Response to reviewers for the paper "In situ secondary organic aerosol formation from ambient pine forest air using an oxidation flow reactor."

B. B. Palm, J. L. Jimenez, et al.

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper (**in bold text**).

Anonymous Referee #1

Overview

R1.0. The paper summarizes observations of SOA formation and evolution in the ambient air and oxidized ambient air in a flow tube reactor at a forested site in Colorado. The paper is well thought (especially the extent of corrections performed for possible losses in the sampling lines, etc.) and results are clearly presented. The main conclusion of the paper is that oxidation of the measured VOCs is not enough to explain the formation of SOA upon aging. This is not a new finding, but the value of the paper in my opinion is to attempt a mass closure and determine the necessary SOA formation yields for the measured S/IVOCs to explain the observed increase in OA mass after photochemical aging. The analysis for relevant time scales for a typical OFR operation is also valuable for the community. I suggest publishing the manuscript after my comments below are addressed.

We thank the reviewer for his/her input. However, we disagree that showing that oxidation of the measured VOCs is not enough to explain the formation of SOA *formed in-situ from ambient air in a forest* is not a new finding. We believe that it is a new finding in at least two ways: (1) To our knowledge that has only been shown before through more complex analyses that join together VOCs and SOA measured at different points in time, and not when comparing SOA formation and VOCs measured simultaneously in ambient air in a forest. (2) The underestimation of SOA has only been consistently observed for urban air, and not in biogenically-dominated air.

We have modified the text in the abstract at P30411 L25 to read:

"Approximately 4.4 times more SOA was formed in the reactor from OH oxidation than could be explained by the VOCs measured in ambient air. To our knowledge this is the first time that this has been shown when comparing VOCs and SOA formation measured at the same time, rather than comparing measurements made at different times."

We have also modified the introduction at P30413 L5 to read:

"Aerosol models using traditional (pre-2007) aerosol yields for volatile organic compounds (VOCs) from chamber studies generally underpredict SOA mass by a factor of 10 in urban areas (Volkamer et al., 2006; Hodzic et al., 2010; Hayes et al., 2015). More recent models are able to better predict SOA mass in urban areas by using higher VOC yields and adding previously ignored semivolatile and intermediate volatility organic compounds (S/IVOCs; Hodzic et al., 2010; Hayes et al., 2015). Model comparisons for biogenically-dominated areas have not shown such systematic underpredictions even when using older models (e.g., Tunved et al., 2006; Chen et al., 2009; Hodzic et al., 2009; Slowik et al., 2010)."

We added the following sentence to the conclusions at P30444 L5:

"To our knowledge, this is the first time this has been demonstrated by comparing simultaneous VOC measurements with in situ SOA formation, particularly in a biogenic environment."

R1.1. P 30412, L20: consider changing to ". . ..functionalized products" and ". . . fragmented products."

We have modified the text at P30412, L20 as suggested.

R1.2. P 30422, L25: Max SOA is observed over night when in reality oxidation by OH in the ambient air would be low and oxidation by O3 would be high, but OFR185 doesn't include much of an oxidation by O3, so how relevant are these observations to understanding the ambient SOA formation at the site?

The reviewer raises a good question that we have discussed at various points during analysis of this dataset and others using the OFR, but may have not made clear enough in the manuscript. We did not mean to suggest that SOA formation from OH oxidation is actually producing more SOA in the forest at night. Rather we are reporting the observation that the SOA formation potential from OH oxidation of nighttime air is larger and quantifiable. In fact the lack of much OH in nighttime air is likely an important factor to explain why the potential for OH-produced SOA is higher at night: the longer lifetime of monoterpenes and their oxidation products allows building up higher concentrations in nighttime air. During this study we also investigated O_3-produced and NO_3-produced SOA in the OFR which, together with these OH oxidation results, can provide a more complete picture of the complex interplay between different oxidant-driven SOA formation processes. The O_3 and NO_3 oxidation results will be the subject of an upcoming manuscript, as it was too much material to attempt to cover in one manuscript. We have modified the text in several places to clarify how OFR measurements can be related to ambient SOA formation:

P30411 L2: "An oxidation flow reactor (OFR) is a vessel inside which the concentration of a chosen oxidant can be increased for the purpose of studying SOA formation and aging by that oxidant. During the BEACHON-RoMBAS field campaign, ambient pine forest air was oxidized by OH radicals in an OFR to measure the amount of SOA that could be formed from the real mix of ambient SOA-precursor gases, and how that amount changed with time as precursors changed."

P30411 L28: "An SOA yield of 18-58% from those compounds can explain the observed SOA formation. This work suggests that these typically unmeasured gases play a substantial role in ambient SOA formation."

P30412 L3: "These measurements help clarify the magnitude of potential SOA formation from OH oxidation in forested environments, and demonstrate methods for interpretation of ambient OFR measurements."

P30419 L2: "This allows the potential of SOA formation from OH oxidation to be studied over the whole range of exposures as functions of time of day and the concentration of precursors that change on that time scale."

P30424 L3: "Under typical operation, an OFR is used to study oxidation dominated by a single oxidant, similar to typical large chamber experiments. In the case of a field application (as in this study) the sample is a complex and time-varying mixture of ambient precursors that enter the OFR. Importantly, the $OH:O_3:NO_3$ oxidant ratios produced within the OFR are generally not the same as the changing

ambient ratios. Therefore SOA formation in the OFR does not, and is not meant to, reproduce in situ ambient SOA formation at each point in time. In other words, the OFR can be used as a tool to determine the amount of SOA from a single oxidant that would form upon oxidation of ambient gases (both identified and unidentified) at any time of day.

Typical OFR operation of OH oxidation using the OFR185 method is illustrated…"

P30433 L22: "SOA will be formed in the OFR from these changing VOC mixtures and any other gases present in the ambient air that enters the reactor, so it might be expected that different amounts of SOA production would be observed during daytime vs. nighttime."

P30434 L10: "In other words, this OH oxidation in the OFR is not meant to reproduce true ambient nighttime chemistry, rather it allows us to measure SOA formation from OH oxidation of the true mix of ambient gases as it evolves with time of day, including nighttime. In fact, the lack of ambient nighttime OH oxidation may help explain the increased SOA formation potential when nighttime air is oxidized by OH in the OFR."

R1.3. P. 30435, L15-20: authors suggest that ORF185 is more suitable for forested environments. I don't agree with this statement since comparisons could not be carried out for short aging times and since OFR185 does not allow for significant O3 oxidation whereas MTs have a high reactivity with O3. Plus, for some long aging times, there is a non-negligible difference between OA enhancements observed in OFR185 and OFR254.

Please see our response to R1.2 for an explanation that the OFR is used to study oxidation by a single oxidant at a time. In our opinion, it is more informative to perform O_3-only oxidation and OH-dominated oxidation separately and compare the results than to try to perform simultaneous oxidation by several oxidants, which is more complex to interpret.

We have modified P30435, L18-19 to read:

"… we recommend the OFR185 mode of operation for future OFR studies of OH oxidation in forested areas."

The reviewer is correct that a comparison of OH oxidation between the two methods could not be made for short aging times, but this is because of limitations of the OFR254 method, which are discussed starting on P30421 L3. The OFR185 method allowed for studying OH oxidation at ages <1 eq. day, whereas the OFR254 method did not during this study. Therefore, the OFR185 mode was more useful for a forested environment where many of the ambient SOA-forming gases will react during these short aging times.

For completeness, we have also added the following text to P30421 L13:

"Measuring the decay of a compound that reacts relatively quickly with OH but does not react with O_3 could allow for better OH_{exp} quantification at low ages for OFR254-70."

