

Point-by-point response to reviewer 1

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 concentration-discharge 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 ($C \cdot Q$) 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 viscosity 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.

We improved the terminology and added the word “saturated” when talking about the 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.

We subtract the original time series from the time series with the daily moving average. This results in a time series (that we call anomaly time series) where shorter timescales are not filtered out.

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 ($SUVA_{254} = A_{254}/DOC$). Consequently, an increase in $SUVA_{254}$ is based on an increase in A_{254} that is larger than the increase in DOC concentration. Therefore an 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.11.15: 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 an 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.

We described that in a better way in the discussion.

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.

Point-by-point response to reviewer 2

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 below 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):

$$\eta(T) = e^{(3.7188 + 578.919 / (137.546 + T))}$$

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 $\eta = 164$ Pa.s
for T=20 Celsius deg (293 Kelvin deg) the formula gives $\eta = 161 = 164 - 2\%$

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

$$(\eta) = e^{(-3.7188 + 578.919 / (-137.546 + T))}$$

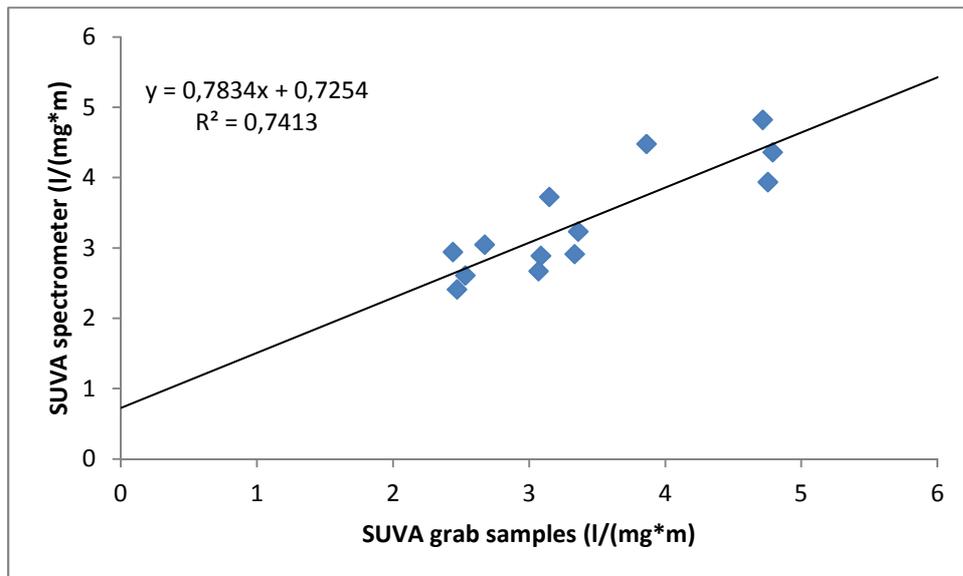
<http://ddbonline.ddbst.de/VogelCalculation/VogelCalculationCGI.exe>

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%.

The equation has been already corrected by WRR.

p. 4 lines 26-31: Did you compare also the absorbance values at 254 nm from spectrophotometer 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

It is difficult to compare the end member values with the stream flow values as the measurements were done at different time intervals. Therefore we preferred only showing to end members in this figure.

Discussion

p. 10 lines 5-9: Correlation between DOC and SUVA₂₅₄ fluctuations sounds consistent and I certainly agree with the authors on the value of SUVA₂₅₄ 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 spectrophotometer 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 lines 26-31)

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). SUVA₂₅₄ is calculated as the absorbance at 254nm normalized by the DOC concentration ($SUVA_{254} = A_{254}/DOC$). Consequently, an increase in SUVA₂₅₄ is based on an increase in A_{254} that is larger than the increase in DOC concentration. Therefore an 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 in 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 changed the hypothesis from “controlled” to “mainly controlled”

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

It is difficult to compare the end member values with the stream flow values as the measurements were done at different time intervals. Therefore we preferred only showing to end members in this figure.

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?

O₂ probes would have been very helpful for studying metabolic activity. Unfortunately, no O₂ 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.

Most relevant changes in the manuscript

Figure 1: new

Figure 3: background shading depending on seasons

Figure 4: color change of the dots (no red-green)

Study Site and Methods

- Improved description of the hydrological process understanding of the Weierbach catchment
- Clarification of the measurement location in the riparian area: riparian water temperature is measured in the saturated riparian area

Discussion

- Explanation why a correlation between SUVA₂₅₄ and DOC concentration is not disagreeing with our results: SUVA₂₅₄ is the absorbance at 254 nm NORMALIZED by the DOC concentration.
- Clarification that we did not intend to neglect to existence of instream processes. But the external input is mainly explaining the diel DOC fluctuations.
- More detailed discussion on diel discharge fluctuations and the interplay between evapotranspiration and the viscosity effect

Diel fluctuations of viscosity-driven riparian inflow affect streamflow DOC concentration

Michael P. Schwab^{1,2}, Julian Klaus¹, Laurent Pfister¹, Markus Weiler²

¹Catchment and Eco-Hydrology Research Group, Luxembourg Institute of Science and Technology, Belvaux, 4422, Luxembourg

²Hydrology, Faculty of Environment and Natural Resources, University of Freiburg, Freiburg, 79098, Germany

Correspondence to: Michael P. Schwab (michaelschwab.fr@gmx.de)

Abstract. Diel fluctuations of streamwater DOC concentrations are generally explained by a complex interplay of different instream processes. We measured the light absorption spectrum of water and DOC concentrations *in-situ* and with high-frequency by means of a UV-Vis spectrometer during 18 months at the outlet of a forested headwater catchment in Luxembourg (0.45 km²). We generally observed diel DOC fluctuations with a maximum in the afternoon during days that were not affected by rainfall-runoff events. We identified an increased inflow of terrestrial DOC to the stream in the afternoon, causing the DOC maxima in the stream. The terrestrial origin of the DOC was derived from the SUVA-254 (specific UV absorbance at 254 nm) index, which is a good indicator for the aromaticity of DOC. In the studied catchment, the ~~only possible~~most likely process that can explain the diel DOC input variations towards the stream is the so-called viscosity effect. The water temperature in the upper parts of the saturated riparian zone is increasing during the day, leading to a lower viscosity and therefore a higher hydraulic conductivity. Consequently, more water from areas that are rich in terrestrial DOC passes through the saturated riparian zone and contributes to streamflow in the afternoon. We believe that not only diel instream processes, but also viscosity driven diel fluctuations of terrestrial DOC input should be considered for explaining diel DOC patterns in streams.

1 Introduction

Dissolved organic matter (DOM) is a major constituent of the carbon cycle and aquatic biogeochemistry, eventually linking terrestrial and aquatic ecosystems (Battin et al., 2008; Lee et al., 2016; Saraceno et al., 2009). The largest component of DOM in forested stream ecosystems is dissolved organic carbon (DOC) (McLaughlin and Kaplan, 2013). DOC has a multifaceted chemical character that is mainly determined by its origin and its biogeochemical transformation (Hanley et al., 2013; Ruhala and Zarnetske, 2017). DOC in streams is mainly derived from external terrestrial sources (allochthonous) like plants and soils or from instream microbial sources (autochthonous). With increasing stream orders, autochthonous sources become more important (Dawson et al., 2001; Nimick et al., 2011). While DOC from allochthonous sources is characterized by fulvic and humic acids with high molecular weight and aromaticity, DOC from autochthonous sources has a lower molecular weight and is less aromatic (Hood et al., 2006; Saraceno et al., 2009; Spencer et al., 2012).

Different techniques have been used to gain information on the composition and the concentration of DOC. Two frequently used optical methods to characterize bulk DOC are UV-Vis spectroscopy and fluorescence spectroscopy (Minor et al., 2014). For identifying the aromaticity of DOC in aqueous systems, the specific UV absorbance at 254 nm (SUVA-254) is a commonly used index. SUVA-254 is calculated as the UV absorbance of water at the wavelength of 254 nm (A_{254}) that is normalized for DOC concentration (Weishaar et al., 2003). A higher SUVA-254 value indicates a higher aromatic DOC content and is therefore a valuable index for distinguishing between allochthonous and autochthonous origins of DOC.

