Anonymous Referee #2

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The study deals with an original time scale of dissolved organic matter variations as diel cycles have been less studied than event responses or seasonal patterns and long-term trends. DOM is described via 2 parameters: DOC concentration and its properties through SUVA index as a proxy of the aromaticity. The studied hypothesis is also original and mainly supported by a previous work by Schwab et al in 2016 that compared the respective role of evapotranspiration and riparian inflow changes (due to temperature-driven viscosity changes) on diel fluctuations of stream flow. For riparian GW temperature, DOC stream concentration and corresponding SUVA-254, diel cycles are in phase over the whole time series with daily max occurring in the afternoon (between 2pm and 6 pm). Amplitude of the cycles is minimal in winter. Amplitude of riparian shallow groundwater and DOC concentration cycles is relatively constant during the rest of the period. Amplitude of SUVA-254 cycles is high in spring (at the end of the dormant period) and small in summer (middle of the growing period). For discharge, diel cycles change in phase between the dormant season (morning max) and the growing season (afternoon max) and disappear during winter (start of the dormant period). Amplitude of the discharge diel cycles seems higher in spring (end of dormant period) than in the growing period. From these observations the authors suggest that the variations of riparian flow (due to water viscosity variations with the temperature) are the major control of DOM diel cycles. I found the manuscript well written with clear messages. The analyses and supporting data set are valuable. However I found the conclusion on the respective hypothesized controlling processes (in-stream biology versus riparian flow conductivity) quite hasty and maybe too categorical regarding what is effectively observed and demonstrated. The results support the hypothesis but some questions remain and interpretation should remain more careful in my point of view (please see specific comments).

We thank the reviewer for her/his supportive assessment.

Detailed comments and questions

Introduction

p.2 line 3: Do you have an idea of the relative concentration levels of DOC and DIC in the study stream?

We have some measurements of HCO_3^- which is the biggest component of DIC in the stream. HCO_3^- values in the stream are generally around 0.1 meq/l.

p.5 line 5 indeed photodegradation has been shown significant on highly brown DOM coming from peatlands (references cited by the authors). I am not sure that it has been reported as important on forested-derived DOM

Indeed, the references cited in the manuscript are from peatlands. We will clarify that photodegradation has been shown significant on DOM coming from peatlands and that we have a forest catchment without peatlands.

Methods

p.4 lines 5-6 This point may be an output from previous research conducted on this well-studied catchment but how the significance of riparian zone contribution has been demonstrated? And quantifications if available would be useful

The flow from the riparian zone to the stream is continuously monitored by thermal cameras and the contribution from different sections of the riparian zone to discharge is measured by dense discharge measurements (salt dilution method) along the stream. This is still work in progress as part of two PhD projects. We know that the hydraulic gradient is towards the stream and that our measurement location is constantly saturated.

p. 4 lines 11-13 provide information about average annual pattern of flow. Similar information about the annual behaviour of DOC concentration and SUVA-254 would be useful to understand the catchment: from Fig. 2 it seems that mean DOC and mean SUVA-254 are maximal in summer low-flow period (increase from Feb to Aug 2014 and from Feb to June 2015). If riparian subsurface flow is the main source of aromatic DOC, I expected this contribution being higher in high flow periods and lower in low flow periods when catchment saturation decreases and therefore minimal DOC and SUVA values in this low flow period

This data is clearly interesting, yet we want to focus, within this manuscript, on diel fluctuations in this manuscript. The reviewer's observations from Fig. 2 are right. We addressed this in another manuscript that is currently under review and that focuses on the event and annual time scale

(Schwab et al., 2017). After reaching a storage threshold during wet conditions (and therefore during high flows) an additional runoff process is playing an important role: subsurface flow / shallow groundwater flow with low DOC and SUVA-254 values.

p. 4 lines 16-17 I think there is an error: unless I am mistaken a variation of 5_C leads to a viscosity change of 2% only. Using Eq. 3 from Schwab et al. (2016):

_(T_)=e^(3.7188+578.919/(137.546+T_))

If T_ is the temperature in Kelvin degree (as said "T in K"). I think that the 12 to 15% of change of viscosity have been deduced by applying the formula with Temp in Celsius degree, right?

