

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) can contribute significantly to the overall nitrogen
14 budget, but is not routinely measured in precipitation or stream water. In order to
15 investigate the contribution of DON to deposition and export of N, precipitation, stream
16 and soil water samples were collected from an ombrotrophic peatland and analysed for
17 DON over a two year period. In wet only deposition DON contributed up to 10% of the
18 total dissolved nitrogen (TDN), ~~and was the most dominant fraction in~~ soil water
19 ~~(99%), and 75% in~~ stream water ~~(75%). No correlations were observed between DIN and~~
20 ~~DON in precipitation stream water or soil water.~~

21 ~~NH₄⁺ was the most dominate form of N in precipitation, with NO₃⁻ contributing the least~~
22 ~~to precipitation, soil water and stream water.~~

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

27 ~~Precipitation DIN showed a loose seasonal pattern, with peak concentrations occurring~~
28 ~~between January and June, while DON concentrations tended to be lower in the winter~~
29 ~~months. Stream water DON and NH₄⁺ showed no obvious seasonal pattern but NO₃⁻~~
30 ~~showed larger concentrations in cooler months and the smallest during warmer months,~~
31 ~~with the exception of June and July 2010, when concentrations were high.~~

32 Precipitation and stream DON was qualitatively analysed using GC×GC-NCD. ~~Only 10%~~
33 ~~of DON was able to be assessed, with ten~~ unique compounds ~~were~~ detected, ~~of which~~
34 ~~only~~ five could be identified: pyrrole, benzonitrile, dodecylamine, N-

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35 nitrosodipropylamine and decylamine. Five compounds were present in both
36 precipitation and stream samples: pyrrole, benzonitrile and three unidentified compounds.
37 A more detailed DON speciation may be used to identify sources and pathways of DON.

38

39 *Keywords: organic nitrogen, ammonium, nitrate, precipitation, stream, GC×GC-NCD*

40 **1 Introduction**

41 Atmospheric deposition of nitrogen (N) has increased dramatically over the last century
42 as a result of industrial and agricultural activities (Galloway et al., 2004). In the last 150
43 years, the amount of global anthropogenic reactive nitrogen has increased by a factor of
44 12.5; from ~15 Tg N y⁻¹ in 1860 to ~187 Tg N y⁻¹ in 2005 (Galloway et al., 2008). The
45 total deposition of N in the UK was estimated to be approximately 330 Gg in 2004, with
46 wet and cloud deposition accounting for approximately 211 Gg (63.9%), and the rest
47 consisting of dry deposition (Fowler et al., 2009, Hertel et al., 2011).

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

53 Wet deposition of the dissolved inorganic nitrogen (DIN) compounds ammonium (NH₄⁺)
54 and nitrate (NO₃⁻) has been studied over many years (Violaki et al., 2010, Cape et al.,
55 2011, Zhang et al., 2012). The former is produced by the dissolution of ammonia gas
56 (NH₃) and the scavenging of NH₄⁺ aerosol, and the latter by the dissolution of nitric acid
57 gas (HNO₃) and the scavenging of NO₃⁻ aerosol (Russell et al., 1998, Cornell et al., 2003,
58 Tian et al., 2011). The dissolved organic nitrogen (DON) fraction is less well
59 documented due to difficulties in measuring it, but it can be an important fraction of the
60 total dissolved nitrogen (TDN) deposited, and can potentially be biologically available as
61 a source of N (Russell et al., 1998, Neff et al., 2002, Cornell et al., 2003, Cape et al.,
62 2004). The sources of DON are not well understood, but it is known to be ubiquitous in
63 the environment, present in particulate, gaseous and aqueous phases (Cornell et al., 2003,
64 Cape et al., 2004, Özel et al., 2011). Studies have shown that DON can contribute 30-
65 50% of the wet deposition of water soluble N (Neff et al., 2002, Cape et al., 2004, Zhang
66 et al., 2008, Cape et al., 2011, Cornell, 2011, Zhang et al., 2012).

67 Several atmospheric species of DON are considered hazardous to human health, and
68 appear on the Environment Protection Agency (EPA) hazardous air pollutant list (Özel et
69 al., 2011). Sources of DON are believed to include: pollen; sea spray; soil dust; deposits
70 from fauna and flora; the scavenging of aerosols; and reactions in the atmosphere
71 between inorganic gaseous nitrogen species and organic compounds (Prospero et al.,
72 1996, Russell et al., 1998, Cornell et al., 2003, Calderon et al., 2007, Zhang et al., 2008,
73 Violaki et al., 2010). Some work has been done to identify organic N compounds, so that
74 their sources can be traced. Amino acids, urea, aliphatic amines and peptides have all
75 been found in the atmosphere from naturally occurring sources (Calderon et al., 2007,
76 Violaki et al., 2010). The main anthropogenic organic compounds are believed to be N-
77 heterocyclic compounds, nitrophenols and nitro-polycyclic aromatic hydrocarbons
78 (Violaki et al., 2010). Alky amides have also been identified and are believed to result
79 from reactions between NH_3 and fatty acids at high temperatures (Cheng et al., 2006);
80 photochemical reactions are believed to be responsible for the presence of alky nitrates
81 and peroxyacyl nitrates (Violaki et al., 2010).

82 As with wet deposition, N is present in streams as both DIN and DON, with most focus
83 usually being on the DIN fraction. DIN, in particular NO_3^- , is often used as an indicator
84 of N saturation, with higher stream concentrations and changes in seasonal patterns
85 indicating an increase in the leaching of DIN from the catchment (Cundill et al., 2007,
86 Daniels et al., 2012). DON, however, is not often measured in spite of being the most
87 dominant fraction in waters draining peatland catchments; DON is known to contribute
88 60-90% of the TDN load in peatland streams (Yesmin et al., 1995).

89 Various techniques have been developed to characterise DON, including FT-ICR Mass
90 spectrometry (Altieri et al., 2009) and NMR spectrometry (Maie et al. 2006), with these
91 methods focusing on the more on groups of compounds rather than individual species.
92 ~~identify individual organic nitrogen compounds, but m~~Many techniques are not sensitive
93 enough to detect ~~these individual organic nitrogen~~ compounds in low concentrations
94 (Özel et al., 2010). Solid phase extraction (SPE) is a technique used to separate organic
95 compounds from aqueous systems, and has successfully been applied in many cases
96 (Moret & Conte, 2002, Özel et al., 2003, Özel et al., 2011). The SPE method has given
97 better DON recovery than solvent extraction from the aqueous phase (Özel et al., 2011)
98 and the extracted samples can be analysed using Gas chromatography (GC). By using a
99 multi-dimensional GC-technique and comprehensive two-dimensional GC, GC×GC, and
100 coupling it with a nitrogen chemiluminescence detector (NCD), better separation and

101 improved limits of detection can be achieved than by conventional one-dimensional GC
102 (Özel et al., 2006, Adam et al., 2007, Adahchour et al., 2008, Özel et al., 2010). GC×GC-
103 NCD has recently been used to investigate the presence of organic nitrogen compounds in
104 diesel fuel, atmospheric aerosol, nitrosamines in meat and vegetables, and nicotine and
105 N-nitrosamines in house dust (Adam et al., 2007, Özel et al., 2010, Özel et al., 2011,
106 Kocak et al., 2012, Ramirez et al., 2012).

