Atmospheric deposition of inorganic nitrogen in Spanish holm oak forests measured with ion-exchange resins and conventional collectors

Héctor García-Gomez[1,6], Sheila Izquieta-Rojano[2], Laura Aguillaume[3], Ignacio González-Fernández[1], Fernando Valiño[1], David Elustondo[2], Jesús M. Santamaría[2], Anna Àvila[4], Mark E. Fenn[5], Rocío Alonso[1]

[1] Ecotoxicology of Air Pollution, CIEMAT, Av. Complutense 40, Ed.70, 28040 Madrid, Spain.
[2] LICA, Universidad de Navarra, C. Irunlarrea 1, 31009 Pamplona, Spain.
[3] CREAF, Campus de Bellaterra (UAB), Edifici C, 08193Cerdanyola del Vallès, Spain.
[4] Universitat Autònoma de Barcelona (UAB), Campus de Bellaterra, 08193 Cerdanyola del Vallès, Spain.
[5] USDA Forest Service, Riverside, CA, 92507, USA
[6] Technical University of Madrid, School of Agriculture, Avd. Complutense s/n, 28040 Madrid, Spain.

1. Introduction

A continuous increase of nitrophilous species of plants, lichens and mosses in the Iberian Peninsula (Ariño et al., 2011); an increase in the N content of bryophytes during the last half of the 20th century (Peñuelas and Filella, 2001); an increase in nitrate concentration in headwater streams (Àvila and Rodà, 2012; Camarero and Aniz, 2010); and nutritional imbalances in forests of *Abies pinsapo* and *Pinus silvestris* attributed to atmospheric N inputs (Blanes et al., 2013; Sardans et al., 2015). Furthermore, interactions of N enrichment with ozone, the most important air pollutant in the Mediterranean region, have been described for plant species in Spain (Calvete-Sogo et al., 2014; Sanz et al., 2015).

A recent model-based assessment of N deposition threats to habitats within the Spanish Natura 2000 network showed that the most threatened habitat-types were in mountainous and alpine areas (natural grasslands and heathlands in the Pyrenees and Cantabrian Ranges, *Pinus uncinata* and *Abies pinsapo* forests), and in mountain forests and scrublands close to high emission sources such as the big cities of Madrid and Barcelona, and sclerophyllous forests of *Quercus ilex* in NE Spain (García-Gómez et al., 2014). These high-altitude and orographically-complex areas are difficult to

access for monitoring purposes. Besides, current chemical transport models do not adequately simulate small-scale variations in deposition regimes in these areas (Boutin et al., 2015; García-Gómez et al., 2014; Simpson et al., 2006). Further monitoring efforts in such areas would be useful for ground validation of transport models and for ecosystem conservation assessments..

Although the use of automatic wet-only samplers is widely recommended for monitoring atmospheric wet deposition, the expansion of monitoring networks has been urged by using less expensive methods, easy to operate, and without requiring frequent visits to the field (Erisman et al., 2005; Clow et al., 2015). Throughfall or precipitation collectors using ion exchange resins (IER) combine all these conditions. They usually consist of a collector funnel connected to an IER-containing column instead of a collection bottle. Inside the tube, the precipitation flows through the resin during rain or snowmelt events and the ionic solutes are adsorbed to the resin. Collectors using IER have been employed to monitor atmospheric N input to forest ecosystems since the early 2000s (e.g. Fenn et al., 2002; Fenn et al., 2015). This technique appears highly suitable for the Mediterranean region where complex orography complicates field sampling. To our knowledge, there are not published studies applying this technique in Mediterranean forests of Europe. In this study, three monitoring sites in three Spanish forests of *Q. ilex* were equipped with conventional and IER collectors to monitor bulk and throughfall deposition of inorganic N (nitrate and ammonium) during two years. In addition, a review of the published works using IER for collecting N deposition was performed and compared with our results. This study was part of the EDEN project (*Effects of nitrogen deposition in Mediterranean evergreen holm oak forests*), for which one of the objectives was to evaluate different measurement methodologies for determining atmospheric N deposition.

2. Methodology

2.1. Study sites

Three holm-oak (*Q. ilex*) forests in Spain, influenced by different pollution sources, soil and climatic conditions were selected for this study (Fig. 1). The Can Balasc (CB) site is in a forest located within a natural protected area 4 km from Barcelona. This site

is characterized by acidic soils and a Mediterranean sub-humid climate. The Carrascal site (CA) is located in an agricultural area close to Pamplona (15 km), with calcareous soil and a Mediterranean humid climate. This site is the most agriculturally-influenced among the three forests. The Tres Cantos site (TC) is a forest located in a natural protected area 9 km from Madrid, growing on acidic sandy soil and with a Mediterranean semi-arid climate. The vegetation at TC was historically managed as a traditional dehesa (a savannah-like agrosilvopastoral system) of *Q. ilex*, but the low management intensity during the last decades has allowed vegetation to grow as a moderately open forest. Meteorological variables were monitored in the CB and TC sites, and data from the closest meteorological station were collected for the CA site. Further information on the monitoring sites can be found in García-Gómez et al. (2015).

