On seasonality of stratomesospheric CO above midlatitudes: New insight from solar FTIR spectrometry at Zugspitze and Garmisch

Tobias Borsdorff[1] and Ralf Sussmann[1]

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[1] A significant seasonality in stratomesospheric CO (24–100 km) above mid-latitudes is derived from FTIR via a new regularization scheme. Half hourly means from the Zugspitze (47.42°N, 10.98°E, 2964 m a.s.l.) and nearby Garmisch (745 m a.s.l.) measurements show excellent agreement (R = 0.94, slope 0.91, standard deviation 12%). Mean seasonality of the Zugspitze series (1999–2008) shows a November–April enhancement (February maximum 3.63×10^{16} cm^{-2}) and a summer background (1.64×10^{16} cm^{-2}) which agrees with the WACCM model. Measured monthly means reveal a year-to-year variability of up to 32% (1-sigma) in winter not reproduced by WACCM (R = −0.13). Frequency distributions of daily means are right skewed in winter due to enhancements by vortex air transport (1–3 days duration) which typically reflect CO levels of the vortex border and may even reach vortex-center levels (≈300% of the multi-annual monthly median). **Citation:** Borsdorff, T., and R. Sussmann (2009), On seasonality of stratomesospheric CO above midlatitudes: New insight from solar FTIR spectrometry at Zugspitze and Garmisch, *Geophys. Res. Lett.*, *36*, L21804, doi:10.1029/2009GL040056.

1. Introduction

[2] CO in the middle atmosphere is produced by photolysis of CO_2 in the thermosphere and destroyed by the reaction with OH in the stratomesosphere [*Rinsland et al.*, 1992]. Its photochemical lifetime is comparable to vertical and horizontal transport timescales. This makes CO an ideal tracer for the global transport in the middle atmosphere [*Allen et al.*, 1999].

[3] This transport is part of a complex mechanism, i.e., photochemistry produces more CO in summer than in winter [*López-Valverde et al.*, 1996], and horizontal transport through the meridional circulation enhances CO abundances in the winter thermosphere [*Dupuy et al.*, 2004]. Subsequent downward transport by vertical advection then greatly enhances the CO mixing ratios in the winter stratomesosphere relative to the summer, because of reduced OH densities in winter [*Solomon et al.*, 1985].

[4] Already the study by *Solomon et al.* [1985] called for a continuous observation program at mid-latitudes to analyze the displacement of CO enriched vortex air towards mid-latitudes in wintertime [*López-Valverde et al.*, 1996]. However, this could not be realized until now. Retrievals from ground-based FTIR measurements at high latitudes were performed by *Kasai et al.* [2005] and transferred to other stations by *Velazco et al.* [2007]. But still two years of microwave measurements [*Forkman et al.*, 2003] constitute the longest time series of stratomesospheric CO above mid-latitudes.

[5] This paper presents an improved FTIR retrieval for stratomesospheric CO. About 10 years of measurements above the mid-latitude NDACC (Network for the Detection of Atmospheric Composition Change, http://www.acd.ucar.edu/irwg/) stations Zugspitze and Garmisch are analyzed giving new insight into seasonality, inter-annual and day-to-day variability.

2. Method

[6] Solar FTIR measurements were performed with a Bruker IFS 125 HR Interferometer at the Zugspitze since 1995 [e.g., *Sussmann and Schäfer*, 1997; *Sussmann et al.*, 2005] and coincident FTIR measurements are performed at Garmisch since 2004 [e.g., *Sussmann et al.*, 2009]. The Zugspitze (Garmisch) retrieval is implemented via the SFIT2 algorithm ver. 3.9 [*Rinsland et al.*, 2000] and uses 29 (30) equidistant layers between the station altitude and 100 km. The CO a priori profile is the average of the volume mixing ratio (VMR) profiles modeled by WACCM (1999–2006). WACCM is a General Circulation Model developed at the National Center for Atmospheric Research [*Garcia et al.*, 2007]. All further retrieval settings (e.g., microwindows, HITRAN version) were taken from *Sussmann and Borsdorff* [2007].

