The HDO/H_2O relationship in tropospheric water vapor in an idealized "last-saturation" model

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Received 9 May 2012; revised 17 August 2012; accepted 27 August 2012; published 5 October 2012.

[1] Previous model studies have shown that the isotopic composition of tropospheric water vapor is sensitive to atmospheric water transport processes, but compositional information is difficult to interpret due to the complexity of the models. Here an attempt is made to clarify the sensitivity by computing the relationship between tropospheric HDO (via δD) and H_2O (via specific humidity q) in an idealized model atmosphere based on a "last-saturation" framework that includes convection coupled to a steady large-scale circulation with prescribed horizontal mixing. Multiple physical representations of convection and mixing allow key structural as well as parametric uncertainties to be explored. This model has previously been shown to reproduce the essential aspects of the humidity distribution. Variations of δD or q individually are dominated by local dynamics, but their relationship is preserved advectively, thus revealing conditions in regions of convection. The model qualitatively agrees with satellite observations, and reproduces some parametric sensitivities seen in previous GCM experiments. Sensitivity to model assumptions is greatest in the upper troposphere, apparently because in-situ evaporation and condensation processes in convective regions are more dominant in the budget there. In general, vapor recycling analogous to that in continental interiors emerges as the crucial element in explaining why δD exceeds that predicted by a simple Rayleigh process; such recycling involves coexistent condensation sinks and convective moisture sources, induced respectively by (for example) waves and small-scale convective mixing. The relative humidity distribution is much less sensitive to such recycling.

Citation: Sherwood, S. C., and C. Risi (2012), The HDO/H_2O relationship in tropospheric water vapor in an idealized "last-saturation" model, *J. Geophys. Res.*, *117*, D19205, doi:10.1029/2012JD018068.

1. Introduction

[2] Atmospheric processes related to phase changes of water (including cloud formation and moist convection) continue to be a central uncertainty in large-scale simulations of the atmosphere. Observational constraints on the systematic aspects of such processes relevant to climate are particularly important, and particularly elusive. Clouds are complex, cannot by fully characterized observationally, and are sensitive to hydro-meteor microphysics and atmospheric dynamics on all timescales. This makes the use of cloud observations directly to constrain convective models a grand-challenge problem in atmospheric sciences that will not be solved soon.

[3] In recent years investigators have proposed that the isotopic composition of water vapor could provide an important and novel constraint on the behavior of convection and/or cloud microphysical processes [e.g., *Moyer et al.*, 1996; *Schmidt et al.*, 2005; *Lee et al.*, 2007]. The most useful measure so far has been the ratio of the amount of deuterated water HDO to the amount of H_2O, commonly expressed in the form of

$$\delta\mathrm{D} = 1000\left(\frac{R}{R_{\mathrm{sample}}} - 1\right), \tag{1}$$

where R is the ratio of concentrations of HDO to H_2O, and R_{sample} is this ratio in Standard Mean Ocean Water, 3.115×10^{-4}. (In principle $H_2^{18}O$ could also be exploited, or even better the two in tandem, but the greater measurement accuracy required for this is much harder to achieve.)

[4] Aircraft observations in the late 20th century found that HDO (δD) in the mid-troposphere either matched or exceeded that expected for a pseudoadiabatically lifted air parcel (a so-called Rayleigh calculation), clearly exceeding such values in the upper troposphere [*Gedzelman*, 1988; *Smith*, 1992; *Webster and Heymsfield*, 2003; *Ehhalt et al.*, 2005]. Sampling was however severely limited until the recent advent of satellite observations. *Kuang et al.* [2003] found a very weak vertical gradient in remotely sensed δD within the tropical tropopause region, suggesting significant convective

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0148-0227/12/2012JD018068

mixing throughout this region [see *Dessler and Sherwood*, 2003].

[5] More recently, several satellites have become available that can see down into the troposphere including the Tropospheric Emission Spectrometer (TES) [*Worden et al.*, 2006] which observes the lower to mid-troposphere; SCIAMACHY [*Frankenberg et al.*, 2009], which detects total column amounts (emphasizing the lower troposphere), and MIPAS [*Steinwagner et al.*, 2007] and ACE [*Nassar et al.*, 2007] which measure in and above the upper troposphere. Continuous in-situ analyzers that are of useful accuracy are also now available and are increasingly being deployed in field programs [e.g., *Noone et al.*, 2011].

[6] Efforts to interpret the TES observations directly using simple parcel or trajectory calculations [e.g., *Brown et al.*, 2008; *Lee et al.*, 2011] have tended to suggest a complex array of contributions to water vapor from a variety of convective pathways. However, the TES weighting function in these studies extends well down into the boundary layer, which is a problem for interpretation given that very different processes govern water vapor in the boundary layer versus the free troposphere [e.g., *Sherwood*, 1996].

[7] Other studies [*Galewsky et al.*, 2007; *Frankenberg et al.*, 2009; *Wright et al.*, 2010; *Galewsky and Hurley*, 2010; *Galewsky et al.*, 2011] have found that the isotopic composition of air in very dry free-tropospheric regions has not significantly changed during its trajectory after leaving convective systems and subsiding significantly to arrive at a low relative humidity. This result is consistent with the "last saturation" model of free-tropospheric humidity [see *Sherwood et al.*, 2010b], in which air exits convective regions with a nearly saturated specific humidity and then retains this value as it wanders horizontally while subsiding through isentropic surfaces until reaching the boundary layer or another convective system—except that, unlike the initial specific humidity, the initial δD may not match that obtained from a simple pseudo-adiabatic calculation. These results support earlier suggestions that isotopic ratios are informative about convective processes, even if they are measured far away from convection. It must not be forgotten however that land-surface interactions can dominate any signal measured near the surface and can affect the isotopic characteristics of air within deep convection near or over land [*Salati et al.*, 1979; *Frankenberg et al.*, 2009; *Risi et al.*, 2010; *Lee et al.*, 2012]. Also, some GCM studies have found that significant variations in relative humidity not predicted by the advection-condensation model can be brought about by sufficiently large changes to model microphysics [*Wright et al.*, 2010; *Risi et al.*, 2012b].

[8] Indeed, GCM studies (or single-column equivalents) using models equipped with isotopes enable a more quantitative investigation of specific physical mechanisms affecting either the humidity field or its isotopic composition. Comparisons of the simulated δD in vapor to those from the new satellites often find widespread biases, which could be attributed to general biases in the model or to satellite calibration or retrieval biases. However, when these biases are put aside, the agreement in global patterns is often quite good, except for a tendency toward underestimated equator-to-pole gradients in simulated total column HDO compared to SCIAMACHY [*Yoshimura et al.*, 2011; *Werner et al.*, 2011; *Risi et al.*, 2012b]. The pattern agreement is especially good for TES data if clear-sky sampling biases are properly accounted for [*Risi et al.*, 2012b], which is interesting given the presumed sensitivity of HDO to convective processes that are so hard to represent in global-scale models, and the large departures from equilibrium (i.e., low relative humidities) found in many regions. Comparison with upper-tropospheric observations tend to reveal greater biases [*Risi et al.*, 2012b] and sensitivity to model parameters [*Risi et al.*, 2012a] than at lower levels, for reasons that are not yet clear.

[9] Diagnosis of the factors that control δD in atmospheric vapor and precipitation is possible with GCM sensitivity experiments. Interestingly, recent studies have concluded that the so-called "amount effect" (observed anti-correlation between δD in rainfall and rain rate) is largely modulated by the δD of water vapor in the lower to mid-troposphere. In conditions of weak or infrequent rainfall, precipitation re-evaporates relatively quickly or at relatively high altitudes, causing ambient vapor to acquire a relatively high δD characteristic of moisture from near the surface. But in persistently rainy and more humid conditions, precipitation tends to evaporate more slowly while falling more rapidly, thus allowing relatively depleted rainwater formed aloft to equilibrate with vapor at low levels such that this vapor gradually becomes depleted as well [*Lawrence et al.*, 2004]; as this air is recycled back into storms, the δD of the rain itself ratchets downward [*Risi et al.*, 2008; *Lee and Fung*, 2008]. This process is evident in variations of the MJO [*Kurita et al.*, 2011]. The specific importance of re-equilibration (as opposed to net evaporation) of the rain has been pointed out by *Field et al.* [2010].

