

THE TOTAL HYDROGEN BUDGET OF THE EQUATORIAL UPPER STRATOSPHERE

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1) INTRODUCTION

The chemical process of methane oxidation is believed to be reasonably well understood such that the complete oxidation of one methane molecule produces two water vapor molecules [Brasseur and Solomon, 2005]. Studies with LIMS/SAMS and HALOE data have revealed significant deviations in the ratio of the changes of H₂O to CH₄ from 2.0 in the equatorial and mid-latitude upper stratosphere [Hansen and Robinson, 1989; Remsberg et al., 1996] with values significantly greater than 2.0. The implication of H₂O to CH₄ ratios greater than two in the upper stratosphere is that there exists an additional source of water vapor in addition to methane oxidation. As discussed by Le Texier et al. [1988], the water vapor budget of the stratosphere is not complete without consideration of the oxidation of molecular hydrogen.

This study uses observational data of water vapor and methane from the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) [Russell et al., 1993], the SCISAT-1 Atmospheric Chemistry Experiment (ACE) [Bernath et al., 2005], and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on the European Environmental Satellite (Envisat) [Fischer et al., 2008] to study the hydrogen budget in the upper stratosphere.

2) INSTRUMENTS AND DATA

The HALOE instrument uses solar occultation to measure absorption of solar energy in several broadband and gas filter spectral bands at infrared wavelengths. The measurements in the atmosphere are ratioed to the unattenuated measurements outside the atmosphere to create transmission profiles which are inverted to infer profiles of H₂O and CH₄, among other gases. Version 19 data are used for this study.

The ACE-FTS instrument (hereafter referred to simply as ACE) is a high resolution Fourier Transform Spectrometer which measures atmospheric absorption spectra between 2.2 and 13.3 μm . Transmission profiles of the spectra are calculated and fitted to obtain profiles of temperature, pressure, and over 20 atmospheric trace gases [Boone et al., 2005]. Version 2.2 data are used for this study.

The MIPAS instrument is a Fourier transform emission spectrometer which measures limb spectra with high spectral resolution over the wavelength range of 4.15 to 14.6 μm . Measurements are from the upper troposphere to the lower mesosphere, and are inverted to obtain profiles of temperature, pressure, and over 25 trace gases along with cloud distributions. This study uses data produced by a retrieval processor designed at the Institute for Meteorology and Climate Research (IMK) [von Clarmann et al., 2003] and the Instituto de Astrofísica de Andalucía [Funke et al., 2001].

3) CREATION OF A UNIFORM DATASET

Comparison of mixing ratio profiles from HALOE to a variety of coincident profiles from other instruments [Harries et al., 1996; Park et al., 1996; McHugh et al., 2005] consistently show that HALOE H₂O and CH₄ mixing ratios are biased low. Since the ATMOS and ACE instruments are thought to have very good absolute accuracy, and the H₂O and CH₄ differences with HALOE are similar, we have used these as the standards and have modified the HALOE profiles to remove the relative bias. This bias correction is done explicitly through a

comparison of HALOE and ACE equatorial profiles. Comparisons of MIPAS H₂O and CH₄ data to ACE [Engelhardt et al., unpublished results, 2007; Carleer et al., 2008] show that the MIPAS data have small biases, as well. In order to minimize the possible influence of these biases, we correct for the biases in the MIPAS H₂O and CH₄ profiles by comparing them directly to the HALOE corrected profiles.

The upper panel of Figure 1 shows the monthly zonal mean time series of the corrected HALOE, ACE and corrected MIPAS H₂O and CH₄ data at 2.2 hPa averaged over 10°S-10°N. While the H₂O+2*CH₄ time series in Figure 1 (lower panel) clearly shows smaller variations than either the H₂O or the CH₄ time series, there remain significant variations. Clearly, H₂O+2*CH₄ is not conserved over this time period in the three data sets, with the variations themselves averaging about +/- 0.2 ppmv, or 3 % of the total H₂O+2*CH₄ mixing ratio.