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

111 2 Site and methods

112 2.1 Study area

113 Auchencorth Moss (Fig. 4.1) is an ombrotrophic peat bog located in south Scotland,
114 approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat.
115 55°47'34 N; long. 03°14'35 W). The site is used primarily for low intensity sheep
116 grazing (less than one livestock unit km⁻²) and in 2009 a small herd of cows (15-20) also
117 grazed on the site.

118 The volume of peat in the catchment is estimated to be ~50 million m³, with depths up to
119 5 m, and an average depth of 50 cm. The total peat coverage is ~1214 ha, of which
120 approximately 170 ha is extracted (located 1.75 - 3.4 km W-SW of the monitoring
121 station) (Mitchell and Mykura, 1962, Dinsmore, 2008).

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

130 The vegetation is arranged into ~~consists of~~ numerous hummocks and hollows. The
131 hollows are depressions up to 30 cm deep and are dominated by blankets of *Sphagnum*
132 mosses, with various sedges, monocotyledons and other bryophytes also present; the
133 hummocks can be up to 30 cm high, and although *Sphagnum* mosses are present, there is

134 a larger density of vascular plants with the dominant species being *Deschampsia*
135 *flexuosa*, *Eriophorum vaginatum* and *Juncus effusus*. Flechard and Fowler (1998) and
136 Dinsmore (2008) have presented more detailed vegetation information for Auchencorth
137 Moss.

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

141

142 2.2 Wet-only precipitation

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

156 A Metrohm 761 Compact Ion Chromatograph (IC) connected in parallel with a Metrohm
157 733 IC Separation Centre to a Metrohm 766 IC sample processor (Metrohm Ltd.,
158 Herisau, Switzerland) measured NO_3^- and NH_4^+ respectively. NO_3^- was determined by
159 pumping an eluent solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate
160 through a Metrosep A Supp 5 column. For NH_4^+ determination, an eluent solution of 24
161 mM boric acid, 5 mM tartaric acid and 0.7 mM dipicolinic acid, was pumped through a
162 Metrosep C1 column. Typical detection limits were $1 \mu\text{mol N l}^{-1}$ for both NO_3^- and NH_4^+ .
163 For analysis of TDN (TDN = DIN + DON) subsamples were obtained (a minimum of 5
164 ml) where possible, and filtered using Millipore Hydrophilic PTFE (0.45 μm pore size)
165 syringe filters prior to freezing and later analysed for TDN by high-temperature catalytic
166 oxidation using an ANTEK 8060-M Nitrogen Specific HPLC Detector (ANTEK

167 Instruments Inc., Houston, TX, USA). The analysis was conducted in flow-injection
168 mode, in which 20 μl samples were introduced into an eluent stream of 10% methanol in
169 deionised water at a flow rate of 250 $\mu\text{l min}^{-1}$. It was then combusted in oxygen at 1050
170 $^{\circ}\text{C}$, producing nitric oxide (NO) which was detected by chemiluminescence. The
171 detection limit for TDN was $\sim 1 \mu\text{mol N l}^{-1}$. DON was determined by subtracting DIN
172 from TDN.

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

178 The uncertainty in DON values is greater than for DIN as a result of errors associated
179 with measuring TDN and DIN compounding and thus reducing the accuracy of the DON
180 calculation (Cornell et al., 2003). A negative bias may result from these combined
181 uncertainties, from DON not being fully converted during the total N analysis, and from
182 losses due to the collection and storage procedure (Russell et al., 1998, Cornell et al.,
183 2003). A positive bias results from setting small negative values of DON to zero; small
184 negative values of DON were included in the data analyses here in order to prevent this
185 source of bias. The limit of detection of DON was determined by the summation of the
186 detection limits of the 3 independent measured concentrations (NH_4^+ , NO_3^- and TDN)
187 and was $3 \mu\text{mol N l}^{-1}$.

188 2.3 Soil water

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

196 2.4 KCl-extractable mineral N

197 Soil cores were collected at a depth of 0-10 cm at three locations (next to the dip wells),
198 in spring and autumn in 2009 and in spring, summer and winter in 2010. NH_4^+ and NO_3^-
199 were extracted from soil samples using KCl; 15 g of soil were shaken for 1 hour with 50

200 ml of 1M KCl solution at a rate of 100 rpm. Samples were then filtered using Whatman
201 42 filter papers and frozen prior to analysis by IC. TDN was not measured, so DON could
202 not be determined.

203 2.5 Stream water

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

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

219 2.6 GC×GC-NCD

220 Comprehensive two-dimensional gas chromatography coupled to a nitrogen
221 chemiluminescence detector (GC×GC-NCD) was used to separate DON into different
222 peaks and identify individual components where possible. The samples were extracted by
223 solid phase extraction (SPE), in order to trap the DON, using Superclean ENVI-18 SPE
224 tube 20 µm polymeric C_{18} -reverse phase 500 mg-3 ml SPE cartridges (SUPELCO,
225 Bellefonte, PA, USA). C_{18} material has been used in many SPE applications for
226 extraction of organic compounds from the aqueous phase. It has been found that there is
227 almost no change in the composition of the sample before and after the application of
228 SPE of the C_{18} material (Özel et al., 2003). Cartridges were conditioned with 5 ml
229 methanol followed by 5 ml of water at a rate of 2-5 ml min^{-1} . Between 5 and 18 ml of
230 precipitation and 9 and 24 ml of stream water was passed through the cartridge at a rate
231 of 2-5 ml min^{-1} . The cartridge was thoroughly dried under vacuum for ~30 minutes.

232 Following drying, the cartridge was eluted with 5 ml dichloromethane (DCM), and then
233 concentrated in a stream of nitrogen to a volume of ~ 0.1 ml. The GC×GC-NCD was an
234 Agilent 7890 GC coupled with an Agilent 255 NCD (Agilent Technologies, Palo Alto,
235 CA, USA). 1 µl extracts were injected in pulsed splitless mode at a temperature of 280 °C
236 and a pressure of 30 psi for 2 min, using a Gerstel automated liquid injector (Gerstel,
237 Mulheim an der Ruhr, Germany). The first dimension column was a non-polar BPX5 (30
238 m x 0.32 mm i.d. x 0.25 µm film thicknesses), set to an initial temperature of 55 °C for 1
239 min. The temperature was then increased at a rate of 5°C min⁻¹ until 305 °C where it was
240 isothermally held for 1 min. The second column was a BPX50 (1.5 m x 0.10 mm i.d. x
241 0.10 µm film thickness) set to an initial temperature of 70 °C for 1 min, the temperature
242 was then increased at a rate of 5 °C min⁻¹ until 320 °C where it was isothermally held for
243 1 min. Both columns were from SGE Analytical Science (VIC, Australia). Helium was
244 used as a carrier gas at a constant flow of 1 mL min⁻¹ and the data was collected at 50 Hz.
245 Pyrolysis was carried out at 900 °C with a hydrogen flow rate of 4 ml min⁻¹ and oxygen
246 flow rate of 10 ml min⁻¹.