[7] *Kasai et al.* [2005] revealed that the true variability of stratomesospheric CO can be suppressed in FTIR retrievals by an inappropriate regularization of the profile retrieval above 20 km. They overcame this problem by heavily weighting the core of the weak isotopic CO lines, i.e., empirical tuning of the measurement covariance. In our study the problem is rigorously addressed in retrieval space.

[8] A regularization matrix is designed which assures that the variability of the retrieved stratomesospheric CO is not damped, i.e., free scaling of three parts of the VMR profile is emulated by a 3-block Tikhonov-L1 scheme – the generation of such a matrix is presented in *Sussmann and Borsdorff* [2007, equation 11]. The altitude borders of the blocks are selected to separate vertical domains with different atmospheric characteristics and take the attainable altitude resolution into account: The lowermost block ends at 11 km, which corresponds to the tropopause altitude. The second block ends at 30 km, above which no altitude resolution can be retrieved from solar spectra. The last block ends at 100 km. Due to the free scaling of each block the signal of stratomesospheric CO is not dampened by the regularization. The resulting degrees of freedom of signal are $dofs \equiv 3$ (trace of the averaging kernel matrix [*Rodgers*, 2000]).

[1] Karlsruhe Institute of Technology, IMK-IFU, Garmisch-Partenkirchen, Germany.

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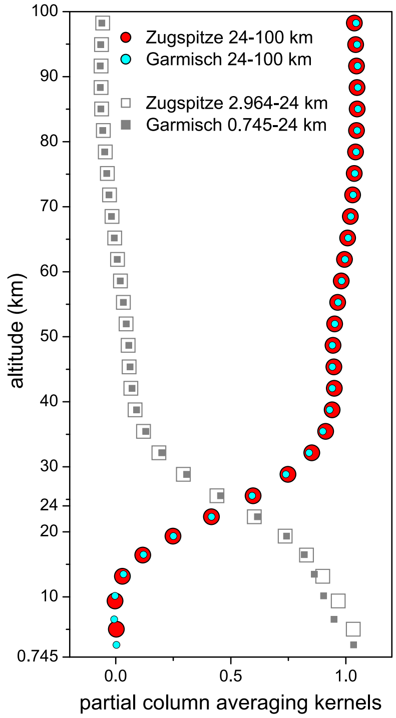

Figure 1. Characterization of the optimized FTIR retrieval of stratomesospheric CO at mid-latitudes. Mean averaging kernels for all states measured in 2004–2008.

[9] We obtain a twofold proof that our retrieval approach is not limited to mountain stations and is thus applicable to mid-latitude FTIR stations in general:

[10] 1. Figure 1 shows that the theoretical sensitivity for the CO partial column above 24 km is nearly identical for the FTIR system at the Zugspitze summit (2964 m a.s.l.) and the nearby Garmisch ground site (745 m a.s.l.).

[11] 2. Figure 2 shows that the stratomesospheric CO columns retrieved from these two FTIR measurement sites located at different altitudes (but only 7 km horizontal distance) show a good correlation of half-hourly mean values; i.e., R = 0.94, the slope is 0.91 and the standard deviation is 12% of the mean stratomesospheric column of 2.25×10^{16} cm^{-2}.

[12] In this study, we selected only retrieval results which fulfill the following criteria at the same time: *i*) solar zenith angle < 85°, *ii*) root mean square of the spectral fitting residuals (measured minus calculated) < 1%.

3. Results: Variability of Stratomesospheric CO

3.1. Seasonal Cycle and Inter-annual Variability at Mid-latitudes

[13] Early microwave studies indicated that CO columns above 60 km are about twice as large in mid-latitude winter as in summer [*Clancy et al.*, 1984]. This was assumed to be a result of CO transport through the meridional circulation [*Solomon et al.*, 1985]. Satellite observations proved this transport on the global scale [*López-Valverde et al.*, 1996] and gave evidence for its seasonal reversal [*Dupuy et al.*, 2004]. Our measurements exhibit a significant seasonality in stratomesospheric CO on the monthly scale, which agrees with previous studies.

