

THESIS

MULTI-DAY EVOLUTION OF ORGANIC AEROSOL MASS AND COMPOSITION FROM
BIOMASS BURNING EMISSIONS

Submitted by

Abraham C Dearden

Department of Mechanical Engineering

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Master's Committee:

Advisor: Shantanu Jathar

Tami Bond

Jeffrey Pierce

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ABSTRACT

MULTI-DAY EVOLUTION OF ORGANIC AEROSOL MASS AND COMPOSITION FROM BIOMASS BURNING EMISSIONS

Biomass burning is an important source of primary and secondary organic aerosol (POA, SOA, and together, OA) to the atmosphere. The photochemical evolution of biomass burning OA, especially over long photochemical ages, is highly complex and there are large uncertainties in how this evolution is represented in models. Recently, we performed photooxidation experiments on biomass burning emissions using a small environmental chamber (~150 L) to study the OA evolution over multiple equivalent days of photochemical aging. In this work, we use a kinetic, process-level model (SOM-TOMAS; Statistical Oxidation Model-Two Moment Aerosol Sectional) to simulate the photochemical evolution of OA in 18 chamber experiments performed on emissions from 10 different fuels. A base version of the model was able to simulate the time-dependent evolution of the OA mass concentration and its oxygen-to-carbon ratio (O:C) at short photochemical ages (0.5 to 1 equivalent days) but substantially underestimated the enhancement in both metrics at longer photochemical ages (>1 equivalent day). The OA after several days of equivalent photochemical aging was dominated by SOA (58%, on average) with the remainder being POA (42%, on average). Semi-volatile organic compounds, oxygenated aromatics, and heterocyclics accounted for the majority (86%, on average) of the SOA formed. Experimental artifacts (i.e., particle and vapor wall losses) were found to be much more important in influencing the OA evolution than other processes (i.e., dilution, heterogeneous chemistry, and oligomerization reactions). Adjustments to the kinetic

model seemed to improve model performance only marginally indicating that the model was missing precursors, chemical pathways, or both, especially to explain the observed enhancement in OA mass and O:C over longer photochemical ages. While far from ideal, this work contributes to a process-level understanding of biomass burning OA that is relevant for its evolution at regional and global scales.

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CHAPTER 1 - INTRODUCTION

Biomass burning, which includes wildfires, prescribed burning, agricultural burning, and residential wood combustion, is the largest combustion-related source of primary organic aerosol (POA) and volatile organic compounds (VOCs) to the atmosphere.¹⁻⁴ Some of the biomass-burning VOCs undergo photochemical reactions in the atmosphere to form secondary organic aerosol (SOA), which together with POA, is labeled organic aerosol (OA).^{5,6} Biomass burning OA contributes significantly to the global atmospheric aerosol burden⁷ and consequently has large impacts on climate,^{8,9} air quality,¹⁰ and human health.¹¹ Although a large body of research has made significant contributions in characterizing the emissions, chemistry, microphysics, and atmospheric properties (e.g., water uptake, volatility, nuclei for cloud formation, optics) of biomass burning OA, its physicochemical evolution is extremely complex and aspects of this atmospheric evolution still remain uncertain.

In a recent critical review, Hodshire et al.¹² analyzed the ‘near-field’ evolution of wildfire OA, characterized across 13 field and 4 laboratory campaigns.¹³⁻²⁹ They concluded that, with photochemical aging, the OA mass burden in real wildfire plumes remained relatively constant while the OA mass concentrations consistently increased in laboratory experiments. They further showed that the degree of oxygenation (i.e., oxygen-to-carbon ratio or O:C) for OA, as well as its increase with photochemical age, was larger in real wildfire plumes relative to laboratory experiments. Hodshire et al.¹² laid out several hypotheses to explain differences between the field and laboratory observations. Some of these hypotheses, such as the substitution of evaporated POA with SOA production to keep the OA mass approximately constant with plume age,^{30,31} have been examined in some detail.^{32,33} Yet, other hypotheses, such as the OA evolution close to the fire or differences in the emissions composition between the field and laboratory, remain

untested. Regardless, the field campaign data included in Hodshire et al.¹² focused on quantifying the wildfire OA evolution in diluting and chemically reacting plumes over a few hours of photochemical aging and transported over a few hundred kilometers. Understandably, this is because it is challenging to study biomass burning emissions in the real atmosphere over multiple days as the OA dilutes, mixes and interacts with OA from other sources, and is subjected to varying photochemical and environmental conditions (e.g., temperature, relative humidity, clouds, precipitation). So, in addition to the discrepancies between field and laboratory observations outlined in Hodshire et al.,¹² the multi-day evolution of biomass burning OA remains highly uncertain and a topic of significant interest.

Over the past decade, the photochemical evolution of biomass-burning OA has been extensively studied in laboratory experiments using environmental chambers. Although a full literature review remains beyond the scope of this work, we highlight some of the important studies, first for residential wood combustion and then for open burning. Grieshop et al.^{34,35} and Heringa et al.³⁶ studied the photochemistry of emissions from three different residential wood stoves using several different fuels and one pellet burner. Over a total of 25+ experiments, both studies found strong evidence for SOA formation where the OA mass was enhanced by factors of 1.5 to 4 after photochemical aging. Bruns et al.³⁷ performed five experiments on emissions from a modern wood stove and measured an OA mass enhancement between 3 and 7. They reported, for the first time, that the OA mass enhancement could mostly be attributed to SOA production from oxidation of phenolic compounds and aromatic hydrocarbons. Hennigan et al.¹⁵ performed experiments on combustion emissions from fuels and fuel complexes found in the western United States (US) and saw an OA mass enhancement of 1.7 ± 0.7 . They further argued that the POA mass (i.e., fresh OA) was rapidly and chemically processed such that it accounted

for less than 20% of the net OA after several hours of photochemical aging. Tkacik et al.¹⁴ used a novel approach to study the oxidation chemistry of biomass-burning OA. They used a dual chamber setup in which emissions were added to both chambers but only one of the chambers was perturbed (e.g., exposure to UV, exposure to O₃, addition of NO to vary VOC:NO_x) with the other chamber serving as a control. Although the perturbations were generally found to enhance OA mass (1.78±0.91), they found that the OA mass enhancement was insensitive to the perturbation performed. Relying on the data published by Tkacik et al.¹⁴, Ahern et al.¹³ improved corrections for particle wall losses (average OA mass enhancement was reduced to 1.48, 17% smaller than Tkacik et al.¹⁴) and showed that the VOCs quantified using two-dimensional gas-chromatography were responsible for the most of the observed SOA. Biogenic VOCs were found to be the dominant SOA precursors for coniferous fuels and furans were found to be similarly important for grasses. Finally, Akherati et al.³⁸ performed chamber experiments similar to Hennigan et al.¹⁵ and Tkacik et al.¹⁴ and leveraged detailed speciation of SOA precursors to show that the majority of the SOA formed in these experiments was from the oxidation of oxygenated aromatic (e.g., phenols, methoxyphenols) and heterocyclic (e.g., furans) VOCs. Although these chamber data have been extremely insightful in understanding the photochemical evolution of biomass burning OA, the experiments have only been performed over short photochemical ages (typically, <12 equivalent hours at an OH concentration of 1.5×10⁶ molec. cm⁻³). While these data can and have been used to predict and interpret OA evolution close to the source (<100 km),³³ they say little about the multi-day/week evolution, relevant for regional and global scales.

Only two studies so far have attempted to study the photochemical evolution of biomass burning OA over multiple days and up to a week in laboratory experiments. Ortega et al.²⁹

sampled and oxidized smoke using an oxidation flow reactor (OFR, 13 L) and performed 25 different experiments on emissions from 16 different fuels. The smoke was sampled from a large room (3000 m³) that was filled by combusting a small amount of fuel (0.1-1 kg). When aged over an equivalent of five days, they found an average increase of 42% ($\pm 36\%$) in OA mass concentrations. The enhancement in OA mass was not found to correlate with the mass of speciated VOCs but did correlate with the initial POA, indicating a key role for semi-volatile organic compounds (SVOCs) as SOA precursors. Lim et al.³⁹ sampled and oxidized smoke using a small chamber (150 L) and analyzed 20 different experiments performed on 11 different fuels; there was significant overlap with the fuels used in Ortega et al.²⁹ The smoke was sampled from a large exhaust stack that ported biomass burning emissions from a small fire (0.25-6 kg of fuel). Lim et al.³⁹ saw a much larger enhancement in OA mass concentrations ($250\% \pm 70\%$) compared to Ortega et al.²⁹ and the chamber studies described earlier^{13-15,34-38} but argued that the higher enhancement could be explained by differences in photochemical age. In contrast to Ortega et al.,²⁹ Lim et al.³⁹ found that the OA mass enhancement correlated with fresh emissions of non-methane organic compounds, specifically those that were smaller than monoterpenes (molecular weight < 136 g mol⁻¹). Both studies undertook an empirical investigation of the changes in OA mass and composition with oxidation but neither leveraged models to better understand the precursors, processes, and properties of OA with photochemical age.

Over the past few decades, chambers and OFRs have served as workhorses, providing the underlying data needed to develop, evaluate, and optimize gas/aerosol chemical mechanisms and parameterizations for use in air quality and climate models. But while chambers and OFRs aim to simulate the photochemical evolution in the real atmosphere, this oxidation chemistry and microphysics is subject to experimental artifacts. For example, chambers and flow reactors are

subject to both particle and vapor wall losses, artifacts that can significantly influence measurements of aerosol mass and properties. Particle wall losses are relatively easy to correct for, if size and time dependent loss rates can be measured.⁴⁰ Vapor wall losses, on the other hand, require a kinetic treatment of the uptake and release of organic species, which have been shown to depend on volatility and composition.^{41,42} Furthermore, at the unusually high oxidant concentrations encountered, especially in OFRs (factors of 20 to 100 higher than those in the ambient atmosphere), the timescales for oxidation are much shorter than those for gas/particle partitioning.^{43,44} This timescale difference leads to an organic species undergoing multiple generations of oxidation in the gas phase without partitioning to the particle phase, leading to highly oxygenated products and conditions ripe for new particle formation, processes that are much less frequent in the real atmosphere. Finally, high oxidant concentrations in OFRs also tend to elevate the importance of heterogeneous oxidation reactions, which tend to reduce aerosol mass through fragmentation reactions followed by evaporation of the semi-volatile/volatile products.^{45,46} Recently, He et al.⁴⁷ showed that when different aerosol processes and their corresponding timescales were appropriately simulated using a kinetic model, the model was able to reproduce observed differences in aerosol formation and composition between a chamber and OFR study for α -pinene SOA. Similar kinetic models need to be used to simulate and interpret chamber and OFR data.

In this work, we combined laboratory data (Lim et al.)³⁹ and a process-level kinetic model (SOM-TOMAS) to simulate the photochemical evolution of OA in 18 environmental chamber experiments performed on combustion emissions from 10 different fuels. The model-simulated dilution, multigenerational gas-phase chemistry, phase-state-influenced gas/particle partitioning, heterogeneous oxidation, oligomerization reactions, and experimental artifacts (i.e., particle and

vapor wall losses). Model predictions were compared to measurements of VOCs and OA mass and composition. A suite of sensitivity simulations were performed to study the influence of individual processes on OA evolution and to diagnose model performance at higher photochemical ages.

CHAPTER 2 - MATERIALS AND METHODS

2.1 Environmental Chamber Data

Table 1: Summary of initial and final data for the 18 chamber experiments performed on 10 different fuels by Lim et al.³⁹ Experiments are ordered alphabetically by fuel.

Fire ID	Fuel	Initial OA [$\mu\text{g m}^{-3}$]	Initial OA O:C	Initial SOA Precursors [ppbv]	Initial Seed Surface Area [m^2]	Final OA [$\mu\text{g m}^{-3}$]	Final O:C	OH Exposure [molec. cm^{-3}]	Dilution Rate (hr^{-1}) [#]
62	Bear Grass	120	0.33	67	2.4×10^{-9}	60	0.70	2.1×10^{11}	2.8
28	Chaparral #1	84	0.29	70	4.3×10^{-9}	9.1	0.81	6.8×10^{11}	2.9
30	Chaparral #2	130	0.32	117	5.5×10^{-9}	26	0.69	2.2×10^{11}	3.2
33	Chaparral #3	96	0.32	91	4.1×10^{-9}	101	0.90	8.9×10^{11}	2.7
31	Douglas Fir #1	240	0.62	153	4.9×10^{-9}	4.5	0.83	14×10^{11}	2.6
57	Douglas Fir #2	120	0.48	53	3.7×10^{-9}	14	0.93	10×10^{11}	2.8
64	Douglas Fir #3	330	0.39	202	7.7×10^{-9}	37	0.74	1.2×10^{11}	3.6
50	Dung	300	0.21	134	6.0×10^{-9}	33	0.85	7.1×10^{11}	3.0
25	Engelmann Spruce #1	16	0.35	11	6.9×10^{-10}	8.8	0.71	5.9×10^{11}	2.2
26	Engelmann Spruce #2	33	0.20	40	6.7×10^{-10}	10	0.76	8.8×10^{11}	2.4
52	Engelmann Spruce #3	47	0.40	27	1.9×10^{-9}	11	1.21	14×10^{11}	3.1
61	Excelsior	56	0.52	48	3.2×10^{-9}	15	1.02	6.4×10^{11}	2.0
53	Loblolly Pine	66	0.35	52	1.8×10^{-9}	24	0.96	5.3×10^{11}	2.8
21	Lodgepole Pine #1	48	0.25	15	9.8×10^{-10}	18	0.74	6.8×10^{11}	2.1
41	Lodgepole Pine #2	23	0.38	12	4.2×10^{-10}	22	1.28	8.2×10^{11}	2.1
38	Ponderosa Pine #1	29	0.36	18	1.1×10^{-9}	9.9	0.92	8.6×10^{11}	2.4
39	Ponderosa Pine #2	240	0.31	123	4.4×10^{-9}	38	0.76	3.4×10^{11}	2.9
56	Subalpine Fir	42	0.24	96	8.5×10^{-10}	39	0.76	2.5×10^{11}	3.5
63*	Lodgepole Pine #3	180	0.37	85	7.8×10^{-9}	1.0	0.64	N/A	3.3

[#]First-order dilution rate from single exponential fit; *Dark experiment used to determine the bulk particle wall loss rate

In this work, we simulated the photochemical evolution of biomass burning OA for the chamber experiments described in Lim et al.³⁹ We take advantage of the knowledge gained from

prior papers written using FIREX data (Hatch et. al., Ahern et. al., Hennigan et. al.),^{64,13,15} and build on the tools from another (Akherati et. al.) to explore the following experiments. A detailed account of the physical and instrument setup, design of experiments, and chamber operation is provided in Lim et al.,³⁹ with additional details in McClure et al.⁴⁸ and Cappa et al.⁴⁹ A brief description, relevant to the data used in this work, is provided below. The chamber experiments outlined in Lim et al.³⁹ were performed at the Fire Sciences Laboratory (FSL) in Missoula, MT as part of the Fire Influence on Regional and Global Environments Experiment in 2016 (FIREX-2016).⁵⁰ During these experiments, a small amount of fuel (0.25 to 6 kg) was combusted using an electric igniter and emissions from these burns were channeled into a large stack (1.6 m diameter, 17 m tall), located right above the fuel bed. A long duct (0.2 m diameter, 30 m long) was used to port emissions from the stack and eventually into one of two PFA (perfluoroalkoxy) environmental chambers using an ejector-diluter system. The scope of this work includes only experiments where emissions were sent from the stack to the “mini” (150L) environmental chamber. Residence times in the duct were about 2 s, which should have minimized losses of gasses and particles during transport. Ozone (O_3) was continuously added to the chamber after smoke addition and a single UV-C light with a peak at 254 nm was used to photolyze the O_3 to produce high concentrations of hydroxyl radicals (OH). The photooxidation experiments were performed for a length of 30 to 60 minutes before the chamber was flushed with clean air to prepare for the next experiment.

A Scanning Electrical Mobility Spectrometer (SMPS), High-Resolution Aerosol Mass Spectrometer (HR-AMS), and Single-Particle Soot Photometer (SP2) were used to characterize aerosol mass concentrations and composition. A Proton Transfer Reaction - Time of Flight - Mass Spectrometer (PTR-ToF-MS) was used to measure mixing ratios for VOCs that included

key SOA precursor classes: oxygenated aromatics, heterocyclics, aromatic hydrocarbons, and biogenic VOCs.^{51–53} We should note that measurements from the same instrument were used in Akherati et al.³⁸ to analyze and simulate SOA formation from biomass burning VOCs. Lim et al.³⁹ performed a total of 56 chamber experiments but characterized the photochemical evolution in only half of those experiments. In this work, we simulated the OA evolution for 18 chamber experiments where complete VOC, aerosol, and environmental data were available. Experimental details including the fuels used are listed in Table 1.

