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Temporal and spatial patterns in the chemistry of wet deposition in Southern Alps

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HIGHLIGHTS

- A trend analysis of atmospheric deposition in an area south of the Alps is presented.
- Ammonium and nitrate deposition decreases only in the most recent period (after 2005).
- Nitrogen wet deposition is still high, ranging from 60–70 meq L^{-1} to 120–140 meq L^{-1}.
- Precipitation amount is relevant in the temporal and spatial patterns of deposition.
- Alkaline rain events markedly contribute to the deposition of base cations and alkalinity.

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ABSTRACT

In the last decades, in Europe a large effort was carried out to reduce sulphur and nitrogen emission in the atmosphere, in order to improve air quality and reduce the acidity of atmospheric deposition and the amount of nitrogen compounds it carries to terrestrial and aquatic ecosystems. This resulted in a sharp decrease in the deposition of sulphate and acidity, while until recently a decrease of the atmospheric load of nitrogen compounds was not evident.

In this paper, we focus on the subalpine and alpine areas in North-Western Italy and Southern Switzerland (Canton Ticino), receiving high deposition of atmospheric pollutants transported from emission sources in the Po Valley, one of the most urbanised and industrialised areas of Europe. Long-term studies, covering a 30-year period (1984–2014), were carried out on the chemistry of atmospheric deposition in this area and its effects on surface water bodies through a cooperation between Swiss and Italian research institutions.

A total of 14 atmospheric deposition wet-only sampling sites operate in this area, covering a wide latitudinal and altitudinal range (about 200–1900 m a.s.l.).

A spatial gradient in the deposition of sulphate and nitrogen compounds was evident both in the 1990s and in recent times (2008–2012), with highest values in the south-eastern part of the area, close to the major emission sources. Deposition also varied depending on local topography.

The analysis of long-term trends revealed a large proportion of significant decreasing trends in the concentration of both sulphate and nitrogen compounds. Deposition changes were less evident, due to the high interannual variability in the data, caused by the highly variable precipitation amount, ranging from 1200–1300 mm in dry years to 3000 mm in wet years.

Sulphate concentrations and deposition decreased steadily since the 1980s, while ammonium and nitrate showed a widespread decrease only in the most recent period (after 2006). However, nitrogen wet deposition is still high with respect to critical loads: inorganic N deposition ranges from 60–70 meq m^{-2} y^{-1} (as the sum of ammonium and nitrate) at the alpine sites to 120–140 meq m^{-2} y^{-1} at the southern lowland sites. Deposition of ammonium has acquired an increasing importance in time, especially at the southern, more polluted sites: the relative contribution of reduced N to wet N deposition passed from about 50% in the early 1990s to 56–57% in recent years.

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The observed temporal changes in nitrogen deposition followed the emission decrease but with a delay. This aspect may be relevant in monitoring the effects of emission reductions as a result of the enforcements of international and national regulations.

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1. Introduction

For many decades, human activities have caused the emission into the atmosphere of large amounts of air pollutants, such as sulphur (S) and nitrogen (N) oxides and ammonia (NH_3). These compounds are transformed in the atmosphere to sulphuric and nitric acid and to ammonium (NH_4), which become important components of the ionic content of atmospheric deposition. The resulting ions, i.e. nitrate (NO_3), sulphate (SO_4) and ammonium, may have two different effects on natural and artificial receptors, such as forests, lakes, cultivated land and buildings. They can directly cause water and soil acidification and/or damages due to the acidity of nitric and sulphuric acid or indirectly, because ammonium generates acidity by nitrification and assimilation (Rodhe et al., 2002). Nitrogen compounds also act as nutrients for plants and algae, stimulating growth and causing eutrophication in coastal waters and nutrition unbalance in forest trees (Rabalais, 2002; Aber et al., 1998; Fenn et al., 1998).

Efforts to reduce the effects of acid and N-enriched deposition have led to the definition of protocols for the reduction of their emission through the Convention on Long-range Transboundary Air Pollution. As an effect of emission regulations, rates of acid and N deposition have decreased since the 1980s and 1990s, respectively, across large portions of North America and Europe (e.g. Shannon, 1999; Waldner et al., 2014).

In particular, in both Italy and Switzerland, emissions of sulphur dioxide (SO_2) reached its maximum between 1965 and 1980, while nitrogen oxides (NO_x) peaked around 1985. From 1980 to 2012, the decrease of anthropogenic sulphur and nitrogen oxides emissions in Switzerland was 90% and 59%, respectively. The reduction in emissions of anthropogenic ammonia was much lower: 25% with respect to 1980 (Heldstab et al., 2014). In Italy, emissions decreased similarly, by 90%, 58% and 14%, respectively for SO_2, NO_x and NH_3 compared to the values in 1990 (Romano et al., 2014). The reduction of SO_2 emissions has been mainly caused by a reduction of the sulphur content in heating oils and the partial substitution of sulphur rich coal with other fossil fuels, while the decrease of NO_x emissions has been mainly determined by the equipment of cars with catalytic converters and stationary combustion sources with DeNOx-systems (Steingruber, 2015a, b). Agriculture is by far the main source of NH_3 emissions (95% of the total). Emissions from agriculture have decreased because of the reduction in the number of animals, the trend in agricultural production and the introduction of abatement technologies due to the implementation of the EU IPPC Directive (Romano et al., 2014).

As an effect of decreasing emissions, a substantial reduction in sulphate and acidity (H^+) deposition has occurred in Italy and Switzerland, as in most of Europe (Waldner et al., 2014; Karlsson et al., 2011). Deposition of oxidized and reduced nitrogen has not changed to the same extent, showing a slight tendency to decrease only in the 2000s (Rogora et al., 2012; Steingruber, 2015a).

An extensive network for the study of atmospheric deposition chemistry exists in the area of Lake Maggiore watershed, located between North-Western Italy and Southern Switzerland (Canton Ticino). Surface water chemistry has been monitored in this area since the late 1970s (Mosello et al., 2001; Barbieri et al., 2004), while wet-only deposition sampling sites have operated since the 1980s with collaborations from Swiss and Italian research institutions to better understand the effects of atmospheric deposition on surface waters. Selected sites (alpine lakes and subalpine rivers) have contributed data to ICP Waters (International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes; Mosello et al., 2001).

Of particular interest in this area are the long-term trends of nitrogen compounds in both atmospheric deposition and surface water (Barbieri et al., 2004; Rogora et al., 2012) to assess the possible ecosystem impacts of atmospheric N inputs. Indeed, previous studies pointed out an advanced stage of N saturation of several catchments in the subalpine areas, with consequent NO_3 release to surface water (Rogora, 2007). Lake Maggiore itself experienced an increasing trend of NO_3 concentration since the 1990s, mainly due to the atmospheric input (Rogora et al., 2006). A reversal was detected in the last decade, when decreasing trends of NO_3 were observed in several rivers and lakes in response to changing deposition (Rogora et al., 2012). The situation also improved as regards the acidifying effect of NO_3 and SO_4 on sensitive ecosystems such as high altitude lakes; however, the situation may still be critical at a few sites at snowmelt, when the very limited alkalinity pool of these lakes can be depleted (Rogora et al., 2013).

