

DISSERTATION

UNDERSTANDING THE PHOTOCHEMICAL EVOLUTION OF ORGANIC AEROSOL
FROM MOBILE SOURCES AND WILDFIRES

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Ali Akherati

Department of Mechanical Engineering

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Doctoral Committee:

Advisor: Shatanu H. Jathar

Co-Advisor: Jeffrey R. Pierce

Tami C. Bond

John Volckens

Delphine K. Farmer

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ABSTRACT

UNDERSTANDING THE PHOTOCHEMICAL EVOLUTION OF ORGANIC AEROSOL FROM MOBILE SOURCES AND WILDFIRES

Atmospheric aerosols affect climate, air quality, and human health. Primary organic aerosol (POA), directly emitted from a variety of sources, and secondary organic aerosol (SOA), formed when gas-phase organic compounds (OC) are oxidized in the atmosphere, account for a large fraction of the submicron atmospheric aerosol mass globally. The atmospheric evolution of SOA is poorly understood due to a wide range of natural and anthropogenic sources of gas-phase OC, the complex chemical composition of gas-phase OC and SOA and chemical pathways through which SOA forms. Semivolatile and intermediate-volatility organic compounds (SVOCs and IVOCs, respectively) from anthropogenic sources (e.g., gasoline, diesel, residential wood burning, and cooking) are likely to be important precursors of SOA. Additionally, gas-phase oxidation of organic precursors to form SOA is impacted by the presence of nitric oxide (NO), but this influence is poorly constrained in organic aerosol models. Furthermore, SOA parameterizations used in organic aerosol models often do not account for laboratory experimental artifacts, such as particle and vapor wall losses to Teflon walls during laboratory chamber experiments, which impacts the SOA mass and composition predicted by models.

This dissertation combines extensive data analysis of laboratory and field-campaign data, new state-of-the-art organic aerosol box modeling, and regional chemical transport modeling to explore the physicochemical evolution of POA and SOA from different combustion sources (e.g. gasoline, diesel, and biomass burning). We used several novel modeling tools to (i) quantify the SOA and POA contributions in an urban airshed from combustion sources, (ii) investigate the importance of different SOA precursors in biomass burning laboratory experiments, (iii) and explore the key

processes and mechanisms driving the discrepancies between laboratory and field biomass burning measurements.

In Chapter two, we updated an organic aerosol model (i.e. the Statistical Oxidation Model) in UCD/CIT (the University of California, Davis/California Institution of Technology) chemical transport model to include (i) a semivolatile and reactive treatment of POA and SVOCs, (ii) emissions and SOA formation from IVOCs, (iii) NO_x -dependent SOA formation, and (iv) updated SOA parameterizations to account for the influence of vapor wall loss artifacts encountered in Teflon chamber experiments. Using these updates, we ran a chemical transport model over the state of California for a summertime episode during the SOAR (Study of Organic Aerosols at Riverside) field campaign in 2005. Treatment of POA as semi-volatile resulted in a 15-40% reduction of estimated OA in Southern California. Adding IVOCs did not result in as much SOA enhancement as other SOA precursors (e.g. alkanes and aromatics). Accounting for the effects of NO_x using NO_x :VOC ratios and vapor wall loss artifacts of chamber experiments in the model produced better OA estimates in both urban and remote areas when compared to ambient measurements during SOAR. Despite updating the model, the model still underestimated OA by a factor of two in this urban environment suggesting that some sources may be missing (i.e. volatile chemical products such as personal care products, solvents, and pesticides) or that IVOC emissions and IVOC SOA parameterizations may not be accurately modeled.

The third and fourth research chapters in this thesis focus on biomass burning, one of the major sources of OA globally. There are large uncertainties around IVOC and VOC, POA emissions, thermodynamic properties, and physical and chemical evolution. Further, recent studies have shown contradictory results on OA evolution between the laboratory and field measurements. A state-of-the-science OA model (i.e. SOM-TOMAS) is developed to investigate the OA evolution of recent laboratory and field campaigns with a focus on wildfires in the western United States. The SOM-TOMAS model was used to examine the influence of different processes and mechanisms that drive OA discrepancies.

In Chapter three, we used the NOAA FIREX (Fire Influence on Regional and Global Environments Experiment) laboratory campaign data to analyze and model biomass burning OA evolution. In this study, we showed that oxygenated aromatics play an important role in forming a large fraction of the biomass burning SOA measured in laboratory experiments. Accounting for vapor wall loss artifacts in Teflon chamber experiments and losses of IVOC species in the transfer tubing during injection of smoke to the chamber resulted in doubling the SOA productions in our modeling work. In addition, using temperature-dependent emission profiles and campaign average emission profiles in modeling sets produced relatively similar results as using fire-specific emission profiles.

In Chapter four, we utilized the data from the Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) field campaign to explore the laboratory and field OA mass and composition discrepancies. We used a modified plume version of the SOM-TOMAS model to simulate the dilution, oxidation chemistry, thermodynamic properties, and microphysics of OA in wildfire plumes. Our data analyses suggest that SOA precursors, on average, have been lower in the field than the laboratory measurements. Our model results also showed that dilution-driven evaporation of POA with simultaneous photochemical production of SOA is likely to explain the measured trends in OA mass and composition. The rapid transformation of SOA precursors within the first hour after emission resulted in OA enhancement because of higher OH concentrations. Semivolatile, heterocyclics, and oxygenated aromatics were the most important SOA precursors in these large wildfire plumes.

The aim of my dissertation was to better understand the composition and evolution of organics from combustion sources in the atmosphere. Through this work, we developed a novel OA box model (i.e. SOM-TOMAS) and data analysis tools for laboratory and field campaigns. My work demonstrated the importance of (i) IVOC and gas-phase oxygenated organic compound emissions, (ii) SVOC treatments and dilution-driven evaporation of SVOCs in large wildfire plumes, and (iii) accounting for the smog chamber experimental artifact (e.g., vapor wall losses). Future work could involve (i) addition of newly found sources of SOA precursors in chemical transport model emission inventories (e.g., volatile chemical product), (ii) performing laboratory experiments to

better understand the volatility and chemical composition of biomass burning POA, and (iii) better estimates and understanding of oxidant concentrations driving SOA formation in large wildfire plumes (e.g., hydroxyl radical).

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DEDICATION

To my mother, Vida Bahmani, and my father, Alireza Akherati, who unconditionally love me and support me.

TABLE OF CONTENTS

ABSTRACT	ii
ACKNOWLEDGEMENTS	vi
DEDICATION	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
Chapter 1 Introduction	1
Chapter 2 Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 3: Assessing the influence of semi- volatile and intermediate volatility organic compounds and NO _x	6
2.1 Introduction	6
2.2 Methods	11
2.2.1 Chemical Transport Model	11
2.2.2 Organic Aerosol Model	12
2.2.3 Simulations	27
2.2.4 Measurements for Model Evaluation	31
2.3 Results	32
2.3.1 POA and SOA Precursor Emissions	32
2.3.2 Spatial Distribution of OA Concentrations and Bulk Composition	35
2.3.3 Precursor Contributions to OA and SOA	38
2.3.4 Influence of Vapor Wall Losses	44
2.3.5 Sensitivity Analysis	47
2.3.6 NO _x -Adjusted SOA Formation	49
2.4 Model Evaluation	53
2.4.1 SOA Precursors	53
2.4.2 OA Mass Concentrations	56
2.4.3 POA and SOA Mass Concentrations	61
2.4.4 OA Elemental Composition	64
2.5 Summary and Discussion	65
Chapter 3 Oxygenated Aromatic Compounds are Important Precursors of Secondary Organic Aerosol from Biomass Burning	71
3.1 Introduction	71
3.2 Materials and Methods	73
3.2.1 Environmental Chamber Measurements	73
3.2.2 SOM-TOMAS Modeling	75
3.3 Results	83
3.4 Discussion	89

Chapter 4	Dilution and Photooxidation Driven Processes Explain the Evolution of Organic Aerosol in Wildfire Plumes	91
4.1	Introduction	91
4.2	Materials and Methods	94
4.2.1	Aircraft Measurements	94
4.2.2	OH Concentration and Exposure Estimates	97
4.2.3	Organic Aerosol Model	101
4.2.4	SOA Formation from VOCs	104
4.2.5	Treatment of POA and SVOCs	106
4.2.6	Model Configuration and Simulations	108
4.3	Results	110
4.3.1	OA Mass and Composition Evolution	110
4.3.2	Model Sensitivity to the Treatment of POA and SVOCs	115
4.3.3	Model Sensitivity to OH, ‘First’ Transect, and Background Correction	118
4.3.4	Summary and Implications of the Base Results	119
4.4	Discussion	121
Chapter 5	Conclusion and summary of science findings	126
Bibliography		130
Appendix A	Supplementary information for Chapter 2	183
Appendix B	Supplementary information for Chapter 3	193
Appendix C	Supplementary information for Chapter 4	221

LIST OF TABLES

2.1	SOA precursors and SOM parameters used in this work. VWL=Vapor Wall Loss Corrected, Δ LVP = change in vapor pressure linked to addition of one oxygen atom, P_{func} = molar yields of species that add 1 to 4 oxygens per reaction (Pf_1 through Pf_4), m_{frag} = exponent influencing the probability of fragmentation.	16
2.2	Low and high VOC:NO _x ratios in ppb ppb ⁻¹ from chamber experiments used to model the influence of NO _x on SOA formation.	26
2.3	Names and descriptions of the simulations performed in this work	28
2.4	Statistical metrics of averages, fractional bias, fractional error, and R ² for the model-measurement comparison in southern California.	59
4.1	OH concentration and exposure estimates based on the laboratory-normalized and reactivity-differentiated VOC decay for the five transect sets.	102
A.1	Hydrocarbon distribution used to distribute POA emissions.	192
B.1	Fuel, oxidant, and variables of interest (see column headings) for the eleven chamber experiments performed during FIREX. Note that the table is split into three sections for visual clarity, keeping the first two columns the same.	194
B.2	Table B1 continued	195
B.3	Table B1 continued	196
B.4	Emissions ratios of SOA precursors with acetonitrile (g g ⁻¹) used to calculate SOA precursor concentrations in the 11 chamber experiments	197
B.5	VOC species measured by the PTR-ToF-MS (Koss et al.10) and considered as SOA precursors in our model.	200
B.6	SOM grids, surrogates, and parameters used in this work.	204
C.1	Precursor classes, surrogates, and parameters used in this work.	222
C.2	SOA precursors measured by the PTR-ToF-MS and included in the SOM-TOMAS model.	223

LIST OF FIGURES

2.1	Episode-averaged gas- and particle-phase organic emissions in tons per day over the 8 km southern California domain resolved by source. POA and SVOC represent the particle- and gas-phase emissions partitioned to an OA mass concentration of $9 \mu\text{g m}^{-3}$. SVOC, IVOC, long alkanes, aromatics, and biogenics represent gas-phase emissions of precursor species that are modeled to form SOA. We note that recent measurements suggest that POA from food cooking sources is less volatile than assumed in these results.	34
2.2	14-day averaged model predictions of mass concentrations for OA, POA, SOA, aV-SOA, aS/I-SOA, and bV-SOA in $\mu\text{g m}^{-3}$ over the southern California domain from the Base simulation. We note that recent measurements suggest that POA from food cooking sources is less volatile than assumed in these results.	36
2.3	14-day averaged model predictions of POA and SOA mass concentrations and precursor contributions at the central Los Angeles site from the sensitivity simulations that examined the influence of updates made in this work. Panel (a) shows absolute concentrations and panel (b) shows precursor contributions. The legend at the bottom tracks how the different pathways (i.e., SOA formation from SVOCs, SOA formation from IVOCs, and correction for chamber vapor wall losses (VWL)) were turned on for the different simulations. Model predictions from the low and high NO_x simulations are shown separately. Model predictions to the extreme right are from accounting for the influence of NO_x on SOA formation using equation 2. We note that recent measurements suggest that POA from food cooking sources is less volatile than assumed in these results.	40
2.4	Ratio of model predictions from the Base simulation that accounts for the influence of vapor wall losses to model predictions from the IVOC simulation that does not account for the influence of vapor wall losses. Ratios are calculated from the 14-day averaged results for the whole domain and are resolved by precursor. Panels (a) and (b) show results from the low and high NO_x simulations respectively.	45
2.5	14-day averaged model predictions of POA and SOA mass concentrations and precursor contributions from the sensitivity simulations. Panel (a) shows absolute concentrations and panel (b) shows precursor contributions. Model predictions from the low and high NO_x simulations are shown separately. Simulation legend: Base = Base case, No Aging = only models first generation chemistry in the SOM, SVOC_{max} = all POA treated as semi-volatile, IVOC_{max} = all combustion sources assumed to have 20% IVOC emissions and a C_{15} SOA yield, $\text{S-IVOC}_{aromatic}$ = SVOCs and IVOCs modeled as high-yield aromatic compounds, VOC_{spec} = mobile source emissions profiles based on May et al. (2014), $\text{SVOC}_{cooking}$ = POA volatility distribution for food cooking sources based on the measurements of Louvaris et al. (2017). All simulations besides $\text{SVOC}_{cooking}$ assumed food cooking POA to have the same volatility as biomass burning POA. More details about these simulation inputs can be found in Section 2.2.3.	50
2.6	14-day averaged ratio of the SOA_{eff} mass concentration to the SOA mass concentration from the (a) high NO_x and (b) low NO_x Base simulations.	51

2.7	(a) Mass concentrations of single-ring aromatics in southern California at different sites between 2000 and 2011. Measurements show the temporal trend in the summer-time mean (solid line) and 10 th -90 th percentile (bands) at Los Angeles, Riverside, and Long Beach from 2000 to 2011 (ARB, 2017) and the campaign-averaged measurement from CalNex at the Pasadena ground site in 2010 (Zhao et al., 2014). Model predictions show the 14-day averaged concentration simulated in this work at four different sites (solid symbols) in 2005. (b) Mass concentrations of single-ring aromatics and IVOCs compared between the model predictions from 2005 (this work) to measurements in 2010 (Zhao et al., 2014).	55
2.8	Model-measurement comparison for daily-averaged OA mass concentrations at (a) CSN and (b) IMPROVE sites in southern California. Panel (c) shows the geographic locations where the comparisons were made.	56
2.9	(a) Diurnal profile of the modeled and measured OA/ Δ CO ratios at Riverside, CA. The box plots capture the 10 th -25 th -50 th -75 th -90 th in model predictions over the simulated episode while the gray bands and solid orange line represent the 10 th and 90 th percentile and median of the measured data. (b) Modeled and measured OA mass concentrations plotted against CO concentrations between 10 am and 8 pm local time. The solid and dashed black lines represent lines fitted to the modeled and measured data by forcing the X-intercept to be the corresponding modeled and measured background CO concentration. Diurnal profiles of the modeled and measured (c) H:C and (d) O:C ratios of the OA (corrected as per Canagaratna et al. (2015)). The three different predictions show results from the Base simulations for OA assuming no change, the POA O:C was fixed to 0.078 based on the measurements of Docherty et al. (2011), and no POA.	62
2.10	Ratios of 14-day averaged model predictions of (a) OA, (b) POA, (c) SOA, and (d) OH from 2035 to those from 2005. The 2035 simulations were performed with 2005 meteorological inputs but scaling the anthropogenic emissions for CO, NO _x , VOC, PM _{2.5} , SO ₂ , and NH ₃ based on changes projected by the California Emission Projections and Analysis Model (CARB, 2018).	69
3.1	(a) Decay of D9 (deuterated butanol, pink) and VOCs, summed by class, with time and the OH exposure estimated based on the decay of D9; color scheme for VOCs can be found in the legend to the extreme right. (b) Model predictions of OA mass concentrations (green) and O:C ratio (blue) compared with measurements. Both results are for a lodgepole pine experiment performed at high NO _x conditions (Fire007). (c) The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	79
3.2	End-of-experiment model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ($\mu\text{g m}^{-3}$), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments. Statistical metrics based on a linear fit to the model-measurement comparison are presented at the bottom of each panel. RMSE = Root Mean Squared Error.	82

3.3	Normalized emissions and OH reactivity of the SOA precursors and their contribution to SOA production for the average of the eleven chamber experiments analyzed in this work. Some of the SOA precursor classes are lumped for clarity (e.g., alkanes+partially speciated, reduced aromatics). Top panels show results for all SOA precursors and bottom panels show results for just the oxygenated aromatic precursors.	84
3.4	Model predictions of end-of-experiment SOA mass concentrations compared between simulations performed (a) with and without experimental artifacts and (b) with fire-specific and averaged emissions profiles.	87
4.1	Field-to-laboratory ratios of the VOC-to-CO ratio in the wildfire plume to the average VOC-to-CO emissions ratio measured in laboratory experiments plotted against k_{OH} . Results are shown for the first transect measured for the (a) Taylor Creek, (b) Sharps, (c) Bear Trap 1, (d) Bear Trap 2, and (e) Silver Creek transect sets. Solid red lines represent the linear fit to the data and the red bands capture the uncertainty in the fit (1σ). The table lists statistics based on the linear fit including the OH concentration and exposure. The time-varying OH exposures for all five transect sets are shown in Figure 4.2 and the OH concentrations are listed in Table 4.1.	99
4.2	Time-varying OH exposures estimated for the five transects sets: (a) Taylor Creek, (b) Sharps, (c) Bear Trap 1, (d) Bear Trap 2, and (e) Silver Creek. The solid red lines are linear fits to time periods after the first transect while the dotted red lines represent the estimated OH exposure prior to the first transect.	100
4.3	Field-to-laboratory ratios of the ratios of SOA precursor class to CO in the wildfire plume to the average emissions ratios of SOA precursor class to CO measured in laboratory experiments at $t=0$ and the first transect. SOA precursors are aggregated by organic class: biogenics, oxygenated aromatics, heterocyclics, reduced aromatics, and alkanes. Data are presented together for all five transect sets.	105
4.4	Predictions of (a) OA NEMR and (b) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. Model predictions are shown for five different simulations that vary in their assumptions about POA volatility and oxidation chemistry. Model predictions were always constrained to the measurements of OA NEMR and OA O:C at the 1 st transect, marked by the red solid circle. Predictions of the normalized OA composition from the base simulations are shown in panel (c).	110
4.5	Predictions of (a-e) OA NEMR and (f-j) OA O:C from the SOM-TOMAS model compared against measurements from four different wildfire transect sets (Sharps, Bear Trap×2, Silver Creek) . Model predictions are shown for five different simulations that vary in their assumptions about POA volatility and oxidation chemistry. (k-o) Model predictions of the normalized OA composition from the base simulations (SV-POA+FullChem).	112
4.6	Predictions of (a,b,c) OA NEMR and (d,e,f) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (g,h,i) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for the SVOC oxidation chemistry (a,d,g), POA volatility and SVOC oxidation chemistry (b,e,h), and POA+SVOC mass distribution in the SOM grid. . . .	116

4.7	Predictions of (a,b,c) OA NEMR and (d,e,f) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (g,h,i) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for OH (a,d,g), ‘first’ transect (b,e,h), and approach to perform background corrections.	120
4.8	Model predictions of OA and SOA precursor NEMRs at t=0 (‘Fresh Emission’) and the first and last transects for all five transect sets. Observations of OA NEMR are also presented for the first and last transects in light grey with error bars.	122
A.1	Model domains showing the 24 km grid (top) used for the state of California simulations and the 8 km nested grid (bottom) used for the southern California simulations. Symbols show the Chemical Speciation Network (CSN) and Interagency Monitoring of Protected Visual Environments (IMPROVE) network sites in both domains.	183
A.2	Ratio of the 14-day averaged POA mass concentration to SOA_{eff} mass concentration in the Base simulation.	184
A.3	14-day averaged model predictions of POA and SOA mass concentrations and precursor contributions at the (a) Riverside and (b) Simi Valley site from the sensitivity simulations that examine the influence of updates made in this work. Panel (a) shows absolute concentrations and panel (b) shows precursor contributions. The legend at the bottom tracks how the different pathways (i.e., SOA formation from SVOCs, SOA formation from IVOCs, and correction for chamber vapor wall losses (VWL)) were turned on for the different simulations. Model predictions from the low and high NO_x simulations are shown separately. Model predictions to the extreme right are from accounting for the influence of NO_x using equation 2 in the main text (logarithmic dependence on $VOC:NO_x$).	185
A.4	Ratio of the 14-day averaged POA mass concentration from the SVOC simulation to that from the Traditional simulation.	186
A.5	Vapor wall loss-related enhancements in SOA mass yield calculated using a box model version of the SOM for different precursor species at an organic aerosol mass concentration of $9 \mu g m^{-3}$	186
A.6	Ratio of the 14-day averaged OA mass concentration from the (a) $IVOC_{max}$ and (b) $IVOC_{aromatic}$ simulation to that from the Base simulation.	187
A.7	Modeled (2005) and measured (2010) diurnal profiles of (a) OH, (b) HO_2 (model), HO_2^* (measurements) (c) NO_2 and (d) NO concentrations over Pasadena. Model predictions are shown as box plots while measurements are show as bands (10-90 th percentiles) and a solid black line (median).	188
A.8	Scatter plots comparing model predictions of SOA_{eff} using equation 2 (logarithmic dependence on the $VOC:NO_x$ ratio) to those predicted using (a) equation 1 (linear dependence on the $VOC:NO_x$ ratio), (b) equation 3 (linear dependence on the NO_x concentration), and (c) equation 4 (logarithmic dependence on the NO_x concentration).	189
A.9	14-day averaged (a) $VOC:NO_x$ ratios (ppbv ppbv ⁻¹) and (b) NO_x concentrations (ppbv) in southern California.	189

A.10	Model-measurement comparison for daily-averaged OA mass concentrations at (a) CSN and (b) IMPROVE sites across California. Panel (c) shows the color-coded geographic locations where the comparisons were made.	189
A.11	(a) Diurnal profile of the modeled and measured OA/ Δ CO ratios at Riverside, CA. The box plots capture the 10 th -25 th -50 th -75 th -90 th in model predictions over the simulated episode while the gray bands and solid orange line represent the 10th and 90th percentile and median of the measured data. (b) Modeled and measured OA mass concentrations plotted against CO concentrations between 10 am and 8 pm local time. The solid and dashed black lines represent lines fitted to the modeled and measured data by forcing the X-intercept to be the corresponding modeled and measured background CO concentration. Diurnal profiles of the modeled and measured (c) H:C and (d) O:C ratios of the OA. The three different predictions show results from the Base simulations for OA assuming no change, the POA O:C was fixed to 0.078, and no POA. Model predictions are from three different simulations: Base, IVOC _{max} , and S-IVOC _{aromatic}	190
A.12	Ratios of 14-day averaged model predictions of (a) CO, (b) NO, (c) NO ₂ , and (d) VOC from 2035 to those from 2005. The 2035 simulations were performed with 2005 meteorological inputs but scaling the anthropogenic emissions for CO, NO _x , VOC, PM _{2.5} , SO ₂ , and NH ₃ based on changes projected by the California Emission Projections and Analysis Model (CARB, 2018).	191
B.1	Scaling factor (SF) as a function of the oxidation state (OSc) for six different experiments. The OSc was approximated as 2×O:C-H:C (Kroll et al., 2011). The relatively larger variability in SF for Fire001 and Fire002 can be attributed to low initial OA mass concentrations in those experiments (<4 μg m ⁻³) compared to the rest (>20 μg m ⁻³). Gas-phase data were unavailable for Fire001 and Fire002 and hence were not modeled in this study. Fire011 was a nitrate (NO ₃) radical experiment performed in the dark and the oxidation results from that experiment will be discussed in a companion paper.	205
B.2	Scatter plot comparing the acetonitrile concentration measured by the PTR-MS and PTR-ToF-MS in the MIT/UCD mini-chamber over 30 experiments (Tkacik et al., 2017). The slope was used to correct the acetonitrile concentrations in the CSU chamber before being used to determine the initial concentrations of SOA precursors.	206
B.3	Averaged fate of the RO ₂ radical with reaction with NO, NO ₂ , HO ₂ , and RO ₂ , based on predictions from the Master Chemical Mechanism (MCM) over the entire duration of the chamber experiment (Coggon et al, 2019). Here, we only calculated the fate of RO ₂ radicals with a carbon number larger than or equal to 4.	207
B.4	Model predictions of SOA mass concentrations and O:C ratios for (a) phenol, (b) guaiacol, and (c) syringol compared against measurements from Yee et al. (2013) and Chhabra et al. (2011)	208
B.5	Particle-wall-loss-corrected OA mass concentrations measured by the HR-AMS at a mass-to-charge ratio of 60.02113 for all eleven chamber experiments. Except for Fire003, the mass was found to be relatively constant during the lights-on period of the experiment, which we concluded as little indication of oxidation of POA	208

B.6	Emissions ratios of individual SOA precursors to acetonitrile ratioed between those measured in the chamber to those measured in the stack for Fire007. The data are resolved by SOA precursor class. A ratio of 1 indicates no loss in the transfer duct and a ratio of 0 indicates a complete loss in the transfer duct. The time series of these species in the chamber were relatively flat during the dark period indicating that the losses were from those in the transfer duct and not to the walls of the chamber. The solid black line represents the chamber-to-stack ratio if the species were binned by volatility.	209
B.7	Modeled (solid black line) and measured (peach circles) decay of reduced hydrocarbons identified by the PTR-ToF-MS for the chamber experiments performed on Fire007.	210
B.8	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high NO _x conditions (Fire003). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	211
B.9	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high NO _x conditions (Fire004). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	211
B.10	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed without added oxidants (Fire016). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	212
B.11	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Douglas fir experiment performed without added oxidants (Fire022). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	212
B.12	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a chaparral (manzanita) experiment performed at high NO _x conditions (Fire028). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	213
B.13	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high NO _x conditions (Fire037). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	213
B.14	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Lodgepole pine experiment performed at high NO _x conditions (Fire042). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	214

B.15	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for an Engelmann spruce experiment performed at high NO _x conditions (Fire054). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	214
B.16	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Lodgepole pine experiment performed at high NO _x conditions (Fire063). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	215
B.17	Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a subalpine fir experiment performed with additional ozone (Fire067). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.	215
B.18	Model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ($\mu\text{g m}^{-3}$), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments at four different time percentiles: 25%, 50%, 75%, and 100%.	216
B.19	Model error in OA mass enhancement ratio, SOA production, and OA O:C regressed against lights-on period, OH exposure, and initial concentrations of seed surface area, OA mass, O:C, NO, NO ₂ , O ₃ , and SOA precursors.	217
B.20	(a) SOA mass concentrations apportioned by precursor class and (b) normalized precursor contributions to SOA arising from oxygenated aromatics. Data presented for all eleven chamber experiments.	218
B.21	(a) SOA precursor classes as a mass fraction of the total VOCs and (b) normalized distribution of SOA precursor emissions in volatility space. (c) SOA precursor classes as a fraction of the total VOC reactivity and (d) normalized distribution of SOA precursor reactivity in volatility space. Data are presented as an average of the emissions over the eleven chamber experiments.	219
B.22	Box plots for initial and final OA O:C ratios from the chamber experiments performed during FIREX and a host of field studies. The field studies are summarized in Hodshire et al. (2019) The orange horizontal lines are medians and the dotted horizontal lines are means. Solid circles are outliers.	220
B.23	End-of-experiment model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ($\mu\text{g m}^{-3}$), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments for three different assumptions about the scaling factor: constant scaling factor of 0.5 and 1 and a scaling factor as a function of the OA oxidation state.	220
C.1	Physical age plotted against the sampling time for the five transect sets and four wildfire plumes.	227
C.2	Box plots for (a) pressures and (b) temperatures encountered during the pseudo-Lagrangian evolution of smoke in the five transect sets and four wildfire plumes.	228

C.3	(a) POA volatility from May et al. (2013) and that used in this work expressed as the aerosol mass fraction against the OA mass concentration. The POA volatility based on the use of multi-ring aromatics was used with the base configuration of the SOM-TOMAS model while the POA volatility based on the use of other organic classes was used to perform sensitivity simulations. (b) Dependence of the OA O:C ratio as a function of the OA mass concentration. (c) Model species, shown in yellow, in the SOM grid used to represent the POA and SVOC mass. This distribution was informed based on the Monte-Carlo simulations performed and discussed in Section 3.2.	229
C.4	Predictions of the (a) OA and (b) CO concentrations from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. Model predictions are shown for five different simulations that vary in their assumptions about POA volatility and oxidation chemistry.	230
C.5	Same as Figure 4.4 but with the standard error in the mean for the observations.	230
C.6	Predicted POA (dotted lines) and SOA (solid lines) ratios with OA for the base simulation results presented in Figures 4 and 5.	231
C.7	Averaged and normalized, (a) volatility distribution and (b) mass distribution in carbon-oxygen space for the POA and SVOC emissions and (c) O:C ratio behavior with respect to total organic aerosol concentration quantified by Jen et al. (2019). Jen et al. (2019) only quantified 10 to 65% of the POA and SVOC mass collected on quartz filters. The volatility (c^*) was calculated for the POA and SVOC species using EPISuite v4.11 (EPA, 2021), and the Statistical Oxidation Model (SOM) parameterizations based on different surrogate (Cappa and Wilson, 2012; Jathar et al., 2015).	232
C.8	(a) POA volatility from May et al. (2013) and 1000 Monte Carlo simulations. The POA volatility based on the use of linear alkanes was used to perform Monte Carlo sensitivity simulations. (b) Dependence of the OA O:C ratio as a function of the OA mass concentration for all simulations. (c) Model volatility class from which one species was chosen randomly to perform Monte Carlo simulations.	233
C.9	Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the four different fires. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for the SVOC oxidation chemistry.	234
C.10	Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the four different fires. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for the POA volatility and SVOC oxidation chemistry.	234
C.11	Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for OH.	235

C.12 Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying ‘first’ transect.	235
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Chapter 1

Introduction

Overview

Atmospheric aerosols or particulate matter, defined as suspended tiny particles in the air, play a key role in air pollution and atmospheric processes (Seinfeld and Pandis, 2016). Air pollution reduces atmospheric visibility and has adverse effects on human health (Charlson, 1969; Nel, 2005) and climate. Currently, air pollution is recognized as a leading risk factor for human health globally (Fann et al., 2012; Stanaway et al., 2018). Adverse health effects of aerosols have been seen with increases in mortality, and cardio-pulmonary, respiratory and allergic diseases (Bernstein et al., 2004). In addition, aerosols have direct radiative effects and indirect radiative effects (Boucher et al., 2013; Charlson et al., 1992; Forster et al., 2007; Hobbs et al., 1997; Mahowald, 2011; Myhre, 2009). Aerosols scatter or absorb solar radiation, which directly impacts the energy budget of the Earth (Charlson et al., 1992). Aerosols can act as cloud-condensation nuclei and alter the cloud droplet number concentrations. Altering the cloud droplet number concentrations has two indirect effects on cloud properties and how they interact with solar radiation; the cloud droplet number concentrations affect (i) change in the reflectivity and brightness of clouds and (ii) the cloud lifetime and distribution in the atmosphere (Ackerman et al., 2004; Albrecht, 1989; Anderson et al., 2003; Charlson et al., 1992; Morgan et al., 2006; Penner, 2004; Pincus and Baker, 1994; Rosenfeld, 2006). Aerosols can also suppress precipitation regionally, which may impact global food security and human life (e.g. agriculture, land use, and water supply) (Givati and Rosenfeld, 2004; Rosenfeld, 2005).

Organic aerosol (OA) makes up a large fraction ($\sim 50\%$ on average) of submicron atmospheric particulate matter (de Gouw and Jimenez, 2009; Jimenez et al., 2009). The sources, atmospheric processes, and fate of OA are highly uncertain. Secondary OA (SOA) is formed when volatile organic compounds from various sources (e.g. biomass burning (Shrivastava et al., 2017), gasoline and diesel engines (Gentner et al., 2012), personal-care products (McDonald et al., 2018)) are

oxidized resulting in low volatility products that can partition to particles. Combustion sources contribute significantly to OA (both through primary OA emissions and emissions of SOA precursor vapors), especially in urban environments (e.g. gasoline and diesel engines) (Bond et al., 2004; Gentner et al., 2012; Jathar et al., 2014). However, a recent study showed that volatile chemical products (VCPs) not associated with combustion (such as the chemical compounds giving cleaning and personal-care products their scents) can contribute up to 50% of anthropogenic SOA in urban environments (McDonald et al., 2018). Biomass burning— including wildfire, agricultural fires, and prescribed burning— is also a large source of OA and combustion-related gas-phase organic compounds (OC) (Akagi et al., 2011; Andreae, 2019; Andreae and Merlet, 2001; Crutzen and Andreae, 1990; Granier et al., 2011; Lamarque et al., 2010; Reid et al., 2005; Westerling, 2016). Studies have shown that the frequency and intensity of wildfires has been increasing as the climate changes (Ford et al., 2018; Meehl and Tebaldi, 2004; Westerling, 2016; Westerling et al., 2006). The contribution of biomass burning to SOA is highly uncertain at both regional and global scales (Shrivastava et al., 2017). Since OA is a large fraction of atmospheric aerosol, it is critical to study where it comes from and how it evolves as it is transported in the atmosphere.

This thesis examines a variety of previously unconstrained factors that affect atmospheric OA. Each of these factors is explored in this thesis and is described in the paragraphs that follow.

OA Modeling: Atmospheric models are used both in research and regulatory applications to understand the impact of air pollution sources on air quality, human health, and climate. Improving atmospheric models will help us to come up with better solutions for mitigating the negative impacts of air pollution. Models can help us identify potential missing processes that lead to SOA formation and sources of OA and gas-phase OC. In urban environments, where combustion-related sources are the dominant sources of pollution, atmospheric models often underpredict the OA mass concentration suggesting that more work needs to be done to understand the underlying physical and chemical processes (Akherati et al., 2019; Carlton et al., 2010; Jathar et al., 2017; Volkamer et al., 2006).

Semivolatile organic compounds (SVOCs) and importance for OA: Studies have shown that primary organic aerosol (POA) that comes from combustion sources is semi-volatile (Grieshop et al., 2009a, 2009b; Huffman et al., 2009; Kuwayama et al., 2015; Lipsky and Robinson, 2006; May et al., 2013a, 2013b, 2013c; Robinson et al., 2007). After POA is released into the atmosphere and is diluted, it partitions between the gas and particle phases, which leads to (i) reduced particle-phase OA mass concentrations as POA evaporates and (ii) further gas-phase reactions of evaporated POA that potentially lead to SOA production. It is important to emphasize that meteorological factors (e.g. temperature, pressure, transport) play a role in the partitioning of OA.

Emission of intermediate volatility organic compounds (IVOCs) and associate SOA formation: IVOCs are organic species that are generally too volatile to contribute much to the particle-phase but lower in volatility than the more well-studied VOCs. IVOCs come from a variety of different sources (e.g. combustion sources, personal-care products) (Jathar et al., 2014; Koss et al., 2018; McDonald et al., 2018) and they are a complex mixture of different compounds. Due to the complexity of the IVOC chemical composition, IVOCs used to be defined as a fraction of total non-methane organic gases (NMOG) (Jathar et al., 2014). Recent studies have tried to quantify the direct emission of IVOCs (Koss et al., 2018). Importantly, it has been suggested, based on chamber experiments, that IVOCs form substantial amounts of SOA (Chan et al., 2009; Lim and Ziemann, 2009; Presto et al., 2010; Tkacik et al., 2017).

NO_x effects on SOA formation: NO_x concentrations, which are higher in urban areas and lower in remote continental/marine regions, affect organic chemistry and SOA production (Camredon et al., 2007; Chhabra et al., 2010; He et al., 2020; Loza et al., 2014; Ng et al., 2007a, 2007b; Yee et al., 2013). Under high NO_x regimes, RO₂ radicals, which are produced when VOCs react with an oxidant (e.g. hydroxyl radical, ozone, and nitrate radical), react with NO instead of HO₂. This leads to SOA formation pathways which may result in higher volatility and less SOA in the condensed phase. In contrast, in the absence of NO_x, RO₂ radicals react with either HONO₂ or RO₂ and produce lower volatility compounds, which increases SOA production (Ehn et al., 2014; Kroll and Seinfeld, 2008; Praske et al., 2018).

Vapor-wall-loss chamber artifacts in SOA chamber experiments: The SOA parameterizations commonly used in models mainly come from environmental chamber laboratory experiments and generally do not account for experimental artifacts, such as vapor wall losses (VWL). Gas-wall partitioning of oxidation products reduces the apparent SOA production during chamber experiments (Grosjean, 1985; Krechmer et al., 2016; La et al., 2016; Matsunaga and Ziemann, 2010; McMurry and Grosjean, 1985; Yeh and Ziemann, 2015; Zhang et al., 2014). During these experiments, oxidation products that have lower volatilities that can contribute to SOA formation condense strongly onto the Teflon® walls of the chamber and do not undergo further oxidation. As a result of VWL, these low-volatility oxidation products do not participate in SOA formation. However, in the atmosphere, these low-volatility oxidation products would mainly condense onto the particle-phase. Therefore, it is crucial to account for VWL artifacts in OA models to have a better representation of SOA production in models.

Objectives and research questions

In the second chapter, I tried to investigate SOA production 1) from POA evaporation and SVOC photochemistry, 2) from mobile source IVOCs, 3) under high and low NO_x conditions, and 4) accounting for vapor wall loss chamber experiment artifacts. To answer these questions, I improved a chemical transport model (UCD/CIT) by (i) allowing POA to be semivolatile, (ii) including IVOC emissions, (iii) accounting for the effect of NO_x and (iv) accounting for the effect of vapor wall losses in SOA parameterizations. Then, I tested the effects of these improvements by comparing model estimates to data from a field campaign over Southern California to examine whether OA prediction was improved.

In the third chapter, the research questions are whether I was able to explain the observed change in OA mass and composition and which gas-phase SOA precursors account for the SOA formation in biomass burning laboratory experiments. I developed and used a coupled chemistry-thermodynamics-microphysics organic aerosol model (SOM-TOMAS) to simulate the formation and composition of OA from new chamber experiments performed on emissions from burning biomass fuels representative of those found in the western US. This work provided insights into

how different classes of SOA precursors from biomass burning (BB) emissions behave when BBOA evolves in the atmosphere. I also investigated the effect of chamber experiment artifacts such as loss of gas-phase organic gases to the Teflon wall of the chamber and transfer ducts and quantified how these experimental artifacts could influence our OA estimates in the real world. Finally, I investigated how various emissions profiles can affect OA mass and composition predictions.

In the fourth chapter, I ask the following questions: 1) Does the OA evolve physically and chemically between the wildfire source and the first aircraft measurements? For safety considerations, aircraft often miss 20 minutes to an hour of photochemical aging. 2) What processes drive the differences between laboratory experiments and field measurements? 3) What gas-phase SOA precursors account for SOA formation in wildfire field campaign measurements? I used a plume version of SOM-TOMAS to simulate organic aerosol from aircraft measurements sampled over wildfires in the western US. I used this method to explore which processes drive the evolution of OA mass and composition and discussed differences between the laboratory and field measurements. I conducted sensitivity studies to test which assumptions about OA processes lead to the largest uncertainties in our predictions of OA mass and composition. Finally, I discuss how these findings address the known gaps between the laboratory experiments, field measurements, and modeling.

Chapter 2

Simulating secondary organic aerosol in a regional air quality model using the statistical oxidation model – Part 3: Assessing the influence of semi-volatile and intermediate volatility organic compounds and NO_x

2.1 Introduction

Organic aerosol (OA) is an important yet uncertain component of atmospheric aerosol (Fuzzi et al., 2015; Jimenez et al., 2009) and has large impacts on air quality, climate, and human health (Pachauri et al., 2014). Combustion sources such as motor vehicles, biomass burning, and food cooking are significant contributors to atmospheric OA from urban to regional to global scales (Bond et al., 2004). Yet, in urban environments where combustion emissions are a dominant source, atmospheric models often underpredict total OA mass concentrations (e.g., Carlton et al. (2010)). Models based on older parameterizations also predict much lower contributions of secondary organic aerosol in urban areas (e.g., Volkamer et al. (2006); Jathar et al. (2017a)), and may overemphasize the role of mobile sources (e.g., Ensberg et al. (2014)), suggesting that combustion-related OA and other urban sources may not be well represented in models. There is a need to improve the treatment of combustion-related OA in atmospheric models since these improvements will allow for better predictions of air quality that are needed to mitigate climate and health impacts from anthropogenic combustion sources, and will facilitate improved understanding of additional potentially missing sources.

Research over the past decade has made major inroads in understanding the sources and properties of combustion-related OA (Gentner et al., 2017). Combustion sources directly emit organic particles (primary organic aerosol, POA) and also emit gaseous organic compounds that are oxidized in the atmosphere to form secondary organic aerosol (SOA). A significant fraction of the combustion-related POA mass is now understood to be semi-volatile, that is material that exists in a dynamic equilibrium between the vapor and particle phases (Grieshop et al., 2009a, 2009b; Huffman et al., 2009; Kuwayama et al., 2015; Lipsky and Robinson, 2006; May et al., 2013a, 2013b, 2013c; Robinson et al., 2007). This POA is formed as vapors in the combustion exhaust cool down to become supersaturated and condense on existing seed aerosol (Robinson et al., 2010). After emission, some of this POA evaporates with atmospheric dilution since the aerosol mass available for partitioning decreases as the POA is transported away from source regions. Further, diurnal changes in temperature leading to changes in the vapor pressure can also cycle POA between the two phases. Both vapor and particle forms of semi-volatile POA have been shown to photochemically react in the atmosphere to add or remove organic material from the particle-phase (Miracolo et al., 2010) and become more oxygenated (Kroll et al., 2009), although the vapors react much faster. In addition, all combustion processes are now believed to include emissions of an important additional class of SOA precursors: intermediate-volatility organic compounds (IVOCs) (Jathar et al., 2014). Gas-chromatography mass-spectrometry applications have suggested that they are primarily composed of high molecular weight linear, branched, and cyclic alkanes (carbon numbers greater than 12) and aromatics (Gentner et al., 2012; Zhao et al., 2014, 2017). Model IVOCs have been shown to form SOA efficiently in chamber experiments (Chan et al., 2009; Lim and Ziemann, 2009; Presto et al., 2010; Tkacik et al., 2012) and have been hypothesized to account for a large fraction of the SOA formed from the photooxidation of motor vehicle exhaust and biomass burning emissions (Jathar et al., 2014; Zhao et al., 2017). The emissions and atmospheric properties (e.g., volatility, reactivity, SOA mass yields) of POA and IVOCs are known (or very likely) to vary by source (e.g., mobile sources versus biomass burning) and hence atmospheric models need

to include a source-resolved treatment to accurately predict source contributions to OA and fine particulate matter.

Most commonly used chemical transport models (e.g., CMAQ, CAMx, PMCAMx, WRF-Chem, GEOS-Chem) have been updated to include a semi-volatile and reactive treatment of POA and emissions and SOA formation from IVOCs (Ahmadov et al., 2012; Koo et al., 2014; Murphy and Pandis, 2009; Pye and Seinfeld, 2010). However, their representation in models has been based on limited data and there are major differences between the implementations in different models. For example, in most models, with a few exceptions (e.g., most recent research version of the OA model in CMAQ developed by Koo et al. (2014)), the gas/particle partitioning of POA was modeled based on measurements performed on a small off-road diesel engine from more than a decade ago (Robinson et al., 2007) and IVOC emissions were based on data gathered from two medium duty diesel vehicles from two decades ago (Schauer et al., 1999). Models have assumed that these data are representative of emissions from modern diesel-powered sources and the POA/IVOC properties from diesel sources are similar to those from other sources. New source data are now available to update POA and IVOC emissions estimates in chemical transport models. Further, the most common schemes to model SOA formation from POA vapors and IVOCs use a single lumped precursor to simulate SOA formation from all sources (e.g., Pye and Seinfeld (2010)) or use an ad hoc aging routine that continuously reduces the volatility of the precursor/oxidation products until they partition into the particle phase (Robinson et al., 2007). While some of these schemes have been validated against experimental data (Fountoukis et al., 2016; Hodzic and Jimenez, 2011; Murphy et al., 2017; Zhang et al., 2015), most have assumed that all sources have the same rate and potential to form SOA and, in some cases, ignore fragmentation reactions tied to multigenerational chemistry. Ad hoc aging schemes can overestimate net aerosol mass yields from an SOA precursor and can sometimes overpredict ambient SOA mass concentrations too, especially over larger regional scales (Dzepina et al., 2009, 2011; Hayes et al., 2015; Jathar et al., 2016). Recently, a host of studies have quantified the volatility of POA emissions from over 100 unique sources and measured SOA formation in more than 100 chamber experiments across six broad source classes:

on- and off-road gasoline and diesel sources, wood stoves, and biomass burning (Gordon et al., 2014a, 2014b; Hennigan et al., 2011; May et al., 2013a, 2013b, 2013c, 2014; Tkacik et al., 2017). These data offer a comprehensive set of measurements to inform and update the source-resolved semi-volatile and reactive behavior of POA and the emissions and SOA formation from IVOCs in atmospheric models.

SOA formation is strongly influenced by the presence of NO_x (Camredon et al., 2007; Chhabra et al., 2010; Loza et al., 2014; Ng et al., 2007b). For most SOA precursors, with the exception of alkanes (Loza et al., 2014) and certain sesquiterpenes (Ng et al., 2007b), environmental chamber data suggest that the reaction chemistry at low NO_x , or more precisely low NO, conditions (<2 ppbv) produces more SOA than at high NO_x conditions (>50 ppbv and up to ~ 1 ppmv) (Camredon et al., 2007; Chhabra et al., 2010; Loza et al., 2014; Ng et al., 2007; Zhang et al., 2014). The consensus seems to be that at low NO_x conditions such as those found in remote continental or marine regions the peroxy radical (RO_2) – formed immediately after the reaction of the precursor with the oxidant – combines with the hydroperoxy radical (HO_2) or RO_2 to form lower volatility hydroperoxides or organic peroxides (Kroll and Seinfeld, 2008). Low NO conditions in remote regions, and in some cases in urban regions that have recently witnessed dramatic reductions in NO_x concentrations, can promote autooxidation reactions to form extremely low-volatility organic compounds (Ehn et al., 2014; Praske et al., 2018). At high NO_x , or more precisely high NO, conditions such as those found in urban regions or biomass burning plumes, the RO_2 reaction with NO either leads to the formation of alkoxy radicals that can then fragment the carbon backbone, or to the formation of organic nitrates where both reactions result in more volatile products (Kroll and Seinfeld, 2008). Most atmospheric models (e.g., CMAQ, WRF-Chem, GEOS-Chem) have incorporated this knowledge to account for the influence of NO_x on the magnitude, composition, and spatial distribution of SOA.

In the mostly commonly used scheme (i.e., Henze et al. (2008)), RO_2 reacts with HO_2 to form ‘low-NO’ SOA or with NO to form ‘high-NO’ SOA. The HO_2 :NO ratio determines the branching ratio for RO_2 and controls the SOA formed under varying NO_x levels. The SOA yields under

the low and high NO_x conditions are parameterized based on chamber data gathered under low and high NO_x conditions respectively. Despite being widely implemented, this scheme has one key limitation that might tend to bias the NO_x -dependent predictions of SOA. This scheme relies on an accurate prediction of NO and HO_2 to determine the branching ratio for the RO_2 radical. Although NO predictions can be validated against routine measurements and most chemical mechanisms seem to predict NO_x ($\text{NO} + \text{NO}_2$) within a factor of 2, there are very few ambient data to validate model predictions of HO_2 . For example, as will be shown later, we find that predictions of HO_2 concentrations from the use of a typical gas-phase chemical mechanism (SAPRC-11) in a 3D model at Pasadena, CA were almost an order of magnitude lower when compared against measurements at the same site in 2010 (Griffith et al., 2016). In this case, underpredicting HO_2 concentrations by an order of magnitude could shift the scheme to produce most of the SOA via the high NO pathway. In contrast, box models that have used the regional atmospheric chemistry mechanism (RACM) have shown good model-measurement comparisons for HO_2 concentrations in polluted regions (Griffith et al., 2016; Hofzumahaus et al., 2009). Regardless, gas-phase chemical mechanisms that use the aforementioned scheme need to ensure accurate predictions of HO_2 and NO concentrations to simulate the influence of NO_x on SOA formation.