Several studies used SUVA-254 to identify DOC from different origins in combination with changing contributions from different water sources and flowpaths. Hood et al. (2006) observed an increase of SUVA-254 during a 6-day storm event in three catchments of the H.J Andrews Experimental Forest, Oregon (USA) and suggested SUVA-254 as a useful tracer for identifying different flowpaths through mineral soils. Also at HJ Andrews, Lee et al. (2016) observed lower SUVA-254 values during the dry season low flows and suggest, supported by fluorescence indices, that in those conditions the stream water originates from more microbiallymicrobial-processed sources. Fasching et al. (2016) described similar observations in an Austrian, alpine second-order stream. They related the increase in SUVA-254 values during high flows mainly to a rise in terrestrial DOC contributions. Likewise, they correlated the decrease in SUVA-254 values during baseflow conditions to larger contributions from autochthonous DOC sources. As an alternative, Catalan et al. (2013) identified seasonality as the main factor controlling SUVA-254 patterns in an ephemeral Mediterranean catchment, because vegetation is accumulated during the dry period. In comparison to mechanistic studies focusing at seasonal and event timescales, investigations combining diel DOC fluctuations with SUVA-254 calculations are rather scarce. While Fasching et al. (2016) did not find clear diurnal SUVA-254 patterns in their stream, they were able to document diel DOC fluctuations with recurrent maxima around 19:30 h. They linked this pattern to a decrease in Photosynthetically Active Radiation (PAR).

Diel DOC fluctuations in streams are generally explained by a complex interplay of different instream processes. They cannot be observed in every stream, but when they occur, DOC concentrations are often increasing during daytime and decreasing at night (Nimick et al., 2011 and reference therein). Throughout daytime, autotrophic organisms like algae

excrete labile DOC during their photosynthesis, which depends on stream temperature and the amount of sunlight. On the contrary, more instream DOC is consumed at night by heterotrophic organisms (Chittoor Viswanathan et al., 2015; Fasching et al., 2016; Nimick et al., 2011; Parker et al., 2010; Spencer et al., 2007). This interplay of autotrophic and heterotrophic organisms is generally used to explain diel DOC fluctuations in streams. ~~Other studies~~ Studies from catchments with peatlands observed diel DOC fluctuations with DOC maxima in the early morning due to the absence of photic removal processes of DOC during the night (Worrall et al., 2015; Worrall and Moody, 2014). Tunaley et al. (2017) observed DOC maxima in the early morning for a peatland catchment, whereas a proximate catchment had its DOC maxima in the afternoon. Spencer et al. (2007) reported two DOC maxima per day in the San Joaquin River (California, USA).

In our study, we observed diel DOC concentration fluctuations at the outlet of a 0.45 km² forested headwater catchment. ~~Throughout~~ During baseflow conditions throughout the year, the maximum diel DOC concentrations occurred in the afternoon ~~during baseflow conditions~~. Based on our literature review of mechanistic explanations of DOC fluctuations our first hypothesis states that diel fluctuations in DOC concentrations are mainly controlled by instream microbial processes. Our second hypothesis stipulates that diel fluctuations in DOC concentrations can be explained by an increased input of terrestrial DOC to the creekstream during daytime. This second hypothesis is a follow-up on previous work by Schwab et al. (2016) carried out the Weierbach catchment. They linked diel fluctuations in discharge to increased inflow from the saturated riparian zone in the afternoon due to variations in viscosity (viscosity effect). Before the growing season, Schwab et al. (2016) observed diel discharge fluctuations with maxima in the afternoon that can be explained by riparian water temperature fluctuations and therefore viscosity fluctuations. Warmer riparian water ~~temperature~~ temperatures in the afternoon led to a lower viscosity of water, resulting in a higher hydraulic conductivity and therefore an increasing inflow of water to the creekstream when passing through the saturated riparian zone. During the growing season, discharge minima were observed in the afternoon due to the stronger influence of evapotranspiration. Nevertheless, Schwab et al. (2016) concluded that the viscosity effect was still present during the growing season, but not visible anymore in the diel discharge fluctuations as a result of the increased importance of the counteracting evapotranspiration. We intend to leverage these findings through our second hypothesis, stating that the viscosity effect could possibly increase the input of terrestrial DOC in the afternoon all year long.

We used SUVA-254 for testing both hypotheses. A decrease in SUVA-254 values during the afternoon would lead to the rejection of the second hypothesis, stating that an augmented input of terrestrial DOC can explain the DOC concentration maxima in the creekstream. Increased SUVA-254 values would lead to the rejection of the first hypothesis, where instream processes are supposed to control fluctuations in DOC concentrations.

22 Study Site and Methods

We measured the DOC concentration and the light absorption spectrum with a UV-Vis spectrometer in the Weierbach creekstream in Luxembourg from December 2013 to May 2015- (Figure 1). The Weierbach is a headwater catchment with a

size of 0.45 km² and elevations ranging from 450 to 512 m a.s.l. Beech (*Fagus sylvatica*) and in a smaller part spruce (*Picea abies*) are the dominant tree species in this forested catchment. The soils are shallow Cambisols with a depth of generally less than one meter and the bedrock geology consists of Devonian metamorphic slate and overlying Pleistocene Periglacial Slope Deposits (Moragues-Quiroga et al., 2017). In the vicinity of the ~~creekstream~~, the hillslopes are gentle on the right bank side and steep on the left bank side, while further uphill slopes tend to plateau. Along most parts of the ~~creekstream~~ a riparian zone extends ~~up 1 m~~ to ~~3 meters~~ ~~5 m~~ away from the channel and connects the hillslopes to the ~~creekstream~~. Water passing through the ~~saturated~~ riparian zone contributes significantly to discharge, both during wet and dry conditions.

At the outlet of the Weierbach catchment, we measured water levels with a pressure transducer (ISCO 4120 Submerge Probe) at 5 minute intervals. Water levels were converted into discharge via a rating curve. We corrected the temperature sensitivity of the probe according to the stream water temperature (Schwab et al., 2016). Precipitation was measured with a tipping bucket rain gauge at the meteorological station of Roodt, 3.5 km outside the Weierbach catchment. Precipitation had no distinct seasonality and the long term annual average was approximately 950 mm. During the observation period, no substantial snowfall was observed. The annual rainfall runoff ratio was around 50% with higher discharge volumes in winter than in summer (Glaser et al., 2016; Martínez-Carreras et al., 2015; Pfister et al., 2017; Schwab et al., 2016).

~~In one part of the riparian zone with high subsurface flow to the creek, we measured the riparian groundwater temperature every 30 min at 10 cm depth. We calculated the viscosity of the~~

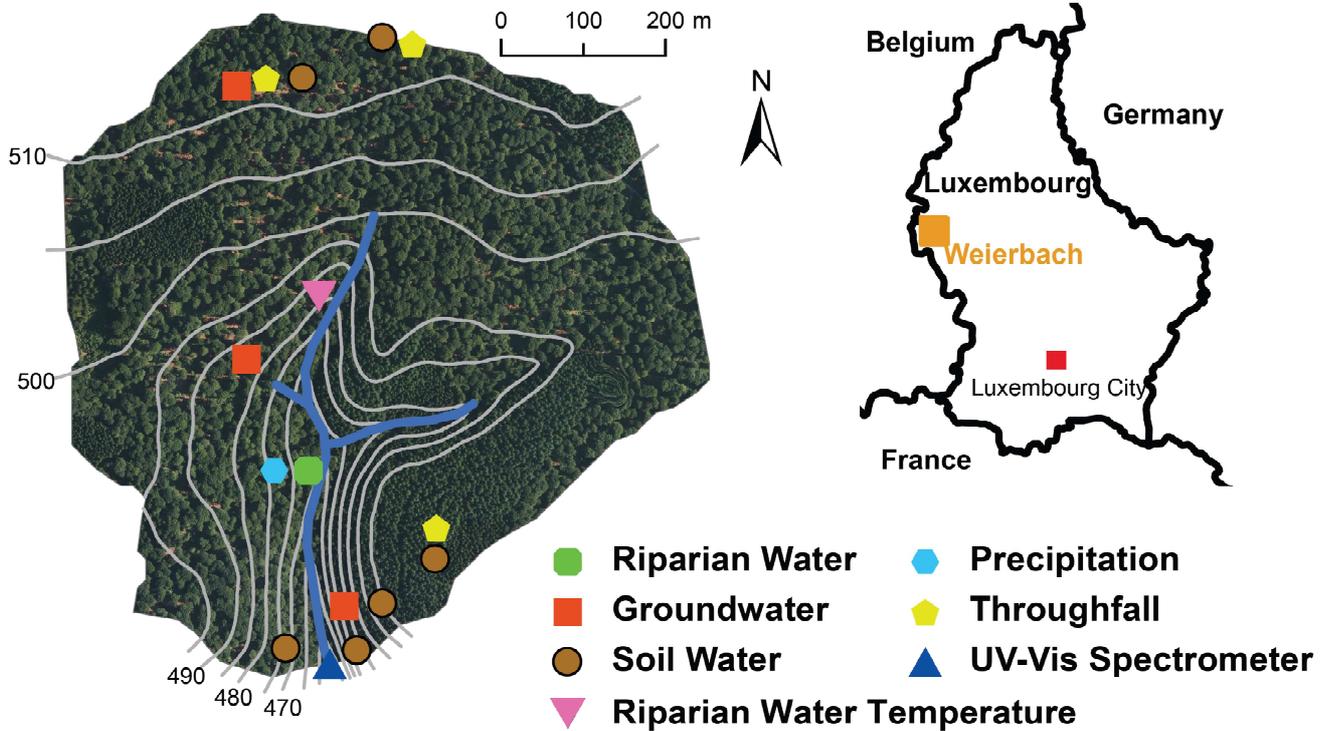


Figure 1: The Weierbach catchment: Location of the spectrometer, the end-member sampling points and the measurement location of the riparian water temperature (modified from Schwab et al., 2017).

