

Latitude and altitude variability of carbon monoxide in the Atlantic detected from ship-borne Fourier transform spectrometry, model, and satellite data

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[1] Carbon monoxide (CO) volume mixing ratio (VMR) profiles have been retrieved from ship-borne solar absorption spectra recorded in the Atlantic between 80°N and 70°S. CO profiles can be retrieved up to 30 km with a maximum altitude resolution of 4 km for a few layers. CO enhancements due to biomass burning have been detected. Recurring enhancements of CO were detected in the upper troposphere (10–15 km) in the equatorial regions and in the southern Atlantic (20°S–30°S). These enhancements could be traced back to African biomass burning sources as well as sources as far as South America. Similar results are observed in CO measurements from space by the Measurements of Pollution in the Troposphere (MOPITT) instrument. However, some enhancements in the upper troposphere especially above the source regions are difficult to distinguish from the MOPITT data. Results from the Model of Atmospheric Transport and Chemistry from the Max Planck Institute for Chemistry (MATCH-MPIC) show good agreement with the FTIR results. An analysis of the model data allows the quantification of the contributions of different sources such as biomass burning, fossil fuel combustion, and oxidation of methane (CH₄) and nonmethane hydrocarbons (NMHC).

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1. Introduction

[2] Measurements of the global variations of trace gases are important for the understanding of chemical and dynamical processes that control the distribution of these trace gases both in the free troposphere and in the stratosphere. Fourier Transform Infrared (FTIR) spectroscopy has been found to be one of the most suitable instruments for the measurements of atmospheric trace gases [Rao and Weber, 1992].

[3] Measurements of the trace gas CO are discussed and utilized in this paper. CO is primarily produced from biomass burning, oxidation of CH₄ and other biogenic hydrocarbons, and fossil fuel combustion. It has a lifetime ranging from weeks to a few months, and it 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. Atmospheric CO is responsible for more than half of the total turnover of OH [Crutzen and Zimmermann, 1991]. In the tropics, CO from biomass burning events can be effectively transported upward by deep convection and can reach high altitudes in the tropical troposphere [Krishnamurti *et al.*, 1996; Sherwood and Dessler, 2000; Notholt *et al.*, 2003].

[4] Along with other pollutants, biomass burning releases a significant amount of CO. Estimates to this amount range from about 300 Tg of CO per year to more than 700 Tg of CO per year [e.g., Bergamaschi *et al.*, 2000; Holloway *et al.*, 2000; Intergovernmental Panel for Climate Change (IPCC), 1996, 2001]. Biomass burning also controls the CO concentration in localized regions near the surface, primarily in the tropics, yielding a 15–30% contribution to CO concentrations throughout most of the troposphere [Holloway *et al.*, 2000].

[5] Owing to the localized intermittent sources and its short lifetime, CO is not homogeneously distributed in the atmosphere. In the Atlantic, backward trajectories starting at different altitude levels indicate that air parcels originate from the African, American, and European continents, depending on the altitude. Upwelling in the tropical Atlantic also plays an important role in transporting pollutants to the free troposphere [Holton *et al.*, 1995; Talbot *et al.*, 1996]. All these processes lead to very uneven distributions of CO

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in the troposphere. Ship-borne in situ and surface measurements of total columns are not able to provide information on the vertical distribution of CO. Therefore there is not enough information about the transport of CO based on these measurements alone. In order to achieve a better picture of the transport of CO it is crucial to measure VMR profiles with a sufficient altitude resolution. In our case, CO VMR profiles could be retrieved up to 30 km with a resolution of up to 4 km for some layers.

[6] The retrieval algorithm is based on the optimal estimation method [Rodgers, 2000]. This method requires an accurate knowledge of the experimental geometry, the meteorological conditions along the sampled path, and realistic a priori information of the relevant atmospheric gases. This causes us a particular concern regarding the contribution of the a priori information to the retrieval. As part of this study, we attempt to provide an illustrative view of the dependence of the retrievals on the a priori information and to show that the derived information mostly comes from the measurement, an indication that the retrieval is robust. A sensitivity study on the data from one of the cruises is presented. The spectra were measured from a ship cruise that covers the latitudes 79°N to 70°S. This provides us a large ensemble of different CO profiles from different latitudes.

[7] In the second part we show the results of CO retrievals from five different ship cruises within the period 1996–2003 in the northern and southern Atlantic Ocean. The cruises in the Southern Hemisphere took place within a common period (i.e., during or close to the Southern Hemisphere summer). Although the results of CO profiles do not represent all seasons, they allow us to draw important conclusions on the transport of CO. The variability of CO volume mixing ratios with respect to latitude and altitude is discussed. Three-dimensional figures including backward trajectories and fire data are provided in order to give a better overview on the transport of pollutants and biomass burning on the sampled locations. Satellite data from the MOPITT instrument on board the Terra spacecraft as well as output data from the MATCH-MPIC model will also be shown to augment the analysis of the FTIR data.

2. Experimental Methods

2.1. FTIR Data

[8] The experiments were performed using a Bruker 120M interferometer. The instrument was installed in a climate controlled laboratory container placed on top of the helicopter deck/upper deck of the German research vessel (RV) *Polarstern*. A solar tracker mounted on the container's roof was modified to react faster in order to cope with the ship's movements. It is driven to follow the sun using a quadrant diode controller [Notholt et al., 2000]. The spectra were recorded between 750 and 6000 cm^{-1} using the sun as the light source. Measurements were made with an optical path difference of up to 200 cm corresponding to an unapodized resolution of 0.005 cm^{-1} . Strict visual inspection by the personnel made sure that only spectra during cloud-free measurements were evaluated.

[9] CO spectra were analyzed in three micro windows: 2057.70–2057.90 cm^{-1} , 2069.55–2069.80 cm^{-1} , and 2157.30 cm^{-1} –2159.35 cm^{-1} . The interfering gases H_2O ,

N_2O , and O_3 are taken into account in all of the three micro windows. Their total columns are retrieved at the same time.

[10] In order to study the dependency of the results on the a priori profiles, the retrievals at all latitudes were repeated with the CO a priori profile scaled by different factors, assigned a constant value and shifted in altitude. This was done to the combined cruise data in December 1999 through January 2000 and July 2000. The cruise data cover the Southern Hemisphere summer and the following Northern Hemisphere summer. Only the sensitivity of the retrievals with respect to the a priori is shown. Sensitivity studies of the retrieved profile to other parameters such as temperature, instrumental noise, etc., are discussed by Pougatchev and Rinsland [1995].

