Ethane, ethyne and carbon monoxide concentrations in the upper troposphere and lower stratosphere from ACE and GEOS-Chem: a comparison study

G. González Abad¹, N. D. C. Allen¹, P. F. Bernath¹, C. D. Boone², S. D. McLeod², G. L. Manney³,⁴ G. C. Toon³, C. Carouge⁵, Y. Wang⁶, S. Wu⁷, M. P. Barkley⁸,⁹, P. I. Palmer⁹, Y. Xiao¹⁰, and T. M. Fu¹¹

¹Department of Chemistry, University of York, York, UK
²Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada
³NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA
⁴Department of Physics, New Mexico Institute of Mining and Technology, Socorro, New Mexico, USA
⁵Department of Earth and Planetary Sciences and Division of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA
Department of Environmental Science and Engineering, Tsinghua University, Beijing, China
Dept. of Geological and Mining Engineering and Sciences & Dept. of Civil and Environmental Engineering, Michigan Technological University, Houghton MI, USA
EOS Group, College of Science and Engineering, University of Leicester, UK
School of GeoSciences, University of Edinburgh, UK
Atmospheric and Environmental Research, Inc., Lexington, MA, USA
Department of Atmospheric and Oceanic Science, School of Physics, Peking University, China

Received: 26 November 2010 – Accepted: 12 April 2011 – Published: 28 April 2011

Correspondence to: G. González Abad (gga500@york.ac.uk)

Published by Copernicus Publications on behalf of the European Geosciences Union.
Abstract

Near global upper tropospheric concentrations of carbon monoxide (CO), ethane (C$_2$H$_6$) and ethyne (C$_2$H$_2$) from ACE (Atmospheric Chemistry Experiment) Fourier transform spectrometer on board the Canadian satellite SCISAT-1 are presented and compared with the output from the Chemical Transport Model (CTM) GEOS-Chem. The retrievals of ethane and ethyne from ACE have been improved for this paper by using new sets of microwindows compared with those for previous versions of ACE data. With the improved ethyne retrieval we have been able to produce a near global upper tropospheric distribution of C$_2$H$_2$ from space. Carbon monoxide, ethane and ethyne concentrations retrieved using ACE spectra show the expected seasonality linked to variations in the anthropogenic emissions and destruction rates as well as seasonal biomass burning activity. The GEOS-Chem model was run using the dicarbonyl chemistry suite, an extended chemical mechanism in which ethyne is treated explicitly. Seasonal cycles observed from satellite data are well reproduced by the model output, however the simulated CO concentrations are found to be systematically biased low over the Northern Hemisphere. An average negative global mean bias of 12% and 7% of the model relative to the satellite observations has been found for CO and C$_2$H$_6$ respectively and a positive global mean bias of 1% has been found for C$_2$H$_2$. ACE data are compared for validation purposes with MkIV spectrometer data and Global Tropospheric Experiment (GTE) TRACE-A campaign data showing good agreement with all of them.

1 Introduction

The Volatile Organic Compounds (VOCs) ethane (C$_2$H$_6$) and ethyne (C$_2$H$_2$) are two of the most important tropospheric organic trace gases. Ethane is the second most abundant hydrocarbon in the atmosphere and has a lifetime of approximately two months (Rudolph, 1995) whereas ethyne has a shorter lifetime estimated to be between two
and four weeks (Logan et al., 1981). The main sink for non methane hydrocarbons (NMHC) in the free troposphere are reactions with hydroxyl radical (OH). Ethane has a significant impact on air quality as it is a strong source of PAN (peroxyacetyl nitrate), a reservoir for nitrogen dioxide. PAN has a major effect on tropospheric ozone, which is a strong greenhouse gas and also a toxic air pollutant (Rudolph, 1995). The main sources of ethane include biomass burning emissions, natural gas loss and biofuel consumption (Rudolph, 1995; Xiao et al., 2008). Ethyne’s main sources include natural gas, biofuel combustion products and biomass burning emissions (Gupta et al., 1998; Logan et al., 1981; Rudolph, 1995; Xiao et al., 2007; Zhao et al., 2002). Ethyne may act as a precursor of Secondary Organic Aerosols (SOA) through the formation of glyoxal, a by-product from its oxidation by OH (Volkamer et al., 2009).

Carbon monoxide (CO) is a key gas tracer in the troposphere. Sources in the troposphere include oxidation of methane and other hydrocarbons, biomass burning, and anthropogenic emissions. Reaction with the hydroxyl radical is the main sink of CO. Carbon monoxide’s lifetime in the troposphere is about two months. Its reaction with OH has an impact on the tropospheric chemistry of ozone and other important greenhouse gases such as methane (Logan et al., 1981; Turquety et al., 2008).

All together these species are three of the most important NMVOCs (Non Methane Volatile Organic Compounds) in the free troposphere. They play a key role in ozone chemistry through their reactions with OH, and therefore are important for air quality and human health.

