



## First ground-based FTIR observations of the seasonal variation of carbon monoxide in the tropics

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[1] We present the first ground-based solar absorption Fourier Transform Infrared (FTIR) spectrometric measurements in the inner tropics over several years. The FTIR observations agree well with satellite data from the MOPITT instrument. MATCH-MPIC model simulations reproduce the mean vertical structure of the FTIR observations. The model is generally not able to reproduce the extreme enhancements seen during the specific biomass burning events by both observation instruments. Nevertheless, the model indicates that beyond the background source of CO from methane oxidation, the main contributions to the CO mixing ratios are the episodic convective injection of NMHCs and CO from South American biomass burning into the upper troposphere, along with long range transport of African biomass burning CO, particularly during spring. In future studies with more extensive observed time series, observations such as these will be valuable for evaluating ongoing improvements in global chemistry transport models. **Citation:** Petersen, A. K., T. Warneke, M. G. Lawrence, J. Notholt, and O. Schrems (2008), First ground-based FTIR observations of the seasonal variation of carbon monoxide in the tropics, *Geophys. Res. Lett.*, 35, L03813, doi:10.1029/2007GL031393.

### 1. Introduction

[2] The composition of the tropical atmosphere and its changes over time are of significant importance for global climate. Currently large uncertainties in the budgets of many trace gases in the tropics exist, mainly due to a lack of measurements. Emissions within the tropics, especially from biomass burning, contribute substantially to the global budgets of many important trace gases [Andreae and Merlet, 2001; Intergovernmental Panel on Climate Change, 2001]. Carbon monoxide (CO) is primarily produced from biomass burning, oxidation of methane and other biogenic hydrocarbons, and fossil fuel combustion. It has a lifetime ranging from weeks to a few months and is an effective indicator of how transport processes distribute atmospheric pollutants from biomass and fossil fuel burning on a global scale. The main sink of CO is oxidation by OH [Crutzen and Zimmermann, 1991]. In the tropics, CO from biomass burning events can be effectively transported upwards by deep convection and can reach high altitudes in the tropical troposphere [e.g., Pickering *et al.*, 1992; Notholt *et al.*,

2003]. Along with CO, biomass burning releases significant amounts of other trace gases, among them hydrogen cyanide (HCN), acetylene (C<sub>2</sub>H<sub>2</sub>) and ethane (C<sub>2</sub>H<sub>6</sub>). We present the first tropical ground-based solar absorption Fourier Transform Infrared (FTIR) spectrometric measurements performed at 5.8°N in Suriname over several years. FTIR spectrometry is able to resolve 3–4 vertical layers of CO concentrations in the troposphere [Velazco *et al.*, 2005]. We compare FTIR observations of CO with satellite data from the MOPITT instrument on board the Terra spacecraft as well as with simulations by the MATCH-MPIC model. The vertical information that can be obtained from ground-based FTIR measurements is important for satellite validation and especially relevant for the evaluation of models. Currently neither satellite nor any other ground-based remote sensing instrument can provide such vertical resolution. Aircraft in situ measurements could provide vertical profiles, but are expensive and therefore sparse. In addition to total columns and profiles of carbon monoxide, we also present total columns of hydrogen cyanide, ethane and acetylene.

### 2. Data Analysis

[3] The FTIR measurements were performed at the Meteorological Service (MDS) in Paramaribo, Suriname (5.8°N, 55.2°W) during five consecutive dry seasons between September 2004 and November 2006. Campaigns during short dry seasons (SDS, February to March) are denoted as SDS campaigns, while campaigns during long dry seasons (LDS, August to November) as LDS campaigns. The Intertropical Convergence Zone (ITCZ) migrates twice a year over the measurement site. During the SDS, Paramaribo belongs to the meteorological northern hemisphere (NH), during the LDS, it belongs to the meteorological southern hemisphere (SH) [Fortuin *et al.*, 2007]. Besides the FTIR measurements, atmospheric observations at MDS include LIDAR [Immmler *et al.*, 2007] and MAX-DOAS measurements, weekly ozone- and Snow-White-soundings [Fortuin *et al.*, 2007; Verver *et al.*, 2006; Peters *et al.*, 2004].

