

1 **Novel approaches for monitoring of water vapor isotope ratios:**

2 **Plants, lasers and satellites**

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Brent R. Helliker

5

*Department of Biology,*

6

*University of Pennsylvania*

7

*Philadelphia, PA, USA*

8

*(helliker@sas.upenn.edu)*

9

10

and

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David Noone

13

*Department of Atmospheric and Oceanic Sciences, and*

14

*Cooperative Institute for Research in Environmental Sciences,*

15

*University of Colorado*

16

*Boulder, CO, USA*

17

*(dcn@colorado.edu)*

18

1 **Abstract**

2 Atmospheric water vapor is a major component of the global hydrological cycle and the  
3 isotope ratio of that vapor is a key tracer for both hydrological and biological processes.  
4 Yet little is know of the isotopic composition of vapor over any spatial scale and through  
5 time because of challenges associated with collecting water vapor samples. Here we  
6 discuss alternate methods for measuring water vapor isotopes. The first approach  
7 capitalizes on the unique physiology and broad distribution of the epiphytic plant  
8 *Tillandsia usneoides* (Spanish Moss) to reconstruct a growing-season-integrated isotope  
9 ratio of water vapor. The second approach utilizes infrared spectroscopy to measure the  
10 isotopic composition without sample collection. In situ laser-absorption instruments and  
11 emission spectrometers aboard satellites employ similar optical measurement approaches,  
12 and while the former lends itself to developing very detailed time series the latter offers  
13 resolution of global-scale spatial distributions. These new approaches, while highly  
14 disparate, represent novel methods that compliment existing collection techniques and  
15 enable improved knowledge of both the spatial mean and variation of isotopes in  
16 atmospheric water vapor.

17

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19 Keywords: Isotope, proxy, satellite, spectroscopy, water vapor,

20

# 1 **1. Introduction**

2 Water vapor is central to understanding the water balance in the terrestrial biosphere,  
3 surface landscapes and in the atmosphere. As such measurements of the isotopic  
4 composition of atmospheric vapor are highly desirable. In the past measurements of  
5 water vapor isotopes has been particularly laborious, and consequently sparse. Here we  
6 discuss new methods that are emerging that will make water vapor isotope measurement  
7 a more practical endeavor, and thereby facilitate better mapping of the spatial and  
8 temporal variations. To date the interest in water vapor isotope measurements has been in  
9 the context of understanding processes governing hydrologic balance at local scales since  
10 spatially distributed measurements, such as those available for precipitation, have been  
11 unavailable. Emerging measurement techniques have changed this landscape, and the  
12 potential to construct empirically based isoscapes of water vapor isotopes has arrived.

13  
14 The methods examined here lend themselves to developing new comprehensive isotopic  
15 datasets. Specifically, plant material that preserves the isotopic composition represents  
16 archive of the water vapor isotopic history, which can be exploited to infer spatial  
17 gradients of the isotopic composition. Using plants to provide samples gives a time  
18 integrated proxy measurement, and avoids some of the technical limitations that arise  
19 when collecting vapor samples. Similarly, direct measurements using optical approaches  
20 removes the need to capture samples completely. In situ laser-based spectroscopy  
21 provides a method that simplifies the measurement of the vapor phase; however the  
22 observational detail is obtained in time domain though continuous operation and spatial  
23 mapping will require deployment of sensor arrays. Measurement of spatial distributions

1 of water vapor isotopes in the mid-troposphere is obtained through satellite-remote  
2 sensing, yet there remains questions on the ability to measure the isotopic composition in  
3 the boundary layer and at the surface from space. In this chapter, our aims are to outline  
4 the importance of spatially resolving the isotope ratio of atmospheric water vapor, to  
5 describe both the plant-based and the optical approaches, and discuss the strength and  
6 weaknesses of these new measurement methods.

7

## 8 **2. Water vapor isotopes and measurement challenges**

9 The isotope ratio of atmospheric water vapor is controlled by many exchange  
10 mechanisms that reflect the isotope ratio of water in biological water pools (i.e. plant  
11 stems and leaves), soils, open water bodies, precipitation and air mass movement from  
12 the local scales up to general circulation (Craig and Gordon 1965; Ehleringer et al. 2002;  
13 Gat 1996; Yakir and Sternberg 2000; Noone 2008). Many of these processes are  
14 understood in detail and can be accounted for in comprehensive models (Noone and  
15 Sturm, this volume). Recent attention has been drawn to the study of the isotope ratio of  
16 atmospheric water vapor, particularly in an attempt to partition the fluxes of surface  
17 evaporation from plant transpiration, to enhance our understanding of precipitation  
18 processes and to balance hydrological budgets at the basin-scale (Helliker et al. 2002;  
19 Williams et al. 2004; Yakir and Wang 1996; Yopez et al. 2003). In addition to these  
20 efforts, regular measurements of water vapor isotope ratios can significantly enhance our  
21 understanding of a wide range of topics from leaf-scale isotope studies (Farquhar and  
22 Cernusak 2005; Roden and Ehleringer 1999) to climate reconstruction through isotopes

1 in tree rings to global-scale estimates of productivity (Brunel et al. 1992; Ciais et al.  
2 1997; Farquhar et al. 1993).

3

4 Improved estimates of either spatial averages or variation in water vapor isotopes will  
5 lead to a substantial improvement in applications of stable water isotopes to  
6 understanding life and earth processes and function. Yet in many applications of stable  
7 isotopes, the isotope ratio of water vapor is either not measured or measured infrequently.  
8 In these cases, one common procedure to estimate near surface water vapor isotope ratios  
9 is to assume a temperature-based equilibrium with the isotope ratio of precipitation,  
10 which is more readily measurable (IAEA 2001). While there are a variety of plausible  
11 choices as to what precipitation inputs and what temperature should be used to arrive at  
12 an assumed equilibrium value (e.g., mean annual temperature and mean annual  
13 precipitation or growing season temperature and growing season precipitation or some  
14 combination thereof) the existence of a robust relationship is neither guaranteed nor  
15 unambiguous. While the equilibrium approach is often necessary in the lieu of little real  
16 data availability, it should be approached with caution as the isotope ratio of precipitation  
17 can vary seasonally and can be substantially different from the isotope ratio of water  
18 entering plant roots. As such, any simple estimation approach is difficult to defend. An  
19 alternative is to use estimates from global and regional dynamical models that also  
20 simulate isotopes (Ciais, et al. 1997; Riley et al. 2003; Buening et al. 2007; Noone and  
21 Sturm, this volume), although there remains question as to the quantitative reliability of  
22 such models for accurately constraining estimate of, for instance, CO<sup>18</sup>O (Buening and  
23 Noone 2008).

