General comments:
The paper presents methods to estimate organic nitrogen concentration in precipitation and wet deposition, as well as results obtained across Europe. Since organic nitrogen represents a significant part of total nitrogen, classical approaches taking into account inorganic nitrogen only lead to biases and underestimates of deposited nitrogen. The presented results are new at the whole European scale and deserve publication in Biogeosciences. The paper is well-written and clear except a few sentences (see "Specific comments"). The following points need to be addressed before publication.

The results section is not enough detailed and figures are missing to make the reader able to evaluate the results and the discussion (see details below). Only one figure is included and it presents results on inorganic N, whereas the paper addresses organic N in the title.

Further figures have been added to address this point, and the text has been extended. Details are given below in response to specific points

Several protocols are described in the methods section and a large part of the discussion deals with these protocols. Choosing and discussing the protocols is a very important issue in such a study. Methods of sampling and analysis may lead to large uncertainties, especially when organic N is calculated as the difference of two measured variables (total N and inorganic N). Results of method comparison must be deeply presented with a more robust statistical analysis.

We agree completely with the reviewer, yet there is such a large variety of methods and protocols used in the literature that a full comparison is not possible in this paper. However, reference has been made to a recent review (Cape et al., 2011) in which these confounding factors (and others) are discussed in detail. The discussion should leave the reader in no doubt that methodological differences have greatly inhibited the utility of the published data on organic N. The text now reads:

4.2   Comparison with the literature

Comparison of precipitation chemistry data from studies with very different sampling and analytical methods is not straightforward, particularly where the analyte of interest (WSON) is determined by difference, and where contamination and sampling artefacts are handled differently in different studies (Cape et al., 2011). Nevertheless, the present study does need to be set in context. In terms of the inorganic N component, the annual average concentrations across Europe show a similar range and geographical pattern to those measured in the EMEP Network (www.emep.int), as shown in Figure 1.

The last discussion section (4.2) presents a comparison of the results obtained for organic N with several references corresponding to local or regional results. However, there is no discussion dealing with spatial patterns at the European scale according to natural and anthropogenic characteristics of the sites/regions. Such a discussion would bring a new contribution at the European scale in comparison with individual/local results.

Discussion has been added – see below under the specific item.

Specific comments:
p.8094, l.8: seasonal trends are not shown in the paper (see below, to be presented in the results section).

Please see below.

p.8094, l.9: "simple statistics": the statistical analysis must be more detailed in the results section (see below).

Please see below

p.8094, l.10: "organic N vary in precipitation across Europe": the discussion has to be extended (see "General comments" and below).

Please see below

p.8095, l.7-21: this part should be at the beginning of the methods section. This section 1 "Background" should be renamed "Introduction" and end by a clear statement of the objectives of the paper, instead of starting the description of the methods.

Changed as requested. Text added at end of Introduction:

> In this paper we present the results of measurements of total water-soluble nitrogen in rain samples from sites across Europe, which when combined with data on the inorganic components (ammonium and nitrate) allow the estimation of the water-soluble organic nitrogen content of precipitation. The data are discussed in terms of spatial and temporal variation, and in comparison with the inorganic nitrogen composition.

p.8095, l.8-9: what are the characteristics of the "Level 1" sites? The reader may be not familiar with the Nitroeurope project. Moreover, the authors mentioned "Level 3" sites (Table 1 caption) and other data sources obtained by other research groups (section 2.2). Data origin should be presented clearer. Are Level 3 groups and other groups the same?

New text added:

> At 'Level 1' sites the concentrations of nitrogen compounds in air and precipitation were measured using time-averaged methods, to provide a basic understanding of the spatial and temporal patterns of reactive N in the atmosphere over Europe, and to permit the estimation of wet and dry deposition, the latter using inferential methods (Flechard et al., 2011;Tang et al., 2009). These sites can be described as 'rural', and were chosen to provide a regionally representative estimate of air composition. At 'Level 3' sites more detailed measurements were made, usually at higher time resolution, and with the use of wet-only samplers rather than bulk samplers for measuring wet deposition (Skiba et al., 2009), but not all the 'Level 3' sites participated in this study.

p.8098, l.14-18: a scatterplot and more summary statistics (for instance RMSE, standard deviation) are needed to make the reader able to evaluate the results. R2 is not sufficient to represent the distribution of values.

