

Balloon-borne in situ measurements of stratospheric H₂O, CH₄ and H₂ at midlatitudes

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Abstract. Using a new Lyman α hygrometer, balloon-borne measurements of H₂O were performed on September 20, 1993 at midlatitudes (43° N). A cryogenic whole air sampler to measure CH₄ and H₂ amongst other long-lived trace gases was operated on the same payload. The profile of the water vapor mixing ratio showed a well-pronounced hygropause of 4 ppmv at $\theta = 420$ K increasing to 6.0 ppmv at $\theta = 920$ K. For $\theta > 400$ K, total hydrogen $\Sigma\text{H}_2 = \text{H}_2\text{O} + 2\cdot\text{CH}_4 + \text{H}_2$ appeared to be constant at a mean value of 7.72 ± 0.13 ppmv; the overall accuracy of this value is 0.65 ppmv. From the correlation functions of CH₄ with H₂ and H₂O the water vapor yield from methane oxidation is determined with high precision to be 1.975 ± 0.030 . The globally averaged water vapor mixing ratio entering the stratosphere from the troposphere was found to be 3.9 ± 1.0 ppmv. Intercomparison with H₂O and CH₄ profiles obtained nearby from the Halogen Occultation Experiment (HALOE) on board the UARS satellite showed good agreement within the experimental errors.

1. Introduction

The major hydrogen-containing species in the stratosphere are water vapor, methane, and molecular hydrogen. Their stratospheric distribution is determined by exchange of air masses with the troposphere and the mesosphere, transport processes within the stratosphere and photochemistry [e.g., *Ehhalt and Tönnissen*, 1979; *Le Texier et al.*, 1988; *Rosenlof et al.*, 1997]. Regionally, the distribution of water vapor may be determined in addition by condensation and subsequent sedimentation processes as observed in the Antarctic polar vortex [e.g., *Kelly et al.*, 1989].

In the stratosphere above approximately 450 K potential temperature, mass transport is controlled by nonlocal dynamical processes. *Rosenlof et al.* [1997] denoted this part of the stratosphere as the “overworld” while *Holton et al.* [1995] used this term to describe the part of the stratosphere whose isentropes no longer cross the tropopause, that is, above approximately 380 K. In the following, “overworld” is used according to the notation of *Rosenlof et al.* Here, above 450 K, the seasonal cycle of CO₂ mixing ratios has been attenuated enough that residence times of the air of several years can be determined from measurements of CO₂ [e.g., *Schmidt and Khedim*, 1991]. In this region the chemical lifetime of CH₄ and H₂ becomes comparable to the residence time of the air, and thus oxidation of CH₄ and H₂ as a source of stratospheric H₂O determines the vertical distribution of hydrogen species: Water vapor mixing ratios increase with

altitude, while mixing ratios of methane decrease. At higher altitudes, in the mesosphere, photodissociation of H₂O becomes dominant and the water vapor mixing ratio again decreases. The oxidation of CH₄ is initiated by its reactions with O(¹D), OH, and to a lesser extent Cl, forming formaldehyde and finally H₂O, H₂, CO and HO_x (for a more detailed description see *Ehhalt and Tönnissen* [1979] and *Le Texier et al.* [1988]). The competition between H₂O and H₂ from the oxidation of methane depends mainly on the OH concentration, which favors the production of H₂O from formaldehyde at the expense of H₂. Molecular hydrogen itself reacts with O(¹D), OH and Cl with reaction rates comparable to those for methane and has therefore to be considered in calculations of the total hydrogen budget. Transport processes on global scales result in vertical gradients of CH₄, H₂O, and H₂ varying with latitude and season as observed, for example, by *Rosenlof et al.* [1997]. However, the mixing ratio of total hydrogen, defined as

$$\Sigma\text{H}_2 = 2\cdot\text{CH}_4 + \text{H}_2\text{O} + \text{H}_2 \quad (1)$$

is assumed to be conserved in the “overworld” in the absence of local sources and sinks. However, recent evaluation of data of the Halogen Occultation Experiment (HALOE) on the Upper Atmosphere Research Satellite (UARS) showed peak values up to 8 ppmv H₂O in parts of the mesosphere, indicating a violation of conservation of total hydrogen in the middle atmosphere [*Summers et al.*, 1997].