2.2. Sampling and analytical methodologies

Atmospheric deposition of ammonium (NH_4^+) and nitrate (NO_3^-) was monitored for two years (spring 2011 – winter 2013) in open-field plots (bulk deposition) and below the forest canopy (throughfall deposition) by means of IER collectors (IECs). These collectors were manufactured following Fenn and Poth (2004), and consisted of a funnel (10 cm radius; NILU - Norwegian Institute for Air Research, Kjeller, Norway) attached to a PVC tube with an inner diameter of 15 mm filled with a mixed-bed IER (Amberlite™ IRN150) and a valve at the bottom for drainage (Fig. A1). Generic residue-free synthetic filter wool was inserted in both ends of the resin tube. Replicate IECs were placed in the field with the collection surface at 1.5 m height during periods of 3 to 5 months. For bulk deposition measurements, 4 collectors were deployed in TC and CA, and 2 collectors in CB, in open-field locations; for throughfall deposition measurements, 12 collectors were deployed in TC and CA, and 8 collectors in CB, below the forest canopy. The entire collector devices were replaced in the field at the end of each sampling period, and visually inspected for signs of bird fouling or other potential contaminations of the sample. Once in the laboratory, the columns were pre-rinsed with 100 ml of deionized water and the ions extracted by percolating 200 ml aliquotes of 2*M* solution of KCl two times, representing two consecutive extractions. Extracts were measured for pH as an additional quality control of this methodology since liquid samples can lose NH_4^+ via NH_3 volatilization as the pH increases (Vlek

and Stumpe, 1978). Background levels of NO_3^- and NH_4^+ in resin columns unexposed to atmospheric deposition and stored at room temperature were also determined and used as blanks. Finally, a set of IECs were spiked with known quantities of NO_3^- and NH_4^+ in laboratory conditions and were extracted and analysed following the same procedure to determine the adsorption and recovery efficiencies of the IECs for this experiment (Table 1).

Available published studies using similar IECs (or at least applying similar laboratory tests to them) were collected, and their methodological data (when available) were recorded or estimated from tables or figures. Results from this methodological review are presented in Table A-1.

Nitrogen deposition was additionally monitored by means of conventional collectors using bottles instead of resin tubes (conventional bottle collectors; CBCs). These CBCs were collocated with the IECs, applying the same replication, funnel type and height. The CBC samples were collected on a weekly-basis by replacing the collection bottle. During periods without rain, the CBC funnels were rinsed with 100 ml of deionised water every two weeks before replacing the bottle, in order to collect and measure the dry deposition into the funnel. The sampling procedure, storage, analysis by ion chromatography (Dionex, Sunnyvale, USA) and quality control of the analytical results of the CBC samples were performed following the recommendations of the ICP Forests Manual (Clarke et al. 2010), and it is further described in Izquieta-Rojano et al. (2016).

For both measurement methodologies, a filter mesh was fixed on top of the funnel walls to prevent the accumulation of litterfall in the funnels and a bug-sieve (NILU, Kjeller, Norway)was placed at the bottom the funnel to protect the resins from further small particle contamination. The upper edges of the funnels were equipped with an external metal ring to prevent birds from perching on the tube perimeter (Fig. A1).

2.3. Calculations and statistical analysis

Nitrogen deposition in each IEC was calculated multiplying the concentration of nitrate-N (NO_3-N) and ammonium-N (NH_4-N) by the volume of the extracting solution and adding the results from the two extractions. Then the background levels measured in the unexposed blank IER tubes were subtracted, and the result divided by

the collection surface. Finally, these results were corrected by the recovery efficiency factor. For the CBCs, the deposition was calculated for each collection bottle by multiplying the sample concentration by the volume collected (or the rinsing volume for the rainless periods). Deposition values from the replicated samples were then averaged for each period and plot for both methodologies. Deposition of total inorganic nitrogen (TIN) was calculated by adding NO_3-N and NH_4-N deposition values. Annual deposition values were calculated as the sum of the sampling period values during the year. When the sum of periods did not exactly match with the duration of a natural year, values were weighted by their added-up sampling time. Deposition values (means and standard deviations) of the CBC periods were combined to match the IEC periods for comparison purposes, and also grouped and combined on a monthly basis to summarize and describe the intra-annual variability of the N deposition. Net throughfall deposition was calculated subtracting bulk deposition values from throughfall deposition values for every period and methodology.

To compare the two methods, the Pearson correlation coefficient (r) was calculated for NO_3-N, NH_4-N and TIN deposition data from both methods. Correlation between variables was tested using Statistica version 12 (StatSoft, Inc. Tule, OK, USA) with the Pearson correlation coefficient, and with Spearman rank order correlation when the data were not normal. Alpha level was set at 0.05. Additionally, two metrics commonly used in model evaluation (García-Gómez et al., 2014; Boylan and Russell, 2006), the mean fractional bias (MFB) and root mean square error (RMSE), were calculated following eq.1 and eq. 2, respectively.

eq. 1 $$MFB = \frac{1}{N}\sum\left(\frac{IEC_i - CBC_i}{\frac{IEC_i + CBC_i}{2}}\right)$$

eq. 2 $$RMSE = \left[\frac{1}{N}\sum(IEC_i - CBC_i)^2\right]^{\frac{1}{2}}$$

,where N is the number of data pairs from the IEC and CBC methods, and the index *i* is over the time series, and including all the monitoring sites for each method. Variability of deposition values among collectors (referred herein as precision of the method) was calculated as the coefficient of variation (CV = standard deviation / mean) for every plot and period with two or more sampling data available.