Previous research on atmospheric deposition in the Lake Maggiore area has focused on effects on surface waters (acidification and N enrichment; Mosello et al., 2001; Rogora et al., 2012; Steingruber and Colombo, 2010) and tended to have a narrow focus in space (only a few sites). Spatial and long term temporal trends are lacking in the current body of literature from this region and episodic inputs like those associated with Saharan dust events (Rogora et al., 2004) have not been comprehensively examined even though they can have significant impacts on ecosystems in remote areas (Psenner, 1999; Hannes et al., 2014).

In this paper, we analyse long-term data available at the Italian and Swiss sites, with the aim to assess if there has been a widespread and coherent response of deposition in the area of Lake Maggiore to emission changes. To this aim, (i) we assess trends of precipitation volume and of the main chemical compounds, both as concentration and deposition, at each site; (ii) we evaluate trends at a regional level, by identifying the main temporal patterns for H^+, SO_4, NO_3, NH_4 and base cations; (iii) we assess spatial trends and geographical gradients in SO_4 and N deposition; (iv) we analyse short term changes in the chemistry of precipitation at one of the study sites, where sampling is performed after each precipitation event, focusing on the role of alkaline events in the total input of alkalinity and base cations to ecosystems. Finally (v), we compare the emissions of S and N compounds affecting the study area with measured deposition to assess the relative role of emissions and meteorology (precipitation volume) in deposition change.

2. Study area and methods

The watershed of Lake Maggiore is an area of about 6600 km^2, shared almost equally between Italy and Switzerland (Fig. 1). This area receives a high amount of orographic precipitation and

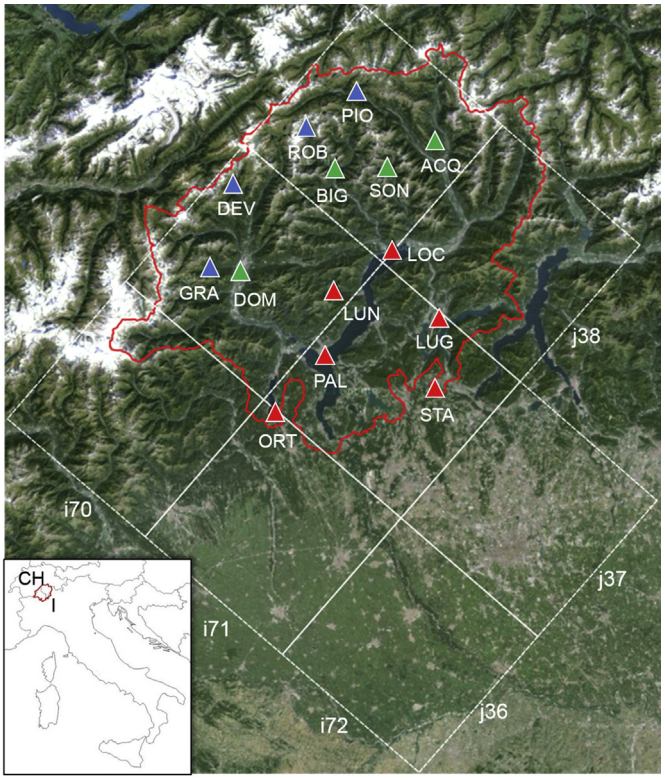

Fig. 1. Location of the study area (watershed of Lake Maggiore, in red) and of the 14 atmospheric deposition sampling sites (triangles). Acronyms as in Table 1. The 50 × 50 km EMEP (European Monitoring and Evaluation Programme) grid cells considered for emission calculation are also shown. Red, green and blue triangles represent low-altitude south-eastern (L), mid-altitude (M) and high-altitude north-western (H) sites, respectively (see Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

deposition of pollutants, due to its location at the foothills of the Alps, in proximity of the most industrialised part of Italy, the Po Valley, which includes cities such as Milan and Turin (Mosello et al., 2001). The mean precipitation amount in this area is high (1720 mm per year as average value for the period 1978–2008), with the highest amount occurring in autumn (550–600 mm during the whole season) and the lowest in winter (200–250 mm) (Rogora et al., 2012).

Monitoring of atmospheric deposition in the area of Lake Maggiore watershed started, in the 1980s, at 9 sites. A few sites were included in the network at a later stage (between 1990 and 2001; Table 1). In this paper we considered 14 sites in total, with continuous data series and with data covering at least 10 years: 6 of them are located in Italy (Pallanza, Lunecco, Orta, Domodossola, Graniga, Devero) and 8 in Switzerland (Acquarossa, Bignasco, Locarno-Monti, Lugano, Robiei, Piotta, Sonogno, Stabio) (Table 1, Fig. 1). Sampling sites span a wide latitudinal and altitudinal range (200–1900 m a.s.l.). They can be divided into three categories according to their location and their proximity to the main emission sources, located south-east of the Lake Maggiore watershed: low-altitude south-eastern sites (L), mid-altitude sites (M), and high-altitude north-western sites (H) (Table 1; Fig. 1).

Sampling frequency was weekly at all the sites, with the exception of Pallanza, where sampling and analysis were performed after each rain event. Deposition samples were analysed for pH, conductivity, alkalinity, ammonium, main cations (calcium, magnesium, sodium, potassium) and anions (sulphate, nitrate, chloride). All the analysis were performed on filtered samples (0.45 μm). Samples from Italian and Swiss sites were analysed at the chemical laboratories of the CNR Institute of Ecosystem Study (CNR ISE) in Verbania Pallanza and of the Territory Department of Canton Ticino in Bellinzona, respectively. The analytical methods and QA/QC adopted in the two laboratories are described by Tartari and Mosello (1997), Steingruber and Colombo (2010) and Steingruber (2015a). The analytical quality and the comparability of the data provided by the two laboratories were guaranteed by regular participations in intercomparison exercises (e.g., Dahl, 2012).

Monthly, yearly and 5-years mean concentrations were calculated by weighting weekly concentrations with the sampled precipitation volume. Monthly and yearly deposition values were calculated by multiplying monthly and yearly concentration weighted means by the precipitation amount for the same period.

We analysed trends at site level for key variables (precipitation, H^+, alkalinity, sulphate, nitrate, ammonium, base cations: $Ca^{++} + Mg^{++} + Na^+ + K^+$) by means of the Seasonal Kendall Test (SKT; Hirsch et al., 1982), with the approach described in Marchetto et al. (2013). The analysis was applied to the data of the period 1988–2014, (1990–2014 for STA, ACQ and PIO; 1994–2010 for GRA), divided into two sub-periods (1988–2000 and 2001–2014). According to Waldner et al. (2014), time series of about 10 years are required to detect significant trends in deposition data. For this reason, in the trend assessment for the first period we only included sites with at least 10 years of data (9 sites; Table 1). All trend analysis were calculated in R 3.0.2. (R Core Team, 2013) with the CRAN package "rkt" ver. 1.4 (Marchetto, 2015).

