitrogen, reactive silica, total organic carbon and trace metals.

Table 2 Main characteristics of the atmospheric deposition sampling sites and meteorological stations

Site	Acronym	Lat. N	Long. E	Alt.	Data	Frequency	Period
				m a.s.l.			
Devero	DEV	46°20'03"	8°16'54"	1,634	Atmospheric deposition chemistry	Weekly	1996–2011
Domodossola	DOM	46°07'12"	8°17'55"	270	Atmospheric deposition chemistry	Weekly	1986–2011
Toggia	TOG	46°20'01"	8°25'50"	2,170	Temperature, precipitation, snow cover	Daily	1980–2011
Robiei	ROB	46°26'43"	8°30'51"	1,898	Atmospheric deposition chemistry	Weekly	1996–2011
					Temperature, precipitation, snow cover	Daily	1991 (1980 for snow cover) to 2011

We measured alkalinity by Gran's titration and used this variable to assess the acidification status of the lakes, according to Henriksen (1979). However, because ANC is also commonly used as a classification criterion, we also calculated charge balance ANC for all lakes as the equivalent sum of base cations ($\text{Ca}^{++} + \text{Mg}^{++} + \text{Na}^{+} + \text{K}^{+}$) minus the equivalent sum of strong acid anions ($\text{SO}_4^{=} + \text{NO}_3^{-} + \text{Cl}^{-}$) (Reuss and Johnson 1986).

Details on sampling and analytical procedures can be found in Tornimbeni and Rogora (2012) and Steingruber and Colombo (2010a). The two laboratories regularly perform QA/QC programmes. A comparison between the sum of anions and cations and between measured and calculated conductivity was performed for each analysis. Further quality assurance measures involved the use of control charts, the analysis of synthetic samples on a regular basis and participation in inter-laboratory comparisons on surface water analysis, such as those organised within the ICP Waters (e.g. Dahl and Hagebø 2011).

Sampling of the lakes in Ticino started in 1980, 1983 or 1986 (eight, seven and five lakes, respectively). Until 2000, sampling occurred occasionally, while since 2000 sampling has occurred two or three times per year (in June–July, September and October). However, at least 15 years of data exist for all the lakes in Ticino in the period between 1980 and 2011. Four lakes in the Ossola Valley (PAI, PAS, BOI and BOS) were also sampled each year since 1984 (from a minimum of one to a maximum of eight samples per year), usually in late summer/autumn. The remaining lakes were sampled during occasional surveys: The first sampling took place between 1984 and 1987 depending on the lake and the following ones occurred in 2000, 2001, 2007, 2008, 2010 and 2011.

These characteristics of the dataset do not allow applying the same statistical analysis to all the lakes, with the exception of the regional trend analysis. The lakes were first divided into subgroups according to their chemical characteristics using a cluster analysis (Ward's method, Euclidean distance). This was applied to the average chemical data (conductivity and concentrations of the major ions) of 2010–2011.

The Regional Kendall Test (RKT; Helsel and Frans 2006) was then applied to the main subgroups to identify overall trends in water chemistry for the study region. The RKT was applied to the following four blocks of data: values of the samples collected in the 1980s (a year between 1984 and 1987, according to the lake) and the average values of the surveys performed in 2000–2001, 2007–2008 and 2010–2011. The main aim of the RKT, compared with the trend analysis at site level, is to describe the global variation occurred in the chemistry of lakes in the study area, and to assess the overall extent of acidification recovery.

Trend analysis was also performed at the site level by means of the Mann Kendall Test (MKT) applied to the lakes with at least 15 years of data within 1986–2011 (all the lakes in Ticino and four lakes in the Ossola valley, Italy). Only the autumn data, representative of stable chemical conditions, were considered. Trend significance and slope were calculated with the MKT (Hirsch and Slack 1984) and Sen's methods, respectively (Sen 1968). Trend slope and significance were calculated for each lake and for the following chemical variables: pH, conductivity, alkalinity, SO_4 , NO_3 and base cations.

The availability of data collected during both snow-melt and late summer period for the Ticino lakes allowed the evaluation of seasonal differences in the main hydrochemical characteristics. For each parameter and lake, a Student *t* test was applied to determine the

significance of the difference between average summer and average autumn values for the period 2000–2011.

At the atmospheric deposition sampling stations of Robiei and Devero, located in proximity of the lakes, wet-only samples have been collected since 1996 and analysed for pH, conductivity and major ions (Rogora et al. 2012; Steingruber and Colombo 2010b). Longer series of atmospheric deposition data are available for some sites in the southern part of the area, at a lower altitude with respect to Devero and Robiei: For example, data have been collected at Domodossola since 1986 (Fig. 1, Table 2). These data were also considered to assess the overall trend of deposition during the period covered by lake data. Annual mean deposition was calculated from the product of annual average concentrations (obtained from the volume-weighted weekly concentrations) and mean annual precipitation.

Two meteorological stations, Toggia and Robiei, were considered to assess changes in meteorological drivers during the period covered by lake data. Annual and summer averages of temperature and precipitation were calculated for both sites. The summer values (June through October) were examined because this is the ice-free season for the lake, when the samplings take place; furthermore ground temperatures, which can be relevant for weathering processes and permafrost melting, are expected to be influenced by air temperatures in the summer, when the ground is not covered by snow. Mean and maximum snow height were calculated for the period November–May of each year. The length of the snow cover season was calculated as the number of days in the period November–May with the presence of at least 5 cm of snow on the ground.

In an attempt to assess the role of the various drivers on lake chemistry, we applied a multiple regression analysis to the four lakes (PAS, PAI, LAS and LAI) with the most continuous data series. Autumn data of the period 1986–2011 were used. Response variables considered in the analysis were: H^+ , conductivity, alkalinity, SO_4 , NO_3 and base cations. As explanatory variables, we used the average annual and summer air temperature and precipitation, annual deposition of sulfate and total inorganic nitrogen, and snow cover data calculated for the winter before lake sampling. A backward selection procedure was used and regression model selected on the basis of the Akaike Information Criteria (AIC).

All the statistical analyses were performed using Brodgar vers. 2.5.1 (Highland Statistics Ltd), S-plus

2000 (Math Soft) and the Kendall.exe program (Helsel and Frans 2006).

3 Results

3.1 Meteorology and Atmospheric Deposition Chemistry

Mean annual and summer air temperatures (calculated as average values of the last decade) at Toggia were 0.82 and 7.05 °C, respectively. Corresponding values at Robiei were slightly higher (3.40 and 9.27 °C, respectively) due to the lower altitude of this site. Air temperature at Toggia (Fig. 2) showed a slight increasing trend in the period 1980–2011, with an overall change of mean annual air temperature (MAAT) and mean summer air temperature (MSAT) of 0.93 and 0.83 °C, respectively. The short data series available for Robiei does not allow an assessment of trends.

Precipitation at Toggia did not show any tendency towards increase or decrease over the 30-year period (Fig. 2). In general, precipitation showed a high interannual variability at both the two sites, for instance, at Robiei annual precipitation, can range between 1,350 (e.g. 2005) and 3,300 mm (2002).

A slight tendency towards a decrease in the amount of snow in time was highlighted by the data, in particular in regard to the length of the snow cover period calculated for the Toggia site (Fig. 2). The last decade was characterised by a very high variability, consisting of some snowy years (2000–2001, 2003–2004, 2008–2009) but also winters with extremely scarce snow (e.g. 2001–2002, 2004–2005).

