Free tropospheric CO, C₂H₆, and HCN above central Europe: Recent measurements from the Jungfraujoch station including the detection of elevated columns during 1998

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Abstract. Time series of free tropospheric carbon monoxide (CO), ethane (C₂H₆), and hydrogen cyanide (HCN) column abundances have been derived from observations at the International Scientific Station of the Jungfraujoch (ISSJ) at 3.58-km altitude in the Swiss Alps (latitude 46.55°N, 7.98°E longitude). The free troposphere was assumed to extend from 3.58 to 11 km altitude, and the related columns were derived for all three molecules from high spectral resolution infrared solar spectra recorded between January 1995 and October 1999. The three molecules show distinct seasonal cycles with maxima during winter for CO and C₂H₆, and during spring for HCN. These seasonal changes are superimposed on interannual variations. The tropospheric columns of all three molecules were elevated during 1998. Increases were most pronounced for HCN with enhanced values throughout the year, up to a factor of 2 in January 1998 when compared to averages of the other years. The increased tropospheric columns coincide with the period of widespread wildfires during the strong El Niño warm phase of 1997–1998. The emission enhancements above ISSJ are less pronounced, and they peaked after the increases measured above Mauna Loa (19.55°N, 155.6°W). Tropospheric trends for CO, C₂H₆, and HCN of (2.40 ± 0.49) , (0.47 ± 0.64) , and $(7.00 \pm 1.61)\% \text{ yr}^{-1}$ (1 sigma) were derived for January 1995 to October 1999. However, if 1998 measurements are excluded from the fit, CO and HCN trends that are not statistically significant, and a statistically significant decrease in the C₂H₆ tropospheric column, are inferred. Comparisons of the infrared CO columns with CO in situ surface measurements suggest that the CO free tropospheric vertical volume mixing ratio profile generally decreases with altitude throughout the year.

1. Introduction

Carbon monoxide (CO), ethane (C₂H₆), and hydrogen cyanide (HCN) are important indicators of tropospheric pollution readily measured in the infrared with ground-based solar absorption spectroscopy. Measurements of these molecules (and of over a dozen others) have been performed routinely since 1984 at the International Scientific Station of the Jungfraujoch (ISSJ), located at 3.58 km altitude in the Swiss Alps (46.55°N latitude, 7.98°E longitude). These observations and the earlier solar measurements obtained at 0.1 to 0.3 cm⁻¹ spectral resolution in 1950–1951 [Migeotte *et al.*, 1956] are unique databases for assessing changes in the atmospheric chemical composition above central Europe during the second half of the twentieth century [Zander *et al.*, 1993, 1994a].

Carbon monoxide is released at the ground as a byproduct of combustion and is also produced as an intermediate in the oxidation of methane (CH₄) and nonmethane hydrocarbons. Reaction of CO with the hydroxyl radical (OH) accounts for

more than 90% of the loss of CO in the troposphere [Logan *et al.*, 1981] and about 75% of the OH removal [Thompson, 1992]. Consequently, changes in CO emissions will have an important effect on OH levels and hence on the oxidizing capacity of the troposphere [Sze, 1977; Levine *et al.*, 1985; Thompson, 1992].

The presence of carbon monoxide in the Earth's atmosphere was first reported by Migeotte [1949] based on CO lines observed in the (1-0) band of solar spectra recorded in 1948 near Columbus, Ohio. Since that time, numerous measurements of CO have been reported with ground-based [e.g., Zander *et al.*, 1989; Pougetchev and Rinsland, 1995; Rinsland *et al.*, 1998a; Notholt *et al.*, 2000], aircraft-based [McMillan *et al.*, 1996; Worden *et al.*, 1997], and space-based [e.g., Reichle *et al.*, 1990; Rinsland *et al.*, 1998b; Connors *et al.*, 1999] remote sensing techniques. In situ samplings of tropospheric CO from networks of surface sites [Novelli *et al.*, 1994, 1998; Forrer *et al.*, 2000] and from aircraft-based samplers [Sachse *et al.*, 1991; Herman *et al.*, 1999] have provided additional information on the temporal, spatial, and vertical distribution of tropospheric CO. Maximum annually averaged lower tropospheric CO concentrations are measured at northern middle and high lati-

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tudes [Novelli *et al.*, 1998, Figure 7], where both maximum industrial activity and fossil fuel usage occur.

Comparisons of ISSJ solar absorption spectra recorded in 1950–1951 and during the 1970s and early 1980s showed a significant long-term CO total column abundance increase of about 0.7 to 1%/yr [Rinsland and Levine, 1985; Zander *et al.*, 1989]. However, subsequent solar observations at ISSJ up to early 1995 indicated that this trend in total column CO above central Europe had inverted. Although spring 1992 measurements were relatively high, record low CO total columns were measured above ISSJ during the second half of 1992 and throughout 1993 [Mahieu *et al.*, 1997, Figure 3]. These observations of an abrupt shift in the CO trend from an increase to a decrease around the mid-1980s are consistent with surface sampling measurements from stations in both hemispheres [Khalil and Rasmussen, 1994; Novelli *et al.*, 1994, 1998]. The recent trend in tropospheric CO has varied interannually and with location [Novelli *et al.*, 1998]. The variations are driven by imbalances between sources and sinks. They reflect the relatively short tropospheric lifetime of CO (~2 month global average [Volz *et al.*, 1981]), variations in source emissions, transport from source regions to sampling stations, and possible changes in OH tropospheric levels.

Ethane (C₂H₆) is the most abundant nonmethane hydrocarbon in the atmosphere. The molecule is released at the surface principally by natural gas leaks in the northern hemisphere and biomass burning in the tropics [Rudolph, 1995]. Removal of C₂H₆ from the troposphere is primarily due to reaction with OH radicals, and the average global C₂H₆ lifetime is also about 2 months [Rudolph and Ehhalt, 1981]. The concentration of C₂H₆ drops rapidly with increasing altitude above the tropopause because C₂H₆ reacts rapidly with both OH and atomic chlorine [Rudolph *et al.*, 1981; Goldman *et al.*, 1984; Coffey *et al.*, 1985]. Maximum and minimum concentrations of tropospheric C₂H₆ are generally measured at high northern latitudes during spring and autumn, respectively [e.g., Ehhalt *et al.*, 1991]. The 1951 Jungfraujoch spectra had sufficient spectral resolution to show C₂H₆ spectral features in the 3 μ m region [Rinsland and Levine, 1986; Ehhalt *et al.*, 1991]. Analysis of ISSJ spectra from 1951 and 1984–1988 showed a long-term increase in the C₂H₆ tropospheric burden between 1951 and 1984–1988 of $(0.85 \pm 0.3)\%$ yr⁻¹ [Ehhalt *et al.*, 1991]. However, an analysis of the ISSJ database of measurements spanning 1985–1995 showed the increase had reversed to a decline [Mahieu *et al.*, 1997, Figure 4]. The observation of a decrease over this time span is consistent with measurements of tropospheric C₂H₆ columns above the Kitt Peak National Solar Observatory in Arizona (31.9°N latitude, 111.6°W longitude, 2.09 km altitude) between May 1977 and December 1997 [Rinsland *et al.*, 1998a].

