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Trend of lower stratospheric methane (CH_4) from atmospheric chemistry experiment (ACE) and atmospheric trace molecule spectroscopy (ATMOS) measurements

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ABSTRACT

The long-term trend of methane (CH_4) in the lower stratosphere has been estimated for the 1985–2008 time period by combining spaceborne solar occultation measurements recorded with high spectral resolution Fourier transform spectrometers (FTSs). Volume mixing ratio (VMR) FTS measurements from the ATMOS (atmospheric trace molecule spectroscopy) FTS covering 120–10 hPa (~16–30 km altitude) at 25°N–35°N latitude from 1985 and 1994 have been combined with Atmospheric Chemistry Experiment (ACE) SCISAT-1 FTS measurements covering the same latitude and pressure range from 2004 to 2008. The CH_4 trend was estimated by referencing the VMRs to those measured for the long-lived constituent N_2O to account for the dynamic history of the sampled airmasses. The combined measurement set shows that the VMR increase measured by ATMOS has been replaced by a leveling off during the ACE measurement time period. Our conclusion is consistent with both remote sensing and *in situ* measurements of the CH_4 trend obtained over the same time span.

1. Introduction

Atmospheric methane (CH_4) is the second most important anthropogenic greenhouse gas with a radiative forcing half that of carbon dioxide (CO_2) [1]. Both natural (e.g. wetlands, termites, oceans, hydrates) and anthropogenic (e.g., rice paddies, gas extraction leaks, domestic heating, ruminants, biomass burning, landfills) sources contribute to total CH_4 emissions [1–3]. Atmospheric methane contributes about 20% of the increased direct radiative forcing by greenhouse gases compared with preindustrial times [2–5] with an increase in the total abundance of a factor of 2.5 since the pre-industrial era [6]. Observations of its abundance and long-term trend have been obtained with a variety of techniques, including infrared remote sensing (e.g. [7–11]). However, since the early 1990s its abundance has varied some 10 ppbv (1 ppbv = 10^{-9} per unit volume) with no clear quantitative explanation for this variability and the processes governing its trend, limiting

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confidence in potential methods for CH_4 emission controls [12,13]. Recently, renewed growth starting near the beginning of 2007 was reported from all advanced global atmospheric gases (AGAGE) and Commonwealth Scientific and Industrial Research Organization (CSIRO) surface station networks [14].

Surface emissions of methane are transported to higher altitudes where they can be measured by remote sensing techniques, for example high resolution solar occultation Fourier transform spectrometers (FTSs). High precision solar occultation measurements were first obtained from the US Space Shuttle during missions in 1985, 1992, 1993, and 1994 [15,16]. More recently, the Atmospheric Chemistry Experiment (ACE) solar occultation FTS was launched into a 74° inclined orbit on 12 August 2003 and has been recording measurements [17] since its science operations phase began on 21 February 2004 [18].

An important geographic measurement overlap occurs near 30°N latitude during the ATMOS 1985 (Spacelab 3), ATMOS 1994 (ATLAS 3), and ACE missions. Previously we reported trends of HF, HCl, CCl_2F_2, CCl_3F, $CHClF_2$, and SF_6 in the lower stratosphere from comparison of those measurement data sets by referencing the measured volume mixing ratios (VMRs) at 100–10 hPa (16–30 km) to those of the long-lived constituent N_2O to account for variations in the dynamic history of the sample air masses [19]. The purpose of this study is to apply a similar procedure to the analysis of CH_4 by combining ATMOS 1985 and 1994 measurements with ACE measurements from 2004 to 2008.

2. ATMOS/ACE CH_4 trend analysis

Fig. 1 illustrates ACE version 2.2 measured VMRs of CH_4 (upper left panel) and N_2O (lower left panel) for latitudes of 25°N–35°N from 2004–2008 vs. pressure between 120 and 10 hPa. Profiles with N_2O VMRs above 320 ppbv and CH_4 VMRs above 2000 ppbv have been deleted. The vertical distributions of both constituents are consistent with the location of sources at the ground and sinks at higher altitudes. The lifetime of CH_4 is about 8–9 years with the dominant CH_4 loss