The trends in the deposition of acidity, sulfate and nitrogen compounds on two sites in the lake area, Devero and Robiei, and the lower altitude site of Domodossola are shown in Fig. 3. Concentrations of the main chemical compounds were very similar in the three sites, while deposition tended to be higher in Robiei, as a consequence of the higher amount of precipitation.

Spatial variability in precipitation can be very high; for instance, very abundant rainfalls affected the whole area in the autumn of 2002, but they were more copious in the southern region (e.g. 758 mm in November 2002 at Devero versus 311 mm at Robiei); the opposite occurred in the autumn of 2000, another period characterised by heavy precipitation, with the highest

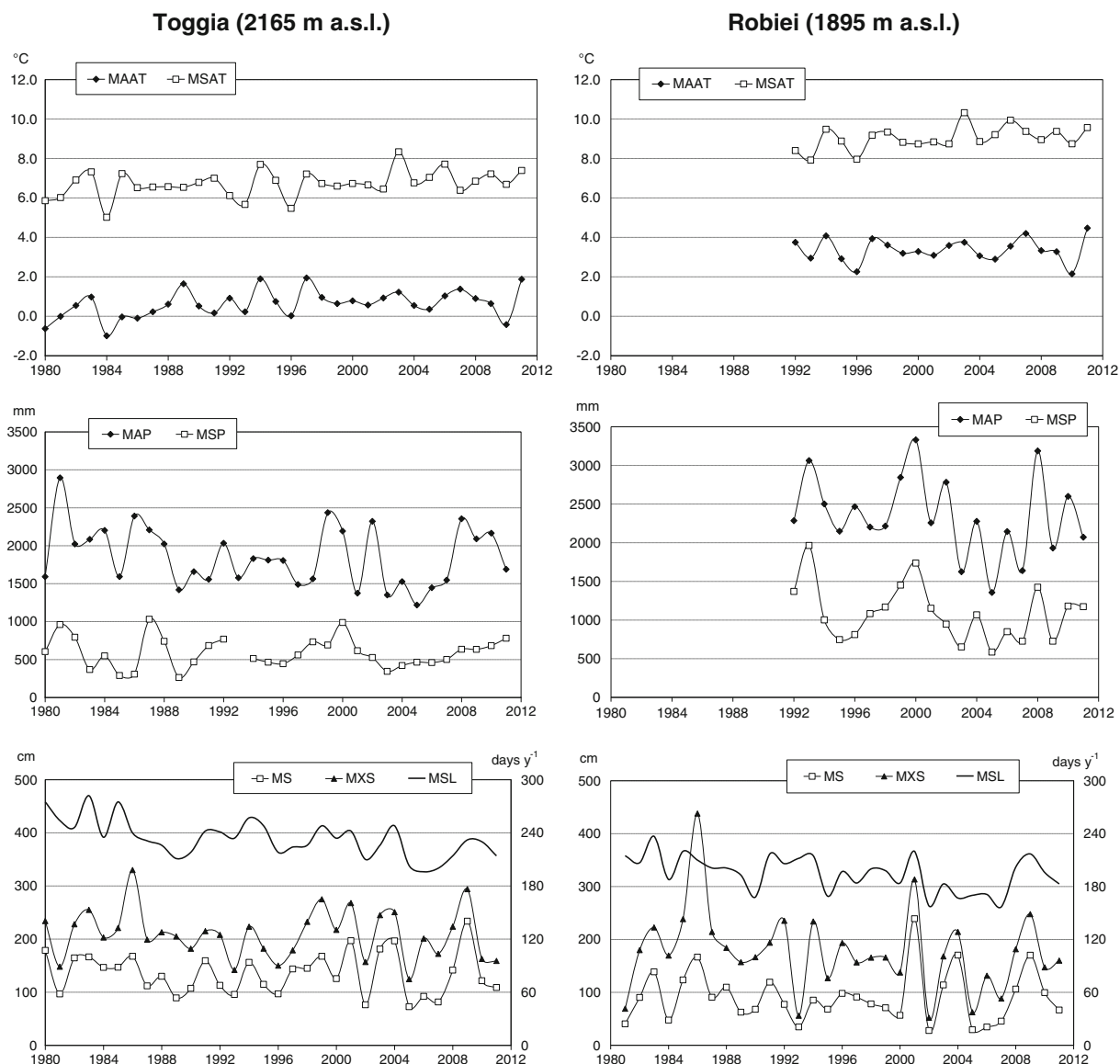


Fig. 2 Mean annual values of selected meteorological variables at the station of Toggia and Robiei. *MAAT*: mean annual air temperature; *MSAT*: mean summer air temperature; *MAP*: mean

annual precipitation; *MSP*: mean summer precipitation; *MS*: mean snow height; *MXS*: maximum snow height; *MSL*: length of the snow cover period

volume recorded in the northern part of the area. Concentrations of chemical compounds in deposition may also vary spatially, depending on long-range transport from lowland areas, and consequently from geographical and morphological attributes of the sampling sites such as altitude, orientation of the valley and exposure to the main wind directions (Rogora et al. 2006; Steingruber and Colombo 2010b). As a result, annual deposition of acidity, SO_4 and N compounds may differ among the sites.

A trend towards decreasing acidity and sulfate was found both in Robiei and Devero, particularly from 1996 to 2004. Annual fluxes of these two variables decreased from 25–30 and 50–60 $\text{meq m}^{-2} \text{ year}^{-1}$, respectively, in the late 1990s to about 10 and 25 $\text{meq m}^{-2} \text{ year}^{-1}$ in recent years (Fig. 3). These negative trends were mainly caused by decreasing concentration of H^+ and SO_4^{2-} , but a contribution also came from the lower precipitation which characterised some of the recent years (e.g. 2003, 2004, 2005, 2009).

