

Seasonal and latitudinal variations of column averaged volume-mixing ratios of atmospheric CO₂

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[1] Column-averaged volume mixing ratios of CO₂ have been obtained by ground based high-resolution solar absorption spectrometry at Ny-Alesund (Spitsbergen, 79°N) in 2002–2003 and during two ship cruises (54°N–34°S) on the Atlantic in 2003. Precisions are better than 0.4% at Ny-Alesund and better than 0.6% for the cruises. The observed 11 ppmv (part per million by volume) seasonal amplitude of the CO₂ column at Ny-Alesund is about 5 ppmv smaller than surface in situ data and 2–4 ppmv greater than model-predictions. The latitudinal gradient of column CO₂ inferred from shipborne measurements is less than 2 ppmv in Oct/Nov 2003. During the cruise in Jan/Feb 2003 the observed latitudinal variation is about 7 ppmv. This strong variation is caused by pollution events (biomass burning) and natural variations. Low CO₂ columns observed between 5°S–15°S are attributed to a strong seasonal amplitude of CO₂ over Central Africa. **Citation:** Warneke, T., Z. Yang, S. Olsen, S. Körner, J. Notholt, G. C. Toon, V. Velazco, A. Schulz, and O. Schrems (2005), Seasonal and latitudinal variations of column averaged volume-mixing ratios of atmospheric CO₂, *Geophys. Res. Lett.*, 32, L03808, doi:10.1029/2004GL021597.

1. Introduction

[2] Currently information about atmospheric CO₂ is mainly inferred from in situ measurements. The main limitation of these measurements is their sparse spatial distribution. Future Satellite measurements will provide a global coverage, placing important constraints on the carbon cycle. The first satellite mainly dedicated to CO₂ measurements is the Orbiting Carbon Observatory (OCO, <http://oco.jpl.nasa.gov/>) whose launch is planned for 2007. Satellites measure the atmospheric CO₂ column, a different kind of information than the atmospheric CO₂ in situ measurements. Furthermore, directly measured column values are potentially a valuable input for atmospheric CO₂ inversion calculations because of much lower impact from errors in modeled vertical convection. However,

currently the understanding of the information content of column CO₂ is largely limited to model evaluations [e.g., Rayner and O'Brien, 2001; Olsen and Randerson, 2004] and few column measurements are available.

[3] The atmospheric column of CO₂ can be also measured from the ground by solar absorption Fourier transform infrared (FTIR) spectrometry. These measurements will play a vital role for the validation of satellites. In addition they provide complementary information to the satellite measurements (e.g., diurnal variation). It has been shown that the atmospheric CO₂ column can be retrieved with a precision of better than 0.5% by ground-based solar absorption FTIR spectroscopy [Yang *et al.*, 2002; Dufour *et al.*, 2004].

[4] In this paper we present ground based solar absorption measurements of the atmospheric CO₂ column performed at Spitsbergen (79°N) and on the research vessel Polarstern during two cruises on the Atlantic, one in Jan/Feb 2003 and another one in Oct/Nov 2003. We investigate the seasonal and latitudinal variation of column CO₂ mixing ratios by comparison with in situ measurements and model calculations.

2. Measurements and Data Analysis

[5] Solar absorption Fourier transform (FT) measurements have been performed at the primary “Network for the Detection of Stratospheric Change (NDSC)”-station at Ny-Alesund (Spitsbergen, 79°N, 12°E, 20 masl) and aboard the research vessel Polarstern during two cruises on the Atlantic. The first cruise started in Cape Town (33.9°S, 18.4°E) on January 24, 2003 and ended in Bremerhaven (53.5°N, 8.6°E) on February 17, 2003. The second cruise started in Bremerhaven on October 22, 2003 and ended in Cape Town on November 15, 2003. The experimental set-up is described elsewhere [Notholt *et al.*, 1997, 2000].

