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

M. Rogora [a], [*], L. Colombo [b], A. Marchetto [a], R. Mosello [a], S. Steingruber [c]

[a] *CNR Institute of Ecosystem Study, Largo Tonolli 50, I-28922 Verbania Pallanza, Italy*
[b] *University of Applied Sciences and Arts of Southern Switzerland (SUPSI), CH-6952 Canobbio, Switzerland*
[c] *Ufficio dell'aria, del clima e delle energie rinnovabili, Dipartimento del territorio del Cantone Ticino, CH-6501 Bellinzona, Switzerland*

## 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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[*] Corresponding author.
*E-mail addresses:* m.rogora@ise.cnr.it (M. Rogora), luca.colombo@supsi.ch (L. Colombo), a.marchetto@ise.cnr.it (A. Marchetto), r.mosello@ise.cnr.it (R. Mosello), sandra.steingruber@ti.ch (S. Steingruber).

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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.

## 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