In this work, we update the organic aerosol model in the UCD/CIT chemical transport model to include a semi-volatile and reactive treatment of POA, emissions and SOA formation from IVOCs, the NO_x influence on SOA formation, and SOA parameterizations for SVOCs and IVOCs that are corrected for vapor wall loss artifacts during chamber experiments. All of these updates are implemented in the statistical oxidation model (SOM) that simulates the oxidation chemistry, thermodynamics, and gas/particle partitioning of OA. Model inputs for POA and IVOCs are based on an interpretation of a comprehensive set of source measurements and resolved broadly by the source type. The NO_x influence on SOA formation is calculated offline based on measured and modeled $\text{VOC}:\text{NO}_x$ ratios and NO_x concentrations. And finally, the SOA formation from SVOCs and IVOCs is modeled based on recently derived parameterizations that account for vapor wall loss artifacts in chamber experiments. Building on our earlier work (Cappa et al., 2016; Jathar et al.,

2015, 2016), these updates within the framework of the SOM have improved the representation of OA in a chemical transport model.

To help the reader, we provide a brief overview of the different sections in this manuscript (section numbers in parentheses). Section 2.2 discusses details of the chemical transport model (2.2.1), organic aerosol model (2.2.2), simulations performed (2.2.3), and measurements used for model evaluation (2.2.4). In Section 2.3, we first describe the emissions (2.3.1), spatial distribution (2.3.2), and precursor contributions to OA (2.3.3), followed by the influence of vapor wall losses (2.3.4) and NO_x (2.3.6) on SOA formation. In the same section, we describe results from sensitivity simulations performed on the most sensitive inputs (2.3.5). Next, we compare model predictions of SOA precursors (2.4.1), OA (2.4.2), POA, and SOA (2.4.3) mass concentrations, and OA elemental composition (2.4.4) against measurements in southern California. Finally, we highlight key findings from this work in the summary and discussion section (2.5).

2.2 Methods

2.2.1 Chemical Transport Model

We used the UCD/CIT regional chemical transport model (Kleeman and Cass, 2001) to simulate the emissions, transport, chemistry, and deposition of air pollutants over the state of California at a grid resolution of 24 km and over southern California (see Fig. S1) using a nested 8 km grid from 20th July to 2nd August 2005. The results and analysis were focused on model predictions over Southern California because the region, with approximately 15 million people, is home to one of the most polluted cities in the United States (Los Angeles; ALA (2017)). The time period for simulation was primarily chosen because the model has been previously evaluated for this time period (Jathar et al., 2016) and applied to examine important sources and formation pathways of OA (Cappa et al., 2016; Jathar et al., 2015, 2016, 2017b). The recent literature describes the latest version of the UCD/CIT model but we provide a very brief description of the models and inputs used in this work. Anthropogenic emissions for California were developed using the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) inventory of 2000 but scaled to match

conditions in 2005. Wildfire emissions were based on the model FINN (Fire Inventory for National Center for Atmospheric Research) (Wiedinmyer et al., 2011) although they were not found to significantly contribute to OA during the simulated time period (Docherty et al., 2011). Biogenic emissions were based on the model MEGAN (Model of Emissions of Gases and Aerosols from Nature) (Guenther et al., 2006). The Weather Research and Forecasting (WRF) v3.4 model (www.wrf-model.org) was used to produce hourly meteorological fields. National Center for Environmental Protection's NAM (North American Mesoscale) analysis data were used to set the initial and boundary conditions for WRF. The gas- and particle-phase initial and hourly varying boundary conditions were based on the results from the global model MOZART-4/NCEP (Emmons et al., 2010). The gas-phase chemistry was modeled using SAPRC-11 (Carter, 2010).

2.2.2 Organic Aerosol Model

Statistical Oxidation Model (SOM)

In this work, we use the Statistical Oxidation Model (SOM) developed by (Cappa and Wilson, 2012). The SOM is a semi-explicit and parameterizable model that simulates the oxidation chemistry, thermodynamics, and gas/particle partitioning of OA and its precursors. The SOM has been used to model SOA formation in chamber (Cappa et al., 2013; Cappa and Wilson, 2012; Zhang et al., 2014) and flow reactor (Eluri et al., 2017) experiments. and was recently coupled with SAPRC-11 (gas-phase chemical mechanism) in the UCD/CIT model (Jathar et al., 2015) to investigate the role of chamber-based vapor wall losses (Cappa et al., 2016) and multigenerational aging (Jathar et al., 2016) on the ambient SOA burden. In this work, we used an updated version of the SAPRC-SOM model embedded in the UCD/CIT model that included the POA and IVOC updates described in Section 2.2.2. A detailed description of the mathematical and numerical formulation of the SOM can be found in earlier literature but a brief description of the SOM framework follows. The SOM uses a 2-dimensional carbon-oxygen grid to describe and track the evolution of the gas- and particle-phase organic carbon that is known to yield OA. Each grid cell in the SOM represents an organic species with the molecular formula: $C_xH_{2X+2-Z}O_Z$, where $X=N_C$,

and $Z=N_O$. This species is expected to capture the average properties (e.g. volatility, reaction rate constants) of species with the same number of carbon (N_C) and oxygen (N_O) atoms that are formed from a given SOA precursor. Each species, in the gas and particle phases, is assumed to react with the hydroxyl radical (OH). Operationally, OH is not consumed within the SOM as the chemistry captured in the SOM overlaps with that represented in the gas-phase mechanism (i.e., SAPRC-11). Reactions with the OH radical result in functionalization or fragmentation of the organic species and the distribution of the reaction products is tracked in the carbon-oxygen grid. Six precursor-specific adjustable parameters are assigned for each SOM grid: four parameters that define the molar yields of the four functionalized, oxidized products (P_{func}), one parameter that determines the probability of functionalization or fragmentation (m_{frag}) and one parameter that describes the relationship between N_C , N_O and volatility (ΔLVP). In the model, the probability of fragmentation is modeled as a function of the O:C ratio since species with higher O:C ratios have been shown to fragment much more easily than species with lower O:C ratios (Chacon-Madrid and Donahue, 2011). All SOM species properties (e.g., OH reactivity, volatility) are described in terms of N_C and N_O .

Seven SOM grids were used to represent SOA formation from nine different precursor classes: (i) long alkanes, (ii) benzene, (iii) high-yield aromatics, (iv) low-yield aromatics, (v) isoprene, (vi) monoterpenes, (vii) sesquiterpenes, (viii) semi-volatile POA (SVOC), and (ix) IVOCs. Long alkanes as a precursor class includes linear, branched, and cyclic alkanes roughly up to a carbon number of C_{13} and represent they speciated alkanes present in existing emissions inventories. These long alkanes are distinct from the alkanes that might be present in SVOC and IVOCs. High-yield and lower-yield aromatics include all speciated aromatic compounds present in existing emissions inventories and, similar to the long alkanes precursor class, are distinct from the aromatics that might be present in SVOC and IVOCs. Classes (i) through (vii) have been included in previous applications of the SOM and we refer the reader to our earlier publications for more details (Cappa et al., 2016; Jathar et al., 2015, 2016). Classes (viii) and (ix) were included in this work for the first time. The SOA formation from monoterpenes and sesquiterpenes (classes vi and vii) was modeled

in the same SOM grid since both precursors used the SOM parameter sets for α -pinene. Similarly, the SOA formation from SVOCs and IVOCs was modeled in the same SOM grid and both used the SOM parameter sets for n-dodecane; sensitivity simulations were performed using the SOM parameter set for toluene. SOM parameters were determined from fitting the observed SOA volume produced in chamber experiments, with and without accounting for losses of vapors to the chamber walls. Details about how the vapor wall losses were modeled are described in Zhang et al. (2014) and Cappa et al. (2016). Briefly, loss of vapors to the Teflon walls of the chamber was modeled reversibly where the first-order uptake to the walls was assumed to be $2.5 \times 10^{-4} \text{ s}^{-1}$ and the release of vapors from the walls was modeled using absorptive partitioning theory with the Teflon wall serving as an absorbing mass with an effective mass concentration of 10 mg m^{-3} . Recent work has argued that vapor wall loss rates in Teflon chambers are much higher (larger than a factor of 5) than those used by Cappa et al. (2016) to derive the SOM parameterizations (Huang et al., 2018; Krechmer et al., 2016; Sunol et al., 2018). The use of a higher wall loss rate will tend to increase SOA aerosol mass yields further. This new understanding will need to be considered in the future.

We used low and high NO_x -specific parameter sets to simulate SOA formation separately under low and high NO_x conditions respectively since the current version of the SOM cannot account for continuous variation in NO_x . The SOM parameters used for the nine different classes and seven different grids are listed in Table 2.1. Parameters for all species except for isoprene were from Cappa et al. (2016). The parameters for isoprene were from Hodzic et al. (2016) that included updates for the reactions rate constants for the first generation products from isoprene photooxidation. Jathar et al. (2016) investigated the influence of oligomerization reactions by allowing irreversible conversion of particle-phase SOM species into a single non-volatile species and found that the oligomerization pathway (as simulated) did not substantially affect the OA mass concentration in Southern California. Hence, the oligomerization pathway was not considered in this work. We also did not include the formation of extremely low-volatility organic compounds from oxidation of SOA precursors such as α -pinene (Ehn et al., 2014) and alkanes (Praske et al.,

2018) through autooxidation pathways, which will very likely be addressed in future versions of the SOM.

array

Table 2.1: SOA precursors and SOM parameters used in this work. VWL=Vapor Wall Loss Corrected, Δ LVP = change in vapor pressure linked to addition of one oxygen atom, P_{func} = molar yields of species that add 1 to 4 oxygens per reaction (Pf_1 through Pf_4), m_{frag} = exponent influencing the probability of fragmentation.

SOA Precursors	SAPRAC Species /SOM Grid	SOM Surrogate	VWL	NO _x	ΔLVP	P _{func}				m _{frag}	Reference
						Pf ₁	Pf ₂	Pf ₃	Pf ₄		
SVOC/ IVOC	POA+IVOC	n-dodecane/ toluene	No	Low	1.54	0.717	0.278	0.0028	0.0022	0.122	Loza et al. (2014)
Alkanes	ALK			High	1.39	0.927	0.0101	0.018	0.0445	0.098	
			Yes	Low	1.83	0.999	0.001	0.001	0.001	2	
High	1.47			0.965	0.001	0.002	0.032	0.226			
Benzene	BENZ	benzene	No	Low	2.01	0.769	0.001	0.0505	0.180	2.010	Ng et al. (2007a)
				High	1.70	0.079	0.001	0.919	0.001	0.535	
			Yes	Low	1.97	0.637	0.001	0.002	0.360	0.0807	
				High	1.53	0.008	0.001	0.991	0.001	0.824	
High-yield aromatics	ARO1	toluene	No	Low	1.84	0.561	0.001	0.001	0.438	0.010	Zhang et al. (2014)
				High	1.24	0.003	0.001	0.001	1.010	0.222	
			Yes	Low	1.77	0.185	0.001	0.002	0.812	1.31	
				High	1.42	0.856	0.001	0.002	0.141	4.61	
Low-yield aromatics	ARO2	m-xylene	No	Low	1.76	0.735	0.001	0.002	0.262	0.010	Ng et al. (2007a)
				High	1.68	0.936	0.001	0.002	0.061	0.010	
			Yes	Low	2.05	0.102	0.001	0.878	0.019	1.08	
				High	1.46	0.001	0.001	0.942	0.056	0.0671	
Isoprene	ISOP	isoprene	No	Low	2.26	0.973	0.001	0.001	0.026	0.010	Chhabra et al. (2011); Hodzic et al. (2016)
				High	1.94	0.952	0.001	0.030	0.016	0.063	
			Yes	Low	2.25	0.1646	0.5164	0.3012	0.0179	0.0244	
				High	1.93	0.998	0.0002	0.0116	0.0009	0.51	
Monoterpenes /Sesquiterpenes	TRP	α-pinene	No	Low	1.87	0.001	0.869	0.078	0.053	0.010	Chhabra et al. (2011)
				High	1.62	0.068	0.633	0.275	0.024	0.035	
			Yes	Low	1.97	0.419	0.426	0.140	0.014	0.305	
				High	1.91	0.500	0.422	0.070	0.008	0.16	

Model Inputs

Semi-Volatile and Reactive POA (SVOC). POA from gasoline, diesel, biomass burning, and food cooking sources was treated as semi-volatile and reactive. POA from all other sources (e.g., marine, dust) was assumed to be non-volatile in all simulations except one where we explored the sensitivity in model predictions to this assumption (see Section 2.2.3 for more details). Semi-volatile POA was modeled by distributing POA emissions from the emissions inventory in the SOM grid as hydrocarbon species modeled as linear alkanes, i.e. as species with no oxygen (i.e., C_XH_Y). The hydrocarbon/linear alkane distribution in the SOM grid was determined by refitting the volatility distributions published by May and coworkers (May et al., 2013a, 2013b, 2013c) such that the hydrocarbon distribution reproduced the observed gas/particle partitioning behavior; the hydrocarbon distributions are listed in Table A.1. We assumed all on- and off-road gasoline exhaust POA to have the same hydrocarbon/linear alkane distribution as the volatility distribution determined by May et al. (2013a) from data for 51 light-duty gasoline vehicles. Almost three-quarters of the light-duty gasoline vehicles used in May et al. (2013a) were manufactured in or prior to 2005 (the year modeled in this work) and they did not find the POA volatility distribution data to be sensitive to the model year of the vehicle. Hence, the volatility distribution used in this work should still be representative of the vehicle fleet in 2005. Based on tests performed on eight light-duty gasoline vehicles, Kuwayama et al. (2015) found that the POA volatility for their vehicles was consistent with that determined by (May et al., 2013a) for about half the vehicles but substantially lower for the other half. They hypothesized that the lower POA volatility could be attributed to fuel oxidation products. The findings of Kuwayama et al. (2015) suggest that the volatility distribution used in this work may overestimate the evaporation of POA with dilution. We assumed all on- and off-road diesel exhaust POA to have the same hydrocarbon/linear alkane distribution as the volatility distribution determined by May et al. (2013b) from data for two medium-duty diesel trucks, three heavy-duty diesel trucks, and a single off-road diesel engine. May et al. (2013b) did not report on differences in the POA volatility distribution between vehicles that did or did not use a modern emissions control system (diesel particulate filter (DPF) and/or

diesel oxidation catalyst (DOC)). Hence, we assumed that the volatility distribution used here was still representative of the mostly non-DPF and non-DOC vehicle fleet in 2005. We assumed residential wood combustion and wildfires to have the same hydrocarbon/linear alkane distribution as the volatility distribution determined by May et al. (2013c) from a selection of fifteen different fuels. We assumed food cooking to have the same hydrocarbon/linear alkane distribution as that for wildfires. Recent work suggests that food cooking OA may be significantly less volatile than wildfire OA (Louvaris et al., 2017; Woody et al., 2016). To examine the influence of this finding, we performed sensitivity simulations to model the POA from food cooking sources using the volatility distribution of Louvaris et al. (2017). This work, similar to the most recent implementation in the Community Multiscale Air Quality (CMAQ) model (Koo et al., 2014; Woody et al., 2016), included a source-resolved treatment of semi-volatile POA that was tied to a comprehensive set of source measurements.

The reactive behavior of POA was modeled by assuming that the POA vapors (i.e. SVOCs) (represented as a hydrocarbon distribution) and their products participated in gas-phase oxidation and formed SOA similar to linear alkanes and utilized the SOM parameter set for n-dodecane. The surrogate, in this case n-dodecane, only informs the multi-generational oxidation chemistry of the precursor and the actual compound of interest (e.g., a C_{15} linear alkane) can have a different SOA mass yield than that of n-dodecane. The reaction rate constants with OH for the parent hydrocarbons were assumed to be similar to the carbon-equivalent linear alkane. We should note that the presence of branched/cyclic alkane and aromatic compounds in the SVOCs would require the use of a higher reaction rate constant with OH as these compounds are more reactive with OH than carbon-equivalent linear alkanes. The equivalence to linear alkanes while not perfect was probably a good assumption for gasoline and diesel sources since alkanes account for a substantial fraction of gasoline and diesel fuel (Gentner et al., 2012) and lubricating oil (Caravaggio et al., 2007) and are a dominant organic class in both gas- and particle-phase emissions from mobile sources (Brandenberger et al., 2005; Hays et al., 2017; Schauer et al., 1999, 2002b)(Worton et al., 2014). However, alkanes do not make up a significant fraction of the gas- and particle-phase emissions

from biomass burning (Hatch et al., 2015; Schauer et al., 2001; Stockwell et al., 2015) or food cooking (Schauer et al., 2002a) and hence it is unlikely that linear alkanes are good surrogates to model the oxidation of SVOCs from these sources. To test the sensitivity of the model predictions to the surrogate used to model SOA formation from SVOCs, we ran sensitivity simulations where we modeled the SVOCs as a mixture of aromatic compounds using the SOM parameter set for toluene (see rationale in Section 2.2.4).

Intermediate-Volatility Organic Compounds. We included IVOC emissions from gasoline, diesel, and biomass burning. We assumed none of the other sources emitted IVOCs for all simulations except one where we explored the sensitivity in model predictions to this assumption (see Section 2.2.4 for more details). The IVOC emissions estimates and their potential to form SOA was based on the work of Jathar et al. (2014). In Jathar et al. (2014), IVOC emissions, defined as the sum of all unspciated compounds, were determined as a mass fraction of the total non-methane organic gas (NMOG) emissions for three different source categories: gasoline vehicles, diesel vehicles, and biomass burning. Here, the IVOCs, as unspciated organic compounds, are new SOA precursors added to the emissions inventory and regardless of their chemical makeup are distinct from the speciated precursors such as long alkanes and aromatics already present in existing emissions inventories. IVOCs were assumed to be 25% of the NMOG emissions for on- and off-road gasoline exhaust, 20% of the NMOG emissions for on- and off-road diesel exhaust, and 7% of the NMOG emissions for residential wood combustion and wildfires. The IVOC:NMOG fractions did not appear to be statistically different for the gasoline and diesel sources manufactured before or after 2005 and hence those fractions were assumed to be representative of the source fleet in 2005. No IVOCs were considered for the food cooking source but recent work suggests that they might play a role in influencing the OA evolution from a multitude of food cooking sources (Kaltsonoudis et al., 2017; Liu et al., 2017). We assumed that the NMOG emissions in the emissions inventory accounted for most of the gas-phase organic compound mass that included the IVOCs and hence the addition of IVOC emissions meant that the non-IVOC emissions had to be reduced to conserve total NMOG mass. Recent literature suggests that IVOCs could be lost to walls of the sampling

hardware (e.g., tubing, bags) (Pagonis et al., 2017) and therefore would be excluded in the NMOG measurement. Our assumption should result in conservative estimates for the influence of IVOC emissions on SOA formation.

Following Jathar et al. (2014), the IVOCs were modeled as a C_{13} hydrocarbon for those from on- and off-road gasoline sources and as a C_{15} hydrocarbon for those from on- and off-road diesel sources and biomass burning. The oxidation of the IVOC hydrocarbons and their reaction products and the subsequent SOA formation was modeled assuming equivalence to a linear alkane and used the SOM parameter set for n-dodecane. As mentioned earlier, n-dodecane only informs the multi-generational oxidation chemistry of the precursor and the actual compound of interest (e.g., a C_{13} or C_{15} linear alkane) can have a different SOA mass yield than that of n-dodecane. The equivalent linear alkane to model SOA formation from IVOCs in Jathar et al. (2014) was based on fitting the SOA formation observed in chamber experiments (Gordon et al., 2014a, 2014b; Hennigan et al., 2011) and hence the choice of the hydrocarbon in this work was experimentally constrained. Jathar et al. (2014) used linear alkanes as a surrogate as the SOA formation from linear alkanes was well studied when they developed the parameterization and the SOA mass yields increased predictably with the carbon number of the precursor. Recent application of gas-chromatography mass-spectrometry to combustion emissions has found that IVOCs are mostly composed of branched/cyclic alkane and aromatic compounds (Gentner et al., 2012; Koss et al., 2018; Zhao et al., 2016, 2017). So while it would have been more appropriate to model the IVOCs as an alkane-aromatic mixture, this choice would not have substantially changed the model predictions in the work as the SOA formation from this alkane-aromatic mixture would still be constrained to the same chamber experiments. We will consider the recent detailed speciation work surrounding IVOCs in future applications of this model. In this work, we also investigated the sensitivity in model predictions to the use of an aromatic compound (i.e., toluene) as a surrogate instead of an alkane (i.e., n-dodecane) to model SOA formation from IVOCs (see rationale in Section 2.2.4).

Recently, Zhao and coworkers (Zhao et al., 2015, 2016) used thermal desorption gas-chromatography mass spectrometry (TD-GC-MS) to measure IVOC emissions in gasoline and diesel exhaust and speciated/classified the IVOCs as a mixture of linear, branched, and cyclic compounds resolved by carbon number. We should note that Zhao et al. (2015, 2016) defined IVOCs as the sum of speciated and unspeciated hydrocarbons roughly larger than a C12 alkane, which was different from the definition adopted by Jathar et al. (2014). In their first paper, Zhao et al. (2015) found IVOCs to be about 60% of the NMOG mass emissions for tailpipe exhaust from older diesel vehicles/engines (ones without particle filters or oxidation/reduction catalysts). In this work we used an IVOC:NMOG ratio of 0.2 and likely underestimated IVOC emissions from diesel sources by a factor of 2.5. Zhao et al. (2015) concluded that the effective IVOC yield based on their speciation was comparable to the yield of the C15 linear alkane used in this work but the application of that yield over-predicted the chamber SOA data from Gordon et al. (2014a) by a factor of 1.8; virtually all of the SOA predicted by Zhao et al. (2016) was from the oxidation of IVOCs. If one assumed that the effects from lower IVOC emissions (factor of 2.5) were roughly balanced by the use of higher SOA yields (factor of 1.8), then the SOA formation from diesel sources was probably well represented in our work.

In their second paper, Zhao et al. (2016) found the IVOCs to be only about 4% of the NMOG mass emissions in gasoline exhaust but we used an IVOC:NMOG ratio of 0.25 in this work. This suggests that we may be overestimating the gasoline exhaust IVOC emissions by approximately a factor of six in this work. Based on the speciation performed, Zhao et al. (2016) estimated that the IVOCs collectively had an SOA yield between 19 and 24% at an OA mass concentration of $9 \mu\text{g m}^{-3}$ ($9 \mu\text{g m}^{-3}$ was the average end-of-experiment concentration in the chamber experiments of Gordon et al. (2014a)), which was slightly more than twice the SOA yield for a C13 linear alkane (7-12%) – used to model gasoline IVOCs in this work – at the same OA mass concentration. However, application of the Zhao et al. (2016) SOA yields for IVOCs underpredicted the observed chamber SOA formation for newer gasoline vehicles by a factor of ~ 2 . Since IVOC oxidation accounted for slightly less than half of the SOA formed (with the other half coming from single-

ring aromatics), the IVOC SOA yields in Zhao et al. (2016) would need to be tripled to explain the chamber SOA measurements. If we assumed that the effects from higher IVOC emissions (factor of 6) were approximately balanced by the use of lower SOA yields (factor of $2 \times 3 = 6$), then the SOA formation from gasoline sources in this work was probably well represented in our work. To summarize, the IVOC emissions estimates and the surrogates used to model SOA formation from IVOCs from gasoline and diesel sources in this work, while different from those suggested in Zhao et al. (2015, 2016), are still consistent with the SOA measurements made by Gordon et al. (2014a, 2014b). In a future version of the model, we will aim to include the IVOC emissions estimates of Zhao et al. (2015, 2016) and update the SOA parameterizations accordingly. It is likely that these might slightly alter the spatiotemporal distribution of IVOC SOA in the modeled domain.

Modeling the NO_x Dependence on SOA Formation

Previous applications of the SOM have simulated SOA under low and high NO_x conditions separately since the SOM, in its current form, cannot model the continuous evolution of SOA under varying NO_x conditions using the local NO/HO_2 . Predictions from either of these simulations (Jathar et al., 2016) or the average of these simulations (Cappa et al., 2016) likely do not accurately characterize the evolution or spatial distribution of SOA since NO_x concentrations exhibit strong spatial variability with higher concentrations in urban (e.g., traffic) and source (e.g., wildfires) regions. For example, since most precursors have higher SOA yields under low NO_x conditions than under high NO_x conditions, the use of an average is expected to overestimate SOA in high- NO_x urban areas and underestimate SOA in low- NO_x rural/remote continental areas.

In this work, we used two different offline techniques to account for the influence of NO_x on SOA formation. For both methods, we assumed that the 3D model predictions based on the low and high NO_x SOA parameterizations bounded the minimum and maximum ambient SOA mass concentrations. Xu et al. (2015) found that the SOA formation from isoprene photooxidation was maximized at intermediate NO_x levels with lower values at the extreme NO_x levels, suggesting that our bounding assumption may not necessarily hold for all precursor species. Presto and Donahue (2006) found that the SOA from α -pinene ozonolysis under varying NO_x conditions could be

estimated by interpolating the SOA formed between the low and high NO_x conditions using the $\text{VOC}:\text{NO}_x$ ratio. Hence, in the first method, we used the $\text{VOC}:\text{NO}_x$ ratios from the low and high NO_x chamber experiments as our bounds and used the 3D model predicted $\text{VOC}:\text{NO}_x$ ratio to interpolate between the minimum and maximum SOA mass concentrations predicted from the low and high NO_x simulations. Previous work (e.g., Camredon et al. (2007), Xu et al. (2015)) has also found SOA formation to vary along a NO_x scale and hence, in the second method, we used NO_x concentrations from the low and high NO_x chamber experiments and the 3D model predictions to perform the interpolation. For each method, we performed the interpolation on the SOA mass concentrations assuming a linear or logarithmic dependence on the $\text{VOC}:\text{NO}_x$ ratios and NO_x concentrations. The linear dependency was chosen for simplicity while the logarithmic dependency was chosen to mimic the visual trends in SOA and $\text{VOC}:\text{NO}_x$ or NO_x reported in previous work and also to produce the highest response in the SOA formation with NO_x . The $\text{VOC}:\text{NO}_x$ ratio and the NO_x concentration served as an approximate surrogate for the $\text{HO}_2:\text{NO}$ ratio used in most atmospheric models to simulate the NO_x -dependent SOA formation. The NO_x -adjusted SOA concentrations (SOA_{eff}) from each precursor at each grid cell were calculated from model predictions from the low and high NO_x simulations using the following equations:

$$\text{SOA}_{\text{eff}} = \text{SOA}_{\text{high NO}_x} + \frac{\text{SOA}_{\text{low NO}_x} - \text{SOA}_{\text{high NO}_x}}{(\text{VOC} : \text{NO}_x)_{\text{low NO}_x} - (\text{VOC} : \text{NO}_x)_{\text{high NO}_x}} \times ((\text{VOC} : \text{NO}_x)_{\text{model}} - (\text{VOC} : \text{NO}_x)_{\text{high NO}_x}) \quad (2.1)$$

$$\text{SOA}_{\text{eff}} = \text{SOA}_{\text{high NO}_x} + \frac{\text{SOA}_{\text{low NO}_x} - \text{SOA}_{\text{high NO}_x}}{\log(\text{VOC} : \text{NO}_x)_{\text{low NO}_x} - \log(\text{VOC} : \text{NO}_x)_{\text{high NO}_x}} \times (\log(\text{VOC} : \text{NO}_x)_{\text{model}} - \log(\text{VOC} : \text{NO}_x)_{\text{high NO}_x}) \quad (2.2)$$

$$\text{SOA}_{\text{eff}} = \text{SOA}_{\text{low NO}_x} - \frac{\text{SOA}_{\text{low NO}_x} - \text{SOA}_{\text{high NO}_x}}{(\text{NO}_x)_{\text{high NO}_x} - (\text{NO}_x)_{\text{low NO}_x}} \times ((\text{NO}_x)_{\text{model}} - (\text{NO}_x)_{\text{low NO}_x}) \quad (2.3)$$

$$\text{SOA}_{\text{eff}} = \text{SOA}_{\text{low NO}_x} - \frac{\text{SOA}_{\text{low NO}_x} - \text{SOA}_{\text{high NO}_x}}{\log(\text{NO}_x)_{\text{high NO}_x} - \log(\text{NO}_x)_{\text{low NO}_x}} \times (\log(\text{NO}_x)_{\text{model}} - \log(\text{NO}_x)_{\text{low NO}_x}) \quad (2.4)$$

where SOA_{lowNO_x} and SOA_{highNO_x} are model predictions of SOA from using the low and high NO_x parameterizations respectively, $(VOC:NO_x)_{lowNO_x}$ and $(VOC:NO_x)_{highNO_x}$ are the initial VOC: NO_x ratios from the chamber experiments used to develop the low and high NO_x SOA parameterizations, $(VOC:NO_x)_{model}$ is the model predicted VOC: NO_x ratio in the model grid cell, $(NO_x)_{lowNO_x}$ and $(NO_x)_{highNO_x}$ are the NO_x concentrations from the chamber experiments used to develop the low and high NO_x parameterizations, and $(NO_x)_{model}$ is the model predicted NO_x concentration in the model grid cell. Equations (1) and (3) assume linear dependence while equations (2) and (4) assume logarithmic dependence. For the $(VOC:NO_x)_{model}$ ratio, the VOC is the sum of all organic species tracked in the SAPRC-11 gas-phase chemical mechanism, including all IVOCs and gas-phase SVOCs. NO_x is the sum of NO and NO_2 . The $(VOC:NO_x)$ ratios and the NO_x concentrations from the chamber experiments used in the equations were gathered directly from the primary references and are listed in Table 2.2. When the $(VOC:NO_x)_{model}$ or $(NO_x)_{model}$ values were lower or higher than the chamber values in Table 2.2, the SOA formation was set to model predictions from the bounding simulations.

Table 2.2: Low and high VOC:NO_x ratios in ppb ppb⁻¹ from chamber experiments used to model the influence of NO_x on SOA formation.

SOM surrogate	(VOC:NO _x) _{lowNO_x}	(NO _x) _{lowNO_x}	(VOC:NO _x) _{highNO_x}	(NO _x) _{highNO_x}	References
<i>n</i> -dodecane	17.0 ^{&}	<2 ppbv	0.09	343	Loza et al. (2014)
benzene	207 ^{&}	<2ppbv	1.98	169	Ng et al. (2007a)
toluene	46.3 ^{&*}	<0.8 ppbv	0.76 [*]	50	Zhang et al. (2014)
<i>m</i> -xylene	12.1 ^{&#}	<2 ppbv	0.10	943	Ng et al. (2007a)
isoprene	24.5 ^{&}	<2 ppbv	0.29	937	Chhabra et al. (2010)
α-pinene	33.1 ^{&}	< 2 ppbv	0.05	844	Chhabra et al. (2010)

[&] minimum VOC:NO_x ratios since these assume a NO_x concentration of 0.8 ppbv in the chamber

^{*} average of six experiments performed by Zhang et al. (2014)

[#] average of two experiments performed by Ng et al. (2007a)

We acknowledge that this approach to modeling the NO_x influence on SOA formation is limited and is sensitive to the following assumptions: (i) the $\text{VOC}:\text{NO}_x$ ratio plus NO_x concentration is a good proxy to model the $\text{HO}_2:\text{NO}$ ratio and the branching between low and high NO_x SOA formation, (ii) the low and high NO_x chamber experiments for a particular precursor bound the minimum and maximum SOA formed, (iii) the SOA response between the low and high NO_x levels varies linearly or logarithmically with $\text{VOC}:\text{NO}_x$ ratios/ NO_x concentrations, and (iv) the model predicted VOC concentrations at each grid cell, summed across a mixture of organic compounds, are analogous to the initial VOC concentrations from the chamber experiment to calculate $\text{VOC}:\text{NO}_x$ ratios. There are few experimental data to test these assumptions and these need to be investigated in future work. In addition to modeling the influence of NO_x on ambient SOA concentrations, this approach allowed us to explore the influence of reductions in NO_x emissions and concentrations on ambient OA concentrations in the future.

2.2.3 Simulations

Table 2.3: Names and descriptions of the simulations performed in this work

No.	Name	Semi-Volatile & Reactive POA (SVOC)	IVOC	Vapor Wall Losses for SVOC, IVOC, and VOC	Additional Details
1	Traditional	No	No	No	Same as model of Cappa et al. (2016)
2	SVOC	Yes ²	No	No	-
3	IVOC	Yes ²	Yes	No	-
4	Base	Yes ²	Yes	Yes	Base case model used in this work
5	SVOC _{max} ¹				SVOCs modeled as per diesel parameterization
6	IVOC _{max} ¹				IVOCs modeled as per diesel parameterization
7	No-Aging ¹				No multi-generational aging
8	VOC _{spec} ¹				VOC speciation from May et al. (2014)
9	Aromatic ¹				S/IVOCs modeled using the toluene parameterization
10	SVOC _{cooking} ¹	Yes ³			SVOCs from food cooking modeled using the volatility distribution of Louvaris et al. (2017).

¹Same as the Base simulation but with differences noted in the ‘Additional Details’ section.

²Assumes volatility of food cooking POA to be similar to volatility of biomass burning.

³Uses measured volatility of food cooking POA.

The Base simulation – representing our most comprehensive simulation – included the updates described in Section 2.2.2; a source-resolved semi-volatile and reactive treatment of POA, source-resolved SOA formation from SVOCs and IVOCs, and correction of the subsequent SOA formation for vapor wall losses in chambers. The Base simulation included sub-simulations at two resolutions (24 km and 8 km) with two NO_x parameterizations (low and high NO_x).

Additional simulations were designed and performed with two objectives in mind: (i) to examine the influence of each update included in this work and (ii) to test the sensitivity in model predictions to uncertainties inherent in the updates and other model inputs. A set of four simulations were performed to systematically study the influence of model updates. These included the following simulations where only one update (as underlined) was made over the previous configuration: (1) Traditional – Non-volatile POA, no IVOCs, SOA from VOCs, and no correction for chamber vapor wall losses, (2) SVOC – Semi-volatile POA, no IVOCs, SOA from SVOCs and VOCs, and no correction for chamber vapor wall losses, (3) IVOC – Semi-volatile POA, IVOCs, SOA from SVOCs, IVOCs, and VOCs, and no correction for chamber vapor wall losses, and (4) Base – Semi-volatile POA, IVOCs, SOA from SVOCs, IVOCs, and VOCs, and correction for chamber vapor wall losses. Successive differences in model predictions between the Traditional, SVOC, IVOC, and Base simulations were used to systematically examine the influence of the semi-volatile and reactive POA, IVOCs, and chamber vapor wall losses respectively.

A set of six simulations were performed to study uncertainties in model inputs. The SVOC_{max} simulation (5) assumed that POA from all sources (all POA except marine POA) was semi-volatile and modeled using the volatility distribution for diesel exhaust POA. Diesel POA was chosen since it was the most volatile of the volatility distributions used in this work. This simulation bounded the maximum loss in POA mass to evaporation. The IVOC_{max} (6) simulation assumed that all sources (combustion and non-combustion except biogenic sources) emitted IVOCs, which were estimated using an IVOC:NMOG ratio of 0.2 and allowed to form SOA equivalent to a C_{15} alkane. This simulation provided an upper bound estimate to the contribution of IVOCs to ambient SOA although the IVOC emissions and their potential to form SOA could be even higher than

that assumed here. The No-Aging (7) simulation assumed no multi-generational aging or in other words, the emitted precursor was allowed to react with OH and form four functionalized products with no further oxidation. This simulation investigated the influence of multi-generational aging on ambient SOA. The VOC_{spec} (8) simulation updated the VOC speciation for on- and off-road gasoline and diesel vehicles based on a comprehensive set of measurements performed on an in-use fleet (May et al., 2013a, 2013b). This simulation examined the influence of updated emissions profiles on the non-IVOC contribution to SOA. The Aromatic (9) simulation assumed that the oxidation of SVOCs and IVOCs to form SOA was modeled using toluene. There were two reasons for choosing toluene. First, both mono- and poly-cyclic aromatic compounds are found in gasoline and diesel fuel (Gentner et al., 2012) and in tailpipe emissions from mobile sources (Zhao et al., 2015, 2016), and oxygenated aromatic compounds such as phenols, guaiacols, and syringols are found in biomass burning emissions (Schauer et al., 2001; Stockwell et al., 2015). Second, aromatic compounds, similar to alkanes, have been studied in detail for their potential to form SOA and are recognized to form more SOA than linear alkanes for the same carbon number. This simulation provided an upper bound estimate for SOA formation from the oxidation of SVOCs and IVOCs. Finally, the SVOC_{cooking} (10) simulation used a hydrocarbon/linear alkane distribution based on the measured volatility distribution of Louvaris et al. (2017) to represent POA from food cooking sources. This simulation examined the effect a more realistic volatility distribution for food cooking POA on mass concentrations of POA and SOA from SVOCs.

The UCD/CIT model was run on the High Performance Computing cluster run by Engineering Network Services at Colorado State University. Although the number of cores varied based on availability, on average each simulation used 96 cores and required 5 days to execute 19 simulated days. Since each set included four sub-simulations, each simulation required ~5 days and all simulations in this work required ~180 days of computational time.

2.2.4 Measurements for Model Evaluation

Model predictions were evaluated against gas-phase measurements of SOA precursors and particle-phase measurements of OA mass concentrations and composition. Here, we briefly describe the primary measurement data and any post-processing of the data we performed prior to undertaking the model evaluation.

Gas-phase measurements of SOA precursors were from two different sources. The first source was routine daily-averaged measurements of single-ring aromatics made by the South Coast Air Quality Management District (SCAQMD, 2017) in southern California at three different sites: North Los Angeles, Riverside, and Long Beach. While measurement data were available at three other sites, data were not available for 2005, our modeled year and hence not included. These gas-chromatography-based measurements were available every twelfth day and included the following aromatic species: benzene, toluene, *o/m/p*-xylene, ethyl-benzene, and styrene. Since there was little overlap between the modeled episode (14 day period over July-August) and available aromatic data, the measurement data were averaged over a three month period in the summer (May 15th to September 15th) and then compared to the episode-averaged model predictions. The second source was gas-chromatography mass-spectrometry measurements of single-ring aromatics (Borbon et al., 2013) and IVOCs (Zhao et al., 2014) made at the Pasadena ground site in the months of May and June of 2010 as part of the CalNex campaign. The single-ring aromatics were measured every hour and included the following species: benzene, toluene, *o/m/p*-xylene, ethyl-benzene, and styrene. The IVOCs were measured every three hours and included most of the reduced and oxidized organic species with a carbon number larger than 12. Since these measurements were from a different time period, we compared campaign-averaged measurements against episode-averaged model predictions.

Particle-phase measurements were from two different sources as well. The first source was routine daily-integrated measurements of organic carbon (OC) in southern California from four sites in the Chemical Speciation Network (CSN; Central Los Angeles, Riverside, Simi Valley, and Escondido) and six sites in the Interagency Monitoring of Protected Visual Environments (IM-

PROVE) network (San Rafael, Rubidoux-Riverside, San Gorgonio Wilderness, Joshua Tree NP, Agua Tibia, and San Gabriel). The CSN is a network of ~ 50 urban measurement sites across the United States where pollutant concentrations are typically higher, more variable, and representative of local sources and measurements are made once every three days. The IMPROVE is a network of ~ 200 rural/remote continental sites typically located in national parks across the United States where pollutant concentrations are lower, less variable, and representative of regional influences and measurements are made once every three days. Over the 14 day episode modeled in this work, three measurements from the CSN and five measurements from the IMPROVE network were available for comparison. We used an organic aerosol to organic carbon ratio (OA:OC) of 1.6 to calculate OA at the CSN sites (Docherty et al. (2011) measured an OA:OC ratio of 1.77 during the SOAR-1 campaign, after correction with the updated calibration of Canagaratna et al. (2015)) and a ratio of 2.1 to calculate OA at the IMPROVE sites (Turpin and Lim, 2001). The CSN data are artifact corrected but we subtracted $0.5 \mu\text{g m}^{-3}$ from the calculated OA mass concentrations to blank correct the data (Subramanian et al., 2004). The IMPROVE data are both blank and artifact corrected. We note that a negative evaporation artifact has been reported for at IMPROVE sites in the southeast US (Kim et al., 2015) but it is not known whether such an artifact may be present in this region and no correction has been made. The second source was particle measurements made at the ground site in Riverside as part of the SOAR-1 campaign during the summer of 2005 (Docherty et al., 2008, 2011). These measurements included hourly-averaged mass concentrations and elemental ratios of H:C and O:C for OA, and estimates of the POA-SOA split based on results from a positive matrix factorization analysis.

2.3 Results

2.3.1 POA and SOA Precursor Emissions

Gas- and particle-phase emissions of organic compounds in the 8 km southern California domain, averaged over the 14-day episode, are shown in Figure 2.1. The 8 km domain, shown in Figure A.1, includes the entire Los Angeles metropolitan statistical area, parts of the Pacific

Ocean, and forested areas surrounding the urban area. The emissions are color-coded by source type and include all species that contribute to direct emissions and atmospheric formation of OA. These do not include emissions of marine POA since those were calculated inline in the UCD/CIT model. Since the POA repartitioned between the gas and particle phases after emission, POA was split into POA and SVOC that represented the particle and gas portions of POA partitioned at an urban OA mass concentration of $9 \mu\text{g m}^{-3}$. We chose $9 \mu\text{g m}^{-3}$ to partition POA because the campaign-averaged OA mass concentration at Riverside during SOAR-1 was $9 \mu\text{g m}^{-3}$. If one discounts the POA emissions in the ‘Other’ category (which is mostly made of road, agricultural, and construction dust), the re-partitioning resulted in about 60% of the POA emitted to evaporate as SVOC vapors; these vapors will oxidize in the atmosphere to form SOA. As noted earlier, a relatively more volatile treatment compared to that described in the recent literature suggests that we may have overestimated the POA evaporation from food cooking sources. Mobile sources accounted for 20% of the POA and 35% of the SVOC vapors and competed with food cooking as an important source of primary emissions and one which accounted for 15% of the POA and 44% of the SVOC vapors. IVOC, long alkane, and aromatic emissions were roughly on the same order of magnitude but taken together were approximately an order of magnitude larger than the POA emissions. This suggests that even at low SOA mass yields (say <10%), the OA formed from the oxidation of these precursors could quickly exceed direct emissions of POA.

Emissions of total IVOCs were slightly lower than those for long alkanes (by $\sim 30\%$) and aromatics (by $\sim 40\%$) but a factor of 2 higher than the sum of POA and SVOCs. Previously, IVOC emissions have been estimated by scaling POA emissions by a factor of 1.5 to 4 derived from gas/particle partitioning calculations (Dzepina et al., 2009; Shrivastava et al., 2008) and from atmospheric measurements (Ma et al., 2017). While our estimate for IVOC emissions are within the previously used range, our estimates were informed by a broader suite of source measurements, which will help reduce the uncertainty in IVOC emissions and related SOA formation in atmospheric models. IVOC emissions from mobile sources were similar to aromatic emissions but twice the long alkane emissions. Hence, we anticipated IVOCs to contribute meaningfully to the

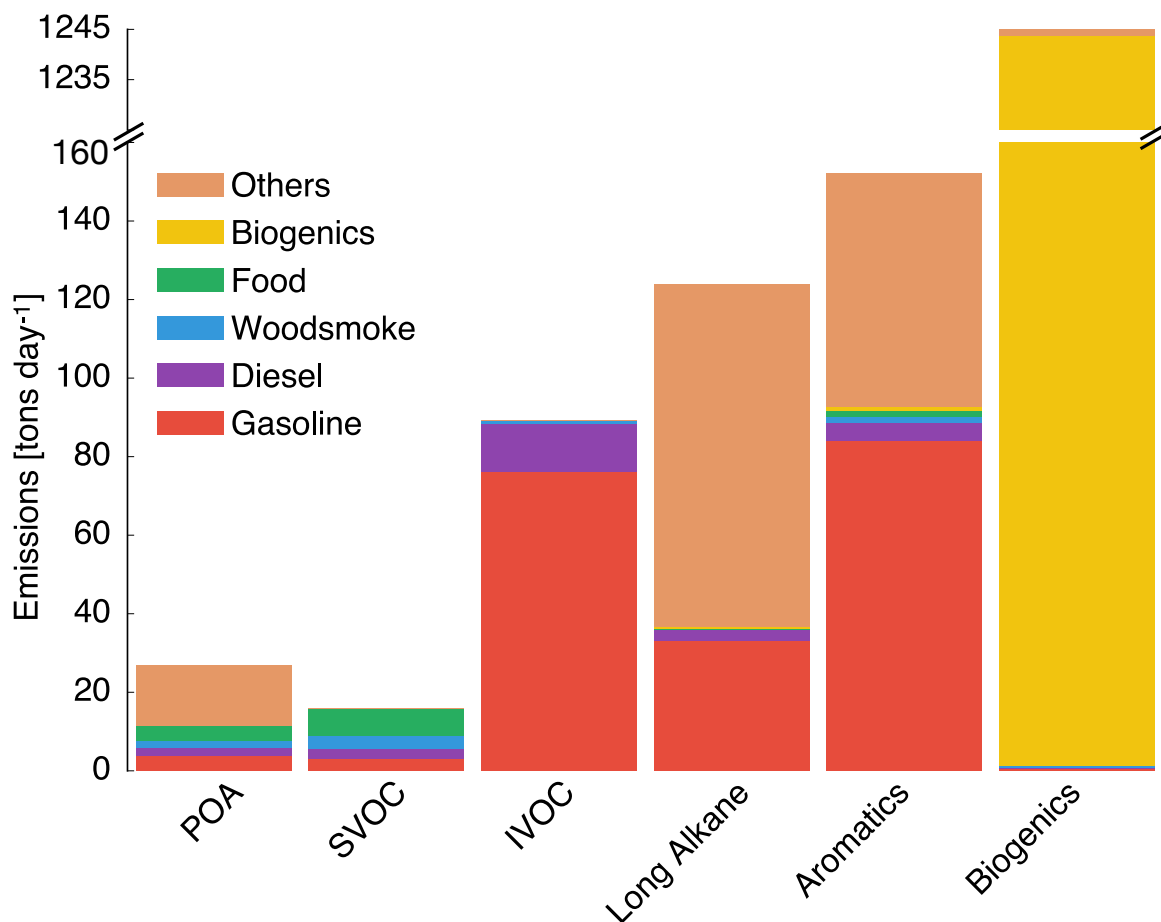


Figure 2.1: Episode-averaged gas- and particle-phase organic emissions in tons per day over the 8 km southern California domain resolved by source. POA and SVOC represent the particle- and gas-phase emissions partitioned to an OA mass concentration of $9 \mu\text{g m}^{-3}$. SVOC, IVOC, long alkanes, aromatics, and biogenics represent gas-phase emissions of precursor species that are modeled to form SOA. We note that recent measurements suggest that POA from food cooking sources is less volatile than assumed in these results.

anthropogenic SOA burden. We note that in this work we only considered IVOC emissions from combustion sources but recent work suggests that volatile chemical products present in sources such as pesticides, coatings, cleaning agents, and personal care products may be a large source of SVOCs and IVOCs in urban environments (McDonald et al., 2018).

Mobile sources – dominated by gasoline use – accounted for a much larger fraction of the anthropogenic SOA precursors (85% of IVOCs, 27% of long alkanes, and 55% of aromatics) in this study. Hence, mobile source regulation on precursor emissions from gasoline vehicles (e.g., limits on emissions of unburned hydrocarbons) has and could have a much larger influence on controlling ambient OA than regulating direct emissions of POA, although this ultimately depends on the extent of conversion of these species to SOA. Finally, biogenic precursor emissions of isoprene, monoterpenes, and sesquiterpenes were about a factor of three higher than the combined emissions of SVOCs, IVOCs, long alkanes, and aromatics and will continue to be an important source of SOA in southern California. However, their impact on urban OA/SOA will be smaller since these emissions are primarily limited to regions outside the urban areas.

