Stratospheric abundances of water and methane based on ACE-FTS measurements

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[1] We present solar occultation measurements of H_2O and CH_4 by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS). The data used here were selected from occultations spanning February to April 2004 from 0 to 79.8°N. The midlatitude volume mixing ratio (VMR) of potential water is determined as $[H_2O] + 2[CH_4]$ and from $[H_2O]$ versus $[CH_4]$ correlations, then used to calculate the VMR of water vapor entering the stratosphere. We obtain 7.14 ± 0.23 ppm for potential water and 3.65 ± 0.29 ppm for water entering the stratosphere in 2004 for direct comparison with Atmospheric Trace Molecule Spectroscopy (ATMOS) data (1985–1994). We find a very small change in potential water and no change in water entering the stratosphere relative to the 1994 ATMOS data, indicating that increases observed by ATMOS and other instruments from that time period have not continued. This halt in stratospheric water vapor increases is consistent with recent water vapor measurements by other instruments.
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1. Introduction

[2] The amount of water vapor in the stratosphere plays an important role in the climate and the chemistry of our atmosphere. Elevated levels of water, an important greenhouse gas, are known to enhance tropospheric warming and stratospheric cooling [*Rind and Lonergan*, 1995; *Shindell*, 2001]. Although numerous greenhouse gases contribute to changes in the temperature profile of the atmosphere, the presence of water in the stratosphere, accompanied by enhanced cooling, increases the formation of polar stratospheric clouds (PSCs) during the polar winter. PSCs then enable heterogeneous reactions to produce species that can catalytically destroy polar stratospheric ozone in the spring. Recent research indicates that the total volume of PSCs formed during a particular winter is perhaps the most important climate parameter driving the evolution of Arctic ozone loss [*Rex et al.*, 2004].

[3] Water primarily enters the stratosphere through vertical transport across the tropical tropopause layer (TTL). This is part of Brewer-Dobson circulation, which proceeds with the tropical air circulating to stratospheric midlatitudes then descending at the poles. The removal of stratospheric water (dehydration) occurs frequently in the Antarctic vortex and sporadically in the Arctic vortex by sedimentation of water in PSCs, which can rapidly fall to lower altitudes. The descent of water vapor in the vortex without sedimentation may also alter water vapor profiles significantly, particularly when the vortex is strong [*Nassar et al.*, 2005]. The major photochemical source of water in the stratosphere is oxidation of CH_4 by the net reaction $CH_4 + 2O_2 \rightarrow 2H_2O + CO_2$, in which one CH_4 molecule creates two H_2O molecules. The oxidation of all other hydrocarbons makes a negligible contribution to $[H_2O]$ (where the square brackets denote VMR). A high level of variability is often observed if one treats H_2O and CH_4 independently but the quantity $[H_2O] + 2[CH_4]$, referred to as potential water (PW), is essentially conserved with CH_4 oxidation. Total hydrogen, a truly conserved quantity, is often estimated by the sum of PW and $[H_2]$.

[4] Numerous studies have detected an increase in stratospheric water vapor occurring over time periods as short as a few years and as long as the past half-century [*Oltmans et al.*, 2000; *Michelsen et al.*, 2000; *Rosenlof et al.*, 2001]. The increase can partially be attributed to an increase in CH_4 emissions but the remainder is attributed to an increase in water vapor entering the stratosphere across the TTL. More recent evidence indicates that the increase in stratospheric $[H_2O]$ has ceased in the last few years and has even shown a temporary decrease on the order of 3–4 years [*Nedoluha et al.*, 2003; *Randel et al.*, 2004]. Understanding changes in stratospheric water vapor and water vapor entering the stratosphere or $[H_2O]_e$, requires a better understanding of the relative importance of the numerous tropical dehydration processes and processes that control humidity near the TTL.

[5] Determination of trends in water data is complicated by long-term variability, the quasi-biennial oscillation, as well as the seasonal variability of water vapor entering the stratosphere, with maximum water ascending through the TTL during the Northern Hemisphere (NH) summer and a minimum during the NH winter. This seasonal variability creates a pattern in the stratosphere that is a record of the amount of water that has passed the TTL and is often referred to as the tape recorder effect [*Mote et al.*, 1996]. In addition to issues regarding the variability of water vapor, comparisons between the many water datasets are complicated by the different types of measurements (in situ or remote sounding), numerous different types of instruments (hygrometers, radiometers, spectrometers, etc.) and mea-

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surement platforms (ground, aircraft, balloon, or satellite) but extensive attempts at comparison for the purpose of establishing water trends as well as measurement validation continue to be made [*Stratospheric Processes and Their Role in Climate (SPARC)*, 2000; *Michelsen et al.*, 2002].

