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Title: Dry deposition and canopy uptake in Mediterranean holm-oak forests estimated with a canopy budget model: a focus on N estimations

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Abstract: Bulk/wet and throughfall fluxes of major compounds were measured from June 2011 to June 2013 at four Mediterranean holm-oak (Quercus ilex) forests in the Iberian Peninsula. Regression analysis between net throughfall fluxes and precipitation indicated that the best defined canopy process was leaching for K+ and uptake for NH4+ at all sites. A more variable response between sites was found for Na+, Ca2+, SO42- and Cl-, which suggests that the interplay of dry deposition, leaching and uptake at the canopy was different depending on site climate and air quality characteristics.
A canopy budget model (CBM) was used to try to discriminate between the canopy processes and enable to estimate dry deposition and uptake fluxes at three of the sites that complied with the model specifications. To derive N uptake, an efficiency factor of NH4+ vs. NO3- uptake (xNH4) corresponding to moles of NH4+ taken up for each NO3- mol, has to be determined. Up to now, a value of 6 has been proposed for temperate forests, but we lack information for Mediterranean forests. Experimental determination of N absorption on Quercus ilex seedlings in Spain suggests efficiency factors from 1 to 6. Based on these values, a sensitivity analysis for xNH4 was performed and the NH4 -N and NO3-N modeled dry deposition was compared with dry deposition estimated with independent methods (inferential modeling and washing of branches). At two sites in NE Spain under a milder Mediterranean climate, the best match was obtained for xNH4 = 6, corroborating results from European temperate forests. Based on this value, total DIN deposition was 12-13 kg N ha-1 y-1 at these sites. However, for a site in central Spain under drier conditions, variation of the NH4+ efficiency factor had little effect on DD estimates (which ranged from 2 to 2.6 kg N ha-1 y-1 with varying xNH4); when added to wet deposition, this produced a total N deposition in the range 2.6 to 3.4 kg N ha-1 y-1. Dry deposition was the predominant pathway for N, accounting for 60-80% of total deposition, while for base cations wet deposition dominated (55-65%). Nitrogen deposition values at the northwestern sites were close to the empirical critical load proposed for evergreen sclerophyllous Mediterranean forests (15-17 kg N ha-1 y-1).

When organic N deposition at these forests is added (3 kg N ha-1 y-1), the total N input to the sites in NE Spain are close to the critical loads for Mediterranean evergreen oak forests.

***Highlights (for review)**

A canopy budget model is used to estimate dry deposition and canopy uptake

A sensitivity analysis is carried out to determine NH4 canopy uptake

Dry deposition accounts for 60-80% of total N deposition in 2 oak forests in the NE Iberian Peninsula

Dry deposition and canopy uptake in Mediterranean holm-oak forests estimated with a canopy budget model: a focus on N estimations

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Keywords,

Wet deposition, throughfall, canopy exchange, Mediterranean, nitrogen, critical loads

Abstract

Bulk/wet and throughfall fluxes of major compounds were measured from June 2011 to June 2013 at four Mediterranean holm-oak (*Quercus ilex*) forests in the Iberian Peninsula. Regression analysis between net throughfall fluxes and precipitation indicated that the best defined canopy process was leaching for K^+ and uptake for NH_4^+ at all sites. A more variable response between sites was found for Na^+, Ca^{2+}, SO_4^{2-} and Cl^-, which suggests that the interplay of dry deposition, leaching and uptake at the canopy was different depending on site climate and air quality characteristics.

A canopy budget model (CBM) was used to try to discriminate between the canopy processes and enable to estimate dry deposition and uptake fluxes at three of the sites that complied with the model specifications. To derive N uptake, an efficiency factor of NH_4^+ *vs.* NO_3^- uptake (xNH_4) corresponding to moles of NH_4^+ taken up for each NO_3^- mol, has to be determined. Up to now, a value of 6 has been proposed for temperate forests, but we lack information for Mediterranean forests. Experimental determination of N absorption on *Quercus ilex* seedlings in Spain suggests efficiency factors from 1 to 6. Based on these values, a sensitivity analysis for xNH_4 was performed and the NH_4-N and NO_3-N modeled dry deposition was compared with dry deposition estimated with independent methods (inferential modeling and washing of branches). At two sites in NE Spain under a milder Mediterranean climate, the best match was obtained for xNH_4 = 6, corroborating results from European temperate forests. Based on this value, total DIN deposition was 12-13 kg N ha^{-1} y^{-1} at these sites. However, for a site in central Spain under drier conditions, variation of the NH_4^+ efficiency factor had little effect on DD estimates (which ranged from 2 to 2.6 kg N ha^{-1} y^{-1} with varying xNH4); when added to wet deposition, this produced a total N deposition in the range 2.6 to 3.4 kg N ha^{-1} y^{-1}. Dry deposition was the predominant pathway for N, accounting for 60-80% of total deposition, while for base cations wet deposition dominated (55-65%). Nitrogen deposition values at the northwestern sites were close to the empirical critical load proposed for evergreen sclerophyllous Mediterranean forests (15-17 kg N ha^{-1} y^{-1}). When organic N deposition at these forests is added (3 kg N ha^{-1} y^{-1}), the total N input to the sites in NE Spain are close to the critical loads for Mediterranean evergreen oak forests.

1. Introduction

Atmospheric deposition has an impact on forest ecosystem functioning, forest health and biodiversity. However, quantification of atmospheric total deposition is scarce for Iberian Peninsula forests. In general, the Iberian Peninsula is little affected by acidification, partly due to the important neutralizing role of carbonate-rich dust deposition from North African events (Avila et al., 1998; Rodà et al., 1993). However, this region is currently receiving substantial nitrogen (N) deposition (Aguillaume et al., 2016, Izquieta-Rojano et al., 2016; Fowler et al., 2007) which is expected to increase in the future (Dentener et al., 2006). Nitrogen deposition may adversely affect biodiversity (Ochoa-Hueso et al., 2011; Phoenix et al 2006). The Iberian Peninsula has been considered as one of the 25 Global Biodiversity Hotspots for conservation priorities (Myers et al., 2000), and N deposition may exacerbate the threats to biodiversity. In fact, N empirical critical loads established for the protection of terrestrial habitats under the UNECE CLRTAP Convention (Convention on Long-Range Transboundary Air Pollution) seem to be currently exceeded in some habitats of Community interest of the Spanish Natura 2000 network (García-Gómez et al., 2014).

Quantifying total atmospheric deposition entails some difficulties. Wet (WD) and bulk (BD) atmospheric deposition can be directly measured by using wet-only or bulk collectors. However, the estimation of dry deposition (DD) is still challenging. Throughfall (TF) deposition has been widely used to indicate total deposition (TD) to the forest soil (De Schrijver et al., 2007). However, exchanges at the canopy level, either from leaching or uptake, complicate the quantification of DD. Methods for separating in-canopy sources from external sources in TF deposition rely on two broad type of approaches: 1) regression models relating net throughfall fluxes (netTF) and rainfall, such as those described by Lovett and Lindberg (1984) and Lovett et al. (1996), and 2) canopy budget models (CBM) such as the one first proposed by Ulrich (1983) and subsequently extended by several authors (Adriaenssens et al., 2012; Balestrini and Tagliaferri, 2001; Draaijers and Erisman, 1995; Zhang et al., 2006). Canopy budget models estimate total deposition of major ions by using a tracer ion, based in the following assumptions: (1) the tracer ion is not influenced by canopy exchange processes, and (2) aerosols containing the other ions have similar deposition behavior than the ion chosen for reference.

