**Atmospheric
Chemistry
and Physics
Discussions**

Co-located column and in situ measurements of CO_2 in the tropics compared with model simulations

T. Warneke[1], A. K. Petersen[1], C. Gerbig[2], A. Jordan[2], C. Rödenbeck[2], M. Rothe[2],
R. Macatangay[1,2], J. Notholt[1], and O. Schrems[3]

[1]Institute of Environmental Physics, University of Bremen, Bremen, Germany
[2]Max Planck Institute for Biogeochemistry (MPI-BGC), Jena, Germany
[3]Alfred Wegener Institute for Polar and Marine Research (AWI), Bremerhaven, Germany

Correspondence to: T. Warneke (warneke@iup.physik.uni-bremen.de)

Abstract

The first ground-based remote sensing measurements of the column averaged volume mixing ratio of CO_2 (XCO_2) for the inner tropics have been obtained at Paramaribo, Suriname (5.8° N, 55.2° W). The remote sensing observations are complemented by
5 surface air-samples collected at the site, analyzed for CO_2 and $^{13}CO_2$. The surface in-situ measurements are strongly influenced by local sources. From the isotopic composition of the air samples the local source component is suggested to be dominated by the terrestrial biosphere. Using $\delta^{13}C$ from the NOAA/ESRL stations Ascension Is. (ASC), 7.9° S, 14.4° W, and Ragged Point (RPB), 7.9° S, 14.4° W, the data has been
10 corrected for the local source component. Due to the migration of the ITCZ over the measurement site the probed air masses belong to the Northern or Southern Hemisphere depending on the time of the year. Comparison to analyzed CO_2 fields based on TM3 model simulations using optimized fluxes indicate agreement for XCO_2 as well as for the corrected CO_2 mixing ratios at the surface for the long dry season, when
15 Paramaribo belongs to the Southern Hemisphere. A slightly worse agreement during the short dry season is attributed to a larger representation error during this time of the year. Overall the comparison demonstrates that the TM3 model is capable to simulate surface concentrations as well as column densities of CO_2 correctly at the same location.

20 **1 Introduction**

CO_2 is the most important anthropogenic greenhouse gas. Human activities, primarily fossil fuel combustion and deforestation, are responsible for a continuing increase of its atmospheric concentration. The oceans and terrestrial ecosystems currently act as sinks for atmospheric CO_2 and absorb approximately half of the anthropogenic
25 emissions (IPCC, 2007). Inverse models have been used to infer the geographical distribution of the sinks from atmospheric measurements. Until recently inverse mod-

elling studies were solely based on a network of in-situ boundary layer measurement stations. This approach is limited by the sensitivity of the sink estimates to vertical transport and by the sparse spatial coverage of the sampling sites.

The tropics are the geographic region of the Earth, where the atmospheric composition is least constraint by measurements. Ground-based column CO_2 measurements in the tropics are performed at only two sites, at Darwin (Australia) in the outer tropics as part of TCCON and at the inner-tropical site at Paramaribo (Suriname), which is presented in this work. Ground-based column measurements will play a vital role for the validation of current and upcoming satellite measurements, enabling the correction of a potential spatial bias and/or temporal drift in the satellite retrievals. This is especially important in the tropics since a spatial bias is likely to arise from (a) the frequent occurrence of (subvisual) cirrus clouds, which are suggested to be a significant error source in CO_2 retrievals from SCIAMACHY (Schneising et al., 2008) and (b) the high abundance of water vapour, an inferring gas in the spectral region of the satellite retrievals, which has shown to have a strong impact on the CH_4 retrievals from SCIAMACHY in the tropics (Frankenberg et al., 2008).

Recent studies showed that a large set of atmospheric inverse model results, using only in-situ boundary layer measurements, were inconsistent with total column measurements and vertical aircraft profiles as a result of incorrect vertical transport in the models (Stephens et al., 2007; Yang et al., 2007). In contrast to previous studies Stephens et al. (2007) suggests that the tropics are not a net source, but that the uptake of CO_2 in the tropics balances deforestation.