247 The detector shows an equimolar response regardless of the chemical state of the organic
248 nitrogen (except azo compounds), allowing nitrogen-containing compounds to be
249 quantified without the need for a separate calibration standard for each compound (Yan,
250 2002, Özel et al., 2011). Details of the optimization of the NCD response and the
251 analytical performance with respect to equimolar response using standards was evaluated
252 by Özel et al., (2011).

253 **3 Results**

254 3.1 Meteorology

255 Total rainfall was determined from the volume of rain collected in the wet only analyser.
256 In 2009 the total rainfall was 902 mm with monthly totals varying from 16 mm in
257 February to 180 mm in November. The mean monthly temperature varied from 0.5 °C in
258 December to 13.7 °C in July, with a yearly mean of 7.6 °C. In 2010 the total rainfall was
259 732 mm with monthly totals varying from 21 mm in May to 128 mm in November.
260 However, in 2010 a significant amount of snow fell, interfering with the wet-only
261 collector and resulting in less precipitation collection during January-March. It is
262 estimated that 423 mm of precipitation fell during these months (an additional 291 mm),
263 making the total precipitation collected for 2010 approximately 1023 mm. This additional
264 precipitation was estimated from the ratio of discharge and precipitation, measured at the

265 stream sampling site by the Black Burn (Dinsmore et al., 2013, Skiba et al., 2013). The
266 mean monthly temperature varied from -2.0 °C in December to 13.6 °C in July, with a
267 yearly mean of 6.6 °C.

268 3.2 Wet-only N deposition

269 Figure 2 shows the volume-weighted monthly mean concentrations of N in precipitation.
270 The temporal variation of NH_4^+ and NO_3^- follow a similar pattern, with DON differing. In
271 both 2009 and 2010 (Table 1), NH_4^+ was the dominant component of wet-only deposition
272 with annual mean concentrations of $27.2 \mu\text{mol N l}^{-1}$ (58% of TDN) and $30.7 \mu\text{mol N l}^{-1}$
273 (53% of TDN) respectively. The contribution of NO_3^- was greater in 2010 than in 2009,
274 with mean concentrations of $15.0 \mu\text{mol N l}^{-1}$ (32% of TDN) in 2009 and $22.7 \mu\text{mol N l}^{-1}$
275 (39% of TDN) in 2010. Although DON contributed the least to annual concentrations in
276 both years, on a monthly timescale there were a few occasions when DON exceeded NO_3^-
277 (March 2009, June 2009, Aug 2009 and Oct 2010). A loose seasonal pattern can be
278 observed for NH_4^+ and NO_3^- , with peak concentrations occurring between January and
279 June. This is more obvious in 2010. DON has no clear seasonal pattern, although the
280 lowest concentrations seem to occur in the winter months (Nov- Jan). A weak, but
281 significant correlation was found between NH_4^+ and NO_3^- in 2009 ($R^2 = 0.45$, $p < 0.001$).
282 In 2010, a stronger correlation between NH_4^+ and NO_3^- was also observed ($R^2 = 0.62$, $p <$
283 0.001). No correlations were observed between NH_4^+ , DON, temperature, rainfall or
284 precipitation; NO_3^- , DON, temperature, rainfall or precipitation; or DON, temperature,
285 rainfall or precipitation.

286 3.3 Soil water and KCl-extractable N

287 Due to gaps in the data, caused by the dip wells being dry and thus no sample to be
288 collected, it is difficult to assess seasonal patterns. What is clear, is that DON clearly
289 dominates the TDN. From the data available, it appears that DON concentrations were
290 larger in the warmer months compared to cooler months (November to March) and that
291 peak concentration for DON occurred in September in both years (Figure 3). The
292 contribution of DON to TDN was higher in 2010 at 99% compared to 85% in 2009
293 (Table 2). NH_4^+ and NO_3^- followed similar patterns, with concentrations in 2009
294 appearing to increase in the spring, peaking in August. In 2010, both NH_4^+ and NO_3^-
295 concentrations generally remained low, with much smaller peak concentrations occurring
296 in July. NO_3^- mean annual concentrations were $1.2 \mu\text{mol N l}^{-1}$ (2% of TDN) in 2009 and

297 0.2 $\mu\text{mol N l}^{-1}$ (0.3% of TDN) in 2010. NH_4^+ mean annual concentrations were also larger
298 in 2009 than in 2010; 8.6 $\mu\text{mol N l}^{-1}$ compared to 0.2 $\mu\text{mol N l}^{-1}$. The contribution of
299 NH_4^+ to TDN was thus much larger in 2009 at 13% and just 0.4% in 2010.
300 Soil extractions from 2 samples in 2009 and 3 samples in 2010 found no detectable NO_3^- ,
301 and NH_4^+ concentrations of $29 \pm 12 \mu\text{mol N l}^{-1}$ and $39 \pm 20 \mu\text{mol N l}^{-1}$ for 2009 and
302 2010, respectively.

303 3.4 Concentration and forms of N in stream water

304 Monthly mean discharge-weighted concentrations of NO_3^- , NH_4^+ and DON are presented
305 in Figure 4, and a basic statistical analysis of annual stream water chemistry is presented
306 in Table 3. DON is the dominant N species found in the stream water contributing, on
307 average, 74.6% (in 2009) and 74.3% (in 2010) of TDN., with the highest concentrations
308 in summer/autumn, however no clear seasonal pattern was evident. ~~Monthly mean DON~~
309 ~~concentrations ranged from 9.8 to 96.4 $\mu\text{mol N l}^{-1}$ in 2009 and 15.5 to 104.2 $\mu\text{mol N l}^{-1}$ in~~
310 ~~2010. Annual mean concentrations were 48.1 $\mu\text{mol N l}^{-1}$ in 2009 and 50.0 $\mu\text{mol N l}^{-1}$ in~~
311 ~~2010, contributing, on average, 74.6% and 74.3% of TDN.~~

312 Monthly mean concentrations of NO_3^- ranged from 0.0 to 13.7 $\mu\text{mol N l}^{-1}$ in 2009 and 0.0
313 to 15.2 $\mu\text{mol N l}^{-1}$ in 2010. Annual mean concentrations were 2.3 $\mu\text{mol N l}^{-1}$ in 2009 and
314 4.5 $\mu\text{mol N l}^{-1}$ in 2010. In 2009, concentrations varied seasonally; largest NO_3^-
315 concentrations were measured during the cooler months and the smallest during the
316 warmer months. In summer 2009 there was no detectable NO_3^- . In 2010 stream water
317 NO_3^- concentrations initially followed a similar pattern as in 2009, with concentrations
318 increasing during the winter months and decreasing as temperature increased and summer
319 approached. However, there was a large increase in NO_3^- concentrations in June and July
320 2010. Consequently, average annual NO_3^- concentrations in 2010 were nearly double
321 those in 2009, contributing 6.6% of TDN compared to 3.6% of TDN (Table 3). Monthly
322 median concentrations for NO_3^- for the whole period showed a similar pattern to monthly
323 discharge-weighted mean concentrations, with the exception of June 2010, which is
324 reduced to a summer low of 0 $\mu\text{mol N l}^{-1}$, suggesting the monthly mean value was
325 skewed by an unusually large value. Median concentrations made little difference to the
326 July 2010 maximum. July 2010 also showed a maximum in the mean concentrations of
327 DON and NH_4^+ .

