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The influence of biogenic emissions on upper-tropospheric methanol as revealed from space

G. Dufour[1,*], **S. Szopa**[2], **D. A. Hauglustaine**[2], **C. D. Boone**[3], **C. P. Rinsland**[4], and **P. F. Bernath**[3,5]

[1]Laboratoire de Météorologie Dynamique/Institut Pierre Simon Laplace (LMD/IPSL), Palaiseau, France
[2]Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), CNRS-CEA-UVSQ Gif-sur-Yvette, France
[3]Department of Chemistry, University of Waterloo, Ontario, N2L 3G1, Canada
[4]NASA Langley Research Center, Hampton, VA, USA
[5]Deparment of Chemistry, University of York, Heslington, York, YO10 5DD, UK
[*]now at: Laboratoire Inter-universitaire des Systèmes Atmosphériques (LISA), Universités Paris 12 et Paris 7, CNRS, Créteil, France

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Correspondence to: G. Dufour (dufour@lisa.univ-paris12.fr)

Abstract

The distribution and budget of oxygenated organic compounds in the atmosphere and their impact on tropospheric chemistry are still poorly constrained. Near-global space-borne measurements of seasonally resolved upper tropospheric profiles of methanol by the ACE Fourier transform spectrometer provide a unique opportunity to evaluate our understanding of this important oxygenated organic species. The comparison with distributions simulated by a state-of-the-art chemistry transport model shows fair agreement during the March 2004 to August 2005 period with about 50% of the measurements reproduced by the model within 50%. However, in the northern hemisphere and during summertime, the satellite measurements reveal that the emissions from the continental biosphere lead to upper-tropospheric methanol concentrations significantly higher than expected.

1 Introduction

Methanol (CH_3OH) is the second most abundant organic molecule in the atmosphere after methane (Singh et al., 2001) and is the predominant oxygenated organic compound in the mid to upper troposphere (Heikes et al., 2002). Furthermore, primary methanol emissions constitute about 6% of the total terrestrial biogenic organic carbon emissions (Heikes et al., 2002). Oxygenated species such as methanol also influence the oxidizing capacity of the atmosphere by reacting with the hydroxyl radical, OH, to produce HO_2 and formaldehyde (Tie et al., 2003). As such, methanol represents an important source of radicals in the dry upper troposphere and affects the budget of tropospheric ozone (Tie et al., 2003; Folberth et al., 2006). However, the existing measurements of methanol suffer from a very limited spatial and temporal coverage and, as a consequence, large uncertainties exist in our knowledge of the methanol distribution and budget in the atmosphere (Jacob et al., 2005).

The global distribution of methanol has been assessed using global chemical-transport-models (Tie et al., 2003; Von Kuhlmann et al., 2003; Jacob et al., 2005; Folberth et al., 2006). However, the few available surface sites (e.g., Heikes et al., 2002; Karl et al., 2003; Schade and Goldstein, 2006) and aircraft measurements (e.g., Singh et al., 2000; Singh et al., 2003) do not provide a sufficient constraint on the simulated methanol distribution. In particular, little is known about the seasonal variation of methanol, especially in the mid- to upper-troposphere. The origin of methanol in the atmosphere is largely dominated by biogenic emissions (Galbally and Kristine, 2002). Plant growth represents up to 60–80% of this source and is responsible for a strong seasonal cycle in methanol abundance, especially in the northern hemisphere where vegetated land surfaces prevail (Jacob et al., 2005; Galbally and Kristine, 2002; Folberth et al., 2006). Methanol release from plants is higher for young leaves than for mature leaves (Galbally and Kristine, 2002; Jacob et al., 2005; Lathière et al., 2006) implying peak emissions in spring and early summer (Karl et al., 2003; Schade and Goldstein, 2006). The biogenic sources of methanol from plant growth and also plant decay are subject to large uncertainties and current best estimates range from 77 to 312 Tg/year (Galbally and Kristine, 2002; Heikes et al., 2002; Tie et al., 2003; Von Kuhlmann et al., 2003; Jacob et al., 2005). Biomass burning, urban activities and atmospheric oxidation of hydrocarbons are also identified as methanol sources and together contribute 27–55 Tg/year (Singh et al., 2001; Jacob et al., 2005). The major sink of methanol in the atmosphere is from gas-phase oxidation by the hydroxyl radical OH (Heikes et al., 2002, Jacob et al., 2005). Other sinks arise from dry deposition, wet removal and oceanic uptake. These loss terms result in a methanol atmospheric lifetime in the atmosphere of 1–2 weeks (Galbally and Kristine, 2002; Heikes et al., 2002; Jacob et al., 2005). This medium range lifetime implies that the methanol distribution is not only affected by surface emissions and chemistry but also by atmospheric transport.

