

Seasonal variations of acetone in the upper troposphere–lower stratosphere of the northern midlatitudes as observed by ACE-FTS



G. Dufour^{a,*}, S. Szopa^b, J.J. Harrison^{c,d}, C.D. Boone^e, P.F. Bernath^{e,f}

^a Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Universités Paris-Est Créteil et Paris Diderot, CNRS, Créteil, France

^b Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), CEA-CNRS-UVSQ, Gif-sur-Yvette, France

^c Department of Physics and Astronomy, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

^d National Centre for Earth Observation, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

^e Department of Chemistry, University of Waterloo, Ontario N2L 3G1, Canada

^f Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA

ARTICLE INFO

Article history:

Received 14 September 2015

In revised form 3 February 2016

Accepted 9 February 2016

Available online 10 February 2016

Keywords:

Acetone

Teledetection

Satellite

Atmospheric chemistry

Upper troposphere

ABSTRACT

This study reports on the climatological acetone distribution and seasonal variations in the upper troposphere and lower stratosphere of the northern midlatitudes, derived from observations by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) onboard SCISAT. The acetone profiles retrieved from 5 to ~20 km cover the period from January 2004 to September 2010. The 1σ statistical fitting errors are typically ~5–20% within the upper troposphere (UT), increasing in the lower stratosphere (LS) with decreasing acetone. The systematic errors range between 15% and 20%. The largest UT acetone mixing ratios (~1200 ppt on average in July over Siberia) are observed in summer in the northern mid- and high latitudes. Mixing ratios are larger over continental regions than over the ocean. Comparisons with airborne measurements available in the literature point toward a possible underestimation in acetone retrieved from ACE-FTS. The largest differences occur primarily in winter and for the background values. This underestimation is attributed to the complexity of the spectral region used for the retrieval. The annual cycle of acetone for the 30–70°N midlatitude band shows a maximum during summer, reflecting the annual cycle of the primary terrestrial biogenic source of acetone. By comparison with ACE-FTS, the LMDz-INCA global climate-chemistry model systematically overestimates acetone mixing ratios lower than 400 ppt. This overestimation is thus generalized for the lower stratosphere, the Tropics and beyond 70°N for the upper troposphere. In contrast, in the upper troposphere of the 30–70°N region, where the acetone levels are the highest (>450 ppt on average), the model–observation differences are in the range of the observation uncertainty. However, in this region, the model fails to capture the annual cycle of acetone, culminating in July. A seasonal cycle can only be obtained by considering high biogenic emissions but this cycle is shifted toward autumn, likely indicating an underestimation of the chemical destruction in the northern high latitudes.

© 2016 Published by Elsevier Inc.

1. Introduction

Acetone (CH_3COCH_3) is one of the most abundant oxygenated volatile organic compounds (OVOCs) in the troposphere [1,2]. Its impact on the oxidative capacity of the dry extratropical upper troposphere, as a HOx source, was thought to be one of the most important until mid-2000s, e.g. [2–6]. Its major contribution in the upper troposphere (UT) and the lowermost stratosphere (LMS) has been confirmed, especially in summer and autumn. It has been recently quantified based on the CARIBIC experiment

(Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) and the model ECHAM5/MESSy [7], assuming the recently revised acetone photolysis quantum yield [8,9].

Large uncertainties remain in the acetone budget [10]. The main sources of acetone are primary terrestrial biogenic and biomass burning emissions, secondary chemical production, and a small contribution from the decay of dead plant matter. The ocean is either a source or a sink depending on microbial activity, light and temperature [10–12]. Photolysis, oxidation and dry deposition over land and ocean are the main sinks of acetone [1,10,13]. Many of the acetone budget studies have been constrained using data from aircraft field campaigns compiled by Emmons et al. [14].

* Corresponding author.

E-mail address: dufour@lisa.u-pec.fr (G. Dufour).

However, given the variability of acetone and the scarcity of campaigns, the dataset is not representative of a complete acetone climatology. More recently, the availability of the CARIBIC aircraft measurements has improved our knowledge of the description of the acetone distribution in the UT/LMS (lowermost stratosphere), especially in the northern midlatitude band between 35°N and 56°N [7,15]. Space-borne instruments are powerful tools to complement in situ measurements since they provide global distributions of the atmospheric composition, especially those of VOCs, e.g. [16–22]. Retrieving acetone from remote-sensing instruments is very challenging because: (i) acetone absorbs in the infrared in a particularly dense spectral region, (ii) the acetone absorption cross-sections are weak and (iii) the concentration of acetone in the atmosphere is rather low (0.2–3 ppb, e.g. [10]). First retrievals from infrared spectrometers were performed from balloon-borne instruments [23] and from the spaceborne ACE-FTS in biomass burning plumes [19]. The first global distribution has been retrieved from MIPAS for one month in August 2003 [21].

In this study, we present a recent acetone ACE-FTS research product based on ACE processing version 3.0 [24]. The principal objective of the study is to evaluate the capability of this new ACE-FTS acetone product to describe the global distribution of acetone in the UTLS as well as the seasonal variations and the transport occurring in this region. Comparisons with measurements available from the literature, and in particular CARIBIC observations in the UTLS [15], are used for this purpose. Comparisons with the state-of-the-art global chemical transport model LMDz-INCA [25] are also discussed. The acetone profile retrievals are described and evaluated in Section 2. The model is described in Section 3. Sections 4 and 5 discuss the global acetone distribution in the UTLS and its annual cycle as observed by ACE-FTS and simulated by LMDz-INCA. Section 6 summarizes the conclusions of the study.

2. ACE-FTS observations

2.1. Retrieval of acetone from ACE-FTS spectra

The ACE-FTS instrument, which covers the spectral region 750–4400 cm^{−1} with a ±25 cm maximum optical path difference, uses the sun as a light source to record limb transmission through the

Earth's atmosphere during sunrise and sunset ('solar occultation'). Transmittance spectra are obtained by ratioing against exoatmospheric 'high sun' spectra measured each orbit. These spectra, with high signal-to-noise ratios, are recorded through long atmospheric limb paths (~300 km effective length), thus providing a low detection threshold for trace species. ACE has an excellent vertical resolution of about 2–3 km in the troposphere and can measure up to 30 occultations per day, with each occultation sampling the atmosphere from 150 km down to the cloud tops (or 5 km in the absence of clouds). The locations of ACE occultations are dictated by the low Earth circular orbit of the SCISAT satellite and the relative position of the sun. Over the course of a year, the ACE-FTS records atmospheric spectra over a large portion of the globe [26].

Version 3.0 of the ACE-FTS retrieval software was used for the acetone volume mixing ratio (VMR) retrievals. Vertical profiles of trace gases (along with temperature and pressure) are derived from the recorded transmittance spectra via a nonlinear least squares global fit to the selected spectral region(s) for all measurements within the altitude range of interest. The microwindow set consists of 16 microwindow 'slices' across the acetone spectral feature, with a common set of fitted baseline parameters (a baseline scaling factor and a baseline slope); all microwindows are listed in Table 1 and an example of fit is given in Fig. 1. An additional four microwindows are utilized to improve the retrieval of various interferers; see the footnotes to Table 1. The 16 'slices' lie between CH₄ and H₂O lines and were chosen to avoid CH₄ line mixing effects. The atmospheric pressure and temperature profiles, and the tangent heights of the measurements were taken from the v3.0 processing of the ACE-FTS data. The abundances of most molecules with absorption features in the microwindow (see Table 2) were adjusted simultaneously with the acetone VMR, except for CFC-12, CFC-114, CFC-115, HCFC-22, HFC-125, CBrF₃, CFC-13 and HFC-143a. Contributions from CFC-12 and HCFC-22 were calculated directly using the v3.0 VMRs, with assumed constant VMR profiles that did not vary with time for the others. Spectroscopic line parameters and absorption cross sections for most molecules were taken from the HITRAN 2004 database [27], with the exception of CHF₃ [28] and CBrF₃ (PNNL; <http://nwr.pnl.gov>), water vapor and ozone [29]. The acetone cross-section dataset, recently included in HITRAN 2012 [30], was obtained from Harrison et al.

Table 1
Summary of the microwindows used in the acetone retrieval.

