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Atmospheric deposition of inorganic nitrogen in Spanish forests of *Quercus ilex* measured with ion-exchange resins and conventional collectors☆

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ABSTRACT

Atmospheric nitrogen deposition is one of the main threats for biodiversity and ecosystem functioning. Measurement techniques like ion-exchange resin collectors (IECs), which are less expensive and time-consuming than conventional methods, are gaining relevance in the study of atmospheric deposition and are recommended to expand monitoring networks. In the present work, bulk and throughfall deposition of inorganic nitrogen were monitored in three different holm oak forests in Spain during two years. The results obtained with IECs were contrasted with a conventional technique using bottle collectors and with a literature review of similar studies. The performance of IECs in comparison with the conventional method was good for measuring bulk deposition of nitrate and acceptable for ammonium and total dissolved inorganic nitrogen. Mean annual bulk deposition of inorganic nitrogen ranged 3.09–5.43 kg N ha^{-1} according to IEC methodology, and 2.42–6.83 kg N ha^{-1} y^{-1} using the conventional method. Intra-annual variability of the net throughfall deposition of nitrogen measured with the conventional method revealed the existence of input pulses of nitrogen into the forest soil after dry periods, presumably originated from the washing of dry deposition accumulated in the canopy. Important methodological recommendations on the IEC method and discussed, compiled and summarized.

1. Introduction

The global alteration of the N cycle has led to an increased deposition of atmospheric nitrogen (N) which could be threatening the extraordinary biological richness of the Mediterranean Basin (García-Gómez et al., 2014; Myers et al., 2000; Rockström et al., 2009). However, limited information is available on atmospheric N deposition and possible effects on the natural ecosystems of Spain. A recent model-based assessment of N deposition threats to habitats within the Spanish Natura 2000 network showed that most of the threatened habitats are located in mountainous and alpine areas in the North (Pyrenees, Cantabrian Range) and mountain areas 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 find challenging to simulate small-scale variations in deposition regimes in these areas (Boutin et al., 2015; García-Gómez et al., 2014; Simpson et al., 2006). Thus, monitoring efforts in such areas would be useful for ecosystem conservation assessments and could be applied for validation and improvement of air quality models.

The use of automatic wet-only samplers, in which the collector is open to the atmosphere only during precipitation events, is widely recommended for monitoring atmospheric wet deposition. But the need to expand monitoring networks has impelled the use

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of less expensive methods, easy to operate, and without requiring frequent visits to the field (Clow et al., 2015; Erisman et al., 2005). The common alternative is using open samplers (bulk deposition collectors), which have no provision to exclude dry deposition during rainless periods. They basically consist on collection surfaces, typically funnels, ending in containers where the sample is stored until collected for analysis. These conventional collectors are inexpensive and can be easily replicated, but they still require frequent visits to the field. The use of ion-exchange resins (IER) in deposition collectors can dramatically reduce the number of trips to the monitored sites, as well as the number of samples and, therefore, the cost of the analysis (Fenn et al., 2009). The IER collectors are designed and used similarly to conventional collectors, except that instead of storing the collected sample, the solution is funnelled through an IER column where ions are reversibly adsorbed on the resin. The use of this technique should avoid some of the uncertainties found in deposition measurements with conventional collectors, such as increases or decreases in ammonium concentration ascribed (among others) to biological activity in the solution or adsorption on the bottle walls (Thimonier, 1998) and other changes in sample composition driven by microbiological activity (Dämmgen et al., 2005). Moreover, IER collectors allow long sampling periods (e.g., up to 12 months; Fenn and Poth, 2004), appearing as a suitable tool for monitoring atmospheric deposition in remote locations.

Collectors using IER have been employed to measure atmospheric N input to forest ecosystems since the early 2000s mainly in the USA (e.g. Fenn et al., 2002). To our knowledge, there are not published studies applying this monitoring 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 with the following objectives: (1) to test the performance of IER collectors in relation to the conventional methodology, (2) to provide recommendations for measuring in Mediterranean environments with IER collectors and (3) to study the bulk and throughfall deposition of N in these characteristic Mediterranean forests. In addition, a review of the published works using IER for collecting N deposition was performed and compared with our results.

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 (Table 1). The Can Balasc (CB) site is located in a forest within a natural protected area 4 km from Barcelona. This site is characterized by acidic soils and a Mediterranean sub-humid climate. This is the site with the highest influence of urban pollutants such as nitrogen dioxide (NO_2) due to its short distance to traffic and urban sources (Table 1). 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, with the highest atmospheric concentrations of ammonia (Table 1). The proximity of this site to a highway originates NO_2 values similar to those recorded in suburban background monitoring stations (García-Gómez et al., 2016). 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 agro-silvopastoral system) of *Q. ilex*, but the low management intensity during the last decades has allowed vegetation to grow as a moderately open forest (72% of tree cover in the monitored area). 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 Table 1.

2.2. Sampling and analytical methodologies

Atmospheric deposition of ammonium (NH_4^+) and nitrate (NO_3^-) was monitored in precipitation 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 (20 cm diameter; 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. Each tube was placed in field inside a PVC cylinder to shield it from solar radiation and prevent warming. Replicate IECs were placed in the field with the collection surface at 1.5 m height during periods of 3–5 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 collectors were deployed randomly in forest with continuous canopy cover. In the case of TC, due to the open structure of the forest, the collectors were randomly placed under dominant trees changing orientations among trees. The entire collector devices were replaced or cleaned in the field at the end of each sampling period, and visually inspected for signs of bird dropping 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 two 200 ml aliquots of 2*M* solution of KCl (i.e., two consecutive extractions). Extracts were measured for pH as an additional quality control since liquid samples can lose NH_4^+ via NH_3 volatilization as the pH increases (Vlek and Stumpe, 1978). Ammonium and nitrate concentrations in the KCl extracts were determined by automated colorimetric determination using a flow injection analyser (Perkin Elmer, Rodgau, Germany). 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 2).

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 Tables 2 and A1.

Nitrogen deposition was additionally monitored by means of conventional collectors using high-density polyethylene bottles to store the sampled solution (conventional bottle collectors; CBCs) instead of tubes containing IER (see Fig. A1 for comparison). These bottles were also solar-shielded by PVC tubes. These CBCs were deployed in the study sites paired with the IECs at a distance of 1–1.5 m from each other, applying the same replication, funnel type and height. The CBC samples were collected on a weekly-basis by replacing the collection bottle. During the longest rainless periods, the CBC funnels were rinsed with 100 ml of deionized water every two weeks before replacing the bottle, in order to collect and measure the dry deposition into the funnel. The sampling

Table 1
Characterization of the study sites.