[4] Solar absorption spectra were recorded using a Bruker 120M interferometer. Total column amounts and volume mixing ratio (vmr) profiles were retrieved using the algorithm SFIT-2. Details on the measurement technique are given, for example, by Velazco *et al.* [2005]; details on the retrieval are in the auxiliary material<sup>1</sup>. In Table 1 the microwindows in which the spectra were analysed and the interfering molecules which were fitted at the same time

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**Table 1.** Microwindows and Interfering Gases

	Microwindow, $\text{cm}^{-1}$	Interfering Gases
CO	2057.70 – 2057.95	$\text{H}_2\text{O}$ , $\text{N}_2\text{O}$ , $\text{O}_3$ , OCS
	2069.55 – 2069.72	$\text{H}_2\text{O}$ , $\text{N}_2\text{O}$ , $\text{O}_3$ , OCS
	2157.30 – 2159.92	$\text{H}_2\text{O}$ , $\text{N}_2\text{O}$ , $\text{O}_3$
HCN	3268.18 – 3268.30	$\text{H}_2\text{O}$
	3286.60 – 3288.00	$\text{H}_2\text{O}$
	3305.30 – 3305.60	$\text{H}_2\text{O}$ , $\text{CO}_2$
$\text{C}_2\text{H}_2$	3250.43 – 3250.77	$\text{H}_2\text{O}$
	3304.78 – 3305.12	$\text{CO}_2$ , $\text{N}_2\text{O}$ , HCN, $\text{H}_2\text{O}$
$\text{C}_2\text{H}_6$	2976.62 – 2976.92	$\text{H}_2\text{O}$ , $\text{CH}_4$ , $\text{O}_3$

by profile scaling are specified. Solar lines are generally simulated in the retrieval.

[5] Global fire maps (ATSR World Fire Atlas, [dup.esri-n.esa.int/ionia/wfa/index.asp](http://dup.esri-n.esa.int/ionia/wfa/index.asp)) were used together with back-trajectory analysis (BADC Trajectory Service, [badc.nerc.ac.uk](http://badc.nerc.ac.uk)) to identify the impact of biomass burning (see auxiliary material). Data for CO from the MOPITT instrument onboard the TERRA satellite were obtained from the NASA Langley Research Center Atmospheric Science Data Center ([eosweb.larc.nasa.gov/PRODOCS/mopitt/table\\_mopitt.html](http://eosweb.larc.nasa.gov/PRODOCS/mopitt/table_mopitt.html)). We used MOPITT level 3 gridded daily averaged data for the comparison. Only cloud free pixels within a radius of 200 km from the FTIR measurement site were selected. The comparison of vmr profiles from FTIR measurements with MOPITT data has been done by *Velazco et al.* [2005], showing good agreement. Here we concentrate on the comparison of total columns.

