Biogeosciences Discuss., 12, 515–554, 2015
www.biogeosciences-discuss.net/12/515/2015/
doi:10.5194/bgd-12-515-2015

Biogeosciences
Discussions
Open Access

The import and export of organic nitrogen species at a Scottish ombrotrophic peatland

R. M. McKenzie[1,2,*], M. Z. Özel[3], J. N. Cape[1], J. Drewer[1], K. J. Dinsmore[1], E. Nemitz[1], J. F. Hamilton[3], M. A. Sutton[1], M. W. Gallagher[2], and U. Skiba[1]

[1]Centre for Ecology and Hydrology, Edinburgh, Bush Estate, Penicuik, EH26 0QB, UK
[2]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Williamson Building, Oxford Road, Manchester, M13 9PL, UK
[3]Department of Chemistry, The University of York, York, YO10 5DD, UK
[*]now at: Environmental Research Institute, Castle Street, Thurso, KW14 7JD, UK

Received: 10 November 2014 – Accepted: 12 December 2014 – Published: 9 January 2015

Correspondence to: R. M. McKenzie (rebecca.mckenzie@uhi.ac.uk)

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

Abstract

Dissolved organic nitrogen (DON) can contribute significantly to the overall nitrogen budget, but is not routinely measured in precipitation or stream water. In order to investigate the contribution of DON to deposition and export of N, precipitation, stream and soil water samples were collected from an ombrotrophic peatland and analysed for DON Over a two year period. In wet only deposition DON contributed up to 10 % of the total dissolved nitrogen (TDN), 99 % in soil water, and 75 % in stream water. No correlations were observed between DIN and DON in precipitation stream water or soil water.

DIN is an important source of nutrients and in ombrotrophic peatlands, is only deposited via precipitation. Too much nitrogen to a sensitive ecosystem can result in problems with the way in which it is processed, such as an increase in the export of N via nearby water bodies. It is therefore important to monitor N deposition and export.

Precipitation DIN showed a loose seasonal pattern, with peak concentrations occurring between January and June, while DON concentrations tended to be lower in the winter months. Stream water DON and NH_4^+ showed no obvious seasonal pattern but NO_3^- showed larger concentrations in cooler months and the smallest during warmer months, with the exception of June and July 2010, when concentrations were high.

Precipitation and stream DON was qualitatively analysed using GC × GC-NCD. Ten unique compounds were detected, of which only five could be identified: pyrrole, benzonitrile, dodecylamine, N-nitrosodipropylamine and decylamine. Five compounds were present in both precipitation and stream samples: pyrrole, benzonitrile and three unidentified compounds. A more detailed DON speciation may be used to identify sources and pathways of DON.

1 Introduction

Atmospheric deposition of nitrogen (N) has increased dramatically over the last century as a result of industrial and agricultural activities (Galloway et al., 2004). In the last 150 years, the amount of global anthropogenic reactive nitrogen has increased by a factor of 12.5; from ~ 15 Tg N y^{-1} in 1860 to ~ 187 Tg N y^{-1} in 2005 (Galloway et al., 2008). The total deposition of N in the UK was estimated to be approximately 330 Gg in 2004, with wet and cloud deposition accounting for approximately 211 Gg (63.9 %), and the rest consisting of dry deposition (Fowler et al., 2009; Hertel et al., 2011).

Altering the chemistry of precipitation inputs to ecosystems which are dependent on atmospheric deposition for nutrients, such as N, can disturb the way in which N is utilised. Problems such as N-saturation may result in N being leached from the soil and into nearby water bodies (Adamson et al., 1998). Eutrophication and acidification may occur in both terrestrial and aquatic ecosystems.

Wet deposition of the dissolved inorganic nitrogen (DIN) compounds ammonium (NH_4^+) and nitrate (NO_3^-) has been studied over many years (Violaki et al., 2010; Cape et al., 2011; Zhang et al., 2012). The former is produced by the dissolution of ammonia gas (NH_3) and the scavenging of NH_4^+ aerosol, and the latter by the dissolution of nitric acid gas (HNO_3) and the scavenging of NO_3^- aerosol (Russell et al., 1998; Cornell et al., 2003; Tian et al., 2011). The dissolved organic nitrogen (DON) fraction is less well documented due to difficulties in measuring it, but it can be an important fraction of the total dissolved nitrogen (TDN) deposited, and can potentially be biologically available as a source of N (Russell et al., 1998; Neff et al., 2002; Cornell et al., 2003; Cape et al., 2004). The sources of DON are not well understood, but it is known to be ubiquitous in the environment, present in particulate, gaseous and aqueous phases (Cornell et al., 2003; Cape et al., 2004; Özel et al., 2011). Studies have shown that DON can contribute 30–50 % of the wet deposition of water soluble N (Neff et al., 2002; Cape et al., 2004, 2011; Zhang et al., 2008, 2012; Cornell, 2011).

Several atmospheric species of DON are considered hazardous to human health, and appear on the Environment Protection Agency (EPA) hazardous air pollutant list (Özel et al., 2011). Sources of DON are believed to include: pollen; sea spray; soil dust; deposits from fauna and flora; the scavenging of aerosols; and reactions in the atmosphere between inorganic gaseous nitrogen species and organic compounds (Prospero et al., 1996; Russell et al., 1998; Cornell et al., 2003; Calderon et al., 2007; Zhang et al., 2008; Violaki et al., 2010). Some work has been done to identify organic N compounds, so that their sources can be traced. Amino acids, urea, aliphatic amines and peptides have all been found in the atmosphere from naturally occurring sources (Calderon et al., 2007; Violaki et al., 2010). The main anthropogenic organic compounds are believed to be N-heterocyclic compounds, nitrophenols and nitro-polycyclic aromatic hydrocarbons (Violaki et al., 2010). Alky amides have also been identified and are believed to result from reactions between NH_3 and fatty acids at high temperatures (Cheng et al., 2006); photochemical reactions are believed to be responsible for the presence of alky nitrates and peroxyacyl nitrates (Violaki et al., 2010).

As with wet deposition, N is present in streams as both DIN and DON, with most focus usually being on the DIN fraction. DIN, in particular NO_3^-, is often used as an indicator of N saturation, with higher stream concentrations and changes in seasonal patterns indicating an increase in the leaching of DIN from the catchment (Cundill et al., 2007; Daniels et al., 2012). DON, however, is not often measured in spite of being the most dominant fraction in waters draining peatland catchments; DON is known to contribute 60–90 % of the TDN load in peatland streams (Yesmin et al., 1995).

Various techniques have been developed to identify individual organic nitrogen compounds, but many are not sensitive enough to detect these compounds in low concentrations (Özel et al., 2010). Solid phase extraction (SPE) is a technique used to separate organic compounds from aqueous systems, and has successfully been applied in many cases (Moret and Conte, 2002; Özel et al., 2003, 2011). The SPE method has given better DON recovery than solvent extraction from the aqueous phase (Özel et al., 2011) and the extracted samples can be analysed using Gas chromatography (GC).

By using a multi-dimensional GC-technique and comprehensive two-dimensional GC, GC×GC, and coupling it with a nitrogen chemiluminescence detector (NCD), better separation and improved limits of detection can be achieved than by conventional one-dimensional GC (Özel et al., 2006, 2010; Adam et al., 2007; Adahchour et al., 2008). GC×GC-NCD has recently been used to investigate the presence of organic nitrogen compounds in diesel fuel, atmospheric aerosol, nitrosamines in meat and vegetables, and nicotine and N-nitrosamines in house dust (Adam et al., 2007; Özel et al., 2010, 2011; Kocak et al., 2012; Ramirez et al., 2012).

The aim of this study was to investigate the contribution of DON to TDN of wet deposition and TDN export via a stream at a typical NW European ombrotrophic peatland over a two year period. In addition to this, an attempt was made to identify individual DON compounds present in a selection of precipitation and stream samples.

2 Site and methods

2.1 Study area

Auchencorth Moss (Fig. 1) is an ombrotrophic peat bog located in south Scotland, approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat. 55°47′34′′ N; long. 03°14′35′′ W). The site is used primarily for low intensity sheep grazing (less than one livestock unit km^{-2}) and in 2009 a small herd of cows (15–20) also grazed on the site.

The volume of peat in the catchment is estimated to be ~ 50 million m^3, with depths up to 5 m, and an average depth of 50 cm. The total peat coverage is ~ 1214 ha, of which approximately 170 ha is extracted (located 1.75–3.4 km W-SW of the monitoring station) (Mitchell and Mykura, 1962; Dinsmore, 2008).

The Black Burn runs SW to NE of the CEH atmospheric monitoring station at Auchencorth Moss, and drains into the North Esk river. It has a catchment area of approximately 335 ha, which is fed by numerous tributaries, including one which originates in the area of peat extraction. There are a number of overgrown ditches laid out in parallel which is evidence of past drainage activities. The elevation of the catchment is approximately 250–300 m and the main soil type is Histosols (85 % coverage), with Gleysol (9 %), Humic Gleysol (3 %) and Cambisols (3 %) present mostly at the margins of the catchment (Billett et al., 2004).

The vegetation consists of numerous hummocks and hollows. The hollows are depressions up to 30 cm deep and are dominated by blankets of *Sphagnum* mosses, with various sedges, monocotyledons and other bryophytes also present; the hummocks can be up to 30 cm high, and although *Sphagnum* mosses are present, there is a larger density of vascular plants with the dominant species being *Deschampsia flexuosa*, *Eriophorum vaginatum* and *Juncus effusus*. Flechard and Fowler (1998) and Dinsmore (2008) have presented more detailed vegetation information for Auchencorth Moss.