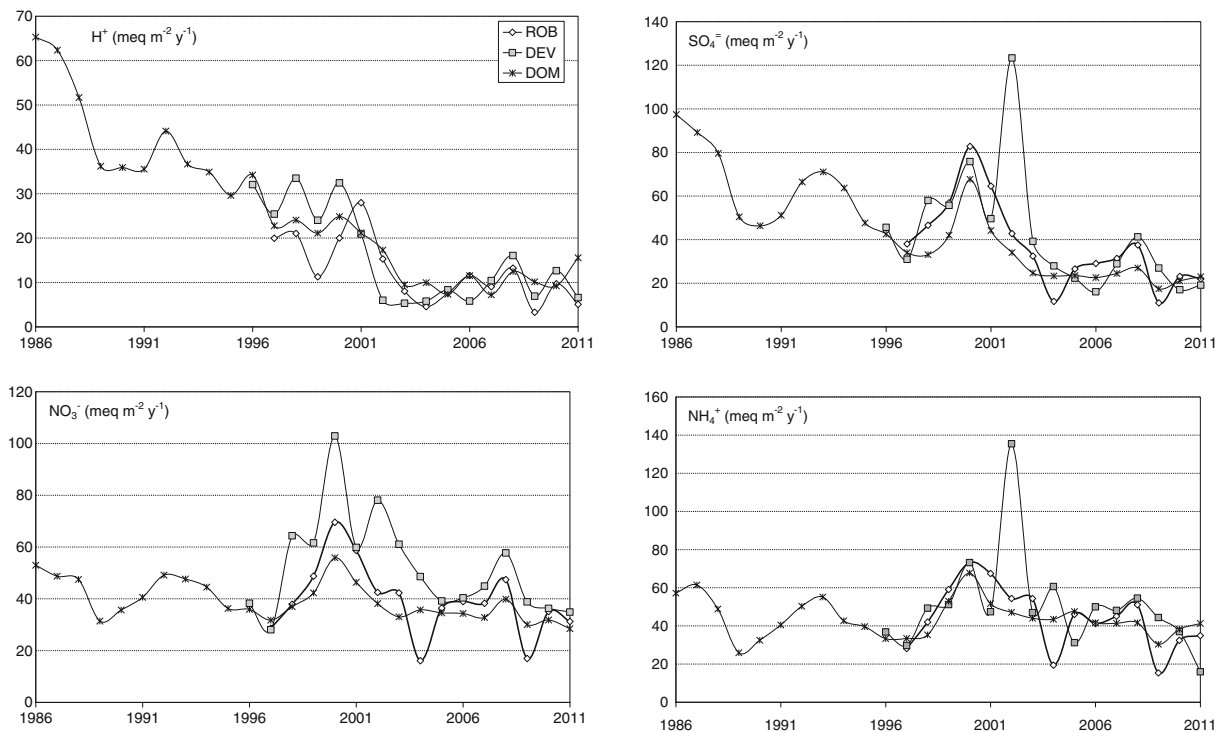


Fig. 3 Trends of atmospheric deposition of selected chemical variables at the sites of Robiei (ROB), Devero (DEV) and Domodossola (DOM)

Slightly lower levels of N deposition have been recorded in the last few years (2009–2011), particularly of NO_3^- (Fig. 3). However, deposition values are still high (42 and 48 $\text{meq m}^{-2} \text{ year}^{-1}$ at Robiei and 32 and 27 $\text{meq m}^{-2} \text{ year}^{-1}$ at Devero for ammonium and nitrate, respectively) compared with those commonly found on mountains or remote areas (Rogora et al. 2008; Nanus et al. 2009).

Even if located at a lower altitude, the site of Domodossola showed deposition levels comparable to those measured at the higher sites. Therefore, the trends in SO_4 and inorganic nitrogen deposition observed in Domodossola probably affected the northern and higher part of the area too, where the lakes are located. Data collected in Devero and Robiei since the mid-1990s captured only the most recent phase of the decrease in acid deposition.

3.2 Lake Chemistry

3.2.1 Present Chemistry of the Lakes

A summary of the lake water chemistry according to the mean values of 2010–2011 is shown in Table 3. The lakes cover a wide range of chemical characteristics, as

shown by the high variability (about one order magnitude) of both conductivity (from 7 to more than 80 $\mu\text{S cm}^{-1}$) and total ionic content (from 100 up to 2,000 $\mu\text{eq L}^{-1}$). 25 % of the lakes have alkalinity below 30 $\mu\text{eq L}^{-1}$. Charge balance ANC and alkalinity values showed the same distribution in the lakes as an effect of the low organic acid content of lake water. Phosphorus content was very low: The lakes can be classified as oligotrophic or ultraoligotrophic according to total phosphorus concentrations (1–10 $\mu\text{g P L}^{-1}$). Total nitrogen was below 0.5 mg N L^{-1} , and inorganic nitrogen forms dominated (75 % of IN with respect to 15 % of ON). Dissolved organic carbon was generally around 0.5 mg C L^{-1} .

Cluster analysis identified three main groups, named A, B and C, according to a linkage distance of 0.5. The average chemical characteristics of each group are shown in Table 3, while the group to which each lake belongs is shown in Table 1. Group A consist of ten lakes, all located in the Ossola Valley; they can be classified as not sensitive to acidification, according to pH and alkalinity values (7.77 ± 0.24 and $461 \pm 199 \mu\text{eq L}^{-1}$, respectively). These lakes were also characterised by the highest ionic content (conductivity of $56.3 \pm 18.4 \mu\text{S cm}^{-1}$ at 20 °C), with higher sulfate ($121 \pm 69 \mu\text{eq L}^{-1}$) and base cations (e.g.

Table 3 Mean chemical characteristics of the studied lakes ($n=41$; average values of the surveys performed in 2010 and 2011) and of the groups of lakes (mean \pm standard deviation) resulting from the cluster analysis

	pH	Cond.	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	Alk.	Cl ⁻	SO ₄ ⁼	NO ₃ ⁻	RSi	TP	TN	DOC	ANC
Min	5.43	6.5	27	5	7	3	0	2	16	2	0.24	1	0.09	0.13	-3
25 percentile	6.48	7.7	48	7	11	5	27	2	25	11	0.66	2	0.23	0.30	28
Mean	6.89	21.7	167	26	15	10	143	3	57	14	0.87	3	0.31	0.46	144
75 percentile	7.30	20.3	134	21	18	12	112	3	68	19	1.03	4	0.37	0.52	106
Max	8.21	87.3	846	146	28	32	857	4	244	26	1.68	10	0.62	1.09	854
SD	0.68	21.9	206	36	5	7	207	1	52	6	0.31	2	0.12	0.24	205
Cluster A $n=10$	7.77 \pm 0.24	56.3 \pm 18.4	482 \pm 198	73 \pm 48	17 \pm 6	19 \pm 9	461 \pm 199	3 \pm 1	121 \pm 69	10 \pm 6					
Cluster B $n=15$	6.04 \pm 0.42	7.5 \pm 0.6	42 \pm 10	7 \pm 2	11 \pm 2	5 \pm 2	19 \pm 11	3 \pm 0.4	25 \pm 6	17 \pm 4					
Cluster C $n=16$	6.83 \pm 0.21	13.4 \pm 3.0	88 \pm 25	14 \pm 6	17 \pm 5	10 \pm 3	61 \pm 22	3 \pm 0.5	47 \pm 23	14 \pm 6					

Ionic concentrations in milliequivalents per litre

Cond. conductivity (microsiemens per centimetre at 20 °C), RSi reactive silica (micrograms Si per litre), TP total phosphorus (micrograms P per litre), TN total nitrogen (milligrams N per litre), DOC dissolved organic carbon (milligrams C per litre)

calcium 482 \pm 198 $\mu\text{eq L}^{-1}$) concentration. The 15 lakes in group B were the most sensitive to acidification: Mean pH and alkalinity were 6.04 \pm 0.42 and 19 \pm 11 $\mu\text{eq L}^{-1}$, with some lakes in Ticino reaching pH values as low as 5.4–5.5 and alkalinity below 5 $\mu\text{eq L}^{-1}$. These lakes also showed the lowest concentrations of all ions, except nitrate, which was slightly higher than in groups A and C. Group C consists of 16 lakes with intermediate characteristics: pH ranged between 6.6 and 7.3 and alkalinity between 29 and 112 $\mu\text{eq L}^{-1}$; however, alkalinity certainly reached lower values at snowmelt and probably fell below 50 $\mu\text{eq L}^{-1}$ in most of the lakes, so that they can be considered as moderately sensitive to acidification. Because of the shared sensitivity to acidification, lakes of group B and C were grouped for the regional trend analysis.

