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**Atmospheric C₂–C₅
alkanes**

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Observed and simulated global distribution and budget of atmospheric C₂–C₅ alkanes

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Abstract

The primary sources and atmospheric chemistry of C₂–C₅ alkanes have been incorporated into the atmospheric chemistry general circulation model EMAC. Model output is compared with new observations from the NOAA/ESRL GMD cooperative air sampling network. Based on the global coverage of the data, two different anthropogenic emission datasets for C₄–C₅ alkanes, widely used in the modelling community, are evaluated. We show that the model reproduces the main atmospheric features of the C₂–C₅ alkanes (e.g., seasonality). While the simulated values of ethane and propane are within a 20% range of the measurements, larger deviations are found for the other tracers. Finally the effect of C₃–C₅ alkanes on the concentration of acetone and acetaldehyde are assessed. Their chemical sources are largely controlled by the reaction with OH, while the reactions with NO₃ and Cl contribute only to a little extent. The total amount of acetone produced by propane, *i*-butane and *i*-pentane oxidation is 11.2 Tg/yr, 4.2 Tg/yr and 5.8 Tg/yr, respectively. Moreover, 3.1, 3.3, 1.4 and 4.8 Tg/yr of acetaldehyde are formed by the oxidation of propane, *n*-butane, *n*-pentane and *i*-pentane, respectively.

1 Introduction

Non Methane Hydrocarbons (NMHC) play an important role in tropospheric chemistry and ozone formation. They significantly influence the hydroxyl radical HO_x (=OH+HO₂) budget through many complex reaction cycles (Logan, 1985; Houweling et al., 1998; Seinfeld and Pandis, 1997; Atkinson, 2000). For example, NMHC are precursors of the formation of oxygenated volatile organic compounds (OVOC) such as acetone, formaldehyde and acetaldehyde. The seasonal and spatial distribution of NMHC is determined by:

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- emission strength (Singh et al., 2001, 2003; Singh and Zimmermann, 1992),
- photochemical reactions (Cardelino and Chameides, 1990; Singh et al., 1995; Neeb, 2000),
- atmospheric transport (Rood, 1987; Brunner et al., 2003),
- dilution due to atmospheric mixing (Roberts et al., 1985; Parrish et al., 2007).

Three-dimensional (3-D) global models, which represent both transport and chemical processes, allow to study and predict the spatial distribution and the temporal development of these species (Gupta et al., 1998; Roelofs and Lelieveld, 2000; Poisson et al., 2000; von Kuhlmann et al., 2003b; Folberth et al., 2006). Here we compare results of the EMAC (ECHAM5/MESSy1 Atmospheric Chemistry) model with data based on flask measurements (see Sect. 3) collected at remote locations across the globe during the years 2005–2008. The NMHC flask measurements (Pollmann et al., 2008) include ethane (C₂H₄), propane (C₃H₈), butane (or *n*-butane, C₄H₁₀), isobutane (or *i*-butane, I-C₄H₁₀), pentane (or *n*-pentane, C₅H₁₂) and isopentane (or *i*-pentane, I-C₅H₁₂).

In Sect. 2 the model is presented: two simulations (“E1” and “E2”), based on two different emission databases for butanes (i.e. *n*-butane plus *i*-butane) and pentanes (i.e. *n*-pentane plus *i*-pentane), are described. Then, the observational data set (Sect. 3) is described, followed by a comparison between model results and observations (Sect.4). Finally, we discuss the contribution of C₂–C₅ alkanes to the atmospheric production and mixing ratios of the most important OVOC (Sect. 5), with a focus on the acetone budget.

2 Model description and setup

EMAC is a combination of the general circulation model ECHAM5 (Roeckner et al., 2006) (version 5.3.01) and the Modular Earth Submodel System (MESSy, version 1.1, Jöckel et al., 2005). A first description and evaluation of the model system has been

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published by Jöckel et al. (2006) and Pozzer et al. (2007). Details about the model system can be found at <http://www.messy-interface.org>. The setup is based on that of the evaluation simulation “S1”, described by Jöckel et al. (2006). It was modified by adding the emissions of butane and pentane isomers, and their corresponding oxidation pathways (see Sect. 2.2 and Sect. 2.1).

The simulation period covers the years 2005–2008, plus two additional months of spin-up time. The initial conditions are taken from the evaluation simulation “S1” of the model. Dry and wet deposition processes are described by Kerkweg et al. (2006a) and Tost et al. (2006), respectively, while the tracer emissions are described by Kerkweg et al. (2006b). As in the simulation “S1”, the spectral truncation of the ECHAM5 base model is T42, corresponding to an horizontal resolution of $\approx 2.8^\circ \times 2.8^\circ$ of the quadratic Gaussian grid. The applied vertical resolution is 90 layers, with about 25 levels in the troposphere. The model setup includes feedbacks between chemistry and dynamics via radiation calculations. The model dynamics was weakly nudged (Jeuken et al., 1996; Jöckel et al., 2006; Lelieveld et al., 2007) towards the analysis data of the ECMWF (European Center Medium-range Weather Forecast) operational model (up to 100 hPa) to realistically represent the tropospheric meteorology of the selected period. This allows the direct comparison of model results with observations.

2.1 Chemistry

The chemical kinetics within each grid-box is calculated with the submodel MECCA (Sander et al., 2005). The set of chemical equations solved by the Kinetic PreProcessor (KPP, Damian et al. (2002); Damian-lordache (1996)) in this study is essentially the same as in Jöckel et al. (2006). However, the propane oxidation mechanism (which was already included in the original chemical mechanism) has been slightly changed, and new reactions for the butane and pentane isomers have been added.

The complete list of differences from the original chemical mechanism used in Jöckel et al. (2006) is presented in the electronic supplement (<http://www.atmos-chem-phys-discuss.net/10/615/2010/acpd-10-615-2010-supplement.pdf>). The

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new reactions are a reduction of the corresponding detailed Master Chemical Mechanism (MCM, Saunders et al., 2003). In order to keep the number of reactions as low as possible for 3-D global simulations, the first generation products of the reactions of butanes and pentanes with OH, NO₃, and Cl were directly substituted with their final degradation products formaldehyde, acetaldehyde and acetone. This substitution includes the production of corresponding amounts of a model peroxy radical (RO₂), which has generic properties representing the total number of RO₂ produced during the “instantaneous oxidation”. With this approach we take into account the NO → NO₂ conversions and the HO₂ → OH interconversion. It is assumed that the reactions with OH and NO₃ have the same product distribution. The Cl distribution was nudged with monthly average mixing ratios taken from Kerkweg et al. (2008a,b, and references therein). Thus, both alkanes and Cl are simulated without the need of a computationally expensive chemical mechanism.

Finally, the OH concentration is very important for a correct simulation of NMVC. Jöckel et al. (2006) performed a detailed evaluation of the simulated OH abundance. In summary, OH compared very well with that of other models of similar complexity. Compared to Spivakovsky et al. (2000), the EMAC simulation of OH indicated slightly higher values in the lower troposphere and lower values in the upper troposphere. We refer to Jöckel et al. (2006) for further details.

2.2 Emissions

2.2.1 Anthropogenic emissions

As pointed out by Jobson et al. (1994) and Poisson et al. (2000), the seasonal change in the anthropogenic emissions of NMHC are thought to be small, due to their relatively constant release from fossil fuel combustion and leakage from oil and natural gas production (Middleton et al., 1990; Blake and Rowland, 1995; Friedrich and Obermeier, 1999). The most detailed global emission inventory available is EDGAR (Olivier et al., 1999, 1996; van Aardenne et al., 2001), Emission Database

for Global Atmospheric Research, which was applied for the evaluation simulation of EMAC (Jöckel et al., 2006).

In the evaluation simulation “S1” of the model (Jöckel et al., 2006), the anthropogenic emissions were taken from the EDGAR database (version 3.2 “fast-track”, van Aardenne et al., 2005) for the year 2000. In order to keep the model as consistent as possible with the evaluation simulation “S1”, the ethane and propane emissions were not changed and an annual global emission of 9.2 and 10.5 Tg/yr respectively, as reported by Pozzer et al. (2007) was applied.