[6] The retrieval and the calculation of the column-average volume mixing ratio (vmr) are based on Yang *et al.* [2002]. CO₂ and O₂ were retrieved from the same spectra using the GFIT spectral fitting algorithm, developed at NASA/JPL [e.g., Toon *et al.*, 1992]. O₂ was analysed between 7765 cm⁻¹–8005 cm⁻¹ (O₂ 0-0¹Δg – ³Σg – band) and CO₂ between 6297 cm⁻¹–6382 cm⁻¹ (2ν₁ + 2ν₂ + ν₃ band centered at 6348 cm⁻¹). The pressure-weighted dry vmr of CO₂ was calculated by scaling the CO₂/O₂ column ratio with the mean O₂ vmr (0.2095), which is constant in the atmosphere. The only interfering gas in the used spectral region is water. The initial vmr-profiles for water and profiles of pressure and temperature are taken from sondes that were launched daily at Ny-Alesund and from the ship. A constant initial vmr (volume mixing ratio)

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profile of 20.95% is assumed for O₂. The assumed initial vmr profile of CO₂ is 370 ppmv at the ground and decreases by 17 ppmv over the first 50 km. The spectral line parameters were taken from an updated version (version July 2004) of the “Atmospheric Trace Molecule Spectroscopy (ATMOS)” linelist [Brown *et al.*, 1996]. The near-IR spectra cover the 5900–11000 cm⁻¹ region at 0.075 cm⁻¹ resolution. Between five and fifty scans were averaged for each spectrum to produce high signal to noise ratios.

[7] Solar absorption measurements in the near-infrared (NIR) have been performed at Ny-Alesund since 2002. Here we present measurements for the years 2002 and 2003. In total 184 NIR-spectra were recorded during these two years. Additionally, during the three cruises from Bremerhaven to Cape Town 128 spectra in the NIR were obtained. Between 2 and 15 spectra were recorded per measurement day.

3. Results

3.1. Precision of the Column Measurements

[8] The rms spectral fitting residuals at Spitsbergen are 0.5–0.8% for CO₂ and 0.4–0.75% for O₂. In the case of the ship spectra, the residuals indicate that the instrumental line shape (ILS) deviates from the calculated one, which has been derived from the finite optical path difference and the size of the entrance aperture. This results in higher residuals of 0.7–1.1% for CO₂ and of 0.55–1.0% for O₂. Yang *et al.* [2002] suggested to use the diurnal variation (Figure 1) of the column averaged vmr (or equivalent the diurnal variation of the column ratio CO₂/O₂) as a measure of precision. Part of the diurnal variation will be caused by real variations in the CO₂ over the day. However, a lower limit for the precision can be estimated from the observed diurnal variation.

[9] The observed diurnal variation of the column ratios CO₂/O₂ is smaller than the diurnal variations of the CO₂ and O₂ columns. This is expected because many systematic errors are common to CO₂ and O₂ (e.g., surface pressure, solar zenith angle, instrumental line shape) and will be partially cancelled in the CO₂/O₂ ratio. A sensitivity study for a typical scenario showed that errors in the solar zenith angle are the dominant limit for the precision of the columns of CO₂ and O₂. We estimated that the error of the solar zenith angle could be up to 0.3 degrees. This error would change the CO₂ and O₂ columns by 1.15% and the CO₂/O₂ only by 0.003%. The pressure-weighted dry vmr of CO₂ is obtained by scaling the column ratio CO₂/O₂ by the vmr of O₂. For the vast majority of the measurements the diurnal variation of the CO₂/O₂ is smaller than 0.4% at Ny-Alesund (Figure 1) and smaller than 0.6% for the measurements during the cruise (Figure 1). Currently no satellite instrument can achieve this precision and it is also sufficient for the validation of proposed satellite missions (e.g., the OCO – satellite). The higher diurnal variation observed for the ship-borne measurements is most likely due to the lower quality of the spectra compared to Spitsbergen. There are several reasons for the lower quality: Instrumental differences (Bruker120M on the ship and a 120HR at Spitsbergen) are responsible for a less stable ILS. Besides that during the ship cruise it was aimed to record spectra whenever possible, whereas in Spitsbergen spectra were only recorded under very good weather conditions (clear