3.2.2 Long-Term Trends

The regional trend analysis (RKT) was performed using the whole set of data ($n=41$; Table 4). This dataset includes 19 lakes, which cannot be tested for trends by means of MKT due to the lack of continuous data; these lakes are located in Italy, in the southern part of the study area, and include both not sensitive ($n=10$) and sensitive ($n=9$) lakes. The analysis was done both considering the whole set of lakes ($n=41$) and splitting them into two subgroups (not sensitive lakes, cluster A, and sensitive lakes, clusters B+C).

pH and alkalinity increased significantly ($p<0.001$), both in sensitive and not sensitive lakes, while nitrate showed a widespread decrease (Table 4). Sulfate decreased significantly in sensitive lakes, and base cations increased, even if not significantly. On the other hand, conductivity, base cations and sulfate tended to increase in buffered lakes. ANC showed a very similar pattern to alkalinity, with a slightly higher slope for the acid-sensitive lake group.

A trend analysis by means of the MKT was performed for 24 lakes with an almost complete series of data for the period 1986–2011 (Table 5). The dataset for this analysis included exclusively acid-sensitive sites (moderately or highly sensitive according to the cluster analysis). The analysis at site level provided insights into the inter-site variability of lake response to acidification.

Almost all the lakes (18 of 24) showed significant positive trends for pH, alkalinity and ANC. Trends in

Table 4 Results of the regional Kendall test (*p* levels and slopes) applied to lake chemical data collected during different periods

	All lakes (n=41)			Not sensitive lakes (n=10)			Sensitive lakes (n=31)		
		<i>p</i>	slope		<i>p</i>	slope		<i>p</i>	slope
pH	+	***	0.0155	+	***	0.0141	+	***	0.0157
Cond.	-	n.s.	-0.0186	+	**	0.4425	-	*	-0.0576
Alk.	+	***	0.7479	+	***	2.994	+	***	0.6414
SO ₄ ⁼	-	***	-0.4795	+	n.s.	0.4748	-	***	-0.6178
NO ₃ ⁻	-	***	-0.1921	-	***	-0.2194	-	***	-0.1789
BC	+	n.s.	0.0647	+	*	3.227	-	n.s.	-0.1052
ANC	+	***	0.7669	+	*	2.567	+	***	0.6932

The plus and minus symbols indicate increasing and decreasing trends, respectively. Results are shown both for the whole set of lakes and for two subgroups, sensitive and not sensitive lakes, identified by means of a cluster analysis (see Table 2). Slope units: Cond. in microsiemens per centimetre per year; Alk., SO₄⁼, NO₃⁻, BC, ANC in milliequivalents per litre per year

n.s. not significant

****p*<0.001, ***p*<0.01, **p*<0.05, significance levels

these variables were positive but not significant at some sites (e.g. MOR, MOG, ANT, POZ) that were moderately sensitive to acidification according to the cluster analysis (group C; Table 1).

The overall increases of pH and alkalinity over the 25-year period were 0.7 units of pH and 28 µeq L⁻¹, respectively, as average values. ANC slopes were slightly higher in some of the lakes, with an overall increase of 32 µeq L⁻¹ as an average value. A widespread decrease was observed in sulfate concentration, with significant negative trends in 16 sites and an overall decrease between 9 and 34 µeq L⁻¹. In contrast with this general pattern, five lakes showed significant positive trends (LEI, MOR, MOG, BOS, BOI), with an increase in concentration over the study period ranging between 7 and 60 µeq L⁻¹.

Nitrate concentration decreased at all sites, with significant trends in 20 lakes. The overall change of concentration was between 4 and 9 µeq L⁻¹. Base cations showed a more variable response at site level, with seven positive and five negative significant trends. Base cations increased in the sites where sulfate also increased. Conversely, the decrease in BC mainly occurred at acid-sensitive sites (e.g. STA, TOM, POZ, SAS and PAS).

A trend analysis of Al concentration in the lakes was not performed due to the lack of continuous data for a long period. However, even if not tested for trends, Al concentration showed a decrease in all the lakes, as an effect of acidification recovery. Nevertheless, some of

the most sensitive lakes are still affected by low pH values (below 5.7) and concentration of aluminium between 25 and 50 µg L⁻¹. As an example, trends of pH and aluminium in three highly sensitive lakes (STA, GAR, TOM) within 2000 and 2011 are shown in Fig. 4, including data recorded in early summer. In lake TOM, pH rarely fell below 5.6 and showed a tendency to increase during the study period; Al decreased from 50–100 µg L⁻¹ in 2000–2003 to values generally below 30 µg L⁻¹ in recent years. Despite the positive trend of pH in STA, pH values at snowmelt still dropped below 5.5–5.6 and aluminium increased up to 70–90 µg L⁻¹. In lake GAR, the situation is even more critical: pH has remained steadily below 5.5 during the last decade, and Al varied between 40 and 130 µg L⁻¹ (Fig. 4). GAR was one of the few lakes which were not affected by significant change in alkalinity and ANC; furthermore SO₄ decreased to a lesser extent in this lake than in others (Table 5) and BC did not change at all, highlighting the lack of a recovery pattern.

To investigate if the proportion of acidifying anions in lake water has changed in time, we evaluated the temporal trends of SO₄, NO₃ and Cl contribution to the sum of acid anions (SAA) in a group of sensitive lakes (lakes with alkalinity below 20 µeq L⁻¹) (Fig. 5). The contribution of Cl has remained stable in time, contributing between 5 and 10 % to SAA. The contribution of SO₄ has declined in most of the lakes, from 60–70 % in the 1980s to about 50 %, and

Table 5 Results of the Mann Kendall test applied to chemical data (autumn data, period 1986–2011) of 24 lakes

Lake	pH		Cond.		Alk.		SO ₄ ⁼		NO ₃ ⁻		BC		ANC	
	p	B	p	B	p	B	p	B	p	B	p	B	p	B
STA	***	0.040	***	-0.359	**	1.056	***	-1.436	**	-0.730	***	-0.997	***	0.834
TOM	**	0.025	***	-0.176	*	0.333	***	-0.822	*	-0.376	***	-0.869	*	0.565
POR	*	0.024	n.s.	0.070	*	0.864	n.s.	0.403	*	-0.474	n.s.	0.913	**	1.438
BAR	*	0.030	***	-0.081	***	0.657	***	-0.374	**	-0.259	n.s.	0.047	**	0.787
GAR	**	0.020	***	-0.126	n.s.	0.000	*	-0.221	**	-0.262	n.s.	-0.110	*	0.343
LEI	***	0.023	***	0.203	***	0.694	***	2.084	***	-0.365	***	2.589	**	0.896
MOR	n.s.	0.019	n.s.	0.061	***	0.943	***	0.298	**	-0.188	***	1.266	**	1.397
MOG	n.s.	0.011	n.s.	0.046	n.s.	0.321	**	0.374	**	-0.246	**	1.216	**	1.305
LAI	***	0.035	**	-0.111	***	0.967	***	-0.833	**	-0.452	n.s.	-0.324	***	1.114
LAS	***	0.036	**	-0.074	***	1.100	***	-0.847	***	-0.457	n.s.	0.137	***	1.636
NER	*	0.018	n.s.	0.043	***	0.858	n.s.	0.036	*	-0.168	**	1.009	***	1.519
FRO	***	0.027	n.s.	-0.040	**	0.648	n.s.	-0.160	***	-0.451	**	1.078	***	1.681
ANT	n.s.	0.017	**	-0.124	n.s.	0.555	***	-0.677	**	-0.284	n.s.	0.262	**	1.533
CRO	***	0.029	***	-0.085	***	0.772	***	-0.787	n.s.	-0.082	n.s.	-0.151	***	0.895
ORS	***	0.042	***	-0.165	***	1.168	***	-1.039	**	-0.462	n.s.	-0.175	***	1.384
SCH	**	0.025	**	-0.192	n.s.	0.667	***	-1.026	**	-0.540	n.s.	-0.593	**	1.108
POZ	n.s.	0.017	***	-0.171	*	0.600	***	-1.169	*	-0.231	**	-0.654	**	1.058
SFI	**	0.071	***	-0.153	***	0.850	***	-0.987	**	-0.403	n.s.	-0.514	**	0.970
SAS	**	0.026	***	-0.187	**	0.568	***	-0.971	*	-0.344	**	-0.667	**	0.754
ALZ	**	0.025	**	-0.087	***	1.162	***	-0.922	*	-0.240	n.s.	0.364	***	1.554
PAS	***	0.034	***	-0.111	***	0.917	***	-1.163	**	-0.407	*	-0.552	***	0.917
PAI	*	0.014	*	-0.063	**	0.959	***	-1.279	n.s.	-0.153	n.s.	-0.661	**	0.936
BOS	n.s.	0.006	***	0.624	***	4.750	***	1.353	n.s.	-0.178	***	6.176	***	4.850
BOI	n.s.	-0.008	***	0.716	***	5.272	***	2.394	n.s.	-0.133	**	8.690	**	6.313

