



Supplement of

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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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 S3 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 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.

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 (¼" 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.

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^* of $10^{-1} \mu\text{g m}^{-3}$	VROCN1ALK	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 $1 \mu\text{g m}^{-3}$	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

Table S4. Slopes for the linear fits without a fixed intercept in Fig. 9.

	Ambient	All precursors	VOCs + $\frac{1}{3}$ IVOCs	$\frac{2}{3}$ IVOCs + SVOCs
CRACMM	0.89	0.35	0.41	0.17
Caltech Model	0.76	0.80	1.36	0.19

Table S5. Results for the VOC-SOA-FP regression from Eq. (3) for each OFR.

Coef	Corresponding VOC (O-OFR)	Fit Coef. ($\mu\text{g m}^{-3} \text{ ppt}^{-1}$)	SOA mass yield from literature	Maximum SOA based on 7:00 conc. ($\mu\text{g m}^{-3}$)	Fit Coef. * conc. at 7:00 ($\mu\text{g m}^{-3}$)
a	C ₁₁ Aromatics	0.042	0.15 ^a	0.013	0.61
b	Sesquiterpenes	0.045	1 ^b	0.32	1.7
c	CH ₃ SH	0.22	-	-	1.7
d	Styrene	0.0050	0.023 ^c	0.012	0.58
e	C ₆ Carbonyls	0	0.013 ^a	0.0035	0
	Corresponding VOC (I-OFR)	Fit Coef. ($\mu\text{g m}^{-3} \text{ ppt}^{-1}$)	SOA mass yield from literature	Maximum SOA based on 7:00 conc. ($\mu\text{g m}^{-3}$)	Fit Coef. * conc. at 7:00 ($\mu\text{g m}^{-3}$)
a	C ₆ Carbonyls	0.0085	0.013 ^a	0.0037	0.59
b	Ethanol	0	-	-	0
c	Sesquiterpenes	0.038	1 ^b	0.33	1.5
d	C ₁₁ Aromatics	0	0.15 ^a	0.013	0
e	Styrene	0.0049	0.023 ^c	0.011	0.55

^a McDonald et al. (2018), ^b Hoffman et al. (1997), ^c Schueneman et al. (2024), “-” no evidence of SOA formation

The maximum SOA was calculated by converting the average concentration at 7:00 in the morning for each precursor into mass, then multiplying by the reported literature yields (thus considering it reacts to completion with OH). The fit coefficients were multiplied by the average concentration at 7:00 to calculate simulated SOA formation values. The maximum SOA values are much lower than the simulated SOA formation values, therefore, the precursors are understood as tracers. The precursors cannot make much SOA mass on their own, but can capture the variance of the SOA-FP throughout the day well, and represent all compounds that correlate with them.

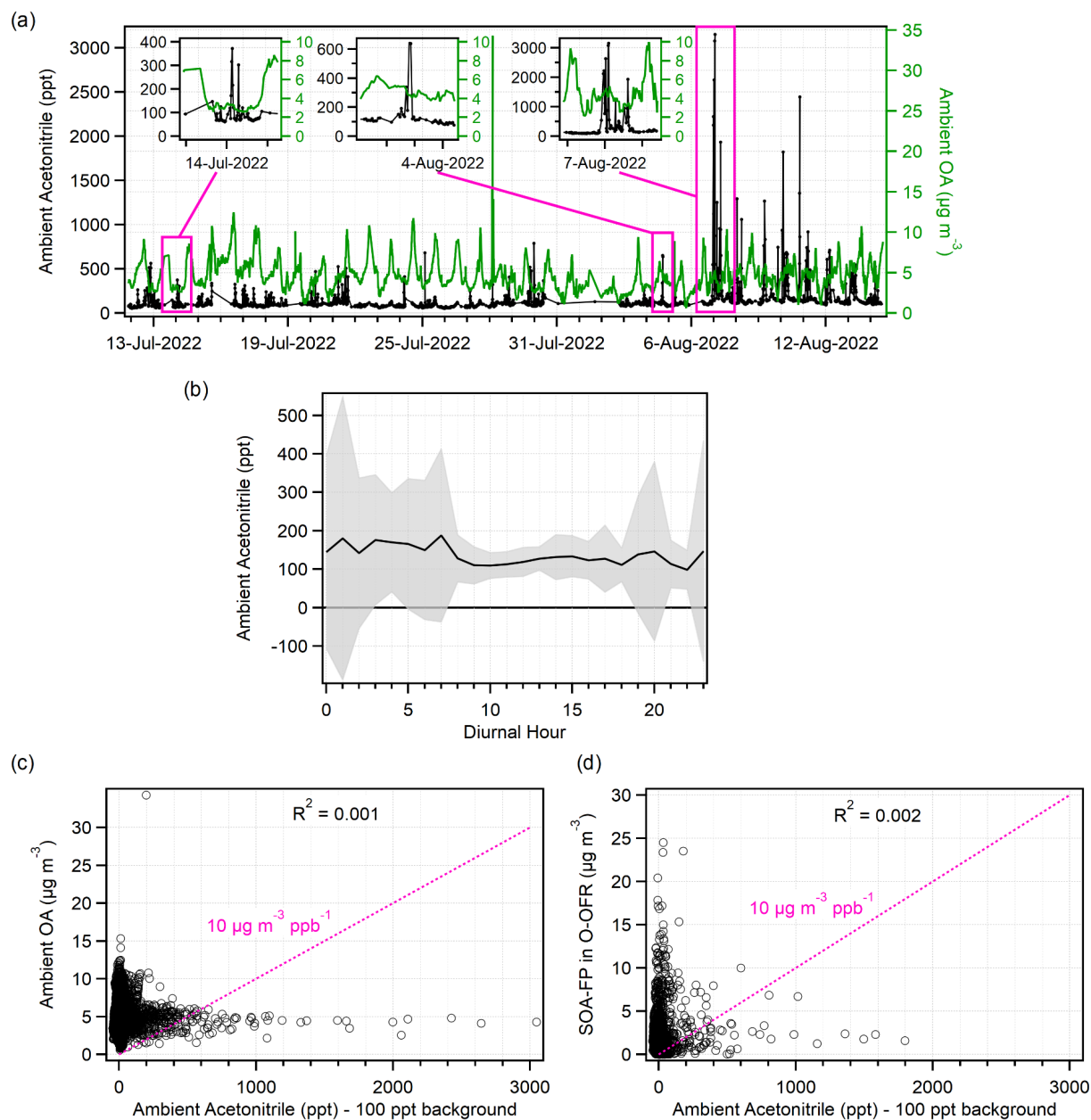


Figure S1. (a) A time series of measured ambient acetonitrile and ambient organic aerosol, with insets zoomed in to several acetonitrile spikes. (b) A campaign average diurnal of measured acetonitrile, with 1 standard deviation shown in grey. (c) Ambient organic aerosol vs ambient acetonitrile that has been background subtracted. A typical biomass burning organic aerosol to acetonitrile ratio from the literature is shown as a pink line (Aiken et al., 2010). Given the lack of correlation between acetonitrile and OA, we conclude that acetonitrile is arising from non-biomass burning sources in this campaign, and that the biomass burning influence on OA is very low. (d) Secondary organic aerosol formation potential in the O-OFR vs ambient acetonitrile that has been background subtracted, leading to similar conclusions.

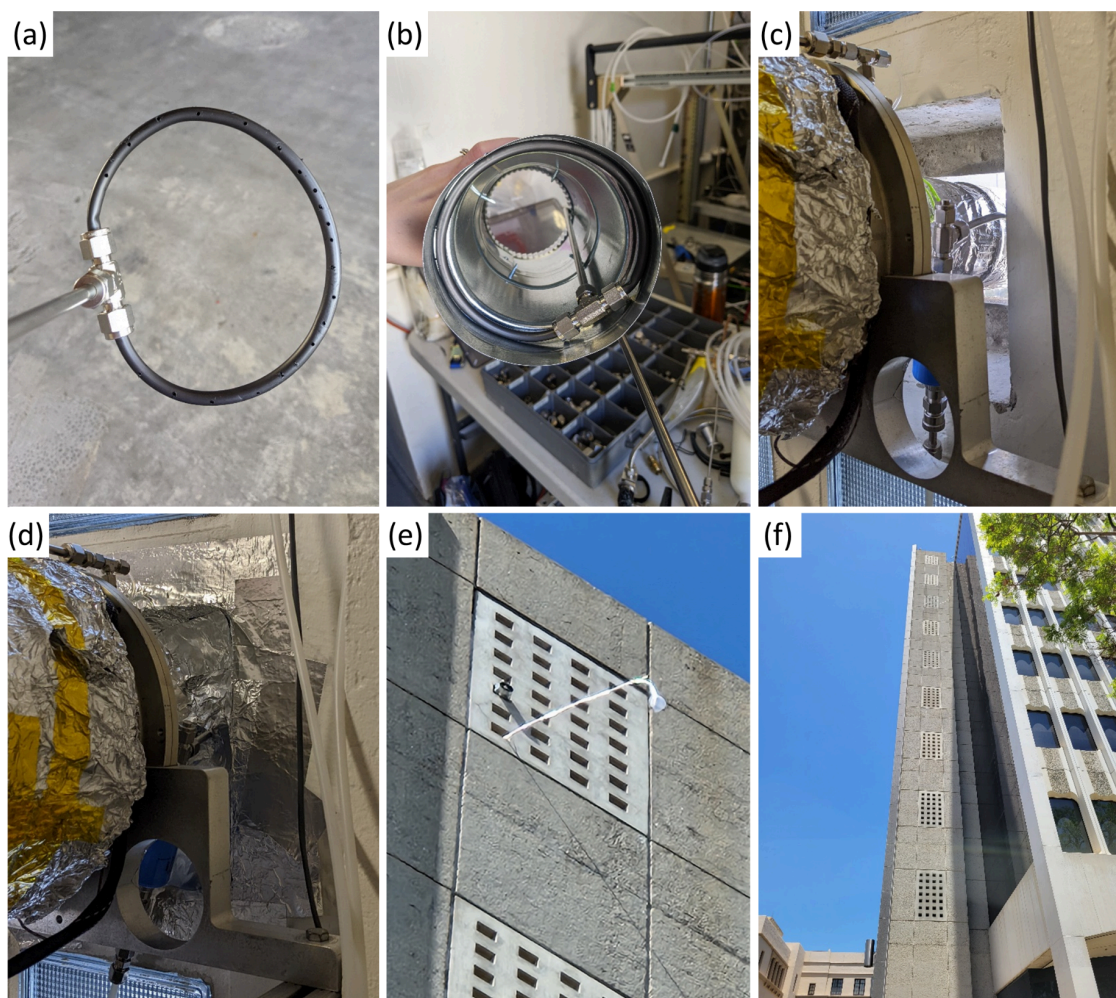


Figure S2. The O-OFR needed to sample air outside the concrete port, so a metal cone system was developed to seal it off from the indoor air and from wall effects from the concrete. (a) A custom vacuum line (made of electrically conductive PFA tubing) was built to remove any air from the ambient stream that had come in contact with the walls of the metal cone. (b) The custom vacuum line was installed close to the O-OFR face and the plumbing was routed out the front and around the metal cone. The flow rate through the vacuum port was nominally 3.5 LPM. (c) The metal cone was sealed to the O-OFR face using aluminum foil and aluminum foil tape. Careful attention was made so adhesive from the tape was never in contact with the sample stream. The seal on the cone was leak checked using CO₂ measurements throughout the campaign. (d) The O-OFR was sealed off from the room using the same aluminum foil and aluminum foil taping technique. (e) A zoomed in photo of the O-OFR metal cone from the outside, with the Vocus sampling line underneath. (f) A zoomed out version of photo E to show the height of the sampling.

