



## Long-term changes of methane and hydrogen in the stratosphere in the period 1978–2003 and their impact on the abundance of stratospheric water vapor

S. Rohs,<sup>1</sup> C. Schiller,<sup>1</sup> M. Riese,<sup>1</sup> A. Engel,<sup>2</sup> U. Schmidt,<sup>2</sup> T. Wetter,<sup>2</sup> I. Levin,<sup>3</sup> T. Nakazawa,<sup>4</sup> and S. Aoki<sup>4</sup>

Received 10 November 2005; revised 24 January 2006; accepted 20 March 2006; published 28 July 2006.

[1] The long-term changes of the stratospheric mixing ratio of CH<sub>4</sub> over the period of 1978–2003 are derived from balloon-borne data of H<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O. The data were obtained by collecting whole air samples and subsequent gas chromatographic analyses. To eliminate the short-term variability attributed to dynamical processes, the N<sub>2</sub>O mixing ratio is used as a proxy for altitude. A correlation analysis for the individual years is applied and the CH<sub>4</sub> mixing ratios are interpolated to four different levels of N<sub>2</sub>O, corresponding to altitudes of approximately 17, 23, 26 and 30 km at midlatitudes. For the investigated period of 1978 to 2003 we find increases at the four levels of 207 ± 32 ppb, 159 ± 21 ppb, 140 ± 34 ppb and 111 ± 60 ppb, respectively. The CH<sub>4</sub> trend has slowed down in recent years and is best fitted by a second-order polynomial. The increase of CH<sub>4</sub> can account for only 25–34% of the increase in stratospheric H<sub>2</sub>O of 1%/yr over the last decades as derived from previous studies. The simultaneously measured time series of stratospheric H<sub>2</sub> mixing ratios shows that the contribution of stratospheric H<sub>2</sub> to the H<sub>2</sub>O trend in the period 1988–2003 is minor.

**Citation:** Rohs, S., C. Schiller, M. Riese, A. Engel, U. Schmidt, T. Wetter, I. Levin, T. Nakazawa, and S. Aoki (2006), Long-term changes of methane and hydrogen in the stratosphere in the period 1978–2003 and their impact on the abundance of stratospheric water vapor, *J. Geophys. Res.*, *111*, D14315, doi:10.1029/2005JD006877.

### 1. Introduction

[2] The major hydrogen-containing species in the stratosphere are CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub>. They play a central role in stratospheric chemistry, being the primary precursor of HOx radicals. These radicals participate in the heterogeneous reactions that destroy stratospheric ozone. However, methane also impacts the ozone loss rate as it reacts with atomic chlorine atoms to form HCl, the major reservoir gas via the reaction: CH<sub>4</sub> + Cl ⇒ HCl + CH<sub>3</sub> [*World Meteorological Organization*, 1998]. Further, stratospheric H<sub>2</sub>O is the major condensate in polar stratospheric clouds (PSCs), which are prerequisites for chlorine activation and ozone destruction during ozone hole events in the polar vortex [*Solomon*, 1999]. As a consequence of increasing stratospheric water vapor, the critical temperature below which PSCs can exist, rises. There are indications that increasing H<sub>2</sub>O (and CH<sub>4</sub> itself) alters the radiation budget of the atmosphere resulting in a cooler stratosphere [*Forster and Shine*, 1999, 2002;

*Oinas et al.*, 2001]. Both effects could lead to a more frequent formation of PSCs and, thus, enhanced destruction of O<sub>3</sub> [*Shindell*, 2001]. As a feedback, the increment of stratospheric water vapor is believed to contribute to global warming. From these findings it becomes clear, that the mixing ratios and trends of CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub> in the stratosphere are of great relevance for atmospheric chemistry and climate and have to be determined very precisely.

[3] In the lower stratosphere H<sub>2</sub>O mixing ratios are very low because of dehydration processes in air masses entering the stratosphere when passing through the cold tropical tropopause region. In the middle stratosphere, the mixing ratios of CH<sub>4</sub> and H<sub>2</sub>O are tightly coupled, because the photochemical oxidation of each molecule of CH<sub>4</sub> produces approximately two molecules of H<sub>2</sub>O. A model study by *Le Texier et al.* [1988] indicates that deviations from this ratio are possible. *Engel et al.* [1996] derived a ratio of 1.81 ± 0.21 from near simultaneous observations of CH<sub>4</sub> and H<sub>2</sub>O. From the correlation of CH<sub>4</sub>, H<sub>2</sub>O and H<sub>2</sub> *Zöger et al.* [1999] calculated a ratio of 1.975 ± 0.030. Nevertheless, as a first approximation the quantity H<sub>2</sub>O + 2 CH<sub>4</sub> is conserved, and CH<sub>4</sub> oxidation is the primary reason for the increase of H<sub>2</sub>O with altitude from its entry value of approximately 3.6 ppm at the tropopause [e.g., *Engel et al.*, 1996] to more than 7.0 ppm in the upper stratosphere.

[4] Since 1981, stratospheric water vapor, measured with balloon-borne hygrometers over Boulder, Colorado, has shown a statistically significant trend with an average

<sup>1</sup>ICG-I: Stratosphäre, Forschungszentrum Jülich, Jülich, Germany.

<sup>2</sup>Institut für Atmosphäre und Umwelt, J. W. Goethe Universität, Frankfurt, Germany.

<sup>3</sup>Institut für Umweltphysik, Universität Heidelberg, Heidelberg, Germany.

<sup>4</sup>Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai, Japan.

increase between 1.0% and 1.3% per year at levels between 16 and 28 km [Oltmans *et al.*, 2000]. This trend was confirmed by observations compiled in the SPARC Assessment of Upper Tropospheric and Stratospheric Water Vapor [Kley *et al.*, 2000] and more recent investigations [e.g., Rosenlof *et al.*, 2001].

[5] The reasons for this trend are still not understood completely. A warming of the tropical tropopause could be a plausible explanation, however, the average temperature in this region is observed to decrease [Zhou *et al.*, 2001]. Transport studies of Rosenlof [2002] provide an indication that an increase in the tropical upwelling in the season, when water vapor values are highest, has occurred between 1997 and 2001. This increase could possibly contribute to the observed H<sub>2</sub>O trend.

[6] Rosenlof *et al.* [2001] derived that the increase in tropospheric CH<sub>4</sub> (see below) could at maximum cause 50% of the H<sub>2</sub>O trend, provided that the additional CH<sub>4</sub> gets oxidized completely. If, however, the additional CH<sub>4</sub> from the troposphere is not oxidized completely but instead results in a stratospheric CH<sub>4</sub> increase, then the contribution of CH<sub>4</sub> to the stratospheric H<sub>2</sub>O trend would even be less. Therefore, for a first step toward a reasonable explanation of the water vapor trend, it is important to estimate the contribution of CH<sub>4</sub> and H<sub>2</sub> oxidation as exact as possible; that is, it is necessary to know the tropospheric and stratospheric CH<sub>4</sub> and H<sub>2</sub> trends.

[7] CH<sub>4</sub> is emitted to the atmosphere by natural sources, for example wetlands, but about 60% of the emissions are due to anthropogenic activities such as fossil fuel production and distribution, cultivation of rice, stock farming and landfills [Intergovernmental Panel on Climate Change (IPCC), 2001]. During the last decades the globally averaged tropospheric CH<sub>4</sub> concentration has increased significantly. Blake and Rowland [1988] found a CH<sub>4</sub> increase ranging from 1520 ppb in 1978 to 1684 ppb in 1987, according to an increment of  $16 \pm 1$  ppb per year. Similar results are reported by Khalil and Rasmussen [1990], who calculated an average rate of increase of  $16.6 \pm 0.4$  ppb per year in the period 1980–1988. Since 1984 the globally averaged tropospheric CH<sub>4</sub> concentration is monitored by the globally distributed NOAA/CMDL Climate Monitoring and Diagnostic Laboratory network. During this period global mean tropospheric CH<sub>4</sub> mixing ratios have increased from 1625 ppb in 1984 to 1751 ppb in 2002 with a slowdown in CH<sub>4</sub> growth rate being observed. This could be explained by stagnant CH<sub>4</sub> emissions and lifetime in a system approaching steady state [Dlugokencky *et al.*, 2001, 2003]. Most studies seeking to explain the decline in the CH<sub>4</sub> increase rate focus on only one or a few processes. A good overview of the various studies and a 3-D model analysis of the slowdown in the methane growth is given by Wang *et al.* [2004]. According to them the slowdown is attributed to a combination of slower growth of sources like decline in the global cattle production, changes in rice cultivation, decreases due to the economic downturn of the former Soviet Union and an increased methane sink due to increased OH because of the stratospheric ozone depletion.

[8] The tropospheric trend is well recorded. However, the long-term temporal variation of CH<sub>4</sub> in the stratosphere is less well characterized and subject of the analysis presented

in this paper. Not much is known about the stratospheric long-term trends, because 20 years ago only a few appropriate instruments for the detection of methane in the stratosphere existed. From 1991 to 2005 the Halogen Occultation Experiment HALOE delivered data of stratospheric CH<sub>4</sub> and H<sub>2</sub>O. These data show slightly negative CH<sub>4</sub> trends in the upper stratosphere and a positive trend in the middle stratosphere (100–22 hPa) [Randel *et al.*, 1999].

[9] We also analyze stratospheric H<sub>2</sub>, which originates mainly from oxidation of CH<sub>4</sub> (and from transport out of the troposphere) and is removed by OH initiated oxidation to H<sub>2</sub>O. The mixing ratio of H<sub>2</sub> does not change significantly with altitude because the production and loss rates of H<sub>2</sub> are nearly balanced [Le Texier *et al.*, 1988; Dessler *et al.*, 1994; Hurst *et al.*, 1999]. Reports about the tropospheric H<sub>2</sub> trend are inconsistent with one another. During 1991–1996 data from the NOAA/CMDL network show a decline of the tropospheric H<sub>2</sub> mixing ratio of  $-2.3 \pm 0.1$  ppb/yr [Novelli *et al.*, 1999] whereas the data from the CSIRO Commonwealth Scientific and Industrial Organization result in a global mean growth rate of tropospheric H<sub>2</sub> of +1.4 ppb/yr during 1992–1999 [Langenfelds *et al.*, 2002].