Site code	CB	TC	CA
Altitude (m)	255	705	592
Longitude	2° 04′ 54″ E	3° 43′ 59″ O	1° 38′ 40″ O
Latitude	41° 25′ 47″ N	40° 35′ 17″ N	42° 39′ 13″ N
Mean annual temperature (°C) [a]	15.3	14.4	12.3
Mean annual rainfall (mm y^{-1}) [a]	580	386	656
Leaf area index (m^2 m^{-2})	3.3	3.1	5.3
Tree density (number of trees ha^{-1})	1429	491	1760
Distance to the nearest big city (km)	4	9	15
Distance to the nearest highway (m)	150	1500	50
Agricultural land-use cover [b]	23%	21%	62%
Livestock density (LU km^{-2})[c]	14.5	13.7	26.9
NO_2 concentration (μg m^{-3})[d]	16.2	11.1	10.6
NH_3 concentration (μg m^{-3}) [d]	1.0	0.7	2.5
HNO_3 concentration (μg m^{-3})[d]	2.7	1.5	2.3

[a] Mean values calculated for the study period.
[b] 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.
[c] From the Spanish National Statistic Institute (http://www.ine.es), using a buffer of 25 km radius around the sampling sites.
[d] Mean concentration of the main nitrogen gaseous pollutants (García-Gómez et al., 2016).

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 they are further described in Izquieta-Rojano et al. (2016).

For both measurement methodologies, a filter mesh was placed moderately tight into all the funnels to avoid, as much as possible, the accumulation of litterfall at the bottom of the funnels and a bug-sieve (NILU, Kjeller, Norway), consisting in a perforated plastic disk, was included inside the connection to the bottle. 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, comparison metrics 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 (Table 2). 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 (open-field and below-canopy plots) for both methodologies. Deposition of total dissolved inorganic nitrogen (DIN) 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, three accuracy metrics commonly used in model evaluation (Boylan and Russell, 2006; García-Gómez et al., 2014) were calculated for NO_3-N, NH_4-N and DIN deposition data obtained with both methods: the mean fractional bias (MFB; eq. (1)) the root mean square error (RMSE eq. (2)) and the Pearson correlation coefficient (r; eq. (3)).

$$MFB = \frac{1}{N}\sum \frac{IEC_i - CBC_i}{\frac{IEC_i + CBC_i}{2}} \quad (1)$$

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

$$r = \frac{\sum\left(CBC_i - \overline{CBC}\right)\left(IEC_i - \overline{IEC}\right)}{\sqrt{\sum\left(CBC_i - \overline{CBC}\right)^2 \sum\left(IEC_i - \overline{IEC}\right)^2}} \quad (3)$$

where N is the number of data pairs from the IEC and CBC methods, $\overline{CBC}$ and $\overline{IEC}$ are the mean values for the N data and the index i is over the time series, including all the monitoring sites.

Variability of deposition values among collectors (precision of the measurements) was calculated as the coefficient of variation (CV = standard deviation/mean) for every plot and period with two or more sampling data available. Correlations between environmental variables and deposition values were tested using Statistica version 12 (StatSoft, Inc. Tule, OK, USA) with the Pearson correlation coefficient, or with Spearman rank order correlation when the data were not normal. Statistical significance level was set at 0.05.

3. Results and discussion

3.1. Laboratory testing of ion-exchange resin collectors

The values of nitrate obtained in blank unexposed IECs (0.001–0.006 mg NO_3-N per gram of resin) were similar to previously reported ones (Table 2). In the case of ammonium, mean values of 0.048, 0.060 and 0.074 mg NH_4-N per gram of resin for CB, CA and TC, respectively, were obtained. This blank correction was higher than those shown in Table 2, except for one that was somewhat similar: 0.014 mg NH_4-N g^{-1} (Boutin et al., 2015). Resins made of quaternary ammonium compounds, like the one used in

Table 2
Compilation of data from different studies reporting blank values, details of bulk deposition sampling and laboratory tests of performance for ion exchange resins.

Study	Ion exchange resin	Number and type of blanks	NO_3^-				NH_4^+			
			Blank correction (mg N g^{-1})[a]	Intra-site variability (CV)	Adsorption efficiency	Recovery efficiency	Blank correction (mg N g^{-1})[a]	Intra-site variability (CV)	Adsorption efficiency	Recovery efficiency
Boutin et al., 2015	Mixed-bed IONAC® NM-60	3 in total; field blanks	Non detected	12% [b]			0.014 ± 0.006	19% [b]		
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% [b]		100%	<0.003	21% [b]		88%
Fang et al., 2011	Mixed bed 201×7[717] & 001×7[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% [c]	Approx. 100%	90–91%	≤0.001	7–89% [c]	Approx. 100%	74–96%
Simkin et al., 2004	Anion-exchange Dowex™ Monosphere 550-A	3; lab. blanks	< DL		100%	93.9 −100.4%				
Tulloss 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 per period; lab. blanks	<0.001 −0.002	2–66%			0.024–0.061	0–141%		
Present work (CA)	Mixed bed Amberlite®IRN150	2 per period; lab. blanks	<0.001 −0.006	5–67%			0.039–0.071	25–66%		
Present work (TC)	Mixed bed Amberlite®IRN150	1 per period; lab. blanks	0.001 −0.004	2–20%	100%	99%	0.054–0.103	4–27%	100%	112%

[a] Milligram of N released per gram of resin.
[b] Not CV (coefficient of variation).
[c] Collectors distributed along a larger area.

this study, can release NH_4^+ (Hansen, 2012; Langlois et al., 2003), which could explain the relatively high NH_4^+ found in the blanks. Although having such high blank values is not expected to cause accuracy problems, it could contribute to a decrease in the precision of the measurement of low deposition values. The adsorption efficiency of the IER tubes was close to 100% for both ions, the same as in most of the reviewed experiments from the literature (Table 2). The recovery efficiency for NO_3^- was comparable to that previously reported, whereas it was higher for NH_4^+. In this case, more NH_4^+ was recovered from the spiked resins than the quantity added, giving a recovery factor of 112%. Recovery factors above 100% have been previously described using the same IER (Fenn et al., 2002, Table 2). These results highlight the importance of lab tests to explore the performance of the resin used and to provide with suitable correction factors.