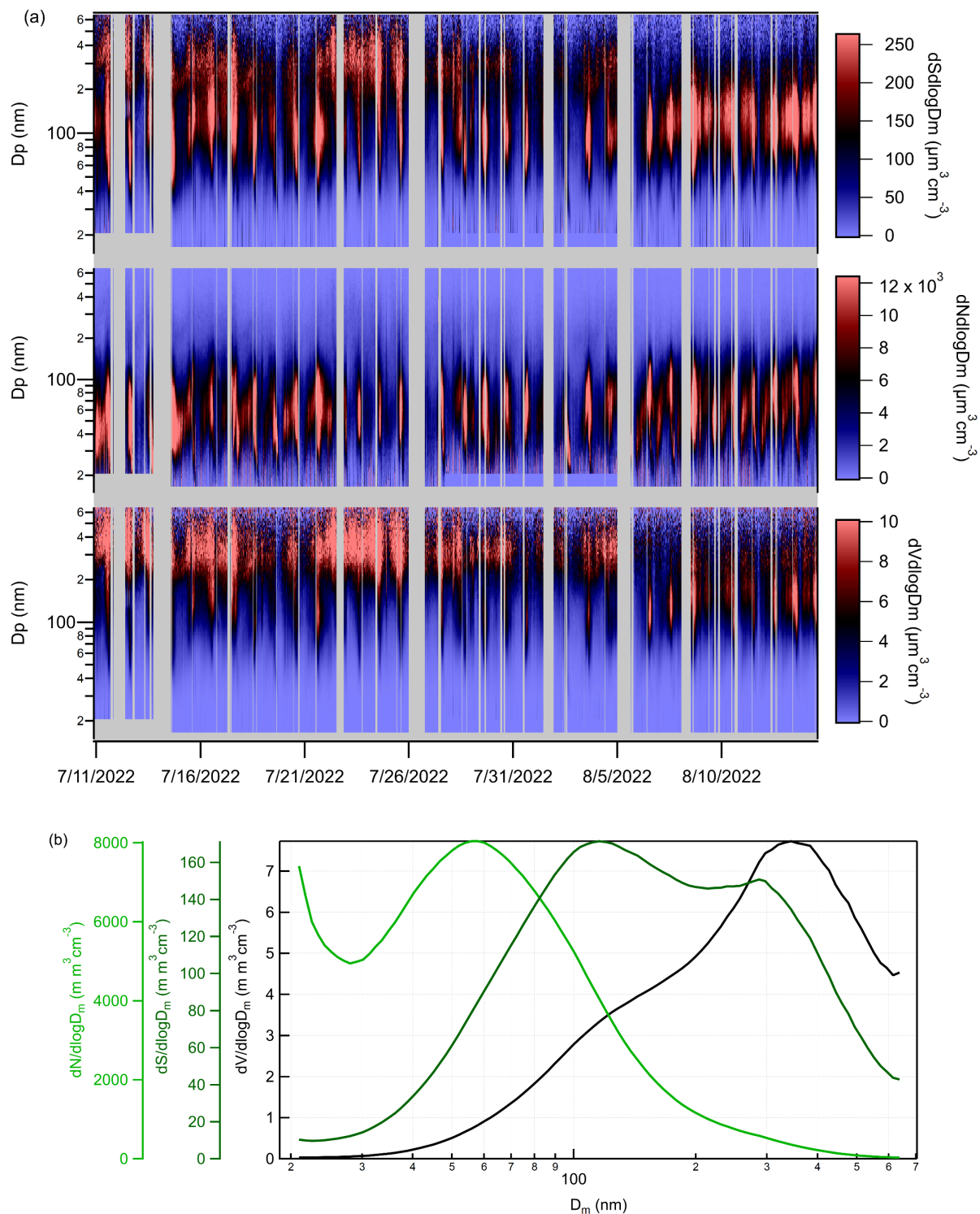


Figure S3. a) An image plot showing the size distribution measured by the SMPS. Data is colored by particle surface area, number and volume (top to bottom). b) The average SMPS size distribution for the campaign, based on particle surface area, number and volume.

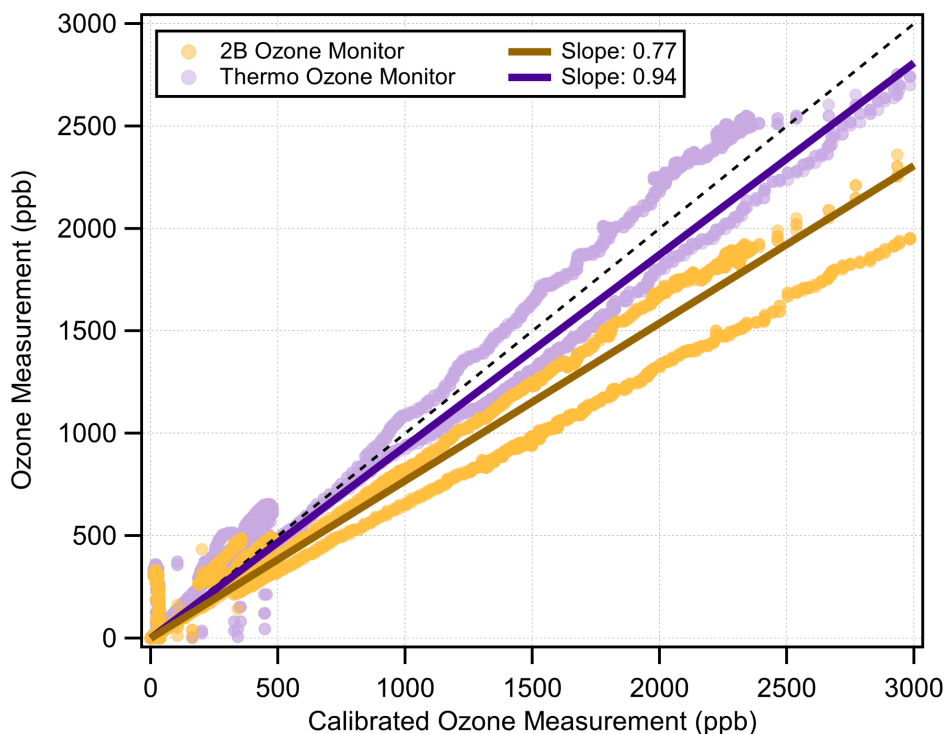


Figure S4. Prior to the campaign, the two field ozone instruments were compared to a third, calibrated ozone measurement (Thermo Scientific, Model 49i) in the laboratory. All three ozone instruments sampled the same OFR as the lights were ramped to produce ozone. The data appears as two lines per instrument, one for increasing ozone concentration and one for decreasing ozone concentration during the experiment; the average of all data was taken for the reported slopes. The slopes were used to correct the ozone data collected in the field. When applied, these corrections only changed the estimation of OH exposure from the estimation equation shown in Fig. S20. Analysis of toluene decay in each OFR was calculated to replace the results from the estimation equation.

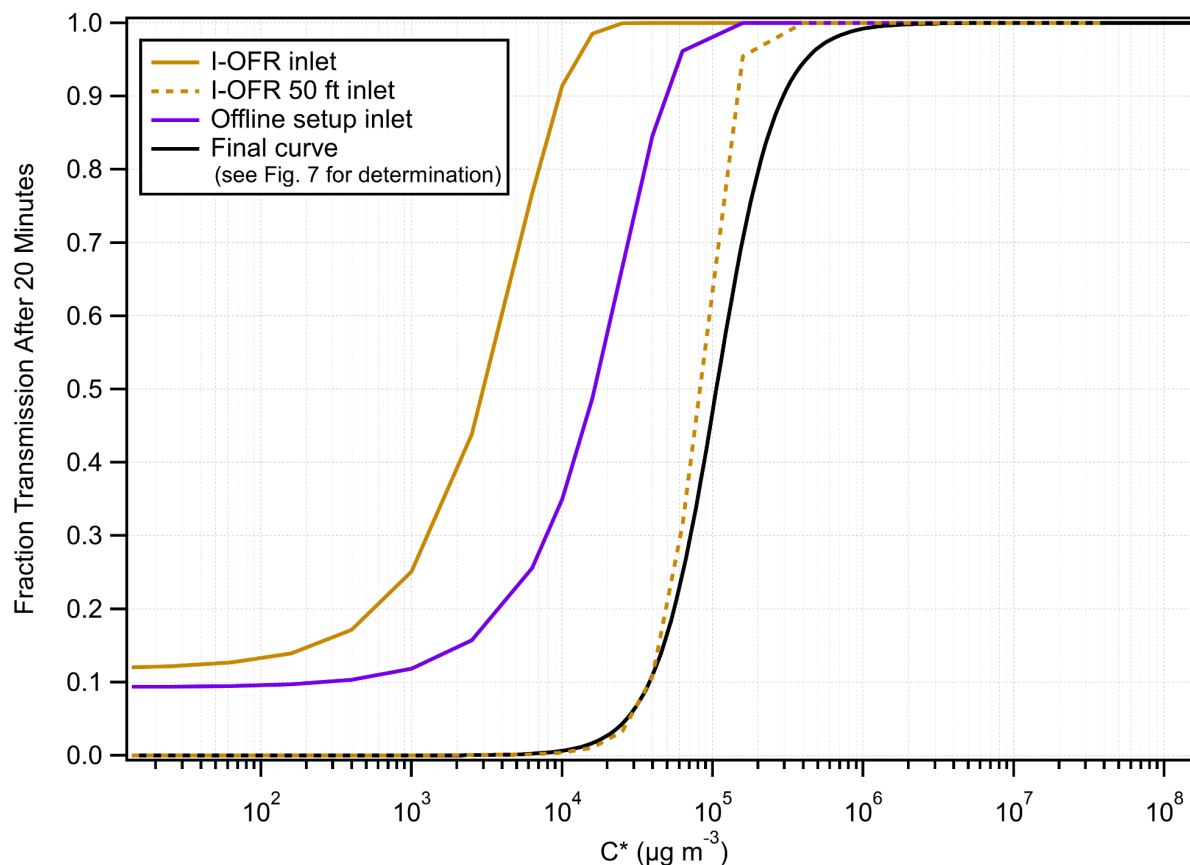


Figure S5. The tubing model published in Pagonis et al. (2017) was used to simulate several inlets: the predominant I-OFR inlet (cPFA, 3.5 m long, ¼" OD), a longer test I-OFR inlet (cPFA, 15 m long, ¼" OD) and the inlet used for the offline setup (PTFE, 1.5 m long, ¼" OD). Importantly, this prediction is only for the polymer tubing in the sampling setups. The sampled gas stream for the I-OFR also passed through 2 Teflon solenoid valves. The sampled gas stream for the offline setup also passed through a PTFE filter for particulate matter. Both of these are expected to increase the denuding of the sampling systems. We note that the shorter modeled tubes do not denude lower volatility species. This is because not all air touches the walls of the tubing in the model, which is assumed to be perfectly straight. In reality, our experimental setup included many bends, which would increase air mixing. Additionally, the model is only valid under a laminar flow regime, which we were at the upper limit of. See Fig. 3 for an experimental determination of the transmission curve for this work.

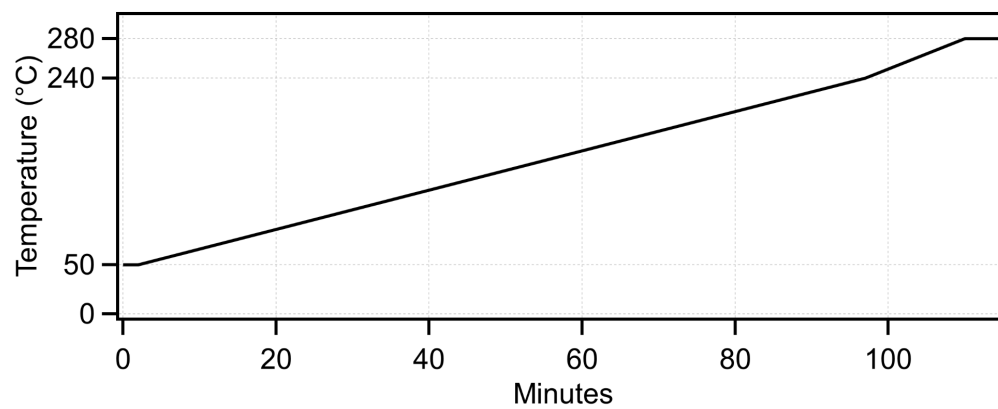


Figure S6. Temperature ramp used for the cartridge analysis at Riverside.