At lower altitudes the hydrogen budget is strongly influenced by input of water vapor from the troposphere, which occurs predominantly in the tropics. In previous studies, the phenomenon of the existence of the tropical hygropause has been attributed to dehydration in convective systems in connection with overshooting cloud turrets [e.g., *Danielsen*, 1993]. The H₂O mixing ratio entering the stratosphere is determined by the temperature at the tropical tropopause, that is, at $\theta \approx 380$ K, and thus varies with season. Analyzing satellite data, *Mote et al.* [1996] found that in the

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tropics this seasonal signature in the H_2O mixing ratio propagates upward well above $\theta \approx 450$ K. A seasonal cycle of H_2O and CO_2 was also found at midlatitudes in this part of the stratosphere [e.g., McCormick *et al.*, 1993; Hints *et al.*, 1994; Boering *et al.*, 1995, 1996; Rosenlof *et al.*, 1997]. Effective isentropic transport out of the tropics in the lowest few kilometers of the stratosphere on timescales of a few months, which is also confirmed by wind field analysis [Chen *et al.*, 1994; Waugh, 1996] is believed to be the reason for these observations. Following the notation of Rosenlof *et al.* [1997], the region between $\theta = 380$ K and 450 K is referred to as the “tropically controlled transition region”.

Among other recent findings, the study of Mote *et al.* [1996] implies that exchange is effective more or less continuously at all tropical longitudes, which is in contrast to the hypothesis that troposphere-stratosphere exchange occurs predominantly in tropical regions with the lowest tropopause temperature driven by convection. Both approaches certainly result in a different mean input of H_2O into the stratosphere, owing to seasonal and regional variability of temperatures. Unfortunately, existing data sets of hydrogen species do not yield a consistent picture of the absolute amount of total hydrogen in the stratosphere.

At middle and high latitudes, one has to consider that below a potential temperature surface of $\theta \approx 380$ K, in the “lowermost stratosphere” or the stratospheric part of the “middleworld”, isentropic exchange between the troposphere and stratosphere can occur [e.g., Holton *et al.*, 1995]. Thus highly variable and high mixing ratios of H_2O up to 40 ppmv are observed in the lowest part of the stratosphere [e.g., Dessler *et al.*, 1995; Pan *et al.*, 1997].

Various in situ and remote instruments exist to measure stratospheric water vapor from different platforms. However, few in situ data exist for the midlatitude “overworld” at altitudes which can be probed only by balloons. In particular, Lyman α fluorescence hygrometers have been used on balloons very rarely in the past [Kley *et al.*, 1979; Weinstock *et al.*, 1990]. Systematic differences between different measurement techniques have been identified but not yet understood [e.g., World Meteorological Organization (WMO), 1986; Dessler *et al.*, 1994; Vömel *et al.*, 1995] demonstrating the need for intercomparative studies. Further, measurements of H_2 are very limited; thus most recent studies of total hydrogen in the stratosphere are based on CH_4 and H_2O measurements only. To our knowledge, only one recent study using in situ CH_4 and H_2O data in the middle stratosphere has been reported, but it was for high-latitude winter [Engel *et al.*, 1996].

2. Experiment

The combined balloon payload for this study consisted of an in situ hygrometer, a cryogenic whole air sampler, and an electrochemical concentration cell (ECC) ozone sonde. The fast in situ stratospheric hygrometer (FISH) [Zöger *et al.*, this issue] is based on the photofragment fluorescence technique as first developed by Kley and Stone [1978] and Bertaux and Delannoy [1978]. Water vapor is dissociated by Lyman α radiation (121.6 nm) emitted by a hydrogen plasma light source [Woyke *et al.*, 1995] forming electronically excited OH and H. The excited OH relaxes to its ground state either by fluorescence or quenching. The fluorescence radiation is

detected with a photomultiplier tube through a narrow band filter with maximum transmittance at 313 nm and full width at half maximum of 12 nm. The background signal, which is mainly caused by lamp stray light, and the intensity of the Lyman α radiation are monitored and taken into account in the data processing. Since solar UV stray light can strongly affect the measurement, the inlet of the instrument is designed as a light trap. In order to avoid wall contaminations, all inner surfaces are made of polished and gold-plated stainless steel. A constant airflow through the instrument of 3–5 L/s is maintained by a modified turbomolecular pump.

The instrument used for this study is the prototype version of FISH, whose basic design is described by Mörschel *et al.* [1991] with several modifications. For a more detailed technical description of the instrument and more recent improvements the reader is referred to Zöger *et al.* [this issue]. For the flight discussed below, the high background signal caused by the light source and the nonoptimized fluorescence cell of the prototype FISH reduced the precision of the water vapor measurement to 0.5 ppmv for a 90 s integration time, which is far below the precision achieved using the improved hygrometers [Zöger *et al.*, this issue].

While Mörschel *et al.* [1991] calibrated the fluorescence hygrometer in flight using the tropospheric absorption signal, a new calibration bench has been developed for this study: FISH is calibrated in the laboratory preflight and postflight using a dynamic dilution system. The generated H_2O mixing ratio is traced to a frost point hygrometer reference [Zöger *et al.*, this issue]. Thus calibrations down to a few ppmv can be performed. From the known systematic errors of the calibration the accuracy of the instrument is calculated to be ± 0.43 ppmv for stratospheric water vapor mixing ratios.