[10] In this paper we use the longest data set of high-precision balloon measurements available for a comprehensive analysis of the stratospheric CH<sub>4</sub> and H<sub>2</sub> trends [Engel and Schmidt, 1998; Engel *et al.*, 2002]. The results will be used for an assessment of the contribution of these trace gases to the unexplained positive trend in stratospheric H<sub>2</sub>O.

## 2. Evolution of Stratospheric CH<sub>4</sub> and H<sub>2</sub> Trends: Data and Methods

[11] From 1978 to 2003 a series of stratospheric observations has been obtained by means of three neon-cooled, balloon-borne cryogenic whole air samplers. The data from two flights (1978 and 1979) stem from the sampler CRYO MPI [Fabian *et al.*, 1981]. Since 1982 data from 32 flights of the cryosampler BONBON form the main database of this study. BONBON is operated in cooperation between the University of Frankfurt and the Institute for Stratospheric Research of the Research Centre Jülich. The measurements were performed at mid latitudes in Aire sur l'Adour and Gap in France (44°N) and since 1987 also at high latitudes in Kiruna, Sweden (68°N). During a flight, 15 air samples were collected in the altitude range between 10 and 35 km by opening and closing evacuated stainless steel cylinders immersed in liquid neon. Subsequently the content of H<sub>2</sub>, N<sub>2</sub>O and other long-lived trace gases was analyzed by gas chromatography at the Institute for Atmosphere and Environment of the University of Frankfurt. CH<sub>4</sub> was analyzed at the Institut für Umweltphysik, University of Heidelberg. All data can be traced to long-term standard gases, which were carefully calibrated and intercompared. The details of the instruments and intercomparisons with other instruments are described elsewhere [Schmidt *et al.*, 1987; Engel *et al.*, 1997; Levin *et al.*, 1999]. For the precisions of the single measurements ( $1\sigma$ ) see Table 1.

[12] Additionally, data from 8 flights of the balloon-borne cryogenic sampler SAKURA, which was launched from Sanriku Balloon Center of the Institute of Space and Astronautical Science, Japan (39°N), are used. The collection of air samples with SAKURA over Japan, initiated in

**Table 1.** Precisions of the Single Measurements ( $1\sigma$ )

	N <sub>2</sub> O	CH <sub>4</sub>	H <sub>2</sub>
CRYO MPI (1978–1981)	15 ppb or 5%	10 ppb or 2.0%	10 ppb or 2.0%
BONBON (1982–1996)	15 ppb or 5%	10 ppb or 2.0%	10 ppb or 2.0%
BONBON (1997–1999)	5.0 ppb or 2%	3.0 ppb or 0.2%	10 ppb or 2.0%
BONBON (since 2000)	2.0 ppb or 0.5%	3.0 ppb or 0.2%	10 ppb or 2.0%
SAKURA (since 1991)	1.0 ppb	1.5 ppb	...

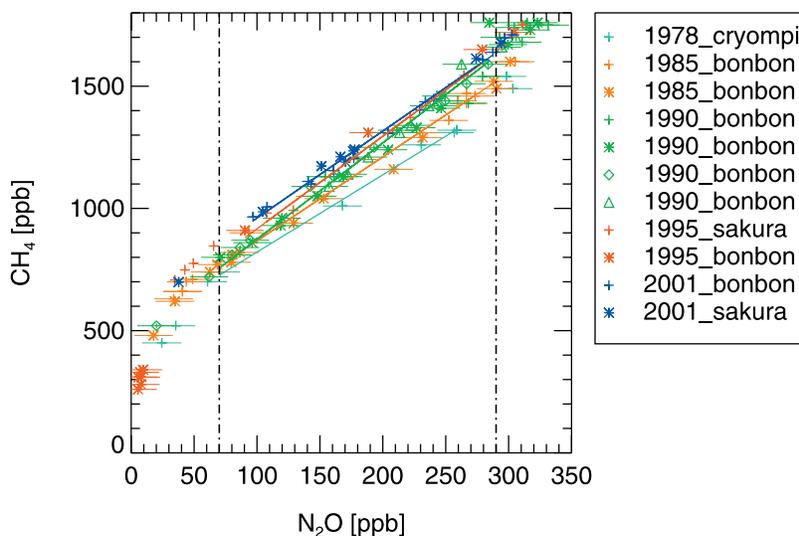
1985, has been made almost once a year for measurements of various stratospheric trace gases [Nakazawa *et al.*, 1995, 2002], and the CH<sub>4</sub> and N<sub>2</sub>O concentration data since 1991 are available for this study. The air samples of about 25 L<sub>STP</sub> were collected into 760 mL stainless steel samples tubes cooled by liquid helium at 11 different altitudes in the stratosphere. The CH<sub>4</sub> and N<sub>2</sub>O concentrations of the sample air were analyzed against gravimetrically prepared standard gases at Tohoku University, using gas chromatographs equipped with the respective detectors of FID and ECD. Details of the CH<sub>4</sub> and N<sub>2</sub>O concentration analyses have been described by Aoki *et al.* [1992] and Ishijima *et al.* [2001].

[13] For the calculation of the long-term variations of CH<sub>4</sub> the data from all flights accomplished during one year were combined. Then, a correlation analysis with N<sub>2</sub>O as vertical coordinate was performed. The mixing ratio of CH<sub>4</sub> in the stratosphere decreases rapidly with altitude. Using the geometric altitude or potential temperature as a vertical coordinate, the CH<sub>4</sub> mixing ratio at a defined altitude depends on latitude and season. Moreover, the profiles show strong short-term variability caused by stratospheric

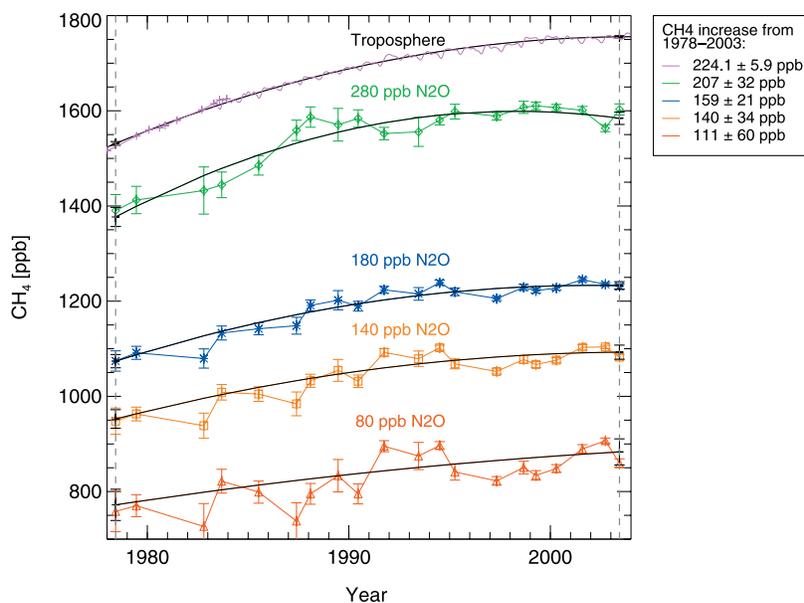
dynamics. This variability impedes the determination of the long-term temporal variation of CH<sub>4</sub>. The problem can be solved, when the mixing ratio of the long-lived tracer N<sub>2</sub>O is used as a proxy vertical coordinate [Engel and Schmidt, 1998]. In the stratosphere, the only significant loss process for N<sub>2</sub>O is photochemical decomposition. The stratospheric lifetime of both, N<sub>2</sub>O and CH<sub>4</sub> are approximately 120 years [IPCC, 2001]. Therefore the vertical profiles of N<sub>2</sub>O comprise similar dynamical structures as those of CH<sub>4</sub>. At each N<sub>2</sub>O level, air masses of comparable dynamical history are assorted [Engel and Schmidt, 1998]. N<sub>2</sub>O has only a small tropospheric trend. To account for this trend, the stratospheric N<sub>2</sub>O values are normalized to the year 1993, assuming that the tropospheric increase of 0.25% per year [IPCC, 2001] propagates into the stratosphere. This is a rough estimate, but should be expedient for the further analysis. The possible systematic deviation of the calculated stratospheric CH<sub>4</sub> trends due to this normalization will be discussed later.

[14] For N<sub>2</sub>O values between 70 and 290 ppb, a linear correlation between N<sub>2</sub>O and CH<sub>4</sub> is observed. In order to weight the data points of the different instruments equally, we use the worst case estimate of the error of all instruments for each year. The correlation in this range yields linear fits with an average squared correlation coefficient of  $r^2 = 0.98$ . Single correlations for five different years are shown in Figure 1.

[15] In individual cases, the data points from the flights in one year might be better grouped along more than one line. Such a separation can occur for two flights of the same instrument or for flights of two different instruments. For example in the year 2001, the CH<sub>4</sub> mixing ratio at the 80 ppb N<sub>2</sub>O level is increased slightly from  $886 \pm 11$  ppb (excluding the SAKURA data) to  $889 \pm 9$  ppb (including the SAKURA data). Overall, using both, the data from



**Figure 1.** Correlation plots of CH<sub>4</sub> versus N<sub>2</sub>O observed during 1978–2003. For eliminating variability attributed to short-term dynamical processes and to varying latitudinal and seasonal coverage of the measurements, N<sub>2</sub>O is used as a vertical coordinate. This filtering samples air of approximately the same average stratospheric residence time. The N<sub>2</sub>O values are normalized to the year 1993, assuming an increase of 0.25% per year and the linear regression is limited to a range from 70 to 290 ppb N<sub>2</sub>O (dashed vertical lines), where no deviations from the linear relationship are observed.



