Seasonal variations of CO and HCN in the troposphere measured by solar absorption spectroscopy over Poker Flat, Alaska

Y Kasai
National Institute of Information and Communications Technology, Japan

A. Kagawa
National Institute of Information and Communications Technology, Japan

Nicholas B. Jones
University of Wollongong, njones@uow.edu.au

A. Fujiwara
Tokyo University of Science

K. Seki
National Institute of Information and Communications Technology, Japan

See next page for additional authors

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Abstract

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Keywords

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Authors

Y Kasai, A. Kagawa, Nicholas B. Jones, A. Fujiwara, K. Seki, Y. Murayama, and F Murcray

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Yasuko J. Kasai,[1] Akiko Kagawa,[1,2] Nicholas Jones,[3] Akimitsu Fujiwara,[1,4] Koji Seki,[1] Yasuhiro Murayama,[1] and Frank Murcray[5]

[1] Tropospheric partial column abundances of CO and HCN have been retrieved from infrared solar spectra observed with a ground-based spectrometer at Poker Flat Alaska (65°N, 147°W) over the time period from 2000 to 2004. From these data we report the transpacific transport induced inter-annual variability of tropospheric CO over Poker Flat. This is the first report of solar infrared data from the Poker Flat station, where the geographical location of the site means that remote sensing measurements are sampling the transport of transpacific air parcels going to Northern America from Eastern Siberia and Asia. The five year time-span of the data also show significant differences in year to year CO and HCN tropospheric column enhancements driven by changes in Siberian/Asian pollution sources. **Citation:** Kasai, Y. J., A. Kagawa, N. Jones, A. Fujiwara, K. Seki, Y. Murayama, and F. Murcray (2005), Seasonal variations of CO and HCN in the troposphere measured by solar absorption spectroscopy over Poker Flat, Alaska, *Geophys. Res. Lett.*, *32*, L19812, doi:10.1029/2005GL022826.

1. Introduction

[2] Carbon monoxide (CO) is one of the most important molecules in the troposphere. The reaction of CO with the hydroxyl radical OH is the primary sink for tropospheric OH, which controls the oxidizing capacity of trace gases in the troposphere [e.g., *Logan et al.*, 1981]. The distribution of CO is interesting not only for it's role in tropospheric chemistry but also as a primary and secondary determinant of air quality via its use as an atmospheric tracer with a relatively long life-time, that is, as an indicator of how transport redistributes pollutants. It is therefore important to understand the driving force behind locally observed CO variations.

[3] Poker Flat is a good site to detect polluted air transported because of its' relatively clean background tropospheric air and isolation from most local industrial activity. Except for occasional local burn-offs, there are no significant regional sources of pollution. Poker Flat is the entrance for transpacific transport of air parcels going to Northern America from Eastern Siberia and Asia, and biomass burning affected air masses that have been transported from Siberia [*Jaffe et al.*, 2004].

[4] The Siberian region holds one of the largest pools of terrestrial carbon. Siberia is also located where some of the largest temperature increases are expected to occur under current climate change scenarios [*Soja et al.*, 2004]. It is therefore interesting to understand the behavior and impact of polluted air due to Siberian fires on the Alaska region, where the background air is relatively clean.

[5] CO and hydrogen cyanide (HCN) are common atmospheric tracers of biomass burning. The lifetime of CO in the Arctic is estimated to be 15 days in summer and more than 1 year in winter in the Northern polar region [*Holloway et al.*, 2000]. Recently, there have been many reports of CO generated by fossil fuel emissions, fire, or biomass burning plumes being transported from East Asian-Siberia region to the continental US [*Kar et al.*, 2004; *de Gouw et al.*, 2004; *Jaffe et al.*, 2004; *Heald et al.*, 2003; *Yurganov et al.*, 2004, 2005]. Ocean uptake has been hypothesized as the dominant sink of HCN [*Li et al.*, 2003; *Singh et al.*, 2003]. The residence time of HCN is estimated to be 63 months due to the OH reaction, and 5.3 months due to the ocean sink [*Singh et al.*, 2003], therefore, HCN is known to be a good tracer of the remote transport of biomass burning polluted air. A number of ground and space based observation of its total atmospheric column have been made [for example, *Zhao et al.*, 2002].