The mean water table depth was determined from nine dip wells located close to the monitoring station (Fig. 1) and was −14.8 cm, ranging from −52.4 to 7 cm above the peat surface during the study period (January 2009–December 2010).

2.2 Wet-only precipitation

Auchencorth Moss is a European Monitoring and Evaluation Programme (EMEP) supersite contributing to the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (http://www.emep.int/index_facts.html). Precipitation was collected daily using an automated wet-only collector (Eigenbrodt NSA 181/KS, Königsmoor, Germany). A sensor detected when rain fell, opening the lid and allowing rain to be collected in a PTFE-coated funnel draining to refrigerated polyethylene bottles. When rainfall ceased, the sensor closed the lid, protecting the samples from contamination from dry deposition and animal inputs. The collector was kept at 4 °C by an internal cooling system and samples were manually emptied once a week, where they were stored in a cool room, also at 4 °C. Samples were analysed by Ion Chromatography (IC) for NH_4^+ and NO_3^-, following EMEP protocols (http://www.nilu.no/projects/ccc/manual/index.html).

A Metrohm 761 Compact Ion Chromatograph (IC) connected in parallel with a Metrohm 733 IC Separation Centre to a Metrohm 766 IC sample processor (Metrohm Ltd., Herisau, Switzerland) measured NO_3^- and NH_4^+ respectively. NO_3^- was determined by pumping an eluent solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate through a Metrosep A Supp 5 column. For NH_4^+ determination, an eluent solution of 24 mM boric acid, 5 mM tartaric acid and 0.7 mM dipicolinic acid, was pumped through a Metrosep C1 column. Typical detection limits were 1 µmol NL^{-1} for both NO_3^- and NH_4^+.

For analysis of TDN (TDN = DIN + DON) subsamples were obtained (a minimum of 5 mL) where possible, and filtered using Millipore Hydrophilic PTFE (0.45 µm pore size) syringe filters prior to freezing and later analysed for TDN by high-temperature catalytic oxidation using an ANTEK 8060-M Nitrogen Specific HPLC Detector (ANTEK Instruments Inc., Houston, TX, USA). The analysis was conducted in flow-injection mode, in which 20 µL samples were introduced into an eluent stream of 10 % methanol in deionised water at a flow rate of 250 $\mu L\,min^{-1}$. It was then combusted in oxygen at 1050 °C, producing nitric oxide (NO) which was detected by chemiluminescence. The detection limit for TDN was ~ 1 µmol NL^{-1}. DON was determined by subtracting DIN from TDN.

The subsamples were also analysed for NO_3^- and NH_4^+ at the same time DON was analysed and compared to the EMEP samples. The samples compared well with an average standard error of ±0.22 $\mu mol\,N\,L^{-1}$ between NO_3^- samples and ±1.45 $\mu mol\,N\,L^{-1}$ between NH_4^+ samples. The analysis was carried out according to the IC description above.

The uncertainty in DON values is greater than for DIN as a result of errors associated with measuring TDN and DIN compounding and thus reducing the accuracy of the DON calculation (Cornell et al., 2003). A negative bias may result from these combined uncertainties, from DON not being fully converted during the total N analysis, and from losses due to the collection and storage procedure (Russell et al., 1998; Cornell et al., 2003). A positive bias results from setting small negative values of DON to zero; small negative values of DON were included in the data analyses here in order to prevent this source of bias. The limit of detection of DON was determined by the summation of the detection limits of the 3 independent measured concentrations (NH_4^+, NO_3^- and TDN) and was 3 µmol N L^{-1}.

2.3 Soil water

Soil water was collected once or twice per month from nine dip wells, from which the water table was also measured. They were filtered within 24 h of collection, using Millipore Hydrophilic PTFE (0.45 µm pore size) syringe filters and stored frozen until analysis. The dip wells consisted of high-density polyethylene perforated pipes (0.04 m diameter) buried in the ground, with rubber bungs to prevent contamination. Samples were analysed for NH_4^+, NO_3^- and TDN by the IC and ANTEK methods described previously. DON was determined by subtracting DIN from TDN.

2.4 KCl-extractable mineral N

Soil cores were collected at a depth of 0–10 cm at three locations (next to the dip wells), in spring and autumn in 2009 and in spring, summer and winter in 2010. NH_4^+ and NO_3^- were extracted from soil samples using KCl; 15 g of soil were shaken for 1 h with 50 mL of 1 M KCl solution at a rate of 100 rpm. Samples were then filtered using Whatman 42 filter papers and frozen prior to analysis by IC. TDN was not measured, so DON could not be determined.

2.5 Stream water

Stream water spot samples were collected by dipping a 300 mL glass bottle once a week from the Black Burn, to the north of the field station. The samples were filtered within 24 h of collection, using Millipore Hydrophilic PTFE (0.45 µm pore size) syringe filters and frozen until ready for analysis. Samples collected from January 2009–October 2009 were analysed for TDN, NH_4^+ and NO_3^- using a San^{++} Automated Wet Chemistry Analyzer/Continuous Flow Analyzer (SKALAR, the Netherlands). Samples from November 2009–November 2010 were analysed for NH_4^+, NO_3^- and TDN using the IC and ANTEK methods described above. In both cases, DON was determined by subtracting DIN from TDN.

Discharge was determined from water height using manually calibrated rating curves ($R^2 > 0.90$) based on measurements of dilution gauging (Dinsmore, personal communication, 2013). Pressure transducers were used to measure water height at 10 min intervals. Until April 2009, a Druck PDCR 1830 series pressure transducer was used at the sample site (Fig. 1). After April 2009, an In Situ Inc. Level Troll® pressure transducer located ∼ 2 km downstream was used.

2.6 GC×GC-NCD

Comprehensive two-dimensional gas chromatography coupled to a nitrogen chemiluminescence detector (GC×GC-NCD) was used to separate DON into different peaks and identify individual components where possible. The samples were extracted by solid phase extraction (SPE), in order to trap the DON, using Superclean ENVI-18 SPE tube 20 µm polymeric C_{18}-reverse phase 500 mg-3 mL SPE cartridges (SUPELCO, Bellefonte, PA, USA). C_{18} material has been used in many SPE applications for extraction of organic compounds from the aqueous phase. It has been found that there is almost no change in the composition of the sample before and after the application of SPE of the C_{18} material (Özel et al., 2003). Cartridges were conditioned with 5 mL methanol followed by 5 mL of water at a rate of 2–5 mL min^{-1}. Between 5 and 18 mL of precipitation and 9 and 24 mL of stream water was passed through the cartridge at a rate of 2–5 mL min^{-1}. The cartridge was thoroughly dried under vacuum for ∼ 30 min. Following drying, the cartridge was eluted with 5 mL dichloromethane (DCM), and then concentrated in a stream of nitrogen to a volume of ~ 0.1 mL. The GC×GC-NCD was an Agilent 7890 GC coupled with an Agilent 255 NCD (Agilent Technologies, Palo Alto, CA, USA). 1 µL extracts were injected in pulsed splitless mode at a temperature of 280 °C and a pressure of 30 psi for 2 min, using a Gerstel automated liquid injector (Gerstel, Mulheim an der Ruhr, Germany). The first dimension column was a non-polar BPX5 (30 m × 0.32 nm i.d. × 0.25 µm film thicknesses), set to an initial temperature of 55 °C for 1 min. The temperature was then increased at a rate of 5 °C min^{-1} until 305 °C where it was isothermally held for 1 min. The second column was a BPX50 (1.5 m × 0.10 mm i.d. × 0.10 µm film thickness) set to an initial temperature of 70 °C for 1 min, the temperature was then increased at a rate of 5 °C min^{-1} until 320 °C where it was isothermally held for 1 min. Both columns were from SGE Analytical Science (VIC, Australia). Helium was used as a carrier gas at a constant flow of 1 mL min^{-1} and the data was collected at 50 Hz. Pyrolysis was carried out at 900 °C with a hydrogen flow rate of 4 mL min^{-1} and oxygen flow rate of 10 mL min^{-1}.

The detector shows an equimolar response regardless of the chemical state of the organic nitrogen (except azo compounds), allowing nitrogen-containing compounds to be quantified without the need for a separate calibration standard for each compound (Yan, 2002; Özel et al., 2011). Details of the optimization of the NCD response and the analytical performance with respect to equimolar response using standards was evaluated by Özel et al., (2011).

3 Results

3.1 Meteorology

Total rainfall was determined from the volume of rain collected in the wet only analyser. In 2009 the total rainfall was 902 mm with monthly totals varying from 16 mm in February to 180 mm in November. The mean monthly temperature varied from 0.5 °C in December to 13.7 °C in July, with a yearly mean of 7.6 °C. In 2010 the total rainfall was 732 mm with monthly totals varying from 21 mm in May to 128 mm in November. However, in 2010 a significant amount of snow fell, interfering with the wet-only collector and resulting in less precipitation collection during January–March. It is estimated that 423 mm of precipitation fell during these months (an additional 291 mm), making the total precipitation collected for 2010 approximately 1023 mm. This additional precipitation was estimated from the ratio of discharge and precipitation, measured at the stream sampling site by the Black Burn (Dinsmore et al., 2013; Skiba et al., 2013). The mean monthly temperature varied from −2.0 °C in December to 13.6 °C in July, with a yearly mean of 6.6 °C.

