

Seasonal variations of HCN over northern Japan measured by ground-based infrared solar spectroscopy

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Abstract. Ground-based infrared solar spectra were recorded at Rikubetsu (43.5°N) and Moshiri (44.4°N) in Japan using Fourier transform infrared (FTIR) spectrometers from 1995 to 1997. Total column amounts and tropospheric mixing ratios of HCN were derived from these spectra in the 3287.05-3287.40 cm⁻¹ micro-window using a nonlinear least squares spectral fitting method. The HCN values at these two locations showed significant seasonal variations. The HCN total column reached a maximum value of $6.57 \pm 0.84 \times 10^{15}$ molecules cm⁻² in summer (June-August) and a minimum value of $3.97 \pm 0.30 \times 10^{15}$ molecules cm⁻² in winter (December-February). The maximum and minimum tropospheric HCN mixing ratios were 333 ± 44 (summer) and 195 ± 16 (winter) parts per trillion by volume (pptv), respectively. These seasonal variations suggest that the lifetime of HCN is shorter than one year. The enhancement of HCN above its seasonal mean (Δ HCN) was correlated with the enhancement of CO (Δ CO). A constant Δ HCN/ Δ CO ratio suggests biomass burning as a source of HCN.

1. Introduction

It is likely that atmospheric HCN is produced near the Earth's surface by biomass burning and biological activities [Cicerone and Zellner, 1983; Mahieu *et al.*, 1995]. The principal HCN sink is likely to be ocean uptake [Li *et al.*, 2000], with much smaller losses due to chemical reactions with OH and O(¹D) [Cicerone and Zellner, 1983], leading to an estimated lifetime of a few months [Li *et al.*, 2000]. Concentrations of HCN should reflect distributions of sources and sinks coupled with transport, all of which are still poorly understood. In addition, interest in measuring tropospheric HCN for NO_y studies has grown because conversion of HCN into NO by gold catalytic converters can cause interference in NO_y measurements [Kliner *et al.*, 1997; Kondo *et al.*, 1997].

Spring enhancements of HCN have previously been derived from ground-based infrared solar spectra recorded at Kitt Peak (32°N, 112°W, 2.1 km a.s.l.) and at the

International Scientific Station of the Jungfraujoch (ISSJ) (47°N, 8°E, 3.6 km a.s.l.) [Mahieu *et al.*, 1995]. The HCN measurements at the subtropical station of Mauna Loa Observatory (MLO) (20°N, 156°W, 3.4 km a.s.l.) also showed an enhancement up to a factor of 3 above the background level, most likely due to biomass burning [Rinsland *et al.*, 1999]. Since at present there is very limited knowledge regarding the causes for seasonal variability in HCN, long-term observations at various locations could provide useful information on the temporal and spatial variations in HCN. In this paper, we present seasonal variations in the total column amounts and tropospheric mixing ratios of HCN derived from ground-based infrared solar spectra observed at Rikubetsu (43.5°N, 143.8°E, 0.2 km a.s.l.) and Moshiri (44.4°N, 142.3°E, 0.2 km a.s.l.) in Japan.

2. Observations

A Bruker IFS 120M Fourier transform infrared (FTIR) spectrometer was installed at Rikubetsu in May 1995. The maximum optical path difference (OPD) of the instrument is 257 cm, resulting in the maximum resolution (RES) of 0.0035 cm⁻¹ (RES = 0.9/OPD). Another FTIR spectrometer (Bruker IFS 120HR) was installed at Moshiri in April 1996. Its OPD and RES are 450 cm and 0.0020 cm⁻¹, respectively. Ground-based infrared solar spectra were recorded with the two FTIR instruments generally at the maximum spectral resolution. The spectra from May 1995 to December 1997 were analyzed to obtain HCN for this study. An example of a ground-based infrared solar spectrum in the 3287.25 cm⁻¹ micro-window, i.e., the P8 line of the ν₃ fundamental vibration-rotation band of HCN, recorded at Rikubetsu on April 22, 1996 is shown in the lower portion of Figure 1.

