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Monoterpene chemical speciation in the Amazon tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO)

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Speciated monoterpene measurements in the Amazon rainforest air are scarce, but important in order to understand their contribution to the overall reactivity of volatile organic compound (VOCs) emissions towards the main atmospheric oxidants, such as hydroxyl radical (OH), ozone (O_3) and nitrate radical (NO_3). In this study, we present the chemical speciation of gas phase monoterpenes measured in the tropical rainforest at the Amazon Tall Tower Observatory (ATTO, Amazonas, Brazil). Samples of VOCs were collected by two automatic sampling systems positioned on a tower at 12 and 24 m height and analysed using Gas Chromatography Flame Ionization Detection (GC-FID). The samples were collected in October 2015, representing the dry season, and compared with previous wet and dry season studies at the site. In addition, vertical profile measurements (at 12 and 24 m) of total monoterpene mixing ratios were made using Proton-Transfer Reaction Mass Spectrometry (PTR-MS). The results showed a distinctly different chemical speciation between day and night. For instance, α-pinene was more abundant during the day, whereas limonene was more abundant at night. Reactivity calculations showed that the most abundant compounds may not be the most atmospheric chemically relevant compounds. Furthermore, inter- and intra-annual results demonstrate similar chemodiversity during the dry seasons analysed. Simulations with a canopy exchange modelling system compare relatively well with the observed temporal variability in speciated monoterpene mixing ratios, but also indicate the necessity of more experiments to enhance our understanding of in-canopy sinks of these monoterpenes.

1. Introduction

Isoprenoids such as isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) are considered to be key contributors to the production of biogenic secondary organic aerosol (SOA), which affect cloud condensation nuclei production (Engelhart et al., 2008; Jokinen et al., 2015; Pöschl et al., 2010). While isoprene has been shown to be a globally significant source of SOA (Claeys et al., 2004), it's presence has been also shown to inhibit SOA formation under certain conditions (Kiendler-Scharr et al., 2009). By virtue of their lower volatility and higher ozone reactivity, monoterpenes and sesquiterpenes are strong sources of secondary organic aerosol (SOA) through the generation of low-volatility oxidation products formed via ozonolysis and hydroxyl radical oxidation (Bonn and Moortgat, 2003; Zhao et al., 2015).

The main source of monoterpenes to the global atmosphere is emission from vegetation, with smaller contributions from soil (Kesselmeier and Staudt, 1999; Kuhn et al., 2002; Ormeno et al., 2007). Synthesis of the monoterpene species occurs via the non-mevalonate pathway within the plant chloroplast (Kesselmeier and Staudt, 1999; Lichtenthaler, 1999; Schwender et al., 1996), which explains the light dependency also known to determine isoprene synthesis and emission. These commonly emitted compounds have been identified as important signalling compounds through plant-to-plant, plant-insect or plant-microbe interactions (Gershenzon, 2007; Gershenzon and Dudareva, 2007; Kishimoto et al., 2006; Maag et al., 2015) and they are thought to protect photosynthetic membranes against abiotic stresses (Jardine et al., 2017; Penuelas and Llusia, 2002; Vickers et al., 2009).

Despite having a common sum formula, variations in the molecular structure of the various monoterpenes result in large variations (over two orders of magnitude) of their reaction rate coefficients with the hydroxyl radical (OH), ozone (O_3) and nitrate radical (NO_3). Current quantification methods for monoterpenes include the fast (ca. 30 seconds) but unspecific total monoterpene measurement by the proton transfer reaction mass spectrometer (PTR-MS) (Lindinger and Jordan, 1998) and the slower (ca. 1 hour) but chemically speciated gas chromatographic methods. In order to gauge the role of these species in atmospheric chemistry, chemical speciation needs to be provided by the gas chromatographic techniques while the on-line mass spectrometer can assess how the total mass changes over time. It should be noted that the structure and reactivity of the monoterpenes can also have implications for the efficiency of SOA formation (Hallquist et al., 2009; Kiendler-Scharr et al., 2009; Mentel et al., 2009; O'Dowd et al., 2002). In most cases, SOA products are poorly characterized due to a scarcity of measurements (Martin et al., 2010).

Considering the overall size of the Amazon rainforest (5.4 million km^2 in 2001; Malhi et al., 2008) and the significant contribution of BVOC emissions from this vast forest to the global VOC budget (globally 1000 Tg of carbon yr^{-1}; Guenther et al., 2012), measurements of total monoterpene emissions and mixing ratios from this ecosystem are scarce (Greenberg and Zimmerman, 1984; Helmig et al., 1998; Jardine et al., 2015, 2011, 2017; Karl et al., 2007; Rinne et al., 2002; Yáñez-Serrano et al., 2015). Speciated measurements are even more scarce (Jardine et al., 2015, 2017; Kesselmeier et al., 2002; Kuhn et al., 2004). Yet, this information is essential to our understanding of the functioning of the Amazon rainforest in atmospheric chemistry-climate interactions. Knowledge of these processes also serves to improve predictions of future changes in atmospheric composition and to assess the impact of changes in regional emissions and land use on global climate caused by Amazon deforestation.

In this study, we evaluate measurements of speciated rainforest monoterpene mixing ratios as a function of height in the canopy, season and diel cycle. This evaluation includes a comparison with an offline version of the Multi-Layer Canopy Chemistry Exchange model (MLC-CHEM), driven by observed micro-meteorology and ozone surface layer mixing ratios, to support analysis of the measured temporal variability in speciated rainforest monoterpene mixing ratios as a function of height in the canopy. The MLC-CHEM was chosen for this purpose since it has been already extensively applied for site- to global-scale studies on atmosphere-biosphere exchange for tropical rainforest ecosystems (Ganzeveld et al., 2008, 2002a; Ganzeveld and Lelieveld, 2004; Kuhn et al., 2010).

2. Methodology

2.1. Site

The site chosen for this study was the Amazon Tall Tower Observatory, ATTO (Andreae et al., 2015). This site is located in Central Amazonia (S 02° 08.647' W 58° 59.992'), 150 km NE of the closest populated city, Manaus, Brazil. Due to the prevailing north-easterly wind direction, the influence of the Manaus plume is negligible and the measurements at this site can be considered to reflect pristine tropical forest conditions affected by air masses that passed over 1000 km of undisturbed rainforest. The site is equipped with a 325 m tall tower as well as two smaller towers. This study was carried out on the INSTANT tower, an 80-m walk-up tower located 600 m from the tall tower in easterly direction. For a comprehensive site description see Andreae et al. (2015). Sampling was performed on this tower at two different heights (12 m and 24 m).

2.2. Air sampling

Collection of ambient air samples on adsorbent tubes, for subsequent analysis by Gas Chromatography – Flame Ionization Detector (GC-FID), was made with two automated cartridge samplers described earlier (Kesselmeier et al., 2002; Kuhn et al., 2002, 2005). The samples were collected from 17 to 20 October 2015. Furthermore, additional sampling was performed at 24 m with a GSA SG-10-2 personal sampler pump during the years 2012-2014. Measurements took place on 19 and 28 November 2012, 22, 25 and 26 September 2013, 17 and 21 August 2014, with the measurements presented in this study in more detail having been taken from 17 to 20 October 2015 (dry season); 1, 3 and 4 March 2013 (wet season) and 11 to 14 June 2013 (wet-to-dry transition). Briefly, the samplers consist of two main units, a cartridge magazine that holds the adsorbent-filled tubes and the control unit timing the process and recording the data. This latter unit also houses the pumps (Type N86KT, KNF Neuberger, Freiburg, Germany), pressure gauges, mass flow controllers and power supply. The cartridge magazine is equipped with solenoid valves controlling the inlet and outlet of up to 20 individual sampling adsorbent tubes. The system is a constant-flow device, with one cartridge position per loop used as a bypass for purging the system. Due to the compact weatherproof housings and the low power consumption, we were able to position one sampler at 24 m and the other one at 12 m, attached to the INSTANT tower booms with commercially available 50 mm aluminium clamps. The height of the canopy is approximately 35 m (Andreae et al., 2015).

The adsorbent tubes used for VOC sampling were filled with 130 mg of Carbograph 1 (90 m^2 g^{-1}) followed by 130 mg of Carbograph 5 (560 m^2 g^{-1}) sorbents. The size of the Carbograph particles was in the range of 20–40 mesh. Carbographs 1 and 5 were provided by L.A.R.A s.r.l. (Rome, Italy) (Kesselmeier et al., 2002). Samples were taken for 30 min at a flow of 200 cm^3 min^{-1} (STP), leading to a collection of 6 L of air.

2.3. Instruments for chemical analysis

2.3.1. Gas Chromatography –Flame Ionization Detector (GC-FID)

After collection, the adsorbent tubes were analysed at the Max Planck Institute for Chemistry (MPIC) using a Gas Chromatograph equipped with a Flame Ionization Detector (GC-FID, Model Auto-System XL, Perkin Elmer GmbH, Germany) for identification and quantification of the monoterpene species. Helium was used as carrier gas. Separation occurred on a 100 meter HP-1 column with 0.22 mm inner diameter and coated with the non-polar dimethylpolysiloxane as stationary phase. The compound mixture collected in the adsorbent tubes was discharged into the gas stream with the help of a two-step desorption system (Model ATD400, Perkin Elmer, Germany). The samples were cryofocused in a cold trap at -30 °C filled with Carbograph 5, providing better defined peaks in the chromatograms. Afterwards the cold trap was rapidly heated to 280°C and the pre-concentrated sample injected onto the column. The following temperature programme was used: (-10 to 40 °C at 20 °C min^{-1}, 40 to 145 °C at 1.5 °C min^{-1}, and 145 to 220 °C at 30 °C min^{-1}). The separated compounds were quantified with a Flame Ionization Detector (FID). Identification was achieved through spiked injection of pure compounds. For a more detailed description see Kesselmeier et al., (2002).

Calibration for VOCs containing no heteroatoms was achieved by using a standard gas mixture of isoprene and several n-alkanes (n-pentane, n-hexane, n-heptane, n-octane, n-nonane, and n-decane) (Apel-Riemer Environmental Inc., USA). In this case, it is assumed that the “effective carbon number” (Sternberg et al., 1962) is equal to the real carbon number of the molecules (Komenda, 2001), yielding a signal response that is proportional to the real carbon number. The monoterpenes identified and quantified were α-pinene, camphene, sabinene, β-pinene, myrcene, α-phellandrene, 3-carene, α-terpinene, ρ-cymene, limonene and γ-terpinene. The detection limit for the GC-FID was 2 ppt (Bracho-Nunez et al., 2011).