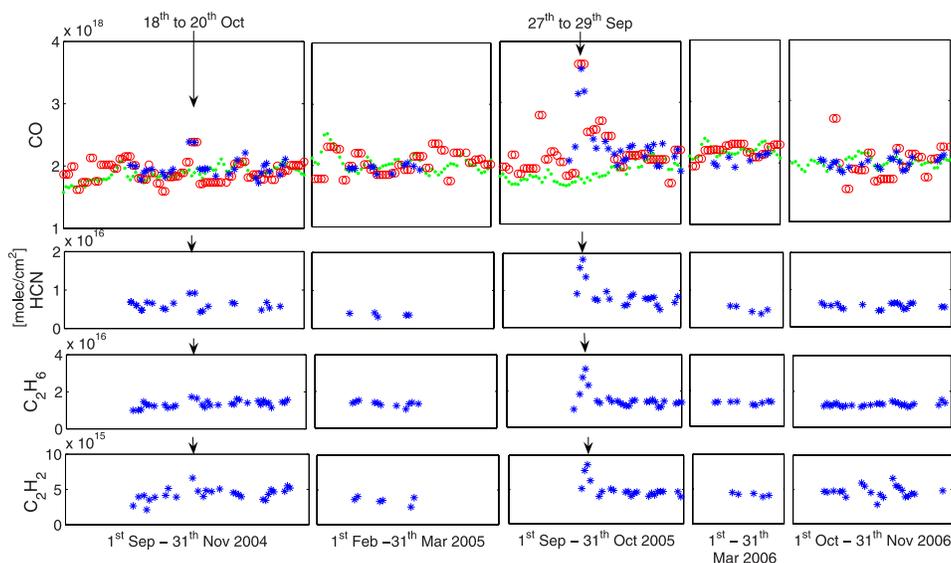
[6] MATCH-MPIC, the Model of Atmospheric Transport and Chemistry, has been developed for the investigation of global tropospheric chemistry [*Rasch et al.*, 1997; *Lawrence et al.*, 1999, 2003; *von Kuhlmann et al.*, 2003]. It is an offline model that reads in gridded time-dependent values for the basic meteorological parameters, e.g. temperature, surface pressure, and horizontal winds. It then uses these parameters to calculate further meteorological parameters

like cloud fields and convective mass fluxes that are required for atmospheric chemistry simulations. MATCH-MPIC employs monthly-mean biomass burning emissions which do not vary from year to year. The MATCH-MPIC model, in the forecast and analysis configuration [*Lawrence et al.*, 2003], has been used to calculate vmr profiles for Paramaribo for the same time periods as the measurement campaigns.

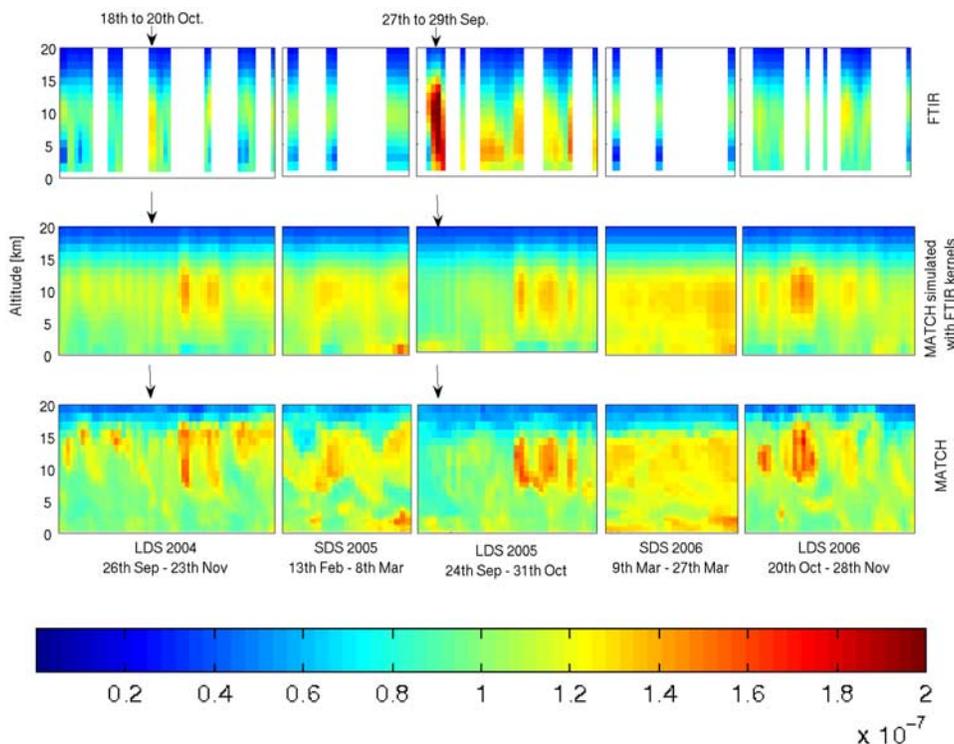
### 3. Ground-Based and Space-Borne Measurements