2.3.2 Spatial Distribution of OA Concentrations and Bulk Composition

In Figure 2.2 we plot predictions of the 14-day averaged mass concentrations for OA, POA, SOA, and contributions from three lumped SOA precursors (long alkanes and aromatics, SVOC and IVOCs, and biogenic VOCs) from the Base case simulation. We used the terminology developed by Murphy et al. (2014) to describe the SOA from the different sources. To reiterate, the Base case simulation included a semi-volatile treatment of POA, SOA formation from oxidation of SVOCs, IVOCs, and VOCs, multi-generational aging, and SOA parameterizations that accounted for the influence of chamber vapor wall losses. The mass concentrations in Figure 2.2 account for SOA formation under varying NO_x levels as per equation 2 (logarithmic dependence on the $\text{VOC}:\text{NO}_x$ ratio). We chose equation 2 because it produced the highest SOA mass concentrations and presented an upper bound on SOA formation.

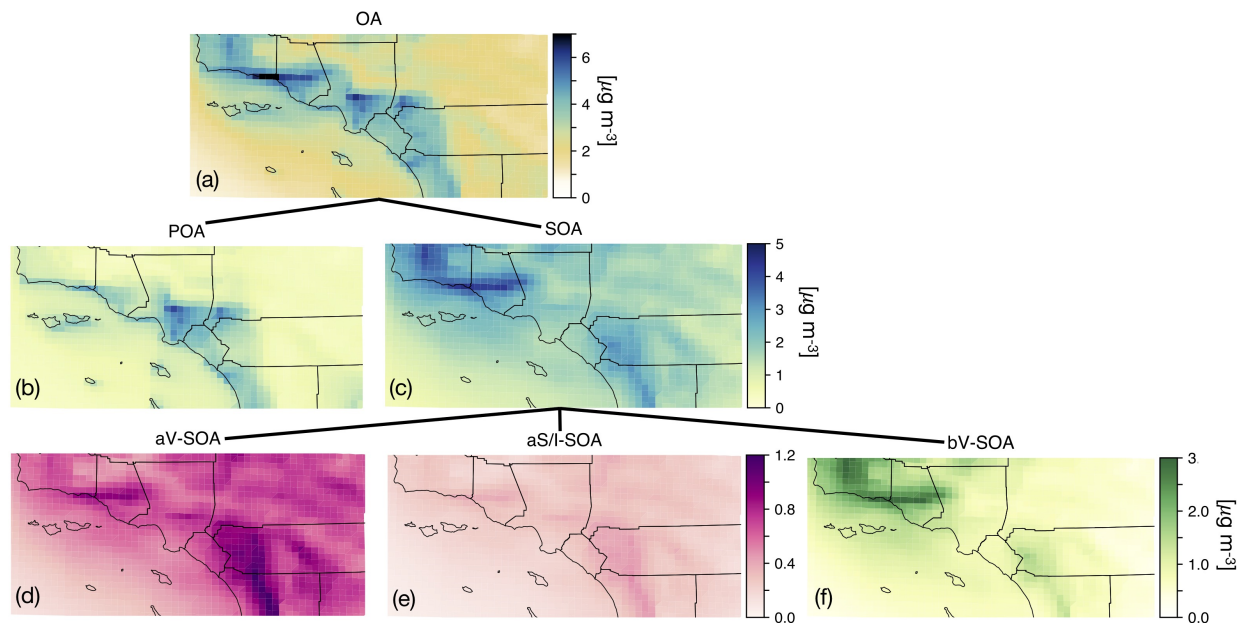


Figure 2.2: 14-day averaged model predictions of mass concentrations for OA, POA, SOA, aV-SOA, aS/I-SOA, and bV-SOA in $\mu\text{g m}^{-3}$ over the southern California domain from the Base simulation. We note that recent measurements suggest that POA from food cooking sources is less volatile than assumed in these results.

The highest OA mass concentrations were found in three general regions: the densely-populated Los Angeles-Orange-Riverside County region likely attributed to heavy transportation emissions, along the coast as a result of sea spray emissions, and in biogenic VOC dominated areas. In central Los Angeles (grid cell containing the CSN site), OA accounted for 38% of the modeled non-refractory PM_{2.5} mass concentration with 20, 25, and 18% contributions from sulfate, nitrate, and ammonium aerosol. A sensitivity simulation that turned emissions of marine POA off suggested that the marine POA mass concentrations in central Los Angeles were $\sim 0.9 \mu\text{g m}^{-3}$, which were considerably higher than the coastal measurements made during CalNex in 2010 (Hayes et al., 2013). Measured mass concentrations of POA over the open ocean west of California were $\sim 0.2 \mu\text{g m}^{-3}$ during CalNex in 2010 and it was expected that these mass concentrations would be substantially lower by the time they were transported to central Los Angeles (Hayes et al., 2013). Sea spray emissions in the UCD/CIT model are based on the parameterization of Gong et al. (2003) and may need to be revisited in the future.

The broader spatial trends of OA, POA, and SOA were in line with results from earlier chemical transport model studies that have treated POA as semi-volatile and modeled SOA formation from SVOCs and IVOCs (Ahmadov et al., 2012; Jathar et al., 2017a; Koo et al., 2014; Robinson et al., 2007; Tsimpidi et al., 2010). POA mass concentrations were highest in upwind (e.g., $3.4 \mu\text{g m}^{-3}$ in central Los Angeles) and lower in downwind (e.g., $2.7 \mu\text{g m}^{-3}$ in Riverside) locations as the POA emissions that were transported away from the source region evaporated with dilution. SOA mass concentrations, in contrast to POA, had a more regional presence with lesser differences between the upwind and downwind regions (e.g., $2.4 \mu\text{g m}^{-3}$ in Riverside versus $2.2 \mu\text{g m}^{-3}$ in central Los Angeles) or in regions with high emissions of biogenic VOCs (e.g., $2.5 \mu\text{g m}^{-3}$ inside the Los Padres National Forest). To assess the relative contribution of POA and SOA to total OA, we plot the POA:SOA ratio in Figure A.2, which suggests a POA:SOA ratio of ~ 1.6 in near-source regions and lower elsewhere, e.g., ~ 0.4 , 0.8 , and 1.2 in representative marine, biogenic-dominated, and urban downwind regions. These POA:SOA splits qualitatively aligned with the hydrocarbon-like and oxygenated organic aerosol (HOA and OOA) splits estimated in aerosol mass spectrometer datasets in urban locations worldwide (Jimenez et al., 2009; Zhang et al., 2007). However, we predict POA:SOA ~ 1 for Riverside during SOAR-1, compared to a measured ratio of ~ 0.25 (Docherty et al., 2008), which indicates that SOA may still be underestimated in the model. A comparison of the OA composition predictions with the aerosol mass spectrometer measurements is described in Section 2.4.

Panels (d) through (f) show contributions of three distinct SOA precursor classes to total SOA. Alkane and aromatic VOCs – included as SOA precursors in most atmospheric models – appeared to contribute a maximum of $1.2 \mu\text{g m}^{-3}$ of what we refer to as aV-SOA downwind of the source region. The majority of this aV-SOA (75%) originated from aromatic precursors implying that alkane VOCs are unlikely to contribute much to the anthropogenic SOA or total OA burden in urban areas, consistent with our earlier work (Cappa et al., 2016; Jathar et al., 2016). We note that emissions inventories typically only include alkane species with carbon numbers less than 12 (Pye and Pouliot, 2012) and longer alkanes with carbon numbers larger than 12 are included as part of

the POA, SVOC, and IVOC emissions. Together aS-SOA and aI-SOA mass concentrations exhibited a similar spatial pattern over the domain but were substantially lower than the aV-SOA mass concentrations – reaching a maximum of only $0.5 \mu\text{g m}^{-3}$. The lower aS-SOA and aI-SOA mass concentrations were somewhat contrary to earlier work that has argued that SVOCs and IVOCs are an equal or dominant precursor of anthropogenic SOA when compared to aV-SOA, especially in urban areas (Jathar et al., 2014, 2017a; Woody et al., 2016). The reason for these lower concentrations can be partially attributed to the precursor-dependent influence of accounting for vapor wall losses in chamber experiments (probed in greater detail in Section 2.3.4). Biogenic SOA or bV-SOA mass concentrations exceeded $2.3.2 \mu\text{g m}^{-3}$ in regions with high biogenic emissions but were slightly less than $1 \mu\text{g m}^{-3}$ in urban regions where the POA mass concentrations were the highest. Previous work has suggested that the bV-SOA in urban regions is formed outside but later transported to the urban region (Hayes et al., 2015; Heo et al., 2015). Overall, the averaged results over the urban areas appeared to be split evenly between POA, anthropogenic SOA (aV-SOA+aS-POA+aI-SOA), and biogenic SOA (bV-SOA).

2.3.3 Precursor Contributions to OA and SOA

We examined the absolute OA mass concentrations and precursor contributions to SOA in central Los Angeles across four different simulations to better understand the effect of successive updates: semi-volatile and reactive POA, IVOCs, and accounting for vapor wall losses. We chose central Los Angeles (grid cell containing the CSN site) as our study area as it is representative of an urban location with a large population density and suffers from some of the poorest air quality in the United States (ALA, 2017); results from the sensitivity simulations in Section 2.3.5 are also discussed at this specific site. Results at other urban locations (e.g., Riverside, Simi Valley) had similar SOA precursor fractional contributions although the absolute concentrations did vary a little (see Figure A.3). In Figure 2.3, we plot the 14-day averaged, precursor-resolved OA mass concentrations and precursor contributions to SOA in Los Angeles from two pairs of four

different simulations. The two pairs represent model predictions based on the low and high NO_x parameterizations.

Semi-volatile and Reactive POA. Differences in the Traditional and SVOC simulations were used to highlight the influence of including a semi-volatile and reactive treatment of POA. The semi-volatile POA treatment resulted in evaporation of the primary POA emissions from combustion sources (on- and non-road gasoline and diesel, woodsmoke, biomass burning, and food cooking) and reduced POA mass concentrations by 35% in central Los Angeles. A ratio of the POA mass concentrations from the SVOC simulation to those from the Traditional simulation suggested that the POA mass was reduced by approximately 30 to 50% in the urban environment around the central Los Angeles site (Figure A.4). Overall, the POA reductions appeared to be smaller than those implied by the volatility distributions of May and coworkers (May et al., 2013a, 2013b, 2013c) and those simulated in other atmospheric models (Robinson et al., 2007). For gasoline, diesel, and biomass burning, May and coworkers (May et al., 2013a, 2013b, 2013c) proposed a 45 to 80% reduction in POA mass concentrations at ambient OA mass concentrations between 1 and $10 \mu\text{g m}^{-3}$. This difference was mainly because we only modeled certain combustion-related POA to be semi-volatile (i.e., gasoline, diesel, biomass burning, and food cooking sources) while earlier modeling work has considered POA from all sources to be semi-volatile (e.g., marine, dust). The use of a less volatile and more realistic food cooking POA than that used in this work (informed by the works of Woody et al. (2016) and Louvaris et al. (2017)) would tend to further increase the discrepancy between our work and the findings of May and coworkers. Hu et al. (2014) found that the combustion sources considered to be semi-volatile in this work accounted for about half of $\text{PM}_{2.5}$ mass concentrations in Los Angeles. The POA mass reductions shown here are conservative and might have been larger if there was evidence that sources other than those considered here (e.g., marine, dust) produced POA that was semi-volatile too, although this scenario seems unlikely.

Allowing the POA vapors or SVOCs to react resulted in only a small fraction of their oxidation products to condense back as aS-SOA. For example, of the $1.75 \mu\text{g m}^{-3}$ of POA lost at the

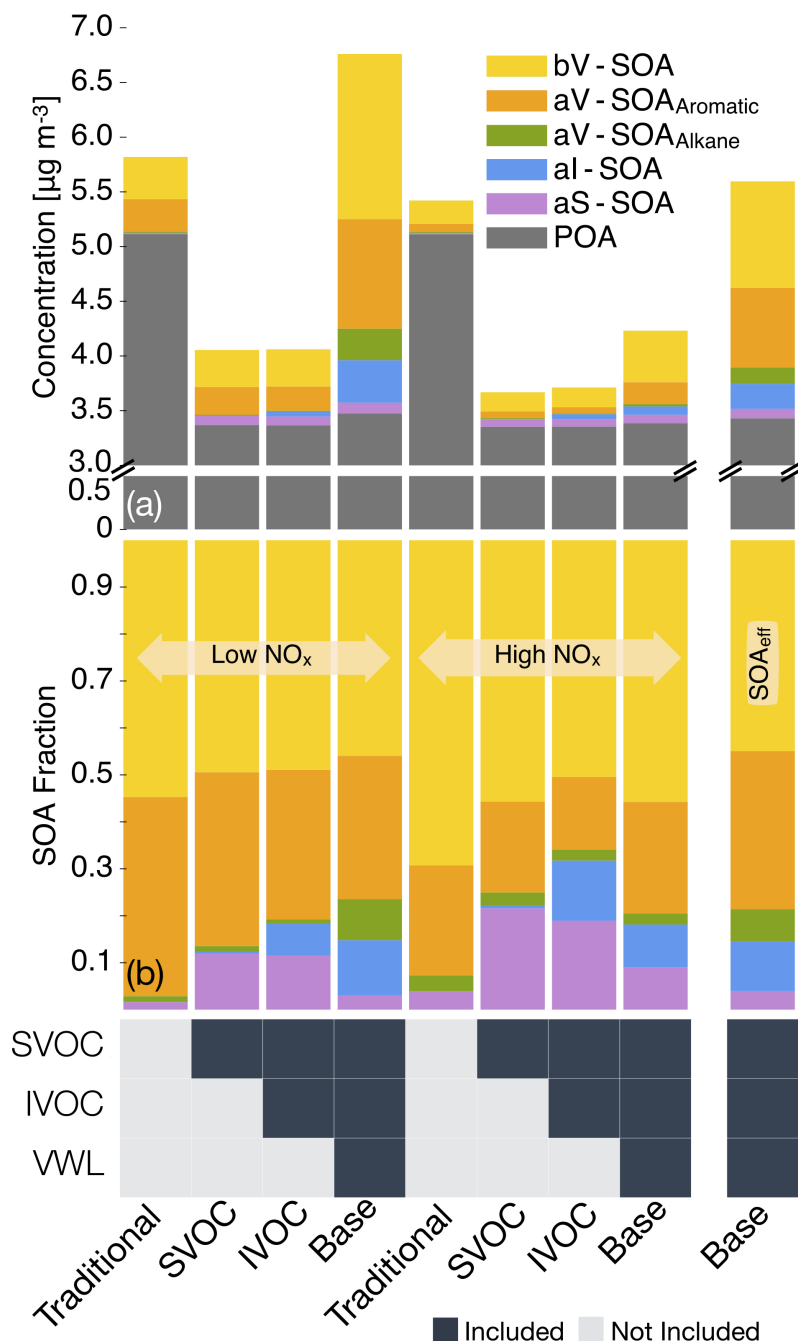


Figure 2.3: 14-day averaged model predictions of POA and SOA mass concentrations and precursor contributions at the central Los Angeles site from the sensitivity simulations that examined the influence of updates made in this work. Panel (a) shows absolute concentrations and panel (b) shows precursor contributions. The legend at the bottom tracks how the different pathways (i.e., SOA formation from SVOCs, SOA formation from IVOCs, and correction for chamber vapor wall losses (VWL)) were turned on for the different simulations. Model predictions from the low and high NO_x simulations are shown separately. Model predictions to the extreme right are from accounting for the influence of NO_x on SOA formation using equation 2. We note that recent measurements suggest that POA from food cooking sources is less volatile than assumed in these results.

central Los Angeles site, only $0.082 \mu\text{g m}^{-3}$ for the low NO_x and $0.068 \mu\text{g m}^{-3}$ for the high NO_x simulations was regained as aS-SOA from oxidation reactions. This implied a very low chemical conversion efficiency ($\sim 4\%$) for the POA-to-SVOC-to-aS-SOA pump within the urban area (Mira-colo et al., 2010). The SVOCs, at an ambient concentration of $9 \mu\text{g m}^{-3}$, from gasoline exhaust, diesel exhaust, and biomass burning emissions had an average carbon number between 18 and 20. Calculations with a box model version of the SOM suggested that the SOA mass yields for C_{18} and C_{20} alkanes were between 33 and 86% where the range includes yields for low NO_x and high NO_x parameterizations. One possible explanation for the difference between the chemical conversion efficiency in the 3D model and box model yields was that only a small fraction of the SVOCs had the opportunity to react with OH and form SOA before they were transported out of the urban area. If we assume that most of the sS-SOA in the grid cell that contains the Los Angeles site was from the oxidation of SVOCs released in that grid cell and from grid cells that are up to two grid cells away, our results do not appear unrealistic. For example, for an SOA precursor with an OH reaction rate constant of $2.4 \times 10^{-11} \text{ cm}^{-3} \text{ molecules}^{-1} \text{ s}^{-1}$ (average value from a C_{18} and C_{20} linear alkane) and an SOA mass yield of 60% (average from the SOA mass yield range described earlier for a C_{18} and C_{20} linear alkane), the chemical conversion efficiency would be 3.5-15% with a daily-averaged OH concentration of $1.5 \times 10^6 \text{ molecules cm}^{-3}$ and a reaction time of 0.5-2.3 hours. A reaction time of 0.5 to 2.3 hours corresponds to a transport of 2.5 (half a grid cell) and 12.5 (2.5 grid cells) miles at an average wind speed of 5.4 miles per hour (Weather Spark).

The low and high NO_x parameterizations had little effect on the aS-SOA mass concentrations presumably because the n-dodecane based parameterization used for semi-volatile POA exhibited marginal differences in SOA production under low and high NO_x environments (Loza et al., 2014). Finally, SOA parameterizations based on including the vapor wall loss effect only marginally increased the aS-SOA mass concentrations, especially when viewed in light of the SOA increases from other precursors. We examine the precursor-resolved vapor wall loss effect in more detail in Section 2.3.4. For the Base simulations, the aS-SOA mass concentrations were a factor of 10

and 2 lower than the aV-SOA mass concentrations for the low and high NO_x parameterizations respectively.

IVOC. Differences in the SVOC and IVOC simulations were used to determine the influence of including SOA formation from IVOCs. For both the low and high NO_x simulations, IVOCs contributed marginally to the aI-SOA mass concentrations in Los Angeles ($\sim 0.045\text{-}\mu\text{g m}^{-3}$) and elsewhere too (see Figures A.3 and A.4). The aI-SOA mass concentrations were about half of the aS-SOA mass concentrations for both the low and high NO_x simulations. When compared to the aV-SOA mass concentrations, the aI-SOA mass concentrations were slightly lower for the high NO_x simulations ($\sim 40\%$) but about a factor of five lower for the low NO_x simulations. The inclusion of vapor wall losses seemed to make aI-SOA as or more important than aS-SOA but still less important than aV-SOA; the aI-SOA mass concentrations were a factor of 3.3 and 2.9 lower than the aV-SOA mass concentrations for the Base simulations for the low and high NO_x simulations respectively. Our simulations imply that IVOCs might be as influential as SVOCs as a bulk class of SOA precursors but they were still less important than the traditional SOA precursors (that included long alkanes and aromatics) in contributing to ambient SOA levels. In this work, the IVOC contribution to SOA was smaller compared to that from traditional SOA precursors mostly because IVOC emissions were only about a third of the traditional SOA precursors (see Section 2.3.1 for details on emissions). So although IVOCs have higher SOA yields than most of the traditional SOA precursors, the significantly lower IVOC emissions more than offset the increased SOA formation from higher yields. While there are exceptions (e.g., Tsimpidi et al. (2010); Jathar et al. (2017a)), our results did not align with previous box (e.g., Dzepina et al. (2009); Hayes et al. (2015); Ma et al. (2017)) and 3D (e.g., Bergstrom et al. (2012); Zhang et al. (2013)) modeling literature that has found IVOCs to be similar or more important than traditional SOA precursors in contributing to ambient SOA levels. Below we discuss three main reasons for this inconsistency.

First, some previous estimates of IVOC emissions are likely to be less representative of the in-use gasoline- and diesel-powered sources and unconstrained for biomass burning sources. IVOC emissions in most atmospheric models have previously been determined by scaling emissions of

POA or by calculating partitioning with the measured POA, with scaling factors typically on the order of 1.5 (e.g., Shrivastava et al. (2008)) but as large as 3 (e.g., Dzepina et al. (2009)). These factors have been calculated from emissions data from two medium-duty gasoline vehicles built more than two decades ago and a POA volatility distribution from a small off-road diesel engine (Robinson et al., 2007). Additionally, since POA is semi-volatile the POA mass in the particle phase will change with OA loading, which can complicate the use of a scaling based on POA (but this is addressed by the partitioning method used in some studies). Zhao et al. (2015) provided some evidence for this where they found that the POA-based scaling did not work that well for modern diesel vehicles and instead recommended the use of an NMOG-based scaling. We note that Ma et al. (2017) used the IVOC estimates of Zhao et al. (2015) and still found IVOCs to be comparable to VOCs in terms of SOA production in the Los Angeles area. Second, the SOA formation from IVOCs in most models to date has not been experimentally constrained. Most schemes to model SOA formation from IVOCs have relied on an ad hoc aging scheme where IVOCs and their oxidation products react with the OH radical to form lower volatility products with ultimate SOA yields of 100% (Robinson et al., 2007). These schemes do not account for fragmentation reactions and have not been comprehensively validated against experimental data. Jathar et al. (2016) showed that such schemes may significantly overestimate the net aerosol production from SOA precursors. And finally, most models do not use SOA parameters that yet account for the effect of vapor wall losses in chamber experiments. This effect and its particular influence on the IVOC contribution to SOA is discussed in Section 2.3.4. In this work, we (i) rely on a comprehensive set of IVOC emissions estimates made from measurements performed on more representative sources, (ii) model fragmentation reactions during IVOC oxidation, (iii) to some degree constrain SOA formation from IVOCs with chamber experiments, (iv) to some degree account for the influence of vapor wall losses in chamber experiments, and (v) include all of the previously mentioned updates in a chemical transport model. Hence, we argue that our findings on the IVOC contribution to SOA might be more robust than those modeled in earlier studies.

Traditional VOCs. For the Base simulations in Los Angeles, aromatics accounted for 33% of the total SOA in Los Angeles and were the most important anthropogenic precursor of SOA. Alkane contributions to SOA were less than 10% for both the low and high NO_x simulations. Biogenic VOCs accounted for 46% and 55% of the total SOA for the low and high NO_x simulations respectively and were clearly the most important precursor of SOA at the central Los Angeles site. After accounting for the influence of NO_x based on equation (2), the isoprene, monoterpene, and sesquiterpene contributions to bV-SOA were 23%, 68%, and 9% respectively, suggesting a strong monoterpene contribution to SOA in southern California. As biogenic VOCs react very quickly with OH and O_3 (chemical lifetimes of a few hours), most of the biogenic SOA at this site was likely formed outside the urban airshed and transported to this location, as suggested by Kleeman et al. (2007), Hayes et al. (2015) and Heo et al. (2015).

2.3.4 Influence of Vapor Wall Losses

SOA parameterizations that accounted for the influence of vapor wall losses in chambers seemed to have had a large effect on the absolute mass concentrations of SOA. This can be seen by comparing model results between the IVOC and Base simulations in Figure 2.3. The SOA mass concentrations were enhanced by a factor of 10.1 and 2.6 for the low and high NO_x simulations respectively and consistent with previous 3D simulations (Cappa et al., 2016). However, they were slightly higher than the range of enhancements reported by Zhang et al. (2014) and estimated by Krechmer et al. (2016) based on analyses of chamber data. The SOA enhancements resulted in an OA enhancement of 1.66 and 1.14 in the low and high NO_x simulations, which were lower than the SOA enhancements since SOA only accounted for a fraction of the OA mass. Differences in enhancements in the low and high NO_x simulations suggest that the vapor wall loss effect was modified by the NO_x level where the enhancement may be lower in urban/source regions with higher NO_x but higher in rural/remote continental regions with lower NO_x . Since urban SOA mass concentrations are usually higher than those in rural/remote continental regions, an implication of this NO_x -modified enhancement is that accounting for vapor wall loss artifacts will tend to reduce

gradients in SOA mass concentrations between urban and rural/remote continental regions and make SOA more of a regional pollutant similar to ozone (O_3).

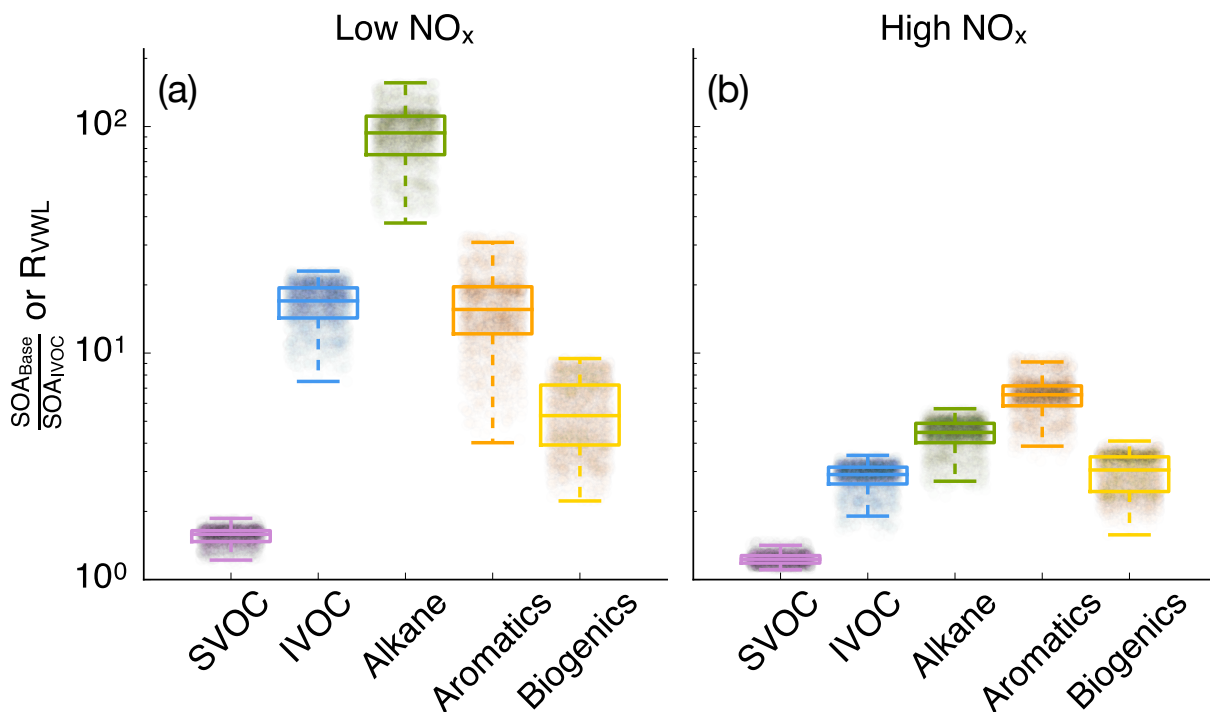


Figure 2.4: Ratio of model predictions from the Base simulation that accounts for the influence of vapor wall losses to model predictions from the IVOC simulation that does not account for the influence of vapor wall losses. Ratios are calculated from the 14-day averaged results for the whole domain and are resolved by precursor. Panels (a) and (b) show results from the low and high NO_x simulations respectively.

Different precursors contributed in varying degrees to the SOA enhancement. The precursor-resolved enhancements are visualized in Figure 2.4 where we plot the ratio of the 14-day averaged model predictions of the SOA mass concentrations from the Base simulation to those from the IVOC simulation for each grid cell in the southern California domain (dots) and overlay box-whisker plots based on those data. For all precursors the enhancements were higher for the low NO_x simulations compared to the high NO_x simulations. SVOCs showed the smallest enhancement at both the low and high NO_x levels (median of 1.6 and 1.2) and hence their fractional contribution to total SOA was reduced in the Base simulation when compared to the IVOC simulation. Alkanes showed the largest enhancement in the low NO_x simulations (median of 94) and

the second largest enhancement in the high NO_x simulations (median of 4.5). Despite the large enhancements, alkanes still contributed marginally to total SOA in the Base simulations because the baseline contribution of alkanes to SOA was small in the IVOC simulations ($<3\%$). IVOCs exhibited a larger enhancement (median of 17 and 2.9) compared to SVOCs and a smaller enhancement compared to alkanes in both simulations, despite using the same surrogate (i.e., *n*-dodecane) to model SOA formation. The reason for varying enhancements in SVOC, IVOCs, and alkanes, despite using the same surrogate (i.e., *n*-dodecane), was that the vapor wall loss-related enhancement was inversely related to the carbon number where larger carbon number precursors (e.g., SVOC that had an average carbon number of 18 to 20) showed smaller enhancements and smaller carbon number precursors (e.g., alkanes that included species between carbon numbers of 6 and 12) showed larger enhancements. The simplest explanation for this inverse relationship is that larger precursors and their oxidation products, relatively speaking, have shorter chemical lifetimes and undergo fewer chemical reactions before condensing, which make them less susceptible to being lost to the walls (see Figure A.5 where we plot the vapor wall loss-related enhancement in SOA yields as a function of the carbon number at an OA mass concentration of $9 \mu\text{g m}^{-3}$). Of the two other important precursors, aromatics displayed the largest enhancement in the high NO_x simulations (median of 6.6) and were tied with IVOCs for the second largest enhancement in the low NO_x simulations (median of 16) while biogenic VOCs showed the lowest enhancement after SVOC in both the low NO_x and high NO_x simulations. Accounting for vapor wall loss artifacts is expected to result in an increase in the aromatic contribution to SOA when compared against biogenic VOCs. Vapor wall loss rates in Teflon chambers might be much higher ($\sim$ factor of 5) than those used in this work to develop the SOM parameterizations ((Huang et al., 2018; Krechmer et al., 2016; Sunol et al., 2018), the use of which will be will tend to increase SOA mass concentrations even further. This new understanding will need to be considered in the future.

2.3.5 Sensitivity Analysis

Results from the sensitivity simulations that examined uncertainties in select model inputs are shown in Figure 2.5 where we plot the 14-day averaged model predictions from these simulations at the central Los Angeles site. We also plot model predictions from the Base simulations as all the sensitivity simulations have been performed using the Base simulation as the reference (see Table 2.3 for details about the simulations). Model predictions from the low and high N simulations are shown separately. The No Aging simulations decreased the SOA mass concentrations by almost an order of magnitude demonstrating the importance of modeling multi-generational aging in the SOM. The inclusion of oligomerization reactions that may enhance the partitioning of semi-volatile species may alter this finding. The No-Aging simulations produced a very different precursor contribution to total SOA compared to the Base simulations and the changes in the precursor contribution were also different between the low and high NO_x simulations. For instance, the aV-SOA contributions to total SOA increased from 39% to 41% for the low NO_x simulations but decreased from 26% to less than 5% in the high NO_x simulations. This implied that the treatment of multi-generational aging in the SOM did not proportionately enhance the SOA mass concentrations from the different precursors but rather produced varying levels of enhancement for the different precursors that was further modified by the NO_x levels. This finding is of note because CTMs that have employed schemes such as the volatility basis set (VBS) have typically assumed that multi-generational aging has an approximately similar effect on SOA mass concentrations from different precursors, regardless of the NO_x levels, and one which does not significantly change the precursor contribution to SOA. With the VBS, one may observe some differences with multi-generational aging from the use of different starting VBS distributions for SOA from different precursors.

The SVOC_{max} simulations that assumed all POA (except marine POA) to be semi-volatile saw POA mass concentrations decrease by 36% compared to the Base simulations and by 56% compared to the Traditional simulations (not shown here but inferred from results in Figure 2.3). The increase in SVOCs from the additional evaporation of POA mass resulted in about a three-fold

increase in the aS-SOA mass concentrations and a proportionate increase in the SVOC contribution to total SOA. Similar to the findings discussed in Section 2.3.3, only a fraction of the evaporated POA mass lost was regained as aS-SOA mass concentrations. For instance, when compared to the Traditional simulations, of the 2.9/3.3 $\mu\text{g m}^{-3}$ of POA mass lost 0.32/0.22 $\mu\text{g m}^{-3}$ was regained as aS-SOA reflecting a chemical conversion efficiency of 11/7% for the low/high NO_x simulations. These simulations predicted the maximum decrease in POA mass concentrations from treating all POA as semi-volatile and reactive but the results still found POA to be 40% and 69% of the total OA in the low and high NO_x simulations respectively. Direct emissions of POA were still a sizeable fraction of the ambient OA and PM burden using the current state-of-the-science treatment.

Estimating IVOCs to be 20% of the NMOG emissions for all combustion sources and modeling the SOA formation from IVOCs using a C15 linear alkane – as modeled in the IVOC_{max} simulations – resulted in an approximately four-fold increase in the aI-SOA mass concentrations over the Base simulations. The increases were partly attributed to additional IVOC emissions from sources other than mobile and biomass burning (factor of 2.8 compared to IVOC emissions from the Base simulations) and partly to using a larger alkane (C15 linear alkane) with a higher SOA mass yield to model SOA formation from IVOCs emitted by gasoline sources. Simulating SOA formation from IVOCs using an aromatic surrogate in the $\text{S-IVOC}_{aromatic}$ simulations had the same effect as the IVOC_{max} simulations and increased aI-SOA mass concentrations by a factor of 2.6/6.3 for the low/high NO_x simulations. The aI-SOA mass concentrations were higher because aromatics for the same carbon number have a higher SOA mass yield than alkanes. The IVOC_{max} and $\text{S-IVOC}_{aromatic}$ simulations potentially present an upper bound contribution of IVOCs to SOA formation and in both these simulations were $\sim 30\%$ of the total SOA and a factor of ~ 1.5 -2 larger than the aromatic VOC contribution. While the IVOC_{max} and $\text{S-IVOC}_{aromatic}$ simulations dramatically increased the aI-SOA mass concentrations, these simulations only modestly increased the total OA mass concentrations over the low and high NO_x simulations (average increase of 10%). Over the urban area, the OA mass concentrations in the IVOC_{max} and $\text{S-IVOC}_{aromatic}$ simulations were on average 10-12% higher compared to the Base simulations (see Figure A.6). Updating the

emissions profiles based on the work of May et al. (2014) had a negligible effect on the SOA mass concentrations and its precursor contribution implying that the emissions profiles from more than a decade and a half ago may be sufficient to model the modern mobile source fleet. Finally, a lower volatility (i.e., more realistic) POA in the $\text{SVOC}_{\text{cooking}}$ simulations, informed by the measurements of Louvaris et al. (2017), resulted in a 20% increase in POA mass concentrations when compared to both the low and high NO_x Base simulations. POA mass concentrations in these low and high NO_x simulations accounted for approximately 55 and 85% of the OA respectively. The SOA mass concentrations between the $\text{SVOC}_{\text{cooking}}$ and Base simulations remained the same.

2.3.6 NO_x -Adjusted SOA Formation

The SOM currently does not model the continuous evolution of SOA under varying NO_x concentrations. One of the challenges in modeling the NO_x influence on SOA formation has been in quantifying the branching of the VOC oxidation under low and high NO_x conditions. Most commonly used schemes in atmospheric models use the $\text{NO}:\text{HO}_2$ ratio to determine the initial branching of the precursor to form SOA via the low or the high NO_x pathway. However, this scheme depends on an accurate prediction of NO and HO_2 . To assess, at least qualitatively, the ability of the model to capture NO and HO_2 concentrations, we compare 14-day averaged diurnal profiles from this work to those measured in Pasadena in 2010 during the CalNex campaign in Figure A.7. We found that the model predictions were within a factor of two for NO concentrations but were about a factor of 10 lower than the measured HO_2^* concentrations. We should note that the HO_2^* measurements included HO_2 and a fraction of RO_2 radicals, where RO_2 radicals contributed to $\sim 30\%$ of the HO_2^* measurements (Griffith et al., 2016). The inclusion of RO_2 should not change the findings reported here. If the results from our modeling are representative of results from other atmospheric models that use SAPRC or other gas-phase chemical mechanisms, underestimating the HO_2 concentrations may lead $\text{NO}:\text{HO}_2$ ratio-based schemes to overestimate the SOA formed via the high NO_x pathway. Given this limitation and the fact that the SOM does

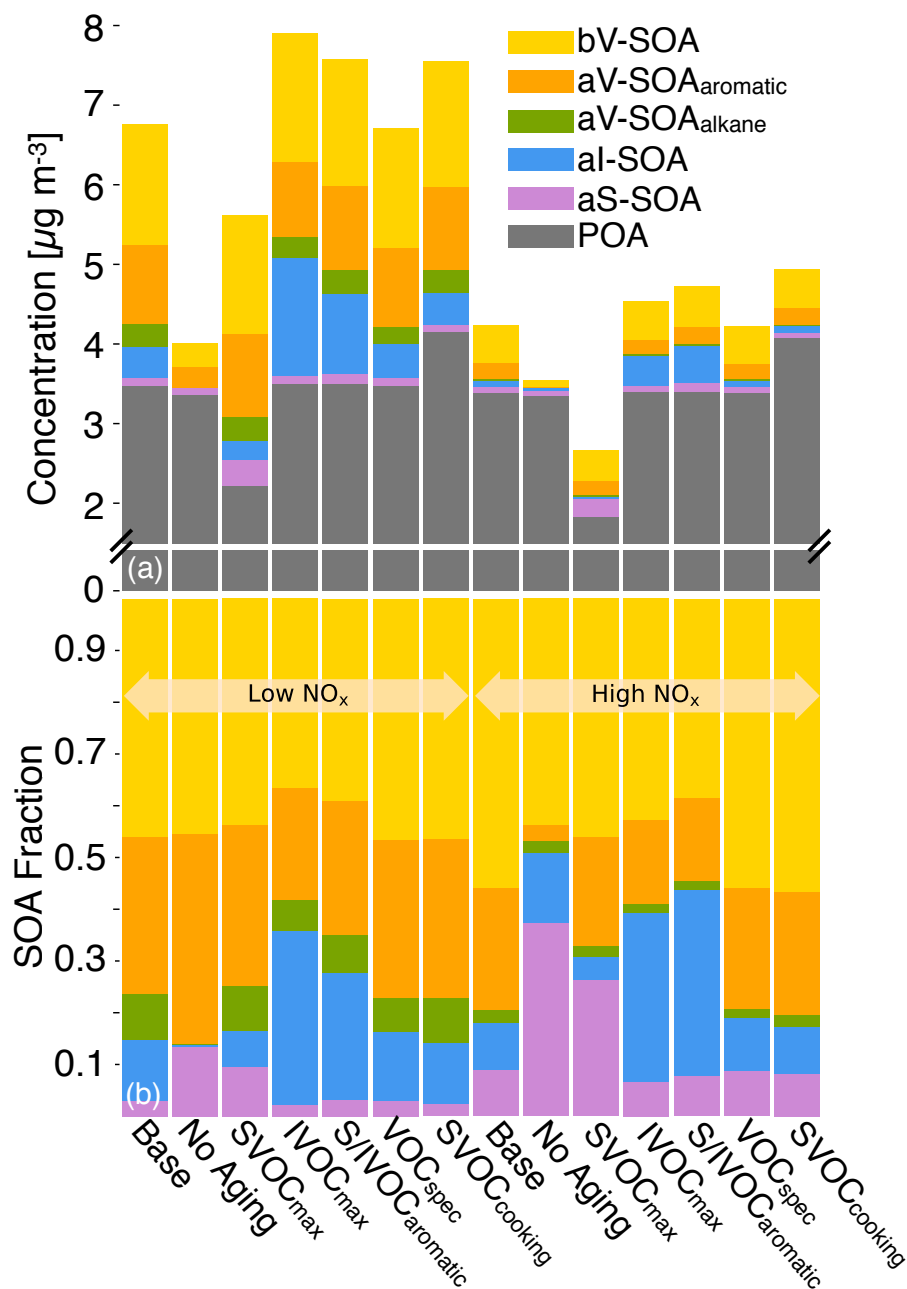


Figure 2.5: 14-day averaged model predictions of POA and SOA mass concentrations and precursor contributions from the sensitivity simulations. Panel (a) shows absolute concentrations and panel (b) shows precursor contributions. Model predictions from the low and high NO_x simulations are shown separately. Simulation legend: Base = Base case, No Aging = only models first generation chemistry in the SOM, SVOC_{max} = all POA treated as semi-volatile, IVOC_{max} = all combustion sources assumed to have 20% IVOC emissions and a C_{15} SOA yield, S-IVOC_{aromatic} = SVOCs and IVOCs modeled as high-yield aromatic compounds, VOC_{spec} = mobile source emissions profiles based on May et al. (2014), SVOC_{cooking} = POA volatility distribution for food cooking sources based on the measurements of Louvaris et al. (2017). All simulations besides SVOC_{cooking} assumed food cooking POA to have the same volatility as biomass burning POA. More details about these simulation inputs can be found in Section 2.2.3.

not model the continuous evolution of SOA under varying NO_x concentrations, we attempted to model the NO_x -dependent SOA formation using VOC: NO_x ratios and NO_x concentrations.

Four different methods – described in equations (1) through (4) – were used to adjust the SOA mass concentrations from each individual precursor to account for the influence of NO_x . To remind the reader, equations (1) and (2) assume a linear and logarithmic dependence respectively between the SOA mass concentration and the VOC: NO_x ratio. Equations (3) and (4) assume a linear and logarithmic dependence respectively between the SOA mass concentration and the NO_x concentration. The adjusted SOA mass concentrations, referred to as SOA_{eff} , were summed to calculate the total SOA mass concentrations. Equation (2) produced the highest SOA mass concentrations while equation (3) produced the lowest SOA mass concentrations amongst the four equations. Scatter plots comparing the SOA mass concentrations calculated using equation (2) to those calculated using other equations, in Figure A.8, show that the SOA mass concentrations based on equation (2) were, on average, a factor of 1.27, 3.19, and 1.92 higher than those with equations (1), (3), and (4) respectively. This meant that a calculation based on the VOC: NO_x ratio produced a stronger response of NO_x on SOA mass concentrations than the NO_x concentrations themselves. In the subsequent sections, where we evaluate the model predictions (Section 2.4) and predicted future changes in the OA burden (Section 2.5), we used the SOA_{eff} calculations based on equation 2 since they represented an upper bound estimate of the NO_x effect on SOA mass concentrations. The validity of equation 2 needs to be examined in future work.

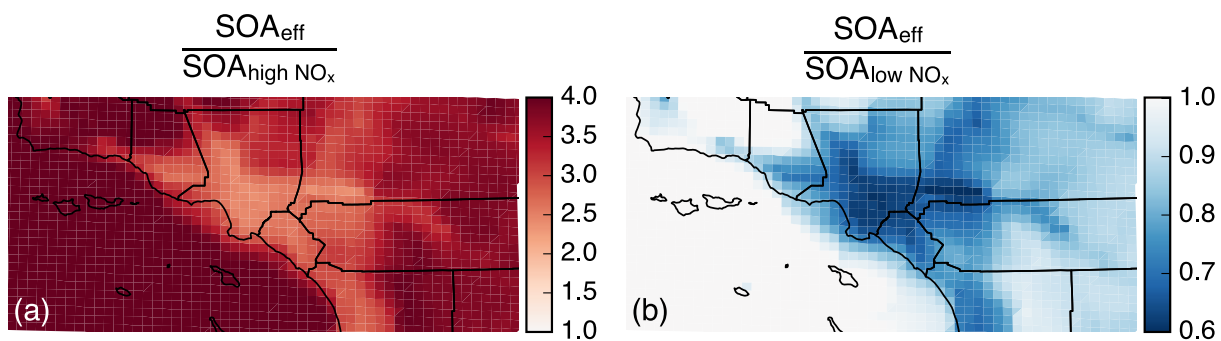


Figure 2.6: 14-day averaged ratio of the SOA_{eff} mass concentration to the SOA mass concentration from the (a) high NO_x and (b) low NO_x Base simulations.

In Figure 2.6, we plot the ratio of the total SOA_{eff} mass concentrations based on equation (2) to the total SOA mass concentrations from the (a) high NO_x and (b) low NO_x Base simulations. The SOA_{eff} mass concentrations were higher than the SOA mass concentrations predicted using the high NO_x parameterizations, with an average factor of two increase in urban areas and a maximum factor of four increase in non-urban areas. This was because the model predicted VOC:NO_x ratios in the urban areas were higher than the VOC:NO_x ratios produced in the high NO_x chamber experiments and based on equation (2) the SOA mass concentrations were adjusted upwards to include the SOA predicted using the low NO_x parameterizations. The adjustments increased the SOA mass concentrations because the SOA mass concentrations from each precursor were universally higher with the use of the low NO_x parameterizations compared to the high NO_x parameterizations. The SOA_{eff} mass concentrations were 30-40% lower than the SOA mass concentrations predicted using the low NO_x parameterizations in urban areas, suggesting that the SOA_{eff} mass concentrations were approximately midway between the SOA predictions using the high and low NO_x parameterizations. In contrast, the SOA_{eff} mass concentrations were only marginally lower (10-20%) in the non-urban areas implying that the VOC:NO_x ratios in these regions were very similar to the VOC:NO_x ratios produced in the low NO_x chamber experiments. In summary, a modest fraction of the SOA mass may be formed through the ‘low-NO_x’ pathway in high NO_x urban areas, which may result in substantial increases in the predicted SOA mass concentration when compared against predictions purely based on the use of high NO_x parameterizations. This low-NO_x SOA will continue to increase in the future as NO_x concentrations are reduced in urban areas through controls on mobile sources. In contrast, only a small fraction of the SOA mass may be formed through the ‘high-NO_x’ pathway in low NO_x non-urban areas and the use of a low NO_x parameterization in these regions will only marginally bias model predictions of SOA mass concentrations.

2.4 Model Evaluation

Model predictions from the Base simulation were evaluated against gas-phase measurements of SOA precursors and particle-phase measurements of OA mass concentrations and composition. For the particle-phase measurements, we focused the model evaluation on predictions adjusted for the NO_x influence on SOA formation using equation 2 (logarithmic dependence on $\text{VOC}:\text{NO}_x$ ratio).

2.4.1 SOA Precursors

In Figure 2.7(a), we compare 14-day averaged model predictions of aromatic concentrations for our 2005 episode against measured temporal trends in summer-averaged single-ring aromatic concentrations at three different sites in Southern California (Los Angeles-North Main Street, Riverside-Rubidoux, and Long Beach) (SCAQMD, 2017); model predictions of aromatic concentrations are a sum of the benzene, ARO1, and ARO2 concentrations. On the same figure, we also plot model predictions of aromatic concentrations at Pasadena for our 2005 episode and measured single-ring aromatic concentrations made at the Pasadena ground site in 2010 as part of the CalNex campaign (Zhao et al., 2014). The summertime single-ring aromatic concentrations in southern California have decreased by a factor of 2 to 3 between 2000 and 2011 presumably from regulations that have targeted emissions from mobile sources. These reductions agreed well with reported temporal trends in carbon monoxide, nitrogen oxides, and non-methane organic compounds for Los Angeles over the same time period (Warneke et al. (2012); MacDonald et al. (2013)). Aromatic measurements at Pasadena in 2010 compared well with the 2010 measurements made ~ 12 km southwest of Pasadena at the Los Angeles-North Main Street location suggesting that the summer/campaign-averaged aromatic concentrations were spatially homogeneous over urban Los Angeles and findings from the model-measurement comparison at a particular site could be generalized for the larger modeled domain. The model-measurement comparison for aromatics in 2005 was mixed. Concentrations were overpredicted by a factor of ~ 1.5 at the Los Angeles-North Main Street and Long Beach sites but agreed well with measurements at Riverside-Rubidoux. The

predictions might have been overestimated because we were using an older emissions inventory developed for the year 2000 but adapted for use for the year 2005 based on activity data (Hu et al., 2015). Another possibility for the over prediction was that the lumped model species ARO1 and ARO2 in SAPRC-11 also included emissions from oxygenated aromatic (e.g., phenols) and aromatic-like compounds (e.g., furans) while the measurements were limited to a handful of single-ring reduced aromatic compounds. Despite differences in the absolute concentrations, the model seemed to capture the measured spatial differences between the three sites, i.e. Los Angeles-North Main Street > Riverside-Rubidoux > Long Beach.

