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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. Among terrestrial ecosystems, heathlands are characterised by low nutrient status and highly affected by N deposition. However, few studies have been developed under natural field conditions to evaluate the amount of N deposition in these ecosystems. Therefore, a field experiment was carried out to investigate the 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 N-sensitive ecosystems. Three replicated bulk collectors and one rain gauge were installed at each study site to collect monthly rainwater samples over three years. Wet bulk N deposition was different between the study areas (2.81 kg N ha-1 year-1 in La Majúa and 4.56 kg N ha-1 year-1 in San Isidro), but showed the same temporal pattern, with the highest N deposition rate observed in April and the lowest in August-September. In general, annual wet bulk NO3--N deposition was higher than NH4+-N, reflecting the prevailing NOX emission sources. Depositions of NO3--N were mostly originated by NOX emissions from northern highly industrialized and populated areas of North Spain. The lower NH4+/NO3- ratio in rainwater observed in the study area could be due to the decline of traditional land uses (livestock grazing, heath burning and croplands) associated with NHY emissions. Despite the low rates of N deposition observed in this study, N-sensitive heathlands in North-Western Spain could be threatened by N depositions.

Dear Editor,

I send you the manuscript entitled "Atmospheric inorganic nitrogen inputs in mountainous heathland ecosystems in North-Western Spain" to be evaluated to publish in the journal "Atmospheric Research".

This manuscript is a novel contribution about the inorganic nitrogen depositions in NW Spain that could affect the functioning and biodiversity of hot spot ecosystems. For this reason, updated nitrogen deposition rate is necessary to know if these N-sensitive ecosystems are affected by currently N deposition rates. This is the first study that assess field measured of nitrogen depositions in North West Spain and we quantify the prevailing chemical form of inorganic nitrogen deposition (oxidized/reduced) in order to determine the potential nitrogen emission sources and its consequences in N-sensitive ecosystems.

Yours sincerely

Javier Calvo-Fernández

Highlights

Wet bulk inorganic N depositions range between 2.81 to 4.56 kg N ha^{-1} $year^{-1}$ in mountainous heathlands of North-Western Spain.

Wet bulk NO_3^--N depositions were higher than NH_4^+-N depositions.

The NO_3^--N depositions are from northern industrialized and populated areas.

The decline of traditional land uses gives lower NH_4^+-N depositions.

N-sensitive heathlands of North-Western Spain could be threatened by current N depositions rates.

Atmospheric inorganic nitrogen inputs in mountainous heathland ecosystems in North-Western 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. Among terrestrial ecosystems, heathlands are characterised by low nutrient status and highly affected by N deposition. However, few studies have been developed under natural field conditions to evaluate the amount of N deposition in these ecosystems. Therefore, a field experiment was carried out to investigate the 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 N-sensitive ecosystems. Three replicated bulk collectors and one rain gauge were installed at each study site to collect monthly rainwater samples over three years. Wet bulk N deposition was different between the study areas (2.81 kg N ha^{-1} $year^{-1}$ in La Majúa and 4.56 kg N ha^{-1} $year^{-1}$ in San Isidro), but showed the same temporal pattern, with the highest N deposition rate observed in April and the lowest in August-September. In general, annual wet bulk NO_3^--N deposition was higher than NH_4^+-N, reflecting the prevailing NO_X emission sources. Depositions of NO_3^--N were mostly originated by NO_X emissions from northern highly industrialized and populated areas of North Spain. The lower NH_4^+/NO_3^- ratio in rainwater observed in the study area could be due to the decline of traditional land uses (livestock grazing, heath burning and croplands) associated with NH_Y emissions. Despite the low rates of N deposition observed in this study, N-sensitive heathlands in North-Western Spain could be threatened by N depositions.

Key Words

Wet bulk nitrogen deposition; nitrogen emission source; ammonium/nitrate ratio; heathland ecosystem; North-Western Spain.

1. Introduction

Anthropogenic activities have contributed, mainly since the 1970s, to a significant increase in nitrogen (N) compound creation, including aerosols and particulate material into the atmosphere (Galloway et al., 2014), which are generated from the emissions of oxidized (NO_Y) and reduced (NH_X) N compounds. Estimations of global N emissions point out that N oxide (NO_X) emissions will increase from 46.0 Tg N $year^{-1}$ in the 1990s to 81.5 Tg N $year^{-1}$ in 2050, and ammonia (NH_3) emissions will increase from 52.6 Tg N $year^{-1}$ to 113.0 Tg N $year^{-1}$ in the same period (Galloway et al., 2004) due to the increasing world population (Galloway et al., 2014). However, this global pattern of increasing N emissions showed different tendencies in the analysis of a shorter time period in developed areas such as Europe, in which a decrease in N emissions has been detected from 1990 to 2013, with a reduction of 54% for NO_X and 27% for NH_3 (EEA, 2015). A similar trend was observed for NO_X emissions in Spain, with a decrease of 41% in the period 1990-2013 (MAGRAMA, 2015a). This decreasing pattern could be explained by the effects of the world economic crisis and, at the same time, by the implementation of anthropogenic NO_X emission control policies (Castellanos and Boersma, 2012; Vedrenne et al., 2015). In Spain the North-Western region represents the area with the greatest decrease in NO_X emissions (Cuevas et al., 2014) about 52% in the last eight years (MAGRAMA, 2015b) related to the decline in mining and industrial activities. However, an opposite trend to the rest of Europe has been observed for NH_3 emissions in Spain, with an increase of 11% from 1990 to 2013 (MAGRAMA, 2015a).