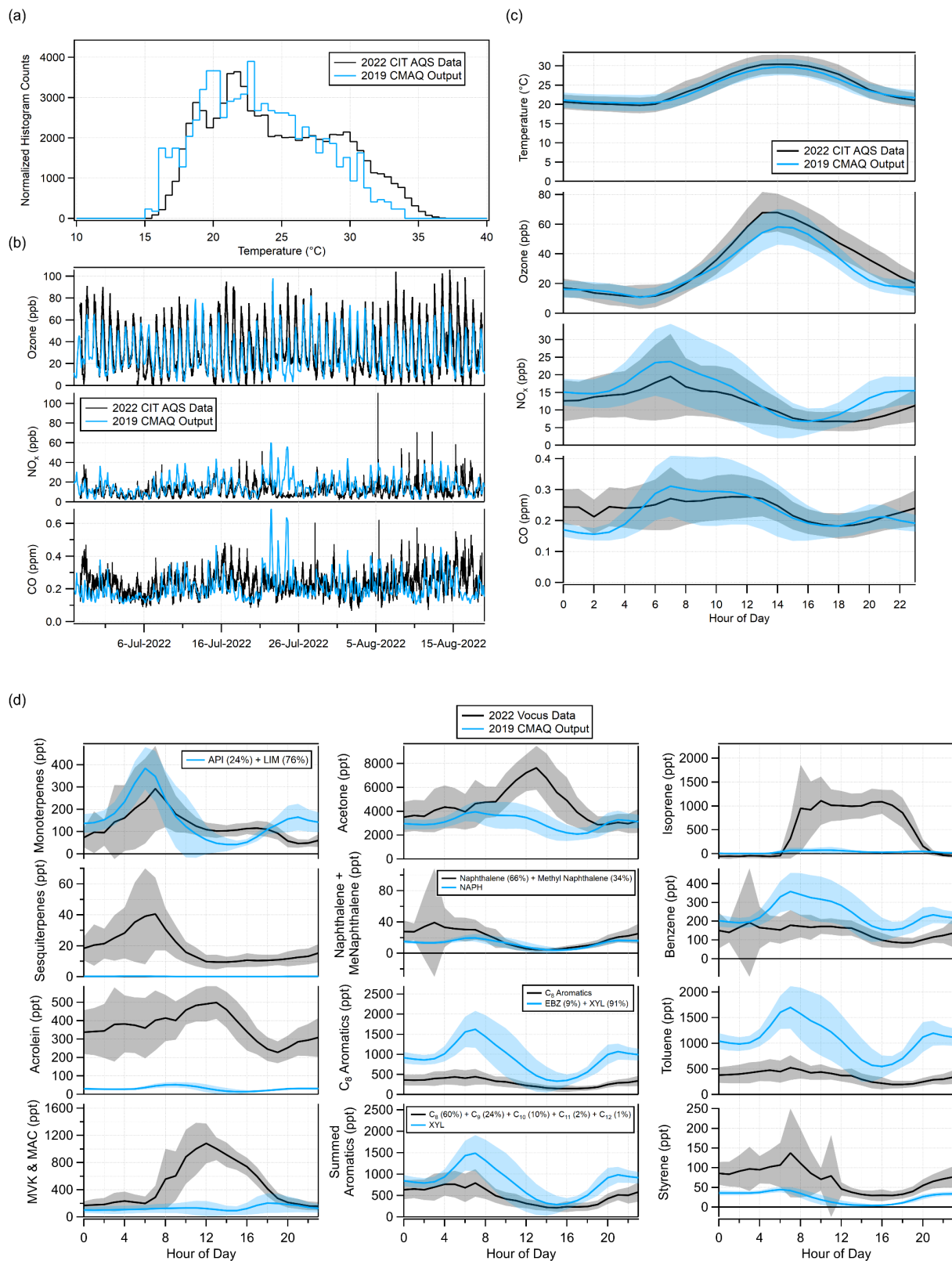


Figure S7. Comparison of temperature, ozone, NO_x, CO and gas phase precursors between the measured data (2022) and model results (2019). CITAQS is the Caltech air quality system. (a) Normalized histograms of temperature. (b) Time series of ozone, NO_x and CO. (c) Diurnals of temperature, ozone, NO_x and CO. (d) Diurnal comparisons of gas phase precursors.

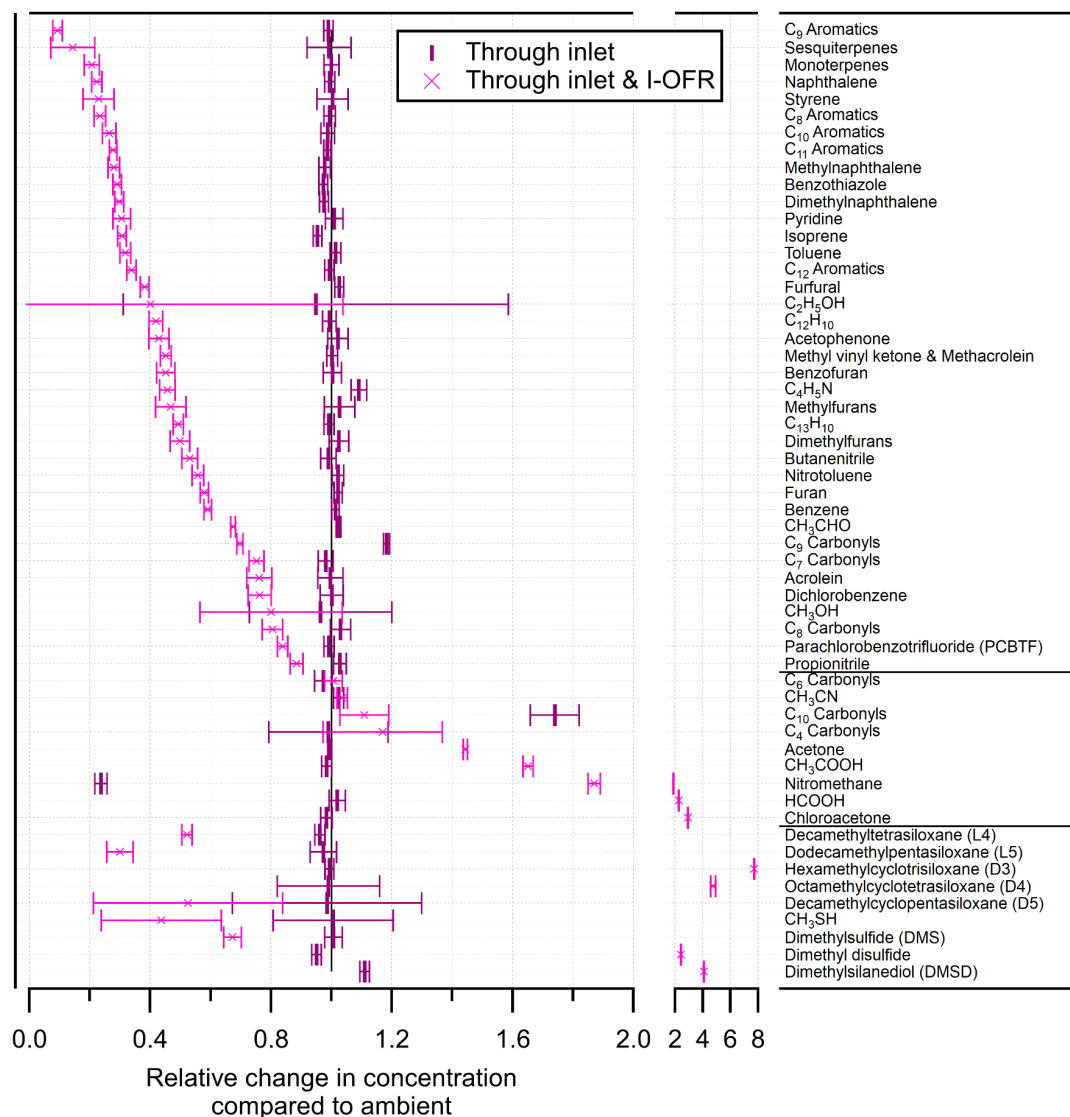


Figure S8. Fraction transmission of all gas-phase species measured by the Vocus through just the inlet of the I-OFR or the inlet and I-OFR combined. When measured through the I-OFR, some species decay due to oxidation (top category), while other species are enhanced because they are oxidation products (middle category). The bottom category contains sulfur-containing and siloxane species. A few species (C₉ carbonyls 54 ppt ambient average; C₁₀ carbonyls 24 ppt; DMSD 68 ppt) show increases through the tubing, for reasons that are unclear. In any case their contribution to SOA-FP should be minimal.

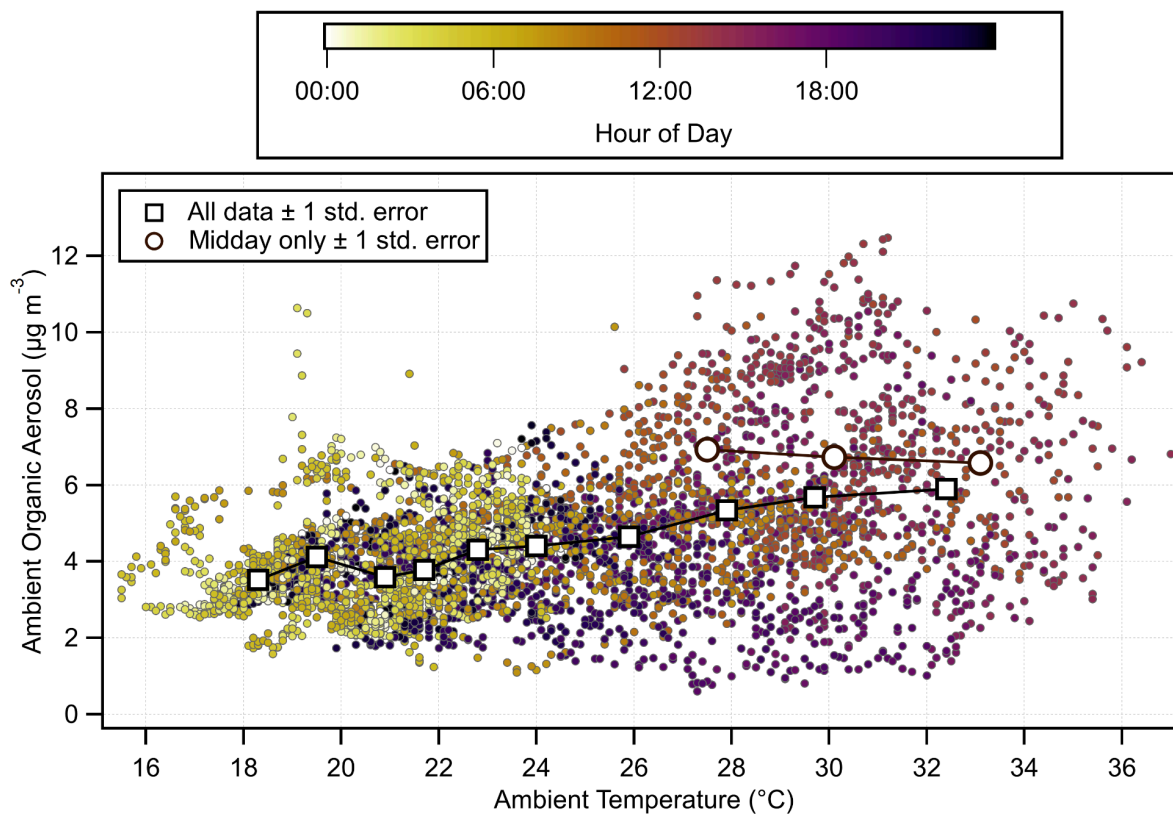


Figure S9. Measured ambient organic aerosol vs ambient temperature, colored by time of day. Quantiles of all data and midday only (11:00-16:00) are shown with vertical error bars being the std. error. All error bars are smaller than the markers.

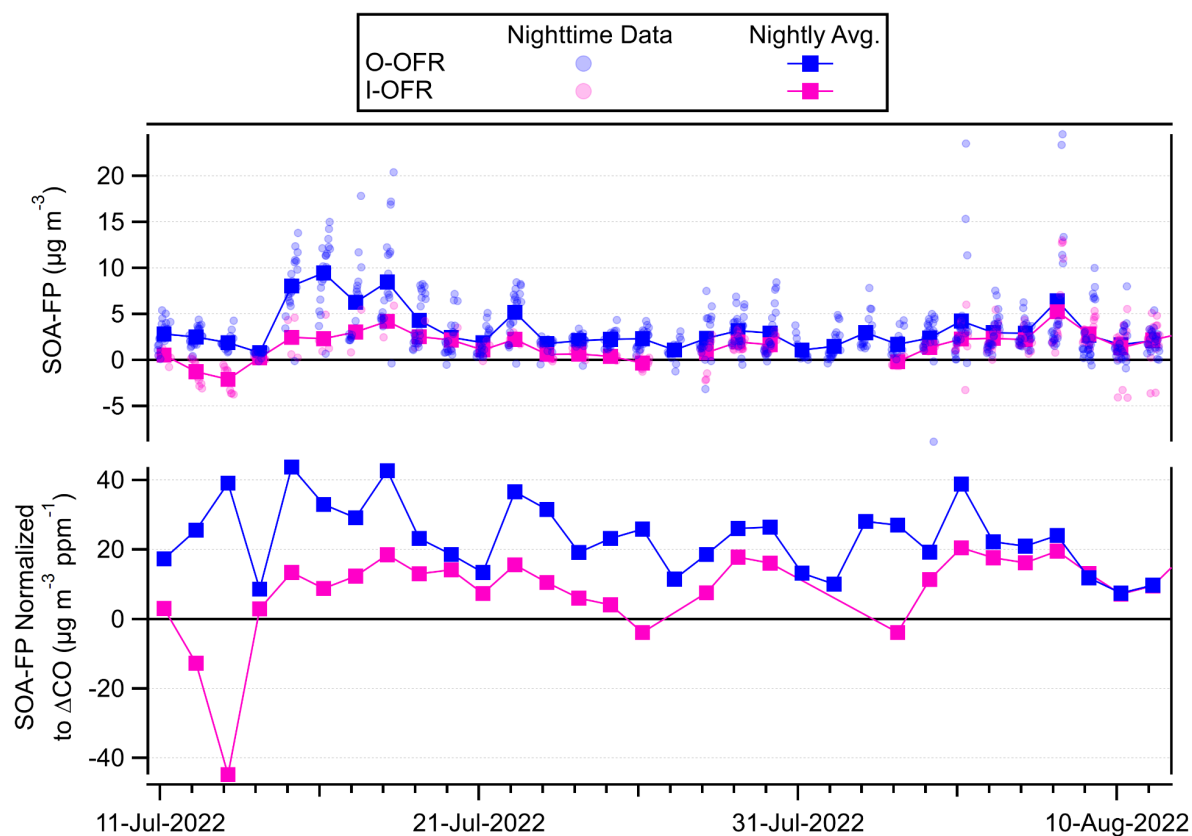


Figure S10. Top: Nighttime data and nightly average of SOA-FP. Bottom: Nightly averages normalized to average background-subtracted CO concentrations.