2.3.2. Proton Transfer Reaction - Mass Spectrometer (PTR-MS)

Online total monoterpene mixing ratios were determined by a quadrupole Proton Transfer Reaction - Mass Spectrometer, PTR-MS (Ionicon Analytic, Austria). The PTR-MS was operated under standard conditions (2.2 mbar drift pressure, 600 V drift voltage, 142 Td). Periodic background measurements and humidity dependent calibrations were performed. A gravimetrically prepared multicomponent standard for calibration was obtained from Apel & Riemer Environmental, USA. The measurements were carried out at eight different heights (0.05, 0.5, 4, 12, 24, 53 and 79 m) with the PTR-MS switching sequentially between each height at 2 min intervals and only data from 12 and 24 m is shown. The inlet lines were made of PTFE (9.5 mm OD), insulated and heated to 50 ºC, and had PTFE particle inlet filters at the intake end. More information about the gradient system and PTR-MS operation at ATTO can be found elsewhere (Nölscher et al., 2016; Yáñez-Serrano et al., 2015). The limit of detection (LOD) of the PTR-MS for total monoterpenes was 0.1 ppb, determined as 2σ of the background noise.

2.4. Multi-Layer Canopy Chemistry Exchange model (MLC-CHEM)

To analyse the magnitude and temporal variability in the observed monoterpene concentrations inside and above the forest canopy, we applied the Multi-Layer Canopy Chemistry Exchange Model (MLC-CHEM), driven by the observed micro-meteorology and ozone surface layer mixing ratios. The MLC-CHEM model was originally developed and implemented as a single-column model (SCM) as well as in a global chemistry and climate-modelling system to assess the role of canopy processes in local- to global-scale atmosphere-biosphere exchange of nitrogen oxides (Ganzeveld et al., 2008, 2002b; Kuhn et al., 2010). The MLC-CHEM generalized representation of chemistry, dry deposition, emissions and turbulent mixing allows to study the role of canopy interactions in determining atmosphere-biosphere exchange fluxes and in-canopy and surface layer concentrations of biogenic volatile organic compounds (BVOCs). BVOC emissions are calculated according to MEGAN (Guenther et al., 2006), considering the vertical distribution of biomass and direct as well as diffuse radiation to calculate leaf-scale BVOC emissions. The current implementation of canopy chemistry in MLC-CHEM considers, in addition to standard photo-chemistry (O_3, NO_x, CH_4, CO), the role of non-methane hydrocarbons including isoprene, and a selection of hydrocarbon oxidation products such as formaldehyde, higher aldehydes and acetone. Oxidation of the monoterpenes by OH, O_3 and NO_3 is taken into account to simulate their chemical destruction, but the role of the oxidation products in photo-chemistry is not considered in the current implementation of the chemistry scheme in MLC-CHEM. For this study, we have extended MLC-CHEM to consider, besides the already included compounds α-pinene and β-pinene, the observed monoterpene species α-terpinene, limonene and myrcene. The monoterpene relative emission ratios used for this simulation (relative to the selected initial leaf-scale MT emission factor (EA) of 0.4 µg C g^{-1} hr^{-1}) were: α-pinene = 0.45 x EA, β-pinene = 0.10 x EA, α-terpinene = 0.27 x EA, limonene = 2.25 x EA and myrcene = 0.45 x EA. Note that for limonene, only the selected high basal emission flux would result in simulated mixing ratios comparable to the observed ones. Regarding the physical sinks; dry deposition of gases including the BVOC compounds depends on their uptake resistances calculated according to Wesely's (1989) parameterization, which estimates these uptake resistances based on the compounds' solubility and reactivity.

The simulations with MLC-CHEM were constrained with the observed surface layer net radiation, wind speed, relative humidity and O_3 concentrations as well as the temperature measured above and inside the canopy from 17 to 20 October 2015. Note that unfortunately no high-quality micrometeorological observations were available for 18 October 2015, so we modelled a diurnal cycle based on the previous and subsequent meteorological parameters, which drive MLC-CHEM quite close to the observed diel cycles for the other three days of the measurement period.

3. Results

3.1. Time series and diel cycles

Continuous online PTR-MS measurements were compared with off-line GC-FID samples over the course of 3 days in October 2015 (Figure 1). The close agreement between the two measurement techniques provides confidence that almost all monoterpenes present at ambient air in the site were being measured. Note that in this comparison, ρ-cymene was removed from the calculations as the PTR-MS does not detect it on m/z 137.

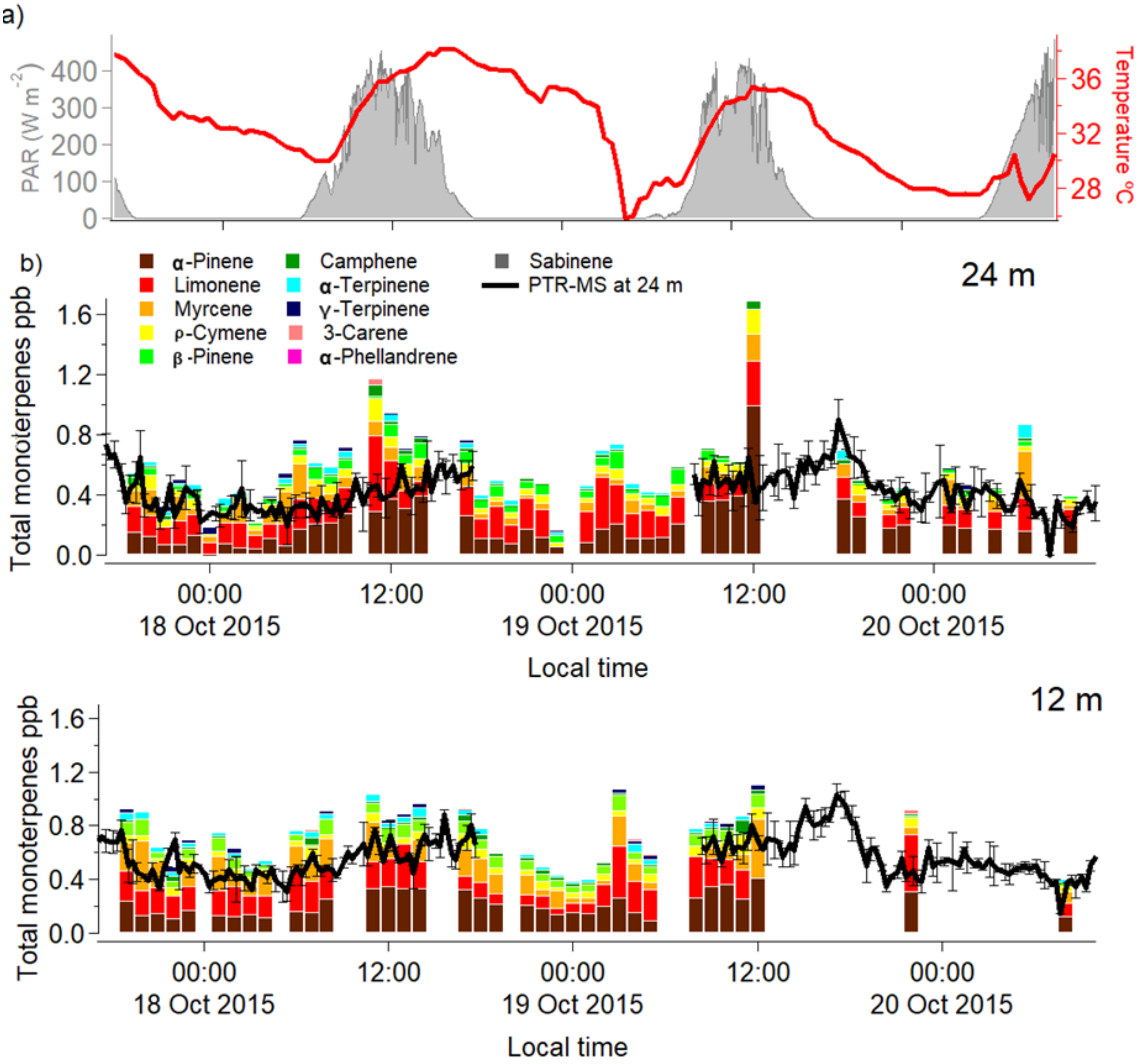

Figure 1: Graph showing the speciated monoterpene mixing ratios measured hourly from 17 to 20 October 2015 for b) 24 m and c) 12 m. The colours on the stacked bar plot indicate the different monoterpene species as they are denoted in the legend. The black line represents the PTR-MS total monoterpene mixing ratio, with a gap of data on the 19 October 2015. Temperature at 80 m is shown in the red thick line and photosynthetically active radiation at 39 m is shown in the shaded areas in a).

The total monoterpene mixing ratios were higher during the day when temperature and solar radiation were at their maxima. Most of the observed distinct diurnal cycle in total monoterpene mixing ratios can be attributed to α-pinene, which was the dominant species during the daytime with mixing ratios large as 0.33±0.04 and 0.38±0.21 ppb at 12 and 24 m respectively, and 0.15±0.05 and 0.11±0.06 ppb for the night at 12 and 24 m. The second most abundant monoterpene species was limonene, with observed average daytime mixing ratios of 0.18±0.09 and 0.19±0.12 ppb at 12 and 24 m, respectively, and 0.18±0.01 and 0.14±0.07 ppb for the night time at 12 and 24 m.

Table 1: Mixing ratios in ppb at 24 and 12 m of the measured monoterpene species for 17 to 20 October 2015 as determined by the GC-FID analysis. The daytime period was considered from 0900h to 1700h and the night time period from 2000h to 0500h (Local time). BLD stands for below detection limit.

Compound	Day 12 m	Night 12 m	Day 24 m	Night 24 m
α-Pinene	0.33 ± 0.04	0.15±0.05	0.38±0.21	0.11±0.06
Limonene	0.18±0.09	0.18±0.10	0.19±0.12	0.14±0.07
Myrcene	0.16±0.14	0.12±0.09	0.09±0.04	0.07±0.06
P-Cymene	0.07±0.03	0.04±0.01	0.08±0.04	0.04±0.02
β-Pinene	0.08±0.03	0.06±0.03	0.05±0.03	0.04±0.02
Camphene	0.03±0.03	0.02±0.01	0.03±0.02	0.01±0.01
α-Terpinene	0.03±0.02	0.03±0.02	0.01±0.02	0.02±0.02
γ-Terpinene	0.02±0.01	0.01±0.01	0.01±0.01	0.01±0.01
3-Carene	0.001±0.003	0.003±0.008	0.003±0.011	0 or BLD
α-Phellandrene	0 or BLD	0 or BLD	0 or BLD	0 or BLD
Sabinene	0 or BLD	0 or BLD	0 or BLD	0 or BLD
MT Sum – GC-FID	0.91±0.10	0.62±0.19	0.82±0.34	0.45±0.13
MT Sum – PTR-MS	0.96±0.27	0.54±0.17	0.77±0.22	0.56±0.16

The difference between the 12 and 24 m height total monoterpene mixing ratios is minor given the variance of the measurements, but there is a tendency for the difference to be more pronounced during night time (Table 1). This could be due to higher biogenic emissions at 12 m compared to 24 m during the night, differences in reactivity within the canopy leading to different oxidation regimes, or more stagnant conditions leading to higher accumulation.

