

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,¹ C. Schiller,¹ M. Riese,¹ A. Engel,² U. Schmidt,² T. Wetter,² I. Levin,³ T. Nakazawa,⁴ and S. Aoki⁴

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[1] The long-term changes of the stratospheric mixing ratio of CH₄ over the period of 1978–2003 are derived from balloon-borne data of H₂, CH₄ and N₂O. 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 N₂O mixing ratio is used as a proxy for altitude. A correlation analysis for the individual years is applied and the CH₄ mixing ratios are interpolated to four different levels of N₂O, 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 CH₄ trend has slowed down in recent years and is best fitted by a second-order polynomial. The increase of CH₄ can account for only 25–34% of the increase in stratospheric H₂O of 1%/yr over the last decades as derived from previous studies. The simultaneously measured time series of stratospheric H₂ mixing ratios shows that the contribution of stratospheric H₂ to the H₂O trend in the period 1988–2003 is minor.

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1. Introduction

[2] The major hydrogen-containing species in the stratosphere are CH₄, H₂O and H₂. 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: CH₄ + Cl => HCl + CH₃ [*World Meteorological Organization*, 1998]. Further, stratospheric H₂O 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 H₂O (and CH₄ 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 O₃ [*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 CH₄, H₂O and H₂ in the stratosphere are of great relevance for atmospheric chemistry and climate and have to be determined very precisely.

[3] In the lower stratosphere H₂O 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 CH₄ and H₂O are tightly coupled, because the photochemical oxidation of each molecule of CH₄ produces approximately two molecules of H₂O. 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 CH₄ and H₂O. From the correlation of CH₄, H₂O and H₂ *Zöger et al.* [1999] calculated a ratio of 1.975 ± 0.030. Nevertheless, as a first approximation the quantity H₂O + 2 CH₄ is conserved, and CH₄ oxidation is the primary reason for the increase of H₂O 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

¹ICG-I: Stratosphäre, Forschungszentrum Jülich, Jülich, Germany.

²Institut für Atmosphäre und Umwelt, J. W. Goethe Universität, Frankfurt, Germany.

³Institut für Umweltphysik, Universität Heidelberg, Heidelberg, Germany.

⁴Center 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 H₂O trend.

[6] Rosenlof *et al.* [2001] derived that the increase in tropospheric CH₄ (see below) could at maximum cause 50% of the H₂O trend, provided that the additional CH₄ gets oxidized completely. If, however, the additional CH₄ from the troposphere is not oxidized completely but instead results in a stratospheric CH₄ increase, then the contribution of CH₄ to the stratospheric H₂O 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 CH₄ and H₂ oxidation as exact as possible; that is, it is necessary to know the tropospheric and stratospheric CH₄ and H₂ trends.

[7] CH₄ 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 CH₄ concentration has increased significantly. Blake and Rowland [1988] found a CH₄ increase ranging from 1520 ppb in 1978 to 1684 ppb in 1987, according to an increment of 16 ± 1 ppb per year. Similar results are reported by Khalil and Rasmussen [1990], who calculated an average rate of increase of 16.6 ± 0.4 ppb per year in the period 1980–1988. Since 1984 the globally averaged tropospheric CH₄ concentration is monitored by the globally distributed NOAA/CMDL Climate Monitoring and Diagnostic Laboratory network. During this period global mean tropospheric CH₄ mixing ratios have increased from 1625 ppb in 1984 to 1751 ppb in 2002 with a slowdown in CH₄ growth rate being observed. This could be explained by stagnant CH₄ emissions and lifetime in a system approaching steady state [Dlugokencky *et al.*, 2001, 2003]. Most studies seeking to explain the decline in the CH₄ 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 CH₄ 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 CH₄ and H₂O. These data show slightly negative CH₄ 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 H₂, which originates mainly from oxidation of CH₄ (and from transport out of the troposphere) and is removed by OH initiated oxidation to H₂O. The mixing ratio of H₂ does not change significantly with altitude because the production and loss rates of H₂ are nearly balanced [Le Texier *et al.*, 1988; Dessler *et al.*, 1994; Hurst *et al.*, 1999]. Reports about the tropospheric H₂ trend are inconsistent with one another. During 1991–1996 data from the NOAA/CMDL network show a decline of the tropospheric H₂ mixing ratio of -2.3 ± 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 H₂ 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 CH₄ and H₂ 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 H₂O.