[14] Figure 3a compares the multi-annual, monthly mean seasonal cycle derived from ground-based FTIR measurements at Zugspitze and Bremen. To be directly comparable, the data of the two sites is presented as column average mixing ratios. (Each individual partial column is divided by its dry airmass calculated from NCEP PTU profiles). The seasonal cycles are calculated by averaging daily means from the same month of the years. The Zugspitze seasonal cycle is based on 871 daily means calculated from individual FTIR column measurements (≈9 min integration) between 1999 and 2008. The Bremen data are 71 daily mean values taken from *Velazco et al.* [2007, Figure 7] (measured between 2002 and 2006). The error bars in Figure 3a are the 95% confidence of the multi-annual monthly means. The dotted line is the average of the 12 multi-annual monthly means of the Bremen data.

[15] Figure 3a shows that a significant seasonality can be derived from the FTIR daily means at Zugspitze. The Bremen daily means are in good agreement; i.e., peak and minimum values show similar magnitudes as the Zugspitze results. In spite of this agreement, i.e., even though the Bremen data show some winter enhancements in 2003 and 2005 the previous study by *Velazco et al.* [2007] stated in the abstract: "Generally, the mid-latitude stations show no significant annual variability of strato-mesospheric CO columns." This conclusion was a result of the sparse data coverage available at the time of their study, leading to large uncertainties on the Bremen data, as indicated in our Figure 3a by error bars. Therefore, based on Zugspitze FTIR data, containing more years and denser measurements, the Bremen data can be re-interpreted, concluding now the opposite, namely that a seasonality of stratomesospheric CO at mid-latitudes can be derived from FTIR measurements in a significant manner.

[16] Figure 3b compares the multi-annual, monthly mean seasonal cycle derived from ground-based FTIR measurements at the Zugspitze between 1999 and 2006 with the WACCM model. The WACCM results were provided in a monthly mean output. Consequently the WACCM seasonal cycle has been calculated by averaging monthly mean values from the same month of the years studied. The year-to-year variability is indicated in Figure 3b by 1-sigma error bars.

[17] First of all, Figure 3b shows from the FTIR measurements a broad winter enhancement of stratomesospheric CO between November and April (full width at half maximum) with a maximum in February (3.63×10^{16} cm^{-2}) which

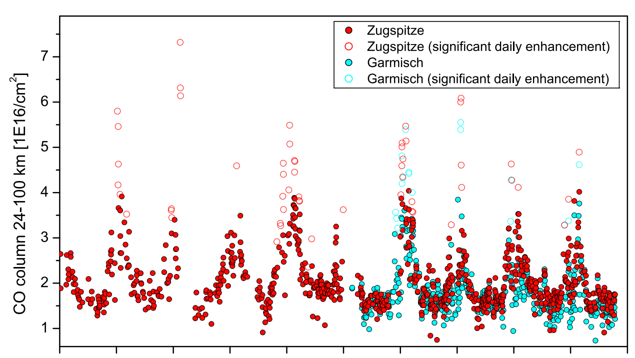

Figure 2. Stratomesospheric CO measured by FTIR at Zugspitze and Garmisch (daily means).