Regarding the "non-negligible differences between OA enhancements observed in OFR185 and OFR254" at high ages, please see the response to R3.20 below.

R1.4. P. 30432, L24: It's unclear to me why SO4 mass should be scaled by Faer? Is this the correction that's referenced in line 27? Similarly, I don't understand why a correction for LVOC condensation needs to be applied. Is the idea to account for the max possible amount of SOA formed beyond the time scales of residence in the flow tube?

The reasoning for including an LVOC fate correction is discussed in the first paragraph of Sect. 3.3.1, starting on P30426 L25. To clarify, we have changed the text starting at P30427 L11 to read:

"However, if they are subject to one of the other three fates, then the AMS + SMPS measurements would underestimate the amount of SOA that would form in the atmosphere at the same level of OH exposure. Similar to loss of gases to large Teflon chamber walls (e.g., Matsunaga and Ziemann, 2010), these other three fates are experimental limitations of the OFR technique that need to be corrected in order to relate OFR measurements to real atmospheric SOA formation processes."

To clarify why SO4 mass also needs to be corrected by F_{aer}, we have replaced the first sentence of Sect 3.3.2 at P30432 L11 to read:

"In addition to LVOCs, H_2SO_4 can also be produced in the OFR from OH oxidation of SO_2. H_2SO_4 molecules can also condense onto OFR or sampling line walls (but not be lost to further reaction with OH). These limitations of the OFR technique need to be corrected in order to relate OFR measurements to real atmospheric processes. H_2SO_4 formation is an analogous yet much simpler system compared to LVOC formation, so it can be used to validate the LVOC fate model."

This is indeed the correction referenced in P30432 L27, and we have clarified the text at that line to read:

"After applying the correction for H_2SO_4 wall and sampling line losses as described in the previous paragraph, the measured …"

R1.5. P. 30437, L 20: Are the mentioned SOA yield values the chamber-derived yield values, just scaled accordingly for ~5 ug/m3 of OA? If so, what formulation was used to scale down the yields?

To clarify the manuscript, we have added a new table (Table 2) and modified the text starting at P30437 L12 to read:

"SOA formation was predicted by applying low-NO_x, OA-concentration-dependent, chamber derived aerosol yields to the ambient VOC concentrations predicted to react in the OFR based on OH_{exp}. Estimated fractions reacted were >99% of ambient MT, SQT, and isoprene, and ~45% of toluene+*p*-cymene in the age range of 0.4–1.5 eq. days. The yields used to predict SOA formation were calculated for each individual data point as a function of the OA mass concentration measured after oxidation in the OFR, using the two- or four-product basis set parameterizations listed in Table 2 (Henze and Seinfeld, 2006; Tsimpidi et al., 2010). With an average post-oxidation OA concentration of 4.1 g m^{-3} when the LVOC fate correction was applied, this resulted in campaign-average SOA yields of 12.5, 13.2, 13.8, and 3.2% for MT, SQT, toluene, and isoprene, respectively. Previous experiments have shown SOA yields from various precursor gases oxidized in the OFR to be of the same order as yields from large environmental chambers (Kang et al., 2007, 2011; Lambe et al., 2011, 2015)."

See also the response to R2.1 discussing the new table of SOA yield parameters.

R1.6. P. 30443, L11-12: Please add the aging times when OFR185 and 254 were compared (comparison wasn't possible at short photochemical times and so a general statement on the similarity of the results is not warranted).

We have modified the text starting at P30443 L12 to read:

"Similar amounts of SOA formation were observed from both the OFR185 and OFR254-70 methods for the overlapping range of eq. ages (~1-30 days). Comparison at shorter ages was not possible because the OFR254-70 method, especially as it was employed during this campaign, was not suitable for measuring <1 eq. day of OH aging."

Please see the response to comment R1.3 for an explanation of why comparison between OFR185 and OFR254-70 was not possible at short photochemical ages for this study.

R1.7. Section S1: Particle loss correction: Adding in particle mass to what the AMS measured based on the volume fraction of different species is valid only if there is no size dependent composition differences. Is that a valid assumption in this data set?

To address this comment, we have modified Fig. S1 and its caption to read:

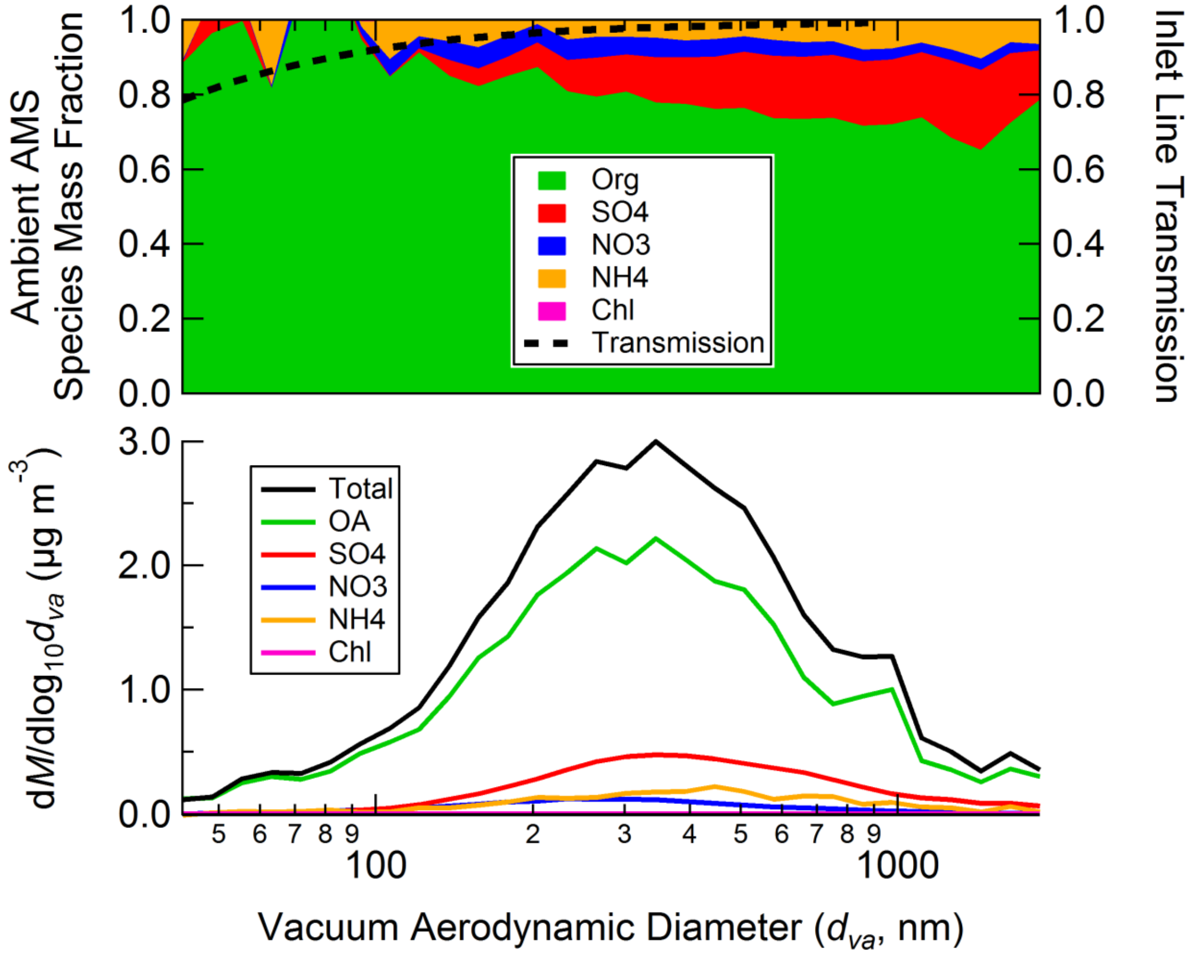

Fig. S1. Top: Average species mass fraction of ambient aerosol measured by the AMS, and inlet sampling line particle transmission efficiency. The transmission efficiency was estimated using the Max Planck Institute for Chemistry Particle Loss Calculator (von der Weiden et al., 2009). This transmission curve was used to correct SMPS size distributions for particle losses in the ambient and OFR sampling lines. Particle losses to surfaces inside the OFR are discussed in Sect. S3. Bottom: Average species mass size distribution of ambient aerosol measured by the AMS.