3.2. Comparison of methods

3.2.1. Variability of the measurements

In our study, the IEC extractions from CA exhibited a higher pH than the other sites (mean of 4.9 *vs.* 3.6 and maximum of 13.1 *vs.* 6.3, respectively). Significant negative correlations were found between the pH of the extracts and NH_4^+ concentrations within some periods at CA (data not shown) and a remarkable reduction in NH_4^+ concentration were noticed at pH values higher than 7. Because of this, ammonium values from extracts with a pH value higher than 6.5 (25% of 266 extracted samples from CA) were removed from the dataset before deposition calculations, which reduced the replication of measurements (Table 3). The precipitation in CA was much more alkaline (with a mean pH of 7.3 and a mean alkalinity of 141.1 μeq l^{-1}) than in CB or TC (with mean pH of 6.3 and 6.0; and mean alkalinity of 67.6 and 27.5 μeq l^{-1}, respectively) during the study period (Aguillaume, 2015). It may therefore occur that carbonates and bicarbonates present in the rain in this site increased the pH of the extracts provoking the loss of NH_4^+ via volatilization of NH_3 before the analysis (Cape et al., 2012; Izquieta-Rojano et al., 2016). However, such high values may also be originated partially from hydroxide anions which could be leached from the IER; and this possibility and the processes involved merit further study.

Variability among IECs for bulk deposition was lower in TC

Table 3
Bulk and throughfall deposition (kg N ha^{-1}) using ion-exchange resin collectors.

Site	Start date	End date	Season[a]	Rain (mm)	Bulk[b]		Throughfall[b]	
					NO_3^-	NH_4^+	NO_3^-	NH_4^+
CB	05/04/11	28/06/11	SPR	181.0	0.54 (2)	0.33 (2)	1.66 (8)	2.01 (8)
	05/07/11	27/09/11	SUM	120.2	0.42 (2)	0.86 (2)	1.22 (8)	0.94 (8)
	04/10/11	10/01/12	AUT	268.1	0.43 (2)	1.03 (2)	1.35 (8)	0.81 (5)
	17/01/12	18/04/12	WIN-SPR	100.0	0.39 (2)	0.01 (2)	1.40 (7)	0.85 (7)
	14/05/12	03/07/12	SPR	50.7	0.49 (2)	0.43 (2)	1.92 (8)	0.59 (8)
	11/07/12	01/10/12	SUM-AUT	112.1	0.29 (2)	0.01 (2)	1.01 (7)	0.30 (7)
	16/10/12	25/02/13	AUT-WIN	213.4	0.30 (2)	0.61 (2)	0.86 (7)	0.65 (7)
CA	25/02/11	31/05/11	SPR	118.3	0.57 (4)	0.41 (1)	1.04 (12)	0.23 (12)
	31/05/11	31/08/11	SUM	66.8	0.59 (4)	0.66 (1)	0.51 (8)	0.23 (12)
	31/08/11	13/12/11	AUT	119.3	0.35 (4)	0.26 (1)	0.80 (7)	0.33 (12)
	13/12/11	13/03/12	WIN	64.6	0.63 (3)	0.40 (2)	0.67 (7)	0.12 (12)
	13/03/12	19/06/12	SPR	267.8	1.07 (3)	2.11 (1)	1.37 (2)	0.76 (11)
	19/06/12	25/09/12	SUM	31.0	0.58 (2)	0.29 (4)	0.92 (11)	0.49 (9)
	25/09/12	06/03/13	AUT-WIN	660.4	1.41 (2)	1.54 (1)	1.29 (2)	0.49 (11)
TC	23/03/11	21/06/11	SPR	173.0	0.73 (3)	1.03 (3)	0.54 (11)	1.55 (11)
	28/06/11	27/09/11	SUM	17.5	0.16 (4)	0.16 (4)	0.80 (11)	0.28 (11)
	11/10/11	21/02/12	AUT-WIN	115.0	0.36 (4)	0.49 (4)	0.77 (11)	0.67 (11)
	06/03/12	21/06/12	WIN-SPR	127.4	0.37 (4)	0.76 (4)	0.64 (12)	0.77 (12)
	26/06/12	23/10/12	SUM-AUT	103.4	0.32 (4)	0.42 (4)	1.69 (11)	1.12 (11)
	30/10/12	25/03/13	AUT-WIN	197.7	0.38 (4)	0.57 (4)	0.25 (7)	0.66 (7)

[a] SPR: spring; SUM: summer; AUT: autumn; WIN: winter.
[b] The number of collected samples used to calculate the mean deposition value is shown in brackets.

(mean CV of 12% and 11% for NO_3-N and NH_4-N, respectively) than in the other two sites, with mean CVs of 22% and 37% for NO_3-N and 79% and 46% for NH_4-N in CB and CA, respectively (ranges shown in Table 2). These high values may be caused by the lower replication in these sites: in CB, only two IECs were installed in open field, while in CA the above-mentioned reduction in the dataset provoked a drastic reduction in the actual replication (Table 3). The variability found with IECs was similar to that found using CBCs, with the exception of NH_4-N in CB (79%), which was largely higher (29% using CBCs). It might indicate that a higher replication than two funnels is needed for monitoring N deposition with IER in Mediterranean humid and sub-humid climates. Moreover, a higher replication allows detecting and removing questionable data, as was done for the CA dataset. In the present study, the intra-plot variability of the IEC methodology for bulk deposition measurements was in a similar range to the set of previous experiments shown in Table 2, with the exception of NH_4-N in CB.

3.2.2. Comparison metrics and plots

The comparison metrics and graphics were performed only for bulk deposition values, since throughfall deposition is subjected to a higher variability not directly related to the method used, but related to canopy interactions with atmospheric N, canopy heterogeneity, and biochemical transformations provoked by litterfall or algae in the collectors (Bleeker et al., 2003; Fenn and Poth, 2004). This comparison was performed using the CBC results as the reference for assessing the IEC results, but the former methodology is likewise not without uncertainty (Bleeker et al., 2003; Dämmgen et al., 2005).

