Anonymous Referee #2

Received and published: 5 September 2017

Manuscript presents results of intensive, 2-year high-frequency monitoring campaign of streamwater DOC and nitrate in a forested catchment in Luxembourg by using UVVis 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 highfrequency 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.

We appreciate the constructive comments made by the reviewer. Referring to the value for small catchments is a good suggestion that we will include in the manuscript.

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 withgrab water samples.

We can include that in the revised manuscript. It is of importance to take grab samples at different flow stages and during first and second peaks and during base flow conditions.

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.

Showing a 1:1 line might be misleading for the reader, as we did not expect to have a 1:1 agreement. An offset and a slope different from 1 has to be expected when comparing the in-situ spectrometer measurements with grab samples that are analyzed in the lab (the manufacturer of the spectrometer also points this out in the spectrometer manual). Stream water has a different background matrix compared to calibration standards that are used in the lab. Therefore it is essential, to take grab samples directly in the stream to compare them with the spectrometer measurements. We can point this out more clearly in the manuscript.

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?

This is roughly visible in figure 10. We will include the exact percentages in the text.

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.

Indeed, this technique is not something new. We did not intend to introduce a new technique. We tried to keep it as simple and reproducible as possible.

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.

We will improve this section.

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”?

We will improve the discussion related to other studies in the catchment.

We have a high porosity and hydraulic conductivity in the catchment – especially in the periglacial slope deposits (Glaser et al. 2016, Jackisch et al. 2016). The second peaks are most likely controlled

by a storage threshold (Martinez-Carreras et. Al 2016). The rainfall intensity is not a controlling factor (Scaini et al. 2016).

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.).

We will include that in the revised manuscript.

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?

A rainfall event of 5mm is already causing a discharge peak in the stream. This is the reason why we chose 5mm as the lower limit for a rainfall event.

We will cite Pfister et al. 2017 for the interception and evapotranspiration

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

We will rewrite this sentence

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

This is a good suggestion. We will change that.

Figure 5 caption: Does Fig. 5 really show discharge volumes, units are in m3/s?

Fig.5 shows the probability density plots of DOC and nitrate. In Fig. 5 c and d, the probability density plots are grouped in different discharge classes and the discharge has units of l/s

Page9, line 14: I suggest changing the statement to: : : :similarly increased during first and second peaks.

This is a good suggestion. We will change this sentence.

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?

For some second peaks we took grab samples that were analyzed in the lab. Those results verified the UV-Vis spectrometer measurements.

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

Indeed, we need to clarify more specifically which comment is related to which Figure

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.

An offset and a slope different from 1 have to be expected when comparing the in-situ spectrometer measurements with grab samples that are analyzed in the lab (the manufacturer of the spectrometer also points this out in the spectrometer manual). Stream water has a different background matrix compared to calibration standards that are used in the lab. Therefore it is essential, to take grab samples directly in the stream to compare them with the spectrometer measurements. We can point this out clearer in the manuscript.

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.

We will check for some reference. This sentence is mainly based on oral communication with other researchers that used the same spectrometer and our own experience in two different catchments (those studies are not yet published).

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

See our answer to your previous comment. We consider our linear regression as good. We cannot expect a 1:1 line.

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

Hortonian overland flow has not been observed in the catchment. We have near surface flow from the hillslopes and overland flow from saturated areas. A physically based modeling approach by Glaser et al. 2016 confirmed this. Additional confirmation comes from the reaction of the soil moisture sensors in the catchments (not yet published)

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.

This is a good advice. We will change this accordingly.

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.

Indeed, we fully agree with this comment. Nevertheless, we decided that the focus of the manuscript will be: runoff components explaining export behavior. But we will add here a statement on the fact that vice-versa is also true.

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

We are referring to Krause et al. (2015) who used to expression “hot moments”. We introduced this expression on page 3, line 5-7: Catchments generally exhibit a pulsed and highly nonlinear behavior 5

for flow and solute transport. Consequently, monitoring protocols that are too coarse are likely to miss important information during those pulses or so-called hot moments (Krause et al., 2015).

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.

Indeed, this is not a conclusion. It is rather an outlook. We will change that accordingly. We will change the title of section 5 to Conclusions and Outlook.

.