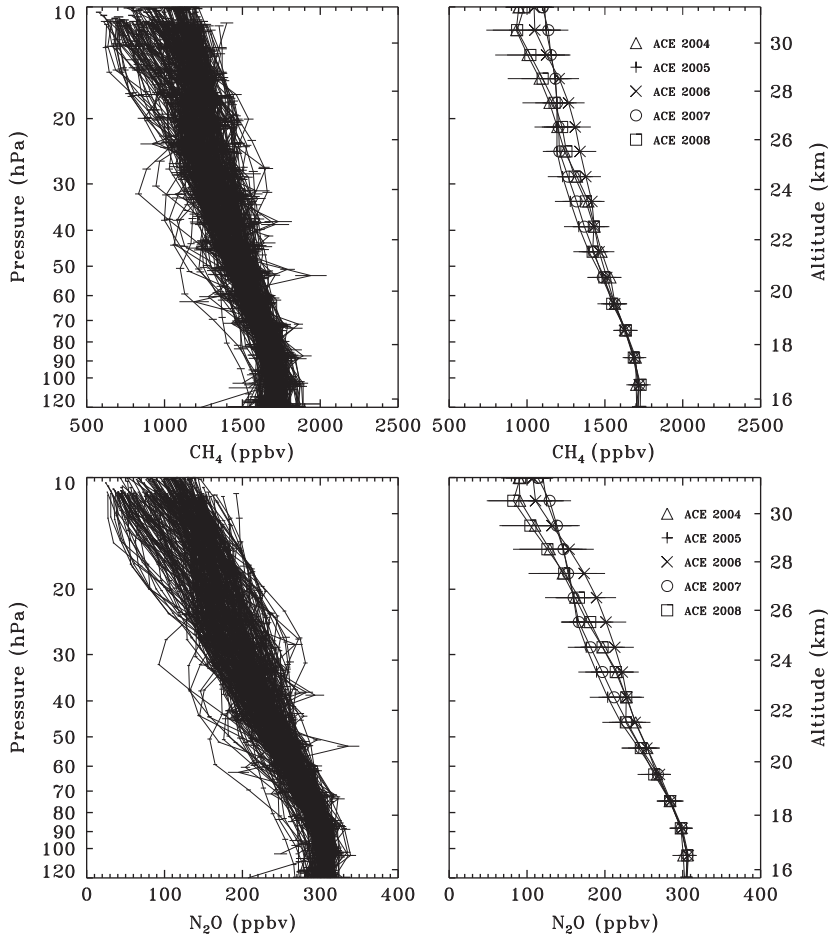

Fig. 1. ACE version 2.2 CH_4 (upper left panel) and N_2O (lower left panel) vs. pressure at 120–10 hPa and 25°N–35°N latitude for 2004–2008. The two right panels show the averaged results for the same latitude and pressure range [for each of the 5 years of ACE measurements of CH_4 (upper right) and N_2O (lower right)]. Different symbols are used to identify the measurements for each year, and the corresponding standard deviations are represented by horizontal bars. Approximate altitude is shown on both the upper and lower right vertical axis.

pathway, reaction with the hydroxyl radical (OH) in the troposphere [11]. The two right panels show the averaged results for the same latitude and pressure range for each of the 5 years of ACE measurements of CH_4 (upper right) and N_2O (lower right). Different symbols are used to identify the measurements for each year, and the corresponding standard deviations are represented by horizontal bars. Previously we assumed a linear N_2O VMR growth rate based on surface sampling measurements from the Climate Monitoring and Diagnostics Laboratory (CMDL) surface stations in the northern and southern hemispheres [19]. We adopted the same approach here and again assume an N_2O increase rate measured at the surface. The trend was derived from a fit to monthly mean surface sampling measurements at Niwot Ridge, Colorado (40.0°N, 105.5°W, 3013 m altitude) obtained between 1977 and August 2008. The time series was obtained by gas chromatography [10] with a best-fit to the full time series assuming a linear rate of change as a function of time correspond to an increase rate of $0.249 \pm 0.003\%$ yr^{-1}. The time series is well fitted and has a 1 sigma uncertainty of 0.00915 ppbv. We assumed the same percent rate of increase in the stratosphere and a 4 year time delay to account for the transport of surface air to the lower stratosphere based on model predictions for 38° latitude [20]. The corrected N_2O VMRs are noted hereafter by N_2O^*. Although stratospheric N_2O VMRs were obtained from ATMOS version 3 retrievals [21] and ACE version 2.2 retrievals [22] show an increase as a function of time, those results are not sufficiently precise and consistent to allow an accurate determination of the N_2O trend in the lower stratosphere.

3. Results, comparison with previous measurements, and uncertainties

Methane (CH_4) VMRs were binned by 5 ppbv N_2O^* increments to obtain averages and standard deviations for similar N_2O^* intervals. The combined ATMOS and ACE lower stratospheric measurements of CH_4 and N_2O^* analyzed in this manner over 25°N–35°N latitude and 120–10 hPa pressure range are depicted in the upper panel of Fig. 2. As can be seen in this panel, the total range of N_2O^* bins for each of the 7 missions (75–315 ppbv range) is very similar. Seven different symbols were used to characterize ATMOS Spacelab 3 1985 and 1994 shuttle flight version 3 [21] and version 2.2 results from ACE [22] measurements during 2004, 2005, 2006, 2007, and 2008 [22]. Each symbol and the accompanying vertical bar represents the averages and standard deviations of CH_4 VMR for each year and for each N_2O^* bin.

