JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 116, D19301, doi:10.1029/2011JD016243, 2011

Within-canopy sesquiterpene ozonolysis in Amazonia

K. Jardine,[1] A. Yañez Serrano,[2] A. Arneth,[2,3] L. Abrell,[4] A. Jardine,[1] J. van Haren,[1]
P. Artaxo,[5] L. V. Rizzo,[6] F. Y. Ishida,[7] T. Karl,[8] J. Kesselmeier,[9] S. Saleska,[10]
and T. Huxman[1,10]

Received 12 May 2011; revised 28 June 2011; accepted 8 July 2011; published 1 October 2011.

[1] Through rapid reactions with ozone, which can initiate the formation of secondary organic aerosols, the emission of sesquiterpenes from vegetation in Amazonia may have significant impacts on tropospheric chemistry and climate. Little is known, however, about sesquiterpene emissions, transport, and chemistry within plant canopies owing to analytical difficulties stemming from very low ambient concentrations, high reactivities, and sampling losses. Here, we present ambient sesquiterpene concentration measurements obtained during the 2010 dry season within and above a primary tropical forest canopy in Amazonia. We show that by peaking at night instead of during the day, and near the ground instead of within the canopy, sesquiterpene concentrations followed a pattern different from that of monoterpenes, suggesting that unlike monoterpene emissions, which are mainly light dependent, sesquiterpene emissions are mainly temperature dependent. In addition, we observed that sesquiterpene concentrations were inversely related with ozone (with respect to time of day and vertical concentration), suggesting that ambient concentrations are highly sensitive to ozone. These conclusions are supported by experiments in a tropical rain forest mesocosm, where little atmospheric oxidation occurs and sesquiterpene and monoterpene concentrations followed similar diurnal patterns. We estimate that the daytime dry season ozone flux of −0.6 to −1.5 nmol m^{-2} s^{-1} due to in-canopy sesquiterpene reactivity could account for 7%–28% of the net ozone flux. Our study provides experimental evidence that a large fraction of total plant sesquiterpene emissions (46%–61% by mass) undergo within-canopy ozonolysis, which may benefit plants by reducing ozone uptake and its associated oxidative damage.

Citation: Jardine, K., et al. (2011), Within-canopy sesquiterpene ozonolysis in Amazonia, *J. Geophys. Res.*, *116*, D19301, doi:10.1029/2011JD016243.

1. Introduction

[2] Monoterpenes (MTs, $C_{10}H_{16}$) and sesquiterpenes (SQTs, $C_{15}H_{24}$) are two diverse classes of volatile terpenoids produced by plants. These compounds have been hypothesized to function as endogenous antioxidants within plants, protecting them from oxidative damage during the stress-induced accumulation of reactive oxygen species [*Vickers et al.*, 2009]. Within ecosystems, they may also mediate an array of antagonistic and beneficial interactions among organisms such as acting as defensive agents against herbivores or as semiochemicals during plant to plant and plant to insect communication [*Gershenzon and Dudareva*, 2007; *Laothawornkitkul et al.*, 2009]. SQTs and MTs are also increasingly receiving attention in atmospheric chemistry and climate research, in part, owing to their proposed large contribution to aerosol particle nucleation and growth that arises from the semivolatile nature (and hence easy condensability) of their atmospheric oxidation products [*Bonn and Moortgat*, 2003; *Hallquist et al.*, 2009; *Li et al.*, 2011]. Once secondary organic aerosols are formed in the atmosphere, they become increasingly oxidized and hygroscopic [*Jimenez et al.*, 2009], growing to larger sizes and interacting with solar radiation. Simulation experiments that account explicitly for particle nucleation and subsequent growth

---

[1] Biosphere 2, University of Arizona, Tucson, Arizona, USA.

[2] Department of Physical Geography and Ecosystems Analysis, Lund University, Lund, Sweden.

[3] Institute for Meteorology and Climate Research/Atmospheric Environmental Research, Karlsruhe Institute of Technology, Garmisch-Partenkirchen, Germany.

[4] Department of Chemistry and Biochemistry and Department of Soil, Water, and Environmental Science, University of Arizona, Tucson, Arizona, USA.

[5] Instituto de Fisica, Universidade de Sao Paulo, Sao Paulo, Brazil.

[6] Department of Exact and Earth Sciences, Federal University of Sao Paulo, Diadema, Brazil.

[7] Large Biosphere-Atmosphere Experiment, Instituto Nacional de Pesquisas da Amazônia, Manaus, Brazil.

[8] Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA.

[9] Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany.

[10] Department of Ecology and Evolutionary Biology, University of Arizona, Tucson, Arizona, USA.

0148-0227/11/2011JD016243

estimated a total present-day secondary organic and sulfate aerosol indirect and direct radiative forcing of near-similar magnitude to that of CO_2, but opposite in sign (R. Makkonen et al., Air pollution control and decreasing new particle formation lead to strong climate warming, manuscript in preparation, 2011). This provides quantitative support for the suggested sensitivity in the climate system to a doubling of CO_2 that is drastically larger than commonly thought [*Andreae et al.*, 2005]. A recent review of aerosol climate interactions found that aerosol model studies to date only include MTs as the biogenic precursor for organic aerosol [*Carslaw et al.*, 2010] as no global SQT emission inventory is available [*Duhl et al.*, 2008]. Therefore the strength of aerosol cooling forcing estimates likely needs to be increased especially since SQTs are known to generally have higher aerosol yields than MTs and up to 100 times higher reactivity toward ozone than MTs [*Bonn and Moortgat*, 2003; *Griffin et al.*, 1999]. Secondary organic particle formation in the atmosphere may not be initiated by MT oxidation products, but by very low volatility substances produced during SQT ozonolysis reactions [*Bonn and Moortgat*, 2003].

[3] Therefore, SQT emissions, transport, and ozonolysis within plant canopies represent fundamental uncertainties in our understanding of the complex interactions of air pollution and climate change (O_3 formation and depletion, secondary organic aerosol formation and growth) [*Andreae et al.*, 2005; *Arneth et al.*, 2009]. However, while a large number of studies have quantified ecosystem-scale MT emission rates [*Baker et al.*, 2005; *Baraldi et al.*, 2004; *Jordan et al.*, 2009; *Karl et al.*, 2004; *Raisanen et al.*, 2009; *Rinne et al.*, 2002], to our knowledge, only a few studies to date have attempted to quantify ambient SQT concentrations [*Bouvier-Brown et al.*, 2009; *Boy et al.*, 2008; *Kim et al.*, 2009, 2010] including one attempt to quantify ecosystem-scale SQT emission rates using the vertical gradient technique [*Kim et al.*, 2009]. The lack of information is largely due to the very low ambient concentrations of SQT (<200–800 pptv) owing to rapid reactions with ozone of some common SQTs such as β-caryophyllene (1–2 min atmospheric lifetime), and technical difficulties in quantifying gas-phase SQTs [*Ortega and Helmig*, 2008]. A modeling study suggested that forest canopies can be a significant source of aerosol precursors via SQT ozonolysis; during the summertime in North Carolina, USA, an estimated 70% of the emitted β-caryophyllene (a reactive SQT), was lost within the canopy owing to ozonolysis [*Stroud et al.*, 2005]. Similarly, a coupled measurement/modeling study in California estimated that 50% of very reactive VOCs are lost owing to within-canopy ozonolysis [*Wolfe et al.*, 2011]. But our understanding of the processes that control within-canopy SQT emissions and oxidation is insufficient to provide a robust assessment of regional and global emissions of SQTs and their oxidized aerosol precursors as well as the related impacts on ground level ozone dynamics.

[4] In this study, we present real-time ambient concentration measurements of SQTs (without long-term averaging or sample preconcentration) within and above a primary rain forest canopy in central Amazonia during the 2010 dry season. By simultaneously quantifying ozone above the canopy and estimating the within-canopy SQT ozonolysis rates, we present evidence that within-canopy ozonolysis impacts the vertical and temporal patterns of SQT ambient concentrations which can account for a large fraction of ecosystem-scale emissions. We also use whole tropical rain forest mesocosm SQT ambient concentrations measurements at Biosphere 2 (with low ambient ozone concentrations) during a 3 month period from winter to spring 2010 to better understand the role of temperature versus light on influencing ecosystem-scale SQT emissions from tropical forests.

