Anonymous Referee #1

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General comments:

The paper analyses diel concentration dynamics of DOC in a headwater stream. The analysis explicitly addresses dry conditions and thus focuses on the internal controls of the system rather than external hydrological drivers such as snowmelt and rainfall. I think it has an important and general value to better understand stream concentrations dynamics and moreover to disentangle responses of external forcing and internal controls.

In this paper the authors argue that diel DOC concentration variability is driven by temperature-induced changes of hydraulic conductivity (via water viscosity) which leads to changes in the magnitude of groundwater discharge and the associated discharge of DOC and ultimately to variations of instream concentrations. Although the authors claim that this is the only mechanism that can explain the observed pattern, they do not provide enough evidence. I would like to challenge the interpretation by asking to perform a mixing analysis. Assume that all variations in discharge are driven by viscosity-induced discharge of groundwater (or water from the riparian zone if you like) what would be the DOC concentration in this water that explains the observed DOC concentrations in the stream. Do these concentrations match the observed DOC concentrations in the riparian zone? This would be a simple test to check the plausibility of the proposed mechanism. Moreover one could have a look at the concentrationdischarge relationships: From Figure 1 c and d I see a dilution pattern in DOC concentrations at multi-day timescales. Low discharge=High concentration which means that the load (C*Q) remains broadly constant, indicating a constant source.

This relationship does not hold for the diurnal discharge peaks, here we see increasing concentrations with increasing discharge - suggesting a temporarily dynamic source, potentially viscosity effects.

We realize that we have to clarify some important things in the manuscript to avoid misunderstandings: the time scale of interest and our process understanding of the Weierbach catchment in general.

In this manuscript, we only focus on diel fluctuations and not on the event, multiday, seasonal or annual time scales. The viscosity effect is only of importance for variations on a daily time scale and we do not attempt to explain differences in DOC concentrations on longer time scales or between seasons. We do not assume that all variations in discharge are driven by viscosity-induced discharge of groundwater, but only the diel variations of discharge and DOC under very specific conditions. We will clarify this in the revised manuscript. Hence, we do not believe, that a mixing analysis can improve our process understanding on a daily time scale.

We addressed the event and seasonal patterns of DOC 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. This leads to decreasing DOC and SUVA254 values with increasing discharge and vice versa (Figure 1 b,c,d; Figure 2 b,c,d).

In g and h this seems reversed. DOC follows discharge at the multiday time scale- meaning a drastic reduction of DOC load, while daily DOC peaks occur at daily discharge minima. This last fact largely counteracts the "viscosity hypothesis".

Thus for _50% of the data the viscosity hypothesis must be rejected.

I encourage the authors to "harvest" their data in multiple ways to support their hypothesis or better to explain the multiple processes rather than focusing on a one-sided interpretation.

Given the fact that the study was conducted in a potentially well studied catchment,

Figure 1 g,h is not a good example for the multiday relationship between DOC and discharge; it is not representative for the multiday timescale. Yet DOC does not follow discharge during the growing season (see Figure 2; daily mean values of DOC and discharge). Figure 1 is focusing on the diel fluctuations.

The discharge minima in the afternoon during the growing season are triggered by evapotranspiration. This does not exclude the presence of the visoscosity effect. Most likely, the viscosity effect is only hidden by the effect of evapotranspiration. This was already discussed in (Schwab et al., 2016).

The SUVA254 peak occurs always in the afternoon, both during the growing and the dormant season. This indicates that an increasing amount of terrestrial DOC is entering the stream in the afternoon. And this correlates well with the viscosity effect.

I wonder why the data is so sparse. The entire line of argumentation is based on a single temperature observation location which is used to explain catchment scale effects. I think this "extrapolation" is not justified. Moreover, the authors claim that at this location, there is high subsurface flow. However, they do not provide any data to

support this. How do I know that this location is representative for the entire catchment?
Indeed, we have to explain that better in this manuscript. We observed the temperature fluctuations at different locations. However, we only had one spot, where we had high-frequency data for the entire observation period and therefore selected this observation.
We will revise this in the revision and describe the locations and the other observations to show that this observation is representative for water temperature fluctuation in the riparian zone.

I strongly recommend better explaining the hydrologic aspects of how this catchment functions. I mostly missed some hydraulic gradients between the stream and the groundwater, some numbers on the amount of GW discharge and its spatial distribution and how temperatures, particularly streambed temperatures vary spatially. I am aware of the Schwab et al. 2016 study but also there, these essential information are not provided.

