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Key Points:

- Mixing ratios of 12 Amazon monoterpenes reflect vertical forest structure
- Light-dependent reactive monoterpene leaf emissions observed in ambient air
- Monoterpene ozonolysis rates suggest important local aerosol precursor source

Supporting Information:

- Readme
- Figure S1
- Figure S2
- Figure S3
- Figure S4
- Text S1

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Highly reactive light-dependent monoterpenes in the Amazon

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Abstract Despite orders of magnitude difference in atmospheric reactivity and great diversity in biological functioning, little is known about monoterpene speciation in tropical forests. Here we report vertically resolved ambient air mixing ratios for 12 monoterpenes in a central Amazon rainforest including observations of the highly reactive cis-β-ocimene (160 ppt), trans-β-ocimene (79 ppt), and terpinolene (32 ppt) which accounted for an estimated 21% of total monoterpene composition yet 55% of the upper canopy monoterpene ozonolysis rate. All 12 monoterpenes showed a mixing ratio peak in the upper canopy, with three demonstrating subcanopy peaks in 7 of 11 profiles. Leaf level emissions of highly reactive monoterpenes accounted for up to 1.9% of photosynthesis confirming light-dependent emissions across several Amazon tree genera. These results suggest that highly reactive monoterpenes play important antioxidant roles during photosynthesis in plants and serve as near-canopy sources of secondary organic aerosol precursors through atmospheric photooxidation via ozonolysis.

1. Introduction

Many tree species produce monoterpenes ($C_{10}H_{16}$), a diverse class of volatile terpenoids, which can be emitted into the atmosphere at high rates [*Kesselmeier and Staudt*, 1999; *Fuentes et al.*, 2000]. Within ecosystems, monoterpenes mediate plant-microbe [*Dorman and Deans*, 2000] and plant-insect [*Beyaert and Hilker*, 2014] interactions and protect photosynthesis during abiotic stress [*Peñuelas and Llusià*, 2002; *Vickers et al.*, 2009]. Fueled by large total monoterpene emissions from forested ecosystems [*Karl et al.*, 2002, 2003, 2004], atmospheric photochemical oxidation of monoterpenes generates low-volatility oxidation products that can partition to the particle phase [*Yu et al.*, 1999; *Fuentes et al.*, 2000; *Kurpius and Goldstein*, 2003; *Mcfrederick et al.*, 2008; *Martin et al.*, 2010]. These oxidation products, along with the oxidation products of isoprene (C_5H_8), sesquiterpenes ($C_{15}H_{24}$), and possibly higher-order terpenoids ($C_{20}H_{32}$ and above), play important roles in the formation and growth of secondary organic aerosol (SOA) particles that can activate into cloud condensation nuclei [*Claeys et al.*, 2004; *Pöschl et al.*, 2010].

Monoterpene ozonolysis reactions are important for SOA formation [*Presto et al.*, 2005; *Zhao et al.*, 2014] and postnucleation growth processes [*Presto et al.*, 2005; *Hao et al.*, 2009]. Further, the studies of *Goldstein et al.* [2004] and *Fares et al.* [2010] demonstrated that O_3 fluxes above a ponderosa pine forest (*Pinus ponderosa*) were dominated by gas phase chemistry, and their results suggested highly reactive monoterpenes likely contributing to a "missing" within-canopy O_3 sink. Thus, characterization of speciated monoterpenes and their associated ozonolysis reactions in the atmosphere is important for a comprehensive understanding of SOA sources [*Chen et al.*, 2009].

Little is known about monoterpene composition in the tropics—a widely recognized major global source of terpenoids to the atmosphere [*Guenther et al.*, 1995]. To date, only a few field observations targeting plant and atmospheric monoterpenes have been reported from the Amazon. Ambient levels of monoterpenes including α-pinene, β-pinene, and *p*-cymene have been reported [*Helmig et al.*, 1998; *Rinne et al.*, 2002; *Kuhn et al.*, 2007] as well as low levels of highly reactive monoterpenes including myrcene, terpinolene, α-phellandrene and α-terpinene [*Kesselmeier et al.*, 2000]. Other atmospheric monoterpene studies in the Amazon used the online technique of proton transfer reaction-mass spectrometry (PTR-MS), which is capable of high temporal resolution measurements but only reports total monoterpene mixing ratios [*Rizzo et al*., 2010; *Jardine et al*., 2011].

