

Response to reviewers for the paper “Measurements and modeling of urban secondary organic aerosol formation potential as a function of precursor volatility class in the Los Angeles area during summer 2022”

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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**. All line numbers refer to the originally submitted manuscript.

Anonymous Referee #1

Overview

R1.0. This manuscript presents measurements of secondary organic aerosol formation potential (SOA-FP) in the Los Angeles basin during summer 2022 using a novel dual oxidation flow reactor (OFR) system. By employing an electrically conductive perfluoroalkoxy alkane inlet upstream of one OFR, the authors separate ambient precursors according to volatility and experimentally quantify the relative contributions of higher- and lower-volatility compounds to SOA formation. The measurements are further compared with predictions from two box models.

Overall, this is a well-written, carefully executed, and comprehensive study. The experimental approach is novel and represents an important advance in the direct characterization of SOA precursor volatility classes in ambient air. The manuscript is clearly structured, the methodology is described in sufficient detail, and the interpretation is generally well supported by the observations. I believe that this work is suitable for publication after the authors address the comments below

We thank the reviewer for their accurate summary of our paper and the overall positive assessment.

R1.1. The manuscript discusses SOA formation primarily in terms of volatility classes. However, recent laboratory and field studies have demonstrated that rapid autoxidation and HOM formation can substantially enhance SOA yields even for relatively volatile precursors, especially monoterpenes and aromatic compounds. Given that OFRs can efficiently generate HOMs under low-NO conditions, could the authors comment on how autoxidation chemistry may influence the inferred SOA-FP distribution across volatility classes? This may be

particularly relevant when comparing the measurements with mechanisms such as CRACMM that contain simplified autoxidation treatments.

The authors thank the reviewer for this important point. This was already mentioned in the submitted manuscript (L114) as:

“Fast autoxidation reactions are still competitive at this level of exposure, while slower ones have reduced importance compared to ambient conditions (Peng et al., 2019).”

The reviewer is asking whether the remaining deviations between average OFR oxidation conditions and average ambient conditions could bias the measurement in favor of VOCs or S/IVOC precursors. Given the state of the knowledge about ambient SOA-FP, oxidation mechanisms, and oxidation conditions, we feel that this question cannot be precisely answered at this time. A detailed study could be conducted using e.g. GECKO, along the lines of Peng et al. (2020), but that is beyond the scope of this manuscript. Additionally, it would be subject to the current limitations and uncertainties regarding concentrations, SOA yields and mechanism correctness for VOCs and SVOCs both in ambient air and GECKO. What we can do is to add a clearer explanation of what the reactor conditions are and how they compare to ambient conditions. The paragraph starting on L106 has been expanded to read:

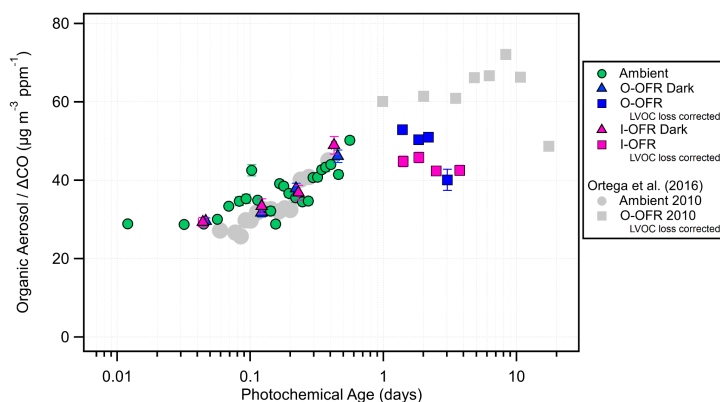
“Both of the OFRs deployed in this study were **manufactured by Penn State Univ. and** run in OFR185-mode (Peng and Jimenez, 2020). In this mode, two Teflon-sleeved low-pressure mercury lamps (model no. 82-9304-03, BHK Inc., Ontario, CA) with discrete emission peaks at 185 and 254 nm, photolyze water and ozone inside the OFR to generate hydroxyl (OH) radicals. A steady flow (~30 ccm) of nitrogen **passed** through each Teflon lamp sleeve to cool and protect the lamps. No ozone was injected into the OFRs. While both OH radicals and ozone are formed in the OFR, the ratio of OH to ozone exposure is ~100 times larger than in the atmosphere (at the surface). Even for species like limonene that react quickly with ozone, OH chemistry is dominant in the OFR (Peng et al., 2016; Peng and Jimenez, 2020). **Since the midday photochemical age of ambient air was 0.5 days (as discussed in Sect. 3.4), and the OFRs were achieving an additional 2 days of aging in a 3 minute residence time, we estimate that the concentration of OH radicals in the OFR was ~240 times that of ambient air.** The rapid consumption of NO_x leads to low-NO conditions in the reactor (Peng and Jimenez, 2017). **As discussed in Peng et al. (2020), in order to maintain atmospheric relevance under low-NO conditions, OFRs need to be tuned carefully. OH concentrations should be high enough to minimize non-tropospheric VOC photolysis, but low enough so that fast autoxidation reactions can occur. In this work we targeted an OH exposure of ~2 equivalent days, to exhaust SOA precursors and measure the full SOA-FP of ambient air** (Hayes et al., 2015; Ortega et al., 2016). Fast autoxidation reactions are still competitive at this level of exposure, while slower ones have reduced importance compared to ambient conditions (Peng et al., 2019). **This exposure, along**

with the humidity of ambient air and the estimated total external OH reactivity of 20 s^{-1} , puts the OFR in “safe” operating conditions (Peng et al., 2020). In a previous campaign, the SOA yields in the OFR for several terpene species were probed using standard addition, and found to be comparable to those of low- NO_x chamber studies (Palm et al., 2018). Given the state of the knowledge about ambient SOA-FP, oxidation mechanisms, and oxidation conditions, it is still unclear whether other deviations between average OFR oxidation conditions and average ambient conditions could bias the experimental VOC to S/IVOC SOA-FP apportioning. To quantify ambient gas and aerosol transmission in the absence of oxidation, the OFR lamps were turned off for 40 min every 6 hours.”

R1.2. The manuscript attributes the lower SOA formation potential observed in 2022 relative to CalNex 2010 to a combination of reduced precursor concentrations and enhanced ambient OH exposure, which presumably leads to greater consumption of SOA precursors prior to sampling. However, increased atmospheric oxidation can also generate lower-volatility products that remain available for further SOA formation in the OFR. Could the authors discuss how multigenerational oxidation influences the interpretation of SOA-FP? Specifically, does increased photochemical age necessarily imply lower SOA-FP, or could aging shift the precursor distribution toward more oxygenated, lower-volatility species that are not fully captured by the present framework?

The reviewer highlights an important point.

First, we can address potential multigenerational oxidation in the photochemical aging done by the reactors. The question, “Does increased photochemical age necessarily imply lower SOA-FP?” has already been partially addressed through the analysis of Fig. 7, reproduced below:



In Fig. 7, the naturally formed SOA in ambient air increases with ambient photochemical age. When we further age the air by ingesting through the OFRs, an increased photochemical age causes a plateau in SOA-FP. L524 in the submitted paper states:

“OA generation in OFRs has been shown to have a non-linear dependence on OH exposure: for up to 1 day of aging OA generation is positively correlated with OH exposure, at 1-10 days of aging OA generation plateaus and does not have a dependence on OH exposure, and at ages higher than 10 days OA may begin to be destroyed as OH exposure increases (Ortega et al., 2016).”

Therefore, it is unlikely that the photochemical aging done by the OFRs is generating a substantial amount of lower-volatility gas-phase products that remain available for further SOA formation.

The discussion of Fig. 7 has been expanded with the bolded text as follows (L465):

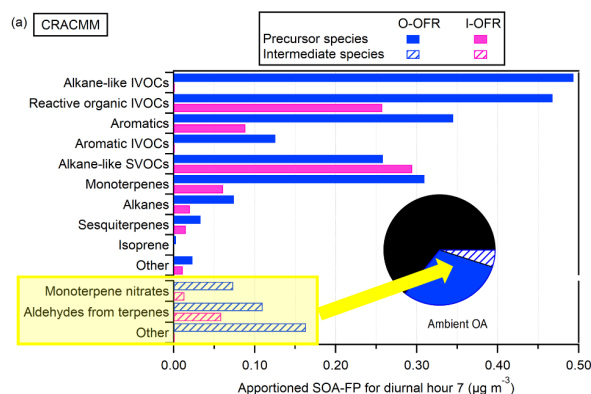
“In this photochemical age range (1-10 days), we do not expect SOA formation to be dependent on age, based on previous campaigns (Ortega et al., 2016; Palm et al., 2016). **The plateau of SOA-FP / Δ CO as photochemical age increases was measured in both 2010 and 2022, and indicates that SOA precursors are being exhausted by the photochemical aging level reached by the OFRs.**”

Second, we can address potential multigenerational oxidation in the ambient aging, prior to ingestion by the OFRs, in three ways: a) using the CMAQ-CRACMM simulation results, b) empirically based on the diurnal cycle of the measured SOA-FP, and c) through a new analysis of oxygenated gas phase species.