2. Evolution of Stratospheric CH₄ and H₂ 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 H₂, N₂O and other long-lived trace gases was analyzed by gas chromatography at the Institute for Atmosphere and Environment of the University of Frankfurt. CH₄ 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 (1σ) 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 (1σ)

	N ₂ O	CH ₄	H ₂
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 CH₄ and N₂O concentration data since 1991 are available for this study. The air samples of about 25 L_{STP} were collected into 760 mL stainless steel samples tubes cooled by liquid helium at 11 different altitudes in the stratosphere. The CH₄ and N₂O 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 CH₄ and N₂O 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 CH₄ the data from all flights accomplished during one year were combined. Then, a correlation analysis with N₂O as vertical coordinate was performed. The mixing ratio of CH₄ in the stratosphere decreases rapidly with altitude. Using the geometric altitude or potential temperature as a vertical coordinate, the CH₄ 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 CH₄. The problem can be solved, when the mixing ratio of the long-lived tracer N₂O is used as a proxy vertical coordinate [Engel and Schmidt, 1998]. In the stratosphere, the only significant loss process for N₂O is photochemical decomposition. The stratospheric lifetime of both, N₂O and CH₄ are approximately 120 years [IPCC, 2001]. Therefore the vertical profiles of N₂O comprise similar dynamical structures as those of CH₄. At each N₂O level, air masses of comparable dynamical history are assorted [Engel and Schmidt, 1998]. N₂O has only a small tropospheric trend. To account for this trend, the stratospheric N₂O 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 CH₄ trends due to this normalization will be discussed later.

[14] For N₂O values between 70 and 290 ppb, a linear correlation between N₂O and CH₄ 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 CH₄ mixing ratio at the 80 ppb N₂O level is increased slightly from 886 ± 11 ppb (excluding the SAKURA data) to 889 ± 9 ppb (including the SAKURA data). Overall, using both, the data from

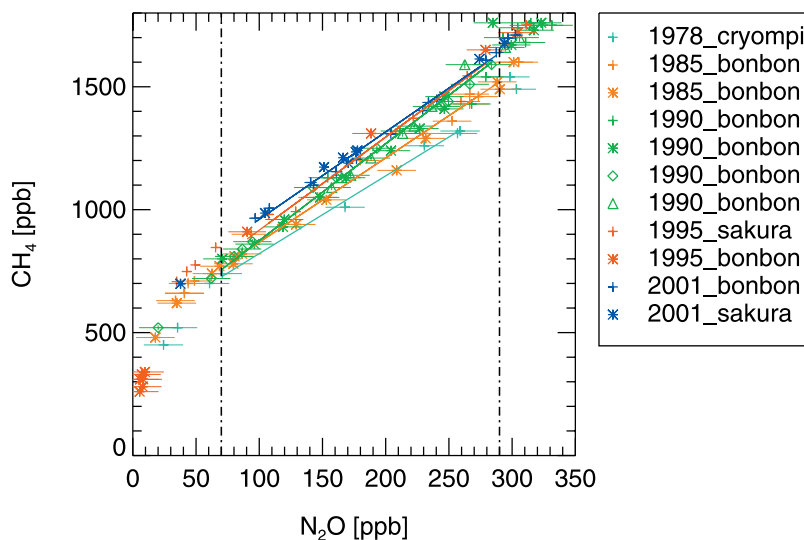


Figure 1. Correlation plots of CH₄ versus N₂O observed during 1978–2003. For eliminating variability attributed to short-term dynamical processes and to varying latitudinal and seasonal coverage of the measurements, N₂O is used as a vertical coordinate. This filtering samples air of approximately the same average stratospheric residence time. The N₂O 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 N₂O (dashed vertical lines), where no deviations from the linear relationship are observed.

