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Multiyear infrared solar spectroscopic measurements of HCN, CO, C2H6, and C2H2 tropospheric columns above Lauder, New Zealand (45 S Latitude)

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Publication Details
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Abstract
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Keywords
45, zealand, lauder, columns, latitude, c2h2, c2h6, co, hcn, measurements, spectroscopic, solar, infrared, above, tropospheric, multiyear, GeoQuest

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INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: tropospheric chemistry, biomass burning, tropospheric sources and sinks, pollution

1. Introduction

Multiyear measurements of trace gases in the middle and upper troposphere are rare in the extratropical southern hemisphere (ETSH, defined as 30°S–90°S by Manning et al. [1997] and 35°S–90°S by Rudolph [1995]). This region includes some of the cleanest tropospheric air in the world and as such, it is important for studying atmospheric chemical budgets and cycles. The purpose of this paper is to report and interpret time series of HCN, C$_2$H$_2$, CO, and C$_2$H$_6$, tropospheric columns retrieved from infrared solar absorption spectra recorded at high resolution (0.0035 or 0.007 cm$^{-1}$) from Lauder, New Zealand (latitude 45.04°S, 169.68°E, altitude 0.37 km). The measurements were obtained at the Network for the Detection of Stratospheric Change (NDSC) [Kurylo, 1991; Kurylo and Zander, 2000] (data available at http://www.ndsc.ncep.noaa.gov) primary station with a high spectral resolution Fourier transform spectrometer. Measurements of HCN and C$_2$H$_2$ began in November 1997 and are reported to November 2000 for over 350 days for both molecules. The CO and C$_2$H$_6$ time series extend by 2.5 years a previously long-term data set [Rinsland et al., 1998a] with improved sensitivity for CO in the lower and middle troposphere.

The molecules analyzed in this investigation are sensitive indicators of tropospheric pollution and transport. They can be measured throughout the year from high spectral resolution infrared ground-based solar spectra, even at the low abundances in the extratropical Southern Hemisphere troposphere. Measured 0.37- to 12-km columns of CO and C$_2$H$_6$, with peak sensitivity in the upper troposphere show maxima in August–November with high variability at that time [Rinsland et al., 1998a, Figure 10...
and Tables 2 and 3]. The elevated tropospheric columns originate from tropical biomass burning emissions lofted by frequent, deep convection from surface air to the upper troposphere [e.g., Rinsland et al., 1998a, 1998b; Matsueda et al., 1998, 1999]. The strong westerly upper tropospheric winds measured around the subtropical jet at that time are sufficient to transport biomass burning products thousands of kilometers on a timescale of about a week [Matsueda et al., 1998; Fuellberg et al., 1999]. Only minor losses occur for long-lived species. Back trajectories calculated for regions of enhanced midtropospheric nonmethane hydrocarbons and halocarbons over the remote western south Pacific tropics and subtropics indicate the polluted air masses originated from biomass burning in South America, southern Africa, and possibly Australia. [Blake et al., 1999a, 1999b]. The high variability of CO and C$_2$H$_6$ tropospheric columns during austral spring above Lauder result from sampling either tropical biomass burning plumes or relatively clean air from high southern latitudes. Changes between the two states occur irregularly on a timescale of several days [Pougatchev et al., 1999]. Few long-term atmospheric chemistry datasets are available from this region for either background or biomass-burning-influenced time periods, particularly in the middle and upper troposphere. Potentially they could reveal trends due to changing emissions or transport.

