The influence of convection on the water isotopic composition of the TTL and tropical stratosphere

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Abstract. We present the first in situ measurements of HDO across the tropical tropopause, obtained by the ICOS and Hoxotope water isotope instruments during the CR-AVE and TC4 aircraft campaigns out of Costa Rica in winter and summer, respectively. We use these data to explore the role convection plays in delivering water to the tropical tropopause layer (TTL) and stratosphere. We find that isotopic ratios within the TTL are inconsistent with gradual ascent and dehydration by in-situ cirrus formation and suggest that convective ice lofting and evaporation play a strong role throughout the TTL. We use a convective influence model and a simple parameterized model of dehydration along back trajectories to demonstrate that the convective injection of isotopically heavy water can account for the predominant isotopic profile in the TTL. Although ice particles from convection at these altitudes were not directly observed during the flight campaigns, observations include clear examples of residue of individual convective injections of water vapor to near-tropopause altitudes. Air parcels with significantly enhanced water vapor and isotopic composition can be linked via trajectory analysis to specific convective events in the Western Tropical Pacific and Southern Pacific Ocean. The results suggest that deep convection is significant for the moisture budget of the tropical near-tropopause region and must be included to fully model the dynamics and chemistry of the TTL and lower stratosphere.
1. Introduction

Water vapor and ice exert a controlling influence on the radiative and dynamical balance of the upper troposphere and lower stratosphere (UT/LS) and are key constituents in determining this region’s response to climate forcing [Smith et al., 2001; Fasullo and Sun, 2001; Minschwaner and Dessler, 2004]. The concentration of water vapor in the stratosphere also impacts the dosage of UV radiation reaching the surface through water’s control of heterogeneous stratospheric ozone depletion [Dvortsov and Solomon, 2001; Kirk-Davidoff et al., 1999]. In the UT/LS water vapor concentrations are central to the formation, evolution, and lifetime of cirrus that not only play a critical role in the radiative balance in the UT/LS but also in the dehydration of air ascending through the tropical tropopause layer (TTL). Changes in water vapor concentrations and the cirrus associated therewith control the radiative imbalance that amplifies climate forcing by CO$_2$ and CH$_4$ release at the surface and therefore quantifying the mechanisms that control water vapor in the TTL are key to predicting future changes in the climate system.

Quantifying the importance of convection in transporting boundary layer air to the TTL and lowermost stratosphere is pivotal for understanding the mechanisms that control the stratospheric water vapor budget and accordingly that of other trace gases and particulates. Due to this importance much emphasis has been put on understanding the mechanisms that control the water vapor budget of the TTL and UT/LS. In general, water vapor in the TTL is removed by in-situ condensation and cirrus formation on cooling during ascent or advection through local cold regions [Holton et al., 1995; Holton and Gettelman, 2001; Fueglistaler et al., 2005]. Convection can however provide additional
sources of water via evaporation of convective ice in undersaturated TTL air [Fu et al., 2006; Hanisco et al., 2007; Dessler et al., 2007]. Distinguishing the relevant mechanisms will allow models to better simulate how water vapor pathways linking the troposphere and stratosphere will change with increased climate forcing by CO$_2$ and CH$_4$. Many modeling studies that attempt to reproduce the observed water vapor mixing ratio of the TTL have suggested that convective ice lofting and evaporation may be unimportant to the region’s water budget, and that mixing ratios of water vapor in air crossing the tropical tropopause can be well explained simply by the minimum temperature experienced by those air parcels [Fueglistaler et al., 2004, 2005; Gulstad and Isaksen, 2007; Cau et al., 2007]. However, attempts to simultaneously model HDO mixing ratios find that convection is necessary to accurately reproduce observed profiles of both H$_2$O and HDO [Dessler et al., 2007; Bony et al., 2008]. Because water vapor isotopic composition is altered by all processes involving condensation or evaporation, the ratio of water vapor isotopologues (HDO/H$_2$O or H$_2^{18}$O/H$_2$O) can act as a tracer of an air parcel’s convective history [Pollock et al., 1980; Moyer et al., 1996; Keith, 2000]. Therefore, adding HDO to models constrains the amount of convection allowable in the model. Any model that attempts to explain the water vapor mixing ratio must also explain the water vapor isotopologue ratio which is usually written as the ratio of the heavier isotope (e.g. HDO or H$_2^{18}$O) to the more abundant lighter isotope (H$_2$O) referenced to a standard. In the case of water the reference is the ratio in Vienna Standard Mean Ocean Water ($R_{VSMOW}$) [Craig, 1961a]. Deviations from the standard, $\delta$, are reported in permil ($\%_\circ$) where for the HDO/H$_2$O ratio $\delta D = 1000(\text{HDO}/\text{H}_2\text{O}/R_{VSMOW} - 1)$. Values of $\delta D \approx 0\%_\circ$ are found
close to the boundary layer and more negative values (e.g. $\delta D = -600\%$) are found in highly dehydrated air masses near the tropopause.

