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Joining empirical and modelling approaches to estimate dry deposition of nitrogen in Mediterranean forests☆

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ABSTRACT

In Mediterranean areas, dry deposition is a major component of the total atmospheric N input to natural habitats, particularly to forest ecosystems. An innovative approach, combining the empirical inferential method (EIM) for surface deposition of NO_3^- and NH_4^+ with stomatal uptake of NH_3, HNO_3 and NO_2 derived from the DO_3SE (Deposition of Ozone and Stomatal Exchange) model, was used to estimate total dry deposition of inorganic N air pollutants in four holm oak forests under Mediterranean conditions in Spain. The estimated total deposition varied among the sites and matched the geographical patterns previously found in model estimates: higher deposition was determined at the northern site (28.9 kg N ha^{-1} $year^{-1}$) and at the northeastern sites (17.8 and 12.5 kg N ha^{-1} $year^{-1}$) than at the central-Spain site (9.4 kg N ha^{-1} $year^{-1}$). On average, the estimated dry deposition of atmospheric N represented 77% ± 2% of the total deposition of N, of which surface deposition of gaseous and particulate atmospheric N averaged 10.0 ± 2.9 kg N ha^{-1} $year^{-1}$ for the four sites (58% of the total deposition), and stomatal deposition of N gases averaged 3.3 ± 0.8 kg N ha^{-1} $year^{-1}$ (19% of the total deposition). Deposition of atmospheric inorganic N was dominated by the surface deposition of oxidized N in all the forests (means of 54% and 42% of the dry and total deposition, respectively). The relative contribution of NO_2 to dry deposition averaged from 19% in the peri-urban forests to 11% in the most natural site. During the monitoring period, the empirical critical loads provisionally proposed for ecosystem protection (10–20 kg N ha^{-1} $year^{-1}$) was exceeded in three of the four studied forests.

1. Introduction

Atmospheric deposition of nitrogen (N) in the European Mediterranean region, and particularly in Spain, is lower than in central Europe (Lorenz and Becher, 2012; Nyíri and Gauss, 2010). However, N deposition has been identified as a potential threat for some valuable Spanish ecosystems, such as alpine grasslands and heathlands or mountainous forest of holm oak (*Quercus ilex*) in NE Spain (García-Gómez et al., 2014, 2017). In Mediterranean areas, dry deposition of atmospheric N compounds may play a major role in the total N deposition to natural vegetation, particularly to forest ecosystems (Fenn et al., 2009).

Dry deposition of N on vegetation can occur either via surface or stomatal deposition. Surface deposition is referred to gaseous and particulate N species that are adsorbed by the vegetation surfaces, while stomatal deposition represents the gaseous species absorbed through stomatal pores followed by their dissolution in the apoplast. Many factors can potentially regulate the deposition rates onto vegetation surfaces (Fowler et al., 2009), with highly reactive and water soluble species, like HNO_3 and NH_3, being readily

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deposited to leaf surfaces and plant canopies (Hanson and Lindberg, 1991). On the other hand, the flux of nitrogen dioxide (NO_2) to vegetation is mainly controlled by stomatal uptake (Saxe, 1986; Raivonen et al., 2009). Stomatal deposition of gaseous N pollutants is controlled by the degree of stomatal aperture and by gas concentrations in the sub-stomatal cavity (Massad et al., 2010). This concentration is particularly important for NH_3 flux estimation, since plants can act as either a sink or as a source of NH_3, depending on the relative concentration gradient between the near atmosphere and the stomatal cavity, defining a stomatal compensation point (Massad et al., 2010; Raivonen et al., 2009).

Since dry deposition cannot be readily measured, several approximations exist to estimate this input into the ecosystems. The inferential methods are often considered the best for assessing long term dry deposition on wide scales, despite the presence of some uncertainties (Vet et al., 2014; Wesely and Hicks, 2000). These methods calculates dry-deposition fluxes to the ecosystems based on measurements of atmospheric concentrations of the pollutants of interest and their velocity deposition rates, which are mainly driven by meteorological conditions and the physical characteristics of surfaces (Fenn et al., 2009). These deposition rates are commonly estimated by using a multiple resistance analogy approach in which the deposition process is considered as a series of resistances, by analogy with an electrical circuit (Monteith and Unsworth, 2008). Deposition rates can be also obtained from micrometeorological studies (Fowler et al., 2009), which are complex and expensive systems, and, therefore, difficult to replicate in different sites.