Center frequency (cm ^{−1})	Microwindow width (cm ^{−1})	Lower altitude (km)	Upper altitude (km)
1184.65	0.22	7 – 2sin ² (latitude°)	22
1189.38	0.28	7 – 2sin ² (latitude°)	22
1191.72	0.24	7 – 2sin ² (latitude°)	22
1194.50	0.50	7 – 2sin ² (latitude°)	22
1204.59	0.70	7 – 2sin ² (latitude°)	22
1206.85	0.50	7 – 2sin ² (latitude°)	22
1208.25	0.30	7 – 2sin ² (latitude°)	22
1214.00	0.40	7 – 2sin ² (latitude°)	22
1217.00	0.35	7 – 2sin ² (latitude°)	22
1227.85	0.30	7 – 2sin ² (latitude°)	22
1231.25	0.70	7 – 2sin ² (latitude°)	22
1232.10	0.40	7 – 2sin ² (latitude°)	22
1200.40	0.40	8 – 2sin ² (latitude°)	22
1222.25	0.30	10 – 2sin ² (latitude°)	22
1233.95	0.30	9 – 2sin ² (latitude°)	22
1241.53	0.26	9 – 2sin ² (latitude°)	22
1937.15 ^a	0.70	8	21
1950.10 ^b	0.35	10 – 2sin ² (latitude°)	22
2566.22 ^c	0.26	9	22
2623.87 ^d	0.90	8 – 2sin ² (latitude°)	22

^a Included to improve results for interferers H₂¹⁸O and H₂¹⁷O.

^b Included to improve results for interferer H₂O.

^c Included to improve results for interferers N¹⁵NO.

^d Included to improve results for interferers HDO, OC¹⁸O, and CH₄.

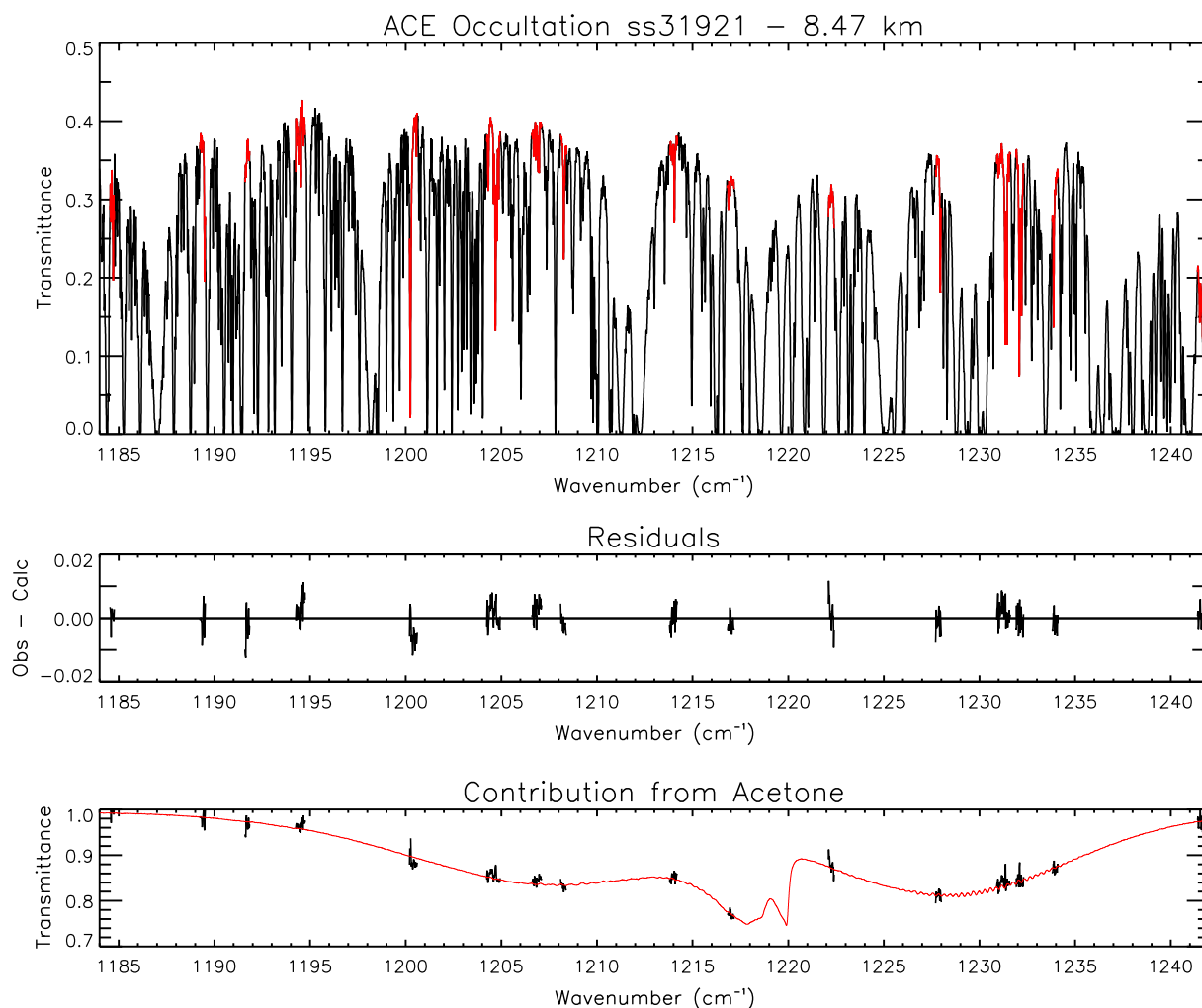


Fig. 1. Top panel: an ACE-FTS transmittance spectrum over the 1184–1242 cm⁻¹ region for occultation ss31921 (recorded on 17 July 2009 over central Russia) at a tangent height of 8.47 km. The features in red represent the microwindows used in the acetone retrieval. Middle panel: the total observed – calculated residuals for the acetone retrieval. Bottom panel: Obs/calc ratio (without the inclusion of acetone in the forward model), with the calculated acetone transmittance contribution to the measurement overlaid.

[31]. The lower altitude limits of the microwindows vary with latitude, as reflected by the phenomenological expression $\sin^2$ (latitude°), due to the saturation of microwindow spectral features. In total, retrieved acetone VMR profiles from 17,689 occultation measurements taken between January 2004 and September 2010 were used for this work.

2.2. Error estimates and detection limit

For a single ACE-FTS acetone VMR profile, the 1σ statistical fitting errors are typically ~5–20% within the troposphere, increasing in the lower stratosphere where the VMRs tend to be smaller. These errors are random in nature and are largely determined by the measured signal-to-noise ratios of the ACE-FTS spectra, i.e. measurement noise. For averaged profiles, the random errors are small (reduced by a factor of $1/\sqrt{N}$, where N is the number of profiles averaged) and the systematic errors dominate.

Spectroscopic sources of systematic error predominantly arise from the acetone absorption cross sections (~5%), with minor contributions from interfering species in the microwindows. Since the baselines of the ACE-FTS transmittance spectra and the VMRs of the interferers (Tables 1 and 2) are fitted simultaneously with the acetone VMR, it is not a trivial exercise to determine how much

these contribute to the overall systematic error of the acetone retrieval. Due to the dense spectral region used for the acetone retrieval, the fitting residuals remain above the noise level for some of the microwindows. However, acetone has a very broad spectral feature in this region and the remaining residuals do not have a major impact on the retrieved profile. We then consider that these contributions to the systematic error are small. Since there are a large number of interferers, it is assumed that the total contribution is at most ~5%.

In addition to spectroscopic errors, uncertainties in temperature, pressure, tangent altitude (i.e. pointing) and instrumental line shape (ILS) all contribute to systematic errors in the retrieved acetone profiles. To estimate the overall systematic error, the retrieval was performed for small subsets of occultations by perturbing each of these quantities (b_j) in turn by its assumed 1σ uncertainty (Δb_j), while keeping the others unchanged. The fractional retrieval error, μ_j , is defined as

$$\mu_j = \left| \frac{\text{VMR}(b_j + \Delta b_j) - \text{VMR}(b_j)}{\text{VMR}(b_j)} \right|. \quad (1)$$

Note that for the ACE-FTS retrievals, pressure, temperature and tangent height are not strictly independent quantities; tangent heights are determined from hydrostatic equilibrium, and so these

Table 2

Summary of the molecules included in the microwindows for the ACE acetone retrieval.