Furthermore, the total butanes and pentanes emissions from EDGARv2.0 were used, being 14.1 Tg/yr and 12.3 Tg/yr, respectively. The simulation with these emissions for butanes and pentanes is further denoted as “E1”. Based on speciation factors described below, the totale emissions are 9.9 Tg/yr for *n*-butane (70% of all butanes), 4.2 Tg/yr for *i*-butane (30% of all butanes), 4.3 Tg/yr for *n*-pentane (35% of all pentanes) and 8.0 Tg/yr for *i*-pentane (65% of all pentanes).

It must be stressed that the EDGAR database was criticized for the inaccuracies in the C₄–C₅ alkanes emissions. As pointed out by Jacob et al. (2002), “. . . the EDGAR inventory underestimates considerably the observed atmospheric concentration of propane and *i*-butane over Europe, over the United States and downwind Asia”. Based on these considerations, Jacob et al. (2002) suggested a different emission inventory distribution, as described by Bey et al. (2001). From this distribution, Jacob et al. (2002) estimated a total of of 9.9, 4.2, 3.2 and 6.0 Tg/yr emission of *n*-butane, *i*-butane, *n*-pentane and *i*-pentane respectively, with the same isomer speciation factors used before.

To evaluate which emissions database describes butanes and pentanes most realistically, an additional simulation (denoted “E2”) was performed, with butanes and pentanes emissions distribution as suggested by Bey et al. (2001). The total butanes emission used in simulation “E2” is the one estimated by Jacob et al. (2002), which are also the same total emission of butanes from the EDGARv2.0 database. Differently, for pentanes, the total emission estimated by Jacob et al. (2002) seriously

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underestimates the observed mixing ratios of these tracers in a sensitivity simulation (not shown). Hence, the total amount of pentanes used in simulation “E2” was scaled to 12.3 Tg/yr, the same total amount estimated from the EDGARv2.0 database. In conclusion, the same total emissions for butanes and pentanes are used in both simulation “E1” and “E2”, although with a different spatial distribution. The total amount emitted in both simulation “E1” and “E2” is 9.9, 4.2, 4.3, 8.0 Tg/yr for *n*-butane *i*-butane, *n*-pentane and *i*-pentane, respectively.

The speciation fractions used for *i*-butane (30%) and *n*-butane (70%), and for *i*-pentane (65%) and *n*-pentane (35%) are from the calculation of Saito et al. (2000) and Goldan et al. (2000), respectively.

These fractions have been confirmed by McLaren et al. (1996), who showed that the ratio of *n*-pentane to *i*-pentane is 0.5 (i.e. a fraction of ~66% for *i*-pentane and ~34% for *n*-pentane over total pentanes). The long measurement from the NOAA flask data set also confirm these speciation factors. Almost all the measurements present in the database, independent on the spatio/temporal location, are shown in Fig. 1, with the exception of data with very high uncertainties, i.e. observations of mixing ratios lower than 1 pmol/mol or greater than 1000 pmol/mol. As shown in Fig. 1, the fraction of *i*-butane of the total butanes is ~0.33, while the fraction of *i*-pentane of the total pentanes is ~0.65. These values are in close agreement with the speciation factors present in previous literature.

2.2.2 Biomass burning

Biomass burning is a large source of ethane and propane, and a negligible source of butane and pentane isomers (Andreae and Merlet, 2001; Guenther et al., 2000). Blake et al. (1993) extrapolated the total emission from biomass burning of 1.5 Tg/yr for ethane, and 0.6 Tg/yr for propane. Rudolph (1995) suggested instead 6.4 Tg/yr for ethane. The biomass burning contribution was added using the Global Fire Emissions Database (GFED version 1, Van der Werf et al. (2004)) for the year 2000 (without interannual variability) scaled with different emissions factors (Andreae and Merlet,

2001; von Kuhlmann et al., 2003a). The total amounts calculated are 2.76 Tg/yr and 0.86 Tg/yr for ethane and propane, respectively. No biomass burning emission was included for C₄–C₅ alkanes, due to its low impact in the global budget of these tracers.

2.2.3 Biogenic emissions

5 Biogenic sources of C₂–C₅ alkanes appear to be negligibly small (Kesselmeier and Staudt, 1999; Guenther et al., 1995). Other measurements in rural environments (Johnson et al., 1994; Goldan et al., 1995) show no evidence of biogenic emissions of saturated C₂–C₅ NMHC.

2.2.4 Oceanic emissions

10 Alkanes are also emitted by the oceans. Plass-Dülmer et al. (1995) estimated 1 Tg/yr as upper limit for the global emission of C₂–C₄ alkanes: 0.54 Tg/yr of ethane, 0.35 Tg/yr of propane and 0.11 Tg/yr of butanes (*n*-butane + *i*-butane). Broadgate et al. (1997) extrapolated global oceanic emissions to 0.04 Tg/yr for *i*-butane, 0.17 Tg/yr for *n*-butane, 0.03 Tg/yr for *i*-pentane, and 0.06 Tg/yr for *n*-pentane.

15 While oceanic emissions for ethane and propane were included in this study, oceanic emissions of higher alkanes were neglected due to their small impact and largely unknown spatio-temporal distributions.

2.2.5 Other sources

20 Etioppe and Ciccioli (2009) proposed a geophysical (volcanic) source of ethane and propane. Based on observations of gas emissions from volcanoes, they estimated an emissions of 2 to 4 Tg/yr for ethane and of 1 to 2.4 Tg/yr for propane. However, since the emission distribution is unknown, it is not yet feasible to include this source into the model. In addition, results from our simulations do not support a further increase in the emissions of these tracers (see below, Sects. 4.1–4.2).

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3 Observations

The NOAA ESRL GMD (National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division, Boulder, CO, USA) cooperative air sampling network currently includes 59 active surface sampling stations, where usually one pair of flask samples is collected every week. This network is the most extensive global flask sampling network in operation, both in terms of number of sites and total number of samples collected. NMHC data are available from approximately 40 of these sampling stations (see <http://www.esrl.noaa.gov/gmd/>), covering the latitudes from 82° N (ALT, Alert, Canada) to 89.98° S (SPO, South Pole). However, the measurements collected from the stations are not homogeneously distributed in time and some gaps are present in the data. A variable number of measurements have been used to form the monthly averages used here, and the relative monthly variability was calculated as the monthly standard deviation of the measurements. Air samples are typically taken during pre-defined clean air periods, i.e., from specific wind directions only.

A detailed description of the flask instrument and a full evaluation of the analytical technique was previously published (Pollmann et al., 2008).

An intercomparison with the WMO GAW (World Meteorological Organization, Global Atmospheric Watch) station in Hohenpeissenberg, Germany showed that flask measurements meet the WMO data quality objective (World Meteorological Organization, 2007). These findings were confirmed during a recent audit by the World Calibration Center for Volatile Organic Compound (WCC-VOC, <http://imk-ifu.fzk.de/wcc-voc/>).

4 Comparison of the model results with observations

In this section results from only a selected number of sites are presented. The complete series of figures can be found in the electronic supplement of this paper (<http://www.atmos-chem-phys-discuss.net/10/615/2010/acpd-10-615-2010-supplement.pdf>). For

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ethane and propane, only results from the simulation “E1” are shown, as in simulation “E2” the same sources are applied for these tracers. Results from both simulations are presented for butanes and pentanes.

As explained in Sect. 1 and also confirmed by measurements (Gautrois et al., 2003; Lee et al., 2006; Swanson et al., 2003), the seasonal cycle of NMHC exhibits a maximum corresponding to the local winter and a minimum corresponding to the local summer. Hagerman et al. (1997) and Sharma et al. (2000) showed that the seasonal cycle of C₂–C₅ alkanes is anti-correlated with the production rate of the main atmospheric oxidant (OH, see Spivakovsky et al., 2000; Jöckel et al., 2006). The flask measurements used in this study confirm this and the model is able to reproduce the observed seasonal signal, with high mixing ratios during winter and low mixing ratios during summer.