Notholt et al., 1997; Rinsland et al., 2002 and Zhao et al., 2002 have all retrieved CO, C_2H_6 and C_2H_2 using ground based FTIRs (Fourier Transform Infrared Spectrometers) from solar and lunar measurements. Carbon monoxide concentrations from space have been obtained by many different instruments such as SCIAMACHY, MOPITT, and TES (Buchwitz et al., 2006; Deeter et al., 2003; Luo et al., 2007) that have a nadir viewing geometry and the ATMOS, MIPAS, SMR, ACE and MLS (Barret et al., 2006; Clerbaux et al., 2008; Funke et al., 2007; Rinsland et al., 2000; Pumphrey et al., 2007) instruments with a limb viewing geometry. Ethane concentrations have been
retrieved previously by MIPAS and ACE (Glatthor et al., 2009; Rinsland et al., 2005) from enhanced concentrations in biomass burning plumes. So far, ethyne has been retrieved extensively from space by ACE, for example as reported by Park et al., 2008 in the Asian monsoon anticyclone and by MIPAS (Glatthor et al., 2007; Parker et al., 2010) some more limited retrievals were made previously by ATMOS for both ethane and ethyne (Irion et al., 2002).

Concentrations of these molecules have been retrieved using data from the ACE Fourier Transform Spectrometer (FTS) and compared with aircraft data from the GTE (Global Tropospheric Experiment) TRACE-A (Transport and Atmospheric Chemistry near the Equator-Atlantic) field mission (Blake et al., 1996; Chatfield et al., 1998; Fishman et al., 1996) and from the MkIV balloon-borne FTIR flights near Fort Sumner (Toon, 1991). A detailed discussion of these comparisons will show that ACE retrieved concentrations are in good agreement with correlative measurements.

In addition, we compare the ACE measurements with carbon monoxide, ethane and ethyne concentrations simulated by the GEOS-Chem chemical transport model (Bey et al., 2001). In these comparisons seasonal variations and hemispheric asymmetries observed with ACE data are reproduced with good accuracy by the model output. The structure of the paper is as follows. Section two includes a description of the ACE-FTS and the retrieval process for carbon monoxide, ethane and ethyne as well as the data subset used in the paper. We will analyze the errors in the retrieval process for ethane and ethyne. The ACE CO product has been validated extensively so we simply cite the previous work (Clerbaux et al., 2008). In section three the retrieved ACE concentrations will be compared with TRACE-A and MkIV data. The fourth section is focused on the GEOS-Chem model in which the set up of the model used in this paper is explained and discussed. In section five the data from ACE and GEOS-Chem are analyzed, discussed and compared; the final section is a conclusion.
2 ACE-FTS measurements and data

The ACE-FTS (Atmospheric Chemistry Experiment – Fourier Transform Spectrometer) is the main instrument on board the Canadian satellite SCISAT-1 launched by NASA in August 2003 (see http://www.ac.uwaterloo.ca/). Working primarily in solar occultation with a resolution of 0.02 cm$^{-1}$ in the 2.2 to 13.3 µm (750–4400 cm$^{-1}$) spectral range, the instrument provides altitude profile information for temperature, pressure and volume mixing ratios (VMRs) for numerous molecules of atmospheric interest between 85° N and 85° S (Bernath et al., 2005).

The CO retrievals reported in this paper are the standard version 2.2 set of the ACE–FTS retrievals (Boone et al., 2005) using the same linelist that was used by Clerbaux et al., 2008. We use the first overtone of CO when the fundamental lines become saturated allowing us to retrieve CO concentrations down to 5 km.

The C$_2$H$_6$ and C$_2$H$_2$ are a research version based on the same global-fit coupled with a Lenvenberg-Marquardt non linear least-square algorithm used in the version 2.2 of the ACE–FTS data (Boone et al., 2005). Pressure and temperatures used in the retrieval are from version 2.2. C$_2$H$_6$ retrievals use the $P$ $Q$$_3$ branch in the $\nu$$_7$ band located around 3 µm. A 2 cm$^{-1}$ microwindow centred at 2976.5 cm$^{-1}$ has been used. The retrieval altitude range is between 5 and 20 km. Interferers in this microwindow are H$_2$O, H$^{18}$OH, O$_3$, CH$_4$ and CH$_3$D with VMR profiles retrieved for each of these isotopologues. Figure 1 shows, as an example, synthetic spectra calculated with the forward model, the observed spectra and the residuals with and without ethane included in the forward model. The reduction of the residuals when ethane is included in the forward model shows the viability of the retrieval in this microwindow.

C$_2$H$_2$ retrievals use the $\nu$$_3$ and $\nu$$_2 + \nu$$_4 + \nu$$_5$ bands in the 3 µm region. A complete list of the fourteen microwindows used for its retrieval is reported in Table 1. As stated above this selection of microwindows improves the retrieval in comparison with previous versions of the ACE ethyne product. The new ACE version 3.0 ethyne product makes use of these microwindows. The retrieval altitude range extends between 5
and 15 km. Interferers for the retrieval of ethyne are H$_2$O, H$^{18}$OH, H$^{17}$OH, N$_2$O, CO$_2$, C$^{13}$OO, C$^{18}$OO, O$_3$ and HCN. The spectroscopic data used for the retrieval of all three molecules is in the HITRAN 2004 database (Rothman et al., 2005). The errors associated with the CO retrievals have been reported previously to be smaller than 2% (Clerbaux et al., 2005). The errors for C$_2$H$_6$ and C$_2$H$_2$ in a typical VMR profile are dominated by statistical errors. For ethane the errors are usually between 30% in tropical regions and improve to 20% towards the poles. Ethyne errors are less than 25% near the North Pole and less than 30% near the South Pole increasing towards the equator and with altitude. A more detailed analysis of the retrieval error for these two molecules is to follow in Sect. 2.1.

