Measurements of water vapor D/H ratios from Mauna Kea, Hawaii, and implications for subtropical humidity dynamics

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[1] Water vapor D/H ratios were measured from samples collected on Mauna Kea, Hawaii, in July 2006, and provide new constraints on the processes that control subtropical humidity. D/H ratios ranged from -88‰ at sea level to -321‰ on the summit of Mauna Kea, with sharply decreased D/H ratios above the trade inversion. A simple Rayleigh distillation model underpredicts the observed clear-sky D/H ratios by as much as 160‰ at the summit. A model that accounts for large-scale condensation, fractionation, mixing, and transport of water vapor, but ignores more detailed microphysical processes, is able to reproduce the first-order characteristics of the clear-sky free troposphere relative humidity and D/H ratios. These results are consistent with remote sensing studies of subtropical D/H ratios and suggest that subtropical clear-sky water vapor isotopologues may be relatively insensitive to microphysical processes. **Citation:** 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.

1. Introduction

[2] The subtropical atmosphere is characterized by an extensive and persistent structure consisting of a well-mixed, humid subcloud layer, a layer of trade cumulus clouds capped by a temperature inversion, and an arid, subsiding free troposphere. The aridity of the subtropical troposphere plays an important role in the radiative balance of the Earth's climate, so knowledge of the processes that control the humidity in these regions is of prime importance for understanding past and future climate change.

[3] An especially challenging problem in climate studies involves quantifying the relative importance of small-scale microphysical processes and large-scale mixing processes for controlling the subtropical hydrologic cycle. On the one hand, several studies [*Sun and Lindzen*, 1993; *Rennó et al.*, 1994; *Emanuel and Zivkovic-Rothman*, 1999; *Bacmeister et al.*, 2006] have argued that microphysical cloud processes related to moist convection and condensate re-evaporation play a central role in the subtropical hydrologic cycle and that detailed representations of microphysics are thus required for accurately simulating the Earth's climate. On the other hand, other studies [*Sherwood*, 1996; *Salathe and Hartmann*, 1997; *Pierrehumbert*, 1998; *Dessler and Sherwood*, 2000; *Galewsky et al.*, 2005] have shown that subtropical humidity can be remarkably well simulated in

terms of the large-scale advection and condensation of water vapor, without the inclusion of detailed microphysics. The class of models used in the latter studies have been referred to as large-scale control (LSC) models.

[4] The stable isotope chemistry of water is a potentially useful tool for probing the relative roles of microphysics and the large-scale circulation in the atmospheric hydrologic cycle because of the isotopic fractionation that occurs during phase transformations [*Sharp*, 2007]. Water isotopologues have been successfully used to constrain humidity dynamics of the upper troposphere and lower stratosphere [*Moyer et al.*, 1996; *Johnson et al.*, 2001; *Webster and Heymsfield*, 2003] and may provide an equally powerful probe of lower subtropical troposphere humidity [*Worden et al.*, 2007].

[5] Previous studies of subtropical humidity dynamics have used a combination of modeling, global atmospheric reanalysis, and remote sensing data. In-situ data can provide an independent probe into the processes that control subtropical humidity and may thus be used to validate and extend remote sensing and reanalysis results. The Island of Hawaii (Figure 1) is uniquely situated for the collection of such data because of its subtropical location (20 degrees north latitude) and because its high elevation (4205 m) allows easy surface sampling of water vapor from sea level, through the trade inversion, and into the free troposphere. Here we report measurements of atmospheric water vapor D/H ratios from the Island of Hawaii and use these data to explore models of subtropical humidity dynamics.

2. Measurements of Water Vapor D/H Ratios

[6] Between July 25 and July 29, 2006, we obtained 13 near-surface air samples from the Island of Hawaii along an elevation transect from sea level to the summit of Mauna Kea at 4205 m (Figure 1). Meteorological conditions during the field program were characterized by typical subtropical trade conditions, with a humid lower level, scattered trade cumuli, an inversion at around 800 hPa, and an arid lower free troposphere. Temperature and dew point measurements were obtained at each sample location with an Extech RH390 digital psychrometer. With one exception (sample MK1), all of the samples obtained above 2500 m were collected under early morning clear-sky conditions, well above the elevation of the cumulus layer. Sample MK1 was collected in the early afternoon, when the top of the cumulus layer had reached the summit. Conditions below 2500 m were more variable, ranging from clear sky to drizzle.