2.2. Retrieval Algorithm

[11] The program used for the retrieval is SFIT-2 (Spectral Least Squares Fitting Program) developed at NASA Langley Research Center and the National Institute for Water and Atmospheric Research in New Zealand (for further descriptions see, for example, Rinsland et al. [1998]). The main element of the software is the forward model that creates a synthetic spectrum from a simulated atmosphere. It then fits the measured spectrum and the synthetic spectrum using optimal estimation [Rodgers, 2000]. The pressure and temperature profiles necessary for the forward model were obtained from balloon sondes that were launched daily from the ship.

[12] Since the retrieval problem is an underdetermined problem, the true profile of the atmosphere can never be known. All the unknown parameters that will be estimated from the measurements by the retrieval are contained in the state vector \mathbf{x} . These parameters may be molecular profiles that describe the state of the atmosphere and instrument related parameters. What we get is the estimated state vector $\hat{\mathbf{x}}$, which is a weighted contribution of the true state vector and the a priori state vector \mathbf{x}_a ; these are related by

$$\hat{\mathbf{x}} = \mathbf{x}_a + \mathbf{A}(\mathbf{x} - \mathbf{x}_a) + \epsilon, \quad (1)$$

where \mathbf{A} is the matrix whose rows are called the averaging kernels and ϵ represents the error terms. In the ideal case, the averaging kernel matrix is a unit matrix. It indicates the resolution and, in principle, reflects how close the retrieved $\hat{\mathbf{x}}$ to the true state \mathbf{x} is.

[13] For our SFIT-2 retrieval, the state vector $\hat{\mathbf{x}}$ contains the profiles of one or more atmospheric molecules, the total columns of interfering molecules, and other parameters, for example, instrument-related parameters such as frequency shift between the measured and the simulated spectrum, the slope of the background level, and the offset of the zero transmission level (see also Rinsland et al. [1998], Barret et al. [2003], and Rodgers and Connor [2003] for more discussions). The subspace of the state vector $\hat{\mathbf{x}}$ concerning one atmospheric molecular profile has 29 elements. Each element represents the volume mixing ratio of the target molecule in one of the layers from the atmospheric model. In this subspace, the averaging kernels are bell-shaped functions (see Figure 1). The amplitudes of the averaging kernels give an indication of the sensitivity of the retrieval in each layer, and the widths indicate the resolution for that layer.

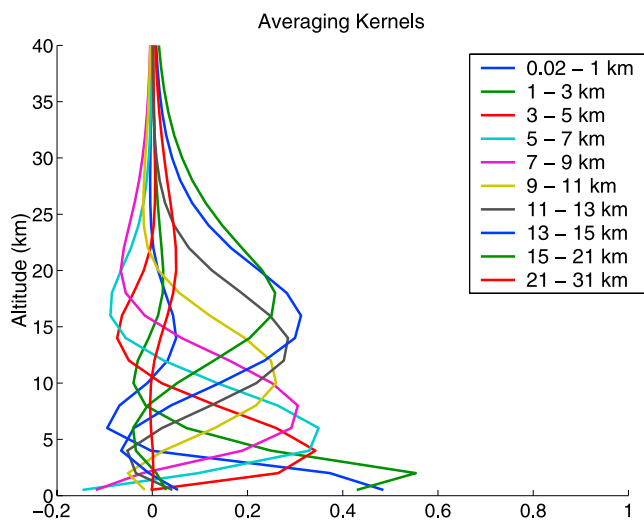


Figure 1. Averaging kernels for an optical path difference (OPD) of 90 cm, solar zenith angle (SZA) of 51° , and a signal-to-noise ratio of 500. The amplitudes of the kernels give an indication of the sensitivity of the retrieval in each layer. The widths of the averaging kernels can be regarded as an indicator of the vertical resolution for that layer.

[14] The trace of the averaging kernel matrix gives the so-called degrees of freedom (DOF) for signal [Rodgers, 2000]. This is an indication of the number of independent pieces of information contained in the measurement. Depending on some parameters (e.g., solar zenith angle, a priori and measurement error covariance, etc.), we have calculated that the DOF for signal for our CO retrieval typically ranges between 4.0 and 5.0.

[15] The a priori and the measurement covariance matrices are ad hoc matrices chosen so that the best possible fit is obtained without undesired oscillations in the retrieved profiles. The ad hoc CO a priori covariance matrix (S_a) has diagonal values corresponding to a standard deviation of 20% for all layers. These settings provide weak constraints to account for variability in the CO profile. The measurement covariance matrix (S_e) is diagonal with values corresponding to signal-to-noise ratio of 500. A diagonal S_e assumes that the measurement errors at each wavelength are independent. Consequently, the retrieval will not be strictly optimal [Rodgers and Connor, 2003]. Moreover, the information content of a retrieval depends on the a priori covariance matrix. With an S_a having diagonal values corresponding to 1% to up to 21%, the DOF for signal in our retrieval increases drastically from about 1.18 to about 4.00, respectively. Further increasing the S_a does not yield a

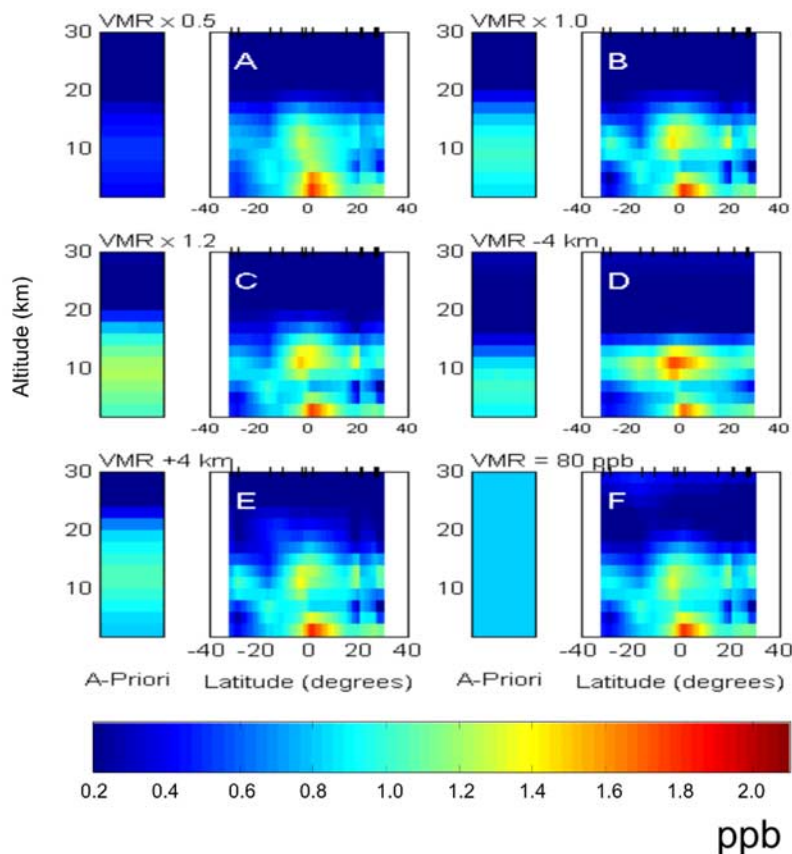


Figure 2. Latitude transects of the retrieved volume mixing ratios of CO and the corresponding a priori VMR profiles used. The measurements were taken from 70°S to 79°N . The CO enhancement at around 10–15 km in the equatorial region can still be resolved using different values of the a priori. The a priori VMR profiles were multiplied by (a) 0.5, (b) 1.0, and (c) 1.2, (d) shifted down by 4 km, (e) shifted up by 4 km, and (f) assigned a constant value of 80 ppb.