To orient the reader, we describe the OA data from Lim et al.⁴⁰ used in this work (i.e., 18 chamber experiments). Two-thirds of the chamber experiments were performed on coniferous fuels (Douglas Fir, Engelmann Spruce, Loblolly Pine, Lodgepole Pine, Ponderosa Pine, and Subalpine Fir) and the remaining third were performed on a variety of different fuels (grass (Bear Grass), shrub (Chaparral), and other (Excelsior or wood shavings, Dung)). The dilution and particle-wall-loss corrected OA mass concentrations and OA O:C are shown in Figures S1 for all 18 chamber experiments. The initial OA mass concentrations and O:C varied between 16 and 330 $\mu\text{g m}^{-3}$ and between 0.20 and 0.62, respectively. With photochemical aging, the OA mass concentrations and OA O:C increased in nearly all chamber experiments with significant variability in the enhancement across experiments (0.9–4.8 $\times$ for OA mass concentrations and 1.3–4.0 $\times$ for OA O:C). The final photochemical age varied between slightly less than 1 equivalent day to nearly 11 equivalent days. We did not observe a relationship between initial OA and O:C (not shown) but the initial OA mass concentrations showed a strong positive correlation with several SOA precursor classes (Figure S1a–e). On average, the total SOA precursors were more than a factor of two larger than the initial POA, highlighting the large potential to form SOA with oxidation (Figure S1a). The SOA precursor composition varied some

between the chamber experiments but had an average profile of 40% heterocyclics, 29% oxygenated aromatics, 20% aromatic hydrocarbons, and 11% biogenic VOCs, roughly consistent with Akherati et al.³⁹ SVOCs were considered to be SOA precursors but since they were estimated in this work from the initial OA measurements (see Section 2.2.2), they were expected to correlate with initial OA and hence not shown in Figure S1. The OA mass enhancement, calculated as an initial value subtracted from the final value, exhibited a positive correlation with the initial POA mass concentrations ($R^2=0.54$) (Figure S2a), similar to what Ortega et al.²⁹ discovered, and with the initial SOA precursor concentrations ($R^2=0.43$) (Figure S3c). In contrast, the O:C enhancement, calculated as an initial value subtracted from the final value, exhibited a weaker negative correlation with the initial POA mass concentrations ($R^2=0.17$) (Figure S2e) and with the initial SOA precursor concentrations ($R^2=0.20$) (Figure S2g). The correlations were much weaker when the OA mass and O:C enhancement were calculated as a ratio of the final value to the initial value (Figure S2b, S2d, S2f, S2h). Regardless, Figure S2a-d suggest that the OA enhancement might be driven by the oxidation of SVOCs, which are in equilibrium with POA, in addition to the VOCs.

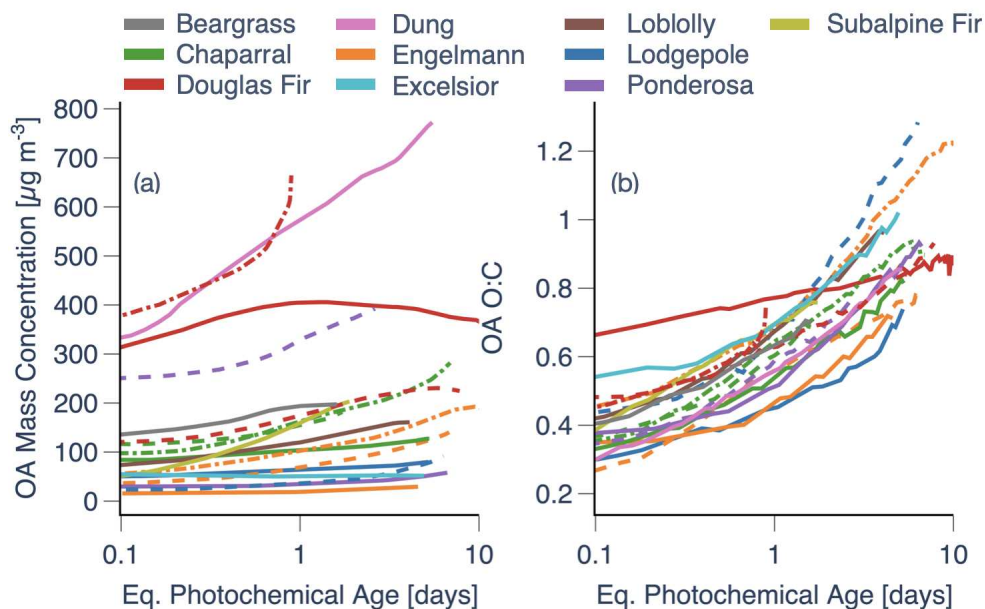


Figure 1: (a) Dilution and particle-wall-loss corrected measurements of OA mass concentration and (b) suspended OA O:C for the 18 chamber experiments studied in this work. Colors indicated different fuels. Different lines (solid, dashed, dash-dotted) with the same color are used to show experiments with the same fuel.

2.2 Kinetic Organic Aerosol Model

2.2.1 SOM-TOMAS Model

The SOM-TOMAS model, or Statistical Oxidation Model (SOM)-Two Moment Aerosol Sectional (TOMAS) model, was used to simulate the photochemical evolution of OA for the 18 chamber experiments described above. The SOM uses a two-dimensional carbon-oxygen grid and a statistical approach to simulate the multigenerational oxidation chemistry of organic compounds and its oxidation products, in addition to calculating the volatility of the oxidation products.⁵⁴ The TOMAS model uses a two-moment scheme to track number and mass size distributions and simulates the microphysical processes of coagulation, condensation, evaporation, and nucleation.⁵⁵ The SOM-TOMAS model has been used extensively to study the formation and evolution of OA in laboratory experiments^{32,47,56,57} and field environments.⁵⁸ More specifically, it has been used to study the photochemical evolution of OA in chamber

experiments performed on biomass burning emissions³⁸ and in wildfire plumes sampled during an aircraft-based field campaign.³³ The primary difference between the chamber experiments of Akherati et al.³⁸ and Lim et al.³⁹ is the size of the chamber and the photochemical exposure achieved in those two studies (<10 hours versus up to 11 days, respectively).

A detailed description of the SOM-TOMAS model and the governing equations can be found in previous publications.^{38,47} A brief overview is provided below. Within SOM, five parameters are used to track the oxidation chemistry of the VOC and its oxidation products (i.e., model species) by explicitly simulating functionalization and fragmentation reactions: (i-iv) $p_{f,1}$ to $p_{f,4}$, mass yields for four functionalized products that add one, two, three, and four oxygen atoms to the carbon backbone, respectively; and (v) m_{frag} , a parameter used to calculate the probability of fragmentation (P_{frag}) based on the O:C ratio of the model species ($P_{frag} = (O:C)^{m_{frag}}$). ΔLVP , a sixth parameter, is used to quantify the decrease in volatility of the model species with the addition of an oxygen atom. The volatility (c^*) and reaction rate constant with OH (k_{OH}) are parameterized as a function of the model species' carbon (N_C) and oxygen (N_O) number. Based on the diffusive-reactive framework described in Zaveri et al.,⁵⁹ the SOM-TOMAS model simulates the kinetic gas/particle partitioning of the model species by considering the particle-phase diffusivity of the absorbing organic aerosol. The SOM-TOMAS model was recently updated to simulate autoxidation reactions, heterogeneous oxidation via OH, and oligomerization reactions.⁴⁷ Autoxidation is modeled by directly prescribing an empirical yield for highly oxygenated organic molecules (HOM), informed by previous laboratory experiments.⁶⁰ Heterogeneous oxidation is modeled as a surface reaction of a model species in the particle phase with OH and assuming that the subsequent chemistry is the same as that in the gas phase; collisions between the model species and OH that lead to a chemical reaction are

modulated by the uptake coefficient (γ).⁴⁶ Finally, oligomerization is modeled by tracking the reversible formation and dissociation of dimers, characterized by forward and reverse reaction rates, respectively.⁶¹

The SOM-TOMAS model can simulate size-dependent losses of particles to the chamber walls. However, in this study, only a single, bulk particle wall-loss rate was available to model particle wall losses (details described in Section 2.2.2). Vapor losses to the chamber walls are modeled, following the work Matsunaga and Ziemann.⁶² Here, the first-order uptake to the walls is assumed to be equal to $k_{\text{vap,on}}$ and the release of vapors from the walls ($k_{\text{vap,off}}$) is modeled using absorptive partitioning theory with the chamber wall serving as an absorbing mass with an effective mass concentration of C_w mg m⁻³; C_w is parameterized as a function of the partitioning model species's c^* , following Krechmer et al.⁴¹

2.2.2 Model Inputs

Select measurements were used to create experiment-specific inputs to initialize and run the SOM-TOMAS model. Below, we describe the inputs used to model dilution, initialize SOA precursors, POA, and SVOCs, prescribe OH concentrations, and inform particle and vapor wall losses.

Lim et al.³⁹ diluted the chamber with clean air to offset the volume sampled out by the instruments and to keep the chamber volume constant at 150 L. This dilution was significant enough (2 to 3.6 hr⁻¹) that dilution ended up being the most important process that affected concentrations inside the chamber. Therefore, we decided to explicitly model dilution in the SOM-TOMAS model since it was likely to strongly affect gas/particle partitioning of OA. The dilution rate was calculated by first fitting a double exponential function to the mixing ratios for hydrogen cyanide (HCN) and then using the function to determine a time-dependent dilution rate, fitted to a double exponential decay that was specific to each chamber experiment. We assumed HCN to be an inert tracer that did not react with OH or O₃ and was not lost to the walls.

Previous work has tended to use acetonitrile as an inert tracer but we did not find significant differences in the bulk dilution calculated using HCN or acetonitrile. The HCN data were preferred since they were both smoother and larger in concentration than that of acetonitrile. Numerically, dilution was modeled at each model time step by multiplying the chamber concentrations in the model with the incremental dilution rate. Time series data for HCN for a representative chamber experiment (Ponderosa Pine) and the corresponding time-dependent dilution rate are shown in Figure 2.

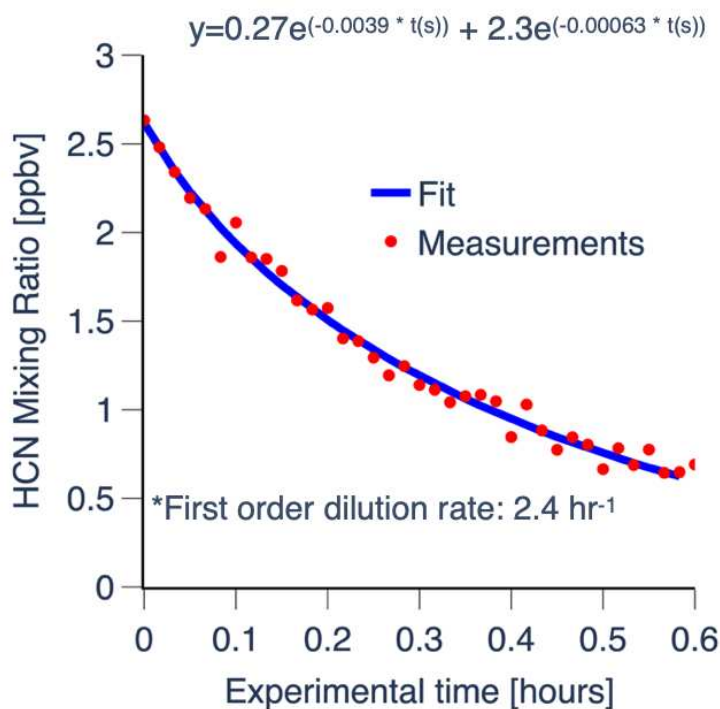


Figure 2: An example of the measured hydrogen cyanide (HCN) mixing ratios and the double exponential fit (where t is time in seconds) used to calculate time-dependent dilution rate for one such chamber experiment performed on Ponderosa Pine emissions (Fire 38). An interpretable first order dilution rate is shown, calculated using a single exponential decay for demonstrational purposes only.

PTR-ToF-MS data were used to initialize mixing ratios for the SOA precursors. The PTR-ToF-MS data have been described in detail in Coggon et al.⁵³ and the SOA precursor treatment was identical to that described in Akherati et al.³⁸ A total of 86 unique VOCs were

considered to form SOA and the full list of precursors is provided in Table S1 (reproduced from Akherati et al.).³⁸ The 86 VOCs were assigned to one of nine SOA precursor surrogates (benzene, toluene, *m*-xylene, naphthalene, isoprene, α -pinene, phenol/guaiacol, syringol, alkyl furans) for which SOM-TOMAS parameters have been developed from historical chamber data. SOM-TOMAS parameters for these surrogates are provided in Table S2a (reproduced from Akherati et al.),³⁸ noting that these parameters are representative of SOA formation under high NO_x conditions. Coggon et al.⁵³ argued, based on simulating the gas-phase chemistry for a few of the Lim et al.³⁹ fires, that peroxy radicals (RO₂) from higher carbon number VOCs exclusively reacted with the hydroperoxyl radical (HO₂) (~75%) or with itself (i.e., forms gas-phase dimers) (~25%). Accordingly, the oxidation chemistry is expected to be more representative of that encountered under low NO_x conditions. Chamber walls, however, can serve as a source for NO in the presence of NO₂, a pathway Coggon et al.⁵³ did not consider, and may confound the choice between using high versus low NO_x parameters to simulate SOA formation. Because of this, we decided to run a Low NO_x simulation as a model sensitivity case. SOM-TOMAS parameters for surrogates in this use case can be found in table S2b. We should point out that since the SOM parameters only inform the trajectory of the oxidation chemistry in the carbon-oxygen grid, model predictions of the SOA mass yield for a specific precursor are likely to be different from that for the surrogate. Although the SOM-TOMAS model was run to simulate the oxidation chemistry separately for each of the 86 VOCs, VOC and SOA data were aggregated to present results across four broad precursor classes: oxygenated aromatics, heterocyclics, aromatic hydrocarbons, and biogenic VOCs.

POA from biomass burning sources is known to be semi-volatile and reactive.^{63–65} Hence, we used the volatility distribution reported in May et al.⁶⁵ to distribute POA and the semi-volatile

organic compounds (SVOCs) in equilibrium with POA, within the SOM grid. This was done by first determining the POA+SVOC mass distribution in a volatility basis set (VBS) and then mapping the mass from each c^* bin in the VBS to the SOM model species that had a matching c^* . The mapping was done while ensuring that the SOM-predicted POA O:C aligned with initial observations of POA O:C. The chemical evolution of the POA+SVOC mass was simulated assuming that the oxidation chemistry was the same as that for multi-ring aromatics (naphthalene served as the surrogate), based on the work of Akherati et al.³³

Following Barmet et al.,⁶⁶ dilution-corrected mixing ratios of deuterated butanol (D9) were used to calculate time-dependent OH concentrations, specific to each chamber experiment. Dilution-corrected data for D9 and the corresponding OH concentrations and exposures for a representative chamber experiment (Ponderosa Pine) are shown in Figure 3. The average OH concentration was 4×10^8 molec. cm^{-3} and the OH exposure by the end of the experiment was equivalent to 6.6 days of photochemical aging at an OH concentration of 1.5×10^6 molec. cm^{-3} .

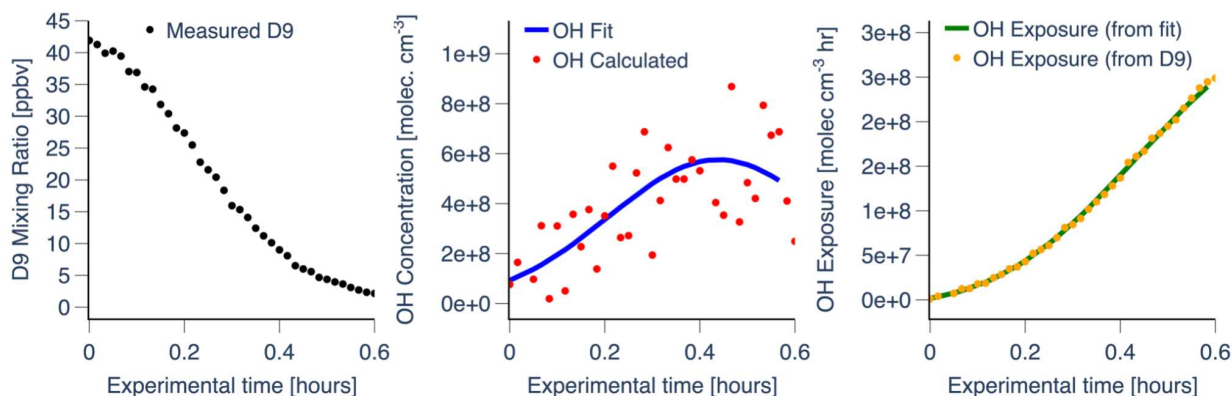


Figure 3: (a) Dilution-corrected mixing ratios for deuterated butanol (D9). (b) OH concentrations estimated from D9 decay and the Gaussian fit to the data. (c) Raw and fit OH exposure. All data are from the chamber experiment performed on Ponderosa Pine emissions (Fire 38)

Lim et al.³⁹ determined a bulk particle wall loss (PWL) rate ($k_{\text{PWL}}=0.028 \text{ min}^{-1}$, $\tau_{\text{PWL}}=36 \text{ min}$) by fitting an exponential function to dilution-corrected POA mass concentration data from a ‘dark’ chamber experiment performed on Lodgepole Pine; in this specific experiment the lights were not turned on and there was no photochemistry. This particle wall loss rate represents an upper bound estimate since the POA mass could have evaporated with dilution⁶⁷ or from losses of semi-volatile vapors in equilibrium with the POA to the chamber walls.⁶⁸ To account for these additional loss processes, we ran the SOM-TOMAS model for this dark experiment and simulated dilution, kinetic gas/particle partitioning, and particle and vapor wall losses; all chemical reactions were turned off. The model was run with several particle wall loss rates ($\tau_{\text{PWL}} = 36, 72, 108, \text{ and } \infty \text{ min}$) and results are presented in Figure 4. We found that a particle wall loss rate of $k_{\text{PWL}}=0.014 \text{ min}^{-1}$ ($\tau_{\text{PWL}} = 72 \text{ min}$) best reproduced the observations, indicating that the rate presented in Lim et al.³⁹ was likely overestimated. The same bulk particle wall loss rate was used to model losses of particles to the chamber walls for all 18 chamber experiments.