In this paper, we report on the first satellite observations of the global methanol distribution in the upper troposphere and lower stratosphere using the Atmospheric Chemistry Experiment infrared Fourier transform spectrometer (ACE-FTS) onboard the

SCISAT satellite.

2 ACE-FTS measurements

The ACE-FTS records solar occultation measurements with coverage between approximately 85° S and 85° N, and with a majority of observations over the Arctic and the Antarctic (Bernath et al., 2005). The ACE-FTS has high spectral resolution (0.02 cm^{-1}) in the 750 to 4400 cm^{-1} range. Vertical profiles of temperature, pressure and various atmospheric constituents are retrieved from ACE-FTS spectra using a global fit approach (Boone et al., 2005). In our previous work, we were able to retrieve methanol profiles with enhanced concentrations in biomass burning plumes (Dufour et al., 2006). We have improved our methanol retrievals by adding a supplementary 6.4-cm^{-1}-width microwindow centred at 1001.9 cm^{-1} (Fig. 1). This improves the fitting error for concentration profiles at background levels and hence permits the investigation of near global distributions for this species. In order to assess the performances of our new retrieval setup, we compared the error budget obtained with one and two windows using a method similar to that used in our previous work (Dufour et al., 2006) on a subset of 12 tropical occultations recorded in October 2004. The resulting relative and absolute errors are shown in Fig. 2. The relative error at the maximum of the profile is about 17% with a two-window retrieval and about 20% with a one-window retrieval. The errors are also more constant below the tropopause with two windows and increase rapidly in the lower stratosphere. We also determined the error budget for 5 individual occultations that are representative of the different types of profiles encountered for different latitudes and seasons (Fig. 3). For high southern latitudes, where the methanol vmr is small (~250 pptv), the total error reaches 80% in the troposphere and is larger than 100% in the lower stratosphere (>10 km). For other occultations, the errors usually stay below 30% in the troposphere and also increase rapidly in the lower stratosphere where the methanol values decrease rapidly. For the present study, we used a selection of profiles from March 2004 to August 2005 that sample low in the troposphere and for which the quality of the retrieval has been checked. Observed methanol in the upper troposphere ranges from 200 pptv (especially during winter) to 2000 pptv on average (above northern hemisphere continents in summer) and agrees well with previous aircraft measurements (Singh et al., 1995; Singh et al., 2000; Singh et al., 2001; Singh et al., 2004). The background methanol vmr measured, for instance, from aircraft in the free troposphere over the Pacific is about 600 pptv (Singh et al., 2000; Singh et al., 2001), in agreement with the mean value observed by the ACE-FTS. It is also worth pointing out that the measured profiles show a rapid decrease above the tropopause and reach values close to the detection limits of the ACE-FTS (~100 pptv). These values and their uncertainties (>100%) are similar to aircraft measurements performed in the lower stratosphere during the SONEX campaign (104±102 pptv) (Singh et al., 2000).

3 LMDz-INCA chemistry transport model

The ACE-FTS measurements are compared with the results of the LMDz-INCA state-of-the-art global three-dimensional chemistry transport model. LMDz is a grid point General Circulation Model (GCM) coupled on-line to INCA (Interactive Chemistry and Aerosols) (Hauglustaine et al., 2004; Folberth et al., 2006). The version of INCA used in this study simulates tropospheric chemistry, emissions, and deposition of primary tropospheric trace species including non-methane hydrocarbons. The ORCHIDEE (Organizing Carbon and Hydrology in Dynamic Ecosystems) dynamical vegetation model has been used to calculate the seasonal and geographical distribution of methanol biogenic emissions (Lathière et al., 2005). These emissions are rescaled to a global mean best estimate for plant growth and plant decay of 151 Tg/year (Jacob et al., 2005). The methanol biomass burning emissions from wild fires is 12 Tg/year (Van der Werf et al., 2006) and we consider a minor urban source of 4 Tg/year (Jacob et al., 2005). In the model, we calculate a total methanol photochemical production of 20 Tg/year from hydrocarbon oxidation. The photochemical destruction is 141 Tg/year and the surface dry deposition accounts for 40 Tg/year. We derive a methanol lifetime in the atmosphere of 9 days. For comparison with the ACE occultations, the simulated daily averaged methanol profiles are interpolated to the measurement locations.

