Response to reviewer comments RC1

We thank you for your thoughtful comments and making us aware of open questions.

Please find below a list of specific responses to the individual points.

Responses to comments are shown in blue.

Hydrol. Earth Syst. Sci. Discuss.,

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Interactive comment on "Real-time observations of stable isotope dynamics during rainfall and throughfall events" by Barbara Herbstritt et al.

Anonymous Referee #1

Received and published: 19 July 2018

In this manuscript, the authors present results of a novel method to determine stable isotope ratios of H and O (delta2H and delta18O values) in water of incident rainfall and throughfall below a selected individual tree in high temporal resolution making use of the latest developments in infrared laser spectroscopy.

Overall, the conducted research is sound and the manuscript is well structured. However, the language is sloppy and imprecise and needs to be considerably improved.

In the following, I offer a number of line-by-line comments to improve the manuscript before it can be accepted for publication in Hydrology and Earth System Sciences:

Comment: p. 1, l. 1-2: The title is misleading and incomplete. The measurement is not real-time but highly resolved (but with a temporal delay), the considered stable isotope ratios must be specified, because rainfall and throughfall do not only consist of water but include numerous solutes, which also have to a large part several stable isotopes. Therefore, the title should be something like "Temporally highly resolved measurement of stable hydrogen and oxygen isotope ratios in water of rainfall and througfall with a novel infrared laser-based method"

Response: We agree that the stable isotopes have to be specified. Therefore we now inserted "water" before "…stable isotope dynamics…". Regarding time delay we agree that strictly speaking the isotope measurements are not real-time. However, when comparing the time delay of our method (few minutes) to the time delay accompanying assays based on discrete liquid samples (days, even weeks depending on the number of samples and laboratory capacities) we considered it justified to call it "real-time". Further, we feel that this should be seen in the context of the research conducted. Ultimately, our setup is intended to be employed in combination with observations of soil or runoff water which will eventually carry the isotopic signature first observed in gross precipitation and canopy throughfall.

Compared to the timescale that can be expected for these reactions we argue that "real-time" is not too far-fetched.

Comment: p. 1, l. 6: Like in the title the considered isotopes and their molecule need to be mentioned.

Response: We inserted "water" before "…isotopic composition…" in this rather general introductory sentence. Further, we specified the molecule and isotopes in line 10. The sentence now reads "For the quasi real-time observation of the water isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) of…".

Comment: p. 1, l. 6: It is unclear what the difference between exchange and mixing is. Add an explanation.

Response: We refer to diffusive exchange between liquid water and ambient vapour, while mixing refers to conservative mixing of different liquid water reservoirs.

We inserted "diffusive" before "…exchange…".

Comment: p. 1, l. 8 (and throughout the manuscript): It is unclear what you mean by "amount". Do you talk about the rainfall/throughfall rate or volume? Be clear.

Response: We refer to depth. We found that amount and depth are used synonymously in literature. Nonetheless, we replaced "amount" by "depth" in most places of the manuscript.

Comment: p. 1, l. 10: What do you mean by "gross precipitation"? The water of the incident rainfall?

Response: Gross precipitation is the community-used term for open site rainfall.

Comment: p. 1, l. 16-18: This threeline statement has (almost) no content. Specify, what exactly makes your method to a tool for more insight.

Response: We rephrased the sentence. It now reads:

"The achieved evolution from discrete liquid or event-based bulk samples to continuous measurements allows for direct comparison with common meteorological measurements. This makes our approach a powerful tool towards more insight into the dynamic processes contributing to interception during rainfall events."

Comments: p. 1, l. 20: Tracers of what? Water sources? Water flow paths? Mixing processes? All of them? But then it would no longer be ideal, because usually a tracer is

expected to be specific for a single source or a single process. & p. 1, l. 21-22: This is again too unspecific. What exactly were water isotopes used for?

Response p.1 l. 20-22: p. 1, l. 20: *This is an introductory sentence. We kept it but rephrased the following sentence* (p. 1, l. 21-22). *It now reads:*

"They have proven to be powerful tools for the characterisation of water flow and transport processes with a long record of applications at different spatial and temporal scales and in all parts of the water cycle (Kendall and McDonnell, 1998; Vitvar et al., 2005)."

Comment: p. 1, l. 24: What is crucial? The knowledge of the isotope ratios? But there was also a catchment hydrology before the isotopes could be measured and there are catchment hydrologists who do not use water isotope ratios.

Response: We rephrased the sentence to:

"The isotopic composition of precipitation ultimately cascades through the entire hydrologic system affecting soil water, groundwater, evapotranspiration, and stream water isotopic signatures. Knowledge about the isotopic composition of precipitation is therefore crucial for isotope studies in catchment hydrology."

Comment: p. 1, l. 27: "important role" for what? Location, rate and volume of water input into the soil?

Response: we replaced "…play an important role…" by "…have a significant impact on the input function…"

Comment: p. 2, l. 1: The parentheses should be around the year only.

Response: Changed as suggested.

Comment: p. 2, l. 3: Why should "redistribution in the canopy" have an isotope effect?

Response: We meant to express that redistribution, i.e. movement of water to or from a specific place e.g. via flow along branches, may have an effect on the isotopic composition observed as it also changes the (unknown) spatial pattern of precipitation water isotopes. We addressed this issue in the discussion where it now reads:

"Water redistribution in the canopy, i.e. movement of water to or from a specific place e.g. via flow along branches, may have an effect on the isotopic composition observed as it also changes the unknown spatial pattern of precipitation water isotopes."

Comment: p. 2, l. 5: The mixing was already mentioned in l. 4.

Response: The study cited in l. 4 refers to intra-storm mixing, while the study cited in l. 5 refers to mixing with water from previous events.

Comments: p. 2, l. 6: Perhaps better “deciduous and coniferous” in context with “type”, because spruce and beech are plant species. & p. 2, l. 7: To what do the numbers refer? Interception loss? Throughfall in % of the rainfall? Vegetation cover? & p. 2, l. 8: Enrichment of which isotopes in which compound?

Response p. 2, l. 6-8: We replaced “type” by “species” and rearranged the sentence to:

“Depending on the species (spruce and beech) and on the density of the vegetation cover the volume weighted mean of the interception loss was in a range of 12% to 41%. It was typically higher for small events and therefore generally led to enrichment of heavy isotopes in TF (Brodersen et al., 2000).”

Comment: p. 2, l. 8-10: Is this really done? The following sentence is much more plausible.

Response: The authors found significant differences between P_g and TF depth in their study and argued not to ignore the differences.

We replaced “…is…” by “…would…be…”

Comment: p. 2, l. 13-15: This sentence is confusing. I do not understand it.

Response: We rephrased the sentence to:

”High spatial intra- and inter-storm variabilities have been found in depth and isotopic composition of TF. A synthesis study analysed the spatial variabilities of TF from 18 selected studies at a global scale. The study showed that the spatial patterns of TF, when related to leaf area index (LAI) as well as to spatial variability in general, were very heterogeneous and ecosystem dependent (Levia, 2011).”

Comment: p. 2, l. 16-18: The temporal persistence of spatial throughfall patterns clearly depends on the length of the observation period and on the vegetation type. Please specify both. Furthermore, it is unclear what the cited authors studied: throughfall volume, rate or water isotope composition?

Response: Regarding the vegetation type we added “(coniferous and deciduous)”

The cited authors studied throughfall amounts (l. 17), we added “…(storm-total) for three to seven storms in a six months period...“ before “…with a geostatistical approach…”

Comments: p. 2, l. 20: Are you talking about the same study that you cited just before? Who “hypothesized”? You? & p. 2, l. 21: The collection of representative throughfall volume/rate

data is a classic in ecosystem sciences and it is rather well known how it can be reached. See e.g., Kimmins, J.P., 1973. Some statistical aspects of sampling throughfall precipitation in nutrient cycling studies in British Columbian coastal forests. Ecology 54, 1008–1019. Do you refer to representative stable water isotope ratios?

Response p. 2, l. 20-22: We moved the citation from l. 19 to l.22

The authors referred to stable isotope ratios, therefore we added "… for isotope studies…" before "…is still missing…"

Comment: p. 3, l. 12-14: However, if you want to investigate the mean water isotope ratios of throughfall, you also need a high spatial resolution of your samples to collect a representative throughfall sample as stated earlier in your introduction. Just one pair of samplers above and below the canopy is not sufficient for this purpose.

Response: We are aware of this issue and fully agree. However, we argue that before a setup for TF sampling can be employed multiple times in the field in order to cover the spatial variability of TF isotope patterns the technical challenges need to be solved first. The present paper is meant to aim at this goal.

Comment: p. 3, l. 24-25: Perhaps, the explanation can be a little bit expanded to avoid that the reader has to consult the cited paper.

Response: The method of the cited paper is summarized in l. 19-29. For clarification we modified the sentence in l. 24-25 to

At the membrane's surface, dry carrier gas (e.g. N_2) mixes with vapour diffusing through the pores across the membrane from the liquid phase. Moist air then leaves the contactor…

Comment: p.3 l. 30: The spatial variability of throughfall cannot be appropriately measured with a single collector of limited size. Usually, a large number of collectors is needed to collect a representative sample. I suggest that you make clear that your results refer to a point measurement, which is very likely not representative for the throughfall at larger scale.

Response:

In this study we did not intend to investigate the spatial variability. Therefore, we modified the last paragraph of the introduction to:

"Therefore, the aim of this study is to develop an approach for the analysis of P_g and TF depth and isotopic composition at the point level at high temporal resolution based on the membrane contactor method, to compare and validate the continuous isotope measurements with discrete liquid samples as well as with event-based bulk samples. With this approach the dynamics in amount and isotopic composition of P_g and TF and hence, interception processes influencing amount and isotopic composition of TF can be investigated in unprecedented high temporal resolution."

Comment: p. 4, l. 19: Where was incident rainfall measured? Above the canopy or in an adjacent forest clearing?

Response: We replaced "…10 m apart…" by "…with 10 m horizontal distance from each other…"

Comment: p. 4, l. 20: Acer campestre (in italics) L. - i.e. spell genus name with upper scale A and include author Abbreviation.

Response: Changed as suggested.

Comment: p. 5, l. 10: What does this deviation from the meteoric line tell us? What is the reason for nonequilibrium fractionation? The d value only appears in Fig. 6 but is not addressed in the discussion.

Response: The d values are now considered in the discussion. The respective paragraph reads:

"The lower intensity and total depth of TF as compared to P_g is indicative for evaporation from the canopy. However, this is not reflected in continuous d_{TF} values (Fig. 6) which were expected to follow the trend of d_{Pg} values while being lower after evaporative non-equilibrium fractionation."

Comment: p. 5, l. 14 (and troughout the manuscript): Capdelta values are given without the lower case delta (i.e. DELTA18O, not DELTAdelta18O).

Response: Which guideline do you refer to? DELTAdelta18O is mathematically correct and it is common in the community. Therefore we defined it like this in Eq. (2) and (3).

Comment: p. 5, l. 20: Why did you chose exactly this event? Add properties of the event (date, total volume, intensity).

Response: We added the date to the figure and the caption as suggested. In Fig. 2 we intended to show the temporal variability in both isotope ratios ($\delta^{18}O$ and $\delta^{2}H$) during one 'long' (2 h) event without bubbles at the contactor, the continuous readings, the noise reduction by the moving average, and to illustrate the stepwise loss of information with discrete liquid samples and moreover with the one event-based bulk sample.

Comment: p. 5, l. 21: "grab" samples, anyway being sloppy jargon, sounds strange in the context of water. I at least cannot grab water…

Response: We replaced "… liquid grab…" by "… isotope ratios of discrete…". Throughout the manuscript we replaced "liquid grab samples" by "discrete liquid samples".

Comment: p. 6, l. 13: Usually, one starts with the left figure and then goes to the right one.

Response: Changed as suggested.

Comment: p. 6, l. 29: "cm3" is not the unit of an area.

Response: Changed to cm².

Comment: p. 6, l. 33: "without bubbles at any contactor"

Response: Changed as suggested.

Comment: p. 7, l. 11-13: This statement seems almost trivial. What do we really gain by this higher temporal resolution? How do you interpret Fig. 2? I am a bit disappointed of the depth of the discussion.

Response: We think that the value of our study is, that the high temporal resolution achieved now matches the resolution of routine meteorological observations and thus allows for comparison with these. Consequently, as explained in the revised discussion, continuous P_g and TF isotope data enable new mechanistic modeling approaches aiming at a more realistic simulation of physical processes being effective when P_g becomes TF.

Figure 2 is now addressed several times in the revised discussion:

"*The modified setup of the method developed by Herbstritt et al. (2012) adapted to continuous rainfall and throughfall isotope measurement worked quite well in terms of providing continuous, thermo-regulated flows of water to the membrane modules and delivering reliable liquid water stable isotope data. The latter became evident by the good agreement of continuous measurements and single liquid samples (**Fig. 2** and also Fig. 6) which was in the order of the measurement uncertainty for both isotope ratios under investigation. Large intra-storm variabilities exist in the isotopic signature of P_g and TF, which would have been impossible to detect when solely relying on commonly taken event-based bulk samples or even on data representing a higher sampling interval of typically 5 mm precipitation depth. We found that the variability of the continuous P_g isotope data is higher than the variability of the continuous TF data (Fig. 6). For the latter, the signal is more dampened probably due to mixing processes, which was also found in other studies (Qu et al., 2013). The lower intensity and total depth of TF as compared to P_g is indicative for evaporation from the canopy. However, this is not reflected in continuous d_{TF} values (Fig. 6) which were expected to follow the trend of d_{Pg} values while being lower after evaporative non-equilibrium fractionation."*

…

*"Depletion in heavy isotopes in open site rainfall was observed in the last ~30 minutes of the event presented in **Figure 2**. Several effects could cause such a pattern. The amount effect, reported for lower latitudes (Moore et al., 2014), can be ruled out due to the fact that at the same time rainfall intensity was quite low compared to other periods of this particular rainfall event. Also a rainout effect cannot be attributed to our data as it is only detectible on a spatial scale considering the movement of air masses and rain clouds. Rather, the simultaneous decrease of air temperature indicates the passing of a weather front which appears to be the relevant explanation for the observed changes in precipitation isotope values."*

…

*"Highest $\Delta\delta^{18}O$ values were found in the cases of the continuous observations. One reason could be that the continuously analysed events are shorter and therefore potentially capturing extreme values while bulk samples represent flux-weighted mean isotopic signatures of the entire periods of rainfall and throughfall. On the other hand, we are aware that the calculation and interpretation of synchronous $\Delta\delta^{18}O$ and $\Delta\delta^{2}H$ data are disputable given assumable, yet unknown, time lags between P_g and TF. Within each rainfall event, also past trends and variabilities of the P_g isotopic compositions must be assumed to be reflected in instantaneous TF isotopic compositions, but are not considered with the proposed approach. However, a quite common intra-event P_g isotopic depletion trend (**Fig. 2** and Fig. 6) combined with any positive time lag between P_g and TF would result in higher synchronous $\Delta\delta^{18}O$ values compared to estimates derived from bulk sample data."*

Comment: p. 7, l. 21-22 and Fig. 3: Why do you highlight a non-significant correlation between interception loss and D18O?