The model is based on the balance between fluxes above and below the canopy: TF = PD + DD + CE, where PD stands for precipitation deposition (which can be wet or bulk deposition) and CE for canopy exchange. Once DD is known, the CE flux can be estimated from subtraction in the above equation. Negative values of CE are due to canopy uptake (CU) while positive values, to canopy leaching (CL). Some ions do not comply with the above assumptions (e.g. NH_4^+ and H^+), and DD cannot be estimated with this approach. In this case, the calculation process is reversed: first the CE flux is estimated and then DD is obtained from the balance equation (Staelens et al., 2008; ICP-Forest Manual, 2010).

Up to now, and to our knowledge, no studies have applied the canopy budget model to determine dry deposition and canopy exchange in Mediterranean European forests, in contrast to various studies in temperate and boreal European forests (Adriaenssens et al., 2012; Kirchner et al., 2014; Staelens et al., 2008; Thimonier et al., 2005). Moreover, in the Mediterranean as in other aridic regions, DD may be very important (García-Gómez et al., 2014). For N, canopy uptake can be biogeochemically significant because N has been found to limit productivity in Mediterranean forests (Rodà et al., 1999), foliar N uptake for *Quercus ilex* and other Mediterranean species has been demonstrated experimentally (Uscola Fernández et al., 2014), and foliar nutrition has been found to play relevant role in forest productivity (Sparks, 2009).

Holm-oak (*Quercus ilex* L.) is a typical broadleaf evergreen sclerophyllous tree widely distributed in the Mediterranean Basin, whose traditional management has led to a diversity of forest types differing in structure and maturity. Nitrogen DD has been found to make an important contribution to total deposition inputs in Mediterranean forests as derived from modeling exercises (García-Gómez et al., 2014) or from branch and surrogate surfaces washing experiments in holm-oaks (Avila and Rodà, 2012; Rodrigo and Àvila, 2002). In spite of this research, more work is needed to define atmospheric N inputs to the Iberian Peninsula, as model predictions presented a poor match with measurements in some regions, notably for the Northeastern Iberian fringe (García-Gómez et al., 2014), and measurements of deposition in the Iberian Peninsula (e.g. Camarero and Catalan 1996; Morales-Baquero et al., 2006; Sanz et al., 2002) comprise a low spatial coverage.

This work attempts to fill this gap by modeling DD of the major ions in Iberian Peninsula holm-oak forests with a canopy budget model, with a special focus on N deposition. Total N deposition (obtained from the sum of dry plus wet deposition) will then permit to assess the status of these forests regarding the N critical loads proposed for Mediterranean sclerophyllous forests.

2. Material and methods

2.1 Locations and experimental sites

The study was conducted at 4 holm-oak forests (*Quercus ilex* L.) in the north, center and north-east of the Iberian Peninsula (Fig. 1). Two sites were located in Catalonia (La Castanya and Can Balasc, LC and CB respectively), one in Madrid (Tres Cantos, TC) and another site in Navarra (Carrascal, CA). The main characteristics of the sampling sites are shown in Table 1.

The LC site (41º46'N, 2º21'E, 696 m.a.s.l.) is located in the Montseny Mountains of the Pre-littoral Catalan Range, 40 km to the NNW of Barcelona city. This site is considered as a rural background station, even though pollution from the Barcelona metropolitan area may reach it transported by sea-land breezes (Pérez et al., 2008). Vegetation at LC consists of a closed canopy forest dominated by holm-oak (*Quercus ilex* L.) trees. Lithology at this area is composed by schists and granodiorites. Climate is Mediterranean, with a clear seasonal cycle with lower precipitation in summer and winter.

The CB site (41º25'N, 2º04'Eº, 255 m.a.s.l.) is located in the Collserola Natural Park, a protected lying to the west of the Barcelona Metropolitan Area (3.5 million inhabitants). The plot lies at 4 km linear distance from Barcelona outskirts. A moderate to heavy traffic highway (C-16) runs about 150 m from the study plot. Vegetation at CB is characterized by a continuous cover of holm-oak (*Quercus ilex* L.)

mixed with *Quercus humilis* Mill. Lithology consists of shales and slates with granitic outcrops. Climate is Mediterranean.

The CA site (42º39'N, 1º38'W, 645 m.a.s.l.) is situated at the foot of the Alaitz-Izco hills, in central Navarra. The nearest larger city, Pamplona (197 604 inhabitants) is 15 km to the North. The site lies at ~100 m from a heavy traffic highway (AP-15) and is surrounded by fields of irrigated cereal. An opencast limestone quarry is located approximately 2 km to the north of the plots. The forest comprises mostly *Quercus ilex* L. trees with scattered *Quercus faginea* Lam. and *Quercus humilis* Mill. individuals. The site lies on calcareous soils mainly composed by washed clays. The climate at CA is Mediterranean continental with oceanic influence from the Atlantic sea.

The TC site (40º35'N, 3º43'W, 705 m.a.s.l.) is located 9 km NE from Madrid outskirts (3.2 million inhabitants). The site lies in the north-eastern border of the holm-oak forest of El Pardo, which extends over an area of 170 km^2 and is a protected area. Vegetation was historically managed as a traditional 'dehesa', a savannah-type managed formation of low density isolated trees. The low management level during the last decades has allowed the vegetation to grow as an open forest with an understory of shrubs and grasslands. Lithology is composed by sandy arkoses sediments from granites and gneisses. A moderate to high traffic intensity highway (M-607) is located at 2 km from the monitoring site. The climate is continental Mediterranean, characterized by long dry periods and a more contrasted seasonality than the typical Mediterranean climate.

2.2 Field sampling and chemical analysis

In every location, an open-field (for WD and BD) and a below-canopy plot (for TF) were instrumented. The same model of sampler was used to collect bulk and throughfall deposition at all sites. It was composed of an ISO-standardized funnel (Norwegian Institute for Air Research, NILU) with a 314 cm^{-2} horizontal interception surface, connected to a polypropylene 2 L bottle. A bugsieve was placed at the funnel neck to prevent leaves and other materials from entering into the bottle. The upper edge of the funnel was equipped with an external ring to prevent contamination from bird droppings. The rim of the funnel stood approximately at 1.5 m above ground level. For bulk sampling, two collectors were used per site at LC and CB, and 4 at CA and TC. For throughfall sampling, 12 collectors were used at all sites; they were randomly located in a forest plot of 30*30 m^2 at LC, CB and CA. At TC, which had a more open canopy, each collector was placed in the mid-distance between the trunk and the canopy border in 12 trees encompassing the range of diameters. Collectors were permanently open to the atmosphere, so they collected dry deposited coarse particles onto the funnel. During no-rain periods the funnel was rinsed with 100 ml of deionized water in order to collect particles that settle gravitationally, corresponding to coarse dry deposition. The recovered dry deposition during dry periods made a low contribution to the total bulk deposition, but nevertheless it was added to BD and TF deposition collected in the next period. WD was also measured at LC and TC in the open-field plot, by means of an automatic Andersen sampler (ESM Andersen instruments, G78-1001) at each site. All funnels and WD buckets were thoroughly cleaned in the field with deionized water after each sampling. Bulk and throughfall sampling bottles were retrieved and replaced by clean ones at each site. Field blanks (recovered distilled water after rinsing the funnels and buckets in the field) were periodically obtained and analyzed.

