TIME SERIES of ^{12}CO and ^{13}CO at NORTHERN MID-LATITUDES: DETERMINATION of PARTIAL COLUMN and $\delta^{13}C$ SEASONAL and INTERANNUAL VARIATIONS

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1. INSTRUMENTATION AND OBSERVATIONAL DATABASE

- Two high-resolution Fourier Transform Infrared (FTIR) spectrometers operated under clear-sky conditions at the International Scientific Station of the Jungfraujoch (ISSJ, 46.5ºN, 8.0ºE, 3580m a.s.l.) which is part of the Network for Detection of Atmospheric Composition Change (NDACC, formerly NDSC, http://www.ndacc.org) Alpine station.
- More than 7000 high-resolution (0.003 to 0.005 cm^{-1}) IR absorption solar spectra relevant to the present study have been recorded regularly at the Jungfraujoch, essentially since the early 1990s.

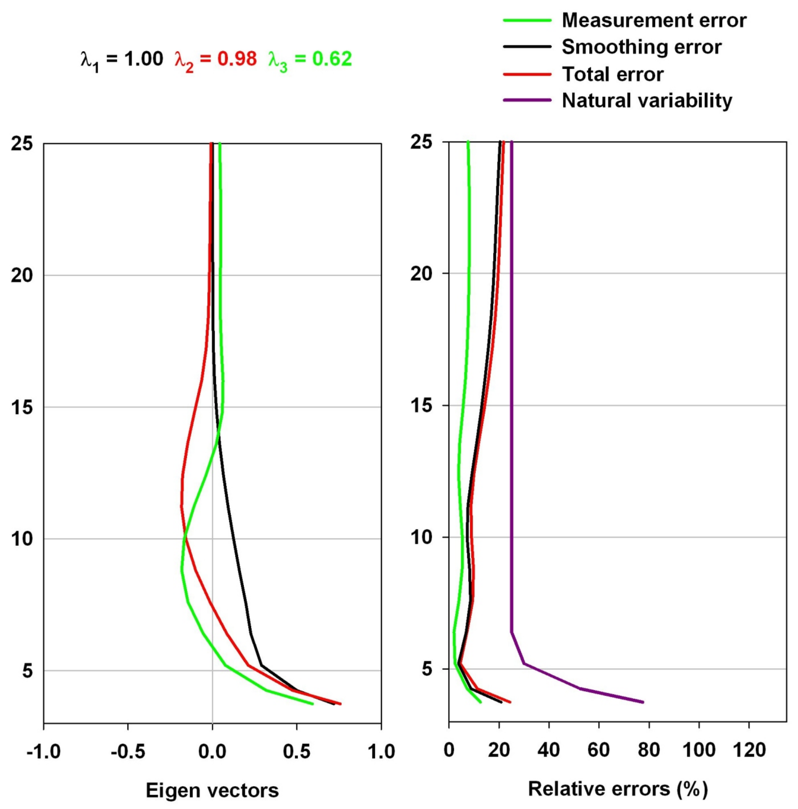

FIGURE 1. Information content calculated for vmr, for typical ^{12}CO retrievals at the Jungfraujoch station. Left frame shows the three first eigenvectors, with corresponding eigenvalues (λ_i) provided above. Right frame gives the error budget, with identification of the main error components, as well as the assumed natural variability.

