

## Secular trend and seasonal variability of the column abundance of N<sub>2</sub>O above the Jungfraujoch station determined from IR solar spectra

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**Abstract.** Infrared solar spectra recorded at the International Scientific Station of the Jungfraujoch (3580 m altitude), Switzerland, in 1950–1951 and from 1984 to 1992 have been analyzed to determine vertical column abundances of nitrous oxide (N<sub>2</sub>O) above the station. The best fit to the relatively dense set of measurements made between 1984 and 1992 indicates a mean exponential rate of increase equal to  $0.36 \pm 0.06\% \text{ yr}^{-1}$  ( $1 \sigma$ ) and a seasonal modulation of 7.2% peak to peak, the minimum occurring at the end of the winter and the maximum in early September. The column abundances for April of the years 1951, 1984, and 1992 were found equal to  $3.49 \times 10^{18}$ ,  $3.76 \times 10^{18}$ , and  $3.87 \times 10^{18}$  molecules cm<sup>-2</sup>, respectively; they translate into N<sub>2</sub>O concentrations at the altitude of the Jungfraujoch equal to 275, 296, and 305 parts per billion by volume. These results indicate that the exponential rate of increase for 1951–1984 was equal to  $0.23 \pm 0.04\% \text{ yr}^{-1}$  ( $1 \sigma$ ), thus substantially lower than for the 1984–1992 time interval and that the so-called preindustrial levels of N<sub>2</sub>O pertained until 1951 with most of the increase in atmospheric N<sub>2</sub>O occurring thereafter.

### Introduction

The existence of nitrous oxide, N<sub>2</sub>O, in the Earth's atmosphere was proposed at the turn of the twentieth century by Langley [1900], who reported the presence of two N<sub>2</sub>O infrared bands in solar spectra recorded in 1876 from Mount Whitney, California, while Adel [1939] added further evidence to that fact. Its quantitative evaluation evolved along the exploration and identification of N<sub>2</sub>O absorption features observed in infrared solar spectra recorded from the ground with increasing spectral resolution during the late 1940s and early 1950s [e.g., McMath and Goldberg, 1949; Goldberg and Müller, 1953; Goody and Walshaw, 1953; Migeotte et al., 1956]. On the basis of these early investigations, it became clear that nitrous oxide was present as a minor tropospheric constituent all around the globe and that its main sources were to be located at the ground [Adel, 1951; Goody and Walshaw, 1953].

In an attempt to study any variability in the abundance of N<sub>2</sub>O near the ground, Birkeland and Shaw [1959] investigated the P branch of the 4.5- $\mu\text{m}$  band of N<sub>2</sub>O in spectra recorded at Columbus, Ohio, through a multiple-pass cell totaling 706 m, filled with ambient air, as well as over open horizontal paths. The multiple-pass cell spectra were carefully calibrated against laboratory spectra for interference corrections and N<sub>2</sub>O concentration determinations. During the 3-month period of measurements (July, August, and September 1957), Birkeland and Shaw found a mean atmo-

spheric N<sub>2</sub>O concentration of  $(270 \pm 50)$  parts per billion by volume (ppbv), with a reproducibility of 20 ppbv; the variation in the N<sub>2</sub>O abundance over the 3-month time base never exceeded 30 ppbv.

More modern methods of investigation and extensive observational campaigns have been initiated since about 1970 to monitor the content and variability of N<sub>2</sub>O in the Earth's atmosphere at various sites around the globe. This was originally motivated by the concern that its atmospheric concentration may accumulate as a result of increasing release to the atmosphere due to nitrogenous fertilizer use. The technique most widely used today for tropospheric N<sub>2</sub>O measurements is the in situ gas chromatography in combination with electron capture detection. Since the mid-1970s, intensive programs measuring the tropospheric background concentrations of N<sub>2</sub>O have been carried out. From these measurements the present-day (1992) N<sub>2</sub>O sea level background concentration is found equal to 310 ppbv. The different measurement series indicate an average increase of N<sub>2</sub>O in the background troposphere equal to 0.6 to 1.0 ppbv yr<sup>-1</sup>. An overview is given by the *World Meteorological Organization (WMO)* [1992, and references therein]. A detailed description and analysis of the global distribution of N<sub>2</sub>O and its changes is presented by Prinn et al. [1990].

The in situ measurements of N<sub>2</sub>O do not directly provide information about its column abundance, but there have been several such measurements made of the vertical distribution of N<sub>2</sub>O in the upper troposphere and lower and middle stratosphere. Such measurements are made by whole air collection at various altitudes with balloon-borne samplers and subsequent analysis for N<sub>2</sub>O in the air samples by electron capture gas chromatography in the laboratory; column abundances can then be calculated from integration over the vertical volume mixing ratio (VMR) profiles. The first in situ measurements of stratospheric N<sub>2</sub>O have already

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been reported in 1970 [Schütz *et al.*, 1970], and a large number of measurements of the vertical distribution of N<sub>2</sub>O in the stratosphere have been made since. Details regarding stratospheric air sampling with balloon-borne cryogenic whole air samplers and the subsequent gas chromatography analysis have been described by Fabian *et al.* [1981] and Schmidt *et al.* [1983, 1985]. Early infrared remote measurements of N<sub>2</sub>O throughout the free troposphere and lower stratosphere were reported by Goldman *et al.* [1970, 1973].

The investigations of the last two decades, backed by theoretical studies, have revealed a number of N<sub>2</sub>O characteristics influencing our environment, i.e., (1) its global increase in the boundary layer at an exponential rate of 0.20 to 0.31% yr<sup>-1</sup> (e.g., Fraser *et al.*, chap. 1 [WMO, 1992]); (2) its indirect role in the erosion of the stratosphere as the major source of nitrogen oxides above 15 km altitude (via the reaction N<sub>2</sub>O + O(<sup>1</sup>D) → 2NO [e.g., Crutzen, 1975]); (3) its direct warming potential likely to influence the evolution of the Earth's climate [Ramanathan *et al.*, 1985; Ramanathan, 1988; WMO, 1992]; (4) its long lifetime in the atmosphere, of over 150 years [Mahlman *et al.*, 1986; Prinn *et al.*, 1990]; (5) its atmospheric burden being more and more affected by anthropogenic activities (caused by increased usage of nitrogen fertilizers [Crutzen and Ehhalt, 1977; McElroy *et al.*, 1977; Johnston, 1977; Eichner, 1990], tropical deforestation, and biomass burning [Crutzen and Andreae, 1990; Cofer *et al.*, 1991]); and (6) a latitude-dependent vertical gradient decline in the volume mixing ratio of N<sub>2</sub>O above the tropopause [Ehhalt, 1980].

Despite substantial progress in the identification of sources and sinks of atmospheric N<sub>2</sub>O, the global budget of nitrous oxide remains controversial, with large uncertainties affecting the sources (both natural and anthropogenic) whose sum is not sufficient to balance the calculated atmospheric sink [Prinn *et al.*, 1990; Khalil and Rasmussen, 1992]. The present knowledge of atmospheric distributions, global trends, and mass balances of N<sub>2</sub>O have been summarized recently by Fraser *et al.* [WMO, 1992, chap. 1], and by Khalil and Rasmussen [1992].

In this paper we attempt to provide more information on the atmospheric trend of N<sub>2</sub>O over the last 40 years. To do so, we describe the database and analysis procedure used to obtain a consistent series of vertical column abundances of nitrous oxide integrated through the atmosphere above the Jungfraujoch station and derive their variability and secular evolution.

