Anonymous Referee #1

This manuscript reports the use of high frequency measurement of DOC and nitrate using UV VIS spectrophotometer in a forested headwater catchment, Weierbach. The scope of the manuscript is relevant to HESS and presents on the use of relatively new tools –high frequency, automated sensor data to understand the dynamics of DOC and nitrate in the catchment. Rigorous evaluation of these emerging technologies is a pressing need. The aim of this manuscript was to demonstrate that these high frequency automated sensor data add value to understanding event and seasonal dynamics of DOC and nitrate in this catchment. Indeed, the manuscript reaches a confirmatory conclusion that the sensors add value in detecting event peaks and seasonal trends. However, at the end of the manuscript, it is not clear to the reader how transferable these methods are to other catchments; the methods and limitations of the sensors remain poorly articulated in this manuscript.

We thank the reviewer for his constructive comments on this manuscript.

The main objective of the paper was on the export of DOC and nitrate and its relationship with to rainfall-runoff processes. Yet, we acknowledge that more information about the limitations of the sensor is beneficial. We will do that in the revised manuscript in more detail.

In particular, a number of concerns are raised concerning detail of the methods and assumptions. These concerns include 1) details on methods for filtering samples and calibration of sensor seemed inadequate to reproduce,

We will improve that in our manuscript.

2) the adequacy of use of linear regression for calibrating sensor data to manual grab samples

We followed the instructions of the manufacturer of the spectrometer that advices a linear calibration. The results shown in Figure 2 support our decision to use a linear regression.

and well as 3) use of non-conservative tracers as end members to attribute to sourcing.

We are aware of the limitations of DOC and nitrate as tracers – therefore we do not use them for classical mixing calculations. The information that we use for the sources does not only come from DOC and nitrate, but is also based on previous work in the catchment by other authors. We will discuss the available Weierbach literature on this topic in more detail. However, the main goal of this manuscript is on export of DOC and nitrate and not on sources.

Most studies in the literature use concentrations obtained from grab samples as the known concentration values (X axis) and sensor data as the response variable (Y axis). Uncertainty in both the x and y as well as self-correlations (see Worrall et al. 2015 should be given consideration and

other models (possibly orthogonal regression or other models (see Vaughan et al. 2017)) should be adopted to address uncertainty in x and y values.

We could change the x- and y values, but this will not considerably alter the results on the correlation between the two variables. Self-correlations should not be an issue, as the water samples were taken at bi-weekly interval. Since we used the regression to test how well the spectrolyser can describe lab samples, we do not see the necessity to consider the uncertainty of the measurements.

Finally, this manuscript is not as fluent as it could be, and it could be more concise. There were numerous grammatical and tense agreement issues as well as awkward statements that made accessing the results and discussion a bit challenging. I believe that there could be better use of figures and some figures could be combined and/or possibly put into supplemental materials.

We will improve this in the revised version.

Standard hydrograph separation techniques should be used or better referenced

We will improve the reference.

Adequate referencing of description of prior research in the Weierbach is needed in the introduction to understand the research gap but also the rationale behind single and double peak separation. Some of these studies are cited in the discussion but this discussion comes too late. Finally, putting these data into context of other studies is desperately needed to improve the manuscript.

We will improve that in the manuscript. However, previous research is somewhat ambiguous about the underlying processes generating the first and second peaks are.

Specific comments

Page 4, line 1-5: Hypotheses are a bit awkward; what is meant by individual concentration signals?

We hypothesis, that the response of DOC and nitrate concentrations during rainfall-runoff events help us to identify the relevant flow paths in the catchment.

Page 5, line 4: Need more details on global calibration provided by manufacturer.

The manufacturer does not provide more details on the global calibration. However, we will better explain what is meant by the term global calibration.

Page 5, line 7: filter through what kind of filter? Need more details here. And were the samples run for NPOC or TC-TIC? Then you are sparging the samples?

We will provide more details on that.

Page 5, line 10: if only using nitrate samples, how did you cover the full range of nitrate concentrations at high discharges?

The maximum concentration that we collected with the grab samples was 1.2 mg/l. This covered the vast majority of the measured nitrate concentration. Indeed, we did not cover all the whole concentration range with our grab samples. In some rare cases, the measured nitrate concentration reached almost 2 mg/l.

Page 5, lines 10-15: Most studies found in the literature (e.g. Vaughan et al. 2017) use concentrations obtained from grab samples as the known concentration values (X axis) and sensor data as the response variable (Y axis). This is the reverse of what has been done in Figure 2. Uncertainty in both the x and y as well as selfcorrelations (see Worrall et al. 2015 should be given consideration and other models (possibly orthogonal regression or other models (see Vaughan et al. 2017)) should be adopted to address uncertainty in x and y values. Were the residuals of the line regression examined to determine if they are normally distributed? They appear at bit heteroscedastic, especially for DOC.

see comment and response above

Finally, this section is awkward and could use a rewrite. Here the manuscript starts to switch back and forth. For example, it should read DOC concentrations of grab samples "were" linearly correlated to stay consistent with past tense used throughout paragraph.

