Biogeosciences Discuss., 9, 8093–8109, 2012
www.biogeosciences-discuss.net/9/8093/2012/
doi:10.5194/bgd-9-8093-2012

Biogeosciences Discussions

Organic nitrogen in precipitation across Europe

J. N. Cape[1], Y. S. Tang[1], J. González-Benítez[1,2], M. Mitošinková[3], U. Makkonen[4], M. Jocher[5], and A. Stolk[6]

[1]Centre for Ecology & Hydrology, Edinburgh, EH26 0QB, UK
[2]School of Chemistry, University of Edinburgh, EH9 3JJ, UK
[3]Slovak Hydrometeorological Institute, 833 15 Bratislava, Slovak Republic
[4]Finnish Meteorological Institute, 00560 Helsinki, Finland
[5]Agroscope Reckenholz-Tänikon ART, 8046 Zürich, Switzerland
[6]RIVM, 3720 BA Bilthoven, The Netherlands

Received: 8 June 2012 – Accepted: 12 June 2012 – Published: 5 July 2012

Correspondence to: J. N. Cape (jnc@ceh.ac.uk)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Measurements of total nitrogen and inorganic nitrogen in precipitation samples from NitroEurope sites across Europe permit the calculation of organic nitrogen concentrations and wet deposition, by difference. The contribution of organic N to total N in precipitation ranged from only a few % to around 40 % across sites from Northern Finland to Italy, similar to results from previous individual studies. This paper presents the absolute and relative contributions of organic N to wet N deposition across Europe, and examines seasonal trends. There were only weak correlations with other solutes in precipitation. These simple statistics indicate that sources of organic N in precipitation vary across Europe, and that no single source is responsible. The organic N contributes to total N deposition, yet this input is rarely quantified in nitrogen budgets.

1 Background

The effects of nitrogen (N) deposition on ecosystems is often expressed in terms of the wet deposition of inorganic nitrogen, as ammonium (NH_4^+) and nitrate (NO_3^-) ions in precipitation. Sometimes, the additional dry deposition of nitrogen-containing gases and particles is included in the deposition estimate, but rarely is the contribution of organic nitrogen (ON) included. This is partly because of the difficulty in characterising the various individual components of ON, even the water-soluble organic nitrogen (WSON) in precipitation. However, the significant contribution of WSON to wet N deposition is now beyond doubt, given the many measurements from around the world (Cornell, 2011; Cornell et al., 2003; Neff et al., 2002). Although WSON is usually estimated from the difference between the total N content of precipitation and the inorganic N, a process which can lead to large uncertainties, some data are also available on the role of individual compounds or groups of compounds, such as urea, amines or amino-acids, but these generally only contribute a small proportion of the WSON. Some WSON is associated with large macromolecules, or humic-like substances (Kieber et al., 2005). The

BGD
9, 8093–8109, 2012

lack of data on the chemical form of WSON has greatly hampered attempts at identifying sources, and therefore the possibility of controls on emissions, many of which are likely to be of biological origin (Cape et al., 2011). Nevertheless, the observation that, on average, WSON contributes around 30 % of total wet-deposited N (Cornell, 2011) means that its role should not be ignored when attempting to quantify the deposition of N.

This study was part of the EU Framework Programme 6 Integrated Project "NitroEurope" (www.nitroeurope.eu). Wet deposition of N was measured at a network of "Level 1" sites across Europe, and originally only the inorganic ions (NH_4^+ and NO_3^-) were measured. Inclusion of a measurement of total N concentration in precipitation samples, combined with the measured inorganic ion concentrations, permitted an estimate to be made of the WSON, and its contribution to the total wet deposition of N at the "Level 1" sites. Moreover, several other research groups who were part of NitroEurope, but not involved in "Level 1" activities, agreed to participate, bringing the total number of sites up to over 20. Several of these sites proved to have consistent problems with loss of samples from contamination, and have not been used here, but 18 sites (Table 1) provided sufficient valid samples for analysis. The opportunistic nature of this approach, relying on a single central laboratory for total N analysis, led to some additional uncertainties in the final data, as explained below. However, without these measurements, the quantification of wet N deposition across Europe would have been systematically under-estimated.