4.1 Ethane, C₂H₆

In Fig. 2 a comparison of the observations and the model simulation is shown for a number of locations. Both simulations (“E1” and “E2”) present the same model results, having the same chemistry/meteorology and the same emissions for this tracer; hence simulated results from one simulation only are shown. Notice that the seasonal cycle is correctly reproduced, although the model simulates a too low mixing ratio of ethane during the Northern Hemisphere (NH) winter (e.g., Alert, Canada (ALT) and Barrow, Alaska (BRW)). On the other hand, the NH summer mixing ratios are reproduced correctly within the model/observation monthly variability (calculated as the monthly standard deviation of the observations). In the Southern Hemisphere (SH) the results are more difficult to interpret. Although the southern extratropics seem to be well simulated (see CRZ, Crozet Island, France), for polar sites (as an example HBA, Halley Station, Antarctica) the model tends to simulate higher mixing ratios than observed. Fig. 3 shows the latitudinal gradients and the seasonal cycle from observations and as calculated by the model. The model is able to reproduce the correct latitudinal gradients during all seasons with a strong north-south gradient at the equator.

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4.2 Propane, C₃H₈

As also shown in a previous analysis (Poizzer et al., 2007), the model simulation reproduces the main features observed for propane. The amplitude and phase of the simulated seasonal cycle also agree well with this new observational data set. As shown in Fig. 4, the seasonal cycle is well reproduced at the Northern Hemispheric sites (ALT and BRW) representing background conditions. Moreover, Fig. 5 shows that not only the seasonal cycle is correctly reproduced, but also the latitudinal gradient.

Generally, the model simulations agree very well with the observations in the NH (where most of the emissions are located). However, at some locations (for example MHD, Mace Head, Ireland and LEF, Park Falls, USA) the model slightly overestimates the observed mixing ratios of propane.

In addition, in the SH the simulated mixing ratios seem to be somewhat higher than the observations, especially during the SH winter (June, July and August) in remote regions, and during summer (January and February) in the SH extratropics.

Clearly, these findings do not support a further increase of the emissions compared to the data used here.

4.3 *n*-butane, C₄H₁₀

As mentioned in Sect. 4, the phase of the seasonal cycle of *n*-butane calculated from model results from “E1” and “E2” reproduces the observations (Fig. 6). As observed by Blake et al. (2003) during the TOPSE campaign and also shown by the model, *n*-butane is removed quite rapidly at the onset of summer in all regions, and it is reduced to low levels (almost depleted, with single digit ppt levels) by late spring, except at the highest latitudes. Examples are given in Fig. 6 for ALT and BRW, where the simulated mixing ratios (both in simulation “E1” and “E2”) decrease from ~300–400 pmol/mol in April to ~1–2 pmol/mol in June and remain at this level during the NH summer (July and August).

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In general, simulation “E1” (based on anthropogenic emissions taken from the EDGAv2.0 database) produces higher mixing ratios at almost all locations in the NH compared to simulation “E2”. The opposite is the case in the SH, with lower mixing ratios in “E1” than in “E2”.

Simulation “E1” seems to systematically overestimate the winter maximum in the NH (see Fig. 6, ALT and CBA, Cold Bay, USA, and many others) while simulation “E2” is closer to the observed mixing ratios.

Overall, for many stations, simulation “E2” better represents the observed mixing ratios than “E1”. This is evident at some locations (for example MHD).

Although a fair agreement of simulation “E2” with the observations is achieved at Midway Island (MID), and Cape Kumukahi (KUM), two typical marine boundary layer (MBL) background stations, the model underestimates the observed mixing ratios in the NH summer at these locations. This indicates that a nearby source of *n*-butane may be present, hence that oceanic emissions potentially play a significant role.

In the SH, both model simulations seem to underestimate *n*-butane mixing ratios, with almost a total depletion during SH summer at remote locations, which is not observed in the flask data. While both model set-ups simulate values below 1 pmol/mol (~ 0.5 – 0.6 pmol/mol) during SH summer (December, January and February), the observations indicate ~ 10 pmol/mol. This difference suggests localized *n*-butane emissions from the ocean. Additional high precision measurements of this tracer are needed to assess the role of the ocean in these remote areas.

4.4 *i*-butane, I–C₄H₁₀

A different picture arises for *i*-butane, for which it is difficult to clearly establish which simulation reproduces the observed mixing ratios better, due to the different performance of the model simulations at different locations.

Generally, the simulated mixing ratios from “E1” are at the high end of the observed range for stations in the NH during the NH winter. In contrast, simulated mixing ratios from “E2” are at the low end of the observed range for the same locations

(see, for example, Fig. 7, ALT, and CBA, Cold Bay, USA). As for *n*-butane, in the SH both model simulations underestimate the observed mixing ratios (see Fig. 7, HBA). Please note that these measurements are close to the NMHC method detection limit, causing an increase of the analytical uncertainty in these data.

Simulation “E1” does not underestimate *i*-butane in the USA and Europe, in contrast to the results obtained by Jacob et al. (2002). On the contrary, for the USA stations (see Fig. 7, LEF) “E1” shows a slight overestimation or (see Fig. 7, UTA) a good agreement with the observations, whereas simulation “E2” is too high. For Europe, both simulations “E1” and “E2” overestimate the observed mixing ratios (see Fig. 7, Ochsenkopf station, OXK, Germany), where the discrepancy is largest for “E2”. It must be stressed that both simulations present a large variability at Ochsenkopf station.

The coarse grid resolution hence prevents us from deciding which emission database is best in reproducing European or USA emissions. It is actually expected that simulation “E2” reproduces observations in the USA better than simulation “E1”, because the Bey et al. (2001) emissions database was calculated based on USA data (see Wang et al., 1998). However, this is not always the case; in particular, at Park Falls (LEF), simulation “E2” is better than simulation “E1” and, in contrast, at Wendorfer (UTA) simulation “E1” is better than “E2”.

For the SH, due to the low mixing ratios of *i*-butane (close to instrumental detection limit) and the high variability of the observations, it is difficult to draw a firm conclusion. However, at Halley Bay Station (HBA, Antarctica) simulation “E2” reproduces the first year of observation (2005) better than “E1”.

4.5 *n*-pentane, C₅H₁₂

As for *i*-butane, also for this tracer it is difficult to establish clearly which simulation better represents the observations, as both agree well with the observed values at the remote locations in the NH. For example (see Fig. 8) at BRW simulation “E1” reproduces very well the observed mixing ratios, while in contrast at Storhofdi, Iceland (ICE), the results from simulation “E2” are better in agreement with the measurements.

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The simulated mixing ratios are lower than observed throughout all seasons in the tropics and in the SH (Fig. 8, BKT, Bukit Kototabang, Indonesia, and HBA, Antarctica) in both simulations “E1” and “E2”. However, as mentioned earlier, in SH remote regions the mixing ratios are close to the instrumental detection limits and the instrumental error could be relatively large. Nevertheless, a bias between the model results and the observations is evident; the short lifetime of C₅H₁₂ (shorter than the interhemispheric exchange time), indicates that the emissions are generally underestimated in the SH. This is corroborated by similar results for *i*-pentane (see also Sect. 4.6).

4.6 *i*-pentane, I–C₅H₁₂

In contrast to *n*-pentane, in the NH the mixing ratios from simulation “E2” agree rather well with the observations (see Fig. 9) while results from simulation “E1” generally overestimate the measurements. In simulation “E1” the overestimation in the NH remote regions (see Fig. 9, ALT) is strongest during the NH winter, with a difference of a factor of 2. On the other hand, the model (both simulation “E1” and “E2”) tends to underestimate the mixing ratios of I–C₅H₁₂ in the NH subtropics and in the SH (see Fig. 9, MID and KUM). As mentioned in Sect. 4.5, this points to a partially wrong distribution of the emissions in the model, which are located almost exclusively in the NH, notably in the industrialised regions.

4.7 Global C₂–C₅ alkanes budgets

Following the analyses performed in Sects. 4.1–4.6, a global inventory of C₂–C₅ alkanes emissions is shown in Table 1. Anthropogenic emissions are the most important sources in the budget of these tracers, ranging from ~75% (for ethane) to ~98% (for butanes and pentanes) of the total emissions. For butanes and pentanes, the dataset presented by Bey et al. (2001) (with an increase total emissions for pentanes) gives the best results with the EMAC model, and is recommended for future studies of these

tracers. For ethane and propane, the model simulation with the EDGARv3.2 fast-track database gives satisfactory results.