2. RETRIEVAL STRATEGY

- For the Jungfraujoch spectra, all retrievals have been performed with the SFIT-2 algorithm (v3.91) which is based on a semi-empirical implementation of the Optimal Estimation Method formalism of Rodgers [1]. This code allows to determine information on the vertical distribution of most of the species accessible to the ground-based FTIR technique.
- The HITRAN-2004 spectroscopic compilation used here includes the latest August 2006 updates for water vapor. The carbon monoxide (CO) a priori information is essentially based on ATMOS occultation measurements which were performed in the 39-49ºN latitude range during the ATLAS-3 mission of November 1994. Assumed daily pressure-temperature profiles were provided by the National Centers for Environmental Prediction (NCEP, USA).
- Two approaches have been developed and optimized to independently retrieve abundances of ^{12}CO and ^{13}CO. In both cases, several lines of the target gases have been carefully selected in the so-called INSB spectral domain, more precisely in the 2055-2155 and 4205-4295 cm^{-1} ranges, for ^{13}CO and ^{12}CO respectively. Since the broadband spectra encompassing these lines are not recorded with the same optical filter, no strict timely coincident measurements of the two isotopologues are available from our database. Ratio have therefore been computed allowing for a maximum time difference of 1 hour, compatible with CO intra-day variability at our site.
- The following four microwindows have been simultaneously fitted for ^{13}CO: 2057.78-2057.91; 2069.61-2069.71; 2117.355-2117.447 and 2153.36-2153.56 cm^{-1}. Ozone and the solar spectrum are the major interferences in these domains.
- For the main isotopologue, 6 microwindows were used: 4209-2-4209.55; 4227.09-4227.8; 4231.47-4231.97; 4274.63-4274.965; 4284.82-4285.36 and 4291-4292.14 cm^{-1}. Absorptions by methane, HDO and the solar spectrum have to be accounted for.

Poster presented at the EGU General Assembly 2009, Vienna, Austria, 19-24 April 2009.

3. CHARACTERIZATION OF THE RETRIEVED PRODUCTS

Information content and error budget have been carefully evaluated. FIGURE 1 displays typical results computed for vmr, in the case of ^{12}CO. A very similar picture is obtained for ^{13}CO, hence it is not shown here.

- The three first eigenvectors and corresponding eigenvalues (see left frame, in black, red and green, respectively) show that information on the ^{12}CO tropospheric column is only coming from the retrieval, this is also true for the discrimination between partial columns below and above 8.2 km (98%). Further vertical resolution is available as indicated by the third eigenvector (in green), but with a more significant contribution from the a priori (38%). The situation is a little less favorable for ^{13}CO, with corresponding typical values of 99, 81 and 71 %.
- The error budget affecting the retrieved vmrs below 25 km is given in the right panel of FIGURE 1. Total and individual error profiles are provided and identified (see color codes). These typical errors correspond to 2% [5% for ^{13}CO] of the tropospheric column, to 3%[10%] of the 3.58-8.2 km partial column, to 5% [8%] of the 8.2-15.4 km partial column.