The continuous online measurements by the quadrupole PTR-MS indicate a clear diurnal cycle in the measured mixing ratios of the sum of monoterpenes, which has been reported previously from this site (Yáñez-Serrano et al., 2015). In order to assess the effect of each individual monoterpene species, we further investigated their diurnal cycles as obtained by the off-line GC-FID samples. The measured diel cycles for the most relevant monoterpene species at the ATTO site were very similar at both heights. We also compared the measured diel cycles of isoprene with the observed diel cycle for the different monoterpene species. The compounds that showed a diurnal cycle similar to isoprene were α-pinene and ρ-cymene (Figure 2). This could be due to the emission of α-pinene and ρ-cymene being dependent on light and temperature, analogous to isoprene. However, during the night both monoterpenes were also present, albeit at lower mixing ratios, and the nocturnal mixing ratios of the monoterpenes did not decrease as much as isoprene. This has also been noted in previous studies (Yáñez-Serrano et al., 2015).

Despite the higher mixing ratios of limonene compared to other monoterpene species (other than α-pinene), it was not possible to distinguish any clear diel pattern in the average data for this species (see Figure 2). β-Pinene and α-terpinene likewise show no obvious diel pattern in the rainforest air, despite the detection limit of the GC-FID being 2 ppt.

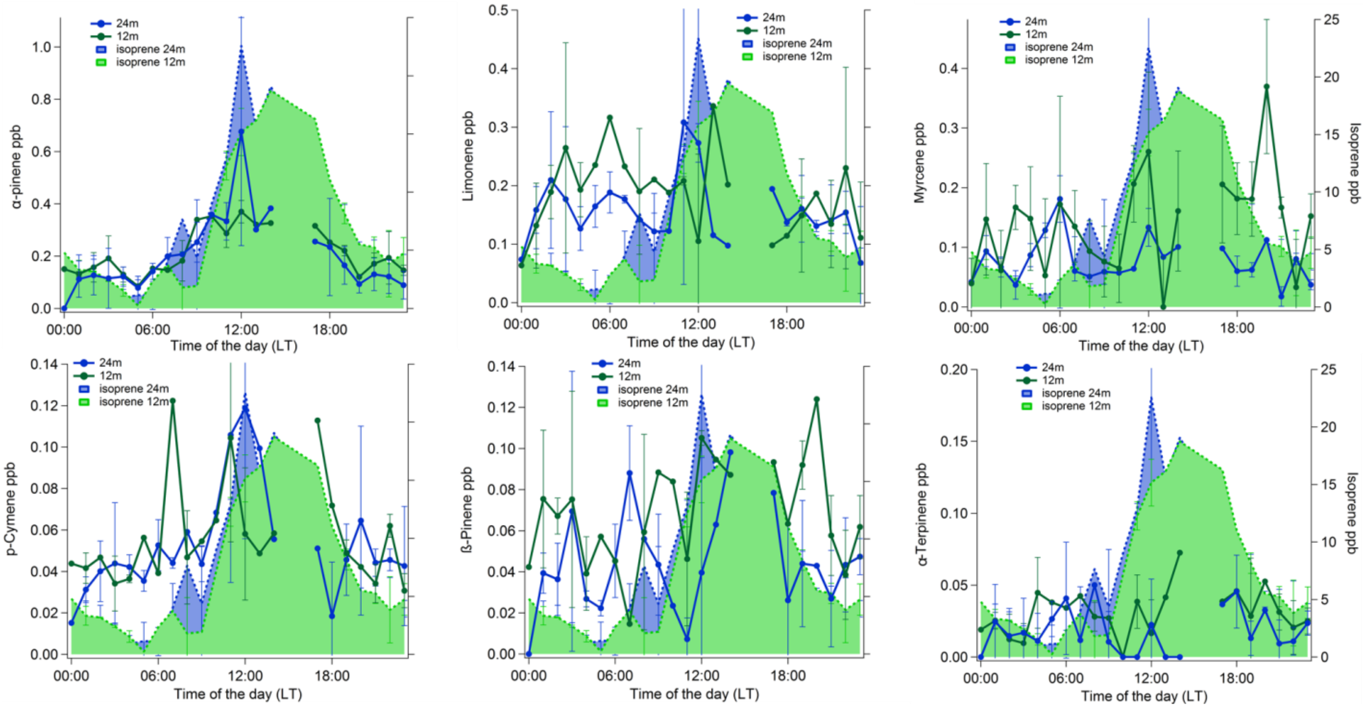

Figure 2: Graphs showing the average diel cycles for 24 m (in blue) and for 12 m (in green) for α-pinene, limonene, myrcene, ρ-cymene, β-pinene and α-terpinene, individually. All graphs have the isoprene diel cycle for both heights in the back.

3.2. Chemodiversity

The chemical speciation (or chemodiversity) of monoterpenes relates to the relative abundances of the different monoterpene species in the sampled air. α-Pinene, limonene, myrcene, ρ-cymene and β-pinene represented more than 85% of the total MT mixing ratio (Figure 3). During the day, α -pinene had an average abundance of 50% and 36% of the total monoterpene mixing ratios at 24 and 12 m, respectively, and was the dominant monoterpene in this study overall. However, during the night, its relative abundance dropped to 32% and 29% at 24 and 12 m, respectively. In contrast, limonene made up 19% and 20% of the MT at 24 and 12 m, respectively, by day, and increased during night time to 33% and 32% at 24 and 12 m. Thus, there are clear differences in monoterpene species abundance between day and night.

These are mainly due to the nocturnal decreases in α-pinene and the nocturnal relative increase in limonene. It is plausible that the observed decrease in α-pinene mixing ratios could be due to a decreased vegetation emission, as reduced chemical destruction due to very low OH concentrations at night, would lead to an increase in the nocturnal α-pinene mixing ratios.

Even though there are clear differences between the absolute and relative abundances of some monoterpene species during day and night, there are no clear changes in the in the vertical gradients (e.g. for α-pinene night time averages were 0.15±0.05 for 12 m and 0.11±0.06 at 24 m). For the day, the apparent difference in the abundance of α-pinene is due to a single outlier data point covering 30 minutes at noon on 19 October 2015 at 24 m, when the α-pinene mixing ratio doubles. This increase could not be explained, although it could be related to a strong change in wind speed an hour before the measurement, when the wind was blowing from the North. In general, our observations indicate that the abundance of monoterpene species does not vary much over the heights selected (12 and 24 m) within the canopy. This is consistent with the results by Kesselmeier et al. (2000), where the monoterpene composition at the rain forest floor was comparable to the above-canopy composition at their site.

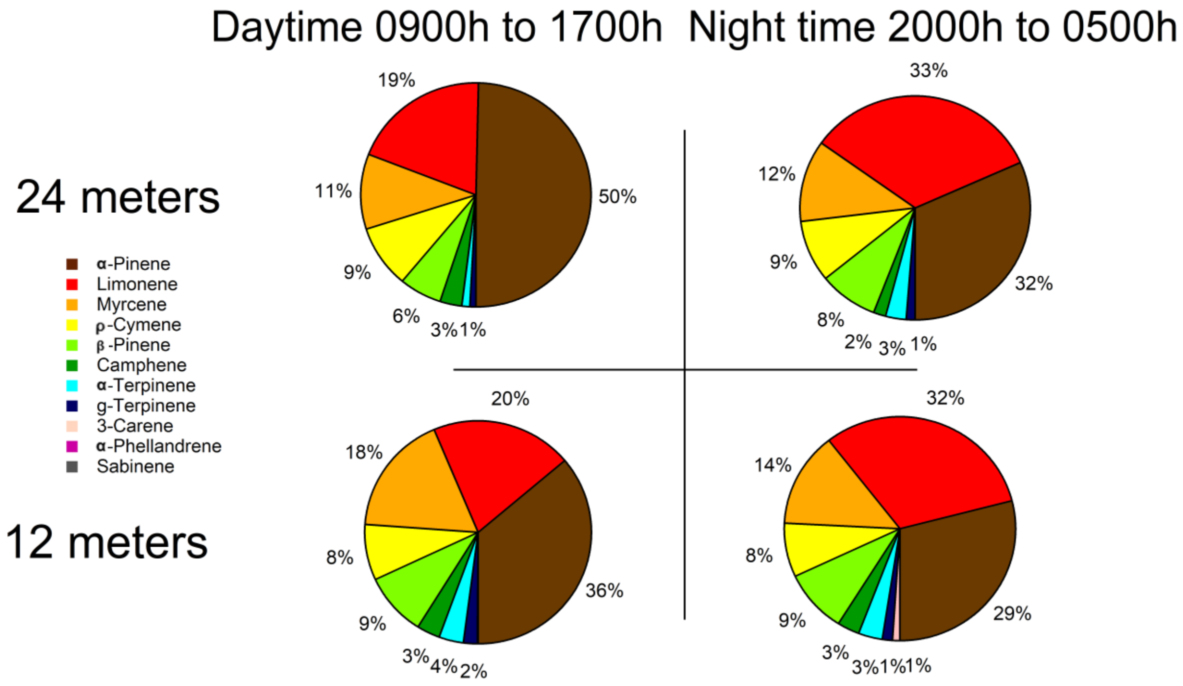

Figure 3: Pie charts representing day and night monoterpene species abundance.

3.3. Reactivity

The variability of the oxidants (OH, O_3 and NO_3) present in the Amazon air is important when considering the impact that monoterpenes can have in the oxidative regime in the Amazon region and Brazil. Hydroxyl radicals are produced mainly during the day via ozone photolysis and O^1D reaction with water. Low levels of OH can be also generated by the reaction of ozone with doubly bonded species (e.g. monoterpenes and sesquiterpenes) even at night. In this assessment, we consider the monoterpene contributions to OH reactivity by day only. In contrast, NO_3 is photolytically destroyed during the day, but can become significant at night so we assess the impact of monoterpenes on NO_3 reactivity at night. Even though in the Amazon rainforest ozone levels are low (~10-20 ppb) compared to other areas of the world (e.g. Williams et al., 2016), it is nevertheless present, and some monoterpenes are extremely reactive towards ozone. Table 2 gives an overview of the lifetime and reactivity to 1 ppb of all the investigated monoterpene species for these three oxidants. For this Table 2, typical oxidant concentration for the Amazon rainforest conditions were used. For OH a mean value of $7x10^5$ molecules cm^{-3}

was used as representative of the site (Spivakovsky et al., 2000). During the measurement period the observed average ozone value was 12 ppb at 24 m (Andreae et al., 2015), whereas the NO_3 mixing ratios were taken from the MLC-CHEM model simulations that predicted mixing ratios of ~0.4 ppt.