B: trend's slope according to Sen (1968). Slope units: Cond. in microsiemens per centimetre per year; Alk., SO₄⁼, NO₃⁻, BC in milliequivalents per litre per year

n.s. not significant

*** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$ significance levels

while the importance of NO₃ has increased, at least until early 2000. In some lakes NO₃ has become the most important acidifying agent (CRO, ORS), representing 50–55 % of SSA. However, in the very last few years, a decrease in NO₃ concentrations was observed in the lakes, leading again to a prevalence of SO₄. Furthermore, some of the most sensitive lakes, like GAR and BAR, did not show any changes in the relative proportion of SO₄ and NO₃. Focusing on the last decade, when more regular data are available, it can be seen that NO₃ is often prevailing over SO₄ at snowmelt (June–July). From these data, it can be concluded that there is a general balance between the contribution of SO₄ and NO₃ to lake acidity, with a more relevant role played by NO₃ in the early

summer period, when the highest flushing of water to the lakes occurs.

3.2.3 Seasonal Changes and Interannual Variability

A subgroup of 20 lakes, located in the Swiss part of the study area, has been regularly monitored since 2000 also during snowmelt (late June or early July of each year). The differences between these values and those collected in autumn (late September and/or early October) were tested for each lake and parameter by means of a *t* test (Table 6). For most parameters (base cations, sulfate, alkalinity, SiO₂, DOC and ANC) and lakes, values at the beginning of the summer are significantly lower than in autumn (Table 3). However, H⁺ and

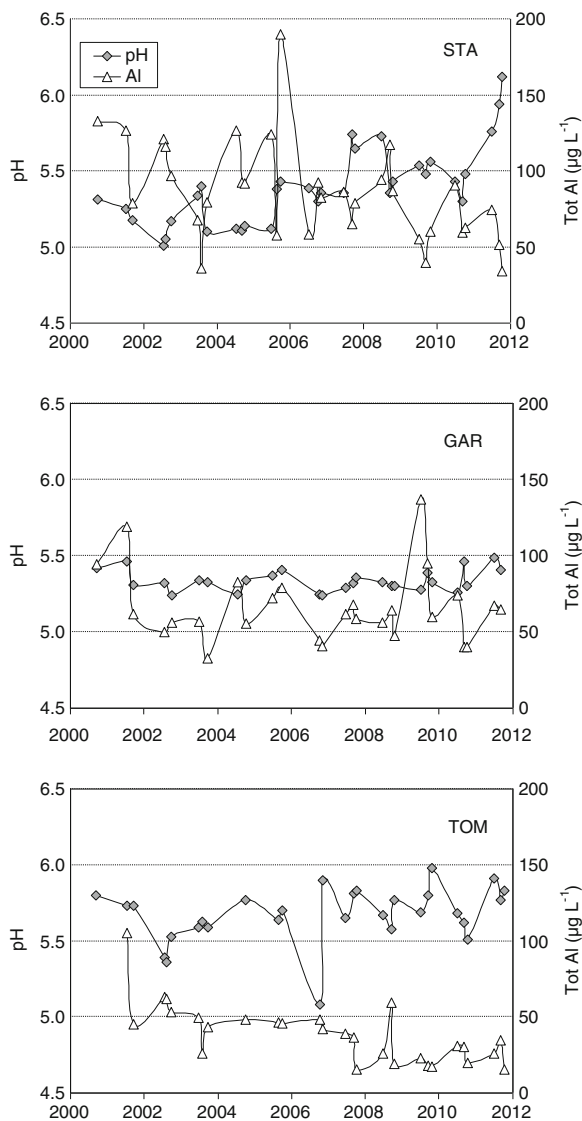


Fig. 4 Trends of pH and aluminium concentrations in the period 2000–2011 in lakes Starlaresc (STA), Gardiscio (GAR) and Tomè (TOM)

nitrate frequently have significantly higher concentrations during snowmelt. Concentrations of chloride and aluminium mostly do not show significant differences between the two periods, although aluminium concentration was higher during snowmelt in the majority of the lakes. Significant differences between early summer and autumn in SiO_2 , DOC, base cations, alkalinity, sulfate and nitrate are on average $0.13 \text{ mg Si l}^{-1}$, 0.15 mg C l^{-1} , $18 \text{ } \mu\text{eq l}^{-1}$, $8 \text{ } \mu\text{eq l}^{-1}$, $8 \text{ } \mu\text{eq l}^{-1}$, $-0.2 \text{ } \mu\text{eq l}^{-1}$, respectively. Conductivity is on average $1.55 \text{ } \mu\text{S cm}^{-1}$ higher in autumn than during snowmelt (Table 6). Lakes

classified as highly sensitive to acidification (e.g. GAR, BAR, STA, TOM) did not show significant seasonal changes in alkalinity or ANC values, which can be even lower in autumn than in summer. However, alkalinity significantly increased at the end of the summer period in lakes only moderately sensitive to acidification (average alkalinity above $50 \text{ } \mu\text{eq l}^{-1}$) and with more mineralised water (conductivity $>10 \text{ } \mu\text{S cm}^{-1}$; e.g. ANT, POR, FRO, MOG). In these lakes, base cations, sulfate and conductivity are also higher in autumn, showing a trend towards greater solute content in time.

Beside seasonal changes, lake chemistry also showed a high interannual variability. Both atmospheric deposition and meteorology also varied sharply from one year to the other (Figs. 2 and 3) with possible counteracting effects on the lakes.