1  
2 The potential offset between the isotope ratio of plant root water and any equilibrium  
3 assumption of water vapor isotopes can lead to large errors in the interpretation of the  
4  $\delta^{18}\text{O}$  of  $\text{CO}_2$ ,  $\text{O}_2$  and the  $\delta^{18}\text{O}$  and D/H of plant organic material. For an example with  
5  $\delta^{18}\text{O}$ , an error of 2 ‰ in water-vapor  $\delta^{18}\text{O}$  translates into an error of about 1.5 ‰ in leaf-  
6 water  $\delta^{18}\text{O}$  under global estimates for evaporative enrichment (e.g., Craig and Gordon  
7 1965; Ciais et al 1997). A consistent 1.5 ‰ error in leaf-water  $\delta^{18}\text{O}$  results in an  
8 approximate 10 % error in the calculated photosynthetic effect on the  $\delta^{18}\text{O}$  of  
9 atmospheric  $\text{CO}_2$ , this is significant considering global estimates for average leaf water  
10 range from 4 ‰ to 8 ‰. A 1.5 ‰ error in leaf-water  $\delta^{18}\text{O}$  results in a 1 ‰ error in the  
11  $\delta^{18}\text{O}$  of tree-ring cellulose, equivalent to 10 to 66 percent of observed tree-ring  $\delta^{18}\text{O}$   
12 signals (Poussart and Schrag 2005; Verheyden et al. 2004; Evans and Schrag 2004).  
13 Many of these uncertainties are minimized if the isotopic composition of vapor was  
14 indeed known.

15  
16 While the importance of stable isotopic measurements of atmospheric water vapor to the  
17 above applications is without doubt, so too is the fact that there is a paucity of  
18 measurements. The reason for this is, in part, due to current methods of obtaining  
19 atmospheric water vapor samples for isotopic analysis. Reliable methods to collect  
20 atmospheric water vapor exist, but the logistical constraints inherent to these methods  
21 either limit wide spread use in field-based sampling campaigns or severely limit spatial or  
22 temporal coverage. There are four primary methods in common use for ground-based  
23 sampling atmospheric water vapor: cryogenic condensation traps, trapping with Peltier

1 coolers, chemical capturing with molecular sieves, and vapor collection with vacuum  
2 flasks. However, each of these methods is not without their limitations.  
3  
4 To ensure accurate isotopic analysis via trapping liquid samples for subsequent standard  
5 isotope ratio mass spectrometric analysis, nearly complete removal of all water molecules  
6 from the air needs to be achieved. Water-condensing traps that are cooled below  $-70^{\circ}\text{C}$   
7 have been used successfully in numerous studies (Blaga and Blaga 1977; Helliker et al.  
8 2002; Huebner et al. 1978; Yakir and Wang 1996; Yopez et al. 2003; Sharp 2007) and the  
9 efficiency of this method is not questioned. However, this method requires a continuous  
10 supply of dry ice or liquid nitrogen, which raises problems for field work and for long  
11 sampling periods. Additionally, the flow rate of air through cryogenic traps is often  
12 unacceptably high ( $> 1 \text{ L/min}$ ) resulting in fractionation or direct loss of ice crystals.  
13 Further, with the use of very cold cryogenes,  $\text{CO}_2$  and explosive  $\text{O}_2$  can condense, which  
14 yields practical constraints at very low temperature. The Peltier method produces a  
15 minimum temperature of about  $-50^{\circ}\text{C}$ , which avoids condensing some other gasses.  
16 However, this temperature is not low enough to quantitatively trap water vapor below the  
17 working precision of an isotope ratio mass spectrometer and leads to enrichment of heavy  
18 isotopes in the sampled water (Schoch-Fischer et al. 1983). Corrections for this  
19 enrichment require precise measurements of flow rate, condenser temperature, ambient  
20 temperature and ambient humidity during the period of sampling. These ancillary  
21 measurements propagate error through to the determination of the final isotope ratio.  
22 Molecular sieves have been shown to precisely and accurately capture water vapor  
23 isotope ratios and can potentially be deployed to gain large spatial coverage (Han et al.

1 2006). But the molecular sieve method needs further testing for a variety of potential  
2 problems, including: long and short-term storage of samples on the molecular sieve,  
3 recovery of samples from saturated versus unsaturated states and tests to determine if  
4 exchange occurs when moist air continues to be drawn through a saturated column. Also,  
5 a modular system of field sampling and laboratory extraction from the molecular sieve  
6 columns must be developed for the method to be fully field-deployable. A method to  
7 directly analyze small amounts of water vapor that has been captured in very dry and  
8 clean vacuum flasks has been successful for measuring HDO abundance, but can not be  
9 used to measure  $^{18}\text{O}$  in such low volumes (Strong et al. 2007). This method avoids some  
10 of the problems associated with trapping the vapor in liquid forms, but there remains a  
11 requirement to ensure there is no condensation within the flask (Sharp 2007)

12  
13 With a clear need to obtain water vapor isotope data, new techniques have emerged in  
14 recent years that compliment the existing direct collection sampling. Specifically, optical  
15 methods using laser-based spectroscopy allow direct in situ measurement. While there are  
16 specific challenges in using these new instruments, their strength is in avoiding the need  
17 to collect samples for later laboratory analysis. Similarly, high-resolution emission  
18 spectrometers that are able to discern individual water isotopologue emission lines from  
19 the background atmospheric emission, and are beginning to find homes on space based  
20 platforms which enables global-scale monitoring of the isotopic composition of  
21 atmospheric water. So too the advance in understanding of the linkage between the  
22 isotopic composition of vapor and the isotopic composition of plant material yields novel  
23 opportunities to estimate water vapor isotopes from natural archives. These emerging

1 techniques provide valuable new capabilities to map the spatial and temporal distribution  
2 of water vapor isotopes, but like more traditional sampling techniques, have their  
3 limitations.

4

### 5 **3. Motivation for plant-based proxies**

6 Plants can operate as bio-recorders of water vapor isotopes if a few environmental and  
7 physiological requirements are met. The necessary environmental condition is that of  
8 relative humidity being near or greater than 90 percent, which drives leaf water isotopes  
9 to be reasonably close to equilibrium with the isotopes of atmospheric vapor. The  
10 physiological patterns necessary for plants to act as bio-recorders are that plants must  
11 lose water during periods that satisfy the environmental conditions above— this would  
12 most likely be at night. To the best of our knowledge, the only plants that satisfy these  
13 conditions are epiphytic plants with Crassulacean acid metabolism (CAM).

14

15 CAM photosynthesis is characterized by nocturnal assimilation of CO<sub>2</sub> and,  
16 consequently, nocturnal water loss. The CO<sub>2</sub> that is assimilated at night is converted to  
17 malic acid and stored within cell vacuoles. Upon the next day's light, the malic acid is  
18 decarboxylated and the liberated CO<sub>2</sub> is used, along with incident sunlight, in the normal  
19 photosynthetic carbon reduction cycle to produce simple carbohydrates that are the  
20 building blocks for all plant organic material. Through the diel cycle there is tight control  
21 over the leaf pores, or stomata, of CAM plants so that during the day little water or CO<sub>2</sub>  
22 is lost from inside the plant. Therefore CAM photosynthesis represents a physiological  
23 mechanism to maximize CO<sub>2</sub> gain while minimizing water loss. The cost of this

1 mechanism is two-fold: first, there is a chemical-energy cost to storing CO<sub>2</sub> as malic acid  
2 and second, there is a restricted amount of CO<sub>2</sub> that can be stored as malic acid, thus the  
3 growth rate of CAM plants is limited in comparison to plants that assimilate CO<sub>2</sub> only  
4 during the day (Martin 1994).