The Weierbach catchment exhibits a distinct rainfall-runoff behavior, characterized by marked differences between dry and wet conditions. During dry conditions rainfall events trigger only one single discharge peak. During wet conditions an additional second discharge peak occurs with a delay of one to several days. The first discharge peak is probably caused by near surface and near stream runoff processes, while the second discharge peak is likely generated by “subsurface flow through the highly conductive saprolite layers” on the hillslopes (Glaser et al., 2016). This subsurface flow is initiated once a certain wetness threshold is reached in the catchment. DOC concentrations increased only during the first peaks. During wet conditions the DOC concentration in the stream was generally lower as more DOC poor subsurface flow contributed to streamflow (Schwab et al., 2017). The behavior of DOC concentrations at the seasonal and event time scales will not be analyzed in this study. We focus solely on diel fluctuations of DOC concentrations during days without rainfall events.

In one part of the riparian zone with high subsurface flow to the stream, we measured the riparian groundwater temperature every 30 min at 10 cm depth (Figure 1). We could only rely on one location with high-frequency riparian groundwater temperature data for the entire observation period. However, saturated riparian water temperature measurements along several profiles from previous years showed temperature fluctuations down to 15 cm depth that were consistent with the fluctuations that we observed at the selected location (Schwab et al., 2016). Based on our high-frequency temperature measurements at this location we calculated the viscosity of the saturated riparian water according to the Vogel equation (Schwab et al., 2016; Vogel, 1921). An increase of water temperature by 5 °C leads to a decrease (given the observed temperature range of groundwater) in viscosity by 12 % to 15 % and therefore to an increase in hydraulic conductivity in the same range (Tipler and Mosca, 2008). We consider the riparian zone being saturated during most of the year. In the vicinity of the temperature sensor, the soil was saturated during the whole observation period. The riparian zone extends 1 to 5 meters from the stream and is up to 1 m deep. The stream flows on solid, rather unpermeable, mostly unweathered slate bedrock. Hence, most of the groundwater is entering the stream through the riparian zone with hydraulic gradients from the riparian groundwater to the stream.

The DOC concentrations and the light absorption spectrum were measured *in-situ* in the Weierbach creekstream (Figure 1) at an interval of 15 minutes with the UV-Vis spectrometer spectrolyser (scan Messtechnik GmbH). The spectrometer measured the light absorption spectrum of the stream water between 220 and 720 nm in 2.5 nm resolution with a xenon flash lamp, 256 photo diodes and a two-beam instrument. The optical path length was 35 mm. The spectrometer probe was fixed to a metal plate that was placed on the streambed of the Weierbach creekstream. The orientation of the probe was horizontal and in stream direction with the measuring window facing towards the riverbed to avoid direct solar radiation. Every three hours, the measuring window of the spectrometer probe was cleaned automatically with pressurized air that was produced by an air compressor. We cleaned the spectrometer manually every two weeks.

We adapted the global calibration of the spectrometer that was provided by the manufacturer of the instrument to the local conditions by applying a local calibration. For this, we manually sampled the stream water weekly to biweekly and took

automatic samples during several rainfall events. We analyzed the grab samples in the laboratory for DOC with a combustion analyzer (Apollo 9000 - Teledyne Tekmar) and compared the results with the *in-situ* DOC concentration measurements of the spectrometer at the collection time of the grab samples. The linear regression for the local calibration between the lab values and the spectrometer values resulted in a good fit with an R^2 of 0.96. In the lab, we additionally measured SUVA-254 values of grab samples from the stream and compared them with *in-situ* SUVA-254 values from the spectrometer. The linear regression between them resulted in a good fit with an R^2 of 0.74.

A long time series of end-member chemistry data is available for the Weierbach catchment (Martínez-Carreras et al., 2015). DOC concentration values of biweekly sampled end-members are available since 2009, while biweekly UV-absorbance values at 254 nm (A254) are available since 2012. The sampled end-members included throughfall, soil water, saturated riparian water and shallow groundwater. Throughfall was collected as bulk samples over two weeks at three different locations. Soil water was sampled by applying a vacuum to suction cups that were installed at six different locations in the soil at depths of 10 cm to 100 cm. At one location in the riparian zone, saturated riparian water was collected with the same method. The biweekly grab samples of shallow groundwater were pumped from three wells in the catchment. The wells were screened for the lowest 50 cm to one meter and had a depth of two to three meters. (Figure 1).

SUVA-254 is a commonly applied index for characterizing the aromaticity and the terrestrial origin of DOC. SUVA-254 ($l\ mg^{-1}\ m^{-1}$) is calculated as the UV absorbance at 254 nm (A254 in m^{-1}) divided by the DOC concentration ($mg\ l^{-1}$) (Weishaar et al., 2003). For the SUVA-254 data of the end-members, A254 and the DOC concentrations of the biweekly grab samples were measured in the laboratory. To calculate the high-frequency SUVA-254 values of the stream water, we used the *in-situ* spectrometer measurements of DOC and the light absorbance measurements. Due to the 2.5 nm intervals of the spectrometer, the absorbance data at 254 nm (A254) was not available. Therefore we calculated A254 as the weighted mean between the absorbance at 252.5 nm and the absorbance at 255 nm. We eliminated potential outliers in the SUVA-254 time series by applying a 3 hours moving median to the entire time series.

For analyzing the diel fluctuations of DOC concentrations, SUVA-254, viscosity and discharge, we selected the days with diel fluctuations during the observation period from December 2013 to May 2015. Days that were influenced by rainfall-runoff events were not included in the analysis. According to this criteria, many short and several longer periods were removed. Especially the two winter seasons and August 2014 were particularly rainy periods. From the remaining days, additional days were removed from further analysis if at least one of the four variables showed unreliable or no values, especially due to problems with the used sensors. A longer period had to be removed in October 2014 because of that same reason.

We first analyzed the diel fluctuation patterns of DOC, SUVA-254, viscosity and discharge by comparing their daily minima, maxima and amplitude. For each day with diel fluctuations, we calculated the time of the day, when the minima and maxima occurred. The daily amplitude resulted from the difference between the values of the daily maximum and minimum. For further analysis, we calculated the anomaly of the time series of each of the four variables, (DOC, SUVA-254, viscosity and discharge, around their daily moving average from) by subtracting the values of the original time series with from those

of the ~~15-minute~~ daily moving average time intervals series. The daily moving average time series was calculated from the original time series with a window size of 24 hours and did not show diel fluctuations anymore. The calculations were based on the time series with 15 minute intervals and resulted in anomaly values for every 15 minutes.

We studied the anomalies of the four variables by comparing them with the corresponding values at the same time of another variable using scatterplots. With four different variables (DOC, SUVA-254, viscosity, discharge), this resulted in six different combinations. For each combination, linear regressions were calculated separately for each month, for the dormant and growing season and for the entire observation period. Due to the absence of days with diel fluctuations, we could not compute a linear regression for January. We defined the growing season as the period between the 15th of May and the end of September and the dormant season from the beginning of October until the 15th of April. To clearly distinguish between the two seasons, we introduced a transition period. As a transition period, we considered the time between mid-April and mid-May, when not all plants are yet fully active and developed. A transition period was not defined in fall, due to the lack of days with diel fluctuations around the end of September and the beginning of October.