[10] Some investigators have noted that GCMs tend to be too humid above the boundary layer. *Risi et al.* [2012a] sought to explain this using isotopic information, concluding based on sensitivity studies with the LMDZ model that while several types of model error could in principle produce the bias, the seasonal cycle of δD in vapor aloft was a fingerprint of excessive vertical diffusion being the true culprit. Other studies have however shown that horizontal model resolution of at least T85 or so is necessary across many GCMs to simulate dry regions correctly regardless of vertical resolution [*Sherwood et al.*, 2010a], and that sufficient resolution in both directions is important for correct isotopic simulation in the ECHAM5 GCM [*Werner et al.*, 2011]. It thus remains unclear exactly how important mixing (real or numerical, vertical or horizontal) is in affecting the isotopic composition or overall amount of water vapor. Encouragingly, however, none of the aforementioned studies suggest that numerical impacts on isotopic signatures dominate physical ones. Thus these models should still be useful for diagnosing the behavior of physical processes.

[11] The above studies have identified a number of processes that affect δD. However, they arguably have not yet produced any clear advice on how to model convection or clouds, nor yielded a concise explanation of what causes the observed departure of δD from the Rayleigh model. One limitation of GCM studies is that they are rather challenging to interpret. Also, it is usually not practical to alter the structural assumptions in a given GCM, but some model-data biases appear to be resistant to changes in parameters alone [*Risi et al.*, 2012a]. Single-column studies [*Bony et al.*, 2008; *Risi et al.*, 2008] have been very helpful in elucidating basic

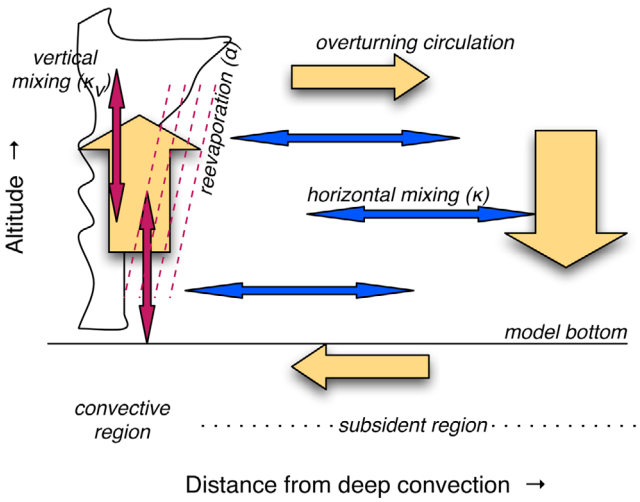

Figure 1. Cartoon showing the processes in the model. Yellow arrows indicate prescribed overturning circulation, blue arrows parameterized horizontal mixing, red arrows parameterized vertical mixing, and red dotted lines the parameterized reevaporating precipitation.

mechanisms, but lack an explicit representation of the large-scale circulation which is crucial for properly simulating water vapor even in an idealized setting [*Sherwood and Meyer*, 2006]. Finally, parcel calculations have proven useful but do not incorporate the energy and water conservation constraints that are crucial in determining the global characteristics of water vapor. Interestingly, many different modeling approaches, including all of the above plus cloud resolving models [*Smith et al.*, 2006; *Blossey et al.*, 2010], are able to obtain roughly similar departures from the Rayleigh process. This makes it hard to see what exactly is needed to obtain a given δD or what, if any, reasonable model can be rejected by the observations.

[12] We therefore bridge the above approaches by extending the idealized 2-D modeling approach of *Sherwood and Meyer* [2006, hereafter SM06] to include HDO. The next section reviews this model and the isotopic calculations, with section 3 discussing the results.

2. Model

2.1. Transport

[13] The transport model, described fully by SM06, is a simple, two-dimensional implementation of the advection-condensation paradigm for predicting humidity [e.g., *Sherwood et al.*, 2010b]. Its vertical coordinate spans the free troposphere (at 5 hPa resolution), and its horizontal coordinate (10 positions) notionally represents distance from convection. Four variables are predicted for each grid cell: in addition to the water vapor mixing ratio q within the cell and precipitation flux P out the bottom of the cell, examined by SM06, we add the HDO mixing ratio q_D and precipitation P_D. A steady, horizontally uniform, large-scale subsidence everywhere energetically balances a prescribed net radiative cooling profile with the temperature profile also prescribed. The subsidence is mass balanced by net ascent in deep convective clouds, taken to occur in clouds of negligible area occurring within only 10% of the domain denoted the "convective region" (as shown by SM06 results are not sensitive to reasonable variations of the size of the convective region). These upward injections of mass provide water vapor, which is then advected by the winds. The remainder of the domain is free of phase changes, isotopic exchanges or vertical mixing. Horizontal winds satisfy continuity, and are thus strongly divergent aloft in the convective region and weakly convergent elsewhere (see Figure 1).

[14] Additional horizontal transport is parametrized in three alternative ways. The simplest, and default way is advection by a mean, uniform horizontal wind superimposed on the divergent wind. The second way is by relaxation of quantities toward their horizontal mean; this seems very artificial, but can be taken to represent what would happen if air masses were rearranged randomly on some timescale. The third way is by horizontal diffusion. The mixing rate in each case is determined by a parameter, κ.

[15] Since detrainment of water vapor from net upward convective motions alone cannot account for most of the vapor present at levels below about 10 km [*Sun and Lindzen*, 1993], some type of convective moistening is essential. Two alternative schemes are considered. In the first (EVAP) scheme, all water condensed in the net upward convective motions is detrained with the air, and then rains downward through the convective region, evaporating as it falls according to

$$E = \alpha(q_s - q)P \tag{2}$$

where α is a height-independent, tunable constant representing the propensity of falling hydro-meteors to re-evaporate and q_s is the saturation mixing ratio. Evaporated water E within a given cell is added to the cell's q and subtracted from the P leaving through the bottom of the cell. In the second (MIX) scheme, $E = 0$ and water vapor is instead subjected to strong vertical diffusion in the convective region only, quantified by a diffusion constant κ_V. This assumption implies transport by many small eddies or highly entraining and detraining thermals or small plumes, for example, as opposed to the single troposphere-spanning updrafts implied in EVAP. When running with MIX, portions of the model domain are sometimes brought above saturation, in which case in-situ dehydration is invoked to return the air to saturation (the importance of this is discussed later in section 4).

2.2. Treatment of Isotopes

[16] Vertical and horizontal diffusion, advection and relaxation processes operate independently on each isotopologue and thus do not alter isotopic ratios (we note that *Berkelhammer et al.* [2012] report evidence of MIX-style, non-fractionating transport in the early stages of MJO events but rainfall evaporation signatures in later stages). However isotopic ratios are affected by phase change processes. To treat this, we follow the relatively simple treatment of *Dessler and Sherwood* [2003].

[17] Equilibrium fractionation by so-called "Rayleigh distillation" process is assumed for condensation within convective updrafts or during in-situ removal of supersaturated vapor. In a Rayleigh process the condensate and vapor are assumed to remain in equilibrium as conditions change slowly, and condensate is assumed to be removed immediately so that there is no subsequent effect of lofted condensate

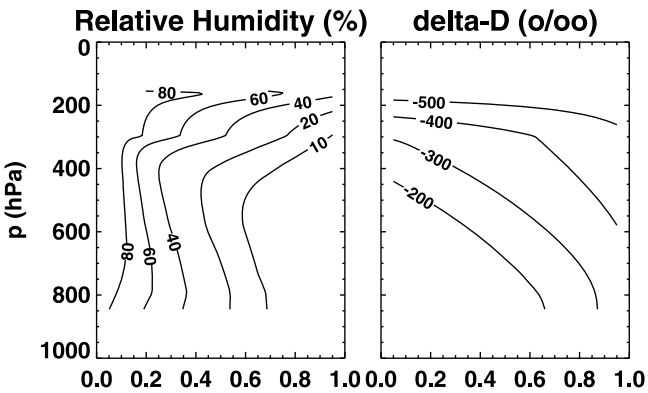

Figure 2. (left) Relative humidity and (right) δD versus pressure and horizontal position from the model.

on the vapor, consistent with classical pseudoadiabatic calculations. Condensate will be more enriched in HDO than the vapor from which it condenses, thus the vapor will gradually become more depleted in HDO as cooling and condensation proceed. This is a standard reference calculation. We do not consider non-equilibrium or lofting effects sometimes considered in more complicated calculations.