4 Results and discussion

The methanol satellite observations reveal a pervasive imprint of surface sources and in particular of biogenic emissions on the upper tropospheric mixing ratio. The zonally-averaged ACE-FTS methanol measurements show a strong seasonal cycle in the northern hemisphere (Fig. 4). The upper tropospheric vmr increases progressively from less than 500 pptv during northern winter to about 2000 pptv in summer. This seasonal increase starts in April-May at mid-latitudes and in early summer at high latitudes, in agreement with the plant growth cycle. The measured distribution at 8.5 km confirms a higher vmr and a stronger seasonal variation of methanol over the continents than over the ocean (especially the Northern Pacific), in agreement with the biogenic origin of this species (Fig. 5). Large vmrs are however sampled over the Northern Atlantic reflecting intercontinental transport. In the southern hemisphere, the seasonal variation is less pronounced since most of the land masses are located in the tropics where the seasonal cycle of the vegetation and hence of biogenic emissions is weak. The satellite measurements also show the clear influence of biomass burning emissions on the methanol distribution in the tropics. This is particularly the case during March-April-May (MAM) and September-October-November (SON) 2004 with zonally-averaged vmrs up to 1500 pptv (Fig. 4). Biomass burning plumes with methanol vmrs reaching more than 2000 pptv and emanating from southern Africa to the Indian and southern Atlantic oceans are also clearly detected in SON during the peak burning season in the southern hemisphere. The biomass burning origin of these plumes is confirmed by the positive correlation observed between methanol and both CO and HCN, two tracers of biomass burning emissions in the atmosphere (Rinsland et al., 2005; Dufour et al., 2006).

A fair general agreement between the model and the measurements is obtained considering the large uncertainties in surface emissions, and about 50% of the model results reproduce the measurements within 50% (Table 1). Overall, the model overestimates the satellite observations by 20% in the March 2004 to August 2005 period in the upper troposphere (Table 1). A seasonal comparison reveals however a strong underestimation of upper-tropospheric methanol by the model during spring and summer seasons when the influence of biogenic sources on the measured vmr is large at northern mid-to-high latitudes (Fig. 4). During the northern hemisphere summer (JJA), the simulated mixing ratios are only 60% of the measured values at the maximum of the profile for latitudes higher than 50° N. This disagreement arises mostly from continental regions (Fig. 5). Measured methanol values over the continents in the northern hemisphere are much larger than the simulated values (e.g., up to 34% in 2005 over North America) whereas they are in good agreement over the ocean (North Pacific: 2% in 2005) (Table 1). This disagreement points towards an underestimate of methanol biogenic emissions during the plant growth cycle in the model. To test this hypothesis, an additional model run was performed with biogenic emissions increased by 50% (not shown) and in this case, the disagreement is significantly reduced over land in spring and summer. This disagreement between model results and measurements is not only associated with the magnitude of the biogenic source but also arises from the seasonal cycle of this source. The model results peak in early fall whereas the observations reach a maximum in early summer (Figs. 5 and 6). This feature causes an overestimate of methanol vmrs in the model in the fall persisting through the winter season at high northern latitudes and is confirmed and exacerbated in the 50% increased biogenic emission sensitivity experiment. The comparison of the measured and simulated vertical profiles provides another perspective on this strong influence of biogenic emissions on methanol in the upper troposphere during summer in the northern hemisphere (Fig. 7). Over Europe and Asia, the observed vmrs reach a maximum of 2000–2500 pptv in summer 2004 and 2005 at an altitude of 7–9 km and decrease to only 300 pptv in DJF. The model clearly underestimates this signature of biogenic emissions.