3 Results

In our long-term high-frequency time series, we observed many days and periods with diel fluctuations in viscosity, SUVA-254, DOC and discharge. In the afternoons of rainless periods during the dormant and the growing season, we observed the diel minima of viscosity and the diel maxima of SUVA-254 and DOC (Figure 42). During the dormant season, we observed diel discharge minima in the morning, whereas we observed diel discharge minima in the afternoon during the growing season. The diel amplitudes of viscosity, SUVA-254 and DOC are changing in similar ways from one day to the other (Figure 42 e-g).

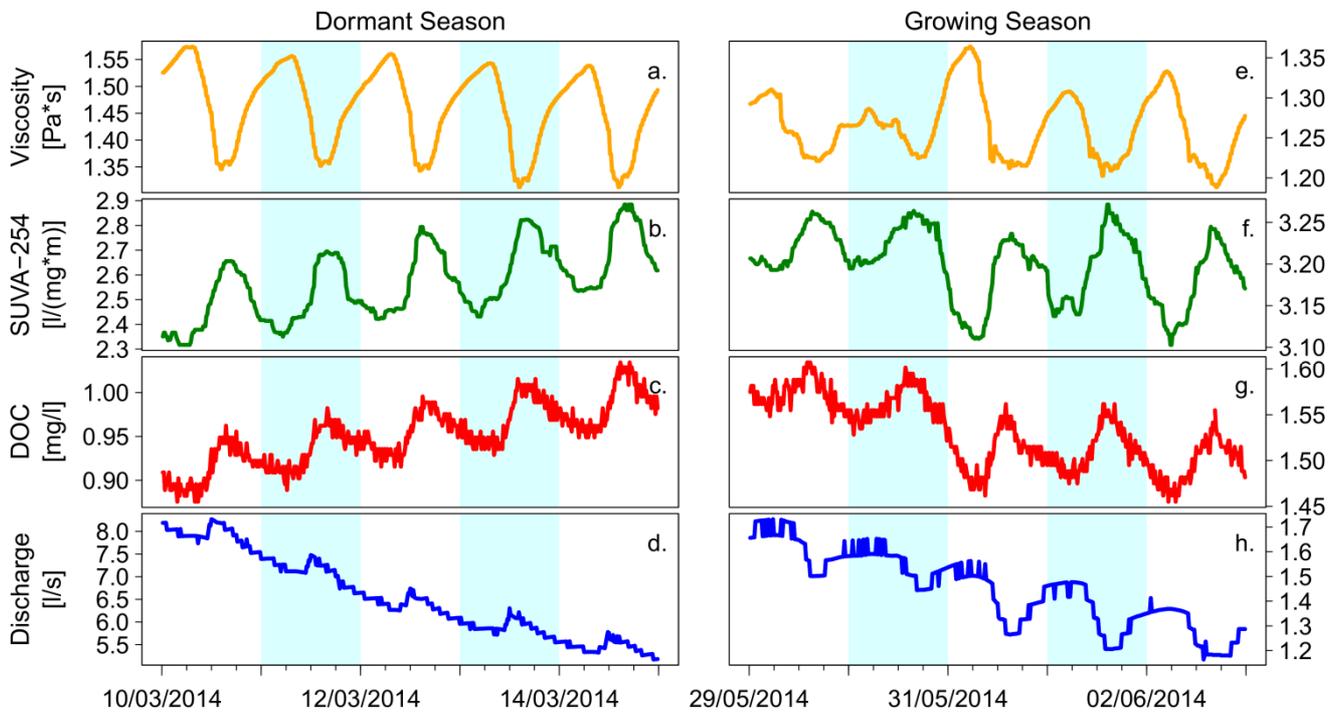
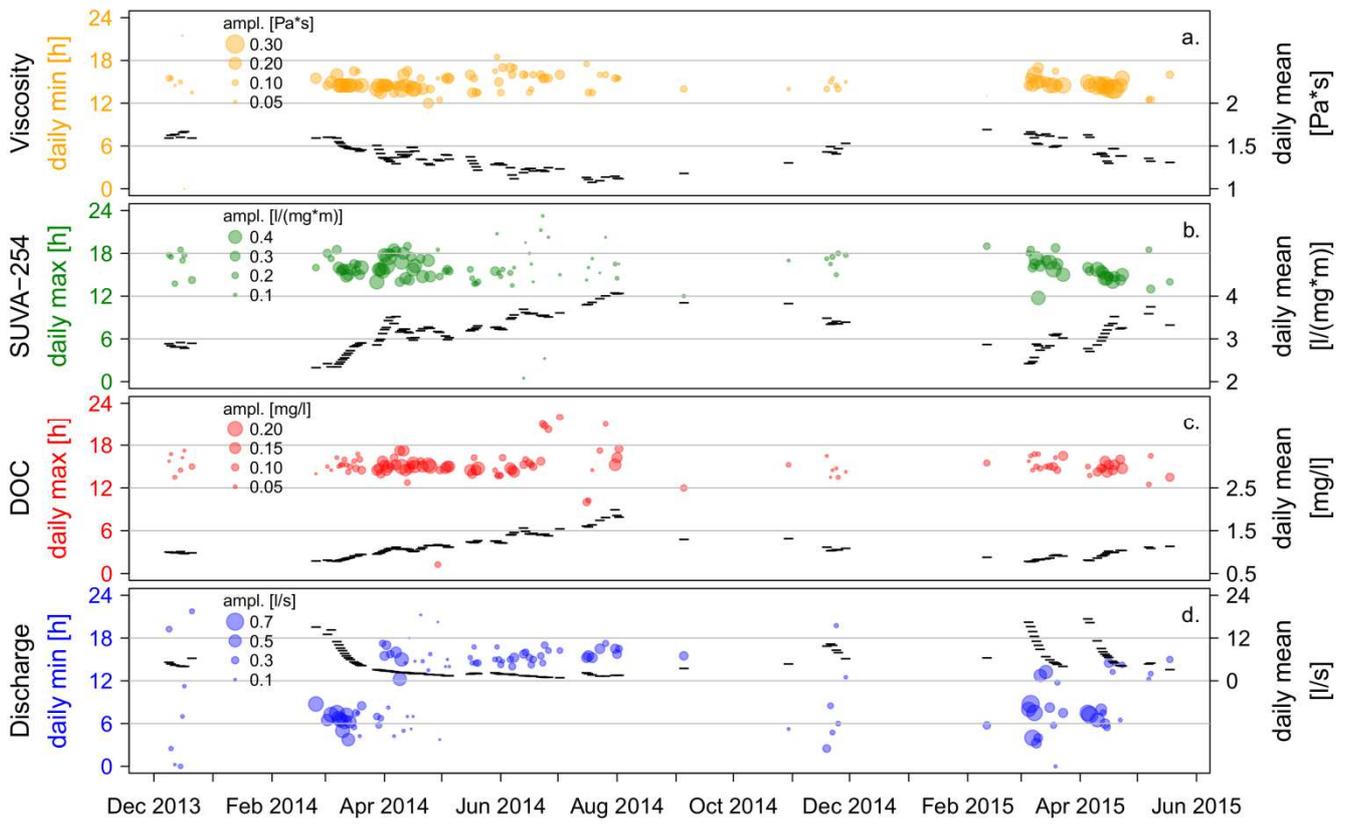


Figure 4-2: Diel fluctuations of viscosity of saturated riparian water, SUVA-254, DOC and discharge during a representative rainless period in the dormant season and the growing season.

Over the whole time series of 18 months, the minima in viscosity and the maxima in SUVA-254 and DOC occurred in the afternoon between 14:00 h and 18:00 h for both, the growing and the dormant season (Figure 23 a-c). For discharge, the time of the minima switched from early morning in the dormant season to the afternoon in the growing season both in 2014 and 2015 (Figure 243d). In winter, we only observed a few rainless days outside rainfall-runoff events with diel fluctuations (Figure 23). During that time (December 2013 and November 2014) no clear diel discharge pattern is visible (Figure 243d) and the diel amplitudes of all four variables are relatively small. The diel amplitudes of DOC and viscosity stayed relatively constant over the 18 months with lowest amplitudes of DOC in winter and spring and slightly higher viscosity amplitudes during the growing season than during the dormant season (Figure 23 a,c). The amplitudes of SUVA-254 changed more markedly over the 18 months. SUVA-254 had its highest amplitudes in spring and very low amplitudes in summer (Figure 2b3b).

