Response to Reviewers for “Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet and dry seasons”

The authors thank both referees for their helpful comments towards improving this manuscript. All referee comments are addressed below. Author comments are formatted in blue text. Page numbers and line numbers are according to the ACPD published manuscript.

Response to Anonymous Referee #1 Comments:

Technical Comments

1. In section 2.2, what was done to ensure that the denuder efficiency was 100%? Or was this efficiency calculated in previous publications? If so, please provide the number and appropriate citation - and if appropriate, discuss how this efficiency was taken into account during quantification.

   We have added after the discussion pg. 4, line 36:
   As described in Isaacmann-VanWertz et al., (2016), regular checks of denuder efficiency were done by inserting a filter upstream of the denuder to remove particles, and sampling the normal volume of air through this “blank” system so the measured signal would indicate any breakthrough. Any remaining mass signal was subtracted from the sample mass signal as part of data correction before quantification. Previous laboratory testing of the denuder efficiency was also performed by sending gas standards (e.g. the sesquiterpene longifolene) through the denuder and measuring the sesquiterpene signal upstream and downstream using proton-transfer-reaction-mass-spectrometry. This led to a calculated penetration value on average of <5% for a single denuder and a predicted penetration of <0.5% for the two denuders used in series on SVTAG.

2. In section 2.2.1, please define the match statistic. It is clear that a maximum value is 999, but it is not clear how the values are obtained.

   The “match statistic” is the same as the “match factor” calculated within the NIST/EPA/NIH Mass Spectral Library program in accordance to the methods described in (Stein, 1994). To be more precise and consistent, we have changed the term to “match factor” throughout the manuscript and an additional sentence has been added in section 2.2.1, “A match factor is calculated from a comparison function outlined in Stein et al., 1994 as a measure of the overall probability that an obtained spectral match is correct. Spectral matches are considered …”

3. In some cases, abbreviations/acronyms/chemical symbols are defined prior to use. In others, they are not. In some cases, they are not used consistently. Please make this consistent.

   This has now been addressed. Thank you for noticing this.

4. In section 2.2.3, Tables S4 and S5 are cited – but Tables S1-S3 have not been called out yet. This is simply a matter of reordering the tables in the SI.

   Thank you for catching this. The tables have been properly reordered in the SI to match the order of reference in the main text.

5. On page 7, line 14. Can the authors explain why dry season filter samples are not included here? It seems odd that wet and dry season SVTAG output is included, but only wet season filter samples are. Do these samples not exist? It would strengthen the paper greatly if both season's filter results were included, allowing comparison of seasons and discussion of 'representativeness.'

   As only selected wet and dry season filter samples have been analyzed thus far (complete set will be analyzed for an upcoming publication), we merely meant to show a representative sample that would be rich in a variety of sesquiterpene oxidation products. A similarly targeted filter sample from the dry season was also analyzed and similar to the sample presented for the wet season. We do understand the question raised, so we have adjusted the text further to explain this accordingly:

   Filter samples collected during IOP2 (dry season) are not presented in this analysis as the wet season filters were more ideal for targeted isolation and detection of sesquiterpene oxidation products. Similarly targeted samples from the dry season had similar chemical composition in terms of terpene oxidation as that presented in Section 3.3 for the wet season so this presentation is not repeated, though there are certainly contributions from additional OA sources (e.g. biomass burning compounds are more prominent in dry than wet season) as well. A more complete analysis of all samples from both seasons will be presented in separate forthcoming publication. The goal in the current analysis is to simply demonstrate the number and chemical complexity of the observed sesquiterpene-derived compounds and the potential for their significance in contributing to overall OA mass.

6. On page 10, line 8, the statement 'or obtained from the literature where available' seems to contradict the previous statement about lack of availability of rate constant data. I could simply be misunderstanding, but please clarify?

   The authors acknowledge that the text is confusing here and have deleted the phrase, "or obtained from the literature where available."

7. On page 10, line 17, where transport to the site is discussed as the reason for lack of observation of more quickly reacting sesquiterpenes, please discuss what the typical transport time to the site from the canopy is.

   We have included the following sentence, "Based on average wind speed (2 m s-1), transport time from the nearest surrounding trees (1 km) to the measurement site is on the order of at least 8 minutes, longer than the chemical lifetime of some of the more highly reactive sesquiterpenes."

8. On Figure 5, what is the maximum to which the concentrations are normalized? The aldehyde product? The acid product? Both have values that are 1 around sundown.

   Each of these series is normalized to its own average maximum concentration observed. This makes every series have 1 as the relative maximum concentration as plotted in Figure 5. To be more clear, we have added text in the caption of Figure 5 to describe this, "For each series, data are normalized by the maximum observed concentration within the series and shown as concentration relative to max."

9. In the SI, is Figure S3 called out/cited anywhere?

   We have added reference to this figure at the end of Section 2.2 describing deployment of SV-TAG to explain how continuous time series of total sesquiterpenes were generated. As each sesquiterpene typically made up a small fraction of total ion signal in derivatized runs, we utilized the less frequent (~ every 13 hrs) runs without derivatization to speciate all sesquiterpenes and obtain total sesquiterpene concentration.

   "To generate continuous time series of total sesquiterpenes concentration as presented in section 3.2.1, we assumed that the longer-lived and regularly detected α-copaene comprised 6% of total sesquiterpenes concentration at all times, since this was the average % composition during runs without derivatization (Figure S3)."

Editorial Corrections/Recommendations (other very minor typos should be found when proofs are reviewed)

1. In several places throughout the manuscript, the authors need to format citations that appear in the main text (as opposed to in the parentheses). For example, page 3, line 20, 'Khan et al., 2017' should be 'Khan et al. (2017)'.

   Thank you for catching this, we have adjusted all references accordingly.

2. On page 8, lines 34+, numbers in chemical formulae should be subscripted.

   These changes have been addressed.

3. I would recommend replacing '%' with 'percentage' in several places where it appears as part of the text – for example, page 13, line 39. This is simply preference.

   These changes have been addressed.

4. Caption to Table S3 in SI. There appears to be an extra 'in' Caption to Figure S1 in SI. There appears to be an 'in' at the end that is not necessary.

The unnecessary “in” has been deleted. Thank you for catching this.

Response to Anonymous Referee #2 Comments:

General comments:

1. The calibration procedure has to be described and presented in greater detail. Please include further details on how the calibrations were performed, how often and with what technical characteristics (e.g. detection limits, precision, accuracy).

   We have adjusted Section 2.2.2 Compound quantification as follows:

   a) We have started the section now with, "In-field calibrations on SV-TAG were performed using an auto liquid injection system (Isaacman et al., 2011) to deliver customized standard solutions. A calibration point was obtained every 6-7 hrs, rendering a complete six-point calibration curve within 48 hrs."

   b) We have added pg. 5, line 38 after "…relative response factors to β-caryophyllene," the following sentence, "A range of instrument responses to sesquiterpene standards was observed. For example, on-column lower detection limits were 0.14, 0.01, 0.05, and 0.08 ng with precision of 14%, 21%, 9.5%, and 13% and accuracy of 12%, 7.4%, 25%, and 17%, for β-caryophyllene, longifolene, alloaromadendrene, and α-copaene, respectively."

   c) We have added after the sentence pg. 6, line 2, "Calculated on-column lower detection limit is 0.07 ng with typical precision on the order of 14% and accuracy errors within 30%. Additional details of error analysis for SV-TAG data are detailed in Isaacman et al., (2014)."

2. There has to be a section over which the observations are thoroughly presented. The results section starts with a subchapter named "Chemical characterization of observed sesquiterpenes" but there is mainly technical descriptions and not presentation of the observations. In addition, only selected time frames are presented in both manuscript and supplement. I would encourage the authors to include a complete timeline of their measurements and certainly move the largest part of this section (3.1) in the methods.

   We have now moved the majority of the text from this section to Section 2.2.1 Compound Identification per recommendation and have adjusted Section 3.1 to more thoroughly describe the observations and include a full timeline of the speciated sesquiterpene and diterpene measurements as follows:

   3.1 Chemical characterization of observed sesquiterpenes

   Thirty sesquiterpene species were observed regularly in the gas phase in SV-TAG chromatograms during the GoAmazon campaign at T3 (Figure 1). Compound names for those compounds positively identified via MS matching and retention index are labelled accordingly in chromatograms and listed with mean concentrations observed during the wet and dry seasons in Table 1. Most sesquiterpene species were observed at mean levels above 100 ppq$_v$, ranging 1-529 ppq$_v$ in the wet season and 1-670 ppq$_v$ in the dry season. While mean observed concentrations differed for some species observed in the wet and dry season, overall summed mean concentrations of sesquiterpenes was similar in both seasons (~4-5 ppq$_v$).

   Complete timelines of speciated sesquiterpens are presented in Figure 2 wet season and Figure 3 dry season. In panel a), six species are presented with hourly time-resolution under regularly derivatized run conditions. In panel b), occasional runs without derivatization allow for complete speciation of sesquiterpene/diterpene species and to calculate summed concentration of sesquiterpenes and diterpenes as overlaid in panel a). For both seasons, sesquiterpenes exhibit highest concentrations overnight. Note also that a more dynamic range of summed sesquiterpene concentrations were observed during the wet season (spanning across 15 ppt$_v$), whereas in the dry season the range is closer to 8 ppt$_v$. Further, the wet season exhibits the greater chemodiversity of observed sesquiterpenes and terpenes compared to the dry season.

New figures:

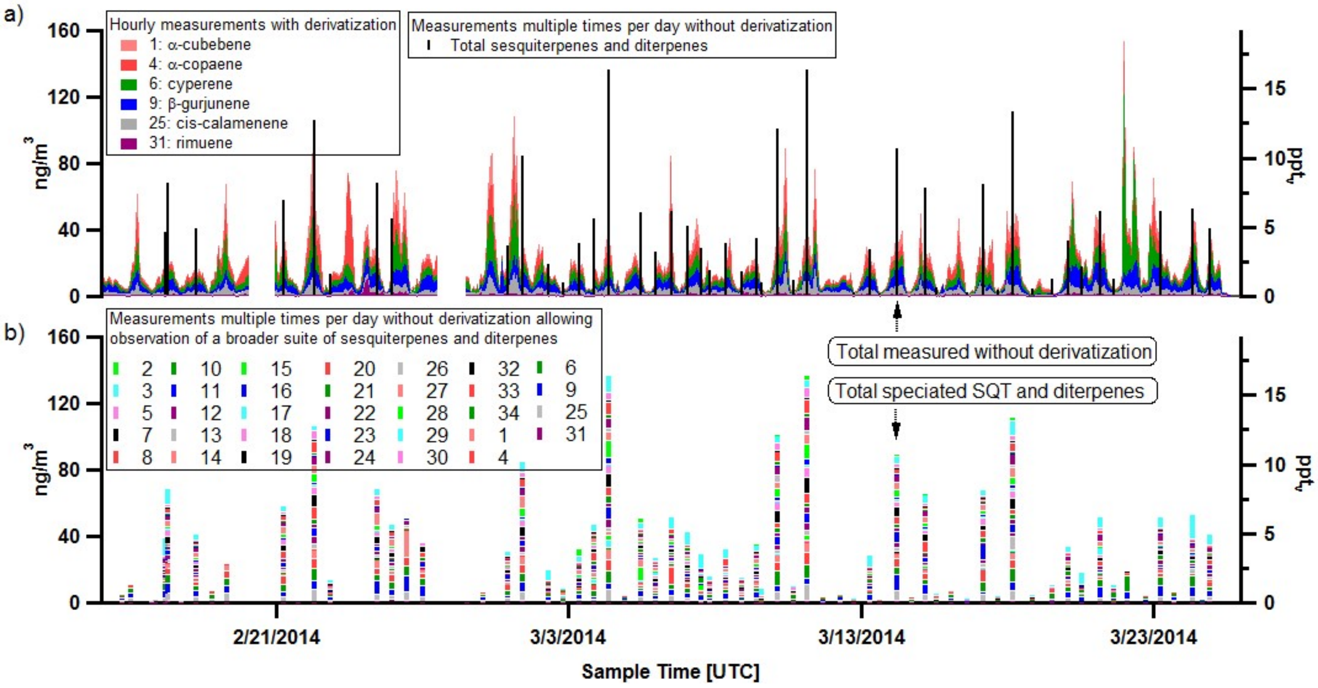

Figure 2: Wet season timeline of sesquiterpene (SQT) and diterpene species for those measured with hourly time resolution with derivatization (shaded colors) a) and those measured multiple times per day at lower time-resolution without derivatization b). Legend entries correspond to compound numbers in Table 1. Total SQT and diterpenes quantified during runs without derivatization are overlaid in black for reference in panel a). Concurrent speciation shown in b).

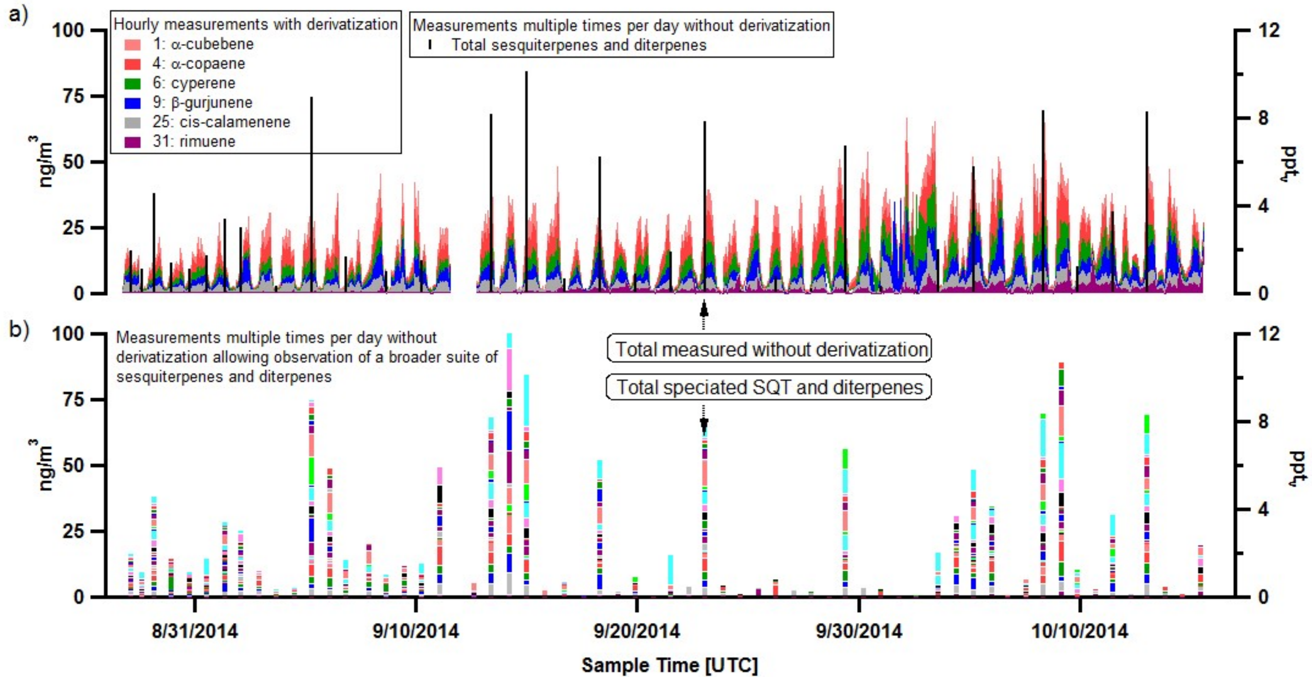

Figure 3: Dry season timeline of sesquiterpene (SQT) and diterpene species for those measured with hourly time resolution with derivatization (shaded colors) a) and those measured multiple times per day at lower time-resolution without derivatization b). Legend entries correspond to compound numbers in Table 1 and colors in b) same as that used in Figure 1. b). Total SQT and diterpenes quantified during runs without derivatization are overlaid in black for reference in panel a). Concurrent speciation shown in b).

3. While the uncertainties on the reaction rate constants are discussed for sesquiterpenes, the same rate constant as a-pinene has been applied for monoterpenes. Yanez-Serrano et al. (2018) demonstrated a similar chemodiversity of monoterpenes for both wet and dry season inside the Amazon rainforest. Therefore, the uncertainties of monoterpene reactivity (and hence the relative contribution to isoprene and sesquiterpenes) can be minimized. I recommend re-calculation of the O3 reactivity based on the monoterpene speciation from the literature with the respective reaction rates and relative abundance.

The authors appreciate that the referee has brought up this point for discussion. The analysis recommended by the referee was considered in original preparation of the manuscript, but was then simplified to the current version for several reasons which we expand on here. First of all, while the ideal constraint on monoterpenes contribution to O$_3$ reactivity at the measurement site is to have speciated measurements of monoterpenes at T3, these data unfortunately do not exist. To simply assume that the chemodiversity of monoterpenes observed within-canopy presented in Yanez-Serrano et al., (2018) and Jardine et al., (2015) applies to T3 would also introduce uncertainty to this analysis and may even be more erroneous than using the selected rate constant for α-pinene for the following reasons:

a) Mean concentration of total monoterpenes measured within-canopy at several sites around the region are 0.82 ± 0.34 ppbv day 24m height, 0.45 ± 0.13 ppbv night 24 m height for the dry season (Yáñez-Serrano et al., 2018), 0.67 ± 0.3 ppbv for the wet season and 0.47 ± 0.2

ppbv for the dry season (Alves et al., 2016), and 1.3 ppbv averaged for a period spanning the dry-to-wet transition, wet, and wet-to dry transition seasons (Jardine et al., 2015). At T3, mean concentrations of monoterpenes were 0.15 ± 0.09 ppbv for the wet season and 0.21 ± 0.12 ppbv for the dry season. The comparison of monoterpene concentrations within canopy presented in these literature and that at T3 suggests that there has been significant losses (reactive, deposition, etc.) within the canopy and during transport outside of the canopy.

b) Since the kO3 rate constants for the observed monoterpenes near the source of emission span over two orders of magnitude, this also means that the monoterpene composition at T3 will be dissimilar to that within the canopy. If the within-canopy monoterpene speciation were assumed to be the same at T3 as in the literature, then certainly O3 reactive loss due to reaction with monoterpenes would be more evenly spread across more reactive species (e.g. d-limonene, α-terpinene, cis-β-ocimene) rather than α-pinene, which would make up < 10%, but we know this to be an incorrect approach because of a) above and c) below.

c) If one were to "react" the within canopy-level monoterpenes speciated in Yáñez-Serrano et al., (2018) with even 30 ppbv O3 levels (representative of daytime O3 concentrations during dry season at T3) to achieve the monoterpenes concentrations measured at T3, this would be equivalent to 8 hours of reaction time, which is much longer than the expected transport time (~8 mins) from the nearest surrounding trees (~2.5 km, ~5 m/s wind speeds). For reference, the measurement site, T0a/ATTO, of Yáñez-Serrano et al., (2018) is ~225 km northeast of T3, which would be approximately 12.5 hrs transport time. This mismatch in transport timescales and summed monoterpene concentrations supports that the chemodiversity and concentrations of monoterpenes must vary dramatically in space and time. At T3, the less chemically reactive species will remain. In fact, to render the observed monoterpenes concentration at T3 via reaction with O3 starting with canopy-level monoterpenes speciation, the O3 reactivity associated with monoterpenes left at T3 would be dominated by α-pinene (81%), β-pinene (10%), and d-limonene (5%). No other reported monoterpene species would make up > 1% of the O3 reactivity from monoterpenes. The selection of using the reaction rate constant from α-pinene vs. an assumed monoterpene chemical composition as stated previously would render an "overestimate" of O3 reactive loss due to monoterpenes by a factor of 2.8. Using an average kO3 for the monoterpenes observed at T0a/ATTO by Yáñez-Serrano et al., (2018) would render an even greater overestimate by a factor of 100. An analogous analysis using the monoterpene speciation at T0k measurement site in Jardine et al., (2015), approximately 100 km northeast of T3 with 20 ppbv O3 levels (representative of daytime O3 concentrations during wet season at T3) requires 6 hours of reaction time to achieve T3 monoterpene levels. While O3 reactivity at T3 would be largely attributed to α-pinene (43%), d-limonene (30%), sabinene (18%), and β-pinene (6%), using the α-pinene rate constant only results in an overestimate of monoterpene reactivity by a factor of 1.3. Using an average kO3 for the monoterpene speciation at T0k results in an "overestimate" by a factor of 7.7. Thus, the selection of using α-pinene rate constant is not unreasonable given that much greater error could be introduced assuming that T3 monoterpene speciation is the same as that within the canopy.

In light of the above considerations, we have adjusted the text pg. 10, lines 14-16 to the following:

“Further, the estimate for monoterpene contribution to O3 reactivity assumes that all monoterpenes here have the same rate constant as α-pinene, as monoterpene measurements were not speciated here and it is one of the more dominant (17% and 45% by mass) and longer-lived monoterpenes as observed in upwind forested sites by Jardine et al., (2015) and Yáñez-Serrano et al., (2018). As observed concentrations of monoterpenes within canopy are a factor of 3-4 higher than those observed at T3, it is reasonable to expect that O3 loss due to reaction with monoterpenes at this measurement site will become increasingly dominated by reaction with α-pinene.”