153 **3. Results and Discussion**

154 **3.1. Laboratory testing of ion-exchange resin collectors**

155 The values of nitrate obtained in blank unexposed IECs were 0.001 - 0.006 mg NO_3-N
156 per gram of resin. These values were similar to previously reported ones (Table 1). In
157 the case of ammonium, mean values of 0.048; 0.060 and 0.074 mg NH_4-N per gram of
158 resin were obtained. This blank correction was higher than those shown in Table 1,
159 which were 0.001 mg NH_4-N g^{-1}, except for Boutin et al. (2015) who nonetheless
160 reported a blank value aat least 4 times lower.. Resins made of quaternary ammonium
161 compounds, like the one use in this study, can release NH_4^+ (Hansen 2012; Langlois et
162 al., 2003), which could explain the relatively high NH_4^+ found in the blanks. Although
163 having such high blank values is not expected to cause accuracy problems, it could
164 contribute to a decrease in the precision of the measurement of low deposition values.
165 The adsorption efficiency of the IER tubes was close to 100% for both ions, the same
166 as in most of the reviewed experiments from the literature (Table 1). The recovery
167 efficiency for NO_3^- was comparable to that reported in other studies, but the recovery
168 efficiency was higher for NH_4^+. In this case, more NH_4^+ was recovered from the
169 spiked resins than the quantity previously added, giving a recovery factor of 112%.
170 Recovery factors above 100 % have been previously described using the same IER
171 (Fenn et al., 2002; Table 1). These results highlight the importance of lab tests to
172 explore the performance of the resin used and to provide with suitable correction
173 factors.

174 **3.2. Comparison of methods**

175 The comparison metrics and graphics were performed only for bulk deposition values,
176 since throughfall deposition is subjected to a higher variability due to canopy
177 interactions with atmospheric N, canopy heterogeneity, and biochemical
178 transformations provoked by litterfall or algae in the collectors (Bleeker et al., 2003;
179 Fenn and Poth, 2004).

180 In our study, a considerable number of the IEC extracts from CA exhibited a high pH
181 (mean of 4.9, maximum of 13.1), while for the other two sites a mean pH of 3.6 and a
182 maximum value of 6.3 were found. Significant negative correlations were found
183 between the pH of the extracts and NH_4^+ concentrations within some periods at CA

184 (data not shown) and a remarkable reduction in NH_4^+ concentration occurred generally
185 at pH values higher than 5.5. Because of this, ammonium values from extracts with a
186 pH value higher than 5 (34% of 246 extracted samples) were removed from the dataset
187 before deposition calculations, which reduced the replication of measurements (Table
188 2). The precipitation in CA was much more alkaline (with a mean pH of 7.3 and a
189 mean alkalinity of 1411 µeq l^{-1}) than in CB or TC (with mean pH of 6.3 and 6.0; and
190 mean alkalinity of 67.6 and 27.5 µeq l^{-1}, respectively) during the study period
191 (Aguillaume, 2015). It may therefore be that carbonates and bicarbonates present in
192 the rain at this site increased the pH of the extracts provoking the loss of NH_4^+ via
193 volatilization of NH_3 before the analysis (Cape et al., 2012; Izquieta-Rojano et al.,
194 2016).

195 Variability among IEC samplers for bulk deposition was lower in TC (mean CV of
196 12% and 11% for NO_3-N and NH_4-N, respectively) than in the other two sites: mean
197 CV of 22% and 35% for NO_3-N and 79% and 22% for NH_4-N in CB and CA,
198 respectively. These high values are similar to the highest reported ones in Table 1 and
199 they may be caused by a low replication in these sites. In CB, only two IECs were
200 installed in the open, while in CA the above-mentioned reduction in the dataset
201 provoked a drastic reduction in the actual replication. In the present study, the intra-
202 plot variability of the IEC methodology for bulk deposition measurements was in a
203 similar range to the set of previous experiments shown in Table 1. The variability
204 found with IECs was similar to that found using CBCs, with the exception of NH_4-N
205 in CB (79%), which was largely higher (29% using CBCs). It might indicate that a
206 higher replication than two funnels is needed in this type of forests when IER are used
207 to measure NH_4-N deposition. Moreover, the higher replication allows detecting and
208 removing questionable data, as was done for the CA dataset.

209 Comparison of IEC and CBC measurements of N bulk deposition showed a good
210 agreement for NO_3-N and acceptable for NH_4-N and TIN (Fig. 2). Nitrate deposition
211 estimations showed lower error (RMSE = 0.15 kg N ha^{-1}) and a better fit to the 1:1 line
212 than NH_4-N measurements. Ammonium measurements with IECs tended to
213 overestimate the lowest range and underestimate the highest ones, in relation with the
214 CBC values. The bias for NH_4-N deposition was low and positive (MFB = 6% for the
215 entire dataset) and the error was about 0.56 kg N ha^{-1}. In consequence, TIN

measurements showed an acceptable accuracy between methods (Fig. 2) but a lower precision (RMSE = 0.63). This comparison was performed using the CBC results as the reference for assessing the IEC results, but it must be taken into account that the former methodology is not free of uncertainty (Bleeker et al. 2003; Dämmgen et al., 2005). Moreover, there are also differences in the quality control of the data, since a thorough validation of the analytical results was not possible for IEC data (because only NO_3^- and NH_4^+ were analyzed in these samples).