Figure 23 shows a seasonal pattern for the daily mean values of all four variables. The viscosity of the saturated riparian water is lower during the growing season than during the dormant season (Figure 2a3a), while the mean daily SUVA-254 values and the mean daily DOC concentrations are higher during the growing season than during the dormant season (Figure 23 b,c). The discharge in the Weierbach creekstream was lower in summer and higher in winter and early spring (Figure 243d).



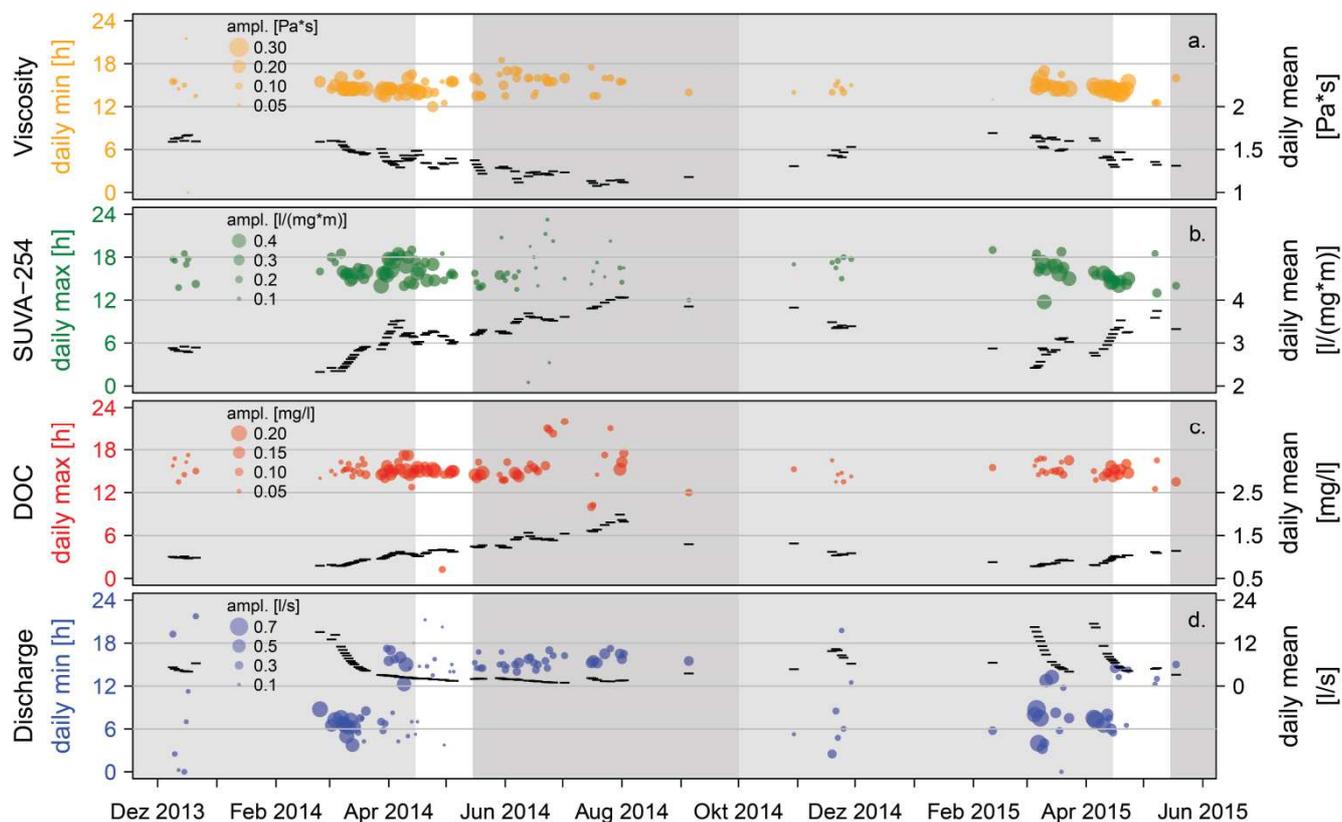
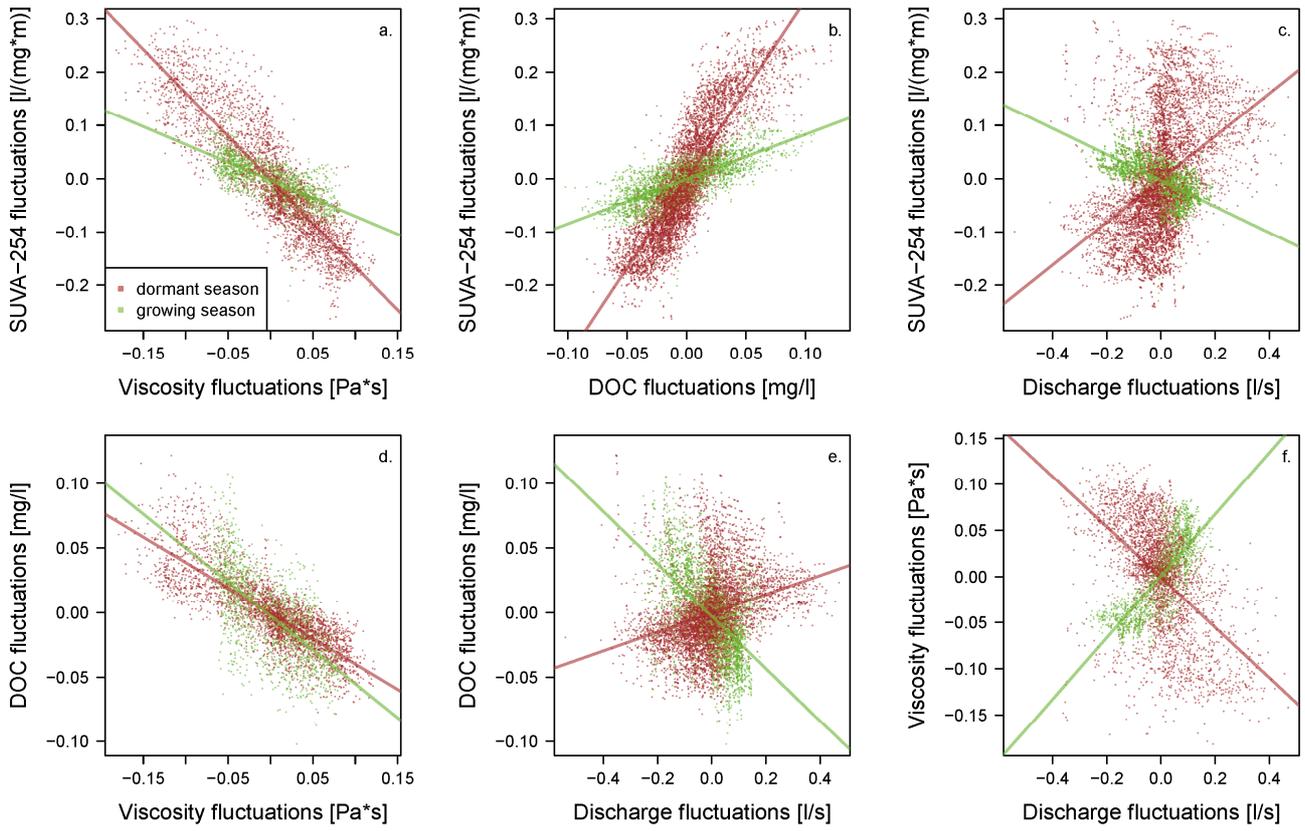


Figure 23: The time of day of the daily minima/maxima of saturated riparian water viscosity, SUVA-254, DOC and discharge over 18 months. Only rainless days with diel fluctuations and without the influence of rainfall-runoff events are represented. The points are scaled by the daily amplitude between the daily minimum and maximum. Black dashes (-) are the daily mean values of the respective variables. **Background: dark grey (growing season), light grey (dormant season), white (transition period).**

After identifying the strong similarity in the timing of the diel extreme of viscosity, SUVA-254 and DOC, we analyzed the relationship between the 15 minute anomalies of viscosity, SUVA-254, DOC and discharge. Figure 34 and Figure 45 show a strong linear relationship between SUVA-254 and viscosity, SUVA-254 and DOC as well as between DOC and viscosity for the dormant season, the growing season and the entire time series of 18 months with R^2 larger than 0.6. The slope of the linear regression between the viscosity anomalies and the SUVA-254 anomalies is negative, meaning that the viscosity of the saturated riparian water was decreasing during the day, while SUVA-254 values were increasing (Figure 3a4a). During the growing season, the slope was less negative than during the dormant season (Figure 3a4a and Figure 4a5a). The values of the slopes show an annual pattern, with the least negative slopes occurring in June and July (Figure 4a5a). The slope of regression between the DOC anomalies and the SUVA-254 anomalies is positive (Figure 3b4b). An increase of SUVA-254 during the day leads to an increase in DOC concentrations. This relationship is less strong during the growing season, with the smallest slopes occurring in June, July and August (Figure 3b4b and Figure 4b5b). The slope of the regression between

viscosity and DOC is negative, meaning that a decrease in viscosity during the day leads to an increase in DOC (Figure 3d4d). These negative slopes are relatively constant over the year and between the seasons (Figure 3d4d and Figure 4d5d).