The lower panel in Fig. 2 illustrates the best-fit (black curve) to the combined time series of averaged 120–10 hPa CH_4 VMRs from the 7 time periods using Eq. (1) with open triangles and the corresponding vertical bars showing the

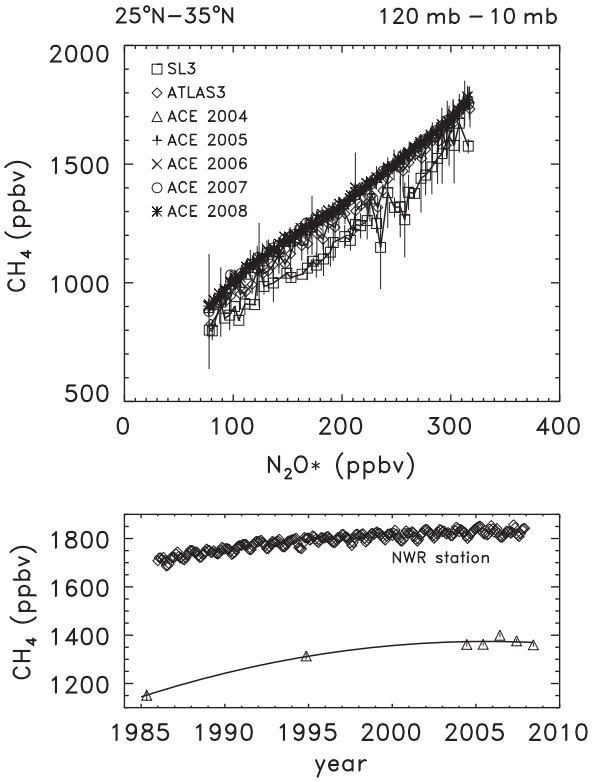

Fig. 2. Upper panel: Measurements of CH_4 volume mixing ratio (VMR) at 25°N–35°N latitude and 120–10 hPa vs. N_2O^* from the combined ATMOS and ACE time series. Lower panel: temporal evolution of the CH_4 trend (black curve) derived from a fit to the combined ATMOS 1985 and 1994 and the ACE for 2004–2008 time series with Eq. (1). An open triangle displays the mean VMR and a vertical bar indicates the standard deviation for each measurement year. Monthly mean measurements from the Niwot Ridge (NWR) surface station are shown as open diamonds.

measurements and the standard deviations for each year of the time series. Monthly mean surface measurements from the Niwot Ridge station (open triangles) are presented for comparison. We adopted the empirical polynomial expression assumed previously [19] to determine the time dependence of V from fits to the 1985 and 1994 ATMOS and the 2004–2008 ACE VMRs.

$$V = a_0 + a_1(t - t_0) + a_2(t - t_0)^2 \quad (1)$$

In Eq. (1), t is time and t_0 is the time of the measurements from the first ATMOS mission. The coefficients a_0, a_1, and a_2 and their statistical uncertainties were determined from a least-squares fit to average VMRs from each measurement set with the number of occultations from each year, the best-fit obtained with Eq. (1), and the number of occultations for each year reported in Table 1. The average measured VMR, the standard deviation, the corresponding best-fit CH_4 VMR, the measured minus calculated difference, and the number of occultations are reported. Table 2 presents the calculation of the rate of change and uncertainty in the CH_4 VMR and its uncertainty derived from the best-fit to the average VMRs from time series. The summary of the results is provided for each year. As can be seen from the tables, the rate of change in the lower stratospheric CH_4 over the time span is small, though the trend analysis shows that the statistically significant increase measured during the ATMOS time period changed to a trend that is not statistically significant during the time span measured by the ACE instrument. Although the best-fit for the trend reported in Table 2 from the combined time series indicates a maximum in 2005, the uncertainty is too large to infer a statistically-significant trend for the ACE measurement time period. As shown in Table 1, fewer occultations were obtained by ATMOS in 1985 and 1994 as compared to those from each year of the ACE time series (2004–2008). The increasing lower stratospheric VMRs measured in 1985 and 1994 have been replaced by no statistically-significant trend in the lower stratospheric CH_4 VMR.