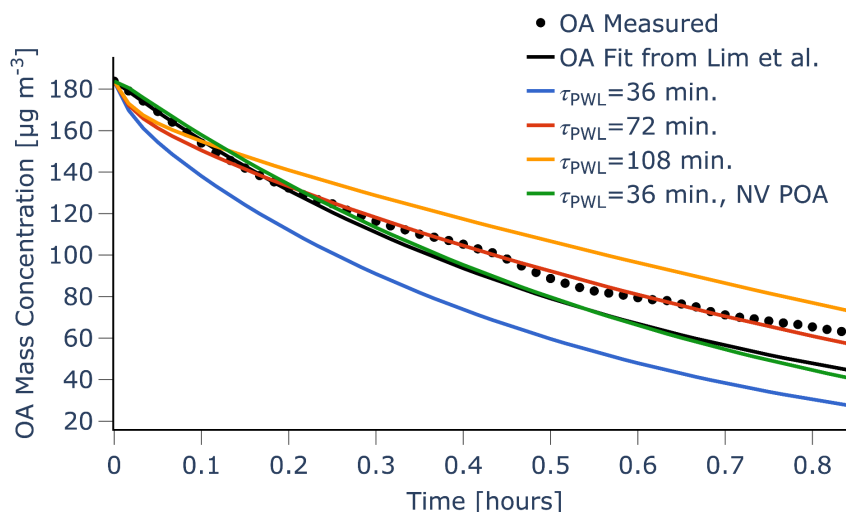


Figure 4: Dilution-corrected predictions of OA mass concentrations compared against measurements for different particle wall loss rates (τ of 36, 72, and 108 minutes) and assumptions about POA (semi-volatile versus non-volatile). Also shown is the particle wall loss rate used estimated in Lim et al.³⁹ Model predictions and measurements are from a ‘dark’ experiment performed on a Ponderosa Pine Fire.

The vapor wall loss rate has not been quantified for the chamber used by Lim et al.³⁹ Assuming that the vapor wall loss rate scales as a linear function of the surface area to volume ratio for the chamber,⁶⁹ we used historical estimates for five separate environmental chambers to calculate a $k_{\text{vap,on}}$ of $2 \times 10^{-2} \text{ s}^{-1}$ ($\tau_{\text{VWL}} = 0.8 \text{ min}$) for the Lim et al.³⁹ chamber; Paul Scherrer Institute (5.5 m^3 , $k_{\text{vap,on}}$ of $3.3 \times 10^{-3} \text{ s}^{-1}$, $\tau_{\text{VWL}} = 5 \text{ min}$),⁷⁰ University of Colorado Boulder (8 m^3 , $k_{\text{vap,on}}$ of $1.7 \times 10^{-3} \text{ s}^{-1}$, $\tau_{\text{VWL}} = 10 \text{ min}$),⁴¹ Colorado State University (10 m^3 , $k_{\text{vap,on}}$ of $1.3 \times 10^{-3} \text{ s}^{-1}$, $\tau_{\text{VWL}} = 13 \text{ min}$),⁵⁶ Georgia Institute of Technology (13 m^3 , $k_{\text{vap,on}}$ of $6.1 \times 10^{-4} \text{ s}^{-1}$, $\tau_{\text{VWL}} = 27 \text{ min}$),⁷¹ and California Institute of Technology (30 m^3 , $k_{\text{vap,on}}$ of $4 \times 10^{-4} \text{ s}^{-1}$, $\tau_{\text{VWL}} = 42 \text{ min}$).⁴²

2.2.3 Simulations and Sensitivity Analysis

The primary results in this work are from simulations performed with the ‘Base’ configuration of the SOM-TOMAS model. In this configuration, we modeled dilution, multigenerational gas-phase chemistry, phase-state-influenced kinetic gas/particle partitioning, heterogeneous oxidation, oligomerization, and particle and vapor wall losses. The end result is temporal model outputs of OA mass, and OA composition (O:C and OA precursor contribution to OA). We assumed a liquid-like phase state for OA (particle-phase diffusion coefficient (D_b) of $10^{-10} \text{ m}^2 \text{ s}^{-1}$) and an uptake coefficient (γ) of 1 to simulate heterogeneous oxidation reactions. For oligomerization, we used dimer formation ($k_f = 10^{-24} \text{ cm}^3 \text{ molec.}^{-1} \text{ s}^{-1}$) and dissociation ($k_r = 1.6 \times 10^{-2} \text{ s}^{-1}$) rates based on our previous work with α -pinene SOA.⁵⁷ All SOM species were assumed to participate in oligomerization reactions. In addition, we performed two types of sensitivity simulations. In the first type, we performed simulations where a single process was turned off or scaled to examine the sensitivity in model predictions to that specific process (e.g., dilution, particle wall losses, heterogeneous oxidation, etc.).

In the second type, we performed simulations to examine the sensitivity in model predictions to several adjustments in model inputs or chemical schemes. These are described below. First, the heterogeneous oxidation scheme was simplified such that the model species' reaction with OH was assumed to form a single oxidation product with four oxygen atoms added to the reactant. This scheme, which simulated an aggressive uptake of oxygen into the particle phase, was used to run simulations with two different uptake coefficients ($\gamma = 1, 6$). Second, Coggon et al.⁵³ were able to speciate more than 150 VOCs using the PTR-ToF-MS, of which only 86, as identified by Akherati et al.,³⁸ were considered to form SOA. To investigate whether the remaining 42 VOCs were responsible for SOA formation, we aggregated the VOCs by carbon and oxygen number, inputted them into a SOM grid, and simulated their oxidation chemistry using *n*-dodecane as a surrogate. Third, we explored how an average SOA precursor profile based on an average of 57 fires sampled during FIREX-2016⁵¹ affected model predictions. Initial SOA precursor concentrations for each chamber experiment were determined by multiplying the emissions ratio of the SOA precursor with acetonitrile with the initial acetonitrile concentrations. Finally, we performed 100 Monte-Carlo simulations where we randomized the distribution of POA+SVOC mass in the SOM grid while ensuring that the mass distribution reproduced the volatility behavior observed by May et al.⁶⁵ and matched the initial OA O:C. The Base and both types of sensitivity simulations were performed on all 18 chamber experiments.

CHAPTER 3 - RESULTS

3.1 Example Results from a Ponderosa Pine Chamber Experiment

Predictions from simulations performed with the SOM-TOMAS model for a representative fuel and experiment (Ponderosa Pine, Fire 38 in Table 1) are compared against measurements in Figure 5. This specific experiment was chosen since it was illustrative of the model performance across all 18 chamber experiments (described in Section 3.2 and showcased in Figures 2, 3, and 4). Model predictions in Figure 5a and 5b are from the Base simulation (solid line) and from sensitivity simulations (dash-dotted lines) performed by systematically turning off or adjusting a specific process. Predictions and measurements of OA mass concentrations presented in panels (a), (b), and (d) have been corrected for dilution and particle wall losses; being a ratio, the O:C data remain uncorrected and represent those for the suspended OA.

As shown in Figure 5a, predictions from the Base simulation seemed to reproduce the increase in OA mass concentrations, within the range of the measurement uncertainty, over the entire experiment. By the end of the experiment, predictions for OA mass concentrations showed a net increase of 33% while measurements had increased by 99%, relative to the initial OA. However, the modeled trends with photochemical age did not align with trends in the measurements. For instance, over one equivalent day of photochemical aging, the model produced a rapid increase in OA mass concentrations while the measurements were relatively flat. At photochemical ages longer than one equivalent day, the model produced a marginal increase in the OA mass concentrations, which deviated from the measurements that continued to rise sharply. Model predictions of OA O:C, as shown in Figure 5b, closely followed the measurements up to one equivalent day of photochemical aging. While model predictions of OA O:C continued to increase after one equivalent day of photochemical aging, the modeled increase

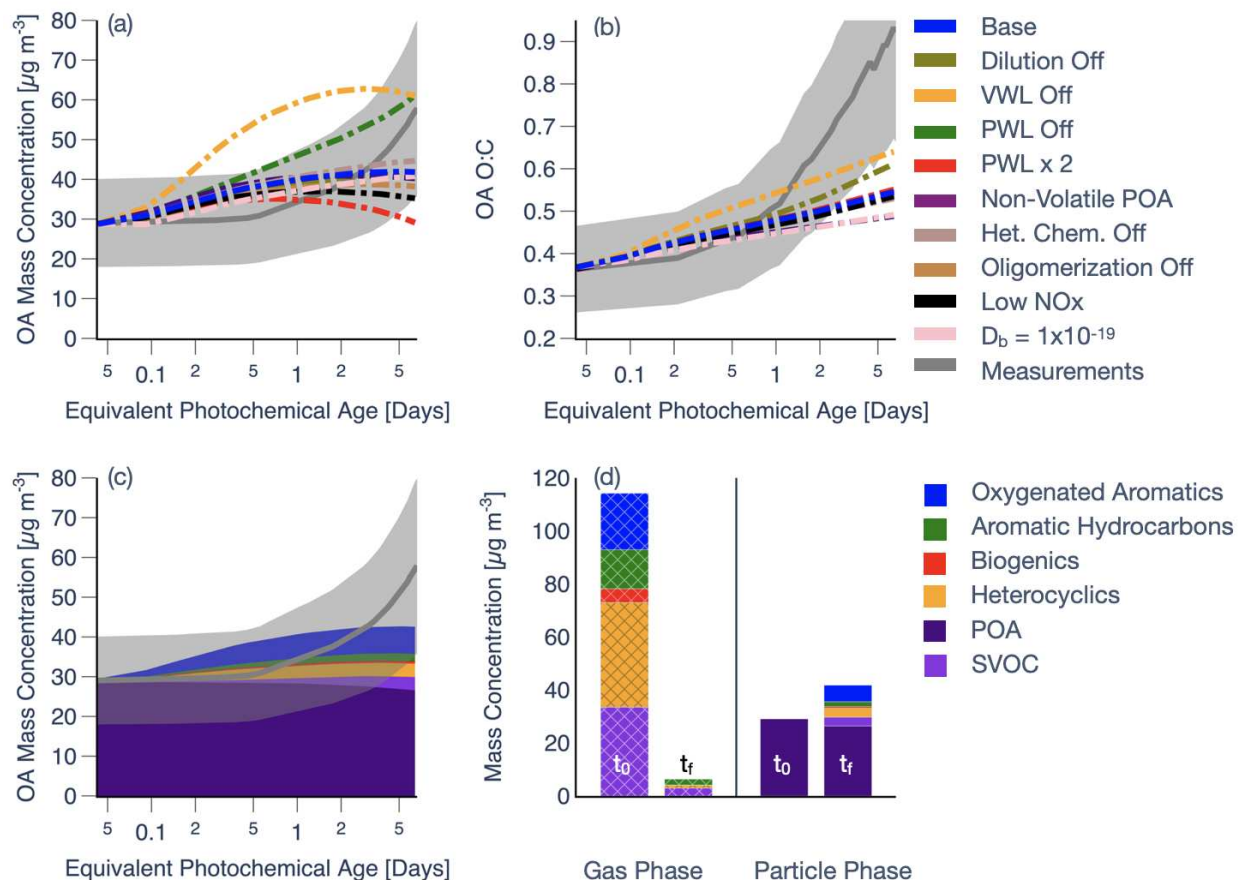


Figure 5: SOM-TOMAS model predictions for (a) OA mass concentration and (b) OA O:C compared against measurements as a function of photochemical age (assuming an OH concentration of $1.5 \times 10^6 \text{ molec. cm}^{-3}$) for the Ponderosa Pine chamber experiment (Fire 38). (c) 'Base' model predictions resolved by precursor class compared against bulk measurements of OA mass concentration. (d) Initial (t_0) and final (t_f) gas- and particle-phase predictions resolved by precursor class from the 'Base' simulation. In panels (a-c), mean measurements are shown with a gray solid line with the shaded region representing the 2- σ uncertainty. Sensitivity simulation results in (a) and (b) are shown with dash-dotted lines. The hatching in (d) shows precursor concentrations in the gas-phase. The OA mass concentrations in panels (a,b,d) have been corrected for dilution and particle wall losses.

with respect to the initial OA O:C was dwarfed (50%) relative to the increase experienced by the measurements (157%). The increase in the predicted OA and O:C stemmed from the production of SOA (Figure 5c), primarily driven by the oxidation of SVOCs, oxygenated aromatics, and heterocyclics, with minor contributions from aromatic hydrocarbons and biogenic VOCs. After

slightly more than six equivalent days of photochemical aging, the OA was dominated by POA (56%) with a smaller contribution from SOA (44%).

The temporal trends in OA mass concentrations, shown in Figure 5, can be explained as follows. The OH reactivities (i.e., reaction rate constant with OH $\times$ OH concentration) for the key SOA precursor classes (i.e., SVOCs, oxygenated aromatics, heterocyclics) were high enough that the precursor mixing ratios were depleted within 1 equivalent day of photochemical aging. Model predictions and measurements of precursor decay, summed and resolved by precursor class, with photochemical age are shown in Figure 6 for this experiment. Model predictions of precursor decay seemed to agree the most with observations for aromatic hydrocarbons but were largely inconsistent with the measurements for the three other precursor classes. This was mostly likely because there were significant interferences at the mass-to-charge ratios used to track the precursors, from fragmentation of oxidation products during ionization in the PTR-ToF-MS.⁵³ The high OH reactivities and rapid precursor decay resulted in an initial burst in SOA production. However, with few precursors left after one equivalent day, the model was unable to produce any more SOA. This also indicated that there were minor contributions to SOA from slower reacting precursors (i.e., aromatic hydrocarbons) and from the multigenerational chemistry of the residual oxidation products left behind after the initial SOA burst. Furthermore, any SOA production past one equivalent day of photochemical aging was balanced by evaporation of POA and SOA from dilution of the chamber volume (2.4 hr⁻¹). The end result was that the predictions of OA mass concentrations increased earlier in the experiment but continued to slow down with aging.

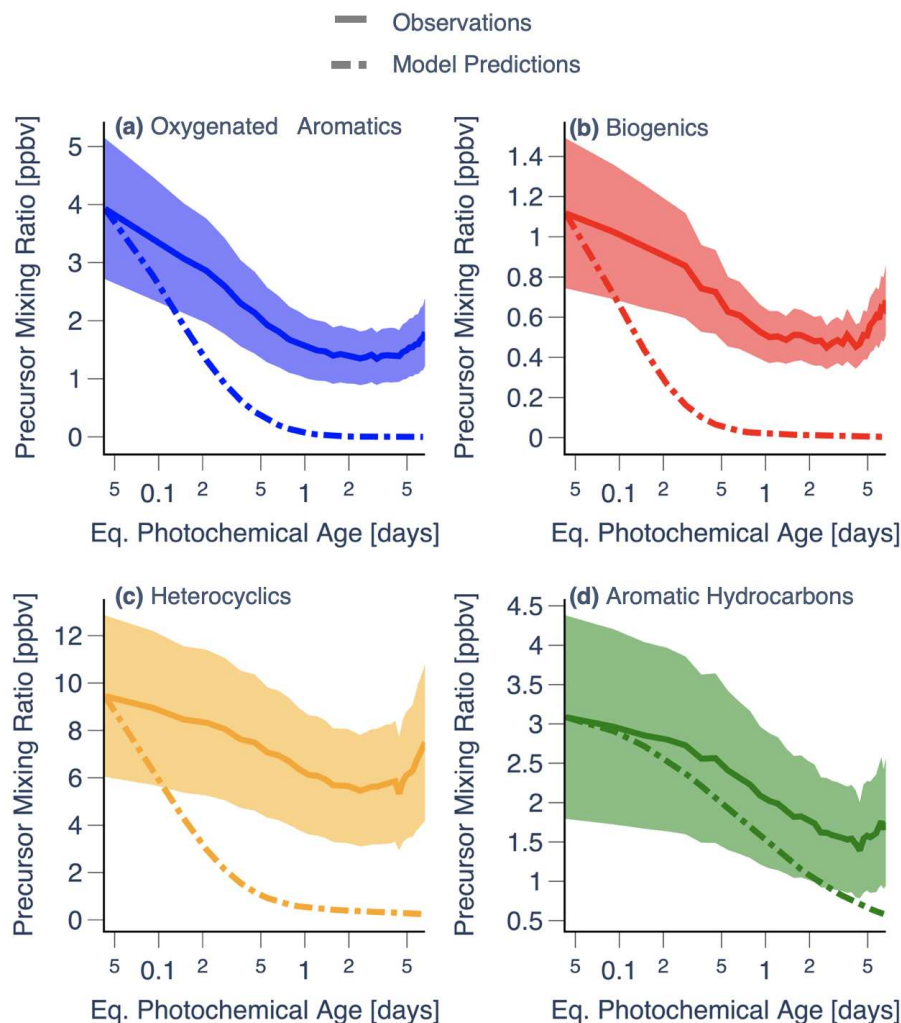


Figure 6: Model predictions of dilution-corrected SOA precursor mixing ratios compared against measurements for the chamber experiment performed on Ponderosa Pine emissions (Fire 38). Individual SOA precursors were aggregated by the precursor class.

Results from the sensitivity simulations provided additional insight on the relative importance of the various processes. Simulations performed with no dilution, heterogeneous oxidation, and oligomerization and a non-volatile and non-reactive POA, individually, resulted in no significant change in OA mass concentrations ($\pm 10\%$), relative to the Base simulation. Also included is a sensitivity simulation using model parameters conducive to a low NO_x environment. This had a medium effect, but brought OA further from the measurements. In contrast, simulations performed with particle wall losses turned off (PWL Off) or particle wall

loss rates doubled ($\text{PWL} \times 2$) seemed to produce a stronger change in OA mass concentrations ($\pm 45\%$). While the PWL-Off simulation produced slightly better agreement with the OA mass concentration measurements, it is unlikely that there were no losses of particles to the chamber walls. Rather, this suggests that a bulk, time-independent particle wall-loss rate informed by a single dark experiment and used to correct for losses in all experiments may add to the uncertainty in simulating the experiment-specific trends in OA evolution. The VWL-Off simulation predicted a large spike in OA mass concentrations at short photochemical ages highlighting that vapor wall losses are an important artifact to consider for this small chamber. We should note that VWL likely plays a dynamic role in these experiments since vapors lost to the walls initially when the concentrations are higher may be released from the walls later in the experiment when the concentrations are depleted from continuous dilution of the chamber volume. The run using low NO_x parameters impacted results, but not significantly enough to justify using these parameters as a new base case. Most of the sensitivity simulations produced a smaller spread in the OA O:C evolution and even when they did (i.e., dilution off, VWL off), the predictions significantly underestimated the change in measured OA O:C after one equivalent day of photochemical aging.

