

# 1 The import and export of organic nitrogen species at a Scottish ombrotrophic 2 peatland

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## 12 **Abstract**

13 Dissolved organic nitrogen (DON) contributes significantly to the overall nitrogen budget,  
14 but is not routinely measured in precipitation or stream water. In order to investigate the  
15 contribution of DON to the deposition and export of N, precipitation, stream and soil water  
16 samples were collected from an ombrotrophic peatland and analysed for DON over a two  
17 year period. In wet only deposition DON contributed up to 10% of the total dissolved  
18 nitrogen (TDN), and was the most dominant fraction in soil water (99%), and stream water  
19 (75%).  $\text{NH}_4^+$  was the most dominate form of N in precipitation, with  $\text{NO}_3^-$  contributing the  
20 least to precipitation, soil water and stream water.

21 Precipitation and stream DON was qualitatively analysed by GCxGC NCD after trapping  
22 onto C18 SPE cartridges. Ten unique compounds were detected and five identified as  
23 pyrrole, benzonitrile, dodecylamine, N-nitrosodipropylamine and decylamine. Five  
24 compounds were present in both precipitation and stream samples: pyrrole, benzonitrile  
25 and three unidentified compounds. The SPE extraction efficiency for DON was very low  
26 (11%), but with improvements DON speciation could become a valuable tool to provide  
27 information on its sources and pathways and inform chemical transport models.

28  
29 *Keywords: organic nitrogen, ammonium, nitrate, precipitation, stream, GCxGC-NCD*

## 30 **1 Introduction**

31 The total deposition of N in the UK was estimated to be approximately 330 Gg in 2004,  
32 with wet and cloud deposition accounting for approximately 211 Gg (63.9%), and the rest  
33 consisting of dry deposition (Fowler et al., 2009, Hertel et al., 2011).

34 Wet deposition of the dissolved inorganic nitrogen (DIN) compounds ammonium ( $\text{NH}_4^+$ )  
35 and nitrate ( $\text{NO}_3^-$ ) has been studied over many years (Violaki et al., 2010, Cape et al., 2011,  
36 Zhang et al., 2012). The former is produced by the dissolution of ammonia gas ( $\text{NH}_3$ ) and  
37 the scavenging of  $\text{NH}_4^+$  aerosol, and the latter by the dissolution of nitric acid gas ( $\text{HNO}_3$ )  
38 and the scavenging of  $\text{NO}_3^-$  aerosol (Russell et al., 1998, Cornell et al., 2003, Tian et al.,  
39 2011). The dissolved organic nitrogen (DON) fraction is less well documented due to  
40 difficulties in measuring it, but it can be an important fraction of the total dissolved nitrogen  
41 (TDN) deposited, and can potentially be biologically available as a source of N (Russell et  
42 al., 1998, Neff et al., 2002, Cornell et al., 2003, Cape et al., 2004). The sources of DON  
43 are not well understood, but it is known to be ubiquitous in the environment, present in  
44 particulate, gaseous and aqueous phases (Cornell et al., 2003, Cape et al., 2004, Özel et al.,  
45 2011). Studies have shown that DON can contribute 30-50% of the wet deposition of water  
46 soluble N (Neff et al., 2002, Cape et al., 2004, Zhang et al., 2008, Cape et al., 2011, Cornell,  
47 2011, Zhang et al., 2012).

48 Several atmospheric species of DON are considered hazardous to human health, and appear  
49 on the Environment Protection Agency (EPA) hazardous air pollutant list (Özel et al.,  
50 2011). Sources of DON are believed to include: pollen; sea spray; soil dust; deposits from  
51 fauna and flora; the scavenging of aerosols; and reactions in the atmosphere between  
52 inorganic gaseous nitrogen species and organic compounds (Prospero et al., 1996, Russell  
53 et al., 1998, Cornell et al., 2003, Calderon et al., 2007, Zhang et al., 2008, Violaki et al.,  
54 2010). Some studies have identified organic N compounds, so that their sources can be  
55 traced. Amino acids, urea, aliphatic amines and peptides have all been found in the  
56 atmosphere from naturally occurring sources (Calderon et al., 2007, Violaki et al., 2010).  
57 The main anthropogenic organic compounds are believed to be N-heterocyclic compounds,  
58 nitrophenols and nitro-polycyclic aromatic hydrocarbons (Violaki et al., 2010). Alky  
59 amides have also been identified and are believed to result from reactions between  $\text{NH}_3$   
60 and fatty acids at high temperatures (Cheng et al., 2006); photochemical reactions are  
61 believed to be responsible for the presence of alky nitrates and peroxyacyl nitrates (Violaki  
62 et al., 2010).

63 As with wet deposition, N is present in streams as both DIN and DON, with most focus  
64 usually being on the DIN fraction. DIN, in particular  $\text{NO}_3^-$ , is often used as an indicator of  
65 N saturation, with higher stream concentrations and changes in seasonal patterns indicating  
66 an increase in the leaching of DIN from the catchment (Cundill et al., 2007, Daniels et al.,  
67 2012). DON, however, is not routinely measured in spite of being the most dominant

68 fraction in waters draining peatland catchments; DON is known to contribute 60-90% of  
69 the TDN load in peatland streams (Yesmin et al., 1995).

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

## 74 **2 Site and methods**

### 75 2.1 Study area

76 Auchencorth Moss (Fig. 4.1) is an ombrotrophic peat bog located in south Scotland,  
77 approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat.  
78 55°47'34 N; long. 03°14'35 W). The site is used primarily for low intensity sheep grazing  
79 (less than one livestock unit km<sup>-2</sup>) and in 2009 a small herd of cows (15-20) also grazed on  
80 the site.

81 The volume of peat in the catchment is estimated to be ~50 million m<sup>3</sup>, with depths up to  
82 5 m, and an average depth of 50 cm. The total peat coverage is ~1214 ha, of which  
83 approximately 170 ha is extracted (located 1.75 - 3.4 km W-SW of the monitoring station)  
84 (Mitchell and Mykura, 1962, Dinsmore, 2008).

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

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

99 The mean water table depth was determined from nine dip wells located close to the  
100 monitoring station (Figure1) and was -14.8 cm, ranging from -52.4 to 7 cm above the peat  
101 surface during the study period (January 2009 - December 2010).

102

## 103 2.2 Wet-only precipitation

104 Auchencorth Moss is a European Monitoring and Evaluation Programme (EMEP)  
105 supersite contributing to the Co-operative Programme for Monitoring and Evaluation of  
106 the Long-range Transmission of Air Pollutants in Europe  
107 ([http://www.emep.int/index\\_facts.html](http://www.emep.int/index_facts.html)). Precipitation was collected daily using an  
108 automated wet-only collector (Eigenbrodt NSA 181/KS, Königsmoor, Germany). A sensor  
109 detected when rain fell, opening the lid and allowing rain to be collected in a PTFE-coated  
110 funnel draining to refrigerated polyethylene bottles. When rainfall ceased, the sensor closed  
111 the lid, protecting the samples from contamination from dry deposition and animal inputs.  
112 The collector was kept at 4°C by an internal cooling system and samples were manually  
113 emptied from the daily collector once a week, where they were stored in a cool room, also  
114 at 4°C. Samples were analysed by Ion Chromatography (IC) for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , following  
115 EMEP protocols (<http://www.nilu.no/projects/ccc/manual/index.html>).

116 A Metrohm 761 Compact Ion Chromatograph (IC) connected in parallel with a Metrohm  
117 733 IC Separation Centre to a Metrohm 766 IC sample processor (Metrohm Ltd., Herisau,  
118 Switzerland) measured  $\text{NO}_3^-$  and  $\text{NH}_4^+$  respectively.  $\text{NO}_3^-$  was determined by pumping an  
119 eluent solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate through a  
120 Metrosep A Supp 5 column. For  $\text{NH}_4^+$  determination, an eluent solution of 24 mM boric  
121 acid, 5 mM tartaric acid and 0.7 mM dipicolinic acid, was pumped through a Metrosep C1  
122 column. Typical detection limits were  $1 \mu\text{mol N l}^{-1}$  for both  $\text{NO}_3^-$  and  $\text{NH}_4^+$ .

123 Whenever enough precipitation was collected, the EMEP sample was subsampled (5 ml)  
124 for analysis of TDN (TDN = DIN + DON). Samples were filtered using Millipore  
125 Hydrophilic PTFE (0.45 $\mu\text{m}$  pore size) syringe filters prior to freezing and later analysed  
126 for TDN by high-temperature catalytic oxidation using an ANTEK 8060-M Nitrogen  
127 Specific HPLC Detector (ANTEK Instruments Inc., Houston, TX, USA). The analysis was  
128 conducted in flow-injection mode, in which 20  $\mu\text{l}$  samples were introduced into an eluent  
129 stream of 10% methanol in deionised water at a flow rate of 250  $\mu\text{l min}^{-1}$ . It was then  
130 combusted in oxygen at 1050 °C, producing nitric oxide (NO) which was detected by

131 chemiluminescence. The detection limit for TDN was  $\sim 1 \mu\text{mol N l}^{-1}$ . DON was determined  
132 by subtracting DIN from TDN.

133 Subsamples were also analysed for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  on the IC at CEH and where compared  
134 to the EMEP samples. The agreement was good, with an average standard error of  $\pm 0.22$   
135  $\mu\text{mol N l}^{-1}$  between  $\text{NO}_3^-$  samples and  $\pm 1.45 \mu\text{mol N l}^{-1}$  between  $\text{NH}_4^+$  samples.