Response: The correlation between interception loss and intensity as well as the correlation between interception loss and $\Delta\delta^{18}O$ were selected due to their relatively high Pearson correlation coefficients and their relatively low p-values. Furthermore we expected to see a significant correlation as it has been shown in the cited literature.

Furthermore, you should not show a regression line for non-significant correlations.

Response: We added data to the scatterplot matrix in Fig. 3. Detailed figures with regression lines have been removed.

Comment: p. 7, l. 22: It is unclear what you mean by "There is no clear pattern…" Perhaps: "The explained variance by any of the considered variables alone was generally small, illustrating the complexity of the processes…"

Response: Thank you for the suggestion which was followed.

Comment: p. 7, l. 24-25: This sentence is confusing. It is clear that a bulk sample represents a mean isotopic signature, while at higher resolution the extreme values can be seen, which is trivial.

Response: We agree that this may appear trivial. The point we are trying to emphasize is that depending on the scale of an isotope study high-resolution data is crucial but was not accessible so far with more traditional approaches. Furthermore this sentence was meant to be rather introductory.

Comment: p. 8, l. 1-2: Furthermore, there is a pronounced spatial variation of throughfall quantity and quality, which cannot be captured with a single collector (see above).

Response: We did not intend to cover the spatial variation. We tried to make this point clearer when stating the aims of our study as well as in the revised conclusions. The respective segments now read:

"Therefore, the aim of this study is to develop an approach for the analysis of P_g and TF depth and isotopic composition at the point level at high temporal resolution based on the membrane contactor method, to compare and validate the continuous isotope measurements with discrete liquid samples as well as with event-based bulk samples. With this approach the dynamics in amount and isotopic composition of Pg and TF and hence, interception processes influencing amount and isotopic composition of TF can be investigated in unprecedented high temporal resolution."

…

"We are therefore confident that our setup, especially when employed across larger spatial scales, will contribute to the aim of thorough isotopic sampling of TF, which is crucial in hydrological studies in particular for forested sites but also for other vegetated areas."

Comment: p. 8, l. 4: This repeats l. 22 (as the whole Fig. 6 is repetitive of Fig. 2 – albeit for another arbitrarily selected rainfall event).

Response: We added the date to the figure and the caption as suggested. In Fig. 2 we intended to show the temporal variability in both isotope ratios ($\delta^{18}O$ and $\delta^{2}H$) during one 'long' (2 h) event without bubbles at the contactor, the continuous readings, the noise reduction by the moving average, and to illustrate the stepwise loss of information with discrete liquid samples and moreover with the one event-based bulk sample.

In Fig. 6 only the moving average is shown, no continuous readings and no bulk sample data. P_g- and TF-data of the parallel measurements are shown, including potential artefacts due to bubbles in the contactor when intensities get below a certain threshold. Additionally, meteorological variables are shown that may influence the isotopic signature.

Comment: p. 8, l. 7: extent

Response: Changed as suggested.

Comment: p. 8, l. 11: The ultimate objective would be the prediction of the mean input signal of throughfall into soil for a whole forested catchment or even the spatial distribution of this input signal, which would require much more extensive instrumentation.

Response: We fully agree, but we did not intend to cover the spatial variation as pointed out above.

Comment: p. 8, l. 14: I think that "point" level is more appropriate, because you cannot extrapolate your measurement with a single collector to a larger area. Plots I think of are at least 10 x 10 m large and on such plots you might easily need > 10 collectors to measure the mean throughfall properties with an acceptable uncertainty.

Response: We deleted "…at the plot level…" and instead addressed this issue a few lines later:

"We are therefore confident that our setup, especially when employed across larger spatial scales, will contribute to the aim of thorough isotopic sampling of TF, which is crucial in hydrological studies in particular for forested sites but also for other vegetated areas."

Comment: p. 8, l. 18: I would really be keen to learn about what we can gain by measuring the stable isotope ratios of water at this high resolution. Can we distinguish different processes or even quantify the contributions of these processes to the total throughfall?

Response: We agree that effort should be made to identify the different processes contributing to total throughfall. We are confident that the method described here has the potential to contribute to this goal. Further, in the revised manuscript we sketched a modeling approach aiming at this goal.

Comment: p. 8, l. 22: I agree that this is crucial, but again point at the problem of spatial representativity of the measurements which cannot be reached with the approach used in this paper.

Response: We rephrased the respective sentence which now reads:

"We are therefore confident that our setup, especially when employed across larger spatial scales, will contribute to the aim of thorough isotopic sampling of TF, which is crucial in hydrological studies in particular for forested sites but also for other vegetated areas."

Comment: p. 8, l. 28: I wonder whether the authors are aware of the modelling efforts of Rutter et al. (1971), Agric. Meteorol., Gash and Morton (1978), J. Hydrol. and Gash (1979), Q. J. R. Meteorol. Soc. I think that it could be a way forward to add an isotope module to these models.

Response: We are aware of these publications and agree that this could be a way forward. Our perception is that the issues of intra-canopy mixing and the time lag between P_g and TF need to be addressed before further modelling efforts are feasible.

Comment: Fig. 3: Add how many events were sampled to the figure legend. Furthermore, part of the lettering is too small.

Response: Added and changed as suggested.

Comment: Fig. 4: Number subfigures.

Response: Changed as suggested.

Comment: Fig. 6: I suggest to combine this figure with Fig. 2. Both figures show stable isotope results for arbitrarily chosen individual events but only Fig. 6 is accompanied by the necessary information about the (micro-)meteorologic conditions.

Response: Both figures are now addressed to a greater extent in the revised discussion. We therefore considered it justified to present them both individually.

Furthermore, the d values are only shown but not interpreted. Either you add an interpretation of these results or remove the d values entirely.

Response: The d values are now considered in the revised discussion. The respective paragraph reads:

"The lower intensity and total depth of TF as compared to P_g is indicative for evaporation from the canopy. However, this is not reflected in continuous d_{TF} values (Fig. 6) which were expected to follow the trend of d_{Pg} values while being lower after evaporative non-equilibrium fractionation."

Furthermore, I am confused by the legend stating "in vapour". I understood that you indeed measured isotope ratios in vapour produced from a liquid sample in your contactor but you referred these values back to the liquid sample via a temperature-dependent calibration function. Do you indeed want to show the isotope ratios in vapour (not referred back to the liquid sample)? Why?

Response: We regret the confusion. You understood right that all vapour data is back calculated to the liquid phase. By referring to 'vapour' in figure caption and legend we meant to indicate where our continuous data were derived from.

We added "…derived from…" in the figure caption to avoid this confusion.

Response to reviewer comments RC2

We thank you for your thoughtful comments and making us aware of open questions.

Please find below a list of specific responses to the individual points.

Responses to comments are shown in blue.

Hydrol. Earth Syst. Sci. Discuss.,

https://doi.org/10.5194/hess-2018-301-RC2, 2018

Interactive comment on “Real-time observations of stable isotope dynamics during rainfall and throughfall events” by Barbara Herbstritt et al.

Anonymous Referee #2

Received and published: 20 July 2018

The manuscript “Real-time observations of stable isotope dynamics during rainfall and throughfall events” by Herbstritt et al. presents and discusses an experimental setup designed to monitor in parallel the stable isotope composition of rainfall (Pg) and throughfall (TF) at high resolution during several summer rainfall events. High resolution stable isotopes in rainfall have already been observed and documented in previous studies. Yet, this study is the first I am aware of that compared the rapid dynamics of rainfall and throughfall and looked into their mass weighted average difference over several rainfall events. In the abstract and the introduction, the authors summarize the importance, extent, and main reasons of the difference between isotopic composition of throughfall and that of rainfall. The authors justify the need for a comparison of these signatures at a higher resolution than in the past, which reflects their measurement setup. This is described in the method section and well-illustrated in Figure 1. The results show time series of stable isotopes in TF and Pg, differences between them (dynamics and means), and an attempt to find correlations between such differences and meteorological variables. The discussion essentially deals with some of the limitations of the approach.

The manuscript is clear and concise, and the figures are of good quality.

Yet, no or only minor mechanistic understanding is provided. It will be a good contribution to isotope hydrology, after having addressed several comments and after some questions are clarified.

The **introduction** and the **discussion** need to state clearer in what way this measurement setup can provide a more accurate estimate of the isotopic recharge in the catchments for typical applications in isotope hydrology.

Why is it not enough to just consider the average mass weighted difference between isotopes in TF and Pg?

What is a necessary detail of measurement?

One figure that would improve in the manuscript in that regard is the relationship between precipitation intensity and $\Delta\delta$ for each measured storm. Are isotopic differences larger for higher intensities during a single event?

A more detailed description of the applications of tracers in isotope hydrology is also needed in the introduction. The discussion needs to argue for which application this time-varying difference really is important. For instance, are End Member Mixing Analysis (Hooper et al., 1990), isotope hydrograph separation (Klaus & McDonnell, 2013), or travel time modeling (McGuire & McDonnell, 2006; Rinaldo et al., 2015; Hrachowitz et al., 2016) able to incorporate such high-frequency data and distinguish between Pg and TF?

Some clarifications of details in the method sections will be necessary (see details below), as some important information was skipped.

Furthermore, the English is somewhat bumpy especially in the first half of the introduction, and should be carefully revised before the manuscript is resubmitted.

Eventually, one may consider to change the manuscript into a technical note, since many of the hydrological aspects are discussed rather briefly and the key contribution is the measurement of high-frequency variations in stable isotopes of Pg and TF and their characteristics. No mechanistic understanding is provided by the manuscript. The main conclusion also starts with the technological aspect.

Specific comments:

Abstract

line 15 The 4 min time-lag information can be confusing with respect to the 2 sec reading interval. Please make it clearer that the time-lag is the transfer time from the collector to the laser in the instrument. How does dispersion/ diffusion potentially influence this?

Response: We inserted "…from rainfall collector to isotope analyser…" after "…four minutes…". Dispersion in the small funnel must be assumed which is why we calculated a

moving average. Dispersion and diffusion can be considered neglectable in the tubing given the small diameters.

page 1: line 1ff. Please tighten up and do a better job in pointing out the relevance of isotopes from here until page 2 line 12.

Response: We rephrased major parts of the introduction, pointing out the importance of isotope studies for the determination of water flow and transport processes.

line 20 I would omit the word “signature”, since the stable isotopes are the tracers, while their signatures are measurements.

Response: Changed to “ratios”.

line 25 Move the citations (Kendall and McDonnell [. . .]) to line 22 after “water cycle” line 25 “There is. . . hydrology” I would omit that sentence which looks somehow too isolated, see previous comment.

Response: Changed as suggested.

line 26 “residence times” is vague. Is it canopy, soil, or catchment residence times? Please be more precise.

Response: We inserted “catchment”.

Line28 New sentence after “Allen et al. . .”. Delete “Since” Line 28 Citations after “forested” needed.

Response: We rephrased to

“Many studies have used the temporal dynamics in the isotopic composition of precipitation for estimating catchment residence times, but especially in forested catchments, when meteorological and isotopic reference stations are in the open, interception losses and accompanying isotope effects have a significant impact on the input function (Xu et al., 2014;

Stockinger et al., 2015; Allen et al., 2017). The importance of understanding rainfall interception processes is presented in a thorough review by Allen et al. (2017).”

page 2: line 1 must be . . .”Allen et al. (2017).”

Response: Changed as suggested.

line 13 delete “Typically”; found for what? Precip? TF? Runoff? References needed

and

line 15 “spatial variability in general” is to general. Please elaborate

Response: We rephrased the respective segment to:

”High spatial intra- and inter-storm variabilities have been found in depth and isotopic composition of TF. A synthesis study analysed the spatial variabilities of TF from 18 selected studies at a global scale. The study showed that the spatial patterns of TF, when related to leaf area index (LAI) as well as to spatial variability in general, were very heterogeneous and ecosystem dependent (Levia et al., 2011).”

line 17 Ref needed after “diameters”. Replace “They” by “The authors” or “Keim et al.”

Response: A reference was added. We replaced “They” by “The authors”.

page 3: line 18 in-situ

Response: Changed as suggested.

line 24,27 SPACE between numeric value and unit needed

Response: Changed as suggested.

page 4: lines 2-4 What is the dead volume inside smaller funnel just before the pump? How is it made sure that all the water exceeding the pump flowrate Qp is spilled into the bulk sample?

Response: after "...was spilled…" we inserted

"… and collected via an additional funnel into a sampling bottle. This overflow was volume-weighted, contributing…"

In my perception, if Vd is the dead volume of the smaller funnel (let's assume Vd = 3 mL), then assuming complete mixing, the isotope signature effectively recorded is a moving average of the precipitation, with a time window of length Vd/Qp, i.e. about 36 sec. Please elaborate on this!

Response: We see your point and agree. However, time windows shorter than 90 s yielded quite "noisy" data.

lines 14-16 Were these discrete samples analyzed later in the lab?

Response: Yes, these samples were analyzed later in the lab. For clarification we changed the sentence to

"…discrete liquid samples were taken every five minutes at the liquid outlet port of the membrane module and analysed later in the laboratory."

line 19 Is 10 m really sufficient to make sure that there are no effects of the trees at all on the gross precipitation? Did you see an effect of wind direction etc?

Response: Due to the height where the samplers were installed and the size of the tree the distance was considered sufficient (45° vertical clearance, WMO guidelines). We did not observe meaningful effects of wind direction.

line 20 How many events were recorded in total? It is never mentioned in the text. It also makes it difficult to follow the results. Add also more details about the events in tables.

Response: The number of recorded events is added as suggested:

"In total 28 bulk samples and nine continuously analysed events were obtained in August-September 2015 and throughout the vegetation period (May-September) of 2016."

A table has been added listing the characteristics of the continuously analysed events.

page 5: lines 2-9 How was calibration applied? Did you apply an individual correction for each rainfall event based on the 3 measured standards? More details are needed here. Also, how did you ensure that there were no memory effects between standards when measuring them consecutively?