[4] Although the lifetime of HCN was initially estimated as 2.5 years [Cicerone and Zellner, 1983], upper tropospheric enhancements and large variability have been measured in both hemispheres [Mahieu et al., 1995, 1997; Rinsland et al., 1998a, 1998b, 1999, 2000, 2001a, 2001b; Notholt et al., 2000; Zhao et al., 2000, 2002]. Reaction of HCN with OH radicals (which consumes about 0.17 Notholt et al. measured in both hemispheres [2.5 years estimated as 2.5 years [Cicerone and Zellner, 1983]]). This implies that other important sinks must exist, such as uptake by oceans or plants [Lobert et al., 1990]. Based on atmospheric remote sensing observations such as those noted above, the HCN lifetime has been estimated as 2–4 months with biomass burning the main source and ocean uptake suggested as the missing sink [Li et al., 2000]. A wide range of global atmospheric HCN emission rates has been estimated [e.g., Holzinger et al., 1999; Lobert et al., 1990; Li et al., 2000]. Atmospheric HCN emissions from “well-aged” remote upper tropospheric air masses are likely to at least partially explain the large systematic differences between the higher total reactive nitrogen (NO$_x$) direct measurements and lower values from a sum of individual components (HCN not included) obtained during a recent NASA Global Tropospheric Experiment (GTE) airborne field campaign [Bradshaw et al., 1998]. Emissions of HCN relative to CO vary widely depending on fuel type and burning phase [e.g., Lobert et al., 1991], but for some smoldering organic soils HCN is the dominant detected nitrogen-containing emission relative to CO [Yokelson et al., 1997].

[5] The combustion product C$_2$H$_2$ (acetylene or ethyne) has a shorter lifetime (global average of 1 month) [Gupta et al., 1998] than CO and C$_2$H$_6$ (global average of about 2 months [Hough, 1991]). Infrared absorption features of C$_2$H$_2$ are weak and significantly more difficult to measure than those of the other three molecules in this study at the low tropospheric C$_2$H$_2$ concentrations typically above Lauder. However, such measurements are potentially valuable as the ratio of the C$_2$H$_2$ mixing ratio to the CO mixing ratio is a sensitive indicator of the combined effects of photochemistry and dynamical mixing with background air [McKeen et al., 1996; Smyth et al., 1996, 1999; Talbot et al., 1999]. The dominant sink for both molecules is the reaction with OH and the dominant source for both is production from combustion. The C$_2$H$_2$/CO ratio decreases with increased atmospheric processing as the air mass travels away from the source region (which is often but not necessarily proportional to the time after emission) [McKeen et al., 1996; Smyth et al., 1996, 1999]. The tropospheric distribution of C$_2$H$_2$/CO mixing ratio versus 0–12 km pressure altitude was measured in situ in the central and south Pacific during the austral spring GTE Pacific Exploratory Mission-Tropics (PEM-Tropics) aircraft flights. The measurements of 0.2–2.2 ppbv/ppbv for the C$_2$H$_2$/CO mixing ratio (1 pptv = 10$^{-12}$ per unit volume, 1 ppbv = 10$^{-9}$ per unit volume) [Talbot et al., 1999, Figure 3] and the chemical composition of the sampled air parcel have been interpreted as having sampled primarily aged biomass combustion emissions [Talbot et al., 1999].

[6] The Lauder infrared spectroscopic observations sample a broad altitude region. Daily average 0.37- to 12-km altitude columns are reported. The 12-km altitude limit corresponds to the approximate annual mean tropopause height above the station and was assumed to maintain consistency with respect to our earlier study [Rinsland et al., 1998a]. We refer to 0.37- to 12-km columns as tropospheric columns throughout the remainder of the paper for convenience, though the altitude of the tropopause above Lauder varies between 11 and 17 km (G. Bodeker, private communication, 1997). Lauder CO tropospheric mixing ratios and aerosol vertical profiles from monthly balloon-borne backscatter measurements between 1994 and the end of 1998 also show elevated values during the austral spring peak of the tropical biomass burning season superimposed on interannual variations [Jones et al., 2001; Liley et al., 2001].