2 Methods

2.1 Main network

As part of the NitroEurope IP wet deposition was measured at the primary network sites (Level 1) across Europe (Flechard et al., 2011). The network comprised bulk Rotenkamp samplers (Dämmgen et al., 2005); each unit consisted of two samplers

BGD
9, 8093–8109, 2012

(to provide replicate samples) mounted 1.5 m above ground, or in the case of forest sites, above the canopy. Samples were taken monthly, and sent to a central laboratory for analysis (Slovak Hydrometeorological Institute, Bratislava, Slovak Republic). Samples were protected during and after sampling by the addition of the biocide thymol (2-isopropyl-5-methylphenol). Major inorganic ion composition was measured using ion chromatography (IC) (Dionex 3000, with column CS12A for cations: NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} and AS4A-SC for anions: SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}. In addition pH and conductivity were measured. At the time of ion analysis, two 2 ml filtered (0.45 µm) subsamples were taken into vials prepared with additional thymol (200 µg) and shipped to the laboratory at CEH, where they were analysed for total N using high-temperature chemiluminescence in flow injection mode (ANTEK 8060M). Triplicate 20 µl injections were made into a flow of 10 % methanol in water, and multi-point calibrations were made using both $(NH_4)_2SO_4$ and $NaNO_3$ to ensure correct operation of the detector (both salts should give identical responses). The method provides linear equimolar response to all but a few N-containing compounds, both inorganic and organic, the exceptions being molecules containing a $-C{\equiv}N$ bond or some heterocyclic compounds. The detection limit for total N was 1 µM. Reproducibility of triplicate analyses was better than 1 %.

Inorganic ion concentrations determined by IC were then subtracted from the total N concentrations to obtain the "organic N" concentrations, referred to as "water soluble organic N" (WSON). This process inevitably leads to increased uncertainties, and occasional (small) negative values which are retained in the statistical analysis. Contaminated samples, as evidenced by high potassium and/or phosphate concentrations (from bird excreta), and samples where the calculated WSON concentration was large and negative (i.e. calculated negative WSON was more than 20 % of the measured total N, see discussion below for possible reasons for this) were excluded from the analysis.

For quality control, analytical standards (CRM – certified reference material) from the Slovak lab were sent to CEH for analysis as samples; agreement was within the

BGD
9, 8093–8109, 2012

combined uncertainties of the two laboratories. The Slovak laboratory also participates once annually in the EMEP "round robin" for rain water samples on major inorganic anions and cations, pH, conductivity and heavy metals, and twice annually in the GAW WMO Laboratory Intercomparison Study (LIS) for rain water samples on major inorganic anions and cations, pH and conductivity as an accredited EMEP laboratory.

A list of the sites from the main NitroEurope network is given in Table 1. Only sites with at least one year's valid data have been used. At some sites contamination was too frequent to permit construction of a valid data set.

2.2 Other data sources

Other research groups in the NitroEurope IP have been making their own measurements of rainfall composition as part of ongoing projects. Although several different methods have been employed, a similar "opportunistic" approach was taken to estimate WSON. Empty sample vials, treated with thymol, were sent from CEH to each of the participating laboratories, and subsamples taken at the time of inorganic analysis, then sent back to CEH for analysis of total N. The inorganic N measurement data from these laboratories were then used to calculate WSON from the measured total N for each sample.

3 Results

3.1 Concentrations and deposition

The average data for all sites are shown in Table 2, together with the period over which they provided samples for WSON analysis, and the % data capture expressed in terms of the proportion of rainfall sampled (i.e. excluding periods when samples were contaminated, or data were missing). Average concentration data are expressed as the precipitation-weighted mean over the period; annual deposition data show the product of the precipitation-weighted mean concentration and the calculated annual

BGD
9, 8093–8109, 2012

precipitation (total sample volume/sampling period in years). The precipitation volume of excluded samples was included in calculating annual precipitation.