Molecule	Lower altitude limit (km)	Upper altitude limit (km)	Nature of spectroscopic data
CH ₃ COCH ₃	7 – 2sin ² (latitude°)	22	Cross sections
HCFC-142b (CH ₃ CClF ₂)	7 – 2sin ² (latitude°)	20	Cross sections
CFC-113 (CCl ₃ CF ₃)	7 – 2sin ² (latitude°)	20	Cross sections
CH ₄	7 – 2sin ² (latitude°)	22	Line parameters
¹³ CH ₄	7 – 2sin ² (latitude°)	22	Line parameters
CH ₃ D	7 – 2sin ² (latitude°)	22	Line parameters
N ₂ O ₅	7 – 2sin ² (latitude°)	22	Cross sections
HFC-134a (CFH ₂ CF ₃)	7 – 2sin ² (latitude°)	20	Cross sections
H ₂ O	7 – 2sin ² (latitude°)	22	Line parameters
H ₂ ¹⁸ O	7 – 2sin ² (latitude°)	21	Line parameters
H ₂ ¹⁷ O	7 – 2sin ² (latitude°)	21	Line parameters
HDO	7 – 2sin ² (latitude°)	22	Line parameters
OC ¹⁸ O	7 – 2sin ² (latitude°)	22	Line parameters
O ¹³ C ¹⁸ O	7 – 2sin ² (latitude°)	22	Line parameters
O ₃	7 – 2sin ² (latitude°)	22	Line parameters
N ₂ O	7 – 2sin ² (latitude°)	22	Line parameters
N ¹⁵ NO	7 – 2sin ² (latitude°)	22	Line parameters
¹⁵ NNO	7 – 2sin ² (latitude°)	22	Line parameters
N ₂ ¹⁸ O	7 – 2sin ² (latitude°)	22	Line parameters
N ₂ ¹⁷ O	7 – 2sin ² (latitude°)	22	Line parameters
HNO ₃	7 – 2sin ² (latitude°)	22	Line parameters
H ₂ O ₂	7 – 2sin ² (latitude°)	22	Line parameters
COF ₂	7 – 2sin ² (latitude°)	22	Line parameters
CHF ₃	7 – 2sin ² (latitude°)	20	Pseudo-line parameters

quantities are strongly correlated. For the purposes of this work, only two of these quantities are altered: temperature is adjusted by 2 K and tangent height by 150 m [16,32]. Additionally, ILS uncertainty is induced by adjusting the field of view by 5% [16,32]. A subset of occultations recorded on 29–31 July 2009 between 43.28° and 49.47°N was selected for this analysis. The fractional value estimates of the systematic uncertainties, and their symbols, are given in Table 3. Assuming these quantities are uncorrelated, the overall systematic error in the acetone retrieval can be calculated as

$$\mu_{\text{systematic}}^2 = \mu_{\text{spec}}^2 + \mu_{\text{int}}^2 + \mu_T^2 + \mu_z^2 + \mu_{\text{ILS}}^2. \quad (2)$$

The total systematic error contribution to the ACE-FTS acetone retrieval, based on known sources, is estimated to be ~15%.

Careful investigation of the retrieved acetone VMRs has revealed an additional source of bias which is particularly evident at high latitudes (50–90°S and 50–90°N) and manifests as negative VMRs (peaking at ~–50 ppt) between ~10 and ~15 km. The exact source of this negative bias is unknown, as is its manifestation at lower altitudes and latitudes where acetone VMRs are higher, but the likely explanation is that some of the microwindows are actually affected by CH₄ line mixing; certainly none of the interferers with assumed profiles appear to be the source.

Considering the signal-to-noise ratio is around 350:1 in the acetone spectral region, the detection limit for a single observation is estimated to be ~100 ppt.

2.3. Dataset preparation

The vertical resolution of the ACE-FTS measurements is largely limited by the field of view of the instrument, which is 2–3 km in the UTLS. For that reason, it is more reasonable to consider mean upper tropospheric (UT) acetone VMRs and mean lower stratospheric (LS) acetone VMRs to compensate for an oversampling of the acetone profile. Except in Fig. 4, in which monthly mean VMR profiles on a 1-km grid are used, we consider the mean upper tropospheric acetone VMR, calculated as the average of the VMRs for altitude levels within 3 km below the tropopause (included), and the mean lower stratospheric acetone VMR, calculated as the average for the altitude levels within 3 km above the tropopause

(excluded). We use the dynamical tropopause from the ACE-FTS Derived Meteorological Products (DMPs) [33] calculated for each occultation to identify the tropopause height. The results are mainly presented as mean UT or LS acetone VMRs for grid cells, latitude bands or large-scale regions. Only acetone VMRs larger than the detection limit of 100 ppt are included in the averages. Fig. 2 displays the number of individual VMRs averaged over the entire period for grid cells with 20° × 20° latitude and longitude resolution in the UT and the LS respectively. Due to the orbit of the ACE-FTS, large variations in the number of averaged VMRs are observed with latitude. The northern mid- and high latitudes have a high sampling rate whereas the tropics and the latitudes south of 70°S are much less sampled. The difference between the number of averaged VMRs between the UT and the LT in the mid and high latitudes is mainly due to the tropopause height. Its lower altitude at these latitudes does not allow a full 3 km-range-below-the-tropopause selection of the UT VMRs because of the lower altitude limit of the retrieval. In the tropics, it is the contrary: the tropopause is at high altitudes and the 3 km-range-above-the-tropopause section criterion for the LS average is limited by the upper altitude limit of the retrieval. Moreover, the acetone VMR in the LS at these high altitudes VMR are more often smaller than the 100 ppt-detection limit, reducing the number of averaged compared to the UT.

In addition, we use the LMDz-INCA model, described in Section 3, in order to evaluate the representativeness of the ACE-FTS observations, considering the limited sampling. We compare the UT and LS acetone distributions based on the climatological mean of model simulations for the 2004–2010 period and on the mean of simulated concentrations interpolated to the measurement points

Table 3

Sources of systematic uncertainty in the ACE-FTS acetone research product, based on v3.0 processing.

Source	Symbol	Fractional value
Acetone spectroscopy	μ_{spec}	0.05
Spectral interferers	μ_{int}	0.05
Temperature	μ_T	0.05
Altitude	μ_z	0.12
ILS	μ_{ILS}	0.04

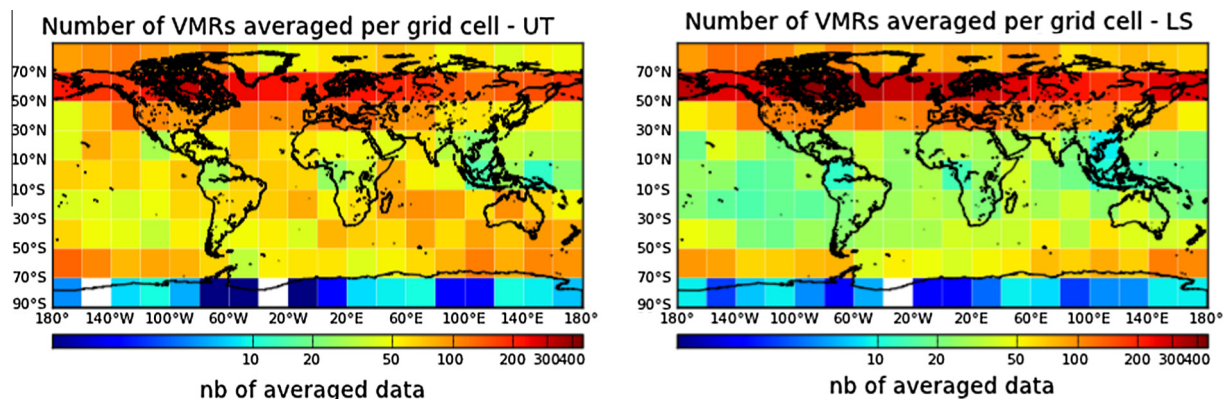


Fig. 2. Number of VMRs averaged per grid cell of $20^\circ \times 20^\circ$ latitude and longitude resolution for the 2004–2010 period.

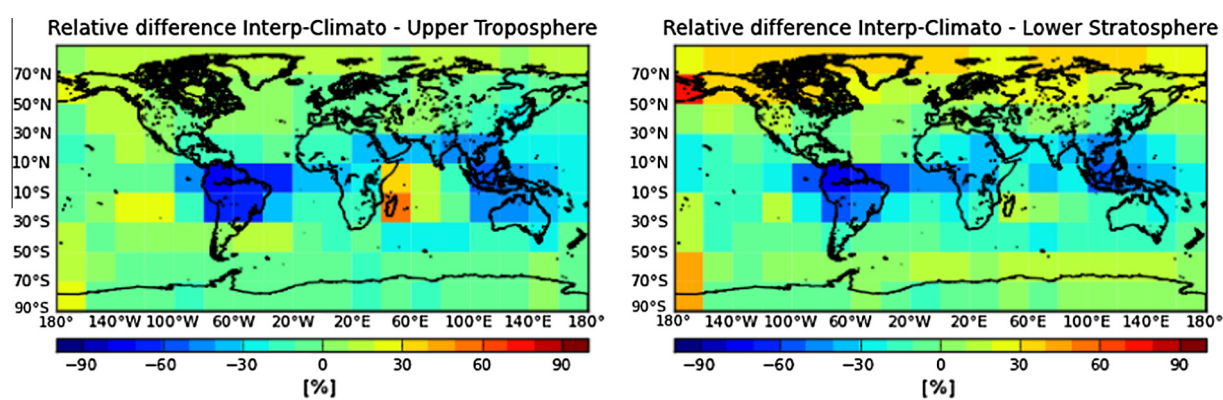


Fig. 3. Relative difference (%) between a climatology of acetone distribution based on LMDz-INCA simulation over the 2004–2010 period and the acetone distribution computed using the same simulation but with simulated concentrations interpolated at the ACE-FTS observation points.