In Figure 2.7(b), model predictions of aromatics and IVOCs in Pasadena in 2005 are compared against measurements made at the Pasadena ground site in 2010. The model predictions in Pasadena were calculated by averaging predictions from the grid cell that contained the Pasadena ground site and the grid cell immediately to the south. This was done because the ground site location was very close to the cell boundary to the south and the grid cell containing the Pasadena ground site included mountains to the north of Pasadena that tended to dilute the concentrations in that grid cell. The measurements in Figure 2.7(b) included primary IVOCs but did not include the oxygenated IVOCs measured by Zhao et al. (2014) since the primary IVOCs, according to the authors, relate most closely to IVOC emissions from mobile sources. The IVOCs included in this work were mostly (>95%) from mobile sources (see Figure 2.1) and the hence the comparison with primary IVOCs was appropriate. The model predicted aromatic concentrations at Pasadena in 2005 were twice the measured aromatic concentrations at Pasadena in 2010. This 2005(modeled)-to-2010(measured) ratio was slightly higher but still consistent with the measured 2005-to-2010 ratio in aromatic concentrations at the Los Angeles-North Main Street site (1.67). That the 2005(modeled)-to-2010(measured) ratio for IVOCs in Pasadena was ~ 1.0 is some evidence that the model predictions of IVOCs might be underpredicted in 2005, assuming that the ambient IVOC-to-aromatic ratio did not change between 2005 and 2010. The IVOC_{max} sensitivity simulation (the only sensitivity simulation that modeled an increase in IVOC emissions) predicted a 2005(modeled)-to-2010(measured) ratio of 3.15 for IVOCs in Pasadena, which was closer to the

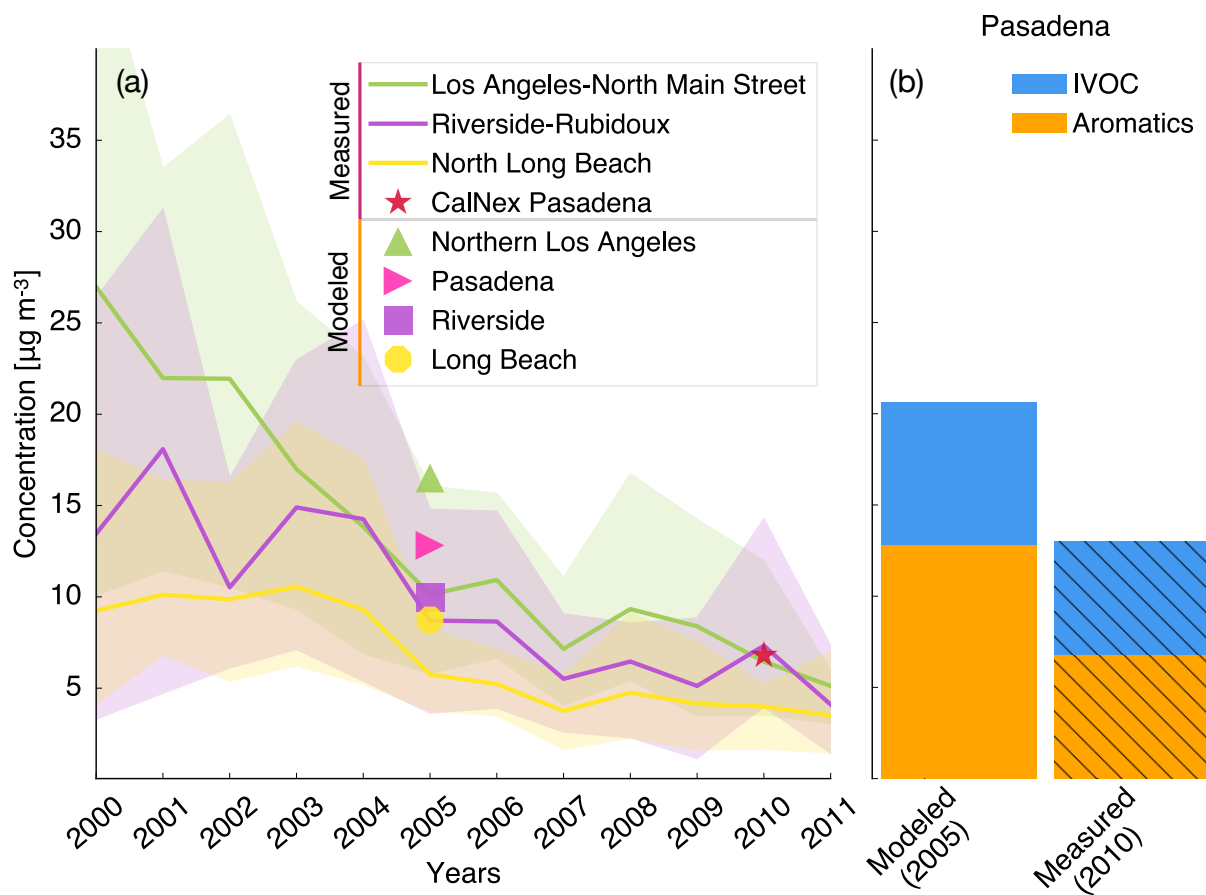


Figure 2.7: (a) Mass concentrations of single-ring aromatics in southern California at different sites between 2000 and 2011. Measurements show the temporal trend in the summertime mean (solid line) and 10th-90th percentile (bands) at Los Angeles, Riverside, and Long Beach from 2000 to 2011 (ARB, 2017) and the campaign-averaged measurement from CalNex at the Pasadena ground site in 2010 (Zhao et al., 2014). Model predictions show the 14-day averaged concentration simulated in this work at four different sites (solid symbols) in 2005. (b) Mass concentrations of single-ring aromatics and IVOCs compared between the model predictions from 2005 (this work) to measurements in 2010 (Zhao et al., 2014).

measured aromatic concentrations ratios between 2005 and 2010 at the Los Angeles-North Main Street site. This provides additional evidence for higher IVOC emissions to be included in the model and it is possible that these additional IVOC emissions might come from volatile chemical products such as pesticides, coatings, cleaning agents, and personal care products (McDonald et al., 2018). While this model-measurement comparison validates the aromatic SOA precursors and to some extent the mobile source IVOC SOA precursors, our model does not account for the oxygenated IVOCs that Zhao et al. (2014) measured and we recommend that future work investigate the sources, composition, and the SOA potential for these IVOCs.

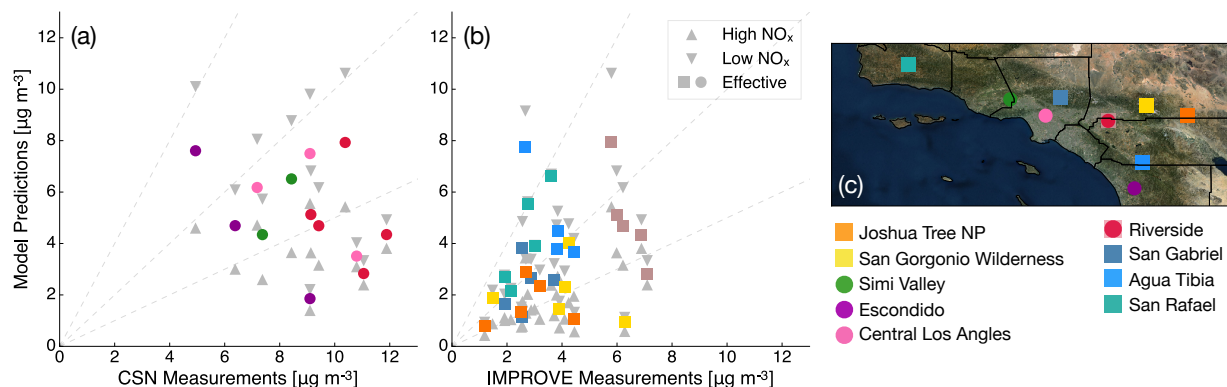


Figure 2.8: Model-measurement comparison for daily-averaged OA mass concentrations at (a) CSN and (b) IMPROVE sites in southern California. Panel (c) shows the geographic locations where the comparisons were made.

2.4.2 OA Mass Concentrations

Scatter plots comparing model predictions of OA from the Base simulations to (a) CSN and (b) IMPROVE measurements in southern California are shown in Figure 2.8(a) and 2.8(b). Predictions from the low and high NO_x simulations are presented in grey while predictions accounting for the influence of NO_x are shown in color. The colors denote different sites and the site locations are shown in Figure 2.8(c). The model-measurement performance is also captured using statistical metrics of fractional bias, fractional error, and the coefficient of determination in Table 2.4. At all CSN sites, model predictions of OA that included SOA mass concentrations adjusted for the

influence of NO_x were in-between those predicted between the low and high NO_x simulations. As explained earlier, this was because the VOC: NO_x ratios at all these sites (see Figure A.9(a)) were always higher than those in the high NO_x chamber experiments (see Table 2.2) and hence the SOA mass concentrations calculated using equation 2 were always higher than those predicted in the high NO_x simulations. At all the CSN sites, correcting for NO_x improved model performance compared to the high NO_x experiments but was still inferior compared to the predictions from the low NO_x simulations (see Table 2.4). The mean predicted OA mass concentration across all the CSN sites was about 30% lower than the measurements (5.96 versus $8.86 \mu\text{g m}^{-3}$). Model predictions of OA were very similar to those predicted in the low NO_x simulations at the IMPROVE sites where the VOC: NO_x ratios were higher (e.g., San Rafael–green square). But, similar to the finding at the CSN sites, model predictions of OA were in-between the predictions between the low and high NO_x simulations at the IMPROVE sites where the VOC: NO_x ratios were lower as a result of their proximity to urban areas (e.g., Agua Tibia–blue square and Riverside–brown square). Accounting for NO_x seemed to improve the model performance at the IMPROVE sites when compared to predictions from the high NO_x simulations and were slightly inferior to those from the low NO_x simulations (see Table 2.4). Of the 27 IMPROVE measurements available for comparison, 22 or $\sim 80\%$ of the model predictions corrected for NO_x were within a factor of two of measurements with little bias (fractional bias= -16.63%). The model skill, captured by the R^2 values, for all model simulations at both the CSN and IMPROVE sites was quite poor, but still slightly better than that found in earlier work for the southern California region with the CMAQ model (Baker et al., 2015). However, the model skill was much worse than that reported in earlier work with CMAQ (e.g., Murphy et al. (2017)) and WRF-Chem (e.g., Ahmadov et al. (2012)) over regions other than southern California, suggesting that there might be missing emissions sources and/or chemical pathways or meteorological considerations that contribute to the poor model skill in southern California.

Given the differences in the model-measurement comparison between the CSN (or urban) and IMPROVE (rural/remote continental) sites, the underprediction at the CSN sites might be indica-

tive of a missing urban source or pathway of OA formation. Recently, McDonald et al. (2018) found that volatile chemical products such as pesticides, coatings, cleaning agents, and personal care products may contribute substantially to IVOC emissions and account for more than half of the anthropogenic SOA formation in southern California. Our underprediction at urban sites might be evidence of missing SOA from volatile chemical product-related IVOC emissions. However, it is also possible that the urban versus rural/remote continental difference is an artifact of how the SOM models the oxidation chemistry and/or accounts for the influence of vapor wall losses. Within the CSN and IMPROVE sites, we did not find the model-measurement comparison to vary systematically by location. The model-measurement comparison over all of California using the 24 km simulations produced a similar result (Figure A.10).

Table 2.4: Statistical metrics of averages, fractional bias, fractional error, and R^2 for the model-measurement comparison in southern California.

Simulation	CSN					IMPROVE				
	Measured Average ($\mu\text{g m}^{-1}$)	Modeled Average ($\mu\text{g m}^{-1}$)	Fractional Bias	Fractional Error	R^2	Measured Average ($\mu\text{g m}^{-1}$)	Modeled Average ($\mu\text{g m}^{-1}$)	Fractional Bias	Fractional Error	R^2
Base- Low NO_x	8.86	7.96	-31.5%	46.0%	0.16	3.27	4.87	-1.38%	42.8%	0.116
Base- Effective	8.86	5.96	-53.4%	49.2%	0.13	3.72	4.02	-16.6%	44.8%	0.079
Base- High NO_x	8.86	3.97	-83.1%	83.1%	0.013	3.72	2.00	-74.1%	75.9%	0.317

Model predictions of the OA: Δ CO diurnal profile and daytime OA versus CO (between 10 am and 8 pm local time) are compared against measurements made at the Riverside site during the SOAR-1 campaign in Figure 2.9(a) and (b); SOA mass concentrations have been adjusted for the influence of NO_x using equation (2). The Δ CO for the measurements was calculated by assuming a background concentration of 105 ppbv (Hayes et al., 2013) while the Δ CO for the model predictions was calculated by using the model predicted background concentration of CO over the ocean to the west of Los Angeles. This model-measurement comparison was not completely coincident in time since the model results were between July 20 and August 2 while the SOAR-1 campaign spanned from July 15 to August 15. The measurements did not point to any substantial differences in results between the coincident and non-coincident time and hence we did not anticipate any issues in our comparisons here. The model predictions were able to capture the general trends in the measured diurnal profile in Figure 2.9(a) with low ratios during the night, high ratios attributed to photochemistry in the mid-afternoon, and a peak between 1 and 2 pm (local time). However, the modeled OA: Δ CO ratios at all times in the diurnal profile in Figure 2.9(a) and the slope of the OA:CO ratios in Figure 2.9(b) was approximately a factor of 2 to 3 lower than the measured ratios, indicating a significant underprediction of urban SOA, which was consistent with the much higher POA/SOA ratios predicted by the model compared to the observations, as discussed above. This underprediction cannot be blamed on the model grid resolution since a ratio with CO should to first order account for the influence of dilution in the grid cell. Cappa et al. (2016) showed much better model performance than this work when they assumed a non-volatile POA and SOA formed under low NO_x conditions. In this work, despite forming additional SOA from SVOCs and IVOCs, the evaporation of the POA mass and an SOA estimate adjusted for NO_x meant that the model performance was worse in comparison to Cappa et al. (2016). The sensitivity simulations of IVOC_{max} and $\text{S-IVOC}_{aromatic}$ produced slightly higher OA mass concentrations (10-15%) compared to the Base simulations but not dramatically different to influence the comparison in Figure 2.9(a) and (b). As mentioned earlier, SOA formation from

IVOC emissions from volatile chemical products, or other future improvements in the SOM, have the potential to reduce the model underprediction at Riverside during the SOAR-1 campaign.

2.4.3 POA and SOA Mass Concentrations

The 14-day averaged results predicted POA and SOA mass concentrations of 3.4 and $2.2 \mu\text{g m}^{-3}$ and an approximate 60:40 POA-SOA split at Riverside. Docherty et al. (2011) estimated average POA and SOA mass concentrations of 1.9 and $7.0 \mu\text{g m}^{-3}$ and a POA-SOA split of 20:80 at Riverside during the SOAR-1 campaign. On an absolute basis model predictions of POA mass concentrations were overpredicted by $\sim 80\%$. A sensitivity simulation that turned sea spray emissions off suggested that the 14-day averaged marine POA mass concentrations at Riverside were $0.8 \mu\text{g m}^{-3}$, which are very likely to be overestimated (Hayes et al., 2013). If the emissions of marine POA were updated to align better with the observations and in the limiting case where the marine POA mass concentrations at Riverside were negligible, model predicted POA mass concentrations at Riverside ($3.4 - 0.8 = 2.6 \mu\text{g m}^{-3}$) would compare well with the measured values ($1.9 \mu\text{g m}^{-3}$). As the POA mass concentrations in the SVOCcooking simulations increased and the SOA mass concentrations remained the same compared to the Base simulations, a low volatility and more realistic treatment of the POA from food cooking sources increased the discrepancy in the modeled and measured POA:SOA ratio at Riverside. It is also possible that the model might be over predicting POA because we only considered POA from certain sources (gasoline and diesel use, woodsmoke, and food cooking) to be semi-volatile.

Figure 2.1 shows that more than half of the partitioned POA (that excludes marine POA) in southern California belonged to other sources (e.g., road and construction dust) and this POA was treated as non-volatile in the Base simulations. Model predictions from the SVOC_{max} simulations that treated all POA except marine POA as semi-volatile predicted a 14-day averaged POA mass concentration of $2.1 \mu\text{g m}^{-3}$, which was much closer to the measured value of $1.9 \mu\text{g m}^{-3}$. This suggests that all POA, regardless of source, might be semi-volatile and could be modeled so in atmospheric models. While these results are in better agreement with measurements, $\text{PM}_{2.5}$ from

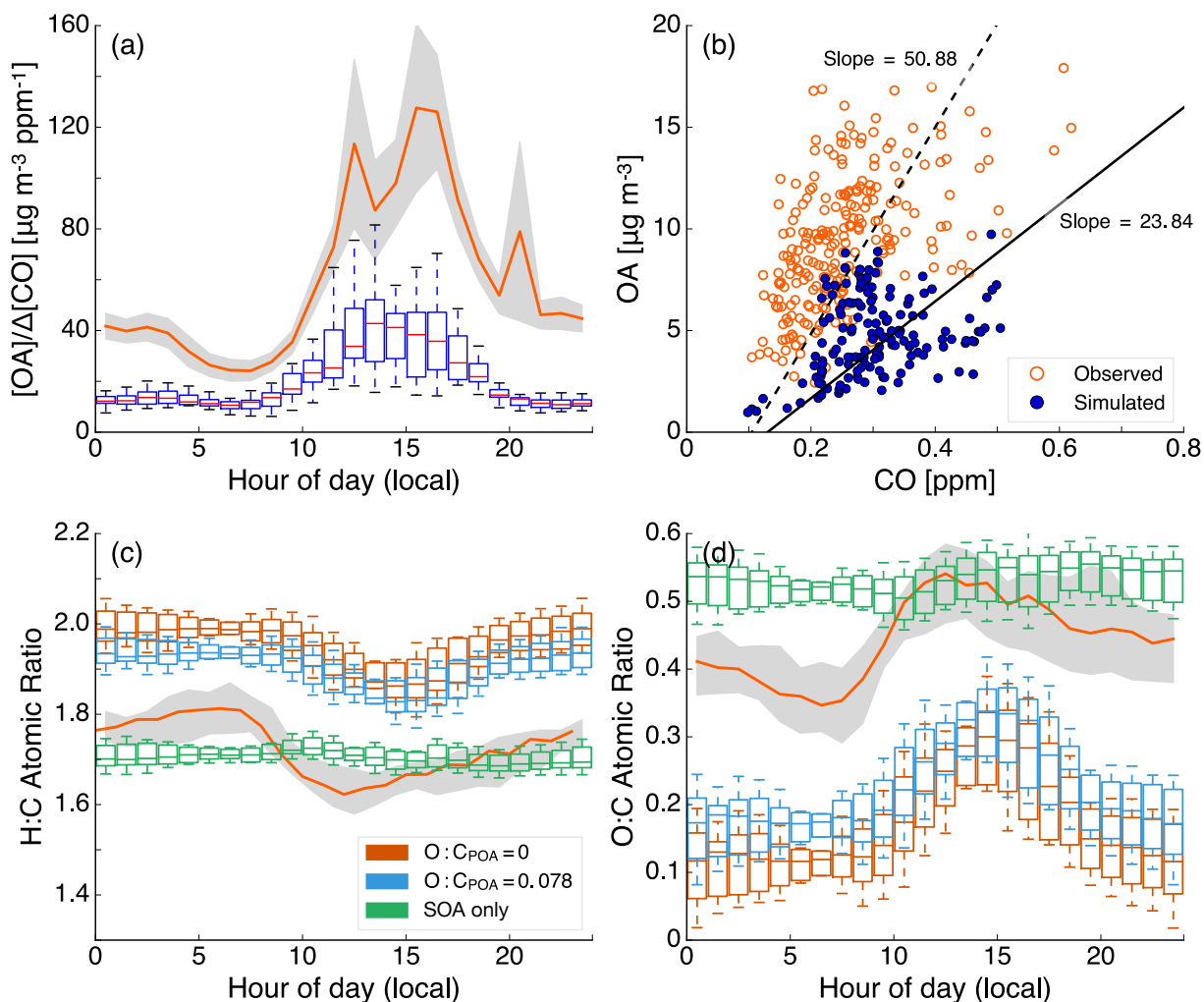


Figure 2.9: (a) Diurnal profile of the modeled and measured OA/ΔCO ratios at Riverside, CA. The box plots capture the 10th-25th-50th-75th-90th in model predictions over the simulated episode while the gray bands and solid orange line represent the 10th and 90th percentile and median of the measured data. (b) Modeled and measured OA mass concentrations plotted against CO concentrations between 10 am and 8 pm local time. The solid and dashed black lines represent lines fitted to the modeled and measured data by forcing the X-intercept to be the corresponding modeled and measured background CO concentration. Diurnal profiles of the modeled and measured (c) H:C and (d) O:C ratios of the OA (corrected as per Canagaratna et al. (2015)). The three different predictions show results from the Base simulations for OA assuming no change, the POA O:C was fixed to 0.078 based on the measurements of Docherty et al. (2011), and no POA.

road and construction dust sources is not created in a high temperature process followed by rapid cooling and so it is unknown whether the POA portion in it would evaporate with atmospheric dilution. We also compared the hydrocarbon-like OA (HOA) estimate from the measurements, which was more representative of POA from mobile sources, against model predictions of POA from mobile sources. We did not model POA from mobile sources separately but if we assumed that mobile sources only accounted for about a quarter of the partitioned POA mass in southern California (based on Figure 2.1), our estimated Base model predictions of POA mass concentrations from mobile sources of $0.85 \mu\text{g m}^{-3}$ ($=3.4 \times 0.25$) would compare reasonably with the measured HOA mass concentrations of $1.20 \mu\text{g m}^{-3}$.

On an absolute basis, SOA mass concentrations were underpredicted by a factor of 3 compared to measurements. Based on the discussion in the previous paragraph, if we added the non-mobile source POA to SOA, the net SOA mass concentration ($3.4 \times 0.75 + 2.2 = 4.75 \mu\text{g m}^{-3}$) was still 33% lower than the measured value. The SOA mass concentrations in the IVOC_{max} simulations – sensitivity simulations that modeled a fixed IVOC:NMOG ratio of 20% for all sources except biogenic sources, assumed IVOCs formed SOA similar to a C15 linear alkane, and which produced the maximum SOA mass concentrations amongst all the simulations – were 33% higher than those in the Base simulation but still 60% lower than the measured SOA mass concentration of $7 \mu\text{g m}^{-3}$. A combination of the two, i.e., adding the non-mobile source POA to the SOA formation in the IVOC_{max} simulations, resulted in a net SOA mass concentration that was only 22% lower than the measured SOA value. Since the IVOC_{max} simulations produced ambient IVOC concentrations that were more in line with the measurement trends (see Section 2.4.1), it is likely that the IVOC_{max} simulations were better in predicting IVOC concentrations and their contribution to SOA. However, there are no bottom up (i.e., source) or top down (i.e., atmospheric) data to directly constrain the emissions of and SOA formation from IVOCs in the IVOC_{max} simulations and hence this finding provides motivation for more detailed studies of IVOCs in the future.

2.4.4 OA Elemental Composition

The SOM tracks the carbon and oxygen numbers for the OA species and hence we were able to compare model predictions of the diurnal profiles for the OA H:C and O:C ratios to measurements made at the Riverside site during the SOAR-1 campaign. The comparisons are shown in Figure 2.9(c) and (d). For the Base simulations (shown as orange box plots), model predictions of H:C were significantly overpredicted and those for O:C were significantly underpredicted although the predictions did capture dips in the H:C and the peaks in the O:C ratios in the mid-afternoon, coincident with peak photochemical activity. The model predictions did not capture the slight increase in H:C and the decrease in O:C in the early morning attributed to emissions from rush hour traffic. The high H:C and low O:C predictions were a result of OA being dominated by POA (~60%), which in this work was modeled as a hydrocarbon distribution that had an H:C slightly larger than 2.0 and an O:C of 0. Docherty et al. (2011) found that POA had a campaign-averaged H:C of 1.92 and an O:C of 0.078. If the POA O:C were fixed to the values estimated by Docherty et al. (2011), model predictions (shown as blue box plots) improved – as shown in Figure 2.9(c) and (d) – but still over and under predicted the H:C and O:C, respectively; since SOM only tracks carbon and oxygen numbers for an organic species and determines the hydrogen number based on the remaining valence, specifying the O:C dictates the H:C. To assess the ability of the model to predict the elemental composition of SOA, we plot the diurnal profile of H:C and O:C of the SOA in Figure 2.9(c) and (d). Model predictions of SOA H:C and O:C (shown as green box plots) compared well with the measured range of values but did not reproduce the diurnal changes. Docherty et al. (2011) argued that the H:C and O:C of OA at Riverside was mostly controlled by the SOA composition, which did not change dramatically during the day, and was modified by POA at certain times when POA emissions dominated over SOA production (e.g., nights, rush-hour traffic). This suggests that if absolute predictions of the SOA mass concentrations and the POA-SOA splits were improved, our model would be able to predict both the magnitude and diurnal changes in OA H:C and O:C ratios. We found that the SOA H:C and O:C ratio predictions did not vary significantly and produced similarly flat diurnal profiles across a subset of sensitivity

simulations performed (Figure A.11), suggesting that the modeled elemental composition of SOA was not very sensitive to the distribution of precursor contributions to SOA.

2.5 Summary and Discussion

Organic aerosol (OA) is an important contributor to urban fine particle pollution yet remains one of its most uncertain components. In this work, we updated the organic aerosol treatment in the UCD/CIT chemical transport model to include a semi-volatile and reactive treatment of POA, emissions and SOA formation from IVOCs, the NO_x influence on SOA formation, and SOA parameterizations for SVOCs and IVOCs that were corrected for vapor wall loss artifacts during chamber experiments. All updates were implemented in the statistical oxidation model (SOM), which simulates the multigenerational aging and gas/particle partitioning of organic aerosol and is embedded in the UCD/CIT model (Cappa et al., 2016; Jathar et al., 2015, 2016). POA, SVOC, and IVOC updates were based on an interpretation of a comprehensive set of source measurements. The influence of NO_x on SOA formation was estimated offline using methods based on the $\text{VOC}:\text{NO}_x$ ratios/ NO_x concentrations.

Despite treating the POA from gasoline, diesel, biomass burning, and food cooking sources as semi-volatile, the updated model only predicted a 30-50% decrease in POA mass concentrations in the urban airshed even when the volatility data used to simulate POA projected a much larger decrease (45 to 80%). The primary reason for the weaker response was that a large fraction of the POA mass came from sources other than those modeled as semi-volatile, e.g., road and construction dust, marine. When all POA, except for marine POA, was modeled as semi-volatile, more than 60% of the POA mass evaporated and the POA mass concentrations under this scenario compared well with measurements made in Riverside, CA as part of the SOAR-1 field campaign. While this sensitivity analysis was informative, it is unlikely that the POA from sources such as road and construction dust is semi-volatile and recent measurements suggest that POA from food cooking sources has much lower volatility than assumed in the Base simulations in this work. These findings indicate that model predictions continue to overestimate POA relative to measured

concentrations. Sea spray emissions accounted for a quarter of the POA mass concentrations in the urban airshed but more recent observations suggest that the sea spray emissions or the organic fraction attributed to the sea spray emissions might be overestimated (Hayes et al., 2013). This needs to be examined in future applications of the UCD/CIT model. Atmospheric oxidation of the evaporated POA vapors or SVOCs did not contribute significantly to the SOA burden ($<0.1 \mu\text{g m}^{-3}$), even after accounting for the influence of vapor wall loss artifacts, since the timescales for SOA production appeared to be longer than the timescales for transport out of the urban airshed.

We found IVOCs to be more important than SVOCs but less important than traditional VOCs such as single-ring aromatics and biogenics in forming SOA. IVOCs accounted for less than $0.5 \mu\text{g m}^{-3}$ of SOA while single-ring aromatics and biogenics each contributed to approximately $1 \mu\text{g m}^{-3}$ in the Base simulations. The IVOC contribution to SOA was smaller than that for aromatics partly because IVOC SOA was relatively less sensitive to corrections of vapor wall loss artifacts in chamber experiments. Another reason for the small IVOC contribution to SOA was that we only considered IVOC emissions from gasoline, diesel, and biomass burning. On analyzing trends in SOA precursor concentrations in southern California, the modeled IVOC concentrations in this scenario appeared to be underpredicted by a factor of ~ 2 . Allowing all sources that emit non-methane organic gases (NMOG) to emit IVOCs (using an IVOC:NMOG ratio of 0.2) and form SOA similar to a C_{15} linear alkane seemed to increase the IVOC contribution to SOA ($\frac{1}{3}$ of total SOA) and produced better comparisons against ambient measurements of IVOC concentrations, OA composition, and SOA mass concentrations. This might be indicative of missing IVOC emissions in the model. These missing emissions might be from volatile chemical products such as pesticides, coatings, cleaning agents, and personal care products, which have been found to contribute substantially to urban SOA burdens (McDonald et al., 2018). It is also likely that the missing IVOC emissions are from sources considered in this work (i.e., gasoline, diesel, and biomass burning sources) but were not accounted in the emissions inventories because they have been shown to be very easily lost to sampling tubes (Pagonis et al., 2017). The IVOCs in this work were modeled using a linear alkane surrogate despite recent evidence that IVOCs in combustion emissions

are a mixture of branched and cyclic alkanes, aromatics, and oxygenated compounds with very few linear alkanes (Koss et al., 2018; Zhao et al., 2016, 2017). A more chemically appropriate representation of the IVOCs would not have substantially changed the findings in this work since the linear alkane surrogates were chosen to reproduce the SOA formation in chamber experiments performed on combustion emissions. However, future work should incorporate the more detailed speciation available to model the emissions and SOA formation from IVOCs.

Loss of vapors to the Teflon walls has been shown to significantly bias SOA formation in environmental chamber experiments (Krechmer et al., 2016; Zhao et al., 2014). Cappa et al. (2016) studied the influence of vapor wall loss artifacts on ambient SOA mass concentrations from VOC precursors. In this work, we extended the work of Cappa et al. (2016) by considering additional precursors of SOA, i.e., S/IVOCs. Correcting for vapor wall loss artifacts seemed to increase SOA mass concentrations for all precursors but the enhancement varied by precursor. With a few exceptions, the SOA enhancements correlated with carbon number where larger carbon number precursors had lower enhancements and vice versa. The reason for this inverse relationship was that larger precursors and their oxidation products have shorter chemical lifetimes and undergo fewer chemical reactions to form SOA, which made them less susceptible to being lost to the chamber walls. Recent work suggests that the vapor wall loss rates to the Teflon wall might be two or more times larger than the rates used in this work to develop the SOM parameters (Huang et al., 2018; Krechmer et al., 2016). The use of these faster rates will tend to increase the model predicted SOA mass concentrations and help explain the underpredictions with ambient measurements.

The emissions inputs and chemical treatment for OA was varied substantially in the sensitivity simulations performed in this work. Yet, the simulations seemed to change the OA by less than a factor of 2 suggesting that the model framework, except for the treatment of NO_x , was generally reasonable in constraining the total OA mass concentrations in southern California. The total SOA enhancement was modified by the NO_x level where low NO_x regions might see higher enhancements compared to high NO_x regions. In southern California where urban SOA mass concentrations might be higher than rural/remote continental SOA mass concentrations, the NO_x -

mediated enhancement will tend to reduce the spatial gradients in SOA mass concentrations and make SOA a regional pollutant like O₃. Accounting for the influence of NO_x seemed to improve OA model performance against routine measurements in rural/remote environments (i.e., Interagency Monitoring of Protected Visual Environments network) where OA model predictions were within a factor of 2 with very little bias (e.g., fractional bias of -16.6%). However, model predictions of OA at routine monitoring sites in urban environments (i.e., Chemical Speciation Network) and at the Riverside site during the SOAR-1 field campaign were still underpredicted by at least a factor of 2 (e.g., fractional bias of -49.2%). This suggested a missing emissions or chemical source of OA in urban areas.

The future OA burden in southern California will depend not only on reductions in POA and SOA precursor emissions but also on changes in oxidant concentrations and VOC:NO_x ratios. We used the Base model to simulate the same time period, July 20 to August 2, for the year 2035 to determine how emissions reductions and atmospheric conditions may change in a future year to influence ambient OA-POA-SOA mass concentrations. The same meteorology and environmental conditions were assumed, with the understanding that climatological changes in the future may alter the findings presented here. Emissions reductions in CO, NO_x, VOC, PM_{2.5}, SO₂, and NH₃ were informed by net reductions in statewide emissions between 2005 and 2035 as projected by the California Emission Projections and Analysis Model (CARB, 2018). The 2005 inventory was scaled based on these emissions reductions for anthropogenic sources but the biogenic emissions and VOC emissions profiles were kept the same. We did not resolve the emissions reductions in these pollutants by source or by region since the goal was to examine the general trend in the OA-POA-SOA system and not to predict future air quality; heterogeneity in the reduction in pollutant emissions by source and geography may alter the results. Statewide emissions reductions in CO, NO_x, and VOC of 78%, 83%, and 33% resulted in approximately 50%, 75%, 75%, and 30% reductions in ambient concentrations of CO, NO, NO₂, and VOC in the urban airshed (Figure A.12 plots the ratio of CO, NO, NO₂, and VOC concentrations in 2035 to those in 2005). Here, VOC is the sum of all organic species tracked in the SAPRC-11 gas-phase chemical mechanism

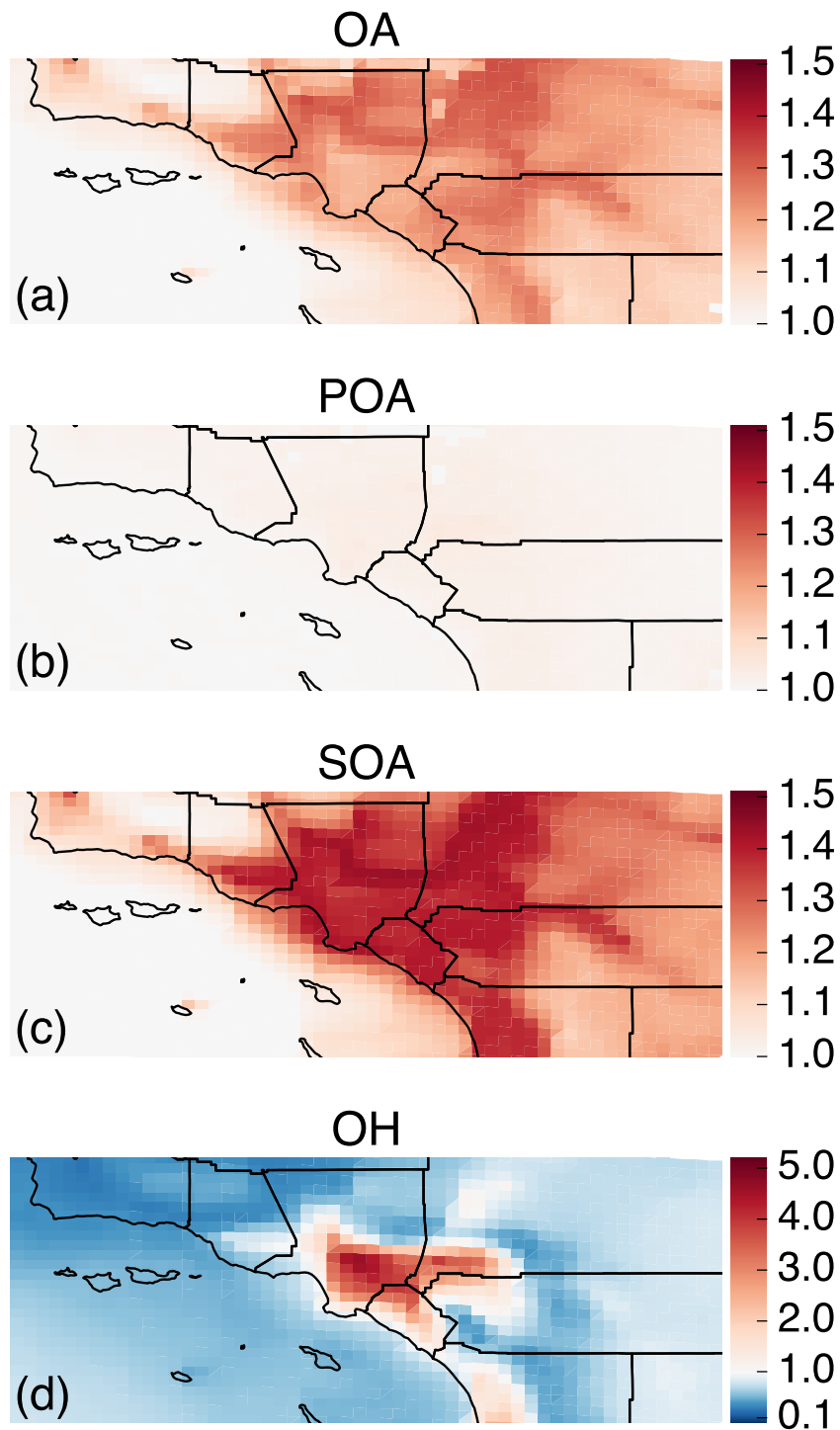


Figure 2.10: Ratios of 14-day averaged model predictions of (a) OA, (b) POA, (c) SOA, and (d) OH from 2035 to those from 2005. The 2035 simulations were performed with 2005 meteorological inputs but scaling the anthropogenic emissions for CO, NO_x, VOC, PM_{2.5}, SO₂, and NH₃ based on changes projected by the California Emission Projections and Analysis Model (CARB, 2018).

(excludes methane). Since the NO_x reduction was much more dramatic than that for VOCs, the VOC: NO_x ratio in the urban airshed increased from ~ 1 to ~ 5 between 2005 and 2035, which was in line with recent modeled estimates by Fujita et al. (2016).

We plot the ratio of the mass concentrations for OA, POA, and SOA in 2035 to those in 2005 in Figure 2.10(a), (b), and (c) respectively. SOA mass concentrations have been adjusted for the influence of NO_x using equation 2. POA mass concentrations in the urban airshed in 2035 were slightly higher ($\sim 5\%$) than those in 2005 primarily because $\text{PM}_{2.5}$ emissions were higher in 2035 compared to 2005; according to CEPAM, increases in $\text{PM}_{2.5}$ emissions were mostly from increases in area source emissions and not mobile source emissions. Surprisingly, SOA mass concentrations in the urban airshed were 30-40% higher in 2035 compared to 2005 despite a 30% reduction in VOC emissions and concentrations. Some of the increase in the SOA mass concentrations was from a shifting VOC: NO_x ratio that produced more SOA via the low- NO_x pathway. However, the primary reason for the SOA increase was that OH concentrations in the urban area had increased by a factor of 2 to 4 (see Figure 2.10(d)) and had reacted more of the SOA precursors. The OH concentrations were presumably higher in 2035 because lower NO_x emissions resulted in a higher OH lifetime since the $\text{NO}_2 + \text{OH}$ reaction is the primary sink for OH in polluted environments (Jacob, 1999), including the Los Angeles area (Griffith et al., 2016). These findings suggest that the SOA and OA mass concentrations may not necessarily respond linearly to reductions in VOC and NO_x emissions in the future but rather will be strongly influenced by the changes in chemical regime. Similarly, Praske et al. (2018) argue that dramatic reductions in NO_x emissions and concentrations in urban environments may increasingly lead to SOA formation through autooxidation pathways and alter the rate and quantity of SOA formed. Hence, attention needs to be paid to appropriately simulate the chemical regime (e.g., oxidant concentrations, VOC: NO_x ratios, autooxidation reactions) if we are to accurately simulate the SOA burden in urban environments in the future.

Chapter 3

Oxygenated Aromatic Compounds are Important Precursors of Secondary Organic Aerosol from Biomass Burning

3.1 Introduction

Volatile organic compounds (VOCs) participate in photochemical reactions to form secondary organic aerosol (SOA), which accounts for a significant fraction of the sub-micron atmospheric aerosol mass (Jimenez et al., 2009). Biomass burning, which includes wildfires, prescribed burning, agricultural fires, and residential wood combustion, is the largest combustion-related source of VOCs to the atmosphere (Reid et al., 2005; Lamarque et al., 2010; Granier et al., 2011). However, the contribution of biomass burning to the regional and global SOA burden is quite uncertain (Shrivastava et al., 2017), and consequently the impacts of biomass burning aerosols on climate, air quality, human health, and visibility (McClure et al., 2018; Ford et al., 2018; O'Dell et al., 2019) are uncertain as well. There is a need to better understand the precursors and formation pathways of SOA from biomass burning sources.

Laboratory experiments performed on biomass burning emissions, using environmental chambers and oxidation flow reactors, have shown that VOC oxidation results in SOA production and an enhancement in OA mass (Hennigan et al., 2011; Ortega et al., 2013; Tkacik et al., 2017; Ahern et al., 2019; Lim et al., 2019). In instances where the OA mass increased with photochemical aging, the observed SOA production in these experiments varied substantially, with SOA production between zero to six times the primary aerosol emissions. While some prior work has found it challenging to explain the variability in the SOA produced across different fires, these studies have concluded that precursors, such as alkanes and single-ring aromatics that are important for fossil fuel combustion, contribute little to the measured SOA mass (Ahern et al., 2019; Jathar et al.,

2014; Bruns et al., 2016). Thus, an improved understanding of the VOCs responsible for biomass burning-related SOA is needed.

Detailed speciation of VOCs in biomass burning emissions are now available through measurements using one- and two-dimensional gas chromatography-mass spectrometry (GC/MS) (Gilman et al., 2015; Hatch et al., 2015; Hatch et al., 2017; Hatch et al., 2018; Jen et al., 2019) and chemical ionization mass spectrometry (CIMS) (Stockwell et al., 2015; Bruns et al., 2016; Bruns et al., 2017; Koss et al., 2018; Sekimoto et al., 2018). By linking the detailed VOC speciation to the laboratory-measured SOA formation, several studies have attributed a substantial fraction of the SOA mass to a few VOC classes of SOA precursors: monoterpenes (e.g., α -pinene), oxygenated aromatics (e.g., phenols), heterocyclic compounds (e.g., furans), and polycyclic aromatic hydrocarbons (PAHs, e.g., naphthalene) (Ahern et al., 2019; Bruns et al., 2016; Stefenelli et al., 2019). Ahern et al. (2019) found monoterpenes to be important for two conifers (i.e., black spruce, ponderosa pine) and furans to be important for grasses (i.e., wiregrass) while Bruns et al. (2016) and Stefenelli et al. (2019) found oxygenated aromatics and PAHs to be important for SOA from wood stoves. Lim et al. (2019) found tight correlations between the SOA produced and the initial VOC mass, with stronger correlations observed for VOCs more volatile than monoterpenes. These earlier studies suggest that the dominant SOA precursors vary widely based on the fuel and there is a continued need to better understand these precursors across the diversity of fuel types found within the broad source category of biomass burning.

Finally, studies that have modeled SOA formation from biomass burning emissions in laboratory experiments have not systematically accounted for the influence of vapor losses to the chamber walls (Zhang et al., 2014; Hodshire et al., 2019; He et al., 2020), multi-generational aging (Jathar et al., 2016), or kinetic gas/particle partitioning (Shiraiwa et al., 2012), all of which could influence SOA formation and the interpretation of the chamber data. It is likely that some, if not all, of the differences between earlier studies could be attributed to differences in the experimental methods (e.g., aging timescales) and artifacts (e.g., particle and vapor wall loss rates). There is a need to

use models that simulate the detailed physicochemical evolution of the OA mixture and account for experimental artifacts.

In this work, we develop and use a coupled chemistry-thermodynamics-microphysics organic aerosol model to simulate the formation and composition of SOA from new chamber experiments performed on biomass burning emissions representative of those found in the western US. The primary finding of this work is that oxygenated aromatics are important precursors of SOA formation in chamber experiments performed on the biomass burning emissions.

3.2 Materials and Methods

3.2.1 Environmental Chamber Measurements

We performed a total of eleven photooxidation experiments using the Colorado State University (CSU) 10 m³ Teflon® environmental chamber on emissions from six western US fuels (Ponderosa pine, Lodgepole pine, Douglas fir, manzanita, Engelmann spruce, or subalpine fir), as part of the FIREX (Fire Influence on Regional and Global Environments) laboratory campaign conducted at the Fire Sciences Laboratory in Missoula, MT in 2016 (Selimovic et al., 2018; Koss et al., 2018). Some fuels were studied in multiple experiments (e.g., Ponderosa pine) while some were studied only once (e.g., Engelmann spruce). Details for all eleven chamber experiments are provided in Tables B.1, B.2, and B.4. Briefly, a known mass of a single fuel (298-4376 g) placed on a concrete pallet was electrically ignited and the smoke from the fire was diverted into a large stack. Smoke from the stack was drawn and injected into the chamber and irradiated with UV-A lights (32 W × 80=2.6 kW) to simulate photochemical oxidation. Five of the chamber experiments were performed at high NO_x conditions (>400 ppbv) with HONO added as an OH precursor. Three experiments were performed at modest NO_x conditions (2-20 ppbv) with H₂O₂ added as an OH precursor; NO_x in these experiments was limited to that generated by the fire. One experiment was performed with UV lights only (no intentional addition of HONO or H₂O₂) and two experiments used ozone (O₃) as an oxidant (400 ppbv). During the O₃ experiment, oxidation was first per-

formed with O₃ in a dark chamber, and after slightly more than 2 hours the UV lights were turned on.

A high-resolution aerosol mass spectrometer (HR-AMS) was used to estimate OA mass concentrations and the elemental composition (e.g., O:C ratio). The raw OA mass concentrations were corrected for losses and artifacts in the HR-AMS using a scaling factor (SF), which was determined by comparing measurements of non-refractory aerosol from the HR-AMS to those estimated from measurements made by a scanning mobility particle sizer (SMPS) and single particle soot photometer (SP2). The SF accounts for instrument-specific factors, including transmission, collection, and ionization efficiencies (See SI Section ‘Scaling Factor Calculation’). We also used the Composition Dependent Collection Efficiency (CDCE) approach proposed by Middlebrook et al. (2012) to correct the OA mass concentrations but this approach seemed to produce similar results to those from the use of the SF. Following Ahern et al. (2019), suspended OA mass concentrations were corrected for particle wall losses by assuming that the loss of OA mass at a mass-to-charge ratio of 95.086067 (C₇H₁₁⁺), which was assumed to be a non-volatile and non-reactive marker for POA, was purely from particle losses to the walls. These corrections resulted in two estimates for OA mass concentrations assuming: (i) SOA vapors only condensed on the suspended particles (w=0) and (2) SOA vapors condensed on both the suspended particles and the particles deposited on the walls (w=1) (He et al., 2020; Hildebrandt et al., 2009). The central estimate in the particle-wall-loss-corrected OA mass concentrations was calculated as an average of these estimates. The uncertainty was approximated by assuming that the two estimates were separated by four standard deviations. For simplicity, the particle-wall-loss-corrected OA mass concentration at lights on was defined as POA and any increase in OA mass was defined as SOA. We assumed that particle-wall-loss-corrected POA mass concentrations remained constant during the experiment; more details about this assumption are discussed in ‘Treatment of POA’ below in Section 3.2.2. We assumed an uncertainty of 28% on the O:C measurements based on previous laboratory work performed with the HR-AMS (Canagaratna et al., 2015).

The modeling relied on OH estimates and O₃ measurements to determine the oxidation chemistry of the SOA precursors. The OH concentrations and exposure were estimated by tracking the decay of deuterated butanol (D9) as measured by a quadrupole proton transfer reaction mass spectrometer (PTR-MS) (Rogers et al., 2006; Barnet et al., 2012). O₃ was directly measured with a reference instrument. We used the number size distributions measured by the SMPS to determine the initial particle size distributions at the beginning of the experiment.