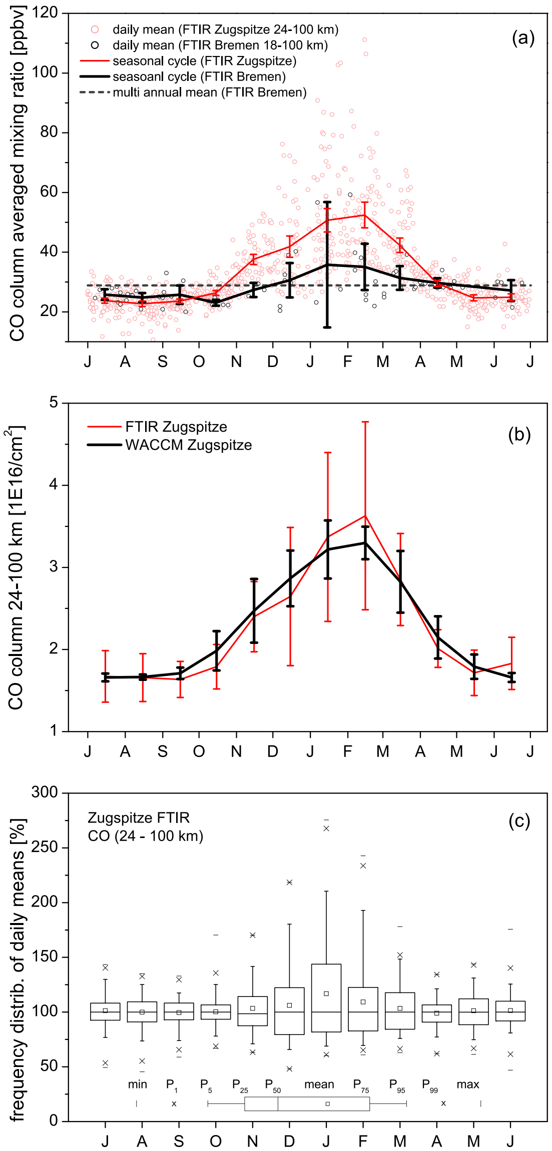

Figure 3. (a) Significance of seasonal cycles (error bars are the 95% confidence statistical errors of the multi-annual monthly means). Bremen data were taken from *Velazco et al.* [2007, Figure 7]. (b) Inter-annual variability (1-sigma bars) on the monthly scale. (c) Frequency distributions of Zugspitze FTIR daily means in percent of the multi-annual median (P are percentiles).

represents a seasonality factor of ≈2.2 relative to the minimum of the summer background of 1.64×10^{16} cm^{-2}. This seasonality factor agrees with earlier microwave studies at mid-latitudes [*Forkman et al.*, 2003]. Figure 3b also shows that this seasonality is in good agreement with the WACCM calculations and therefore is consistent with the study by *Dupuy et al.* [2004], which compared WACCM with UARS/ISAMS CO profiles on the monthly scale [*Taylor et al.*, 1993].

[18] Another result from Figure 3b is that the year-to-year variability of monthly means (1-sigma bars) calculated from the FTIR measurements (up to 32% in winter) is significantly larger than that calculated by WACCM. *Forkman et al.* [2003] assumed that WACCM underestimates the true year-to-year variability. This conclusion was only based on observations for one season and thus required additional confirmation. We can now prove this assumption by analyzing a decade of measurements.

[19] In this context, we found that WACCM not only underestimates the magnitude of the true year-to-year variability, but in addition, there is no correlation between the modeled year-to-year variability and the year-to-year variability derived from the FTIR measurements. This was proven by calculating the deviation of each monthly mean value from a common, multi-annual, seasonal cycle for FTIR and WACCM - which were not correlated ($R = -0.13$). (The common, multi-annual, seasonal cycle is the mean of the multi-annual monthly mean, seasonal cycles derived from FTIR and WACCM). This means that WACCM is not able to realistically model the measured year-to-year variability on a monthly scale, even though it has a built-in capability for this: *Forkman et al.* [2003] remarked that the modeled intra-seasonal and inter-annual variability in WACCM arises from meridional transport of CO-rich polar air by planetary waves. Our finding could be interpreted to mean that strong enhancements on the daily scale due to meridional transport impacting the measured monthly means are not captured by WACCM.