**Figure 2.** Time series of CRYO MPI, BONBON and SAKURA CH<sub>4</sub> mixing ratios for the lower stratosphere over the period 1978–2003. The globally averaged tropospheric CH<sub>4</sub> measurements are from the NOAA CMDL cooperative air sampling network (E. J. Dlugokencky, personal communication, 2005) and prior to 1984 from *Blake and Rowland* [1986]. The mixing ratios of CH<sub>4</sub> are interpolated to the levels of 80, 140, 180 and 280 ppb N<sub>2</sub>O. The increases over the observed period, determined by using second-order polynomial fits ( $1\sigma$  uncertainties calculated with the bootstrap method), are annotated in the plot.

SAKURA and from BONBON results in slightly but insignificantly lower CH<sub>4</sub> mixing ratios at 280 ppb N<sub>2</sub>O and in slightly but insignificantly higher CH<sub>4</sub> mixing ratios at 80 ppb N<sub>2</sub>O. The resulting effect for the trend calculation in Chapter 3 is minor. Excluding the 8 flights from SAKURA shifts the calculated trends of CH<sub>4</sub> (see below) by 0.0–0.3% and therefore well within the error ranges calculated below (i.e., 2–7%).

[16] The linear fit method is damping effects as they appeared in situations when abrupt changes of the CH<sub>4</sub> concentration took place, as were observed in the troposphere after the eruption of Mt. Pinatubo in 1991 [*Dentener et al.*, 2003]. Unfortunately, no stratospheric measurements were performed in 1992. Anyhow, in the year 1993 no anomalous deviation of single data points from the fitted regression line can be observed in the lower stratosphere. As an additional test we divided the data into three N<sub>2</sub>O ranges (not shown here) and calculated linear fits for each compartment. Similar results were obtained, although, because of the diminished number of data points in the single bins, with higher fluctuation. This shows that indeed the relationship between N<sub>2</sub>O and CH<sub>4</sub> is close to linear over the range of mixing ratios used in this study.

[17] For the further analysis, four N<sub>2</sub>O levels, i.e., 280, 180, 140 and 80 ppb, corresponding to different stratospheric altitude regions of approximately 17, 23, 26 and 30 km or 90, 35, 20 and 10 hPa at midlatitudes are chosen. Using the functions of the individual linear fits, the CH<sub>4</sub> mixing ratios, which correspond to these N<sub>2</sub>O levels are calculated for each year and provide the data of the time series. The errors of these interpolations are derived from the precisions of the single measurements weighted by the distance to the

barycenter of the correlation fit. The observations used in this study have all been obtained at northern mid and high latitudes. This might lead to a systematic deviation in the calculated trends from the global trends, albeit this error should be diminished because of the use of N<sub>2</sub>O as vertical coordinate. Further uncertainties of the calculated time series result from the limited data basis and will be discussed later.

[18] The mixing ratios of H<sub>2</sub> and N<sub>2</sub>O show no correlation, similarly to the behavior observed between CH<sub>4</sub> and H<sub>2</sub> [*Zöger et al.*, 1999], because in contrast to N<sub>2</sub>O or CH<sub>4</sub>, H<sub>2</sub> does not vary systematically with altitude. For this reason the H<sub>2</sub> data of the whole altitude range from 280 to 80 ppb N<sub>2</sub>O are averaged for each year to derive the time series.

### 3. Results: Stratospheric Changes of CH<sub>4</sub> and H<sub>2</sub>

#### 3.1. CH<sub>4</sub> Trend

[19] The temporal development of the CH<sub>4</sub> mixing ratios for the N<sub>2</sub>O levels of 280, 180, 140 and 80 ppb (approximately 17, 23, 26 and 30 km altitude at mid latitudes) is shown in Figure 2. Because of increasing photochemical decomposition rate, CH<sub>4</sub> mixing ratios decrease with altitude. A positive trend of the CH<sub>4</sub> mixing ratio over the whole observational period is evident for all altitude levels. However, the increase of CH<sub>4</sub> has not been constant but slowed down or even ceased in recent years at all altitudes. As for the tropospheric trend, the beginning of this slowing down cannot be attributed to a specific year or event. Therefore, if the average increase of CH<sub>4</sub> for the whole period is determined by fitting the curve with two succes-

**Table 2.** Calculated CH<sub>4</sub> Increase for Different Time Periods, N<sub>2</sub>O Normalized to 1993, to Account for the N<sub>2</sub>O Trend

N <sub>2</sub> O, ppb	1978/06–2003/06		1980/01–2000/01	
	ppb	Percent	ppb	Percent
Troposphere <sup>a</sup>	224.1 ± 5.9	13.4 ± 0.4	192.0 ± 4.3	11.5 ± 0.3
280 (17 km, 90 hPa)	207 ± 32	13.4 ± 2.1	187 ± 21	12.1 ± 1.4
180 (23 km, 35 hPa)	159 ± 21	13.4 ± 1.8	138 ± 15	11.6 ± 1.3
140 (26 km, 20 hPa)	140 ± 34	13.4 ± 3.3	120 ± 23	11.4 ± 2.2
80 (30 km, 10 hPa)	111 ± 60	13.2 ± 7.1	92 ± 38	10.9 ± 4.6

<sup>a</sup>Referring to *Dlugokencky et al.* [2003] and *Blake and Rowland* [1986].

sive linear regressions, the obtained result is depending on the chosen partitioning date of the two fits.

[20] A more suitable method, which accounts for the long-term slowing in the rate of CH<sub>4</sub> increase, is the fitting of the CH<sub>4</sub> data of the different N<sub>2</sub>O levels by second-order polynomials. This method is applied in the following. The 1  $\sigma$ -errors of these second-order polynomial fits are computed with the bootstrap method, taking into account the errors of the single data points and the variance of the data points around the fitted curve. From these second-order polynomial functions the CH<sub>4</sub> increases for different periods, for example 1978–2003 or 1980–2000 (Table 2) have been calculated.

[21] From 1978 to 2003 at the 280 ppb N<sub>2</sub>O level, i.e., in the lower stratosphere, a mean increase of 207 ± 32 ppb (13.4 ± 2.1%) is observed; at 140 ppb N<sub>2</sub>O the increase is 140 ± 34 ppb (13.4 ± 3.3%) and at 80 ppb N<sub>2</sub>O 111 ± 60 ppb (13.2 ± 7.1%). For the determination of the tropospheric CH<sub>4</sub> increase the annual trends from the globally distributed NOAA/CMDL Climate Monitoring and Diagnostic Laboratory network are used [*Dlugokencky et al.*, 2001, 2003; E. J. Dlugokencky, personal communication, 2005]. Prior to 1984 there are no global CH<sub>4</sub> data from NOAA/CMDL. Therefore, for the years 1978–1983 the mean trend during this period of 18 ± 1 ppb CH<sub>4</sub>/yr [*Blake and Rowland*, 1986] was adopted. By fitting the tropospheric CH<sub>4</sub> data with a second-order polynomial, from 1978/06 to 2003/06 we calculate a tropospheric CH<sub>4</sub> increase of 224.1 ± 5.9 ppb (13.4 ± 0.4%).

[22] Because of the proximity to the troposphere, the CH<sub>4</sub> increase in the lower stratosphere should be similar to the tropospheric increase. This is in accordance with our findings. The tropospheric CH<sub>4</sub> increase over the entire time period corresponds well with our data for the lower stratosphere. Moreover, if we calculate the CH<sub>4</sub> increase from the derived second-order polynomial fit for the two periods 1978/06–1993/06 and 1993/06–2003/06, again, the increases in the troposphere and in the lower stratosphere are in good agreement. In the lower stratosphere the growth rate decreased from 13.9 ± 1.7 ppb/yr (0.9 ± 0.1%/yr) in 1978/06–1993/06 to −0.1 ± 1.9 ppb/yr (−0.0 ± 0.1%/yr) in 1993/06–2003/06. Similarly, the tropospheric growth rate decreased from 12.4 ± 0.3 ppb/yr (0.7 ± 0.0%/yr) in 1978/06–1993/06 to 3.8 ± 0.3 ppb/yr (0.2 ± 0.0%/yr) in the period 1993/06–2003/06.

[23] To detect changes on shorter time periods, the balloon-borne data are too limited because of the low sampling frequency. For example, the 5-year gliding average of the annual growth rate of stratospheric CH<sub>4</sub> shows a

high variability (−15 to + 20 ppb/yr at the 80 ppb N<sub>2</sub>O level). In addition, the derived “trends” in this short time range are highly influenced by variations at both ends of the record.

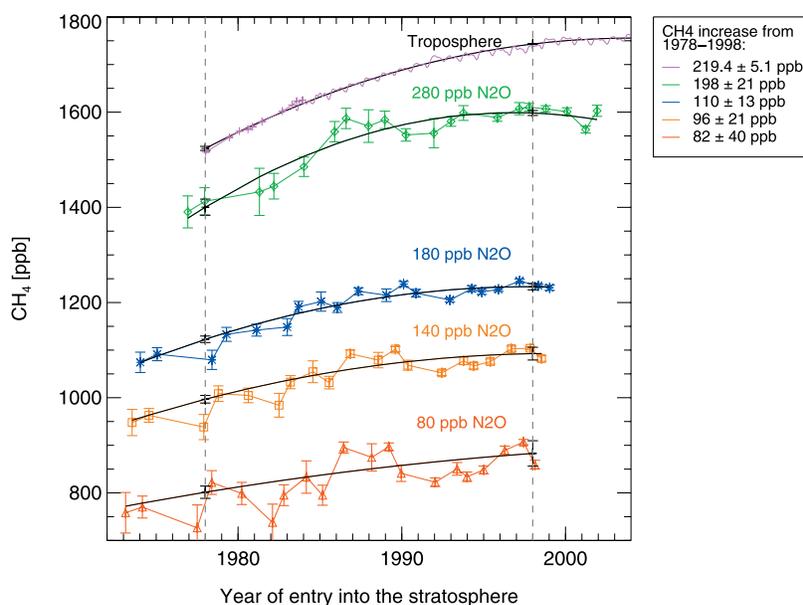
[24] Therefore comparison of our balloon-borne data with short stratospheric data sets is suitable to a limited extent only. The so far longest reported continuous data set for detection of long-term variations of CH<sub>4</sub> in the stratosphere originates from the HALOE instrument on the Upper Atmosphere Research Satellite (UARS) and dates back to 1992. From 1992 to 1997 at 100–22 hPa, a global mean CH<sub>4</sub> increment of 0.86 ± 0.40% per year is found, which remains relatively constant over this altitude range. In the middle stratosphere between 10 and 3 hPa in the Northern hemisphere, negative trends of 0 to −3% per year are observed and in the upper stratosphere (≤3 hPa) HALOE measures decreasing CH<sub>4</sub> abundances (up to −5% CH<sub>4</sub> per year) [*Randel et al.*, 1999].

