

Flux estimates of isoprene, methanol and acetone from airborne PTR-MS measurements over the tropical rainforest during the GABRIEL 2005 campaign

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Abstract

Tropical forests are a strong source of biogenic volatile organic compounds (BVOCs) to the atmosphere and such emissions can impact the atmospheric oxidation capacity. Here we present airborne and ground-based BVOC measurements performed during the long dry season in October 2005 during the GABRIEL (Guyanas Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet) project, which covered a large area of the northern Amazonian rainforest ($6\text{--}3^\circ \text{N}$, $50\text{--}59^\circ \text{W}$). The vertical (35 m to 10 km) and diurnal (09:00–16:00) profiles of selected BVOCs like isoprene, its oxidation products methacrolein and methyl vinyl ketone, methanol and acetone, measured by PTRMS (Proton Transfer Reaction Mass Spectrometry), have been used to empirically estimate their emission fluxes from the forest canopy on a regional scale. The mixed layer isoprene emission flux, inferred from the airborne measurements above 300 m, is $4.1 \text{ mg isoprene } \text{m}^{-2} \text{ h}^{-1}$ whereas the surface flux is $7.3 \text{ mg isoprene } \text{m}^{-2} \text{ h}^{-1}$ after compensating for chemistry. This surface flux is in general agreement with previous tropical forest studies. Mixed layer fluxes of $0.8 \text{ mg methanol } \text{m}^{-2} \text{ h}^{-1}$ and $0.35 \text{ mg acetone } \text{m}^{-2} \text{ h}^{-1}$ were found. The BVOC measurements were compared with fluxes and mixing ratios simulated with a single-column model (SCM). The isoprene flux inferred from the measurements is substantially smaller than that simulated with an SCM implementation of MEGAN (Model of the Exchange of Gases between the Atmosphere and Nature) though consistent with global emission estimates. The exchanges of methanol and acetone can be reasonably well described using a compensation point approach.

1 Introduction

Tropical ecosystems are important sources and sinks for many gas and aerosol species, producing almost half of the estimated 1.3 Pg C yr^{-1} globally emitted biogenic volatile organic compounds (BVOCs) (Guenther, 2002). These biogenic emissions are

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thought to exceed the anthropogenic emissions by a factor of 10 (Miller, 1992; Guenther et al., 1995) and are important to both atmospheric chemistry and climate e.g. Fehsenfeld et al. (1992), Sanderson et al. (2003). The tropical forest ecosystem is the largest single source of isoprene, which makes up almost half of all BVOC emissions (Guenther et al., 1995; Guenther, 2002). Currently the oxidation chemistry of BVOCs over tropical ecosystems is not well understood, as evidenced by large discrepancies reported between measured and modelled isoprene concentrations from these regions (Ehhalt and Prather, 2001; von Kuhlmann et al., 2004).

Global atmospheric chemistry models rely on emission inventories to provide accurate fluxes of BVOCs. Such emissions vary as a function of many parameters e.g. temperature, light, species, age etc. (Monson and Fall, 1989; Monson et al., 1992; Guenther et al., 1995; Kesselmeier and Staudt, 1999) and hence are subject to large uncertainty due to enormous species diversity, uncharacterised landscapes and limited datasets. Guenther et al. (1995) estimated that 1.15 Pg C of volatile organic compounds are emitted each year into the atmosphere from vegetation, comprising 44% of isoprene, 11% of monoterpenes, 22.5% of other reactive VOCs and 22.5% of other VOCs. Recently a new parameterised inventory named the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006), has been developed to better quantify net terrestrial biosphere BVOC emissions. The driving parameters within MEGAN include temperature, solar radiation, leaf area index, and plant functional type. The annual global isoprene emission estimated with MEGAN ranges from about 500 to 750 Tg C yr⁻¹ depending on the driving variables used. Estimated emissions can, however, vary by more than a factor of 3 for specific times and locations. It is therefore important to compare in situ measurements and empirically derived fluxes with those predicted by models using the MEGAN inventory. This applies not only to isoprene but also to biogenic oxygenated compounds such as acetone and methanol which will be introduced in future versions of the inventory. Both these compounds are strongly emitted by terrestrial vegetation but their budgets are currently not well constrained (Galbally and Kirstine, 2002; Jacob, 2002).

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Globally, an estimated 128 Tg yr^{-1} of methanol is released naturally through plant growth and a further 23 Tg yr^{-1} from plant decay. The plant growth source is a factor of 3 higher for young than from mature leaves (Jacob et al., 2005). The estimated acetone release from terrestrial vegetation is 35 Tg yr^{-1} and 2 Tg yr^{-1} from plant decay (Jacob, 2002). Therefore the direct emission of methanol and acetone from the terrestrial biosphere represents a major source term in the budgets of both compounds. Nonetheless photochemical sources of methanol and acetone can be significant: a globally estimated 38 Tg yr^{-1} of methanol is formed from the self-reaction of the methyl peroxy radical (CH_3O_2) and other organic peroxy radicals; and 7 Tg yr^{-1} of acetone is produced from the oxidation of monoterpenes and methylbutenol. For both components gas-phase oxidation by OH and deposition are the main removal processes.

In this study we present in situ airborne measurements of BVOCs monitored by a Proton Transfer Reaction Mass Spectrometer (PTR-MS) together with other trace gases over Guyana's tropical rainforest. Most notable within the context of this study are the hydroxyl (OH) and hydroperoxy (HO_2) radicals, reactive oxidized nitrogen (NOx) and ozone (O_3), during the GABRIEL (Guyana's Atmosphere-Biosphere exchange and Radicals Intensive Experiment with the Learjet) campaign. The GABRIEL campaign, which took place in the long dry season in October 2005, was a successor to the LBA/CLAIRe (Large-scale Biosphere-Atmosphere experiment) which was conducted in the short dry season in March 1998 e.g. Crutzen et al. (2000). The main focus of GABRIEL was to concurrently quantify OH and key BVOC species over the Amazonian rainforest and to compare these values to those simulated by state of the art models. Ten flights were performed between 300 m to 10 km altitude, at different times of day and extents of rainforest influence, providing a data set suitable for studying horizontal, vertical and diurnal profiles over the pristine rainforest. This large scale approach is inherently less prone to scaling errors than single leaf or tower based studies (Greenberg and Zimmerman, 1984; Rinne et al., 2002; Greenberg et al., 2004a; Karl et al., 2004). The spatial and temporal distribution of isoprene, its oxidation products methacrolein and methyl vinyl ketone, methanol and acetone during the GABRIEL

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campaign were used together with an empirically derived convective boundary layer (CBL) height (also known as the “mixing height”) to estimate their emission fluxes as a function of time. Profiles and inferred fluxes are also compared with data derived from a Single-Column atmospheric chemistry and climate Model (SCM) (described in detail elsewhere Ganzeveld and Lelieveld, 2004; Ganzeveld et al., 2006; Ganzeveld et al., 2008). Interpretation of the observations is facilitated by the use of this model to complement the observations through the explicit simulation of a selection of processes and parameters that were not measured but which are important in controlling the trace gas distribution including boundary layer and free troposphere mixing conditions.

10 2 Site description and meteorology

Meteorological conditions over the northeast coast of South America are strongly influenced by the annual migration of the inter-tropical Convergence Zone (ITCZ). Two rainy and two dry seasons can be distinguished: a short rainy season from early December till the end of January, a short dry season from early February till the end of April, a long rainy season from early May to mid August, and finally a long dry season from mid August till end November (Teunissen et al., 2001). In October 2005 the ITCZ was located north of Suriname at approximately 10–15° N. Thus at that time of the year, although geographically in the northern hemisphere, the atmosphere over the Guyana's reflects mostly southern hemisphere air mass conditions under the influence of the south-easterly trade winds. They advect clean marine boundary layer air westwards over the pristine tropical rainforests of French Guyana and Suriname allowing analysis of the transition in reactive trace gas exchanges and atmospheric chemistry from a marine to pristine tropical forest regime.

Despite the fact that GABRIEL was conducted during the dry season, meteorological observations indicate that the region was still relatively moist with almost daily rain showers subsequent to the development of shallow cumuli in the afternoon and increasing cloudiness towards the evening. The low level cloud base over land dur-

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- ing the GABRIEL-campaign varied from 300–550 m in the morning, to 900–1200 m in the afternoon (based on visual, civil aircraft and satellite observations) and the cloud coverage has been comparable over Suriname and French Guyana during this campaign; generally up to 3/8, occasionally 5/8 in the afternoon (Scheeren et al., 2007).
- 5 The average surface temperature for October 2005 was 33°C and the relative humidity generally varied between ~70% (morning) and ~50% (afternoon) with surface easterlies of 5–6 m/s.

3 Experimental set-up

3.1 Proton transfer reaction mass spectrometer

- 10 The proton transfer reaction mass spectrometer (PTRMS) technique has been described in detail elsewhere e.g. Lindinger et al. (1998), Hansel et al. (1999), de Gouw et al. (2003a) and this instrument was employed during the GABRIEL-campaign to measure mass over charge ratios (m/z) 69, 71, 33 and 59. These m/z 's have been attributed to protonated isoprene, the sum of methacrolein and methyl vinyl ketone, 15 methanol and acetone respectively. These identifications are consistent with previous studies although minor contributions from other isobaric compounds, such as protonated propanal to m/z 59 (Lindinger et al., 1998; Williams et al., 2001) and fragments of 2-methyl-3-buten-2-ol (MBO) to m/z 69 (Eerdekens, 2001; de Gouw et al., 2003a) cannot be ruled out.
- 20 Measurement on board the Learjet (35A) aircraft during the GABRIEL campaign were performed to monitor the distribution of species vertically (0–10 km), and horizontally (range ca. 1800 km) by day. Morning-, noon- and afternoon-time flights were conducted to obtain data following latitudinal and longitudinal grid patterns within the boundary layer and the free troposphere. Details on the airborne instrumentation for the measurements of CO₂, H₂O, CO, O₃, NO, JNO₂, H₂O₂, total peroxides, OH, HO₂, HCHO, besides VOCs can be found elsewhere (Stickler et al., 2007;
- 25

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Martinez et al., 2008¹). The measurement of volatile organic compounds by the air-borne PTRMS are described here, whereas VOCs measured with Thermo Desorption-Gas chromatography – Mass Spectrometry (TD-GCMS) and halogenated VOC canister GC-MS analysis are described by Williams et al. (2007) and Gebhardt et al. (2008), respectively. A similar PTRMS instrument was located in the rainforest at the remote Suriname meteorological station of Brownsberg National Park, to monitor diel cycles of the same species at canopy level and further details of this PTR-MS and measurements performed with it are available in (Sinha et al., 2008).

3.1.1 Airborne instrumentation

- A main flow of more than 10 l min^{-1} was drawn through a 9 mm I.D. forward facing stainless steel fast flow inlet (length ~30 cm) coupled inside the aircraft to a 6.35 mm I.D. (length 1 m) Teflon tube. From the fast flow inlet, the PTR-MS system drew a flow of between 1.5 L min^{-1} at ground level to 150 ml min^{-1} at 10 km, through 2.5 m of 3.18 mm I.D. Teflon tubing. A fraction of this flow was sampled at between $25\text{--}30 \text{ ml min}^{-1}$ directly into the drift tube. Measurements by PTR-MS are usually performed under isobaric and isothermal conditions for the drift tube. The drift tube pressure was set at 2.2 mbar and was automatically adjusted to its set point value in flight. The drift tube was temperature controlled to 40°C when the cabin air was sufficiently cool. However, under the extremely hot cabin temperatures which were often experienced at the end of the flights this was not possible. Under such circumstances the drift tube temperature has been assumed to be equal to the cabin temperature for the calculation of concentration. Data were obtained from 8 of the 10 flights. Measurement of each species was made once almost every 30 s.

¹Martinez, M., Harder, H., Kubistin, D., M., R., Bozem, H., Butler, T., Eerdekkens, G., Fischer, H., Gurk, C., Königstedt, R., Klüpfel, T., Lawrence, M., Parchatka, U., Schiller, C., Stickler, A., Williams, J., and Lelieveld, J.: Hydroxyl Radicals in the Tropical Troposphere over the Suriname rain forest: Airborne Measurements, *Atmos. Chem. Phys. Discuss.*, submitted, 2008.

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3.1.2 Ground-based measurements

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Brownsberg National Park was more or less centrally situated with regard to the operational area of the aircraft, which ranged from 6–3.5° N and 57–50° W. The Brownsberg measurement site (4°53' N, 55°13' W, ~500 m) was situated on the Mazaroni Plateau ca. 450 m above the surrounding lowlands and adjacent to a 55×40 km² lake situated east of the measurement site. Upwind from the site is 250–300 km of pristine rainforest before the coast of French Guyana.

An existing radio communication tower situated in a jungle clearing served as a stand for the inlet line. A membrane pump pulled down air sampled at canopy top level (~35 m) through a 50 m PFA tubing (6.35 mm I.D.) towards the instrument. The flow rate was restricted to 5 L min⁻¹ mainly by a 5 μm Teflon filter. The PFA tubing was shrouded with black tubing to minimise the potential of photochemically induced artefact signals. Continuous monitoring of the aforementioned BVOCs by PTR-MS at the ground based site was only possible for ~3 days starting from 3 until 6 October from midday to midday.