Aguillaume et al. (2016) have related the amount of atmospheric emissions of NO_X, NH_3, N_2O and NO_3^- to the deposition rates of NO_Y and NH_X. Global total deposition of N was estimated at 106.3 Tg N in 2001, comparable to the global N emissions (Vet et al., 2014). Estimates of global N depositions point out that NO_Y and NH_X depositions will increase from the 1990s to 2050 (Galloway et al., 2004). However, different patterns for N depositions have been observed

in Europe, as the decrease in N emissions in Europe since the 1990s has involved a decrease in N depositions of about 25% 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 N deposition rates being 12-23 kg N ha^{-1} $year^{-1}$ for Central Europe and 3-15 kg N ha^{-1} $year^{-1}$ for Spain (EMEP, 2015). Furthermore, oxidized N depositions in Spain dominate reduced N depositions, patterns opposite to those of Central Europe (Fagerli et al., 2006). In mountainous areas in North Spain a decrease in oxidized and reduced N depositions has been observed in response to the decrease in N emissions in recent years (Izquierdo and Avila, 2012). Nonetheless, it has been estimated that the predicted slight increase in NO_X and NH_3 emissions in the next five years will produce a simultaneous increase in both oxidized and reduced N depositions (Vedrenne et al., 2015). Atmospheric N can be deposited by two processes: wet deposition, N which enters ecosystems via precipitation, and dry deposition, which is the direct input of atmospheric N gasses and aerosols by wind and gravity (Avila et al., 2010; Javid et al., 2015; Stevens et al., 2011). In southern Europe dry deposition tends to dominate wet (Im et al., 2013; Simpson et al., 2006). In this sense, in Spain, different authors (Rodà et al., 2002; Vet et al., 2014) estimated that wet deposition of N represents about 40% of total N deposition.

Chemical compounds of N in rainwater are the result of precipitation scavenging processes of nitrogenous gases and aerosols from the atmosphere (Al-Khashman, 2009; Avila et al., 2010). The concentration of N chemical compounds in precipitation depends mainly on meteorological factors such as prevailing wind direction and wind speed (Gómez-Carracedo et al., 2015; Pineda Rojas and Venegas, 2010) and the type and distribution of N emission sources (Calvo et al., 2010; Celle-Jeanton et al., 2009; Niu et al., 2014). So, atmospheric N depositions can originate from local emission sources or from distant sources by long-range transport (Al-Khashman, 2009). In relation to the type of emissions, the sources of NH_X in Spain were 94%

from the volatilization of NH_3 from agricultural and farming activities in 2012 (EEA, 2014), and the sources of NO_Y were mainly from combustion processes of power plants and industrial processes (57%) and road traffic (34%) in 2012 (EEA, 2014). Although N emissions mainly have an anthropogenic origin (Javid et al., 2015), there are N emissions produced by natural sources, such as soil emission, biomass burning and lighting (Cuevas et al., 2014; Jia et al., 2010).

In recent years new environmental legislation on emission control (Castellanos and Boersma, 2012; Cuevas et al., 2014) and land abandonment in mountainous areas (Morán-Ordóñez et al., 2013) has led to a reduction in N depositions in these areas of North Spain. However, protected areas such as the Cantabrian Mountains (NW Spain) could be receiving N deposition rates above their tolerance threshold (Bleeker et al., 2011), which may affect these natural ecosystems, recognized as a biodiversity hotspot (Morán-Ordóñez et al., 2011). 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 affected by current N deposition rates (Calvo et al., 2007; Marcos et al., 2003). One of the most representative ecosystems in the mountainous areas of North-Western Spain is *Calluna-vulgaris*-heathland, which represents a habitat of high conservation importance at a European level (Habitats Directive 92/43/EEC). These *Calluna* heathlands are adapted to low-N conditions (Calvo-Fernández et al., 2015) and knowledge of N depositions 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). For this reason, modelled N deposition maps have been created in order to complement the measurement data by filling the large spatial gaps between measurement points (Vet et al., 2014). However, only modelled N deposition data for the last few years are available for the mountainous areas 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 predicted 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 inorganic wet bulk N depositions in N-sensitive ecosystems of North-Western Spain in order to find temporal patterns of the N deposition rate. We also proposed quantifying the different inorganic N chemical forms of wet bulk deposition (oxidized/reduced). Finally, we proposed analysing the relationship between N depositions and N emission sources in North-Western Spain.

2. Materials and Methods

2.1. 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., 43º01'N, 6º05'W) within the Babia Biosphere Reserve and San Isidro is located in a mountain pass (1636 m.a.s.l., 43º03'N, 5º21'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. These study sites have a Eurosiberian climate that is characterized by a dry period of less than two months in summer and snowfall events in winter. Mean annual temperature is 8.9 ºC for La Majúa and 5.5 ºC for San Isidro. Prevailing winds are from north to northeast 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. Field sampling and chemical analysis

Three replicated rainfall collectors were installed at each study site on 1st July 2011 in open areas. We used bulk deposition collectors recommended by Izquierdo and Avila (2012) for this type of studies. The bulk collector consisted of a 500 ml PVC bottle coupled to a 12 cm diameter PVC funnel (113 cm^2 horizontal interception surface). The bottle was supported by a metal bar placed above a grass surface at ≈ 1m height (to avoid ground contamination), inside a PVC opaque tube, protected from direct sunlight and biological transformations. The funnel also limited the evaporation of rainwater. The funnel was covered by a 1 mm pore size mesh to avoid contamination by insects, debris and other contaminants. The bottle was washed and rinsed with deionized water and dried after each sampling. Bulk collectors were permanently open to the atmosphere, collecting a fraction of total dry deposition, so not only wet deposition was collected. Besides, a Hellmann rain gauge (200 cm^2 collection area) was installed at each study site in order to measure the amount of precipitation.