Average concentrations of total water-soluble N ranged from 0.3 mg N l^{-1} in Northern Finland to 1.5 mg N l^{-1} in the Netherlands, while annual wet deposition ranged from 1.4 kg N ha^{-1} to 10 kg N ha^{-1}. The proportion of WSON was from 2 % in the Netherlands to 38 % at Fontainebleau, France. Precipitation-weighted average concentrations of inorganic N (NH_4^+ and NO_3^-) can be compared with wet-only concentrations of inorganic N from the EMEP monitoring network (Hjellbrekke and Fjaeraa, 2011) for 2009 in Fig. 1. The sites used in this study cover the range of rain composition observed across Europe. Annual average deposition of ammonium and nitrate was highly correlated across all sites excluding the Netherlands ($r^2 = 0.42$, $n = 15$), whereas the Dutch samples showed a much greater contribution from ammonium. Across sites, the deposition of WSON was not correlated with reduced, oxidised or total N deposition, but the proportion of WSON was significantly negatively correlated with total wet N deposition (WSON%TN = 33–3.2 · wet dep N (kg ha^{-1}), $r^2 = 0.50$) across all the sites, but with large scatter. The inverse relationship with wet deposited nitrate (WSON%TN = 36–9.2 · wet dep NO_3–N (kg ha^{-1}), $r^2 = 0.72$) was much stronger than for ammonium (WSON%TN = 25–3.7 · wet dep NH_4–N (kg ha^{-1}), $r^2 = 0.37$).

3.2 Seasonal patterns

Seasonality in each data series was measured by fitting a sine curve through the monthly data. Significant ($P < 0.05$) seasonal patterns in concentration of ammonium and nitrate were observed at approximately half of the sites, with a spring maximum between February and May. 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.

BGD
9, 8093–8109, 2012

3.3 Correlations in space and time

Despite the lack of correlation across sites for annual-average data, WSON concentrations and/or deposition were correlated in time with inorganic N at some 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. There were no statistically significant correlations at most sites, but WSON 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. No clear pattern emerged over Europe.

4 Discussion

4.1 Uncertainties

With this type of project, involving sub-sampling and analysis in two different laboratories, the possibility of artefacts is increased, with increases in the uncertainty associated with the results. 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 bias (Cornell and Jickells, 1999). However, on some occasions the measured total N at CEH was significantly less than the sum of the NH_4^+ and NO_3^- concentrations reported by the originating laboratory, implying artefacts during the sub-sampling process, and/or systematic differences in calibrations between the laboratories. The latter possibility was checked by the analysis of analytical standards, shipped from the Slovak laboratory to CEH. No bias could be detected, implying no systematic difference. A second check was direct comparison of total N (measured by CEH using high-temperature combustion and chemiluminescence) with total N (measured by RIVM using persulphate oxidation) for samples from the Dutch sites.

BGD
9, 8093–8109, 2012

Orthogonal regression of these two datasets shows a small negative bias of the persulphate data compared with chemiluminescence (slope = 0.95, intercept $-0.12\,\mathrm{mg\,N\,l^{-1}}$), 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). However, these small differences do not account for the occasional large discrepancy between total N measurement and prior inorganic N analyses. The addition of thymol has been shown to be effective as a biocide in rain samples (Cape et al., 2001; Ayers et al., 1998; Hadi and Cape, 1995), so it is unlikely that there would have been large biotic changes in sample composition during shipping. There remains the possibility of abiotic losses caused by chemical reactions during shipping. In some cases, the pH and NH_4^+ concentrations measured in the laboratory would, at equilibrium at 20 °C, imply transfer of NH_3 to the gas phase, which could have been lost from the vial when sampled. Although weak, there was a correlation between the WSON deficit and NH_4^+ concentration, which would be consistent with this explanation. It is possible that at some sites, inclusion of sub-micron particles of minerals could have increased the pH during transit and led to losses of NH_3. Although a small proportion of the overall samples, these anomalies suggest that at some sites the concentration of WSON may have been underestimated; any losses of N from the sample between the ion analyses and the analysis for total N would lead to a low value for the calculated WSON.