We will better describe the hydrologic aspects of the catchment in the revised manuscript. The riparian zone extends 1 to 5 meter from the stream and is around 1m deep. The stream flows on solid, impermeable, unweathered bedrock. Hence, most of the groundwater is flowing through the riparian zone into the stream (hydraulic gradients from the riparian groundwater to the stream).

My main technical concern is the position of the temperature sensor. If I understand correctly temperatures are measured at 10 cm below the land surface in the unsaturated zone. I wonder how this temperature can be representative for the water that is discharging into the stream. In the unsaturated zone water flows vertically, driven by gravity. Thus more or less horizontal flow, discharging into the stream is bound to saturated, Darcian flow. Moreover the relationship between hydraulic conductivity and viscosity is for saturated conditions. Under variably saturated conditions, saturation should have a much larger influence. No data on water saturation is reported. Anyway I doubt that the unsaturated zone is the source for the stream water. Thus to evaluate the effects of viscosity temperatures should be measured at groundwater discharge locations directly in the streambed.

We consider the riparian zone as being saturated. At least the parts with high inflow to the stream are saturated during most parts of the year. At the location of the sensor the soil is saturated during

the whole observation period and most of the inflow must enter the stream through the riparian zone.
Review #1 clearly points to our limited description of the catchment in the current manuscript. This needs further clarification in the revised manuscript and the specific site characteristics of the Weierbach catchment will be better discussed.

In summary, this manuscript presents only a modest amount of (spatial) data to support the "viscosity hypothesis". My impression is that the interpretation of the data is onesided towards this hypothesis. I encourage the authors to acknowledge the pattern which are obviously in their data and provide an analysis that is accounting for the different controls of DOC concentration which vary between seasons.

As already mentioned before, this paper explicitly focuses on the explanation of diel DOC fluctuations and not on the seasonal pattern of DOC. The seasonal patterns cannot explain the diel DOC pattern that we observed in the stream.
What we clearly see in our observations is the fact that the diel SUVA254 maxima are in the afternoon, both during the growing and the dormant season. An elevated SUVA254 value indicated an increased amount of aromatic/terrestrial DOC in the stream. This increased amount of DOC likely comes from the riparian zone, where the viscosity effect takes place. In general, science develops by testing alternative hypothesis (viscosity effects) and to show evidence for this hypothesis. As we can only reject hypothesis, but not completely proof, we can only show the indications we have and mention the other hypothesis which we rejected.

Specific comments:

I find "riparian water" is a misleading term - hydrologically there is no difference between soil and riparian water - both are in the unsaturated zone. So at least it should be defined what exactly is meant here.
We will define this more precise in the revised manuscript. Yet we disagree. The riparian zone can be saturated and unsaturated. We could either use the term saturated near stream areas or saturated riparian areas.

P.3. 15-20: This is exactly the point where the authors are on the wrong track. Water (groundwater - saturated zone) cannot flow through the unsaturated zone (I guess that the riparian zone is unsaturated because of 1) p5.l.3 sampling of riparian water was with suction cups, and 2) sampling depth is 10 cm below the ground) and then entering the stream. I encourage the authors to provide a conceptual model on the water fluxes and heat transport at the site

Our sampling location in the riparian zone is always saturated up to the soil surface. It is possible to sample with suction cups in the saturated zone – the suction cups were installed in the beginning to allow sampling under saturated and unsaturated conditions in the whole catchments – this location, however is saturated throughout the year. We will state this clearer in the revised manuscript.

P.4.l.14-15: Please provide a reference, better data confirming that this location has high GW inflow.

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 have to admit that the statement ("location of high GW inflow") is somewhat vague. We know that the hydraulic gradient is towards the stream and that the location is constantly saturated.

Moreover the sampling and measuring locations should be provided, in a way that the reader knows if the riparian water was sampled in 10 cm, 1m or 10m distance from the stream. Also: where are the GW wells? I think the spatial relationships are important. Please provide this in a map or a cross-section.

We will include a map with the sampling and measurement locations. Maps with the sampling and measurement locations are already published/under review in (Schwab et al., 2016, 2017).

p.5 l.24.: I don't understand what is meant by anomaly. This seems important for the further analysis but I don't get it. Is it a time shift between the variables? Or is it the difference between the 24h moving average time series and the original time series? I guess the latter. If so, what has been done is a simple form of spectral high pass filtering. You cancel out the low frequencies and only keep high frequencies of 1/24 d^-1. This should be better explained, best in terms of common time series analysis terminology.