Fig. 2 shows a very good performance of IEC method for NO_3-N measurements, with only one period slightly out of the ±50% lines. In the case of NH_4-N deposition, the values with the highest deviation were from two sampling periods during the second year in CA, with exceptionally low values in the IECs (2.12 and 1.54 kg NH_4-N ha^{-1}) compared to the CBC values (3.15 and 3.29 kg NH_4-N ha^{-1}). These two periods showed the highest mean hourly precipitation of the entire study (0.11 and 0.17 mm h^{-1}) and an elevated maxima hourly precipitation (9.9 and 18.2 mm h^{-1}). The lower deposition values could be therefore related to collection problems during those heavy rains To protect the resins IECs have additional filters and stoppers that may impede the rainwater flux during very intense storms and rainwater may temporarily accumulate in the funnel, exposing a relatively large surface of sample to the atmosphere. This could provoke a loss of NH_4^+ via volatilization of NH_3, particularly from rain samples with high alkalinity and pH like those found in CA. Hourly averaged rainfall showed a slight positive correlation with the differences found for NH_4^+ concentration at CA ($r = -0.48$; $p = 0.059$), which totally disappeared once the two above-mentioned periods from CA were removed, suggesting that only during these two periods the measurements were affected by heavy rains. When excluding these two sampling periods at CA, the deposition of NH_4-N estimated with the IEC method was generally higher (59%) than with the CBC method.

Previous studies have reported that NH_4^+ in bulk deposition tends to be greater in IECs than in CBCs (Clow, et al, 2015; Fenn and Poth, 2004; Hansen, 2012; Langlois et. al., 2003). There are three processes that could account for this discrepancy: 1) release of NH_4^+ from the amine groups of the IER, 2) nitrification in the CBC samped solution and 3) volatilization losses of NH_3 in the CBC liquid samples (Fenn and Poth, 2004). The high temperatures that are common in the Mediterranean climate could favor any

of the three potential processes (Fenn and Poth, 2004) and, in fact, there was a positive relationship between the mean temperature of the sampling periods and positive discrepancies of IEC over CBC for NH_4-N deposition (n = 11; r = 0.66).

Field blanks are recommended to correct for ammonium release from the IER (Fenn and Poth, 2004). However, we used laboratory blanks (i.e. IER tubes not exposed to field condition), which may release less amount of NH_4^+ than field blanks because they are not submitted to the stronger temperature oscillations experienced in the field that may enhance NH4 release from resins. This could account for part of the overestimation of NH_4^+ deposition of IECs at low concentrations.. After the study period, two sealed IECs (field control) were deployed in TC during 6 months, one under the canopy and the other in the open. The blank NH_4^+ value from the field control in the open-field plot was the only one showing a clear difference with the laboratory control for the same period, being 29% higher which corresponds to an overestimation of 0.23 kg NH_4-N ha^{-1} for bulk deposition for that period and site. Regarding the other two processes, nitrification is not expected to occur in the open-field CBCs, since the bottles are protected from solar radiation by PVC tubes , but this possibility cannot be totally discarded. Secondly, the volatilization of NH_3 from liquid samples in open field is highly possible in this warm climate, although the narrow passage through the bug-sieve in the funnel neck is expected to meaningfully reduce the rate of ammonia volatilization, since this process is known to be severely restricted by limiting the movement of air above the water (Vlek and Stumpe, 1978).

3.3. Annual nitrogen deposition to holm oak forests

Mean annual N deposition estimated with IECs and CBCs is presented in Fig. 3. TIN bulk deposition ranged from 2.42–3.85 and 3.09–5.41 kg N ha^{-1} among the sites according to CBC and IEC methodologies respectively. TIN in throughfall ranged from 2.33–8.20 and 4.52–8.91 kg N ha^{-1} among the sites with CBC and IEC respectively. The highest N bulk deposition occurred in CA, with an annual average of 2.69 kg NO_3-N ha^{-1} and 4.15 kg NH_4-N ha^{-1} according to the CBC method and 2.60 kg NO_3-N ha^{-1} and 2.81 kg NH_4-N ha^{-1}according to IECs. Throughfall deposition, on the other hand, was the highest in CB, with an annual average of 5.83 kg NO_3-N ha^{-1} and

278 2.36 kg NH_4-N ha^{-1} according to CBC method and 5.50 kg NO_3-N ha^{-1} and 3.41 kg
279 NH_4-N ha^{-1}, according to IECs.
280 The IEC method estimated on average a bulk deposition 0.20 kg NO_3-N ha^{-1} y^{-1} and
281 0.17 kg NH_4-N ha^{-1} y^{-1} lower than the CBC method, representing a MFB of -9% and -
282 5%, respectively. The comparison of annual values for throughfall showed a marked
283 difference for NH_4^+ in TC, where the IEC method estimated 2.25 kg NH_4-N ha^{-1} y^{-1}
284 more than the CBC method. This discrepancy could be related to the high uncertainty
285 of the CBC method when concentrations are close to or below detection limits
286 (Köhler, et al., 2012), as was here the case with 30% of NH_4^+ throughfall samples
287 below the detection limit. Besides, the open structure of this dehesa forest enhances
288 the heating of the collectors through direct radiation and, therefore, biological
289 processes in the liquid samples (nitrification) or in the accumulated debris at the
290 bottom of the IEC funnels (decomposition). Both possibilities are equally possible,
291 although collectors are shaded by PVC tubes and no correlation was found between
292 mean temperature and the discrepancies between methods for throughfall deposition at
293 this site. Despite bird dropping cannot be totally disregarded, the largest discrepancy
294 was found in spring of 2011, the period in which more inflorescences were collected
295 in litterfall samplers (55.2 g m^{-2}). Inflorescences of *Q. ilex* are the smallest and most
296 easily decomposable part of the litterfall with a high N content (close to 1.5 %; Bellot
297 et al., 1999). Thus, inflorescence can mean a high return of N to the soil in the years
298 with high production of flowers (Escarré et al., 1999), such as 2011. It is therefore
299 recommended to clean or change the funnels when this situation occurs. On the other
300 hand, some of the CBC samples at TC which stood uncollected in field for 2-3 days
301 after summer rains showed algal growth in the below-canopy plot but not in the open-
302 field one. The use of biocide in the collection bottles (faltan 2 refs) is therefore
303 recommended under Mediterranean conditions, particularly under semi-arid regimes
304 like at TC site and in throughfall deposition collectors. Besides, further quality control
305 can be included by analyzing phosphates in the IEC samples to identify bird-fouling
306 contamination (Fenn et al., 2015). All these results show that, IECs seem a suitable
307 method for monitoring annual deposition in this type of forest with lower cost and
308 effort than CBC methods, once precautions mentioned above are considered.