The second artefact applies only to the samples from the Netherlands. We have already shown good agreement for total N measured by the RIVM and CEH laboratories, but for these samples the NH_4^+ concentrations were measured colorimetrically rather than by ion chromatography. It has been shown that amines and amino acids produce positive artefacts in the indophenol blue method for measuring ammonium (Cape et al., 2001). Consequently, the reported "NH_4^+" concentrations are likely to be over-estimates of the true NH_4^+ concentrations, leading to a systematic under-estimate of WSON concentrations at the 4 Dutch sites.

As seen from Table 1, some of the (non-NitroEurope) sites used wet-only rather than bulk samplers. While this is likely to have led to a lower relative measurement

BGD
9, 8093–8109, 2012

of concentration and deposition, because of additional dry deposition of gases and particles on the bulk collector surfaces, the effect on the proportion of WSON is not known. In the only study to have investigated the potential bias (González Benítez et al., 2009), the difference between wet-only and bulk samplers was up to 50 %, but with no clear indication of a difference in the proportion of WSON. Consequently, the overall deposition data for the "wet-only" sites may be biased low relative to the other sites studied.

4.2 Comparison with the literature

The annual average concentrations of inorganic N across Europe show a similar range and geographical pattern to those measured in the EMEP Network (www.emep.int), as shown in Fig. 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. The concentration of WSON as a proportion of total N in this study is approximately inversely related to the total N, 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). For reviews of global and historical datasets see Cornell (2011), Cornell et al. (2003) and Neff et al. (2002).

BGD
9, 8093–8109, 2012

5 Conclusions

This study, despite the obvious drawbacks of its opportunistic nature, has confirmed the importance of WSON as a component of wet deposition across Europe, as illustrated by a growing number of individual studies. However, no clear patterns have emerged as to the likely sources, or rather, the lack of pattern has shown that the contribution of WSON to total N is not unequivocally linked to either ammonium or nitrate across the continent. The relative contribution of WSON to total N is greater where total N concentrations and deposition are smallest, but again, there are no consistent temporal or spatial patterns, reflecting earlier conclusions on the varied sources and chemical composition of WSON (Cape et al., 2011).

However, the study has reinforced the fact that wet deposition of nitrogen to European ecosystems is systematically underestimated by the use of inorganic N data alone. Although the bioavailability of WSON may be less than for inorganic N, there is sufficient evidence that at least some components are bioavailable (Liu et al., 2011; Peierls and Paerl, 1997; Wedyan et al., 2007; Krab et al., 2008; GalletBudynek et al., 2009; Nasholm et al., 2009; Xu et al., 2006). Consequently, Critical Loads for N deposition may need to be revised, particularly for sensitive ecosystems where deposition is close to the Critical Load based on inorganic N alone. Where the empirical Critical Load has been established on the basis of field measurements of ambient deposition then the role of WSON will have been included implicitly, but where the Critical Load has been established on the basis of additions of inorganic N the translation of these data to the real world, where WSON is also a contributory factor, needs to be re-examined. Similarly, where processes such as species change (Stevens et al., 2010) are described or modelled using deposition of inorganic N as an explanatory variable, the potential role of WSON should not be ignored.

Acknowledgements. The authors gratefully acknowledge financial support from the European Commission 6th Framework Programme for the NitroEurope IP, and from the NERC Centre for

BGD
9, 8093–8109, 2012

Ecology & Hydrology. J. M. G.-B. also acknowledges support from the School of Chemistry, University of Edinburgh.

References

Ayers, G. P., Fukuzaki, N., Gillett, R. W., Selleck, P. W., Powell, J. C., and Hara, H.: Thymol as a biocide in Japanese rainwater, J. Atmos. Chem., 30, 301–310, 1998.

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, Atmos. Environ., 43, 3786–3798, doi: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 UK, Water Air Soil Pollut., 4, 25–35, 2004.

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

Cornell, S. E.: Atmospheric nitrogen deposition: revisiting the question of the importance of the organic component, Environ. Pollut., 159, 2214–2222, 2011.