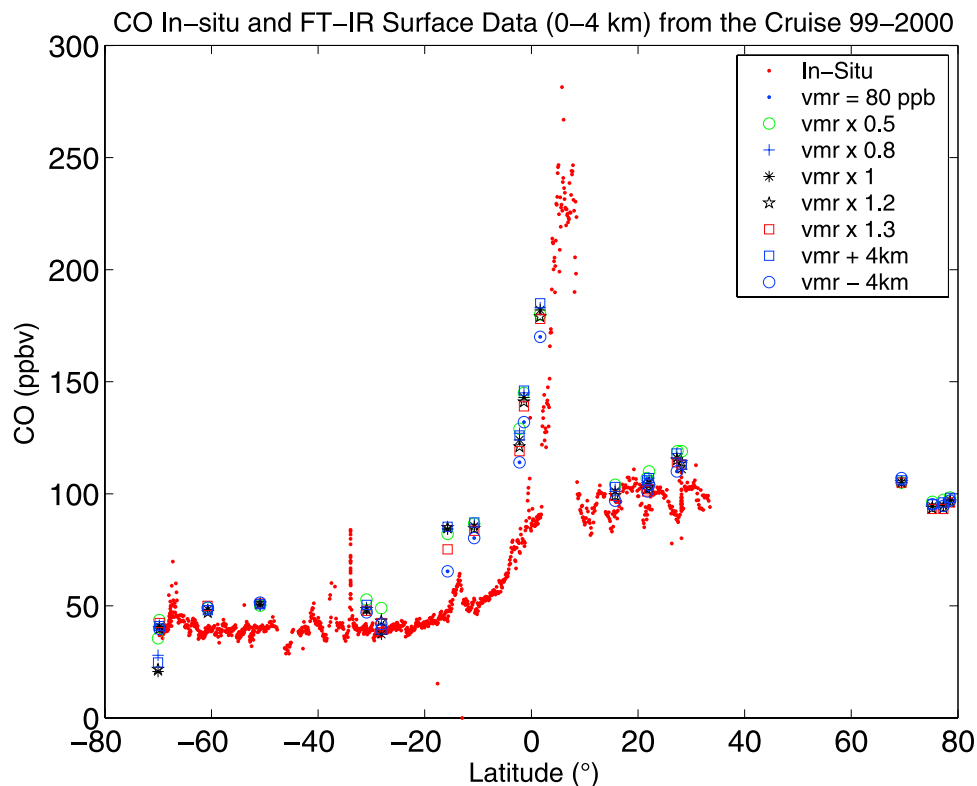


Figure 3. Comparison between in situ CO data and CO as measured with the FTIR spectrometer on board the RV *Polarstern* by using different values of the a priori (the standard VMR used is labeled “VMR \times 1”). The FTIR surface data were averaged from 0 to 4 km. Spikes from the in situ measurements are attributed to background CO from the ship’s exhaust and other local sources (e.g., harbor in Cape Town at 33°S).

substantial increase in the DOF for signal. For an S_a corresponding to 100%, the DOF for signal is about 5.19.

2.3. MOPITT Data

[16] Data from space-borne measurements of CO were obtained from the MOPITT instrument on board the Terra spacecraft launched in December 1999. Terra has a Sun-synchronous orbit at an altitude of 705 km. The MOPITT instrument retrieves CO mixing ratios using gas correlation radiometry at 4.7 μm and 2.3 μm [Drummond, 1992]. The instrument measures in the nadir direction with a 22 km \times 22 km pixel resolution. Global coverage is achieved in about 4 days. The retrieval algorithm is also based on the optimal estimation technique, which requires an a priori CO profile [Deeter *et al.*, 2003]. The retrieval algorithm is discussed in more detail in the works of Pan *et al.* [1998] and Deeter *et al.* [2003]. From the analysis of the MOPITT averaging kernels, the retrieved CO profile has essentially two independent pieces of information; at 500–800 hPa and 150–350 hPa [Bremer *et al.*, 2004]. The retrievals were done only for cloud-free daytime data. The pixels were selected within a radius of 200 km from the position of the RV *Polarstern* and averaged for ± 2 days.

2.4. Model Data From MATCH-MPIC

[17] MATCH-MPIC, the Model of Atmospheric Transport and Chemistry has been developed for the investigation of global tropospheric chemistry. It has been described in

detail in several publications [Rasch *et al.*, 1997; Lawrence *et al.*, 1999, 2003; von Kuhlmann *et al.*, 2003]. It is described as an “offline” model that reads in gridded time-dependent values for the basic meteorological parameters, for example, temperature, surface pressure, and horizontal winds. It then employs these parameters to diagnose further meteorological parameters such as cloud fields and convective mass fluxes that are required for atmospheric chemistry simulations.

[18] MATCH-MPIC has been used to calculate CO mixing ratios along the track of RV *Polarstern*. The positions of the ship every 3 hours (the model output frequency) were used to yield interpolated CO VMR profiles at the location of the FTIR measurements. This allows for a direct comparison of the latitude transects both from the ship measurements and the model results. The contributions of regional CO tracers from various sources (e.g., biomass burning, fossil fuel combustion, and oxidation of methane and NMHCs) were also calculated from the model; the regions are the same as defined by Lawrence *et al.* [2003], with the addition of a breakdown of the CO tracers into source categories.