New text and figures added:

> Across all sites, the deposition of WSON was not correlated with reduced, oxidised or total N deposition, but the proportion of WSON was significantly ($P<0.001$) negatively correlated with total wet N deposition (Figure 2). Orthogonal regression across all the sites gave (uncertainty in parameters is s.e. of estimate):

WSON%TN = 33(±5) – 3.2(±0.8) * wet dep N/kg ha^{-1}y^{-1}; r^2 = 0.51

The inverse relationship with wet deposited nitrate (Figure 3) was:

WSON%TN = 36(±4) – 9.2(±1.5) * wet dep NO$_3$-N/kg ha^{-1}y^{-1}; r^2 = 0.71

and was much stronger than for ammonium (data not shown):

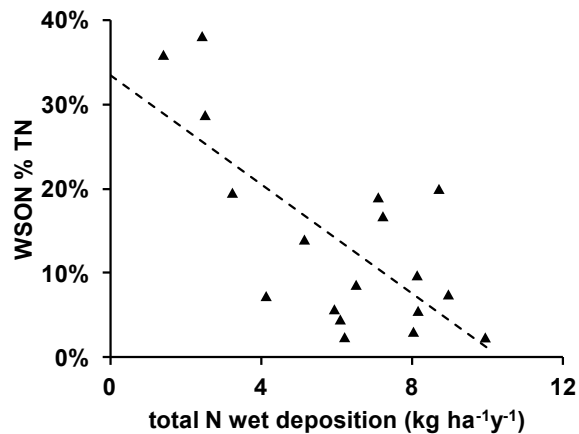WSON%TN = 25(±4) – 3.7(1.2) * wet dep NH$_4$-N/kg ha^{-1}y^{-1}; r^2 = 0.38.

Figure 2. Relationship between the proportion of Total N represented by WSON, and the wet deposition of total N at each site, showing the strong inverse relationship.
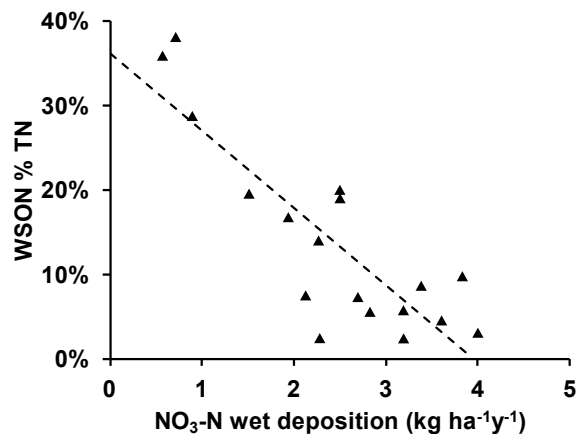

Figure 3. As for Figure 2, but showing WSON as % of Total N in terms of wet deposition of NO$_3$-N at each site.

p.8098, l.20-25: section 3.2 must be extended by presented seasonal patterns graphically, in particular N concentrations. "Significant (P<0.05) seasonal patterns. . ." needs more explanation.

3.2 Seasonal patterns

Seasonality in each data series was measured by fitting a sine curve through the monthly data using non-linear regression in SigmaPlot,v10 (Systat Software Inc.). Significant seasonal patterns in concentration of ammonium and nitrate were observed at approximately half of the sites (Table 3), with a spring maximum between February and May (e.g. Figure 4). At some sites there was a seasonal pattern in deposition, slightly later in the year (data not shown), but at no site was there a statistically significant seasonal pattern in either the concentration or deposition of WSON. Although this is a crude measure of seasonality, it is the simplest indicator for such a short dataset, and does show the lack of seasonal patterns in all components at the more southerly sites compared with central Europe; the two Finnish sites had no data from the winter period.