We have also added the following text to L29 of Sect. S1:

"As seen in Fig. S1, there was on average only a slight size dependence to the species mass fractions of ambient aerosol. The mass fractions are also particularly noisy at smaller particle sizes due to small mass concentrations. Ideally, the species size distributions measured at each point in time could be used to allocate the sampling line particle losses to each species. In practice, the AMS size-distribution measurement mode is not sensitive data point. Thus, we have applied the best correction possible and expect that it should improve quantification. Regardless, the small size dependence of species mass fractions would have a minimal impact on this analysis since the correction is at most 20% at the smallest sizes."

R1.8. Figure S3 and S6. I'm confused as to why the right panels that plot AMS or SMPS volume added after oxidation show negative values. Please clarify.

Figures S3 and S6 include all OFR185 data, over the entire range of eq. OH ages. To clarify the negative values in these figures, we have added the following text to the captions of Figs. S3 and S6:

"At the highest ages, heterogeneous oxidation led to fragmentation/volatilization of preexisting OA, resulting in a net loss of OA."

We have also modified the text to say **"change in volume"** throughout the manuscript.

Anonymous Referee #2

Overview

R2.0. This study is focused on using an oxidation flow reactor to study secondary organic aerosol formation in a forest environment. During the BEACHON-RoMBAS field study multiple VOC species and organic aerosol concentrations were measured. The authors predicted the SOA concentrations by using the measured VOCs and known SOA yields. The predicted SOA concentrations show that still there are unmeasured SOA precursors in the forest environment. The findings of this study could help to better understand and model the SOA formation in an environment dominated by biogenic VOCs. The study demonstrates that the oxidation flow reactor is a powerful tool to study the contribution of different unidentified species to SOA formation. The paper is well written. I have some minor comments on the paper.

R2.1. Show all the SOA yields used in the calculations in a separate table. In SOA calculations do you take into account BVOC oxidation by ozone?

For typical yields under the conditions of our study, see the response to comment R1.5.

To document the full details, we have added Table 2 (reproduced below) to the revised paper. Note that the SOA yield values used for isoprene have been updated compared to the ACPD version, leading to slightly larger yields. This change has no consequence for the conclusions drawn in this analysis, as isoprene is a very minor contribution to the predicted SOA amounts.

Table 2. Low-NO_x SOA yield parameters using basis sets, used to estimate SOA yields from VOCs in the OFR (Sect. 3.6.1).

	C^* saturation vapor concentrations at 298K ($\mu g\ m^{-3}$)			
SOA precursor	**1**	**10**	**100**	**1000**
MT[a]	**0.107**	**0.092**	**0.359**	**0.600**
SQT[a]	**0.075**	**0.150**	**0.750**	**0.900**
Toluene[a]	**0.075**	**0.225**	**0.375**	**0.525**
	C^* saturation vapor concentrations at 295K ($\mu g\ m^{-3}$)			
	0.6		**116**	
Isoprene[b]	**0.0288**		**0.232**	

[a](Tsimpidi et al., 2010), not including the chemical "aging" parameterization

[b](Henze and Seinfeld, 2006)

Regarding BVOC oxidation by ozone, please see our response to R3.4 below.

R2.2. You use a number of abbreviations, please put them in one table so it's easier to follow. For example, what is "CS"?

We have added a Glossary after the main text:

OFR	**Oxidation flow reactor**
SOA	**Secondary organic aerosol**
LVOC	**Low volatility organic compound**
OA	**Organic aerosol**
VOC	**Volatile organic compound**

S/IVOC	**Semi- and intermediate-volatility organic compound**
PTR-TOF-MS	**Proton transfer reaction time-of-flight mass spectrometer**
OH	**Hydroxyl radical**
O_3	**Ozone**
NO_3	**Nitrate radical**
MBO	**2-methyl-3-buten-2-ol**
MT	**Monoterpenes**
SQT	**Sesquiterpenes**
OHR_{ext}	**External OH reactivity**
OHR_{int}	**Internal OH reactivity**
OH_{exp}	**OH exposure**
eq.	**Equivalent**
SMPS	**Scanning mobility particle sizer**
AMS	**Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)**
k_{OH}	**Rate constant for reaction with OH**
k_{O3}	**Rate constant for reaction with** O_3
TD-EIMS	**Thermal desorption electron impact mass spectrometer**
C^*	**Effective saturation vapor concentration**
τ_{aer}	**Lifetime of LVOCs (or** H_2SO_4**) for condensation onto aerosols**
τ_{wall}	**Lifetime of LVOCs (or** H_2SO_4**) for loss to OFR walls**
τ_{OH}	**Lifetime of LVOCs for reaction with OH**
τ_{total}	**Total lifetime for loss of LVOCs (or** H_2SO_4**)**
CS	**Condensational sink**
D	**Gas diffusion coefficient**
r	**Particle radius**
$N(r)$	**Particle number size distribution**
α	**Sticking coefficient**
Kn	**Knudsen number**
λ_g	**Mean free path of gas molecules**
A/V	**Surface-area-to-volume ratio of OFR**
k_e	**Coefficient of eddy diffusion**
F_x	**Fraction of LVOCs (or** H_2SO_4**) lost to pathway** x
SO_4	**Sulfate aerosol**

R2.3. Section 3.6.2: You didn’t use any aging in calculation of SOA formation from measured VOCs. Here you state that "At night, O3 and NO3 may react with the C=C-containing MT and SQT emissions leading to a buildup of S/IVOC oxidation products that lack C=C double bonds, molecules with which O3 and NO3 generally do not react". Doesn’t this imply that these first generation oxidation products of monoterpenes will produce more SOA by further oxidation? Therefore, applying aging in the calculations would reduce the gap between predicted and measured SOA. I’m aware that there are some uncertainties related to using aging in the SOA predictions. Nevertheless, there are several papers based on laboratory studies, which show multi-generational SOA production from alpha-pinene.

To address this point we have added the following text at P30437 L22:

"These yield values reflect the amount of SOA that forms after several generations of gas-phase oxidation of precursor gases. We do not include additional "aging" of the precursors through additional oxidation steps, as such parameterizations are not well-supported experimentally."

This comment is also addressed as part of the restructuring of Sect. 3.6.2 as part of the response to R3.24 below.

We agree that additional oxidation by OH of products of e.g. terpene oxidation by NO_3 or O_3 may be part of the missing SOA precursors observed at night (see last paragraph of Sect. 3.6.2).