Monthly samples of rainwater from wet bulk depositions were collected from July 2011 to September 2014. These samples were transported in dark conditions in order to prevent any sunlight effects. Prior to analyses, the samples were filtered through a 25mm Ø cellulose acetate membrane filter (0.45 µm pore size). We analysed the ammonium concentration using the salicylate method (Reardon et al., 1966) less than 24 hours after sample collection. Nitrate concentration was determined by ion chromatography (Tabatabai and Dick, 1983) from filtered samples stored in a freezer.

2.3. Measurements

Monthly means of NO_3^--N and NH_4^+-N deposition rates (referred to as inorganic wet bulk depositions) for each study site were calculated as follows:

$$D = \sum_{i=1}^{n} Ci \; x \; Li \; x \; 0.01 \; x \; f \; / \; n, \quad (1)$$

where *D* refers to monthly means of NO_3^--N or NH_4^+-N wet bulk depositions (kg N ha^{-1}); *Ci* is the NO_3^- or NH_4^+ concentration in rainwater for each individual sample (mg l^{-1}); *Li* is the amount of precipitation corresponding to each sample (mm); *f* is the conversion factor which is necessary to calculate NO_3^--N deposition (f=14/62) and NH_4^+-N deposition (f=14/18); *n* refers to the number of samples.

Annual wet bulk deposition for NO_3^--N and NH_4^+-N at each study site was also calculated as the sum of monthly means of wet bulk depositions.

Monthly and annual volume-weighted means of NO_3^- and NH_4^+ concentrations in rainwater for each study site were calculated separately with the following equation (Zhao et al., 2009):

$$C = \sum_{i=1}^{n} Ci \; x \; Li \; / \sum_{i=1}^{n} Li, \quad (2)$$

where *C* refers to volume-weighted means of NO_3^- or NH_4^+ concentrations in rainwater (mg l^{-1}); *Ci* is the NO_3^- or NH_4^+ concentration in rainwater for each individual sample (mg l^{-1}); *Li* is the amount of precipitation corresponding to each sample (mm); *n* refers to the number of samples.

NH_4^+/NO_3^- ratio was also calculated from volume-weighted means of NO_3^- and NH_4^+ concentrations in rainwater for each study site.

2.4. Potential sources of N emissions in the study area

We identified the main N emission sources surrounding the La Majúa and San Isidro study sites in order to find a possible relationship between patterns of atmospheric N depositions in relation to N emissions. We selected an area from 30 km south of the study sites as far as the coastline in the north (more than 50 km away from the study sites, since the prevailing winds are from the north (Fig. 2)). A map of N emission sources was created using ArcGis v.10.3. We reclassified the CORINE Land Cover 2006 map (http://centrodedescargas.cnig.es/CentroDescargas/) in seven categories: human infrastructure, mineral extraction sites, croplands, pasturelands, forest, shrub, and water and rocks. We also represented the main stationary N emission sources (http://www.prtr-es.es/Informes/InventarioInstalacionesIPPC.aspx) over the land use map in the following categories: shipyard, feedstuff factory, farm, brick factory, metal smelter plant, coking plant, fertilizer plant, cement factory, and coal power plant.

2.5. Statistical Analyses

Monthly differences in NO_3^- and NH_4^+ concentration, NH_4^+/NO_3^- ratio, wet bulk NO_3^--N and NH_4^+-N deposition were tested using a two-way repeated measures ANOVA, with time as the repeated measure. A Pearson correlation was used to analyse the relationship among monthly precipitation with NO_3^- and NH_4^+ concentration, NH_4^+/NO_3^- ratio, wet bulk NO_3^--N and NH_4^+-N deposition. All statistical analyses were performed using SPSS v.20.0 (SPSS Inc., Chicago, IL, USA).

3. Results

3.1. Wet bulk N deposition

Annual wet bulk N-(NO_3^- + NH_4^+) deposition was 2.81 kg N ha^{-1} $year^{-1}$ and 4.56 kg N ha^{-1} $year^{-1}$ in La Majúa and San Isidro, respectively. Annual wet bulk NO_3^--N deposition was higher than NH_4^+-N (1.42 vs. 1.39 kg N ha^{-1} $year^{-1}$ and 2.89 vs. 1.67 kg N ha^{-1} $year^{-1}$ for La Majúa and San Isidro, respectively). Monthly differences in wet bulk NO_3^--N ($F_{(11, 44)}$ = 52.869; $p<0.05$) and NH_4^+-N deposition ($F_{(11, 44)}$ = 10.273; $p<0.05$) were found, with the highest deposition rates in April and the lowest in August or September (Fig. 3). Precipitation is significantly correlated with NO_3^--N (r^2 = 0.56; $p<0.01$) and NH_4^+-N (r^2 = 0.46; $p<0.01$) deposition. Also, there were significant differences between the two study sites for monthly wet bulk NO_3^--N depositions ($F_{(1, 4)}$ = 115.622; $p<0.05$), with higher NO_3^--N deposition rates in San Isidro, except for September (Fig. 3). However, no significant differences were found for wet bulk NH_4^+-N deposition between the two study sites.