136 The uncertainty of DON is greater than for DIN as a result of errors associated with  
137 measuring TDN and DIN compounding (Cornell et al., 2003). A negative bias may result  
138 from these combined uncertainties, from DON not being fully converted during the total N  
139 analysis, and from losses due to the collection and storage procedure (Russell et al., 1998,  
140 Cornell et al., 2003). A positive bias results from setting small negative values of DON to  
141 zero. To avoid this bias small negative values of DON were included in the data analyses  
142 here. The limit of detection of DON was determined by the summation of the detection  
143 limits of the 3 independent measured concentrations ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN) and was 3  
144  $\mu\text{mol N l}^{-1}$ .

### 145 2.3 Soil water

146 Soil water was collected once or twice per month from nine dip wells, from which the water  
147 table was also measured. They were filtered within 24 hours of collection, using Millipore  
148 Hydrophilic PTFE ( $0.45 \mu\text{m}$  pore size) syringe filters and stored frozen until analysis. The  
149 dip wells consisted of high-density polyethylene perforated pipes ( $0.04 \text{ m}$  diameter) buried  
150 in the ground, with rubber bungs to prevent contamination. Samples were analysed for  
151  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and TDN by the IC and ANTEK methods described previously. DON was  
152 determined by subtracting DIN from TDN.

### 153 2.4 KCl-extractable mineral N

154 Soil cores were collected at a depth of 0-10 cm at three locations (next to the dip wells), in  
155 spring and autumn in 2009 and in spring, summer and winter in 2010.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were  
156 extracted from soil samples using KCl; 15 g of soil were shaken for 1 hour with 50 ml of  
157 1M KCl solution at a rate of 100 rpm. Samples were then filtered using Whatman 42 filter  
158 papers and frozen prior to analysis by IC. TDN was not measured, so DON could not be  
159 determined.

### 160 2.5 Stream water

161 Stream water spot samples were collected from the Black Burn, to the north of the field  
162 station by dipping a 300 ml glass bottle once a week. The samples were filtered within 24

163 hours of collection, using Millipore Hydrophilic PTFE (0.45 $\mu$ m pore size) syringe filters  
164 and frozen until ready for analysis. Samples collected from January 2009 – October 2009  
165 were analysed for TDN, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> using a San<sup>++</sup> Automated Wet Chemistry  
166 Analyzer/Continuous Flow Analyzer (SKALAR, The Netherlands). Samples from  
167 November 2009-November 2010 were analysed for NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and TDN using the IC and  
168 ANTEK methods described above. In both cases, DON was determined by subtracting DIN  
169 from TDN.

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

## 176 2.6 GC×GC-NCD

177 Comprehensive two-dimensional gas chromatography coupled to a nitrogen  
178 chemiluminescence detector (GC×GC-NCD) was used to separate DON into different  
179 peaks and identify individual components where possible. To trap DON samples were  
180 extracted by solid phase extraction (SPE), using Superclean ENVI-18 SPE tube 20  $\mu$ m  
181 polymeric C<sub>18</sub>-reverse phase 500 mg-3 ml SPE cartridges (SUPELCO, Bellefonte, PA,  
182 USA). Cartridges were conditioned with 5 ml methanol followed by 5 ml of water at a rate  
183 of 2-5 ml min<sup>-1</sup>. Between 5 and 18 ml of precipitation and 9 and 24 ml of stream water was  
184 passed through the cartridge at a rate of 2-5 ml min<sup>-1</sup>. The cartridge was thoroughly dried  
185 under vacuum for ~30 minutes, eluted with 5 ml dichloromethane (DCM), and then  
186 concentrated in a stream of nitrogen to a volume of ~ 0.1 ml prior analysis by GC×GC-  
187 NCD. We investigated the extraction efficiency retrospectively on rainwater and river  
188 water samples collected in October 2015 from the same locations the precipitation and  
189 stream water samples were collected in 2009 and 2010, and analysed these for DIN and  
190 TDN as described in section 2.2. As expected the C18 SPE cartridges did not retain NH<sub>4</sub>  
191 and NO<sub>3</sub> on the SPE cartridges, but unfortunately also the retention of DON was low (9%  
192 for the precipitation and 18% for the river waters).

193 The GC×GC-NCD was an Agilent 7890 GC coupled with an Agilent 255 NCD (Agilent  
194 Technologies, Palo Alto, CA, USA). 1  $\mu$ l extracts were injected in pulsed splitless mode at  
195 280 °C and a pressure of 30 psi for 2 min, using a Gerstel automated liquid injector (Gerstel,

196 Mulheim an der Ruhr, Germany). The first dimension column was a non-polar BPX5 (30  
197 m x 0.32 mm i.d. x 0.25  $\mu\text{m}$  film thicknesses), set to an initial temperature of 55  $^{\circ}\text{C}$  for 1  
198 min. The temperature was then increased at a rate of 5  $^{\circ}\text{C min}^{-1}$  until 305  $^{\circ}\text{C}$  where it was  
199 isothermally held for 1 min. The second column was a BPX50 (1.5 m x 0.10 mm i.d. x 0.10  
200  $\mu\text{m}$  film thickness) set to an initial temperature of 70  $^{\circ}\text{C}$  for 1 min, then increasing the  
201 temperature at a rate of 5  $^{\circ}\text{C min}^{-1}$  until 320  $^{\circ}\text{C}$  where it was isothermally held for 1 min.  
202 Both columns were from SGE Analytical Science (VIC, Australia). Helium was used as a  
203 carrier gas at a constant flow of 1  $\text{mL min}^{-1}$  and the data was collected at 50 Hz. Pyrolysis  
204 was carried out at 900  $^{\circ}\text{C}$  with a hydrogen flow rate of 4  $\text{ml min}^{-1}$  and oxygen flow rate of  
205 10  $\text{ml min}^{-1}$ .  
206 The detector shows an equimolar response regardless of the chemical state of the organic  
207 nitrogen (except azo compounds), allowing nitrogen-containing compounds to be  
208 quantified without the need for a separate calibration standard for each compound (Yan,  
209 2002, Özel et al., 2011). Details of the optimization of the NCD response and the analytical  
210 performance with respect to equimolar response using standards was evaluated by Özel et  
211 al., (2011).

## 212 **3 Results**

### 213 3.1 Meteorology

214 Total rainfall was determined from the volume of rain collected in the wet only analyser.  
215 In 2009 the total rainfall was 902 mm with monthly totals varying from 16 mm in February  
216 to 180 mm in November. The mean monthly temperature varied from 0.5  $^{\circ}\text{C}$  in December  
217 to 13.7  $^{\circ}\text{C}$  in July, with a yearly mean of 7.6  $^{\circ}\text{C}$ . In 2010 the total rainfall was 732 mm  
218 with monthly totals varying from 21 mm in May to 128 mm in November. However, a  
219 significant amount of snow fell, which was not recorded by the wet-only collector. Based  
220 on the ratio of discharge and precipitation (Dinsmore et al., 2013, Skiba et al., 2013) it was  
221 estimated that snow accounted for an additional 291 mm, making the total precipitation  
222 collected for 2010 approximately 1023 mm. The mean monthly temperature varied from -  
223 2.0  $^{\circ}\text{C}$  in December to 13.6  $^{\circ}\text{C}$  in July, with a yearly mean of 6.6  $^{\circ}\text{C}$ .

### 224 3.2 Wet-only N deposition

225 Figure 2 shows the volume-weighted monthly mean concentrations of N in precipitation.  
226 The temporal variation of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  follow a similar pattern, with DON differing. In  
227 both 2009 and 2010 (Table 1),  $\text{NH}_4^+$  was the dominant component of wet-only deposition

228 with annual mean concentrations of 27.2  $\mu\text{mol N l}^{-1}$  (58% of TDN) and 30.7  $\mu\text{mol N l}^{-1}$   
229 (53% of TDN) respectively. The contribution of  $\text{NO}_3^-$  was greater in 2010 than in 2009,  
230 with mean concentrations of 15.0  $\mu\text{mol N l}^{-1}$  (32% of TDN) in 2009 and 22.7  $\mu\text{mol N l}^{-1}$   
231 (39% of TDN) in 2010. Although DON contributed the least to annual concentrations in  
232 both years, on a monthly timescale there were a few occasions when DON exceeded  $\text{NO}_3^-$   
233 (March 2009, June 2009, Aug 2009 and Oct 2010). A loose seasonal pattern was observed  
234 for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , with peak concentrations occurring between January and June,  
235 especially in 2010. DON has no clear seasonal pattern, although the lowest concentrations  
236 seem to occur in the winter months (Nov- Jan). A weak, but significant correlation was  
237 found between  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in 2009 ( $R^2 = 0.45$ ,  $p < 0.001$ ) and a slightly stronger  
238 correlation in 2010 ( $R^2 = 0.62$ ,  $p < 0.001$ ). No correlations were observed between  $\text{NH}_4^+$ ,  
239 DON, temperature, rainfall or precipitation;  $\text{NO}_3^-$ , DON, temperature, rainfall or  
240 precipitation; or DON, temperature, rainfall or precipitation.

### 241 3.3 Soil water and KCl-extractable N

242 As expected for a peatland, DON dominates TDN concentrations in the soil water. The  
243 contribution of DON to TDN was higher in 2010 at 99% compared to 85% in 2009 (Table  
244 2). Mean annual  $\text{NO}_3^-$  concentrations were 1.2  $\mu\text{mol N l}^{-1}$  (2% of TDN) in 2009 and 0.2  
245  $\mu\text{mol N l}^{-1}$  (0.3% of TDN) in 2010. Mean annual  $\text{NH}_4^+$  concentrations were also larger in  
246 2009 (8.6  $\mu\text{mol N l}^{-1}$ ) than in 2010 (0.2  $\mu\text{mol N l}^{-1}$ ). The contribution of  $\text{NH}_4^+$  to TDN was  
247 thus much larger in 2009 at 13% and just 0.4% in 2010. Due to data gaps, caused by dip  
248 wells remaining empty in low rainfall periods, or frozen in winter 2010, it was difficult to  
249 assess seasonal patterns.