[7] Total columns of CO,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_2$  and HCN retrieved from ground based solar absorption measurements in Paramaribo, Suriname, are shown in Figure 1. The CO total column averaged over all of the campaigns is about  $2.0 \pm 0.3 \times 10^{18}$  molec/cm<sup>2</sup>. During the LDS campaign in 2005 it is about 11.4% higher than the average. The LDS campaigns (SH) are more strongly impacted by biomass burning emissions than the SDS campaigns (NH). Variability is also much higher during LDS than during SDS campaigns. This is especially so during the LDS 2005, when very high total column amounts of CO were observed. Statistics on the fire counts during the LDS 2004 and 2005 give no evidence for enhanced biomass burning during the LDS 2005, neither in Africa nor in South America. However, back-trajectories indicate that during the LDS of 2005, a higher percentage of air masses are coming from South America compared to the same season in the years 2004 and 2006, so that greater levels of regional biomass burning pollution are experienced.

[8] CO total columns from MOPITT measurements are plotted together with the FTIR observations in Figure 1. There is a very good agreement between the FTIR and MOPITT data, especially for the significant enhancements during 18–20 October 2004 and 27–29 September 2005, which are observed by the FTIR as well as by the MOPITT



**Figure 1.** Total columns of CO, HCN,  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_2$  retrieved from FTIR measurements (blue stars). (top) The comparison of CO total columns from FTIR measurements with cloud free data from the MOPITT instrument (red circles) within a radius of 200 km around the FTIR measurement site. Also shown are corresponding CO total columns of the MATCH-MPIC model runs for Paramaribo (green dots).



**Figure 2.** CO vmr data (in ppb) from (bottom) MATCH-MPIC and the (top) FTIR in Paramaribo for five consecutive measurement campaigns between September 2004 and November 2006. The time axis covers the time periods of the FTIR measurements. (middle) CO profiles from MATCH-MPIC smoothed by FTIR averaging kernels are shown.

instrument. The back-trajectory analysis shows that the enhancements are affected by polluted air masses from biomass burning events, coming from South America. For the sake of completeness, the CO total columns of the MATCH-MPIC model for Paramaribo are also plotted. Apart from the LDS 2005, the CO total columns of the model are in good agreement with both the FTIR and the MOPITT observations (for details see Section 4).