3.2. NO_3^- and NH_4^+ concentrations in rainwater

Annual precipitation was 858 mm in La Majúa and 1,645 mm in San Isidro, although unevenly distributed throughout the year (Fig. 4). We observed a high precipitation period from October to April and a low one from May to September. NO_3^- concentration in rainwater was always higher than NH_4^+ concentration throughout the year; but both N compounds are significantly correlated (r^2 = 0.79; $p<0.01$). A temporal pattern with significant differences in time was observed for NO_3^- concentration in rainwater ($F_{(11, 44)}$ = 40.306; $p<0.05$), with the highest values reached during summer months (June, July, August and September). NH_4^+ concentration also showed a temporal pattern ($F_{(11, 44)}$ = 8.210; $p<0.05$), with the highest values reached during spring and summer months. It was observed that NO_3^- and NH_4^+ concentration in

rainwater were negatively correlated with precipitation rates (r^2 = -0.65 and r^2 = -0.59, respectively; $p<0.01$). There were no significant differences between the study sites in the annual weighted mean of NO_3^- concentration in rainwater. On the contrary, the annual weighted mean of NH_4^+ concentration was significantly ($F_{(1, 4)} = 10.669$; $p<0.05$) higher in La Majúa (0.206 mg l^{-1}) than San Isidro (0.134 mg l^{-1}).

3.3. NH_4^+/NO_3^- ratio in rainwater

Significant differences over time in the study sites were found for the NH_4^+/NO_3^- ratio in rainwater ($F_{(11, 44)} = 2.057$; $p<0.05$). The highest NH_4^+/NO_3^- ratio in rainwater was observed in May, and the lowest in September-October (Table 1). The annual NH_4^+/NO_3^- ratio was higher in La Majúa than San Isidro, with values of 0.29 and 0.16, respectively ($F_{(1, 4)} = 9.387$; $p<0.05$) (Table 1).

3.4. Potential sources of N emissions

The study area is a mountainous system mainly dominated by shrub, pastureland and forest land uses. 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 (Fig. 5). Prevailing winds in the two study sites are from the highly industrialized and populated area of Central-Northern Asturias (North Spain), carrying the NO_Y emissions originated by combustion processes towards the study sites. Air masses in San Isidro are more influenced by NO_Y emissions, since prevailing winds carry the N emissions more directly from coal power plants, cement factories, metal smelter plants and road traffic compared to La Majúa. Besides, the San Isidro study site is located less than 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, mainly related to traditional land uses. However, land uses in La Majúa are potentially greater emitters of NH_X compared to San Isidro, because La Majúa is surrounded by larger areas of pasturelands and croplands, associated with volatilization of NH_X from livestock excreta and nitrogenous fertilizers, respectively.

4. Discussion

Wet N depositions are conditioned by several factors, such as the volume of precipitation and the seasonal influence of emission sources (Alastuey et al., 1999; Cape et al., 2015; Izquieta-Rojano et al., 2016; Liang et al., 2015; Zhan et al., 2015), as well as the chemical and physical N removing processes from the atmosphere (de Souza et al., 2015). In our study, we observed higher wet bulk NO_3^--N depositions in the winter months compared to the summer. It could be explained because NO_2 emissions to the atmosphere in North-Western Spain are higher during winter due to fossil fuel consumption in building heating systems (Cuevas et al., 2014; Gómez-Carracedo et al., 2015). Wet bulk NO_3^--N depositions observed in our field studies are consistent with the modeled estimation for North-Western Spain (1.5-2.0 kg N ha^{-1} $year^{-1}$; Vet et al., 2014) and also with others studies carried out for all Spain (2.33 kg N ha^{-1} $year^{-1}$; García-Gómez et al., 2014). The highest wet bulk NH_4^+-N depositions in our study were obtained in April, reflecting the emissions of volatilized NH_3 from nitrogenous fertilizers spread over croplands in late-winter and spring (Asman et al., 1998; Rodà et al., 2002; Zhan et al., 2015). Wet bulk NH_4^+-N depositions in our field study are within the range of the modeled estimate for North-Western Spain (1.0-2.0 kg ha^{-1} $year^{-1}$; Vet et al., 2014), but lower than the average measured for all Spain (2.08 kg N ha^{-1} $year^{-1}$; García-Gómez et al., 2014). Total annual wet bulk N deposition observed in the study sites was lower compared to other mountainous areas

of Spain, as Pyrenees (Rodà et al., 2002; Sanz et al., 2002; Izquierdo and Avila, 2012). This could be explained by greatly reduced industrial and mining activities in recent years in North-Western Spain, which has resulted in a drastic reduction in atmospheric NO_2 emissions (MAGRAMA, 2015b), since NO_3^--N deposition patterns mimic the general NO_X emission patterns of the surrounding area (Vet et al., 2014; Aguillaume et al., 2016). Besides, the prevalence of unpolluted air masses from the Atlantic Ocean crossing the study area could also support the observed low N deposition rates (Santos et al., 2011). Despite low rates of N deposition, protected habitats such as mountainous heathlands could be receiving an exceedance of N empirical critical load (García-Gómez et al., 2014) and affect their high diversity (Boutin et al., 2015; Morán-Ordóñez et al., 2013) in poor-N ecosystems.

Wet bulk NO_3^--N and NH_4^+-N depositions in our field studies were consistent with total national emissions of NO_X and NH_3, since NO_X were higher than NH_3 emissions for the period 2011-2013 (MAGRAMA, 2015a). This is in agreement with the estimates obtained for modeled N deposition in North-Western Spain, which showed a dominance of oxidized N over reduced N (García-Gómez et al., 2014). These differences between wet bulk NO_3^--N and NH_4^+-N depositions could be explained by the diversity of N sources (Li et al., 2013). Prevailing wet bulk NO_3^--N depositions could be explained to the great influence of airborne NO_X from industrialized and populated areas of the northern region of Asturias (Vedrenne et al., 2015). However, NH_4^+-N depositions are lower due to it is mainly influenced by local sources such as pasturelands and croplands (Asman et al., 1998). In these mountainous systems the NH_3 emissions are lower than in intensive agriculture of the southern lowlands (MAGRAMA-C.H.D., 2010) with higher level of N fertilization. Furthermore, land abandonment in these mountainous areas over the last 50 years also contributes to lower wet bulk NH_4^+-N deposition, since the decline of traditional management of pasturelands has led to a reduction in NH_3

emissions associated with traditional practices such as livestock grazing by sheep transhumance and heath burning (Morán-Ordóñez et al., 2013).