[6] In this paper, we present ACE-FTS profiles of mid-latitude $[H_2O]$, $[CH_4]$, and PW from the mid-troposphere to the mesopause. We also include $[H_2O]$ versus $[CH_4]$ correlations to facilitate the direct comparison of potential water with past measurements made by the ATMOS instrument and furthermore compare our calculated value of water entering the stratosphere to ATMOS values.

2. ACE-FTS Water and Methane Retrievals

[7] The Atmospheric Chemistry Experiment (ACE) satellite also known as SCISAT-1, makes solar occultation measurements during up to 15 sunrises and 15 sunsets per day. The primary instrument on SCISAT-1 is the ACE-FTS, a high resolution Fourier transform spectrometer (FTS) operating in the $750-4400 \, cm^{-1}$ range [*Bernath et al.*, 2005]. During each occultation, the ACE-FTS can measure spectra at a series of tangent heights, which are inverted to give profiles of temperature, pressure, and molecular VMRs with a vertical resolution of 3–4 km. The inversion process first requires the retrieval of temperature and pressure by fitting measured CO_2 spectral lines to calculated spectral lines from a forward model. After retrieving temperature and pressure, VMR profiles for numerous molecules are retrieved in a similar manner (C. D. Boone et al., Retrievals for the Atmospheric Chemistry Experiment Fourier Transform Spectrometer, submitted to *Applied Optics*, 2005) (hereinafter referred to as Boone et al., submitted manuscript, 2005).

[8] The H_2O retrieval utilizes 52 microwindows, which fall in the $1362-2137 \, cm^{-1}$ range to retrieve profiles from 7 to 90 km altitude. The 64 CH_4 microwindows in the $1245-2889 \, cm^{-1}$ range are used to retrieve profiles from 4 to 63 km altitude. Above the highest measured tangent point for each molecule, VMR values are derived by assuming the shape of a climatological a priori VMR profile and multiplying it by a constant determined from fitting the lower portion (Boone et al., submitted manuscript, 2005). The retrieved H_2O and CH_4 profiles each have statistical uncertainties (a measure of the random error in the fitting process that does not include systematic errors) of less than 2.0% for the stratosphere but higher in the troposphere and mesosphere. A complete error analysis has not yet been carried out for all species measured by the ACE-FTS, however *Clerbaux et al.* [2005] have done an error analysis for ACE-FTS CO measurements. Their analysis suggests that the total error is mainly due to measurement error with smaller contributions from other sources such as smoothing, instrument line shape and temperature retrievals. With the large number of microwindows used in the H_2O and CH_4 retrievals, we expect measurement error to be relatively small, thus exerting a negligible influence on our final results, but a more thorough error analysis is left for future work.

3. Results and Analysis

[9] The data used in this work consist of NH measurements spanning February to April of 2004 scattered over a
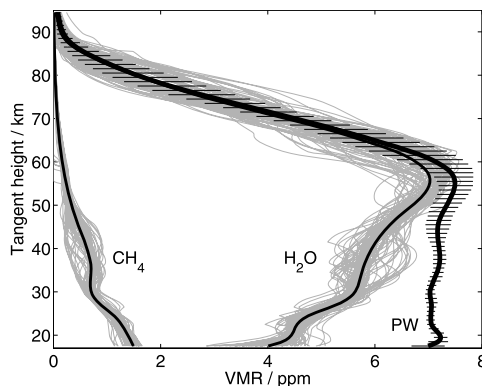

Figure 1. Midlatitude $[H_2O]$, $[CH_4]$ and PW profiles from 21 March to 2 April 2004 with latitude decreasing during this time period from 66°N to 30°N. The thick black lines are the averaged profiles taken from the 83 individual profiles shown as thin lines. The derivation of the error bars for PW is explained in section 3.

range of latitudes from 0 to 79.8°N. We classified the occultations using a combination of potential vorticity data and $[CH_4]$ versus $[N_2O]$ correlations [*Nassar et al.*, 2005]. In this work, we will refer to occultations that have been classified to be in the extratropical extravortex region as midlatitude occultations.