Measurements of bulk deposition of N using the IEC method showed a good agreement with the corresponding CBC values for NO_3-N, and an acceptable one for NH_4-N and DIN, based on the overall values of the calculated metrics (Fig. 1). The graphical comparison showed a very good performance of the IEC method in relation to the CBC for NO_3-N measurements, with only one period slightly out of the ±50% lines (Fig. 1). Nitrate deposition estimations with IECs compared to CBCs showed a lower error (RMSE = 0.15 kg N ha^{-1}) and a better fit to the 1:1 line than NH_4-N measurements. Measurements with IECs tended to overestimate the NH_4-N low values (which are the majority of the data) and underestimate the high NH_4-N compared to CBC values (Fig. 1). The general bias for NH_4-N deposition was low and positive (MFB = 6% for the entire dataset) and the error was about 0.56 kg N ha^{-1}. The values with the highest deviation came from two sampling periods during the second year in CA, with exceptionally low values in the IECs (2.11 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 measured with the IEC could therefore be related to a collection problem during those heavy rains. The slower flux of the rainwater through the IEC collector can cause a temporal accumulation of water 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 elevated pH like those found in CA. Indeed, hourly averaged rainfall showed a slight positive correlation with the differences between methods found for NH_4-N deposition ($r = 0.48$; $p = 0.059$), 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 the most influencing NH_4-N values on Pearson's *r*, this metric became lower (≤0.70), while better results were found for RMSE (0.29), and MFB showed and overall overestimation of NH_4-N bulk deposition (27%). Other authors have reported similar overestimations of bulk deposition of NH_4-N when using IECs compared to CBCs (Clow et al., 2015; Fenn and Poth, 2004; Hansen, 2012; Langlois et al., 2003). There are three main processes that could account for the discrepancy between methods: release of NH_4^+ from the amine groups of the IER, and nitrification or volatilization losses of NH_3 in the liquid samples of the CBCs (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). The utilization of field blanks (i.e., sealed tubes containing IER, placed in the field) is recommended to avoid the discrepancies caused by ammonium release from the IER (Fenn and Poth, 2004). In our study, we used laboratory blanks (i.e., sealed IER tubes not exposed to field condition), which may release less amount of NH_4^+ since they are not exposed to the stronger

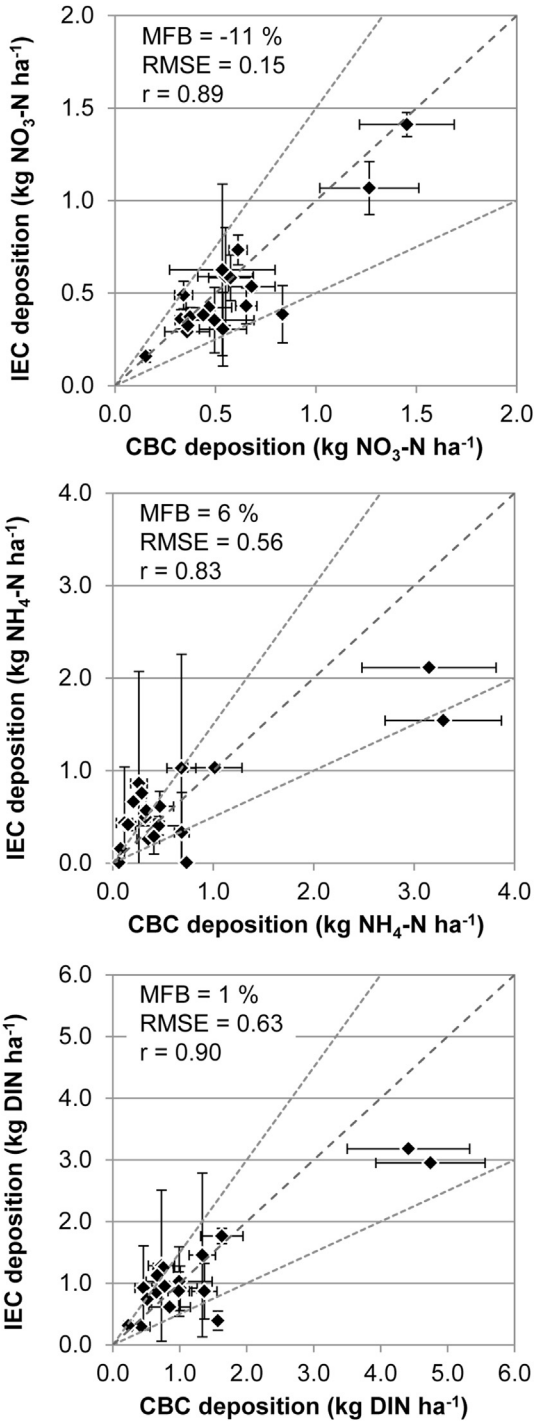

Fig. 1. Comparison of bulk deposition values of nitrate, ammonium and dissolved inorganic nitrogen (DIN) measured with conventional bottle collectors (CBC) and ion-exchange resin collectors (IEC). Data from all sites and sampling periods included. Comparison metrics are added in the graphic: mean fractional bias (MFB), root mean square error (RMSE) and Pearson correlation coefficient (r; all values are statistically significant with $p < 0.01$). Dashed lines represent the line 1:1 (perfect fit) and lines 1:1.5 and 1:0.5 (±50%). Error bars correspond to standard deviation of the sampling period mean.

temperature oscillations experienced in the field. This could account for part of the overestimation of NH_4-N deposition found in IECs when comparing to CBCs that occurred at the lowest deposition range. In any case, the field blanks will never undergo the same conditions as the operational IECs, since they remain sealed in the field without experiencing the drying and rewetting cycles. Regarding the other two processes, nitrification is not expected to occur in the open-field CBCs, since these samples are not expected to be colonized by nitrifier communities (Fenn and Poth, 2004) and the bottles are protected from solar radiation (Thimonier, 1998), 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 installed in the connection with the bottle 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).

Overall, and taking into account all these considerations, the performance of IECs for N deposition measurements in comparison with the CBC method showed an acceptable accuracy, with an error of 0.63 kg DIN ha^{-1} (Fig. 1). All these results show that IECs seem a suitable method for monitoring N atmospheric deposition in these environmental conditions with lower cost and effort than CBC methods, once precautions mentioned above are considered.

3.3. Nitrogen deposition in holm oak forests

Mean annual deposition of N for the 2-year period of the study estimated with IECs and CBCs is presented in Fig. 2. Bulk deposition of DIN ranged 2.42–6.83 and 3.09–5.43 kg N ha^{-1} among the sites according to CBC and IEC methodologies, respectively. Throughfall deposition of DIN ranged 2.33–8.20 and 4.59–8.91 kg N ha^{-1} among the sites with CBC and IEC, respectively. The highest bulk deposition of N occurred in CA and the highest throughfall deposition was recorded in CB. These two sites are located in the North of Spain where high wet deposition has been linked to the high industrialization and population in the region, higher precipitation and transboundary pollution (García-Gómez et al., 2014).