Response: Yes, we applied an individual calibration for each rainfall event. For clarification we added "…until a plateau in the isotope readings was reached (~ 10 minutes)…" after "…each rainfall event…".

line 6 What is meant by "long term changes in the membranes"? Please elaborate

Response: Small particles could be removed by back flushing, whereas the built-up of biofilms or mechanical changes of the membrane ("membrane fouling") would change its characteristics over time. We inserted "…e.g. built-up of biofilms or mechanical changes (small cracks, fissures) at the membrane…" after "…long term changes…".

line 17 It should be mentioned here already why the VPD is calculated.

Response: We inserted "…to indicate potentially high or low evaporation…" after "…is calculated…".

line 20 What date did the event happened? This also needs to appear in the caption of Figure 2. Why not show directly the comparison between isotopes in Pg and TF in Figure 1, as in Figure 6?

Response: We added the date to the figure and the caption as suggested. In Fig. 2 we intended to show the temporal variability in both isotope ratios ($\delta^{18}O$ and $\delta^{2}H$) during one 'long' (2 h) event without bubbles at the contactor, the continuous readings, the noise reduction by the moving average, and to illustrate the stepwise loss of information with discrete liquid samples and moreover with the one event-based bulk sample.

page 6: line 1 It looks like the isotopes in Pg are getting lighter while rainfall intensities are getting lower. Is that not contradictory with the amount effect?

Response: At the end of this specific rainfall event air temperature dropped, which could explain this effect. For clarification we added the temperature data to the figure. Further, we added the following paragraph to the revised discussion:

"Depletion in heavy isotopes in open site rainfall was observed in the last ~30 minutes of the event presented in Figure 2. Several effects could cause such a pattern. The amount effect, reported for lower latitudes (Moore et al., 2014), can be ruled out due to the fact that at the same time rainfall intensity was quite low compared to other periods of this particular rainfall event. Also a rainout effect cannot be attributed to our data as it is only detectible on a spatial scale considering the movement of air masses and rain clouds. Rather, the simultaneous decrease of air temperature indicates the passing of a weather front which appears to be the relevant explanation for the observed changes in precipitation isotope values."

lines 3-4 I suppose the interception loss is (Pg-TF)/Pg*100. It should be stated clearly how you calculated it.

Response: This is correct. We added this equation to the method section.

line 13 Were the interception losses and the $\Delta\delta^{18}$O greater with time and plant growth from May to September? A plot with $\Delta\delta^{18}$O in time during the growing season could be useful here. Any data on LAI?

Response: We looked at potential effects of the vegetation period without finding meaningful relationships. We added the following sentence to the manuscript:

"In any case, the measurements were carried out during the period when the leafs had reached their full size, in order to minimize the influence of the growing season."

Unfortunately, we did not have any LAI data.

line 15 Is this mean difference flux weighted? I think this is important to emphasize.

Response: Yes, the mean of each event (P_g and TF separately) was flux weighted and the difference was calculated from the flux weighted means. We added this information to the manuscript.

Line 21 “all events”, see above, more information needed

Response: We replaced “…all events…” by “…nine continuously observed events…”.

line 29: cm3 should be cm2

Response: Changed as suggested.

page 7: lines 1-2 Why is the TF signature more damped than the Pg signature?

Response: We assume that this is due to mixing in the canopy. This issue is now addressed in the revised discussion:

“We found that the variability of the continuous P_g isotope data is higher than the variability of the continuous TF data (Fig. 6). For the latter, the signal is more dampened probably due to mixing processes, which was also found in other studies (Qu et al., 2013).”

Lines 2-4 Maybe it is because of the scale, but it does not seem like the VPD is decreasing on figure 6. Please clarify. Also, why not look at the relationship between VPD, Ta, and time-variable $\Delta\delta$ for all events? Some meaningful correlation could exist.

Response: We looked at these relationships without finding meaningful relations.

lines 10- 11 Some statistics about the differences between continuous measurements and the single liquid samples would be nice here to emphasize that point, even though it looks valid just when looking at the figures. For example, what was the average difference between the single liquid samples and the corresponding moving average values for each event? For all events? Does that vary a lot between events?

Response: This information can be found in the results section of the revised manuscript:

“Mean absolute deviation between the moving average of the continuously analysed vapour data and the discrete liquid samples was 0.11‰ and 1.35‰ with standard deviations of 0.096‰ and 0.81‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively.”

We also extended the discussion by inserting:

"…which was in the order of the measurement uncertainty for both isotope ratios under investigation."

lines 17-18 How are "wet", and "dry" canopies defined?

Response: We defined "dry" by adding "…i.e. 6 hours without rainfall,…" to the results section.

line 25 So, why are the average differences in bulk samples and continuous samples so different? I think this is a crucial part of the manuscript showing why the measurement protocol proposed here is valuable!

Response: We discussed this issue now in greater detail and also provided a possible explanation for the observed discrepancies:

"Comparing $\Delta\delta^{18}O$ data during continuously measured events with those derived from event-based bulk samples, the differences are larger during the shorter continuously measured periods (Fig. 4). It should be noted that in this case the definition of a rainfall event is not consistent. Bulk samples cover the entire time period of rainfall regardless of intensity at the point of observation and mere existence of rainfall at the complementary observation point (P_g vs. TF). In contrast, continuous events are defined by sufficient simultaneous rainfall intensity at both points of observation due to our setups' properties. Therefore, natural rainfall events can only partially be captured by continuous synchronous observations. At the same time bulk samples represent the flux-weighted mean of all conditions constituting the respective event."

…

"Highest $\Delta\delta^{18}O$ values were found in the cases of the continuous observations. One reason could be that the continuously analysed events are shorter and therefore potentially capturing extreme values while bulk samples represent flux-weighted mean isotopic signatures of the entire periods of rainfall and throughfall. On the other hand, we are aware that the calculation and interpretation of synchronous $\Delta\delta^{18}O$ and $\Delta\delta^{2}H$ data are disputable given assumable, yet unknown, time lags between P_g and TF. Within each rainfall event, also past trends and variabilities of the P_g isotopic compositions must be assumed to be reflected in instantaneous TF isotopic compositions, but are not considered with the proposed

approach. However, a quite common intra-event P_g isotopic depletion trend (Fig. 2 and Fig. 6) combined with any positive time lag between P_g and TF would result in higher synchronous $\Delta\delta^{18}O$ values compared to estimates derived from bulk sample data."

line 27 What process could explain that a wet canopy leads to an even stronger enrichment?

Response: We added the following sentence to the discussion:

"The fact that wet canopies lead to an even stronger enrichment in heavy isotopes can probably be attributed to partly evaporated and therefore isotopically enriched pre-event water that mixes with new rainfall water."

Figure 1 Is the beginning of the event missed because of the stabilization of T? That info would be nice in the figure caption.

Response: Yes, the beginning of the event was missed. Therefore, we inserted

"…starting after temperature at the contactor was stable".

Figure 5 A legend with the date of each event and the corresponding lines would be nice here.

Response: We added a legend with IDs to every line in Fig. 5. Further, we added a table listing the date and further characteristics of each event.

Figure 6 The points for d_Pg and d_TF in the legend are too small and hard to distinguish. The date of the event is missing.

Response: We changed the color to make the symbols more distinguishable. Further, the date of the event was added to the figure caption.

Thanks for the interesting contribution to isotope hydrology!

☺

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Response to reviewer comments RC3

We thank you for your thoughtful comments and making us aware of open questions.

Please find below a list of specific responses to the individual points.

Responses to comments are shown in blue.

Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2018-301-RC3, 2018

Interactive comment on "Real-time observations of stable isotope dynamics during rainfall and throughfall events" by Barbara Herbstritt et al.

Anonymous Referee #3

Received and published: 26 July 2018

The discussion paper "Real-time observations of stable isotope dynamics during rainfall and throughfall events" presents an suitable approach for continuous observation of stable water isotope composition in precipitation and throughfall at the plot level. The paper is very well structured and written. The presentation of results is in general very clear and straight forward. I think, however, that the discussion could be extended in order to explain the findings or show that with the given data no explanation is possible.

The focus of the paper is to test the methodological approach. But as the approach was tested in a natural environment, possible natural influences should be discussed e.g. the possible effect of different initial rainfall d18O values for different events and and its possible relation to low isotopic ratios for events with antecedent dry conditions.

This could be linked to the level of rainout of the air mass before the events.

The discussion also lacks relating the results to the existing literature. Some examples are given below, but the revision should not be restricted to these examples. Right now, the discussion only provides two citations and one of it is a self-citation. Beside this, the following specific comments should be addressed before the publication of the manuscript in HESS.

Page 2, Line 5: "These effects": The before mentioned effects include "mixing with water from previous events", which does not affect the mean amount of weekly sampled TF compared to Pg. Please improve the wording.

Response: Thanks. You are absolutely correct. We accidently mixed up two literature sources. We replaced "…weekly…" by "…event-based…" to be in concordance with Allen et al. (2014).

Line7: Not the absolute interception loss is higher for small events, but the relative loss compared to rainfall.

Response: We rephrased the sentence to "…the volume weighted mean of the relative interception loss…"

Line 8: Insert "depth" after TF at the end of the line.

Response: Changed as suggested.

Line 13: "isotopic composition" please indicate whether this is related to TF or something else?

Response: We inserted "…of TF".

Line 16: "94 gauges" These are TF collectors?

Response: We replaced "gauges" by "TF collectors".

Line 18: Change "temporal" to "spatiotemporal".

Response: Changed as suggested.

Page 3, Methods: The bulk sampling method needs to be added to the methods section.

Response: We rephrased the respective segment. It now reads:
"From there, a stream of water was pumped to the membrane contactor with a peristaltic pump at a constant flowrate of 5 mL/min while at the same time water exceeding this flowrate was spilled and collected via an additional funnel into a sampling bottle. This overflow was volume-weighted, contributing to the event-based bulk sample."

Line 32: Delete “when measured below the canopy” as TF can’t be measured elsewhere than below the canopy.

Response: Changed as suggested.

Page 4, Line 7: “periodical back flushing” How often was this done?

Response: We rephrased the sentence to:
“… could be facilitated by back flushing with deionized water as needed or periodical rinsing (every 2 to 4 weeks) with weak acids, respectively.”

Line 17: As it hasn’t be said until this point that there was 1 collector for rainfall and one for throughfall the reader can’t understand to what “each collector” is referring to. Please clarify.

Response: Thanks, we replaced “each” by “the”.

Line 23-25: Were all these meteorological variables used in the publication? If not than keep only those that were used.

Response: Changed as suggested.

Page 5, Line 20: “high rainfall intensities” Consider rewording as the reader does not know if “high” is related to this event or to all events sampled.

Response: “(Fig. 2)” was added for clarification.

Line 22-23: Please reword as it is not the samples that are shown but the isotopic ratios of these samples.

Response: We inserted “…isotope ratios of discrete liquid, …” and replaced “sampling” by “analysing”.

Page 6, Line 4: Change “compared” to “correlated to each other”.

Response: Changed as suggested.

Line 5: The authors might add that the correlation is significant, but rather moderate.

Response: Added as suggested.

Line 6: Insert “percentage of” before “interception loss” as the absolute interception loss is probably higher for greater rainfall intensities.

Response: Changed as suggested.

Line 8: There is no positive correlation. The weak correlation is not significant.

Response: Rephrased as suggested.

Line 13: Please rephrase this sentence. “2-2.5 per mille” were not found “in d18O values”.

Response: We rephrased the sentence to
“The data of the bulk samples (Fig. 4, right) were grouped into 0.5‰-classes. The maximum of 2 - 2.5‰ in $\Delta\delta^{18}O$ values was calculated only for two events, while for 23 of the 28 events $\Delta\delta^{18}O$ was 1.5‰ or less.”

Line 17: How was dryness or wetness of the canopy before an event started monitored? I assume that dry and wet is interfered from a certain period of time without rainfall. This should be described in the revised manuscript.

Response: We inserted “…, i.e.after at least 6 hours without rainfall…” after “dry canopy”

Line 23: If the information about Dd2H is important then I suggest to take it out of the brackets and include it in the sentence with “and” and “respectively”. Otherwise it should be omitted.

Response: Changed as suggested.

Page 7, Line 11-12: Is this in line with the literature? E.g. see (Qu et al., 2014). Please extend the discussion.

Response: The discussion has been extended accordingly:
"Large intra-storm variabilities exist in the isotopic signature of P_g and TF, which would have been impossible to detect when solely relying on commonly taken event-based bulk samples or even on data representing a higher sampling interval of typically 5 mm precipitation depth. We found that the variability of the continuous P_g isotope data is higher than the variability of the continuous TF data (Fig. 6). For the latter, the signal is more dampened probably due to mixing processes, which was also found in other studies (Qu et al., 2013)."

Line 21-22: Figure 3 only shows one significant correlation. Please correct this sentence.

Line 21: An explanation should be given why there is a negative correlation of rainfall intensity with interception loss. I can imagine that this is in line with what others have found for bulk samples. If possible respective references should be added.

Line 21-22: Is this in line with results reported in the literature? See e.g. (Dewalle and Swistock, 1994; Kato et al., 2013)

Response: Figure 3 has been reworked and also covers more variables now. The respective paragraph has been rephrased to:
"In the data of the collected bulk samples a significant negative correlation between interception loss and the meteorological variable rainfall intensity as well as a moderate negative correlation between relative interception loss and depth of incident rainfall could be observed (Fig. 3).This means that the highest interception losses were found during events with either lowest rainfall intensities or with lowest depths. A weak positive relationship also existed between $\Delta\delta^{18}O$ and interception loss, indicating that $\Delta\delta^{18}O$ increases with increasing interception losses. This is in line with results found in other studies (Dewalle and Swistock, 1994; Brodersen et al.; 2000, Keim et al.; 2005, Kato et al., 2013; Allen et al., 2017). Only non-significant correlations were found between the other investigated quantities. …"

Line 22: I don't understand what the authors mean with "There is no clear pattern for only one of these variables. . ."

Response: We rephrased the respective sentence. It now reads:

"The small explained variance between any of the considered variables illustrates the complexity of the processes contributing to interception loss and the transformation of P_g isotope ratios when becoming TF."

Line 26-27: This needs to be related to what was reported earlier in the literature (e.g. Allen et al., 2013).

Response: We rephrased the respective sentence to:

"This supports the interpretation that antecedent conditions have a clear impact on isotopic enrichment of TF which was also described in previous studies (Keim et al., 2005; Allen et al., 2014; Stockinger et al., 2015; Allen et al., 2017).

There is more room for interpretation here. For instance, the difference of d18O in rainfall and throughfall is presented for different events and discussed, but the level of d18O of rainfall for different events is not presented.