About 11,000 occultations recorded between January 2004 and February 2007 have been used in this study. We have used the DMPs (Derived Meteorological Products) (Manney et al., 2007) to filter out data within or at the edge of the polar vortex (Nassar et al., 2005). 8200 occultations remain for the study after applying the polar vortex filter. The inclination of the SCISAT-1 orbit (74° to the equator) (Bernath, 2006) provides a large number of occultations at high latitudes therefore we decided to discard the occultations perturbed by the descent of the cold, isolated air in the polar vortex. The locations of the occultations used are plotted in Fig. 2. Note that there is an uneven distribution of data, with many occultations available near the poles and just a few hundred in tropical regions.

2.1 C$_2$H$_6$ and C$_2$H$_2$ retrieval error analysis

Error analysis of VMRs retrieved by ACE-FTS has to consider two components: the statistical or random error and the systematic error. The statistical part of the error corresponds to the error provided by the fitting algorithm (Boone et al., 2005). The 1σ error for the state variable $x_j$ in a Levenberg-Marquardt fitting algorithm is:

$$\sigma_m(x_j) = \sqrt{(K^T S_y^{-1} K)^{-1}}$$  \hspace{1cm} (1)
where $\mathbf{K}$ is the Jacobian of the forward model and $\mathbf{S}_y$ is the covariance matrix of the measurements, assumed to be diagonal. This error, often called measurement noise, is plotted in Figs. 3 and 4 in orange for the average of 25 representative occultations selected for the error analysis.

Analysis of systematic errors needs to be considered to quantify the effect of the variability of important parameters in the retrieval algorithm. Systematic errors are caused by the uncertainty of relevant parameters ($b_j$) in the retrieval process. The effects of these uncertainties in the retrieved VMRs ($\Delta x_j$) have been quantified using Eq. (2):

$$\Delta x_j = |x(b_j) - x(b_j + \Delta b_j)|$$

where $x(b_j)$ is the standard retrieved VMR and $x(b_j + \Delta b_j)$ is the retrieved VMR after perturbation of the relevant parameter ($b_j$) in the retrieval process. The relevant parameters have been perturbed by $1\sigma$ of its assumed uncertainty, one at a time while keeping the others unchanged. The relevant parameters considered and their $1\sigma$ uncertainties are: temperature ($2\,\text{K}$), tangent height ($150\,\text{m}$), instrumental line shape ($5\%$ of field of view) (Dufour et al., 2009), mixing ratio uncertainties of the main interferers, $10\%$ for $\text{H}_2\text{O}$, $1\%$ for $\text{CO}_2$, $5\%$ for $\text{O}_3$ and $25\%$ for $\text{N}_2\text{O}$ (McHugh et al., 2005) and spectroscopic data uncertainties assumed to be $5\%$ for $\text{C}_2\text{H}_2$ (Rothman et al., 2005) and $10\%$ for $\text{C}_2\text{H}_6$. A restricted subset of 25 occultations covering all latitudes and seasons has been selected for this analysis.

Figures 3 and 4 summarize the impact of the different parameters on the quality of the retrieval. In general the perturbation of these parameters has a relatively small impact on the retrieved VMRs of ethane and ethyne with changes less than $5\%$ for all of them. Only the perturbation of the tangent height causes a change in the retrieved VMRs which is big enough to change the effective error, at altitudes above $9\,\text{km}$ in the case of $\text{C}_2\text{H}_6$ and over the full range of altitudes for $\text{C}_2\text{H}_2$. The effective error for $\text{C}_2\text{H}_6$ is between $20\%$ and $30\%$ over the $6\,\text{km}$ to $12\,\text{km}$ altitude range increasing to $40\%$ for altitudes between $12\,\text{km}$ and $14\,\text{km}$. At higher altitudes the random error
increases sharply due to the low atmospheric concentrations of ethane near the limits of the retrieval. For $\text{C}_2\text{H}_2$ the effective error is slightly larger than for $\text{C}_2\text{H}_6$. Ethyne errors at altitudes below 10 km are less than 30% and increase to values between 40% and 50% for the altitude range between 10 km and 14 km. This error analysis shows that the VMRs errors are mainly dominated by the random component of the error with a small systematic error component caused mainly by uncertainties in the knowledge of the tangent height. Errors for single profiles are generally less than 30% in the troposphere for both molecules.