- a) This was already partially addressed in the submitted manuscript through the application of CMAQ-CRACMM. That mechanism predicts the formation of nighttime intermediate oxidation products from terpenoids, which can then react with OH during the daytime to form SOA. L791 states,

“In terms of our model results, Figure 11 shows that the Caltech model attributes a total of 2.6 % SOA-FP at 7 am (peak of measured SOA-FP) to monoterpenes, of which 0.8 % is anthropogenic (VCP terpenes) and 1.8 % is biogenic (Fig. S20). CRACMM shows isoprene contributing near zero to SOA-FP at this time, monoterpenes contributing 12.5 % and sesquiterpenes contributing 1 %. However, monoterpenes have an additional contribution to SOA-FP in CRACMM through partially oxidized gas-phase monoterpene products (nitrates and aldehydes), likely from nighttime chemistry. These species were responsible for 7.5 % of modeled total SOA-FP in CRACMM at 7 am (Fig. 11a). Adding this to the direct contribution of monoterpenes and sesquiterpenes brings the terpenoid and terpenoid oxidation products SOA-FP to ~21 % of the peak value in our study. The CRACMM model input does not differentiate between biogenic vs anthropogenic terpenes.”

We have highlighted the relevant data in Fig. 11a for this comment in yellow below. The figure was already in the submitted paper and has not been changed for this revision.:

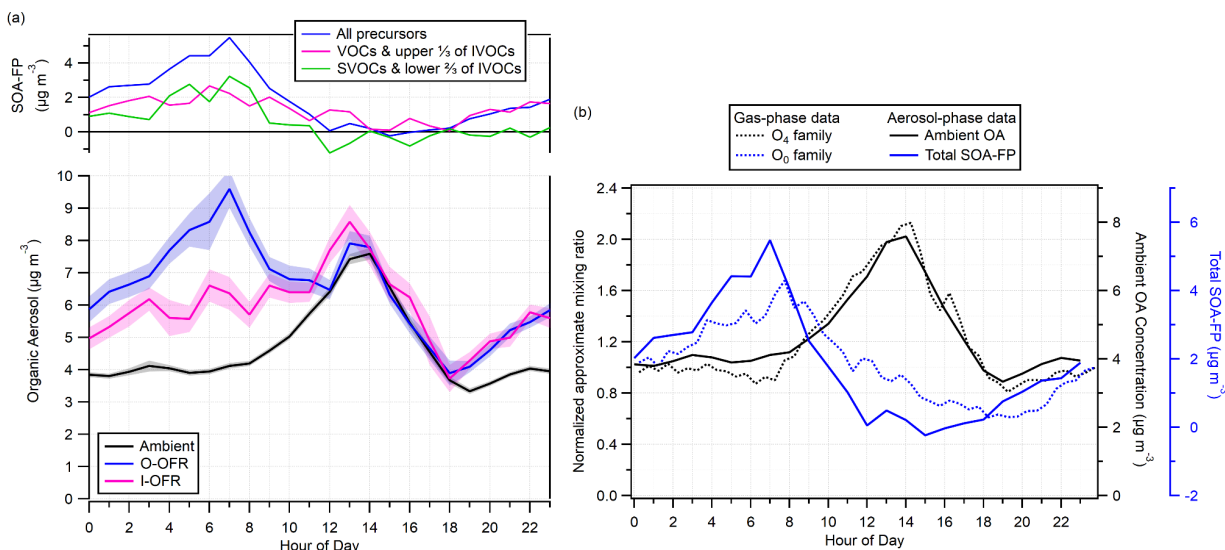


- b) The empirical SOA-FP data in Fig. 6 (reproduced in its revised form for point c) below) shows that when ambient photochemical aging is highest, SOA-FP is the lowest. We've added the following text to L442 to expand this discussion:

“In Fig. 6, the growth of SOA-FP due to lower volatility precursors starts to be significant around midnight and peaks at 7:00 in the morning. When the photochemical age is highest (afternoon), the measured SOA-FP drops to zero. Since the contribution of lower volatility precursors is highest when the photochemical age is lowest, this suggests that the dominant source of lower volatility precursors is primary emission, rather than multigenerational oxidation. One exception are products of NO₃ radical oxidation of monoterpenes, that do accumulate at night. Fig. 11a shows the relatively small contribution to SOA-FP from these intermediate species. The lack of measurable SOA-FP in the afternoon also indicates that oxidation has exhausted SOA-FP, and there is no further SOA to be formed by aging multigenerationally across days.”

- c) For a separate manuscript, a colleague has been analyzing the gas phase data from this campaign to compare with another location. As part of that analysis, the PTRMS gas phase data has been grouped into families according to the number of oxygens in all the measured ions. We are including a new figure here from that analysis to highlight a striking comparison.

Figure 6 is now multipanel:



“Figure 6: (a) Bottom: Diurnal cycles (1 h time resolution) of OA through each sampling pathway: ambient air, O-OFR and I-OFR. **Shaded regions indicate ± 1 standard error.** (a) Top: SOA-FP from **all precursors (O-OFR minus ambient)**, precursors in the VOC & upper 1/3 of IVOCs volatility range (I-OFR minus ambient) and SOA-FP from all lower volatility precursors (O-OFR minus the I-OFR). (b) **A comparison of the ambient OA and total SOA-FP from (a) with families of gas phase species based on the number of oxygens.**”

A discussion of Fig. 6b has been added on L443:

“Further evidence to support the lower volatility precursors being emitted rather than formed is shown in Fig. 7b. In their analysis of the Vocus data from this campaign Blauth et al. (2026) grouped the gas phase species according to the number of oxygens. The least and most oxygenated O_x families are plotted in Fig. 6b, with concentrations normalized to be 1 at midnight. The O_4 family peaks in the afternoon, and its diurnal cycle nearly identical to the ambient SOA trace when overlaid. The O_4 family anti-correlates with the total SOA-FP measured in the O-OFR. Despite the presence of these highly oxygenated VOCs in the afternoon there is no measured SOA-FP. Again, this strongly suggests that the dominant source of lower volatility precursors is primary emission, rather than multigenerational oxidation. The O_0 family peaks in the morning, similar to the total SOA-FP, and is anti-correlated with ambient SOA. This is consistent with the analysis we present in Sect. 3.8, where we find that non-oxygenated species correlate best with total SOA-FP.”

We have also added this to the abstract on L33:

“The dual-OFR measurements suggest ~31 % of the total SOA-FP is due to compounds with volatilities in the SVOC and lower IVOC ranges. **Evidence suggests these lower volatility**

precursors are mainly from direct emissions, rather than oxidation products from upwind aging.”

R1.3. One important aspect of the experimental design that may influence the interpretation of the results is the performance of the c-PFA inlet as a volatility filter. While the authors characterize the transmission efficiency, it remains unclear whether multifunctional compounds with moderate volatility and strong polarity may experience enhanced wall interactions beyond those predicted solely from volatility. Previous studies have shown substantial wall losses of oxygenated organics in sampling lines (e.g., Pagonis et al., 2017; Deming et al., 2019). Could the authors discuss whether differential losses of highly functionalized species could bias the inferred partitioning between higher and lower-volatility precursor classes?

This topic had already been addressed in the submitted manuscript (L387-397) that read:

“In the analysis above it has been assumed that the absorptive mass of the tubing is independent of the C^* of the partitioning species. Krechmer et al. (2016) showed that highly oxidized, low volatility vapors needed to be modeled with decreasing absorptive mass of the fluorinated ethylene propylene (FEP) Teflon chamber walls than higher volatility hydrocarbons and lightly oxidized species. Those authors suggested that activity coefficients of these highly oxidized species onto nonpolar Teflon films may explain the observed behavior. Huang et al. (2018) proposed a quantitative parameterization of the activity coefficient of these highly oxidized, low volatility gas species vs. C^* that can explain the partitioning data for Krechmer et al. (2016). The activity coefficient increases as the species become more oxidized and less volatile, causing them to behave as if their vapor pressures were larger (Huang et al., 2018). However, in this study the SVOCs that are SOA precursors may be primarily emitted or lightly oxidized, and thus may not have such high activity coefficients on Teflon. We do not see evidence of higher than expected transmission of low volatility species in Fig. 3b; the final transmission curve appears to fit all the data.”