Short Comment: “Relevant Reference”, C.N. Hewitt, 9 Nov 2015

The authors of this interesting manuscript may wish to refer to a paper we published in ACP in 2014 in which we studied the formation of aerosol particles in a reaction chamber into which gas-phase emissions from trees where fed:

Emissions of biogenic volatile organic compounds and subsequent photochemical production of secondary organic aerosol in mesocosm studies of temperate and tropical plant species (2014) K.P. Wyche, A.C. Ryan, C. N. Hewitt, M. R. Alfarra, G. McFiggans, T. Carr, P.S. Monks, K.L. Smallbone, G. Capes, J.F. Hamilton, T.A.M. Pugh, and A. R. MacKenzie, Atmospheric Chemistry and Physics, 14, 12781 – 12801

We have modified the text at P30413 L26:

“Also, while chamber experiments have been performed using emissions from mesocosm (e.g., whole tree) systems in the laboratory (e.g., Wyche et al., 2014), it is difficult to perform field experiments with ambient air in chambers (Tanaka et al., 2003).”

Anonymous Referee #3

Overview

The authors present results from measurements of SOA formation made using an oxidation flow reactor in a forested environment. They provide a detailed discussion of the physical mechanisms at play, and find some interesting relationships between the SOA formation potential and the ambient concentrations of monoterpenes, in particular. They find that the SOA that they would predict to form based on the observed MT concentrations is lower than the observed formation. They use this, along with some direct measurements of the concentrations of S/IVOCs, to estimate effective yields for these species and to explain the observation-prediction gap. I find this section to be a bit weaker than it could be, I think because the authors are working to not show data that is under review elsewhere (Hunter et al., Submitted to Nat. Geosci.). I suggest that the authors be more direct in this section. Overall I think that this study is well done, provides interesting results and should be publishable once the authors address the comments below.

R3.1. P30414, L13: Although it seems very likely that S/IVOCs are contributors to SOA formation from biomass burning and vehicle exhaust, some of the difference between the observed and predicted SOA formation from VOCs in the two cited studies (Ortega et al., 2013; Tkacik et al., 2014) could potentially be explained by the assumed SOA yields used to make the predictions being too low, a consequence of the losses of semivolatile gases alluded to on the previous page. It seem appropriate to also mention this here.

We have modified the text at P30414 L 13 to clarify this point as:

"Bruns et al. (2015) found that for a wood combustion system, the amount of SOA formed in an OFR compared to a large chamber agreed reasonably well. Tkacik et al. (2014) and Ortega et al. (2013) showed substantially more SOA formation than could be explained from speciated VOCs. Despite relying on SOA yields measured in large chambers, which can be affected by the aforementioned wall losses of semivolatile gases, these results suggest that S/IVOCs contribute to SOA formation in biomass burning plumes and vehicle exhaust."

R3.2. P30415, L25: I find the statement here regarding the NO+ ion to be a bit unclear how specifically this links to the first part of the sentence. Do the authors mean whole air samples analyzed using a CIMS technique with NO+ as the reagent ion?

For clarification, we have modified the text at P30415 L25 to clarify this point as:

"The relative ratio of isoprene/(MBO + isoprene) at this field site was estimated using a combination of GC-MS, PTR-TOF-MS, and whole air sample measurements during summer 2010 (Kaser et al., 2013) and using NO^+ ionization mass spectrometry during the BEACHON-RoMBAS campaign (Karl et al., 2012) to be approximately 20%."

R3.3. P30416, L13: Is the mesh smaller than the ID of the OFR body (14 vs. 19.7 cm)? This makes it difficult to understand how this really acted as a screen (not that this really matters to the results of this study, but it could be clarified in case someone else wants to apply this methodology).

The text at P30416 L10 has been modified to clarify this point as:

“The 14 cm diameter inlet plate was removed from the intake end of the OFR to reduce possible losses of semivolatile SOA precursors to the inlet plate inferred in a previous study (Ortega et al., 2013) and to reduce the width of the residence time distribution in the reactor (Ortega et al., 2015). Air was sampled into the reactor through this 14 cm diameter opening, which was covered with a coarse-grid mesh screen to reduce turbulence in the reactor and prevent insects and debris from entering the reactor.”

It is correct that that inlet plate is of smaller diameter than the diameter of the body of the OFR. There is a solid ring on the front face of the reactor that seals the region between the inlet plate (or mess screen) and the outer diameter of the reactor. This can roughly be seen in Fig. 2 (solid black line) and more clearly in the photo in Fig. 1b in Ortega et al. (2015). The reason for this difference in diameters is that the UV lamps and mounting hardware are located the other diameter of the reactor.

R3.4. P30417, L22: It would be useful if the authors were to elaborate as to what “a small number means.” If, for example, the number of compounds influenced is small but they are the most abundant, then the influence on the system would not be small.

We have modified the text at P30417 L16 to address this point as:

“According to Fig. 5 of Peng et al. (2015b), O_3 in the OFR185 method during this study likely contributed only a minor (< 20%) role in the oxidation of a few biogenic VOCs with the largest k_{O_3}/k_{OH} ratios (e.g., β-caryophyllene, α-terpinene, α-humulene), and only at the lowest OH exposures (OH_{exp}) equivalent to several hours of aging. With the OFR254-70 method though, the ratio of O_3 exposure to OH_{exp} was as high as 10^6 for the lowest OH_{exp} in this study. Under these conditions, O_3 may have played a substantial role in the initial oxidation of a larger number of species of biogenic VOCs (e.g., reacting with ~100% of β-caryophyllene and α-terpinene, ~60% of α-pinene and limonene, ~20% of 3-carene and β-pinene, 10% of isoprene).”

R3.5. P30418, L2: It would be useful if the authors were to define “external OH reactivity” further here, so the reader doesn’t have to look this up in the Li et al. paper. Additionally, the authors could elaborate as to how this was estimated.

The text starting at P30417 L28 was modified to:

“OH_{exp} for the OFR185 method was estimated in part based on a model-derived equation, which uses measurements of ambient water vapor concentration, O_3 produced in the reactor, and estimated external OH reactivity (OHR_{ext}) as equation parameters (Li et al., 2015). OHR_{ext} is the OH reactivity from ambient gases such as VOCs, CO, SO_2, and is accounted for separately from the “internal OH reactivity (OHR_{int})” from species such as $HO_x/H_2O_2/O_3$ that are greatly enhanced by the reactor. For this study, OH_{exp} was calculated using an estimated $OHR_{ext} = 10\ s^{-1}$, based on measurements at the same field site and season during previous campaigns (Kim et al., 2013; Nakashima et al., 2014).”

R3.6. I suggest the authors just write out “equivalent” rather than using the abbreviation “eq.”, which I find awkward.

We thank the reviewer for this suggestion, but prefer to keep using the abbreviation “eq.” This term has been defined on first use, is included in Table 2 as part of the response to R2.2, and is used consistently throughout the manuscript.

R3.7. Line 30420, L24 and elsewhere: Given that the net change in the amount of particle volume observed can either increase or decrease, I suggest that the authors move away from using the terminology “volume added,” which to me implies that things only increase, to something like deltaV (where delta is the delta symbol) to capture that this is not unidirectional.

Please refer to the response to R1.8.

R3.8. P30421: Although I understand the arguments as to why the OFR185 and OFR254 measurements are different, given that they apparently “give consistent results” I do not see why the OFR254 measurements would be excluded from the bulk of the analysis. Why not merge the data sets, which should be straight forward if they are “consistent”.

To clarify why we have chosen to not merge the OFR254-70 measurements into the analysis, we have added this sentence to P30421 L5 to read:

“The analysis of SOA mass formed vs. predicted in Sect. 3.6 was done using the age range that produced the maximum SOA formation (0.4–1.5 eq. days). However, determination of ages below approximately 1 eq. day using the OFR254-70 method was limited by the ability to accurately measure the amount of injected O_3 that was consumed in the reactor.”