Sampling took place from June 2011 to June 2013 in a weekly schedule (biweekly in case of rainless weeks). All collected samples were kept refrigerated (4ºC) in the darkness until analyzed for conductivity, pH and alkalinity (within 24–48h of collection). Alkalinity was measured by a conductivity titration (Golterman et al., 1978) at LC, CB, and TC and Gran titration at CA. Samples were filtered with 0.45 μm size pore membrane filters of cellulose (Millipore) and frozen until analysis. The ionic measurements from the LC and CB were performed at CREAF by ionic chromatography as described in Izquierdo and Avila (2012). In samples from CA and TC, ammonium and anions were determined by ion chromatography, whereas cations were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) as described in Izquieta-Rojano et al. (2016).

Analytical accuracy was checked with internal control samples of known concentrations, with differences being lower than 10% except for K^+ and NH_4^+ (12 and 15%). The balance of the sum of cations *vs.* the sum of anions was also scrutinized. A systematic excess of cations was found in all sample types, especially for TF. Since the analytical accuracy was acceptable, the anion deficit was attributed to the anions of weak acids, as done elsewhere (Balestrini and Tagliaferri, 2001; Hoffman et al., 1980).

2.3 Data handling and statistical analysis

Annual mean concentrations were calculated as volume-weighted means (VWM, expressed as μeq L^{-1}). Annual WD, BD and TF fluxes were obtained as the product of their respective VWM by the annual precipitation (for WD and BD) or throughfall volume for TF fluxes.

Precipitation-ion and pair-wise ion relationships were analyzed with Spearman regressions using weekly/biweekly data.

Model calculations in the CBM were performed in terms of equivalents (in meq m^{-2} y^{-1}) and were then transformed into kg ha^{-1} y^{-1}. The CBM is based on the following balance between fluxes above and below the canopy:

TF+SF = PD + DD + CE (1)

where TF stands for throughfall, SF for stemflow, PD for Precipitation Deposition, DD for Dry Deposition and CE for Canopy Exchange. **Canopy exchange can arise from leaching of ions from the leaf pool (canopy leaching, CL) or from the uptake of deposited ions (canopy uptake, CU)**.

Stemflow at the LC site contributed only 3% of total rainfall (Rodrigo et al., 2003) and because of its small contribution and to optimize sampling time and efforts, SF was not measured in this study. Regarding PD, either WD or BD can be used, but WD is recommended (Staelens et al., 2008) since BD includes the fraction of DD corresponding to coarse particle deposition.

Then,

TF-WD = net TF = DD + CE (2)

In this study we have used WD measurements at LC (measured in parallel to BD), and applied the ratio WD/BD from this site to derive WD fluxes at CB which is only ~ 40 km distant. For TC, WD and BD measurements were available for 6 months (January to June 2013), and the ratios WD/BD for this period were applied to the 2011-2013 period (Table 2). To ascertain the validity of a short term period to infer yearly ratios, we took advantage of the data series at LC. BD/WD ratios at LC from January to June 2013 were compared to the annual values (June 2012 - June 2013) with an unpaired Student t-test, and differences were non-significant ($p>0.05$) for all ions, except for H^+ and alkalinity. While acknowledging a degree of uncertainty due to site differences, we have considered this result to back up the use of the half-year ratios at TC. At CA, only bulk deposition measurements were available, and because of the probable influence of local agriculture and due to the carbonate lithology at this site, WD/BD ratios from the other sites were considered not to apply for CA. Therefore, CBM calculations were not performed at CA.

For ions such as Na^+, SO_4^{2-} and Cl^- it is often assumed that the exchange between precipitation and plant tissue is negligible and that their netTF fluxes represent their dry deposition; i.e., they are considered as tracer ions. However, in this study we have chosen Na^+ as tracer since it is the most commonly recommended tracer (Staelens et al., 2008) and previous research in the LC forest has shown it to be mostly derived from dry deposition (Rodrigo et al., 2003).

To obtain DD of an ion x (DD_x), the dry deposition factor based on Na^+ (TF_{Na} - WD_{Na} / WD_{Na}) is multiplied by the WD of this particular ion:

$$DD_x=(TF-WD)_{Na}/WD_{Na})*WD_x \quad (3)$$

This approach is quite straightforward for estimating DD for base cations and sulphate aerosols, assuming that the particles containing them are deposited at similar deposition velocities as the Na^+ particles.

For N to in its reduced or oxidized forms, which are mostly present as gases at the study sites (García-Gomez et al., 2016), the above assumptions do not hold and other approaches must be implemented. Furthermore, N compounds are known to be retained at the canopy level (and H^+ as well), thus netTF does not represent DD or canopy leaching (Brumme et al., 1992; Ferm, 1993; Geßler et al., 2002). It has been proposed (Balestrini and Tagliaferri, 2001; Staelens et al., 2008) that the NH_4^+ exchange flux can be estimated by considering that its canopy uptake equals the canopy leaching of base cations (the sum of leaching of Ca^{2+}, Mg^{2+} and K^+) once corrected by the anion leaching (Staelens et al., 2008; Zhang et al. 2006). **Several studies have only taken into account the leaching of anions of weak acids (corresponding to $HCO3^-$ and organic acids in the form of $RCOO^-$) to compensate base cation leaching (Adrianssens et al., 2012; Balestrini and Tagliaferri 2001; Thimonier et al. 2005). Our data suggested that Cl^- was also leached from the canopy, thus, it was also included in equation 4 (**CL_{Cl^-}**) as suggested in Staelens et al. (2007). Evidence of Cl^- leaching in our study sites was indicated by the correlation analysis (Section 3.2).**

Uptake of NH_4^+ **has been then equated to:**

$$CU_{NH4+} = CL_{bc} - [CL_{Cl^-} + CL_{wa}] \qquad (4)$$

Where CU_{NH4+} = canopy uptake of NH_4^+

CL_{bc} = Canopy leaching of base cations

CL_{wa} = Canopy leaching of anions of weak acids

CL_{Cl^-} = Canopy leaching of Cl.

The leaching of anions of weak acids (CL_{wa}) was calculated based in eq. 2 as $CL_{wa} = TF_{wa} - WD_{wa} - DD_{wa}$. Thus, an estimation of the concentrations of anions in weak acids in TF, WD and DD was required; however, the concentrations of bicarbonate and organic acids were not measured directly in these water fluxes. Several methods exist to estimate the concentrations of weak acids in water samples (Staelens et al. 2008). One of the mostly used is the ion charge balance, the difference in concentration of major cations minus strong acid anions (De Vries et al., 2001) and is

the procedure we employed here to estimate WD_{wa} and TF_{wa}. For DD_{wa}, the same procedure as with the other ions was considered, based on equation 3.