The model reproduces with some accuracy the high methanol levels of biomass burning origin in the tropics. This is in particular the case in MAM and SON 2004 for the zonal mean distributions (Fig. 4) and is also visible in SON 2004 over southern Africa (Fig. 5). This strong influence of biomass burning also appears in the measured 10.5 km height distribution (Fig. 6) and on the vertical profiles over Africa (Fig. 7). Over this region, during the biomass burning period the bias between model values and measurements is only 8% (Table 1). Not surprisingly, in this model designed for tropospheric studies, the coarse resolution in the stratosphere and upper-troposphere does not reproduce the rapid decrease with height observed by ACE-FTS above the tropopause (Figs. 4 and 7) and the model results overestimate the measurements by 70% in the lower stratosphere (Table 1). However, the degree of overestimation by the model in the lower stratosphere has to be taken carefully because of the large uncertainties in the observations above the tropopause. It is also worth noting that the ACE-FTS is also able to detect a strong signature from pollution sources in the upper troposphere. The satellite measurements reveal large methanol concentrations above China and India during MAM 2005 (Fig. 4). These enhanced values are reproduced by the model but to a much lesser extent. This disagreement points to underestimated anthropogenic emissions of hydrocarbons in currently available emission inventories over these regions, a conclusion also reached by other studies for carbon monoxide (Kasibhatla et al., 2002; Heald et al., 2004).

5 Conclusions

Global measurements from a space-borne infrared limb-viewing instrument can measure the height-resolved distribution of methanol in the mid and upper troposphere. These measurements provide a unique view of the pervasive influence of biogenic emissions on the composition of the upper troposphere at northern mid and high latitudes. Furthermore, the satellite observations reveal how the upper troposphere is directly affected by surface and lower-tropospheric processes. The integration of these global methanol measurements from space with model results and airborne observations should significantly improve our understanding of the atmospheric budget of this important oxygenated species and the role played by the vegetation as a source of chemical species. It should also help to improve model simulations in future studies. The measured profiles will also help to better quantify the role played by methanol as a major source of radicals in the upper troposphere.

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Table 1. Correlation coefficients (R^2) and mean arithmetic biases (%) between simulated and observed methanol and ratios (%) of measurements reproduced within 50% by the model in the upper troposphere. Correlation coefficients and mean arithmetic biases for the lower stratosphere. The tropopause height is based on the NCEP tropopause products.

Region	Latitude	Longitude	Period	Upper troposphere			Lower stratosphere	
				R^2	bias	<=50%	R^2	bias
global	90° S–90° N	180° W–180° E	Entire period	0.33	19	46	0.35	73
North America	20° N–80° N	180° W–50° W	Entire period	0.23	13	42	0.18	66
			MAM2004	0.08	17	38	0.11	54
			JJA2004	0.20	–25	57	0.26	63
			SON2004	0.15	33	48	0.31	81
			DJF2005	0	55	36	0.02	78
			MAM2005	0.36	–14	50	0.44	54
			JJA2005	0.17	–34	52	0.14	66
North Pacific	0° N–50° N	130° E–120° W	Entire period	0.32	–5	64	0.19	64
			MAM2004	0.66	–23	46	0.29	49
			JJA2004	0.26	–1	69	0.36	75
			SON2004	0.02	39	56	0.42	83
			DJF2005	0	40	39	0.01	65
			MAM2005	0.11	–21	60	0.60	49
			JJA2005	0.34	–2	69	0.22	71
South Pacific	40° S–0° S	150° E–90° W	Entire period	0.05	13	59	0.06	58
			MAM2004			NO DATA		
			JJA2004	0	23	72	0.02	39
			SON2004	0	–28	51	0.11	54
			DJF2005	0.07	–20	54	0.15	64
			MAM2005	0.20	22	74	0.10	59
			JJA2005	0.24	44	52	0.20	58
Europe – Asia	35° N–80° N	20° W–180° E	Entire period	0.45	15	50	0.31	70
			MAM2004	0.10	21	60	0.10	63
			JJA2004	0.23	–31	53	0.38	74
			SON2004	0.52	44	52	0.28	82
			DJF2005	0.05	48	48	0.03	76
			MAM2005	0.39	13	53	0.45	66
			JJA2005	0.03	–27	52	0.25	75
Africa	40° S–35° N	20° W–60° E	Entire period	0.30	12	68	0.33	60
			MAM2004	0.23	–35	61	0.87	51
			JJA2004	0.32	28	66	0.35	60
			SON2004	0.43	–8	55	0.42	66
			DJF2005	0.15	20	57	0	59
			MAM2005	0.17	15	71	0.14	54
			JJA2005	0.20	24	71	0.47	68