Biomass burning is the second major source, being very important for ethane and propane, within $\sim 22\%$ and $\sim 7\%$ of the total sources, respectively. As shown by Helmig et al. (2008), biomass burning effects on C_3 – C_5 alkanes is generally sporadic. Hence, the monthly average values of the observational dataset used here generally masked the biomass burning signal that could be observed. In addition the model resolution and the low estimated value limited the possible informations to evaluate realistically this type of emission. These values could hence not be confirmed by our study and are reported as suggested in the literature.

Oceanic emissions play a small role in the budget only for ethane and propane. The theoretical magnitude of oceanic emission for C_4 – C_5 is comparable to the one of biomass burning, and hence too weak to be clearly distinguished in the observational dataset. Nevertheless, our analysis suggests that oceanic emissions can play a more significant role also for butanes and pentanes, at least at some locations.

5 Contributions to the atmospheric budget of some OVOC

5.1 Acetone formation

Acetone (CH_3COCH_3), due to its photolysis, plays an important role in the upper tropospheric HO_x budget (Singh et al., 1995; McKeen et al., 1997; Müller and Brasseur, 1995; Wennberg et al., 1998; Jaeglé et al., 2001). Moreover, this trace gas is essential to correctly describe the ozone enhancement in flight corridors (Brühl et al., 2000; Folkins and Chatfield, 2000). Oxidation of propane and C_4 – C_5 isoalkanes (Singh et al., 1994) has been estimated to be $\sim 22\%$ of the total sources of acetone (Jacob et al., 2002).

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The transport and chemical production of acetone were explicitly calculated with EMAC. Globally, the total production of acetone from C₃–C₅ alkanes is 21.2 Tg/yr in both simulation “E1” and simulation “E2”. The propane decomposition, with a yield of 0.73, produces ~11.2 Tg/yr of acetone, which is higher than the total production of acetone from C₄–C₅ isoalkanes oxidation, namely 10 Tg/yr. In fact, *i*-butane oxidation produces 4.2 Tg/yr acetone, while 5.8 Tg/yr of acetone are produced by *i*-pentane oxidation. This is the same for both simulations, because total emissions are equal.

Despite the fact that both simulations produce the same amount of acetone, the production is distributed quite differently in the two simulations.

As shown in Fig. 10, simulation “E1” indicates a pronounced acetone production over the middle East and Persian Gulf, northern Europe and western USA, compared to simulation “E2”. On the other hand, simulation “E2” indicates stronger production of acetone in the eastern USA, China and in the SH. In both model simulations, CH₃COCH₃ is produced almost solely by the reaction of the iso-alkanes with OH; the contributions of the reactions with Cl and NO₃ are negligible, being less than 0.5% of the total.

Our result partially confirms the conclusion of Jacob et al. (2002), who calculated an acetone production of 14 Tg/yr, 4.0 Tg/yr and 2.6 Tg/yr from propane, *i*-butane and *i*-pentane, respectively. The different acetone production between the work of Jacob et al. (2002) (present for propane and *i*-pentane decomposition) arise from the different emissions and/or the acetone yield. For instance, Jacob et al. (2002) used an acetone yield of 0.52 for *i*-pentane (from the reaction with OH). In our study an acetone yield of ~0.90 from *i*-pentane was obtained. In addition the *i*-pentane emissions are substantially different, being 6.0 and 8.0 Tg/yr in the work of Jacob et al. (2002) and our work, respectively. For propane, the acetone yield is very similar (0.72) to the one obtained here (0.73), but a difference in the emissions (13.5 vs 11.7 Tg/yr) causes a slight difference in the acetone production.

Because the “E2” results reproduce *i*-butane and *i*-pentane better, we use this model simulation for the comparison to the evaluation simulation “S1” (see Sect. 2). The “S1” analysis did not account for NMHC with more than 4 carbons and their subsequent atmospheric reactions. This allows us to evaluate the effect of higher NMHC on acetone.

The resulting increase of the acetone mixing ratios is evident, especially in the NH. As shown in Fig. 11, the acetone mixing ratio increased at the surface between 100 and 300 pmol/mol in NH remote regions, with the highest values reached in locations downwind of polluted regions (for example over the Pacific and Atlantic Ocean). The relative effect in polluted regions is smaller (maximum increase ~30%) due to the strong anthropogenic emission of acetone. However, the contributions from the alkanes oxidation are significant (up to 1 nmol/mol). The strongest production regions are located over polluted regions such as the eastern USA, the Mediterranean area and the China-Japan region. Here the maximum effect of C₄–C₅ alkanes on acetone is achieved, with an increase of ~1 nmol/mol. The mixing ratio of acetone in the SH is practically not affected by chemical formation from iso-alkanes, with the exception of a few locations in South America, simply because they are mainly emitted in the NH. This, combined with their short lifetime (shorter than the interhemispheric exchange time), confine the iso-alkanes to decompose and produce acetone only in the NH.

To confirm the improvements in the acetone budget obtained by including the C₄–C₅ alkanes, the model simulation was compared with field data reported by Emmons et al. (2000). In Fig. 12, we show only campaigns performed in the NH where the differences between simulations “E2” and “S1” are largest. We refer to Pozzer et al. (2007) and the electronic supplement (<http://www.atmos-chem-phys-discuss.net/10/615/2010/acpd-10-615-2010-supplement.pdf>) for the complete comparison.

The inclusion of the C₄–C₅ alkanes chemistry substantially increases the mixing ratios of acetone in the North Pacific region (PEM-Tropics-B and PEM-West-B). In these cases, the increase is ~50% compared to a simulation without C₄–C₅ alkanes. The simulated mixing ratios thus agree much better with the measurements. Especially

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below 5 km altitude, the simulated vertical profiles are closer to the observations, being improved compared to simulation “S1”. In a polluted region (TRACE-P, Fig. 12) downwind of China, the inclusion of C₄–C₅ compounds improves the simulation of acetone. The underestimation of the free-troposphere mixing ratios seems to support the revision of the acetone quantum yield, as proposed by Blitz et al. (2004). Arnold et al. (2005), in fact, calculated an average increase of ~60–80% of acetone in the upper troposphere. It must be stressed however, that in two cases the comparison between the model results from simulation “E2” and field campaigns deteriorates compared to the evaluation simulation “S1”. These are presented in Fig. 12 (bottom). Both cases are located in Japan, where the model, after the inclusion of C₄–C₅ oxidation pathways in the chemistry scheme, simulates too high mixing ratios of acetone. This could be due to a too strong source of C₄–C₅ alkanes in the region in simulation “E2”, or alternatively, an overestimation/underestimation of direct acetone emissions/depositions.

5.2 Acetaldehyde formation

Acetaldehyde (CH₃CHO) is also formed during the chemical degradation of C₃–C₅ alkanes. This tracer is a short-lived compound, with an average lifetime of several hours (Tyndall et al., 1995, 2002). It is an important precursor of PAN (peroxyacetyl nitrate), being a reservoir species of NO_x (see Singh et al., 1985; Moxim et al., 1996).

In this study, using the EMAC model, the calculated global production of acetaldehyde from C₃–C₅ alkanes is 12.6 Tg/yr. In both simulations “E1” and “E2”, 3.1 Tg/yr of acetaldehyde are formed by the oxidation of propane (C₃H₈).

In addition, 3.3 Tg/yr, 1.4 Tg/yr and 4.8 Tg/yr of acetaldehyde results from the oxidation of *n*-butane (C₄H₁₀), *n*-pentane (C₅H₁₂) and *i*-pentane (C₅H₁₂), respectively.

These amounts are almost exclusively produced by the reaction with OH; in fact, the reaction of C₃–C₅ alkanes with NO₃ produces only 0.1% of the total acetaldehyde.

6 Conclusions

We compared the EMAC model results of C_2 – C_5 alkanes with new observational data obtained from flask measurements from the NOAA/ESRL flask sampling network. Two emission distribution databases for butanes and pentanes (and associates isomers) were evaluated, new emissions of C_2 – C_5 estimated, and the effect of C_3 – C_5 alkanes on the concentrations of acetone and acetaldehyde calculated.