Large seasonal variability of NO_3^- and NH_4^+ concentrations in rainwater were found in the study area, which showed the existence of an annual cycle for oxidized and reduced N concentrations in rainwater (Avila et al., 2010; de Souza et al., 2015; Niu et al., 2014). The highest NO_3^- and NH_4^+ concentrations in rainwater are related to the lowest precipitation rates during summer months (Izquierdo and Avila, 2012; Park et al., 2002; Pineda Rojas and Venegas, 2010). This can be explained because the first drops of rainfall perform an intense atmospheric N scavenging, which increases the rainwater N concentration in low rainfall events (Al-Khashman, 2009; Sanz et al., 2002; Zhang et al., 2008).

The chemical form of N inputs is an important factor regulating plant nutrient assimilation processes in a wide variety of ecosystems (Harmens et al., 2014; Izquieta-Rojano et al., 2016; Pornon et al., 2007). So, the high NO_3^- and NH_4^+ concentrations in rainwater found during summer could affect the nutrient balance of N-poor ecosystems such as mountainous heathlands (Calvo-Fernández et al., 2015), since this period is the growing season and the highest amount of N is uptaken by vegetation. Previous studies have demonstrated that an increase of N depositions in heathland ecosystems could involve higher shoot N content, inducing heather defoliation by leaf beetles, such as *Lochmaea suturalis* (Cuesta et al., 2008; Torres, 2010), as well as a rise in soil nutrient content and higher species richness (Marcos et al., 2015). The amount of NO_3^- and NH_4^+ concentrations in rainwater reflects the composition of the nitrogenous gases and aerosols in the atmosphere (Calvo et al., 2010; Celle-Jeanton et al., 2009; Niu et al., 2014). For this reason, the NH_4^+/NO_3^- ratio in rainwater is a useful value to find out the prevailing sources of N depositions in a delimited area (Li et al., 2013). Zhao et al. (2009) defined a NH_4^+/NO_3^- ratio in rainwater <1 within industrialized regions and >1 within

intensive agricultural regions. Our field study sites showed NH_4^+/NO_3^- ratios much smaller than 1 over time, pointing out a greater contribution of industrial activities on total N deposition.

5. Conclusions

Field measured wet bulk depositions of inorganic N in North-Western Spain were evaluated in this study. Annual wet bulk deposition was 2.81 kg N ha^{-1} $year^{-1}$ and 4.56 kg N ha^{-1} $year^{-1}$ for the La Majúa and San Isidro study sites, respectively. A similar temporal pattern was found for wet bulk NO_3^--N and NH_4^+-N depositions in the study area. This temporal pattern was dependent on the precipitation rate, with the highest monthly NO_3^--N and NH_4^+-N depositions in the rainiest months. It was found that wet bulk depositions of oxidized N (NO_3^--N) were higher than reduced N (NH_4^+-N) depositions, consistent with the observed NH_4^+/NO_3^- ratio in rainwater <1. This prevailing wet bulk NO_3^--N deposition was associated with airborne NO_X emissions from the northern industrialized region. Land abandonment in mountainous areas has had a great effect on reduced wet bulk NH_4^+-N deposition due to the decline of traditional management associated with NH_Y emissions. Despite the low rates of N deposition observed in this study, N-sensitive heathlands in mountainous areas could be receiving an exceedance of N affecting their structure and functioning.

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Tables

Table 1: NH_4^+/NO_3^- ratio in rainwater for La Majúa and San Isidro. Data are monthly and annual volume-weighted means with volume-weighted SD in parentheses.

	La Majúa		San Isidro	
January	0.38	(0.14)	0.13	(0.05)
February	0.32	(0.13)	0.15	(0.05)
March	0.38	(0.16)	0.18	(0.06)
April	0.35	(0.12)	0.19	(0.07)
May	0.44	(0.28)	0.31	(0.18)
June	0.19	(0.30)	0.14	(0.05)
July	0.25	(0.08)	0.21	(0.08)
August	0.20	(0.52)	0.22	(0.09)
September	0.11	(0.56)	0.29	(0.14)
October	0.19	(0.10)	0.11	(0.09)
November	0.17	(0.08)	0.12	(0.06)
December	0.31	(0.12)	0.23	(0.11)
Annual	0.29	(0.15)	0.16	(0.08)

Figure captions

Fig. 1. Location of La Majúa and San Isidro study sites.