To assess trends on a regional basis and to evaluate the presence of common temporal patterns at the various sites, we applied the min-max autocorrelation factor analysis (MAF; Zuur et al., 2007) to the time series of SO_4, NO_3, NH_4 and base cations concentration and deposition. A subgroup of 9 sites with data available since the late 1980s or early 1990s was considered for this analysis (Table 1). MAF is a type of principal component analysis (PCA) in which the axes represent a measure of autocorrelation and give an indication of the association between variable Y_t and Y_{t+k}, where k is a time-lag (k = 1, 2, …). This technique is particularly suitable for relatively short (15–25 years), non-stationary multivariate time-series (Solow, 1994; Zuur and Pierce, 2004). It can be used to extract and identify common trends (axes) from multiple time-series. The axes are independent and an autocorrelation coefficient (Ac) and a significance level (p-value) can be estimated for each of them (Zuur et al., 2007). Similarly to the factors in a PCA, axes can be interpreted as the main components describing the temporal variability in the data. For each variable, we identified the most significant axis for both concentration and deposition data and plotted the axis score against time. An Ac value was also provided for each axis: this can be interpreted as a measure of the level of autocorrelation among the time series. This analysis was performed with the software Brodgar vers. 2.5.6 (Highland Statistics Ltd).

Maps of precipitation and deposition of SO_4, NO_3 and NH_4 were calculated for the 5-year periods 1993–1997 and 2008–2012. We used 5-year average data to reduce the effect of the high inter-annual variability in deposition, due to the highly variable precipitation amount recorded in different years (Rogora et al., 2012). Deposition maps were obtained by multiplying precipitation maps with concentration maps. The former were obtained on the basis of a network of over 110 meteorological stations spread over the study area (Mosello et al., 2001). The latter were obtained calculating concentration values as a function of latitude, longitude and altitude, based on multiple linear regression equations describing concentrations as a function of the three parameters above, as described in Steingruber (2015a). All maps have a resolution of 1 km × 1 km and were produced using QGIS Version 2.14.0.

Table 1
Main characteristics of the atmospheric deposition sampling sites and results of the trend analysis by Seasonal Kendall Test (SKT) applied to monthly data of concentration and deposition. §: Sites with the longest data series (included in the MAF analysis). I: Italy; CH: Switzerland. Cat: category of the site (L: low-altitude south-eastern sites, M: mid-altitude sites, H: high-altitude north-western sites). Prec: precipitation amount. Alk: alkalinity. BC: base cations. Blue: negative trends. Red: positive trends. Level of significance: $^{***}p < 0.001$; $^{**}p < 0.01$; $^{*}p < 0.05$.

Station	Cat.	Acronym	Country	Altitude (m a.s.l.)	Data since	Periods for trend analysis	Prec	Concentration						Deposition					
								H^+	NH_4	Alk	SO_4	NO_3	BC	H^+	NH_4	Alk	SO_4	NO_3	BC
Pallanza§	L	PAL	I	208	1984	1988-2000		***		*	***		*	**		**			
						2001-2014		***	***	**	***	***	***	*	*	**	***	**	
Domodossola§	M	DOM	I	270	1986	1988-2000		***		**	***	*	***	***		**	***		**
						2001-2014		***	***	**	***	***	**	*		**	**	*	
Lugano§	L	LUG	CH	350	1982	1988-2000		***		**	***		*	***	**	***			
						2001-2014		**	***		***	***	***	*	***	*	***	***	***
Stabio§	L	STA	CH	353	1990	1990-2000	**	***		***	***	**	**	*		***			
						2001-2014		***	***	***	***	***	***	***	*	***	***	*	
Orta§	L	ORT	I	360	1984	1988-2000	**	***		***	***			**	*	***		**	**
						2001-2014		***		*	***	***		*		**	*		
Locarno-Monti§	L	LOC	CH	380	1982	1988-2000		***		***	***		**	***		***	***		
						2001-2014	*	***	***	**	***	***	**	***		**	***		
Lunecco§	L	LUN	I	415	1988	1988-2000		***		**	***			*		***			
						2001-2014	*	***	***	***	***	***		***		***	*		***
Bignasco	M	BIG	CH	443	2001	2001-2014		***		***	***	**	*	**		***	**		
Acquarossa§	M	ACQ	CH	575	1990	1990-2000		***		***				***		***			
						2001-2014					***	***	***				***	*	***
Sonogno	M	SON	CH	918	2001	2001-2014		***		***	***	**		***		***	*		
Piotta§	H	PIO	CH	1007	1990	1990-2000		***		*	*			**		*			
						2001-2014		***	***		***	***		*		*	**	*	
Graniga	H	GRA	I	1080	1994-2010	2001-2010		**	*		***	**	*				**		
Devero	H	DEV	I	1634	1996	2001-2014		**	***		***	***	***		**		**	***	**
Robiei	H	ROB	CH	1890	1996	2001-2014		***	***	**	***	**		*	**	***	**		

Emission data for SO_2, NO_x and NH_3 were downloaded from the EMEP (European Monitoring and Evaluation Programme) activity data and emission database (WebDab) at http://www.ceip.at/. We calculated average emission values from 8 cells (Fig. 1), 6 of which partly included in the study area (watershed of Lake Maggiore). Two further cells (i 72 j 36 and i 72 j 37), located south of the watershed and including the major emission sources, were also considered, to get a more reliable estimate of the emission affecting the deposition on the study area.

3. Results and discussion

3.1. Long-term trends in precipitation amount and rain chemistry

The study area is characterised by a very irregular distribution of precipitation, due to the complex topographic pattern (Fig. 2). As an example, the average annual precipitation during the period 2008–12 ranged from 800–900 to above 2000 mm y^{-1}. Despite the presence of local maxima and minima, mainly due to geographical features, the driest zones are located in the western part of the area, where the highest mountains are located (Massif of Mount Rosa), while the wettest zones are situated in the central part, on Lake Maggiore and its shores.

A wide variability in precipitation can be observed also from the temporal point of view (Fig. 3a): the long-term trends of yearly precipitation at the study sites show coherent patterns and a very high inter-annual variability. As an example, annual average values vary between 600 and 2000 mm at Piotta and between 1000 and 3000 mm at Pallanza. No clear trend can be seen from the data, as put in evidence also by detailed analysis of precipitation time series available in the study area (Ambrosetti et al., 2006; MeteoSvizzera, 2012). Other studies (Andersson et al., 2007; Kryza et al., 2012) confirmed that meteorology and particularly precipitation quantity can lead to an interannual variability of SO_4 and inorganic N deposition up to 20%. Our study showed that this variability can be much higher: considering sulphate, for instance, which concentration has remained stable in the last 10 years, deposition may differ up to 40% from one year to the other (Fig. 3e).

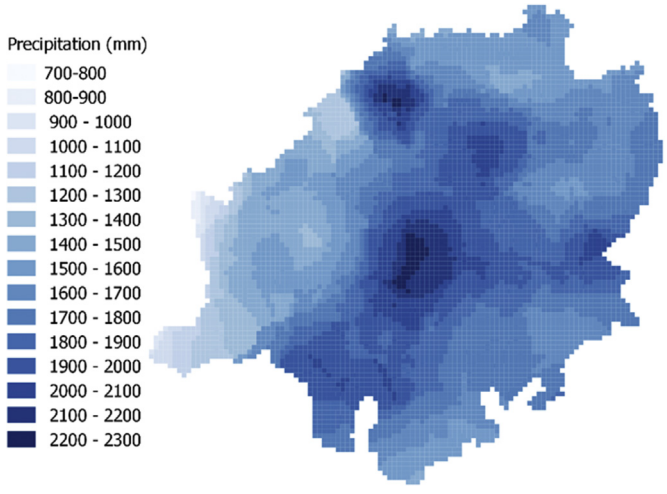

Fig. 2. Map of precipitation (mm) over the study area. Average values of the period 2008–2012. Data from about 110 meteorological stations.