3.1.3 Calibration

Both PTR-MS instruments were calibrated against a gravimetric prepared synthetic mix (Apel-Riemer Environmental, Inc., Denver, USA) comprising 13 non-methane hydrocarbons in the order of ~500 ppbv per substance, stated accuracy 5%. This standard was diluted dynamically for calibration with synthetic air to achieve atmospheric mixing ratios (covering ppbv to pptv levels). In-field and post-flight calibrations started and ended with measurements of synthetic air cleaned by passing it through a catalytic converter. The catalytic converter (Platinum on quartz wool at 360°C) strips the air of organics and converts them to CO₂ and H₂O. It has been used in all flights to provide a background signal, and the difference of this to the sample signal is used to determine the mixing ratios present in the ambient air. The targeted species over the rainforest included substances that mostly have shown NO significant humidity dependence on sensitivity under the operating conditions of 2.5 mbar drift tube pressure

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and 65 V cm^{-1} used by Warneke et al. (2001b), which are comparable to our operating conditions of 2.2 mbar drift tube pressure and 66 V cm^{-1} ($\sim 120 \text{ Td}$). Thus for methacrolein and methyl vinyl ketone (*m/z* 71), acetone (*m/z* 59) and methanol (*m/z* 33) calibration with dry gas was considered sufficient. Under more humid conditions,
5 sensitivity for isoprene (*m/z* 69) declines (Warneke et al., 2001b). Our measurements have been performed in an environment with relative humidities of 40–80% in the lowest 4 km, whereas calibrations were done using dry synthetic air. Although calculations of mixing ratios have been done taking H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ into account, the lower sensitivity for isoprene under ambient conditions (relative humidity of 50–80% in the
10 lowest 1700 m) could lead to an underestimation of the isoprene mixing ratios in the ambient air by several percent.

The precision or statistical uncertainty in the volume mixing ratio was calculated conservatively using the Gaussian error propagation. Measurement of each species was made once almost every 30 s with dwell times of 0.9–2 s per mass. The average speed of the Learjet above the rainforest was $\sim 128 \pm 6 \text{ m/s}$. The overall accuracy of the determination depends on the accuracy of each signal used in the calculation and their respective systematic errors. Reported values should be accurate to within 5–10% assuming NO unaccounted-for systematic errors are present and using the stated accuracy of the calibration standard and measurements of calibrated instrument response. The total measurement error (calculated as the geometric sum of accuracy and precision) for isoprene ranged from 25% (at 0.5 ppbv), and 8% (at 6 ppbv). For MACR+MVK volume mixing ratios between 0.4 and 2.5 ppbv the corresponding total measurement errors were between 20% and 9%. For acetone the total measurement errors were 25–10%, for measurements ranging between 0.4–1.5 ppbv;
15 and 50–20% for methanol between 2–6 ppbv. If noise at each channel is taken as the signal observed upon sampling zero air (sampling with a catalytic converter in-line), the detection limits for the unsmoothed data using a threshold signal-to-noise ratio of three were 0.27 ppbv (methanol), 0.07 ppbv (acetonitrile), 0.09 ppbv (acetone), 0.10 ppbv (isoprene) and 0.09 ppbv (MVK).

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3.2 Measurements of VOCs by TD-GCMS

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The sampling and analysis procedures for isoprene and monoterpenes are described in detail in Williams et al. (2007). Briefly, sampling for isoprene over the tropical rainforest was performed using a custom built cartridge sampling device installed within a standard aircraft wing pod. The device was mounted underneath the port wing of the Learjet aircraft and operated from within the cabin via a communication cable. The system was designed to collect ambient air in flight within 18 cartridges. A flight was typically 3 h in duration so that a cartridge was filled every 10 min. Three identical systems were built to allow rapid changeovers between flights. Within the wing pod, outside air was drawn by a metal bellows pump, into the system through an 8.5 mm diameter stainless steel inlet located on the wing pod nose. The pump was connected to the cartridge sampling sections by heated 6.35 mm stainless steel tubing. Calibrated mass flow-controllers regulated the air flow through the system and a custom made processor was used to set the parameters and record the sampling processes. The sample tubes were fitted into the flowpath approximately 80 cm after the pump with Swagelok Ultra-Torr stainless steel fittings and sealed with 2-way electromagnetic valves at the entrance and the exit. The valves could be opened and closed simultaneously via the software. During the sampling, the inlet and outlet valves of the selected cartridge are opened and the sample flow (80 ml/min) passed through the sorbent filled cartridge for 5 min. Cartridges were filled every 10 min and, up to 17 of the 18 available cartridges (at least one blank was flown i.e. cartridge that was not opened in flight) were filled per measurement flight. To minimise the sample contamination from airport air, the pump was generally started 15 min after take-off.

Prior to flight, the stainless steel, two-bed sampling cartridges (Carbo-graph I/Carbo-graph II; Markes International, Pontyclun, UK) were cleaned with the Thermoconditioner. All pertinent analysis parameters and further details on the Thermo Desorption-GCMS analysis system can be found in Williams et al. (2007). Laboratory multipoint calibrations showed good linearity within the concentration ranges

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measured. Blanks, namely cartridges that were flown but not opened, were taken regularly and showed NO high levels for the compounds discussed. One-point calibrations of 250 ml VOC standard (Apel-Riemer Environmental, Inc., Denver, USA) and 100 ml of a terpene (Apel-Riemer Environmental, Inc., Denver, USA, stated accuracy 5%) standard mixture were carried out at the beginning and the middle of each flight analysis.
5 The total measurement uncertainties were around 15% and the detection limit ranged from 0.5 pptv to 5 pptv.

3.3 Comparison PTRMS-GCMS

GC-MS techniques are inherently more sensitive and selective than the PTR-MS by virtue of the pre-separation step performed prior to introduction of sample into the mass spectrometer (de Gouw et al., 2003a; Williams, 2006). However, for the same reason the PTR-MS has a much higher measurement frequency which is highly desirable on an aircraft. In order to compare the TD-GC-MS and the PTR-MS, the later data have been averaged around the centred measurement time of the cartridges which were sampled every 10 min for 5 min.
10 The number of PTR-MS data points per sampling interval of the cartridges varied, because of the unequal sampling rates and because the PTR-MS periodically measured background values through the aforementioned catalytic converter. The cartridges continuously collect organic compounds for the whole 5 min of sampling, in effect taking a 5 min integrated sample. Within this period
15 the PTR-MS takes approximately 10 measurements of 1.5 s in duration for m/z 69.
20

In the analysis of the PTR-MS versus the TD-GC-MS, flight data are only used for cases where more than 5 PTR-MS data points were present over the cartridge sampling interval of 5 min. For isoprene, the results of 62 analysed cartridges from 6 flights were used in the orthogonal distance regression which is presented in Fig. 1. Although
25 both systems have been calibrated against the same standard their correlation deviates from unity.

The error bars indicate the total measurement uncertainty for isoprene. They were found to be less than 16% for values higher than the median mixing ratios measured

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by the PTR-MS and 15% for the TD-GC-MS. Some 69% of the data in this comparison were within the uncertainty limits, while of the remaining 31% the PTR-MS measured isoprene mixing ratio was lower than the cartridge data in most cases. While the regression correlation R^2 of 0.72 is good, the reported slope of 0.75 ± 0.18 suggests that
5 the PTR-MS system systematically underestimates the volume mixing ratio for isoprene in comparison to the GC cartridge analysis. From all the diagnostic information we have on both measurement systems, NO irregularities have been found. Since GC-PTR-MS measurements were not performed, the relative contributions from known and unknown interferences (protonated molecules, or fragments e.g. from m/z 87 to m/z 69)
10 could not be determined, although since the PTR-MS data are slightly lower than the cartridge data such interferences are assumed to be minor in this case.

A similar linear correlation (0.84) has been found for the PTR-MS isoprene data obtained during the LBA/CLAIRe campaign in 1998, by comparing with the isoprene canister data analysed by GC-FID (Warneke et al., 2001a). However, their offset (668 pptv)
15 was larger. In 2005, the cartridges were analysed immediately after each flight in order to minimise possible storage time artefacts. Storage tests on alkenes including isoprene have shown that these species tend to grow in concentration in canisters after storage (Colomb et al., 2006) and this is a possible explanation for the larger offset seen in 1998 since these canisters were measured several months after sampling.

20 Here we make the assumption that the slightly lower values for isoprene determined by the PTR-MS are due to the calibration in dry rather than humid air. Therefore for the remainder of this study we use PTR-MS data corrected with respect to the aforementioned comparison to the TD-GC-MS in our calculations. In doing so we use the high resolution PTR-MS data with the humidity independent calibration of the GC-MS
25 system.

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4 SCM Model description and initialization

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The measurement data have been compared with results generated by a Single-Column, chemistry climate Model (SCM). The SCM includes an explicit representation of atmosphere-biosphere trace gas exchanges using a multi-layer canopy exchanges model. In this study we focus on the BVOCs, however, in a companion paper, Ganzeveld et al. (2008), the local chemistry of NO_x and ozone is discussed in detail. Since its first application by Ganzeveld et al. (2002a), the atmosphere-biosphere model has been further updated and improved, as described in detail elsewhere (Ganzeveld et al., 2002b; Ganzeveld and Lelieveld, 2004; Ganzeveld et al., 2005; Ganzeveld et al., 2006). Therefore only the salient features of the model are summarised below.

Model simulations have been performed in the “Lagrangian mode”, described by Ganzeveld and Lelieveld (2004), which implies that during the simulations, the air column is advected from the Atlantic Ocean over the Amazon rainforest along a transect along 4.5° N from 45° E to 60° E at a speed of the average PBL wind speed (~6 m/s). In three days the air masses are first advected over the ocean (1 day, 2 October) and then for 2 days over land (3–4 October), simulating the response of the column to changes in surface cover properties including the transition from atmosphere-ocean to the atmosphere-land-biosphere exchanges properties. The land cover properties, including parameters such as Leaf Area Index (LAI), Leaf Area Density (LAD), surface roughness and the NO and VOC emission factors are determined by the distribution of the 72 ecosystem classes of the Olson (1992) ecosystem database.

The SCM’s chemistry scheme, based on the CBM4 mechanism (Roelofs and Lelieveld, 1995, 2000), has been modified to include the oxidation of terpenes by ozonolysis (Ganzeveld et al., 2006). In addition to the primary impact of terpene oxidation on OH and HO₂ production, H₂O₂ production through the formation and decomposition of long-chain hydroxyalkyl-hydroperoxides has also been included (Valverde-Canossa, 2004).

The SCM includes an explicit atmosphere-biosphere trace gas exchange model that

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accounts for dry deposition processes, biogenic emissions, extinction of radiation (relevant to in-canopy photochemistry) and turbulence within the canopy as a function of the SCM's meteorological, hydrological and atmospheric chemistry parameters, distinguishing a crown- and understorey layer. Biogenic NO emissions are calculated
5 according to Yienger and Levy (1995) whereas volatile organic compound emissions are simulated using either, the well-established Guenther et al. (1995) or alternatively the recent MEGAN (Model of Emissions of Gases and Aerosols from Nature) algorithm (Guenther et al., 2006). It should be noted that in this study the MEGAN algorithm only provides isoprene emission fluxes in the SCM implementation; all other biogenic fluxes,
10 including terpenes, oxygenated VOCs) are based on alternative algorithms (Ganzeveld et al., 2008). In the SCM, methanol and acetone biogenic exchanges are described using a compensation point approach since bi-directional exchanges (emissions and deposition) have been reported in the field e.g. Kesselmeier 2001 in this approach, the compensation point concentration is defined as the concentration for which the uptake
15 reaction is equal to the simultaneous operating production rate for a net zero flux. The compensation concentration for methanol is prescribed such that with the simulated stomatal exchange we arrive at a maximum daytime emission flux comparable to those inferred from the observed boundary layer mixing ratios (see Ganzeveld et al., 2008)

Note that the model simulates, in contrast to daytime emissions, nocturnal deposition
20 fluxes from dry deposition velocities that mostly reflect assumptions on non-stomatal uptake, i.e. the dry and wet cuticular and soil uptake resistances. The latter are estimated from the solubility and reactivity of methanol and acetone according to the Wesely (1989) approach (see also Ganzeveld et al., 2006).

The integrations within the SCM are performed using the default ECHAM4 vertical
25 coordinate system of 19 atmospheric levels (L19), with 5 layers representing the daytime the Convective Boundary Layer (CBL), 9 in the free troposphere, and 5 in the stratosphere. The model is initialised with vertical profiles of temperature, moisture, wind speed and with trace gas concentrations if measured upwind over the Atlantic Ocean and otherwise from the chemistry and transport model TM3 (Houweling et al.,

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1998). Since isoprene mixing ratios over the ocean were close to or below the detection limit, its vertical initialisation profile was set to zero on all levels in the SCM. The North Atlantic Oceanic vertical profiles of methanol and acetone used to initialise the model at six levels up to 5 km are shown in Fig. 2 (01/10/2005 21:00 LT). The vertical profiles of acetone and methanol maintain a good agreement with the observations throughout the transport over the ocean as shown by the profiles around sunrise (05:00–07:00 LT) of the 3rd day of the simulation, when the airmass reaches land. The sharp decrease in mixing ratios from 3 km to the marine boundary layer is probably due to an oceanic uptake of methanol (Williams et al., 2004; Sinha et al., 2007), acetone (Marandino et al., 2005) and acetonitrile (Hamm et al., 1984; de Gouw et al., 2003b). The ratio of acetone to methanol varied between 0.25–0.35 in the Marine Boundary Layer (MBL) and 0.20–0.25 aloft.