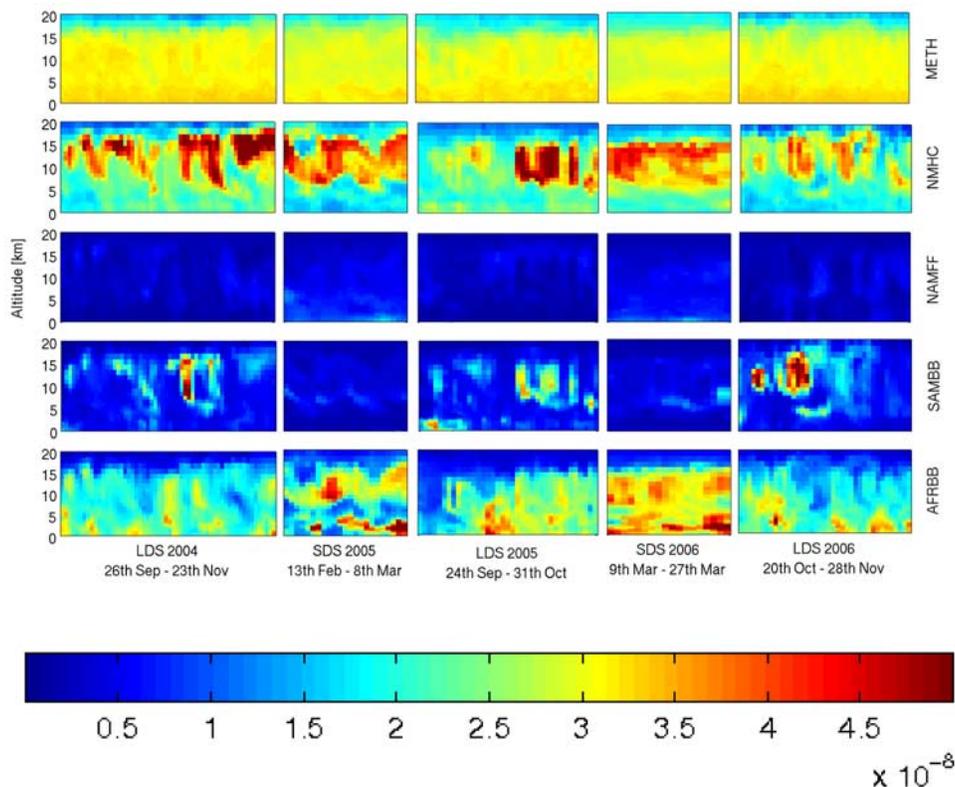
[9] Differences between the NH and SH are seen for both the HCN and  $C_2H_2$  total columns, showing that the sources of these two gases in the NH are not as abundant as in the SH. The HCN and  $C_2H_2$  total columns are on average about  $7.0 \pm 2.7 \times 10^{15}$  molec/cm<sup>2</sup> and  $4.6 \pm 1.0 \times 10^{15}$  molec/cm<sup>2</sup>, respectively, during the LDS (SH) campaigns. During the SDS (NH) campaigns they are about 40% and 17.4% lower than during the LDS campaigns (averaging  $4.2 \pm 0.9 \times 10^{15}$  and  $3.8 \pm 0.5 \times 10^{15}$  molec/cm<sup>2</sup>, respectively). As for CO, especially in the LDS 2005 campaign, high HCN and  $C_2H_2$  total columns were observed. Further, the variation during LDS campaigns is larger than during the SDS measurement periods. These two differences are also seen for the  $C_2H_6$  measurements, though the hemispheric differences are not as clear.

#### 4. Comparison of Model Output With FTIR Measurements

[10] CO mixing ratio profiles for Paramaribo have been calculated from MATCH-MPIC output by interpolation from the 4 surrounding grid points. Figure 2 shows the corresponding FTIR measurements and model output for all

campaigns. The profiles from MATCH-MPIC have a higher vertical resolution compared to the FTIR profiles. To make allowance for characteristics of the observing remote sensing instrument, it is necessary to take the averaging kernels into account when intercomparing the observations with model simulations [Rodgers and Connor, 2003; Palm *et al.*, 2005]. Owing to the nature of the retrieval problem being underdetermined, the FTIR averaging kernels tell us that the retrievals at each designated atmospheric layer have contributions from neighbouring layers. In the middle panel of Figure 2, the model smoothed by the averaging kernels is shown (details on similar profiles and averaging kernels are given by Velasco *et al.* [2005]). The middle panel shows what would be seen by FTIR spectrometry if the MATCH-MPIC profiles represented the true CO profile. For visual clarity, FTIR measurements are interpolated in this plot for days without measurements if the gaps do not exceed three days. Gaps in the measurements are due to unsuitable weather or solar viewing conditions, and to various logistical problems.

[11] As can be seen by comparing the upper with the middle panel of Figure 2, the model generally reproduces the vertical structure with a peak in the middle to upper troposphere. This is well illustrated in the mean vertical profiles for each season (see auxiliary material). The model tends to overestimate the observed mixing ratios, generally by about 10–30%, and has a broader pollution peak in the upper troposphere, presumably due to smearing out of plumes by numerical diffusion which is inherent in the transport algorithms used in the model. The overall seasonal differences are also reproduced, with greater CO mixing