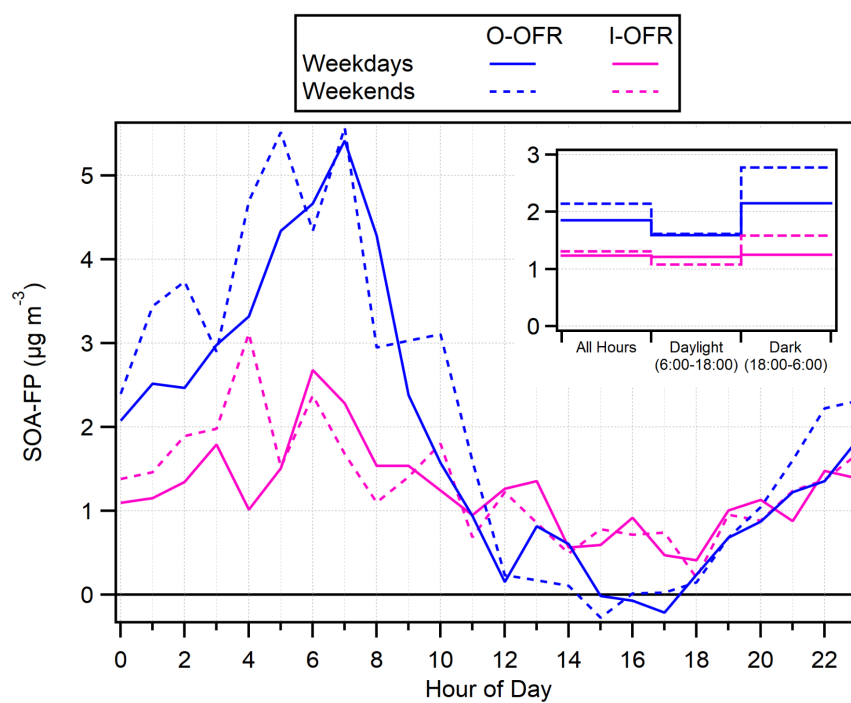


Figure S11. The campaign-average diurnal of SOA-FP measured in each OFR from Fig. 6 split between weekdays and weekends. An inset bar chart shows averages for specified time ranges.

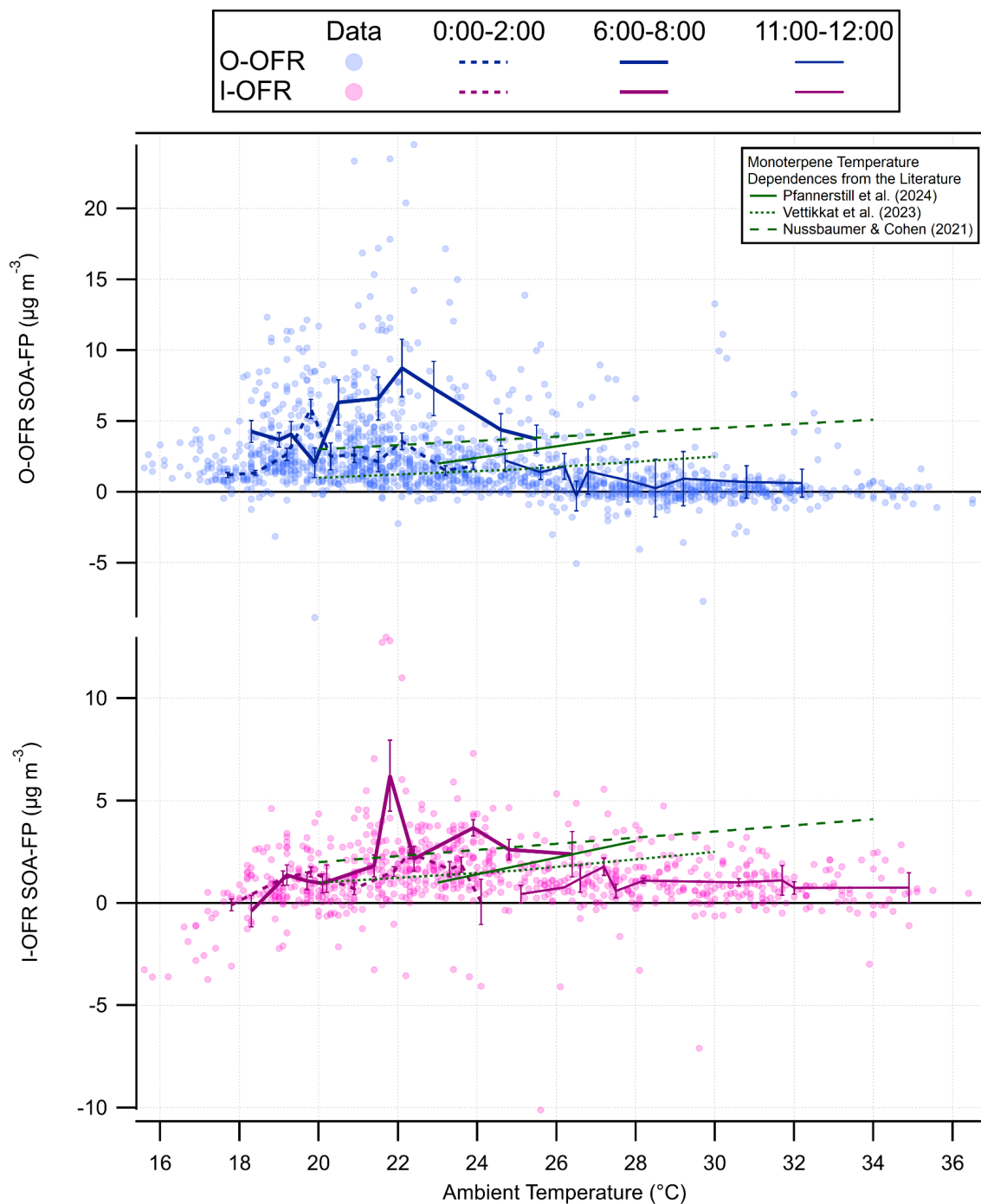


Figure S12. Measured SOA-FP for both OFRs according to ambient temperature. Deciles for the described time periods are shown as lines, with vertical error bars as the standard error. Some outlying data points are outside the y-axis ranges so that trends can be better analyzed visually. The green lines show relative expected SOA-FP enhancements from the literature for monoterpenes (Nussbaumer and Cohen, 2021; Pfannerstill et al., 2024; Vettikkat et al., 2023). The relative slope was calculated from the literature and added with an arbitrary y-offset for ease of visual comparison.

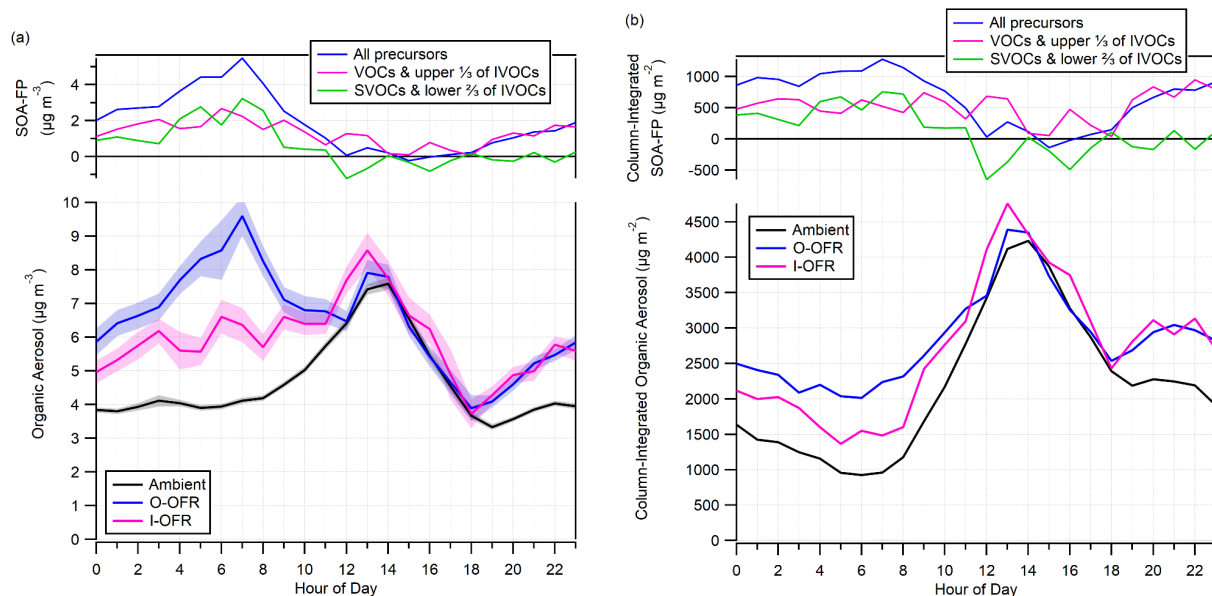


Figure S13. a) A reprint of Fig. 6a from the manuscript, for comparison. b) The same data in a) but multiplied by the estimated planetary boundary layer height. To estimate the PBL height, we averaged the estimate from the 2010 Cal-Nex campaign (Hayes et al., 2013) with an estimate from the Ontario International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

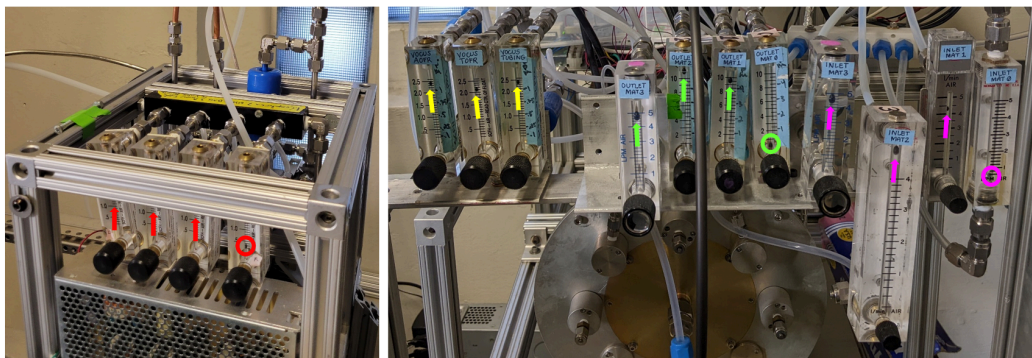


Figure S14. There were 15 rotameters installed in the system that could be read to understand how air was flowing. No rotameters were installed in the critical sampling path - all rotameters were installed on exhaust ports and zero air intakes. The red rotameters indicate which sampling pathway the aerosol instruments were measuring. Since 3 options were flowing to exhaust, the fourth option (ambient air) was being sampled. The yellow marked rotameters indicate which sampling pathway the gas instruments were measuring. Since all OFR-related options were flowing to exhaust, the system was sampling ambient air. The pink and green rotameters show if zero air is flowing to the I-OFR inlets and if the air through those inlets is being exhausted, respectively. In the photo, inlets 1-3 have zero air flowing through them to the exhaust, and inlet 0 is being sampled by the I-OFR.