With the cryosampler, whole air samples were taken and subsequently analyzed in the laboratory using gas chromatography. In addition to other long-lived atmospheric trace gases like CFCs and N_2O , the mixing ratios of CH_4 and H_2 can be determined by this technique. The calibration is traced to a primary standard provided by Rasmussen and Khalil [1984]. For CH_4 and H_2 the agreement with this standard is determined to be better than 1% and 5%, respectively. The precision is 1% for CH_4 and better than 5% for H_2 , resulting in a total accuracy of a single measurement of 2% and 7%, respectively. For a more detailed description of the cryosampling technique see Schmidt *et al.* [1987].

Simultaneous measurements of water vapor, methane, hydrogen and other tracers were performed on September 20, 1993, on a balloon launched from Aire sur l'Adour (France; 43.7°N, 0.1°W) at the CNES (Centre National d'Etudes Spatiales) launch facility. The measurements were performed during a valve-controlled descent at a rate of 3–5 m/s in order to avoid contamination by balloon outgassing.

3. Results and Discussion

3.1 Profiles of Water Vapor, Methane, Molecular Hydrogen and Ozone

Figure 1 shows the vertical profiles of the water vapor, methane and molecular hydrogen mixing ratio as measured on September 20, 1993. In the upper troposphere the H_2O mixing ratio shows a strong gradient. The thermal tropopause is situated at a potential temperature of $\theta = 350$ K (13 km, 173

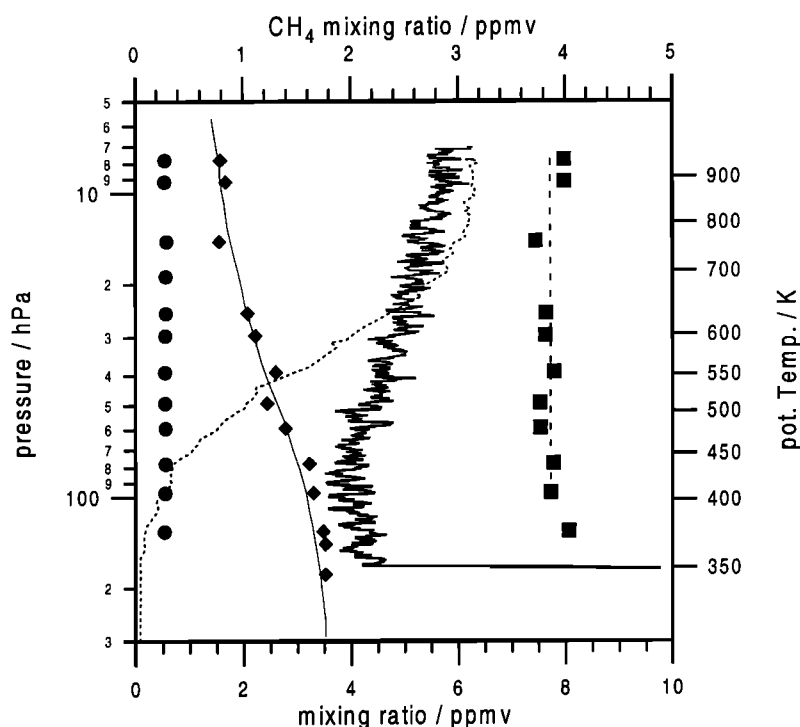


Figure 1. Simultaneously measured mixing ratio of CH_4 (diamonds) and H_2 (circles) obtained from cryosampler measurements and H_2O (thick solid line) by FISH. From the data above the hygropause, total hydrogen (squares) has been calculated, yielding a mean value of $\Sigma\text{H}_2 = 7.72 \pm 0.65$ ppmv. The thin line denotes the average profile from more than 10 summertime profiles of methane. The dotted line is the ozone mixing ratio (bottom scale) as measured by an ECC sonde on board the gondola.

hPa) with 8 ppmv water vapor mixing ratio. Above the tropopause it decreases rapidly to 5.0 ppmv and then further to a minimum, defining the hygropause, of 4.0 ppmv at $\theta = 420$ K (17 km, 87 hPa). Between the hygropause and the ceiling altitude at $\theta = 920$ K (33 km, 7.5 hPa) the mixing ratio of H_2O increases due to CH_4 oxidation to a value of 5.5–6.0 ppmv. Correspondingly, the CH_4 mixing ratio decreases with altitude from its tropospheric value of 1.74 ppmv down to 0.79 ppmv at $\theta = 920$ K. The mixing ratio of H_2 is nearly constant in the stratosphere at 0.55 ppmv with $\text{STD} \pm 0.01$ ppmv.