[6] The purpose of this paper is to report that the seasonal variation of tropospheric CO over Poker Flat, Alaska, is qualitatively explained by long-range transport of air masses, in combination with forest fire activity from the Asian-East Siberian region.

2. CO Seasonal Variations and Correlation of CO With HCN

[7] The spectrometer in this experiment is located at the Poker Flat Research Range (PFRR: Altitude 0.61 km; latitude 65.11°N; longitude 147.42°W) of the Geophysical Institute at the University of Alaska Fairbanks (GI/UAF). The solar absorption spectra have been recorded with a high spectral resolution Fourier Transform Infrared (FTIR) spectrometer (Bruker 120HR, 0.0019 cm^{-1} resolution) from February 2000 to June 2004. The reported tropospheric partial columns were obtained using the software SFIT2 v3.8 [*Pougatchev and Rinsland*, 1995; *Rinsland et al.*, 1998], which retrieves the vertical profiles of atmospheric constituents using Rodger's Optimal Estimation Method (OEM) [*Rodgers*, 2000]. The CO and HCN absorption lines and the parameterization of the CO and HCN state vector
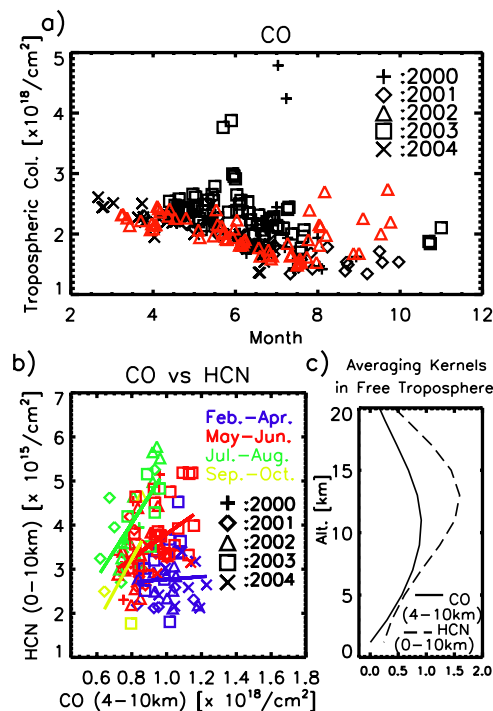
[1]National Institute of Information and Communications Technology (NICT), Koganei, Tokyo, Japan.
[2]Fujitsu FIP Corporation, Koto, Tokyo, Japan.
[3]Department of Chemistry, University of Wollongong, Wollongong, New South Wales, Australia.
[4]Tokyo University of Science, Shinjyuku, Tokyo, Japan.
[5]Department Physics, University of Denver, Denver, Colorado, USA.

Figure 1. a) Seasonal variation of the CO tropospheric partial column from the ground to 10 km in 2000–2004. b) Correlation between HCN (1–10 km) and CO (4–10 km) in the free troposphere. See the text for details. c) Partial column averaging kernels for CO (4–10 km) and HCN (1–10 km).

elements employed in this retrieval study are similar to those used in previous work by *Rinsland et al.* [2002] and *Zhao et al.* [2002]. The HITRAN2k line list was used for all spectroscopic lines. Temperature and water vapor profiles were obtained from daily 1500 hour National Centers for Environmental Prediction (NCEP) measurements. Temperature was smoothly connected to the daily UK Meteorological Office (UKMO) data for 30–50 km, and CIRA86 data above 50 km.

[8] Figure 1a displays the seasonal variation of CO tropospheric column amount over Poker Flat from 2000 to 2004, with April maximum and July minimum, with the exception of 2003. As the purpose of this paper is to discern the behavior of tropospheric CO at Poker Flat, the altitude profiles have been processed for the 1–10 km region. The 10 km limit was selected to correspond to the average altitude of the tropopause (by temperature) above the station. The precision of the CO partial columns are estimated as 2% (1–10 km), and 4% (4–10 km), respectively, which includes error terms for spectral noise, a priori error, and temperature uncertainty. Details of the error budget including systematic errors is described fully in [*Rinsland et al.*, 2000].