[25] If we use the second-order polynomial fit for the whole period and calculate with this function the CH<sub>4</sub> increase from 1991 to 1997, at 280 ppb N<sub>2</sub>O (90 hPa) the increase is 0.3 ± 0.1%/yr and at 80 ppb N<sub>2</sub>O (ca. 10 hPa) it is 0.5 ± 0.6%/yr. This is not in agreement with the HALOE CH<sub>4</sub> trend. However, the unfitted CH<sub>4</sub> data at 280 ppb N<sub>2</sub>O level for the period 1991–1997 suggest a similar pattern as HALOE: in the lower stratosphere a small positive trend and at 10 hPa a very small decrease. However, this is not significant because of the large variation caused by the low sampling frequency. Thus, for a reliable comparison with the HALOE data, a longer HALOE time series is needed.

[26] A possible systematic error could originate from normalizing the N<sub>2</sub>O values to the year 1993, assuming that the stratospheric N<sub>2</sub>O trend approximates the tropospheric trend. To estimate an upper limit of this uncertainty, the correlation fits were also performed without accounting for the N<sub>2</sub>O trend. This yielded a lower limit for the stratospheric CH<sub>4</sub> increases (Table 3). At the 280 ppb N<sub>2</sub>O level an increase of 147 ± 31 ppb (9.5 ± 2.0%) would result for the period from 1978 to 2003 and at the 80 ppb N<sub>2</sub>O level the increase would account to 95 ± 60 ppb (11.3 ± 7.1%). Thus the annual increase of CH<sub>4</sub> would be considerably reduced in comparison with the rate of increase derived for N<sub>2</sub>O mixing ratios normalized to 1993. The largest reduction occurs in the lower stratosphere, where the calculated trend would drop from 13.4% to 9.5%, but especially here in close proximity to the troposphere correcting N<sub>2</sub>O mixing ratios with the tropospheric N<sub>2</sub>O trend should be a good estimate. This is supported by the good agreement between the tropospheric CH<sub>4</sub> increase and the CH<sub>4</sub> increase at the 280 ppb N<sub>2</sub>O level (see above). Nevertheless, the uncertainty resulting from

**Table 3.** Calculated CH<sub>4</sub> Increase for Different Time Periods, N<sub>2</sub>O Not Normalized to 1993

N <sub>2</sub> O, ppb	1978/06–2003/06		1980/01–2000/01	
	ppb	Percent	ppb	Percent
280 (17 km, 90 hPa)	147 ± 31	9.5 ± 2.0	138 ± 21	8.9 ± 1.3
180 (23 km, 35 hPa)	120 ± 22	10.1 ± 1.8	107 ± 16	9.0 ± 1.3
140 (26 km, 20 hPa)	111 ± 34	10.6 ± 3.3	97 ± 23	9.2 ± 2.2
80 (30 km, 10 hPa)	95 ± 60	11.3 ± 7.1	79 ± 38	9.4 ± 4.6



**Figure 3.** Same as Figure 2 but  $x$  axis shows the year of entry of the air parcel into the stratosphere.

the N<sub>2</sub>O correction must be kept in mind during the further discussion.

[27] From the analysis of our stratospheric CH<sub>4</sub> data, two major findings are obvious: First, as anticipated, CH<sub>4</sub> has also increased in the stratosphere in the last 25 years. Second, CH<sub>4</sub> concentrations level off at present, also in the stratosphere. The reasons for this leveling off are, however, not yet understood.

[28] As shown in Table 2, the increase of the CH<sub>4</sub> abundance from 1978 to 2003 is approximately 13% for all altitude ranges. This feature does not indicate that the increase proceeds uniformly at all altitude ranges. Instead, it has to be taken into account that different levels of N<sub>2</sub>O have different mean ages of the air. With decreasing normalized N<sub>2</sub>O levels (i.e., increasing geometric altitude) the air parcels are getting older and entered the stratosphere at a time, when CH<sub>4</sub> was still increasing at a high rate, while at higher N<sub>2</sub>O level (nearer to the tropopause) the air parcels stem from a time when, in the troposphere, the CH<sub>4</sub> trend had already weakened. An indication for this argument is the fact that at higher altitudes the flattening of the curves in Figure 2 occurs at a later date.

[29] A more meaningful comparison of the CH<sub>4</sub> trends can be obtained, if the mean age of the air, i.e., the average

time since entry of the probed air mass into the stratosphere, is considered. Using the SF<sub>6</sub> and CO<sub>2</sub> data obtained from the same data set since 1997, Engel *et al.* [2002] deduced correlations between N<sub>2</sub>O and mean age of the air. According to this analysis, a N<sub>2</sub>O mixing ratio of 280 ppb corresponds approximately to a mean age of 1.5 years, 180 ppb correspond to 4.4 years, 140 ppb to 4.9 years, and 80 ppb to 5.3 years, respectively. The age of air in the stratosphere is not a single value for a given air parcel, but rather a distribution over a large number of transport pathways with associated different transit times, the so-called age spectrum. The mean age is the first moment of this distribution [Hall and Plumb, 1994].

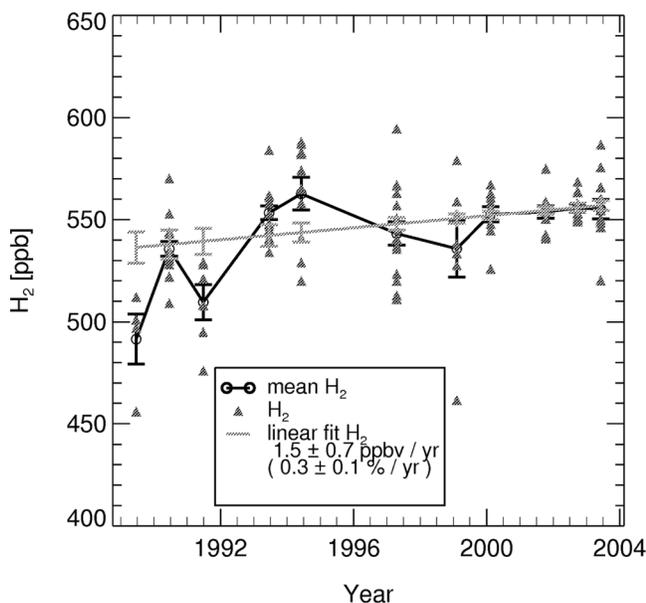
[30] In Figure 3, the CH<sub>4</sub> mixing ratios at the different N<sub>2</sub>O levels are plotted against the estimated mean year of entry of the air parcel into the stratosphere. For example, the trend curve for the 280 ppb N<sub>2</sub>O level is shifted 1.5 years back and that for the 80 ppb N<sub>2</sub>O level is shifted 5.3 years back. Again, the average increases of the time series are determined by using second-order polynomial fits and the bootstrap method. Table 4 shows the results of this calculation for the period 1978 to 1998. The increase at the 280 ppb N<sub>2</sub>O level of  $12.8 \pm 1.4\%$  is still in good agreement with the tropospheric increase of  $13.1 \pm 0.3\%$ . Since the

**Table 4.** Calculated CH<sub>4</sub> Increase for Different Time Periods, Age of Air Considered, N<sub>2</sub>O Normalized to 1993, to Account for the N<sub>2</sub>O Trend

N <sub>2</sub> O, ppb	$\Delta$ Time, years	Increase (1978–1998) <sup>a</sup>		Increase (1978–1995) <sup>a</sup>	
		ppb	Percent	ppb	Percent
Troposphere <sup>b</sup>	0	219.4 ± 5.1	13.1 ± 0.3	203.9 ± 5.0	12.2 ± 0.3
280 (17 km, 90 hPa)	+ 1.5	198 ± 21	12.8 ± 1.4	197 ± 21	12.7 ± 1.3
180 (23 km, 35 hPa)	+ 4.4	111 ± 13	9.3 ± 1.1	108 ± 12	9.1 ± 1.0
140 (26 km, 20 hPa)	+ 4.9	96 ± 21	9.1 ± 2.1	92 ± 16	8.8 ± 1.5
80 (30 km, 10 hPa)	+ 5.3	82 ± 40	9.7 ± 4.8	73 ± 27	8.7 ± 3.2

<sup>a</sup>Year of entrance of the air parcel into the stratosphere.

<sup>b</sup>Referring to Dlugokencky *et al.* [2003] and Blake and Rowland [1986].



**Figure 4.** Time series of BONBON H<sub>2</sub> measurements over the period 1988–2000. The H<sub>2</sub> data show no correlation with N<sub>2</sub>O or altitude. Therefore the temporal development of the mean H<sub>2</sub> mixing ratio in the 80–280 ppb N<sub>2</sub>O range (10–90 hPa) is presented. The increase over the observed period, determined by using a linear fit (1  $\sigma$  uncertainty calculated with the bootstrap method), is annotated on the plot.

years 1998–2003 with the relative weak CH<sub>4</sub> increase are not considered, the averaged tropospheric increase per year is  $11.0 \pm 0.3$  ppb/yr, compared to  $9.0 \pm 0.2$  ppb/yr over the whole period 1978–2003. When comparing air parcels of the same age, the mean increases of CH<sub>4</sub> are significantly smaller for lower N<sub>2</sub>O levels (between  $9.1 \pm 2.1\%$  and  $9.7 \pm 4.8\%$  at the 80–180 ppb N<sub>2</sub>O levels compared to of  $12.8 \pm 1.4\%$  at the 280 ppb N<sub>2</sub>O level).