Branch-level studies of *Apeiba tibourbou* in Rôndonia, Brazil, revealed emissions of sabinene, α-pinene, β-pinene, myrcene, and *d*-limonene in a pattern consistent with light-dependent emissions [*Kuhn et al*., 2002]. However, in midlatitude sites, light-independent temperature-driven foliar evaporation of monoterpenes from storage pools has been demonstrated [*Niinemets et al*., 2004] and $^{13}CO_2$ labeling demonstrated significant storage emissions versus de novo production [*Ghirardo et al*., 2010]. Although monoterpene emissions from tropical plants are generally assumed to be light dependent (i.e., emissions of near zero at night), the relative importance of monoterpene emissions due to evaporation from storage pools versus de novo production in tropical plants is not known. Given limited field studies in the Amazon, improvements in our understanding of the speciation of monoterpene composition in ambient air along with speciated emissions from tropical vegetation and associated abiotic controls (i.e., light and temperature) will enhance our predictive capabilities of monoterpene functioning within and above the Amazon forest [*Martin et al*., 2010].

Over a 9 month period (November 2013 to July 2014), we collected vertically resolved ambient air profiles of individual monoterpenes within and above a mature terra firma rainforest in the central Amazon Basin as part of the Green Ocean Amazon 2014/15 experiment (GoAmazon2014/5). We examined the results in the context of the vertical distribution of leaf area index (LAI) and combined monoterpene and ozone mixing ratios to calculate individual monoterpene ozonolysis rates. Finally, we investigated the potential light-dependent nature of monoterpene emissions from leaves of pioneer and climax tree species at the field site and also found in wide distribution across the Amazon Basin. The results are discussed in terms of the potential importance of highly reactive monoterpenes as ozonolysis-driven SOA precursors in the Amazon Basin as well as ecosystem antioxidation roles during photosynthesis. A brief discussion is given on the possible selective advantages of trees that produce highly reactive monoterpenes during photosynthesis under future climate and land use change scenarios in the Amazon Basin [*Unger*, 2014].

2. Methods

2.1. Overview

The field site (Reserva Biologica da Cuieiras; also referred to as ZF2 and T0k for GoAmazon 2014/5 experiment) in central Amazonia is approximately 60 km NNW of Manaus, Brazil (2°35′48.09″S, 60°13′11.43″W), and managed by the National Institute for Amazon Research (INPA). Ambient air measurements were made at the K34 tower, situated on a plateau surrounded by primary forest (dominated by climax tree species). A leaf area index (LAI) vertical profile showed a canopy top at 29 m and a subcanopy top at 17 m (section 1.1 in Text S1 and Figure S1 in the supporting information).

2.2. Vertically Resolved Speciated Monoterpene Ambient Mixing Ratios

Nine-point vertical profiles of the identified monoterpenes were collected at the K34 tower (heights of 0, 13, 17, 21, 25, 29, 34, 38, and 50 m and one blank tube) by drawing 1.0 L of ambient air through a conditioned stainless steel thermal desorption tube fitted with internal SafeLok caps and packed with Tenax-TA 35/60, Carbograph 1TD 40/60, and Carboxen 1003 40/60 sorbents. Each sample was collected within 4 min using a volumetrically calibrated hand pump (EasyVOC, Markes International, UK), and each nine-point vertical profile was completed in about 60 min. Eleven vertical ambient air profiles were collected between 8 November 2013 and 17 July 2014 during rain-free afternoon periods (13:00–16:30 local time) as detailed in the supporting information Table S1. In addition, within-canopy turbulence profiles were obtained using 3-D sonic anemometers on the tower (section 1.2 in Text S1 and Figure S2 in the supporting information).

2.3. Light-Dependent Leaf Photosynthesis and Monoterpene Emissions From Amazonian Trees

Coupled photosynthesis and monoterpene emission measurements were conducted on sun-exposed leaves from several tree species at the field site along the access road ~2 km from the K34 tower (two pioneer tree species, intact branches) and along the established north-south and east-west transects [*Da Silva et al*., 2002] within the forest (five climax tree species, detached upper canopy branches), ~1 km from the K34 tower (supporting information Table S2). Leaf photosynthesis measurements together with monoterpene emissions during controlled photosynthetically active radiation (PAR) curves from 0 to 2000 $\mu mol\ m^{-2}\ s^{-1}$ at constant CO_2 (400 ppm) and leaf temperature (30°C) were collected using a portable photosynthesis system (LI-6400 XT, Licor