[9] *Holloway et al.* [2000] compared the modeled CO with measured data at 6 arctic sites including Barrow, Alaska, (71.19°N, 156.36°W), and reported on the seasonal variations of CO and its components in Alaska. Their modeled seasonal variation is qualitatively consistent with our observation. They showed that the main contribution to

this seasonal variation is not caused by methane oxidation chemistry (less than 10 percent), but rather transport of air masses affected by fossil fuel and biomass burning. *Allen et al.* [1996] also supports this view. More recently, *Yurganov et al.* [2004, 2005] reported anomalous CO column enhancements in 1998, 2002 and 2003 above background levels from a number of Northern Hemisphere sites, including global CO MOPITT data, that was ascribed to forest fires in Russia.

[10] If the seasonal variation of CO were due to transport from Asia and Siberia via biomass burning emissions and residential coal burning, one would expect that the correlation of CO and HCN would also be linked to its seasonal variation. Figure 1b are scatter plots of CO and HCN from 2000 to 2004 in the free troposphere (defined here as the altitude range from 4 to 10 km for CO and 1–10 km for HCN).

[11] The different altitude ranges were chosen for the two gases so that the relative atmospheric sampling of these species was similar based on their averaging kernel functions. Thus the abundances of CO and HCN were weighed to the free troposphere. The averaging kernel functions for CO (4–10 km) and HCN (1–10 km) are shown in Figure 1c.

[12] The correlations in Figure 1b are classified bimonthly, represented by symbol color; blue for February–April, red for May–June, green for July–August, and yellow for September–October. Years are shown by symbol shapes; cross 2000, diamond 2001, triangle 2002, and square 2003, and 'x' 2004. The correlations are calculated for each two-monthly period between CO and HCN (the correlation coefficients, detailed below, range from r = 0.69 to r = 0.05, showing a seasonal dependence). The amounts of the HCN tropospheric columns ($2\text{-}5 \times 10^{15}$ molecules cm^{-2}) are reasonably consistent with the measurements over Japan ($3\text{-}6 \times 10^{15}$ molecules cm^{-2}) from January to April [*Singh et al.*, 2003].

[13] The slope of CO-HCN scatter plots tends to increase during the course of the season, that is, the HCN amount relative to the CO amount increases from spring to autumn. The slope values for February–April, May–June, July–August, and September–October are 0.3 (correlation coefficient r = 0.05), 2.8 (r = 0.44), 6.2 (r = 0.69), and 7.3 (r = 0.53) respectively.

[14] The presence of fossil fuel or biomass burning emissions in the transported air parcel is suggested for the following three reasons. First, the value of the spring-time slope (2.8 in May–June) is consistent with measurements in the free troposphere over the Pacific ocean in 2001 by*Singh et al.* [2003], who also suggest that this air-mass originated from East Siberia and Asian sources.

[15] Second, the HCN/CO slope increases from spring to summer. The slope for July–August (6.2) is larger than that of Feb.–April (0.3). In the summer the contribution from transported CO relative to the total CO distribution decreases as the lifetime of CO over continental source regions drops to about 15 days. If the origin of the CO air during the spring maximum is caused by transport of the pollutant air, the slope should be increasing from March through to August as shown in Figure 1b.

[16] Third, the correlation of HCN/CO is higher in summer than in spring. The correlation coefficients are r =
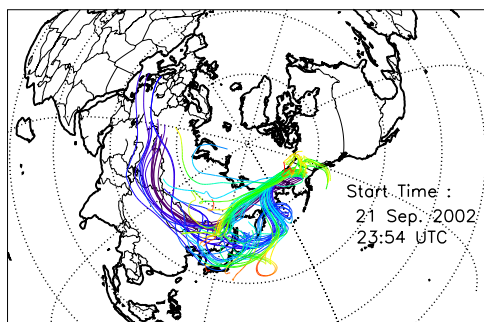
Figure 2. An example of the backward trajectories over 7 days on nine isentropes from 100–900 hPa, starting at Poker Flat, Alaska at 23:54 UTC on 21 September 2002 when the observed CO was significantly enhanced.