2. Experimental

2.1. Proton Transfer Reaction–Mass Spectrometry (PTR-MS)

[5] Ambient concentrations of total MTs and total SQTs were quantified using a commercial high-sensitivity proton transfer reaction–mass spectrometer (PTR-MS, IONICON, Austria). The PTR-MS was operated in standard conditions with a drift tube voltage of 600 V and drift tube pressure of 2.0 mb (E/N, 136 Td). Optimization of PTR-MS conditions resulted in extremely high and sustained primary ion intensities (20–40 MHz H_3O^+) with low water cluster and O_2^+ formation (water cluster and $O_2^+ < 4\%$ H_3O^+). The following mass to charge ratios (m/z) were sequentially monitored during each PTR-MS measurement cycle; 21 ($H_3{}^{18}O^+$), 32 (O_2^+), 37 (H_2O-H_3O^+) with a dwell time of 20 ms each and 137 (MT-H^+) and 205 (SQT-H^+) with a dwell time of 5 s each. While adsorptive losses to surfaces during sampling are potentially a major issue for quantifying SQTs in air samples, β–caryophyllene line losses were negligible in a heated (40°C) 40 m Teflon line (1/4″ O.D.) flushed with sample air [*Kim et al.*, 2009]. Therefore, to minimize losses during sampling, all Teflon gas inlets were continuously heated to ~50°C using self-regulating heating tape (Omega Engineering) in an insulated jacket. Raw signals (counts per second, cps) were normalized by the adjusted primary ion signal (cps_{21}) and background subtracted from measurements of ultra high purity nitrogen (Brazil) or zero air (Biosphere 2) to obtain normalized counts per second (ncps, equation (1)). The adjusted primary ion signal (cps_{21}) was obtained by measuring the signal at m/z 21 ($H_3^{18}O^+$) and multiplying it by the oxygen isotopic ratio of a representative natural abundance water sample ($^{16}O/^{18}O = 500$):

$$\mathrm{ncps} = (\mathrm{cps}/\mathrm{cps}_{21})_{\mathrm{sample}} - (\mathrm{cps}/\mathrm{cps}_{21})_{\mathrm{background}}. \quad (1)$$

Calibration slopes (m, ppbv/ncps) for MTs and SQTs were obtained at Biosphere 2 and twice in the field (Brazil) using the dynamic solution injection (DSI) technique [*Jardine et al.*, 2010a]. Solutions were prepared by diluting 5 μL of authentic α-pinene and β-caryophyllene standards, (>95% purity, Biosphere 2: Sigma-Aldrich, Brazil: Merck) in 100 mL of cyclohexane. The solution was injected into the mixing vial at 0.5, 1.0, 2.0, and 3.0 μL/min. Calibrations showed good linearity for α-pinene: (r^2 of 0.98–0.99) and β-caryophyllene (r^2 of 0.90–0.98). Sample air total MT and SQT concentrations were calculated by multiplying the calibration slope by ncps (average of two calibration slopes used in Brazil). The repeat measurement of calibration slopes obtained on 20 October 2010 in Brazil showed good stability within 10% relative to those from the initial calibration on 11 September 2010 (α-pinene −8.2% and β-caryophyllene −2.5%). However, a previous detailed study of SQT detection with PTR-MS

[*Demarcke et al.*, 2009] showed that for all four sesquiterpenes investigated (β-caryophyllene, α-humulene, α-cedrene, and longifolene), the major product ion is the protonated molecule (m/z 205) with yields ranging from 30% (β-caryophyllene) to 65% (α-cedrene) at the highest *E*/*N* value of 140 Td. Therefore, given our similar operating conditions of 136 Td (E/N), the presence of SQTs other than β-caryophyllene in ambient air may lead to an overestimation of total SQT concentrations by as much as 50%.

2.2. Biosphere 2 Tropical Rain Forest Mesocosm

[6] The 27,000 m^3 tropical rain mesocosm at Biosphere 2 currently encompasses 91 species of tropical plants from 41 families, including 73 trees under a flat-topped pyramidal glass enclosure operated as a semiclosed system. Typical of neotropical forests, the trees are dominated by Fabaceae (pea family) and Arecaceae (palm family). Although not quantified, the mesocosm ventilation rate was controlled by a large vent at the top on the mesocosm which was opened during the day and closed at the night to help regulate air temperature. This is qualitatively similar to the vertical mixing pattern in a natural forest where transport of materials and energy out of the canopy is much larger during the day, owing to increased vertical mixing, than during the night. However, due the extremely large volume of the mesocosm (2.7×10^7 L) and the relatively low estimated ventilation rate ($<1 \times 10^5$ L min^{-1}), the air residence time is much larger than in a natural forest (>270 min). Photosynthetically active radiation (PAR) and ambient air temperatures were monitored continuously along three vertical profile towers. Details of the volatile organic compound (VOC) measurement methods at the whole-mesocosm scale can be found elsewhere [*Jardine et al.*, 2010b]. Briefly, ambient air at 16 m height and zero air were analyzed (15 min each) continuously for VOC concentrations. Ambient air from the tropical rain forest biome was pumped through heated Teflon tubing (PFA, 1/4″ O.D. 75m length) into the adjacent laboratory for VOC analysis by PTR-MS. Ten 6–10 day measurement periods were made during the winter and spring of 2010 (22 January 2010 to 14 April 2010).

2.3. BrazilianAir 2010 Field Campaign

[7] The BrazilianAir 2010 study was carried out at the TT34 tower (2°35.37′S, 60°06.92′W) in the Reserva Biologica do Cueiras in central Amazonia, 60 km NNW of the city of Manaus, Brazil. The site is run by the Instituto Nacional de Pesquisas da Amazonia (INPA) under the Large-Scale Biosphere-Atmosphere Experiment in Amazonia (LBA) program [*Martin et al.*, 2010]. The vegetation in this area is considered to be undisturbed, mature, *terra firme* rain forest, with a leaf area index of 5–6 and an average canopy height of 30 m. The dry season measurements described in this manuscript occurred between 2 September 2010 and 5 December 2010.

[8] The VOC gradient measurement scheme employed was based on that used in the AMAZE 2008 campaign [*Karl et al.*, 2009] with six ambient air inlets at different tower heights (2, 11, 17, 24, 30, and 40 m) sequentially analyzed for VOCs (10 min at each inlet, one complete canopy profile per hour). The air sample tubing lengths were equal to the inlet heights plus an additional 4 m each to reach the detector in the instrument trailer directly adjacent to the tower. Ambient air was drawn through 1/4 in O.D. Teflon PFA tubing using an oil free diaphragm pump (KNF Neuberger). The sample airflow rates through each inlet was set to ~4.0 slpm each using needle valves downstream of the PTR-MS resulting in a range of air sample point to detector delay times of ~6 s (2 m height inlet) to ~15 s (40 m height inlet).

[9] While no effort was made to remove ozone from the ambient air samples, the estimated daytime (10:00–16:00 LT) and nighttime (22:00–04:00 LT) SQT lifetime above the canopy (40 m) during the dry season with respect to ozonolysis ([SQT]/ozonolysis rate) was 133 s and 270 s, respectively (using the ozonolysis rate constant for β-caryophyllene, see below). This corresponds to a maximum relative SQT concentration loss of 11% (daytime) and 6% (nighttime) due to ozonolysis in the inlets during transport to the detector (assuming the dominant SQT is β-caryophyllene).