[10] We created average profiles of midlatitude $[H_2O]$ and $[CH_4]$ and determined potential water as PW = $[H_2O]$ + 2$[CH_4]$. Figure 1 shows 83 individual midlatitude profiles of $[H_2O]$ and $[CH_4]$ as well as the mean profiles. The PW profile is also plotted and appears nearly vertical from ~20–50 km as expected. It is shown without individual profiles but rather error bars indicating one standard deviation variability from the mean PW. The statistical fitting uncertainties were ignored when calculating the error bars because they were typically small compared to the variability between profiles. Error bars could have been plotted for $[H_2O]$ and $[CH_4]$ independently and propagated to obtain an error on PW, however this would ignore the anti-correlation between $[H_2O]$ and $[CH_4]$ which accounts for most of the observed variability in the middle to upper stratosphere (~30–48 km).

[11] In Figure 2, $[H_2O]$ and $[CH_4]$ correlations were plotted in the same manner as carried out with ATMOS data by *Michelsen et al.* [2000], which was based on earlier work by *Abbas et al.* [1996]. The 83 occultations used here and in the profiles were selected to minimize seasonal variation when comparing to ATMOS. To be consistent with the analysis by *Michelsen et al.* [2000], points from 18 to 40 km were plotted as open circles. The points in this range were fit to a line (and others ignored) for which the slope is approximately −2 (implying one CH_4 molecule oxidizes to two H_2O molecules) and the intercept represents the PW or the $[H_2O]$ when CH_4 is fully oxidized. By this method, the slope is -2.02 ± 0.06 and the intercept PW is 7.14 ± 0.05 ppm. From the profiles, PW is calculated to be 7.12 ± 0.02 ppm by taking the average PW at tangent heights from 18 to 40 km. The above uncertainty stated for the PW fit comes from the error in determining the intercept and the uncertainty stated for PW from the profiles is the
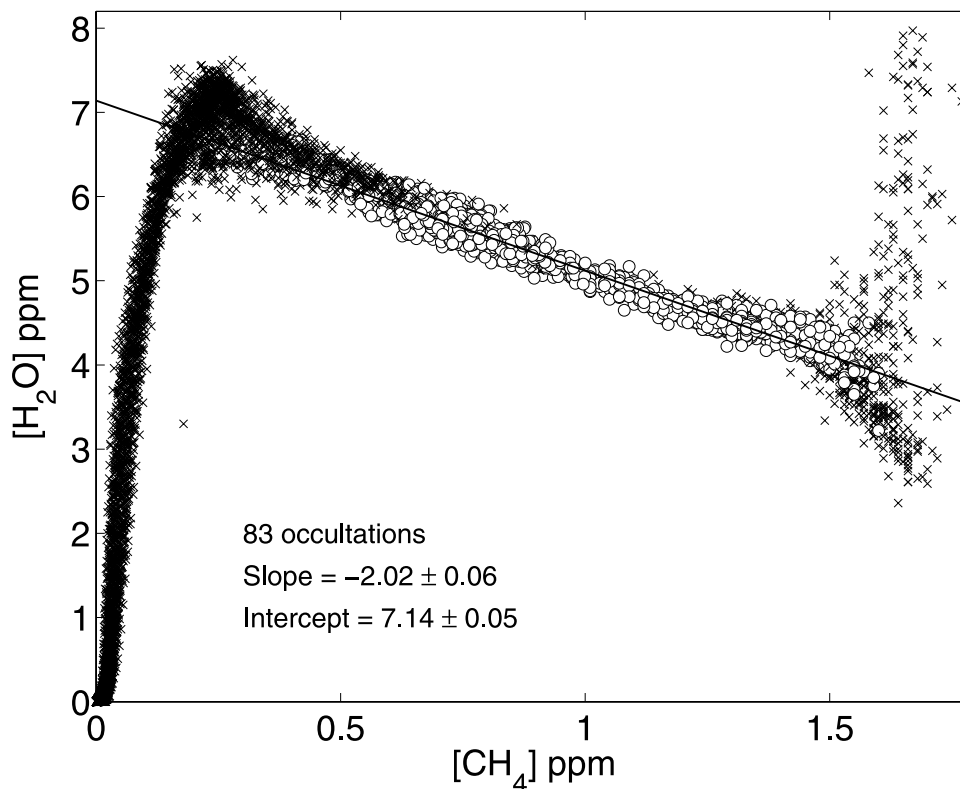
Figure 2. Correlation between midlatitude $[H_2O]$ and $[CH_4]$ to determine potential water, based on the same 83 occultations as in the previous figure. A linear fit was carried out for points between 18 and 40 km (open circles) to determine the slope and intercept.