The difference between throughfall and bulk deposition (net throughfall) of N reflects the interaction between the atmosphere and the canopy, including both the wash-off of dry deposited N and the exchange with leaf surfaces. Negative values of net throughfall indicate that at least part of the wet deposited N is being effectively retained in the canopy, while positive values indicate that at least part of the dry deposited N is reaching the forest floor. Annual net throughfall values were positive for NO_3-N with the two measurement methods at all sites (Fig. 2). This result indicates a net flux of oxidized N to the forest soil coming from dry deposition, even though some canopy nitrate retention could be occurring. This input of dry deposited NO_3-N is very high at CB, the most urban-influenced site, which experiences the highest concentrations of gaseous oxidized-N compounds (García-Gómez et al., 2016) and high dry deposition of N (Aguillaume, 2015). On the other hand, net throughfall values for NH_4-N were only clearly positive in CB and negative in CA, while in TC depended on the method used and could be considered close to zero. Consequently, the forest canopy at CA seems to retain more NH_4^+ than at CB; especially considering that dry deposition of reduced N is expected to be higher than in CB, since CA is the most agriculture-influenced site with the highest NH_3 concentrations (Table 1). Canopy uptake of NH_4^+ has been described to be larger at lower nitrogen foliar content (de Vries et al., 2001), which is coincident with the stoichiometry of these sites, since CA showed the lowest leaf N content (1.44%) and CB the highest one (1.61%). The fact that the forest canopy at CB seems to retain less deposited N than the other two sites (positive and higher net throughfall of both NO_3-N and NH_4-N), agrees with the observation of a lower retention of atmospheric gaseous N (García-Gómez et al., 2016). These results indicate that the *Q. ilex* canopy in this forest cannot retain as much N as the other sites. Interestingly, other *Q. ilex* forests close to this experimental site and with

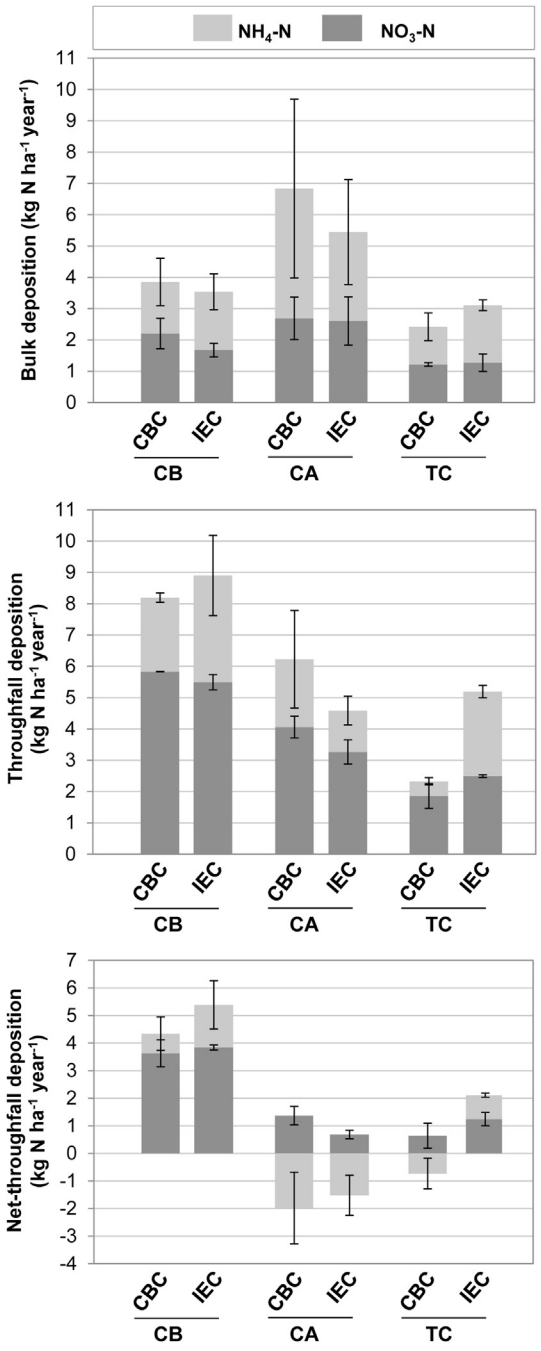

Fig. 2. Mean of annual bulk, throughfall and net throughfall deposition of inorganic N for the 2-year sampling period. Methodologies: conventional bottle collector (CBC) and ion-exchange resin collector (IEC). Error bars represents the standard error of the mean (n = 2 years).

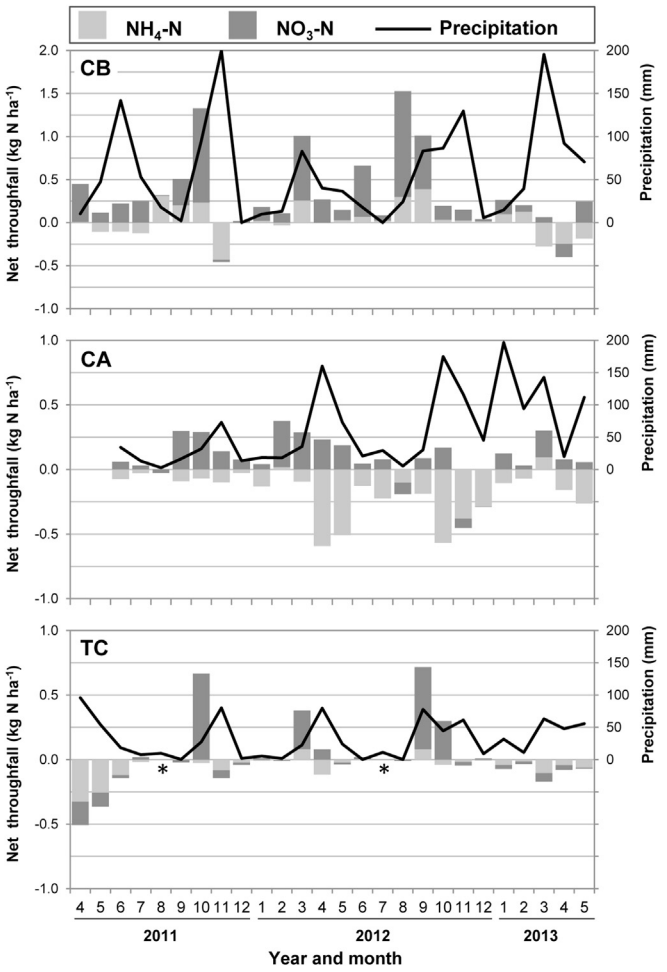

Fig. 3. Net throughfall deposition of N and collected precipitation on a monthly basis at the three study sites using CBCs. *: bars not shown because of the presence of missing data for this month.

similar deposition load have been considered at a first stage of eutrophication (Àvila and Rodà, 2012).