[10] Prior to each vertical gradient ambient air measurement period (lasting 4–7 days), ultra high purity nitrogen was run directly into the inlet of the PTR-MS (bypassing the ambient inlets) for 2 h to obtain instrument background signals. Vertical gradients were calculated by averaging the last 7 min of each 10 min measurement period. Average vertical gradients for daytime (10:00–16:00 LT) and nighttime (22:00–04:00 LT) were calculated for the dry season data. Ozone measurements were made above the canopy (40 m) every 5 min on the tower by thermoluminescence, with a Thermo Environment model 49i and averaged every hour. Ozone concentrations within the canopy were estimated from the above canopy measurements and by assuming the same relative concentration decrease within the canopy as determined by *Karl et al.* [2009] (97% at 30 m, 93% at 24 m, 87% at 17 m, 77% at 11 m, and 37% at 2 m). This was treated as an upper limit for ozone concentrations within the canopy and an additional ozone profile was calculated as the lower limit with a more extreme relative loss of ozone within the canopy (80% at 30 m, 60% at 24 m, 40% at 17 m, 20% at 11 m, and 1% at 2 m). We estimate from Figures 8a and 8b of *Rummel et al.* [2007] that the average daytime (10:00–16:00 LT) fraction of remaining ozone near the ground (1 m) relative to above the canopy (52 m) in southwestern Amazonia is ~32% (dry season) and ~11% (wet season). Therefore, these observations fall within the range of our lower (1%) and upper (37%) limit for remaining ozone near the ground (2 m). Although difficult to estimate from *Rummel et al.* [2007, Figures 8a and 8b], owing to the extremely low ozone concentrations near the ground which approach zero at night, the lower limit of 1% remaining ozone near the ground may represent what might be expected for nighttime conditions when SQT emissions persist and vertical mixing is slow.

[11] SQT ozonolysis rates at each of the six measurement heights were estimated using the dry season hourly averaged O_3 and SQT concentrations (molecules cm^{-3}) in equation (2), with k equal to the ozonolysis rate constant for β-caryophyllene (1.16×10^{-14} $molecule^{-1}$ cm^{-3} s^{-1}) [*Shu and Atkinson*, 1994]:

$$\text{SQT ozonolysis rate} = k[O_3][SQT]. \qquad (2)$$

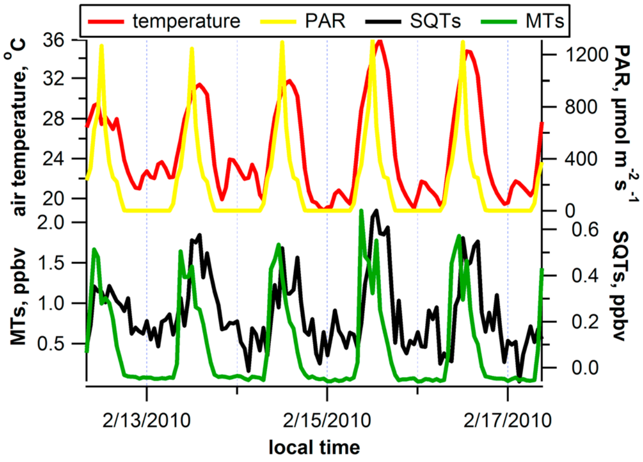

Figure 1. Example of diurnal patterns in SQT and MT ambient concentrations (16 m height) in the Biosphere 2 tropical rain forest mesocosm plotted together with PAR and ambient temperature (20 m height). Note that the MTs appear to be more closely related to PAR, whereas the SQTs appear to be more closely related to temperature.

While several SQTs have high reported ozonolysis rate constants similar to β-caryophyllene (e.g., α-humulene, 1.2×10^{-14} molecule^{-1} cm^{-3} s^{-1}), others are nearly 2 orders of magnitude lower (e.g., α-copaene, 1.6×10^{-16} molecule^{-1} cm^{-3} s^{-1}) [*Shu and Atkinson*, 1994]. However, in a review of SQT emissions from vegetation, β-caryophyllene was found to be the most frequently reported SQT emitted and the most abundant SQT within many emission profiles [*Duhl et al.*, 2008]. Preliminary research using GC-MS suggests that β-caryophyllene is the dominant sesquiterpene in ambient air near the TT34 flux tower in Amazonia (C. P. da Silva, manuscript in preparation, 2011). Nonetheless, while our assumption that β-caryophyllene is the dominant SQT in ambient air at the TT34 tower may be valid, calculated SQT ozonolysis rates based only on the β-caryophyllene rate constant should be considered an upper limit.

[12] The average daytime (10:00–16:00 LT) ecosystem-scale SQT ozonolysis flux was estimated by integrating the average ozonolysis rates over the height of the entire vertical profile (0–40 m). Ecosystem-scale MT and SQT vertical fluxes were estimated using the average daytime concentration gradients throughout the canopy and applying an inverse Lagrangian transport model [*Raupach*, 1989]. Total MT and SQT fluxes were computed according to $\vec{C} - \vec{C}_{ref} = \overleftrightarrow{D} \cdot \vec{S}$, where C is the concentration (μg m^{-3}) vector for each level, C_{ref} is the concentration (μg m^{-3}) at reference height (e.g., 40 m), D represents a dispersion matrix and S (mg m^{-2} h^{-1} layer^{-1}) the resulting source/sink vector. D can be expressed as a function of Lagrangian time scale and profiles of the standard deviation of the vertical wind speed (σ_w) divided by the friction velocity (u*, 0.5 m/s). The Lagrangian time scale was parameterized according to *Raupach* [1989], and the parameterization of D was based on turbulence measurements inside and above the canopy during the AMAZE 2008 experiment [*Karl et al.*, 2009] and calculated using the far- and near-field approach described by *Raupach* [1989]. This method has been estimated to have an uncertainty in flux estimates of +/− 20% [*Karl et al.*, 2004]; model inputs, including profiles of σ_w divided by u*, were obtained during the wet season at the TT34 tower in 2008 [*Karl et al.*, 2009], and therefore the source/sink vectors S (for total MTs and SQTs, mg m^{-2} h^{-1} layer^{-1}) are considered pseudo-quantitative. However, the use of turbulence parameters from a different year and season may be reasonable in light of previous micrometeorology research at the K34 tower (<5 km from the TT34 tower). A study that overlapped with AMAZE 2008 demonstrated that both the 2008 wet and dry seasons have similar average daytime values of friction velocities above the canopy (~0.35 m s^{-1} in the wet season and ~0.40 m s^{-1} in the dry season [*Ahlm et al.*, 2010, Figure 2i]). Another earlier study at the K34 tower which continuously measured the friction velocity above the canopy between July 1999 and September 2000 (and therefore spanned both dry and wet seasons) observed comparable average daytime friction velocities of ~0.40 m s^{-1} [*Araujo et al.*, 2002, Figure 5b]. Similar daytime friction velocities were observed above the canopy at the K34 tower during the 1995 dry season [*Kruijt et al.*, 2000].

3. Results and Discussion

3.1. Biosphere 2 Tropical Rain Forest Mesocosm

[13] We investigated whether we could detect both MT and SQT emissions from tropical vegetation at the scale of the whole 0.5 ha tropical rain forest mesocosm at Biosphere 2. We took advantage of the fact that the Biosphere 2 glass absorbs all ultraviolet photons (<385 nm) that drive the generation of atmospheric oxidants like ozone [*Cockell et al.*, 2000], thereby enabling us to ignore the complicating effects of gas phase SQT ozonolysis, and isolate the role of plant emissions at the ecosystem scale. Ambient concentrations of SQTs and MTs (and therefore implied ecosystem-scale emission rates) showed strong diurnal patterns matching the same general pattern as temperature and PAR (for example, 6 day data set shown in Figure 1). For each data set (N = 10), ambient SQT and MT concentrations were linearly regressed against ambient PAR and air temperature (20 m, midheight). Ambient SQT concentrations correlated more strongly with ambient temperature ($R^2_{temp} = 0.56$ +/− 0.09) than with PAR ($R^2_{PAR} = 0.43$ +/− 0.07), (t test, $\alpha = 0.05$, $R^2_{temp} \neq R^2_{PAR}$). In contrast, ambient MT concentrations correlated more strongly with PAR ($R^2_{PAR} = 0.69$ +/− 0.07), than with ambient temperature ($R^2_{temp} = 0.60$ +/− 0.08), (t test, $\alpha = 0.05$, $R^2_{temp} \neq R^2_{PAR}$). While maximum PAR typically occurred at 12:00 LT, maximum air temperatures typically occurred at 14:00 LT (Figure 1). In all data sets, we observed a similar lag between maximum MT concentrations (which typically occurred at 12:00 LT) and SQT concentrations (which typically occurred at 14:00 LT). These observations suggest that SQT emissions from the tropical plants inside the Biosphere 2 rain forest mesocosm are more temperature dependent than light dependent and imply evaporation from storage pools or de novo biosynthesis in the cytosol derived from carbon sources not strongly connected with recently assimilated carbon. The secondary peak in air temperature that often occurs at night (Figure 1) is caused by the heating of the mesocosm by air handlers which recirculate the air within the mesocosm. Heating of the ambient air is used to prevent cold damage to the plants when the air temperature drops