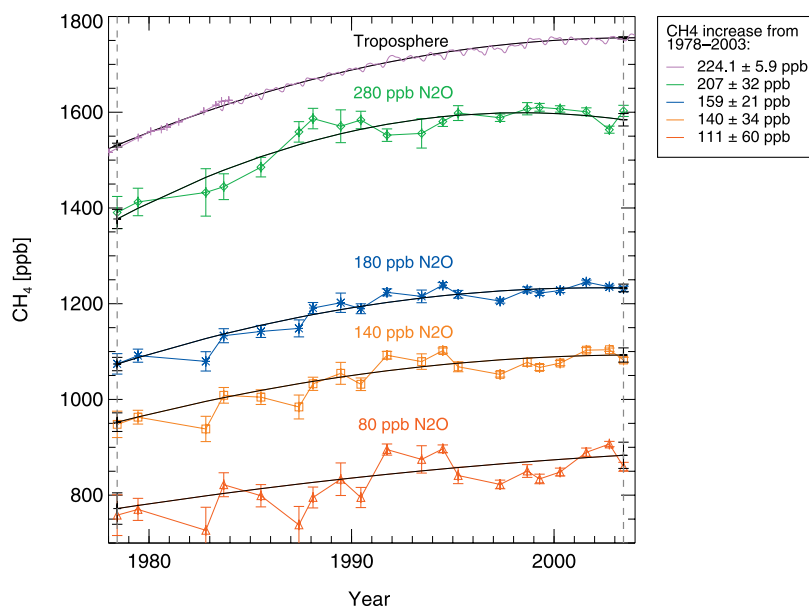


Figure 2. Time series of CRYO MPI, BONBON and SAKURA CH₄ mixing ratios for the lower stratosphere over the period 1978–2003. The globally averaged tropospheric CH₄ measurements are from the NOAA CMDL cooperative air sampling network (E. J. Dlugokencky, personal communication, 2005) and prior to 1984 from *Blake and Rowland* [1986]. The mixing ratios of CH₄ are interpolated to the levels of 80, 140, 180 and 280 ppb N₂O. The increases over the observed period, determined by using second-order polynomial fits (1σ uncertainties calculated with the bootstrap method), are annotated in the plot.

SAKURA and from BONBON results in slightly but insignificantly lower CH₄ mixing ratios at 280 ppb N₂O and in slightly but insignificantly higher CH₄ mixing ratios at 80 ppb N₂O. The resulting effect for the trend calculation in Chapter 3 is minor. Excluding the 8 flights from SAKURA shifts the calculated trends of CH₄ (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 CH₄ 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 N₂O 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 N₂O and CH₄ is close to linear over the range of mixing ratios used in this study.

[17] For the further analysis, four N₂O 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 CH₄ mixing ratios, which correspond to these N₂O 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 N₂O 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 H₂ and N₂O show no correlation, similarly to the behavior observed between CH₄ and H₂ [*Zöger et al.*, 1999], because in contrast to N₂O or CH₄, H₂ does not vary systematically with altitude. For this reason the H₂ data of the whole altitude range from 280 to 80 ppb N₂O are averaged for each year to derive the time series.

3. Results: Stratospheric Changes of CH₄ and H₂

3.1. CH₄ Trend

[19] The temporal development of the CH₄ mixing ratios for the N₂O 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, CH₄ mixing ratios decrease with altitude. A positive trend of the CH₄ mixing ratio over the whole observational period is evident for all altitude levels. However, the increase of CH₄ 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 CH₄ for the whole period is determined by fitting the curve with two succes-

Table 2. Calculated CH₄ Increase for Different Time Periods, N₂O Normalized to 1993, to Account for the N₂O Trend

N ₂ O, ppb	1978/06–2003/06		1980/01–2000/01	
	ppb	Percent	ppb	Percent
Troposphere ^a	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

^aReferring 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 CH₄ increase, is the fitting of the CH₄ data of the different N₂O levels by second-order polynomials. This method is applied in the following. The 1 σ -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 CH₄ 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 N₂O level, i.e., in the lower stratosphere, a mean increase of 207 ± 32 ppb (13.4 ± 2.1%) is observed; at 140 ppb N₂O the increase is 140 ± 34 ppb (13.4 ± 3.3%) and at 80 ppb N₂O 111 ± 60 ppb (13.2 ± 7.1%). For the determination of the tropospheric CH₄ 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 CH₄ data from NOAA/CMDL. Therefore, for the years 1978–1983 the mean trend during this period of 18 ± 1 ppb CH₄/yr [*Blake and Rowland*, 1986] was adopted. By fitting the tropospheric CH₄ data with a second-order polynomial, from 1978/06 to 2003/06 we calculate a tropospheric CH₄ increase of 224.1 ± 5.9 ppb (13.4 ± 0.4%).