for the same period. The distribution based on interpolated concentrations provides a similar picture of the acetone distribution as the climatology in the extratropical upper troposphere (Fig. 3). This would suggest that the limited horizontal sampling of ACE-FTS is not an issue (in the extratropics) and that the distribution given by ACE-FTS is likely representative of the actual acetone UT distribution. In the tropics, the limited sampling of ACE-FTS leads to a strong underestimation of acetone ($>30\%$), especially over the regions impacted by the biomass burning. ACE-FTS acetone observations are then not well suitable to evaluate acetone distribution in the tropical band. In the lower stratosphere, significant differences occur in the tropical latitudinal band and in the high northern latitudes (Fig. 3). This leads us to focus more on the northern midlatitudes in the following sections, where ACE-FTS acetone observations are more reliable according to the sampling issue. In the following, we will focus preferably on the $30\text{--}70^\circ\text{N}$ latitude band, where the sampling rate is the best and which is rather uniformly sampled every month. This will allow a good description of the seasonal cycle (Section 5).

2.4. Northern midlatitude upper tropospheric and lower stratospheric acetone from ACE-FTS

Fig. 4 provides a plot of the monthly variations of acetone VMRs in the midlatitude band as retrieved from ACE-FTS between 6 and 18 km. Upper tropospheric acetone ranges from ~ 180 ppt to ~ 1100 ppt with a maximum in July. A strong vertical gradient is observed across the tropopause during summer with stratospheric acetone ranging from ~ 130 ppt to ~ 350 ppt. Note that the minimum mean VMRs derived from ACE-FTS are likely overestimated

due to the detection limit being rather high (100 ppt). However, this probable overestimation has a lesser effect on the higher acetone levels.

In order to determine whether the retrieved ACE-FTS profiles provide a realistic picture of the acetone vertical distribution in the northern midlatitudes, we compare ACE-FTS data with CARIBIC acetone measurements reported by Sprung and Zahn [15], and with UTLS observations from aircraft campaigns (TRACE-P, SONEX, PEM-WEST, STREAM) available in the literature for northern latitudes [14,34,35]. We also consider satellite observations provided by MIPAS on August 2003 [21]. The different datasets used for the comparison are reported in Table 4.

Without considering the observation year, a detailed comparison between the different datasets is limited by the differences in the sampling and subsequent representativity of the ACE-FTS, aircraft campaigns and CARIBIC.

The top panels of Fig. 5 display the UT and LS monthly variations of acetone as observed by ACE-FTS in the $30\text{--}70^\circ\text{N}$ latitude band. The 1σ -standard deviations are plotted, and represent the natural acetone variability combined with the spread due to the observation errors. For comparison, CARIBIC, different aircraft campaign, and MIPAS measurements are plotted. For CARIBIC, we consider the seasonal cycle fitted by [15] as representative of the observations. In the upper troposphere, the comparison points toward a possible underestimation of ACE-FTS acetone, all the others observations being larger. This is particularly the case for winter months. In the lower stratosphere, it seems to be the contrary: ACE-FTS acetone appears to be systematically larger than the CARIBIC estimates, but it is not the case with the other available datasets (Fig. 5). In both the UT and the LS, the differences

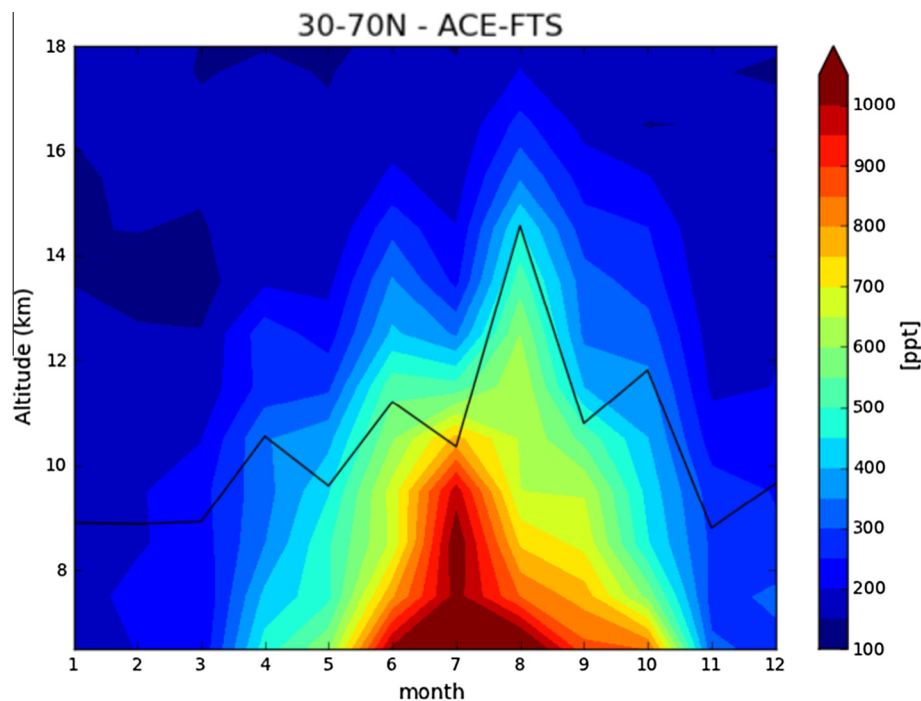


Fig. 4. Monthly acetone profiles retrieved from ACE-FTS for the 30–70°N latitude band over the 2004–2010 period. The mean tropopause, computed from the DMP corresponding to each individual occultation, is displayed in black.

Table 4
Aircraft and satellite measurement datasets used for the evaluation of ACE-FTS acetone. Only the datasets corresponding to northern mid and high latitudes are considered.

Name of observations	Observation type/sampling	Vertical regions used for comparison	Comment
CARIBIC [15]	Airborne 106 flights sampling mainly over continents 33–56°N Period 2006–2008	Tropopause level 2 km above the tropopause	
STREAM [34]	3 airborne campaigns Nov/Dec 1995 (Amsterdam) March 1997 (Kiruna) July 1998 (Timmings, Amsterdam)	Upper troposphere Lower stratosphere ($\Theta > 30$ K)	
TRACE-P [35]	Airborne campaign 32–40°N March/April 2001	Upper troposphere (8–10 km)	– Unpolluted dataset – Use the tropopause height derived from ACE-FTS to determine UT and LS
PEM-WEST B [14]	Airborne campaign Japan (25–40°N) February 1994	Upper troposphere (6–9 km) Lower stratosphere (10 km)	– Use the tropopause height derived from ACE-FTS to determine UT and LS
SONEX [14]	Airborne campaign 3 sites: Newfoundland, Ireland, East Atlantic (35–60°N) October 1997	Upper troposphere (9–12 km)	– The 3 sites are merged together – Use the tropopause height derived from ACE-FTS to determine UT and LS
MIPAS [21]	Satellite observations 45–90°N band August 2003	277 hPa	– Values estimated from Fig. 12 in [21]

between the different datasets remain mainly within the respective errors of the observations. It is then difficult to firmly conclude and quantify the possible under- or overestimation of ACE-FTS, especially as the definition of the UT and the LS as well as the observation years differ from one dataset to another. The main conclusion of these comparison is that ACE-FTS provides a reasonable picture of acetone in the northern midlatitudes, and reproduces the main seasonal features depicted by the CARIBIC data, the best available dataset in terms of sampling. In particular, we

have checked that the vertical gradient across the tropopause is correctly reproduced by ACE-FTS. Acetone distribution in the northern midlatitudes provided by ACE-FTS is relevant for climatological analyses.