In this paper we present co-located surface and column measurements of CO_2 from the inner-tropical measurement site at Paramaribo (Suriname) and compare the results to TM3 model simulations.

3175

2 Measurements and data analysis

Solar absorption Fourier-transform near infrared (FT-NIR) measurements were performed at the Meteorological Service (MDS) in the south-western outskirts of Paramaribo, Suriname (5.8 N, 55.2 W) during six dry seasons between September 2004 and November 2007. The Intertropical Convergence Zone (ITCZ) migrates twice a year over the measurement site resulting in two dry and two rainy seasons. During the short dry season from February to March the measurement site belongs to the meteorological Northern Hemisphere and during the long dry season from August to November to the meteorological Southern Hemisphere.

Solar absorption spectra were recorded by a Bruker 120M FTIR spectrometer using a 18 cm optical path difference. An InSb-detector, a CaF_2 beamsplitter and an optical infrasil-glass filter were used for the measurements. The recorded spectra were analysed using the line-by-line code GFIT, developed at NASA/JPL (e.g. Toon et al., 1992). Profiles of pressure, temperature and relative humidity up to the 10 mbar level are taken from NCEP re-analysis data. Above 10 mbar a typical stratospheric profile was attached. The initial vmr-profiles are taken from the GFIT-package and are based on balloon observations at Ft Sumner (35° N, 104° W) using the JPL MkIV Interferometer. The initial vmr-profiles of CO_2 and O_2 are constant in time.

O_2 was analysed between $7765\,\text{cm}^{-1}$–$8005\,\text{cm}^{-1}$ ($O_2 0$–$0^1 \Delta g$–$^3\Sigma g^-$ band) and CO_2 between $6297\,\text{cm}^{-1}$–$6382\,\text{cm}^{-1}$ ($2\nu_1 + 2\nu_2 + \nu_3$ band centered at $6348\,\text{cm}^{-1}$). Spectral line parameters for the O_2 retrieval were taken from an updated version (December 2006) of the ATMOS database (Brown et al., 1996). For the CO_2 retrieval spectroscopic parameters from Toth et al. (2008) and for H_2O parameters from Jenouvrier et al. (2007) have been used. The pressure-weighted dry vmr of CO_2 was calculated by scaling the CO_2/O_2 column ratio with the mean O_2 vmr (0.2095), which is, to the degree required, constant in the atmosphere.

Surface air was collected with a portable sampling system consisting of a pump and glass flasks from October 2005–November 2007. The air samples were collected at

3176

the site of the FTIR measurements. For the campaigns in 2007 additional samples were taken at a coastal location north-west of Paramaribo, about 10 km away from the Meteorological Service (MDS). The flask samples were analyzed for CO_2, CH_4, CO, N_2O, SF_6, and H_2. The isotopic composition of CO_2 was also determined, except for the measurements in autumn 2007. Average relative precisions are 0.07% for CH_4 (1.3 ppb at atmospheric mixing ratio levels), 0.02% for CO_2 (0.08 ppm), 0.04% for N_2O (0.13 ppb), 0.3% for CO (0.5 ppb), 0.5% for SF_6 (0.03 ppt) and 0.4% for H_2 (2 ppb). The precision is 0.013‰ for $\delta^{13}C$ and 0.025‰ for $\delta^{18}O$.

3 Results

3.1 CO_2 in surface air

The air is transported from the Atlantic Ocean to the measurement site by the easterly tradewinds. During the short dry season (SDS) from February to March the air passes directly over the Surinamese coastal region to the measurement site. During the long dry season (LDS) from August to November the air passes frequently over French Guiana resulting in a longer passage of the air over the South American continent, which can also be seen in stronger impact by biomass burning during the LDS (Petersen et al., 2008). During both dry seasons the air might be impacted by emissions from the City of Paramaribo.