5

6 The eco-physiological significance of CAM photosynthesis is that it allows for survival  
7 in areas that are typified by low water availability and high solar radiation inputs—  
8 explicitly including desert biomes and functionally including the epiphytic lifeform. An  
9 epiphyte is a non-parasitic plant that grows on another plant (known as the porophyte) for  
10 support and has no continuous source of water. Examples of epiphytes include the  
11 symbiotic organisms known as lichens and higher plants such as bromeliads and orchids.  
12 Lichens are active only immediately after a rain event, whereas epiphytic bromeliads and  
13 orchids with the CAM pathway are capable of maintaining physiological activity long  
14 after the rains have passed. Fortunately, the distributional constraints for epiphytic  
15 CAM plants mirror the environmental conditions required for them to act as bio-recorders  
16 of water vapor isotopes.

17

18 The physical requirements for a plant to act as a recorder of water vapor isotopes are best  
19 described (following Helliker and Griffiths 2007), by starting with the standard Fick's  
20 law approach to estimate net transpiration from a plant ( $E$ ,  $\mu\text{mol m}^{-2} \text{s}^{-1}$ ),

$$21 \quad E = g(w_i - w_a) \quad (1)$$

22

1 Where  $g$  is stomatal conductance ( $\text{mol m}^{-2} \text{s}^{-1}$ ) and  $w_i$  and  $w_a$  are the mole fractions of  
2 water vapor in the substomatal cavity and ambient air, respectively. Thus, net diffusion  
3 of water from the leaf is characterized by the difference of two real, one-way fluxes of  
4 water vapor from the leaf to the atmosphere ( $gw_i$ ) and from the atmosphere into the leaf  
5 ( $gw_a$ ).

6

7 Following Craig and Gordon (1965), the flux of heavy water molecules out of the leaf  
8 can be written as

$$9 \quad R_E E = \frac{g}{\alpha_K} \left( \frac{R_L}{\alpha_e} w_i - R_a w_a \right) \quad (2)$$

10

11 where  $R$  is the molar isotope ratio of transpiration ( $E$ ), leaf water ( $L$ ) and water vapor ( $a$ ),  
12  $\alpha_e$  is the temperature dependent equilibrium fractionation factor, and  $\alpha_K$  is a balance of  
13 the ratio of diffusivities of light to heavy water molecules through the stomata and  
14 through the leaf boundary layer (Farquhar and Cernusak 2005; Farquhar and Lloyd 1993;  
15 Flanagan et al. 1991)(Farquhar and Cernusak 2005; Farquhar and Lloyd 1993; Flanagan  
16 et al. 1991).

17

18 By rearranging equation (**Error! Reference source not found.**) to solve for  $R_L$  and  
19 relating the water vapor mole fractions to leaf-based relative humidity where  $h = w_a/w_i$   
20 we arrive at,

21

$$22 \quad R_L = \alpha_e [\alpha_K R_E (1-h) + R_a h]. \quad (3)$$

1

2 For an epiphyte, tissue water content is recharged by each precipitation event, either  
3 rainfall or dewfall. The gross flux of water from the plant,  $gw_i$ , is drawn from a finite and  
4 small volume of water. Whereas the gross flux of water into the plant from the  
5 atmosphere,  $gw_a$ , is a finite but dramatically larger volume of water. Therefore, over time  
6 the volume of water within the epiphyte is exchanged by atmospheric water vapor. From  
7 **(Error! Reference source not found.)** it can be seen that as  $w_a$  increases relative to  $w_i$   
8 (i.e., as  $h$  increases), the isotope ratio of water remaining in the plant becomes dominated  
9 by atmospheric water vapor.

10

11 Under constant or nearly constant environmental conditions with  $h$  near unity, the isotope  
12 ratio of water vapor exiting ( $R_E$ ) the leaf approaches that remaining in the leaf ( $R_L$ ) and  
13 we can write:

14 
$$R_L \approx \frac{\alpha_e R_a h}{1 - \alpha_e \alpha_K (1 - h)} \quad (4)$$

15

16 In the limit when  $h = 1$ , the denominator vanishes and the isotopic enrichment in a  
17 steadily evaporating CAM epiphyte is equal to the isotope composition of atmospheric  
18 water vapor, corrected for the equilibrium fractionation factor,

19 
$$R_L = \alpha_e R_a . \quad (5)$$

20 As such, the main limitation in existing trapping based vapor sampling methods can be  
21 avoided by simply collecting the entire water sample that is enclosed in the leaf material  
22 of an appropriate candidate species. The water can be obtained from the leaf using

1 traditional vacuum extraction methods, then analyses using traditional isotope mass  
2 spectrometry. Once known, (**Error! Reference source not found.**) can be applied to  
3 estimate the water vapor isotopes for the time over which the leaf recently transpired.  
4 Similarly, to the degree to which this water is used in cellulose production, the isotopic  
5 composition of cellulose can be used to develop a history of isotopic composition. This in  
6 turn holds potential for developing records of isotopic composition that extend beyond  
7 the modern era.

8

#### 9 **4. Application of plant proxy estimates**

10 *Tillandsia usneoides* (Spanish Moss) is an ideal candidate organism for testing the  
11 efficacy of a plant-water-vapor-isotope proxy. *T. usneoides* is a subtropical to tropical  
12 epiphyte that ranges from coastal Virginia, USA through the tropics to Argentina. The  
13 distribution is determined by high nocturnal relative humidity (Garth 1964) and it is a  
14 constitutive CAM plant. The plant achieves a net gain of water solely from rain or  
15 dewfall by absorption through a heavy cover of modified, hygroscopic trichomes. The  
16 trichomes also directly adsorb atmospheric water vapor as a function of  $h$ , however the  
17 water potential gradients from the trichomes to cellular water mitigates use of this water  
18 for plant metabolism (Martin and Schmitt 1989). The plant hangs from the branches of  
19 trees and grows as a series of ramets that, while physically connected, are isolated in  
20 terms of CO<sub>2</sub> assimilation and metabolite translocation (Martin 1982). The epiphytic  
21 lifeform and the isolation of each ramet allows for *T. usneoides* to be modelled, in terms  
22 of water loss, as an evaporating cup that slowly loses water during a high humidity night  
23 and is refilled infrequently with each precipitation event. *T. usneoides* exhibits slow

1 growth rates of about 1cm/month and new ramets are produced at the tip of a given strand  
2 (Martin 1980). Therefore, the growth of *T. usneoides* strands can be viewed as analogous  
3 to a tree ring recording growth environment from year to year. The results discussed here  
4 may hold true for other species of epiphytic plants with CAM photosynthesis within and  
5 outside of the western hemisphere. Therefore, our approach can potentially be expanded  
6 to tropical and subtropical regions throughout the world.