3.2 Wet-only N deposition

Figure 2 shows the volume-weighted monthly mean concentrations of N in precipitation. The temporal variation of NH_4^+ and NO_3^- follow a similar pattern, with DON differing. In both 2009 and 2010 (Table 1), NH_4^+ was the dominant component of wet-only deposition with annual mean concentrations of 27.2 µmol N L^{-1} (58 %) and 30.7 µmol N L^{-1} (53 %) respectively. The contribution of NO_3^- was greater in 2010 than in 2009, with mean concentrations of 15.0 µmol N L^{-1} (32 %) in 2009 and 22.7 µmol N L^{-1} (39 %) in 2010. Although DON contributed the least to annual concentrations in both years, on a monthly timescale there were a few occasions when DON exceeded NO_3^- (March 2009, June 2009, August 2009 and October 2010). A loose seasonal pattern can be observed for NH_4^+ and NO_3^-, with peak concentrations occurring between January and June. This is more obvious in 2010. DON has no clear seasonal pattern, although the lowest concentrations seem to occur in the winter months (November–January). A weak, but significant correlation was found between NH_4^+ and NO_3^- in 2009 ($R^2 = 0.45$, $p < 0.001$). In 2010, a stronger correlation between NH_4^+ and NO_3^- was also observed ($R^2 = 0.62$, $p < 0.001$). No correlations were observed between NH_4^+, DON, temperature, rainfall or precipitation; NO_3^-, DON, temperature, rainfall or precipitation; or DON, temperature, rainfall or precipitation.

3.3 Soil water and KCl-extractable N

Due to gaps in the data, caused by the dip wells being dry and thus no sample to be collected, it is difficult to assess seasonal patterns. From the data available, it appears that DON concentrations were larger in the warmer months compared to cooler months (November to March) and that peak concentration for DON occurred in September in both years (Fig. 3). The contribution of DON to TDN was higher in 2010 at 99 % compared to 85 % in 2009 (Table 2). NH^{4+} and NO_3^- followed similar patterns, with concentrations in 2009 appearing to increase in the spring, peaking in August. In 2010, both NH^{4+} and NO_3^- concentrations generally remained low, with much smaller peak concentrations occurring in July. NO_3^- mean annual concentrations were 1.2 µmol N L^{-1} (2 % of TDN) in 2009 and 0.2 µmol N L^{-1} (0.3 % of TDN) in 2010. NH^{4+} mean annual concentrations were also larger in 2009 than in 2010; 8.6 µmol N L^{-1} compared to 0.2 µmol N L^{-1}. The contribution of NH^{4+} t TDN was thus much larger in 2009 at 13 % and just 0.4 % in 2010.

Soil extractions from 2 samples in 2009 and 3 samples in 2010 found no detectable NO_3^-, and NH^{4+} concentrations of 29 ± 12 µmol N L^{-1} and 39 ± 20 µmol N L^{-1} for 2009 and 2010, respectively.

3.4 Concentration and forms of N in stream water

Monthly mean discharge-weighted concentrations of NO_3^-, NH_4^- and DON are presented in Fig. 4, and a basic statistical analysis of annual stream water chemistry is presented in Table 3. DON is the dominant N species found in the stream water, with the highest concentrations in summer/autumn, however no clear seasonal pattern was evident. Monthly mean DON concentrations ranged from 9.8 to 96.4 µmol N L^{-1} in 2009 and 15.5 to 104.2 µmol N L^{-1} in 2010. Annual mean concentrations were 48.1 µmol N L^{-1} in 2009 and 50.0 µmol N L^{-1} in 2010, contributing, on average, 74.6 and 74.3 % of TDN.

Monthly mean concentrations of NO_3^- ranged from 0.0 to 13.7 µmol N L^{-1} in 2009 and 0.0 to 15.2 µmol N L^{-1} in 2010. Annual mean concentrations were 2.3 µmol N L^{-1} in 2009 and 4.5 µmol N L^{-1} in 2010. In 2009, concentrations varied seasonally; largest NO_3^- concentrations were measured during the cooler months and the smallest during the warmer months. In summer 2009 there was no detectable NO_3^-. In 2010 stream water NO_3^- concentrations initially followed a similar pattern as in 2009, with concentrations increasing during the winter months and decreasing as temperature increased and summer approached. However, there was a large increase in NO_3^- concentrations in June and July 2010. Consequently, average annual NO_3^- concentrations in 2010 were nearly double those in 2009, contributing 6.6 % of TDN compared to 3.6 % of TDN (Table 3). Monthly median concentrations for NO_3^- for the whole period showed a similar pattern to monthly discharge-weighted mean concentrations, with the exception of June 2010, which is reduced to a summer low of 0 µmol N L^{-1}, suggesting the monthly mean value was skewed by an unusually large value. Median concentrations made little difference to the July 2010 maximum. July 2010 also showed a maximum in the mean concentrations of DON and NH_4^+.

Monthly mean concentrations of NH_4^+ ranged from 5.4 to 21.9 µmol N L^{-1} with an annual mean of 14.1 µmol N L^{-1} in 2009, and 0.0 to 52.3 µmol N L^{-1} with an annual mean of 12.9 µmol N L^{-1} in 2010. Concentrations of NH_4^+ were consistently higher than NO_3^- and there was no clear seasonal pattern. No correlation was observed between NH_4^+, NO_3^-, DON, discharge, temperature, rainfall (both air and stream) or precipitation.

3.5 DON speciation by GC×GC-NCD

Tables 4 and 5 display breakdowns of the individual DON compounds detected by the GC×GC-NCD and their concentrations for precipitation and stream water, respectively. The plasticiser N-butyl-benzenesulphonamide (not included in tables) was a prominent compound in all samples, with extremely high concentrations, sometimes higher than TDN detected in the precipitation by ANTEK. We assume that the N-butyl-benzenesulphonamide detected was most likely to be a sampling contaminant from the storage bottles. This contamination was not detected by the ANTEK as samples run on this machine were filtered directly into glass vials for storage before analysis. The source of this contamination is discussed later and the compound was thus excluded from the results.

In 13 of the 31 precipitation samples, and 2 of the 21 stream samples, no DON compounds were detected or the peaks were too small to be distinguishable from background noise. The limit of detection (LOD) using the optimized method has been determined between 0.16–0.27 pg N using GC×GC-NCD of standard mixtures (Özel et al., 2011).

Peak identification was carried out by comparing the two retention times (Rt_1 and Rt_2) of the peaks observed in the samples with the retention times of known standards. This could lead to misidentification of peaks, however co-elution is greatly reduced using GC×GC and there is very good retention time stability between runs. There were several peaks, consistently present in some samples, that could not be identified as they did not match any of the retention times of standards already run, so have been labelled "Unknown" A–F. In total 10 unique compounds were found to be present in the stream and precipitation, of which only 5 could be identified. Tables 4 and 5 present a summary of the compounds identified in precipitation and stream water DON, respectively. Both the precipitation and the stream water contained 8 distinct compounds, 5 of which were in common.

The most common compound identified in the precipitation samples was Unknown E, present in 10 samples, followed by Unknown D in 6 samples and Unknown B in 5 samples, with mean concentrations of 0.3, 0.14 and 0.2 $\mu mol\,N\,L^{-1}$, respectively assuming an equimolar response and 100 % recovery during SPE. Two precipitation samples contained pyrrole, with a mean concentration of 0.03 $\mu mol\,N\,L^{-1}$. Unknown F was in 3 samples (mean concentrations of 0.1 $\mu mol\,N\,L^{-1}$), dodecylamine was in 2 samples (mean concentration of 0.02 $\mu mol\,N\,L^{-1}$), and Unknown C was in one sample (concentration of 0.02 µmol N L^{-1}). The precipitation samples did not contain any Unknown A, N-nitrosodipropylamine or decylamine, which were found in the stream samples.

The most common compound identified in the stream samples was Unknown A, the mean concentration was 2.0 µmol N L^{-1} (Table 5). Pyrrole was the next most common compound, found in 18 of the stream samples, with a mean concentration of 1.2 µmol N L^{-1}. Unknowns E and F both appeared in 9 stream samples, with mean concentrations of 0.5 and 0.4 µmol N L^{-1}. N-nitrosodipropylamine (NDPA) was present in 4 stream samples, followed by Unknown B and decylamine in 3 stream samples. Mean concentrations were 0.2 µmol N L^{-1} for all three compounds. Unknown D, Unknown C and dodecylamine, which were found in the precipitation samples, were not present in the stream samples.

In both the stream and precipitation samples, only one sample contained benzonitrile, with means of 0.01 (precipitation) and 0.1 µmol N L^{-1} (stream).

Figures 5a and 6a display breakdowns of the monthly means of individual DON compounds detected by the GC×GC-NCD and the remaining DON detected by ANTEK for precipitation and stream water, respectively. Figures 5b and 6b show the monthly means of individual DON compounds detected by the GC×GC-NCD only, to make this fraction more visible. In both cases, the majority of DON was “unidentified”, contributing a mean of 86 and 92 % of total DON detected in precipitation and stream water, respectively. This represents the DON not detected by the GC×GC-NCD, but measured as TDN by the ANTEK, and indicates that the GC×GC-NCD was only able to speciate a small fraction of the DON present. This is likely to be in part a result of losses of highly polar DON compounds during the SPE step and large molecular weight species that are not volatile enough to be analysed by GC. In the precipitation samples, Unknown E is the only compound present in all 5 sampling months, and is the only compound identified in September. October had the most identified compounds present, with 6 of the 8 compounds measured (Fig. 5b). In the stream samples, pyrrole and Unknown A were present in all 4 sampling months. October also had the most identified compounds present, with 7 of the 8 compounds present (Fig. 4).