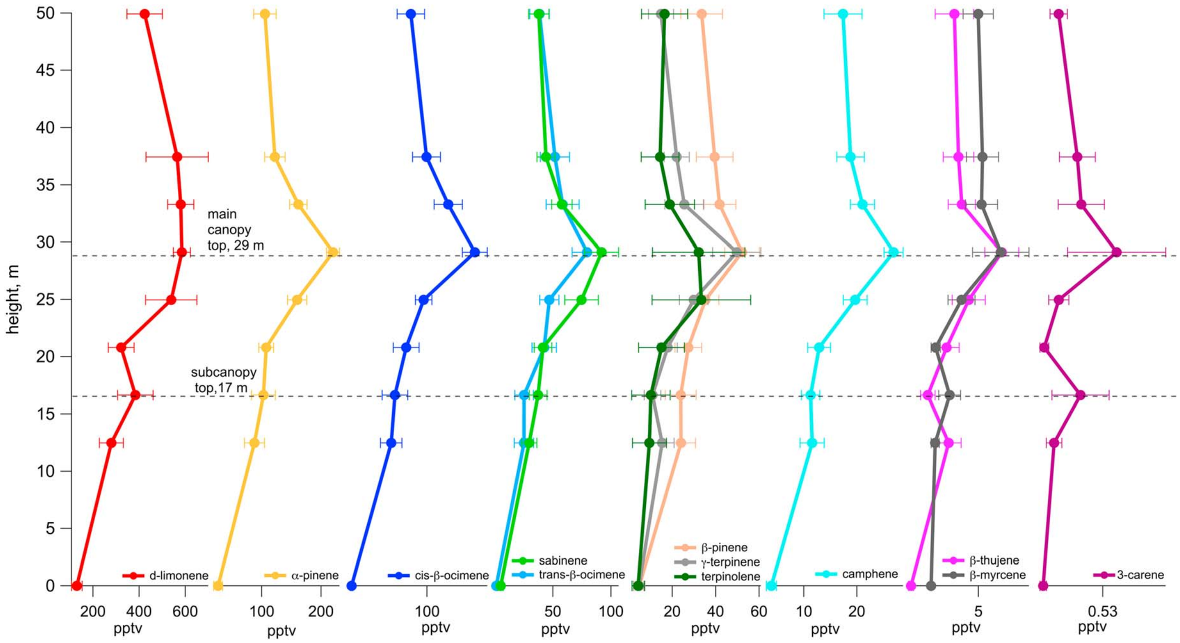

Figure 1. Average afternoon (13:00–16:30) ambient air mixing ratio profiles ($n = 11$) for 12 monoterpenes collected at the K34 walkup tower at the central Amazon field site between 8 November 2013 and 17 July 2014. Error bars represent ±1 mean standard error.

Biosciences, USA) coupled to a portable thermal desorption tube autosampler (Less-P, Signature Science, USA) as described in section 1.3 in Text S1.

2.4. TD-GC-MS Analysis

Thermal desorption tube samples were stored no more than 2 days following collection and analyzed with a thermal desorption-gas chromatograph-mass spectrometer (TD-GC-MS) at the INPA laboratory in Manaus, Brazil, using the TD-GC-MS instrumentation and methods described in *Jardine et al*. [2014] in simultaneous scan and selective ion monitoring (SIM) modes (scan: mass/charge ratio (m/z) range = 35–240, $n = 2$ samples averaged, SIM: target $m/z = 93$ and 68 with 20 ms dwell times each).

Monoterpenes were identified with the 2011 National Institute of Standards and Technology Mass Spectral Library (NIST, USA) and by retention time and mass spectral comparisons with authentic liquid standards (Restek, USA). Monthly five-point calibrations were conducted throughout the study using the dynamic solution injection technique [*Jardine et al*., 2010b]. Liquid standards and five-point monthly calibration curves are described in section 1.4 in Text S1.