We have measured $\delta^{13}C$ in the samples to distinguish between different sources. For each of the measurement campaigns a very high linear correlation between the $\delta^{13}C$ and the inverse of CO_2 concentration has been observed (Fig. 1). This shows that the measurements can be described by mixing of background CO_2 with CO_2 from one local source (e.g. Pataki et al., 2003), assuming the $\delta^{13}C$ of the background CO_2 and the CO_2 from the local source are constant over the time of measurement campaigns. The $\delta^{13}C$ is not strongly changed by ocean exchange, but by the biosphere. Therefore it can be assumed that the local source is either the terrestrial biosphere

3177

or fossil fuel combustion. The intercept of the mixing line with the vertical axis corresponds to the isotopic composition of the local-source component. The $\delta^{13}C$ of the local source component is around −25.3‰ during the LDS and approximately 3‰ higher during the SDS. Plant CO_2 uptake via photosynthesis discriminates against ^{13}C resulting in a smaller $\delta^{13}C$ in plant tissues compared to atmospheric CO_2. Plant respiration does not change the isotopic composition of CO_2, hence the CO_2 emitted to the atmosphere via plant respiration is also depleted in ^{13}C. The depletion is strong for C3 plants and small for C4 plants and also depends on plant physiological parameters. Due to the biological origin of fossil energy sources, fossil fuel emissions are also depleted in ^{13}C. Depending on the type of fuel and its region of origin, the $\delta^{13}C$ ranges from $\delta^{13}C=-30‰$ to −6.4‰ for oil, natural gas has a signature of about $\delta^{13}C=-44‰$ and coal of about $\delta^{13}C=-24.1‰$ (Andres et al., 1999). The emissions in the City of Paramaribo are predominantly from cars and natural gas. The isotopic signature of the local source component as well as that the calculated CO_2 for the local source does not correlate with the measured CO in the flasks (not shown) suggests that the measurements are not strongly influenced by urban pollution and the local source component is the terrestrial biosphere. This is also supported by three samples from a remote location in the coastal region at the border to French Guiana, which are on the mixing line.

Measured surface air mixing ratios of CO_2 vary between 377 ppm and 433 ppm. As inferred from the $\delta^{13}C$ the strong variation is most likely arising from emissions from the terrestrial biosphere during the passage of the air from the ocean to the measurement site. The background CO_2 mixing ratio has been calculated using the linear mixing lines (Fig. 1). For this calculation a $\delta^{13}C$ for background air has been taken from NOAA/ESRL flask measurements on Ascension Is. (ASC) for the LDS and from Ragged Point (RPB) for the SDS. $\delta^{13}C$ is only marginal influenced by ocean exchange and therefore not changed during transport from the two NOAA/ESRL sites to the east coast of South America. For each year the mean $\delta^{13}C$ and its standard deviation for the NOAA/ESRL flask measurements has been calculated for the time period

3178

15 September–15 December for the LDS and 15 January–15 April for the SDS. This time period corresponds to approximately one month before the start and one month after the end of the measurement campaigns. The mean $\delta^{13}C$ at the NOAA/ESRL stations are −8.16+/−0.05‰ for the LDS 2005, −8.31+/−0.04‰ for the SDS 2006, −8.16+/−0.04‰ for the LDS 2006 and −8.36+/−0.07‰ for the SDS 2007.

For comparison global spatio-temporal CO_2 concentration fields have been calculated by the atmospheric tracer transport model TM3 driven with re-analysed meteorological data (NCEP) (Roedenbeck, 2005). Surface CO_2 fluxes supplied to the model comprise detailed representations of fossil fuel emissions, land biosphere exchange, and oceanic exchange, as well as an inversely calculated correction flux ensuring consistency with measured atmospheric CO_2 concentrations at many sites around the globe. Details about the model are described by Roedenbeck (2005), and data are available online (http://www.bgc-jena.mpg.de/~christian. roedenbeck/download-CO2-3D/).