328 Monthly mean concentrations of NH_4^+ ranged from 5.4 to 21.9 $\mu\text{mol N l}^{-1}$ with an annual
329 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 annual mean of 12.9

330 $\mu\text{mol N l}^{-1}$ in 2010. Concentrations of NH_4^+ were consistently higher than NO_3^- and there
331 was no clear seasonal pattern. No correlation was observed between NH_4^+ , NO_3^- , DON,
332 discharge, temperature, rainfall (both air and stream) or precipitation.

333 3.5 DON speciation by GC×GC-NCD

334 Tables 4 and 5 display breakdowns of the individual DON compounds detected by the
335 GC×GC-NCD and their concentrations for precipitation and stream water, respectively.
336 The plasticiser N-butyl-benzenesulphonamide (not included in tables) was a prominent
337 compound in all samples, with extremely high concentrations, sometimes higher than
338 TDN detected in the precipitation by ANTEK. We assume that the N-butyl-
339 benzenesulphonamide detected was most likely to be a sampling contaminant from the
340 storage bottles. This contamination was not detected by the ANTEK as samples run on
341 this machine were filtered directly into glass vials for storage before analysis. The source
342 of this contamination is discussed later and the compound was thus excluded from the
343 results. Since this study involved screening for unknown DON components, the SPE
344 recoveries of the identified species could not be determined in advance. Therefore the
345 concentrations provided should be considered as a lower limit assuming 100 % recovery
346 from the water sample. Reverse phase SPE will by its nature not retain the most polar
347 DON species and so this analysis targets only the GC amenable fraction of water soluble
348 volatile/semi-volatile mid-polarity compounds.

349 In 13 of the 31 precipitation samples, and 2 of the 21 stream samples, no DON
350 compounds were detected or the peaks were too small to be distinguishable from
351 background noise. The limit of detection (LOD) using the optimized method has been
352 determined between 0.16-0.27 μgN using GC×GC-NCD of standard mixtures (Özel et al.,
353 2011).

354 Peak identification was carried out by comparing the two retention times (R_{t1} and R_{t2}) of
355 the peaks observed in the samples with the retention times of known standards. This
356 could lead to misidentification of peaks, however co-elution is greatly reduced using
357 GC×GC and there is very good retention time stability between runs. There were several
358 peaks, consistently present in some samples, that could not be identified as they did not
359 match any of the retention times of the standards available to us already run, so have
360 been and therefore were labelled “Unknown” A-F. In total 10 unique compounds were
361 found to be present in the stream and precipitation, of which only 5 could be identified.
362 Tables 4 and 5 present a summary of the compounds identified in precipitation and

363 stream water DON, respectively. Both the precipitation and the stream water contained 8
364 distinct compounds, 5 of which were in common.

365 The most common compound identified in the precipitation samples was Unknown E,
366 present in 10 samples, followed by Unknown D in 6 samples and Unknown B in 5
367 samples, with mean concentrations of $0.3 \mu\text{mol N l}^{-1}$, $0.14 \mu\text{mol N l}^{-1}$ and $0.2 \mu\text{mol N l}^{-1}$,
368 | respectively assuming an equimolar response ~~and 100 % recovery during SPE~~. Two
369 precipitation samples contained pyrrole, with a mean concentration of $0.03 \mu\text{mol N l}^{-1}$.

370 Unknown F was in 3 samples (mean concentrations of $0.1 \mu\text{mol N l}^{-1}$), dodecylamine was
371 in 2 samples (mean concentration of $0.02 \mu\text{mol N l}^{-1}$), and Unknown C was in one sample
372 (concentration of $0.02 \mu\text{mol N l}^{-1}$). The precipitation samples did not contain any
373 Unknown A, N-nitrosodipropylamine or decylamine, which were found in the stream
374 samples.

375 The most common compound identified in the stream samples was Unknown A, the
376 mean concentration was $2.0 \mu\text{mol N l}^{-1}$ (Table 5). Pyrrole was the next most common
377 compound, found in 18 of the stream samples, with a mean concentration of $1.2 \mu\text{mol N}$
378 l^{-1} . Unknowns E and F both appeared in 9 stream samples, with mean concentrations of
379 $0.5 \mu\text{mol N l}^{-1}$ and $0.4 \mu\text{mol N l}^{-1}$. N-nitrosodipropylamine (NDPA) was present in 4
380 stream samples, followed by Unknown B and decylamine in 3 stream samples. Mean
381 concentrations were $0.2 \mu\text{mol N l}^{-1}$ for all three compounds. Unknown D, Unknown C
382 and dodecylamine, which were found in the precipitation samples, were not present in the
383 stream samples.

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

386 Figures 5a and 6a display breakdowns of the monthly means of individual DON
387 compounds detected by the GC×GC-NCD and the remaining DON detected by ANTEK
388 for precipitation and stream water, respectively. Figures 5b and 6b show the monthly
389 means of individual DON compounds detected by the GC×GC-NCD only, to make this
390 fraction more visible. In both cases, the majority of DON was “unidentified”,
391 contributing a mean of 86% and 92% of total DON detected in precipitation and stream
392 water, respectively. This represents the DON not detected by the GC×GC-NCD, but
393 measured as TDN by the ANTEK, and indicates that the GC×GC-NCD was only able to
394 | speciate a very small fraction of the DON present. This is likely to be in part a result of
395 losses of highly polar DON compounds during the SPE step and large molecular weight

396 species that are not volatile enough to be analysed by GC. In the precipitation samples,
397 Unknown E is the only compound present in all 5 sampling months, and is the only
398 compound identified in September. October had the most identified compounds present,
399 with 6 of the 8 compounds measured (Fig. 5b). In the stream samples, pyrrole and
400 Unknown A were present in all 4 sampling months. October also had the most identified
401 compounds present, with 7 of the 8 compounds present (Fig. 4).