[22] Because of the proximity to the troposphere, the CH₄ increase in the lower stratosphere should be similar to the tropospheric increase. This is in accordance with our findings. The tropospheric CH₄ increase over the entire time period corresponds well with our data for the lower stratosphere. Moreover, if we calculate the CH₄ 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 CH₄ shows a

high variability (−15 to + 20 ppb/yr at the 80 ppb N₂O 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 CH₄ 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 CH₄ 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 CH₄ abundances (up to −5% CH₄ 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 CH₄ increase from 1991 to 1997, at 280 ppb N₂O (90 hPa) the increase is 0.3 ± 0.1%/yr and at 80 ppb N₂O (ca. 10 hPa) it is 0.5 ± 0.6%/yr. This is not in agreement with the HALOE CH₄ trend. However, the unfitted CH₄ data at 280 ppb N₂O 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 N₂O values to the year 1993, assuming that the stratospheric N₂O trend approximates the tropospheric trend. To estimate an upper limit of this uncertainty, the correlation fits were also performed without accounting for the N₂O trend. This yielded a lower limit for the stratospheric CH₄ increases (Table 3). At the 280 ppb N₂O 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 N₂O level the increase would account to 95 ± 60 ppb (11.3 ± 7.1%). Thus the annual increase of CH₄ would be considerably reduced in comparison with the rate of increase derived for N₂O 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 N₂O mixing ratios with the tropospheric N₂O trend should be a good estimate. This is supported by the good agreement between the tropospheric CH₄ increase and the CH₄ increase at the 280 ppb N₂O level (see above). Nevertheless, the uncertainty resulting from

Table 3. Calculated CH₄ Increase for Different Time Periods, N₂O Not Normalized to 1993

N ₂ 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

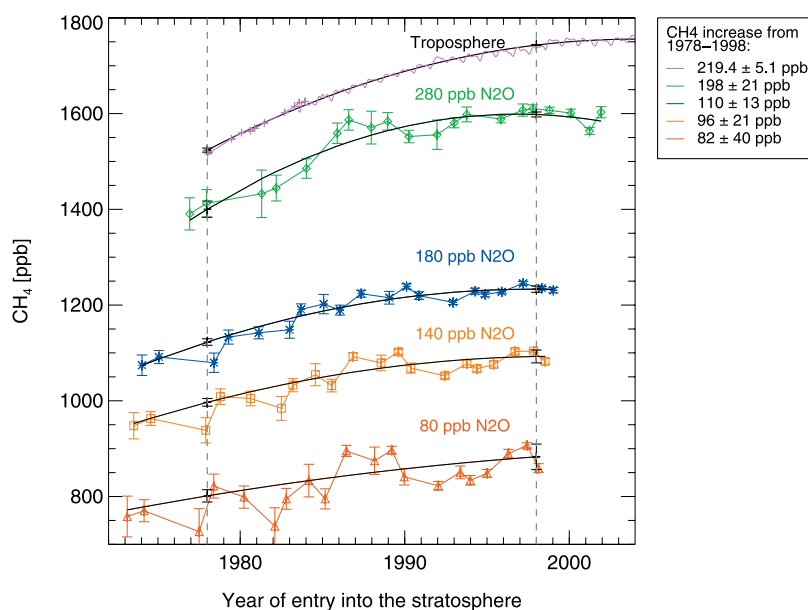


Figure 3. Same as Figure 2 but x axis shows the year of entry of the air parcel into the stratosphere.

the N₂O correction must be kept in mind during the further discussion.

