Response to **Anonymous Referee #2**

"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 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 gererally 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 frequence 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.

(R2GC1)

We appreciate the honest opinion of Referee #2. There are four general points raised by the reviewer which we want to address to in the following.

1.1- Referee #2 recommends adding a discussion section where

- we mark down similarities and differences to other studies which broadly show the same results and conclusions
- sensitivity and potential limitations of predictors including the characteristics of the catchment should be addressed.

We agree that there have been studies carried out, which point in the same direction, but we disagree with the opinion of Referee#2: “I don’t think that the paper really provides more understanding than what is already known”. A comparison with other studies can help to define what is new in this study and thus will be incorporated in the MS:

a) In general most of other studies related to this topic are of a lower frequency and do not consider DOC composition. As also stated from Referee#2, to our knowledge there is no other study using a combination of “really” high frequent DOC concentration and composition time series for over one year. Yet, seeing that results of the here proposed high frequency method incorporates findings of other papers which used lower frequency measurements is an important and promising finding on its own, since it strengthens our proposed method, but also findings from other (lower frequency) papers. Please see also the discussion of 1.2 in this reply.

b) The mentioned studies from Referee#2 were conducted in a peatland which is included in a forest catchment with peaty riparian zone. Especially the DOC concentration dynamics of peatland C-Q relationships differ from that of riparian DOC mobilization dynamics (dilution vs. enrichment patterns with increasing discharge). An interesting question is if the different patterns also hold for DOC quality. Such a discussion could be fruitful, because it helps to unravel whether mobilization mechanisms are really the same in two catchments (then DOC concentration and composition dynamics in these catchments should be also comparable). In terms of DOC quality, this is not the case between these two catchments, which leads us to the conclusion that our riparian zone study site adds valuable data to complement the data for peats and peaty riparian zones provided by the studies cited by the Referee (a discussion on that will be added to the MS).

c) High frequent DOC concentration and quality is dependent on seasonal antecedent hydroclimatic changes. In order to better model and understand DOC export dynamics at such a high frequency, it is crucial to also understand the changes and interaction between the antecedent conditions at a similar time scale. This has been done in our paper and we believe highlighting the importance of continuous, interacting, hydroclimatic variables for modelling high frequency DOC data is an important contribution to former high frequency DOC export analysis. The study gives the opportunity to easily compare our findings and depicted mechanisms with other catchments which use similar (high frequency DOC concentration and composition) set ups. In terms of reproducibility, it is therefore easier to conduct in comparison to a study which uses e.g. trace metal contaminations as tracer (because such contaminations do not occur everywhere) and thus represents a potentially powerful methodological tool for examination. However, with regards to biogeochemistry and its mobilization processes, a further combination with (trace) metal export /element stoichiometry (see R#3) could turn out to be quite synergetic.

The discussion will be further complemented by a section with limitations of the predictors. In general, the statistical relationships established for predictors and DOC response cannot account for situations outside of the measurement range (extreme droughts and floodings, which are out of

calibration have to be treated with care). Furthermore, validity and sensitivity of the statistical relationships with the predictors does not account for long-term changes in biogeochemical and hydroclimatical factors (pH, ionic strength, sulfate and nitrate, annual mean temperature…) which all can influence DOC export behavior on its own.

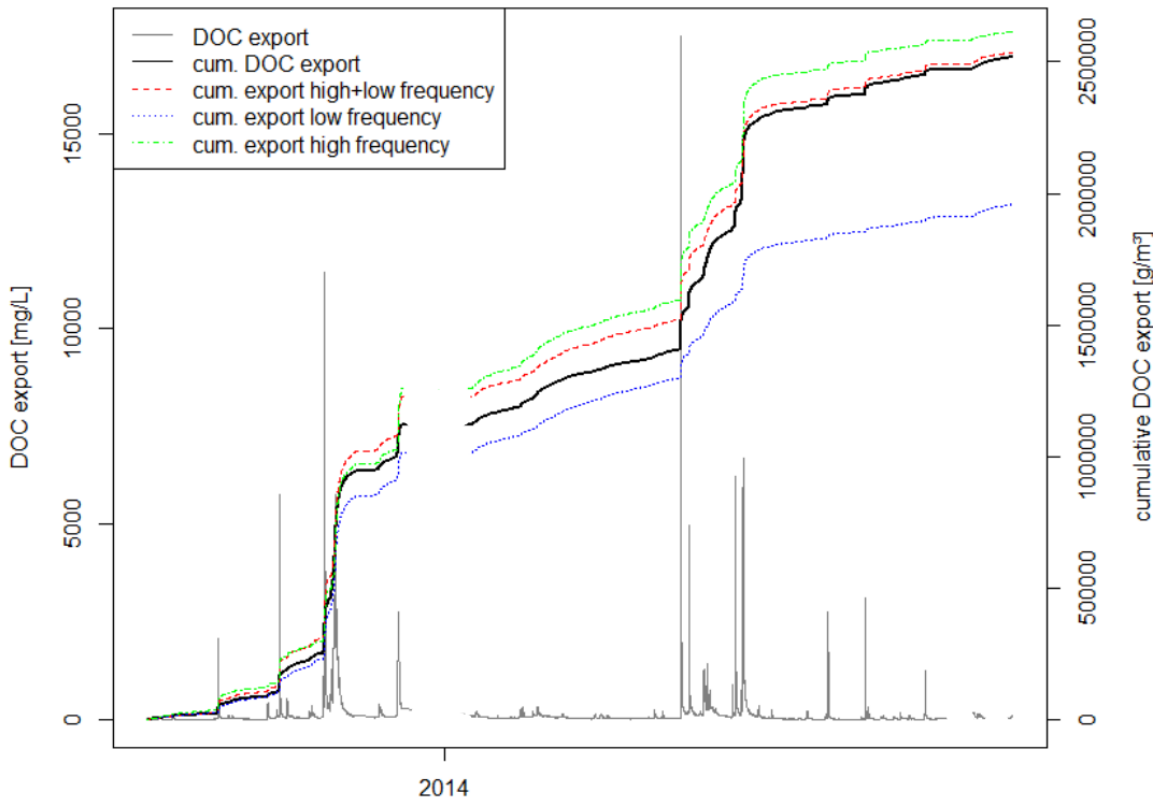
1.2- Referee #2 recommends adding a section about the meaning and benefit of the high frequency DOC monitoring in comparison to lower frequent monitoring.