To illustrate the highly oxidizing environment inside the chamber, we plot the initial and final precursor (and OA) concentrations in Figure 5d. Over the course of six equivalent days of photochemical aging (~ 35 mins of clock time), nearly all of the primary precursors (oxygenated aromatics, heterocyclics, aromatic hydrocarbons, and biogenic VOCs) were consumed. Although it might appear that only a small fraction of the SVOCs (semi-volatile vapors in equilibrium with the POA) reacted by the end of the experiment, the net change in SVOCs was a result of competing processes: reaction with OH (loss), evaporation of POA with dilution (gain), and

exchange of SVOCs between the chamber and the chamber walls (loss initially but gain later). Based on the net loss of VOC and net production of SOA, we calculated an end-of-experiment SOA mass yield of 13% for the SOA precursors. A similar mass yield calculation was not possible to perform for the SVOCs due to the reasons mentioned above.

3.2 Photochemical Evolution of OA from Eighteen Different Fires

Model predictions of OA mass concentrations and O:C are compared against measurements for 18 chamber experiments in Figures 2 and 3, respectively. Results are shown for the Base simulations and also for simulations where particle wall losses were turned off since this simulation offered the most optimal performance for the Ponderosa Pine chamber experiment shown in Figure 5. In addition, predictions of the normalized OA composition from the Base simulations for the 18 chamber experiments are shown in Figure 9 at two different time points: 0.5 equivalent days and at the end of the experiment. In Figures 2 and 3, the model-measurement comparison was highly variable (more so for OA mass concentrations) but there were still a few findings of note. First, generally speaking, model predictions of OA mass concentrations seemed to agree with the measurements at shorter photochemical ages but the model-measurement comparison varied quite significantly at longer photochemical ages; a logarithmic scale was used for photochemical age to highlight this finding. Yet, the heterogeneity in photochemical ages across the chamber experiments makes this hard to notice in Figure 7 and we reexamined this comparison, resolved by photochemical age, in Figure 10 (described later in this section). In 6 out of 18 chamber experiments, the model-predicted OA mass concentration was outside the measured uncertainty range by the end of the experiment; overestimated in 3 and underestimated in 3 chamber experiments. The modeled OA mass concentration profile with photochemical age was contained within the measurement uncertainty envelope in 9 out of the

18 chamber experiments and in only 4 out of 18 chamber experiments did the model predictions follow the mean in the measurements.

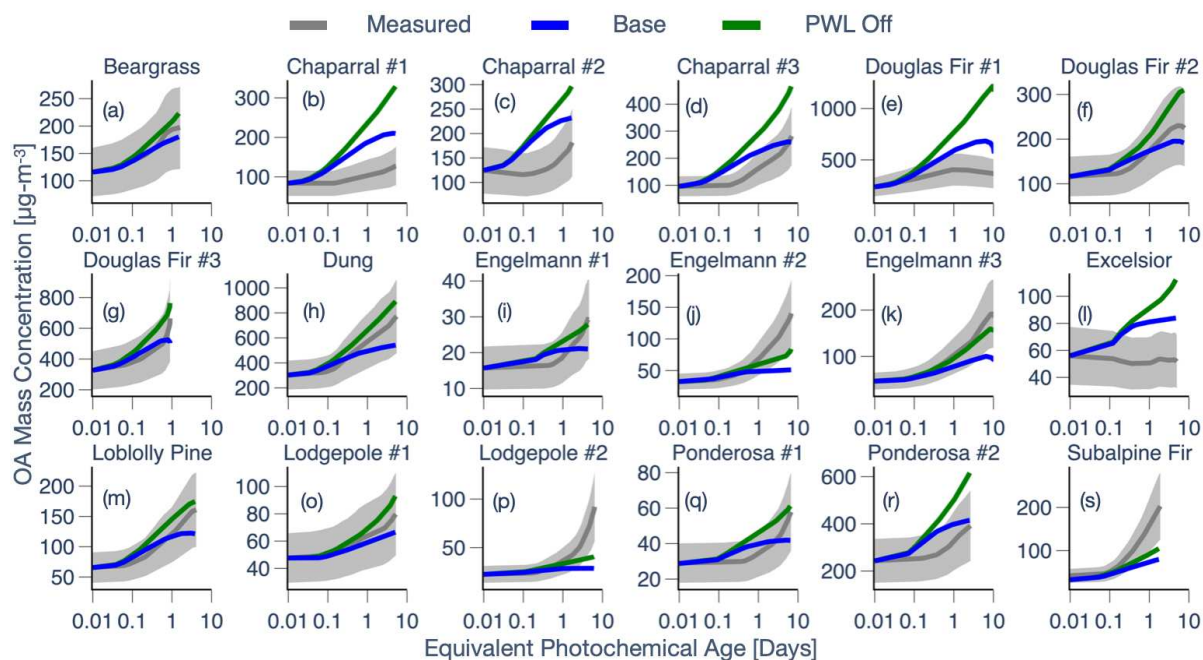


Figure 7: SOM-TOMAS model predictions from the Base and PWL-Off simulations compared against measurements of OA mass concentration. Each panel has a unique y-axis scale but the same x-axis scale. Experiments based on the same fuel have been numbered serially and the panels have been organized alphabetically by fuel. Mean measurements are shown with a gray solid line with the shaded region representing the 2- σ uncertainty. All OA mass concentrations have been corrected for dilution and particle wall losses.

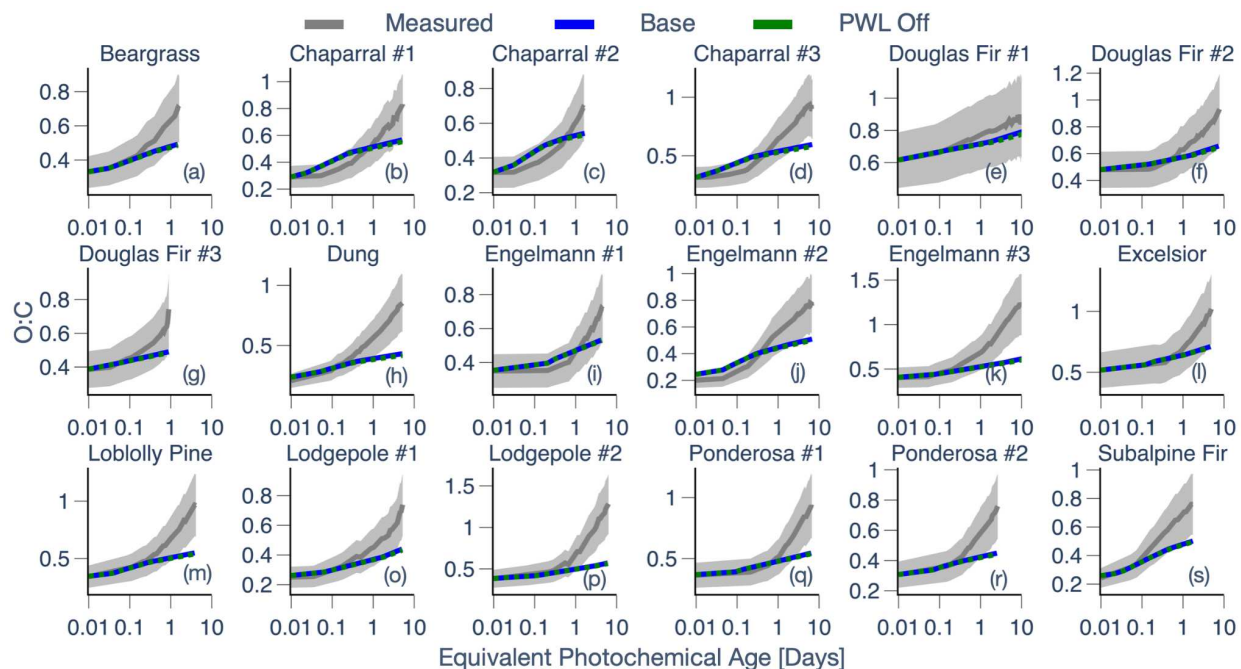


Figure 8: Same as Figure 7 but for OA O:C. The OA O:C is calculated for the suspended OA and it did not require corrections for dilution or particle wall losses. Model predictions from the PWL-Off simulation are hidden behind those for the Base simulation and, hence, they cannot be seen.

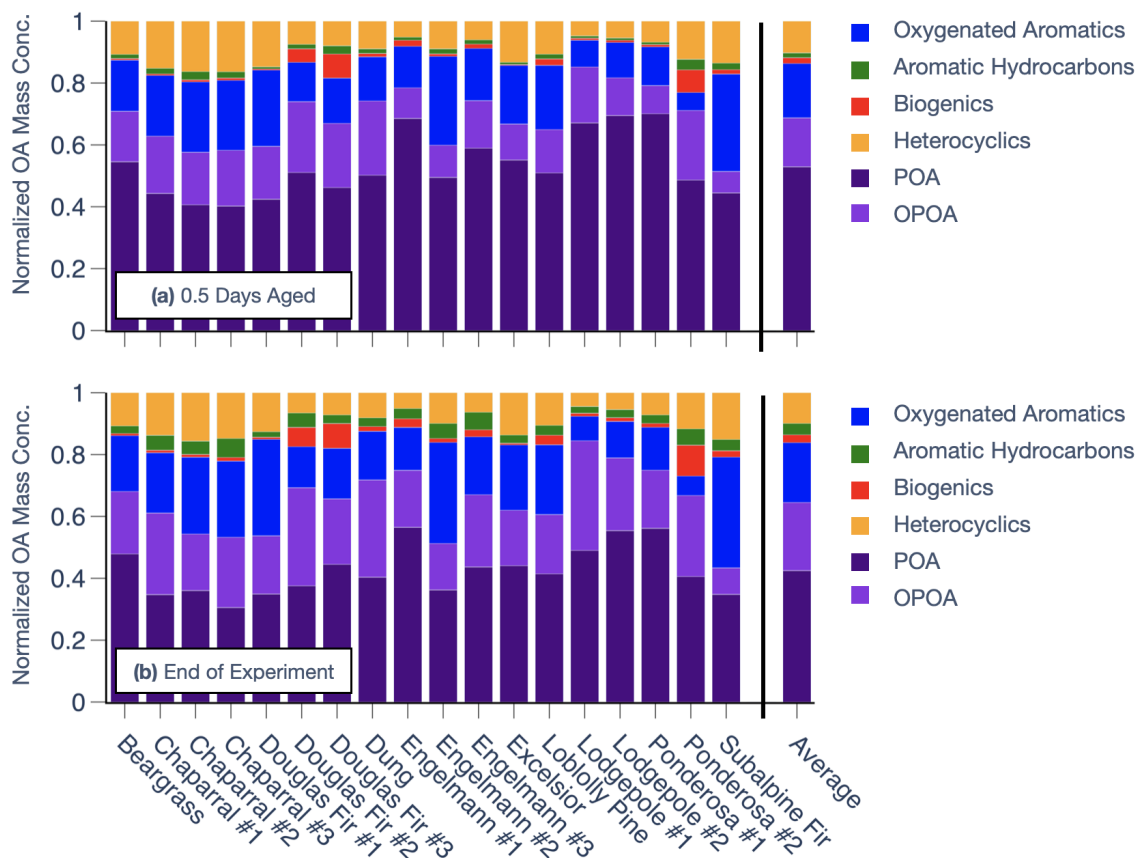


Figure 9: Model-predicted, normalized OA composition for all 18 chamber experiments as well as the arithmetic average. Composition includes POA and SOA resolved by precursor class. Results are presented at 0.5 equivalent days of photochemical aging and at the end of the experiment.

Second, VOC oxidation led to SOA formation in all 18 experiments and contributed to the increase in model predictions of OA mass concentrations and O:C. While there was some variability in SOA formation across chamber experiments, SOA contributed to 30% to 60% of the total OA at 0.5 equivalent days of photochemical aging and 44 to 70% of the total OA by the end of the chamber experiment. On average, SOA accounted for 47% and 58% of the total OA at those two time points, respectively. The end-of-experiment SOA mass yield across all 18 chamber experiments ranged from 11% to 38%. Similar to the conclusions made by Akherati and

coworkers who simulated the OA evolution in laboratory fires³⁸ and wildfire plumes,³³ the SOA formation was dominated by oxidation of SVOCs (average contribution of 37%), oxygenated aromatics (primarily, phenols and methoxyphenols; average contribution of 33%), and heterocyclics (primarily, furanic VOCs; average contribution of 17%). Biogenic VOCs also contributed to SOA formation but it was limited to a handful of chamber experiments performed on coniferous fuels; 3 out of 18 where biogenic SOA was ~8% of total SOA. Differences in the OA mass composition between 0.5 equivalent days (Figure 9a) and the end of the experiment (Figure 9b) were marginal with the exception that the SOA contribution from aromatic hydrocarbons at 0.5 equivalent days was much smaller (average contribution of 3%), relative to that at the end of the experiment (average contribution of 4.3%). Similar to the trends observed in Figure 5, SOA formation slowed after one equivalent day of photochemical aging in nearly all chamber experiments and this was linked to the near depletion of dominant SOA precursors over that timescale. Overall, that SOA could be up to half of biomass burning OA with prolonged aging aligns well with recent findings from empirical analyses of aircraft measurements,⁵ numerical modeling,^{12,72} and studies that have combined both³³ for wildfire OA.

Third, while there were a couple of exceptions (e.g., Dung, Subalpine Fir), model predictions of OA O:C from the Base simulations matched the observed increase in OA O:C over 12 to 24 equivalent hours (0.5 to 1 day) of photochemical aging but systematically underestimated the observed O:C increase with additional aging. Except for Douglas Fir #1, the model heavily underestimated the OA O:C for 17 fires by the end of the experiment. Across all 18 chamber experiments, the model-predicted increase in OA O:C was primarily linked to SOA production. This was because the fresh POA had an initial O:C of 0.35 and the SOA added from oxidation of SVOCs, oxygenated aromatics, and heterocyclics had a higher O:C (0.4-0.6, 0.8-1,

and 0.85, respectively)^{56,73}. Hence, SOA condensation onto existing POA coupled with heterogeneous oxidation of POA led to an increase in OA O:C, at least until SOA production was sustained. The model performance was unaffected by the treatment for particle wall losses.

Finally, we make two additional comments about the model-measurement comparisons for multiple experiments performed on the same fuel. The model appeared to do well on both OA mass concentrations and OA O:C for two of the three chamber experiments performed on Chaparral and two of the three chamber experiments performed on Douglas Fir. In contrast, the model systematically underestimated both the OA mass concentrations and O:C for all chamber experiments performed on Engelmann, Lodgepole Pine, and Ponderosa Pine, except for OA mass on one Ponderosa Pine chamber experiment. Regardless, there were no discernible differences in the model performance across the different fuel types (conifer, shrub, grass, and dung) although the ability to distinguish was affected by the small sample size of the dataset.

To investigate the model performance at the same photochemical age, we compared model predictions of the OA mass and O:C enhancement ratios (final to initial) against measurements at four different photochemical ages - 0.5, 1, 2, and 4 days - in Figure 10. Since there was significant variability in the maximum photochemical age achieved across the 18 chamber experiments, the model-measurement comparisons had to be performed on a sample size that decreased with photochemical age (from $N=18$ at 0.5 days to $N=13$ at 4 days). For OA mass enhancement ratios at 0.5 equivalent days of photochemical aging, the model exhibited little to no bias (Normalized Mean Bias (NMB)=9%) and a modest error (Normalized Mean Error (NME)=20%), alongside poor model skill. A small bias meant that the average and range of the OA mass enhancement ratios predicted by the model (average=1.5, range=1.1-2.0) were very similar to that for the measurements (average=1.4, range=0.9-2.5). With one exception, the

bias (i.e., NMB), error (i.e., NME), and skill in model predictions got progressively worse with photochemical aging. At 4 equivalent days of photochemical aging, the model exhibited a negative bias (NMB=-25%), a larger error (NME=40%), and little to no model skill. While most of the model predictions for the OA mass enhancement ratio were within 50% of the measurements at 0.5 and 1 equivalent days (14/18 and 14/17, respectively), only 6 of the 13 chamber experiments were within the 50% envelope at 4 equivalent days. The model performance for OA mass enhancement ratios at the shorter photochemical ages (0.5 and 1 equivalent days) was consistent with two previous modeling studies based on chamber experiments specifically performed over short photochemical ages (<12 equivalent hours).^{13,38}

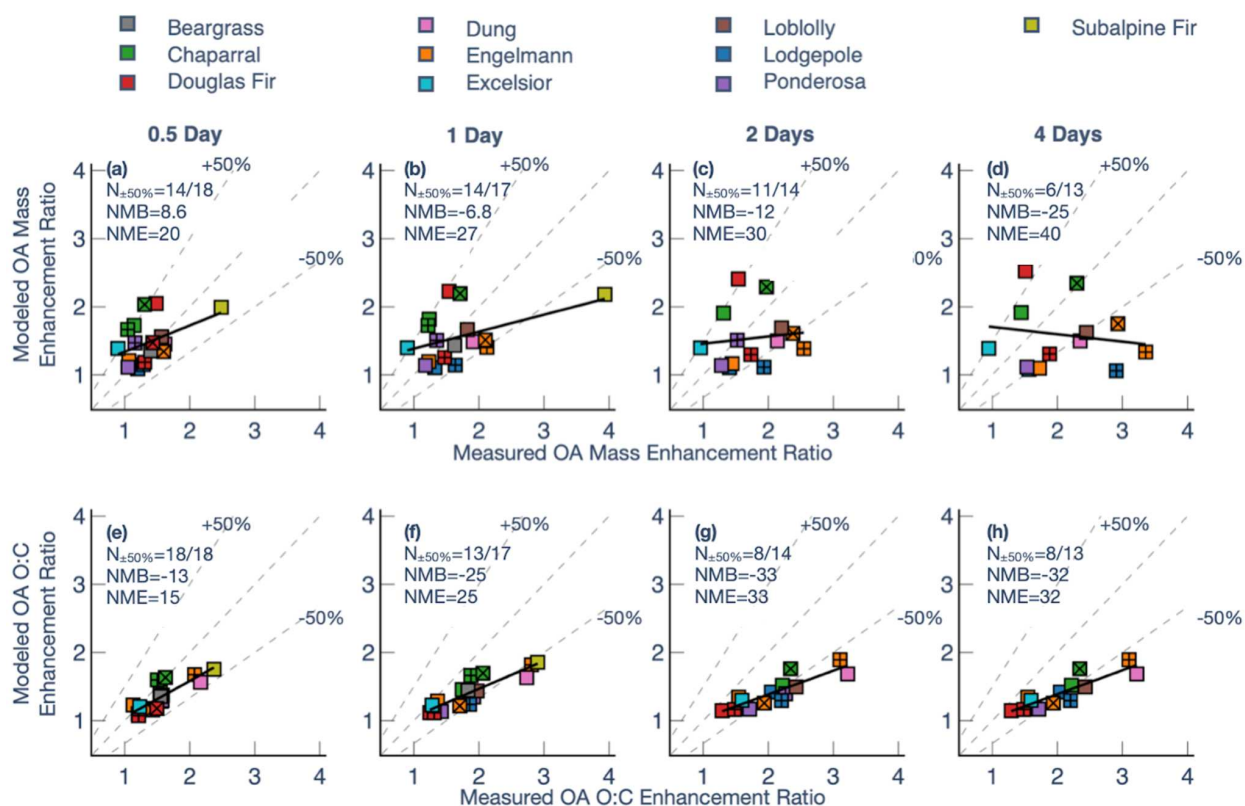


Figure 10: Model predictions of (a-d) OA mass enhancement ratio and (e-h) OA O:C enhancement ratio compared to measurements at four different photochemical ages (a,e) 0.5 days, (b,f) 1 day, (c,g) 2 days, and (d,h) 4 days. Different colors are used to denote different fuels with the patterns (plus, cross) used to separate multiple experiments performed on the same fuel.

