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Atmospheric Chemistry and Physics
Discussions

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

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See attached pdf for formatted version with author responses in color.

Authors' Responses to Reviewer 2 âĂć Author responses are indicated in blue font. âĂć Locations of our edits in the "strike-through" and final versions of the manuscript are provided with the following convention: ([strike-through version] pg. #, ln # / [final version] pg. #, ln #).

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. To address the Reviewer's comment, we have consolidated the case studies' results (originally Sect. 3.1-3.3) and discussion sections (originally Sect 4.1-4.3) so that each case study's key isotope features are identified, and their possible cause(s) immediately discussed. The consolidated sections are now located in Section 4.1-4.3. We have also extensively revised Section 3.3 (now Section 4.3), which presents the DBL case study results.

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 semidehydrated 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. We thank the Reviewer for identifying Section 4.2 as an area that could see improvement. We have chosen to remove the cloud evaporation equations (see our response to comment #4), and by association, the paragraphs which discussed the degree of droplet evaporation under two scenarios. In their place, we have added text which evaluate the likelihood of cloud evaporation and its impact on d-excess under meteorologically-relevant time scales. We believe our changes have greatly improved the clarity of Section 4.2. (pg 24, ln 19 – pg 25, ln 39 / pg 10, ln 17 – pg 11, ln 2)

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 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. We thank the Reviewer for these suggested literature citations. We have revised our interpretation of the RAY (now CLR) case study to express that the Rayleigh-consistent observations likely reflect the isotopic imprint of prior condensation under saturated conditions, followed by advection of this imprinted signal to the Indianapolis study site. Additionally we note that the lower free troposphere measurements appear more consistent with mixing lines, which is indicative of mixing between subsiding free troposphere air and boundary layer air. We include the some of the suggested references to support this discussion (pg 19, ln 2-28 / pg 8, ln 10-33). 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). The reviewer make an excellent point that our fight conditions during the RAY (now CLR) flights are not consistent with moist adiabatic conditions. However, the Rayleigh prediction is most consistent with our observations, compared to mixing scenarios. We have changed this discussion to indicate that observed profile is an imprint of previous airmass dehydration conditions, and cite the suggested studies (pg 19, ln 17-28 / pg

8, ln 22-33). 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. The Reviewer makes a good point. We do note, however, that our Rayleigh curves are calculated using an objective method (Sect. 2.5; Eq (1)). The initial isotopic composition of the Rayleigh air parcel (Ro) is determined from the average observed boundary layer delta values. The equilibrium fractionation factors are calculated for the lifting condensation level temperature. We also demonstrate in Fig. S4 that varying the equilibrium fractionation factor by observed temperature does not lead to significantly different shaped Rayleigh curves. We now note that mixing endmembers are informed by actual observed delta values in different atmospheric layers (pg 10, ln 26 / pg 6, ln 26). Figure 7 now makes a direct comparison of our observations to Rayleigh theory and mixing scenarios.

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

nal paper, and there is an alpha missing in the denominator of the beta equation. We have opted to remove the Worden et al, 2007 and Stewart, 1975 equations from the paper for the reasons that both reviewers mention. Instead of calculating the impact different degrees of evaporation could have on surrounding vapor, we have reframed this discussion by evaluating the likelihood of cloud droplet evaporation impacts based on transport and equilibration time scales. We now show that a droplet would isotopically equilibrate with surrounding vapor faster than the time required for transport of a droplet from the bottom to the top of the inversion (Equation B5 in Bolot et al., 2013). These calculations suggest cloud droplet evaporation may not be responsible for the observed d-excess minimum during the STC flight. However, we maintain that a negative d-excess signal resulting from cloud or rain droplet evaporation could have been transported from an area upwind of the STC measurements. (pg 24, ln 19 – pg 25, ln 39 / pg 10, ln 17 – pg 11, ln 2)

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. The Reviewer brings up an excellent point. We have deleted any reference to research flight codes (RF#), and now refer to the flights by date. We maintain pseudonyms for the case study flights, but we have made sure that figures include both the flight date and case study pseudonym where appropriate. We have renamed the RAY case study to CLR (for clear skies) so that the pseudonym characterizes the day's meteorology, rather than a possible interpretation of the isotopologue data.