4. ^{12}CO and ^{13}CO TOTAL COLUMN TIME SERIES

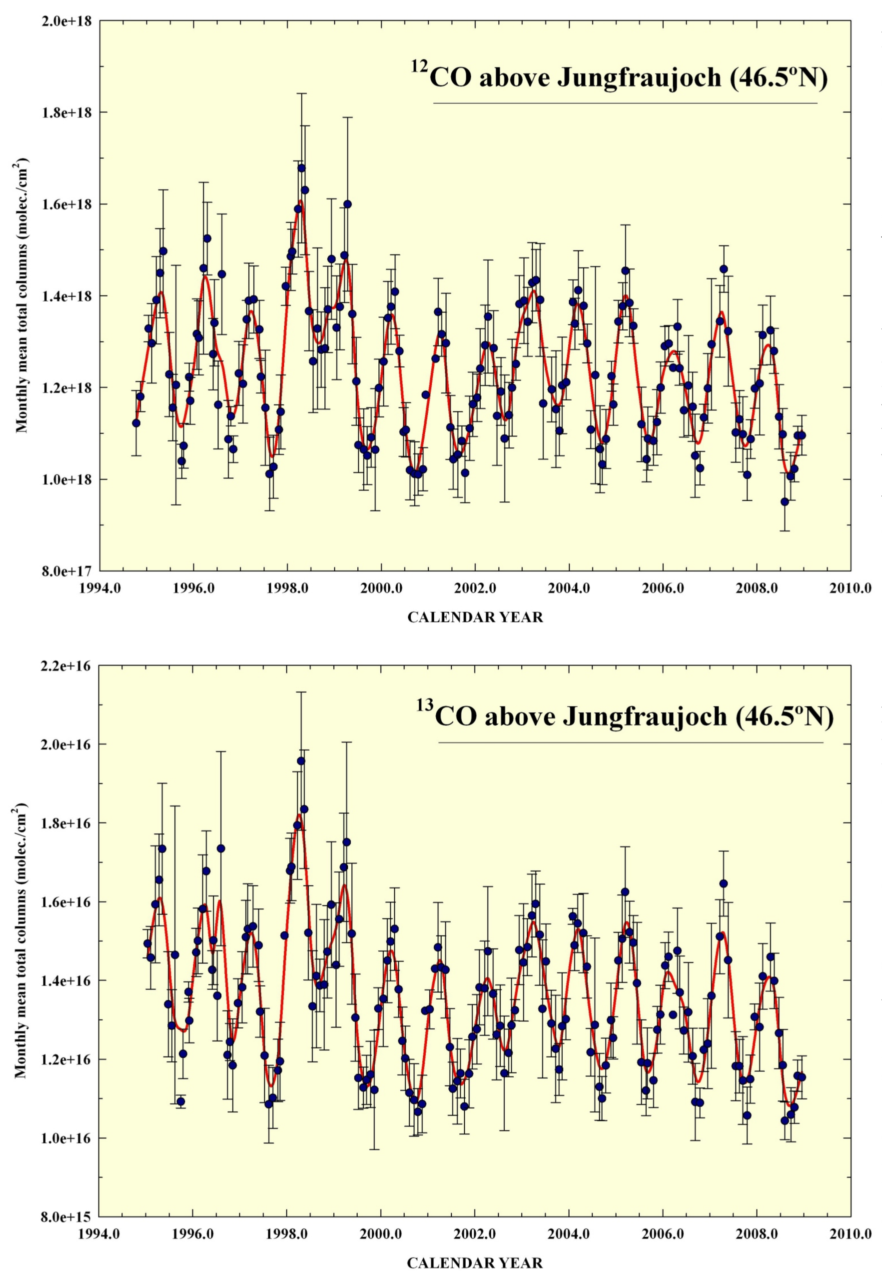

FIGURE 2. Time series of monthly mean total columns of ^{12}CO (upper frame) and ^{13}CO (lower frame) above the Jungfraujoch station. Error bars correspond to the standard deviations around the monthly means. Running mean functions help to appraise the short-term and interannual variations.

The two time series exhibit similar features with strong seasonal cycles for both isotopologues, showing maximum columns in March/April and minimum abundances in September. Interannual variability is also obvious, with years like 1998 showing very high columns in both sets, over the whole season, resulting from high biomass burning. This is also true -although in a lesser extent- in 2002 and 2003, with emission anomalies attributed to strong boreal forest fires [2].

BACKGROUND INFORMATION ON CARBON MONOXIDE (CO)

- Carbon monoxide (CO) is an important reactive gas in the troposphere. It is emitted at the Earth's surface by fossil fuel combustion and biomass burning, it is further transported and mixed into the troposphere. Biogenic sources as well as oxidation of methane and non-methane hydrocarbons complete the emission budget.
- Large uncertainties still affect the relative contributions of the identified anthropogenic and natural sources.
- Destruction by the hydroxyl radical (OH) is the main removal process for CO in both the troposphere and the stratosphere. The resulting average tropospheric lifetime of CO varies from several weeks to a few months.