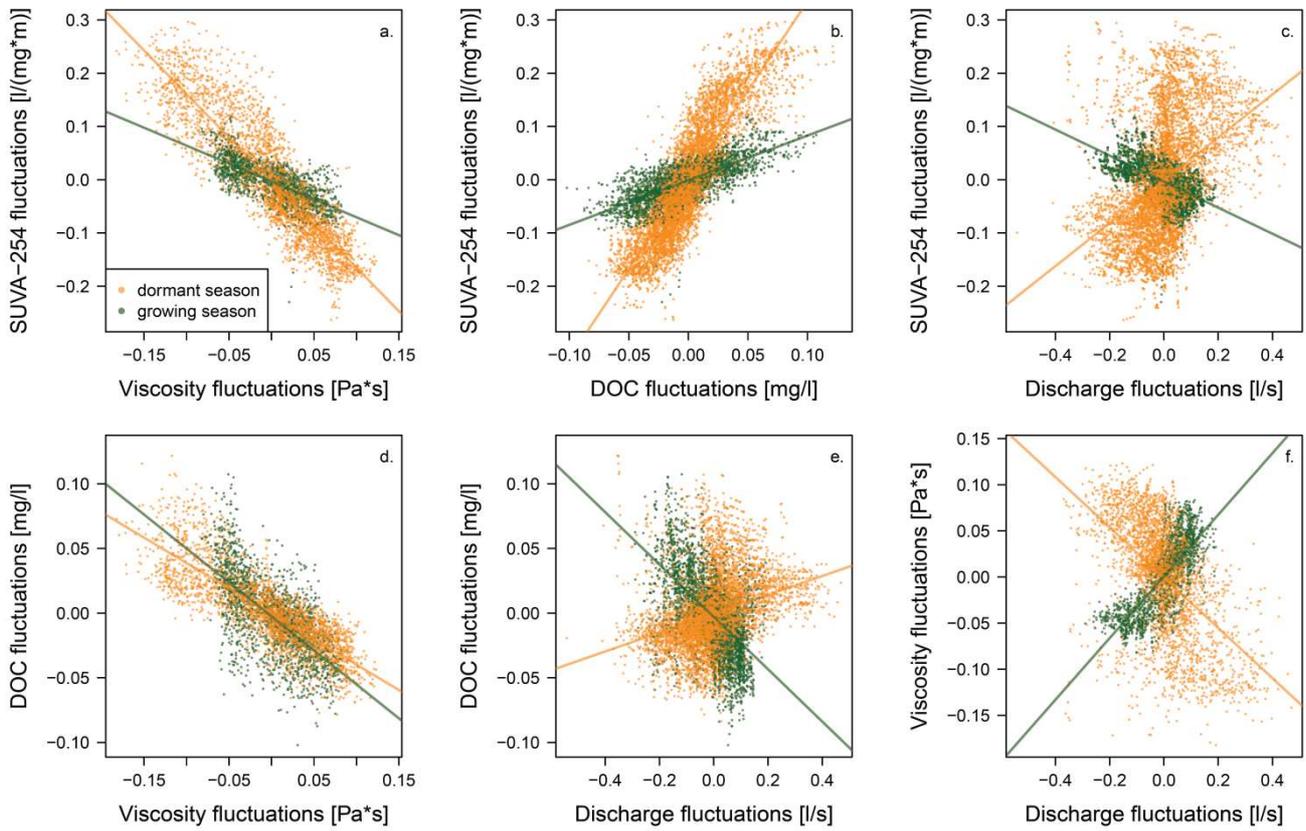


Figure 34: Scatterplots and linear regression between the 15 minute anomalies of the four variables for the growing and dormant period. Only rainless days with diel fluctuations and without the influence of rainfall-runoff events are shown (corresponding to the days in Figure 23).

- 5 For the combinations that included discharge, we generally observed weaker and more heterogeneous relationships (Figure 34 c,e,f and Figure 45 c,e,f). The linear regressions between discharge and SUVA-254, discharge and DOC, as well as between discharge and viscosity resulted in contrary signs of their slopes between the dormant season and the growing season. Moreover, the R^2 of the linear regressions where discharge was involved, were generally smaller than for the linear regressions in absence of discharge (Figure 45).

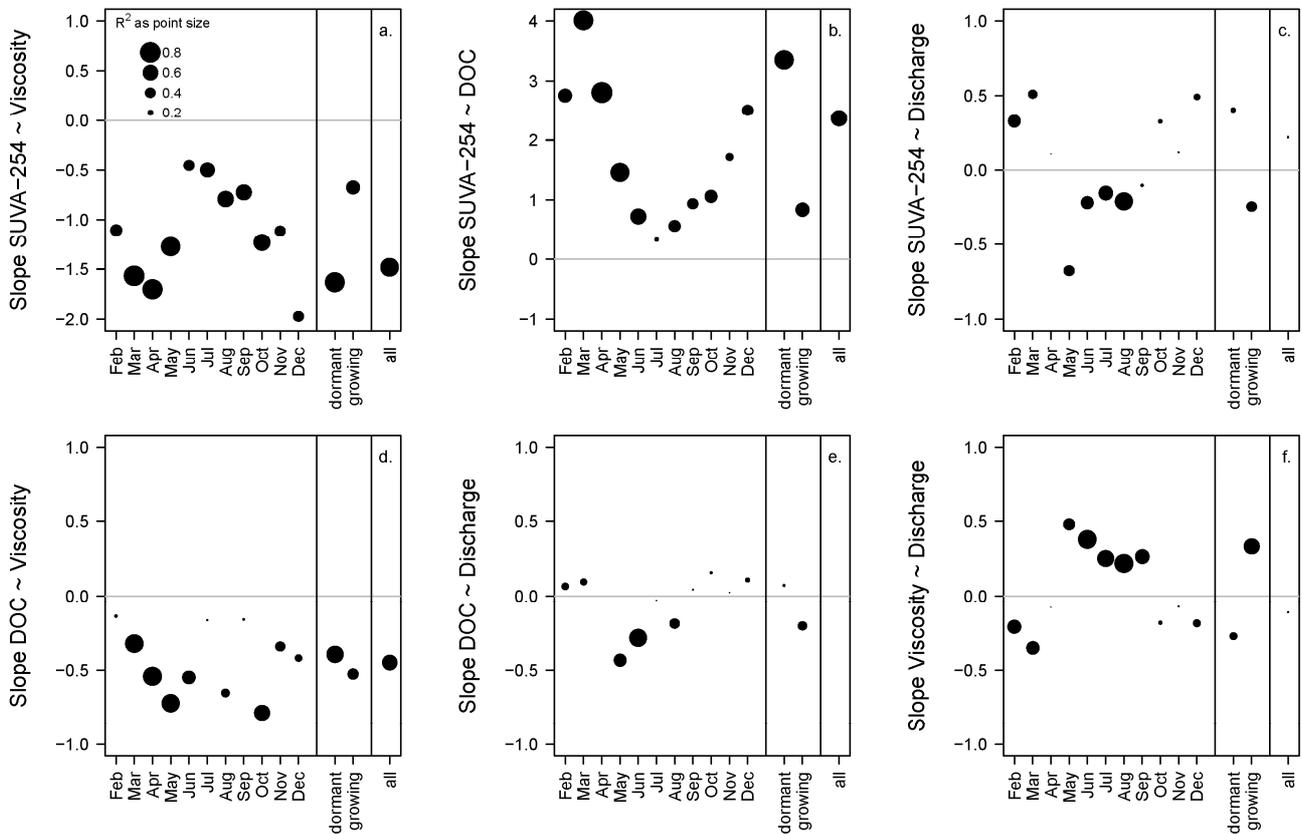


Figure 45: Slope and explained variance (R^2) of the linear regression between the 15 minute anomalies of the four variables. Slope and R^2 are separately calculated for each month, for the dormant and the growing season and for all values. All the p-values are generally highly significant. Only rainless days with diel fluctuations and without the influence of rainfall-runoff events are shown (corresponding to the days in Figure 23).