[18] As noted in the section 2.1, we follow SM06 in assuming that all water that condenses in deep convection in EVAP is carried to the highest convective level before falling as precipitation. Since at the highest level nearly all the initial total water content has condensed, the isotopic composition of the precipitation is simply set to that of the subcloud-layer vapor. This assumption is not strictly consistent with the pseudoadiabatic calculation for vapor, since the precipitation obviously must be retained in the air to reach the highest level. For the part of the ascent where condensate is liquid, we are therefore neglecting the continuing effect of this liquid on the vapor as it is carried upward. This effect would add some HDO back to the vapor at the expense of the condensate. Once the condensate freezes, the neglected effect should be negligible for reasons given in more detail in section 4.2.

[19] This simplification in EVAP is partly offset by another, which is that no fractionation is allowed for the condensate as it falls and re-evaporates. This is again a significant omission for liquid precipitation, since falling liquid droplets will equilibrate with ambient vapor independently of any net phase change [*Friedman et al.*, 1962; *Field et al.*, 2010]. We thus expect that vapor below the melting level (roughly 600 hPa in the tropics and lower at higher latitudes) will be insufficiently depleted in our calculations. The effect of this on the global mean was estimated by *Field et al.* [2010] at roughly 50‰. However, we will show that the region of primary interest is the upper troposphere where nearly all falling precipitation is likely to be in the ice phase. This is discussed further in section 4.2.

2.3. Boundary Conditions

[20] The horizontal boundary conditions are periodic. H_2O and HDO profiles are initialized to an observed sounding and a Rayleigh profile respectively, and run to steady state via a standard time stepping mode. The final state is not sensitive to the initial condition, but is affected by the upper and lower boundary conditions.

[21] At 850 hPa the boundary values (relevant only for MIX) are 13.0 g kg^{-1} and, in the default case, δD of -120‰. For EVAP runs, updrafts carry 15 g kg^{-1} of total water with a δD of -90‰, close to values observed near the surface over warm tropical oceans [e.g., *Kurita et al.*, 2011]. To assess the importance of these values, we repeated the calculations with an 850 hPa δD of -60‰ and with undepleted updraft water content (δD = 0). For all runs an upper boundary condition is introduced for practical reasons but has little effect except very near the tropopause (see section 3.4).

3. Results

[22] The H_2O and HDO fields produced by the model are shown in Figure 2, with H_2O shown as a relative humidity and HDO shown as a δD. SM06 compared the histograms of relative humidity thus obtained at each pressure level against those from satellite observations and found them to be reasonably close to observed. At any given pressure level there is a close relationship between δD and relative or specific humidity, as reported in many studies [*Galewsky et al.*, 2007; *Frankenberg et al.*, 2009; *Galewsky and Hurley*, 2010; *Noone et al.*, 2011; *Galewsky et al.*, 2011; *Risi et al.*, 2012b]. This arises because very dry air has subsided considerably since having been last saturated at a high, cold level; air in higher parts of a cumulus cloud is more depleted of HDO by fractionation during condensation, and this low δD property is retained during the air's subsequent, slow ascent as discussed previously.

[23] The close isobaric relationship between humidity and δD means that variations in the latter, either in space or time, will tend to mirror changes in relative or specific humidity if the comparison is done between air masses at a similar pressure or temperature. This begs the question of how much independent information one can get from HDO beyond what can be gleaned from humidity. Indeed, either the relative humidity or δD are primarily indicators of how long the particular air mass has subsided since last saturation.

[24] The best way to examine the data, therefore, is to focus not on variations in δD alone but on relatively smaller variations in the HDO-H_2O relationship, as has been done by many (though by no means all) previous efforts to use isotopes to constrain atmospheric processes. Since each of these variables is conserved away from deep convection (especially in the model, though apparently also to a useful level of approximation in reality), deviations in the relationship should reveal convective or microphysical effects most clearly. We therefore present all data in the form of this relationship, for the remainder of the article.

3.1. Overall Results, and the Role of Convective Transport Type

[25] Figure 3 compares the isotopic relationship simulated by the model for EVAP versus MIX convection, with default parameter settings. The colored zones show the range of the data in δD-q space, while the symbols identify where three different pressure levels fall on the graph; for example, data from 700 hPa can be found all the way from the bottom of the graph (10+ g/kg) up to 0.2 g/kg depending on horizontal location in the model (the former being in the convective region, and the latter in the driest region).

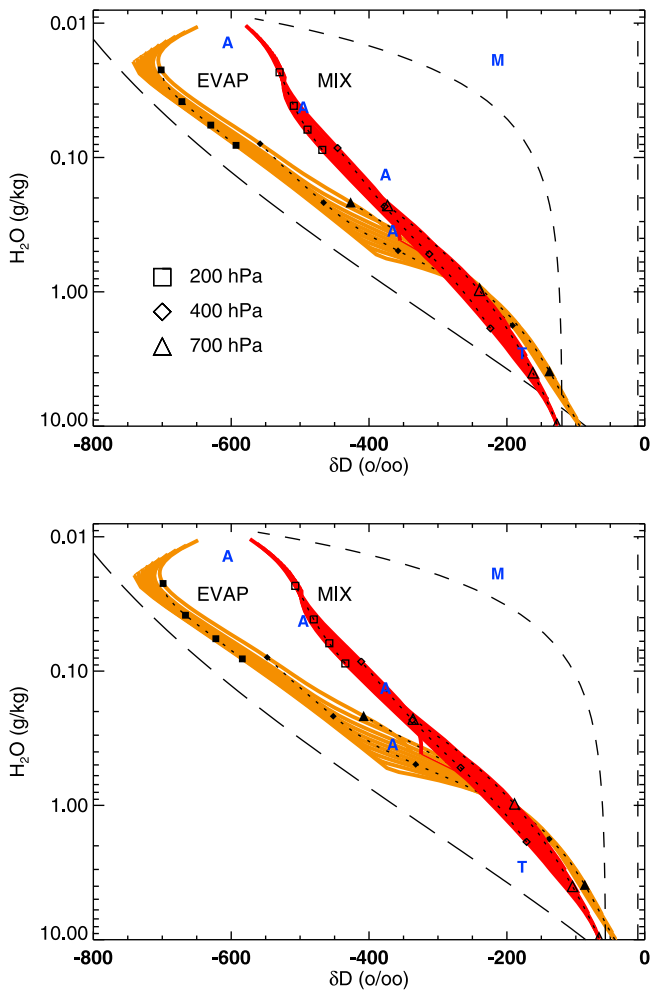

Figure 3. Comparison of EVAP and MIX simulations with (top) default parameter settings and (bottom) higher boundary-layer δD. Envelope of results across levels and horizontal positions for each simulation is shown with colored shading. Within this, markers for three chosen pressure levels (see legend) are shown, with dotted lines connecting the markers for different horizontal locations in the model. The Rayleigh curve is shown as a long dashed line, the mixing line between air from lower and upper boundaries is shown by a short dashed line, and the δD value of falling precipitation at its level of origin is shown by the vertical short-dashed line at right. Blue letters show satellite retrievals averaged between 30 S–30 N from three satellites (A = ACE, M = MIPAS, T = TES), with each letter showing the mean δD and q at a selected retrieval level. The MIPAS value appears to be strongly affected by the retrieval process (see text).