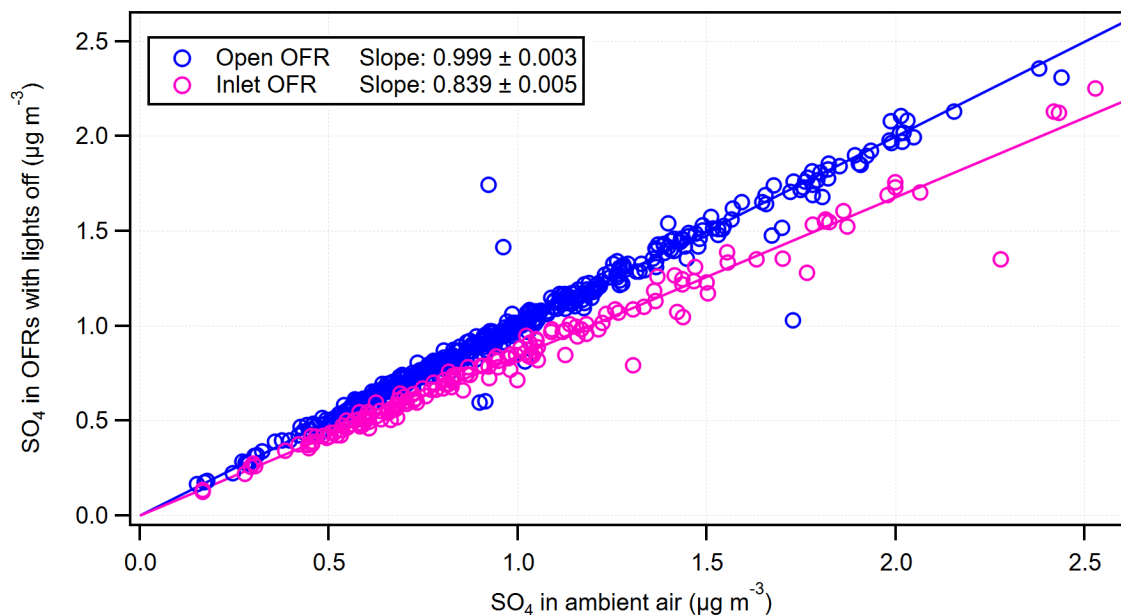


Figure S15. Correlation of SO_4 in the OFRs during periods where the lights were turned off, plotted against SO_4 in ambient air. Since the O-OFR had a slope of ~ 1 , no correction for aerosol transmission was needed compared to the ambient inlet. Since the I-OFR had a slope of 0.839, the I-OFR OA values were corrected according to Eq. 1.

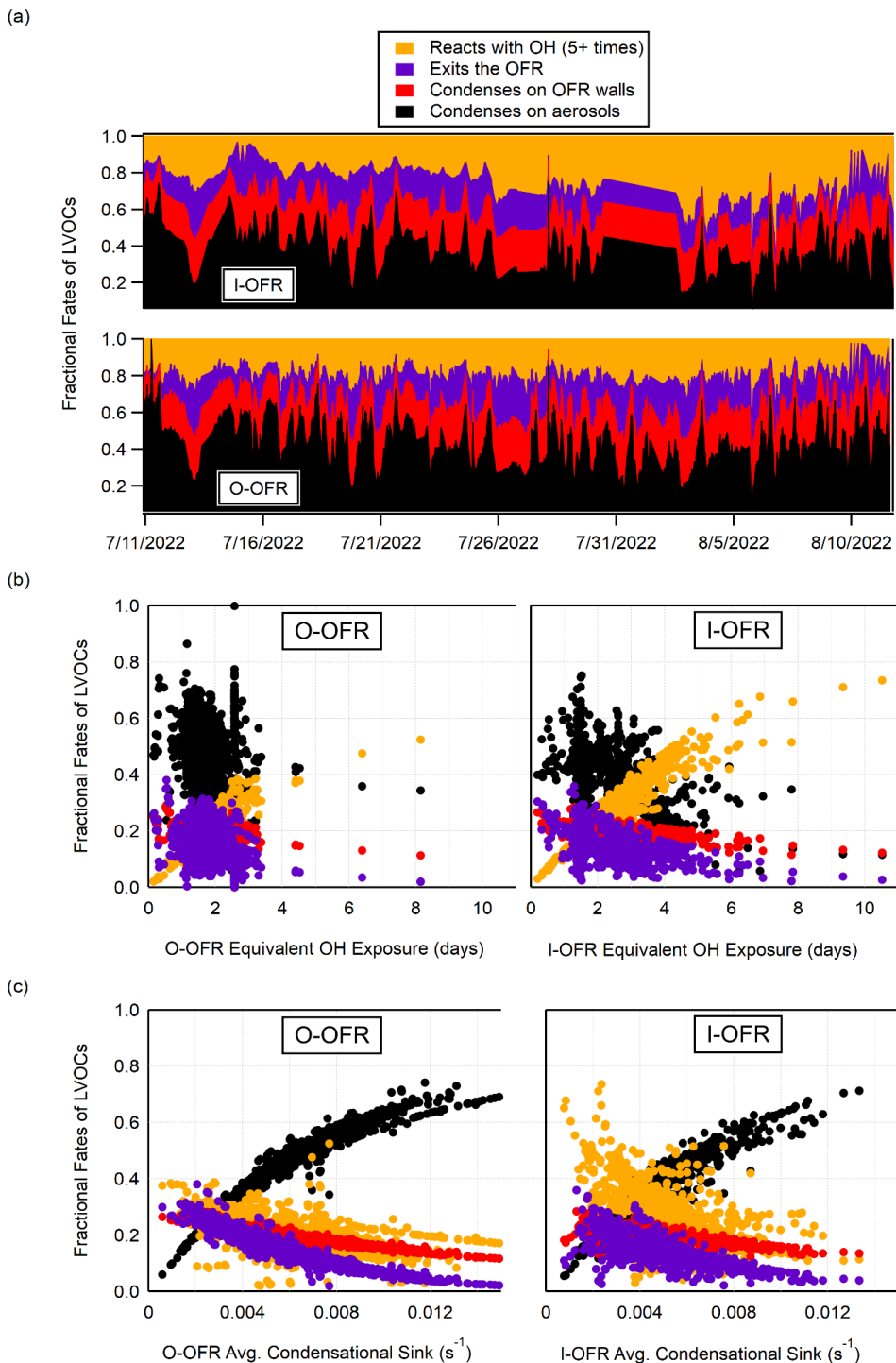


Figure S16. Results from the LVOC loss calculator for both OFRs (Palm et al., 2016). (a) Time series of fractional LVOC fates through various pathways. Since, on average, 43% and 38% of the LVOCs were properly condensing on aerosols in the O-OFR and I-OFR respectively, a correction was necessary and applied as in Eq. (2). (b) Fractional LVOC fates plotted vs OH exposure. (c) Fractional LVOC fates plotted vs average condensational sink (average of the input and output of the OFRs).

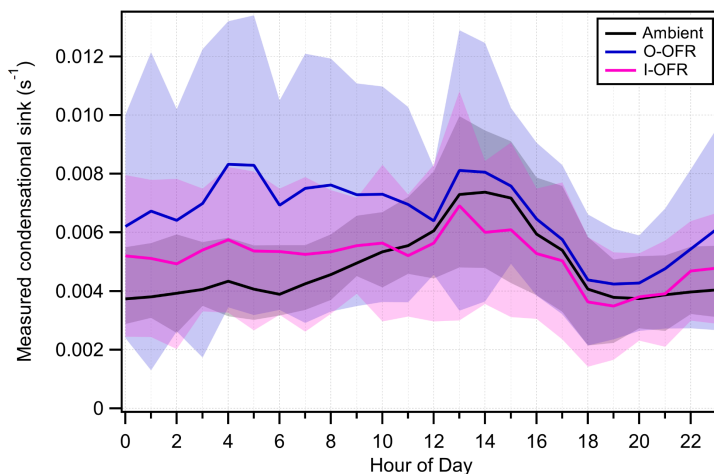


Figure S17. Average campaign diurnals of the measured condensational sink for ambient air, the output of the O-OFR and the output of the I-OFR, with shading representing one standard deviation. For the LVOC loss calculator, we estimated the condensational sink in each OFR by averaging the input (ambient air) and output condensational sink values.

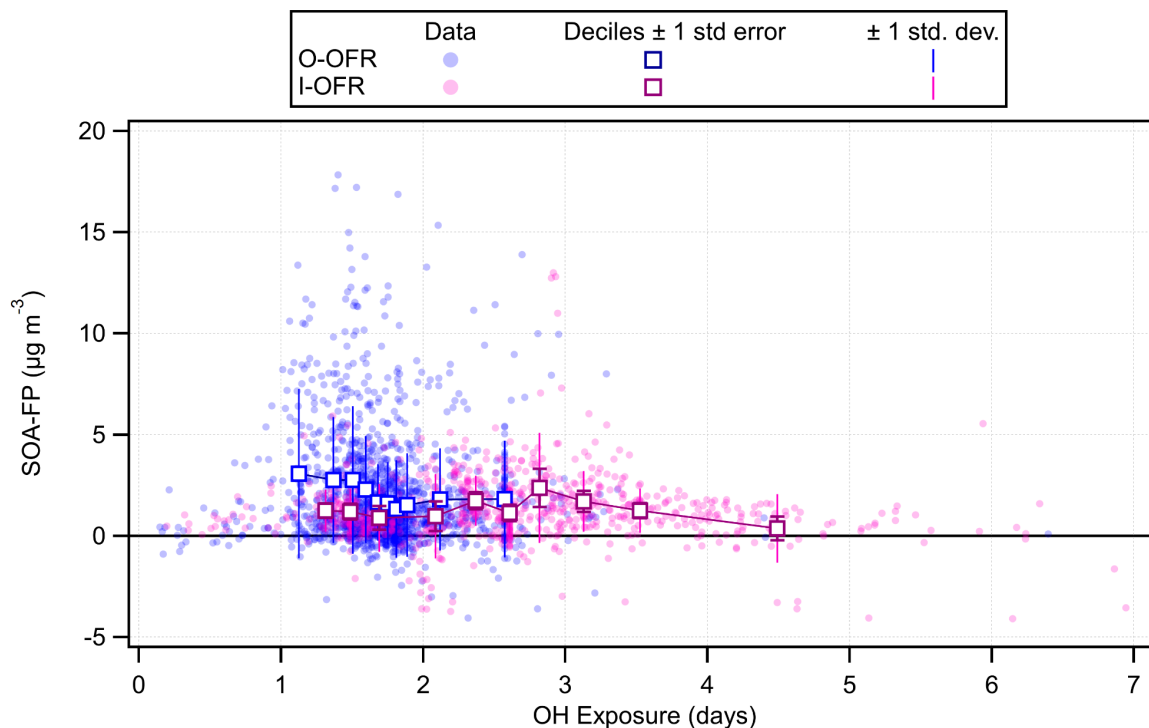


Figure S18. SOA-FP for both OFRs according to OH exposure (assuming a 24-h average OH concentration of $1.5 \times 10^6 \text{ molec cm}^{-3}$). Deciles are shown as squares, with vertical error bars being the standard error (with caps). Some error bars are smaller than the markers. Standard deviations are shown as vertical lines (without caps). As discussed in the main text, no SOA formation dependence on OH exposure is expected or seen in this range of ages.