[7] Samples were collected and analyzed using the method of *Strong et al.* [2007]. Water vapor D/H ratios (Figure 2a) from samples below 2500 m showed little

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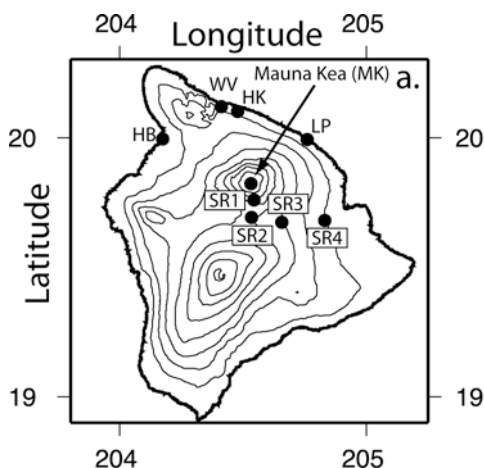
Figure 1. Topography of the Big Island of Hawaii (contour interval 500 m) and locations of water vapor sampling sites (black dots). Four samples (MK1-MK4) were obtained from the summit of Mauna Kea. Samples SR1-SR4 were collected on the Saddle Road; samples HB, WV, HK, and LP were collected at Hapuna Beach, Waipio Valley, Honokaa, and Laupahoehoe, respectively.

variation with elevation, with values ranging between −86‰ (LP) and −109‰ (SR2). Four samples were obtained at sea level (two from Laupahoehoe, and one each from Waipio and Hapuna beaches) and ranged from −86‰ to −94‰. Repeated measurements at Laupahoehoe varied by 7‰ between July 26 and July 27. Sea water samples were obtained at Waipio, Laupahoehoe, and Hapuna, although the two samples from Laupahoehoe (2.7‰ and −3.2‰) were obtained from a partially enclosed bay and may be unreliable indicators of open ocean values. The sea water D/H ratios from Waipio and Hapuna were −0.3‰ and −1.5‰, respectively. The water vapor D/H ratios of the sea level samples is in line with previous sea level measurements and are consistent with disequilibrium evaporation from the sea surface [*Craig and Gordon*, 1965; *Sharp*, 2007].

[8] Samples obtained above 2500 m had substantially lower D/H ratios, ranging from −186‰ at 2800 m (SR1) to −321‰ at the summit of Mauna Kea (MK4). Four samples were obtained from the summit of Mauna Kea. Sample MK1, collected when the top of cumulus layer had reached the summit, had the highest D/H ratio at −238‰. Sample MK2 (−242‰) was obtained 15 minutes prior to sample MK3 (−254‰) on the same morning under clear skies. Sample MK4 had the lowest D/H ratio at −321‰ and was collected just after sunrise under clear skies.

[9] The isotopic measurements generally correlate with dewpoint (Figure 2b), with the highest D/H ratio of −86‰ corresponding to a dewpoint temperature of 20°C and the lowest D/H ratio of −321‰ corresponding to a dewpoint of −27°C. Samples MK1 and MK2 have similar D/H ratios (−238‰ and −242‰, respectively), but sample MK1, which was obtained near the top of the cumulus layer, had a much higher dewpoint than MK2 (−7C° and −17°C, respectively).

[10] A potential complication for interpreting water vapor data from Hawaii involves the impact of evapotranspiration.

With the exception of MK1, the high elevation samples were collected in the early morning, well above the trade inversion, under clear sky, subsiding conditions above surfaces of bare bedrock. While we cannot entirely rule out the possible influence of evapotranspiration on these samples, the meteorological and surface conditions lead us to believe that such influences are minimal and that the high-elevation samples represent air from the free troposphere.