[26] The relation is very tight for either model configuration, with a given value of q always paired with nearly the same δD value (within $\pm$50‰ or so) regardless of pressure or horizontal location. This simply shows the approximately conservative behavior of both HDO and H_2O away from the convective region in the model. The calculation shown in the lower panel with higher boundary-layer δD values produces somewhat higher δD throughout the troposphere, but the sensitivity to model details described in this paper is essentially the same in either case.

[27] The results overall are qualitatively consistent with previously reported characteristics. Both the EVAP and MIX curves are less depleted in HDO than indicated by a Rayleigh calculation (long-dashed line), but are nonetheless highly depleted compared to vapor in the subcloud layer or the precipitation in EVAP (shown by a vertical dashed line). Likewise, they are much more depleted than the air one would obtain by mixing subcloud-layer and near-tropopause air (curving dashed line).

[28] Comparing the locations of the pressure symbols in the two results, we see that the MIX distribution is displaced significantly along the (horizontal) δD-axis but hardly at all along the (vertical) q-axis compared to the EVAP distribution. As reported in SM06, and in accord with the advection-condensation approximation, varying the nature or strength of convective transport has little impact on q, but here we see that it can significantly affect δD at least in the upper troposphere. In the lower troposphere there is little difference between the two curves. The behavior near the tropopause is discussed in section 3.4.

[29] Also shown in Figure 3 are data from three satellites: ACE, MIPAS and TES (see section 1). In each case we have averaged the retrieved values on pressure levels over the tropics (30S-30N) and shown levels where $q > 0.01$g kg^{-1}: a single value at 250 hPa for MIPAS, four values from 475 hPa to 175 hPa for ACE, and one value near 600 hPa for TES. Absolute calibration is a significant issue for these satellites, as evident from the huge discrepancy between ACE and MIPAS and documented biases in other instruments [e.g., *Worden et al.*, 2011]. Thus, these instruments are more useful for identifying geographic variations in properties than for constraining the average isotopic relationship simulated by our model. Following the procedure of *Risi et al.* [2012a], however, who tested the ability of satellite averaging kernel-based retrievals to reproduce the original humidity values on particular pressure levels simulated by a GCM, we find that simulated MIPAS-retrieved values of δD and q at 250 hPa are too high by 250‰ and too low by 56%, respectively, compared to the actual values in the original field. Accounting for these retrieval biases moves the MIPAS observation close to that implied by ACE (for which a similar test revealed only small retrieval errors). In any case it is encouraging that our model is not too far off of the TES observations, and in the MIX configuration, it falls nearly on top of the ACE observations. The results agree reasonably well with TES at low levels, but this does not mean too much given our neglect of precipitation re-equilibration and the sensitivity of results to the lower boundary condition.

3.2. The Roles of Vertical Versus Horizontal Transport Rates

[30] Figures 4 and 5 show the isotopic relations in two particular horizontal locations in the model: the convective region (Figure 4) and the driest region (Figure 5). Each plot shows two vertical locations for each of EVAP and MIX, comparing results from a sweep of both parameters: α (for EVAP) or κ_V (for MIX), and κ.

[31] As shown by SM06, stronger convective moistening (increase in either α or κ_V) increases q everywhere, but not by very much. As explained by SM06, this is because the

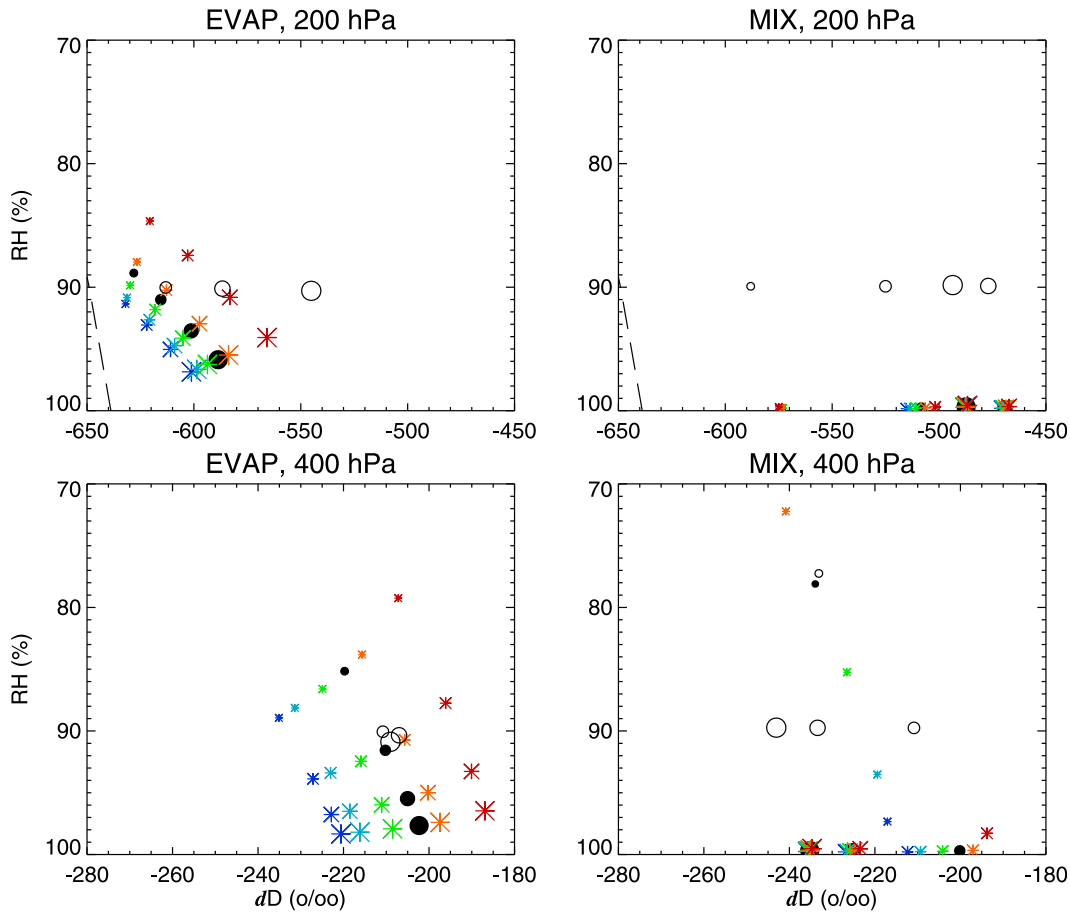

Figure 4. Humidity (vertical axis) versus δD (horizontal axis), at (top) 200 hPa or (bottom) 400 hPa in the convective region of the model. (left) EVAP and (right) MIX, both with advective mixing. For EVAP, smallest asterisks show α = 0.0025 with larger ones showing 0.005, 0.01, 0.02; for MIX, the corresponding κ_V are 100, 300, 3000, 10000 hPa^2 d^{-1}. Asterisk color indicates horizontal mixing rate, ranging from 0.025 (blue) to 0.4 (red). The circles show runs with the best-guess κ, with standard assumptions (filled circles) or with large-scale condensation limiting RH to 90% (open circles).

convective region is already near saturation and its humidity is therefore difficult to budge by changing convective behavior; meanwhile humidity in the rest of the domain is set by that in the convective region and by horizontal transport. Also as shown by SM06, stronger horizontal mixing (κ) significantly moistens the domain, except for the convection region which it slightly dries. Thus horizontal mixing is much more important for determining overall humidity than is convection, in this model (and as argued by SM06, probably in the real world).

[32] The behavior of EVAP is relatively smooth, with parameter variations causing modest and monotonic changes. MIX is much more nonlinear since the convective upper troposphere is brought to saturation for sufficiently large κ_V and/or small κ. Once this happens, humidity loses all sensitivity to κ_V, but when moisture is below saturation (seen at 400 hPa in Figure 4 for the lowest value of κ_V), it is more sensitive than in EVAP.