3.2.2 SOM-TOMAS Modeling

We developed the Statistical Oxidation Model-Two Moment Aerosol Sectional (SOM-TOMAS) model to simulate the chemistry, thermodynamic properties, and kinetic gas/particle partitioning of SOA produced during photooxidation of biomass burning emissions. A detailed description of the SOM and TOMAS models can be found in earlier work (Zhang et al., 2014; Cappa et al., 2012; Adams et al., 2002; Pierce et al., 2011). Briefly, the SOM uses a carbon-oxygen grid to track the chemical evolution of the gas- and particle- phase species arising from VOC oxidation. Each cell in the carbon-oxygen grid is a model species that represents the average properties of the oxidation products with the same carbon (N_C) and oxygen (N_O) number. All properties of each model species (e.g., reactivity (k_{OH}), volatility (C^*)) are expressed in terms of N_C and N_O . The following six parameters determine the formation, evolution, and thermodynamic properties of the oxidation products in a SOM grid: (i–iv) p_1 – p_4 , the yields of four functionalized products that add one, two, three, and four oxygen atoms to the carbon backbone respectively; (v) m_{frag} , the parameter that characterizes the fragmentation probability, $P_{frag} = (O:C)^{m_{frag}}$; and (vi) ΔLVP , the decrease in the saturation vapor pressure (or C^*) of the model species per addition of an oxygen atom. The SOM has been previously used to model SOA formation from individual VOCs (Zhang et al., 2014; Cappa et al., 2012), VOC mixtures (He et al., 2020), engine emissions (Eluri et al., 2018), and precursors in an urban airshed (Jathar et al., 2016; Akherati et al., 2019; Cappa et al., 2016). The SOM and TOMAS models are coupled in that the particle-phase species in SOM are tracked in the TOMAS size sections. TOMAS in our setup has 36 size sections spanning dry diameters of

approximately 3 nm to 10,000 nm. In each size section, TOMAS tracks the number of particles as well as the mass of each SOM model species in the particle phase. In this work, TOMAS simulates coagulation between size sections and kinetic condensation/evaporation of mass between the particle and vapor phases for all SOM model species.

SOA Precursors. Koss et al. (2018) used a proton transfer reaction - time of flight - mass spectrometer (PTR-ToF-MS) to measure stack emissions of ~ 150 unique hydrocarbons and lightly oxygenated gas-phase organic compounds and ~ 370 partially speciated gas-phase organic compounds from 57 separate fires during FIREX. The PTR-ToF-MS was able to identify molecules with up to 4 oxygen atoms per molecule and up to an O:C ratio of 2. Partially speciated VOCs were those where Koss et al. (2018) could not determine an exact speciation and assumed that the detected species only comprised of C, H, and O. Alkanes and partially speciated compounds larger than C_{10} , reduced and oxygenated aromatics, heterocyclics, and biogenics were considered to form SOA in this work. Altogether, 86 speciated VOCs and 61 partially speciated VOCs that were lumped by carbon and oxygen number were modeled to form SOA. Concentrations of SOA precursors measured in the stack were averaged over the duration of the fire and ratioed with acetonitrile to calculate fire-specific emissions ratios (i.e., $VOC_i:Acetonitrile$). Acetonitrile was chosen over other inert tracers such as CO because the background (room) concentrations of acetonitrile were relatively much lower than those in the stack. The PTR-ToF-MS instrument measured emissions in the stack and not in the chamber (except for Fire007). Hence, initial concentrations of the SOA precursors at the beginning of the chamber experiment were calculated by multiplying the stack-based emissions ratios with the acetonitrile concentrations measured by a different quadrupole PTR-MS that sampled from the chamber (de Gouw et al., 2007; Coggon et al., 2019). Based on simultaneous measurements made during FIREX in a different chamber across 30 individual experiments (Lim et al., 2019), we found that the acetonitrile concentrations measured by the quadrupole PTR-MS were 38% higher than those measured by the PTR-ToF-MS (Figure B.2), possibly from multiple isobaric interferences from the unit mass resolution of the quadrupole PTR-MS. The initial concentrations of the SOA precursors were scaled by 0.62 to ac-

count for this difference. Stack emissions data from the PTR-ToF-MS were directly available for five of the eleven chamber experiments. For the remainder, PTR-ToF-MS-derived emissions ratios (to acetonitrile) from all fires performed with the same fuel as that used in the chamber experiment were averaged before being used for that particular chamber experiment. Emissions ratios for the SOA precursors, lumped by VOC class, for each of the eleven chamber experiments is presented in Table ???. We also considered the uncertainty reported in the PTR-ToF-MS measurements and examined its influence on model predictions of SOA. Lower- and upper-bound estimates for SOA production due to these uncertainties in the emissions measurements were calculated by running two sets of simulations for each experiment, assuming that all SOA precursors were either at their lower or upper bounds, based on the 95th percentile confidence interval documented in Koss et al. (2018). The uncertainty varied by VOC (15% to 100%; 2σ) with lower uncertainties for smaller carbon number VOCs and hydrocarbons and larger uncertainties for larger oxygenated VOCs. The uncertainty in the model predictions for SOA was approximated by assuming that the lower and upper bounds were separated by four standard deviations. We should note that we did not consider the SOA formation from semi-volatile organic compounds (SVOCs) emitted by biomass burning (Jen et al., 2019) and recommend that this be examined in the future.

SOM Parameterizations for Traditional Precursors. Each SOA precursor based on the PTR-ToF-MS data and its reaction with OH/O₃ was modeled explicitly in the SOM-TOMAS model. The parent VOC is allowed to react with OH (for all SOA precursors) and O₃ (biogenic SOA precursors only). In modeling the SOA formation, the 147 (86+61) potential SOA precursors were assigned to one of nine surrogate compounds or compound classes: (i) *n*-dodecane, (ii) benzene, (iii) toluene, (iii) *m*-xylene, (iv) naphthalene, (v) isoprene, (vi) α -pinene, (vii) an alkylfuran mixture consisting of 60% dimethylfuran and 40% 2-methylfuran, (viii) phenol and guaiacol, and (ix) syringol; more details can be found in Table B.5. This is in line with other approaches (Carlton et al., 2010) and necessary because experimental observations and parameterizations of SOA formation are not available for each individual compound. The SOM parameters for each of these surrogates were developed based on high-NO_x chamber experiments and are listed in Table B.6.

We chose to use SOM parameters for the high NO_x chamber experiments because simulations performed with a modified version of the Master Chemical Mechanism (MCM) suggested that the peroxy radicals (RO_2) predominantly reacted with NO in nine of the eleven chamber experiments, even those in which no additional HONO was added (Coggon et al., 2019); the branching ratio (β) that quantifies the RO_2 fate, was calculated for all of the experiments and is presented in Figure B.3. Although not definitive, the MCM simulations helped minimize the uncertainty linked to extrapolating the high- NO_x SOA parameters based on single VOC experiments to the biomass burning experiments analyzed in this work. Alkanes larger than C_{10} were modeled as *n*-dodecane, C_8 and larger single-ring aromatics were modeled as *m*-xylene, all monoterpenes and sesquiterpenes were modeled as α -pinene, and all PAHs were modeled as naphthalene. Although SOA mass yields for the different monoterpenes found in biomass burning emissions may vary by more than a factor of 2 (Hatch et al., 2015), Ahern et al. (2019) showed that the use of α -pinene as a surrogate to model SOA formation from all monoterpenes only marginally changed model predictions. For these traditional SOA precursors, the surrogate choice was similar to that used in previous applications of the SOM (Akherati et al., 2019) and the SOM parameters for these surrogates were corrected for the influence of vapor wall losses based on the loss rates estimated by Zhang et al. (2014) ($k_{\text{vap, on}} = 2.5 \times 10^{-4} \text{ s}^{-1}$). Heterocyclic compounds that included furans and substituted furans were modeled using the alkylfuran mixture while oxygenated aromatics, except for syringol, were modeled as phenol or guaiacol (more details in the next paragraph). In the absence of additional information, partially speciated SOA precursors larger than C_{10} were modeled as *n*-dodecane.

The surrogates and SOM parameters used to model the SOA precursors in this work only inform the statistical trajectory for the oxidation chemistry and it is very likely that the surrogate itself and the SOA precursor (as long as they are not identical) have different SOA mass yields (Eluri et al., 2018). For example, SOA precursors with a carbon number larger than the surrogate will have higher SOA mass yields and vice versa. This approach has been found to work well (Cappa et al., 2012) and is generally consistent with observations for alkane (Tkacik et al., 2017;

Lim et al., 2009; Presto et al., 2010) and alkene (including biogenic) VOCs (Forstner et al., 1997; Griffin et al., 1999; Keywood et al., 2004). The SOA mass yields for C₈ and larger single-ring aromatics do not seem to vary strongly with carbon number so this approach likely overestimates the SOA contribution from these precursors. There is limited evidence on how SOA mass yields for heterocyclics and oxygenated aromatics vary by carbon number. As discussed in the next section, the SOM parameters used to model the SOA formation from heterocyclics and oxygenated aromatics were determined in a way to approximately account for the influence of carbon number on the SOA mass yields.

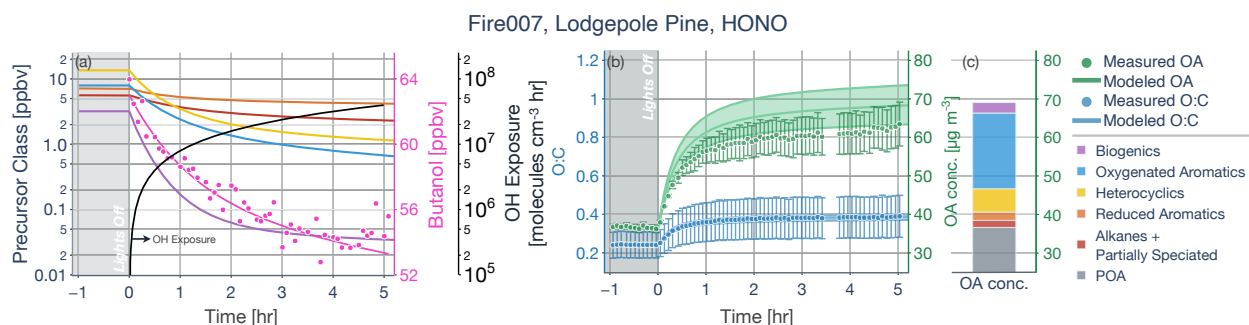


Figure 3.1: (a) Decay of D9 (deuterated butanol, pink) and VOCs, summed by class, with time and the OH exposure estimated based on the decay of D9; color scheme for VOCs can be found in the legend to the extreme right. (b) Model predictions of OA mass concentrations (green) and O:C ratio (blue) compared with measurements. Both results are for a lodgepole pine experiment performed at high NO_x conditions (Fire007). (c) The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

SOM Parameterizations for Heterocyclics and Oxygenated Aromatics. Recently, He et al. (2020) performed high NO_x chamber experiments with an alkylfuran mixture (60:40 mixture of 2-methylfuran and dimethylfuran by mass) and developed SOM parameters (i.e., p_1 - p_1 , m_{frag} , and ΔLVP described earlier) to simulate the SOA formation and O:C ratio from that mixture; these parameters were corrected for vapor wall losses using an estimated vapor wall loss rate coefficient ($k_{vap,on}$) of $1.28 \times 10^{-3} \text{ s}^{-1}$ for that specific chamber. Furans and substituted furans account for a substantial fraction of heterocyclic compounds in biomass burning emissions (Koss et al., 2018), and hence we used the SOM parameters for the alkylfuran mixture, in the absence of SOA mass

yield data, to represent the SOA formation from all heterocyclic compounds. SOM parameters for all oxygenated aromatics were developed here using the high-NO_x chamber experiments of Yee et al. (2013) for phenol and guaiacol. The chamber SOA mass yields for phenol and guaiacol in Yee et al. (2013) were similar to those observed in other experiments performed with phenolic species (Yee et al., 2013; Coeur-Tourneur et al., 2010; Nakao et al., 2011; Lauraguais et al., 2014; Liu et al., 2019; Finewax et al., 2018; Finewax et al., 2019). A single SOM parameter set was able to explain the evolution of the SOA mass concentrations in the phenol and guaiacol experiments when differences in their molecular formulas were accounted for, indicating that the oxidation chemistry of these two species might be similar. A separate SOM parameter set was developed for syringol since the phenol- and guaiacol-based parameters overestimated the SOA formation from syringol by nearly a factor of two. The model-measurement comparisons for the phenol, guaiacol, and syringol experiments are shown in Figure B.4. The SOA parameters for the phenolic species slightly under-predicted the O:C values measured for SOA from those species (between 0.8 and 1) (Chhabra et al., 2011). The oxygenated aromatics parameters were corrected for the influence of vapor wall losses based on the loss rates estimated by Zhang et al. (2014) ($k_{\text{vapor}}=2.5 \times 10^{-4} \text{ s}^{-1}$) as these experiments were performed in the same chamber.

Treatment of POA. Previous work has found POA from biomass burning emissions to be semi-volatile (Huffman et al., 2009; May et al., 2013). Bian et al. (2015), based on the results of a kinetic model, argued that the loss of semi-volatile POA vapors to the Teflon® walls can lead to substantial evaporation of the suspended POA mass in chamber experiments performed on biomass burning emissions. Hennigan et al. (2011) suggested that POA can undergo heterogeneous oxidation on the time scale of a chamber experiment. In contrast to these earlier studies, we did not find evidence for evaporation or photochemical processing of POA during the FIREX chamber experiments. This is consistent with findings from experiments performed with a smaller chamber during FIREX (Cappa et al., 2020). In at least one experiment where the chamber contents were monitored in the dark for more than an hour, the particle-wall-loss-corrected POA mass concentrations did not vary much (~2-3%) during the dark period (see Figure 3.1(a) for Fire007). This could mean that the

POA was primarily composed of sufficiently low-volatility material to not be affected by the loss of semi-volatile vapors to the Teflon® walls that could lead to evaporation of the suspended POA mass. Alternatively, it is possible that the evaporation rates linked to the loss of semi-volatile POA vapors to the Teflon® walls were too slow to be observed during the dark period in that experiment. The slow evaporation rates could indicate a mass transfer limitation due to a viscous or semi-solid aerosol, which has been previously observed for combustion-related POA (Grieshop et al., 2009; Takhar et al., 2019). Furthermore, particle-wall-loss-corrected concentrations of the OA mass at a mass-to-charge ratio of 60.02113 ($\text{C}_2\text{H}_3\text{O}_2^+$), one that includes contributions from directly-emitted compounds such as levoglucosan, mannosan, and galactosan (Hennigan et al., 2011; Simoneit et al., 1999; Aiken et al., 2009; Cubison et al., 2011), did not change much during the photooxidation periods for all chamber experiments (Figure B.5). This might suggest that POA was not being photochemically processed during our chamber experiments. Based on the available evidence in our specific experiments, we assumed in our simulations that the particle-wall-loss-corrected POA mass concentrations remained constant during the photooxidation experiments. Future modeling studies may need to explicitly model the POA volatility and the phase state of OA and their impacts on gas/particle partitioning. This assumption also allowed us to calculate the lower limit of SOA mass produced during the experiment by subtracting the initial POA from the particle-wall-loss-corrected OA mass concentrations. Any loss of POA, either through evaporation or photochemical oxidation, should increase the SOA estimates.

Accounting for Experimental Artifacts. In the SOM-TOMAS model, losses of vapors to the walls of the Teflon® chamber are modeled here following Zhang et al. (2014) and Krechmer et al. (2016). Briefly, the first-order loss rate of vapors to the walls is assumed to be equal to $k_{vap,on}$ and the release of vapors from the walls is modeled using absorptive partitioning theory where the Teflon® wall is assumed to have an equivalent mass concentration that varies based on the volatility of the model species ($C_{wall} = 16 \mu\text{g m}^{-3}$ to 10 mg m^{-3}) (Krechmer et al., 2016). Recently, He et al. (2020) estimated an average $k_{vap,on}$ of $1.28 \times 10^{-3} \text{ s}^{-1}$ for the CSU chamber from the observed loss rates of small, electrically-neutral particles ($<100 \text{ nm}$). In addition to losses

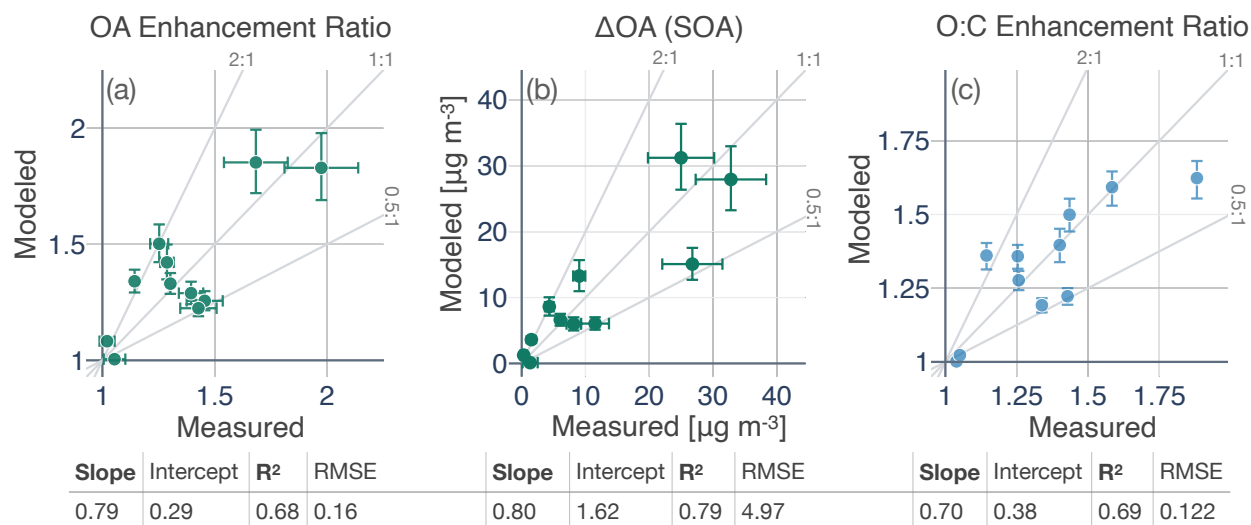


Figure 3.2: End-of-experiment model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ($\mu\text{g m}^{-3}$), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments. Statistical metrics based on a linear fit to the model-measurement comparison are presented at the bottom of each panel. RMSE = Root Mean Squared Error.

of vapors to the chamber walls, vapors were also lost to the flexible aluminum transfer duct that brought smoke from the stack to the chamber (ID ~ 20 cm $\times$ length ~ 20 m, volumetric flow rate of $0.47 \text{ m}^3 \text{ s}^{-1}$, residence time of 1.5 s) or in the ejector-diluters used to fill the chamber with smoke. To investigate the losses of SOA precursors to the walls of the transfer duct, we compared emissions ratios of SOA precursors in the stack to those in the chamber for Fire007 (Figure B.6); this was the only experiment where the PTR-ToF-MS sampled from both the stack (during the burn) and the chamber (after the burn and chamber filling were complete). We found that the intermediate-volatility SOA precursors ($10^4 < C^* < 10^6 \mu\text{g m}^{-3}$) were moderately lost in the transfer duct with the largest losses seen for oxygenated aromatics (average of $\sim 30\%$). These precursor loss percentages parameterized to C^* , based on the Fire007 experiment, were applied to determine the initial concentrations of SOA precursors for all chamber simulations.

Simulations. We performed the following sensitivity simulations to investigate the influence of model inputs on SOA production: (i) no losses of vapors to the walls of the Teflon® chamber, (ii) no losses of SOA precursors to the transfer duct, (iii) no losses of vapors to the walls of the Teflon chamber and no losses of SOA precursors to the transfer duct, (iv) initial concentrations of SOA

precursors calculated using a campaign-averaged emissions profile, and (v) initial concentrations of SOA precursors calculated using the low- and high-temperature pyrolysis profiles of Sekimoto et al. (2018). For (iv), the emissions profiles for all 57 fires measured by Koss et al. (2018) during the FIREX laboratory campaign were first normalized and then averaged to determine a campaign-averaged emissions profile. Sekimoto et al. (2018) performed positive matrix factorization on all the emissions data measured by Koss et al. (2018) and found that two emissions profiles, namely a low- and high-temperature pyrolysis profile, were able to explain the variability in emissions across those 57 fires. In (v), we used the low- and high-temperature pyrolysis profiles identified by Sekimoto et al. (2018) and combined them using averaged, experiment-specific low- and high-temperature weights to calculate a fire-specific emissions profile. The base, Koss et al. (2018), and Sekimoto et al. (2018) emissions profiles as an emissions ratio with acetonitrile, aggregated by SOA precursor class, and for all fires analyzed in this work are listed in Table ??.

3.3 Results

Example Experiment. In Figure 3.1(a), we show the modeled decay of SOA precursors with time and the measured decay of D9 and the fit used to determine the OH exposure for the chamber experiment performed on emissions from lodgepole pine (Fire007). We left out the measured decay for visual clarity but the model-measurement comparison in SOA precursor decay is shown in Figure B.7. In Figure 3.1(b), we show the modeled and measured temporal evolution of the OA mass concentration and O:C ratio for that same experiment. In this experiment, HONO was added as an OH precursor to the chamber, which resulted in high NO_x concentrations (~ 900 ppbv at lights on) and a high OH exposure (1.4×10^7 molecules-h cm^{-3} or 9.3 photochemical hours at an OH concentration of 1.5×10^6 molecules-h cm^{-3}). The SOM-TOMAS model was able to reasonably reproduce the magnitude and evolution of the OA mass concentration and O:C ratio during the photooxidation period. The average modeled OA mass concentrations were slightly higher than the average measured OA mass concentrations but with significant overlap of the uncertainty ranges. In contrast, predictions of the average O:C ratio agreed very well with the measurements.

Sensitivity simulations performed by gradually decreasing the initial SOA precursor concentrations to match the average predicted SOA mass concentrations with the measurements resulted in an under-prediction of the O:C, highlighting the tight coupling between SOA mass concentrations and O:C ratios for the predictions. The use of a constant POA reproduced the flat POA profile measured during the dark period. As shown in the bar chart in Figure 3.1(c), while POA continued to account for a substantial fraction of the aged OA (>50%), the majority of the modeled SOA mass seemed to arise from the oxidation of oxygenated aromatics. Time-series comparisons for OA mass concentrations and O:C ratios for all chamber experiments are shown in Figures S.8 through S.17.

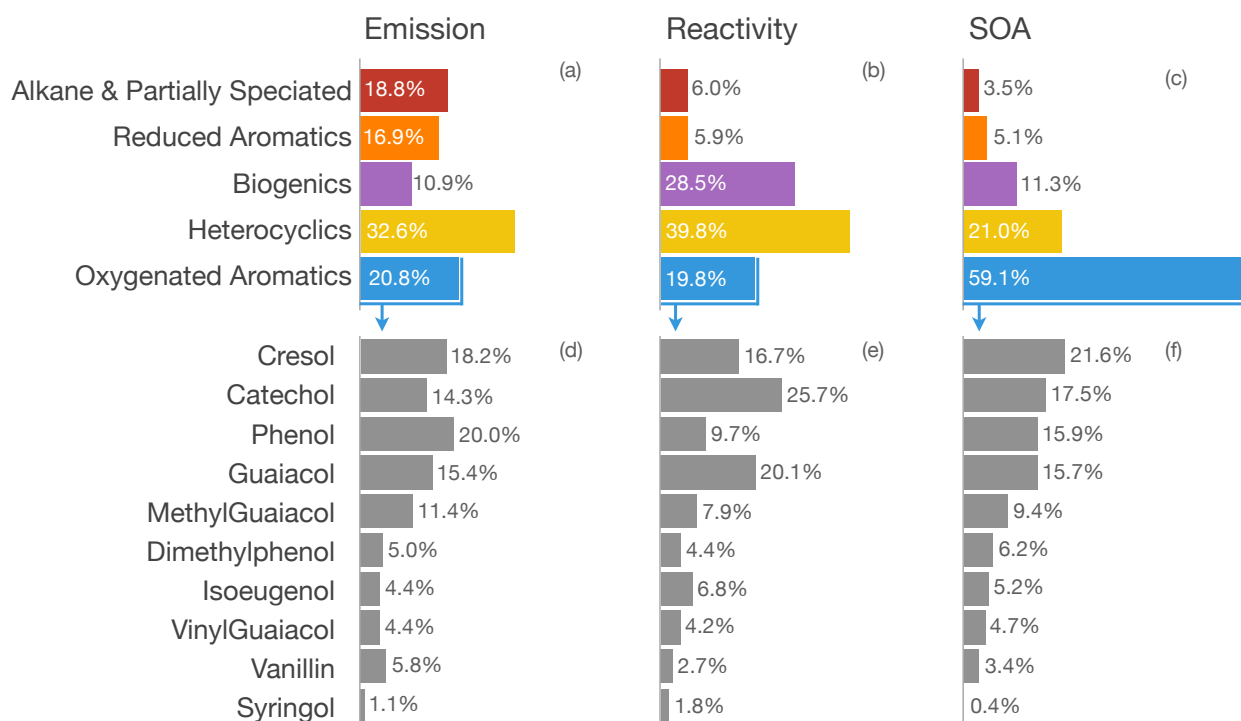


Figure 3.3: Normalized emissions and OH reactivity of the SOA precursors and their contribution to SOA production for the average of the eleven chamber experiments analyzed in this work. Some of the SOA precursor classes are lumped for clarity (e.g., alkanes+partially speciated, reduced aromatics). Top panels show results for all SOA precursors and bottom panels show results for just the oxygenated aromatic precursors.

Study-wide Comparison for OA and SOA Mass and O:C. The model-measurement comparisons for the end-of-experiment OA mass enhancement ratio (the ratio of the final to initial OA masses),

SOA production, and O:C enhancement ratio for all eleven chamber experiments are shown in Figure 3.2. For most experiments, the model was able to generally track the measured temporal evolution in the OA mass concentrations and O:C ratios (see Figures B.8-B.17), and hence we only compared end-of-experiment values in Figure 3.2. An analog of Figure 3.2, but one where the model predictions are compared to the measurements at four different points during each experiment, is provided in the SI (Figure B.18). The SOM-TOMAS model was able to reproduce the OA mass enhancement ratio (Figure 3.2(a)) and SOA production (Figure 3.2(b)) to within a factor of 2 across all chamber experiments, despite significant differences in the fuel type (pines to shrubs), initial OA loading (10 to $58 \mu\text{g m}^{-3}$), initial seed surface area (120 to $740 \mu\text{m}^2 \text{cm}^{-3}$), and OH exposure ($<10^6$ to 1.4×10^7 molecules-h cm^{-3} or <1 to ~ 10 hours of photochemical aging assuming an OH concentration of 1.5×10^6 molecules cm^{-3}). For both the OA mass enhancement ratio and SOA production, the model was able to explain 68% and 79% of the observed variability, respectively. The model was able to reproduce the measured enhancement in the O:C ratio and the model explained 69% of the observed variability. We also compared model predictions of the SOA O:C ratio to the measurements. We calculated the SOA O:C ratio for the measurements by assuming that the measured change in the O:C ratio was purely from the condensation of SOA (rather than through the evaporation or oxidation of POA). Across the eleven chamber experiments, the model predicted SOA O:C ratio of 0.64 ± 0.04 was slightly higher than the measurement-derived SOA O:C ratio was 0.58 ± 0.2 (mean $\pm$ standard deviation). Since there were significant differences in the model-measurement comparison across experiments, we examined if the model error correlated with any of the input variables (Figure B.19). We did not find any strong correlations possibly because there are many more variables than chamber experiments that are contributing to differences between experiments. Analysis of a larger dataset might be required to identify deficiencies in the model to simulate certain physical and chemical processes. Overall, the model-measurement comparison for the OA mass enhancement ratio, SOA production, and O:C enhancement ratio indicated that the model was able to represent the majority of the key precursors and processes needed to simulate the OA evolution during photooxidation of biomass burning emissions. We did not

model the SOA formation from SVOCs (Jen et al., 2019; Hatch et al., 2018) and it is possible that the model performance could be improved if these precursors were considered.

Precursor Contributions to SOA. The contribution of the different SOA precursors to gas-phase emissions, OH reactivity, and SOA production is shown in Figure 3.3 as an average over the eleven chamber experiments and results for each individual experiment are shown in Figure B.20. Heterocyclic compounds, which were mostly composed of furans and substituted furans, accounted for nearly a third of the SOA precursor emissions by mass while oxygenated aromatics, which were exclusively composed of phenols and methoxyphenols, accounted for a fifth. Altogether, the SOA precursors (excluding the partially speciated compounds) were about 38% of the total VOC emissions (Figure B.21(a)) and, interestingly, similar to SOA precursor fractions found in gasoline, diesel, and aircraft exhaust (Lu et al., 2018). As heterocyclic compounds, oxygenated aromatics, and biogenic VOCs have a much higher reactivity with OH relative to alkanes and reduced aromatics (Atkinson and Arey, 2003), these three classes accounted for almost 90% of the initial OH reactivity linked to SOA precursors. Koss et al. (2018) showed that together these classes accounted for a large fraction (60%) of the total OH reactivity (Figure B.21(b)).

Model predictions suggested that oxygenated aromatics contributed up to 60% of the SOA mass produced in our chamber experiments, despite this class contributing to only a fifth of the emissions and OH reactivity linked to the SOA precursors. Heterocyclic compounds and biogenic VOCs, respectively, were estimated to contribute $\sim 20\%$ and $\sim 10\%$ each to the total SOA mass while alkanes and reduced aromatic compounds made even smaller contributions ($<6\%$ each). The heterocyclic compounds did not contribute significantly to SOA production due to their small SOA mass yield (He et al., 2020; Joo et al., 2019), despite accounting for a substantial fraction of the emissions and OH reactivity of the SOA precursors. Amongst the oxygenated aromatics, five species, namely phenol, cresol, guaiacol, methylguaiacol, and catechol, accounted for slightly less than half of the total SOA and $\sim 80\%$ of the SOA from oxygenated aromatics. The relative contribution of the different oxygenated aromatics to the emissions, OH reactivity, and SOA production

was roughly similar, especially for the five major contributors. This is despite having a slightly different potential to form SOA on account of their different carbon and oxygen numbers.

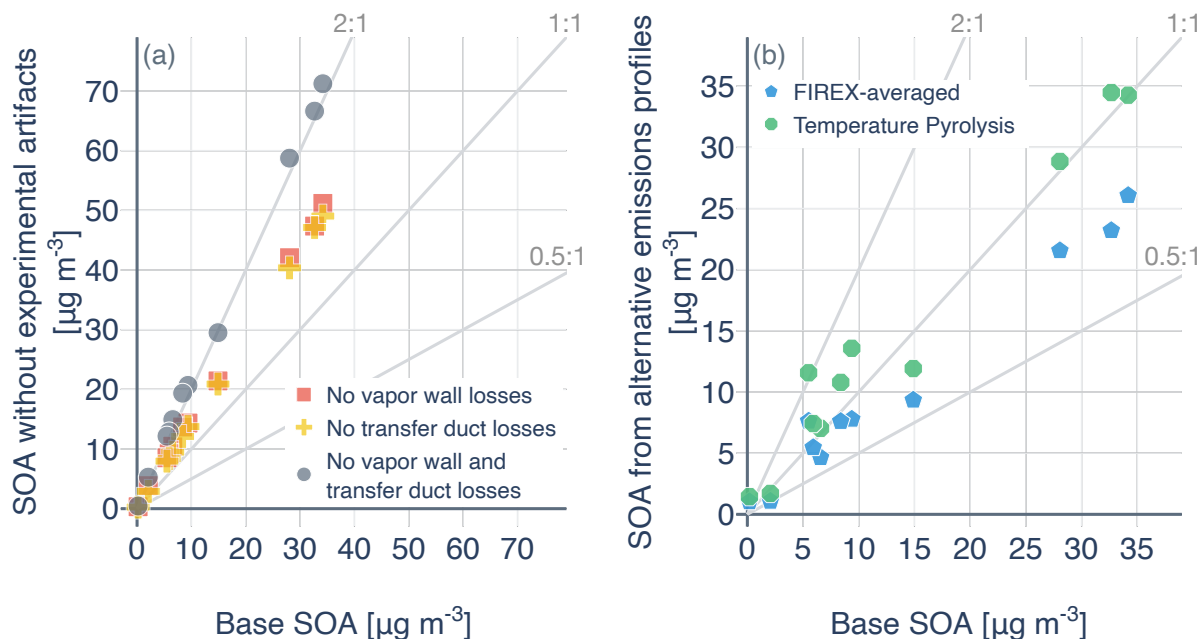


Figure 3.4: Model predictions of end-of-experiment SOA mass concentrations compared between simulations performed (a) with and without experimental artifacts and (b) with fire-specific and averaged emissions profiles.

Influence of Experimental Artifacts. We investigated the influence of the experimental artifacts, namely those associated with the transfer duct and chamber walls, on model predictions of SOA. Results from those simulations are shown in Figure 3.4(a), where we compare the SOA predicted without the experimental artifacts to the SOA predicted in the base simulations with artifacts accounted for. Simulations performed without the loss of SOA precursors in the transfer duct resulted in an average increase of 44% in SOA mass concentrations compared to those in the base simulations. The increase was roughly proportional to the 30% increase in initial concentrations of oxygenated aromatics in the simulations where transfer duct losses were not considered. Similarly, turning vapor wall losses off inside the chamber resulted in an average increase of 47% in SOA predictions compared to those in the base simulations. This relative level of increase in SOA mass concentrations appears to be similar to the average increase of 40% estimated previously for several

SOA precursors under high NO_x conditions (Zhang et al., 2014). The vapor-wall-loss effect was smaller than what would be expected given a short gas/wall partitioning timescale (~ 13 minutes). This is because oxygenated aromatics and their oxidation products, on account of their relatively higher OH reactivity, are likely to proceed quickly through the cascade of oxidation reactions to form SOA (Finewax et al., 2018), which should make the precursors and oxidation products less susceptible to vapor wall losses (Akherati et al., 2019). When considered together, i.e., on turning transfer duct and chamber losses off, the model predicted a combined increase of 105% in SOA mass concentrations. These results imply that in the absence of dilution and similarity in chemistry, photochemical oxidation within biomass burning plumes should have twice the potential to form SOA as in the chamber.

Impact of Average Emissions Profiles. We simulated the SOA production using two additional approaches to calculate the initial SOA precursor concentrations: (i) campaign-averaged emissions profile for fuels found in the western US (Koss et al., 2018) and (ii) use of the temperature pyrolysis profiles of Sekimoto et al. (2018). Both approaches simulate the calculation of an emissions profile in the absence of direct measurements. Predictions from these simulations are compared against those from the base simulations in Figure 3.4(b). The use of the temperature pyrolysis profiles produced slightly higher SOA mass concentrations ($\sim 20\%$) while the campaign-averaged emissions profile produced slightly lower SOA mass concentrations ($\sim 20\%$) when compared to the base simulations. These differences could be attributed to a proportionate increase and decrease in the initial concentrations of oxygenated aromatics and heterocyclics calculated from the emissions profiles. These emissions profiles are listed in Table ???. These results indicate that, in the absence of direct measurements, averaged or pyrolysis-based emissions profiles may be used to determine the SOA precursor concentrations in biomass burning emissions with the understanding that these may add an additional layer of uncertainty (found to be 30% for the fires investigated in this work) in representing the potential of those emissions to form SOA during photooxidation.

3.4 Discussion

While laboratory experiments have typically shown clear evidence for SOA production and an enhancement in OA mass with photochemical aging, field measurements have not observed an enhancement in OA mass with aging in biomass burning plumes; see Hodshire et al. (2019) and references therein. Since oxygenated aromatics have relatively short atmospheric lifetimes with respect to OH, they will, depending on the OH concentrations, rapidly form SOA in the first few hours after emission. If oxygenated aromatics contribute to most of their SOA close to the fire, it might partly explain why aircraft-based measurements, which are limited in how close they can get to the fire (~ 15 -60 minutes after emission), do not consistently show an enhancement in OA mass (i.e., the SOA formation has happened prior to the closest measurement). An additional piece of evidence that oxygenated aromatics might be forming SOA before or close to the first aircraft transect is that, on average, the initial O:C observed in the field on the first transect was higher than the initial O:C in the chamber (and closer to the final O:C observed in the chamber; Figure B.22). This however neither agrees with the findings from the smaller chamber during FIREX (Shrivastava et al., 2017) nor does it explain field observations of an increasing O:C of the OA with age beyond the first transect that could be linked to heterogeneous chemistry (Hodshire et al., 2019; Garofalo et al., 2019).

Several studies have hypothesized that the lack of an enhancement in OA mass in the field could be explained if the photochemistry-driven SOA formation was balanced by dilution-driven POA evaporation (Garofalo et al., 2019; Hodshire et al., 2019; Ramnarine et al., 2019). In this work, based on the available evidence, we assumed that the POA mass concentrations did not vary during the chamber experiment but note that there was very little dilution in our experiments compared to what would be observed in a biomass burning plume. This hypothesis currently remains untested for field data and any hypothesis testing would need to not only model the SOA formation from oxygenated aromatics and heterocyclic compounds but also model the evaporation kinetics of the POA and subsequent oxidation of the evaporated vapors to correctly interpret the field observations.

In both chamber studies performed during the FIREX laboratory campaign, namely the data used in this work and the data from Lim et al. (2019), the scaling factor, used to correct the raw OA mass concentrations from the HR-AMS, seemed to vary with photochemical oxidation. In both instances, the scaling factor seemed to decrease with oxidation, which produced a larger correction in the OA mass concentrations as the emissions were aged. In contrast to these studies, Liu et al. (2017) found little evidence for the scaling factor changing with time when sampling aerosol from wildfires during Biomass Burning Observation Project (BBOP). Differences in the laboratory and the field could arise from differences in the relative humidity: mostly dry in the current laboratory case (<20%) but higher in the field (>40%), which may lead to differences in the particle phase state. Regardless, laboratory and field measurements of OA made with an HR-AMS need to be carefully corrected before being used to evaluate models. We note that in sensitivity simulations performed with bounds on the scaling factor (0.5 to 1), the model measurement comparison did not change dramatically and did not affect the key findings from this work (Figure B.23).

One of the limitations of the chamber experiments here was that the experiments were performed in dry conditions (relative humidity<20%) where the only pathway for SOA formation was through gas-phase oxidation followed by partitioning of lower volatility products to the particle phase. In a biomass burning plume, where the relative humidity is likely to be much higher, oxygenated VOCs such as phenols and furans, which are somewhat water-soluble, could partition into aerosol water and undergo a different chemical fate than that explored in this work (Sengupta et al., 2020; Smith et al., 2014; Yu et al., 2014; Huang et al., 2018). The simultaneous, but competing, production of SOA from oxygenated VOCs through gas- and aqueous-phase pathways needs to be better understood in the future.

Chapter 4

Dilution and Photooxidation Driven Processes

Explain the Evolution of Organic Aerosol in Wildfire Plumes

4.1 Introduction

Wildfires are an important source of organic aerosol (OA) and OA precursors to the atmosphere (Akagi et al., 2011; Andreae and Merlet, 2001; Reid et al., 2005; Van der Werf et al., 2010; Yokelson et al., 2013). Wildfire OA, as a major component of the submicron atmospheric aerosol mass (Jimenez et al., 2009; Schill et al., 2020), has been estimated to exert a strong influence on the Earth's radiative budget (Hobbs et al., 1997; Ramnarine et al., 2019) and adversely affect regional and global air quality (McClure and Jaffe, 2018; O'Dell et al., 2019; Schill et al., 2020; Yue et al., 2013), human health (Chen et al., 2017; Ford et al., 2018), and visibility (Ford et al., 2018; Spracklen et al., 2009). Yet, there are large uncertainties surrounding the emissions and processes that control the abundance, distribution, and properties of wildfire OA in the atmosphere. For example, annual emissions and production rates of biomass burning OA, which includes OA from wildfires, agricultural fires, and biofuel combustion, have been shown to vary over two orders of magnitude in several recent global modeling studies ($1\text{-}100\text{ Tg yr}^{-1}$) (Shrivastava et al., 2017). These uncertainties have made it extremely challenging to represent wildfire OA in large-scale atmospheric models, which, in part, has limited the ability of these regional and global models to predict the atmospheric and environmental impacts of wildfires and atmospheric aerosols.

Wildfires directly emit particles that are dominated by primary organic aerosol (POA) with smaller amounts of black carbon (BC) and inorganic species (e.g., sulfate, nitrate, potassium) (Akagi et al., 2011; Lewis et al., 2009). Wildfire POA has been shown to be semivolatile and evaporates with dilution (Hatch et al., 2018; Huffman et al., 2009b; May et al., 2013). Further, the

POA and the vapors in equilibrium with the POA (or semivolatile organic compounds, SVOC) are also known to be reactive (Hatch et al., 2018; Hennigan et al., 2010; Jen et al., 2019). Wildfires emit OA precursors that include intermediate-volatility and volatile organic compounds (IVOC and VOC) (Hatch et al., 2017; Koss et al., 2018; Smith et al., 2014) and these oxidize in the atmosphere to form secondary organic aerosol (SOA) (Jathar et al., 2014)). In addition to emissions of reduced hydrocarbons such as alkane, aromatic, and biogenic VOCs (Akagi et al., 2011), wildfires also emit oxygenated IVOCs and VOCs (Hatch et al., 2015, 2017, 2018; Koss et al., 2018; Sekimoto et al., 2018; Stockwell et al., 2015). These include oxygenated aromatic and heterocyclic organic compounds that have recently been shown to be important precursors for SOA formation (Ahern et al., 2019; Akherati et al., 2020; Bruns et al., 2017; Stefenelli et al., 2019). Globally, wildfires are the largest source for POA and the largest combustion-related source for SOA to the atmosphere (Shrivastava et al., 2017). Although a lot has been understood about the emissions (e.g., Koss et al. (2018)), chemistry (e.g., Akherati et al. (2020)), and properties (Jen et al., 2019; May et al., 2013) of POA and SOA from biomass burning emissions in laboratory experiments, a detailed understanding of their physicochemical evolution in real wildfire plumes remains uncertain.

Recently, Hodshire et al.(2019a) undertook a comprehensive review of wildfire OA data gathered in four laboratory campaigns and thirteen field campaigns over the past two decades. A meta-analysis of these data suggested that while photooxidation of biomass burning emissions resulted in an enhancement in OA mass in laboratory experiments (mean=1.25, median=1.44, and IQR=1.1-1.54) (Ahern et al., 2019; Akherati et al., 2020; Hennigan et al., 2011; Lim et al., 2019; Ortega et al., 2013; Tkacik et al., 2017), a similar enhancement was missing for the OA tracked in real wildfire plumes (mean=1.1, median=1.0, and IQR=0.77-1.0) (Akagi et al., 2012; Alvarado and Prinn, 2009; Brito et al., 2014; Capes et al., 2008; Collier et al., 2016; Cubison et al., 2011; DeCarlo et al., 2008; Forrister et al., 2015; Hobbs et al., 2003; Jolleys et al., 2012, 2015; Liu et al., 2016; May et al., 2015; Morgan et al., 2019; Vakkari et al., 2014, 2018; Yokelson et al., 2009). In contrast to the findings for OA mass, the OA measured within wildfire plumes closest to the fire was not only more oxidized (i.e., a higher oxygen-to-carbon (O:C) ratio for the OA) than the initial

OA measured in laboratory experiments but the OA O:C exhibited a stronger enhancement with photochemical age in the field (median=1.85, and IQR=1.5-2.0) versus the laboratory (median=1.5, and IQR=1.3-1.8). Similar to the trends in OA O:C, a different enhancement was also observed for the ratio of two mass fragments (m_{44}/m_{60}) measured by the aerosol mass spectrometer between the field (median=3.8, and IQR=2.3-6.7) and the laboratory (median=3.0 and IQR=1.8-3.6). m_{44} refers to the mass measured for the CO_2^+ ion and is representative of low-volatility organic compounds found in SOA (Ng et al., 2011) while m_{60} refers to the mass measured for the $\text{C}_2\text{H}_4\text{O}_2^+$ ion arising from primary emissions of anhydrous sugars such as levoglucosan (Cubison et al., 2011).

Based on this meta analysis, Hodshire et al. (2019a) put forth four hypotheses to explain this field versus laboratory difference. First, they argued that the dilution of the wildfire plume could result in evaporation of POA and this evaporation could be approximately balanced by SOA production to result in a small change in the OA mass with photochemical aging. Since the condensing SOA is likely to have a higher O:C ratio than the evaporating POA, this POA-SOA swap, they argued, would not affect the OA mass but would produce an increase in the O:C ratio with aging. This hypothesis has been supported by theoretical calculations (Bian et al., 2017; Hodshire et al., 2019b). Second, they hypothesized that because wildfire plumes are generally sampled for the first time at least 15 minutes after emission (often longer), the plume measurements could have missed the OA evolution that happened prior to the first measurement. If rapid chemistry does indeed occur early on, this may not only explain the higher O:C ratio measured in the field but also explain the reduced propensity to form SOA after the first aircraft pass was made. Third, they postulated that the field and laboratory differences could arise from differences in the emissions and chemistry of OA and OA precursors, attributed to differences in the fuel complex, burn conditions, combustion efficiency, and environmental conditions (e.g., temperature, relative humidity) and regimes (e.g., photolytic rates, NO_x). Finally, they commented that there were several experimental artifacts linked to laboratory experiments, including losses of OA and OA precursors to transfer ducts (Akherati et al., 2020) and walls of the environmental chamber (Krechmer et al., 2016; Matsunaga and Ziemann, 2010; Zhang et al., 2014), that could drive differences between laboratory and field

measurements. For the most part, these hypotheses remain untested and will serve as the basis for this work. So far, only a single study has come close to testing the first hypothesis above, that dilution-driven evaporation of POA is roughly balanced by SOA production in wildfire plumes. Based on wildfire plumes sampled in the western US, Palm et al. (2020) studied trends in OA mass as a function of dilution and photochemical age. They found that plumes that had diluted but had not undergone photooxidation showed evidence for POA evaporation and plumes that had both diluted and undergone photooxidation showed evidence for replacement of the lost POA mass with SOA. However, Palm et al. (2020) did not account for the photochemical evolution prior to the first aircraft pass nor did they account for the oxidation of all potential precursors (i.e., semivolatile organic compounds) leading to SOA formation. To the best of our knowledge, no bottom-up, detailed models have been used to simulate and evaluate the OA mass and composition evolution in wildfire plumes. In this study, we simulated the physicochemical evolution of OA in a subset of wildfire plumes sampled during a recent aircraft-based field campaign (Western wildfire Experiment for Cloud chemistry, Aerosol absorption, and Nitrogen (WE-CAN)). The OA evolution was simulated using a state-of-the-science model (SOM-TOMAS) that simulates dilution, oxidation chemistry, thermodynamic properties, and microphysics of OA. A novel contribution of this work is that based on estimates of dilution and photochemical age before the first transect sampled by the aircraft, we were able to simulate the OA evolution from very close to the fire to several hours downwind. Model results of mass and composition were compared to plume measurements to study the contribution of precursors and processes to OA evolution.