Mixed methodologies using modelled and empirical approximations might improve the estimation of the dry atmospheric input, particularly in arid and semi-arid ecosystems (Cook et al., 2018). The empirical inferential method (EIM), inserting empirical results from branch-washing experiments into inferential modelling methodology, was recently proposed by Bytnerowicz et al. (2015) for evaluation of N deposition in Mediterranean-type ecosystems. It involves the use of values of surface deposition rates experimentally estimated at branch level (conductance), instead that at canopy level (deposition velocity). Surface conductance values can be more easily obtained from branch-washing experiments than from micrometeorological studies, and produce site-specific values. Branch-washing techniques use deionized water to rinse the dry-deposited ions from the vegetation surfaces, although cannot distinguish the sources of the surface-deposited NO_3^- (HNO_3 or particulate NO_3^-), nor NH_4^+ (NH_3 or particulate NH_4^+) (Dasch, 1989). Besides, it may underestimate deposition to foliar surfaces due to the transcuticular uptake, translocation processes of the deposited chemical species and volatilization of the deposited compounds (Garten and Hanson, 1990). However, the branch-rinsing method may be very useful for the development of estimation models for forest with different environmental conditions and pollution exposures. Regarding stomatal deposition of reactive N gases, in the EIM approximation it has been estimated so far from measurements of stomatal conductance values for H_2O vapour of several species, temporally and spatially extrapolated regardless the environmental conditions. In this work, we propose an improvement through estimating stomatal conductance values depending on the environmental conditions using a stomatal conductance model (CLRTAP, 2004) parameterized based on measurements performed in the studied species, i.e. holm oak (Alonso et al., 2008).

The main objectives of the study were: (1) to estimate the dry deposition of atmospheric N in Spanish holm oak forests by means of the empirical inferential method, (2) to complement the EIM methodology with the modelling of stomatal conductance values using a standard modelling approach, (3) to compare surface flux and conductance values of pollutants to living and lyophilized branches of holm oak, and (4) to estimate and describe the total input of atmospheric inorganic N to these forests.

2. Material and methods

2.1. Study sites

Four monitoring plots were located in four holm oak (*Q. ilex*) forests located in three areas of the Iberian Peninsula characterized by different climatic and soil conditions, as well as canopy structure and distance to main sources of pollutants (Table 1). Tres Cantos (TC) site is located in the central region of the Peninsula, near Madrid city (9 km), with a Mediterranean semi-arid climate. The historical management of this forest has produced a moderately open woodland (72% of tree cover). Can Balasc (CB) and La Castanya (LC) sites are located in the North-eastern Spain, with a sub-humid Mediterranean climate. Whereas CB is close to Barcelona city (4 km), LC is far from this city (40 km) and relatively sheltered from

Table 1
Characterization of the study sites.

Site code	CB	TC	CA	LC
Type of location	Peri-urban	Peri-urban	Peri-urban	Rural
Longitude	2° 04′ 54″ E	3° 43′ 59″ O	1° 38′ 40″ O	2° 21′ 29″ E
Latitude	41° 25′ 47″ N	40° 35′ 17″ N	42° 39′ 13″ N	41° 46′ 47″ N
Altitude (m)	255	705	592	696
Leaf area index ($m^2\ m^{-2}$)	3.3	3.1	5.3	6.1
Tree density (number of trees ha^{-1})	1429	491	1760	2571
Mean diameter at breast height (cm)	13	41[d]	16	13
Mean annual temperature (°C) [a]	15.2	14.6	12.3	13.7
Mean annual rainfall (mm y^{-1}) [a]	652	348	681	812
Mean annual relative humidity (%) [a]	71.3	54.6	73.7	70.3
Mean annual wind speed (%) [a]	0.8	1.3	6.2	0.9
Distance to the nearest big city (km)	4	9	15	40
Population of the nearest big city [b]	1.6	3.2	0.2	1.6
Agricultural land-use cover [c]	23%	21%	62%	23%

[a] Mean values calculated for the study period February 2011–February 2013;
[b] Million inhabitants;
[c] From the CORINE Land Cover 2006 (http://www.eea.europa.eu/data-and-maps/data/corine-land-cover-2006-raster-3) using a buffer of 25 km radius around the sampling sites;
[d] Measured in the dominant cohort.