Hydrogen cyanide (HCN) was first detected in the stratosphere based on infrared solar spectra recorded with a high-altitude aircraft [Coffey *et al.*, 1981]. Initial analysis of ground-based infrared solar spectra recorded from Kitt Peak indicated that HCN is nearly uniformly distributed in the troposphere with an average mixing ratio of ~166 parts per trillion by volume (pptv) or 10⁻¹² per unit volume, between 2 and 12 km [Rinsland *et al.*, 1982]. Subsequent time series of ground-based solar measurements from ISSJ and Kitt Peak showed spring-time tropospheric HCN enhancements with the elevated HCN levels tentatively attributed to biological activity [Mahieu *et al.*, 1995, 1997].

Recently, spectra of laboratory fires, ground-based infrared

solar spectra, solar occultation spectra, and airborne field measurements have shown that HCN emissions from fires are likely to contribute significantly to the budget of reactive nitrogen in the troposphere, particularly in the tropics where intense burning occurs most frequently [see Rinsland *et al.*, 1999, section 4.3, and references therein]. An initial evaluation of the chemistry of HCN suggested that the principal pathway for HCN loss is its reaction with atmospheric OH and O(¹D), leading to an estimated atmospheric residence time of 2.5 years [Cicerone and Zellner, 1983]. However, the large variations in HCN tropospheric measurements have prompted a reevaluation of the chemistry of HCN. Li *et al.* [2000] proposed that biomass burning is the primary source of HCN and that ocean uptake provides the main sink. They estimate a HCN atmospheric lifetime of 2 to 4 months on the basis of a comparison of infrared solar absorption measurements with simulations calculated with their global three-dimensional (3-D) model. Zonal averaged model calculations performed for ISSJ with these assumptions, a prescribed CO emissions inventory, and a constant HCN/CO emissions ratio of 1.1% show a predicted HCN total column maximum in spring. Although the timing of the maximum is generally consistent with the ISSJ measurements through 1996, the model HCN total column seasonal maximum, it is significantly broader than the ISSJ seasonal measurements [Li *et al.*, 2000, Figure 1]. Hence the origin of HCN spring peak above ISSJ remains not well understood.

The purpose of this paper is to report the time series of CO, C₂H₆, and HCN tropospheric column measurements derived from infrared solar observations made at ISSJ between January 1995 and October 1999. The selected time period includes the strong El Niño warm phase of 1997–1998 when related Southeast Asian tropical fires [Liew *et al.*, 1998; Levine, 1999; United Nations Environment Programme (UNEP), 1999] significantly perturbed tropospheric chemistry in Asia and the Pacific [see Rinsland *et al.*, 1999, and references therein]. We evaluate the possible effects of these fires by comparing tropospheric CO, C₂H₆, and HCN columns above the ISSJ station during the El Niño warm phase with corresponding measurements from the other time periods. The data reported here are complementary to a large list of atmospheric compounds more specifically monitored at ISSJ as part of the Belgian commitment toward the Network for the Detection of Stratospheric Change (NDSC) [Kurylo, 1991; Zander *et al.*, 1999; URL: <http://www.ndsc.ncep.noaa.gov/>]. We also compare our IR remote spectroscopic CO observations with in situ CO sampling measurements made at ISSJ between January 1997 and December 1999 with a commercial instrument. The in situ measurements were acquired by the Air Pollution/Environmental Technology group in Duebendorf, Switzerland. Information resulting from this comparison is discussed in section 5.1.

2. Infrared Solar Spectroscopic Measurements

The infrared solar absorption measurements are recorded at ISSJ with two Fourier transform spectrometer (FTSs). The first is a homemade instrument which began operation in 1984. The second is a commercial BRUKER IFS 120-HR. Both instruments can operate in the 1–5.4 μ m (InSb detector) and 8–14 μ m (HgCdTe detector) domains. The measurements for CO and C₂H₆ reported here were obtained with the BRUKER instrument in combinations with an InSb detector. The HCN measurements were recorded with both instruments and InSb

detectors. Solar spectra from both instruments are recorded in the air. The homemade instrument is installed at the coudé focus of a 76-cm diameter, 33-m focal length telescope; the spectrometer focal length is 700 mm, and the HCN spectra obtained with it were recorded with an entrance aperture diameter of 2.4 mm (3.4-mrad field of view) and a resolution of 0.017 cm⁻¹ (defined as 0.9 divided by the maximum optical path difference). The BRUKER spectrometer focal length is 418 mm; it is fed by a homemade coelostat. Entrance aperture diameters range from 1.1 to 1.6 mm, which corresponds to 2.6 to 3.7 mrad fields of view. Although this instrument can achieve a resolution of 0.002 cm⁻¹, most spectra were recorded unapodized with spectral resolutions of 0.005 to 0.008 cm⁻¹.

After discarding fittings of lower quality based on realistic criteria described by Rinsland *et al.* [1998a, Figure 9], the solar spectral database reported here contains measurements on 406, 452, and 352 days between January 1995 and October 1999 for CO, C₂H₆, and HCN, respectively. The selected time period provides overlap with the earlier reported time series of ISSJ solar measurements extending from 1984 to mid-1995 for these three molecules [Mahieu *et al.*, 1997]. The solar measurement time series also overlaps with a CO and C₂H₆ solar absorption measurement time series recorded synchronously with a mobile high-resolution FTS installed in the nearby Grindelwald valley at an altitude of 1070 m [Barret *et al.*, 1999]. Measurements at ISSJ and the Grindelwald site were recorded during a first measurement campaign in May and June 1998. Average mixing ratios between the altitudes of the two stations were derived for both CO and C₂H₆ from concurrent measurements analyzed with the same methods and spectroscopic parameters. The results are briefly discussed in relation to the additional boundary layer concentration information and validations they provided.