2. Infrared Spectroscopic Observations

[7] The Lauder station is located in an isolated region near the middle of the South Island of New Zealand, an area with minimal industrial activity. Except for occasional local burn-offs [Rinsland et al., 1998a; Jones et al., 2001], there are no significant regional sources of pollution. The infrared solar measurements were recorded with a Bruker model 120-M Fourier transform spectrometer (FTS) operated typically at an unapodized resolution of 0.0035 or 0.007 cm$^{-1}$ (defined as 0.9 divided by the maximum optical path difference). Optical filters limited the spectral band pass to measure three microwindows in the CO (1→0) band at 2143 cm$^{-1}$, the unresolved C$_2$H$_6$ ν$_7$ band $Q_o$ subbranch at 2976.8 cm$^{-1}$, the C$_2$H$_2$ line at 3250.6624 cm$^{-1}$ of the ν$_2$ + ν$_4$ + ν$_5$ band [Rinsland et al., 1985], and three lines of the HCN ν$_1$ band at 3312 cm$^{-1}$. The CO (2–0) band R(3) and R(6) lines at 4274.7047 and 4284.8911 cm$^{-1}$ were analyzed previously, but observations of those transitions are not included in this study because the sensitivity in the lower troposphere is relatively poor [Rinsland et al., 1998a, Figure 2]. Microwindows, target, interfering species, and
the assumed signal-to-noise ratios are listed in Table 1. Measurement time record to time a full resolution spectrum was 104 s with typically two or three spectra recorded per day [Rinsland et al., 1998a, section 2.1].

The C2H2 and HCN measurements began in November 1997 with a filter centered at 3300 cm\(^{-1}\) with a width of 700 cm\(^{-1}\) to half power points. Signal-to-noise ratios of full resolution measurements of HCN are typically 400:1. Absorption by C2H2 is very weak in the Lauder spectra and close to the noise level in full spectral resolution solar spectra. Improved retrievals of both C2H2 and HCN were achieved with an algorithm developed by one of us (N. Jones) for reducing the spectral resolution in the Fourier transform domain to an optical path difference of 50 cm. The truncated interferograms were then transformed with a triangular apodization function to further reduce the high-frequency noise. The depths of the C2H2 and HCN features are reduced only slightly in the lower-resolution solar spectra because the width of both lines is dominated by pressure broadening and the molecules are located primarily in the troposphere. The signal-to-noise in the reprocessed spectra is increased to 1000:1. A previous attempt to detect the same C2H2 feature in Southern Hemisphere extratropical solar spectra was unsuccessful due to the lower signal-to-noise of those measurements [Rinsland et al., 2001b].

The extended CO and C2H6 measurement database contains over 1000 measurements for both molecules on over 500 days beginning in January 1994 for CO and in March 1993 for C2H6 and extending to October 2000 for both molecules. After excluding lower-quality observations based on objective criteria based on the signal-to-noise ratio and absorption depth of the target absorption feature [Rinsland et al., 1998a, Figure 9], the HCN and C2H2 measurements reported here span December 1997 through October 2000 and March 1998 through October 2000 on over 350 days. In contrast to our previous Lauder study of CO and C2H6 [Rinsland et al., 1998a], no lengthy measurement gaps occurred during the extended observational period.

### 3. Analysis

Retrievals from the infrared solar spectra were performed with the SFIT2 algorithm, which has been developed jointly by the NASA Langley and Lauder groups for the retrieval of molecular vertical profiles from ground-based infrared solar absorption spectra. The algorithm is based on a semiempirical implementation [Connor et al., 1995; Parrish et al., 1992] of the Rodgers [1990] optimal estimation method. Profiles of one or more molecules are 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 algorithm includes a crude model for simulating and fitting the absorption by solar CO lines [Rinsland et al., 1998a, section 3.2.2]. As noted previously [Rinsland et al., 1998a, section 3.2.3], the Lauder instrument line shape function is slightly broader than the theoretical one calculated from instrumental parameters. An effective instrument line shape function was derived from fits to nearby O3 lines in the spectrum assuming O3 profiles derived from ozonesonde measurements launched from the Lauder station within one day of the spectroscopic measurement. The line shape correction has only a minor impact (~5%) on the retrieved tropospheric columns because the target tropospheric absorption features are significantly pressure broadened in the spectra. Inspection of the solar spectra and the fits to the present observations indicate the instrument alignment has been well maintained recently.