We have also modified the text at P30421 L18 to read:

“This short time period of OFR254-70 measurements combined with the difficulty of sampling at short eq. ages with this particular experimental setup meant that there were few OFR254-70 measurements relative to OFR185 measurements for the analysis in Sect. 3.6. Also, there were no concurrent measurements of S/IVOC concentrations and SOA formation using OFR254-70 available for the analysis in Sect. 3.6.2. If these analyses would have been performed on a combined dataset using both OH production methods, the results would be driven almost completely by OFR185 measurements. For these reasons, the analyses were performed and conclusions reached using only OFR185 measurements. Regardless, we document below that both OH oxidation methods gave consistent results for SOA production over the range of overlapping ages (~1-30 eq. days) used during this campaign (Sect. 3.4).”

R3.9. P30424, L14: The authors note that as the OH exposure is increased the SO4 mass formed continued to increase. However, in looking at Fig. 2 it appears that the SO4 mass increases to a point, but plateaus at high OH exposure. Is this generally true? If so, it should be mentioned.

At P30424 L12, the text has been modified as follows:

“As the eq. age continued to increase, OA mass enhancement decreased, eventually resulting in net OA loss. These high ages led to a lack of formation of SOA as well as heterogeneous oxidation of the preexisting OA, leading to fragmentation and evaporation (Ortega et al., 2015). The amount of SO_4 aerosol production increased with eq. age, and plateaued with no further production at ages above ~10 days. This behavior is consistent with theory, since SO_2 has a lifetime of ~8 days with respect to oxidation by OH (Sander et al., 2011). Also, as expected, SO_4 aerosol (and H_2SO_4 gas) was not consumed by excess OH_{exp} in the same way as OA (and SOA precursor gases).”

R3.10. P30426, L5: The authors here note that the accuracy of the model-derived OH exposures could be assessed by comparing the measured vs. predicted depletion curves. However, since the factor of 2 scaling was determined by comparing the model results with the observations, I don't really think that this is an assessment of the accuracy of the "model-derived OHexp". I realize the authors have the caveat "(including the factor of two decrease)", but I don't find this sufficient. I suggest that the authors very simply replace "accuracy" with "reasonableness".

We have replaced the word "accuracy" with **"reasonableness"** in P30426 L5 as suggested.

R3.11. P30427, L2: I think that here the authors are more specifically defining LVOCs as species that "irreversibly" condense, not just condense. I suggest they add this word.

The words **"(effectively) irreversibly"** have been added to P30427 L2.

R3.12. P30427: Regarding the fates of the LVOCs relative to their fate in the atmosphere, given that this study focuses on a forested area where the available surface area may be low, do they think that (perhaps) the LVOCs may condense onto things like leaves, trees, rather than onto particles? If this were to occur, then some of the loss processes discussed here might actually be relevant to this particular environment. I am speculating here, but perhaps something to consider adding a note about? Of course, such high exposures as considered here would not be relevant for the particles within the canopy, in general, but for those transported far downwind and so perhaps this line of thinking on my part is generally irrelevant.

We have changed P30427 L4 to:

"In the atmosphere, the dominant fate of these LVOCs is to condense onto aerosols (lifetime of ~minutes), as dry and wet deposition of even fast-depositing species are generally slower sinks (lifetime of ~hours; Farmer and Cohen, 2008; Knote et al., 2015; Nguyen et al., 2015)."

We have also added the following sentence to P30427 L14:

"As mentioned above, this correction takes into account that dry deposition of such LVOCs is not competitive with condensation onto particles in the atmosphere (Knote et al., 2015; Nguyen et al., 2015)."

R3.13. P30427, L20: The authors here seem to be implying that the low volatility of SOA results solely from the condensing species being low volatility. However, this neglects that some of the low volatility nature of SOA may result from condensed phase reactions involving SVOCs. If such condensed phase reactions are fast, then distinguishing between SVOC and LVOC condensation may not be important.

We have modified the text at P30427 L20 to:

"Some semivolatile species (SVOC) will likely also be produced. However, we focus on irreversibly condensing LVOCs, both for simplicity and based on the observation that most of the OA has low volatility at this site, according to thermal denuder measurements (Hunter et al., 2016), and consistent with measurements at other locations (Cappa and Jimenez, 2010; Lopez-Hilfiker et al., 2016). If the low volatility of OA is a result of condensation of SVOC followed by fast particle-phase reactions to produce low-volatility species, then the distinction between LVOC and SVOC would be irrelevant for this analysis."

R3.14. P30427, L25: I find this to be an odd way to start a sentence.

We have added the following text to the end of P30427 L24:

"The lifetimes of LVOCs against different processes are estimated as follows:"

R3.15. P30429, L13: I think the units are incorrect on the surface area concentration.

Thanks for the catch. The units have been changed from "µm cm^{-3}" to **"µm^2 cm^{-3}"** in three places: P30429 L13, P30429 L15, and P30467, L5 of Fig. 9 caption.

R3.16. P30432, L24: Do the authors mean by dividing the newly produced SO4 mass, and not the total SO4 mass, which would include pre-existing SO4 that is not influenced by the loss to walls or exiting the OFR?

The sentence starting at P30432 L22 has been changed as follows to clarify this point:

"Using the model results, the fraction of H_2SO_4 that does not condense onto aerosol was corrected for by dividing the newly produced SO_4 mass measured with the AMS by F_{aer}."

R3.17. Figure 6: There does not appear to be a blue curve, as indicated in the legend. Do the authors mean black?

The word "blue" has been changed to **"black"** in L5 of the Fig. 6 caption on P30464.

R3.18. P30433: I agree that the H2SO4 results suggest a strong potential for the LVOC correction method to help/work, however I think that the authors should also note that there is a great deal of scatter at low enhancements, when the corrections are particularly large, meaning that these values are particularly uncertain.

The following detail has been added to the captions of Fig. 6 and Fig. S10:

"Ambient SO_2 concentrations <0.2 ppb have been excluded from this analysis."

We have also modified the text starting at P30433 L5 to read:

"Generally, the amount of SO_4 formed after applying the H_2SO_4 wall and sampling line loss correction was consistent with the expected amount within the uncertainties. The amount of scatter introduced by applying the correction was larger when the amount of SO_4 produced (and predicted) was close to zero, when the F_{aer} correction factor was less than ~0.3. This suggests that the LVOC fate model becomes more uncertain when the correction factors are large and F_{aer} is close to zero. However, this analysis demonstrates that a correction can be successfully applied for H_2SO_4 condensation, and that a similar correction should also be applied for LVOC condensation to more accurately interpret the results of SOA formation in an OFR."

R3.19. P30435, L5: I suggest a reference to (Lambe et al., 2015) would be good here, as they compare OFR to chamber experiments for isoprene SOA.

We have modified the text at P30435 L2 to read:

"This includes the IEPOX pathway from isoprene (Paulot et al., 2009) and the similar pathway proposed for MBO (Zhang et al., 2012). While SOA formation from isoprene in an OFR has been

demonstrated (Lambe et al., 2015), the total SOA formation potential from MBO + isoprene may be underestimated in our study."

R3.20. P30435, L14: In Fig. 7, comparing the daytime points, the difference between OFR185 and OFR254 at the lowest OH exposure was fairly large. Although I agree that there are no major differences between the OFR185 and OFR254, I am not entirely convinced that "significant" is justified here.