Isoprene mixing ratios simulated by the SCM using the Guenther et al. (1995) algorithm as well as the MEGAN algorithms, were found to be much higher above the rainforest than the measured values. This is in agreement with previous model/measurement comparisons (von Kuhlmann et al., 2004). For the analysis of the role of isoprene chemistry in the inversion of surface emissions from mixed layer isoprene mixing ratios, the modelled emission flux has been scaled down by an arbitrary factor of 2 (indicated in all graphs by $F_{\text{emiss, isoprene}} * 0.50$) to arrive at a reasonable agreement between the isoprene flux inferred from the measurements and the model, as will be shown and discussed in the following sections.

5 Results and discussion

5.1 GABRIEL 2005 boundary layer conditions

At the outset of this study it is important to characterise the evolution and structure of the CBL over the tropical forest. This evaluation of the CBL is particularly important when estimating trace gas concentration and fluxes from the forest since the bound-

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ary layer dynamics control the dilution and vertical turbulent transport of the chemical species. In the meteorological section we have described that scattered clouds form near the top of the CBL in the afternoon over the rainforest. The sub-cloud layer buoyancy is driven by upward thermals, and in the cloud layer the positive buoyant motions are due to the release of latent heat by the condensation process. Both sub-layers are components of the CBL or mixed layer. As a result, chemical compounds are transported to higher vertical heights compared to clear sky conditions (Schumann et al., 2002; Vilà-Guerau de Arellano et al., 2005). Clouds also reduce radiation dependent biogenic emissions, photolysis rates and photochemical processes underneath (Lelieveld and Crutzen, 1991; Tang et al., 2003).

Figure 3 shows the characteristic thermodynamic vertical profiles during GABRIEL in 5–95 percentile box and whisker plots with highlighted means and medians (13:00–15:00 LT, LT=UTC–3) over the rainforest for the first day over land (see below for further details of how the data was filtered). These are used here to characterize the CBL as well as to compare with the simulated profiles by the SCM. The virtual potential temperature (θ_v) has been calculated according to Bolton (1980) from the static air temperature and the water vapour mixing ratio measured by a NDIR absorption spectrometer FABLE (Fast AirBorne Licor Experiment)(Gurk, 2003). There generally is a good agreement between the model simulated and measured temperature. However, the model simulates a lower virtual (θ_v) and equivalent (θ_e) potential temperatures and a slightly reversed lapse rate below 800 m in the afternoon as a result of the large difference in the specific humidity profile. The observations (09:00–16:00 LT) show that the specific humidity remains between 14–16 g/kg throughout the day below 900 m whereas the model simulates a higher moisture content (16–17 g/kg) in the boundary layer, despite an imposed substantial smaller evapotranspiration in the SCM (Ganzeveld et al., 2008).

Vertical profiles for the wind direction and wind speed for the whole campaign (see Fig. 2 of Gebhardt et al., 2008) show that the vertical structure of the troposphere (mixed layer and free troposphere) has been rather constant (surface easterlies of 5–6 m/s) throughout the campaign, which is consistent with stable trade wind conditions.

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Figure 3c here, shows that the SCM is able to simulate these wind speeds in the afternoon, though slightly lower wind speeds are calculated in the model for the lower 500 m of the CBL.

In order to determine the CBL height over the rainforest as a function of time of day we have used inversions (fluctuations) in the static air temperature measured on-board the aircraft. An example of such a capping inversion (at 941 m) is shown in Fig. 4a, and those from the entire dataset in Fig. 4b. Note there are several inversions present in most vertical profiles and these inversions generally occur at comparable levels above the rainforest for a particular time in the day.

The observed morning profiles of θ_v are typical for dry convective boundary layers without clouds and strong persistent winds above the CBL (marked by clear differences in temperature and humidity). The exchange of compounds with the layer above occurs particularly when the CBL develops. The growth may continue in the afternoon or the CBL height may stabilize, depending on the synoptic conditions and the amount of surface buoyancy flux. Vilà-Guerau de Arellano et al. (2005) suggest that a possible exchange flux between the sub-cloud and the cloud layers allows species to be transported upwards or downwards, causing the CBL mixing ratios of emitted compounds to change (see next sections).

In the course of a day, as clouds are being formed, the profiles show a conditionally unstable layer caused by the high moisture content, above the first virtual temperature inversion. The cloud top, which normally defines the top of the CBL, has not been uniform for the whole GABRIEL domain due to partial cloudiness meaning that sometimes species can be transported to higher levels (up to ~ 2.5 km).

For this study we assume that the cloud tops delineate our lower estimate of the convective boundary layer height. We assume here that the fit through the aforementioned first inversion points (see Fig. 4b), describes the development of the CBL throughout a day above the rainforest for the first day over land. Two kinds of fits have been applied: a sinusoidal fit and a 5th order polynomial fit to study the uncertainty in the inferred inversion height dependent on the selected fit. The uncertainty of the estimate is di-

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rectly related to the scatter and the number of observed temperature inversions. Data from coastal areas, (25 km from the coastline), were omitted in these estimates (see next section for further details of data filters). We therefore determine empirically that between 09:00 and 15:00 LT the boundary layer over the forest grows from ~500 to ~1450 m (bottom curve in Fig. 4b). Nonetheless, in many cases several inversions occurred beyond the 1st inversion above the rainforest, generally up to ~2550 m (open squares in Fig. 4b). Occasionally there may have been uninterrupted clouds to this level. Weather observations by Scheeren et al. (2007) report higher altitude scattered clouds which could be passive remnants that are no longer connected to the boundary layer. Therefore, we assume the second average level at which the inversions occurred is represented by the second curve in Fig. 4b with an average afternoon level of ~1900 m.

To support our observational analysis and to verify the occurrence of clouds, we have used a parcel method calculation. In short, we release a parcel with initial surface values $\theta_v = 310.2\text{ K}$ and $q_t = 16\text{ g/kg}$ which follows a dry adiabatic until it condensates at the lifting condensation level (LCL: 1590 m). After this level the parcel follows a moist adiabatic. The results are shown in Fig. 3a indicating a well-mixed sub-cloud layer below the LCL. By comparing the slope of the observed virtual potential temperature gradient with the moist adiabatic, we can conclude that the stratification is conditionally unstable, characteristic for shallow cumuli. The analysis does not show a clear limit of free convection (LFC), which may indicate that the cloud extension could be higher than 5000 m. We are aware that this situation is not in a steady-state and other important processes like horizontal and vertical advection are not included. However, the parcel method allows us to gain a better impression of the boundary layer dominated by clouds (Siebesma et al., 2003; Vilà-Guerau de Arellano, 2007).

The SCM suggests a slightly deeper boundary layer before noon for the first day over land compared to our lowest estimated CBL height due to the higher moisture content. Before 10:00 the difference was 200 m, about 100 m around 12:00, and around 14:00 the simulated and measured CBL heights are at comparable altitudes, about 1450 m.

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In contrast to SCM simulations, we observed little difference between the CBL height for the first day over land (east of 55° W) compared to the second day over land (west of 56° W).

The modelled boundary layer grows remarkably faster than observed between 07:30 and 08:30 (363 m h^{-1}) and subsequently it grows more slowly ($130\text{--}40 \text{ m h}^{-1}$) than the growth rate inferred from the observations ($220\text{--}130 \text{ m h}^{-1}$) until noon, the repercussions of which are discussed by Ganzeveld et al. (2008). Our observationally inferred boundary layer evolutions compare reasonably well with the findings by Martin et al. (1998) who investigated regions further inland and with the studies by Krejci et al. (2005) who reported mixing layer heights from observed during the LBA-CLAIRES 1998 project over the same area of 1200–1500 m and a cloud base of 1600–1800 m altitude.

It is not expected that the depth of the marine boundary layer (MBL) varies much over the course of the day. The observed inversions occurred at $\sim 460 \text{ m}$ pressure altitude at 08:30, around 575 m around noontime, and $\sim 500 \text{ m}$ around 15:15.

5.2 Data selection criteria

BVOC emissions are inherently highly variable, being a function of plant type, solar intensity, temperature and other factors. In order to present the flight data as clearly as possible and to ensure interpretation of pristine tropical forest exchange fluxes and a fair comparison with the simulated fluxes and CBL concentrations, a number of geographical, temporal and altitude filters have been applied. The intention is to reduce the possibility masking trends in the dataset. Details of each filter applied are presented below.

Biogeographical filter: a vegetation map of South-America (Eva et al., 2004) was used to filter only data collected over rainforested regions for analysis. The northernmost 100 km of Suriname is covered along the coast by mangrove forest, fresh water swamp forest (wetland forest) and cultivated crops and non-forest land cover (UNEP-WCMC). Data from this region was filtered out so as to leave only rainforested areas

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under analysis (see Fig. 5). The total rainforested area under investigation was approx. 775 km by 220 km.

Vertical filter: data were also filtered for the time evolution of the CBL height as discussed in the section on the GABRIEL 2005 boundary layer conditions. Hereafter, 5 only data within the mixed layer are retained.

Temporal filter: to ensure fluxes were derived from airmasses that had spent the entire daylight period over the rainforest, the “startpoint” of the measured air parcel at sunrise (ca. 06:25) was calculated based on the specific wind direction and wind speed measured by the aircraft. If the airmass at dawn, for a certain data point measured in 10 flight, was situated above the Atlantic Ocean or the coastal periphery, the data point was not considered.

The remaining datapoints therefore represent the emissions of the rainforest in air masses which crossed land between dawn and the moment of measurement and are characterised by their Forest Contact Time (FCT) with the Guyana's rainforest. The

15 FCT has been defined as the time an air parcel spends in the CBL above the rainforest starting from the rainforest periphery near the east coast. With an average wind speed of 5.4 m/s within the mixed layer and a FCT between sunrise and sunset (~ 12 h), the transect is restricted to the eastern shore of the reservoir close to the surface site (54.9–55.16° W). This transect will from here on be referred to as “the first day over 20 land”. Filtered data are used to infer the diurnal cycle of BVOCs above the rainforest and will be compared to the simulated diurnal cycle for the 3 October.

Note that the simulated mixing ratios included in the figures concerning the vertical and diurnal distribution of the BVOCs over the rainforest discussed in the following sections are base on the emission fluxes that are inferred from the airborne measurements 25 by the Convective Boundary Layer Budgeting Approach which will not be discussed until Sect. 5.7.

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5.3 Isoprene chemistry

Following emission from the rainforest, isoprene is oxidised primarily by reaction with OH (and to a lesser extent with ozone), forming methacrolein (MACR), methyl vinyl ketone (MVK) and formaldehyde as first order products (Carter and Atkinson, 1996).

- 5 Several previous studies e.g. Montzka et al. (1993), Goldan et al. (1995), Biesenthal et al. (1998), Stroud et al. (2001) have shown that ambient NO_x levels can influence the relationship between isoprene and MACR+MVK. Laboratory studies have shown that under high NO_x conditions the yield of the primary oxidation products was 55±6% (22±2% for MACR, 32±5% for MVK) and 57±6% for formaldehyde (Lee et al., 2005; Zhao et al., 2004) and references therein. In the absence of NO, Miyoshi et al. (1994) reported oxidation product yields of 22% for MACR, 17% for MVK and 34% for formaldehyde in addition to organic hydroperoxides. Another study by Ruppert and Becker (2000) indicated the NO_x free yields to be 17.8%, 15.3% and 33% for MACR, MVK and formaldehyde, respectively. Using online mass spectrometry, Lee et al. (2005) determined the yields of MACR, MVK, at 323 K to be 19.0±0.2% and 14.4±0.1% respectively, under NO_x-free conditions. NO has been measured during the GABRIEL campaign and its average mixing ratios were found to be generally less than 40 pptv (Ganzeveld et al., 2008). At these low values isoprene oxidation is expected to produce MACR and MVK with a yield resembling that for the low NO_x studies. This is essential to this analysis in which we infer the isoprene flux from the CBL mixing ratios of the chemically conservative tracer that consists of the sum of the measured isoprene, the measured MACR+MVK mixing ratios and a remaining amount of unaccounted oxidation products (indicated in the text by ISOP+MACR+MVK+others). For this study we have assumed the 39% yield of MACR and MVK production from isoprene oxidation as suggested by Miyoshi et al. (1994) and Benkelberg et al. (2000) and hence we calculate the remaining oxidation products, the “others”, as 61% based on the measured MACR+MVK. It should be noted that the assumed MACR+MVK oxidation yield in the SCM’s chemistry scheme is 55%.

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5.4 Vertical profiles

Figures 6 and 7 show vertical profiles of the measured BVOC mixing ratios, between 14:00–16:15, as a function of the height of measurement (z) normalised to the prevalent boundary layer height (z_i) as shown in Fig. 4b. Measured data are presented in 5p–95p box and whisker plots of $z/z_i=0.1$ (~140 m as of 14:00 LT). Figures 6 and 7 also contain the simulated, mixing ratio vertical profiles based on the inferred fluxes as discussed in Sect. 5.7.