4 Discussion

4.1 The composition of N in precipitation

Cape et al. (2004) studied several sites in the UK on a range of land uses and noted an annual cycle for DIN and DON, with peak concentrations for NH^{4+} and NO_3^- occurring in the late spring (April–June 2000–2002) and a DON peak occurring in late summer (June–August 2000–2002). Both DIN and DON showed minima in winter. The data presented here are similar, but with earlier DIN maxima in early spring (February–April in 2009 and February–June 2010) followed by lower values in the autumn and beginning of winter. DON also peaked earlier than reported by Cape et al. (2004) but roughly a month after DIN peaks in both 2009 and 2010. Generally, sources of NH^{4+} in precipitation tend to be agricultural in origin and sources of NO_3^- in precipitation from combustion activities (Cape et al., 2011). Although Auchencorth Moss is located in a rural setting and with minimal agricultural activity on the peatland itself; there are several chicken farms in the area. Chickens farms emit ammonia (NH_3), which when dissolved in rainwater, produces NH^{4+} (Schlesinger, 1997). NH_4^+ also makes up a large fraction of atmospheric aerosols and is often transported further downwind of its source (Nieder and Benbi, 2008), where it can then be washed out and deposited by precipitation.

Sources of NO_3^- include motor vehicles and stationary combustion sources (power stations, domestic heating) following atmospheric oxidation of the emitted nitrogen oxides. As a secondary pollutant, nitric acid and nitrates are less easily traced back to sources. The sources of DON are more difficult to generalise, but spring maxima may be due to the release of pollen, plant debris and spores during the spring, which have been suggested as sources of DON (Violaki et al., 2010), or to seasonal patterns in spreading manure. Conversely, an autumn maximum may be linked to decomposition of vegetation (Cape et al., 2004). The contribution of DON to TDN is low at Auchencorth – 10.0 and 8.3 % in 2009 and 2010, respectively – when compared to the literature average of 30 % (Cornell et al., 2003; Cape et al., 2004, 2011; Zhang et al., 2008, 2012), which is likely to be the result of differing sources and varying contributions from anthropogenic inputs. This 10 % contribution is markedly less than for a nearby study in the grounds of the Centre for Ecology and Hydrology (10 km north of Auchencorth Moss), a rural science park, where the contribution of DON to TDN was 24 % for the period June 2005 to April 2007 (Gonzalez Benitez et al., 2009). This site was within 1 km of an intensively managed agricultural area (Easter Bush) dominated by sheep grazed grasslands and receiving high rates mineral nitrogen fertiliser (~ 200 kg N ha^{-1} y^{-1}). In areas of intensive agricultural activity DON in precipitation increases, and is thought to be due to the addition of N fertilisers, especially urea (Neff et al., 2002; Zhang et al., 2012). Auchencorth Moss does not receive fertilisers and the number of sheep/cattle on site was low. Also, many of these earlier studies used bulk precipitation collectors instead of wet-only collectors, and these are likely to have additional water-soluble organic N deposited via dry deposition, and thus larger DON concentrations (Gonzalez Benitez et al., 2010).

Previous studies of precipitation DIN and DON have reported varying degrees of correlation between DON, NH^{4+} and NO$_3^-$. For example, Violaki et al. (2010) found no correlation between DON, NH$_4^+$ and NO$_3^-$ in wet deposition in the Eastern Mediterranean. Zhang et al. (2008) also did not observe correlation between DON, NH^{4+} and NO$_3^-$ in precipitation at 15 sites in China. However, when an additional 37 sites from across the globe were added to the study, positive relationships were found, suggesting a common or similar sources of DON and DIN on a global, but not regional, scale. In a number of studies, DON and NH^{4+} were correlated, or at least more closely correlated than DON and NO$_3^-$, suggesting DON is more closely associated with agricultural sources than with combustion processes (Cape et al., 2004, 2011; Chen et al., 2008; Zhang et al., 2012). Our study showed weak to moderate correlations between NH^{4+} and NO$_3^-$ but no correlation between DIN and DON. This suggests that whilst the DIN compounds might share a common source (e.g. secondary aerosol), DON does not. This is further supported by the later seasonal maxima of DON compared to those of the DIN compounds (Cape et al., 2011).

4.2 N in the soil solution

August 2009 had the highest DIN concentrations and was the driest month that still produced enough sample for analysis. Samples collected in drier periods or from dipwells situated in drier parts of the moss were more viscous and contained much particulate matter, making filtering difficult. In contrast, DIN concentrations in dipwells during wetter periods or in wetter parts of the moss were more dilute and samples contained much less particulate matter. Adamson et al. (2001) found higher NH^{4+} concentrations, but lower DON concentrations, duringperiods of low water table in a blanket bog in England. They suggested that the microbial community responsible for ammonification benefited from the fluctuating water table to a higher degree than nitrifying organisms, resulting in enhanced NH^{4+} concentrations, which then accumulated if the fluctuation continued (Adamson et al., 2001; Daniels et al., 2012). This may be due to nitrifiers being less able to cope with the stress caused by fluctuating conditions than ammonifiers (Voroney, 2007). Although the mean water table was lower in 2010, 2009 saw a greater degree of water table fluctuation (Fig. 4).

Interestingly, the TDN and DIN deposited as precipitation in 2010 was larger than in 2009, but the soil chemistry showed larger concentrations of TDN and DIN in 2009 than in 2010. The larger DIN concentrations in 2009 may be due to the activities of sheep which grazed on this moorland at very low livestock density of less than 1 ewe per ha and also a small herd of 15–20 cattle. In 2009, sheep and sheep droppings were observed in and around the vicinity of the dip wells and where the soil cores were collected; the small cattle herd (15–20) also had access to this area. However, in 2010, there were no cattle on site and the sheep frequented an alternative area of the peatland.

The type of vegetation present in an ecosystem is known to have an effect on the availability of N. Bog vegetation and the associated litters, such as the *Sphagnum* mosses found at Auchencorth, can strip N, particularly NO_3^-, from precipitation, depending on rainfall and vegetation N requirements (Adamson et al., 1998). This would likely result in less N detected in the soil and associated waters. The vegetation cover at Auchencorth does not change significantly year on year, but the location, type and density of livestock does vary unpredictably.

4.3 The composition of N in stream water

Numerous studies have found DON to be the dominant form of stream water N, with contributions varying from 54 to 82 % annually (Chapman et al., 2001; Cundill et al., 2007; Helliwell et al., 2007a). Similarly, NO_3^- is commonly the second most dominant species reported, with NH^{4+} being present in much lower concentrations. For example, Cundill et al. (2007) conducted a study at several points along a blanket peat-dominated catchment in the North Pennine uplands and found the annual mean concentrations of DON, NO_3^- and NH^{4+} to be 32.5 μmol N L^{-1} (82.1 %), 6.2 μmol N L^{-1} (15.7 %), and 0.9 μmol N L^{-1} (2.2 %), respectively. At Auchencorth Moss, the Black Burn DON concentrations were also the dominant form of N, at 75 % (48.1 μmol N L^{-1} and 74 % (50.0 μmol N L^{-1}) for 2009 and 2010, respectively. These high TDN contributions of DON are typical of waters that drain peatlands due to their high organic matter content, often steep slopes promoting surface runoff, and high rainfall. In addition, anaerobic and acidic conditions reduce mineralisation of DON and nitrification to NO_3^- (Yesmin et al., 1995; Adamson et al., 1998; Chapman et al., 2001). However, in contrast to the studies highlighted above, water draining from Auchencorth Moss had higher mean annual NH^{4+} than NO_3^- concentrations in both 2009 and 2010, with means of 14.1 μmol N L^{-1} (22 %) in 2009 and 12.9 μmol N L^{-1} (19 %) in 2010 for NH^{4+}, and 2.3 μmol N L^{-1} (3.6 μmol N L^{-1} (6.6 %) in 2010 for NO_3^-. Helliwell et al. (2007a) compared four upland regions in the UK and found NO_3^- concentrations were lower when waters drained peaty soils than those which drained more mineral soils. Usually, the leaching of inorganic N is dominated by NO_3^-, whereas NH^{4+} remains in the soil in weak association with organic matter and incorporation into clay lattices (Scherer, 1993; Chapman and Edwards, 1999; Davies et al., 2005; Helliwell et al., 2007a). The anaerobic conditions resulting from waterlogged soils may inhibit the oxidation of NH^{4+} to NO_3^-, resulting in a higher incidence of NH^{4+} leaching into nearby water bodies(Helliwell et al., 2007a). Fluctuating water tables have also been linked to higher NH^{4+} concentrations from the mineralisation of organic nitrogen (Daniels et al., 2012; Paul and Clark, 1996). Vegetation can also influence river water N-chemistry; peatlands with extensive blanket bog vegetation often exhibit lower NO_3^- concentrations than those that drain mineral soils (Chapman et al., 2001; Cundill et al., 2007).

A previous study carried out at the Black Burn in 2008, approximately 2.5 km downstream from the sampling site reported here, also found DON to be the dominant species (mean concentration of 47.9µmol N L^{-1}) contributing71 % of the TDN, followed by NH^{4+} (mean concentration 10.7 µmol N L^{-1}), contributing 16 NO_3^- (mean concentration 8.6 µmol N L^{-1}), contributing13 % of TDN (Vogt, 2011). The DON values are comparable to the study reported here, but the Vogt study found lower $NH^{4+}$and higher NO_3^- values. These differences may be due to the location of the Vogt study site, which was further downstream, next to a busy road, and was frequented by sheep more regularly than the upstream site from this study. This may have resulted in addition N inputs from the sheep and road traffic, increasing the amount of N leached/deposited into the stream as NO_3^-. Also, some NH^{4+} may have been nitrified to NO_3^- as it was transported downstream towards the Vogt sampling sit (Helliwell et al., 2007a). No correlation was found between the wet deposition of atmospheric N and stream concentrations suggesting that precipitation does not represent a major source of stream water N.

