Science of the Total Environment 544 (2016) 919–928

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Long-term effects of changing atmospheric pollution on throughfall, bulk deposition and streamwaters in a Mediterranean forest

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HIGHLIGHTS

- Rain chemistry at a site NE Spain tracks SO_2 and NO_x Spanish emissions.
- NO_x emission and rainfall NO_3 decline is attributed to a shift to renewable energy.
- Increased stream N export in a recent period suggests the onset of N saturation.

ARTICLE INFO

Article history:
Received 14 September 2015
Received in revised form 3 December 2015
Accepted 4 December 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Emission reductions
Atmospheric deposition
Nitrogen
Sulfate
Throughfall
Canopy

ABSTRACT

The abatement programs implanted in Europe to reduce SO_2, NO_2 and NH_3 emissions are here evaluated by analyzing the relationships between emissions in Spain and neighboring countries and atmospheric deposition in a Mediterranean forest in the Montseny mountains (NE Spain) for the last 3 decades. A canopy budget model was applied to throughfall data measured during a period of high emissions (1995–1996) and a period of lower emissions (2011–2013) to estimate the changes in dry deposition over this time span.

Emissions of SO_2 in Spain strongly decreased (77%) and that was reflected in reductions for nssSO_4^{2-} in precipitation (65% for concentrations and 62% for SO_4^{2}-S deposition). A lower decline was found for dry deposition (29%). Spanish NO_2 emissions increased from 1980 to 1991, remained constant until 2005, and decreased thereafter, a pattern that was paralleled by NO_3^- concentrations in bulk precipitation at Montseny. This pattern seems to be related to a higher share of renewable energies in electricity generation in Spain in recent years. However, dry deposition increased markedly between 1995 and 2012, from 1.3 to 6.7 kg ha^{-1} year^{-1}. Differences in meteorology between periods may have had a role, since the recent period was drier thus probably favoring dry deposition.

Spanish NH_3 emissions increased by 13% between 1980 and 2012 in Spain but NH_4^+ concentrations in precipitation and NH_4^+-N deposition showed a decreasing trend (15% reduction) at Montseny, probably linked to the reduction ammonium sulfate and nitrate aerosols to be scavenged by rainfall. NH_4^+-N dry deposition was similar between the compared periods.

The N load at Montseny (15–17 kg ha^{-1} year^{-1}) was within the critical load range proposed for Mediterranean sclerophyllous forests (15–17.5 kg ha^{-1} year^{-1}). The onset of N saturation is suggested by the observed increasing N export in streamwaters.

1. Introduction

High atmospheric deposition of sulfur (S) and nitrogen (N) in the last century has lead to the acidification and eutrophication of many terrestrial ecosystems in Europe and North America, peaking in the 1970–1980 (Aber et al., 1998; EC, 2001; Reuss and Johnson, 1986). To counteract these adverse effects, transboundary amendment programs were launched by the Convention on Long-Range Transboundary Air Pollution (CLRTAP) in the frame of the United Nations Economic Commission for Europe (UNECE, 2011). Upon the implementation of national emission limits, significant declines were observed since the mid 1980s in SO_2 emissions and S in precipitation in Europe (Tørseth et al., 2012). Nitrogen emissions were also significantly reduced in many European countries, although higher variability was found among regions and the changes were different for oxidized or reduced N (Fagerli and Aas, 2008; Konovalov et al., 2008; Lövblad et al., 2004). A summary of the major results following the implementation of pollution control measures can be found in Grennfelt and Hov (2005). Concerning Spain, SO_2 emissions

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http://dx.doi.org/10.1016/j.scitotenv.2015.12.017
0048-9697/

were readily cut, but the country still exceeded in 2012 the NO_x and NH_3 emissions ceilings for 2010, established at 847 and 353 Gg respectively (EC, 2001). The link between emissions, air concentrations and deposition is complex because of the interplay of the meteorological conditions, the chemical interaction between pollutants in the atmosphere and the spatial scale of the region of influence. In this sense non-linearities have been found between emission reductions and the decline in rainwater concentration (Fowler et al., 2007).

Dry deposition of airborne pollutants makes also a significant contribution to the atmospheric load of most ecosystems. However, long time records of changes in dry deposition for the last decades are scarce. Changes in dry deposition have also been found to change non-linearly with emissions (Fowler et al., 2005). This has been attributed to the fact that for SO_2, the deposition velocity (V_d) is controlled by the NH_3/SO_2 ratio, where SO_2 deposition increases as leaf pH raises in response to NH_3 deposition (Erisman et al., 1998; Fowler et al., 2001). Thus, dry deposition will not only depend on SO_2 concentrations, but also on its relative abundance respect to NH_3. Also, declining air SO_2 concentrations will affect the partitioning of gaseous NH_3 and particulate NH_4^+, which in turn will affect the spatial range affecting deposition, since NH_3 will tend to be locally deposited while fine-sized NH_4^+-sulfate aerosols have a longer residence time in the atmosphere and will be mostly transported to longer distances (van Jaarsveld et al., 2000).

Throughfall (TF), the water flux collected under the forest canopy, has been widely used to provide an estimation of dry deposition (De Vries et al., 2003; Lindberg and Lovett, 1992). However, throughfall does not truly represent total deposition, since it also is affected by chemical exchanges at the canopy level (Parker, 1983). When using throughfall measurements to derive dry deposition fluxes, a distinction has to be made between dry deposition and canopy exchange processes. These include the leaching of elements from internal plant pools and/or the uptake by the canopy of gases or dissolved solutes (Lovett and Lindberg, 1984; Schaefer and Reiners, 1990). To sort this out, a canopy budget model has been widely used (Draaijers and Erisman, 1995; Staelens et al., 2008) and will be here applied to estimate dry deposition from throughfall measurements.