The multiple regression analysis performed on selected lakes and variables (Table 7) failed to identify significant factors explaining the variability in NO_3 concentrations. In contrast, significant regression models were found for H^+ , alkalinity (two lakes), SO_4 (three lakes) and BC (one lake). SO_4 deposition was the most relevant driver of change, especially for SO_4 , alkalinity and H^+ concentrations in lake water. Climate drivers were also selected as predictive variables, even if with low significance levels. Air temperature had a positive effect on BC in PAI and a negative one on H^+ concentration in PAS. The mean summer precipitation and the length of the snow cover period influenced negatively alkalinity (LAI and PAI) and partly BC (PAI), meaning that a higher amount of snow in winter and/or more abundant precipitation in summer led to lower alkalinity and BC values in the lakes. Precipitation and snow height were also negatively related to SO_4 concentration in all four lakes (Table 7).

4 Discussion

4.1 Lake Long-Term Chemical Changes and Their Drivers

The results of the trend analysis, both at site and regional levels, highlighted a widespread chemical recovery of the studied lakes, more pronounced in highly acid-sensitive sites. The long-term trends of pH, alkalinity and aluminium showed clearer responses to decreasing acid deposition in the sites that were more severely affected by acidification in the 1980s. The

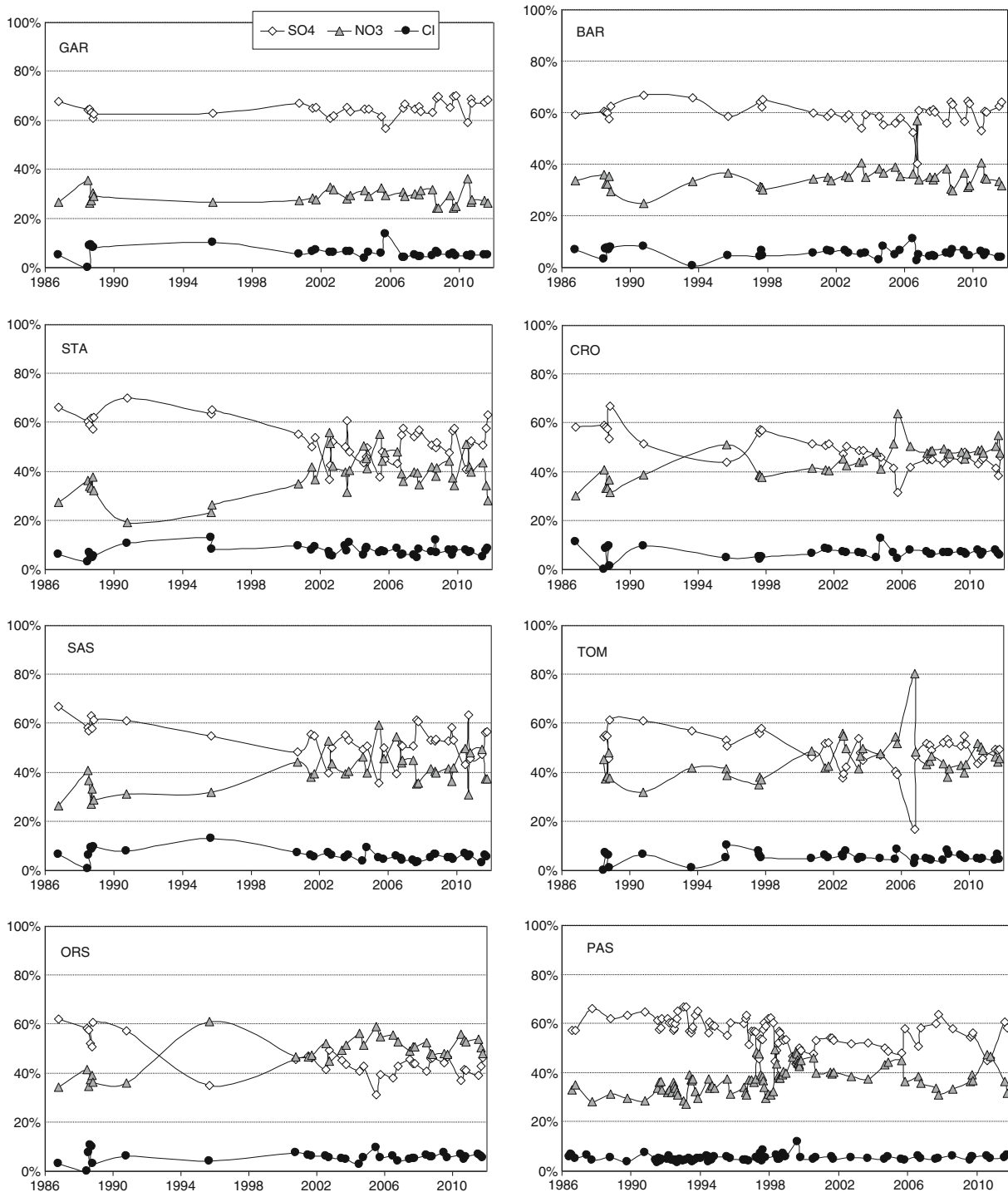


Fig. 5 Trends of the relative contribution of SO_4 , NO_3 and Cl to the sum of acid anions in eight sensitive lakes (alkalinity below $20 \mu\text{eq L}^{-1}$). For the lake acronyms, see Table 1

lake response in terms of ANC was even more evident, with significant positive trends in all the lakes and higher slopes than those of alkalinity (Table 5).

Waller et al. (2012) also detected a different response between charge balance ANC and ANC determined by Gran plot analysis (coincident with alkalinity) and

Table 6 Mean differences between the values of the main chemical variables in autumn (late September or early October) and at snowmelt (late June or early July) calculated for 20 lakes with seasonal data

	Cond.	H ⁺	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	Alk.	SO ₄ ⁼	NO ₃ ⁻	Cl ⁻	RSi	DOC	ANC
Mean diff.	1.55	-0.01	12.75	1.72	2.34	1.16	8.18	7.59	-0.23	0.11	0.13	0.15	10.49
<i>N</i> (<i>t</i> test)	14	6	16	15	13	10	14	17	4	–	13	13	12

Differences are calculated from the mean values of the period 2000–2011. The number (*N*) of significant differences according to a *t* test is also shown. Abbreviations and units as in Table 3

suggested that the increasing concentrations of organic acids were the explanation for this discrepancy. Unfortunately, long-term series of DOC data were not available to assess trend in this variable (DOC measurements only started in early 2000). Because an increase in organic acids may partly counteract the effects of acid deposition decrease, an assessment of DOC levels and trends in our lakes will warrant further investigation in the future.

The change in the deposition of acidifying compounds, mainly as sulfate, was the main driver of change for lake chemistry, as indicated by the multiple regression analysis conducted at the selected sites. According to the long-term data available for some subalpine sites in Ticino or in the Ossola Valley, it can be hypothesised that SO₄ deposition affecting the lakes decreased of more than 70 % since the 1980s. On the other hand, as the data from Domodossola show, there were no substantial changes in the deposition of N compounds in the last 25 years. A more extended analysis of long-term change of N deposition in North-Western Italy confirmed a very recent decrease, mainly due to the reduction of emissions and partly to the lower amount of precipitation occurred between 2003 and 2009 (Rogora et al. 2012).

At sensitive lakes, sulfate and base cations decreased, although only sulfate did drop significantly; this type of response, together with significant increases of pH, alkalinity and ANC, is consistent with the dominant mechanism in recovery from acidification, i.e. lower concentrations of mobile acid anions, reduced leaching of base cations from soils and decreasing concentrations of BC in lake water (Reuss and Johnson 1986).