We have modified the text at P30435 L 13 to read:

"From Fig. 7, we conclude that there were no major differences in the amount of SOA formation between the OFR185 and OFR254-70 methods over the range of ages measured in this campaign. Minor differences in SOA formation between the two methods are likely a result of limits on the ability to determine the proper eq. age (especially for low ages in OFR254-70 as discussed in Sect. 2.3) or due to real changes in ambient SOA precursor gases, since the measurements using each method were not simultaneous. Additional comparisons of both methods sampling the same air, carefully designed and controlled to more accurately determine low ages in OFR254-70, would be useful to further explore this issue. Since the OFR185 mode is experimentally simpler and does not require addition of O_3 (with associated issues of mixing, dilution, possible contamination, etc.), and since the OFR185 mode more faithfully simulates OH chemistry due to reduced O_3 concentrations (Peng et al., 2015b), we recommend the OFR185 mode of operation for future OFR studies of OH oxidation in forested areas."

R3.21. P30439, L7: Given the authors acknowledgement on the previous page that the yields of SOA in chamber experiments due to losses of S/IVOCs to chamber walls might be low, I think that the authors should change their language to indicate that other S/IVOCs "contribute" to the discrepancy, don't "cause" the discrepancy.

The text has been modified at P30439 L6 to:

"The gases that enter the OFR as S/IVOCs are the most likely source of SOA formation contributing to the factor of 6 discrepancy in Sect. 3.6.1."

We have also changed the word "explained" to **"completely explained"** in P30444 L6.

R3.22. Section 3.6.2: Given that the Hunter et al. manuscript is not yet published and not available for consideration, I find it difficult to really assess this section. For example, the authors report here measurements of MT concentrations that are typically around 0.5-1 ppb, which corresponds to 2.5-5 ug/3m. The logC* of MTs is around 6 or 7. Either way, they should fall in one of the TD-EIMS bins shown in Fig. 12. However, the max concentration in those bins is only 0.5 ug/m3. Where are the MTs? I see the argument that "the TD-EIMS instrument experiences a loss of sampling efficiency in that bin and MT are not expected to be measured," but without being able to read the Hunter paper I do not understand how one specific class within a bin would be missed (which is implied by the statement). If the authors simply mean that the overall efficiency in this bin is low, that I can understand.

We have modified the sentence at P30440 L13 to read:

"While MT are in the $C^* = 10^7$ µg m^{-3} volatility bin, that bin is at the upper volatility limit of the TD-EIMS measurement capability. Some gases in that bin were sampled, but MT were expected to be too volatile to be measured (Hunter et al., 2016). This was supported by the fact that the campaign-

average mass in the $C^* = 10^7$ μg m^{-3} bin was only 0.43 μg m^{-3}, which would correspond to only approximately 0.1 ppbv MT, if there were no other gases in that bin. The campaign-average in-canopy MT concentration measured by the PTR-TOF-MS was approximately 0.8 ppbv."

R3.23. S/IVOCs Diurnal Dependence? The authors note a substantial difference in day/night SOA formation. This correlates really well with the day/night variation in MT concentrations. What about for S/IVOCs?

We have added the diurnal trace of S/IVOCs measured by the TD-EIMS instrument to Fig. 11, shown below.

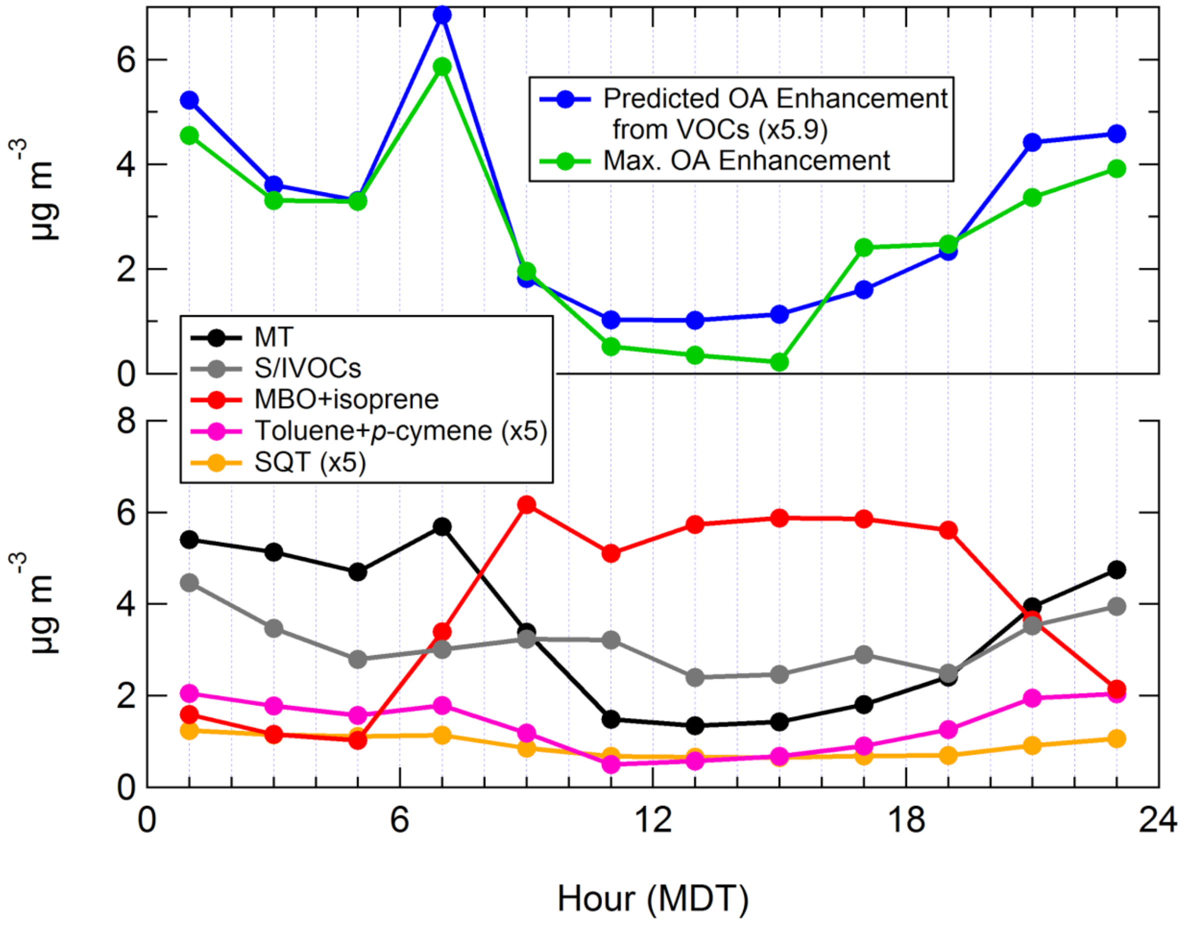

Fig. 11. Top: diurnal maximum measured OA enhancement (all data from 0.4–1.5 eq. days aging, LVOC fate corrected) in the OFR from OH oxidation using the OFR185 method, and predicted OA formation from measured VOCs (x4.4). Bottom: ambient MT, SQT (x5), toluene+*p*-cymene (x5), MBO+isoprene, and S/IVOC mass concentrations vs. time of day.

We also added or modified the following text:

P30438 L11: **"A diurnal plot of the measured maximum (0.4–1.5 eq. days age) and predicted SOA formation is shown in Fig. 11, along with ambient MT, SQT, toluene+*p*-cymene, and MBO+isoprene concentrations (and S/IVOC concentrations, discussed in Sect. 3.6.2)."**

See also the response to R3.24 for discussion of the diurnal S/IVOC concentrations.