250 Soil extractions of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  using 1 M KCl on two occasions in 2009 and 3 three  
251 occasions in 2010 showed similar trends; no detectable  $\text{NO}_3^-$ , and  $\text{NH}_4^+$  concentrations of  
252  $29 \pm 12 \mu\text{mol N l}^{-1}$  and  $39 \pm 20 \mu\text{mol N l}^{-1}$  for 2009 and 2010, respectively.

### 253 3.4 Concentration and forms of N in stream water

254 DON is the dominant N species found in the stream water. Monthly mean discharge  
255 weighted concentrations contributed on average 74.6% (in 2009) and 74.3% (in 2010) to  
256 TDN; with the highest concentrations in summer/autumn, however no clear seasonal  
257 pattern was evident (Figure 4, Table 3). Monthly mean discharge weighted concentrations  
258 of  $\text{NO}_3^-$  ranged from 0.0 to 13.7  $\mu\text{mol N l}^{-1}$  in 2009 and 0.0 to 15.2  $\mu\text{mol N l}^{-1}$  in 2010.  
259 Annual mean concentrations were 2.3  $\mu\text{mol N l}^{-1}$  in 2009 and 4.5  $\mu\text{mol N l}^{-1}$  in 2010. In



260 2009, concentrations varied seasonally; largest  $\text{NO}_3^-$  concentrations were measured during  
261 the cooler months and the smallest during the warmer months. In summer 2009 there was  
262 no detectable  $\text{NO}_3^-$ . In 2010 stream water  $\text{NO}_3^-$  concentrations initially followed a similar  
263 pattern as in 2009, with concentrations increasing during the winter months and decreasing  
264 as temperature increased and summer approached. However, there was a large increase in  
265  $\text{NO}_3^-$  concentrations in June and July 2010. Consequently, average annual  $\text{NO}_3^-$   
266 concentrations in 2010 were nearly double those in 2009, contributing 6.6% of TDN  
267 compared to 3.6% of TDN (Table 3). Monthly median concentrations for  $\text{NO}_3^-$  for the  
268 whole period showed a similar pattern to monthly discharge-weighted mean  
269 concentrations, with the exception of June 2010, which is reduced to a summer low of 0  
270  $\mu\text{mol N l}^{-1}$ , suggesting the monthly mean value was skewed by an unusually large value.  
271 Median concentrations made little difference to the July 2010 maximum. July 2010 also  
272 showed a maximum in the mean concentrations of DON and  $\text{NH}_4^+$ .  
273 Monthly mean discharge weighted concentrations of  $\text{NH}_4^+$  ranged from 5.4 to 21.9  $\mu\text{mol}$   
274  $\text{N l}^{-1}$  with an annual mean of 14.1  $\mu\text{mol N l}^{-1}$  in 2009, and 0.0 to 52.3  $\mu\text{mol N l}^{-1}$  with an  
275 annual mean of 12.9  $\mu\text{mol N l}^{-1}$  in 2010. Concentrations of  $\text{NH}_4^+$  were consistently higher  
276 than  $\text{NO}_3^-$  and there was no clear seasonal pattern. No correlation was observed between  
277  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON, discharge, temperature, rainfall (both air and stream) or precipitation.

### 278 3.5 DON speciation by GC×GC-NCD

279 Tables 4 and 5 display breakdowns of the individual DON compounds detected by the  
280 GC×GC-NCD and their concentrations for precipitation and stream water, respectively.  
281 The plasticiser N-butyl-benzenesulphonamide (not included in tables) was a prominent  
282 compound in all samples, with extremely high concentrations, sometimes higher than TDN  
283 detected in the precipitation by ANTEK. We assume that the N-butyl-  
284 benzenesulphonamide detected was most likely to be a sampling contaminant from the  
285 storage bottles during storage in the freezer prior to analysis, or from SPE extraction tubes  
286 by reaction with the DCM. This contamination was not detected in blank water samples  
287 (deionised water) or by the ANTEK as samples run on this machine were filtered directly  
288 into glass vials for storage before analysis. The source of this contamination is discussed  
289 later and the compound was thus excluded from the results.  
290 In 13 of the 31 precipitation samples, and 2 of the 21 stream samples, no DON compounds  
291 were detected or the peaks were too small to be distinguishable from background noise.

292 The limit of detection (LOD) using the optimized method was determined between 0.16-  
293 0.27  $\mu\text{gN}$  using GC $\times$ GC-NCD of standard mixtures (Özel et al., 2011).

294 Peak identification was carried out by comparing retention times and  $R_{t2}$ ) of sample peaks  
295 ( $R_{t1}$ ) with retention times of known standards ( $R_{t2}$ ). This could lead to some  
296 misidentification, however co-elution is greatly reduced using GC $\times$ GC and there is very  
297 good retention time stability between runs. Several peaks, consistently present in some  
298 samples, could not be identified as they did not match any of the retention times of the  
299 standards available, and therefore were labelled “Unknown” A-F. In total 10 unique  
300 compounds were found to be present in the stream and precipitation, of which only 5 could  
301 be identified. Tables 4 and 5 present a summary of the compounds identified in  
302 precipitation and stream water DON, respectively. Both the precipitation and the stream  
303 water contained 8 distinct compounds, 5 of which were in common.

304 The most common compound identified in the precipitation samples was Unknown E,  
305 present in 10 samples, followed by Unknown D in 6 samples and Unknown B in 5 samples,  
306 with mean concentrations of  $0.3 \mu\text{mol N l}^{-1}$ ,  $0.14 \mu\text{mol N l}^{-1}$  and  $0.2 \mu\text{mol N l}^{-1}$ . Two  
307 precipitation samples contained pyrrole, with a mean concentration of  $0.03 \mu\text{mol N l}^{-1}$ .  
308 Unknown F was in 3 samples (mean concentrations of  $0.1 \mu\text{mol N l}^{-1}$ ), dodecylamine was  
309 in 2 samples (mean concentration of  $0.02 \mu\text{mol N l}^{-1}$ ), and Unknown C was in one sample  
310 ( $0.02 \mu\text{mol N l}^{-1}$ ). The precipitation samples did not contain Unknown A, N-  
311 nitrosodipropylamine or decylamine, which were found in the stream samples.

312 The most common compound identified in the stream samples was Unknown A, the mean  
313 concentration was  $2.0 \mu\text{mol N l}^{-1}$  (Table 5). Pyrrole was the next most common compound,  
314 found in 18 of the stream samples, with a mean concentration of  $1.2 \mu\text{mol N l}^{-1}$ . Unknowns  
315 E and F both appeared in 9 stream samples, with mean concentrations of  $0.5 \mu\text{mol N l}^{-1}$   
316 and  $0.4 \mu\text{mol N l}^{-1}$ . N-nitrosodipropylamine (NDPA) was present in 4 stream samples,  
317 followed by Unknown B and decylamine in 3 stream samples. Mean concentrations were  
318  $0.2 \mu\text{mol N l}^{-1}$  for all three compounds. Unknown D, Unknown C and dodecylamine,  
319 present in the precipitation samples, were absent from the stream samples.

320 In both the stream and precipitation samples, only one sample contained benzonitrile, with  
321 means of  $0.01 \mu\text{mol N l}^{-1}$  (precipitation) and  $0.1 \mu\text{mol N l}^{-1}$  (stream).

322 Figures 5a and 6a display breakdowns of the monthly means of individual DON  
323 compounds extracted with the C18 SPE cartridges prior identification by the GC $\times$ GC-NCD  
324 method and the remaining DON measured by ANTEK for precipitation and stream water,

325 respectively. Figures 5b and 6b show the monthly means of individual DON compounds  
326 detected by the GC×GC-NCD only, to make this fraction more visible. In both cases, the  
327 majority of DON was not was “unidentified”, contributing a mean of 91% and 82% of total  
328 DON detected in precipitation and stream water, respectively. In the precipitation samples,  
329 Unknown E is the only compound present in all 5 sampling months, and is the only  
330 compound identified in September. October had the most identified compounds present,  
331 with 6 of the 8 compounds measured (Fig. 5b). In the stream samples, pyrrole and  
332 Unknown A were present in all 4 sampling months. October also had the most identified  
333 compounds present, with 7 of the 8 compounds present (Fig. 4).

## 334 **4 Discussion**

### 335 4.1 The composition of N in precipitation

336 Cape et al., (2004) studied several sites in the UK on a range of land uses and noted an  
337 annual cycle for DIN and DON, with peak concentrations for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  occurring in  
338 April-June 2000-2002 and a DON peak occurring later (June-August 2000-2002). Both  
339 DIN and DON showed minima in winter. The data presented here are similar, but with  
340 earlier DIN maxima in (Feb-April in 2009 and Feb-June 2010) followed by lower values  
341 in the autumn and beginning of winter. DON also peaked earlier than reported by Cape et  
342 al. (2004) but roughly a month after DIN peaked in both 2009 and 2010. Generally, sources  
343 of  $\text{NH}_4^+$  in precipitation tend to be of agricultural origin, and sources of  $\text{NO}_3^-$  in  
344 precipitation from combustion activities (Cape et al., 2011). Although Auchencorth Moss  
345 is located in a rural setting and with minimal agricultural activity on the peatland itself;  
346 there are several chicken farms in the area. Chickens farms emit ammonia ( $\text{NH}_3$ ), which  
347 when dissolved in rainwater, produces  $\text{NH}_4^+$  (Schlesinger, 1997).  $\text{NH}_4^+$  also makes up a  
348 large fraction of atmospheric aerosols and is often transported further downwind of its  
349 source (Nieder and Benbi, 2008), where it can then be washed out and deposited by  
350 precipitation.