Because the intensity of solar radiation within this spectral region was weak due to strong absorption by H₂O, the signal-to-noise ratio (SNR) of the infrared solar spectra at 3287.25 cm⁻¹ was relatively low, ranging from 10 to 70. The spectrum in Figure 1 is a typical one, having an intermediate SNR of 28. In order to reduce the error caused by random noise, spectra with a RMS noise higher than 0.3% were excluded. In order to increase the SNR, between 2 and 8 interferograms were co-added to create an infrared solar spectrum. In addition, lower resolution (0.0035 cm⁻¹) was sometimes adopted for the Moshiri FTIR measurements.

The CO column amounts derived from the micro-windows at 2111.00-2112.00 cm⁻¹ and 2157.40-2159.20 cm⁻¹ at the same two sites [Zhao *et al.*, 1997] are also discussed in this study.

3. Methods of Analysis

Total column amounts of HCN were derived from the ground-based infrared solar spectra using a nonlinear least

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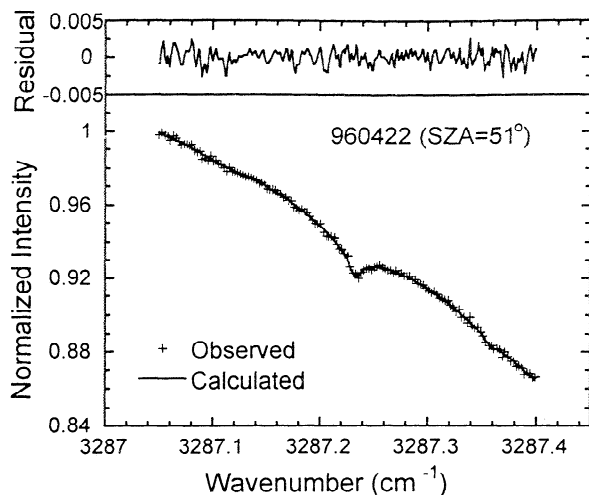


Figure 1. An example of a ground-based infrared solar spectrum, the corresponding fit, and residual of the fit in the micro-window of the HCN P8 line at 3287.25 cm^{-1} .

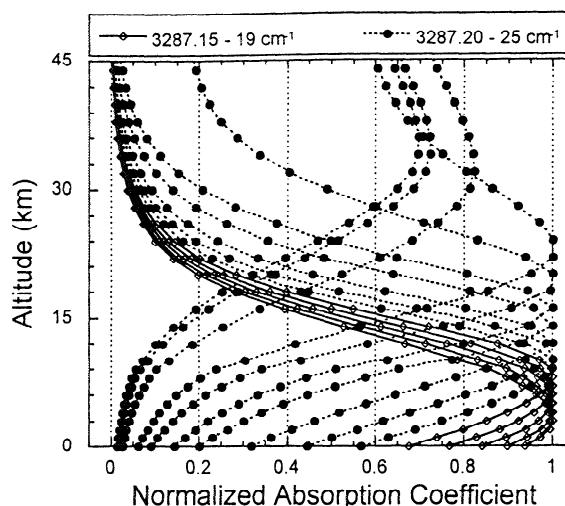


Figure 2. Normalized absorption coefficients of the HCN P8 line at selected wavenumbers.

squares spectral fitting (SFIT) method developed by *Rinsland et al.* [1982].

It was found that the initial guess for the HCN profile was very important for SFIT retrievals, particularly the HCN values at lower altitudes [*Rinsland et al.*, 1982; *Mahieu et al.*, 1995]. Because the HCN lines in the ground-based infrared solar spectra are pressure broadened, the HCN spectra contain information on the HCN absorption at various altitudes. Figure 2 shows normalized absorption coefficients of the HCN P8 line at selected wavenumbers in the ranges from 3287.15 to 3287.19 cm^{-1} (the line wing) and from 3287.20 to 3287.25 cm^{-1} (near the line center) as functions of altitude. Because the spectral resolution used in this study is relatively high and the HCN line shape is dominated by pressure broadening (i.e., the Lorentz line shape) for the lower part of the atmosphere, the absorption coefficients in Figure 2 have not been convolved with the instrument function. The absorption coefficients in the line wing peak at altitudes between 5 and 10 km, while those near the line center peak above 10 km. In comparison, the HCN absorption in this spectral region is much smaller at altitudes below about 5 km. Therefore, little information on the HCN abundance below 5 km is available. Because the spectra are thus insensitive to the changes in HCN at lower altitudes, the tropospheric HCN mixing ratio was assumed to be uniform in the present method of analysis. Errors associated with this assumption will be discussed below. In order to keep the tropospheric HCN mixing ratio uniform, the initial HCN profile in the troposphere was adjusted by a single scaling factor and the tropopause height was shifted between 8 and 20 km. The final results were obtained when the residual between the calculated and observed spectra reached a minimum. The tropopause height determined by this spectral fitting was highest in summer and lowest in winter, consistent with the seasonal variation of the tropopause determined from rawinsonde data obtained daily at Sapporo (43.1°N, 141.3°E).