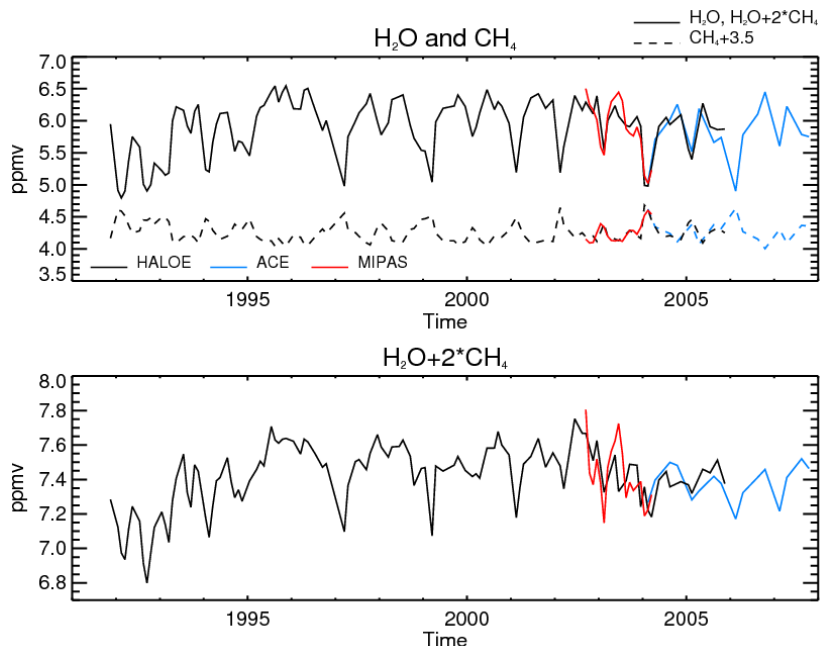


Figure 1. Time series of corrected HALOE (black), ACE (blue), and corrected MIPAS (red) water vapor and methane (top panel) and H₂O+2*CH₄ (lower panel) at 2.2 hPa averaged over 10°S-10°N.

4) CORRELATION ANALYSIS

We define the inverse of the slope of the changes of H₂O to the changes of CH₄ as β [Le Texier et al., 1988]:

$$\Delta[\text{H}_2\text{O}] = -\beta * \Delta[\text{CH}_4] \quad (1)$$

We calculate β using regression fits both for H₂O versus CH₄ changes at one pressure level (single-level β) and for H₂O versus CH₄ changes over a range of pressures (multi-level β). The single-level β values are particularly sensitive to assumptions about errors in measurement precision, while the multi-level β values are sensitive to level-dependent systematic errors in the measurements. Unless chemistry changes quickly with altitude, the methods should give similar results.

In Figure 2a, we show an example of the regression plot for deriving β values at 1.5 (blue points) and 2.2 hPa (red points) from HALOE measurements from 1996-2005. The best fit lines shown here (same color connotations) are calculated by assuming half the CH₄ random error and twice the H₂O random error at this level. For comparison to the best fit lines, a dashed line with a slope of -2.0 representing the conservation of H₂O+2*CH₄ is also shown in Figure 2a. Figure 2a shows a good agreement between the single and multi-level β values between 1.5 and 2.2 hPa, with values in all cases exceeding 2.0. Figure 2b shows the correlation of ACE H₂O and CH₄ data from 2004-2007 showing similar β values to the HALOE values. Values of single and multi-level β were then

calculated on five pressure surfaces between 1.5 and 6.8 hPa for the HALOE, ACE, and MIPAS data. These calculations yielded values greater than 2.0 for all cases, implying that more than two molecules of H₂O are produced for each CH₄ molecule oxidized in this region of the atmosphere.

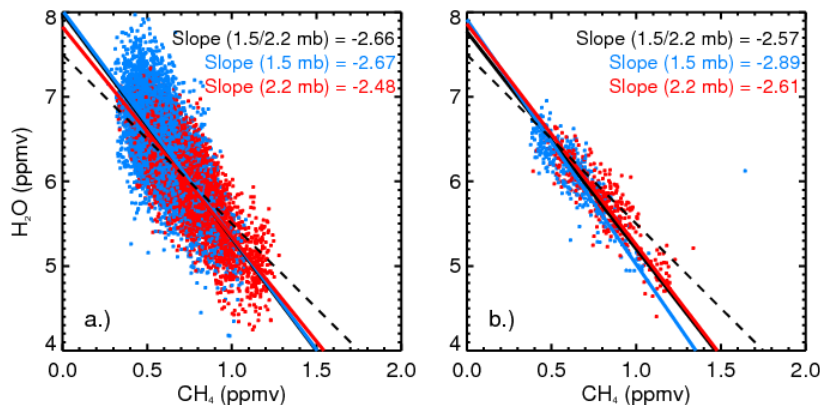


Figure 2. Water vapor versus methane at a) 1.5 and 2.2 hPa measured by HALOE from 1996-2005 and b) 1.5 and 2.2 hPa measured by ACE from 2004-2007. The best fit line through the cumulative distribution of points at 1.5 and 2.2 hPa is shown in black. All data shown are for the latitude range of 10°S-10°N. The slopes of the best fit lines are shown in the upper right hand corner of each plot. The dashed lines have slopes of -2.0.