3.2. Day-to-Day Variability at Mid-latitudes

[20] The global distribution of stratomesospheric CO shows a strong latitudinal gradient with highest mixing ratios at the winter pole and large accumulation takes place in the polar night stratomesosphere, due to the lack of OH [*Solomon et al.*, 1985; *López-Valverde et al.*, 1996; *Dupuy et al.*, 2004; *Clerbaux et al.*, 2005]. From the existence of this north-south gradient *Solomon et al.* [1985] concluded that mid-latitudes can exhibit strong enhancements in stratomesospheric CO due to transport of polar vortex air, triggered by planetary wave activity. This mechanism was confirmed by UARS/ISAMS CO measurements performed during the early northern winter 1991/1992 [*Allen et al.*, 1999]. We thereafter derive the first statistics of the frequency, magnitude, and seasonality of such mid-latitude enhancements in stratomesospheric CO based on more than 10 years of continuous measurements at 47.42°N.

[21] Figure 3c shows the frequency distribution of the magnitude of FTIR daily means as a function of season (monthly bins). In order to make the frequency distributions of different months comparable, the seasonal cycle was removed. This was done by representing the daily means for each month as percent of the corresponding monthly median calculated from all FTIR, daily means of this month using all years of the Zugspitze time series (1999–2008).

[22] Figure 3c reveals that the frequency distributions are subject to a strong seasonal change. From November to March the distributions are right skewed (i.e., the mean is significantly larger than the median). This is caused by strong isolated enhancements of stratomesospheric CO on the daily scale (due to meridional transport events) that exceed the multi-annual monthly median by up to ≈300% (e.g., in February 2001, see Figure 2). For the rest of the year, the frequency distributions are symmetric.

[23] The duration of these strong enhancements of stratomesospheric CO varies between 1–3 days. This was derived

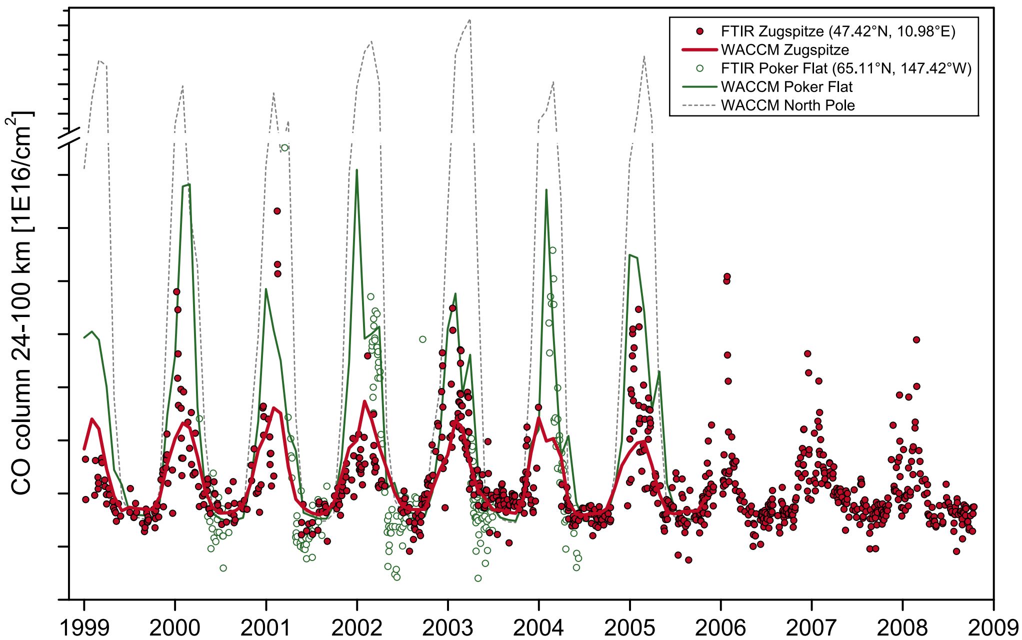

Figure 4. Stratomesospheric CO measured by the Zugspitze FTIR (daily means) and WACCM model results for different latitudes (monthly means). Poker Flat FTIR data were taken from *Jones et al.* [2007].