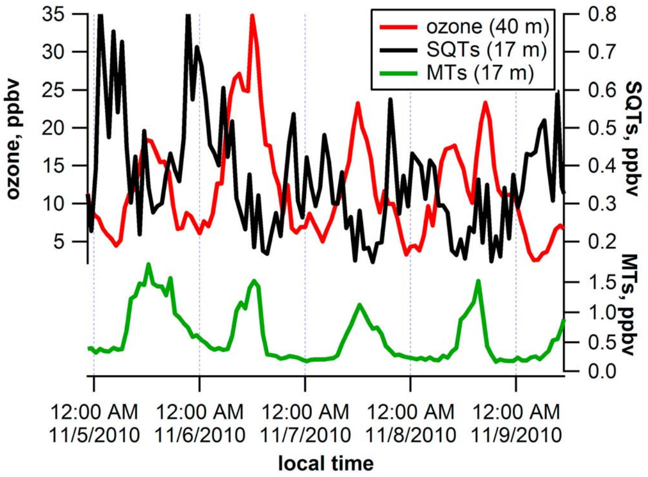

Figure 2. Example time series plot showing the inverse relationship between ozone concentrations above the canopy (40 m) and SQTs' concentrations within the canopy (17 m) during the 2010 dry season in central Amazonia. For comparison, MT concentrations in the canopy (17 m) showed the expected diurnal pattern with noontime maxima.

below the 22°C threshold at night. Potentially in response to this heating at night, SQT but not MT ambient concentrations often increase slightly providing additional evidence for temperature-dependent SQT emissions from tropical plants. This is in agreement with most of the published literature on SQT emissions from plants which conclude that dependencies on temperature are much stronger than those for light [*Duhl et al.*, 2008]. In contrast, a stronger correlation between MT concentrations and light than with temperature from the tropical plants in the mesocosm implies that emissions are mainly controlled by de novo biosynthesis from recent carbon assimilation inside chloroplasts. This is in agreement with the findings that MT emissions from many plants (mostly broadleafed) are light dependent with emission rates determined by de novo biosynthesis rates [*Kesselmeier et al.*, 1997; *Kesselmeier and Staudt*, 1999; *Schuh et al.*, 1997; *Staudt and Seufert*, 1995]. Our observations add to the emerging view that MT emissions from many tropical plants are strongly light dependent [*Kuhn et al.*, 2002, 2004; *Wang et al.*, 2007]. In support of these conclusions, despite the much higher ambient concentrations of MTs than SQTs during the day (2–4 ppbv versus 0.5–1.0 ppbv), we observed significantly higher SQT concentrations (0.1–0.4 ppbv) than MTs (<0.1 ppbv) at night, implying that SQT emissions can continue at night whereas light-dependent MT emissions cease.

3.2. BrazilianAir 2010

[14] To date, real-time in situ SQT concentration dynamics have not been reported in ambient air without long-term averaging or sample preconcentration [*Bouvier-Brown et al.*, 2009; *Boy et al.*, 2008; *Kim et al.*, 2009, 2010]. Despite the fact that we operated our high-sensitivity PTR-MS in standard conditions (600 V drift tube voltage and 2.0 mbar pressure), we were able to resolve real-time in-canopy and above-canopy concentration dynamics owing to a number of technical, biological, and environmental reasons including (1) the use of heated gas inlets (~50°C) which minimized the loss of SQT to tubing walls, (2) the achievement of extremely high sustained primary ion intensities (20–40 MHz H_3O^+) and low contaminant O_2^+ and H_2O-H_3O^+ ion intensities (<4% H_3O^+), (3) high ecosystem SQT emission rates due to high light and temperatures during the 2010 dry season and high biomass densities in the primary tropical forest in central Amazonia, and (4) relatively low ambient ozone concentrations (<40 ppbv, dry season) that exhibited strong diurnal patterns. These conditions allowed for real-time quantification of ambient SQT concentrations due to relatively high ambient concentrations (up to 800 pptv) and PTR-MS detection sensitivity (24 cps/ppbv for SQTs).

[15] During the 2010 dry season in central Amazonia at the TT34 flux tower, SQT ambient concentrations at all heights displayed pronounced variation throughout the day, especially at night when maxima occurred typically around midnight (see Figure 2). Ambient SQT concentrations were inversely related to ozone, which generally peaked around midday. This is in contrast with the SQT and MT pattern in the Biosphere 2 tropical rain forest mesocosm (Figure 1) and MTs in Amazonia (Figure 2) which showed expected diurnal concentrations patterns with midday maxima. Higher ambient SQT concentrations at night than during the day were also observed in the mean vertical concentration profiles (Figure 3b). Our observations indicate the mean vertical concentration pattern for SQTs to be very different from those of MTs. While daytime concentrations of MTs peaked within the canopy (17 m), those of SQTs peaked near the ground (2 m). In addition, when ozone concentrations within the canopy were estimated, again an inverse relationship was observed between the mean daytime vertical profiles of SQTs and ozone (Figure 4). This suggests that SQTs are rapidly oxidized by ozone, contributing to the scarcity of SQTs above the canopy and ozone near the ground.

[16] In photosynthetically active plant cells, MTs and SQTs are known to be produced by two different biosynthetic pathways; the cytosolic mevalonate (MVA) pathway and the plastidic 2-C-methyl-D-erythritol 4-phosphate (MEP) pathway [*Lichtenthaler et al.*, 1997]. However, while MTs are thought to be mainly produced in chloroplasts via the MEP pathway, SQTs are thought to mainly be produced in the cytosol via the MVA pathway. The direct connection to recently assimilated carbon may result in a strong light dependence on de novo MT production/emission whereas de novo SQT production/emission may be more temperature dependent. Therefore, similar to vegetation inside the Biosphere 2 rain forest mesocosm (Figure 1), SQT emission rates from plants near the TT34 tower may be mainly light independent and continue at night via temperature driven processes (both de novo biosynthesis and evaporation from storage pools) whereas MT emissions are mainly light dependent. At night, ambient MT concentrations crash owing to the lack of plant emissions and the perseverance of sinks like deposition whereas SQT concentrations could accumulate within the canopy owing to continued emissions (albeit at much lower rates) and greatly reduced vertical mixing.