Table 2: Lifetime of the different monoterpene species related to OH, O3 and NO3 for the OH daytime conditions at 24 m and at 12 m. In addition, the reactivity to 1 ppb of the different monoterpene species is calculated.

Monoterpenes investigated	Formula	Lifetime (minutes)			Reactivity to 1 ppb s^{-1}		
		OH	O_3	NO_3	OH	O_3	NO_3
α-Pinene	$C_{10}H_{16}$	449	615	250	1.42	2.3E-06	0.17
Camphene	$C_{10}H_{16}$	447	57422	2461	1.43	2.4E-08	0.02
Sabinene	$C_{10}H_{16}$	400	623	155	1.60	2.2E-06	0.27
β-Pinene	$C_{10}H_{16}$	320	3445	618	2.00	4.0E-07	0.07
Myrcene	$C_{10}H_{16}$	71	110	141	8.98	1.3E-05	0.30
α-Phellandrene	$C_{10}H_{16}$	132	17	21	4.84	8.1E-05	1.96
Δ3-Carene	$C_{10}H_{16}$	271	1397	170	2.37	9.9E-07	0.24
α-Terpinene	$C_{10}H_{16}$	103	2	11	6.24	5.6E-04	3.76
ρ-Cymene	$C_{10}H_{14}$	1577	>90000	>90000	0.41	1.3E-09	2.7E-05
Limonene	$C_{10}H_{16}$	145	246	127	4.41	5.6E-06	0.33
γ-Terpinene	$C_{10}H_{16}$	140	369	53	4.57	3.8E-06	0.78
Isoprene	C_5H_8	238	4069	238	2.69	3.4E-07	0.02

The most abundant species are α-pinene, limonene and myrcene. However, with respect to their reactivities towards the different oxidants, their relative contribution to total monoterpene reactivity dramatically changes and α-pinene is not the dominant species anymore. For instance, α-terpinene dominates ozone reactivity associated with monoterpene abundance both during the day and night, as well as the nocturnal nitrate reactivity, despite the low mixing ratios measured for this compound.

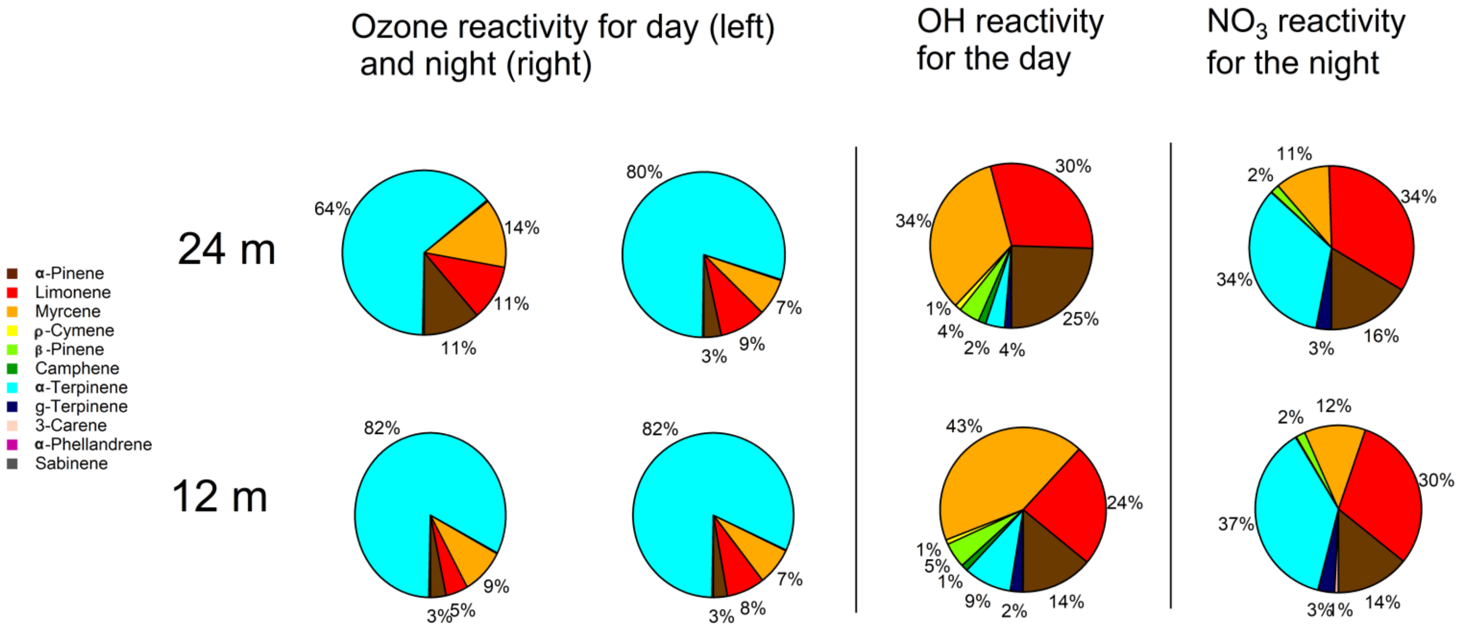

Figure 4: Pie charts representing day and night ozone reactivity, and OH reactivity (only for day) and NO_3 reactivity (only for night), for 12 m on the bottom and 24 m on the top.

The monoterpene ozone reactivity seems to be quite similar between day ($1.37\text{x}10^{-06}$ s^{-1}) and night ($1.12\text{x}10^{-06}$ s^{-1}). α-Terpinene dominates the monoterpene-ozone chemistry, followed by myrcene and limonene. Despite the relatively high abundance of α-pinene (50%, average mixing ratio during the day was 0.34±0.04 ppb at 12 m), its contribution to ozone reactivity with respect to other monoterpene species was only 11% and 3% during the day and night, respectively at 24 m, and 3% for both day and night at 12 m. As previously noted, the differences between heights are negligible for the night and slightly higher at 24 m during the day. As ozone mixing ratios are quite similar for both heights during day and night (11.4 ppb at 12 m and 10.4 ppb at 24 m during night, and 16.1 ppb at 12 m and 15.6 at 24 m during the day), the higher abundance of α-pinene during the day, and the lower α-terpinene mixing ratios at 24 m during the day mainly explain these changes in monoterpene-ozone reactivity. It is important to note that these results are derived from a relative abundance analysis, and unmeasured monoterpene species could change the proportions, although given the close similitude between PTR-MS and GC-FID measurements shown in Figure 1 this is unlikely. On the other hand, very reactive species

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which could dominate reactivity, may be present in very low concentrations, and our measurements capabilities would not allow for its monitoring.

The monoterpene reactivity towards NO_3 radical during the night in this study is also dominated by α-terpinene (34 and 37%, respectively for 24 and 12 m), although contributions of limonene (30 and 34%, respectively for 24 and 12 m), α-pinene (16 and 14%, respectively for 24 and 12 m), and myrcene (11 and 12%, respectively for 24 and 12 m) are also significant. There seem to be no significant differences between the reactivity at different heights, suggesting a rather homogeneous chemical regime regarding monoterpene chemical destruction within the canopy (from 12 to 24 m). However, note that this finding reflects the use of a single simulated NO_3 concentration due to the absence of direct measurements in the Amazon rainforest, which prevents us from drawing any further conclusion. The OH reactivity estimates demonstrate the important role of myrcene with its higher reactivity towards OH due to its acyclic nature, especially at 12 m where myrcene is more abundant. The total OH reactivity for the sum of monoterpenes was calculated to be 2.3 and 3.4 s^{-1} for 24 and 12 m, respectively.

3.4. Seasonality

By examining GC-FID data collected in previous campaigns, an intra- and inter-annual comparison can be made. These earlier samples were collected using a GSA SG10-2 personal pump sampler. Adsorbent tubes were filled at 167 cm^3 min^{-1} (STP) air flow for 20 min. Total monoterpene averages for each season were calculated from 1100 to 1600 LT at 24 m. Based on these data, we distinguished the monoterpene mixing ratios representative for the dry season, the wet season and the wet-to-dry transition. The dry season conditions were represented by measurements collected in November 2012, September 2013, August 2014, and the measurements from this study in October 2015. The wet season measurements were collected in March 2013 and the wet-to-dry transition measurements were collected in June 2013. For the dry season conditions, the total monoterpene mixing ratios were substantially higher (1.02 ppb) compared to the observed monoterpene mixing ratios in the wet season (0.14 ppb) and the wet-to-dry transition season (0.18 ppb) (Figure 5). This coincides with the occurrence of the highest radiation levels and temperatures as well as the lowest precipitation during these dry season measurement campaigns. During the wet season, the total monoterpene mixing ratios are lowest, while during the transition season in June, they are slightly higher.

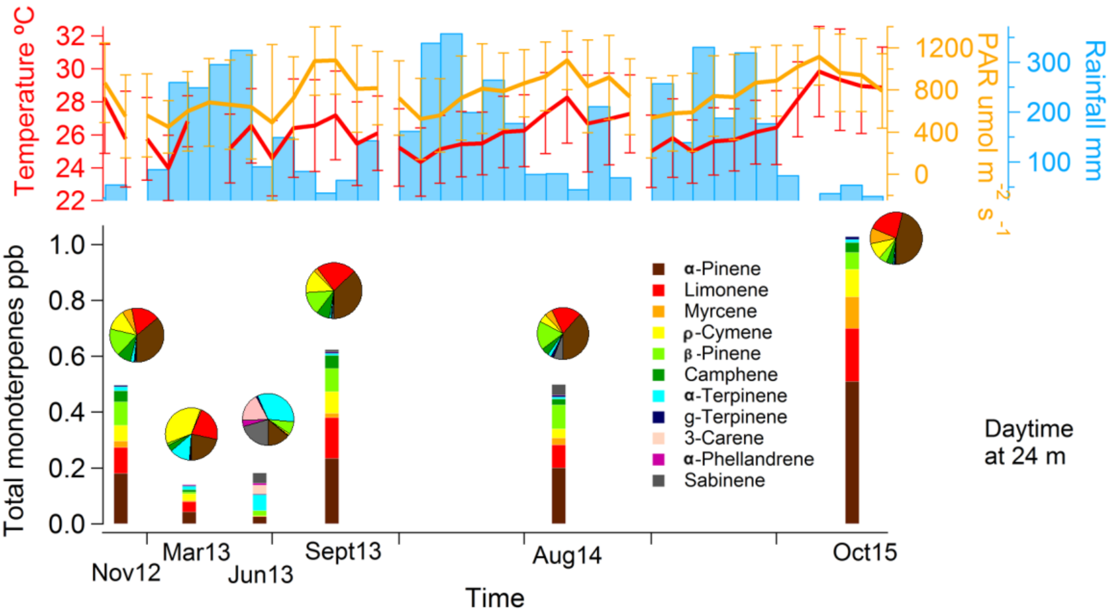

Figure 5: Graph showing the monoterpene speciation during the seasons of measurements. In the top, the monthly average of temperature (in red) and photosynthetically active radiation (in orange) are displayed with their standard deviations for the 80 m height. The rain, also on top, is displayed as mm per month (bars). In the bottom the different monoterpene species are differentiated by colours, stacked together adding up to the sum of monoterpenes. On top of each bar, a chart pie with the chemical speciation is shown for easier visualization.