As brief example, for T=15 Celsius deg (288 Kelvin deg) I found Nu=164 Pa.s

for T=20 Celsius deg (293 Kelvin deg) the formula gives Nu=161 = 164 -2%

Yes, there is a mistake in (Schwab et al., 2016). Two minus signs are missing. The equation should be (with T in Kelvin):

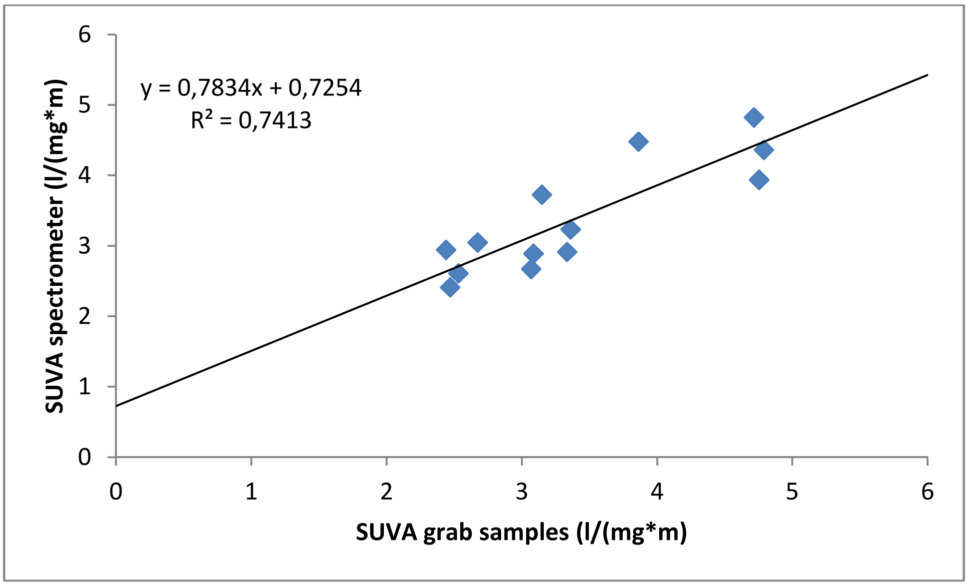
(Nu)=e^(-3.7188+578.919/(-137.546+T))

http://ddbonline.ddbst.de/VogelCalculation/VogelCalculationCGI.exe

With the corrected equation (we performed the calculations based on the correct equation in both papers, but reported the equation not correctly in the WRR paper), a temperature change of 5 °C leads to viscosity changes of 12 % to 15%.

p. 4 lines26-31: Did you compare also the absorbance values at 254 nm from spectro::
lyser and from the lab? (Since Absorbance values are available for the endmembers
- p4 lines 33-34- I suppose that some exist for the stream as well: : :?)

Some grab samples from the stream were analyzed for absorbance 254 nm in the lab. In the figure below we compared the grab samples with the in-situ spectrometer values.



p. 5 lines 1-5 sampling points for the end-members, as well as the stream station and the temperature monitoring point should be located on a map of the site.

We will include a map with the sampling and measurement locations

p. 5 line 3 Regarding the method to sample riparian water, I wonder if the riparian area was effectively fully saturated?

Yes, at the sampling location, the riparian area was fully saturated during the sampling period

On another hand, viscosity of riparian water is calculated from a temperature sensor located in the riparian groundwater at 10 cm depth so I imagine that riparian groundwater remains shallower than those 10 cm depth?

The sampling was done in a saturated area.

Is the water table level in this specific zone monitored (that could help giving the local hydraulic gradient with the stream)?

Unfortunately, the water level was not monitored in this specific zone. Yet, we have TIR images from the area that show how GW enters the stream.

Is riparian water sampled at 6 different depths too or only at 10 cm? Do you observe any vertical variability of DOC and SUVA in this riparian zone as shown for soil water in Fig 5 b,d?

The riparian water was only sampled at 10cm depths.

Regarding Fig 5a, the DOC richness is finally much closer between riparian water and groundwater and low.

Riparian water is likely a mixture between groundwater and soil water components.

p.5 line 13 It is not clear in the following which analyses do use this smoothed SUVA time series (obtained from 3 hours moving window) or the raw time series: p. 5 line 25 "the original time series with the 15 min time intervals" is used to compute the distance to daily average

Indeed, this needs some clarification. The smoothed SUVA time series was used for all the following SUVA analysis and is considered as the original time series. We will clarify this in the revised manuscript.

Results

p.7 The difference in amplitude of diel discharge cycle between dormant and growing period is not characterized but amplitude of the discharge diel cycles seems higher in spring (end of dormant period) than in the growing period? Maybe a scale effect to due difference in base flow?