### 3.1. A Priori Mixing Ratio Profiles and Covariance Matrix Parameters

The a priori mixing ratio profiles of CO and C2H6 [Rinsland et al., 1998a, section 3.2.1] assumed previously were adopted to maintain a consistent analysis method. Retrievals of HCN were performed assuming a constant a priori mixing ratio of 185 pptv below 12 km. At higher altitudes the vertical a priori distribution was scaled to connect smoothly to the reference profile given by Mahieu et al. [1995, Table III]. A constant C2H2 mixing ratio of 60 pptv was adopted in the troposphere based on averages of in situ measurements during GTE PEM-Tropics A during August through early October 1996 [Blake et al., 1999a, Figure 10]. A priori volume mixing ratio profiles for interfering species were taken from reference compilations [e.g., Smith, 1982].

The covariance matrix was assumed diagonal for all four molecules. Uncertainties were selected semiempirically to achieve stable retrievals and good fits to the target absorption features. An increase with altitude in the mixing ratio uncertainty of CO, C2H6, and C2H2 relative to the mixing ratio in the a priori profile was assumed for each of

### Table 1. Microwindows, Interfering Molecules, and Signal-to-Noise Ratios Assumed in the Analysisa

<table>
<thead>
<tr>
<th>Target Molecule</th>
<th>Microwindows, cm(^{-1})</th>
<th>Interfering Molecules</th>
<th>SNR</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>2057.684–2058.000, 2069.5500–2069.760, 2157.400–2159.200</td>
<td>Solar CO, N2O, H2O, O3</td>
<td>150</td>
</tr>
<tr>
<td>C2H6</td>
<td>2976.62–2976.94</td>
<td>CO2, H2O, CH4, O3</td>
<td>200</td>
</tr>
<tr>
<td>C2H2</td>
<td>3250.00–3251.12</td>
<td>H2O, CH4, O3</td>
<td>1000</td>
</tr>
<tr>
<td>HCN</td>
<td>3268.18–3268.27</td>
<td>H2O, CO2, O3</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>3287.15–3287.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3299.46–3299.58</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Spectral intervals containing strong absorption by solar CO were assigned a reduced signal-to-noise ratio in the CO retrievals. Each interfering molecule was retrieved by multiplying the a priori volume mixing ratio in all layers by a single factor and retrieving the scale factor. Isotopes of H2O were fitted.
the 29 layers in the model atmosphere extending from the surface (0.37 km) to 100 km [Rinsland et al., 1998a]. An uncertainty equal to 0.5 times the a priori mixing ratio was assumed for HCN.

Temperature profiles assumed in the analysis were taken from daily mean National Centers for Environmental Prediction (NCEP) measurements. They were smoothly connected to the 1976 U.S. Standard Atmosphere above 65 km.

### 3.2. Spectroscopic Parameters and Microwindows

Spectroscopic parameters adopted in the present study were mostly the same as assumed in recent ground-based studies [Rinsland et al., 1998a, 1999, 2000, 2001a, 2001b; Jones et al., 2001]. Except for C2H6, and updates to H2O and its isotopes, parameters were taken from the 1996 HITRAN compilation [Rothman et al., 1998]. Improved values [Rinsland et al., 1998a, section 4.1] were adopted for C2H6 based on updates to the analysis of Pine and Stone [1996]. Updated parameters for H2O and its isotopes from HITRAN 2000 or 2001 (available from http://www.hitran.com) were assumed. The three microwindows for CO have been used in previous studies [e.g., Rinsland et al., 2000; Jones et al., 2001]; they provide improved sensitivity in the lower troposphere. Molecule-by-molecule simulations of the transmission in the selected C2H2 microwindow have been reported [Meier et al., 1997]. The line is located in the far wing of two strong H216O lines and is also close to lines of H217O and H218O. The individual water vapor isotopes were fitted separately. The selected windows and spectroscopic parameters for the four target species provide a consistent set of the best currently available spectroscopic parameters for the target and interfering lines.