7  
8 To test the controls of water vapor on leaf water we placed strands of *T. usneoides* in a  
9 climate-controlled chamber that was fed water vapor and air from a 23 L temperature-  
10 controlled “water tower.” Using the water-tower setup a constant water vapor  $\delta^{18}\text{O}$  for  
11 several weeks with  $h = 0.97$  and temperature = 27.5 °C could be maintained (Figure 1). In  
12 contrast to most studies of isotopic enrichment in leaf water during evaporation, leaf  
13 water  $\delta^{18}\text{O}$  in *T. usneoides* became depleted during transpiration. The large gross flux of  
14 water into the leaves replaced the initial leaf water by water vapor that entered the leaf  
15 and condensed. After a period of about 4 days, leaf water  $\delta^{18}\text{O}$  was in equilibrium with  
16 observed water vapor  $\delta^{18}\text{O}$ . This was a similar period of turnover time that we observed  
17 in a previous study (Helliker and Griffiths 2007). This slow leaf-water turnover time in *T.*  
18 *usneoides* acts as a buffer against rapid, short-term changes in water vapor isotopes that  
19 have been observed in field studies (Helliker et al., 2002, Lai et al., 2006) and suggest  
20 that *T. usneoides* leaf water will act as a long-term integrator of water vapor isotopes.

21  
22 On August 2, 2007 a large-scale sampling effort for *T. usneoides* leaf water was  
23 conducted as a first step to characterize regional variation in atmospheric water vapor.

1 The samples were collected within a couple of hours either side of solar noon by  
2 volunteers at various colleges and universities. Figure 2 shows the mean leaf-water  $\delta^{18}\text{O}$   
3 for each sample site and the reconstructed water-vapor  $\delta^{18}\text{O}$ . While a preliminary effort,  
4 it is clear that there is a regional coherence of water vapor  $\delta^{18}\text{O}$  as reconstructed by leaf  
5 water. There was a consistently enriched value around the Gulf Coast of Texas and water  
6 vapor  $\delta^{18}\text{O}$  became more depleted towards the eastern Gulf states. There were marked  
7 differences across the Florida peninsula with the east coast sample sites being more  
8 enriched than the gulf coast sites.

9

10 With a view to extending this analysis approach, we note that leaf-water isotopes are  
11 recorded in leaf cellulose and the analysis of *T. usneoides* cellulose  $\delta^{18}\text{O}$  along with basic  
12 climate data allows for the reconstruction of water vapor  $\delta^{18}\text{O}$  from herbarium  
13 specimens. To demonstrate this, the  $\delta^{18}\text{O}$  of bulk organic material was determined on  
14 samples obtained from Miami, Florida in September of 2005 and compared to herbarium  
15 specimens which were originally collected in Miami in the late 19<sup>th</sup> and early 20<sup>th</sup>  
16 centuries (Figure 3). Miami is a good location to examine our approach because of the  
17 availability of herbarium specimens and Miami is near the southern tip of an oceanic  
18 peninsula that has little weaker variation in mean temperature and  $\delta^{18}\text{O}$  of precipitation  
19 compared to continental regions (Bowen and Revenaugh 2003). Therefore, we would  
20 expect that water vapor  $\delta^{18}\text{O}$  is near equilibrium with precipitation  $\delta^{18}\text{O}$  throughout the  
21 growing season.

22

1 We first reconstructed leaf-water  $\delta^{18}\text{O}$  values by using a leaf-water-to-bulk-leaf  
2 fractionation factor of 23.4 ‰. Bulk material of *T. usneoides* has a large lignin  
3 component and it was assumed that bulk organic offset of *T. usneoides* strands to leaf  
4 cellulose was similar to that of whole wood *versus*  $\alpha$ -cellulose obtained by a weighted  
5 average of published fractionation factors (Barbour et al. 2001; Ferrio and Voltas 2005).  
6 The  $\delta^{18}\text{O}$  water vapor was estimated using the reconstructed leaf water  $\delta^{18}\text{O}$  using the  
7 equilibrium offset, as before. To obtain mean values of  $h$  we used mean annual nocturnal  
8 relative humidity from the Miami area for the years 2001-2005. The same value for  $h$  was  
9 used for the herbarium specimens due to a lack of temperature and humidity records for  
10 the period spanning 1878 to 1930. While this assumption introduces a large uncertainty  
11 when one considers the role of  $h$  in (**Error! Reference source not found.**), one should  
12 note that the selection of *T. usneoides* was motivated by its distribution in regions with  
13 very high and constant humidity. Given this, the observed bulk organic  $\delta^{18}\text{O}$  and  
14 calculated leaf water and water vapor  $\delta^{18}\text{O}$  were nearly constant from 1878 to 1930  
15 (average water vapor  $\delta^{18}\text{O} = -15.5 \pm 0.25$  ‰). Contemporary  $\delta^{18}\text{O}$  in Miami was more  
16 enriched than the average values from the past by 2.3 ‰. The 2005 value for water vapor  
17  $\delta^{18}\text{O}$  ( $-13.1 \pm 0.5$  ‰) was similar to what would be expected by water vapor  $\delta^{18}\text{O}$  being,  
18 on average, in equilibrium with the  $\delta^{18}\text{O}$  of annual rainfall at the mean annual  
19 temperature ( $-13$  ‰). It is worth noting that this reconstructed value from Miami in  
20 2005, the leaf water value obtained in the survey sampling for Miami two years later ( $-$   
21  $12.7 \pm 0.3$  ‰; Figure 2) and the average measured water vapor from a field experiment  
22 near Miami a week after the survey sampling ( $-12.0 \pm 0.8$  ‰) are all similar.  
23

1 *T. usneoides* records water vapor  $\delta^{18}\text{O}$  of nocturnal periods while the majority of plants  
2 (and hence Isoscape applications) will be affected by daytime values of water vapor  $\delta^{18}\text{O}$ .  
3 Any systematic offset between nocturnal and diurnal  $\delta^{18}\text{O}_a$  would lessen the importance  
4 of reconstructing water vapor  $\delta^{18}\text{O}$  via *T. usneoides*. In recent direct observations water  
5 vapor  $\delta^{18}\text{O}$  at a Florida field site there has been no clear diel pattern. In general, changes  
6 in observed water vapor  $\delta^{18}\text{O}_a$  in Florida seem to be governed more by synoptic-scale  
7 weather patterns than diel cycles. This observation is consistent with observations of  
8  $\delta^{18}\text{O}_a$  in a New England forest, but contrary to those of a forest site in the Pacific  
9 Northwest (Lai et al. 2006; Lee et al. 2006). Additionally, precipitation inputs have an  
10 immediate effect on *T. usneoides* leaf water  $\delta^{18}\text{O}$ , but these effects are short-lived and do  
11 not appear to change the long-term control of water vapor  $\delta^{18}\text{O}$  on leaf water  $\delta^{18}\text{O}$ . In lab  
12 and field experiments, any measurable effect of the precipitation water on leaf water  $\delta^{18}\text{O}$   
13 is typically gone within two days. However, carbon is being assimilated during the  
14 periods following a precipitation event while leaf water  $\delta^{18}\text{O}$  approaches equilibrium  
15 with water vapor  $\delta^{18}\text{O}$ . Therefore, through future research we must gain a better  
16 understanding of the relationship between precipitation and leaf water  $\delta^{18}\text{O}$  to more  
17 accurately reconstruct water vapor  $\delta^{18}\text{O}$  through leaf water and plant organic material.  
18  
19 The tropical epiphytic CAM plant *T. usneoides* offers a means to reconstruct past and  
20 present water vapor isotopic signals. In the future, we hope to develop an Isoscape of  
21 water vapor  $\delta^{18}\text{O}$  across the entire southeastern US coastal plain. Further, there are  
22 similar plants throughout the tropical Americas for which reconstructions of water vapor