6. The Isotope Theory section suggests there are "three common ways the isotopic composition of the atmospheric H2Ov 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. We have reworded this section to indicate that we employ different models to represent condensation and mixing processes. Please refer to our response to comment #4 for our explanation for removing the cloud evaporation equations. (pg 9, ln 24-26 / pg 6, ln 1-4)

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 18O. 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 4.4. The Reviewer is correct that evaporation (from an infinitely large source) typically imparts a positive d-excess signal on the surrounding vapor. This is why we believe cloud evaporation to be responsible for the slight increase in d-excess in the middle of the inversion (Fig. 6b). As a droplet evaporates, its own d-excess signal becomes more negative, so subsequent complete evaporation of the droplet in another region would act to decrease the surrounding vapor d-excess (Aemisegger et al., 2015; Sodemann et al., 2017). We also now include a calculation (Bolot et al., 2013) showing that a droplet would isotopically equilibrate with surrounding vapor faster than the time a droplet would be transported from the bottom of the inversion to the top of the inversion. This calculation indicates cloud evaporation during the STC flight may not be responsible for the observed d-excess minimum. We do, however, maintain that evaporation of cloud/rain droplets upwind might have caused the d-excess minimum. We support this possible explanation with references that show that stratocumulus cloud droplet evaporation occurs at different altitude in and above the cloud layer, and that the inversion layer above stratocumulus clouds are not homogeneous in terms of depth or thermodynamic properties. (pg 24, ln 19 – pg 25, ln 39 / pg 10, ln 17 – pg 11, ln 2)

8. The calibration documentation is quite thorough and comprehensive. I was prompted, however, to ask a few follow up questions regarding the variations in con-

centration 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? Our calibration procedure does begin with concentration-dependence corrections (Sect. S2; note that the Appendix has been merged with the SI). We determined that VSMOW scaling of the concentration dependence-corrected delta values was not necessary (Figure S2.3). The Reviewer makes an interesting point about the apparent dD irreproducibility. However, we note that the "irreproducibility" at mid-range humidities (3000-8000 ppmv) only lie on one side of the correction curve (Fig. S2.2b), so it is an offset. On the other hand, variability on either side of the correction curve is observed for drier conditions (550-3000 ppmv; Fig. S2.2b), which indicates the low precision idea could be a possible explanation. We note that the uncertainty is only consequential for very low H2Ov mole fractions, where these depleted delta values are observed. We have added a sentence discussing the possible low precision and offset ideas (strike-through SI: pg 5, ln 5 / final SI: pg 5, ln 7).

Minor comments Page 1 Line 35 – no need for ":" after "include" The ":" has been removed.

Page 2 Line 10 –I had trouble distinguishing the conditions at a moisture source region from "surface H2Ov 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?" This sentence has been changed to reflect the Reviewer's suggestion.

Page 2 Line 19 – I think "further exchange" is meant instead of "equilibrium?" "Equilibrium" has been replaced by "further exchange".

Page 3 Line 3 – I might remove "point in" before time, since I initially confused "point" with space. "Point in" has been removed.

Page 3 Line 6 – Perhaps best to say "higher. . .resolution" since aircraft is not as high resolution as slower-moving platforms. This is a good point, "high" has been changed to "higher".

Page 3 Line 11 – Perhaps best to say that "measurements of vertical profiles" were conducted. We have incorporated this suggestion.

Page 4 Line 28 – Perhaps "produce" for "emit?" Thank you for this suggestion, we have replaced "emit" with "produce".

Page 6 Figure 2 – Could the three analyzed flights be emphasized, perhaps by making the other flight lines dashed? This is a good suggestion, the case study flight paths are now indicated with solid lines, and all other flight paths are indicated with dashed lines.