Cornell, S. E. and Jickells, T. D.: Water-soluble organic nitrogen in atmospheric aerosol: a comparison of UV and persulfate oxidation methods, Atmos. Environ., 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, Atmos. Environ., 37, 2173–2191, 2003.

Dämmgen, U., Erisman, J. W., Cape, J. N., Grünhage, L., and Fowler, D.: Practical considerations for addressing uncertainties in monitoring bulk deposition, Environ. Pollut., 134, 535–548, 2005.

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, Atmos. Chem. Phys., 11, 2703–2728, doi:10.5194/acp-11-2703-2011, 2011.

BGD
9, 8093–8109, 2012

GalletBudynek, A., Brzostek, E., Rodgers, V. L., Talbot, J. M., Hyzy, S., and Finzi, A. C.: Intact amino acid uptake by northern hardwood and conifer trees, Oecologia, 160, 129–138, 2009.
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, Atmos. Environ., 43, 4087–4094, 2009.
Hadi, D. A. and Cape, J. N.: Preservation of throughfall samples by chloroform and thymol, Int. J. Environ. An. Ch., 61, 103–116, 1995.
Hjellbrekke, A. G. and Fjaeraa, A. M.: Data Report 2009: acidifying and eutrophying compounds and particulate matter. EMEP-CCC Report 1/2011, NILU, Kjeller, Norway, 139, 2011.
Kieber, R., Long, M., and Willey, J.: Factors influencing nitrogen speciation in coastal rainwater, J. Atmos. Chem., 52, 81–99, 2005.
Kopacek, J., Prochazkova, L., Hejzlar, J., and Blazka, P.: Trends and seasonal patterns of bulk deposition of nutrients in the Czech Republic, Atmos. Environ., 31, 797–808, 1997.
Krab, E. J., Cornelissen, J. H. C., Lang, S. I., and van Logtestijn, R. S. P.: Amino acid uptake among wide-ranging moss species may contribute to their strong position in higher-latitude ecosystems, Plant Soil, 304, 199–208, 2008.
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.
Liu, H., Jeong, J., Gray, H., Smith, S., and Sedlak, D. L.: Algal uptake of hydrophobic and hydrophilic dissolved organic nitrogen in effluent from biological nutrient removal municipal wastewater treatment systems, Environ. Sci. Technol., 46, 713–721, doi:10.1021/es203085y, 2011.
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, J. Geophys. Res. Atmos., 108, 4320, doi:10.1029/2002JD002997, 2003.
Michalzik, B. and Matzner, E.: Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem, Eur. J. Soil Sci., 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 Environ. Res., 13, 3–21, 2008.
Nasholm, T., Kielland, K., and Ganeteg, U.: Uptake of organic nitrogen by plants, New Phytol., 182, 31–48, doi:10.1111/j.1469-8137.2008.02751.x, 2009.

BGD
9, 8093–8109, 2012

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.

Peierls, B. L. and Paerl, H. W.: Bioavailability of atmospheric organic nitrogen deposition to coastal phytoplankton, Limnol. Oceanogr., 42, 1819–1823, 1997.

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 Soil Pollut., 105, 165–174, 1998.

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, doi:10.5194/bg-6-2743-2009, 2009.

Stevens, C. J., Duprè, C., Dorland, E., Gaudnik, C., Gowing, D. J. G., Bleeker, A., Diekmann, M., Alard, D., Bobbink, R., Fowler, D., Corcket, E., Mountford, J. O., Vandvik, V., Aarrestad, P. A., Muller, S., and Dise, N. B.: Nitrogen deposition threatens species richness of grasslands across Europe, Environ. Pollut., 158, 2940–2945, 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, Environ. Pollut., 158, 1857–1869, doi: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, doi:10.1016/j.marchem.2009.08.004, 2010.

Wedyan, M. A., Fandi, K. G., and Al-Rousan, S.: Bioavailability of atmospheric dissolved organic nitrogen in the marine aerosol over the Gulf of Aqaba, Aust. J. Basic Appl. Sci., 1, 208–212, 2007.