Trends of yearly volume weighted average concentrations of the main chemical compounds at the 14 study sites are shown in Fig. 3.

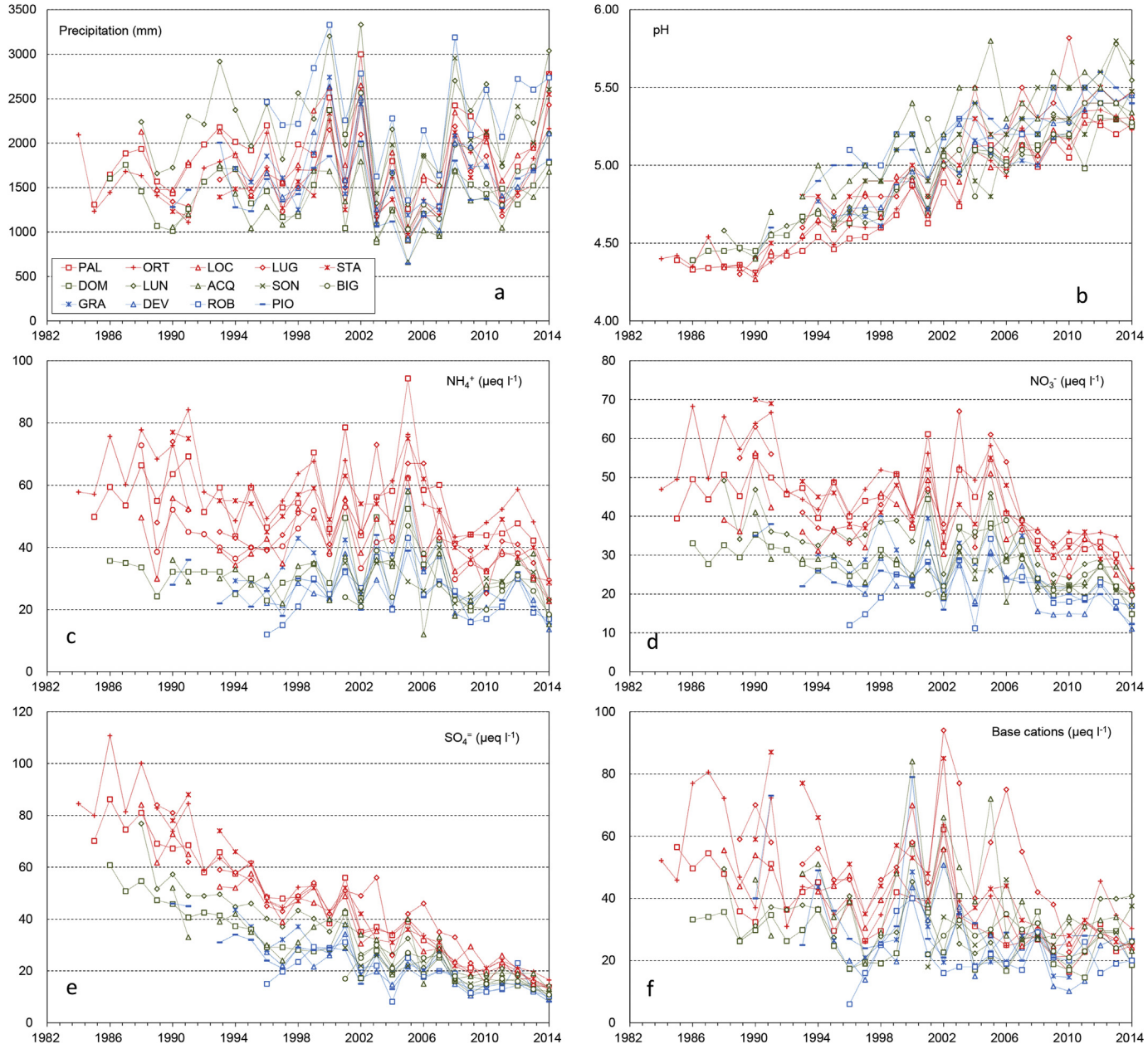

Fig. 3. Trends of yearly average precipitation (a) and concentration (µeq L^{-1}) of the main chemical compounds at 14 sites in the period 1988–2014: (b) pH; (c) ammonium; (d) nitrate; (e) sulphate; (f) base cations. Red lines: low-altitude south-eastern sites (L in Table 1); green lines: mid-altitude sites (M in Table 1); blue lines: high-altitude north-western sites (H in Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Sites were divided into three categories according to their location (Table 1), from the lowland southern sites to the alpine ones, to better identify possible gradients.

As for the amount of annual precipitation, concentrations were highly variable form one site to the other, even though coherent patterns can be detected from the data. In general, the highest concentrations of both sulphur and nitrogen compounds, and the lowest pH, are recorded at the sites located in the central southern part of the area (e.g. Pallanza, Orta, Locarno, Lugano) while the lowest at the northernmost and highest sites (Devero, Robiei, Piotta). For instance, nitrate and ammonium varied from 15–20 and 20–25 µeq L^{-1}, respectively, at the alpine sites to 30–35 and 45–50 µeq L^{-1} at the subalpine stations (Fig. 3c, d). Beside altitude, the location of the sites with respect to the major emission sources, located South-East of Lake Maggiore watershed (e.g. the metropolitan area of Milan), also affected the concentration of pollutants. For instance, the site DOM (270 m a.s.l.) is characterised by fairly lower concentrations of SO_4 and N compounds with respect to stations located at similar altitude or latitude (e.g. PAL, ORT, LOC, LUG): this is due to the location of DOM, westernmost than the other sites and partly sheltered by the mountains from the main trajectories of polluted air masses.

Sulphate concentrations, which have steadily decreased during the study period, were much more variable among the sites in the 1980s and 1990s (40–80 µeq L^{-1}) with respect to the 2000s, when concentrations were between 15 and 20 µeq L^{-1} at all the sites (Fig. 3e). pH values increased of more than 1 unit in the 30-year period, from values below 4.5 at the southern, most affected sites

to values slightly below 5.5 (Fig. 3b). Differently from sulphate and pH, nitrogen compounds did not show a coherent trend: concentrations were fairly stable in the 1980s and 1990s, with sharp interannual variability, particularly evident in the early 2000s. A tendency towards lower and more consistent concentrations can be seen only after 2006, both for ammonium and nitrate (Fig. 3c, d).

Base cations showed the most scattered distribution of concentrations: no clear trend or coherent pattern emerged from the data. However, lower concentrations were detected in the second half of the period (after 2000) at most sites i.e. 20–30 μeq L^{-1} as average values with respect to 40–60 μeq L^{-1} in the 1980s and 1990s (Fig. 3f).

In general, pH, SO_4 and partly NO_3 concentrations showed a more limited spreading among the sites than NH_4 and base cations. The latter variables are indeed more subject to the effects of local emission sources, such as farms and livestock in the case of reduced N (Waldner et al., 2014) or cement manufacturing and wind-blown dust from soils for base cations (Lee et al., 1999).