0.69 and r = 0.05 in summer (July–August) and spring (February–April), respectively. The tropospheric column amounts of CO are also more scattered about the seasonal trend in summer than in spring.

[17] A likely explanation for the seasonal variation of CO profiles is the transport of fossil fuel emissions, fire, or biomass burning plumes being transported over the Poker Flat site from elsewhere. In the next section we will check this scenario using meteorological data.

3. Backward Trajectory Analysis

[18] Backward trajectory analysis is used to document the histories of air parcels observed by the FTIR system at Poker Flat. We used the trajectory calculation tool developed by Y. Tomikawa and K. Sato at National Institute of Polar Research, Japan [*Yamanouchi et al.*, 2005]. Our trajectories utilized global gridded meteorological analysis prepared by the European Centre for Medium-Range Weather Forecasts (ECMWF). 7-day backward trajectories were calculated using a kinematic model, i.e., employing horizontal and vertical wind components from the ECMWF data. Additional details about the trajectory model are given in *Yamanouchi et al.* [2005]. The 9 isobaric vertical levels were used from 900 to 100 hPa, interpolated onto a 2.5° by 2.5° latitude-longitude horizontal grid. The trajectories were calculated with 9 clusters, the center point at Poker Flat with the surrounding 8 points at each vertical level. Since the life-time of middle-upper tropospheric CO and related pollutant molecules are relatively long (>15 days), this 7-day period generally provides sufficient information about long-range transport of the air masses without resorting to an even longer period whose results would be subject to greater uncertainty.

[19] Figure 2 shows an example of backward trajectories over 7 days on nine isentropes in the range of 100–900 hPa, starting at Poker Flat, Alaska at 23:54 UTC on 21 September 2002 when the observed CO was significantly enhanced. The trans-Pacific transport to Poker Flat, Alaska from the Asian region is clearly shown. This air mass passed over the area burned in Siberia in 2002 as shown by *Soja et al.* [2004].

[20] The enhanced CO column on 21 September 2002 (Figure 1) was likely to have been affected by Siberian biomass burning, which is consistent with the evidence of

increased HCN on the same day. It should also be noted that large wild fires were reported in the eastern Asian-Russian region during 18–27 Sept. 2002 [*Sukhinin et al.*, 2004]. It is also note that this timeframe is relatively unusual as it
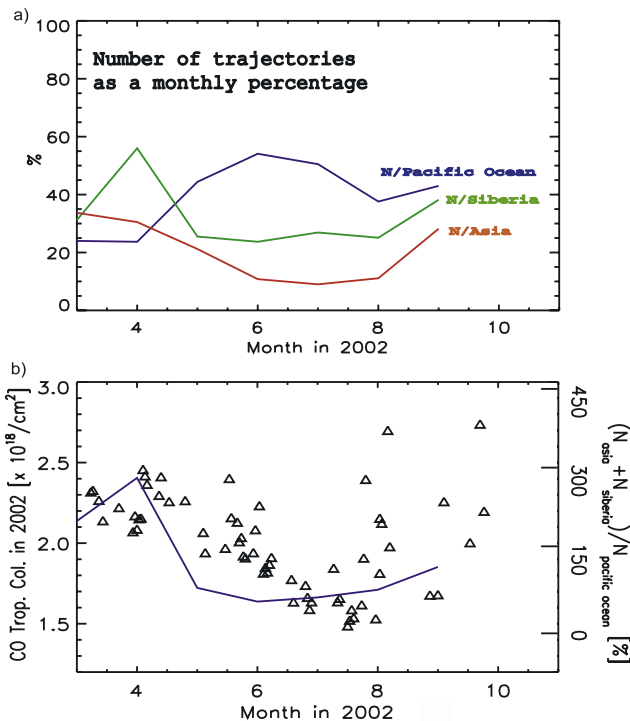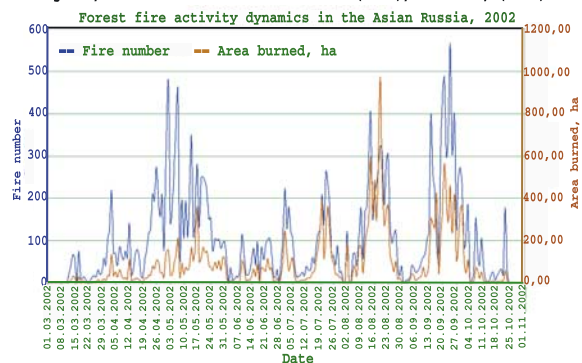
Figure 3. a) The seasonal variation of the percentage of backward trajectories from Poker Flat which passes through Asia (red), East Siberia (green) and Pacific Ocean only (blue) for the 2002 year. X-axis is the month in 2002. b) A comparison of the seasonal variation of the origin of the air parcel with that of tropospheric CO in 2002. The seasonal variation of this air parcel is calculated from Figure 3a, using the equation $(N_{SIBERIA} + N_{ASIA})/N_{PACIFIC}$, where N_{AREA} represents the number of trajectories passing over AREA. The y-axis is the tropospheric CO daily mean, while the x-axis is the month in 2002. c) Forest fire activity dynamics in the Asian-Russian region in 2002. The number of biomass burning events in the Asian-Russian region in 2002 has a triple peak, i.e., from the end of April to the middle of May, the middle of August, and the end of October [*Sukhinen et al.*, 2004].