When comparing the CH_4 profile to the average profile determined from more than 10 balloon profiles in the summer (thin solid line in Figure 1) a couple of slight but significant deviations can be observed: The layer around 770 K shows a rather low mixing ratio of CH_4 , and lamination is also observed in the region of 500–550 K. The same structure is also visible in the vertical profiles of other tracers measured simultaneously, such as N_2O and CF_2Cl_2 (not shown). Within the precision of the hygrometer (Figure 1 shows 90 s running average values corresponding to 0.5 ppmv precision), no corresponding significant structure is resolved in the water vapor profile above the hygropause. Lamination was also not found in the profile of the ozone mixing ratio measured by an onboard ECC sonde (Figure 1, dotted line). This observation agrees with climatological studies by, for example, Reid and Vaughan [1991] that the occurrence of ozone laminae at midlatitudes has a minimum in autumn.

3.2 Total Hydrogen

From the simultaneous in situ measurements of CH_4 and H_2 by the cryosampler and H_2O using FISH, total hydrogen is calculated using (1). For this purpose, H_2O values are averaged over the same time period over which the atmosphere was probed by the cryosampler. Within experimental error, total hydrogen remains constant above $\theta = 400$ K, that is, in the overworld and the hygropause region (Figure 1). Therefore in the major part of the “tropically controlled transition region” the same value is observed as in the “overworld”, a hint that the air masses might be well mixed at these altitudes and no longer show a signature of the seasonal variation from the tropics. However, from this single measurement this observation and its consequences cannot be generalized.

A mean value of stratospheric total hydrogen, $\Sigma\text{H}_2 = 7.72 \pm 0.13$, is determined for $\theta > 400$ K. This error consists of the 2σ precision of the mean value (95% confidence interval) considering Student’s *t* distribution. Including the systematic errors of the CH_4 , H_2 and H_2O measurements, a total uncertainty $\sigma = \pm 0.65$ of ΣH_2 is calculated. Since measurements of molecular hydrogen are rare, the quantity $2\cdot\text{CH}_4 + \text{H}_2\text{O}$ is often cited in the literature. For comparison with such data the mean value of $2\cdot\text{CH}_4 + \text{H}_2\text{O} = 7.17 \pm 0.13$ ppmv (including systematic errors: ± 0.62 ppmv) is calculated for our data set. This value is in good agreement with most of the recent in situ and satellite measurements of $2\cdot\text{CH}_4 + \text{H}_2\text{O}$ listed in Table 1. Since total hydrogen is expected to be

Table 1. Values of $2\text{CH}_4 + \text{H}_2\text{O}$ Measured in the Northern Hemisphere in the Last Decade Using in Situ and Remote Sensing Techniques

$2\text{CH}_4 + \text{H}_2\text{O}$, ppmv	Instrument ($\text{H}_2\text{O}/\text{CH}_4$)	Platform	Reference
7.17 ± 0.62	FISH / cryosampler	balloon	this work
6.91 ± 0.15	HALOE V18	UARS	this work
7.24 ± 0.44	ATMOS	shuttle	Abbas <i>et al.</i> [1996]
6.91 ± 0.41	frost point / cryosampler	balloon	Engel <i>et al.</i> [1996]
6.6 - 7.6	NOAA-AL Lyman α / N_2O TDL	ER-2	Kelly <i>et al.</i> [1990]
7.6 ± 0.6	Harvard Lyman α / ALIAS	ER-2	Dessler <i>et al.</i> [1994]

FISH denotes fast in situ stratospheric hygrometers; HALOE denotes Halogen Occultation Experiment; ATMOS denotes Atmospheric Trace Molecule Spectroscopy Experiment; TDL denotes tunable diode laser; and ALIAS denotes Aircraft Laser Infrared Absorption Spectrometer.

conserved and the H_2 mixing ratio can be assumed as constant to first order in the middle stratosphere, measurements of $2\text{CH}_4 + \text{H}_2\text{O}$ are suitable to compare different instruments at different locations and times.

HALOE measurements of CH_4 and H_2O from a nearby overpass on the same day are presented below. They yield $2\text{CH}_4 + \text{H}_2\text{O} = 6.91$ ppmv (retrieval software V18, $\text{STD} = \pm 0.15$ ppmv), in agreement with the FISH value within the error bars. Also, data obtained in November 1994 by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment aboard the space shuttle [Abbas *et al.*, 1996] do not show significant differences from $2\text{CH}_4 + \text{H}_2\text{O}$ derived by our balloon data.

Engel *et al.* [1996] calculated the mixing ratio of $2\text{CH}_4 + \text{H}_2\text{O}$ to be 6.91 ± 0.41 ppmv analysing balloon-borne in situ measurements of H_2O by a frost point hygrometer [Ovarlez and Ovarlez, 1994] and methane by the cryosampler. These data have been obtained in the Arctic winter, and consequently the individual profiles of CH_4 and H_2O show different vertical distributions due to subsidence inside the polar vortex [Schiller *et al.*, 1996]. However, no significant difference of $2\text{CH}_4 + \text{H}_2\text{O}$ could be derived for data inside and outside the vortex. Since CH_4 was measured with the same instrument as the one used in this study, the agreement is a strong indication that H_2O measurements by FISH compare well with those of the frostpoint hygrometer.