R3.24. P30440/L28: I don't fully follow what is being compared here. I thought that the SOA yields from S/IVOCs were just derived by comparing the S/IVOCs to the SOA. But then here they are comparing the SOA predicted from S/IVOCs (and VOCs) to the observed SOA. Isn't this circular? Is the point here only the R2 value since the slope was effectively forced to one? This should be clarified. But given that the authors seem to use campaign-average values, not time-dependent values, for the S/IVOC concentrations it is not especially surprising to me that the R2 decreases from when compared to just the SOA predicted from VOCs. Or am I missing that, in fact, time dependent S/IVOC concentrations were used here? I think I am confused because of the statements on the previous page that a "full time series analysis" was not possible. I suggest that this section could be somewhat clearer regarding what specifically is being done with the S/IVOC measurements. (I suspect the authors are trying to not show too much of this data given the other pending publication. If the Hunter paper has been published by the time this is revised, I strongly encourage the authors to use a figure to help facilitate understanding here.)

We have restructured Sect. 3.6.2 as follows to clarify these topics:

P30439 L15-16: this last sentence of the paragraph has been removed.

Starting at P30439 L23: **"With the substantial temporal overlap between OFR185 operation and TD-EIMS measurements, it is feasible to perform a point-by-point analysis using the full TD-EIMS time series (shown in Fig. S7) to determine what the SOA yield of the lower limit S/IVOC mass would need to be in order to fully explain the amount of SOA formed from OH oxidation in the OFR.**

Ideally, the total mass of S/IVOCs at each data point that would be converted into SOA by oxidation would be determined by multiplying the mass in each volatility bin by the SOA yields of each bin. Since experimental measurements of the aerosol yields of such gases are generally not available and the ambient mixture of S/IVOCs was not fully speciated, we instead proceed under the assumption that all of the SOA formation that was not due to the previously discussed PTR-TOF-MS-measured VOCs came instead from the mass measured in the $C^* = 10^1$–10^7 μg m^{-3} volatility bins, with one correction. Since SQT are typically in the $C^* = 10^5$ μg m^{-3} range, we subtracted the SQT mass measured by the PTR-TOF-MS from the bulk S/IVOC mass (a subtraction of 6% of the total TD-EIMS measurement), to avoid double-counting due to this expected measurement overlap. While MT are in the $C^* = 10^7$ μg m^{-3} volatility bin, that bin is at the upper volatility limit of the TD-EIMS measurement capability. Some gases in that bin were sampled, but MT were expected to be too volatile to be measured (Hunter et al., 2016). This was supported by the fact that the campaign-average mass in the $C^* = 10^7$ μg m^{-3} bin was only 0.43 μg m^{-3}, which would correspond to only approximately 0.1 ppbv MT, if there were no other gases in that bin. The campaign-average in-canopy MT concentration measured by the PTR-TOF-MS was approximately 0.8 ppbv.

For the lower limit S/IVOC mass case, the average SOA yield of the total S/IVOCs was determined by finding the yield value that made the slope of SOA measured vs. predicted from VOCs + S/IVOCs equal to one. As shown in Fig. 12, an average SOA yield of 58% for the bulk S/IVOC mass was required in order to bring the measured vs. predicted SOA formation into optimal agreement in this time series analysis. The correlation between measured and predicted SOA formation including the S/IVOCs and VOCs was R^2=0.66. Attempts were made to optimize the correlation between measured and predicted SOA formation by applying arbitrary *C-dependent yields, but this did not result in significantly better correlations. Since speciated S/IVOC measurements as well as yields for each volatility bin (which may have varied with diurnal changes in the composition of each bin) were not available, we concluded that further detailed interpretation of SOA production from the measured S/IVOCs would be under-constrained.**

As mentioned above, this average SOA yield for S/IVOCs of 58% was estimated by assuming the lower limit case where the total ambient S/IVOC mass was sampled using only the TD-EIMS. The upper limit mass case in Hunter et al. (2016) assumed that the several instruments that measured S/IVOCs were measuring different subsets of total S/IVOCs, so the measurements needed to be summed in order to determine the total mass concentration. Due to limited temporal overlap between all instruments, the analysis in Hunter et al. (2016) was performed on campaign average measurements. For this reason, the average SOA yield of S/IVOCs for the upper limit case is also done using the campaign average values instead of the time series analysis that was possible for the lower limit case. The average upper and lower limit S/IVOC mass concentrations were 10 and 3.1 µg m^{-3}. To estimate the SOA yield of S/IVOCs in the upper limit case, the TD-EIMS time series data was multiplied by 3.2, so that it reflected a campaign average of 10 µg m^{-3}. Using this upper limit mass time series, an average SOA yield for S/IVOCs of 18% was needed to bring measured vs. predicted SOA formation in the OFR into agreement. This makes the assumption that the ratio of S/IVOC mass measured by each technique was constant.

While measurements of SOA yields for speciated S/IVOCs are limited, especially for the relatively low OA concentrations in this study, previous work suggests that this range of 18-58% yield is reasonable. A yield of 51% was measured for n-heptadecane ($C^* = 10^4$ µg/m^3) with OA = 15.4 µg/m^3 under high-NO_x conditions (Presto et al., 2010). Yields can be even higher from cyclic compounds (Lim and Ziemann, 2009; Tkacik et al., 2012) and under low-NO_x conditions (Ng et al., 2007; Lane et al., 2008). SOA yields from several other IVOCs (naphthalene and alkylnapthalenes) under low-NO_x conditions were determined to be 58-73% with OA concentrations of 10–40 µg/m^3 (Chan et al., 2009).

This analysis suggests that OH oxidation of organic gases in a parcel of ambient pine forest air will produce approximately 3.4 times more SOA from S/IVOC gases than from VOCs. This does not provide information about the sources of the lower volatility organic gases. They may be directly emitted, formed as oxidation products of VOCs that were emitted upwind of this parcel, or some combination of these two options. Ambient MT measured by the PTR-TOF-MS and S/IVOC concentrations measured by the TD-EIMS exhibit a modest correlation (R^2 = 0.43, shown in Fig. S13), suggesting that the S/IVOCs may at least partially come from a biogenic source related to the emission of MT. For

example, O_3 and NO_3 may react with the C=C-containing MT and SQT emissions during nighttime, leading to a buildup of oxidation product S/IVOCs that lack C=C double bonds and would generally not react further with O_3 and NO_3 (Atkinson, 1997). If this occurs, then OFR oxidation is merely starting with precursors that are partway through the "aging" process from VOC emission to SOA formation. Variations in the ratio of measured to predicted SOA formation in Figs. 10 and 12 could be due partly to variations in the ratio of the concentrations of S/IVOCs to VOCs due to changes in the meteorological or chemical conditions of the atmosphere, or from periodic changes in the biogenic and/or anthropogenic sources of S/IVOCs. However, as shown in Fig. 11, the diurnal profile of S/IVOC concentrations showed a relatively smaller increase in concentrations at night compared to MT or measured SOA formation. Since emissions and losses (e.g. OH oxidation) generally change with time of day, it would not be unreasonable to expect the speciation and SOA formation potential of ambient S/IVOCs to also change with time of day. Until the S/IVOCs in a dataset such as this can be better speciated and quantified, these conclusions remain speculative."

R3.25. P30441, L8: I think the authors need to change "will produce" to "can potentially produce." As I see what the authors have done, it is simply a matching exercise that does not definitively indicate that S/IVOCs form this much more SOA compared to VOCs in this environment because the authors have not addressed the issue of potential yield underestimates for VOCs in a quantitative manner.

We have changed the words "will produce" to **"can potentially produce"** in P30441 L8, as suggested.

R3.26. P30441/L12: The authors here discuss how the correlation between SOA and MT concentrations indicates that S/IVOCs come from biogenic sources related to MTs. I believe it would be much more straight forward to compare the SOA formation to the S/IVOC concentrations or the MT concentrations to S/IVOC concentrations directly to make this point. As written, this conclusion seems one step removed from the desired actual comparison.