1 isotopes can potentially be made. While little knowledge is available of epiphytic CAM  
2 plants in African or Pacific tropical systems, the same ecological niche exists in these  
3 biomes so there is certainly a potential similar plants exist and we can expand the spatial  
4 extent of water vapor reconstruction beyond the Americas. Continued examination of  
5 herbarium material will extend this analysis to allow for the temporal reconstruction of  
6 isotopic ratios of water vapor for a large portion of the terrestrial biosphere through a  
7 period of rapid climate change during the past century. However there remains a need to  
8 validate the plant-derived samples with a direct field measurement in modern  
9 environments before these proxies can be used with confidence.

10

## 11 **5. Direct measurement by optical methods**

12 While collecting physical samples for later laboratory analysis has had success in many  
13 cases, the issues associated with capturing liquids from the vapor phase without  
14 fractionation and the intricacies associated with proxy sampling leave great potential for  
15 direct in situ measurement of water vapor isotopes. Spectrometric isotopic analysis (with  
16 Isotope Ratio Mass Spectrometers) in a laboratory setting is highly precise and is in  
17 common use, but is not presently a field portable technology. Similarly, it is particularly  
18 laborious to develop time series data with traditional sampling or proxy methods since  
19 each individual measurement needs lengthy collection, preparation and transport to a  
20 laboratory. On the other hand, laser-based spectroscopic analyzers can be deployed in a  
21 field setting, run in an almost continuous sampling mode and thereby offer substantial  
22 potential to improved measurement density.

23

1 Estimation of isotopic abundance from either absorption or emission spectroscopy entails  
2 measuring some fraction of the spectrum at sufficiently high resolution to be able to  
3 quantitatively identify individual spectroscopic line features associated with the  
4 isotopologues of interest. Figure 4 shows a section of the infrared absorption spectrum of  
5 a gas in which water isotopologues are found. Given accurate measurement of a  
6 spectrum, the line features (peak shape and size) can be mapped to the concentration of  
7 each isotopologue identified in the spectrum, and the isotope ratio constructed. This is  
8 typically performed using an estimation approach in which the concentration is found as  
9 a best fit between the measured spectrum and a spectrum based on physical  
10 considerations in light of known uncertainties. Alternatively, the concentration estimate  
11 can simply be made by finding the integral of a specific line feature as a function of  
12 frequency, and again using the physical expectation to map the integrated quantity back  
13 to the of number of molecules of the species within the gas sample.

14

15 While a number of different optical configurations are possible, two variations of the  
16 spectroscopic approach have emerged as useful in developing commercial field-  
17 deployable instruments, and both of which use Tunable Diode Lasers (TDL) to accurately  
18 probe a small region of the spectrum. Integrated Cavity Output Spectroscopy (ICOS;  
19 Baer et al., 2008) illuminates the sample gas and directly measure the absorption  
20 spectrum from light that leaks from optical cell. The second approach is Wavelength  
21 Scanning - Cavity Ring-Down Spectroscopy (WS-CRDS; Crosson 2008) in which the  
22 optical cavity is filled with a pulse of light and the measurement is of the decay in light  
23 intensity as a function of time when the laser is switched off. While there are some

1 technical advantages for either method, both approaches are fast enough that in field  
2 applications, measurements can be made in a near continuous manner with measurements  
3 made every few seconds. It has been shown that the precision and accuracy of these types  
4 of instruments now rivals that of the laboratory based isotope ratio mass spectrometers.  
5 Gupta et al., (in review) reports the precision on continuous (12 second) samples to be  
6 0.17 ‰ for  $\delta^{18}\text{O}$  and 1.1 ‰ for  $\delta\text{D}$  even at very low water vapor concentrations.  
7  
8 Figure 5 shows an example of a time series of hourly  $\delta^{18}\text{O}$  and deuterium excess data  
9 measured over a 10-day period in New Haven (L. Welp and X. Lee, personal  
10 communication, 2008) using a direct absorption method as described by Wen et al.  
11 (2008), which yields a measurement precision around 0.07 ‰ for  $\delta^{18}\text{O}$  and 1.1 ‰ for  $\delta\text{D}$   
12 and an absolute accuracy of 1.2‰ for  $\delta^{18}\text{O}$  and 1.1 ‰ for  $\delta\text{D}$  for hourly average data.  
13 The figure shows clear diurnal variability that is tied to the daily transpiration cycle and  
14 boundary layer activity at the measurement site in New Haven, Connecticut. Both longer  
15 term weather-scale variability, and higher frequency variability associated with local  
16 conditions are also seen. Rain occurred on 17 August (day 229) and 20-21 August (day  
17 232-233) and likely linked to the more depleted  $\delta^{18}\text{O}$  values measured at those times  
18 because of both local recycling by evaporation of fallen water and that the rain is  
19 associated with arrival of different prevailing air masses. Being able to examine this fine  
20 scale structure in the time domain as a function of meteorological controls is not readily  
21 possible from traditional methods and is a clear advance provided by optical systems.  
22

1 The ability to use a network of such instruments to map spatial variations in water vapor  
2 isotopes is of great interest in the future but to date is lacking. On the other hand, the  
3 scientific benefit for surrendering spatial detail is in the advantages offered by what is  
4 learned from the structure found the temporal domain. Time series data lend themselves  
5 to improving understanding of the controlling processes and the ability to resolve isotope  
6 variability from the order of seconds, upwards though the diurnal cycle, weather  
7 timescales, the annual cycle and beyond, cannot be understated.

8

9 Until the recent appearance of commercial analyzers, the use of laser-based instruments  
10 has been the domain of specialist research groups. For instance, there have been  
11 applications that focused on upper tropospheric water with high frequency measurements  
12 needed for fast moving high altitude aircraft (Webster and Heymsfield 2003; Hanisco et  
13 al, 2007), and specialist surface studies are beginning to appear (e.g., Welp et al., in  
14 press). With the availability of commercial analyzers in 2007 and 2008, wider use of such  
15 instruments is likely, and there is great potential for continuous in situ instruments to  
16 revolutionize water isotope science. At this early stage of their availability, care is needed  
17 to demonstrate the accuracy of laser-based measurements relative to exiting sample  
18 collection and mass spectrometer methods. While decades of experience with mass  
19 spectrometry has lead to many refinements in laboratory practices that allow reliability in  
20 measurements, there remains a number of technical issues that can scientifically degrade  
21 performance of optical analyzers if not kept in check. For instance the polar nature of the  
22 water molecules provides special concern in continuous flow systems since the water can  
23 “stick” to sample inlet tubes and surfaces with the optical cavity. Sticking can lead to an

1 isotopic fractionation and degrade the precision of the instrument. Further, the use of  
2 multiple passes of the laser through the sample cavity requires high quality and well  
3 calibrated optical components such as mirrors. Similarly, the most accurate  
4 measurements require accurate and well calibrated lasers that can be precisely tuned.  
5 Nonetheless, while obtaining lasers of appropriate quality remains a particular  
6 technological issue, gaining confidence in the measurements from existing instruments  
7 remains a scientific endeavor and indeed there remains some question as to how such  
8 systems can be reliably calibrated against known liquid standards.

