

## ***Interactive comment on “Vertical profile observations of water vapor deuterium excess in the lower troposphere” by Olivia E. Salmon et al.***

**Anonymous Referee #2**

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This paper describes vertical profiles of water vapor isotope ratios (e.g.  $dD$ ,  $d18O$ ) collected by aircraft in the lower atmosphere. The majority of the paper focuses on three case study flights, which took place around Indianapolis, USA. Additional flights were conducted both around Indianapolis and the Washington DC-Baltimore urban area, though much less is said about these. The paper pays particular attention to the utility of deuterium excess ( $dxs$ , defined as  $dD - 8 \times d18O$ ) as a tracer of distinct air masses and of evaporating cloud condensate. The three case studies presented are purportedly illustrative of Rayleigh distillation, evaporation of stratocumulus clouds, and erosion of a residual layer as the boundary layer develops. The key points of the paper appear to be that Rayleigh distillation plays a dominant role in setting boundary layer water vapor isotope ratios and that deuterium excess is a useful tracer of mixing

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between distinct air masses (and moisture sources) near the inversion layer.

The data collected are an important addition to the growing record of high-resolution water vapor isotope ratio measurements, and the attention to detail in the calibration and characterization of the measurements (reported in the Appendices) is quite impressive. The analysis also clearly demonstrates the utility of using deuterium excess to distinguish air masses, as compared to the individual isotope ratios. Nevertheless, I believe one of the main conclusions should be revisited and the clarity of the presentation improved.

Major Comments

1. The results could be better distilled. The paper is quite lengthy and detailed. As a result, it is easy for key points to become buried. Usually, I would not list this as a major concern, but in this case, I found much of the critical interpretation for the analysis was lost among the long-winded descriptions of the data. It might help readers if the critical arguments and conclusions were emphasized near the beginning and/or end of each sub-section. One place where this is very much needed is in Section 3.3, which discusses the developing boundary layer case (DBL). Here, more time could be spent on the interpretation of the causes of the fascinating differences in atmospheric structure among the profiles rather than on re-describing Figure 6.
2. Section 4.2 is another section that is somewhat difficult to follow, largely because of confusing terminology. How do the “scenarios” relate back to the equations presented in the methods? Also, “partial evaporation” and “near complete evaporation of a semi-dehydrated drop” could easily be confused as one and the same. As a result, it is not at all clear which “scenario” best represents the data.
3. I am not convinced by the analysis that Rayleigh distillation is the dominant process determining the vertical isotopic structure of the boundary layer. First and foremost, there are many papers that show the contrary; a few case studies are not sufficient to prove otherwise. Previous papers that have measured water vapor isotope ratio

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vertical profiles in situ (and have shown profiles consistent with processes other than distillation) include He and Smith 1999, Galewsky et al 2007, Noone et al 2013, Bailey et al 2013, Sodemann et al 2017, and Kelsey et al 2018. These studies contrast, to some degree, with the early work of Ehhalt, which was re-published as Ehhalt et al 2005.

Second, I am not entirely convinced that Rayleigh distillation gives the best physical interpretation for the Indianapolis “Ray” profiles. The paper argues that Rayleigh distillation is a good model when the boundary layer is dry adiabatic (and therefore that no clouds or precipitation exist). This is contrary to expectation: distillation depends on condensation and precipitation. Furthermore, other studies (see above) have shown nearly the opposite: that Rayleigh is appropriate when the boundary layer follows a moist adiabat but not when it follows a dry one. A clear exception, of course, is if the distillation occurs upwind and imprints an isotopic signature that is then advected downwind. One of the earliest papers discussing this phenomenon is Gedzelman 1988. Is it possible that advection is affecting the Indianapolis isotope ratio profiles? If so, this could make for an interesting discussion on whether moist convective processes regionally set the humidity structure of the lower atmosphere locally, which others have argued for tropical/subtropical regions (e.g. Brown et al 2008, Lee et al 2011, Bailey et al 2013).

Third, extra care must be taken in matching data to hypothetical Rayleigh curves since these can be designed to fit many data. A good example of this is found in Noone et al 2013. Consequently, it may be difficult to truly distinguish Rayleigh from mixing processes unless the theoretical end-members are well constrained. It is not clear in the manuscript from whence the theoretical end-members for Figure 4 are derived. Some description of the assumptions made would be a valuable addition to the analysis and perhaps make the case that the Ray flights are, in fact, illustrative of (upwind?) Rayleigh distillation in a much more compelling manner.

4. Some care should be taken in describing the Worden et al 2007 and Stewart 1975

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models and applying them to the case of stratiform clouds. Both models were designed to describe freely falling raindrops. In the original presentation of the model, Worden suggests raindrops undergo both an equilibrium fractionation and an effective fractionation, and that “this assumption is unlikely to be valid when raindrops are small. . .”. I note that Equation 3 substitutes a kinetic fractionation coefficient in place of the effective factor. What impact does this have? How does the model work if the assumptions of large falling drops are violated? The Worden model describes isotopic depletion with a loss of water from an air parcel. How can it be applied to describe a gain of moisture by the atmosphere? I have similar concerns with use of the Stewart model and would like to see more justification for these model choices for the case of stratiform clouds. Also, the equations presented from Stewart are from Equations 2 and 3 of the original paper, and there is an alpha missing in the denominator of the beta equation.