In other words, we may be *overestimating* the losses of highly functionalized species through the inlet.

We realize that this text may have been too focused on the history of those observations, and therefore unclear for readers in terms of the implications. We have attempted to clarify these ideas and have rewritten the paragraph above as:

“Papers that have studied oxygenated organics in Teflon sampling lines and chamber walls (Krechmer et al., 2016; Pagonis et al., 2017; Huang et al., 2018; Deming et al., 2019 and Liu et al., 2019) found that species with oxygenated functional groups partitioned to surfaces less efficiently than species without oxygen (for the same saturation concentration). This is

likely due to an increased activity coefficient compared to non-oxygenated species (Krechmer et al., 2016; Huang et al., 2018). Therefore, the transmission of moderate volatility oxygenated species could be underestimated in this work, since we predicted inlet transmission based on volatility alone. However, we do not see evidence of higher than expected transmission of moderate volatility species in the transmission measurements in Fig. 3b; the final transmission curve appears to fit all the data.”

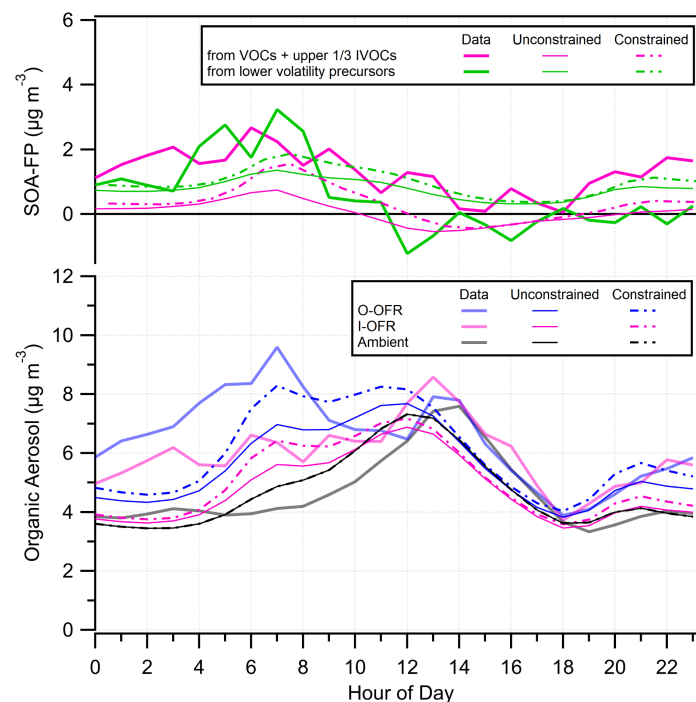
R1.4. The comparison between model performance and observations provides useful insight. This study shows that CRACMM reproduces ambient OA reasonably well but substantially underpredicts SOA-FP, while the Caltech model exhibits the opposite behavior (underestimates OA and overestimates SOA-FP). Although the model–measurement discrepancies are clearly presented, it remains somewhat unclear which processes are primarily responsible for these biases. Could the authors further discuss whether the disagreement mainly arises from uncertainties in emissions, gas-phase oxidation chemistry, volatility distributions, or gas-particle partitioning or some other factors? Such discussion would really strengthen the implications for future model development.

The authors agree that understanding possible reasons for the measurement-model discrepancies would be very helpful for future efforts. However, we do not have a simple way of deconvolving the many possible reasons mentioned in the reviewer’s comment.

One specific point we were able to explore was the effect of emission uncertainty for CRACMM. In Figure S21, we compared the CRACMM model output when it was initialized with the unconstrained CMAQ output vs. with the constrained CMAQ output (where some of the model emissions were replaced with Vocus measurements). L591 discussing Fig. S21 originally read (in the submitted manuscript):

“As a sensitivity study, CRACMM was also run with the unconstrained CMAQ output as input. This resulted in enhanced SOA-FP in the O-OFR and I-OFR from 5:00-12:00, but otherwise looked very similar to the constrained results (Fig. S21).”

Fig. S21 is reproduced below, unchanged from the manuscript:



“Figure S21. A modeling sensitivity study comparing CRACMM results when the input is unconstrained (raw CMAQ output) vs constrained (when Vocus measurements are used to constrain the CMAQ output, as is done in the main paper). Top: Campaign-averaged diurnal of SOA-FP according to the volatility split. Bottom: Campaign-averaged diurnal of total OA through the different sampling pathways.”

We have expanded the quoted text on L591 to read:

“There are many possible reasons for the model-measurement discrepancies discussed above, including uncertainties in emissions, gas-phase oxidation chemistry, volatility distributions, or gas-particle partitioning yields. To test if uncertainties in emissions affect the amount of SOA-FP, CRACMM was also run with the unconstrained CMAQ output as input. This resulted in enhanced SOA-FP in the O-OFR and I-OFR from 5:00-12:00, bringing the model into slightly better agreement, but otherwise looked very similar to the constrained results (Fig. S21). Unfortunately, we do not currently have a way to deconvolve the possible effects of the other listed factors from one another.”

Another way to address this point (and several others in both reviews) would be to simulate our observations within a 3D regional air quality model. This is obviously outside the scope of the present manuscript, but we hope to motivate some collaborators to explore that topic in a future study.

R1.5. (a) The present study attributes only a modest fraction of SOA-FP to terpenoids. However, because biogenic oxidation products can undergo extensive multigenerational oxidation and partition into lower-volatility bins, is it possible that some SOA-FP attributed to lower-volatility precursors originated from earlier terpenoid oxidation? How does the volatility-based framework distinguish between primary terpenoid precursors and their aged oxidation products?

This is an excellent question. We had already addressed it in the submitted manuscript. See the response to R1.2 in response a) for the previous text and the changes to clarify this topic.

R1.5. (b) Also, the OFRs were operated in OFR185 mode at approximately two equivalent days of OH exposure under low-NO conditions. Since terpenoid oxidation chemistry and SOA yields are strongly dependent on NO_x, it would be useful to discuss in more detail how representative the inferred terpenoid SOA-FP is of summertime atmospheric conditions in Los Angeles, where oxidation frequently occurs under moderate-to-high NO_x conditions. Could the OFR operating conditions systematically bias the estimated contribution of terpenoids?

The following text has been added to L804 to address this question:

“In this work, the OFRs were run in 185-mode, creating low-NO conditions. Modeling work for LA showed that in 2010, the fate of ambient RO₂ radicals in the morning was dominated (weekday branching ratio of 99%) by the RO₂+NO rather than low-NO oxidation pathways (Hayes et al., 2013). However, Schulze et al. (2025) cite a 40% decrease in NO_x emissions from 2010 to 2022. Robinson et al. (2026) also describe a decrease in the fraction of isoprene RO₂ radicals going through the RO₂+NO pathway for LA to as low as 80% (and as low as 60% for New York City). Thus even the largest US urban areas are shifting from a NO_x-saturated regime to a NO_x-sensitive one. Ambient NO_x concentrations are shown in Fig. S7b, with a campaign average of 12 ppb.

The presence of NO_x in ambient air may have an effect on the SOA yields of terpenes and other VOCs. Early chamber work studying isoprene (Kroll et al., 2006) and α -pinene and sesquiterpenes (Ng et al., 2007a) reported NO_x-dependent SOA yields in opposite directions (decreasing yields for isoprene and α -pinene, and increasing yields for sesquiterpenes as NO_x increases). Ng et al. (2007b) reported substantially lower yields for high-NO compared to low-NO conditions for three aromatic compounds studied. Those studies suggest effects on yields can be as large as factors of 2. However, the “high-NO_x” conditions of these experiments ranged from 100-800 ppb, much higher than the concentration measured in this work (12 ppb). Stirnweis et al. (2017) found that α -pinene SOA yields generally decrease with increasing NO_x/VOC ratios, but that relative humidity, aerosol concentration and initial VOC concentrations also had significant effects. Given this, it is unclear how differences in NO_x concentrations between ambient LA air and the OFR would affect overall SOA-FP or from different compounds or classes. However, likely the overall effects on yields of operating under low-NO conditions in the OFR (compared to ambient conditions) are not nearly as large as a factor of 2, due to the relatively extreme conditions of those high-NO chamber studies, offsetting effects of different compounds (e.g., differing signs) and less sensitive species, and that overall RO₂ fate is no longer NO_x-saturated in LA.”