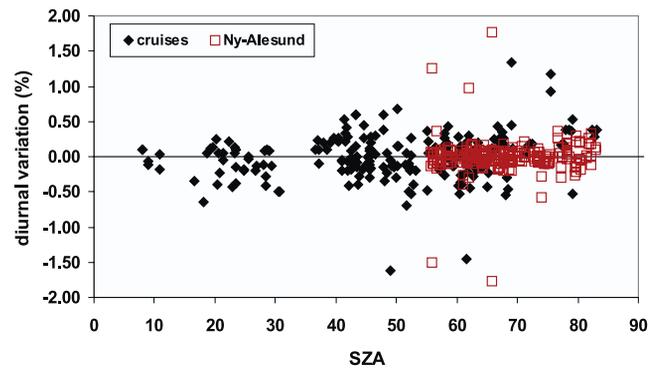


Figure 1. Diurnal variations of the column averaged vmr of CO₂. The diurnal variation in percent is defined as $100 \times \left(\frac{x}{\langle x \rangle} - 1 \right)$ where x is one measurement and $\langle x \rangle$ the mean of the day.

sky). A higher content of atmospheric water vapor during the cruise results in stronger intensity fluctuations than in Spitsbergen. Though the quality of the cruise spectra is worse than the quality of the Spitsbergen spectra, the diurnal variation is only slightly greater. We assume that this can be explained by the cancellation of systematic errors in the CO₂/O₂ ratio.

3.2. Comparison of Column CO₂ With in Situ Data and Models

[10] The in situ sampling at Ny-Alesund is taking place on Zeppelin mountain (475 masl) about 2 km away from the Fourier transform spectrometer. In situ flask sampling is performed by the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory (NOAA/CMDL) [Carbon Cycle Greenhouse Gases Group (CCGG), 2003] and continuous in situ measurements are performed by the Norwegian Institute for Air Research (NILU) [Stordal *et al.*, 2003].

[11] Two different three-dimensional global atmospheric transport models are used for comparison. The Model of Atmospheric Transport and Chemistry (MATCH-model) by Olsen and Randerson [2004] provides monthly mean data for both the surface and the column. It uses meteorological fields representative for a climatologically average year. The model is based on emissions for the year 1990 (5.8 Gt C yr⁻¹) and does not include a “missing sink” which would be necessary to balance fossil fuel carbon sources with the atmospheric growth rate. The model data is provided relative to the mean CO₂ south of 60°S from the model run [Olsen and Randerson, 2004]. To compare the model data with the measurements, performed in 2002 and 2003, a constant value, equivalent to the subtracted CO₂ south of 60°S, has to be added to the model data. In agreement with the in situ measurements at South Pole station (89.98°S, 24.80°W, 2810 masl) [CCGG, 2003] for 2002 a constant of 371 ppmv and for 2003 a constant of 273 ppmv were added to the model. The second model (MPI-model) by Heimann and Körner [2003] uses meteorological fields from the 6-hourly “National Center for Environmental Prediction (NCEP)” re-analysis (NCEP/DOE AMIP-II). The CO₂ source/sink fields for this model originate from Takahashi *et al.* [2002], the version 3.2 of the “Emission Database for

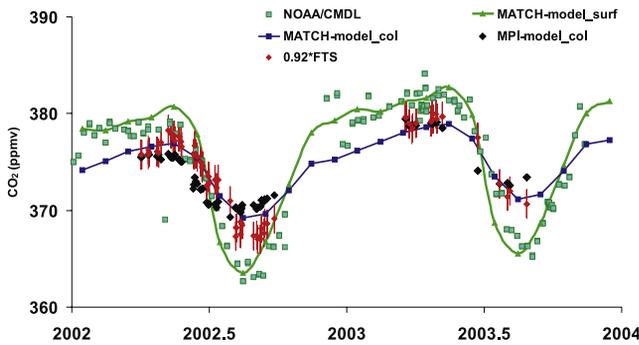


Figure 2. Seasonality of column averaged vmr of CO₂ measured by ground-based Fourier transform spectroscopy (red). NOAA/CMDL surface sampling (green squares) is performed at Zeppelin mountain (475 masl) about 2 km away from the Fourier transform spectrometer. Monthly mean model values from the MATCH-model [Olsen and Randerson, 2004] for the surface (green) and the column (blue) are connected with a line. The black diamonds represent the CO₂ columns from the MPI-model [Heimann and Körner, 2003].

