Total nitrogen analysis in water samples collected at Auchencorth Moss station and five monitoring sites in Spain, OrganicNwetdep

Sheila Izquieta Rojano

- Introduction and motivation

Anthropogenic activities, like fertilizer application and fossil fuel burning, have doubled levels of reactive nitrogen in circulation. This massive alteration of the nitrogen cycle has resulted in changes in the atmospheric composition, with detectable consequences for the climate system, food security, energy security, human health and ecosystem services (Erisman et al. 2011).

In the 1970s two important monitoring programs, the US National Atmospheric Deposition Program (NADP) and the European Monitoring and Evaluation Program, began to work on the study of nitrogen deposition and its management to prevent environmental and human harms, but in both cases monitoring programs addressed only inorganic N (Cape et al. 2011). Since that period, many punctual surveys have been carried out taking into account organic nitrogen. These studies have highlighted the important contribution of this form of nitrogen to total N deposition, ranging from 10 to 40% depending on the study area (Neff et al. 2002; Cornell 2003). The exclusion of this fraction introduces significant uncertainty in the determination of nitrogen deposition, with implications for the critical loads approach (Cornell 2011).

Robust emission inventories of atmospheric pollutants are critical for understanding and predicting impacts, identifying key sources and mitigation opportunities. These inventories are also important in providing information to policy makers on the key polluting sources, so that informed decisions can be made in developing mitigation strategies. Significant uncertainties or omissions from such inventories may result in significant errors in the prediction of potential policy impacts and the implementation of inappropriate measures (Misselbrook et al. 2011).

- Scientific objectives

Considering the above mentioned context, the aim of the stay was to determine the amount of organic nitrogen in water samples collected at Auchencorth Moss (AMO) (wet-only rain collector), and throughfall and bulk deposition samples collected in five monitoring forest sites of Spain.

The AMO samples were taken from July to November during an intensive field campaign, and are framed on the 'Aerosols, Clouds, and Trace gases Research InfraStructure' network (ACTRIS).

The sites from Spain are three holm oak forests distributed in different regions of the Iberian Peninsula in the frame of EDEN project (Effects of nitrogen deposition in Mediterranean evergreen holm oak forests). Within this project the different inorganic forms of N are being routinely measured, but not the organic ones, which are known to constitute a significant percentage of the total N deposition.

Similarly, a beech and an oak forest are being currently monitored with the aim to estimate the nitrogen critical loads. The oak forest is part of a project focused on the characterization of the atmospheric deposition and its effect over the biodiversity. Finally, the beech site is located in the "Señorío de Bertiz" Natural Park, and constitutes the only monitoring site of the International Cooperative Programme (ICP) on Integrated Monitoring in Spain.

- Reason for choosing station

The Centre for Ecology and Hydrology from Edinburgh has been a pioneer in the determination of organic N in forest ecosystems in the UK (Cape et al. 2001), so the stay that arises can be a quantum leap for research taking place in Mediterranean countries, where such measurements are practically nonexistent.

- Method and experimental set-up

Samples from Auchencorth Moss (AMO) station (wet-only rain collector) were kept filtered in 2ml chromatography vials and immediately frozen at -20^{o}C after collection.

In Spain, in each site, four throughfall and one bulk deposition samples were taken fortnightly. They were immediately filtered and frozen after collection. Before fill the chromatography vials, 200μg of Thymol were added as biocide.

Approximately 700 samples (from AMO and Spain projects) have been analysed.

The determination of the organic nitrogen was carried out with a total-N analyzer (ANTEK 8060) at the Centre for Ecology and Hydrology in Penicuik.

The ANTEK 8060-M is a specific instrument for nitrogen analysis used to determine the total dissolved nitrogen (TDN) concentrations in aqueous samples.
There is not a direct method to quantify the dissolved organic nitrogen (DON) in aqueous samples. Thus, the quantification of this fraction (DON) involves three steps: 1) determination of the total dissolved nitrogen (TDN) concentration, 2) determination of the dissolved inorganic nitrogen (DIN) species in the sample, 3) subtraction of the DIN concentrations from the TDN concentrations.

Ammonium and nitrate standards were used to make the calibration curves and ensure that the instrument worked properly. The standards, both for ammonium and nitrate, ranged from 0 to 200 μM.
Both sets of standards should produce the same signal in the detector. In other words, the same calibration line (with the same slope) should be obtained (Figure 1). This was the main indicator to check if the instrument was working properly or not. It was generally considered that the operation conditions were optimal when the difference between the slope produced by both the ammonium and the nitrate standards was lower than 4%.

The total dissolved nitrogen (TDN) in the samples was determined using the calibration curves equations. Replacing the area obtained in the equation we got the TDN concentration in μM for each sample.