3 Balloon and aircraft comparisons

We have compared our retrieved concentrations with those obtained by a similar instrument, the MkIV FTS, and with concentrations obtained with in situ instruments deployed on the DC-8 aircraft in the TRACE-A field campaign. The MkIV-FTS records solar occultation spectra from a high altitude balloon in the $650–5640\,\text{cm}^{-1}$ spectral range with a spectral resolution of $0.01\,\text{cm}^{-1}$ (Toon, 1991). MkIV data obtained in five flights carried out from Ft. Sumner, New Mexico ($34.4^\circ\text{N}, 104.2^\circ\text{W}$) during September 2003, 2004, 2005 and 2007 have been compared with the ACE–FTS retrievals. These flights took place during the autumn turn-around period when the stratospheric winds are light enough to permit long duration (15–30 h) flights. The VMR retrievals extend from the cloud tops up to the float altitude (typically 38 km) with 2–3 km vertical resolution. The MkIV retrieval used the JPL retrieval code GFIT (Sen et al., 1998). Figure 5 shows the result of this comparison between MkIV–FTS and ACE–FTS retrievals. Only ACE occultations within the same time period of the year (September, October, November) and within latitudes and longitudes similar to Ft. Sumner have been used to carry out these comparisons. Very few ACE occultations are near New Mexico and for this reason an average of occultations from the continental USA ($30^\circ\text{N}–54^\circ\text{N}$ and $85^\circ\text{W}–115^\circ\text{W}$) for the fall season has been used. This comparison shows most of the MkIV-FTS profiles are within one standard deviation of the ACE–FTS average profile for all three molecules.
The TRACE-A field campaign aircraft flights took place between 21 September and 24 October 1992. The flights were located around 12° S and between 40° E and 70° W (Blake et al., 1996; Fishman et al., 1996) and only ACE–FTS occultations situated near this location and occurring in the same season have been used to compare with the aircraft data. Figure 6 shows carbon monoxide, ethane and ethyne concentrations from the TRACE-A measurements and the ACE–FTS. Values from satellite and aircraft are in good agreement with aircraft concentrations falling within one standard deviation of the average satellite values.

The MkIV and TRACE-A correlative comparisons show that the concentrations retrieved using ACE recorded spectra are generally reliable in the upper troposphere and lower stratosphere region.

4 GEOS-Chem

GEOS-Chem version v8-02-03 (http://acmg.seas.harvard.edu/geos/) is a global 3-D chemical transport model able to simulate trace gases and aerosol distributions in the troposphere (Bey et al., 2001). The model is driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modelling and Assimilation Office (GMAO). We have used here the GMAO GEOS-5 operational meteorology data. GEOS-5 meteorological fields have a temporal resolution of 6 h (3 h for surface variables), a horizontal resolution of 0.5° latitude by 0.667° longitude and a vertical resolution of 72 eta hybrid levels extending from the surface up to 0.01 hPa. The resolution of these meteorological data is degraded for model input to a horizontal resolution of 4° latitude by 5° longitude and with vertical resolution reduced to 47 eta levels by lumping levels above ~80 hPa.

For this paper we need the model predictions for ethyne, ethane and carbon monoxide with the appropriate spatial and temporal resolution. Twenty four hour average concentrations have been considered in this paper given the lifetimes of the molecules. Since the satellite data have a very uneven geographical and temporal distribution only...
model data coincident in time, average of a given day, and space with each ACE oc-
cultation has been used. The GEOS-Chem data have been interpolated to the satellite
altitude grid of 1 km resolution.

The GEOS-Chem chemical mechanism used in this study is the standard NOx-Ox-
Hydrocarbon-Aerosol simulation (Horowitz et al., 1998; Martin et al., 2003) with the
dicarbonyls chemistry extension (Fu et al., 2008) in order to include explicit ethyne
chemistry and updated VOCs including aromatics and dicarbonyls. The main sink
for ethane is oxidation with OH. Another minor ethane sink included in the model is
oxidation by NO$_3$. Ethyne oxidation with OH is the only sink included in the model for
this species.

Carbon monoxide and ethane emissions include anthropogenic emissions based on
the Global Emission Inventory Activity (GEIA) (Wang et al., 1998) for ethane and on
the Emission Database for Global Atmospheric Research (EDGAR) for carbon mono-
oxide. Scaling factors have been used to scale the emissions to present-day values.
Updates with regional inventories are used where available: The European Monitoring
and Evaluation Programme (EMEP) for Europe (Auvray and Bey, 2005) designed for
the year 2005, the Big Bend Regional Aerosol and Visibility Observational (BRAVO)
Study Emissions Inventory for Mexico (Kuhns et al., 2005) designed for the year 1999,
the Streets inventory for South East Asia (Zhang et al., 2009) with base years 2000,
2004 and 2006, the Criteria Air Contaminant inventory (CAC) over Canada with 2002
and 2005 base years and the Environmental Protection Agency/National Emission In-
ventory (EPA/NEI) (Hudman et al., 2008) for USA with base years 1999 and 2004.
Biofuel emissions of CO and C$_2$H$_6$ are included in the model (Yevich and Logan, 2003)
as well as biomass burning emissions from the monthly data of the Global Fire Emis-
sion Database version 2 (GFEDv2) (Giglio et al., 2006). For C$_2$H$_2$ biomass burning
emissions, anthropogenic emissions and biofuel emissions the model uses the ap-
proach followed by Xiao et al., 2007 based on emission factors of ethyne relative to
CO. Using this set up for the emissions the following total global budgets are produced
by GEOS-Chem. For carbon monoxide for the year 2005 the total emission budget
is 1178 Tg with 340 Tg contribution of anthropogenic origin, 173 Tg from biofuel emissions, 610 Tg due to biomass burning and 53 Tg from monoterpene oxidation. The ethane budget for 2005 is 12 Tg C with 7.5 Tg having an anthropogenic origin, 2 Tg C from biofuel and 2.5 Tg from biomass burning. Finally the ethyne budget is 5 Tg C with 1.25 Tg C having an anthropogenic origin, 2.75 Tg C produced due to the usage of biofuel and 1.25 Tg C coming from biomass burning. Figs. S1, S2 and S3 (Supplement) show a global map with the total emissions for each molecule.