3. Results

3.1. Sensitivity Studies

[19] A latitude transect of the retrieved volume mixing ratio for CO during the cruise of 10 December 1999 to

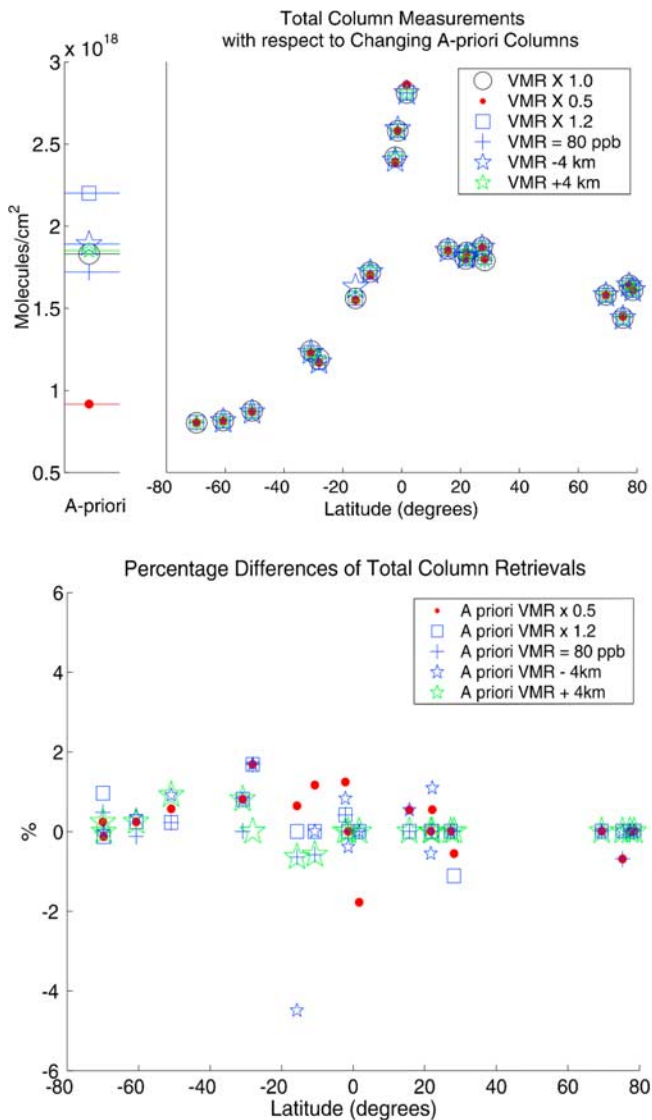


Figure 4. (top) Total CO column measurements with respect to different a priori VMR profiles. (bottom) The corresponding percentage difference of the total column retrievals with respect to the standard retrieval.

18 January 2000 (Southern Hemisphere summer) combined with the cruise from 1–26 July 2000 (Northern Hemisphere summer) is shown in Figure 2c. Also shown is the a priori VMR used for the retrieval. The ad hoc a priori uncertainty was set to 20% for all layers. The averaging kernels for the retrieval shown in Figure 1 have been calculated for the micro-windows used, an optical path difference (OPD) of 90 cm, a solar zenith angle (SZA) of 51°, and a typical signal-to-noise ratio (S/N) of 500. The averaging kernels for the averaged layers indicate that the CO retrieval is sensitive until about 20–30 km. Above this, the retrieval eventually approaches the value of the a priori.

[20] To show the dependency of the results on the a priori profiles, the retrievals at all latitudes were repeated with the CO a priori profile multiplied by 0.5, 0.8, 1.2, and 1.3. Selected results are shown in Figures 2a–2f. The studies were done for the measurements between 40°S

and 40°N. It has been shown that there is no strong variation in CO in the region south of 40°S [Notholt *et al.*, 2003]. Therefore this region has been excluded. As can be seen, the retrievals are only slightly influenced by the a priori depending on the scaling factor used. Note that the features are well retained. The CO enhancement just below the tropical tropopause is still clearly visible. The figures also show the clean Southern Hemisphere and the presence of pollution below 4 km in the Northern Hemisphere.

[21] Even when the whole a priori profile is shifted downward and upward by 4 km (Figures 2d and 2e, respectively), the CO enhancements near the equator between 10 and 15 km along with other features remain, although they are changed in intensity.

[22] Finally, a CO a priori profile having equal values of 80 ppbv at all layers was used (Figure 2f). Even with this unrealistic a priori profile, the CO enhancements near the equatorial region could still be resolved and the clean Southern Hemispheric air can be reconstructed despite the retrievals having yielded unrealistic and negative values above 30 km.

[23] The retrievals were compared to in situ measurements during the cruise (Figure 3). The measurements were taken from an in situ monitor, measuring the ultraviolet resonance fluorescence of CO at 150 nm. The instrument has an accuracy of ± 1.3 ppbv and a detection limit of 3 ppbv (2σ) for an integration time of 1 s [Notholt *et al.*, 2003]. The FTIR surface layer data (0–4 km) showed good correlations with the in situ data with the exception of a few measurements between the equator and 20°S. In this region, the FTIR surface layer data showed greater values compared to the in situ data. Despite the perturbations in the a priori, the FTIR surface layer data showed small deviations.

[24] Total CO column measurements are shown in Figure 4 (top). Using different a priori profiles has proven to have very little effect on the retrieval of the total column. The percentage differences of the total columns with respect to the original CO column using the standard retrieval (“VMR 1.0”) are mostly within $\pm 2\%$ (Figure 4, bottom).

3.2. Five RV *Polarstern* Cruises From 1996–2003

[25] A total of five cruises with the FTIR have been carried out on board the RV *Polarstern* within 1996–2003. The retrieved volume mixing ratio profiles for the cruises ANT-XIV (12 October through 4 November 1996), ANT XVII-1 and 2 + ARK XVI-1 (10 December 1999 through 18 January 2000, and 1–26 July 2000), ANTXX-1 (7–20 November 2002), ANTXX-3 (25 January through 14 February 2003), and ANT XXI-1 (21 October through 13 November 2003) are shown in Figures 5a–5e. In the lower troposphere, the typical features are: the relatively CO-rich Northern Hemisphere, high CO volume mixing ratio profiles in the equatorial regions and a relatively clean lower troposphere in the Southern Hemisphere. The CO enhancement in the upper troposphere (between 10 and 15 km) in the tropical regions is worth noting. This is evident in all the cruises. These enhancements can also be seen to extend to 20°S to 30°S also at the 10–15 km level.

[26] A three-dimensional slice of the atmosphere along the track of the RV *Polarstern* showing the VMR of CO at different altitude levels viewed from the west and east is shown in Figure 6. The measurements took place in

