Interactive comment on "How runoff components affect the export of DOC and nitrate: a long-term and high-frequency analysis" by Michael P. Schwab et al.

Anonymous Referee #3

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Overview: Recent technological developments have enabled watershed researchers to monitor important biogeochemicals at high frequency for long periods. Sensors that measure both carbon and nitrate are uniquely suited to study the coupling of nitrogen and carbon cycles across varying temporal scales. The authors present a highfrequency, multi-year data set of nitrate and dissolved organic concentration over a range of hydrological and climatological conditions in a forested watershed. The authors leverage this high density dataset to examine rain-fall runoff responses of nitrate and DOC over varying climatological conditions. The authors suggest that antecedent moisture conditions, and as a result, groundwater levels, drives the relative fluxes of nitrate and DOC form the basin.

General comments: This study was well conceived and the results are clearly presented. However, several elements of the manuscript need attention before this study warrants publication.

1. Further, claims that seasonal differences in nitrate/doc fluxes were observed, are not clearly supported by the data presented in this manuscript.

Rather, initial dryness is the direct driver. Consider including data that clearly links the occurrence of preceding dry conditions to season over a longer period of time (longer than two years) to support the seasonal link to hydrologic conditions over the period of this study.

We thank the reviewer for the constructive comments. Indeed, initial dryness is the direct driver for differences in nitrate/doc fluxes through differences in rainfall-runoff processes. In the Weierbach catchment, dryness is generally linked to the growing season. We can proof that with time series of several years of discharge, groundwater and soil moisture. We will either present those time series in the revised manuscript or refer to already published articles about the Weierbach catchment showing these effects.

However, the pattern of dry=growing season, wet=dormant season is not always true. In some years some exceptions existed. We should therefore be more careful when talking about seasonal differences. We will consider that in the revised manuscript.

2. The authors fail to put the implications of the study- that “dry”/”reduced wetness” antecedent conditions results in larger fluxes in nitrate to the stream-into a larger context.

Larger context: We can discuss the implication of climate change to the nitrate export in the Weierbach catchment and in other catchments that behave similar to the Weierbach catchment (catchments with double peak behavior that depend on the initial wetness or catchments where subsurface stormflow is existing but not materialized as a second peak).

3. Consider removing “long-term”, as data collected for less than three years hardly justifies the use of this term.

In the context of high-frequency monitoring we consider two years as being long-term measurements. Conventional high-frequency sampling approaches (e.g. with autosamplers) are generally restricted to much shorter time periods of several events. Thus we want to stick to our terminology if the editor supports it.

4. The authors should consider using an outside editing service, given the occurrence of several awkward statements throughout the text (e.g. Pg 2, Line 5; Pg.3 lines 28-30; Pg 12, lines 10-13). We will improve the language quality of the manuscript.

Specific comments: Abstract: Pg 1 Line 11: Define “dry”, as this definition is critical in the interpretation of the results as well as applying the findings to other locales and placing the implications of this study into a larger context.

It is difficult to exactly define “dry” as it is a relative term. Dry enough that no second discharge peaks occur. There is an ongoing debate about the dryness threshold for second peaks in the Weierbach catchment. In figure 4 it is possible to compare discharge and the periods with and without second peaks. It might be useful to include groundwater levels and soil moisture content time series.

Introduction: Well cited, however, consider adding Pellerin et al., given the similarity in use of continuous DOC and nitrate sensors to document varying biogechemical yield over different hydrological conditions in a forested watershed.

We will include this article in the introduction.

Methods: I was puzzled as to how the probability density plots were developed, and the source of the data. Please explain in detail which if not all storms were considered and how these distribution plots were generated/modeled.

We will better explain the methods that we used for the probability density plots. There was not modeling involved. We used the entire 2 year time series and divided it into periods with first peaks,

second peaks, baseflow and also into classes of different discharge amounts and derived the probability density plots using R.

The deployment techniques should be more clearly documented to ease duplication of the study. Was the approach modeled after the used in another study? If so please cite. For example, one important aspect is how the sensor cleaned (Birgand et al., 2016, Etheridge et al., 2013)? Pg 5, line 6-7.

We will improve the description of the deployment technique. The sensor was manually cleaned every two weeks with a brush and a detergent that was provided by the manufacturer. Every 3 hours, the sensor was cleaned with air pressure.

This was not modeled after another study.

What was the typical (or max) holding time before analysis of discrete samples?

The samples were filtered and cooled the same day they were taken. We also tried to use autosamplers that were emptied weekly. For nitrate, the samples from the autosamplers were not usable, for DOC it was possible to include the samples.

Results: Consider moving Figure 1 to supplemental material. Characterize the model fits and explain or speculate when/why the outliers tended to occur, especially high residuals for DOC in late 2015.

We guess that the reviewer is referring to figure 2 and not figure 1. We will consider removing figure 2 to supplemental material and try to explain or speculate when the outliers occurred. However, since the other 2 reviewers were quite keen on the results of this figure, we have to balance all suggestions

Placing discrete sample data on the time series Figure 4, would help interpret the limitation of this measurement strategy, i.e. non-linearity due to fouling, light blockage, high turbidity, etc.

There is no pattern visible when displaying the discrete samples in the time series of figure 4. The Weierbach catchment was very suitable for the use of the spectrometer. Due to the low nutrient content, disturbance by biofilm was almost never a problem and the turbidity was generally low.

Please explain the DOC/nitrate data gaps in the summers of 2014/2015.Are these gaps a result of sensor limitations, or were the data otherwise removed? Also, what is the presumed influence of these missing data on cumulative DOC/NO3 export presented in Figure 10.

The gaps in summer 2014 were rather short and were caused by a failure of the sensor due to a cut in power supply. The gaps in summer 2015 were caused by the fact that the stream was nearly dry. No discharge was in the stream for several weeks. This is a natural effect and cannot be considered as missing data but as 0 values.

Figures 3, panel b and Figure 4, panel e and Figure 6, panels d, h, nitrate trace is almost illegible given the color selection. Consider a darker color for the trace and y-axis font.

We will adapt the color.

Figure 4 Justify the presentation of was daily mean values rather than another descriptive statistic (mean,max, etc).

We wanted to show how the variables behave over the 2 years – general behavior like recession periods, periods with high discharge/concentration. Therefore we considered the daily mean as the best way to display the variables in an averaged way.

Pg 9, line3: If the data is sampled to daily mean, how are sub-daily peaks resolved? Pg 11, line 3: replace remarkable to “notable” or equivalent.

Indeed, this is misleading. The subdaily peaks are not visible in figure 4.

Pg.11, Line 3-5/Figure 6. Do the authors speculate on the mechanism for a steady decline/recession in DOC, despite the rise in discharge during second peak?

We do not understand what the reviewer is intending to express.

Pg 12, lines 10-13: be specific about which end members

We will be more specific about that

Consider replacing figure 8, which is unclear and messy and rather plot a few select storms that illustrate hysteresis loops.

We believe that figure 8 contains relevant information. We will try to do it in a less messy way or using a second figure showing individual events

Pg 12, line 18. Change “increasing” to “variable”

Ok.

Pg 13 Lines 10-13.More detail needed here, e.g. what direction were hysteresis loops, for example?

We will provide more details. However, we did not do a detailed analysis of the hysteresis loops. This could be a completely new study.

Discussion: Pg 16, lines 5-7.Citation suggested here instead of personal experience not included in this study.

ok

Pg 16, line 29-30.Where is the evidence of a rise on groundwater table to support this claim?

We will provide some references.

Pg 17, line 26.Consider changing “concur to the” to “suggests that”

ok