Measurements of $\delta D$ from canisters and remote observations have reported enriched values of HDO compared to what would be expected from simple thermally controlled dehydration mechanisms [Moyer et al., 1996; Johnson et al., 2001; Kuang et al., 2003; Ehhalt et al., 2005]. To try to better model the observed $\delta D$ ratio Dessler et al. [2007], hereafter Dessler07, used the Fueglistaler et al. [2005] trajectory model and added a representation of convective ice flux to demonstrate that addition of water from evaporating convective ice was indeed a plausible explanation for isotopic enhancements observed by remote sensing instruments. Dessler07 was able to reproduce the $\delta D$ profile from remote observations with only a small perturbation to the water vapor mixing ratio produced from the Fueglistaler et al. [2005] model. However, the lack of direct in situ observations of $\delta D$ in Dessler07 means that the parcel trajectories followed in the model can not be directly tied to the data which makes validation of the theory difficult. In addition, the range of $\delta D$ observations used is sparse both spatially and temporally which makes regional, seasonal, and yearly variability not well quantified further complicating the comparison of the model to the remote observations.

In this paper we present the first in situ tropical measurements of HDO during both winter and summer. The high spatial and temporal resolution of the in situ data offer a more detailed test case than did the relatively coarse remote sensing data used in Dessler07. The in situ data are tied directly to diabatic back trajectories from the point of the measurement to identify sources of recent convective influence and to estimate the effect of convection on the $\delta D$ ratio and the water vapor mixing ratio. We then use our own
convective influence scheme to evaluate whether a measurable difference in $\delta D$ and water vapor mixing ratio is observed between data recently influenced by convection. Finally, as with Dessler07, we simulate the motion of air parcels along trajectories, tracking both water vapor and HDO in order to test if our model reproduces the profiles from the in situ data. However, we use real-time convection observations as opposed to the climatology of Dessler07.

2. Measurements

Isotopologue ratios were measured in situ aboard NASA’s WB-57 high-altitude research aircraft during the Costa Rice Aura Validation Experiment (CR-AVE) in January and February, 2006 and the Tropical Composition, Cloud and Climate Coupling (TC4) campaign in August, 2007, both based out of Alajuela, Costa Rica, at 9.9° North latitude. Measurements of $\text{H}_2\text{O}$, HDO, and $\text{H}_2^{18}\text{O}$ were obtained during these campaigns using the Harvard ICOS isotope instrument [Sayres et al., 2009]. We focus here primarily on HDO which, although less abundant than $\text{H}_2^{18}\text{O}$, experiences stronger fractionation on condensation, giving isotope ratio observations more robustness against any instrument systematics. For TC4, $\text{H}_2\text{O}$ and HDO measurements were also obtained by the total water Hoxotope instrument [St. Clair et al., 2008]. Water vapor mixing ratios are reported using the Harvard Lyman-α hygrometer [Weinstock et al., 1994], which has a long heritage on the WB-57 aircraft.