9  
10 Due to their fledgling status, laser-based instruments are presently not being used to  
11 provide information on spatial gradients at any scale, although the opportunity certainly  
12 exists. An ideal platform for monitoring global scale spatial distributions is provided by  
13 satellites. The use of high resolution space-borne spectrometers to obtain the spectra of  
14 natural emission of infrared radiation from satellite can be used to estimate the isotopic  
15 composition. Due to the temperature of the atmosphere, radiative emission is mostly in  
16 the infrared, but the specific frequencies at which radiation is emitted depends on the  
17 abundance of each nuclide in the mixture of gases in the atmosphere at any time. Of  
18 interest, all water vapor isotopologues emit radiation that leads to specific spectral  
19 features that can be measured by precise space-based spectrometers. To date, four Fourier  
20 transform infrared spectrometers have been flown and provided demonstration of the  
21 methodology. The Interferometric Monitor for Greenhouse-gasses (IMG) instrument on  
22 the Japanese Advanced Earth Observing System spacecraft operated for nine months at  
23 the end of 1996 and 1997. Zakharov et al. (2004) used these data to estimate the total

1 column mean HDO abundance and demonstrated that the latitudinal gradient could be  
2 recovered. The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS)  
3 was flown on the Envisat satellite and operated at high resolution between 2002 and  
4 2004. This limb scanning instrument was used to retrieve HDO from 6 km upwards to the  
5 top of the mesosphere, and is most reliable in the stratosphere (Payne et al. 2007). The  
6 Tropospheric Emission Spectrometer (TES) on NASA's Aura spacecraft was launched in  
7 2004, and continues to recover spectra from which global maps of HDO can be  
8 constructed at approximately 5x5 degree resolution every two days from observations  
9 taken at local 2am and 2pm as an operational product from that mission (Worden et al.  
10 2006, 2007). Because of the accuracy and operational nature, these results are a  
11 remarkable leap in the ability to monitor naturally occurring isotopes. The Infrared  
12 Atmospheric Sounding Interferometer (IASI) instrument on Eumetsat has similar optical  
13 characteristics to TES, and while isotope retrievals have been done in an experimental  
14 capacity (Herbin et al. 2007) have not been used to obtain in an operational manner.  
15 IMG, TES and IASI are all downward looking instruments and recover the isotopic  
16 composition in the lower-mid troposphere above the boundary layer.

17

18 Figure 6 shows a climatology of the TES HDO measurements for the layer between 800  
19 and 500 hPa based on measurements between December 2004 and February 2008. Many  
20 aspects of the large scale spatial structure of the free tropospheric  $\delta D$  distribution  
21 emerge, including a latitude effect, continental-oceanic contrasts, and both enriching and  
22 depleting influences of convective activity. Analysis of the data show that the large scale  
23 atmospheric hydrology can be directly inferred from the isotopes (Brown et al. 2008;

1 Noone 2008). It is important to recognize that satellite derived data are not for vapor at  
2 the surface but in the free troposphere and as such do not necessarily match the isotopic  
3 composition of boundary layer vapor or precipitation which are governed by different  
4 sets of processes. Also, while the spectroscopic methodology used by space-based  
5 sensors is fundamentally similar to in situ instruments, they are less precise because of  
6 measurement and retrieval uncertainty. As a case in point, TES obtains  $\delta D$  with a  
7 precision of 10 ‰, compared to the in situ instruments at around 1 ‰, and traditional  
8 mass spectrometry of around 0.2 ‰. Similarly, is it more difficult to estimate  $\delta^{18}O$  since  
9 the  $H_2^{18}O$  lines are less well separated from the  $H_2O$  lines even though the abundance of  
10  $H_2^{18}O$  molecules is greater, and contain little information beyond that provided by  $\delta D$ .  
11 Even so, the ability of space platforms to provide spatial context and make regular  
12 isotopic measurements of otherwise unobserved parts of the atmosphere leads them to  
13 hold observational advantages that compliment in situ measurements.

14

## 15 **6. Final remarks**

16 There is now a range of measurement techniques available that will greatly advance the  
17 ability to map the spatial and temporal distributions of water vapor isotopes near the  
18 surface and in the free atmosphere. These new methods are not without their limitations,  
19 but provide new strengths that compliment existing techniques. To this end, new  
20 measurements provide opportunities to pose new scientific problems in the realm of  
21 isotope hydrological studies. Importantly, since water vapor abundance is a measure of  
22 the atmospheric state (as compared to precipitation, which is a flux) better constraint on  
23 theoretical models and explanations of water exchange can be investigated in a more

1 integrated manner. Also, with a wider range of water vapor isotope measurements that  
2 span from the stratosphere, through the troposphere, and to the surface, the pathways of  
3 water movement in the atmosphere and surface hydrological systems can be better  
4 understood. Given improved understanding, more detailed mapping of water vapor  
5 isotopes will allow better constraint on developing secondary isoscapes of, for instance,  
6 leaf water isotopes.

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17

18

1 **Figure captions**

2 Figure 1: Observed leaf water loss and  $\delta^{18}\text{O}$  for *T. usneoides*. Panel A, water loss as a  
3 percent of full saturation. Panel B, changes in the  $\delta^{18}\text{O}$  through time. The day/night  $h$   
4 was 94/98 percent, respectively and water loss was determined by weighing the  
5 individual strands.  $n = 5$  for each day.

6

7 Figure 2: Observed leaf water  $\delta^{18}\text{O}$  (the first number) and reconstructed water vapor  $\delta^{18}\text{O}$   
8 (the second number) for August 2, 2007. All samples were taken within 2 hours of solar  
9 noon during a coordinated survey. The dashed line is the fall line for *T. usneoides*  
10 distribution in the US. The black dot is a field site where mean, measured water vapor  
11  $\delta^{18}\text{O}$  was  $-12.0 \pm 0.8$  from 8/9/2007 to 8/13/2007.