3. In Situ Sampling Measurements

Surface level measurements of CO at ISSJ by the Swiss Federal Laboratories for Materials Testing and Research (EMPA) began in spring 1996. The in situ measurements have been recorded continuously since that time with a commercially available instrument (HORIBA APMA-360) using the Nondispersive Infrared (NDIR) technique. Calibration of the instrument is performed using CO calibration gas traced back to Reference Material of the National Institute of Standards and Technology (NIST). The accuracy is estimated to be 6 ppbv (level of confidence 95% for an hourly mean value). The instrument is calibrated twice a month using zero air and CO calibration gas (1–10 ppmv (10⁻⁶ per unit volume)) of CO in 4.7 ppmv of N₂. Estimated overall uncertainty is ~10% (95% confidence level) for hourly mean values [Forrer *et al.*, 2000].

Back trajectories corresponding to the measurement times and ending at the Jungfraujoch and 700 hPa have been calculated with the TRAJEC DWD model [Fay *et al.*, 1995] and wind fields from the Swiss Model (SM). These calculations have been used to classify the measurements into two periods, that is, undisturbed free tropospheric conditions and periods possibly influenced by one or more meteorological processes leading to nonbackground concentration levels (C. Zellweger *et al.*, A 2-year record of reactive nitrogen (NO_y) at a high-alpine site (Jungfraujoch, 3580 m asl, Switzerland), submitted to *Journal of Geophysical Research*, 2000). We used this filter to exclude nonbackground CO measurements for the time period when the trajectory results were available, namely, January 1,

1997, to December 31, 1999. Results of the trajectory analysis were not available for the earlier measurements, and therefore they are not included here.

Although the meteorological filter mentioned above proved highly successful in identifying and removing nonbackground measurement of NO_x and NO_y, which are also measured in situ at ISSJ, this approach was not entirely successful for CO, probably because its lifetime is significantly longer than those of NO_x and NO_y. Vertical exchange may occur outside the range of the trajectory calculations, and there are inherent uncertainties in calculating trajectories over the complex terrain of the ISSJ region. Therefore we also excluded days from the database when the standard deviation of the measurements exceeded the mean value by more than 10%. While these samples may represent true CO background variations, they were regarded as suspect. In addition, December 1997 was removed because of construction activities that could have occasionally influenced the measurements [Forrer *et al.*, 2000, section 2].

4. Spectral Retrievals

4.1. Method

The infrared solar spectra were analyzed with the SFIT2 algorithm, which has been developed for the retrieval of molecular vertical profiles from ground-based infrared solar observations made with high-quality FTIR spectrometers. With this algorithm the vertical profiles of one or two molecules can be retrieved by simultaneously fitting one or more narrow spectral intervals (microwindows) in one or more solar spectra. The forward and inverse models in SFIT2 have been described previously [Pougatchev *et al.*, 1995; Rinsland *et al.*, 1998a]. The inversion technique is based on a semiempirical application of the optimal estimation technique [Rodgers, 1990]. The algorithm includes a model for simulating and fitting the absorption by solar CO lines [Rinsland *et al.*, 1998a, section 3.2.2]. In the present applications the modeling of instrument performance-related characteristics included a parameter to retrieve the wavelength shift between the measured and calculated spectra and another one to fit for the slope of the background in each microwindow. The latter parameter was required primarily because of uncertainties in modeling the absorption by lines outside the fitted regions, particularly those of H₂O and its continuum, also to account for the overall transmission response of the instruments.

Refractive ray-tracing paths were performed for the solar zenith angle of the observations with the FSCATM program described by Gallery *et al.* [1983]. Daily pressure-temperature-altitude profiles were calculated from P-T profiles provided by the National Centers for Environmental Prediction (NCEP). Above 55 km these values were extended based on the 1976 U.S. Standard Atmosphere.

4.2. A Priori Profiles and Covariance Matrix Parameters

As summarized by Logan *et al.* [1981, Figure 10], CO aircraft measurements over Europe show large scatter with, on average, higher CO mixing ratios near the surface than in the upper tropospheric layers. The a priori profile adopted for the CO ISSJ retrievals reflects this gradient and was taken from Zander *et al.* [1989, Table 2]. The profile decreases from 83 ppbv (1 ppbv = 10⁻⁹ per unit volume) at 3.58 km, the altitude of ISSJ, to 62 ppbv at 12 km, and reaches a minimum of 16 ppbv at 38 km. Higher up, the profile increases with altitude, reflecting

the increasing contribution of CO₂ photolysis as a source of CO molecules in the mesosphere and lower thermosphere [Solomon *et al.*, 1985]. This a priori profile was extrapolated from 58 to 100 km by data from Smith [1982].

The tropospheric portion of the a priori profile for C₂H₆ is based on the two-dimensional model calculations of Kanakidou *et al.* [1991]. We adopted an average of March and December profiles for the latitude of the Jungfraujoch and extended this profile above 17 km to connect with a reference profile constructed by Smith [1982]. For HCN a constant mixing ratio of 185 pptv was assumed below 11 km. At higher altitudes the ISSJ reference profile given by Mahieu *et al.* [1995, Table 3] was adopted.

Covariances for the CO, C₂H₆, and HCN mixing ratio vectors were assumed to be diagonal. We expressed the uncertainties relative to the a priori mixing ratio in the layer. For CO the assumed values ranged from 0.2 above 40 km, increasing to 0.4 below 30 km. For C₂H₆ and HCN, relative mixing ratio uncertainties of 1.0 and 0.5 were assumed for all 29 layers in the atmospheric model, respectively. The selected parameters provide weak constraints as demonstrated from retrievals performed from simulated spectra calculated for realistic ranges in atmospheric variability [Rinsland *et al.*, 1998a, Figure 1].

4.3. Microwindows and Spectroscopic Parameters

The CO retrievals were performed by simultaneously fitting measurements in three narrow intervals, 2057.78–2057.91, 2069.61–2069.71, and 2157.30–2159.15 cm⁻¹. As illustrated by Pougetchev and Rinsland [1995, Figure 1], these intervals contain the weak P(10) line of ¹³CO at 2057.8578 cm⁻¹, the weak P(7) ¹³CO line at 2069.6559 cm⁻¹, and the strong R(3) line of ¹²CO at 2158.2997 cm⁻¹. In the first two windows, interfering absorptions by atmospheric O₃ and N₂O were fitted by single multiplicative factors applied to reference a priori profiles taken from Smith [1982]. Similarly, a priori profiles [Smith, 1982] for CO₂, O₃, N₂O, and H₂O were each scaled by a single multiplicative factor to improve the fits to the atmospheric absorption lines in the third window. Solar CO lines produce additional features in all three windows. Modeling of the absorption by the overlapping solar CO lines followed the approach described previously [e.g., Rinsland *et al.*, 1998a, sections 3.1 and 3.2.2].

