

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

Anonymous Referee #2

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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

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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.

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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? 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. line 20 I would omit the word "signature", since the stable isotopes are the tracers, while their signatures are measurements. 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. line 26 "residence times" is vague. Is it canopy, soil, or catchment residence times? Please be more precise. Line 28 New sentence after "Allen et al....". Delete "Since" Line 28 Citations after "forested" needed.

page 2: line 1 must be ..."Allen et al. (2017)." line 13 delete "Typically"; found for what? Precip? TF? Runoff? References needed line 15 "spatial variability in general" is to general. Please elaborate line 17 Ref needed after "diameters". Replace "They" by "The authors" or "Keim et al." page 3: line 18 in-situ line 24,27 SPACE between numeric value and unit needed

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

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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? line 6 What is meant by "long term changes in the membranes"? Please elaborate line 17 It should be mentioned here already why the VPD 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?

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? lines 3-4 I suppose the interception loss is $(Pg-TF)/Pg * 100$. It should be stated clearly how you calculated it. line 13 Were the interception losses and the $\Delta\delta^{18}\text{O}$ greater with time and plant growth from May to September? A plot with $\Delta\delta^{18}\text{O}$ in time during the growing season could be useful here. Any data on LAI? line 15 Is this mean difference flux weighted? I think this is important to emphasize. Line 21 "all events", see above, more information needed line 29: cm3 should be cm2

page 7: lines 1-2 Why is the TF signature more damped than the Pg signature? 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. 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? lines 17-18 How are "wet", and "dry" canopies defined? 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! line 27

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What process could explain that a wet canopy leads to an even stronger enrichment? Figure 1 Is the beginning of the event missed because of the stabilization of T? That info would be nice in the figure caption. Figure 5 A legend with the date of each event and the corresponding lines would be nice here. 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.

Thanks for the interesting contribution to isotope hydrology!

References: Hooper, R.P., Christophersen, N., Peters, N.E., 1990. Modelling streamwater chemistry as a mixture of soilwater end-members – an application to the Panola Mountain catchment, Georgia, USA. *J. Hydrol.* 116 (1), 321–343. Hrachowitz, M., Benettin, P., van Breukelen, B. M., Fovet, O., Howden, N. J. K., Ruiz, L., et al. (2016). Transit times—The link between hydrology and water quality at the catchment scale. *Wiley Interdisciplinary Reviews: Water*, 3(5), 629–657. <https://doi.org/10.1002/wat2.1155> Klaus, J., McDonnell, J.J., 2013. Hydrograph separation using stable isotopes: Review and evaluation. *J. Hydrol.* 505, 47–64. doi:10.1016/j.jhydrol.2013.09.006 McGuire, K. J., & McDonnell, J. J. (2006). A review and evaluation of catchment transit time modeling. *Journal of Hydrology*, 330(3–4), 543–563. <https://doi.org/10.1016/j.jhydrol.2006.04.020> Rinaldo, A., Benettin, P., Harman, C. J., Hrachowitz, M., McGuire, K. J., van der Velde, Y., et al. (2015). Storage selection functions: A coherent framework for quantifying how catchments store and release water and solutes. *Water Resources Research*, 51, 4840–4847. <https://doi.org/10.1002/2015WR017273>

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