[17] Another process that may differentially affect ambient MT and SQT concentrations in addition to plant emissions and vertical transport is the rapid gas-phase ozonolysis of SQTs [*Bonn et al.*, 2007]. Because ozone concentrations peak during midday, rapid SQT ozonolysis reactions could

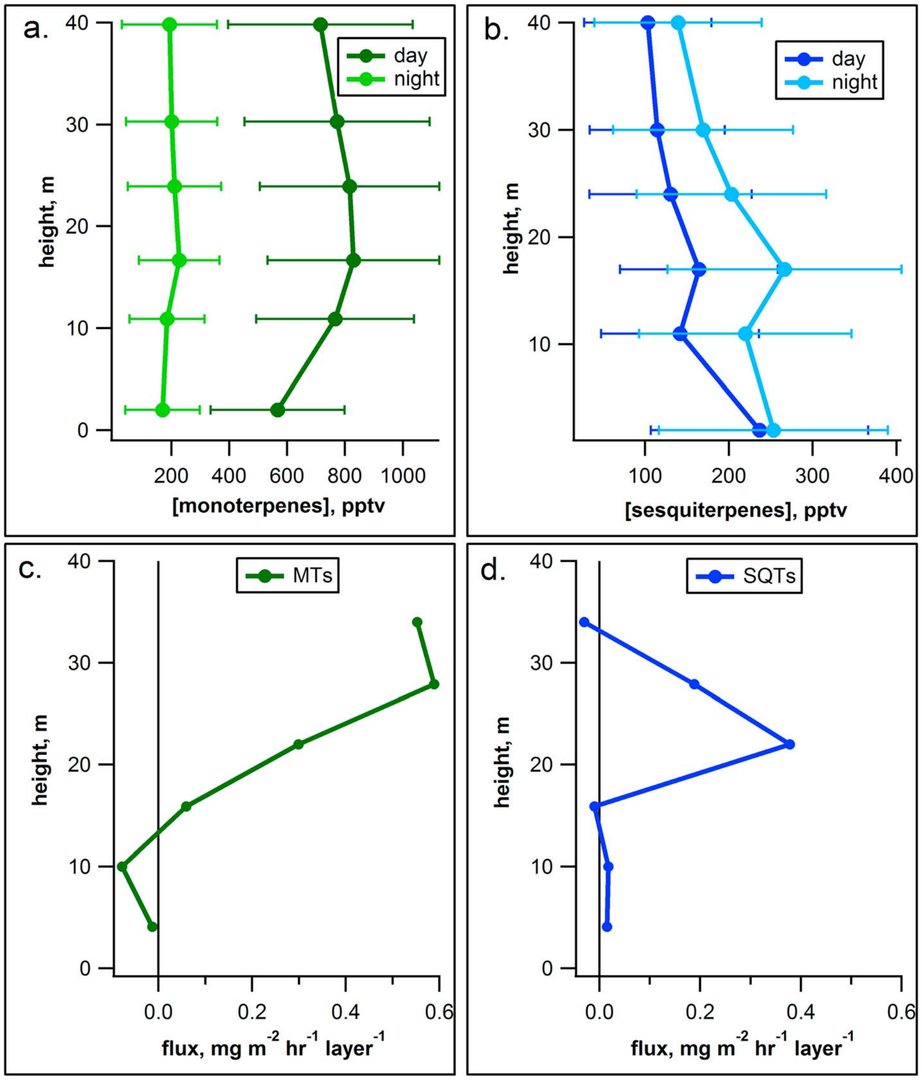

Figure 3. (a, b) Mean daytime and nighttime MT and SQT concentrations ± 1 standard deviation at each height during the 2010 dry season in central Amazonia. (c, d) Estimated vertical flux distributions for MTs and SQTs during the 2010 dry season.

represent a much larger sink for ambient SQTs during the day than at night; which could mean that SQTs are not emitted at low rates but rather quickly oxidized within the canopy. Therefore, the divergence in MT and SQT temporal (Figure 2) and vertical (Figure 3) patterns must, at least in part, be related to the high reactivity of SQTs with ozone. The results from the SQT ozonolysis calculations reveal that despite higher SQT concentrations at night, higher ozone concentrations during the day leads to elevated SQT ozonolysis rates (SQT lifetime with respect to ozonolysis above the canopy at 40 m; day: 2 min, night: 5 min) (Figure 5b). Moreover, despite higher SQT concentrations near the ground, ozonolysis rates are highest within the canopy where the product of ozone and SQT concentrations reaches a maximum (using estimated ozone concentrations within the canopy based on the work of *Karl et al.* [2009]).

[18] When the mean daytime vertical fluxes of MTs and SQTs were estimated using the inverse Lagrangian transport model (with the mean 2010 concentration gradients and the 2008 within canopy turbulence parameters measured during the AMAZE campaign), both MTs and SQTs showed a strong source within the canopy (Figures 3c and 3d). However, while MT fluxes remained strong near the top of the canopy, net SQT fluxes dramatically declined. One potential explanation for this is the loss of SQTs via ozonolysis within and above the canopy. The two different daytime ozone profiles representing the lower and upper limits in ozone concentrations within the canopy were used to estimate the mean daytime SQT ozonolysis fluxes integrated throughout the 40 m profile (−0.6 and −1.1 mg SQT m^{-2} h^{-1}, respectively). When compared with the total canopy-scale emission rate estimated as the sum of SQT fluxes in each layer throughout the profile (Figure 3d, 0.7 mg SQT m^{-2} h^{-1}), SQT canopy escape efficiency during the dry season is estimated to be 39%–54% (46%–61% oxidized within the canopy by mass). This is consistent with an escape efficiency estimate of 50% for very reactive VOCs in a Ponderosa Pine forest in California [*Wolfe et al.*, 2011]

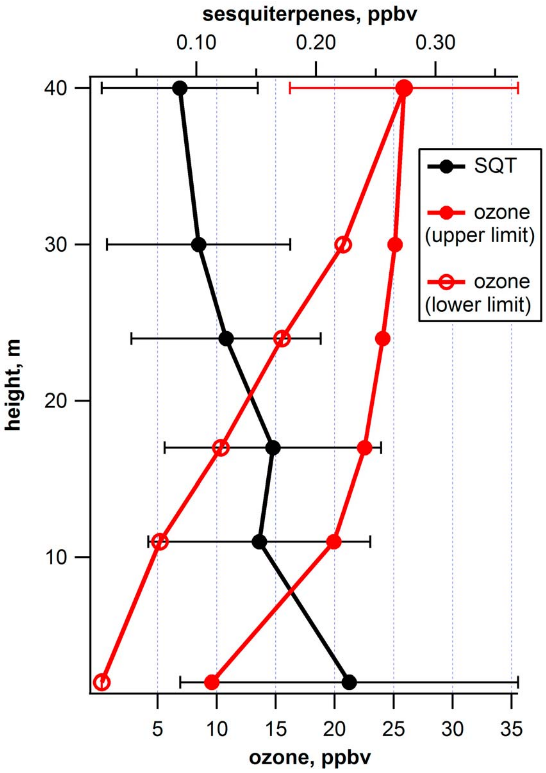

Figure 4. Mean noontime (12:00–13:00 LT) vertical concentration profiles for SQTs and ozone through the 30 m canopy in central Amazonia during the 2010 dry season showing the inverse relationship with height. Ozone concentrations within the canopy are estimated from the above canopy measurements (40 m) and assuming the same relative concentration decrease within the canopy as that determined by *Karl et al.* [2009] (upper limit) and a larger relative decrease with only 1% remaining at 2 m height (lower limit). Error bars represent ±1 standard deviation.

and comparable to an estimated 30% SQT escape efficiency based on model calculations for summertime conditions in a hardwood forest in North Carolina [*Stroud et al.*, 2005]. Although the estimated canopy-scale SQT emission rates can only be considered pseudo-quantitative owing to the use of the within-canopy turbulence parameters from the AMAZE 2008 campaign, our results provide vertically resolved evidence to substantiate the role of SQTs as in-canopy ozone sinks with a large fraction of emitted SQTs being lost to ozonolysis [*Ciccioli et al.*, 1999]. Future studies should aim to quantitatively investigate the SQT canopy escape efficiency in order to better understand biological and environmental influences on the fate of SQTs within plant canopies.

[19] The involvement of plant volatiles in destroying ozone may have a significant impact on the interpretation of the role of such emissions. Previous studies estimated that total ozone fluxes to plant canopies in midlatitude forests can be dominated by gas-phase chemistry and not by stomatal uptake as generally assumed [*Fowler et al.*, 2001; *Kurpius and Goldstein*, 2003; *Mikkelsen et al.*, 2000]. However, in Amazonia during the dry season, mean daytime ozone fluxes measured by eddy covariance above the canopy was found to be between -6.6 and -10.9 nmol m^{-2} s^{-1} in southwest Amazonia [*Rummel et al.*, 2007], and the authors assumed the stomatal uptake to sufficiently explain the observed ozone flux. Furthermore, enclosure studies with Amazonian plants [*Gut et al.*, 2002] indicated that the uptake of ozone was completely under stomatal control. Thus, any decomposition of ozone by volatiles would limit the impact of ozone on plant metabolism.