In addition to the high-frequency instream observations and temperature measurements of the saturated riparian zone, we sampled end-members in the catchment and analyzed them in the laboratory for SUVA-254 and the DOC concentrations. We observed the highest DOC concentrations in throughfall and soil water, lower concentrations in saturated riparian water and lowest DOC concentrations in the groundwater (Figure 5a6a). We found a decrease of DOC concentrations in soil with depth. The highest DOC concentrations were observed in the upper part of the soil profile (Figure 5b6b). The SUVA-254 values in soil water behave similarly to the DOC concentrations, having the highest values in the upper part of the soil profile (Figure 5e6c). Soil water, throughfall and saturated riparian water have similar SUVA-254 values, while groundwater has the smallest SUVA-254 values (Figure 5d6d).

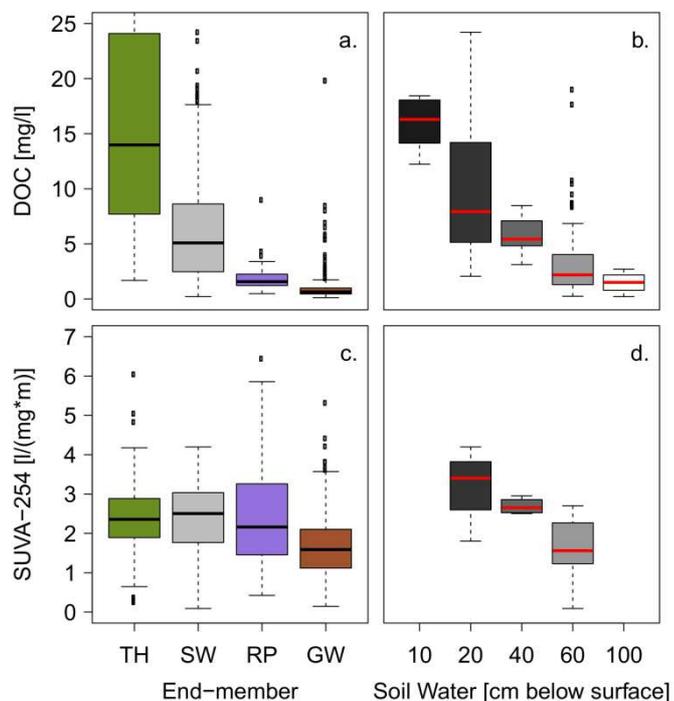


Figure 56: DOC concentrations and SUVA-254 values of the biweekly sampled end-members and the detailed information for soil water at different depths. TH = throughfall, SW = soil water, RP = saturated riparian water, GW = groundwater.

4 Discussion

5 Based on our measurements in the Weierbach catchment, we are convinced that SUVA-254 is a suitable proxy for identifying terrestrial DOC in diel DOC fluctuations. Several studies already demonstrated that SUVA-254 is a valid index to characterize the origin of DOC (Catalán et al., 2013; Fasching et al., 2016; Lee et al., 2016; Weishaar et al., 2003). We found strong evideneeindices in the Weierbach catchment for rising SUVA-254 values serving as a valid index of higher terrestrial DOC input to the ereekstream. Immediately after rain events, discharge, DOC concentrations and SUVA-254 rapidly increased. This increase in discharge is related to surface or near-surface runoff processes (Glaser et al., 2016; Klaus et al., 2015). Therefore it is likely that the increase in DOC concentrations was induced by terrestrial DOC input that eventually led to a rise in measured SUVA-254 values. Although our data showed a correlation between absorbance at 254 nm (A254) and the DOC concentration, an increase in SUVA254 is not (only) related to an increase of DOC concentration in general, but to an increase in more aromatic DOC components. According to the measurement methods of the spectrometer,

10 A254 is only one wavelength among several other wavelengths that have been used to calculate the DOC concentration. SUVA 254 is calculated as the absorbance at 254 nm normalized by the DOC concentration ($SUVA_{254} = A_{254}/DOC$). Consequently, an increase in SUVA254 is based on an increase in A254 that is larger than the increase in DOC concentration.

15

We tested our two hypotheses on processes controlling diel DOC fluctuations. For the days with diel fluctuations we generally observed both DOC and SUVA-254 maxima in the afternoon. Thus we could reject our first hypothesis that ~~the DOC maxima in the afternoon are controlled by microbial autochthonous instream processes. Moreover microbial autochthonous instream processes are the dominant control of the DOC maxima in the afternoon. However, we need to keep in mind that biological processes that recycle DOC are manifold leading to complex antagonistic results and that SUVA-254 is only a proxy of the complex composition of DOC computed from absorbance properties.~~ Nevertheless, the increased SUVA-254 values in the afternoon are a strong support for our second hypothesis that the DOC maxima in the afternoon are triggered by an increase in terrestrial DOC input to the stream in the afternoon. Another support for the second hypothesis is that the high-frequency anomalies of DOC and SUVA-254 behave in a similar way as suggested by the good fit of the regression between those two variables. Additionally, the SUVA-254 values and DOC concentrations of the end-members are a strong indicator of the origin of the stream water ~~origin~~ in the afternoon (when SUVA-254 and DOC are on the rise). For both DOC and SUVA-254, soil water and saturated riparian water had higher values than groundwater and the values in the topsoil were higher than in the subsoil for both variables. ~~Rejecting the first hypothesis and supporting the second hypothesis does not imply that biological processes were absent. Yet, these processes were not the dominant control for the diel DOC fluctuations (Figure 7).~~

Our study provides strong experimental evidence for viscosity-controlled diel DOC fluctuations in the Weierbach. Previous work by Schwab et al. (2016) in the Weierbach catchment had shown that an increase in riparian water temperature during the day led to a decrease in riparian water viscosity and subsequently to an increase in hydraulic conductivity. This viscosity effect resulted in an increased inflow of riparian groundwater to the stream in the afternoon – from the topsoil of the saturated riparian zone to the ereekstream. The timing of the daily minima of viscosity in the afternoon is consistent with the timing of the daily maxima of DOC and SUVA-254. Besides the timing of the viscosity minima, the high-frequency anomalies provide another solid indication that the viscosity effect triggers an increased inflow of terrestrial DOC to the ereekstream in the afternoon. The strong regression between the viscosity and the SUVA-254 anomalies and especially the regression between the viscosity and the DOC anomalies showed that viscosity, SUVA-254 and DOC had very similar diel dynamics.

The regressions between the discharge anomalies and the anomalies of viscosity, SUVA-254 and DOC resulted in different slope directions and values depending on the season. This behavior can be explained by the existence of two different opposing processes that are controlling the diel discharge fluctuations: the viscosity effect during the dormant season and evapotranspiration during the growing season. ~~We argue that different spatial impacts are the reason, why during the growing season evapotranspiration is controlling discharge but the viscosity effect is controlling the DOC concentrations and the SUVA values in the stream.~~ (Schwab et al., 2016). However, we believe that the viscosity effect is always present, even when its effect on diel discharge fluctuations is hidden by the stronger, counteracting influence of evapotranspiration during the growing season. As the viscosity effect is present all year long, it can control the diel fluctuations of DOC concentration

and SUVA-254 values both during the dormant and the growing seasons. Evapotranspiration cannot hide the influence of the viscosity effect on diel DOC and SUVA-254 fluctuations during the growing season as evapotranspiration and the viscosity are impacting different water sources with dissimilar DOC concentrations and SUVA-254 values. While the viscosity effect

is only present in the topsoil of the riparian zone, the plants transpire water from deeper soil depths (Bond et al., 2002; Schwab et al., 2016). Especially the upper parts of the soil had high SUVA-254 and DOC concentration values.

Different models for simulating autochthonous DOC dynamics exist (Fasching et al., 2016; Worrall and Moody, 2014). However, these models are partly contradictory and no state-of-the-art model has been established so far. In addition, we did not have all the data required to run these models. Consequently, we did not simulate the autochthonous DOC dynamics.