12

13 Figure 3: Reconstructed leaf water ( $\delta^{18}\text{O}_L$ ) and water vapor ( $\delta^{18}\text{O}_a$ )  $\delta^{18}\text{O}$  in Miami,  
14 Florida. Leaf water and water vapor  $\delta^{18}\text{O}$  were calculated from whole-leaf  $\delta^{18}\text{O}$  of *T.*  
15 *usneoides* of fresh material sampled in September of 2005 and herbarium specimens  
16 sampled from 1878 to 1930. See text for details of the calculations. The horizontal dash  
17 for 2005 is the calculated modern equilibrium value for  $\delta^{18}\text{O}_a$  using the 30-year mean  
18 annual temperature in Miami of 23.3 °C and surface water  $\delta^{18}\text{O} = -3.5 \text{‰}$ .  $n = 2$  for 1930,  
19  $n = 5$  for 2005,  $n = 1$  for all other years, error bars represent one standard error mean.  
20 Reprinted from Helliker and Griffiths (2007) with permission from Blackwell Scientific.

21

1 Figure 4: An example section of the infrared ring-down spectrum showing the signature  
2 of water isotopologues measured by a Picarro G1102-I Water Vapor Isotope Analyzer in  
3 the region scanned by a tunable diode laser as part of the CRDS measurement. The shape  
4 and size of each line feature is related to the number of molecules in the sample. (P.  
5 Gupta, personal communication, 2009).

6

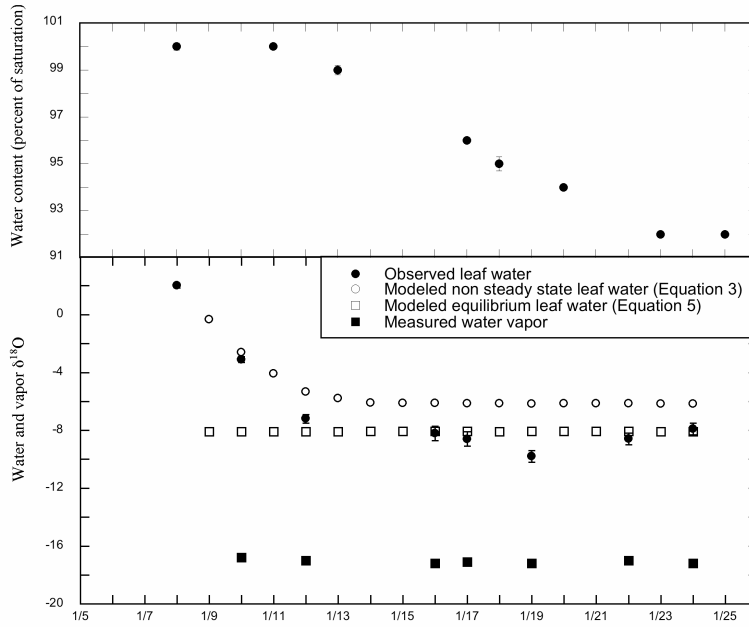
7 Figure 5: Example of an hourly time series of  $\delta^{18}\text{O}$  (upper panel) and deuterium excess  
8 (lower panel) measured via infrared absorption spectroscopy between measured 13-23  
9 August 2007 in New Haven (L. Welp and X. Lee, personal communication, 2008).

10

11 Figure 6: DJF and JJA mean  $\delta\text{D}$  for the atmosphere between 800 and 500 hPa derived  
12 from the infrared spectra measured by the NASA Tropospheric Emission Spectrometer  
13 on the Aura spacecraft. Observations were taken between December 2004 and February  
14 2008. Contour interval is 10 ‰ and the data are most reliably between 30°N and 30°S.

15

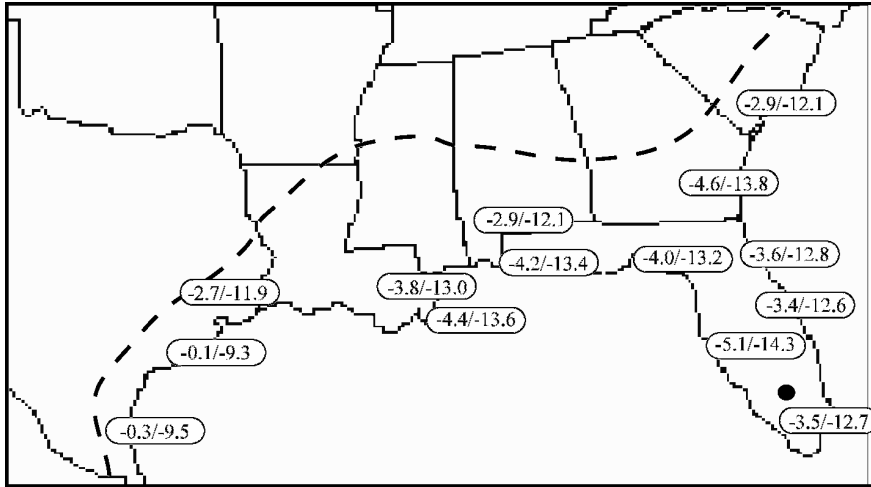
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1

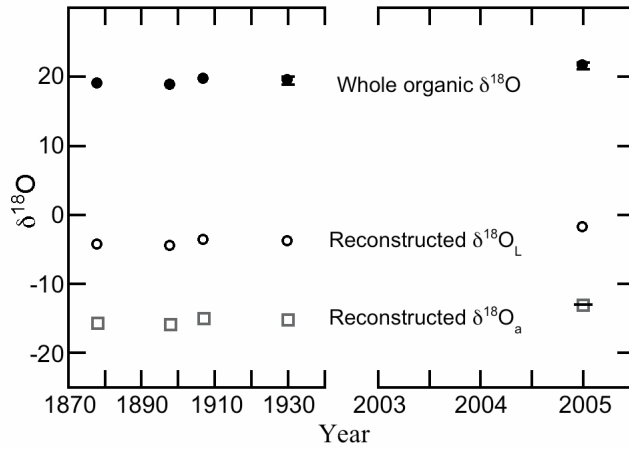


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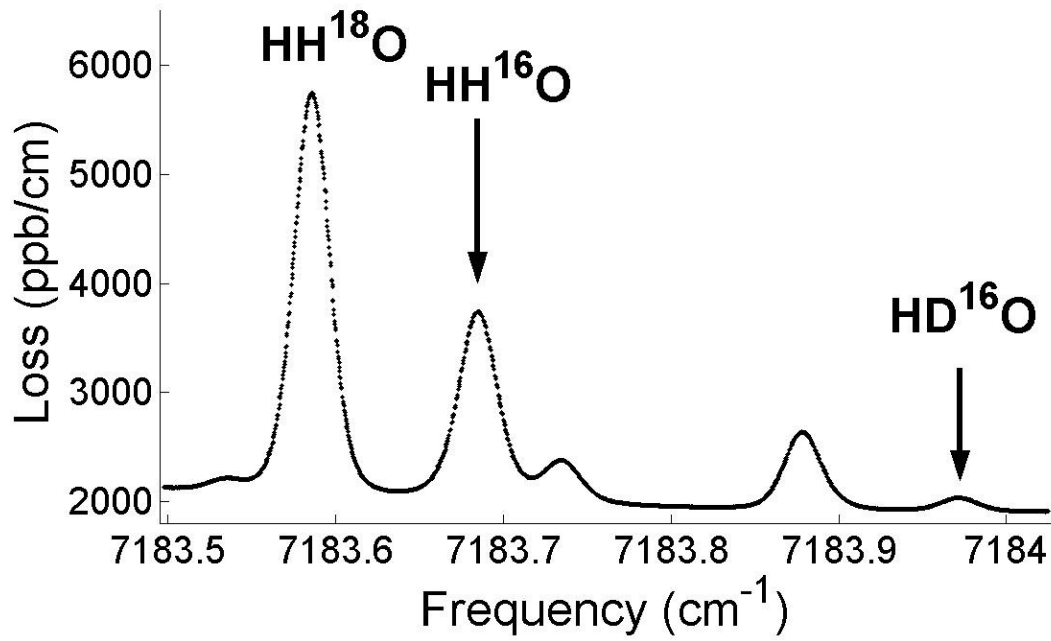
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10 Reprinted from Helliker and Griffiths (2007) with permission from Blackwell Scientific.