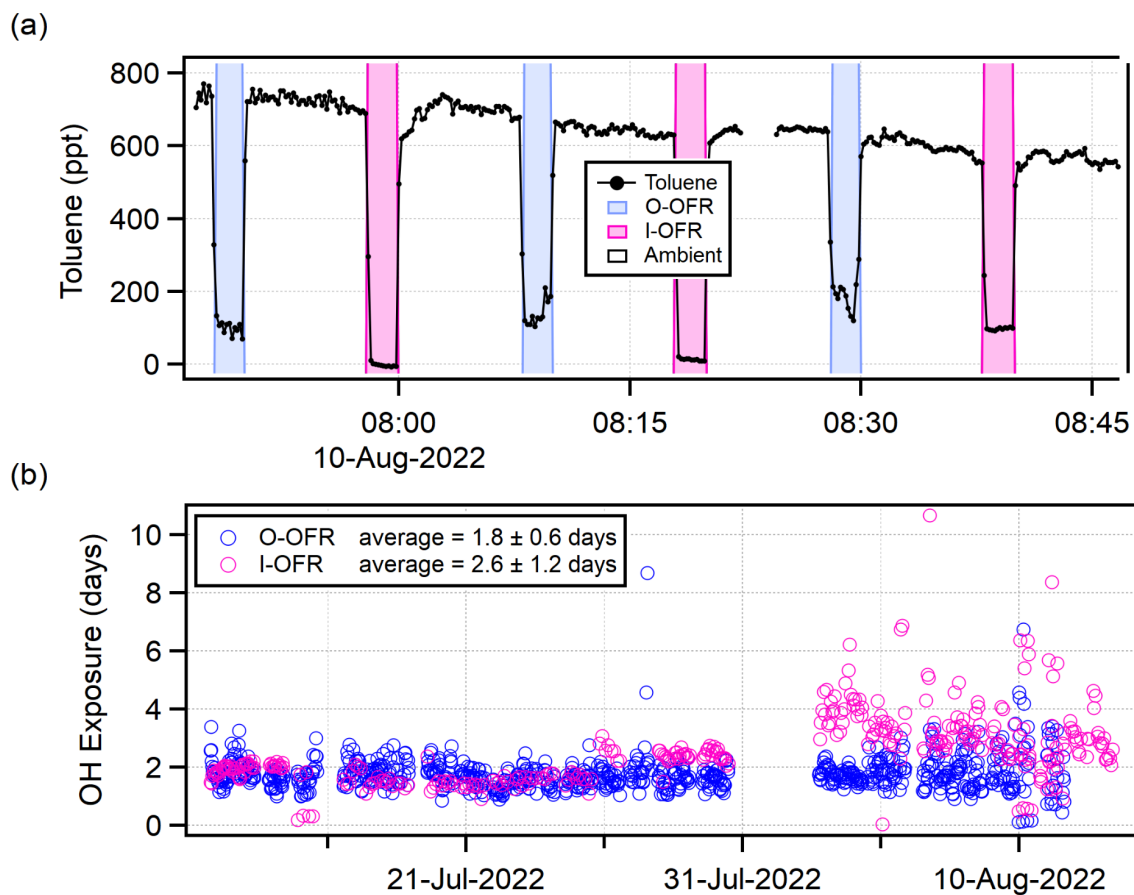


Figure S19. (a) A typical time series showing the decay of toluene in the OFRs compared to toluene in ambient air. (b) Calculated OH exposure (assuming a 24-h OH average concentration of 1.5×10^6 molec cm^{-3}) for each of the OFRs, in time. Averages are reported with one standard deviation.

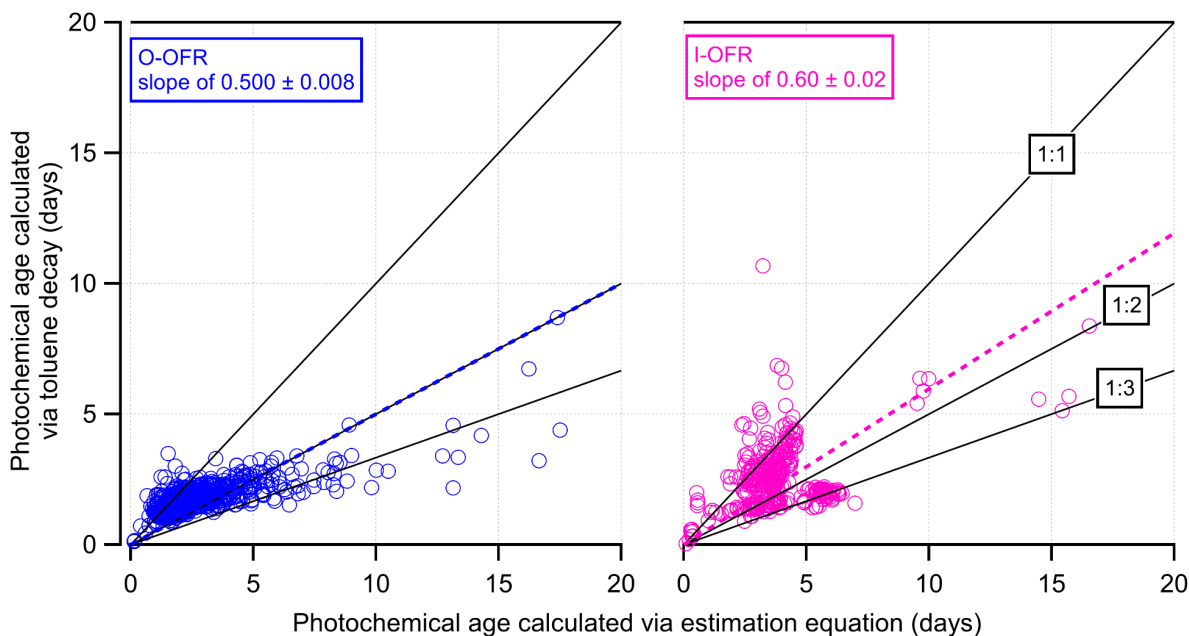


Figure S20. A comparison of OH exposures for both OFRs calculated from decays of toluene vs with the estimation equation from Li et al. (2015). The estimation equation results were used during the campaign to monitor the system, and the toluene decays were calculated post-campaign to refine the OH exposures.

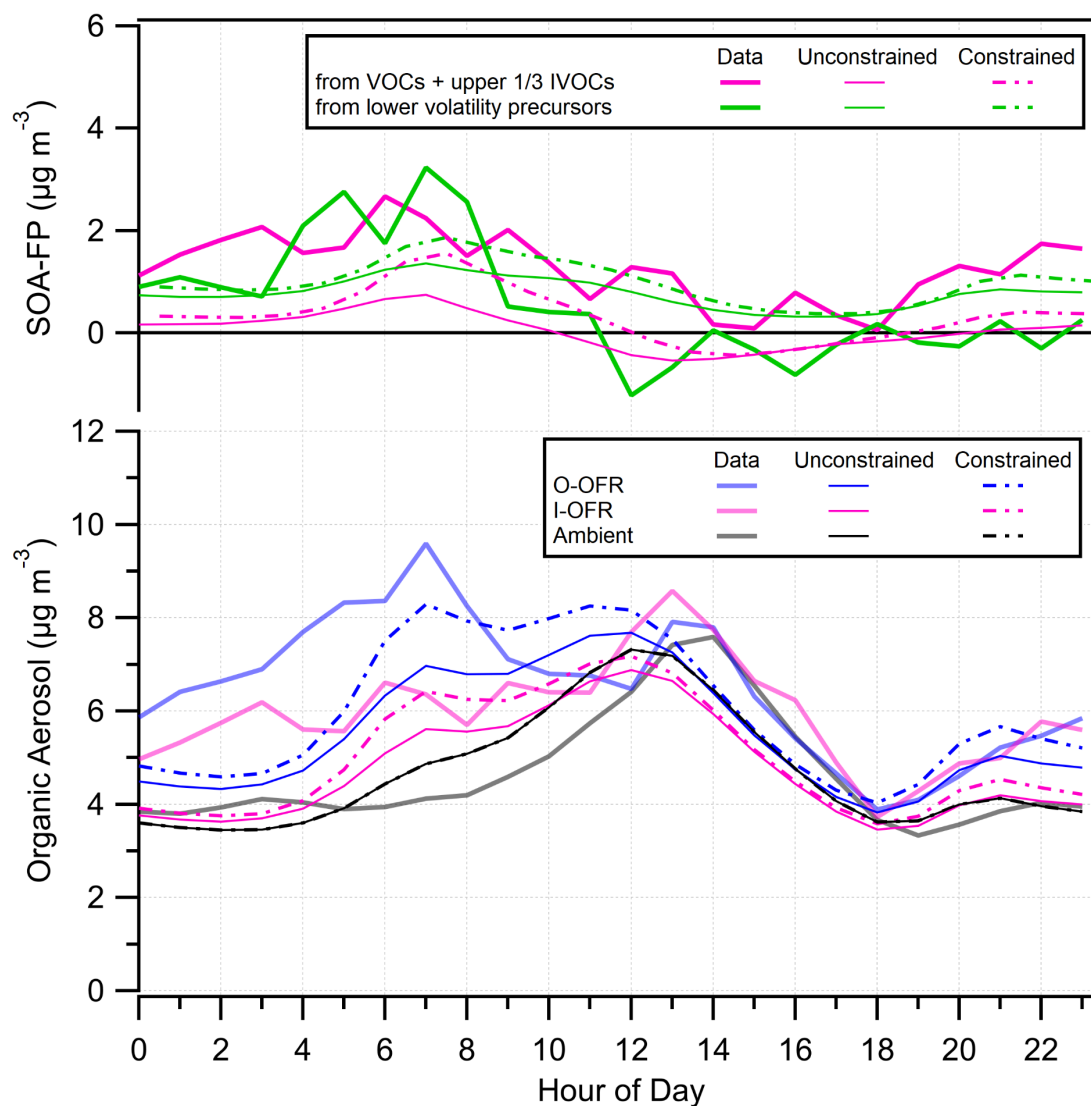


Figure S21. A modeling sensitivity study comparing CRACMM results when the input is unconstrained (raw CMAQ output) vs constrained (when Vocus measurements are used to constrain the CMAQ output, as is done in the main paper). Top: Campaign-averaged diurnal of SOA-FP according to the volatility split.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

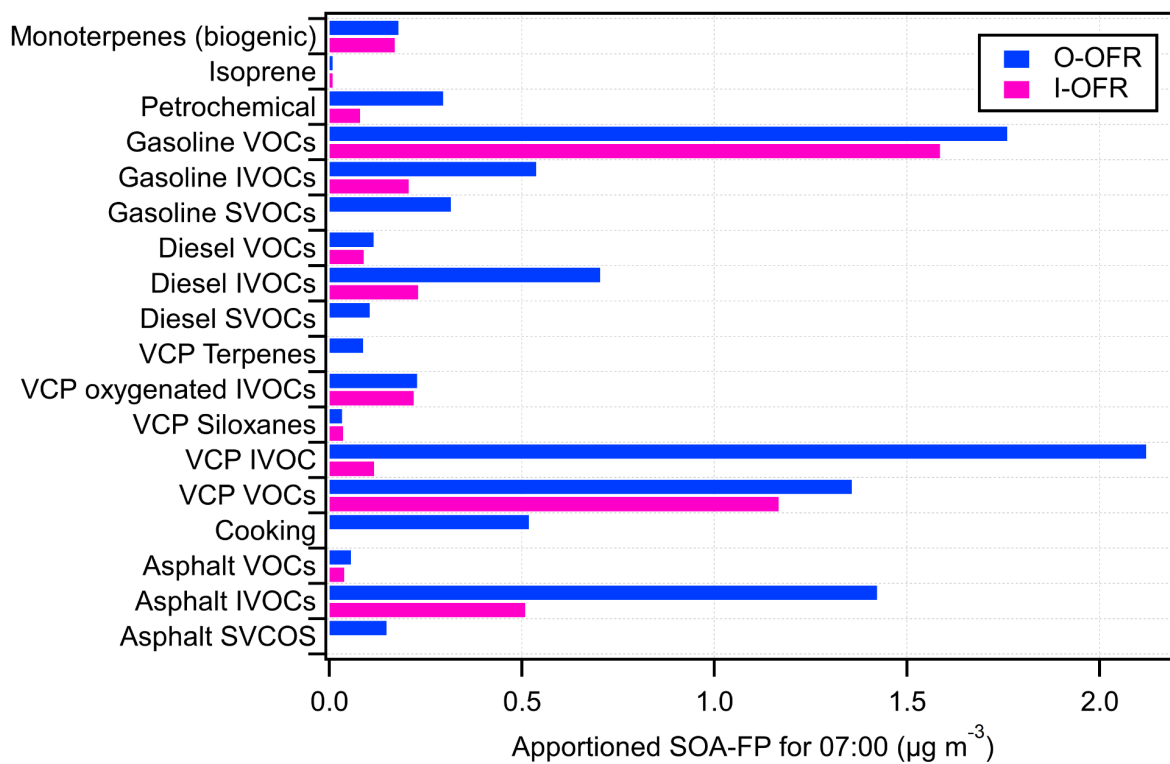


Figure S22. Breakdown of SOA-FP for 7:00 in the Caltech model according to sources and volatility. Contributions to ambient SOA have been subtracted off.