For the analysis of the HCN P8 line, absorptions by atmospheric H_2O , C_2H_2 , CO_2 , and solar OH lines were taken into account in the SFIT parameters. The initial guess for the HCN profile was taken from the “realistic” profile of *Mathieu*

et al. [1995] (i.e., an HCN mixing ratio of 185 pptv in the troposphere, decreasing slowly with altitude in the stratosphere). All spectral parameters for the absorption lines were from the 1996 HITRAN database [*Rothman et al.*, 1998]. The temperature profiles observed at Sapporo (below 30 km) were used in conjunction with the US Standard Atmosphere at 45°N (above 30 km) for the present analysis. The tropospheric H_2O mixing ratios derived from the rawinsonde data were also used. Figure 1 shows an example of a typical spectral fit and the resulting residual.

Errors in the retrieved HCN columns were estimated using artificial infrared solar spectra in the 3287.25 cm^{-1} micro-window. The artificial spectra were created using two HCN profiles. One was the realistic profile of *Mahieu et al.* [1995]. The other was a modification of the realistic profile in which HCN below 15 km was 310 pptv, a value close to the summer maximum level of HCN observed at northern Japan (see Section 4). Then the HCN column amounts and mixing ratios in the troposphere were retrieved from the artificial spectra using the algorithm described above. The difference between the artificial and retrieved HCN column amounts was 5%, which is defined as the error due to the algorithm as given in Table 1. The uncertainty in the HCN line parameters was estimated to be $\pm 2\%$ [*Rinsland et al.*, 1999]. Assuming 0.3% as the maximum RMS noise in HCN spectra and $\pm 5^\circ\text{C}$ uncertainty in the temperature measurements, random errors due to these two parameters were calculated and are listed in Table 1. The total uncertainty was estimated to be 8%.

4. Results and Discussion

Daily averages of the total column abundance of HCN and CO over Rikubetsu and Moshiri from 1995 to 1997 are shown

Table 1. Error Budget for the HCN Column.

Systematic errors (%)		Random errors (%)	
Algorithm	5	Random noise	6
Line intensity	2	Temperature	2

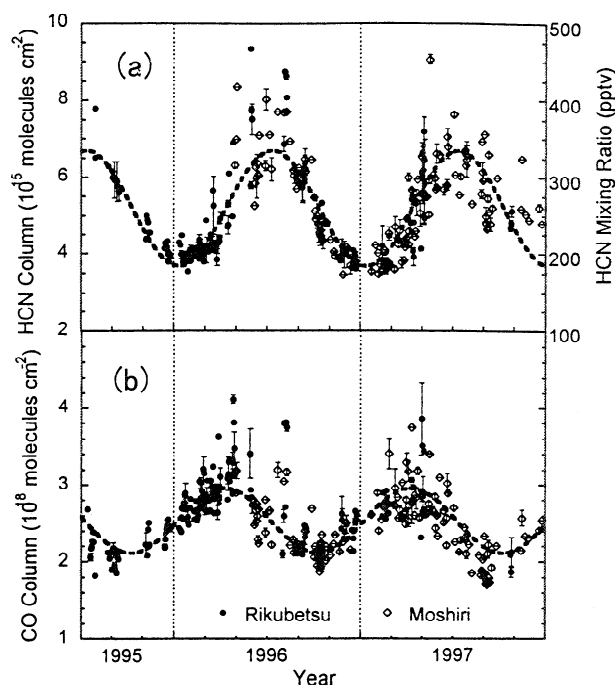


Figure 3. Daily averages of (a) total column abundance and tropospheric mixing ratio of HCN, and (b) total column abundance of CO. Cosine curves fitted to the total column amounts of HCN and CO are also shown. Vertical bars represent one standard deviation in the daily averages.