coincides with the peak in springtime biomass burning in the southern hemisphere.

4. Statistical Characteristics of Trajectory Results

[21] Figure 3a illustrates the number of trajectories, as a monthly percentage, which had originated from the Asian, East-Siberian, and Pacific Ocean regions in 2002. For the trajectories through Asia, a seasonal trend is seen with a maximum in February and a minimum in June–April. For the Siberian case, however, a season maximum occurs later in March, with a minimum from May to August. The number of trajectories passing through the Pacific Ocean (a non-polluted area) increases from spring to summer.

[22] Figure 3b is a comparison of the seasonal variation of air parcel origin with that of tropospheric CO column amounts in 2002. The solid line in Figure 3b shows the ratio $(N_{SIBERIA} + N_{ASIA})/N_{PACIFIC}$, where N_{AREA} represents the number of trajectories passing over AREA. The regular CO seasonal trend of a spring maximum and summer minimum is reasonably consistent with the long-range transport from the Asia-Siberian region as suggested by the $(N_{SIBERIA} + N_{ASIA})/N_{PACIFIC}$ trajectory source ratio. In addition, 3 anomalously high CO peaks can be seen in mid May, late July-early August, and late September in the CO seasonal trend (Figure 3b). Figure 3c is the forest fire activity dynamics in the Asian-Russian region in 2002 [*Sukhinin et al.*, 2004]. One can recognize the more frequent forest fire events and larger area of burned land in the eastern Russian region, and in particular, three periods of larger fire activity in late April-mid May, mid August, and late September (Figure 3c), consistent with the Poker Flat CO enhancements (Figure 3b).

[23] Thus the seasonal variation of the tropospheric CO column amounts in 2002 is qualitatively explained by long-range transport of CO from the Asian-East Siberian region in combination with forest fire activity in the Asian-Russian region.

5. Summary

[24] The seasonal variation of the tropospheric column amount of CO was observed over Poker Flat, Alaska, with maxima in April and minima in July. CO and HCN amounts were well correlated when they are classified bimonthly. The seasonal behavior and variation of the HCN/CO ratio implies that the measured air parcels underwent similar dilution processes. The ratio in spring was consistent with past measurements over the Pacific Ocean. A trajectory analysis indicated that the trans-Pacific transport of air from Eastern Siberia and Asia to Poker Flat, Alaska, is consistent with the observed seasonal variation and scatter of CO over Poker Flat in 2002. Incorporating the trajectory analysis results, it is suggested that transport processes are the primary driver of the CO season dependence, and that the observed sporadic CO enhancements are due to superimposed Asian/Siberian forest fires.

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A. Fujiwara, A. Kagawa, Y. J. Kasai, Y. Murayama, and K. Seki, National Institute of Information and Communications Technology (NICT), Koganei, Tokyo 184–8795, Japan. (ykasai@nict.go.jp)

N. Jones, Department of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia.

F. Murcray, Department Physics, University of Denver, Denver, CO 80208, USA.