by first identifying days with significantly enhanced stratomesospheric CO (Figure 2, open circles) and then searching for continuous enhancement periods which were captured without gap by the FTIR measurements. Significant daily enhancements were identified by selecting all daily means larger than the 95th percentile after removing the seasonal cycle from the time series. The seasonal cycle was removed by representing the FTIR daily means as percent of the multi-annual median cycle (i.e., the seasonal cycle was derived by calculating the monthly median of all FTIR daily means of all the different years). The next section will identify the origin of these strong enhancements on a daily scale.

3.3. Variability at Different Latitudes

[24] In this section we investigate how the seasonal variability of stratomesospheric CO on the daily and monthly time scales depends on latitude. Figure 4 shows the time series of ground-based FTIR measurements (daily means) at the Zugspitze (42.42°N) and at Poker Flat (65.11°N); the latter were taken from *Jones et al.* [2007]. For comparison, the WACCM series of stratomesospheric CO above 24 km between 1996 and 2006 for both sites are shown (monthly means), plus one additional WACCM series for the North Pole. We want to point out four striking features of Figure 4:

[25] 1. The maximum level of the winter enhancement of the Zugspitze FTIR daily means is similar to the maximum level measured by the Poker Flat FTIR study.

[26] 2. In February 2001 both the Zugspitze and Poker Flat FTIRs show the highest values of the whole time series. This is the only time that the magnitude of the measured daily means reaches the level of the WACCM result calculated for the North Pole.

[27] 3. Zugspitze FTIR daily means show sporadic winter enhancements on a daily scale. These enhancements are not reproduced by WACCM (monthly means).

[28] 4. Poker Flat FTIR daily means show a monotonous fall-winter increase and a winter-spring decrease which is reproduced by the WACCM monthly means.

[29] Our interpretation of feature 1 is that the mid-latitude winter enhancements are due to the rapid transport of CO enriched air from higher latitudes and reflect CO levels otherwise typical for latitudes comparable to Poker Flat (65.11°N, vortex border). Feature 2 shows that the mid-latitude region is only rarely affected by rapid transport of air directly from the North Pole (vortex center). Features 3 and 4 can be interpreted to be due to the difference in latitudes, i.e., the Zugspitze with isolated winter enhancements on a time scale of 1–3 days due to meridional transport events, and Poker Flat showing a more monotonous fall-winter increase and winter-spring decrease because it is located within or close to the vortex. WACCM data is only available as monthly means and cannot capture the sporadic, daily enhancements at the Zugspitze, although it is able to simulate the smoother seasonality at Poker Flat.

4. Conclusions

[30] Due to our measurement-site location at 47.42°N we were able to detect both monthly-scale signatures of CO transport induced by meridional circulation [*Dupuy et al.*, 2004] and daily-scale effects due to vortex-air distortions [*Allen et al.*, 1999]. In detail, this study i) fills the lack of long term observations at mid-latitudes with 10 years of continuous measurements, ii) presents a new FTIR retrieval approach for CO above 24 km applicable to all mid-latitude stations, iii) derives a significant seasonality with a seasonality factor of ≈2.2 relative to the summer background which agrees to WACCM calculations, iv) proves the assumption of *Forkman et al.* [2003] that WACCM is not able to reflect the real year-to-year variability at mid-latitudes ($R = -0.13$), v) identifies strong enhancements

on the daily scale (up to 300%) as meridional excursions of vortex air through mid-latitudes, and vi) derives first statistics of this vortex-air transport, which shows that winter mid-latitudes are seasonally affected by vortex-border air and only rarely by vortex-center air (with a duration of 1 – 3 days).

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T. Borsdorff and R. Sussmann, Karlsruhe Institute of Technology, IMK-IFU, 40109 D-82467 Garmisch-Partenkirchen, Germany. (tobias.borsdorff@kit.edu)