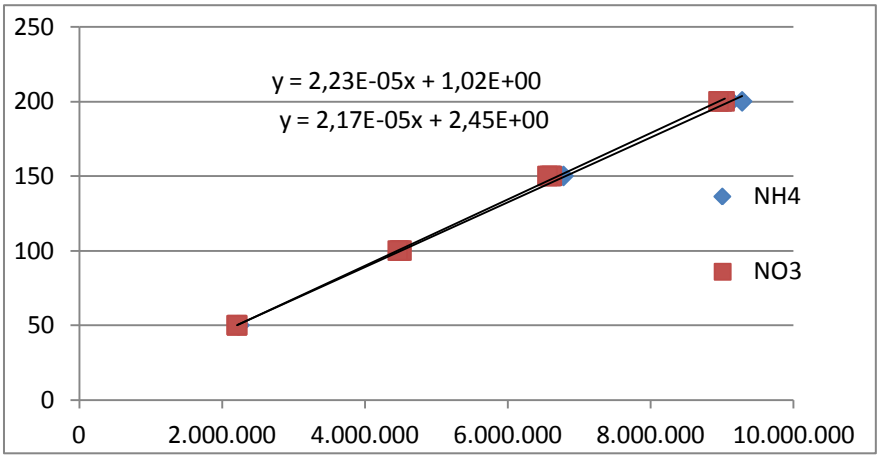


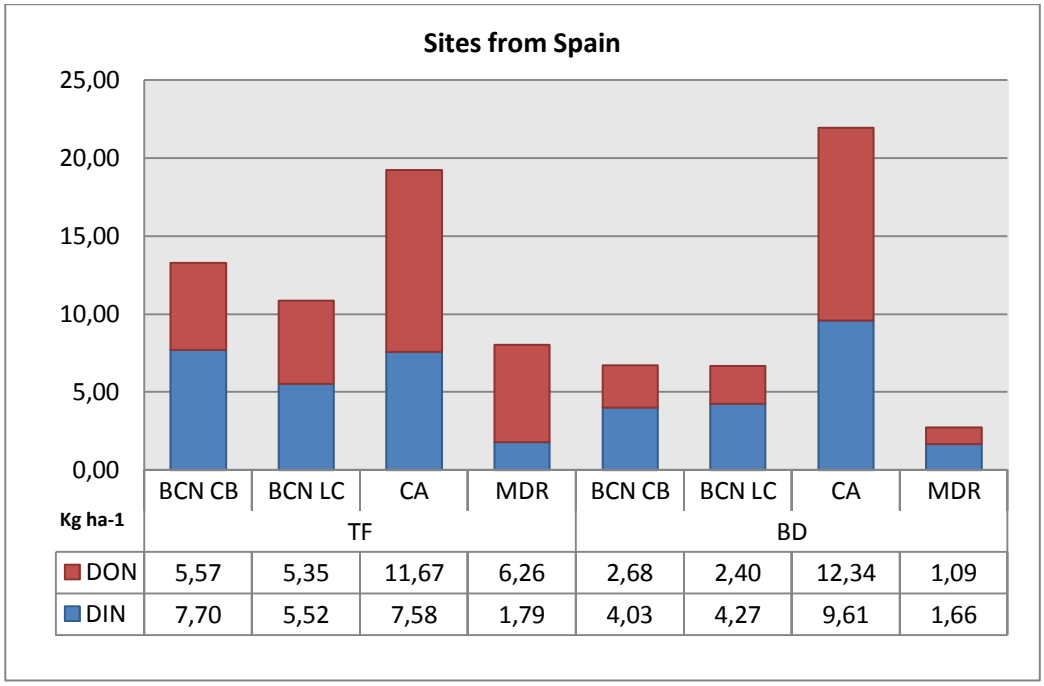
Figure 1. Calibration Curve.

- Preliminary results and conclusions

- Auchencorth Moss station results:

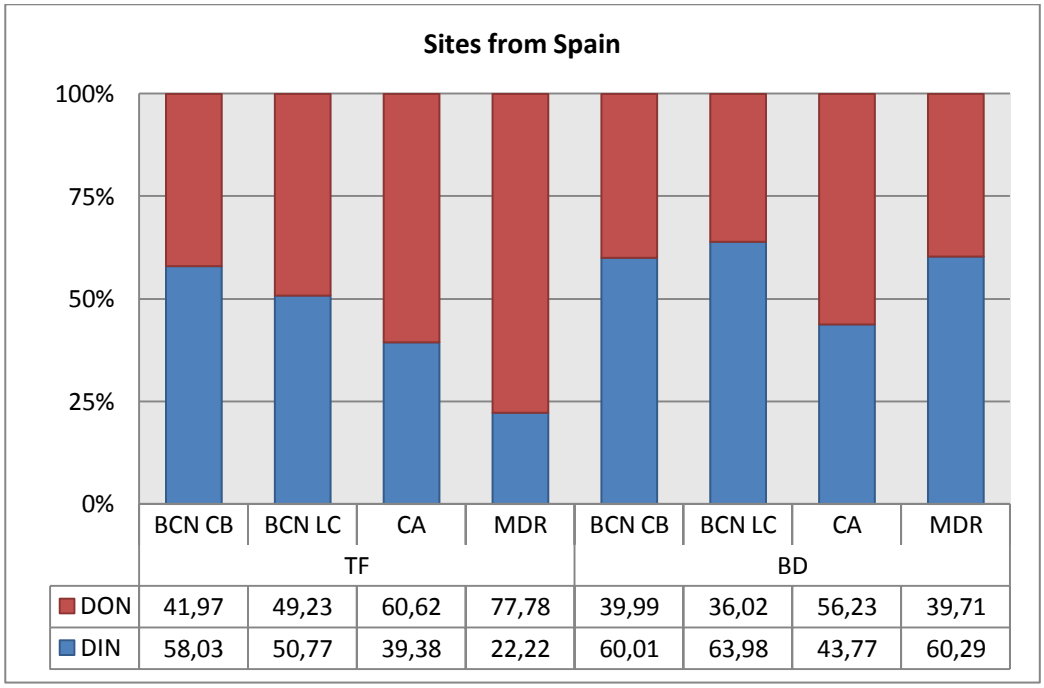
ID	Sample	Date	[TDN] mM	[TDN] ppm
1 AUCH	WOC	12/07/2014	30,5184	0,4276
2 AUCH	WOC	26/07/2014	94,3459	1,3218
3 AUCH	WOC	31/07/2014	45,7176	0,6405
4 AUCH	WOC	02/08/2014	62,0773	0,8697
5 AUCH	WOC	03/08/2014	29,1188	0,4080
7 AUCH	WOC	06/08/2014	27,2103	0,3812
8 AUCH	WOC	08/08/2014	104,7841	1,4680
9 AUCH	WOC	10/08/2014	18,0441	0,2528
10 AUCH	WOC	12/08/2014	10,9910	0,1540
11 AUCH	WOC	14/08/2014	24,4062	0,3419
12 AUCH	WOC	20/08/2014	44,0538	0,6172
13 AUCH	WOC	21/08/2014	13,4484	0,1884
14 AUCH	WOC	29/08/2014	13,1534	0,1843
15 AUCH	WOC	31/08/2014	30,5942	0,4286
16 AUCH	WOC	23/09/2014	26,6704	0,3737
17 AUCH	WOC	03/10/2014	7,6710	0,1075
18 AUCH	WOC	05/10/2014	16,8048	0,2354
19 AUCH	WOC	13/10/2014	30,9984	0,4343
20 AUCH	WOC	17/10/2014	24,9287	0,3493
21 AUCH	WOC	18/10/2014	8,7138	0,1221
22 AUCH	WOC	26/10/2014	14,2856	0,2001
23 AUCH	WOC	28/10/2014	5,3309	0,0747
24 AUCH	WOC	31/10/2014	21,4094	0,2999
25 AUCH	WOC	04/11/2014	21,3704	0,2994
26 AUCH	WOC	06/11/2014	15,5420	0,2177
27 AUCH	WOC	14/11/2014	12,6338	0,1770
28 AUCH	WOC	16/11/2014	37,5487	0,5261

- Barcelona (BCN CB and LC), Madrid (MDR) and Carrascal (CA) (Navarra) reuslts:



Kg ha-1	TF				BD			
	BCN CB	BCN LC	CA	MDR	BCN CB	BCN LC	CA	MDR
DON	5,57	5,35	11,67	6,26	2,68	2,40	12,34	1,09
DIN	7,70	5,52	7,58	1,79	4,03	4,27	9,61	1,66

Figure 2. Dissolved Organic and Inorganic Nitrogen rates in throughfall and bulk deposition for each sampling site (Kg ha^{-1}).



	TF				BD			
	BCN CB	BCN LC	CA	MDR	BCN CB	BCN LC	CA	MDR
DON	41,97	49,23	60,62	77,78	39,99	36,02	56,23	39,71
DIN	58,03	50,77	39,38	22,22	60,01	63,98	43,77	60,29

Figure 3. Dissolved Organic and Inorganic Nitrogen percentage in throughfall and bulk deposition for each sampling site.

As it can be seen in the above graphics, the DON load in the monitoring sites ranges, in throughfall, from 41.97% in Barcelona Can Balasc (BCN-CB) to 77,78% in Madrid, and in bulk deposition, from 36,02% in Barcelona La Castanya (BCN-LC) to 56,23% in Carrascal (CA), Navarra.

These data are very interesting because they suggest that the nitrogen load in throughfall in Mediterranean ecosystems could be being underestimated up to a 70%, with all the possible consequences mentioned in the first section of this report.

Results from Señorío de Bértiz station are still being processed.

- Outcome and future studies

When the data are totally processed and results are validated, conclusions will be published as scientific papers.
In light of the preliminary results here presented, we think that our study of the organic nitrogen in the Mediterranean area will be highly interesting for the scientific community.

The EDEN project is already finished, but pollution monitoring in the Señorío de Bértiz station still continue, and our purpose is continue including organic nitrogen in the target pollutants that reach this beech forest.

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