Global Atmospheric Research (EDGAR 3.2)'' and from biosphere fluxes obtained by the BIOME-BGC (BioGeochemical Cycles) model. While monthly mean mixing ratios are used in the case of the MATCH-model, daily means were extracted from the MPI-model.

[12] At Ny-Alesund the seasonal cycle of column CO₂ mixing ratios has been compared with in situ measurements and model data (Figure 2). At the surface the MATCH-model compares well with in situ measurements. Although the emissions for the MATCH-model are based on 1990 the seasonality is well reflected. This is expected because the emissions used for the model are uniformly distributed throughout the year, hence an update of the emissions to current values would not change the seasonality. The good agreement between the in situ surface data and the MATCH-model for the surface provides confidence that adding of 371 ppmv for 2002 and 373 ppmv for 2003 is also a good representation of the modeled column for the years 2002 and 2003.

[13] The accuracy of the measured column is currently limited by errors in the spectroscopic and solar line lists. Laboratory measurements are expected to improve the accuracy of the spectral line list in the future. However, to overcome this limitation in this work we scaled the retrieved vmr of CO₂ at Spitsbergen by a constant factor of 0.92. This factor was empirically determined by minimizing the bias between the measured column and the surface data.

[14] Surface and column data at Ny-Alesund (Figure 2) show qualitatively the same seasonal variability. A peak-to-trough amplitude of the seasonal cycle of about 16 ppmv at the surface and about 11 ppmv for the column has been observed. A smaller amplitude in the column is expected because the processes responsible for the seasonality, namely plant photosynthesis sinks and plant and microbial respiration, take place at the earth's surface. The measured columns suggest that the seasonal amplitude of the column is larger (~2–4 ppmv) than predicted by both models for the column. Possible reasons for the difference in amplitude between the observed and modelled column could be that the models do

not include the weighting function of the remote sensing measurements or that convection is not well modeled, which influences vertical mixing and therefore plays an important role in the relation between the surface and column measurements. Photosynthesis and vertical atmospheric mixing over land are both forced by solar radiation at the surface and therefore correlated. The covariance between seasonal exchange and seasonal transport is called 'seasonal rectifier effect' [Denning *et al.*, 1995]. The importance of the rectifier effect is that its uncertainty is responsible for a significant portion of the spread between inverse models [Gurney *et al.*, 2002]. Column and surface measurements at the same location, as presented here, constrain vertical transport and the rectifier effect.

[15] The latitudinal variation of column CO₂ was investigated during two cruises on the Atlantic between 55°N and 35°S, one in Jan/Feb 2003 and another one in Oct/Nov 2003. Since no CO₂ surface air sampling was undertaken on the ship, the only means for comparison is model data. The MATCH-model has deficiencies in describing the latitudinal gradient of CO₂ for two reasons: First it has no representation of the 'missing' CO₂ sink and second the update of the emissions to current values will change the gradient. For this reason only the MPI-model is used for comparison.

[16] During the cruise in Jan/Feb 2003 latitudinal variations of up to 7 ppmv are observed (Figure 3 (bottom)). The general pattern of the latitudinal variations of column CO₂ is predicted by the model. However, differences between the model and the measurements are clearly observed. In the latitude band between 15°N and 30°N the model predicts consistently higher values than observed during the ship cruise. Between the equator and 10°N the observed values are higher than the modeled ones. Trajectory calculations and measurements of biomass related gases like CO [Warneke *et al.*, 2005] reveal biomass burning in West