3. Results

3.1. Vertical Profiles of LAI and 12 Monoterpenes in the Central Amazon

GC-MS analysis of ambient air revealed the presence of 12 individual monoterpenes (supporting information Figure S3). The average of 11 vertical mixing ratio profiles, each collected in approximately 1 h between November 2013 and July 2014 during rain-free afternoon periods (13:00–16:30) at the K34 tower, is shown in Figure 1. When compared with the vertical profile of LAI, the largest mixing ratios for all monoterpenes other than terpinolene occurred in the high light/temperature environment of the upper canopy (29 m), where the average total monoterpene mixing ratio was 1.3 ppb. These values are in good agreement with afternoon total monoterpene mixing ratios made by PTR-MS at the same site in 2010–2011 (1.5 ppb) [*Jardine et al*., 2011]. While PTR-MS methods can provide high temporal information on total monoterpene mixing ratios, the GC-MS method presented here allows for rapid speciation of the ambient air monoterpene composition.

At the top of the canopy (29 m), *d*-limonene (585 ppt) was the dominant monoterpene followed by α-pinene (220 ppt), cis-β-ocimene (160 ppt), sabinene (92 ppt), trans-β-ocimene (79 ppt), β-pinene (52 ppt), γ-terpinene

(50 ppt), terpinolene (32 ppt), camphene (27 ppt), *β*-myrcene (6 ppt), *β*-thujene (6 ppt), and 3-carene (1 ppt). Secondary peaks were observed at the top of the subcanopy (17 m) for *d*-limonene (383 ppt), *β*-myrcene (3 ppt), and 3-carene (0.4 ppt). These subcanopy peaks were observed in 7 of the 11 individual ambient air profiles collected.

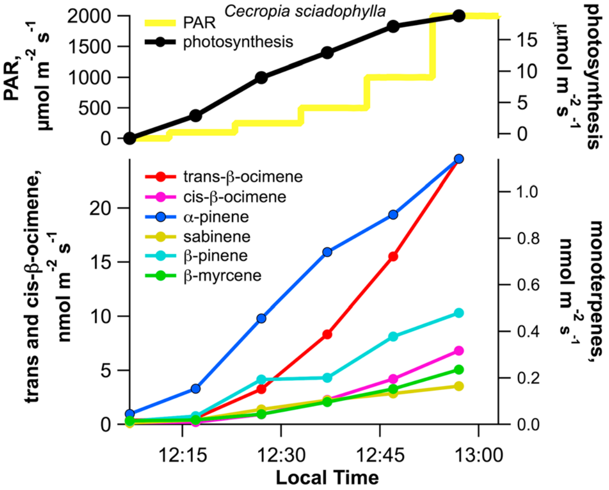

Figure 2. Light dependence of monoterpene emissions from *C. sciadophylla* (a common pioneer species in the Amazon Basin) together with photosynthesis rates measured at the field site. See supporting information Figure S4 for similar observations from additional pioneer and climax tree species at the Amazon field site.

3.2. Light-Dependent Leaf Photosynthesis and Monoterpene Emissions

Coupled leaf monoterpene emissions and photosynthetic rates as a function of light intensity at constant leaf temperature (30°C) were collected from trees found at the field site (supporting information Table S1) and also found in abundance across the Amazon Basin [*Ter Steege et al*., 2013]. Measurements on *Cecropia sciadophylla* leaves at the site showed light-dependent emissions of six monoterpenes (Figure 2). As PAR intensities increased, both photosynthesis and monoterpene emission rates from the *C. sciadophylla* leaf increased strongly to the maximum PAR intensity (PAR: 2000 μmol m^{-2} s^{-1}; photosynthesis: 19.0 μmol m^{-2} s^{-1}; and total monoterpene emissions of 35.8 nmol m^{-2} s^{-1}). Across all PAR intensities, monoterpene emissions correlated with net photosynthetic rates ($R^2 = 0.86$) with 1.91 ± 0.44% of recently assimilated carbon reemitted to the atmosphere as monoterpenes. Trans-*β*-ocimene and cis-*β*-ocimene dominated the light-dependent emissions, which had maximum emission rates of 24.5 nmol m^{-2} s^{-1} and 6.8 nmol m^{-2} s^{-1}, respectively, at maximum PAR. Additional light-dependent monoterpenes with emission rates at maximum PAR include *α*-pinene (1.5 nmol m^{-2} s^{-1}), *β*-pinene (0.5 nmol m^{-2} s^{-1}), *β*-myrcene (0.23 nmol m^{-2} s^{-1}), and sabinene (0.16 nmol m^{-2} s^{-1}). Thus, at high light intensities, leaf emissions of trans- and cis-*β*-ocimene accounted for 87.6% of total light-dependent monoterpene emissions.