309 The difference between throughfall and bulk deposition (net throughfall) reflects the
310 interaction between the atmosphere and the canopy including both the wash-off of dry
311 deposited N and the exchange with the leaf surfaces, which in the case of N iscan
312 have an important adsorption component (Lindberg et al., 1986). Negative values of
313 net throughfall indicate that at least part of the wet deposited N is being effectively
314 retained in the canopy, while positive values indicate that at least part of the dry
315 deposited N is reaching the forest floor. Annual net throughfall values were positive
316 for NO_3-N with the two measurement methods at all sites (Fig. 3). This result indicates
317 a net flux of oxidized N to the forest soil at all sites coming from dry deposition, even
318 though some canopy nitrate retention could be occurring. This input of dry deposited
319 NO_3-N is very high at CB, the most urban-influenced site wich experiences the highest
320 concentrations of gaseous oxidized-N compounds (García-Gómez et al., 2015). On the
321 other hand, net throughfall values for NH_4-N were only clearly positive in CB and
322 negative in CA, while in TC depended on the method used and could be considered
323 close to zero. The forest canopy at CB seems to be retaining less NH_4^+ than CA, even
324 though dry deposition of reduced N is expected to be lower at this site than in CA
325 which is a highly agriculture-influenced site with higher NH_3 concentrations (García-
326 Gómez et al., 2015). Canopy uptake of NH_4^+ has been described to be larger at lower
327 nitrogen foliar content (de Vries et al., 2001), which is coincident with the
328 stoichiometry of these sites, since CA showed the lowest leaf N content (1.44%) and
329 CB the highest one (1.61%). On the other hand, the apparent retention of N by the
330 canopy of *Q. ilex* forest needs further investigation, particularly for NH_4^+. The fact that
331 the forest canopy at CB seems to retain less deposited N than the other two sites,
332 together with the observation of lower retention of atmospheric gaseous N (García-
333 Gómez et al., 2015) could indicate that the *Q. ilex* trees in this forest cannot retain as
334 much N as the other sites. Interestingly, *Q. ilex* forests close to this experimental site
335 and with similar deposition load have experienced rises of NO_3^- concentration in
336 headwater streams considered as a sign of the onset of eutrophication (Àvila and Rodà,
337 2012).

338 Seasonality

339 In Mediterranean areas, the seasonal variability of N deposition is expected to be high
340 because of the particularities of the Mediterranean precipitation regime, in which

rainfall is not equally distributed over the year. IEC data showed seasonal variations (Table 2), such as higher deposition in spring and autumn (the wettest periods), and a lower deposition during the rest of the year. Data from CBCs can be better used for studying intra-annual variability in detail because deposition can be presented monthly; Fig. 4 and A2). Negative values for net throughfall were most commonly observed with NH_4^+ (Fig. 4), indicating that canopy retention occurred more often in the reduced form, as usually found in the literature. Relatively high positive values of net throughfall can be noticed in TC during September and October in 2011 and 2012, during the first rains after the summer droughts occurred, and also in March 2012, after a particularly dry winter (Fig. 4). These values of positive net throughfall imply relatively large and ephemeral pulses of N into the soil after the first rainfall events, as those previously described in other semi-arid Mediterranean ecosystems (e.g. Meixner and Fenn, 2004; Vourlitis et al., 2009). These pulses can be noticed also in CB, but they rarely occurred in the CA site (Fig. A2). These ephemeral inputs, among others effects, can trigger pulses of NO emissions from soil (Homyak and Sickman; 2004) which can affect the atmospheric photochemistry of the forest, involved in ozone (O_3) and nitric acid formation (HNO_3). Besides, they can provoke a flushing of inorganic N to groundwater if the pulse occurs when plants and soil communities are not able to use this dissolved N (like at the end of the summer, when they are withstanding drought stress). This effect, known as the asynchrony hypothesis (Meixner and Fenn, 2004), is corroborated in TC, where high concentrations of NO_3^- in the soil water (up to 2.01 and 0.35 mg NO_3^- l^{-1} at 20 and 40 cm depth, respectively) have been found after pulses of N during late-summer and early-autumn, but not during early spring, when understory annual pastures were emerged and growing and soil communities were active.