351 Sources of  $\text{NO}_3^-$  include motor vehicles and stationary combustion sources (power stations,  
352 domestic heating) following atmospheric oxidation of the emitted nitrogen oxides. As a  
353 secondary pollutant, nitric acid and nitrates are less easily traced back to sources. The  
354 sources of DON are more difficult to generalise and the magnitude of DON is likely to be  
355 the result of different contributions of biological and anthropogenic local origin and those  
356 deposited through long range transport. Spring maxima of DON may be due to the release  
357 of pollen, plant debris and spores (Violaki et al., 2010), or spreading of manure and mineral

358 N fertilisers (Neff et al., 2002, Zhang et al., 2012). Conversely, autumn maxima may be  
359 linked to decomposition of vegetation (Cape et al., 2004). The contribution of DON to  
360 TDN is low at Auchencorth – 10.0% and 8.3% in 2009 and 2010, respectively, when  
361 compared to the 24% (June 2005 to April 2007) measured at Bush Estate, an agricultural  
362 area 10 km north of Auchencorth Moss dominated by grazed grasslands with high stocking  
363 densities and receiving high rates of mineral nitrogen fertiliser ( $\sim 200 \text{ kg N ha}^{-1} \text{ y}^{-1}$ ,  
364 Gonzalez Benitez et al., 2009). The literature average from a range of environments is  
365 30% (Cornell et al., 2003, Cape et al., 2004, Zhang et al., 2008, Cape et al., 2011, Zhang  
366 et al., 2012).

367 Previous studies of precipitation DIN and DON reported varying degrees of correlation  
368 between DON,  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . For example, Violaki et al. (2010) found no correlation  
369 between DON,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in wet deposition in the Eastern Mediterranean. Zhang et  
370 al. (2008) also did not observe correlation between DON,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in precipitation  
371 at 15 sites in China. However, when an additional 37 sites from across the globe were added  
372 to these data, positive relationships between DON and DIN were found, suggesting that  
373 broadly similar sources of DON and DIN at the global, but not regional, scale. In a number  
374 of studies, DON and  $\text{NH}_4^+$  were correlated, or at least more closely correlated than DON  
375 and  $\text{NO}_3^-$ , suggesting DON is more closely associated with agricultural sources than with  
376 combustion processes (Cape et al., 2004, Chen et al., 2008, Cape et al., 2011, Zhang et al.,  
377 2012). Our Auchencorth Moss study showed weak to moderate correlations between  $\text{NH}_4^+$   
378 and  $\text{NO}_3^-$  but no correlation between DIN and DON. This suggests that whilst DIN  
379 compounds might share a common source (e.g. secondary aerosol), DON does not. This is  
380 further supported by the later seasonal maxima of DON compared to those of the DIN  
381 compounds (Cape et al., 2011).

#### 382 4.2 N in the soil solution

383 Interestingly, the TDN and DIN deposited as precipitation in 2010 was larger than in 2009,  
384 but the soil chemistry showed the opposite. The larger soil water DIN concentrations in  
385 2009 may be due to the activities of sheep which grazed on this moorland at very low  
386 livestock density of less than  $1 \text{ ewe ha}^{-1}$  and also a small herd of 15 – 20 cattle. In 2009,  
387 sheep and sheep droppings were observed in and around the vicinity of the dip wells and  
388 where the soil cores were collected; the small cattle herd (15-20) also had access to this  
389 area. However, in 2010, there were no cattle on site and the sheep frequented another area  
390 of this large peatland.

391

#### 392 4.3 The composition of N in stream water

393 DON is the dominant form of stream water N in high rainfall areas, catchments with steep  
394 slopes and those draining peatlands. Typical DON contributions vary from 54% to 82%  
395 annually (Chapman et al., 2001, Cundill et al., 2007, Helliwell et al., 2007a), which is  
396 similar to the 75% and 74% measured in the Black Burn for 2009 and 2010, respectively.  
397 Mean annual  $\text{NH}_4^+$  concentrations (22% in 2009 and 19% in 2010) were larger than  $\text{NO}_3^-$   
398 concentrations (3.6% in 2009 and 6.6% in 2010). This was also observed by Helliwell et  
399 al. (2007a) in four upland regions in the UK. Usually, the leaching of inorganic N is  
400 dominated by  $\text{NO}_3^-$ , whereas  $\text{NH}_4^+$  remains in the soil in weak association with organic  
401 matter and incorporation into clay lattices (Scherer, 1993, Chapman and Edwards, 1999,  
402 Davies et al., 2005, Helliwell et al., 2007a).

403 A previous study carried out at the Black Burn in 2008, approximately 2.5 km downstream  
404 from the sampling site reported here, also found DON to be the dominant species (mean  
405 concentration of  $47.9 \mu\text{mol N l}^{-1}$ ) contributing 71 % of the TDN, followed by  $\text{NH}_4^+$  (mean  
406 concentration  $10.7 \mu\text{mol N l}^{-1}$ ), contributing 16% of TDN, and  $\text{NO}_3^-$  (mean concentration  
407  $8.6 \mu\text{mol N l}^{-1}$ ), contributing 13% of TDN (Vogt 2011). The DON values are comparable  
408 to the study reported here, but the Vogt study found lower  $\text{NH}_4^+$  and higher  $\text{NO}_3^-$  values.  
409 These differences may be due to the location of the Vogt study site, which was further  
410 downstream, next to a busy road, and was frequented by sheep more regularly than our  
411 upstream site. No correlation was found between the wet deposition of atmospheric N and  
412 stream concentrations suggesting that precipitation does not represent a major source of  
413 stream water N.

#### 414 4.4 Seasonal patterns of N in stream water

415 No clear seasonal pattern was identified for DON, although the general trend was higher  
416 concentrations in the warmer months. Also Chapman et al. (2001), who studied 28  
417 Scottish upland streams, found DON to be larger in the summer than winter months. They  
418 suggested that this was due to an increase of in-stream biological DON production,  
419 mediated by algae and microorganisms, rather than increased leaching from the soil.  
420 The seasonal pattern of  $\text{NO}_3^-$ , where concentrations were higher in cooler months and lower  
421 in warmer months has been observed in numerous upland studies (Black et al., 1993,  
422 Chapman et al., 2001, Daniels et al., 2012). In warmer months, the biological uptake of

423 NO<sub>3</sub><sup>-</sup> by plants and microbes both in the terrestrial and aquatic systems is at its highest,  
424 immobilising NO<sub>3</sub><sup>-</sup>. In winter, productivity declines, increasing the amount of NO<sub>3</sub><sup>-</sup>  
425 available to be leached into the stream and its residence time in the stream (Black et al.,  
426 1993, Chapman et al., 2001, Helliwell et al., 2007b). The summer peaks in June and July  
427 2010 are unusual and different to the summer lows observed in 2009. The high June value  
428 appears to be due to one high concentration, skewing the mean monthly concentration; the  
429 median value for June was 0 μmol N l<sup>-1</sup>. The high July 2010 peak is also evident in the  
430 mean concentrations of DON, and NH<sub>4</sub><sup>+</sup>, and is still reflected in median values. The reason  
431 for these high values are unclear, however the differences in discharge and precipitation  
432 between the two sampled years may be a contributing factor.

#### 433 4.5 DON speciation by GC×GC-NCD

434 More than 82% of the DON was not trapped by the SPE cartridges. This low retention  
435 implies that further work is needed to improve the extraction procedure and maximise the  
436 applicability of this technique, or alternatives, such as liquid-liquid extractions or stir bar  
437 sorptive extraction, and thereby provide a more comprehensive picture of the DON species  
438 in precipitation and stream waters. For example, it is noticeable that highly polar and large  
439 molecular weight DON species were not detected by the GC×GC-NCD, and presumably  
440 also not retained by the C18 SPE cartridges.

441 Whilst some of the compounds detected by the GC×GC-NCD appear in the precipitation  
442 and the stream water, the two main compounds identified in the stream water were only  
443 present in precipitation in small amounts or not present at all. This suggested that at least  
444 some sources of DON in precipitation and stream waters are different. Schulten and  
445 Schnitzer, (1998) investigated the chemistry of organic matter of humic substances and  
446 soils. Amongst other compounds they identified pyrrole and benzonitrile, along with  
447 derivatives of pyrrole. Pyrrole and pyrrolic compounds are a major N source in coal and  
448 are often found in peats (van Smeerdijk and Boon, 1987, Schulten and Schnitzer, 1998). It  
449 is therefore likely that the source of pyrrole in the streams was the peat in the surrounding  
450 catchment. Pyrrole has also been identified in fog waters where it was found to be quickly  
451 degraded during transport by photochemistry (Anastasio and McGregor, 2000). It is  
452 thought to be present in the atmosphere originating from soil dust rich in humic/fluvic  
453 material (Schulten and Schnitzer, 1998, Anastasio and McGregor, 2000). This may explain  
454 the presence of a small amount of pyrrole found in the precipitation samples. The three  
455 other compounds identified were all amines: dodecylamine (found only in the

456 precipitation), NDPA and decylamine (both only found in the stream). The number of  
457 unknown compounds detected may be reduced by running more standards for comparison.  
458 In spite of the low DOC retention by the SPE cartridges, our attempt to describe the DON  
459 speciation in precipitation and streams, suggests that further investigation could provide  
460 some insight into the temporal and sector dependent speciation of DON and their sources.