In Mediterranean areas, the intra-annual variability of N deposition is expected to be high because of the particularities of the Mediterranean precipitation regime, in which rainfall is not equally distributed over the year. Data from CBCs can be better used for studying intra-annual variability in detail, because deposition can be observed almost on an event basis. In this study, data were monthly aggregated in order to summarize the results (Fig. 3). Negative values for net throughfall were most commonly observed with NH_4^+ (Fig. 3), indicating that canopy retention of wet-deposited N in these forests occurred more often in the reduced form. Relatively high positive values of net throughfall can be noticed in TC during the months of September and/or October in 2011 and 2012, during the first rains after the summer droughts, and also in March 2012, after a particularly dry winter. 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. 3). These ephemeral inputs, among other effects, can trigger pulses of NO emissions from soil (Homyak and Sickman, 2014) or provoke a flushing of inorganic N to ground- or stream waters 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 relatively high concentrations of NO_3^- in the soil water (up to 28.15 and 4.90 mg NO_3-N l^{-1} at 20 and 40 cm depth, respectively, using tension lysimeters) have been found after these pulses of N during late-summer and early-autumn, but not during the early spring of 2012, when understory annual pastures were emerged and growing and soil communities were active.

3.3.1. Arising issues for measuring N deposition in open forests of holm oak

Measuring N throughfall deposition in the open forest of holm oak in TC highlighted some discrepancies between IEC and CBC methods for NH_4-N throughfall deposition estimations (Fig. 2). The IEC method estimated a value 2.25 kg NH_4-N ha^{-1} y^{-1} larger than the CBCs at this site but those differences were not observed in the other sites. This discrepancy could be partially related to the high uncertainty of the CBC method when concentrations are close to or below detection limits (Köhler et al., 2012), as it happened to 30% of the throughfall samples in TC. Also some nitrification processes in CBC samples at TC could be occurring, since some throughfall samples collected 2–3 days after summer rains showed algal growth (while it did not happened in the open-field bulk samples). The addition of a biocide in the collection bottles as a sample preservative (Cape et al., 2010) is therefore recommended under Mediterranean conditions, particularly under semi-arid regimes like at TC site. Bird dropping cannot be disregarded as a cause of the discrepancy either, since visual inspections might not be effective when enough precipitation has occurred to rinse the funnels. Further quality control including analysis of phosphates in the IEC samples could aid to detect bird dropping contamination (Fenn et al., 2015). The largest discrepancy in NH_4-N estimations at TC was found in spring of 2011, the period in which more inflorescences were collected (55.2 g m^{-2}) in the litterfall samplers. Inflorescences of *Q. ilex* are small and easily decomposable while presenting high N content (close to 1.5%; Bellot et al., 1992). Since the flowers remained longer in the IECs compared to the CBCs, more NH_4^+ could therefore be leached out from older decomposing litter, originating this greater discrepancy. It is therefore recommended to clean or change the funnels of the IECs when big amounts of debris are accumulated in them. The open structure of the canopy in TC might facilitate both, bird dropping and litterfall accumulation, which together with the high temperatures might explain the discrepancies in NH_4-N throughfall estimations observed only at this site.

3.4. Summary of methodological considerations

Some methodological recommendations on the IEC method arising from the present study have been already reported in previous works (e.g. Cape et al., 2010; Fenn et al., 2015). 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-N deposition due to the release of NH_4^+ 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-N deposition could also occur when a large amount of leachable debris is accumulated during the long sampling periods of IECs and it can be taken into consideration when planning the duration of the different sampling periods along the year. In *Q. ilex* forests it could particularly occur during the flowering period. Consequently, periodic cleaning of sampling devices is advised during those sensitive periods. On the other hand, NH_4^+ deposition could be underestimated when the flow of the rain 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), particularly with alkaline rain. A modification in the design could be studied in those areas withstanding intermittent heavy rains. Our results recommend deploying at least three replicate IECs at every bulk deposition sampling plot. 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 particular kind of forest stands. An additional quality control method for IEC by analysing phosphates in the extracts is also recommended. 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 seasonal variability of N deposition and the use of biocides is recommended in these climatic conditions, especially for throughfall measurements.

4. Conclusions

The results of the present study showed that collection methods for N deposition based on ion-exchange resins can be recommended for long-term studies in the Mediterranean region, since its performance in measuring NO_3^- deposition was good and acceptable for NH_4^+ and DIN, in comparison with conventional methods. This methodology is particularly recommended in remote areas and when the nitrogen concentration in rain is low. However, the methodological recommendations on the IEC method arising from the present study should be taken into consideration in the monitoring design.

Mean annual bulk deposition of DIN in holm oak forests in Spain ranged 2.42–6.83 and 3.09–5.43 kg N ha^{-1} according to CBC and IEC methodologies, respectively. Intra-annual variability showed significant input pulses of N into the forest soil after dry periods. These pulses are 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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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.06.027.

References

Aguillaume, L., 2015. Nitrogen Deposition at Mediterranean Holm Oak Forests: Loads and Indicators (PhD. thesis),. CREAF - Universitat Autònoma de Barcelona (UAB), Barcelona, Spain, 201 pp.

Àvila, A., Rodà, F., 2012. Changes in atmospheric deposition and streamwater chemistry over 25 years in undisturbed catchments in a Mediterranean mountain environment. Sci. Total Environ. 434, 18–27. http://dx.doi.org/10.1016/j.scitotenv.2011.11.062.

Bellot, J., Sánchez, J.R., Lledó, M.J., Martínez, P., Escarré, A., 1992. Litterfall as a measure of primary production in Mediterranean holm-oak forest. Vegetatio 99–100, 69–76. http://dx.doi.org/10.1007/BF00118211.