3.4. Summary of methodological considerations

Some methodological recommendations on the IEC method arising from the present study (some of them have been already reported in previous works) must be taken into consideration. Preliminary laboratory tests on adsorption and recovery efficiency need to be done in order to know the performance of the resin. The IEC method poses a potential overestimation of NH_4^+ deposition due to the release of ammonium from the

amine groups of the IER. To avoid that, field blanks consisting of sealed IECs deployed in the field are recommended over unexposed laboratory blanks in Mediterranean conditions. An overestimation of NH_4^+ deposition could also occur when a large amount of leachable debris is accumulated during the long sampling periods of IECs. In *Q. ilex* forests it could particularly occur during the flowering period and/or in open forests, like dehesas, because the structure of the canopy allows high radiation exposure and heating of the collectors. Periodic cleaning of sampling devices is advised during those sensitive periods. On the other hand, NH_4^+ deposition could be underestimated when rain flow across the different parts of the IECs during heavy rains is made difficult (e.g. by small nominative diameter of any part of the collector, or very dense filters or sieves). A modification in the design could be studied in those areas withstanding intermittent heavy rains. It is recommended to deploy at least three replicate IECs at every bulk deposition sampling plot, so questionable samples can be removed if necessary. There would not be a recommended replication for throughfall measurements, since it may vary depending on the vegetation cover type, canopy characteristics and its distribution throughout the stand; however, based on the intra-site variability found in this study, at least ten replicates are recommended in this kind of forest stands. Finally, we also recommend to measure the pH of the sample IEC extracts, and to acidify the extract if the pH is too high. Regarding the CBC method, it has proven useful for studying the temporal variability of N deposition, and the use of biocides is recommended in these climatic conditions and especially for throughfall measurements. An additional quality control method for IEC by analysing phosphates in the extracts is also recommended.

4. Conclusions

The results of the present study show that collection methods for N deposition based on ion-exchange resins can be recommended for long-term studies in the Mediterranean region, since its measuring good performance was found for NO_3^- deposition and an acceptable for NH_4^+ and TIN, in comparison with conventional methods. This methodology is particularly recommended in remote areas and when the nitrogen concentration in rain is low. However, throughfall measurements of ammonium in low density forests (like dehesas) or any measurement with alkaline rain

should be considered with caution. Besides, possible contamination from the accumulation of debris in the funnels must be contemplated when planning the duration of the different sampling periods along the year. Absorption and recovery efficiencies from the IER need to be tested in the lab to derive possible correction factors needed.

Mean annual bulk deposition of TIN in Holm oak forests ranged from 2.42–3.85 and 3.09–5.41 kg N ha^{-1} according to CBC and IEC methodologies, respectively. Analogous throughfall deposition fluxes of TIN ranged from 2.33–8.20 and 4.52–8.91 kg N ha^{-1}. On average, bulk deposition estimated by the IEC method was 0.20 kg NO_3-N ha^{-1} y^{-1} and 0.17 kg NH_4-N ha^{-1} y^{-1} lower than the CBC method. Intra-annual variability studied with the CBC data showed significant input pulses of N into the forest soil after dry periods. These pulses presumably originated from the washing of dry deposition accumulated in the canopy and were particularly noticeable in the forest site with a semiarid climate. The implication of these nutrient pulses for ecosystem functioning, atmospheric chemistry and N leaching should be further investigated.

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615

Table 1. Compilaton of data from different studies reporting field blanks, field sampling details and laboratory tests of performance for ion exchange resins collectors.

Study	Ion exchange resin	Number and type of blanks	NO_3^-				NH_4^+			
			Blank correction (mg N g^{-1})[b]	Intra-site variability (CV)	Adsorption effiency	Recovery efficiency	Blank correction (mg N g^{-1})[b]	Intra-site variability (CV)	Adsorption effiency	Recovery efficiency
Boutin et al., 2015	Mixed-bed IONAC® NM-60	3 in total; field blanks	Non detected	12 %[a]			0.014 ± 0.006	19 %[a]		
Brumbaugh et al., 2012	2-stage columns	9; field blanks	Near detection limits	8–10 %		106 ± 7 %	Near detection limits	5–10 %		101 ± 3 %
Cerón et al., 2015	Mixed bed Amberlite™ IRN150	3; field blanks				98.6 %				98.6 %
Clow et al., 2015	Mixed bed Amberlite™ IRN150	1 per site; field blank	< 0.003	16 %[a]		100 %	< 0.003	21 %[a]		88 %
Fang et al., 2011	Mixed bed 201x7[717] & 001x7[732]	2 per site; field blank	0.003–0.028	9–34 %	90–99 %	90 %	< 0.001	5–23 %	94–100 %	97 %
Fenn et al., 2002	Mixed bed Amberlite™ IRN150	5; lab. blanks	< 0.001			104.4 %	0.001			104.5 %
Fenn and Poth, 2004	Mixed bed Amberlite™ IRN150	Lab. blanks	< 0.001	1–16 %			0.001	13–27 %		
Hansen, 2012	mixed bed Rexin®	1 per plot; field blanks	< 0.001				< 0.001			
Köhler et al., 2012	Mixed bed Amberlite™ MB 20	1; lab. blank	0.001			95%				
Sheibley et al., 2014	Mixed bed Amberlite™ IRN150	1 field blank (per site) and 3 lab. blanks	0.001–0.003	9–36 %	Approx. 100 %	90 - 91 %	≤ 0.001	7–89 %	Approx. 100 %	74–96 %
Simkin et al., 2004	Anion-exchange Dowex™ Monosphere 550-A	3; lab. blanks	< DL		100 %	93.9 - 100.4 %				
Tuloss and Cadenasso, 2015	Mixed bed Amberlite™ IRN150					90 - 95 %				90–95 %
van Dam et al., 1991	Mixed bed Dowex™ 1-X8 and 50W-X8			18 %				8 %		
Wieder et al., 2010	Mixed bed Amberlite™ IRN150	3–5 per period; lab. blank								
Yamashita et al., 2014	Mixed bed Amberlite™ MB-1	1 per period; field blank		< 10–50 %				< 8–25 %		
Zhan et al., 2015	Mixed bed of #717 anion and #732 cation	2 field blanks			> 99 %	90.3 - 95.5 %			> 99 %	90.9–100 %
Present work (CB)	Mixed bed Amberlite™ IRN150	1–3; lab. blanks	< 0.001–0.002	2–66 %			0.024–0.061	0–141 %		
Present work (CA)	Mixed bed Amberlite™ IRN150	2; lab. blanks	< 0.001–0.006	5–67 %			0.039–0.071	22 %		
Present work (TC)	Mixed bed Amberlite™ IRN150	1; lab. blanks	0.001–0.004	2–20 %	100 %	99 %	0.054–0.103	4–27 %	100 %	112 %