In contrast, the model performance for OA O:C enhancement ratios was much easier to interpret. The model exhibited good skill in predicting the enhancement in OA O:C, that improved at longer photochemical ages. As shown in Figure 8, the model was able to generally reproduce the observed O:C enhancement up to one equivalent day of photochemical aging (NMB=-25%, NME=25%) but the model steadily underestimated the observed OA O:C enhancement with additional aging. By 4 equivalent days of photochemical aging, the model underestimated the OA O:C enhancement ratio by ~50% (NMB=-32%, NME=32%). All or most of the model predictions for the OA O:C enhancement ratio were within 50% of the measurements at 0.5 and 1 equivalent days (18/18 and 13/17, respectively) while only 8 of the 13 chamber experiments were within the 50% envelope at 4 equivalent days. Tentatively, the comparisons in Figure 10 suggest that the model is missing precursors, processes, or both that may be relevant for OA mass and O:C enhancement linked to POA processing and SOA production at longer photochemical ages (>1 days).

We probed the model's underestimation and poor skill by performing a variance analysis on the OA mass concentrations at 4 equivalent days of photochemical aging. By fixing the photochemical age to 4 equivalent days, we were analyzing the model performance in a region where it performed poorly, noting that our analysis was limited to a subset of experiments ($N=13$). Using values from the end of the experiment would have increased the sample size to 18 but would have made it difficult to account for differences in photochemical age. Results from the variance analysis, which included variables present within the model (initial POA, SOA precursors, and OA O:C) and those not considered in the model (modified combustion efficiency, fuel moisture content, fuel type), are shown in Figure 11. The model error in OA mass, expressed as a ratio of modeled to measured OA, showed a weak positive correlation with initial

concentrations of SOA precursors ($R^2=0.25$) and POA ($R^2=0.13$) (Figure 11b). Specifically, the model underestimated the OA mass when the SOA precursor and POA concentrations were lower suggesting that a different set of SOA precursors than those measured by the PTR-ToF-MS might be responsible for SOA formation in these experiments. Defining the model error as [modeled OA - measured OA] or a ratio of the modeled Δ OA to measured Δ OA produced a variance analysis that was identical to that shown in Figure 11 (not shown). The model error exhibited a poor relationship, or the absence of one, with the remaining variables: modified combustion efficiency ($R^2=0.03$), fuel moisture content ($R^2=0.07$), and fuel type. We admit that we do not know how to interpret the weak positive correlation of the model error in OA mass with the initial O:C.

3.3 Model Sensitivities

We studied sensitivity in model predictions to individual processes and results from this analysis for all 18 chamber experiments are shown in Figure S10. Here, we compared model predictions of OA mass concentration and O:C from the sensitivity simulations to those from the Base simulations. The presentation of the sensitivity analysis ($N=13$) was done at four equivalent days of photochemical aging as one of the reasons for performing the sensitivity analysis was to study the reasons for the model's poor performance at longer photochemical ages. Analogous to the findings in Figure 5, turning particle and vapor wall losses off resulted in the largest change in OA mass concentrations (median increase of 60% and 45%, respectively), relative to the Base results. In contrast, turning dilution, heterogeneous oxidation, and oligomerization off resulted in much smaller changes in the OA mass concentrations (median change of 7%, 15%, and -10%, respectively). Treating POA as non-volatile and non-reactive had the least effect on OA mass concentrations (median increase of 5%). Except for dilution, the model response (i.e., sensitivity)

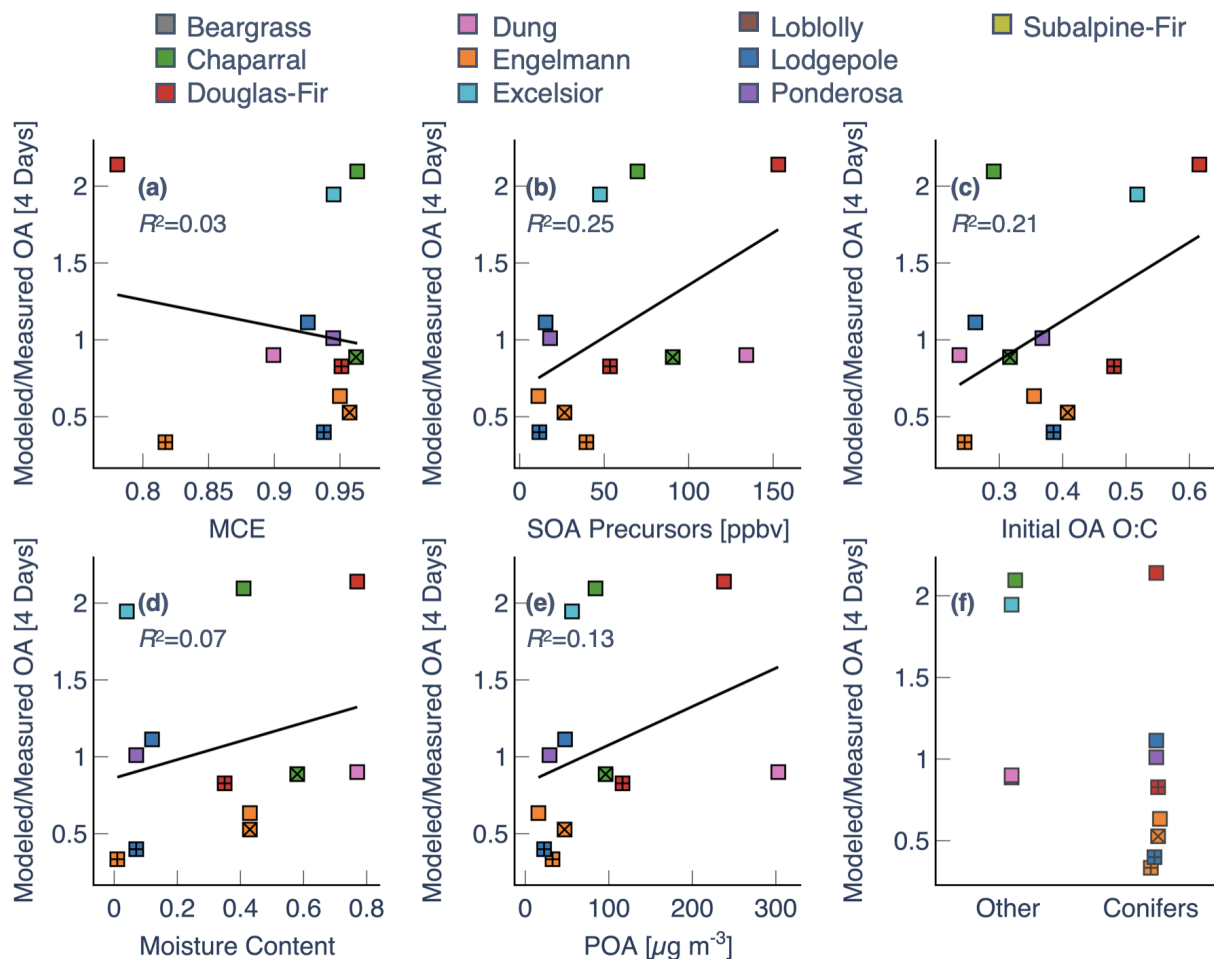


Figure 11: Model variance in OA mass expressed as a ratio of the modeled to measured OA compared against (a) MCE, (b) initial SOA precursors, (c) initial OA O:C, (d) fuel moisture content, (e) initial POA, and (f) fuel type (conifers versus others). Variance analysis is performed at a photochemical age of 4 equivalent days.

the findings in Figure 5, turning particle and vapor wall losses off resulted in the largest change in OA mass concentrations (median increase of 60% and 45%, respectively), relative to the Base results. In contrast, turning dilution, heterogeneous oxidation, and oligomerization off resulted in much smaller changes in the OA mass concentrations (median change of 7%, 15%, and -10%, respectively). Treating POA as non-volatile and non-reactive had the least effect on OA mass concentrations (median increase of 5%). Except for dilution, the model response (i.e., sensitivity) to a particular process varied modestly across the 18 chamber experiments, despite comparisons

in the model output at the same photochemical age. Given that particle and vapor wall losses influence model predictions significantly, one potential reason for the poor model performance at longer photochemical ages might be the use of a single, time-independent value to determine those wall loss rates. Interestingly, model predictions of OA O:C were only mildly sensitive to turning dilution and vapor wall losses off (median increase of 12% and 8%, respectively) and nearly insensitive to all other processes. Therefore, an experiment-specific particle or vapor wall loss rate is unlikely to influence the model performance for OA O:C.

Results from simulations performed with model adjustments for the Ponderosa Pine chamber experiment are shown in Figure 12. Similar to the motivation for performing the sensitivity analysis described earlier, these simulations were used to study reasons for the model's poor performance at longer photochemical ages. The heterogeneous oxidation schemes that rapidly produced lower-volatility and more oxygenated products increased model predictions of OA mass concentrations and O:C modestly (up to a 18% increase in OA mass and 15% increase in OA O:C by the end of the experiment), relative to the Base results. Despite this increase, model predictions of OA O:C were still significantly underestimated at higher photochemical ages. As expected, the smaller but slower-reacting VOCs, which were nearly similar in magnitude to the initial SOA precursors, did not affect SOA production significantly to alter the OA evolution. The use of an average SOA precursor profile boosted OA mass concentrations and O:C much more so than the modified heterogeneous oxidation schemes. This was because the average SOA precursor profile, based on measurements in the stack,⁵¹ resulted in higher initial precursor concentrations compared to the direct chamber measurements described in Coggon et al.⁵³ and Lim et al.³⁹ We did not find this to be surprising. Akherati et al.³⁸ had shown that there were meaningful losses of SOA precursors in the duct used to port smoke

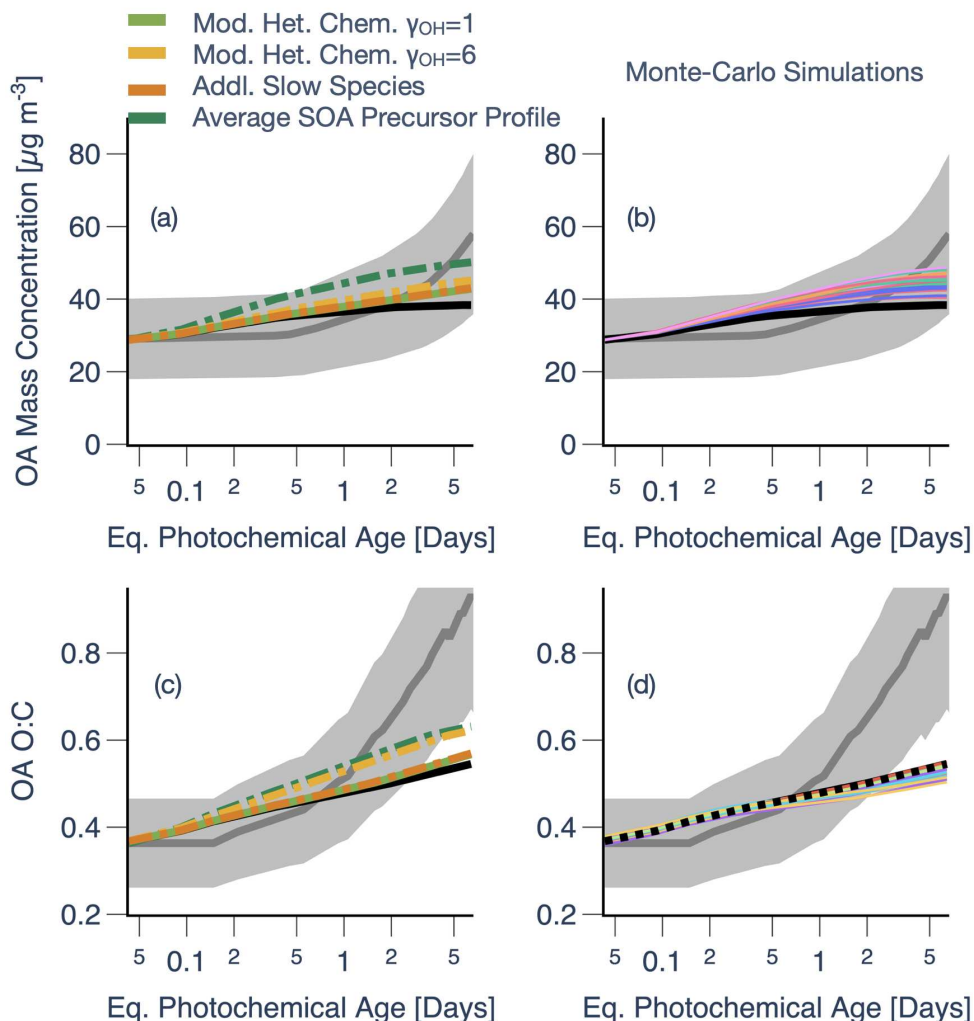


Figure 12: Model predictions of (a,b) OA mass concentrations and (c,d) OA O:C compared against measurements. Predictions are from simulations performed with a modified treatment for heterogeneous oxidation, SOA formation from smaller and slower-reacting VOCs, and Monte-Carlo simulations.

from the stack to their larger chamber. These losses were found to be a function of c^* with higher losses observed for lower c^* species and vice versa (c.f. Figure S6 in Akherati et al.)³⁸; Lim et al.³⁹ had used a similar duct setup to port smoke emissions into their smaller chamber. As to why the initial SOA precursor concentrations would be larger than those directly measured in the chamber and used in the Base simulations is unclear to us. Randomly varying the distribution of POA+SVOC mass in the SOM grid seemed to produce some variability in model predictions of

OA mass concentrations ($\pm 27\%$) and O:C ($\pm 8\%$) but these variations were not significant enough to explain the underestimation in at longer photochemical ages.

Overall, of the model adjustments undertaken here, the use of an alternative heterogeneous oxidation scheme and an average SOA precursor profile helped marginally improve the model performance at longer photochemical ages without significantly affecting the performance at shorter photochemical ages (Figure 13). Broadly, the sensitivity simulations and model adjustments discussed in this section strengthen the argument that the model is missing precursors, pathways, or both that can help explain the strong increase in OA mass concentrations and O:C at longer photochemical ages.