General technical comments:

1. Please ensure that the supplementary material is appropriately cited in the main text.

   The cross-references to supplementary material have been revised and appropriately cited.

2. Please ensure that your references conform to the ACP style.

   The references have been revised to conform to the ACP style.

Specific comments:

1. P3L25-28. No need to repeat the measurement challenges as they were already mentioned above.

   The measurement challenges here refer to those associated with measurement of tracers of oxidation of terpenes, some of which also apply to the measurement of the terpenes themselves mentioned above. We prefer to keep this text here to keep the distinction.

2. P4L5. You may keep the definition of IOP but it would be better if you refer to your periods as wet and dry season thereafter.

   We have adjusted singular references to IOP1 and IOP2 and replaced them with wet and dry seasons, respectively.

3. P4L17. There is no need for this last sentence.

   This sentence has been deleted.

4. P8L31. Please rename as “Results and discussion”. As mentioned above, I would recommend to include a section over which the observations are described.

   The section has been renamed as suggested and we have included a section for describing the observations according to General Comment 2 above.

5. P8L36. This class of compounds is referred as sesquiterpenoids in Chan et al. (2016).

   We have revised this class to be referred to as "sesquiterpenoids", and these lines have been moved to Section 2.2.1 Compound Identification.

6. P9L24. Please site the "previous literature". P9L34-36. Did you observe such case? Is there a possibility of presenting a case study?

   We refer to the analysis in which we compare with the sesquiterpene concentrations observed by Alves et al. (2016) to those that we have measured. We have changed "previous literature" to cite Alves et al. (2016) specifically.

7. P10L10-14 and L30. It would be interesting if an upper end of sesquiterpene estimated O3 reactivity is presented as well.

   While we agree that this would be interesting, we found original analyses in this regard to be highly speculative to include in this manuscript. For the referee's interest, when we considered an estimate of β-caryophyllene that may have reacted by scaling the observed α-copaene concentration by the ratio of β-caryophyllene: α-copaene in copaiba essential oil (Table S3, Young Living Essential Oil, origin Brazil), we calculated that sesquiterpene reactivity would be higher by a factor of ~4 and would then contribute approximately equally to if not the majority of the reactive O_3 loss. Reaction of O_3 with isoprene would account for 31%, 33%, monoterpenes for 30%, 31%, and sesquiterpenes for 39%, 36% during the wet, dry seasons respectively. Still, as the referee points out

8. P10L14-16. Please see my general comment.

   This has been addressed in General Comment 4 above.

9. P11L21-22. Nonetheless, this is your practice for monoterpenes. Please discuss a quantitative

   This comment was cut off in the submitted text from the reviewer so we could not read it or address it.

10. Figure 6. The filter tracers are not visible. Maybe the use of log scale would help?

    Thank you for the suggestion, though unfortunately log scale does not help significantly.

References:

Yáñez-Serrano, A. M., Nölscher, A. C., Bourtsoukidis, E., Gomes Alves, E., Ganzeveld, L., Bonn, B., Wolff, S., Sa, M., Yamasoe, M., Williams, J., Andreae, M. O., and Kesselmeier, J.: Monoterpene chemical speciation in a tropical rainforest:variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO), Atmos. Chem. Phys., 18, 3403-3418, https://doi.org/10.5194/acp-18-3403-2018, 2018.

Additional changes by authors:

Improvements in calibration for beta-nocaryophyllonic acid using an authentic standard for UHPLC-MS analyses have occurred and data and analyses are updated accordingly in the revised manuscript.

References in authors' response:

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

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Isaacman, G. A., Kreisberg, N. M., Worton, D. R., Hering, S. V and Goldstein, A. H.: A versatile and reproducible automatic injection system for liquid standard introduction: Application to in-situ calibration, Atmos. Meas. Tech., 4(9), 1937–1942, doi:10.5194/amt-4-1937-2011, 2011.

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.

Stein, S. E.: Estimating probabilities of correct identification from results of mass spectral library searches, J. Am. Soc. Mass Spectrom., 5(4), 316–323, doi:10.1016/1044-0305(94)85022-4, 1994.

Yáñez-Serrano, A. M., Nölscher, C., Bourtsoukidis, E., Gomes Alves, E., Ganzeveld, L., Bonn, B., Wolff, S., Sa, M., Yamasoe, M., Williams, J., Andreae, M. O. and Kesselmeier, J.: Monoterpene chemical speciation in a tropical rainforest: variation with season, height, and time of day at the Amazon Tall Tower Observatory (ATTO), Atmos. Chem. Phys, 185194, 3403–3418, doi:10.5194/acp-18-3403-2018, 2018.

Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet and dry seasons

Lindsay D. Yee[1], Gabriel Isaacman-VanWertz[1*], Rebecca A. Wernis[2], Meng Meng[3**], Ventura Rivera[3], Nathan M. Kreisberg[4], Susanne V. Hering[4], Mads S. Bering[5], Marianne Glasius[5], Mary Alice Upshur[6], Ariana Gray Bé[6], Regan J. Thomson[6], Franz M. Geiger[6], John H. Offenberg[7], Michael Lewandowski[7], Ivan Kourtchev[8], Markus Kalberer[8], Suzane de Sá[9], Scot T. Martin[9,10], M. Lizabeth Alexander[11], Brett B. Palm[12], Weiwei Hu[12], Pedro Campuzano-Jost[12], Douglas A. Day[12], Jose L. Jimenez[12], Yingjun Liu[9***], Karena A. McKinney[9****], Paulo Artaxo[13], Juarez Viegas[14], Antonio Manzi[14], Maria B. Oliveira[15], Rodrigo de Souza[15], Luiz A. T. Machado[16], Karla Longo[17], and Allen H. Goldstein[1]

[1]Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley, 94720, USA
*Now at Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, 24061, USA
[2]Department of Civil and Environmental Engineering, University of California, Berkeley, Berkeley, 94720, USA
[3]Department of Chemical Engineering, University of California, Berkeley, Berkeley, 94720, USA
**Now at Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, CA
[4]Aerosol Dynamics Inc., Berkeley, 94710, USA
[5]Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark
[6]Department of Chemistry, Northwestern University, Evanston, 60208, USA
[7]National Exposure Research Laboratory, Exposure Methods and Measurements Division, United States Environmental Protection Agency, Research Triangle Park, 27711, USA
[8]Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom
[9]School of Engineering and Applied Sciences, Harvard University, Cambridge, 02138, USA
***Now at Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley,
****Now at Department of Chemistry, Colby College, Waterville, Maine, 04901, USA
[10]Department of Earth and Planetary Sciences, Harvard University, Cambridge, 02138, USA
94720, USA
[11]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, 99352, USA
[12]Dept. of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, 80309, USA
[13]Department of Applied Physics, University of São Paulo, SP, Brazil
[14]Instituto Nacional de Pesquisas da Amazonia, Manaus, AM, Brazil
[15]Universidade do Estado do Amazonas, Manaus, AM, Brazil;
[16]Instituto Nacional de Pesquisas Espiacais, São José dos Campos, SP, Brazil
[17]Instituto Nacional de Pesquisas Espiacais, Cachoeira Paulista, SP, Brazil

Correspondence to: Lindsay D. Yee (lindsay.yee@berkeley.edu)

Abstract. Biogenic volatile organic compounds (BVOCs) from the Amazon forest region represent the largest source of organic carbon emissions to the atmosphere globally. These BVOC emissions dominantly consist of volatile and intermediate volatility terpenoid compounds that undergo chemical transformations in the atmosphere to form oxygenated condensable gases and secondary organic aerosol (SOA). We collected quartz filter samples with 12-hour time resolution and performed hourly in-situ measurements with the Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SV-TAG) at a rural site ("T3") located to the west of the urban center of Manaus, Brazil as part of the Green Ocean Amazon (GoAmazon2014/5) field campaign to measure intermediate volatility and semi-volatile BVOCs and their oxidation products during the wet and dry seasons. We speciated and quantified 30 sesquiterpenes and four diterpenes with concentrations in the range 0.01–6.04 ng m^{-3} (1–670 ppq$_v$). We estimate that sesquiterpenes contribute approximately 14% and 12% to the total reactive loss of O$_3$ via reaction with isoprene or terpenes during the wet and dry seasons, respectively. This is reduced from ~50-70% for within-canopy reactive O$_3$ loss, attributed to ozonolysis of highly reactive sesquiterpenes (e.g. β-caryophyllene) that are reacted away before reaching our measurement site. We further identify a suite of their oxidation products in the gas and particle phases and explore their role in biogenic SOA formation in the Central Amazon region. Synthesized authentic standards were also

used to quantify gas- and particle-phase oxidation products derived from β-caryophyllene. Using tracer-based scaling methods for these products, we roughly estimate that sesquiterpene oxidation contributes at least ~~1-18~~0.4-5% (median ~~5~~1%) of total submicron OA mass. However, this is likely a low-end estimate, as evidence for additional unaccounted sesquiterpenes and their oxidation products clearly exists. By comparing our field data to laboratory-based sesquiterpene oxidation experiments we confirm more than 40 additional observed compounds produced through sesquiterpene oxidation are present in Amazonian SOA, warranting further efforts towards more complete quantification.

1 Introduction

Emission of biogenic volatile organic compounds (BVOCs) from terrestrial vegetation represents a large source of organic carbon to Earth's atmosphere. These emissions comprise a wide array of chemical species, including known terpenoids: isoprene (C_5), monoterpenes (C_{10}), sesquiterpenes (C_{15}), and diterpenes (C_{20}). Isoprene, 2-methyl-1,3-butadiene (C_5H_8), is a hemi-terpene and the most dominant non-methane hydrocarbon emitted to the atmosphere at levels of ~500 TgC/year globally (Guenther et al., 2006, 2012). Global emissions of terpenes are estimated for monoterpenes ($C_{10}H_{16}$) at ~160 TgC/year, sesquiterpenes ($C_{15}H_{24}$) at ~30 Tg/year, and global emission estimates for diterpenes ($C_{20}H_{42}$) have yet to be made (Guenther et al., 2012).

In the atmosphere, such compounds undergo chemical transformations that lead to the formation of biogenic secondary organic aerosol (BSOA) and affect local radical budgets (Kesselmeier et al., 2013; Lelieveld et al., 2008, 2016) and carbon cycling (Bouvier-Brown et al., 2012; Guenther, 2002). Globally, the majority of organic aerosols stem from oxidation of biogenic carbon, yet their role in affecting Earth's radiative balance remains unclear (NAS, 2016). This is largely due to limited observations of the speciated precursors and identification of their oxidation products, which are crucial for understanding their chemical pathways and fate in Earth's atmosphere (Worton et al., 2012).

While laboratory measurements simulating oxidation of BVOCs provide insight into atmospheric chemistry, challenges still exist for making ambient, high time-resolution, speciated measurements of the higher carbon number terpenes and their oxidation. These compounds present measurement challenges due to several reasons. First, their relatively low vapour pressure makes sample collection more challenging due to line losses. Second, they tend to be present at lower ambient concentrations due to lower emission and higher reactivity, therefore requiring very sensitive detection methods and/or lower time-resolution. These measurement challenges have resulted in more research focused on highly volatile and higher concentration BVOCs (i.e. isoprene, monoterpenes), but there is less understanding of sesquiterpenes (Bouvier-Brown et al., 2009a, 2009b; Chan et al., 2016), and almost no data on concentrations or chemical reaction pathways of diterpenes.

Isoprene has a laboratory determined SOA yield of <6% (Dommen et al., 2006; King et al., 2010; Kroll et al., 2005, 2006; Xu et al., 2014) and an estimated 3.3% yield in the ~~SE~~Southeast U.S. (Marais et al., 2016), but nevertheless contributes a major fraction of organic aerosol over forested regions because it is emitted in such high quantities relative to other BVOCs ~~(Carlton et al., 2009; Hu et al., 2015)~~(Carlton et al., 2009; Hu et al., 2015). Though other terpenes are present in the atmosphere at much lower concentrations, they generally react faster with oxidants such as OH, O_3, and NO_3 (Atkinson, 1997), and have higher SOA yields at typical atmospheric OA concentrations, ~5-10% for monoterpenes as reported in ~~Griffin et al., 1999a, 1999b~~Griffin et al., (1999a, 1999b) and ~20-70% for sesquiterpenes as reported in ~~Chen et al., 2012; Griffin et al., 1999b; Hoffmann et al., 1997; Jaoui et al., 2013; Lee et al., 2006a, 2006b.~~Chen et al., (2012); Griffin et al., (1999b); Hoffmann et al., (1997); Jaoui et al., (2013); Lee et al., (2006a, 2006b). SOA yields from diterpenes have not yet been quantified, though they are likely higher than those of sesquiterpenes due to their higher carbon number and lower volatility. While emitted mass generally decreases with decreasing volatility (and increasing carbon number), the concomitant rise in sheer possible number of compounds from C_5 to C_{10} to C_{15} to C_{20} backbones and associated SOA yields and oxidant reactivity indicates that lower-volatility terpenes may have an important impact on regional chemistry and BSOA formation.

Using the BVOC emission model, MEGAN2.1, it is predicted that ~80% of terpenoid emissions come from tropical trees that cover about 20% of the global land surface (Guenther et al., 2012), yet very few observations of sesquiterpenes exist from these regions. Chemical characterization of tropical plant tissue shows the presence of an abundance of sesquiterpenes (Chen et al., 2009a; Courtois et al., 2012) and suggests their widespread emission from such vegetation (Chen et al., 2009a; Courtois et al., 2009). Previous branch enclosure measurements of native Amazon saplings found that sesquiterpene emission was below detection limits (Bracho-Nunez et al., 2013) even though sesquiterpenes have been observed within and outside the canopy of the Central Amazon ~~(Alves et al., 2016; Jardine et al., 2012)~~(Alves et al., 2016; Jardine et al., 2012). Further, ~~Chen et al., 2009a observed higher sesquiterpene emissions from wounded seedlings of the tropical tree, *Copaifera officinalis*, with similar composition and quantity to that in the leaves.~~Chen et al., (2009a) observed higher sesquiterpene emissions from wounded seedlings of the tropical tree, *Copaifera officinalis*, with similar composition and quantity to that in the leaves. However, while ambient concentrations of sesquiterpenes have been measured by field-deployable mass spectrometers such as Proton Transfer Time-of-Flight Mass Spectrometry (Jordan et al., 2009), previous measurements have provided little or no separation of isomers, which can vary substantially (orders of magnitude) in their reactivity and SOA yields, so a significant knowledge gap remains regarding the contribution of these compounds to organic aerosol.

Aerosols play a critical role in cloud formation and the hydrologic cycle of the Brazilian Amazon (Fan et al., 2018; Pöschl et al., 2010; Wang et al., 2016), which is also one of the major source regions of global BVOCs. Previous studies have found the aerosols over this region (Martin et al., 2010) to be primarily composed of organic material (Artaxo et al., 2013) derived from BVOCs (Chen et al., 2009b, 2015). While isoprene oxidation has been estimated to contribute ~50% of OA in Amazonia (Chen et al., 2015), of which a large portion is attributed to uptake of isoprene-epoxydiols ~~(Hu et al., 2015; de Sá et al., 2017)~~(Hu et al., 2015; de Sá et al., 2017), the remaining contribution to OA from other BVOC precursors such as monoterpenes and sesquiterpenes remains largely unconstrained. ~~Khan et al., 2017 report that including updated sesquiterpene emissions and SOA pathways (all represented by β-caryophyllene mechanism) in the STOCHEM global chemical transport model led to a 48% increase in global SOA burden and 57% increase in SOA production rate.~~Khan et al., (2017) report that including updated sesquiterpene emissions and SOA pathways (all represented by β-caryophyllene mechanism) in the STOCHEM global chemical transport model led to a 48% increase in global SOA burden and 57% increase in SOA production rate. In addition, the highest concentrations of sesquiterpene-derived SOA were modelled to be present over central Africa and South America. However, the general lack of available time-resolved measurements of speciated sesquiterpenes and their oxidation products in either the gas or particle phase has precluded fully constraining their contribution to BSOA formation. For terpenes in general there are even greater measurement challenges associated with observation of tracers of their oxidation: the gas-phase component of these semi-volatile compounds may condense in sample lines or be lost by wet/dry deposition, or quickly react to form compounds sufficiently ubiquitous to be disconnected from a specific precursor. Particle-phase composition is therefore critical for studying the importance of individual terpenes and terpene classes, but dynamic gas-particle partitioning of these semi-volatile products requires the contemporaneous measurement of the difficult-to-measure gas-phase components. Measurements of gas/particle partitioning and concentrations of biogenic OA tracers from isoprene and monoterpene oxidation have been reported previously as part of the Green Ocean Amazon (GoAmazon2014/5) field campaign (Isaacman-VanWertz et al., 2016), but few, if any, sesquiterpene oxidation products were identified in the dataset at that time. To fully characterize the sources of OA in the region, molecular-level and chemically specific signatures of oxidation products from a more complete range of BVOC precursors need to be identified and quantified.

Here we report the first speciated measurement of 30 sesquiterpenes and four diterpenes in the Central Amazon and assess their role in reactive oxidant losses during the wet and dry seasons through in-situ observations with the Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SV-TAG) and off-line measurements of quartz filter collected aerosol samples. We further report measurements of specific oxidation products of the sesquiterpene β-caryophyllene that were synthesized in the laboratory and attribute more than 40 additional species observed on a representative filter sample from the wet season to sesquiterpene oxidation based on comparison to products found in laboratory-based oxidation experiments. Finally, we provide a rough low-end estimate of the contribution of sesquiterpene oxidation to OA in the region.

2 Experimental section

2.1 Green Ocean Amazon (GoAmazon2014/5) field campaign: "T3" site description

Measurements were conducted as part of the Green Ocean Amazon (GoAmazon2014/5) field campaign, for which the scientific objectives and measurement sites are described in an overview paper by ~~Martin et al., 2016.~~Martin et al., (2016). We present observations from the wet and dry seasons of 2014, respectively referred to as Intensive Operating Periods 1 and 2 (IOP1 and IOP2). ~~IOP1~~Wet season measurements were taken 1 February to 31 March 2014 and ~~IOP2~~dry season measurements were taken 15 August to 15 October 2014 at the "T3" Manacapuru rural site, located 70 km downwind of urban Manaus. The T3 site was located on a cleared pasture site (−3.2133°, −60.5987°) and 2 km north of the nearest heavily travelled road which connects Manaus to Manacapuru. The immediate surrounding forest (∼~~2.5~~1 km away) consisted primarily of secondary forest, and prevailing meteorological conditions (northeasterly winds) resulted in regional transport of clean air from the primary forest north and east of the site mixed with the outflow of Manaus pollution from the east.

Several instruments for investigating gas and particle phase chemistry were housed at T3 alongside the instrument suite of the United States Department of Energy Atmospheric Radiation Measurement (ARM) Climate Research Facility. ARM Trailers consisted of the Atmospheric Radiation Measurement Facility One (AMF-1) and Mobile Aerosol Observing System (MAOS) (Mather and Voyles, 2013). Here we focus on measurements conducted using a Semi-Volatile Thermal desorption Aerosol Gas Chromatograph (SV-TAG) and quartz filters collected using a custom-designed sequential filter sampler.~~ Additional details of these and supporting measurements follow.~~

~~2.2 Deployment of a Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SV-TAG)~~

~~We deployed a Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SV-TAG) housed in one of the instrument trailers at T3. Details of the instrument development and operation have been published previously (Isaacman-VanWertz et al., 2016; Isaacman et al., 2014; Kreisberg et al., 2009; Williams et al., 2006; Zhao et al., 2013) and we describe SV-TAG deployment in brief here. During the campaign, ambient air was pulled through a 15.24 cm I.D. duct at ~5 m above ground level. Flow through the ducting was maintained at laminar flow conditions with minimal residence time to minimize loss of semi-volatile species from the center-line of flow. Air was then sub-sampled from the center of the sampling duct at 20 lpm for 22 min through a cyclone (PM_1 cutpoint) to SV-TAG's dual collection cells held at 32 °C. Concentrations and gas-particle partitioning were measured through a combination of particle-only measurements, in which gas-phase components were removed through a multi-channel carbon monolith denuder (500 channels, 30 mm OD x 40.6 cm; MAST Carbon) upstream of one collection cell, and total gas-plus-particle measurements, with no removal of the gas-phase component. One collection cell always sampled total gas-plus-particle concentrations, while the other cell alternated between particle-only samples and total gas-plus-particle samples, which were used to remove any bias between collection cells. Particle fraction, F_p, is calculated comparing the particle-only signal from the denuded channel to the gas and particle signal from the other cell. Measurements of F_p for many tracers of biogenic origin from this campaign were presented previously in Isaacman-VanWertz et al., 2016 and an intercomparison of SV-TAG and other instrumentation for measuring F_p is described in Thompson et al., 2017. We found here that sesquiterpenes and their oxidation products detected by SV-TAG were completely in the gas phase (F_p was zero, as discussed in Sections ~~

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), so we do not present time-dependent F_p measurements for these compounds. As described in Isaacmann-VanWertz et al., (2016), regular checks of denuder efficiency were done by inserting a filter upstream of the denuder to remove particles, and sampling the normal volume of air through this “blank” system so the measured signal would indicate any breakthrough. Any remaining mass signal was subtracted from the sample mass signal as part of data correction before quantification. Previous laboratory testing of the denuder efficiency was also performed by sending gas standards (e.g. the sesquiterpene longifolene) through the denuder and measuring the sesquiterpene signal upstream and downstream using proton-transfer-reaction-mass-spectrometry. This led to a calculated penetration value on average of <5% for a single denuder and a predicted penetration of <0.5% for the two denuders used in series on SV-TAG.