Anonymous Referee #2

Overview

Article describes novel measurement concept utilizing open-OFR and inlet-OFR systems and preliminary results with the new system. The topic is timely and it is very important to develop further the OFR measurement systems to be more flexible for different purposes. Especially it would be very important to have a “standardized and repeatable” approaches for the OFR measurements and reporting of the results.

We thank the reviewer for the summary. We share similar hope that this dual-OFR technique will be used in other locations in future works.

R2.1. I have few major comments; Firstly, I propose removing/reducing the Los Angeles focus of the article to make it less locally focused, as the method is applicable anywhere and the results are representing significantly larger area than LA alone. I propose removing LA from the title and moving the LA specific discussion from introduction chapter to experimental/results. In contrast, more discussion to the introduction could be related to OFR setups, what kind of chemistry happens in those, and how representative it is.

We thank the reviewer for this suggestion. We agree that the dual-OFR technique is widely applicable. This is why we have included Section 3.10, "Outlook for the dual-tubing-OFR technique", in which we discuss where and how this technique might be most usefully deployed in the future.

We understand that the reviewer would prefer to highlight the technique over the specific results from this Los Angeles based campaign. During the manuscript drafting, we discussed the possibility of writing a methods paper and an LA results paper. However, we concluded that such a pair of papers would separate critical material and at the end make the work harder to understand and less impactful. Therefore, we will leave the paper title and introduction as is.

R2.2. Secondly, I propose reporting systematically e.g. in a table all the PAM chamber measurement parameters (OH- exposure and its deviations, calibrations, target age, flows, what kind of corrections were done, ozone concentrations etc) for both chambers. Now this information is mostly there, but really hard to find as it is scattered in so many chapters. It is great that authors have already included a chapter about quality assurance and corrections! A list of other comments below.

This is an excellent idea. On L105 we added the following text:

“A list of OFR configuration details is included in Table S2.”

and we have included the following table in the SI:

Table S2. Summary of oxidation flow reactor configuration details

Parameter	O-OFR	I-OFR	Units
OFR operation mode	OFR185	OFR185	-
Intake configuration	Circular opening (14 cm diameter) with Silconert coated coarse mesh screen	Front plate with conductive PFA inlet (1/4" OD, 3.5 m)	-
Number & type of UV lamps	2 BHK lamps	2 BHK lamps	-
Flow of N ₂ through each Teflon lamp sleeve for cooling	~30	~30	sccm
Flow through ring port on back end (to sample gases)	2.4	2.4	LPM
Flow through straight port on back end (to sample aerosols)	2	2	LPM
Target OH exposure on top of ambient age	2 [2.6 x 10 ¹¹]	2 [2.6 x 10 ¹¹]	eq. days [molec cm ⁻³ s]
Average OH exposure on top of ambient (calculated from toluene decay)	1.8 ± 0.6 [2.3 x 10 ¹¹]	2.6 ± 1.2 [3.4 x 10 ¹¹]	eq. days [molec cm ⁻³ s]
Average ozone concentration in OFR output (no O ₃ injection)	~2	~2.5	ppm
Average aerosol transmission (with lights off)	0.999 ± 0.003	0.839 ± 0.005	-

Uncertainties represent one standard deviation.

Introduction:

R2.3. (a) The introduction chapter is quite focused on LA studies and results. Would it be possible to focus on the introduction more to the literature across the world and move the LA related information and discussion to experimental/results?

Please see our response to R2.1 on this topic. LA is a major megacity that has been the subject of many air quality and in particular SOA formation studies. Thus, we prefer to make the LA results central to the paper, including in the introduction.

R2.3. (b) Please, also add something about previous studies related to openOFR + using inlets/tubing in front of it and what is known about their effectivity..

To our knowledge, this is the first time an inlet has purposefully been put in front of an OFR to denude gases, so we cannot introduce previous studies about it. We can, however, include one published qualitative observation that inspired this technique (L67):

“When deployed in the field, OFRs typically ingest ambient air without any upstream separation techniques. The use of an inlet or inlet plate on the front of the OFR was qualitatively observed to result in reduced SOA formation, presumably from the loss of lower volatility gas precursors, so OFRs are typically run with an open front end (Ortega et al., 2013).”

The introduction in the submitted manuscript already includes a summary of OFR use in urban areas, as well as a summary of the time one was used specifically in LA. For additional OFR context, on L52 we have added:

“OFRs are field-deployable reactors that can ingest and photochemically age ambient air. (Peng and Jimenez, 2020; Zhang et al., 2024a).”

R2.4. Line 53: clarify how these contribute? Do you mean traffic emissions or roadways (e.g. asphalt) emissions? How do urban centers contribute? “Specific sources that contribute to SOA formation include roadways and urban centers”

This is a useful clarification. The quoted text starting on L53 has been replaced with:

“OFR studies have identified emissions from traffic, volatile chemical products, cooking and biogenics as sources of SOA-FP in urban areas (Hu et al., 2021; Liao et al., 2021; Liu et al., 2018, 2019a; Ortega et al., 2016; Saha et al., 2018; Shah et al., 2020; Tkacik et al., 2014; Zhang et al., 2024b).”

Experimental

R2.5. For the wood burning influence; maybe add information about general temperature during the period and if possible diurnal variation of e.g. OA. These typically tell also about the need to burn something (e.g. due to cold temperature at night) or if there is evening spikes in OA during e.g. Friday/Saturday this often indicates burning emissions e.g. from grills also.. were any other episodes, e.g. long-range transport, seen during the period?

The author brings up a good point to clarify. The analysis about biomass burning was primarily to understand if there was transported wildfire influence on the data set. We analyzed the trends of the biomass burning tracer, acetonitrile, to see if urban or transported smoke plumes were present. Neither transported nor local biomass burning from e.g. grilling are apparent from the measured acetonitrile concentration. Regarding this analysis, L89 originally stated:

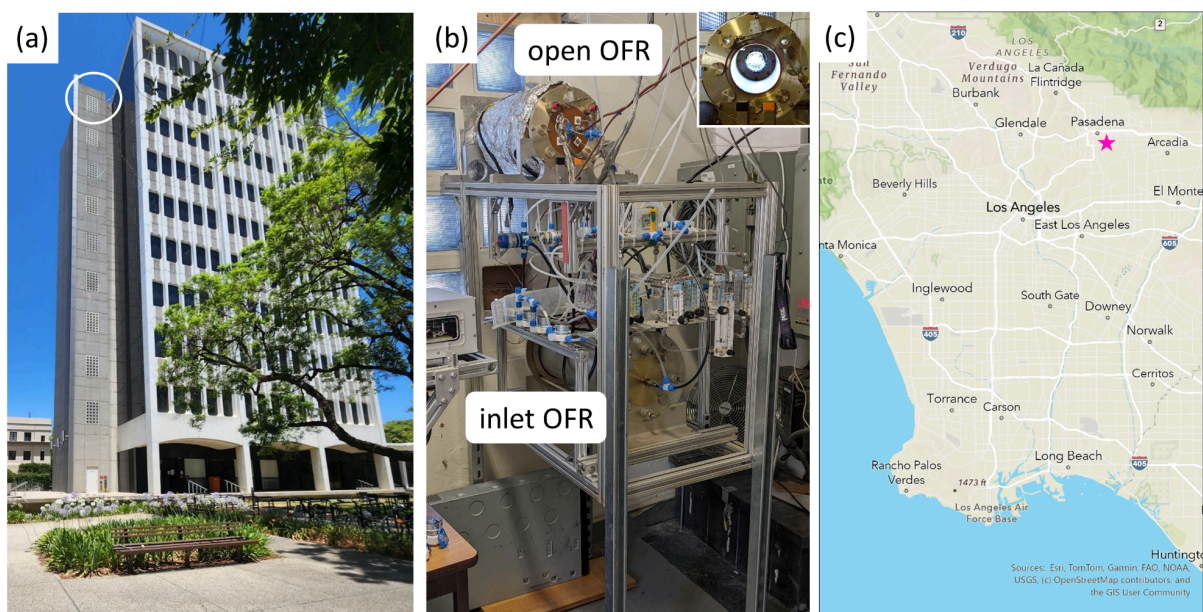
“We used measured ambient acetonitrile to investigate biomass burning influence during this campaign. Acetonitrile and OA would be expected to be correlated during periods of such influence (Aiken et al., 2010). The time series of acetonitrile in Fig. S1a shows some spikes, but these do not correlate with ambient OA or SOA-FP enhancements (Fig. S1c,d), and are likely from solvent use or other urban sources. Therefore, there is no known biomass burning influence on this campaign data.”