Table 3: Seasonal variations in ammonium and nitrate concentrations (mg N l^{-1}) from non-linear fitting of a sine function to monthly data, where C(m) = C$_0$ + A.sin(π/6.(m-m$_0$+3)), and C$_0$, A and m$_0$ are fitted parameters for the annual mean, seasonal amplitude and month of maximum amplitude, respectively. Data are shown only for sites where the probability of A>0 exceeds 95%. Standard errors of fitted parameters are shown in parentheses.

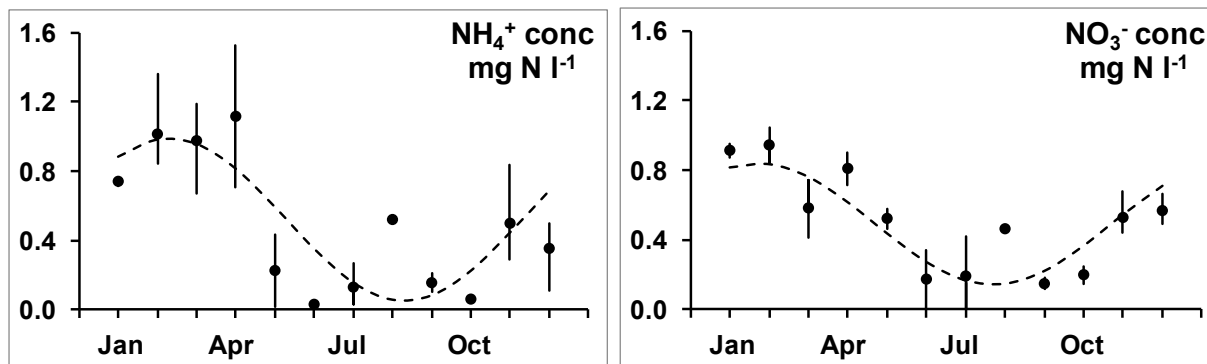| site	NH_4^+ C_0		NH_4^+ A		max m_0		NO_3^- C_0		NO_3^- A		max m_0	
Pallas												
Virolahti												
Polwet	0.56	(0.09)	0.51	(0.10)	2.1	(1.1)	0.52	(0.07)	0.37	(0.07)	1.7	(1.3)
Hainich	0.38	(0.07)	0.27	(0.09)	3	(1.6)	0.51	(0.05)	0.17	(0.07)	3	(2.1)
Grillenburg	0.52	(0.07)	0.47	(0.09)	2.3	(1.0)	0.49	(0.05)	0.35	(0.05)	1.7	(1.0)
Wetzstein	0.54	(0.07)	0.23	(0.07)	2.8	(2.4)						
Vielsalm	0.26	(0.06)	0.18	(0.08)	3	(1.9)						
Oensingen	0.53	(0.10)	0.19	(0.09)	5.6	(2.7)	0.26	(0.05)	0.14	(0.05)	5.1	(1.7)
Lägeren							0.31	(0.04)	0.23	(0.05)	2.4	(1.0)
Fontainebleau												
Puéchabon												
Le Bray												
San Rossore												
Roccarespampani												
Rotterdam	0.89	(0.09)	0.62	(0.12)	4.6	(0.6)	0.47	(0.04)	0.25	(0.05)	4.5	(0.7)
Speulderveld	0.96	(0.06)	0.45	(0.07)	4.6	(0.6)	0.47	(0.02)	0.19	(0.03)	4.3	(0.6)
Vredepeel	1.28	(0.08)	0.45	(0.11)	4.4	(0.8)						
Wieringerwerf	0.81	(0.07)	0.49	(0.09)	4.8	(0.6)	0.47	(0.03)	0.18	(0.04)	4.3	(0.7)

Figure 4. Seasonal variation in concentrations of inorganic ions at Grillenburg. Points show monthly mean data, and bars show ranges. The parameters of the fitted sine function are shown in Table 3.

p.8099, l.1-10: see previous comment, section 3.3 must also be extended.