We have run the model between February 2004 and February 2007, the period of time for which ACE–FTS data was available for this study. The model was spun-up with a 3 month run from November 2003 before restarting it in February 2004.

5 ACE – FTS and GEOS-chem data analysis and comparison

Figure 7 shows ACE data available at 7.5 km altitude for all three molecules during the period between February 2004 and February 2007. The hotspots are due to biomass burning plumes and high anthropogenic emissions. Concentrations as high as 250 ppb for CO, 2.50 ppb for C$_2$H$_6$ and 0.5 ppb for C$_2$H$_2$ are observed at 6.5 km, which is usually the lowest altitude retrieved. However, a number of occultations have retrievals at 5.5 km. The average profiles obtained for the entire period of study are available in supplementary Tables S1, S2 and S3 (CO, C$_2$H$_6$ and C$_2$H$_2$ respectively) and altitude-latitude cross sections are shown in Fig. S4 (Supplement). The hemispherical asymmetry of concentrations in the middle and upper troposphere with higher values in the Northern Hemisphere is observed in this figure for all three molecules.

Only GEOS-Chem data that has been sampled to the same times and locations as the ACE–FTS occultations has been used to make a meaningful comparison between the model output and the satellite retrievals. The horizontal resolution used for the model is 4° latitude by 5° longitude; the grid is roughly 330 km by 640 km. This allows us to compare it with the 500 km horizontal resolution ACE data (Sica et al., 2008). ACE data above the tropopause have been discarded for the comparison between
the model and the satellite using the information available in the DMPs (Manney et al., 2007). After the collocation the data have been averaged in 10° latitude bins and into temporal seasons for the period February 2004 to February 2007. December-January-February 2004–2005 (DJF0405), March-April-May 2005 (MAM05), June-July-August 2005 (JJA05) and September-October-November 2005 (SON05) are selected to carry out a more detailed study due to the substantial amount of ACE data available during 2005.

Figure 8 shows the altitude-latitude cross sections for CO. We clearly see the hemispherical asymmetry and the seasonal variation of CO concentrations in the upper and middle troposphere linked mainly to anthropogenic emissions and biomass burning seasons over South America, Africa and boreal regions. High concentrations of CO in the Southern Hemisphere (SON season) are linked to biomass burning episodes. This is the strongest feature for CO in Southern latitudes and the model underestimates it, simulating concentrations around 17% lower that the satellite retrieved concentrations. In the Northern Hemisphere the biomass emissions do not have such a strong impact on tropospheric CO concentrations and anthropogenic emissions are dominant. The seasonal variation is therefore not as strong as in the Southern Hemisphere and this can be observed clearly in the ACE data (Clerbaux et al., 2008). Although GEOS-Chem is able to capture this feature, it underestimates CO concentrations in the Northern Hemisphere (Kopacz et al., 2010) by a 15%. The hemispheric asymmetry is also well represented by the model.

Ethane altitude-latitude cross sections are presented in Fig. 9. Once again the seasonal variation and the hemispheric asymmetry are well simulated by the model. Human activity is the main reason for the hemispheric asymmetry and biomass burning emissions contribute strongly to the seasonal variation in both Hemispheres. The first results obtained for ethane from the model showed an unrealistic high positive bias in the Southern Hemisphere, which led us to fix a small bug in the C$_2$H$_6$ emissions over Africa. Emission factors were unrealistically large over Namibia leading to anomalously high emissions. It was estimated that the emissions were two orders of magnitude
bigger than what they should be. Therefore to give the ethane model output a more reasonable value, emissions were reduced by 99%. After this modification the model does well in the Southern Hemisphere where the effects of the bug in the emissions over Africa were dramatic. A more detailed comparison between the model and the ACE data is given below.

Figure 10 shows a near global middle to upper tropospheric ethyne concentration distribution observed from space. Due to ethyne's low concentrations the signature associated with it is sometimes weak in the ACE spectra, and fewer measurements are available for it than for CO and C₂H₆. These altitude-latitude cross sections of C₂H₂ show the expected features: hemispheric asymmetry with higher ethyne concentrations in the Northern Hemisphere, obviously linked to human activities and the use of biofuels, and the superimposed seasonal variation linked to emissions from fires and biomass burning episodes. High pollution episodes were also observed from the satellite but it is difficult to separate them from biomass burning plumes. Elevated upper troposphere concentrations from biomass burning emissions are easier to observe in the Southern Hemisphere where background concentrations are lower.