After sample collection, material was thermally desorbed from the collection cells into helium (He) at a rate of 35° C min^{-1} up to 320 ° C, taking approximately 8 mins. The helium was saturated with a derivatization agent N-methyl-N-(trimethylsilyl) trifluoroacetamide (“MSTFA”), which converts polar –OH moieties to $–OSi(CH_3)_3$ (trimethylsilyl ester) groups for separation on a gas chromatography column (Isaacman et al., 2014). Desorbed material was focused onto a pre-concentrator held at 30 °C, and then transferred onto a gas chromatography column (Restek, Rtx-5Sil MS, 20 m × 0.18 mm × 0.18 µm) via a valveless injector (Kreisberg et al., 2014). Analysis was performed using an Agilent 7890A/5975 Gas Chromatograph (GC) coupled to a quadrupole mass spectrometer (MS). The GC program consisted of He flow at 1 sccm and a ramp from 50 °C to 330 °C (ramp rate 23.6 °C min^{-1}), then holding at 330 °C for 2.2 min while He flow ramped to 3 sccm. The use of online-derivatization greatly extends the use of SV-TAG for analysis of highly oxygenated species typical of BVOC oxidation, but it also renders more complex chromatograms. For many of the observed sesquiterpenes, their individual contributions to the total ion signal within a chromatogram were low. Thus, analysis was occasionally performed (~every 13 hrs) without derivatization to allow for clearer identification and quantification of all detected sesquiterpene species. To generate continuous time series of total sesquiterpenes concentration as presented in section 3.2.1 Sesquiterpene contribution to total O_3 reactivity, we assumed that the longer-lived and regularly detected α-copaene comprised 6% of total sesquiterpenes concentration at all times, since this was the average % composition during runs without derivatization (Figure S1).

2.2.1 Compound identification

A typical sample total ion chromatogram (TIC) contains hundreds to thousands of compounds. For peak deconvolution, compound peaks are separated and quantified using a characteristic (“selected”) ion fragment. Chemical identification is aided by comparing the peak’s background-subtracted mass spectrum and *n*-alkane based retention index to those of authentic standards run on SV-TAG or presented in the literature and available mass spectral libraries. The 2014 NIST/EPA/NIH Mass Spectral Library (Stein et al., 2014), the Adams essential oil library (Adams, 2007), and a proprietary library from a flavour and fragrance company (MANE) were used for mass spectral matching. A match factor is calculated from a comparison function outlined in Stein et al., 1994 as a measure of the overall probability that an obtained spectral match is correct. Spectral matches are considered perfect if the match ~~statistic~~factor (Stein, 1994) is 999, excellent if >900, good if 800–900, and fair if 700–800. Further, additional work using electron impact (EI) mass spectral matching to identify components of a complex OA sample found that the probability of incorrect identification was low (30% and 14%) for match ~~statistics~~factors between 800–900 and >900, respectively (Worton et al., 2017). Here we present proposed identities if the spectral match factor is >800 and the retention index is reasonable with the proposed identity. Retention index (RI) is helpful for determining elution order of compounds and narrowing the possible compound identities for species such as the sesquiterpenes with similar mass spectra. We calculate *n*-alkane based retention index for compound *i*, using Eq. (1) below

$$\boldsymbol{RI = 100 \times \left[n + \frac{t_i - t_n}{t_{n+1} - t_i}\right]} \qquad \textbf{(1)}$$

where *n* is the number of carbon atoms of the *n*-alkane that elutes before species *i*, and *t* represents retention time.

Sesquiterpenes with chemical formula $C_{15}H_{24}$ were mostly resolved within single ion chromatograms (Figure 1) by a characteristic ion, *m/z* 161, $C_{12}H_{17}^{+}$, typically coincident with the molecular ion, *m/z* 204. In addition, a few sesquiterpenoids with chemical formula $C_{15}H_{22}$ were resolved at their molecular ion (*m/z* 202), as well as a few diterpenes with chemical formula $C_{20}H_{32}$, resolved using characteristic ion, *m/z* 257. In some cases, peak signal was too low to provide good mass spectra (MS) matching, so retention index information was also used to propose identities.

While many sesquiterpenes observed in ambient chromatograms are not available as authentic standards, sesquiterpene-rich essential oils from Amazonian trees were injected on SV-TAG for chromatographic separation and to aid in identification. These included Copaiba essential oil and Andiroba essential oil obtained from a local pharmacy in Manacapuru, Brazil, and additional bottles of Copaiba essential oil from Young Living Essential Oils, Lehi, UT, and through personal communication (origin, Bolivia). Copaiba essential oil originates from trees of the genus *Copaifera*, comprising over 70 species (Plowden, 2003), several of which are distributed throughout the greater Amazon region (SpeciesLink, 2018) While copaiba trees are commonly referred to as the "diesel" or "kerosene" tree due to the oil's limited use as a biofuel, the essential oil is extracted primarily for medicinal purposes. Andiroba essential oil is derived from *Carapa guianensis*, also widely used for medicinal purposes.

While the exact composition, grade, and quality of the essential oils depends on multiple factors (e.g. ~~While many sesquiterpenes observed in ambient chromatograms are not available as authentic standards, sesquiterpene-rich essential oils from Amazonian trees were injected on SV-TAG for chromatographic separation and to aid in identification. These included Copaiba essential oil and Andiroba essential oil obtained from a local pharmacy in Manacapuru, Brazil, and additional bottles of Copaiba essential oil from Young Living Essential Oils, Lehi, UT, and through personal communication (origin, Bolivia).~~

extraction method, species, origin), we hypothesized that the essential oils may serve as a proxy for emissions of terpenes within the canopy and that the ambient sesquiterpene composition might reflect similar composition to the essential oils. Studies have previously observed the chemical similarity between that of terpene emissions and within plant content (Ormeno et al., 2010), and specifically so for *Copaifera officinalis* (Chen et al., 2009a). Most of the sesquiterpenes observed in ambient samples (13 Feb 2014 06:47 UTC (02:47 LT)) coincide with those observed in copaiba essential oil (Figure 1, black and red traces respectively). This similarity between the ambient sesquiterpenes composition and essential oil composition also allowed for positive identification of some of the peaks in the ambient chromatogram. Sesquiterpene standards that were commonly available and brought to the field as standards included (+)-longifolene, β-caryophyllene, and alloaromadendrene with their chromatographic retention times indicated in Figure 1. Further, the essential oils injected on SV-TAG have relatively similar sesquiterpene composition (Table S3) and are comparable to previously analysed essential oils/tissue from Amazonian trees (Table S4).

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2.2.2 Compound quantification

In-field calibrations on SV-TAG were performed using an auto liquid injection system (Isaacman et al., 2011) to deliver customized standard solutions. A calibration point was obtained every 6-7 hrs, rendering a complete six-point calibration curve within 48 hrs. Within a selected ion chromatogram (SIC), peak signal is integrated at the quantification ion and calibrated based on the best available authentic standard. Peak-integrated ion signal of both the analyte and the standard is normalized by the integrated ion signal of an isotopically-labelled internal standard in each sample to account for differences in recovery by compound functionality in SV-TAG as well as changing MS detector response over time. For the sesquiterpenes, n-tetradecane d_{30} (CAS # 204244-81-5) was selected as the internal standard to normalize by. Reported oxidation products are normalized using 2-C^{13}-pentaerythritol. Compounds were quantified using authentic standards whenever possible, though analytical grade standards for many of the observed sesquiterpenes are not commercially available and/or were not present in the custom standard solution that was used for in-field calibrations. Longifolene, β-caryophyllene, and alloaromadendrene were the only sesquiterpenes present in the calibration solution during deployment, and only β-caryophyllene and alloaromadendrene were occasionally detected in ambient air. Post-deployment calibrations were performed in the laboratory with newly acquired sesquiterpene ~~and sesquiterpene-derived oxidation product~~ standards using relative response factors to β-caryophyllene. A range of instrument responses to sesquiterpene standards was observed. For example, on-column lower detection limits were 0.14, 0.01, 0.05, and 0.08 ng with precision of 14%, 21%, 9.5%, and 13% and accuracy of 12%, 7.4%, 25%, and 17%, for β-caryophyllene, longifolene, alloaromadendrene, and α-copaene, respectively. An average response factor for several sesquiterpenes was used to quantify compounds for which authentic standards were not available (Chan et al., 2016). All sesquiterpenes are quantified on $m/z = 161$; average sensitivity of most sesquiterpenes to quantification on this ion is 6.4 ± 6.0 times more sensitive than for β-caryophyllene. Calculated on-column lower detection limit is 0.07 ng with typical precision on the order of 14% and accuracy errors within 30%. Additional details of error analysis for SV-TAG data are detailed in Isaacman et al., (2014).

Standards of several oxidation products from β-caryophyllene ozonolysis were custom-synthesized at Northwestern University. The oxidation products synthesized were β-caryophyllene aldehyde, β-nocaryophyllone aldehyde, β-caryophyllonic acid, β-nocaryophyllonic acid, β-caryophyllinic acid, and β-nocaryophyllinic acid. Synthesis details and procedures are outlined in ~~(Be et al., 2017).~~Bé et al., (2017). Each standard was analysed in the laboratory by SV-TAG and by two-dimensional gas chromatography with high-resolution-time-of-flight mass spectrometry (GC×GC-HR-ToFMS) to obtain MS and retention time information to aid identification of these compounds in SV-TAG chromatograms. Relative response factors of the synthesized standards to pinonic acid, a compound in the regular standard solution for SV-TAG during deployment, were obtained and used for quantification.

2.2.3 Laboratory-generated SOA from sesquiterpenes

Filter samples from laboratory oxidation experiments of several sesquiterpenes were analysed by GC×GC-HR-ToFMS to provide mass spectral information for identification of potential sesquiterpene-derived oxidation products in ambient samples. Mass spectra of resolved peaks from these and previously analysed filters were added to custom MS libraries and are listed in ~~Table S4.~~Table S1. Sesquiterpenes were oxidized in the U.S. EPA National Exposure Research Laboratory reactors ~~(Table S5)~~(Table S2) in the dark via ozonolysis; some were also oxidized under conditions of OH oxidation in the presence of NO_x according to methods described previously ~~(Jaoui et al., 2003, 2004, 2013, 2016; Offenberg et al., 2017)~~(Jaoui et al., 2003, 2004, 2013, 2016; Offenberg et al., 2017). The following sesquiterpene systems were studied: β-caryophyllene, α-cedrene, α-copaene, aromadendrene, β-farnasene, and α-humulene. In addition, a complex mixture rich in sesquiterpenes (copaiba essential oil, Amazon origin) was also oxidized under ozonolysis conditions as a representation of the potential mixture expected in the Amazon atmosphere.

2.3 Supporting measurements

Several supporting measurements were made that allow for interpretation of the chemistry observed. These include gas-phase measurements of BVOCs from a Proton Transfer Time-of-Flight Mass Spectrometer (PTR-ToF-MS, Ionicon Analytik) and particle-phase measurements from an Aerodyne High Resolution Aerosol Mass Spectrometer (HR-ToFAMS), hereinafter referred to as the AMS (DeCarlo et al., 2006). Operation and analysis procedures are outlined elsewhere for the PTR-ToF-MS ~~(Liu et al., 2016)~~(Liu et al., 2016) and for the AMS ~~(de Sá et al., 2017).~~(de Sá et al., 2017). Positive matrix factorization analysis of AMS data was performed to resolve the statistical factor, isoprene epoxydiol-SOA (IEPOX-SOA~~,~~), which is considered to be a tracer for organic aerosol formed through particle uptake of isoprene epoxydiols and has been previously described ~~(de Sá et al., 2017).~~(de Sá et al., 2017). Filter-based measurements were also taken using a custom-built sequential filter sampler. Selected filter samples were analysed using various chromatographic, ionization, and mass spectrometric techniques to provide additional chemical insight. The sequential filter sampler and filter analysis techniques are described in brief in the following sections. Routine meteorology data and gas-phase measurements (e.g. O_3) were provided by the Atmospheric Radiation Measurement (ARM) Climate Research Facility, a U.S. Department of Energy Office of Science user facility sponsored by the Office of Biological and Environmental Research.

2.3.1 Sequential filter sampler

Aerosol samples were collected on quartz-fiber filters using a custom-built sequential filter sampler (Aerosol Dynamics, Inc.). Ambient air was sampled at 120 LPM through a 2.4 cm I.D. stainless steel tube 4 m above ground level. Sampled air passed through 2.7 m of 2 cm I.D. copper tubing kept at temperatures below the dew point of the trailer temperature for trapping excess water with periodic manual removal. The sample inlet geometry and flow conditions minimized particle losses (< 5%) for those between 10 and 1000 nm. We estimate 70% removal of intermediate volatility organic compounds (IVOCs), minimizing adsorption of gas-phase organics onto the filters. Previous filter measurements have noted sampling artefacts due to O_3 penetration (Dzepina et al., 2007). We estimate 90% removal of O_3 (estimated diffusive losses) for the sampler design used in this study, which should minimize further reaction of organics collected on filters.

Following the water removal stage was a pair of greaseless cyclones operating in parallel with aerodynamic diameter cutpoints of 1 μm. The cyclones are equivalent to the AIHL cyclone (John and Reischl, 1980) originally designed for $PM_{2.5}$ collection at 21.7 LPM but experimentally verified to provide PM_1 separation at 60 LPM. The sample was then introduced into a 91 cm length of 32 mm I.D. aluminium tubing, to one of six filter housings (HiQ, ILPH-102) containing a 101.6 mm diameter quartz fiber filter (Whatman, QM-A Quartz). Filter housings were modified from the manufacturer to remove all adhesives to prevent potential off-gas and contamination of the filter samples. Further modifications to the housings included replacing filter supports with custom etched 316L stainless steel support screens and utilizing an o-ring face seal not in contact with the sample flow or filter.

Before deployment filters were pre-treated by baking at 550°C for 12 hours. During IOP1 (wet season), samples were collected at approximately 12-hour time resolution, from 06:15-18:00 and 18:30-06:15, local time (LT) basis. Filter changes occurred daily from 18:00-18:30 LT. Field blanks were also collected weekly in each filter holder. ~~Filter samples collected during IOP2 (dry season) are not presented in this analysis. Removed filters~~Filter samples collected during IOP2 (dry season) are not presented in this analysis as the wet season filters were more ideal for targeted isolation and detection of sesquiterpene oxidation products. Similarly targeted samples from the dry season had similar chemical composition in terms of terpene oxidation as that presented in Section 3.3 Contribution of sesquiterpene oxidation to secondary organic aerosol for the wet season so this presentation is not repeated, though there are certainly contributions from additional OA sources (e.g. biomass burning compounds are more prominent in dry than wet season) as well. A more complete analysis of all samples from both seasons will be presented in separate forthcoming publication. The goal in the current analysis is to simply demonstrate the number and chemical complexity of the observed sesquiterpene-derived compounds and the potential for their significance in contributing to overall OA mass. Filter samples were kept frozen (or transported on ice) until analysis. Switching valves were automated to time sample collection appropriately over each filter throughout the day. Flow rates were logged in LabView using a TSI mass flow meter (TSI, model 4045).

2.3.2 Two-dimensional gas chromatography with high-resolution-time-of-flight mass spectrometry (GC×GC-HR-ToFMS)

Selected filter samples and standards were analysed in the laboratory using two-dimensional gas chromatography with high-resolution-time-of-flight mass spectrometry. Aliquots of samples (multiples of ovoid filter punches with an area of 0.4 cm^2 each) were introduced into the gas chromatograph using a thermal-desorption autosampler (Gerstel, TDS-3 and TDSA2) with built-in derivatization using MSTFA. Compounds were separated first on a nonpolar column (Restek, Rxi-5Sil-MS, 60 m × 0.25 mm ×250 µm), then transferred to a Zoex Corporation cryogenic dual-stage thermal modulator comprised of guard column (Restek, 1.5 m × 0.25 mm, Siltek). The modulation period was 2.3 s, followed by separation on a secondary column (Restek, Rtx-200MS, 1 m × 0.25 mm ×250 µm) to separate polar compounds. The GC temperature program ramped from 40 °C to 320 °C at a rate of 3.5 °C min^{-1}, holding for 5 min, and the He carrier gas flow was 2 mL min^{-1}. Following chromatographic separation, analysis was performed with a Tofwerk high-resolution $\left(\frac{m}{\Delta m} \approx 4000\right)$ mass spectrometer employing electron impact (70 eV) ionization.

To correct for compound transmission efficiency through the system, total ion signal for each peak was corrected based on a volatility curve comprising even-carbon numbered perdeuterated alkanes as internal standards (from $C_{12}D_{26}$ through $C_{36}D_{74}$. The custom-synthesized β-caryophyllene oxidation products (described in Section 2.2.2 Compound quantification) and several filter samples containing sesquiterpene-derived SOA from laboratory oxidation experiments (described in Section 2.2.3 Laboratory-generated SOA from sesquiterpenes) were analysed to create characteristic mass spectra of sesquiterpene-derived oxidation products. These mass spectra were put into custom MS libraries and added to the available NIST 14 MS libraries within NIST MS Search v.2.2 software to be searched against when analysing sample chromatograms. Custom MS libraries comprising mass spectra of products from previous laboratory oxidation experiments of the monoterpenes α-pinene, myrcene, and d-limonene were also included in MS searches. These custom MS libraries ~~will be made~~are available online for the use of the atmospheric chemistry community as indicated in the Data availability section and are the subject of a future publication. Published MS in the literature were also used to identify previously reported tracers of isoprene and terpene oxidation as described in Section 3.3.2 Additional identification of terpene oxidation products by mass spectral matching. For peaks with "good" MS match factors > 800 out of 1000 (Stein, 1994) and an alkane-based retention index matching within ± 10 of that of the library entry, a tentative match was considered at least for source categorization of the peak. Some peaks with <800 MS match factors were included after manual review accounting for co-elutions and other factors affecting MS quality and MS matching.

2.3.3 Ultra-High Performance Liquid Chromatography Mass Spectrometry (UHPLC-MS)

A subset of filters were extracted and analysed using Ultra-High Performance Liquid Chromatography coupled to quadrupole time-of-flight MS (UHPLC-qTOF-MS) for carboxylic acids and organosulfates. ~~The method was based on Kristensen and Glasius, 2011 and Kristensen et al., 2016. Monoterpene oxidation products were analysed using these methods and further optimized for analysis of sesquiterpene products. Filters were extracted in 1:1 methanol:acetonitrile assisted by sonication, evaporated to dryness using nitrogen gas, and reconstituted in 200 µL MilliQ water with 10% acetonitrile and 0.1% acetic acid. The UHPLC system used an Acquity T3 column (1.8 µm, 2.1 × 100 mm, Waters) with a mobile phase of eluent A: 0.1% acetic acid in MilliQ water and eluent B: acetonitrile with 0.1% acetic acid (eluent flow was 0.3 mL min^{-1}). The 18 min gradient was: Eluent B increased from 3% to 80% from 1 min to 12 min, and then increased to 100% (during 0.5 min) where it was held for 3 minutes, before returning to initial conditions. The qTOF-MS had an electrospray ionization source~~

~~and was operated in negative ionization mode with a nebulizer pressure of 3.0 bar, dry gas flow 7.0 L min^{-1}, source voltage 3.0 kV, and transfer time of 50 µs. Oxidation products of β-caryophyllene were identified by comparison of their mass spectra with previous work (Alfarra et al., 2012; Chan et al., 2011; van Eijck et al., 2013; Jaoui et al., 2003) as well as products obtained from a smog chamber study of ozonolysis of β-caryophyllene. Quantification of β-caryophyllinic and β-nocaryophyllonic acid was performed using a synthesized standard provided by Dr. J. Parshintsev, Helsinki University following previously reported synthesis procedures (Parshintsev et al., 2010)~~The method was based on Kristensen and Glasius (2011) and Kristensen et al., (2016). Monoterpene oxidation products were analysed using these methods and further optimized for analysis of sesquiterpene products. Filters were extracted in 1:1 methanol:acetonitrile assisted by sonication, evaporated to dryness using nitrogen gas, and reconstituted in 200 µL MilliQ water with 10% acetonitrile and 0.1% acetic acid. The UHPLC system used an Acquity T3 column (1.8 µm, 2.1 × 100 mm, Waters) with a mobile phase of eluent A: 0.1% acetic acid in MilliQ water and eluent B: acetonitrile with 0.1% acetic acid (eluent flow was 0.3 mL min^{-1}). The 18 min gradient was: Eluent B increased from 3% to 80% from 1 min to 12 min, and then increased to 100% (during 0.5 min) where it was held for 3 minutes, before returning to initial conditions. The qTOF-MS had an electrospray ionization source and was operated in negative ionization mode with a nebulizer pressure of 3.0 bar, dry gas flow 7.0 L min^{-1}, source voltage 3.0 kV, and transfer time of 50 µs. Oxidation products of β-caryophyllene were identified by comparison of their mass spectra with previous work (Alfarra et al., 2012; Chan et al., 2011; van Eijck et al., 2013; Jaoui et al., 2003) as well as products obtained from a smog chamber study of ozonolysis of β-caryophyllene. Quantification of β-caryophyllinic acid was performed using a synthesized standard provided by Dr. J. Parshintsev, Helsinki University following previously reported synthesis procedures (Parshintsev et al., 2010), and quantification of β-nocaryophyllonic acid was performed using the custom-synthesized standard at Northwestern University described in Bé et al., (2017).