For each season, an average monoterpene chemodiversity distribution is shown in Fig. 5. During the dry seasons the chemodiversity seems relatively similar (39.4±4% for α-pinene, 20.3±3% for limonene), whereas it slightly changes during the wet season, and dramatically changes during the wet-to-dry transition. The reason for this difference in June could be related to changes in the phenology, as demonstrated at a Central Amazonian site (Alves et al., 2016; Lopes et al., 2016). Furthermore, during the dry season of 2015 a very strong *El-Niño* event was taking place, leading to extremely dry conditions observed region-wide (Jardine et al., 2017).

3.5. Modelling with MLC-CHEM

To further support our analysis of the observed magnitude as well as temporal variability in the monoterpene mixing ratio inside the forest canopy, we used MLC-CHEM to: 1) explore how well the model represents the measured mixing ratios and 2) to assess the role of the different in-canopy processes in explaining the diel cycle of the observed monoterpene mixing ratios at the ATTO site. We used the observed meteorological parameters and above-canopy O_3 concentration from the ATTO site during the period of measurement to constrain these simulations with MLC-CHEM. Meteorological observations for 18 October were missing and therefore, for this day the MLC-CHEM was driven by first-order estimates of the diurnal cycles in radiation, air and surface temperatures, relative humidity and wind speed based on the previous day's meteorological information. These simulations represent a set-up of MLC-CHEM distinguishing six canopy levels with a canopy height of 30 m, implying canopy layers with a thickness of 5 m. Furthermore, we assumed a Leaf area index (LAI) of 5 m^2 m^{-2} and a Leaf Area Density (LAD) profile such that about 70% of this biomass is present in the top 15 m of the canopy. Monoterpene emissions by vegetation were simulated using a temperature-only dependent emission as a function of the amount of biomass in each layer and the measured canopy temperature profiles interpolating between the 0.4 m and 26 m temperature sensors.

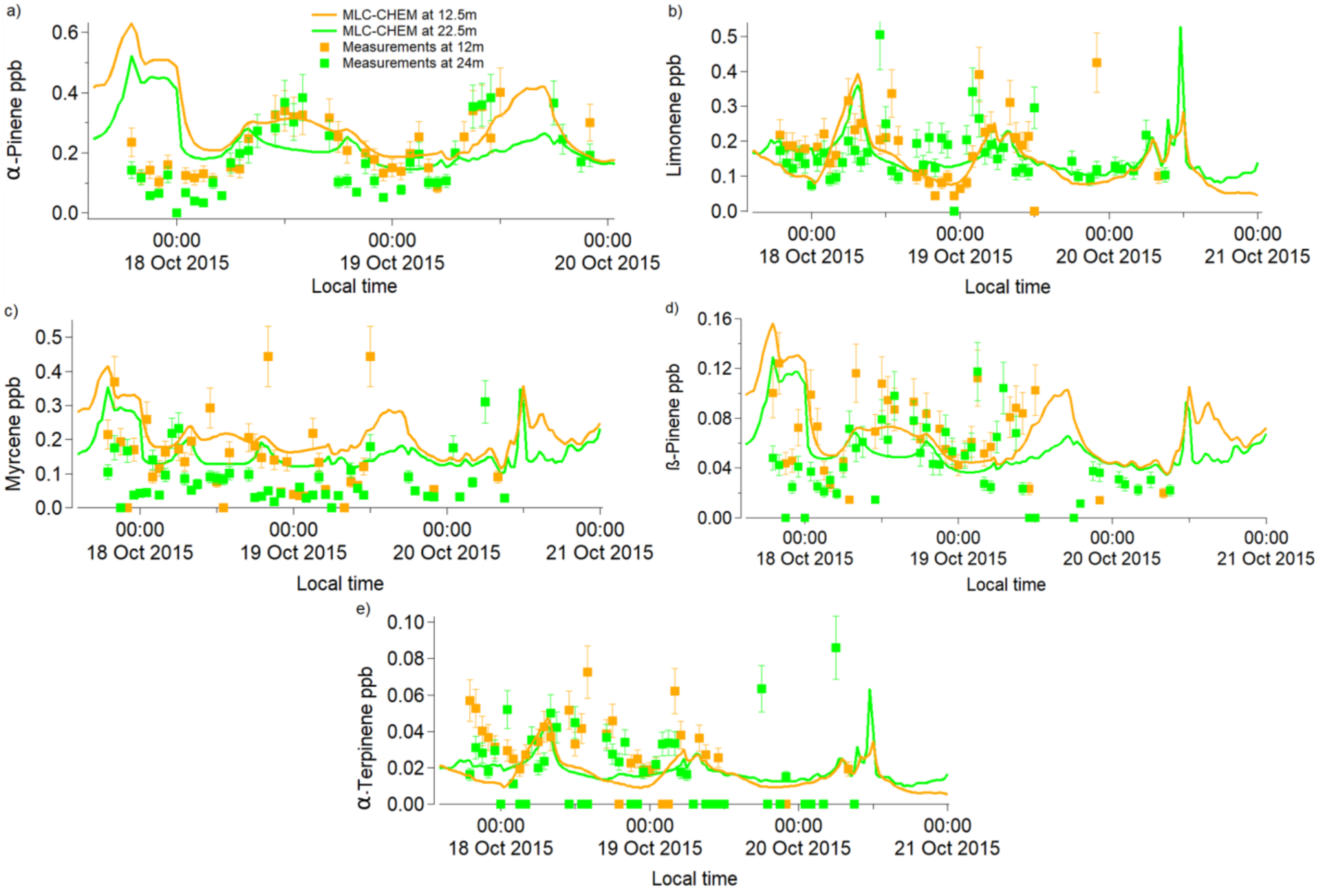

Figure 6: Graphs showing the simulated results (solid lines) for 12.5 m (orange) and 22.5 m (green) from the MLC-CHEM, with the GC-FID speciated mixing ratios measurements for the most important monoterpene species at ATTO. The error bars represent the 20% uncertainty involved in the GC-FID measurements.

From Fig. 6, which shows a comparison of the simulated (12.5 and 22.5 m) and observed (12 and 24 m) speciated monoterpene mixing ratios from 17 to 20 October 2015, it can be inferred that the simulated speciated monoterpene mixing ratios are of comparable magnitude to the measured observations. Furthermore, it seems that overall the diurnal variability is well captured by the model. The processes involved in explaining the simulated temporal variability in the canopy monoterpene mixing ratios are: vegetation emission as a function of the basal emission factor and temperature dependency, leaf biomass and the canopy temperature measurements, turbulent mixing, chemical destruction and deposition to surfaces. Note that a temperature and light dependent emission algorithm was performed and the modelling results did not follow the observed magnitudes and temporal variability as good as the modelling simulations using temperature only dependent emission. For instance, the comparison for the night of 17 to 18 October 2015 reflects the potentially important role of deposition to wet leaf surfaces. MLC-CHEM uses relative humidity as a proxy for the fraction of the leaf surface being wet. This seems to result in substantially smaller estimates of canopy wetness on 17 October 2015 compared to the following days, which explains also the simulated high nocturnal α-pinene mixing ratios, whereas the observations show actually minimum mixing ratios similar to those observed for the night of 18 to 19 October 2015. The simulated α-pinene mixing ratios for that night as well as for the remainder of the measurement period are in much better agreement with the observations. Regarding the comparison of the simulated observed mixing ratios for some of the other monoterpenes, the simulated ß-pinene, limonene, and myrcene mixing ratios, especially at 12.5 m seem to capture the observed temporal variability quite well. Note that this result for limonene reflects the use of a high leaf basal emission factor (2.25 µg C g^{-1} hr^{-1}) required to simulate mixing ratios reaching up to 0.4 ppb. MLC-CHEM was applied to infer how much of the actual emission flux escapes the canopy expressed by the calculated atmosphere-biosphere limonene flux divided by the canopy emission flux of limonene. This ratio reaches a maximum value of 0.5 around noontime implying that these model simulations indicate that at the middle of the day, about 50% of the emitted limonene is removed inside the canopy by in-canopy chemistry and deposition. During night time, this ratio reaches a minimum < 0.1 indicating simulation of very efficient in-canopy removal.

4. Discussion

The observed differences in the monoterpene chemodiversity of the Amazon rainforest canopy atmosphere are driven by differences in emission, reactivity to the oxidizing species, physical removal processes and turbulent mixing conditions. As demonstrated in this data set, chemically speciated measurements are very important for understanding how monoterpenes affect Amazon air chemistry dependent on time of day and season. When comparing our results to previously published studies, we observe consistent differences with other regions of the Amazon rainforest. For instance, Kesselmeier et al.

(2002), studied the seasonal monoterpene speciation in the Rondonia rainforest. Even though they found the same monoterpene species as presented in this study, their individual abundances were very different compared to the mixing ratios for the dry season at the ATTO site. In the case of β-pinene, the abundance measured at ATTO was much lower than at other Amazonian sites (Andreae et al., 2002; Karl et al., 2007). These differences show that it cannot be assumed that the same speciation and emission rates of monoterpenes exist throughout the vast Amazon basin.

The emission of monoterpenes has generally been thought to be from storage glands in specialized structures like resin ducts, glandular trichomes or related structures (Schürmann et al., 1993; Steinbrecher, 1989). The release from these pools is governed by leaf temperature (Fall et al., 1999; Kesselmeier and Staudt, 1999; Monson et al., 1995), but other studies on monoterpene emissions have indicated that these emissions originate from recently photosynthetically fixed carbon (Staudt et al., 2017; Staudt and Bertin, 1998). In particular, Amazonian species have been found to show an emission dependency on light and temperature (Bracho-Nunez et al., 2013; Jardine et al., 2015; Kuhn et al., 2002, 2004). This could partly explain the diurnal pattern of α-pinene, which resembles the observed diurnal cycle in mixing ratios of VOCs such as isoprene with a light and temperature dependent emission flux (Kuhn et al., 2002; Rinne et al., 2002; Williams et al., 2007). However, this behaviour is not observed for all monoterpene species. Therefore, analysis of the observed diurnal cycles in some monoterpene species might lead to the conclusion, based on the assumption that this temporal variability is mainly determined by emissions and turbulent mixing ratios, that these emissions are both light and temperature dependent. Our analysis combining the observations and the canopy exchange modelling system, however indicates that this temporal variability seems to be well explained using temperature dependent emissions alone, combined with the role of the in-canopy chemical destruction as well as the potentially important role of canopy deposition, in part to wet leaf surfaces.