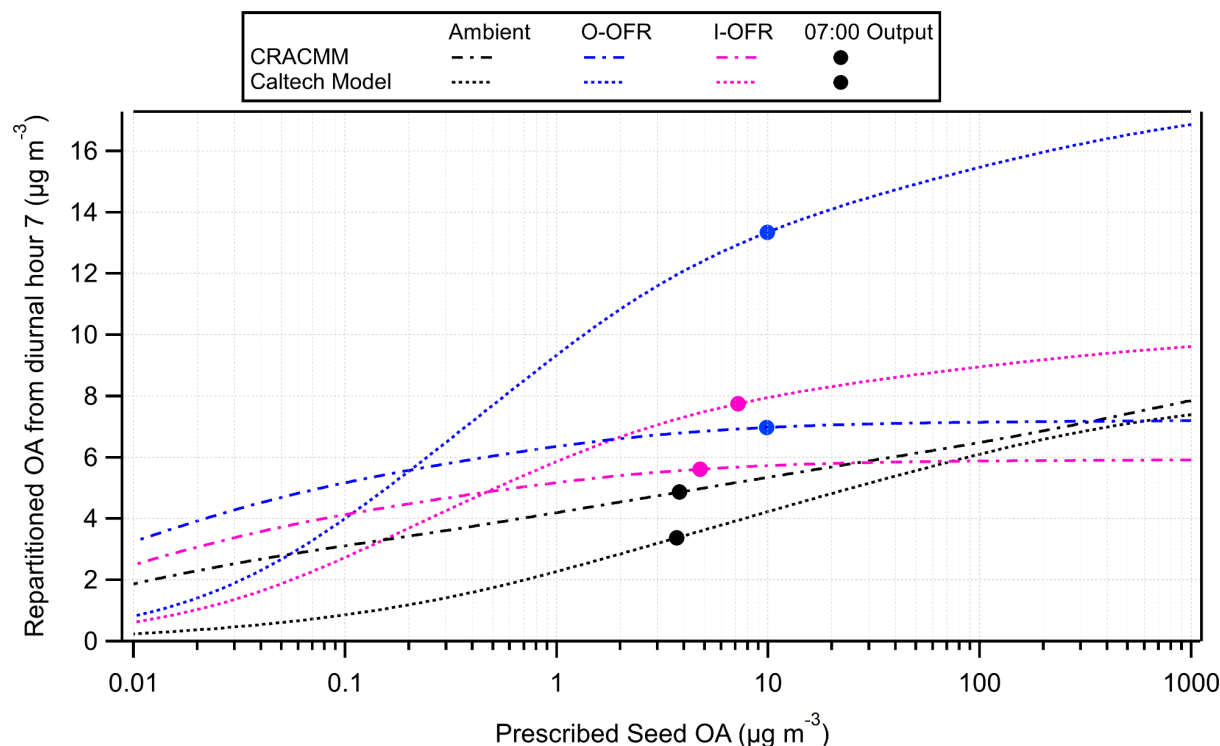


Figure S23. The total OA from 7:00 in the morning (as indicated by the circle markers) was input into a separate model experiment, in which all chemistry was turned off and the OA was allowed to repartition according to a prescribed seed concentration, with a constant condensational sink of 1 s^{-1} . This calculation was done for both models for all three sampling pathways. By exposing the OA to lower prescribed seed OA concentrations we can quantify the amount of expected OA evaporation, and by exposing the OA to higher prescribed seed OA concentrations we can quantify the amount of expected OA condensation. This gives an indication of how sensitive each model is to evaporation and condensation. For example, if the OA from 7:00 of the ambient CRACMM model run was exposed to an order of magnitude less seed OA, only $\sim 2 \mu\text{g m}^{-3}$ would evaporate, and conversely only $\sim 0.5 \mu\text{g m}^{-3}$ would condense if the seed OA was increased by an order of magnitude.

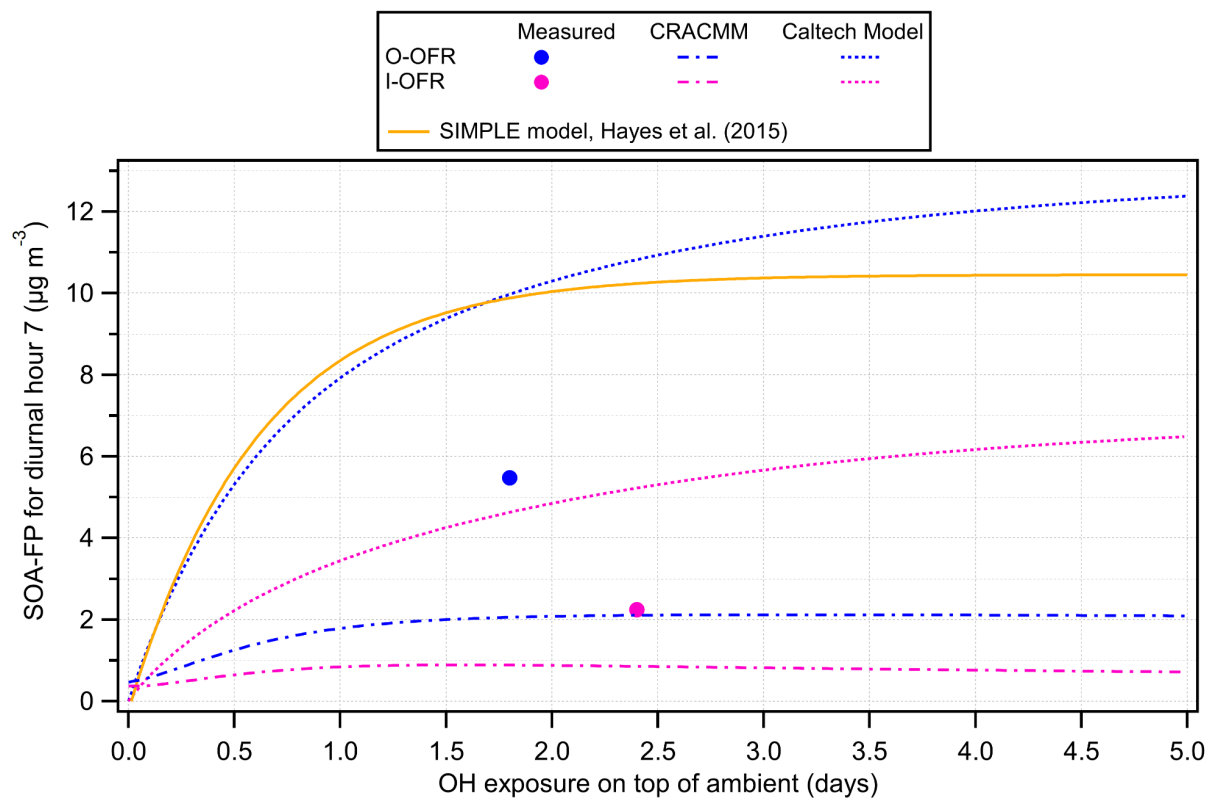


Figure S24. SOA-FP for 7:00 as a function of photochemical age (on top of ambient age) for both models described in this work, the SIMPLE model from Hayes et al. (2015), and measurements. The ambient age determined in Jensen et al. (2024) for 7:00 was 0.11 days, which has been subtracted on the x-axis.

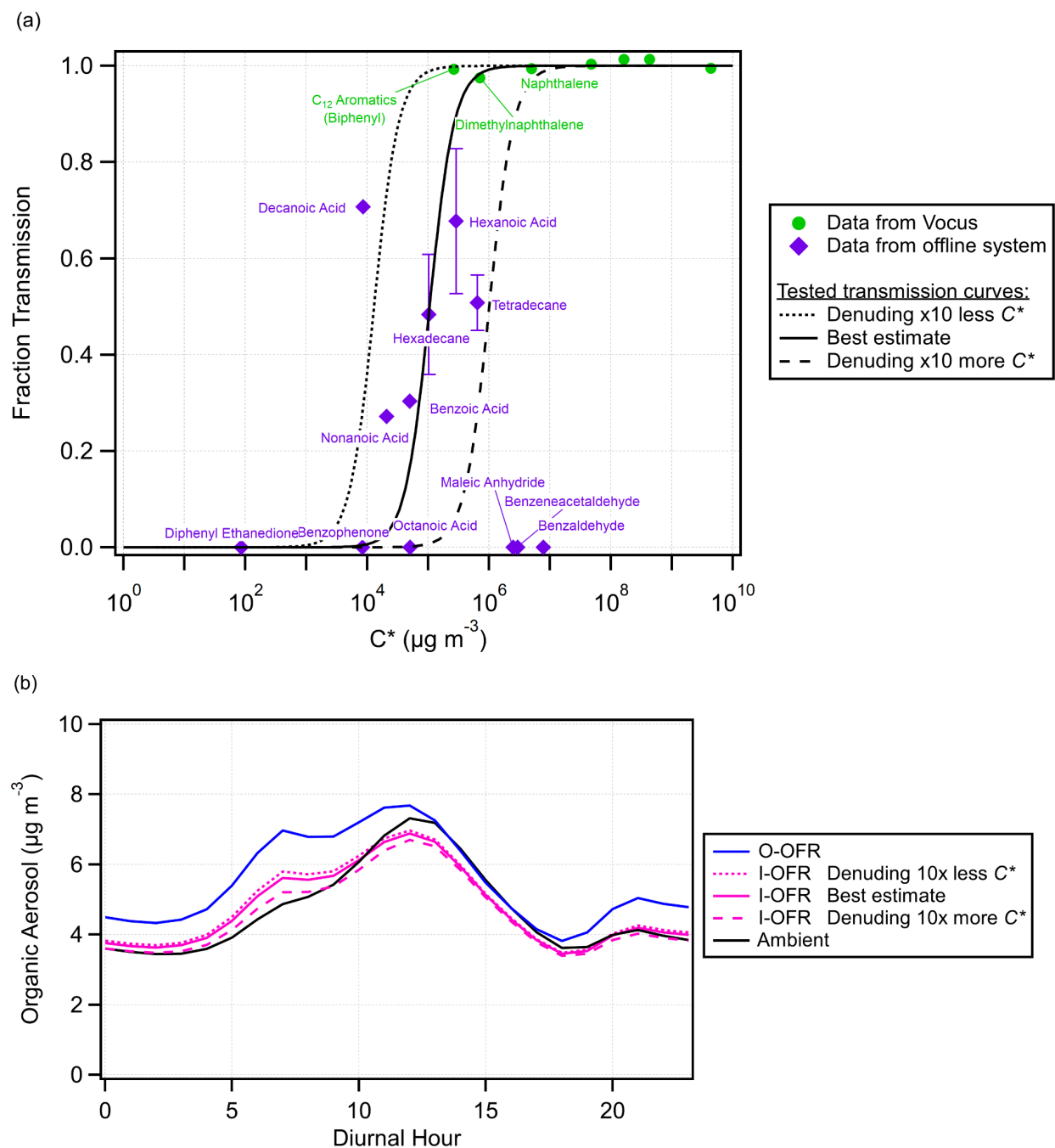


Figure S25. Sensitivity study for the CRACMM model to quantify the effect of shifting the volatility transmission curve on the modeled I-OFR OA. (a) The three transmission curves used for testing. (b) The resulting OA as a function of diurnal hour for the different transmission curves.

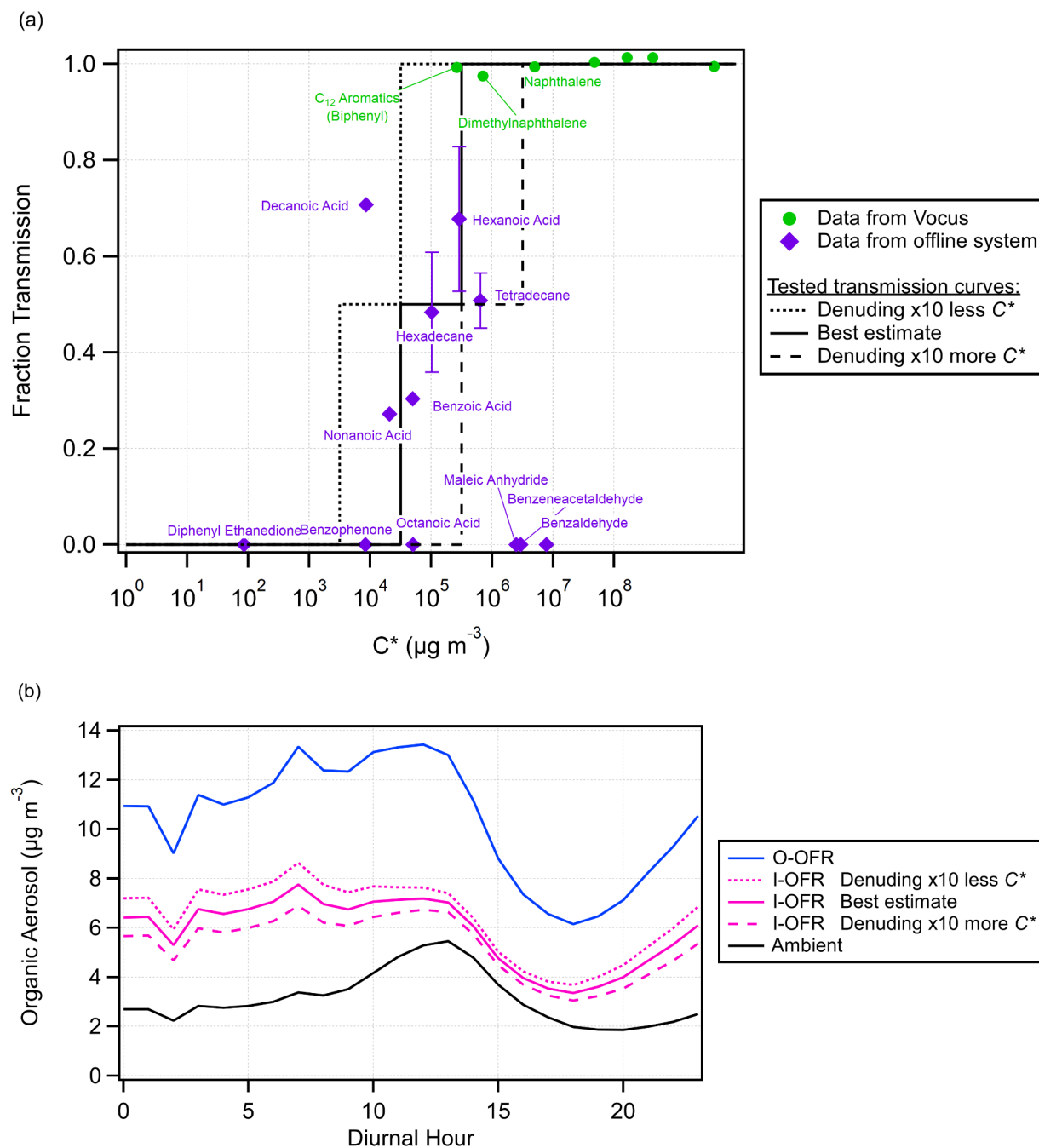


Figure S26. Sensitivity study for the Caltech model to quantify the effect of shifting the volatility transmission curve on the modeled I-OFR OA. (a) The three transmission curves used for testing. (b) The resulting OA as a function of diurnal hour for the different transmission curves.