2.3.4 Nanoelectrospray (nanoESI) Ultra-High Resolution Mass Spectrometry (UHRMS)

Selected filter samples from the wet season were extracted and analysed by direct infusion ultra-high-resolution LTQ Orbitrap Velos mass spectrometer (Thermo Fisher, Bremen, Germany) equipped with a TriVersa Nanomate robotic nanoflow chip-based ~~ESI~~electrospray ionization (nanoESI, Advion Biosciences, Ithaca NY, USA) source according to methods described previously (Kourtchev et al., 2013, 2014, 2015, 2016). This analysis provided mass resolution power of ≥ 100 000 and mass accuracy <1 ppm to provide molecular assignments. The direct infusion nanoESI parameters were as follows: the ionization voltage and back pressure were set at −1.4 kV and 0.8 psi, respectively. The inlet temperature was 200 °C. The sample flow rate was approximately 200-300 nL min^{-1}. The negative ionization mass spectra were collected in three replicates over ranges *m/z* 100–650 and *m/z* 150–900 and processed using Xcalibur 2.1 software (Thermo Scientific). Chemical formulae of the form $C_cH_hN_nO_oS_s$ were made according to analysis procedures presented in Kourtchev et al., ~~Kourtchev et al., 2013, 2015; Zielinski et al., 2018~~(2013, 2015) and Zielinski et al., (2018) and only ions that were observed in all three replicate extract analyses were kept for evaluation. All sample intensities were normalized to the aerosol organic carbon loading as well.

3 Results and Discussion

3.1 Chemical characterization of observed sesquiterpenes

Thirty sesquiterpene species were observed regularly in the gas phase in SV-TAG chromatograms during the GoAmazon campaign at T3~~.~~ (Figure 1). ~~Sesquiterpenes with chemical formula $C_{15}H_{24}$ were mostly resolved within single ion chromatograms (Figure 1) by a characteristic ion, *m/z* 161, $C_{12}H_{17}^{+}$, typically coincident with the molecular ion, *m/z* 204. In addition, a few sesquiterpenes with chemical formula C15H22 were resolved at their molecular ion (m/z 202), as well as a few diterpenes with chemical formula C20H32, resolved using characteristic ion, m/z 257.~~ Compound names for those

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compounds positively identified via MS matching and retention index are labelled accordingly in chromatograms and listed with mean concentrations observed during the wet and dry seasons in Table 1. ~~In some cases, peak signal was too low to provide good MS matching, so retention index (RI) information was also used to propose identities.~~Most sesquiterpene species were observed at mean levels above 100 ppq$_v$, ranging 1-529 ppq$_v$ in the wet season and 1-670 ppq$_v$ in the dry season. While mean observed concentrations differed for some species observed in the wet and dry season, overall summed mean concentrations of sesquiterpenes was similar in both seasons (∼4-5 ppq$_v$).

~~While many sesquiterpenes observed in ambient chromatograms are not available as authentic standards, sesquiterpene-rich Copaiba and Andiroba essential oils from Amazonian trees were injected on SV-TAG for chromatographic separation and to aid in identification.~~Complete timelines of speciated sesquiterpens are presented in Figure 2 wet season and Figure 3 dry season. In panel a), six species are presented with hourly time-resolution under regularly derivatized run conditions. In panel b), occasional runs without derivatization allow for complete speciation of sesquiterpene/diterpene species and to calculate summed concentration of sesquiterpenes and diterpenes as overlaid in panel a). For both seasons, sesquiterpenes exhibit highest concentrations overnight. Note also that a more dynamic range of summed sesquiterpene concentrations were observed during the wet season (spanning across 15 ppt$_v$), whereas in the dry season the range is closer to 8 ppt$_v$. Further, the wet season exhibits the greater chemodiversity of observed sesquiterpenes and terpenes compared to the dry season.

~~Copaiba essential oil originates from trees of the genus *Copaifera*, comprising over 70 species (Plowden, 2003), several of which are distributed throughout the greater Amazon region (SpeciesLink, 2018) While copaiba trees are commonly referred to as the “diesel” or “kerosene” tree due to the oil’s limited use as a biofuel, the essential oil is extracted primarily for medicinal purposes. Andiroba essential oil is derived from *Carapa guianensis*, also widely used for medicinal purposes.~~

~~While the exact composition, grade, and quality of the essential oils depends on multiple factors (e.g. extraction method, species, origin), we hypothesized that the ambient sesquiterpene composition might reflect similar chemical composition to the essential oils of tree species prevalent in the area. Studies have previously observed the chemical similarity between that of terpene emissions and within plant content (Ormeno et al., 2010), and specifically so for *Copaifera officinalis* (Chen et al., 2009a). Most of the sesquiterpenes observed in ambient samples (13 Feb 2014 06:47 UTC (02:47 LT)) coincide with those observed in copaiba essential oil (Figure 1, black and red traces respectively). This similarity between the ambient sesquiterpenes composition and essential oil composition also allowed for positive identification of some of the peaks in the ambient chromatogram. Sesquiterpene standards that were commonly available and brought to the field as standards included (+)-longifolene, β-caryophyllene, and alloaromadendrene with their chromatographic retention times indicated in Figure 1. Further, the essential oils injected on SV-TAG have relatively similar sesquiterpene composition (Table S1) and are comparable to previously analysed essential oils/tissue from Amazonian trees (Table S2).~~

3.2 Sesquiterpene oxidation

We further explore in this section indicators for sesquiterpene oxidation in the region. First, by comparing relative concentrations of isoprene, monoterpenes, and sesquiterpenes at T3 compared to those made within the canopy at an upwind Amazon forest site ~~(from previous literature),~~(Alves et al., 2016), we confirm that the majority of sesquiterpene oxidation must occur within/near the canopy. Second, differences in chemical composition between ambient samples at our site away from the canopy and that of sesquiterpene-rich essential oils (used as a proxy for emission profile within the canopy) reveals that the most reactive sesquiterpenes in the oils (e.g. β-caryophyllene) are reacted away to levels below detection by SV-TAG before reaching the sampling location at T3. Third, we observe known oxidation products of β-caryophyllene in SV-TAG and on filter samples collected at T3.

3.2.1 Sesquiterpene contribution to total O_3 reactivity

Sesquiterpenes are observed at concentrations much lower than those of the monoterpenes and isoprene (Figure Figure 4a and Figure 5a). They generally react relatively quickly with O_3, which dominates their reactive loss, and thus a strong anti-correlation with O_3 concentration is observed (Figure 4a and Figure 5a). During daytime, the levels of photochemically produced O_3 keep sesquiterpenes concentrations low. In addition, downward transport of ozone-rich air during convective storms in the Amazon that typically occur during late morning or early afternoon hours (Gerken et al., 2016) also contribute to the temporal concentration profile observed with highest concentrations at night (Figure 6). This is in contrast with typically observed daytime maxima for isoprene and monoterpenes ~~(Alves et al., 2016; Yáñez-Serrano et al., 2015)~~(Alves et al., 2016; Yáñez-Serrano et al., 2015), for which their reactive loss is dominated by reaction with OH and with OH/O_3, respectively (Atkinson, 1997; Kesselmeier et al., 2013; Kesselmeier and Staudt, 1999), and whose daytime emissions are likely more associated with immediate release following production as a function of solar radiation input ~~(Alves et al., 2014; Bracho-Nunez et al., 2013; Harley et al., 2004; Jardine et al., 2015; Kuhn, 2002; Kuhn et al., 2004)~~(Alves et al., 2014; Bracho-Nunez et al., 2013; Harley et al., 2004; Jardine et al., 2015; Kuhn, 2002; Kuhn et al., 2004).

To better understand reactive loss of O_3, the estimated cumulative loss of O_3 by reaction with sesquiterpenes compared to that by reaction with isoprene and monoterpenes is shown for the wet and dry seasons in Figure 4b and Figure 5b), respectively. O_3 reactivity (s^{-1}) is defined as the summed product of each terpene concentration (molec cm^{-3}) and its second order rate constant ($molec^{-1}$ cm^3 s^{-1}) for reaction with O_3. Of the approximately 20 regularly observed sesquiterpenes by SV-TAG, only two species (α-copaene and α-cedrene) have their reaction rate constants with all three major atmospheric oxidants (O_3, OH, and NO_3) measured in the laboratory (Atkinson and Arey, 2003; Shu and Atkinson, 1994). For the remaining sesquiterpenes, reaction rate constants were estimated using the Environmental Protection Agency's Estimation Program Interface Suite (U. S. EPA, 2000)~~ or obtained from the literature where available.~~. Reaction rate constants (estimated/measured) are listed in Table 1 for the observed sesquiterpenes. Additional reaction rate constants for other sesquiterpenes that are commonly reported but unobserved in this study are provided for comparison. The estimated contribution to O_3 reactivity from sesquiterpenes remains uncertain, as one to two orders of magnitude discrepancy sometimes exist between measured and estimated reaction rate constants. For example, the estimated reaction rate constant for β-caryophyllene is 44.2 x 10^{-17} cm^3 $molec^{-1}$ s^{-1} and the experimentally determined rate is 1170 x 10^{-17} cm^3 $molec^{-1}$ s^{-1}, leading to calculated lifetimes via ozonolysis at 20 ppb_v O_3 of 77 min and 3 min, respectively. Further, the estimate for monoterpene contribution to O_3 reactivity assumes that all monoterpenes here have the same rate constant as α-pinene, as monoterpene measurements were not speciated here and it is one of the more dominant (17% and 45% by mass) and longer-lived monoterpenes ~~emitted from the canopy~~as observed in upwind forested sites by Jardine et al., ~~(Jardine et al., 2015).~~ (2015) and Yáñez-Serrano et al., (2018). As observed concentrations of monoterpenes within canopy are a factor of 3-4 higher than those observed at T3, it is reasonable to expect that O_3 loss due to reaction with monoterpenes at this measurement site will become increasingly dominated by reaction with α-pinene.

At T3, the observed sesquiterpenes are estimated to have a measurable though smaller contribution (~10-15%) to the reactive losses of O_3 compared to isoprene (~40%) and monoterpenes (~45%) for both seasons. The contribution of sesquiterpenes to total O_3 loss varies dramatically in space and time, being highest right near the sources of emission. Based on average wind speed (2 m s^{-1}), transport time from the nearest surrounding trees (1 km) to the measurement site is on the order of at least 8 minutes, longer than the chemical lifetime of some of the more highly reactive sesquiterpenes. Ozonolysis of sesquiterpenes within the canopy has been estimated to account for about 50% of sesquiterpenes' reactivity during the daytime, suggesting significant losses of these compounds before escaping the Amazon forest canopy (Jardine et al., 2011). This is reflected in our measurements of daytime minima being located far from and outside the canopy (Figure 4a and Figure 5a). This is also evident for monoterpenes, for which their concentrations and associated O_3 reactivity at the top of the canopy at an upwind forest site (Jardine et al., 2015) are both approximately ten times higher than those at the measurement site in this study. ~~Further, the ratio between monoterpene and sesquiterpene concentrations typical within canopy sites upwind during the wet (7.4) and dry (2.35) seasons (Alves et al., 2016)~~Further, the ratio between monoterpene and sesquiterpene concentrations typical within canopy sites upwind during the wet (7.4) and dry (2.4) seasons (Alves et al., 2016) and that observed at our measurement site for both seasons (~17) indicate that the majority of sesquiterpenes have reacted away before our measurement. This is consistent with the fact that lifetimes of all 30 sesquiterpene species detected in SV-TAG with respect to loss via reaction with O_3 tend to be >20 minutes, whereas more highly reactive and more commonly studied sesquiterpenes were below detection (Table 1, "Unobserved/Below Detection"). Hence, sesquiterpene contributions to O_3 loss in our study represents a low-end estimate of an undoubtedly important contribution of sesquiterpenes affecting ozone chemistry in the region.

3.2.2 Differences in chemical composition between sesquiterpene-rich essential oils and ambient samples

While it is clear that the sesquiterpenes measured at our site represent only a subset of what is emitted from regional vegetation, we further explored the compositional differences between those at our site and those in sesquiterpene-rich copaiba and andiroiba essential oils as proxies for sesquiterpene composition at the site of emission. A major difference between the ambient sesquiterpenes content (13 Feb 2014 06:47 UTC (02:47 LT)) and that of the essential oils~~,~~ (Figure 1, black and red traces respectively) is the general absence of β-caryophyllene (Figure 1, blue label) in ambient samples and its presence in copaiba essential oil (Figure 1 and ~~Table S1),~~Table S3), Andiroiba oil ~~(Table S1),~~(Table S3), and previously analysed essential oils of Amazon origin ~~(Table S2).~~(Table S4). The chemical reactivity of β-caryophyllene with 20 ppb$_v$ of ozone typical of polluted conditions from Manaus (Gerken et al., 2016; Trebs et al., 2012) results in a chemical lifetime of 3 minutes compared to that of α-copaene which is more than 3 hours, so any emissions are expected to be quickly depleted through reaction near the emission location. β-Caryophyllene is detected in ambient samples at our measurement site very rarely, and only when ozone is near zero ppb. This is also expected to be the case with α-humulene, which also has a chemical lifetime just under 3 minutes due to reaction with O_3, though it is not as abundant as β-caryophyllene in copaiba essential oil. Some sesquiterpenes are routinely observed in ambient air that are not in the analysed copaiba essential oil (e.g. cyperene and β-gurjunene), which is expected given the rich diversity of plant species in the Amazon that should all have unique terpene contents. The difference in relative abundances of sesquiterpenes in ambient and the analysed essential oils ~~(Table S1)~~(Table S3) also reflects many other variables: additional vegetation with similar sesquiterpenes emission profiles, actual emission relative to tissue content, and chemical fate of the sesquiterpenes once emitted.

Based on the sesquiterpenes profile in various essential oils serving as a proxy for sesquiterpene composition upon emission, it becomes clear that the majority of potential O_3 reactivity from sesquiterpenes is dominated by β-caryophyllene (>80% even if only comprising approximately 20% of total sesquiterpene mass; ~~Table S1~~Table S3), This demonstrates that the estimate of O_3 reactivity via reactive loss with sesquiterpenes at our measurement site is a significant underestimate and not representative of near-field O_3 chemistry. For example, taking typical terpenoid concentrations within canopy as reported in Alves et al., 2016 and assuming monoterpene and sesquiterpene speciation within canopy to be that of Jardine et al., 2016 (for monoterpenes) and that of Copaiba Essential Oil (for sesquiterpenes), near-field or in-canopy loss of O_3 is dominated (> 50%) by reaction with sesquiterpenes for both seasons (Figure S2). Within the transport time to T3~~,~~ (> 8 mins), the most reactive sesquiterpenes have been reacted away, and observed contribution to O_3 reactivity becomes diminished by a factor of ~5 for both seasons. This analysis also highlights the importance of using speciated terpene measurements for calculating oxidative loss of radical species. For example, while the relative contributions to total terpene VOC concentrations are such that isoprene > monoterpenes > sesquiterpenes near the canopy (Figure S2) and at T3 (Figure 4a and Figure 5a), the large differences seen in terms of their relative contribution to O_3 reactivity at the two locations result from the terpene species prevalent at each site (Figure S2, Figure 4b, and Figure 5b). In addition, while it is typical practice to take total sesquiterpene concentration and use $k_{O3+\beta\text{-caryophyllene}}$ for all sesquiterpenes (Jardine et al., 2011; Khan et al., 2017), this would result in an overestimate of sesquiterpene reactivity with O_3 by an order of magnitude at T3. Thus, with the majority of sesquiterpene ozonolysis occurring within/just outside the canopy, we expect to observe less sesquiterpenes at our measurement site, but that their oxidation products may be observed even when the primary sesquiterpenes are not.

3.2.3 Observation of β-caryophyllene oxidation products

β-Caryophyllene was infrequently observed in ambient samples despite its prevalence in copaiba essential oil, consistent with its rapid reaction with ozone during transport from the canopy to the measurement site. However, with SV-TAG we regularly observed β-caryophyllene oxidation products (specifically β-caryophyllene aldehyde and β-caryophyllonic acid) in both the gas and particle phases. These products have maxima at local night time hours (Figure 7) of at most a few ng m^{-3} (Figure S3~~), and exist predominantly in the gas-phase despite previous observations of these products in filter-based measurements (Chan et al., 2011; van Eijck et al., 2013; Jaoui et al., 2003; Li et al., 2011; Winterhalter et al., 2009). Based on saturation vapour pressure estimates for several β-caryophyllene oxidation products presented in Li et al., 2011~~), and exist predominantly in the gas-phase despite previous observations of these products in filter-based measurements (Chan et al., 2011; van Eijck et al., 2013; Jaoui et al., 2003; Li et al., 2011; Winterhalter et al., 2009). Based on saturation vapour pressure estimates for several β-caryophyllene oxidation products presented in Li et al., (2011) the gas-phase only observation of β-caryophyllene aldehyde (therein referred to as P-236, $C^* = 4.0 \times 10^3$ μg m^{-3}) is consistent with the typical organic loadings of sampled air at T3 (~1 μg m^{-3} during wet season), though β-caryophyllonic acid (therein referred to as P-252-5, $C^* = 8.7 \times 10^{-1}$ μg m^{-3}) might be expected to have some contributions to the particle phase.

Speciation of additional oxidation products β-nocaryophyllonic acid and β-caryophyllinic acid (typically observed at sub ng/m^3 levels, Figure S3) were obtained from UHPLC-qTOF-MS analysis of selected filters. These products were observed to have daily maxima during local daytime hours (Figure 7). The differing diel profiles between the four observed β-caryophyllene oxidation products likely reflects differences in chemical lifetimes of each product and multiple possible reaction pathways of formation (i.e. β-caryophyllene initiated oxidation by O_3 followed by continued ozonolysis or continued OH oxidation during daytime). Further, both of these acids are estimated to have atmospheric lifetimes 2–10 days (Nozière et al., 2015), consistent with the flatter diel profile observed. In addition, because the filter-based measurements have approximately 12-hour time resolution and only a selected period representing significant influence from the Manaus plume was analysed, the diurnal dynamics of these concentration profiles may not be fully captured.

3.3 Contribution of sesquiterpene oxidation to secondary organic aerosol

3.3.1 Identification and quantification of common terpenoid SOA tracers

Here, we roughly examine the contribution of isoprene and terpene oxidation to total submicron organic aerosol (OA). Figure 8 shows a selected timeline from the wet season of the total observed OA from the AMS (averaged over the same time frame as our filter samples) and the summed contributions of positively identified molecular tracers from isoprene, monoterpene, and sesquiterpene oxidation. This analysis combines observed tracers from both SV-TAG (particle phase measurements, averaged to 12-hour time resolution to match the filter sampling times) and the UPLC filter-based measurements of monoterpene and sesquiterpene-derived tracers, as listed in Table 2. Estimated contributions to total OA from oxidation of isoprene has a lower limit of SOA formed through the uptake of isoprene epoxydiol (IEPOX) based on positive matrix factorization (PMF) analysis of AMS data ~~(de Sá et al., 2017)~~(de Sá et al., 2017). This statistical factor, known as the IEPOX-SOA factor, represents OA mass formed from isoprene under sufficiently low NO_x conditions such that IEPOX forms in the gas phase (Paulot et al., 2009), followed by uptake to the particle phase to form SOA ~~(Lin et al., 2012; Ngyuen et al., 2014; Liu et al; 2015);~~(Lin et al., 2012; Liu et al., 2015; Nguyen et al., 2014); it is estimated to account for approximately half of total isoprene-derived SOA in environments with low levels of NO_x (Liu et al., 2015). Tracers associated with the IEPOX channel of SOA formation include 2-methyltetrols ("2-MTs") observed previously in the Amazon by ~~Claeys et al.,~~

~~2004~~Claeys et al., (2004) and C5-alkene triols ~~(Surratt et al., 2006b, 2010)~~(Surratt et al., 2006b, 2010), both of which are measured by SV-TAG ~~(Isaacman-VanWertz et al., 2016)~~(Isaacman-VanWertz et al., 2016) and correlate well with OA mass attributed to the AMS IEPOX-SOA factor ~~(de Sá et al., 2017)~~(de Sá et al., 2017). For this reason they are presented in Figure 8 as separate from the remaining IEPOX-SOA factor mass (i.e. IEPOX-SOA factor subtracting SV-TAG measured 2-methyltetrols and C_5-alkene triols). In the presence of NO_x, there is also production of 2-methylglyceric acid, another tracer of isoprene chemistry (Surratt et al., 2006a) measured at the molecular level by SV-TAG and also presented in Figure 8. Lower-limit estimates to total OA from oxidation of monoterpenes (MT) comprises ~~MT~~ filter tracers (DTAA (Iinuma et al., 2009), MBTCA (Szmigielski et al., 2007), pinic acid (Yu et al., 1999), pinonic acid (Yu et al., 1999), and terpenylic acid ~~(Claeys et al., 2009)). Finally, lower-limit estimates to total OA from oxidation of sesquiterpenes~~(Claeys et al., 2009)). Finally, lower-limit estimates to total OA from oxidation of sesquiterpenes (SQT) includes the two filter-quantified β-caryophyllene oxidation products (β-nocaryophyllonic acid and β-caryophyllinic acid). Only approximately 20% of all OA mass is composed of these identified tracer species/statistical factor, almost all of which (18%) is represented by known IEPOX products. However, the yields of known tracer compounds typically represent only a minor fraction of total terpene SOA in laboratory studies: MT acid tracers used here contribute <10% of monoterpene SOA (Kristensen et al., 2016), and the SQT acid tracers contribute <5% of sesquiterpene SOA ~~(van Eijck et al., 2013; Jaoui et al., 2003)~~(van Eijck et al., 2013; Jaoui et al., 2003). Significant work therefore remains for the scientific community to resolve and identify a large fraction of terpene products to understand sources and formation processes. However, these laboratory studies provide an opportunity to estimate total contribution of monoterpene and sesquiterpene oxidation products to OA using an approximate tracer-based scaling method.