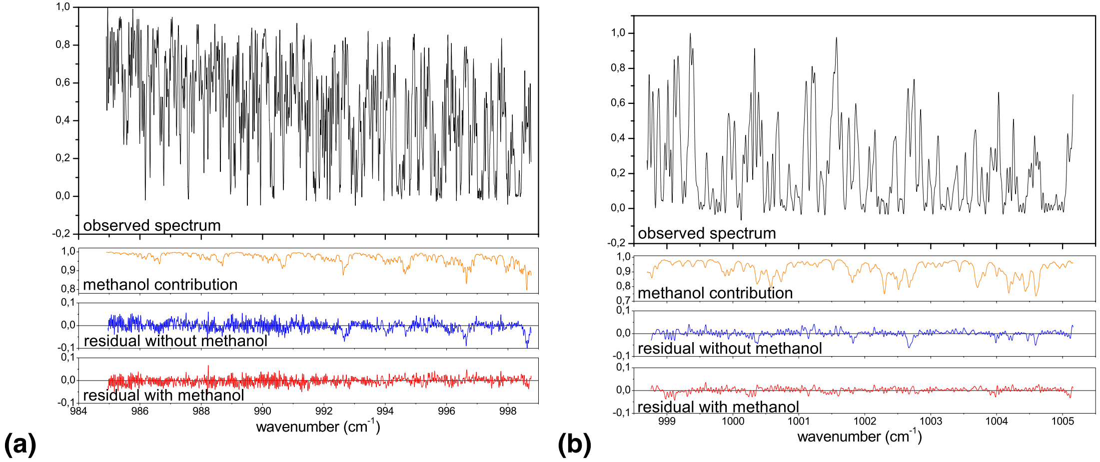

Fig. 1. (a) Spectral window used for the retrieval in (Dufour et al., 2006). **(b)** Additional window used for this study (see text for details). The upper panels show a spectrum observed at 10 km in the tropics during October 2004. The second panels represent the methanol contribution to the spectrum. The third and the last panels give the residuals (observed-calculated) when methanol is excluded or included in the calculation, respectively.

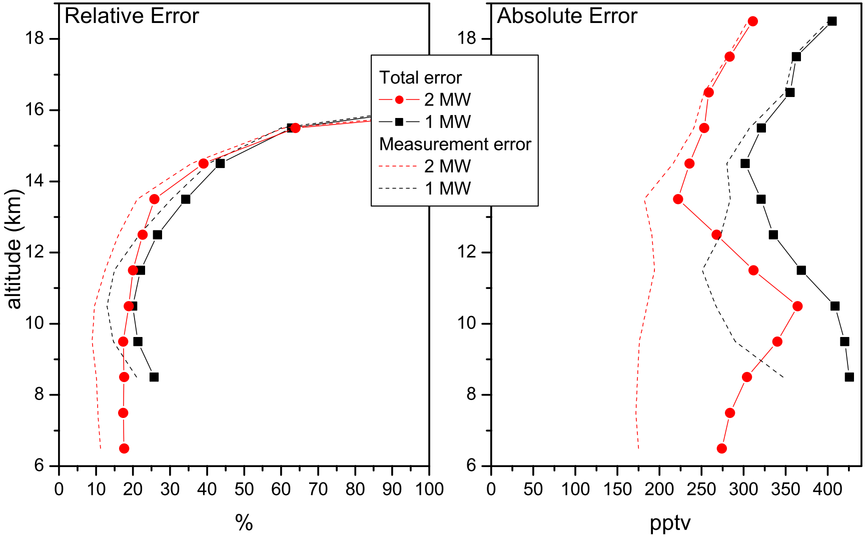

Fig. 2. Comparison of the total and measurement error profiles obtained using one or two windows for the methanol retrieval.