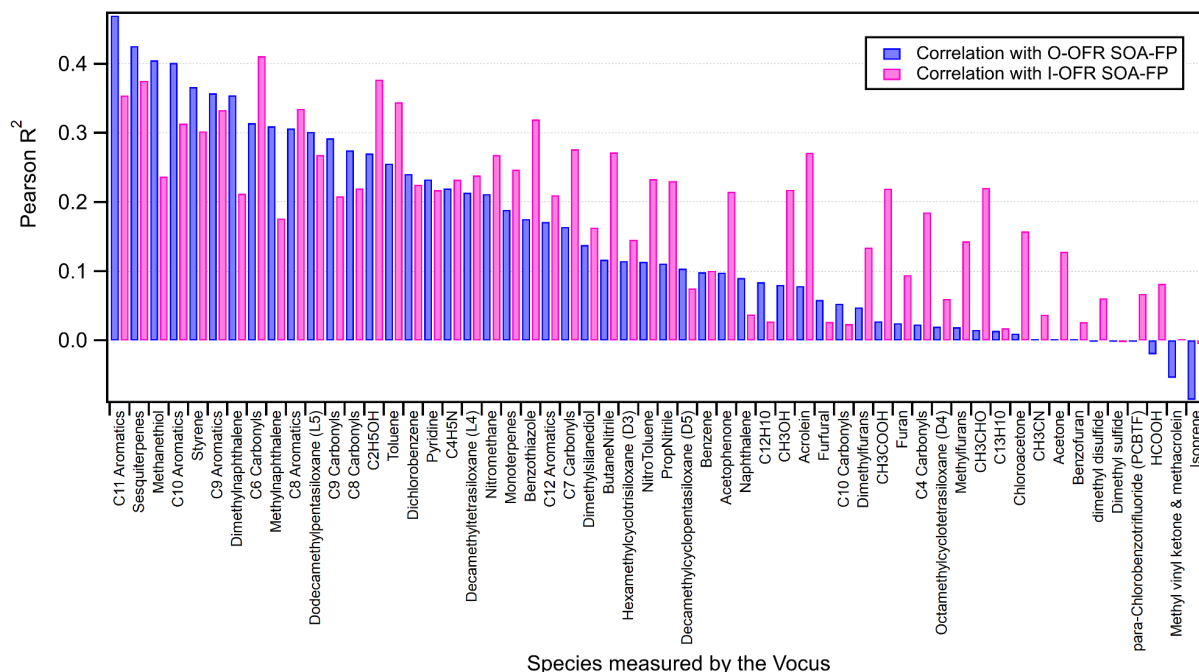


Figure S27. Bar chart showing Pearson R^2 values of all gas phase species (measured with the Vocus) with SOA-FP measured in each OFR.

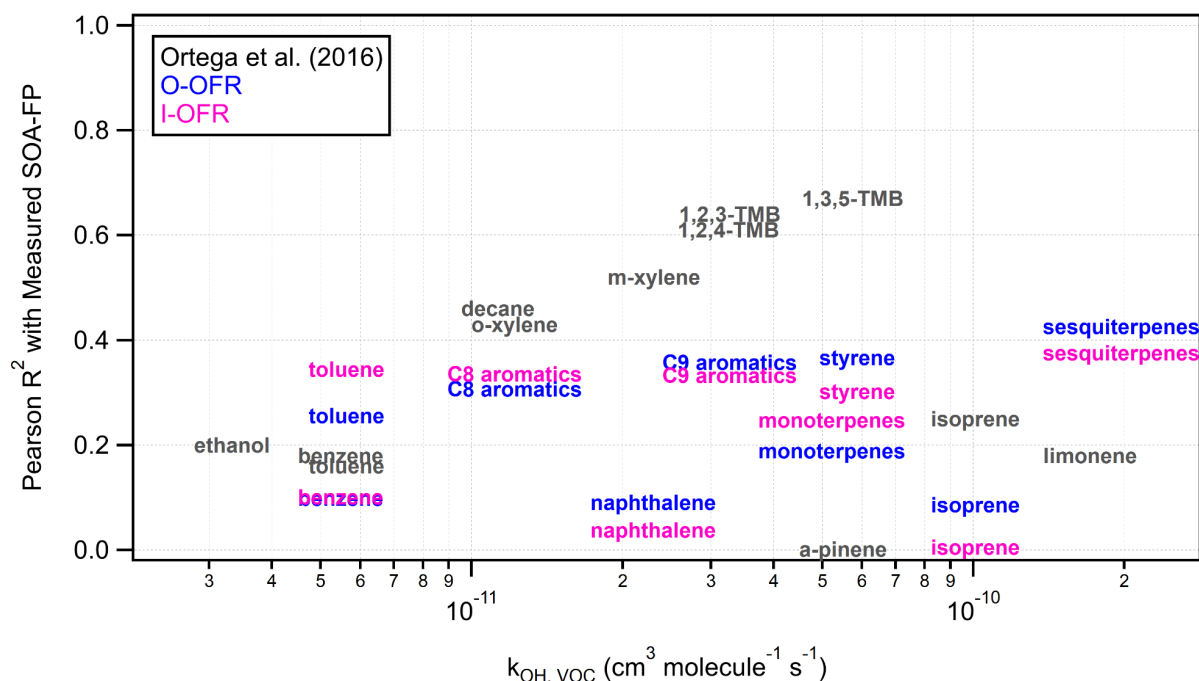


Figure S28. A comparison between 2022 and 2010 data (Ortega et al., 2016) showing correlations of VOCs with measured SOA-FP as a function of the rate coefficient constant for reaction with OH radicals. The formulas for C₈ and C₉ aromatics are C₈H₁₀ and C₉H₁₂ respectively.

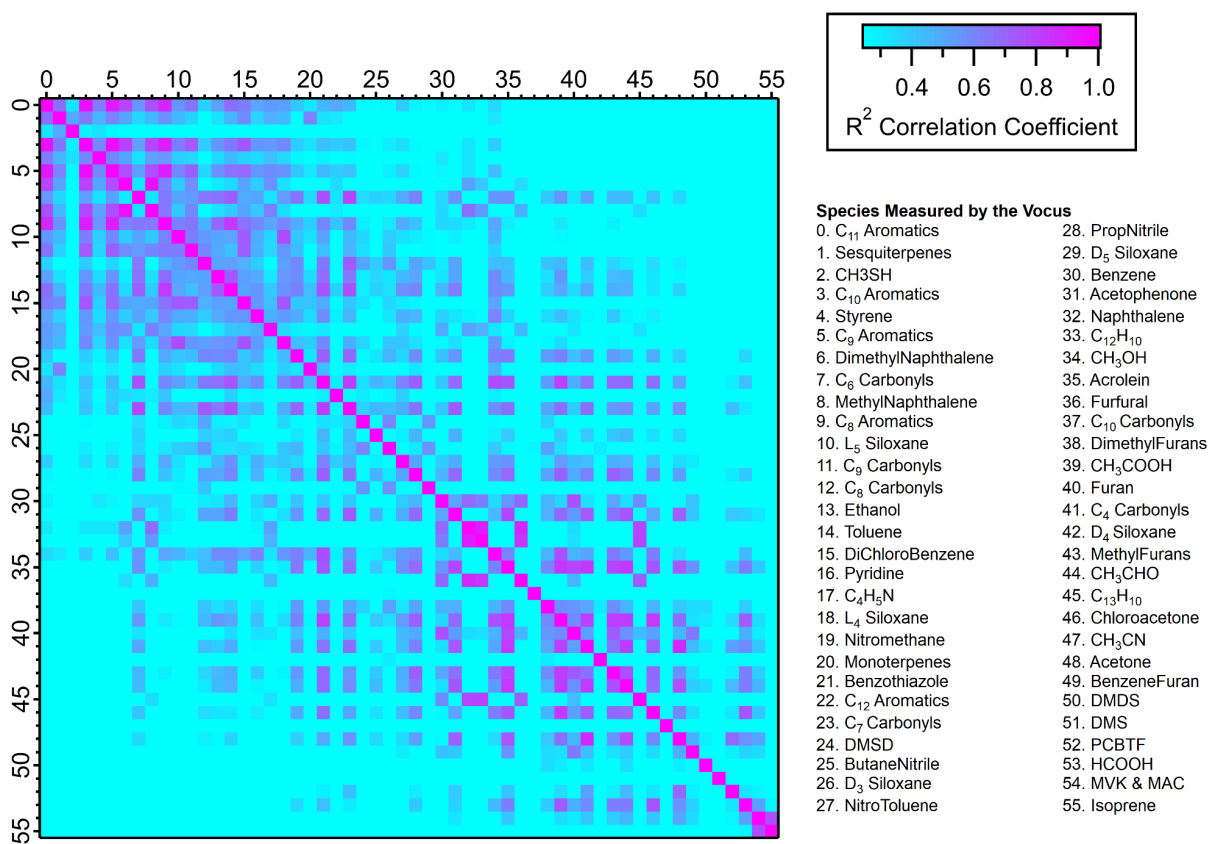


Figure S29. Matrix of Pearson R^2 values showing correlation between gas phase species measured by the Vocus in ambient air.

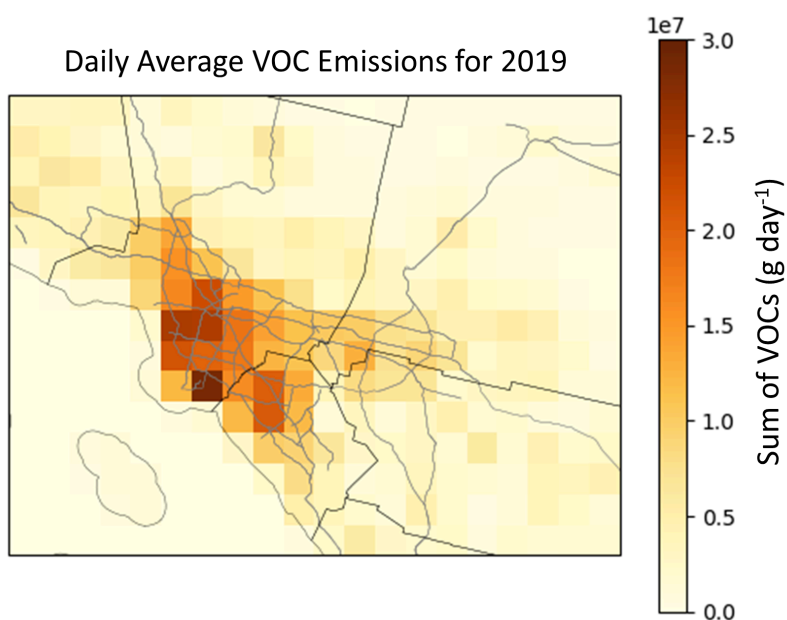


Figure S30. CMAQ model output of total VOC emissions for 2019 in the LA area.

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