4.4 Seasonal patterns of N in stream water

Although no clear seasonal pattern was identified for DON, the general trend was higher concentrations in warmer months. Chapman et al. (2001) studied 28 Scottish upland streams and found DON to be larger in the summer than winter months. It was suggested that this was due to an increase of in-stream DON production, rather than increased leaching from the soil, as a result of algae/microorganisms in stream. Winter months would have cooler temperatures, less sunlight and a higher frequency of storm events, resulting in less primary production and DON being washed away more frequently.

The seasonal pattern of NO_3^-, where concentrations were higher in cooler months and lower in warmer months has been observed in numerous upland studies (Black et al., 1993; Chapman et al., 2001; Daniels et al., 2012). In warmer months, the biological uptake of NO_3^- by plants and microbes is at its highest, immobilising NO_3^-. In winter, productivity declines, increasing the amount of NO_3^- available to be leached into the stream (Black et al., 1993; Chapman et al., 2001; Helliwell et al., 2007b). The summer peaks in June and July 2010 are unusual and different to the summer lows observed in 2009. The high June value appears to be due to one high concentration, skewing the mean monthly concentration; the median value for June was 0 $\mu mol\,N\,L^{-1}$. The high July 2010 peak is also evident in the mean concentrations of DON, and NH_4^+, and is still reflected in median values. The reason for these high values are unclear, however the differences in discharge and precipitation between the two sampled years may be a contributing factor. The monthly discharge was 59 % higher in June 2009 and 11 % higher in July in 2009 than in the corresponding months in 2010. Likewise, precipitation was 39 % higher in June 2009 and 24 % higher in July 2009 than in the corresponding months in 2010. Stream temperatures were similar but overall cooler in 2009.

4.5 DON speciation by GC×GC-NCD

Most of the compounds contributing to DON in both the precipitation and stream samples could not be identified. Whilst some of the compounds detected by the GC×GC-NCD appear in both sets of data, the two main compounds identified in the stream water were either present in precipitation only in small amounts or not present at all. This suggested that at least some sources of DON in precipitation and stream waters are different.

Schulten and Schnizer, (1998) investigated the chemistry of organic matter of humic substances and soils. Amongst other compounds they identified pyrrole and benzonitrile, along with derivatives of pyrrole. They concluded that heterocyclic N compounds, of which pyrrole is one, were an important constituent of soil organic matter, contributing up to 35 % of total N. Pyrrole and pyrrolic compounds are a major N source in coal and are often found in peats; they can result from the aerobic breakdown of the tetrapyrrole ring found in chlorophyll or from the breakdown of extensin, which is a type of hydroxyproline-rich polymer found in the cell walls of plants (van Smeerdijk and Boon, 1987; Schulten and Schnizer, 1998). It is therefore likely that the source of pyrrole in the streams was the peat in the surrounding catchment. Pyrrole has also been identified in fog waters where it was found to be quickly degraded during transport by photochemistry (Anastasio and McGregor, 2000). It is thought to be present in the atmosphere originating from soil dust rich in humic/fluvic material (Schulten and Schnizer, 1998; Anastasio and McGregor, 2000). This may explain the presence of a small amount of pyrrole found in the precipitation samples.

The three other compounds identified were all amines: dodecylamine (found only in the precipitation), NDPA and decylamine (both only found in the stream).

4.6 GC×GC-NCD limitations

Although the application of GC×GC-NCD to precipitation and stream water samples was largely successful, there were a number of issues. The main issue was the presence of what appeared to be a contamination peak. Blank water samples were included before sample analysis and N-butyl-benzenesulphonamide was not detected. N-butyl-benzenesulphonamide is a plasticiser, and may have leached into the samples from the storage bottles when stored in the freezer prior to analysis, or from SPE extraction tubes by reaction with the DCM. This warrants further investigation.

In order to remove the DIN and water prior to analysis, solid phase extraction was used. The most polar, water-soluble compounds, such as amino acids and urea, will be lost during this step. Further work is needed to improve the extraction procedure to maximise the applicability of the technique. Alternative approaches include liquid–liquid extractions or stir bar sorptive extraction. Another issue is the small sample size of precipitation samples, which combined with low concentrations, means that many of the compounds are below the detection limit. In the stream samples, part of the DON may be in less volatile forms that, although they can be measured by the ANTEK, are not amenable to a GC analysis.

Identification of the peaks of unknown compounds may be improved by including standards of more chemical compounds.

5 Conclusions

DON is an important source of nitrogen both in streams and precipitation and must not be ignored in measurements of atmospheric nitrogen deposition rates or stream water nitrogen balances. The mean volume-weighted concentration of DON found in the precipitation over the total study period was 4.8 µmol N L^{-1}, with a mean contribution of 9 % to TDN.

DON in stream water was a major contributor to TDN (with an overall mean of 75 %) and showed no clear seasonal pattern. The presence of pyrrole, the large DON concentrations and the high NH_4^+ in stream water, suggest mineralisation of organic N stored in peat was one of the sources.

In soil water, DON contributed an overall mean of 92 % to TDN. The mean concentrations of DON did not vary greatly between the years but the concentration of NH_4^+ did (8.6 µmol N L^{-1} in 2009 and 0.2 µmol N L^{-1} in 2010), possibly due to localised impact of animal waste and the importance of water table variation on the availability of N to plants and on immobilisation.

GC×GC-NCD shows promise as a technique to identify compounds in stream water/precipitation and their potential sources. The number of unknown compounds detected may be reduced by running more standards for comparison. The contamination issue needs to be investigated to determine when/how a plasticiser was leached into the samples.

Acknowledgements. This work was funded by the UK Natural Environment Research Council (NERC) through a PhD studentship grant number NE/H526351/1 and standard grant ((NE/F01905X/1) and the EU projects NitroEurope IP (FP6 proposal number 017841) and ECLAIRE “Effects of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems” (FP7-ENV-2011/282910). The authors would like to gratefully acknowledge the assistance of Ian Leith, Ivan Simmons and Netty van Dijk, with sample collection, and Harwell Analytics laboratory for analysis of the EMEP samples.

References

Adahchour, M., Beens, J., and Brinkman, U. A. T.: Recent developments in the application of comprehensive two-dimensional gas chromatography, J. Chromatogr. A, 1186, 67–108, 2008.

Adam, F., Bertoncini, F., Brodusch, N., Durand, E., Thiebaut, D., Espinat, D., and Hennion, M.-C.: New benchmark for basic and neutral nitrogen compounds speciation in middle distillates using comprehensive two-dimensional gas chromatography, J. Chromatogr. A, 1148, 55–64, 2007.

Adamson, J. K., Scott, W. A., and Rowland, A. P.: The dynamics of dissolved nitrogen in a blanket peat dominated catchment, Environ. Pollut., 99, 69–77, 1998.

Adamson, J. K., Scott, W. A., Rowland, A. P., and Beard, G. R.: Ionic concentrations in a blanket peat bog in northern England and correlations with deposition and climate variables, Eur. J. Soil Sci., 52, 69–79, 2001.

Anastasio, C. and McGregor, K. G.: Photodestruction of dissolved organic nitrogen species in fog waters, Aerosol Sci. Tech., 32, 106–119, 2000.

Billett, M. F., Palmer, S. M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K. J., Flechard, C., and Fowler, D.: Linking land–atmosphere-stream carbon fluxes in a lowland peatland system, Global Biogeochem. Cy., 18, GB1024, doi:10.1029/2003GB002058, 2004.

Black, K. E., Lowe, J. A. H., Billett, M. F., and Cresser, M. S.: Observations on the changes in nitrate concentrations along streams in seven upland moorland catchments in Northeast Scotland, Water Res., 27, 1195–1199, 1993.

Calderon, S. M., Poor, N. D., and Campbell, S. W.: Estimation of the particle and gas scavenging contributions to wet deposition of organic nitrogen, Atmos. Environ., 41, 4281–4290, 2007.

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

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

Chapman, P. J. and Edwards, A. C.: The impact of atmospheric nitrogen deposition on the behaviour of nitrogen in surface waters, in: The Impact of Nitrogen Deposition on Natural and Semi-Natural Ecosystems, edited by: Langan, S. J., Kluwer Academic Publishers, Dordrecht, the Netherlands, 153–212, 1999.

Chapman, P. J., Edwards, A. C., and Cresser, M. S.: The nitrogen composition of streams in upland Scotland: some regional and seasonal differences, Sci. Total Environ., 265, 65–83, 2001.

Chen, N.-W., Hong, H.-S., and Zhang, L.-P.: Wet deposition of atmospheric nitrogen in Jiulong River Watershed, Huanjing Kexue, 29, 38–46, 2008.

Cheng, Y., Li, S.-M., and Leithead, A.: Chemical characteristics and origins of nitrogen-containing organic compounds in $PM_{2.5}$ aerosols in the Lower Fraser Valley, Environ. Sci. Technol., 40, 5846–5852, 2006.

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., 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.