Once CU of NH_4^+ is obtained, and assuming that there is no leaching of NH_4^+, the NH_4^+ DD flux can be derived from equation 2. Besides, there might be also NO_3^- canopy uptake and a further step is therefore needed to estimate the NO_3 canopy retention flux. For this, we followed an approach that considers a proportional uptake of NO_3^- related to that of NH_4^+:

$$CU_{(NH4^+ + NO3^-)} = [\, x\, NH_4^+ \cdot (TF_{NH4^+} + TF_{NO3^-}) / x\, NH_4^+ \cdot TF_{NH4^+} \,] \cdot CU_{NH4^+} \qquad (5)$$

An efficiency factor of NH_4^+ *vs.* NO_3^- uptake of 6 (x NH_4^+ = 6) has been generally applied for temperate forests (de Vries et al., 2003). For Mediterranean vegetation, the experimental work of Uscola Fernández et al. (2014) has shown this factor to vary in the range 1 to 6.5. Thus, here xNH_4^+ has been here varied between 1.5 to 6 based on literature proposed values (De Vries et al., 2003; Schmitt et al., 2005; Thimonier et al., 2005; Uscola Fernández et al. 2014; Zhang et al., 2006).
Finally, to maintain the charge balance, CU of H^+ was equated to the uptake of NO_3^- (Stachurski and Zimka, 2002; Staelens et al., 2008).

The CBM calculations considered the average fluxes for the 2 years at all sites. The dry deposition factor based on Na^+ varied between 0.5 at CB to 0.8 at TC.

For a further check of the N compound DD estimates from the CBM, the modeled values were compared with those obtained with two independent methods: inferential modeling and washing of branches. The inferential method is a combination of measurement and modelling that involves indirect estimation of dry deposition rates on the basis of routinely measured air concentrations and meteorological parameters. The method is based on an assumed steady-state relationship $F = V_d * C$, where the dry deposition flux or rate (F) is a product of the dry deposition velocity (V_d) and the concentration (C) of an airborne pollutant.

For inferential calculations we have used the gas and particle atmospheric information of N compounds from García-Gómez et al., (2016) which sampled gases (February 2011 to February 2013) and aerosols (February 2012 to February 2013) during periods encompassing the period of throughfall measurements, while V_d values were selected from literature reports of deposition unto forests: for NH_3 and HNO_3, 2.0 cm s^{-1}; for NO and NO_2, 0.1 cm s^{-1}, from Holland et al., (2005), Kalina et al., (2002), Krupa (2003) and Muller et al., (1993). Particulate nitrate and ammonium was not included in these calculations. A study in NE Spain indicates that particle N deposition can represent 4-8% of total N dry deposition (Avila and Rodà, 2012).

Branch washing was performed as described in Rodrigo and Avila (2002). In brief, 8 to 10 top holm oak branches were obtained at LC during rain-free periods in 1996 and again in 2016. Collected branches were included in a plastic bag carefully keeping branch tips out of the bag and were rinsed for 3 minutes with distilled water. The branch foliar surface was measured at CREAF with a Li-Cor 3100 area meter, and the liquid samples from the washes were filtered and frozen until analysis. Analytical routine was similar to the one for BD, WD and TF sample types.

3. Results and Discussion

3.1. Water and nutrient fluxes

The annual BD and TF water fluxes are shown in Table 3. Rainfall amount differed markedly between the studied sites, with TC being the driest site. These differences in rainfall amount are explained by the climatic characteristics of the study regions and are in accordance with the precipitation patterns and inter-annual variability in Spain (Rodriguez-Puebla et al., 1998). TC, located at the center of the Iberian Peninsula is under a continental Mediterranean climate, drier and colder than the coastal Mediterranean. By contrast, the CA site receives an important oceanic influence from the Cantabric Ocean while the sites in NE Spain are influenced by the Mediterranean Sea. Throughfall water volume represented on average a 66-77% of precipitation (Table 3). The lowest percentage was at TC, which can be explained by lower weekly precipitation which would favor higher interception. Since BD and TF fluxes depend on the amount of precipitation, lower BD and TF fluxes were found at the driest TC site compared to the other sites (Table 3).

Calcium, followed by Cl^- and K^+, were the most abundant ions transferred to soils through bulk and throughfall deposition. Except for NH_4-N (and for SO_4-S at TC where it was near zero), TF fluxes were always enriched in relation to BD and thus, netTF fluxes were positive (Table 3). The negative netTF of NH_4-N indicates that retention within the tree crowns is greater than any DD that may have occurred.

Alkalinity fluxes were higher than those of H^+, indicating the non-acidic nature of deposition at these sites probably due to the neutralizing role of bicarbonate dust deposited on leaves (Rodrigo et al. 2003), even at sites with non-calcareous litologies such as in LC, CB and TC. When acid and alkaline episodes alternate in a year, as was here the case at all sites, the conservative variable that indicates the acid status of the solution is the net alkalinity instead of H^+ (Liljestrand, 1985; Stumm and Morgan, 1981). Therefore, H^+ fluxes are given here only for comparison with other studies. Alkalinity fluxes in TF about doubled those in BD, and presented very higher enrichments at CA, suggesting the washing of calcareous soil dust deposited on the canopy at this site that may derive from the calcareous nature of soils, the influence of fugitive emissions from a nearby quarry and the important resuspension of soil dust due to a windy meteorology**.** Consistently, calcium TF and netTF fluxes were higher at CA than at the other sites. Also, at this site, the influence of the intense agricultural activities in its surroundings was reflected in NH_4-N fluxes in BD and TF higher than at the other sites (Table 3).

Bulk and TF deposition of anthropogenic related compounds were not negligible at LC, being similar to fluxes at CB and CA (Table 3). Thus, this site, which a priori was considered as a background station, is receiving similar loads of pollutants than sites closer to traffic and urban pollution. This suggests the influence of pollutants carried by rain from regional and long-range transport to the Montseny Mountains, as already found for aerosols (Pérez et al. 2008; Pey et al. 2009). The forest close to Barcelona (CB) registered the highest NO_3-N and SO_4-S netTF loads (Fig.2), suggesting higher dry deposition, which is consistent with its higher concentrations of gaseous pollutants (NO_2, HNO_3) found at this site compared to the other sites of this study (García-Gómez et al., 2016).

3.2. Main canopy processes

In order to understand and describe canopy processes, the correlations between weekly/biweekly rainfall amount and net TF fluxes were explored. It has been proposed that, for individual events, a positive correlation between net throughfall and rainfall amount will indicate leaching, a negative correlation will indicate uptake, while the absence of correlation may be attributed to dry deposition (Balestrini and Tagliaferri, 2001; Kopáček et al., 1997; Lovett and Lindberg, 1984; Rodrigo et al., 2003). This approach is based on the assumptions that dry deposition is completely and quickly removed from the canopy by the rain and that foliar leaching proceeds unstopped as precipitation washes the leaves, being therefore correlated to the amount of rain.

The results of Spearman correlations between rainfall amount and netTF fluxes (Table 4) showed a consistent behavior at the 4 sites for some elements (K^+, NH_4-N, SO_4-S) and marked differences for other elements (NO_3-N, Na^+, Cl^-, Ca^{2+} and Mg^{2+}). Based on the previous assumptions, K^+ in netTF should derive from leaching (positive relationship with $p<0.05$), NH_4^+-N should result from uptake (negative relationship with $p<0.05$, except at CB where $p<0.1$), and SO_4^{2-}-S would derive from dry deposition (non significant relationships). For NO_3-N, results suggested uptake at LC and TC (the later with $p<0.1$), but leaching at CA and dry deposition at CB.