## Observational Database

The vertical column abundances of N<sub>2</sub>O reported here have been derived from infrared (IR) solar spectra recorded at the International Scientific Station of the Jungfraujoch (ISSJ), located at 3580 m altitude in the Swiss Alps (latitude 46.5°N; longitude 8.0°E). The solar recordings were obtained with both a double-pass grating spectrometer (DPGS; spectral resolution of 0.02 cm<sup>-1</sup>) during the period from 1984 to 1989 and a Fourier transform spectrometer (FTS; spectral resolution from 0.003 to 0.005 cm<sup>-1</sup> for the present data) from 1984 to present. The main characteristics and performances of these two instruments developed at the Institute of Astrophysics of Liège have been described by Delbouille *et al.* [1973] for the DPGS and by Demoulin *et al.* [1991]

regarding the FTS. The observations were made during regular stays at ISSJ (mainly by P.D., G.R., and A.J.S.), as part of an effort to monitor the state and evolution of our atmosphere. The observed database has been exploited, so far, to determine and monitor the evolution of the vertical column abundances of some 15 telluric gases above ISSJ [Zander *et al.*, 1993].

Nitrous oxide, N<sub>2</sub>O, possesses over 140 absorption bands in the 570- to 5100-cm<sup>-1</sup> infrared region [Brown *et al.*, 1987; Rothman *et al.*, 1992]. Many of these bands occur in spectral intervals with complete absorption at the ground (mainly due to H<sub>2</sub>O and to CO<sub>2</sub>). An important selectivity criterion is to choose individual absorption lines with small temperature dependence, therefore relaxing the need to use accurate atmospheric temperature profiles. For a linear type molecule such as N<sub>2</sub>O, temperature insensitive lines ought to have lower-state energies,  $E''$ , so that their line intensity  $S_T$  at atmospheric temperature  $T$  remains close to the  $S_0$  value given in the line parameters' compilations at a reference temperature  $T_0$  equal to 296 K. As  $S_T$  is related to  $S_0$  by the simplified formulation (for details, see Brown *et al.* [1992])

$$S_T = S_0(T_0/T)^n [V(T_0)/V(T)] \exp - \{1.4387(T_0 - T)/T_0 T\} E''$$

where  $n$  is equal to 1 for a linear molecule such as N<sub>2</sub>O and  $V(T_0)/V(T)$  is the vibrational partition function term also close to 1 for N<sub>2</sub>O, it is found that a nitrous oxide line with  $E''$  near 200 cm<sup>-1</sup> is indeed temperature independent. In selecting the lines with a weak temperature dependence, it was further necessary to reject those which were significantly affected by interfering absorptions from either solar target or/and nontarget telluric origin, as well as those for which the spectroscopic parameters are not known with satisfactory accuracy. And finally, those lines satisfying the above conditions were to be recorded as often as possible and measurable with good precision when obtained under extreme observational conditions (high signal-to-noise ratio in the central part of the line for high- and low-Sun observations) so as to create a set of data points as dense as possible. As a consequence of these restrictions, the N<sub>2</sub>O line centered at 2439.632 cm<sup>-1</sup> was selected as the "target" transition to be primarily used in the investigation of all post-1984 modern spectra. Its lower-state energy is equal to 294.06 cm<sup>-1</sup>, corresponding to a mean temperature dependence equal to 0.15% K<sup>-1</sup> in the 240 to 280 K range; its strength and air-broadened half width are equal to 3.50 × 10<sup>-21</sup> cm<sup>-1</sup>/molecules cm<sup>2</sup> at 296 K and 0.0723 cm<sup>-1</sup> at 296 K and 1 atm, respectively, as given in the HITRAN 1986 database [Rothman *et al.*, 1987]. The precision and consistency with which the N<sub>2</sub>O column abundance could be derived from one line were assessed by analyzing various transitions present in the same spectrum; when dealing with high-quality recordings, the small relative differences among the results from such individual lines could be assigned to relative uncertainties in the spectroscopic parameters of these individual transitions and to their different relative temperature dependences.

The total number of "modern" solar spectra making up the database analyzed in this work (DPGS and FTS observations combined) is in excess of 900; they were recorded at solar zenith angles smaller than 75°, on 240 different days between May 1984 and December 1992. The limitation of the

**Table 1.** Solar Sample Spectra Recorded at ISSJ in 1950–1951 and Analyzed in This Research to Derive Vertical Column Abundances Above the Site at That Time

Date	Local Time	Spectral Interval, cm <sup>-1</sup>	Mode of Analysis*	Column Abundance, × 10 <sup>18</sup> molecules cm <sup>-2</sup>	Relative Weight
Aug. 21, 1950	0835	1187.5–1190.0	LSF	3.25	1
	0848	1181.5–1187.0	LSF	3.37	2
	1103	1153.0–1160.0	EQW	3.63	1
April 20, 1951	0932	2571.5–2580.5	LSF	3.49	2
		2565.5–2583.0	EQW	3.56	2
	0953	2538.0–2550.7	LSF	3.58	2
		2540.0–2560.0	EQW	3.64	2
		2538.0–2556.0	EQW	3.56	2
June 7, 1951	1456	2538.0–2555.0	LSF	3.50	2
July 10, 1951	1835	1157.0–1161.0	LSF	3.52	1
	1917	1142.5–1148.5	EQW	3.60	1
Aug. 21, 1951	0848	1181.5–1187.0	LSF	3.37	2
Sept. 20, 1951	1046	2571.5–2580.5	LSF	3.51	2
	1108	2539.0–2555.0	LSF	3.52	1

\*LSF, least squares curve fitting; EQW, equivalent width measurement.

error caused by possible departure of the real N<sub>2</sub>O VMR distribution from that adopted as “reference” profile (see later discussion and Figure 4).