[33] These figures show that the departure between EVAP and MIX in Figure 3 depends on κ_V in MIX. When this is low enough so that the convective region is no longer saturated (such that no large-scale condensation occurs), δD drops to roughly match that in EVAP; this is seen in both regions and pressure levels (compare the smallest symbols at right with the EVAP results at left).

[34] In both versions of the model, increasing the convective moistening parameter (larger asterisks in the figures) shifts the isotopic relationship toward higher δD for a given q. A shift in this direction was also found in a GCM by *Risi et al.* [2012a] when decreasing the precipitation efficiency. However, successive doublings of κ_V produce steadily diminishing increases in δD in MIX and are always small in EVAP. The range of isotopic relationships for different convective moistening parameter for either version is much smaller than the difference between MIX and EVAP.

3.3. Impact of Easing Large-Scale Condensation

[35] Motivated by the above results, we conducted additional simulations (all with advective horizontal mixing) where the relative humidity threshold for in-situ condensation was lowered from 1.0 to 0.9. This allows condensation to occur in EVAP, while producing it at lower humidities in MIX.

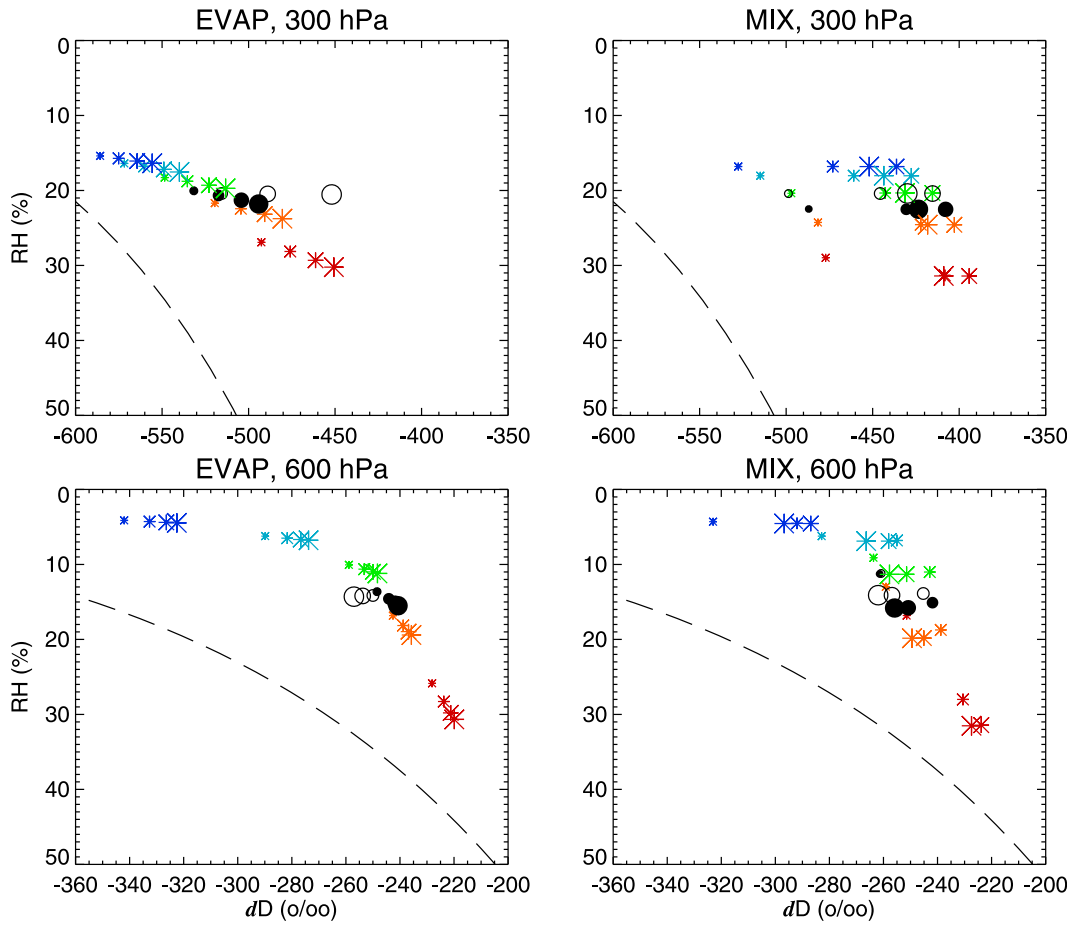

Figure 5. As in Figure 4, but for the driest model region. Note that higher pressure levels are shown and scales are different than in Figure 4, and pressure levels were chosen to intersect approximately the same isopleth of q as in the Figure 4.

[36] The results of this, shown as open circles in Figures 4 and 5, are interesting. In MIX, the only impact is to reduce all humidities in the model by a small percentage, with essentially no impact on the isotopic relationship. But in EVAP, the δD values are increased, provided that relative humidities reach 0.9 which occurs when α is above a minimum required value. As α is further increased, q cannot rise any further due to the ceiling imposed by the condensation process, but δD continues to increase and approaches values seen, up to this point, only in the MIX configuration.

[37] This result is curious because the proximate impact of in-situ condensation is to *deplete* the vapor of heavy isotopes, and yet the end result in the EVAP case is that the vapor is becoming more *enriched*. This paradoxical result is explained in section 4. In the MIX case we do not see this enrichment, but also do not see any depletion even though one might expect it. *Risi et al.* [2012a] found essentially the same result as in our MIX case, when increasing a parameter in their GCM (the breadth of the sub-grid scale humidity variations) having an effect equivalent to our threshold reduction. This suggests that their GCM behaves more like the MIX version of our simple model; indeed, the detrainment of condensed water by the convective scheme in their GCM is unaffected by ambient relative humidity (unlike in equation (2)) and leads to large-scale saturation and subsequent in-situ condensation.

3.4. Role of the Stratosphere and Tropopause Layer

[38] Isotopic behavior near the tropopause was examined in a model somewhat similar to the present one by *Dessler and Sherwood* [2003], who included effects from lofted ice and slow advection by the stratospheric circulation. That study found that evaporating ice significantly affected the isotopic composition of air entering the stratosphere, but in a way that was sensitive to the history and isotopic composition of ice particles. We do not include these effects here and do not attempt to predict the isotopic composition of water vapor entering the stratosphere.

[39] Accordingly, and to simplify the calculation of advection, the SM06 model predicted values only where the vertical velocity was downward, specifying the value at 150 hPa as a boundary condition. We tested to make sure this does not affect results by changing the boundary value from −600‰ to −900‰; this affected results only for the very driest values of q, below 0.02 g/kg, where the EVAP curve can be seen in Figure 3 to bend upward toward the prescribed value. This

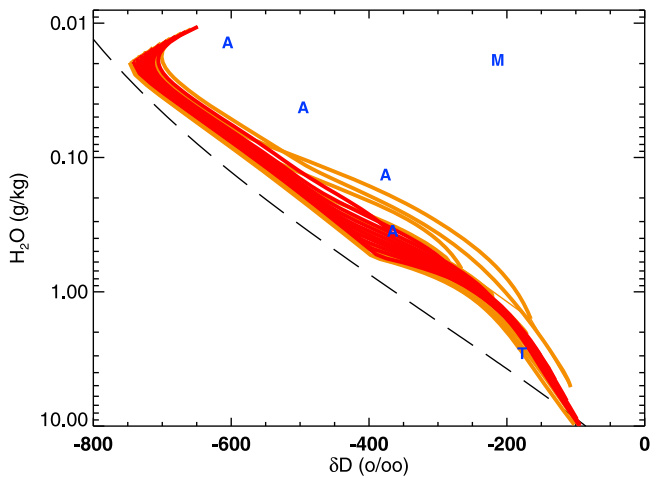

Figure 6. As in Figure 3, but comparing advective and diffusive advection for the EVAP case. The broader distribution shown (brown) is the diffusive one.

uppermost region should therefore be disregarded in our calculations.