We have modified the text as part of the response to R3.24, and have included the following Fig. S13 in the supplemental information:

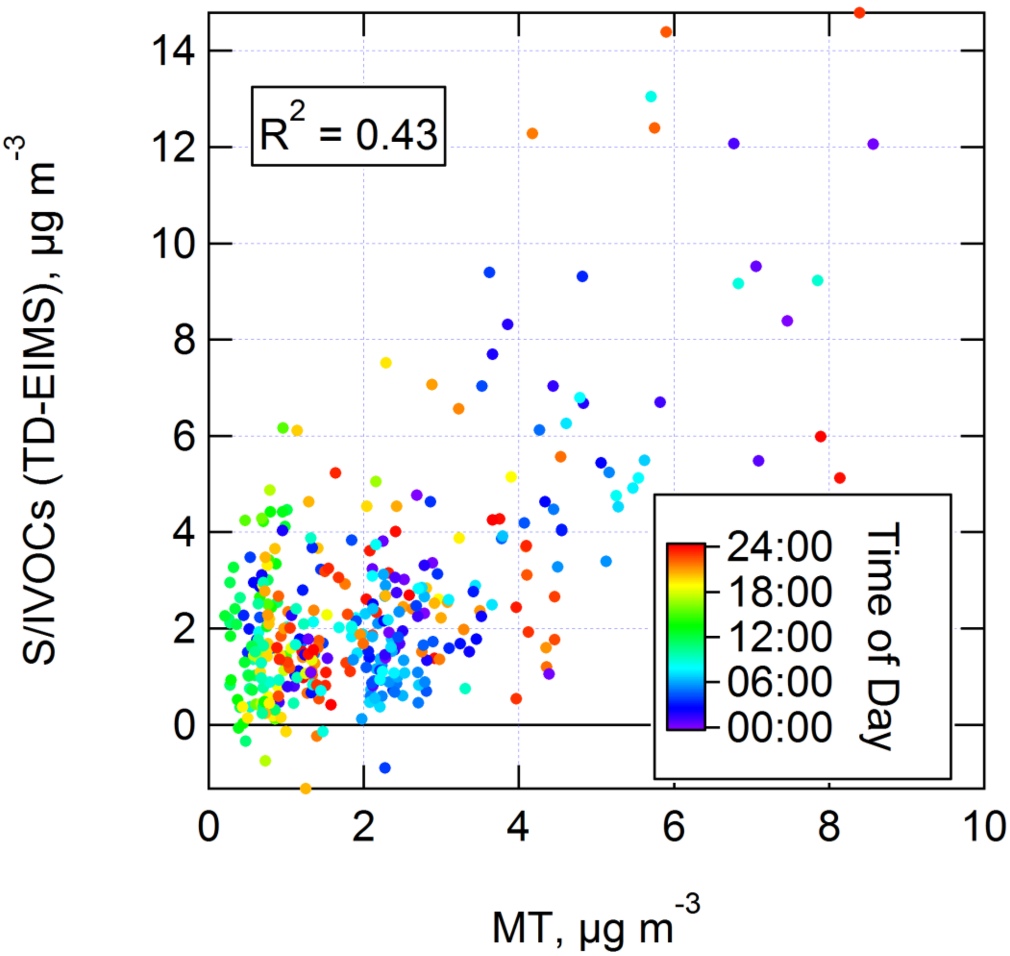

Fig. S13. Scatterplot of mass concentration of ambient S/IVOCs (lower limit measured by TD-EIMS) vs. ambient MT measured by PTR-TOF-MS. Data are shown colored by local time of day.

Other Changes:

In order to conform with the terminology introduced by Peng et al. (2015a), we have changed from "OFR254" to **"OFR254-70"** at all relevant references, signifying the typical injection of 70 ppm of O_3 during this campaign. This detail is relevant for understanding the oxidant chemistry in the OFR, which will assist with any future comparisons that are made with this dataset. To this end, we have modified the text at P30417 L9 to read:

"In the OFR254 method, the mercury lamps were mounted inside Teflon-coated quartz sheaths, which blocked transmission of 185 nm light into the OFR, and only (R4-5) produced OH by photolysis of injected O_3. Following the terminology introduced by Peng et al. (2015a), the method used in this work can be referred to as OFR254-70, signifying that typically 70 ppm of O_3 was injected when using the OFR254 method."

We have also introduced an additional correction to the LVOC fate modeling. Previously, the condensational sink (*CS)* was calculated using the dry SMPS measurements. However since oxidation in the OFR took place under ambient RH, the *CS* would be larger due to hygroscopic growth of particles in the atmosphere. We have now accounted for the added *CS* due to particle water, and the details were added starting at P30427 L25, which now reads:

"- τ_{aer}: Following Pirjola et al. (1999), the lifetime for LVOC condensation onto aerosols was calculated as

$$\tau_{aer} = \frac{1}{4\pi \cdot CS \cdot D} \qquad (1)$$

with a diffusion coefficient *D* = 7 x 10^{-6} m^2 s^{-1} representative of an oxidized organic molecule with a molecular weight of approximately 200 g mol^{-1} at the field site ambient pressure (Tang et al., 2015). *CS* is the "condensational sink"

$$CS = \int_0^\infty r\beta(r)N(r)dr \qquad (2)$$

which is the integral of the first moment of the particle size distribution, where *r* is the wet particle radius, *N(r)* is the particle number size distribution, and

$$\beta(r) = \frac{Kn+1}{0.377Kn+1+\frac{4}{3}\alpha^{-1}Kn^2+\frac{4}{3}\alpha^{-1}Kn} \qquad (3)$$

is the Fuchs-Sutugin correction for gas diffusion to a particle surface in the transition regime, calculated using the sticking coefficient *α* of the condensing species (Seinfeld and Pandis, 2006). *CS* was calculated using the average of the size distributions of ambient air entering the OFR and of air exiting the OFR after oxidation, as a best approximation of the actual *CS* experienced by LVOCs in the OFR. Since LVOC condensation in the OFR took place under ambient RH, the dried SMPS particle size

distribution measurement was corrected to account for the increase in *CS* from hygroscopic particle growth as a function of RH. For each data point, a growth factor (*gf*) was calculated from the equation

$$\boldsymbol{\kappa = \sum \varepsilon_i \kappa_i = (gf^3 - 1)(1 - a_w)a_w^{-1}} \tag{4}$$

from Petters and Kreidenweis (2007) and Nguyen et al. (2015), where ε_i is the volume fraction of aerosol species *i*, κ_i is the hygroscopicity parameter of aerosol species *i*, κ is the hygroscopicity parameter of the total aerosol, and a_w is water activity. We approximate a_w as being equal to RH, between 0 and 1. Total κ was estimated using κ_{OA} = 0.13 as previously reported for this site and campaign (Levin et al., 2014) and $\kappa_{inorganic}$ = 0.6, using the volume mixing rule (Petters and Kreidenweis, 2007). The volume fractions were calculated from AMS measurements in ambient air or after OFR oxidation, using estimated component densities (Salcedo et al., 2006; Kuwata et al., 2012). The *gf* ranged between 1 and 2.3 with an average of 1.2. It was applied to the dry SMPS particle diameter before calculating *CS*.”

This correction to *CS* for hygroscopic growth of particles resulted in minor updates to values quoted throughout the manuscript, as well as Figs. 5–8, 10–13, S10, and S12. None of these updates resulted in substantial changes to the interpretation of our results.

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