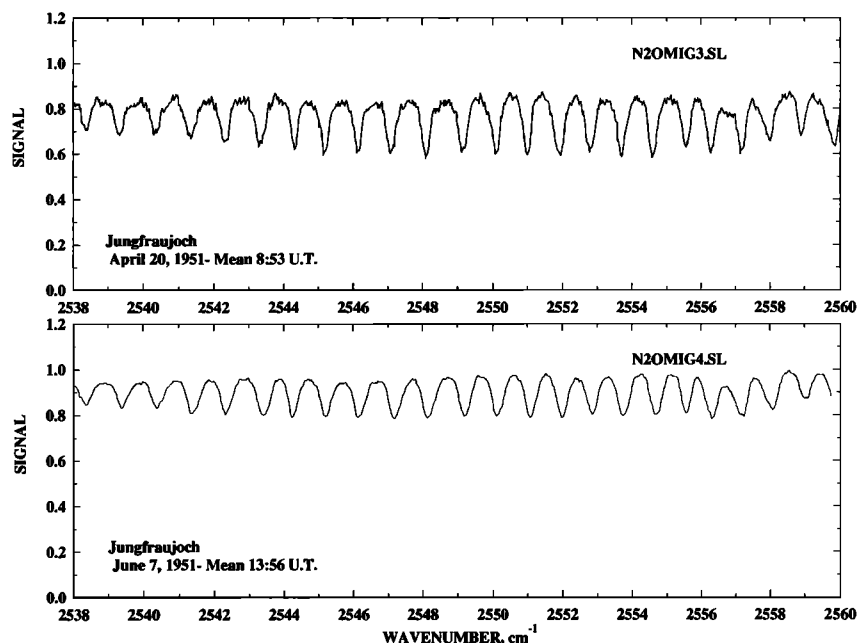
In addition to the modern solar observations spanning the 1984 to present time period, infrared solar spectra recorded at ISSJ during 1950–1951 by M. Migeotte and collaborators have also been investigated here to provide a meaningful vertical column abundance of N<sub>2</sub>O above the Jungfraujoch at the middle of the twentieth century. The old Migeotte recordings cover limited spectral intervals which were recorded with a Pfund type grating spectrometer on various days during 1950–1951; a spectral resolution between 0.12 and 0.44 cm<sup>-1</sup> was achieved using a thermocouple as a detector [Migeotte *et al.*, 1956]. The observations were intended to provide an ensemble of solar tracings, from which the best ones were selected to produce an atlas of the solar spectrum from 2.7 to 23.7 μm [Migeotte *et al.*, 1956]. Most of the original recordings have been saved by one of us (R.Z.); they appear in the form of analog traces of ink drawn on paper strip chart rolls. Some of the 1950–1951 observations have been investigated elsewhere to contribute information on the atmospheric burdens of CO [Zander *et al.*, 1989a], CH<sub>4</sub> [Rinsland *et al.*, 1985; Zander *et al.*, 1989b], and C<sub>2</sub>H<sub>6</sub> [Ehhalt *et al.*, 1991] at that time. In order to retain a reasonable set of N<sub>2</sub>O sample spectra making up a valid 1950–1951 database, the selection criteria applied to the modern 1984–1992 observations had to be relaxed somewhat. For instance, as the signal-to-noise ratio of the old spectra is relatively low (about 50 to 75), a larger temperature dependence of the lines selected could be tolerated without affecting significantly the uncertainty of the overall results, and reasonable interferences, both telluric and solar, could further be accommodated, provided they were identified from inspection of modern high-quality spectra and taken into account in the spectral retrievals and in the evaluation of the columns’ uncertainties. Even sets of lines of N<sub>2</sub>O occurring in the 1140- to 1190-cm<sup>-1</sup> region were retained as part of the 1950–1951 database; care was taken in the fitting process of these transitions to properly account for interferences produced by weak but numerous ozone absorptions. According to R. A. Toth (private communication, 1992), the spectroscopic parameters of the N<sub>2</sub>O lines in the

regions 2438–2440, 2530–2590, and 1140–1195 cm<sup>-1</sup> are known with very good accuracy, and any relative biasing among results derived from these regions should not exceed ±1%.

Nine spectral regions recorded independently on six different days of 1950–1951 were finally retained on the basis of their satisfactory spectral quality and the availability of related ancillary information such as day and time of observation, local pressure and temperature, and spectral resolution; they are listed in Table 1, along with their relative weights which reflect the quality and extent of the spectral intervals fitted as part of this research.

## Data Analysis

The bulk of the vertical column abundances reported here has been derived through nonlinear least squares curve fitting of calculated spectra to those observed; this was performed for all the FTS spectra of 1984–1992 and for the nine older 1950–1951 recordings mentioned in Table 1. A fitting algorithm developed at the Langley Research Center (LRC), Hampton, Virginia, during the early 1980s [e.g., Rinsland *et al.*, 1984] and steadily updated since by one of us (C.P.R.) was used. Its atmospheric transmission calculations are based on an atmosphere divided into 29 curved layers extending from the altitude of the ISSJ station (3.58 km) to 100 km, with the first one ranging from 3.58 to 4.0 km and the next ones being spaced by 1 km from 4 to 16 km, by 2 km from 16 to 32 km, by 3 km from 32 to 35 km, by 5 km from 35 to 50 km, and by 10 km from 50 to 80 km altitude; one layer accounts for the atmosphere from 80 to 100 km. Each layer is considered homogeneous in pressure, temperature, and constituents’ volume mixing ratios. The physical model adopted incorporated typical seasonal temperature profiles with relative uncertainties evaluated from comparison with radiosonde measurements made at Payerne, Switzerland. Initial “reference” volume mixing ratio (VMR) profiles were taken from Smith [1982], with appropriate updates whenever justified. In general, the fitting procedure with the LRC algorithm involves multiplicative scaling of the entire VMR profiles of up to five different species (i.e., the target and four interfering gases), with the absorption of up to 15 other gases



**Figure 1.** Two samples of solar spectra recorded at ISSJ in 1951 by M. Migeotte [Migeotte *et al.*, 1956] reproduced here, after having been digitized then linearized in terms of their abscissa frequency scale. Wide sections of these spectra have been used in the present investigation, as most absorption features are produced by telluric N<sub>2</sub>O.

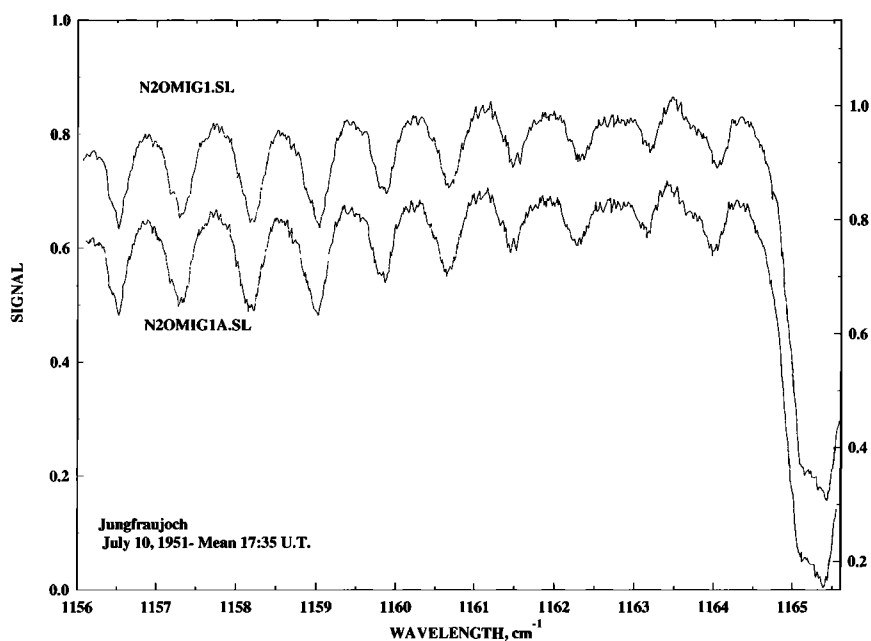
also included (but with their VMR profiles kept fixed), until the root-sum-square of the residuals between the discrete observed and calculated transmissions converge to a minimum. Tests with VMRs modified in specific layers of the profile or shifted vertically up and down were also performed for fitting improvements as well as for sensitivity studies and error evaluations (see example in Figure 3).

The spectroscopic parameters necessary to calculate the absorption over the spectral intervals retained as microwindows were essentially those found in the HITRAN line parameter compilations of 1986 [Rothman *et al.*, 1987]. While more recent HITRAN versions [Rothman *et al.*, 1992] contain improved parameters for various molecules, only minor changes were noticed regarding the target molecule N<sub>2</sub>O in the intervals analyzed here, and therefore the line parameters of the 1986 compilation were kept throughout this investigation, in order to maintain consistency in the database.