### 3.3. Retrieval Characterization

Averaging kernels provide a direct assessment of the theoretical altitude sensitivity of the observations in the absence of errors in the measurements and model parameters [Rodgers, 1990, section 4]. They are a function of the retrieval intervals selected, the spectral resolution of the observations, the assumed signal-to-noise of the measurements, and the selections of the retrieval parameters, such as the a priori profile and its covariance matrix.

Figure 1 displays averaging kernels for profile retrievals of the 0.37- to 12-km columns of the four molecules plotted versus altitude. The 12-km limit was selected to correspond to the average altitude of the tropopause above the station. Calculations were performed for the typical spectral resolution of 0.0035 cm⁻¹ and the microwindows listed in Table 1. The column averaging kernels are broad with maximum sensitivity for CO at the surface. The surface peak reflects the added sensitivity of measurements with

![Figure 1. Averaging kernels for tropospheric columns calculated for profile retrievals of CO, C2H6, HCN, and C2H2 with the microwindows and signal-to-noise ratios in Table 1 and spectroscopic parameters described in the text.](image)

### Table 2. Estimated CO, C2H6, C2H2, and HCN Tropospheric Column Uncertainties

<table>
<thead>
<tr>
<th>Error Source</th>
<th>CO</th>
<th>C2H6</th>
<th>C2H2</th>
<th>HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Instrumental noise</td>
<td>1</td>
<td>8</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Interfering lines</td>
<td>3</td>
<td>2</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Solar zenith angle uncertainty</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>A priori profile</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Root-sum-square total error</td>
<td>4</td>
<td>8</td>
<td>15</td>
<td>11</td>
</tr>
</tbody>
</table>

**Random Error Budget**

| Spectroscopic parameters | 3  | 5    | 5    | 5   |
| Instrument line shape     | 2  | 2    | 2    | 2   |
| A priori profile           | 1  | 1    | 1    | 1   |
| Forward model Approximation | 15 | 2    | 2    | 2   |

**Systematic Error Budget**

| Root-sum-square total error | 15 | 6    | 6    | 6   |

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"Includes the estimated uncertainty in the retrieval due to errors in simulating the absorption by overlapping solar CO lines."
both strong and weak lines; the vertical distribution is more uniform with altitude when displayed with volume mixing ratio averaging kernels [Jones et al., 2001, Figure 1]. The tropospheric column averaging kernels of HCN, C2H6, and C2H2 increase with altitude.

3.4. Error Analysis

[17] In Table 2 we report estimates of the uncertainties in the tropospheric columns of HCN, CO, C2H6, and C2H2. The approach used to estimate the uncertainties is the same as adopted previously [Rinsland et al., 1998a].

[18] The sources of random error considered are the temperature uncertainty, the effect of random instrumental noise, and errors in calculating the absorption by interfering lines. We estimated the uncertainty due to errors in the temperature profile by performing retrievals with 2 K added to the NCEP temperature at each altitude. Changes in the columns are shown in Table 2; the values reported for temperature are the mean offset obtained from retrievals performed with three randomly selected spectra on different days.

[19] The contribution of instrumental noise was evaluated by generating random numbers with zero mean, a normal distribution, and a root-mean-square deviation equal to 0.005 times the maximum transmission in the spectral interval. The selected noise level is typical of the Lauder observations. The mean difference between tropospheric columns retrieved from the noisy spectra and the values obtained without noise is given in the table. As we report only daily average partial columns, the error due to random noise will be generally less than the values in Table 2.