From airborne measurements during the Airborne Arctic Stratospheric Experiment I mission in 1989 using the National Oceanic and Atmospheric Administration Aeronomy Laboratory (NOAA-AL) Lyman α hygrometer and CH_4 mixing ratios derived from the correlation with N_2O , mixing ratios of $2\text{CH}_4 + \text{H}_2$ between 6.6 to 7.6 ppmv can be calculated from 'residual water' profiles shown by Kelly *et al.* [1990] for $\theta > 450$ K; at 400 - 450 K, even higher values up to 8.2 have been observed. A somewhat higher value of 7.6 ± 0.6 ppmv in the "overworld" was measured by Dessler *et al.* [1994] during the Stratospheric Photochemistry Aerosols and Dynamics Expedition (SPADE) employing the Harvard Lyman α hygrometer and a tunable diode laser spectrometer to measure CH_4 . During this campaign, water vapor was simultaneously measured by the NOAA-AL hygrometer, yielding approximately 15% lower values for H_2O [Dessler *et al.*, 1994].

From the $\text{CH}_4 - \text{H}_2\text{O}$ correlation at middle and high latitudes the average input of H_2O into the stratosphere can be determined [e.g., Engel *et al.*, 1996]. Using the intercept of

the linear fit of the $\text{CH}_4 - \text{H}_2\text{O}$ correlation of 7.3 ± 1.0 ppmv and assuming a tropospheric methane mixing ratio of 1.7 ppmv for 1993 [Dlugokencky *et al.*, 1994; Khalil *et al.*, 1993], the mean input of water vapor is calculated to be 3.9 ± 1.0 ppmv. The relatively large uncertainty is mainly caused by the small number of data points. However, this value is in good agreement with previous calculations, for example, that of Engel *et al.* [1996] of 3.61 ± 0.28 ppmv and reviewed data therein.

3.3 The Water Vapor Yield

To first order, the oxidation of one CH_4 molecule produces two molecules of H_2O . However, Le Texier *et al.* [1988] showed that the so-called net chemical yield factor

$$\beta = -\Delta\text{H}_2\text{O}/\Delta\text{CH}_4 \quad (2)$$

should vary with altitude, latitude, and season in the stratosphere and could be slightly less than or greater than 2, depending on the competing effects of the chemical production and destruction of H_2 and the intermediate species CH_2O . Values of β less than 2 are expected in the tropical and midlatitude lower stratosphere and values exceeding 2 between 40 and 50 km altitude. In the polar winter, downward transport of mesospheric hydrogen-rich air is also expected to influence the ratio of $\Delta\text{H}_2\text{O}$ to ΔCH_4 .

In Figure 2a, H_2O data are plotted versus those of CH_4 for this flight (diamonds). Assuming a linear correlation between methane and water vapor, the water vapor yield from methane oxidation can be evaluated by linear regression. A linear fit of the measured mixing ratios above the hygropause yields a slope of $\Delta\text{H}_2\text{O}/\Delta\text{CH}_4 = -2.10 \pm 0.83$. Data points with major deviations from the regression line are those corresponding to the laminae features in the CH_4 profile as discussed above. The large experimental error of the slope is caused by the scatter of the data due to the high background signal combined with the low number of data points of the cryosampler. Considering the large error, an interpretation of β from the $\text{H}_2\text{O}/\text{CH}_4$ correlation is not useful.

As stated above, the only long-lived products of methane oxidation are hydrogen and water. Thus in regions of high methane oxidation rates, indicated by a significant decrease of methane with height, deviations of the water vapor yield should be visible in the hydrogen profile. Analyzing the correlation of the simultaneously measured CH_4 and H_2 mixing ratios allows a more precise evaluation of β . The