[a]: not CV

[b]: milligram of N released per gram of resin

620

621 **Table 2.** Bulk and throughfall deposition (kg N ha^{-1}) using ion-exchange resin collectors.

				Bulk			Throughfall		
	Start date	**End date**	**Season[1]**	**n[2]**	**NO_3^-**	**NH_4^+**	**n**	**NO_3^-**	**NH_4^+**
CB	05/04/11	28/06/11	SPR	2	0.54	0.33	8	1.66	2.01
	05/07/11	27/09/11	SUM	2	0.42	0.86	8	1.22	0.94
	04/10/11	10/01/12	AUT	2	0.43	1.03	8	1.35	0.81
	17/01/12	18/04/12	WIN-SPR	2	0.39	0.01	7	1.40	0.85
	14/05/12	03/07/12	SPR	2	0.49	0.43	8	1.92	0.59
	11/07/12	01/10/12	SUM-AUT	2	0.29	0.01	7	1.01	0.30
	16/10/12	25/02/13	AUT-WIN	2	0.30	0.61	7	0.86	0.65
CA	31/05/11	31/08/11	SUM	1	0.67	0.50	8	0.50	0.15
	31/08/11	13/12/11	AUT	1	0.35	0.26	1	0.80	0.27
	13/12/11	13/03/12	WIN	3	0.58	0.37	7	0.67	0.12
	13/03/12	19/06/12	SPR	1	1.07	2.12	1	1.37	0.76
	19/06/12	25/09/12	SUM	2	0.58	0.39	11	0.92	0.49
	25/09/12	06/03/13	AUT-WIN	1	1.41	1.54	2	1.29	0.49
TC	23/03/11	21/06/11	SPR	3	0.73	1.03	11	0.54	1.55
	28/06/11	27/09/11	SUM	4	0.16	0.16	12	0.80	0.28
	11/10/11	21/02/12	AUT-WIN	4	0.36	0.49	12	0.85	0.71
	06/03/12	21/06/12	WIN-SPR	4	0.37	0.76	12	0.64	0.77
	26/06/12	23/10/12	SUM-AUT	4	0.32	0.42	11	1.69	1.12
	30/10/12	25/03/13	AUT-WIN	4	0.38	0.57	12	0.22	0.65