Following the approach of Kleindienst et al., ~~(Kleindienst et al., 2007)~~(2007), we take the average summed concentration of β-nocaryophyllonic acid and β-caryophyllinic acid (0.~~51~~15 ng m^{-3}) and scale by their summed product yields (0.045) from laboratory ozonolysis of β-caryophyllene ~~(Jaoui et al., 2003)~~(Jaoui et al., 2003). This suggests that the contribution of β-caryophyllene to typical wet season OA concentrations of 1000 ng m^{-3} is approximately ~~1~~0.3%. However, β-caryophyllene represents only a minor fraction (median: 22%, range 6-83%) of the total sesquiterpene content of analysed essential oil/plant tissues ~~(Table S2).~~(Table S3). This suggests that the sesquiterpene SOA contribution should be approximately ~~5~~1% (range ~~1-18~~0.4-5%). This is only a rough low-end estimate because: 1) it derives from scaling two molecular tracers of β-caryophyllene oxidation; the actual SOA yield of β-caryophyllene and other sesquiterpenes oxidation is not known under conditions relevant to the Amazon, and yields likely vary as a function of air pollution and other environmental variables. Further, vapour-phase wall losses of the more semi-volatile and lower-volatility oxidation products such as these in environmental chambers may result in non-atmospherically relevant phase partitioning and underestimated product and SOA yields ~~(Krechmer et al., 2016; La et al., 2016; Loza et al., 2010; Matsunaga and J., 2010; McMurry and Grosjean, 1985; McVay et al., 2014; Ye et al., 2016; Yeh and Ziemann, 2014; Zhang et al., 2014, 2015)~~(Krechmer et al., 2016; La et al., 2016; Loza et al., 2010; Matsunaga and Ziemann, 2010; McMurry and Grosjean, 1985; McVay et al., 2014; Ye et al., 2016; Yeh and Ziemann, 2014; Zhang et al., 2014, 2015). 2) This estimate derives from the available analysis of three essential oil types derived from Amazonian tree species: copaiba essential oil (this study; Chen et al., 2009a; Soares et al., 2013), rosewood essential oil (Fidelis et al., 2012), and andiroiba essential oil (this study). While these essential oils typically comprise on order ~30 sesquiterpenes, Courtois et al., ~~Courtois et al., 2009 report 169 sesquiterpenes emitted by 55 species of tropical trees.~~(2009) report 169 sesquiterpenes emitted by 55 species of tropical trees. Thus, the impact of additional sesquiterpenes reported to be emitted from these plants but not found in the essential oils presented here is unaccounted for. Nevertheless, this estimate demonstrates that sesquiterpene oxidation contributes measurably to SOA based on scaling from specific identified tracers. In addition, previous analysis for the region utilizing PMF during the AMAZE-08 campaign suggests that 50% of freshly produced secondary organic material may derive from isoprene, 30% from monoterpenes, and 20% from sesquiterpenes (Chen et al., 2015). This suggests that a considerable fraction of OA from sesquiterpene oxidation remains to be accounted for through speciated measurements. Considering the chemical diversity of the sesquiterpenes observed here, it would be most ideal to have additional representative tracers and authentic standards to perform a more accurate scaling estimate. While this remains a challenge due to the enormous range of sesquiterpenes and their oxidation products, we provide new tracers and data below.

3.3.2 Additional identification of terpene oxidation products by mass spectral matching

It is clear that the majority of oxidation products and SOA mass from β-caryophyllene and other sesquiterpenes (i.e. beyond β-nocaryophyllonic acid and β-caryophyllinic acid) were not identified, and thus a vast array of additional oxidation products must be present. To explore the contributions of additional sesquiterpene oxidation products to OA, non-targeted chemical characterization was performed on selected filters from ~~IOP1~~the wet season that were collected during times when sesquiterpenes were prevalent. The compounds observed in these analyses were uniquely identified by their first and second dimension retention times, and their mass spectra. The observed compounds in ambient air samples were compared to the laboratory-generated SOA compounds from sesquiterpene oxidation, as well as a subset of known products from isoprene and monoterpene oxidation.

Figure 9 is a GCxGC chromatogram of a night time filter sample taken Feb. 12, 2014 18:30-06:15 LT (22:30-10:15 UTC) when sesquiterpenes were relatively abundant. Approximately 460 sample peaks were separated in the chromatogram and their mass spectra and retention indices searched using NIST MS Search via GC Image (Zoex, LLC). A table of the peaks in this sample that could be attributed as BVOC oxidation products, their compound names (if positively identified), and their assigned source category is available in Table S5. Source categories and number of peaks, n, assigned to each category in the present analysis include the following: isoprene-derived oxidation products (ISOPOX, n = 6), monoterpene-derived oxidation products (MTOX, n = 13), sesquiterpenes-derived oxidation products (SQTOX, n = 41), terpene-derived oxidation products (TERPOX, n = 10), and other organic aerosol constituents (some not easily categorized) as BVOC oxidation products (Other OA, n = 385). The TERPOX category represents compounds that are suspected to derive from monoterpene and/or sesquiterpene oxidation based on MS similarity. That is, good MS matches include oxidation products observed in samples of laboratory monoterpene and sesquiterpene oxidation experiments (some may be overlapping products), but there was no positive delineation between MTOX or SQTOX. Categorized peaks accounted for 45% of total signal for this sample, the rest is labelled as Other OA.

The pie chart inset of Figure 9 shows the ~~%~~percentage of the sample signal (Total Ion Chromatogram, TIC, corrected for compound transmission efficiency) associated with each source category. The peaks associated with SQTOX account for 9% of the corrected TIC, and the peaks associated with TERPOX account for another 5%, at least part of which are likely from sesquiterpene oxidation. This sample highlights the chemical complexity still to be elucidated and quantified in forthcoming analyses of these filter samples to constrain source contributions to total SOA, while demonstrating that numerous unidentified oxidation products derived from sesquiterpenes in this region are present during local nighttime hours. This is consistent with sesquiterpenes dominating ozone reactivity during nighttime hours (Figure 4b and Figure 5b).

3.3.3 Identification of terpene oxidation products by chemical formulae

Five filter samples from IOP1 (wet season) during the period Feb 09 18:30 LT to Feb 11 18:30 LT were analysed according to procedures described in Section 2.3.4 Nanoelectrospray (nanoESI) Ultra-High Resolution Mass Spectrometry (UHRMS) to provide additional insight into the chemical identity (by chemical formula) of sample compounds. The presence of ions with chemical formulae consistent with oxidation products identified in the chromatography-MS methods (SV-TAG, GCxGC~~-~~-HR-~~TOFMS~~ToFMS, and UPLC-MS) provides additional support for their prevalence throughout the wet season and is presented in Table 2 for β-caryophyllene oxidation products and Table 3 for monoterpene oxidation products. Note that this ESI-UHRMS method is not sensitive to the isoprene oxidation products specified in Table 3, thus entries of not applicable (N/A) for observation of their chemical formulae are used. An average ~~%~~percentage of signal intensity for each UHRMS *m/z*

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is also presented for reference, but these should not be directly interpreted as the ~~%~~percentage of total OA. Rather these are the ~~%~~percentage of sample that this technique is sensitive to, as these samples have complex matrices of organic species which also affect ionization efficiencies.

4 Conclusion

We have provided speciated time-resolved measurement of 30 sesquiterpenes, four diterpenes, and have observed a broad array of sesquiterpene oxidation products in Amazonia, demonstrating that the emitted sesquiterpenes and their oxidation products in this region are both relatively abundant and highly chemically diverse. Most of the observed oxidation products have yet to be fully chemically characterized and quantified, which will be the subject of forthcoming publications. Our observations provide a low-end estimate of the sesquiterpenes in the atmosphere closer to the forest and suggest that sesquiterpene oxidation via ozonolysis is likely the primary reactive fate of these compounds in the region. They exhibit nighttime maxima, anti-correlated with ozone, and contribute at least 10% to reactive loss of O_3 compared to that from reaction with isoprene and monoterpenes at our measurement site and >50% within/near the canopy. As ozone levels in this region are directly influenced by the outflow of the Manaus plume, we would expect contributions of sesquiterpene-derived SOA to also depend highly on anthropogenic activities. In addition, since ozone enhancements at ground-level can result from downdrafts of convective storms, sesquiterpenes are part of an intricate aerosol-oxidant-cloud life cycle. Based on the observation of two β-caryophyllene oxidation products in aerosols, we estimate that sesquiterpene oxidation contributes at least ~~1-18~~0.4-5% (median ~~5~~1%) of observed submicron organic aerosol. As the within/near canopy reactive loss of sesquiterpenes to O_3 is significant, the measurements at T3 cannot account for the most reactive sesquiterpene species, and their contributions to SOA formation in the region likely remain underestimated by the estimates reported here.

Because several of the observed sesquiterpenes have not been studied in terms of their reaction kinetics with various oxidants (i.e. O_3, OH, NO_3) or their oxidative pathways leading to SOA, it is still challenging to fully constrain their role in the atmospheric chemistry of the region. Part of this challenge is stymied by the lack of available authentic standards, so further work in separation of complex mixtures (e.g. essential oils) to isolate pure sesquiterpenes and chemical synthesis of oxidation products would prove beneficial for furthering our knowledge of sesquiterpene chemistry. Future field work should focus on performing speciated sesquiterpene measurements within the canopy and connecting the chemical fate and transport from emission to regional atmospheric chemistry. Further, laboratory oxidation experiments of newly-observed sesquiterpenes or relevant mixtures could be used to improve estimates of reactive oxidant loss and contributions to SOA.

Data availability

The data sets used in this publication are available at the ARM Climate Research Facility database for the GoAmazon2014/5 campaign ~~(https://www.arm.gov/research/campaigns/amf2014goamazon).~~(https://www.arm.gov/research/campaigns/amf2014goamazon). Mass spectra of observed terpene oxidation products are available at: https://nature.berkeley.edu/ahg/data/MSLibrary/ within the file GoAmazon2014_terpox_v1.msp.

Competing Interests

The authors declare that they have no conflict of interest

Author contribution

AG, LM, RdS, AM, PA, JJ, and SM designed, coordinated, and supervised the GoAmazon field campaign and LY, GI, RW, NK, SV, SdS, LA, BB, WH, PC, DD, YL, KM, JV, MO, and KL carried out the measurements and model simulations. LY, GI, MM, VR, RW, SdS, BB, and YL performed data analysis. MB, MG, IK, and MK performed additional analysis of collected filter samples. MA, AB, RT, and FG synthesized and provided chemical standards. JO and ML provided supplementary filter samples from laboratory oxidation experiments to aid data interpretation. LY prepared the manuscript with contributions from all co-authors.

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Tables

Table 1. Sesquiterpene and terpenoids observed in the gas phase during GoAmazon2014/5 with proposed identification and their alkane-based retention index, Chemical Abstract Service (CAS) #, mean concentration during wet/dry season, reaction rate constant with O_3 (k_{O3}), and estimated chemical lifetime in the presence of 20 ppb_v O_3. k_{O3} estimated using EPA EPI Suite 4.1 AOPWIN where literature data unavailable. Concentrations of each species estimated by using an average instrument response factor for several sesquiterpene standards unless otherwise noted that an authentic standard was used. Other commonly studied sesquiterpenes typically below detection or unobserved are also included for comparison of reactive timescales.

#	Compound	Retention Index	CAS #	Wet Season Mean Concentration		Dry Season Mean Concentration		k_{O3} x 10^{17} (cm^3 $molec^{-1}$ s^{-1})	τ for $[O_3]$ = 20 ppb_v (min)
				($ng\ m^{-3}$)	(ppq_v)	($ng\ m^{-3}$)	(ppq_v)		
Sesquiterpenes									
1	α-cubebene	1355	17699-14-8	2.25	250	1.90	211	43.0	78.9
2	unidentified	1380		2.86	318	1.12	125		
3	cyclosativene	1383	22469-52-9	2.86	317	1.16	129	7.4	458.7
4	α-copaene	1387	3856-25-5	3.75[1]	417	3.92[1]	435	16[2]	212.0
5	β-elemene	1397	515-13-9	2.08	231	1.46	163	2.6	1317.2
6	cyperene	1420	2387-78-2	1.61	179	0.81	90	NE[3]	
7	α-cedrene	1435	469-61-4	0.25[1]	28	0.45[1]	49	2.8[2]	78.9
8	unidentified	1443		4.76	529	6.04	670		
9	β-gurjunene	1447	17334-55-3	0.88	97	0.88	98	7.4	458.7
10	unidentified	1453	26620-71-3	0.32	35	0.01	2		
11	unidentified	1462		1.61	179	1.38	153		
12	α-patchoulene	1471	560-32-7	0.27	30	1.01	113	7.4	458.7
13	unidentified; SQT202	1474		0.29	33	0.43	49		
14	(-) alloaromadendrene[1]	1476	025246-27-9	1.93[1]	214	1.72[1]	191	1.2	2826.4
15	γ-muurolene	1486	30021-74-0	0.18	20	0.11	12	44.2	76.7
16	unidentified; SQT202	1486		2.36	265	4.89	548		
17	α-amorphene	1490	20085-19-2	1.23	136	1.03	114	86.0	39.4
18	β-selinene	1505	17066-67-0	0.45	50	2.38	264	2.4	1413.2
19	α-muurolene	1509	31983-22-9	1.50	166	1.45	161	86.0	39.4
20	unidentified	1512		2.14	237	1.50	167		
21	β-bisabolene	1513	495-61-4	1.24	138	0.32	36	87.20	38.9
22	cuparene	1524	16982-00-6	1.13	127	0.62	69		
23	γ-cadinene	1526	39029-41-9	1.75	194	1.18	131	44.2	76.7
24	δ-cadinene	1529	483-76-1	0.95	105	0.81	90	163.0	20.8
25	cis-calamenene~~;~~	1534	72937-55-4	0.81	91	0.32	35	NE[3]	
26	selinene <7-epi-α>	1537	6813-21-4	0.14	15	0.22	25	163.0	20.8
27	γ-cuprenene	1545	4895-23-2	0.32	35	0.14	15	50.4	67.3
28	α-cadinene	1549	24406-05-1	0.17	18	0.06	7	86.0	39.4
29	unidentified	1553		0.01	1	0.13	14		
30	Selina-3,7(11)-diene	1558	6813-21-4	0.07	8	0.10	11	163.0	20.8
Below Detection/Unobserved									
	β-caryophyllene	1427	87-44-5	N/A	N/A	N/A	N/A	1160.0	2.9
	trans-α-bergamotene	1442	13474-59-4	N/A	N/A	N/A	N/A	86.0	39.4
	aromadendrene	1450	489-39-4	N/A	N/A	N/A	N/A	1.2	2826.4
	α-humulene	1471	6753-98-6	N/A	N/A	N/A	N/A	1170.0	2.9
	β-farnesene		18794-84-8	N/A	N/A	N/A	N/A	40.1[4]	84.6
	α-farnesene	1509	502-61-4	N/A	N/A	N/A	N/A	104.0	32.6
	valencene	1523	4630-07-3	N/A	N/A	N/A	N/A	8.6	394.7
Diterpenes									
31	rimuene	1958	1686-67-5	0.21	18	0.22	19	7.6	448.1
32	pimaradiene	1977	1686-61-9	0.11	10	0.14	12	7.6	448.1
33	Sandaracopimaradiene	1995	1686-56-2	0.38	33	0.15	13	7.6	448.1
34	kaurene	2085	34424-57-2	0.97	86	0.69	60	1.1	2981.7
Total Sesquiterpenes + Diterpenes:				**41.8**	**4611**	**38.8**	**4285**	N/A	N/A

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[1] Authentic standard used for quantification

[2] (Shu and Atkinson, 1994)

[3] NE=No estimate in EPISuite

[4] (Kourtchev et al., 2009)

Table 2: Oxidation products from beta-caryophyllene observed in Central Amazonia in gas and/or particle phases by listed analysis method. These products are attributed to oxidation from sesquiterpenes (SQTOX) source category. Synthesized standards for tracers 1–6 were used to confirm identification and for quantification.

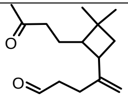
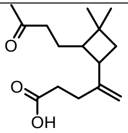
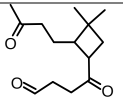
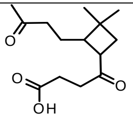
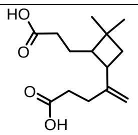
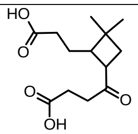
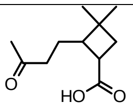
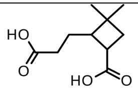
#	Tracer Name	Structure	Source Category	Analysis Methods	Chemical Formula	Molecular Weight (g/mol)	UHRMS Measured *m/z* [M-1]$^-$	UHRMS Average % of Total Signal Intensity
1	β-caryophyllene aldehyde		SQTOX	SV-TAG; Filter GCxGC HR-TOF-MS; Filter ESI-UHRMS	$C_{15}H_{24}O_2$	236.35	235.17023	1.2
2	β-caryophyllonic acid		SQTOX	SV-TAG; Filter GCxGC HR-TOF-MS; Filter ESI-UHRMS	$C_{15}H_{24}O_3$	252.35	251.1652	0.74
3	β-nocaryophyllone aldehyde		SQTOX	Filter GCxGC HR-TOF-MS; Filter ESI-UHRMS	$C_{14}H_{22}O_3$	238.32	237.14943	0.37
4	β-nocaryophyllonic acid		SQTOX	Filter UPLC-MS; Filter ESI-UHRMS	$C_{14}H_{22}O_4$	254.32	253.14448	0.81
5	β-caryophyllinic acid		SQTOX	Filter UPLC-MS; Filter ESI-UHRMS	$C_{14}H_{22}O_4$	254.32	253.14448	0.81
6	β-nocaryophyllinic acid		SQTOX	Filter ESI-UHRMS	$C_{13}H_{20}O_5$	256.29	255.12378	0.69
7	DCCA or 3,3-dimethyl-2-(3-oxobutyl)-cyclobutanecarboxylic acid		SQTOX	Filter ESI-UHRMS	$C_{11}H_{18}O_3$	198.26	197.11828	1.25
8	2-(2-carboxyethyl)-3,3-dimethylcyclo-butanecarboxylic acid		SQTOX	Filter ESI-UHRMS	$C_{10}H_{16}O_4$	200.23	199.09755	1.36

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Table 3: Oxidation products from isoprene (ISOPOX) and monoterpenes (MTOX) in Central Amazonia in gas and/or particle phases. Only particle-phase measurement presented in this study. Products marked not applicable (N/A) are not detected in the UHRMS analysis method.