3. Interpretation of Subtropical D/H Ratios

[11] One of the simplest models for atmospheric water vapor D/H ratios is based on the Rayleigh distillation model. In a Rayleigh model, it is assumed that condensate is continuously removed in isotopic equilibrium with vapor from an ascending, condensing air parcel, resulting in rapidly decreasing D/H ratios. The equation describing this process is:

$$d \ln R = (\alpha(T) - 1) d \ln q \qquad (1)$$

where $R = [HDO]/[H_2O]$ is the isotopic mixing ratio in the vapor, q is the specific humidity, T is the temperature, and α
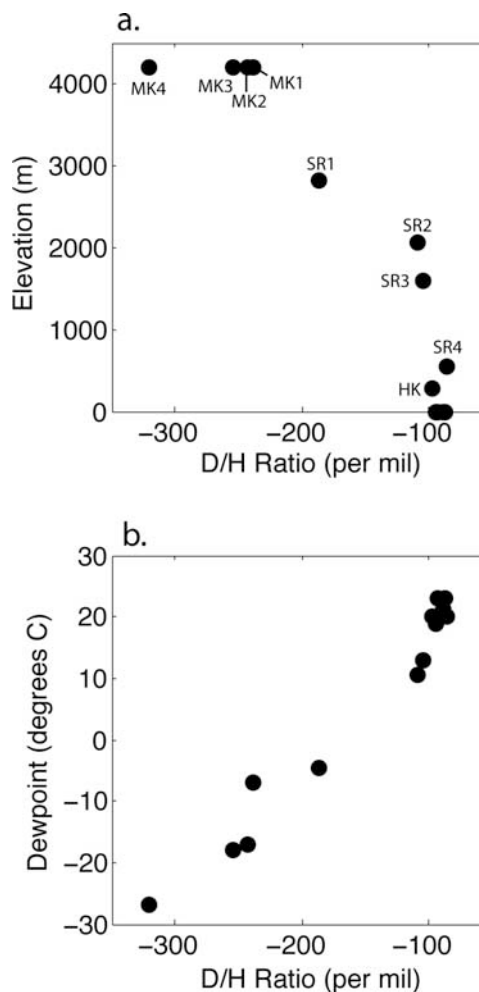
Figure 2. (a) Water vapor D/H ratios versus elevation; (b) dewpoint temperature (degrees C). Samples collected at sea-level (HB, WV, and LP) are not labeled. Samples are reported relative to SMOW in per mil notation.
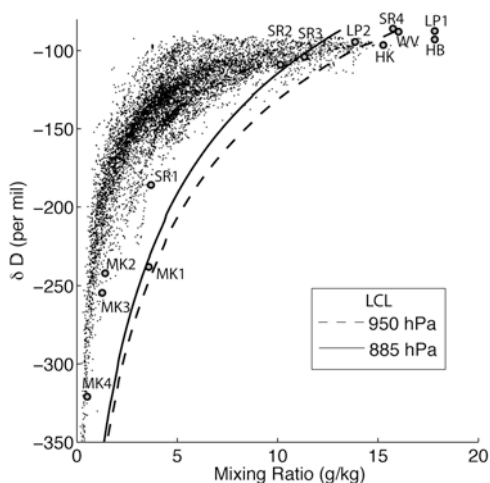
Figure 3. Water vapor D/H ratios (per mil) versus water vapor mixing ratio (g/kg). Measurements are shown by solid circles, the Rayleigh distillation curves by the solid and dashed lines for lifted condensation levels of 885 hPa and 950 hPa, respectively, and the 6-hour average MATCH advection-condensation isotope model for the subtropical Pacific basin at 0000Z July 27, 2006, shown by black dots.

is the temperature-dependent equilibrium fractionation factor between vapor and condensate. Standard equilibrium fractionation factors were used in all of the calculations [*Majoube*, 1971; *Merlivat and Nief*, 1967]. The temperature profile is the average sounding from Hilo, Hawaii, during the July 25–29, 2006, period starting from the lifted condensation level (LCL), which ranged from 950 hPa to 885 hPa. The initial D/H ratio was set to −90‰, reflecting the measured value at sea level.

