

## ***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 #3**

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General Comments: In this paper entitled “High-frequency measurements of dissolved organic carbon quantity and quality in a headwater catchment” Benedikt et al. report the results of a high-frequency monitoring study in a small, alpine catchment in Germany. Using 15-minute interval data, the authors analyzed correlations between temporal variation in dissolved organic carbon (DOC) quantity and optical properties on event and seasonal scales with antecedent weather conditions. They found that seasonal state influenced DOC concentration as well as the response to change in discharge. This work is a strong, observational study that build off the growing literature on high-frequency DOC dynamics. The paper is well written and citations are generally appropriate, though there are gaps, which is inevitable in large field such as

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this. I was also impressed by the clarity and creativity of the figures, which can be challenging for an observational paper with so much data. The combination of high-quality and unique data with a thoughtful statistical framework makes this a compelling and complex study. With a thorough revision, this paper would be a strong contribution to Biogeosciences. A few general comments and suggestions below:

1. There is a clear goal stated at the end of the introduction, but there are not clear hypotheses until the conceptual model is presented (Figure 6). I think that putting the conceptual framework at the front of the paper (introduction or at latest the methods) would help the reader understand how the authors are viewing the system, better appreciate the findings, and better grasp why certain methods were used.
2. The paper spends quite a bit of time discussing long-term trends in DOC attributed to changes in acid deposition, land use, and climate change. This focus was something of a red herring, as the paper is strongest on a much shorter timescale, which does not speak directly to this literature. Additionally, most of the cited papers on DOC trends are older, which I think is a recognition that while many regional trends exist (for either increasing or decreasing DOC), there is not a clear pattern or signal of anthropogenic effects on DOC concentration. There is more evidence of anthropogenic effects on DOC properties (e.g. Butman et al., 2014), and this could be fruitful, but, I think the ecohydrological focus on sources and fate of DOC is most compelling. This fits in better with the conceptual model and approach of the paper. There are many other reasons to study DOC, many of which are brought up elsewhere in the introduction (Zarnetske et al., 2018), so starting the paper with this observation is less effective.
3. The discussion seemed somewhat uneven to me—with the authors still defining some concepts and findings and even describing methods. I think that reorganizing the paper around a clear set of hypotheses would strengthen this already interesting piece of work.
4. Throughout the paper, I was surprised at the lack of discussion of interactions with other elements. DOC does not cycle in isolation, and stoichiometry can have a strong influence on DOC production and consumption (Helton et al., 2015). not to find greater discussion of DOC removal mechanisms, including heterotrophic respiration and abi-

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otic removal (Raymond et al., 2016). I imagine that nitrogen and phosphorus data are available (NO<sub>3</sub> data, specifically should be available through the whole time period), and including and integrating them could greatly strengthen the paper. For example, how do N and P vary during the chosen seasonal periods and how might that influence temporal patterns currently attributed to changes in source and transport limitation?

References Butman DE, Wilson HF, Barnes RT, Xenopoulos MA, Raymond PA. 2014. Increased mobilization of aged carbon to rivers by human disturbance. *Nature Geoscience* 8 (2): 112–116 DOI: 10.1038/ngeo2322 Helton AM, Ardón M, Bernhardt ES. 2015. Thermodynamic constraints on the utility of ecological stoichiometry for explaining global biogeochemical patterns (P Jeyasingh, ed.). *Ecology Letters* 18 (10): 1049–1056 DOI: 10.1111/ele.12487 Raymond PA, Saiers JE, Sobczak WV. 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. *Ecology* 97 (1): 5–16 DOI: 10.1890/14-1684.1 Zarnetske JP, Bouda M, Abbott BW, Saiers J, Raymond PA. 2018. Generality of Hydrologic Transport Limitation of Watershed Organic Carbon Flux Across Ecoregions of the United States. *Geophysical Research Letters* 45 (21): 11,702-11,711 DOI: 10.1029/2018GL080005

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