The TM3 model does not capture the high variations observed in the surface air samples (Fig. 2, upper panel). The surface samples are likely be influenced by local sources, which are averaged out in the large grid of the model of 3.8×5.0 degrees. Therefore we have compared the surface data corrected for the local source component with an eastward model grid, which mostly contains ocean. Due to the trade winds the airmasses pass this model grid prior to the measurements. The corrected mixing ratios compare well with TM3 model simulations for the long dry seasons (Fig. 2, lower panel). During the SDS 2007 the variation of $\delta^{13}C$ at Ragged Point results in higher uncertainties in the corrected mixing ratios compared to the other campaigns and the modeled values are within the errors of the corrected vmrs. During the SDS 2006 the corrected mixing ratios are on the average about 1–2 ppm lower than the model. The reason for the slightly worse agreement during the short dry season might arise from the large grid size of the model, which comprises part of the ITCZ during the short dry seasons.

3179

3.2 Column averaged volume mixing ratios of CO_2

The column averaged volume mixing of CO_2 (XCO_2) was calculated by scaling the CO_2/O_2 column ratio with the mean O_2 vmr (0.2095), which is, to the degree required, constant in the atmosphere. The accuracy of the measured column is limited by errors in the spectroscopic and solar linelists. Recent laboratory measurements have improved the accuracy of the spectral data for CO_2 (Toth et al., 2008) and the main limitation for the accuracy of the CO_2/O_2 column ratio is assumed to be the spectral data of O_2. To overcome this limitation in this work we have scaled the XCO_2 at Paramaribo with a factor of 1.018. This factor was derived from a least square fit of measured XCO_2 with TM3 model simulations at the TCCON site at Spitsbergen for the years 2005–2006. TM3 model simulations for surface CO_2 show a good agreement with NOAA/ESRL flask measurements at Spitsbergen and therefore we derived the scaling factor for the measured XCO_2 at Spitsbergen from a comparison with the modeled XCO_2 for Spitsbergen.

The measurements of XCO_2 at Paramaribo show a higher scatter than the ones at the TCCON site at Spitsbergen (Warneke et al., 2005). Partly this can be attributed to a less stable instrumental lineshape (ILS) of the Bruker 120M spectrometer used at Paramaribo compared to the Bruker 120HR spectrometer used at Spitsbergen. However, the main limitation for the solar absorption measurements at Paramaribo is assumed to be the impact by clouds. Spectra at Paramaribo were recorded whenever possible and many spectra are impacted by the frequent occurrence of cirrus clouds. Keppel-Aleks et al. (2007) presented a method to correct for source brightness fluctuations caused by clouds which would help to overcome this problem. However, this method requires the DC recording of the interferogram, which is unfortunately not feasible with the instrument used at Paramaribo due to its analog-to-digital converter. To sort out the spectra, which are affected by clouds we use the column averaged vmr of O_2, which is, to the degree required, constant in the atmosphere. Only spectra with an O_2 vmr within 2.5% of the mean retrieved vmr of O_2 were used for this study.

3180

The average of the XCO_2 was calculated for each measurement campaign (red diamonds in Fig. 3) at Paramaribo. For the southern hemishere (LDS) XCO_2 measurements are available for four consecutive years. The measurement campaigns in the LDS took place during the same months of each year. The mean annual increase of XCO_2 from 2004 to 2007 is about 2.2 ppm, which agrees well with the modeled annual increase. The measurements agree very well with the model simulations for the SDS and LDS in 2006. For the other LDS the mean measured XCO_2 are about 0.6 ppm higher and for the SDS 2007 about 1 ppmv lower than the model. Given the standard deviation of 0.9 ppm of the mean in the measurements the deviation from the model it is not significant and it can be concluded that the measurements agree with the model within the uncertainties.

4 Conclusions

The first ground-based remote sensing measurements of XCO_2 for the inner tropics have been obtained at Paramaribo (Suriname). Due to the migration of the ITCZ over the measurement location the probed air masses belong to the Northern or Southern Hemisphere depending on the time of the year. The XCO_2 show a mean annual increase of 2.2 ppm in the column averaged volume mixing ratio between 2004 and 2007 for the Southern Hemisphere.