Data reported here are screened for both potential contamination and potential instrument systematics. To preclude inclusion of any ICOS data subject to contamination from water desorbing off the instrument walls, we report only ICOS data where ICOS water vapor is less than 0.5 ppmv greater than that reported by Harvard Lyman-α. The
Hoxotope instrument uses the technique of photofragment fluorescence and therefore is far less subject to wall contamination. An additional potential source of measurement uncertainty in the ICOS data is optical fringing and other artifacts in the baseline power curve, which can produce measurement biases that manifest themselves as offsets in measured $\delta D$. While fitting routines developed for ICOS (as described in Sayres et al. [2009]) mitigate some potential sources of bias, residual offsets on the order of 50% to 100% are still occasionally present. Periods of high potential bias are however readily identified and for this work we have removed all data with potential biases greater than the short term 1-$\sigma$ measurement precision. Quality-controlled ICOS data during CR-AVE in the driest, most signal-limited conditions ($H_2O < 10$ ppmv) show a maximum uncertainty in $\delta D$ of 30% (10 sec., 1-$\sigma$). (In wetter air, signal to noise is higher and therefore isotopic ratio uncertainty lower). For the TC4 mission, a laser change in the ICOS instrument resulted in increased bias uncertainty in low-signal conditions. We therefore show here ICOS data from TC4 only for wetter conditions ($H_2O > 10$ ppmv) and use Hoxotope data for dry conditions or for flights when ICOS did not report data. The base Hoxotope precision is 85% (10 sec., 1 $\sigma$). Although these uncertainties exceed those of laboratory-based mass spectrometers, they represent the most sensitive in situ water isotope measurements made in these conditions, and are comparable with the performance of remote sensing instruments while providing far higher spatial and temporal resolution.

In order to restrict our analysis to true tropical airmasses we show here only data from tropical flight segments out of Alajuela, Costa Rica in which the WB-57 aircraft made vertical transects through the tropopause while in the deep tropics, i.e. at latitudes below 10° North. Flights with segments meeting both the geographic and data quality criteria...
in the wintertime (CR-AVE) campaign occurred on January 30, and February 1, 2, and 7, 2006; in the summertime (TC4) campaign on August 6, 8, and 9, 2007 (Hoxotope) and August 8 and 9, 2007 (ICOS). We include water vapor data from the Lyman-\(\alpha\) instrument for all these flight legs and in addition for the qualifying flight of August 5, 2007, during which no isotopic data was available.

3. Mean tropical \(\delta D\) profiles

The isotopic composition of water vapor in the tropical atmosphere shows a sharp distinction in behavior between the bulk of the troposphere and the TTL (Figure 1). Below the TTL, both water vapor and \(\delta D\) fall off with altitude much as expected in pure Rayleigh distillation, where preferential removal of heavier condensate leaves the residual vapor progressively lighter [Jouzel et al., 1985; Ehhalt et al., 2005]. In the TTL water vapor concentrations continue to decrease to the tropopause while isotopic composition remains roughly constant. This feature is persistent in both summertime and wintertime observations, but some seasonal difference is evident. The TTL is isotopically lighter in the wintertime CR-AVE data with a mean \(\delta D\) of -650\(^\circ\)e, and shows a discontinuity starting at 370 K to isotopically heavier air with a mean of -500\(^\circ\)e. This shift is not well correlated with the slight increase in the water vapor measurements above the tropopause as the shift in \(\delta D\) starts below the tropical tropopause. In the stratosphere proper, the \(\delta D\) measurements are invariant within the precision limits of the data, while the water vapor mixing ratio increases linearly. In the summertime TC4 data, with nearby ITCZ convection, the TTL is isotopically heavier with a mean \(\delta D\) of -550\(^\circ\)e and its composition is continuous with the stratosphere proper. All these results suggest that evaporation of convective ice is a significant factor in affecting the isotopic composition of TTL water.
in both the summertime and wintertime. While in both campaigns the WB-57 did not directly intercept convective outflow at the top of the TTL or stratosphere, evidence of evaporation of convective ice is found in the summertime data which show two plumes of enhanced water vapor at 390 and 405 K and a second profile between 390 and 420 K that is 0.5 ppmv wetter than the mean profile (denoted by arrows in Figure 1). The two plumes were sampled during August 5th when no isotope data are available.

