

Transport of water through the tropopause studied from its isotopic fractionation

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Introduction

Air enters the stratospheric overworld (above 380 K potential temperature) in the tropics. Subsequently, air rises over the tropics, and descends over the extra-tropics (the wave-driven Brewer-Dobson circulation). The temperatures in the vicinity of the tropical tropopause control water vapour concentrations of the entire stratospheric overworld, except for the contribution from methane oxidation and dehydration in the polar vortices. In the lowermost stratosphere, other processes may also play a secondary role.

Recent modelling work (Fueglistaler and Haynes 2005) showed that interannual variations in water entering the stratosphere (H_2O^{entry}) can be understood essentially from variations in tropopause temperatures alone. However, postulated long-term trends (Rosenlof *et al.* 2001) are at odds with this finding (see also Zhou *et al.* 2001).

Water that enters the stratosphere in the particulate phase can by-pass the direct temperature control at the cold point, and could reconcile opposing trends of tropopause temperature and stratospheric water vapour concentrations. Particulate water entering the stratosphere could stem from

- (a) incomplete fall-out of in-situ formed cirrus clouds;
 - (b) very deep convective injection into the lower stratosphere.
- Here, we present the first measurements that allow to constrain the role of particulate water for stratospheric water trends.

Method

Condensation processes lead to modification of the water isotopic composition. Here, we focus on the concentration of deuterated water, HDO, commonly expressed in the delta-notation for isotopic depletion:

$$\delta D = ((D/H)_{sample} / (D/H)_{snow} - 1) * 1000$$

In the stratosphere, total hydrogen (H) and deuterium (D) are conserved, and the main species are: H_2O , CH_4 and H_2 for hydrogen, and HDO, CH_3D and HD for deuterium.

The dehydration during ascent from surface to tropopause is associated with a strong fractionation of water vapour, but not for methane and hydrogen. Consequently, at entry into the stratosphere HD^{entry} and CH_3D^{entry} are known from tropospheric measurements (superscript 'tr'), and we can determine HDO^{entry} from measurements of HDO and CH_3D in the stratosphere (similar to H_2O^{entry}):

$$HDO^{entry} = HDO - (CH_3D^{tr} - CH_3D) - (HD^{tr} - HD)$$

$$H_2O^{entry} = H_2O - 2(CH_4^{tr} - CH_4) - (H_2^{tr} - H_2)$$

$$\delta D^{entry} = ((HDO^{entry}/H_2O^{entry}) / (D/H)_{snow} - 1) * 1000$$

We show results obtained from MkIV solar occultation FTIR profile measurements of H_2O , HDO, CH_4 and CH_3D obtained at 35N and 60N over the period 1991 - 2007 at a vertical resolution of about 2-3 km. These measurements are complemented with information of tropospheric HD, CH_4 and CH_3D .

Variability vs. Trends

We analyse results separately for two layers:

- (a) lower stratosphere (380-425K), with rapid transport (months) from tropics to higher latitudes, large variability in H_2O and HDO.
- (b) middle stratosphere (500-800K), well-mixed air masses with mean age of order years.