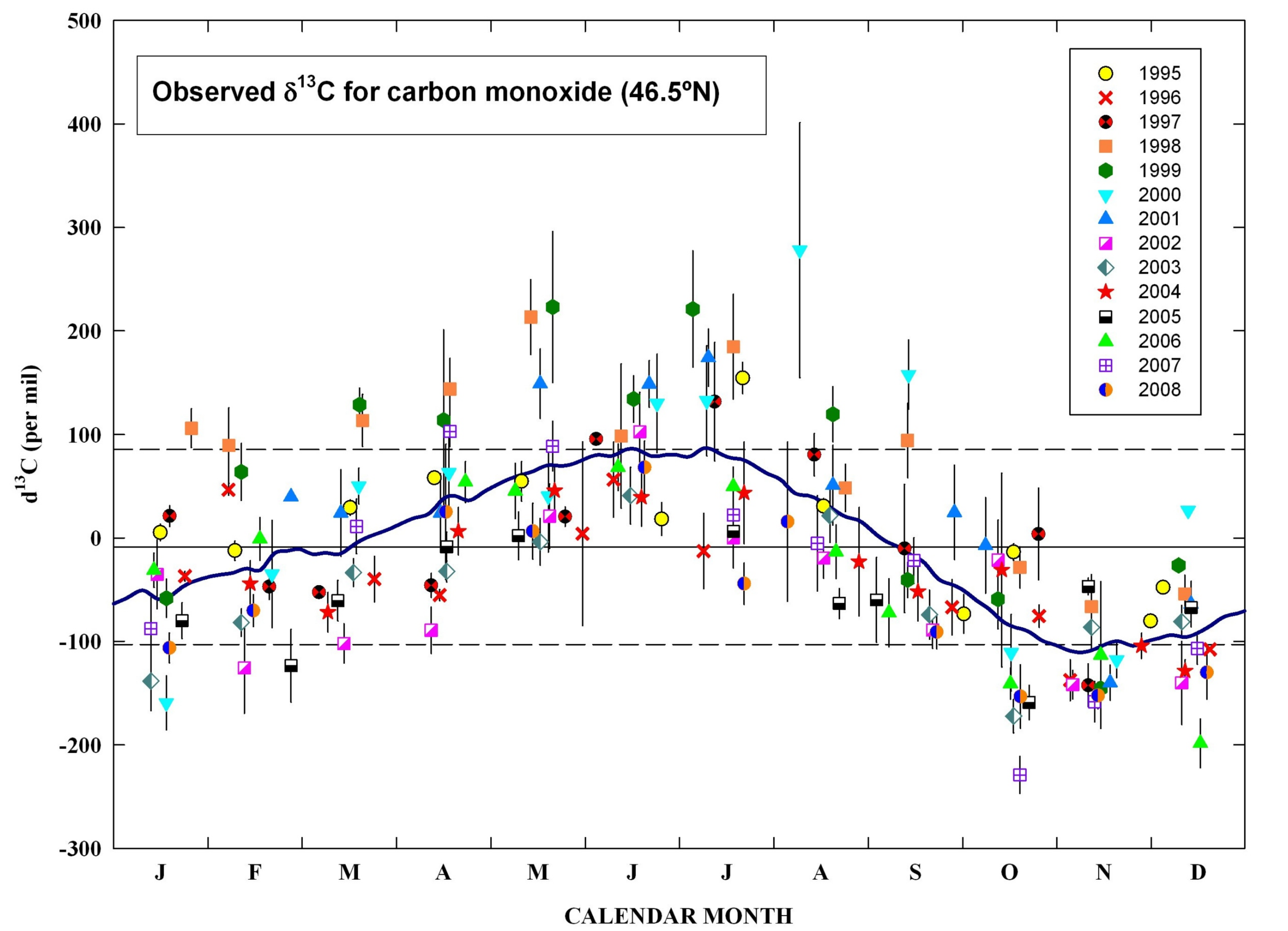

FIGURE 3. Seasonal variations of the $\delta^{13}C$, derived from quasi-simultaneous measurements of the ^{12}CO and ^{13}CO mean vmr in the 3.58-8.2 km atmospheric layer. Vertical bars give the standard errors around the monthly means.