[20] Using deposition velocities of 0.5 and 1.0 cm s^{-1} for midday conditions in the dry season, we calculate similar ozone fluxes in central Amazonia (between -5.4 and -10.8 nmol m^{-2} s^{-1}) to those measured in southwest Amazonia [*Rummel et al.*, 2007]. Therefore, our estimated dry season SQT ozonolysis loss term of -0.6 to -1.1 mg m^{-2} h^{-1} (-0.8 to -1.5 nmol m^{-2} s^{-1}), accounting for 7%–28% of the net ozone flux would demonstrate a substantial reduction of the ozone burden for the plants.

4. Summary and Conclusions

[21] While a large number of studies have observed SQT emissions from plants using leaf, branch, and whole plant enclosures, because of reported high sensitivity of SQT emissions to mechanical and heat disturbances [*Duhl et al.*, 2008] and their high reactivity toward ozone [*Bonn and Moortgat*, 2003], enclosure approaches cannot be used to estimate ambient concentrations or ecosystem-scale emission rates without the exclusion or corrections of ozone and disturbance effects during the studies. Because of analytical difficulties in quantifying ambient SQTs, attempts have been made to indirectly quantify them by correlation with air ions [*Bonn et al.*, 2007, 2008]. While recent studies have successfully directly quantified ambient SQTs with long-term averaging using PTR-MS [*Kim et al.*, 2009] and air sample preconcentration coupled with GC-MS [*Bouvier-Brown et al.*, 2009], we report real-time in situ ambient SQT concentration measurements within a controlled rain forest mesocosm and a natural primary rain forest in the central Amazon. We found that within both the tropical rain forest mesocosm at Biosphere 2 and a natural primary rain forest in the central Amazon, SQT emissions rates from plants were mostly temperature dependent whereas MT emissions were mostly light dependent. This combined with strong diurnal patterns of vertical mixing and within canopy ozonolysis of highly reactive SQTs likely contributes to the divergence in MT (daytime maxima) and SQT (nighttime maxima) ambient concentration patterns in the Amazon. In contrast, MT and SQT concentrations in Biosphere 2 are primarily controlled by emission rates as gas-phase oxidants and ventilation were notably lower than in a natural forest.

[22] Our observations in the dry season in the Amazon provide vertically resolved experimental evidence to support conclusions of photochemical modeling studies that a large fraction of SQTs emitted by plant canopies do not escape the canopy owing to reactions with ozone [*Stroud et al.*, 2005; *Wolfe et al.*, 2011], possibly leading to high yields of secondary organic aerosol [*O'Dowd et al.*, 2002] and OH production [*Paulson et al.*, 1999]. These processes have important implications for tropospheric chemistry and climate. In addition, many studies have indirectly suggested that a substantial amount of unmeasured and unidentified highly reactive VOCs are emitted by forests [*Di Carlo et al.*,

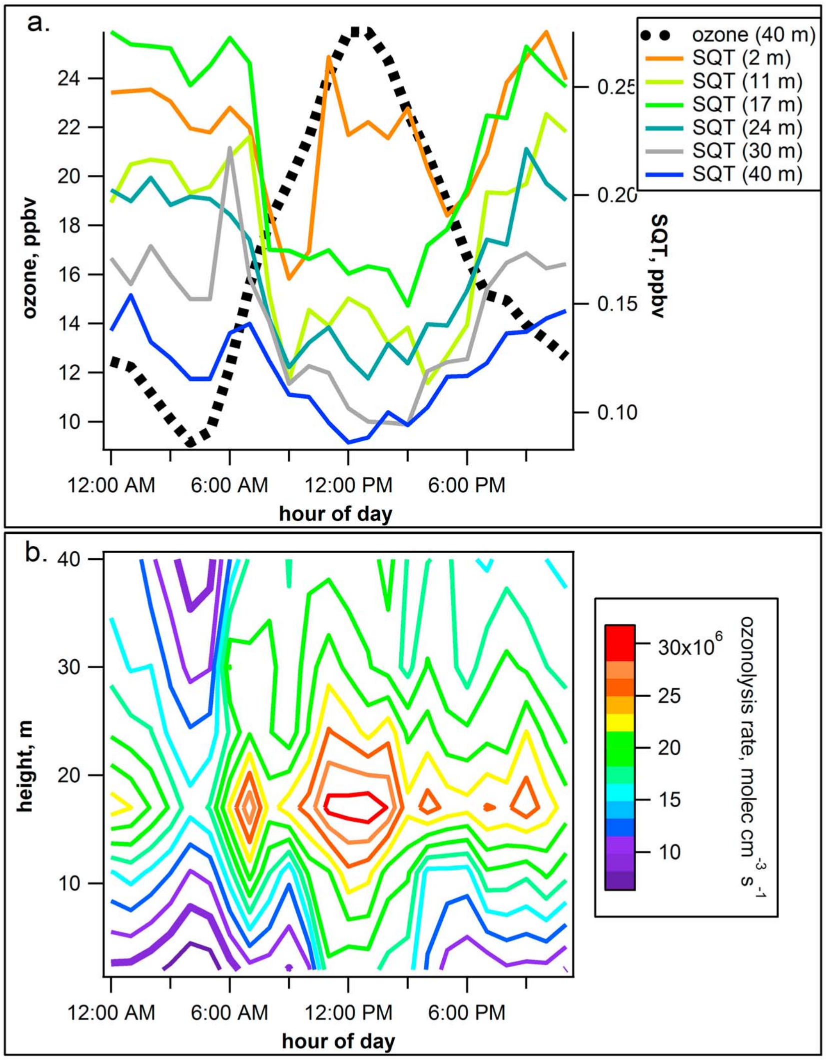

Figure 5. (a) Mean diurnal patterns of ozone (40 m) and SQTs during the 2010 dry season in central Amazonia. (b) Estimated mean diurnal pattern of SQT ozonolysis rates throughout the canopy in central Amazonia during the 2010 dry season. Ozone concentrations within the canopy were estimated by assuming the same relative concentration decrease within the canopy as that determined by *Karl et al.* [2009] (upper limit).

2004; *Goldstein et al.*, 2004; *Holzinger et al.*, 2005]. Our observations demonstrate that SQTs are an important component of these highly reactive compounds, which to date have not been measured using standard vertical flux techniques (e.g., eddy covariance) owing to their high within-canopy loss rates and analytical difficulties associated with measuring them quantitatively.

[23] Both MTs and SQTs have been proposed to serve roles as endogenous antioxidants in plants by reducing oxidative damage during the stress induced accumulation of reactive oxygen species [*Vickers et al.*, 2009]. Given the analytical challenges involved, no experimental evidence has emerged to date to support this role for SQTs, but studies have shown that MTs protect photosynthesis against high temperatures [*Delfine et al.*, 2000; *Loreto et al.*, 1998] and elevated ozone concentrations [*Loreto and Fares*, 2007]. Our estimation of mean daytime ozone loss within the central Amazon canopy during the dry season due to gas-phase reactions with SQTs represents a significant fraction (7%–28%) of calculated ozone fluxes. Therefore, by acting as effective ozone sinks within plant canopies, emissions of SQTs may significantly reduce harmful ozone uptake and its associated oxidative damage. The reduction of within canopy ozone through gas-phase reactions with SQTs may be particularly important for future plant survival in Amazonia given that regular exposure of tropical trees to mixing ratios (>50 ppbv) can cause permanent plant damage [*Rummel et al.*, 2007] and that plants in Amazonia have only recently been exposed to high levels of ozone. For example, as recently as 1987 the maximum daytime ozone in the central Amazon during the dry season was only 12 ppbv [*Kirchhoff et al.*, 1990], compared with over 40 ppbv observed during the 2010 dry season. Therefore, while the evolution of SQT emissions by plants may be related to its role as an antioxidant within plants, we propose a new protective role of SQTs as an exogenous antioxidant within plant canopies.

