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Bulk deposition of atmospheric inorganic nitrogen in mountainous heathland ecosystems in North-Western Spain

Javier Calvo-Fernández *, Elena Marcos, Leonor Calvo

Area of Ecology, Faculty of Biological and Environmental Sciences & Institute of Environment, Natural Resources and Biodiversity, University of León, 24071 León, Spain

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ABSTRACT

Nitrogen (N) deposition has been identified as one of the main traits of terrestrial ecosystems, affecting their structure and functioning. However, few studies have been developed under natural field conditions to evaluate the amount of N deposition in low nutrient status heathland ecosystems. Therefore, a field experiment was carried out to investigate the bulk inorganic N inputs in mountainous heathlands of North-Western Spain. Two study sites (La Majúa and San Isidro) were selected on the south side of the Cantabrian Mountains, as a representative monitoring of N-sensitive ecosystems. Three replicated bulk collectors and one rain gauge were installed at each study site to collect monthly bulk deposition samples over three-year period (2011–2014). Bulk inorganic N deposition was different between the study sites (2.81 kg N ha^{-1} yr^{-1} in La Majúa and 4.56 kg N ha^{-1} yr^{-1} in San Isidro), but showed the same seasonal dynamic, with higher N deposition rate in the wet period (October to April) compared to the dry period (May to September). Annual bulk NO_3^- deposition was comparable to annual bulk NH_4^+ deposition in La Majúa (1.42 vs. 1.39 kg N ha^{-1} yr^{-1}), and higher in San Isidro (2.89 vs. 1.67 kg N ha^{-1} yr^{-1}). San Isidro displayed a characteristic bulk NH_4^+/NO_3^- deposition ratio below 1 of industrialized areas (0.58), while La Majúa displayed a bulk NH_4^+/NO_3^- deposition ratio close to 1 (0.98), distinctive of an intermediate situation between industrialized and agricultural areas. Total bulk inorganic N depositions observed in the present field study are consistent with the modelled estimation of N depositions for North-Western Spain, but only San Isidro was consistent with the estimated dominance of oxidized N over reduced N.

1. Introduction

Anthropogenic activities have contributed, mainly since the 1970s, to a significant increase in reactive nitrogen (Nr), including aerosols and particulate material into the atmosphere (Galloway et al., 2014), which are generated from the emissions of oxidized NO_Y (NO_X, HNO_3, N_2O_5, particulate NO_3^-, organic nitrates…) and reduced NH_X (NH_3 and particulate NH_4^+) compounds (Galloway et al., 2004). However, a different tendency compared to this global dynamic was displayed in the analysis of a shorter time period in Spain, in which decreases of 41% and 11% have been observed for NO_X and NH_3 emissions from 1990 to 2013 (MAGRAMA, 2015). The amounts of these atmospheric emissions of NO_X, NH_3 and NO_3^- have been related to the deposition rates of NO_Y and NH_X (Aguillaume et al., 2016). Estimates of global total N depositions in 2001 were also comparable to the global total N emissions for the same year (106.3 vs. 105.1 Tg N; Vet et al., 2014). Predictions point out that global NO_Y and NH_X depositions will increase from the 1990s to 2050 (Galloway et al., 2004), although in developed areas such as Europe a decrease in N deposition of about 25% has been observed from 1990 to 2009 (Tørseth et al., 2012). In Spain, atmospheric N depositions are lower than values recorded in Central Europe (Lorenz and Becher, 2012), with estimates of current rates being 12–23 kg N ha^{-1} yr^{-1} for Central Europe and 3–15 kg N ha^{-1} yr^{-1} for Spain (EMEP, 2015). In addition, oxidized N deposition tends to dominate over reduced N in Spain (Fagerli et al., 2006), even after the decrease in NO_Y and NH_X depositions observed in mountainous areas of Northern Spain in response to the lessening in N emissions in recent years (Izquierdo and Avila, 2012). These atmospheric N depositions depend mainly on meteorological factors such as prevailing wind direction and wind speed (Gómez-Carracedo et al., 2015; Javid et al., 2015; Pineda Rojas and Venegas, 2010), as well as the type and distribution of N emission sources (Calvo et al., 2010; Celle-Jeanton et al., 2009; Niu et al., 2014). In Spain, the sources of atmospheric NH_3 in 2012 were 92% from the volatilization of NH_3 from agricultural and farming activities (EEA, 2014), and the sources of NO_X were mainly from combustion processes of industrial activities (57%) and road traffic (34%) (EEA, 2014).