It has been shown previously that the amounts and speciation of monoterpenes vary strongly according to plant species and leaf developmental stage. For instance, Bracho-Nunez et al. (2011) found young leaves of the some Mediterranean plant species to emit more α-pinene and mature leaves to emit *e*-ocimene, *z*-ocimene and myrcene, but not α-pinene. Some species have been found to be higher emitters of α-pinene (i.e. *Hevea spruceana*), whereas others are higher emitters of myrcene (i.e. *Quercus coccifera,* Bracho-Nunez et al., 2013). The leaf developmental stage is also important, as reported for flushing young leaves emitting monoterpenes in contrast to the isoprene emission of mature leaves of the same plant species (Kuhn et al., 2004). Such a behaviour could explain the lower mixing ratios and different chemodiversity found in June. During this time of the year, leaf flushing takes place in the Central Amazon region (Alves et al., 2016; Lopes et al., 2016). Under these conditions, lower α-pinene mixing ratios were found as compared to the dry season, when young leaves reach mature levels. Therefore, the seasonality in Amazon forest monoterpene emissions might depend more on the changes in aggregated canopy phenology than on the seasonality of climate drivers (Wu et al., 2016). In this study we have shown that chemodiversity remained relatively constant during at least the dry seasons, but changed between different seasons, and that the implications to the atmosphere are different for each monoterpene species. Kesselmeier et al. (2002) also showed this type of behaviour in their study, where they did not find a strong difference in total mixing ratios, but different chemodiversity, between seasons, likely expressing differences in seasonal plant developments and reactivities, which should be accounted for model implementation at the ATTO site.

Another driver for the observed difference in chemodiversity in the Central Amazon rainforest canopy is the difference in oxidation rates. Therefore, a lower abundance of a certain monoterpene species could not only be related to a lower vegetation emission, but also to a higher reactivity with atmospheric oxidant species. Despite the small amount of α-terpinene present in the atmosphere, it can profoundly affect reactivity due to its fast reaction rate (its lifetime, according to the oxidant mixing ratios stated above, can be 103, 2 and 11 minutes to OH, O_3 and NO_3, respectively (Neeb et al., 1997). In terms of total OH reactivity accounted for by the MTs, the values of this study are very low compared to the total OH reactivity measurements by Nölscher et al. (2016), with a mean of total OH reactivity for the dry season of 32 s^{-1}, mostly dominated by isoprene chemistry. This suggests that the monoterpenes contribute only a small fraction to the total OH reactivity at the ATTO site. This study demonstrates that the abundance does not relate to the importance in chemical reactivity, and species that are usually not considered into atmospheric chemistry models due to their modest mixing ratios might actually play a dominant role in the monoterpene atmospheric chemistry. Therefore, it is not correct to generalize the representation of terpene chemistry in models (Hallquist et al., 2009) using one or two monoterpene species only.

The gas-phase oxidation of the monoterpenes in the Amazon has numerous impacts on the environment including the production of a multitude of new compounds that are generally longer lived than the primary emissions, increasing the lifetimes and particle production potential of certain compounds by suppressing oxidant availability. Moreover, production of OH due to the ozonolysis of monoterpenes is known to occur (Paulson et al., 1999). The production strength varies depending on the position of the double bonds (if there is more than one) (Herrmann et al., 2010). Furthermore, the products of the reaction can be manifold. For instance, when α-pinene is oxidized by OH, especially at low nitrogen oxides mixing ratios, pinonaldehyde is formed in high yields (Eddingsaas et al., 2012). Chemical processing of α-pinene can also result in a further production of different monoterpenes such as the reaction of α-pinene with nitrate during the night, which can lead to the formation of ρ-cymene (Gratien et al., 2011).

The implications of the measured monoterpene abundances for SOA formation at the ATTO site are difficult to quantify. For an aerosol to be formed certain conditions must be met, as the aerosol yield of the parent biogenic hydrocarbon depends on the concentration of organic aerosol into which these products can be absorbed (Griffin et al., 1999). This is the reason why in regions with similar monoterpene mixing ratios and different aerosol loading, the SOA yield can vary. For instance, α-pinene forms no aerosol under NO_3 oxidation (Fry et al., 2014), whereas there is production of aerosols when the oxidation of α-pinene involves O_3 (Ehn et al., 2014) and OH (Eddingsaas et al., 2012). Monoterpenes containing endocyclic double bonds (e.g. α-pinene, 3-Carene) or open chains (e.g. myrcene) tend to form less aerosols from ozonolysis than monoterpenes with exocyclic double bonds (e.g. β-pinene, sabinene, Hatakeyama et al., 1989; Hoffmann et al., 1997). Following the equation established by Bonn et al. (2014), we were able to quantify the potential aerosol growth from the monoterpene species alone

($5x10^{-6}$ to $5x10^{-5}$ molec cm^{-3} at 24 m) being two orders of magnitudes less than the potential aerosol production from sesquiterpenes, assuming mixing ratios of the latter of 0.2 ppb ($5.21x10^{-4}$ and $3.43x10^{-3}$ molec cm^{-3} at 24 m) based on previous measurements in the Amazon (Jardine et al., 2011). Furthermore, the level of NO (nitric oxide) present also affects severely the potential aerosol growth, for instance in the atmosphere a change from 0.2 ppb to 1 ppb of NO leads to a decrease in the formation rate. This interdependence calls for a consistent consideration of the BVOC and NO_x exchange in aerosol formation and growth studies. For both species, consideration of the demonstrated canopy interactions are very important, not only in terms of determining the overall average flux out of the canopy, but also in terms of the temporal variability in atmosphere-biosphere fluxes.

The modelling results have indicated gaps in the understanding of the common processes affecting the monoterpene species dynamics. Based on the observations from this study, deposition to wet surfaces may play an important role in the removal of monoterpene species with different reactivities and solubility. This potentially important role of canopy deposition could have two important implications: 1) the effective emissions into the atmosphere are substantially smaller compared to leaf-scale based emission flux estimates and 2) monoterpene emission flux estimates based on above-canopy mixing ratio measurements can be substantially smaller than the actual leaf-scale monoterpene emission flux. These findings should be considered in the further development of inventories for application in large/scale chemistry models.

5. Conclusions

This study presents an analysis of the measured monoterpene chemodiversity at the Amazon tropical forest measurement site, ATTO. The results showed a distinctly different chemical speciation between day and night, whereas there were little vertical differences in speciation within the canopy (12 and 24 m). Furthermore, inter- and intra-annual results demonstrate similar chemodiversity during the dry seasons analysed, but this chemodiversity changed with season, similar to the seasonal measurements performed by Kesselmeier et al. (2002). Furthermore, reactivity calculations demonstrated that the most abundant compounds may not be the most atmospheric chemically relevant compound, and therefore it is not correct to generalize the representation of terpene chemistry in models. Moreover, simulations with a canopy exchange modelling system to assess the role of canopy interactions compared relatively well with the observed temporal variability in speciated monoterpenes, but also indicate the necessity of more experiments to enhance our understanding of in-canopy sinks of these monoterpenes.

6. Data Availability

Even though the data are still not available in any public repository, the data are available upon request from the main author.

7. Acknowledgements

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8. References

Alves, E. G., Jardine, K., Tota, J., Jardine, A., Yãnez-Serrano, A. M., Karl, T., Tavares, J., Nelson, B., Gu, D., Stavrakou, T., Martin, S., Artaxo, P., Manzi, A. and Guenther, A.: Seasonality of isoprenoid emissions from a primary rainforest in central Amazonia, Atmos. Chem. Phys., 16(6), 3903–3925, doi:10.5194/acp-16-3903-2016, 2016.

Andreae, M. O., Artaxo, P., Brandao, C., Carswell, F. E., Ciccioli, P., da Costa, A. L., Culf, A. D., Esteves, J. L., Gash, J. H. C., Grace, J., Kabat, P., Lelieveld, J., Malhi, Y., Manzi, A. O., Meixner, F. X., Nobre, A. D., Nobre, C., Ruivo, M., Silva-Dias, M. A., Stefani, P., Valentini, R., von Jouanne, J. and Waterloo, M. J.: Biogeochemical cycling of carbon, water, energy, trace gases, and aerosols in Amazonia: The LBA-EUSTACH experiments, J. Geophys. Res., 107(D20), 8066, doi:8066 10.1029/2001jd000524, 2002.

Andreae, M. O., Acevedo, O. C., Araùjo, A., Artaxo, P., Barbosa, C. G. G., Barbosa, H. M. J., Brito, J., Carbone, S., Chi, X., Cintra, B. B. L., da Silva, N. F., Dias, N. L., Dias-Júnior, C. Q., Ditas, F., Ditz, R., Godoi, A. F. L., Godoi, R. H. M., Heimann, M., Hoffmann, T., Kesselmeier, J., Könemann, T., Krüger, M. L., Lavric, J. V., Manzi, A. O., Lopes, A. P., Martins, D. L., Mikhailov, E. F., Moran-Zuloaga, D., Nelson, B. W., Nölscher, A. C., Santos Nogueira, D., Piedade, M. T. F., Pöhlker, C., Pöschl, U., Quesada, C. A., Rizzo, L. V., Ro, C.-U., Ruckteschler, N., Sá, L. D. A., de Oliveira Sá, M., Sales, C. B., dos Santos, R. M. N., Saturno, J., Schöngart, J., Sörgel, M., de Souza, C. M., de Souza, R. A. F., Su, H., Targhetta, N., Tóta, J., Trebs, I., Trumbore, S., van Eijck, A., Walter, D., Wang, Z., Weber, B., Williams, J., Winderlich, J., Wittmann, F., Wolff, S. and Yáñez-Serrano, A. M.: The Amazon Tall Tower Observatory (ATTO): overview of pilot measurements on ecosystem ecology, meteorology, trace gases, and aerosols, Atmos. Chem. Phys., 15(18), 10723–10776, doi:10.5194/acp-15-10723-2015, 2015.

Bonn, B. and Moortgat, G. K.: Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons, Geophys. Res. Lett., 30(11), doi:Artn 1585Doi 10.1029/2003gl017000, 2003.

