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 #2

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Manuscript presents results of intensive, 2-year high-frequency monitoring campaign of streamwater DOC and nitrate in a forested catchment in Luxembourg by using UV-Vis spectrometer, which is relatively new and emerging technology in field monitoring systems. Credible assessments of UV-Vis spectrometer advantages and limitations in different hydrological conditions is undoubtedly of high value. By obtaining high-frequency data, authors aimed to identify relevant flow paths in the catchment which regulate individual DOC and nitrate concentration signs.

I find the manuscript in line with aims and scope of HESS. Generally, the paper is well written, however there here are some grammatical issues and weird statements that

made it somewhat difficult to follow the link between the results and the discussion section. The discussion section needs to be improved, related especially to other studies at the same study site which also aimed to identify preferential flow paths during different hydrological conditions. Details are provided bellow.

General comments:

The introduction section provides a good overview of the governing biogeochemical and hydrological processes regulating DOC and nitrate exports.

While mentioning the benefits of high frequency monitoring techniques it would be worth noting that the high frequency water quality measurement are valuable especially in small catchments where hydrological mechanisms usually respond to rainfall inputs very quickly and there is usually a strong interconnection between soil biogeochemical conditions (usually the main controlling factors of DOC and nitrate mobilization or retention) and hydrological processes.

The comparison of grab water sample concentration and in-situ concentrations of DOC and nitrate are very informative. I would suggest the authors to point out in conclusions (related to their experiences) how they suggest to combine UV-Vis measurements with grab water samples. I would also suggest to show 1:1 line in fig. 2a and 2c which would illustrate the agreement between the two datasets. Namely, in the case of nitrate, the regression line is close to 1:1 line whereas in the case of DOC there seems to be quite a discrepancy especially for high DOC concentrations (regardless of the fact that linear correlation is good) which indicates that one should be careful when using UV-Vis concentrations without additional grab sampling control.

What is the proportion (e.g. in %) of the total annual DOC and nitrate flux that is exported by the baseflow and by events as defined in the study? Overall, I agree with the authors opinion that the proposed methodology for separating the baseflow DOC and nitrate from events fluxes is simple and could be used elsewhere. However, the method is in principle based on graphical baseflow separation techniques and is not

something new.

In the Discussion section, the authors refer to other studies at the same experimental catchment. But there is relatively poor discussion of the results in relation to process understanding. I miss more tangible discussion on how the results of the DOC and nitrate fit into other studies mentioned in the discussion that were done at the same study site. Do they agree well or do the show that some of the explanations proposed in other studies are not in line with the results shown here.

Another thing that in my opinion strongly influences preferential flow paths (such as flow paths near the surface or in top soils) is the influence of antecedent wetness, rainfall abundancy and intensity in relation to soli infiltration capacity. Was anything done in this direction? Have authors of this or some other studies in the experimental catchment observed some "boundary conditions" which could be related to the solute concentrations behavior in wet periods and so formation of so called "second peaks"?

Specific comments:

Page 4, lines 16-18: What are the technical characteristics of the UV-Vis spectrometer in terms of the DOC and nitrate concentrations (min, max concentration, detection limits, accuracy, etc.).

Page 7, line 12: The rainfall amount of 5 mm seems rather small in order to be considered as a rainfall events. Any additional comment on rainfall losses and rainfall interception, average monthly evapotranspiration from the forested catchment?

Page 7, lines 9-12: The sentence is unclear and need to be rewritten.

Page 7, line 13: I suggest changing: . . .with a minimum 5 h time gap. . .

Figure 5 caption: Does Fig. 5 really show discharge volumes, units are in m3/s? Page 9, line 14: I suggest changing the statement to: . . .similarly increased during first and second peaks.

Page 11, line 5: Authors mention increase of nitrate concentration during second peak. Looking at Fig. 6d, this increase is very small (from approx. 0.8 mg/l (pre-event concentration) to 0.9-1.0 mg/l. I wonder how can this "slight" increase in nitrate concentration be explained in view of UV-Vis spectrometer accuracy?

Page 14, line 2: Is the comment on the results related to Figs. 10 c and d?

Page 16, lines 1-2: I believe the discussion on the goodness-of-fit between laboratory DOC concentrations ad in-situ UV-Vis concentrations should be further discussed accosting to my comment provided above.

Page 16, lines 5-7: Please add some references (if available) while mentioning potential problems with the use of measuring equipment in environmental settings different than the presented study site.

Page 16, line 2: Was the fit between UV-Vis and lab measurement really good (seem my previous comment regarding DOC measurements)?

Page 16, line 22-23: Are there any field evidences that preferential overland or near surface flow paths really occur at the studied catchment?

Page 16, line 24: The flushing hypothesis was not originally proposed by Weiler and McDonnell (2006), one of the first that proposed the flushing hypothesis were Hornberger et al. (1994). Therefore I suggest changing the order of the listed references.

Page 17, line 9-12: I believe that vice-versa is also true. So the export behavior of DOC or nitrate (or maybe some other dissolved substances) can be very helpful for explaining various runoff components.

Page 17, Line 34: What is meant by "hot moments"?

Page 18, lines 15 – 18: Last paragraph of the Conclusion section seems rather general and is in my view not in line with the main theme of the study.

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