Until the LRC algorithm became available, the DPGS measurements were mainly analyzed for vertical column abundances by the equivalent width (EQW) method, for example, for HCl, HF, CO, and CH<sub>4</sub>, and N<sub>2</sub>O was treated similarly. The procedure followed in the application of that method, and reasons for having adopted it as well as its limitations, have been described in detail by Zander *et al.* [1989a, 1989b]. Comparisons between results obtained on various days during the years 1984–1989 when both the DPGS and the FTS instruments were in operation (the DPGS was removed from ISSJ in October 1989 and replaced with a commercial Bruker-120HR Fourier transform spectrometer) showed that within their respective uncertainties (a few percent, combined), the columns derived by application of the EQW method to DPGS measurements were equal to those obtained from fitting FTS observations, with no sys-

tematic biasing. Therefore N<sub>2</sub>O columns derived by the EQW method from DPGS measurements have been included here on 17 days when no FTS data were available. Note here that only on rare occasions did the standard deviation around the mean exceed the sum of the observational and analytical uncertainties, indicating that the N<sub>2</sub>O column abundance above ISSJ does not change substantially during the course of a day, typically less than 2%.

In order to analyze the 1950–1951 sample spectra (see Table 1) by the curve-fitting procedure, their analog tracings had to undergo the following treatments: (1) digitization of the tracings using a SummaSketch II-Graphics tablet; (2) linearization of their frequency scale (using the positions of the successive N<sub>2</sub>O transitions given in the HITRAN 1986 compilation [Rothman *et al.*, 1987]), as these spectra were recorded with a grating spectrometer producing a wavelength dispersion modulated by a sinusoidal component and showing further “local” anomalies likely to be associated with periodic type errors in the grating drive mechanism [Zander *et al.*, 1989b]; and (3) resampling of the linearized spectra with a constant frequency spacing consistent with the resolution of the spectra and the format appropriate for their fitting with the LRC algorithm. Figure 1 reproduces two sample spectra extending from 2538 to 2560 cm<sup>-1</sup>, recorded at ISSJ in 1951; the main and regularly spaced absorption lines clearly observed in both spectra are the P27 to P4 transitions of the (2000–0000) band of N<sub>2</sub>O. Notice the “perturbation” of the absorption pattern above 2556 cm<sup>-1</sup> caused by interfering solar lines identified in “pure” solar spectra recorded from space with the atmospheric trace molecule spectroscopy (ATMOS) instrument [Farmer and Norton, 1989]. The top spectrum of Figure 1 was recorded on April 20, 1951, at a mean solar zenith angle of 51.0° and published in the Migeotte *et al.* [1956, Plate 20] solar atlas.



**Figure 2.** Sample spectrum recorded by M. Migeotte [Migeotte *et al.*, 1956] on July 10, 1951, reproduced twice to show the reproducibility of independent digitization and linearization processes. With the exception of the strong H<sub>2</sub>O absorption at the right edge of the figure, all other absorption features are essentially attributable to telluric N<sub>2</sub>O, with some interferences by ozone.

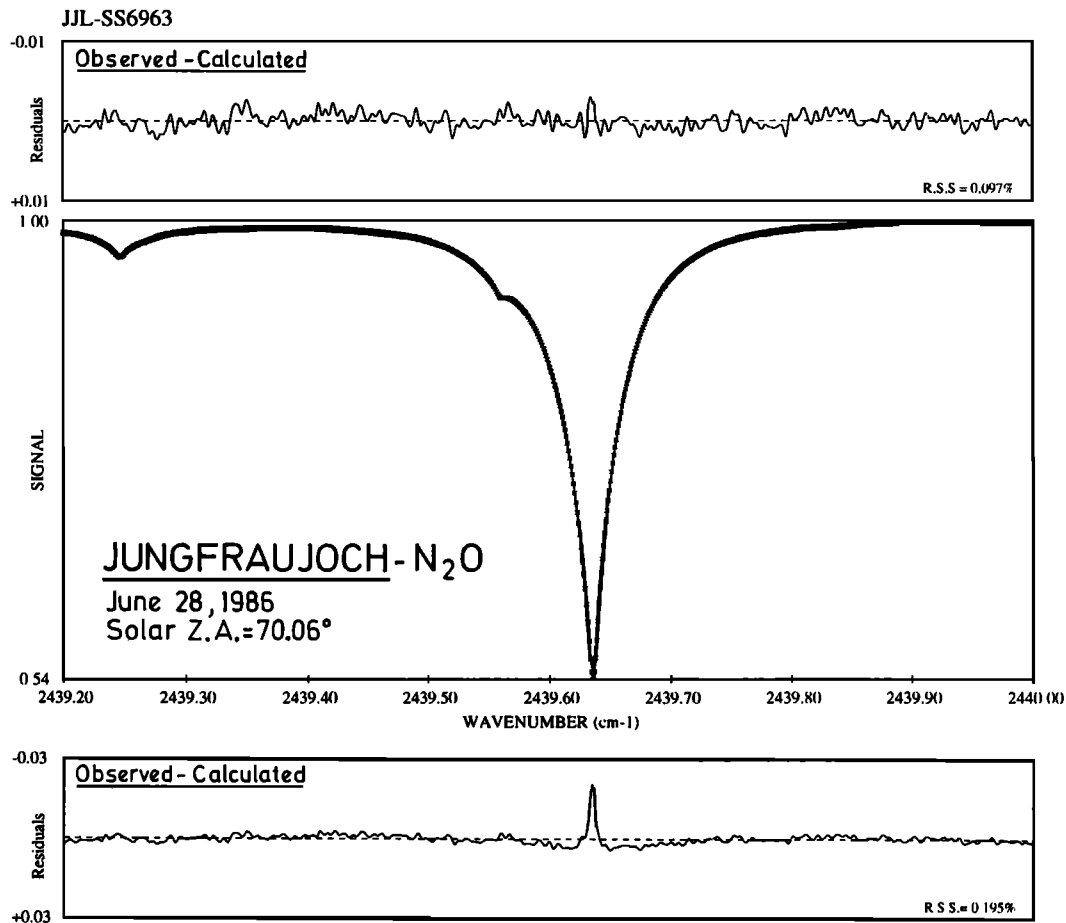
The bottom tracing of Figure 1 was obtained on June 7, 1951, at a mean solar zenith angle of 38.3° but was never published. Figure 2 reproduces two independent digitizations of the 1156 to 1165.5 cm<sup>-1</sup> spectral region recorded on July 10, 1951, around 1735 local time; it shows the good reproducibility of the digitization and linearization procedure. When fitting identical intervals of either of these processed tracings, the retrieved N<sub>2</sub>O columns never differed by more than 1.5%. Today's modern spectra recorded over the 1156- to 1166-cm<sup>-1</sup> interval reveal drastically different absorption characteristics caused by the presence of CF<sub>2</sub>Cl<sub>2</sub> ("Freon 12") in the Earth's atmosphere, an anthropogenic molecule which was not contributing any absorption in the early 1950s [Brown *et al.*, 1992].

As the instrumental line shape function of the grating spectrometer used to record the spectra in 1950–1951 was unknown, a Gaussian function with a half width equal to the instrument spectral resolution was adopted in the fitting procedure (such a function has been shown to closely represent the instrumental response of a grating spectrometer [Kostkowski and Bass, 1956]); the Gaussian function half width was occasionally allowed to vary in the fitting process as one of the adjustable parameters in the LRC algorithm. The need for linearization of the old 1950–1951 tracings, as well as good fittings achieved when using a Gaussian instrument function, have been discussed and demonstrated by Rinsland *et al.* [1985, 1991]. Occasional N<sub>2</sub>O column abundances were also derived from 1950–1951 spectra using the EQW procedure (which is independent of the distortion due to the finite band pass of the spectrometer), in order to check the validity of the columns retrieved with the fitting method. The results agreed to within 4% when the same spectral intervals were investigated by the two methods.