The observed tropical TTL isotopic profile is incompatible with simple dehydration during gradual ascent, which would produce isotopic depletion along with dehydration. In the bulk of the troposphere, from the lowest observations to the base of the TTL (θ = 355-360 K), observed water isotopic composition is roughly consistent with Rayleigh distillation. Water vapor concentrations fall by over two orders of magnitude and isotopic composition drops to approximately -700‰. Within the TTL, however, observed near-constant isotopic composition cannot be explained by a simple Rayleigh distillation model. (Model calculations are shown for comparison in Figure 1, in gray, with the range representing condensate retention between 0 and 80%). Gradual ascent and pure Rayleigh distillation within the TTL would have further reduced vapor isotopic composition to some -900‰. In the stratosphere proper, we would expect no further change save a slight increase due to methane oxidation as air ages. To within the precision of the data, δD is indeed invariant above the tropopause; the aircraft flights do not sample high enough altitudes or old enough air ages for methane oxidation to be significant.

Thus far we have evaluated the water vapor and δD measurements separately even though when in equilibrium they follow a very tight relationship that can be seen by plotting the logarithm of the water vapor mixing ratio versus δD (Figure 2). As in Figure
1 the data are isotopically heavy compared to a simple Rayleigh model. The Rayleigh relationship modeled here assumes that the air parcels sampled followed a single Rayleigh distillation curve given by the temperature profile measured by the WB-57 out of Costa Rica. Even if this temperature profile is representative of the tropics, ice evaporation in the free troposphere or lower part of the TTL would have the effect of shifting the Rayleigh curve. As an example, if the Rayleigh curve is shifted by 200% below the TTL, the subsequent relationship between water vapor and $\delta D$ would follow the light-gray shaded region shown in Figure 2. The CR-AVE data and most of the TC4 data greater than 10 ppmv water vapor fall on this shifted curve indicating that convection at or below the base of the TTL is important for setting the $\delta D$ value at the base of the TTL. The enrichment at the base of the TTL therefore may be due to convective ice evaporation in the mid-troposphere, more likely in summertime. In the wintertime that enrichment may have taken place in a different part of the tropics or perhaps even reflect an influx of midlatitude air [Hanisco et al., 2007; James and Legras, 2009]. However, below water vapor mixing ratios of 10 ppmv, corresponding to the upper TTL and lower stratosphere the simple relationship between water vapor and $\delta D$ is no longer valid. This implies that convective enhancements lower in the troposphere can only explain the data up to the middle of the TTL. To account for the enriched water vapor sampled at the top of the TTL and lower stratosphere, convection must reach the top of the TTL.

One other possible mechanism that would shift the Rayleigh curve is ice formation under supersaturated conditions. When ice forms under these conditions, kinetic effects between the isotopologues dominate over the thermodynamics with the result that $\delta D$ is
shifted to less depleted values as shown in Figure 1 by the solid and dashed black lines representing condensation at 120% and 150% relative humidity over ice.

Whether condensation at high supersaturation is a major factor in determining the $\delta D$ ratio can be evaluated by looking at the relationship between $\delta D$ and $\delta^{18}O$. If condensation follows a Rayleigh process (i.e. is in thermodynamic equilibrium) then the slope of the $\delta D$ to $\delta^{18}O$ relationship follows the well known meteoric water line (MWL) (Figure 3, thick black curved line) [Craig, 1961b]. As the level of supersaturation increases, the heavier $H_2^{18}O$ isotopologue is less depleted relative to HDO resulting in the slope between $\delta D$ and $\delta^{18}O$ becoming shallower as shown by the dashed lines in Figure 3. Data falling below the MWL can occur from mixing between parcels with $\delta$ ratios at different points along the MWL. Data from CR-AVE and TC4 are plotted in blue and cyan respectively and lie either on the MWL or below in the mixed region. We therefore conclude that condensation at high supersaturation is not a major factor controlling the shift in $\delta D$ away from the Rayleigh curve and leaves convective ice lofting and subsequent evaporation as the sole possible mechanism for the observed enhancements in $\delta D$.

To confirm the implication that convection within the TTL is a source of isotopic enhancement, we conduct two modeling studies. First, we use a back-trajectory model and maps of past convection to examine the isotopic impact of convection. Second, we model isotopic evolution along those trajectories to verify that addition of convective ice can produce the observed enhancements.