Bleeker, A., Draaijers, G., van der Veen, D., Erisman, J.W., Möls, H., Fonteijn, P., Geusebroek, M., 2003. Field intercomparison of throughfall measurements performed within the framework of the Pan European intensive monitoring program of EU/ICP Forest. Environ. Pollut. 125, 123–138. http://dx.doi.org/10.1016/S0269-7491(03)00142-8.

Boutin, M., Lamaze, T., Couvidat, F., Pornon, A., 2015. Subalpine Pyrenees received higher nitrogen deposition than predicted by EMEP and CHIMERE chemistry-transport models. Sci. Rep. 5, 12942. http://dx.doi.org/10.1038/srep12942.

Boylan, J.W., Russell, A.G., 2006. PM and light extinction model performance metrics, goals, and criteria for three-dimensional air quality models. Atmos. Environ. 40, 4946–4959.

Brumbaugh, W., Earhart, S., Linder, G., Neitlich, P., 2012. Determination of Annual Loads of Inorganic Atmospheric Contaminants in Northern Alaska by Measurement in Snowpack and Passive Ion Collectors. In: 33rd SETAC Conference. Long Beach.

Cape, J.N., Sheppard, L.J., Crossley, A., van Dijk, N., Tang, Y.S., 2010. Experimental field estimation of organic nitrogen formation in tree canopies. Environ. Pollut. 158, 2926–2933. http://dx.doi.org/10.1016/j.envpol.2010.06.002.

Cape, J.N., Tang, Y.S., González-Benítez, J.M., Mitošinková, M., Makkonen, U., Jocher, M., Stolk, A., 2012. Organic nitrogen in precipitation across Europe. Biogeosciences 9, 4401–4409. http://dx.doi.org/10.5194/bg-9-4401-2012.

Cerón, R., Cerón, J., Aguilar, C., Montalvo, C., Rustrian, E., Houbron, E., Ramórez, E., Muriel, M., Córdova, A., Carballo, C., García, A., Chi, H., Hernández, M., 2015. Spatial and temporal throughfall deposition patterns on two regions at the center and at the Southeast of Mexico. WSEAS Trans. Environ. Dev. 11, 57–72.

Clarke, N., Zlindra, D., Ulrich, E., Mosello, R., Derome, J., Derome, K., König, N., Lövblad, G., Draaijers, G.P.J., Hansen, K., Thimonier, A., Waldner, P., 2010. Part XIV. Sampling and analysis of deposition, 66 pp.. In: Manual on Methods and Criteria for Harmonized Sampling, Assessment, Monitoring and Analysis of the Effects of Air Pollution on Forests. UNECE, ICP Forests, Hamburg.

Clow, D.W., Roop, H.A., Nanus, L., Fenn, M.E., Sexstone, G.A., 2015. Spatial patterns of atmospheric deposition of nitrogen and sulfur using ion-exchange resin collectors in Rocky Mountain National Park, USA. Atmos. Environ. 101, 149–157. http://dx.doi.org/10.1016/j.atmosenv.2014.11.027.

De Vries, W., Reinds, G.J., van der Salm, C., Draaijers, G.P.J., Bleeker, A., Erisman, J.W., Auée, J., Gundersen, P., Kristensen, H.L., van Dobben, H., de Zwart, D., Derome, J., Voogd, J.C.H., Vel, E.M., 2001. Intensive Monitoring of Forest Ecosystems in Europe, 2001 Technical Report. EC, UN/ECE, Brussels, Geneva, 177 pp.

Dämmgen, U., Erisman, J.W., Cape, J.N., Grünhage, L., Fowler, D., 2005. Practical considerations for addressing uncertainties in monitoring bulk deposition. Environ. Pollut. 134, 535–548. http://dx.doi.org/10.1016/j.envpol.2004.08.013.

Erisman, J.W., Hensen, A., Mosquera, J., Sutton, M., Fowler, D., 2005. Deposition monitoring networks: what monitoring is required to give reasonable estimates of ammonia/ammonium? Environ. Pollut. 135, 419–431. http://dx.doi.org/10.1016/j.envpol.2004.11.015.

Fang, Y., Yoh, M., Koba, K., Zhu, W., Takebayashi, Y., Xiao, Y., Lei, C., Mo, J., Zhang, W., Lu, X., 2011. Nitrogen deposition and forest nitrogen cycling along an urban-rural transect in southern China. Glob. Chang. Biol. 17, 872–885. http://dx.doi.org/10.1111/j.1365-2486.2010.02283.x.

Fenn, M.E., Poth, M.A., Arbaugh, M.J., 2002. A throughfall collection method using mixed bed ion exchange resin columns. ScientificWorldJournal 2, 122–130. http://dx.doi.org/10.1100/tsw.2002.84.

Fenn, M.E., Poth, M.A., 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: a field test in the San Bernardino Mountains. J. Environ. Qual. 33, 2007–2014.

Fenn, M.E., Sickman, J.O., Bytnerowicz, A., Clow, D.W., Molotch, N.P., Pleim, J.E., Tonnesen, G.S., Weathers, K.C., Padgett, P.E., Campbell, D.H., 2009. Methods for measuring atmospheric nitrogen deposition inputs in arid and montane ecosystems of western North America. In: Legge, A.H. (Ed.), Developments in Environmental Science, Air Quality and Ecological Impacts: Relating Sources to Effects, vol. 9. Elsevier, Amsterdam, pp. 179–228.

Fenn, M.E., Bytnerowicz, A., Schilling, S.L., Ross, C.S., 2015. Atmospheric deposition of nitrogen, sulfur and base cations in jack pine stands in the Athabasca Oil Sands Region, Alberta, Canada. Environ. Pollut. 196, 497–510.

García-Gómez, H., Garrido, J.L., Vivanco, M.G., Lassaletta, L., Rábago, I., Àvila, A., Tsyro, S., Sánchez, G., González Ortiz, A., González-Fernández, I., Alonso, R., 2014. Nitrogen deposition in Spain: modeled patterns and threatened habitats within the Natura 2000 network. Sci. Total Environ. 485–486, 450–460. http://dx.doi.org/10.1016/j.scitotenv.2014.03.112.