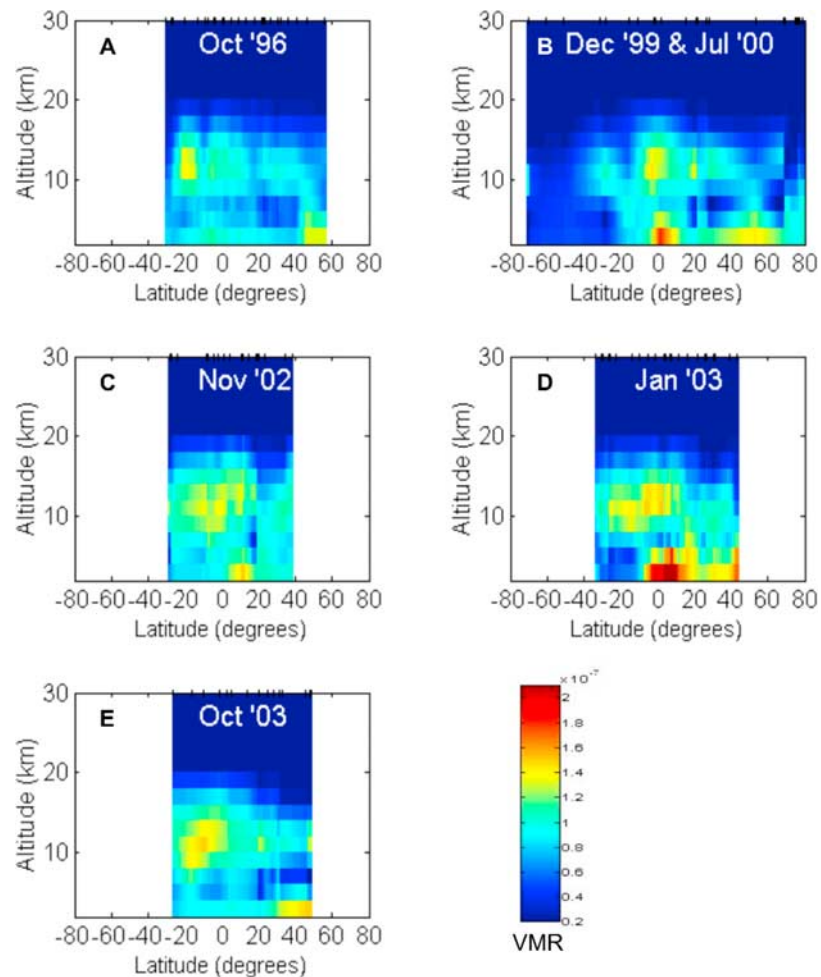


Figure 5. Variations of CO volume mixing ratios with latitude and altitude measured from five different cruises in the Atlantic Ocean. The CO enhancement in the upper troposphere (about 10–15 km) in the tropics and sometimes extending to 20°S–30°S is evident in all of the cruises. A biomass-burning plume was directly encountered during the cruise in January–February 2003 (Figure 5d), resulting in high mixing ratios (red) near the equator.

January–February 2003. The red dots correspond to fires measured by the MODIS web fire mapper for the same months (<http://maps.geog.umd.edu/default.asp>). The backward trajectories correspond to different pressure levels along the track: 700 hPa or about 2.6 km (green), 300 hPa or about 8.7 km (blue), and 140 hPa or about 14.2 km (magenta). The trajectories were obtained from the Deutsche Wetter Dienst (German Weather Service, <http://www.dwd.de>). They were calculated using three-dimensional winds. Note the vertical circulation of air parcels in the southern Atlantic indicated by the trajectories at 300 hPa and 140 hPa as well as the CO enhancements in this region. Air parcels directly coming from areas with high concentration of fires could be seen to contribute to high CO mixing ratios (reddish color) near the equator.

3.3. FTIR, Model, and Satellite Data

[27] CO volume mixing ratio profiles from the MATCH-MPIC model, the FTIR on RV *Polarstern* and MOPITT on the Terra satellite are shown in Figure 7. The data are shown

for the three cruises in November 2002 (Figures 7a–7c), January–February 2003 (Figures 7g–7i) and October–November 2003 (Figure 7j–7l). Data from MOPITT and from MATCH are also shown corresponding to the positions of the RV *Polarstern* on these dates. The color plots are latitude transects along the track of the RV *Polarstern*. All three data sets show similar structures regarding the CO profiles near the equator below 5 km and for most of the measurements in the lower troposphere in the Northern Hemisphere. For visual clarity, some of the FTIR measurements are interpolated in this plot (true measurements are indicated by a marker on top of each plot, and interpolation, if necessary, is made without exceeding 15° of distance between the data points). Where data are absent, for instance near the equator during the cruise in October 2003, some disagreement is expected. The MOPITT data reach only up to 16 km. Owing to MOPITT's coarse resolution, some features may not be resolved, such as the second maximum in the CO VMR profile near the equator during the cruise in January 2003, which can be seen in the

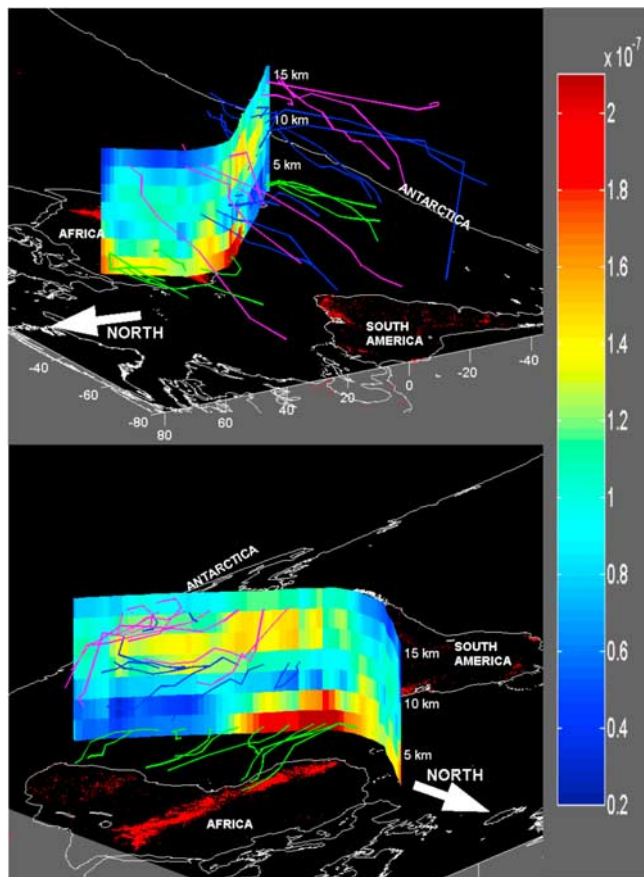


Figure 6. A slice of the atmosphere along the track of the RV *Polarstern* showing the CO VMRs at different altitude levels viewed from the west and the east. The red dots correspond to fires measured by the MODIS web fire mapper (<http://maps.geog.umd.edu/default.asp>). The backward trajectories correspond to different pressure levels along the track: 700 hPa or about 2.6 km (green), 300 hPa or about 8.7 km (blue), and 140 hPa or about 14.2 km (magenta). Note the vertical circulation of air in the southern Atlantic indicated by the trajectories at 300 hPa and 140 hPa near the African continent as well as the CO enhancements in this region. (Backward trajectories are from the German Weather Service, <http://www.dwd.de>.)

FTIR and the model data. CO enhancements at high altitudes near 20°S that could be seen from the model and the FTIR data are also visible in the MOPITT measurements but to a certain extent are difficult to distinguish owing to the limited vertical resolution.