We have updated it to:

“During periods of transported wildfire smoke or biomass burning activity, we expect acetonitrile and OA to be correlated (Aiken et al., 2010; deGouw et al., 2003). To understand if this campaign was influenced by wildfire smoke plumes or other biomass burning, we used the ambient acetonitrile measurements. The time series of acetonitrile in Fig. S1a shows some spikes, but these do not correlate with ambient OA or SOA-FP enhancements (Fig. S1c,d), and thus are likely from solvent use or other urban sources. We conclude that there is no significant biomass burning influence on this campaign data. Additionally, ambient temperatures (shown in Fig. S6c) were too high to expect local wood burning for warmth, as nighttime temperatures only dropped to ~20 °C.”

R2.6. Figure 1. Please add a map so reader can see the surrounding area (e.g. roadways etc) better.

We have updated Figure 1 with a map:



“Figure 1: (a) A photo of Caltech Hall, where all instruments were located in a rooftop

penthouse. Ambient inlets for the Vocus and inlet OFR were put out the circled windows. The ambient inlet for the aerosol mass spectrometer (AMS) was located through a hole in the roof. (b) The dual-OFR system was mounted against the windows. The top “open” OFR sampled ambient air through an open window without an inlet, and the bottom “inlet” OFR sampled ambient air through a tubing inlet. The inset shows a photo of the top OFR when open for servicing. For more details about the open OFR, see Fig. S2. **(c) A map of the campaign location, with a pink star indicating the sampling site at Caltech, which was ~3 hours downwind of LA.”**

R2.7. How did the measurement height impact results? Quite many emission sources are on street level and some dilution and aging probably happens before the pollutants reach the chamber.

For this campaign our goal was to measure the well-mixed air of the Los Angeles basin, rather than point sources. In Shah et al. (2020) an OFR was put on a mobile laboratory and driven around the city of Pittsburgh, PA. They found that local sources varied significantly at ground level. For this campaign, we put the instruments in the top of one of the tallest buildings in Pasadena to attempt to sample well-mixed urban air.

We agree that there is ambient aging happening in the plume from Los Angeles to the sampling site in Pasadena (which is ~3 hours downwind) when the sun has risen and photochemistry is active. We were interested in how SOA-FP would evolve over the course of a day, so having ambient aging occur was expected and critical to the results. We partially addressed this in the submitted manuscript on L824:

“Our analysis focuses on the SOA-FP that is present in the gas-phase ambient air, which has not yet formed SOA. Any SOA-FP that has already been converted to SOA is not included in our analyses in this paper. As discussed above this would reduce the contribution of very fast-reacting species such as sesquiterpenes to our measured SOA-FP.”

For added clarity on our method design, we have added (L84):

“To measure the well-mixed air of the Los Angeles basin, we measured downwind of LA from as high a site as possible.”

To better understand the effects of planetary boundary layer height on our analysis, we have added the following figure to the SI:

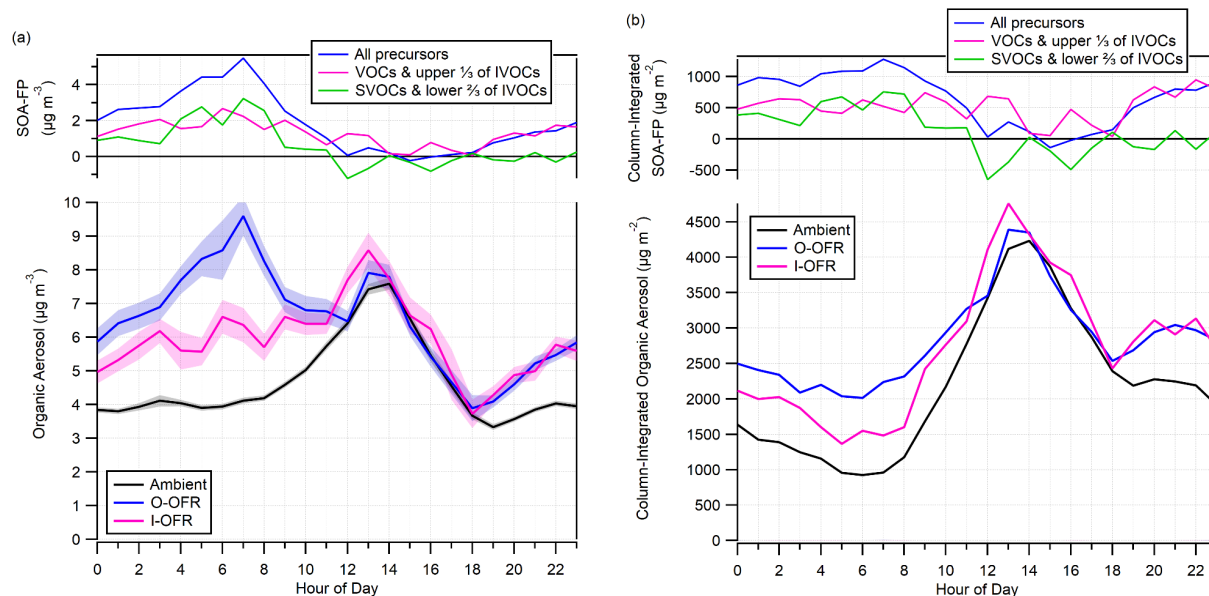


Figure S13. a) A reprint of Fig. 6a from the manuscript, for comparison. b) The same data in a) but multiplied by the estimated planetary boundary layer height. To estimate the PBL height, we averaged the estimate from the 2010 Cal-Nex campaign (Hayes et al., 2013) with an estimate from the Ontario International Airport (~30 miles east of the sampling location) (Rahn et al., 2016).

In the main manuscript, on L447 we have added the following text to introduce this figure:

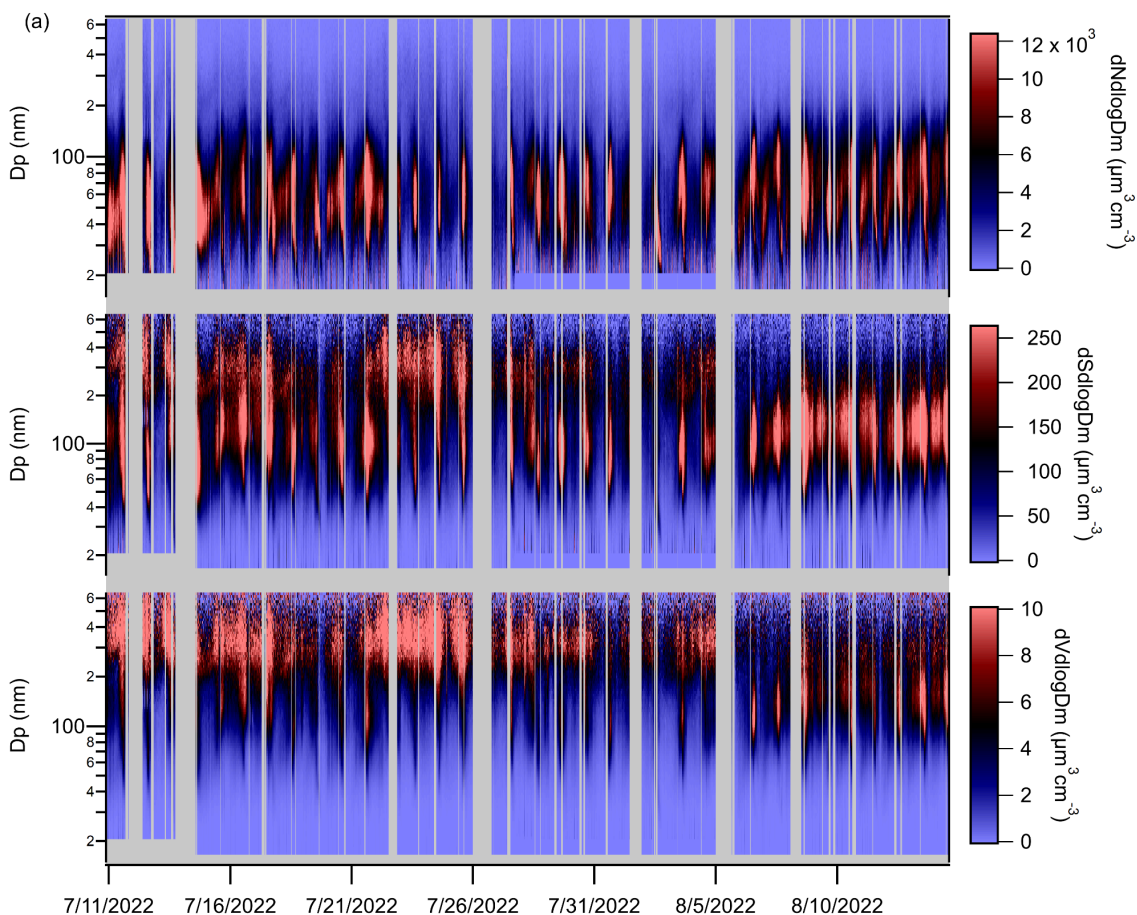
“To understand the effect of the diurnal cycle of the planetary boundary layer (PBL) height on these measurements, Fig. S13 compares the surface concentrations of OA from Fig. 6a with estimated column-integrated concentrations. The column-integrated concentrations show more moderate variations at night and the early morning, due to the effect of the changing PBL height. The column-integrated SOA-FP still collapses onto the ambient data at noon.”