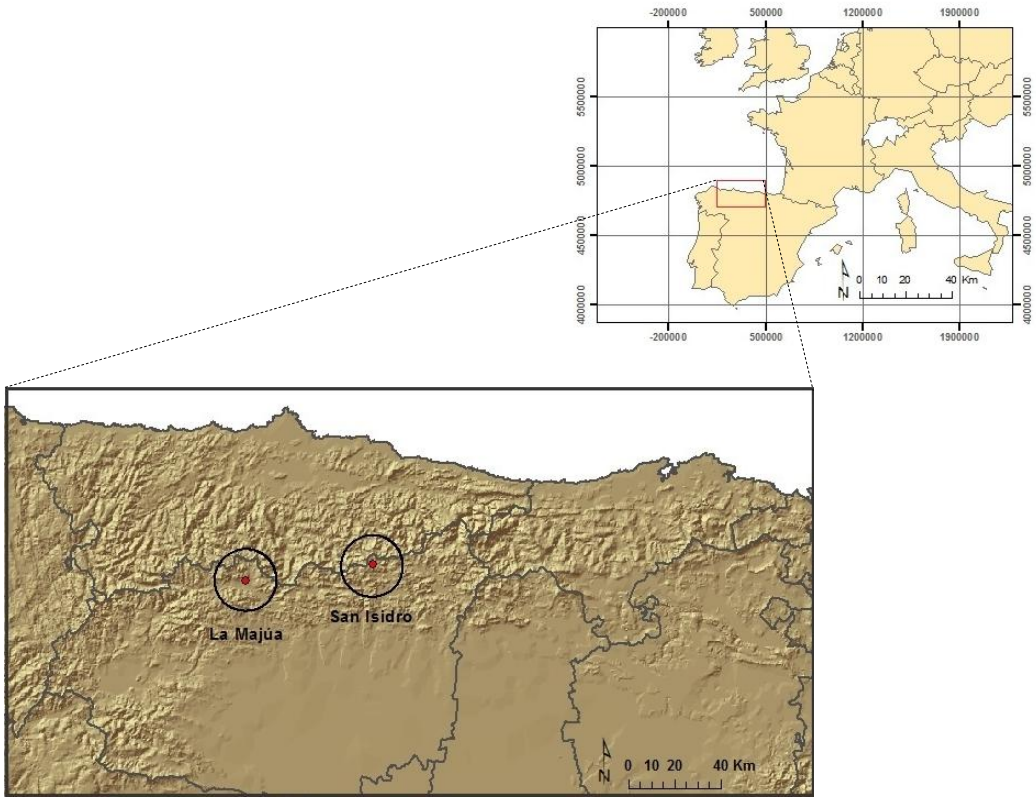
Fig. 2. Wind roses for (a) Miñera de Luna (16 km from La Majúa) and (b) Puerto de San Isidro. They represent the wind proportion for each direction (%) and the speed range for each direction (km h^{-1}). They also show the windless period (%). Data are from 2009 to 2011 in La Majúa and from 2000 to 2011 in Puerto de San Isidro. Adapted from: http://www.atlas.itacyl.es.

Fig. 3. Monthly means of wet bulk N depositions for La Majúa and San Isidro expressed as kg N ha^{-1}: a) wet bulk NO_3^--N deposition, b) wet bulk NH_4^+-N deposition.

Fig. 4. Monthly volume-weighted mean of NO_3^- concentrations in rainwater (expressed as hatched bars; in mg l^{-1}), monthly volume-weighted mean of NH_4^+ concentrations in rainwater (expressed as filled bars; in mg l^{-1}), and monthly mean precipitation (expressed as solid line; in mm) in the two study sites: (a) La Majúa and (b) San Isidro.

Fig. 5. Land cover and main stationary N emission sources surrounding the study site.

Figure 1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La Majúa
San Isidro
0 10 20 40 Km
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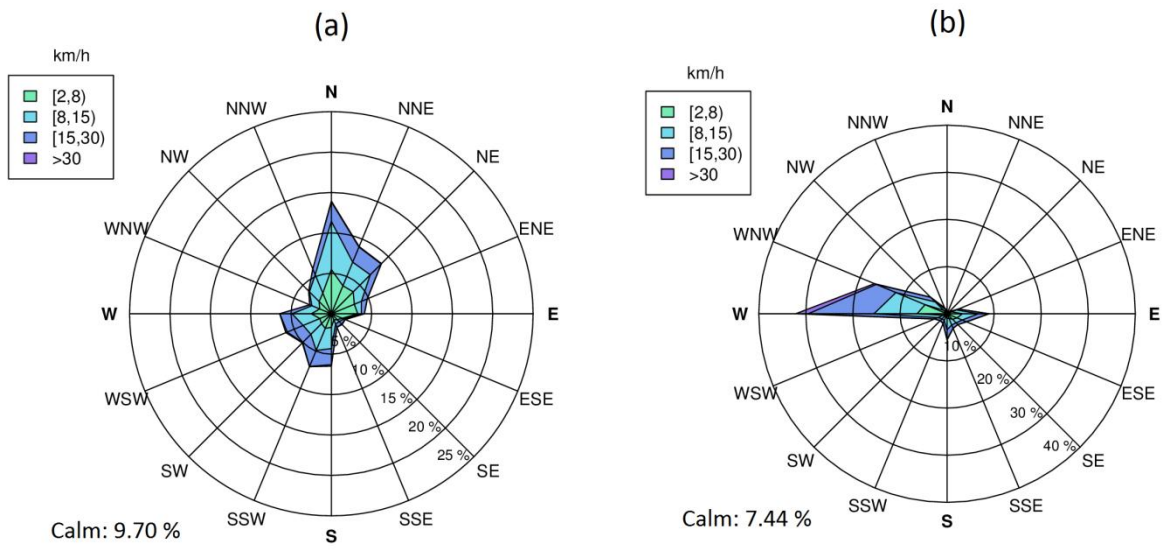
Figure 2


(a)
km/h
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>30
N
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NE
ENE
E
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S
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SW
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W
WNW
NW
NNW
5 %
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20 %
25 %
Calm: 9.70 %
(b)
km/h
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Calm: 7.44 %

