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

2 peatland

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13 **Abstract**

14 Dissolved organic nitrogen (DON) contributes significantly to the overall nitrogen

15 budget, but is not routinely measured in precipitation or stream water. In order to

16 investigate the contribution of DON to the deposition and export of N, precipitation,

17 stream and soil water samples were collected from an ombrotrophic peatland and

18 analysed for DON over a two year period. In wet only deposition DON contributed up to

19 10% of the total dissolved nitrogen (TDN), and was the most dominant fraction in soil

20 water (99%), and stream water (75%). NH_4^+ was the most dominate form of N in

21 precipitation, with NO_3^- contributing the least to precipitation, soil water and stream

22 water.

23 Precipitation and stream DON was qualitatively analysed by GCxGC NCD after trapping

24 onto C18 SPE cartridges. Ten unique compounds were detected and five identified as

25 pyrrole, benzonitrile, dodecylamine, N-nitrosodipropylamine and decylamine. Five

26 compounds were present in both precipitation and stream samples: pyrrole, benzonitrile

27 and three unidentified compounds. The SPE extraction efficiency for DON was very low

28 (11%), but with improvements DON speciation could become a valuable tool to provide

29 information on its sources and pathways and inform chemical transport models.

30

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

1 Introduction

The total deposition of N in the UK was estimated to be approximately 330 Gg in 2004, with wet and cloud deposition accounting for approximately 211 Gg (63.9%), and the rest consisting of dry deposition (Fowler et al., 2009, Hertel et al., 2011). Wet deposition of the dissolved inorganic nitrogen (DIN) compounds ammonium (NH_4^+) and nitrate (NO_3^-) has been studied over many years (Violaki et al., 2010, Cape et al., 2011, Zhang et al., 2012). The former is produced by the dissolution of ammonia gas (NH_3) and the scavenging of NH_4^+ aerosol, and the latter by the dissolution of nitric acid gas (HNO_3) and the scavenging of NO_3^- aerosol (Russell et al., 1998, Cornell et al., 2003, Tian et al., 2011). The dissolved organic nitrogen (DON) fraction is less well documented due to difficulties in measuring it, but it can be an important fraction of the total dissolved nitrogen (TDN) deposited, and can potentially be biologically available as a source of N (Russell et al., 1998, Neff et al., 2002, Cornell et al., 2003, Cape et al., 2004). The sources of DON are not well understood, but it is known to be ubiquitous in the environment, present in particulate, gaseous and aqueous phases (Cornell et al., 2003, Cape et al., 2004, Özel et al., 2011). Studies have shown that DON can contribute 30-50% of the wet deposition of water soluble N (Neff et al., 2002, Cape et al., 2004, Zhang et al., 2008, Cape et al., 2011, Cornell, 2011, Zhang et al., 2012).

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

65 As with wet deposition, N is present in streams as both DIN and DON, with most focus

66 usually being on the DIN fraction. DIN, in particular NO_3^-, is often used as an indicator

67 of N saturation, with higher stream concentrations and changes in seasonal patterns

68 indicating an increase in the leaching of DIN from the catchment (Cundill et al., 2007,

69 Daniels et al., 2012). DON, however, is not routinely measured in spite of being the most

70 dominant fraction in waters draining peatland catchments; DON is known to contribute

71 60-90% of the TDN load in peatland streams (Yesmin et al., 1995).

72 The aim of this study was to investigate the contribution of DON to TDN of wet

73 deposition and TDN export via a stream at a typical NW European ombrotrophic peatland

74 over a two year period. In addition to this, an attempt was made to identify some of the

75 less polar individual DON compounds present in a selection of precipitation and stream

76 samples. A comparison between possible sources of compounds detected in both the

77 precipitation and stream water was also discussed

78 **2 Site and methods**

79 2.1 Study area

80 Auchencorth Moss (Fig. 4.1) is an ombrotrophic peat bog located in south Scotland,

81 approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat.

82 55°47'34 N; long. 03°14'35 W). The site is used primarily for low intensity sheep

83 grazing (less than one livestock unit km^{-2}) and in 2009 a small herd of cows (15-20) also

84 grazed on the site.

85 The volume of peat in the catchment is estimated to be ~50 million m^3, with depths up to

86 5 m, and an average depth of 50 cm. The total peat coverage is ~1214 ha, of which

87 approximately 170 ha is extracted (located 1.75 - 3.4 km W-SW of the monitoring

88 station) (Mitchell and Mykura, 1962, Dinsmore, 2008).

89 The Black Burn runs SW to NE of the CEH atmospheric monitoring station at

90 Auchencorth Moss, and drains into the North Esk river. It has a catchment area of

91 approximately 335 ha, which is fed by numerous tributaries, including one which

92 originates in the area of peat extraction. There are a number of overgrown ditches laid out

93 in parallel which is evidence of past drainage activities. The elevation of the catchment is

94 approximately 250-300 m and the main soil type is Histosols (85% coverage), with

95 Gleysol (9%), Humic Gleysol (3%) and Cambisols (3%) present mostly at the margins of

96 the catchment (Billett et al., 2004).

97   The vegetation is arranged into numerous hummocks and hollows. The hollows are

98   depressions up to 30 cm deep and are dominated by blankets of *Sphagnum* mosses, with

99   various sedges, monocotyledons and other bryophytes also present; the hummocks can be

100   up to 30 cm high, and although *Sphagnum* mosses are present, there is a larger density of

101   vascular plants with the dominant species being *Deschampsia flexuosa, Eriophorum*

102   *vaginatum* and *Juncus effusus.* Flechard and Fowler (1998) and Dinsmore (2008) have

103   presented more detailed vegetation information for Auchencorth Moss.

104   The mean water table depth was determined from nine dip wells located close to the

105   monitoring station (Figure1) and was -14.8 cm, ranging from -52.4 to 7 cm above the

106   peat surface during the study period (January 2009 - December 2010).

107

108   2.2 Wet-only precipitation

109   Auchencorth Moss is a European Monitoring and Evaluation Programme (EMEP)

110   supersite contributing to the Co-operative Programme for Monitoring and Evaluation of

111   the Long-range Transmission of Air Pollutants in Europe

112   (http://www.emep.int/index_facts.html). Precipitation was collected daily using an

113   automated wet-only collector (Eigenbrodt NSA 181/KS, Königsmoor, Germany). A

114   sensor detected when rain fell, opening the lid and allowing rain to be collected in a

115   PTFE-coated funnel draining to refrigerated polyethylene bottles. When rainfall ceased,

116   the sensor closed the lid, protecting the samples from contamination from dry deposition

117   and animal inputs. The collector was kept at 4°C by an internal cooling system and

118   samples were manually emptied from the daily collector once a week, where they were

119   stored in a cool room, also at 4°C. Samples were analysed by Ion Chromatography (IC)

120   for NH_4^+ and NO_3^-, following EMEP protocols

121   (http://www.nilu.no/projects/ccc/manual/index.html).

122   A Metrohm 761 Compact Ion Chromatograph (IC) connected in parallel with a Metrohm

123   733 IC Separation Centre to a Metrohm 766 IC sample processor (Metrohm Ltd.,

124   Herisau, Switzerland) measured NO_3^- and NH_4^+ respectively. NO_3^- was determined by

125   pumping an eluent solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate

126   through a Metrosep A Supp 5 column. For NH_4^+ determination, an eluent solution of 24

127   mM boric acid, 5 mM tartaric acid and 0.7 mM dipicolinic acid, was pumped through a

128   Metrosep C1 column. Typical detection limits were 1 μmol N l^{-1} for both NO_3^- and NH_4^+.

129 Whenever enough precipitation was collected, the EMEP sample was subsampled (5 ml)
130 for analysis of TDN (TDN = DIN + DON). Samples were filtered using Millipore
131 Hydrophilic PTFE (0.45μm pore size) syringe filters prior to freezing and later analysed
132 for TDN by high-temperature catalytic oxidation using an ANTEK 8060-M Nitrogen
133 Specific HPLC Detector (ANTEK Instruments Inc., Houston, TX, USA). The analysis
134 was conducted in flow-injection mode, in which 20 μl samples were introduced into an
135 eluent stream of 10% methanol in deionised water at a flow rate of 250 μl min^{-1}. It was
136 then combusted in oxygen at 1050 ºC, producing nitric oxide (NO) which was detected
137 by chemiluminescence. The detection limit for TDN was ~ 1 μmol N l^{-1}. DON was
138 determined by subtracting DIN from TDN.
139 Subsamples were also analysed for NO_3^- and NH_4^+ on the IC at CEH and where
140 compared to the EMEP samples. The agreement was good, with an average standard
141 error of ± 0.22 μmol N l^{-1} between NO_3^- samples and ± 1.45 μmol N l^{-1} between NH_4^+
142 samples.
143 The uncertainty of DON is greater than for DIN as a result of errors associated with
144 measuring TDN and DIN compounding (Cornell et al., 2003). A negative bias may result
145 from these combined uncertainties, from DON not being fully converted during the total
146 N analysis, and from losses due to the collection and storage procedure (Russell et al.,
147 1998, Cornell et al., 2003). A positive bias results from setting small negative values of
148 DON to zero. To avoid this bias small negative values of DON were included in the data
149 analyses here. The limit of detection of DON was determined by the summation of the
150 detection limits of the 3 independent measured concentrations (NH_4^+, NO_3^- and TDN)
151 and was 3 μmol N l^{-1}.

152 2.3 Soil water

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

160   2.4 KCl-extractable mineral N

161   Soil cores were collected at a depth of 0-10 cm at three locations (next to the dip wells),

162   in spring and autumn in 2009 and in spring, summer and winter in 2010. NH_4^+ and NO_3^-

163   were extracted from soil samples using KCl; 15 g of soil were shaken for 1 hour with 50

164   ml of 1M KCl solution at a rate of 100 rpm. Samples were then filtered using Whatman

165   42 filter papers and frozen prior to analysis by IC. TDN was not measured, so DON could

166   not be determined.

167   2.5 Stream water

168   Stream water spot samples were collected from the Black Burn, to the north of the field

169   station by dipping a 300 ml glass bottle once a week. The samples were filtered within 24

170   hours of collection, using Millipore Hydrophilic PTFE (0.45μm pore size) syringe filters

171   and frozen until ready for analysis. Samples collected from January 2009 – October 2009

172   were analysed for TDN, NH_4^+ and NO_3^- using a San^{++} Automated Wet Chemistry

173   Analyzer/Continuous Flow Analyzer (SKALAR, The Netherlands). Samples from

174   November 2009-November 2010 were analysed for NH_4^+, NO_3^- and TDN using the IC

175   and ANTEK methods described above. In both cases, DON was determined by

176   subtracting DIN from TDN.

177   Discharge was determined from water height using manually calibrated rating curves

178   (R^2>0.90) based on measurements of dilution gauging (Dinsmore, per. com.). Pressure

179   transducers were used to measure water height at 10 minute intervals. Until April 2009, a

180   Druck PDCR 1830 series pressure transducer was used at the sample site (Fig 1). After

181   April 2009, an In Situ Inc. Level Troll® pressure transducer located ~2 km downstream

182   was used.

183   2.6 GC×GC-NCD

184   Comprehensive two-dimensional gas chromatography coupled to a nitrogen

185   chemiluminescence detector (GC×GC-NCD) was used to separate DON into different

186   peaks and identify individual components where possible. To trap DON samples were

187   extracted by solid phase extraction (SPE), using Superclean ENVI-18 SPE tube 20 μm

188   polymeric C_{18}-reverse phase 500 mg-3 ml SPE cartridges (SUPELCO, Bellefonte, PA,

189   USA). Cartridges were conditioned with 5 ml methanol followed by 5 ml of water at a

190   rate of 2-5 ml min^{-1}. Between 5 and 18 ml of precipitation and 9 and 24 ml of stream

191   water was passed through the cartridge at a rate of 2-5 ml min^{-1}. The cartridge was

192   thoroughly dried under vacuum for ~30 minutes, eluted with 5 ml dichloromethane

193   (DCM), and then concentrated in a stream of nitrogen to a volume of ~ 0.1 ml prior

194   analysis by GC×GC-NCD. We investigated the extraction efficiency retrospectively on

195   rainwater and river water samples collected in October 2015 from the same locations the

196   precipitation and stream water samples were collected in 2009 and 2010, and analysed

197   these for DIN and TDN as described in section 2.2. As expected the C18 SPE cartridges

198   did not retain NH_4 and NO_3 on the SPE cartridges, but unfortunately also the retention of

199   DON was low (9% for the precipitation and 18% for the river waters).

200   The GC×GC-NCD was an Agilent 7890 GC coupled with an Agilent 255 NCD (Agilent

201   Technologies, Palo Alto, CA, USA). 1 µl extracts were injected in pulsed splitless mode

202   at 280 °C and a pressure of 30 psi for 2 min, using a Gerstel automated liquid injector

203   (Gerstel, Mulheim an der Ruhr, Germany). The first dimension column was a non-polar

204   BPX5 (30 m x 0.32 nm i.d. x 0.25 µm film thicknesses), set to an initial temperature of

205   55 °C for 1 min. The temperature was then increased at a rate of 5°C min^{-1} until 305 °C

206   where it was isothermally held for 1 min. The second column was a BPX50 (1.5 m x 0.10

207   mm i.d. x 0.10 µm film thickness) set to an initial temperature of 70 °C for 1 min, then

208   increasing the temperature at a rate of 5 °C min^{-1} until 320 °C where it was isothermally

209   held for 1 min. Both columns were from SGE Analytical Science (VIC, Australia).

210   Helium was used as a carrier gas at a constant flow of 1 mL min^{-1} and the data was

211   collected at 50 Hz. Pyrolysis was carried out at 900 °C with a hydrogen flow rate of 4 ml

212   min^{-1} and oxygen flow rate of 10 ml min^{-1}.

213   The detector shows an equimolar response regardless of the chemical state of the organic

214   nitrogen (except azo compounds), allowing nitrogen-containing compounds to be

215   quantified without the need for a separate calibration standard for each compound (Yan,

216   2002, Özel et al., 2011). Details of the optimization of the NCD response and the

217   analytical performance with respect to equimolar response using standards was evaluated

218   by Özel et al., (2011).

219   **3 Results**

220   3.1 Meteorology

221   Total rainfall was determined from the volume of rain collected in the wet only analyser.

222   In 2009 the total rainfall was 902 mm with monthly totals varying from 16 mm in

223   February to 180 mm in November. The mean monthly temperature varied from 0.5 °C in

224   December to 13.7 °C in July, with a yearly mean of 7.6 °C. In 2010 the total rainfall was

225   732 mm with monthly totals varying from 21 mm in May to 128 mm in November.

226   However, a significant amount of snow fell, which was not recorded by the wet-only

227   collector. Based on the ratio of discharge and precipitation (Dinsmore et al., 2013, Skiba

228   et al., 2013) it was estimated that snow accounted for an additional 291 mm, making the

229   total precipitation collected for 2010 approximately 1023 mm. The mean monthly

230   temperature varied from -2.0 °C in December to 13.6 °C in July, with a yearly mean of

231   6.6 °C.

232   3.2 Wet-only N deposition

233   Figure 2 shows the volume-weighted monthly mean concentrations of N in precipitation.

234   The temporal variation of NH_4^+ and NO_3^- follow a similar pattern, with DON differing. In

235   both 2009 and 2010 (Table 1), NH_4^+ was the dominant component of wet-only deposition

236   with annual mean concentrations of 27.2 μmol N l^{-1} (58% of TDN) and 30.7 μmol N l^{-1}

237   (53% of TDN) respectively. The contribution of NO_3^- was greater in 2010 than in 2009,

238   with mean concentrations of 15.0 μmol N l^{-1} (32% of TDN) in 2009 and 22.7 μmol N l^{-1}

239   (39% of TDN) in 2010. Although DON contributed the least to annual concentrations in

240   both years, on a monthly timescale there were a few occasions when DON exceeded NO_3^-

241   (March 2009, June 2009, Aug 2009 and Oct 2010). A loose seasonal pattern was

242   observed for NH_4^+ and NO_3^-, with peak concentrations occurring between January and

243   June, especially in 2010. DON has no clear seasonal pattern, although the lowest

244   concentrations seem to occur in the winter months (Nov- Jan). A weak, but significant

245   correlation was found between NH_4^+ and NO_3^- in 2009 ($R^2 = 0.45$, $p < 0.001$) and a

246   slightly stronger correlation in 2010 ($R^2 = 0.62$, $p < 0.001$). No correlations were

247   observed between NH_4^+, DON, temperature, rainfall or precipitation; NO_3^-, DON,

248   temperature, rainfall or precipitation; or DON, temperature, rainfall or precipitation.

249   3.3 Soil water and KCl-extractable N

250   As expected for a peatland, DON dominates TDN concentrations in the soil water. The

251   contribution of DON to TDN was higher in 2010 at 99% compared to 85% in 2009

252   (Table 2). Mean annual NO_3^- concentrations were 1.2 μmol N l^{-1} (2% of TDN) in 2009

253   and 0.2 μmol N l^{-1} (0.3% of TDN) in 2010. Mean annual NH_4^+ concentrations were also

254   larger in 2009 (8.6 μmol N l^{-1}) than in 2010 (0.2 μmol N l^{-1}). The contribution of NH_4^+ to

255   TDN was thus much larger in 2009 at 13% and just 0.4% in 2010. Due to data gaps,

256　caused by dip wells remaining empty in low rainfall periods, or frozen in winter 2010, it

257　was difficult to assess seasonal patterns.

258　Soil extractions of NO_3^- and NH_4^+ using 1 M KCl on two occasions in 2009 and 3 three

259　occasions in 2010 showed similar trends; no detectable NO_3^-, and NH_4^+ concentrations of

260　29 ± 12 µmol N l^{-1} and 39 ± 20 µmol N l^{-1} for 2009 and 2010, respectively.

261　3.4 Concentration and forms of N in stream water

262　DON is the dominant N species found in the stream water. Monthly mean discharge

263　weighted concentrations contributed on average 74.6% (in 2009) and 74.3% (in 2010) to

264　TDN; with the highest concentrations in summer/autumn, however no clear seasonal

265　pattern was evident (Figure 4, Table 3). Monthly mean discharge weighted concentrations

266　of NO_3^- ranged from 0.0 to 13.7 µmol N l^{-1} in 2009 and 0.0 to 15.2 µmol N l^{-1} in 2010.

267　Annual mean concentrations were 2.3 µmol N l^{-1} in 2009 and 4.5 µmol N l^{-1} in 2010. In

268　2009, concentrations varied seasonally; largest NO_3^- concentrations were measured

269　during the cooler months and the smallest during the warmer months. In summer 2009

270　there was no detectable NO_3^-. In 2010 stream water NO_3^- concentrations initially

271　followed a similar pattern as in 2009, with concentrations increasing during the winter

272　months and decreasing as temperature increased and summer approached. However, there

273　was a large increase in NO_3^- concentrations in June and July 2010. Consequently, average

274　annual NO_3^- concentrations in 2010 were nearly double those in 2009, contributing 6.6%

275　of TDN compared to 3.6% of TDN (Table 3). Monthly median concentrations for NO_3^-

276　for the whole period showed a similar pattern to monthly discharge-weighted mean

277　concentrations, with the exception of June 2010, which is reduced to a summer low of 0

278　µmol N l^{-1}, suggesting the monthly mean value was skewed by an unusually large value.

279　Median concentrations made little difference to the July 2010 maximum. July 2010 also

280　showed a maximum in the mean concentrations of DON and NH_4^+.

281　Monthly mean discharge weighted concentrations of NH_4^+ ranged from 5.4 to 21.9 µmol

282　N l^{-1} with an annual mean of 14.1 µmol N l^{-1} in 2009, and 0.0 to 52.3 µmol N l^{-1} with an

283　annual mean of 12.9 µmol N l^{-1} in 2010. Concentrations of NH_4^+ were consistently higher

284　than NO_3^- and there was no clear seasonal pattern. No correlation was observed between

285　NH_4^+, NO_3^-, DON, discharge, temperature, rainfall (both air and stream) or precipitation.

286   3.5 DON speciation by GC×GC-NCD

287   Tables 4 and 5 display breakdowns of the individual DON compounds detected by the
288   GC×GC-NCD and their concentrations for precipitation and stream water, respectively.
289   The plasticiser N-butyl-benzenesulphonamide (not included in tables) was a prominent
290   compound in all samples, with extremely high concentrations, sometimes higher than
291   TDN detected in the precipitation by ANTEK. We assume that the N-butyl-
292   benzenesulphonamide detected was most likely to be a sampling contaminant from the
293   storage bottles during storage in the freezer prior to analysis, or from SPE extraction
294   tubes by reaction with the DCM. This contamination was not detected in blank water
295   samples (deionised water) or by the ANTEK as samples run on this machine were filtered
296   directly into glass vials for storage before analysis.The source of this contamination is
297   discussed later and the compound was thus excluded from the results.

298   In 13 of the 31 precipitation samples, and 2 of the 21 stream samples, no DON
299   compounds were detected or the peaks were too small to be distinguishable from
300   background noise. The limit of detection (LOD) using the optimized method was
301   determined between 0.16-0.27 pgN using GC×GC-NCD of standard mixtures (Özel et al.,
302   2011).

303   Peak identification was carried out by comparing retention times and Rt_2) of sample
304   peaks (Rt_1) with retention times of known standards (Rt_2). This could lead to some
305   misidentification, however co-elution is greatly reduced using GC×GC and there is very
306   good retention time stability between runs. Several peaks, consistently present in some
307   samples, could not be identified as they did not match any of the retention times of the
308   standards available, and therefore were labelled "Unknown" A-F. In total 10 unique
309   compounds were found to be present in the stream and precipitation, of which only 5
310   could be identified. Tables 4 and 5 present a summary of the compounds identified in
311   precipitation and stream water DON, respectively. Both the precipitation and the stream
312   water contained 8 distinct compounds, 5 of which were in common.

313   The most common compound identified in the precipitation samples was Unknown E,
314   present in 10 samples, followed by Unknown D in 6 samples and Unknown B in 5
315   samples, with mean concentrations of 0.3 μmol N l^{-1}, 0.14 μmol N l^{-1} and 0.2 μmol N l^{-1}.
316   Two precipitation samples contained pyrrole, with a mean concentration of 0.03 μmol N
317   l^{-1}. Unknown F was in 3 samples (mean concentrations of 0.1 μmol N l^{-1}), dodecylamine
318   was in 2 samples (mean concentration of 0.02 μmol N l^{-1}), and Unknown C was in one

319 sample (0.02 μmol N l^{-1}). The precipitation samples did not contain Unknown A, N-
320 nitrosodipropylamine or decylamine, which were found in the stream samples.

321 The most common compound identified in the stream samples was Unknown A, the
322 mean concentration was 2.0 μmol N l^{-1} (Table 5). Pyrrole was the next most common
323 compound, found in 18 of the stream samples, with a mean concentration of 1.2 μmol N
324 l^{-1}. Unknowns E and F both appeared in 9 stream samples, with mean concentrations of
325 0.5 μmol N l^{-1} and 0.4 μmol N l^{-1}. N-nitrosodipropylamine (NDPA) was present in 4
326 stream samples, followed by Unknown B and decylamine in 3 stream samples. Mean
327 concentrations were 0.2 μmol N l^{-1} for all three compounds. Unknown D, Unknown C
328 and dodecylamine, present in the precipitation samples, were absent from the stream
329 samples.

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

332 Figures 5a and 6a display breakdowns of the monthly means of individual DON
333 compounds extracted with the C18 SPE cartridges prior identification by the GC×GC-
334 NCD method and the remaining DON measured by ANTEK for precipitation and stream
335 water, respectively. Figures 5b and 6b show the monthly means of individual DON
336 compounds detected by the GC×GC-NCD only, to make this fraction more visible. In
337 both cases, the majority of DON was not was "unidentified", contributing a mean of 91%
338 and 82% of total DON detected in precipitation and stream water, respectively. In the
339 precipitation samples, Unknown E is the only compound present in all 5 sampling
340 months, and is the only compound identified in September. October had the most
341 identified compounds present, with 6 of the 8 compounds measured (Fig. 5b). In the
342 stream samples, pyrrole and Unknown A were present in all 4 sampling months. October
343 also had the most identified compounds present, with 7 of the 8 compounds present (Fig.
344 4).

345 **4 Discussion**

346 4.1 The composition of N in precipitation

347 Cape et al., (2004) studied several sites in the UK on a range of land uses and noted an
348 annual cycle for DIN and DON, with peak concentrations for NH_4^+ and NO_3^- occurring
349 in April-June 2000-2002 and a DON peak occurring later (June-August 2000-2002). Both
350 DIN and DON showed minima in winter. The data presented here are similar, but with

351   earlier DIN maxima in (Feb-April in 2009 and Feb-June 2010) followed by lower values

352   in the autumn and beginning of winter. DON also peaked earlier than reported by Cape at

353   al. (2004) but roughly a month after DIN peaked in both 2009 and 2010. Generally,

354   sources of NH_4^+ in precipitation tend to be of agricultural origin, and sources of NO_3^- in

355   precipitation from combustion activities (Cape et al., 2011). Although Auchencorth Moss

356   is located in a rural setting and with minimal agricultural activity on the peatland itself;

357   there are several chicken farms in the area. Chickens farms emit ammonia (NH_3), which

358   when dissolved in rainwater, produces NH_4^+ (Schlesinger, 1997). NH_4^+ also makes up a

359   large fraction of atmospheric aerosols and is often transported further downwind of its

360   source (Nieder and Benbi, 2008), where it can then be washed out and deposited by

361   precipitation.

362   Sources of NO_3^- include motor vehicles and stationary combustion sources (power

363   stations, domestic heating) following atmospheric oxidation of the emitted nitrogen

364   oxides. As a secondary pollutant, nitric acid and nitrates are less easily traced back to

365   sources. The sources of DON are more difficult to generalise and the magnitude of DON

366   is likely to be the result of different contributions of biological and anthropogenic local

367   origin and those deposited through long range transport. Spring maxima of DON may be

368   due to the release of pollen, plant debris and spores (Violaki et al., 2010), or spreading of

369   manure and mineral N fertilisers (Neff et al., 2002, Zhang et al., 2012). Conversely,

370   autumn maxima may be linked to decomposition of vegetation (Cape et al., 2004). The

371   contribution of DON to TDN is low at Auchencorth – 10.0% and 8.3% in 2009 and 2010,

372   respectively, when compared to the 24% (June 2005 to April 2007) measured at Bush

373   Estate, an agricultural area 10 km north of Auchencorth Moss dominated by grazed

374   grasslands with high stocking densities and receiving high rates of mineral nitrogen

375   fertiliser (~ 200 kg N ha^{-1} y^{-1}, Gonzalez Benitez et al., 2009). The literature average from

376   a range of environments is 30% (Cornell et al., 2003, Cape et al., 2004, Zhang et al.,

377   2008, Cape et al., 2011, Zhang et al., 2012).

378   Previous studies of precipitation DIN and DON reported varying degrees of correlation

379   between DON, NH_4^+ and NO_3^-. For example, Violaki et al. (2010) found no correlation

380   between DON, NH_4^+ and NO_3^- in wet deposition in the Eastern Mediterranean. Zhang et

381   al. (2008) also did not observe correlation between DON, NH_4^+ and NO_3^- in precipitation

382   at 15 sites in China. However, when an additional 37 sites from across the globe were

383   added to these data, positive relationships between DON and DIN were found, suggesting

384   that broadly similar sources of DON and DIN at the global, but not regional, scale. In a

385　number of studies, DON and NH_4^+ were correlated, or at least more closely correlated

386　than DON and NO_3^-, suggesting DON is more closely associated with agricultural

387　sources than with combustion processes (Cape et al., 2004, Chen et al., 2008, Cape et al.,

388　2011, Zhang et al., 2012). Our Auchencorth Moss study showed weak to moderate

389　correlations between NH_4^+ and NO_3^- but no correlation between DIN and DON. This

390　suggests that whilst DIN compounds might share a common source (e.g. secondary

391　aerosol), DON does not. This is further supported by the later seasonal maxima of DON

392　compared to those of the DIN compounds (Cape et al., 2011).

393　4.2 N in the soil solution

394　Interestingly, the TDN and DIN deposited as precipitation in 2010 was larger than in

395　2009, but the soil chemistry showed the opposite.　The larger soil water DIN

396　concentrations in 2009 may be due to the activities of sheep which grazed on this

397　moorland at very low livestock density of less than 1 ewe ha^{-1} and also a small herd of 15

398　– 20 cattle. In 2009, sheep and sheep droppings were observed in and around the vicinity

399　of the dip wells and where the soil cores were collected; the small cattle herd (15-20) also

400　had access to this area. However, in 2010, there were no cattle on site and the sheep

401　frequented another area of this large peatland.

402

403　4.3 The composition of N in stream water

404　DON is the dominant form of stream water N in high rainfall areas, catchments with

405　steep slopes and those draining peatlands. Typical DON contributions vary from 54% to

406　82% annually (Chapman et al., 2001, Cundill et al., 2007, Helliwell et al., 2007a), which

407　is simlar to the 75% and 74% measured in the Black Burn for 2009 and 2010,

408　respectively. Mean annual NH_4^+ concentrations (22% in 2009 and 19% in 2010) were

409　larger than NO_3^- concentrations (3.6% in 2009 and 6.6% in 2010). This was also observed

410　by Helliwell et al. (2007a) in four upland regions in the UK. Usually, the leaching of

411　inorganic N is dominated by NO_3^-, whereas NH_4^+ remains in the soil in weak association

412　with organic matter and incorporation into clay lattices (Scherer, 1993, Chapman and

413　Edwards, 1999, Davies et al., 2005, Helliwell et al., 2007a).

414　A previous study carried out at the Black Burn in 2008, approximately 2.5 km

415　downstream from the sampling site reported here, also found DON to be the dominant

416　species (mean concentration of 47.9 µmol N l^{-1}) contributing 71 % of the TDN, followed

417   by NH_4^+ (mean concentration 10.7 μmol N l^{-1}), contributing 16% of TDN, and NO_3^-

418   (mean concentration 8.6 μmol N l^{-1}), contributing 13% of TDN (Vogt 2011). The DON

419   values are comparable to the study reported here, but the Vogt study found lower NH_4^+

420   and higher NO_3^- values. These differences may be due to the location of the Vogt study

421   site, which was further downstream, next to a busy road, and was frequented by sheep

422   more regularly than our upstream site. No correlation was found between the wet

423   deposition of atmospheric N and stream concentrations suggesting that precipitation does

424   not represent a major source of stream water N.

425   4.4 Seasonal patterns of N in stream water

426   No clear seasonal pattern was identified for DON, although the general trend was higher

427   concentrations in the warmer months. Also Chapman et al. (2001), who studied 28

428   Scottish upland streams, found DON to be larger in the summer than winter months.

429   They suggested that this was due to an increase of in-stream biological DON production,

430   mediated by algae and microorganisms, rather than increased leaching from the soil.

431   The seasonal pattern of NO_3^-, where concentrations were higher in cooler months and

432   lower in warmer months has been observed in numerous upland studies (Black et al.,

433   1993, Chapman et al., 2001, Daniels et al., 2012). In warmer months, the biological

434   uptake of NO_3^- by plants and microbes both in the terrestrial and aquatic systems is at its

435   highest, immobilising NO_3^-. In winter, productivity declines, increasing the amount of

436   NO_3^- available to be leached into the stream and its residence time in the stream (Black et

437   al., 1993, Chapman et al., 2001, Helliwell et al., 2007 b). The summer peaks in June and

438   July 2010 are unusual and different to the summer lows observed in 2009. The high June

439   value appears to be due to one high concentration, skewing the mean monthly

440   concentration; the median value for June was 0 μmol N l^{-1}. The high July 2010 peak is

441   also evident in the mean concentrations of DON, and NH_4^+, and is still reflected in

442   median values. The reason for these high values are unclear, however the differences in

443   discharge and precipitation between the two sampled years may be a contributing factor.

444   4.5 DON speciation by GC×GC-NCD

445   More than 82% of the DON was not trapped by the SPE cartridges. This low retention

446   implies that further work is needed to improve the extraction procedure and maximise the

447   applicability of this technique, or alternatives, such as liquid-liquid extractions or stir bar

448   sorptive extraction, and thereby provide a more comprehensive picture of the DON

species in precipitation and stream waters. For example, it is noticeable that highly polar and large molecular weight DON species were not detected by the GC×GC-NCD, and presumably also not retained by the C18 SPE cartridges.

Whilst some of the compounds detected by the GC×GC-NCD appear in the precipitation and the stream water, the two main compounds identified in the stream water were only present in precipitation in small amounts or not present at all. This suggested that at least some sources of DON in precipitation and stream waters are different. Schulten and Schnitzer, (1998) and Leinweber et al., (2013) investigated the chemistry of organic matter of humic substances and soils. Amongst other compounds they identified pyrrole and benzonitrile, along with derivatives of pyrrole. Pyrrole and pyrrolic compounds are a major N source in coal and are often found in peats (van Smeerdijk and Boon, 1987, Schulten and Schnitzer, 1998). It is therefore likely that the source of pyrrole in the streams was the peat in the surrounding catchment. Pyrrole has also been identified in fog waters where it was found to be quickly degraded during transport by photochemistry (Anastasio and McGregor, 2000). It is thought to be present in the atmosphere originating from soil dust rich in humic/fluvic material (Schulten and Schnitzer, 1998, Anastasio and McGregor, 2000). This may explain the presence of a small amount of pyrrole found in the precipitation samples. The three other compounds identified were all amines: dodecylamine (found only in the precipitation), NDPA and decylamine (both only found in the stream). The number of unknown compounds detected may be reduced by running more standards for comparison.

In spite of the low DOC retention by the SPE cartridges, our attempt to describe the DON speciation in precipitation and streams, suggests that further investigation could provide some insight into the temporal and sector dependent speciation of DON and their sources.

5 Conclusions

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

DON in stream water was a major contributor to TDN (with an overall mean of 75%) and showed no clear seasonal pattern. The presence of pyrrole, the large DON concentrations

483 and the high NH_4^+ in stream water, suggest mineralisation of organic N stored in peat was

484 one of the sources.

485 In soil water, DON contributed an overall mean of 92% to TDN. The mean

486 concentrations of DON did not vary greatly between the years but the concentration of

487 NH_4^+ did (8.6 μmol N l^{-1} in 2009 and 0.2 μmol N l^{-1} in 2010), possibly due to localised

488 impact of animal waste and the importance of water table variation on the availability of

489 N to plants and on immobilisation.

490 GC×GC-NCD shows promise as a technique to identify compounds in stream

491 water/precipitation and their potential sources, but requires further development.

492 **6 Acknowledgements**

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679   and Zhang, F. S. (2008) 'Evidence for organic N deposition and its anthropogenic
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681   Table 1. Statistics of annual concentrations of NH_4^+, NO_3^-, DON and TDN for 2009 and

682   2010 in wet-only precipitation. Values are based on individual samples collected over the

683   two year period. N^* indicates the number of samples collected.

	NO_3^- μmol N l^{-1}	NH_4^+ μmol N l^{-1}	DON μmol N l^{-1}	TDN μmol N l^{-1}
2009				
Mean	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
2010				
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

684 Table 2. Statistics of annual concentrations of NH_4^+, NO_3^-, DON and TDN for 2009 and

685 2010 in soil water. Values are based on individual samples collected from dip wells over

686 the two year period. N^* indicates the number of samples collected.

	NO_3^- $\mu mol\ N\ l^{-1}$	NH_4^+ $\mu mol\ N\ l^{-1}$	DON $\mu mol\ N\ l^{-1}$	TDN $\mu mol\ N\ l^{-1}$
2009				
Mean	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
2010				
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

687

688   Table 3. Statistics of annual concentrations of NH_4^+, NO_3^-, DON and TDN for 2009 and

689   2010 in stream water. Values are based on individual samples collected over the two year

690   period. N^* indicates the number of samples collected.

	NO_3^- μmol N l^{-1}	NH_4^+ μmol N l^{-1}	DON μmol N l^{-1}	TDN μmol Nl^{-1}
2009				
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
2010				
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

691

693

694 Table 4. Summary of compounds and their concentrations (μmol N l^{-1}) detected by the GC×GC-NCD, and overall DON concentrations (μmol N l^{-1})

695 derived from TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations

696 by the GC×GC-NCD. Blank spaces indicate a value below the detection limit. Rt$_1$ and Rt$_2$ are retention times in seconds for the first and second GC

697 columns.

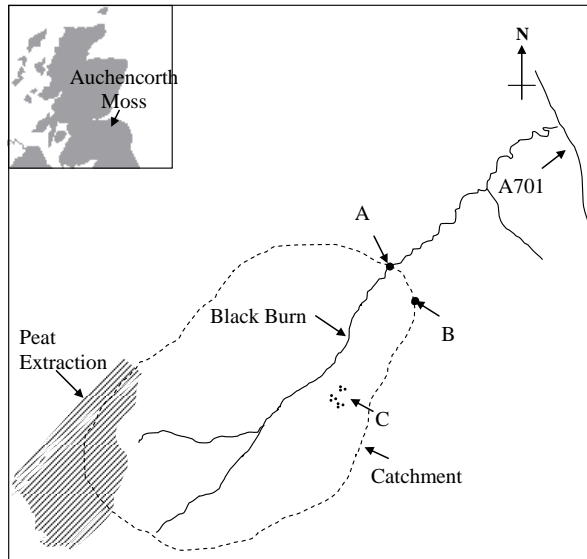| Sample Rt$_1$/Rt$_2$	DON (TDN-DIN)	Pyrrole 375/1.24	Benzonitrile 825/1.8	Unknown B 11.45/1.52	Unknown C 1218/1.48	Dodecylamine 1590/1.5	Unknown D 1615/1.7	Unknown E 1910/1.7	Unknown F 2200/2.09
09/07/2010	9.2							1.6	1.7
13/07/2010	13.8		0.4				0.5		
14/07/2010	6.5								
15/07/2010	5.5								
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		

698

699

700

701   Table 4. continued. Summary of compounds and their concentrations (μmol N l^{-1}) detected by the GC×GC-NCD, and DON concentrations (μmol N l^{-1})

702   as TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the

703   GC×GC-NCD. Blank spaces indicate a value below the detection limit. Rt_1 and Rt_2 are retention times in seconds for the first and second GC columns.

704

| Sample Rt_1/Rt_2	DON (TDN-DIN)	Pyrrole 375/1.24	Benzonitrile 825/1.8	Unknown B 11.45/1.52	Unknown C 1218/1.48	Dodecylamine 1590/1.5	Unknown D 1615/1.7	Unknown E 1910/1.7	Unknown F 2200/2.09
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	

705

Table 5. Summary of compounds and their concentrations (μmol N l^{-1}) detected by the GC×GC-NCD, and DON concentrations (μmol N l^{-1}) detected by ANTEK in stream water samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the GC×GC-NCD. Blank spaces indicate a measured value of below the detection limit.. Rt$_1$ and Rt$_2$ are retention times in seconds for the first and second GC columns.

| Sample Rt$_1$/Rt$_2$	DON (TDN-DIN)	Pyrrole 375/1.24	Unknown A 415/1.24	Benzonitrile 825/1.8	N-nitrosodipropylamine 970/1.4	Unknown B 11.45/1.52	Decylamine 1295/1.64	Unknown E 1910/1.7	Unknown F 2200/2.09
11/08/2010	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

710

711 Figure 1: Schematic map of catchment and sampling sites at Auchencorth Moss. Key: (A)

712 study catchment outlet and stream sampling site; (B) monitoring station (wet only analyser);

713 (C) dip wells. Adapted from Dinsmore et al., (2010).

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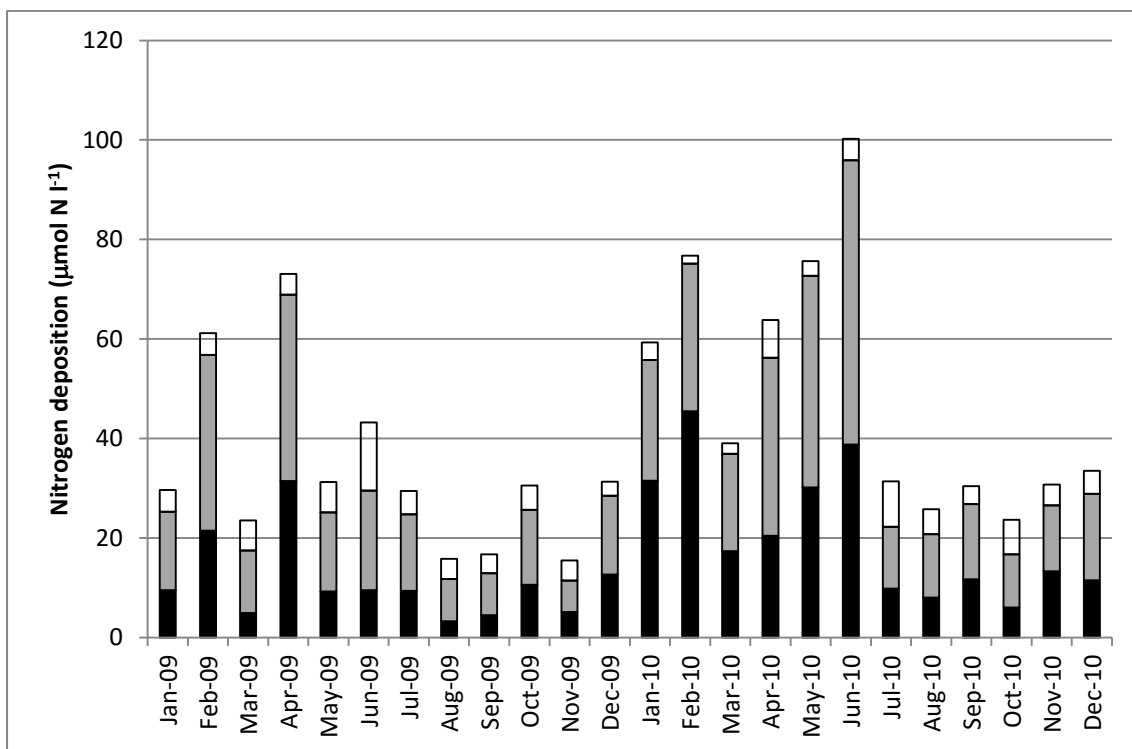
716 Figure.2. Volume-weighted monthly average concentrations of NH_4^+ (grey), NO_3^- (black) and

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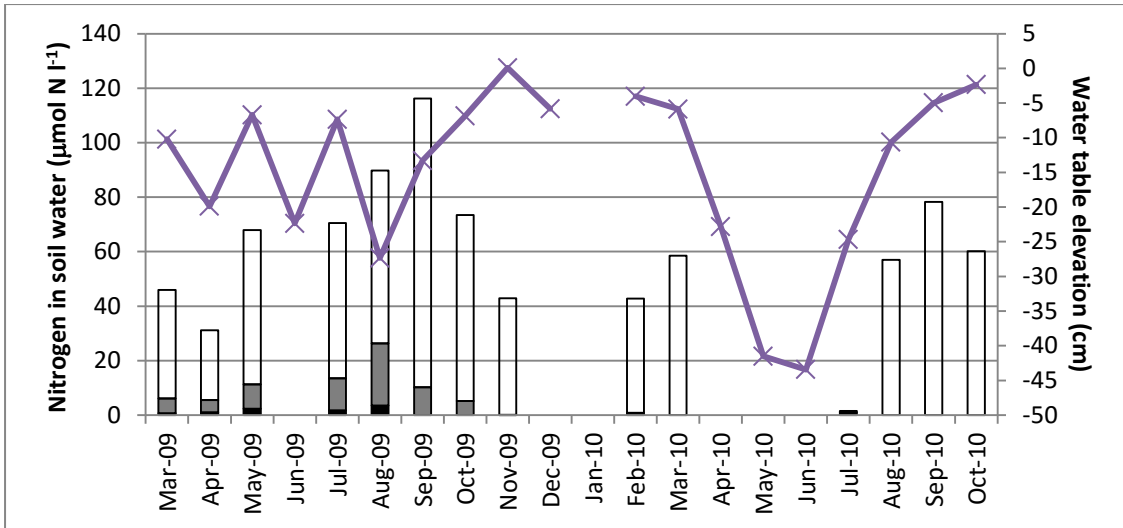
Figure 3. Monthly concentrations of NH_4^+ (grey), NO_3^- (black) and DON (white) in soil water. The line represents monthly water table elevation. The June-09 sample was misplaced and Dec-09 and Jan 2010 were frozen, the remaining blank spaces indicate the dip wells were dry on the day of collection.
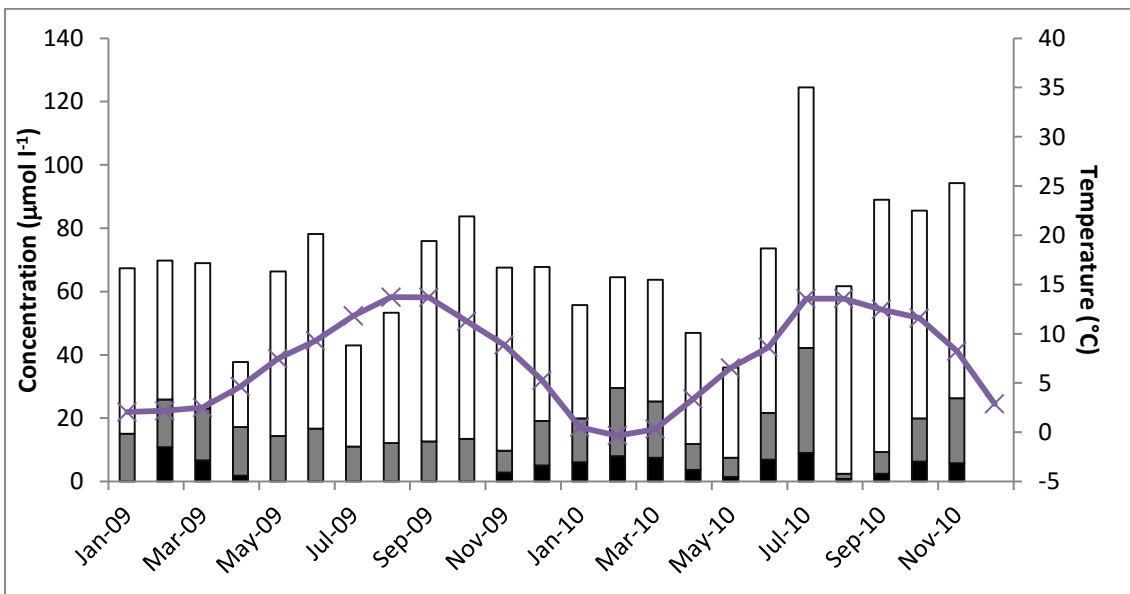

Figure 4. Discharge-weighted monthly mean concentrations of NH_4^+ (grey), NO_3^- (black) and DON (white) in stream water. The line represents mean monthly air temperature.
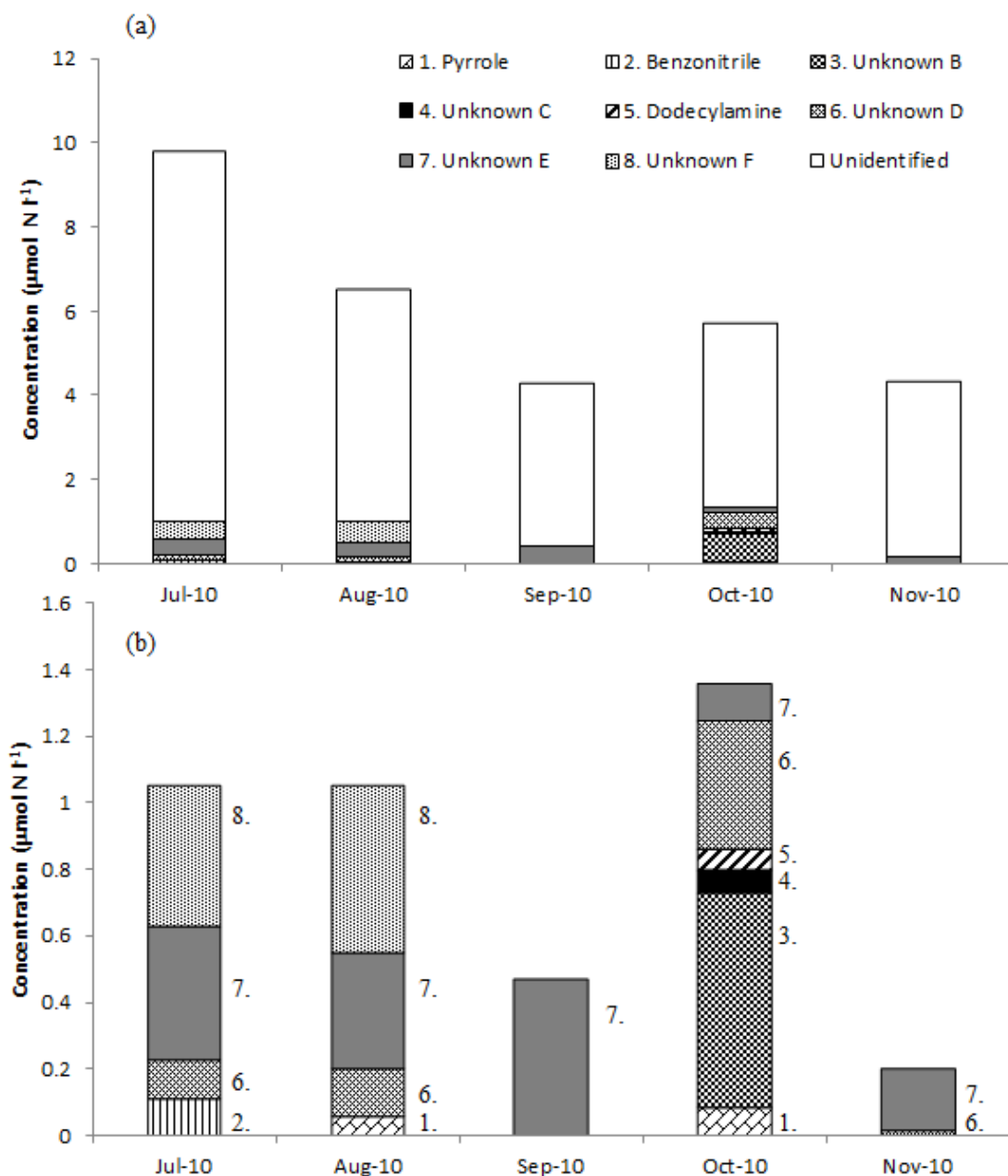
Figure 5. Mean monthly concentrations of the individual DON compounds found in precipitation water. (a) includes the DON fraction identified from the ANTEK (white bar). (b) excludes the unidentified fraction, so that the speciation achieved by GC×GC-NCD is more clearly seen.
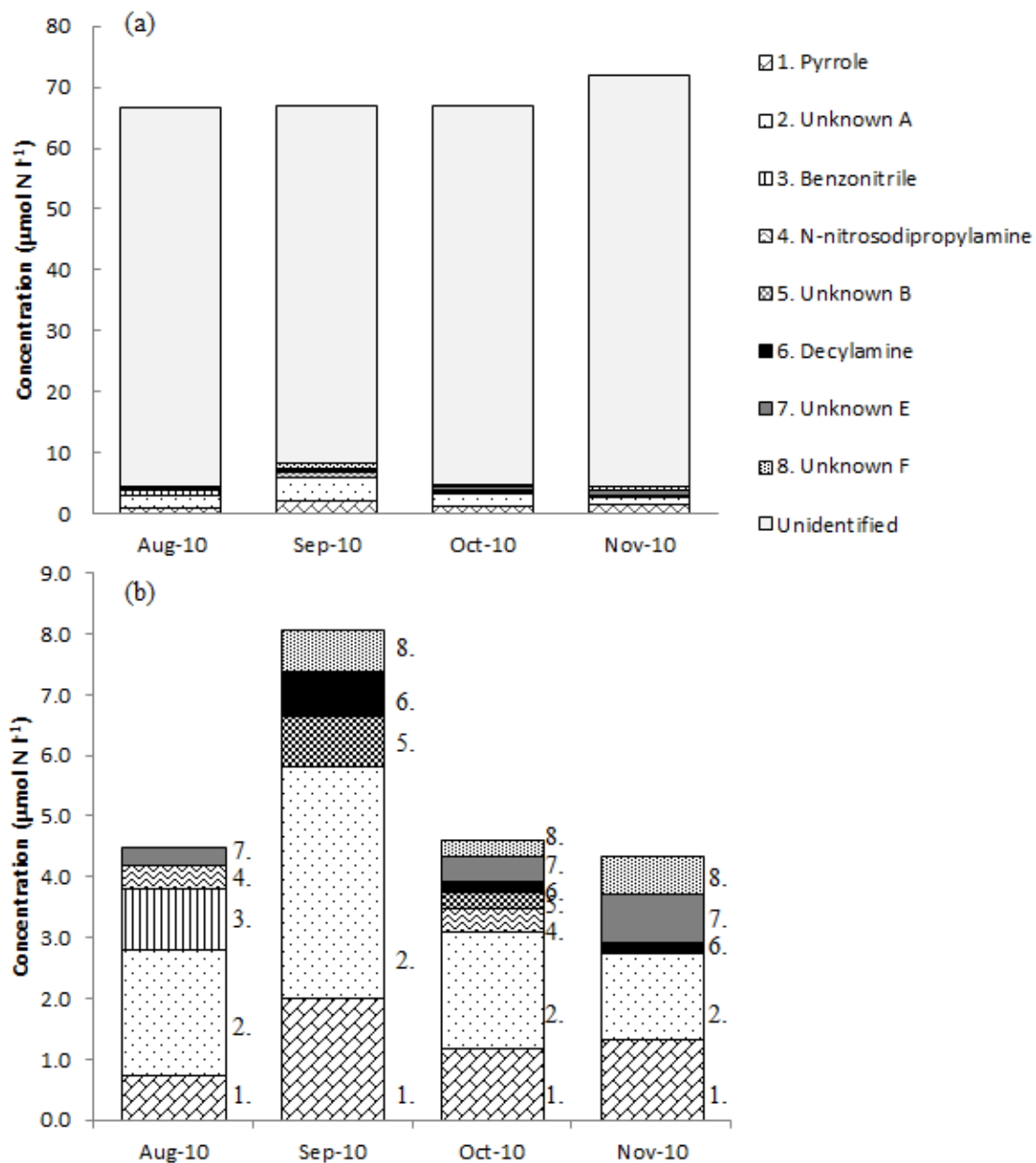
Figure 6. Mean monthly concentrations of the individual compounds found in stream water. (a) includes the DON fraction identified from the ANTEK (white bar) (b) excludes the 'unidentified' fraction, so the fraction detected by GC×GC-NCD is more clearly seen.