3.5. Role of Horizontal Transport Type

[40] Figure 6 compares results for advective and diffusive forms of horizontal transport, for the EVAP case (the impact of changed transport is very similar in MIX, but with both distributions shifted in the manner shown in Figure 3). The dispersion of the isotopic relation is clearly broader when using diffusive transport (a third option, relaxation transport, yields intermediate results and is not shown). The broadening is most evident in the middle and lower troposphere, as expected since the air at these levels has on average spent longer subsiding and therefore has experienced more diffusion. The dispersion is associated with a shift in the mean, as dry regions experience increases in δD for a given H_2O while moister regions see little change. Note that in our model, since HDO and q isopleths are everywhere almost exactly parallel and the circulation is steady, diffusion must have qualitatively the same effect whether vertical or horizontal.

[41] Since diffusive vertical transport might occur in a GCM with a coarse horizontal grid or poor numerics, the above result agrees with that of *Risi et al.* [2012a], who found that a poor numerical representation of vertical advection increased δD in their GCM. Given the extreme nature of the diffusion used here, our results suggest that numerical diffusion in GCMs is unlikely to be a first-order problem in simulating isotopes, although it probably causes some overestimation of δD values in dry regions. Some studies have found horizontal resolution changes to have more of an effect on simulated isotopic relationships [*Werner et al.*, 2011], but this could be due to the knock-on effects of improving other aspects of the simulation (the circulation, for example) at higher resolution, rather than necessarily resulting from less diffusion.

4. The Vapor Budget

[42] The above results show that the EVAP model produces δD values too close to the Rayleigh result compared to observations, even with very large α. This is surprising when one considers that in the EVAP model, the precipitation is isotopically very rich, with an initial composition matching that of the boundary-layer air ($\sim$−50‰). This is very much richer than the ambient vapor, especially in the upper troposphere, and probably richer than most real precipitation at mid or upper levels [see *Bony et al.*, 2008] especially if one considers that lofted ice particles are likely to have a radial gradient of δD within, with the earliest (hence richest) condensate near the core and relatively depleted condensate nearer the surface. Yet despite this, no matter how large we make α, the δD of the upper tropospheric water vapor remains stubbornly low.

4.1. H_2O

[43] To see why, we begin with the local humidity budget,

$$\frac{dq}{dt} = A + M - C, \tag{3}$$

where A is convergence of transport of water vapor by the large-scale circulation, including convection and its detrainment of vapor, and horizontal mixing; M is the additional source of moisture from the model convection scheme (equalling E in EVAP and the convergence of diffusive transport in MIX); and C is in-situ condensation. For the equilibrium model solutions considered here, the left-hand side is zero. Outside the convective region, each individual term is zero.

[44] If the system is perturbed, its distribution of $q(x, z)$ will change in response until a new distribution is found that rebalances the budget. To quantify this requires knowing the sensitivity of each term to changes in q. Roughly speaking, we expect A to scale with q assuming that changes in q are smooth and broad-scale in (x, z). M scales with $q_s - q$ in EVAP, and with q in MIX (again assuming a spatially smooth change). C scales with $q - q_s$, although in a highly nonlinear way; in practice C will increase very rapidly with mean q once sufficiently close to saturation, but will be negligible otherwise. In the convective region q is close to q_s, so any process that scales with $q - q_s$ will change much more in a relative sense for any given change in q than will a process that scales with q. Perturbation to the system will therefore be compensated mainly by changes in C and M rather than by changes in A.

[45] Now in EVAP (with standard assumptions), $C = 0$, and A balances M. It will thus be very difficult to change M (say by increasing α) because of the difficulty of changing A. Instead a small increase in q (as shown in Figure 4) will mostly offset the increase in α, so as to keep changes in A and M small. This underlies both the resistance of q to changes in α, and the stubbornly low δD in the upper troposphere in EVAP.

[46] In MIX, on the contrary, C and M are both significant as long as M is large enough to bring about in-situ condensation. Moreover, M scales with q, thus neither it nor A will be very responsive to changes in q. Instead the most responsive term will be C, and M will therefore be much easier to change than in EVAP. A doubling of κ_V should approximately double both M and C. This again happens without significant changes in q, so that large-scale humidity is not affected, but implies an intensification of "recycling"

of water vapor locally in the convection region through convective source and condensational sink processes.

[47] The same is true in EVAP if we allow condensation to occur before $q = q_s$: the rigidity of the budget is thereby relaxed, allowing increases in M to freely occur in response to changes in convection, balanced by changes in C.

[48] To summarize, we conclude that robust in-situ drying and convective moistening processes must coexist in the convective region in order for either process to be sensitive to changes in its governing parameters. This insight is not necessarily intuitive, would not be evident in a parcel-type calculation, nor be easy to draw out of GCM experiments, but it should apply to any model of the atmosphere in the absence of significant temperature or dynamical changes.

4.2. The δD: The Importance of the Ice Phase

[49] The arguments so far apply to terms in the H_2O budget; we now turn to the implications for δD. First, the convective source M is quite rich for both EVAP and MIX, as shown in Figure 3 (for MIX the effective source is the difference between the isotopic character of a mixture of air from above and below a level compared to that at the level itself, which in the limiting case is shown by the dashed line). This accounts for why δD falls above the Rayleigh curve in both versions of the model. Depletion by in-situ condensation is relatively weak compared to the enrichment of adding an equivalent amount of such rich vapor. Thus, a corresponding increase in both M and C will in this model increase the HDO of the vapor.

[50] This explains the paradox noted earlier, whereby allowing in-situ condensation in EVAP raised the δD: this occurred because the increase in C permitted a similar increase in M, and the latter had a stronger effect on δD. It also explains why the isotopic relationship is more sensitive to model parameters in the upper troposphere than lower down (as also found by, e.g., *Risi et al.* [2012a]), since in-situ dehydration only occurs in the upper troposphere in this model. Most in-situ condensation is also likely to be confined to the upper troposphere in GCMs and the real world.

[51] The above reasoning considers only net phase changes, ignoring the fact that gross fluxes between the phases occur strongly in both directions. In liquid droplets, these fluxes quickly bring the two phases to an isotopic equilibrium. The importance of this was noted in section 1 and analyzed recently by *Field et al.* [2010].

[52] However, in ice this effect is strongly suppressed because molecules cannot escape unless they are in the top one or two monolayers of the ice lattice, and diffusion within the ice is usually assumed negligible. Thus, it is only the top surface of the ice particle that can equilibrate with the vapor. Since this layer is of order a few tenths of a nanometer in thickness, while ice crystals are typically of order 10 micron diameter or larger, only a minute fraction ($\sim 10^{-7}$ or less) of the ice can interact with the vapor in the absence of net ablation of the ice to liberate more layers of the lattice. However, HDO diffusion may not be negligible (T. Peter, personal communication, 2012) in the ice phase; if not, this could lead to isotopic exchanges even in the absence of net sublimation, which would provide another means of elevating δD in the ambient vapor.

[53] Since falling precipitation is typically in the ice phase until below the melting level, which is near 600 hPa or lower, our neglect of fractionation other than that associated with net phase changes should be justified in the upper troposphere where we have found the most interesting behavior.

[54] An additional issue is the internal heterogeneity of the ice particle. We have assumed ice particles are well-mixed (as assumption also made in most if not all current atmospheric models), but in reality the exterior of a lofted ice particle would presumably be relatively depleted while the interior would be enriched, having formed from vapor at lower levels. Taking this into account would weaken the enrichment effect of precipitation in EVAP, making it even more necessary to have recycling processes to bring δD up to realistic values.

5. Conclusion

[55] We find, as have others using GCMs, that the isotopic composition of ambient water vapor is sensitive to convective processes in ways that the overall specific humidity is not. We emphasize moreover that to isolate these effects requires looking simultaneously δD and specific humidity q. Either one of these on its own informs mainly about local air history, rather than phase-change processes.