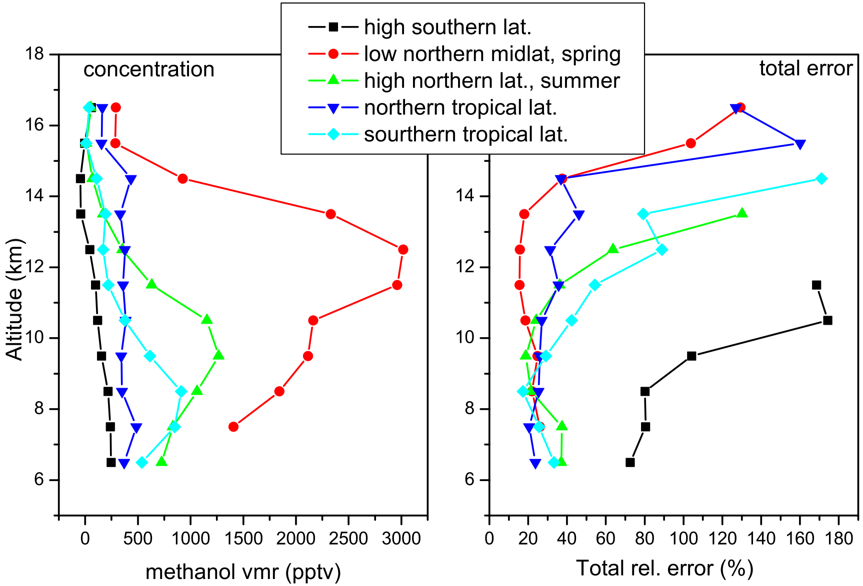

Fig. 3. Methanol profiles and the associated total error profile for 5 individual occultations representative of different latitudes and seasons. The error profile is given only for altitudes with methanol values above the detection limit (>100 pptv).

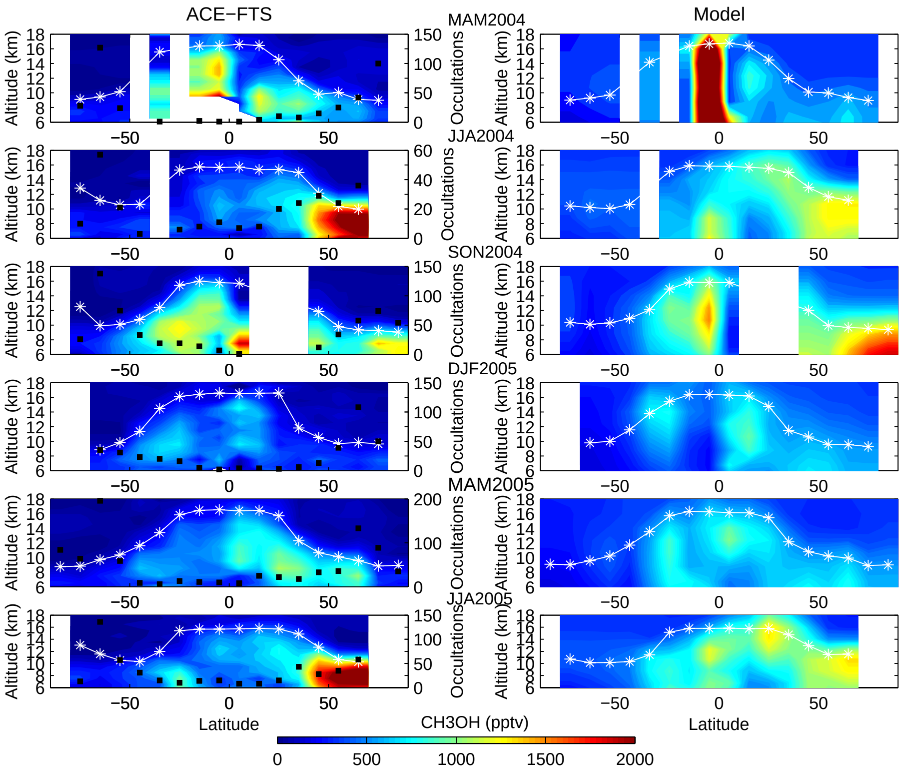

Fig. 4. Zonal mean CH_3OH volume mixing ratio profiles observed by the ACE-FTS (left) and simulated with the LMDz-INCA model (right) for each season from March 2004 to August 2005. The number of profiles averaged in each 10° latitude band is indicated on the left panels (black squares). A mean tropopause height is calculated based on NCEP meteorological fields for each measured methanol profile and from the model for the calculated distributions (white stars).

