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Discussions

Interactive comment on "Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements?" *by* A. M. Ågren et al.

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Response to Interactive comment on "Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements?" by A. M. Ågren et al. D. D'amore (Referee) ddamore@fs.fed.us Received and published: 18 December 2013

General overview: This study is a welcome addition to the field of catchment biogeochemical modeling. The data on DOC concentrations and patterns in the landscape is an important contribution to the growing body of data and conditions around the world. I would have welcomed some estimates of fluxes, but understand that this material is an

important precursor to those calculations. I did find that the number of landscape variables seemed very numerous for the final model (see comments below). Many studies of DOC concentrations have reduced the predictor variables to a few key landscape attributes. I think this approach could improve the presentation and use of the proposed model. One other technical improvement that the authors might consider is trying the new Bayeseian approach INLA (http://www.r-inla.org/). This is an alternative to MCMC stochastic modeling. I believe this technique offers great promise to researchers that use time series measurements.

Yes the field of Bayesian statistics is certainly growing and there are many new interesting approaches that could be tested, however, for this study we chose a frequentist approach. Our landscape mixing model is based on the mixing-model by (Cooper et al., 2000) . Cooper writes:

"If a single spatial classification is available, then suitable landscape types may be defined directly using Eq. (1) in an iterative fashion using measured stream water concentrations from a sample of subcatchments within a catchment of interest. The regression model is first fitted to all spatial classes. This is likely to indicate that estimated concentrations from some classes are not statistically distinguishable. If this is true for all water chemistry variables of interest, then the classes concerned are merged. This merging continues until either an acceptably small number of merged classes have been defined, or until all classes have statistically distinguishable concentrations. This point may be judged to have been reached when no merging of classes gives a reduction in the residual mean squared error. Merging classes is to some extent subjective and may depend on prior scientific knowledge of the relationship between classes. Before starting regression analysis, it may also be useful to create preliminary groupings based on the frequency of occurrence of classes within the catchment."

Previous research in the study catchments has identified three source types which might account for the concentrations of DOC (Ågren et al., 2007;Buffam et al., 2008): peat, till, and fine sorted sediments. We chose to build the landscape-mixing model

based on these three aggregated classes. However, this gives concern that by aggregating the classes and only include the variability in the quaternary deposits we are throwing away "landscape variability" that can also explain stream DOC variability. That is the reason for collecting numerous landscape variables and using them in the PLS residual analysis as that would indicate other controlling processes.

General comments: 1. The abstract could be more specific and concise.

We have now rewritten the abstract to make it more concise.

2. A theme is the evaluation of the models is that they are 'okay'. I am curious if the authors are satisfied with this first approximation, or did it fall well short of the expectations of the study?

We were of course hoping that this approach would generate a good model, and our simple landscape mixing-model give predictions of the same quality (during high/intermediate flow) as the much more complex process based DOC-3 model (Jutras et al., 2011). Because of the complex spatial and temporal variability of DOC we did not expect it to work everywhere or every-when and the residual analysis with the PLS method is an important part of the article to identify where and why the landscape mixing model failed.

3. What do the parameter estimates represent in equation (1). Are the parameter values percentages? If 'peat' is an area, is 'A' a modifier for the concentration or a percent of the area? This equation needs to have a bit more explanation to be clear.

The parameter values are flow ratios, as indicated by dividing equation 1 above (the flux equality) by the total discharge. We assume the flow ratio is equivalent to the areal ratio of specific landscape to whole catchment. So A, B etc are proprtional areas input to the model.

We have now clarified this and now write: "Based on the 15 selected headwater sites in the construction dataset, a regression model (Eq. 1) was constructed to calculate

the end-member concentrations for each landscape type and on each sample date by multiplying the concentration with the areal coverage for each landscape type (A-D). By setting the intercept to 0 in the model and using the areal coverage of the landscape types in proportions (0-1) instead of percentages, the estimates (A-D) were expressed directly as the end-member concentration for DOC in mg L-1 for each landscape type.

$[DOC]$ (mg L^{-1})= A×$[DOC]$_Peat+ B×$[DOC]$_Till+ C×$[DOC]$_(Sorted sediment)+ D×$[DOC]$_Other

Eq. (1)"

4. There are many variables selected for input, but these variables don't appear to play a major role in the evaluation. The landscape variables are generally used as predictors. However, the authors note that prediction isn't a goal (section 4.1). Could this model be used for prediction? What are the shortcomings?

The following paragraph have now been inserted in the discussion:

"Whether the landscape-mixing model is good enough to be used for prediction, depends on what the predictions are to be used for, and how much error is acceptable. However, our simple landscape mixing model produces similar results to the more complicated process based DOC-3 model (Jutras et al., 2011) where RMSE ranged from 2.4 - 5.1 mg L-1 and R2 0.27 - 0.55 (cf. Table 2) in three Nova Scotia streams with stream DOC concentrations 4 - 40 mg L-1, similar values to the Krycklan catchment (Figure 4). Based on the many model measurements calculated (RMSE, RSR, NSE, PBIAS) we assess that the model performed well for two campaigns (May 2003 and Sept 2008), unsatisfactorily for the one winter campaign (Feb 2005), and satisfactorily for the remaining four campaigns."