Co-located in-situ measurements of surface air exhibit a strong variation. Using the δ^{13}C determined in the air samples the strong variation has been attributed to local emissions from the terrestrial biosphere. δ^{13}C data from NOAA/ESRL measurements on Ascension Is. (ASC) and at Ragged Point (RPB) have been used to calculate the background volume mixing ratios of CO_2 from the surface measurements at Paramaribo.

Column averaged volume mixing ratios and background mixing ratios for surface air, derived from the in-situ measurements are compared with TM3 model simulations. Except for the surface background data for the SDS 2006 the background mixing ratios for

3181

the surface as well as the XCO_2 agree well with the model simulations. This demonstrates that the TM3 model is capable to simulate surface concentrations as well as column densities of CO2 correctly at the same location.

References

Andres, R. J., Marland, G., and Bischof, S.: Global and latitudinal estimates of δ^{13}C from fossil-fuel consumption and cement manufacture, Carbon Dioxide Information Center, Oak Ridge National Labaratory, Oak Ridge, Tenn., USA, 1999 (available on Internet via ftp://cdiac.ornl.gov/pub/db1013/).

Brown, L. R., Gunson, M. R., Toth, R. A., Irion, F. W., Rinsland, C. P., and Goldman, A.: "The 1995 Atmospheric Trace Molecule Spectroscopy (ATMOS) linelist", Appl. Opt., 35, 2828–2848, 1996.

Frankenberg, C., Bergamaschi, P., Butz, A., Houweling, S., Meirink, J. F., Notholt, J., Petersen, A. K., Schrijver, H., Warneke, T., and Aben, I.: Tropical methane emissions: A revised view from SCIAMACHY onboard ENVISAT, Geophys. Res. Lett., 35, L15811, doi:10.1029/2008GL034300, 2008.

IPCC, 2007: Climate Change 2007: The Physical Science Basis, in: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Jenouvrier, A., Daumont, L., R'egalia-Jarlot, L., Tyuterev, V. G., Carleer, M., Vandaele, A. C., Mikhailenko, S., and Fally, S.: Fourier transform measurements of water vapor line parame-

3182

ters in the 4200–6600 cm^{-1} region, J. Quant. Spectrosc. Radiat. Transfer, 105(2), 326–355, 2007.

Keeling, C. D.: The concentration and isotopic abundance of carbon dioxide in rural and marine air, Geochim. Cosmochim. Acta, 24, 277–298, 1961.

5 Keppel-Aleks G., Toon, G. C., Wennberg, P. O., and Deutscher N. M.: Reducing the impact of source brightness fluctuations on spectra obtained by Fourier-transform spectrometry, Appl. Opt., 46, 4774–4779, 2007.

Pataki, D. E., Ehleringer, J. R., Flanagan, L. B., Yakir, D., Bowling, D. R., Still, C. J., Buchmann, N., Kaplan, J. O., and Berry, J. A.: The application and interpretation of
10 Keeling plots in terrestrial carbon cycle research, Global Biogeochem. Cy., 17(1), 1022, doi:10.1029/2001GB001850, 2003.

Petersen, A. K., Warneke, T., Lawrence, M. G., Notholt, J., and Schrems, O.: First ground-based FTIR observations of the seasonal variation of carbon monoxide in the tropics, Geophys. Res. Lett., 35, L03813, doi:10.1029/2007GL031393, 2008.

15 Rödenbeck, C.: Estimating CO_2 sources and sinks from atmospheric mixing ratio measurements using a global inversion of atmospheric transport Tech. Rep. 6, Max Planck Institute for Biogeochemistry (MPI-BGC), Jena, Germany, available on Internet http://www.bgc-jena. mpg.de/mpg/websiteBiogeochemie/Publikationen/Technical_Reports/tech_report6.pdf, 2005.

20 Schneising, O., Buchwitz, M., Burrows, J. P., Bovensmann, H., Reuter, M., Notholt, J., Macatangay, R., and Warneke, T.: Three years of greenhouse gas column-averaged dry air mole fractions retrieved from satellite –Part 1: Carbon dioxide, Atmos. Chem. Phys., 8, 3827–3853, 2008,
http://www.atmos-chem-phys.net/8/3827/2008/.

