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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.

R. M. McKenzie et al.

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General comments In their manuscript McKenzie et al describe and analyze concentrations and composition of inorganic and organic N forms in precipitation, shallow groundwater and river water in an ombrotrophic peatland in Scotland. In summary, nitrogen inputs into the peatland with wet-only precipitation were dominated by inorganic N forms, while nitrogen stored in the peat in groundwater as well as nitrogen exports with river water were dominated by dissolved organic nitrogen (DON). The role of the peat as a source of organic N forms is not very surprising given the high organic matter contents of Histosols and the poor retention of dissolved organic matter in Histosols. A comparison of DON quality by means of GCxGC-NCD revealed that the peat not only changed the quantity of DON in water, but also its composition. While wet-only

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precipitation was dominated by unidentified compounds E and F, DON in stream water was dominated by Pyrrole and an unknown compound A. Overall, I think that the manuscript provides valuable information, but the text can probably be condensed by some 30% without significant loss of information. AUTHOR REPLY: Thank you for your positive comments. We have managed to condense the text a bit, but prefer not to condense it by 30%, some of the information we provide may be rather helpful for the reader.

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

To compensate for such “concentration-dilution” effects, I suggest normalizing NH₄, NO₃, and DON concentrations in soil water for example to chloride concentrations or at least to electrical conductivity. Chloride concentrations might be available, because the samples were analyzed using an ion chromatograph that is commonly also quantifying chloride concentrations. AUTHOR REPLY: The dissolved nitrogen concentrations are volume weighted. We do not have the chloride data to normalise the N concentrations. But we have written at the start of section 4.2 that the differences are likely a dilution effect. ‘... situated in drier parts of the moss were more viscous and contained much particulate matter making filtering difficult. In contrast, DIN concentrations in dipwells during wetter periods or in wetter parts of the moss were more dilute and samples contained much less particulate matter’.

In contrast to the authors, I would regard the characterization of DON composition with the GCxGC-NCD technique as not particularly successful, because only a few percent of the DON compounds could be assessed using this technique. AUTHORS REPLY: The GC*GC analysis of peatland water samples is almost pioneering work. We

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recognise our measurements are not absolutely perfect, however they provide some valuable information for future research to improve.

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

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

In the discussion regarding the chemical nature of DON, I missed information and papers using other techniques such as NMR spectroscopy (e.g., McCarthy et al., 1997 Nature 390, 150-154; Maie et al. 2006. Geochim Cosmochim Acta 70, 4491-4506), Py-FIMS or XANES (e.g., Kruse et al. 2010, Sci. Total Environ. 408, 4910-4915). **AUTHORS REPLY:** we have added a reference to NMR spectrometry in the introduction.

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

ATHOURS REPLY: As mentioned to reviewer 1: 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.

Specific comments The structure of the abstract appears a little “jumpy” to me and probably needs to be revised. Which numbers below to the introductory part of the abstract, which ones are results of the study that is presented? AUTHORS REPLY: The abstract has been altered to improve its readability.

Page 521-Line 14: DON analysis. Were DOC concentrations analyzed as well using a TOC-analyzer? Having DOC concentrations in conjunction with DON concentrations would be very nice. AUTHORS REPLY: Unfortunately we did not have the opportunity to analyse our samples for TOCs.

Page 523-lines17ff: What was the recovery of DON by the C18-SPE cartridges? I strongly doubt the statement that the SPE procedure does not alter the DON composition. Ozel et al 2003 is not an appropriate reference, since this reference refers to oils and not to water samples! AUTHORS REPLY: The reason for using this reference is that this involves a sub-critical water extract of the essential oils. This was then subjected to the same SPE approach. Therefore in both cases the matrix is water. The response here is similar to the other reviewer. 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. This is a limitation of the study and so we have shortened this section as recommended. However, this data allows us in the future to carry out these

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sorts of studies and include recovery tests as appropriate.

Page 528-Line 25: Assuming a 100% DON recovery during SPE is not realistic... Page 529-Lines 20ff: It is not only that the GC captures only a fraction of the DON, also the SPE procedure likely recovers only a limited DON fraction. AUTHORS REPLY: We agree with the reviewer that for many species the recovery is likely to be less than 100 %. We have clarified this in the text and made the limitations of the approach clearer.

Page 530-Line 25: Consider adding “in precipitation” after “TDN” AUTHORS REPLY: This information has been added

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C2526/2015/bgd-12-C2526-2015-supplement.pdf>

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