#	Tracer Name	Source Category	Analysis Methods	Chemical Formula	Molecular Weight (g/mol)	UHRMS Measured *m/z* [M-1]$^-$	UHRMS Average % of Total Signal
1	2-MT 1 or 2-methylerythritol	ISOPOX	SV-TAG; Filter GCxGC HR-TOF-MS	$C_5H_{12}O_4$	136.15	N/A	N/A
2	2-MT 2 or 2-methylthreitol	ISOPOX	SV-TAG; Filter GCxGC HR-TOF-MS	$C_5H_{12}O_4$	136.15	N/A	N/A
3	C5 alktriol 1 or 3-methyl-2,3,4-trihydroxy-1-butene	ISOPOX	SV-TAG; Filter GCxGC HR-TOF-MS	$C_5H_{10}O_3$	118.13	N/A	N/A
4	C5 alktriol 2 or cis-2-methyl-1,3,4-trihydroxy-1-butene	ISOPOX	SV-TAG; Filter GCxGC HR-TOF-MS	$C_5H_{10}O_3$	118.13	N/A	N/A
5	2-MGA or 2-methylglyceric acid	ISOPOX	SV-TAG; Filter GCxGC HR-TOF-MS	$C_4H_8O_4$	120.10	N/A	N/A
6	DTAA or diaterpenylic acid acetate	MTOX	Filter UPLC-MS; Filter ESI-UHRMS	$C_{10}H_{16}O_6$	232.23	231.08728	0.57
7	MBTCA or 3-methyl-1,2,3-butanetricarboxy	MTOX	Filter GCxGC HR-TOF-MS; Filter UPLC-MS; Filter ESI-UHRMS	$C_8H_{12}O_6$	204.18	203.05606	0.87
8	Pinic acid	MTOX	Filter GCxGC HR-TOF-MS; Filter UPLC-MS; Filter ESI-UHRMS	$C_9H_{14}O_4$	186.21	185.08186	0.96
9	Pinonic acid	MTOX	Filter UPLC-MS; Filter ESI-UHRMS	$C_{10}H_{16}O_3$	184.23	183.10259	2.73
10	Terpenylic acid	MTOX	Filter UPLC-MS; Filter ESI-UHRMS	$C_8H_{12}O_4$	172.18	171.06618	0.78
11	*cis*-norpinic acid	MTOX	Filter GCxGC HR-TOF-MS; Filter ESI-UHRMS	$C_9H_{16}O_3$	172.22	171.10252	2.97

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Figures

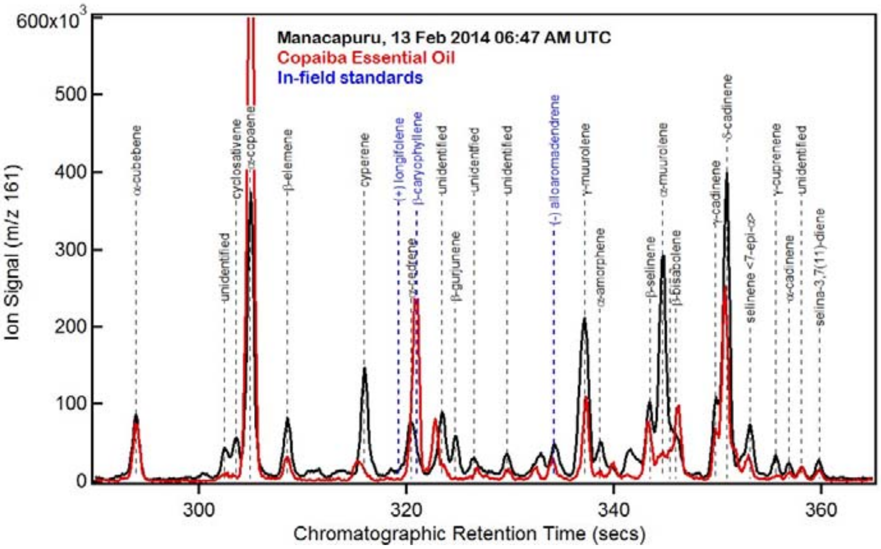

Figure 1: Selected ion chromatograms at sesquiterpene characteristic ion *m/z* 161 of ambient air (black) and copaiba essential oil (red). Sesquiterpenes in ambient air were measured in the gas phase. Copaiba essential oil analysed from direct liquid injection on SV-TAG collection cells. Retention times for standards analysed in the field indicated in blue.

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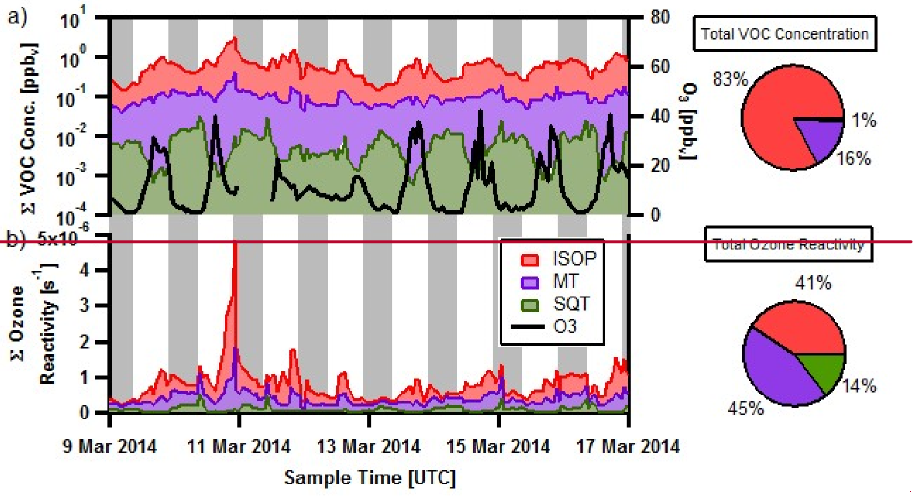

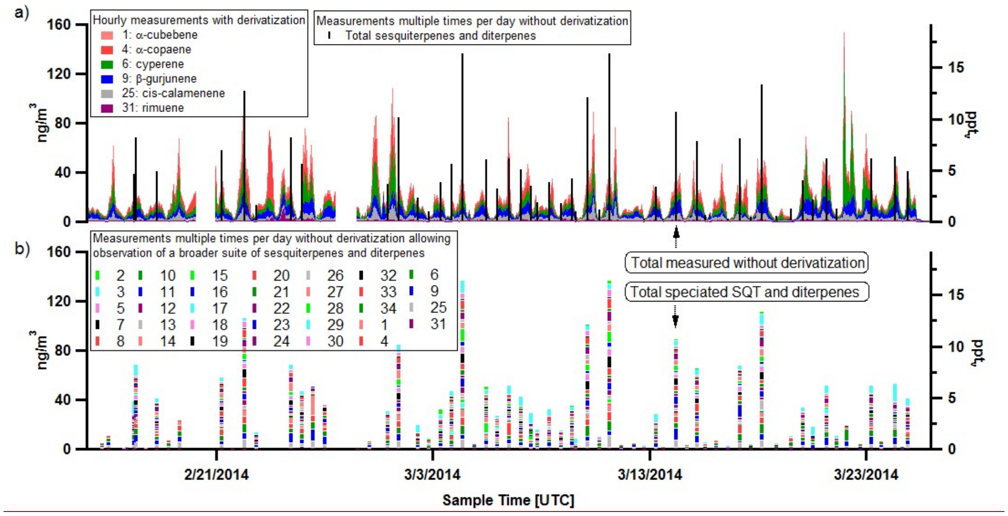

Figure 2: Wet season timeline of sesquiterpene (SQT) and diterpene species for those measured with hourly time resolution with derivatization (shaded colors) a) and those measured multiple times per day at lower time-resolution without derivatization b). Legend entries correspond to compound numbers in Table 1. Total SQT and diterpenes quantified during runs without derivatization are overlaid in black for reference in panel a). Concurrent speciation shown in b).

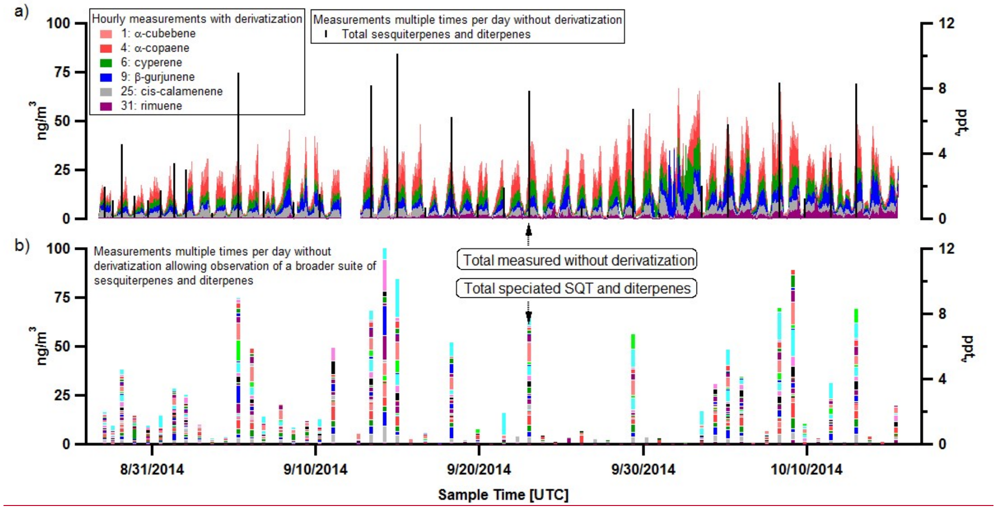

Figure 3: Dry season timeline of sesquiterpene (SQT) and diterpene species for those measured with hourly time resolution with derivatization (shaded colors) a) and those measured multiple times per day at lower time-resolution without derivatization b). Legend entries correspond to compound numbers in Table 1 and colors in b) same as that used in Figure 1b). Total SQT and diterpenes quantified during runs without derivatization are overlaid in black for reference in panel a). Concurrent speciation shown in b).

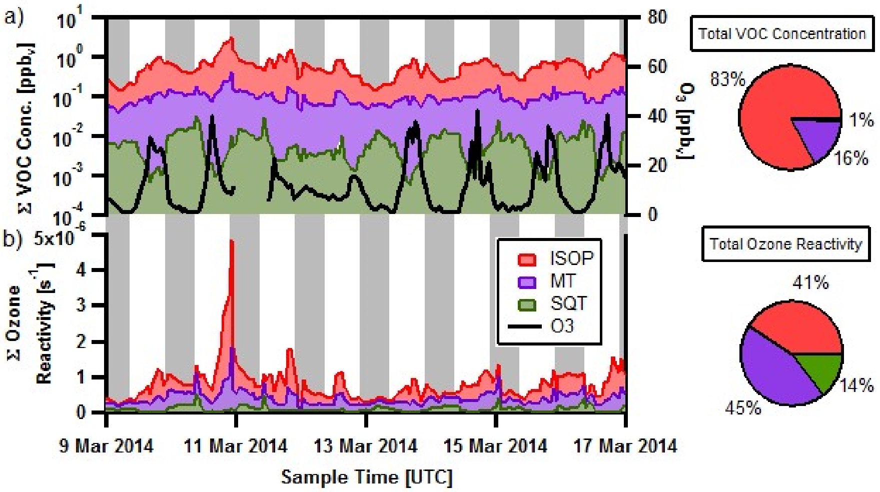

Figure 4: Wet season selected timeline of summed gas-phase VOC concentrations, isoprene (ISOP, red), monoterpenes (MT, purple), and estimated sesquiterpenes (SQT, green) and ozone concentration (O_3, black) in panel a). Average ~~%~~percentage contributions during wet season for each group to total VOC concentration during also shown in top pie chart. Panel b) depicts summed contribution to ozone reactivity from isoprene, monoterpenes, and sesquiterpenes. Average ~~%~~percentage contributions during wet season for each VOC to total ozone reactivity shown in bottom pie chart. Local nighttime hours indicated in grey. Local time is -4 h relative to UTC.

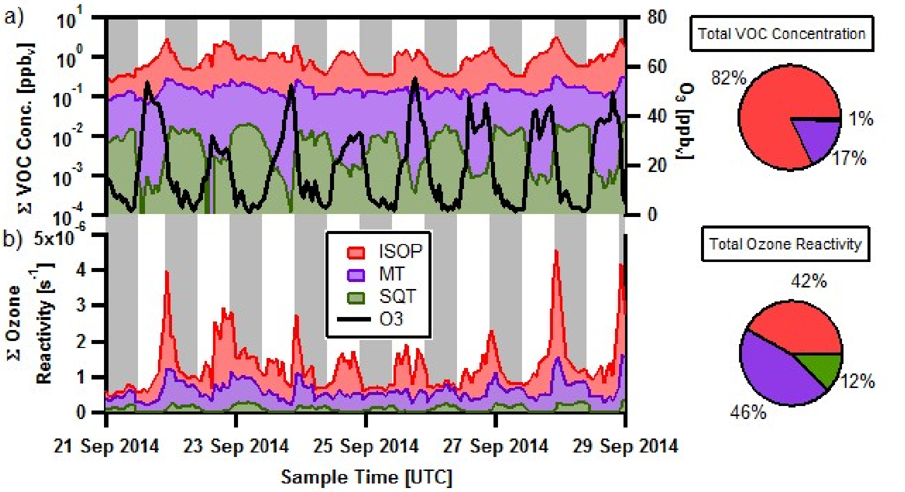

Figure 5: Dry season selected timeline of summed gas-phase VOC concentrations, isoprene (ISOP, red), monoterpenes (MT, purple), and estimated sesquiterpenes (SQT, green) and ozone concentration (O_3, black) in panel a). Average ~~%~~percentage contributions during dry season for each group to total VOC concentration during also shown in top pie chart. Panel b) depicts summed contribution to ozone reactivity from isoprene, monoterpenes, and sesquiterpenes. Average ~~%~~percentage contributions during dry season for each VOC to total ozone reactivity shown in bottom pie chart. Local nighttime hours indicated in grey. Local time is -4 h relative to UTC.

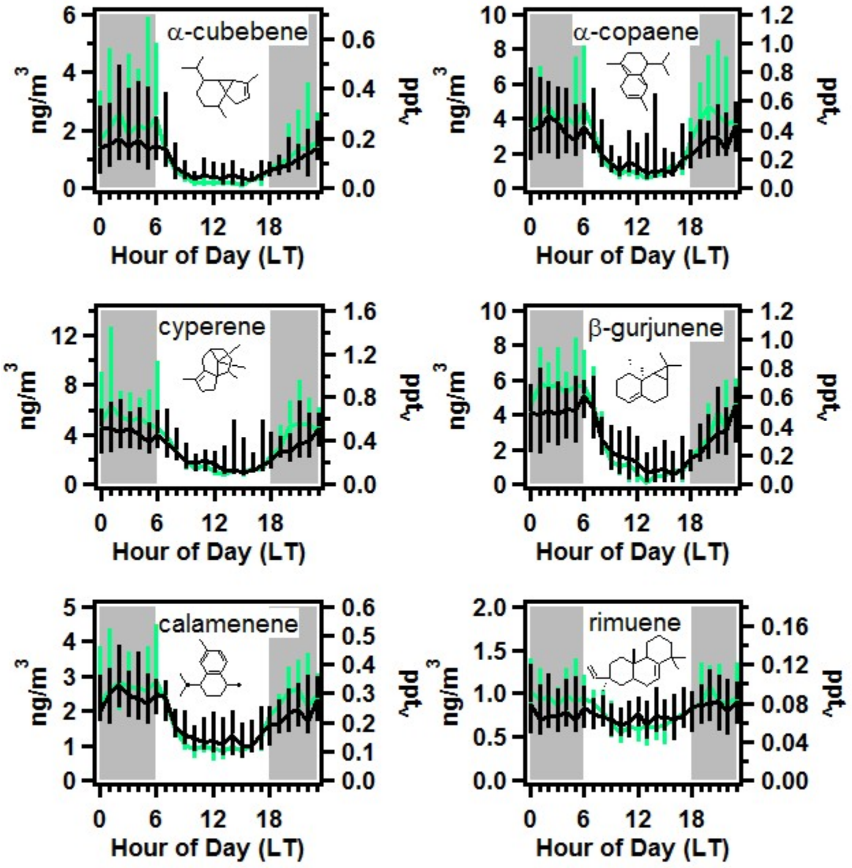

Figure 6: Average diel profiles of selected sesquiterpenes and one diterpene (rimuene) for wet season (light green) and dry season (black) in gas phase. Solid line is drawn through median values, and bars indicate range from 25- to 75- percentiles. Local night time hours are indicated in grey shading.

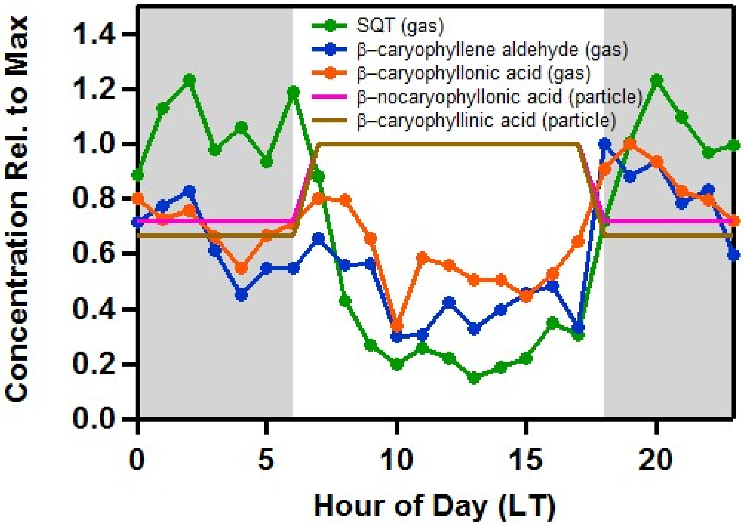

Figure 7: Diel profiles during wet season of total sesquiterpenes (SQT) and four β-caryophyllene oxidation products in gas and particle phases. For each series, data are normalized by the maximum observed concentration within the series and shown as concentration relative to max. Local night time hours indicated in grey.

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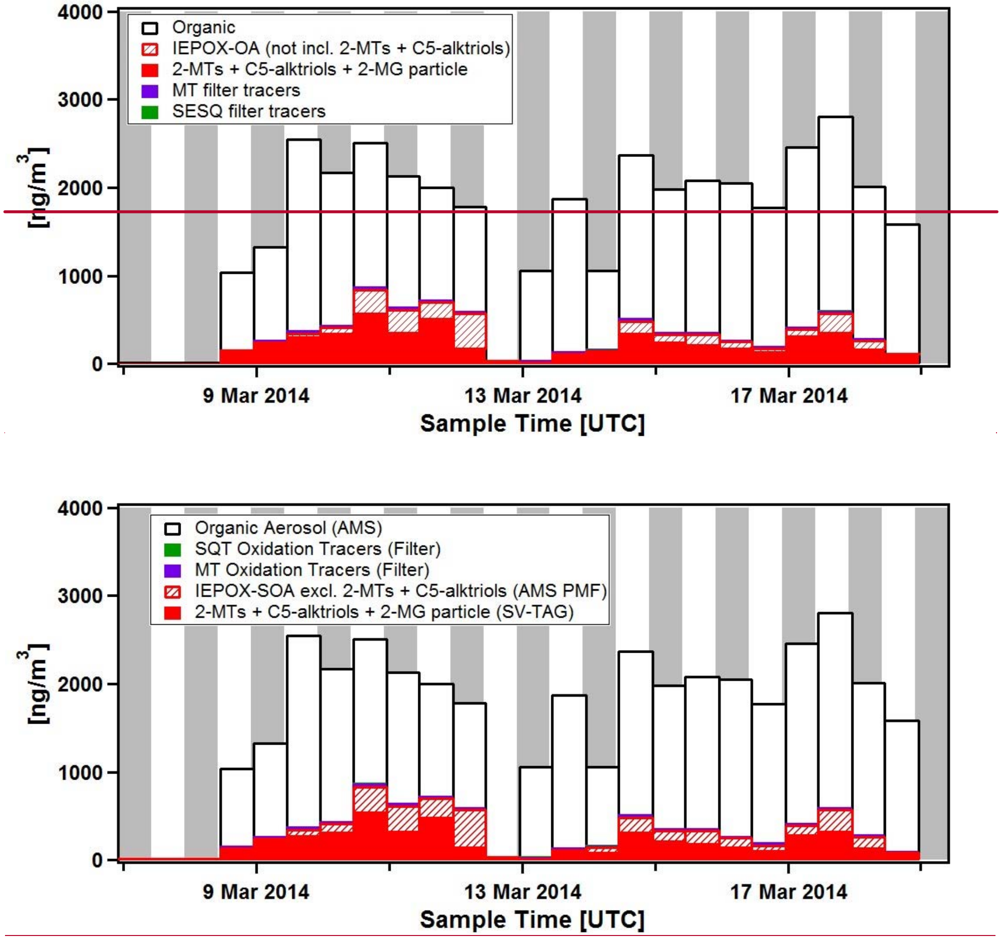

Figure 8: Estimated contributions to total organic aerosol from particle-phase tracers/statistical factors attributed to oxidation of isoprene (red) (IEPOX-SOA, 2-MTs + ~~C5alktriols~~C5-alktriols + 2-MG), monoterpene (purple) (MT filter tracers), and sesquiterpene (green) (~~SESQ~~SQT filter tracers). 2-MTs = 2-methyl tetrols, 2-MG = 2-methylglyceric acid, and C5alktriols is C5-alkene triols. Local night time hours indicated in grey.