Cundill, A. P., Chapman, P. J., and Adamson, J. K.: Spatial variation in concentrations of dissolved nitrogen species in an upland blanket peat catchment, Sci. Total Environ., 373, 166–177, 2007.

Daniels, S. M., Evans, M. G., Agnew, C. T., and Allott, T. E. H.: Ammonium release from a blanket peatland into headwater stream systems, Environ. Pollut., 163, 261–272, 2012.

Davies, J. J. L., Jenkins, A., Monteith, D. T., Evans, C. D., and Cooper, D. M.: Trends in surface water chemistry of acidified UK freshwaters, 1988–2002, Environ. Pollut., 137, 27–39, 2005.

Dinsmore, K. J.: Atmosphere–Soil-Stream Greenhouse Gas Fluxes from Peatlands, unpublished thesis, The University of Edinburgh, 2008.

Dinsmore, K. J., Billett, M. F., Skiba, U. M., Rees, R. M., Drewer, J., and Helfter, C.: Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland catchment, Glob. Change Biol., 16, 2750–2762, 2010.

Dinsmore, K. J., Billett, M. F., and Dyson, K. E.: Temperature and precipitation drive temporal variability in aquatic carbon and GHG concentrations and fluxes in a peatland catchment, Glob. Change Biol., 10, 2133–2148, 2013.

Flechard, C. R. and Fowler, D.: Atmospheric ammonia at a moorland site. I: The meteorological control of ambient ammonia concentrations and the influence of local sources, Q. J. Roy. Meteor. Soc., 124, 733–757, 1998.

Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S. A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Kruit, R. W., Bahl, K. B., Flechard, C., Tuovinen, J. P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T. N., Poulsen, H. R., Cellier, P., Cape, J. N., Horváth, L., Loreto, F., Niinemets, Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüeggemann, N., Boltenstern, S. Z., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A., Chaumerliac, N., and Erisman, J. W.: Atmospheric composition change: ecosystems–atmosphere interactions, Atmos. Environ., 43, 5193–5267, 2009.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., and Vorosmarty, C. J.: Nitrogen cycles: past, present, and future, Biogeochemistry, 70, 153–226, 2004.

Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z. C., Freney, J. R., Martinelli, L. A., Seitzinger, S. P., and Sutton, M. A.: Transformation of the nitrogen cycle: recent trends, questions, and potential solutions, Science, 320, 889–892, 2008.

Gonzalez Benitez, J. M., Cape, J. N., Heal, M. R., van Dijk, N., and Diez, 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.

Helliwell, R. C., Coull, M. C., Davies, J. J. L., Evans, C. D., Norris, D., Ferrier, R. C., Jenkins, A., and Reynolds, B.: The role of catchment characteristics in determining surface water nitrogen in four upland regions in the UK, Hydrol. Earth Syst. Sci., 11, 356–371, doi:10.5194/hess-11-356-2007, 2007a.

Helliwell, R. C., Davies, J. J. L., Evans, C. D., Jenkins, A., Coull, M. C., Reynolds, B., Norris, D., and Ferrier, R. C.: Spatial and seasonal variations in nitrogen leaching and acidity across four acid-impacted regions of the UK, Water Air Soil Pollut., 185, 3–19, 2007b.

Hertel, O., Reis, S., Skjøth, C. A., Bleeker, A., Harrison, R., Cape, J. N., Fowler, D., Skiba, U., Simpson, D., Jickells, T., Baker, A., Kulmala, M., Gyldenkærne, S., Sørensen, L. L., and Erisman, J. W.: Nitrogen processes in atmosphere, in: The European Nitrogen Assessment: Sources, Effects and Policy Perspectives, edited by: Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., and Grizzetti, B., Cambridge University Press, Cambridge, UK, 117–210, 2011.

Kocak, D., Özel, M. Z., Gogus, F., Hamilton, J. F., and Lewis, A. C.: Determination of volatile nitrosamines in grilled lamb and vegetables using comprehensive gas chromatography – nitrogen chemiluminescence detection, Food Chem., 135, 2215–2220, 2012.

Mitchell, G. H. and Mykura, W.: The Geology of the Neighbourhood of Edinburgh, 3rd edn., H. M. S. O. Publishing, Edinburgh, 1962.

Moret, S. and Conte, L. S.: A rapid method for polycyclic aromatic hydrocarbon determination in vegetable oils, J. Sep. Sci., 25, 96–100, 2002.

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.

Nieder, R. and Benbi, D. K.: Carbon and Nitrogen in the Terrestrial Environment, illustrated edn., Springer, Netherlands, 2008.

Özel, M. Z., Gogus, F., and Lewis, A. C.: Subcritical water extraction of essential oils from *Thymbra spicata*, Food Chem., 82, 381–386, 2003.

Özel, M. Z., Gogus, F., and Lewis, A. C.: Determination of *Teucrium chamaedrys* volatiles by using direct thermal desorption-comprehensive two-dimensional gas chromatography-time-of-flight mass spectrometry, J. Chromatogr. A, 1114, 164–169, 2006.

Özel, M. Z., Gogus, F., Yagci, S., Hamilton, J. F., and Lewis, A. C.: Determination of volatile nitrosamines in various meat products using comprehensive gas chromatography-nitrogen chemiluminescence detection, Food Chem. Toxicol., 48, 3268–3273, 2010.

Özel, M. Z., Hamilton, J. F., and Lewis, A. C.: New sensitive and quantitative analysis method for organic nitrogen compounds in urban aerosol samples, Environ. Sci. Technol., 45, 1497–1505, 2011.

Paul, E. A. and Clark, F. E.: Soil Microbiology and Biochemistry, Academic Press, London, 1996.

Prospero, J. M., Barrett, K., Church, T., Dentener, F., Duce, R. A., Galloway, J. N., Ii, H. L., Moody, J., and Quinn, P.: Atmospheric deposition of nutrients to the North Atlantic Basin, Biogeochemistry, 35, 27–73, 1996.

Ramirez, N., Özel, M. Z., Lewis, A. C., Marce, R. M., Borrull, F., and Hamilton, J. F.: Determination of nicotine and N-nitrosamines in house dust by pressurized liquid extraction and comprehensive gas chromatography-Nitrogen chemiluminiscence detection, J. Chromatogr. A, 1219, 180–187, 2012.

Russell, K. M., Galloway, J. N., Macko, S. A., Moody, J. L., and Scudlark, J. R.: Sources of nitrogen in wet deposition to the Chesapeake Bay region, Atmos. Environ., 32, 2453–2465, 1998.

Scherer, H. W.: Dynamics and availability of the non-exchangeable NH_4-N: a review, Eur. J. Agron., 2, 149–160, 1993.

Schlesinger, W. H.: Biogeochemistry: an Analysis of Global Change, 2nd edn., Academic Press, San Diego, Calif., London, 1997.

Schulten, H. R. and Schnizer, M.: The chemistry of soil organic nitrogen: a review, Biol. Fert. Soils, 26, 1–15, 1998.

Skiba, U., Jones, S. K., Drewer, J., Helfter, C., Anderson, M., Dinsmore, K., McKenzie, R., Nemitz, E., and Sutton, M. A.: Comparison of soil greenhouse gas fluxes from extensive and intensive grazing in a temperate maritime climate, Biogeosciences, 10, 1231–1241, doi:10.5194/bg-10-1231-2013, 2013.

Tian, Y. H., Yang, L. Z., Yin, B., and Zhu, Z. L.: Wet deposition N and its runoff flow during wheat seasons in the Tai Lake region, China, Agr. Ecosyst. Environ., 141, 224–229, 2011.

van Smeerdijk, D. G. and Boon, J. J.: Characterisation of subfossil *Sphagnum* leaves, rootlets of ericaceae and their peat by pyrolysis-high-resolution gas chromatography-mass spectrometry, J. Anal. Appl. Pyrol., 11, 377–402, 1987.

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, 2010.

Vogt, E.: Nitrogen Fluxes at the Landscape Scale: a Case Study in Scotland, unpublished thesis, The University of Edinburgh, 2011.

Voroney, R. P.: The soil habitat, in: Soil Microbiology, Ecology and Biochemistry, third edn., edited by: Paul, E. A., Academic Press, San Diego, 25–49, 2007.

Yan, X. W.: Sulfur and nitrogen chemiluminescence detection in gas chromatographic analysis, J. Chromatogr. A, 976, 3–10, 2002.

Yesmin, L., Gammack, S. M., Sanger, L. J., and Cresser, M. S.: Impact of atmospheric N deposition on inorganic- and organic-N outputs in water draining from peat, Sci. Total Environ., 166, 201–209, 1995.

Zhang, Y., Zheng, L. X., Liu, X. J., Jickells, T., Cape, J. N., Goulding, K., Fangmeier, A., and Zhang, F. S.: Evidence for organic N deposition and its anthropogenic sources in China, Atmos. Environ., 42, 1035–1041, 2008.

Zhang, Y., Song, L., Liu, X. J., Li, W. Q., Lu, S. H., Zheng, L. X., Bai, Z. C., Cai, G. Y., and Zhang, F. S.: Atmospheric organic nitrogen deposition in China, Atmos. Environ., 46, 195–204, 2012.

Table 1. Statistics of annual concentrations of NH_4^+, NO_3^-, DON and TDN for 2009 and 2010 in wet-only precipitation. Values are based on individual samples collected over the two year period. N^* indicates the number of samples collected.