On the other hand, for Na^+, Ca^{2+}, Mg^{2+} and Cl^-, highly significant positive relationships were found at CA and TC, while they were non-significant at LC and CB (Table 4). Therefore, results at the Catalan sites would suggest dry deposition for these elements, which is consistent with previous research in Montseny (Rodrigo and Avila, 2002; Rodrigo et al., 2003). However, results at CA and TC suggested leaching of these ions from internal canopy pools, which is a non-expected result.

This unexpected result may derive from the fact that the above approach has been usually employed to describe canopy processes in temperate forests, but under the Mediterranean drier climate the relationships between net throughfall and rainfall may be complicated by the fact that events with low precipitation may not provide enough water to wash the accumulated dry deposition from previous events, or that small events may evaporate leaving their content to be washed in future rainier events. This may be the case at the driest site TC (annual precipitation of only 346 mm during the study period, half of that at CB and CA and one third of that at LC and showing the highest water interception rates). On the other hand, CA received very high amounts of dust deposition and the amount of weekly rain might not have been enough to wash all the deposited material in some sampling periods. Therefore, positive relationships for Na^+, Ca^{2+} and NO_3^- that conventionally would be interpreted as leaching, in these cases may in fact indicate a delayed washout of dry deposition due to low rain amount and elevated dry deposition. This casts doubts on the application of the correlational procedure for semi-arid environments.

On the other hand, correlation results clearly suggested uptake of NH_4^+ by *Quercus ilex* canopies at all sites. This is also corroborated by the significant negative relationships between NH_4^+ in netTF and BD fluxes (Fig. 3) suggesting NH_4 uptake by the leaves in the canopy, since lichen and mosses are scarce in these forests. In this figure, outliers above the regression line corresponded to rainfall events after long dry periods, thus corroborating the mentioned assumption of dry deposition accumulation during dry spells at the Mediterranean sites.

3.3. Estimating total atmospheric inputs with the canopy budget model

3.3.1. *Base cations, Cl^- and SO_4-S*

Dry deposition fluxes of Ca^{2+}, Mg^{2+} and K^+ estimated with the CBM were, respectively, 6.5, 0.8 and 0.5 kg $ha^{-1}y^{-1}$ at the Catalan sites (two-site means), and 1.3, 0.2, 0.5 kg $ha^{-1}y^{-1}$ at TC (Table 5). Values at the Catalan sites can be compared with those from a previous study at the Montseny Mountains in which DD fluxes were obtained by washing surrogate plates and branches (Rodrigo and Avila, 2002). For Ca^{2+}, DD fluxes from the CBM were similar to those of the mentioned study when considering foliage washes (6.6 kg ha^{-1} y^{-1}) but not when compared with plate washes (3.8 kg ha^{-1} y^{-1}). On the other hand, CBM results for Mg^{2+} and K^+ were consistent with those from plate washing (1.0 and 0.24 kg $ha^{-1}y^{-1}$) but not from foliage washing (2.0 and 18 kg $ha^{-1}y^{-1}$). This indicated that foliage-washes better represent DD since branches are organized in the three dimensions of the canopy, except for K^+ and Mg^{2+} which are strongly leached ions (Parker 1983; Tukey, 1970). Dry deposition of base cations (Ca^{2+}, Mg^+ and K^+) contributed 40, 34, and 45% of their total deposition at LC, CB, and TC, respectively. Thus, for base cations, wet deposition was the dominant deposition pathway.

Potassium was the most leached base cation (Table 5), which was consistent with the correlational analysis as K^+ netTF fluxes always presented the highest correlation coefficients with precipitation (Table 4). Leaching of K^+ is a common result in TF studies (Langusch et al., 2003; Likens et al., 1994; Tukey, 1970; Vitousek and Sanford, 1986). In general, K^+ leaching is accompanied by weak acid leaching and/or K^+ ions are exchanged cations, typically NH_4^+ (Stachurski and Zimka, 2002).
Dry deposition of SO_4^{2-}-S ranged between 0.8 to 1.7 kg $ha^{-1}y^{-1}$ at the study sites. At LC, SO_4^{2-} canopy exchange was near zero, indicating DD as the main netTF component at this site. At CB and TC, the CBM indicates leaching and uptake, respectively, with the leached/ taken up amounts of similar size as dry deposition (Table 5).

The CBM indicated that canopy leaching was the dominant flux for Cl^- at LC and CB, which is not consistent with results from regression analysis, where dry deposition was suggested. For Cl^-, both processes may have a significant influence in netTF. At sites receiving marine air masses, as is the case in these two sites not far from the Mediterranean Sea, sea-salt aerosols may be responsible of Cl^- dry deposition. But on the other hand, the Na/Cl ratios in TF were significantly lower than in BD (t-test of paired observations, p<=0.0001 at both sites), and Cl^- was highly correlated with K, a ion representative of leaching (r=0.71, p<0.0001 and =0.44; p<0.05 at LC and CB, respectively). Therefore, the interplay of dry deposition and canopy leaching is responsible of Cl^- netTF fluxes at these sites.

3.3.2. *Nitrogen compounds*

To calculate DD for N compounds, an efficiency coefficient for the uptake exchange between NH_4^+ and NO_3^- (x NH_4^+) has to be defined in the CBM (ICP-Forest, 2010). Up to now, a value of 6 moles of NH_4^+ exchanged per each each mol of NO_3^- has been commonly accepted (De Vries et al. 2003; Staelens et al. 2008). To check whether this value was adequate for a Mediterranean species such as the holm-oak, we took advantage of the work of Uscola Fernández et al. (2014) which determined N foliar absorption from oxidized (NO_3) and reduced (NH_4^+ and urea) forms in *Quercus ilex* seedlings. From these experiments, xNH_4^+ = 1.5 (in equivalents) was obtained when considering only the NO_3^- and NH_4^+ forms, but when considering the NO_3^- absorption *vs.* [NH_4^+ + urea], a value of xNH_4^+ = 6.5 was obtained. It is possible that part of the sprinkled urea in fact might be taken up as NH_4^+ since urea deposited on leaves can undergo a rapid conversion to NH_4^+ by the enzyme ureasa present in bacterial and fungal populations that colonize the phyllosphere (Peñuelas and Terradas, 2013; Redford et al., 2010) and then be absorbed as NH_4^+. Also urea can decompose to NH_3 and NH_4^+ at high pH values on wetted surfaces, though we do not know the extent of these transformations. To account for the possible range of exchange values pointed out from this study and the usual values in the literature (xNH_4^+ = 6) we performed a sensitivity analysis with xNH_4^+ = 1.5, 3 and 6 in the CBM. Dry deposition resulting from this exercise was compared with N dry deposition derived from the inferential model and with results from leaf washing experiments conducted in 1996 (Rodrigo and Avila, 2002) and repeated again in 2016 at LC (Table 6).

Dry deposition of NH_4-N estimated with the CBM varied between 0.25 to 4.0 kg N ha^{-1} y^{-1}, with the lowest dry deposition at the TC site and the highest at the CB site near Barcelona (Table 6). The CMB approach used here equates NH_4^+ uptake with the net canopy leaching of base cations once corrected for anion leaching (eq. 4) and this is constant along the sensitivity analysis. At LC (where this comparison is possible) dry deposition of NH_4^+-N estimated with the CBM was closer to inferential estimations (77%) than to leaf washes. This is attributed to the probable NH_4^+ uptake at the leaf surfaces during the washings, as seen in other works (Adrianssens et al., 2011;

Ignatova and Dambrine, 2000). Therefore, for NH_4^+-N, the CBM and the inferential calculations seem to be better descriptors of dry deposition than the leaf washes.