4. Back Trajectories and Convective Influence Model

The high spatial and temporal resolution of the in situ data allow us to use back trajectories to determine which sampled air parcels have been influenced by recent convective
events and evaluate whether convective influence is indeed correlated with isotopic enhancement. We use for this purpose an analysis framework similar to Pfister et al. [2001] and briefly documented in Pfister et al. [2009, this issue]. Diabatic back-trajectories (BTs) are performed along the flight tracks of the WB-57 aircraft using the GSFC trajectory model [Schoeberl and Sparling, 1995] driven by the GEOS-4 analysis [Bloom et al., 2005] and radiative heating rates. For the TC4 calculations, we used the mean July clear-sky radiative heating rates from Rosenfield [1991]. For CR-AVE, we used mean winter all-sky heating rates calculated by Yang et al. [2009]. For each aircraft point, a cluster of 14 day BTs are calculated in order to minimize errors from the BTs and also to allow for a gradient in convective influence, as the convective systems in the TTL are narrow and scarce. Each cluster has 15 points at 3 altitudes; 0.5 km above the aircraft level, at the aircraft level, and 0.5 km below the aircraft level. At each level there are 5 points along a line perpendicular to the aircraft flight track, each separated by 0.3 degrees. The BTs are run along theta surfaces, with the parcels moving across theta surfaces as indicated by the GEOS-4 heating rates. To calculate convective influence, the BTs are run through a time varying field of satellite brightness temperature, using global geostationary, 8 km resolution, 3 hourly satellite imagery. Convective influence is defined as occurrences along the BTs where the satellite brightness temperature is less than or equal to the trajectory temperature. Convective encounters are allowed even if the trajectory is as much as 0.25 degrees distant from the cold temperature.

The CR-AVE trajectories (Figure 4, plots A and C) show a clear separation in the origin of the air near the tropopause. Air from the free troposphere and throughout the TTL up to 390 K originates in the Western Tropical Pacific (WTP) and Southern...
Pacific Ocean. Air above 390 K mostly originates from over the Caribbean or has been sitting over the northern part of South America for much of the 14 day trajectories. A few trajectories also follow the tropospheric air that originates from the Southern Pacific. The trajectories from TC4 (plot B and D) are more uniform with air throughout the TTL and stratosphere originating either from the Asian monsoon region moving westward or from the southern Pacific Ocean and moving eastward. This is also consistent with the uniform $\delta^D$ measurements made during TC4. The model indicates that convective events reach as high as 410 K in the WTP and over South America during TC4. During CR-AVE deep convection occurs over South America and the Southern Pacific Ocean. Both patterns are consistent with observed isotopic profiles, with a sharper discontinuity in tropopause $\delta^D$ during CR-AVE and more uniform $\delta^D$ measurements during TC4.

The convective influence model, however, only indicated the possibility that convection has influenced the water vapor mixing ratio, as the amount of detrained ice that can evaporate depends on the level of saturation of the ambient air. For the convection to affect the water vapor mixing ratio we add a constraint to the model that requires the mixing ratio of water vapor to be below the saturation mixing ratio calculated along the trajectory at the point of potential convective influence. Only if this criteria is met can convection meaningfully moisten the air parcel. We attempt to identify such undersaturated parcels by constructing a pseudo-relative humidity using measured water vapor along the flight track and pressure and temperature along the back-trajectory. For example, the convective events over the Southern Pacific Ocean during CR-AVE reach up to 405 K (Figure 4, plot C) and the air during this time is undersaturated compared with the measured water vapor mixing ratio with pseudo relative humidity below 60% (Figure 4, plot E). These
convective events would be expected to hydrate the air parcels with evaporated ice. The convective events over South America that reach up to 410 K but occur when the air parcels are near saturation are less likely to influence the water vapor mixing ratio as the ice particles will likely fall before evaporating.

This protocol has one obvious weakness, that we cannot discriminate between humidity that pre-dates convective influence and that derived from convection itself. A parcel with 100% relative humidity at the point of convection may have been saturated beforehand, and therefore experienced no convective influence, or it may have become saturated from evaporating ice, and therefore experienced maximum convective influence. However, in the atmosphere we do not expect convective ice evaporation to bring parcels completely to saturation, and in this case the pseudo-relative humidity test remains meaningful. Furthermore, even a small change in water content can produce a large change in isotopic composition. We therefore define our complete convective influence criterion as that more than 50% of cluster BTs intersect convection (as defined above) and that pseudo-relative humidity at the point of intersection is less than 80%.