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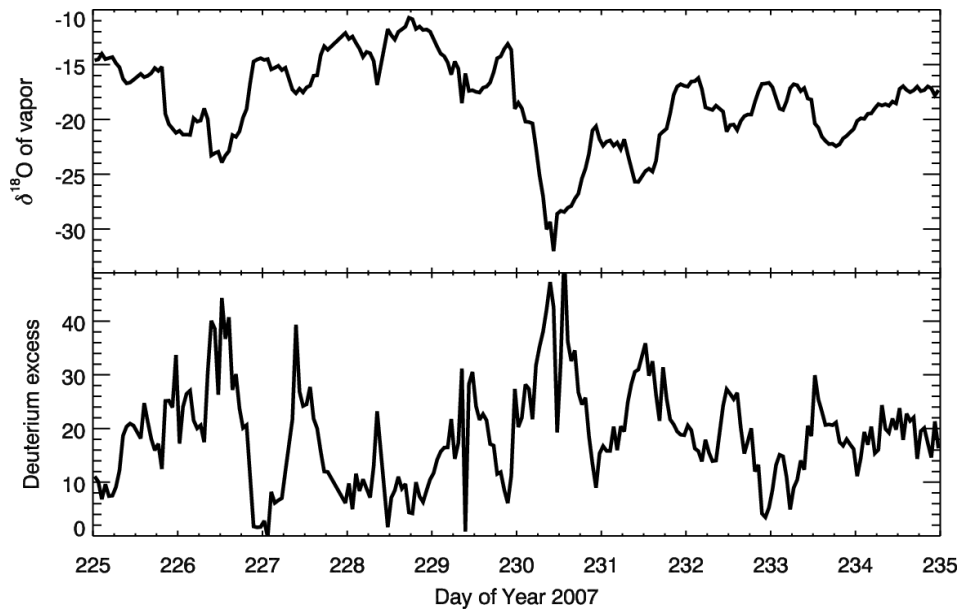
2

3 Figure 4: An example section of the infrared ring-down spectrum showing the signature  
4 of water isotopologues measured by a Picarro G1102-I Water Vapor Isotope Analyzer in  
5 the region scanned by a tunable diode laser as part of the CRDS measurement. The shape  
6 and size of each line feature is related to the number of molecules in the sample. (P.

7 Gupta, personal communication, 2009).

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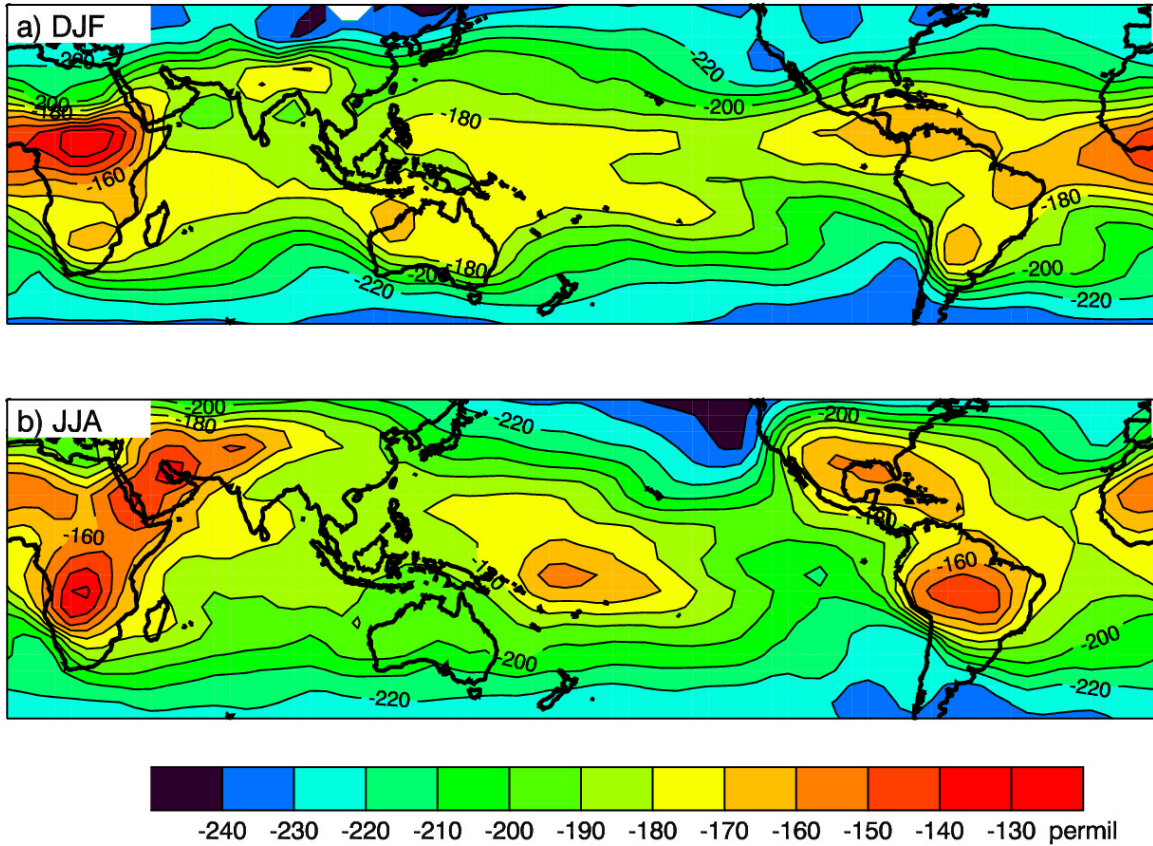
3 Figure 5: Example of an hourly time series of  $\delta^{18}\text{O}$  (upper panel) and deuterium excess

4 (lower panel) measured via infrared absorption spectroscopy between measured 13-23

5 August 2007 in New Haven (L. Welp and X. Lee, personal communication, 2008).

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3 Figure 6: DJF and JJA mean  $\delta D$  for the atmosphere between 800 and 500 hPa derived  
4 from the infrared spectra measured by the NASA Tropospheric Emission Spectrometer  
5 on the Aura spacecraft. Observations were taken between December 2004 and February  
6 2008. Contour interval is 10‰ and the data are most reliably between 30°N and 30°S.

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