[20] Estimates for the random errors due to interfering atmospheric lines have been reported previously for CO and...
The relatively high estimated uncertainty for $\text{C}_2\text{H}_6$ reflects the potential for error in the calculation of the $\text{H}_2\text{O}$ absorption line overlapping the target $\text{C}_2\text{H}_6$ spectral feature at $2976.8 \text{ cm}^{-1}$ [Rinsland et al., 1998a, Figure 5]. The HCN retrievals account for interference from nearby $\text{H}_2\text{O}$, $\text{CO}_2$, and $\text{O}_3$ lines by independent multiplicative scaling of the a priori profiles of each molecule by a single factor.

Four sources of systematic error were considered: (1) errors in the assumed spectroscopic line parameters, (2) uncertainties in the forward model, (3) errors in the a priori profiles, and (4) errors in the instrument line shape function. The forward model is also the same as adopted previously [Rinsland et al., 1998a], though additional recent validations have led us to reduce the estimate uncertainties for some cases [Goldman et al., 1999].

We estimated the effect of uncertainty in knowledge of the instrument line shape function by generating a synthetic spectrum for each molecule based on the instrument line shape function assumed in the retrievals. We then performed a retrieval from the synthetic spectrum with the coefficient of the “straight line” effective apodization coefficient [Park, 1983] offset from the nominal value of 0.0 to −0.2. This calculation simulates an error in the apodizing function with the error increasing from zero at the zero path difference to 20% at the maximum path difference. Changes in the tropospheric columns were less than 0.4%.

We compared CO tropospheric columns retrieved with the three windows listed in Table 1 with the values derived previously with the lines at $4274.7047$ and $4284.8911 \text{ cm}^{-1}$. Same day tropospheric columns show a high correlation coefficient (>0.95), but with 15% higher values from the revised (three window) dataset. The cause of the difference is likely related to the uncertainties in modeling the absorption by overlapping solar CO lines and the difference in the averaging kernels. As both
4. Results

[23] Figure 2 presents a sample HCN three-window fit from an observation recorded in April 1999 at near the minimum in the seasonal cycle when no significant biomass burning occurs in the Southern Hemisphere tropics. The retrieval yields a total HCN column of \(1.77 \times 10^{15}\) molecules cm\(^{-2}\) and the root-sum-square residual of 0.09\%. The residuals (plotted above the measured and calculated spectrum) illustrate the consistency of the fit to the three HCN lines and the high signal-to-noise achieved after processing the observation to a reduced spectral resolution from the transform of the truncated and apodized interferogram. The average tropospheric mixing ratio calculated from the two retrievals from that day is 0.08 ppbv, lower than typical minimum values observed in the Northern Hemisphere troposphere [e.g., Rinsland et al., 1998b, section 4.3; Mahieu et al., 1985]. However, the low mean value is reasonably consistent with an annual mean predicted by a 3-D model simulation for the latitude of Lauder [Li et al., 2000, Figure 2].

[24] Figure 3 illustrates measured and best-fit calculated spectra from near the time of maximum biomass burning in the Southern Hemisphere tropics. The retrieved tropospheric HCN column of \(6.86 \times 10^{15}\) molecules cm\(^{-2}\) from this spectrum corresponds to an average mixing ratio of 0.35 ppbv. The low root-sum-square residual (0.097\%) again reflects the consistency of the three-window fit and the increase in the signal-to-noise obtained from the reduced resolution and apodized solar spectrum.

datasets are consistent with the limited available correlative measurements (see below), it is not yet possible to distinguish which is more reliable.
Figure 4 presents sample fits for C$_2$H$_2$ obtained on 9 July 1999 (top two panels) and 4 September 1999 (bottom two panels) in the same format as Figures 2 and 3. The target C$_2$H$_2$ feature and a nearby H$_2$O$^{18}$O line are marked in the spectra, which are displayed on an expanded vertical scale to reveal the weak C$_2$H$_2$ line. The root-sum-square residuals are 0.063 and 0.083%, respectively.