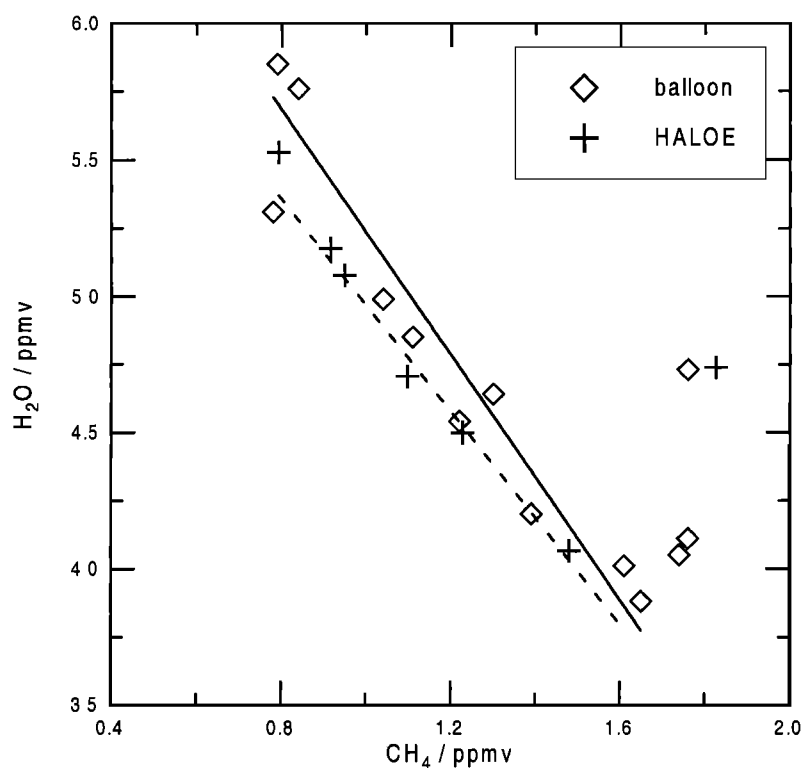


Figure 2a. Correlation of water vapor and methane measured on September 20, 1993 by the FISH/cryosampler (diamonds, solid regression line) and by HALOE (pluses, dashed regression line).

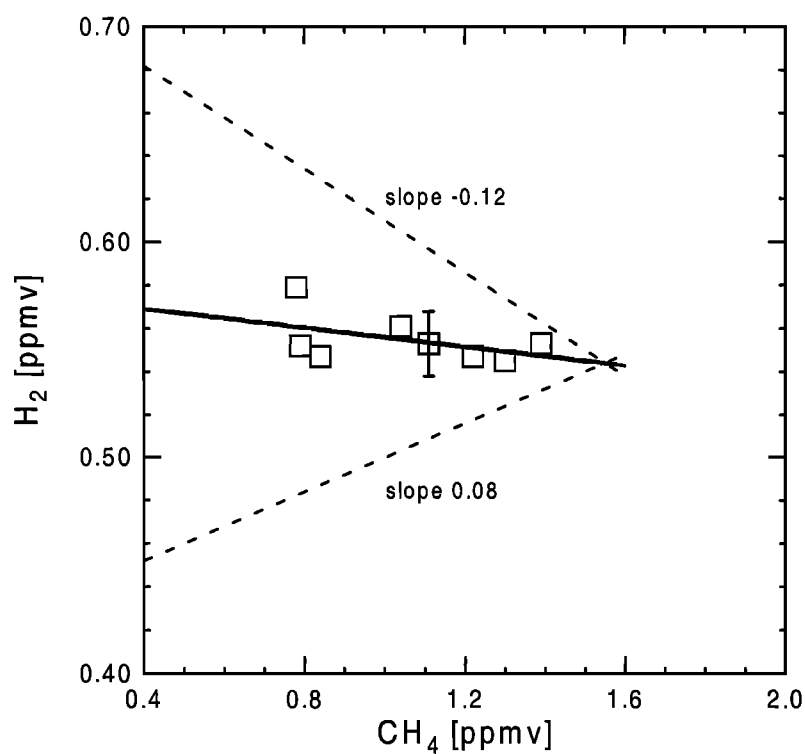


Figure 2b. Correlation of methane and hydrogen measured on September 20, 1993, yielding a slope of -0.018 ± 0.028 . Assumed H_2 gradients corresponding to deviations from β of 0.1 are drawn as dashed lines.

linear regression of the H_2/CH_4 correlation yields a slope of $\Delta\text{H}_2/\Delta\text{CH}_4 = -0.018 \pm 0.028$. Assuming total hydrogen to be conserved in equation (1), equation (2) can be transformed to

$$\beta' = \Delta\text{H}_2/\Delta\text{CH}_4 + 2 \quad (2')$$

Since the mixing ratios of other hydrogen-containing species as $\text{X} = \text{HCl}$, HF and HNO_3 are considerably lower than that of H_2 , they do not need to be considered in the approximation of equation (1). However, the ratios $\Delta\text{X}/2\Delta\text{CH}_4$ may become of the same magnitude as $\Delta\text{H}_2/\Delta\text{CH}_4$ due to the small gradient of the H_2 mixing ratio. Thus we extend equation (2')

$$\beta'' = \Delta\text{H}_2/\Delta\text{CH}_4 + \Sigma\Delta\text{X}/2\Delta\text{CH}_4 + 2 \quad (2'')$$

The gradients of the other hydrogen-containing substances HCl and HF can be obtained from HALOE measurements on the same day. HNO_3 is calculated from the N_2O mixing ratio measured by the cryosampler using the $\text{NO}_y/\text{N}_2\text{O}$ correlation given by *Kondo et al.* [1996] and the mixing ratio of $\text{NO}+\text{NO}_2$ measured by HALOE. From these data a maximum gradient of $\Sigma\Delta\text{X}/2\Delta\text{CH}_4 = -0.007 \pm 0.002$ is derived. Further hydrogen-containing species like H_2SO_4 , CH_2O , OH and H_2O_2 are assumed to show stratospheric mixing ratios well below 1 ppbv and can thus be neglected.