3.4. Simulating High-Resolution Retrievals With Low-Resolution Retrievals

[28] The profiles from MATCH have a higher resolution compared to the FTIR and MOPITT. Owing to the nature of the retrieval problem being underdetermined, the averaging kernels of the FTIR and MOPITT tell us that the retrievals at each designated atmospheric layer have contributions from neighboring layers. To account for the different characteristics of the FTIR and MOPITT instruments, especially the averaging kernels, we have included a study

using the method of retrieval simulation, which is discussed by *Rodgers and Connor* [2003] and *Palm et al.* [2005]. The FTIR retrievals were done with the same a priori profile (until 24 km) as used in the MOPITT retrievals. The MOPITT retrievals were then simulated by the FTIR retrievals using the averaging kernels of MOPITT. A similar method has been applied to the profiles from MATCH using the FTIR and MOPITT averaging kernels with the assumption that MATCH is the true profile.

[29] The results of the measurements from November 2002 are shown in Figures 7a–7c. Figures 7a–7c show the original retrievals from the three platforms. Figure 7d shows profiles from MATCH smoothed by the averaging kernels of the FTIR. Figure 7e shows the FTIR profiles smoothed with the averaging kernels of MOPITT. The MATCH profiles smoothed with the MOPITT averaging kernels are shown in Figure 7f.

[30] The true VMR at a layer can never be known. Using the method of retrieval simulation, it can be said that Figures 7d and 7f would show what the FTIR and MOPITT would have seen if the MATCH profiles would represent the true CO profile. On the other hand, the plot in Figure 7e would show what MOPITT would have seen if the FTIR profiles represent the true CO profile.

3.5. CO Sources

[31] In order to assess the origins of the CO enhancements, we have calculated the contributions of regional tracer fields from the MATCH-MPIC model. A selection of the most significant sources for the three cruises and their percentage contribution is shown in Figure 8. The absolute contributions are shown in Figure 9. Most of the CO in the equatorial regions come from African biomass burning (AFRBB), with more than 40% contribution during the cruise in January 2003. Oxidation of nonmethane hydrocarbons (NMHC) gives about 20–30% contribution to the enhancements in the upper troposphere in the Southern Hemisphere with the largest contribution during the cruise in January 2003, where air parcels seem to have been entrained in vertical circulations. South American biomass burning (SAMBB) also contributes to the enhancements in the upper troposphere in the SH, especially for the cruise in November 2002 and October 2003, but SAMBB for the same region is almost absent during the cruise in January 2003. Fossil fuel combustion from the North American continent (NAMFF) has a relatively stable contribution (up to about 20–25%) to the Northern Hemisphere CO measured in all three cruises. The most dominant source of the background CO is the oxidation of methane (see Figure 9). It covers large regions of the Northern and Southern Hemisphere including the stratosphere with contributions well above 30%.

4. Discussions

[32] CO can be retrieved up to 20–30 km with FTIR spectrometry. The sensitivity studies show that the basic vertical structure of the CO profile with regards to the location of enhanced layers of CO is well captured despite the differences in the choice of the a priori profile. The retrievals cover the Northern Hemisphere, where industrial

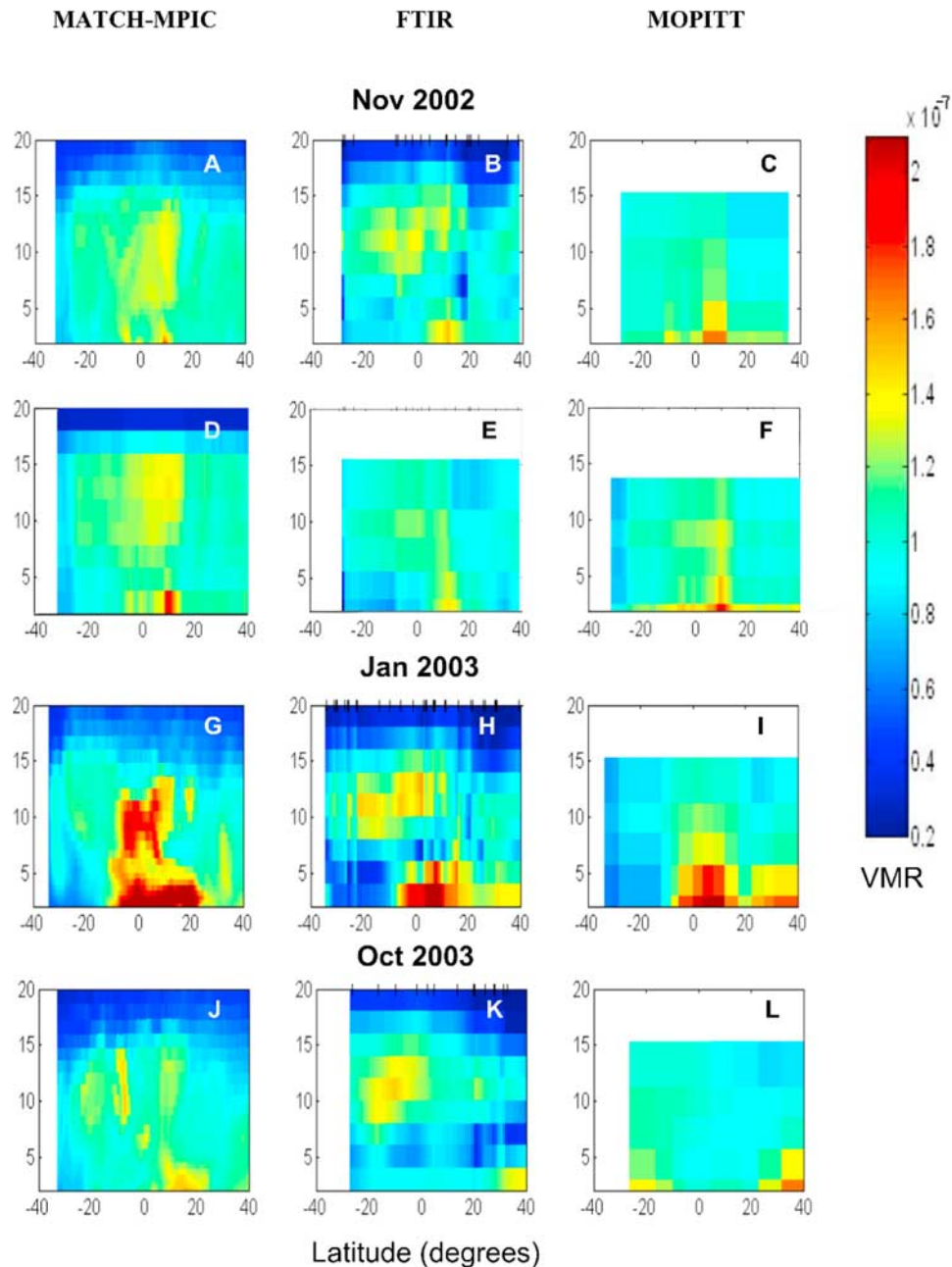


Figure 7. A–C, G–I, J–L. (a, g, j) CO volume mixing ratio data from MATCH-MPIC (left column), (b, h, k) the FTIR on RV *Polarstern*, and (c, i, l) MOPITT on the Terra satellite. The color plots are latitude transects along the track of the RV *Polarstern*. The MOPITT data reaches only up to 16 km. (d) CO profiles from MATCH for October 2002 smoothed by FTIR averaging kernels. CO profiles (e) from the FTIR and (f) from MATCH for October 2002 smoothed by MOPITT averaging kernels.