A further contribution to base cation in rain samples may be the input of dust, usually of Saharan origin, with a high content of calcium and bicarbonate. For instance, high base cations concentrations were recorded in 2000 and 2002, in particular at the south-eastern sites (e.g. LOC, LUG, ACQ; Fig. 3f). In these years, alkaline rain events (pH above 6.5, relatively high concentrations of alkalinity and base cations, mainly as calcium) were more frequent than usual (Steingruber, 2015a).

When considering the relative contribution of oxidized and reduced N to wet N deposition, it can be seen that ammonium is presently the dominant form of N in deposition and its importance has progressively increased in time (Fig. 4): the relative contribution of the two forms of N changed from 50% in the early 1990s to 56–57% and 43–44% for NH_4 and NO_3, respectively, in recent years (average values for the 9 sites with the longest data series). The highest relative increase in NH_4 compared to NO_3 deposition was detected at the southernmost sites (e.g. PAL, ORT) which bear the greatest impact of the emission of reduced N from agricultural and stock rearing activities in the Po Valley (Rogora et al., 2012).

3.1.1. Single site trends

Statistical significance of temporal trends was assessed using the SKT applied to monthly data (Table 1). In particular, we evaluated trends for each variable and site, splitting the time series into two periods, from 1988 (1990 for three sites) to 2000 and from 2001 to 2014 (2010 for one site).

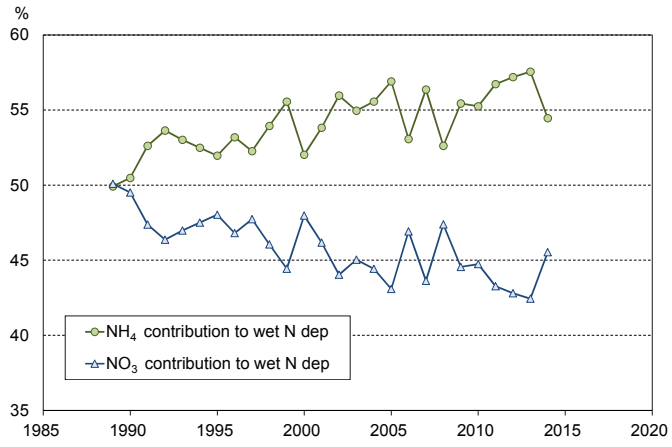

Fig. 4. Long-term trends of the percent contribution of oxidized (NO_3) and reduced (NH_4) nitrogen wet deposition (average values from 9 sites with the longest data series).

Precipitation amount did not show any trend, with the exception of a slight increase at a few sites. The decrease of acidity and sulphate concentrations affected the majority of the sites both in the 1980s/1990s (8 out of 9 sites) and in the 2000s (13 out of 14 sites). A more widespread decrease in the 2000s can be seen for ammonium and nitrate concentrations: ammonium did not change at any sites in the 1980s and 1990s, while a negative trend was detected at 10 sites in the 2000s. Similarly, nitrate was essentially stable in the first period, while a significant decrease affected all the sites in the second one. Alkalinity increased in most of the sites, but with a higher significance at the southern lowland sites than at the high altitude ones. Base cations showed a tendency towards decreasing concentrations, more evident in the 2000s and at the lowland stations.

Rain acidity decreased as a response to decreasing concentration of strong acids (H_2SO_4 and HNO_3) in rain samples; this also favoured increasing concentration of alkalinity, especially at the most impacted sites (Table 1). In fact, positive values of alkalinity were rarely measured in the 1980s, when the alkalinity pool was fully depleted by the high levels of acidity (pH values were close to 4.5 and acidity ranged between 60 and 90 μeq L^{-1}). Positive values of alkalinity became common in rain samples only in the 2000s, with average annual values around 10 μeq L^{-1}. Base cation concentrations also changed in response to acidity levels: neutralization of H^+ by the dissolution of soil dust (e.g. $CaCO_3$) explains the higher concentrations of calcium and the other base cations in the 1980s and 1990s with respect to the recent period (Fig. 3f). However, base cations concentrations may be also affected by local sources and by the long-range transport of soil dust (see paragraph 3.3).

In general, trends of deposition were less evident than those of concentrations, as can be expected from the dependency of deposition values from precipitation. Deposition showed a consistent response only in the case of alkalinity (increasing), acidity and sulphate (decreasing) (Table 1).

3.1.2. Regional trends

To extract the main temporal patterns from concentration and deposition data and to assess the level of temporal coherence among sites, we performed a MAF analysis. The main axis extracted for each variable is shown in Fig. 5, together with the autocorrelation coefficient (Ac) and the significance level.

In general, higher autocorrelation or coherence among the sites were found for concentrations, as can be expected from the higher site-to-site variability in deposition values. The most coherent patterns, according to the Ac coefficient, were found for acidity and sulphate, for both concentration and deposition (Fig. 5a, b), and base cations concentrations (Fig. 5e). On the other hand, the lowest level of autocorrelation among the sites was found for ammonium (Fig. 5d). Ammonium concentration and deposition are more subject to the effect of local emission sources (Waldner et al., 2014); furthermore, emissions from agricultural land in the form of NH_3 are themselves strongly influenced by local weather conditions (Wichink Kruit et al., 2012). As a result, temporal patterns of NH_4 deposition differed more among sites (Fig. 3d).

Regarding the shape of the trends, acidity and sulphate showed a quite regular decrease, with a tendency towards stable values in the last few years (Fig. 5a, b). Indeed, pH values and SO_4 concentration are no more changing at the study sites since 2010 (Fig. 3b, e). Trends of nitrogen compounds were much more irregular, with a shift towards lower concentrations after 2005 and a further decrease in the last 2–3 years of the record (Fig. 5c, d). Deposition showed a temporary increase in 1998–2002, as an effect of a sequence of rainy years, then moved towards values lower than those of the 1990s. Similarly, base cations deposition peaked