5) CHEM2D MODELING

CHEM2D is a global middle atmosphere model with interactive radiative, photochemical and dynamical schemes which successfully simulates the general distribution and variability of tracers such as H₂O, CH₄, and N₂O [Summers et al., 1997; McCormack and Siskind, 2002]. Here we analyze monthly zonal mean H₂O, CH₄ and H₂ fields from a 30-year CHEM2D simulation. Figure 3 shows H₂O, CH₄, H₂O+2*CH₄, H₂, and H₂O+2*CH₄+H₂ at a pressure of 1.4 hPa for years 20-25 of the simulation averaged over 10°S to 10°N. While the variability in H₂O and CH₄ is somewhat different than that seen in the HALOE data, the CHEM2D model shows H₂O+2*CH₄ variations which are anti-correlated with the CH₄ variations in the same sense as the observations. Also, the H₂O+2*CH₄ variations are anti-correlated with the variations in H₂, such that H₂O+2*CH₄+H₂ is nearly constant in time.

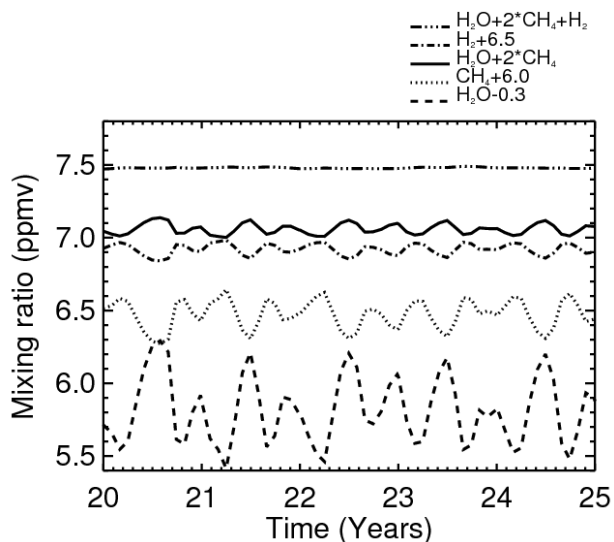


Figure 3. Time series of water vapor, methane, molecular hydrogen, H₂O+2*CH₄, and H₂O+2*CH₄+H₂ at 1.4 hPa averaged over 10°S-10°N from CHEM2D. The time series shown is for years 20-25 of a thirty year simulation where the line description for each time series is shown above the figure. Note that some of the time series have been shifted to fit the plot.

6) MEASUREMENT TIME SERIES

Model results from CHEM2D show $H_2O+2*CH_4$ variations which are balanced primarily by H_2 variations, so that total hydrogen, H_y , is conserved by adding H_2 to $H_2O+2*CH_4$:

$$H_y = H_2O + 2*CH_4 + H_2 \quad (2)$$

Variations in total hydrogen can then be calculated as a function of pressure and time from the observational data by relating the H_2 term in equation (2) with the variations in $H_2O+2*CH_4$. If the H_2 term is expanded into a mean and residual term and equation (1) is substituted in (2), then H_y at pressure level p_i can be expressed solely in terms of H_2O , CH_4 , and the β values (along with an assumed constant H_2 mixing ratio of 0.55 ppmv at 7 hPa (level 1 in (3)):

$$H_y(p_i,t) = H_2O(p_i,t) + 2*CH_4(p_i,t) + \langle H_2(7 \text{ hPa}) \rangle + \sum_{i=1,j} \{ [0.5*(\beta(p_i)+\beta(p_{i-1}) - 2)] * [\langle CH_4(p_i) \rangle - \langle CH_4(p_{i-1}) \rangle] \} + (\beta(p_i)-2)*dCH_4(p_i,t) \quad (3)$$

The third term of equation (3) is the long-term average H_2 mixing ratio at 7 hPa (assumed to be 0.55 ppmv [Zöger et al., 1999; Rohs et al., 2006]), while the fourth term is the summation of the changes in the long-term average CH_4 mixing ratio between 7 hPa and the pressure of interest multiplied times $(\beta-2)$ where β is an average of the value at the chosen pressure and one level below.