Retrievals of C₂H₆ and HCN were both performed with single microwindows. As described previously [Rinsland *et al.*, 1998a], interferences by weak O₃ lines and the wings of nearby H₂O and CH₄ lines need to be fitted in the C₂H₆ retrievals, particularly from low-altitude stations. Reference volume mixing ratio profiles [Smith, 1982] for each interferent were scaled by a single multiplicative factor to minimize the residuals. The HCN window lies on the wing of a strong and broad H₂O line, but otherwise it is free of interferences [Mahieu *et al.*, 1995].

Spectroscopic parameters for atmospheric CO and HCN lines were taken from the 1996 HITRAN compilation [Rothman *et al.*, 1998]; those adopted for C₂H₆ have been described by Rinsland *et al.* [1998a, section 4.1].

4.4. Retrieval Characterization

Figure 1 illustrates CO, C₂H₆, and HCN averaging kernels computed for profile retrievals from columns integrated from layers with boundaries of 3.58–11.0 and 11.0–100.0 km. The 3.58–11 km layer corresponds roughly to the free troposphere above ISSJ, as the height of the tropopause above the station varies from about 10 km during winter to nearly 12.5 km during

summer. A typical spectral resolution corresponding to a maximum optical path difference of 175 cm and signal-to-noise ratios of 200, 300, and 2000 were assumed for CO, C₂H₆, and HCN, respectively. These values were selected empirically to obtain averaging kernels with similar altitude distributions. As can be seen from Figure 1, the averaging kernels for the bottom layer are broad with maxima in the middle to upper troposphere. The kernel peaks for the 3.58–11.0 km layer are located at 5.2, 8.0, and 8.9 km for CO, C₂H₆, and HCN, respectively.

4.5. Error Analysis

Table 1 lists the error budgets for the 3.58 to 11.0 km free tropospheric columns, resulting from the most important random and systematic sources of uncertainty. The approach used to estimate these uncertainties is similar to that adopted in several previous studies [e.g., Zander *et al.*, 1994b; Rinsland *et al.*, 1998a, 1999].

Sources of random errors considered were uncertainties in temperature profiles and in the effective solar zenith angles, as well as retrieval errors due to random instrument noise and interfering absorptions. We estimated the temperature error by offsetting the nominal temperatures by 2 K in all atmospheric layers. This offset is larger than the typical quoted NCEP error in the troposphere, but it is less than that quoted by NCEP for the upper atmosphere.

Spectra recorded with the BRUKER interferometer are typically generated from 15 interferograms under high Sun conditions. A total of nine and three interferograms are usually averaged for solar zenith angles ranging from 70° to 80° and 80° to 85°, respectively. Observations with the homemade instrument are recorded more slowly; therefore three interferograms are typically averaged for solar zenith angles smaller than 75°, and individual recordings are used for larger zenith angle observations.

Effective solar zenith angles of the averaged spectra were calculated from the mean air mass of the observations on the basis of the time of the zero path difference crossing of each interferogram. The error on this time is of the order of 1 s and has a negligible effect on the retrieved columns. Spectra with solar zenith angles larger than 75° and 80° were not included in the respective analysis of CO and C₂H₆. A maximum solar zenith angle of 87° was adopted for HCN. Errors due to random noise were evaluated based on estimates for typical ISSJ measurements.

Sources of systematic errors considered in the analysis include the spectroscopic parameters, the a priori profile, forward model approximations, and errors in the instrument line shape function. The largest errors are attributed to inaccuracies in simulating solar CO lines in the three CO microwindows and potential biases in the retrievals due to errors in modeling weak interfering and/or wide overlapping wing absorptions of H₂O for all three target species.

The error in the 3.58–11 km column determinations resulting from an uncertainty in the instrument line shape function was calculated as described previously [Rinsland *et al.*, 1999, section 3.5]. The estimated error is <1% for all three molecules. The total random and systematic errors arrived at in Table 1 are 2.6 and 4.5% for CO, 6.6 and 5.9% for C₂H₆, and 6.5 and 6.3% for HCN, respectively. The most important sources of error appear to be instrument noise for the weak absorbers C₂H₆ and HCN, and solar line modeling for CO. The air-broadening coefficient assumed for the HCN target

Figure 1. Averaging kernels for CO, C₂H₆, and HCN profile retrievals calculated for a typical ISSJ solar absorption observation. Values are shown for 3.58–11.0 km. This altitude range corresponds approximately to the free troposphere above ISSJ. Kernels for 11–100 km altitude are also shown.

Table 1. CO, C₂H₆, and HCN 3.58–11 km Partial Column Measurement Uncertainties

Error Source	Relative Error, %		
	CO	C ₂ H ₆	HCN
<i>Random Error Budget</i>			
Temperature	2.2	1.3	1.7
Instrument noise	1.3	6.5	6.3
Zenith angle	<1	<1	<1
Interfering lines	<1	<1	<1
RSS total random error	2.6	6.6	6.5
<i>Systematic Error Budget</i>			
Spectroscopic parameters	2	5	5
A priori profile	0.5	2.4	3.2
Forward model approximations ^a	4	2	2
Instrument line shape function	<1	<1	<1
RSS total systematic error	4.5	5.9	6.3

^aIncludes the estimated uncertainty in the retrieval due to errors in computing the absorption by overlapping solar CO lines.

line on HITRAN 1996 originates from the HITRAN 1986 compilation [Rothman *et al.*, 1987]. It was computed by multiplicatively scaling the 0.06-cm⁻¹ resolution room temperature N₂-broadening measurement for the line [Smith *et al.*, 1984] by 0.9. The relative uncertainties in the individual HCN air-broadening coefficients on HITRAN are quoted as 10–20% [Rothman *et al.*, 1987]. We estimate that a 5% relative error in the 3.4–11 km column results from the uncertainties in the current HCN spectroscopic parameters. It is only through additional laboratory measurements of HCN air-broadened widths and intensities that more accurate retrievals of atmospheric hydrogen cyanide will be possible.