in Figure 3. The vertical bars represent one standard deviation (SD) in these averaged values. Those data without error bars in Figure 3 are single measurements within one day. It can be seen that the observations at Rikubetsu and Moshiri were very similar, and they were combined for this analysis. Averages of the HCN total column amounts in summer (June–August) and winter (December–February) resulted in a maximum of $6.57 \pm 0.84 \times 10^{15}$ molecules cm^{-2} and a minimum of $3.97 \pm 0.30 \times 10^{15}$ molecules cm^{-2} , i.e., the HCN total column amounts increased in summer by a factor of 1.7. Since tropospheric HCN makes the largest contributions to the HCN total column, the tropospheric mixing ratio is proportional to the total column. The derived tropospheric HCN mixing ratios are shown in Figure 3a with an approximate scale on the right hand side of the plot. The summer and winter averages were 333 ± 44 pptv and 195 ± 16 pptv, respectively. These seasonal variations suggest that the lifetime of HCN is shorter than one year. The CO column amounts measured simultaneously with HCN generally decreased from spring to summer due partly to the loss of CO through the reaction with OH [Zhao *et al.*, 1997], while HCN increased from winter to summer. Cosine curves fitted to the seasonal variation in the total column amounts of HCN and CO are also shown in Figure 3. It can be seen that high HCN column amounts above the seasonal mean were sometimes observed in spring and summer.

The HCN values observed in Japan agree with the measurements at Kitt Peak and ISSJ, for which the background HCN mixing ratios above the two stations were about 190 pptv and the spring increase was more than 60% [Mahieu *et al.*, 1995]. In order to compare the HCN column over Japan with the measurements at Kitt Peak (2.1 km a.s.l.)

and ISSJ (3.6 km a.s.l.), the HCN column amounts above 2.1 and 3.6 km were derived from the Rikubetsu and Moshiri data, respectively, and are given in Table 2. The maximum HCN columns in northern Japan agree well with those over Kitt Peak and ISSJ, when the differences in altitude are taken into account. The minimum HCN column also agrees well with the ISSJ measurements, while it is 14% higher than the Kitt Peak results.

Latitudinal variations in HCN over the central Atlantic have been measured using high-resolution infrared solar spectroscopy during a ship cruise in October 1996 [Notholt *et al.*, 2000]. The total column amount and tropospheric mixing ratio of HCN at 25–30°N (the highest latitudes of their HCN measurements) were 4.81×10^{15} molecules cm^{-2} and 220 pptv, respectively. Fourteen infrared HCN spectra were observed over ten days in October 1996 in Japan, yielding an average of $4.79 \pm 0.23 \times 10^{15}$ molecules cm^{-2} for the total column and 230 ± 15 pptv for the tropospheric mixing ratio, in excellent agreement with the results of Notholt *et al.* [2000].

Anthropogenic sources that do not undergo strong seasonal variations, such as fossil fuel combustion, cannot explain the spring–summer maximum in HCN. However, the production and release of HCN from biological sources (plants, bacteria, and fungi) could cause the HCN enhancements in summer because the effects of these sources tend to be amplified during the summer season. Mahieu *et al.* [1995] suggested that the increases in HCN observed at Kitt Peak and ISSJ in spring were likely due to processes associated with spring vegetation. Li *et al.* [2000] have shown that a three-dimensional chemistry–transport model, including biomass burning as the major HCN source, can generally reproduce the seasonal variations observed at northern Japan. In their model, the high HCN values over northern Japan in spring–summer are mainly due to the northward transport of HCN produced by biomass burning in the tropics in February. The HCN column amounts above MLO also showed increases up to a factor of 3 above the background in September–December, 1997 [Rinsland *et al.*, 1999]. Simultaneous measurements of HCN, CO, and C_2H_6 for air masses transported from South East Asia indicated that active biomass burning in tropical Asia in 1997 was also the most probable cause of the HCN enhancements observed by Rinsland *et al.* [1999].