Both the summertime (TC4) and wintertime (CR-AVE) data show convective influence throughout the TTL and into the lower tropical stratosphere, with summertime convection extending higher than wintertime (Figure 5). Though convection was not directly measured above the base of the TTL during TC4 or CR-AVE, there is clear observational evidence of convection penetrating above 400 K in the tropics. Kelly et al. [1993] and Pfister et al. [1993] noted hydration associated with convection up to 410 K in northern Australia. More recently, Corti et al. [2008] have noted hydration up to 420 K, both in Australia and South America. As noted earlier, the data presented here show residual
evidence of convection indicated by the water vapor measurements shown in Figure 5 where between 390 K and 420 K there are two distinct profiles which differ by 0.5 ppmv water vapor, the wetter profiles being labeled as air parcels that have been recently influenced by convection. While not all wet points coincide with convectively influenced points, trajectories beyond seven days are not accurate enough to correctly identify specific convective events. Even with this uncertainty, the trajectories still have statistical validity. We would expect to see some convective influence in data taken over several flight days where the model indicates overall convective influence over the same flights in the same area. The 14 day time period is also significant because the back trajectories do not always reach the Asian monsoon region in that time (TC4), or the deepest convection in the Western Pacific (CR-AVE).

With the definitions for positive influence of convection on the water vapor mixing ratio defined above, we find that during the summertime a larger percentage of the data within the last 14 days has been influenced by convection. During the wintertime 37% of the data were influenced by convection within the TTL with a sharp cut off around 390 K. During the summertime 56% of the data samples were influenced by convection within the TTL and 37% of data samples were influenced by convection above 390 K. The highest potential temperatures that convective influence was observed at was 388 K and 414 K during winter and summer, respectively. Both convective events occurred over South America.

The convective influence calculations do not themselves show that convection can influence the isotopic composition of TTL water, as within the precision of the measurements, the δD data within the TTL do not show a quantitative separation between data that
is identified as with or without convective influence. (Above 380 K, the convectively influenced data for the $\delta D$ measurements tend to lie to the heavier side of the measured prole, though this difference is within the uncertainty of the measurements). This lack of discrimination is likely due to mixing during the 14 day trajectories and error in back trajectories. The model results do however highlight the extent of convection within the TTL and lower stratosphere.

5. Isotope Simulation

To help establish whether evaporating convective ice can indeed explain the observed non-Rayleigh isotopic profiles in the tropical TTL, we have added a simulation of isotopic evolution to the back-trajectories and convective influence model described above. We use a Rayleigh model and NCEP reanalysis temperatures to provide initial water vapor and HDO concentrations for the start of each trajectory assuming that the initial water vapor mixing ratio is equal to the saturation mixing ratio. We run two cases of $\delta D$ assumptions, the first assuming a start value set by simple Rayleigh distillation and the second an initial value enhanced by 200%, reflecting the observed tropospheric enhancements. Temperature and relative humidity are then calculated along the trajectory. As the trajectory is run forward, if the air parcel cools the relative humidity is kept equal to 100% and it is assumed that any removal of water by condensation follows Rayleigh distillation and this provides the resultant $\delta D$. If the temperature increases and the air becomes undersaturated then the concentrations of H$_2$O and HDO are left constant unless there is convective influence. If there is convective influence the model hydrates the air to saturation with evaporated ice that has a $\delta D$ of -100% (see ice data highlighted in Figure 1 and Hanisco et al. [2007])
The results of this simple model, using trajectories from TC4 that start between 350 and 360 K, suggest that observed convection over just 14 days can produce significant isotopic enhancement in the TTL (Figure 6, with trajectories that were influenced by convection plotted in red). Most trajectories ascend to their final potential temperature of between 370 and 390 K in 14 days. During that time water vapor decreases to between 3 and 7 ppmv. Convective enhancements of water vapor and HDO occurred throughout the TTL with events above 370 K being more pronounced in both water vapor and $\delta$D. However, by the time the trajectories reach the top of the TTL or lower stratosphere (where they would be sampled by the WB-57) the enhanced water vapor signature has been mostly washed out by desiccation in the model; though in the atmosphere it can also be washed out by mixing. The exception is the event at 385 K in which water vapor remains high (8 ppmv) since this event occurred above the tropopause and did experience further cooling. On the other hand, the $\delta$D signature is very distinct as the amount of subsequent depletion is small since only a few ppmv of water vapor is removed. The difference between trajectories that encountered convection and those that did not is between 200$\%$ and 300$\%$ (Figure 6, plot A). Convection at the base of the TTL does not greatly affect the final mean value of $\delta$D for the profiles that have subsequent convective influence (red profiles in plots A and B). However, for the profiles that are not otherwise convectively influenced (blue profiles), a shift of 200$\%$ at the start of the trajectory produces a shift ranging from 0$\%$ to 200$\%$ in the final $\delta$D value, with the result that the mean $\delta$D value has been shifted by 150$\%$ and the spread of values broadened (Figure 6, plot B). This makes the separation in $\delta$D between the parcels that were influenced by convection in the TTL and those that were not much smaller. This is consistent with the in situ data that show little difference in
δD between data marked as being convectively influenced in the TTL. Since the model only starts at the beginning of the 14 trajectories, it will not account for convection that occurred prior to this period. In addition, the absence of mixing and diffusion in the model tends to enhance the differences between convectively and non-convectively influenced air. All these limitations in the simulation and model will tend to make the separation between convectively and non-convectively influenced data greater in the simulation as compared to the actual in situ data.