Overall, the model reproduces the observations of ethane and propane mixing ratios well using the EDGARv3.2 emission database (van Aardenne et al., 2005). The seasonal cycle is correctly reproduced, and the mixing ratios are generally within 20% of the observations. The simulation of ethane (C_2H_6) shows good agreement with the observations, both with respect to the spatial and the temporal distribution, although with some underestimation in the NH during winter. In the SH a general overestimation is found, especially during the SH summer. Propane (C_3H_8) is reproduced well in the NH, while in the SH an overestimation occurs during the SH winter.

To compare two different emissions databases, two sensitivity simulations were performed. In simulation “E1” the EDGARv2 (Olivier et al., 1999) emissions for butanes and pentanes, while in simulation “E2” the emissions distribution suggested by Bey et al. (2001) were used. Generally, the simulated seasonal cycles of the butanes and pentanes agree well with the observations in both simulations. However, simulation “E2” reproduces more realistically both, *n*-butane and *i*-pentane, while for *i*-butane and *n*-pentane it is not evident which simulation is better, one being at the higher end of the observations (“E1”) and the other at the lower end (“E2”).

In conclusion, we recommend the emission database suggested by Bey et al. (2001) (with increased pentanes emissions) for future studies of these tracers.

Results of a high resolution simulation would be necessary to enable us to draw a firm conclusion regarding the ability of the model to represent C_4 – C_5 alkanes in remote areas. Nevertheless, our analysis suggests a larger source from the ocean than what is currently assumed. In addition, an higher resolution simulation would also

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give additional information on the global impact of biomass burning on these tracers, which, due to the low emitted amount compared to anthropogenic emissions, is difficult to analyse and quantify with low resolution model.

The inclusion of C₄–C₅ alkanes in the model improves the representation of acetone (CH₃COCH₃). Based on simulation “E2”, *i*-butane and *i*-pentane degradation produces ~4.2 and ~5.8 Tg/yr of acetone, respectively. At the same time, the formation of acetaldehyde was also calculated, resulting in a production rate of 3.3 Tg/yr, 1.4 Tg/yr and 4.8 Tg/yr from the oxidation of *n*-butane, *n*-pentane and *i*-pentane, respectively. The role of NO₃ and Cl radicals in the degradation of C₃–C₅ isoalkanes and the formation of acetone and acetaldehyde is negligible, contributing less than 1% to the total chemical production.

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Table 1. Global source estimates of C₂–C₅ alkanes based on the present EMAC simulations.

	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	I–C ₄ H ₁₀	C ₅ H ₁₂	I–C ₅ H ₁₂
anthropogenic	9.2 ^b	10.5 ^b	9.9 ^a	4.2 ^a	4.3 ^a	8.0 ^a
biomass burning	2.8 ^d	0.9 ^d	0.2 ^d	0.07 ^d	0.1 ^d	0.08 ^d
oceanic	0.5 ^c	0.3 ^c	–	–	–	–
total	12.5	11.7	10.1	4.3	4.4	8.1

^a simulation “E2”, with emissions distribution from Bey et al. (2001)

^b based on EDGARv3.2, fast-track 2000

^c based on Plass-Dülmer et al. (1995)

^d based on Van der Werf et al. (2004) and Andreae and Merlet (2001) for the year 2000 (see Sect. 2.2.2)

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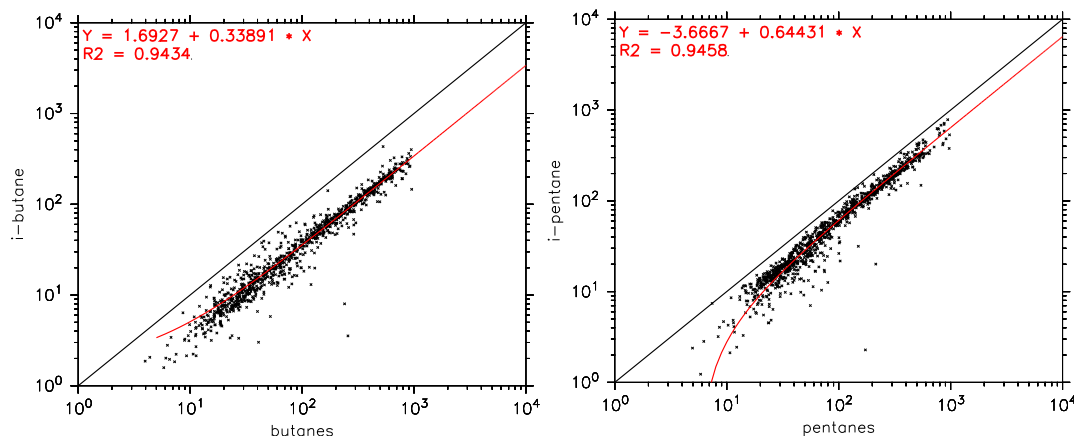


Fig. 1. *i*-butane versus total butanes (left) and *i*-pentane versus total pentanes (right) measurements in pmol/mol. The black line represents the 1 to 1 line while the red line represent the linear fit of the data. In the upper left corner the fitting parameters are presented in red. Note the logarithmic scale of the axes.

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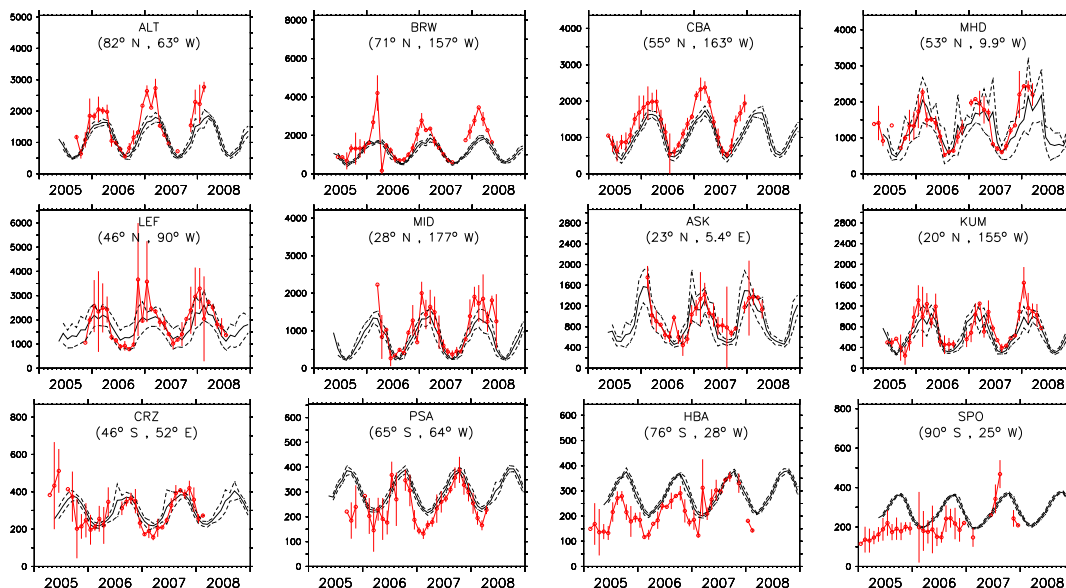


Fig. 2. Comparison of simulated and observed C₂H₆ mixing ratios in pmol/mol for some selected locations (ordered by latitude). The red lines and the bars represent the monthly averages and variability (calculated as the monthly standard deviations) of the measurements. The simulated monthly averages are indicated by the black lines and the corresponding simulated monthly variability (calculated as the monthly standard deviations of the simulated mixing ratios) by the dashed lines. The three letters at the center of each plot denote the station code (see <http://www.esrl.noaa.gov/gmd/ccgg/flask.html>). Note the different scales of the vertical axes.