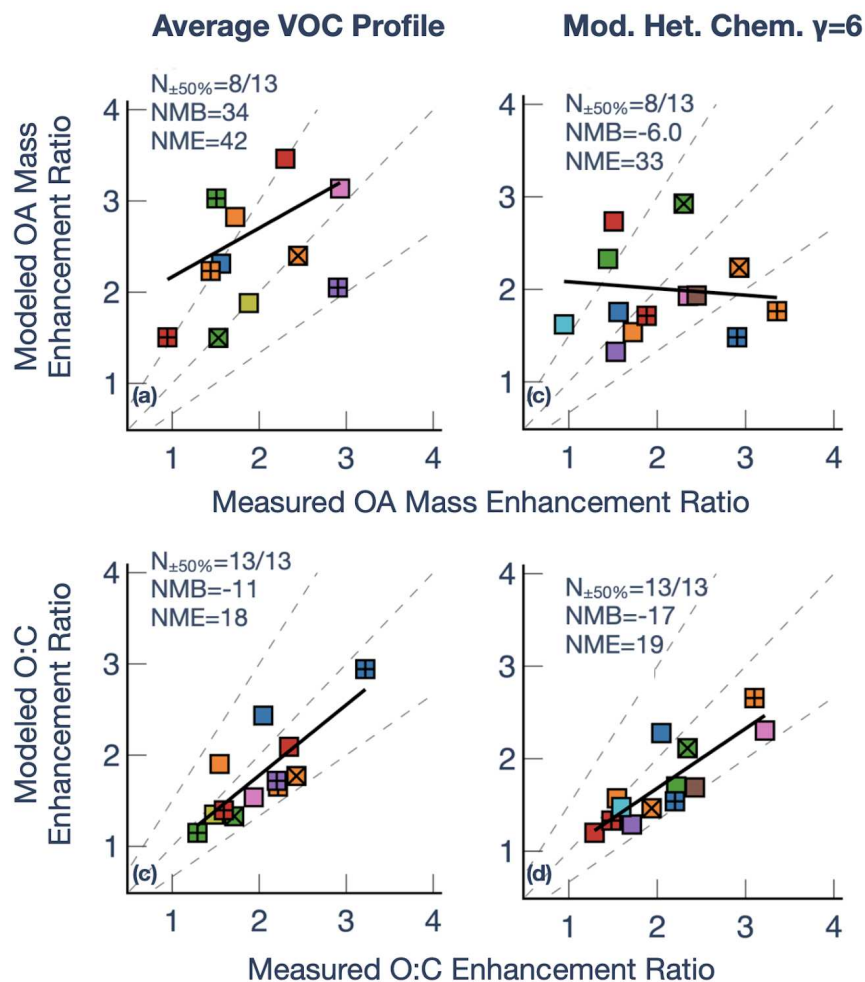


Figure 13: Model predictions of (a,b) OA mass enhancement ratio and (c,d) OA O:C enhancement ratio compared to measurements at 4 photochemical days for two model adjustments, an Average VOC profile based on initial acetonitrile (a,c), and an alternative heterogeneous oxidation scheme (b,d).

CHAPTER 4 - SUMMARY, DISCUSSION, AND FUTURE WORK

In this work, we simulated the photochemical evolution of biomass burning OA in 18 separate chamber experiments performed in a small environmental chamber. The simulations were performed with a process-level kinetic model (i.e., SOM-TOMAS) that simulated dilution, multigenerational gas-phase chemistry, phase-state-influenced gas/particle partitioning, heterogeneous oxidation, oligomerization reactions, and chamber artifacts (i.e., particle and vapor wall losses). We found that the model was able to generally reproduce the OA mass and O:C evolution at short photochemical ages (0.5-1 equivalent days), consistent with earlier work, but the model performed less optimally at longer photochemical ages (>1 equivalent day). For instance, at four equivalent days of photochemical aging, the model underestimated both the enhancement in OA mass and O:C but showed good skill in predicting the increase in OA O:C. Neither the variance analyses nor the sensitivity simulations were able to provide conclusive evidence for why the model performance deteriorated with photochemical age. We tentatively argue that the model performance would have been better if we had access to experiment-specific and time-dependent particle and wall loss rates although neither of these would have helped with the model's ability to accurately predict the increase in OA O:C. Simulations performed with adjustments made to the heterogeneous oxidation scheme and higher inputs for initial SOA precursor concentrations offered modest improvements in model performance at longer photochemical ages.

The SOM-TOMAS model can be used to determine aerosol mass yields for SOA precursors that would be relevant for photochemical evolution over multiple days. The dilution- and particle-wall-loss-corrected SOA mass yields from the end of the experiment varied between 11% and 38% over the 18 chamber experiments. If these were further corrected for vapor wall

losses, the SOA mass yields increased to between 22% and 40%. In these chamber experiments where the SOA precursors were $2.4\times$ the initial POA emissions (Figure S3), these yields were found to enhance the OA mass burden even when some of the POA was lost to dilution-driven evaporation. However, Akherati et al.³³ discovered that SOA precursor emissions were on the same order as POA emissions in real wildfire plumes sampled using a research aircraft in the western US. Hence, these SOA mass yields are likely to boost OA mass burdens by at least $\sim 30\%$ over regional scales even if the emitted POA is not subject to evaporation. Furthermore, this SOA is bound to alter the chemical, microphysical, and optical properties of biomass burning aerosol with photochemical age. Biomass burning is an important source of SOA precursor emissions, just like it is for POA emissions, and these precursors have significantly large yields that they need to be considered in air quality climate models if we are to simulate SOA production and the physicochemical evolution of biomass burning OA.

The SOM-TOMAS model currently does not account for aqueous processing or photolysis of organic compounds in the particle phase. Both of these processes have been shown to alter SOA production and loss rates in model systems.^{74,75} We do not anticipate the lack of aqueous chemistry to be a severe limitation since the Lim et al.³⁹ chamber experiments were performed under low relative humidity conditions (25-40%). However, we cannot fully discount the effects from water taken up by a rapidly evolving OA. Coggon et al.⁵³ argued that except for a few photolabile species (e.g., furfural), the 254 nm UV-C light used by Lim et al. (2019) had a negligible impact on the photooxidation of biomass burning VOCs. Yet, the impact from absorption of UV-C light by OA remains uncertain. Aqueous processing and photolysis will need to be explicitly modeled.

Our work was motivated to better understand the chemistry and microphysics of biomass burning OA at long photochemical ages, which could shed light on its evolution in the real atmosphere at regional and global scales. Results from this work provided key insights on the transformation of OA mass and composition with aging while indicating that we may be missing key precursors, processes, or both that become more important at longer photochemical ages. We recommend future work should continue to combine kinetic modeling with laboratory and field datasets to improve our understanding of biomass burning aerosol. Such modeling will be important in developing mechanisms and parameterizations to represent biomass burning aerosol in three-dimensional models, a prerequisite to studying the impact of biomass burning on climate, air quality, and human health.

REFERENCES

- 1 J. S. Reid, R. Koppmann, T. F. Eck and D. P. Eleuterio, *Atmospheric Chemistry and Physics*, 2005, **5**, 799–825.
- 2 J.-F. Lamarque, T. C. Bond, V. Eyring, C. Granier, A. Heil, Z. Klimont, D. Lee, C. Liousse, A. Mieville, B. Owen and Others, *Atmos. Chem. Phys.*, 2010, **10**, 7017–7039.
- 3 C. Granier, B. Bessagnet, T. Bond, A. D’Angiola, H. Denier van der Gon, G. J. Frost, A. Heil, J. W. Kaiser, S. Kinne, Z. Klimont, S. Kloster, J.-F. Lamarque, C. Liousse, T. Masui, F. Meleux, A. Mieville, T. Ohara, J.-C. Raut, K. Riahi, M. G. Schultz, S. J. Smith, A. Thompson, J. van Aardenne, G. R. van der Werf and D. P. van Vuuren, *Clim. Change*, 2011, **109**, 163–190.
- 4 M. O. Andreae, *Atmos. Chem. Phys.*, 2019, **19**, 8523–8546.
- 5 B. B. Palm, Q. Peng, C. D. Fredrickson, B. H. Lee, L. A. Garofalo, M. A. Pothier, S. M. Kreidenweis, D. K. Farmer, R. P. Pokhrel, Y. Shen, S. M. Murphy, W. Permar, L. Hu, T. L. Campos, S. R. Hall, K. Ullmann, X. Zhang, F. Flocke, E. V. Fischer and J. A. Thornton, *Proc. Natl. Acad. Sci. U. S. A.*, 2020, **117**, 29469–29477.
- 6 W. Permar, Q. Wang, V. Selimovic, C. Wielgasz, R. J. Yokelson, R. S. Hornbrook, A. J. Hills, E. C. Apel, I.-T. Ku, Y. Zhou, B. C. Sive, A. P. Sullivan, J. L. Collett Jr, T. L. Campos, B. B. Palm, Q. Peng, J. A. Thornton, L. A. Garofalo, D. K. Farmer, S. M. Kreidenweis, E. J. T. Levin, P. J. DeMott, F. Flocke, E. V. Fischer and L. Hu, *J. Geophys. Res.*, , DOI:10.1029/2020jd033838.
- 7 M. Shrivastava, C. D. Cappa, J. Fan, A. H. Goldstein, A. B. Guenther, J. L. Jimenez, C. Kuang, A. Laskin, S. T. Martin, N. L. Ng, T. Petaja, J. R. Pierce, P. J. Rasch, P. Roldin, J. H. Seinfeld, J. Shilling, J. N. Smith, J. A. Thornton, R. Volkamer, J. Wang, D. R. Worsnop, R. A. Zaveri, A. Zelenyuk and Q. Zhang, *Rev. Geophys.*, 2017, **55**, 509–559.
- 8 Y. Jiang, Z. Lu, X. Liu, Y. Qian, K. Zhang, Y. Wang and X.-Q. Yang, *Atmos. Chem. Phys.*, 2016, **16**, 14805–14824.
- 9 N. Bellouin, J. Quaas, E. Gryspeerdt, S. Kinne, P. Stier, D. Watson-Parris, O. Boucher, K. S. Carslaw, M. Christensen, A.-L. Daniau, J.-L. Dufresne, G. Feingold, S. Fiedler, P. Forster, A. Gettelman, J. M. Haywood, U. Lohmann, F. Malavelle, T. Mauritsen, D. T. McCoy, G. Myhre, J. Mülmenstädt, D. Neubauer, A. Possner, M. Rugenstein, Y. Sato, M. Schulz, S. E. Schwartz, O. Sourdeval, T. Storelvmo, V. Toll, D. Winker and B. Stevens, *Rev. Geophys.*, 2020, **58**, e2019RG000660.
- 10 C. D. McClure and D. A. Jaffe, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 7901–7906.
- 11 B. Ford, M. Val Martin, S. E. Zelasky, E. V. Fischer, S. C. Anenberg, C. L. Heald and J. R. Pierce, *Geohealth*, 2018, **2**, 229–247.
- 12 A. L. Hodshire, A. Akherati, M. J. Alvarado, B. Brown-Steiner, S. H. Jathar, J. L. Jimenez, S. M. Kreidenweis, C. R. Lonsdale, T. B. Onasch, A. M. Ortega and J. R. Pierce, *Environ. Sci. Technol.*, 2019, **53**, 10007–10022.
- 13 A. T. Ahern, E. S. Robinson, D. S. Tkacik, R. Saleh, L. E. Hatch, K. C. Barsanti, C. E. Stockwell, R. J. Yokelson, A. A. Presto, A. L. Robinson, R. C. Sullivan and N. M. Donahue, *J. Geophys. Res.*, 2019, **124**, 3583–3606.
- 14 D. S. Tkacik, E. S. Robinson, A. Ahern, R. Saleh, C. Stockwell, P. Veres, I. J. Simpson, S. Meinardi, D. R. Blake, R. J. Yokelson, A. A. Presto, R. C. Sullivan, N. M. Donahue and A. L. Robinson, *J. Geophys. Res.*, 2017, **122**, 6043–6058.
- 15 C. J. Hennigan, M. A. Miracolo, G. J. Engelhart, A. A. May, A. A. Presto, T. Lee, A. P. Sullivan, G. R. McMeeking, H. Coe, C. E. Wold and Others, *Atmos. Chem. Phys.*, 2011, **11**,

- 7669–7686.
- 16 P. V. Hobbs, P. Sinha, R. J. Yokelson, T. J. Christian, D. R. Blake, S. Gao, T. W. Kirchstetter, T. Novakov and P. Pilewskie, *J. Geophys. Res.*, DOI:10.1029/2002jd002352.
 - 17 X. Liu, Y. Zhang, L. G. Huey, R. J. Yokelson, Y. Wang, J. L. Jimenez, P. Campuzano-Jost, A. J. Beyersdorf, D. R. Blake, Y. Choi, J. M. St. Clair, J. D. Crounse, D. A. Day, G. S. Diskin, A. Fried, S. R. Hall, T. F. Hanisco, L. E. King, S. Meinardi, T. Mikoviny, B. B. Palm, J. Peischl, A. E. Perring, I. B. Pollack, T. B. Ryerson, G. Sachse, J. P. Schwarz, I. J. Simpson, D. J. Tanner, K. L. Thornhill, K. Ullmann, R. J. Weber, P. O. Wennberg, A. Wisthaler, G. M. Wolfe and L. D. Ziemba, *J. Geophys. Res.*, 2016, **121**, 7383–7414.
 - 18 P. F. DeCarlo, E. J. Dunlea, J. R. Kimmel, A. C. Aiken, D. Sueper, J. Crounse, P. O. Wennberg, L. Emmons, Y. Shinozuka, A. Clarke and Others, *Atmos. Chem. Phys.*, 2008, **8**, 4027–4048.
 - 19 V. Vakkari, V.-M. Kerminen, J. P. Beukes, P. Tiitta, P. G. Zyl, M. Josipovic, A. D. Venter, K. Jaars, D. R. Worsnop, M. Kulmala and L. Laakso, *Geophys. Res. Lett.*, 2014, **41**, 2644–2651.
 - 20 A. A. May, T. Lee, G. R. McMeeking, S. Akagi, A. P. Sullivan, S. Urbanski, R. J. Yokelson and S. M. Kreidenweis, *Atmos. Chem. Phys.*, 2015, **15**, 6323–6335.
 - 21 S. K. Akagi, J. S. Craven, J. W. Taylor, G. R. McMeeking, R. J. Yokelson, I. R. Burling, S. P. Urbanski, C. E. Wold, J. H. Seinfeld, H. Coe and Others, *Atmos. Chem. Phys.*, 2012, **12**, 1397–1421.
 - 22 M. J. Cubison, A. M. Ortega, P. L. Hayes, D. K. Farmer, D. Day, M. J. Lechner, W. H. Brune, E. Apel, G. S. Diskin, J. A. Fisher and Others, *Atmos. Chem. Phys.*, 2011, **11**, 12049–12064.
 - 23 J. Brito, L. V. Rizzo, W. T. Morgan, H. Coe, B. Johnson, J. Haywood, K. Longo, S. Freitas, M. O. Andreae and P. Artaxo, *Atmos. Chem. Phys.*, 2014, **14**, 12069–12083.
 - 24 H. Forrister, J. Liu, E. Scheuer and J. Dibb, *Geophysical*, DOI:10.1002/2015GL063897.
 - 25 S. Collier, S. Zhou, T. B. Onasch, D. A. Jaffe, L. Kleinman, A. J. Sedlacek 3rd, N. L. Briggs, J. Hee, E. Fortner, J. E. Shilling, D. Worsnop, R. J. Yokelson, C. Parworth, X. Ge, J. Xu, Z. Butterfield, D. Chand, M. K. Dubey, M. S. Pekour, S. Springston and Q. Zhang, *Environ. Sci. Technol.*, 2016, **50**, 8613–8622.
 - 26 G. Capes, B. Johnson and G. McFiggans, *Journal of*, DOI:10.1029/2008JD009845.
 - 27 M. D. Jolleys, H. Coe, G. McFiggans, J. W. Taylor, S. J. O’shea, M. Le Breton, S.-B. Bauguutte, S. Moller, P. Di Carlo, E. Aruffo and Others, *Atmos. Chem. Phys.*, 2015, **15**, 3077–3095.
 - 28 M. D. Jolleys, H. Coe, G. McFiggans, G. Capes, J. D. Allan, J. Crosier, P. I. Williams, G. Allen, K. N. Bower, J. L. Jimenez, L. M. Russell, M. Grutter and D. Baumgardner, *Environ. Sci. Technol.*, 2012, **46**, 13093–13102.
 - 29 A. M. Ortega, D. A. Day, M. J. Cubison, W. H. Brune, D. Bon, J. A. De Gouw and J. L. Jimenez, *Atmos. Chem. Phys.*, 2013, **13**, 11551–11571.
 - 30 L. A. Garofalo, M. A. Pothier, E. J. T. Levin, T. Campos, S. M. Kreidenweis and D. K. Farmer, *ACS Earth Space Chem.*, 2019, **3**, 1237–1247.
 - 31 Y. Liang, C. N. Jen, R. J. Weber, P. K. Misztal and A. H. Goldstein, *Atmos. Chem. Phys.*, 2021, **21**, 5719–5737.
 - 32 L. A. Garofalo, Y. He, S. H. Jathar, J. R. Pierce, C. D. Fredrickson, B. B. Palm, J. A. Thornton, F. Mahrt, G. V. Crescenzo, A. K. Bertram, D. C. Draper, J. L. Fry, J. Orlando, X. Zhang and D. K. Farmer, *Environ. Sci. Technol.*, 2021, **55**, 15637–15645.