R2.8. AMS was HR-ToF-AMS? Was size distribution measured or only MS mode? would be great to have at least very short summary of the instrument, even though there is a link to other study, but not everybody follows it.

We have added the bolded text below to include more details on the particle instruments (L162) and discuss the measured size distribution, which has been added as Fig. S3 and is reproduced below:

“A high-resolution time-of-flight aerosol mass spectrometer (AMS) (Canagaratna et al., 2007; DeCarlo et al., 2006) was operated by Caltech and used to monitor chemical composition of non-refractory submicron aerosol with 1 minute resolution. Schulze et. al. (2025) provide a

detailed summary of the AMS sampling setup and ambient data, and compare the results with those from 2010 and 2020 campaigns (Schulze et al., 2025). **The instrument was run in “V-mode”. Sensitivity calibrations were made ~weekly using dry ammonium nitrate and ammonium sulfate aerosols.** A scanning mobility particle sizer (SMPS) with a condensation particle counter (TSI, Model 3775, Shoreview, MN), **differential mobility analyzer (TSI, Model 3081)** and classifier (TSI, Model 3080) quantified the size distribution of measured aerosols with 2.5 minute resolution, always sampling the same air as the AMS. **The time series of the SMPS size distribution is shown in Fig. S3a. The average size distribution is shown in Fig. S3b. Schulze et al. (2025) report a regression slope of 1.03 between the AMS and SMPS particle volume for this campaign.”**



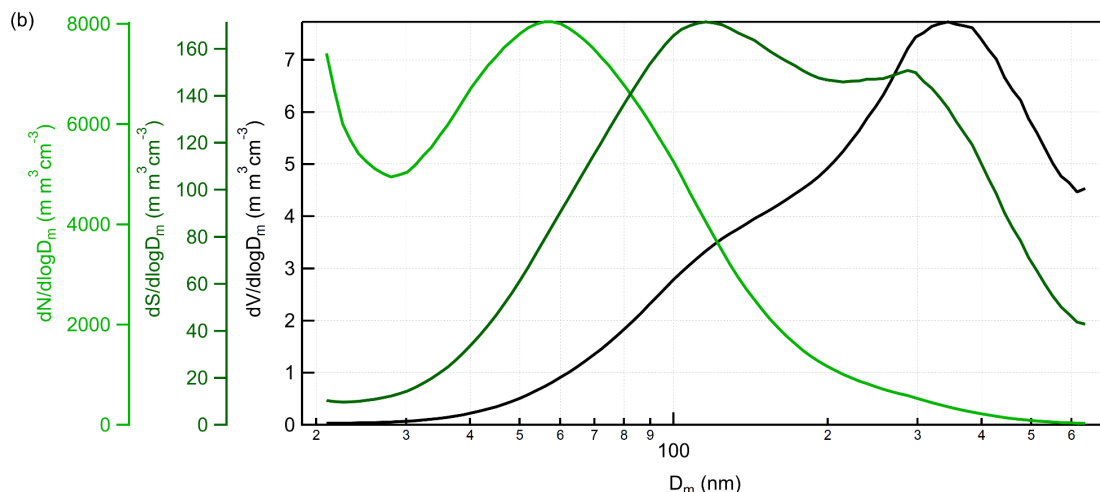
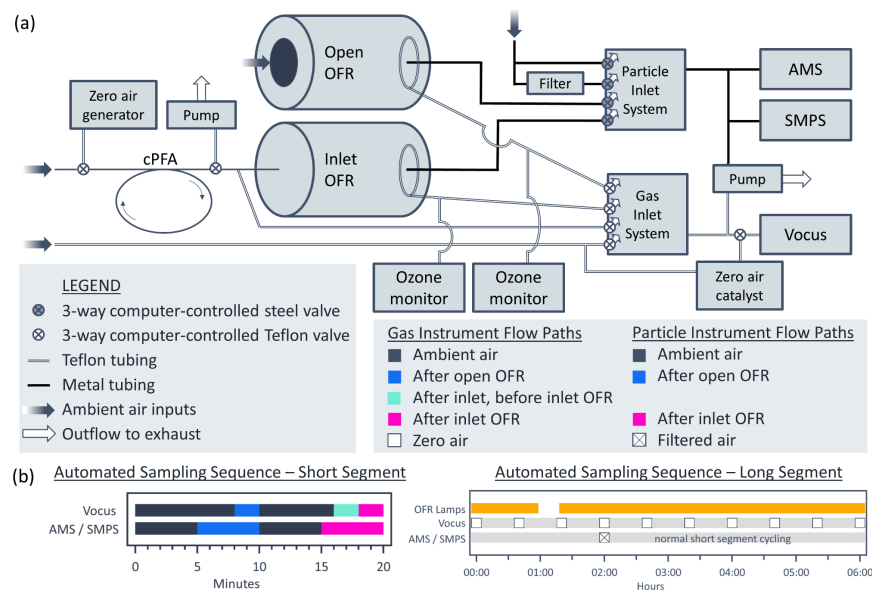


Figure S3. a) An image plot showing the size distribution measured by the SMPS. Data is colored by particle number, surface area and volume (top to bottom). b) The average SMPS size distribution for the campaign, based on particle surface area, number and volume.

R2.9. Figure 2. Would it be possible to indicate here the sampling points? It gets complicated to understand fig. 3, without this information. Also, the colors indicating “Teflon and metal tubing lines” are very similar and when figure is small it’s hard to separate them.

There were 5 sampling pathways for the gas-phase instruments and 4 pathways for the aerosol instruments, which can all be traced in the figure. The authors have done their best to make this clear, but understand that it is complicated. The pathways used for the data in Figure 3a are already shown. We have updated the color scheme to increase the difference between the Teflon and metal tubing:



R2.10. Line 198: Add atmospheric to the sentence "average 24-hour concentration of OH radical" to ensure reader understand where this number is coming..

Thank you for the suggestion. L198 has been updated to:

"Coupled with a reference average 24-hour **atmospheric** concentration of OH radical (1.5×10^6 molecules cm^{-3}) (Mao et al., 2009), OH exposures can be translated into photochemical ages, in days, and are then comparable to atmospheric aging outdoors."

R2.11. Line 260: I am not sure what this means "We estimated ambient gas-phase monoterpenes as half of the Vocus measurements.". Please clarify.

L259-262 originally read:

"Therefore, we adapted the Caltech model to perform this aging. We estimated ambient gas-phase monoterpenes as half of the Vocus measurements. We assume the other half of the measured monoterpenes come from anthropogenic sources (Katz et al., 2025; Tasnia et al., 2026) and are therefore already accounted for by the VCP emissions in the model."

and have been updated to:

"Therefore, we adapted the Caltech model to perform this aging. **We initialized the biogenic concentration of ambient gas-phase monoterpenes as half the measured concentration of monoterpenes using the Vocus.** We assume the other half of the measured monoterpenes come from anthropogenic sources (Katz et al., 2025; Tasnia et al., 2026) and are therefore already

accounted for by the VCP emissions in the model.”