[27] From the analysis of our stratospheric CH₄ data, two major findings are obvious: First, as anticipated, CH₄ has also increased in the stratosphere in the last 25 years. Second, CH₄ 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 CH₄ 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 N₂O have different mean ages of the air. With decreasing normalized N₂O levels (i.e., increasing geometric altitude) the air parcels are getting older and entered the stratosphere at a time, when CH₄ was still increasing at a high rate, while at higher N₂O level (nearer to the tropopause) the air parcels stem from a time when, in the troposphere, the CH₄ 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 CH₄ 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 SF₆ and CO₂ data obtained from the same data set since 1997, Engel *et al.* [2002] deduced correlations between N₂O and mean age of the air. According to this analysis, a N₂O 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 CH₄ mixing ratios at the different N₂O 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 N₂O level is shifted 1.5 years back and that for the 80 ppb N₂O 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 N₂O 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 CH₄ Increase for Different Time Periods, Age of Air Considered, N₂O Normalized to 1993, to Account for the N₂O Trend

N ₂ O, ppb	Δ Time, years	Increase (1978–1998) ^a		Increase (1978–1995) ^a	
		ppb	Percent	ppb	Percent
Troposphere ^b	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

^aYear of entrance of the air parcel into the stratosphere.

^bReferring to Dlugokencky *et al.* [2003] and Blake and Rowland [1986].

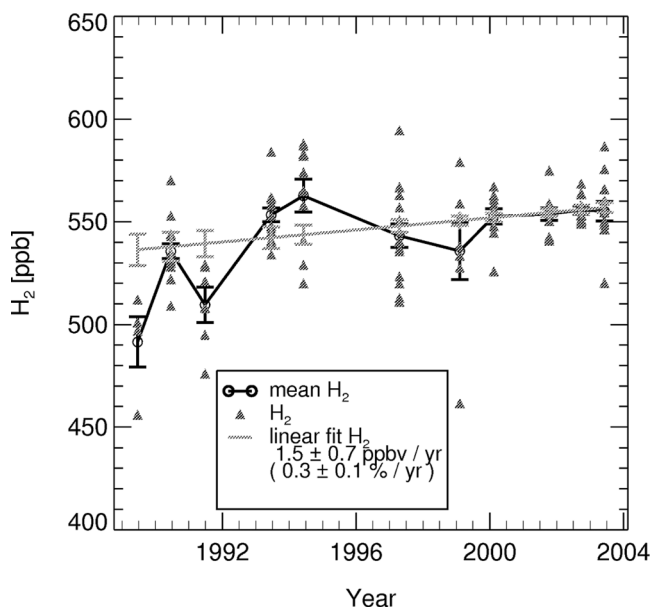


Figure 4. Time series of BONBON H₂ measurements over the period 1988–2000. The H₂ data show no correlation with N₂O or altitude. Therefore the temporal development of the mean H₂ mixing ratio in the 80–280 ppb N₂O range (10–90 hPa) is presented. The increase over the observed period, determined by using a linear fit (1 σ uncertainty calculated with the bootstrap method), is annotated on the plot.

years 1998–2003 with the relative weak CH₄ increase are not considered, the averaged tropospheric increase per year is 11.0 ± 0.3 ppb/yr, compared to 9.0 ± 0.2 ppb/yr over the whole period 1978–2003. When comparing air parcels of the same age, the mean increases of CH₄ are significantly smaller for lower N₂O levels (between $9.1 \pm 2.1\%$ and $9.7 \pm 4.8\%$ at the 80–180 ppb N₂O levels compared to of $12.8 \pm 1.4\%$ at the 280 ppb N₂O level).

[31] Box model results by Röckmann *et al.* [2004] reveal that enhanced OH in the stratosphere due to increased stratospheric H₂O leads to more efficient oxidation of CH₄, which in turn produces more H₂O. This effect, namely a compensation of the increase by a stronger sink, could explain our findings. So, the temporal development of the stratospheric CH₄ abundance can be qualitatively understood by taking changing entry levels of CH₄ into the stratosphere and a more efficient oxidation of CH₄ at high altitudes into account. Changes in vertical transport rates as discussed by Rosenlof [2002] also affect the CH₄ mixing ratio at different altitudes. However, this effect should be diminished in our study because of the elimination of dynamic effects by choosing N₂O as a vertical coordinate.