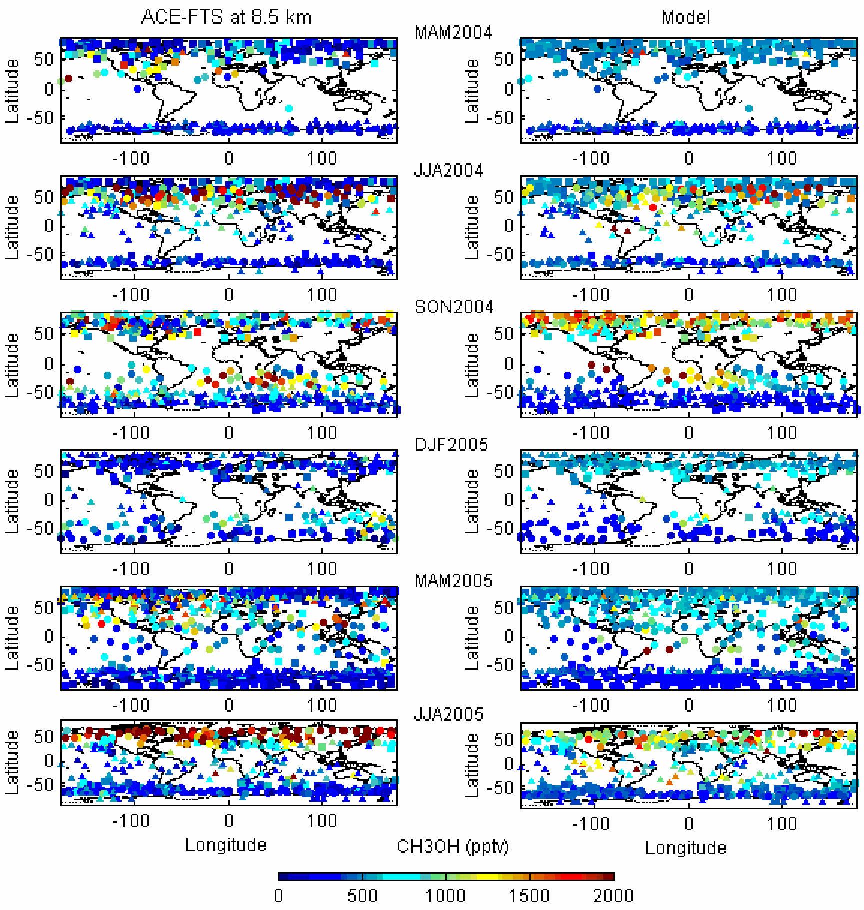

Fig. 5. Methanol volume mixing ratios at 8.5 km height observed by the ACE-FTS (left) and simulated by LMDz-INCA (right) for each season from March 2004 to August 2005. Squares, circles and triangles represent the first, second and the third month of the period, respectively.