Response: We added the range of $\delta^{18}O$ for the observed events to the results section. For the interpretation of interception processes we preferred to focus on the changes of the isotopic compositions ($\Delta\delta^{18}O$) rather than the absolute numbers ($\delta^{18}O$).

For events for which the degree of rainout from Ocean to inland is low, levels of d18O of rainfall could be higher. Would it be possible that high initial levels d18O in rainfall lead to rather smaller increases of d18O from rainfall to throughfall?

Response: We see your point but currently can't think of a physical reason that would support this hypothesis. We additionally looked at the relationship without finding any significant correlation.

Page 8, Line 7-9: Scatterplots only presented for bulk samples.

Response: We refer to the results shown in Fig. 4 to 6.

Figure 1: For me it is not absolutely clear whether Pg is collected by the same collector for the water that goes through the tipping bucket and that one that is sampled. So is there only

one collector for each, Pg and TF, and the water go first through the tipping bucket and then the pump samples the water? Please clarify this in the figure. I think that the triangle within the box illustrates the tipping bucket, right? This must be shown more clearly.

Response: We reworked Figure 1 as suggested to clarify this point.

Figure 2: Add “depth” after “Time series of rainfall”.

Response: Changed as suggested.

Figure 2: In the text it says that the event duration was only 2 hours, but in the legend a “three-hour bulk sample” is mentioned.

Response: In order to also collect the water dripping from the canopy, the throughfall sampler was emptied later. We changed the legend to “bulk sample”.

Figure 2: Please provide the date of this event in the legend.

Response: Added as suggested.

Figure 3: I don’t the point in part a) and b) of figure 3. The only additional information is the p-value. But the p-value should be added to the left side figure part for all correlations, e.g. in parentheses below the correlation coefficients. If the reason for a) and b) was to have interception on the x-axis, then it should be plotted as the first variable in the left side figure.

Response: Figure 3 has been reworked and also covers more variables now. Detailed figures (a) an (b) have been removed. Levels of significance for all correlations have been integrated into the main figure as suggested.

Figure 3: This is not a scatter plot of throughfall samples. Please rephrase the figure caption.

Response: Changed as suggested.

Figure 3: Please indicate in the figure that the intensity is that one of rainfall (and not throughfall).

Response: Changed as suggested.

Figure 3: Please explain in the legend what is shown the lower left und the upper right part of the figure on the left side. Include an explanation, why the size of the correlation coefficients differ. Is that really needed? The small numbers are hard to read.

Response: In the reworked Figure 3 an explanation in the figure caption is added as suggested. The font size of the correlation coefficients has been unified.

Figure 3: I suggest adding d18O of rainfall and throughfall and the length of the antecedent dry period to the scatter plot.

Response: $\delta^{18}O$ data have been added to the scatter plot as suggested. We didn't show the data about the length of the antecedent dry periods because not all relevant time scales were sufficiently represented in our dataset.

Figure 4: Please shift the right figure to the left side as it is mentioned first in the text.

Response: Changed as suggested.

Figure 5: Which of these events are shown in figures 2 and 6?

Response: The event shown in Fig. 2 is not represented in Fig. 5. Information about which events are shown in Fig. 6 can be found in the new Table 1. A legend with the respective event IDs is added to Fig. 5.

Figure 5: There are events for which Dd18O increases with time and others with an opposite trend. Does Dd18O correlate with d18O of rainfall per event?

Response: We looked at this relationship without finding a significant correlation.

Figure 6: Indicate the date of this event.

Response: Changed as suggested.

Figure 6: Delete “amounts,” from the first line of the figure caption.

Response: Changed as suggested.

Figure 6: The colours of d_Pg and d_TF are hard to distinguish.

Response: We changed the color to make the symbols more distinguishable.

Figure 6: Why did throughfall start before rainfall?

Response: Rainfall started before 19:27 already, but data are shown from the time when temperature at the contactor was stable.

References:

Allen, S.T., Brooks, J.R., Keim, R.F., Bond, B.J., McDonnell, J.J., 2013. The role of preâˇARˇ event canopy storage in throughfall and stemflow by using isotopic tracers. Ecohydrology 7, 858–868. https://doi.org/10.1002/eco.1408

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Real-time observations of water stable isotope dynamics during rainfall and throughfall events

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Abstract. The water isotopic composition of throughfall is affected by complex diffusive exchange, evaporative enrichment of heavy isotopes, and mixing processes in the tree canopy. All interception processes occur simultaneously in space and time generating a complex pattern of throughfall ~~amount~~ depth and isotopic composition. This pattern ultimately cascades through the entire hydrologic system and is therefore crucial for isotope studies in catchment hydrology where recharge areas are often forested while reference meteorological stations are generally in the open. For the quasi real-time observation of the water isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) of both gross precipitation and throughfall we developed an approach combining a~~n off the shelf~~ membrane contactor (Membrana) with a laser-based Cavity Ring-Down Spectrometer (CRDS, Picarro), obtaining isotope readings every two seconds. ~~For the continuous observation of the temporal effect of interception processes two~~A setup~~s~~ with two CRDS instruments in parallel ~~were used~~ analysing gross precipitation and throughfall simultaneously was used for the continuous observation of the temporal effect of interception processes. All devices were kept small to minimize dead volume and thereby, with time-lags of only four minutes for water from the rainfall collectors to the isotope analysers, to increase the temporal resolution of isotope observations. Complementarily, meteorological variables were recorded ~~in~~ at high temporal resolution at the same location. ~~Comparing these high temporally resolved continuous measurements with discrete liquid or event based bulk samples, this approach proves to be a powerful tool towards more insight in the very dynamic processes contributing to interception during rainfall events.~~ The achieved evolution from discrete liquid or event-based bulk samples to continuous measurements allows for direct comparison with common meteorological measurements. This makes our approach a powerful tool towards more insight in the dynamic processes contributing to interception during rainfall events.

1 Introduction

Stable isotope ratios ~~signatures~~ of water ($\delta^{18}O$ and $\delta^{2}H$) are ideal tracers due to the fact that they are part of the water molecule itself (Gonfiantini, 1986). They have proven to be powerful tools ~~in hydrology~~for the characterisation of water flow and transport processes with a long record of applications at different spatial and temporal scales and in all parts of the water cycle (Kendall and McDonnell, 1998; Vitvar et al., 2005). The isotopic composition of precipitation ultimately cascades through the entire hydrologic system affecting soil water, groundwater, evapotranspiration, and stream water

isotopic signatures. Knowledge about the isotopic composition of precipitation ~~and~~ is therefore crucial for isotope studies in catchment hydrology. ~~There are extensive reviews of stable isotope applications in catchment hydrology (Kendall and McDonnell, 1998; Vitvar et al., 2005).~~ Many studies have used the temporal dynamics in the isotopic composition of precipitation for estimating catchment residence times, but especially in forested catchments, when meteorological and isotopic reference stations are in the open, interception losses and accompanying isotope effects ~~play an important role~~have a significant impact on the input function (Xu et al., 2014; Stockinger et al., 2015; Allen et al., 2017)~~.~~. ~~since recharge areas are often forested whereas meteorological and isotopic reference stations are generally in the open.~~ The importance of understanding rainfall interception processes is presented in a thorough review by ~~(~~Allen et al.~~,~~ (2017). The reasons for the differences in amount and isotopic composition of gross precipitation (P_g) and throughfall (TF) are complex, since multiple interacting processes affect TF. They are driven by evaporation from the canopy during or between storms, ~~isotopic~~ diffusive exchange with ambient vapour, redistribution in the canopy, and storage effects where water is differentially retained or mixed. Also sub-canopy water recycling i.e. evapotranspiration and re-condensation (Green et al., 2015) as well as mixing with water from previous events (Allen et al., 2014) has been described. These effects reduced the mean ~~amount~~ depth and the difference in isotopic composition of ~~weekly~~ event-based sampled TF compared to P_g. ~~Depending on the type (spruce and beech) and density of the vegetation cover in a range of 12% to 41% (Brodersen et al., 2000) the interception loss has typically been higher for small events and generally leading to isotopic enrichment of TF.~~ Depending on the species (spruce and beech) and on the density of the vegetation cover the volume weighted mean of the relative interception loss was in a range of 12% to 41%~~.~~. It was typically higher for small events and generally led to enrichment of heavy isotopes in TF (Brodersen et al., 2000). However, ignoring the differences between P_g and TF depth results in an overestimation of the input amount to the system and ~~is~~ would therefore be a source of error in hydrograph separation (Kubota and Tsuboyama, 2004) and other isotope related analyses. In ungauged catchments or when only P_g instead of TF data are available, isotopic correction factors were determined empirically (Stockinger et al., 2015; Calderon and Uhlenbrook, 2016) serving as surrogates to compensate for the lack of respective TF isotope data.

~~Typically h~~High spatial intra- and inter-storm variabilities have been found in ~~amount~~ depth and isotopic composition of TF. ~~In a~~A synthesis study analys~~ed~~~~ing~~ the spatiotemporal variabilities of TF from 18 selected studies at a global scale. ~~It~~ The study showed that the~~ir~~ spatial patterns of TF, when related to leaf area index (LAI) as well as to spatial variability in general, were very heterogeneous and ecosystem dependent (Levia et al., 2011). Another study used a set of 94 ~~gauges~~ TF collectors at three different forested sites, covering different ~~species~~ types (coniferous and deciduous) and ages of trees, canopy densities and canopy diameters. The~~y~~re the authors investigated the spatial dependence of TF ~~amount~~depth (storm-total) for three to seven storms in a six months period with a geostatistical approach finding a high spatiotemporal persistence (Keim et al., 2005). Recently, the observation of high spatial variability in collected TF stable isotopic compositions could be improved by using a set of roving collectors (Allen et al., 2015). Although hypothesized by the authors, intra- and inter-storm variabilities of TF amount did not necessarily correspond with variations in isotopic

composition. Consequently, collecting representative TF input data for isotopes studies is still missing and an observational challenge (Allen et al., 2015).

Traditionally, the isotopic composition of liquid water is determined with discrete samples being analysed in the laboratory, hence conducting isotope studies always implied a trade-off between limited spatio-temporal resolution and extensive (and expensive) lab work. With the recent development of laser-based isotope analysers like off-axis integrated cavity output spectroscopy (OA-ICOS) or Cavity Ring-Down Spectroscopy (CRDS), there is now the possibility to analyse water stable isotopes faster and less expensive. The fact that water vapour is analysed directly 'as water' together with the field-deployability of the analysers and the virtually instant availability of isotope readings made way for several attempts aiming at in-situ isotope observations with high temporal resolutions. Berman et al. (2009) and Pangle et al. (2013) combined an autosampler with a flow-through system and were able to reveal otherwise unnoticed fine-scale (5-minutes) variations of precipitation isotopic compositions. A commercially available VALCO® valve unit coupled with laser spectrometers for high-resolution sampling (9.5-minutes) was used by Leis et al. (2011) to investigate spring water isotope dynamics. Koehler and Wassenaar (2011) employed a marble-filled equilibrator and a minimodule device for producing and subsequently analysing a constant stream of vapour being in isotopic equilibrium with and therefore carrying in a known manner the isotopic information of the liquid phase of interest. Following the same principle, other researchers used gas-permeable ePTFE surgical tubings for the investigation of precipitation trajectories (Munksgaard et al., 2012a) or seawater-freshwater mixing ratios (Munksgaard et al., 2012b). For the continuous investigation of rapid water isotope changes in a soil column experiment, Herbstritt et al. (2012) employed a commercially available hydrophobic membrane contactor for converting a small fraction of liquid water continuously into a stream of vapour, which was directly analysed by the coupled isotope analyser. However, none of these approaches have attempted to observe rainfall and throughfall in parallel.

Recent interception studies, mostly based on bulk sampling data and focusing on spatial variations, are especially lacking an appropriate temporal resolution to be comparable with the available temporal resolution of meteorological input data and hence to describe and better understand the physics controlling the differences in isotopic composition between P_g and TF.

Therefore, the aim of this study is to develop an approach for the analysis of P_g and TF depth and isotopic compositionanalysis at the point level at high temporal resolution based on the membrane contactor method, to compare and validate the continuous isotope measurements with discrete liquid samples as well as with event-based bulk samples. With this approach the dynamics in amount and isotopic composition of P_g and TF and hence, interception processes influencing amount and isotopic composition of TF can be investigated in unprecedented high temporal resolution.

2 Methods and Material

2.1 Sampling

We modified the setup developed and used previously for the in-situ observation of water stable isotopes in a soil column experiment (Herbstritt et al, 2012). A commercially available hydrophobic membrane contactor of 1 x 1 x 0.5 inch

(MicroModule®, Membrana, Charlotte, NC, USA, www.liquicel.com) was combined with a CRDS isotope analyser (L2120-*i*, Picarro, Inc., Santa Clara, CA, USA, www.picarro.com). The contactor, originally designed for degassing liquids, was used in the so called 'sweep-mode' in order to continuously transform a small fraction of liquid water of interest with flowrates of 5-30 mL/min, according to manufacturer specifications, into a water vapour stream. Inside the contactor a microporous, hydrophobic, PP-based membrane (A = 100 cm²) divides the liquid from the gaseous phase. At the membrane's surface, dry carrier gas (e.g. N_2) mixes with vapour ~~evolving~~ diffusing ~~through the pores across the membrane~~ from the liquid phase through the pores across the membrane. ~~water flowing through the contactor and m~~Moist air then leaves the contactor at the gas outlet port (Fig. 1, right) which is directly connected to the CRDS. In the analyser-controlled stream of moist air (flow rate ~35 mL/min), readings of water vapour, $\delta^{18}O$ and $\delta^{2}H$ are given every two seconds. The method requires a thorough determination of the temperature to account for the temperature-dependent isotope fractionation factors of the membrane as described in detail by Herbstritt et al. (2012).

Several modifications of the original setup were made for the quasi real-time observation of water stable isotopes in rainfall. A standard rainfall collector was enlarged from 200 to 1810 cm² with a PP-funnel to ensure sufficient water flow in case of low rainfall intensities and also to account for small-scale spatial variabilities in TF ~~when measured below the canopy~~. To protect against clogging by litter fall, a metal mesh with 1 x 1 mm covered the funnel. At the bottom end, a smaller funnel with a volume of 3 mL was installed. From there, a stream of water was pumped to the membrane contactor with a peristaltic pump at a constant flowrate of 5 mL/min while at the same time water exceeding this flowrate was spilled and collected via an additional funnel into a sampling bottle. This overflow was volume-weighted, contributing to the event-based bulk sample.