[32] Nedoluha *et al.* [1998] assess the importance of different processes for the observed CH₄ 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 CH₄, 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 CH₄ 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 N₂O as vertical coordinate, because a reduced tropical upwelling results also in a decrease in stratospheric N₂O 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. H₂ Trend

[33] The long-term temporal variation of stratospheric H₂ is estimated by a linear fit to the mean values of the H₂ mixing ratios measured at all levels (80–280 ppb N₂O) 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 H₂ trend of 1.5 ± 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 H₂ 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 H₂ mixing ratio of -2.3 ± 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 CH₄) and sinks (microbial uptake in soils), as well as reaction with tropospheric OH [IPCC, 2001]. On the other hand, the stratospheric H₂ abundance depends mainly on H₂ formation via oxidation of CH₄, and H₂ removal by reaction with stratospheric OH. To investigate the reasons for the observed stratospheric H₂ increment, an examination of the altitude dependency of this trend would be necessary but is not subject of this paper.

4. Discussion: Contribution of CH₄ and H₂ Trends to the Stratospheric Increase of H₂O

[35] A major goal of this paper is to investigate the contribution of CH₄ 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 H₂O 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 H₂O 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 CH₄ 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 H₂O Trend From 1980 to 2000 Over Boulder, Colorado, Obtained From Balloon-Borne, Chilled Mirror Hygrometers [Kley *et al.*, 2000]

Altitude, km	Corresponding N ₂ 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 ^a
24–26	140	1.0 ± 0.3	45 ± 14

^aEstimated from the two adjacent layers.

limit estimate is based on the assumption that the additional stratospheric CH₄ originating from the increase in tropospheric CH₄ is oxidized completely in the stratosphere. However, only the difference between the tropospheric and stratospheric CH₄ mixing ratio can have reacted to water, whose fraction depends on altitude. Up to now, an estimate of the long-term stratospheric CH₄ increase for a more exact calculation was missing, and therefore the tropospheric CH₄ increase was used as an upper estimate. The assessment of the long-term increase of stratospheric CH₄ presented in this study enables to estimate the contribution of CH₄ to the H₂O increase more accurately by applying the difference between the tropospheric and stratospheric CH₄ 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).

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

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

where C_{abs} is absolute contribution of CH₄ to the increase of stratospheric H₂O, C_{rel} is relative contribution of CH₄ to the increase of stratospheric H₂O increase, CH₄_{trop} is tropospheric CH₄ increase in a given time range, increase CH₄_{strat} is stratospheric CH₄ increase in a given time range, Δ years = time range, and trend H₂O_{strat} is stratospheric H₂O 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 CH₄ to the Stratospheric H₂O Increase for Key Data (Consideration of the Age of Air, N₂O Correction)

N ₂ O Level, ppb	Δ Time, years	CH ₄ Increase, ppb	Δ CH ₄ Increase (Trop.–Strat.), ppb	C _{abs} , ppb/yr	H ₂ O Trend, ^a ppb/yr	C _{rel} (Mean H ₂ O Increase), ^a %	C _{rel-95} ^b (Range of H ₂ O Increase), ^a %
<i>Case 1: Best Estimate^c</i>							
Troposphere ^d	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^e</i>							
Troposphere ^d	...	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^f</i>							
Troposphere ^d	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^g</i>							
Troposphere ^d	...	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

^aReferring to SPARC.

^bC_{rel-95} = relative contribution of CH₄ to the increase of stratospheric H₂O under consideration of the 95% confidence interval of the H₂O trend.

^cAge of air considered, entrance of air into stratosphere: 1978–1995, N₂O normalized to 1993.

^dReferring to Dlugokencky *et al.* [2003] and Blake and Rowland [1986].

^eAge of air not considered, 1980–2000 (SPARC time period), N₂O normalized to 1993.

^fAge of air considered, entrance of air into stratosphere: 1978–1995, N₂O not normalized.

^gAge of air not considered, 1980–2000 (SPARC time period), N₂O not normalized.