New text and table added:

3.3 Correlations in space and time

Despite the lack of correlation across sites for annual-average data (Section 3.1), WSON concentrations and / or deposition were correlated in time with inorganic N at some individual sites. Given the strong inverse dependence of concentrations on precipitation amounts (small amounts tend to have high concentrations), within-site correlations were analysed using deposition data (mg N m^{-2} month^{-1}) rather than concentration data, and Spearman's rank correlation coefficient to test for significant correlations over time within a site. There were no statistically significant correlations at most sites, but WSON deposition was significantly negatively correlated with both NH_4^+ and NO_3^- at San Rossore and at Vielsalm, and significantly positively correlated with NH_4^+ (only) at Lägeren, and with both NH_4^+ and NO_3^- at Pallas (Table 4). No clear spatial pattern in correlations emerged over Europe.

Table 4. Correlations of WSON deposition with NH_4^+ and NO_3^- deposition over time within individual sites, as Spearman rank correlation coefficient (ρ) with associated significance probability (GenStat13, VSN International Ltd). Only significant (p<0.05) correlations are shown.

site	WSON vs. NH_4^+	WSON vs. NO_3^-
San Rossore	-0.52 (0.004)	-0.44 (0.011)
Vielsalm	-0.68 (0.006)	-0.66 (0.007)
Lägeren	+0.51 (0.002)	
Pallas	+0.69 (<0.001)	+0.73 (<0.001)

p.8099, l.16-17: the sentence "small, apparently negative. . .to avoid bias" is not clear, not enough explicit. Be clearer, develop.

New text added:

Typical uncertainties in calculating individual WSON concentrations are 0.08 mg N L^{-1}, and small, apparently negative, concentrations have been included in the above calculations to avoid the bias caused by ignoring (or treating as zero) the small negative values which arise as a result of uncertainties in the total N and inorganic N concentrations (Cornell and Jickells, 1999).

p.8100, l.1-2: slope and intercept are not sufficient to judge the regression (see previous comments).

Text amended:

A second check was direct comparison of total N (measured by RIVM using persulphate oxidation) for samples from the Dutch sites with total N (measured by CEH using high-temperature combustion and chemiluminescence) on the same samples. Orthogonal regression of data from these two independent analyses shows a small negative bias of the persulphate data compared with chemiluminescence, with slope (RIVM:CEH) = 0.95 (±0.03 s.e.) and intercept (RIVM-CEH) = -0.12 (±0.04 s.e.) mg N L^{-1}, consistent with the observation that chemiluminescence is slightly more effective (at least for rain samples) in measuring total N than persulphate digestion (Cape et al., 2001).

p.8100, l.13-14: to which result refers this sentence?

Text amended:

Although weak, there was a correlation between the WSON deficit and NH_4^+ concentration, i.e. samples with higher initial NH_4^+ concentrations were more likely to show a lower total N concentration than the sum of NH_4^+ and NO_3^- (negative WSON), implying loss of NH_3 from the vial.

p.8101, l.12-13: the sentence "By contrast. . ." should refer to a figure. The reader cannot evaluate ranges and geographical patterns of WSON concentrations. It should be useful for a paper entitled organic N across Europe.