The pioneer species *Croton lanjouwensis* also showed strong light-dependent emissions of cis-*β*-ocimene (up to 1.1 nmol m^{-2} s^{-1}, supporting information Figure S4a). Similar light-dependent emissions of cis-*β*-ocimene (up to 1.0 nmol m^{-2} s^{-1}) were observed from three climax tree species from the genera *Protium*, *Inga*, *and Eschweilera* (supporting information Figures S4b–S4d, respectively). These tree genera have been identified as hyperdominant in the Amazon Basin [*Ter Steege et al*., 2013]. Two additional climax tree species at the site showed clear light-dependent emissions of *α*-pinene, sabinene, and *β*-myrcene (*Scleronema micranthum*, supporting information Figure S4e) and sabinene (*Pouteria anomala*, supporting information Figure S4f).

4. Discussion

In this study, Tenax-TA was selected as the adsorbent to quantitatively trap the monoterpenes as previous studies have found that it is highly inert without significant interconversions between monoterpenes under similar analytical conditions [*Hollender et al*., 2002]. In addition, the sample storage time was low (1–2 days) with demonstrated stability of monoterpenes on Tenax-TA over this time frame [*Sunesson et al*., 1999]. While ozone was not removed from the ambient air samples, low volumes of ambient air were collected (1.0 L) and its atmospheric mixing ratios were < 10 ppb on the majority of measurement days. Nonetheless, as reactions between highly reactive monoterpenes and ozone on the thermal desorption tubes cannot be ruled out, our monoterpene mixing ratio measurements should be considered as a lower limit. However, similar total monoterpene mixing ratios in the afternoon observed in this study by GC-MS (1.3 ppb) were previously observed at the field site using PTR-MS (up to 1.5 ppb) [*Jardine et al*., 2011].

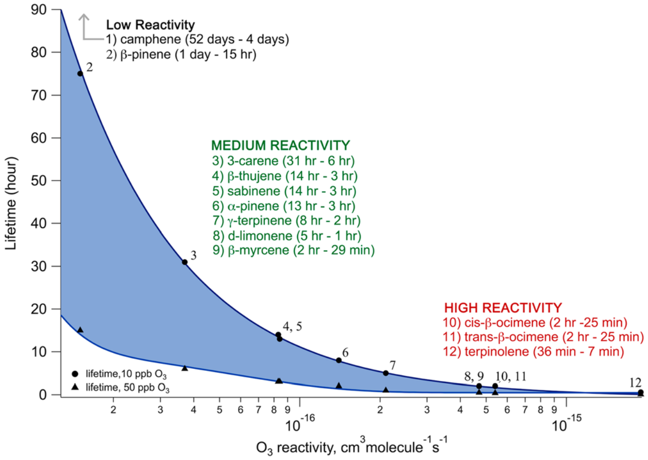

Figure 3. Estimated atmospheric lifetimes for the 12 monoterpenes quantified in this study with respect to ozonolysis as three reactivity groups (low, black; medium, blue; and high, red). Representative ozone mixing ratios represent the central Amazon Basin during in the wet season (10 ppb, upper line) and dry season (50 ppb, lower line); these values were used as upper and lower limits of monoterpene atmospheric lifetimes with respect to ozonolysis.

4.1. Atmospheric Oxidation via Ozonolysis

A large ecosystem-scale source of missing reactive volatiles has been previously suggested based on measurements of total ozone deposition fluxes to canopies of midlatitude forests [*Mikkelsen et al.*, 2000; *Fowler et al.*, 2001; *Barr et al.*, 2003; *Kurpius and Goldstein*, 2003]. The highly reactive monoterpenes quantified in this study including terpinolene, trans-β-ocimene, and cis-β-ocimene (Figure 1) may contribute to this missing reactivity balance. To our knowledge, this study represents the first observations of ambient trans- and cis-β-ocimene. To evaluate the potential importance of these reactive monoterpenes in atmospheric ozonolysis chemistry important for SOA formation and growth, we first estimated the atmospheric lifetimes of each monoterpene with respect to maximum afternoon ozone mixing ratios representative of the central Amazon (Figure 3, where the upper line represents a typical Amazon wet season clean atmosphere (10 ppb O_3) [*Rinne et al.*, 2002] and the lower line represents a polluted dry season Amazonian atmosphere (50 ppb O_3) [*Pacifico et al.*, 2014]). Monoterpene ozonolysis reactivities span more than 2 orders of magnitude [*Atkinson and Arey*, 2003] resulting in atmospheric lifetimes of days, hours, and minutes for low, medium, or highly reactive monoterpenes, respectively. Low reactive monoterpenes with respect to ozonolysis have atmospheric lifetimes on the order of days and include camphene (4–52 days), β-pinene (0.6–1 day), and 3-carene (0.25–1.3 days). Medium reactive monoterpenes having lifetimes on the order of hours include β-thujene and sabinene (3–14 h), α-pinene (3–13 h), γ-terpinene (2–8 h), *d*-limonene (1–5 h), and β-myrcene (0.5–2 h). Finally, highly reactive monoterpenes having lifetimes on the order of minutes include cis- and trans-β-ocimene (25–120 min) and terpinolene (7–36 min).