We believe an assessment about the necessity and potential of "really" high frequency measurements will highlight the findings of our study and sufficiently demarcate new findings. Within one year, DOC concentration and quality dynamics fluctuate on event and seasonal scale. Our model showed that seasonal scale drivers alone (30 d and 60 d) are able to explain the same amount of variability than hydrological event-scale drivers (≤ 5d). However, it is the superposition of both which provides the more complete information to explain DOC concentration and quality dynamics throughout the year. High frequency measurements can integrate both, the high frequent part but also by (different aggregation forms) the lower frequent part of DOC variability. As presented in this paper, one can determine the optimal frequency of the low and high frequent variations, all together necessary to explain most of the DOC variance with least variables.

A comparison of our high frequency study with a low frequency study from Köhler et al. (2009) concretizes the benefit from high frequency measurements: The frequency used in our model was hourly values (~17,000 values in ~ 1.5 years) whereas Köhler et al. (2009) took 470 stream water samples in 14 years based on Köhler et al. (2008). Therefore the variance which needs to be explained shifts from a focus on seasonality and interanual variations towards high frequent fluctuations on top of the seasonal shifts. Furthermore, Köhler did not analyze the factors which are responsible for the shifts between the snow covered, melting and snow free period models. We continuously modeled discharge events throughout the whole year, as it turned out that it is exactly these shifts which could be represented by interaction of seasonal and event type predictors and they are important to understand DOC mobilization dynamics in a more holistic way through several seasons. Therefore, event based variance is needed to get better ideas of the explicit source zone activation of DOC. This frequency is in the scale of minutes to several hours.

A comparison of our high frequency and low frequency parts of our model concretizes the benefit from high frequency measurements: The Figure below shows the cumulative DOC export when just using low frequency measurements (DNT_{30} + AI_{60}+DNT_{30}xAI_{60}), high frequency measurements (Q_{hf} + Q_b+Q_{hf}xQ_b) or both, high and low frequency measurements. NSE of DOC export was 0.998, 0.979 and 0.783 for the "high+ low frequency", high frequency and low frequency, respectively indicating that low frequency measurements alone are not able to explain DOC export as adequate as the higher frequencies and its combination. The different export behavior of low and high frequent DOC modeling gets most pronounced during events (see Figure below).

The discussion and Figure will be analogously implemented in the manuscript and SI, respectively.



2- Title, aim and hypothesis (introduction) of the paper are too general.

We agree to reorganize the introduction (c.f. also Referee#3, R3GC1 and #4 R4GC1). The critique that a clear hypothesis is lacking implies the valuable suggestion to add a crisply formulated hypothesis, and we will endeavor to formulate one.

3- It seems that the authors cannot really decide if this is an eco-hydrochemical or a statistical-hydrological study.

We argue that no clear separation should be made between eco-hydrochemical and a statistical-hydrological study at such high frequency. We think both approaches are important and interacting during different hydroclimatic situations throughout the year, if viewed at high frequency.

4- The data could be used for something else

Obviously, with such a dataset there are plenty different questions to analyze. Yet we think in terms of readability, it is important to not lose the focus here. This is also why we decided to keep the biogeochemical discussion section as well as sensitivity analyses brief. Note that the data set is freely available and may be used by others (see section Data availability).

References cited in response to Reviewer #2

Köhler, S. J., Buffam, I., Laudon, H., and Bishop, K. H.: Climate's control of intra-annual and interannual variability of total organic carbon concentration and flux in two contrasting boreal landscape elements, Journal of Geophysical Research, 113, doi:10.1029/2007jg000629, 2008.
Köhler, S. J., Buffam, I., Seibert, J., Bishop, K. H., and Laudon, H.: Dynamics of stream water TOC concentrations in a boreal headwater catchment: Controlling factors and implications for climate scenarios, Journal of Hydrology, 373, 44-56, doi:10.1016/j.jhydrol.2009.04.012, 2009.