Science of the Total Environment 434 (2012) 18–27

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Changes in atmospheric deposition and streamwater chemistry over 25 years in undisturbed catchments in a Mediterranean mountain environment

Anna Àvila [a,*], Ferran Rodà [a,b]

[a] Center for Ecological Research and Forestry Applications (CREAF), Universitat Autònoma de Barcelona, 08193, Bellaterra, Spain
[b] Department of Animal Biology, Plant Biology and Ecology, Universitat Autònoma de Barcelona, 08193, Bellaterra, Spain

ARTICLE INFO

Article history:
Received 28 April 2011
Received in revised form 8 November 2011
Accepted 9 November 2011
Available online 24 December 2011

Keywords:
Nitrogen
Sulphate
Alkalinity
Base cations
Streamwater chemistry
Quercus ilex

ABSTRACT

Surface water chemistry has changed in response to reduced atmospheric deposition of sulphur and acidity in many regions of Europe and North America. Most of these studies come from acidic or low-alkalinity surface waters under high acidic deposition. Mediterranean climates offer a different biogeochemical context, characterised by streamwaters of higher alkalinity and low acid inputs. In this paper, we use surveys of streamwater chemistry conducted in 1981–1984 and again in 2007 in the Montseny natural park (NE Spain) to test whether streamwaters of these well-buffered catchments respond to changes in atmospheric deposition, which has declined for S during the last decades in NE Spain while remaining about stable for nitrogen. The 23 sampled streams drained heathland, beech forests and evergreen oak forests in relatively undisturbed small catchments underlain by silicate bedrock. Bulk deposition of sulphate at Montseny decreased by 54% while nitrate bulk deposition increased (non-significantly) by 30% in this period. Total N deposition is estimated in the range 15–30 kg N ha^{-1} y^{-1} for NE Spain. This is well above threshold values (e.g. 10 kg N ha^{-1} y^{-1}) reported as starting nitrogen saturation symptoms in forest ecosystems in Europe. Baseflow sulphate concentrations decreased on average by 47 μeq L^{-1} or 29% of early 1980s concentrations. Baseflow mean nitrate concentrations increased significantly but only from 5.5 to 8.9 μeq L^{-1}. Thus, despite decades of high N deposition, these ecosystems appear to be still far from N saturation. Baseflow alkalinity and base cation concentrations increased substantially, probably a combined result of decreased S deposition, enhanced silicate weathering under current higher temperatures, reduced plant cation uptake as vegetation matures, and slightly drier conditions in the survey of 2007. Overall, these well-buffered catchments have shown sizable changes in baseflow chemistry in response to changed atmospheric deposition and other environmental changes.

1. Introduction

Emissions of oxidised nitrogen species from fossil fuel combustion and of reduced N from livestock raising and field fertilisation have increased in Spain in the last two decades (EMEP, 2010). In Europe, N emissions also increased, peaking in the 1980s and subsequently leveling off or slightly decreasing in some European countries (Tarrasón and Schaug, 2000). To curb these and other pollutant emissions, such as SO_2, control programs have been set at national and international levels under the initiative of the Convention of Long-range Transboundary Air Pollution (Bull et al., 2001). These programs have succeeded in reducing S deposition, and this has been reflected in terrestrial and aquatic ecosystems (Kahl et al., 2004; Skjelkvale et al., 2005; Stoddard et al., 1999). However, the control on N emissions has not been as successful across Europe and many regions exhibit an absence of changes in soil and streamwater N concentrations (Skjelkvale et al., 2005; Wright et al., 2001) or even an increase (Rogora, 2007; Whitehead et al., 2002).