For a more detailed analysis of the model performance the data has been split into four geographical regions of particular interest (shown in Fig. 11). These regions are: North America (formed by two rectangular areas 170°W, 40°W, 80°N, 50°N and 130°W, 40°W, 20°N, 50°N), Eurasia (20°W, 160°E, 80°N, 50°N), Southern Hemisphere (180°W, 180°E, 0°S, 40°S) and Antarctica (180°W, 180°E, 50°S, 90°S). In Figs. 12, 13 and 14 time series of average ACE concentrations at 8.5 km (representative of the upper troposphere) have been plotted alongside the GEOS-Chem concentrations sampled in the same way as the satellite data. Figure 12 presents the results for CO, Fig. 13 for C₂H₆ and Fig. 14 for C₂H₂ respectively. These three plots illustrate the seasonal variation for all three molecules as well as the hemispheric asymmetry in their concentrations fairly well. For these selected regions the mean bias (bias), the mean absolute bias (|bias|) and the correlation coefficient between satellite and model data have been calculated as:
bias = \frac{\text{meanVMRmodel} - \text{meanVMRsatellite}}{\text{meanVMRsatellite}} \times 100 \quad (3)

|\text{bias}| = \frac{1}{n} \sum_i |\text{VMRmodel}_i - \text{VMRsatellite}_i| \times 100 \quad (4)

This statistical analysis is summarized in Table 2 for CO, Table 3 for C$_2$H$_6$ and Table 4 for C$_2$H$_2$. The CO mean bias between ACE and GEOS-Chem is less than 30 percent for all the regions and seasons. Only North America and Eurasia JJA05 and Antarctica DJF0405 have greater mean biases. In general the model underestimates the CO concentration in the Northern Hemisphere while overestimating it in the Southern Hemisphere and the mean bias is always negative over North America and Eurasia but is always less than 40%. For the case of the C$_2$H$_6$ the mean bias is smaller than 35% in all regions for all seasons and only in the Antarctic region does the model significantly overestimate the concentrations. As discussed above, the C$_2$H$_6$ emissions were modified in the model after finding a problem in the Southern regions of Africa; a more detailed study is needed to assess and improve the model performance in the polar latitudes of the Southern Hemisphere. Finally the analysis of C$_2$H$_2$ shows a high mean bias in North America for the DJF0405 season and in Antarctica for the MAM05 and JJA05 seasons. In general the seasonal variation of ethyne at 8.5 km is small according to the ACE data, while the model predicts a greater seasonal variation, linked to the emissions especially in the Northern Hemisphere.

6 Conclusions

The near global tropospheric distributions of CO, C$_2$H$_6$ and C$_2$H$_2$ have been presented using data from the ACE satellite. Approximately 8200 extravortex profiles were used in this study covering the period between February 2004 and September 2007. It has been possible to observe seasonal variations, and to relate these variations with the main sources of these trace gases: biomass burning and anthropogenic emissions.
Values up to 250 ppb have been observed for individual profiles of CO up to 2.5 ppb for ethane and up to 0.5 ppb for ethyne that are likely associated with biomass burning plumes or strong pollution events. The GEOS-Chem model has been run with the dicarbonyls extended chemistry and has been compared with the ACE-FTS observations. Agreement between the model and the satellite data is good having mean bias values smaller than 40% for all three molecules in all regions and seasons at 8.5 km in altitude. The mean bias of the model relative to the observations for all data at 8.5 km is −12% for CO, −7% for C₂H₆ and 1% for C₂H₂. The hemispheric asymmetry and seasonal variation observed for all three molecule concentrations has been linked to changes in anthropogenic and biomass burning emissions. The ACE data have been compared with similar measurements made by the balloon-borne MkIV-FTS and with aircraft data obtained in the GTE TRACE-A campaign showing that the ACE retrievals are reliable in the upper troposphere lower stratosphere region.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/13099/2011/acpd-11-13099-2011-supplement.pdf.

Acknowledgements. The ACE mission is funded primarily by the Canadian Space Agency. Funding was also provided by the UK Natural Environment Research Council (NERC), in part through the National Centre for Earth Observation (NCEO). Gonzalo González Abad thanks the Wild Fund for support. Work at the Jet Propulsion Laboratory, California Institute of Technology, was done under contract with the National Aeronautics and Space Administration.
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Rothman, L. S., Jacquemart, D., Barbe, A., Chrus Benner, D., Birk, M., Brown, L. R.,, Carleer,


Table 1. Microwindows used for the retrieval of $\text{C}_2\text{H}_2$ in this paper.

<table>
<thead>
<tr>
<th>Centre wavenumber (cm$^{-1}$)</th>
<th>Microwindow width (cm$^{-1}$)</th>
<th>Lower altitude (km)</th>
<th>Upper altitude (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3268.30</td>
<td>0.80</td>
<td>8–3$</td>
<td>\sin(\text{latitude})</td>
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<td>3270.20</td>
<td>1.00</td>
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</tr>
<tr>
<td>3286.00</td>
<td>1.60</td>
<td>12–4$</td>
<td>\sin(\text{latitude})</td>
</tr>
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</tr>
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<td>3335.57</td>
<td>0.45</td>
<td>9–3$</td>
<td>\sin(\text{latitude})</td>
</tr>
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Table 2. Statistical comparison between ACE retrieved CO concentrations and GEOS-Chem output at 8.5 km altitude; VMRs are expressed in ppb: \( n \) is the number of data taken into account, bias is the Mean Bias as defined by Eq. (1), |bias| is the Mean Absolute Bias as defined by Eq. (2) and \( r \) is the correlation coefficient.