In order to study the short-term variability of HCN and CO over Japan, deviations of HCN column amounts from the mean seasonal values represented by the cosine fitting (ΔHCN) are plotted against similar deviations of CO (ΔCO) in Figure 4. Most of the significant positive ΔHCN occurred during the March–August period in 1996 and 1997. The ΔHCN values are positively correlated with ΔCO where $r^2 = 0.44$ (r is the correlation coefficient). The good correlation holds even during the decreasing phase of CO seasonal variation, indicating that additional production of HCN and

Table 2. HCN Column Amounts (10^{15} molecules cm^{-2}) over Kitt Peak, ISSJ, and Northern Japan.

Station	Japan (0.2 km)	Japan (>2.1 km)	Kitt Peak (2.1 km)	Japan (>3.6 km)	ISSJ (3.6 km)
Max.	6.57 ± 0.84	5.22 ± 0.65	5.10 ± 1.10	4.29 ± 0.54	4.16 ± 0.64
Min.	3.97 ± 0.30	3.13 ± 0.23	2.75 ± 0.30	2.53 ± 0.19	2.55 ± 0.30

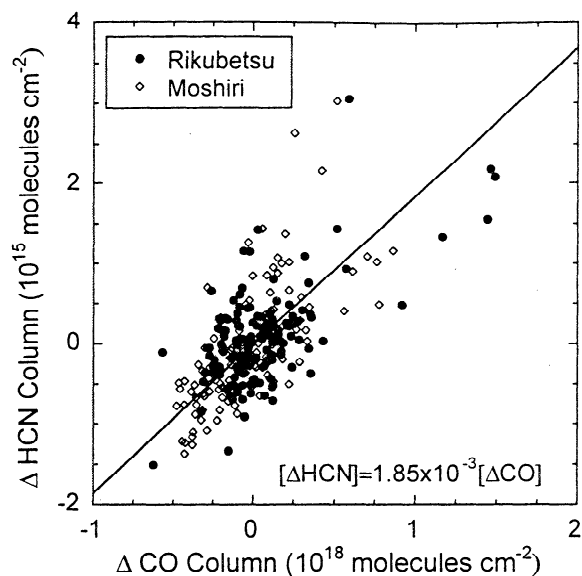


Figure 4. Δ HCN versus Δ CO column amounts. See text for details.

CO occurred simultaneously. Laboratory experiments [Yokelson *et al.*, 1997; Holzinger *et al.*, 1999] have shown that both HCN and CO are emitted by biomass burning. The Δ HCN values in Figure 4 can be expressed as Δ HCN = $1.85 \times 10^{-3} \Delta$ CO using a linear least squares fit. The slope of 1.85×10^{-3} falls between the minimum and maximum values of 0.4×10^{-3} and 2.6×10^{-3} of the HCN/CO emission ratios measured during the laboratory burning experiments [Holzinger *et al.*, 1999]. It is likely that the enhancements of HCN and CO above the regular seasonal variations over Japan in spring-summer were due to biomass burning. It should be mentioned that relative proportions of the emission products are highly dependent on fire type and biomaterials burned and vary throughout a single fire [Yokelson *et al.*, 1996, 1997; Holzinger *et al.*, 1999].

Back trajectory calculations were performed in order to obtain some insight into the origin of the high HCN and CO amounts observed simultaneously at northern Japan. The trajectories showed that the air masses over northern Japan at 800–300 hPa between April and November were predominantly transported from the West, often covering latitudes from 30 to 60°N. From the World Fire Web (<http://ptah.gvm.sai.jrc.it/wfw/>) and the ATSR World Fire Atlas (<http://shark1.esrin.esa.it/FIRE/AF/ATSR/>), it can clearly be seen that biomass burning occurred in China and Mongolia between 30–60°N from March through November 1997 with intensive activities from April to July, resulting in the enhanced HCN and CO levels observed over northern Japan. Considering the lifetime of HCN, it is expected that HCN emitted from Mongolia and China can also contribute to its enhancement at other northern midlatitudes, including Kitt Peak and ISSJ. The present results indicate the importance of HCN emissions from biomass burning at northern midlatitudes.

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