The middle frame of Figure 3 shows a fit (crosses) to a typical ISSJ sample spectrum encompassing the target N<sub>2</sub>O

line at 2439.632 cm<sup>-1</sup> (continuous trace) recorded with the FTS instrument on June 28, 1986, at a solar zenith angle of 70.06°. The N<sub>2</sub>O "reference" VMR profile reproduced in Figure 4 was adopted in that fit and scaled over its entire altitude span until the residuals between observed and calculated traces were minimized (on average the fitting process takes six to eight iterations); these residuals (observed minus calculated signals) are displayed in the top frame of Figure 3, showing excellent consistency over the 2439.20- to 2440.00-cm<sup>-1</sup> interval reproduced here. The root-sum-square (rss) of the residuals over that interval is equal to 0.097%, consistent with the signal-to-noise ratio of the observation. To evaluate the sensitivity of the fitting method, the reference profile of Figure 4 was then shifted one layer upward and the corresponding fitting was repeated; this led to the residuals displayed in the bottom frame of Figure 3, indicating a substantial deterioration near the line center. The vertical column abundances of N<sub>2</sub>O returned for the two cases described above were equal to 3.99 × 10<sup>18</sup> and 3.95 × 10<sup>18</sup> molecules cm<sup>-2</sup>, or a decrease in the column of 1.0% for the profile that was shifted one layer up. When such discrepancies showed up in the residuals from any modern spectrum's fitting, they were quantified and corrected through vertical shifting of the VMR profile and a refitting, so that the retrieved vertical column abundances of N<sub>2</sub>O reported for 1984–1992 can be considered to have a relative precision better than 1% based on the fitting only. Notice that a similar fitting exercise has been reported by Barbe and Marché [1985]. Besides the main N<sub>2</sub>O target line of 2439.6316 cm<sup>-1</sup>, two weak N<sub>2</sub>O features appear in the window displayed in Figure 3, i.e., at 2439.5576 and at 2439.2445 cm<sup>-1</sup>.

Figures 5 and 6 show two fittings performed on 1951 spectra recorded at ISSJ by M. Migeotte [see Migeotte *et al.*, 1956]. The thin light spectral trace in the bottom frame of



**Figure 3.** Example of the “target” microwindow encompassing the N<sub>2</sub>O transition at 2439.632 cm<sup>-1</sup>, used predominantly in the determination of the N<sub>2</sub>O vertical column abundances from 1984 to 1992. Shown is the nonlinear least squares fitting (middle) achieved over the 2439.20 to 2440.00 cm<sup>-1</sup> interval, with the residuals reproduced at the top. Also reproduced (bottom) is the departure of the fit when the “reference” volume mixing ratio of Figure 4 is shifted up by one layer.

Figure 5 reproduces the first three N<sub>2</sub>O lines of the bottom spectrum of Figure 1; the fitting to these lines is represented by the ensemble of crosses appearing as a heavy trace. The N<sub>2</sub>O vertical column abundance retrieved from that fit is equal to  $3.43 \times 10^{18}$  molecules cm<sup>-2</sup>. Similarly, Figure 6 reproduces the fit achieved over the 1157.0- to 1161.0-cm<sup>-1</sup> interval of the spectrum given in Figure 2, recorded at ISSJ on July 10, 1951; the vertical column abundance obtained here is equal to  $3.52 \times 10^{18}$  molecules cm<sup>-2</sup>.

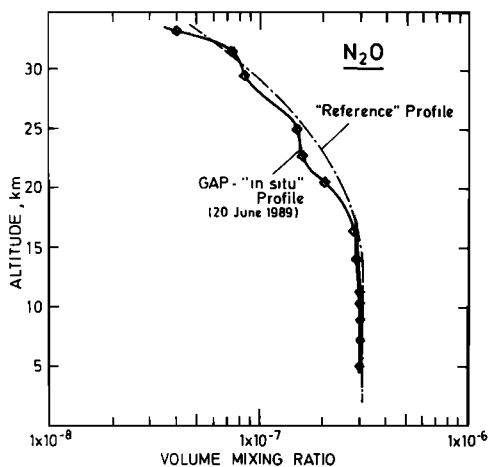
Table 2 lists the major error sources which need to be considered in evaluating the random and systematic uncertainties on the derived vertical column abundances, with evaluations being made separately for the old 1950–1951 measurements and for the modern 1984–1992 investigations. The error magnitudes, reported in terms of percent of the total N<sub>2</sub>O columns at the 1- $\sigma$  level, were mostly based on sensitivity tests by changing various parameters separately and then repeating the fitting process; they apply to individual spectral fittings or EQW measurements. When more than one spectrum or independent spectral interval was included in a daily column determination, some of the random errors could still be reduced by the square root of the number of spectra or intervals involved. The largest sources of random uncertainty in the 1950–1951 columns are clearly related to

the limited signal-to-noise ratio of the tracings and the setting of their zero-transmission level, while the adopted PT and VMR profiles prevail in the precision of the modern 1984–1992 data.

## Results and Discussion

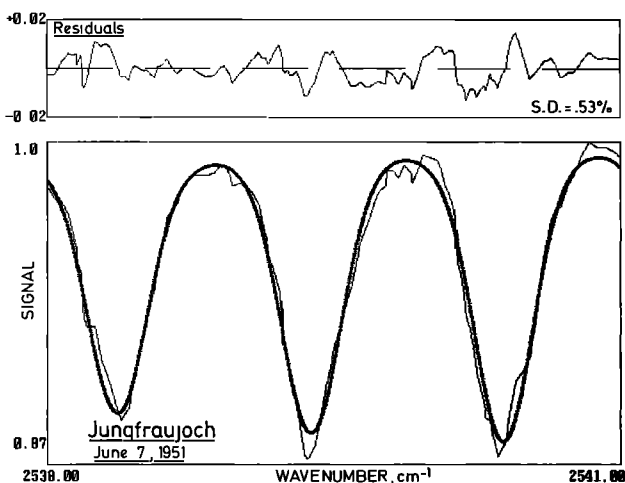
The ensemble of the observational results derived in this research is reproduced versus time in Figure 7. The error bars combine the random uncertainty evaluation of Table 2, the number of individual measurements making up each data point, the standard deviation around the mean of these individual measurements, and the relative weights of the individual measurements of 1950–1951 (see Table 1). Figure 7 indicates a significant increase of the vertical column abundance of N<sub>2</sub>O above ISSJ between 1950–1951 and the present. When fitting the entire database by an exponential function (see the dashed line in Figure 7), the rate of increase was found equal to  $(0.30 \pm 0.03)\% \text{ yr}^{-1}$  (all uncertainties given in this section are also 1  $\sigma$ ).