| Region           | Period | \( n \) | ACE-FTS VMR (ppb) | GEOS-Chem VMR (ppb) | Bias | |bias| | \( r \) |
|------------------|--------|--------|------------------|-------------------|------|---|------|------|
| Global           | Full   | 2084   | 94               | 82                | -12  | 24 | 0.46 |
| North America*   | DJF0405| 6      | 122              | 102               | -16  | 19 | 0.50 |
|                  | MAM05  | 20     | 132              | 95                | -28  | 28 | 0.40 |
|                  | JJA05  | 24     | 119              | 71                | -40  | 41 | 0.08 |
|                  | SON05  | 26     | 101              | 79                | -21  | 30 | 0.18 |
| Eurasia*         | DJF0405| 19     | 111              | 96                | -13  | 17 | 0.77 |
|                  | MAM05  | 19     | 124              | 94                | -24  | 25 | 0.22 |
|                  | JJA05  | 56     | 111              | 71                | -35  | 36 | 0.49 |
|                  | SON05  | 43     | 106              | 77                | -28  | 30 | 0.45 |
| Southern Hemisphere* | DJF0405| 45     | 74               | 81                | -12  | 23 | 0.10 |
|                  | MAM05  | 38     | 75               | 82                | 9    | 15 | 0.67 |
|                  | JJA05  | 58     | 88               | 77                | -17  | 21 | 0.52 |
|                  | SON05  | 81     | 116              | 95                | -17  | 21 | 0.52 |
| Antarctic*       | DJF0405| 12     | 49               | 66                | 36   | 41 | 0.39 |
|                  | MAM05  | 39     | 56               | 71                | 27   | 28 | 0.48 |
|                  | JJA05  | 33     | 61               | 77                | 25   | 26 | 0.10 |
|                  | SON05  | 29     | 77               | 92                | 18   | 24 | 0.11 |

* North America (170° W, 40° W, 80° N, 50° N), Eurasia (20° W, 160° E, 80° N, 50° N), Southern Hemisphere (180° W, 180° E, 0° S, 40° S) and Antarctica (180° W, 180° E, 50° S, 90° S).
Table 3. Statistical comparison between ACE retrieved C$_2$H$_6$ concentrations and GEOS-Chem output at 8.5 km altitude; VMRs are expressed in ppb: \( n \) is the number of data taken into account, bias is the Mean Bias as defined by Eq. (1), \(|\text{bias}|\) is the Mean Absolute Bias as defined by Eq. (2) and \( r \) is the correlation coefficient.

| Region             | Period | \( n \) | ACE-FTS VMR (ppb) | GEOS-Chem VMR (ppb) | Bias \( \% \) | \(|\text{bias}|\) \% | \( r \) |
|--------------------|--------|---------|------------------|---------------------|--------------|----------------|-----|
| Global             | Full   | 1626    | 0.59             | 0.55                | -7           | 28             | 0.65|
| North America*     | DJF0405| 3       | 1.01             | 1.20                | 18           | 18             | 0.81|
|                    | MAM05  | 9       | 1.13             | 1.17                | 4            | 14             | 0.29|
|                    | JJA05  | 22      | 0.81             | 0.72                | -10          | 21             | 0.39|
|                    | SON05  | 22      | 0.76             | 0.73                | -5           | 25             | 0.23|
| Eurasia*           | DJF0405| 13      | 0.86             | 0.87                | 0.3          | 17             | 0.43|
|                    | MAM05  | 10      | 0.97             | 1.09                | 13           | 18             | 0.24|
|                    | JJA05  | 46      | 0.77             | 0.69                | -10          | 21             | 0.30|
|                    | SON05  | 35      | 0.78             | 0.68                | -13          | 22             | 0.51|
| Southern Hemisphere*| DJF0405| 31      | 0.36             | 0.39                | 8            | 30             | 0.47|
|                    | MAM05  | 27      | 0.40             | 0.44                | 10           | 28             | 0.72|
|                    | JJA05  | 53      | 0.38             | 0.42                | 10           | 30             | 0.15|
|                    | SON05  | 65      | 0.60             | 0.49                | -19          | 32             | 0.52|
| Antarctic*         | DJF0405| 2       | 0.21             | 0.29                | 33           | 33             | 1.00|
|                    | MAM05  | 22      | 0.31             | 0.32                | 2            | 36             | 0.19|
|                    | JJA05  | 25      | 0.29             | 0.38                | 31           | 40             | 0.10|
|                    | SON05  | 27      | 0.34             | 0.51                | 47           | 50             | 0.23|

* North America (170° W, 40° W, 80° N, 50° N), Eurasia (20° W, 160° E, 80° N, 50° N), Southern Hemisphere (180° W, 180° E, 0° S, 40° S) and Antarctica (180° W, 180° E, 50° S, 90° S).
Table 4. Statistical comparison between ACE retrieved C$_2$H$_2$ concentrations and GEOS-Chem output at 8.5 km altitude; VMRs are expressed in ppb: $n$ is the number of data taken into account, bias is the Mean Bias as defined by Eq. (1), |bias| is the Mean Absolute Bias as defined by Eq. (2) and $r$ is the correlation coefficient.