[31] Box model results by Röckmann *et al.* [2004] reveal that enhanced OH in the stratosphere due to increased stratospheric H<sub>2</sub>O leads to more efficient oxidation of CH<sub>4</sub>, which in turn produces more H<sub>2</sub>O. This effect, namely a compensation of the increase by a stronger sink, could explain our findings. So, the temporal development of the stratospheric CH<sub>4</sub> abundance can be qualitatively understood by taking changing entry levels of CH<sub>4</sub> into the stratosphere and a more efficient oxidation of CH<sub>4</sub> at high altitudes into account. Changes in vertical transport rates as discussed by Rosenlof [2002] also affect the CH<sub>4</sub> mixing ratio at different altitudes. However, this effect should be diminished in our study because of the elimination of dynamic effects by choosing N<sub>2</sub>O as a vertical coordinate.

[32] Nedoluha *et al.* [1998] assess the importance of different processes for the observed CH<sub>4</sub> trend from HALOE between 30°S and 30°N from 1991 to 1997 (see above) with 2 D model calculations. They discuss important contributions, which are the increase in tropospheric CH<sub>4</sub>, the increase in CFCs, the decrease in solar radiation from solar maximum to solar minimum and the decrease in tropical upwelling. The model can reproduce the observed

decrease in CH<sub>4</sub> from 35 to 65 km only when also the reduced tropical upward transport is considered. Again, this effect should be mostly compensated in our study using N<sub>2</sub>O as vertical coordinate, because a reduced tropical upwelling results also in a decrease in stratospheric N<sub>2</sub>O mixing ratios. Additionally, our data do not stem from the tropics but from middle and high latitudes, where the variability of upwelling has a minor effect, in particular when trends over longer periods are determined. Concerning a potential variability with solar cycle, the data in Figure 3 at higher altitudes seem to feature, at least since 1990, an oscillation with a duration of approximately 11 years. However, the length and quality of the data set is not sufficient to assess a possible correlation with the solar cycle.

### 3.2. H<sub>2</sub> Trend

[33] The long-term temporal variation of stratospheric H<sub>2</sub> is estimated by a linear fit to the mean values of the H<sub>2</sub> mixing ratios measured at all levels (80–280 ppb N<sub>2</sub>O) during the years 1988–2003. The error bars are calculated with the bootstrap method and comprise the standard deviation and the statistical spread of the mean values (Figure 4).

[34] The linear fit indicates a small positive stratospheric H<sub>2</sub> trend of  $1.5 \pm 0.7$  ppb/yr. This finding is in accordance with the tropospheric data from CSIRO, which show a global mean growth rate of +1.4 ppb H<sub>2</sub> per year during 1992–1999 [Langenfelds *et al.*, 2002]. It does, however, not follow the data record of the NOAA/CMDL network which shows a decline of the tropospheric H<sub>2</sub> mixing ratio of  $-2.3 \pm 0.1$  ppb/yr from 1991–1996 [Novelli *et al.*, 1999]. However, the stratospheric trend is not necessarily expected to be similar to the tropospheric trend. The tropospheric trend is mainly driven by the sources (combustion of fossil fuels and oxidation of CH<sub>4</sub>) and sinks (microbial uptake in soils), as well as reaction with tropospheric OH [IPCC, 2001]. On the other hand, the stratospheric H<sub>2</sub> abundance depends mainly on H<sub>2</sub> formation via oxidation of CH<sub>4</sub>, and H<sub>2</sub> removal by reaction with stratospheric OH. To investigate the reasons for the observed stratospheric H<sub>2</sub> increment, an examination of the altitude dependency of this trend would be necessary but is not subject of this paper.

## 4. Discussion: Contribution of CH<sub>4</sub> and H<sub>2</sub> Trends to the Stratospheric Increase of H<sub>2</sub>O

[35] A major goal of this paper is to investigate the contribution of CH<sub>4</sub> oxidation to the trend in stratospheric humidity. From 1981 to 2000 the stratospheric humidity shows a statistically significant linear trend of about 1% increase per year at levels between 16 and 28 km [Oltmans *et al.*, 2000; Kley *et al.*, 2000]. In a recent study by Randel *et al.* [2004], HALOE H<sub>2</sub>O data show very low values in the years 2001 and 2002, which is corroborated also in other data sets after 2000, including that of the Boulder frostpoint record. The long-term H<sub>2</sub>O trend is not well understood at present. Several studies [e.g., Rosenlof *et al.*, 2001; Kley *et al.*, 2000] draw the conclusion that the tropospheric CH<sub>4</sub> increase can only account for at maximum 50% of the observed increase of stratospheric water vapor. This upper

**Table 5.** The 2 km Layer Average H<sub>2</sub>O Trend From 1980 to 2000 Over Boulder, Colorado, Obtained From Balloon-Borne, Chilled Mirror Hygrometers [Kley *et al.*, 2000]

Altitude, km	Corresponding N <sub>2</sub> O Level, ppb	Trend, %/yr	Inferred Trend, ppb/yr
16–18	280	1.3 ± 0.4	53 ± 16
20–22	...	1.0 ± 0.2	42.0 ± 8.4
23	180	...	44 ± 11 <sup>a</sup>
24–26	140	1.0 ± 0.3	45 ± 14

<sup>a</sup>Estimated from the two adjacent layers.

limit estimate is based on the assumption that the additional stratospheric CH<sub>4</sub> originating from the increase in tropospheric CH<sub>4</sub> is oxidized completely in the stratosphere. However, only the difference between the tropospheric and stratospheric CH<sub>4</sub> mixing ratio can have reacted to water, whose fraction depends on altitude. Up to now, an estimate of the long-term stratospheric CH<sub>4</sub> increase for a more exact calculation was missing, and therefore the tropospheric CH<sub>4</sub> increase was used as an upper estimate. The assessment of the long-term increase of stratospheric CH<sub>4</sub> presented in this study enables to estimate the contribution of CH<sub>4</sub> to the H<sub>2</sub>O increase more accurately by applying the difference between the tropospheric and stratospheric CH<sub>4</sub> increase in a given time period (see

formulas (1) and (2)). For this calculation the age of the stratospheric air should be taken into account (for details see Appendix A).

$$C_{\text{abs}}[\text{ppb}/\text{yr}] = [(\text{increase CH}_{4\text{trop}}[\text{ppb}] - \text{increase CH}_{4\text{strat}}[\text{ppb}]) * 2] / \Delta \text{ years} \quad (1)$$

$$C_{\text{rel}}[\%] = [C_{\text{abs}}[\text{ppb}/\text{yr}] / \text{trend H}_{2}\text{O}_{\text{strat}}[\text{ppb}/\text{yr}]] * 100 \quad (2)$$

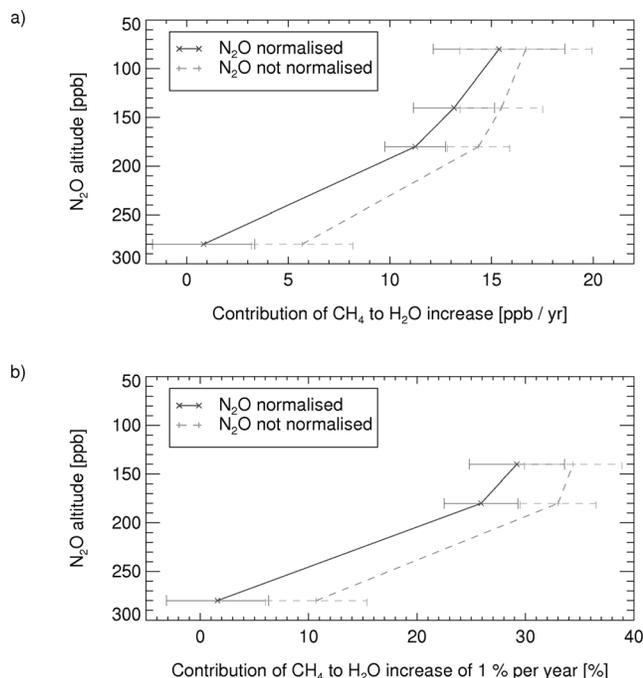
where  $C_{\text{abs}}$  is absolute contribution of CH<sub>4</sub> to the increase of stratospheric H<sub>2</sub>O,  $C_{\text{rel}}$  is relative contribution of CH<sub>4</sub> to the increase of stratospheric H<sub>2</sub>O increase, CH<sub>4trop</sub> is tropospheric CH<sub>4</sub> increase in a given time range, increase CH<sub>4strat</sub> is stratospheric CH<sub>4</sub> increase in a given time range,  $\Delta$  years = time range, and trend H<sub>2</sub>O<sub>strat</sub> is stratospheric H<sub>2</sub>O trend.