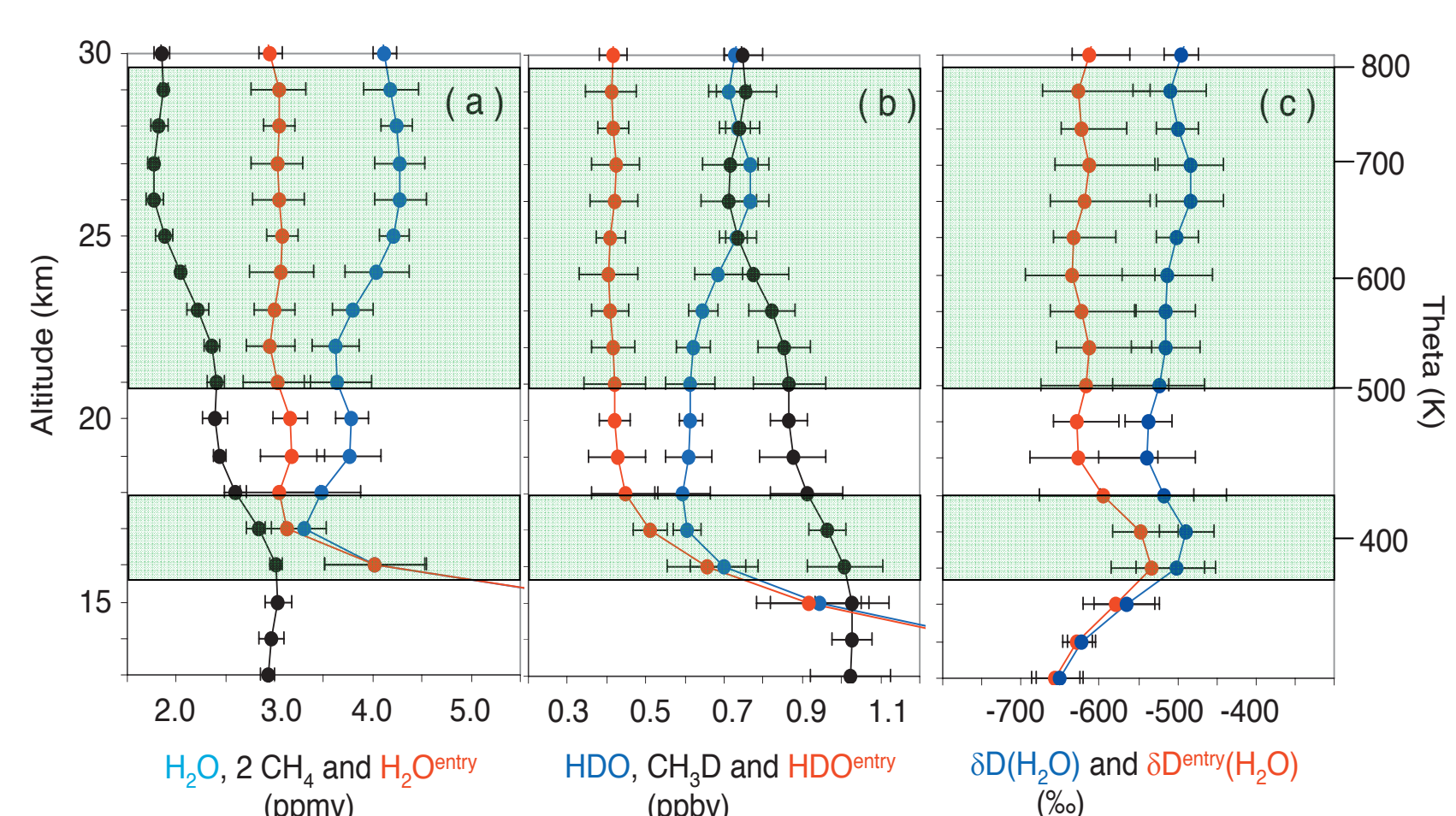


Figure 1: (a) Profiles of measured water vapour (H_2O) and methane (CH_4), and deduced water entry mixing ratio (H_2O^{entry}). (b) Profiles of measured deuterated water (HDO) and deuterated methane (CH_3D), and deduced deuterated water entry mixing ratio (HDO^{entry}). (c) Same as in (b), but expressed in delta-Notation.

Summary

Recent work demonstrated that interannual variation in water entering the stratosphere is well understood (Randel *et al.* 2004; Fueglistaler and Haynes 2005), but postulated long-term trends of stratospheric water vapour remain poorly understood. Trends in particulate water entering the stratosphere could resolve the paradox of apparently increasing water despite a (small) cooling trend at the tropical tropopause.

Because of differing isotopic signatures of water entering the stratosphere in the gas- and particulate phase, the isotopic composition of stratospheric water is expected to be highly sensitive to trends in particulate water.