3. LMDz-INCA chemical transport model and acetone budget

The Interaction between Chemistry and Aerosols (INCA) model, coupled to the LMDz General Circulation Model (GCM), is used to

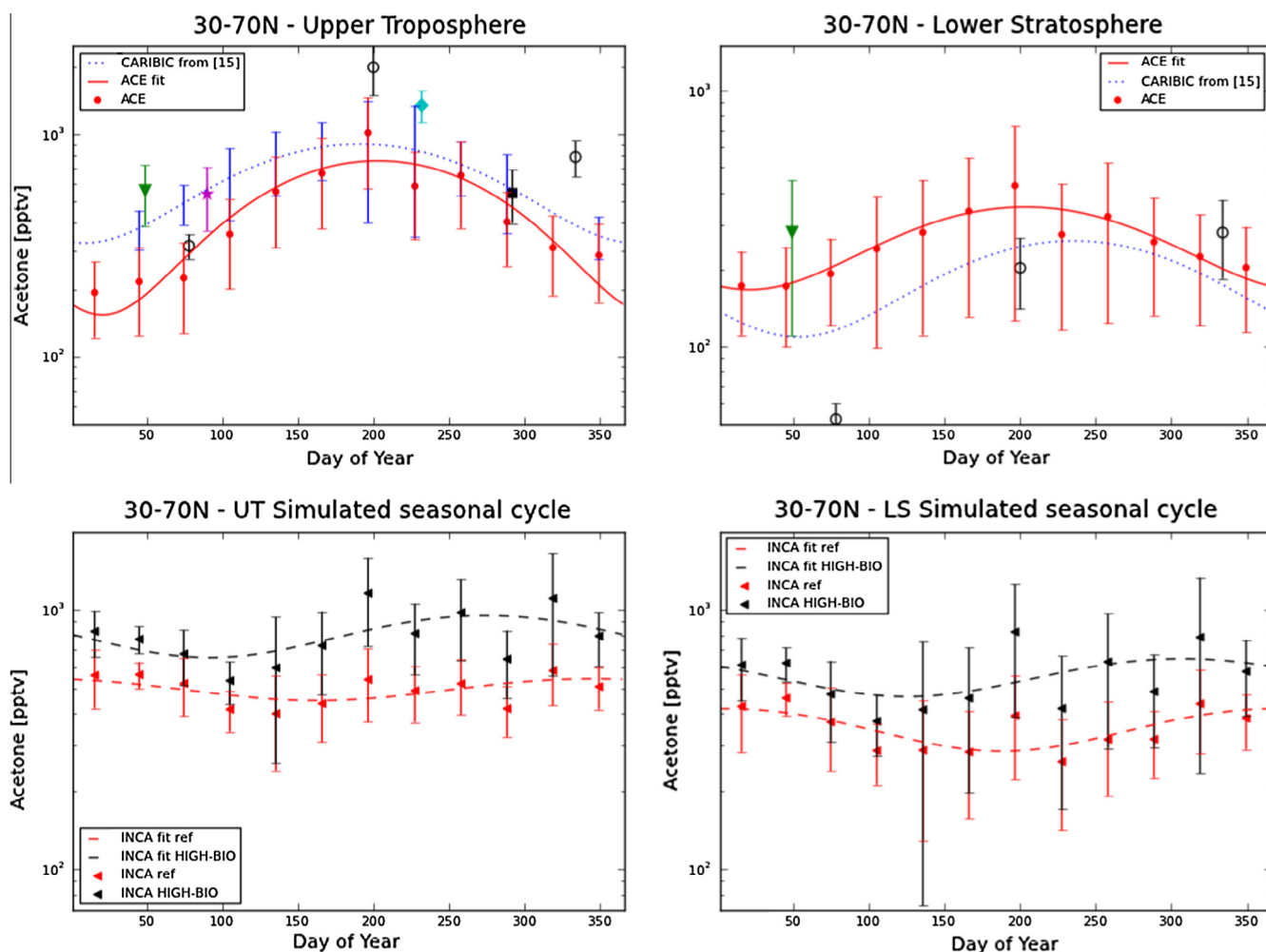


Fig. 5. Seasonal cycle of acetone in the upper troposphere (UT) (left), in the lower stratosphere (LS) (right), for the 30–70°N latitude band as inferred from ACE-FTS (upper) and LMDz-INCA – reference and HIGH-BIO simulation (lower). The acetone cycles reported by Sprung and Zahn [15] at the tropopause and 2 km above and representative of the 33–56°N region are displayed in blue. The associated 1σ -standard deviations have been taken from Fig. 8 of [15]. Acetone VMRs from the airborne campaigns SONEX (black squares), PEM-WEST B (green triangles), TRACE-P (magenta star), and STREAM (black open circles), and from MIPAS (cyan diamonds) are displayed on top panels. Note that the symbols are slightly shifted in time for clarity when necessary. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5

Acetone tropospheric budget computed by the LMDz-INCA model for the reference simulation and the HIGH-BIO simulation.

Simulation	Main simulation	HIGH-BIO
Global tropospheric burden (Tg)	4.2	6
Primary emissions (Tg/year)	62 (20 from ocean and 40 from vegetation)	98 (20 from ocean and 76 from vegetation)
Chemical production (Tg/year)	22	25
Deposition (Tg/year)	26	39
Chemical destruction (Tg/year)	55	78

simulate the distribution of gaseous reactive species in a 39 level atmosphere extending from the surface to 4.3 hPa. INCA considers primary emissions and computes chemical sources and sinks as well as deposition with a time-step of 30 min. In the simulations described here, LMDz is coupled with the ORCHIDEE (Organizing Carbon and Hydrology in Dynamic Ecosystems) dynamic global vegetation model [36] for soil/atmosphere exchanges of water and energy [37]. The LMDz general circulation model is nudged on ERA-interim data for wind fields and sea surface temperatures (SST). The general functioning of INCA and the basic gas phase chemistry are presented in Hauglustaine et al. [25] and results with the full tropospheric gaseous chemical scheme are gathered by

Folberth et al. [38] and Szopa et al. [39]. The oxidative tropospheric photochemistry is described through 85 chemical species and 264 chemical reactions, including non-methane hydrocarbon oxidation. As described in Hauglustaine et al. [25], the stratospheric ozone concentrations are relaxed toward the monthly mean 3D climatologies of Li and Shine [40] at the altitudes having potential temperatures above 380 K.

The LMDz-INCA model has been run over the 2003–2011 period with the first year considered as a spin-up. The anthropogenic emissions used correspond to the year 2010 in the RCP8.5 projection (Representative Concentration Pathways reaching 8.5 W m^{-2} in 2100). They include ship and aircraft emissions. This dataset is

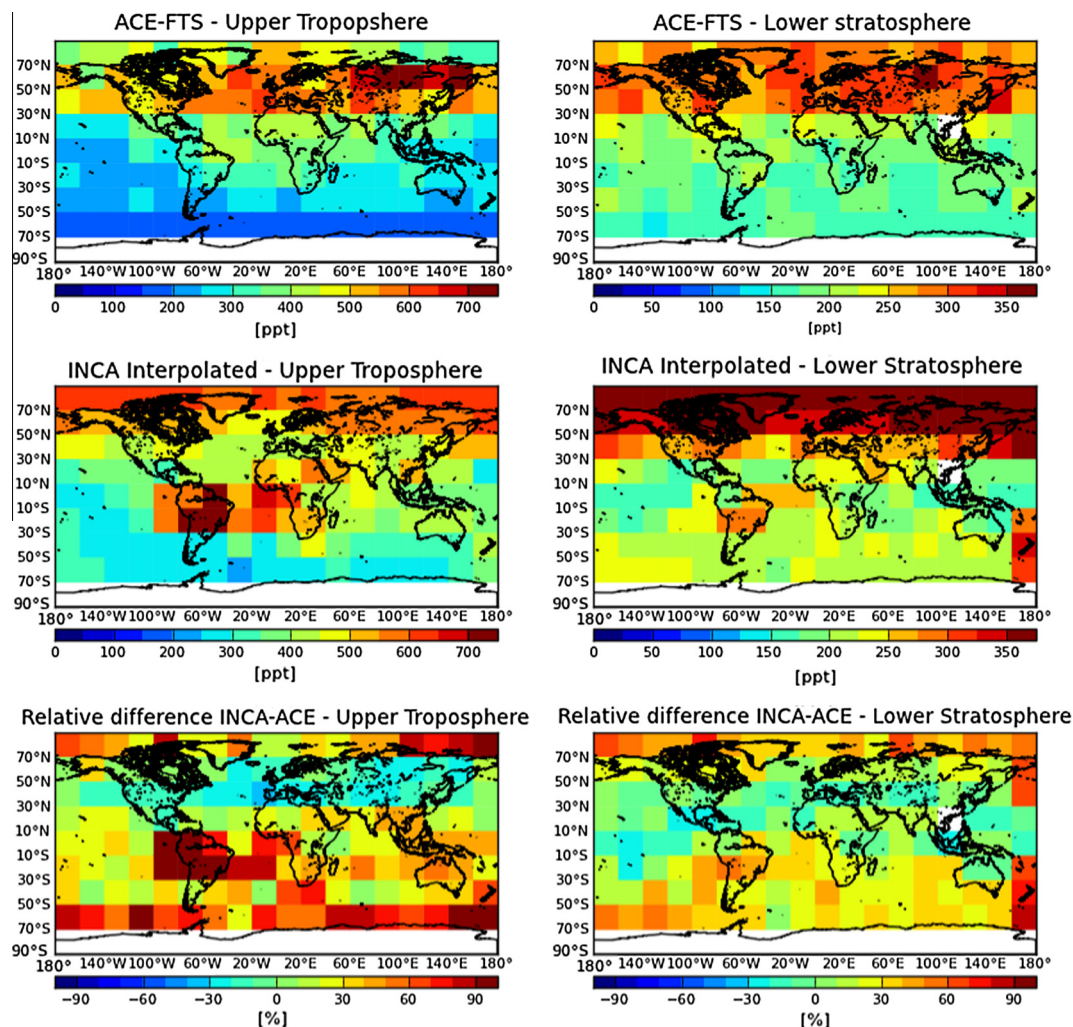


Fig. 6. Global annual distribution of acetone in the upper troposphere (left) and the lower stratosphere (right) observed by ACE-FTS (upper panel), simulated by LMDz-INCA (middle panel) and the relative difference between ACE-FTS and INCA (lower panel). The distribution is calculated over the 2004–2010 period with a $20^\circ \times 20^\circ$ latitude and longitude resolution. The modeled distributions are computed from the simulated acetone profiles interpolated at the observation points. Grid boxes with less than 10 observed profiles are not displayed.