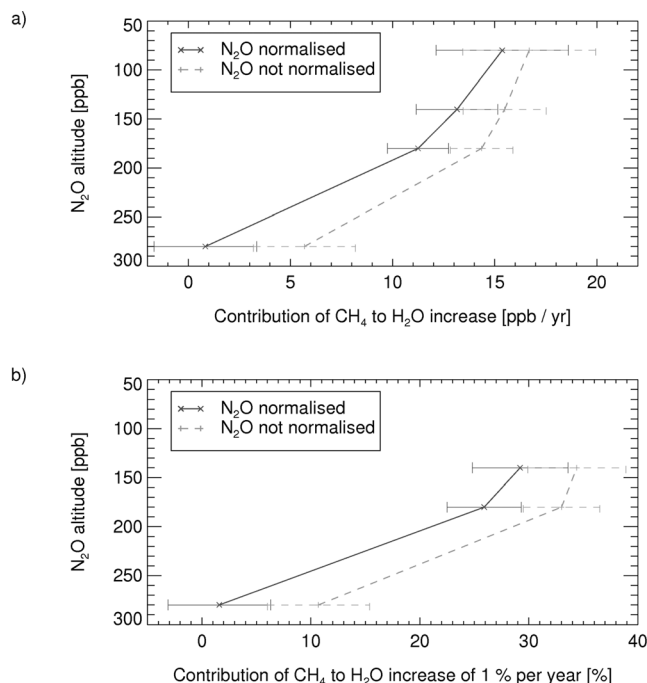


Figure 5. (a) C_{abs} , the contribution of CH₄ oxidation to the stratospheric H₂O increase (in ppb/yr). The age of air is considered and the calculations are performed for 1978–1995 as entrance of the air into the stratosphere, the period of the H₂O trend derived from the SPARC report (see text for details). (b) As Figure 5a but x axis shows C_{rel} , the relative contribution of CH₄ oxidation to the stratospheric H₂O 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 H₂O trend are attributed to N₂O mixing ratio levels. This results only in a negligible effect on our calculation, since the H₂O trend has a weak vertical gradient. Furthermore, supported by the normalization of the N₂O mixing ratios, no significant trend of the N₂O 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_{abs} and C_{rel} , Table 6 summarizes the fraction of CH₄ oxidation to the H₂O trend, determined on the basis of different assumptions. First, the difference between the tropospheric and stratospheric CH₄ 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 N₂O normalization. C_{abs} and C_{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 CH₄ mixing ratio (and, thus, the formation of H₂O) on its way from the troposphere to different altitudes in the stratosphere has to be investigated.

[39] Since the stratospheric N₂O trend is estimated from the tropospheric trend, its incorporation in the calculation is more ambiguous. However, the N₂O mixing ratios must be corrected for this trend as the actual stratospheric CH₄ mixing ratio is growing faster than it would appear relative to uncorrected N₂O values.

[40] Therefore, from our study the best estimate for the contribution of CH₄ to the stratospheric H₂O increase (case 1 in Table 6) is derived, by including the age correction and the N₂O normalization. For the highest altitude (140 ppb N₂O, 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 CH₄ 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 CH₄ increase and the CH₄ increase at 20 hPa (140 ppb N₂O level) from 1978–1995 results in an H₂O increase due to CH₄ increase of 13.2 ± 2.0 ppb/yr. This corresponds to $29.2 \pm 4.4\%$ of the mean H₂O 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 CH₄ increase during the period 1978–1998 with the mean H₂O increase, assuming that the H₂O trend did not change after 1995 (as year of entrance of the air into the stratosphere). The H₂O trend itself has a relative high uncertainty. Consideration of the 95% confidence interval of the H₂O trend suggests that stratospheric CH₄ contributes to the H₂O trend by 22.5–41.8%.

[42] Without considering the age of air, at 20 hPa (140 ppb N₂O) from 1980 until 2000 (the period of the SPARC H₂O trend) only 7.2 ± 2.3 ppb/yr H₂O ($16.0 \pm 5.2\%$ of the mean stratospheric water vapor increase) can be attributed to the CH₄ trend (case 2, Table 6). These low values are generated artificially in the calculation, while comparing young tropospheric air, in which the CH₄ trend has already slowed down, with older stratospheric air, which stems from the troposphere in times when there still was a strong increase in CH₄.