[36] Different trends of water vapor are reported in the literature [see, e.g., Kley *et al.*, 2000; Rosenlof *et al.*, 2001; Randel *et al.*, 2004], which are based on different data sets derived for different periods. The NOAA-CMDL frostpoint hygrometer balloon measurements performed over Boulder, Colorado are the only available continuous multidecadal measurements [Oltmans *et al.*, 2000]. For the time period 1992–2002 the trend derived from this data set is in disagreement with satellite observations made by the Halogen Occultation Experiment HALOE, which suggests a small negative trend of water vapor (less than  $-0.5\%/yr$ ) in

**Table 6.** Calculation of the Contribution of CH<sub>4</sub> to the Stratospheric H<sub>2</sub>O Increase for Key Data (Consideration of the Age of Air, N<sub>2</sub>O Correction)

N <sub>2</sub> O Level, ppb	$\Delta$ Time, years	CH <sub>4</sub> Increase, ppb	$\Delta$ CH <sub>4</sub> Increase (Trop.–Strat.), ppb	$C_{\text{abs}}$ , ppb/yr	H <sub>2</sub> O Trend, <sup>a</sup> ppb/yr	$C_{\text{rel}}$ (Mean H <sub>2</sub> O Increase), <sup>a</sup> %	$C_{\text{rel-95}}$ <sup>b</sup> (Range of H <sub>2</sub> O Increase), <sup>a</sup> %
<i>Case 1: Best Estimate<sup>c</sup></i>							
Troposphere <sup>d</sup>	0	203.9 ± 5.0	...	...	...	...	...
280	+ 1.5	197 ± 21	7 ± 21	0.8 ± 2.5	53 ± 16	1.6 ± 4.7	1.2–2.3
180	+ 4.4	108 ± 12	96 ± 13	11.2 ± 1.5	44 ± 11	25.9 ± 3.4	20.6–34.6
140	+ 4.9	92 ± 16	112 ± 17	13.2 ± 2.0	45 ± 14	29.2 ± 4.4	22.5–41.8
80	+ 5.3	73 ± 27	131 ± 28	15.4 ± 3.2	...	...	...
<i>Case 2: Sensitivity Test<sup>e</sup></i>							
Troposphere <sup>d</sup>	...	192.0 ± 4.3	...	...	...	...	...
280	...	187 ± 21	5 ± 21	0.5 ± 2.1	53 ± 16	1.0 ± 4.0	0.8–1.4
180	...	138 ± 15	54 ± 16	5.4 ± 1.6	44 ± 11	12.5 ± 3.7	10.0–16.7
140	...	120 ± 23	72 ± 23	7.2 ± 2.3	45 ± 14	16.0 ± 5.2	12.3–22.9
80	...	92 ± 38	100 ± 39	10.0 ± 3.9	...	...	...
<i>Case 3: Sensitivity Test<sup>f</sup></i>							
Troposphere <sup>d</sup>	0	203.9 ± 5.0	...	...	...	...	...
280	+ 1.5	156 ± 21	48 ± 21	5.7 ± 2.5	53 ± 16	10.7 ± 4.7	8.2–15.4
180	+ 4.4	82 ± 12	122 ± 13	14.4 ± 1.5	44 ± 11	33.0 ± 3.5	26.3–44.2
140	+ 4.9	72 ± 17	132 ± 17	15.5 ± 2.0	45 ± 14	34.4 ± 4.5	26.5–49.2
80	+ 5.3	62 ± 27	142 ± 28	16.7 ± 3.3	...	...	...
<i>Case 4: Sensitivity Test<sup>g</sup></i>							
Troposphere <sup>d</sup>	...	192.0 ± 4.3	...	...	...	...	...
280	...	138 ± 21	54 ± 21	5.4 ± 2.1	53 ± 16	10.1 ± 3.9	7.7–14.6
180	...	107 ± 16	86 ± 17	8.6 ± 1.7	44 ± 11	19.7 ± 3.8	15.7–26.3
140	...	97 ± 23	95 ± 24	9.5 ± 2.3	45 ± 14	21.1 ± 5.2	16.2–30.2
80	...	79 ± 38	113 ± 39	11.3 ± 3.9	...	...	...

<sup>a</sup>Referring to SPARC.<sup>b</sup> $C_{\text{rel-95}}$  = relative contribution of CH<sub>4</sub> to the increase of stratospheric H<sub>2</sub>O under consideration of the 95% confidence interval of the H<sub>2</sub>O trend.<sup>c</sup>Age of air considered, entrance of air into stratosphere: 1978–1995, N<sub>2</sub>O normalized to 1993.<sup>d</sup>Referring to Dlugokencky *et al.* [2003] and Blake and Rowland [1986].<sup>e</sup>Age of air not considered, 1980–2000 (SPARC time period), N<sub>2</sub>O normalized to 1993.<sup>f</sup>Age of air considered, entrance of air into stratosphere: 1978–1995, N<sub>2</sub>O not normalized.<sup>g</sup>Age of air not considered, 1980–2000 (SPARC time period), N<sub>2</sub>O not normalized.



**Figure 5.** (a)  $C_{\text{abs}}$ , the contribution of CH<sub>4</sub> oxidation to the stratospheric H<sub>2</sub>O increase (in ppb/yr). The age of air is considered and the calculations are performed for 1978–1995 as entrance of the air into the stratosphere, the period of the H<sub>2</sub>O trend derived from the SPARC report (see text for details). (b) As Figure 5a but  $x$  axis shows  $C_{\text{rel}}$ , the relative contribution of CH<sub>4</sub> oxidation to the stratospheric H<sub>2</sub>O increase in% (derived from the SPARC report).

the lower stratosphere over Boulder [Randel *et al.*, 2004]. However, since the Boulder frostpoint hygrometer trend is the only reliable long-term measure, it is compared to our findings using the values given in the SPARC report [Kley *et al.*, 2000] (Table 5). The Boulder frostpoint hygrometer trend is given for several geometric altitude ranges. With the limited data set of our balloon measurements it is, as discussed above, not advisable to use the geometric altitude as a vertical coordinate. Therefore the given altitude ranges from the Boulder H<sub>2</sub>O trend are attributed to N<sub>2</sub>O mixing ratio levels. This results only in a negligible effect on our calculation, since the H<sub>2</sub>O trend has a weak vertical gradient. Furthermore, supported by the normalization of the N<sub>2</sub>O mixing ratios, no significant trend of the N<sub>2</sub>O mixing ratio at a specific geometric altitude can be observed during the time range of this study.

[37] In order to demonstrate the sensitivity of several parameters on  $C_{\text{abs}}$  and  $C_{\text{rel}}$ , Table 6 summarizes the fraction of CH<sub>4</sub> oxidation to the H<sub>2</sub>O trend, determined on the basis of different assumptions. First, the difference between the tropospheric and stratospheric CH<sub>4</sub> mixing ratio is calculated with or without taking into account the age of the stratospheric air, and second, the calculation is carried out with or without applying the N<sub>2</sub>O normalization.  $C_{\text{abs}}$  and  $C_{\text{rel}}$  of case studies 1 and 3 (including the age correction) are shown in Figures 5a and 5b.

[38] The inclusion of the age of air is fundamental, because the alteration of the CH<sub>4</sub> mixing ratio (and, thus, the formation of H<sub>2</sub>O) on its way from the troposphere to different altitudes in the stratosphere has to be investigated.

[39] Since the stratospheric N<sub>2</sub>O trend is estimated from the tropospheric trend, its incorporation in the calculation is more ambiguous. However, the N<sub>2</sub>O mixing ratios must be corrected for this trend as the actual stratospheric CH<sub>4</sub> mixing ratio is growing faster than it would appear relative to uncorrected N<sub>2</sub>O values.

[40] Therefore, from our study the best estimate for the contribution of CH<sub>4</sub> to the stratospheric H<sub>2</sub>O increase (case 1 in Table 6) is derived, by including the age correction and the N<sub>2</sub>O normalization. For the highest altitude (140 ppb N<sub>2</sub>O, 24–26 km), which is reported in the SPARC report, the mean age of the air is 4.9 years. From this, it follows that the air masses of the time period of the SPARC report (1980–2000) entered the stratosphere in the years 1975–1995. Since prior to 1978 there are no global tropospheric CH<sub>4</sub> data available, we performed our calculation for the years 1978–1995 (as years of entrance of the air into the stratosphere).

[41] The difference between the tropospheric CH<sub>4</sub> increase and the CH<sub>4</sub> increase at 20 hPa (140 ppb N<sub>2</sub>O level) from 1978–1995 results in an H<sub>2</sub>O increase due to CH<sub>4</sub> increase of  $13.2 \pm 2.0$  ppb/yr. This corresponds to  $29.2 \pm 4.4\%$  of the mean H<sub>2</sub>O trend, referring to Kley *et al.* [2000]. Very similar results ( $27.5 \pm 5.1\%$ , not shown in Table 6) are obtained from the comparison of the CH<sub>4</sub> increase during the period 1978–1998 with the mean H<sub>2</sub>O increase, assuming that the H<sub>2</sub>O trend did not change after 1995 (as year of entrance of the air into the stratosphere). The H<sub>2</sub>O trend itself has a relative high uncertainty. Consideration of the 95% confidence interval of the H<sub>2</sub>O trend suggests that stratospheric CH<sub>4</sub> contributes to the H<sub>2</sub>O trend by 22.5–41.8%.

[42] Without considering the age of air, at 20 hPa (140 ppb N<sub>2</sub>O) from 1980 until 2000 (the period of the SPARC H<sub>2</sub>O trend) only  $7.2 \pm 2.3$  ppb/yr H<sub>2</sub>O ( $16.0 \pm 5.2\%$  of the mean stratospheric water vapor increase) can be attributed to the CH<sub>4</sub> trend (case 2, Table 6). These low values are generated artificially in the calculation, while comparing young tropospheric air, in which the CH<sub>4</sub> trend has already slowed down, with older stratospheric air, which stems from the troposphere in times when there still was a strong increase in CH<sub>4</sub>.

[43] Another uncertainty arises from the correction of the stratospheric N<sub>2</sub>O mixing ratios for the tropospheric N<sub>2</sub>O trend. To estimate this potential error, the calculations are performed also without a correction of the N<sub>2</sub>O mixing ratio. Considering of the age of the air (case 3, Table 6) results in a contribution of CH<sub>4</sub> to the stratospheric H<sub>2</sub>O increase at 20 hPa of  $15.5 \pm 2.0$  ppb/yr, corresponding to  $34.4 \pm 4.5\%$  of the mean stratospheric H<sub>2</sub>O increase (or 26.5–49.2% for the 95% confidence interval of the stratospheric H<sub>2</sub>O increase). Because of this uncertainty in the stratospheric N<sub>2</sub>O trend, the CH<sub>4</sub> contribution to the mean H<sub>2</sub>O increase could be up to 5% higher than our best estimate.

[44] In summary, from the best estimate of our study (case 1) 25–34% of the mean water trend (referring to

SPARC) at an altitude of 20 hPa originates from the oxidation of CH<sub>4</sub>.