García-Gómez, H., Aguillaume, L., Izquieta-Rojano, S., Valiño, F., Àvila, A., Elustondo, D., Santamaría, J.M., Alastuey, A., Calvete-Sogo, H., González-Fernández, I., Alonso, R., 2016. Atmospheric pollutants in peri-urban forests of *Quercus ilex*: evidence of pollution abatement and threats for vegetation. Environ. Sci. Pollut. R. 23, 6400–6413. http://dx.doi.org/10.1007/s11356-015-5862-z.

Hansen, J., 2012. Assessment of Atmospheric Nitrogen Deposition : Possible Effects on Alpine Ecosystems above 9000 Feet in Grand Teton National Park (PhD. thesis). Utah State University, 172 pp.

Homyak, P.M., Sickman, J.O., 2014. Influence of soil moisture on the seasonality of nitric oxide emissions from chaparral soils, Sierra Nevada, California. USA. J. Arid Environ. 103, 46–52. http://dx.doi.org/10.1016/j.jaridenv.2013.12.008.

Izquieta-Rojano, S., García-Gomez, H., Aguillaume, L., Santamaría, J.M., Tang, Y.S., Santamaría, C., Valiño, F., Lasheras, E., Alonso, R., Àvila, A., Cape, J.N., Elustondo, D., 2016. Throughfall and bulk deposition of dissolved organic nitrogen to holm oak forests in the Iberian Peninsula: flux estimation and identification of potential sources. Environ. Pollut. 210, 104–112. http://dx.doi.org/10.1016/j.envpol.2015.12.002.

Köhler, S., Jungkunst, H.F., Gutzler, C., Herrera, R., Gerold, G., 2012. Atmospheric ionic deposition in tropical sites of central Sulawesi determined by ion exchange resin collectors and bulk water collector. Water. Air. Soil Pollut. 223, 4485–4494. http://dx.doi.org/10.1007/s11270-012-1211-8.

Langlois, J.L., Johnson, D.W., Mehuys, G.R., 2003. Adsorption and recovery of dissolved organic phosphorus and nitrogen by mixed-bed ion-exchange resin. Soil Sci. Soc. Am. J. 67, 889–894.

Meixner, T., Fenn, M., 2004. Biogeochemical budgets in a Mediterranean catchment with high rates of atmospheric N deposition – importance of scale and temporal asynchrony. Biogeochemistry 70, 331–356. http://dx.doi.org/10.1007/s10533-003-4106-3.

Myers, N., Mittermeier, R.A., Mittermeier, C.G., da Fonseca, G.A., Kent, J., 2000. Biodiversity hotspots for conservation priorities. Nature 403, 853–858. http://dx.doi.org/10.1038/35002501.

Rockström, J., Steffen, W., Noone, K., Persson, Å., Chapin, F.S., Lambin, E., Lenton, T.M., Scheffer, M., Folke, C., Schellnhuber, H.J., Nykvist, B., de Wit, C.A., Hughes, T., van der Leeuw, S., Rodhe, H., Sörlin, S., Snyder, P.K., Costanza, R., Svedin, U., Falkenmark, M., Karlberg, L., Corell, R.W., Fabry, V.J., Hansen, J., Walker, B., Liverman, D., Richardson, K., Crutzen, P., Foley, J., 2009. Planetary boundaries: exploring the safe operating space for humanity. Ecol. Soc. 14, 472–475. http://dx.doi.org/10.1038/461472a.

Sheibley, R.W., Enache, M., Swarzenski, P.W., Moran, P.W., Foreman, J.R., 2014. Nitrogen deposition effects on diatom communities in lakes from three national parks in Washington state. Water. Air. Soil Pollut. 225, 1–23. http://dx.doi.org/10.1007/s11270-013-1857-x.

Simkin, S.M., Lewis, D.N., Weathers, K.C., Lovett, G., Schwarz, K., 2004. Determination of sulfate, nitrate, and chloride in throughfall using ion-exchange resins. Water. Air. Soil Pollut. 253, 343–354.

Simpson, D., Fagerli, H., Hellsten, S., Knulst, J.C., Westling, O., 2006. Comparison of modelled and monitored deposition fluxes of sulphur and nitrogen to ICP-forest sites in Europe. Biogeosciences 3, 337–355.

Thimonier, A., 1998. Measurement of atmospheric deposition under forest canopies: some recommendations for equipment and sampling design. Environ. Monit. Assess. 353–387.

Tulloss, E.M., Cadenasso, M.L., 2015. Nitrogen deposition across scales : hotspots and gradients in a California savanna landscape. Ecosphere 6, 167.

van Dam, D., Heil, G.W., Heijne, B., Bobbink, R., 1991. Throughfall below grassland canopies: a comparison of conventional and ion exchange methods. Environ. Pollut. 73, 85–99. http://dx.doi.org/10.1016/0269-7491(91)90016-P.

Vlek, P.L.G., Stumpe, J.M., 1978. Effects of solution chemistry and environmental conditions on ammonia volatilization losses from aqueous systems. Soil Sci. Soc. Am. J. 42, 416–421.

Vourlitis, G.L., Pasquini, S.C., Mustard, R., 2009. Effects of dry-season N input on the productivity and N storage of Mediterranean-type shrublands. Ecosystems 12, 473–488. http://dx.doi.org/10.1007/s10021-009-9236-6.

Wieder, R.K., Vitt, D.H., Burke-Scoll, M., Scott, K.D., House, M., Vile, M.A., 2010. Nitrogen and sulphur deposition and the growth of *Sphagnum fuscum* in bogs of the Athabasca oil sands region, Alberta. J. Limnol. 69, 161–170. http://dx.doi.org/10.3274/JL10-69-S1-16.

Yamashita, N., Sase, H., Kobayashi, R., Leong, K.-P., Hanapi, J.M., Uchiyama, S., Urban, S., Toh, Y.Y., Muhamad, M., Gidiman, J., Chappell, N.A., 2014. Atmospheric deposition versus rock weathering in the control of streamwater chemistry in a tropical rain-forest catchment in Malaysian Borneo. J. Trop. Ecol. 30, 481–492. http://dx.doi.org/10.1017/S0266467414000303.

Zhan, X., Yu, G., He, N., Jia, B., Zhou, M., Wang, C., Zhang, J., Zhao, G., Wang, S., Liu, Y., Yan, J., 2015. Inorganic nitrogen wet deposition: evidence from the north-south transect of Eastern China. Environ. Pollut. 204, 1–8. http://dx.doi.org/10.1016/j.envpol.2015.03.016.