The diel discharge cycles can be explained by two counteracting processes. The viscosity effect is leading to maxima in the afternoon and evapotranspiration is leading to minima in the afternoon. The interplay between those two processes likely affects the diel amplitude of discharge. The viscosity effect is dominant during the dormant season (discharge maxima in the afternoon) and evapotranspiration is dominant during the growing season (discharge minima in the afternoon).

p. 7 Figure 2: It would help to represent dormant and growing periods on the graph by color or shadings or vertical lines for instance

We will improve this in the revised manuscript.

Figure 5: If possible with the scales, the corresponding values in stream water could be added in (a) and (c) to have in mind the relative position of stream between the end members

We will improve that

Discussion

p. 10 lines 5-9: Correlation between DOC and SUVA_254 fluctuations sounds consistent and I certainly agree with the authors on the value of SUVA_254 or such indices as proxy of DOM composition and properties. However, there is a point absolutely not discussed here: the fact that DOC concentration value is computed by the spectro::lyser algorithm using the absorbance value at 254 (or absorbance at 252 & 255nm). Other absorbance values are obviously included in this concentration estimate but the DOC and SUVA variables used here are somehow both functions of measured absorbance at 254 nm, so that their correlation is not fully surprising: : :At least I feel that it deserves a word in the discussion. See also my comment on (p. 4 lines26-31)

As the second reviewer mentioned, there is a correlation between absorbance at 254nm and DOC, as DOC is calculated (measurement method of the spectrometer) based on absorbance 254nm (AND absorbencies at other wavelengths). SUVA 254 is calculated as the absorbance at 254nm normalized by the DOC concentration (SUVA254 = A254/DOC). Consequently, an increase in SUVA254 is based on an increase in A254 that is larger than the increase in DOC concentration. Therefore on increase in SUVA254 is not (only) based on an increase of DOC in general but on an increase in more aromatic DOC.

We will include this into the discussion to clarify this point.

p. 10 lines 14-15 I feel the rejection of the first hypothesis arrives a little bit fast. The absence of in-stream processes is not fully demonstrated to my opinion. Microbial processes are numerous, here you assume DOC concentration increase due to in-stream production should exhibit a low aromaticity and therefore a low SUVA but i) biological processes that recycle the DOC are numerous enough to lead to complex antagonistic results; ii) keep in mind that SUVA is only a proxy of the complex composition of DOC; iii) and again that is this case SUVA is computed using absorbance properties only .

These are valid points. We will take them into consideration to weaken our statement and include the points i) to iii) into the discussion.

On the other hand, all the conclusions are based on relationships between DOC, SUVA and viscosity which is actually an interpretation of measured temperature variations. Therefore, what is established strictly speaking is that DOC and SUVA variations are correlated with temperature in riparian water isn't it? I wonder if the correlations would have been poorer using for instance stream temperature? And temperature is a factor control of viscosity but also many processes, biological processes, evapotranspiration:

Indeed, strictly speaking the DOC and SUVA variations are correlated with riparian water temperature. It is also true, that the temperature is controlling other processes. In (Schwab et al., 2016) we already analyzed the difference between viscosity and evapotranspiration. In this manuscript we show that the SUVA maxima are in the afternoon, which is a strong indication for terrestrial DOC input and not for biological processes that could have been affected by stream temperature variations.

If I didn't make a mistake on comment regarding (p. 4 lines 16-17) above, variations of 5_C would induce a change (in viscosity and thus also) in hydraulic conductivity of 2%, which is a very small change, and even if the 10-15% of variations are right, I wonder how significant it is on the flow from this area. If you had an estimate of the range of hydraulic conductivity and of the hydraulic gradient to stream (via measurement of groundwater level) this would help to understand the relative weight of such an increase of the viscosity?

As already explained above, the 10-15% variations are the correct values. Unfortunately, we cannot quantify to hydraulic gradient to the stream. Nevertheless, in our previous paper (Diel discharge cycles explained through viscosity fluctuations in riparian inflow (Schwab et al., 2016, Water Resources Research) we argued, that around 50% of the inflow to the stream are affected by viscosity fluctuations.

Finally there are still missing pieces of discussion:

(p. 8 & p. 9 lines 1-2) Correlation between DOC and SUVA daily variations are stronger during dormant period: why if their diel fluctuations have the same origin (riparian flow)? Would this be related to a change of riparian DOM composition? If so, such change would be visible on the end-members samples? Looking back at Fig 6, it appears to me that this difference is explained actually by stronger in-stream processes that would have during growing season comparable effects to viscosity fluctuations. So that seasonal processes would be also a dominant control, isn't it?