We present the first measurements of trends in isotopic composition of water into the stratosphere for the period 1991-2007 based on JPL MkIV solar occultation FTIR spectrometer data. We show that :

- (a) variations in HDO^{entry} are correlated to variations in H_2O^{entry} on short timescales
- (b) the correlation follows the theoretical Rayleigh curve
- (c) over the period 1991-2007, no trend in particulate water can be detected.

Interpretation

Previous isotope measurements have highlighted the importance of non-Rayleigh processes (e.g. evaporation of convectively lofted ice) for the water budget of the tropical tropopause layer (and upper troposphere in general).

Our measurements suggest that during the very last stage prior to entry into the stratosphere, temperature dependent Rayleigh fractionation is the governing process. It cannot be excluded that other processes also yield a high correlation between HDO^{entry} and H_2O^{entry} , but that the slope should follow those predicted by Rayleigh fractionation would be quite a coincidence.

Variability of H_2O^{entry} and HDO^{entry}

In the layer 380-425K we observe variability primarily associated with seasonal and shorter-term variations of conditions at entry into the stratosphere.

Figure 2 shows a high correlation between H_2O^{entry} and HDO^{entry} . (Correlation coefficient 0.98.) Moreover, the correlation is well explained by Rayleigh-fractionation (see Notes). (Correlation coefficient 0.96.)