Isoprene mixing ratios decrease with increasing altitude reflecting the role of photo-oxidation chemistry and mixing down of isoprene poor air from above (Fig. 6a). The 10 range of the isoprene mixing ratios (and the products MACR+MVK in Fig. 6b) is small indicating little day to day variability in emissions during the campaign. Occasionally enhanced isoprene and MACR+MVK mixing ratios were observed near the top of the CBL which was probably the result of shallow convection or transport into shallow cumuli. The mean observed isoprene mixing ratio of ~4 ppbv is comparable to the 15 3.3 ppbv obtained by Warneke et al. (2001a) over the southern part of Suriname during LBA-CLAIRe, and less than the 5.2 ppbv observed further inland at Manaus reported by Karl et al. (2007). Greenberg et al. (2004) also reported mixed layer isoprene mixing ratios at various tropical forest sites ranging from 2.9 ppbv in Balbina to 6.7 ppbv in Jaru (Rondônia). GABRIEL median mixing ratios for MACR+MVK in the selected time 20 frame were ~1.5 ppbv and were rather constant with altitude (up to 800 m) indicating a well-mixed layer. Isoprene has been observed above the detection limit up to $z/z_i \sim 1$, MACR+MVK up to $z/z_i \sim 1.7$.

The measured ratio of [MVK+MACR]/[isoprene] was between 0.4 and 0.7 for the lowermost kilometre of the CBL and is comparable to the ratios found by Karl et al. (2007) 25 above Manaus. Similar to the data presented here, Karl et al. (2007) obtained higher and more scattered ratios above the CBL height due to the low mixing ratios for isoprene and the deeper transport of its oxidation products. The interpretation of this ratio is complicated by its dependence on forest contact time, mixing and most impor-

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tantly on chemistry, since the relative levels of OH and O₃ can influence the ratio. The observed O₃ mixing ratios were relatively low, 10–20 ppbv, but the observed OH concentrations were high, $\sim 4.8 \times 10^6$ mol cm⁻³ in the mixed layer above the rainforest and $\sim 8.9 \times 10^6$ mol cm⁻³ between 2 and 3.4 km. The ratio [MVK+MACR]/[isoprene] will be addressed in more detail in section on the chemical and mixing time scales.

Figure 6a indicates that the simulated isoprene mixing ratios, for the same time span as the observations, are higher than observed despite the applied factor of two reduction in the isoprene emission flux. A plausible explanation for this disagreement between the simulated and observed isoprene mixing ratios can also be inferred from the comparison of the simulated and observed MACR+MVK mixing ratios and from the ratio [MACR+MVK]/[isoprene]. This ratio is lower than observed despite the fact that the model simulates a more efficient MACR+MVK production (~16%) per oxidised isoprene molecule than expected for the low NO_x conditions. This suggests a misrepresentation in the gas-phase chemistry model representation (Lelieveld et al., 2008). Comparison to the OH measurements confirms that the measured values exceed the modelled OH-concentrations by an order of magnitude in the afternoon even for the reduced isoprene emissions scenario (see also Fig. 17 for the OH vertical profile in Ganzeveld et al., 2008).

In addition to a disagreement in absolute CBL mixing ratios, there also appears to be a mismatch in the vertical distribution between model and observations. The latter shows a rather well mixed layer profile whereas the modelled isoprene profile decreases rather steeply with height. Note that the discrepancy between the measured and the modelled vertical profiles of BVOCs discussed in this section is the largest for the shown timeframe (14:00–17:00 LT). A higher vertical resolution version of the SCM (60 layers with 13 layers within the CBL), as presented and discussed in more detail by Ganzeveld et al. (2008), shows a better agreement between the observed and simulated vertical profiles. The discrepancies between the model simulated and observed profiles are much smaller in the morning and early afternoon.

In contrast to isoprene, acetone and methanol have much longer atmospheric life-

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times and can consequently serve to interpret the role of transport in and above the CBL. Methanol and acetone vertical profiles shown in Fig. 7 are, as expected, less steep than that of isoprene and MVK+MACR. Methanol and acetone mixing ratios declined to a level of $z/z_i \sim 3.5$ reflecting surface emissions and turbulent transport in the boundary layer and deeper mixing associated with shallow cumulus convection. Their mixing ratios increased again at the level $z/z_i \sim 4-5$ to mixing ratios which were comparable to those observed in the bottom kilometre for the timeframe under discussion.

The GABRIEL campaign average mixing ratios below 3 km were 3.1 ± 0.8 (1σ) ppbv for methanol and 1.0 ± 0.2 ppbv for acetone. The methanol values reported here are therefore significantly higher than the average value of 1.1 ppbv from the 1998 LBA-CLAIRe campaign over the same height range (0–3 km). In contrast, the 2005 acetone data reported here are significantly lower than those reported from 1998, 2.7 ± 0.8 ppbv (Crutzen et al., 2000; Williams et al., 2001).

Figure 7 also shows that the SCM simulated methanol and acetone mixing ratio vertical profiles for 14:00–17:00 LT. Methanol and acetone were prescribed in the model to obtain the maximum flux inferred from the airborne measurements (as discussed in the section “Flux calculations”) and for comparison also to the maximum flux as inferred from the ground-based measurements. The latter, it should be noted, is a point measurement. To a first approximation, measured and modelled profiles are in reasonable agreement for 14:00–17:00 LT. The model slightly overestimates the mixing ratios for acetone and methanol closer to the rainforest (below the cloud layer) and underestimates both tracers above the top of the boundary layer suggesting an underestimation of the simulated convective transport above the CBL. In the model, acetone and methanol mixing ratios remain nearly constant for several times the boundary layer height, in contrast to observations which show quite some variability with altitude and time of the day.

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5.5 Diurnal profile

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In the previous section, we have established that there was little day-to-day variation in meteorology and emissions during the GABRIEL campaign. We therefore have used the entire aircraft dataset, filtered according to the data selection criteria, see Sect. 5.2,
5 to infer area-average diurnal cycles of the studied BVOCs in the mixed layer, over the rainforest (see Fig. 8). Restricting the dataset to the first day over land has the advantage of avoiding influences of residual layers from previous days (discussed in next section and addressed in more detail by Ganzeveld et al., 2008). The diurnal cycles shown are composed of all airborne observations in the morning, early afternoon and
10 late afternoon above 300 m and below the CBL height. The median values of the quarter hourly 5p–95p box and whisker plots have been fitted to both a 5th order polynomial fit and a sinusoidal fit. Such fit is applied in combination with the CBL depth to infer surface fluxes from mixing ratio observations. The green vertical lines shown in these figures at 14:00 and 16:15 indicate the time interval for which the vertical profiles in the
15 previous section have been shown.

Airborne and ground-based observations of isoprene mixing ratios show a distinct diurnal variation (Figs. 8a and 10b), being very low in the morning, reaching peak concentrations during mid-afternoon and decreasing towards the evening along with temperature and sunlight. The ground-based measured values are significantly higher
20 than those taken in the mixed layer above 300 m, indicating the role of turbulent exchange in diluting as well as the high reactivity of isoprene to the oxidants OH and O₃, see Fig. 8a and b. Measured airborne median mixing ratios between 13:00 and 15:00 are 4.7 ppbv with 25p–75p values of 4.2–4.9 ppbv and a maximum of 5.8 ppbv. The mean mixed layer mixing ratios during the TROFFEE-airborne and ground-base campaign performed over Manaus, Brazil, were 5.2 ppbv (Karl et al., 2007) whereas those from the LBA-CLAIRE-2001 campaign were less than 4.7 ppbv (Kuhn et al., 2007).
25

The Brownsberg canopy level median mixing ratio of 6.4 ppbv ranged between 5.0–8.0 ppbv (25p–75p) with a maximum of ~10 ppbv (see Fig. 10b), for the same period of

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the day (after applying the same correction factor as obtained for the airborne intercomparison). Somewhat lower mean canopy level daytime mixing ratios of 3.4 ppbv (with a maximum of 6.6 ppbv) for isoprene have been observed by Kuhn et al. (2007) for isoprene at a measurement tower (K34) near Manaus in July 2001 (beginning of the dry season). Higher mean noontime surface layer isoprene mixing ratios of 7.8 ± 3.7 ppbv with peak values up to 15 ppbv at the Z14 tower in September 2004, and mixed layer mixing ratios between 0.6 and 6.7 ppbv have been observed towards the end of the dry season by Karl et al. (2007) and thereby comparable, yet slightly higher than the mixing ratios reported in this study without compensation for chemical loss.

The GABRIEL vertical profiles and the difference between surface and airborne measurements show strong gradients in isoprene from the canopy source to the top of the mixed layer. These are responsible for the large span of values measured at any given time in the diurnal plot, see Fig. 8. Since the aircraft samples over undulating terrain (particularly south of 5° N, with maximum height of 1280 m a.s.l.), it is in effect sampling at various heights above surface. Figure 8b indicates that mixed layer MACR and MVK mixing ratios show less variability compared to isoprene as they are formed aloft in the well-mixed boundary layer and have significantly longer chemical lifetimes. Their summed median mixing ratio was 1.6 ppbv, ranging between 1.5–1.7 ppbv (25p–75p) with a maximum of 1.8 ppbv comparable to other observations reported e.g. 2.1 ppbv by Karl et al. (2007), 2.5 ppbv by Warneke et al. (2001) whereas the observations by Kuhn et al. (2007) were substantially smaller (~0.5 ppbv). The Brownsberg canopy level MACR+MVK median mixing ratios were 3.2 ppbv, ranging between 2.7–3.6 ppbv (25p–75p) with a maximum of 3.9 ppbv and thereby slightly higher but comparable to the average noontime mixing ratios of 2.3 ppbv reported by Karl et al. (2007) and 2.5 ppbv by Warneke et al. (2001a).

It is important to note that the measured and modelled isoprene values in the mixed layer compared in Fig. 8a show that there is good agreement before 14:00 for simulations that apply a 50% reduction in the emission flux. After 14:00 the model tends to be higher than measured, not only with respect to isoprene but also for MACR and MVK

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as shown in Fig. 8b. All SCM diurnal profiles shown in this paper reflect the average of the 440 m and 870 m output levels of the 19-layer SCM. Measured OH data exhibited a much less pronounced diurnal variation in the mixed layer over the rainforest than in the model (see Fig. 9a). The most reasonable agreement in the simulation of the OH-concentrations occurs only between 09:00 and 09:30 LT when isoprene is still low and quite high simulated NO_x concentrations reflect the release of NOx, accumulated in the nocturnal inversion layer, out of the canopy into the mixed layer. Later in the day the discrepancy between the observed and simulated OH increases. The increasing discrepancy points at a potential misrepresentation in the (late) afternoon sources and/or sinks of isoprene including OH turbulent and convective mixing or emissions. This misrepresentation coincides with a most pronounced role of cloud cover suggesting a possible important role of cloud related processes including radiation, affecting surface emissions and photolysis, and convective mixing.

Reducing the isoprene emission flux in the SCM does lead to higher OH concentrations, however, the isoprene mixing ratios then fall well below the measured values. Increasing the vertical resolution in the SCM also does not result in a sufficient increase in OH to the level measured during this campaign. This apparent inconsistency is likely only to be resolved by significant changes in the models representation of isoprene chemistry including enhanced OH recycling rates for isoprene oxidation. This effect is explored in detail by Lelieveld et al. (2008) and Butler et al. (2008).

The obtained diurnal pattern for the ratio [MACR+MVK]/[isoprene] (not shown) on the 3rd day of the SCM simulation at canopy level shows a constantly increasing ratio between sunrise (zero) and sunset (0.4) without an increase after twelve. The model assumes an equilatitudinal transect (at 4.5° N) exclusively above the ocean before sunrise, which was according to the observed back trajectories not always the case for the airmasses encountered during this campaign. Aloft, both measured and modelled ratios of MACR+MVK to isoprene are found to be in reasonable agreement and varied generally between 0.3–0.4 and 0.4–0.5, respectively in the afternoon. It indicates that drawing conclusions from the ratio of MVK+MACR to isoprene is not straightforward

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since it needs to include an assessment of the role of the non-chemical sources and sinks. In addition, the ratio should also be applied with great care to infer OH concentrations in the field when this radical was not measured directly as has been done in this particular campaign.

In Figure 8c and d we see strong increases in both methanol and acetone within the CBL as a function of time of day. Both compounds have a number of identified biogenic and anthropogenic sources (Heikes et al., 2002; Jacob, 2002). However, we assume here that, because of the rainforest location and absence of significant anthropogenic activity the observed increases are attributable to direct biogenic emission from the rainforest ecosystem and some secondary production from photolysis of glycolaldehyde from isoprene oxidation (Magneron et al., 2005) or from terpene oxidation (Reis-sell et al., 1999). The observed morning mixing ratios varied between 1 and 2 ppbv for methanol, and between 0.5 and 0.7 ppbv for acetone. Afternoon methanol mixing ratios varied between 2 and 3.8 ppbv, and between 0.7 and 1.2 ppbv for acetone. In contrast to acetone, late afternoon methanol mixing ratios kept increasing under a fully developed boundary layer, see Fig. 4b.

From the vertical profiles taken upwind over the ocean shown in Fig. 2 we see that mixing ratios of both species are higher above the mixing layer than below. This raises the possibility that during the first day over land, entrainment of air from above can significantly affect mixing ratios within the mixed layer for these compounds. However, the vertical profiles over the rainforest discussed earlier show highest mixing ratios of both species near the canopy suggesting that biogenic production is more dominant than entrainment in this case.

The average simulated acetone mixing ratios agree well with the measurements whereas methanol mixing ratios are overestimated by the model by about 1 ppbv for the 3rd day of the SCM simulation and this regardless of the good model initialisation above the ocean. This difference is caused by the higher simulated free tropospheric concentrations, shown in Fig. 4 of the paper by Ganzeveld et al. (2008), as the overestimation at sunrise when the SCM column reaches land, is invariable to the imposed

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We calculate for the GABRIEL boundary layer conditions, an average atmospheric lifetime of isoprene, with respect to OH and O₃, of approximately 30 min, and 2 and 5 2.75 h for MACR and MVK, respectively. Compared to isoprene, both acetone and methanol are relatively unreactive towards ozone and OH, with atmospheric lifetimes of 2.5 and 13.5 days, respectively.