Yes, it is the difference between the 24h moving average time series and the original time series. We will revise the explanation.

p.5.l.25-26. If a 24h moving average is applied you filter all fluctuations with shorter timescales.

We do not have significant fluctuations shorter than a daily timescale. In this manuscript, we want to understand the diel fluctuations. Hence, we applied a 24h moving average.

p.5. l 29.-33. Are periods without DOC fluctuation also periods without temperature variation? if so this would support the viscosity hypothesis. Please report temperature and viscosity fluctuations in these periods as well.

The data that we present in our manuscript includes only days that are not influenced by rainfall-runoff processes. Outside rainfall-runoff processes, we observed only minor temperature fluctuations during days with small DOC fluctuations. Days without DOC fluctuations are normally influenced by rainfall-runoff processes, where the diel temperature fluctuation is also disturbed or not existing.

p.10. l.15: What I see in Figure 1 is that for all times SUVA and DOC are highly correlated - also the minima. So far as I can see there is no indication that SUVA is particularly high when DOC is high. This is also supported by the good correlation between SUVA and DOC fluctuation in Fig. 3. Thus SUVA seems a good indicator for DOC concentration and thus not only the maxima, but generally SUVA indicates inputs not changes in DOC quality at this site.

As the reviewer mentioned, there is a correlation between absorbance at 254nm and DOC. According to the measurement method of the spectrometer, DOC is calculated based on absorbance 254nm. However DOC is not only calculated based on the absorbance at 254nm but also based on the 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 information into the discussion to clarify this point.

SUVA254 is indicator for the quality changes of DOC. The quality changes of DOC can be affected by terrestrial input and instream processes.

p.11.l5: Here I would disagree, the evidence is not strong.

We will change the wording in indicate. We think that there is a strong indication due to……

p.11. l.14-20: I think the reversed relationship between concentration and discharge is really striking and is not explained. e.g. p.l.17 "different spatial impacts" what is this exactly, how can you assess this by having only measured at a single location. I think if the authors could figure out how the controls of DOC concentration change over the season because the importance of different controlling factors vary, would make this work a strong contribution.

At first, this work is not about seasonal controls on DOC concentration, but solely explaining the diurnal pattern of DOC and SUVA. The reversed relationship between discharge and viscosity is explained in previous work (Schwab et al., 2016). The viscosity effect (dominant factor controlling discharge fluctuations during the dormant season) has an impact only on the upper part of the saturated riparian zone. Evapotranspiration (dominant factor controlling discharge fluctuations during the growing season) has also on impact on water in deeper layers. The different timing of the diel discharge extrema between growing and dormant season comes from the seasonally changing importance of evapotranspiration and viscosity (Schwab et al., 2016). Nevertheless, we could show in Schwab et al. (2016) that the viscosity effect is always present. As it has only an impact on the upper layer that is richer in DOC, it creates DOC maxima in the afternoon throughout the year. The SUVA254 maxima in the afternoon indicates that the increased DOC input is from terrestrial sources. Hence, this is a strong indication that the increased input comes from near surface layers (with increased SUVA254 and DOC values) where the viscosity effect has an impact.

p.12.l4 ff: I think this perceptual model should be extended by discharge effects. The authors should remember that their main line of argumentation is the increase discharge of water driven by viscosity. Comparing Fig.1 g and h with 6 d I would not bet that DOC inputs are high in the afternoon, concentration is high, but discharge is low. So again, also consider loads, not concentrations alone.

As already mentioned above, the rainfall-runoff responses are not affecting the diel signal. We will carefully revise the manuscript so that it becomes ultimately clear that this study is solely aiming at the diel pattern of DOC and related SUVA. We do not aim at distinguishing seasonal controls on DOC here, which are clearly related to hydrological processes and rainfall-runoff responses. The behavior of DOC on event and seasonal time scale is described in another manuscript (Schwab et al., 2017).

Figure 1: Please provide temperature data as well.

Temperature has the same pattern as viscosity, as viscosity is a function of temperature. Therefore, we decided not to include temperature.

Figure 3: This is a tough one for _8% of male population! Anyway, in 3d the green

regression line does not match the data well - visually it should be steeper.

We will change the colors.

We checked the regression again, and it is the proper regression using least square fit. There are so many data points (especially in the center) that the visual impression can be misleading. The fewer data points outside the center can be less important for the regression.

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.