622

623 [1] : SPR: spring; SUM: summer; AUT: autumn; WIN: winter

624 [2] : number of collectors used to calculate the mean deposition value

625

FIGURES

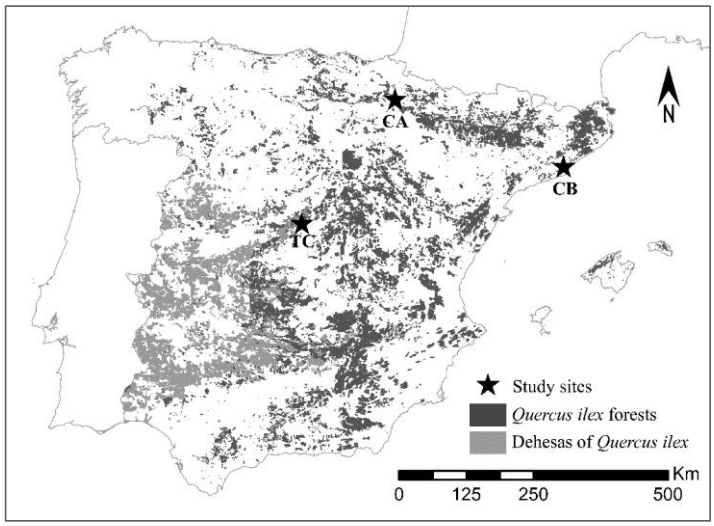
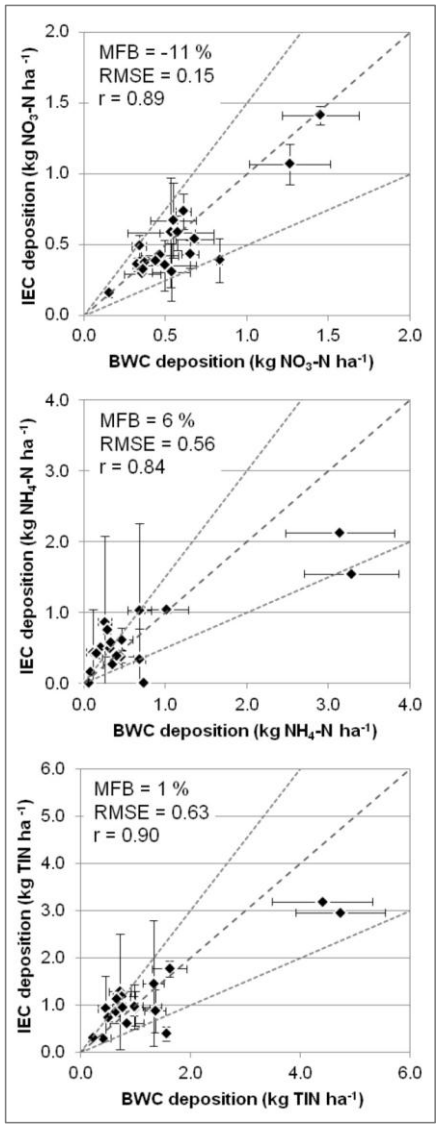
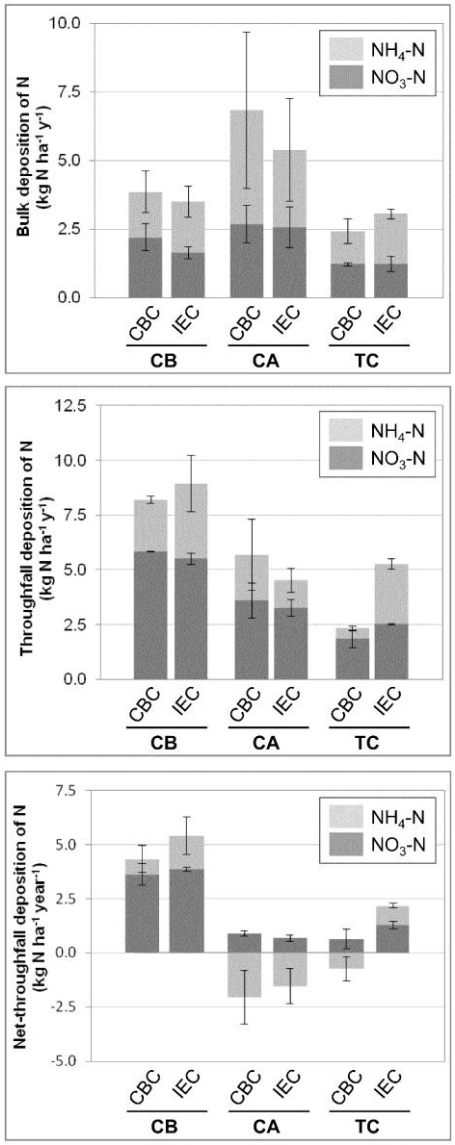


Fig. 1. Location of the study sites: CB, Can Balasc (Barcelona); CA, Carrascal (Pamplona); TC, Tres Cantos (Madrid). Distribution of *Q. ilex* habitats in Spain is added.

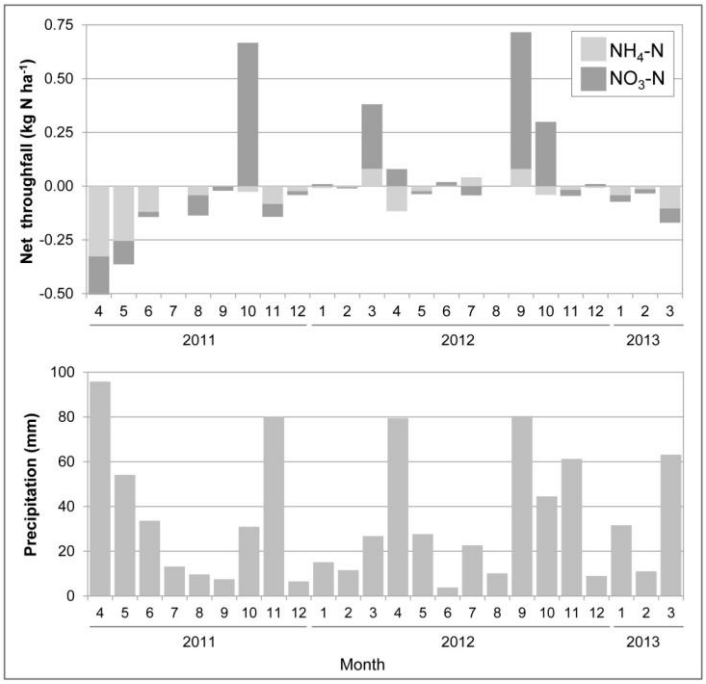


631

632 **Fig. 2.** Comparison of bulk deposition values of nitrate, ammonium and their sum (total
633 inorganic nitrogen; TIN) measured with conventional bulk water collectors (CBC) and ion-
634 exchange resin collectors (IEC). Data from all sites and sampling periods included.
635 Comparison metrics are added in the graphic: mean fractional bias (MFB), root mean square
636 error (RMSE) and Pearson correlation coefficient (r). Dashed lines represent the line 1:1
637 (perfect fit) and lines 1:1.5 and 1:0.5 (±50%). Error bars correspond to standard deviation of
638 the period mean.
639



640 **Fig. 3.** Mean annual bulk, throughfall and net throughfall (throughfall minus bulk) deposition
641 of nitrogen (N) compounds for the 2-year sampling period (2011-2013). Measurements of N
642 deposition are represented for the two methodologies: conventional bottle collector (CBC) and
643 ion-exchange resin collector (IEC). Error bars represents the standard error of the mean (n = 2
644 for CBC and IEC; n = 3 for EMEP).



645 **Fig. 4.** Net throughfall deposition of N and precipitation on a monthly basis at the Tres Cantos
646 (TC) site. *: bars not shown because of the presence of missing data for this month.

647