Xu, X., Ouyang, H., Kuzyakov, Y., Richter, A., and Wanek, W.: Significance of organic nitrogen acquisition for dominant plant species in an alpine meadow on the Tibet Plateau, China, Plant Soil, 285, 221–231, 2006.

BGD
9, 8093–8109, 2012

Table 1. List of sites with locations; those in the NitroEurope Level 1 network (Flechard et al., 2011) are shown by *, and in the NitroEurope Level 3 network by ** (http://www.nitroeurope.eu/sites_data_page).

Name	Country	Latitude	Longitude	Sampler type/frequency
Pallas	Finland	68.00	24.24	bulk/1 week
Virolahti	Finland	60.52	27.64	bulk/1 week
Polwet*	Poland	52.76	16.31	bulk/1 month
Hainich*	Germany	51.08	10.45	bulk/1 month
Grillenburg*	Germany	50.95	13.51	bulk/1 month
Wetzstein*	Germany	50.45	11.46	bulk/1 month
Vielsalm*	Belgium	50.31	6.00	bulk/1 month
Oensingen**	Switzerland	47.17	7.44	wet-only/1–2 week
Lägeren*	Switzerland	47.48	8.37	bulk/1 month
Fontainebleau*	France	48.48	2.78	bulk/1 month
Puéchabon*	France	43.74	3.60	bulk/1 month
Le Bray*	France	44.72	-0.77	bulk/1 month
San Rossore*	Italy	43.73	10.28	bulk/1 month
Roccarespampani*	Italy	42.46	11.93	bulk/1 month
Rotterdam	Netherlands	51.95	4.43	wet-only/2 week
Speulderveld	Netherlands	52.26	5.71	wet-only/2 week
Vredepeel	Netherlands	51.57	5.86	wet-only/2 week
Wieringerwerf	Netherlands	52.80	5.05	wet-only/2 week

BGD
9, 8093–8109, 2012

Table 2a. Average precipitation composition across all sites (precipitation weighted mean concentrations in mg N l^{-1}).

Site	start	end	period y	precipn mm y^{-1}	NH_4^+ mg N l^{-1}	NO_3^- mg N l^{-1}	WSON mg N l^{-1}
Pallas	May 2009	December 2009	0.58	512	0.07	0.11	0.10
Virolahti	May 2009	December 2009	0.59	703	0.16	0.22	0.09
Oensingen	August 2006	December 2008	2.32	984	0.42	0.20	0.12
Fontainebleau	January 2008	January 2011	2.94	634	0.13	0.11	0.15
Grillenburg	January 2008	December 2010	2.91	830	0.42	0.46	0.10
San Rossore	March 2008	December 2010	2.75	939	0.12	0.29	0.03
Roccarespampani	May 2008	January 2011	2.58	835	0.11	0.11	0.09
Puéchabon	February 2008	January 2011	2.66	705	0.34	0.45	0.05
Polwet	January 2008	February 2011	2.93	574	0.38	0.40	0.13
Le Bray	February 2008	January 2009	0.93	801	0.28	0.45	0.03
Lägeren	February 2008	January 2011	2.76	980	0.46	0.26	0.18
Hainich	March 2008	January 2011	2.74	748	0.35	0.45	0.08
Wetzstein	February 2008	January 2011	2.90	807	0.47	0.50	0.03
Vielsalm	January 2008	February 2009	1.07	1354	0.24	0.19	0.10
Rotterdam	September 2008	December 2011	3.22	864	0.57	0.33	0.05
Vredepeel	September 2008	December 2011	3.26	621	0.99	0.34	0.11
Wieringerwerf	September 2008	December 2011	3.26	630	0.60	0.36	0.02
Speulderveld	September 2008	December 2011	3.26	914	0.71	0.35	0.03

BGD
9, 8093–8109, 2012

Table 2b. Average wet deposition of N ($kg\,N\,ha^{-1}\,y^{-1}$) at all sites, from data in Table 2a.