461

462

## 463 5 Conclusions

464 DON is an important source of nitrogen in precipitation and stream water and must not be  
465 ignored in measurements of atmospheric nitrogen deposition rates or stream water nitrogen  
466 balances. The mean volume-weighted concentration of DON found in the precipitation  
467 over the total study period was  $4.8 \mu\text{mol N l}^{-1}$ , with a mean contribution of 9% to TDN.

468 DON in stream water was a major contributor to TDN (with an overall mean of 75%) and  
469 showed no clear seasonal pattern. The presence of pyrrole, the large DON concentrations  
470 and the high  $\text{NH}_4^+$  in stream water, suggest mineralisation of organic N stored in peat was  
471 one of the sources.

472 In soil water, DON contributed an overall mean of 92% to TDN. The mean concentrations  
473 of DON did not vary greatly between the years but the concentration of  $\text{NH}_4^+$  did ( $8.6 \mu\text{mol}$   
474  $\text{N l}^{-1}$  in 2009 and  $0.2 \mu\text{mol N l}^{-1}$  in 2010), possibly due to localised impact of animal waste  
475 and the importance of water table variation on the availability of N to plants and on  
476 immobilisation.

477 GC×GC-NCD shows promise as a technique to identify compounds in stream  
478 water/precipitation and their potential sources, but requires further development.

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487 **References**

- 488 Anastasio, C. and McGregor, K. G. (2000) 'Photodestruction of dissolved organic nitrogen  
489 species in fog waters', *Aerosol Science and Technology*, 32(2), 106-119.  
490
- 491 Billett, M. F., Palmer, S. M., Hope, D., Deacon, C., Storeton-West, R., Hargreaves, K. J.,  
492 Flechard, C. and Fowler, D. (2004) 'Linking land-atmosphere-stream carbon fluxes  
493 in a lowland peatland system', *Global Biogeochemical Cycles*, 18(1), GB1024.  
494
- 495 Black, K. E., Lowe, J. A. H., Billett, M. F. and Cresser, M. S. (1993) 'Observations on  
496 the changes in nitrate concentrations along streams in seven upland moorland  
497 catchments in Northeast Scotland', *Water Research*, 27(7), 1195-1199.  
498
- 499 Calderon, S. M., Poor, N. D. and Campbell, S. W. (2007) 'Estimation of the particle and  
500 gas scavenging contributions to wet deposition of organic nitrogen', *Atmospheric  
501 Environment*, 41(20), 4281-4290.  
502
- 503 Cape, J., Anderson, M., Rowland, A. and Wilson, D. (2004) 'Organic nitrogen in  
504 precipitation across the United Kingdom', *Water, Air, & Soil Pollution: Focus*, 4(6),  
505 25-35.  
506
- 507 Cape, J. N., Cornell, S. E., Jickells, T. D. and Nemitz, E. (2011) 'Organic nitrogen in the  
508 atmosphere - Where does it come from? A review of sources and methods',  
509 *Atmospheric Research*, 102(1-2), 30-48.  
510
- 511 Chapman, P. J. and Edwards, A. C. (1999) 'The impact of atmospheric  
512 nitrogen deposition on the behaviour of nitrogen in surface waters' in Langan, S. J.,  
513 ed. *The Impact of Nitrogen Deposition on Natural and Semi-Natural Ecosystems*,  
514 Dordrecht, The Netherlands: Kluwer Academic Publishers, 153-212.  
515
- 516 Chapman, P. J., Edwards, A. C. and Cresser, M. S. (2001) 'The nitrogen composition of  
517 streams in upland Scotland: some regional and seasonal differences', *Science of the  
518 Total Environment*, 265(1-3), 65-83.  
519
- 520 Chen, N.-W., Hong, H.-S. and Zhang, L.-P. (2008) 'Wet deposition of atmospheric nitrogen  
521 in Jiulong River Watershed', *Huanjing Kexue*, 29(1), 38-46.  
522
- 523 Cheng, Y., Li, S.-M. and Leithead, A. (2006) 'Chemical Characteristics and Origins of  
524 Nitrogen-Containing Organic Compounds in PM<sub>2.5</sub> Aerosols in the Lower Fraser  
525 Valley', *Environmental Science & Technology*, 40(19), 5846-5852.  
526
- 527 Cornell, S. E. (2011) 'Atmospheric nitrogen deposition: Revisiting the question of the  
528 importance of the organic component', *Environmental Pollution*, 159(10), 2214-  
529 2222.  
530
- 531 Cornell, S. E., Jickells, T. D., Cape, J. N., Rowland, A. P. and Duce, R. A. (2003) 'Organic  
532 nitrogen deposition on land and coastal environments: a review of methods and  
533 data', *Atmospheric Environment*, 37(16), 2173-2191.  
534



- 535 Cundill, A. P., Chapman, P. J. and Adamson, J. K. (2007) 'Spatial variation in  
536 concentrations of dissolved nitrogen species in an upland blanket peat catchment',  
537 *Science of the Total Environment*, 373(1), 166-177.  
538
- 539 Daniels, S. M., Evans, M. G., Agnew, C. T. and Allott, T. E. H. (2012) 'Ammonium release  
540 from a blanket peatland into headwater stream systems', *Environmental Pollution*,  
541 163, 261-272.  
542
- 543 Davies, J. J. L., Jenkins, A., Monteith, D. T., Evans, C. D. and Cooper, D. M. (2005)  
544 'Trends in surface water chemistry of acidified UK Freshwaters, 1988-2002',  
545 *Environmental Pollution*, 137(1), 27-39.  
546
- 547 Dinsmore, K. J. (2008) *Atmosphere-Soil-Stream Greenhouse Gas Fluxes from Peatlands*,  
548 unpublished thesis, The University of Edinburgh.  
549
- 550 Dinsmore, K. J., Billett, M. F., Skiba, U. M., Rees, R. M., Drewer, J. and Helfter, C. (2010)  
551 'Role of the aquatic pathway in the carbon and greenhouse gas budgets of a peatland  
552 catchment', *Global Change Biology*, 16, 2750-2762.  
553
- 554 Dinsmore, K. J., Billett, M. F., Dyson, K. E. (2013) 'Temperature and precipitation drive  
555 temporal variability in aquatic carbon and GHG concentrations and fluxes in a  
556 peatland catchment', *Global Change Biology*, 10 (7), 2133-2148  
557
- 558 Flechard, C. R. and Fowler, D. (1998) 'Atmospheric ammonia at a moorland site. I: The  
559 meteorological control of ambient ammonia concentrations and the influence of  
560 local sources', *Quarterly Journal of the Royal Meteorological Society*, 124(547),  
561 733-757.  
562
- 563 Fowler, D., Pilegaard, K., Sutton, M. A., Ambus, P., Raivonen, M., Duyzer, J., Simpson,  
564 D., Fagerli, H., Fuzzi, S., Schjoerring, J. K., Granier, C., Neftel, A., Isaksen, I. S.  
565 A., Laj, P., Maione, M., Monks, P. S., Burkhardt, J., Daemmgen, U., Neiryneck, J.,  
566 Personne, E., Kruit, R. W., Bahl, K. B., Flechard, C., Tuovinen, J. P., Coyle, M.,  
567 Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L., Ammann, C., Cieslik, S.,  
568 Paoletti, E., Mikkelsen, T. N., Poulsen, H. R., Cellier, P., Cape, J. N., Horváth, L.,  
569 Loreto, F., Niinemets, Palmer, P. I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D.,  
570 Pryor, S., Gallagher, M. W., Vesala, T., Skiba, U., Brüeggemann, N., Boltenstern,  
571 S. Z., Williams, J., O'Dowd, C., Facchini, M. C., de Leeuw, G., Flossman, A.,  
572 Chaumerliac, N. and Erisman, J. W. (2009) 'Atmospheric Composition Change:  
573 Ecosystems - Atmosphere interactions', *Atmospheric Environment*, 43(33), 5193-  
574 5267.  
575
- 576 Helliwell, R. C., Coull, M. C., Davies, J. J. L., Evans, C. D., Norris, D., Ferrier, R. C.,  
577 Jenkins, A. and Reynolds, B. (2007a) 'The role of catchment characteristics in  
578 determining surface water nitrogen in four upland regions in the UK', *Hydrology  
579 and Earth System Sciences*, 11(1), 356-371.  
580
- 581 Helliwell, R. C., Davies, J. J. L., Evans, C. D., Jenkins, A., Coull, M. C., Reynolds, B.,  
582 Norris, D. and Ferrier, R. C. (2007b) 'Spatial and seasonal variations in nitrogen  
583 leaching and acidity across four acid-impacted regions of the UK', *Water Air and  
584 Soil Pollution*, 185(1-4), 3-19.  
585