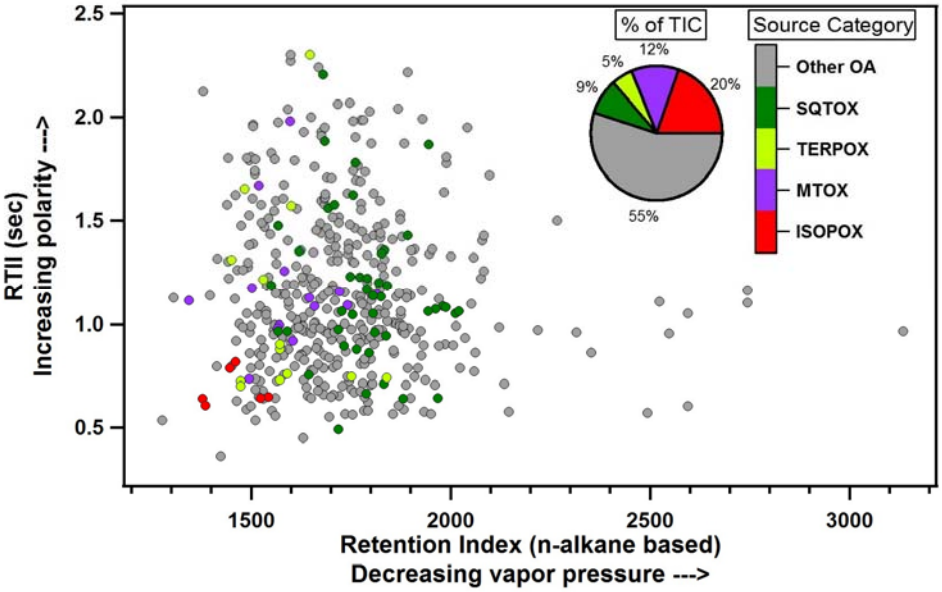

Figure 9: GCxGC Chromatogram of nighttime filter sample during wet season. Peaks are assigned source categories of isoprene oxidation products (ISOPOX) in red, monoterpene oxidation products (MTOX) in purple, terpene oxidation products (TERPOX) in yellow, and sesquiterpene oxidation products (SQTOX) in green. Other unidentified OA in gray. ~~%~~Percentage of total ion chromatogram made up by each source category shown in pie chart.

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Supplementary Information for manuscript:

Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet and dry seasons

Lindsay D. Yee[1], Gabriel Isaacman-VanWertz[1*], Rebecca A. Wernis[2], Meng Meng[3**], Ventura Rivera[3], Nathan M. Kreisberg[4], Susanne V. Hering[4], Mads S. Bering[5], Marianne Glasius[5], Mary Alice Upshur[6], Ariana Gray Bé[6], Regan J. Thomson[6], Franz M. Geiger[6], John H. Offenberg[7], Michael Lewandowski[7], Ivan Kourtchev[8], Markus Kalberer[8], Suzane de Sá[9], Scot T. Martin[9,10], M. Lizabeth Alexander[11], Brett B. Palm[12], Weiwei Hu[12], Pedro Campuzano-Jost[12], Douglas A. Day[12], Jose L. Jimenez[12], Yingjun Liu[9***], Karena A. McKinney[9****], Paulo Artaxo[13], Juarez Viegas[14], Antonio Manzi[14], Maria B. Oliveira[15], Rodrigo de Souza[15], Luiz A. T. Machado[16], Karla Longo[17], and Allen H. Goldstein[1]

[1]Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley, 94720, USA
*Now at Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, 24061, USA
[2]Department of Civil and Environmental Engineering, University of California, Berkeley, Berkeley, 94720, USA
[3]Department of Chemical Engineering, University of California, Berkeley, Berkeley, 94720, USA
**Now at Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, CA
[4]Aerosol Dynamics Inc., Berkeley, 94710, USA
[5]Department of Chemistry, Aarhus University, 8000 Aarhus C, Denmark
[6]Department of Chemistry, Northwestern University, Evanston, 60208, USA
[7]National Exposure Research Laboratory, Exposure Methods and Measurements Division, United States Environmental Protection Agency, Research Triangle Park, 27711, USA
[8]Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, United Kingdom
[9]School of Engineering and Applied Sciences, Harvard University, Cambridge, 02138, USA
***Now at Department of Environmental Science, Policy, and Management, University of California, Berkeley, Berkeley,
****Now at Department of Chemistry, Colby College, Waterville, Maine, 04901, USA
[10]Department of Earth and Planetary Sciences, Harvard University, Cambridge, 02138, USA
94720, USA
[11]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, 99352, USA
[12]Dept. of Chemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, 80309, USA
[13]Department of Applied Physics, University of São Paulo, SP, Brazil
[14]Instituto Nacional de Pesquisas da Amazonia, Manaus, AM, Brazil
[15]Universidade do Estado do Amazonas, Manaus, AM, Brazil;
[16]Instituto Nacional de Pesquisas Espiacais, São José dos Campos, SP, Brazil
[17]Instituto Nacional de Pesquisas Espiacais, Cachoeira Paulista, SP, Brazil

Correspondence to: Lindsay D. Yee (lindsay.yee@berkeley.edu)

SI Tables

Table S1: Custom MS Library Names referred to in **Table S5** with sources of mass spectra. Experimental conditions for sesquiterpene oxidation chamber experiments provided in Table S2.

Custom MS Library Name	**Source of MS$^{\text{Previous Publication}}$**
acedox	α-cedrene + O3
acedox2	α-cedrene + NOx + hv[1]
acopox	α-copaene + O3[2]
ahumox	α-humulene + O3
ahumox2	α-humulene + NOx + hv[1]
apinox	α-pinene + O3[3]
apinox2	α-pinene + O3[3]
aromox	aromadendrene + O3[2]
aromox2	aromadendrene + NOx + hv
bcpox	Synthesized β-caryophyllene oxidation products[4]: β-caryophyllene aldehyde, β-nocaryophyllone aldehyde, β-caryophyllonic acid, β-nocaryophyllonic acid, β-caryophyllinic acid, β-nocaryophyllinic acid
bcpox2	β-caryophyllene + NOx + hv[2]
bcpox3	β-caryophyllene + NOx + acidic seed + hv
bfarnox	β-farnasene + NOx + hv[2]
copox	copaiba oil + O3
limonox	limonene + O3[3]
mainlib	NIST 14 Library
mane2010.hp	proprietary library from a flavour and fragrance company (MANE)
myrcox	myrcene + O3[3]
soasox/soasox2	Previously identified compounds in filters from Southern Oxidant and Aerosol Study (SOAS)[3]

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[1] Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M. and Offenberg, J. H.: Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: alpha-cedrene, beta-caryophyllene, alpha-humulene and alpha-farnesene with O-3, OH and NO3 radicals, Environ. Chem., 10(3), 178–193, doi:10.1071/en13025, 2013.

[2] Offenberg, J. H., Lewandowski, M., Kleindienst, T. E., Docherty, K. S., Jaoui, M., Krug, J., Riedel, T. P. and Olson, D. A.: Predicting Thermal Behavior of Secondary Organic Aerosols, Environ. Sci. Technol., 51, 9911–9919, doi:10.1021/acs.est.7b01968, 2017.

[3] Zhang et al., PNAS

[4] Be, A. G., Upshur, M. A., Liu, P., Martin, S. T., Geiger, F. M., Thomson, R. J. and Paulson, J. A.: Cloud Activation Potentials for Atmospheric α-Pinene and β-Caryophyllene Ozonolysis Products, ACS Cent. Sci., 3(7), 715–725, doi:10.1021/acscentsci.7b00112, 2017.

Table S2: Experimental conditions for sesquiterpene ozonolysis/photolysis experiments performed by U.S. EPA and used for making custom MS libraries as listed in Table S1.

Custom MS Library Name	experiment ID	temp (°C)	RH (%)	hydrocarbon (HC)	initial/final [HC] (ppmC)	initial/steady-state [NO] (ppm)	initial/steady-state [O_3] (ppm)	SOA mass (µg m^{-3})	OM/OC
acedox	ER721	22.3	31.6	α-cedrene	0.68/0.10	N/A	0.203/0.166	230.5	1.4
acedox2	ER649	23.8	27.9	α-cedrene	0.64/0.39	0.108/0.059	0/0.002	33.9	1.4
acopox	ER734	22.1	31.7	α-copaene	0.66/0.01	N/A	0.213/0.156	271.3	1.4
ahumox	ER720	22.1	31.6	α-humulene	0.40/0.00	N/A	0.186/0.061	170.8	1.5
ahumox2	ER648	24.3	27.8	α-humulene	0.63/0.00	0.093/0.028	0/0.004	126.4	N/A
aromox	ER742	22.1	31.5	aromadendrene	0.65/0.06	N/A	0.201/0.147	87.8	1.4
aromox2	ER743	24.7	31.2	aromadendrene	0.66/0.34	0.055/0.039	0/0.004	43.7	1.5
bcpox2	ER716	24.7	29.3	β-caryophyllene	0.58/0.00	0.099/0.052	0/0.002	125.1	1.6
bcpox3	ER717	24.7	29.3	β-caryophyllene	0.54/0.03	0.103/0.061	0/0.002	160.1	1.9
bfarnox	ER711	24.8	31.1	β-farnesene	N/A	0.091/0.009	0/0.025	123.6	1.8
copox	ER722	22.2	31.6	Various in copaiba essential oil (Young Living Essential Oil)	0.25[1]/0.00	N/A	0.198/0.134	271.3	1.4

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[1] Estimated from sum of all major (presumably SQT) peaks measured by GC-FID. Reported value will be underestimate of actual HC in experiment, thus SOA yield likely overestimated.

Table S3: Composition by percent mass of total sesquiterpenes (% $\sum$SQT) and percent contribution to total ozone reactivity (% $\sum kO_{3i}[SQT_i]$) from sesquiterpene ozonolysis at measurement site and in three commercial essential oils. Concentrations of each species estimated by using an average instrument response factor for several sesquiterpene standards unless otherwise noted that an authentic standard was used. For unidentified species, average kO_3 of all sesquiterpene species (from experimental determination or estimated as in Table 1) used for estimated % contribution to total ozone reactivity. BDL = Below Detection Limit, N/A = Not Applicable. Top three values for each column in bold print.

Sample:	Feb 13 2014 06:47 AM UTC		Copaiba Oil		Copaiba Oil		Copaiba Oil		Andiroiba Oil	
Location/Origin:	T3, Manacapuru, AM, Brazil		Young Living Essential Oil, (origin Brazil)		Manacapuru, AM, Brazil		Bolivia		Manacapuru, AM, Brazil	
SQT	% $\sum$SQT	%$\sum kO_{3i}$ [SQT_i]	% $\sum$SQT	%$\sum kO_{3i}$ [SQT_i]	% $\sum$SQT	%$\sum kO_{3i}$ [SQT_i]	% $\sum$SQT	%$\sum kO_{3i}$ [SQT_i]	% $\sum$SQT	%$\sum kO_{3i}$ [SQT_i]
α-copaene	2.5%	0.7%	5.6%	0.1%	4.5%	0.3%	4.8%	0.2%	6.3%	0.2%
cyperene	4.6%	4.0%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
β-gurjunene	1.4%	0.2%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
rimuene	6.4%	0.8%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
cis-calamene	**9.2%**	**7.9%**	1.1%	0.1%	5.0%	1.0%	3.3%	0.4%	BDL	N/A
α-cubebene	3.1%	2.2%	2.6%	0.2%	BDL	N/A	BDL	N/A	BDL	N/A
unidentified	1.2%	1.0%	BDL	N/A	4.9%	1.0%	**10.9%**	**1.3%**	**14.8%**	**1.5%**
cyclosativene	2.2%	0.3%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
β-elemene	2.5%	0.1%	1.1%	0.0%	2.5%	0.0%	2.5%	0.0%	BDL	N/A
α-cedrene	BDL	BDL	BDL	N/A	2.4%	0.0%	3.5%	0.0%	6.4%	0.0%
unidentified	2.8%	2.4%	BDL	N/A	3.9%	0.8%	**7.4%**	0.9%	7.5%	0.8%
unidentified	0.7%	0.6%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
unidentified	BDL	BDL	BDL	N/A	1.1%	0.4%	1.8%	0.4%	BDL	N/A
α-patchoulene	2.5%	0.3%	BDL	N/A	BDL	N/A	0.6%	0.0%	BDL	N/A
SQT202_A	0.7%	0.6%	BDL	N/A	BDL	N/A	1.1%	0.1%	BDL	N/A
γ-muurolene	4.3%	3.1%	1.8%	0.1%	BDL	N/A	BDL	N/A	BDL	N/A
α-amorphene	1.1%	1.6%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
β-selinene	3.4%	0.1%	2.0%	0.0%	**13.8%**	0.1%	3.1%	0.0%	9.1%	0.0%
α-muurolene	**9.0%**	**12.9%**	BDL	N/A	5.8%	1.9%	0.6%	0.1%	BDL	N/A
unidentified	5.7%	4.9%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
β-bisabolene	2.9%	4.2%	BDL	N/A	**16.3%**	**5.5%**	5.0%	1.0%	BDL	N/A
γ-cadinene	3.4%	2.5%	1.7%	0.1%	5.7%	1.0%	3.0%	0.3%	BDL	N/A
δ-cadinene	**13.2%**	**35.7%**	**8.1%**	**1.9%**	2.0%	1.2%	1.1%	0.4%	BDL	N/A
selinene <7-epi-α>	2.6%	7.0%	1.3%	0.3%	BDL	N/A	BDL	N/A	BDL	N/A
γ-cuprenene	0.6%	0.5%	BDL	N/A	BDL	N/A	0.6%	0.1%	BDL	N/A
α-cadinene	0.5%	0.8%	0.6%	0.1%	0.7%	0.2%	0.7%	0.1%	BDL	N/A
unidentified	BDL	BDL	0.6%	0.0%	BDL	N/A	0.7%	0.1%	BDL	N/A
selina-3,7(11)-diene	0.7%	1.9%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
pimaradiene	0.6%	0.1%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
sandaracopimaradiene	5.5%	0.7%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
kaurene	2.1%	0.0%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
SQT202_B	1.3%	1.2%	0.6%	0.0%	1.7%	0.3%	2.3%	0.3%	BDL	N/A
SQT202_C/cuparene	0.7%	0.6%	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
isocaryophyllene	BDL	N/A	2.6%	0.2%	6.2%	1.1%	7.3%	0.7%	**10.9%**	**1.0%**
β-caryophyllene	BDL	N/A	**56.2%**	**95.0%**	**17.8%**	**80.2%**	**32.9%**	**88.2%**	**41.5%**	**95.9%**

trans-α-bergamotene	BDL	N/A	1.0%	0.1%	1.0%	0.3%	4.3%	0.9%	3.5%	0.6%
α-humulene	BDL	N/A	0.7%	**1.1%**	0.7%	**3.3%**	1.6%	**4.3%**	BDL	N/A
(-) alloaromadendrene	1.4%	0.0%	**5.9%**	0.0%	BDL	N/A	BDL	N/A	BDL	N/A
unidentified	BDL	N/A	1.2%	0.1%	BDL	N/A	BDL	N/A	BDL	N/A
unidentified	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
β-bisabolene	BDL	N/A	0.8%	0.1%	3.9%	1.3%	0.7%	0.1%	BDL	N/A
α-selinene	BDL	N/A	3.0%	0.2%	BDL	N/A	BDL	N/A	BDL	N/A
valencene-eremophilene	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A
(+) longifolene	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A	BDL	N/A

Table S4: Comparison of % contribution of three sesquiterpenes: β-caryophyllene, α-copaene, and β-elemene to total sesquiterpenes in ambient air, essential oils, and tissue of Amazonian trees. Major component of sesquiterpene compounds also listed for reference. References listed as footnotes.

	Relative abundance raw integrated area basis				**Relative abundance mass quantified basis**			
Analyte$^{Ref.}$	**% β-caryophyllene**	**% α-copaene**	**% β-elemene**	**Major component**	**% β-caryophyllene**	**% α-copaene**	**% β-elemene**	**Major component**
Ambient air, T3, 13 Feb 2014 06:47 AM UTC[1]	BDL	12.6	2.5	δ-cadinene	BDL	2.5	2.5	δ-cadinene
Copaiba oil, Manacapuru, Brazil[1]	6.9	17.5	1.9	α-copaene	17.8	4.5	2.5	β-caryophyllene
Copaiba oil, Bolivia [1]	12.4	18.3	1.9	α -copaene	32.9	4.8	2.5	β-caryophyllene
Andiroba oil, Manacapuru Brazil[1]	13.7	20.8	BDL	α -cedrene	41.5	6.3	BDL	β-caryophyllene
Copaiba oil, Brazil, Young Living Essential Oils[1]	30.0	30.0	1.0	α -copaene	52.5	5.3	1	β-caryophyllene
Copaifera officinalis, three-week old seedlings (leaves)[2]	N/A	N/A	N/A	N/A	5.8	0.5	0.3	Germacrene D
Copaifera officinalis, three-week old seedlings (stems)[2]	N/A	N/A	N/A	N/A	15.1	0.5	0.4	Germacrene D
Copaifera officinalis, three-week old seedlings (roots)[2]	N/A	N/A	N/A	N/A	82.6	BDL	ND	β-caryophyllene
Copaifera officinalis, two-year old trees (leaves)[2]	N/A	N/A	N/A	N/A	12	1.1	1	Germacrene D
Copaifera officinalis, two-year old trees (stems)[2]	N/A	N/A	N/A	N/A	18	1	0.5	Germacrene D
Copaifera officinalis, two-year old trees (roots)[2]	N/A	N/A	N/A	N/A	67.7	1.7	3.9	β-caryophyllene
Copaifera officinalis, three-week old seedlings injured, emissions[2]	N/A	N/A	N/A	N/A	21.6	1.2	1.9	Germacrene D
Rosewood oil, *Aniba rosaeodora Ducke*[3]	3.4	16.3	6.3	α -copaene	N/A	N/A	N/A	N/A
C1 Commercial copaiba oil, Tarauacá, Acre state, Brazil[4]	56.3	2.0	1.0	β-caryophyllene	N/A	N/A	N/A	N/A
C2 Commercial copaiba oil,	26.5	N/A	N/A	β-caryophyllene	N/A	N/A	N/A	N/A

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[1] This study

[2] Chen et al., 2009

[3] Fidelis et al., 2011

[4] Soares et al., 2013

	Relative abundance raw integrated area basis				**Relative abundance mass quantified basis**			
Analyte[Ref.]	**% β-caryophyllene**	**% α-copaene**	**% β-elemene**	**Major component**	**% β-caryophyllene**	**% α-copaene**	**% β-elemene**	**Major component**
Tarauacá, Acre state, Brazil[4]								
C3 Commercial copaiba oil, Tarauacá, Acre state, Brazil[4]	9.9	32.6	4.3	α -copaene	N/A	N/A	N/A	N/A
C4-VF (volatile fraction, sesquiterpenes only content of C4 copaiba oil), Baía do Portel, PA, Brazil[4]	42.4	11.2	2.0	β-caryophyllene	N/A	N/A	N/A	N/A
Mean	**22.4**	**17.9**	**2.6**		**33.4**	**2.7**	**1.7**	
Standard Deviation	17.9	9.4	1.8		24.9	2.1	1.2	
Median	13.7	17.5	2.0		21.6	1.7	1.5	

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Table S5: Peaks attributed to BVOC oxidation products in shown in GCxGC chromatogram of main text (Figure 9). Best MS matches shown. Library names and source of MS are listed in ~~Table S4.~~Table S1.