5. Results

Figure 2 displays daily average free tropospheric (3.58 to 11 km) columns of CO, C₂H₆, and HCN between January 1995 and October 1999. Values on the right vertical axis represent approximate average mixing ratios calculated by dividing the

Figure 2. Time series of daily average CO, C₂H₆, and HCN 3.58–11.0 km columns (pluses) retrieved from the ISSJ solar spectra. Continuous lines represent the mean trend over the displayed period of observations (January 1995 to October 1999) considered in this work, as well as the superimposed seasonal variation obtained by a fit to the observational time series with equation (1). Measurements obtained with the BRUKER interferometer are displayed with pluses. Some of the HCN measurements were recorded with a homemade instrument and are displayed with open triangles.

3.58–11 km columns by the column of air for this same layer. The solid curves display unweighted least squares fits to the daily average columns calculated with the formula

$$f(t) = a_0 + a_1 t + a_2 \cos 2\pi(t - t_0 - \phi) \quad (1)$$

where t is the time expressed in calendar years and the coefficients a_0 , a_1 , a_2 , and ϕ were derived from the least squares fit to the daily mean partial columns. The parameter t_0 is the first day of the time series. The slope a_1 determined from the time series fit divided by the mean value is defined as the long-term trend over the period of observations; a_2 corresponds to the amplitude of an assumed sinusoidal seasonal cycle; and ϕ is the fraction of the year at which the seasonal maximum occurs. We next discuss the results for each molecule. The in situ surface measurements of CO are included in the overall discussion in section 5.1.

5.1. Carbon Monoxide (CO)

A typical ISSJ solar spectral fit over the three microwindows of CO is illustrated in Figure 3. The high quality of the measurements is apparent. The agreement between the measured and best fit calculated spectra is also very good, though there are minor fitting errors due to the crude model used to represent the solar CO lines. Out of a total of 1093 solar spectra recorded on 406 days between January 1995 and October 1999, there were 1070 that passed our semisubjective criteria to exclude low-quality measurements [Rinsland *et al.*, 1998a, section 5]. The a priori profiles of N₂O and O₃ were also scaled by single multiplicative factors; the latter were required in addition to retrieving the CO vertical profile, in order to fit the measurements to the instrumental noise level.

Table 2 presents monthly averages of the ISSJ measure-

Figure 3. The larger frames reproduce ISSJ sample observations encompassing the three spectral intervals used to retrieve CO, as well as best fits to these data. The measurements in each window are normalized to the peak intensity. Residuals (measured minus calculated signals) are plotted on an expanded vertical scale above each of these frames. The spectrum was recorded on January 6, 1999, at an apparent solar zenith angle of 74.20°.

ments. These values were computed by first generating daily averages from the retained observations. Monthly mean and standard deviations were then computed for two time periods: year 1998 (labeled ENH, for enhanced) and the remainder of the observation period (BKG, for background). The selection of these two time periods is based on the characteristic variations of all three molecules as displayed in Figure 2. Monthly mean CO measurements for the 1998 ENH period are higher by factors of 1.1 to 1.3 as compared to corresponding monthly averages derived from the BKG period observations. Additionally, Figure 2 shows very low column values during 1997, definitely below the average time series fit. The CO trend for the full time period displayed in Figure 2 is equal to $(2.40 \pm 0.49)\% \text{ yr}^{-1}$ (1 sigma); if the 1998 measurements are excluded, the CO trend equals $(0.48 \pm 0.43)\% \text{ yr}^{-1}$ (1 sigma). Hence the statistically significant increase obtained by fitting the entire time period with (1) can be attributed to the elevated measurements during 1998.

Figure 4 displays a comparison of monthly mean CO mixing

ratios calculated from the ISSJ in situ measurements (open circles) and monthly mean 3.58–11 km CO column averages. Average mixing ratios for the 3.58–11 km free troposphere were calculated by dividing the monthly mean CO columns by the corresponding vertical air column (solid circles). Displayed error bars represent standard deviations calculated from the daily means after removal of suspected nonbackground measurements as described in section 3. Both sets of measurements show seasonal and interannual variations with a winter maximum and a summer minimum. Measurements from the spring 1998 maximum are higher than corresponding values from 1997 and those measured through March 1999. The monthly mean surface mixing ratios are a factor of 1.25 ± 0.1 times higher than corresponding monthly mean mixing ratio calculated from the 3.58–11 km column where the error bar represents the standard deviation. The ratio shows no systematic variation with season for the 35 months in common. This result suggests that the free tropospheric CO mixing ratio profile over central Europe decreases with altitude, with minor vari-

Table 2. CO 3.58–11 km Column Monthly Mean Calculations From ISSJ Solar Spectra Recorded During Background (BKG) and Enhanced (ENH) Time Periods^a

Month	Time Period	Mean Column	Standard Deviation	Number of Days
January	BKG	1.007	0.109	24
January	ENH	1.229	0.060	9
February	BKG	1.104	0.093	17
February	ENH	1.234	0.054	7
March	BKG	1.165	0.101	40
March	ENH	1.298	0.091	10
April	BKG	1.206	0.127	37
April	ENH	1.407	0.155	7
May	BKG	1.065	0.122	16
May	ENH	1.294	0.087	10
June	BKG	0.989	0.088	38
June	ENH	1.086	0.093	11
July	BKG	0.888	0.080	24
July	ENH	0.938	0.103	9
August	BKG	0.901	0.224	21
August	ENH	1.076	0.171	13
September	BKG	0.778	0.064	25
September	ENH	1.014	0.085	5
October	BKG	0.850	0.050	42
October	ENH	0.995	0.148	5
November	BKG	0.884	0.098	11
November	ENH	1.114	0.098	5
December	BKG	0.924	0.084	13
December	ENH	1.186	0.162	9

^aENH is 1998; BKG is remainder of January 1995 to October 1999. Units are in 10¹⁸ molecules cm⁻².

ations in the ratio of the surface to the mean free tropospheric mixing ratio. An exception definitely occurred in June 1998 (see Figure 4), when the ratio was close to unity, thus implying that the CO mixing ratio was rather constant throughout the troposphere during that month.

The differential FTS CO volume mixing ratios calculated from nearly time coincident June 1998 solar measurements at the ISSJ and Grindelwald sites have been compared with the time series of in situ sampling measurements recorded from ISSJ [Barret *et al.*, 1999, Figure 5]. The FTS and in situ CO mixing ratios show very similar time variations when nearly time coincident measurements are compared, indicating both have high precision. Absolute values agreed to within ~5 ppbv with no obvious bias between the measured in situ and calculated solar spectroscopic boundary layer mixing ratios. As the in situ and FTS techniques are independent of each other, this comparison provides a validation of the results.