On the other hand, DD estimates varied considerably for NO_3^--N when testing the different efficiency factors: DD estimates decreased as the efficiency factor increased (Table 6). When comparing CBM dry deposition estimates with the other methods, a good match was found at LC and CB between CMB $xNH_4^+ = 6$ and the inferential estimation (80% and 102%, respectively) while $xNH_4^+ = 1.5$ produced too high results both at these sites (Table 6). Leaf wash NO_3^--N dry deposition estimates were similar for the two periods separated by a 20-year lapse (Table 6) and were 70% lower than the inferential result. On the other hand, at TC, variation of the NH_4^+ efficiency factor had little effect on NO_3^--N DD estimates which ranged from 1.2 to 2.0 kg ha^{-1} y^{-1} with the xNH4 variation from 1.5 to 6. The CBM estimates at this site did not adjust to dry deposition derived from the inferential method. This can be attributed to several factors: 1) the low deposition fluxes at this site and its particular dry meteorology during the study years, 2) uncertainties in the parameters for NH4 exchange in the CBM, 3) uncertainties in the inferential model parameters and calculations. While more refinement is needed in this regard, and work is in progress to develop a more accurate inferential model, presently we will use the CBM flux results to provide a range of possible values of dry deposition at TC. On the other hand, for the northwestern sites of LC and CB, the CBM dry deposition estimates with $xNH_4^+ = 6$ were within 77-102% of the estimates obtained from inferential and washing methodologies.

Considering an efficiency factor xNH4 = 6 and based in the assumption NO_3^- **uptake is balanced by** H^+ **uptake,** H^+ **DD and CE fluxes can be calculated (Table 5) . It can be seen that** H^+ **deposition is 2-10 fold higher in DD than in WD, with the highest DD flux at the sites close to Barcelona. This DD may occur under particular atmospheric conditions when air masses carry urban pollutants to the study sites. This does not impede, however, that under other atmospheric scenarios, carbonate dust might also be deposited on the leaves and neutralize acidity on the leaves surface.**

3.4 Assessment of the exceedance of empirical N critical loads proposed for Mediterranean sclerophyllous forests

Dry deposition of N estimated with the CBM using an efficiency factor of 6 was 8.0 and 9.4 kg ha^{-1} y^{-1} at LC and CB, respectively, and the total deposition (sum of wet + dry) of Dissolved Inorganic Nitrogen (DIN) was 12.3 and 12.6 kg ha^{-1} y^{-1} respectively (Table 7). At TC, N dry deposition ranged between 1.5 – 2.3 kg ha^{-1} y^{-1} and total deposition was 2.7 – 3.5 kg ha^{-1} y^{-1} (Table 7). The contribution of DD to TD was between 57-72% for NH_4-N and 71-77% for NO_3-N in the northwestern sites (Table 7), percentages that are in accordance with other deposition studies in the western fringe of the Iberian Peninsula (Avila and Rodà, 2012; Sanz et al., 2002) and in other Mediterranean-type ecosystems as well (Anatolaki and Tsitouridou, 2007; Bytnerowicz and Fenn, 1996). For the site in central Spain, similar dry deposition percentages were obtained for NO_3-N (63-74%), but they were much lower for NH_4-N (33%).

The consistency of the dry deposition estimates using different approaches (CBM, inferential model and branch washing) at the sites with wetter meteorology in NE Spain provides ground for accepting DIN deposition fluxes under these conditions. Accepting the CBM estimates, total deposition of inorganic N (DIN) to LC and CB was around 12 kg ha^{-1} y^{-1}. Recent studies in these sites indicated that dissolved organic nitrogen (DON) would add around 3 kg N $ha^{-1}y^{-1}$ (Izquieta-Rojano et al., 2016), indicating a total N input to the holm-oak forests in Northeastern Spain of 15 kg $ha^{-1}y^{-1}$. Since the current empirical critical loads proposed for sclerophyllous forests are in the range of 15-17 kg N $ha^{-1}y^{-1}$ (Bobbink et al., 2010), these forests are close to the critical value. This is in accordance with results from a modeling exercise for the Iberian Peninsula that suggested that mountain areas in the Northeastern region could be close or even exceed the critical loads in some habitats of Community interest from the Spanish Natura 2000 network (García-Gómez et al., 2014). On the other hand,the study site in central Spain submitted to a drier environment received much lower total DIN deposition inputs (about 3 kg N ha^{-1} y^{-1}), far from the critical loads proposed for sclerophyllous forests.

The high variability of deposition estimates between sites of contrasted climate found in this study and the fact that deposition estimates from the sites under a milder Mediterranean climate showed a higher match with procedures in use for temperate forests, indicates the strong effect of climate in the deposition processes and the need to better understand dry deposition for N compounds in semi-aridic ecosystems.

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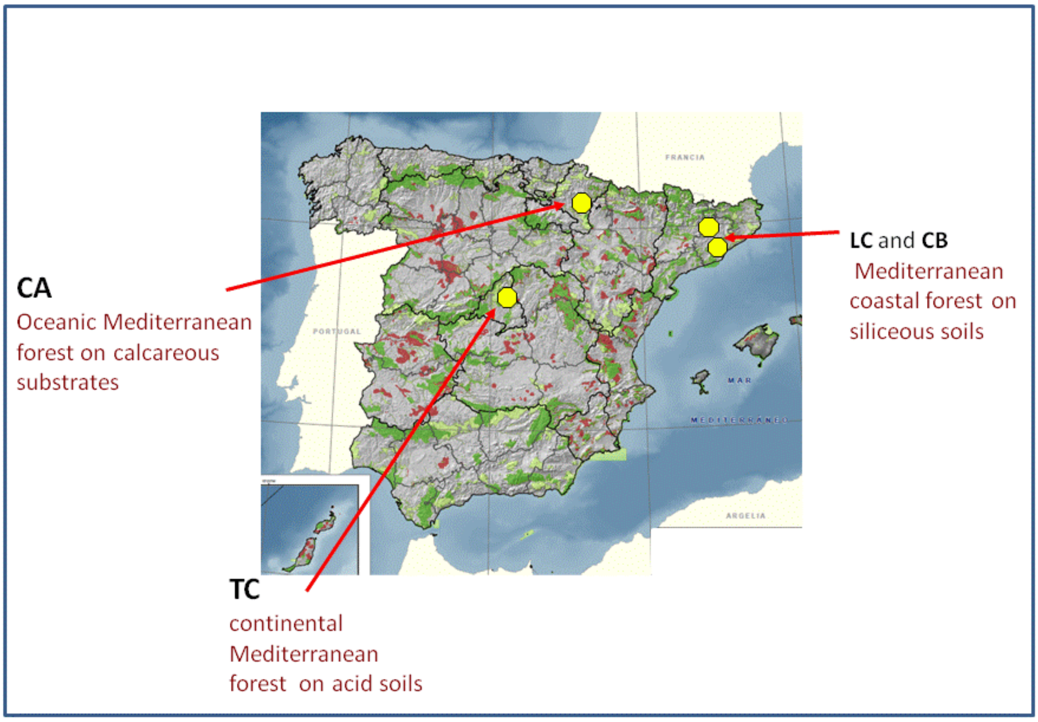

Figure 1. Location of the study sites (name and province) in the Iberian Peninsula. LC = La Castanya (Barcelona), CB = Can Balasc (Barcelona) , CA= Carrascal (Pamplona), and TC = Tres Cantos (Madrid).