Indeed, we explain that difference by stronger in-stream processes during the growing season. As the viscosity effect / the terrestrial input is still stronger than the instream processes (still a peak in the afternoon), we considered the terrestrial input as the dominant control. The reviewer is right, that during the growing season, the instream processes are also an important (if you want a dominant control) control, but not the most dominant control. We will reconsider our wording. Also concerning on how we handle the first hypothesis.

p. 9 lines 10-11 If riparian water is responsible for diel increase of DOC stream concentration, I found it surprising that the DOC concentration in the riparian water is finally rather low compared to soil water in the hillslope

The water in the riparian zone seems to be a mixture of soil water and groundwater. The groundwater is entering the stream through the riparian zone, as the riverbed consists of relatively impermeable, solid, unweathered bedrock.

p. 11 lines 1-4 see my suggestion for Figure 5

We will include the reviewer's suggestion.

p. 11 lines 14-20 Schwab et al. (2016) concluded that Q fluctuations during dormant season was indeed resulting from viscosity changes resulting in variable riparian flow to stream, but in the growing season, the role of evapotranspiration fluctuations was dominant (leading to diel cycle inversion). The authors explain the fact that Q and DOC are not affected by the same processes because of the relative influence of those processes on the respective "sources" of water and DOC. ET controls Q cycle affecting the whole catchment storage while viscosity controls the DOC from riparian upper layers. So at the end, those stream signatures are integrating various catchment processes and disentangling those processes faces the same issue as distinguishing the processes that can control seasonal cycles on water quality. Maybe in further studies, it would be worth to try looking at some other parameters that could play the role of riparian flow tracers to support further the hypothesis.

We fully agree that this work also open new research avenues outlined by the reviewer.

p. 13 lines 5-14: this answers partially my comment on (p. 4 lines 11-13). However I found this seasonal pattern quite surprising. In many study, Hillslope subsurface flows merely active during wet conditions intercept the riparian area flushing somehow their upper soil layers rich in DOC leading to high DOC concentration (and more aromatic as well). During low flow, saturated area extension is decreased, and connection between those DOC sources and the stream can be interrupted. Flow is sustained mainly by groundwater which is poor in DOC so should lead to minimal DOC concentrations excepted if autochthonous production increases this DOC concentration. The proposed interpretation for Weierbach catchment should be discussed regarding general understanding that have been proposed elsewhere.

It would be interesting to have an idea of the importance of the variations we are looking at (as percentage of flow/concentration/SUVA mean value). I do not discuss the interest of the topic that has been scarcely studied so far but I think that keeping in mind the relative orders of magnitude of the studied phenomena sounds relevant

We see the reviewer's point and we will better explain the process understanding of the Weierbach catchment. Nevertheless, we do not want to go too much into detail, as this is the topic of a paper that is currently under review and that focuses on the event and season scale (Schwab et al., 2017). This manuscript here, should focus on diel fluctuations.

We will better explain the following aspect: The DOC and SUVA254 values in Figure 2 are daily mean values of days WITH diel fluctuations. This does NOT include days with rainfall-runoff events. During rainfall-runoff events with peaks in discharge, we clearly have DOC and SUVA254 peaks in the stream (coming from fast runoff components and having nothing to do with the viscosity effect), no matter if we are in the growing or the dormant season. The higher discharge during the dormant season shown in Figure 2 in combination with lower DOC and SUVA254 values can be explained by the fact, that during the dormant season, the wetness threshold is reached and the (shallow) groundwater (low DOC, low SUVA254) is connected to the stream.

Conclusion

p. 13 lines 26-29: I wonder if other tracers unrelated to carbon dynamics could be interesting for tracking independently the riparian flow for instance. I would also suggest the use of O2 probes to try catching indirect information on metabolic activity of the stream?

O_2 probes would have been very helpful for studying metabolic activity. Unfortunately, no O_2 probes were installed in the riparian area.

Citations

Schwab, M., Klaus, J., Pfister, L. and Weiler, M.: Diel discharge cycles explained through viscosity fluctuations in riparian inflow, Water Resour. Res., 52(11), 8744–8755, doi:10.1002/2016WR018626, 2016.

Schwab, M. P., Klaus, J., Pfister, L. and Weiler, M.: How runoff components affect the export of DOC and nitrate: a long-term and high-frequency analysis, Hydrol. Earth Syst. Sci. Discuss., 1–21, doi:10.5194/hess-2017-416, 2017.