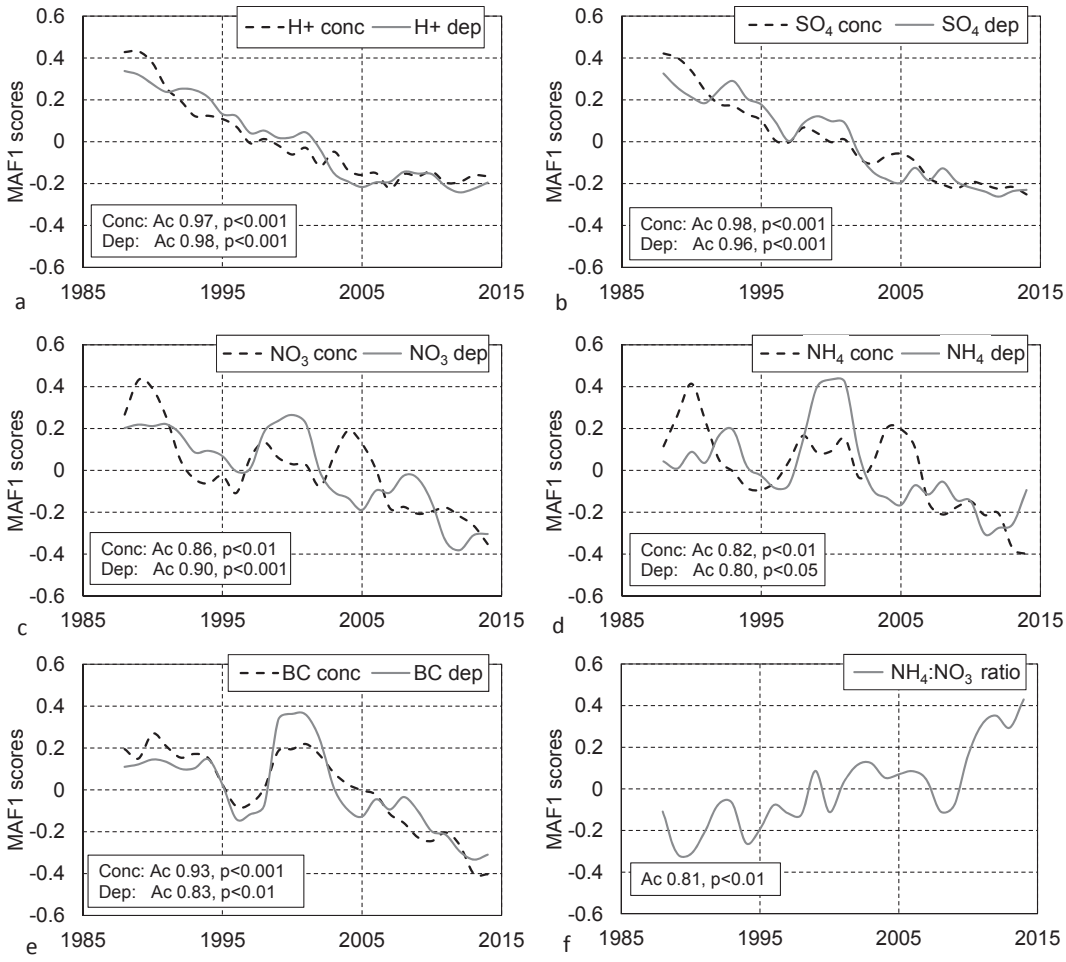

Fig. 5. Main axis extracted for each variable from the time series of 9 sites for concentration and deposition by means of the MAF analysis (see text). Autocorrelation coefficient (Ac) and p-values are also shown. (a) acidity, (b) sulphate; (c) nitrate; (d) ammonium; (e) base cations (BC); (f) ratio between nitrate and ammonium.

around year 2000 (Fig. 5e), as a combined effect of high precipitation amount and above average concentrations recorded in 2000 and 2002 at most sites (Fig. 3f). A positive trend can be seen for the NH_4 to NO_3 ratio, in particular in the last few years (2007–2014): this confirms the increasing importance of reduced N deposition at a regional level.

3.2. Spatial pattern of deposition

Deposition maps were calculated for SO_4 and N compounds over two 5-year periods: 1993–1997 and 2008–2012 (Fig. 6). Nitrogen deposition showed the highest values in the south-eastern part of the area (about 65–70 and 85–100 meq m^{-2} y^{-1} for NO_3 and NH_4, respectively, in 2008–2012) and the lowest in the north-western part and at the highest altitude (25–35 and 35–45 meq m^{-2} y^{-1}, respectively; Figs. 7 and 8). A similar, even sharper gradient can be seen for sulphate deposition, varying from 40–50 meq m^{-2} y^{-1} in the South to 10–15 meq m^{-2} y^{-1} towards the North. These gradients are a direct effect of concentrations (higher values in the south-east, closer to the main emission sources, and lower values in the north-west, at higher altitude). However, the spatial pattern of deposition is also affected by the irregular distribution of the amount of precipitation in the area, with local maxima near the topographic highs (Fig. 2).

Gradients became less and less evident in time: for sulphate, in particular, a gradient of about 100 meq m^{-2} y^{-1} may be seen in the 1990s (from 10–20 meq m^{-2} y^{-1} in the Alps to 110–120 in the subalpine areas), while deposition is presently between 10 and 40 meq m^{-2} y^{-1}. Similarly, much less sharp gradients are observed for NO_3 and NH_4 in 2008–12 with respect to the 1990s (Fig. 6). This is a consequence of the declining concentrations of acidifying compounds observed in the last two decades, which affected in particular the more polluted southern sites.

3.3. Alkaline events and their role in the input of alkalinity and base cations

Single particularly intense rain events with alkaline characteristics can heavily influence yearly mean base cations concentrations and acidity. Exceptionally high calcium and alkalinity concentrations were observed for example at ACQ, LOC, PIO in October 2000 and at LOC, LUG, STA in November 2002. In both cases extreme rainfall amounts were also measured (between 400 and 700 mm per month), so that the overall deposition of calcium and alkalinity in these months was fairly above the average values.

To better investigate the role that outlying events may have in the acidity/alkalinity input from atmospheric deposition, we considered the long-term data series of Pallanza, where sampling and analysis are performed after each precipitation event. To identify events with striking chemical characteristics, we selected events with pH, calcium and alkalinity concentrations above the 90 percentile for the period 2000–2014 (6.6 pH unit, 52 and