standard deviation from the mean. Both values agree within their calculated uncertainties and one would expect to obtain the same value from both methods if the slope of the fit was fixed at exactly −2. Thus although the fit gives a larger uncertainty, we consider it more realistic since it does not exclude the small contributions from side reactions for H_2O and CH_4 in addition to CH_4 oxidation, or other factors that may cause a deviation from an ideal slope of −2. If we apply a systematic error of ±3% and combine this with the precision from the PW fit, then our best value for PW becomes 7.12 ± 0.23 ppm.

[12] The quantity of water entering the stratosphere across the TTL or $[H_2O]_e$ is difficult to determine directly from ACE measurements because of the high degree of variability of water vapor near the TTL. We would need a full year of measurements in order to properly average over both day-to-day variations and the large expected seasonal variation. However, $[H_2O]_e$ can be calculated using a variety of methods [*SPARC*, 2000]. We will utilize the relationship $[H_2O]_e = [H_2O] − \beta([CH_4]_e − [CH_4])$ first proposed by *Hansen and Robinson* [1989], where β is the magnitude of the slope of the correlation plot and $[CH_4]_e$ is the VMR of methane entering the stratosphere across the TTL. This rearranges to $[H_2O]_e = [H_2O] + \beta[CH_4] − \beta[CH_4]_e$ or $[H_2O]_e = PW − \beta[CH_4]_e$. From our measurements, we use the $[CH_4]$ at 16 km (or ∼100 hPa) from 38 tropical occultations (3–9 February and 3–8 April, 0–26°N) to obtain the value of 1.726 ± 0.069 ppm for $[CH_4]_e$, which includes precision and a systematic error of ±3%. The *SPARC* [2000] assessment used a range of estimated values up to $[CH_4]_e$ = 1.72 ppm (with zero uncertainty) in 1999. We calculated $[H_2O]_e$ using various

Table 1. Calculated Values of Water Entering the Stratosphere, $[H_2O]_e$

Parameters Used[a]	$[H_2O]_e$ ppm[b]
Measured $[CH_4]_e$ and $\beta = 2.02 \pm 0.06$	**3.65 ± 0.29**
SPARC $[CH_4]_e$ and $\beta = 2.02 \pm 0.06$	3.67 ± 0.24
Measured $[CH_4]_e$ and $\beta = 2$ (exact)	3.69 ± 0.24
SPARC $[CH_4]_e$ and $\beta = 2$ (exact)	3.70 ± 0.23

[a]The different parameters were used in the equation $[H_2O]_e = PW − \beta[CH_4]_e$, where PW = 7.14 ± 0.23 ppm.

[b]The bold value is likely the most reasonable despite having the highest associated uncertainty.

Table 2. ATMOS-ACE Time Series for PW and $[H_2O]_e$[a]

Mission	Year[b]	PW, ppm	1σ PW ppm[c]	$[H_2O]_e$ ppm	1σ $[H_2O]_e$ ppm[d]
Spacelab-3	1985.42	6.47	±0.40, ±0.47	3.28	±0.47
ATLAS-1	1992.25	6.89	±0.14, ±0.31	3.53	±0.31
ATLAS-2	1993.33	7.05	±0.11, ±0.30	3.67	±0.31
ATLAS-3	1994.92	7.07	±0.08, ±0.29	3.65	±0.30
ACE	2004.33	7.14	±0.05, ±0.23	3.65	±0.29

[a]ATMOS values are taken from Table 3 of *Michelsen et al.* [2000].

[b]The fractional year has been determined from the year and month of the majority of observations.

[c]1σ PW states the precision followed by the estimated accuracy on PW from each mission.