[12] Measured D/H ratios are plotted as solid circles in Figure 3 as a function of water vapor mixing ratio. Results from the Rayleigh distillation model are plotted as solid and dashed lines for the 950 hPa and 885 hPa LCL, respectively. The Rayleigh model underpredicts the observed D/H ratios for the high-elevation clear-sky samples (MK2-MK4 and SR1) by 35‰ to 160‰. The D/H ratio and water vapor mixing ratio for sample MK1, which was collected on the summit at the top of the cumulus layer, is accurately captured by the Rayleigh model.

[13] Several processes could potentially increase the D/H ratios of the clear-sky water vapor relative to the Rayleigh model, including mixing of air parcels, the evaporation of condensate, or kinetic effects [*Gedzelman*, 1988; *Smith*, 1992; *Moyer et al.*, 1996; *Keith*, 2000; *Johnson et al.*, 2001]; in fact, non-Rayleigh processes are probably the dominant processes for controlling D/H values away from sites of active convection.

[14] LSC models have established that large scale mixing of air parcels plays a central role in setting subtropical tropospheric water vapor [*Pierrehumbert*, 1998; *Held and Soden*, 2000; *Galewsky et al.*, 2005], but the impact of mixing on water isotopologues is less well understood. To explore this process, we developed an LSC isotope model, based on the MATCH chemical transport model [*Rasch et al.*, 1997], to simulate the large-scale advection,

condensation, isotopic fractionation, and mixing of water vapor in the subtropical Pacific.

[15] The model was run using 6-hourly NCEP/NCAR reanalysis winds, temperature, and water vapor for the period of June and July 2006, with the first 30 days discarded as model spin-up. The resolution of the reanalysis model is approximately 200 km in the horizontal with 28 unevenly spaced vertical levels. The model consists of two tracers, one representing H2O and the other representing HDO. The tracers below 982 hPa (representing the lowest 2 model levels) are set so that the water vapor mixing ratio in those levels is equal to the reanalysis mixing ratio with a fixed D/H ratio. The tracers are advected by the large-scale reanalysis winds, and condensation is assumed to occur when the grid scale relative humidity exceeds a predetermined threshold. No condensate is retained in the model, and equilibrium isotopic fractionation occurs only upon grid-scale condensation. The model includes convective transport of tracers, but no explicit cloud-scale condensation. No kinetic isotope effects are considered in this model other than the water vapor at sea-level. The model has two free parameters: the boundary layer D/H ratio and the grid-scale relative humidity threshold. The boundary layer D/H ratio was chosen based on the measured ratios at sea-level, which ranged from −86 to −96‰. The results presented here were computed with a boundary layer value of −90‰, and are robust to changes of at least ±10‰. The relative humidity threshold was chosen to be 90%, a value that is consistent with other similar studies [*Sherwood*, 1996; *Galewsky et al.*, 2005; *Dessler and Minschwaner*, 2007].

[16] The model predicts both the humidity and the water vapor D/H ratios. The July 2006 zonal mean Northern Hemisphere subtropical relative humidity from this model
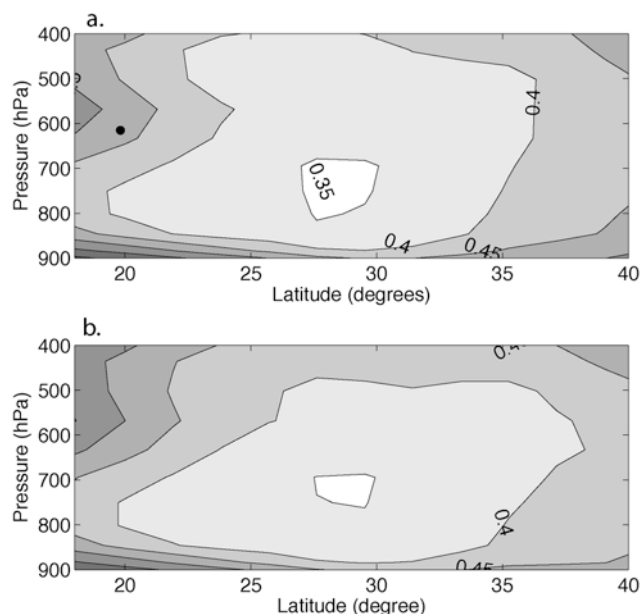
Figure 4. Zonal mean relative humidity over the Northern Hemisphere portion of the Pacific Ocean for July 2006 from (a) NCEP/NCAR Reanalysis; black dot indicates summit of Mauna Kea. (b) MATCH advection-condensation model. Contour interval is 5%.