Figure 4 shows the time series of HALOE, ACE, and MIPAS H_y at 2.2 hPa averaged over $10^\circ S$ to $10^\circ N$ along with the time series of H_2O , CH_4 , H_2 , and $H_2O+2*CH_4$ where the H_2 mixing ratio is calculated from the last three terms of equation (3). For the H_2 and H_y calculations, a 'residual' β value is chosen such that the standard deviation of H_y is minimized. The plot shows that the variations seen in H_y are noticeably reduced compared with those from the $H_2O+2*CH_4$ time series. The overall agreement in H_y between the three instruments is very encouraging and provides confidence in the mixing ratio of total hydrogen. These results highlight the importance of understanding variations in H_2 as well as those of H_2O and CH_4 in this region of the atmosphere.

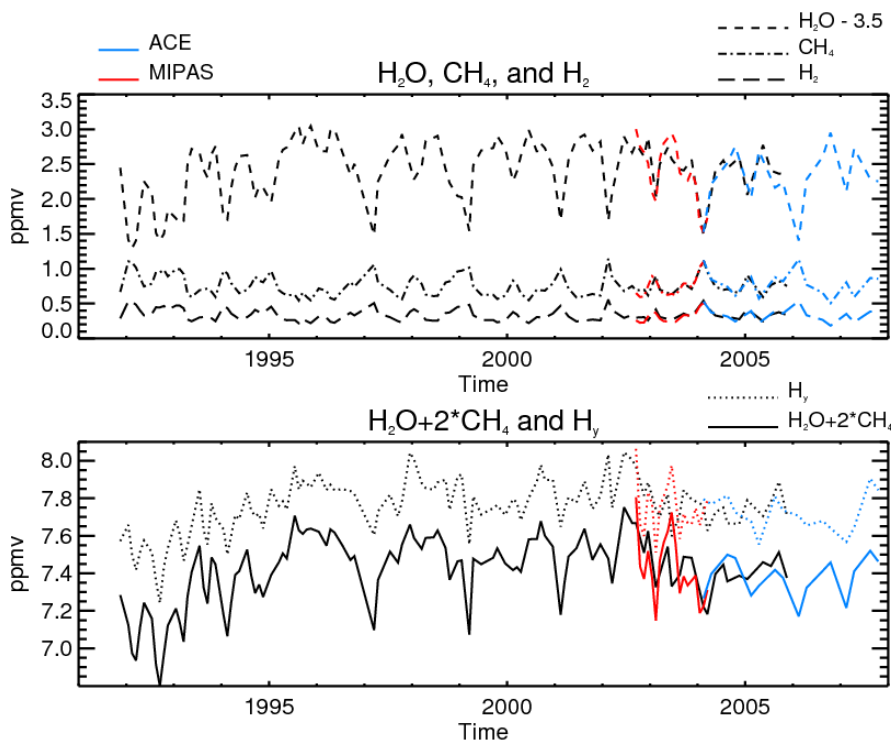


Figure 4. Time series of corrected HALOE (black), ACE (blue), and corrected MIPAS (red) water vapor, methane, and molecular hydrogen (top panel) and $H_2O+2*CH_4$ and H_y (lower panel) at 2.2 hPa averaged over $10^\circ S-10^\circ N$.

7) DISCUSSION AND CONCLUSIONS

We have presented data from the HALOE, ACE, and MIPAS instruments which have shown that the quantity $\text{H}_2\text{O}+2*\text{CH}_4$ is not conserved on individual pressure surfaces over time or as a time-averaged quantity as a function of pressure in the equatorial upper stratosphere. The equatorial upper stratosphere is the ideal region to calculate β values since the CH_4 changes are large, the influence of descending air from higher altitudes is small, and influence of variations in stratospheric entry level H_2O is much smaller than in the lower stratosphere. β values calculated from the HALOE, ACE, and MIPAS showed good agreement both on single pressure surfaces and over a range of pressures in the equatorial upper stratosphere always having values considerably above 2. We calculated values of β which minimized the variability of H_y , or total hydrogen, time series on individual pressure surfaces. The resulting H_y time series can be used to calculate more accurate values of stratospheric entry level H_2O (not shown). The measurements are supported by atmospheric simulations by the CHEM2D model which show not only variations in $\text{H}_2\text{O}+2*\text{CH}_4$ in the upper stratosphere but also variations in H_2 of similar magnitude but anti-correlated in time so that $\text{H}_2\text{O}+2*\text{CH}_4+\text{H}_2$ is nearly conserved. Collectively, these results highlight the importance of the inclusion of molecular hydrogen in the hydrogen budget of the equatorial upper stratosphere.

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