Text amended and figure 5 added:

4.2   Comparison with the literature

Comparison of precipitation chemistry data from studies with very different sampling and analytical methods is not straightforward, particularly where the analyte of interest (WSON) is determined by difference, and where contamination and sampling artefacts are handled differently in different studies (Cape et al., 2011). Nevertheless, the present study does need to be set in context. In terms of the inorganic N component, the annual average concentrations across Europe show a similar range and geographical pattern to those measured in the EMEP Network (www.emep.int), as shown in Figure 1. The largest concentrations are seen in central and western Europe, with smaller values to the north and south. By contrast, concentrations of WSON show a smaller range and a less clear

geographical pattern (Table 2a). The concentration of WSON as a proportion of total N in this study ranges from a few % up to almost 40%. This range is similar to that observed in the UK, between 20 and 50% (Cape et al., 2004;González Benítez et al., 2009;Vanguelova et al., 2010). Other recent European studies have shown up to 15% at the Belgian coast (Bencs et al., 2009) and 30% in Flanders, Belgium (Sleutel et al., 2009), 23% in the Czech Republic (Kopacek et al., 1997), 38% in Poland (Kram, 2008), between 17% and 23% in the eastern Mediterranean (Mace et al., 2003;Violaki et al., 2010), 8% in Germany (Michalzik and Matzner, 1999) and between 14% and 41% in Finland (Mustajarvi et al., 2008;Piirainen et al., 1998). The available data are shown in Figure 5, which suggests that the contribution of WSON to total N in precipitation is greatest to the north and west of Europe, and least in central Europe. However, because the studies cited have all used different methods of sampling and analysis, over different integrating periods and times, such direct comparisons are indicative at best, and may be misleading. For reviews of global and historical datasets see (Cornell, 2011;Cornell et al., 2003;Neff et al., 2002).
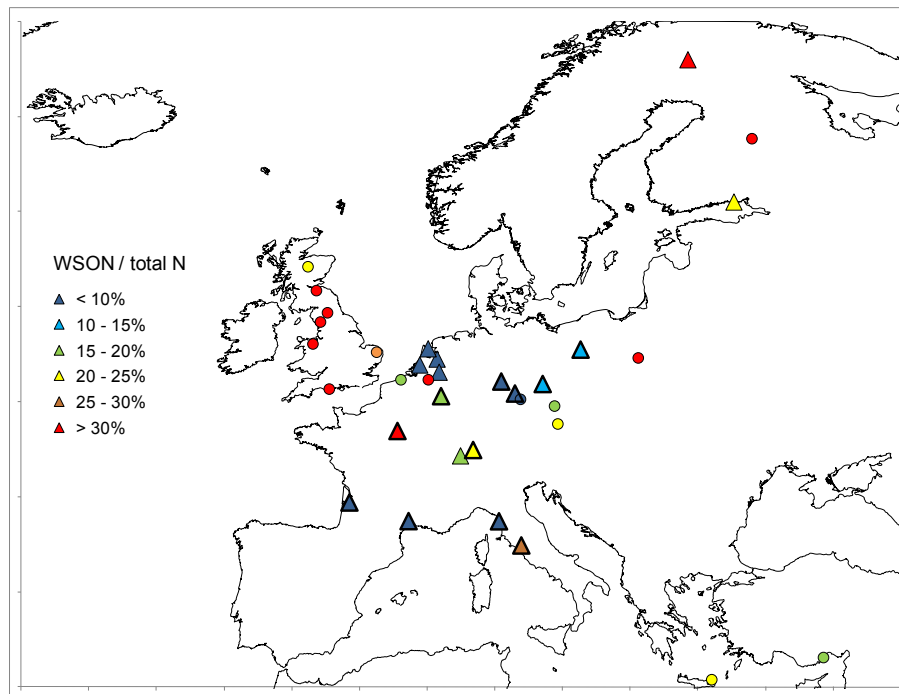

.

Figure 5. WSON as % of total wet-deposited N across Europe, showing results from this study (triangles) and literature data (circles; see text for citations). 'Level 1' sites from this study are shown with bold symbols.

p.8101, l.15-23: a deeper discussion towards geographical patterns across Europe is expected (see general comments). The comparison with local results is interesting, but a general discussion on geographical patterns in relation with site characteristics would be a worthwhile contribution.

See revised text above.

p.8102, l.11: add total in deposition of "total" nitrogen.

Done

p.8102, l.17: give some insights on how to revise critical loads.