**Figure 3.** Absolute contributions of selected regional tracer fields to the CO budget for Paramaribo from MATCH-MPIC (in ppb) for the same time periods as in Figure 2. The CO tracer fields are North American Fossil Fuel (NAMFF), South American Biomass Burning (SAMBB), African Biomass Burning (AFRBB), and methane oxidation (METH). NMHC is the CO source from the chemical oxidation of NMHCs, which originally come from various sources like biomass or fossil fuel burning, plus the surrogate CO that should result from higher NMHCs, such as monoterpenes, which are not represented explicitly in the model.

ratios throughout the troposphere during LDS versus SDS, and more frequent intense pollution events during LDS. However, the very high near-surface CO mixing ratios during SDS are not simulated, nor are the anomalously large CO mixing ratios in the middle troposphere during the LDS 2005. Furthermore, the model fails to reproduce most of the individual observed pollution events, for example, the two periods with enhanced CO levels due to pollution by South American biomass burning discussed in Section 3. This is in contrast to several previous studies [e.g., Lawrence *et al.*, 2003; Velasco *et al.*, 2005], which often showed very good correspondences between observed and modelled pollution plumes, indicating, in particular, a reasonable representation of the outflow meteorology by the model. A likely candidate for the discrepancy here is that climatological monthly mean biomass burning emissions are used, whereas in reality the location of fires varies on a year-to-year basis. Yearly-varying emissions have been used with MATCH-MPIC now in a few specific test cases, showing substantial improvements for comparison to other data sets with observations influenced by biomass burning, though this has not yet been implemented into the operational forecast and analysis system. Nevertheless, the overall good agreement with the statistical characteristics of the observations allows the model output to be used for further analysis of regional CO.

[12] The contributions of CO tracers from various regions and sources (e.g. biomass burning, fossil fuel combustion, and oxidation of methane and NMHCs) were also calculated by the model and are shown in Figure 3. The results show that methane oxidation provides a large background source of CO while biomass burning and other sources largely account for the variability in CO. During the SDS campaigns with the main wind direction from the northeast, the model indicates that biomass burning from the African continent is the main source for enhancements in the simulated CO, whereas biomass burning in South America does not contribute significantly. During the LDS campaigns, with the main wind direction from the southeast, the biomass burning sources from both South America and Africa are largely responsible for variation in the CO concentrations. The oxidation of NMHCs is also a large and variable source, corresponding frequently to the biomass burning CO enhancements, indicating the further importance of biomass burning as an indirect source of CO to the troposphere over Paramaribo.

## 5. Conclusion

[13] Measurements and analysis of CO, HCN, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> were successfully carried out at the tropical site Paramaribo during five consecutive dry seasons. We presented results of vmr profiles for CO and total columns for

CO, HCN, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> and compared our results of CO with space-borne data from the MOPITT instrument and with output from the MATCH-MPIC model. Two significant distinct enhancements in the total column concentrations of all four trace gases occurred on 18–20 October 2004 and on 27–29 September 2005. They are clearly caused by emissions from fires on the South American continent confirmed by back-trajectory analysis and fire counts from satellite measurements. There is a very good agreement between the FTIR and the MOPITT total columns of CO for all of the measurement campaigns; in particular, the enhancements due to biomass burning events are seen by both instruments. The MATCH-MPIC model has been used to calculate vmr profiles for Paramaribo for the same time periods as the measurement campaigns. The model reproduces the mean vertical structure of the FTIR observations, but is generally not able to reproduce the extreme enhancement seen during the biomass burning events in October, 2004, and September, 2005, as well as enhanced CO levels during the first part of the campaign during the LDS in 2005. The model indicates that methane oxidation provides a large background source of CO, while biomass burning and other sources largely account for the variability in CO. During the spring campaigns CO emissions from biomass burning transported from Africa is important, while biomass burning in South America makes no significant contribution. During the LDS campaigns with the main wind direction from the southeast, biomass burning from the African and South American continents are responsible for variation in the CO concentrations. These observations can be valuable for evaluating future improvements in this and similar models, particularly biomass burning emissions and the model resolution and meteorology, to determine which are critical for simulating plumes more accurately in this region.

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