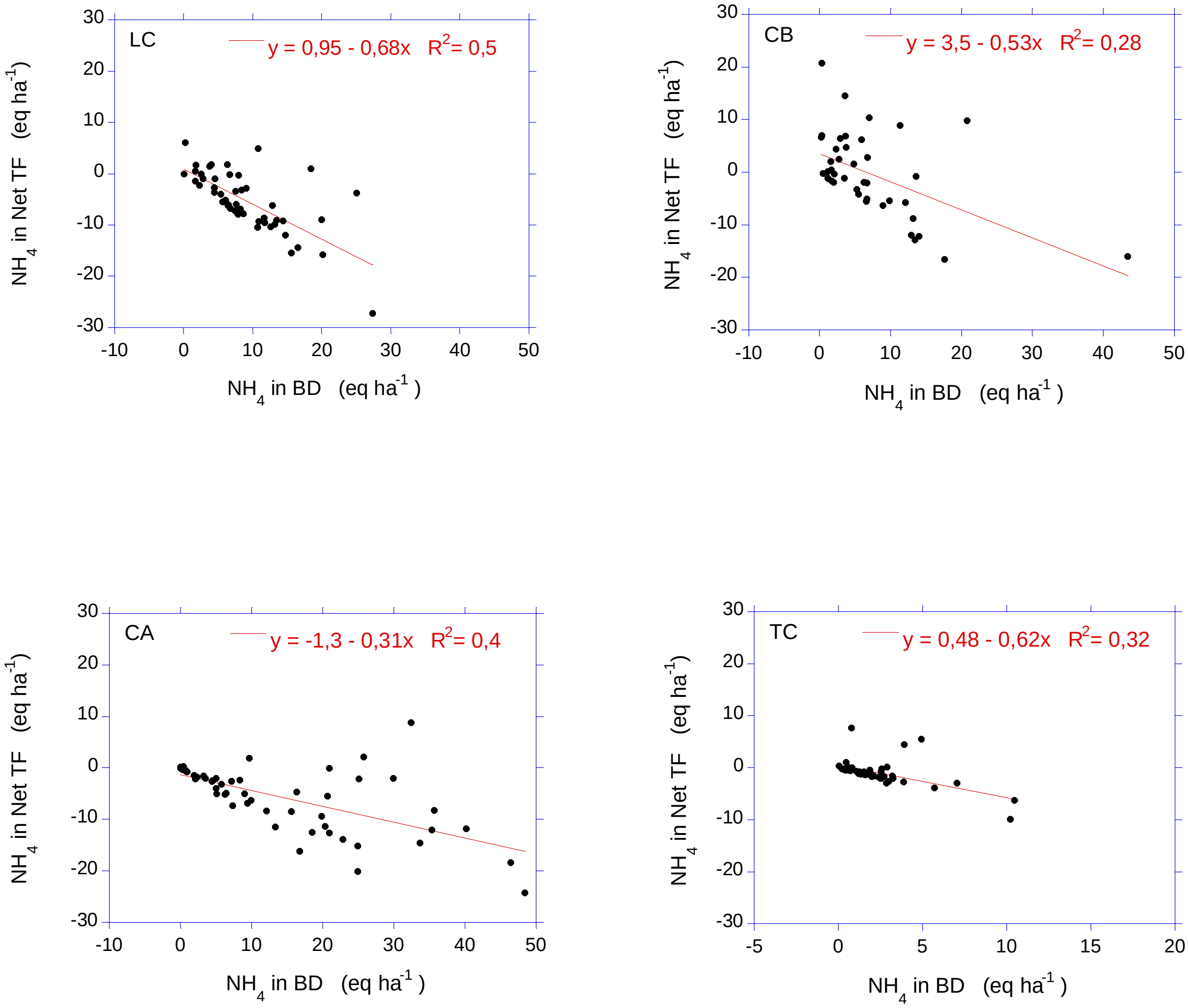

Figure 2. Linear relationships of bulk *vs.* netTF fluxes of NH_4^+ (units in eq ha^{-1} $episode^{-1}$) at each studied site. N= 49 for LC, 41 for CB, 55 for CA and 51 for TC. Notice the different x axis scale for TC.

Table 1. Study site characteristics, climatic features, forest stand parameters, atmospheric information and air quality at the study sites. Climate and pollutant data are mean values for the study period.

		LC	CB	CA	TC
Study site characteristics	Aspect	SE	NE	SE	S
	Distance to the sea (km)	27	11	80	310
Climatic parameters	Climate	Mediterranean	Mediterranean	Mediterranean continental with oceanic influence	Mediterranean continental
	Mean annual Temperature (ºC)	9.0	15.1	12.6	14.4
	Mean annual Rainfall (mm y^{-1})	938	723	786	343
Stand parameters	Leaf area index ($m^2 \cdot m^{-2}$)	6.1	4.7	5.3	3.0
	Number of trees·ha^{-1}	2571	1429	1760	491
	Mean diameter at breast high (cm)	13.0	12.6	16.1	41
Air Quality	NO_2 (µg m^{-3})	4.3	16.2	10.6	11.1
	NH_3 (µg m^{-3})	0.7	1.0	2.5	0.7
	PM_{10} (µg m^{-3})	18.0	-	26.9	23.0
Potential pollution sources		Distant urban agglomerations	Barcelona city	Small urban agglomerations	Madrid city
		Routes within the park	Transportation routes (highways and railways connecting Barcelona to other urban sites)	High traffic intensity highway lying at 100m distance to the study site	High traffic intensity highway lying at 2 km distance to the study site
		Moderate agricultural activities	Air masses influenced by sea traffic	Agriculture in the fields surrounding the studied site	
				Opencast limestone quarry	

Table 2. Ratios between bulk deposition and wet deposition (BD/WD) at LC (June 2011-June 2013) and TC (January to June 2013).

BD/WD	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-
LC	1.39	1.64	1.33	1.63	1.31	1.60	1.36	1.63
TC	1.18	1.39	2.13	1.47	1.45	1.51	1.27	1.17

Table 3. Mean annual precipitation and bulk (BD), throughfall (TF) and net throughfall (netTF) deposition fluxes (kg ha^{-1} y^{-1}) at each studied site. Fluxes for alkalinity are given in eq ha^{-1} y^{-1}. Mean and ± standard deviation for two years are given.