Figure 5 reproduces the extended time series of daily average CO (top) and C$_2$H$_6$ (bottom) tropospheric columns, displayed with plus symbols. Individual tropospheric columns were computed by integrating the vertical profile retrieved from each measurement. Approximate mean mixing ratios calculated by dividing the tropospheric column by the air column in the same layers are shown on the right vertical axis. The high correlation between the day-to-day variations of the tropospheric columns of both molecules is apparent. As found previously, the correlation between tropospheric CO and C$_2$H$_6$ columns varies seasonally with highest correlations measured during the Austral spring biomass burning season [Rinsland et al., 1998a, Table 6].

The time series of daily average tropospheric columns $C_t$ were fitted with the expression

$$C_t = a_0 + a_1(t - t_0) + a_2 \cos 2\pi\left(\frac{t - t_0}{t_1}\right), \quad (1)$$

where $t$ is the time in calendar years, $t_0$ is the time of the first observation in calendar years, $a_0$ is the mean value, $a_1$ is the long-term trend, $a_2$ is the amplitude of the seasonal cycle (assumed to be sinusoidal), and $t_1$ is the fraction of the calendar year corresponding to the time of the seasonal maximum. The best fit to the daily averages and long-term trend (obtained by setting $a_2 = 0$ in equation (1)) are shown in Figure 5 as solid and dashed lines, respectively.

The seasonal variations are similar to those reported previously. Peak tropospheric column amounts are measured near the end of the dry season in the Southern Hemisphere tropics when burning is most intense. Best-fit trends ($a_1/a_0$ of equation (1)) and uncertainties, 1 sigma in % yr$^{-1}$, are ($-0.25 \pm 0.25$) for CO and ($-0.08 \pm 0.30$) for C$_2$H$_6$, respectively. Although the extended time series shows no
evidence for a statistically significant long-term trend in either species, CO interannual variations correlate with the El Niño–Southern Oscillation (ENSO) cycle [Jones et al., 2001].

Figure 6 presents the time series of daily mean HCN and C$_2$H$_2$ tropospheric columns in the same format as Figure 5. Both molecules show distinct seasonal variations similar to those measured for CO and C$_2$H$_6$ with sharp peaks and increased variability during austral spring. For example, HCN rose rapidly from a minimum of $3 \times 10^{15}$ molecules cm$^{-2}$ at 1999.6 to a peak of $6 \times 10^{15}$ molecules cm$^{-2}$ at 1999.7, superimposed on high variability at that time, declining quasiexponentially, through its half maximum on 2000.0 (time constant 4 months), and returning to $3 \times 10^{15}$ molecules cm$^{-2}$ on 2000.4. Although the amplitude of the austral spring peaks of HCN and C$_2$H$_2$ vary from year to year, the rapid austral spring rise and rapid decay provide quantitative support of a 2–4 month HCN lifetime [Li et al., 2000]. Fits to the daily average time series with equation (1) result in trends (1 sigma) of $(-8.60 \pm 1.06)\%$ yr$^{-1}$ for HCN and $(-1.75 \pm 1.66)\%$ yr$^{-1}$ for C$_2$H$_2$, 1 sigma. Although a statistically significant HCN decrease is indicated from the time series fit, the time span of the measurements was less than 3 years.

As mentioned in section 1, few middle and upper tropospheric trace gas measurements are available for comparison with our results, particularly for background time periods. Measurements of CO mixing ratios were obtained in April and October 1994 by the Measurement of Air Pollution from Space (MAPS) instrument during shuttle flights [Connors et al., 1999] with maximum sensitivity in the upper troposphere [Pougatchev et al., 1998]. Total columns of $1.24 \times 10^{15}$ and $1.62 \times 10^{15}$ molecules cm$^{-2}$ were estimated from the MAPS mixing ratio measurements correlative with the Lauder time series during the April and October flights, respectively. The total columns above Lauder obtained from our revised analysis for the same two time periods are $1.00 \times 10^{15}$ and $1.46 \times 10^{15}$ molecules cm$^{-2}$, respectively, based on daily averages of the 7 days in common from each time period. Our total
columns average 0.86 times the corresponding MAPS measurement, a ratio which is within the combined uncertainty of the MAPS total column measurement uncertainty (10%) and the relative uncertainty of our CO measurements (total column uncertainties are close to the tropospheric column uncertainties reported in Table 2).