In summary, β'' for the flight day is calculated to be 1.975 ± 0.030 . Thus both methods yield consistent results, but the analysis of the H_2/CH_4 correlation is more accurate. The high sensitivity of this method is demonstrated in Figure 2b: Assumed H_2 gradients corresponding to deviations from β'' of 0.1 (dashed lines) by far exceed the precision of the hydrogen measurement.

A recent evaluation of global HALOE data yields a range from 1.6 to 2.4 for average seasonal values of β [*Remsberg et al.*, 1996] between 1 and 60 hPa. For the middle stratosphere at midlatitudes during fall, $\beta = 1.8 - 2.0$ is determined in agreement with the balloon measurements presented. The mean value of β derived from four Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) missions is calculated to 2.05 ± 0.16 for the middle stratosphere [*Abbas et al.*, 1996]. *Dessler et al.* [1994] reanalyzed a series of balloon borne measurements of H_2 and CH_4 by *Pollock et al.* [1980] and *Fabian et al.* [1981] obtained in summer and early fall which show that β' is close to 2.0 in the midlatitude lower and middle stratosphere. A value of $\beta = 1.82 \pm 0.21$ was determined by *Engel et al.* [1996], but for the Arctic winter.

Comparison with SPADE measurements in the lower midlatitude stratosphere is ambiguous since different data sets obtained from the same aircraft yield significantly different β between 1.3 and 2.0 [*Dessler et al.*, 1994]. These differences originate from differences in both the H_2O and CH_4 data obtained by different instruments and are presumably still under investigation.

3.4 Satellite Intercomparison

The HALOE instrument on board UARS measured at a tangent point near 48°N 7°W the same day close to the balloon launch site at 44°N 0°W , permitting a comparison of both measurement techniques. Figure 3a shows the H_2O vertical profiles measured by HALOE using retrieval software V18 (J. M. Russell III, private communication, 1997) and data obtained by FISH on September 20, 1993. Within the combined error bars both measurements show good

agreement. Minor discrepancies only occur at lower altitudes close to the tropopause, that is, below 150 hPa, where the precision of the HALOE instrument decreases. Between 20 and 50 hPa, HALOE data of H_2O show a structure that is neither visible in the FISH data nor obviously correlated with the CH_4 profiles. The overall agreement between both measurements indicates that biases of earlier HALOE retrievals [e.g., *Remsberg et al.*, 1996] have been corrected successfully.

CH_4 data of this day measured by HALOE and the balloon-borne cryogenic whole air sampler have been compared previously by *Park et al.* [1996] but still using retrieval software V17. Both profiles agreed well within the error bars. However, HALOE CH_4 data tended to be slightly (by 10%) lower than those obtained by the cryosampler. Figure 3b shows the updated data using the V18 retrieval, which does not cause a major change of the CH_4 determination, yielding similar results of the comparison as those given by *Park et al.* [1996]. Furthermore, the HALOE profile looks smoother, not reproducing the laminae observed by the balloon.

As already mentioned, the mean values of $2\text{CH}_4 + \text{H}_2\text{O}$ derived from both data sets agree even better than expected from the accuracy of both measurements. The variance from the mean values is of comparable magnitude.

Figure 2a also shows the H_2O to CH_4 correlation of the HALOE profile yielding $\beta = 2.09 \pm 0.18$. In comparison with the balloon data, the scatter is lower. However, the scatter of the balloon data originates mainly from those data with the laminae structure in the CH_4 mixing ratio, which either may not be significantly resolved by the H_2O measurements or may reflect real atmospheric variation in the composition of such laminae. Since similar laminae have not been observed or resolved in the HALOE profile, a further evaluation of the intercomparison is ambiguous.

4. Summary

In summary, the discussion of the hydrogen budget derived from the measured midlatitude profile yields a consistent picture for the lower and middle stratosphere. Agreement with other measurements using in situ as well as remote sensing techniques and with other studies of the distribution of hydrogen species and their partitioning is found. In particular, consistent results were obtained with data from the HALOE satellite experiment using profiles of H_2O and CH_4 measured close to the balloon observations for direct intercomparison.

The measurements presented confirm the conservation of total hydrogen in the "overworld" of the stratosphere at midlatitudes and even below down to 400 K. A mixing ratio of $2\text{CH}_4 + \text{H}_2\text{O}$ of 7.2 ± 0.6 ppmv is derived. From the linear correlation of methane and water vapor, the seasonal and global mean mixing ratio of water vapor entering the stratosphere is estimated to be 3.9 ± 1.0 ppmv. The values of $2\text{CH}_4 + \text{H}_2\text{O}$ and the average input derived from our balloon measurements are between the highest and lowest data reported in the literature (see Table 1) and agree within the combined error bars with all these data sets. However, a more accurate determination of H_2O along with an investigation of the causes for the observed discrepancies between extreme data sets is required in the future for appropriate determination of the stratospheric hydrogen budget and its determining processes.