The relationship between isoprene and its oxidation products at a given measurement location is to some extent a reflection of the photochemical age of the air mass, 10 as discussed in Montzka et al. (1993), Biesenthal et al., (1998), Stroud et al. (2001), Apel et al. (2002). Brownsberg data (not shown) revealed a diurnal pattern in the ratio [MACR+MVK]/[isoprene] that drops at sunrise from 0.8 to 0.2 around 08:00 LT, then remains rather constant at 0.20±0.06 until 12:00 LT after which the ratio increases again until sunset. Aloft, the diurnal pattern of the [MACR+MVK]/[isoprene] ratio between 15 09:00–16:00 LT is similar, even though the median and mean ratios are distinctly lower. The airborne ratio fluctuated between 0.3 and 0.4, with the lowest median values between 12:00–14:00 LT. The data scatter was the highest in the morning (0.1–0.5) and lowerest in the afternoon (0.25–0.5).

Using the measured ratio [MACR+MVK]/[isoprene], we investigate the photochemical “age” *t* 20 for the GABRIEL campaign which reflects the time that a tracer spends between the level of emission and the measurement point (incorporating chemistry and mixing). It may be derived according to Eq. (1) and the reactions R1, R2, R3, assuming pseudo first order reactions and a dominance of the OH sink:

$$\frac{\text{MACR} + \text{MVK}}{\text{ISOP}} = \left(\frac{\gamma_{\text{MACR}} k_1}{(k_2 - k_1)} \right) \left(1 - e^{((k_1 - k_2)[\text{OH}]t)} \right) + \left(\frac{\gamma_{\text{MVK}} k_1}{(k_3 - k_1)} \right) \left(1 - e^{((k_1 - k_3)[\text{OH}]t)} \right) \quad (1)$$



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γ_{macr} and γ_{mvk} are the OH oxidation yields for MACR and MVK respectively and the reaction rate constants were taken accordingly as $k_{\text{isop},\text{OH}}=2.7\text{E}-5$

5 $11*\exp(390/T)$; $k_{\text{acr},\text{OH}}=8\text{E}-12*\exp(389/T)$ and $k_{\text{mvk},\text{OH}}=2.6\text{E}-12*\exp(610/T)$.

It should be noted that solving Eq. (1) for t by using high NO_x rather than low NO_x branching yields reveals a 21% longer photochemical age under low NO_x. The photochemical age and the photochemical lifetime of isoprene in the analysed mixed layer air were both between 10 min and 35 min for the first day over land. Interestingly, the diurnal cycle in the photochemical age and lifetime are different with the photochemical time showing a noontime minimum in contrast to the photochemical age which shows its minimum the morning, and thereafter following more or less the boundary layer evolution. The photochemical age of isoprene was shorter than the photochemical lifetime for first day over land. Further land inward, the inferred photochemical age is longer compared to the lifetime in the morning and around noon; in the late afternoon both are comparable.

For the first day over land, the simulated isoprene photochemical age and lifetime of isoprene are much higher and do not follow the observed diurnal profile. The simulated age and lifetime are 0.5 to ~2 h and 1 to 3.5 h, respectively until 14:00 LT, increasing to almost half a day in the following h as a direct consequence of the misrepresentation of OH and mixing. On the second day over land, the model simulates a noontime minimum for the photochemical lifetime as well as for the photochemical age which is in disagreement with the observations. Furthermore, values for these parameters are even higher than obtained for the first day over land.

25 For comparison we may estimate the convective timescale, i.e. the time scale for the air to circulate between the surface and the top of the mixed layer (large Eddy). We assume here typical parameter values for the tropics (as observed during the TROFFEE

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campaign in September 2004, T. Karl, personal communication, 2007) to estimate the timescale for convective mixing (t_*) based on the convective velocity scale (w_*) and the boundary layer height (z_i). We used a maximum sensible heat flux $\sim 200 \text{ W m}^{-2}$ (simulated by the SCM, Ganzeveld et al., 2008) before noon declining to $\sim 100 \text{ W m}^{-2}$ in the afternoon (due to cloud cover) and a surface temperature diurnal profile as observed at Brownsberg (24–26°C). In this way we obtain a maximum convective velocity scale of 2 m/s (Busch et al., 1976; Stull, 1988) which is in range of the convective velocity scale obtained for the TROFFEE campaign. This results in an inferred convective time scale between 8 min in the morning to 16 min in the afternoon which is substantially shorter compared to the chemical time scale and the photochemical age calculated above.

5.7 Flux calculations

In this study, we have attempted to determine trace gas fluxes of isoprene, acetone and methanol from the rainforest throughout the day on a regional scale. Mixed layer fluxes have been determined from the airborne measurements using Eq. (2) which is derived from the conservation equation introduced by McNaughton and Spriggs (1986) in which the change of the concentration of a BVOC as function of time (dC_{BVOC}/dt) represents in principle the sum of the production and loss processes (horizontal and vertical advection, vertical diffusion, dry deposition, convective up and downdrafts, production and loss (gas and aqueous), wet removal, and emissions).

$$20 \quad F_s(t) - F_e(t) = \left(\frac{dC_{\text{BVOC}}}{dt} \right) * z_i(t) \quad (2)$$

In simple terms, we assume that dC_{BVOC}/dt (taken from the inferred diurnal profile), within a boundary layer volume (determined in Sect. 5.1), results in the net flux of the tracer. In the mixed layer, this net flux is mainly the combination of the surface (F_s) and the entrainment flux (F_e). The volume is therefore limited by the convective boundary layer height z_i . This Convective Boundary Layer Budgeting Approach (CBL-BA) assumes a quasi-stationary steady state for the vertical profiles, and as a result

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vertical linear flux profiles can be obtained. The CBL-BA method is time dependent reflecting the role of chemistry and the mixing (vertical transport). It uses the natural integrating properties of the well-mixed atmospheric boundary layer, allowing average surface fluxes to be obtained over relatively large regions for time periods in broad daylight.

In order to estimate the surface flux of isoprene we therefore proceeded as follows. We correct for any chemical loss terms by using the conserved tracer (ISOP+MACR+MVK+others, see Fig. 10a) described previously in Eq. (2). Thereby we obtain the diurnal cycles shown in Fig. 11a and b (blue lines) in which the calculated mixed layer fluxes ($F_s - F_e$) for the observations as well as those simulated by the SCM have been plotted against time of the day. Figure 11a and b show the fluxes of isoprene without correction for chemical loss (dashed line) and the conserved tracer ISOP+MACR+MVK+others (dash double dotted line). The maximum median fluxes (i.e. the maximum flux calculated from the median values for quarter-hourly binned mixing ratios) are summarised in Table 1. By limiting ourselves to the first day over land we have eliminated the influence of residual layer air which complicates interpretation of daytime BVOC exchanges (Ganzeveld et al., 2008). Furthermore we inherently assume that the emissions occur into clean air advected from the ocean during the previous night.

Theoretically, in order to derive a flux the same air mass should be followed as it traverses the landscape as is done by the SCM. Practically, only relatively short (few h), discontinuous periods (spread over 14 days) of airborne measurements were available for analyses, risking that advection of airmasses with different concentrations of the compound of interest can lead to larger variability in regional flux calculations using the CBL method. However, the rather constant boundary conditions in terms of the key meteorological drivers of exchanges and chemistry and little day-to-day variability during the GABRIEL 2005 support the use of this method. Empirically, sinusoidal and 5th polynomial fits through the median values of 15 min binned mixed layer concentrations (in molecules cm^{-3}) for the first day over land have been of equal merit for interpolation.

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The measured median mixed layer isoprene flux without compensation for chemistry and detrainment ($F_e - F_s$) is $\sim 4.1 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ for the Guyana rainforest. This increases to $\sim 7.3 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ by considering the role of chemistry as shown in Fig. 11a. The diurnal profiles of the fluxes calculated here are influenced by the assumed convective boundary layer evolution. Calculating the mixed layer flux ($F_s - F_e$) for a somewhat deeper convective boundary up to $\sim 1900 \text{ m}$ rather than 1450 m in the afternoon (see Fig. 4b), resulted in $\sim 30\%$ higher inferred isoprene emission fluxes into the deeper boundary layer.

As a consistency check, the same budgeting approach has been applied to the CO_2 data measured on board of the Learjet during GABRIEL to determine the daytime CO_2 uptake assuming our lower estimated boundary layer height ($\sim 1450 \text{ m}$). A median value of $2.73 \text{ g CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ and an average of $4 \text{ g CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ (sinusoidal fit through 15 min binned data between 300 and 800 m over the rainforest) are found to be in reasonable agreement with the daytime CO_2 uptake measured under high irradiance state of $2.53\text{--}3.01 \text{ g CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ over an old-growth tropical forest in Para, Brazil from July 2000 to July 2001 using an eddy covariance technique by Goulden et al. (2004).

Air masses in the mixed layer are not only influenced by surface exchanges but also by free tropospheric air masses when the boundary layer grows. The boundary layer over tropical regions involves the development of scattered to broken cloud decks which complicates estimating the entrainment flux. This is especially relevant for relative longer lived tracers like acetone and methanol which can be transported deeper into the troposphere via the clouds compared to a relative short lived tracer like isoprene. Under partially clouded conditions it should be questioned if the role of entrainment or detrainment can be assessed by methods that are strictly speaking valid under clear sky conditions. These methods are usually based on

1. a concentration jump (dC/dz) across the CBL like e.g. $F_e = -w_{\text{entr}} (C_{\text{CBL}} - C_{\text{FT}})$ with w_{entr} being the boundary layer growth on time as used in e.g. Fedorovich (1995), Spirig et al. (2004), or

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2. to relate the overshoot and exchange of heat, moisture and compounds driven by the thermals $F_e = K_e * dC/dz$, where the exchange coefficient K_e is proportional to the convective velocity scaling and inversely proportional to dT/dz .

An accurate correction for mixing and detrainment of isoprene could not be determined

- 5 (inadequate measurements) and applied to Eq. (2) to obtain a surface layer flux (F_s). Karl et al. (2007) calculated the detrainment flux for isoprene to be on the order of 30–40% of the surface flux for a tropical rainforest site near Manaus between 10:00–12:00 LT, and assumed that this decreased with time in the afternoon. In order to estimate the potential significance of detrainment during the GABRIEL campaign we
10 have used the concentration jump method with a concentration difference between the CBL and data from 1 km above it in combination with the CBL growth rate as described above. We calculate a maximum detrainment flux of $1.4 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ around 12:20 LT (~20% of the isoprene mixed layer flux) which decreases fast as the CBL fully develops. This would bring the surface flux to $\sim 8.7 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ but this
15 estimate, as described above is somewhat uncertain.

We now compare the regional flux ($F_s - F_e$) to the Brownsberg surface flux (F_s) determined by the same CBL-budgeting approach with boundary layer evolution as obtained from the airborne data. We calculate using 15 min data intervals for 3–5 October, a maximum median flux of $5.0 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ around 11:00. However, even though
20 the measurements were performed at canopy level, isoprene gets oxidised within the canopy and therefore, this value is the lower limit of our estimate. By considering the sum of ISOP+MACR+MVK+others we obtain a maximum median flux of $11.1 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ which reflects the upper limit in our estimate. Because of the longer atmospheric lifetime of the oxidation products compared to isoprene, we assume the
25 true isoprene emission flux to be closer to the lower than to the higher estimate.

Putting our findings in the context of previous tropical forest isoprene emission studies, as listed in Table 2, we conclude that the isoprene fluxes reported here, are slightly lower than the average eddy covariance surface fluxes of $8.3 \pm 3.1 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ or the average mixed layer gradient surface flux of $12.1 \pm 4.0 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ as

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- described in Karl et al. (2007). These measurements have been conducted under partially cloudy sky and they have defined the top of the CBL as the bottom of the developing cloud layer (~1200 m deep) which is different to our definition as discussed earlier. Kuhn et al. (2007) reported a mean midday isoprene flux of $6.2 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ using the mixed layer gradient method on tower measurement near Manaus in July 2001. However, they state that this flux was on average about a factor two higher than the fluxes derived from tower-based measurements reported in the same study. Karl et al. (2004) observed lower isoprene emissions (on average 1.72 and up to $2.5 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$) for a drought-stressed Costa Rican ecosystem in April–May, 2003.
- Mean REA-measured isoprene fluxes of $2.5 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ were also measured in Costa Rica in October 1999 under cloudy conditions by Geron et al. (2002). These fluxes reflect generally weaker isoprene emissions than the Amazon in the Guyanas.

We compare our results to the simulated surface isoprene flux (green solid line in Fig. 11b) which reflects the canopy-top flux. The modelled mixed layer isoprene flux amounts to $\sim 3.3 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ and $\sim 6.0 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ after compensation for chemical loss. ISOP+MACR+MVK+others is based on high NO_x oxidation yields and reflects the average values of the 440 m and the 880 m level of the SCM. The maximum fluxes obtained for the individual levels were 6.8 and $5.6 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$, respectively indicating a relatively large flux divergence for the boundary layer.