sources influence the atmospheric CO concentration, the tropics where biomass burning contributes to enhanced CO and the relatively clean Southern Hemisphere. The averaging kernels from the retrievals give 4–5 degrees of freedom corresponding to 4–5 independent pieces of information. The shape of the kernels indicates that for a few layers, a maximum altitude resolution of 4–5 km can be achieved for CO retrievals. It is calculated that a relative change of 20% in the a priori VMR (6–20 ppb)

leads to less than 8% (<10 ppb) change in CO concentration for each layer below 16 km. The retrievals also show reasonable results despite assuming a ± 4 km shift in the a priori and even when a constant a priori was used. The retrievals of surface CO concentrations with the FTIR also show good agreement with in situ data. To summarize, we have shown that a single CO a priori profile could be used for FTIR retrievals of CO at all latitudes from the ground up to 16 km.

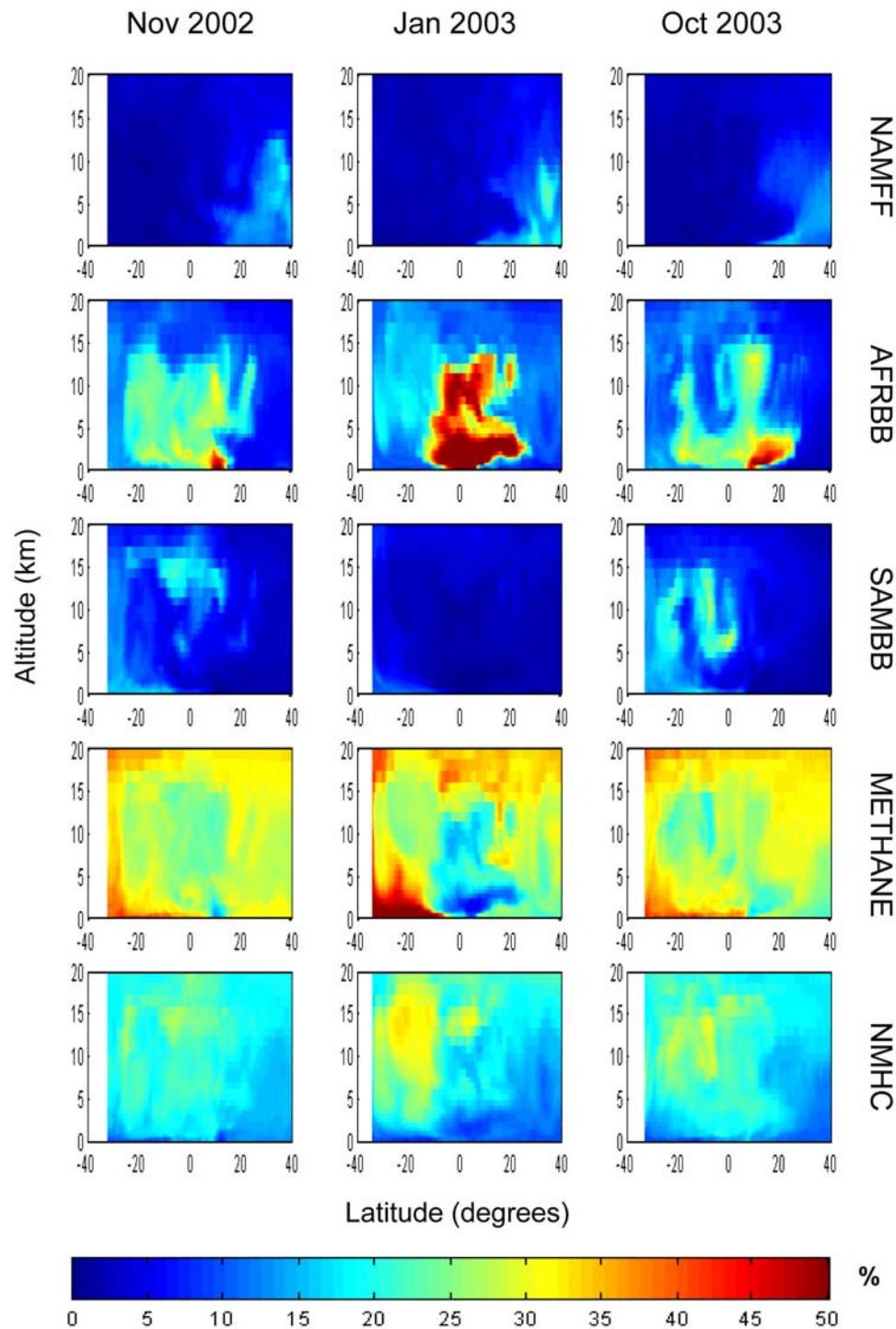


Figure 8. Contributions of each regional tracer field to the CO budget for the three cruises calculated from MATCH-MPIC (in percent). The CO tracer fields are: North American Fossil Fuel (NAMFF), South American Fossil Fuel (SAMFF), and African Biomass Burning (AFRBB). There are also tracer fields of CO from methane oxidation (METHANE) and from NMHC oxidation (NMHC).