| Region               | Period  | $n$ | ACE-FTS VMR (ppb) | GEOS-Chem VMR (ppb) | Bias | |bias| | $r$ |
|----------------------|---------|-----|------------------|---------------------|------|--------|-------|-------|
| Global               | Full    | 1696| 0.071            | 0.072               | 1    | 49     | 0.51  |
| North America*       | DJF0405 | 2   | 0.109            | 0.303               | 179  | 179    | 1.00  |
|                      | MAM05   | 16  | 0.116            | 0.140               | 21   | 32     | 0.38  |
|                      | JJA05   | 22  | 0.089            | 0.056               | −38  | 42     | 0.02  |
|                      | SON05   | 25  | 0.100            | 0.111               | 12   | 47     | 0.02  |
| Eurasia*             | DJF0405 | 13  | 0.118            | 0.173               | 47   | 50     | 0.15  |
|                      | MAM05   | 14  | 0.134            | 0.146               | 8    | 17     | 0.74  |
|                      | JJA05   | 46  | 0.079            | 0.067               | −15  | 37     | 0.41  |
|                      | SON05   | 35  | 0.091            | 0.091               | 1    | 39     | 0.40  |
| Southern Hemisphere* | DJF0405 | 37  | 0.044            | 0.051               | 16   | 66     | 0.28  |
|                      | MAM05   | 30  | 0.044            | 0.053               | 21   | 55     | 0.35  |
|                      | JJA05   | 52  | 0.065            | 0.051               | −21  | 36     | 0.34  |
|                      | SON05   | 57  | 0.083            | 0.051               | −39  | 44     | 0.52  |
| Antarctic*           | DJF0405 | 10  | 0.016            | 0.027               | 66   | 73     | 0.46  |
|                      | MAM05   | 30  | 0.033            | 0.072               | 119  | 139    | 0.10  |
|                      | JJA05   | 32  | 0.043            | 0.092               | 115  | 115    | 0.03  |
|                      | SON05   | 29  | 0.042            | 0.056               | 34   | 45     | 0.71  |

* North America (170° W, 40° W, 80° N, 50° N), Eurasia (20° W, 160° E, 80° N, 50° N), Southern Hemisphere (180° W, 180° E, 0° S, 40° S) and Antarctica (180° W, 180° E, 50° S, 90° S).
Fig. 1. Calculated spectrum, observed spectrum and residuals for occultation ss11613 at 9.76 km. Top panel shows a calculated spectrum without the C$_2$H$_6$ contribution. In the residual plot we can observe the feature due to the absence of C$_2$H$_6$ in the forward model.
Fig. 2. ACE extravortex occultations between January 2004 and February 2007.
Fig. 3. Top panel: mean vmr profile of C$_2$H$_6$ (black) for the 25 occultations selected for the error budget calculations and the absolute value of the contribution of each component. Lower panel: relative contribution of each of the components considered in the error budget calculation. In purple in both panels is the effective total error.
Fig. 4. Top panel: mean vmr profile of C$_2$H$_2$ (black) for the 25 occultations selected for the error budget calculations and the absolute value of the contribution of each component. Lower panel: relative contribution of each of the components considered in the error budget calculation. In purple in both panels is the effective total error.
Fig. 5. Comparison of ACE-FTS average profile and MkIV-FTS profiles. Top left panel CO, top right panel C₂H₆ and lower panel C₂H₂.
Fig. 6. Comparison of ACE-FTS average profiles and GTE, TRACE-A aircraft field campaign concentrations of CO, top left panel, \( \text{C}_2\text{H}_6 \) top right panel and \( \text{C}_2\text{H}_2 \) lower panel.
Fig. 7. CO, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{2} concentrations at 7.5 km retrieved using ACE-FTS spectra during the period between February 2004 and February 2007. Top left panel CO, top right panel C\textsubscript{2}H\textsubscript{6} and bottom panel C\textsubscript{2}H\textsubscript{2}.
Fig. 8. CO altitude-latitude cross sections from ACE (left column), GEOS-Chem (central column) and difference between both data sets (right column). Top panel 2004–2007 time period, second panel December-January-February 2004/2005, third panel March-April-May 2005, fourth panel June-July-August 2005 and fifth panel September-October-November 2005.
Fig. 9. C$_2$H$_6$ altitude-latitude cross sections from ACE (left column), GEOS-Chem (central column) and difference between both data sets (right column). Top panel full study time period, second panel December-January-February 2004/2005, third panel March-April-May 2005, fourth panel June-July-August 2005 and fifth panel September-October-November 2005.
Fig. 10. $\text{C}_2\text{H}_2$ altitude-latitude cross sections from ACE (left column), GEOS-Chem (central column) and difference between both data sets (right column). Top panel full study time period, second panel December-January February 2004/2005, third panel March-April-May 2005, fourth panel June-July-August 2005 and fifth panel September-October-November 2005.
Fig. 11. Geographical regions selected for detailed comparison of ACE and GEOS-Chem data.
Fig. 12. Seasonal and hemispheric variations of CO volume mixing ratios observed (black) and simulated (red) averaged in different regions at 8.5 km.
Fig. 13. Seasonal and hemispheric variations of C$_2$H$_6$ volume mixing ratios observed (black) and simulated (red) averaged in different regions at 8.5 km.
Fig. 14. Seasonal and hemispheric variations of $\text{C}_2\text{H}_2$ volume mixing ratios observed (black) and simulated (red) averaged in different regions at 8.5 km.