However, we developed a perceptual model to explain the observed diel DOC and SUVA-254 anomalies, depending on

instream processes and terrestrial input (Figure 67). The conceptual model follows the main results of Fasching et al. (2016), stipulating that the instream DOC production is higher with increasing stream water temperature and increasing

photosynthetically active radiation (PAR). With the perceptual model that is illustrated in Figure 67, we can also explain the observed smaller slopes resulting from the regression between the SUVA-254 and the DOC anomalies during the growing

season. The amplitudes of the diel DOC anomalies stayed relatively constant over the whole year, while the diel amplitudes

of SUVA-254 decreased during the growing season. We argue that an increasing importance of instream processes during the growing season leads to a decrease in SUVA-254.

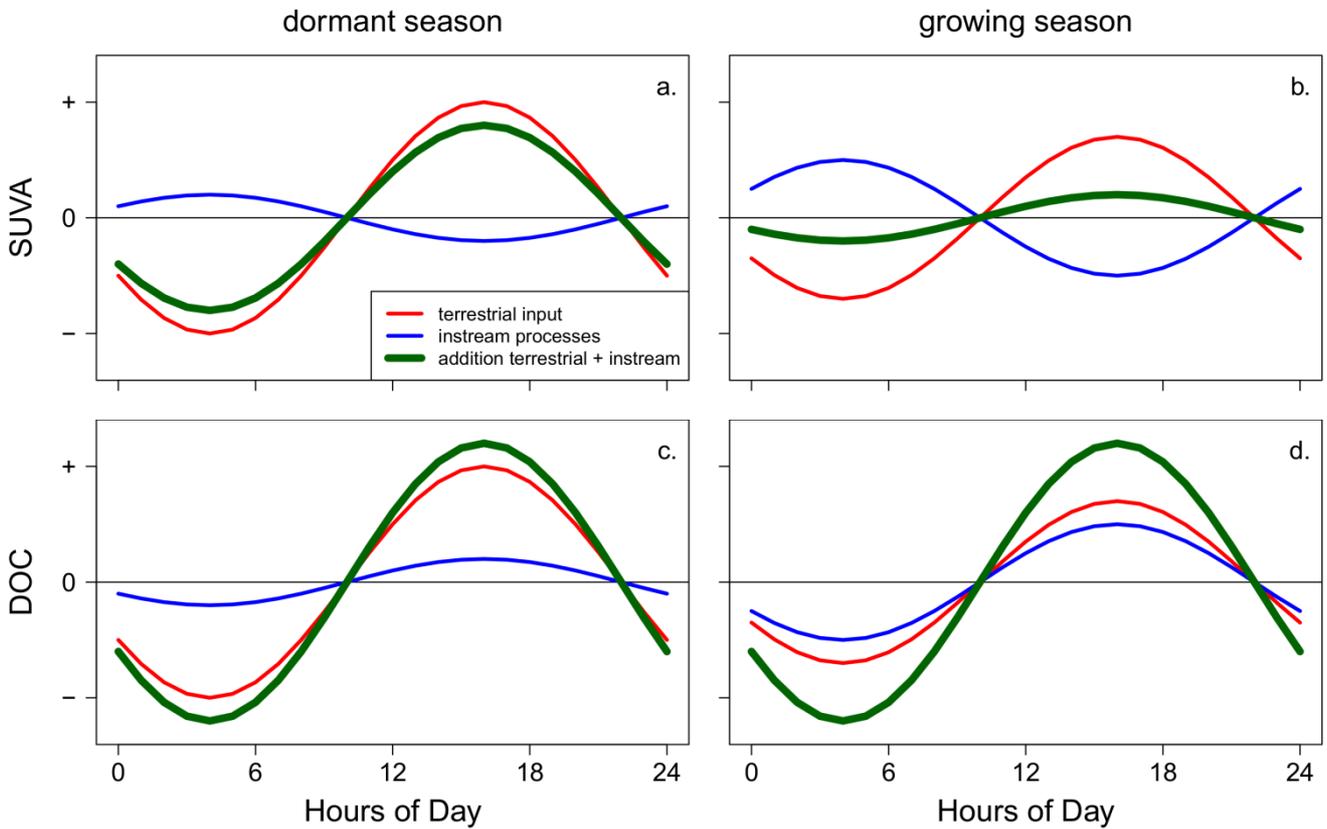


Figure 67: Perceptual understanding on the diel SUVA and DOC fluctuations and its dependence on instream processes or terrestrial input and the resulting superposition of both processes.

In our perceptual model (Figure 67), the diel SUVA-254 fluctuations resulting from instream processes show an opposite pattern compared to the diel SUVA-254 fluctuations resulting from terrestrial DOC input. This can be explained by differences in the aromaticity of DOC of the two processes. Depending on the magnitude of both processes, the resulting superposition of both processes may change the diel pattern or not. As a consequence of the increasing stream water temperature and PAR in summer, SUVA-254 fluctuations resulting from instream processes are much higher during the growing season than during the dormant season (Figure 67 a,b) (Fasching et al., 2016). On the other side, the diel SUVA-254 fluctuations resulting from terrestrial DOC input triggered by viscosity effects are smaller during the growing season due to a decrease of the viscosity fluctuations in summer (Schwab et al., 2016). By overlaying the instream and the terrestrial effect on SUVA-254, the resulting diel SUVA-254 fluctuations are higher in the dormant season than in the growing season.

Contrarily to the SUVA-254 fluctuations, the diel DOC fluctuations resulting from instream processes and terrestrial input are in phase. They have their maxima in the afternoon when the stream water temperature and the PAR (influencing the instream processes) are at their maxima and the riparian water viscosity (influencing the terrestrial input) has its minima. During the growing season (Figure 67d), the diel DOC fluctuations induced by instream processes are higher than during

the dormant season and the DOC fluctuations resulting from terrestrial input are smaller (smaller viscosity fluctuations) than during the dormant season (Figure 6e7c). Consequently, the overlaying of both effects results in similar DOC fluctuations during the growing and the dormant seasons (Figure 6e7c,d). In other catchments the relative proportion of the different processes is probably different, resulting in other overall diel fluctuations.

5 In addition to the diel fluctuations, we observed a seasonal pattern in the daily mean values of SUVA-254 and DOC concentrations. In the Weierbach eekstream we observed higher SUVA-254 values and DOC concentrations during the low flow periods compared to high flow periods, while Lee et al. (2016) and Fasching et al. (2016) described lower SUVA-254 values during dry, respectively baseflow conditions (Figure 23). This could likely be explained by different flow paths of the water contributing to stream flow. During summer low flow, we suspect that only a few source areas in the riparian zone contribute to streamflow. Those riparian source areas have higher SUVA-254 values and DOC concentrations (Figure 10 56). During periods with higher discharge, especially in winter and early spring, a dilution effect leads to decreasing SUVA-254 values and DOC concentrations. Larger areas with lower SUVA-254 values and DOC concentrations contribute to streamflow. During those wet conditions, subsurface flow, whose SUVA-254 and DOC signature is represented by the shallow groundwater end-member (Figure 56), generated a large part of the discharge.

15 5 Conclusion

We observed diel DOC fluctuations in the Weierbach catchment over a complete year during periods that were not affected by rainfall-runoff processes. By means of the SUVA-254 index, serving as an indicator for DOC aromaticity, we found that an increased input of DOC with terrestrial origin was responsible for the peak in DOC concentrations in the afternoon. Higher SUVA-254 values indicate a higher aromaticity of DOC and therefore an increase of DOC from terrestrial 20 (allochthonous) sources. We could explain the increased input of terrestrial DOC in the afternoon with the viscosity effect. Water passing the saturated riparian zone before entering the eekstream is heated in the riparian zone during the day. Warmer water has a decreased viscosity and therefore the hydraulic conductivity increases. Consequently, more water from near surface zones that are rich in terrestrial DOC is entering the eekstream in the afternoon. Our study described a new process that can explain diel DOC fluctuations in streams. We argue that the analysis of diel DOC fluctuations should not 25 only focus on instream processes, but also on surface areas in the vicinity of the eekstream. Moreover, viscosity driven diel hydrological flow processes have to be taken into account for understanding diel DOC dynamics in streams.

For further studies, we suggest to combine the UV-Vis spectrometer measurements with fluorescence spectrometry measurements to gain even more detailed information about the origin of the DOC. Furthermore, a more detailed insight into the instream DOC processes would be an interesting aspect of future research. Oxygen probes could be very helpful for 30 studying metabolic activity in the Weierbach stream. Additionally, we hope that our study could raise the awareness that viscosity driven input of terrestrial DOC can explain diel DOC fluctuations in stream water. We believe that this effect can be also detected in other catchments, but depends on the catchment-specific interplay of both interacting processes.

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Competing interests

The authors declare that they have no conflict of interest.

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