6. COMPARISON WITH ACE-FTS DATA

- The ACE-FTS is a Canadian instrument which was launched onboard the SCISAT satellite on 12 August 2003. Since the beginning of routine operations on 21 February 2004, this Fourier Transform Spectrometer has recorded up to 15 sunrise and sunset occultations per day (about every 90 minutes), with a maximum spectral resolution of 0.02 cm^{-1} in the broad 750-4400 cm^{-1} spectral region [4].
- ACE-FTS products used here for ^{12}CO correspond to the standard version 2.2. ^{13}CO profiles were specifically retrieved for the present study, focusing first on the 41-51ºN latitude range and on the 2004-2005 time period. Over northern mid-latitudes, vmr values are generally available down to at best 7 km. Jungfraujoch and ACE-FTS partial columns are compared in between about 8 and 15 km, since the ground-based retrievals are sensitive in that range, as shown by the information content analysis.
- FIGURE 4 compares the Jungfraujoch and the ACE-FTS data sets for ^{12}CO and ^{13}CO. All occultation measurements obtained between 41 and 51ºN latitude and extending down to at least 8 km are included here.
- The ^{12}CO Jungfraujoch time series (in blue) is characterized by a clear seasonal modulation, showing its maximum around the middle of the year, i.e. somewhat later than the total column signal (see Figure 2). The ACE-FTS data set (in orange) agrees reasonably well with the ground-based data, the higher scatter in the spaceborne data resulting partly from very high values recorded above polluted regions (e.g. China, Russia).
- The seasonal cycle is less obvious in the Jungfraujoch ^{13}CO time series, with significant variations essentially in 1998 and 2007. The ACE-FTS data set is actually too short to draw firm conclusions from the comparison. An extension in time of the ACE-FTS data set and further comparison with model calculations should help to clarify the picture.

References

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Acknowledgments

Work at the University of Liège was primarily supported by the AGACC and the SECPEA projects funded by the Belgian Federal Science Policy Office (SSD and PRODEX Programmes, respectively), Brussels. We thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat (HFSJG, Bern) and the University of Liège for supporting the facilities needed to respectively perform the observations and their analyses. We further acknowledge the vital contribution from all the Belgian colleagues in performing the observations used here.

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5. SEASONAL VARIATION OF THE $\delta^{13}C$ ISOTOPIC RATIO

- Atmospheric isotopic ratio ($^{13}C/^{12}C$) have been computed using the following usual notation:

$$\delta^{13}C = \left(\frac{(^{13}CO/^{12}CO)_{meas}}{(^{13}CO/^{12}CO)_{std}} - 1 \right) \times 1000$$

where $(^{13}CO/^{12}CO)_{std}$ = 0.011237 (Vienna Pedee Belemnite)

- FIGURE 3 shows the seasonal variation of $\delta^{13}C$ above the Jungfraujoch station. The displayed monthly mean values combine quasi-simultaneous measurements (taken within maximum 1 hour) of the ^{12}CO and ^{13}CO mean volume mixing ratio in the atmospheric layer extending from the ground (3.58km) up to 8.2 km. The mean $\delta^{13}C$ deduced from the whole data set is reproduced as a continuous line while the dashed lines correspond to ± one standard deviation around the mean [-9±94].
- Among striking features, we notice a significant seasonal signal (see continuous thick line) with a maximum in June/July, and a minimum around November. The observed phase is in agreement with in situ data sets from northern latitude sites [4]. However, the amplitude of the signal is much larger here, possible causes will be investigated with the help of comparison with GEOS-Chem 3-D transport model (v 7.4.11) calculations.