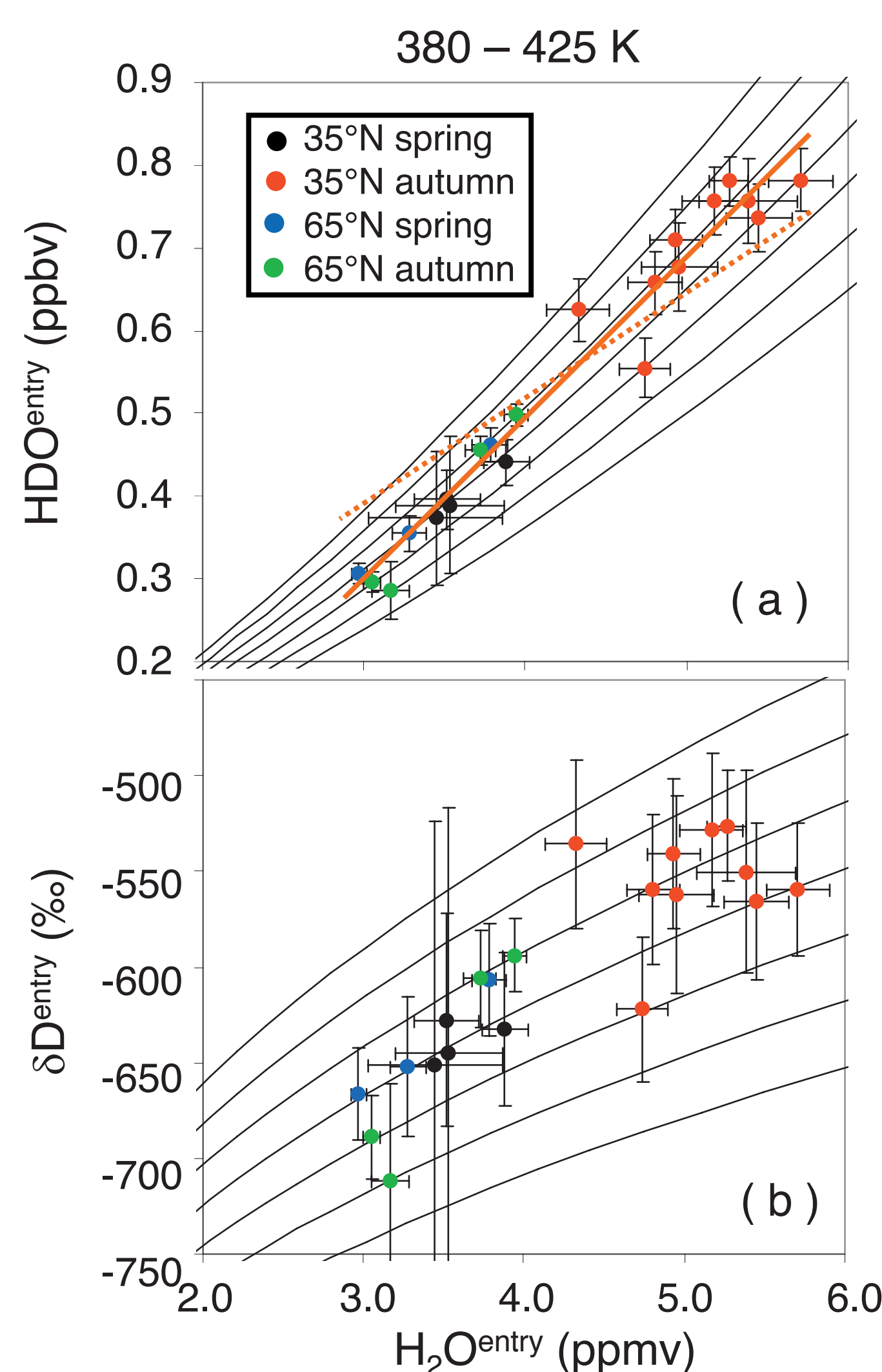


Figure 2: (a) Scatterplot of measured H_2O^{entry} and HDO^{entry} in the layer 380-425K. Color code shows season/latitude of measurement. Brown line is linear least-squares fit (mid-latitude observations only), black lines show Rayleigh-curves. Brown dotted line shows correlation for constant δD . (b) Same as (a), but in delta-Notation.

Trends

In the layer 500 - 800K potential temperature, we observe primarily interannual variations and longer-term trends of conditions at entry into the stratosphere. Consequently, variations in H_2O and HDO are much smaller than those in the layer 380-425K, and a correlation analysis as done in the lower layer is hampered by a low signal to noise ratio.

We therefore directly tackle the question whether the timeseries of H_2O^{entry} and HDO^{entry} show evidence for a trend in the contribution from particulate water. We formulate a simple hypothesis:

Interannual variations and trends in HDO^{entry} are correlated to those in H_2O^{entry} in the same way as the short-term variations.

And the corresponding model:

We predict HDO^{entry} based on H_2O^{entry} , using the correlation between HDO^{entry} and H_2O^{entry} measured in the layer 380 - 425K.

Because the short-term variations can be explained by Rayleigh-fractionation alone without invoking a role for particulate water, it follows that if this model can explain observed HDO^{entry} , we find no evidence for a trend in particulate water over the period 1991 - 2007.