In recent years, new environmental legislation on emission control (Castellanos and Boersma, 2012; Cuevas et al., 2014) and land abandonment in mountainous systems (Morán-Ordóñez et al., 2013) have led to a reduction in N depositions in protected areas such as the Cantabrian Mountains (NW Spain). Updated N deposition data in North Western Spain, and in particular for these protected areas are necessary in order to identify whether their natural ecosystems could be receiving

* Corresponding author.
E-mail address: jcalf@unileon.es (J. Calvo-Fernández).

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N deposition rates above their tolerance threshold (Bleeker et al., 2011). One of the most representative ecosystems in the mountains of North-Western Spain is *Calluna-vulgaris*-heathland, which represents a habitat of high conservation importance at European level (Habitats Directive 92/43/EEC). These *Calluna* heathlands are adapted to low-N conditions (Calvo-Fernández et al., 2015) and the knowledge of N deposition rates in these sensitive-N ecosystems could be necessary to apply appropriate management strategies (Boutin et al., 2015; Calvo et al., 2005, 2007; Marcos et al., 2003). However, only modelled N deposition data for the last few years are available for the mountainous systems of North-Western Spain, with a lack of field measured data in this area (Gómez-Carracedo et al., 2015). Besides, modelled N deposition data should be applied with caution in studies on a small regional scale and in regions with complex topography and the influence of local emissions (García-Gómez et al., 2014), since they cannot be accurate (Im et al., 2013). Boutin et al. (2015) found that mountainous areas could be more threatened by N depositions than the estimates showed by N deposition models, mainly due to the orographic scavenging effect (Cape et al., 2015).

The main aim of this article was to assess the field measured bulk inorganic N depositions in N-sensitive ecosystems of North-Western Spain in order to find seasonal dynamics of the N deposition rate. We also proposed quantifying the different inorganic N chemical forms in bulk deposition (oxidized/reduced). Finally, we proposed to compare our results about N deposition rates with the values obtained for predictive models of N deposition for our study area.

We hypothesized that the frequency and intensity of precipitation are important factors determining N deposition rates, whereby we expect to found elevated inorganic N deposition rates associated with precipitation periods (Izquieta-Rojano et al., 2016; Liang et al., 2015; Zhan et al., 2015). We also hypothesized that oxidized inorganic N deposition is higher than reduced inorganic N deposition, according to modelled N deposition data for North-Western Spain (García-Gómez et al., 2014).

2. Materials and methods

2.1. Study area and monitoring sites

The study area is located in the Cantabrian Mountain range (NW Spain). Two study sites were selected, situated 90 km apart from each other (Fig. 1). La Majúa is located at the top of a valley (1770 m a.s.l., 43°01′N, 6°05′W) within the Babia Biosphere Reserve and San Isidro is located in a mountain pass (1636 m a.s.l., 43°03′N, 5°21′W) at the western limit of the Picos de Europa Regional Park. Both study sites are within *Calluna*-heathland areas of North-Western Spain, which represent the southern distribution range of these heathlands in Europe. The study area has a Eurosiberian climate. Mean annual temperature is 8.9 °C for La Majúa and 5.5 °C for San Isidro. Prevailing winds are from north to northeast direction in La Majúa and from west to west-northwest in San Isidro (Fig. 2). Both study sites are located near mountain passes, which connect the air masses of the northern and southern slopes of the Cantabrian Mountain range, although prevailing northern air masses in San Isidro come from the west due to the orographic conditions of this mountain pass.