The sustained additions of N from the atmosphere, combined with a declining retention capacity as forests mature can lead to "nitrogen saturation", a condition that occurs when the availability of inorganic N is in excess of biological demand (Aber et al., 1989). The nitrogen saturation hypothesis postulates that under elevated atmospheric N deposition, forest ecosystems would undergo changes corresponding to varying degrees of N saturation (Skeffington and Wilson, 1988), eventually leading to NO_3^- losses to drainage waters (Aber et al., 1989; Stoddard et al., 2001). In addition, several studies in temperate and alpine catchments have shown that NO_3^- concentrations in surface waters have also been affected by climate change (Baron et al., 2009; Park et al., 2003; Rogora, 2007; Watmough et al., 2004) as increases in temperature and soil humidity affect biotic-mediated processes such as N mineralization and nitrification.

On the other hand, S deposition has clearly declined in Europe and North America leading to a recovery of lakes and streamwaters from acidification, although the rate of SO_4^{2-} decline in surface waters was

* Corresponding author. Tel.: +34 93 581 46 69; fax: +34 93 581 4151.
E-mail addresses: anna.avila@uab.cat (A. Àvila), ferran.roda@uab.cat (F. Rodà).

0048-9697/$ – see front matter
doi:10.1016/j.scitotenv.2011.11.062

smaller than in deposition for most sites in Europe and North America, indicating a lagged response of soils (Kahl et al., 2004; Skjelkvale et al., 2005).

Since the early 1970s, small catchments have been recognised as a useful tool for investigating how ecosystems respond to changes caused by natural and man-made perturbations (Likens et al., 1977; Likens and Bormann, 1995) and much information on the biogeochemical responses to different impacts, affecting deposition, climate, and land use, has been assembled from temperate ecosystems in central and northern Europe and in North America. However, much less is known for European Mediterranean ecosystems.

In this study we tested whether changing deposition trends of S and N and changes in climate were reflected in the chemistry of small streams draining relatively undisturbed catchments in a span of ca. 25 years for a mountainous system in NE Spain. This was done by re-sampling in 2007 a network of streams that had been sampled in 1981 and 1984. The sampled streams drained heathland, beech forests and evergreen oak forests on silicate bedrocks in the Montseny mountains in NE Spain.

2. Study site

The Montseny mountains (longitude 2° 16′ to 2° 33′ E; latitude 41° 42′ to 41° 52′ N) are situated 40 km to the NNE from Barcelona and are formed by three massifs (Fig. 1): Turó de l'Home–Les Agudes (TH, 1700 m asl), Matagalls (M, 1693 m) and La Calma elevated plateau (LCal, 1300 m). The climate is montane Mediterranean, with mean annual precipitation ranging between 800 and 1200 mm and mean annual air temperature ranging between 7 and 12 °C depending on altitude and slope aspect. Most rainfall occurs in spring and autumn, and summer drought is attenuated by summer storms. A snowpack may develop at higher altitudes but it is usually short-lived. Data from the Meteorological Observatory of Turó de l'Home (1700 m asl) indicate that mean air temperature increased by 0.065 °C per year in the period January 1978 to December 1995. At La Castanya Valley (700 m asl; Fig. 1), mean air temperature increased by 0.081 °C per year in the period January 1993 to December 2009 (unpublished results).

Most of Montseny is underlain by silicated bedrocks: Ordovicic phyllites in the west and central sectors and schists, granites and granodiorites in the north and east sectors. The relief is very steep. Soils have a high level of spatial heterogeneity because of this rugged topography. Most of the soils are colluvial and very stony. They are classified (Soil Survey Staff, 1992) as Entisols (Lithic Xerorthents) or Inceptisols (Typic, Lithic or Dystric Xerochrepts). The main pedogenetic process is the formation of a cambic horizon with moderate illuviation (Hereter, 1990). The soils are moderately acidic, acidity being buffered by silicate weathering and cation exchange. Calcium is the dominant exchangeable base cation (Hereter, 1990).

Slopes are covered by closed-canopy forests of the evergreen holm oak (*Quercus ilex*) and, at higher altitudes, of European beech (*Fagus sylvatica*). Culminal areas of each massif are covered by heathlands, often dominated by *Calluna vulgaris*, and grasslands. The area has been protected as a natural park since 1977–1978.