Text amended:

> In terms of demonstrable effects of deposited N, empirical Critical Loads for different ecosystems have been defined on the basis of the measured or estimated deposition of inorganic N alone (UNECE, 2010). If ecosystems respond similarly to deposition of organic N, then the additional deposition should be taken into account, particularly for sensitive ecosystems where deposition is close to the Critical Load based on inorganic N alone. Although it could be argued that organic N deposition is implicitly included in such estimates, where Critical Loads have been established based on the measured responses to inorganic N deposition in the field, the lack of a clear relationship across Europe between inorganic and organic N deposition means that some ecosystems may be subject to considerably greater total N deposition than that estimated from inorganic N deposition alone, while in other areas the additional deposition of organic N may be negligible. However, this study has shown that the relative importance of organic N is greatest where total N deposition is smallest, i.e. precisely in those areas where sensitive ecosystems are facing pressure from anthropogenic N deposition. Inclusion of organic N in the estimation of empirical Critical Loads would require measurement (ideally) or estimation of the additional wet (and dry) deposition of organic N. Although the need for such measurements is clear, the present study implies that estimating such deposition will be very difficult because of the lack of consistent spatial patterns in WSON, either in absolute amounts or as a fraction of total N.

p.8102, l.19-23: both sentences are not clear and should be reformulated.

See above

p.8109, Fig.1: identify the different sources of data (Level 1, Level 3, other EU sites) since the presented results correspond to different methods of sampling and analysis. Replace mg N.L-1 by mg N l-1.

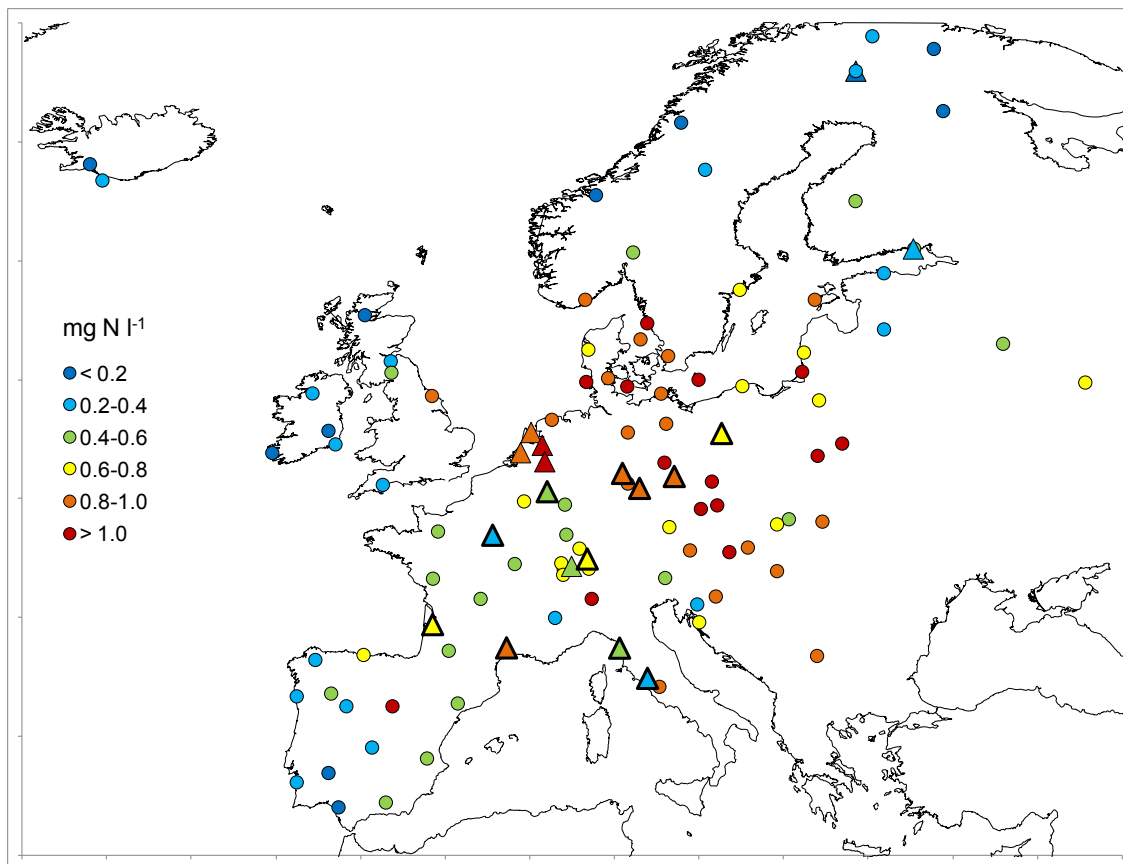*Level 1 sites now indicated on Figures 1 and 5 with bold outline.*