	NO_3^- $\mu mol\,N\,L^{-1}$	NH_4^+ $\mu mol\,N\,L^{-1}$	DON $\mu mol\,N\,L^{-1}$	TDN $\mu mol\,N\,L^{-1}$
2009				
Mean	15	27	5	47
Min	< LOD	< LOD	< LOD	6
Max	148	273	50	426
SD	21	35	4	50
N^*	227	227	63	63
% TDN	32	58	10	100
2010				
Mean	23	31	5	58
Min	2	2	< LOD	8
Max	260	218	45	483
SD	30	33	5	59
N^*	169	169	63	63
% TDN	39	53	8	100

Table 2. Statistics of annual concentrations of NH_4^+, NO_3^-, DON and TDN for 2009 and 2010 in soil water. Values are based on individual samples collected from dip wells over the two year period. N^* indicates the number of samples collected.

	NO_3^- µmol N L^{-1}	NH_4^+ µmol N L^{-1}	DON µmol N L^{-1}	TDN µmol N L^{-1}
2009				
Mean	1	9	57	67
Min	< LOD	< LOD	11	11
Max	6	91	319	389
Median	0	1	48	54
SD	2	15	44	54
N^*	72	72	72	72
% of TDN	2	13	85	100
2010				
Mean	< LOD	< LOD	59	60
Min	< LOD	< LOD	23	23
Max	8	7	285	285
Median	0	0	44	44
SD	1	1	43	43
N^*	54	54	45	45
% of TDN	0.3	0.4	99.3	100

Table 3. Statistics of annual concentrations of NH_4^+, NO_3^-, DON and TDN for 2009 and 2010 in stream water. Values are based on individual samples collected over the two year period. N^* indicates the number of samples collected.

	NO_3^- $\mu mol\,N\,L^{-1}$	NH_4^+ $\mu mol\,N\,L^{-1}$	DON $\mu mol\,N\,L^{-1}$	TDN $\mu mol\ Nl^{-1}$
2009				
Mean	2	14	48	65
Min	< LOD	5	10	25
Max	14	22	96	118
Median	0	14	47	64
SD	4	3	21	21
N^*	43	43	43	43
% of TDN	4	22	75	100
2010				
Mean	5	13	50	67
Min	< LOD	< LOD	16	16
Max	15	52.3	104	145
Median	4	7.9	46	59
SD	4	13.8	20	31
N^*	48	48	48	48
% of TDN	7	19	74	100

Table 4. Summary of compounds and their concentrations (µmol N L^{-1}) detected by the GC×GC-NCD, and overall DON concentrations (µmol N L^{-1}) derived from TDN-DIN in precipitation samples. Samples collected on dates in bold did not contain compounds at measurable concentrations by the GC×GC-NCD. Blank spaces indicate a value below the detection limit. Rt$_1$ and Rt$_2$ are retention times in seconds for the first and second GC columns.

Sample Rt$_1$/Rt$_2$	DON (TDN-DIN)	Pyrrole 375/1.24	Benzonitrile 825/1.8	Unknown B 11.45/1.52	Unknown C 1218/1.48	Dodecylamine 1590/1.5	Unknown D 1615/1.7	Unknown E 1910/1.7	Unknown F 2200/2.09
9 Jul 2010	9.2							1.6	1.7
13 Jul 2010	13.8		0.4				0.5		
14 Jul 2010	6.5								
15 Jul 2010	5.5								
9 Aug 2010	9.4						0.6		1.8
12 Aug 2010	6.5							0.3	0.3
20 Aug 2010	3.5	0.2						0.6	
23 Aug 2010	2.4							0.5	
6 Sep 2010	3.1							1.9	
13 Sep 2010	3.2								
14 Sep 2010	5.8								
18 Sep 2010	3.3								
1 Oct 2010	0.5								
5 Oct 2010	1.0	0.7		2.0					
6 Oct 2010	−2.4								
18 Oct 2010	2.1			0.7			0.7		
21 Oct 2010	19.8			1.3		0.5	2.4		
24 Oct 2010	7.1			1.2					
25 Oct 2010	1.2			0.5		0.7	1.8		
26 Oct 2010	5.8				0.5			0.9	
1 Nov 2010	3.9								
2 Nov 2010	7.0						0.1		
3 Nov 2010	5.1							0.4	
4 Nov 2010	2.9								
5 Nov 2010	3.9								
6 Nov 2010	4.6								
8 Nov 2010	9.9							0.4	
9 Nov 2010	−2.4								
10 Nov 2010	−0.2								
11 Nov 2010	5.0							0.7	
13 Nov 2010	6.1							0.6	

Table 5. Summary of compounds and their concentrations (μmol N L^{-1}) detected by the GC×GC-NCD, and DON concentrations (μmol N L^{-1}) detected by ANTEK in stream water samples. Samples collected on dates in bold did not contain compounds at measurable concentrations by the GC×GC-NCD. Blank spaces indicate a measured value of below the detection limit. Rt_1 and Rt_2 are retention times in seconds for the first and second GC columns.

Sample Rt_1/Rt_2	DON (TDN-DIN)	Pyrrole 375/1.24	Unknown A 415/1.24	Benzonitrile 825/1.8	N-nitrosodipropylamine 970/1.4	Unknown B 11.45/1.52	Decylamine 1295/1.64	Unknown E 1910/1.7	Unknown F 2200/2.09
11 Aug 2010	45.9	1.3	3.2					0.9	
19 Aug 2010	54.8	0.2	0.3		1.2				
26 Aug 2010	85.2	0.7	2.7	3.0					
10 Sep 2010	30.5	0.2	0.8			1.6			1.4
30 Sep 2010	87.2	3.8	6.9				1.5		
06 Oct 2010	57.8	5.0	3.9				1.8		
12 Oct 2010	69.4	0.8	2.1			1.4			
14 Oct 2010	60.1		0.7			1.3			
15 Oct 2010	49.1								
18 Oct 2010	46.1	1.8	3.4						
19 Oct 2010	75.0		1.4		1.3			1.0	0.8
21 Oct 2010	58.2	2.3	4.0						
23 Oct 2010	65.9	0.3	1.9		0.7			1.2	0.5
26 Oct 2010	56.5	1.0							0.9
28 Oct 2010	57.6	0.7	1.8		1.7			1.8	0.6
02 Nov 2010	61.5	0.6	2.3					1.9	1.0
03 Nov 2010	69.5	2.5	3.4					0.4	
04 Nov 2010	79.4	0.6	0.6					0.4	0.7
05 Nov 2010	58.9								
10 Nov 2010	70.7		0.5					0.5	0.4
11 Nov 2010	65.6	4.3	1.8				1.1	1.6	1.7

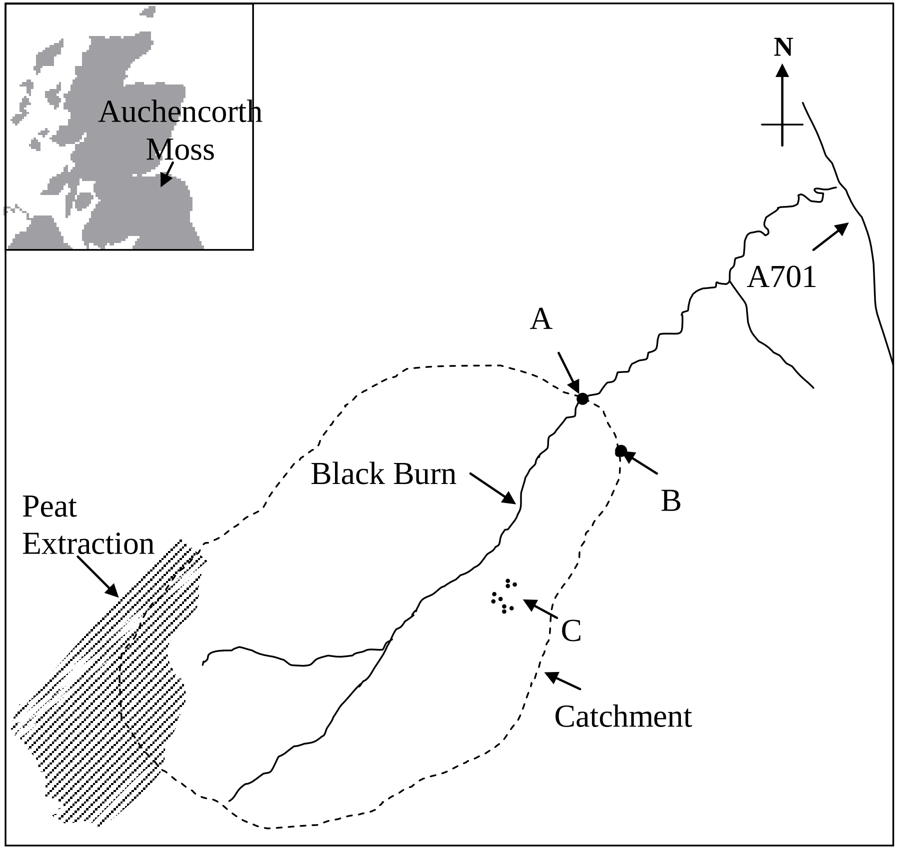

Figure 1. Schematic map of catchment and sampling sites at Auchencorth Moss. Key: (A) study catchment outlet and stream sampling site; (B) monitoring station (wet only analyser); (C) dip wells. Adapted from Dinsmore et al. (2010).

