

Interactive comment on “High-frequency measurements of dissolved organic carbon quantity and quality in a headwater catchment” by Benedikt J. Werner et al.

Anonymous Referee #4

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General Comments: The authors report on a study of DOC concentration and quality over time in a stream using a combination of grab samples and an in situ UV-Vis spectrophotometer. The authors find that during warm, dry periods DOC concentrations were highly responsive to storm events (increases in discharge). As conditions became wetter and cooler, the responsiveness of DOC concentrations decreased. The authors attribute this to differences in hydrologic flowpaths and DOC mobility and production across landscapes. The authors use a thorough analysis to support their arguments and conclude the paper with an interesting conceptual framework that synthesizes their own findings with other existing literature. I think that the authors present a strong study, but have some suggestions for clarity and organization

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I argue that the authors have over-emphasized the trend of increasing DOC flux trends in the abstract and introduction. This is an important reason to study this subject and this work could certainly be used to better understand the mechanisms driving this trend, but the paper includes neither a report on this increasing trend or evidence for a mechanism for this trend. I think that most of the parts of the introduction are there, but I suggest that the text focus more on the aspects of DOC export reported on in the paper (transport of DOC from watersheds across hydrologic regimes and antecedent conditions). One thing that is missing from the introduction is any mention of antecedent moisture conditions. I think that discussing the role of antecedent conditions, discharge-normalized temperature, and their potential role on DOC quantity and quality should be discussed before the methods section since these are a major focus of the paper and the conceptual model discussed later (figure 6).

Specific Comments: Page 3; Lines 14-16: I highlight this sentence because I think that it does an excellent job of encapsulating this study. I suggest the authors reorganize the introduction to better emphasize concepts related to this idea.

Page 4; Line 27: Were grab samples also run for spectral slope values in addition to UVA-254? I also suggest that the authors provide some additional detail about sample collection (e.g., filter size, sample handling).

Page 4; Line 29: Some brief information about methods for DOC analysis (e.g. acidification level) would be of use for the reader.

Page 5; Line 6: I suggest the authors report how closely SUVA values obtained from the sensor match the grab sample values.

Page 6; Line 21: I'm concerned that hysteresis loop size is biasing regression slopes obtained from this method. I would appreciate some support for application of this method to events with varying degrees of hysteresis.

Page 7; Line 27: Reporting an actual mean AI or similar number would be helpful for

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the reader.

Page 8; Line 28: I think that there are better ways to present this information. As written, it is hard for the reader to tell what the readers should take away from this paragraph.

Page 9; Line 16: Presenting this information here is repetitive. I argue this authors should move some of this material to the methods section where similar methods are already covered.

Page 9; Line 30: I am concerned about the interpretation of individual regression coefficients from a multiple regression of observational data due to issues of multicollinearity. In other parts of the analysis, partial least squares regression is used to address this issue, but for this analysis it appears that multiple linear regression was used instead (Page 6, Line 18).

Page 10; Lines 9-20 and Table 3: Values of a change dramatically depending on whether a 15 or 30 day lag is used. For example, a (CDOC) is negatively correlated to T15, but positively correlated to T30. The same is true for Q15 vs Q30. This pattern is reported for a (SUVA254) and a (S275-295). It would be interesting to see if the correlation between a and DNT15 is negative. This would seem to change the implications of the study substantially.

Page 10; Line 28: Referring to this analysis as seasonal-scale is somewhat confusing to me because there is no specific season analysis conducted here (rather variables that change with season are used). I would also like to know if any data were held out for model validation or if the R2 statistics in Table 4 are for the model with reference to the training dataset alone.

Page 13; Lines 9-12: The different weather scenarios make sense, but I think that stating that there are three discrete states is a bit arbitrary and is not supported by any sort of data or analysis. I think the general framework is right and it makes sense

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for the authors to highlight certain scenarios. That said, I don't see evidence in the data for discrete states but for a continuum without jumps from one state to another. I recommend the authors clarify the nature of their conceptual model.

Figure 6: How baseflow DOC concentration changes with season was not supported with particular numbers in the results, but appears to be important for the conceptual framework. It is discussed briefly in a qualitative fashion, but the degree of seasonal differences in DOC concentrations are hard for the reader to infer.

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