Compound Name/Description	d-alkane LRI_I	d-alkane Library LRI_I	Best Match Library_ Name	Library _Match_ Factor	Library_Reverse _Match_Factor	RTI_ min	RTII _sec	Assigned Source Category
ISOP 2-methyltetrol_1	1574	1572	soasox	943	944	37.53	0.65	ISOPOX
ISOP isoprene SOA 1, Surratt 2006	1475	1475	soasox	921	921	34.09	0.79	ISOPOX
ISOP 2-methyltetrol_2	1555	1554	soasox	895	895	36.86	0.64	ISOPOX
ISOP isoprene SOA 2, Surratt 2006	1490	1489	soasox	888	890	34.60	0.82	ISOPOX
ISOP C5alkenetriol 1	1413	1413	soasox	859	868	31.94	0.61	ISOPOX
ISOP C5alkenetriol 2	1407	1406	soasox	786	806	31.70	0.64	ISOPOX
	1525	1523	limonox	855	856	35.81	0.74	MTOX
MT 2-hydroxyglutaric acid	1598	1597	soasox	897	898	38.35	0.98	MTOX
MT MBTCA	1776	1778	soasox	893	894	43.97	1.09	MTOX
	1615	1611	myrcox	815	818	38.89	1.26	MTOX
MT MBTCA isomer	1852	1853	soasox	803	810	46.20	1.14	MTOX
	1680	1679	copox	821	828	40.93	1.13	MTOX
MT pinic acid	1693	1693	soasox	778	796	41.35	1.09	MTOX
MT cis-norpinic acid	1630	1632	soasox2	833	840	39.36	1.98	MTOX
MT 3-hydroxyglutaric acid	1602	1602	soasox	774	785	38.50	1.00	MTOX
MT 3-hydroxy-4,4-dimethylglutaric acid	1637	1636	soasox	818	823	39.60	0.92	MTOX
MT Tricarballylic acid	1757	-1	mainlib	704	731	43.35	1.16	MTOX
	1372	1335	myrcox	800	804	30.38	1.11	MTOX
MT 2,3-dihydroxy-4-oxo pentanoic acid	1533	1532	soasox	684	709	36.08	1.17	MTOX
	1653	1653	copox	914	914	40.10	1.35	SQTOX
β-caryophyllene aldehyde, TMS	1714	1714	bcpox2	899	900	42.02	2.21	SQTOX
	1763	1764	soasox	891	892	43.54	1.06	SQTOX
	1678	1677	copox	883	885	40.89	0.76	SQTOX
	1870	1870	ahumox2	882	883	46.71	0.71	SQTOX
	1744	1746	soasox2	867	870	42.96	1.58	SQTOX
β-nocaryophyllone aldehyde	1754	1757	soasox	861	864	43.27	0.49	SQTOX
	1582	1581	bcpox2	836	847	37.80	1.18	SQTOX
	1843	1850	bcpox3	681	687	45.93	1.14	SQTOX
α-copaene oxidation product	1719	1722	acopox	844	848	42.18	1.88	SQTOX
	2002	2001	copox	794	802	50.42	1.07	SQTOX

Compound Name/Description	d-alkane LRI_I	d-alkane Library LRI_I	Best Match Library_ Name	Library _Match_ Factor	Library_Reverse _Match_Factor	RTI_ min	RTII _sec	Assigned Source Category
	1790	1791	soasox	799	817	44.40	1.05	SQTOX
	1754	1753	aromox2	815	826	43.27	0.98	SQTOX
	2052.63	2053	copox	702	702	51.75	1.05	SQTOX
	1824.83	1824	ahumox2	813	817	45.42	0.66	SQTOX
	1983.45	1985	bcpox2	761	773	49.91	1.06	SQTOX
	1600	-1	mainlib	779	832	38.42	0.97	SQTOX
	1842.76	1844	acopox	767	773	45.93	1.05	SQTOX
	1797.52	1798	bcpox2	788	799	44.64	1.78	SQTOX
	2007.52	2005	bcpox3	794	820	50.58	0.64	SQTOX
	1726.71	1727	bcpox3	785	795	42.41	1.56	SQTOX
	1791.3	-1	mane2010.hp	651	667	44.44	1.62	SQTOX
	1875.86	1876	bfarnox	560	604	46.86	0.94	SQTOX
	1767.7	1768	ahumox	754	761	43.70	0.89	SQTOX
	1826.21	1821	soasox2	688	698	45.46	1.17	SQTOX
	1827.59	1838	bcpox2	626	647	45.50	1.22	SQTOX
	1846.9	1847	ahumox2	615	628	46.04	0.96	SQTOX
	1856.55	1855	bfarnox	656	673	46.32	1.20	SQTOX
β-nocaryophyllonic acid, TMS	1984.83	-1	bcpox	698	714	49.95	1.87	SQTOX
	1862.07	1872	acedox2	592	595	46.47	1.13	SQTOX
	1871.72	1872	aromox2	613	635	46.75	1.36	SQTOX
	1920	1919	ahumox	779	809	48.11	0.64	SQTOX
	1800	1800	ahumox	561	616	44.71	0.88	SQTOX
	1831.72	1828	acopox	568	585	45.61	0.86	SQTOX
	1808.28	1808	bcpox2	617	639	44.95	1.23	SQTOX
	1863.45	1864	soasox2	662	676	46.51	1.34	SQTOX
	2021.05	2020	bcpox2	655	683	50.93	1.09	SQTOX
	2028.57	2029	copox	658	664	51.12	1.08	SQTOX
	1878.62	1879	acedox	548	557	46.94	1.18	SQTOX
β-caryophyllonic acid, TMS	1931.03	1932	bcpox	663	692	48.43	1.43	SQTOX
	2061.65	2063	bcpox2	562	582	51.98	1.06	SQTOX
	1877.24	1879	soasox	890	890	46.90	0.74	TERPOX
	1633.54	1633	ahumox	882	883	39.48	1.57	TERPOX
	1786.34	1786	copox	891	894	44.28	0.75	TERPOX

Compound Name/Description	d-alkane LRI_I	d-alkane Library LRI_I	Best Match Library_ Name	Library _Match_ Factor	Library_Reverse _Match_Factor	RTI_ min	RTII _sec	Assigned Source Category
	1479.78	1479	soasox2	870	873	34.24	1.31	TERPOX
	1513.48	1510	apinox	793	804	35.42	1.65	TERPOX
	1603.73	1602	soasox2	799	808	38.54	0.73	TERPOX
	1680.75	1682	soasox	820	829	40.96	2.30	TERPOX
	1503.37	1504	soasox	805	812	35.06	0.73	TERPOX
	1503.37	1504	soasox	825	835	35.06	0.70	TERPOX
	1561.8	1538	mainlib	669	900	37.10	1.22	TERPOX

~~**Table S4: Custom MS Library Names referred to in Table S3 with sources of mass spectra. Experimental conditions for sesquiterpene oxidation chamber experiments provided in Table S5.**~~

~~**Custom MS Library Name**~~	~~**Source of MS**$^{\text{Previous Publication}}$~~
~~acedox~~	~~α-cedrene + O3~~
~~acedox2~~	~~α-cedrene + NOx + hv[5]~~
~~acopox~~	~~α-copaene + O3[6]~~
~~ahumox~~	~~α-humulene + O3~~
~~ahumox2~~	~~α-humulene + NOx + hv[6]~~
~~apinox~~	~~α-pinene + O3[7]~~
~~apinox2~~	~~α-pinene + O3[3]~~
~~aromox~~	~~aromadendrene + O3[7]~~
~~aromox2~~	~~aromadendrene + NOx + hv~~
~~bcpox~~	~~Synthesized β-caryophyllene oxidation products[8]: β-caryophyllene aldehyde, β-nocaryophyllone aldehyde, β-caryophyllonic acid, β-nocaryophyllonic acid, β-caryophyllinic acid, β-nocaryophyllinic acid~~
~~bcpox2~~	~~β-caryophyllene + NOx + hv[7]~~
~~bcpox3~~	~~β-caryophyllene + NOx + acidic seed + hv~~
~~bfarnox~~	~~β-farnasene + NOx + hv[7]~~
~~copox~~	~~copaiba oil + O3~~
~~limonox~~	~~limonene + O3[3]~~
~~mainlib~~	~~NIST 14 Library~~
~~mane2010.hp~~	~~proprietary library from a flavour and fragrance company (MANE)~~
~~myrcox~~	~~myrcene + O3[3]~~
~~soasox/soasox2~~	~~Previously identified compounds in filters from Southern Oxidant and Aerosol Study (SOAS)[3]~~

~~**Table S5: Experimental conditions for sesquiterpene ozonolysis/photolysis experiments performed by U.S. EPA and used for making custom MS libraries as listed in Table S4.**~~

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[5] ~~Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M. and Offenberg, J. H.: Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes: alpha-cedrene, beta-caryophyllene, alpha-humulene and alpha-farnesene with O-3, OH and NO3 radicals, Environ. Chem., 10(3), 178–193, doi:10.1071/en13025, 2013.~~

[6] ~~Offenberg, J. H., Lewandowski, M., Kleindienst, T. E., Docherty, K. S., Jaoui, M., Krug, J., Riedel, T. P. and Olson, D. A.: Predicting Thermal Behavior of Secondary Organic Aerosols, Environ. Sci. Technol., 51, 9911–9919, doi:10.1021/acs.est.7b01968, 2017.~~

[7] ~~Zhang et al., PNAS~~

[8] ~~Be, A. G., Upshur, M. A., Liu, P., Martin, S. T., Geiger, F. M., Thomson, R. J. and Paulson, J. A.: Cloud Activation Potentials for Atmospheric α-Pinene and β-Caryophyllene Ozonolysis Products, ACS Cent. Sci., 3(7), 715–725, doi:10.1021/acscentsci.7b00112, 2017.~~

~~Custom MS Library Name~~	~~experiment ID~~	~~temp (°C)~~	~~RH (%)~~	~~hydrocarbon (HC)~~	~~initial/final [HC] (ppmC)~~	~~initial/steady-state [NO] (ppm)~~	~~initial/steady-state [O$_3$] (ppm)~~	~~SOA mass (µg m^{-3})~~	~~OM/OC~~
~~acedox~~	~~ER721~~	~~22.3~~	~~31.6~~	~~α-cedrene~~	~~0.68/0.10~~	~~N/A~~	~~0.203/0.166~~	~~230.5~~	~~1.4~~
~~acedox2~~	~~ER649~~	~~23.8~~	~~27.9~~	~~α-cedrene~~	~~0.64/0.39~~	~~0.108/0.059~~	~~0/0.002~~	~~33.9~~	~~1.4~~
~~acopox~~	~~ER734~~	~~22.1~~	~~31.7~~	~~α-copaene~~	~~0.66/0.01~~	~~N/A~~	~~0.213/0.156~~	~~271.3~~	~~1.4~~
~~ahumox~~	~~ER720~~	~~22.1~~	~~31.6~~	~~α-humulene~~	~~0.40/0.00~~	~~N/A~~	~~0.186/0.061~~	~~170.8~~	~~1.5~~
~~ahumox2~~	~~ER648~~	~~24.3~~	~~27.8~~	~~α-humulene~~	~~0.63/0.00~~	~~0.093/0.028~~	~~0/0.004~~	~~126.4~~	~~N/A~~
~~aromox~~	~~ER742~~	~~22.1~~	~~31.5~~	~~aromadendrene~~	~~0.65/0.06~~	~~N/A~~	~~0.201/0.147~~	~~87.8~~	~~1.4~~
~~aromox2~~	~~ER743~~	~~24.7~~	~~31.2~~	~~aromadendrene~~	~~0.66/0.34~~	~~0.055/0.039~~	~~0/0.004~~	~~43.7~~	~~1.5~~
~~bcpox2~~	~~ER716~~	~~24.7~~	~~29.3~~	~~β-caryophyllene~~	~~0.58/0.00~~	~~0.099/0.052~~	~~0/0.002~~	~~125.1~~	~~1.6~~
~~bcpox3~~	~~ER717~~	~~24.7~~	~~29.3~~	~~β-caryophyllene~~	~~0.54/0.03~~	~~0.103/0.061~~	~~0/0.002~~	~~160.1~~	~~1.9~~
~~bfarnox~~	~~ER711~~	~~24.8~~	~~31.1~~	~~β-farnesene~~	~~N/A~~	~~0.091/0.009~~	~~0/0.025~~	~~123.6~~	~~1.8~~
~~copox~~	~~ER722~~	~~22.2~~	~~31.6~~	~~Various in copaiba essential oil (Young Living Essential Oil)~~	~~0.25[9]/0.00~~	~~N/A~~	~~0.198/0.134~~	~~271.3~~	~~1.4~~

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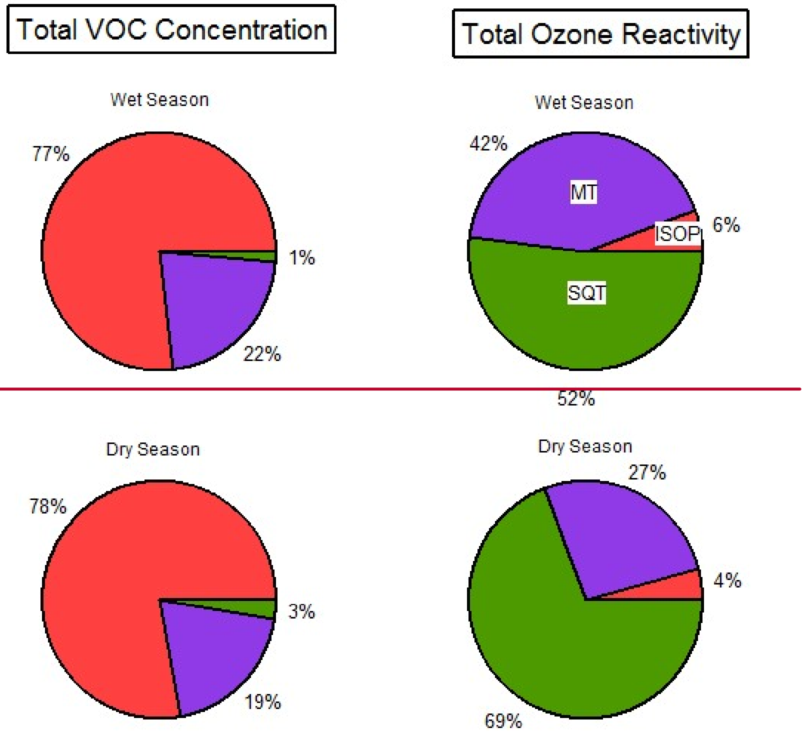
[9] ~~Estimated from sum of all major (presumably SQT) peaks measured by GC-FID. Reported value will be underestimate of actual HC in experiment, thus SOA yield likely overestimated.~~

SI Figures



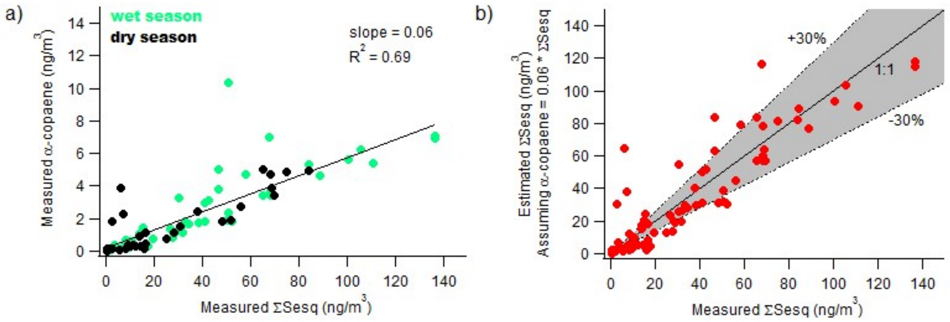


Figure S1~~: Average % of isoprene (ISOP, red), monoterpenes (MT, purple), and sesquiterpenes (SQT, green) during wet and dry seasons contributing to their summed VOC concentration and total ozone reactivity for chemical composition within/near the canopy. VOC concentrations are based on measurements from (Alves et al., 2016) and ozone reactivity calculated using monoterpene composition according to (Shu and Atkinson, 1994) and sesquiterpene composition according to copaiba essential oil (source: Young Living) in~~

: During underivatized runs (n=79), α-copaene on average accounts for 6% of total observed sesquiterpenes in panel a) within +/- 30% in panel b).

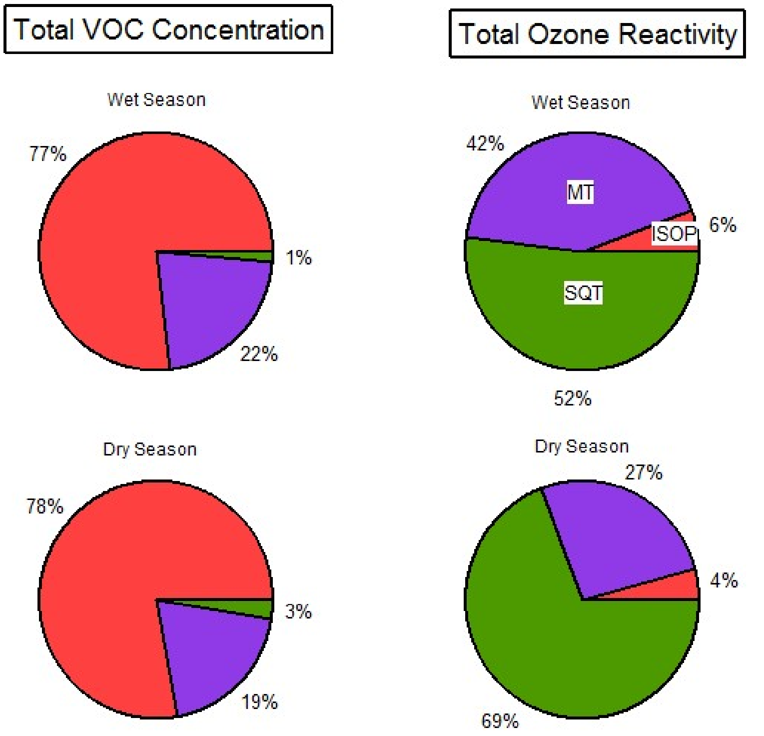
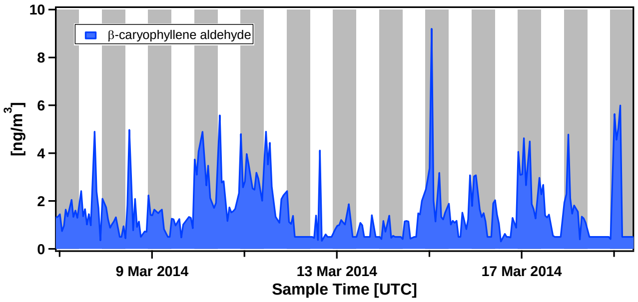


Figure S2: Average percentage of isoprene (ISOP, red), monoterpenes (MT, purple), and sesquiterpenes (SQT, green) during wet and dry seasons contributing to their summed VOC concentration and total ozone reactivity for chemical composition within/near the canopy. VOC concentrations are based on measurements from Alves et al., (2016) and ozone reactivity calculated using monoterpene composition according to Jardine et al., (2015) and sesquiterpene composition according to copaiba essential oil (source: Young Living) analysed in this study.


β-caryophyllene aldehyde
[ng/m^3]
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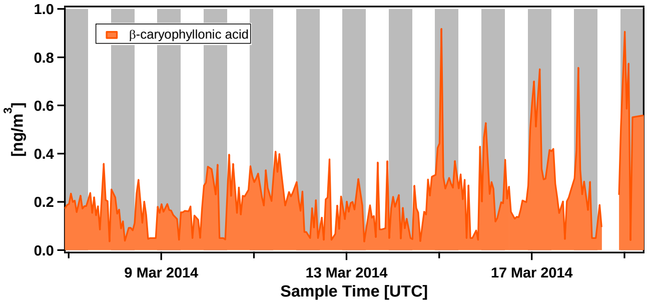
8
6
4
2
0
9 Mar 2014
13 Mar 2014
17 Mar 2014
Sample Time [UTC]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9 Mar 2014
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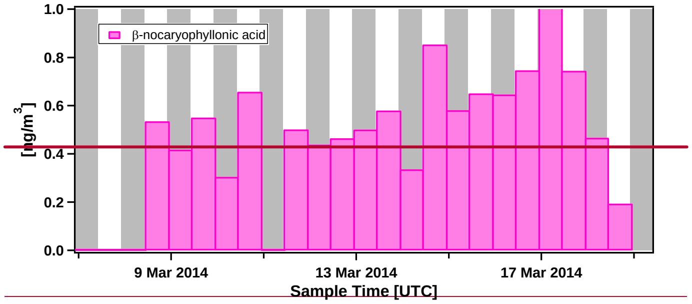
17 Mar 2014
Sample Time [UTC]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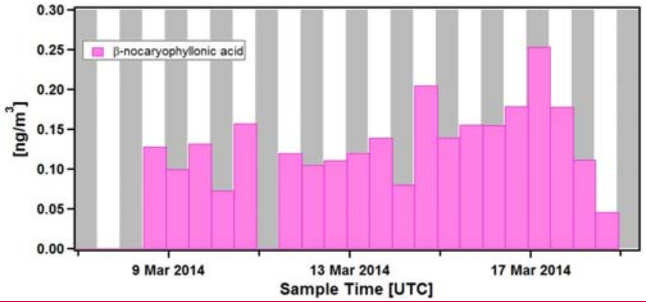
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[ng/m^3]
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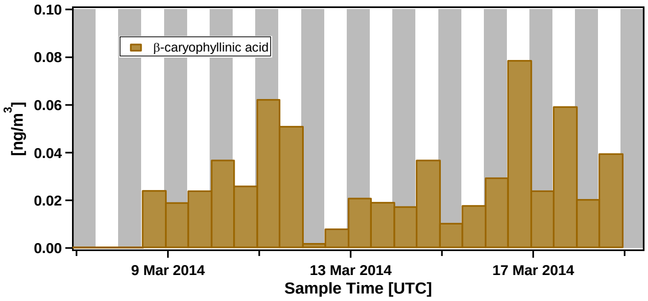
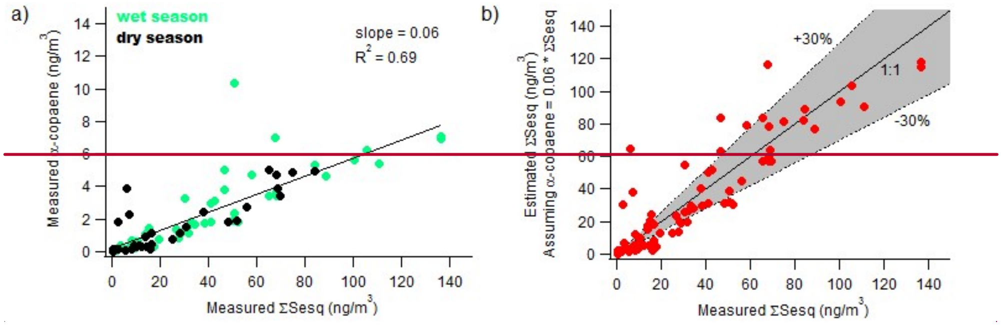


Figure S3: Selected timeline of gas-phase tracers (β-caryophyllene aldehyde, β-caryophyllonic acid) measured with SV-TAG and particle-phase tracers (β-nocaryophyllonic acid, β-caryophyllinic acid) from β-caryophyllene oxidation.



~~**Figure S3: During underivatized runs (n=79), α-copaene on average accounts for 6% of total observed sesquiterpenes in panel a) within +/- 30% in panel b).**~~