- 586 Hertel, O., Reis, S., Skjøth, C. A., Bleeker, A., Harrison, R., Cape, J. N., Fowler, D., Skiba,  
587 U., Simpson, D., Jickells, T., Baker, A., Kulmala, M., Gyldenkerne, S., Sørensen,  
588 L. L. and Erisman, J. W. (2011) 'Nitrogen processes in atmosphere' in Sutton, M.  
589 A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van  
590 Grinsven, H. and Grizzetti, B., eds., *The European Nitrogen Assessment: Sources,  
591 Effects and Policy Perspectives*, Cambridge, UK: Cambridge University Press, pp.  
592 117-210.  
593
- 594 Mitchell, G. H. and Mykura, W. (1962) *The geology of the neighbourhood of Edinburgh*,  
595 3rd ed., Edinburgh: H.M.S.O. publishing.  
596
- 597 Neff, J. C., Holland, E. A., Dentener, F. J., McDowell, W. H. and Russell, K. M. (2002)  
598 'The origin, composition and rates of organic nitrogen deposition: A missing piece  
599 of the nitrogen cycle?', *Biogeochemistry*, 57(1), 99-136.  
600
- 601 Nieder, R. and Benbi, D. K. (2008) *Carbon and Nitrogen in the Terrestrial Environment*,  
602 illustrated ed., Springer.  
603
- 604 Özel, M. Z., Hamilton, J. F. and Lewis, A. C. (2011) 'New Sensitive and Quantitative  
605 Analysis Method for Organic Nitrogen Compounds in Urban Aerosol Samples',  
606 *Environmental Science & Technology*, 45, 1497-1505.  
607
- 608 Prospero, J. M., Barrett, K., Church, T., Dentener, F., Duce, R. A., Galloway, J. N., Li, H.  
609 L., Moody, J. and Quinn, P. (1996) 'Atmospheric Deposition of Nutrients to the  
610 North Atlantic Basin', *Biogeochemistry*, 35(1), 27-73.  
611
- 612 Russell, K. M., Galloway, J. N., Macko, S. A., Moody, J. L. and Scudlark, J. R. (1998)  
613 'Sources of nitrogen in wet deposition to the Chesapeake Bay region', *Atmospheric  
614 Environment*, 32(14-15), 2453-2465.  
615
- 616 Scherer, H. W. (1993) 'Dynamics and availability of the non-exchangeable NH<sub>4</sub>-N: a  
617 review.', *European Journal of Agronomy* 2(3), 149-160.  
618
- 619 Schlesinger, W. H. (1997) *Biogeochemistry : An Analysis of Global Change*, 2nd ed., San  
620 Diego, Calif. ; London: Academic Press.  
621
- 622 Schulten, H. R. and Schnitzer, M. (1998) 'The chemistry of soil organic nitrogen: a review',  
623 *Biology and Fertility of Soils* 26, 1-15.  
624
- 625 Skiba, U., Jones, S. K., Drewer, J., Helfter, C., Anderson, M., Dinsmore, K., McKenzie,  
626 R., Nemitz, E. and Sutton, M. A. (2013) 'Comparison of soil greenhouse gas fluxes  
627 from extensive and intensive grazing in a temperate maritime climate',  
628 *Biogeosciences*, 10, 1231-1241.  
629
- 630 Tian, Y. H., Yang, L. Z., Yin, B. and Zhu, Z. L. (2011) 'Wet deposition N and its runoff  
631 flow during wheat seasons in the Tai Lake Region, China', *Agriculture Ecosystems  
632 and Environment*, 141(1-2), 224-229.  
633
- 634 van Smeerdijk, D. G. and Boon, J. J. (1987) 'Characterisation of  
635 subfossil *Sphagnum* leaves, rootlets of ericaceae and their peat by pyrolysis-high-

- 636 resolution gas chromatography-mass spectrometry', *Journal of Analytical and*  
637 *Applied Pyrolysis*, 11, 377-402.
- 638
- 639 Violaki, K., Zarbas, P. and Mihalopoulos, N. (2010) 'Long-term measurements of dissolved  
640 organic nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean:  
641 Fluxes, origin and biogeochemical implications', *Marine Chemistry*, 120(1-4), 179-  
642 186.
- 643
- 644 Vogt, E. (2011) *Nitrogen fluxes at the landscape scale: A case study in*  
645 *Scotland* unpublished thesis The University of Edinburgh.
- 646
- 647
- 648 Yan, X. W. (2002) 'Sulfur and nitrogen chemiluminescence detection in gas  
649 chromatographic analysis', *Journal of Chromatography A*, 976(1-2), 3-10.
- 650
- 651 Yesmin, L., Gammack, S. M., Sanger, L. J. and Cresser, M. S. (1995) 'Impact of  
652 atmospheric N deposition on inorganic- and organic-N outputs in water draining  
653 from peat', *Science of The Total Environment*, 166(1-3), 201-209.
- 654
- 655 Zhang, Y., Song, L., Liu, X. J., Li, W. Q., Lu, S. H., Zheng, L. X., Bai, Z. C., Cai, G. Y.  
656 and Zhang, F. S. (2012) 'Atmospheric organic nitrogen deposition in China',  
657 *Atmospheric Environment*, 46, 195-204.
- 658
- 659 Zhang, Y., Zheng, L. X., Liu, X. J., Jickells, T., Cape, J. N., Goulding, K., Fangmeier, A.  
660 and Zhang, F. S. (2008) 'Evidence for organic N deposition and its anthropogenic  
661 sources in China', *Atmospheric Environment*, 42(5), 1035-1041.

662 Table 1. Statistics of annual concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON and TDN for 2009 and  
 663 2010 in wet-only precipitation. Values are based on individual samples collected over the  
 664 two year period. N\* indicates the number of samples collected.

	$\text{NO}_3^-$ $\mu\text{mol N l}^{-1}$	$\text{NH}_4^+$ $\mu\text{mol N l}^{-1}$	DON $\mu\text{mol N l}^{-1}$	TDN $\mu\text{mol N l}^{-1}$
<u>2009</u>				
Mean	15	27	5	47
Min	< LOD	< LOD	< LOD	6
Max	148	273	50	426
Standard deviation	21	35	4	50
N*	227	227	63	63
% TDN	32	58	10	100
<u>2010</u>				
Mean	23	31	5	58
Min	2	2	< LOD	8
Max	260	218	45	483
Standard deviation	30	33	5	59
N*	169	169	63	63
% TDN	39	53	8	100

665 Table 2. Statistics of annual concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON and TDN for 2009 and  
 666 2010 in soil water. Values are based on individual samples collected from dip wells over  
 667 the two year period. N\* indicates the number of samples collected.

	$\text{NO}_3^-$ $\mu\text{mol N l}^{-1}$	$\text{NH}_4^+$ $\mu\text{mol N l}^{-1}$	DON $\mu\text{mol N l}^{-1}$	TDN $\mu\text{mol N l}^{-1}$
<u>2009</u>				
Mean	1	9	57	67
Min	< LOD	< LOD	11	11
Max	6	91	319	389
Median	0	1	48	54
Standard deviation	2	15	44	54
N*	72	72	72	72
% of TDN	2	13	85	100
<u>2010</u>				
Mean	< LOD	< LOD	59	60
Min	< LOD	< LOD	23	23
Max	8	7	285	285
Median	0	0	44	44
Standard deviation	1	1	43	43
N*	54	54	45	45
% of TDN	0.3	0.4	99.3	100

668

669 Table 3. Statistics of annual concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , DON and TDN for 2009 and  
 670 2010 in stream water. Values are based on individual samples collected over the two year  
 671 period. N\* indicates the number of samples collected.

672

	$\text{NO}_3^-$ $\mu\text{mol N l}^{-1}$	$\text{NH}_4^+$ $\mu\text{mol N l}^{-1}$	DON $\mu\text{mol N l}^{-1}$	TDN $\mu\text{mol N l}^{-1}$
<u>2009</u>				
Mean	2	14	48	65
Min	< LOD	5	10	25
Max	14	22	96	118
Median	0	14	47	64
Standard deviation	4	3	21	21
N*	43	43	43	43
% of TDN	4	22	75	100
<u>2010</u>				
Mean	5	13	50	67
Min	< LOD	< LOD	16	16
Max	15	52.3	104	145
Median	4	7.9	46	59
Standard deviation	4	13.8	20	31
N*	48	48	48	48
% of TDN	7	19	74	100

673

674

675 Table 4. Summary of compounds and their concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by the GC $\times$ GC-NCD, and overall DON concentrations ( $\mu\text{mol N l}^{-1}$ )  
 676 derived from TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by  
 677 the GC $\times$ GC-NCD. Blank spaces indicate a value below the detection limit.  $R_{t1}$  and  $R_{t2}$  are retention times in seconds for the first and second GC columns.

Sample $R_{t1}/R_{t2}$	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
09/07/2010	9.2							1.6	1.7
13/07/2010	13.8		0.4				0.5		
14/07/2010	6.5								
15/07/2010	5.5								
09/08/2010	9.4						0.6		1.8
12/08/2010	6.5							0.3	0.3
20/08/2010	3.5	0.2						0.6	
23/08/2010	2.4							0.5	
06/09/2010	3.1							1.9	
13/09/2010	3.2								
14/09/2010	5.8								
18/09/2010	3.3								
01/10/2010	0.5								
05/10/2010	1.0	0.7		2.0					
06/10/2010	-2.4								
18/10/2010	2.1			0.7			0.7		
21/10/2010	19.8			1.3		0.5	2.4		
24/10/2010	7.1			1.2					
25/10/2010	1.2			0.5		0.7	1.8		

678

679

680

681 Table 4. continued. Summary of compounds and their concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by the GC $\times$ GC-NCD, and DON concentrations ( $\mu\text{mol N l}^{-1}$ )  
 682 as TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the  
 683 GC $\times$ GC-NCD. Blank spaces indicate a value below the detection limit.  $R_{t1}$  and  $R_{t2}$  are retention times in seconds for the first and second GC columns.