Overall, there is a reasonable agreement between the observations and simulated isoprene emission fluxes for the applied factor 2 decrease in the isoprene emission potential. The comparison also indicates a relative large decrease in the emissions later in the afternoon possibly due to the reduced light and heat flux with the increase in partial cloud cover. However, in the 60-layer version SCM with a more efficient turbulent transport in the CBL, the change of the flux with height becomes much smaller.

Large Eddy Simulations by Vilà-Guerau de Arellano and van den Dries (2008) addresses that fluxes, even for inert or conservative tracers can change with height. Flux divergence depends on the surface and the entrainment flux. Because of quasi steady state conditions, the flux profile is linear with height and holds for dry convective bound-

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ary layers and subcloud layers. By considering isoprene and oxidation products together we assume to have reduced the effect of chemistry on the vertical flux profile (deviation) to a minimum. A possible, additional flux divergence in the cloud layer is depending on the cloud development itself.

The CBL-BA method inherently rejects outliers by using median values over distinct time spans (here 15 min) but remains sensitive to changes in concentrations due to long-range transport, e.g. biomass burning plumes. Data that clearly reflect a role of such events have not been considered in the flux calculation for methanol and acetone using the acetonitrile and CO concentrations as an indicator for such plumes. Elevated acetonitrile and acetaldehyde for Brownsberg have been used as criteria for not considering methanol and acetone data in the flux calculation because of missing CO measurements. From the remaining CBL data, we infer maximum mixed layer fluxes ($F_s - F_e$) of $0.38 \text{ mg acetone m}^{-2} \text{ h}^{-1}$ and a maximum median surface layer of $0.35 \text{ mg acetone m}^{-2} \text{ h}^{-1}$ as shown in Fig. 12 and summarised in Table 3. These fluxes are comparable to the maximum surface layer fluxes of $0.36 \text{ mg acetone m}^{-2} \text{ h}^{-1}$ reported by Karl et al. (2004) but are higher than their average flux of $0.09 \text{ mg acetone m}^{-2} \text{ h}^{-1}$ for 3 weeks of disjunct eddy covariance measurements in Costa Rica during the dry season, bearing the much lower isoprene emission flux from this region in mind. They are nevertheless not as high as the mean REA fluxes of $2.25 \text{ mg acetone m}^{-2} \text{ h}^{-1}$ reported by Geron et al. (2002).

The maximum observed median mixed layer flux of $\sim 0.8 \text{ mg methanol m}^{-2} \text{ h}^{-1}$ is twice the maximum median surface flux of $0.39 \text{ mg methanol m}^{-2} \text{ h}^{-1}$ observed at Brownsberg but there is a close resemblance in the course of the emissions with maximum fluxes around 14:00 LT.

Curiously, the inferred maximum mixed layer methanol flux appears to occur later in the afternoon compared to the maximum fluxes of acetone and isoprene, regardless of the function used for data interpolation, caused by the continuously increasing mixing ratios under a fully developed boundary layer. This suggests the significance of potential additional sources within the convective boundary layer. Methanol has

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been observed as a minor oxidation product of isoprene under low NO_x conditions by Ruppert and Becker (2000), possibly from the photolysis of glycolaldehyde, but this chemical source is not sufficient to explain the extra methanol production.

As the surface diurnal profiles of methanol and acetone have been fairly synchronous to each other and fairly analogous to isoprene, the fluxes are considered predominantly due to emissions from plants and only a relatively small fraction of these fluxes would be attributable to abiotic decay, even at the upper limit of methanol and acetone production rates discussed by Warneke et al. (1999) and the leaf litter fall (which is larger during the dry season) as described by Martius et al. (2004).

Alternatively, the fluxes of acetone and methanol can also be estimated from their longitudinal concentration gradient over the forest that builds up as their emissions accumulate in air traversing the rainforest through analysis of the mixing ratios as a function of time over land (TOL). TOL has been calculated along the back trajectories of the air parcels (as in Gebhardt et al., 2008). It should be noted that during the GABRIEL campaign, methanol and acetone evidently have shown a diurnal cycle with low mixing ratios in the morning and increasing mixing ratios over the course of a day. By interpreting the observations in a Lagrangian sense, i.e. with increasing TOL (max 14 h=sunset to sunrise), time of the day and consequent to the CBL height, fluxes can be determined. In this admittedly cruder approach the obtained mixed layer fluxes are $\sim 0.60 \pm 0.02 \text{ mg methanol m}^{-2} \text{ h}^{-1}$ and $\sim 0.24 \pm 0.01 \text{ mg acetone m}^{-2} \text{ h}^{-1}$ and are thereby comparable but slightly lower than obtained using the CBL-BA. The errors taken into account for the Orthogonal Distance Regression (ODR) are the total measurement uncertainty on the PTR-MS measurements, an uncertainty of 200 m on the CBL height and an error of 20% for the time over land. The number of data points involved in these calculations is much smaller compared to the CBL-BA. Interestingly, this method also indicates a mixed layer methanol flux which is higher than observed for the ground-based measurements. Nevertheless, it results in a lower acetone mixed layer flux than observed for the ground-based measurements.

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Vertical profiles of acetone and methanol have shown deeper mass transport up to several times the CBL height in the afternoon and thereby complicating inferring the emission flux due to the role cloud layer mixing. Due to small concentration differences across the CBL, in contrast to isoprene, the contribution by entrainment/detrainment fluxes for acetone and methanol is difficult to assess. Large Eddy Simulations with detailed representation of cloud dynamics over land by Vilà-Guerau de Arellano and van den Dries (2008) confirm that deeper mass transport can occur even for a generic hydrocarbon with a lifetime in accordance with that of isoprene during the GABRIEL-campaign. Their simulations have been performed with a slightly higher isoprene emission flux ($\sim 10 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$), similar specific humidity and cloud cover as observed during the GABRIEL campaign.

The simulated methanol and acetone fluxes (green solid lines in Fig. 12a and b), which have been adapted to the values inferred from the airborne measurements reflect the canopy-top flux. The driving factor for emission or deposition of methanol and acetone is the concentration difference between the internal leaf concentration and the surrounding air during daytime as the basis of the compensation point approach. A higher leaf level concentration results in a positive flux out of the canopy.

Recent estimates of OH-concentrations over the tropical rainforest (Karl et al., 2007; Kuhn et al., 2007) have been made using, among other methods, the mixed layer technique in which the surface and entrainment fluxes are related to the lifetime of a compound, and the relation has been expressed as

$$F_s - F_e = \frac{C}{\tau} z_i = (k_{\text{isop}, \text{OH}} [\text{OH}]_t + k_{\text{isop}, \text{O}_3} [\text{O}_3]_t) [\text{ISOP}]_t z_i \quad (3)$$

in which F_s and F_e represent the surface and the entrainment flux, respectively; z_i the boundary layer height and C/τ the average concentration at a particular time of a tracer divided by the atmospheric lifetime of that tracer. When the CBL height does not substantially increase anymore, i.e. in the afternoon, it can be assumed that steady state conditions prevail and the mixed layer can be hypothetically treated as a well-mixed volume. Karl et al. (2007) and Kuhn et al. (2007) inferred [OH] con-

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centrations above the rainforest from measured isoprene fluxes and CBL estimates of $1.3 \pm 0.5 \times 10^6 \text{ mol cm}^{-3}$ and $2.5 \pm 1.5 \times 10^6 \text{ mol cm}^{-3}$, respectively. These estimates are substantially smaller compared to the measured OH concentrations during GABRIEL (on average $\sim 5 \times 10^6 \text{ mol OH cm}^{-3}$). Using Eq. (3), with the measured OH values during GABRIEL results in an estimate isoprene emission flux, without considering de-trainment ($F_s - F_e$), of $\sim 20 - \sim 28 \text{ mg isoprene m}^{-2} \text{ h}^{-1}$ (for the first day over land). It is clear from Eq. (3) that the change in concentration is considered from a chemical point of view only and this does not reflect the potentially significant effect of mixing. Furthermore, Eq. (3) calculates very low fluxes for species like acetone and methanol due to their long atmospheric lifetimes.

6 Conclusions

The presented analyses of airborne and ground-based observations of BVOC mixing ratios, in combination with the OH measurements, show that the OH-concentrations above the rainforest have been higher than currently believed leading to fast oxidation of the emitted BVOCs in a convective boundary layer, the dynamics of which have been influenced by shallow cumulus convection.

A comparison of isoprene measurements from cartridge based GC-MS analyses and PTR-MS m/z 69 has shown that the results compare well, with 69% of the dataset within the measurement uncertainty of both systems. The small systematic isoprene underestimation by the PTR-MS could be due the humidity dependence of the m/z 69-signal versus the “dry” calibration performed in between flights. Performing in situ humidity controlled calibrations over the ambient humidity interval is strongly recommended for future rainforest studies.

We have assessed the campaign average mixed layer depth based on the occurrences of temperature inversions to rise from $\sim 500 \text{ m}$ in the morning (09:00) to a maximum of $\sim 1450 \text{ m}$ late in the afternoon. The observations indicate that the short-lived VOCs like isoprene and its slightly longer lived photoproducts MACR+MVK have

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not been significantly transported into the free troposphere. In contrast it has been shown that cloud driven vertical transport can have consequences for the distribution of longer-lived VOCs like acetone and methanol.

For the estimation of isoprene fluxes from the rainforest we have considered the chemically conserved tracer isoprene plus its main oxidation products represented by isoprene, MACR+MVK and an estimate of the remaining oxidation products based on low NO_x chemical yields. We have used the temporal change of this conserved isoprene and the average convective boundary layer evolution for 1 week of measurements to estimate the dry season regional isoprene flux for the tropical rainforest area in the Northeast of South America.

Regional flux estimates using the Convective Boundary Layer Budgeting Approach, accounting for chemical removal and a CBL height up to 1450 m give an isoprene flux of 7.3 mg isoprene m⁻² h⁻¹. This result based on airborne area-average observations has been found to be comparable to the conserved isoprene flux inferred from a point measurement in the same region but does not include a compensation for detrainment. This observed emissions flux resembles a global scale isoprene emission flux of roughly ~0.6 Pg C yr⁻¹ from the estimated 11 million km² of tropical rainforest estimated by Mayaux et al. (1998), being consistent with the global flux obtained by MEGAN (Guenther et al., 2006). In order to estimate the uncertainty in inferred surface emission fluxes we have consequently applied a deeper mixed layer depth that includes the domain affected by clouds of ~1900 m and resulted in a 30% higher flux.

This area- and campaign maximum median isoprene emission flux is about half of the flux simulated with an emission algorithm implemented in 19-layer single-column chemistry and climate model. Consequently, a comparison of observed and simulated CBL BVOC mixing ratios has been based on selected tropical forest emission potential being a factor two smaller compared to the default emission factor. This results in a good agreement in observed and simulated isoprene mixing ratios before 14:00 after which there is an increasing discrepancy between the observations and the model also due to a misrepresentation of isoprene oxidation and shallow clouds in the SCM.

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We determine a median photochemical lifetime in the middle of the mixed layer (850 hPa and 20°C) above the tropical rainforest of ~30 min for isoprene, ~2 h for MACR, 2.75 h for MVK, ~2.5 days for methanol and almost 14 days for acetone. The chemical time scale for these BVOCs is longer than the time scale of mixing which was estimated between 8 min in the late morning to 16 min in the afternoon. The photochemical ages for isoprene in the air masses encountered during GABRIEL were between 10 and 35 min, again indicating the important role of mixing. Consequently, we have observed that the time lag in the diurnal maxima of isoprene and its primary oxidation products is less in the mixed layer than at canopy level.

Here we apply the first simultaneous measurement of isoprene and OH over the tropical rainforest. By applying the mixed box technique also used by Kuhn et al. (2007) and Karl et al. (2007) to estimate OH, though here using the actually measured OH, we derive much larger isoprene fluxes than obtained by the CBL budgeting approach.

The SCM was able to simulate diurnal boundary layer profiles for acetone based on the observed maximum median mixed layer acetone flux ($0.35 \text{ mg acetone m}^{-2} \text{ h}^{-1}$) which has been found to be in good agreement with the scant information available in literature. Similarly for methanol, although its mixing ratios tend to change faster per unit of time in the mixed layer than observed in the surface layer, suggesting an additional, chemical production. The observed mixed layer flux for this tropical region was $\sim 0.8 \text{ mg methanol m}^{-2} \text{ h}^{-1}$. The observations suggest deeper transport of acetone and methanol via shallow cumulus convection. However, we can not exclude a possible downward flux.

Additional regional scale observations of BVOC concentrations and fluxes are needed over tropical continents in combination with high resolution boundary layer meteorological measurements to better constrain the budget of BVOCs emitted by the different tropical ecosystems. Furthermore in-depth investigation of the underlying low NO_x , organic oxidation chemistry in the remote troposphere is needed to improve current atmospheric models.

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Table 1. Maximum median observed and modelled mixed layer and surface layer isoprene emission fluxes for a CBL height up to ~ 1450 m.

	GABRIEL			$SCM F_{emis,isop} \bullet 0.50$		
(mg isoprene $m^{-2} h^{-1}$)	$F_s - F_e^*$	$F_s - F_e^{**}$	$F_s^{\text{Brownsberg,*}}$	$F_s^{\text{Brownsberg,**}}$	$F_s - F_e^{***}$	F_s
Isoprene	3.1	4.1	4.0	5.0	3.2	
Isoprene+MACR+MVK	4.3	5.3			4.8	
Isoprene+MACR+MVK+others	6.3	7.3			6.0	7.1
Time of the day	12:30	12:30	11:00	11:00	13:00	13:00

* Uncorrected PTRMS data

** Data corrected against TD-GCMS (see for details in the text)

*** Data averaged over 440 m and 880 m level of the L19 SCM

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Table 2. Overview of midday isoprene emission fluxes in the literature for the tropical rainforests of South-America.