Acidic atmospheric deposition is not a major issue at Montseny. In the period 1978–1988 only 26% of precipitation samples and 20% of the annual precipitation amount had a pH <4.5 (Rodà et al., 1993). More recent precipitation is even less acidic, and has, on average, positive alkalinity (Àvila and Rodà, 2002). Montseny lies, however, within the polluted air mass of the Barcelona conurbation, with high levels of nitrogen oxides and other pollutants (Pey et al., 2009). Though Montseny ecosystems above ca. 1000 m of altitude are often within clouds, throughfall studies in beech and fir forests at these elevations suggest that occult deposition has a minor contribution to inputs of water and pollutants (Rodà, 1983).

Streamwaters draining silicate-bedrock catchments at Montseny are characterised by medium to high alkalinity, with baseflow alkalinity ranging generally between 300 and 1000 μeq L^{-1}. This testifies to the substantial acid neutralising capacity of these ecosystems. However, first-order rivulets in the uppermost reaches of Montseny show baseflow alkalinities <200 μeq L^{-1} with a few of them under 100 μeq L^{-1}.

2.1. Basin characteristics

The sampled catchments covered the full range of altitudes within the massif above human settlements. Their mean altitude ranged between 805 and 1464 m asl. (Table 1). As they were mostly first- and second-order streams draining the slopes of the main peaks in Montseny, their average slope was quite steep (21°, Table 1). Catchment area ranged from 6 to 600 ha, but the median was 23 ha. Dominant vegetation types in the sampled catchments were the same as in Montseny as a whole: evergreen holm oak forest, beech forest and heathland-grasslands. Catchment characteristics for each vegetation type are also given in Table 1.

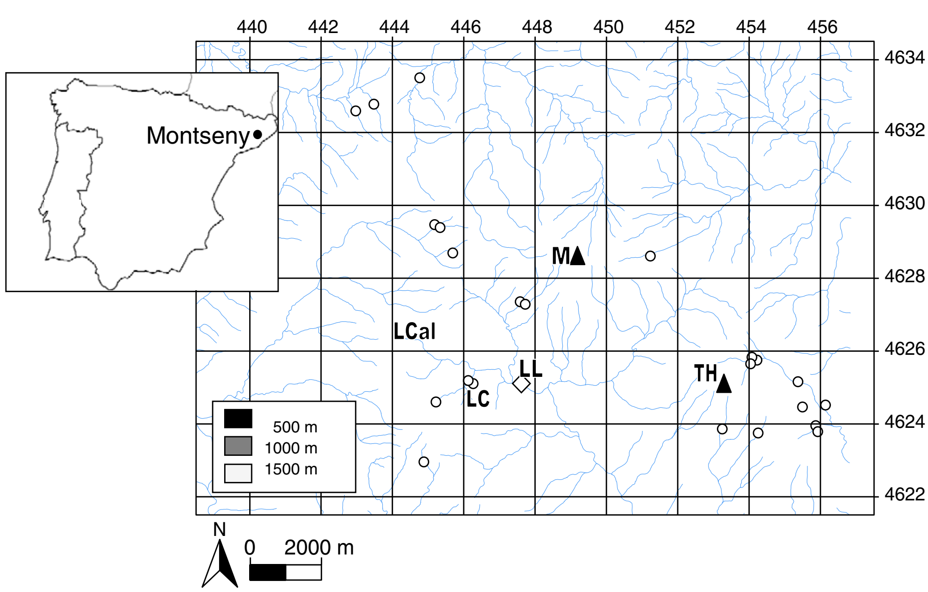

Fig. 1. Map of the streamwater sampling localities (open dots) in the Montseny mountains. Indicated are the main peaks of Turó de l'Home (TH), Matagalls (M) and La Calma (LCal), the intensively studied site of La Castanya (LC) and the gauging station of La Llavina (LL).