described in [41] and can be found at [<http://www.iiasa.ac.at/web-apps/tnt/RcpDb/>]. These $0.5^\circ \times 0.5^\circ$ emission datasets consist of fluxes of methane, carbon monoxide, nitrogen oxides and 23 non-methane explicit or lumped hydrocarbons for ozone precursors. The individual hydrocarbon fluxes are reported on INCA species or surrogate species as described in Folberth et al. [38], and then spatially interpolated to the model resolution ($3.75^\circ \times 1.9^\circ$).

All natural emissions correspond to a single year representative of present-day levels, except lightning NO_x . The lightning NO_x emissions are computed interactively during the simulations depending on the convective clouds, according to [42], with a vertical distribution based on [43] as described in [44]. The biomass burning emissions are from the Global Fire Emissions Database (GFED 4) inventory [45], available at <http://www.globalfiredata.org>. An oceanic source of 20 Tg/year is considered in this simulation. The ORCHIDEE vegetation model was used (offline) to calculate biogenic surface fluxes of isoprene, terpenes, acetone and methanol as well as NO soil emissions as first described by Lathière et al. [46] and recently updated by Messina et al. [47]. As the continental biosphere is the main primary source of acetone in the atmosphere, we carried out a second simulation, similar to the one described previously, but considering the previous biogenic emissions obtained by Lathière et al. [46] and previously used by

Elias et al. [48]. This second simulation is used to support the discussion in Section 5 and is called HIGH_BIO (Table 5).

4. Annual distribution in the upper troposphere and lower stratosphere

Fig. 6 shows the annual global distribution of acetone in the UT and the LS observed by ACE-FTS and simulated by LMDz-INCA. For the comparison, the daily-simulated concentrations are interpolated at the observation points of ACE-FTS. The distributions are calculated over the 2004–2010 period. ACE-FTS observations show a North–South gradient, with acetone concentrations higher in the Northern hemisphere as expected [1,10,21]. The acetone VMRs are usually the largest over land (Fig. 6, Table 6). Siberia, Central Asia and the Euro-Mediterranean regions present the highest acetone VMRs (~ 600 – 700 ppt). The North Atlantic Ocean, North America and North Pacific have acetone VMRs of 530–570 ppt. In the tropics, the highest concentrations (~ 400 ppt) are observed over Africa and the South Atlantic Ocean. Remind that ACE-FTS acetone might be poorly representative of the climatology for this region (Section 2.3). For the other regions, acetone VMRs are ~ 200 ppt. In the lower stratosphere, VMRs between 250 and 350 ppt are

Table 6

Observed and simulated mean annual acetone VMR and associated biases for different regions of the globe, for the upper troposphere.

Regions	Lat bound.	Lon bound.	ACE-FTS mean (standard deviation)	INCA mean (standard deviation)	Relative bias of the model comp. with ACE-FTS (%)
North Atlantic Ocean	[25; 70]	[−60; −10]	568 (362)	422 (116)	−15
North America	[25; 60]	[−120; −60]	538 (340)	473 (120)	−12
Euro-Mediterranean	[30; 50]	[−10; 40]	605 (289)	449 (112)	−26
Siberia	[50; 70]	[40; 160]	673 (533)	571 (101)	−15
Central Asia	[30; 50]	[60; 100]	611 (380)	491 (129)	−20
East Asia	[20; 50]	[100; 150]	490 (270)	485 (136)	−1
North Pacific Ocean	[30; 50]	[140; −120]	560 (332)	481 (140)	−14
Tropical band	[−30; 30]	[−180; 180]	318 (172)	461 (328)	+45

observed at latitudes north of 30°N and between 150 and 200 ppt elsewhere.

Although a north–south gradient is also simulated by LMDz-INCA, the simulated acetone distribution in the UT does not show similar patterns to those observed by the ACE-FTS (Fig. 6). The model simulates very large acetone concentrations for the high northern latitudes (>70°N) that are not observed by ACE-FTS. Similar behavior of the model has previously been observed for methanol, which has similar emission types and chemistry [17], and was attributed to an insufficient destruction of methanol or an unfaithful representation of transport. In addition, compared with ACE-FTS observations the model underestimates acetone midlatitude VMRs. For the upper troposphere, this underestimation varies depending on the region but reaches up to 26% for the Euro-Mediterranean region and 20% in Central Asia whereas it remains within the ACE-FTS uncertainty interval for Siberia, North America, and North Atlantic Ocean (Table 4). In the tropics, the model is significantly larger than the observations. The lack of sampling in this region combined with the low resolution of the emissions considered in the simulation contributes to the differences. As already discussed in Section 2.3, ACE-FTS is not well suited to get insights about the acetone over the tropical band. In the lower stratosphere, the model tends to overestimate acetone compared with observations. Elias et al. [48] when comparing LMDz-INCA outputs with CARIBIC observations have already pointed out such an overestimation. This smoothing of the vertical gradient across the tropopause in the model may be due to the lack of acetone destruction by HO₂ which is suspected to be a significant loss process near the tropopause [49].

5. Seasonal cycle in the northern hemisphere

In this section we investigate the seasonal variations of acetone for the 30–70°N latitude band, where the sampling is the highest. The midlatitude band (30–70°N) is rather uniformly sampled every month allowing for a good description of the seasonal cycle.

Fig. 5 displays the midlatitude acetone seasonal cycle in the UT and the LS, as observed by the ACE-FTS (top panels) and simulated by LMDz-INCA (bottom panels). The monthly averages are calculated over the 2004–2010 period. In the upper troposphere, a clear seasonal cycle is observed with a maximum (~1000 ppt) in July and a minimum in winter (~190 ppt). This reflects the impact of the primary biogenic emissions of acetone that reach a maximum in summer. The width at half maximum of the cycle extends over 6 months from May to October. For comparison, we approximate the ACE-FTS cycle with a sine function (Fig. 5) and compare it with the seasonal cycle observed by CARIBIC, as reported at the tropopause by Sprung and Zahn [15]. These CARIBIC values should provide at least lower limits for the upper tropospheric cycle. As already mentioned, differences of between 10% and 50% are observed between CARIBIC and ACE-FTS. The maximum of both cycles occurs in July: (22 ± 4) for the ACE-FTS and (15 ± 6) for CARIBIC. The width of the CARIBIC cycle is slightly larger from April to October and shifted to spring, but the amplitude is in good agree-

ment (303 ppt for ACE-FTS, 289 ppt for CARIBIC). A similar fit is applied to the cycle derived from the model: however the model fails to reproduce the observed seasonal cycle. Indeed, the model largely overestimates winter acetone VMRs and does not show seasonal cycle for this latitude band considering the up-to-date biogenic emissions. This lack of a seasonal cycle is due to an underestimation of seasonal variations of the biogenic emissions in the model at mid-high latitudes of the northern hemisphere. When using the biogenic emissions used in Elias et al. [48] a seasonal cycle is obtained despite a global overestimation of the acetone concentrations. This modeled cycle is shifted to autumn with a maximum occurring on 1 October.

In the lower stratosphere, a similar cycle with a maximum in summer (425 ppt in July) and a minimum in winter (~170 ppt in January and February) is identified from the observations (Fig. 5). The LS acetone cycle is in rather good agreement with the cycle derived from CARIBIC measurements 2 km above the tropopause [15], apart from in winter and spring. The maximum of both cycles occurs on (22 ± 22) July for ACE-FTS, on (27 ± 14) August for CARIBIC. The LMDz-INCA model does not exhibit a clear seasonal cycle for either the reference or HIGH-BIOG simulations. The simulated LS acetone tends to be overestimated especially during winter when compared to ACE-FTS and CARIBIC.