4.2 Materials and Methods

4.2.1 Aircraft Measurements

The analysis in this work is centered around measurements gathered during the Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) field campaign. An extensive description of the field campaign and instrumentation used can be found in Juncosa Calahorrano et al. (2021) and Lindaas et al. (2021) with additional details found elsewhere

(Garofalo et al., 2019; Palm et al., 2020; Peng et al., 2020). Briefly, during WE-CAN, a research aircraft was deployed between July and September of 2018 to sample the evolution of trace gases and particles in wildfire smoke plumes over the western US. Smoke was sampled from 23 distinct wildfires over this period and for 12 of these wildfires, the aircraft was flown along horizontal transects orthogonal to the wind direction to perform pseudo-Lagrangian sampling of the plume. Multiple transects (4 to 14 per fire) were executed along the length of the wildfire plume over multiple hours (2 to 6 hours of physical age) and several hundred kilometers from the source of the fire (10 to 220 km). We should note that near-Lagrangian sampling was accomplished for only a few of the wildfire plumes (e.g., Taylor Creek, later transects for Sharps) and, in most cases, the sampling was pseudo-Lagrangian. As shown in Figure C.1, the aircraft ended up sampling much faster (twice as fast, on average) than the physical age of the plume for four out of the five sets of transects. The modeling and analysis undertaken in this work assumes that the measurements represent a true Lagrangian dataset and this assumption should be considered while interpreting the results from this and future work. In addition to performing transects through the center/core of the wildfire plume, the aircraft also performed transects at different altitudes to probe the vertical distribution of smoke in the plume. These data were excluded from the analysis presented in this work.

The primary analysis in this work was limited to the following four wildfires: Taylor Creek (southwest Oregon), Sharps (southern Idaho), Bear Trap (eastern Utah), and Silver Creek (northwest Colorado). Two distinct transect sets were executed for Bear Trap and each of these transect sets were modeled and analyzed separately. In total, the analysis focused on five transect sets, one for Taylor Creek, Sharps, and Silver Creek and two for Bear Trap. The fire location and dominant fuel(s) for each fire can be found in Table 4.1 of Lindaas et al. (2020). These wildfires were chosen because they offered the most clear trends in the evolution of OA mass and O:C with time suggesting that they represented pseudo-Lagrangian datasets and we had access to data from all instruments required to perform the proposed OA modeling. In future work, we may extend the modeling to the other fires measured during WE-CAN.

A suite of gas, particle, meteorological, and remote sensing instrumentation was deployed on the aircraft to comprehensively characterize the smoke emissions and its environment. Below, we briefly discuss the measurements and data products that relate to the scope of this work. Pressure and temperature were measured at 1 Hz using base instrumentation available onboard the aircraft (Juncosa Calahorrano et al., 2021; Lindaas et al., 2021). CO concentrations were measured using a Quantum-Cascade Tunable Infrared Laser Direct Absorption Spectrometer (QC-TILDAS, Aerodyne Research) and reported at 1 Hz (Lebague et al., 2016). CO was assumed to be an inert tracer and used to model dilution with the background air as well as to develop convenient metrics to characterize the OA evolution with physical age of the plume. VOC concentrations were measured using a Proton Transfer Reaction - Time of Flight - Mass Spectrometer (PTR-ToF-MS, Ionicon Analytik) at 1 Hz (Permar et al., in review). The PTR-ToF-MS quantified concentrations for 122 reduced and lightly-oxygenated VOCs and included a quantification of the most important SOA precursors that have been identified for biomass burning in previous work (Ahern et al., 2019; Akherati et al., 2020). A High-Resolution Aerosol Mass Spectrometer (HR-AMS; Aerodyne Research) was used to measure the mass concentrations and composition of the sub-micron, non-refractory aerosol (Garofalo et al., 2019) every 5 seconds. Only the observations of aerosol mass concentrations and OA H:C and O:C from the HR-AMS measurements were used in this work. A Single Particle Soot Photometer (SP2; Droplet Measurement Technologies) was used to quantify BC mass concentrations at 10 Hz. Finally, aerosol size distributions were measured using a Passive Cavity Aerosol Spectrometer Probe (PCASP) at 1 Hz (Kupc et al., 2018) and these were used to inform the shape of the initial aerosol size distribution (median and geometric standard deviation).

The quality-controlled measured data, as provided by the instrument leads, were processed before they were used in the OA model and in the analysis. For each transect, we determined average values for OA, non-OA (sulfate+nitrate+ammonium+chloride+BC), CO, and VOC concentrations as well as OA O:C. Following the earlier published work with the WE-CAN data (Garofalo et al., 2019; Juncosa Calahorrano et al., 2021; Lindaas et al., 2021; Palm et al., 2020) we identified the plume-sampling period by visually examining the OA and CO time series for increases and

decreases in concentrations. These averages were then corrected for background concentrations by computing a universal background value for each measured species (e.g., CO, OA, benzene) using data from outside the plume. This method assumes that the concentrations and composition of the gas and aerosol species in the background air remained constant in time and space. We also calculate a normalized excess mixing ratio (NEMR) for OA and VOCs by ratioing its background-corrected concentration (in $\mu\text{g m}^{-3}$ for OA and ppbv for VOCs) with the background-corrected CO (in ppbv). The background-corrected OA O:C was calculated as a ratio of the background-corrected molar concentrations for O and C. For this calculation, we assumed the OA to be only composed of C, H, and O such that the molar concentrations of C, H, and O were determined from the available OA, O:C, and H:C data. Background corrections were performed separately for each wildfire plume. We studied the sensitivity of the findings from this work to other ways in which the background values can be calculated and these are described later.

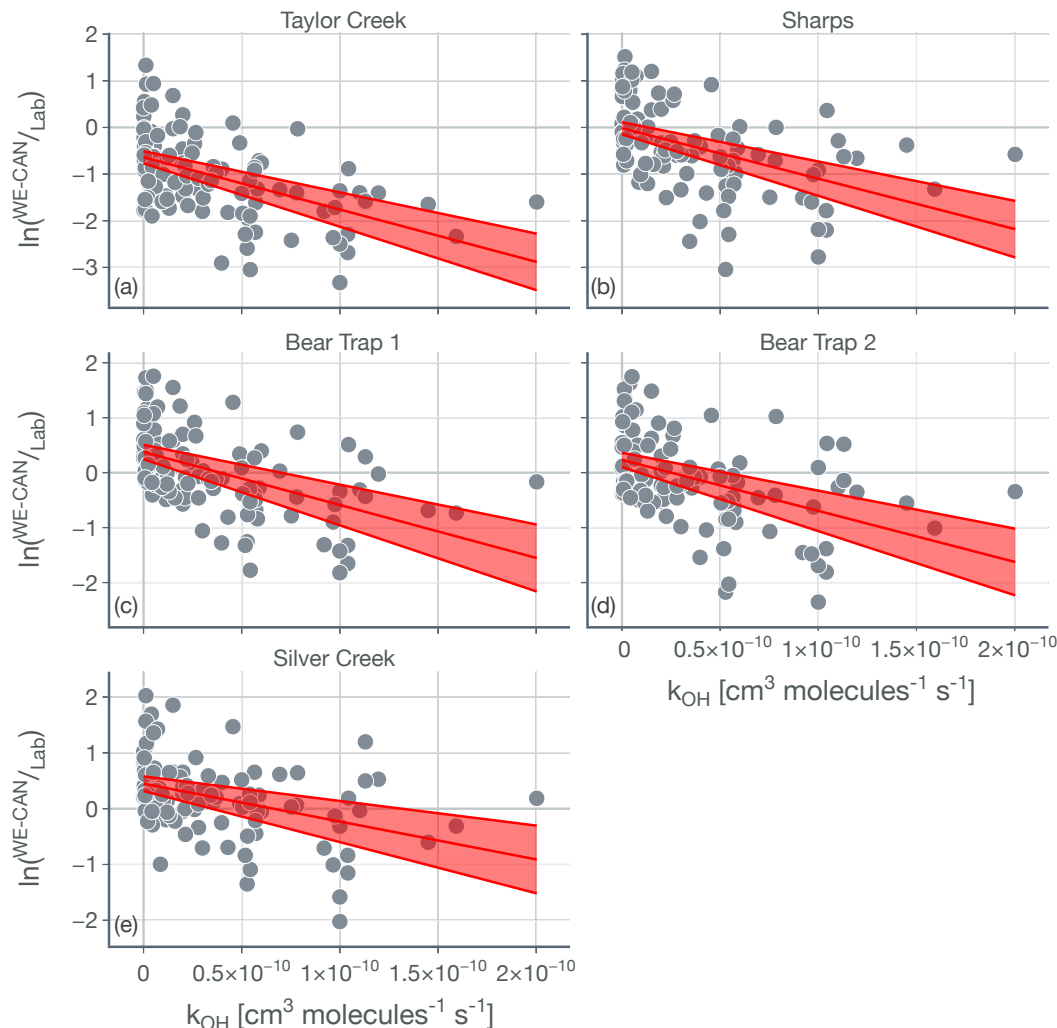
4.2.2 OH Concentration and Exposure Estimates

The hydroxyl radical (OH) exposure in the wildfire plumes was determined by examining the laboratory-normalized and reactivity-differentiated VOC decay. For each transect in a wildfire plume, this was done by first calculating the natural logarithm of the ratio of the background-corrected VOC ratio with CO at that transect to the average, background-corrected VOC emissions ratio with CO measured in laboratory experiments. The VOC emissions ratio with CO from laboratory experiments was based on the work of Koss et al. (2018) who calculated these emissions ratios for 58 separate experiments performed on 18 different fuels. As this calculation could only be performed when the corresponding emissions ratios were also available from the laboratory experiments, we performed this calculation on 106 out of the 122 reduced and lightly-oxygenated VOCs measured by the PTR-ToF-MS. We assumed that the reactive oxygenated VOC concentrations in the wildfire plume were largely from direct emissions from the fire rather than produced through in-plume chemical reactions. This field-to-laboratory ratio of VOC-to-CO ratios was then plotted against the reaction rate constant for those VOCs with OH (k_{OH}). Isoprene, monoterpenes,

and catechol can also react with O_3 in addition to OH and were excluded from the analysis, although including these VOCs did not appear to change the estimated OH exposure (not shown). This was probably because the O_3 concentrations in the wildfire plume were low enough (45-90 ppbv) (Dr. Emily Fisher, personal communication) such that the relative lifetimes of these VOCs with O_3 , at least early on, were much longer compared to those with OH.

Results for an example transect for the four fires analyzed in this work are shown in Figure 4.1. The laboratory-normalized VOC decay exhibited an inverse relationship with k_{OH} . The likely explanation for this inverse trend was that the oxidation chemistry prior to this transect resulted in stronger depletion of VOCs with a higher k_{OH} and weaker depletion of VOCs with a lower k_{OH} ; an alternate explanation is that the field-to-laboratory ratio of VOC-to-CO ratios was biased lower for the higher k_{OH} species compared to the lower k_{OH} species on account of differences in fuel and burn conditions. Assuming this was true, the trend in the field-to-laboratory ratio of VOC-to-CO ratios with k_{OH} was fit to determine an effective OH exposure for the time period before this transect. We should note that we did not assume that the field and laboratory emissions ratios are the same, which would require setting the intercept for the fit to 0, which we did not do. Rather, we assumed that there was no systematic trend or the same exact trend in the field and laboratory emissions ratios for VOCs with k_{OH} . This exercise was repeated for all transects to calculate a time-varying OH exposure estimate for all transect sets, results for which are shown in Figure 4.2(a-e). A line was fit through the OH exposure data to calculate an average OH concentration for the wildfire plume after the first transect. We assumed that the OH exposure changed linearly from zero, close to the fire, to the OH exposure estimated at the first transect, which resulted in a separate, time-invariant OH concentration estimate for the time period before the first transect. The OH concentrations before and after the first transect are tabulated for the five transect sets in Table ??.

For the five transect sets and four wildfire plumes analyzed, the total mean OH exposure varied between 4.58×10^6 (Bear Trap 2) and 6.54×10^6 (Sharps) molecules-hr cm^{-3} to produce 1.7 to 4.4 hours of photochemical aging at an average OH concentration of 1.5×10^6 molecules cm^{-3} . The



Wildfire	Taylor Creek	Sharps	Bear Trap 1	Bear Trap 2	Silver Creek
Physical Age [minutes]	20.9	44.6	52.9	55.6	32.5
OH Exposure [molecules cm ⁻³ hr]	3.11x10 ⁶ ±6.61x10 ⁵	3.00x10 ⁶ ±6.61x10 ⁵	2.67x10 ⁶ ±6.63x10 ⁵	2.58x10 ⁶ ±6.61x10 ⁵	1.88x10 ⁶ ±6.61x10 ⁵
Average OH Conc. [molecules cm ⁻³]	8.92x10 ⁶	4.03x10 ⁶	3.04x10 ⁶	2.78x10 ⁶	3.47x10 ⁶
Intercept	-0.64±0.13	-0.02±0.13	0.02±0.13	0.23±0.13	0.45±0.13
R-squared	0.26	0.23	0.26	0.21	0.16
RMSE	0.768	0.812	0.665	0.735	0.625

Figure 4.1: Field-to-laboratory ratios of the VOC-to-CO ratio in the wildfire plume to the average VOC-to-CO emissions ratio measured in laboratory experiments plotted against k_{OH} . Results are shown for the first transect measured for the (a) Taylor Creek, (b) Sharps, (c) Bear Trap 1, (d) Bear Trap 2, and (e) Silver Creek transect sets. Solid red lines represent the linear fit to the data and the red bands capture the uncertainty in the fit (1σ). The table lists statistics based on the linear fit including the OH concentration and exposure. The time-varying OH exposures for all five transect sets are shown in Figure 4.2 and the OH concentrations are listed in Table 4.1.

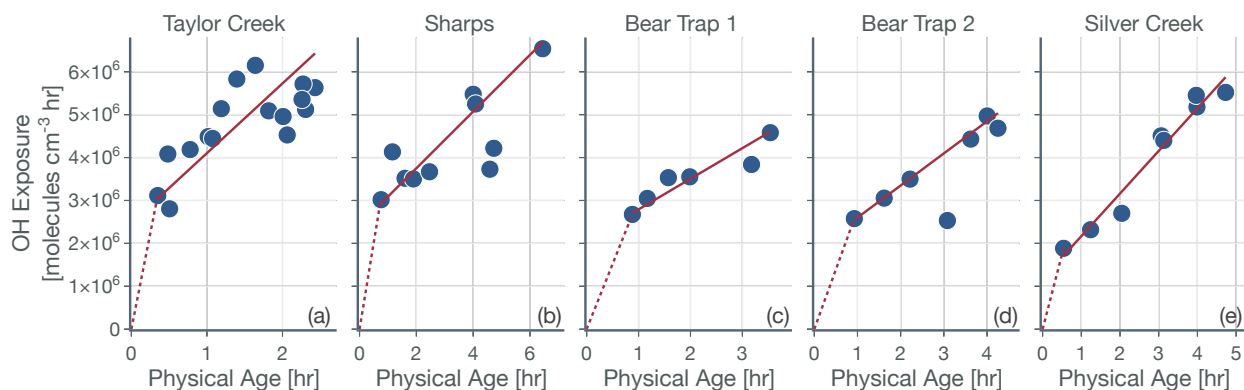


Figure 4.2: Time-varying OH exposures estimated for the five transects sets: (a) Taylor Creek, (b) Sharps, (c) Bear Trap 1, (d) Bear Trap 2, and (e) Silver Creek. The solid red lines are linear fits to time periods after the first transect while the dotted red lines represent the estimated OH exposure prior to the first transect.

OH concentrations varied between 2.78×10^6 (Bear Trap 2) and 8.92×10^6 (Taylor Creek) before the first transect and between 4.72×10^5 (Sharps) and 9.94×10^5 (Silver Creek) beyond the first transect. The OH concentrations, on average, were a factor of six larger before the first transect compared to after the first transect suggesting that photochemical oxidation was as relevant to the wildfire plume in the near field (between the point of emission and the first transect) as it was for the far field (beyond the first transect); the first transect was measured between 21 and 55 minutes of the physical age of the wildfire plume. The OH concentrations in the wildfire plume after the first transect were found to be quite low compared to the average OH concentrations typically found in urban environments and regional backgrounds (Griffith et al., 2016). The low OH concentrations might be a result of the large OH sinks present within the wildfire plume as well as the low photochemical activity expected in optically dense plumes (Peng et al., 2020). Our estimates for OH concentration in the Taylor Creek and Bear Trap wildfire plumes after the first transect were a factor of five smaller than earlier OH estimates for the same wildfire plumes based on the observed decay for a handful of VOCs ($\sim 3 \times 10^6$ and $\sim 5 \times 10^6$ molecules cm⁻³, respectively) (Juncosa Calahorrano et al., 2021). While the two approaches to estimate OH concentrations are structurally similar, the calculations could yield dramatically different results if the background-corrected concentrations are inherently noisy, which is the case for most aircraft data for wildfire plumes. We tentatively argue that Juncosa Calahorrano et al. (2021) estimated very different OH

concentrations because they only used a few species (<5) in their calculation and that our approach which uses a much larger number of species (106) provides a more robust estimate of the mean OH concentrations in the plume. This argument needs to be tested in future work.

Clearly, there is some uncertainty in the OH estimates produced using this approach and, as will be shown later with sensitivity simulations, the assumed OH concentrations had a modest impact on the findings from this work. The OH estimates are likely to be unbiased if the field and laboratory emissions ratios have no systematic relationship with k_{OH} . In case there is a relationship and that this relationship is different between the field and laboratory, our OH estimates could be biased lower or higher. Hence, there is no clear way in which we could argue that our OH estimates bound the range of expected values in a wildfire plume. Since the OH estimates were developed based on the observed decay of all species including reactive oxygenated VOCs, any chemical production of oxygenated species should bias our OH estimate lower. Based on the inclusion of the reactive oxygenated VOCs alone, our OH estimates potentially present a lower bound estimate. When the approach was applied selectively to reduced VOCs measured by the PTR-ToF-MS to eliminate the influence from including oxygenated VOCs, the inverse relationship was weakened and produced OH concentrations that were at least a factor of 2 lower than those listed in Table 4.1, both before and after the first transect. We also applied this approach to estimate OH concentrations beyond the first transect by using the VOC ratios with CO at the first transect as the reference ratio instead of using the emissions ratios from the laboratory. The concentrations so calculated and limited to the time period beyond the first transect were found to be only slightly higher to those listed in Table 4.1 (6.7×10^5 - 1.2×10^6 molecules cm^{-3}). The VOC ratios with CO at the first transect, by definition, cannot be used to determine the OH concentrations prior to the first transect.

4.2.3 Organic Aerosol Model

We developed a plume version of the SOM-TOMAS model to simulate the formation, composition, and evolution of OA in wildfire plumes. SOM, or the statistical oxidation model, uses a statistical approach to track the multigenerational oxidation chemistry and thermodynamic prop-

Table 4.1: OH concentration and exposure estimates based on the laboratory-normalized and reactivity-differentiated VOC decay for the five transect sets

Fire	OH Concentration (molecules cm ⁻³)		OH Exposure (molecules-hr cm ⁻³)	
	Before 1 st transect	After 1 st transect	At 1 st transect	At last transect
Taylor Creek	8.9×10^6	9.7×10^5	3.1×10^6	5.6×10^6
Sharps	4.0×10^6	4.7×10^5	3.0×10^6	6.5×10^6
Bear Trap 1	3.0×10^6	5.7×10^5	2.7×10^6	4.6×10^6
Bear Trap 2	2.8×10^6	6.5×10^5	2.6×10^6	4.7×10^6
Silver Creek	3.5×10^6	9.9×10^5	1.9×10^6	5.5×10^6

erties of OA precursors and its oxidation products (Cappa and Wilson, 2012; Jathar et al., 2015). TOMAS, or the Two Moment Aerosol Sectional model, uses a sectional approach to track the number and mass moments of the aerosol size distribution to simulate the microphysical processes of nucleation, coagulation, and condensation/evaporation (Adams and Seinfeld, 2002; Pierce et al., 2011). The SOM has been extensively used to study the influence of multi-generational aging, (Jathar et al., 2016) intermediate volatility organic compounds (Eluri et al., 2018), NO_x (Akherati et al., 2019), and vapor wall losses in chambers (Cappa et al., 2016; Zhang et al., 2014) on OA evolution. More recently, the SOM-TOMAS model was used to study the SOA formation from biogenic VOCs (He et al., 2021) and evaporated petro- and bio-fuels (He et al., 2020). Pertinent to this work, the SOM-TOMAS model was used to study the SOA formation in chamber experiments performed on wildfire emissions (Akherati et al., 2020). The SOM-TOMAS model configuration described in detail in Akherati et al. (2020) was used in this work with modifications to account for dilution, different environmental conditions (e.g., pressure, temperature) and an updated treatment of POA and SVOCs.

The SOM tracks the chemical evolution of OA and its precursors using a two-dimensional, carbon (N_C) and oxygen (N_O) number grid. The properties of each model species (e.g. reactivity (k_{OH}), volatility (c*)) are parameterized based on their N_C and N_O. The SOM has six adjustable parameters that govern the oxidation chemistry and thermodynamic properties of the model species: (i–iv) p_{f,1}–p_{f,4}, the yields of four functionalized products that add one, two, three, and four oxygen atoms to the carbon backbone, respectively; (v) m_{frag}, the parameter that characterizes the

fragmentation probability (P_{frag}); and (vi) ΔLVP , the decrease in the c^* of the model species per addition of an oxygen atom. The particle-phase species in SOM are tracked in 36 TOMAS size sections that span dry diameters between 3 to 10,000 nm. TOMAS simulates coagulation between size sections and the kinetic condensation/evaporation of mass between the particle and vapor phases for all SOM model species. TOMAS also accounts for formation of highly oxygenated organic molecules (HOMs) and formation/dissociation of oligomers (He et al., 2021) although neither of these processes are modeled in this work since there is little to no evidence for HOM or oligomer formation in wildfire plumes. Recently, SOM-TOMAS was updated with the diffusive-reactive framework described in Zaveri et al. (2014) to model the influence of phase state on the kinetic gas/particle partitioning of OA (He et al., 2021). As part of this framework, the model now accounts for gas-phase diffusion, interfacial mass accommodation, and particle-phase diffusion.

For each wildfire plume, the SOM-TOMAS model was used to simulate the OA evolution from the time just after emission once the plume reaches its equilibrium height (hereafter referred to as ‘ $t=0$ ’) up to the last measured transect. The background-corrected CO concentrations past the first transect were first fit to an exponential function and the CO values including those extrapolated to $t=0$ were then used to determine dilution of the wildfire plume with background air starting at $t=0$. Since we only used background-corrected values in this work, we assumed the background air to be free of any trace gases and particles. This assumption affects non-linear processes, such as equilibrium partitioning and coagulation; however, because background concentrations are generally much lower than in-plume concentrations, this should have a minimal effect (Hodshire et al., 2019b). While the pressure and temperature values changed modestly between wildfire plumes, they were found to be in a relatively narrow range for a given wildfire plume (Figure C.2). Hence, an average pressure and temperature value was used for the entire wildfire plume. Model predictions and measurements of concentrations and mixing ratios were expressed at the plume pressure and temperature.

4.2.4 SOA Formation from VOCs

SOA formation from VOCs was modeled similar to the treatment presented in Akherati et al.(2020) Briefly, we considered five broad classes of SOA precursors, with the surrogates listed in parentheses: (i) alkanes (*n*-dodecane; Loza et al. (2014)), (ii) reduced aromatics (benzene, toluene, *m*-xylene; Ng et al. (2007) and Zhang et al. (2014)), (iii) oxygenated aromatics (phenol, guaiacol, syringol; Yee et al. (2013)), (iv) heterocyclics (2-methylfuran+dimethylfuran; He et al. (2020)), and (v) biogenics (isoprene, α pinene; Chhabra et al.(2011)). We did not model the SOA formation from partially speciated VOCs as we did not find them to be important SOA precursors in our previous work (Akherati et al., 2020). Akherati et al. (2020) found that the five organic classes mentioned above, on average, were able to explain most of the SOA measured in chamber experiments performed on emissions from laboratory fires, with oxygenated aromatics and heterocyclic compounds accounting for 80% of the SOA produced. The SOM-TOMAS parameters, specific to high NO_x conditions, to model SOA formation from these precursors are listed in Table C.1. Each of the 67 SOA precursors in the model were assigned an SOA surrogate, mentioned in parentheses above, and this surrogate assignment along with the molecular weight and k_{OH} value for the precursor is listed in Table C.2. We also modeled SOA formation from SVOCs and that treatment is described in the next section.

The VOC-to-CO ratios at the first transect were extended to $t=0$ by correcting for the OH exposure before the first transect (see Table 4.1 for transect-set-specific OH exposures). These field VOC-to-CO ratios at $t=0$ and the first transect were aggregated by precursor class and compared to the VOC-to-CO emissions ratios measured by Koss et al. (2018) during a recent laboratory campaign. Results of this comparison, combined over all five transect sets and four wildfires, are shown in Figure 4.3. Results when separated by transect set were similar to those presented in Figure 4.3 and, hence, are not shown or discussed. The VOC-to-CO ratios for the five SOA precursor classes at the first transect were substantially lower than those measured in the laboratory. The median values at the first transect were 74%, 58%, 28%, 15%, and 75% lower for the biogenic, oxygenated aromatic, heterocyclic, reduced aromatic, and alkane classes, respectively, compared to

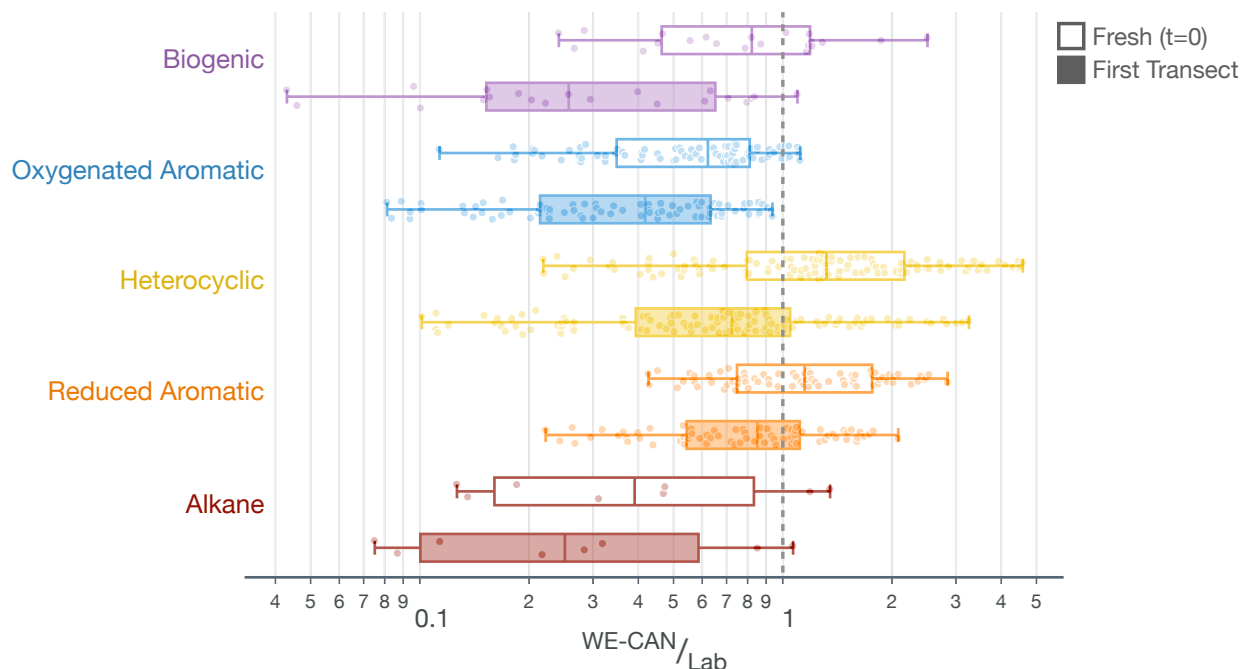


Figure 4.3: Field-to-laboratory ratios of the ratios of SOA precursor class to CO in the wildfire plume to the average emissions ratios of SOA precursor class to CO measured in laboratory experiments at $t=0$ and the first transect. SOA precursors are aggregated by organic class: biogenics, oxygenated aromatics, heterocyclics, reduced aromatics, and alkanes. Data are presented together for all five transect sets.

the laboratory values. The largest differences were observed for the most reactive SOA precursors with respect to OH (e.g., oxygenated aromatics) and the smallest differences were observed for the least reactive SOA precursors with respect to OH (e.g., reduced aromatics), a feature that was leveraged to determine the OH concentrations and exposure in Section 4.2.2. Even after correcting for OH exposure prior to the first transect, the VOC-to-CO ratios for three of the organic classes (i.e., biogenic, oxygenated aromatic, and alkane) were still modestly lower compared to those measured in the laboratory. The median values at $t=0$ were 18%, 38%, and 61% lower for the biogenic, oxygenated aromatic, and alkane classes, respectively, compared to the laboratory values. The median values were 32% and 15% higher for the heterocyclic and reduced aromatic classes, respectively, compared to the laboratory values.

There are two important implications of the differences in the VOC-to-CO ratios shown in Figure 4.3 and described in the previous paragraph. First, field emissions of SOA precursors (those at $t=0$) are lower than those measured in laboratory experiments, for at least a few of the important

organic classes. It is expected then that this SOA precursor mixture would be relatively less potent in forming SOA in wildfire plumes than what has been observed in laboratory experiments (Ahern et al., 2019; Akherati et al., 2020; Hennigan et al., 2011; Lim et al., 2019; Ortega et al., 2013; Tkacik et al., 2017). Second, a significant fraction of the SOA precursor emissions are depleted between $t=0$ and the first transect. This implies that not only is SOA being actively produced in the near field after emission (<1 hour) but also that there is significantly reduced potential for continued production of SOA beyond the first transect. These comparisons partly explain the field versus laboratory differences outlined by Hodshire et al. (2019a).

4.2.5 Treatment of POA and SVOCs

POA was treated as semivolatile and reactive, following a history of observations from laboratory experiments (Grieshop et al., 2009; Huffman et al., 2009b; May et al., 2013). Fresh emissions of POA close to the fire were determined in an iterative manner. Using an initial guess for the POA at $t=0$, we fit a mass distribution for eight model species in the SOM grid that was able to reproduce the average volatility behavior observed by May et al. (2013) for POA emissions (Figure C.3a). May et al. (2013) measured this average volatility behavior by studying the response of fresh POA emissions from 19 separate fires and 12 different fuels to dilution and thermal denuding in laboratory experiments. The model species were placed in a SOM grid for multi-ring aromatics ($\Delta\text{LVP}=1.4922$), the reason for which is discussed later in this section. The number of model species (i.e., 8) used to represent the POA and SVOC mass in the SOM grid was arbitrary and the use of a larger number of model species (e.g., 10, 15) did not seem to affect our results (not discussed further). In addition to constraining the mass distribution in the SOM grid to match observations of POA volatility, the model species were deliberately chosen to produce a specific response in the aerosol O:C with POA mass concentration, following observations of biomass burning OA in laboratory (Huffman et al., 2009b) and field (Huffman et al., 2009a) environments (Figure C.3b): an increasing OA O:C from 0.34 to 0.54 with a decrease in OA mass concentrations from 1000 to $1 \mu\text{g m}^{-3}$. The following species were used to represent the POA/SVOC mass in the

SOM grid, C_5O_7 , C_9O_2 , C_9O_5 , $C_{11}O_2$, $C_{12}O_2$, $C_{12}O_3$, $C_{14}O_5$, $C_{15}O_6$ (Figure C.3c), and an explanation for this distribution is presented later when describing results from the sensitivity simulations. The SOM-TOMAS model was used to simulate the time period between $t=0$ and the first transect using the POA value assumed at $t=0$ and this process was iterated until the OA mass concentration at the first transect was the same as the measured value. This method necessarily assumes that the OA mass and composition at $t=0$ is different than that at the first transect. As the assumptions about POA volatility and oxidation chemistry were varied across different simulations, this iterative approach to determining the POA mass concentration at $t=0$ was done separately for each simulation and transect set.

We used the detailed speciation data for POA and SVOCs from Jen et al. (2019) to create a substitute volatility distribution and to study the sensitivity in model results to the volatility distribution used. Jen et al. (2019) used two-dimensional gas chromatography with time-of-flight mass spectrometry (GC $\times$ GC-ToF-MS) on derivatized samples to measure the detailed chemical composition of POA and SVOC emissions from 29 laboratory-generated fires performed on 24 different fuels. They measured ~ 150 unique species in the sample collected on quartz filters and these amounted to between 10 and 65% of the total POA/SVOC mass. The averaged and normalized, volatility distribution and mass distribution in carbon-oxygen space for the POA and SVOC emissions is shown in Figures S4a and S4b, respectively. The volatility distribution was constructed by binning the ~ 150 species by c^* , which were estimated using EPISuite 4.11 (EPA, 2021).

Jen et al. (2019) found that the SVOCs emissions were dominated by oxygenated organic compounds with major contributions from sugars and terpenoids. These SVOCs have been hypothesized to be important precursors of SOA formation from biomass burning emissions (Garofalo et al., 2019; Palm et al., 2020) but there are few laboratory datasets that can be called upon to inform the oxidation chemistry of SVOCs in our model. In addition to Jen et al. (2019), several studies have measured semivolatile multi-ring aromatics in biomass burning emissions and they are expected to serve as SOA precursors (Bruns et al., 2017; Hatch et al., 2018; Stewart et al., 2021).

Hence, in the absence of any model SOA precursors for which laboratory data are available, we simulated the oxidation chemistry of SVOCs in the base configuration of the SOM-TOMAS model assuming that they have a similar potential to form SOA as multi-ring aromatics (i.e., naphthalene). However, given the uncertainty in this assumption, we performed sensitivity simulations where we modeled the oxidation chemistry of SVOCs as oxygenated aromatics (i.e., phenol), heterocyclics (i.e., alkylfuran), linear alkanes (i.e., n-dodecane), or biogenics (i.e., α -pinene) with the species in parentheses used as the surrogate to model SOA formation.

4.2.6 Model Configuration and Simulations

The base simulations were performed with the following model configuration. We assumed POA to be semivolatile and reactive. The representation of POA/SVOC mass in the SOM grid was based on the volatility distribution of May et al. (2013) and the oxidation chemistry for SVOCs was modeled based on SOM parameters for multi-ring aromatics (naphthalene). We assumed a liquid-like phase state to model the kinetics of OA gas/particle partitioning. All SOA parameters, including those for SVOCs and VOCs, were corrected for the influence of vapor losses to the walls of the Teflon chamber. Background corrections were performed on the raw observations using a background value that was specific to each wildfire plume, but not varying in time or space for that plume. The OH concentrations were based on the laboratory-normalized and reactivity-differentiated analysis with separate but constant values for the time periods before and after the first transect. The first transect for each transect set was hand chosen based on the transect closest to the fire that had the highest observed, background-corrected VOC-to-CO ratios. Simulations performed with this model configuration are hereafter referred to as the ‘base’ or the ‘SV-POA+FullChem’ simulations. Nearly all of the assumptions in the base model were rigorously tested by performing sensitivity simulations, as described below:

1. In addition to the base simulations (SV-POA+FullChem), we performed a systematic sequence of simulations where we tested assumptions about POA volatility and SVOC and VOC chemistry: (i) non-volatile POA and no chemistry (NV-POA+NoChem), (ii) non-

- volatile POA and VOC chemistry (NV-POA+FullChem), (iii) semivolatile POA and no chemistry (SV-POA+No Chem), and (iv) semivolatile POA and SVOC chemistry (SV-POA + NoVOCChem). Results from these simulations are presented in Figures 4.4 and 4.5.
2. Simulations were performed to assess the sensitivity in model results to the treatment of POA and SVOCs: (i) we simulated the oxidation chemistry for SVOCs using the SOM parameters for oxygenated aromatics (i.e., phenol), heterocyclics (i.e., alkylfuran), linear alkanes (i.e., *n*-dodecane), or biogenics (i.e., α -pinene), with the species in parentheses used as the surrogate to model SOA formation, (ii) we used the POA volatility distribution determined from the work of Jen et al. (2019) in combination with the five surrogate species to model the oxidation chemistry of SVOCs, and (iii) we performed a thousand Monte-Carlo simulations where we randomly chose eight species in the SOM grid to represent the POA and SVOC mass and fit a mass distribution with these eight species that reproduced the POA volatility behavior observed by May et al. (2013). Results from these simulations are presented in Figures 4.6 and C.9-C.10.
 3. Simulations were performed to assess the sensitivity in model results to the assumed OH concentrations, ‘first’ transect, and background correction: (i) we assumed a low or high OH concentration over the entire wildfire plume with the low value based on the OH estimate after the first transect and the high value based on the OH estimate before the first transect, (ii) we assumed a time-varying OH concentration that was determined by fitting a power function through the OH exposure data presented in Figure 4.2, (iii) we assumed a constant OH concentration of 1.5×10^6 molecules cm^{-3} , (iv) instead of using the transect closest to the fire as the first transect, we assumed the second or third closest transects to be the ‘first’ transect to perform the simulations, and (v) measurements and model inputs were calculated by performing background corrections by using the transect-specific background concentrations or assuming the concentrations upwind of the fire to be representative of the true background. Results from these simulations are presented in Figures 7 and S11-S12.

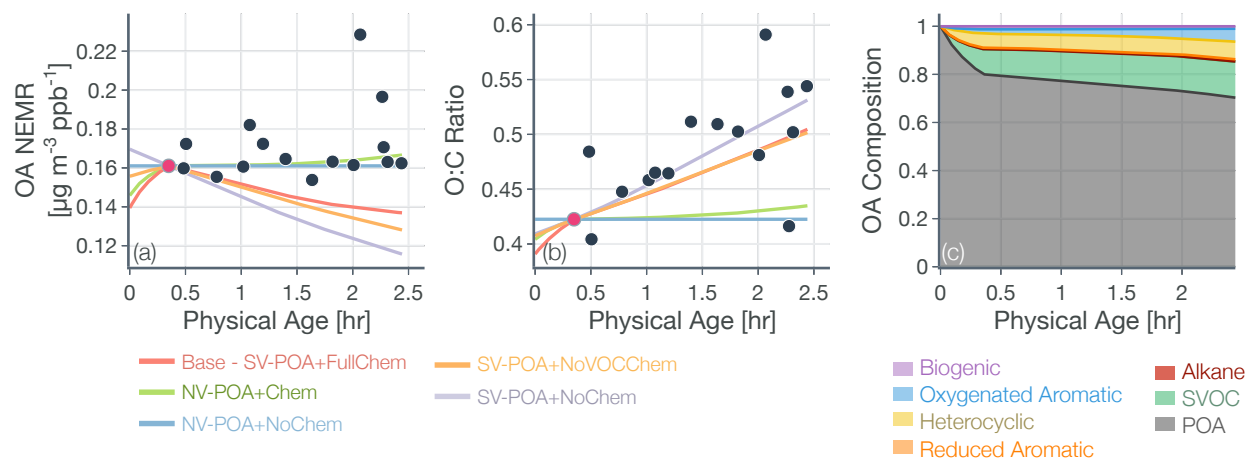


Figure 4.4: Predictions of (a) OA NEMR and (b) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. Model predictions are shown for five different simulations that vary in their assumptions about POA volatility and oxidation chemistry. Model predictions were always constrained to the measurements of OA NEMR and OA O:C at the 1st transect, marked by the red solid circle. Predictions of the normalized OA composition from the base simulations are shown in panel (c).

4.3 Results

4.3.1 OA Mass and Composition Evolution

Results from simulations performed with the base configuration and with assumptions about POA volatility and oxidation chemistry are shown in Figure 4.4 for the Taylor Creek fire. We present results for Taylor Creek first because the plume data for this fire come closest to representing a Lagrangian dataset (Figure C.1). Model predictions and measurements of OA mass are presented using the NEMR metric (Figure 4.4a) and those for OA composition as the background-corrected OA O:C (Figure 4.4b). Model predictions and measurements of the absolute, background-corrected OA and CO concentrations are shown in Figure C.4. The measurements show a nearly constant OA NEMR ($0.16 \mu\text{g m}^{-3} \text{ ppbv}^{-1}$) with a relatively stronger increase in the OA O:C (from 0.42 to 0.54) and these trends were used to evaluate predictions from the five different model simulations. Uncertainties in the observed OA NEMR and O:C were deliberately left out since those were found to be much larger than the overall trend, which made it harder to evaluate the model predictions. A version of Figure 4.4 that includes the standard error in the mean for the observed OA NEMR and O:C is presented as Figure C.5.

For the simulations with non-volatile POA and no oxidation chemistry (NV-POA+NoChem), the model reproduced observations of OA NEMR (Mean Bias Error (MBE)=-0.009, Mean Absolute Error (MAE)=0.011; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$) but, by definition, produced no change in the OA O:C (MBE=-0.061, MAE=0.064). With the oxidation chemistry turned on to produce SOA from VOCs (NV-POA+Chem), the model only produced a marginal increase in the OA NEMR compared to the NV-POA+NoChem simulation and, hence, reproduced observations of OA NEMR (MBE=-0.007, MAE=0.011; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$). The NV-POA+Chem simulation produced a slight increase in OA O:C with physical age compared to the NV-POA+NoChem model but still significantly lower than the observed increase in OA O:C (MBE=-0.057, MAE=0.061). The relatively small increase in OA NEMR and OA O:C can be explained by the marginal amounts of SOA formed from the VOC mixture beyond the first transect. As noted in Section 4.2.4, this VOC mixture was substantially depleted in important SOA precursors by the first transect. For the simulation with semivolatile POA with no oxidation chemistry (SV-POA+NoChem) and the simulation with semivolatile POA with oxidation chemistry for SVOCs alone (SV-POA+NoVOCChem), the model appeared to underestimate the OA NEMR (MBE=-0.035 and -0.028, MAE=0.035 and 0.028, respectively; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$) with a substantial increase in OA O:C. The predicted decrease in OA NEMR compared to the NV-POA+NoChem model stemmed from the evaporation of POA with dilution that was only partly recovered through SOA formation in the SV-POA+NoVOCChem model. Results from the SV-POA+NoChem simulation suggested that POA evaporation alone could explain the increase in the OA O:C with physical age as the lower-volatility material left in the particle phase after evaporation had a relatively higher O:C than the semivolatile material that had evaporated (Figure C.3b). Finally, the base simulation that assumed a semivolatile POA and oxidation chemistry for both SVOCs and VOCs (SV-POA+FullChem) slightly underestimated the OA NEMR compared to observations (MBE=-0.024, MAE=0.024; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$) but produced a large increase in OA O:C consistent with the observations (MBE=-0.019, MAE=0.032; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$). The base simulation predicted a lower increase in O:C compared to the SV-POA+NoChem simulation because the SOA being formed in the base simulation had a lower O:C than the remaining POA. Overall,

two of the simulations appeared to be the most consistent with observations of OA NEMR but significantly underestimated the observations of OA O:C (NV-POA+NoChem and NV-POA+Chem), and two of the simulations came close to reproducing the increase in OA O:C with physical age but underestimated the observations of OA NEMR (SV-POA+NoChem and SV-POA+NoVOCChem). The base or SV-POA+FullChem simulation seemed to offer a balanced comparison with observations where both the OA NEMR and O:C were only slightly underestimated.

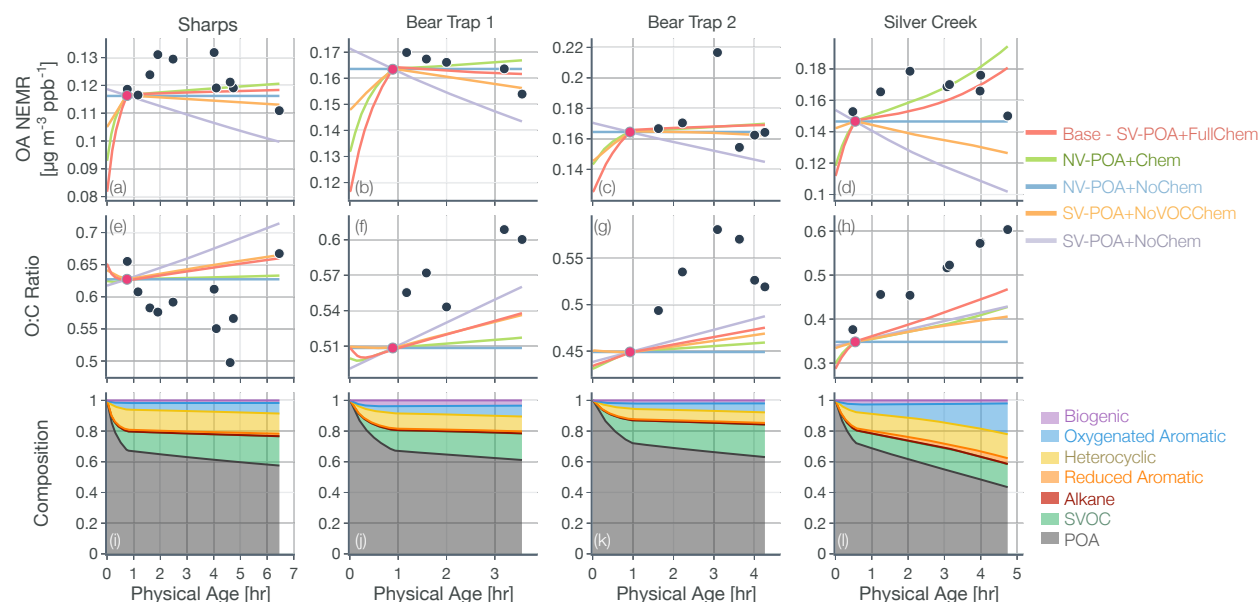


Figure 4.5: Predictions of (a-e) OA NEMR and (f-j) OA O:C from the SOM-TOMAS model compared against measurements from four different wildfire transect sets (Sharps, Bear Trap $\times$ 2, Silver Creek). Model predictions are shown for five different simulations that vary in their assumptions about POA volatility and oxidation chemistry. (k-o) Model predictions of the normalized OA composition from the base simulations (SV-POA+FullChem).

Results from simulations for the remaining fires and transect sets (Sharps, Bear Trap, and Silver Creek) are shown in Figure 4.5(a-l), where the relative trends across the five different simulations were similar between those presented for Taylor Creek in Figure 4.4. Therefore, the differences in these simulations are not described further. However, as discussed below, the absolute performance of the base simulation for these other fires was mixed. The base simulation could not reproduce the initial increase and later decrease in observed OA NEMR for the Sharps and Silver Creek fires. Both of these fires were sampled by the aircraft much faster than the physical

age (Figure C.1) and the measurements reflect changes in emissions rather than those from their evolution. The base simulation produced a gradually increasing OA NEMR for the Sharps fire (MBE=-0.004, MAE=0.006; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$) and a sharply increasing OA NEMR for the Silver Creek fire (MBE=-0.004, MAE=0.012; $\mu\text{g m}^{-3} \text{ ppbv}^{-1}$). Unlike the comparison for the Taylor Creek fire, the base simulation appeared to reproduce the relatively constant observations of OA NEMR for the Bear Trap fire transects. And finally, except for the Sharps fire, the base simulation consistently underestimated the change in OA O:C with physical age with the strongest comparison for the Bear Trap 1 fire (MBE=-0.044, MAE=0.044) and the weakest comparison for the Silver Creek fire (MBE=-0.087, MAE=0.087).

Taken together, we draw the following conclusions from the model-measurement comparisons presented in Figures 4 and 5. First, a non-volatile and non-reactive treatment of POA, regardless of the inclusion of SOA produced from VOC oxidation, is unlikely to explain the combined observations of OA NEMR and O:C. Second, POA evaporation with dilution can potentially explain the change in the OA O:C with time but this loss in POA mass is not consistent with observations of OA NEMR. Finally, we argue that the base simulation best explains the trends in both the OA NEMR and OA O:C across the five transect sets and four wildfires; average MBE=-0.007 and MAE=0.011 ($\mu\text{g m}^{-3} \text{ ppbv}^{-1}$) for OA NEMR and average MBE=-0.033 and MAE=0.055 for OA O:C across all five transect sets. Furthermore, we should note that the model treatment in the base simulation closely reflects our updated understanding of the POA and SOA system from wildfire emissions.

