

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.,

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

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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 ($\delta^2\text{H}$ and $\delta^{18}\text{O}$ 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 throughfall 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 ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) 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.

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 very 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.”

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 of 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. N₂) 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: Will be considered in the discussion.

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 "...in 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 δ value only appears in Fig. 6 but is not addressed in the discussion.

Response: Will be considered in the discussion.

Comment: p. 5, l. 14 (and throughout 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 ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) 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..."

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: Will be extended in the discussion accordingly.

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 $\Delta 18O$ 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: Changed as suggested.

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 spatial scale of an isotope study high-resolution data is crucial but was not accessible so far with more traditional approaches.

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 as pointed out in the aims of this study (p. 3, l. 10-14). See also response to p. 3, l. 12-14.

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 δ^2H) 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 in the aims of this study (p. 3, l.10-14). See also responses to p. 3, l.12-14.

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”.

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.

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: Will be extended in the discussion accordingly.

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: s. response to p. 8, l. 4.

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: Will be added accordingly.

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 was derived from.