25 Stephens B. B., Gurney, K. R., Tans, P. P., Sweeney, C., Peters, W., Bruhwiler, L., Ciais, P., Ramonet, M., Bousquet, P., Nakazawa, T., Aoki, S., Machida, T., Inoue, G., Vinnichenko, N., Lloyd, J., Jordan, A., Heimann, M., Shibistova, O., Langenfelds, R. L., Steele, L. P., Francey, R. J., Denning, A. S.: Weak Northern and Strong Tropical Land Carbon Uptake from Vertical Profiles of Atmospheric CO_2, Science, 316, 1732, doi:10.1126/science.1137004, 2007.

30 Toon, G. C., Farmer, C. B., Schaper, P. W., Lowes, L. L., and Norton, R. H.: Composition Measurements of the 1989 Arctic Winter Stratosphere by Airborne Infrared Solar Absorption Spectroscopy, J. Geophys. Res., 97(D8), 7939–7961, doi:10.1029/91JD03114, 1992.

Toth, R. A., Brown, L. R., Miller, C. E., Devi, V. M., and Benner, D. C.: Spectroscopic database

3183

of CO_2 line parameters: 4300–7000 cm^1, J. Quant. Spectrosc. Radiat. Transfer, 109(6), 906–921, 2008.

Warneke, T., Yang, Z., Olsen, S., Körner, S., Notholt, J., Toon, G. C., Velazco, V., Schulz, A., and Schrems, O.: Seasonal and latitudinal variations of column averaged volume-mixing
5 ratios of atmospheric CO_2, Geophys. Res. Lett., 32, L03808, doi:10.1029/2004GL021597, 2005.

Yang, Z., Washenfelder, R. A., Keppel-Aleks, G., Krakauer, N. Y., Randerson, J. T., Tans, P. P., Sweeney, C., Wennberg P. O.: New constraints on Northern Hemisphere growing season net flux, Geophys. Res. Lett., 34, L12807, doi:10.1029/2007GL029742, 2007.
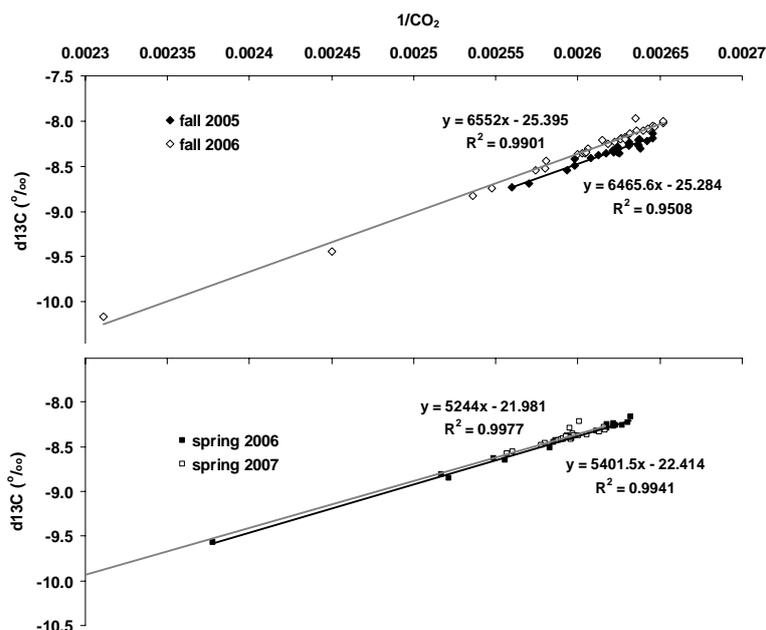
Fig. 1. $\delta^{13}C$ vs. $1/CO_2$ ("Keeling plot" e.g. Keeling, 1961) in flask samples collected at Paramaribo for the different measurement campaigns. The equation of the linear regression and its R2 value is written next to the regression line.
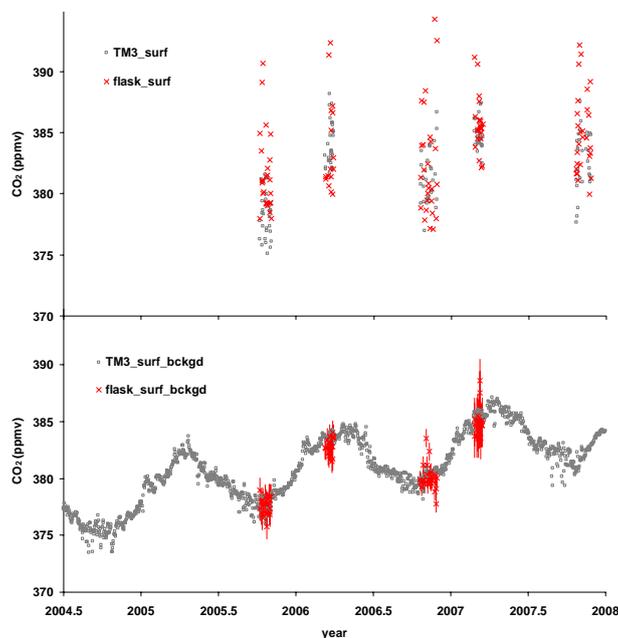
3185