Model predictions of the normalized OA composition with physical age from the base simulations are shown in Figure 4.4c for Taylor Creek and in Figures 5i-5l for all other fires while model predictions of the POA-SOA split with photochemical age for all fires are shown in Figure C.6. There are several interesting features to note. The OA composition began to change rapidly starting at $t=0$ from the dilution-driven evaporation of directly emitted POA and the SOA produced from the oxidation of SVOCs and VOCs. By the first transect, the average OA across all five transect sets, 21 to 55 minutes after emission, was 73% POA and 27% SOA. As the base-simulation-

predicted OA NEMR was found to universally increase during the period before the first transect for all five transect sets, the changes in OA composition were largely driven by SOA condensation rather than POA evaporation. The rapid SOA production was facilitated by the higher OH concentrations experienced before the first transect (see Table 4.1). Generally speaking, the observed and base-simulation-predicted OA NEMRs did not vary much past the first transect for any of the fires. Despite that fact, the base simulations predicted a modest change in the OA composition with physical age after the first transect. Over all five transect sets, POA continued to dominate the total OA mass beyond the first transect (>50%) but there was continued production of SOA over this time period. By the last transect, the SOA contribution to the total OA varied between 30% for the Taylor Creek fire and 56% for the Silver Creek Fire. The base simulations predicted that the majority of the SOA was formed from the oxidation of SVOCs, heterocyclics, and oxygenated aromatics, in that order. On average, these three precursor classes accounted for 45, 25, and 21% of total SOA and 18, 11, and 9% of the total OA by the last transect. Biogenic VOCs that have been found to contribute to SOA formation in laboratory experiments performed on biomass burning emissions (Ahern et al., 2019) accounted for less than 5% of the SOA and 2% of the OA by the last transect. The contributions of the different precursor classes to SOA were nearly identical between the different fires reflecting the uniformity in the SOA precursor emissions across fires.

These simulations provide model-based evidence for dilution-driven evaporation of POA mass being replaced by SOA mass formed from the oxidation of SVOCs and VOCs in wildfire plumes during WE-CAN. This conclusion is consistent with the theoretical findings of Bian et al. ((2017) and Hodshire et al. (2019b), who have argued that POA evaporation can be approximately replaced with SOA condensation under certain conditions pertaining to the fire size, background concentrations, and atmospheric stability. The base simulations predicted a mean POA-SOA split of 59%-41% by the last transect over all five transect sets. These model-predicted POA-SOA splits agreed well with the theoretical findings of Hodshire et al. (2019b), who predicted a minimum POA-SOA split of 75-25% for large fire sizes (>1 km²), and the findings of Palm et al. (2020), who empirically determined a maximum POA-SOA split of 66%-33% for OA measured over sev-

eral wildfire plumes during WE-CAN. Note that Palm et al. (2020) estimated their maximum POA-SOA split assuming that the OA at the first transect was exclusively POA. However, in contrast to the precursor-resolved findings discussed above, Palm et al. (2020) proposed that SVOCs were responsible for nearly 90% of the SOA formed within the plume. They might have overestimated the SVOC contribution to SOA because they arrived at that estimate by performing a closure calculation where they subtracted the SOA estimated from non-SVOC precursors from the total SOA formed.

4.3.2 Model Sensitivity to the Treatment of POA and SVOCs

Results from simulations performed to assess the sensitivity to the treatment of POA and SVOCs are shown in Figure 4.6. Here, we compare model predictions of OA NEMR (top row) and OA O:C (middle row) against measurements for the Taylor Creek fire and plot model predictions of the fractional contributions of POA and SOA to OA (bottom row). We also include predictions from the base simulation shown in Figure 4.4. Results from sensitivity simulations performed for the other fires are shown in Figure C.9-C.12. In the base simulation, SVOCs accounted for $\sim 15\%$ of the total OA by the last transect. Given the relatively small contribution, the use of different surrogate organic classes and species to simulate the oxidation chemistry of SVOCs resulted in a moderate spread in the OA NEMR predictions, with all predictions biased lower than the measurements. The use of a heterocyclic surrogate (i.e., alkylfuran) seemed to agree the best and the use of an oxygenated aromatic surrogate (i.e., phenol) seemed to agree the least with the OA NEMR observations. The differences in the model predictions were understandable since the potential to form SOA is known to vary substantially across the five surrogate species considered: naphthalene, *n*-dodecane, alkylfuran, phenol/guaiacol, and α -pinene. There was a similar spread in the model predictions of OA O:C but, in contrast to the OA NEMR comparisons, all model predictions compared reasonably with the observed increase in OA O:C. By the last transect, the average OA split was 75% POA and 25% SOA. The spread in the model predictions highlights the need for model systems to be identified for the dominant organic compounds found in SVOCs (e.g., sugars)

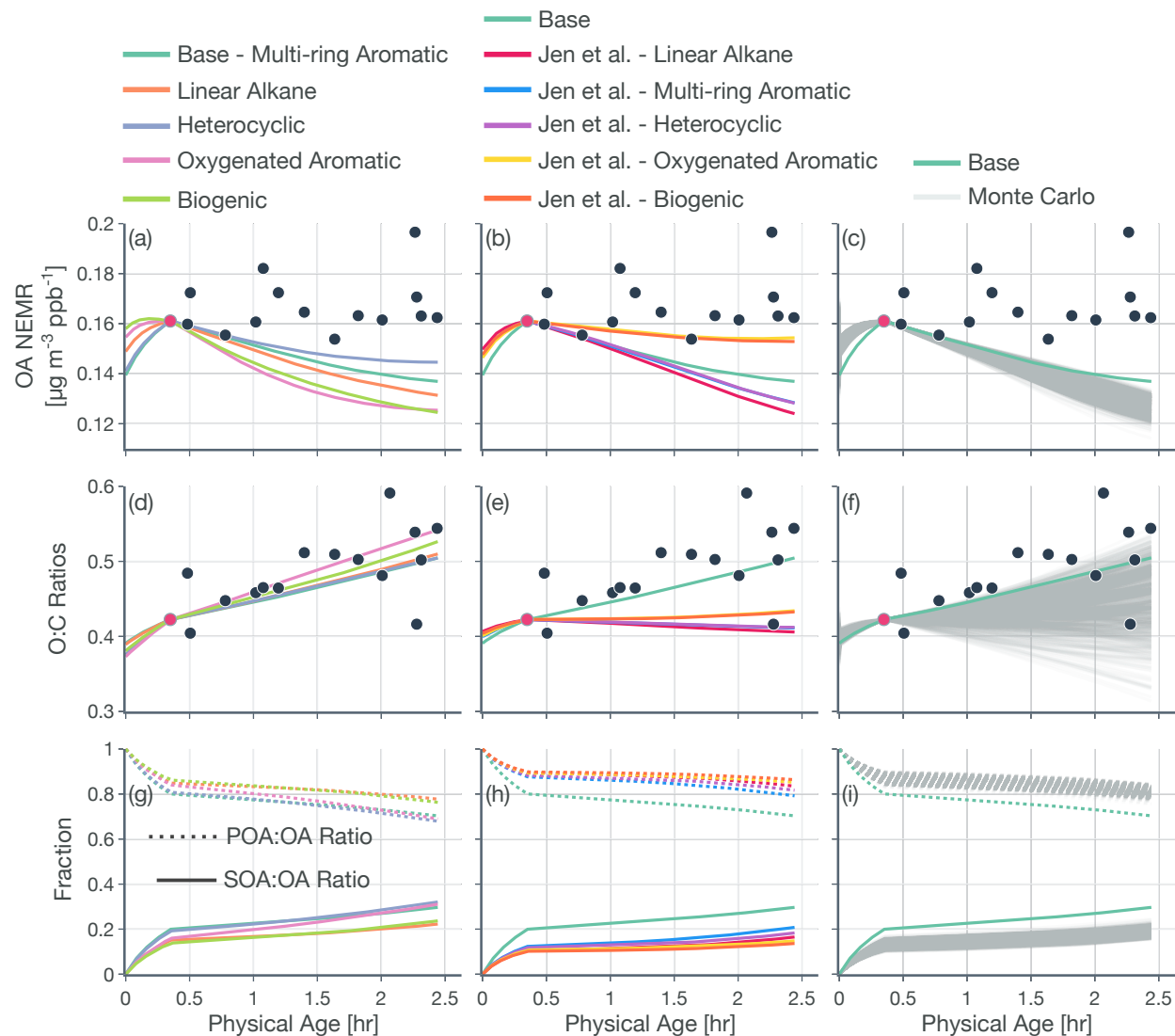


Figure 4.6: Predictions of (a,b,c) OA NEMR and (d,e,f) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (g,h,i) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for the SVOC oxidation chemistry (a,d,g), POA volatility and SVOC oxidation chemistry (b,e,h), and POA+SVOC mass distribution in the SOM grid.

and the need to develop organic class-specific parameters to simulate SOA formation from these SVOCs.

On using the substitute volatility distribution based on the speciation data of Jen et al. (2019) and the five different surrogate species to simulate the oxidation chemistry from SVOCs, the model produced an even larger spread in the OA NEMR predictions compared to the sensitivity result discussed above. The use of an oxygenated aromatic (i.e., phenol/guaiacol) and biogenic (i.e., *alpha*-pinene) surrogate seemed to agree the best and the use of a heterocyclic (i.e., alkylfuran), multi-ring aromatic (i.e., naphthalene), and linear alkane (i.e., *n*-dodecane) surrogate seemed to agree the least with the OA NEMR observations. All simulations produced a flat response in the OA O:C with physical age despite a gradual change in the POA-SOA split and dilution-driven evaporation of the semivolatile material. This flat response was inconsistent with the observed change in the OA O:C. The substitute volatility distribution resulted in a larger POA-SOA split (average of 83%-17%) compared to the first set of sensitivity results (average of 75%-25%) likely because a smaller fraction of the fresh POA mass was lost to evaporation from the use of a less volatile volatility distribution (Figure C.7a). The mixed comparisons for OA NEMR and O:C suggest that model inputs determined from speciation data hold promise but might be limited because, in this specific case, the speciated compounds only represented a fraction (10-65%) of the total POA+SVOC mass. Additional work to fully speciate the POA and SVOC mass to inform the volatility properties of POA and identify surrogate species to model the oxidation chemistry of SVOCs will lead to better model predictions.

Finally, we performed a thousand Monte-Carlo simulations where we randomly specified the mass distribution of the POA+SVOC mass in the SOM carbon- and oxygen-number grid while ensuring that this mass distribution reproduced the POA volatility behavior observed by May et al. (2013) (Figure C.8). The iterations produced a large spread in the OA NEMR predictions but they all seemed to underestimate the observed trends. By the last transect, the predicted OA NEMR was 17 to 29% lower than the average observed OA NEMR at that time. Compared to the OA NEMR, there was an even larger spread in the predicted OA O:C with iterations predicting a decrease in

O:C with physical age at the one end (from 0.41 to 0.31) to reproducing the observed increase at the other end (0.38 to 0.54). The iteration that resulted in the largest absolute OA NEMR at the end of the simulation and then the largest increase in OA O:C was chosen to represent the base simulation results presented in Figures 4 and 5.

4.3.3 Model Sensitivity to OH, ‘First’ Transect, and Background Correction

Results from simulations performed to assess the sensitivity to the OH estimates are presented in the left column in Figure 4.7. The use of a power function fit to the OH exposure data to determine OH concentrations (OH-Power Fit) produced results that were identical to those from the base simulation. To remind the reader, the base simulations used linear fits to the OH exposure data before and after the first transect, which produced constant but separate OH concentration estimates for time periods before and after the first transect, respectively. If we assumed that the lower OH concentration after the first transect was also relevant to the time period before the first transect (OH-Low), the model predictions of OA NEMR and O:C were slightly higher than those from the base simulation. The model predictions were higher likely because a lower OH concentration before the first transect preserved the SVOCs during this period for them to be oxidized to SOA after the first transect. On using a constant OH concentration of 1.5×10^6 molecules cm^{-3} (OH-Ambient) or the higher OH concentration from before the first transect (OH-High) for the entire evolution, the model predicted an even higher OA NEMR and O:C compared to predictions from the base and OH-Low simulations. This was because the OH concentrations in both of these instances were larger than those used in the base and OH-low simulations and these higher OH concentrations promoted SOA formation. For the OH-High simulation, the increase in OA NEMR was found to be inconsistent with the trends in the observations indicating that the high OH concentrations

Qualitatively, the modeled trends in the OA NEMR and OA O:C were not very different when we assigned different transect sets to be the ‘first transect’ where model predictions of OA NEMR and OA O:C were anchored to observations; results are presented in the middle column of Figure

4.7. There appeared to be some tradeoff in the model-measurement comparisons for OA NEMR and OA O:C with the transect chosen. For instance, anchoring the model predictions to the information at the third transect seemed to produce better agreement with observations of OA NEMR but underestimated observations of OA O:C. The opposite was found to be true when anchoring the model predictions to the information at the second transect. Regardless of the variability in the OA NEMR and O:C, the POA-SOA splits were nearly identical between the three simulations. The use of transect-specific or upwind data to calculate values to perform the background corrections did not seem to have any significant effect on model predictions; results are presented in the right column of Figure 4.7.

4.3.4 Summary and Implications of the Base Results

A summary of the model predictions for POA, SOA, and the SOA precursors at $t=0$ and the first and last transects, for all five transect sets is presented in Figure 4.8. Some of these results have been presented in Figures 4 and 5 earlier but this specific presentation of the results provides an opportunity to summarize the modeling effort and draw broader conclusions. First, fresh emissions of POA were found to be consistently larger than those for SOA precursors (factor of 3.4 for Taylor Creek and 30% for the other fires). For reference, for mobile sources, SOA precursor emissions are easily an order of magnitude larger than POA emissions (Lu et al., 2018). This means that direct emissions of POA are likely to be an important constituent of smoke aerosol downwind of the fire, even as some fraction of it is lost to evaporation and surface reactions (not modeled in this work) and SVOCs and VOCs oxidize to form SOA and add to OA mass. Second, up to half of the SOA precursors were rapidly oxidized to form SOA early on, which primarily resulted in an increase in the OA NEMR and O:C prior to the first transect. The rapid evolution in OA mass and composition close to the fire is bound to alter the chemical, microphysical, and optical properties of smoke aerosols early on and confound comparisons of aerosol measurements at the first transect with similar measurements made on fresh emissions in laboratory environments. We should note that the physicochemical evolution prior to the first transect is extremely uncertain and needs to be studied

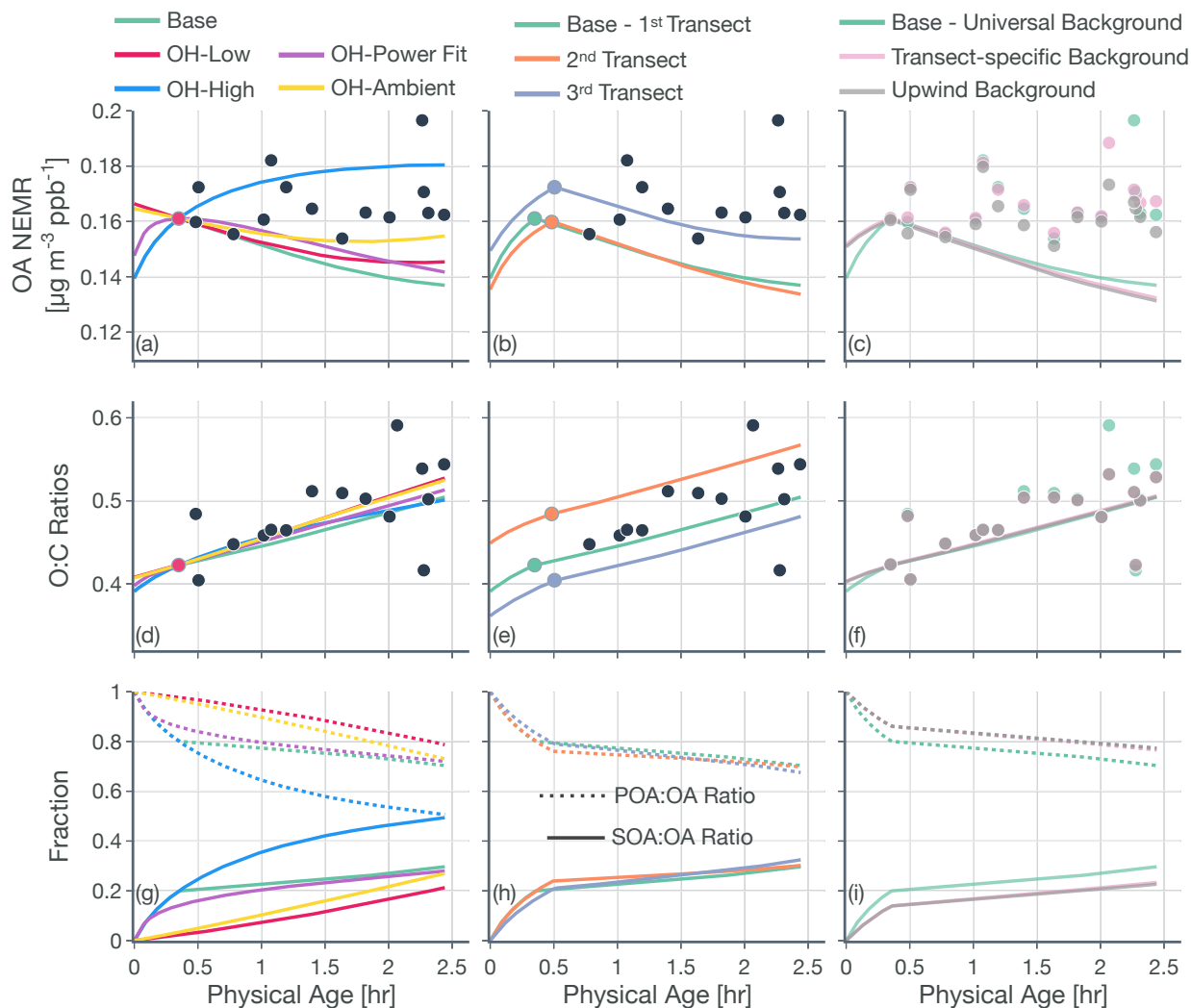


Figure 4.7: Predictions of (a,b,c) OA NEMR and (d,e,f) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (g,h,i) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for OH (a,d,g), ‘first’ transect (b,e,h), and approach to perform background corrections.

in more detail in the future. Third, for four out of the five transect sets (i.e., except Silver Creek), the OA NEMR did not vary much between the first and last transects but there was a gradual change in the OA composition with POA evaporation and SOA formation from SVOCs and VOCs. As the SOA precursors were heavily depleted and the OA mass concentrations ($5\text{--}33\ \mu\text{g m}^{-3}$) were only slightly larger than the background concentrations ($1\text{--}18\ \mu\text{g m}^{-3}$) by the last transect, we postulate that the OA NEMR and O:C are unlikely to change substantially with additional photochemical aging. Finally, by the last transect, SVOCs and VOCs contributed equally to SOA formation in wildfire plumes. Yet, these oxygenated SVOC and VOC classes are not explicitly included in emissions inventories and chemical mechanisms, part of three-dimensional atmospheric models. Hence, the representation of SOA formation, as studied here, is largely missing from atmospheric models.

4.4 Discussion

In this study, we used a plume version of a state-of-the-science model to simulate the dilution and physicochemical evolution of OA in wildfire plumes measured during the WE-CAN field campaign. The model was built on parameterizations developed from laboratory data, initialized using field measurements, and evaluated against the OA mass and composition measurements gathered from pseudo-Lagrangian transect sets. Our work suggests that it is very likely that dilution-driven evaporation of semivolatile POA and simultaneous photochemical production of SOA from SVOCs and VOCs explains the relative invariability in OA enhancements with photochemical age in observations of ambient wildfire plumes. These findings around OA evolution are consistent with the theoretical analysis presented by Bian et al. (2017) and Hodshire et al. (2019a) and the empirical analysis of Palm et al. (2020) for WE-CAN fires. In addition, our model predictions indicate an important role for oxidation chemistry and rapid SOA formation before the first aircraft measurements, which is likely to be driven by higher-than-normal OH concentrations in the wildfire plume ($3\times 10^6\text{--}10^7\ \text{molecules cm}^{-3}$). Notionally, for the fires studied here, we expect the OA measured within an hour after emission to be 80% POA and 20% SOA and 60% POA and 40% SOA

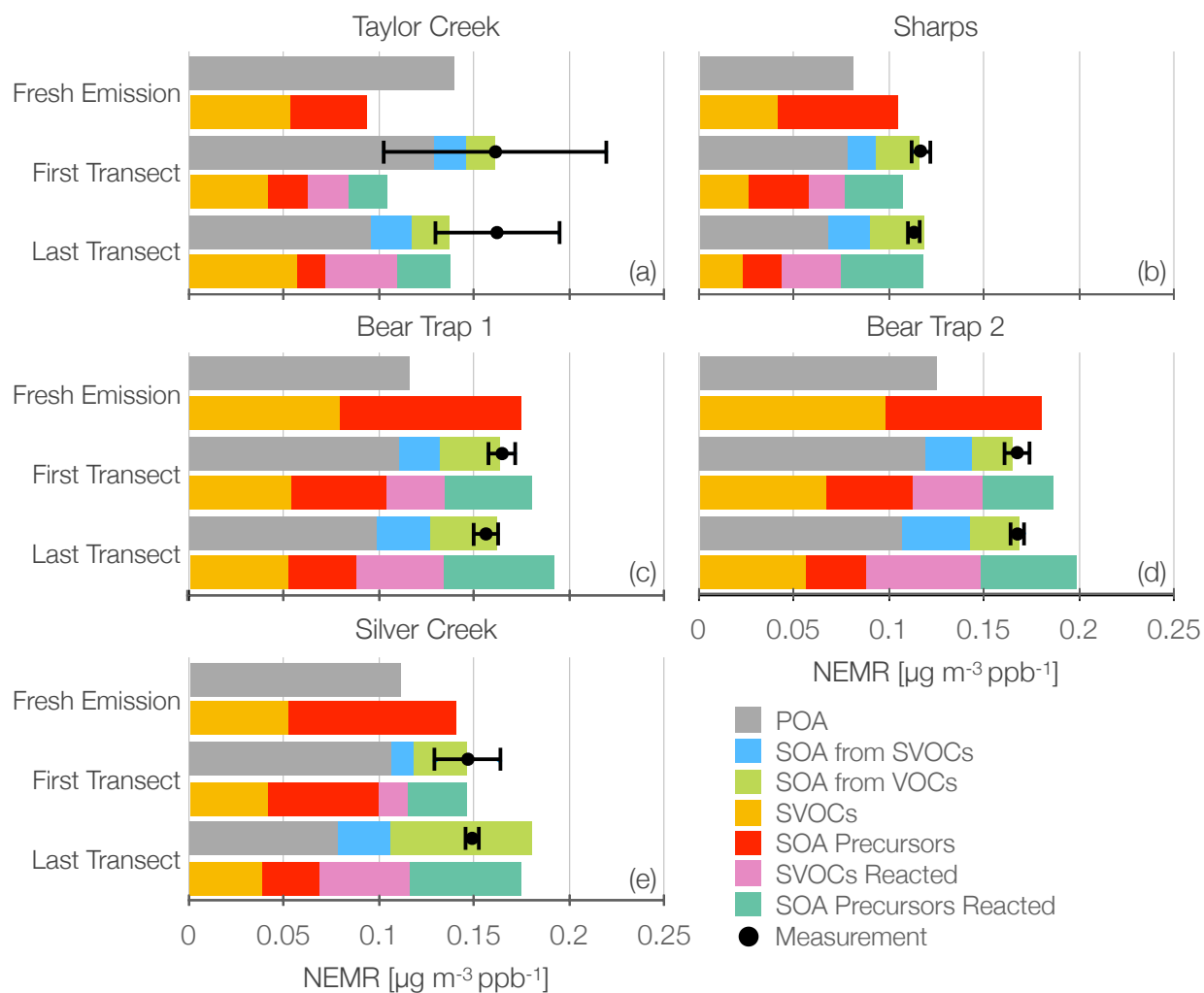


Figure 4.8: Model predictions of OA and SOA precursor NEMRs at $t=0$ ('Fresh Emission') and the first and last transects for all five transect sets. Observations of OA NEMR are also presented for the first and last transects in light grey with error bars.

after several more hours of evolution. Finally, SOA precursor emissions for a few important organic classes (i.e., oxygenated aromatics, biogenics) appear to be systematically lower than those measured in laboratory experiments, and these lower emissions might partly explain the reduced propensity to form SOA in wildfire plumes.

Model results were found to be moderately sensitive to the assumed volatility and oxidation chemistry for POA and SVOCs. Hence, continued work to fully speciate the POA and SVOC mass to inform the volatility properties of POA and to identify surrogate species to model the oxidation chemistry of SVOCs will likely lead to improvements in model predictions. As the model predictions were found to be somewhat sensitive to the OH concentrations assumed in the wildfire plume, the OH estimates developed in this work need to be evaluated in future work. Peng et al. (2020) calculated HO_x ($\text{OH} + \text{HO}_2$) production rates in wildfire plumes sampled during WE-CAN from the photolysis of nitrous acid (HONO), O_3 , and other smaller aldehydes (e.g., formaldehyde) and ozonolysis of alkenes. In theory, these HO_x production rates could be used in conjunction with a gas-phase chemical mechanism to constrain OH concentrations both across and within plume transects and potentially be used to evaluate the OH estimates from this work.

In addition to the uncertainties modeled in this work, there are several additional aspects to consider while modeling the OA evolution in wildfire plumes. First, the model parameterizations in this work (e.g., POA volatility, SOA parameters) were based on simpler model systems studied in laboratory environments and these parameters may not accurately represent the processes in real wildfire plumes. Most obviously, differences in the fuel complex, burn conditions, combustion efficiency, and environmental conditions (e.g., temperature, relative humidity) and regimes (e.g., photolytic rates, NO_x) could produce differences in the emissions, chemistry, and properties of OA and OA precursors between the laboratory and the field (Lindaas et al., 2020). A more specific example is that the parameters that we used to model the SOA formation from SVOCs, heterocyclics, and oxygenated aromatics (precursor classes that contributed the most to SOA production) came from a few environmental chamber experiments performed on a handful of surrogate species (phenol and guaiacol, an alkylfuran mixture, and naphthalene, respectively) under relatively dry

(relative humidity < 20%) and high NO_x conditions (200-800 ppbv) (Chan et al., 2010; He et al., 2020; Yee et al., 2013). While this extrapolation is typical for how laboratory data are translated into parameters for use in atmospheric models, these laboratory versus field differences need to be considered when evaluating model predictions against measurements.

Second, the current version of the SOM-TOMAS model does not simulate the photolysis or aqueous chemistry of OA or OA precursors. Photolysis has been shown to be an important loss pathway for SOA formed from monoterpenes (Henry and Donahue, 2012; Zawadowicz et al., 2020). Oxygenated aromatics that include phenols, methoxyphenols, and phenolic carbonyls, after uptake into aerosol water, can participate in aqueous reactions to form low-volatility and light absorbing SOA (Huang et al., 2018; Smith et al., 2014). Both of these chemical processes are likely occurring in wildfire plumes and, hence, need to be included in future modeling efforts. Third, the model initialization and evaluation in this work only relied on a subset of measurements made during WE-CAN. Future work could certainly benefit from leveraging an extended set of measurements gathered during WE-CAN and similar field campaigns focused on studying biomass burning emissions (e.g., BBOP (Kleinman and Sedlacek, 2016), LASIC (Zuidema et al., 2018), FIREX-AQ (Roberts et al., 2020)). For example, model predictions could be compared against measurements of the evolving composition (e.g., oligomers), size distribution, and thermodynamic (e.g., volatility), optical (e.g., scattering, extinction), and climate (e.g., cloud condensation nuclei) properties. Finally, Peng et al. (2020) and Hodshire et al. (2020) were recently able to study the distinct evolution of trace species resolved over the width of the wildfire plume. Both found evidence for increased photochemical activity near the edges and wings of the plume since these regions diluted much faster and were less optically dense compared to the core of the plume. Modeling in the future could use the information inherent in gradients within the transect to constrain the OA evolution under varying dilution and photochemical conditions.

Our work provides a renewed lens through which OA evolution needs to be viewed in wildfire plumes. The primary findings from this work surrounding the dynamic evolution of OA in wildfire plumes are extremely relevant for interpreting aircraft and ground based measurements of wildfire

smoke and in developing chemical mechanisms and parameterizations to represent the emissions and chemistry of wildfire OA in atmospheric models at all scales.

Chapter 5

Conclusion and summary of science findings

The research presented in this dissertation improves our understanding of the organic aerosol (OA) mass and composition from different sources and precursors. Below, key results and conclusions from each chapter are summarized.

In chapter 2, I updated the organic aerosol model in the UCD/CIT (the University of California at Davis/California Institute of Technology) chemical transport model to include (i) a semi-volatile and reactive treatment of primary organic aerosol (POA), (ii) emissions and secondary organic aerosol (SOA) formation from intermediate volatility organic compounds (IVOCs), (iii) the NO_x influence on SOA formation, and (iv) SOA parameterizations for semi-volatile organic compounds (SVOCs) and IVOCs that are corrected for vapor wall loss artifacts during chamber experiments. Treatment of combustion-related POA as semivolatile in the model resulted in 15-40% reduction of modeled POA mass concentrations in the urban areas in southern California. Model prediction suggested that both SVOCs (evaporated POA vapors) and IVOCs did not contribute as much as other well-known anthropogenic SOA precursors (e.g., alkanes, aromatics) to SOA mass concentrations in the urban areas. Correcting for the chamber-experiment vapor wall loss artifact resulted in positive enhancement of SOA mass concentrations. Accounting for the influence of NO_x using the VOC: NO_x ratios resulted in better predictions of OA mass concentrations in rural/remote environments; however, the model still underpredicted the OA mass in urban environments. The underprediction of modeled OA in urban environments results and data analyses suggested that IVOC emissions were not well-represented in the model and they were low at least by a factor of two. In addition, future simulations performed for the year 2035 showed that, despite reductions in VOC and NO_x emissions in the future, SOA mass concentrations may be higher than in the year 2005, primarily from increased hydroxyl radical (OH) concentrations due to lower ambient NO_2 concentrations.

In chapter 3, I developed a state-of-the-science model, SOM-TOMAS, to simulate the photochemical formation of secondary organic aerosol (SOA) from biomass-burning emissions observed in dry environmental chamber experiments. The modeling work is supported by (i) new oxidation chamber measurements, (ii) detailed concurrent measurements of SOA precursors in biomass-burning emissions, and (iii) development of SOA parameters for heterocyclic and oxygenated aromatic compounds based on historical chamber experiments. I find that oxygenated aromatic compounds, including phenols and methoxyphenols, account for slightly less than 60% of the SOA formed and help our model explain the variability in the organic aerosol mass and O:C enhancement ratios observed across 11 chamber experiments. Despite abundant emissions, heterocyclic compounds that included furans contribute to $\sim 20\%$ of the total SOA. The use of pyrolysis-temperature-based or averaged emission profiles to represent SOA precursors, rather than the emission profiles from each individual fire, provides similar results to within 20%. Our findings demonstrate the necessity of accounting for oxygenated aromatics from biomass-burning emissions and their SOA formation in chemical mechanisms.

In Chapter 4, I developed a plume version of the SOM-TOMAS model to simulate organic aerosol in wildfire plumes. The model was applied to study the in-plume OA measured for four large wildfires during an aircraft-based field campaign in 2018. The model was built on parameterizations developed from laboratory data, initialized using field measurements, and evaluated against the OA mass and composition measurements gathered from pseudo-Lagrangian transect sets. The model results and sensitivity simulations suggested that dilution-driven evaporation of POA and simultaneous photochemical production of SOA are likely to explain the measured trends in OA mass and composition with physical age. I showed that the rapid chemical transformation within the first hour after emission is largely driven by higher-than-ambient OH concentrations and depleted SOA precursors. Model predictions indicate that OA is still dominated by the POA several hours downwind of the fire and the ratio of oxygen to carbon atoms in OA varied between 20% and 50%. Semivolatile, heterocyclic, and oxygenated aromatic compounds, in that order, are

found to contribute substantially to SOA formation. The modeling work undertaken in chapter four is a step forward in bridging laboratory and field observations of wildfire smoke aerosol.

Future work

The findings in chapter 2 indicated that model predictions continue to overestimate POA relative to measured concentrations. Sea-spray emissions accounted for a quarter of the POA mass concentrations in the urban airshed, but more recent observations suggest that the sea-spray emissions or the organic fraction attributed to the sea-spray emissions might be overestimated (Hayes et al., 2013). This needs to be examined in future applications of the UCD/CIT model. The model results also showed that the model still underestimates the ambient OA mass concentration and it is not able to capture OA mass and O:C ratio diurnal cycles for the summer episode. This can be due to missing some sources of SOA precursors and the lack of understanding of the transitional regime between high and low NO_x . Underprediction of IVOC emissions in the model suggests missing sources and emissions of IVOCs. McDonald et al. (2018) found that volatile chemical products such as pesticides, coatings, cleaning agents, and personal care products contribute substantially to urban SOA burdens. So, it is important to examine the SOA production of these sources of IVOCs and have better speciation and representation in the UCD/CIT model.

In chapter 3, biomass burning chamber experiments and modeling have been done under dry conditions. It is important to conduct future experiments and associated modeling at higher relative humidity conditions because wildfire plumes are not always in dry conditions. SOA production, including aqueous-phase chemistry, may change with higher relative humidity, and this work did not explore these differences. Studies have shown that (1) SOA aqueous chemistry of oxygenated aromatic from biomass burning can be important (Huang et al., 2018; Smith et al., 2014) and (2) OA evaporation and the aerosol size distribution are affected by relative humidity through changes in the particle phase state (He et al., 2021; Zaveri et al., 2014), so we should not rely solely on dry experiments. Currently, one of the big uncertainties around biomass burning OA mass and composition evolution is POA speciation and its range of volatilities. Continued work is necessary (1) to fully speciate the POA and SVOC mass to inform the volatility properties of POA and (2) to

identify surrogate species to model the oxidation chemistry of SVOCs in order to improve model predictions and our understanding of biomass burning OA evolution.

In Chapter 4, all biomass burning OA aging was investigated under daytime conditions. However, fresh biomass burning emissions also happen throughout the night, and daytime emissions continue to age overnight. Recent work has shown that there may be significant SOA production in biomass-burning plumes under nighttime oxidation conditions by the nitrate radical (e.g., Finewax et al., 2018, 2019). Further, the FIREX-Lab experiments (many of which were the focus of chapter 3 of this thesis) included “nighttime” nitrate-radical experiments that generally had greater SOA production than the “daytime” experiments; but given the very different chemistry of these “night-time” experiments, I did not include them in my work. Hence, future work should consider the overall effect of daytime and nighttime aging on biomass burning OA in the atmosphere.

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Appendix A

Supplementary information for Chapter 2

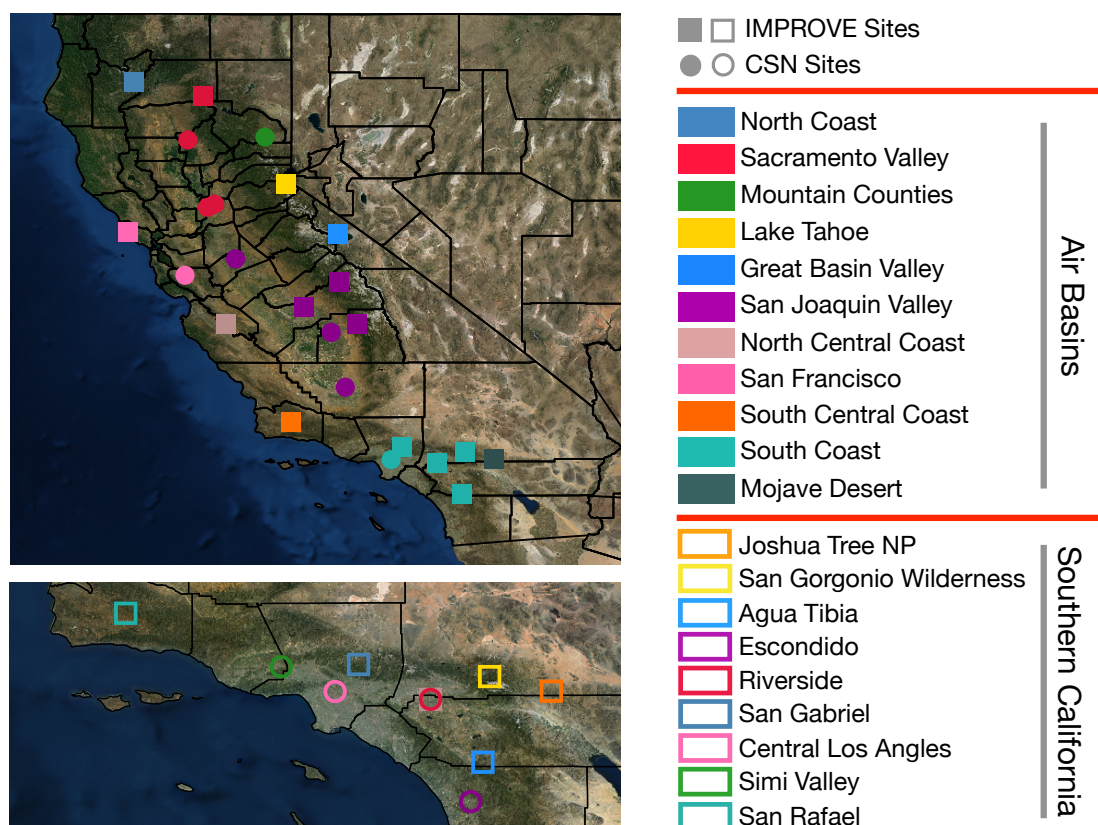


Figure A.1: Model domains showing the 24 km grid (top) used for the state of California simulations and the 8 km nested 18 grid (bottom) used for the southern California simulations. Symbols show the Chemical Speciation Network (CSN) and 19 Interagency Monitoring of Protected Visual Environments (IMPROVE) network sites in both domains.

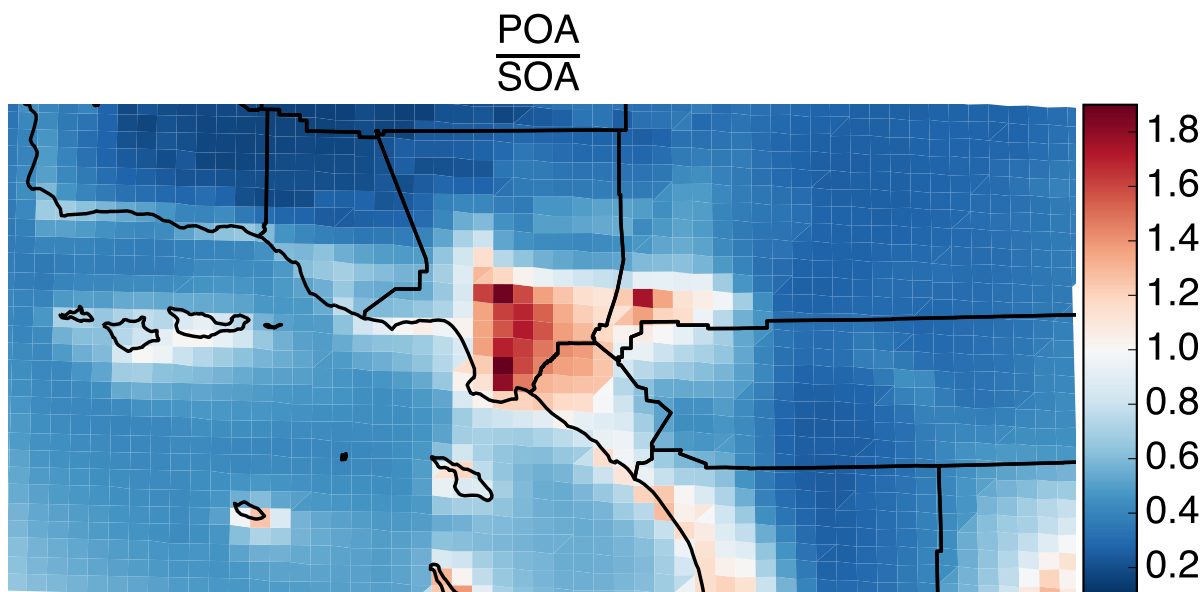


Figure A.2: Ratio of the 14-day averaged POA mass concentration to SOA_{eff} mass concentration in the Base simulation.

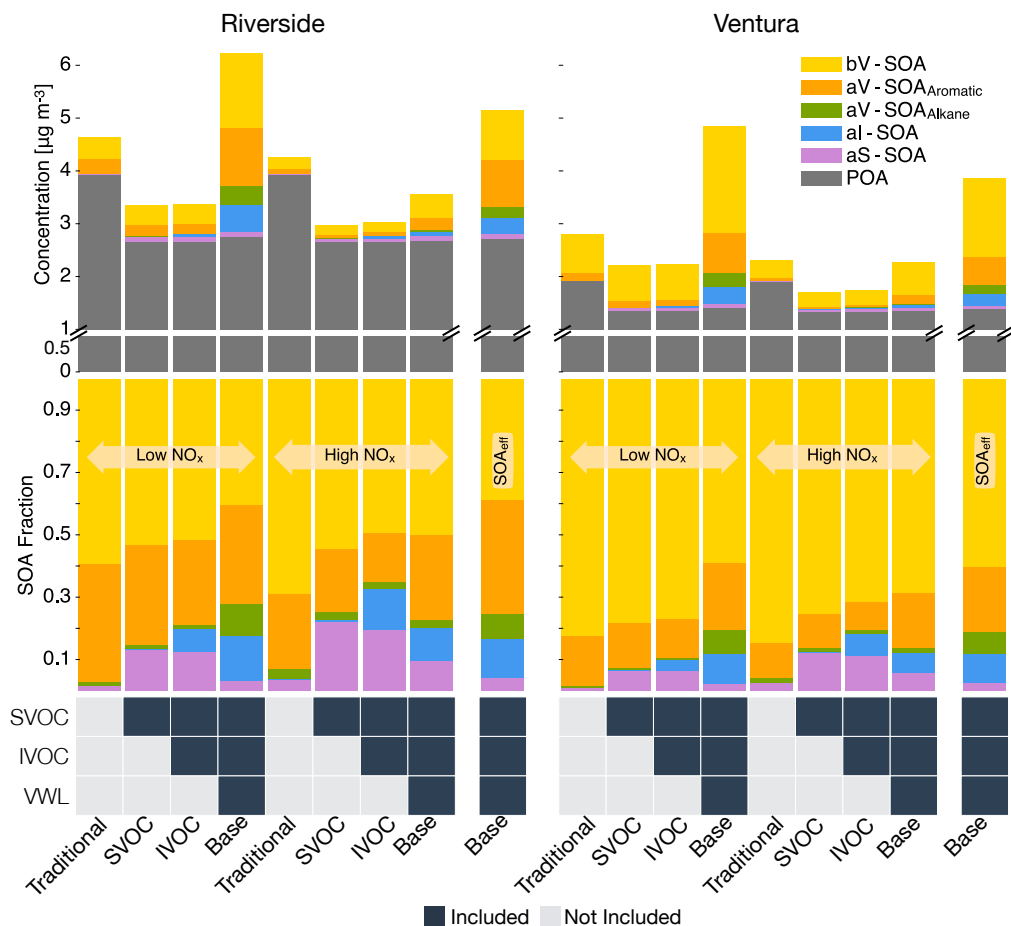


Figure A.3: 14-day averaged model predictions of POA and SOA mass concentrations and precursor contributions at the (a) Riverside and (b) Simi Valley site from the sensitivity simulations that examine the influence of updates made in this work. Panel (a) shows absolute concentrations and panel (b) shows precursor contributions. The legend at the bottom tracks how the different pathways (i.e., SOA formation from SVOCs, SOA formation from IVOCs, and correction for chamber vapor wall losses (VWL)) were turned on for the different simulations. Model predictions from the low and high NO_x simulations are shown separately. Model predictions to the extreme right are from accounting for the influence of NO_x using equation 2 in the main text (logarithmic dependence on $\text{VOC}:\text{NO}_x$).

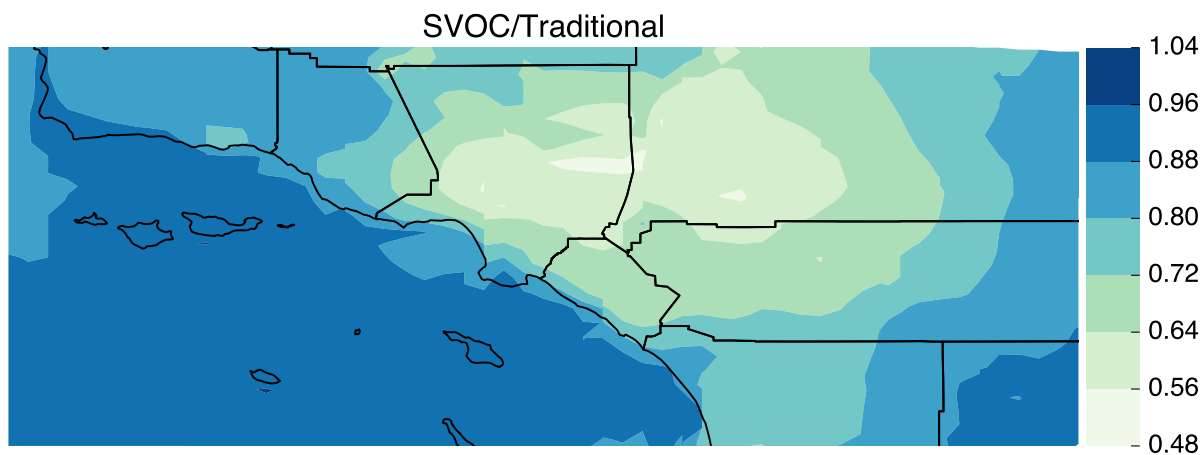


Figure A.4: Ratio of the 14-day averaged POA mass concentration from the SVOC simulation to that from the Traditional simulation.

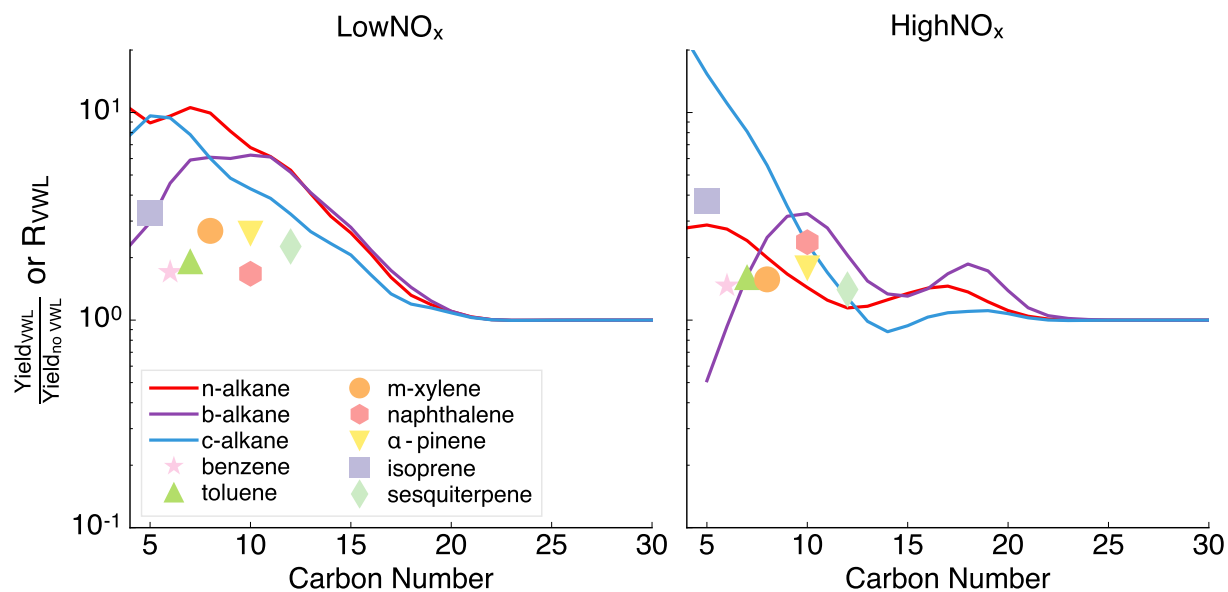


Figure A.5: Vapor wall loss-related enhancements in SOA mass yield calculated using a box model version of the SOM for different precursor species at an organic aerosol mass concentration of $9 \mu\text{g m}^{-3}$.