2.2. Potential sources of N emissions in the study area

The study area is a mountainous system mainly dominated by shrub, pastureland, and forest land uses (Fig. 1). Scattered coal mines are located within the study area, using the extracted coal for combustion processes of a variety of industrial activities situated in lowlands. Prevailing winds in the study sites are from the highly industrialized and populated area of Central-Northern Asturias (North Spain), where are located several NO_Y emission sources such as coal power plants, cement factories, metal smelter plants and intense road traffic. Besides, San Isidro study site is located <1 km from an opencast talc mine, which is an important source of NO_Y emissions due to blasting operations associated with mineral extraction processes. The study area is characterized by scarce NH_X emission sources, although La Majúa is surrounded by larger areas of pasturelands and croplands compared to San Isidro, associated with volatilization of NH_X from livestock excreta and nitrogenous fertilizers, respectively.

2.3. Field sampling and chemical analysis

Three bulk collectors were installed at each study site on 1st July 2011 in open areas. We used the same type of bulk collectors used by Izquierdo and Avila (2012), which consisted of an acid-washed PVC bottle (500 ml) coupled to an acid-washed PVC funnel (12 cm diameter; 113 cm^2 horizontal interception surface). The 500 ml PVC bottle was protected from direct sunlight and biological transformations inside a PVC opaque tube. The PVC funnel was covered by a 1 mm pore size mesh to avoid contamination by insects, debris and other contaminants. Each bulk collector was supported by a metal bar placed above a grass surface at ≈1 m height (to avoid ground contamination). Besides, one Hellmann rain gauge (200 cm^2 collection area) was installed at each study site in order to measure the amount of precipitation.

Bulk precipitation samples were collected monthly basis in 38 sampling occasions at the end of each month from July 2011 to August 2014. After each sampling, the bulk collectors were washed and rinsed with deionized water and dried. These samples were transported in dark conditions in order to prevent any sunlight effects. Prior to analyses, the samples were filtered through a 25 mm Ø cellulose acetate membrane filter (0.45 μm pore size). Ammonium concentration was analysed using the salicylate method (Reardon et al., 1966) <24 h after sample collection, with a detection limit of 0.001 mg L^{-1} (Spectrophotometer UV-1700 PharmaSpec, Shimadzu, Kyoto, Japan). Nitrate concentration was determined by ion chromatography (850 Professional IC, Herisau, Switzerland) according to Tabatabai and Dick (1983) from filtered samples stored in a freezer, with a detection limit of 0.005 mg L^{-1}.

2.4. Calculations

Volume-weighted mean monthly and annual of NO_3^--N and NH_4^+-N concentrations in bulk precipitation (henceforth referred as NO_3^- and NH_4^+ concentrations respectively) for each study site were calculated separately with the following equation (Zhao et al., 2009):

$$C = \sum_{i=1}^{n} Ci\ x\ Li / \sum_{i=1}^{n} Li, \quad (1)$$

where C refers to volume-weighted mean of NO_3^- or NH_4^+ concentration in bulk precipitation (mg N L^{-1}); Ci is the NO_3^- or NH_4^+ concentration in bulk precipitation for each individual sample (mg N L^{-1}); Li is the amount of precipitation corresponding to each sample (mm); and n refers to the number of samples.

Mean monthly of NO_3^--N and NH_4^+-N deposition rates (henceforth referred as NO_3^- and NH_4^+ depositions respectively) for each study site were calculated as follows (Zhao et al., 2009):

$$D = Ci\ x\ Li\ x\ \ 0.01, \quad (2)$$

where D refers to mean monthly of bulk NO_3^- or NH_4^+ deposition (kg N ha^{-1} $month^{-1}$); Ci is the volume-weighted mean monthly of NO_3^- or NH_4^+ concentration in bulk precipitation (mg N L^{-1}); and Li is the mean monthly of precipitation (mm).

Annual bulk NO_3 and NH_4^+ depositions (kg N ha^{-1} yr^{-1}) at each study site was also calculated as the sum of mean monthly of bulk depositions.

NH_4^+/NO_3^- ratio was also calculated from means of monthly and annual bulk NO_3^- and NH_4^+ depositions for each study site.