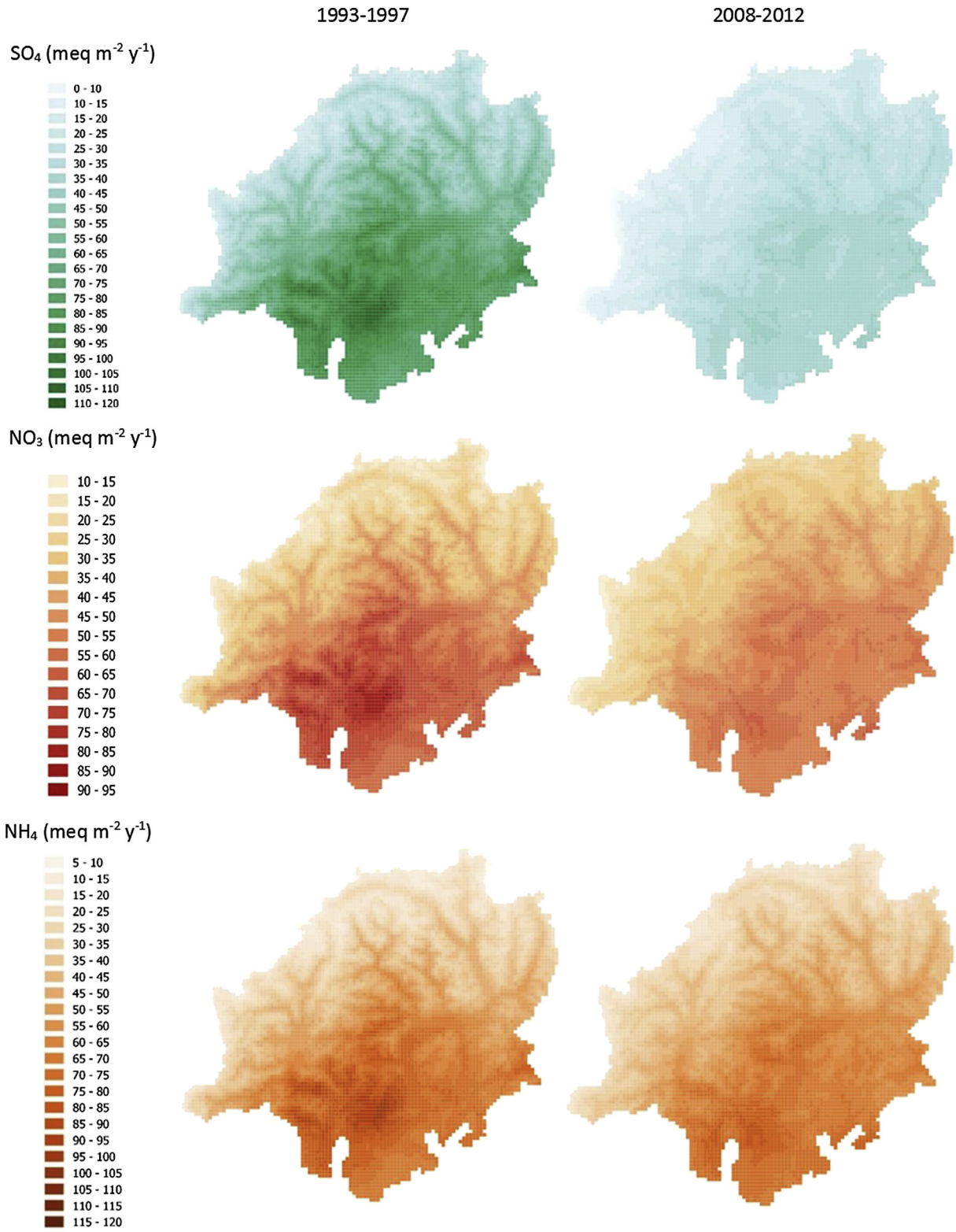

Fig. 6. Maps of SO_4, NO_3 and NH_4 deposition over the study area in the 1990s compared with the recent period (2008–12).

40 μeq L^{-1}, respectively). In total, 26 out of 689 rain events were identified. Eleven of the selected events were characterised by the presence of red dust on the filter used in the sample preparation, which can be assumed as an index of the presence of Saharan dust (Rogora et al., 2004). The alkaline events occurred with a varying frequency from one year to the other, from a minimum of one to a maximum of 4 events per year, and mainly in late spring and early summer (May–July). We calculated the contribution of these events to the total deposition of calcium, base cations and alkalinity on annual basis (Fig. 7). Even if rare, these events proved to be

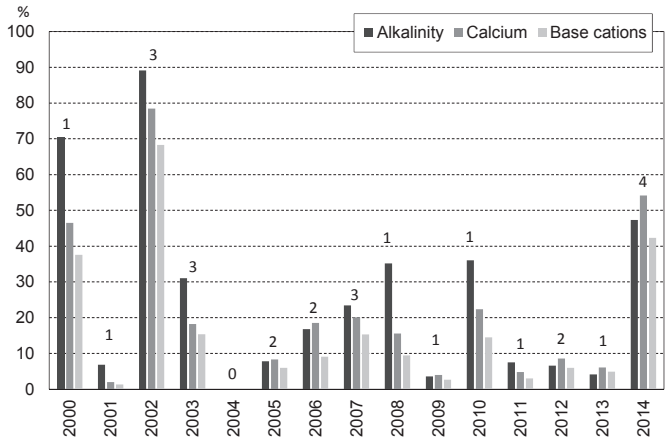

Fig. 7. Percent contribution of alkaline events (selected on the basis of pH, alkalinity and calcium concentrations; see text for the criteria) to the annual deposition of alkalinity, calcium and base cations at the sampling site of Pallanza. The number of alkaline events recorded in each year is also shown.

extremely important from the point of view of alkaline inputs: in some years (e.g. 2000, 2002, 2014) the calcium and alkalinity load associated to these events was more than 50% of the total. Considering the period 2000–2014 as a whole, the alkaline events altogether contributed to 39 and 30% of the alkalinity and calcium deposition.

3.4. Deposition response to emission changes

To assess the relationship between emission and deposition change, we considered the emissions of SO_2, NO_x and NH_3 affecting the study area (Lake Maggiore watershed plus the region South of it, including the metropolitan area of Milan and part of the Po plain; Fig. 1). Emission data are available for 5 year periods since 1990; we compared these data with deposition (also 5-year averages) obtained as mean values from the 9 sites with the longest data series (Fig. 8).

The SO_2 emission affecting the study area almost halved in the first half of the 1990s; a further decrease was observed between 1995 and 2000, then emission levelled off. The overall decrease of SO_2 emission in 2010 compared to 1990 was more than 80%. A much less evident change affected the emissions of NOx and NH_3 (38 and 26%, respectively over the whole period). The effect of technical measures adopted by industry, traffic and agriculture resulted in a clear decrease of S and N emissions in the 1980s and 1990s; then changes became marginal in recent years. Furthermore, increasing traffic partly counteracted the effect of stricter emission norms for vehicles (Verstraeten et al., 2012).

Decrease of N emission began in 1990 (1995 for NH_3). However, deposition at our sites started to decrease only after 2005. A similar situation, with a time lag between emission and deposition change, have been reported also elsewhere (Karlsson et al., 2011; Kernan et al., 2010) and ascribed in some cases to non-linearity in atmospheric chemistry (Fowler et al., 2007; Fagerli and Aas, 2008). Interactions between the different pollutants, variability in precipitation regime, changes in the relative amount and lifetime of the chemical species and in gas-particle partitioning altogether may explain the lack of correlation between emission and deposition trends. For instance, the large decrease in SO_2 emission occurred in the last 20 years may have led to a shift in the equilibrium between nitric acid and ammonium nitrate, contributing to nonlinearities in the oxidized nitrogen budget (Fagerli and Aas, 2008; Fowler et al., 2005).