Bonn, B., Bourtsoukidis, E., Sun, T. S., Bingemer, H., Rondo, L., Javed, U., Li, J., Axinte, R., Li, X., Brauers, T., Sonderfeld, H., Koppmann, R., Sogachev, A., Jacobi, S. and Spracklen, D. V.: The link between atmospheric radicals and newly formed particles at a spruce forest site in Germany, Atmos. Chem. Phys., 14(19), 10823–10843, doi:10.5194/acp-14-10823-2014, 2014.

Bracho-Nunez, A., Welter, S., Staudt, M. and Kesselmeier, J.: Plant-specific volatile organic compound emission rates from young and mature leaves of Mediterranean vegetation, J. Geophys. Res., 116(D16), D16304, doi:10.1029/2010JD015521, 2011.

Bracho-Nunez, A., Knothe, N. M., Welter, S., Staudt, M., Costa, W. R., Liberato, M. A. R., Piedade, M. T. F. and Kesselmeier, J.: Leaf level emissions of volatile organic compounds (VOC) from some Amazonian and Mediterranean plants, Biogeosciences, 10(9), 5855–5873, doi:10.5194/bg-10-5855-2013, 2013.

Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M. O., Artaxo, P. and Maenhaut, W.: Formation of secondary organic aerosols through photooxidation of isoprene., Science, 303(5661), 1173–6, doi:10.1126/science.1092805, 2004.

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Seinfeld, J. H. and Wennberg, P. O.: α-pinene photooxidation under controlled chemical conditions – Part 1: Gas-phase composition in low- and high-NO$_x$ environments, Atmos. Chem. Phys., 12(14), 6489–6504, doi:10.5194/acp-12-6489-2012, 2012.

Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I.-H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurtén, T., Nielsen, L. B., Jørgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petäjä, T., Wahner, A., Kerminen, V.-M., Kulmala, M., Worsnop, D. R., Wildt, J. and Mentel, T. F.: A large source of low-volatility secondary organic aerosol., Nature, 506(7489), 476–9, doi:10.1038/nature13032, 2014.

Engelhart, G. J., Asa-Awuku, A., Nenes, A. and Pandis, S. N.: CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, Atmos. Chem. Phys., 8(14), 3937–3949, doi:10.5194/acp-8-3937-2008, 2008.

Fall, R., Karl, T., Hansel, A., Jordan, A. and Lindinger, W.: Volatile organic compounds emitted after leaf wounding: On-line analysis by proton-transfer-reaction mass spectrometry, J. Geophys. Res., 104(D13), 15963–15974, doi:10.1029/1999jd900144, 1999.

Fry, J. L., Draper, D. C., Barsanti, K. C., Smith, J. N., Ortega, J., Winkler, P. M., Lawler, M. J., Brown, S. S., Edwards, P. M., Cohen, R. C. and Lee, L.: Secondary Organic Aerosol Formation and Organic Nitrate Yield from NO $_3$ Oxidation of Biogenic Hydrocarbons, Environ. Sci. Technol., 48(20), 11944–11953, doi:10.1021/es502204x, 2014.

Ganzeveld, L. and Lelieveld, J.: Impact of Amazonian deforestation on atmospheric chemistry, Geophys. Res. Lett., 31(6), n/a-n/a, doi:10.1029/2003GL019205, 2004.

Ganzeveld, L., Eerdekens, G., Feig, G., Fischer, H., Harder, H., Konigstedt, R., Kubistin, D., Martinez, M., Meixner, F. X., Scheeren, H. A., Sinha, V., Taraborrelli, D., Williams, J., de Arellano, J. V. G. and Lelieveld, J.: Surface and boundary layer exchanges of volatile organic compounds, nitrogen oxides and ozone during the GABRIEL campaign, Atmos. Chem. Phys., 8(20), 6223–6243, 2008.

Ganzeveld, L. N., Lelieveld, J., Dentener, F. J., Krol, M. C. and Roelofs, G. -J.: Atmosphere-biosphere trace gas exchanges simulated with a single-column model, J. Geophys. Res., 107(D16), 4297, doi:10.1029/2001JD000684, 2002a.

Ganzeveld, L. N., Lelieveld, J., Dentener, F. J., Krol, M. C. and Roelofs, G. -J.: Atmosphere-biosphere trace gas exchanges simulated with a single-column model, J. Geophys. Res., 107(D16), 4297, doi:10.1029/2001JD000684, 2002b.

Gershenzon, J.: Plant volatiles carry both public and private messages, Proc. Natl. Acad. Sci. U. S. A., 104(13), 5257–8, doi:10.1073/pnas.0700906104, 2007.

Gershenzon, J. and Dudareva, N.: The function of terpene natural products in the natural world, Nat. Chem. Biol., 3(7), 408–414, doi:10.1038/nchembio.2007.5, 2007.

Gratien, A., Johnson, S. N., Ezell, M. J., Dawson, M. L., Bennett, R. and Finlayson-Pitts, B. J.: Surprising Formation of *p* -Cymene in the Oxidation of α-Pinene in Air by the Atmospheric Oxidants OH, O $_3$, and NO $_3$, Environ. Sci. Technol., 45(7), 2755–2760, doi:10.1021/es103632b, 2011.

Greenberg, J. P. and Zimmerman, P. R.: Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres, J. Geophys. Res., 89(D3), 4767, doi:10.1029/JD089iD03p04767, 1984.

Griffin, R. J., Cocker, D. R., Flagan, R. C. and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res., 104(D3), 3555–3567, 1999.

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I. and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6(11), 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K. and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5(6), 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R. and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9(14), 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Hatakeyama, S., Izumi, K., Fukuyama, T. and Akimoto, H.: Reactions of ozone with α-pinene and β-pinene in air: Yields of gaseous and particulate products, J. Geophys. Res., 94(D10), 13013, doi:10.1029/JD094iD10p13013, 1989.

Helmig, D., Greenberg, J., Guenther, A., Zimmerman, P. and Geron, C.: Volatile organic compounds and isoprene oxidation products at a temperate deciduous forest site, J. Geophys. Res., 103(D17), 22397, doi:10.1029/98JD00969, 1998.

Herrmann, F., Winterhalter, R., Moortgat, G. K. and Williams, J.: Hydroxyl radical (OH) yields from the ozonolysis of both double bonds for five monoterpenes, Atmos. Environ., 44(28), 3458–3464, doi:10.1016/j.atmosenv.2010.05.011, 2010.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C. and Seinfeld, J. H.: Formation of Organic Aerosols from the Oxidation of Biogenic Hydrocarbons, J. Atmos. Chem., 26(2), 189–222, doi:10.1023/a:1005734301837, 1997.

Jardine, A. B., Jardine, K. J., Fuentes, J. D., Martin, S. T., Martins, G., Durgante, F., Carneiro, V., Higuchi, N., Manzi, A. O. and Chambers, J. Q.: Highly reactive light-dependent monoterpenes in the Amazon, Geophys. Res. Lett., 42(5), 1576–1583, doi:10.1002/2014GL062573, 2015.

Jardine, K., Yañez Serrano, A., Arneth, A., Abrell, L., Jardine, A., van Haren, J., Artaxo, P., Rizzo, L. V, Ishida, F. Y., Karl, T., Kesselmeier, J., Saleska, S. and Huxman, T.: Within-canopy sesquiterpene ozonolysis in Amazonia, J. Geophys. Res., 116(D19), D19301, doi:10.1029/2011JD016243, 2011.

Jardine, K. J., Jardine, A. B., Holm, J. A., Lombardozzi, D. L., Negron-Juarez, R. I., Martin, S. T., Beller, H. R., Gimenez, B. O., Higuchi, N. and Chambers, J. Q.: Monoterpene " *thermometer* " of tropical forest-atmosphere response to climate warming, Plant. Cell Environ., 40(3), 441–452, doi:10.1111/pce.12879, 2017.

Jokinen, T., Berndt, T., Makkonen, R., Kerminen, V.-M., Junninen, H., Paasonen, P., Stratmann, F., Herrmann, H., Guenther, A. B., Worsnop, D. R., Kulmala, M., Ehn, M. and Sipilä, M.: Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications., Proc. Natl. Acad. Sci. U. S. A., 112(23), 7123–8, doi:10.1073/pnas.1423977112, 2015.

Karl, T., Guenther, A., Yokelson, R. J., Greenberg, J., Potosnak, M., Blake, D. R. and Artaxo, P.: The tropical forest and fire emissions experiment: Emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia, J. Geophys. Res., 112(D18), D18302, doi:10.1029/2007JD008539, 2007.

Kesselmeier, J. and Staudt, M.: Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, J. Atmos. Chem., 33(1), 23–88, doi:10.1023/A:1006127516791, 1999.

Kesselmeier, J., Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Andreae, M. O., Ciccioli, P., Brancaleoni, E., Frattoni, M., Oliva, S. T., Botelho, M. L., Silva, C. M. A. and Tavares, T. M.: Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia), J. Geophys. Res., 107(D20), 1–13, doi:10.1029/2000jd000267, 2002.

Kiendler-Scharr, A., Wildt, J., Dal Maso, M., Hohaus, T., Kleist, E., Mentel, T. F., Tillmann, R., Uerlings, R., Schurr, U. and Wahner, A.: New particle formation in forests inhibited by isoprene emissions., Nature, 461(7262), 381–4, doi:10.1038/nature08292, 2009.

Kishimoto, K., Matsui, K., Ozawa, R. and Takabayashi, J.: Analysis of defensive responses activated by volatile allo-ocimene treatment in Arabidopsis thaliana, Phytochemistry, 67(14), 1520–1529, doi:10.1016/j.phytochem.2006.05.027, 2006.

Komenda, M.: Investigations of the emissions of monoterpenes from scots pine, Universität Köln, Jülich., 2001.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T. M. and Kesselmeier, J.: Isoprene and monoterpene emissions of Amazonian tree species during the wet season: Direct and indirect investigations on controlling environmental functions, J. Geophys. Res., 107(D20), doi:807110.1029/2001jd000978, 2002.

Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T. M. and Kesselmeier, J.: Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species, Glob. Chang. Biol., 10(5), 663–682, doi:10.1111/j.1529-8817.2003.00771.x, 2004.

Kuhn, U., Dindorf, T., Ammann, C., Rottenberger, S., Guyon, P., Holzinger, R., Ausma, S., Kenntner, T., Helleis, F. and Kesselmeier, J.: Design and field application of an automated cartridge sampler for VOC concentration and flux measurements., J. Environ. Monit., 7(6), 568–76, doi:10.1039/b500057b, 2005.

Kuhn, U., Ganzeveld, L., Thielmann, A., Dindorf, T., Schebeske, G., Welling, M., Sciare, J., Roberts, G., Meixner, F. X., Kesselmeier, J., Lelieveld, J., Kolle, O., Ciccioli, P., Lloyd, J., Trentmann, J., Artaxo, P. and Andreae, M. O.: Impact of Manaus City on the Amazon Green Ocean atmosphere: ozone production, precursor sensitivity and aerosol load, Atmos. Chem. Phys., 10(19), 9251–9282, doi:10.5194/acp-10-9251-2010, 2010.