Sprung and Zahn [15] reported a temporal shift of about 6 weeks between the maximum in the acetone cycle at the tropopause level and 2 km above, which they interpret as the mean transport time of acetone across the extratropical tropopause transition layer. They also noted that this transport time estimate is affected by large uncertainties. Due to the coarser vertical resolution of ACE-FTS compared to CARIBIC, it is difficult to explore the transport time between levels similar to those of CARIBIC. Considering the UT and LS cycles, presented in Fig. 5, the ACE-FTS data do not exhibit any similar temporal shift. However, the ACE-FTS LS acetone data includes measurements at altitudes from the tropopause to 3 km above. If one considers two distinct altitude levels – one lying close to the tropopause (10.5 km) and one lying mainly in the stratosphere (14.5 km) – a temporal shift of 4 weeks is found. Due to the large uncertainties in the fit, it is difficult to estimate a reliable transition time for transport between the UT and the LS.

6. Conclusion

The objective of this study was to (i) present a recent acetone ACE-FTS research product based on v3.0; (ii) evaluate its capability to describe the acetone variability occurring in the UTLS region; and (iii) discuss its main limitations. Two main points have been addressed:

- ACE-FTS provides a climatological global annual distribution of acetone in the UT and in the LS with a better sampling for the northern latitudes. Comparisons with measurements available in the literature suggest an underestimation of acetone

retrieved from ACE-FTS. The large differences are mainly associated with the background values (occurring largely in the southern latitudes and in the lower stratosphere) and are attributed to the complexity of the spectral region used for the retrieval. The relatively poor sampling of regions such as the tropics limits the ability of ACE-FTS to provide a complete representation of acetone in these regions.

- We show that ACE-FTS has the ability to provide reliable seasonal cycles for the northern midlatitudes. Further studies would be necessary to address the transport time across the tropopause transition layer for these regions. Combined with the various species measured by ACE-FTS such as CO, HCN, and methanol, the acetone retrievals form a meaningful dataset to complement in situ measurements and document the transport of reactive gases in the UTLS region.

Comparisons with the state-of-the-art LMDz-INCA model allow us to identify the model weaknesses in reproducing the acetone distribution in the UTLS. First of all, we show that the model likely overestimates acetone concentrations when they are lower than 400 ppt. The seasonal cycle of the biogenic emissions, which are the main primary sources of acetone in the model, is too weak, especially in the high northern latitudes. Moreover, we show that the vertical distribution simulated by the model leads to overestimated acetone concentrations in the lowermost stratosphere. An underestimation of the destruction of acetone might also be an explanation, particularly in the northern high latitudes. This work demonstrates that the novel ACE-FTS dataset can be used, in addition to the existing airborne datasets, to constrain the acetone budget in the northern hemisphere.

Acknowledgments

J.J.H. wishes to thank the UK Natural Environment Research Council (NERC) for funding some of this work through grant NE/I022663/1 and via the National Centre for Earth Observation (NCEO). The ACE mission is funded primarily by the Canadian Space Agency (CSA). This work has been supported by the CNRS/INSU through the LEFE program (BOTOX project).