[33] The issue of choosing an a priori profile is significant for studying combined measurements from different groups and might give rise to problems during comparisons. A study by *Yurganov et al.* [2004] involves several FTIR measurements of CO total columns from different

locations in the Northern Hemisphere. A standard CO a priori profile has not been established among the groups; however, through this study we have shown that the a priori profile could have different values with very small effect on the retrieved column. Moreover, this study

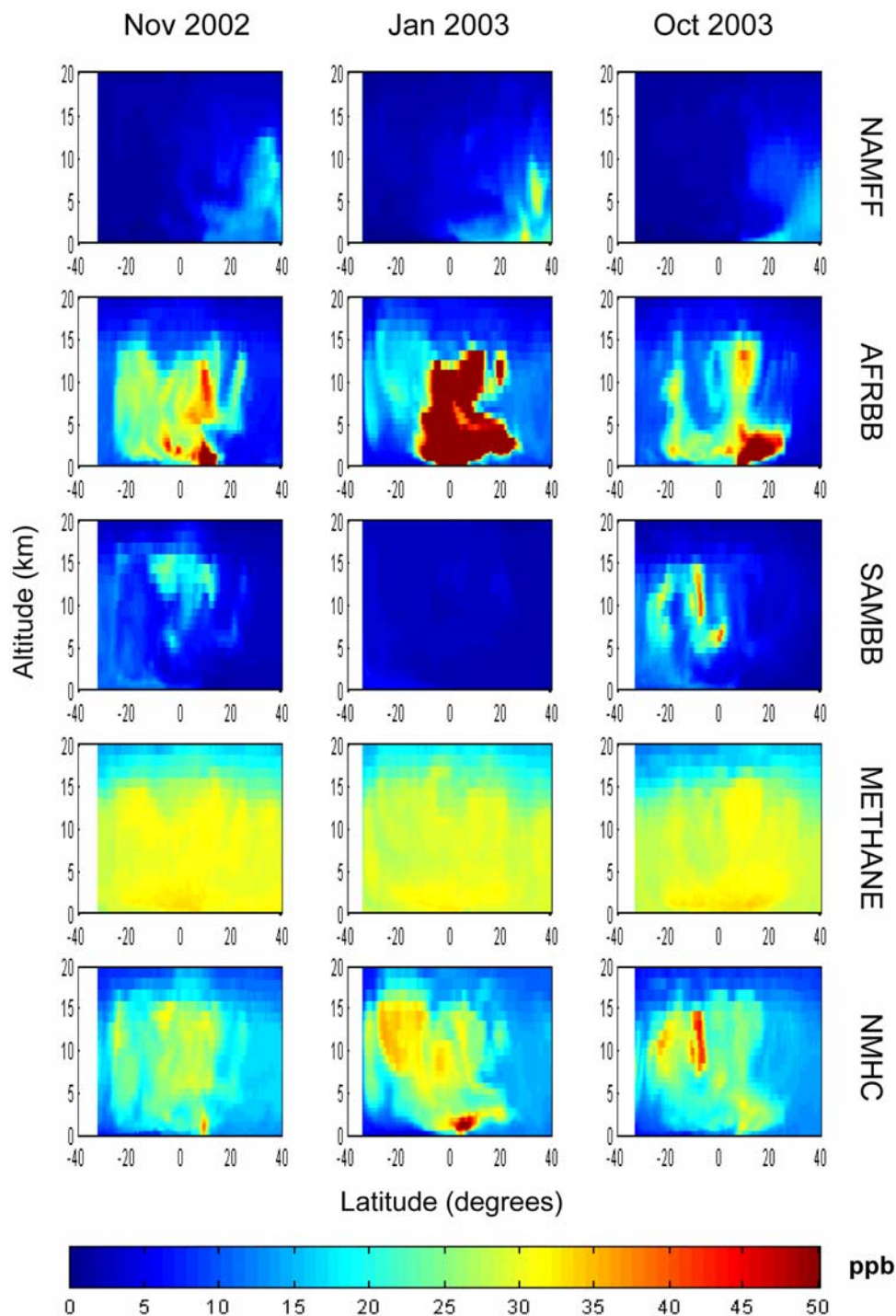


Figure 9. Absolute contributions of each regional tracer field to the CO budget for the three cruises calculated from MATCH-MPIC (in ppb). The CO tracer fields are the same as in Figure 8.

provides complementary information to the total column observations of *Yurganov et al.* [2004] owing to the altitude information that we presented.

[34] In situ measurements are helpful in verifying the surface measurements of the FTIR. Both have been shown to agree well. However, in situ measurements will not be able to represent the whole troposphere owing to the fact that CO shows a strong variability as a function of latitude.

For instance, high CO VMRs are often present on the surface and in the upper troposphere in the equatorial regions as discussed by *Notholt et al.* [2003]. In the Northern Hemisphere, high values of CO VMRs are typical at lower altitudes. In the Southern Hemisphere, high CO VMRs are often only found in the upper troposphere.

[35] A recurring CO enhancement in the upper troposphere (at 10–15 km) in the Southern Atlantic has been

detected with the FTIR spectrometer in five ship cruises spanning a period of 8 years. However, the measurements are limited to one period (during and close to the Southern Hemisphere summer). Backward trajectories calculated for the cruise in January 2003 suggest different sources that account for the CO enhancements at different latitudes. In the equatorial regions down to about 25°S, air parcels mostly originate from the African continent. The scenario is different for regions south of 25°S; air parcels found at about 8 km above the cruise track could have originated from South America, as the trajectories suggest. Convective transport of polluted air from the continents from low to high altitude most likely explains the high CO enhancements in the upper troposphere (10–15 km). Recycling of air in the Atlantic coming from Africa was also observed from the trajectories. This may lead to persistence of pollutants in the southeastern tropical Atlantic as observed by previous studies of Talbot *et al.* [1996] and Garstang *et al.* [1996]. Backward trajectories suggest that some air parcels appear to be carried along for days in vertical circular flow patterns near the coast of the southern African continent. These flow patterns also vary with season because they were not observed in the other cruises.

[36] Measurements from the MOPITT instrument complement the measurements of the FTIR. There is a very good agreement between the FTIR and MOPITT data in the lower troposphere of the Northern Hemisphere. However, some features of CO enhancements (e.g., a second maximum) in the upper troposphere seen in the FTIR data is difficult to detect in the MOPITT data owing to the coarse resolution of MOPITT. Retrieval simulation wherein the averaging kernels are considered leads to a reasonable agreement between MATCH, MOPITT, and the FTIR.

[37] The detected enhancements in the upper troposphere of the Southern Hemisphere by the FTIR agree with results from MATCH-MPIC. It is also important to note that the lower troposphere in the Southern Hemisphere is relatively clean as seen from both data sets; therefore in situ surface and total column measurements alone would not be sufficient to detect the enhancements in this region.

[38] The calculation of the contribution of the major regional tracers shows that methane oxidation provides a large background source of CO while biomass burning and other sources account largely for the variability in CO. Biomass burning emissions from the African continent provide the most dominant source in the equatorial regions. In the 10–15 km region south of 20°S, oxidation of non-methane hydrocarbons seems to contribute more to the CO enhancements than methane oxidation and biomass burning, especially during the cruise in January 2003. South American emissions from biomass burning have a significant contribution in the Southern Hemisphere except for the case during the January 2003 cruise, where air parcels in this region appear to be carried along in circular flow patterns. At the same time, CO from oxidation of NMHCs during the cruise in January 2003 are the highest compared to the two other cruises. This highlights the importance of the transport of pollution on CO concentrations.

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