Decadal trends in atmospheric deposition in a high elevation station: Effects of climate and pollution on the long-range flux of metals and trace elements over SW Europe

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HIGHLIGHTS

- Atmospheric deposition in high mountains captures global fluxes of chemical elements.
- There are three main modes of temporal variation in deposition in the Pyrenees.
- These modes are related to the NAO, precipitation, and human emissions, respectively.

ABSTRACT

Atmospheric deposition collected at remote, high elevation stations is representative of long-range transport of elements. Here we present time-series of Al, Fe, Ti, Mn, Zn, Ni, Cu, As, Cd and Pb deposition sampled in the Central Pyrenees at 2240 m a.s.l, representative of the fluxes of these elements over South West Europe. Trace element deposition did not show a simple trend. Rather, there was statistical evidence of several underlying factors governing the variability of the time-series recorded: seasonal cycles, trends, the effects of the amount of precipitation, climate-controlled export of dust, and changes in anthropogenic emissions. Overall, there were three main modes of variation in deposition. The first mode was related to North Atlantic Oscillation (NAO), and affected Al, Fe, Ti, Mn and Pb. We interpret this as changes in the dust export from Northern Africa under the different meteorological conditions that the NAO index indicates. The second mode was an upward trend related to a rise in the frequency of precipitation events (that also lead to an increase in the amount). More frequent events might cause a higher efficiency in the scavenging of aerosols. As, Cu and Ni responded to this. And finally, the third mode of variation was related to changes in anthropogenic emissions of Pb and Zn.

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1. Introduction

Atmospheric fluxes are an important component of the global cycle of many elements. These fluxes are often caused by long-range transport of elements from distant emission sources to receptor areas, where they are scavenged by precipitation and deposited on land or ocean. In each environment, the atmospherically deposited elements may have an important effect on biogeochemical cycling in the existing ecosystems (Mahowald, 2011), that may have feedback effects on climate (Jickells et al.,

2005). Airborne metals and trace elements play diverse roles in ecosystems; they are micronutrients, but also pollutants with potential toxic effects. They can be used to trace the pathways of atmospheric transport of both natural and human emissions. Crustal elements are indicators of aeolian dust transport, whereas metals emitted in huge amounts by human activities (such as lead, for instance) are tracers of past and present pollution.

Atmospheric long-range transport takes place in the free atmosphere above the mixing boundary layer, which generally has a depth of 1000–1500 m. The chemistry of the free atmosphere can be thus considered to reflect the composition of the global atmosphere better than the boundary layer below it. High mountains protrude above the boundary layer, intercepting the global flux of elements. Therefore, high elevation stations are one of the best

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settings to monitor the long-range (i.e. regional and global) transport of chemical elements. In addition, high mountains are usually free of direct local impacts that could mask global background signals.

International concern about large scale, transboundary pollution by trace metals has led to the establishment of an observation network of trace metal deposition across Europe. However, not all regions are equally covered. Southern Europe has been identified as one of the zones where monitoring is scarce and, therefore, needs more sites with continuous measurements (Ilyin et al., 2016). To our knowledge, there are few publications reporting long-term time-series and trends in metals and trace elements in precipitation at background sites that can be indicative of large-scale transport. The results presented here contribute to fill this gap. Most studies focus on locally polluted areas, or on a few pollutant elements of concern from the ecotoxicological point of view. A number of recent studies use trace element concentration in mosses as a surrogate for deposition; see for instance (Schröder et al., 2016). This method provides useful time-integrated (usually a few years) data at a high spatial resolution. However, it cannot substitute direct observation of actual deposition at a higher time resolution to gain insight into the factors driving the atmospheric transport and delivery of trace elements into various ecosystems.

In this paper we analyze the time series of metal and trace element deposition recorded between 2004 and 2013 at a high elevation station in the Central Pyrenees. Initial results from the two first years of sampling were published elsewhere (Bacardit and Camarero, 2009). In that publication, a first characterization of the depositional fluxes of a suite of metals and trace elements was drawn up. It can be considered representative of background deposition in SW Europe. The effect of meteorology and the geographic provenance of the air masses on the elemental fluxes were also assessed. Here we extend the time frame of our analysis in order to determine the variation in deposition over the past decade, and to examine in greater detail the influence of climate and the changes in anthropogenic emissions on the trends detected.

2. Materials and methods

2.1. Sampling

Atmospheric bulk deposition was collected at Lake Redon (formerly Lake Redó) field station (42° 38′ 36″ N, 0° 46′ 48″ E; 2240 m a.s.l.), in the Central Pyrenees. A detailed description of the station, the lake and its catchment can be found in (Ventura et al., 2000). An automatic weather station (AWS) records air temperature, humidity, wind speed, wind direction, sun radiation and precipitation every 30 min. A field laboratory facilitates on-site work all year round.