- 33 A. Akherati, Y. He, L. A. Garofalo, A. L. Hodshire, D. K. Farmer, S. M. Kreidenweis, W. Permar, L. Hu, E. V. Fischer, C. N. Jen, A. H. Goldstein, E. J. T. Levin, P. J. DeMott, T. L. Campos, F. Flocke, J. M. Reeves, D. W. Toohey, J. R. Pierce and S. H. Jathar, *Environmental Science: Atmospheres*, 2022, **2**, 1000–1022.
- 34 A. P. Grieshop, N. M. Donahue and A. L. Robinson, *Atmos. Chem. Phys.*, 2009, **9**, 2227–2240.
- 35 A. P. Grieshop, J. M. Logue, N. M. Donahue and A. L. Robinson, *Atmos. Chem. Phys.*, 2009, **9**, 1263–1277.
- 36 M. F. Heringa, P. F. DeCarlo, R. Chirico, T. Tritscher, J. Dommen, E. Weingartner, R. Richter, G. Wehrle, A. S. H. Prévôt and U. Baltensperger, *Atmos. Chem. Phys.*, 2011, **11**, 5945–5957.
- 37 E. A. Bruns, I. El Haddad, J. G. Slowik, D. Kilic, F. Klein, U. Baltensperger and A. S. H. Prévôt, *Sci. Rep.*, 2016, **6**, 27881.
- 38 A. Akherati, Y. He, M. M. Coggon, A. R. Koss, A. L. Hodshire, K. Sekimoto, C. Warneke, J. de Gouw, L. Yee, J. H. Seinfeld, T. B. Onasch, S. C. Herndon, W. B. Knighton, C. D. Cappa, M. J. Kleeman, C. Y. Lim, J. H. Kroll, J. R. Pierce and S. H. Jathar, *Environ. Sci. Technol.*, 2020, **54**, 8568–8579.
- 39 C. Y. Lim, D. H. Hagan, M. M. Coggon, A. R. Koss, K. Sekimoto, J. de Gouw, C. Warneke, C. D. Cappa and J. H. Kroll, *Atmos. Chem. Phys.*, 2019, **19**, 12797–12809.
- 40 A. T. Lambe, A. T. Ahern, L. R. Williams, J. G. Slowik, J. P. S. Wong, J. P. D. Abbatt, W. H. Brune, N. L. Ng, J. P. Wright, D. R. Croasdale and Others, *Atmospheric Measurement Techniques*, 2011, **4**, 445–461.
- 41 J. E. Krechmer, D. Pagonis, P. J. Ziemann and J. L. Jimenez, *Environ. Sci. Technol.*, 2016, **50**, 5757–5765.
- 42 Y. Huang, R. Zhao, S. M. Charan, C. M. Kenseth, X. Zhang and J. H. Seinfeld, *Environ. Sci. Technol.*, 2018, **52**, 2134–2142.
- 43 B. B. Palm, S. S. de Sá, D. A. Day, P. Campuzano-Jost, W. Hu, R. Seco, S. J. Sjostedt, J.-H. Park, A. B. Guenther, S. Kim and Others, *Atmos. Chem. Phys.*, 2018, **18**, 467–493.
- 44 S. Eluri, C. D. Cappa, B. Friedman, D. K. Farmer and S. H. Jathar, *Atmos. Chem. Phys.*, 2018, **18**, 13813–13838.
- 45 J. D. Smith, J. H. Kroll, C. D. Cappa, D. L. Che, C. L. Liu, M. Ahmed, S. R. Leone, D. R. Worsnop and K. R. Wilson, *Atmos. Chem. Phys.*, 2009, **9**, 3209–3222.
- 46 J. H. Kroll, J. D. Smith, D. L. Che, S. H. Kessler, D. R. Worsnop and K. R. Wilson, *Phys. Chem. Chem. Phys.*, 2009, **11**, 8005–8014.
- 47 Y. He, A. T. Lambe, J. H. Seinfeld, C. D. Cappa, J. R. Pierce and S. H. Jathar, *Environ. Sci. Technol.*, 2022, **56**, 6262–6273.
- 48 C. McClure, N. R. Pavlovic, S. G. Brown, F. Lurmann, Y. Kimura, E. McDonald-Buller and C. Wiedinmyer, 2019, vol. 2019, p. A23L–2960.
- 49 C. D. Cappa, C. Y. Lim, D. H. Hagan, M. Coggon, A. Koss, K. Sekimoto, J. de Gouw, T. B. Onasch, C. Warneke and J. H. Kroll, *Atmos. Chem. Phys.*, 2020, **20**, 8511–8532.
- 50 V. Selimovic, R. J. Yokelson, C. Warneke, J. M. Roberts, J. De Gouw, J. Reardon and D. W. T. Griffith, *Atmos. Chem. Phys.*, 2018, **18**, 2929–2948.
- 51 A. R. Koss, K. Sekimoto, J. B. Gilman, V. Selimovic, M. M. Coggon, K. J. Zarzana, B. Yuan, B. M. Lerner, S. S. Brown, J. L. Jimenez and Others, *Atmos. Chem. Phys.*, 2018, **18**, 3299–3319.
- 52 K. Sekimoto, A. R. Koss, J. B. Gilman, V. Selimovic, M. M. Coggon, K. J. Zarzana, B.

- Yuan, B. M. Lerner, S. S. Brown, C. Warneke and Others, *Atmos. Chem. Phys.*, 2018, **18**, 9263–9281.
- 53 M. M. Coggon, C. Y. Lim, A. R. Koss, K. Sekimoto, B. Yuan, J. B. Gilman, D. H. Hagan, V. Selimovic, K. J. Zarzana, S. S. Brown and Others, *Atmos. Chem. Phys.*, 2019, **19**, 14875–14899.
- 54 C. D. Cappa and K. R. Wilson, *Atmos. Chem. Phys.*, 2012, **12**, 9505–9528.
- 55 P. J. Adams and J. H. Seinfeld, *J. Geophys. Res. D: Atmos.*, 2002, **107**, AAC 4–1–AAC 4–23.
- 56 Y. He, B. King, M. Pothier, L. Lewane, A. Akherati, J. Mattila, D. K. Farmer, R. L. McCormick, M. Thornton, J. R. Pierce, J. Volckens and S. H. Jathar, *Environ. Sci. Process. Impacts*, 2020, **22**, 1461–1474.
- 57 Y. He, A. Akherati, T. Nah, N. L. Ng, L. A. Garofalo, D. K. Farmer, M. Shiraiwa, R. A. Zaveri, C. D. Cappa, J. R. Pierce and S. H. Jathar, *Environ. Sci. Technol.*, 2021, **55**, 1466–1476.
- 58 O'Donnell, Samuel, Ali Akherati, Yicong He, Anna L. Hodshire, John E. Shilling, Chongai Kuang, Jerome D. Fast, Fan Mei, Siegfried Schobesberger, Joel A. Thornton, James N. Smith, Shantanu H. Jathar, and Jeffrey R. Pierce, *J. Geophys. Res.*
- 59 R. A. Zaveri, R. C. Easter, J. E. Shilling and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2014, **14**, 5153–5181.
- 60 F. Bianchi, T. Kurtén, M. Riva, C. Mohr, M. P. Rissanen, P. Roldin, T. Berndt, J. D. Crounse, P. O. Wennberg, T. F. Mentel, J. Wildt, H. Junninen, T. Jokinen, M. Kulmala, D. R. Worsnop, J. A. Thornton, N. Donahue, H. G. Kjaergaard and M. Ehn, *Chem. Rev.*, 2019, **119**, 3472–3509.
- 61 E. R. Trump and N. M. Donahue, *Atmos. Chem. Phys.*, 2014, **14**, 3691–3701.
- 62 A. Matsunaga and P. J. Ziemann ‡, *Aerosol Sci. Technol.*, 2010, **44**, 881–892.
- 63 J. A. Huffman, K. S. Docherty, A. C. Aiken, M. J. Cubison, I. M. Ulbrich, P. F. DeCarlo, D. Sueper, J. T. Jayne, D. R. Worsnop, P. J. Ziemann and J. L. Jimenez, *Atmos. Chem. Phys.*, 2009, **9**, 7161–7182.
- 64 L. E. Hatch, A. Rivas-Ubach, C. N. Jen, M. Lipton, A. H. Goldstein and K. C. Barsanti, *Atmos. Chem. Phys.*, 2018, **18**, 17801–17817.
- 65 A. A. May, E. J. T. Levin, C. J. Hennigan, I. Riipinen, T. Lee, J. L. Collett Jr, J. L. Jimenez, S. M. Kreidenweis and A. L. Robinson, *J. Geophys. Res.*, 2013, **118**, 11,327–11,338.
- 66 P. Barmet, J. Dommen, P. F. DeCarlo, T. Tritscher, A. P. Praplan, S. M. Platt, A. S. H. Prévôt, N. M. Donahue and U. Baltensperger, *Atmos. Meas. Tech.*, 2012, **5**, 647–656.
- 67 A. P. Grieshop and N. M. Donahue, *Geophys. Res. Lett.*, , DOI:10.1029/2007GL029987.
- 68 Q. Bian, A. A. May, S. M. Kreidenweis and J. R. Pierce, *Atmos. Chem. Phys.*, 2015, **15**, 11027–11045.
- 69 W. H. Brune, *Environ. Sci. Technol.*, 2019, **53**, 3645–3652.
- 70 A. Bertrand, G. Stefenelli, S. M. Pieber, E. A. Bruns, B. Temime-Roussel, J. G. Slowik, H. Wortham, A. S. H. Prévôt, I. El Haddad and N. Marchand, *Atmos. Chem. Phys.*, 2018, **18**, 10915–10930.
- 71 T. Nah, R. C. McVay, X. Zhang, C. M. Boyd, J. H. Seinfeld and N. L. Ng, *Atmos. Chem. Phys.*, 2016, **16**, 9361–9379.
- 72 Q. Bian, S. H. Jathar, J. K. Kodros, K. C. Barsanti, L. E. Hatch, A. A. May, S. M. Kreidenweis and J. R. Pierce, *Atmos. Chem. Phys.*, 2017, **17**, 5459–5475.
- 73 P. S. Chhabra, N. L. Ng, M. R. Canagaratna, A. L. Corrigan, L. M. Russell, D. R. Worsnop,

- R. C. Flagan and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2011, **11**, 8827–8845.
- 74 M. A. Zawadowicz, B. H. Lee, M. Shrivastava, A. Zelenyuk, R. A. Zaveri, C. Flynn, J. A. Thornton and J. E. Shilling, *Environ. Sci. Technol.*, 2020, **54**, 3861–3870.
- 75 L. Yu, J. Smith, A. Laskin, C. Anastasio, J. Laskin and Q. Zhang, *Atmos. Chem. Phys.*, 2014, **14**, 13801–13816.
- 76 C. L. Loza, J. S. Craven, L. D. Yee, M. M. Coggon, R. H. Schwantes, M. Shiraiwa, X. Zhang, K. A. Schilling, N. L. Ng, M. R. Canagaratna and Others, *Atmos. Chem. Phys.*, 2014, **14**, 1423–1439.
- 77 N. L. Ng, J. H. Kroll, A. W. H. Chan, P. S. Chhabra, R. C. Flagan and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2007, **7**, 3909–3922.
- 78 X. Zhang, C. D. Cappa, S. H. Jathar, R. C. McVay, J. J. Ensberg, M. J. Kleeman and J. H. Seinfeld, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 5802–5807.
- 79 L. D. Yee, K. E. Kautzman, C. L. Loza, K. A. Schilling, M. M. Coggon, P. S. Chhabra, M. N. Chan, A. W. H. Chan, S. P. Hersey, J. D. Crounse and Others, *Atmos. Chem. Phys.*, 2013, **13**, 8019–8043.
- 80 Kelsey R. Bilsback, Yicong He, Christopher D. Cappa, Rachel Ying-Wen Chang, Betty Croft, Randall V. Martin, Nga Lee Ng, John H. Seinfeld, Jeffrey R. Pierce, and Shantanu H. Jathar *Environmental Science & Technology* 2023 57 (1), 53–63

SUPPLEMENTARY INFORMATION

Table S1: VOC species measured by the PTR-ToF-MS and considered as SOA precursors in our model. Reproduced from the supporting information in Akherati et al.³⁸

<i>Species name</i>	<i>Species Formula</i>	k_{OH} [s ⁻¹ cm ³ molecules ⁻¹]	c^* [μg m ⁻³]	<i>MW</i> [g mol ⁻¹]	<i>Surrogate</i>
Pyrrole	C4H5N	1.45×10 ⁻¹⁰	5.74×10 ⁷	67.0892	Heterocyclics
Furan	C4H4O	4.00×10 ⁻¹¹	2.23×10 ⁹	68.07356	Heterocyclics
Isoprene	C5H8	1.00×10 ⁻¹⁰	2.05×10 ⁹	68.11702	Biogenics
Dihydropyrrole	C4H7N	1.04×10 ⁻¹⁰	5.15×10 ⁷	69.10508	Heterocyclics
Tetrahydropyrrole	C4H9N	7.85×10 ⁻¹¹	2.44×10 ⁸	71.12096	Heterocyclics
Benzene	C6H6	1.22×10 ⁻¹²	4.05×10 ⁸	78.11184	Aromatics
Pyridine	C5H5N	3.70×10 ⁻¹³	5.28×10 ⁷	79.0999	Heterocyclics
Methylpyrrole	C5H7N	1.10×10 ⁻¹⁰	5.69×10 ⁷	81.11578	Heterocyclics
MethylFuran	C5H6O	7.80×10 ⁻¹¹	7.71×10 ⁸	82.10014	Heterocyclics
Thiophene	C4H4S	9.53×10 ⁻¹²	3.64×10 ⁸	84.13956	Heterocyclics
Furanone	C4H4O2	5.66×10 ⁻¹¹	1.34×10 ⁷	84.07256	Heterocyclics
Ethynylpyrrole	C6H5N	6.45×10 ⁻¹¹	3.95×10 ⁶	92.11854	Heterocyclics
Toluene	C7H8	5.63×10 ⁻¹²	1.42×10 ⁸	92.13842	Aromatics
2-Furancarbonitrile	C5H3NO	7.15×10 ⁻¹²	1.81×10 ⁵	93.08302	Heterocyclics
MethylPyridine	C6H7N	1.10×10 ⁻¹²	4.36×10 ⁷	93.12648	Heterocyclics
Phenol	C6H6O	2.80×10 ⁻¹¹	2.11×10 ⁶	94.11084	Oxygenated Aromatics
4-Pyridinol	C5H5NO	7.65×10 ⁻¹¹	1.81×10 ⁶	95.0989	Heterocyclics
C2-pyrroles	C6H9N	2.00×10 ⁻¹⁰	4.16×10 ⁶	95.14236	Heterocyclics
Furfural	C5H4O2	3.56×10 ⁻¹¹	1.14×10 ⁷	96.08326	Heterocyclics
Dimethylfuran	C6H8O	2.00×10 ⁻¹⁰	1.40×10 ⁷	96.12672	Heterocyclics
Methylthiophene	C5H6S	9.51×10 ⁻¹²	1.28×10 ⁸	98.16614	Heterocyclics
2Methanolfuran	C5H6O2	1.04×10 ⁻¹⁰	3.88×10 ⁶	98.09914	Heterocyclics
Dihydrofurandione	C4H4O3	8.56×10 ⁻¹³	9.00×10 ³	100.0716	Heterocyclics
Phenylacetylene	C8H6	8.02×10 ⁻¹²	2.16×10 ⁶	102.1332	Aromatics
Benzonitrile	C7H5N	3.44×10 ⁻¹³	4.62×10 ⁶	103.1213	Aromatics
Styrene	C8H8	5.80×10 ⁻¹¹	3.43×10 ⁷	104.1491	Aromatics
Vinylpyridine	C7H7N	2.66×10 ⁻¹¹	1.55×10 ⁶	105.1372	Heterocyclics
Benzaldehyde	C7H6O	1.20×10 ⁻¹¹	7.30×10 ⁶	106.1215	Aromatics
C8 Aromatics	C8H10	1.32×10 ⁻¹¹	4.88×10 ⁷	106.165	Aromatics
PyridineAldehyde	C6H5NO	1.71×10 ⁻¹¹	7.85×10 ⁴	107.1096	Heterocyclics
Dimethylpyridine	C7H9N	2.79×10 ⁻¹²	2.05×10 ⁷	107.1531	Heterocyclics
Benzoquinone	C6H4O2	4.51×10 ⁻¹²	8.80×10 ⁵	108.094	Aromatics
Cresol	C7H8O	5.30×10 ⁻¹¹	1.34×10 ⁷	108.1374	Oxygenated Aromatics
Trimethylpyrrole	C7H11N	2.00×10 ⁻¹⁰	1.20×10 ⁷	109.1689	Heterocyclics
Benzenediol	C6H6O2	1.04×10 ⁻¹⁰	1.10×10 ⁶	110.1098	Oxygenated Aromatics
Trimethylfuran	C7H10O	1.59×10 ⁻¹⁰	9.27×10 ⁷	110.1533	Heterocyclics
Dihydroxypyridine	C5H5NO2	4.55×10 ⁻¹¹	3.78×10 ⁴	111.0979	Heterocyclics
5-Hydroxy 2-furfural	C5H4O3	4.90×10 ⁻¹¹	7.36×10 ⁵	112.0823	Heterocyclics
Nitrofuran	C4H3NO3	5.06×10 ⁻¹²	1.64×10 ⁴	113.0703	Heterocyclics
5-hydroxymethyl-2[3H]-furanone	C5H6O3	1.00×10 ⁻¹⁰	2.59×10 ⁵	114.0981	Heterocyclics