R2.12. Chapter 2.6.2 Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM); this is fairly long chapter and bit hard to follow. Would it be possible to add some of this information to the supplement e.g. as a table showing summary of the changes/adjustments made to the model and give here a summary?

The authors agree that some of the details for this section can be moved to the SI. The paragraph starting on L299 originally contained the full description of how we initialized the CRACMM runs. We have removed the bulk of the detail, from L306 to 319, which has been replaced with:

“Key VOCs were adjusted using Vocus measurements from 2022. **Section S1 details how the constraints were used to make these adjustments, and Table S3 lists the constraints by CRACMM species.** By constraining these species with the Vocus measurements, we are able to better evaluate CRACMM as a chemical mechanism rather than the accuracy of the CMAQ output.”

We then added a new section to the SI:

“S1. Constraining the CRACMM inputs

The CMAQ predictions for every CRACMM species were used as a starting point to initialize the CRACMM box model. Table S2. describes the substitutions that were made for specific and bulk species using the Vocus data. A bulk aromatic scaling factor was calculated as the sum of Vocus aromatics (styrene, toluene, benzene, and C₈₋₁₂ aromatics) divided by the sum of CMAQ aromatics (styrene, toluene, benzene, ethylbenzene and XYL = xylenes and other volatile aromatics). For large alkanes (HC10, HC5, HC3 and VROCALK species), the bulk aromatic scaling factor was used to scale half of the CMAQ estimate, and the other half was left unscaled. The scaling was only applied to half of the CMAQ output as there is uncertainty whether alkanes are co-emitted with aromatics or with other VOCs; this decreased the large alkanes by about 20 %.

Table S3. Substitutions made to box model inputs for CRACMM species using Vocus measurements

Species Description	CRACMM Name	Initial concentration source
Acetone	ACT	Vocus measurement
Benzene	BEN	Vocus measurement

Isoprene	ISO	Vocus measurement
Naphthalene and other PAHs	NAPH	Vocus measurements naphthalene + methylnaphthalene
Sesquiterpenes	SESQ	Vocus measurement
Styrene	STY	Vocus measurement
Toluene	TOL	Vocus measurement
Alpha-pinenes and other cyclic terpenes with one double bond	API	The ratio of API : LIM was 24% : 76% in CMAQ. We input 24% of the Vocus monoterpene mixing ratio
D-limonene and other cyclic diene-terpenes	LIM	The ratio of API : LIM was 24% : 76% in CMAQ. We input 76% of the Vocus monoterpene mixing ratio
First generation monoterpene nitrates	TRPN	Scaled down by 59% to account for the average overestimation of monoterpenes at night
Limonene aldehyde and similar LIM-derived aldehydes	LIMAL	Scaled down by 59% to account for the average overestimation of monoterpenes at night
Pinonaldehyde and similar API nitrate-derived aldehydes	PINAL	Scaled down by 59% to account for the average overestimation of monoterpenes at night
Xylenes and other volatile aromatics	XYL	Sum of Vocus measurements for C ₈ - C ₁₂ aromatics
Ethylbenzene	EBZ	Set to zero to avoid double counting with XYL
Alkanes and other species with OH rate constant greater than $6.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	HC10	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkanes and other species with OH rate constant between 3.4×10^{-12} and $6.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	HC5	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkanes and other species with OH rate constant less than $3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	HC3	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10^{-2} \mu\text{g m}^{-3}$	VROCN2ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C*	VROCN1ALK	Half the CMAQ concentration was scaled

of $10^{-1} \mu\text{g m}^{-3}$		by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $1 \mu\text{g m}^{-3}$	VROCP0ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10 \mu\text{g m}^{-3}$	VROCP1ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10^2 \mu\text{g m}^{-3}$	VROCP2ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10^3 \mu\text{g m}^{-3}$	VROCP3ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10^4 \mu\text{g m}^{-3}$	VROCP4ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10^5 \mu\text{g m}^{-3}$	VROCP5ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled
Alkane-like ROC species with C* of $10^6 \mu\text{g m}^{-3}$	VROCP6ALK	Half the CMAQ concentration was scaled by the bulk aromatic scaling factor, the other half was left unscaled

Results

R2.13. Fig 3. I am bit confused of all models/calculation methods used in this manuscript. What is 0D model mentioned in the fig 3. legend? maybe all used models/theoretical calculation methods could be at least very shortly explained in the experimental? LVOC model, 0D, SIMPLE, SIMPOL.. this would also maybe shorten the fairly long results/discussion chapter.

The legend for Fig. 3 should say “**Caltech model**” rather than “0D model”, we have updated this.

The main models used in this work (Caltech model and CRACMM model) are given descriptions in the experimental section. We agree that there are several other small models used in this work, and it can be difficult to keep track of the acronyms. Their descriptions are currently briefly stated before the results obtained from them, and we prefer to keep this organization, since going back to the experimental section would be cumbersome for readers when they encounter the results.

To help readers with the acronyms and models used in this work, we have compiled the following table for the SI:

Table S1. List of acronyms and models used in this work

Acronym	Description
LA	Los Angeles, CA, USA
OA	organic aerosol
SOA	secondary organic aerosol
SOA-FP	secondary organic aerosol formation potential
OFR	oxidation flow reactor
O-OFR	open oxidation flow reactor (no inlet or front plate)
I-OFR	inlet oxidation flow reactor (inlet and front plate installed)
cPFA	electrically conductive perfluoroalkoxy alkane Teflon (inlet material)
PTFE	non-conductive polytetrafluoroethylene
FEP	non-conductive fluorinated ethylene propylene
VOC	volatile organic compound
IVOC	intermediate volatility organic compound
SVOC	semivolatile organic compound
LVOC	low-volatility organic compound
VCP	volatile chemical product
CO ₂	carbon dioxide
OH	hydroxyl radical
ΔCO	background-corrected carbon monoxide
NO	nitric oxide
NO ₂	nitrogen dioxide
NO ₃	nitrate radical
PBL	planetary boundary layer
CalNex 2010	California Research at the Nexus of Air Quality and Climate Change 2010 measurement campaign
CalNexT 2022	this measurement campaign, a follow-up to CalNex
Vocus	Vocus-2R proton-transfer-reaction time-of-flight mass spectrometer
AMS	high-resolution time-of-flight aerosol mass spectrometer
SMPS	scanning mobility particle sizer
ATD	automated thermal desorption

MICAS	Multi-Instrument Control and Acquisition System a software designed for custom acquisition
WRF	Weather Research Forecasting
NEI	National Emissions Inventory
SMILES	Simplified Molecular Input Line Entry System a method for writing out molecular formulas that retains structural information
SIMPOL	A simple group contribution method for predicting saturation vapor pressures of multifunctional organic compounds
Model	Description
CMAQ	Community Multiscale Air Quality Monitoring System A 3-dimensional air quality forecasting model.
CRACMM	Community Regional Atmospheric Chemistry Multiphase Mechanism The chemical mechanism in CMAQ that simulates gas phase reactions and SOA formation. This mechanism can either be run in CMAQ, to predict ambient data, or in a kinetic solver (with modifications) to predict OFR data.
Caltech model	A box model by Schulze et al. (2025) to simulate the formation of SOA from gas phase emissions.
LVOC fate model	A model by Palm et al. (2016) to calculate the estimated fraction of LVOC fates in each OFR. Used to correct the OFR data for non-atmospheric LVOC fates.
SIMPLE	An SOA model with a single lumped precursor and single lumped non-volatile SOA product.

R2.14. Line 315: Clarify what are these; (HC10, HC5, HC3 and VROCALK species),

We have moved this text to the SI and listed out the descriptions for the acronyms in response to comments R2.12 and R2.13.

R2.15. Figures 4,5: how are these days chosen? were all “similar” or was there much variation between days?