Flux (mg isoprene m ⁻² h ⁻¹)	Isoprene	Location, year, (season)
Karl et al., 2007 EC, tower, + airborne	Avg: 7.8±2.3 Max: 12.1±4.0	Manaus September, 2004 (dry)
Karl et al., 2004 DEC, tower, PTRMS	Avg: 1.72 Max: 2.50	Heredia, Costa Rica April and May, 2003 (dry)
Geron et al., 2002 REA, cartridges, GC-FID	Avg: 2.50 Max: ~11	Heredia, Costa Rica October, 1999 (dry)
Kuhn et al., 2007 REA,tower, cartridge, CGMS	Avg: 2.36 Max:~2.40	Manaus, Brazil July, 2001 (dry)
Rinne et al., 2002 DEA, tower, cartridges, FIS	Max:~2.40	Tapajós, Brazil July, 2000 (end of wet)
Greenberg et al., 2004a Tethered balloon, cartridge, CGMS	Max: 2.2*	Tapajós, Brazil February, 2000 (wet)
Greenberg et al., 2004a Tethered balloon, cartridge, CGMS	Max: 5.3*	Balbina, Brazil March, 1998 (wet)
Greenberg et al., 2004a Tethered balloon, cartridge, CGMS	Max: 9.8*	Rondônia, Brazil February, 1999 (wet)

* Maximum midday emission flux, estimated from a box model by Guenther et al. (1999).

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Table 3. Maximum median observed and modelled mixed layer and surface layer methanol and acetone fluxes for a CBL height up to 1450 m.

		GABRIEL		SCM $F_{\text{emis,isop}} \bullet 0.50$
Methanol	(mg m ⁻² h ⁻¹)	$F_s - F_e$	$F_s^{\text{Brownsberg}}$	
		0.8	0.4	0.35
Acetone	Time of the day	13:00	13:27	12:19
		0.4	0.3	0.5
Time of the day		12:50	13:15	12:44
				12:00

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Table 4. Overview of midday OVOC emission fluxes in the literature for the tropical rainforests of South-America.

Flux ($\text{mg m}^{-2} \text{ h}^{-1}$)	Methanol	Acetone	
Karl et al., 2004 DEC, tower, PTRMS	Avg: 0.13 Max: 0.50	Avg: 0.09 Max:0.36	Heredia, Costa Rica April & May 2003
Geron et al., 2002 REA, cartidges, GC-FID	Avg: 1.41	Avg: 2.25	Heredia, Costa Rica October, 1999

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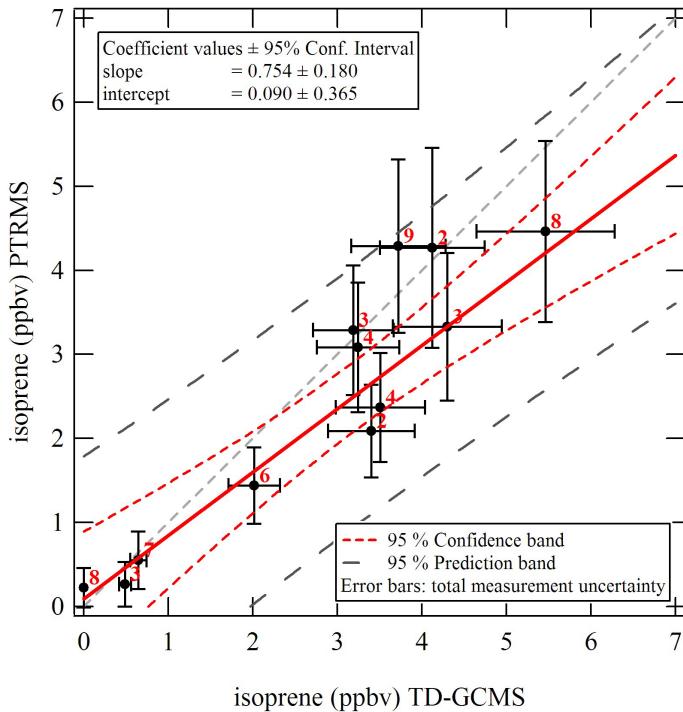


Fig. 1. Orthogonal distance regression of PTRMS vs. TD-GCMS labelled according to flight number; Error bars represent the total measured uncertainty for each measurement technique within each interval of comparison. 95% of the data should fall within the prediction band. By repeating the experiment numerous times, 95% of the fitted line should fall in the confidence band.

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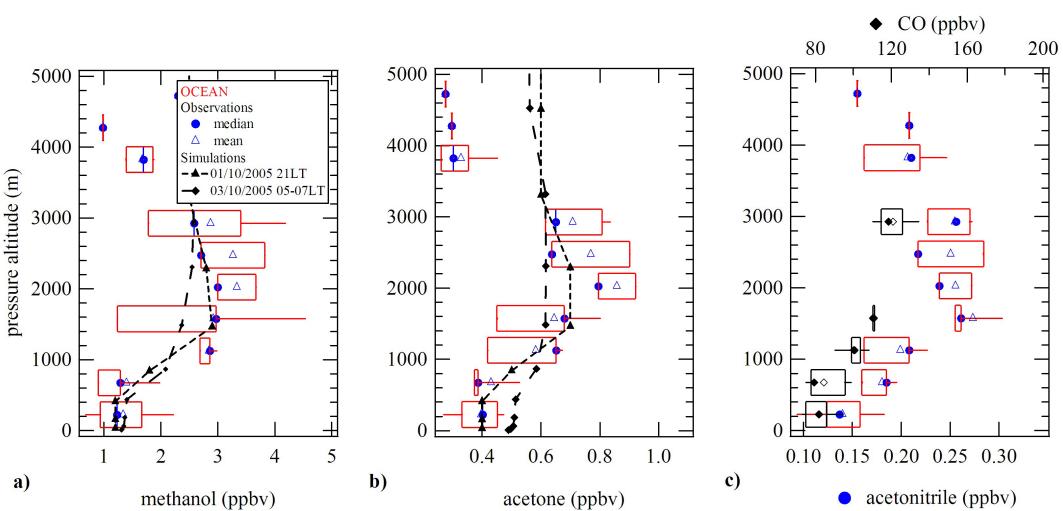


Fig. 2. Oceanic vertical profiles for methanol, acetone and acetonitrile used for SCM-model initialisation.

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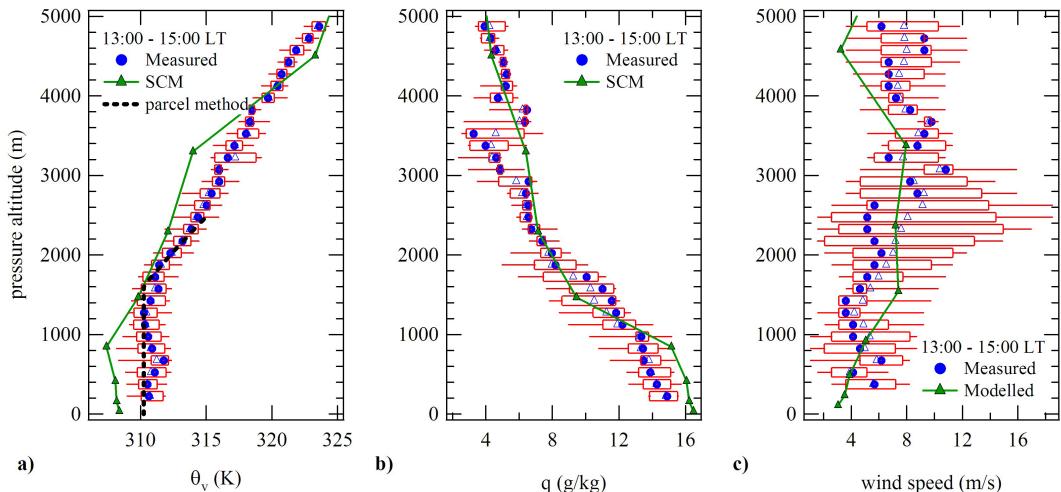


Fig. 3. Virtual potential temperature, specific humidity and wind speed profiles between 13:00 and 15:00 gathered from 10 flights above the Guyana's rainforest in comparison to their SCM simulated profiles.

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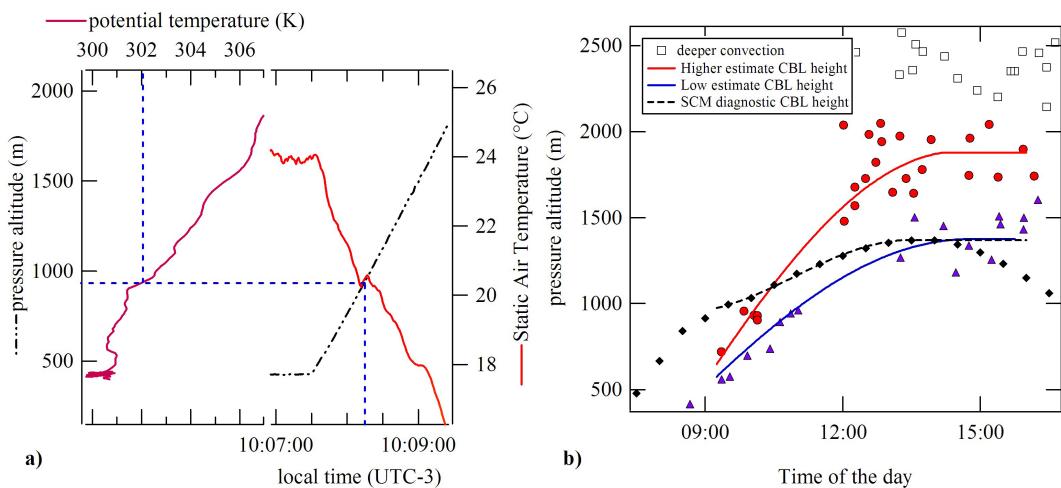


Fig. 4. (a) Fluctuation of the Static Air Temperature (SAT) upon constant climbing of the aircraft; (b) low and higher estimate of the CBL height evolution for the dry season (October) over the Guyana rainforest in comparison to that simulated by the 19 layer MEGAN SCM for the 1st day over land with indication of shallow convection layers.

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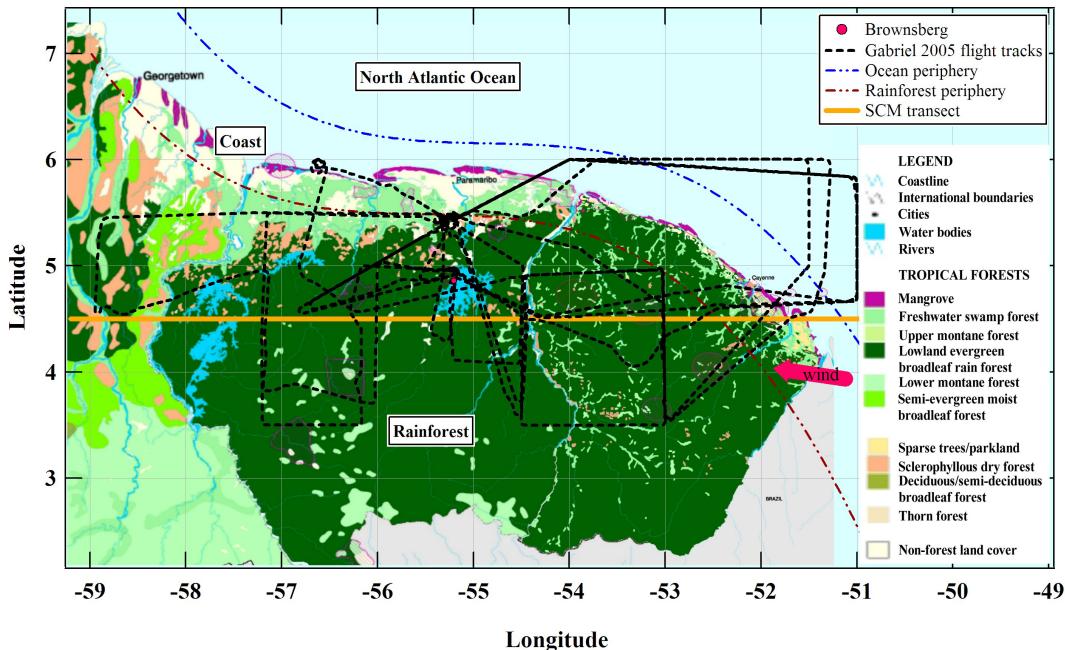


Fig. 5. Map of the geographical area over which the flights were conducted, superimposed onto a vegetation map UNEP-WCMC, 2000.