5.2. Ethane (C₂H₆)

Figure 5 displays a sample fit to the 2976.60–2976.94 cm⁻¹ window selected for the ISSJ C₂H₆ profile retrievals. In addition to the unresolved C₂H₆ ν_7 band ^PQ₃ subbranch, the band pass contains absorption by overlapping H₂O, CH₄, and O₃ lines. A single parameter was used to multiplicatively scale reference a priori profiles [Smith, 1982] for each interfering molecule. The previous ISSJ retrievals were based on analysis of windows containing the unresolved ^PQ₃ and ^TQ₀ subbranches of the ν_7 band. An indication of the improved quality

Figure 4. Monthly average CO mixing ratios (ppbv) for the 3.58–11 km layer derived from the infrared solar measurements (solid circles) investigated in this work and corresponding values calculated from in situ sampling measurements, all performed at ISSJ. The relatively constant difference between the two data sets is a clear indication that the free tropospheric volume mixing ratio profile of CO above ISSJ is, most of the time, decreasing with increasing altitude (an exception is noticeable for June 1998).

Figure 5. Typical C₂H₆ spectral fit displayed in the same format as in Figure 3. The measured spectrum was recorded at an apparent solar zenith angle of 55.63° on October 16, 1999.

obtained in fitting the ^PQ₃ region with the new line parameters relative to the previous results can be noted by comparing our Figure 5 with Figure 3 of *Ehhalt et al.* [1991]. A total of 2087 valid C₂H₆ measurements (out of 2338 observations) was obtained on 452 different days.

Figure 6 reproduces the correlation between C₂H₆ and CO:

3.58 to 11 km columns derived from ISSJ daily averages. Observations for all seasons are included. The high correlation coefficient is indicative of the similar distribution of sources, dilution, and the nearly equal tropospheric photochemical lifetimes of the two molecules. Separation of the measurements by season did not yield a statistically significant difference in the

Figure 6. Correlation plot of daily average 3.58–11 km C₂H₆ versus CO columns. Measurements from all seasons are included. The solid line shows the best fit to the data.

Table 3. C₂H₆ 3.58–11 km Column Monthly Mean Calculations From ISSJ Solar Spectra Recorded During Background (BKG) and Enhanced (ENH) Time Periods^a

Month	Time Period	Mean Column	Standard Deviation	Number of Days
January	BKG	11.362	2.164	40
January	ENH	12.675	2.220	8
February	BKG	11.980	1.566	29
February	ENH	12.457	1.087	8
March	BKG	12.443	1.682	53
March	ENH	12.411	1.743	12
April	BKG	12.217	2.405	47
April	ENH	12.628	1.338	7
May	BKG	11.394	1.984	29
May	ENH	12.303	1.149	12
June	BKG	8.967	1.240	44
June	ENH	9.148	1.094	13
July	BKG	7.082	1.150	42
July	ENH	7.428	0.968	11
August	BKG	7.119	1.424	42
August	ENH	7.700	1.361	15
September	BKG	6.430	1.306	36
September	ENH	7.850	1.603	8
October	BKG	7.057	1.143	49
October	ENH	8.305	2.477	4
November	BKG	9.404	2.115	18
November	ENH	10.609	0.748	7
December	BKG	11.080	2.428	23
December	ENH	12.136	3.002	9

^aENH is 1998; BKG is remainder of January 1995 to October 1999. Units are in 10^{15} molecules cm^{-2} .

slope of the relation. As was found previously [Rinsland *et al.*, 1998a, 1999; Blake *et al.*, 1999], regressions for C₂H₆ versus CO are highly correlated over a wide range of conditions with the slope of C₂H₆/CO higher at northern hemisphere mid to high latitudes than in the southern hemisphere. The ISSJ slope of 0.0129 is slightly lower than the value of 0.0142 determined from fitting measurements at Kitt Peak (31.9°N, 111.6°W, 2.09 km altitude) [Rinsland *et al.*, 1999, Table 6].

As was done for CO, monthly averages of the C₂H₆ 3.58–11 km columns have been calculated separately for the BKG and ENH time periods; they are reported in Table 3. The latter shows that the monthly mean columns were higher by factors of 1.0 to 1.2 during 1998 than during the reference time period. A fit to the entire time series results in a trend of $(0.47 \pm 0.64)\% \text{ yr}^{-1}$, 1 sigma. If the anomalous 1998 measurements are excluded from the fit, the trend is $(-1.20 \pm 0.65)\% \text{ yr}^{-1}$, 1 sigma, which suggests a continuation of the long-term decrease in C₂H₆ measured previously above ISSJ [Mahieu *et al.*, 1997] and Kitt Peak [Rinsland *et al.*, 1998a]. The best fit to the full time series with (1) (see Figure 2) yields an amplitude of 3.08×10^{15} molecules cm^{-2} , which corresponds to a peak-to-peak seasonal cycle amplitude equal to 0.64 times the mean of the 3.58–11 km columns. The peak C₂H₆ 3.58–11 km column occurs during late winter, and the minimum is observed during August. The late winter peak may be due to the accumulation of C₂H₆ at high latitudes during winter because of its long lifetime and slow exchange with lower latitudes, followed by the spring release from this reservoir during the breakup of Arctic circulation [Lightman *et al.*, 1990]. Our conclusions regarding the seasonal changes in C₂H₆ above the ISSJ station are consistent with those reported by Ehhalt *et al.* [1991].

Barret *et al.* [1999, Figure 4] reported C₂H₆ differential columns derived in June 1998 from near-simultaneous solar mea-

surements at the ISSJ station and the nearby Grindelwald valley. The measured average mixing ratio of 1.196 ppbv ($1 \text{ ppbv} = 10^{-9}$ per unit volume) agrees closely with an annual average mixing ratio of 1.150 ppbv determined from northern hemisphere in situ measurements at the ground, as reported by Gupta *et al.* [1998] and the value of 1.030 ppbv reported by Rasmussen and Khalil [1982, Table 1] based on June 1978 in situ measurements. Further validations are needed because of the seasonal and latitudinal changes in C₂H₆ boundary layer concentrations due to variations in emissions and changes in OH levels.