Lichtenthaler, H. K.: The 1-deoxy-d-xylulose-5-phosphate pathway of isoprenoid biosynthesis in plants, Annu. Rev. Plant Physiol. Plant Mol. Biol., 50(1), 47–65, doi:10.1146/annurev.arplant.50.1.47, 1999.

Lindinger, W. and Jordan, A.: Proton-transfer-reaction mass spectrometry (PTR–MS): on-line monitoring of volatile organic compounds at pptv levels, Chem. Soc. Rev., 27(5), 347, doi:10.1039/a827347z, 1998.

Lopes, A. P., Nelson, B. W., Wu, J., Graça, P. M. L. de A., Tavares, J. V., Prohaska, N., Martins, G. A. and Saleska, S. R.: Leaf flush drives dry season green-up of the Central Amazon, Remote Sens. Environ., 182, 90–98, doi:10.1016/j.rse.2016.05.009, 2016.

Maag, D., Erb, M., Köllner, T. G. and Gershenzon, J.: Defensive weapons and defense signals in plants: Some metabolites serve both roles, BioEssays, 37(2), 167–174, doi:10.1002/bies.201400124, 2015.

Malhi, Y., Roberts, J. T., Betts, R. A., Killeen, T. J., Li, W. H. and Nobre, C. A.: Climate change, deforestation, and the fate of the Amazon, Science (80-.)., 319(5860), 169–172, doi:10.1126/science.1146961, 2008.

Martin, S. T., Andreae, M. O., Artaxo, P., Baumgardner, D., Chen, Q., Goldstein, A. H., Guenther, A., Heald, C. L., Mayol-Bracero, O. L., Mcmurry, P. H., Pauliquevis, T., Poschl, U., Prather, K. A., Roberts, G. C., Saleska, S. R., Dias, M. A. S., Spracklen, D. V, Swietlicki, E., Trebs, I., Bracero, O. L. M. and Pöschl, U.: Sources and properties of amazonian aerosol particles, Rev. Geophys., 48(2008), doi:Rg200210.1029/2008rg000280, 2010.

Mentel, T. F., Wildt, J., Kiendler-Scharr, A., Kleist, E., Tillmann, R., Dal Maso, M., Fisseha, R., Hohaus, T., Spahn, H., Uerlings, R., Wegener, R., Griffiths, P. T., Dinar, E., Rudich, Y. and Wahner, A.: Photochemical production of aerosols from real plant emissions, Atmos. Chem. Phys., 9(13), 4387–4406, doi:10.5194/acp-9-4387-2009, 2009.

Monson, R. K., Lerdau, M. T., Sharkey, T. D., Schimel, D. S. and Fall, R.: Biological aspects of constructing volatile organic compound emission inventories, Atmos. Environ., 29(21), 2989–3002, doi:10.1016/1352-2310(94)00360-W, 1995.

Neeb, P., Bode, K., Beck, J., Schafer, L., Kesselmeier, J. and Moortgat: Influence of gas-phase oxidation on estimated emission rates of biogenic hydrocarbons, in The Oxidizing Capacity of the Atmosphere,Proceedings Physico-Chemical, of the 7th European Symposium on the Behaviour of Atmospheric Pollutants, EUR 17482., edited by B. Larsen, B. Versino, and G. Angeletti, p. 295±299, Office for Official Publications of the European Communities, Brussels, Belgium., 1997.

Nölscher, A. C., Yañez-Serrano, A. M., Wolff, S., de Araujo, A. C., Lavrič, J. V., Kesselmeier, J. and Williams, J.: Unexpected seasonality in quantity and composition of Amazon rainforest air reactivity, Nat. Commun., 7, 10383, doi:10.1038/ncomms10383, 2016.

O'Dowd, C. D., Aalto, P., Hameri, K., Kulmala, M. and Hoffmann, T.: Aerosol formation - Atmospheric particles from organic vapours, Nature, 416(6880), 497–498, 2002.

Ormeno, E., Fernandez, C., Bousquet-Melou, A., Greff, S., Morin, E., Robles, C., Vila, B. and Bonin, G.: Monoterpene and sesquiterpene emissions of three Mediterranean species through calcareous and siliceous soils in natural conditions, Atmos. Environ., 41(3), 629–639, doi:10.1016/j.atmosenv.2006.08.027, 2007.

Paulson, S. E., Chung, M. Y. and Hasson, A. S.: OH Radical Formation from the Gas-Phase Reaction of Ozone with Terminal Alkenes and the Relationship between Structure and Mechanism, J. Phys. Chem. A, 103(41), 8125–8138, doi:10.1021/jp991995e, 1999.

Penuelas, J. and Llusia, J.: Linking photorespiration, monoterpenes and thermotolerance in Quercus, New Phytol., 155(2), 227–237, doi:10.1046/j.1469-8137.2002.00457.x, 2002.

Pöschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P., Andreae, M. O., Poschl, U., Martin, S. T., Sinha, B., Chen, Q., Gunthe, S. S., Huffman, J. A., Borrmann, S., Farmer, D. K., Garland, R. M., Helas, G., Jimenez, J. L., King, S. M., Manzi, A., Mikhailov, E., Pauliquevis, T., Petters, M. D., Prenni, A. J., Roldin, P., Rose, D., Schneider, J., Su, H., Zorn, S. R., Artaxo, P. and Andreae, M. O.: Rainforest Aerosols as Biogenic Nuclei of Clouds and Precipitation in the Amazon, Science (80-.)., 329(5998), 1513–1516, doi:10.1126/science.1191056, 2010.

Rinne, H. J. I., Guenther, A. B., Greenberg, J. P. and Harley, P. C.: Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, Atmos. Environ., 36(14), 2421–2426, doi:10.1016/S1352-2310(01)00523-4, 2002.

Schürmann, W., Ziegler, H., Kotzias, D., Schönwitz, R. and Steinbrecher, R.: Emission of biosynthesized monoterpenes from needles of Norway Spruce, Naturwissenschaften, 80(6), 276–278, doi:10.1007/BF01135913, 1993.

Schwender, J., Seemann, M., Lichtenthaler, H. K. and Rohmer, M.: Biosynthesis of isoprenoids (carotenoids, sterols, prenyl side-chains of chlorophylls and plastoquinone) via a novel pyruvate/glyceraldehyde 3-phosphate non-mevalonate pathway in the green alga Scenedesmus obliquus, Biochem. J., 316(1), 73–80, doi:10.1042/bj3160073, 1996.

Spivakovsky, C. M., Logan, J. A., Montzka, S. A., Balkanski, Y. J., Foreman-Fowler, M., Jones, D. B. A., Horowitz, L. W., Fusco, A. C., Brenninkmeijer, C. A. M., Prather, M. J., Wofsy, S. C. and McElroy, M. B.: Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, J. Geophys. Res. Atmos., 105(D7), 8931–8980, doi:10.1029/1999JD901006, 2000.

Staudt, M. and Bertin, N.: Light and temperature dependence of the emission of cyclic and acyclic monoterpenes from holm oak (Quercus ilex L.) leaves, Plant, Cell Environ., 21(4), 385–395, doi:10.1046/j.1365-3040.1998.00288.x, 1998.

Staudt, M., Bourgeois, I., Al Halabi, R., Song, W. and Williams, J.: New insights into the parametrization of temperature and light responses of mono - and sesquiterpene emissions from Aleppo pine and rosemary, Atmos. Environ., 152, 212–221, doi:10.1016/j.atmosenv.2016.12.033, 2017.

Steinbrecher, R.: Gehalt und Emission von Monoterpenen in oberirdischen Organen von Picea abies (L.) Karst., Universität München., 1989.

Sternberg, J. C., Gallaway, W. S. and Jones, D. T. L.: The mechanism of response of flame ionisation detectors, in Gas Chromatography, edited by N. Brenner, J. E. Callin, and M. D. Weiss, Academic press, New York., 1962.

Vickers, C. E., Gershenzon, J., Lerdau, M. T. and Loreto, F.: A unified mechanism of action for volatile isoprenoids in plant abiotic stress, Nat. Chem. Biol., 5(5), 283–291, doi:10.1038/nchembio.158, 2009.

Wesely, M. L.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models, Atmos. Environ., 23(6), 1293–1304, doi:10.1016/0004-6981(89)90153-4, 1989.

Williams, J., Yassaa, N., Bartenbach, S. and Lelieveld, J.: Mirror image hydrocarbons from Tropical and Boreal forests, Atmos. Chem. Phys., 7(3), 973–980, doi:10.5194/acp-7-973-2007, 2007.

Williams, J., Keßel, S. U., Nölscher, A. C., Yang, Y., Lee, Y., Yáñez-Serrano, A. M., Wolff, S., Kesselmeier, J., Klüpfel, T., Lelieveld, J. and Shao, M.: Opposite OH reactivity and ozone cycles in the Amazon rainforest and megacity Beijing: Subversion of biospheric oxidant control by anthropogenic emissions, Atmos. Environ., 125, 112–118, doi:10.1016/j.atmosenv.2015.11.007, 2016.

Wu, J., Albert, L. P., Lopes, A. P., Restrepo-Coupe, N., Hayek, M., Wiedemann, K. T., Guan, K., Stark, S. C., Christoffersen, B., Prohaska, N., Tavares, J. V., Marostica, S., Kobayashi, H., Ferreira, M. L., Campos, K. S., da Silva, R., Brando, P. M., Dye, D. G., Huxman, T. E., Huete, A. R., Nelson, B. W. and Saleska, S. R.: Leaf development and demography explain photosynthetic seasonality in Amazon evergreen forests, Science (80-.)., 351(6276), 972–976, doi:10.1126/science.aad5068, 2016.

Yáñez-Serrano, A. M., Nölscher, A. C., Williams, J., Wolff, S., Alves, E. G., Martins, G. A., Bourtsoukidis, E., Brito, J., Jardine, K., Artaxo, P. and Kesselmeier, J.: Diel and seasonal changes of biogenic volatile organic compounds within and above an Amazonian rainforest, Atmos. Chem. Phys., 15(6), 3359–3378, doi:10.5194/acp-15-3359-2015, 2015.

Zhao, D. F., Kaminski, M., Schlag, P., Fuchs, H., Acir, I.-H., Bohn, B., Häseler, R., Kiendler-Scharr, A., Rohrer, F., Tillmann, R., Wang, M. J., Wegener, R., Wildt, J., Wahner, A. and Mentel, T. F.: Secondary organic aerosol formation from hydroxyl radical oxidation and ozonolysis of monoterpenes, Atmos. Chem. Phys., 15(2), 991–1012, doi:10.5194/acp-15-991-2015, 2015.