The higher sampling frequency in the years 1984 to 1992 permits a separate fit for that time period, which is shown in Figure 8. The corresponding rate of increase derived from that fit (see solid line in Figure 8, also redrawn in Figure 7)

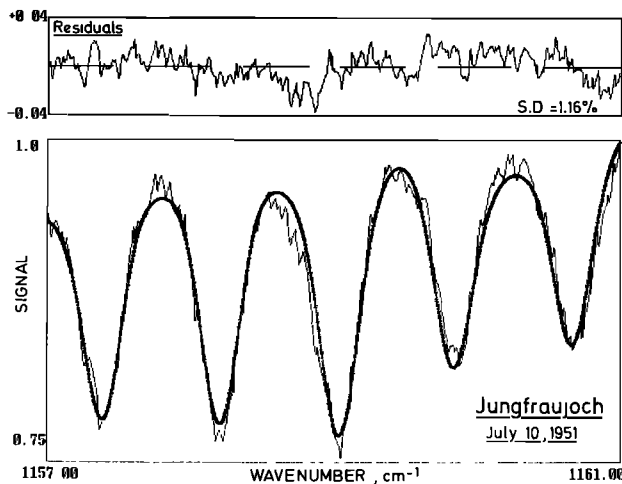


**Figure 4.** Graphical representation of the “reference” volume mixing ratio profile adopted as starting profile in the fitting process performed all along the present work. The profile labeled GAP-“in situ” was obtained from in situ cryogenic air samplings during a balloon flight conducted by KFA-Jülich on June 20, 1989, as part of a validation effort including IR remote measurements at ISSJ; the symbols and their widths indicate the altitudes of sampling and the precision of the measurements.

was equal to  $(0.39 \pm 0.08)\% \text{ yr}^{-1}$ , suggesting a larger rate of increase for the period 1984–1992 than the one derived for the entire database. The relatively dense database of 1984–1992 further revealed a seasonal modulation whose amplitude appears to vary from year to year and to be better defined in some years than in others. As such a modulation affects trend evaluations, a fit combining a sinusoidal seasonal cycle superimposed on an exponential function was applied here to the last 8.5 years of the database. That combined fit is represented by the dash-dotted curve in Figure 8. It returned the following parameters: (1) rate of increase equal to  $(0.36 \pm 0.06)\% \text{ yr}^{-1}$ ; (2) minimum and maximum of the cycle occurring during week 9 and week 36



**Figure 5.** Fitting (heavy trace) performed to the three first N<sub>2</sub>O lines of the June 7, 1951, spectrum shown in Figure 1 (bottom). The residuals of the fit (observed minus calculated signals) are reproduced in the top frame.



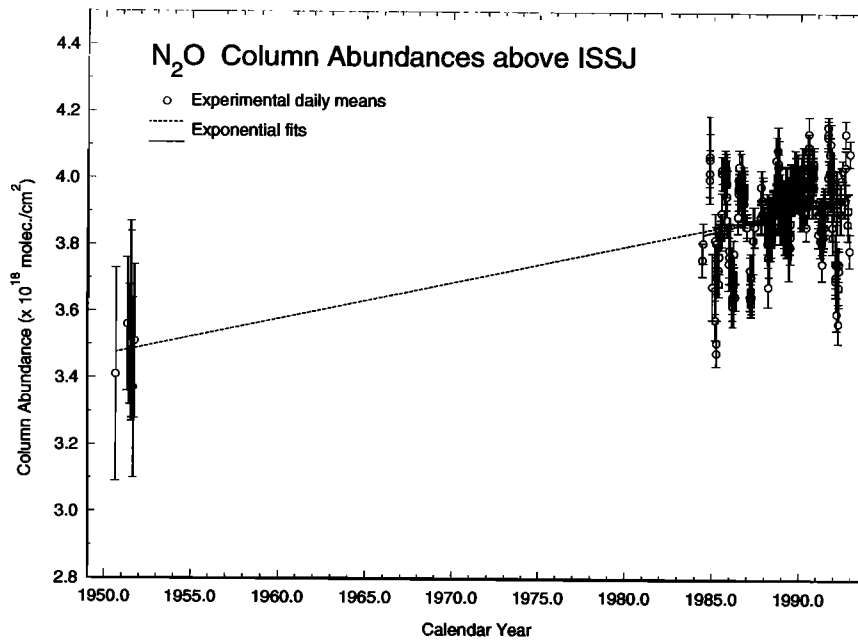
**Figure 6.** Fitting (heavy trace) performed to a section of the July 10, 1951, spectrum shown in Figure 2. The residuals of the fit are reproduced in the top frame.

of the year (i.e., early March and early September); and (3) mean peak-to-peak amplitude of cycle equal to 7.2% of the total column above ISSJ. That retrieved mean peak-to-peak seasonal variation is consistent with an observed 1.5-km average change in the tropopause height above ISSJ. A similar effect was also observed in the CH<sub>4</sub> column abundance investigation [Zander *et al.*, 1989b]. Figure 9 reproduces all data points of Figure 8, normalized with respect to the exponential curve fitted to the data and referenced to the year 1990; the seasonal characteristics, points 2 and 3 above, are clearly noticeable in this figure.

Besides observed year-to-year changes in the seasonal variation of the N<sub>2</sub>O column above ISSJ, other “anomalies” are present in the database; i.e., the columns during the winter of 1984–1985 and 1991–1992 show substantially more variability and lower values, while the winter columns for 1988–1989 and 1989–1990 appear abnormally high. Such

**Table 2.** Random and Systematic Error Sources and Resulting 1σ Uncertainties for a Typical Individual Spectrum Analysis

Error Sources	1σ Uncertainty, % of Column	
	1984–1992	1950–1951
<i>Random</i>		
Finite signal-to-noise ratio	<1.0	2–3
Zero transmission level offset	<1.0	3
Error in 100% transmission level	<1.0	2
Interfering absorption	<0.5	2
PT profile uncertainty	1.0	<2
Variability in assumed VMR profile	1.0	1
Observing geometry	<1.0	2
Spectra processing (digitization and linearization)	...	2
Root-sum-square total random	<2.5	<6.3
<i>Systematic</i>		
Spectroscopic parameters’ uncertainty	1.0	1.0
Bias due to assumed VMR profile	2.0	2.0
Algorithm uncertainty	3.0	3.0
Root-sum-square total systematic	3.7	3.7

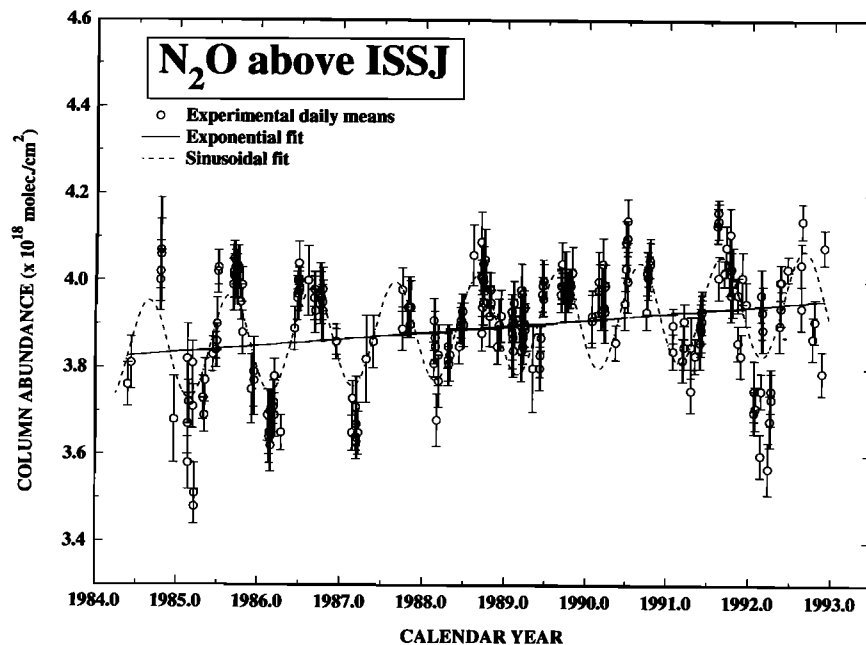


**Figure 7.** Graphical representation of the ensemble of the vertical column abundances derived in this study. Each data point represents a daily mean column above ISSJ, expressed in molecules per square centimeter. The error bars assigned to each daily mean column correspond to one standard deviation.