All connections were made by gas-tight PFA tubings with an inner diameter of 1 mm. Easily replaceable glass fibre syringe filters (pore size 1-2µm) were installed in line to protect the membrane contactor from clogging. Removal of smaller particles or biofilms inside the contactor could be facilitated by ~~periodical~~ back flushing with deionized water as needed or periodical rinsing ~~(~~every 2 to 4 weeks~~)~~ with weak acids, respectively. Temperature of the water in the tubing just before the contactor was stabilized and kept constant at 16°C using a peltier element (UEPT-KIT3) and a controller (UR3274U5, both obtained from uwe electronic, Wachendorf, Germany, www.uweelectronic.de) to avoid super-saturation and condensation of the vapour on the way to the isotope analyser operated at room temperature. Vapour isotope data were recorded as soon as temperature and thus vapour concentration at the membrane contactor was stable, which was usually the case within 5 to 10 minutes after the onset of precipitation sampling. All tubings were kept as short as possible, facilitating a time shift of no more than four minutes between precipitation and the respective readings displayed by the isotope analyser (Fig. 1). During rainfall events, discrete liquid samples were taken every five minutes at the liquid outlet port of the membrane module and analysed later in the laboratory.~~,~~ ~~the~~ The collected overflow plus excess water at the membrane module was volume-weighted and summed up to an event-based bulk sample. In close proximity (1.5 m) to ~~each~~ the collector a tipping bucket (R3, Onset Rain Gauge) was installed. Rainfall was logged in 0.2 mm increments (HOBO UA-003-64 Pendant Event Data Logger, Onset, HOBO®, Bourne, MA, USA, www.onsetcomp.com) and data was aggregated to 1-minute intervals. Two of

these setups were installed with 10 m ~~apart~~horizontal distance from each other, sampling gross precipitation (P_g) and throughfall (TF) ~~separately~~ under a deciduous tree (~~a~~*Acer campestre* L.) separately. In total, 28 bulk samples and nine continuously analysed~~sampled~~ events were obtained~~sampled~~ in August-September 2015 and throughout the vegetation period (May-September) of 2016. In any case, the measurements were carried out during the period when the leafs had reached their full sizes, in order to minimize the influence of the growing season. The meteorological variables air temperature (T_a) and relative humidity (RH) were recorded in 15 m distance to the tree with a CS215 sensor and logged with a CR1000 data logger (both available from Campbell Scientific, Inc., Logan, UT, USA, www.campbellsci.com) every minute. Additionally, the meteorological variables rainfall ~~amount~~ depth (P_g), air temperature (T_a), relative humidity (RH), air pressure, wind speed (v), ~~maximum wind speed (v_max),~~ and wind direction were available in 10 minute resolution from a climate station 250 m away.

Figure 1

2.2 Analyses

All isotope data are expressed in δ-notation calculated with the following ~~Eq. (1)~~equation:

$$\delta = \left(\frac{R_{sample}}{R_{VSMOW2}} - 1\right) * 1000‰ \quad (1)$$

where VSMOW2 is the Vienna Standard Mean Ocean Water and R is the isotope ratio ($^{18}O/^{16}O$ or $^{2}H/^{1}H$). Calibration of the samples was conducted using three in-house standards with distinct isotopic compositions, ~~(~~-16.65‰, -9.59‰, and 0.51‰ for $\delta^{18}O$, -125.05‰, -66.50‰, and -2.40‰ for $\delta^{2}H$~~)~~, referenced to the international VSMOW-SLAP scale (Craig, 1961). They were pumped consecutively through the contactor after each rainfall event until a plateau in the isotope readings was reached (~10 minutes) and treated similar to the continuously sampled precipitation water. Hence, potential long-term changes of the membranes e.g. build-up of biofilms or mechanical changes (small cracks, fissures) at the membrane did not have an effect on calibrated isotope data. For data noise reduction of the continuous measurements we calculated moving averages with an integration time of 90 s.

All liquid water samples were analysed on a CRDS laser spectrometer (Picarro L2130-*i*) with a post-calibration accuracy of ± 0.053‰ for $\delta^{18}O$ and ± 0.34935‰ for $\delta^{2}H$.

D-excess (*d*) was used to indicate the deviation from the global meteoric water line (GMWL) and likely non-equilibrium fractionation by evaporation (Gat, 1996):

$$d = \delta^{2}H - 8 * \delta^{18}O \quad (2)$$

The difference in isotope characteristics between TF and– P_g is indicated by the symbol Δ:

$$\Delta\delta^{18}O = \delta^{18}O_{TF} - \delta^{18}O_{Pg} \quad (3)$$

$$\Delta d = d_{TF} - d_{Pg} \quad (4)$$

Relative interception loss (*Loss*) is the difference in depth between P_g and TF

$$Loss = \frac{P_g - TF}{P_g} * 100\ \% \quad (5)$$

Vapour pressure deficit (VPD) ~~*E - e*~~ is calculated to indicate potentially high or low evaporation with the following equation (modified from Foken, 2008):

$$VPD\sout{E - e} = 6.107hPa * e^{\left(\frac{17.62*T_a}{243.12°C+T_a}\right)} * \left(1 - \frac{RH}{100\ \%}\right) \quad (6)$$

where RH is relative humidity in % and T_a is air temperature in °C.

3 Results

One example rainfall event observed in this study (Fig. 2) had a total depth of 6.8 mm and started with high rainfall intensities followed by more moderate intensities which lasted for roughly two hours. Continuous vapour derived stable isotope measurements, isotope ratios of discrete liquid ~~grab~~ and liquid bulk samples are shown for both isotope ratios investigated to illustrate the increase of temporal information during one single rain event when ~~sampling~~ analysing in high temporal resolution ~~(Fig. 2)~~. The moving average of calibrated vapour derived data ranged between -5.45‰ and -7.53‰ for $\delta^{18}O$ and ~~(~~-27.36‰ and -45.64‰~~)~~ for ~~$\delta^{18}O$ ($\delta^{2}H$)~~ with respective~~a~~ mean precision~~s~~ of ± 0.26‰ ~~(~~and ± 1.53‰~~)~~. Calibrated data of the liquid samples taken simultaneously were in a range of -5.34‰ to -7.43‰ in the case of $\delta^{18}O$ and -28.73‰ to -45.95‰ in the case of $\delta^{2}H$. Mean absolute deviation between the moving average of the continuously analysed vapour data and the discrete liquid samples was 0.11‰ ~~($\delta^{18}O$)~~ and 1.35‰ ~~($\delta^{2}H$)~~ with standard deviations of 0.096‰ and 0.81‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. The isotopic composition of the ~~three hour~~event-based bulk sample during this event was -5.68‰ for $\delta^{18}O$ and -32.67‰ for ~~$\delta^{18}O$ and~~ $\delta^{2}H$~~, respectively~~.

Figure 2

Analysing all 28 event-based bulk samples in this study, the variables rainfall ~~amount~~ depth (P_g), mean rainfall intensity, interception loss, $\delta^{18}O_{Pg}$, $\delta^{18}O_{TF}$, the difference in deuterium excess (Δd) and the isotopic difference $\Delta\delta^{18}O$ ~~were~~ are ~~compared~~ correlated to each other in a scatterplot matrix (Fig. 3)~~. In the upper right part the respective Pearson correlation~~

~~coefficient is shown, indicating a significant~~ . A significant (p-value < 0.05) but moderate negative correlation between the logarithm of rainfall intensity and the relative~~percentage of~~ interception loss ~~is~~ indicat~~e~~ings that the highest interception losses were found during events with lowest rainfall intensities ~~(Fig. 3a)~~. ~~Predominantly~~ The~~the~~ interception loss ~~ranged~~ ranges predominantly between 30% and 50%. Also a weak positive ~~correlation~~ relationship between $\Delta\delta^{18}O$ ~~(the difference in $\delta^{18}O$ between P_g and TF)~~ and interception loss was found ~~(Fig. 3b)~~ which means that the~~-~~ isotopic composition ($\delta^{18}O$) of precipitation when becoming throughfall ~~was~~ is altered to a larger extent ~~in throughfall~~ when interception losses are high. The isotopic composition of P_g ranges from -1.58‰ to -11.69‰ for $\delta^{18}O$ and is significantly correlated to the respective isotopic composition of TF which ranges from -0.88‰ to -10.15‰. Only non-significant correlations were found between the other investigated quantities. The explained variance by any of the considered variables alone was generally small.

Figure 3

In ~~this figure~~Figure 4 (a) the difference of the isotopic signature between TF and P_g ($\Delta\delta^{18}O$) of 28 bulk samples is shown. It was calculated from flux~~-~~-weighted means of $\delta^{18}O$ of TF and P_g. The data of the bulk samples were~~are~~ grouped in ~~0.5 ‰~~ classes of 0.5‰ increments. The maximum difference in $\delta^{18}O$ values of 2 - 2.5‰ was observed only for two events, while for 23 of the 28 events $\Delta\delta^{18}O$ was 1.5‰ or less. In contrast, in the shorter periods of continuous sampling, $\Delta\delta^{18}O$ values up to 3.5‰ were found (Table 1 and Fig. 4 (b)~~)~~. ~~each~~ Each symbol in Figure 4 (b) indicates the mean difference in ~~Δ~~$\delta^{18}O$ (y-axis), whereas the length of the symbol~~s~~ indicates the duration of the continuous sampling (x-axis), including start and end time of the respective events. Two clusters ~~could~~ can be identified w~~h~~ithere one ~~contained~~ containings three single rainfall events on a previously dry canopy, i.e. after at least 6 hours without rainfall, and~~whereas~~ the other ~~was generated by~~containings six events on already wet canopies with markedly higher $\Delta\delta^{18}O$ values.

Table 1: Depth, intensity, and isotope values of continuously sampled P_g and TF. Data of differences in $\delta^{18}O$ ($\Delta\delta^{18}O$ (‰)) are reported as mean ± SD. (* tipping bucket malfunctioned)

			Rain (P_g)		Throughfall (TF)		TF-P_g differences	
Event #	Starting time	Duration (h:mm)	Depth (mm)	Intensity (mm/h)	Depth (mm)	Intensity (mm/h)	Loss (%)	$\Delta\delta^{18}O$ (‰)
1	2015/09/22 20:32	0:25	2.0	4.80	1.20	2.88	40.0	3.45 ± 1.16
2	2015/09/22 21:28	0:32	2.6	4.88	1.60	3.00	38.5	2.49 ± 0.98
3	2016/08/02 17:50	0:59	3.0	3.00	(6.20)*	6.20	(-106.7)	0.95 ± 0.37
4	2016/08/04 19:50	0:42	1.8	2.57	0.80	1.14	55.6	2.14 ± 0.5
5	2016/08/04 20:54	0:22	0.6	1.64	0.40	1.09	33.3	2.68 ± 0.27
6	2016/08/04 21:34	0:24	0.8	2.00	0.40	1.00	50.0	2.31 ± 0.26

7	2016/08/04 22:10	0:15	0.4	1.60	0.20	0.80	50.0	3.31 ± 0.35
8	2016/08/05 18:15	0:08	0.6	4.50	0.40	3.00	33.3	0.86 ± 0.32
9	2016/08/20 18:37	0:46	4.0	4.80	2.80	3.36	30.0	1.00 ± 0.33

Figure 4

Time series of (a) $\Delta\delta^{18}O$, (b) $\Delta\delta^{2}H$, and (c) Δd calculated from continuous isotope data of TF and P_g of all nine ~~events~~ continuously observed events listed in Table 1 are illustrated in Figure 5. Values during events on initially dry ~~canopy~~ canopies ~~did~~ do not exceed 1.5‰ ~~(~~and 10‰~~)~~ for $\Delta\delta^{18}O$ and ~~(~~$\Delta\delta^{2}H$,~~)~~ respectively, with Δd values ranging from +1‰ to -7‰.~~,~~ ~~while~~ In contrast, values from events on wet ~~canopy~~ canopies ~~were~~ are in the range of +1.5‰ to +5‰ for $\Delta\delta^{18}O$ ~~(~~and +11‰ to +43‰~~)~~ for ~~$\Delta\delta^{18}O$~~ ~~(~~$\Delta\delta^{2}H$~~)~~ with Δd values ranging from +12‰ to -6‰.

Figure 5

The combination of collector funnel area (1810 cm^{3}~~)~~ ^{2}~~)~~ and water flow rate (5 mL/min) resulted in a threshold rainfall intensity of 0.03 mm/min that was required to ensure an air bubble-free stream of water being pumped to the membrane contactor. Thus, periods of ~~continuous~~ pure water flow at both (P_g and TF) contactors alternated with periods when air bubbles appeared at either one or both of the contactors in this example event (Fig. 6). Since the presence of bubbles proved to flaw isotope readings, calculations of $\Delta\delta^{18}O$, $\Delta\delta^{2}H$, and Δd were only reasonable~~possible~~ for periods without bubbles at ~~neither~~ any contactor. The variability of the continuous P_g isotope data is higher than ~~that~~ the variability of the continuous TF data, where the signal is more dampened over time. Relative to P_g, TF becomes increasingly enriched in heavy isotopes during the event. The variability of d is in the range of about 5‰ for both P_g and TF, fluctuating initially in a corridor between 10‰ and 15‰. However, d_{Pg} shows a negative trend and decreases by about 10‰ over the course of the event whereas d_{TF} does not follow this trend and remains rather constant. Air temperature as well as vapour pressure deficit ~~become lower~~decrease with event duration.

Figure 6

4 Discussion

The modified setup of the method developed by Herbstritt et al. (2012) adapted to continuous rainfall and throughfall isotope measurement worked quite well in terms of providing continuous, thermo-regulated flows of water to the membrane modules and delivering reliable liquid water stable isotope data. The latter became evident by the good agreement of

continuous measurements and single liquid samples (Fig. 2 and also Fig. 6) which was persistently in the order of the measurement uncertainty for both isotope ratios under investigation. Large inter~~-~~a-storm variabilities exist in the isotopic signature of P_g and TF, which would have been~~were~~ impossible to detect when solely relying on commonly taken event-based bulk samples or even on data representing a higher sampling interval of typically 5 mm precipitation depth. We found that the variability of the continuous P_g isotope data is higher than the variability of the continuous TF data (Fig. 6). For the latter, the signal is more dampened probably due to mixing processes, which was also found in other studies (Qu et al., 2013). The lower intensity and total depth of TF as compared to P_g is indicative for evaporation from the canopy. However, this is not reflected in continuous d_{TF} values (Fig. 6) which were expected to follow the trend of d_{Pg} values while being lower after evaporative non-equilibrium fractionation. The dynamics in the isotopic composition in P_g as well as in TF could ~~nicely~~ be captured by the continuous measurements and also to some degree with the 5-minute discrete liquid ~~grab~~ samples. This provides a good evidence for the applicability of the developed continuous method. On the other hand, it is also an indication that a temporal resolution of around five minutes might be sufficient to capture the isotope dynamics of rainfall events, if continuous sampling is not possible. However, continuous data were instantly available whereas data of sampled liquid water were available not before conventional analysis via CRDS was completed, which lasted for another two days. In contrast, there is obviously a tremendous loss of information about short term dynamics or trends when comparing the results with commonly taken bulk samples or 5 mm depth incremented samples.