Retrievals of CH_4 from Jungfraujoch [7,8], Kitt Peak [10], and ACE [17,21] assumed HITRAN 2004 [23] parameters, though not the same microwindow sets. The ATMOS version 3 retrievals [20] assumed different spectroscopic databases and microwindow sets [24]. Those differences and differences in retrieval techniques introduce biases that are difficult to quantify precisely. A previously estimate of 3% was reported [10]. Kitt Peak (31.9°N latitude, 111.6°W longitude, 2.09 km altitude) solar absorption spectra CH_4 retrievals were compared with monthly gas chromatography measurements at the CMDL Niwot Ridge station for the overlapping October 1983 to December 2003 time period [10]. Both random and systematic errors of retrieved 2.09–10 km mean CH_4 VMRs from the Kitt Peak IR solar spectra were reported. The ratio of the Kitt Peak to the CMDL CH_4 monthly mean VMRs equaled 1.038 ± 0.034. Total random error was estimated as 3%. The estimated uncertainty of 2% in the CH_4 spectroscopic parameters is within the accuracy of 5% estimated for ATMOS version 3 CH_4 results [21]. Although significant updates have been made to the CH_4 parameters that are in the HITRAN 2004 database [23], those changes have only minor impact on the trend determination because of its long time span. Additionally, there is uncertainty in the time delay for transport of surface air to the lower stratosphere [20,25]. A sensitivity test was performed, and it indicates an offset of 6 months with respect to the assumed 4 year time delay for transport from the surface air to the lower stratosphere introduces a bias in the CH_4 trend of 0.01(% yr^{-1}) in the trend reported in Table 2. Based on these considerations, we roughly estimate a total systematic CH_4 error uncertainty of 6%.

Measurements of total columns of CH_4 from the Jungfraujoch station (46.5°N, 8.0°E. 3.578 km altitude) since 1951 provide the longest infrared spectroscopic record of changes in atmospheric composition [8,9]. Results from that station confirm that the rapid growth from the beginning of the time series in 1951 extending to 1998 has been replaced by a

Table 1
Measured and best-fit CH_4 VMRs (25°N–35°N) latitude at 120–10 hPa for the April 1985–March 2008 time period.

Year	Measured CH_4 VMR (ppbv)	Calculated CH_4 (ppbv)	Difference (ppbv)	NOCC
1985	1151.2 ± 24.0	1152.02	−0.79	12
1994	1314.3 ± 14.8	1310.92	3.34	17
2004	1359.6 ± 8.6	1370.42	−10.87	66
2005	1354.9 ± 5.7	1370.82	−15.90	96
2006	1399.1 ± 8.4	1370.15	28.96	46
2007	1374.4 ± 8.5	1368.38	5.99	41
2008	1354.8 ± 8.5	1365.52	−10.72	61

Notes: Error bars show uncertainties calculated as $\sqrt{(n+1)}$, where the standard deviation (STD) is divided by the square root of the number of occultations n+1 and NOCC is the number of retrieved occultations for ATMOS or ACE. 1 ppbv = 10^{-9} per unit volume. Calculated VMRs in column 2 are obtained from a fit to the time series with Eq. (1).

Table 2
Rates of change and uncertainties (% yr^{-1}) from ATMOS and ACE Lower Stratospheric CH_4 VMRs near 30°N latitude.

1985	1994	2004	2005	2006	2007	2008
1.90 ± 0.34	0.87 ± 0.38	0.07 ± 0.54	-0.01 ± 0.57	-0.09 ± 0.57	-0.17 ± 0.60	-0.25 ± 0.63

Notes: Trends and corresponding uncertainties are computed for each year by taking the derivative of V from Eq. (1) and are based on binning the N_2O^* data in $5N_2O^*$ increments.

leveling off of the total column since 2002 with no significant trend through 2007, the end of the current time series (see Fig. 6 from the Ref. [9]).

4. Summary and conclusions

The long-term trend in the lower stratospheric CH_4 VMR has been derived for the 1985–2008 time period by combining solar occultation measurements from ATMOS 1985 and 1994 shuttle flights version 3 retrievals [21] with SCISAT-1 satellite [17] version 2.2 measurements from 2004 to 2008 [22]. The analysis approach follows that adopted in an earlier study [19] by comparing measurements near 30°N latitude with corresponding measurements of N_2O, taking into account its VMR increase as a function of time assuming the same increase rate in percent and 4 years as the time delay for transport of surface air to the lower stratosphere [20]. The selected time span avoids obvious climate anomalous time periods such as the post Mt. Pinatubo-eruption period and strong El Niño/Southern Oscillation (ENSO) events, though a moderate ENSO event occurred in 2006 and 2007 [26]. Measurements from ACE since 2004 show the increase has been replaced by a nearly constant lower stratospheric VMR of ~1370 ppbv during 2004–2008 with no statistically significant change in abundance. Surface measurements covering the same time span at Niwot Ridge also show the early rise in the CH_4 VMR has been replaced by a nearly constant VMR by the end of the time span.

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