temporary perturbations can significantly affect trends' investigations when the data do not extend sufficiently in time. For example, a rate of increase of  $0.8 \pm 0.01\% \text{ yr}^{-1}$  can be identified over the 1985–1990 set of columns, while the 1990–1992 data indicate a negative trend on the order of  $-1\% \text{ yr}^{-1}$ . Despite such temporary perturbations, we believe that the entire 1984–1992 database, which covers nearly a de-

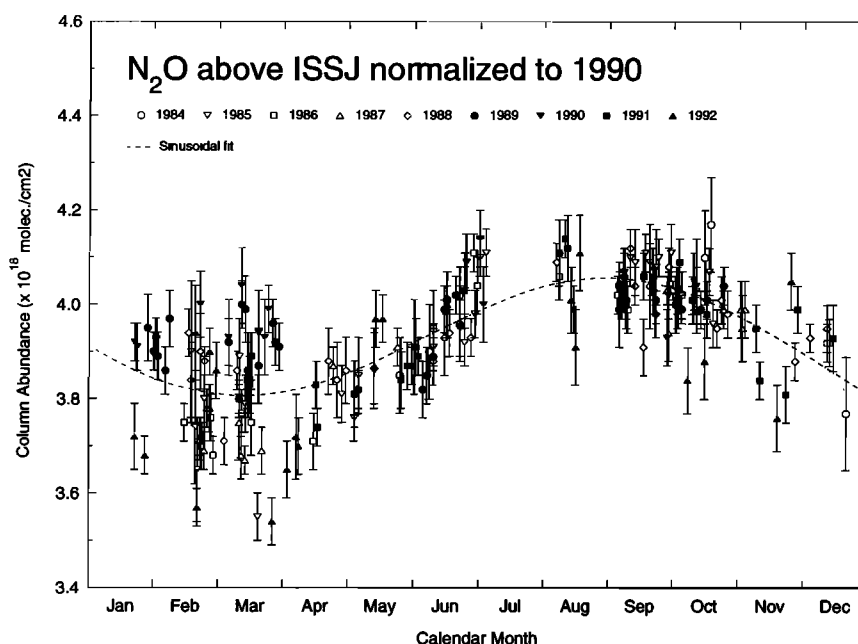
cade, provides an ensemble of measurements from which a statistically significant mean rate of increase can be derived.

By combining the dates of observations, the number of independent column measurements, and their relative weights (see Table 1), the mean time of the 1950–1951 database corresponds to week 16 of 1951, or mid-April 1951, and the mean N<sub>2</sub>O column abundance derived from these



**Figure 8.** Detailed graphical representation of the daily mean vertical column abundances measured above ISSJ between April 1984 and the end of 1992. The solid curve represents the exponential fit to the ensemble of the data points, while the dash-dotted curve reproduces the fit combining a sinusoidal seasonal cycle superposed on the mean exponential increase.





**Figure 9.** Graphical representation of all data points of Figure 8, normalized with respect to the exponential curve fitted to the data points and normalized to the year 1990. The seasonal variation is clearly present in the 1984–1992 ISSJ database.

early observations was found equal to  $(3.49 \pm 0.11) \times 10^{18}$  molecules  $\text{cm}^{-2}$ . The columns for mid-April 1984 and mid-April 1992, read off the best fitting to all 1984–1992 results (dash-dotted curve in Figure 8), are equal to  $3.76$  and  $3.87 \times 10^{18}$  molecules  $\text{cm}^{-2}$ , respectively. The mean exponential rates of increase obtained from these three mid-April columns for 1951, 1984, and 1992 are then found equal to  $0.23 \pm 0.04\% \text{ yr}^{-1}$  for the 1951–1984 time period and  $0.36 \pm 0.06\% \text{ yr}^{-1}$  for the years 1984–1992. As a consequence, the atmospheric burden of N<sub>2</sub>O has increased by some 11% during the past four decades. With the assumption that the “reference” N<sub>2</sub>O profile of Figure 4 is representative of the relative distribution of N<sub>2</sub>O versus altitude that prevailed during the last decades, the three above mentioned columns translate into volume mixing ratios of 275 ppbv, 296 ppbv, and 305 ppbv at the altitude of ISSJ for mid-April of 1951, 1984, and 1992, respectively (notice that these values do not correspond to the average yearly VMRs).

To our knowledge, only two sets of ground-based IR remote measurements of the column abundances of N<sub>2</sub>O have been reported prior to this work. Goody [1969] made such measurements at the Blue Hill Observatory (Milton, Massachusetts, 205 m above sea level; latitude 42.2°N; longitude 71.1°W) on 81 days spanning the period May 1966 to June 1968. During most of that period, Goody found a mean column close to 0.25 cm atm, which translated into a mean atmospheric VMR of ~320 ppbv. Substantially higher values of up to 0.31 cm atm (~380 ppbv) were retrieved from January to March 1968, but this increase could not be explained satisfactorily by Goody in terms of changing meteorological conditions, nor was it established as a repeatable feature from his limited database. Goody’s columns of N<sub>2</sub>O are exceedingly high in comparison to those reported here, and his observed temporal variations are definitely inconsistent with the present findings, perhaps reflecting

effects of local pollution or instrumental calibration difficulties.

The other set of IR remote measurements of N<sub>2</sub>O columns was reported by Wallace and Livingston [1990]. On the basis of the analysis of N<sub>2</sub>O absorption lines observed between 4396 and 4430  $\text{cm}^{-1}$  in solar spectra recorded at Kitt Peak Observatory, Arizona, they derived vertical column abundances of nitrous oxide above that site on 52 days between 1979 and 1985; because of a suspected biasing in the spectroscopic parameters adopted in their analysis, Wallace and Livingston did not derive an original set of VMRs from their measured columns, but rather scaled their data so that the average concentration ratio for January 1, 1980 be equal to 301 ppbv as proposed by Weiss [1981]. Their main findings were that the 1979–1985 N<sub>2</sub>O concentration database of Kitt Peak did not show any significant trend,  $(0 \pm 1)\% \text{ yr}^{-1}$  at the 90% confidence level, nor did it reveal any seasonal variation. While the reported trend is not inconsistent with most findings regarding the rate of increase of N<sub>2</sub>O over the last decades, including ours, its large uncertainty precludes any definite support.

To tie the infrared remote measurements more closely to in situ measurements of the N<sub>2</sub>O trend, a coordinated effort to intercompare IR remote measurements of the N<sub>2</sub>O column abundance above ISSJ and an N<sub>2</sub>O profile obtained in situ was made on June 20, 1989. The Kernforschungsanlage (KFA) cryogenic whole air sampler [Schmidt *et al.*, 1985] was launched at 0700 UT on a large stratospheric balloon from Gap-Tallard (44.5°N; 6.0°E) located in the French Alps, about 250 km to the south of the Jungfraujoch; the balloon traveled essentially westward. Four samples were readily collected in the troposphere (between 5.0 and 11.2 km altitude) during the ascent in the area slightly west of the launch site, in an attempt to obtain the most accurate information about the tropospheric N<sub>2</sub>O burden which con-

stitutes about 70% of the total column amount. The tropopause was observed at 12.1 km altitude. Another series of nine samples was collected between 1115 UT and 1430 UT during the valve-controlled slow descent of the balloon from 33.2 km down to 10.5 km altitude that occurred at a distance of 130 to 190 km west of Gap-Tallard, and correspondingly about 370 km southwest of ISSJ. The height of the sampling intervals decreased from 700 m at altitudes above 30 km to about 200 m at the tropopause level. The samples collected were analyzed within about 2 weeks following the date of the flight in the KFA laboratory using a gas chromatograph equipped with an electron capture detector (ECD). The analytical precision as determined from multiple analyses was about  $\pm 5\%$ . For absolute calibration the collected samples were analyzed against laboratory standard gases prepared by static dilution techniques to an accuracy of about  $\pm 5\%$ . The lower limit of detection achieved during the analyses of the intercomparison samples was about 5.0 ppbv [Schmidt *et al.*, 1987].