684

Sample	DON	Pyrrrole	Benzonitrile	Unknown B	Unknown C	Dodecylamine	Unknown D	Unknown E	Unknown F
Rt <sub>1</sub> /Rt <sub>2</sub>	(TDN-DIN)	375/1.24	825/1.8	11.45/1.52	1218/1.48	1590/1.5	1615/1.7	1910/1.7	2200/2.09
26/10/2010	5.8				0.5			0.9	
01/11/2010	3.9								
02/11/2010	7.0						0.1		
03/11/2010	5.1							0.4	
04/11/2010	2.9								
05/11/2010	3.9								
06/11/2010	4.6								
08/11/2010	9.9							0.4	
09/11/2010	-2.4								
10/11/2010	-0.2								
11/11/2010	5.0							0.7	
13/11/2010	6.1							0.6	

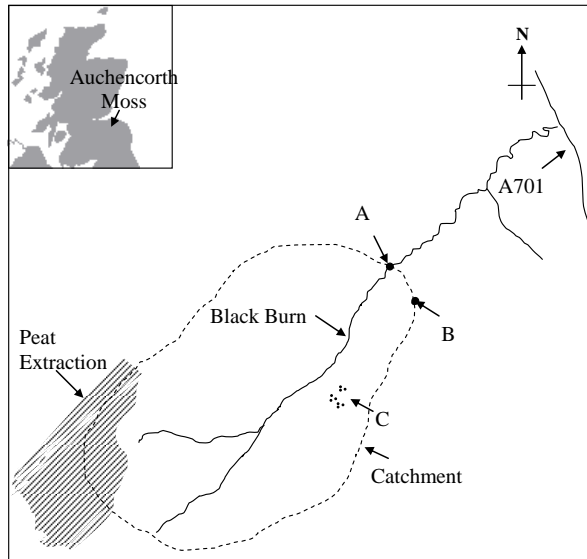
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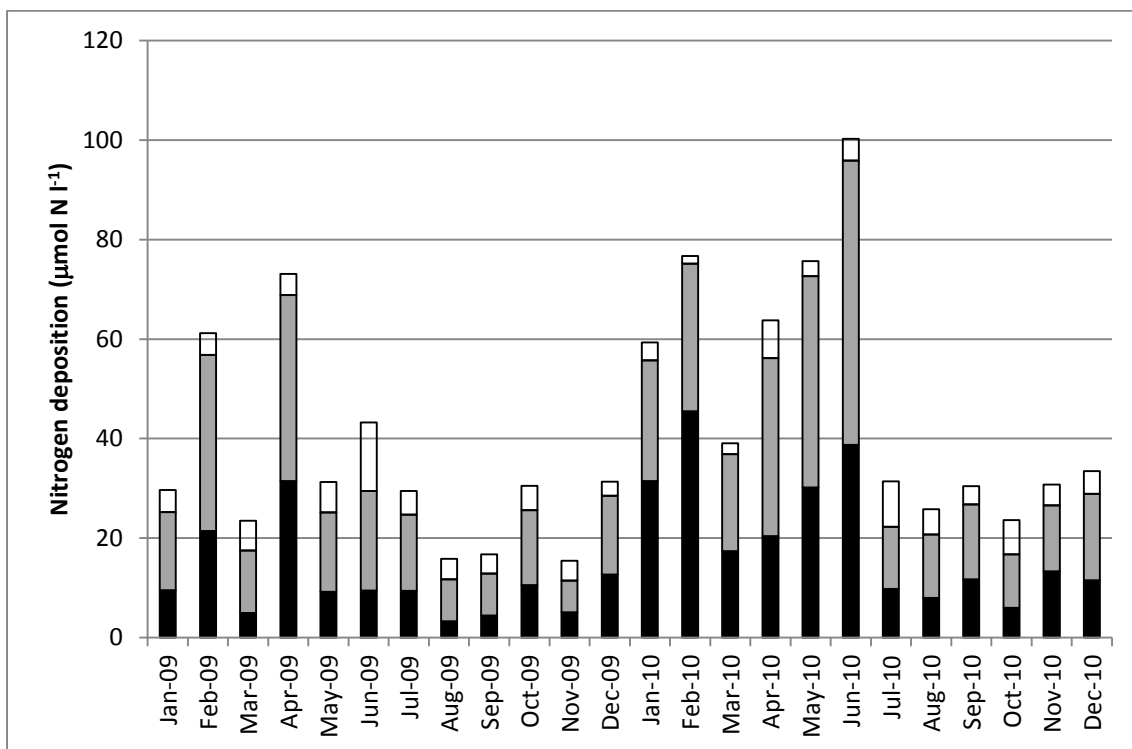
686 Table 5. Summary of compounds and their concentrations ( $\mu\text{mol N l}^{-1}$ ) detected by the GC $\times$ GC-NCD, and DON concentrations ( $\mu\text{mol N l}^{-1}$ ) detected  
 687 by ANTEK in stream water samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the GC $\times$ GC-  
 688 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  
 689 columns.

Sample $Rt_1/Rt_2$	DON (TDN- DIN)	Pyrrole 375/1.2 4	Unknown A 415/1.24	Benzonitril e 825/1.8	N- nitrosodipropylamine 970/1.4	Unknown B 11.45/1.52	Decylamin e 1295/1.64	Unknown E 1910/1.7	Unknown F 2200/2.09
11/08/2010	45.9	1.3	3.2					0.9	
19/08/2010	54.8	0.2	0.3		1.2				
26/08/2010	85.2	0.7	2.7	3.0					
10/09/2010	30.5	0.2	0.8			1.6			1.4
30/09/2010	87.2	3.8	6.9				1.5		
06/10/2010	57.8	5.0	3.9				1.8		
12/10/2010	69.4	0.8	2.1			1.4			
14/10/2010	60.1		0.7			1.3			
15/10/2010	49.1								
18/10/2010	46.1	1.8	3.4						
19/10/2010	75.0		1.4		1.3			1.0	0.8

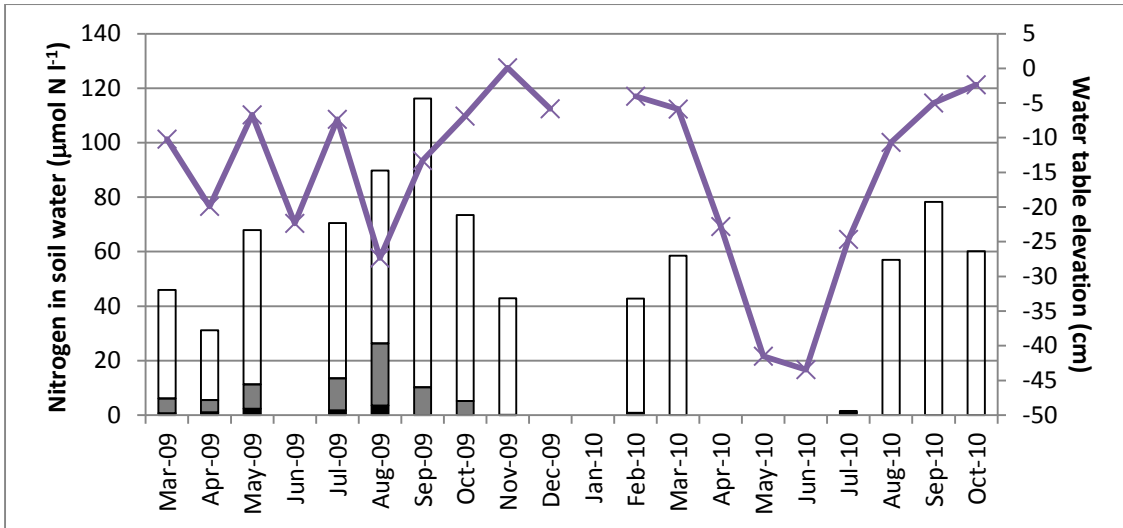
21/10/2010	58.2	2.3	4.0				
23/10/2010	65.9	0.3	1.9	0.7		1.2	0.5
26/10/2010	56.5	1.0					0.9
28/10/2010	57.6	0.7	1.8	1.7		1.8	0.6
02/11/2010	61.5	0.6	2.3			1.9	1.0
03/11/2010	69.5	2.5	3.4			0.4	
04/11/2010	79.4	0.6	0.6			0.4	0.7
05/11/2010	58.9						
10/11/2010	70.7		0.5			0.5	0.4
11/11/2010	65.6	4.3	1.8		1.1	1.6	1.7



691  
 692 Figure 1: Schematic map of catchment and sampling sites at Auchencorth Moss. Key: (A) study  
 693 catchment outlet and stream sampling site; (B) monitoring station (wet only analyser); (C) dip  
 694 wells. Adapted from Dinsmore et al., (2010).  
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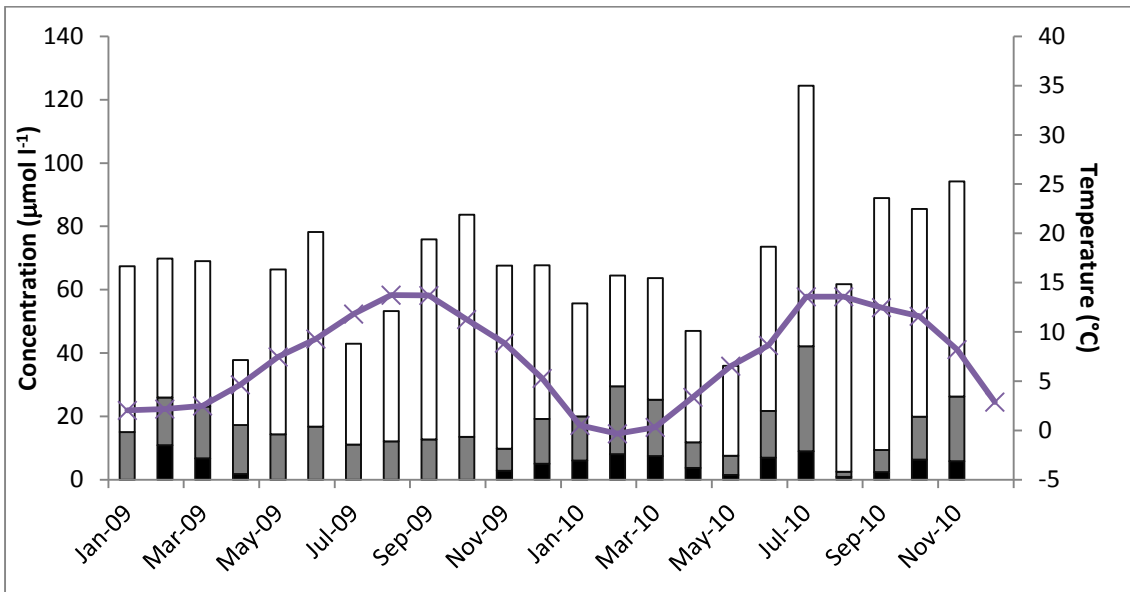


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 697 Figure.2. Volume-weighted monthly average concentrations of NH<sub>4</sub><sup>+</sup> (grey), NO<sub>3</sub><sup>-</sup> (black) and  
 698 DON (white) in wet only precipitation.