[56] Our sensitivity studies imply that some form of "moisture recycling," or the combination of nearby, offsetting convective moistening and condensational drying processes, is ultimately necessary to account for the excess of δD in observed vapor in the upper troposphere relative to a Rayleigh process. This mechanism is directly analogous to the moisture recycling that can cause rainfall in continental interiors to be more enriched than would have been expected if all rain had originated from vapor transported directly from the ocean [*Salati et al.*, 1979; *Frankenberg et al.*, 2009; *Risi et al.*, 2010; *Lee et al.*, 2012]. This recycling is most prevalent in the upper troposphere because it requires substantial in-situ condensation, which in turn requires the high relative humidities typical at deep convective outflow levels.

[57] The physical nature of the recycling process, not fully explicit in our model, could take many forms. For example, transport by highly entraining, small convective eddies (implicit in our MIX model) would provide such recycling. Atmospheric waves can also provoke transient cooling and condensation events, which combined with reevaporation of falling precipitation will also constitute moisture recycling. Rain falling into dry air pockets (not present in our model) and evaporating there would increase recycling if the resulting vapor source were balanced by enhanced condensation in nearby locations, or by advection, but not (at least to first order) if it were balanced by compensating reductions elsewhere in the reevaporation of precipitation.

[58] Our relatively simple generalization of what can lift δD (for a given q) rests on two key constraints in our model, which may only hold approximately in reality. First, we find a strong water-vapor budget constraint mainly in the upper troposphere due to the high relative humidity and the strong sensitivity of phase-change processes to small changes in the saturation deficit. This constraint means that attempts to increase the magnitude of any moisture source are relatively ineffective, unless a condensational sink is also available that is similarly sensitive to small changes in the saturation deficit. Otherwise, the attempted increase in moisture delivery

will be mostly neutralized by a small increase in relative humidity.

[59] The second important constraint is the inability of ice particles to equilibrate with surrounding vapor on relevant timescales. This constraint, commonly assumed in atmospheric models, means that the delivery of HDO to the environment (or uptake therefrom) cannot take place unless there is net sublimation or ablation of ice particles. This net phase change is in turn regulated by the ambient relative humidity, as discussed above. We find that even with unrealistically rich precipitation, δD is difficult to budge by evaporation alone without sufficient large-scale condensation.

[60] The situation described here for the upper troposphere is completely different from that just above the tropical tropopause. There, relative humidity is very low, and added water vapor would be advected into the stratosphere, making the stratospheric isotopic composition relatively sensitive to the availability of lofted ice even in a vapor-conserving model [*Dessler and Sherwood*, 2003].

[61] Despite the simplicity of our model, it does a respectable job—with adequate moisture recycling in the upper troposphere—of reproducing the observed lapse of δD with decreasing q, suggesting that the observed behavior can be explained relatively simply at least to first order. The model is however very simple and excludes many processes, so one would not expect it to agree exactly with real-world observations.

[62] Our results can help to interpret GCMs, and indeed reproduce several of the results of sensitivity tests by *Risi et al.* [2012a] on the LMDZ GCM. This GCM seems to behave more like the MIX version of our model, which may be attributable to the fact that condensed water detrained from convection in that GCM is essentially forced into the large-scale environment regardless of its relative humidity, leading to additional large-scale condensation if the amount detrained increases. Our model is simple and lacks horizontal condensed water transport into drier regions. However, some GCMs may, in effect, overestimate such transport by allowing deep convection to coexist unrealistically with environments that are too dry [e.g., *Derbyshire et al.*, 2004; *Mapes et al.*, 2009].

[63] An implication of our results is that arguably the simplest possible advection-condensation model, exemplified by our EVAP case, is not consistent with isotopic observations. This can be viewed as a generalization of the conclusion of *Moyer et al.* [1996], establishing additional conditions for lofted ice to have a significant effect in the troposphere. Thus, very simple models need to include some form of in-situ condensation and reevaporation processes even though one might get away without them for only the purpose of simulating overall humidity. We find in particular that the MIX model, which can be thought of as an atmosphere with highly entraining cumulus clouds and significant moisture recycling by mixing, is one way of obtaining the recycling required. But there are probably many other ways, which helps to explain why many past studies with various types of models have managed to obtain relatively similar δD profiles.

[64] **Acknowledgments.** We thank Gabriele Stiller and Michael Kiefer for sharing the MIPAS data, Kaley Walker and Peter Bernath for sharing the ACE data and John Worden for sharing the TES data. S.C.S. thanks the ARC and the LMD/IPSL for funding and accommodating a visit to the LMD where a portion of this work was performed.

References

Berkelhammer, M., C. Risi, N. Kurita, and D. C. Noone (2012), The moisture source sequence for the Madden-Julian Oscillation as derived from satellite retrievals of HDO and H_2O, *J. Geophys. Res.*, *117*, D03106, doi:10.1029/2011JD016803.

Blossey, P. N., Z. Kuang, and D. M. Romps (2010), Isotopic composition of water in the tropical tropopause layer in cloud-resolving simulations of an idealized tropical circulation, *J. Geophys. Res.*, *115*, D24309, doi:10.1029/2010JD014554.

Bony, S., C. Risi, and F. Vimeux (2008), Influence of convective processes on the isotopic composition (δ^{18}O and δD) of precipitation and water vapor in the tropics: 1. Radiative-convective equilibrium and Tropical Ocean-Global Atmosphere-Coupled Ocean-atmosphere Response Experiment (TOGA-COARE) simulations, *J. Geophys. Res.*, *113*, D19305, doi:10.1029/2008JD009942.

Brown, D., J. Worden, and D. Noone (2008), Comparison of atmospheric hydrology over convective continental regions using water vapor isotope measurements from space, *J. Geophys. Res.*, *113*, D15124, doi:10.1029/2007JD009676.

Derbyshire, S. H., I. Beau, P. Bechtold, J.-Y. Grandpeix, J.-M. Pirou, J.-L. Redelsperger, and P. Soares (2004), Sensitivity of moist convection to environmental humidity, *Q. J. R. Meteorol. Soc.*, *130*, 3055–3079.

Dessler, A. E., and S. C. Sherwood (2003), A model of isotopes in the tropical tropopause layer, *Atmos. Chem. Phys.*, *3*, 4489–4501.

Ehhalt, D. H., F. Rohrer, and A. Fried (2005), Vertical profiles of HDO/H_2O in the troposphere, *J. Geophys. Res.*, *110*, D13301, doi:10.1029/2004JD005569.

Field, R. D., D. B. A. Jones, and D. P. Brown (2010), Effects of postcondensation exchange on the isotopic composition of water in the atmosphere, *J. Geophys. Res.*, *115*, D24305, doi:10.1029/2010JD014334.

Frankenberg, C., et al. (2009), Dynamic processes governing lower-tropospheric HDO/H_2O ratios as observed from space and ground, *Science*, *325*, 1374–1377.

Friedman, I., L. Machta, and R. Soller (1962), Water-vapor exchange between a water droplet and its environment, *J. Geophys. Res.*, *67*, 2761–2766, doi:10.1029/JZ067i007p02761.

Galewsky, J., and J. V. Hurley (2010), An advection-condensation model for subtropical water vapor isotopic ratios, *J. Geophys. Res.*, *115*, D16116, doi:10.1029/2009JD013651.

Galewsky, J., M. Strong, and Z. D. Sharp (2007), Measurements of water vapor D/H ratios from Mauna Kea, Hawaii, and implications for subtropical humidity dynamics, *Geophys. Res. Lett.*, *34*, L22808, doi:10.1029/2007GL031330.

Galewsky, J., C. Rella, Z. Sharp, K. Samuels, and D. Ward (2011), Surface measurements of upper tropospheric water vapor isotopic composition on the Chajnantor Plateau, Chile, *Geophys. Res. Lett.*, *38*, L17803, doi:10.1029/2011GL048557.

Gedzelman, S. D. (1988), Deuterium in water vapor above the atmospheric boundary layer, *Tellus, Ser. B*, *40*, 134–147.