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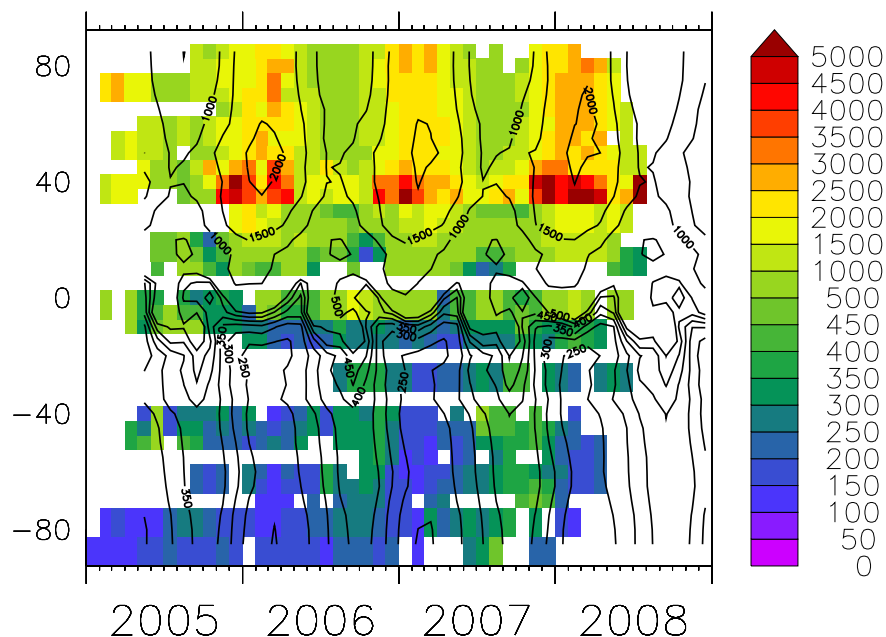
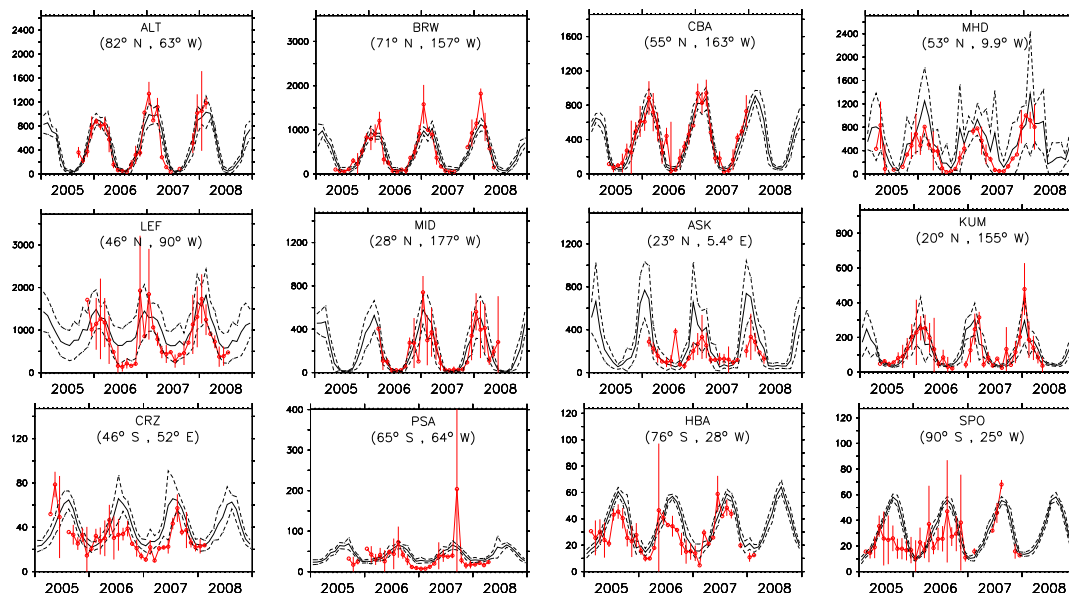


Fig. 3. Seasonal cycle and meridional distribution of ethane (C₂H₆). The colour code denotes the mixing ratios in pmol/mol, calculated as a zonal average of the measurements available in the NOAA/ESRL GMD dataset. The superimposed contour lines denote the zonal averages of the model results.

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Fig. 4. As Fig.2 for C₃H₈.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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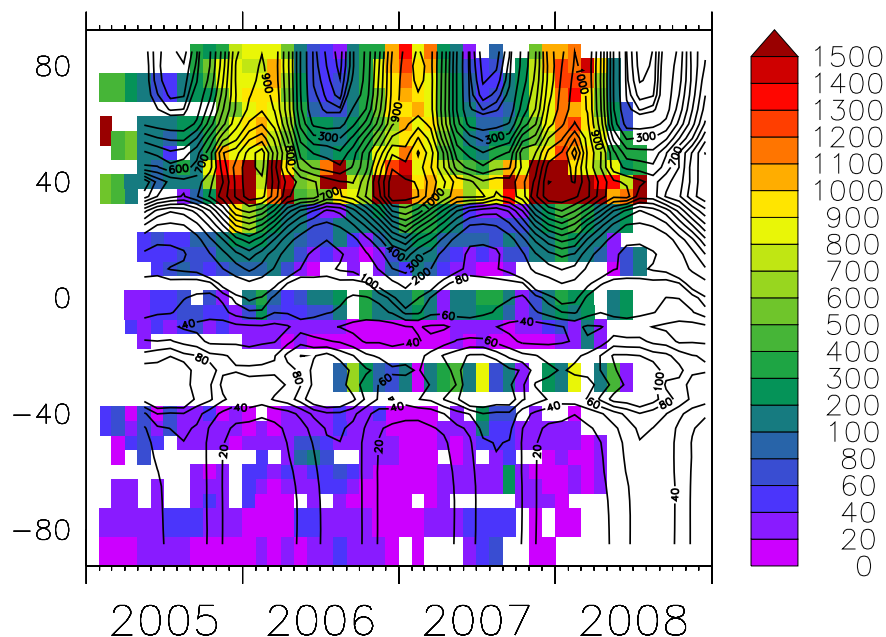


Fig. 5. Seasonal cycle and meridional distribution of propane (C₃H₈). The colour code denotes the mixing ratios in pmol/mol, calculated as a zonal average of the measurements available in the NOAA/ESRL GMD dataset. The superimposed contour lines denote the zonal averages of the model results.

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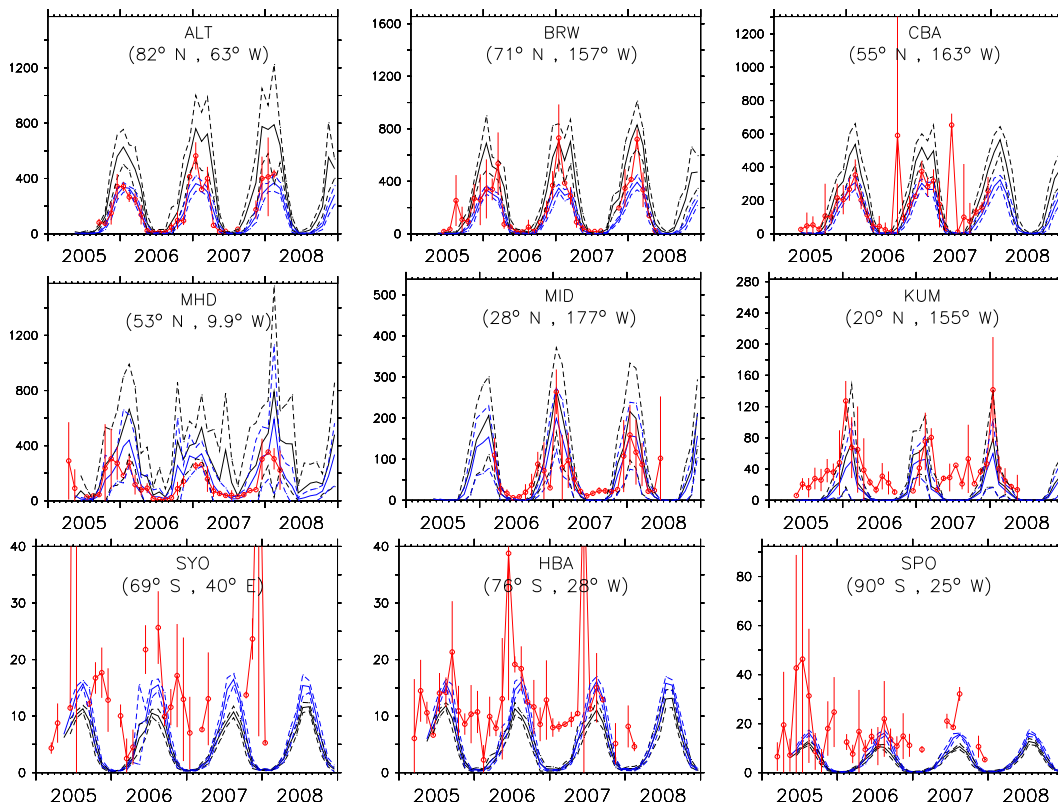


Fig. 6. Comparison of simulated and observed C₄H₁₀ mixing ratios in pmol/mol for some selected locations (ordered by latitude). The red line and the bars represent the monthly average and the variability (calculated as the monthly standard deviations) of the measurements. The simulated monthly average is indicated in the solid line and the corresponding simulated monthly variability (calculated as the monthly standard deviations of the simulated mixing ratios) by the dashed line. The black and blue colours denote results from simulation “E1” and “E2”, respectively. The three letters at the center of each plot denote the station code (see <http://www.esrl.noaa.gov/gmd/ccgg/flask.html>). Note the different scales of the vertical mixing ratio axes.