5. I found it difficult to identify the case studies in the flight figures due to distinct nomenclature. The figures use numbers, the text uses pseudonyms, and only the table provides both these plus dates. I would recommend one naming convention, preferably related to flight number or date. The reason being that a priori, it seems difficult to know whether the “Ray” days will really be Rayleigh-like.

6. The Isotope Theory section suggests there are “three common ways the isotopic composition of the atmospheric H<sub>2</sub>O<sub>v</sub> can change.” I would have thought these would be condensation, evaporation, and mixing. Rayleigh distillation is just an example model for condensation processes. Similarly, cloud evaporation is just one type of evaporation that can affect the atmosphere’s isotopic composition.

7. I have some trouble understanding how partial cloud evaporation can cause a minimum of deuterium excess near the inversion layer. Evaporation tends to favor the diffusion of the D relative to <sup>18</sup>O. Why wouldn’t partial evaporation result in an enrichment of the surrounding vapor? Perhaps I am missing something, but my hunch is most readers will also have this impression. It might be worth explaining the physical underpinning behind these conclusions in greater depth, perhaps in Sections 4.2 or

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4.4.

8. The calibration documentation is quite thorough and comprehensive. I was prompted, however, to ask a few follow up questions regarding the variations in concentration dependence shown for  $dD$ . Is it possible one would get a different answer if concentration biases were adjusted first and VSMOW-scaling applied separately? It also appears that there are higher errors in  $dD$  at low isotopic values at all water vapor concentrations, not just at the low concentrations. Is it possible that lower precision at low isotope ratios causes the appearance of “irreproducibility” in the concentration dependence?

Minor comments

Page 1 Line 35 – no need for “:” after “include”

Page 2 Line 10 –I had trouble distinguishing the conditions at a moisture source region from “surface H<sub>2</sub>O<sub>v</sub> sources.” Perhaps it might be more clear to say “an air parcel’s moisture source region, including the geography of the source and its meteorological conditions?”

Page 2 Line 19 – I think “further exchange” is meant instead of “equilibrium?”

Page 3 Line 3 – I might remove “point in” before time, since I initially confused “point” with space.

Page 3 Line 6 – Perhaps best to say “higher. . . resolution” since aircraft is not as high resolution as slower-moving platforms.

Page 3 Line 11 – Perhaps best to say that “measurements of vertical profiles” were conducted.

Page 4 Line 28 – Perhaps “produce” for “emit?”

Page 6 Figure 2 – Could the three analyzed flights be emphasized, perhaps by making the other flight lines dashed?

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Page 7 Table 1 – Table caption/title should provide some explanation of the “codes” and what is meant by “support study”

Page 9 Line 13 – One of many examples of the great care that was taken in the analysis

Page 9 Line 31 – This appears to be the only place where “q” is used instead of “H<sub>2</sub>O<sub>v</sub>.” Consistency would help.

Page 10 Equations – This appears to be the only place “R<sub>vap</sub>” is used instead of “R<sub>v</sub>.” Again, consistency would help.

Page 11 Figure 4 – All the lines are “solid,” thus it might be best to say the “black” line to distinguish it from the “pink” one. Also, I don’t fully understand how the average mixing ratio is given by a gray envelope. Shouldn’t the average be a point?

Page 12 Line 7+ - Here is an example where it’s easy for the reader to become lost in all the number-reporting. This paragraph would greatly benefit from a sentence that provides a bit more of a picture of what is going on physically.

Page 12 Line 18 – I might say “predictions” instead of “theory.”

Page 13 Figure 5 – Caption should explain what the shaded area for the inversion is and what the envelopes around the profiles are.

Page 14 Line 6 – How was the average range of the inversion calculated? From how many days or which days of data?

Page 14 Line 16 – I’m not sure I agree that the data start “tracking” the mixing line. There just aren’t enough points for me to be convinced of that. Perhaps “approaches” the mixing line?

Page 14 Line 26 – This seems like an important argument explaining how is STC different from Ray, and yet it is buried halfway down the page. Perhaps it could be moved up in the sub-section.

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Page 15 Figure 6 – Most axes appear consistent across panels except for theta. Was this purposeful?

Page 17 subtitle – I'm not really sure what "general observations" means. Would "observations from other flights" be more descriptive?

Page 17 Line 21 – which observations are used here for this argument?

Page 19 Line 19 – A sentence or couple words reminding the reader what "Scenario 1" is would be appreciated.

Page 19 Line 22 – I think "drier" is meant.

Page 21 Figure 9 – I would recommend dots (or some symbol) instead of vertical lines to indicate the values of dxs expected. Otherwise, it is not clear that the reader should look for the intersection of the various lines.

Page 22 Line 24 – Excellent synthesis sentence: highlights the key point nicely.

Page 22 Line 36 – I disagree that these are some of the few data of this kind. There are quite a few studies that are not cited in this work. Please see my major comments for ideas.

Page 23 Line 24 – Kelsey et al 2018 also report dxs profiles.

Page 24 Line 4 – Perhaps "investigate" for "interrogate."

Page 27 Line 5 – "To check calibration. . ." against? of?

Page 30 Line 14 – The notation seems to change here. Should all isotopologues have subscript "v?"

Page 31 Figure D1 – At first I thought the black square was a symbol in the legend. It might be more clear simply to use the caption to say that the striped region shows the expected range for the observations, or something to that effect.

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-1313>, 2019.

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