6. Conclusions

We present the first in situ measurements of δD in the tropics during summertime and wintertime. This represents a unique data set to test models of dehydration in the TTL. In situ profiles of δD measured in the tropics during both summertime and wintertime show enrichment compared to the expected value if water vapor mixing ratio is controlled solely by minimum temperature. The wintertime measurements have a minimum δD of -650‰ at the base of the TTL and are then constant up to 370 K. At the top of the TTL and through the lower tropical stratosphere there is an increase in δD to -500‰ accompanied by a small increase in water vapor mixing ratio. The summertime data show enriched air starting at the base of the TTL and a uniform δD value throughout the TTL and stratosphere with a mean δD of -550‰. Water vapor data show plumes of high water at 390 and 405 K and two distinct profiles between 390 and 420 K, with the wetter profile having a water vapor mixing ratio 0.5 ppmv higher than the dry profile. The data presented here are consistent with the conclusions of Dessler07 and indicate that convection moistens the TTL and is required to explain the enriched δD measurements.
Back-trajectory analysis for the CR-AVE and TC4 data shows that the isotopic discontinuity at the tropopause in the wintertime CR-AVE data is likely real and reflects a different origin for air in TTL and stratosphere. It also supports the conclusion that was also drawn qualitatively from the tropical isotopic profiles that potential convective influence occurs throughout the TTL. The back-trajectory analysis is able to tie air parcels back to specific convective events. The back trajectories from CR-AVE and a convective influence model show the enrichment in both HDO and water vapor above 370 K comes from convection over the southern Pacific Ocean (≈20 °S). There is also strong convection over South America, but as the air is likely saturated during the time of the convection the effect on water vapor is presumably small. The back trajectories from TC4 show air parcels linked to deep convection up to 414 K throughout the Western Tropical Pacific and a few events over South America with the air in both regions being likely unsaturated. The convective influence model identifies the majority of samples from the high water vapor profile as being convectively influenced in the previous 14 days.

The δD data within the TTL do not show a quantitative separation between data that is identified as being convectively influenced within the precision of the measurements. This is in agreement with all data being convectively influenced at the base of the TTL or before the 14 days of the trajectory. Above 380 K, the convectively influenced data for the δD measurements tend to lie to the heavier side of the measured profile, though this difference is within the uncertainty of the measurements. The combination of isotopically enriched air throughout the TTL even as water vapor decreases, the evidence of frequent convective events reaching these particular airmasses, and demonstration that convective ice evaporation can produce the isotopic enhancements seen, all suggest strongly that
the dominant process governing the observed isotopic profiles in the TTL is addition of convective ice. In order to observe this convective effect predicted by the model more directly, and to quantify the $\delta D$ of ice injected into the TTL, measurements should be made closer to the sources of convection. Based on the back trajectory model this would be the Western Tropical Pacific and the southern Pacific Ocean.