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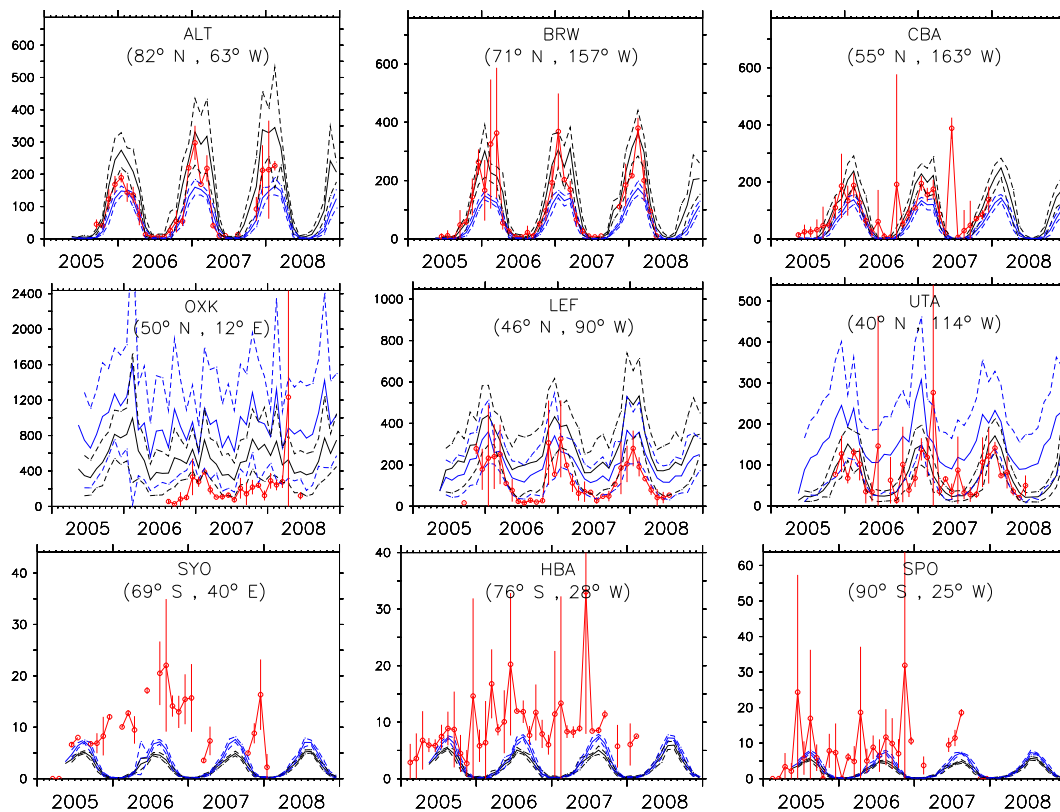
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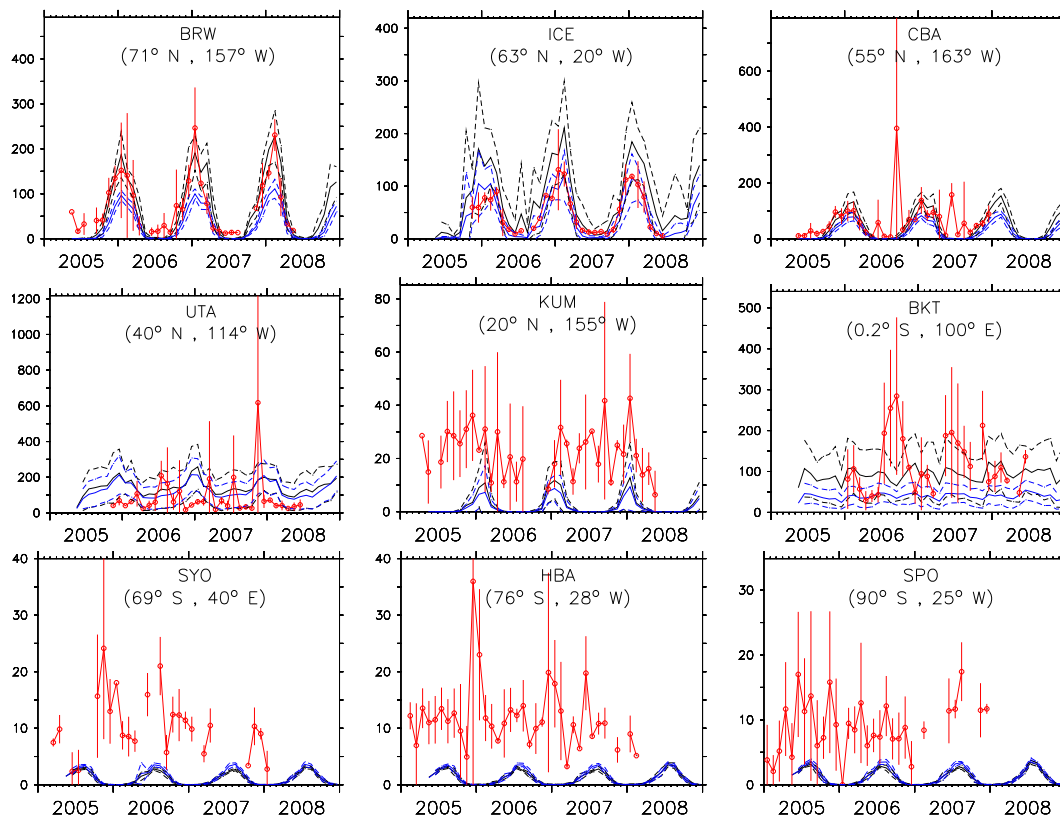
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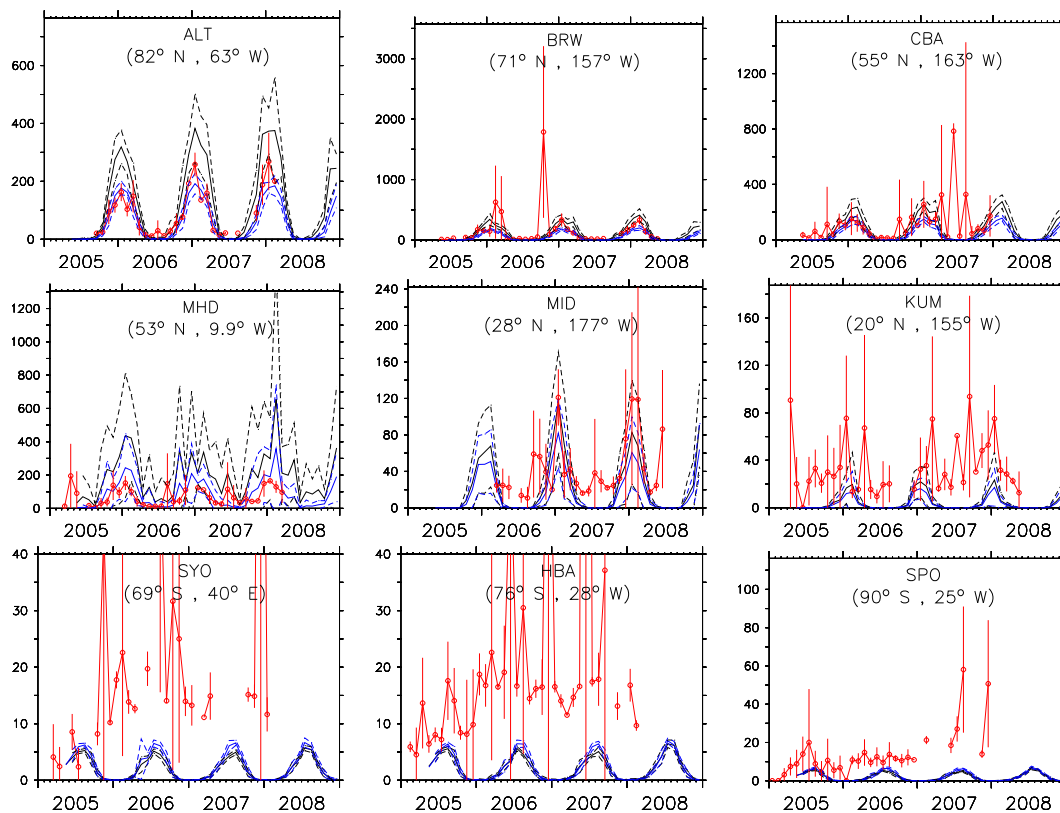