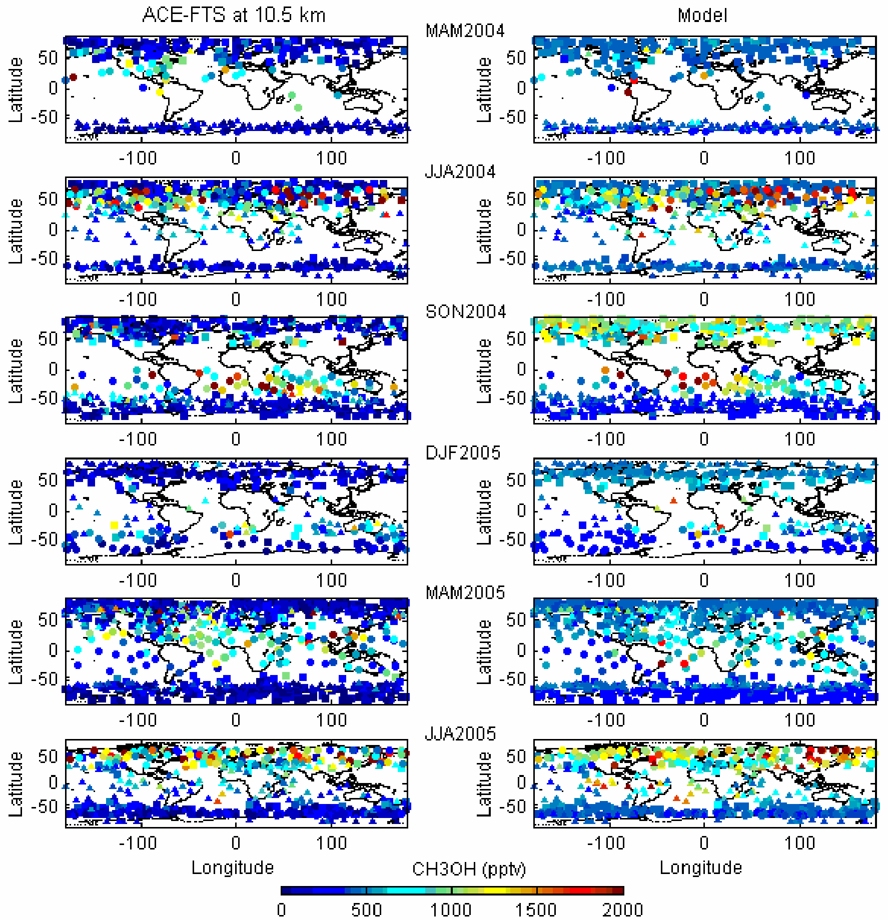

Fig. 6. Same as Fig. 5 but for an altitude of 10.5 km.

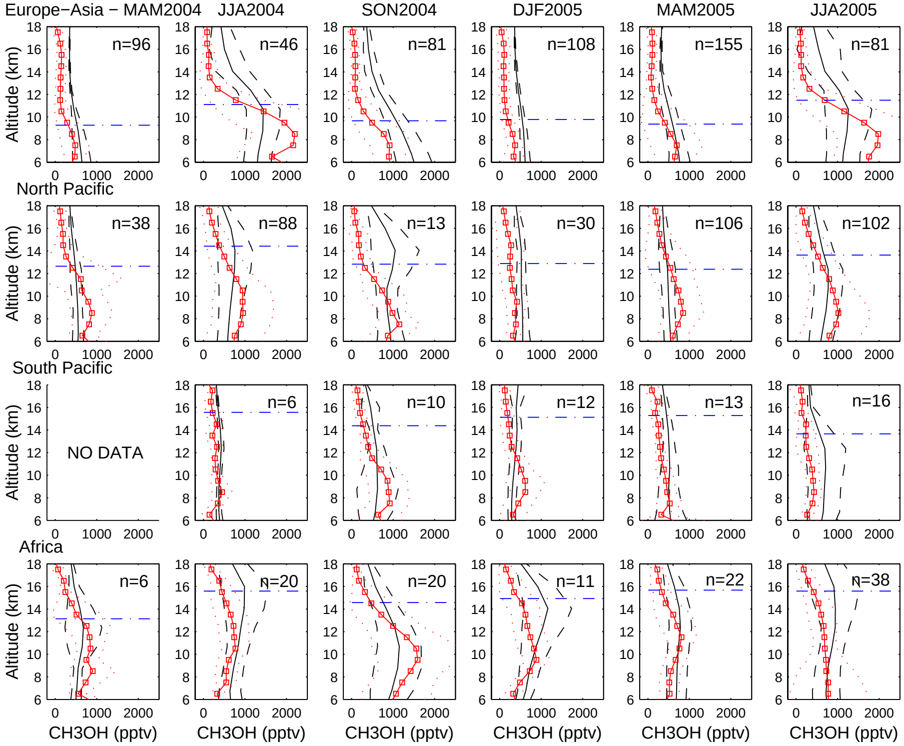

Fig. 7. Observed and simulated volume mixing ratio profiles for each season from March 2004 to August 2005 in 4 different regions: Europe/Asia (35° N–80° N; 20° W–180° E), North Pacific (0–50° N; 130° E–120° W), South Pacific (40–0° S; 150° E–90° W), and Africa (40° S–35° N; 20° W–60° E). Mean observed values are shown as open red squares with dotted red lines marking one standard deviation, whereas mean simulated values are shown as solid black lines with dashed black lines marking one standard deviation. The number of averaged profiles (n) is given for each profile. The tropopause height is based on NCEP tropopause data products (blue dashed-dotted line).