To further investigate the potential importance of monoterpene ozonolysis, the relative contributions of each ambient monoterpene to the total monoterpene mixing ratio (Figure 4a) and total monoterpene ozonolysis rate (Figure 4b) at the top of the main canopy (29 m) were calculated. These estimates suggest that the highly reactive monoterpenes cis-β-ocimene, trans-β-ocimene, and terpinolene accounted for only 21% of the total monoterpene mixing ratio yet accounted for up to 55% of the total monoterpene ozonolysis reactivity. In contrast, the upper canopy α-pinene mixing ratio accounted for 17% of the composition but contributed 5% to the total monoterpene ozonolysis rate.

Thus, these observations suggest that together with their large atmospheric abundances within the Amazon upper canopy and high reactivities to ozonolysis, reactive monoterpenes may serve as a near-canopy source of SOA precursors with their speciation critical to our understanding of SOA total yields and growth processes [*Chen et al.*, 2009; *Hao et al.*, 2009; *Zhao et al.*, 2014]. This may be especially true during the dry season when high light and temperatures stimulate plant emissions of reactive monoterpenes that interact with elevated levels of tropospheric ozone. Thus, enhanced dry season monoterpene and ozone mixing ratios may lead to a strong seasonal pattern in monoterpene ozonolysis rates.

4.2. Light-Dependent Leaf Level Emissions

At the leaf level, monoterpene emissions from middle- and high-latitude species in the Northern Hemisphere have been shown to derive from both stored pools and de novo production within chloroplasts [*Loreto et al.*, 1996; *Lerdau et al.*, 1997; *Ghirardo et al.*, 2010]. Emissions from ecosystems in these regions are often observed to be largely based on temperature-controlled evaporation from storage pools and independent of light

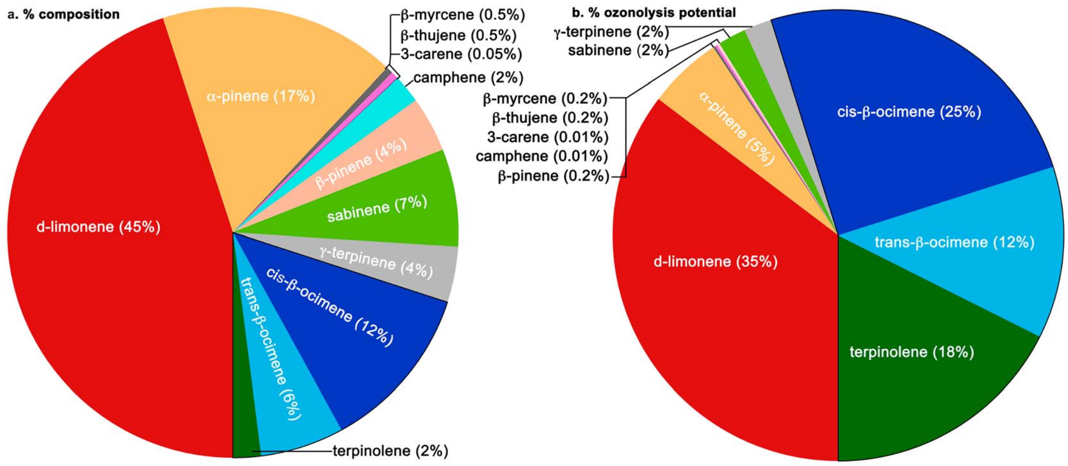

Figure 4. Average relative distribution of the 12 ambient monoterpenes for the top of the main canopy (29 m) at the K34 tower with respect to (a) mixing ratio abundances (% composition) and (b) estimated contribution to the ozonolysis rate (% ozonolysis potential).