[24] **Acknowledgments.** Funding for this project was provided by the Philecology Foundation of Fort Worth, Texas, and the National Science Foundation through the AMAZON-PIRE (Partnerships for International Research and Education) award (0730305) and instrumentation support (CHE 0216226). A.A. and A.Y.S. acknowledge support from the Swedish Research Councils VR and Formas. We would like to thank Allen Goldstein at the University of California at Berkeley for the many helpful discussions on SQTs and several individuals at the Instituto Nacional de Pesquisas da Amazônia (INPA) in Manaus, Brazil, for logistics support, including Roberta Pereira de Souza, Eliane Gomes Alves, Erika Schloemp, and Antonio Manzi.

References

Ahlm, L., et al. (2010), A comparison of dry and wet season aerosol number fluxes over the Amazon rain forest, *Atmos. Chem. Phys.*, *10*(6), 3063–3079, doi:10.5194/acp-10-3063-2010.

Andreae, M. O., et al. (2005), Strong present-day aerosol cooling implies a hot future, *Nature*, *435*(7046), 1187–1190, doi:10.1038/nature03671.

Araujo, A. C., et al. (2002), Comparative measurements of carbon dioxide fluxes from two nearby towers in a central Amazonian rainforest: The Manaus LBA site, *J. Geophys. Res.*, *107*(D20), 8090, doi:10.1029/2001JD000676.

Arneth, A., et al. (2009), Clean the air, heat the planet?, *Science*, *326*(5953), 672–673, doi:10.1126/science.1181568.

Baker, B., et al. (2005), Wet and dry season ecosystem level fluxes of isoprene and monoterpenes from a southeast Asian secondary forest and rubber tree plantation, *Atmos. Environ.*, *39*(2), 381–390, doi:10.1016/j.atmosenv.2004.07.033.

Baraldi, R., et al. (2004), Monoterpene emission responses to elevated CO_2 in a Mediterranean-type ecosystem, *New Phytol.*, *161*(1), 17–21, doi:10.1111/j.1469-8137.2004.00946.x.

Bonn, B., and G. K. Moortgat (2003), Sesquiterpene ozonolysis: Origin of atmospheric new particle formation from biogenic hydrocarbons, *Geophys. Res. Lett.*, *30*(11), 1585, doi:10.1029/2003GL017000.

Bonn, B., et al. (2007), Ambient sesquiterpene concentration and its link to air ion measurements, *Atmos. Chem. Phys.*, *7*(11), 2893–2916, doi:10.5194/acp-7-2893-2007.

Bonn, B., M. Kulmala, I. Riipinen, S.-L. Sihto, and T. M. Ruuskanen (2008), How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particle formation, *J. Geophys. Res.*, *113*, D12209, doi:10.1029/2007JD009327.

Bouvier-Brown, N. C., et al. (2009), In-situ ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during BEARPEX 2007: Implications for gas- and particle-phase chemistry, *Atmos. Chem. Phys.*, *9*(15), 5505–5518, doi:10.5194/acp-9-5505-2009.

Boy, M., et al. (2008), New particle formation in the front range of the Colorado Rocky Mountains, *Atmos. Chem. Phys.*, *8*(6), 1577–1590, doi:10.5194/acp-8-1577-2008.

Carslaw, K. S., et al. (2010), A review of natural aerosol interactions and feedbacks within the Earth system, *Atmos. Chem. Phys.*, *10*(4), 1701–1737, doi:10.5194/acp-10-1701-2010.

Ciccioli, P., et al. (1999), Emission of reactive terpene compounds from orange orchards and their removal by within-canopy processes, *J. Geophys. Res.*, *104*(D7), 8077–8094, doi:10.1029/1998JD100026.

Cockell, C. S., et al. (2000), Lack of UV radiation in Biosphere 2: Practical and theoretical effects on plants, *Ecol. Eng.*, *16*(2), 293–299, doi:10.1016/S0925-8574(99)00057-9.

Delfine, S., et al. (2000), Fumigation with exogenous monoterpenes of a non-isoprenoid-emitting oak (Quercus suber): Monoterpene acquisition, translocation, and effect on the photosynthetic properties at high temperatures, *New Phytol.*, *146*(1), 27–36, doi:10.1046/j.1469-8137.2000.00612.x.

Demarcke, M., et al. (2009), Laboratory studies in support of the detection of sesquiterpenes by proton-transfer-reaction-mass-spectrometry, *Int. J. Mass Spectrom.*, *279*(2–3), 156–162, doi:10.1016/j.ijms.2008.10.023.

Di Carlo, P., et al. (2004), Missing OH reactivity in a forest: Evidence for unknown reactive biogenic VOCs, *Science*, *304*(5671), 722–725, doi:10.1126/science.1094392.

Duhl, T. R., et al. (2008), Sesquiterpene emissions from vegetation: A review, *Biogeosciences*, *5*(3), 761–777, doi:10.5194/bg-5-761-2008.

Fowler, D., et al. (2001), Measurements of ozone deposition to vegetation quantifying the flux, the stomatal and non-stomatal components, *Water Air Soil Pollut.*, *130*(1–4), 63–74, doi:10.1023/A:1012243317471.

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

Goldstein, A. H., M. McKay, M. R. Kurpius, G. W. Schade, A. Lee, R. Holzinger, and R. A. Rasmussen (2004), Forest thinning experiment confirms ozone deposition to forest canopy is dominated by reaction with biogenic VOCs, *Geophys. Res. Lett.*, *31*, L22106, doi:10.1029/2004GL021259.

Griffin, R. J., D. R. Cocker III, R. C. Flagan, and J. H. Seinfeld (1999), Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, *104*(D3), 3555–3567, doi:10.1029/1998JD100049.

Gut, A., et al. (2002), Exchange fluxes of NO_2 and O_3 at soil and leaf surfaces in an Amazonian rain forest, *J. Geophys. Res.*, *107*(D20), 8060, doi:10.1029/2001JD000654.

Hallquist, M., et al. (2009), 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.

Holzinger, R., et al. (2005), Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds, *Atmos. Chem. Phys.*, *5*(1), 67–75, doi:10.5194/acp-5-67-2005.

Jardine, K., et al. (2010a), Dynamic Solution Injection: A new method for preparing pptv-ppbv standard atmospheres of volatile organic compounds, *Atmos. Meas. Tech.*, *3*(6), 1569–1576, doi:10.5194/amt-3-1569-2010.

Jardine, K., et al. (2010b), Gas phase measurements of pyruvic acid and its volatile metabolites, *Environ. Sci. Technol.*, *44*, 2454–2460, doi:10.1021/es903544p.

Jimenez, J. L., et al. (2009), Evolution of organic aerosols in the atmosphere, *Science*, *326*(5959), 1525–1529, doi:10.1126/science.1180353.

Jordan, C., et al. (2009), Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences, *Atmos. Chem. Phys.*, *9*(14), 4677–4697, doi:10.5194/acp-9-4677-2009.

Karl, T., M. Potosnak, A. Guenther, D. Clark, J. Walker, J. D. Herrick, and C. Geron (2004), Exchange processes of volatile organic compounds above a tropical rain forest: Implications for modeling tropospheric chemistry above dense vegetation, *J. Geophys. Res.*, *109*, D18306, doi:10.1029/2004JD004738.

Karl, T., et al. (2009), Rapid formation of isoprene photo-oxidation products observed in Amazonia, *Atmos. Chem. Phys.*, *9*(20), 7753–7767, doi:10.5194/acp-9-7753-2009.

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

Kesselmeier, J., et al. (1997), Emission of short chained organic acids, aldehydes and monoterpenes from *Quercus ilex* L. and *Pinus pinea* L. in relation to physiological activities, carbon budget and emission algorithms, *Atmos. Environ.*, *31*(1), 119–133, doi:10.1016/S1352-2310(97)00079-4.