is shown in Figure 4b, and accurately reproduces the main features from the reanalysis data set (Figure 4a), an expected result that is consistent with other LSC-type models [*Sherwood*, 1996; *Dessler and Sherwood*, 2000; *Galewsky et al.*, 2005]. Tests with other grid-scale saturation thresholds differed from the zonal mean reanalysis relative humidity by several percent, a result that is also consistent with previous studies.

[17] Isotopic results from the LSC model are shown as dots on Figure 3, which shows the 6-hour average of all of the model points from the Pacific troposphere between 915 hPa and 435 hPa, 129°E and 119°W longitude, and 20° and 40° north latitude at 0000Z on July 27, 2006. Sample MK1 is at least 15‰ more depleted in D than predicted by the LSC model at the observed mixing ratio of 3.6 g kg^{-1}, but the other high elevation samples fall within the envelope of D/H ratios predicted by the LSC model. One must exercise caution when comparing instantaneous point measurements with GCM output; nevertheless, these results point to a prominent role for large-scale mixing in setting the D/H ratios of the clear-sky, high-elevation samples.

[18] Our results are consistent with the clear-sky results of *Worden et al.* [2007], who used isotopic data from the Tropospheric Emission Spectrometer aboard the Aura spacecraft to explore the role of rain evaporation in the tropical hydrologic cycle. They successfully modeled clear-sky observations without invoking any condensate evaporation and used a simple model to show that mixing of air parcels yields curves in $\delta - q$ diagrams that are more concave down than curves produced by the Rayleigh model, results that are consistent with our data and model results. Some cloudy regions near tropical convection, however, were more depleted than predicted by a Rayleigh model. This excess depletion in cloudy conditions was attributed to partial rain evaporation near active convection.

[19] While microphysical processes may have a significant influence on the D/H ratios in cloudy conditions, such processes apparently need not be invoked to model the D/H ratios in clear-sky conditions; these ratios can be modeled solely in terms of equilibrium fractionation and large-scale mixing of air parcels. However, because we are measuring and modeling only a single isotopic ratio (D/H, and not also, for example $^{18}O/^{16}O$) we can not entirely rule out the possibility that some microphysical processes would lead to the same observed values. Thus, we do not claim that microphysical processes play no role setting clear-sky subtropical D/H ratios, only that their inclusion is not required for accurate simulation of subtropical water vapor or D/H ratios.

4.   Summary and Conclusions

[20] Measurements of water vapor D/H ratios from Mauna Kea, Hawaii, range from −88‰ at sea level to −321‰ at the summit of Mauna Kea. A Rayleigh condensation model based on an average sounding from Hilo underestimates high elevation clear-sky measurements by as much as 160‰. Results from a model of large-scale condensation, fractionation, mixing, and transport of water vapor are consistent with both the large-scale relative humidity and with the measured D/H ratios of the clear-sky samples.

[21] These results suggest that the simulation of clear-sky water vapor D/H ratios from the subtropical free troposphere may not require a detailed representation of microphysics and may thus extend the concept of large-scale control of subtropical water vapor to include water vapor isotopologues. To the extent this is true, changes in clear-sky water vapor D/H ratios may represent changes in the large scale circulation. Of course, this is a small data set of a single water isotopologue from a single season, so additional measurements of water vapor D/H ratios over several seasonal cycles along with measurements of $^{18}O/^{16}O$ ratios would help to better constrain the relative roles of mixing, condensate evaporation, and convection in the hydrologic cycle of the subtropical troposphere.

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