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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.

Anonymous Referee #2

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GENERAL COMMENTS

This manuscript examines qualitative properties of dissolved organic matter (DOM) and its concentration and load as dissolved organic carbon (DOC) and nitrogen (DON) in two intensive and extensive agricultural rivers of two countries in very different climate zones. These types of comparison are need to better understand how land use influences carbon cycling across rivers. The manuscript combines optical chemical analysis of DOM with size exclusion chromatography to directly determine DOC and DON methods. The manuscript found good evidence that DOM, DOC, and DON measures differed by land use type and country.

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.

SPECIFIC COMMENTS

Please note comment line and page numbers correspond to PDF download of manuscript

Title: The statistical tests focused on main effects. I am not certain that "interaction" properly describes the study design. When the interaction was tested, the evidence for an interaction was significant but weak in magnitude.

Introduction: p137.L3-8 - I found this description of DOC and DON more complex than perhaps it needs to be. Consider simplifying that statement to say that DOM contains N and C and among other elements and then conclude as written with the ecosystem implications for DON and DOC

I think the reader needs more information regarding farming practices in the introduction. It was not immediately clear to me what the difference between intensive and extensive farming practices are. I also wonder how representative pasture lands are when being used as the lone extensive farming practice. These differences might only

be related to terminology, but I feel some clarification is needed for the reader to understand your study's framework. I think adding this information will help the read understand the fourth hypothesis (p139.L20).

Methods:

How do SEC DOC and DON concentrations compare to DOC measured by a TOC analyzer and DON as TDN - DIN? I think some information on this will help assure the reader that your values are comparable to those of other studies. If this work has been completed elsewhere than perhaps included a statement that tells the reader where they can find this information would be useful. Moreover, the study is introduced suggesting that SEC based measures of DON, especially, might provide a better estimate of DON than the common subtraction based approach. I am curious how DON in your study would differ if you used subtraction as opposed to SEC. Hence, I felt the paper never revealed if the insights and results gained from SEC-DON were more insightful than the subtraction method. If these ideas are covered elsewhere than less focus on these methods in the introduction might allow you to focus more on agricultural practices and climate. If these comparisons are novel then I think they should be included in the results and discussed.

In general, I found the statistical description clear and understandable with the correct level of detail needed for a reader to run these tests using their own data. I was curious how the difference in variance rather than normality of each variable influenced the PCA and MANOVA. I general scale (center = T, scale = T) after normalizing the data. This sets the data range to similar units between variables, which I find helps the multivariate data fit better with reduced dimensions. Variables with large ranges can at times disproportionately influence the multivariate analysis over variables with relatively small ranges like the freshness index and FI. I would suggest re-running the PCA and MANOVA using scaled data. If the non-scaled and scaled data are similar then the report analysis are good and you might consider noting that this did not influence the data ordination. If the results differ greatly between scaled and non-scaled, I

recommend using the scaled data.

Results:

Table 1 - I am concerned that the streams understudy do not match fully the study design (County*Land Use). The UY watersheds fit fairly well into agricultural groups but the DK watersheds are a forest with farming vs arable farming. This might explain why DK-Extensive was markedly different based on DOC and DON loads. I think these land use distinctions and possible other underlying differences like soil type should be more clearly stated in the methods and discussed more fully. In other words, I would like more discussion geared to convince the reader that your observations are due to climate and farming practice differences rather than differences in background nutrient levels, hydrology, geology, watershed slope, and the contribution of other land uses.

Table 3 & Figure A1 - I find it surprising that your PARAFAC model does not contain a protein-like peak. Typically, 3 or 4 component models have UV humic-like peak, Vis humic-like peak, and protein-like peak. Upon visual inspection of Figure A1, it looks like the excitation spectra is pretty broad for each component. This might suggest that component number, though reproducible, is not correct for your data. Perhaps adding a few residual and corrected EEMs would be useful for the reader to better understand the PARAFAC output. I am curious if the model systematically misses the protein like peak, which would be evident in the residual EEMs or to see that these samples don't have a protein-like peak. I think some discussion might be needed in order to interpret the model for the reader.

For PC3 - If the three spectral slope indicators are interpreted the same with respect to size why do they show up as opposites? This would suggest that both directions are small and large sized DOM. It wasn't clear to me how this pattern would relate to light exposure differences between watersheds. Perhaps some clarification is need because the smaller sized and lower C:N patterns seem important based on the manuscripts conclusions.

p150.L1-7 & Figure 4 - For individual DOM assessments, I found it unclear why only 6 of the 20 indicates were displayed and presented. Perhaps adding a little more detail regarding why only these variables were selected over others might be useful. Do these factors highlight different components of the PCA? They seem to highlight some of the PCA axes but not all.

Discussion:

I am concerned that the data set might be too focus to resolve strong climate and land use patterns. The N for the study is 4 watersheds (two climate zones and two land use categories). The catchments could just be different and influenced by the observed precipitation patterns rather than broad climatic differences. Differences in climate between Denmark and Uruguay are much greater than the observed differences in DOM quality and quantity. I am uncertain that broad climate generalities in DOM with land use can be drawn from such a small set of watersheds. I agree that the data supports the idea that land use, especially intensive agriculture, has strong affects on DOM and these are seen in two watersheds from countries with very different climate. I am not certain if these results can be generalized. I don't wish to discount the findings but I don't think the evidence was as strong as presented for the hypothesis. There was some evidence that DOM shared similarities between intensive farm systems but the DOM of these watersheds also shared many similarities overall. My interpretation would be that the study found some evidence, rather than strong evidence, in support of the hypothesis that raises important questions and ideas.

p151.L7&8 - I did not understand how Denmark could have a higher water buffering capacity if it is extensively tile drained. Wouldn't this be swamped out by the faster movement of water suggested in the next paragraph?

p152.L14-19 - Could this be due to the fact that this catchment was mostly forested and not as human impacted? This might allow the system to have more stability in discharge and DON/DOC inputs might be controlled by seasonal cycles in litter production

and groundwater vs surface water contributions to stream flow.

p154.L9-11 - Given that DON-agriculture effect was so large, why wasn't this also evident through DOM optical measures? PARAFAC did not identify a protein-like peak, which would suggest there was little DON at least of that type. I feel discussion is needed to explain why these are consistent patterns.

p154.L19-26 - Are you able to check this statement by comparing the subtraction method to the SEC-DON method using your study. If you measured TDN and DIN, this type of discussion would help strengthen the argument for the novel approach used in the your manuscript.

p155.L5-10 - This could be true and is a likely mechanisms. How might the presence of a high percentage of forested land in the Denmark catchment influences these patterns?

TECHNICAL CORRECTIONS

p144.L15 - Do you mean "LMWS" rather than "HMWS"? p147.L7 - Consider simplifying this statement. I think similar works for all catchments p150.L1 - what is meant by "exemplary"? Consider clarifying this statement Figure 3 - I find the dots a little small on these figures. Perhaps changing the shape and color would make it easier to see light blue from blue dots. P150.L9&21 - Did you mean "support" rather than "prove" P152/L14 - Did you mean "in which" rather than "which in which"? Figure 2 - I found it somewhat confusing that this figure shows concentrations paired with percentages for loads. Consider pairing load values with load % and concentration values with concentration %

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