The vertical distribution of the N<sub>2</sub>O mixing ratio derived from the samples collected during the June 20, 1989, flight is reproduced in Figure 4 (full trace). That profile reflects the relatively undisturbed dynamical conditions of the summer-time circulation in the stratosphere.

After extending the Gap profile down to the altitude of ISSJ (3.58 km) by assuming that the mean N<sub>2</sub>O VMR determined during the flight between 5 km and the tropopause (i.e., 305 ppbv) was valid at lower altitudes as well, the N<sub>2</sub>O target line at 2439.63 cm<sup>-1</sup> was fitted in three different spectra recorded at ISSJ on June 20, 1989. The best fits which reproduced the spectra to their noise level were achieved by scaling the Gap profile by factors varying between 1.01 and 1.02, with the corresponding vertical column abundances found equal to 3.94, 3.95, and 3.99  $\times 10^{18}$  molecules cm<sup>-2</sup>. Fittings performed with the "reference" profile of Figure 4 systematically overestimated the central line absorption (with the residuals looking very much like those shown in the bottom frame of Figure 3), because of too large amounts of N<sub>2</sub>O assumed in that profile above about 18 km. The results of the analysis of two June 20, 1989, spectra by the EQW procedure returned columns equal to 3.96 and 3.94  $\times 10^{18}$  molecules cm<sup>-2</sup>, in excellent agreement with the nonlinear least squares curve-fitting results. Furthermore, columns determined at ISSJ on June 19, 1989, were equal to 4.00 and 3.98  $\times 10^{18}$  molecules cm<sup>-2</sup>, similar to the columns found on the day of the intercomparison. Because of the moderate easterly winds observed in the lower and middle stratosphere, we expect little difference in the vertical N<sub>2</sub>O profiles over ISSJ and the region covered by the balloon trajectory. It is, therefore, sound to conclude that the in situ and IR remote-sensing methods agree to within  $\pm 2\%$  for N<sub>2</sub>O-integrated vertical profile investigations.

To further provide a quantitative validation of the local VMRs derived from vertical column abundances obtained remotely from ISSJ, occasional air samples were taken at the ISSJ and analyzed by KFA for various species. A set of three samples collected on August 14, 1991, showed the local N<sub>2</sub>O VMRs to be 321, 325, and 333 ppbv, or an average of (326  $\pm$  5) ppbv; another set made on November 24, 1991, returned 320, 319, and 317 ppbv, or an average of (319  $\pm$  1) ppbv. On these same two days the daily mean N<sub>2</sub>O column abundances derived remotely above ISSJ were found equal

to 4.01  $\times 10^{18}$  and 3.94  $\times 10^{18}$  molecules cm<sup>-2</sup>, respectively, when adjusting the "reference" profile of Figure 3, by both scaling it and shifting it vertically to minimize the residuals of the fits; the corresponding local VMRs are 316 ppbv and 309 ppbv for August 14 and November 24, 1991, respectively. The difference in the local VMRs obtained from the in situ and IR remote results is, therefore, on the order of 3%, with the in situ values being the larger ones. For practical reasons the November 24, 1991, IR remote result was derived from fitting four N<sub>2</sub>O transitions located at 1182.647, 1183.515, 1193.156, and 1194.039 cm<sup>-1</sup>, but as pointed out earlier, it should not preclude a biasing larger than  $\pm 1\%$  with respect to the columns obtained from the primary target line at 2439.632 cm<sup>-1</sup>.

On the basis of these relative findings it seems justified to compare the N<sub>2</sub>O trends derived over ISSJ with those derived from tropospheric in situ measurements. Prinn *et al.* [1990] analyzed the N<sub>2</sub>O volume mixing ratios obtained during the Atmospheric Lifetime Experiment/Global Atmospheric Gases Experiment (ALE/GAGE) experiment between 1978 and 1988. For the two stations at northern midlatitudes (Adrigole/Mace Head in Ireland and Cape Mears in Oregon) they report a trend of 0.88  $\pm$  0.08 ppbv yr<sup>-1</sup>. On the basis of their average value of 303 ppbv this corresponds to a mean relative increase of 0.29% yr<sup>-1</sup>, slightly higher than the relative increase of 0.25% yr<sup>-1</sup> in the N<sub>2</sub>O column densities over ISSJ for the entire data set from 1951 to 1992, but slightly lower than the increase of 0.36% yr<sup>-1</sup> for the period 1984 to 1992. Not only do the relative changes agree, but the absolute values are also very similar: from the average column density for the year 1984 (3.82  $\times 10^{18}$  molecules cm<sup>-2</sup>), we derive an N<sub>2</sub>O mixing ratio of 300.8 ppbv for the free troposphere. This is very close to the 1984 average N<sub>2</sub>O mixing ratio of 303.5 ppbv found at Cape Mears. Measurements made by R. Weiss (private communication, 1968) on air samples collected on oceanographic expeditions by H. Craig and W. Dowd in 1960–1964 returned volume mixing ratios of N<sub>2</sub>O varying between 290 and 296 ppbv, thus showing a bias of some +3% with respect to corresponding values derived by interpolation from the present database.

The early infrared remote measurements of the N<sub>2</sub>O concentrations at the level of the ISSJ site have another important implication: they indicate a N<sub>2</sub>O mixing ratio of 275 ppbv in 1951 over Europe. Although that value refers to the middle troposphere, the troposphere is vertically reasonably well mixed so that the deviations in the boundary layer from that value should not be more than a few parts per billion by volume. Therefore we conclude that the tropospheric N<sub>2</sub>O mixing ratio over Europe in April 1951 was around 275 ppbv. Because of the long lifetime of N<sub>2</sub>O, that value should also be applicable globally within a range of  $\pm 5$  ppbv. On the other hand, the ice core data indicate that the preindustrial N<sub>2</sub>O mixing ratio in the troposphere averaged about 285 ppbv [Khalil and Rasmussen, 1989; Etheridge *et al.*, 1988], with Zardini *et al.* [1989] reporting concentrations of about 270 ppbv approximately 400 years ago and Leuenberger and Siegenthaler [1992] quoting  $\sim 260$  ppbv for preindustrial times. Moreover, the ice core data have been interpreted to show the increase in the atmospheric N<sub>2</sub>O mixing ratio to begin as early as 1700 [Houghton *et al.*, 1990]. The preindustrial N<sub>2</sub>O concentrations from the analysis of ice cores are very similar to the mixing ratio derived

from our Jungfraujoch measurements for 1951. Even if based on the lowest of the ice core derived preindustrial mixing ratio [Leuenberger and Siegenthaler, 1992], the change between preindustrial times and 1951 would still be only 15 ppbv. This indicates that the low preindustrial N<sub>2</sub>O values increased only slightly before 1951 and that most of the increase occurred thereafter.

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