Kuang, Z., G. C. Toon, P. O. Wennberg, and Y. L. Yung (2003), Evidence for convective dehydration from HDO measurements near the tropical tropopause, *Geophys. Res. Lett.*, *30*(7), 1372, doi:10.1029/2003GL017023.

Kurita, N., D. Noone, C. Risi, G. A. Schmidt, H. Yamada, and K. Yoneyama (2011), Intraseasonal isotopic variation associated with the Madden-Julian Oscillation, *J. Geophys. Res.*, *116*, D24101, doi:10.1029/2010JD015209.

Lawrence, J. R., S. D. Gedzelman, D. Dexheimer, H. K. Cho, S. D. Carrie, R. Gasparini, C. R. Anderson, K. P. Bowman, and M. I. Biggerstaff (2004), Stable isotopic composition of water vapor in the tropics, *J. Geophys. Res.*, *109*, D06115, doi:10.1029/2003JD004046.

Lee, J., J. Worden, D. Noone, K. Bowman, A. Eldering, A. LeGrande, J. L. F. Li, G. Schmidt, and H. Sodemann (2011), Relating tropical ocean clouds to moist processes using water vapor isotope measurements, *Atmos. Chem. Phys.*, *11*, 741–752.

Lee, J.-E., and I. Fung (2008), "Amount effect" of water isotopes and quantitative analysis of post-condensation processes, *Hydrol. Processes*, *22*, 1–8.

Lee, J.-E., I. Fung, D. J. DePaolo, and C. C. Henning (2007), Analysis of the global distribution of water isotopes using the NCAR atmospheric general circulation model, *J. Geophys. Res.*, *112*, D16306, doi:10.1029/2006JD007657.

Lee, J.-E., C. Risi, I. Fung, J. Worden, R. A. Scheepmaker, B. Lintner, and C. Frankenberg (2012), Asian monsoon hydrometeorology from TES and SCIAMACHY water vapor isotope measurements and LMDZ simulations: Implications for speleothem climate record interpretation, *J. Geophys. Res.*, *117*, D15112, doi:10.1029/2011JD017133.

Mapes, B., J. Bacmeister, M. Khairoutdinov, C. Hannay, and M. Zhao (2009), Virtual field campaigns on deep tropical convection in climate models, *J. Clim.*, *22*, 244–257.

Moyer, E. J., F. W. Irion, Y. L. Yung, and M. R. Gunson (1996), ATMOS stratospheric deuterated water and implications for troposphere-stratosphere exchange, *Geophys. Res. Lett.*, *23*, 2385–2388, doi:10.1029/96GL01489.

Nassar, R., P. F. Bernath, C. D. Boone, A. Gettelman, S. D. McLeod, and C. P. Rinsland (2007), Variability in HDO/H_2O abundance ratios in the tropical tropopause layer, *J. Geophys. Res.*, *112*, D21305, doi:10.1029/2007JD008417.

Noone, D., et al. (2011), Properties of air mass mixing and humidity in the subtropics from measurements of the D/H isotope ratio of water vapor at the Mauna Loa Observatory, *J. Geophys. Res.*, *116*, D22113, doi:10.1029/2011JD015773.

Risi, C., S. Bony, and F. Vimeux (2008), Influence of convective processes on the isotopic composition (δ^{18}O and δD) of precipitation and water vapor in the tropics: 2. Physical interpretation of the amount effect, *J. Geophys. Res.*, *113*, D19306, doi:10.1029/2008JD009943.

Risi, C., S. Bony, F. Vimeux, M. Chong, and L. Descroix (2010), Evolution of the stable water isotopic composition of the rain sampled along Sahelian squall lines, *Q. J. R. Meteorol. Soc.*, *136*, 227–242.

Risi, C., et al. (2012a), Process-evaluation of tropospheric humidity simulated by general circulation models using water vapor isotopologues: 2. Using isotopic diagnostics to understand the mid and upper tropospheric moist bias in the tropics and subtropics, *J. Geophys. Res.*, *117*, D05304, doi:10.1029/2011JD016623.

Risi, C., et al. (2012b), Process-evaluation of tropospheric humidity simulated by general circulation models using water vapor isotopologues: 1. Comparison between models and observations, *J. Geophys. Res.*, *117*, D05303 ,doi:10.1029/2011JD016621.

Salati, E., A. Dail'Olio, E. Matsui, and J. R. Gat (1979), Recycling of water in the Amazon Basin: An isotopic study, *Water Resour. Res.*, *15*, 1250–1258, doi:10.1029/WR015i005p01250.

Schmidt, G. A., G. Hoffmann, D. T. Shindell, and Y. Y. Hu (2005), Modeling atmospheric stable water isotopes and the potential for constraining cloud processes and stratosphere-troposphere water exchange, *J. Geophys. Res.*, *110*, D21314, doi:10.1029/2005JD005790.

Sherwood, S. C. (1996), Maintenance of the free-tropospheric tropical water vapor distribution. Part I: Clear regime budget, *J. Clim.*, *9*, 2903–2918.

Sherwood, S. C., and C. L. Meyer (2006), The general circulation and robust relative humidity, *J. Clim.*, *19*, 6278–6290.

Sherwood, S. C., W. Ingram, Y. Tsushima, M. Satoh, M. Roberts, P. L. Vidale, and P. A. O'Gorman (2010a), Relative humidity changes in a warmer climate, *J. Geophys. Res.*, *115*, D09104, doi:10.1029/2009JD012585.

Sherwood, S. C., R. Roca, T. M. Weckwerth, and N. G. Andronova (2010b), Tropospheric water vapor, convection and climate, *Rev. Geophys.*, *48*, RG2001, doi:10.1029/2009RG000301.

Smith, J., A. Ackerman, E. Jensen, and O. Toon (2006), Role of deep convection in establishing the isotopic composition of water vapor in the tropical transition layer, *Geophys. Res. Lett.*, *33*, L06812, doi:10.1029/2005GL024078.

Smith, R. B. (1992), Deuterium in North Atlantic storm tops, *J. Atmos. Sci.*, *22*, 2041–2057.

Steinwagner, J., M. Milz, T. von Clarmann, N. Glatthor, U. Grabowski, M. Hopfner, G. P. Stiller, and T. Rockmann (2007), HDO measurements with MIPAS, *Atmos. Chem. Phys.*, *7*, 2601–2615.

Sun, D. Z., and R. S. Lindzen (1993), Distribution of tropical tropospheric water vapor, *J. Atmos. Sci.*, *50*, 1643–1660.

Webster, C. R., and A. J. Heymsfield (2003), Water isotope ratios D/H, O^{18}/O^{16}, O^{17}/O^{16} in and out of clouds map dehydration pathways, *Science*, *302*, 1742–1745.

Werner, M., P. M. Langebroek, T. Carlsen, M. Herold, and G. Lohmann (2011), Stable water isotopes in the ECHAM5 general circulation model: Toward high-resolution isotope modeling on a global scale, *J. Geophys. Res.*, *116*, D15109, doi:10.1029/2011JD015681.

Worden, J., et al. (2006), Tropospheric emission spectrometer observations of the tropospheric HDO/H_2O ratio: Estimation approach and characterization, *J. Geophys. Res.*, *111*, D16309, doi:10.1029/2005JD006606.

Worden, J., et al. (2011), Estimate of bias in Aura TES HDO/H_2O profiles from comparison of TES and in situ HDO/H_2O measurements at the Mauna Loa observatory, *Atmos. Chem. Phys.*, *11*, 4491–4503.

Wright, J. S., A. Sobel, and J. Galewsky (2010), Diagnosis of zonal mean relative humidity changes in a warmer climate, *J. Clim.*, *23*, 4556–4569.

Yoshimura, K., C. Frankenberg, J. Lee, M. Kanamitsu, J. Worden, and T. Rockmann (2011), Comparison of an isotopic atmospheric general circulation model with new quasi-global satellite measurements of water vapor isotopologues, *J. Geophys. Res.*, *116*, D19118, doi:10.1029/2011JD016035.