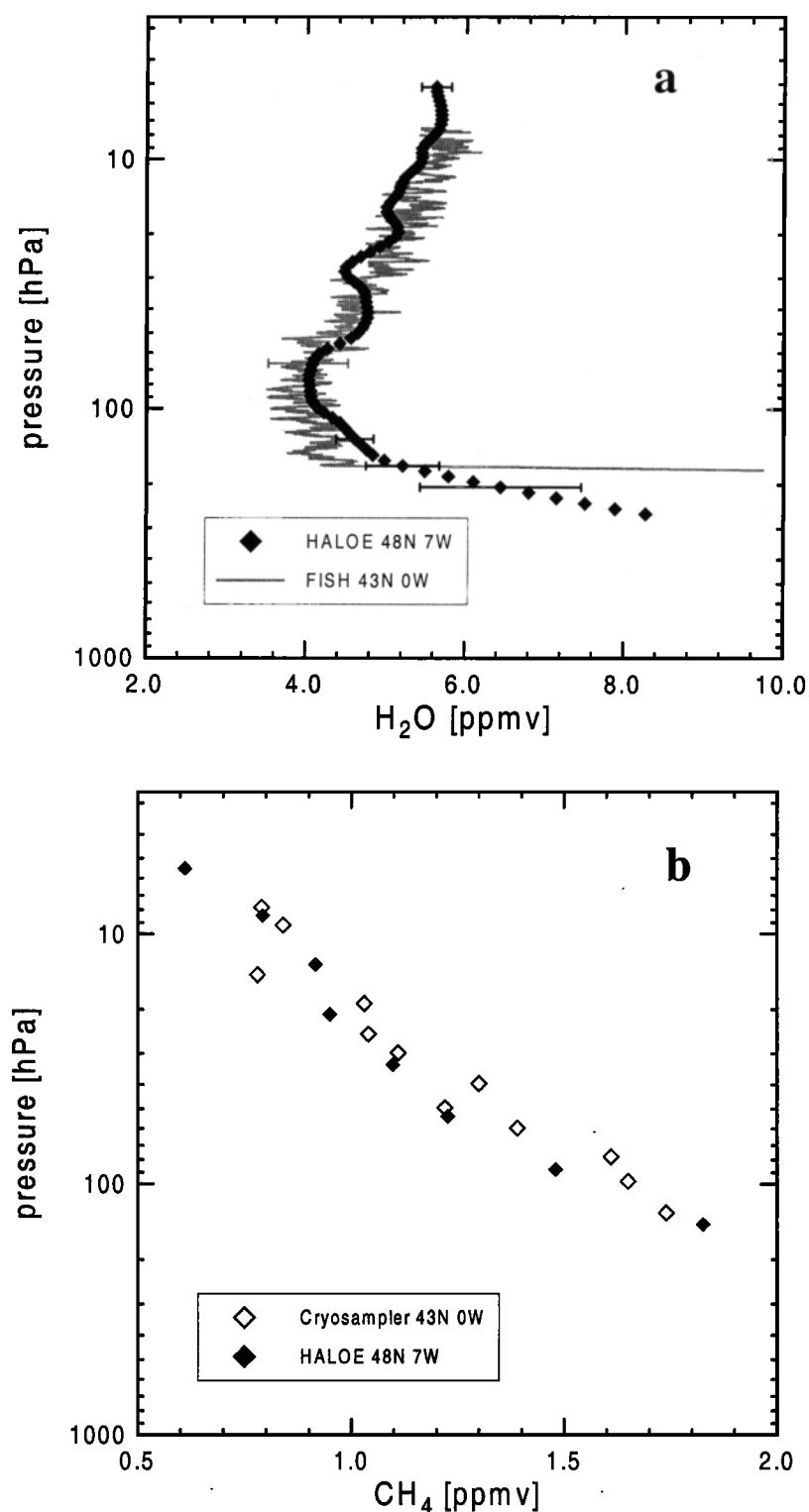


Figure 3. Intercomparison of balloon-borne FISH/cryosampler and HALOE data of (a) H_2O and (b) CH_4 measured the same day at close locations (courtesy of J. Russell III). The error bars denote the precision of both measurements. For H_2O , 300 m resolution data of HALOE are plotted without averaging over the field of view, thus reducing the vertical resolution to > 1 km.

Comparison of the analysis using the correlation between CH_4 and H_2O or H_2 , respectively, shows that due to the higher precision of the H_2 measurement the H_2/CH_4 correlation is much more sensitive to variations of the water vapor yield factor β than the $\text{H}_2\text{O}/\text{CH}_4$ correlation. From the presented measurements, $\beta = 1.975 \pm 0.030$ is derived for the middle stratosphere. This number agrees with the value of 2 predicted by model calculations for this part of the atmosphere [Le Texier et al., 1988] and other measurements.

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