site	NH_4–N	NO_3–N	WSON	total N	WSON % total	% mm sampled
Pallas	0.34	0.58	0.51	1.42	36 %	100
Virolahti	1.10	1.52	0.64	3.25	20 %	96
Oensingen	4.09	1.94	1.21	7.24	17 %	85
Fontainebleau	0.80	0.72	0.93	2.45	38 %	100
Grillenburg	3.52	3.84	0.79	8.15	10 %	85
San Rossore	1.14	2.70	0.30	4.15	7 %	66
Roccarespampani	0.90	0.90	0.73	2.53	29 %	82
Puéchabon	2.42	3.20	0.34	5.96	6 %	68
Polwet	2.17	2.27	0.72	5.16	14 %	97
Le Bray	2.22	3.61	0.28	6.11	5 %	71
Lägeren	4.48	2.51	1.74	8.73	20 %	81
Hainich	2.58	3.39	0.56	6.53	9 %	86
Wetzstein	3.80	4.01	0.25	8.05	3 %	98
Vielsalm	3.26	2.51	1.35	7.12	19 %	74
Rotterdam	4.89	2.83	0.45	8.17	6 %*	94
Vredepeel	6.17	2.13	0.67	8.98	7 %*	95
Wieringerwerf	3.79	2.29	0.15	6.23	2 %*	96
Speulderveld	6.52	3.20	0.24	9.96	2 %*	99

* Possibly underestimated, because colorimetric method used for NH_4^+–N.

BGD
9, 8093–8109, 2012

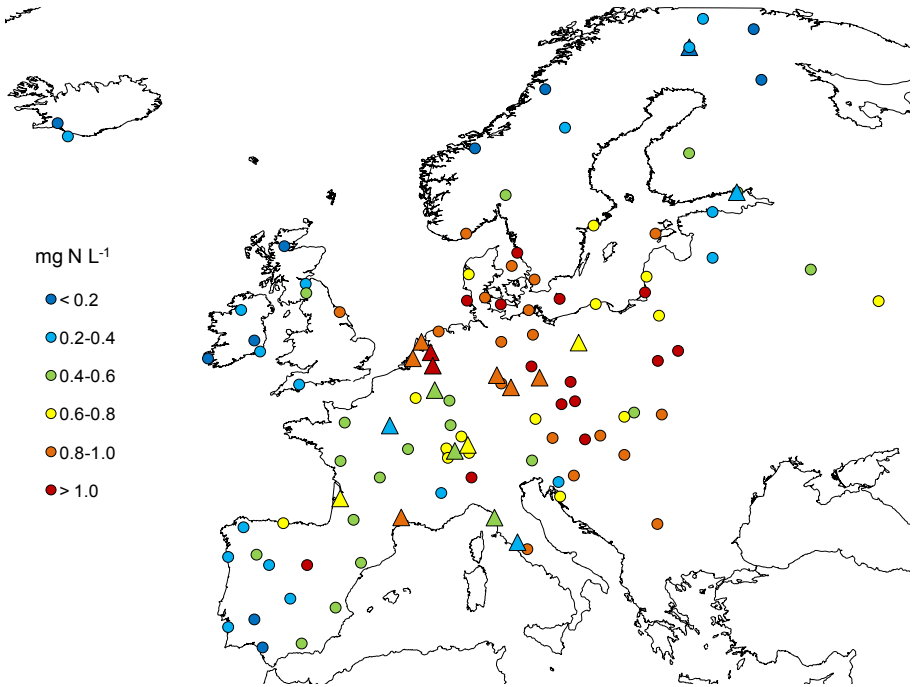

Fig. 1. Annual rainfall-weighted average concentrations ($mg N l^{-1}$) of inorganic N (NH_4^+ and NO_3^-) in precipitation across Europe. The circles show colour-coded concentrations from the EMEP monitoring sites for 2009 (EMEP/CCC-Report 1/2011, available at: http://www.nilu.no/projects/ccc/reports/cccr1-2011.pdf), and the triangles show the data from this study for comparison.

BGD
9, 8093–8109, 2012