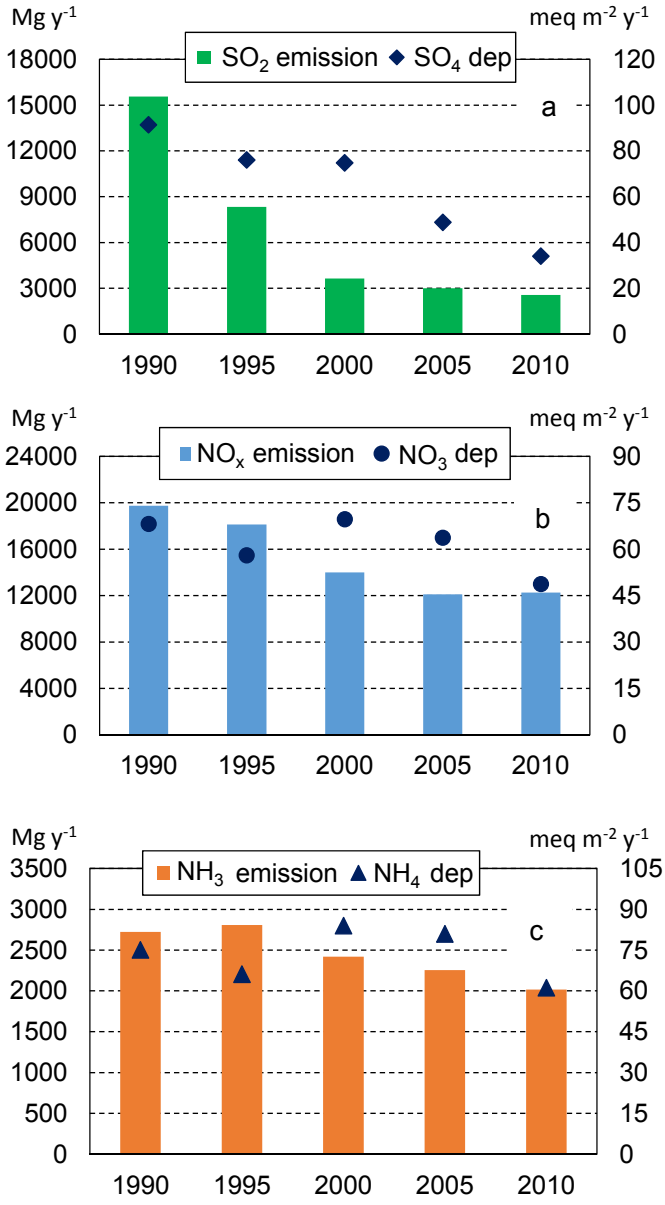

Fig. 8. Emission of SO_2 (a), NOx (b) and NH_3 (c) obtained as average data from 8 EMEP cells (Fig. 1), compared with deposition values in the same periods (mean values from 9 sites, 5-year averages). Emission data from WebDab (http://www.ceip.at/).

Furthermore, the study area is a typical example of a region where concentration and deposition originate to a large extent from sources outside the region itself, so that it is necessary to assess emission changes on a larger scale. To do that, we included two neighbouring cells in the emission calculation (Fig. 1). However, a larger or different area may be needed to estimate the emissions effectively affecting the study area.

3.5. Deposition change and its effects on ecosystems

In the framework of the UNECE Convention on Long-range Transboundary Air Pollution, empirical critical loads of nitrogen (CLN) have been defined for natural and semi-natural ecosystems (Bobbink and Hettelingh, 2011). Among the most sensitive ecosystems there are permanent oligotrophic lakes, ponds and pools, with CLN of 3–10 kg N ha^{-1} y^{-1} (21–71 meq m^{-2} y^{-1}) and raised

bogs and alpine and subalpine grasslands, with CLN of 5–10 kg N ha^{-1} y^{-1} (36–71 meq m^{-2} y^{-1}). These ecosystems are a typical component of the alpine and subalpine landscape in the study area. A further important ecosystem is forest, mainly broadleaves, which covers almost 50% of the total area of Lake Maggiore watershed (Mosello et al., 2001). For forest ecosystems, CLN of 10–15 kg N ha^{-1} y^{-1} (71–107 meq m^{-2} y^{-1}) have been reported (Bobbink and Hettelingh, 2011); for Southern Switzerland in particular, modelled CLN below 10 kg N ha^{-1} y^{-1} have been estimated (Rihm, 1996).

At present, deposition of acidity mostly falls below the critical loads in the areas South of the Alps (Steingruber, 2015b). On the other hand, the atmospheric deposition of nitrogen is still too high with respect to critical levels and further reductions are needed to prevent nitrogen saturation of terrestrial and aquatic ecosystems. Indeed, the measured wet deposition (ranging from 30–40 to 100–120 meq m^{-2} y^{-1} as the sum of ammonium and nitrate) clearly underestimates the total deposition of N, which can be 30–40% higher when including the contribution of dry deposition (Rogora et al., 2006; Steingruber, 2015b). Several studies also put in evidence the role of organic N as an important nitrogen deposition pathway (Beem et al., 2010; Benedict et al., 2013). Unfortunately, long-term continuous data for organic N were not available at the study sites; however, from the data available at a few sites for limited periods, organic N contribution was between 8 and 10% of total N deposition; this contribution varied locally and in different periods of the year and proved to be up to 40–45% during some events. These data confirmed the need to better evaluate this often overlooked N deposition pathway.

At the alpine stations (Piotta, Devero, Robiei), annual deposition of inorganic nitrogen is still often above 70 meq m^{-2} y^{-1} (10 kg N ha^{-1} y^{-1}); at Robiei, in particular, deposition reaches 100–120 meq m^{-2} y^{-1} (>15 kg N ha^{-1} y^{-1}), due to the high amount of precipitation at this site. These levels are still unacceptable if a full recovery of surface water bodies and other sensitive ecosystems has to be achieved. Furthermore, long-term data on NH_4 and NO_3 deposition highlighted the increasing importance of reduced N: ammonium presently represents 56–57% of wet N deposition in the study area. An increasing importance of reduced N with respect to oxidized N in atmospheric deposition has been also reported elsewhere (e.g. Paerl and Whitall, 1999; Fowler et al., 2005). Increases in the ratios of NH_4 to NO_3 may have ecological effects on both terrestrial and surface ecosystems changing for instance community composition (Paerl et al., 2002).

4. Conclusions

This study confirms how the areas South of the Alps in Italy and Switzerland are subject to high N deposition, despite a recent decrease in the atmospheric input of both ammonium and nitrate. While sulphate and acidity trends were more coherent among sites, concentration and deposition of N compounds changed with different temporal patterns at the various sites, probably because of the contribution of local emission sources. The spatial patterns of S and N deposition still show a slight north-south gradient, with higher values in the south-eastern part of the area, but these are much less evident than in the past.

Deposition in this area clearly responded to emission decrease, which has been particularly evident for SO_2. A time lag can be seen between emission and deposition changes for N compounds. This aspect has to be taken into account when monitoring the effects of emission reduction following the enforcements of international and national regulations.

The relative importance of reduced N in wet deposition seems to have grown in time, as a consequence of more effective controls on NO_X emission than on NH_3 emission. Beside further regulations on NO_x emission, agricultural and stock rearing activities, which are by far the main emission sources of NH_3, should be one of the key target of emission reduction policies in the near future.

Precipitation variability, both in the long- and in the short-term, may act as a confounding factor in the response of deposition to emission changes. Yearly average precipitation has not showed any trend in the study area in the last decade; however, short-term variability has changed, with a tendency towards an increasing frequency of extreme precipitation events (Saidi et al., 2015; MeteoSvizzera, 2012). These events may become more and more important in the future, also as a vehicle of chemical compounds from the atmosphere to terrestrial and aquatic ecosystems: brief but very intense rainfalls may deliver acidic but also alkaline compounds, depending on the main storm trajectory, in a very limited time span. These short-term inputs may be relevant, in particular for nutrient limited and acid sensitive ecosystems.

Future trends in air concentration and deposition will be affected directly and indirectly by climate change. Change in precipitation patterns and regime, in particular, will be important in the study area, affecting both the spatial and temporal distribution of deposition.

Base cation deposition decreased in the recent period, even if the trends resulted significant only at a few sites. However, the atmospheric input of base cations can increase significantly in correspondence of alkaline rain events, such as those associated with the transport of Saharan dust. These events, although rare, significantly contribute to the total deposition of base cations and alkalinity. More than the annual average deposition, the frequency and magnitude of these events is crucial in delivering neutralising compounds to the ecosystems.

Despite the recent decrease, deposition of both oxidized and reduced nitrogen is still high, also at the Alpine stations, if compared to the critical loads for the most sensitive ecosystems. From this perspective, further reductions in the emissions of N compounds should be the target of national and international policy.

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