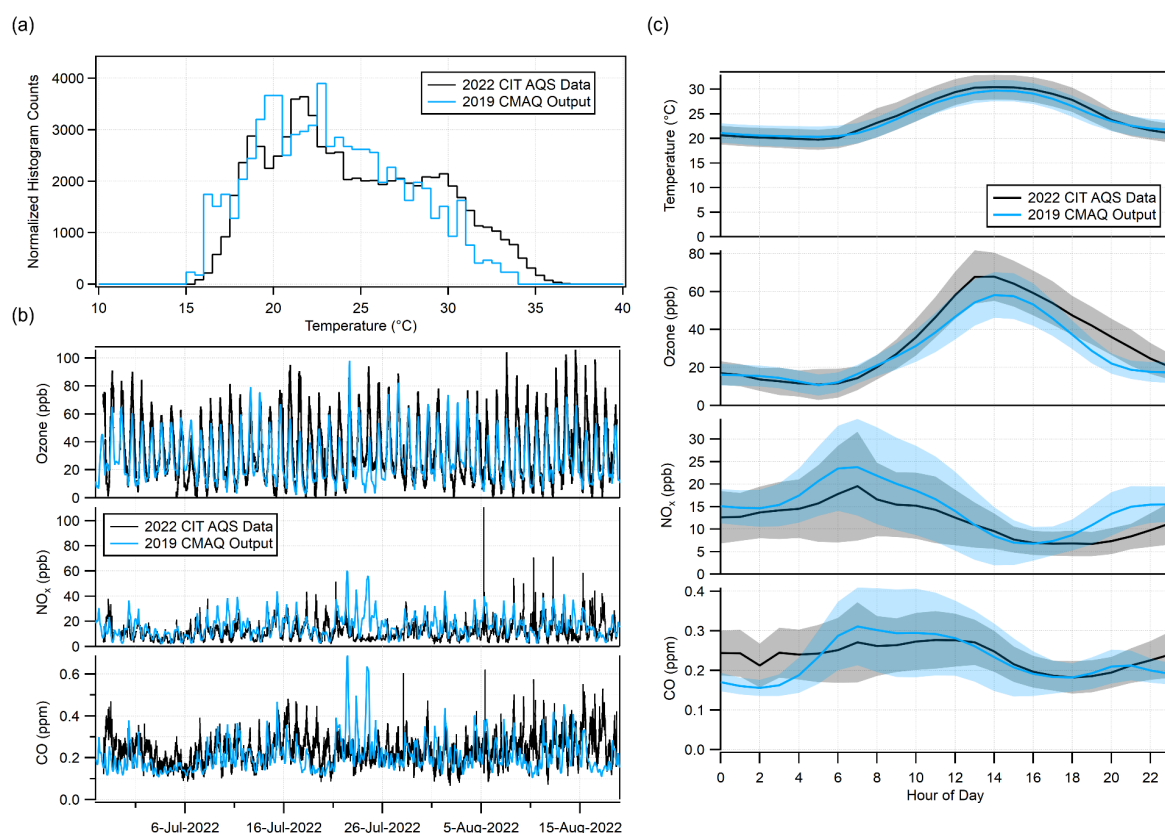
The days were chosen as representative days of the dataset, which had limited variation. This was partially addressed in the submitted manuscript in the discussion about SOA-FP following the introduction of Fig. 6 (L438):

“A nightly average (22:00-08:00) of SOA-FP for both OFRs is shown in Fig. S9, along with the same data normalized to ΔCO . The SOA-FP was fairly constant over the campaign, and did not vary between weekdays and weekends, as shown in Fig. S10.”

On L409 we have added the bold text to discuss this point earlier:

“The measured OA is shown through each pathway for three representative days in Fig. 5. **There was limited day to day variability in the temperature and amounts of ozone, NO_x and CO, as seen in Fig. S7c. There was also limited variability in ambient and OFR OA, as shown in Fig. 6a.”**

The revised Fig. 6a with standard errors is reproduced in our response to R1.2. We realized that Fig. S6c was accidentally missing standard deviation shading for CO, so we have revised it:



R2.16. Figure 6: please add e.g. standard deviation to the diurnal cycles, so that it is possible to understand how much variation was seen in the diurnal cycles during the campaign. Average values can be skewed by single points/days/episodes.

This is an excellent idea. We have added the standard error to each trace as shaded regions. The revised figure is reproduced in our response to R1.2.

R2.17. Line 443: Please clarify what bulk nature means in the sentence: “Due to the diurnal and

bulk nature of the measurement, changes in the precursor identities between morning (when substantial SOA-FP is measured in the OFRs) and afternoon (when SOA-FP is realized via photochemistry in ambient air) are not known.”

“Bulk” refers to the fact that we are not measuring SOA-FP from individual sources or precursors, but all SOA-FP that is present in ambient air at once. The authors thank the reviewer for bringing up this point for clarification. It also gives us an opportunity to point readers to a later section where we explore this limitation using the Caltech model.

The quoted sentence on L443 has been replaced with:

“One limitation of this technique is that we are unable to experimentally determine if precursor identities changed between morning (when substantial SOA-FP is measured in the OFRs) and afternoon (when SOA is realized via photochemistry in ambient air). In Sect. 3.9.4 we explore this topic in more detail via modeling, using the data in Fig. 13C.”

R2.18. Line 542: please add discussion how the different OH-exposures in different chambers may have influenced results and also why they were different?

This explanation was already given in the submitted paper on L524-530. We have moved it to L541 so that all information about OH exposure is together, and have added the following bolded text:

“OA generation in OFRs has been shown to have a non-linear dependence on OH exposure: for up to 1 day of aging OA generation is positively correlated with OH exposure, at 1-10 days of aging OA generation plateaus and does not have a dependence on OH exposure, and at ages higher than 10 days OA may begin to be destroyed as OH exposure increases (Ortega et al., 2016). For this reason both OFRs were tuned to ~2 days of equivalent exposure. **The actual exposures of both OFRs were slightly different, due to the difficulty of precisely tuning the exposure in the field.** Figure S18 shows no correlation between OA and OH exposure for either OFR. Therefore, no correction for differing photochemical ages was necessary to quantitatively compare OA between the two OFRs.”

R2.19. Line 545: was calibration with toluene done after the campaign? why not before? would you expect differences e.g. due to aging of lamps or chamber getting dirty in calibrations done before and after? I am not sure which one (before or after) calibration is more common, but I recall seeing both.

The reviewer brings up an important point to clarify. The analysis was done post-campaign, but the toluene data is from real-time ambient measurements made during the campaign. The text on

L554 originally read:

“A comparison of the OH exposure calculated using toluene decays after the campaign and the estimation equation from Li et al. (2015) used to monitor OH exposure during the campaign is shown in Fig. S20.”

And has been updated to:

“A comparison of the OH exposure calculated using **real-time ambient toluene decays in the OFR and the OFR estimation equation from Li et al. (2015)** is shown in Fig. S18.”

Additionally the text on L208 originally read:

“After the campaign, the measured decay of toluene in the OFRs was used to calculate final OH exposure estimates.”

and has been updated to:

“**During post campaign analysis, the real-time measurements of toluene decay in the OFRs during the campaign were used to calculate final OH exposure estimates.**”

R2.20. chapter 3.4: I was missing this information about calibration already earlier. Maybe this could be shown already in experimental section?

The authors debated about where to put some information in the manuscript, as it could either go in the methods or the results. Since this is a technical result from an analysis we did about the photochemical age using various techniques described in the methods, we would prefer to leave it here.

R2.21. Line 561: Caletch -> should be Caltech?

Yes, thank you for catching this typo.

L597: “the **Caltech** model overpredicts SOA-FP.”

R2.22. Line 612: add why diurnal hour 7 was chosen for modeling? were the other modeled? is this 7 in morning or evening? At least fig 10 uses 24h timestamps, sometimes 7:00 and sometimes 7 is used. Consider using same formats consistently throughout the manuscript.

We added the bolded text to L618 to address the first question:

“To investigate specific contributions to SOA-FP, we ran a source apportioning case study on the OFR modeling results for **7:00 in the morning, when measured SOA-FP was highest.**”

Regarding the time format: for the figures we used 24-hour time for all time series, and diurnal hours for all averaged data.

In several parts of the text (main paper and SI) we had not used a standardized reference to time. We have changed all time references in the text to **24-hour format**. In key places we added the word “morning” for extra clarity.

R2.23. Line 683: Any thoughts why did 1,3,5-trimethylbenzene correlation decreased?

We have added the following bolded text to L184:

“We speculate that since the relative importance of traffic and mobile sources for SOA formation decreased from 50% in 2010 to 25% in 2022 (Schulze et al., 2025), and 1,3,5-trimethylbenzene is an anthropogenic emission (Wyche et al., 2009) associated with gasoline that the correlation would decrease as other sources become important.”

R2.24. Chapter 3.9. why is this chapter limited to terpenes? some of the subchapters have anthropogenic voc results, so I wonder if the title is too limited?

We decided to call out attention to terpenes in particular because this was a specific dissonant result with very recent studies. The authors felt it timely and useful to have a focused discussion about them.

The other VOCs are discussed in terms of their fractional contributions and how they impact the terpene fraction. So we believe the title is accurate and leave it unchanged.