	Prec.	Alk.	H^+	Na^+	K^+	Ca^{2+}	Mg^+	NH_4-N	NO_3-N	SO_4-S	Cl^-
	L m^{-2}	eq ha^{-1} y^{-1}	kg ha^{-1} y^{-1} *10^{-3}	kg ha^{-1} y^{-1}							
BD											
LC	938 ± 46	260± 51	29± 5	6.3 ± 0.9	1.6 ± 0.2	13 ± 2.7	1.9 ± 0.3	3.1 ± 0.6	3.2 ± 0.1	3.4 ± 0.1	11 ± 1.5
CB	723 ± 63	340± 91	14± 7	9.3 ± 2.3	1.3 ± 0.2	17 ± 5.1	2.3 ± 0.6	2.1 ± 0.1	2.6 ± 0.1	4.0 ± 0.5	16 ± 4.0
CA	786 ± 290	670± 210	1 ± 0.1	7.6 ± 1.3	2.4 ± 0.0	24 ± 2.7	1.1 ± 0.2	5.2 ± 1.3	3.0 ± 0.2	3.5 ± 0.6	12 ± 3.2
TC	343 ± 69	62± 12	7 ± 2	1.5 ± 0.1	0.8 ± 0.0	3.4 ± 0.5	0.3 ± 0.0	0.8 ± 0.1	1.0 ± 0.0	1.2 ± 0.2	1.3 ± 0.0
TF											
LC	695 ± 47	620± 15	12± 4	7.5 ± 0.5	17 ± 0.5	17 ± 0.1	4.2 ± 0.1	1.3 ± 0.1	4.5 ± 0.5	4.0 ± 0.6	18 ± 1.2
CB	491 ± 54	620± 14	18± 2	10 ± 0.9	15 ± 0.5	21 ± 0.7	4.3 ± 0.2	2.0 ± 0.1	5.5 ± 0.0	6.1 ± 0.3	23 ± 1.8
CA	607 ± 257	2000± 53	1 ± 0.1	12 ± 0.9	16 ± 2.6	57 ± 3.7	3.1 ± 0.5	3.1 ± 0.9	4.3 ± 0.4	4.6 ± 0.0	20 ± 2.1
TC	230 ± 16	140± 10	14± 1	2.3 ± 0.0	13 ± 1.3	6.6 ± 1.0	1.5 ± 0.2	0.4 ± 0.0	1.6 ± 0.0	0.9 ± 0.2	2.9 ± 0.2
netTF											
LC	-243 ± 1,4	360± 50	-17± 5	1.3 ± 1.3	17± 0.7	4.5 ± 2.8	2.3 ± 0.4	-1.8 ± 0.7	1.3 ± 0.4	0.6 ± 0.5	7.4 ± 2.7
CB	-232± 12	280±45	4 ± 7	0.9 ± 1.4	14 ± 0.3	4.7 ± 4.4	2.0 ± 0.4	0.0 ± 0.3	2.9 ± 0.1	2.1 ± 0.2	7.3 ± 2.2
CA	-179 ± 46	1330± 15	0 ± 0.1	4.0 ± 0.3	12 ± 2.6	35 ± 1.0	2.0 ± 0.2	-2.1 ± 0.4	1.3 ± 0.6	1.2 ± 0.5	8.0 ± 1.1
TC	-113 ± 75	78± 11	7± 2	0.8 ± 0.1	12 ± 1.3	3.2 ± 0.5	1.3 ± 0.1	-0.4 ± 0.1	0.6 ± 0.0	-0.3 ± 0.0	1.6 ± 0.2

Table 4. Spearman correlations (r) between rainfall amount (in mm) and net throughfall fluxes (in eq ha^{-1}) at the four studied sites. The probability value (p) is also given. Number of observations = 49 for LC, 41 for CB, 55 for CA and 51 for TC.

	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-
LC								
r	0.25	0.65	0.15	0.21	-0.28	-0.28	0.02	0.16
p	0.08	0.00	0.30	0.15	0.05	0.05	0.88	0.28
CB								
r	0.25	0.84	0.12	0.09	-0.27	-0.10	0.05	0.21
p	0.12	0.00	0.45	0.59	0.09	0.52	0.76	0.18
CA								
r	0.62	0.89	0.79	0.76	-0.53	0.41	0.20	0.54
p	0.00	0.00	0.00	0.00	0.00	0.00	0.14	0.00
TC								
r	0.33	0.67	0.54	0.62	-0.54	-0.18	-0.27	0.34
p	0.00	0.00	0.00	0.00	0.00	0.11	0.01	0.00

Table 5. Results from the canopy budget model at LC, CB and TC for H^+, base cations, SO_4-S and Cl^- (in kg ha^{-1} y^{-1}) obtained in the Canopy Budget Model with a dry deposition factor based on Na^+. WD= Wet deposition, DD= Dry deposition, CU/CL= Canopy uptake (CU) corresponding to negative CU/CL values and canopy leaching (CL) to positive ones; TD= Total deposition.

	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4-S	Cl^-
LC							
WD	0.03	4.5	1.0	9.7	1.2	2.5	6.4
DD	0.15	3.0	0.7	6.5	0.8	1.7	4.2
CU/CL	-0.18	0.0	17.2	1.2	2.2	-0.1	7.2
TD	0.18	7.5	1.6	16.2	1.9	4.2	10.6
CB							
WD	0.02	6.7	0.8	12.5	1.4	2.9	9.7
DD	0.16	3.5	0.4	6.5	0.7	1.5	5.0
CU/CL	-0.16	0.0	14.1	2.3	2.1	1.7	8.4
TD	0.17	10.2	1.2	19	2.1	4.5	14.7
TC							
WD	0.007	1.2	0.6	1.6	0.2	1.0	1.1
DD	0.015	1.0	0.5	1.3	0.2	0.8	0.9
CU/CL	-0.002	0.0	11.7	3.7	1.2	-0.8	0.8
TD	0.023	2.3	1.1	2.9	0.4	1.8	2.1

Table 6. Dry deposition and canopy uptake fluxes for N compounds (in kg ha^{-1} y^{-1}) estimated with different methods: the CBM with different efficiency factors between NH_4^+ *vs* NO_3^- (xNH_4^+=1.5, 3 and 6), the inferential method based on in situ gas measurements and bibliographic values for V_d and canopy leaf washings in two periods, 1996 and 2016 (only at the LC site).

	Method	LC	CB	TC
Dry Deposition (kg ha^{-1} y^{-1})				
NH4-N	CBM	3.11	4.0	0.25
	inferential	4.0	5.4	3.9
	leaf wash 1996	1.1		
	leaf wash 2016	1.6		
NO3-N	CBM 1.5	12.0	10.3	2.0
	CBM 3	7.3	7.0	1.5
	CBM 6	4.9	5.4	1.2
	inferential	6.2	5.3	4.6
	leaf wash 1996	4.5		
	leaf wash 2016	4.2		
Canopy uptake (kg ha^{-1} y^{-1})				
NH4-N	CBM	-4.1	-3.5	-0.38
NO3-N	CBM 1.5	-9.6	-6.4	-1.03
	CBM 3	-4.8	-3.2	-0.50
	CBM 6	-2.4	-4.6	-0.25

Table 7. N fluxes for NH_4^+-N, NO_3^--N and their sum (Dissolved Inorganic Nitrogen, DIN) in wet deposition (WD), dry deposition (DD) and total deposition (TD) in kg ha-1 y-1. DD estimated with a canopy budget model with xNH_4^+=6 at LC and CB, and a fork comprising from 1.5, 3 and 6 at TC.

		LC	CB	TC
NH_4^+-N	WD	2.33	1.56	0.5
	DD	3.11	3.97	0.25
	TD	5.44	5.53	0.75
	%DD	57	72	33
NO_3^--N	WD	2	1,63	0,67
	DD	4.89	5.43	1.2-2.0
	TD	6.89	7.06	1.9-2.7
	%DD	71	77	63-74
DIN	TD	12.3	12.6	2.7-3.5