Depletion in heavy isotopes in open site rainfall was observed in the last ~30 minutes of the event presented in Figure 2. Several effects could cause such a pattern. The amount effect, reported for lower latitudes (Moore et al., 2014), can be ruled out due to the fact that at the same time rainfall intensity was quite low compared to other periods of this particular rainfall event. Also a rainout effect cannot be attributed to our data as it is only detectible on a spatial scale considering the movement of air masses and rain clouds. Rather, the simultaneous decrease of air temperature indicates the passing of a weather front which appears to be the relevant explanation for the observed changes in precipitation isotope values.

In the data of the collected bulk samples a significant negative correlation~~s~~ between interception loss and the meteorological variable~~s~~ ~~like~~ rainfall ~~amount or~~ intensity as well as a moderate negative correlation between relative interception loss and depth of incident rainfall could be observed (Fig. 3)~~,~~.This means that the highest interception losses were found during events with either lowest rainfall intensities or with lowest depths. A weak positive relationship also existed between $\Delta\delta^{18}O$ and interception loss, indicating that $\Delta\delta^{18}O$ increases with increasing interception losses. This is in line with results found in other studies (Dewalle and Swistock, 1994; Brodersen et al.~~,~~; 2000, Keim et al.~~,~~; 2005, Kato et al., 2013~~,~~; Allen et al., 2017). Only non-significant correlations were found between the other investigated quantities. The small explained variance between any of the considered variables illustrates the complexity of the processes~~There is no clear pattern for only one of these variables, which is evidence for the complexity of processes~~ contributing to interception loss and the transformation of P_g isotope ratios when becoming TF.

Due to required minimum flowrates at the contactor (5 mL/min), the used setup with a collector area of 1810 cm² was limited to minimum rainfall intensities of 0.03 mm/min (1.8 mm/h). The fact that some of the investigated events appear to

have intensities below 1.8 mm/h (Tab. 1) may be due to TF heterogeneities that came into effect at the different locations of the tipping bucket and TF sampling. For sampled intensities below the identified threshold value, a larger or multiple collectors would be necessary, whereby larger collection funnels in combination with low rainfall intensities will increase the risk of evaporative enrichment from the funnel surface, leading to methodological artefacts that need to be avoided. These effects, however, are typical for most throughfall collectors as large and long surfaces are preferred. Therefore, dimensioning the collectors always is a trade-off and the maximum size is limited.

Comparing $\Delta\delta^{18}O$ data during continuously measured events with those derived from~~of~~ event-based bulk samples, the differences are larger during the shorter continuously measured periods (Fig. 4). It should be noted that in this case the definition of a rainfall event is not consistent. Bulk samples cover the entire time period of rainfall regardless of intensity at the point of observation and mere existence of rainfall at the complementary observation point (P_g vs. TF). In contrast, continuous events are defined by sufficient simultaneous rainfall intensity at both points of observation due ~~, owed~~ to our setups' properties. Therefore, natural rainfall events can only partially be captured by continuous synchronous observations. At the same time bulk samples represent the flux-weighted mean of all conditions constituting the respective event. Nonetheless, in the continuously analysed dataset two clusters could be distinguished representing rainfall on already wet and on initially dry canopies (Fig. 4 ~~left~~(b)). The fact that wet canopies lead to an even stronger enrichment in heavy isotopes can probably be attributed to partly evaporated and therefore isotopically enriched pre-event water that mixes with new rainfall water. This supports~~allows for~~ the interpretation that antecedent conditions have a clear impact on isotopic enrichment of TF which was also described in previous studies (Keim et al., 2005; Allen et al., 2014; Stockinger et al., 2015; Allen et al., 2017).

Relative to P_g, TF becomes increasingly enriched in heavy isotopes (Fig. 6), which is similar to our observations of $\Delta\delta^{18}O$ in bulk samples on dry and wet canopies (Fig. 4 and Fig. 5). The additionally calculated Δd values did no~~t~~ show a clear or systematic pattern that would add to previous findings. Meteorological variables also did not provide a clear single evidence for the observed~~is~~ enrichment, indicating that multiple variables ~~take~~ affect the isotopic processes in the canopy. Typically, air temperature as well as vapour pressure deficit slightly decreased over the course of an event, but ~~probably~~ obviously evaporation still ~~took place~~altered the isotopic signal as evidenced by the observed ~~relative~~ interception losses. At the same time mixing of antecedent water with ~~fresh~~ new precipitation water ~~still~~ occurred in the canopy. Therefore, it remains unclear to what ~~extend~~ extent the increase in difference between synchronous P_g and TF isotope data must be attributed to evaporative enrichment or to changing mixing processes following the variable rainfall intensities. Water redistribution in the canopy, i.e. movement of water to or from a specific place e.g. via flow along branches, may have an effect on the isotopic composition observed as it also changes the unknown spatial pattern of precipitation water isotopes. In addition, the spatial scale of mixing, certainly~~probably~~ at the leaf level, but probably also among leafs as~~resulting from~~ water drip~~sping~~ from leaf to leaf, needs to be considered if we would like to ~~simulate~~ decipher the isotope dynamics caused by water mixing and evaporation in the canopy of a tree.

The total number of observed events is lower in the case of the continuously measured events due to a number of events with rainfall intensities below the threshold for the continuous sampling method and due to several events during the night when the sampling setup was not operated. For continuous measurements the differences in the isotopic signature were consistently calculated from isochronic P_g and TF data although we are aware that water falling from the canopy (i.e. TF) is always a mixture of new rainfall (i.e. isochronic P_g) and rainfall that has occurred~~fallen~~ at different points in time before. The time lags depend on canopy storage capacity and rainfall intensity (Allen, 2017) and therefore vary within each single event as well as between different storms. ~~Associating TF to P_g of the same point in time is therefore only partly correct.~~

Highest $\Delta\delta^{18}O$ values were found in the cases of the continuous observations. One reason could be that the continuously analysed events are shorter and therefore potentially capturing extreme values while bulk samples represent flux-weighted mean isotopic signatures of the entire periods of rainfall and throughfall. On the other hand, we are aware that the calculation and interpretation of synchronous $\Delta\delta^{18}O$ and $\Delta\delta^{2}H$ data are disputable given assumable, yet unknown, time lags between P_g and TF. Within each rainfall event, also past trends and variabilities of the P_g isotopic compositions must be assumed to be reflected in instantaneous TF isotopic compositions, but are not considered with the proposed approach. However, a quite common intra-event P_g isotopic depletion trend (Fig. 2 and Fig. 6) combined with any positive time lag between P_g and TF would result in higher synchronous $\Delta\delta^{18}O$ values compared to estimates derived from bulk sample data.

For the quantitative description of processes affecting throughfall depth and isotopic composition, and thus the possible explanation for the discrepancies in $\Delta\delta^{18}O$ values, a mechanistic modeling approach could be envisioned. Such an approach could build on the one developed by Keim et al. (2006) and aim at the quantification of the intensity-dependent canopy storage capacity and hence variable time lags between P_g and TF. The canopy storage capacity has been shown to be a function of leaf area and rainfall intensity and may also depend on wind speed or other meteorological properties. While being attached to the canopy, water is exposed to meteorology-dependent, thus variable, evaporation. This causes the effective cumulative P_g depth to decrease thereby producing variable time lags or rather transit time distributions between P_g and TF. Evaporation also causes enrichment in heavy isotopes of canopy-stored water. Consequently, for every simulation time step the TF isotopic composition needs to be calculated consecutively taking into account the respective fractions of P_g remaining from simultaneous and prior time steps and constituting the instantaneous reservoir releasing TF. In addition, internal mixing will occur at the leaf scale or inter-leaf scale. These mixing assumptions are probably least known and would need to be tested under different conditions. Finally, all relevant model parameters can be assumed to be dependent on meteorological variables thus further complicating this modeling and emphasizing the importance of continuous precipitation data representing different climates and vegetation characteristics.

5 Conclusions

We could demonstrate that the proposed method is suitable for continuously observing the stable water isotope dynamics in precipitation and throughfall ~~at the plot level~~. We facilitated a huge increase in temporal resolution compared to isotope assays based on ~~discrete~~ bulk sampling. Our approach supersedes taking liquid samples and at the same time provides data much faster. The instant data availability enables immediate reactions during rainfall events while the operator is still in the field. Employing our setup, the temporal resolution of the isotope data corresponds with the temporal resolutions that are already common in high frequency meteorological observations.

All components employed in this study are commercially available and can be installed with reasonable effort. In the present design the setup cannot yet be left unattended due to the necessity of periodical cleaning and maintenance like changes of the in-line filters. However, proper precautions excluding clogging by e.g. leaf debris should solve this issue as well. We are therefore confident that ~~this study~~ our setup, especially when employed across larger spatial scales, will contribute to the aim of thorough isotopic sampling of TF, which is crucial in hydrological studies in particular ~~on~~ for forested sites ~~as pointed out repeatedly~~but also for other vegetated areas ~~(Keim et al., 2005; Stockinger et al., 2015; Allen et al., 2017)~~.

Due to the selected ~~setup~~ dimensions of our setup and the resulting minimum rainfall intensity of 0.03 mm/min ~~in this study~~, the system was not able to capture events with low rainfall intensities, e.g. most stratiform rainfall events~~.~~, but this can be changed to make the approach suitable for a wider range of rainfall intensities. The lack of strong correlations between the investigated rainfall characteristics illustrates the complexity of interception processes. ~~Furthermore~~ Especially, knowledge about intra-canopy mixing and the time lags between P_g and TF as required for a precise, physically based calculation of the evaporative enrichment still remains a challenge for future applications.

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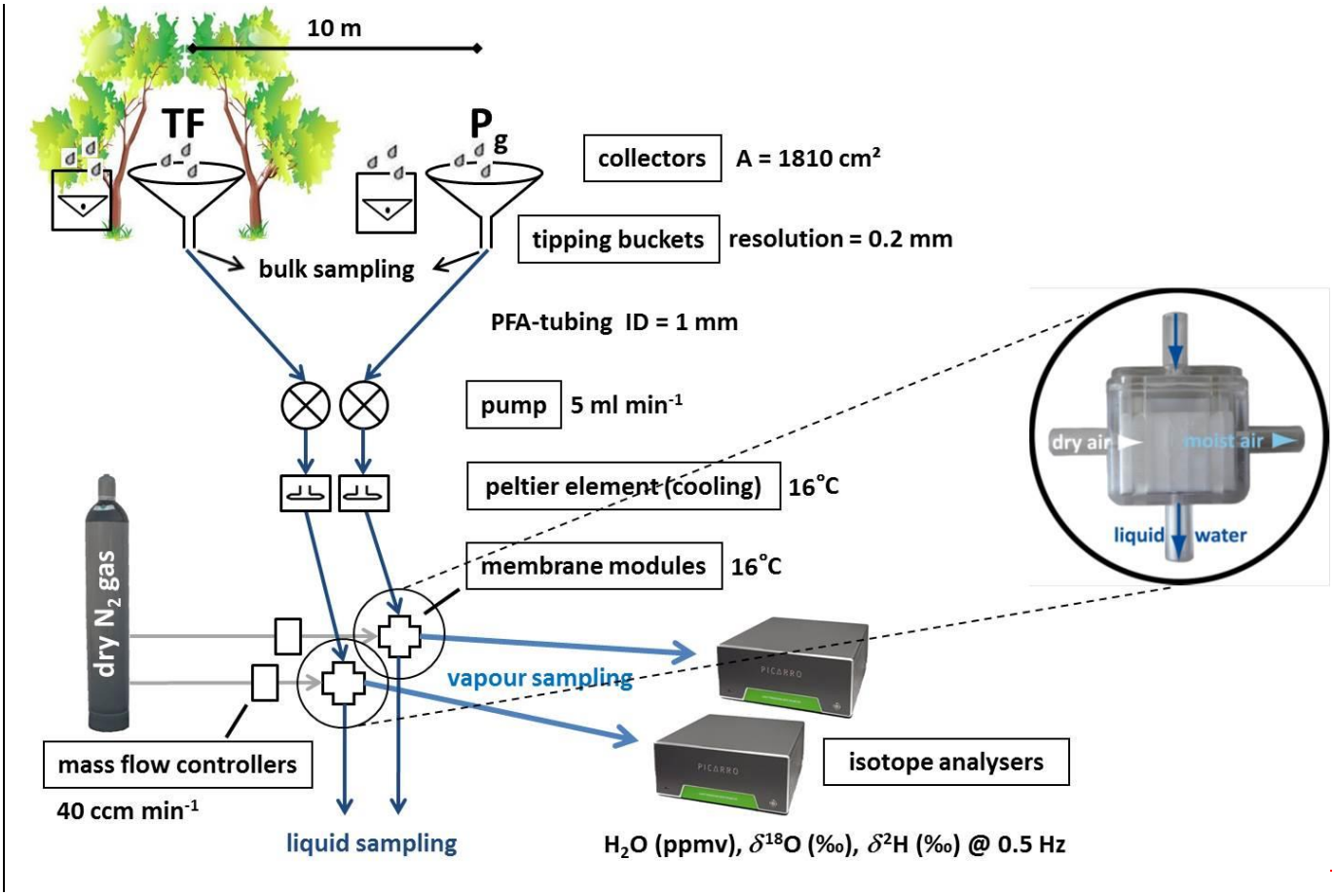

10 m
TF
P g
collectors
A = 1810 cm²
tipping buckets
resolution = 0.2 mm
bulk sampling
PFA-tubing ID = 1 mm
pump
5 ml min-1
peltier element (cooling)
16°C
membrane modules
16°C
dry air
moist air
liquid water
dry N2 gas
vapour sampling
PICARRO
PICARRO
mass flow controllers
40 ccm min-1
isotope analysers
liquid sampling
H2O (ppmv), δ18O (‰), δ2H (‰) @ 0.5 Hz