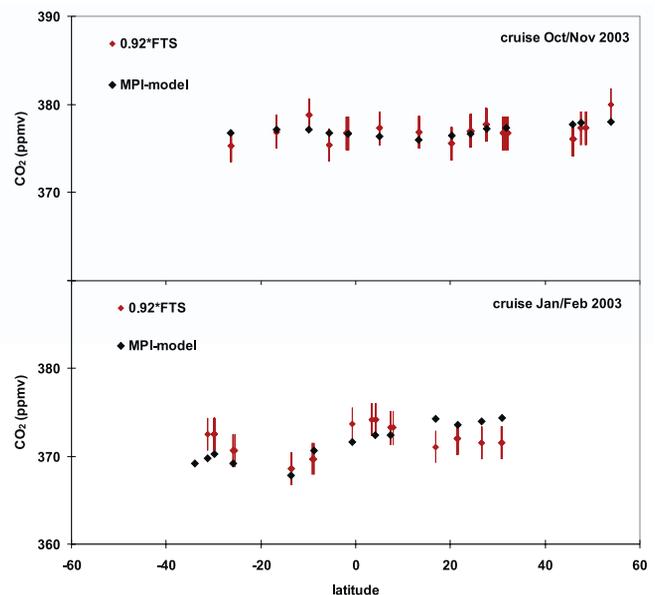


Figure 3. Column averaged vmr of CO₂ (red) measured by Fourier transform spectroscopy (FTS) during a ship cruise on the Atlantic in (top) Oct/Nov 2003 and (bottom) Jan/Feb 2003. Modeled CO₂ columns (black diamonds) are taken from the MPI-model [Heimann and Körner, 2003].

Africa as the apparent source of the CO₂ enhancement between the equator and 10°N. The plumes of the biomass burning are likely to be heterogeneous and the CO₂ enhancements could be very localised. These strong spatial variations are probably not captured by the model. The lowest CO₂ columns have been measured between 5°S–15°S. Low values in this region are also predicted by the model originating from CO₂ depleted air transported out of Central Africa. According to the model the CO₂ depletion centers over Zambia. The reason for the low values over this region is a strong seasonal cycle produced by the biosphere, which is amplified by the meteorology. Southern, subtropical Africa is subject to a persistent high-pressure system causing a large-scale, counterclockwise rotating closed circulation system. This acts as a giant containment reservoir for trace gases. Low CO₂ in this region during that time of the year has also been observed from space by SCIAMACHY [Buchwitz *et al.*, 2004]. The only surface sampling station in this latitude range that is close to the ships track is Ascension Island [CCGG, 2003], but the seasonal cycle at this station does not seem to be impacted by the strong seasonal cycle over Central Africa.

[17] The measurements performed during the cruise in Oct/Nov 2003 were not significantly impacted by pollution events. The measured columns do not exhibit strong variations and the observed latitudinal gradient is less than 2 ppmv, which is in good agreement with the model (Figure 3 (top)).

4. Conclusions

[18] Column averaged volume-mixing ratios of CO₂ have been determined from ground based high-resolution solar absorption spectra obtained at Ny-Alesund (Spitsbergen) and during two ship cruises on the Atlantic. Precisions better than 0.4% at Ny-Alesund and better than 0.6% for the cruises are obtained.

[19] Surface and column data at Ny-Alesund show qualitatively the same seasonal variability. The seasonal amplitude at the surface is about 5 ppmv greater than the one of the column. While the surface data agrees well with model data, the seasonal amplitude of the modeled CO₂ column is about 2–4 ppmv smaller than the measured one. These measurements could be important for the quantification of the rectifier effect, which uncertainty is responsible for a significant portion of the spread between inverse models [Gurney *et al.*, 2002].

[20] The latitudinal variation of column CO₂ was investigated during two cruises on the Atlantic between 55N and 35S, one in Jan/Feb 2003 and another one in Oct/Nov 2003. While during the cruise in Jan/Feb 2003 variations of column CO₂ of up to 7 ppmv were observed, the latitudinal variations during the cruise in Oct/Nov 2003 was less than 2 ppmv. For both cruises the pattern of the latitudinal variation agrees well with model results. According to the MPI-model the low CO₂ columns observed between 5°S–15°S during the cruise in Jan/Feb 2003 have their origin in Central Africa.

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