Fig. 9. As Fig. 6 for I-C₅H₁₂.

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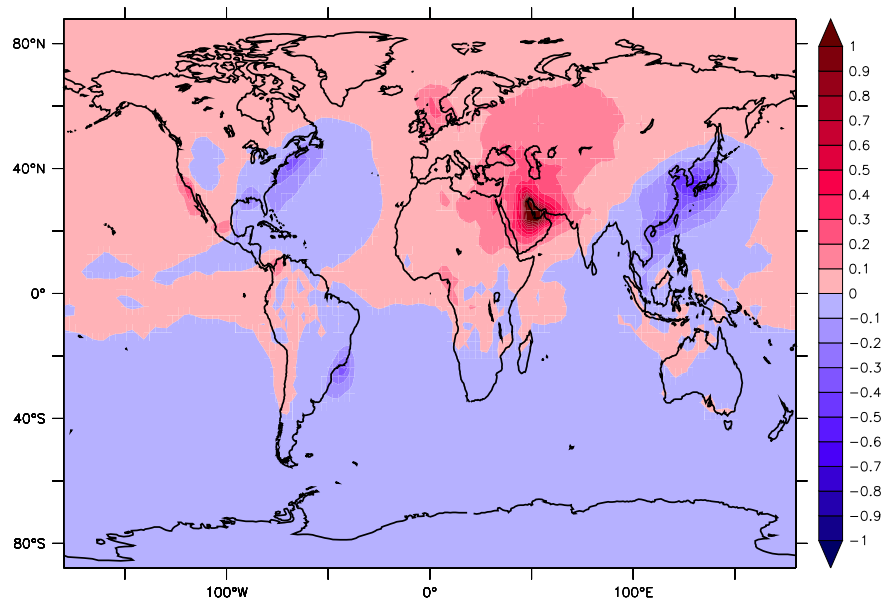


Fig. 10. Difference between the simulated annual average surface mixing ratios of CH₃COCH₃ from simulation “E1” and the simulation “E2”, in nmol/mol (“E1”–“E2”).

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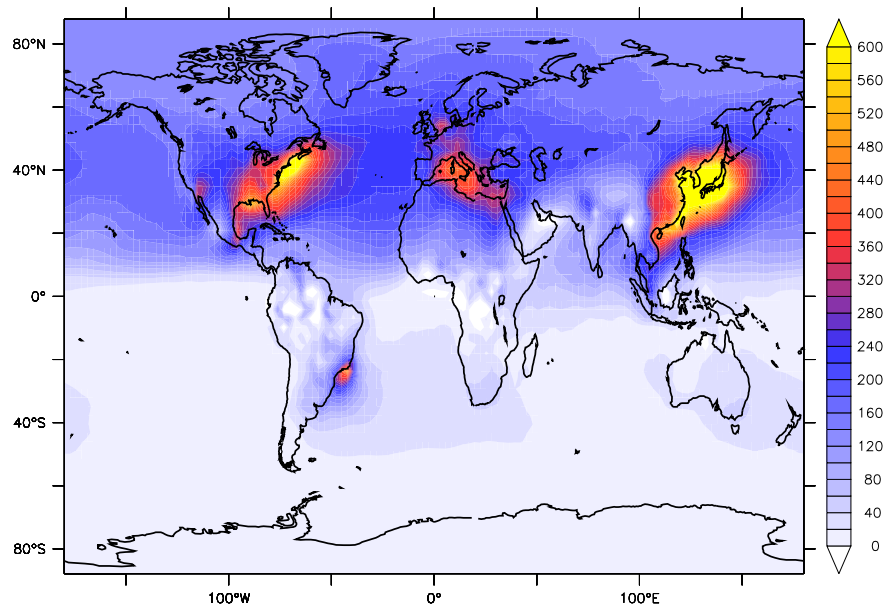


Fig. 11. Difference between the simulated annual average surface mixing ratios of CH₃COCH₃ from simulation "E2" and the evaluation simulation "S1", in pmol/mol ("E2"–"S1").

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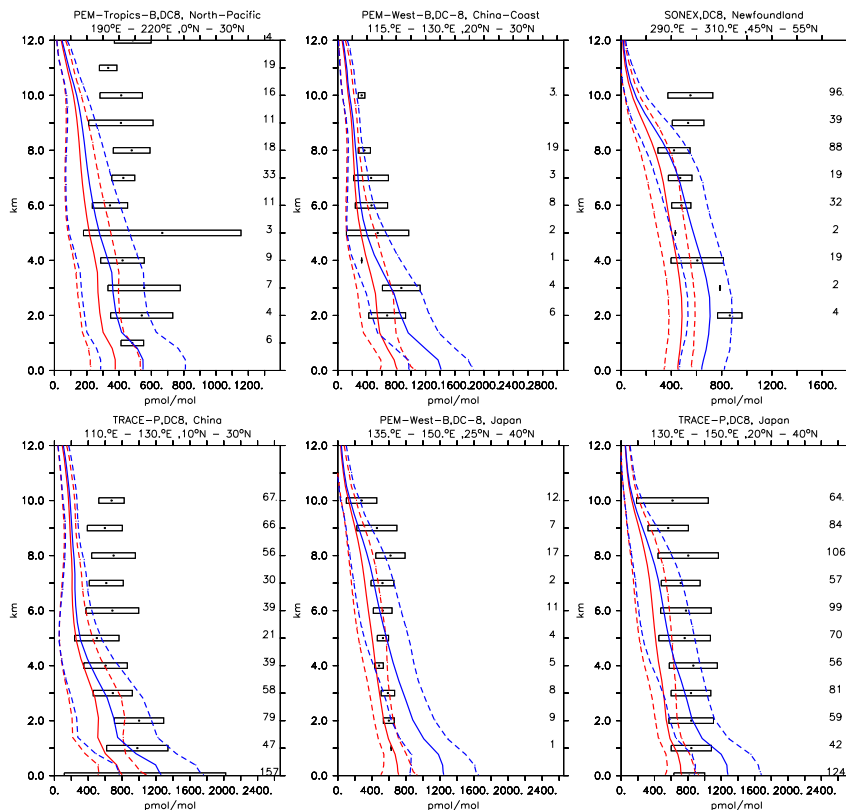


Fig. 12. Vertical profiles of CH₃COCH₃ (in pmol/mol) for some selected campaigns from Emmons et al. (2000). Asterisks and boxes represent the average and the variability (with respect to space and time) of the measurements in the region, respectively. The simulated average is indicated by the solid line and the corresponding simulated variability (calculated as standard deviation with respect to time and space) by the dashed lines. The numbers of measurements are listed near the right axes. The red lines represent the simulation “S1”, the blue lines “E2”. The PEM-West-B, SONEX and TRACE-P campaign took place in March–April (1999), February–March (1994), October–November (1997) and February–April (2001), respectively.

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