Figure 3

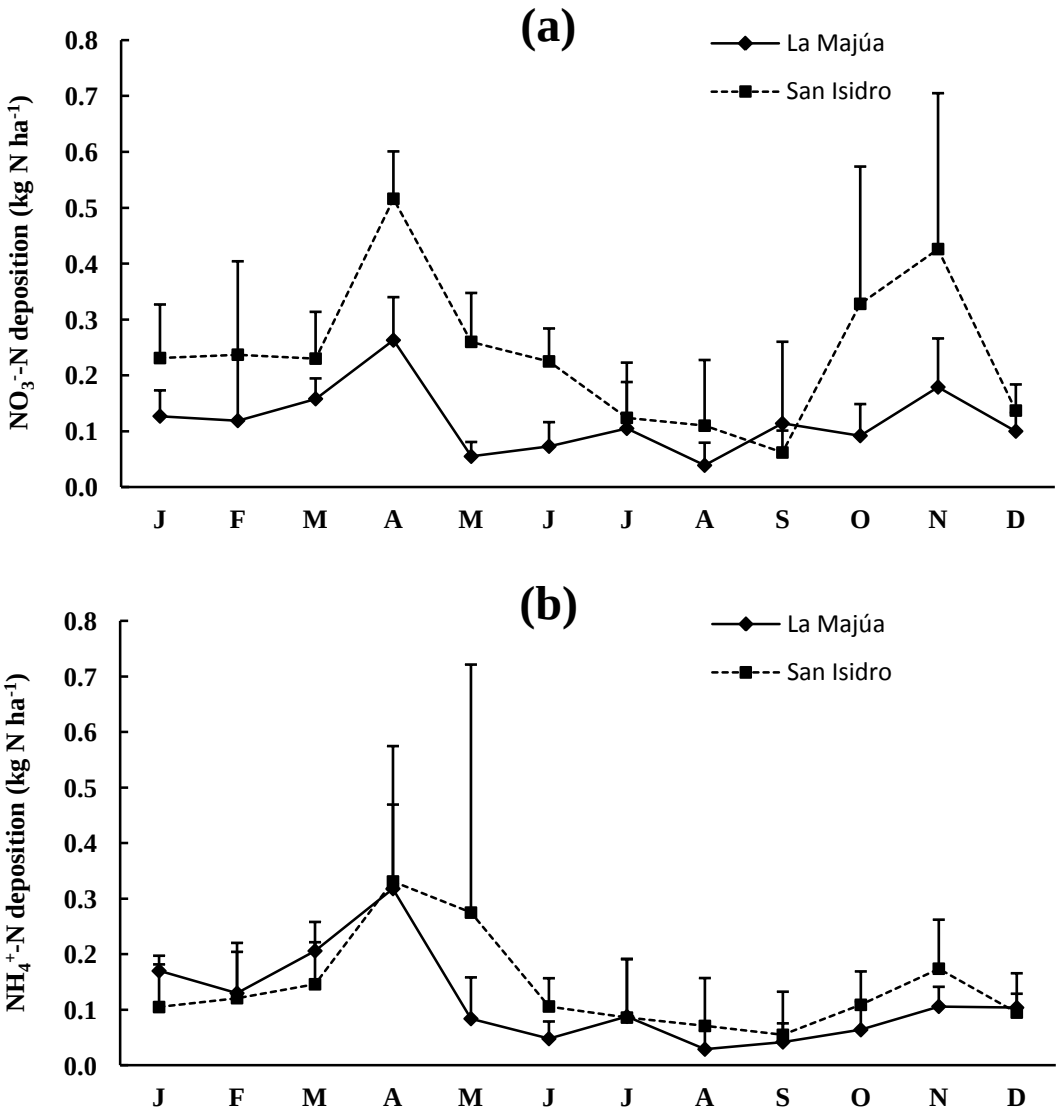

(a)
La Majúa
San Isidro
NO_3^--N deposition (kg N ha^{-1})
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
J F M A M J J A S O N D
(b)
La Majúa
San Isidro
NH_4^+-N deposition (kg N ha^{-1})
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
J F M A M J J A S O N D