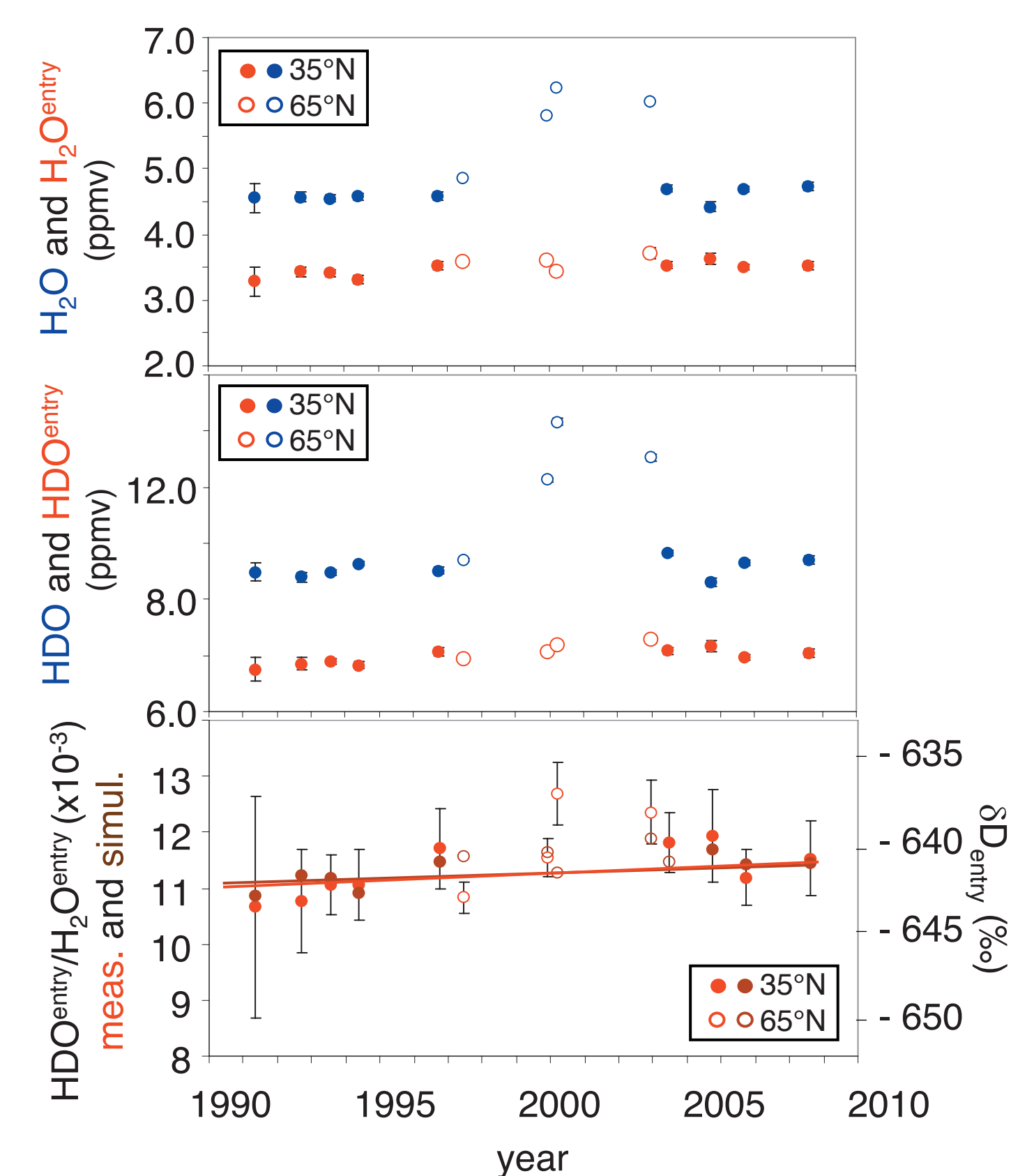


Figure 2: Timeseries of (a) H_2O and H_2O^{entry} ; (b) HDO and HDO^{entry} ; (c) ratio of HDO^{entry}/H_2O^{entry} as measured (red) and predicted (dark red) (measured $18.1 \pm 2.1\%$; model: 15.4% for period 1991-2007).

Figure 3 shows that the isotope measurements show no evidence for a trend in particulate water. This is remarkable, because HDO^{entry} is very sensitive to particulate water. The (statistically insignificant) difference between measured and predicted δD^{entry} trend yields an upper limit of 0.02 ± 0.17 ppmv and 0.06 ± 0.57 ppmv for convectively lofted ice (assumed $\delta D = -200\%$) and in-situ formed ice (assumed $\delta D = -500\%$).

Notes:

Because of different vapour pressures, HDO moves preferentially into the condensed phase. Assuming that the freshly formed condensate is in equilibrium with the gas phase and the formed condensate is sealed from the gas phase (equivalent to instantaneous removal), the isotopic depletion (HDO/H_2O as function of H_2O) is simple to calculate, and is termed **Rayleigh-fractionation**. This should be viewed as the starting point for isotope analysis - there is no *a-priori* reason why the underlying assumptions should hold to a good degree in the atmosphere. Also note that there is not a single Rayleigh curve - rather there is a Rayleigh curve for any arbitrary $[H_2O]/[HDO]$ initial condition, and subsequent pressure/temperature history.

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