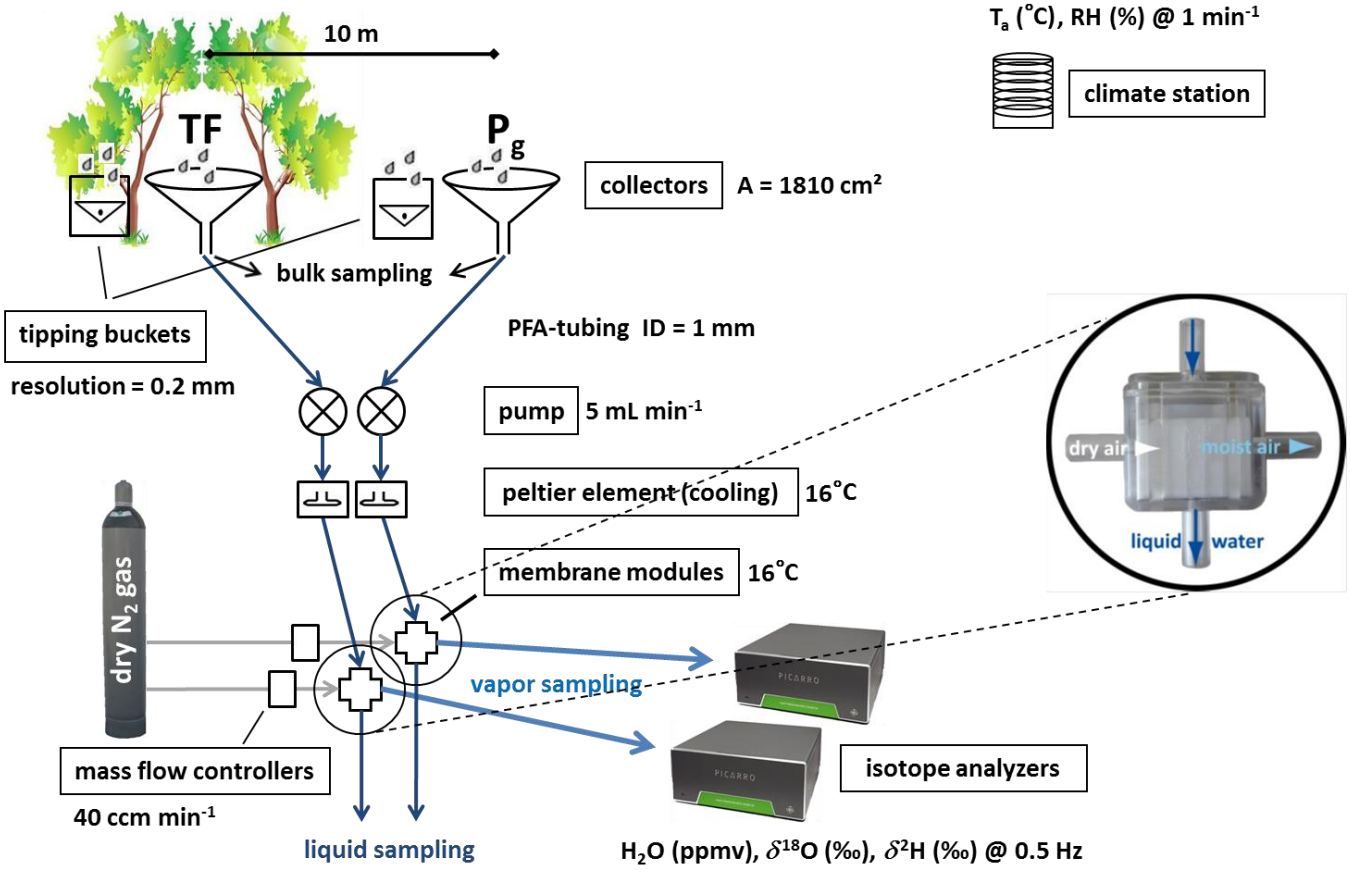


Figure 1: ~~Setup for continuous vapour stable isotope measurements, liquid grab and bulk sampling of gross precipitation (P_g) and throughfall (TF); right: membrane contactor employed for converting liquid water into water vapour.~~ Setup for continuous water vapour stable isotope measurements of gross precipitation (P_g) and throughfall (TF) with two analyzers in parallel; membrane contactor (center-right) employed for continuous production of water vapour; discrete liquid and liquid bulk sampling of P_g and TF; recording of rainfall depth (tipping buckets, upper left) and the meteorological variables T_a and RH (upper right) every minute.

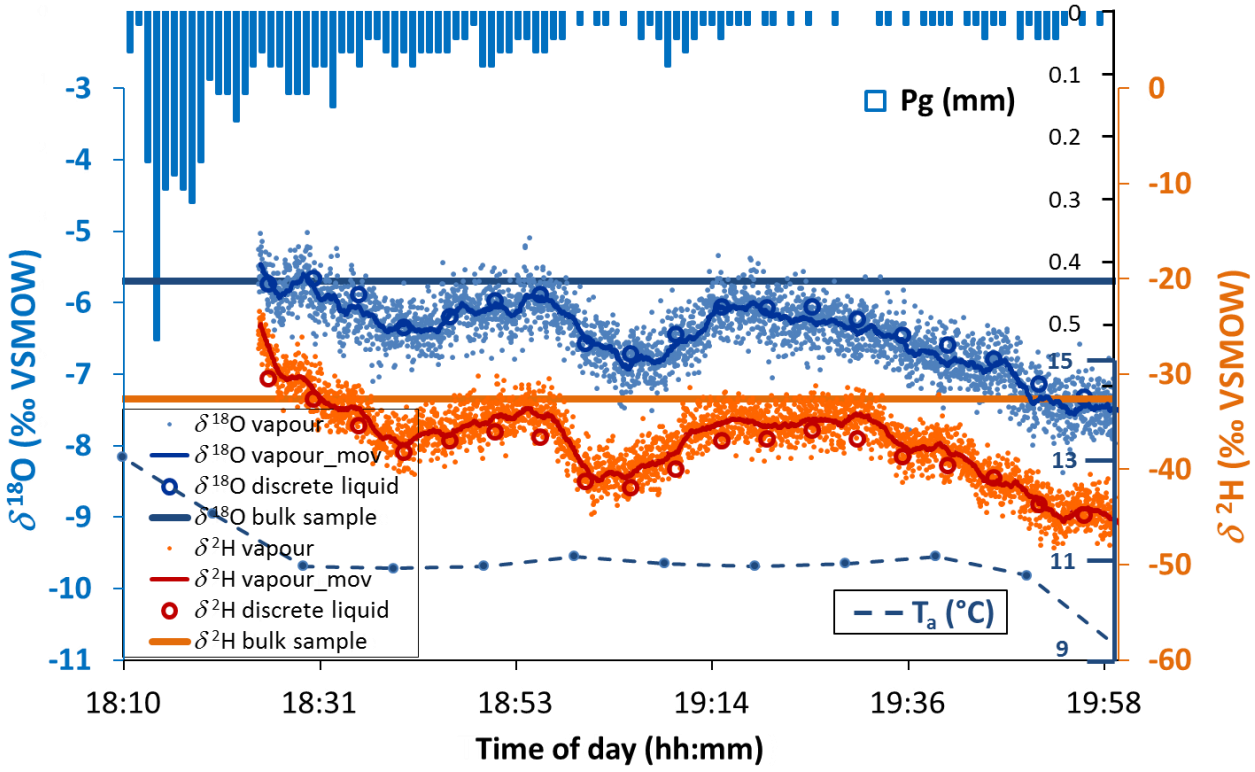
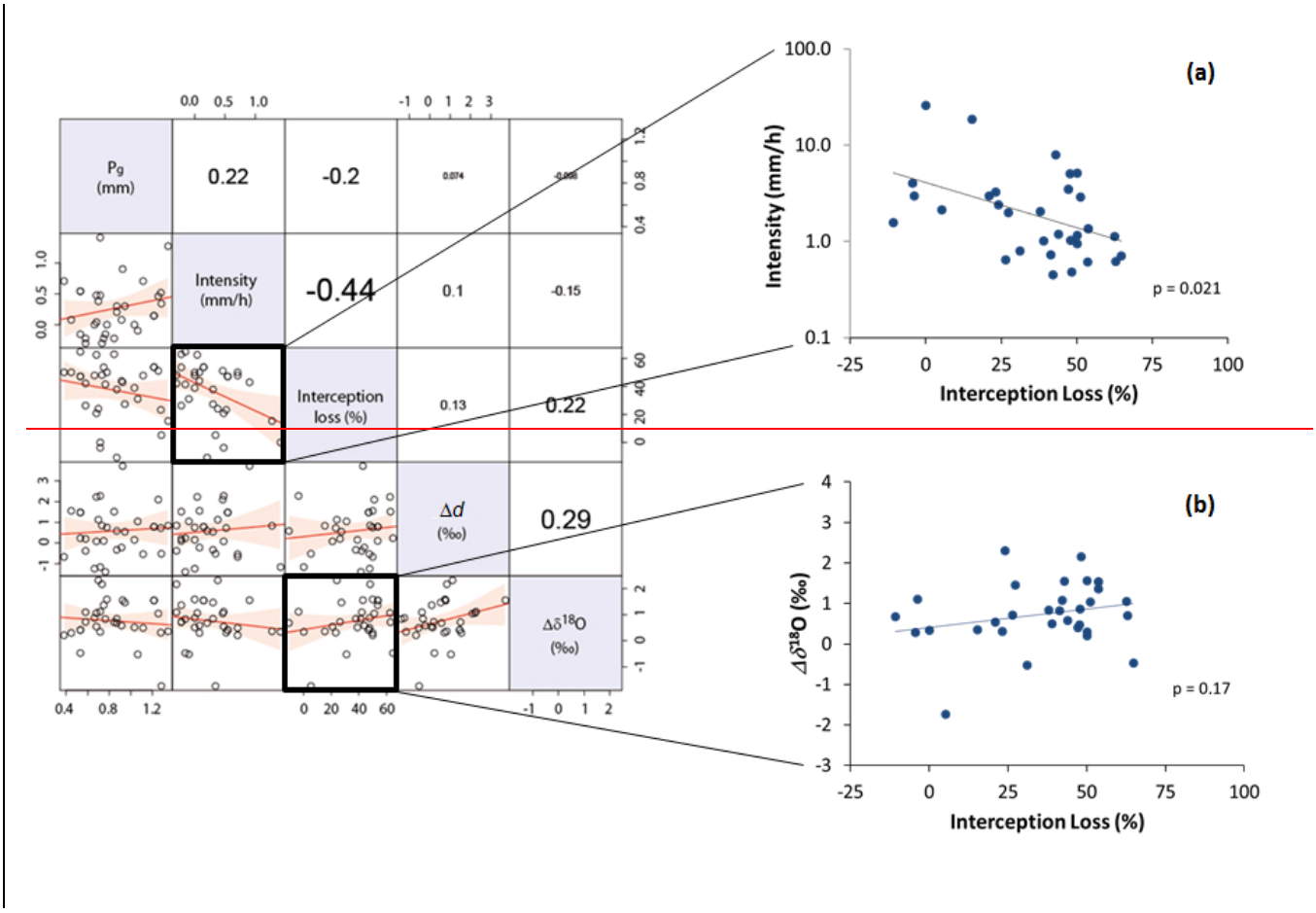


Figure 2: Time series of rainfall (P$_g$) depth per minute (vertical bars); 10-minute data of air temperature (T$_a$) (dashed line) during the ~~one example~~ rainfall event from April 17th 2015; data of δ^{18}O in blue and δ^{2}H in ~~red~~orange; vapour-derived data recorded every two seconds (small dots), starting after temperature at the contactor was stable, 90 sec. moving average (~~thin~~ solid lines), discrete liquid ~~grab~~ samples (open~~big~~ circles) taken every five minutes, ~~three hour~~event-based bulk sample (horizontal bars).


Pg (mm)
0.22
-0.2
0.074
-0.008
Intensity (mm/h)
-0.44
0.1
-0.15
Interception loss (%)
0.13
0.22
Δd (‰)
0.29
Δδ18O (‰)
(a)
Intensity (mm/h)
p = 0.021
Interception Loss (%)
(b)
Δδ18O (‰)
p = 0.17
Interception Loss (%)

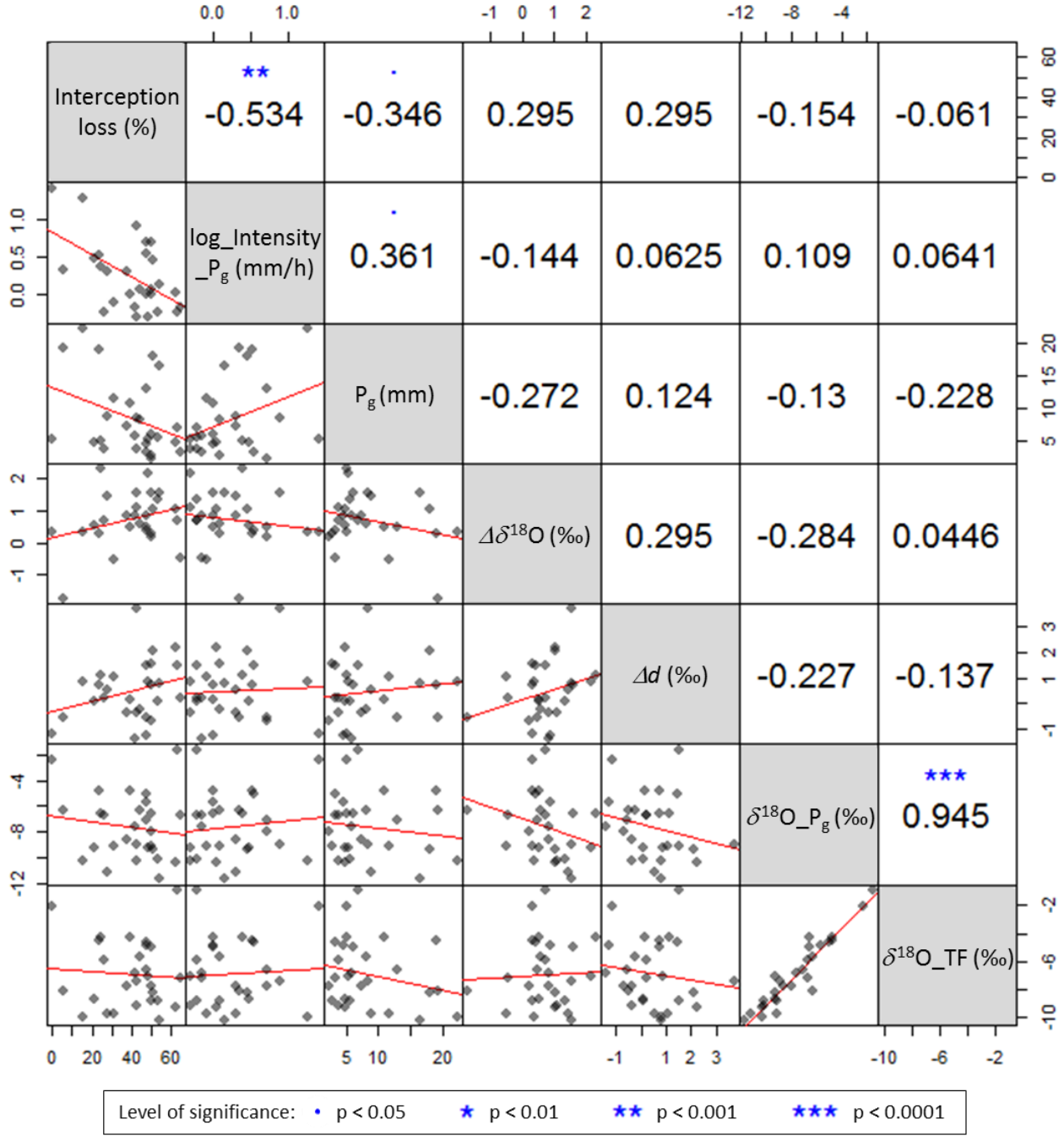


Figure 3: Scatter plot matrix of depths- and isotope-related characteristics derived from 28 event-based bulk samples. ~~in throughfall. a) Correlation between rainfall intensity and interception loss of bulk samples; b) Correlation between $\Delta\delta^{18}O$ and interception loss of bulk samples.~~ Upper right part: Pearson correlation coefficients and level of significance (stars); lower left part: scatter plots and linear regressions (red lines).