Figure 4

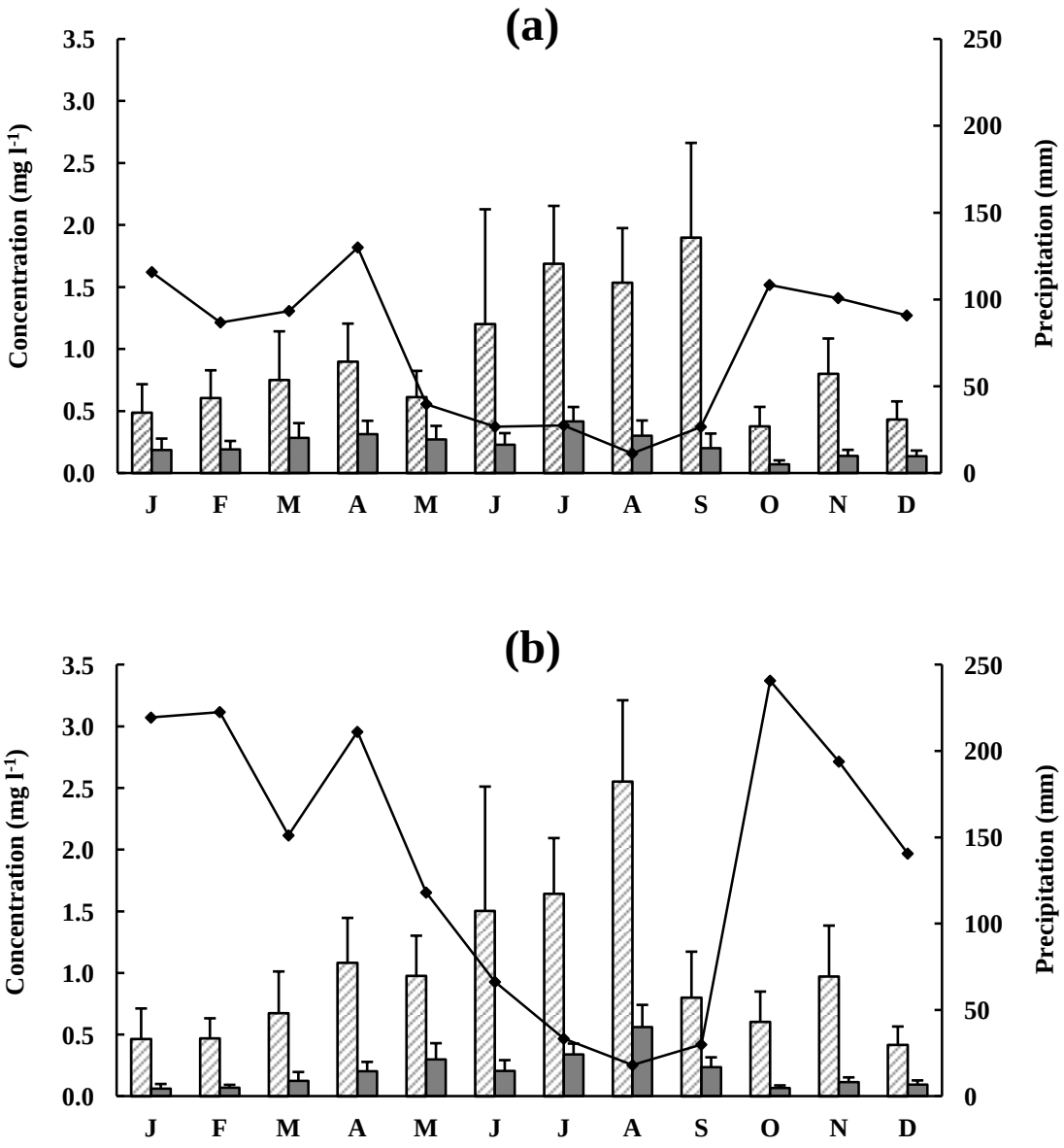
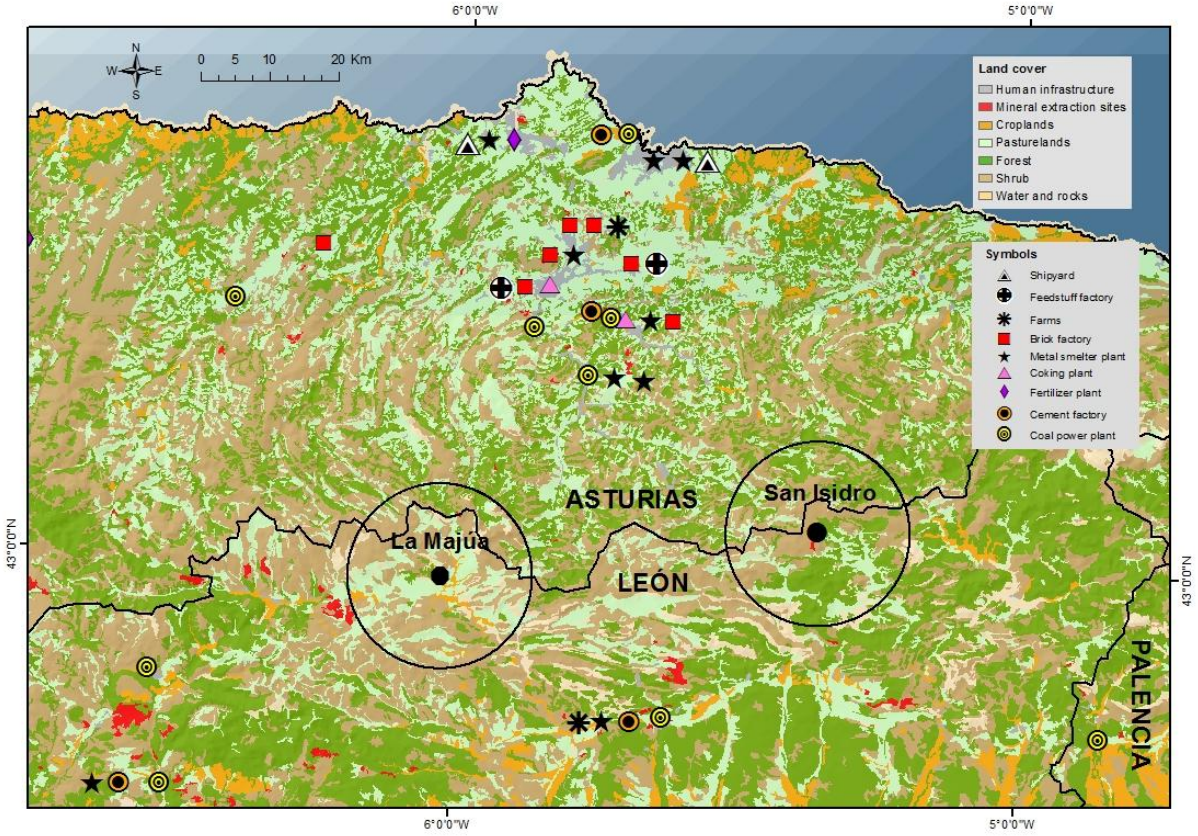

(a)
Concentration (mg l-1)
Precipitation (mm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
250
200
150
100
50
0
J F M A M J J A S O N D
(b)
Concentration (mg l-1)
Precipitation (mm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
250
200
150
100
50
0
J F M A M J J A S O N D

Figure 5


6°0'0"W
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Land cover
Human infrastructure
Mineral extraction sites
Croplands
Pasturelands
Forest
Shrub
Water and rocks
Symbols
Shipyard
Feedstuff factory
Farms
Brick factory
Metal smelter plant
Coking plant
Fertilizer plant
Cement factory
Coal power plant
ASTURIAS
LEÓN
PALENCIA
La Majúa
San Isidro