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Hydrology and Earth System Sciences
Discussions

Interactive comment on "Interacting effects of climate and agriculture on fluvial DOM in temperate and subtropical catchments" *by* D. Graeber et al.

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Reply to the most pressing concerns of Anonymous Referee #2

At first, we want to thank the referee for his/ her indepth review of our manuscript, which surely must have been time consuming. This will help us to detect weak points and to improve the study.

This reply has the aim to answer the most pressing concerns of anonymous referee #2. The detailed reply to the remaining comments will be done within the revision of the manuscript.

General comments by anonymous referee #2: After reviewing the manuscript, I have a few concerns and questions regarding the manuscript that I would like the authors to address. First, the land use groupings used in the manuscript were not fully agricultural differences. One watershed in Denmark had forests as its dominant land use. This watershed seemed to have very different DOM and discharge properties than the other watersheds. I think these differences in land use need to be discussed and acknowledged. Second, I am not certain that the sample size of the study and observed results show strong climate and land use influences on the DOM. There was a lot of overlap for sampling events between rivers. Climate likely has an important influence and this manuscript shows clear evidence of that but I think the evidence is not as strong as the discussion surrounding them implies. Finally, I wondered if data were available to compare the SEC-DON method with the subtraction method in your study. If so adding these comparisons might further strengthen the interesting discussion regarding the SEC-DON method.

Reply to general comments

Concerning the land use:

Both, the extensive catchment in Denmark and the extensive catchment in Uruguay contained a large area of the catchment with extensive land use. Since no forests exist in the prairie of Uruguay, these would also not appear in even completely pristine catchments. In fact, the only larger forests in Uruguay are artificial Eucalyptus plantations, thus, in this case, a forest does not necessarily mean that the land use is pristine. Extensive pasture is the most natural land use in Uruguay, as are commercially used forests in Denmark. We will include a short explanation on the pristine/ near-pristine land-use/ catchment vegetation in both countries in the methods section of the revised manuscript.

Concerning the sample size:

It is clear to the authors, that four catchments are not a large sample size in terms of

spatial sampling, but we had a very large sample size in terms of temporal sampling. To achieve both with a large sample number was difficult to reach due to constraints in time, financial circumstances and manpower. We acknowledge that the low sample size in terms of catchments would limit our conclusions, if this would have been the only study on this topic, but there are many studies with a large spatial dataset (please see discussion section of the manuscript, lines 431-435 & 499-501, and for DOC concentrations especially the cited review of Stanley et al 2012) and, especially for DOM composition measurements, a lack of investigations of temporal variability. Most studies on agricultural catchment effects are limited to one vegetation season (as we write in the introduction, lines 73-79), some to one year (Graeber et al. 2012 and the recently published Heinz et al. 2015, EST, DOI: 10.1021/es505146h) and, apart from our manuscript, none with two years of data and two different climate regions.

Concerning the assessment of climate effects:

We think that our evidence on the presence or absence of climate effects is very strong for the investigated catchments. For the DOM amount, we built a very clear line of evidence, starting with measurements of precipitation, discharge, DOC and DON concentrations and loads (please see discussion of the submitted manuscript, lines 383-403). Furthermore, we found highly significant effects of country (and hence climate region) on DOM composition (PERMANOVA with $p < 0.001$, results section of the submitted manuscript, line 318) and of country on the temporal variability on DOM composition (PERMDISP with $p < 0.001$, results section of the submitted manuscript, lines 322-323). Based on these results the country had a strong effect on DOM composition, but, as we write in the lines 424-425 on the discussion of climate effects on DOM composition: "based only on in-stream measurements, we cannot infer the mechanisms behind the differences of DOM composition in the two climates."

Concerning the further interpretation of climate effects:

We do not want to make final suggestions for the whole climate region or on the act-

ing mechanisms. In fact, we write in the conclusion of the submitted manuscript (lines 517- 522): "Distinct effects of climate on fluvial DOM have been found in this study and support earlier findings that climate is the main driver of DOM export from catchments. However, never before this has been tested for the molecular composition of DOM. We found strong effect between the catchments in the two investigated climate zones but cannot clearly attribute this to one climate or soil factor. Further studies of the DOM sources in the catchments are needed to get a clearer picture why these differences between different climate regions are found." However, we will carefully check the discussion section for any implication that would suggest that we want to make final conclusions for the whole climate region.

Concerning the direct measurement of DON with SEC:

An in-depth comparison of direct (SEC) and indirect DON measurements (by subtraction of DIN from TDN) is available in Graeber et al., 2012a, (Biogeosciences,9,4873-4884). This study is cited several times within the submitted manuscript and one intention to publish the Biogeosciences study was actually to make further laborious comparisons between the direct and indirect measurements in studies with applied SEC for DON measurements unnecessary. The advantages of the direct measurement of DON by SEC are mentioned repeatedly in the submitted manuscript: In the introduction to introduce SEC as a better alternative to the indirect method (page 138, lines 14-21); in the methods, where it is described in detail (page 142, line 11 -page 143, line 5) and it is even mentioned that "the direct measurement of DON with high accuracy was demonstrated in freshwater systems for this SEC system (Graeber et al., 2012a)" (page 142, lines 14-15). Moreover, its mentioned in the discussion, where we discuss the outcome on different measurement types for DON concentrations in the comparison of different literature sources (page 154, lines 4-26). Finally, in the supplement a typical chromatogram of the SEC is shown to explain its mechanism (Figure B1, this is not cited yet in the methods section, but a citation will be included in the revision of the manuscript). Thus, the advantages of the direct measurment over the

indirect measurement of DON are extensively discussed in the submitted manuscript. We believe that further inclusion of methodological data and further methodological discussion is out of the scope of this monitoring study and strongly recommend reading the Biogeosciences publication instead.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 12, 135, 2015.