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Interactive comment on "The import and export of organic nitrogen species at a Scottish ombrotrophic peatland" *by* R. M. McKenzie et al.

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This paper considers the extent and nature of the transmission of organic nitrogen from atmospheric deposition through soils to streamflow in an ombrotrophic bog in Scotland. Organic nitrogen is now recognised as an important component of both atmospheric deposition and fluvial nitrogen and this paper represents one of the first and most comprehensive tests of the links between these. The system in which this is done is well characterised from other studies and the groups involved are very well experienced in both atmospheric and fluvial measurements. I think the paper should be published with some minor modifications. AUTHORS REPLY: We thank the reviewer for the very helpful and encouraging comments. We have modified the manuscript as best as we could as detailed below.

In particular I think it can be shortened and focussed on the main conclusions, rather than minor short term variability and discussion of minor compounds in the largely uncharacterised DON. AUTHORS REPLY: We have removed superfluous discussion points and thereby shortened the manuscript text by ∼340 words. The cuts we have made can be viewed in the track changed document we have submitted together with our replies.

It is also important to note that the fluvial nitrogen transport in streams draining an ombrotrophic bog are probably particularly rich in organic compared to inorganic N, and the conclusions here may not be readily extrapolated to other types of river systems. AUTHORS REPLY: Auchencorth Moss is a peatland not a bog, however your comments still apply, and we agree that our results are not translatable to other river systems, i.e. those fed by mineral soil. The scientists interested in our paper should know this difference and we therefore don't feel that we have to add this information.

Specific points:

Introduction There probably should be a reference to the recent efforts at characterising atmospheric DON using other mass spectrometry systems by Altieri and colleagues (Altieri et al., 2009 ES&T 43, 6950-5). There seems to be little evidence that anthropogenic compounds dominate high molecular weight atmospheric aerosol DON, although of course the potential hazards associated with such compounds cannot be ignored. AUTHOR REPLY: We have now referred to the Altieri paper: 'Various techniques have been developed to characterise DON, including FT-ICR Mass spectormatry (Altieri et al., 2009) and NMR spectrometry (Maie et al. 2006), with these methods focusing on the more on groups of compounds rather than individual species. Many techniques are not sensitive enough to detect individual organic nitrogen compounds in low concentrations (OÌĹzel et al., 2010). '

Line 136 says the samples were collected daily but line 142 says they were collected weekly, which is it? AUTHORS REPLY: we have altered the text to clarify that we are

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dealing with daily samples: 'The collector was kept at 4°C by an internal cooling system and samples were manually emptied from the daily collector once a week, where they were stored in a cool room, also at 4°C.'

In the past this group have used thymol as a preservative, presumably this was not done here, so are the components stable over storage in the field and the laboratory? IN line 565 a freezer is mentioned. AUTHORS REPLY: We were following a common protocol for another project which prohibited the use of Thymol. As shown in the above reply, the daily rainfall collector kept the samples at 4°C. Upon arrival in the lab precipitation, stream and soil water samples were frozen until analysis – this is already mentioned in the methods section for stream and soil water, and has been added for precipitation.

Line 209-218. Was the efficiency of the solid phase extraction for DON specifically tested? AUTHORS REPLY: Since this was a screening study and the identity of the DON species was unknown prior to analysis no SPE recovery was determined in advance. The cartridge uses a C18 stationary phase and so is likely to retain the less polar (but clearly still water soluble) fraction of the DON. This is a necessary step to be able to use GCXGC which has limitations on both the polarity and volatility of species that can be observed. The concentrations given are likely therefore to be underestimates if recovery is low.

Line 262-270 The seasonality is not really particularly obvious but it would be useful to know if it is associated with changing rainfall amounts, changing back trajectories or changing emission. AUTHORS REPLY: There was no correlation between rainfall and DIN or DON which is stated in the text.

Sections 3.3 and 3.4 might be simplified since there is one key and very important conclusion which is that DON completely dominates. AUTHORS REPLY: We have deleted superfluous information.

Section 3.5 Given the very important conclusion at the end of this section that 90%

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of the DON could not be identified, I wonder if some of the detail in this necessary. AUTHORS REPLY: As there are very few such measurements in the literature we feel it is important to provide as much information as possible.

The suggestion at the end of the section is that the DON is lost in the extraction rather than chromatographic steps and this should be discussed as noted above. AUTHORS REPLY: Some text has been added on the lack of information of the SPE recoveries and the limitations of the approach earlier in the section. This makes the discussion here more convincing.

The statement in line 561-2 is probably correct in an analytical chemistry sense but not really in terms of characterising the DON. AUTHORS REPLY: We do not fully understand this comment and therefore are not sure on how to address this. It does not help that our line numbers are very different from those of the reviewers.

In some ways section 4.6 might be more logical within the methods section AUTHORS REPLY: We prefer to keep section 4.6 as it is. The GC*GC analysis of peatland water samples is almost pioneering work, which obviously needs to be advanced in future work. Section 4.6 is the conclusion we have drawn based on our results and methodology used.

Section 4.1 You might note how concentrations compare to the earlier date of Cape and to the other sites they sampled. AUTHORS REPLY: in this paper we are interested in general patterns rather than specific concentrations. As we refer to a number of different papers we prefer not to include too many concentration values, and thereby make it easier for the reader to follow.

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

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

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

Section 4.2 does not seem very concise or well focussed. AUTHORS REPLY: We re-read this section and do not see how we can alter it. Our aim is to portrait the differences in DIN concentrations between the two years, as these effect the overall DON contribution. Perhaps the reviewer has some suggestions on what should be improved.

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

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

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

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

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

Line 257 and 259 what are the percentages in brackets? I assume it is the % of the total N based on Table 1 AUTHORS REPLY: Thank you, we have clarified this in the manuscript

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/12/C2520/2015/bgd-12-C2520-2015-supplement.pdf

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