5. It is not completely clear to me what Figure 8 conveys. Perhaps the discussion of this figure could be expanded."

Citation and extensive discussion of a companion study (Tiwari et al., 2014), where we

further studied the suggested important controls on DOC from this residual analysis, have been added to clarify the discussion of this figure.

6. Section 3.2 and figure 7 are hard to follow. What purpose do the variables play in the model? If there isn't a great deal of use for the variables, shouldn't they be eliminated in the model run? I'd like to see the most parsimonious model described to reveal the most influential landscape factors. For example, what functional role does tree volume play in discharge? Is this variable actually a covariate for some other variable? Is there a subset of influential variables among the 23 predictors in the model?

There is a subset of variables that are important, but this subset is different for the baseflow vs. the intermediate/highflow campaigns (Figure 7). As stated in section 3.2, the purpose of the PLS model in Figure 7 is to give an overview of the data including all flow regimes. Figure 8 shows two distinct refined models, more parsimonious as you suggest, to reveal the most influential landscape factors for each flow condition. We have now clarified section 3.2 so that this is more clearly described.

7. Freezing can reduce DOC concentrations in high DOC samples. Is it possible to improve the model performance if an adjustment to freezing loss is introduced? Perhaps the relationship of the potential loss in samples vs. residuals could be examined.

We have conducted our own freezing experiments on stream water samples from the Krycklan catchment. We have not been able to detect any significant effect on the DOC concentrations. So it is unlikely that this will affect the results in our study.

8. Is there a potential to represent the areas of uncertainty in the hydrologic pathways in a figure? This uncertainty is a concern in the community of biogeochemical transport modeling. What is the role of large valley bottoms on the transport mechanisms? Should there be some discussion of hyporheic dynamics in the sediments?

This issue was further investigated by our group in Tiwari et al (2014), a paper which is now referred to in the discussion of the current manuscript. In Tiwari et al. (2014) we

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show that during baseflow the input of deep groundwater in lower laying catchments was an important control on the DOC concentrations at the outlet. During baseflow 80 % of the water in the outlet originated from deep groundwater flow paths.

In Tiwari et al (2014) we also discuss the reasons for the large input of groundwater: "The question remains whether the large proportion of deep groundwater during baseflow is common for catchments of this size or if our study catchment is a special case? An esker passes through the study catchment which potentially could provide a continuous supply of deeper groundwater that feed into the stream during baseflow. It is plausible that the influx of deep groundwater could be less if the stream only drained till soils instead of the more permeable sorted sediments in the valley. However, our results are consistent with previous findings of Capell et al., [2011], Wu et al., [2004], Shaman et al., [2004] and Ladouche et al., [2000] who also showed that deep groundwater dominates discharge during baseflow in meso-scale catchments. This suggests that the importance of changing hydrological pathways is likely a more generalizable scale process."

Specific comments:

Page 15916:5. Can you provide some examples of 'scale-dependent' processes?

We now write:

"This increased complexity can be related to new/different contributing landscape features becoming increasingly common downstream at lower elevations, but also because there may be scale dependent processes that can have considerable effects on the stream DOC concentrations as the rivers grow, for example changing flowpaths (Cey et al., 1998) or effects of landscape structure (Pacific et al., 2010)."

Section 2.1, Page 15917:15. Are the forests classified as 'forested wetlands'?

No, "forests" are considered upland soils. The peatlands (9%) are divided into forested (2/3) and open(1/3). This has now been clarified.

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P15918:10. Is the other 50% ET or loss through some other pathway?

Yes, mostly ET. It could also be changes in storage but that is less likely in the timescale studied here.

P15919:25. Frozen samples may be subject to DOC loss (see Fellman et al., 2008. Sci. Tot. Env. 392:305-312.

Since Fellman's study showed that freezing of samples can affect the DOC in the samples we have conducted our own freezing experiments on stream water samples from the Krycklan catchment. We have not been able to detect any significant effect on the DOC concentrations. So it is unlikely that this will affect the results in our study.

P15921:0. If riparian zones are important for DOC flux, which grouping includes these landforms? Sorted sediments?

We have not separated the signal from upland soils from the riparian soils in this study. The riparian zones are included in the signal from both the forest on till soils and forest on sorted sediment. However, till and sorted sediment soils have a different riparian DOC signal. Till soils usually have higher DOC concentrations in the riparian soils (on humid and wet sites) than sediment soil. On humid and wet till soils we have a build-up of riparian peat, hence, water draining to a forest stream on till soils will pass through the riparian peat enriched in DOC and give a higher DOC signal to the forest stream than that of a dry till or a sorted sediment (Grabs et al., 2012). This information has been included now in section 4.1 of the Discussion.

P15928.Section 3.2.0. I'm not familiar with PLS so this section was a bit difficult to follow.

We have now extended and clarified this section.

That concludes our answer to the interactive comment.

Anneli Ågren and coauthors

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$$\text{Flux} = \sum_i \text{flux}_i \quad \text{Discharge} \times \text{concentration} = \sum_i \text{discharge}_i \times \text{concentration}_i \qquad (1)$$

Fig. 1.