5.3. Hydrogen Cyanide (HCN)

By far, HCN exhibited the largest enhancements during 1998 relative to the “background” time period. Figure 7 shows ISSJ sample spectra and the corresponding best fits over the microwindow selected for analysis of HCN. The two frames illustrate spectra recorded at nearly the same apparent solar zenith angle but leading to 3.58–11 km columns differing by a factor of 2.2 (1.22×10^{15} and 2.66×10^{15} molecules cm^{-2} on January 27, 1997, and on June 23, 1998, respectively). The HCN trend derived from fitting the January 1995 to October 1999 daily averages (see Figure 2) equals $(7.00 \pm 1.61)\% \text{ yr}^{-1}$, 1 sigma. There were 847 valid measurements (out of a total of 1068 observations) on 352 different days. The trend computed with 1998 measurements excluded from the fit equals $(0.73 \pm 1.38)\% \text{ yr}^{-1}$. Hence the large positive trend can be attributed entirely to the 1998 enhancements. A previous study of HCN columns above ISSJ was based on measurements of the same transition in solar spectra observed from 1984 to the end of 1995 [Mahieu *et al.*, 1997, section 3.6]. Their fit to that ISSJ database indicated a long-term HCN total column trend equal to $(1.24 \pm 0.36)\% \text{ yr}^{-1}$. An increase of $(1.0 \pm 1.0)\% \text{ yr}^{-1}$, 1 sigma, was derived on the basis of a comparison between Atmospheric Trace Molecule Spectroscopy Experiment (ATMOS) lower stratospheric measurements in 1985 and 1994 [Rinsland *et al.*, 1996].

The ISSJ 3.58–11 km HCN seasonal maximum occurs about a month and a half after the seasonal peaks in CO and C₂H₆. During the springtime HCN maximum, observed above both ISSJ and Kitt Peak [Mahieu *et al.*, 1995], the HCN lines were often found to be much broader than during the rest of the year, and significantly larger concentrations in the first kilometer above the sites had to be assumed for achieving good quality fits. This result in combination with evidence for emissions of HCN by higher plants and from bacteria and fungi (see Cicerone and Zellner [1983] for a list of references) gave rise to the hypothesis that enhanced vegetative activity is the primary source of the increased springtime HCN emissions. The later seasonal peak for HCN relative to CO and C₂H₆ remains valid with or without the 1998 observations included in the time series fit. Li *et al.* [2000] have attributed the spring to summer HCN peaks measured at ISSJ and other northern hemisphere stations as due to biomass burning in the northern hemisphere tropics, which peaks in February, combined with the smaller signal from HCN emitted by boreal fires during summer. The high variability and elevated springtime columns observed above ISSJ (see Figure 2 for January 1995 to October 1999 and Figure 3 of Mahieu *et al.* [1995] for June 1984 to June 1993 observations) are consistent with this hypothesis. However, HCN versus CO 3.58–11 km correlation plots derived from the present set of observations as a function of season show only moderately high correlation coefficients ranging from 0.39 in

Figure 7. Examples of ISSJ solar spectra and best fits in the microwindow used to retrieve HCN, presented in the same format as Figure 3. The pair of observations corresponds to similar air masses, but the retrieved 3.58–11 km columns differ by a factor 2.2 which is typical of observed HCN variability. Both measurements were recorded with the ISSJ BRUKER interferometer.

October to December, 0.56 in April to June, 0.84 in July to September, and 0.74 in January to March. The highest correlation is observed during the period of maximum burning in the northern tropics [Li *et al.*, 2000]. The correlation coefficient is much lower than the value of 0.95 derived for the last half of 1999 above Mauna Loa [Rinsland *et al.*, 1999, section 3.4]. A significant contribution from fossil fuel combustion and other nonbiomass burning related sources of CO and HCN are likely to be responsible for the lower correlation between the free tropospheric columns above ISSJ.

At present, it is difficult to reliably test the suggestion of a distant biomass burning source with a model. Emissions by HCN from fires occur primarily during the smoldering rather than the flaming phase of combustion. The emission ratio of HCN relative to that of CO during the smoldering emissions from organic soils [see, e.g., Lobert *et al.*, 1991; Yokelsen *et al.*, 1997] varies by 2 orders of magnitude. As has already been discussed, the lifetime of HCN is uncertain at present with an

important need to quantify the HCN loss rate due to ocean uptake [Li *et al.*, 2000].

6. Discussion

The CO, C₂H₆, and HCN 3.58–11 km columns during 1998 exceeded those measured above ISSJ since intensive monitoring with high-resolution FTS instruments began in 1984 [Mahieu *et al.*, 1997]. Figure 8 provides a plot of the relative enhancements measured during each month of 1998 with respect to monthly averages from the other time periods. Error bars were computed based on the standard deviations presented in Tables 2 to 4. Although the highest 3.58–11 km monthly average columns were measured in May 1998, the relative enhancement in HCN declined from a factor of 1.9 in January to 1.2 in December, whereas the enhancements in CO and C₂H₆ averaged 1.18 to 1.09, respectively, with relatively small variations throughout the year. An understanding of the

Figure 8. Relative enhancements in CO, C₂H₆, and HCN 3.58–11 km columns calculated from the measurements in Tables 2 to 4. Error bars represent values calculated from the standard deviations.

cause of the elevated 1998 free tropospheric columns of the three molecules above ISSJ is not entirely clear. We next speculate on the cause of the increased CO, C₂H₆, and HCN free tropospheric columns based on the information currently available.

Free tropospheric columns of all three molecules derived from infrared solar absorption spectra recorded from the Mauna Loa NDSC station (19.5°N latitude, 155.6°W longitude, 3.4 km altitude) show variable enhancements beginning in about September 1997 [Rinsland *et al.*, 1999, Figure 8] with 3.4–16 km column enhancements peaking at 1.43 ± 0.30 for CO and 1.43 ± 0.41 for C₂H₆ in November 1997. Columns of HCN for 3.4–16 km were elevated by up to a factor of 3 with day-to-day changes that closely paralleled those of CO and C₂H₆. As the global average lifetimes of all three molecules are moderately long in the troposphere (about 2 months for CO and C₂H₆ and a few months to 2.5 years for HCN as already mentioned), the measured free tropospheric columns during 1998 may have been increased by emissions from the intense and widespread fires that burned in Southeast Asia during the strong El Niño of 1997–1998 warm phase, the most intense indicated by El Niño/Southern Oscillation (ENSO) indices compiled for 1970 to 2000 (http://www.coaps.fsu.edu/pub/JMA_SST_Index/jma.gif). However, as can be seen from our Figure 8, the relative enhancements of CO and C₂H₆ are nearly constant throughout the year and different than the seasonal distribution of the HCN enhancements, which showed a gradual decline with time. Rapid losses of CO and C₂H₆ due to reaction with OH radicals in the tropics and the

effects of dilution are likely to have reduced enhancements of both molecules after long-range transport of tropical emissions to above the ISSJ station.