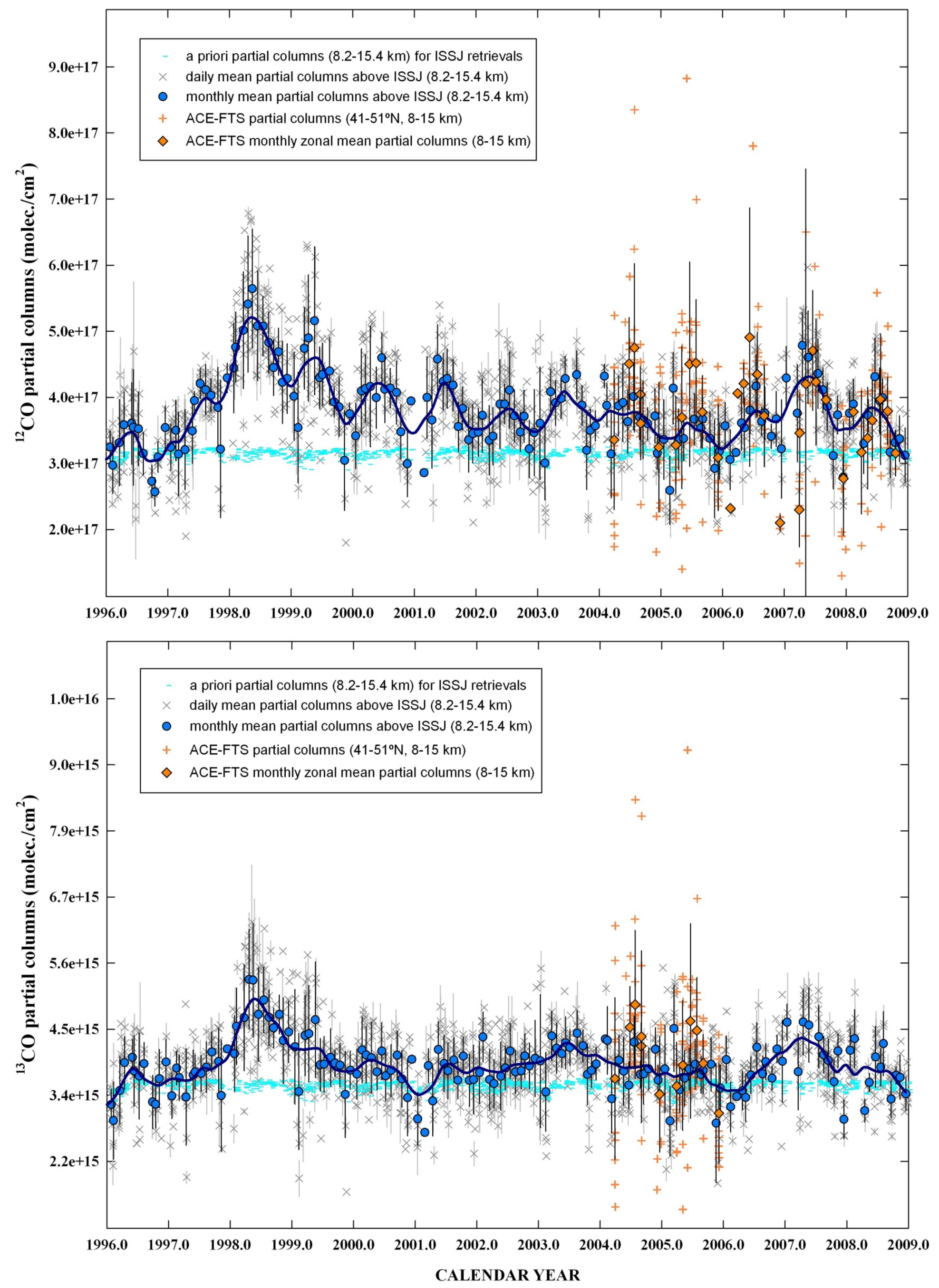

FIGURE 4. Time series of UT/LS partial columns for ^{12}CO (upper frame) and ^{13}CO (lower frame) deduced from the ground-based observations recorded at ISSJ as well as from occultation measurements from the ACE-FTS space-based instrument. Error bars give the standard deviations around the means.