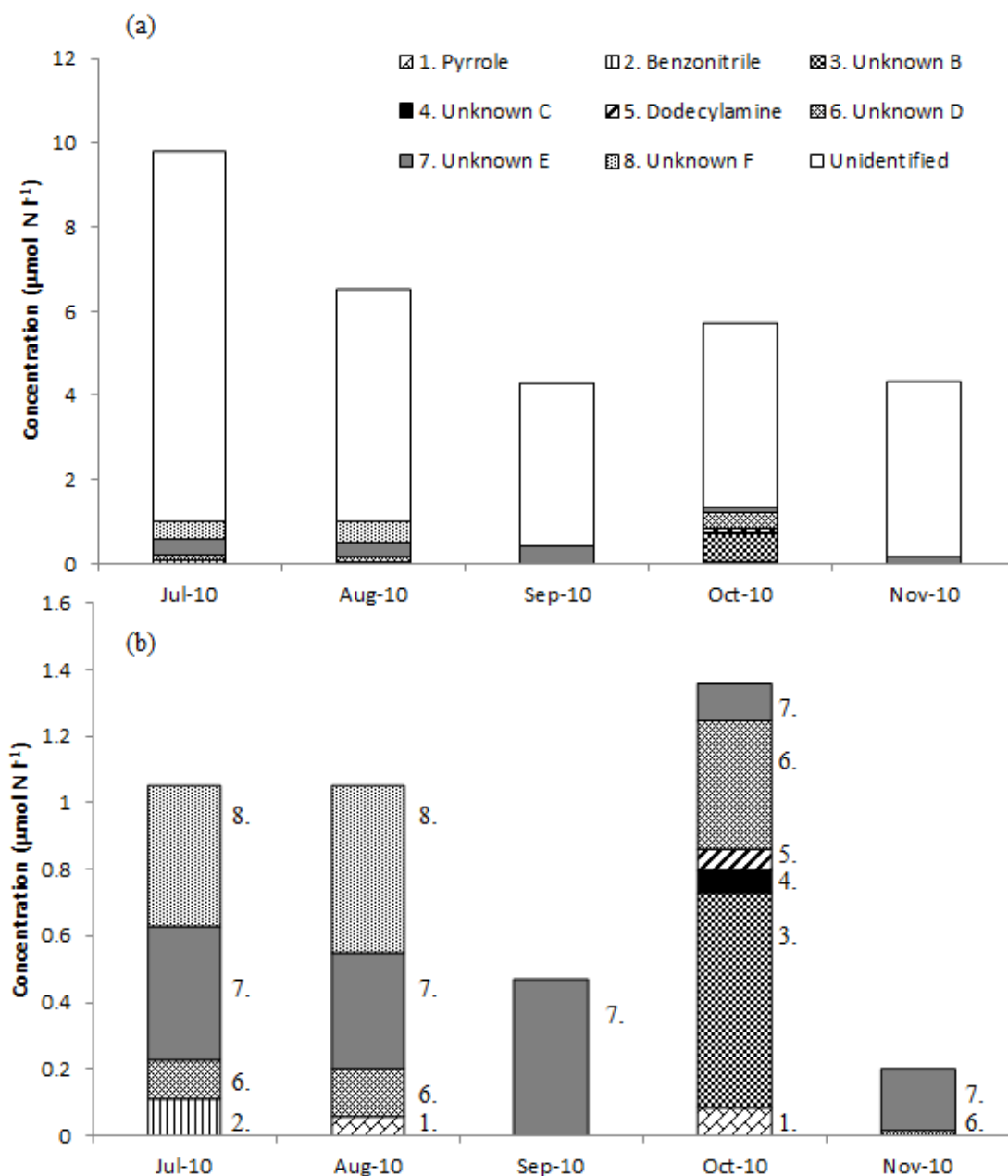
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Figure 3. Monthly concentrations of  $\text{NH}_4^+$  (grey),  $\text{NO}_3^-$  (black) and DON (white) in soil water. The line represents monthly water table elevation. The June-09 sample was misplaced and Dec-09 and Jan 2010 were frozen, the remaining blank spaces indicate the dip wells were dry on the day of collection.



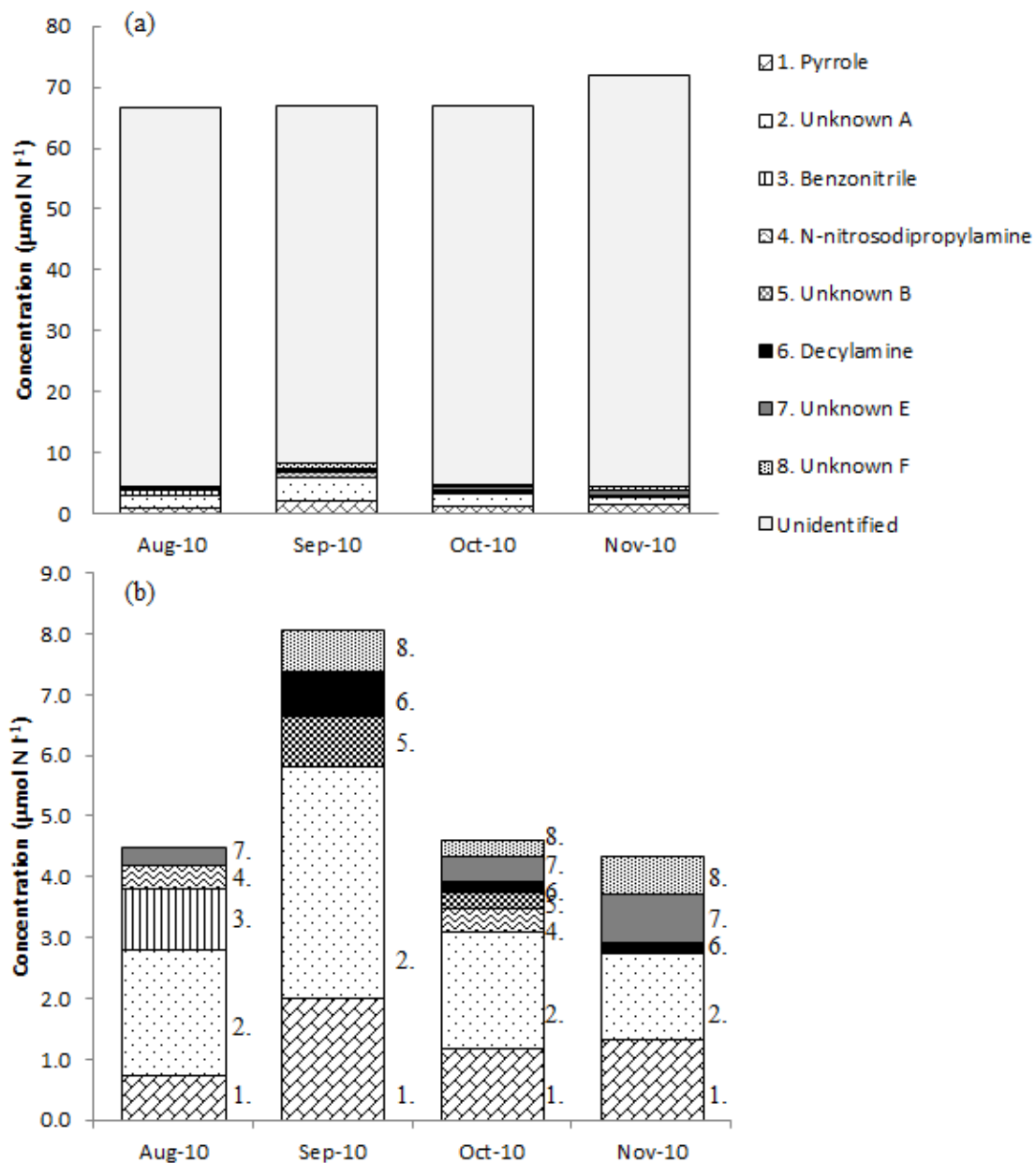
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Figure 4. Discharge-weighted monthly mean concentrations of  $\text{NH}_4^+$  (grey),  $\text{NO}_3^-$  (black) and DON (white) in stream water. The line represents mean monthly air temperature.



708

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



713

714 Figure 6. Mean monthly concentrations of the individual compounds found in stream water.

715 (a) includes the DON fraction identified from the ANTEK (white bar) (b) excludes the

716 'unidentified' fraction, so the fraction detected by GCxGC-NCD is more clearly seen.