Kim, S., et al. (2009), Measurement of atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS), *Atmos. Meas. Tech.*, *2*(1), 99–112, doi:10.5194/amt-2-99-2009.

Kim, S., et al. (2010), Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: Interpretation of PTR-MS mass spectra, *Atmos. Chem. Phys.*, *10*(4), 1759–1771, doi:10.5194/acp-10-1759-2010.

Kirchhoff, V. W. J. H., I. M. O. da Silva, and E. V. Browell (1990), Ozone measurements in Amazonia: Dry season versus wet season, *J. Geophys. Res.*, *95*(D10), 16,913–16,926, doi:10.1029/JD095iD10p16913.

Kruijt, B., et al. (2000), Turbulence statistics above and within two Amazon rain forest canopies, *Boundary Layer Meteorol.*, *94*(2), 297–331, doi:10.1023/A:1002401829007.

Kuhn, U., S. Rottenberger, T. Biesenthal, A. Wolf, G. Schebeske, P. Ciccioli, E. Brancaleoni, M. Frattoni, T. M. Tavares, and J. Kesselmeier (2002), 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), 8071, doi:10.1029/2001JD000978.

Kuhn, U., et al. (2004), Seasonal differences in isoprene and light-dependent monoterpene emission by Amazonian tree species, *Global Change Biol.*, *10*(5), 663–682, doi:10.1111/j.1529-8817.2003.00771.x.

Kurpius, M. R., and A. H. Goldstein (2003), Gas-phase chemistry dominates O_3 loss to a forest, implying a source of aerosols and hydroxyl radicals to the atmosphere, *Geophys. Res. Lett.*, *30*(7), 1371, doi:10.1029/2002GL016785.

Laothawornkitkul, J., et al. (2009), Biogenic volatile organic compounds in the Earth system, *New Phytol.*, *183*(1), 27–51, doi:10.1111/j.1469-8137.2009.02859.x.

Li, Y. J., et al. (2011), Second-generation products contribute substantially to the particle-phase organic material produced by beta-caryophyllene ozonolysis, *Atmos. Chem. Phys.*, *11*(1), 121–132, doi:10.5194/acp-11-121-2011.

Lichtenthaler, H. K., et al. (1997), Two independent biochemical pathways for isopentenyl diphosphate and isoprenoid biosynthesis in higher plants, *Physiol. Plant.*, *101*(3), 643–652, doi:10.1111/j.1399-3054.1997.tb01049.x.

Loreto, F., and S. Fares (2007), Is ozone flux inside leaves only a damage indicator?: Clues from volatile isoprenoid studies, *Plant Physiol.*, *143*(3), 1096–1100, doi:10.1104/pp.106.091892.

Loreto, F., et al. (1998), On the monoterpene emission under heat stress and on the increased thermotolerance of leaves of Quercus ilex L. fumigated with selected monoterpenes, *Plant Cell Environ.*, *21*(1), 101–107, doi:10.1046/j.1365-3040.1998.00268.x.

Martin, S. T., et al. (2010), An overview of the Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08), *Atmos. Chem. Phys.*, *10*(23), 11,415–11,438, doi:10.5194/acp-10-11415-2010.

Mikkelsen, T. N., et al. (2000), Ozone uptake by an evergreen forest canopy: Temporal variation and possible mechanisms, *Environ. Pollut.*, *109*(3), 423–429, doi:10.1016/S0269-7491(00)00045-2.

O'Dowd, C. D., et al. (2002), Aerosol formation: Atmospheric particles from organic vapours, *Nature*, *416*(6880), 497–498, doi:10.1038/416497a.

Ortega, J., and D. Helmig (2008), Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - Part A, *Chemosphere*, *72*(3), 343–364, doi:10.1016/j.chemosphere.2007.11.020.

Paulson, S. E., et al. (1999), 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.

Raisanen, T., et al. (2009), Monoterpene emission of a boreal Scots pine (*Pinus sylvestris* L.) forest, *Agric. For. Meteorol.*, *149*(5), 808–819, doi:10.1016/j.agrformet.2008.11.001.

Raupach, M. R. (1989), Applying Lagrangian fluid-mechanics to infer scalar source distributions from concentration profiles in plant canopies, *Agric. For. Meteorol.*, *47*(2–4), 85–108, doi:10.1016/0168-1923(89)90089-0.

Rinne, H. J. I., et al. (2002), 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.

Rummel, U., et al. (2007), Seasonal variation of ozone deposition to a tropical rain forest in southwest Amazonia, *Atmos. Chem. Phys.*, *7*(20), 5415–5435, doi:10.5194/acp-7-5415-2007.

Schuh, G., et al. (1997), Emissions of volatile organic compounds from sunflower and beech: Dependence on temperature and light intensity, *J. Atmos. Chem.*, *27*(3), 291–318, doi:10.1023/A:1005850710257.

Shu, Y. H., and R. Atkinson (1994), Rate constants of the gas-phase reactions of O_3 with a series of terpenes and OH radical formation from the O_3 reactions with Sesquiterpenes at 296 ± 2 K, *Int. J. Chem. Kinet.*, *26*, 1193–1205, doi:10.1002/kin.550261207.

Staudt, M., and G. Seufert (1995), Light-dependent emission of monoterpenes by Holm Oak (Quercus-Ilex L), *Naturwissenschaften*, *82*(2), 89–92, doi:10.1007/BF01140148.

Stroud, C., P. Makar, T. Karl, A. Guenther, C. Geron, A. Turnipseed, E. Nemitz, B. Baker, M. Potosnak, and J. D. Fuentes (2005), Role of canopy-scale photochemistry in modifying biogenic-atmosphere exchange of reactive terpene species: Results from the CELTIC field study, *J. Geophys. Res.*, *110*, D17303, doi:10.1029/2005JD005775.

Vickers, C. E., et al. (2009), A unified mechanism of action for volatile isoprenoids in plant abiotic stress, *Nat. Chem. Biol.*, *5*(5), 283–291, doi:10.1038/nchembio.158.

Wang, Y. F., et al. (2007), Monoterpene emissions from rubber trees (Hevea brasiliensis) in a changing landscape and climate: Chemical speciation and environmental control, *Global Change Biol.*, *13*(11), 2270–2282, doi:10.1111/j.1365-2486.2007.01441.x.

Wolfe, G. M., et al. (2011), Forest-atmosphere exchange of ozone: Sensitivity to very reactive biogenic VOC emissions and implications for in-canopy photochemistry, *Atmos. Chem. Phys. Discuss.*, *11*(5), 13,381–13,424, doi:10.5194/acpd-11-13381-2011.

L. Abrell, Department of Chemistry and Biochemistry, University of Arizona, PO Box 210041, 1306 East University Blvd., Tucson, AZ 85721-0041, USA.

A. Arneth and A. Yañez Serrano, Department of Physical Geography and Ecosystems Analysis, Lund University, Sölvegatan 12, 223 62 Lund, Sweden.

P. Artaxo, Instituto de Fisica, Universidade de Sao Paulo, Rua do Matao, Travessa R, 187 Sao Paulo, SP 05508-900, Brazil.

T. Huxman, A. Jardine, K. Jardine, and J. van Haren, PO Box 8746, Biosphere 2, University of Arizona, Tucson, AZ 85738, USA. (jardine@email.arizona.edu)

F. Y. Ishida, Large Biosphere-Atmosphere Experiment, Instituto Nacional de Pesquisas da Amazônia, Av. André Araújo, 2936, Aleixo, CEP 69060-001, Manaus, Brazil.

T. Karl, Atmospheric Chemistry Division, National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307-3000, USA.

J. Kesselmeier, Biogeochemistry Department, Max Planck Institute for Chemistry, PO Box 3060, D-55020 Mainz, Germany.

L. V. Rizzo, Department of Exact and Earth Sciences, Federal University of Sao Paulo, Rua Prof. Artur Riedel, 275, Diadema, SP 09972-270, Brazil.

S. Saleska, Department of Ecology and Evolutionary Biology, University of Arizona, PO Box 210088, BioSciences West 310, Tucson, AZ 85721, USA.