The fires of 1997–1998 were not restricted to tropical latitudes, as average OH levels are significantly lower at mid to high latitudes [e.g., Wang *et al.*, 1998, Figure 3] than in the tropics, and increased burning due to changes in weather patterns in extratropical regions could have resulted in enhanced emissions of CO, C₂H₆, and HCN with reduced losses due to lower concentrations of OH radicals. The distribution of fires, their emissions, and their impact on tropospheric chemistry have yet to be quantified for the 1997–1998 period. Changes in OH levels in response to altered O₃ levels could also have played a role in the observed levels of CO and C₂H₆. Elevated columns of CO, C₂H₆, and HCN over northern Japan during summer-fall 1996, 1997, and most significantly 1998 have been reported (Y. Zhao *et al.*, Spectroscopic measurements of tropospheric CO, C₂H₆, and HCN in Japan, submitted to the Quadrennial Ozone Symposium, Sapporo, Japan, 2000). Time series from mid-1995 to mid-1999 show the tropospheric HCN columns above the two stations were well above background from late 1997 through the end of 1998, and both CO and C₂H₆ were also elevated above background levels in late 1998. Back trajectory calculations and National Oceanic and Atmospheric Administration (NOAA) fire imaging measurements during this period originate mostly from the west, often covering 30°N to 60°N latitude. Hence elevated levels of CO and C₂H₆ originated from such enhanced northern midlatitude biomass burning emissions during 1997–1998 could also have been transported above ISSJ. As the average lifetime of HCN may be significantly longer than those of CO and C₂H₆, it is possible that the measured HCN emissions above the ISSJ station originated from both tropical and midlatitude sources. A compar-

Table 4. HCN 3.58–11 km Column Monthly Mean Calculations From ISSJ Solar Spectra Recorded During Background (BKG) and Enhanced (ENH) Time Periods^a

Month	Time Period	Mean Column	Standard Deviation	Number of Days
January	BKG	1.189	0.382	24
January	ENH	2.240	0.365	8
February	BKG	1.455	0.265	15
February	ENH	2.108	0.327	6
March	BKG	1.702	0.517	33
March	ENH	2.453	0.232	10
April	BKG	2.075	0.430	32
April	ENH	3.285	0.699	6
May	BKG	2.224	0.308	17
May	ENH	3.662	0.570	9
June	BKG	1.885	0.359	27
June	ENH	2.926	0.498	11
July	BKG	1.507	0.382	23
July	ENH	2.442	0.550	10
August	BKG	2.194	1.478	11
August	ENH	2.803	0.787	13
September	BKG	1.379	0.368	22
September	ENH	1.849	0.259	6
October	BKG	1.331	0.321	34
October	ENH	1.614	0.491	4
November	BKG	1.177	0.342	8
November	ENH	1.686	0.179	6
December	BKG	1.183	0.364	9
December	ENH	1.395	0.293	8

^a ENH is 1998; BKG is remainder of January 1995 to October 1999. Units are in 10^{15} molecules cm^{-2} .

ison of fire statistics and emission inventories for the El Niño 1997–1998 warm phase with statistics from non-El Niño time periods in combination with tropospheric photochemical-transport model calculations would/should help in assessing the origin of the emissions that caused the increased 1997–1998 free tropospheric CO, C₂H₆, and HCN column enhancements above the ISSJ station.

7. Summary and Conclusions

Time series of high spectral resolution infrared solar spectra have been recorded at the high-alpine Jungfraujoch station at 3.58 km altitude in the Swiss Alps along with surface CO measurements. The solar spectroscopic measurements have been analyzed to derive time series of CO, C₂H₆, and HCN columns between 3.58 and 11 km altitude spanning January 1995 to October 1999. This range in altitude corresponds approximately to the free troposphere above the station with maximum retrieval sensitivity in the middle to upper troposphere.

The infrared solar measurement time series have been used to calculate monthly mean mixing ratios for the 3.58–11 km layer. The values have been compared with monthly average in situ CO measurements from the ISSJ station after filtering to remove suspected nonbackground values. This comparison shows a consistent seasonal cycle with the CO profile generally decreasing with altitude in the free troposphere above the ISSJ station throughout the year.

The time series of infrared measurements of all three molecules show distinct seasonal cycles with late winter or early spring maxima and late summer minima. The best fit trends (% yr⁻¹, 1 sigma) over the full time span equal (2.40 ± 0.49) for CO, (0.47 ± 0.64) for C₂H₆, and (7.00 ± 1.61) for HCN. Trends (% yr⁻¹, 1 sigma) after excluding the anomalous 1998 time period equal (0.48 ± 0.43) for CO, (-1.20 ± 0.65) for C₂H₆, and (0.73 ± 1.30) for HCN. Although the CO and HCN trends are not statistically significant with the 1998 measurements excluded, the decline in the C₂H₆ 3.58–11 km column is statistically significant to about 2 sigma uncertainty and consistent with results of recent northern hemisphere trend studies [Mahieu et al., 1997; Rinsland et al., 1998a].

The cause of the anomalous trends of the three molecules during 1998 is not entirely clear. As shown in Figure 8, the seasonal distribution of the 1998 enhancements in CO and C₂H₆ are similar and indicate average enhancements by factors of 1.18 and 1.09 throughout 1998, whereas the HCN enhancement during that time period declined steadily from a factor of 1.9 at the beginning of the year to 1.2 at the end. The HCN monthly mean peak occurred after the up to a factor of 3 increase in the HCN tropospheric columns measured above the Mauna Loa, Hawaii, NDSC station (19.5°N, 155.6°W, 3.4 km altitude) in November 1997 [Rinsland et al., 1999]. The present results provide further evidence for the importance of biomass burning as a source of tropospheric HCN emissions, though the source of HCN emissions during background time periods is not yet clearly identified. Meteorology and transport vary significantly from year to year. Our measurements show the advantage of recording simultaneous observations of chemically related species to diagnose tropospheric processes and trends. The measurements also demonstrate that pollution from distant fires can have a significant impact on the free tropospheric columns of CO, C₂H₆, and HCN and their trends above central Europe. The regional impact of the 1997–1998

tropical fires on tropospheric chemistry in tropical Asia has been quantified [e.g., Hauglustaine et al., 1999], but to our knowledge, an impact outside of the Pacific region has not been reported. Further work such as analysis of fire statistics, compilation of fire emission inventories, and simulations of atmospheric chemistry and transport for 1997–1998 conditions will be needed to obtain a more complete understanding of the perturbations to tropospheric chemistry and climate that occurred during that time period.

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