[31] Mixing ratios of C2H2 and C2H6 as well as other species were measured in situ over the remote south Pacific ocean during aircraft flights in late November through early December 1995 as part of the first Aerosol Characterization Experiment (ACE 1) [Blake et al., 1999b]. Layers of continental air with elevated mixing ratios of both molecules were measured above 3 km altitude near New Zealand and attributed to aged biomass burning plumes. Aircraft measurements obtained near the same region during the August through early October 1996 PEM-Tropics A mission during the dry season observed similar plumes in the middle and upper troposphere [Blake et al., 1999a].

[32] Figure 7 presents a plot of the daily average HCN tropospheric column versus the daily average CO tropospheric column. The measurements are displayed in four panels as a function of season with a dashed line indicating a least squares best fit assuming a linear relation between the two sets of partial columns. Correlation coefficients are reported in addition to the best-fit slope and its uncertainty (1 sigma).

[33] Layers with correlated chemical variations (e.g., O3 and H2O enhanced) mixing ratios with a range of vertical thickness were detected in the PEM Tropics A September–October 1991 aircraft measurements [Stoller et al., 1999]. The limited vertical resolution of our ground-based meas-
urements and differences in the HCN and CO vertical sampling as indicated by the averaging kernels limits the correlation between the measured HCN and CO tropospheric columns.

5. Summary and Conclusions

[34] We have retrieved tropospheric columns for the biomass burning products HCN, CO, C₂H₆, and C₂H₄ from a time series of infrared solar absorption spectra recorded with a high spectral resolution FTS located at the NDSC primary station in Lauder, New Zealand (45.04°S, 169.68°E, 0.37 km altitude). The HCN and C₂H₂ measurements were obtained on over 350 days between December 1997 and October 2000 for HCN and between March 1998 and October 2000 for C₂H₂. The other observations extend the Lauder database to January 1994 through October 2000 for CO with improved sensitivity in the lower and middle troposphere and to March 1993 through October 2000 for C₂H₄.

[35] The measured tropospheric columns for all four molecules show sharp peaks and high variability during the July–November time period of each year when widespread biomass burning occurs in the Southern Hemisphere tropics near the end of the dry season. The seasonal variations are similar to those of tropospheric aerosols above the station [Jones et al., 2001; Liley et al., 2001]. No statistically significant long-term trend was found for CO or C₂H₆ over the more than 7 years of measurement. This conclusion is relevant to the possibility of long-term changes in the frequency and intensity of the burning or shifts in land usage in the Southern Hemisphere tropics where the fires originate.

[36] The high HCN versus CO tropospheric correlation during austral spring and the well-established link between CO levels and tropical biomass burning emissions provide further evidence that tropical fires are the main HCN source. The measured HCN seasonal cycle is quantitatively consistent with a lifetime estimate of 2–4 months for HCN [Li et al., 2000], though the primary sink of tropospheric HCN remains unidentified. The Lauder time series suggest a possible recent downward trend in the tropospheric HCN column.

[37] Time series of C₂H₂ measurements are reported for the first time based on a new method for increasing the effective signal-to-noise of weakly absorbing tropospheric variations are similar to those of tropospheric aerosols above the station [Li et al., 2000; Liley et al., 2001].

[38] The Lauder database is one of the few multiyear, multispecies observation sets sampling the extratropical Southern Hemisphere middle and upper troposphere during both background and biomass-burning-influenced time periods. The program continues with the goal of providing a long-term record of atmospheric chemistry and climate-related changes.

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