Atmospheric Environment 44 (2010) 582–595

Contents lists available at ScienceDirect

Atmospheric Environment

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

Atmospherically deposited major and trace elements in the winter snowpack along a gradient of altitude in the Central Pyrenees: The seasonal record of long-range fluxes over SW Europe

Montserrat Bacardit*, Lluís Camarero

Centre d'Estudis Avançats de Blanes (CEAB – CSIC), Accés Cala Sant Francesc 14, Blanes 17300, Girona, Spain

ARTICLE INFO

Article history:
Received 2 December 2008
Received in revised form
11 June 2009
Accepted 15 June 2009

Keywords:
Major and trace elements
Long-range pollution
Snowpack
High mountain
Pyrenees

ABSTRACT

The chemistry of high mountain snowpacks is a result of the long-range atmospheric transport and deposition of elements. Pyrenean snowpacks contain information about the fluxes of elements over SW Europe in winter. Here we analysed Al, Ti, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb in the 2004–05 winter snowpack in the Central Pyrenees, at an altitude range of 1820–3200 m a.s.l. Ni, As, Se and Cd were not detected in most cases. The concentrations of the remaining elements were comparable to those found in other high mountain areas in Europe and North America considered representative of regional background of atmospheric deposition in populated areas. In contrast, our measurements were higher than those of polar areas, which represent the global background. Single measurements of concentrations and snow accumulation were subject to considerable spatial variability, which may be attributable to strong wind drift and other post-depositional processes. The major ions chemistry of the snow indicated three possible origins for the solutes: terrigenous dust, sea salt spray and polluting S and N aerosols. We found no association between Cu, Zn and Pb and any of these possible sources. This observation therefore indicates that these elements were not preferentially bound to any particular kind of aerosol. Snow collected at altitudes of up to 2050 m a.s.l. presented higher concentrations of several elements than snow above this altitude, thereby indicating a local influence. Snow collected above 2300 m a.s.l. was therefore more representative of broad regional inputs. At these higher altitudes, snow was not enriched in Al, Ti, Mn, Fe or As compared with the composition of the upper continental crust and the local lithology, and these elements (except Mn) appeared almost exclusively in the particulate fraction. This observation indicates that Al, Ti, Mn, Fe and As were present mainly as part of dust particles of terrigenous origin. In contrast, Cu, Zn, and Pb presented medium to high enrichment factors and showed a higher proportion of soluble forms, thereby indicating their polluting character.

1. Introduction

Cold areas around the world are increasingly recognised as being preferential zones for the accumulation of long-range micropollutants, such as persistent organic pollutants (POPs) and several trace elements. These areas include the poles and high mountains. Evidence is growing that, in the temperate zones, high mountains are 'cold fingers' or regional convergence zones that act as traps where environmentally important compounds accumulate in permanent ice- and snow-fields due to cold condensation and enhanced atmospheric deposition (Loewen et al., 2005). Global warming is likely to release such compounds as ice and snow melt, and thereby affect downstream ecosystems (Meyer and Wania, 2008). Research into the mechanisms and patterns of accumulation, and the speciation of micropollutants in the snow are therefore of general interest.

Mountain emplacements are suitable sites for assessing the degree of background atmospheric pollution caused by long-range transport at both the regional and global scales. This is because they are relatively remote locations generally free from local inputs that mask airborne inputs from long distances (Battarbee et al., 2002). Snowpack measurements are an appropriate method for estimating atmospheric deposition in remote sites where continuous monitoring is logistically unfeasible. The snowpack provides a record of winter atmospheric deposition, which, in the Pyrenees, accounts for at least half the total annual precipitation. The Pyrenees are located at the transition between Atlantic and Mediterranean climate regimes and the chemistry of the snowpack here is

* Corresponding author. Tel.: +34 972 33 61 01; fax: +34 972 33 78 06.
E-mail address: mbacardit@ceab.csic.es (M. Bacardit).

1352-2310/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2009.06.022

therefore representative of the atmospheric fluxes of elements driven by the air masses circulating over SW Europe in winter (Camarero and Catalan, 1996).

Mountain areas have a strong climatic gradient caused by varying altitude. These climatic variations can determine differences in the mechanisms of deposition and storage of environmental pollutants. These mechanisms have been examined for persistent organic pollutants (Wania and Mackay, 1996; Blais et al., 1998; Fernandez and Grimalt, 2003). However, few case studies have addressed the effects of varying altitude on the deposition and accumulation of major and trace elements in mountain areas, and the results are contradictory. On the one hand, several radionuclides and stable elements (^{137}Cs, Pb, Cd, Cs, Hg, Rb and S) show increasing concentrations with altitude in soils along a transect across the Pyrenees (McGee and Vallejo, 1996). A strong correlation between altitude and deposition of metals and metalloids has also been reported for As, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, V, Zn and S in moss shoots (as a record of atmospheric deposition) in the northern and eastern Alps (Zechmeister, 1995). These results support the hypothesis that some pollutants accumulate preferentially in high mountain ecosystems as a result of increased precipitation with altitude. On the other hand, a general trend of decreased concentrations with altitude has been described for Ti, V, Mn, Fe, Co, Cu, Zn, Mo, Ag, Cd, Sb, Ba, Pb, Bi and U in fresh snow collected along two alpine valleys in the French Alps, whereas Li, B, Pd, Sn, Pt and Au concentrations are constant irrespectively of the sampling altitude (Veysseyre et al., 2001). The authors argue that the first group of metals is probably influenced by local sources at low altitude, while the second group originates from long-range transport from distant sources. At higher altitude, no clear trends for element variations with elevation in the northern slope of Mt. Everest between 6500 and 8844 m a.s.l. have been detected (Kang et al., 2007).