[d]1σ $[H_2O]_e$ states the estimated accuracy on $[H_2O]_e$ from each mission.
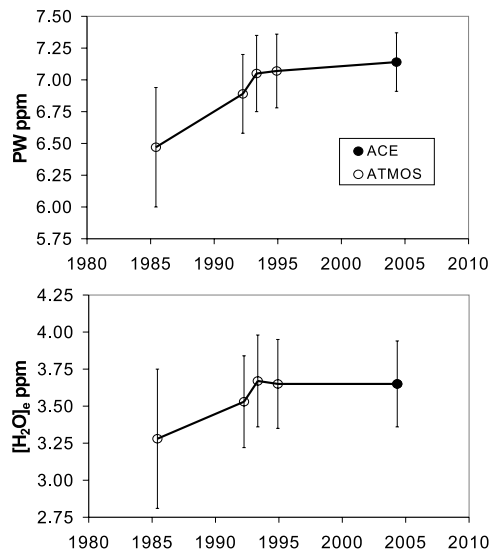
Figure 3. PW and $[H_2O]_e$ from 1985–2004 based on ATMOS and ACE-FTS measurements. The error bars represent the estimated one sigma accuracy on the ATMOS and ACE measurements. A more detailed error analysis for ACE H_2O and CH_4 will be done in the future.

combinations of $[CH_4]_e$ and β values as shown in Table 1. Despite having the highest uncertainty, we consider $[H_2O]_e = 3.65 \pm 0.29$ ppm from the fit and measured $[CH_4]_e$ to be the best value.

4. Discussion and Conclusions

[13] As mentioned in the introduction, many considerations must be taken into account when creating a time series between different instruments, however, we believe that the ATMOS and ACE-FTS instruments, measurement techniques, and retrievals are similar enough to create a time series using ATMOS version 3 data and early ACE-FTS data. By analysis of our data based on the method used for ATMOS data by *Michelsen et al.* [2000], we obtain PW = 7.14 ± 0.23 ppm and $[H_2O]_e = 3.65 \pm 0.29$ ppm from spring 2004 ACE-FTS measurements. In the ATMOS work, both the slope and intercept of the correlation plot were first determined from the fit, followed by redetermination of the intercept with the slope fixed at -2. PW was taken as the intercept with the slope constrained, and $[H_2O]_e$ was calculated based on this value. In our work, we chose not to constrain the slope because we believe that it is reasonable for it to differ slightly from -2. Regardless, our slope of -2.02 was very close to -2, so we directly compare our values to those from ATMOS (see Table 2). This indicates a very small change in PW and no change in $[H_2O]_e$ between the last ATMOS measurements in 1994 and the ACE-FTS measurements in 2004. Thus we conclude that the increase in PW of 0.065 ± 0.008 ppm/yr and the increase in $[H_2O]_e$ of 0.041 ± 0.007 ppm/yr reported by *Michelsen et al.* [2000] for the period of 1985–1994 have not continued (see Figure 3).

[14] The cessation of the $\sim$50 year increase in stratospheric water observed here is consistent with other recent measurements of stratospheric water. For example,

HALOE (The Halogen Occultation Experiment) measurements at 40 km averaged between 50°S and 50°N [*Nedoluha et al.*, 2003] indicate an increase in PW from 1992–1995, a slight decrease from 1996–1999 and a slight increase from 1999–2002. They found that after the greater than 2%/year increase in $[H_2O]$ from 1991–1995, there was little change in $[H_2O]$ from 1996–2002, such that the total increase from 1991–2002 (40–50 km altitude) was slightly less than 1%/year and the increase in PW was only about 0.5%/year [*Nedoluha et al.*, 2003]. More recent HALOE work [*Randel et al.*, 2004] confirms this result. *Considine et al.* [2001] suggest that a fraction of the increase in $[H_2O]$ may be a result of the eruption of Mt. Pinatubo, but the eruption was probably not the sole cause of the observed changes. One can infer from our results that the cessation of the rapid increase in PW is a result of the cessation of the increase in $[H_2O]_e$. However, at the present time, we refrain from making any prediction regarding future stratospheric water vapor levels or trends, and emphasize that further measurements and a better understanding of processes near the TTL are needed to determine whether or not stratospheric water will increase in the coming years.

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