We will improve the language in the revised manuscript.

Page7, line 3: More specifics on rating curve are needed. Are these published rating curves or derived from other publications. If so, please reference or provide more details.

This is a longterm gauging station operated by LIST. The rating curve is based on continuous water pressure (water level) measurements and salt dilution discharge measurements. If we had used discharge data from national gauging sites, we could also not provide the required details as they are not available in most cases.

Page 7, line 4-19: This section needs more referencing to prior research in the catchment as well as referencing for hydrograph separation. If these rainfall runoff characteristics are not reported elsewhere (but it seems like they are based on discussion), these are results and should go into the results section. Also, referencing to standard hydrograph separation or using accepted hydrograph separation would add utility to this paper.

We will explain that in a better way in the revised manuscript.

Page 7, line 24: Figure 3 could be perhaps moved to supplemental if adequate referencing is use.

We believe that figure 3 is of importance to explain the methods.

Page 12, line 4: here the mansuscript using DOC and nitrate endmembers and infers sources without providing additional conservative tracers to determine sources. Did you collect or analyze samples for other conservative tracers for both hydrograph separation and end member mixing analysis. Using a conservative tracer is a central assumption of these analyses (see Barthold et al. (2011)) such that the validity of interpretation of sourcing in this manuscript is questions without additional evidence supporting this conclusion.

Although we are not completely sure about the sources, we do not agree that we necessarily need end-member mixing analysis to determine the sources. We are referring to Glaser et al. (2016), that identified sources based on a modeling approach.

Page 12, line 16. Suggest change paragraph to past tense.

ok

Page 13, line 10, relevant? Suggest a different word choice, suggest substantial

ok

Page 16, line 5: this line refers to other studies and limitation of the sensors. Can you reference to these studies? Perhaps this would be a better method paper if these data were also reported to show the limitation of the sensors?

We will improve the references. However, some of the knowledge about the limitation of the sensor is based on oral communication with other research groups that have use the same sensor. Besides, we do not consider the manuscript as being a method paper.

Page 16, line 8-19: This seems slightly redundant to methods. Perhaps include this section or shortened version thereof in methods. Can you reference other studies that have done this?

We believe that the methods should be discussed in the discussion section. We will improve the referencing.

Page 16, line 20-34. Again, tenses are switched in the paragraph. I'd suggest keeping in past tense.

We will improve that.

Page 17, line 4, suggest delete "have"

ok

Page 17, line 5: awkward sentenceâ˘Aˇ Tsuggest revise

ok

Page 17, line 12 and starting line 20. Here you refer to other studies that have been conducted in the catchment identifying the single and double peaks. This is a strong

rationale for your study, approach, and analysis. I think some of this needs to come up to the introduction or methods.

We will try to find a better balance between introduction, methods and discussion.

Page 17, line 32: Suggest delete second sentence starting "By only: : :" repeat of same sentence.

ok

Figures: Figure 8 and 9 could be combined into one figure with different panels.

We will have a look if that is possible and improve the figures.

Technical corrections: Page 4, Line 8: spell out masl the first time

ok

Page 4, line 9 and 10: italicize Fagus sulvatica and Picea abies

ok

Page 4, Line 10: delete period (.) before (Glaser et al., 2016)

ok

Page 4, line 13: Suggest change "The" to "A" and change "is causing: to "results in"

ok

Page 6, line 3, suggest delete "for" before throughfall

ok

Page 6, line 7, suggest add "(Figure 1)" after location

ok

Page 9, line 6: delete "the" before nitrate and change to "had" to "were" and delete "levels".

ok

Page 9, line 7: Suggest sodify sentence to read "Nitrate concentrations decreased during recession periods, as observed in spring 2014 and 2015: : :

ok

Page 11, line 5: suggest change "reaction" to "response" because you can not infer reaction.

ok

Page 16, line 2: delete "have"

ok

References referred to within comments:

Vaughan, M. C. H., et al. (2017), High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality, Water Resour. Res., 53, 5345–5363,

doi:10.1002/2017WR020491.

Worrall, F., Burt, T. P. & Howden, N. J. K. The problem of self-correlation in fluvial flux data – The case of nitrate flux from UK rivers. Journal of Hydrology 530, 328–335 (2015).

Barthold, F. K., C. Tyralla, K. Schneider, K. B. Vaché, H.-G. Frede, and L. Breuer (2011), How many tracers do we need for end member mixing analysis (EMMA)? A sensitivity analysis, Water Resour. Res., 47, W08519, doi:10.1029/2011WR010604.