

## ***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 #2**

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The manuscript describes a  $\sim$  one year high frequency measurements of dissolved organic carbon (DOC) concentrations and quality in a river draining a headwater catchment in the Harz mountains, Germany. The authors measured DOC-concentrations and SUVA<sub>254</sub> every 15 min by means of a UV-Vis probe and calculated the spectral between 275 and 295 nm as indicator of DOM quality. Validation and calibration of both parameters were performed through SAC<sub>254</sub> and DOC measurements of grab samples. Discharge was calculated from a stage-discharge relationship based on data obtained from pressure transducer and manual discharge measurements. From their DOC measurements the authors concluded that changes in DOC concentrations and quality are mainly determined by antecedent hydroclimatic conditions. Due to this,

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the authors used an aridity index (AI60) as well as temperature and discharge of the preceding 30 days and a so called discharge normalized temperature index as controlling variables/predictors to statistically model DOC concentrations changes in their river. From their data they suggested a conceptual model which differentiates between three hydroclimatic states (warm and dry, cold and wet and intermediate. The authors concluded that the DOC concentration variability in their stream can be predicted by a small number of controlling variable which are linked to DOC source activation, discharge events and seasonal changes in the DOC production in the riparian zone. "High frequency" measurements of DOC release from headwater catchments have been carried out in a number of studies before which showed broadly the same results and conclusions. For example, Broder and Biester, 2015 (also BGC) and Birkel et al 2017 published a study of high frequency measurements of DOC release from a peatland and forest catchment in the Harz (just a few kilometers away) and also modeled DOC release dependent on antecedent moisture conditions. Unfortunately, these papers have not been cited or discussed in the manuscript. What is new in this study is the really high frequency DOC monitoring (15 min) and the different statistically approaches. However, for me it is not really clear what actually the aim of the paper is. One reason for this might be that the paper lacks a clear hypothesis. Even the title does not contain a research question, just a statement of what has been done. The description of the aim of the study (p3) is quite general. . . . to obtain a better understanding. . . Looking at the conclusions, I don't think that the paper really provides more understanding than what is already known. It seems, that the authors cannot really decide if this is a eco-hydrochemical or a statistical-hydrological study. The value of the presented findings is difficult to evaluate as the authors have largely missed to compare and discuss their results to/with those of other studies. From what the authors stated in their (long) conclusions. . . . "Yet, it remains unclear which explicit mechanisms in the riparian zone are responsible for the measured and conceptualized DOC dynamics in the Rappbode stream. . . . Further research is necessary to identify the explicit spatio-temporal mobilization patterns as well as molecular markers that can be used to trace DOC from

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riparian source zones into the stream in order to fully understand DOC mobilization in the riparian zone. "I think that is where other studies have ended before. The biogeochemical findings in this study are quite limited, so that the study has its emphasis on the statistical approach which is clearly necessary to extract a message from the large (high frequency) data set. However, as the authors base their predictors on 60 and 30 means, the meaning of the high-frequency DOC monitoring remains form e unclear. I think it would be interesting to use this data set to evaluate which frequency is at least necessary to capture the role of the predictors and the magnitude of DOC concentration/flux changes (38 discharge events!). Moreover, there are several factors in this data set which might be interesting to evaluate regarding the sensitivity of the model towards the predictors e.g. the magnitude of DOC-flux changes during discharge events, the role of catchment size, DOC-pools etc. but are not discussed.

This manuscript is in general suitable for publication in BGC. I also think that the quality of the data and the approach is good. However, I think before this manuscript can be accepted the authors should try to give their manuscript a clearer aim/hypothesis which goes beyond a generally better understanding of what is already known. I suggest, that the authors extend their introduction by other studies (there are numerous) on this topic. From this they can probably better deviate what is already known and what the (new) aim of their study is (why needs the frequency be higher than in other studies ?). Similar, they should extend their discussion with a comparison to data from other studies and the sensitivity and potential limitations of their predictors including the characteristics of the catchment and a discussion on high frequent high frequency should be.

#### References:

Broder, T., Biester, H. Hydrologic controls on DOC, As and Pb export from a polluted peatland - the importance of heavy rain events, antecedent moisture conditions and hydrological connectivity. Biogeosciences, 12, 4651-4664 (2015).

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