Bulk precipitation samples were collected every fourth week from 29 April 2004 to 28 November 2013. During 2004–2006, the sampling methods were different from those used during the remaining period. The methods (as well as results) used in the first stage were specifically aimed to distinguish between particulate and dissolved fractions in deposition. They are described in detail in Bacardit and Camarero (2009). From 2007 on, the methodology was changed in order to simplify it and make it more suitable for a long term monitoring approach. Basically, we lessened the volume of sample to be handled and reduced the steps for preparation and analysis of the samples. For six months, both methodologies were run in parallel to check their comparability. The only change regarding collectors was the size. In summer, rain was sampled with a polyethylene (PE) funnel (22 cm diameter in 2004–06, 10 cm from 2007 on), connected to a PE reservoir (8 L in 2004–06, 2 L

afterwards) by a tube in which a 250 μm nylon mesh was placed to prevent large particles, such as insects or leaves, from entering the water tank. In winter, when precipitation is in the form of snow, the funnel was substituted with a tube assembled on top of the tank. In 2004–06, a 15 cm diameter, 30 cm long polystyrene (PS) tube and a 30 L (PE) tank were used. From 2007 on, the tube was 7 cm diameter and 50 cm long, made of plexiglas, and the tank was 2 L (the same as for rain). This kind of passive collector was preferred to other active devices that require constant power supply and have mobile mechanical parts with electronic controls, unreliable when they have to be left unattended in high mountain emplacements. The collectors were placed 1.5 m above ground level, close to the AWS precipitation gauge. In 2004–06, the samplers were equipped with wind screens around their mouth to prevent biased precipitation collection due to wind disturbance. The smaller sized collectors used from 2007 on were not fitted with screens. However, precipitation collected in the samplers in all periods was generally in good agreement with measurements from the AWS, suggesting that there was no strong, systematic bias in collection due to wind. Thermophoretic effects could also reduce the collection efficiency of this type of collectors. However, it is assumed to be a minor to neglectable loss of efficiency because: 1) the generally low temperatures in this high mountain setting, and 2) it would affect mainly dry deposition, which is here a low percentage of bulk deposition (Bacardit and Camarero, 2009). Every sampling day, the collection tank with the sample was replaced by a clean tank. The cleaning between uses was done by rinsing the tanks with ultra-pure grade 3 de-ionized water (MilliQ, Millipore) and then filling them with a 5% dilution of Merck Supra-pure nitric acid. Just before new use, the acid solution was removed and the tank was rinsed thoroughly with de-ionized water. This treatment acidified the walls of the tanks, thus preventing the adsorption of trace ions from the sample during the time the collector is exposed to the atmosphere.

In 2004–06, precipitation samples were filtered (snow samples were first melted with a gentle steam bath) to determine metal and trace elements in the particulate and dissolved fractions separately, whereas only the acid leachable fraction was analyzed in the remaining period. The comparability of both approaches is discussed below. In brief, particles in samples from 2004 to 06 were collected on cellulose nitrate filters, and the filters were then extracted with a nitric acid and oxygen peroxide mixture at 95 °C in closed teflon beakers. The extract was used to determine the particulate fraction. See (Bacardit and Camarero, 2009) for further details on the filtration and extraction methods. A 100 mL aliquot of filtered water was acidified with 1% Merck Supra-pure nitric acid, and was used to determine the dissolved fraction. From 2007 on, 100 mL unfiltered subsamples (the whole sample was vigorously shaken before subsampling) were acidified and kept in the fridge (6 °C) for three days to leach metals and trace elements from particles into dissolution. Then, the samples were frozen until analysis.

2.2. Analysis

Until June 2010, analyses were performed at the Analytical Facilities of the University of Barcelona (SCT-UB). After that date, analyses were carried out at the Department of Analytical Chemistry of the University of the Basque Country (UPV-EHU).

Metal and trace element analyses were performed by Inductively Coupled Plasma (ICP). Fe was quantified by Optical Emission Spectrometry (ICP-OES) with a Perkin Elmer OPTIMA 3200 RL instrument (SCT-UB), and Al, Ti, Mn, Ni, Cu, Zn, As, Cd and Pb were measured by Mass Spectrometry (ICP-MS) with a Perkin Elmer ELAN 6000 instrument (SCT-UB), and with a Perkin Elmer Nexion 300 instrument (UPV-EHU; also Fe with this instrument). For