

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

**Anonymous Referee #2**

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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 precipitation was

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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. 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  $\text{NH}_4$ ,  $\text{NO}_3$ , 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.

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. 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 vapor 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;

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Amelung and Zhang *Soil Biol. Biochem.* 33, 553-562). 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). 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...

#### 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?

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.

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!

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.

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

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