[45] For lower altitudes, the relative contribution of CH<sub>4</sub> to the water trend is less important. In the lower stratosphere at 90 hPa (280 ppb N<sub>2</sub>O level) only a little amount of CH<sub>4</sub> is oxidized to water already. The increased CH<sub>4</sub> concentration in this region can only account for  $1.6 \pm 4.7\%$  up to  $10.7 \pm 4.7\%$  (without correction for N<sub>2</sub>O) of the water trend. The additional increment in stratospheric water vapor must be explained for example by a changed transport of water vapor from the troposphere into the stratosphere although the relevant processes are not yet identified [Rosenlof, 2003]. As mentioned above, in a recent study by Randel *et al.* [2004], HALOE H<sub>2</sub>O data show negative or near-zero trends from 1992 to 2002. The downward progression arises from very low values in the years 2001 and 2002, which is corroborated also in other data sets after 2000, including that of the Boulder frostpoint record. Randel *et al.* argue that the changes in global stratospheric water vapor from 1992 to 2002 are primary controlled by changes of the tropical tropopause temperatures, which becomes obvious in particular for the years around and after 2000. Nevertheless, additionally this may be evidence, that the decline of the CH<sub>4</sub> trend becomes apparent in the stratospheric H<sub>2</sub>O trend as well.

[46] Since the cause for the observed increase of stratospheric H<sub>2</sub> is not yet understood, its contribution to the trend in H<sub>2</sub>O remains ambiguous. The linear fit indicates a small positive stratospheric H<sub>2</sub> trend of  $1.5 \pm 0.7$  ppb/yr. If the additional H<sub>2</sub> originates from an increased tropospheric H<sub>2</sub> abundance of +1.4 ppb/yr as is described by Langenfelds *et al.* [2002], then the stratospheric trend does not contribute to the stratospheric increase of H<sub>2</sub>O. If in contrary the H<sub>2</sub> increase originates from incomplete CH<sub>4</sub> oxidation, then actually the existence of this H<sub>2</sub> diminishes the possible contribution of CH<sub>4</sub> to the H<sub>2</sub>O trend by  $3.3 \pm 1.6\%$ . However, at present the contribution of H<sub>2</sub> to the stratospheric H<sub>2</sub>O trend is negligible. This situation could change in the future. The potential for strong increases of H<sub>2</sub> in the atmosphere due to extensive use of the hydrogen technology and its impact on the stratospheric H<sub>2</sub>O budget was recently discussed by Tromp *et al.* [2003] and Schultz *et al.* [2003].

## 5. Summary and Conclusions

[47] On the basis of 42 vertical profiles derived from balloon-borne measurements at mid and high latitudes since 1978, we have calculated stratospheric long-term trends of CH<sub>4</sub> and (since 1988) of H<sub>2</sub>. In the period from 1978 to 2003, stratospheric CH<sub>4</sub> showed a mean increase of  $13.4 \pm 3.6\%$ . In the lower stratosphere at 17 km the overall increase in this 15-year time period was  $207 \pm 32$  ppb, at 23 km  $159 \pm 21$  ppb, at 26 km  $140 \pm 34$  ppb and at 30 km  $111 \pm 60$  ppb. The rate of increase has not been constant but slowed in recent years; at 17 km from  $0.9 \pm 0.1\%/yr$  between 1978 and 1993 to  $-0.0 \pm 0.1\%/yr$  between 1993 and 2003. This is in good agreement with the tropospheric CH<sub>4</sub> trend, whose growth rate decreased as well. Nevertheless, we need further measurements to study, whether the stratospheric CH<sub>4</sub> increase has stopped only temporarily or for a longer period.

[48] This study is unique in terms of its long time period, which basically coincides with that of the Boulder frostpoint hygrometer H<sub>2</sub>O record. This allows inferring the impact of CH<sub>4</sub> on the stratospheric H<sub>2</sub>O trend. To optimize the calculation, the age of air has to be considered and the trend of stratospheric N<sub>2</sub>O has to be corrected. By incorporating these effects, the best estimate from our study shows that at 20 hPa the CH<sub>4</sub> increase can account for an H<sub>2</sub>O increase of  $13.2 \pm 2.0$  ppb/yr. With this result, we are able to calculate the relative contribution of CH<sub>4</sub> to the stratospheric H<sub>2</sub>O increase more precisely than in previous studies. Referring to the stratospheric H<sub>2</sub>O trend from Boulder and to the best estimate from our study only 25–34% of the mean stratospheric H<sub>2</sub>O increase can be explained by the CH<sub>4</sub> increase. This diminishes the estimate of the contribution of CH<sub>4</sub> to the stratospheric H<sub>2</sub>O increase from previous studies of at maximum 50% for this contribution to a considerable degree.

[49] We also find a small positive stratospheric H<sub>2</sub> trend of  $1.5 \pm 0.7$  ppb/yr in the 90–10 hPa range. If this additional H<sub>2</sub> originates from incomplete oxidation of stratospheric CH<sub>4</sub>, then the contribution of CH<sub>4</sub> to the mean stratospheric H<sub>2</sub>O increase would be reduced by  $3.3 \pm 1.6\%$ . If it, in contrast stems from an increase in tropospheric H<sub>2</sub>, then it does not influence the stratospheric H<sub>2</sub>O increase. However, the impact of H<sub>2</sub> is minor. Together, CH<sub>4</sub> and H<sub>2</sub> cannot account for more than 34% of the mean stratospheric H<sub>2</sub>O trend. With our results, compared to previous studies, the main fraction of the stratospheric H<sub>2</sub>O increase must be explained by other changes, e.g., in dynamics, tropical tropopause temperatures or microphysics.

[50] The continuation of our time series will provide further insight, whether the currently observed decline of the stratospheric H<sub>2</sub>O increase is partly caused by the decline of the CH<sub>4</sub> increase.

## Appendix A: Calculation of the CH<sub>4</sub> Increase

[51] The second-order polynomial fits of the measured time series of CH<sub>4</sub> deliver functions, which are dependent from altitude and time.

$$\text{CH}_4(t, z)[\text{ppb}] = a(z) + b(z)t + c(z)t^2 \quad (\text{A1})$$

where CH<sub>4</sub>(t, z) is CH<sub>4</sub> mixing ratio and z is altitude.

[52] For calculating the CH<sub>4</sub> mixing ratio of the air parcel during entry into the stratosphere, the age of the air has to be considered. If species have nonlinear trends in the troposphere, these trends do not simply propagate into the stratosphere with a time lag of the mean age, but a parameterization term, depending on the width of the age spectrum, has to be included [e.g., Hall and Plumb, 1994; Plumb *et al.*, 1999; Volk *et al.*, 1997; Engel *et al.*, 2002].

$$\begin{aligned} \text{CH}_4(t, \text{trop})[\text{ppb}] &= a(\text{trop}) + b(\text{trop})[t - \Gamma(z)] \\ &+ c(\text{trop})[t - \Gamma(\text{strat})]^2 + 2c(\text{trop})\Omega[\Gamma(\text{strat})] \end{aligned} \quad (\text{A2})$$

where a(trop), b(trop), c(trop) are parameters derived from the second-order polynomial fit for the tropospheric CH<sub>4</sub>

mixing ratios;  $\Gamma(\text{strat})$  is mean age of stratospheric air at a given altitude; and  $\Omega$  is width of the age spectrum.

[53] However, since in our case, we calculate the difference between CH<sub>4</sub> ratios at the begin and end of a time period (with the same second-order polynomial correlation function), the parameterization terms  $2c(\text{trop})\Omega[\Gamma(\text{strat})]$  cancel out each other and have not to be incorporated.

$$\begin{aligned} \Delta\text{CH}_4(t_1, t_2, \text{trop})[\text{ppb}] = & b(\text{trop})[t_2 - \Gamma(\text{strat})] \\ & + c(\text{trop})[t_2 - \Gamma(z)]^2 - b(\text{trop})[t_1 - \Gamma(\text{strat})] \\ & - c(\text{trop})[t_1 - \Gamma(\text{strat})]^2 \end{aligned} \quad (\text{A3})$$

where  $\Delta\text{CH}_4$  is  $\Delta\text{CH}_4$  increase in a given time range.

[54] Furthermore, as shown by Plumb *et al.* [1999], the effective distribution of transit times, for an observed tracer with chemical loss is different from the one for a compound without chemical loss. This aspect can also be neglected, because we calculate the tropospheric CH<sub>4</sub> mixing ratio and this value is independent from chemical loss reactions of CH<sub>4</sub> in the stratosphere during the aging of the air.

[55] **Acknowledgments.** We would like to thank E. J. Dlugokencky and the NOAA/CMDL Climate Monitoring and Diagnostic Laboratory network for kindly providing the global surface CH<sub>4</sub> mixing ratio time series. We also thank F. Rohrer for his support by the statistical analysis and R. Müller for many useful discussions on the subject. Furthermore, we extend thanks to our many colleagues who contributed to the experimental part of the work. Finally, we would like to acknowledge the financial support for the balloon observations (e.g., OFP, EASOE, SESAME, THESEO, and ENVISAT-Validation) by the German Ministry of Research and Technology (BMBF) and the European Commission.