402 **4 Discussion**

403 4.1 The composition of N in precipitation

404 Cape et al., (2004) studied several sites in the UK on a range of land uses and noted an
405 annual cycle for DIN and DON, with peak concentrations for NH_4^+ and NO_3^- occurring
406 in the late spring (April-June 2000-2002) and a DON peak occurring in late summer
407 (June-August 2000-2002). Both DIN and DON showed minima in winter. The data
408 presented here are similar, but with earlier DIN maxima in early spring (Feb-April in
409 2009 and Feb-June 2010) followed by lower values in the autumn and beginning of
410 winter. DON also peaked earlier than reported by Cape et al. (2004) but roughly a month
411 after DIN peaks in both 2009 and 2010. Generally, sources of NH_4^+ in precipitation tend
412 to be agricultural in origin and sources of NO_3^- in precipitation from combustion activities
413 (Cape et al., 2011). Although Auchencorth Moss is located in a rural setting and with
414 minimal agricultural activity on the peatland itself; there are several chicken farms in the
415 area. Chickens farms emit ammonia (NH_3), which when dissolved in rainwater, produces
416 NH_4^+ (Schlesinger, 1997). NH_4^+ also makes up a large fraction of atmospheric aerosols
417 and is often transported further downwind of its source (Nieder and Benbi, 2008), where
418 it can then be washed out and deposited by precipitation.

419 Sources of NO_3^- include motor vehicles and stationary combustion sources (power
420 stations, domestic heating) following atmospheric oxidation of the emitted nitrogen
421 oxides. As a secondary pollutant, nitric acid and nitrates are less easily traced back to
422 sources. The sources of DON are more difficult to generalise, but spring maxima may be
423 due to the release of pollen, plant debris and spores during the spring, which have been
424 suggested as sources of DON (Violaki et al., 2010), or to seasonal patterns in spreading
425 manure. Conversely, an autumn maximum may be linked to decomposition of vegetation
426 (Cape et al., 2004). The contribution of DON to TDN is low at Auchencorth – 10.0% and
427 8.3% in 2009 and 2010, respectively – when compared to the literature average of 30%
428 (Cornell et al., 2003, Cape et al., 2004, Zhang et al., 2008, Cape et al., 2011, Zhang et al.,

429 | 2012), which is likely to be the result of different contributions of biological and
430 | anthropogenic local sources and those deposited through long range transport, varying
431 | contributions from anthropogenic inputs. This 10% contribution is markedly less than for
432 | a nearby study in the grounds of the Centre for Ecology & Hydrology (10 km north of
433 | Auchencorth Moss), a rural science park, where the contribution of DON to TDN was
434 | 24% for the period June 2005 to April 2007 (Gonzalez Benitez et al., 2009). This site was
435 | within 1 km of an intensively managed agricultural area (Easter Bush) dominated by
436 | sheep grazed grasslands and receiving high rates mineral nitrogen fertiliser (~ 200 kg N
437 | ha⁻¹ y⁻¹). In areas of intensive agricultural activity DON in precipitation increases, and is
438 | thought to be due to the addition of N fertilisers, especially urea (Neff et al., 2002, Zhang
439 | et al., 2012). Auchencorth Moss does not receive fertilisers and the number of
440 | sheep/cattle on site was low. Unfortunately our experimental set up did not allow us to
441 | investigate the contribution of long range transport to the DON concentrations, which
442 | may have been different between the two sites. These differences may also have a
443 | methodological explanation, as ~~Also~~, many of these earlier studies used bulk precipitation
444 | collectors instead of wet-only collectors, and these are likely to have additional water-
445 | soluble organic N deposited via dry deposition, and thus larger DON concentrations
446 | (Gonzalez Benitez et al., 2010).

447 | Previous studies of precipitation DIN and DON have reported varying degrees of
448 | correlation between DON, NH₄⁺ and NO₃⁻. For example, Violaki et al. (2010) found no
449 | correlation between DON, NH₄⁺ and NO₃⁻ in wet deposition in the Eastern
450 | Mediterranean. Zhang et al. (2008) also did not observe correlation between DON, NH₄⁺
451 | and NO₃⁻ in precipitation at 15 sites in China. However, when an additional 37 sites from
452 | across the globe were added to the study, positive relationships were found, suggesting a
453 | common or similar sources of DON and DIN on a global, but not regional, scale. In a
454 | number of studies, DON and NH₄⁺ were correlated, or at least more closely correlated
455 | than DON and NO₃⁻, suggesting DON is more closely associated with agricultural
456 | sources than with combustion processes (Cape et al., 2004, Chen et al., 2008, Cape et al.,
457 | 2011, Zhang et al., 2012). Our study showed weak to moderate correlations between
458 | NH₄⁺ and NO₃⁻ but no correlation between DIN and DON. This suggests that whilst the
459 | DIN compounds might share a common source (e.g. secondary aerosol), DON does not.
460 | This is further supported by the later seasonal maxima of DON compared to those of the
461 | DIN compounds (Cape et al., 2011).

462 4.2 N in the soil solution

463 August 2009 had the highest DIN concentrations and was the driest month that still
464 produced enough sample for analysis. Samples collected in drier periods or from dipwells
465 situated in drier parts of the moss were more viscous and contained much particulate
466 matter, making filtering difficult. In contrast, DIN concentrations in dipwells during
467 wetter periods or in wetter parts of the moss were more dilute and samples contained
468 much less particulate matter. Adamson et al., (2001) found higher NH_4^+ concentrations,
469 but lower DON concentrations, during periods of low water table in a blanket bog in
470 England. They suggested that the microbial community responsible for ammonification
471 benefited from the fluctuating water table to a higher degree than nitrifying organisms,
472 resulting in enhanced NH_4^+ concentrations, which then accumulated if the fluctuation
473 continued (Adamson et al., 2001, Daniels et al., 2012). This may be due to nitrifiers being
474 less able to cope with the stress caused by fluctuating conditions than ammonifiers
475 (Voroney, 2007). Although the mean water table was lower in 2010, 2009 saw a greater
476 degree of water table fluctuation (Fig. 4).

477 Interestingly, the TDN and DIN deposited as precipitation in 2010 was larger than in
478 2009, but the soil chemistry showed larger concentrations of TDN and DIN in 2009 than
479 in 2010. The larger DIN concentrations in 2009 may be due to the activities of sheep
480 which grazed on this moorland at very low livestock density of less than 1 ewe per ha and
481 also a small herd of 15 – 20 cattle . In 2009, sheep and sheep droppings were observed in
482 and around the vicinity of the dip wells and where the soil cores were collected; the small
483 cattle herd (15-20) also had access to this area. However, in 2010, there were no cattle on
484 site and the sheep frequented an alternative area of the peatland.

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

492 4.3 The composition of N in stream water

493 Numerous studies have found DON to be the dominant form of stream water N [in upland](#)
494 [catchments](#), 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 [in upland catchments](#), 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 $32.5 \mu\text{mol N l}^{-1}$ (82.1%), $6.2 \mu\text{mol N l}^{-1}$ (15.7%), and $0.9 \mu\text{mol N l}^{-1}$ (2.2%), respectively.~~ At Auchencorth Moss, the Black Burn DON concentrations were also the dominant form of N, at 75% ($48.1 \mu\text{mol N l}^{-1}$) and 74% ($50.0 \mu\text{mol N l}^{-1}$) 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 $14.1 \mu\text{mol N l}^{-1}$ (22%) in 2009 and $12.9 \mu\text{mol N l}^{-1}$ (19%) in 2010 for NH_4^+ , and $2.3 \mu\text{mol N l}^{-1}$ (3.6%) in 2009 and $4.5 \mu\text{mol N l}^{-1}$ (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 $47.9 \mu\text{mol N l}^{-1}$) contributing 71% of the TDN, followed by NH_4^+ (mean concentration $10.7 \mu\text{mol N l}^{-1}$), contributing 16% of TDN, and NO_3^- (mean concentration $8.6 \mu\text{mol N l}^{-1}$), contributing 13% of TDN (Vogt 2011). The DON values are comparable to the study reported here, but the Vogt study found lower NH_4^+~~

529 ~~and higher NO₃⁻ values. These differences may be due to the location of the Vogt study~~
530 ~~site, which was further downstream, next to a busy road, and was frequented by sheep~~
531 ~~more regularly than the upstream site from this study. This may have resulted in addition~~
532 ~~N inputs from the sheep and road traffic, increasing the amount of N leached/ deposited~~
533 ~~into the stream as NO₃⁻. Also, some NH₄⁺ may have been nitrified to NO₃⁻ as it was~~
534 ~~transported downstream towards the Vogt sampling site (Helliwell et al., 2007a).~~ No
535 correlation was found between the wet deposition of atmospheric N and stream
536 concentrations suggesting that precipitation does not represent a major source of stream
537 water N.

538 4.4 Seasonal patterns of N in stream water

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

547 The seasonal pattern of NO₃⁻, where concentrations were higher in cooler months and
548 lower in warmer months has been observed in numerous upland studies (Black et al.,
549 1993, Chapman et al., 2001, Daniels et al., 2012). In warmer months, the biological
550 uptake of NO₃⁻ by plants and microbes is at its highest, immobilising NO₃⁻. In winter,
551 productivity declines, increasing the amount of NO₃⁻ available to be leached into the
552 stream (Black et al., 1993, Chapman et al., 2001, Helliwell et al., 2007b). The summer
553 peaks in June and July 2010 are unusual and different to the summer lows observed in
554 2009. The high June value appears to be due to one high concentration, skewing the mean
555 monthly concentration; the median value for June was 0 µmol N l⁻¹. The high July 2010
556 peak is also evident in the mean concentrations of DON, and NH₄⁺, and is still reflected
557 in median values. The reason for these high values are unclear, however the differences
558 in discharge and precipitation between the two sampled years may be a contributing
559 factor. ~~The monthly discharge was 59% higher in June 2009 and 11% higher in July in~~
560 ~~2009 than in the corresponding months in 2010. Likewise, precipitation was 39% higher~~

561 | ~~in June 2009 and 24% higher in July 2009 than in the corresponding months in 2010.~~
562 | ~~Stream temperatures were similar but overall cooler in 2009.~~

563 4.5 DON speciation by GC×GC-NCD

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

569 Schulten and Schnizer, (1998) investigated the chemistry of organic matter of humic
570 substances and soils. Amongst other compounds they identified pyrrole and benzonitrile,
571 along with derivatives of pyrrole. They concluded that heterocyclic N compounds, of
572 which pyrrole is one, were an important constituent of soil organic matter, contributing
573 up to 35% of total N. Pyrrole and pyrrolic compounds are a major N source in coal and
574 are often found in peats; they can result from the aerobic breakdown of the tetrapyrrole
575 ring found in chlorophyll or from the breakdown of extensin, which is a type of
576 hydroxyproline-rich polymer found in the cell walls of plants (van Smeerdijk and Boon,
577 1987, Schulten and Schnizer, 1998). It is therefore likely that the source of pyrrole in the
578 streams was the peat in the surrounding catchment. Pyrrole has also been identified in fog
579 waters where it was found to be quickly degraded during transport by photochemistry
580 (Anastasio and McGregor, 2000). It is thought to be present in the atmosphere originating
581 from soil dust rich in humic/fluvic material (Schulten and Schnizer, 1998, Anastasio and
582 McGregor, 2000). This may explain the presence of a small amount of pyrrole found in
583 the precipitation samples.

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

586 4.6 GC×GC-NCD limitations

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

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

605 **5 Conclusions**

606 DON is an important source of nitrogen both in streams and precipitation and must not be
607 ignored in measurements of atmospheric nitrogen deposition rates or stream water
608 nitrogen balances. The mean volume-weighted concentration of DON found in the
609 precipitation over the total study period was $4.8 \mu\text{mol N l}^{-1}$, with a mean contribution of
610 9% to TDN.

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

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

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

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872 and Zhang, F. S. (2008) 'Evidence for organic N deposition and its anthropogenic
873 sources in China', *Atmospheric Environment*, 42(5), 1035-1041.

874 Table 1. Statistics of annual concentrations of NH_4^+ , NO_3^- , DON and TDN for 2009 and
 875 2010 in wet-only precipitation. Values are based on individual samples collected over the
 876 two year period. N* indicates the number of samples collected.

	NO_3^- $\mu\text{mol N l}^{-1}$	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

877 Table 2. Statistics of annual concentrations of NH_4^+ , NO_3^- , DON and TDN for 2009 and
 878 2010 in soil water. Values are based on individual samples collected from dip wells over
 879 the two year period. N^* indicates the number of samples collected.

	NO_3^- $\mu\text{mol N l}^{-1}$	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

880

881 Table 3. Statistics of annual concentrations of NH_4^+ , NO_3^- , DON and TDN for 2009 and
 882 2010 in stream water. Values are based on individual samples collected over the two year
 883 period. N* indicates the number of samples collected.

	NO_3^- $\mu\text{mol N l}^{-1}$	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

884

885

887 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 ($\mu\text{mol N l}^{-1}$)
 888 derived from TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations
 889 by 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
 890 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		

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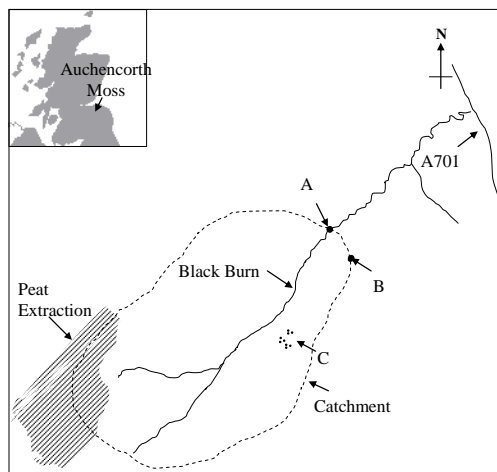
894 Table 4. continued. Summary of compounds and their concentrations ($\mu\text{mol N l}^{-1}$) detected by the GC \times GC-NCD, and DON concentrations ($\mu\text{mol N l}^{-1}$) as TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the
 895 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.
 896
 897

Sample	DON	Pyrrole	Benzonitrile	Unknown B	Unknown C	Dodecylamine	Unknown D	Unknown E	Unknown F
R_{t1}/R_{t2}	(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								
01/11/2010	3.9				0.5			0.9	
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	

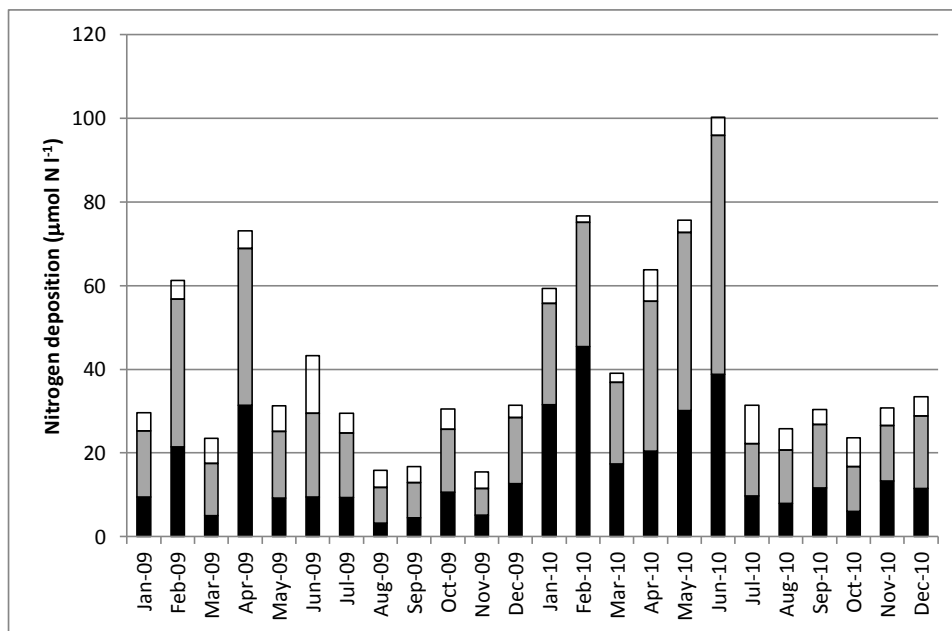
898

899 Table 5. Summary of compounds and their concentrations ($\mu\text{mol N l}^{-1}$) detected by the GC×GC-NCD, and DON concentrations ($\mu\text{mol N l}^{-1}$) detected
 900 by ANTEK in stream water samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the
 901 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
 902 GC columns.

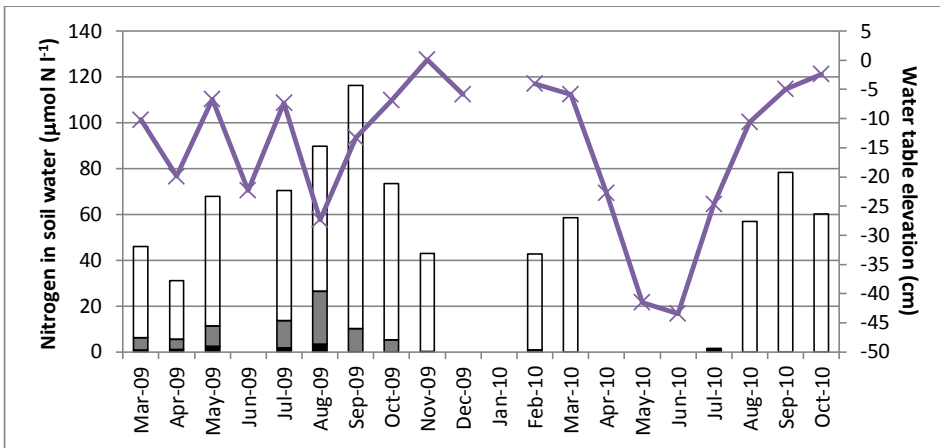
Sample Rt_1/Rt_2	DON (TDN-DIN)	Pyrrole 375/1.24	Unknown A 415/1.24	Benzonitrile 825/1.8	N-nitrosodipropylamine 970/1.4	Unknown B 11.45/1.52	Decylamine 1295/1.64	Unknown E 1910/1.7	Unknown F 2200/2.09
11/08/2010	45.9	1.3	3.2					0.9	
19/08/2010	54.8	0.2	0.3		1.2				
26/08/2010	85.2	0.7	2.7	3.0					
10/09/2010	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



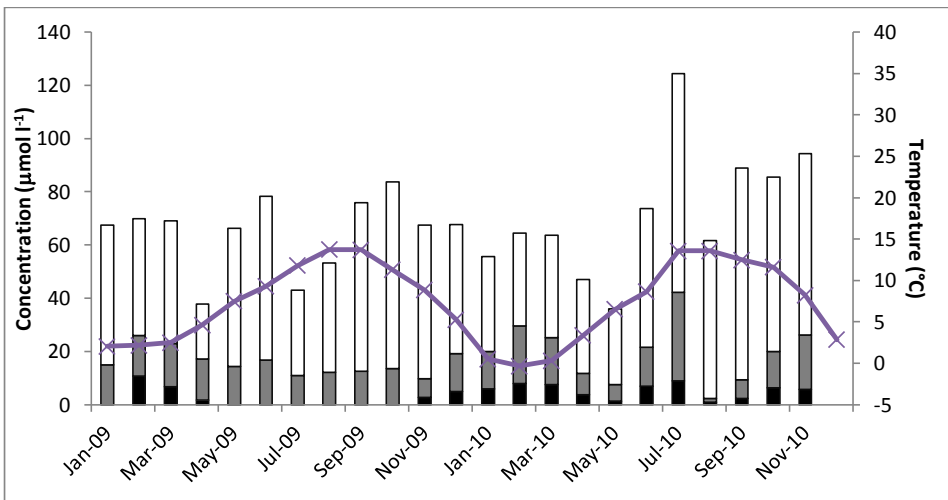
903
 904 Figure 1: Schematic map of catchment and sampling sites at Auchencorth Moss. Key: (A)
 905 study catchment outlet and stream sampling site; (B) monitoring station (wet only analyser);
 906 (C) dip wells. Adapted from Dinsmore et al., (2010).
 907



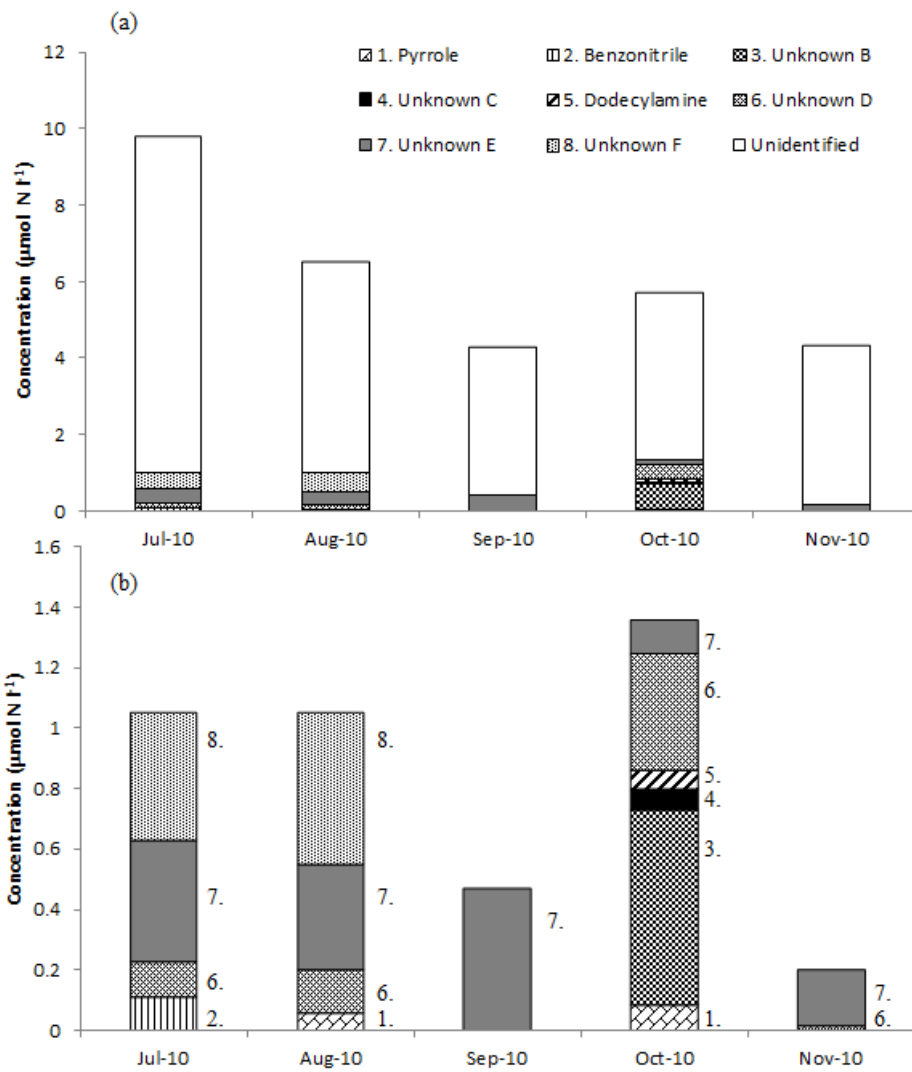
908
 909 Figure.2. Volume-weighted monthly average concentrations of NH₄⁺ (grey), NO₃⁻ (black) and
 910 DON (white) in wet only precipitation.



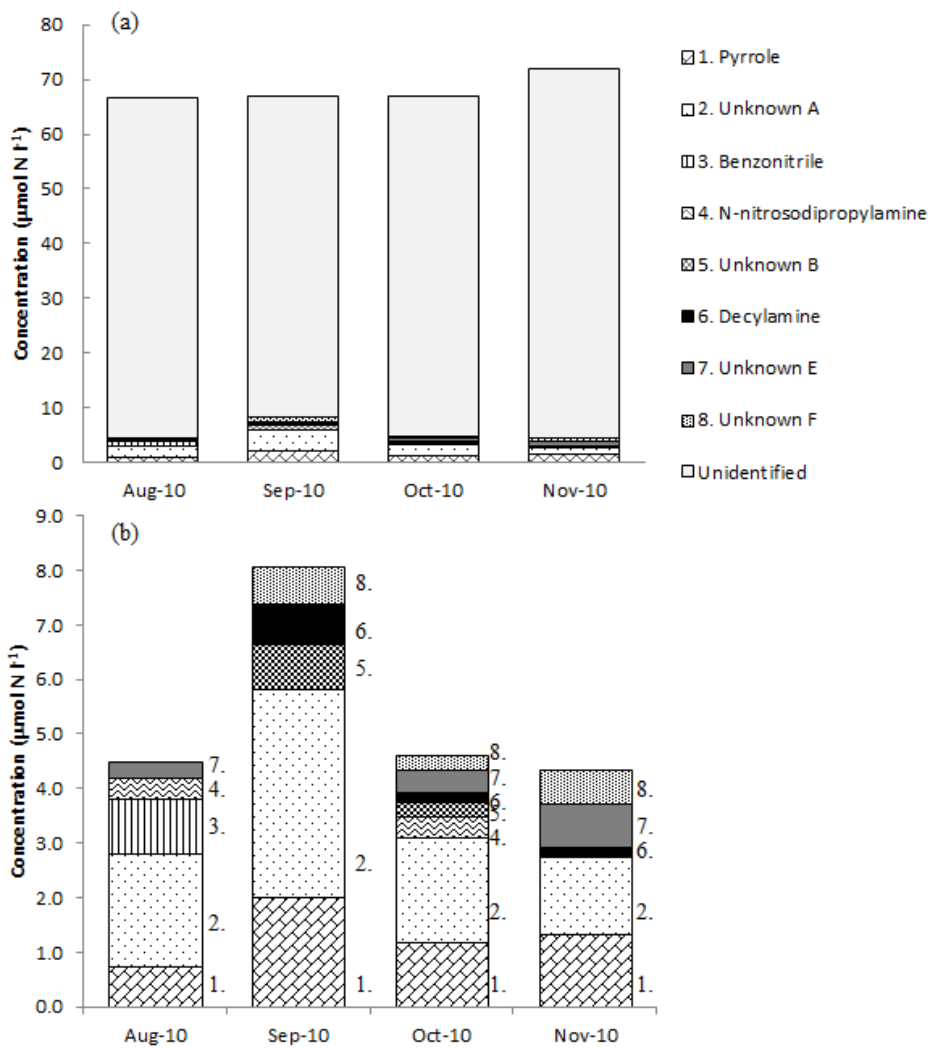
911
 912 Figure 3. Monthly concentrations of NH_4^+ (grey), NO_3^- (black) and DON (white) in soil
 913 water. The line represents monthly water table elevation. The June-09 sample was misplaced
 914 and Dec-09 and Jan 2010 were frozen, the remaining blank spaces indicate the dip wells were
 915 dry on the day of collection.
 916



917
 918 Figure 4. Discharge-weighted monthly mean concentrations of NH_4^+ (grey), NO_3^- (black) and
 919 DON (white) in stream water. The line represents mean monthly air temperature.



920
 921 Figure 5. Mean monthly concentrations of the individual DON compounds found in
 922 precipitation water. (a) includes the DON fraction identified from the ANTEK (white bar).
 923 (b) excludes the unidentified fraction, so that the speciation achieved by GC×GC-NCD is
 924 more clearly seen.



925
 926 Figure 6. Mean monthly concentrations of the individual compounds found in stream water.
 927 (a) includes the DON fraction identified from the ANTEK (white bar) (b) excludes the
 928 'unidentified' fraction, so the fraction detected by GC×GC-NCD is more clearly seen.