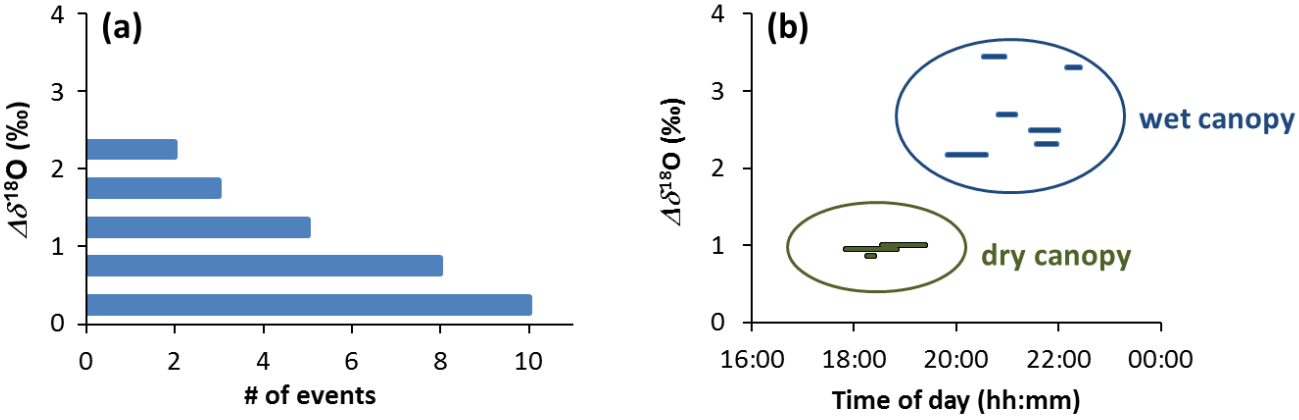


Figure 4: ~~**Deviation**~~ **Difference of the isotopic signature ($\Delta\delta^{18}O$) between TF and P_g for (a) 28 event-based bulk samples and (b) 9 continuously analysed events** ~~**(left) and event-based bulk samples**~~ **of the same period** ~~**(right)**~~**.**

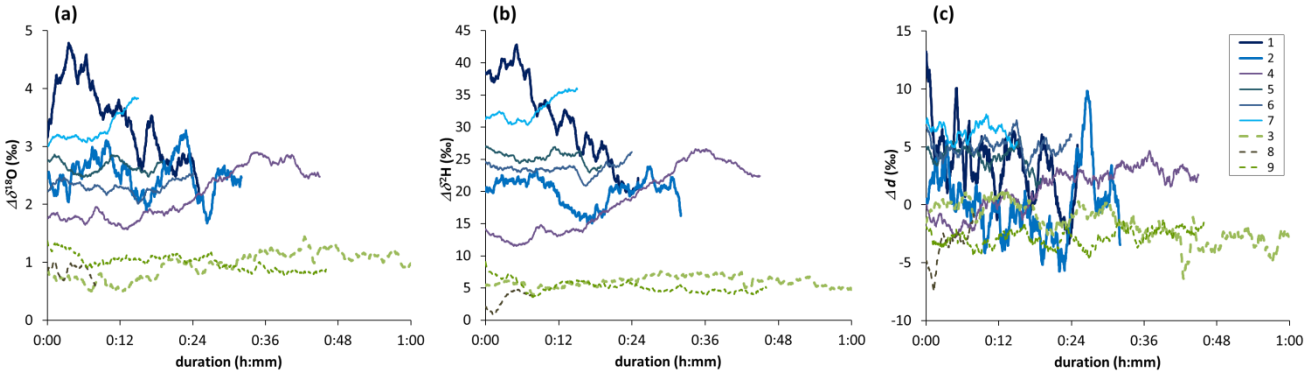
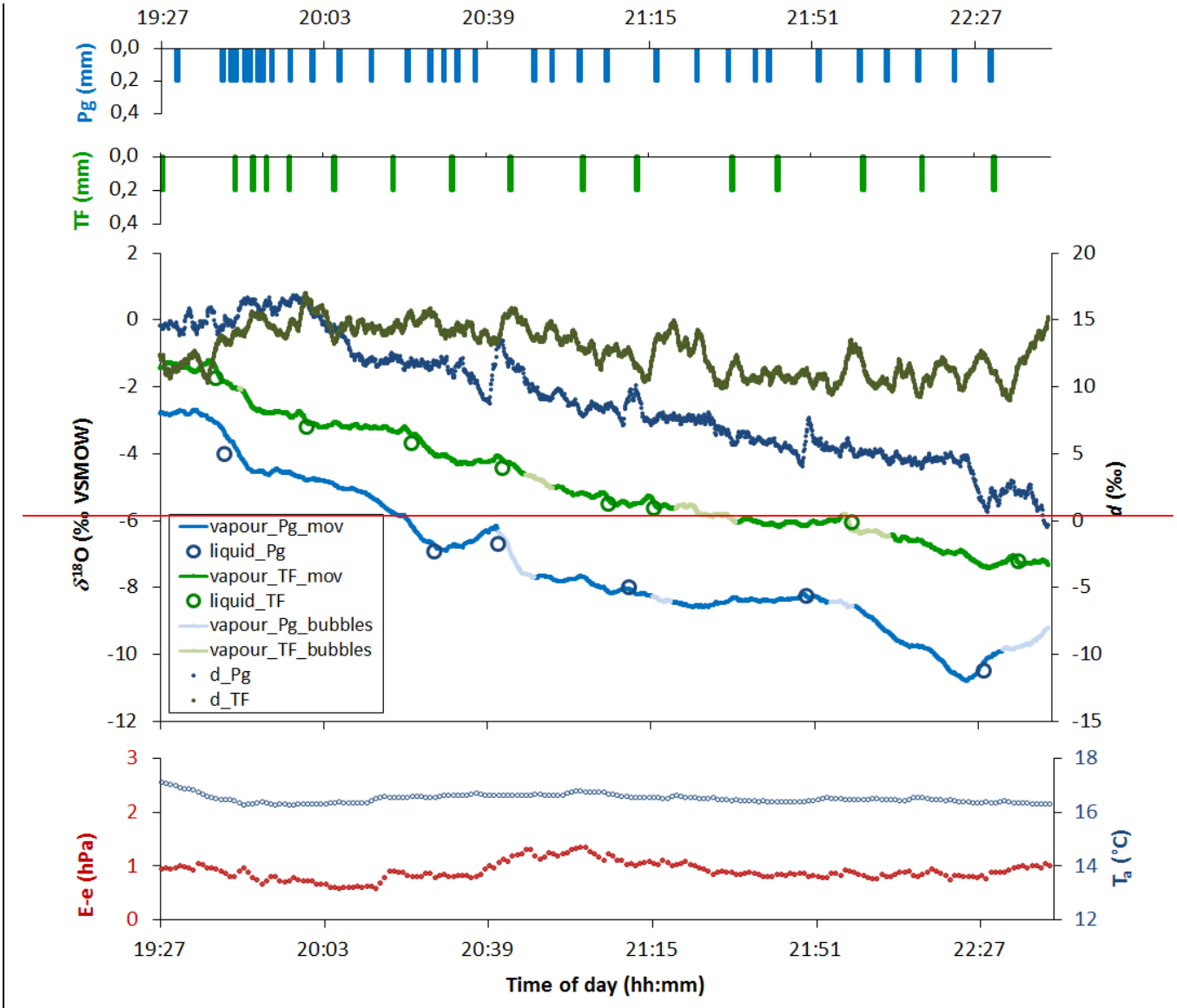


Figure 5: Time series of deviations of isotopic signature between TF and P_g, (a) $\Delta\delta^{-18}O$, (b) $\Delta\delta^{-2}H$, (c) Δd; ~~Dashed lines:~~ events on ~~previously~~ initially dry canopy (dashed line) and~~, solid lines~~ on wet canopy (solid lines).


19:27
20:03
20:39
21:15
21:51
22:27
Pg (mm)
0,0
0,2
0,4
TF (mm)
0,0
0,2
0,4
2
0
-2
-4
-6
-8
-10
-12
20
15
10
5
0
-5
-10
-15
δ18O (‰ VSMOW)
d (‰)
vapour_Pg_mov
liquid_Pg
vapour_TF_mov
liquid_TF
vapour_Pg_bubbles
vapour_TF_bubbles
d_Pg
d_TF
3
2
1
0
18
16
14
12
E-e (hPa)
Ta (°C)
19:27
20:03
20:39
21:15
21:51
22:27
Time of day (hh:mm)

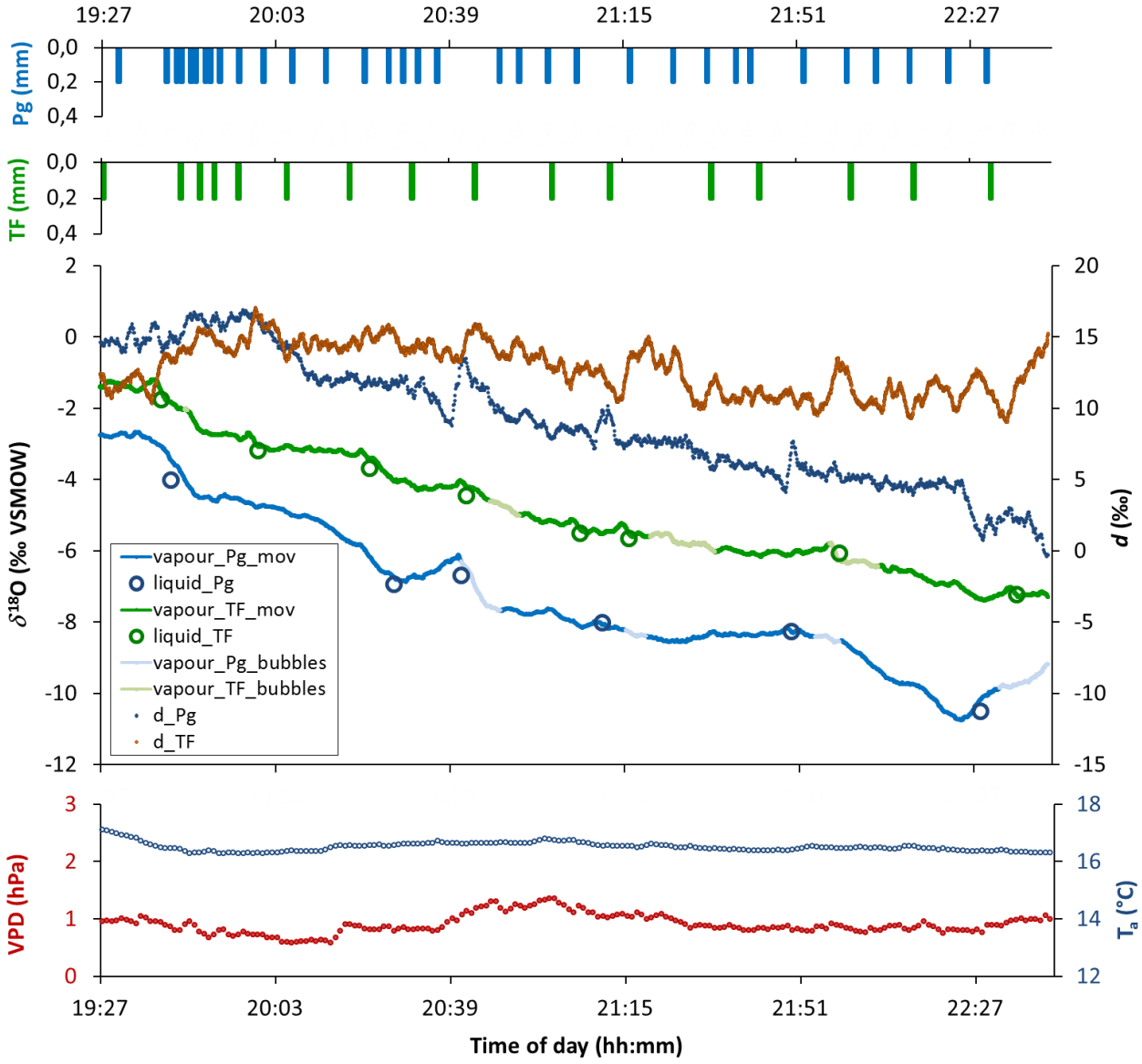


Figure 6: Time series of ~~amounts,~~ $\delta^{18}O$ and *d* ~~in~~ derived from vapour sampling of P_g (blue) and TF (green), discrete liquid samples (big circles), air temperature (T_a) (small blue circles) and vapour pressure deficit (~~E~~ eVPD) (red) of the rainfall event from August 4th 2016. Time series of d_{Pg} (dark blue dots), d_{TF} (brown dots) and T_a are referenced on the right vertical axes. Periods of intensities below threshold for the continuous sampling method (bubbles at membrane contactor) are shown in light blue (P_g) and light green (TF).