A few lakes showed an increase of sulfate concentration, sharply in contrast with the negative trend of sulfate in atmospheric deposition. These lakes also showed increasing values of base cations and conductivity. A climate related effect can be suggested to explain such trends. Several studies showed that climate variation has to be taken into account when evaluating

the response of surface waters to decreasing deposition of acidifying compounds (e.g. Mitchell et al. 2013; Mast et al. 2011; Houle et al. 2010). Recently, some authors emphasised the prominent role that the cryosphere and, particularly, permafrost degradation processes, can have in driving lake chemical changes (Baron et al. 2009; Saros et al. 2010). Rising air temperature may cause the release of highly concentrated meltwater from active rock glaciers (RGs). In particular, the presence of RGs in the catchments has been related to the export of sulfate, heavy metals (Thies et al. 2007) and nitrate (Williams et al. 2007) to surface waters.

An analysis of the meteorological data collected in the Ticino region over more than 100 years put in evidence an increase of air temperature, especially in the last 50 years, with an average increase of 0.5 °C per decade. According to this long-term data collection, the last two decades (1990–2010) have been characterised by the highest temperature rise, and this change mainly affected spring and summer months (Meteo Svizzera 2012). Data collected in Ticino also confirmed a decrease in snowfall (evaluated through the total height of fresh snow and the number of days with fresh snow on the ground during the winter period) as well in the length of the snow cover period (Meteo Svizzera 2012). A decrease of the quantity of snow and its duration was also highlighted by a data series available for Toggia since the 1930s, in particular, the snow cover reduction seemed to be most pronounced after 1985 (Rogora et al. 2003).

As suggested in Rogora et al. (2003), climate warming might play an indirect role in lake chemical changes: the presence of less and less snow on the ground, as revealed by long-term data (Fig. 2) and a more exposed portion of the catchments lead to increasing export of weathering products to lake water. Two lakes in particular (BOS, BOI; Table 5) are characterised by the presence of small amounts of gypsum (CaSO₄ 2H₂O) in their catchments. Enhanced weathering rates of these minerals may explain the significant trend toward increasing sulfate.

Table 7 Results of multiple linear regression applied to four lakes (acronyms as in Table 1) using data of the period 1986–2011

Lake	H ⁺				Alkalinity				SO ₄			
	R ²	P value	Selected variables		R ²	P value	Selected variables		R ²	P value	Selected variables	
LAI	0.467	n.s.	–		0.576	n.s.	SO ₄ dep (-)*		0.955	***	SO ₄ dep (+)*** MSP (-)**	
LAS	0.913	**	SO ₄ dep (+)** TINdep (-)*		0.937	**	SO ₄ dep (-)* MAP (-)**** MSL (-)****		0.934	**	MS (-)* SO ₄ dep (+)*** MAP (+)*	
PAI	0.166	n.s.	–		0.619	.	MSL (-)****		0.839	***	SO ₄ dep (+)*** MAP (-)*	
PAS	0.733	**	SO ₄ dep (+)* MAAT (-)*		0.661	*	SO ₄ dep (-)*		0.610	.	SO ₄ dep (+)* MAP (-)***	
NO ₃												
Lake	R ²	P value	Selected variables		BC	R ²	P value	Selected variables				
LAI	0.459	n.s.	–			0.766	n.s.	MS (-)* MSP (-)****				
LAS	0.630	n.s.	SO ₄ dep (+)*			0.596	n.s.	–				
PAI	0.405	n.s.	TINdep (+)*			0.757	**	SO ₄ dep (+)* MAAT (+)* MAP (-)*				
PAS	0.351	n.s.	TINdep (+)****			0.388	n.s.	–				

Backward model selection based on the AIC. (*Plus sign*): direct relationship; (*minus sign*) inverse relationship

Predictive variables used: *MSAT* (mean summer air temperature), *MSP* (mean summer precipitation), *MS* (mean amount of snow in winter), *MAXS* (maximum amount of snow in winter), *MSL* (length of the snow cover period), *SO₄dep* (SO₄ annual deposition); *TINdep* (total inorganic nitrogen annual deposition)

p*<0.05, *p*<0.01, ****p*<0.001, *****p*<0.1 significance levels

In order to consider the possible role of permafrost features in the lake chemical changes, we collected information about the presence of rock glaciers (RGs) in the lake catchments. To this aim we used: (1) the RGs inventory of the Ticino alpine area (Scapozza and Mari 2010) and (2) the cryosphere map of the Piedmont Alps, in Italy. From these sources, it was possible to identify the presence of active RGs in the area of lakes LEI, MOR and MOG in Switzerland. Interestingly, all these lakes were affected by an increase of sulfate concentrations in time (Table 5). Rock glaciers were also present in the catchments of lakes CAM, BOS and BOI in Italy. For CAM only, scattered survey data are available, so that trend analysis was not performed for this lake; however, SO_4 concentrations increased from $85 \mu\text{eq L}^{-1}$ in the 1980s to about $150 \mu\text{eq L}^{-1}$ in 2007–2010. BOS and BOI were also among the lakes showing significant SO_4 increase in time (Table 5). Even if it was not possible to evaluate the extent to which the RG outflow affects the studied lakes, it can be hypothesised that the presence of RGs has a role in the SO_4 enrichment of these lakes. However, an analysis of the chemical characteristics of the outflowing water from RGs will be necessary to assess their effective role in lake chemical changes.

The widespread decrease of nitrate concentrations in the lakes can be partially justified by the change in deposition, showing slightly lower values in the last few years. Concentrations of nitrate in precipitation ($18\text{--}20 \mu\text{eq L}^{-1}$) were only slightly higher than the values measured in lakes ($14 \mu\text{eq L}^{-1}$). Furthermore, nitrate concentration was quite variable in the lakes, from a few milliequivalents per litre to about $25 \mu\text{eq L}^{-1}$.

Studies performed using isotopes demonstrated that a significant proportion of atmospheric N is cycled before reaching surface water (Campbell et al. 2009; Curtis et al. 2011). Deposition of inorganic N affects the amount of NO_3 in lakes through a combination of direct and indirect processes such as enhanced nitrification (Nanus et al. 2008). Previous studies on high-altitude lakes in the Central Alps highlighted a significant relationship between vegetation cover and NO_3 levels in lakes (Marchetto et al. 1994b). Kopacek et al. (2005) also suggested that the percentage of soil cover and vegetation type explain NO_3 variability in lakes in the Tatras. Beside catchment characteristics, in-lake processes also control NO_3 dynamics (Gerten and Adrian 2002). Lakes are typically experiencing longer ice-free periods due to climate warming, promoting greater biological productivity (Fee et al. 1992).

This could partly explain the overall decrease of NO_3 concentrations in the studied lakes. Unfortunately, no information is available on algal biomass or chlorophyll concentration in the lakes in order to assess possible changes in primary production.