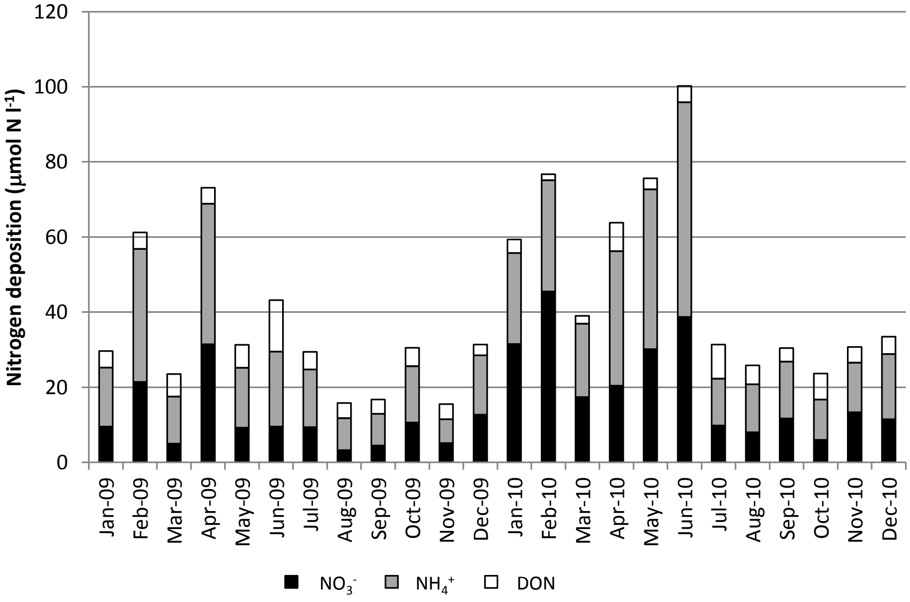

Figure 2. Volume-weighted monthly average concentrations of NH_4^+ (grey), NO_3^- (black) and DON (white) in wet only precipitation.

Title Page
Abstract
Introduction
Conclusions
References
Tables
Figures
◀|
|▶
◀
▶
Back
Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

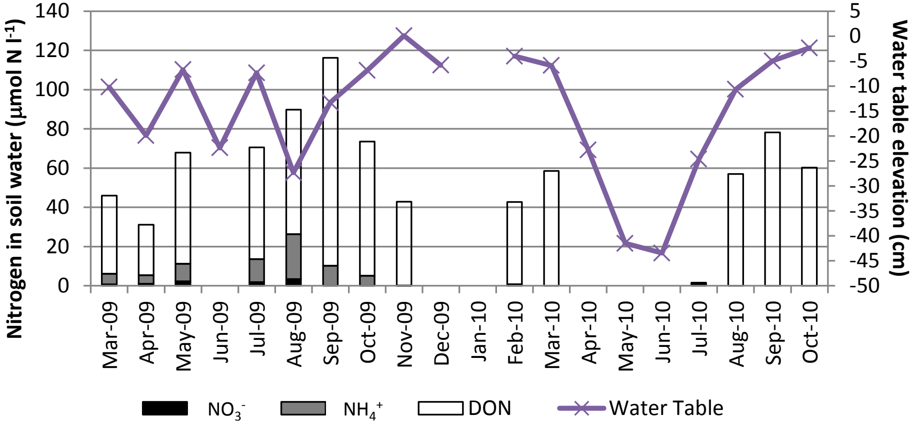

Figure 3. Monthly concentrations of NH^{4+} (grey), NO$_3^-$ (black) and DON (white) in soil water. The line represents monthly water table elevation. The Jun-09 sample was misplaced and Dec-09 and Jan-10 were frozen, the remaining blank spaces indicate the dip wells were dry on the day of collection.

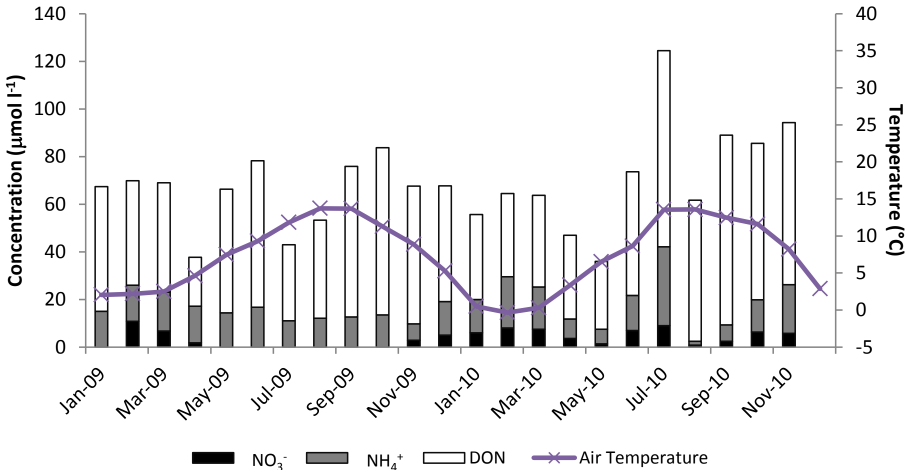

Figure 4. Discharge-weighted monthly mean concentrations of NH_4^+ (grey), NO_3^- (black) and DON (white) in stream water. The line represents mean monthly air temperature.

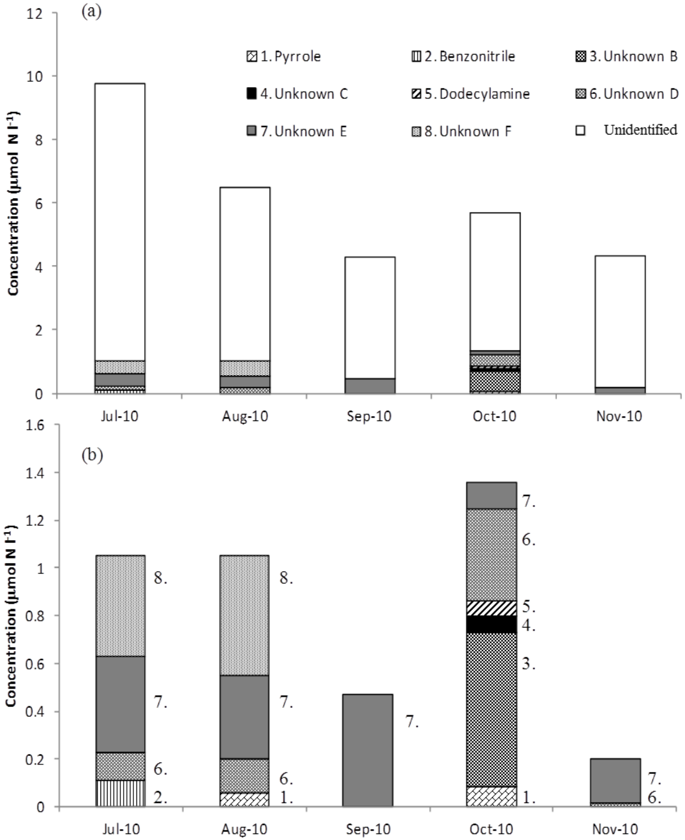

Figure 5. Mean monthly concentrations of the individual DON compounds found in precipitation water. **(a)** includes the DON fraction identified from the ANTEK (white bar). **(b)** excludes the unidentified fraction, so that the speciation achieved by GC×GC-NCD is more clearly seen.

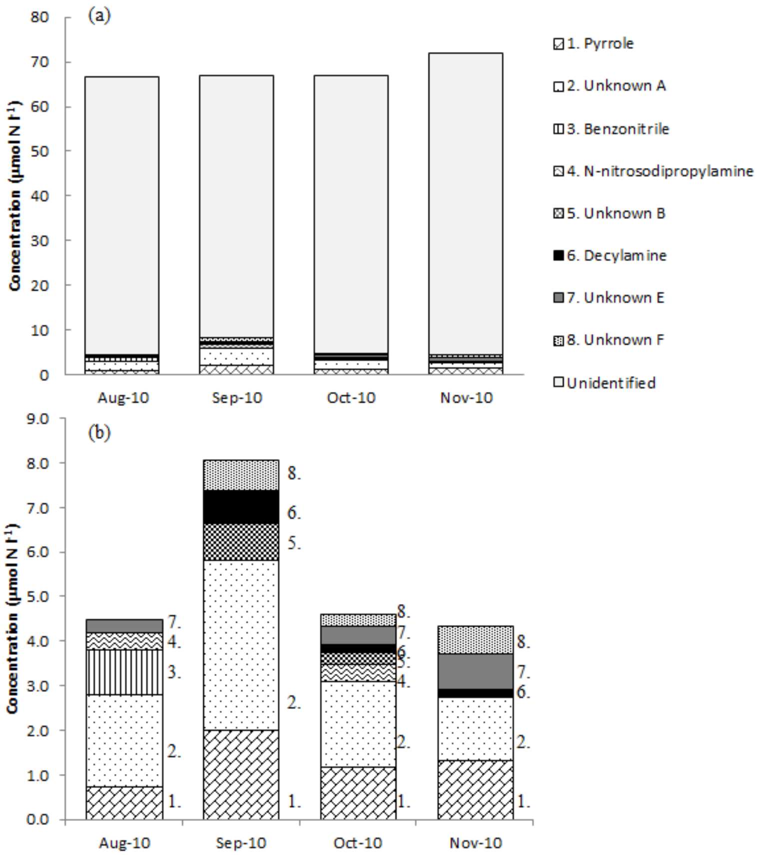

Figure 6. Mean monthly concentrations of the individual compounds found in stream water. **(a)** includes the DON fraction identified from the ANTEK (white bar) **(b)** excludes the "unidentified" fraction, so the fraction detected by GC×GC-NCD is more clearly seen.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀◀ ▶▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion