

1 **Authors reply to the Interactive comment on “The import and export of**
2 **organic nitrogen species at a Scottish ombrotrophic peatland” by R. M.**
3 **McKenzie et al.**
4 **made by Referee #1**
5
6

7 Received and published: 14 January 2015
8

9 This paper considers the extent and nature of the transmission of organic
10 nitrogen from atmospheric deposition through soils to streamflow in an
11 ombrotrophic bog in Scotland.

12 Organic nitrogen is now recognised as an important component of both
13 atmospheric deposition and fluvial nitrogen and this paper represents one of the
14 first and most comprehensive tests of the links between these. The system in
15 which this is done is well characterised from other studies and the groups
16 involved are very well experienced in both atmospheric and fluvial
17 measurements. I think the paper should be published with some minor
18 modifications.

19 **AUTHORS REPLY:** We thank the reviewer for the very helpful and encouraging
20 comments. We have modified the manuscript as best as we could as detailed
21 below.
22

23 In particular I think it can be shortened and focussed on the main conclusions,
24 rather than minor short term variability and discussion of minor compounds in the
25 largely uncharacterised DON.

26 **AUTHORS REPLY:** We have removed superfluous discussion points and
27 thereby shortened the manuscript text by ~340 words. The cuts we have made
28 can be viewed in the track changed document we have submitted together with
29 our replies.
30

31 It is also important to note that the fluvial nitrogen transport in streams draining
32 an ombrotrophic bog are probably particularly rich in organic compared to
33 inorganic N, and the conclusions here may not be readily extrapolated to other
34 types of river systems.

35 **AUTHORS REPLY:** Auchencorth Moss is a peatland not a bog, however your
36 comments still apply, and we agree that our results are not translatable to other
37 river systems, i.e. those fed by mineral soil. The scientists interested in our paper
38 should know this difference and we therefore don't feel that we have to add this
39 information.
40

41 Specific points:
42

43 Introduction There probably should be a reference to the recent efforts at
44 characterising atmospheric DON using other mass spectrometry systems by
45 Altieri and colleagues (Altieri et al., 2009 ES&T 43, 6950-5). There seems to be
46 little evidence that anthropogenic compounds dominate high molecular weight
47 atmospheric aerosol DON, although of course the potential hazards associated
48 with such compounds cannot be ignored.

49 **AUTHOR REPLY:** We have now referred to the Altieri paper: 'Various
50 techniques have been developed to characterise DON, including FT-ICR Mass
51 spectrometry (Altieri et al., 2009) and NMR spectrometry (Maie et al. 2006), with

52 these methods focusing on the more on groups of compounds rather than
53 individual species. Many techniques are not sensitive enough to detect individual
54 organic nitrogen compounds in low concentrations (Özel et al., 2010). ‘
55
56 Line 136 says the samples were collected daily but line 142 says they were
57 collected weekly, which is it?
58 **AUTHORS REPLY:** we have altered the text to clarify that we are dealing with
59 daily samples:
60 ‘The collector was kept at 4°C by an internal cooling system and samples were
61 manually emptied from the daily collector once a week, where they were stored in
62 a cool room, also at 4°C.’
63
64 In the past this group have used thymol as a preservative, presumably this was
65 not done here, so are the components stable over storage in the field and the
66 laboratory?
67 IN line 565 a freezer is mentioned.
68 **AUTHORS REPLY:** We were following a common protocol for another project
69 which prohibited the use of Thymol. As shown in the above reply, the daily rainfall
70 collector kept the samples at 4°C. Upon arrival in the lab precipitation, stream
71 and soil water samples were frozen until analysis – this is already mentioned in
72 the methods section for stream and soil water, and has been added for
73 precipitation.
74
75 Line 209-218. Was the efficiency of the solid phase extraction for DON
76 specifically tested?
77 **AUTHORS REPLY:** Since this was a screening study and the identity of the
78 DON species was unknown prior to analysis no SPE recovery was determined in
79 advance. The cartridge uses a C18 stationary phase and so is likely to retain the
80 less polar (but clearly still water soluble) fraction of the DON. This is a necessary
81 step to be able to use GCXGC which has limitations on both the polarity and
82 volatility of species that can be observed. The concentrations given are likely
83 therefore to be underestimates if recovery is low.
84
85 Line 262-270 The seasonality is not really particularly obvious but it would be
86 useful to know if it is associated with changing rainfall amounts, changing back
87 trajectories or changing emission.
88 **AUTHORS REPLY:** There was no correlation between rainfall and DIN or DON
89 which is stated in the text.
90
91 Sections 3.3 and 3.4 might be simplified since there is one key and very
92 important conclusion which is that DON completely dominates.
93 **AUTHORS REPLY:** We have deleted superfluous information.
94
95 Section 3.5 Given the very important conclusion at the end of this section that
96 90% of the DON could not be identified, I wonder if some of the detail in this
97 necessary.
98 **AUTHORS REPLY:** As there are very few such measurements in the literature
99 we feel it is important to provide as much information as possible.
100
101 The suggestion at the end of the section is that the DON is lost in the extraction
102 rather than chromatographic steps and this should be discussed as noted above.

103 **AUTHORS REPLY:** Some text has been added on the lack of information of the
104 SPE recoveries and the limitations of the approach earlier in the section. This
105 makes the discussion here more convincing.

106

107 The statement in line 561-2 is probably correct in an analytical chemistry
108 sense but not really in terms of characterising the DON.

109 **AUTHORS REPLY:** We do not fully understand this comment and therefore are
110 not sure on how to address this. It does not help that our line numbers are very
111 different from those of the reviewers.

112

113 In some ways section 4.6 might be more logical within the methods section

114 **AUTHORS REPLY:** We prefer to keep section 4.6 as it is. The GC*GC analysis
115 of peatland water samples is almost pioneering work, which obviously needs to
116 be advanced in future work. Section 4.6 is the conclusion we have drawn based
117 on our results and methodology used.

118

119 Section 4.1 You might note how concentrations compare to the earlier date of
120 Cape and to the other sites they sampled.

121 **AUTHORS REPLY:** in this paper we are interested in general patterns rather
122 than specific concentrations. As we refer to a number of different papers we
123 prefer not to include too many concentration values, and thereby make it easier
124 for the reader to follow.

125

126 The suggestion in line 411 is that the results are really quite different to the
127 earlier work and I'm not sure that the argument on line 420 that this reflects large
128 scale dry deposition is credible. The speculation in this section about sources
129 seems entirely focussed on local sources for DON and it is not clear to me why
130 local rather than long range sources are so important.

131 **AUTHORS REPLY:** Thanks for this comment, we have rephrased the below
132 sentences to clarify this:

133 'The contribution of DON to TDN is low at Auchencorth – 10.0% and 8.3% in
134 2009 and 2010, respectively – when compared to the literature average of 30%
135 (Cornell et al., 2003, Cape et al., 2004, Zhang et al., 2008, Cape et al., 2011,
136 Zhang et al., 2012), which is likely to be the result of different contribution of
137 biological and anthropogenic local sources and those deposited through long
138 range transport.'

139

140 And further on in this section:

141 'Unfortunately our experimental set up did not allow us to investigate the
142 contribution of long range transport to the DON concentrations, which may have
143 been different between the two sites. These differences may also have a
144 methodological explanation, as many of these earlier studies used bulk
145 precipitation collectors instead of wet-only collectors, and these are likely to have
146 additional water-soluble organic N deposited via dry deposition, and thus larger
147 DON concentrations (Gonzalez Benitez et al., 2010).'

148

149 Section 4.2 does not seem very concise or well focussed.

150 **AUTHORS REPLY:** We re-read this section and do not see how we can alter it.
151 Our aim is to portrait the differences in DIN concentrations between the two
152 years, as these effect the overall DON contribution. Perhaps the reviewer has
153 some suggestions on what should be improved.

154
155 Section 4.3 Other types of river systems are often dominated by nitrate, so
156 stream systems with these high DON% are typical of only upland sites such as
157 studied here and this should be made clearer.
158 **AUTHORS REPLY:** We have clarified that we are discussing an upland
159 catchment:
160 'Numerous studies have found DON to be the dominant form of stream water N
161 in upland catchments, with contributions varying from 54% to 82% annually
162 (Chapman et al., 2001, Cundill et al., 2007, Helliwell et al., 2007a).'

163
164 As with the previous section, this discussion seems rather general and lacks
165 focus. The simple conclusion is that DON dominates.
166 **AUTHORS REPLY:** We have deleted superfluous text, and hopefully have
167 improved the manuscript.
168

169 Section 4.4 There seems to be limited real evidence of seasonality and no clear
170 explanation of why there should be so I would suggest this section can be
171 shortened.
172 **AUTHORS REPLY:** we have deleted relevant sentences.
173

174 Section 4.5 I think the concentration data alone demonstrates that the DON in
175 soil and stream water cannot all be coming from the atmosphere, an observation
176 that clearly supports the GC analysis results.
177 **AUTHORS REPLY:** We agree, this section is interesting and we hope to
178 continue this research.
179

180 Minor points grammatical errors line 23 line 121 hummocks and hollows are
181 surely not vegetation
182 **AUTHORS REPLY:** Thank you, we have made the relevant changes
183
184

185 Line 257 and 259 what are the percentages in brackets? I assume it is the % of
186 the total N based on Table 1
187 **AUTHORS REPLY:** Thank you, we have clarified this in the manuscript
188 The import and export of organic nitrogen species at a Scottish ombrotrophic
189 peatland

190 **Authors reply to the Interactive comment on “The import and export of**
191 **organic nitrogen species at a Scottish ombrotrophic peatland” by R. M.**
192 **McKenzie et al.**

193 **made by Referee #2**

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195

196 General comments

197 In their manuscript McKenzie et al describe and analyze concentrations and
198 composition of inorganic and organic N forms in precipitation, shallow
199 groundwater and river water in an ombrotrophic peatland in Scotland. In
200 summary, nitrogen inputs into the peatland with wet-only precipitation were
201 dominated by inorganic N forms, while nitrogen stored in the peat in groundwater
202 as well as nitrogen exports with river water were dominated by dissolved organic
203 nitrogen (DON). The role of the peat as a source of organic N forms is not very
204 surprising given the high organic matter contents of Histosols and the poor
205 retention of dissolved organic matter in Histosols. A comparison of DON quality
206 by means of GCxGC-NCD revealed that the peat not only changed the quantity
207 of DON in water, but also its composition. While wet-only precipitation was
208 dominated by unidentified compounds E and F, DON in stream water was
209 dominated by Pyrrole and an unknown compound A. Overall, I think that the
210 manuscript provides valuable information, but the text can probably be
211 condensed by some 30% without significant loss of information.

212 **AUTHOR REPLY:** Thank you for your positive comments. We have managed to
213 condense the text a bit, but prefer not to condense it by 30%, some of the
214 information we provide may be rather helpful for the reader.

215

216 I found the description and discussion of the seasonality of concentrations
217 somewhat lengthy, also when considering the limitations of a two-year time
218 series for interpreting issues of seasonality. When discussing the seasonality in
219 soil water concentrations, I missed the point of “dilution-concentration” effects in
220 shallow groundwater. Can the authors exclude that higher concentrations in
221 summer are simply a consequence of the evapotranspiration of water, leaving
222 more DON behind in the residual water?

223

224 To compensate for such “concentration-dilution” effects, I suggest normalizing
225 NH₄, NO₃, and DON concentrations in soil water for example to chloride
226 concentrations or at least to electrical conductivity. Chloride concentrations might
227 be available, because the samples were analyzed using an ion chromatograph
228 that is commonly also quantifying chloride concentrations.

229 **AUTHOR REPLY:** The dissolved nitrogen concentrations are volume weighted.
230 We do not have the chloride data to normalise the N concentrations. But we have
231 written at the start of section 4.2 that the differences are likely a dilution effect.

232 ‘... situated in drier parts of the moss were more viscous and contained much
233 particulate matter making filtering difficult. In contrast, DIN concentrations in
234 dipwells during wetter periods or in wetter parts of the moss were more dilute and
235 samples contained much less particulate matter’.

236

237 In contrast to the authors, I would regard the characterization of DON
238 composition with the GCxGC-NCD technique as not particularly successful,
239 because only a few percent of the DON compounds could be assessed using this
240 technique.

241 **AUTHORS REPLY:** The GC*GC analysis of peatland water samples is almost
242 pioneering work. We recognise our measurements are not absolutely perfect,
243 however they provide some valuable information for future research to improve.
244

245 The reasons for the suboptimal performance of the combined C18-SPE plus
246 GCxGC-NCD approach are partly discussed by the authors, but some limitations
247 are missing: Most dissolved organic matter (DOM) compounds and even more so
248 the nitrogen-containing compounds of DOM are polar molecules with a high
249 water-solubility (and hence mostly limited vapour pressure and a small octanol-
250 water distribution coefficient). Otherwise, these compounds would not be found
251 dissolved in the soil water. I guess that the efficiency of
252 the C18 SPE cartridges for isolating the DON compounds from the water
253 samples was very limited. The authors should specify the recovery and extraction
254 efficiency of the SPE procedure in the Materials and Methods section. Given their
255 mainly polar character, low vapor pressure and small octanol-water distribution
256 coefficients, most of the DON-compounds are not directly analytically accessible
257 for GC-analysis, but have to be derivatized (see e.g., Zhang and Amelung Soil
258 Biol. Biochem. 28, 1201-1206; Amelung and Zhang Soil Biol. Biochem. 33, 553-
259 562).
260

261 **AUTHORS REPLY:** Pyrrole, benzonitrile, decylamine, dodecylamine and N-
262 nitrosodipropylamine were identified and quantified in this study. They are volatile
263 and suitable to analyse by GC without any derivatization. We clearly will miss the
264 most polar fraction of the DON using this approach. DON is likely to cover a
265 range of water solubility's and polarities, and a single technique will never be
266 able to target all the analytes at the same time. In this study, we have quantified
267 the volatile/semi-volatile DON compounds using SPE followed by GCxGC-NCD.
268

269 In the discussion regarding the chemical nature of DON, I missed information and
270 papers using other techniques such as NMR spectroscopy (e.g., McCarthy et al.,
271 1997 Nature 390, 150-154; Maie et al. 2006. Geochim Cosmochim Acta 70,
272 4491-4506), Py-FIMS or XANES (e.g., Kruse et al. 2010, Sci. Total Environ. 408,
273 4910-4915).
274

274 **AUTHORS REPLY:** we have added a reference to NMR spectrometry in the
275 introduction.
276

277
278 Given the limitations of the C18-SPE/GCxGC-NCD approach, I recommend
279 shortening this part of the manuscript as well. Nevertheless, I would not skip it
280 completely, but focus on the comparison between inputs with precipitation,
281 storage in groundwater, and outputs with river water. Shortening the text will
282 probably help to make the key message of the paper clearer:
283 Peatlands as sources and transformers of DON...
284

285 **ATHOURS REPLY:** As mentioned to reviewer 1: We prefer to keep section 4.6
286 as it is. The GC*GC analysis of peatland water samples is almost pioneering
287 work, which obviously needs to be advanced in future work. Section 4.6 is the
288 conclusion we have drawn based on our results and methodology used.
289
290

291 Specific comments

292 The structure of the abstract appears a little “jumpy” to me and probably needs to
293 be revised. Which numbers below to the introductory part of the abstract, which
294 ones are results of the study that is presented?

295 **AUTHORS REPLY:** The abstract has been altered to improve its readability.

296

297 Page 521-Line 14: DON analysis. Were DOC concentrations analyzed as well
298 using a TOC-analyzer? Having DOC concentrations in conjunction with DON
299 concentrations would be very nice.

300 **AUTHORS REPLY:** Unfortunately we did not have the opportunity to analyse our
301 samples for TOCs.

302

303 Page 523-lines17ff: What was the recovery of DON by the C18-SPE cartridges? I
304 strongly doubt the statement that the SPE procedure does not alter the DON
305 composition.

306 Ozel et al 2003 is not an appropriate reference, since this reference refers to oils
307 and not to water samples!

308 **AUTHORS REPLY:** The reason for using this reference is that this involves a
309 sub-critical water extract of the essential oils. This was then subjected to the
310 same SPE approach. Therefore in both cases the matrix is water. The response
311 here is similar to the other reviewer. Since this was a screening study and the
312 identity of the DON species was unknown prior to analysis no SPE recovery was
313 determined in advance. This is a limitation of the study and so we have
314 shortened this section as recommended. However, this data allows us in the
315 future to carry out these sorts of studies and include recovery tests as
316 appropriate.

317

318

319 Page 528-Line 25: Assuming a 100% DON recovery during SPE is not realistic...

320 Page 529-Lines 20ff: It is not only that the GC captures only a fraction of the
321 DON, also the SPE procedure likely recovers only a limited DON fraction.

322 **AUTHORS REPLY:** We agree with the reviewer that for many species the
323 recovery is likely to be less than 100 %. We have clarified this in the text and
324 made the limitations of the approach clearer.

325

326 Page 530-Line 25: Consider adding “in precipitation” after “TDN”

327 **AUTHORS REPLY:** This information has been added

328

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337 Abstract

338 Dissolved organic nitrogen (DON) can contribute significantly to the overall nitrogen
339 budget, but is not routinely measured in precipitation or stream water. In order to
340 investigate the contribution of DON to deposition and export of N, precipitation, stream
341 and soil water samples were collected from an ombrotrophic peatland and analysed for
342 DON over a two year period. In wet only deposition DON contributed up to 10% of the
343 total dissolved nitrogen (TDN), ~~and was the most dominant fraction in~~ 99% in soil water
344 (99%), and 75% in stream water (75%). ~~No correlations were observed between DIN and~~
345 ~~DON in precipitation stream water or soil water.~~
346 ~~NH₄⁺ was the most dominate form of N in precipitation, with NO₃⁻ contributing the least~~
347 ~~to precipitation, soil water and stream water.~~
348 ~~DIN is an important source of nutrients and in ombrotrophic peatlands, is only deposited~~
349 ~~via precipitation. Too much nitrogen to a sensitive ecosystem can result in problems with~~
350 ~~the way in which it is processed, such as an increase the export of N via nearby water~~
351 ~~bodies. It is therefore important to monitor N deposition and export.~~
352 ~~Precipitation DIN showed a loose seasonal pattern, with peak concentrations occurring~~
353 ~~between January and June, while DON concentrations tended to be lower in the winter~~
354 ~~months. Stream water DON and NH₄⁺ showed no obvious seasonal pattern but NO₃⁻~~
355 ~~showed larger concentrations in cooler months and the smallest during warmer months,~~
356 ~~with the exception of June and July 2010, when concentrations were high.~~
357 Precipitation and stream DON was qualitatively analysed using GC×GC-NCD. Only 10%
358 of DON was able to be assessed, with tTen unique compounds ~~were~~ detected, ~~of which~~
359 ~~e~~ Only five could be identified: pyrrole, benzonitrile, dodecylamine, N-
360 nitrosodipropylamine and decylamine. Five compounds were present in both
361 precipitation and stream samples: pyrrole, benzonitrile and three unidentified compounds.
362 A more detailed DON speciation may be used to identify sources and pathways of DON.
363

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

365 **1 Introduction**

366 Atmospheric deposition of nitrogen (N) has increased dramatically over the last century
367 as a result of industrial and agricultural activities (Galloway et al., 2004). In the last 150
368 years, the amount of global anthropogenic reactive nitrogen has increased by a factor of
369 12.5; from ~15 Tg N y⁻¹ in 1860 to ~187 Tg N y⁻¹ in 2005 (Galloway et al., 2008) . The
370 total deposition of N in the UK was estimated to be approximately 330 Gg in 2004, with
371 wet and cloud deposition accounting for approximately 211 Gg (63.9%), and the rest
372 consisting of dry deposition (Fowler et al., 2009, Hertel et al., 2011).

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

378 Wet deposition of the dissolved inorganic nitrogen (DIN) compounds ammonium (NH₄⁺)
379 and nitrate (NO₃⁻) has been studied over many years (Violaki et al., 2010, Cape et al.,
380 2011, Zhang et al., 2012). The former is produced by the dissolution of ammonia gas
381 (NH₃) and the scavenging of NH₄⁺ aerosol, and the latter by the dissolution of nitric acid
382 gas (HNO₃) and the scavenging of NO₃⁻ aerosol (Russell et al., 1998, Cornell et al., 2003,
383 Tian et al., 2011). The dissolved organic nitrogen (DON) fraction is less well
384 documented due to difficulties in measuring it, but it can be an important fraction of the
385 total dissolved nitrogen (TDN) deposited, and can potentially be biologically available as
386 a source of N (Russell et al., 1998, Neff et al., 2002, Cornell et al., 2003, Cape et al.,
387 2004). The sources of DON are not well understood, but it is known to be ubiquitous in
388 the environment, present in particulate, gaseous and aqueous phases (Cornell et al., 2003,
389 Cape et al., 2004, Özel et al., 2011). Studies have shown that DON can contribute 30-
390 50% of the wet deposition of water soluble N (Neff et al., 2002, Cape et al., 2004, Zhang
391 et al., 2008, Cape et al., 2011, Cornell, 2011, Zhang et al., 2012).

392 Several atmospheric species of DON are considered hazardous to human health, and
393 appear on the Environment Protection Agency (EPA) hazardous air pollutant list (Özel et
394 al., 2011). Sources of DON are believed to include: pollen; sea spray; soil dust; deposits
395 from fauna and flora; the scavenging of aerosols; and reactions in the atmosphere
396 between inorganic gaseous nitrogen species and organic compounds (Prospero et al.,

397 1996, Russell et al., 1998, Cornell et al., 2003, Calderon et al., 2007, Zhang et al., 2008,
398 Violaki et al., 2010). Some work has been done to identify organic N compounds, so that
399 their sources can be traced. Amino acids, urea, aliphatic amines and peptides have all
400 been found in the atmosphere from naturally occurring sources (Calderon et al., 2007,
401 Violaki et al., 2010). The main anthropogenic organic compounds are believed to be N-
402 heterocyclic compounds, nitrophenols and nitro-polycyclic aromatic hydrocarbons
403 (Violaki et al., 2010). Alky amides have also been identified and are believed to result
404 from reactions between NH_3 and fatty acids at high temperatures (Cheng et al., 2006);
405 photochemical reactions are believed to be responsible for the presence of alky nitrates
406 and peroxyacyl nitrates (Violaki et al., 2010).

407 As with wet deposition, N is present in streams as both DIN and DON, with most focus
408 usually being on the DIN fraction. DIN, in particular NO_3^- , is often used as an indicator
409 of N saturation, with higher stream concentrations and changes in seasonal patterns
410 indicating an increase in the leaching of DIN from the catchment (Cundill et al., 2007,
411 Daniels et al., 2012). DON, however, is not often measured in spite of being the most
412 dominant fraction in waters draining peatland catchments; DON is known to contribute
413 60-90% of the TDN load in peatland streams (Yesmin et al., 1995).

414 Various techniques have been developed to [characterise DON, including FT-ICR Mass](#)
415 [spectrometry \(Altieri et al., 2009\) and NMR spectrometry \(Maie et al., 2006\), with these](#)
416 [methods focusing on the more on groups of compounds rather than individual species.](#)

417 ~~identify individual organic nitrogen compounds, but m~~Many [techniques](#) are not sensitive
418 enough to detect ~~these individual organic nitrogen~~ compounds in low concentrations
419 (Özel et al., 2010). Solid phase extraction (SPE) is a technique used to separate organic
420 compounds from aqueous systems, and has successfully been applied in many cases
421 (Moret & Conte, 2002, Özel et al., 2003, Özel et al., 2011). The SPE method has given
422 better DON recovery than solvent extraction from the aqueous phase (Özel et al., 2011)
423 and the extracted samples can be analysed using Gas chromatography (GC). By using a
424 multi-dimensional GC-technique and comprehensive two-dimensional GC, GC×GC, and
425 coupling it with a nitrogen chemiluminescence detector (NCD), better separation and
426 improved limits of detection can be achieved than by conventional one-dimensional GC
427 (Özel et al., 2006, Adam et al., 2007, Adahchour et al., 2008, Özel et al., 2010). GC×GC-
428 NCD has recently been used to investigate the presence of organic nitrogen compounds in
429 diesel fuel, atmospheric aerosol, nitrosamines in meat and vegetables, and nicotine and

430 N-nitrosamines in house dust (Adam et al., 2007, Özel et al., 2010, Özel et al., 2011,
431 Kocak et al., 2012, Ramirez et al., 2012).

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

436 2 Site and methods

437 2.1 Study area

438 Auchencorth Moss (Fig. 4.1) is an ombrotrophic peat bog located in south Scotland,
439 approximately 18 km southwest of Edinburgh (National Grid Reference NT221562; lat.
440 55°47'34 N; long. 03°14'35 W). The site is used primarily for low intensity sheep
441 grazing (less than one livestock unit km⁻²) and in 2009 a small herd of cows (15-20) also
442 grazed on the site.

443 The volume of peat in the catchment is estimated to be ~50 million m³, with depths up to
444 5 m, and an average depth of 50 cm. The total peat coverage is ~1214 ha, of which
445 approximately 170 ha is extracted (located 1.75 - 3.4 km W-SW of the monitoring
446 station) (Mitchell and Mykura, 1962, Dinsmore, 2008).

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

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

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

466

467 2.2 Wet-only precipitation

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

481 A Metrohm 761 Compact Ion Chromatograph (IC) connected in parallel with a Metrohm
482 733 IC Separation Centre to a Metrohm 766 IC sample processor (Metrohm Ltd.,
483 Herisau, Switzerland) measured NO_3^- and NH_4^+ respectively. NO_3^- was determined by
484 pumping an eluent solution of 3.2 mM sodium carbonate and 1.0 mM sodium bicarbonate
485 through a Metrosep A Supp 5 column. For NH_4^+ determination, an eluent solution of 24
486 mM boric acid, 5 mM tartaric acid and 0.7 mM dipicolinic acid, was pumped through a
487 Metrosep C1 column. Typical detection limits were $1 \mu\text{mol N l}^{-1}$ for both NO_3^- and NH_4^+ .
488 For analysis of TDN ($\text{TDN} = \text{DIN} + \text{DON}$) subsamples were obtained (a minimum of 5
489 ml) where possible, and filtered using Millipore Hydrophilic PTFE ($0.45 \mu\text{m}$ pore size)
490 syringe filters prior to freezing and later analysed for TDN by high-temperature catalytic
491 oxidation using an ANTEK 8060-M Nitrogen Specific HPLC Detector (ANTEK
492 Instruments Inc., Houston, TX, USA). The analysis was conducted in flow-injection
493 mode, in which $20 \mu\text{l}$ samples were introduced into an eluent stream of 10% methanol in
494 deionised water at a flow rate of $250 \mu\text{l min}^{-1}$. It was then combusted in oxygen at 1050
495 °C, producing nitric oxide (NO) which was detected by chemiluminescence. The

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

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

503 The uncertainty in DON values is greater than for DIN as a result of errors associated
504 with measuring TDN and DIN compounding and thus reducing the accuracy of the DON
505 calculation (Cornell et al., 2003). A negative bias may result from these combined
506 uncertainties, from DON not being fully converted during the total N analysis, and from
507 losses due to the collection and storage procedure (Russell et al., 1998, Cornell et al.,
508 2003). A positive bias results from setting small negative values of DON to zero; small
509 negative values of DON were included in the data analyses here in order to prevent this
510 source of bias. The limit of detection of DON was determined by the summation of the
511 detection limits of the 3 independent measured concentrations (NH_4^+ , NO_3^- and TDN)
512 and was $3 \mu\text{mol N l}^{-1}$.

513 2.3 Soil water

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

521 2.4 KCl-extractable mineral N

522 Soil cores were collected at a depth of 0-10 cm at three locations (next to the dip wells),
523 in spring and autumn in 2009 and in spring, summer and winter in 2010. NH_4^+ and NO_3^-
524 were extracted from soil samples using KCl; 15 g of soil were shaken for 1 hour with 50
525 ml of 1M KCl solution at a rate of 100 rpm. Samples were then filtered using Whatman
526 42 filter papers and frozen prior to analysis by IC. TDN was not measured, so DON could
527 not be determined.

528 2.5 Stream water

529 Stream water spot samples were collected by dipping a 300 ml glass bottle once a week
530 from the Black Burn, to the north of the field station. The samples were filtered within 24
531 hours of collection, using Millipore Hydrophilic PTFE (0.45µm pore size) syringe filters
532 and frozen until ready for analysis. Samples collected from January 2009 – October 2009
533 were analysed for TDN, NH₄⁺ and NO₃⁻ using a San⁺⁺ Automated Wet Chemistry
534 Analyzer/Continuous Flow Analyzer (SKALAR, The Netherlands). Samples from
535 November 2009-November 2010 were analysed for NH₄⁺, NO₃⁻ and TDN using the IC
536 and ANTEK methods described above. In both cases, DON was determined by
537 subtracting DIN from TDN.

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

544 2.6 GC×GC-NCD

545 Comprehensive two-dimensional gas chromatography coupled to a nitrogen
546 chemiluminescence detector (GC×GC-NCD) was used to separate DON into different
547 peaks and identify individual components where possible. The samples were extracted by
548 solid phase extraction (SPE), in order to trap the DON, using Superclean ENVI-18 SPE
549 tube 20 µm polymeric C₁₈-reverse phase 500 mg-3 ml SPE cartridges (SUPELCO,
550 Bellefonte, PA, USA). C₁₈ material has been used in many SPE applications for
551 extraction of organic compounds from the aqueous phase. It has been found that there is
552 almost no change in the composition of the sample before and after the application of
553 SPE of the C₁₈ material (Özel et al., 2003). Cartridges were conditioned with 5 ml
554 methanol followed by 5 ml of water at a rate of 2-5 ml min⁻¹. Between 5 and 18 ml of
555 precipitation and 9 and 24 ml of stream water was passed through the cartridge at a rate
556 of 2-5 ml min⁻¹. The cartridge was thoroughly dried under vacuum for ~30 minutes.
557 Following drying, the cartridge was eluted with 5 ml dichloromethane (DCM), and then
558 concentrated in a stream of nitrogen to a volume of ~ 0.1 ml. The GC×GC-NCD was an
559 Agilent 7890 GC coupled with an Agilent 255 NCD (Agilent Technologies, Palo Alto,
560 CA, USA). 1 µl extracts were injected in pulsed splitless mode at a temperature of 280 °C

561 and a pressure of 30 psi for 2 min, using a Gerstel automated liquid injector (Gerstel,
562 Mulheim an der Ruhr, Germany). The first dimension column was a non-polar BPX5 (30
563 m x 0.32 mm i.d. x 0.25 μm film thicknesses), set to an initial temperature of 55 $^{\circ}\text{C}$ for 1
564 min. The temperature was then increased at a rate of 5 $^{\circ}\text{C min}^{-1}$ until 305 $^{\circ}\text{C}$ where it was
565 isothermally held for 1 min. The second column was a BPX50 (1.5 m x 0.10 mm i.d. x
566 0.10 μm film thickness) set to an initial temperature of 70 $^{\circ}\text{C}$ for 1 min, the temperature
567 was then increased at a rate of 5 $^{\circ}\text{C min}^{-1}$ until 320 $^{\circ}\text{C}$ where it was isothermally held for
568 1 min. Both columns were from SGE Analytical Science (VIC, Australia). Helium was
569 used as a carrier gas at a constant flow of 1 mL min^{-1} and the data was collected at 50 Hz.
570 Pyrolysis was carried out at 900 $^{\circ}\text{C}$ with a hydrogen flow rate of 4 mL min^{-1} and oxygen
571 flow rate of 10 mL min^{-1} .

572 The detector shows an equimolar response regardless of the chemical state of the organic
573 nitrogen (except azo compounds), allowing nitrogen-containing compounds to be
574 quantified without the need for a separate calibration standard for each compound (Yan,
575 2002, Özel et al., 2011). Details of the optimization of the NCD response and the
576 analytical performance with respect to equimolar response using standards was evaluated
577 by Özel et al., (2011).

578 **3 Results**

579 3.1 Meteorology

580 Total rainfall was determined from the volume of rain collected in the wet only analyser.
581 In 2009 the total rainfall was 902 mm with monthly totals varying from 16 mm in
582 February to 180 mm in November. The mean monthly temperature varied from 0.5 $^{\circ}\text{C}$ in
583 December to 13.7 $^{\circ}\text{C}$ in July, with a yearly mean of 7.6 $^{\circ}\text{C}$. In 2010 the total rainfall was
584 732 mm with monthly totals varying from 21 mm in May to 128 mm in November.
585 However, in 2010 a significant amount of snow fell, interfering with the wet-only
586 collector and resulting in less precipitation collection during January-March. It is
587 estimated that 423 mm of precipitation fell during these months (an additional 291 mm),
588 making the total precipitation collected for 2010 approximately 1023 mm. This additional
589 precipitation was estimated from the ratio of discharge and precipitation, measured at the
590 stream sampling site by the Black Burn (Dinsmore et al., 2013, Skiba et al., 2013). The
591 mean monthly temperature varied from -2.0 $^{\circ}\text{C}$ in December to 13.6 $^{\circ}\text{C}$ in July, with a
592 yearly mean of 6.6 $^{\circ}\text{C}$.

593 3.2 Wet-only N deposition

594 Figure 2 shows the volume-weighted monthly mean concentrations of N in precipitation.
595 The temporal variation of NH_4^+ and NO_3^- follow a similar pattern, with DON differing. In
596 both 2009 and 2010 (Table 1), NH_4^+ was the dominant component of wet-only deposition
597 with annual mean concentrations of $27.2 \mu\text{mol N l}^{-1}$ (58% of TDN) and $30.7 \mu\text{mol N l}^{-1}$
598 (53% of TDN) respectively. The contribution of NO_3^- was greater in 2010 than in 2009,
599 with mean concentrations of $15.0 \mu\text{mol N l}^{-1}$ (32% of TDN) in 2009 and $22.7 \mu\text{mol N l}^{-1}$
600 (39% of TDN) in 2010. Although DON contributed the least to annual concentrations in
601 both years, on a monthly timescale there were a few occasions when DON exceeded NO_3^-
602 (March 2009, June 2009, Aug 2009 and Oct 2010). A loose seasonal pattern can be
603 observed for NH_4^+ and NO_3^- , with peak concentrations occurring between January and
604 June. This is more obvious in 2010. DON has no clear seasonal pattern, although the
605 lowest concentrations seem to occur in the winter months (Nov- Jan). A weak, but
606 significant correlation was found between NH_4^+ and NO_3^- in 2009 ($R^2 = 0.45$, $p < 0.001$).
607 In 2010, a stronger correlation between NH_4^+ and NO_3^- was also observed ($R^2 = 0.62$, $p <$
608 0.001). No correlations were observed between NH_4^+ , DON, temperature, rainfall or
609 precipitation; NO_3^- , DON, temperature, rainfall or precipitation; or DON, temperature,
610 rainfall or precipitation.

611 3.3 Soil water and KCl-extractable N

612 Due to gaps in the data, caused by the dip wells being dry and thus no sample to be
613 collected, it is difficult to assess seasonal patterns. What is clear, is that DON clearly
614 dominates the TDN. From the data available, it appears that DON concentrations were
615 larger in the warmer months compared to cooler months (November to March) and that
616 peak concentration for DON occurred in September in both years (Figure 3). The
617 contribution of DON to TDN was higher in 2010 at 99% compared to 85% in 2009
618 (Table 2). ~~NH_4^+ and NO_3^- followed similar patterns, with concentrations in 2009~~
619 ~~appearing to increase in the spring, peaking in August. In 2010, both NH_4^+ and NO_3^-~~
620 ~~concentrations generally remained low, with much smaller peak concentrations occurring~~
621 ~~in July.~~ NO_3^- mean annual concentrations were $1.2 \mu\text{mol N l}^{-1}$ (2% of TDN) in 2009 and
622 $0.2 \mu\text{mol N l}^{-1}$ (0.3% of TDN) in 2010. NH_4^+ mean annual concentrations were also larger
623 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
624 NH_4^+ to TDN was thus much larger in 2009 at 13% and just 0.4% in 2010.

625 Soil extractions from 2 samples in 2009 and 3 samples in 2010 found no detectable NO_3^- ,
626 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
627 2010, respectively.

628 3.4 Concentration and forms of N in stream water

629 Monthly mean discharge-weighted concentrations of NO_3^- , NH_4^+ and DON are presented
630 in Figure 4, and a basic statistical analysis of annual stream water chemistry is presented
631 in Table 3. DON is the dominant N species found in the stream water contributing, on
632 average, 74.6% (in 2009) and 74.3% (in 2010) of TDN., with the highest concentrations
633 in summer/autumn, however no clear seasonal pattern was evident. ~~Monthly mean DON~~
634 ~~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~~
635 ~~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~~
636 ~~2010, contributing, on average, 74.6% and 74.3% of TDN.~~

637 Monthly mean concentrations of NO_3^- ranged from 0.0 to 13.7 $\mu\text{mol N l}^{-1}$ in 2009 and 0.0
638 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
639 4.5 $\mu\text{mol N l}^{-1}$ in 2010. In 2009, concentrations varied seasonally; largest NO_3^-
640 concentrations were measured during the cooler months and the smallest during the
641 warmer months. In summer 2009 there was no detectable NO_3^- . In 2010 stream water
642 NO_3^- concentrations initially followed a similar pattern as in 2009, with concentrations
643 increasing during the winter months and decreasing as temperature increased and summer
644 approached. However, there was a large increase in NO_3^- concentrations in June and July
645 2010. Consequently, average annual NO_3^- concentrations in 2010 were nearly double
646 those in 2009, contributing 6.6% of TDN compared to 3.6% of TDN (Table 3). Monthly
647 median concentrations for NO_3^- for the whole period showed a similar pattern to monthly
648 discharge-weighted mean concentrations, with the exception of June 2010, which is
649 reduced to a summer low of 0 $\mu\text{mol N l}^{-1}$, suggesting the monthly mean value was
650 skewed by an unusually large value. Median concentrations made little difference to the
651 July 2010 maximum. July 2010 also showed a maximum in the mean concentrations of
652 DON and NH_4^+ .

653 Monthly mean concentrations of NH_4^+ ranged from 5.4 to 21.9 $\mu\text{mol N l}^{-1}$ with an annual
654 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
655 $\mu\text{mol N l}^{-1}$ in 2010. Concentrations of NH_4^+ were consistently higher than NO_3^- and there
656 was no clear seasonal pattern. No correlation was observed between NH_4^+ , NO_3^- , DON,
657 discharge, temperature, rainfall (both air and stream) or precipitation.

658 3.5 DON speciation by GC×GC-NCD

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

674 In 13 of the 31 precipitation samples, and 2 of the 21 stream samples, no DON
675 compounds were detected or the peaks were too small to be distinguishable from
676 background noise. The limit of detection (LOD) using the optimized method has been
677 determined between 0.16-0.27 pgN using GC×GC-NCD of standard mixtures (Özel et al.,
678 2011).

679 Peak identification was carried out by comparing the two retention times (R_{t1} and R_{t2}) of
680 the peaks observed in the samples with the retention times of known standards. This
681 could lead to misidentification of peaks, however co-elution is greatly reduced using
682 GC×GC and there is very good retention time stability between runs. There were several
683 peaks, consistently present in some samples, that could not be identified as they did not
684 match any of the retention times of the standards available to us already run, so have
685 been and therefore were labelled “Unknown” A-F. In total 10 unique compounds were
686 found to be present in the stream and precipitation, of which only 5 could be identified.
687 Tables 4 and 5 present a summary of the compounds identified in precipitation and
688 stream water DON, respectively. Both the precipitation and the stream water contained 8
689 distinct compounds, 5 of which were in common.

690 The most common compound identified in the precipitation samples was Unknown E,
691 present in 10 samples, followed by Unknown D in 6 samples and Unknown B in 5

692 samples, with mean concentrations of 0.3 $\mu\text{mol N l}^{-1}$, 0.14 $\mu\text{mol N l}^{-1}$ and 0.2 $\mu\text{mol N l}^{-1}$,
693 | respectively assuming an equimolar response ~~and 100 % recovery during SPE~~. Two
694 precipitation samples contained pyrrole, with a mean concentration of 0.03 $\mu\text{mol N l}^{-1}$.
695 Unknown F was in 3 samples (mean concentrations of 0.1 $\mu\text{mol N l}^{-1}$), dodecylamine was
696 in 2 samples (mean concentration of 0.02 $\mu\text{mol N l}^{-1}$), and Unknown C was in one sample
697 (concentration of 0.02 $\mu\text{mol N l}^{-1}$). The precipitation samples did not contain any
698 Unknown A, N-nitrosodipropylamine or decylamine, which were found in the stream
699 samples.

700 The most common compound identified in the stream samples was Unknown A, the
701 mean concentration was 2.0 $\mu\text{mol N l}^{-1}$ (Table 5). Pyrrole was the next most common
702 compound, found in 18 of the stream samples, with a mean concentration of 1.2 $\mu\text{mol N}$
703 l^{-1} . Unknowns E and F both appeared in 9 stream samples, with mean concentrations of
704 0.5 $\mu\text{mol N l}^{-1}$ and 0.4 $\mu\text{mol N l}^{-1}$. N-nitrosodipropylamine (NDPA) was present in 4
705 stream samples, followed by Unknown B and decylamine in 3 stream samples. Mean
706 concentrations were 0.2 $\mu\text{mol N l}^{-1}$ for all three compounds. Unknown D, Unknown C
707 and dodecylamine, which were found in the precipitation samples, were not present in the
708 stream samples.

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

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

725 Unknown A were present in all 4 sampling months. October also had the most identified
726 compounds present, with 7 of the 8 compounds present (Fig. 4).

727 **4 Discussion**

728 4.1 The composition of N in precipitation

729 Cape et al., (2004) studied several sites in the UK on a range of land uses and noted an
730 annual cycle for DIN and DON, with peak concentrations for NH_4^+ and NO_3^- occurring
731 in the late spring (April-June 2000-2002) and a DON peak occurring in late summer
732 (June-August 2000-2002). Both DIN and DON showed minima in winter. The data
733 presented here are similar, but with earlier DIN maxima in early spring (Feb-April in
734 2009 and Feb-June 2010) followed by lower values in the autumn and beginning of
735 winter. DON also peaked earlier than reported by Cape et al. (2004) but roughly a month
736 after DIN peaks in both 2009 and 2010. Generally, sources of NH_4^+ in precipitation tend
737 to be agricultural in origin and sources of NO_3^- in precipitation from combustion activities
738 (Cape et al., 2011). Although Auchencorth Moss is located in a rural setting and with
739 minimal agricultural activity on the peatland itself; there are several chicken farms in the
740 area. Chickens farms emit ammonia (NH_3), which when dissolved in rainwater, produces
741 NH_4^+ (Schlesinger, 1997). NH_4^+ also makes up a large fraction of atmospheric aerosols
742 and is often transported further downwind of its source (Nieder and Benbi, 2008), where
743 it can then be washed out and deposited by precipitation.

744 Sources of NO_3^- include motor vehicles and stationary combustion sources (power
745 stations, domestic heating) following atmospheric oxidation of the emitted nitrogen
746 oxides. As a secondary pollutant, nitric acid and nitrates are less easily traced back to
747 sources. The sources of DON are more difficult to generalise, but spring maxima may be
748 due to the release of pollen, plant debris and spores during the spring, which have been
749 suggested as sources of DON (Violaki et al., 2010), or to seasonal patterns in spreading
750 manure. Conversely, an autumn maximum may be linked to decomposition of vegetation
751 (Cape et al., 2004). The contribution of DON to TDN is low at Auchencorth – 10.0% and
752 8.3% in 2009 and 2010, respectively – when compared to the literature average of 30%
753 (Cornell et al., 2003, Cape et al., 2004, Zhang et al., 2008, Cape et al., 2011, Zhang et al.,
754 2012), which is likely to be the result of different contributions of biological and
755 anthropogenic local sources and those deposited through long range transport, varying
756 contributions from anthropogenic inputs. This 10% contribution is markedly less than for
757 a nearby study in the grounds of the Centre for Ecology & Hydrology (10 km north of

758 Auchencorth Moss), a rural science park, where the contribution of DON to TDN was
759 24% for the period June 2005 to April 2007 (Gonzalez Benitez et al., 2009). This site was
760 within 1 km of an intensively managed agricultural area (Easter Bush) dominated by
761 sheep grazed grasslands and receiving high rates mineral nitrogen fertiliser (~ 200 kg N
762 ha⁻¹ y⁻¹). In areas of intensive agricultural activity DON in precipitation increases, and is
763 thought to be due to the addition of N fertilisers, especially urea (Neff et al., 2002, Zhang
764 et al., 2012). Auchencorth Moss does not receive fertilisers and the number of
765 sheep/cattle on site was low. Unfortunately our experimental set up did not allow us to
766 investigate the contribution of long range transport to the DON concentrations, which
767 may have been different between the two sites. These differences may also have a
768 methodological explanation, as ~~Also~~, many of these earlier studies used bulk precipitation
769 collectors instead of wet-only collectors, and these are likely to have additional water-
770 soluble organic N deposited via dry deposition, and thus larger DON concentrations
771 (Gonzalez Benitez et al., 2010).

772 Previous studies of precipitation DIN and DON have reported varying degrees of
773 correlation between DON, NH₄⁺ and NO₃⁻. For example, Violaki et al. (2010) found no
774 correlation between DON, NH₄⁺ and NO₃⁻ in wet deposition in the Eastern
775 Mediterranean. Zhang et al. (2008) also did not observe correlation between DON, NH₄⁺
776 and NO₃⁻ in precipitation at 15 sites in China. However, when an additional 37 sites from
777 across the globe were added to the study, positive relationships were found, suggesting a
778 common or similar sources of DON and DIN on a global, but not regional, scale. In a
779 number of studies, DON and NH₄⁺ were correlated, or at least more closely correlated
780 than DON and NO₃⁻, suggesting DON is more closely associated with agricultural
781 sources than with combustion processes (Cape et al., 2004, Chen et al., 2008, Cape et al.,
782 2011, Zhang et al., 2012). Our study showed weak to moderate correlations between
783 NH₄⁺ and NO₃⁻ but no correlation between DIN and DON. This suggests that whilst the
784 DIN compounds might share a common source (e.g. secondary aerosol), DON does not.
785 This is further supported by the later seasonal maxima of DON compared to those of the
786 DIN compounds (Cape et al., 2011).

787 4.2 N in the soil solution

788 August 2009 had the highest DIN concentrations and was the driest month that still
789 produced enough sample for analysis. Samples collected in drier periods or from dipwells
790 situated in drier parts of the moss were more viscous and contained much particulate

791 matter, making filtering difficult. In contrast, DIN concentrations in dipwells during
792 wetter periods or in wetter parts of the moss were more dilute and samples contained
793 much less particulate matter. Adamson et al., (2001) found higher NH_4^+ concentrations,
794 but lower DON concentrations, during periods of low water table in a blanket bog in
795 England. They suggested that the microbial community responsible for ammonification
796 benefited from the fluctuating water table to a higher degree than nitrifying organisms,
797 resulting in enhanced NH_4^+ concentrations, which then accumulated if the fluctuation
798 continued (Adamson et al., 2001, Daniels et al., 2012). This may be due to nitrifiers being
799 less able to cope with the stress caused by fluctuating conditions than ammonifiers
800 (Voroney, 2007). Although the mean water table was lower in 2010, 2009 saw a greater
801 degree of water table fluctuation (Fig. 4).

802 Interestingly, the TDN and DIN deposited as precipitation in 2010 was larger than in
803 2009, but the soil chemistry showed larger concentrations of TDN and DIN in 2009 than
804 in 2010. The larger DIN concentrations in 2009 may be due to the activities of sheep
805 which grazed on this moorland at very low livestock density of less than 1 ewe per ha and
806 also a small herd of 15 – 20 cattle . In 2009, sheep and sheep droppings were observed in
807 and around the vicinity of the dip wells and where the soil cores were collected; the small
808 cattle herd (15-20) also had access to this area. However, in 2010, there were no cattle on
809 site and the sheep frequented an alternative area of the peatland.

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

817 4.3 The composition of N in stream water

818 Numerous studies have found DON to be the dominant form of stream water N [in upland](#)
819 [catchments](#), with contributions varying from 54% to 82% annually (Chapman et al.,
820 2001, Cundill et al., 2007, Helliwell et al., 2007a). Similarly, NO_3^- is commonly the
821 second most dominant species reported [in upland catchments](#), with NH_4^+ being present in
822 much lower concentrations. ~~For example, Cundill et al. (2007) conducted a study at~~
823 ~~several points along a blanket peat-dominated catchment in the North Pennine uplands~~

824 | ~~and found the annual mean concentrations of DON, NO₃⁻ and NH₄⁺ to be 32.5 μmol N l⁻¹~~
825 | ~~(82.1%), 6.2 μmol N l⁻¹ (15.7%), and 0.9 μmol N l⁻¹ (2.2%), respectively. At~~
826 | Auchencorth Moss, the Black Burn DON concentrations were also the dominant form of
827 | N, at 75% (48.1 μmol N l⁻¹) and 74% (50.0 μmol N l⁻¹) for 2009 and 2010, respectively.
828 | These high TDN contributions of DON are typical of waters that drain peatlands due to
829 | their high organic matter content, often steep slopes promoting surface runoff, and high
830 | rainfall. In addition, anaerobic and acidic conditions reduce mineralisation of DON and
831 | nitrification to NO₃⁻ (Yesmin et al., 1995, Adamson et al., 1998, Chapman et al., 2001).
832 | However, in contrast to the studies highlighted above, water draining from Auchencorth
833 | Moss had higher mean annual NH₄⁺ than NO₃⁻ concentrations in both 2009 and 2010,
834 | with means of 14.1 μmol N l⁻¹ (22%) in 2009 and 12.9 μmol N l⁻¹ (19%) in 2010 for
835 | NH₄⁺, and 2.3 μmol N l⁻¹ (3.6%) in 2009 and 4.5 μmol N l⁻¹ (6.6%) in 2010 for NO₃⁻.
836 | Helliwell et al. (2007a) compared four upland regions in the UK and found NO₃⁻
837 | concentrations were lower when waters drained peaty soils than those which drained
838 | more mineral soils. Usually, the leaching of inorganic N is dominated by NO₃⁻, whereas
839 | NH₄⁺ remains in the soil in weak association with organic matter and incorporation into
840 | clay lattices (Scherer, 1993, Chapman and Edwards, 1999, Davies et al., 2005, Helliwell
841 | et al., 2007a). The anaerobic conditions resulting from waterlogged soils may inhibit the
842 | oxidation of NH₄⁺ to NO₃⁻, resulting in a higher incidence of NH₄⁺ leaching into nearby
843 | water bodies (Helliwell et al., 2007a). Fluctuating water tables have also been linked to
844 | higher NH₄⁺ concentrations from the mineralisation of organic nitrogen (Daniels et al.,
845 | 2012, Paul and Clark, 1996). Vegetation can also influence river water N-chemistry;
846 | peatlands with extensive blanket bog vegetation often exhibit lower NO₃⁻ concentrations
847 | than those that drain mineral soils (Chapman et al., 2001, Cundill et al., 2007).

848 | ~~A previous study carried out at the Black Burn in 2008, approximately 2.5 km~~
849 | ~~downstream from the sampling site reported here, also found DON to be the dominant~~
850 | ~~species (mean concentration of 47.9 μmol N l⁻¹) contributing 71 % of the TDN, followed~~
851 | ~~by NH₄⁺ (mean concentration 10.7 μmol N l⁻¹), contributing 16% of TDN, and NO₃⁻~~
852 | ~~(mean concentration 8.6 μmol N l⁻¹), contributing 13% of TDN (Vogt 2011). The DON~~
853 | ~~values are comparable to the study reported here, but the Vogt study found lower NH₄⁺~~
854 | ~~and higher NO₃⁻ values. These differences may be due to the location of the Vogt study~~
855 | ~~site, which was further downstream, next to a busy road, and was frequented by sheep~~
856 | ~~more regularly than the upstream site from this study. This may have resulted in addition~~
857 | ~~N inputs from the sheep and road traffic, increasing the amount of N leached/ deposited~~

858 | ~~into the stream as NO_3^- . Also, some NH_4^+ may have been nitrified to NO_3^- as it was~~
859 | ~~transported downstream towards the Vogt sampling site (Helliwell et al., 2007a).~~ No
860 | correlation was found between the wet deposition of atmospheric N and stream
861 | concentrations suggesting that precipitation does not represent a major source of stream
862 | water N.

863 | 4.4 Seasonal patterns of N in stream water

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

872 | The seasonal pattern of NO_3^- , where concentrations were higher in cooler months and
873 | lower in warmer months has been observed in numerous upland studies (Black et al.,
874 | 1993, Chapman et al., 2001, Daniels et al., 2012). In warmer months, the biological
875 | uptake of NO_3^- by plants and microbes is at its highest, immobilising NO_3^- . In winter,
876 | productivity declines, increasing the amount of NO_3^- available to be leached into the
877 | stream (Black et al., 1993, Chapman et al., 2001, Helliwell et al., 2007b). The summer
878 | peaks in June and July 2010 are unusual and different to the summer lows observed in
879 | 2009. The high June value appears to be due to one high concentration, skewing the mean
880 | monthly concentration; the median value for June was $0 \mu\text{mol N l}^{-1}$. The high July 2010
881 | peak is also evident in the mean concentrations of DON, and NH_4^+ , and is still reflected
882 | in median values. The reason for these high values are unclear, however the differences
883 | in discharge and precipitation between the two sampled years may be a contributing
884 | factor. ~~The monthly discharge was 59% higher in June 2009 and 11% higher in July in~~
885 | ~~2009 than in the corresponding months in 2010. Likewise, precipitation was 39% higher~~
886 | ~~in June 2009 and 24% higher in July 2009 than in the corresponding months in 2010.~~
887 | ~~Stream temperatures were similar but overall cooler in 2009.~~

888 | 4.5 DON speciation by GC×GC-NCD

889 | Most of the compounds contributing to DON in both the precipitation and stream samples
890 | could not be identified. Whilst some of the compounds detected by the GC×GC-NCD

891 appear in both sets of data, the two main compounds identified in the stream water were
892 either present in precipitation only in small amounts or not present at all. This suggested
893 that at least some sources of DON in precipitation and stream waters are different.
894 Schulten and Schnizer, (1998) investigated the chemistry of organic matter of humic
895 substances and soils. Amongst other compounds they identified pyrrole and benzonitrile,
896 along with derivatives of pyrrole. They concluded that heterocyclic N compounds, of
897 which pyrrole is one, were an important constituent of soil organic matter, contributing
898 up to 35% of total N. Pyrrole and pyrrolic compounds are a major N source in coal and
899 are often found in peats; they can result from the aerobic breakdown of the tetrapyrrole
900 ring found in chlorophyll or from the breakdown of extensin, which is a type of
901 hydroxyproline-rich polymer found in the cell walls of plants (van Smeerdijk and Boon,
902 1987, Schulten and Schnizer, 1998). It is therefore likely that the source of pyrrole in the
903 streams was the peat in the surrounding catchment. Pyrrole has also been identified in fog
904 waters where it was found to be quickly degraded during transport by photochemistry
905 (Anastasio and McGregor, 2000). It is thought to be present in the atmosphere originating
906 from soil dust rich in humic/fluvic material (Schulten and Schnizer, 1998, Anastasio and
907 McGregor, 2000). This may explain the presence of a small amount of pyrrole found in
908 the precipitation samples.
909 The three other compounds identified were all amines: dodecylamine (found only in the
910 precipitation), NDPA and decylamine (both only found in the stream).

911 4.6 GC×GC-NCD limitations

912 Although the application of GC×GC-NCD to precipitation and stream water samples was
913 largely successful, there were a number of issues. The main issue was the presence of
914 what appeared to be a contamination peak. Blank water samples were included before
915 sample analysis and N-butyl-benzenesulphonamide was not detected. N-butyl-
916 benzenesulphonamide is a plasticiser, and may have leached into the samples from the
917 storage bottles when stored in the freezer prior to analysis, or from SPE extraction tubes
918 by reaction with the DCM. This warrants further investigation.
919 In order to remove the DIN and water prior to analysis, solid phase extraction was used.
920 The most polar, water-soluble compounds, such as amino acids and urea, will be lost
921 during this step. Further work is needed to improve the extraction procedure to maximise
922 the applicability of the technique. Alternative approaches include liquid-liquid
923 extractions or stir bar sorptive extraction. Another issue is the small sample size of

924 precipitation samples, which combined with low concentrations, means that many of the
925 compounds are below the detection limit. In the stream samples, part of the DON may be
926 in less volatile forms that, although they can be measured by the ANTEK, are not
927 amenable to a GC analysis.
928 Identification of the peaks of unknown compounds may be improved by including
929 standards of more chemical compounds.

930 **5 Conclusions**

931 DON is an important source of nitrogen both in streams and precipitation and must not be
932 ignored in measurements of atmospheric nitrogen deposition rates or stream water
933 nitrogen balances. The mean volume-weighted concentration of DON found in the
934 precipitation over the total study period was $4.8 \mu\text{mol N l}^{-1}$, with a mean contribution of
935 9% to TDN.

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

940 In soil water, DON contributed an overall mean of 92% to TDN. The mean
941 concentrations of DON did not vary greatly between the years but the concentration of
942 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
943 impact of animal waste and the importance of water table variation on the availability of
944 N to plants and on immobilisation.

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

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1208 sources in China', *Atmospheric Environment*, 42(5), 1035-1041.

1209 Table 1. Statistics of annual concentrations of NH_4^+ , NO_3^- , DON and TDN for 2009 and
 1210 2010 in wet-only precipitation. Values are based on individual samples collected over the
 1211 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

1212 Table 2. Statistics of annual concentrations of NH_4^+ , NO_3^- , DON and TDN for 2009 and
 1213 2010 in soil water. Values are based on individual samples collected from dip wells over
 1214 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

1215

1216 Table 3. Statistics of annual concentrations of NH_4^+ , NO_3^- , DON and TDN for 2009 and
 1217 2010 in stream water. Values are based on individual samples collected over the two year
 1218 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

1219

1220

1222 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 ($\mu\text{mol N l}^{-1}$)
 1223 derived from TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations
 1224 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
 1225 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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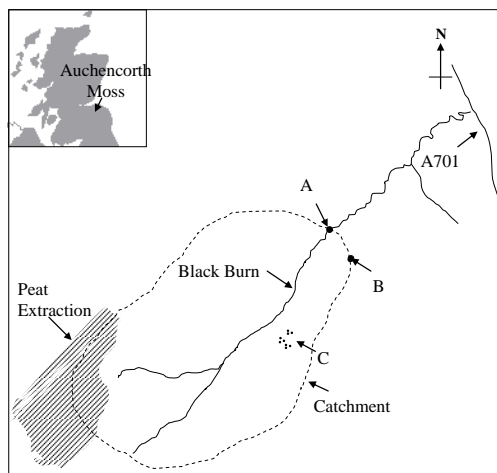
1229 Table 4. continued. Summary of compounds and their concentrations ($\mu\text{mol N l}^{-1}$) detected by the GC \times GC-NCD, and DON concentrations ($\mu\text{mol N l}^{-1}$) as TDN-DIN in precipitation samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the
 1230 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.
 1231
 1232

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				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	

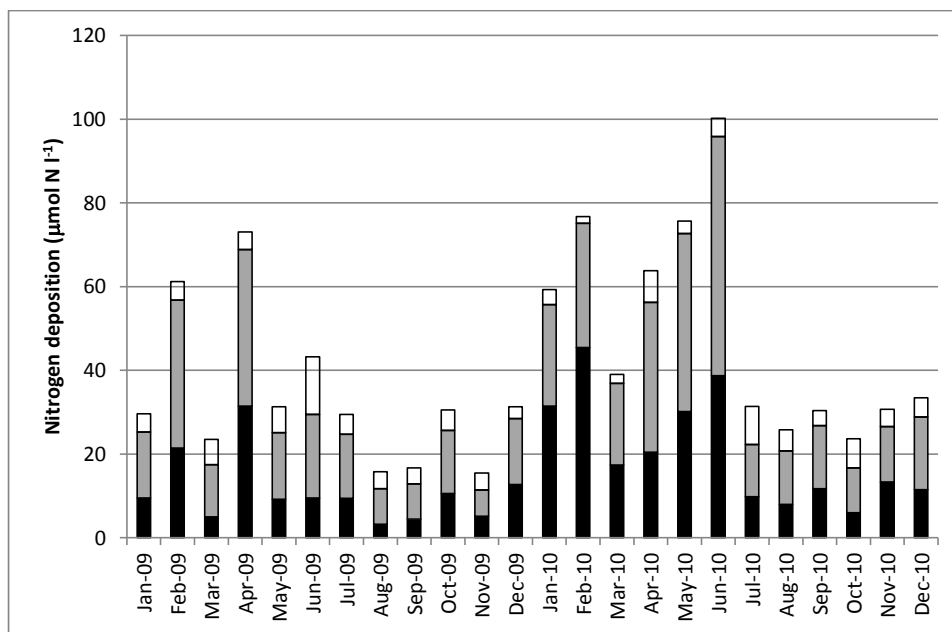
1233

1234 Table 5. Summary of compounds and their concentrations ($\mu\text{mol N l}^{-1}$) detected by the GC \times GC-NCD, and DON concentrations ($\mu\text{mol N l}^{-1}$) detected
 1235 by ANTEK in stream water samples. Samples collected on dates shaded in grey did not contain compounds at measurable concentrations by the
 1236 GC \times GC-NCD. Blank spaces indicate a measured value of below the detection limit.. Rt₁ and Rt₂ are retention times in seconds for the first and second
 1237 GC columns.

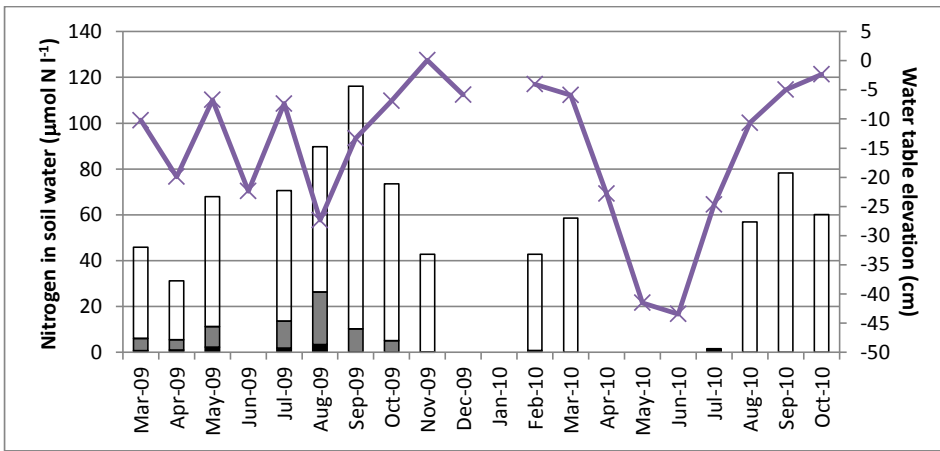
Sample Rt ₁ /Rt ₂	DON (TDN-DIN)	Pyrrole 375/1.24	Unknown A 415/1.24	Benzonitrile 825/1.8	N-nitrosodipropylamine 970/1.4	Unknown B 11.45/1.52	Decylamine 1295/1.64	Unknown E 1910/1.7	Unknown F 2200/2.09
11/08/2010	45.9	1.3	3.2					0.9	
19/08/2010	54.8	0.2	0.3		1.2				
26/08/2010	85.2	0.7	2.7	3.0					
10/09/2010	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



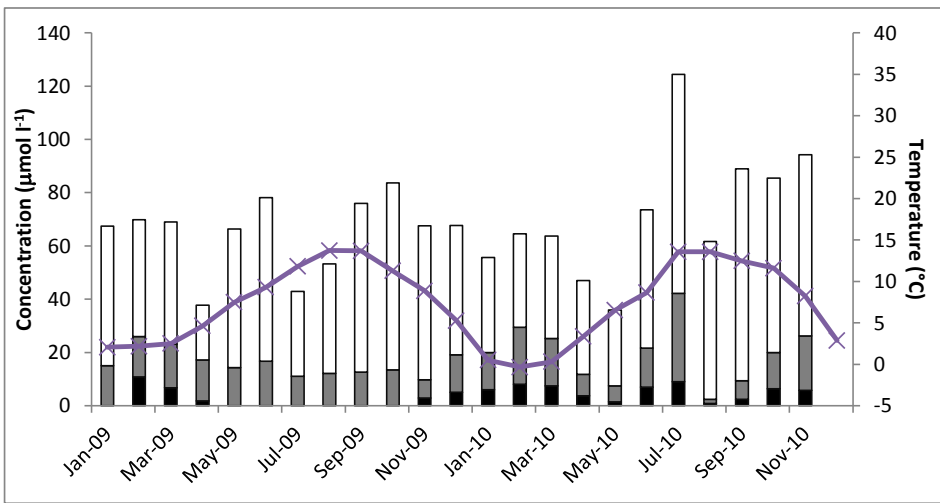
1238
 1239 Figure 1: Schematic map of catchment and sampling sites at Auchencorth Moss. Key: (A)
 1240 study catchment outlet and stream sampling site; (B) monitoring station (wet only analyser);
 1241 (C) dip wells. Adapted from Dinsmore et al., (2010).
 1242



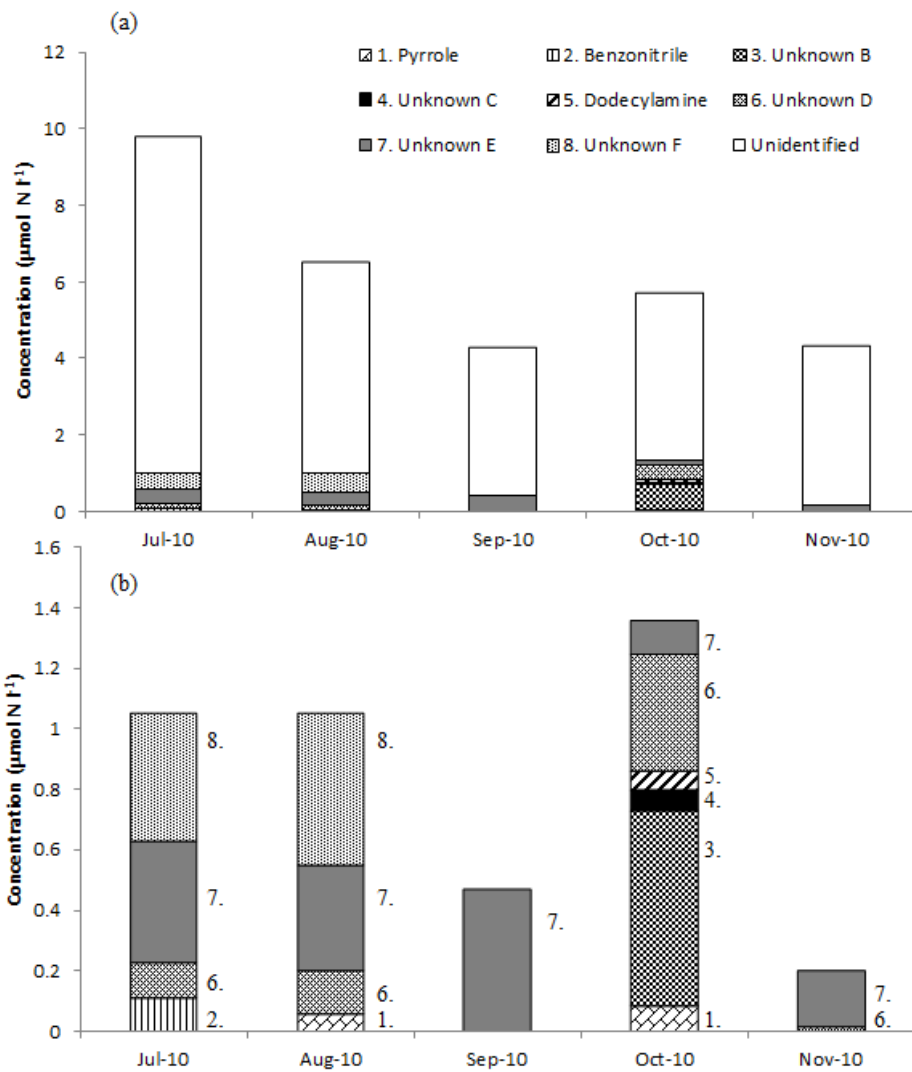
1243
 1244 Figure.2. Volume-weighted monthly average concentrations of NH₄⁺ (grey), NO₃⁻ (black) and
 1245 DON (white) in wet only precipitation.



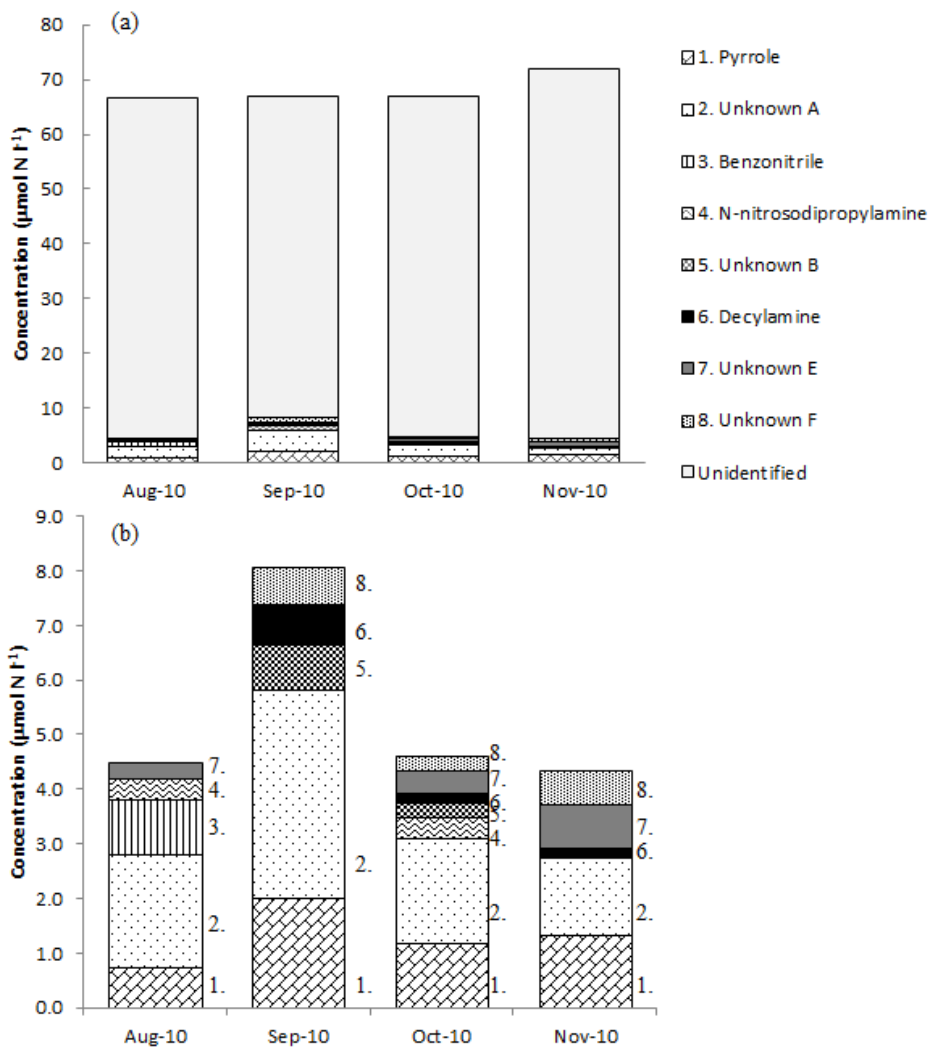
1246
 1247 Figure 3. Monthly concentrations of NH_4^+ (grey), NO_3^- (black) and DON (white) in soil
 1248 water. The line represents monthly water table elevation. The June-09 sample was misplaced
 1249 and Dec-09 and Jan 2010 were frozen, the remaining blank spaces indicate the dip wells were
 1250 dry on the day of collection.
 1251



1252
 1253 Figure 4. Discharge-weighted monthly mean concentrations of NH_4^+ (grey), NO_3^- (black) and
 1254 DON (white) in stream water. The line represents mean monthly air temperature.



1255
 1256 Figure 5. Mean monthly concentrations of the individual DON compounds found in
 1257 precipitation water. (a) includes the DON fraction identified from the ANTEK (white bar).
 1258 (b) excludes the unidentified fraction, so that the speciation achieved by GC×GC-NCD is
 1259 more clearly seen.



1260
 1261 Figure 6. Mean monthly concentrations of the individual compounds found in stream water.
 1262 (a) includes the DON fraction identified from the ANTEK (white bar) (b) excludes the
 1263 'unidentified' fraction, so the fraction detected by GCxGC-NCD is more clearly seen.