[43] Another uncertainty arises from the correction of the stratospheric N₂O mixing ratios for the tropospheric N₂O trend. To estimate this potential error, the calculations are performed also without a correction of the N₂O mixing ratio. Considering of the age of the air (case 3, Table 6) results in a contribution of CH₄ to the stratospheric H₂O increase at 20 hPa of 15.5 ± 2.0 ppb/yr, corresponding to $34.4 \pm 4.5\%$ of the mean stratospheric H₂O increase (or 26.5–49.2% for the 95% confidence interval of the stratospheric H₂O increase). Because of this uncertainty in the stratospheric N₂O trend, the CH₄ contribution to the mean H₂O 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 CH₄.

[45] For lower altitudes, the relative contribution of CH₄ to the water trend is less important. In the lower stratosphere at 90 hPa (280 ppb N₂O level) only a little amount of CH₄ is oxidized to water already. The increased CH₄ concentration in this region can only account for $1.6 \pm 4.7\%$ up to $10.7 \pm 4.7\%$ (without correction for N₂O) 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 H₂O 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 CH₄ trend becomes apparent in the stratospheric H₂O trend as well.

[46] Since the cause for the observed increase of stratospheric H₂ is not yet understood, its contribution to the trend in H₂O remains ambiguous. The linear fit indicates a small positive stratospheric H₂ trend of 1.5 ± 0.7 ppb/yr. If the additional H₂ originates from an increased tropospheric H₂ 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 H₂O. If in contrary the H₂ increase originates from incomplete CH₄ oxidation, then actually the existence of this H₂ diminishes the possible contribution of CH₄ to the H₂O trend by $3.3 \pm 1.6\%$. However, at present the contribution of H₂ to the stratospheric H₂O trend is negligible. This situation could change in the future. The potential for strong increases of H₂ in the atmosphere due to extensive use of the hydrogen technology and its impact on the stratospheric H₂O 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 CH₄ and (since 1988) of H₂. In the period from 1978 to 2003, stratospheric CH₄ 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 ± 32 ppb, at 23 km 159 ± 21 ppb, at 26 km 140 ± 34 ppb and at 30 km 111 ± 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 CH₄ trend, whose growth rate decreased as well. Nevertheless, we need further measurements to study, whether the stratospheric CH₄ 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 H₂O record. This allows inferring the impact of CH₄ on the stratospheric H₂O trend. To optimize the calculation, the age of air has to be considered and the trend of stratospheric N₂O has to be corrected. By incorporating these effects, the best estimate from our study shows that at 20 hPa the CH₄ increase can account for an H₂O increase of 13.2 ± 2.0 ppb/yr. With this result, we are able to calculate the relative contribution of CH₄ to the stratospheric H₂O increase more precisely than in previous studies. Referring to the stratospheric H₂O trend from Boulder and to the best estimate from our study only 25–34% of the mean stratospheric H₂O increase can be explained by the CH₄ increase. This diminishes the estimate of the contribution of CH₄ to the stratospheric H₂O increase from previous studies of at maximum 50% for this contribution to a considerable degree.

[49] We also find a small positive stratospheric H₂ trend of 1.5 ± 0.7 ppb/yr in the 90–10 hPa range. If this additional H₂ originates from incomplete oxidation of stratospheric CH₄, then the contribution of CH₄ to the mean stratospheric H₂O increase would be reduced by $3.3 \pm 1.6\%$. If it, in contrast stems from an increase in tropospheric H₂, then it does not influence the stratospheric H₂O increase. However, the impact of H₂ is minor. Together, CH₄ and H₂ cannot account for more than 34% of the mean stratospheric H₂O trend. With our results, compared to previous studies, the main fraction of the stratospheric H₂O 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 H₂O increase is partly caused by the decline of the CH₄ increase.

Appendix A: Calculation of the CH₄ Increase

[51] The second-order polynomial fits of the measured time series of CH₄ 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 CH₄(t, z) is CH₄ mixing ratio and z is altitude.

[52] For calculating the CH₄ 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 CH₄

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

[53] However, since in our case, we calculate the difference between CH₄ 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 ΔCH_4 is ΔCH_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 CH₄ mixing ratio and this value is independent from chemical loss reactions of CH₄ in the stratosphere during the aging of the air.

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- 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)