## References

- Aoki, S., T. Nakazawa, S. Murayama, and S. Kawaguchi (1992), Measurements of atmospheric methane at Japanese Antarctic station, Syowa, *Tellus, Ser. B*, *44*, 273–281.
- Blake, D. R., and F. S. Rowland (1986), World-wide increase in tropospheric methane, 1978–1983, *J. Atmos. Chem.*, *4*, 43–62.
- Blake, D. R., and F. S. Rowland (1988), Continuing worldwide increase in tropospheric methane, 1978–1987, *Science*, *239*, 1129–1131.
- Dentener, F., M. van Weele, M. Krol, S. Houweling, and P. van Velthoven (2003), Trends and inter-annual variability of methane emissions derived from 1979–1993 global CTM simulations, *Atmos. Chem. Phys.*, *3*, 73–88.
- Dessler, A. E., E. J. Weinstock, E. M. Hints, J. G. Anderson, C. R. Webster, R. D. May, J. W. Elkins, and G. S. Dutton (1994), An examination of the total hydrogen budget of the lower stratosphere, *Geophys. Res. Lett.*, *21*, 2563–2566.
- Dlugokencky, E. J., B. P. Walter, K. A. Masarie, P. M. Lang, and E. S. Kasischke (2001), Measurements of an anomalous global methane increase during 1998, *Geophys. Res. Lett.*, *28*, 499–502.
- Dlugokencky, E. J., S. Houweling, L. Bruhwiler, K. A. Masarie, P. M. Lang, J. B. Miller, and P. P. Tans (2003), Atmospheric methane levels off: Temporary pause or a new steady-state?, *Geophys. Res. Lett.*, *30*(19), 1992, doi:10.1029/2003GL018126.
- Engel, A., and U. Schmidt (1998), Stratospheric trends of CFC-12 over the past two decades: Recent observational evidence of declining growth rates, *Geophys. Res. Lett.*, *25*, 3319–3322.
- Engel, A., C. Schiller, U. Schmidt, R. Borchers, H. Ovarlez, and J. Ovarlez (1996), The total hydrogen budget in the Arctic winter stratosphere during the European Arctic Stratospheric Ozone Experiment, *J. Geophys. Res.*, *101*, 14,495–14,504.
- Engel, A., U. Schmidt, and R. A. Stachnik (1997), Partitioning between chlorine reservoir species deduced from observations in the Arctic winter stratosphere, *J. Atmos. Chem.*, *27*, 107–126.
- Engel, A., M. Strunk, M. Müller, H. Haase, C. Poss, I. Levin, and U. Schmidt (2002), Temporal development of total chlorine in the high-latitude stratosphere based on reference distributions of mean age derived from CO<sub>2</sub> and SF<sub>6</sub>, *J. Geophys. Res.*, *107*(D12), 4136, doi:10.1029/2001JD000584.
- Fabian, P., *et al.* (1981), The vertical distribution of stable trace gases at midlatitudes, *J. Geophys. Res.*, *86*, 5179–5184.
- Forster, P. M. de F., and K. P. Shine (1999), Stratospheric water vapor changes as a possible contributor to observed stratospheric cooling, *Geophys. Res. Lett.*, *26*(21), 3309–3312.
- Forster, P. M. de F., and K. P. Shine (2002), Assessing the climate impact of trends in stratospheric water vapor, *Geophys. Res. Lett.*, *29*(6), 1086, doi:10.1029/2001GL013909.
- Hall, T. M., and R. A. Plumb (1994), Age as a diagnostic of stratospheric transport, *J. Geophys. Res.*, *99*, 1059–1070.
- Hurst, D. F., *et al.* (1999), Closure of the total hydrogen budget of the northern extratropical lower stratosphere, *J. Geophys. Res.*, *104*, 8191–8200.
- Intergovernmental Panel on Climate Change (2001), *Climate Change 2001: The Scientific Basis*, edited by J. T. Houghton *et al.*, Cambridge Univ. Press, New York.
- Ishijima, K., T. Nakazawa, S. Sugawara, S. Aoki, and T. Saeki (2001), Concentration variations of tropospheric nitrous oxide over Japan, *Geophys. Res. Lett.*, *28*, 171–174.
- Khalil, M. A. K., and R. A. Rasmussen (1990), Atmospheric methane: Recent global trends, *Environ. Sci. Technol.*, *24*, 549–553.
- Kley, D., J. M. Russell III, and C. Phillips (Eds.) (2000), Assessment of upper tropospheric and stratospheric water vapour, *SPARC Rep. 2, WMO/TD 1043*, World Meteorol. Organ., Geneva, Switzerland.
- Langenfelds, R. L., R. J. Francey, B. C. Pak, L. P. Steele, J. Lloyd, C. M. Trudinger, and C. E. Allison (2002), Interannual growth rate variations of atmospheric CO<sub>2</sub> and its  $\delta^{13}\text{C}$ , H<sub>2</sub>, CH<sub>4</sub>, and CO between 1992 and 1999 linked to biomass burning, *Global Biogeochem. Cycles*, *16*(3), 1048, doi:10.1029/2001GB001466.
- Le Texier, H., S. Solomon, and R. R. Garcia (1988), The role of molecular hydrogen and methane oxidation in the water vapour budget of the stratosphere, *Q. J. R. Meteorol. Soc.*, *114*, 281–295.
- Levin, I., H. Glatzel-Mattheier, T. Marik, M. Cuntz, M. Schmidt, and D. E. Worthy (1999), Verification of German methane emission inventories and their recent changes based on atmospheric observations, *J. Geophys. Res.*, *104*(D3), 3447–3456.
- Nakazawa, T., T. Machida, S. Sugawara, S. Murayama, S. Morimoto, G. Hashida, H. Honda, and T. Itoh (1995), Measurements of the stratospheric carbon dioxide concentration over Japan using a balloon-borne cryogenic sampler, *Geophys. Res. Lett.*, *22*, 1229–1232.
- Nakazawa, T., *et al.* (2002), Variations of stratospheric trace gases measured using a balloon-borne cryogenic sampler, *Adv. Space Res.*, *30*, 1349–1357.
- Nedoluha, G. E., D. E. Siskind, J. T. Bacmeister, R. M. Bevilacqua, and J. M. Russell III (1998), Changes in upper stratospheric CH<sub>4</sub> and NO<sub>2</sub> as measured by HALOE and implications for changes in transport, *Geophysical Res. Lett.*, *25*, 987–990.
- Novelli, P. C., P. M. Lang, K. A. Masarie, D. F. Hurst, R. Myers, and J. W. Elkins (1999), Molecular hydrogen in the troposphere: Global distribution and budget, *J. Geophys. Res.*, *104*, 30,427–30,444.
- Oinas, V., A. A. Lacis, D. Rind, D. T. Shindell, and J. E. Hanson (2001), Radiative cooling by stratospheric water vapour: Big differences in GCM results, *Geophys. Res. Lett.*, *28*, 2791–2794.
- Oltmans, S. J., H. Vömel, D. J. Hofmann, K. H. Rosenlof, and D. Kley (2000), The increase in stratospheric water vapor from balloon-borne, frostpoint hygrometer measurements at Washington, D.C., and Boulder, Colorado, *Geophys. Res. Lett.*, *27*, 3453–3456.
- Plumb, I. C., P. F. Vohralik, and K. R. Ryan (1999), Normalization of correlations for atmospheric species with chemical loss, *J. Geophys. Res.*, *104*, 11,723–11,732.
- Randel, W. J., F. Wu, J. M. Russell III, and J. Waters (1999), Space-time patterns of trends in stratospheric constituents derived from UARS measurements, *J. Geophys. Res.*, *104*, 3711–3727.
- Randel, W. J., F. Wu, S. J. Oltmans, K. Rosenlof, and G. E. Nedoluha (2004), Interannual changes of stratospheric water vapor and correlations with tropical tropopause temperatures, *J. Atmos. Sci.*, *61*, 2133–2148.
- Röckmann, T., J.-U. Groöf, and R. Müller (2004), The impact of anthropogenic chlorine emissions, stratospheric ozone change and chemical feedbacks on stratospheric water, *Atmos. Chem. Phys.*, *4*, 693–699.
- Rosenlof, K. H. (2002), Transport changes inferred from HALOE water and methane measurements, *J. Meteorol. Soc. Jpn.*, *80*, 831–848.
- Rosenlof, K. H. (2003), How water enters the stratosphere, *Science*, *302*, 1691–1692.
- Rosenlof, K. H., *et al.* (2001), Stratospheric water vapour increases over the past half-century, *Geophys. Res. Lett.*, *28*, 1195–1198.
- Schmidt, U., G. Kulesa, E. Klein, E.-P. Röth, P. Fabian, and R. Borchers (1987), Intercomparison of balloon-borne cryogenic whole air samplers during the MAP/GLOBUS 1983 campaign, *Planet. Space Sci.*, *35*, 647–656.

- Schultz, M. G., T. Diehl, G. P. Brasseur, and W. Zittel (2003), Air pollution and climate-forcing impacts of a global hydrogen economy, *Science*, *302*, 624–627.
- Shindell, D. (2001), Climate and ozone response to increased stratospheric water vapour, *Geophys. Res. Lett.*, *28*, 1551–1554.
- Solomon, S. (1999), Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, *37*, 275–316.
- Tromp, T. K., R.-L. Shia, J. M. Eiler, and Y. L. Yung (2003), Potential environmental impact of a hydrogen economy on the stratosphere, *Science*, *300*, 1740–1742.
- Volk, C. M., J. W. Elkins, D. W. Fahey, G. S. Dutton, J. M. Gilligan, M. Loewenstein, J. R. Podolske, K. R. Chan, and M. R. Gunson (1997), Evaluation of source gas lifetimes from stratospheric observations, *J. Geophys. Res.*, *102*, 25,543–25,564.
- Wang, J. S., J. A. Logan, M. B. McElroy, B. N. Duncan, I. A. Megretskaja, and R. M. Yantosca (2004), A 3-D model analysis of the slowdown and interannual variability in the methane growth rate from 1988 to 1997, *Global Biogeochem. Cycles*, *18*, GB3011, doi:10.1029/2003GB002180.
- World Meteorological Organization (1998), Scientific assessment of ozone depletion: 1998, *Global Ozone Res. and Monit. Proj., Rep. 44*, Geneva, Switzerland.
- Zhou, X. L., M. A. Geller, and M. H. Zhang (2001), The cooling trend of the tropical cold point tropopause temperatures and its implications, *J. Geophys. Res.*, *106*, 1511–1522.
- Zöger, M., A. Engel, D. S. McKenna, C. Schiller, U. Schmidt, and T. Woyke (1999), Balloon-borne in situ measurements of stratospheric H<sub>2</sub>O, CH<sub>4</sub> and H<sub>2</sub> at mid-latitudes, *J. Geophys. Res.*, *104*, 1817–1825.
- 
- S. Aoki and T. Nakazawa, Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai 980-8578, Japan.
- A. Engel, U. Schmidt, and T. Wetter, Institut für Atmosphäre und Umwelt, J. W. Goethe Universität, D-60325 Frankfurt, Germany.
- I. Levin, Institut für Umweltp Physik, Universität Heidelberg, D-69120 Heidelberg, Germany.
- M. Riese, S. Rohs, and C. Schiller, ICG-I: Stratosphäre, Forschungszentrum Jülich, D-52425 Jülich, Germany. (s.rohs@fz-juelich.de)