Figure 1: Annual rainfall-weighted average concentrations (mg N l^{-1}) of inorganic N (NH_4^+ and NO_3^-) in precipitation across Europe. The circles show colour-coded concentrations from the EMEP monitoring sites for 2009 (http://ebas.nilu.no/), and the triangles show the data from this study for comparison (see Table 1 for details). 'Level 1' sites are shown with bold outline.

Figure 1 revised to show 'Level 1' sites with bold outline

References cited in reply:

Bencs, L., Krata, A., Horemans, B., Buczynska, A. J., Dirtu, A. C., Godoi, A. F. L., Godoi, R. H. M., Potgieter-Vermaak, S., and Van Grieken, R.: Atmospheric nitrogen fluxes at the Belgian coast: 2004-2006, Atmospheric Environment, 43, 3786-3798, 10.1016/j.atmosenv.2009.04.002, 2009.

Cape, J. N., Kirika, A., Rowland, A. P., Wilson, D. R., Jickells, T. D., and Cornell, S.: Organic nitrogen in precipitation: real problem or sampling artefact?, The Scientific World, 1, 230-237, 2001.

Cape, J. N., Anderson, M., Rowland, A. P., and Wilson, D.: Organic nitrogen in precipitation across the United Kingdom, Water, Air, & Soil Pollution: Focus, 4, 25-35, 2004.

Cape, J. N., Cornell, S., Jickells, T., and Nemitz, E.: Organic nitrogen in the atmosphere - where does it come from?, Atmospheric Research, 102, 30-48, 2011.

Cornell, S. E., and Jickells, T. D.: Water-soluble organic nitrogen in atmospheric aerosol: a comparison of UV and persulfate oxidation methods, Atmospheric Environment, 33, 833-840, 1999.

Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P., and Duce, R. A.: Organic nitrogen deposition on land and coastal environments: a review of methods and data, Atmospheric Environment, 37, 2173-2191, 2003.

Cornell, S. E.: Atmospheric nitrogen deposition: Revisiting the question of the importance of the organic component, Environmental Pollution, 159, 2214-2222, 2011.

Flechard, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A. T., Bleeker, A., Erisman, J. W., Simpson, D., Zhang, L., Tang, Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, Atmospheric Chemistry & Physics, 11, 2703-2728, 10.5194/acp-11-2703-2011, 2011.

González Benítez, J. M., Cape, J. N., Heal, M. R., van Dijk, N., and Díez, A. V.: Atmospheric nitrogen deposition in south-east Scotland: Quantification of the organic nitrogen fraction in wet, dry and bulk deposition, Atmospheric Environment, 43, 4087-4094, 2009.

Kopacek, J., Prochazkova, L., Hejzlar, J., and Blazka, P.: Trends and seasonal patterns of bulk deposition of nutrients in the Czech Republic, Atmospheric Environment, 31, 797-808, 1997.

Kram, K. J.: Nitrogen deposition and flux through birch stands (Betula pendula Ens Ehrh.) in the Kampinos National Park (central Poland), Pol. J. Ecol., 56, 605-612, 2008.

Mace, K. A., Kubilay, N., and Duce, R. A.: Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: An association with atmospheric dust, Journal of Geophysical Research-Atmospheres, 108, art. no.-4320, 2003.