In this study, we analysed the winter snowpack along an altitudinal transect in the Maladeta valley, Central Pyrenees (Spain), with emphasis on several major and trace elements. We included in our analyses the speciation of these elements between soluble and particulate forms; an approach that is rarely found in previous literature. The study of speciation in soluble and particulate forms offers advantages over simple bulk analysis. It provides information on the origin of the elements and on their availability for biota, as well as providing insight into their potential fate in the environment. Our main aims were to characterize (both quantitatively and qualitatively) the elements in the snowpack, in order to see whether there was a spatial pattern of major and trace element accumulation as a function of altitude, and to assess the value of the snowpack as an indicator of background fluxes of these elements at the broad regional scale.

2. Methods

Snow sampling was conducted in the Maladeta mountain massif (42°41′ N, 0°38′ E, Central Pyrenees, Spain) from 10 to 15 March 2005, after the major winter snowfall had occurred and before the snowpack had started to melt. Snow samples were collected along the Maladeta valley from six altitudes: 1820, 2050, 2315, 2630, 2915 and 3200 m a.s.l. (Fig. 1). The sampling area was located entirely on a lithologically homogeneous area of granite bedrock to prevent interference of local lithologies with distinct element compositions. The yearly precipitation in the valley is between 1800 and 2200 mm, reaching 2500–2600 mm at greater altitudes. The mean annual temperature ranges from 4.5 °C at 1750 m a.s.l. to −4 °C on Aneto peak, at 3404 m a.s.l., the highest summit in the Pyrenean range. In the upper part of the Maladeta valley (2800–3200 m a.s.l.) a small retreating glacier still remains.

In all steps of this study, precautions were taken to prevent sample contamination (Veysseyre et al., 2001). All sampling and laboratory containers and tools were previously cleaned by submerging them in a 5% nitric acid bath overnight. They were then rinsed several times with abundant deionised water (ultra-pure water produced with a MilliQ water purification system, Millipore), air-dried in an isolated area of the lab, and kept in cleaned plastic bags. In all steps, we used latex gloves for sample handling, and extreme care was taken to prevent contact of the sample with materials other than the clean tools and containers. In the field, the personnel conducting the sampling wore clean polyethylene overcoats and hats. Samples were not processed in a fully classified clean

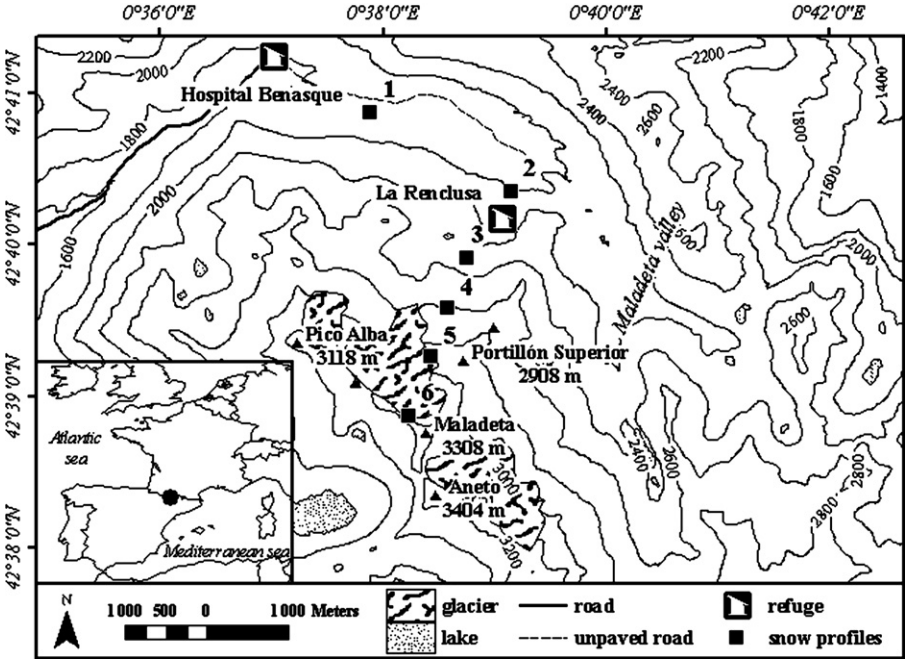

Fig. 1. Location of sampling sites in the Maladeta valley, Spanish Central Pyrenees.