[*Lerdau et al*., 1997] with monoterpenes often observed accumulating within the forest atmosphere at night [*Janson*, 1993; *Rinne et al*., 2000; *Bouvier-Brown et al*., 2009]. However, monoterpene emissions from tropical ecosystems are generally assumed as emitted from de novo production in a light-dependent manner, analogous to isoprene [*Rinne et al*., 2002]. This is supported by observations of much lower mixing ratios of total monoterpenes within the canopy at night compared with the day [*Jardine et al*., 2011]. Additional studies observed branch and ecosystem emissions during covariations in a number of environmental conditions including light, leaf temperature, and CO_2 with stronger correlations with light than with temperature [*Kuhn et al*., 2002, 2004; *Rinne et al*., 2002]. To our knowledge, this is the first study to provide direct evidence for the light-dependent nature of monoterpene emissions from tropical plants in the Amazon by conducting light curves under constant temperature and CO_2. We show that for the pioneer species investigated at the Amazon field site, large leaf emissions of highly reactive monoterpenes (e.g., 25 nmol trans-β-ocimene $m^{-2} s^{-1}$, up to 88% of total monoterpene emissions) can account for a significant fraction of leaf photosynthesis (1.9%).

In addition, light-dependent emissions of cis-β-ocimene were found as a common feature among the abundant climax tree species investigated at the site. As positive correlations between monoterpene emissions and photosynthesis were detected across all tree species investigated, our results suggest that like isoprene, light-dependent monoterpene emissions from tropical trees are produced via the 1-deoxy-D-xylulose-5-phosphate pathway in chloroplasts [*Lichtenthaler*, 1999]. This suggests that monoterpene emissions can be successfully modeled from regional to global scales using current light-dependent algorithms developed for isoprene [*Guenther et al*., 2006, 2012].

4.3. In Plant Antioxidant Roles in Future Climates

As has been demonstrated for isoprene, the results also suggest a potentially important antioxidant role for highly reactive monoterpenes during photosynthesis [*Vickers et al*., 2009; *Jardine et al*., 2010a, 2012, 2013; *Velikova et al*., 2012]. As highly reactive monoterpenes have reactivities with oxidants many orders of magnitude higher than those of isoprene, a selective advantage under abiotic stress can be hypothesized —Amazon tree species that are capable of producing highly reactive monoterpenes may have an advantage in future surface warming scenarios as well as in the high light and temperature environments of degraded secondary rainforests as a result of increasing natural and human disturbances, potentially fueling increased monoterpene emissions to the atmosphere [*Kanakidou et al*., 2005]. For example, *C. sciadophylla*, is a fast-growing pioneer genus specializing in exposed open secondary habitats with high solar radiation [*Mesquita et al*., 2001; *Bentos et al*., 2008] abundant across the Amazon Basin [*Ter Steege et al*., 2013]. In this study with *C. sciadophylla*, nearly 88% of the total light-dependent monoterpenes emitted at maximum PAR were as the highly reactive cis- and trans-β-ocimene.

5. Conclusions

In this study, we confirm the light dependence of leaf monoterpene emissions from tropical trees and show that their ambient air mixing ratios within a primary rainforest canopy reflect the vertical distribution of leaf area. However, the 11 ambient profiles represent a small data set and are only representative of afternoon conditions at one site in the Amazon Basin. Moreover, the leaf emissions from seven tree species represent only a very limited selection of more than 500 tree species previously identified at the field site. Nonetheless, to our knowledge this study represents the first ambient observations of the highly reactive monoterpenes cis- and trans-β-ocimene with high abundance (160 ppt) and observations of large light-dependent emissions from tropical vegetation (32.3 nmol m^{-2} s^{-1}). Undetected highly reactive monoterpene species have precluded a quantitative understanding of monoterpene roles in photochemical processes [*Martin et al.*, 2010] and biological functions [*Gershenzon and Dudareva*, 2007]. Thus, a better understanding of monoterpene impacts on aerosol and cloud life cycles and terrestrial gross primary production may require an explicit treatment of speciated monoterpene biochemistry, emissions, and atmospheric oxidation in Earth system models.

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Erratum

In the originally published version of this article, the last line of the first paragraph of section 4.1 contained an incorrect number: “(25-60 min)” should have read “(25-120 min)”. This number has since been corrected, and this version may be considered the authoritative version of record.