Page 7 Table 1 – Table caption/title should provide some explanation of the "codes" and what is meant by "support study" Per the Reviewer's comment #5, we have modified the flights codes so that the flights are identified by their date.

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 "H2Ov." Consistency would help. Thank you for catching this. As noted in our response to major comment #4, we no longer include the Worden et al., 2007 equation that the Reviewer is referencing.

Page 10 Equations – This appears to be the only place "Rvap" is used instead of "Rv." Again, consistency would help. Thank you for catching this oversight. As noted in our response to major comment #4, we have removed the Stewart, 1975 equation that the Reviewer is referencing.

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? Thank you for these suggestions. We have replaced "solid" with "black", and we have clarified that the grey envelope indicates the inversion layer, which is defined by the average H2Ov mole fraction observed at zINV and zFT during the vertical profiles. (Fig 4 has been split into three figures for each of the case studies, Fig 7- CLR; Fig 9 – STC; Fig 12 – DBL)

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. Thank you for this suggestion. We have added text to identify the important meteorological characteristics of each atmospheric layer on this day, and also decreased the amount of number-reporting. (pg 17, ln 6-19 / pg 7, ln 35 – pg 8, ln 9)

Page 12 Line 18 – I might say "predictions" instead of "theory." We have made this substitution.

Page 13 Figure 5 – Caption should explain what the shaded area for the inversion is and what the envelopes around the profiles are. The caption now indicates that the inversion layer (previously grey bands, now blue bands) lies between zFT and zINV, and that the shading around the isotope VP measurements correspond to total measurement uncertainty. (Now Fig 6)

Page 14 Line 6 – How was the average range of the inversion calculated? From how many days or which days of data? Similar to our changes to the caption of Fig. 4 (now Fig 7, 9 and 12) and Fig. 5 (now Fig. 6), we now specify that the bounds of the inversion layer range, which are unique to each flight, are defined by the average H2Ov mole fractions observed at zFT and zINV for each flight.

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? We have made this substitution.

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. We have moved this sentence to the second paragraph of Sect 4.2. (pg 21, ln 7 / pg 9, ln 18)

Page 15 Figure 6 – Most axes appear consistent across panels except for theta. Was this purposeful? Good catch! We have modified the theta range of Fig 6a (now Fig. 11a) for consistency.

Page 17 subtitle – I'm not really sure what "general observations" means. Would "observations from other flights" be more descriptive? We have renamed this subsection: "Airborne campaign observations of H2Ov isotopologues in the lower troposphere". (Now Sect. 3 title)

Page 17 Line 21 – which observations are used here for this argument? We now specify that the "DBL" case study observations are being discussed in this sentence.

Page 19 Line 19 – A sentence or couple words reminding the reader what "Scenario 1" is would be appreciated. We have revised the STC discussion paragraphs (see our response to major comment #2), and no longer reference cloud evaporation scenarios 1 and 2.

Page 19 Line 22 – I think "drier" is meant. Great catch, we did mean "drier". During our revision of this section, we have deleted "drier".

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. We have revised Section 4.2 per major comment #2, and in doing so, we have removed Figure 9 from the manuscript.

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. We have reworded this sentence to express that there are few studies that report vertical profiles of d-excess.

Page 23 Line 24 – Kelsey et al 2018 also report dxs profiles. Thank you for this suggestion, we now reference the Kelsey et al, 2018 study here, and in the introduction.

Page 24 Line 4 – Perhaps "investigate" for "interrogate." We have made the suggested replacement.

Page 27 Line 5 – "To check calibration. . ." against? of? We have rephrased this sentence.

Page 30 Line 14 – The notation seems to change here. Should all isotopologues have subscript "v?" Thank you for catching this, we have added missing subscripted v's to the isotopologue ratios. (Now in the SI, Section S6)

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. Thank you for this observation. We have modified the legend to better represent the slanted line region, and we have added a sentence to the caption describing the saturation values that the slanted lines represent. (Now in the SI, Figure S6)

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-1313/acp-2018-1313-AC2-supplement.pdf

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