The Iberian Peninsula, in the south-western corner of the European continent, is influenced by air masses from contrasting provenances. Five main air mass movements have been established based on the frequency of back trajectories: 1) European or continental, 2) from the Atlantic Ocean, 3) from North Africa, 4) from the Mediterranean, 5) from shorter pathways, as recirculating air masses over the Iberian Peninsula (Calvo et al., 2012; Escudero et al., 2007; Izquierdo et al., 2012). A cluster classification of daily back-trajectories for the periods 1984–1993 and 1998–2009 indicated that the most frequent air flows at the Montseny mountains in NE Spain were from the Atlantic Ocean (39 and 31% for the two study periods) and the Peninsular recirculation (27–25%). Thus, the major air pollution influence at the north-east coast of Spain may be from emissions from the Iberian Peninsula itself. However, during winter, a good correlation was observed between air masses from the Mediterranean and NO_3^- deposition (Izquierdo et al., 2014). Also, source receptor models indicated the influence of emissions from eastern provenances on the rain chemical composition in NE Spain (Izquierdo et al., 2012).

The aim of this work is to examine the relationships between S and N emissions in Spain and neighboring countries from the early 1980s to 2014 and rain concentrations and deposition at a site in the NE of the Iberian Peninsula, in order to check whether the abatement measures implemented by CLRTAP protocols are reflected in reduced deposition. This has been undertaken by comparing the evolution of bulk deposition trends at a rural forested site (La Castanya, Montseny) in NE Spain and the evolution of emissions in the Iberian Peninsula, France, Italy and the totals for the European Union (EU28) for this period. Previous studies have documented a SO_4^{2-} decrease in bulk deposition in NE Spain (Avila, 1996; Avila and Rodà, 2002); here we expand these studies for a longer time series and incorporate the examination of changes in dry deposition. Changes in dry deposition along the last 3 decades cannot be traced in NE Spain because of the lack of a continuous monitoring scheme for dry deposition. However, throughfall measurements in two contrasting periods over this time span (in 1995–1996, a period of high emissions and in 2011–2013, a period of lower emissions) can provide an insight on dry deposition changes, particularly for S.

Several studies have reported changes in surface stream water chemistry after reduction of pollutant emissions in temperate forests in central and north Europe and North America (Driscoll et al., 1998; Evans et al., 2007; Skjelkvåle et al., 2005). This paper also tackles this issue by exploring the response at the ecosystem level of emissions reductions, by studying changes in streamwater chemistry for a stream draining an undisturbed forested catchment representing a typical Mediterranean forest.

2. Material and methods

2.1. Study site

The study site was located in La Castanya valley (LC, 41°46′N, 2°21′E, 700 m.a.s.l), within the Montseny mountains (Fig. 1) about 40 km NNE from Barcelona and 25 km from the Mediterranean coast. Dominant vegetation is a closed-canopy forest of holm-oak (*Quercus ilex* L.). Forests at La Castanya valley were exploited in the past for charcoal production, but these activities were abandoned about 60 years ago and the forest is increasing in biomass (Rodà et al., 1999).The upper part of La Castanya valley comprises a belt of beech forest at 1100–1200 m, while heathlands and grasslands extend above this altitude up to 1350 m. Dominant lithology is metamorphic schist and phyllite. Soils are shallow with an organic layer 0–5 cm deep and an average total depth of 60 cm (Hereter and Sánchez, 1999). Soils are classified as Entisols or Inceptisols (Soil Survey Staff 1992).

Climate is meso-Mediterranean sub-humid, with a clear seasonal cycle of higher precipitation in spring and summer. Variability among years is very high (Fig. 2). At the LC station, mean precipitation from 1983 to 2014 was 862 mm year^{-1} (range from 518 to 1601 mm year^{-1}; Fig. 2) and mean air temperature 9.5 °C.

This site is considered as a rural background station that is topographically sheltered to some extent from air pollution from the Barcelona metropolitan area. However, during the warm half of the year diurnal sea–land breezes carry pollution from the coast and lowland plains to the upper Montseny slopes, where LC lies, by midday (Pérez et al., 2008).Besides, long-range pollutant transport also influences atmospheric deposition at this site (Izquierdo et al., 2012).

Stream discharge was recorded in a stream named Torrent de la Mina (TM0) which is gauged with a 120° V-notch weir. This catchment has a surface of 205 ha and comprises two distinct zones: an upper plateau with grassland and heathlands (30% of the catchment) and holm-oak forests covering the steep slopes that conform the rest of the catchment (Fig. 1).

2.2. Field sampling

2.2.1. Open field measurements

Weekly bulk deposition samples were obtained from August 1983 to August 2014 (interrupted from September 2000 to March 2002). Wet-only deposition (ESM Andersen instruments) was sampled in parallel to bulk deposition during 2008–2013 but because of the longer bulk deposition record, we will deal here with bulk deposition data for the comparison of emissions and deposition trends. Bulk/wet deposition collectors, a rain tipping bucket gauge and a meteorological station (Campbell with CR1000 data logger) were located at a clearing in the forest close to the throughfall plots (Open field sites, Fig. 1). The open field measurements were located at site LC1 since August 1983 to September 2000. Since March 2002, they were located at site LC2 (Fig. 1), about 850 m distant from the first site. Bulk collectors consisted