References

- [1] H.B. Singh, D. O'Hara, D. Herlth, W. Sachse, D.R. Blake, J.D. Bradshaw, M. Kanakidou, P.J. Crutzen, J. Geophys. Res. 99 (1994) 1805.
- [2] H.B. Singh, M. Kanakidou, P.J. Crutzen, D.J. Jacob, Nature 378 (1995) 50–54.
- [3] F. Arnold, V. Bürger, B. Droste-Fanke, F. Grimm, A. Krieger, J. Schneider, T. Stilp, Geophys. Res. Lett. 24 (1997) 3017–3020.
- [4] L. Jaeglé, D.J. Jacob, P.O. Wennberg, C.M. Spivakovsky, T.F. Hanisco, E.J. Lanzendorf, E.J. Hintsa, D.W. Fahey, E.R. Keim, M.H. Proffitt, E.L. Atlas, F. Flocke, S. Schauffler, C.T. McElroy, C. Midwinter, L. Pfister, J.C. Wilson, Geophys. Res. Lett. 24 (1997) 3181–3184.
- [5] I. Folkins, R. Chatfield, J. Geophys. Res. 105 (2000) 11585.
- [6] L. Jaeglé, Atmos. Environ. 35 (2001) 469–489.
- [7] M. Neumaier, R. Ruhnke, O. Kirner, H. Ziereis, G. Stratmann, C.A.M. Brenninkmeijer, A. Zahn, Geophys. Res. Lett. 41 (2014) 3289–3297.
- [8] M.A. Blitz, D.E. Heard, M.J. Pilling, S.R. Arnold, M.P. Chipperfield, Geophys. Res. Lett. 31 (2004) L06111.
- [9] S.R. Arnold, M.P. Chipperfield, M.A. Blitz, J. Geophys. Res. 110 (2005) D22305.
- [10] D.J. Jacob, B.D. Field, E.M. Jin, I. Bey, Q. Li, J.A. Logan, R.M. Yantosca, H.B. Singh, J. Geophys. Res. 107 (2002) 4100.
- [11] H.B. Singh, A. Tabazadeh, M.J. Evans, B.D. Field, D.J. Jacob, W. Sachse, J.H. Crawford, R. Shetter, W. Brune, Geophys. Res. Lett. 30 (2003) 1862.
- [12] E.V. Fischer, D.J. Jacob, D.B. Millet, R.M. Yantosca, J. Mao, Geophys. Res. Lett. 39 (2012) L01807.
- [13] P.O. Wennberg, T.F. Hanisco, L. Jaeglé, D.J. Jacob, E.J. Hinst, E.J. Lanzendorf, J.D. Anderson, R.-S. Gao, E.R. Keim, S.G. Donnelly, L.A. Del Negro, D.W. Fahey, S.A. McKeen, R.J. Salawitch, C.R. Webster, R.D. May, R.L. Herman, M.H. Proffitt, J.J. Margitan, E.L. Atlas, S. Schauffler, F. Flocke, C.T. McElroy, T.P. Bui, Science 279 (1998) 49–53.
- [14] L.K. Emmons, D.A. Hauglustaine, J.-F. Müller, M.A. Carroll, G.P. Brasseur, D. Brunner, J. Staehelin, V. Thouret, A. Marengo, J. Geophys. Res. 105 (2000) 20497.
- [15] D. Sprung, A. Zahn, J. Geophys. Res. Atmos. 115 (2010) 1–12.
- [16] G. Dufour, C.D. Boone, C.P. Rinsland, P.F. Bernath, Atmos. Chem. Phys. (2006) 3463–3470.
- [17] G. Dufour, S. Szopa, D.A. Hauglustaine, C.D. Boone, C.P. Rinsland, P.F. Bernath, Atmos. Chem. Phys. (2007) 6119–6129.
- [18] G. Dufour, S. Szopa, M.P. Barkley, C.D. Boone, A. Perrin, P.I. Palmer, P.F. Bernath, Atmos. Chem. Phys. 2 (2009) 3893–3910.
- [19] P.-F. Coheur, H. Herbin, C. Clerbaux, D. Hurtmans, C. Wespes, M. Carleer, S. Turquety, C.P. Rinsland, J. Remedios, D. Hauglustaine, C.D. Boone, P.F. Bernath, Atmos. Chem. Phys. 7 (2007) 5437–5446.
- [20] C.P. Rinsland, C.D. Boone, P.F. Bernath, E. Mahieu, R. Zander, G. Dufour, C. Clerbaux, S. Turquety, L. Chiou, J.C. McConnell, L. Neary, J.W. Kaminski, Geophys. Res. Lett. 33 (2006) L23804.
- [21] D.P. Moore, J.J. Remedios, A.M. Waterfall, Atmos. Chem. Phys. 12 (2012) 757–768.
- [22] N. Glatthor, T. von Clarmann, G.P. Stiller, B. Funke, M.E. Koukouli, H. Fischer, U. Grabowski, M. Höpfner, S. Kellmann, A. Linden, Atmos. Chem. Phys. 9 (2009) 9619–9634.
- [23] J.J. Remedios, G. Allen, A.M. Waterfall, H. Oelhaf, A. Kleinert, D.P. Moore, Atmos. Chem. Phys. 7 (2007) 1599–1613.
- [24] C.D. Boone, K.A. Walker, P.F. Bernath, Atmos. Chem. Exp.: ACE, in: Peter F. Bernath (Ed.), A Sol. Occult. Anthol. vol. 10, A. Deep. Publ., Hampton, Virginia, USA, 2013, pp. 103–127.
- [25] D.A. Hauglustaine, F. Hourdin, L. Jourdain, M.-A. Filiberti, S. Walters, J.-F. Lamarque, E.A. Holland, J. Geophys. Res. 109 (2004) D04314.
- [26] P.F. Bernath, C.T. McElroy, M.C. Abrams, C.D. Boone, M. Butler, C. Camy-Peyret, M. Carleer, C. Clerbaux, P.-F. Coheur, R. Colin, P. DeCola, M. DeMazière, J.R. Drummond, D. Dufour, W.F.J. Evans, H. Fast, D. Fussen, K. Gilbert, D.E. Jennings, E.J. Llewellyn, R.P. Lowe, E. Mahieu, J.C. McConnell, M. McHugh, S.D. McLeod, R. Michaud, C. Midwinter, R. Nassar, F. Nichitiu, C. Nowlan, C.P. Rinsland, Y.J. Rochon, N. Rowlands, K. Semeniuk, P. Simon, R. Skelton, J.J. Sloan, M.-A. Soucy, K. Strong, P. Tremblay, D. Turnbull, K.A. Walker, I. Walkty, D.A. Wardle, V. Wehrle, R. Zander, J. Zou, Geophys. Res. Lett. 32 (2005) L15501.
- [27] L.S. Rothman, D. Jacquemart, A. Barbe, D.C. Benner, M. Birk, L.R. Brown, M.R. Carleer, J.C. Chackerian, K. Chance, et al., J. Quant. Spectrosc. Radiat. Transf. 96 (2005) 139–204.
- [28] J.J. Harrison, C.D. Boone, A.T. Brown, N.D.C. Allen, G.C. Toon, P.F. Bernath, J. Geophys. Res. 117 (2012) D05308.
- [29] L.S. Rothman, I.E. Gordon, A. Barbe, D.C. Benner, P.F. Bernath, M. Birk, V. Boudon, L.R. Brown, A. Campargue, J.P. Champion, K. Chance, L.H. Coudert, V. Dana, V.M. Devi, S. Fally, J.M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, I. Kleiner, N. Lacome, W.J. Lafferty, J.Y. Mandin, S.T. Massie, S.N. Mikhailenko, C. E. Miller, N. Moazzen-Ahmadi, O.V. Naumenko, A.V. Nikitin, J. Orphal, V.I. Perevalov, A. Perrin, A. Predoi-Cross, C.P. Rinsland, M. Rotger, M. Šimečková, M. A.H. Smith, K. Sung, S.A. Tashkun, J. Tennyson, R.A. Toth, A.C. Vandaele, J. Vander Auwera, J. Quant. Spectrosc. Radiat. Transf. 110 (2009) 533–572.
- [30] L.S. Rothman, I.E. Gordon, Y. Babikov, A. Barbe, D. Chris Benner, P.F. Bernath, M. Birk, L. Bizzocchi, V. Boudon, L.R. Brown, A. Campargue, K. Chance, E.A. Cohen, L.H. Coudert, V.M. Devi, B.J. Drouin, A. Fayt, J.M. Flaud, R.R. Gamache, J.J. Harrison, J.M. Hartmann, C. Hill, J.T. Hodges, D. Jacquemart, A. Jolly, J. Lamouroux, R.J. Le Roy, G. Li, D.A. Long, O.M. Lyulin, C.J. Mackie, S.T. Massie, S. Mikhailenko, H.S.P. Müller, O.V. Naumenko, A.V. Nikitin, J. Orphal, V. Perevalov, A. Perrin, E.R. Polovtseva, C. Richard, M.A.H. Smith, E. Starikova, K. Sung, S. Tashkun, J. Tennyson, G.C. Toon, V.G. Tyuterev, G. Wagner, J. Quant. Spectrosc. Radiat. Transf. 130 (2013) 4–50.
- [31] J.J. Harrison, N. Humpage, N.D.C. Allen, A.M. Waterfall, P.F. Bernath, J.J. Remedios, J. Quant. Spectrosc. Radiat. Transf. 112 (2011) 457–464.
- [32] J.J. Harrison, M.P. Chipperfield, A. Dudhia, S. Cai, S. Dhomse, C.D. Boone, P.F. Bernath, Atmos. Chem. Phys. 14 (2014) 11915–11933.
- [33] G.L. Manney, W.H. Daffer, J.M. Zawodny, P.F. Bernath, K.W. Hoppel, K.A. Walker, B.W. Knosp, C. Boone, E.E. Remsburg, M.L. Santee, V.L. Harvey, S. Pawson, D.R. Jackson, L. Deaver, C.T. McElroy, C.A. McLinden, J.R. Drummond, H.C. Pumphrey, A. Lambert, M.J. Schwartz, L. Froidevaux, S. McLeod, L.L. Takacs, M.J. Suarez, C.R. Trepte, D.C. Cuddy, N.J. Livesey, R.S. Harwood, J.W. Waters, J. Geophys. Res. 112 (2007) D24S50.
- [34] H.A. Scheeren, H. Fischer, J. Lelieveld, P. Hoor, J. Rudolph, F. Arnold, B. Bregman, C. Brühl, A. Engel, C. van der Veen, D. Brunner, J. Geophys. Res. Atmos. 108 (2003) 4805.
- [35] H.B. Singh, L.J. Salas, R.B. Chatfield, E. Czech, A. Fried, J. Walega, M.J. Evans, B.D. Field, D.J. Jacob, D. Blake, B. Heikes, R. Talbot, G. Sachse, J.H. Crawford, M.A. Avery, S. Sandholm, H. Fuelberg, J. Geophys. Res. 109 (2004) D15S07.
- [36] G. Kriener, N. Viovy, N. de Noblet-Ducoudré, J. Ogée, J. Polcher, P. Friedlingstein, P. Ciais, S. Sitch, I.C. Prentice, Global Biogeochem. Cycl. 19 (2005) GB1015.
- [37] F. Hourdin, M.-A. Foujols, F. Codron, V. Guemas, J.-L. Dufresne, S. Bony, S. Denvil, L. Guez, F. Lott, J. Ghattas, P. Braconnot, O. Marti, Y. Meurdesoif, L. Bopp, Clim. Dyn. 40 (2012) 2167–2192.
- [38] G.A. Folberth, D.A. Hauglustaine, J. Lathière, F. Brocheton, Atmos. Chem. Phys. 6 (2006) 2273–2319.
- [39] S. Szopa, Y. Balkanski, M. Schulz, S. Bekki, D. Cugnet, A. Fortems-Cheiney, S. Turquety, A. Cozic, C. Déandres, D. Hauglustaine, A. Idelkadi, J. Lathière, F. Lefevre, M. Marchand, R. Vuolo, N. Yan, J.-L. Dufresne, Clim. Dyn. 40 (2012) 2223–2250.
- [40] D. Li, K.P. Shine, A 4-D Ozone Climatology for UGAMP Models, UGAMP Internal Report, U. K. Univ. Global Atmos. Model. Programme, Swindon, 1995.
- [41] K. Riahi, A. Gruebler, N. Nakicenovic, Technol. Forecast. Soc. Change 74 (2007) 887–935.
- [42] C. Price, D. Rind, J. Geophys. Res. Atmos. 97 (1992) 9919–9933.

- [43] K.E. Pickering, Y. Wang, W.-K. Tao, C. Price, J.-F. Müller, *J. Geophys. Res.* 103 (1998) 31203.
- [44] L. Jourdain, D.A. Hauglustaine, *Phys. Chem. Earth* 26 (2001) 585–591.
- [45] L. Giglio, J.T. Randerson, G.R. van der Werf, *J. Geophys. Res. Biogeosci.* 118 (2013) 317–328.
- [46] J. Lathière, D.A. Hauglustaine, A.D. Friend, N. De Noblet-Ducoudré, N. Viovy, G. A. Folberth, *Atmos. Chem. Phys.* 6 (2006) 2129–2146.
- [47] P. Messina, J. Lathière, K. Sindelarova, N. Vuichard, C. Granier, J. Ghattas, A. Cozic, D.A. Hauglustaine, Global biogenic volatile organic compound emissions in the ORCHIDEE and MEGAN models and sensitivity to key parameters, *Atmos. Chem. Phys. Discuss.* 15 (2015) 33967–34033, <http://dx.doi.org/10.5194/acpd-15-33967-2015>.
- [48] T. Elias, S. Szopa, A. Zahn, T. Schuck, C. Brenninkmeijer, D. Sprung, F. Slemr, *Atmos. Chem. Phys.* 11 (2011) 8053–8074.
- [49] T.J. Dillon, A. Pozzer, L. Vereecken, J.N. Crowley, J. Lelieveld, *Atmos. Chem. Phys.* 12 (2012) 1339–1351.