

## **General Comments**

In this paper, the authors present a high-resolution time series of water isotope ratios in vapor and precipitation during a rain event in Switzerland. The goal of analyzing both together is to try and improve the understanding of what happens to rain as it falls through the convective boundary layer, where it is subject to a number of processes which can be difficult to observe. The  $\Delta\delta\Delta d$  approach highlighted here is interesting and novel. However, there are some aspects of the paper which need to be clarified better (see specific comments below) and more extensive discussion is needed for the effects of non-equilibrium kinetic fractionation, which is a big gap in the current analysis. While the proposed viewing diagram is novel and would be useful if appropriate, care must be taken into reading too much into the information presented as the current analysis/interpretation is missing some key discussion of how kinetic fractionation would be represented on the  $\Delta\delta\Delta d$  diagram. In addition, the definition of the  $\Delta\delta$  and  $\Delta d$  variables hinges on calculating the vapor-equivalent of rain using surface temperature. Ambient temperature is more likely to reflect the ambient vapor, and therefore I think the analysis should be done using the precipitation-equivalent of vapor and comparing it to the rain samples. This may not make a difference, but should be checked given the non-linearity brought up by the authors and the fact that all conclusions are based on this definition. I would suggest returning the manuscript to the authors for revisions.

Principal criteria	Excellent (1)	Good (2)	Fair (3)	Poor (4)
<b>Scientific significance:</b>  Does the manuscript represent a substantial contribution to scientific progress within the scope of Atmospheric Chemistry and Physics (substantial new concepts, ideas, methods, or data)?		2		
<b>Scientific quality:</b>  Are the scientific approach and applied methods valid? Are the results discussed in an appropriate and balanced way (consideration of related work, including appropriate references)?			3	
<b>Presentation quality:</b>  Are the scientific results and conclusions presented in a clear, concise, and well-structured way (number and quality of figures/tables, appropriate use of English language)?		2		

## **Specific Comments**

### **Abstract**

L11: Does 'equilibration' refer to 'exchange between ambient air and raindrops' or 'temperature-dependent equilibrium fractionation'? The description of the  $\Delta\delta\Delta d$  figure in the previous sentence highlights the latter, but I tend to associate equilibration with the former process. L15 also cites equilibration being less when RH is higher – RH would not affect the temperature-dependent equilibrium but would affect the exchange of isotopes between rain and ambient air through rain evaporation and condensation. See Section 2 of Nusbaumer et al

(2017) for a good description of the microphysical processes needed to describe isotope ratios in rain and vapor (“Evaluating hydrological processes in the Community Atmosphere Model Version 5 (CAM5) using stable isotope ratios of water”, *Journal of Advances in Modeling Earth Systems*, 9:949-977). Non-equilibrium kinetic fractionation must also be included in this analysis.

## Section 1

P2, L30: It might help to insert some explanation about Rayleigh distillation along rain back trajectory, which is the starting point for getting to more depleted rain values at higher latitudes.

P2, L31: as long as the air column is unsaturated

P3, para1: Some introduction about kinetic fractionation would be appropriate here.

## Section 2

P4, L2: How much of the data was discarded for both measurements and calibrations? This is typically done to ensure no memory effects on the final values.

P4, L9: Was any oil added to the funnel to prevent evaporation during collection? Did the authors check for potential sample evaporation over 30 minutes, especially if the air was unsaturated? This could especially complicate the interpretation of *d*-excess values.

P5, L4: This is also complicated by needing to know both temperature of vapor and rain.

P5, L15: Is ambient temperature accurately reflecting raindrop temperature? Wouldn't it be better to look at “*equilibrium precipitation from vapor*”, since ambient temperature is more likely to represent the ambient vapor? I would suggest repeating the analysis using this direction (or at least check to see if it makes a difference). Especially given the authors' explanation for non-linearity in temperature control of isotope ratios.

P5, L24: Do you get the same results using  $\delta^{18}\text{O}$  observations instead for eqn (5)?

## Section 3

P7, L19: I assume the correlations reported here are significant with p values < 0.05? Could add ‘significant’ to line 19. Correlation with *h* has been seen by others (Crawford et al 2016), especially in unsaturated semi-arid environments. Correlation with rain intensity/amount is traditionally assigned to the classic ‘isotopic amount effect’. Some discussion of these would be appropriate here.

P7, L24: Consider: is the ‘surrounding vapor’ simply the vapor coming down with the rain in a downdraft? In which case I would expect them to be closely correlated. Can you distinguish this from non-downdraft/near-surface surface vapor being influenced by rain?

## Section 4

Fig 3 and P7, L30: how do you distinguish ‘rain samples in equilibrium with vapor’ – is this the zero line? I don’t see samples at 17 UTC near the zero line for  $\Delta\delta$  or for  $\Delta d$  at 21 UTC (looks more like 22 UTC). There are several periods where the uncertainty of  $\Delta d$  overlaps the zero line.

P7, L32-33: More negative values of  $\Delta\delta$  are seen before the frontal passage, with  $\Delta d$  trending towards zero. Some explanation of what is going on here? Also, if there is conservation of the depleted isotopic signature from the cloud, I think this should also be reflected in  $\Delta d$  being

zero. Any partial/incomplete tendency towards equilibration should be seen in both signatures from the way equations (5) and (6) are set up. If the argument is for 'conservation', i.e. vapor reflecting the original rain signature in equilibrium (possibly because it is associated with a downdraft associated with the frontal passage), this should be captured in both  $\Delta\delta$  and  $\Delta d$ . Fig 4, P8 L6-7: Some discussion of how non-equilibrium kinetic effects would influence the evolution of the  $\Delta\delta$  and  $\Delta d$  signals would be appropriate here. Why would the early pre-frontal samples be expected to be around the (0,0) point? Falling through an unsaturated atmosphere at 75-85% humidity, I would expect to see more evaporation and kinetic effects. Fig 4a is easier to interpret, the various transitions during the progression of the rain event are harder to read in Fig 4b.

## Section 5

P9, para 2: Here the discussion of  $\Delta\delta$  and  $\Delta d$  is in terms of precipitation, while previously it was defined as the difference in precipitation-equilibrated and surface vapors.

P9, L11: Assuming the precipitation is in equilibrium with the vapor it formed from in the cloud (through temperature equilibration), I would expect the  $\Delta d$  of rain versus 'vapor-where-the-rain-formed-in-the-cloud' to be small, but it could still be vastly different from the  $\Delta d$  at the surface.

P9, L15: Raindrops will also get more enriched during evaporation into an unsaturated atmosphere, because the lighter isotopes are preferentially evaporated, which will make the ambient vapor more depleted.

## Technical Corrections

### Abstract

L4: delete 'to'

L17: either 'this type of rain event' or 'these types of rain events'.

## Section 1

P2, L6: 'but do neither provide' -> 'but provide neither'

P2, L14: Refs in order of date or alphabetical?

P2, Eqn (2): should be a  $\times 1000$  in there

P3, L15: delete 'a'

P3, L24: 'allows to' -> 'allows us to'

## Section 3

P6, L5: 'extends' -> 'extended'

Fig 1 caption: 'measurement site at Zurich'