Fig. 2. Measured surface air mixing ratios of CO_2 compared to model simulations. CO_2 mixing ratios in surface air at Paramaribo (flask_surf) vary between 377 ppm and 433 ppm (values above 395 ppm not shown). In the upper panel the flask data is compared with TM3 model simulations for the model grid containing Paramaribo (grid center 5.81° N 55.21° W). The lower panel shows model data for the adjacent model grid towards the east (grid center 5.81° N 50.21° W), mainly containing ocean compared with calculated background CO_2. The background CO_2 mixing ratio (flask_surf_bckgd) has been calculated using linear mixing lines (Fig. 1) and a background $\delta^{13}C$ from NOAA/ESRL flask measurements from Ascension Is. (ASC) and Ragged Point (RPB). $\delta^{13}C$ values from Ascension Is. are used for the fall-campaigns, when the air at Paramaribo belongs to the Southern Hemisphere and $\delta^{13}C$ values from Ragged Point for the spring campaigns, when the air at Paramaribo belongs to the Northern Hemisphere.

3186

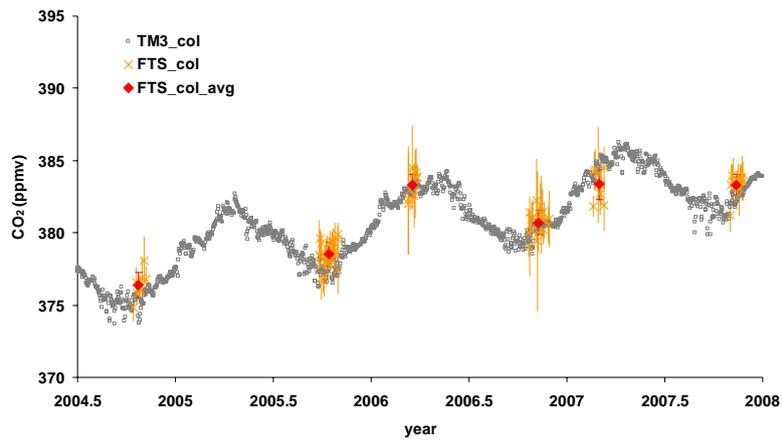**Fig. 3.** Comparison of modeled and measured column averaged vmrs of CO_2. Daily averages (FTS_col) and averages for the measurement campaigns (FTS_col_avg) of column averaged vmrs of CO_2 have been calculated by scaling the column ratio CO_2/O_2 by the vmr of O_2 and a factor 1.018. The scaling factor of 1.018 was derived from a least square fit between FTS measurements and TM3 model simulations at the TCCON site Spitsbergen for the years 2005–2006. The TM3 model simulations (TM3_col) have a grid size of 3.8°×5° and the center coordinate is 5.81° N 55.21° W.

3187