Despite the general tendency towards recovery, a few very sensitive lakes (group B of the cluster analysis), showed only slight evidence of improved chemical conditions. GAR in particular did not show any trend in alkalinity. In this lake, the trend of SO_4 was also weaker than in the other sites. The catchment of this lake is characterised by the same lithology as the other lakes in the area (BAR, POR, TOM) and by similar land cover (less than 10 % of vegetation in the catchment). GAR has a small catchment (12 km^2), and it is the one located at the highest altitude among all the lakes considered (2,580 m a.s.l.): This can lead to a very limited interaction between running water and soil/vegetation, so that both rain and melting water reach the lake without significant change in their chemical composition. The average pH and conductivity of lake water (5.43 and $7.34 \mu\text{S cm}^{-1}$, respectively) are indeed very similar to those of the atmospheric deposition collected at Robiei (5.39 and $6.50 \mu\text{S cm}^{-1}$). Drever and Zobrist (1992) showed how concentrations of the major cations in surface water decreased approximately exponentially with increasing elevation in small granitic basins in southern Switzerland. Lakes located at higher altitude have usually thinner soils, higher catchment slopes, a shorter ice-free season and a lower residence time of water in contact with weatherable minerals.

A further aspect to be considered is that deposition of acidifying compounds may vary slightly from one lake to the other according to their location. Indeed, an analysis of the spatial pattern of deposition in the Ticino region identified latitudinal, longitudinal and altitudinal gradients in the deposition of acidity, sulfate and N compounds (Steingruber and Colombo 2010b). In particular, deposition was inversely related to altitude, as an effect of the increasing distance from emission sources. For such a high-altitude lake as GAR, deposition, and also trends, of SO_4 have been less pronounced compared to lower-altitude lakes. For this lake, acidic water can be a natural state, due to a combination of lithological, geographical and land cover features.

Catchment characteristics and spatial patterns of deposition and meteorology altogether contribute to explain the spatial variability of lake chemistry (and sensitivity to acidification). However, more detailed

information on the lithology of watersheds (at a fine scale) and soils (presence/absence, thickness, chemical composition) would be necessary to get an insight in the differences among the lakes.

4.2 Short-Term Chemical Variations and Episodic Acidification

Despite the overall tendency towards the improving chemical conditions in the lakes, some critical points are still to be considered. Some of the most sensitive lakes still reach low pH values which can lead to the release of Al and other toxic metals. Aluminium is relatively insoluble at pH between 6.0 and 8.0, but its solubility increases under more acid conditions ($\text{pH} < 5$) (Gensemer and Playle 1999). Even small reductions in pH, as those normally occurred during snowmelt, can increase Al solubility (Tornimbeni and Rogora 2012). According to the Canadian Water Quality Guidelines, in freshwaters with $\text{pH} \leq 6$, total aluminium concentration should be $\leq 5 \mu\text{g L}^{-1}$ to avoid toxic effects (CCME 1999). Aluminium concentrations in the most sensitive lakes considered in this study can reach 25–50 $\mu\text{g L}^{-1}$ (Fig. 4). Considering that these lakes are also affected by extremely low alkalinity values (0–5 $\mu\text{eq L}^{-1}$ as mean values of 2010–11), they can be considered still at risk of acidification.

The analysis of the effects of deposition and meteorological drivers on lake chemistry identified sulfate deposition as the primary driver of lake acidity. However, the results also emphasised the acidification effect of wet periods or snow-rich winters (Table 7). These meteorological drivers play the role of confounding factors in the response of lake chemistry to deposition, especially on a short time scale: Above-average precipitation causes a temporary decrease of BC and alkalinity in the lakes by dilution, with an overall acidification effect. Similarly, snowy winters lead to an enhanced dilution effect at snowmelt, when a huge flux of water reaches the lakes. This effect can be hardly seen in the autumn data, as those considered in the regression analysis, but it can influence conditions in early summer. Due to the limited period covered by early summer data (10 years), it was not possible to assess the relative role of deposition and meteorological drivers on the chemical conditions at snowmelt. However, we observed that most of the lakes reached relative minima of BC, alkalinity, silica and sulfate in July of 2001 and 2009. These 2 years were affected by an above-average amount of snow in the winter period

(e.g. 313 and 248 cm at Robiei as maximum height) and by a longer snow cover period (220 and 217 days per year, with respect to a long-term average of 195 days; Fig. 2). This suggests that BC, alkalinity and pH tend to be lower than average when an unusually high amount of snow accumulates in winter and persists on the ground until early summer. As an overall effect, interannual variability in meteorological conditions, especially extreme episodes (e.g. heavy rainfall and snowfall), partly counteracts the effect of decreasing acid deposition.

Our analysis failed to identify any predictor variable for NO_3 in the lakes. However, NO_3 can be an important source of acidity, especially in view of the decreasing sulfate contribution (Curtis et al. 2005; de Wit et al. 2008). When considering both deposition and lake data, it can be clearly seen that N deposition has become increasingly important in regards to its contribution to acidification compared with S deposition (Figs. 3 and 5). Previous studies in Ticino showed that streams in crystalline catchments receiving high N deposition were affected by severe episodic acidification due to the release of NO_3 during spring snowmelt (Lepori et al. 2003a, b). The significantly higher values of nitrate at the beginning of summer in most of our lakes (Table 6) compared with the autumn values are almost certainly caused by release during snowmelt. NO_3 biological uptake during the ice-free period generates alkalinity (Carignan 1985) and contributes to explain the seasonal differences in this variable too. Unfortunately, no seasonal data are available on a regular basis before 2000, so it cannot be assessed if the decreasing trend of nitrate detected at site and regional level (Tables 4 and 5) is affecting summer and autumn values in the same way. However, even if decreasing in the long-term, NO_3 is often prevailing on SO_4 as acidifying agent, especially at snowmelt; this confirms the relevant role of NO_3 in the short-term acidic pulses which still affect the lakes.

5 Concluding Remarks

The results of the trend analysis, both at site and regional levels, revealed a general pattern of chemical recovery from acidification at the study sites. Nevertheless, chemical conditions remain critical at certain sensitive sites, where alkalinity is still depleted and aluminium can reach high concentrations, especially during snowmelt. These lakes experienced the same decrease in the atmospheric input of

sulfate and acidity as the lakes that recovered to a greater extent. We hypothesised that they were characterised by a very limited, if not absent, alkalinity pool, even in pre-acidification times. The alkalinity or ANC critical limits identified at European and international level will be hardly achieved in some of our most sensitive lakes, even under the most optimistic deposition scenarios.

Overall, the results of this study emphasise the benefits of achieving emission reduction targets. Despite the current tendency toward recovery, atmospheric deposition and other global changes will probably keep influencing alpine freshwaters in the future. First of all, unless emissions will be reduced more drastically, nitrogen deposition, both as oxidised and reduced nitrogen, will probably continue to have a prominent role in the acidification processes, especially regarding short-term effects. Moreover, as this study suggests, the recovery trajectory of alpine lakes is influenced by climatic factors, such as snow cover and air temperature. Looking forward, we suggest that studies on the recovery from atmospheric deposition will need to account for a growing array of interacting climatic effects, including melting ice and permafrost.

Acknowledgements This study was supported by the Italian Ministry of the Environment and the Swiss Federal Office for the Environment through the ICP Waters Programme. We are indebted to Dr. Luca Paro (Regional Centre for Territorial and Geological Research, ARPA Piemonte) for providing us with information on the rock glaciers distribution in the Piedmont Alps. Special thanks are given to the staff of the chemical laboratories at CNR Institute of Ecosystem Study and at the Section of air, water and soil protection of Canton Ticino and to all the students and friends participating in the sampling and in the field work.

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