5-hydroxy tetrahydro 2-furfural	C5H8O3	5.00×10^{-12}	7.36×10^5	116.114	Heterocyclics
Indene	C9H8	7.80×10^{-11}	1.06×10^7	116.1598	Aromatics
Benzeneacetonitrile	C8H7N	2.07×10^{-12}	5.72×10^5	117.1479	Aromatics
Benzofuran	C8H6O	3.70×10^{-11}	1.13×10^7	118.1322	Aromatics
Methylstyrene	C9H10	5.40×10^{-11}	1.14×10^7	118.1757	Aromatics
Isoindoline	C8H9N	8.00×10^{-11}	6.08×10^5	119.1638	Heterocyclics
Tolualdehyde	C8H8O	1.60×10^{-11}	2.39×10^6	120.1481	Aromatics
C9 Aromatics	C9H12	2.20×10^{-11}	1.95×10^7	120.1916	Aromatics
Salicylaldehyde	C7H6O2	2.80×10^{-11}	3.72×10^6	122.1205	Aromatics
Dimethylphenol	C8H10O	5.05×10^{-11}	5.31×10^6	122.164	Oxygenated Aromatics
Nitrobenzene	C6H5NO2	1.40×10^{-13}	1.50×10^6	123.1086	Aromatics
Hydroxy benzoquinone	C6H4O3	1.30×10^{-11}	4.11×10^5	124.093	Aromatics
Guaiaicol	C7H8O2	7.53×10^{-11}	9.16×10^5	124.1364	Oxygenated Aromatics
Hydroxymethylfurfural	C6H6O3	1.00×10^{-10}	4.11×10^5	126.1088	Heterocyclics
Dihydroxymethylfuran	C6H8O3	1.29×10^{-10}	4.11×10^5	128.1247	Heterocyclics
Naphthalene	C10H8	2.30×10^{-11}	5.73×10^5	128.1705	Aromatics
dihydronaphthalene	C10H10	6.42×10^{-11}	5.11×10^6	130.1864	Aromatics
Methylindole	C9H9N	2.00×10^{-10}	3.64×10^4	131.1745	Aromatics
Methyl benzofuran	C9H8O	9.75×10^{-11}	3.54×10^6	132.1588	Heterocyclics
Methyl propenyl benzene	C10H12	3.30×10^{-11}	6.76×10^6	132.2023	Aromatics
3-methylacetophenone	C9H10O	2.42×10^{-12}	1.60×10^6	134.1747	Aromatics
C10 Aromatics	C10H14	9.50×10^{-12}	1.04×10^7	134.2182	Aromatics
Methylbenzoicacid	C8H8O2	1.20×10^{-11}	1.66×10^4	136.1471	Aromatics
Monoterpenes	C10H16	1.63×10^{-10}	2.16×10^7	136.234	Biogenics
Nitrotoluene	C7H7NO2	7.72×10^{-13}	5.96×10^5	137.1352	Aromatics
MethylGuaiaicol	C8H10O2	3.98×10^{-11}	5.62×10^5	138.163	Oxygenated Aromatics
Methylnaphthalene	C11H10	5.65×10^{-11}	5.20×10^5	142.1971	Aromatics
Product of levoglucosan dehydration (pyrolysis)	C6H8O4	5.28×10^{-11}	3.81×10^4	144.1237	Alkanes
Naphthol	C10H8O	2.00×10^{-10}	2.71×10^5	144.1695	Aromatics
Ethylindene	C11H12	6.36×10^{-11}	1.67×10^6	144.213	Aromatics
Dimethylbenzofuran	C10H10O	1.20×10^{-10}	2.71×10^5	146.1854	Aromatics
Methylchavicol	C10H12O	5.43×10^{-11}	1.13×10^6	148.2013	Oxygenated Aromatics
C11 aromatics	C11H16	5.00×10^{-11}	4.81×10^6	148.2447	Aromatics
VinylGuaiaicol	C9H10O2	5.44×10^{-11}	2.28×10^5	150.1737	Oxygenated Aromatics
Vanillin	C8H8O3	2.73×10^{-11}	7.00×10^5	152.1461	Oxygenated Aromatics
Acenaphthylene	C12H8	7.55×10^{-11}	6.18×10^4	152.1919	Aromatics
Camphor	C10H16O	4.30×10^{-12}	1.98×10^6	152.233	Biogenics
Syringol	C8H10O3	9.66×10^{-11}	1.00×10^5	154.162	Oxygenated Aromatics
Cineole	C10H18O	2.26×10^{-11}	1.63×10^7	154.2489	Biogenics
1,3-dimethylnaphthalene	C12H12	6.94×10^{-11}	8.57×10^4	156.2237	Aromatics
Decanal	C10H20O	3.45×10^{-11}	1.27×10^6	156.2648	Alkanes
C12 aromatics	C12H18	1.13×10^{-10}	1.17×10^6	162.2713	Aromatics
Isoeugenol	C10H12O2	8.84×10^{-11}	1.94×10^5	188.2217	Oxygenated Aromatics
C13 aromatics	C13H20	1.13×10^{-10}	7.17×10^5	176.2979	Aromatics
Sesquiterpenes	C15H24	3.00×10^{-10}	4.58×10^4	204.3511	Biogenics
5-Methyl furfural	C6H6O2	5.18×10^{-11}	1.10×10^6	110.1098	Heterocyclics

Table S2a: SOM grids, surrogates, and parameters used in this work (High NO_x). Reproduced from the supporting information in Akherati et al.³⁸

Precursor Class	VOC Surrogate	ΔLVP	m_{frag}	$p_{f,1}$	$p_{f,2}$	$p_{f,3}$	$p_{f,4}$	Reference
Long alkanes	<i>n</i> -dodecane	1.4629	0.2627	0.9657	0.0010	0.0020	0.0314	Loza et al. ⁷⁶
Benzene	benzene	1.5495	0.7895	0.0743	0.0213	0.8963	0.0081	Ng et al. ⁷⁷
Toluene	toluene	1.4169	1.3064	0.5634	0.3413	0.0016	0.0937	Zhang et al. ⁷⁸
C ₈₊ single-ring aromatics	<i>m</i> -xylene	1.4601	0.0736	0.1418	0.2971	0.4571	0.1040	Ng et al. ⁷⁷
Polycyclic aromatic hydrocarbons (PAH)	naphthalene	1.4922	0.7673	0.8138	0.0072	0.0635	0.1155	Zhang et al. ⁷⁸
Isoprene	isoprene	1.8742	0.5207	0.9924	0.0003	0.0065	0.0009	Chhabra et al. ⁷³
Terpene	α -pinene	1.9139	0.1312	0.5991	0.2923	0.1079	0.0007	Chhabra et al. ⁷³
Oxygenated aromatics	phenol, guaiacol	2.023	0.315	0.109	0.048	0.439	0.404	Yee et al. ⁷⁹
Oxygenated aromatics	syringol	1.629	0.148	0.394	0.121	0.071	0.414	Yee et al. ⁷⁹
Heterocyclic compounds	2-methylfuran, dimethylfuran	1.459	0.449	0.0005	0.0014	0.998	0.0001	He et al. ⁵⁶

Table S2b: SOM grids, surrogates, and parameters used in this work to perform the low NO_x sensitivity case simulations. Reproduced from the supporting information in Bilsback et al.⁸⁰

Precursor Class	VOC Surrogate	ΔLVP	m_{frag}	$p_{f,1}$	$p_{f,2}$	$p_{f,3}$	$p_{f,4}$	f_{HOMS}	Reference
Benzene	benzene	2.081	0.001	0.122	0.019	0.709	0.151	0.002	Ng et al. ⁴
Toluene	toluene	1.970	0.039	0.197	0.564	0.011	0.228	0.001	Zhang et al. ⁵
C ₈₊ single-ring aromatics	<i>m</i> -xylene	1.994	0.029	0.042	0.045	0.769	0.144	0.014	Ng et al. ⁴
Polycyclic aromatic hydrocarbons (PAH)	naphthalene	1.946	0.029	0.012	0.498	0.48	0.01	0.018	Zhang et al. ⁵
Isoprene	isoprene	1.624	0.107	0.426	0.002	0.558	0.015	0	Chhabra et al. ⁶
Terpene	α -pinene	1.588	0.112	0.431	0.002	0.552	0.015	0.034	Chhabra et al. ⁶
Oxygenated aromatics	phenol	1.977	0.404	0.067	0.096	0.823	0.014	0.001	Yee et al. ⁷
Heterocyclic compounds	2-methylfuran, dimethylfuran	Same as high NO _x parameters from Table S4						0	He et al. ⁸

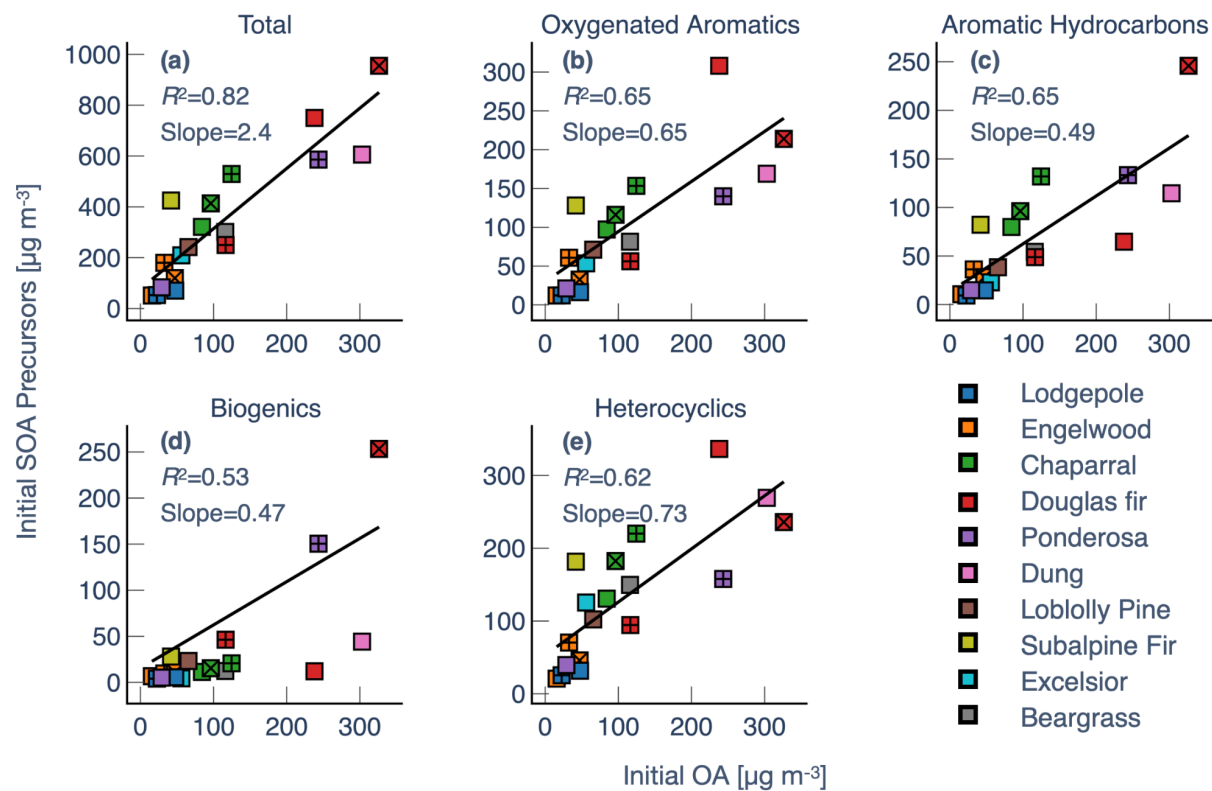


Figure S1: Initial precursor mass concentrations compared against initial OA mass concentrations for (a) all SOA precursors, (b) oxygenated aromatics, (c) aromatic hydrocarbons, (d) biogenic VOCs, and (e) heterocyclics. Data are presented for all 18 chamber experiments.

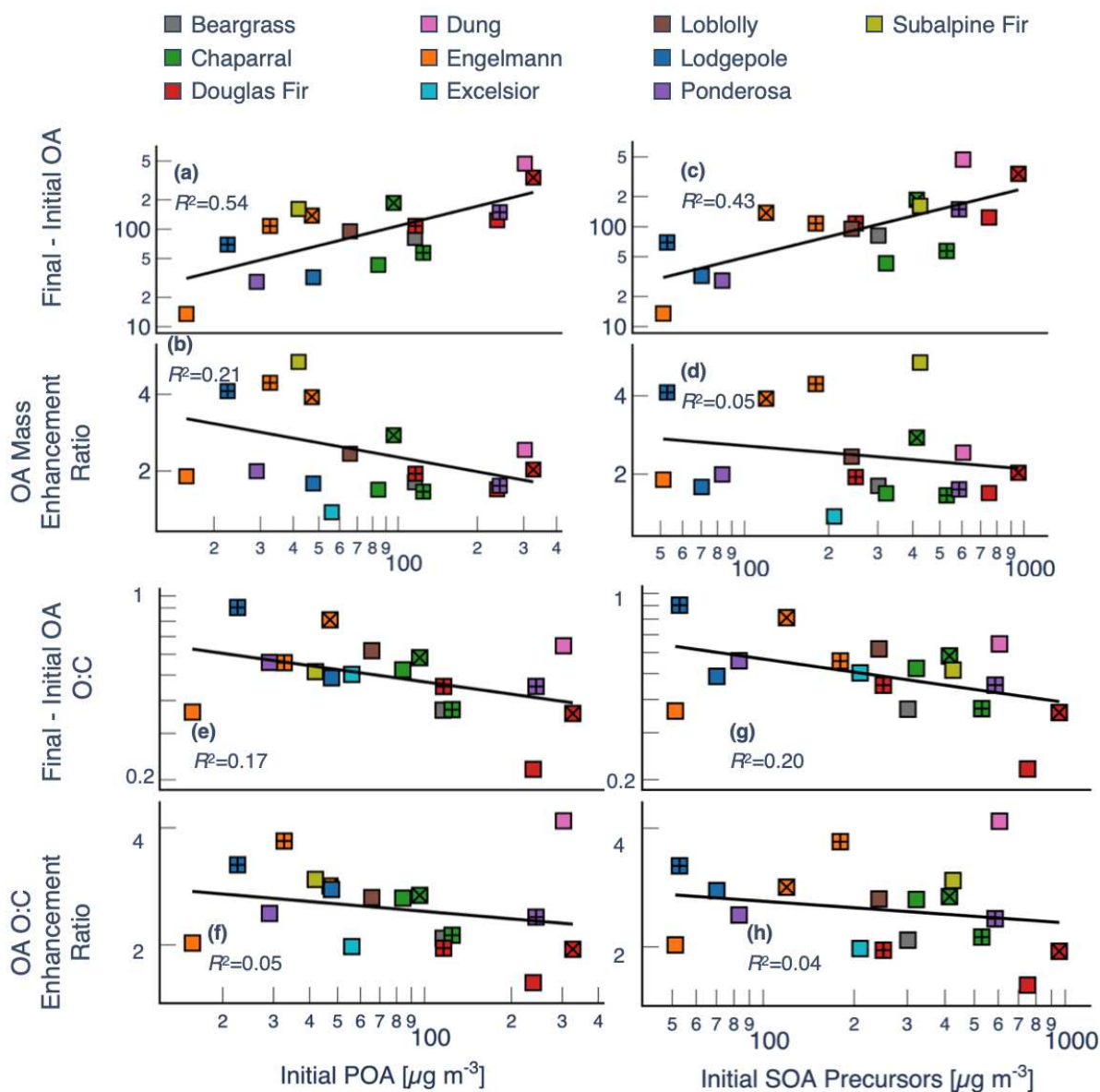


Figure S2: (a,c) OA added (dOA) and (b,d) OA mass enhancement ratio compared to (a,b) initial POA mass concentrations and (c,d) initial SOA precursor mass concentrations for all 18 chamber experiments. (e-h) represent the same for OA O:C. Trend lines are best fits to the data and are meant to guide the eye.

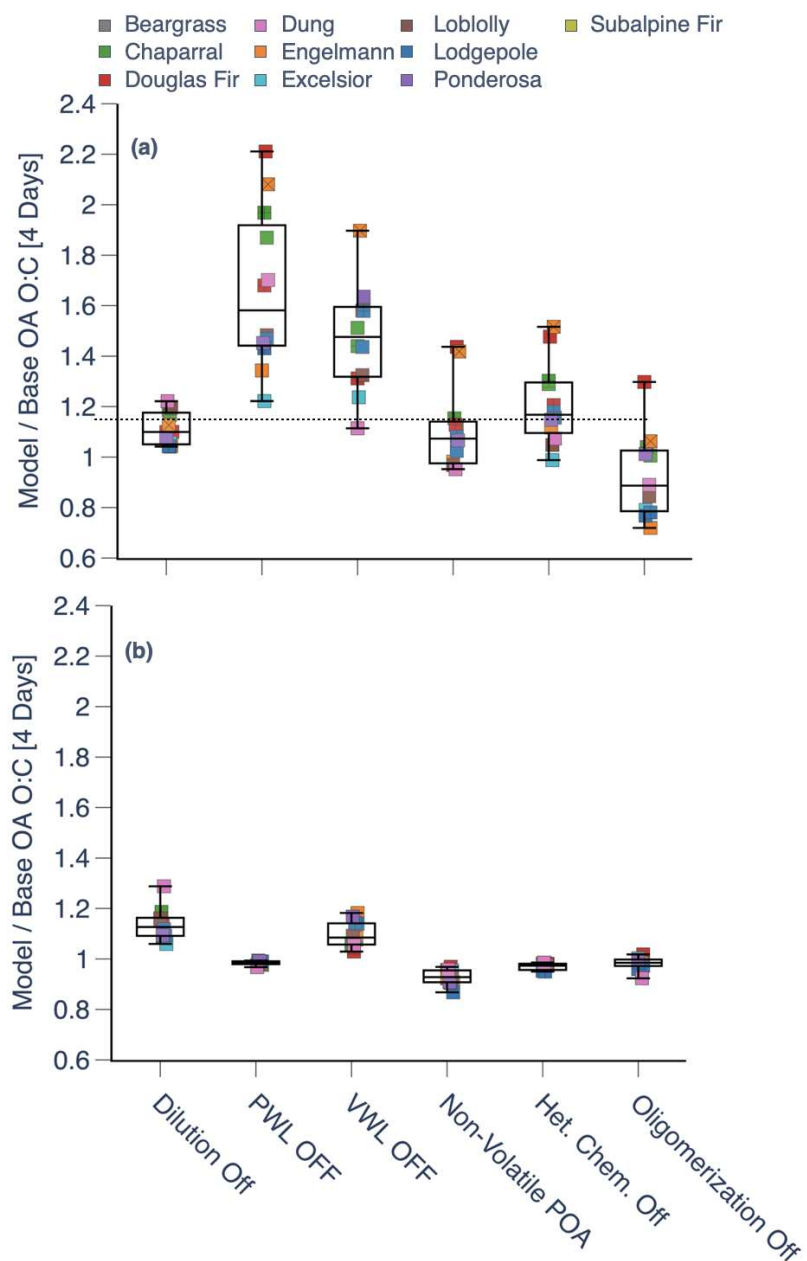


Figure S3: Model predictions from the sensitivity simulations ratioed to those from the Base simulation at four equivalent photochemical days for (a) OA mass concentrations and (b) OA O:C.