Both the convective influence scheme and the $\delta D$ and water vapor measurements show that convection reaches as high as 414 K in the tropics during summertime. As these enhancements in water vapor mixing ratio occur above the local tropopause it is likely that these air parcels will not be further dehydrated and that convection has permanently moistened the tropical stratosphere. Though convective events at altitudes above the tropical tropopause are scarce, these events nevertheless moisten the tropical stratosphere. The importance of this process for the global stratospheric water budget is still not clear due to the small sample size as well as the possibility of large yearly variability. In addition to ice and water vapor, deep convection also may bring into the UT/LS other trace gas species and particulates that can have an effect on ozone chemistry and cloud formation.

Including deep convection in global climate models will be important for predicting the effect of changes in temperature on the climate system. The data clearly show, as Dessler07 and others have also suggested, that to correctly estimate the global amount of water vapor that crossed the tropical tropopause convection must be included. To quantify the water vapor added by deep convection more measurements will be necessary in the tropics particularly in the areas that the convective influence model indicated as being convectively active.
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Figure 1. Profiles of $\delta D$ (left) and water vapor mixing ratio (right) versus potential temperature for flights during CR-AVE (A) and TC4 (B). Only data from tropical flights are shown. For the plots of $\delta D$ the shaded region represents the range of values from a Rayleigh distillation model. The Rayleigh curve plotted here is based on minimum and maximum temperature profiles during each campaign and bounded on the left by an ideal curve where vapor condenses at 100% relative humidity and the condensate is immediately removed and on the right by a curve that includes the effect of 80% condensate retention as the air parcel rises. The shift in the Rayleigh curve due to condensation under supersaturated conditions are shown as solid and dashed black lines for relative humidity of 120% and 150%, respectively. Note that the increased scatter in the summertime data is due to the difference in precision between ICOS and Hoxotope.
**Figure 2.** Plot of $\delta$D versus water vapor with CR-AVE and TC4 data shown in blue and cyan, respectively. The shaded regions represent Rayleigh curves (as in Figure 1) with the light-gray curve shifted by 200% from the dark-gray curve at the base of the TTL.

**Figure 3.** Plot of $\delta^{18}$O versus $\delta$D. Data from CR-AVE and TC4 are plotted in blue and cyan, respectively. Thick black curve represents the meteoric water line with the dashed curves showing the effect of supersaturation on the relationship between $\delta^{18}$O and $\delta$D. Points below the meteoric water line result from mixing of air parcels with different $\delta$ values.
Figure 4. Plots show back-trajectories for aircraft flights during the CR-AVE (left plots) and TC4 (right plots) missions. Top (A and B): Shown are all trajectories that end above the 355 K isentrope and are colored coded by potential temperature as given by the colorbar to the right of each plot. Also shown are points along the trajectory where the air was influenced by convection. The mean latitude and longitude of the convection are plotted as black squares color coded by the potential temperature of the trajectory that intersected each convective event. Middle (C and D): Same as top but for trajectories ending above 380 K. Bottom (E and F): Same as middle but trajectories are color coded by pseudo relative humidity as described in the text.
Figure 5. Same as Figure 1 with profiles of $\delta D$ and water vapor mixing ratio plotted versus potential temperature for flights during the CR-AVE (top plots) and TC4 (bottom plots) missions. Data that are convectively influenced, using the criterion that more than 50% of cluster BTs intersect convection and that pseudo-relative humidity at the point of intersection is less than 80%, are highlighted in red.
Figure 6. Model results of tracking the water vapor mixing ratio and δD of air parcels as they move along diabatic trajectories from TC4 that start between 350 and 360 K. δD (plots A and B) and water vapor (plot C) are plotted versus potential temperature, with trajectories that were influenced by convection plotted in red. Model assumes that parcels are dehydrated to the saturation mixing ratio and trajectories that intersect convection during an unsaturated period are hydrated to a saturation of 100% with ice that has a δD of -100‰. Plot B assumes trajectories start with δD enriched by 200‰ as compared to plot A. Each line represents a single trajectory starting between 350 and 360 K, with water vapor mixing ratio equal to tens of ppmv and typical δD values of between -400‰ and -600‰.