Michalzik, B., and Matzner, E.: Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem, European Journal of Soil Science, 50, 579-590, 1999.

Mustajarvi, K., Merila, P., Derome, J., Lindroos, A. J., Helmisaari, H. S., Nojd, P., and Ukonmaanaho, L.: Fluxes of dissolved organic and inorganic nitrogen in relation to stand characteristics and latitude in Scots pine and Norway spruce stands in Finland, Boreal Environment Research, 13, 3-21, 2008.

Neff, J. C., Holland, E. A., Dentener, F. J., McDowell, W. H., and Russell, K. M.: The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?, Biogeochemistry, 57, 99-136, 2002.

Piirainen, S., Fin,r, L., and Starr, M.: Canopy and soil retention of nitrogen deposition in a mixed boreal forest in eastern Finland, Water, Air and Soil Pollution, 105, 165-174, 1998.

Skiba, U., Drewer, J., Tang, Y. S., van Dijk, N., Helfter, C., Nemitz, E., Famulari, D., Cape, J. N., Jones, S. K., Twigg, M., Pihlatie, M., Vesala, T., Larsen, K. S., Carter, M. S., Ambus, P., Ibrom, A., Beier, C., Hensen, A., Frumau, A., Erisman, J. W., Brüggemann, N., Gasche, R., Butterbach-Bahl, K., Neftel, A., Spirig, C., Horvath, L., Freibauer, A., Cellier, P., Laville, P., Loubet, B., Magliulo, E., Bertolini, T., Seufert, G., Andersson, M., Manca, G., Laurila, T., Aurela, M., Lohila, A., Zechmeister-Boltenstern, S., Kitzler, B., Schaufler, G., Siemens, J., Kindler, R., Flechard, C., and Sutton, M. A.: Biosphere-atmosphere exchange of reactive nitrogen and greenhouse gases at the NitroEurope core flux measurement sites: Measurement strategy and first data sets, Agriculture, Ecosystems & Environment, 133, 139-149, 2009.

Sleutel, S., Vandenbruwane, J., De Schrijver, A., Wuyts, K., Moeskops, B., Verheyen, K., and De Neve, S.: Patterns of dissolved organic carbon and nitrogen fluxes in deciduous and coniferous forests under historic high nitrogen deposition, Biogeosciences, 6, 2743-2758, 2009.

Tang, Y. S., Simmons, I., van Dijk, N., Di Marco, C., Nemitz, E., Dämmgen, U., Gilke, K., Djuricic, V., Vidic, S., Gliha, Z., Borovecki, D., Mitosinkova, M., Hanssen, J. E., Uggerud, T. H., Sanz, M. J., Sanz, P., Chorda, J. V., Flechard, C. R., Fauvel, Y., Ferm, M., Perrino, C., and Sutton, M. A.: European scale application of atmospheric reactive nitrogen measurements in a low-cost approach to infer dry deposition fluxes, Agriculture, Ecosystems & Environment, 133, 183-195, 2009.

UNECE: Empirical critical loads and dose-response relationships, UNECE Working Group on Effects. ECE/EB.AIR/WG.1/2010/14, 8, 2010.

Vanguelova, E. I., Benham, S., Pitman, R., Moffat, A. J., Broadmeadow, M., Nisbet, T., Durrant, D., Barsoum, N., Wilkinson, M., Bochereau, F., Hutchings, T., Broadmeadow, S., Crow, P., Taylor, P., and

Houston, T. D.: Chemical fluxes in time through forest ecosystems in the UK - Soil response to pollution recovery, Environmental Pollution, 158, 1857-1869, 10.1016/j.envpol.2009.10.044, 2010.

Violaki, K., Zarbas, P., and Mihalopoulos, N.: Long-term measurements of dissolved organic nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean: Fluxes, origin and biogeochemical implications, Mar. Chem., 120, 179-186, 10.1016/j.marchem.2009.08.004, 2010.