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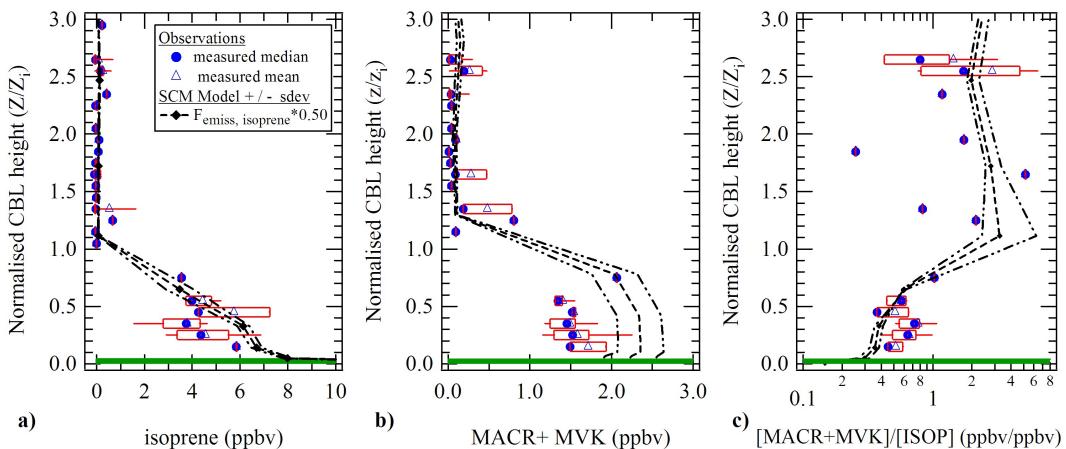


Fig. 6. Vertical profiles for (a) isoprene, (b) the sum of methacrolein and methyl vinyl ketone, (c)) the ratio of oxidation products to isoprene in comparison to the SCM model output for $F_{\text{emiss}, \text{isoprene}} * 0.50$ (14:00–16:15). The green strip signifies the rainforest.

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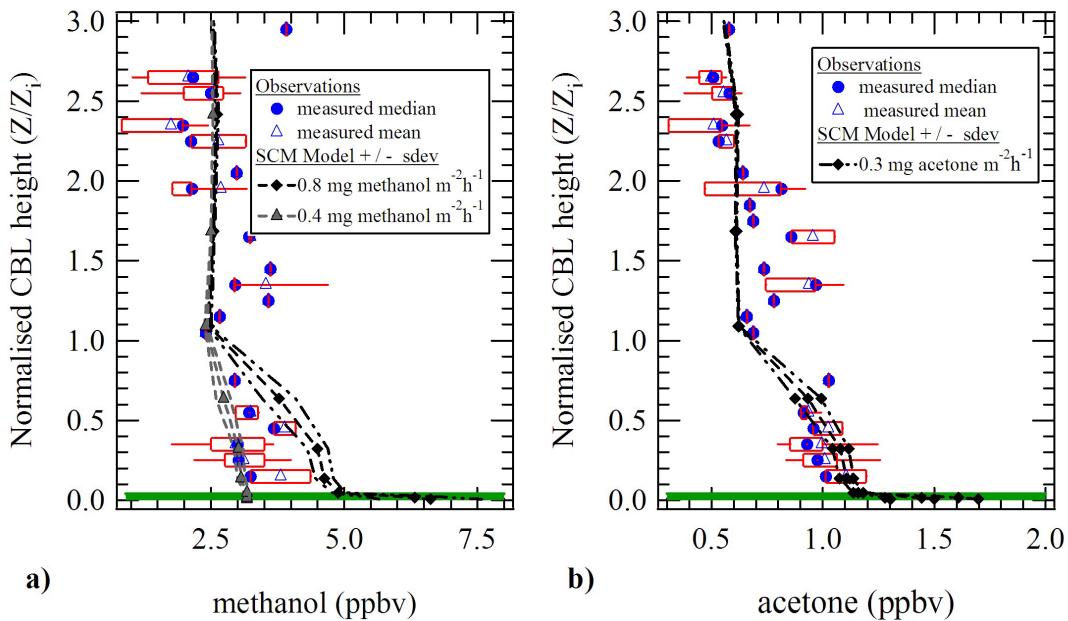


Fig. 7. Vertical profiles (a) for methanol, (b) acetone in comparison to the SCM model output (14:00–16:15).

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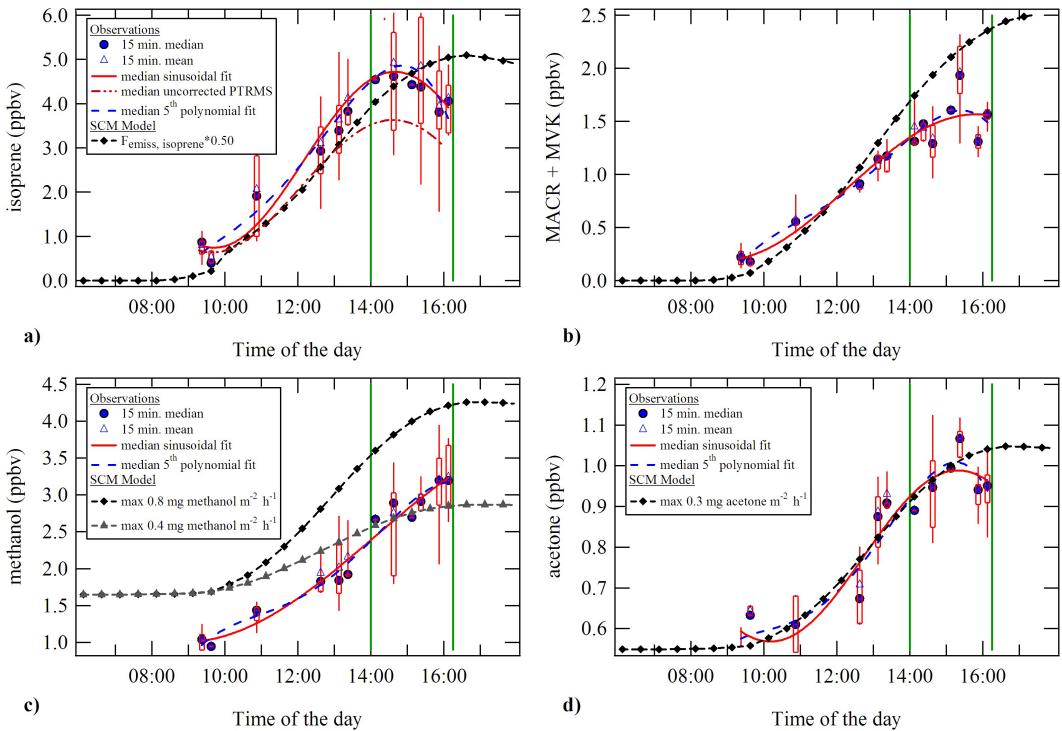


Fig. 8. Mixed layer diurnal cycles for isoprene and its oxidation products, methanol and acetone over the Guyana's rainforest (first day over land).

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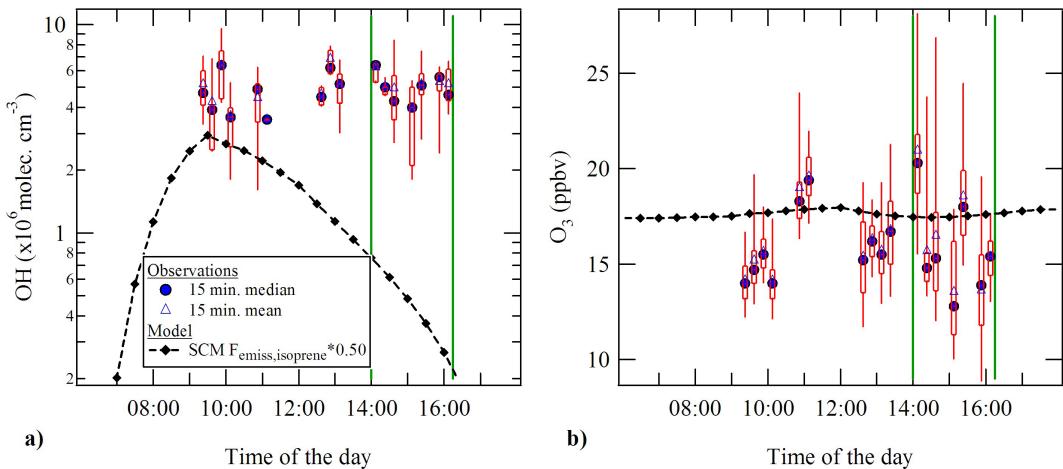


Fig. 9. Diurnal profiles of oxidising agents OH (a) and O_3 (b) measured and modelled above the rainforest for October 2005.

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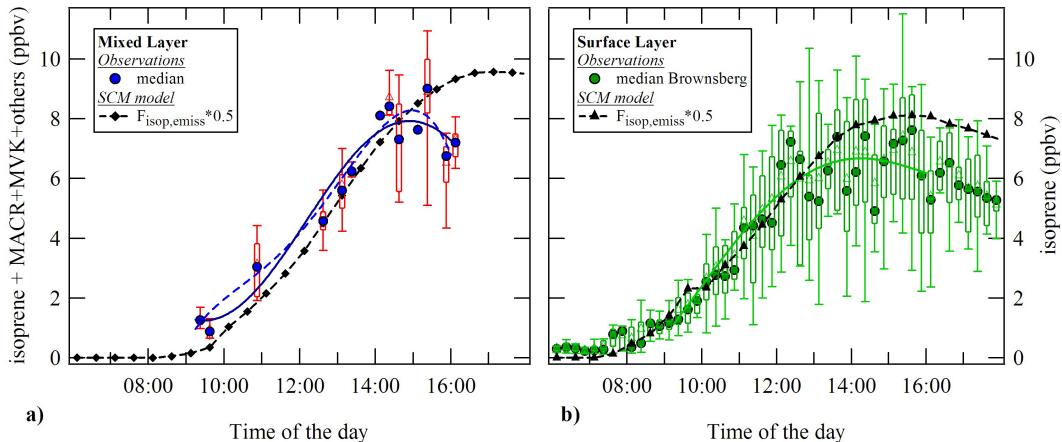


Fig. 10. Comparison of the measured to the modelled diurnal cycle (first day over land) of (a) the conserved tracer isoprene+MACR+MVK+others in the mixed layer and (b) isoprene in the surface layer.

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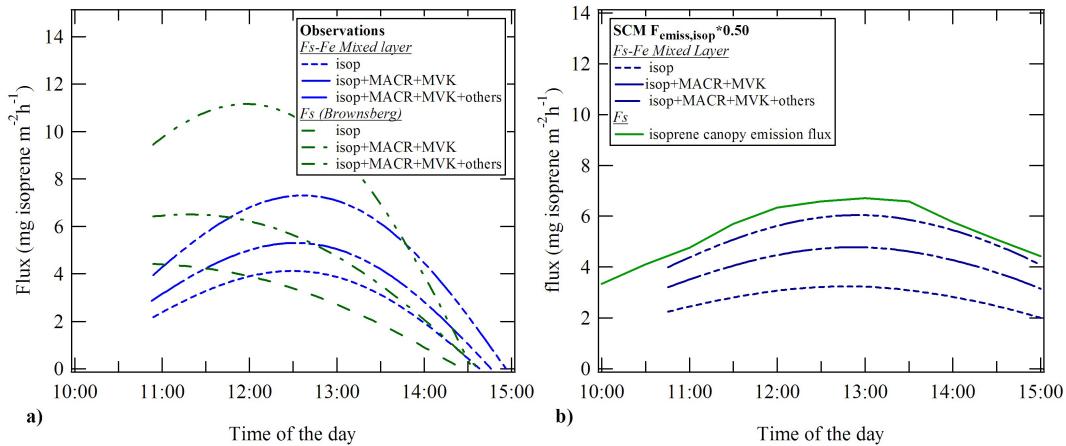


Fig. 11. Comparison of the measured (**a**) and the modelled (**b**) mixed layer isoprene emission flux by compensation for chemical loss.

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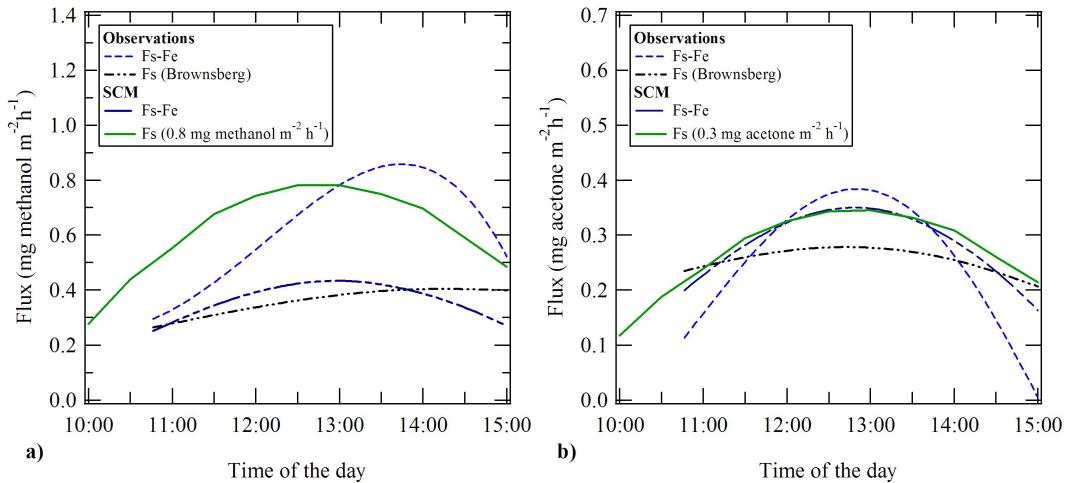


Fig. 12. Mixed layer methanol **(a)** and acetone **(b)** fluxes calculated by the CBL budget approach on measured and modelled data compared to the surface layer fluxes at Brownsberg and the 65 m level of the SCM.

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