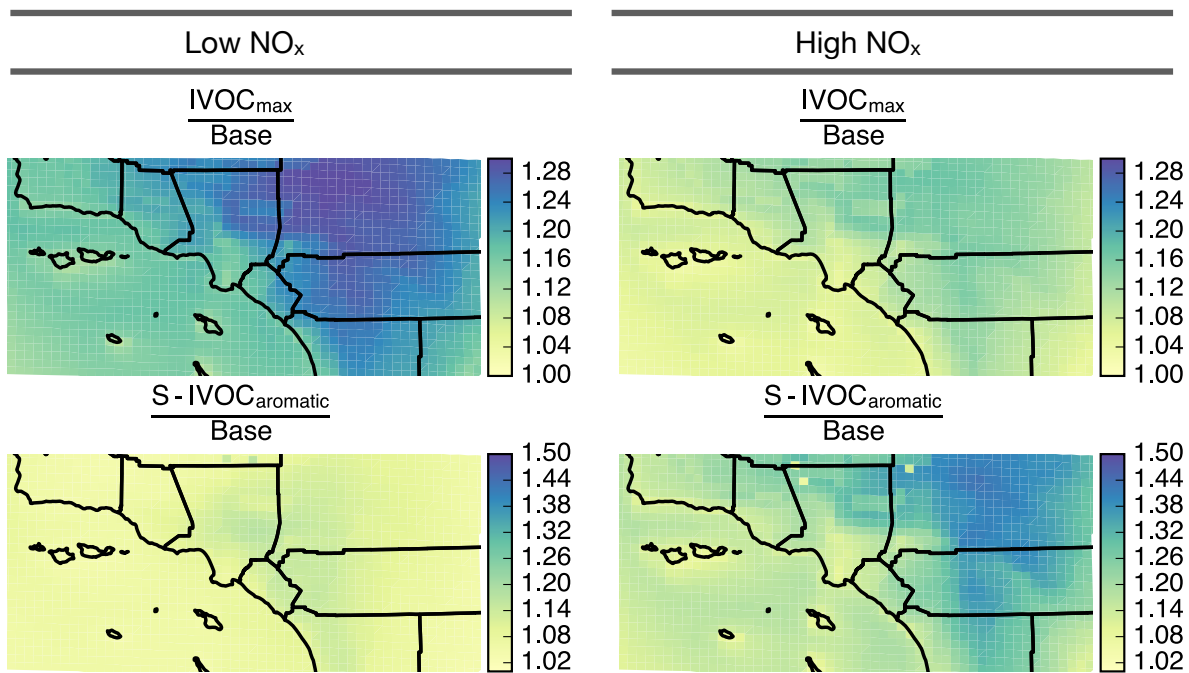


Figure A.6: Ratio of the 14-day averaged OA mass concentration from the (a) IVOC_{max} and (b) IVOC_{aromatic} simulation to that from the Base simulation.

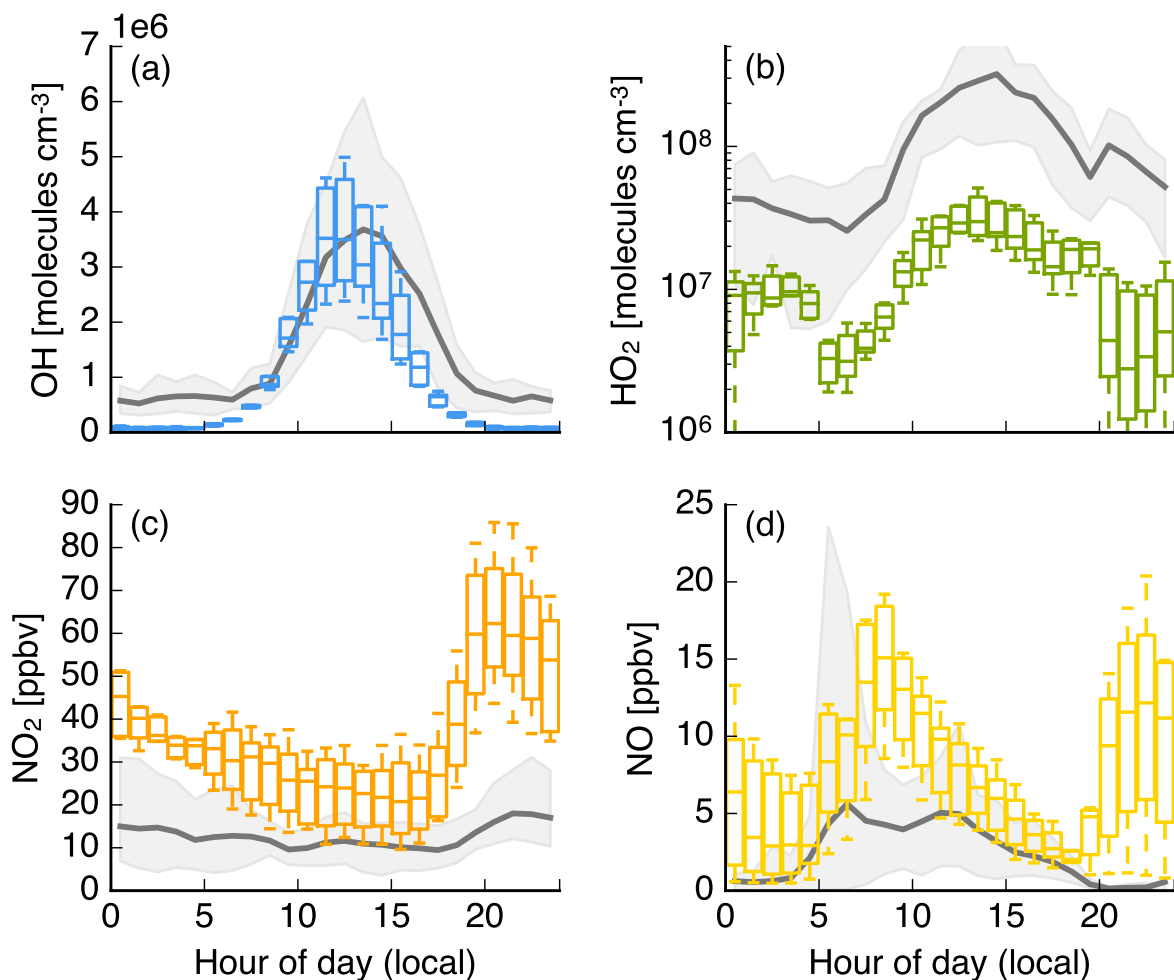


Figure A.7: Modeled (2005) and measured (2010) diurnal profiles of (a) OH, (b) HO₂ (model), HO₂^{*} (measurements) (c) NO₂ and (d) NO concentrations over Pasadena. Model predictions are shown as box plots while measurements are show as bands (10-90th percentiles) and a solid black line (median).

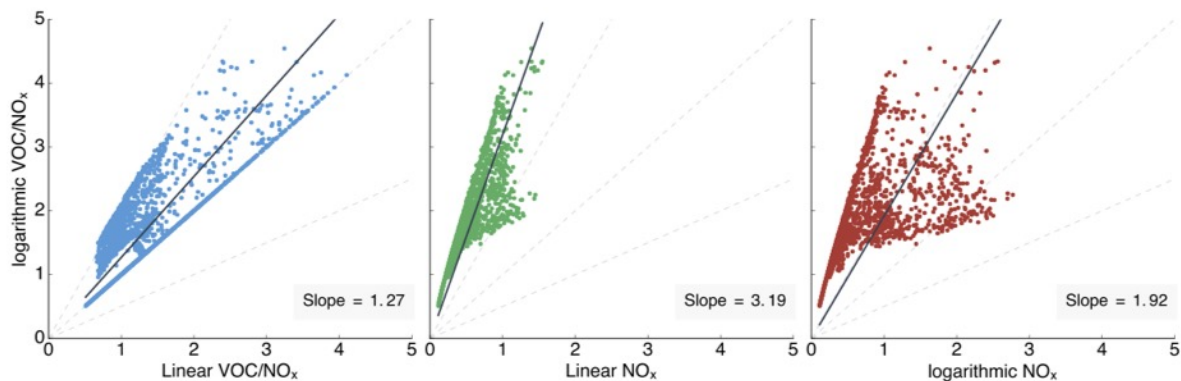


Figure A.8: Scatter plots comparing model predictions of SOA_{eff} using equation 2 (logarithmic dependence on the $VOC:NO_x$ ratio) to those predicted using (a) equation 1 (linear dependence on the $VOC:NO_x$ ratio), (b) equation 3 (linear dependence on the NO_x concentration), and (c) equation 4 (logarithmic dependence on the NO_x concentration).

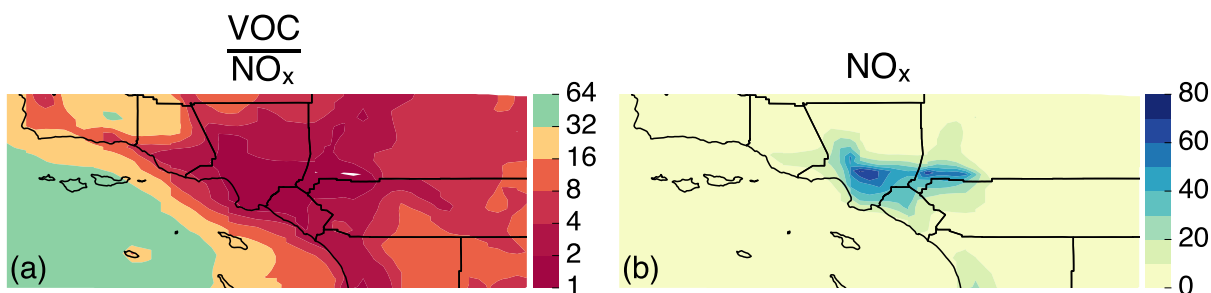


Figure A.9: 14-day averaged (a) $VOC:NO_x$ ratios ($ppbv\ ppbv^{-1}$) and (b) NO_x concentrations ($ppbv$) in southern California.

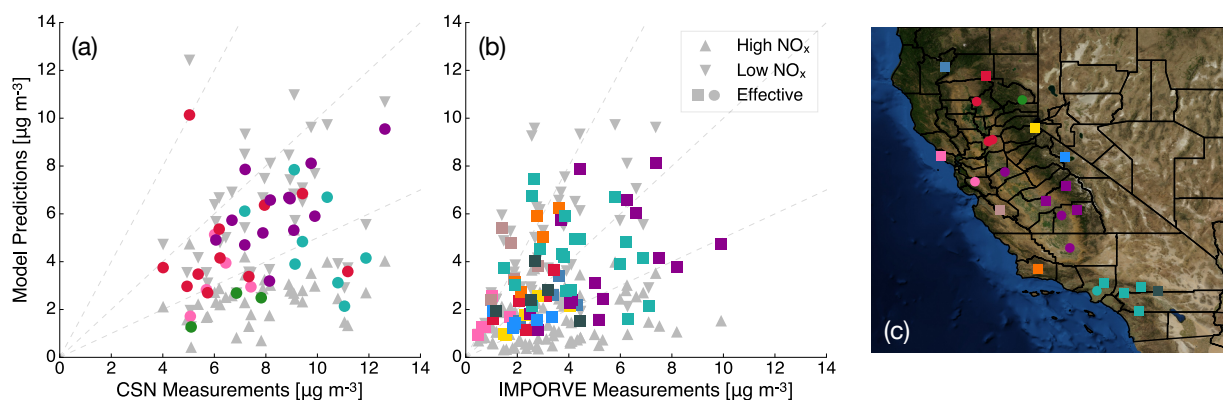


Figure A.10: Model-measurement comparison for daily-averaged OA mass concentrations at (a) CSN and (b) IMPROVE sites across California. Panel (c) shows the color-coded geographic locations where the comparisons were made.

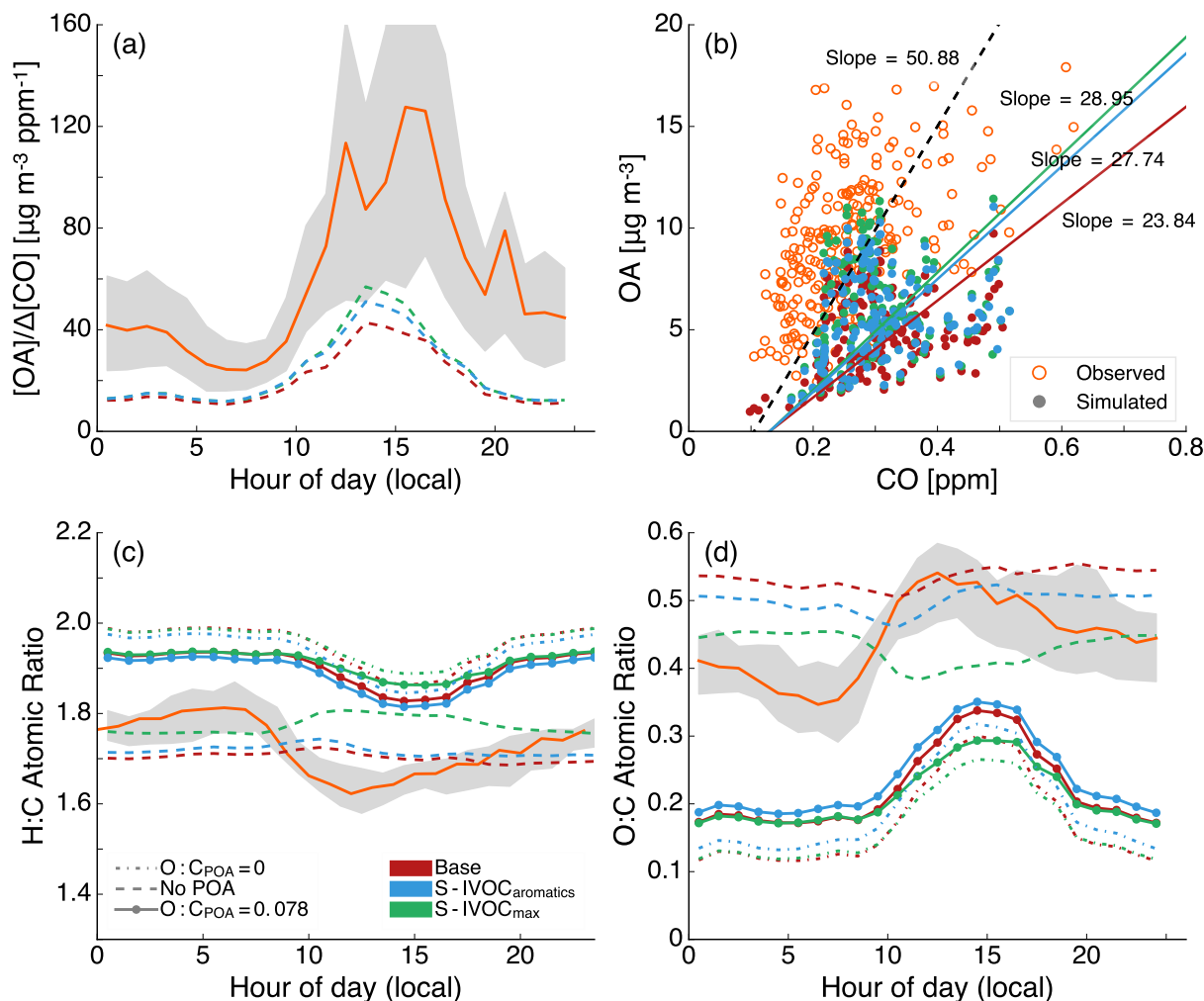


Figure A.11: (a) Diurnal profile of the modeled and measured OA/ΔCO ratios at Riverside, CA. The box plots capture the 10th-25th-50th-75th-90th in model predictions over the simulated episode while the gray bands and solid orange line represent the 10th and 90th percentile and median of the measured data. (b) Modeled and measured OA mass concentrations plotted against CO concentrations between 10 am and 8 pm local time. The solid and dashed black lines represent lines fitted to the modeled and measured data by forcing the X-intercept to be the corresponding modeled and measured background CO concentration. Diurnal profiles of the modeled and measured (c) H:C and (d) O:C ratios of the OA. The three different predictions show results from the Base simulations for OA assuming no change, the POA O:C was fixed to 0.078, and no POA. Model predictions are from three different simulations: Base, IVOC_{max}, and S-IVOC_{aromatic}.

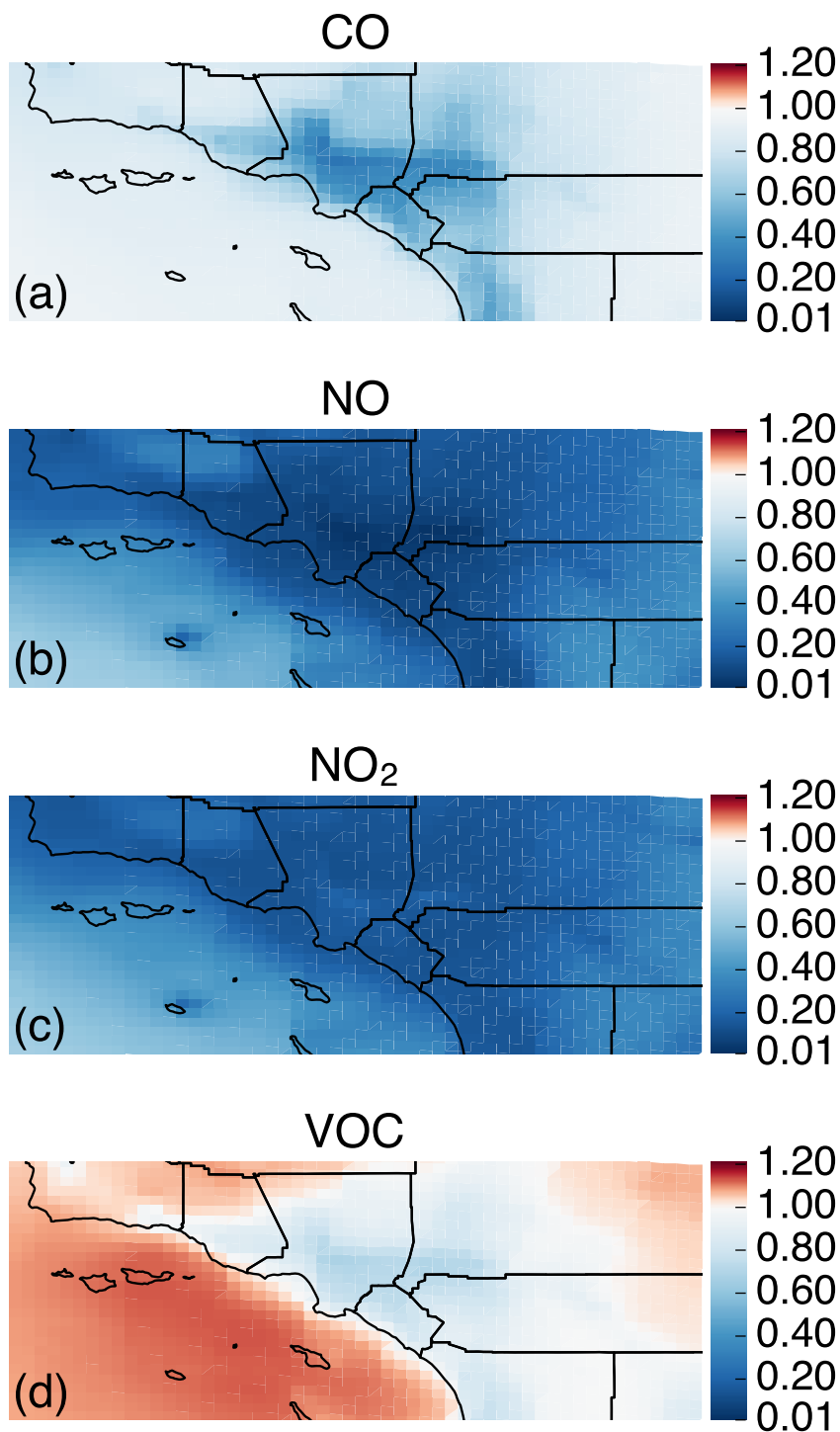


Figure A.12: Ratios of 14-day averaged model predictions of (a) CO, (b) NO, (c) NO₂, and (d) VOC from 2035 to those from 2005. The 2035 simulations were performed with 2005 meteorological inputs but scaling the anthropogenic emissions for CO, NO_x, VOC, PM_{2.5}, SO₂, and NH₃ based on changes projected by the California Emission Projections and Analysis Model (CARB, 2018).

Table A.1: Hydrocarbon distribution used to distribute POA emissions.

Carbon No.	C* ($\mu\text{g m}^{-3}$)	ξ (fraction)		
		Gasolines	Diesel	Biomass Burning / Food Cooking
10	5.95e+06	0.0000	0.0031	0.0000
11	2.01e+06	0.0000	0.0001	0.0166
12	6.78e+05	0.0000	0.0000	0.0386
13	2.29e+05	0.0000	0.0001	0.0391
14	7.72e+04	0.0000	0.0000	0.0405
15	2.60e+04	0.1000	0.0000	0.0443
16	8.79e+03	0.0339	0.0001	0.0534
17	2.96e+03	0.0234	0.0583	0.0678
18	1.00e+03	0.0123	0.0427	0.0717
19	3.38e+02	0.0212	0.0548	0.0668
20	1.14e+02	0.0611	0.0943	0.0966
21	3.80e+01	0.1079	0.1462	0.0947
22	1.30e+01	0.1277	0.1809	0.0329
23	4.38e+00	0.1105	0.1775	0.0299
24	1.48e+00	0.0762	0.1368	0.0870
25	4.98e-01	0.0553	0.0775	0.0159
26	1.68e-01	0.0606	0.0262	0.0000
27	5.67e-02	0.0751	0.0004	0.0000
28	1.91e-02	0.0706	0.0003	0.0873
29	6.46e-03	0.0438	0.0001	0.1167
30	2.18e-03	0.0174	0.0001	0.0000

Appendix B

Supplementary information for Chapter 3

Scaling Factor Calculation

For a few select experiments (Fire001, Fire002, Fire003, Fire004, Fire007, and Fire011), we calculated a scaling factor to correct the raw OA mass concentrations measured by the HR-AMS. Only a few experiments were selected because these were the only experiments where data from the scanning mobility particle sizer (SMPS) was found to be sufficient and not influenced by a second number mode at larger sizes (that prevented complete characterization of the volume concentration and also affected corrections for multiple charges) and synchronization issues between the SMPS and the thermodenuder. The scaling factor is expected to account for losses in the aerodynamic lens, collection efficiency, changes in the relative ionization efficiency, and other potential artifacts associated with the HR-AMS (Middlebrook et al., 2012). A mass-based scaling factor was calculated as a ratio of the total non-refractory aerosol mass concentration measured by the HR-AMS (organic+inorganic aerosol) to that estimated from subtracting the black carbon (BC) measured by the single particle soot photometer (SP2) from the mass concentration estimated from the SMPS data. Total aerosol mass concentrations were estimated from the SMPS data by multiplying the volume concentrations by a density of 1.42 g cm^{-3} based on the work of Tkacik et al. (2017) Figure B.1 shows that the scaling factor for these select experiments varied inversely with the oxidation state of the OA. This is consistent with the finding of Lim et al. (2019) who found the scaling factor to be a function of the OA volatility where the scaling factor was lower for less volatile OA and vice versa. The scaling factor versus oxidation state trends were fit and the fit was used to correct the OA mass concentrations in all experiments.

Table B.1: Fuel, oxidant, and variables of interest (see column headings) for the eleven chamber experiments performed during FIREX. Note that the table is split into three sections for visual clarity, keeping the first two columns the same.

Fire ID	Fuel	Oxidant and precursor	Dark period (hr)	Lights on (hr)	OH exposure (molecules-h cm ⁻³)	Initial surface area (μm ² cm ⁻³)
3	Ponderosa Pine	OH/HONO	0.13	0.85	3.85×10^6	19
4	Ponderosa Pine	OH/H ₂ O ₂	0.34	5.78	7.01×10^6	859
7	Lodgepole Pine	OH/HONO	0.98	4.28	1.40×10^7	735
16	Ponderosa Pine - litter	UV	0.08	4.13	1.51×10^6	345
22	Douglas-fir - litter	UV	2.13	2.82	2.27×10^5	269
28	Chaparral (manzanita)	OH/H ₂ O ₂	0.03	5.47	7.20×10^6	306
37	Ponderosa Pine	OH/HONO	0.32	3.25	1.22×10^7	413
42	Lodgepole Pine	OH/HONO	0.10	4.18	6.38×10^6	287
54	Engelmann spruce	OH/H ₂ O ₂	0.18	2.35	4.14×10^6	117
63	Lodgepole Pine	OH/HONO	0.47	2.3	6.28×10^6	182
67	Subalpine fir	O ₃	2.18	2.57	3.75×10^5	149

Table B.2: Table B1 continued

Fire ID	Fuel	Initial OA ($\mu\text{g m}^{-3}$)	Final OA ($\mu\text{g m}^{-3}$)	OA Mass Enh. Ratio	Initial O:C Ratio	Final O:C Ratio	O:C Enh. Ratio	Final SOA Mass ($\mu\text{g m}^{-3}$)	Final SOA O:C Ratio
3	Ponderosa Pine	34.4	42.9	1.18	0.22	0.26	1.14	8.5	0.403
4	Ponderosa Pine	34.2	79.8	2.17	0.22	0.43	1.92	5.6	0.648
7	Lodgepole Pine	35.1	74.4	1.82	0.24	0.38	1.60	39.3	0.548
16	Ponderosa Pine - litter	20.4	30.1	1.30	0.19	0.27	1.41	9.7	0.476
22	Douglas-fir - litter	24.5	26.2	1.05	0.31	0.31	0.99	1.7	0.251
28	Chaparral (manzanita)	20.5	26.8	1.37	0.18	0.26	1.46	6.3	0.663
37	Ponderosa Pine	60.3	102.2	1.54	0.24	0.35	1.45	42.0	0.558
42	Lodgepole Pine	27.3	42.2	1.41	0.25	0.32	1.30	14.9	0.498
54	Engelmann spruce	10.0	12.3	1.22	0.26	0.33	1.26	2.3	0.948
63	Lodgepole Pine	17.2	25.0	1.34	0.26	0.34	1.29	7.8	0.566
67	Subalpine fir	15.0	15.4	1.28	0.35	0.36	1.07	0.4	0.850

Table B.3: Table B1 continued

Fire ID	Fuel	Initial NO (ppbv)	Initial NO ₂ (ppbv)	Initial O ₃ (ppbv)	Initial NMVOC ($\mu\text{g m}^{-3}$)	Initial NMVOC (ppbv)	Initial SOA Precursors ($\mu\text{g m}^{-3}$)	Initial SOA Precursors (ppbv)
3	Ponderosa Pine	2453.7	BDL	6.5	418.1	183.1	166.3	42.6
4	Ponderosa Pine	28.7	BDL	11.1	491.1	215.1	195.3	50.1
7	Lodgepole Pine	40.3	BDL	5.7	420.0	184.7	160.0	41.1
16	Ponderosa Pine - litter	15.1	37.6	6.8	330.8	143.9	124.6	32.2
22	Douglas-fir - litter	25.1	0.05	504.9	30.4	14.4	10.1	2.6
28	Chaparral (manzanita)	21.7	20.2	3.2	168.8	78.0	60.0	15.9
37	Ponderosa Pine	318.6	166.7	3.4	191.5	82.4	79.9	20.4
42	Lodgepole Pine	346.1	204.5	3.5	143.9	66.2	52.2	13.6
54	Engelmann spruce	2.1	8.4	2.6	94.6	39.8	36.1	9.2
63	Lodgepole Pine	294.1	249.7	4.0	222.3	102.4	80.6	21.1
67	Subalpine fir	0.04	8.8	436.7	217.5	96.0	84.4	21.4

Table B.4: Emissions ratios of SOA precursors with acetonitrile (g g^{-1}) used to calculate SOA precursor concentrations in the 11 chamber experiments

Emissions Profile	Based on	Biogenics	Oxygenated Aromatics	Heterocyclics	Reduced Aromatics	Alkanes + Partially Speciated
Fire003 - this study	Average of Fire 001, 002, 037, 059, 072	12.5	19.3	30.1	15.9	15.2
Fire003 - Sekimoto et al.		9.0	20.9	36.4	19.0	1.5
Fire003 - Koss et al.	All Fires	8.3	15.5	24.8	11.9	15.0
Fire004 - this study	Average of Fire 001, 002, 037, 059, 072	12.8	19.3	30.1	15.9	15.2
Fire004 - Sekimoto et al.		9.2	20.9	36.4	19.0	1.5
Fire004 - Koss et al.	All Fires	8.4	15.5	24.8	11.9	15.0
Fire007 - this study	Fire 007	8.1	22.7	30.7	18.0	19.7
Fire007 - Sekimoto et al.		7.7	25.2	41.6	17.8	2.0
Fire007 - Koss et al.	All Fires	8.3	15.5	24.8	11.9	19.3
Fire016 - this study	Fire 038	3.9	18.0	37.6	9.8	16.8
Fire016 - Sekimoto et al.		7.4	28.0	44.9	17.0	2.2
Fire016 - Koss et al.	All Fires	8.8	15.5	24.8	11.9	15.5

Continuation of Tbl. B.4

Emissions Profile	Based on	Biogenics	Oxygenated Aromatics	Heterocyclics	Reduced Aromatics	Alkanes + Partially Speciated
Fire022 - this study	Average of Fire	0.7	19.4	26.6	15.7	13.4
Fire022 - Sekimoto et al.	014, 018, 031, 043, 057, 064	0.9	23.8	39.9	18.2	1.8
Fire022 - Koss et al.	All Fires	0.6	15.5	24.8	11.9	3.2
Fire028 - this study	Fire	4.1	23.5	38.8	23.8	18.1
Fire028 - Sekimoto et al.	028	8.7	24.8	41.1	17.9	1.9
Fire028 - Koss et al.	All Fires	9.0	15.5	24.8	11.9	18.2
Fire037 - this study	Fire	14.6	24.4	36.0	19.9	15.6
Fire037 - Sekimoto et al.	037	9.6	20.4	35.9	19.1	1.5
Fire037 - Koss et al.	All Fires	8.6	15.5	24.8	11.9	15.2
Fire042 - this study	Average of Fires	9.3	16.6	25.8	16.6	15.1
Fire042 - Sekimoto et al.	006, 007, 058, 063	9.5	21.7	37.4	18.8	1.6
Fire042 - Koss et al.	All Fires	8.8	15.5	24.8	11.9	15.1
Fire054 - this study	Fire	2.0	12.5	17.0	6.6	11.4
Fire054 - Sekimoto et al.	008	8.6	24.1	40.3	18.1	1.8
Fire054 - Koss et al.	All Fires	8.8	15.5	24.8	11.9	11.4

Continuation of Tbl. B.4

Emissions Profile	Based on	Biogenics	Oxygenated Aromatics	Heterocyclics	Reduced Aromatics	Alkanes + Partially Speciated
Fire063 - this study	Fire	8.6	16.8	28.1	16.7	15.9
Fire063 - this study	Fire	8.6	16.8	28.1	16.7	15.9
Fire063 - Sekimoto et al.	063	8.9	22.3	38.2	18.6	1.7
Fire063 - Koss et al.	All Fires	8.5	15.5	24.8	11.9	15.8
Fire067 - this study	Fire	1.2	27.4	39.1	25.7	24.7
Fire067 - Sekimoto et al.	067	0.9	27.1	43.9	17.2	2.2
Fire067 - Koss et al.	All Fires	0.7	15.5	24.8	11.9	24.3

Table B.5: VOC species measured by the PTR-ToF-MS (Koss et al.10) and considered as SOA precursors in our model.

Species name	Species formula	k_{OH} ($s^{-1} cm^3$ molecules $^{-1}$)	Cstar ($\mu g m^{-3}$)	MW ($g mol^{-1}$)	Surrogate
Pyrrole	C ₄ H ₅ N	1.45×10^{-10}	5.74×10^7	67.0892	Heterocyclics
Furan	C ₄ H ₄ O	4.00×10^{-11}	2.23×10^9	68.07356	Heterocyclics
Isoprene	C ₅ H ₈	1.00×10^{-10}	2.05×10^9	68.11702	Biogenics
Dihydropyrrole	C ₄ H ₇ N	1.04×10^{-10}	5.15×10^7	69.10508	Heterocyclics
Tetrahydropyrrole	C ₄ H ₉ N	7.85×10^{-11}	2.44×10^8	71.12096	Heterocyclics
Benzene	C ₆ H ₆	1.22×10^{-12}	4.05×10^8	78.11184	Aromatics
Pyridine	C ₅ H ₅ N	3.70×10^{-13}	5.28×10^7	79.0999	Heterocyclics
Methylpyrrole	C ₅ H ₇ N	1.10×10^{-10}	5.69×10^7	81.11578	Heterocyclics
MethylFuran	C ₅ H ₆ O	7.80×10^{-11}	7.71×10^8	82.10014	Heterocyclics
Thiophene	C ₄ H ₄ S	9.53×10^{-12}	3.64×10^8	84.13956	Heterocyclics
Furanone	C ₄ H ₄ O ₂	5.66×10^{-11}	1.34×10^7	84.07256	Heterocyclics
Ethynylpyrrole	C ₆ H ₅ N	6.45×10^{-11}	3.95×10^6	92.11854	Heterocyclics
Toluene	C ₇ H ₈	5.63×10^{-12}	1.42×10^8	92.13842	Aromatics
2-Furancarbonitrile	C ₅ H ₃ NO	7.15×10^{-12}	1.81×10^5	93.08302	Heterocyclics
MethylPyridine	C ₆ H ₇ N	1.10×10^{-12}	4.36×10^7	93.12648	Heterocyclics
Phenol	C ₆ H ₆ O	2.80×10^{-11}	2.11×10^6	94.11084	Oxygenated Aromatics
4-Pyridinol	C ₅ H ₅ NO	7.65×10^{-11}	1.81×10^5	95.0989	Heterocyclics
C2-pyrroles	C ₆ H ₉ N	2.00×10^{-10}	4.16×10^6	95.14236	Heterocyclics
Furfural	C ₅ H ₄ O ₂	3.56×10^{-11}	1.14×10^7	96.08326	Heterocyclics
Dimethylfuran	C ₆ H ₈ O	2.00×10^{-10}	1.40×10^7	96.12672	Heterocyclics
Methylthiophene	C ₅ H ₆ S	9.51×10^{-12}	1.28×10^8	98.16614	Heterocyclics

2Methanolfuran	C ₅ H ₆ O ₂	1.04×10^{-10}	3.88×10^6	98.09914	Heterocyclics
Dihydrofurandione	C ₄ H ₄ O ₃	8.56×10^{-13}	9.00×10^3	100.0716	Heterocyclics
Phenylacetylene	C ₈ H ₆	8.02×10^{-12}	2.16×10^6	102.1332	Aromatics
Benzonitrile	C ₇ H ₅ N	3.44×10^{-13}	4.62×10^6	103.1213	Aromatics
Styrene	C ₈ H ₈	5.80×10^{-11}	3.43×10^7	104.1491	Aromatics
Vinylpyridine	C ₇ H ₇ N	2.66×10^{-11}	1.55×10^6	105.1372	Heterocyclics
Benzaldehyde	C ₇ H ₆ O	1.20×10^{-11}	7.30×10^6	106.1215	Aromatics
C8_Aromatics	C ₈ H ₁₀	1.32×10^{-11}	4.88×10^7	106.165	Aromatics
PyridineAldehyde	C ₆ H ₅ NO	1.71×10^{-11}	7.85×10^4	107.1096	Heterocyclics
Dimethylpyridine	C ₇ H ₉ N	2.79×10^{-12}	2.05×10^7	107.1531	Heterocyclics
Benzoquinone	C ₆ H ₄ O ₂	4.51×10^{-12}	8.80×10^5	108.094	Aromatics
Cresol	C ₇ H ₈ O	5.30×10^{-11}	1.34×10^7	108.1374	Oxygenated Aromatics
Trimethylpyrrole	C ₇ H ₁₁ N	2.00×10^{-10}	1.20×10^7	109.1689	Heterocyclics
Benzenediol	C ₆ H ₆ O ₂	1.04×10^{-10}	1.10×10^6	110.1098	Oxygenated Aromatics
Trimethylfuran	C ₇ H ₁₀ O	1.59×10^{-10}	9.27×10^7	110.1533	Heterocyclics
Dihydroxypyridine	C ₅ H ₅ NO ₂	4.55×10^{-11}	3.78×10^4	111.0979	Heterocyclics
5-Hydroxy 2-furfural	C ₅ H ₄ O ₃	4.90×10^{-11}	7.36×10^5	112.0823	Heterocyclics
Nitrofuran	C ₄ H ₃ NO ₃	5.06×10^{-12}	1.64×10^4	113.0703	Heterocyclics
5-hydroxymethyl- 2[3H]-furanone	C ₅ H ₆ O ₃	1.00×10^{-10}	2.59E+05	114.0981	Heterocyclics
5-hydroxy tetrahydro 2-furfural	C ₅ H ₈ O ₃	5.00×10^{-12}	7.36×10^5	116.114	Heterocyclics
Indene	C ₉ H ₈	7.80×10^{-11}	1.06×10^7	116.1598	Aromatics
Benzeneacetonitrile	C ₈ H ₇ N	2.07×10^{-12}	5.72×10^5	117.1479	Aromatics

Benzofuran	C ₈ H ₆ O	3.70×10^{-11}	1.13×10^7	118.1322	Aromatics
Methylstyrene	C ₉ H ₁₀	5.40×10^{-11}	1.14×10^7	118.1757	Aromatics
Isoindoline	C ₈ H ₉ N	8.00×10^{-11}	6.08×10^5	119.1638	Heterocyclics
Tolualdehyde	C ₈ H ₈ O	1.60×10^{-11}	2.39×10^6	120.1481	Aromatics
C9_Aromatics	C ₉ H ₁₂	2.20×10^{-11}	1.95×10^7	120.1916	Aromatics
Salicylaldehyde	C ₇ H ₆ O ₂	2.80×10^{-11}	3.72×10^6	122.1205	Aromatics
Dimethylphenol	C ₈ H ₁₀ O	5.05×10^{-11}	5.31×10^6	122.164	Oxygenated Aromatics
Nitrobenzene	C ₆ H ₅ NO ₂	1.40×10^{-13}	1.50×10^6	123.1086	Aromatics
Hydroxy benzoquinone	C ₆ H ₄ O ₃	1.30×10^{-11}	4.11×10^5	124.093	Aromatics
Guaiacol	C ₇ H ₈ O ₂	7.53×10^{-11}	9.16×10^5	124.1364	Oxygenated Aromatics
Hydroxymethylfurfural	C ₆ H ₆ O ₃	1.00×10^{-10}	4.11×10^5	126.1088	Heterocyclics
Dihydroxymethylfuran	C ₆ H ₈ O ₃	1.29×10^{-10}	4.11×10^5	128.1247	Heterocyclics
Naphthalene	C ₁₀ H ₈	2.30×10^{-11}	5.73×10^5	128.1705	Aromatics
dihydronaphthalene	C ₁₀ H ₁₀	6.42×10^{-11}	5.11×10^6	130.1864	Aromatics
Methylindole	C ₉ H ₉ N	2.00×10^{-10}	3.64×10^4	131.1745	Aromatics
Methyl benzofuran	C ₉ H ₈ O	9.75×10^{-11}	3.54×10^6	132.1588	Heterocyclics
Methyl propenyl benzene	C ₁₀ H ₁₂	3.30×10^{-11}	6.76×10^6	132.2023	Aromatics
3-methylacetophenone	C ₉ H ₁₀ O	2.42×10^{-12}	1.60×10^6	134.1747	Aromatics
C10_Aromatics	C ₁₀ H ₁₄	9.50×10^{-12}	1.04×10^7	134.2182	Aromatics
Methylbenzoicacid	C ₈ H ₈ O ₂	1.20×10^{-11}	1.66×10^4	136.1471	Aromatics
Monoterpenes	C ₁₀ H ₁₆	1.63×10^{-10}	2.16×10^7	136.234	Biogenics
Nitrotoluene	C ₇ H ₇ NO ₂	7.72×10^{-13}	5.96×10^5	137.1352	Aromatics
MethylGuaiacol	C ₈ H ₁₀ O ₂	3.98×10^{-11}	5.62×10^5	138.163	Oxygenated Aromatics

Methylnaphthalene	$C_{11}H_{10}$	5.65×10^{-11}	5.20×10^5	142.1971	Aromatics
Product of levoglucosan dehydration (pyrolysis)	$C_6H_8O_4$	5.28×10^{-11}	3.81×10^4	144.1237	Alkanes
Naphthol	$C_{10}H_8O$	2.00×10^{-10}	2.71×10^5	144.1695	Aromatics
Ethylindene	$C_{11}H_{12}$	6.36×10^{-11}	1.67×10^6	144.213	Aromatics
Dimethylbenzofuran	$C_{10}H_{10}O$	1.20×10^{-10}	2.71×10^5	146.1854	Aromatics
					Oxygenated
Methylchavicol	$C_{10}H_{12}O$	5.43×10^{-11}	1.13×10^6	148.2013	Aromatics
C11_aromatics	$C_{11}H_{16}$	5.00×10^{-11}	4.81×10^6	148.2447	Aromatics
					Oxygenated
VinylGuaiacol	$C_9H_{10}O_2$	5.44×10^{-11}	2.28×10^5	150.1737	Aromatics
					Oxygenated
Vanillin	$C_8H_8O_3$	2.73×10^{-11}	7.00×10^5	152.1461	Aromatics
Acenaphthylene	$C_{12}H_8$	7.55×10^{-11}	6.18×10^4	152.1919	Aromatics
Camphor	$C_{10}H_{16}O$	4.30×10^{-12}	1.98×10^6	152.233	Biogenics
					Oxygenated
Syringol	$C_8H_{10}O_3$	9.66×10^{-11}	1.00×10^5	154.162	Aromatics
Cineole	$C_{10}H_{18}O$	2.26×10^{-11}	1.63×10^7	154.2489	Biogenics
1,3-dimethylnaphthalene	$C_{12}H_{12}$	6.94×10^{-11}	8.57×10^4	156.2237	Aromatics
Decanal	$C_{10}H_{20}O$	3.45×10^{-11}	1.27×10^6	156.2648	Alkanes
C12_aromatics	$C_{12}H_{18}$	1.13×10^{-10}	1.17×10^6	162.2713	Aromatics
					Oxygenated
Isoeugenol	$C_{10}H_{12}O_2$	8.84×10^{-11}	1.94×10^5	188.2217	Aromatics
C13_aromatics	$C_{13}H_{20}$	1.13×10^{-10}	7.17×10^5	176.2979	Aromatics
Sesquiterpenes	$C_{15}H_{24}$	3.00×10^{-10}	4.58×10^4	204.3511	Biogenics
5-Methyl furfural	$C_6H_6O_2$	5.18×10^{-11}	1.10×10^6	110.1098	Heterocyclics

Table B.6: SOM grids, surrogates, and parameters used in this work.

Precursor Class	VOC Surrogate	ΔLVP	m_{frag}	p_{10}	p_{20}	p_{30}	p_{40}	Reference
Long alkanes	<i>n</i> -dodecane	1.4629	0.2627	0.9657	0.0010	0.0020	0.0314	Loza et al. (2014)
Benzene	benzene	1.5495	0.7895	0.0743	0.0213	0.8963	0.0081	Ng et al. (2007)
Toluene	toluene	1.4169	1.3064	0.5634	0.3413	0.0016	0.0937	Zhang et al.(2014)
C8+ single-ring aromatics	<i>m</i> -xylene	1.4601	0.0736	0.1418	0.2971	0.4571	0.1040	Ng et al. (2007)
Polycyclic aromatic hydrocarbons (PAH)	naphthalene	1.4922	0.7673	0.8138	0.0072	0.0635	0.1155	Zhang et al. (2014)
Isoprene	isoprene	1.8742	0.5207	0.9924	0.0003	0.0065	0.0009	Chhabra et al. (2011)
Terpene	α -pinene	1.9139	0.1312	0.5991	0.2923	0.1079	0.0007	Chhabra et al. (2011)
Oxygenated aromatics	phenol, guaiacol	2.023	0.315	0.109	0.048	0.439	0.404	Yee et al. (2013)
Oxygenated aromatics	syringol	1.629	0.148	0.394	0.121	0.071	0.414	Yee et al. (2013)
Heterocyclic compounds	2-methylfuran, dimethylfuran	1.459	0.449	0.0005	0.0014	0.998	0.0001	He et al. (2020)

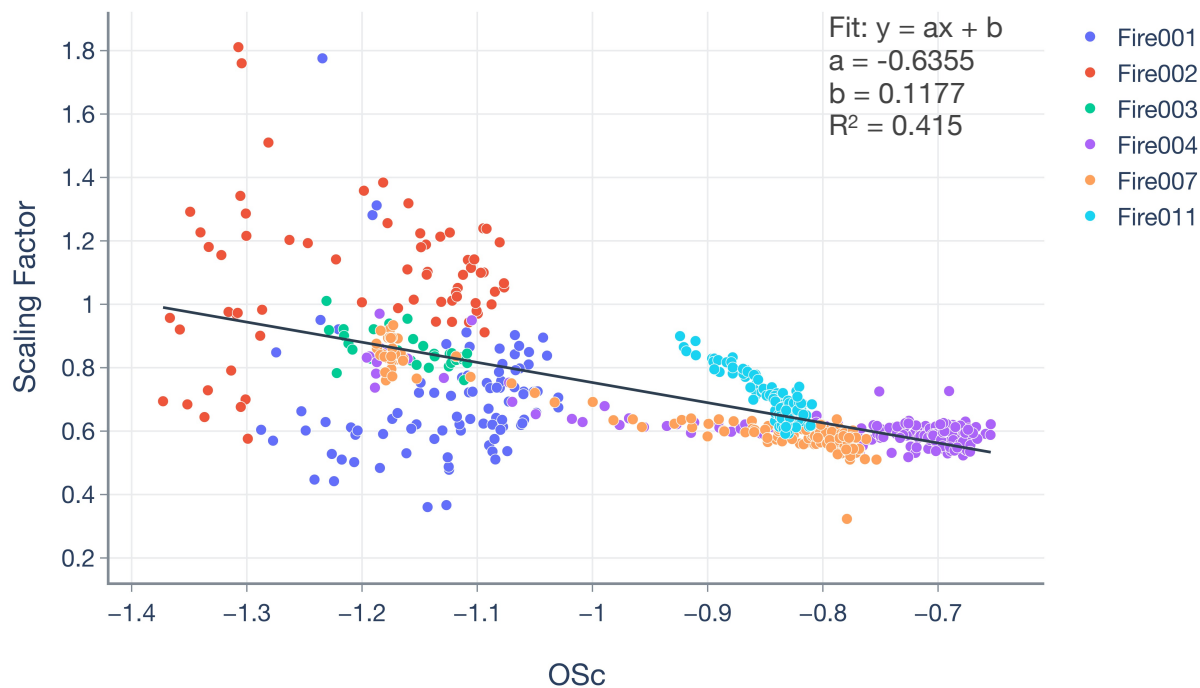


Figure B.1: Scaling factor (SF) as a function of the oxidation state (OSc) for six different experiments. The OSc was approximated as $2 \times \text{O:C-H:C}^{ref11}$. The relatively larger variability in SF for Fire001 and Fire002 can be attributed to low initial OA mass concentrations in those experiments ($<4 \mu\text{g m}^{-3}$) compared to the rest ($>20 \mu\text{g m}^{-3}$). Gas-phase data were unavailable for Fire001 and Fire002 and hence were not modeled in this study. Fire011 was a nitrate (NO_3) radical experiment performed in the dark and the oxidation results from that experiment will be discussed in a companion paper.

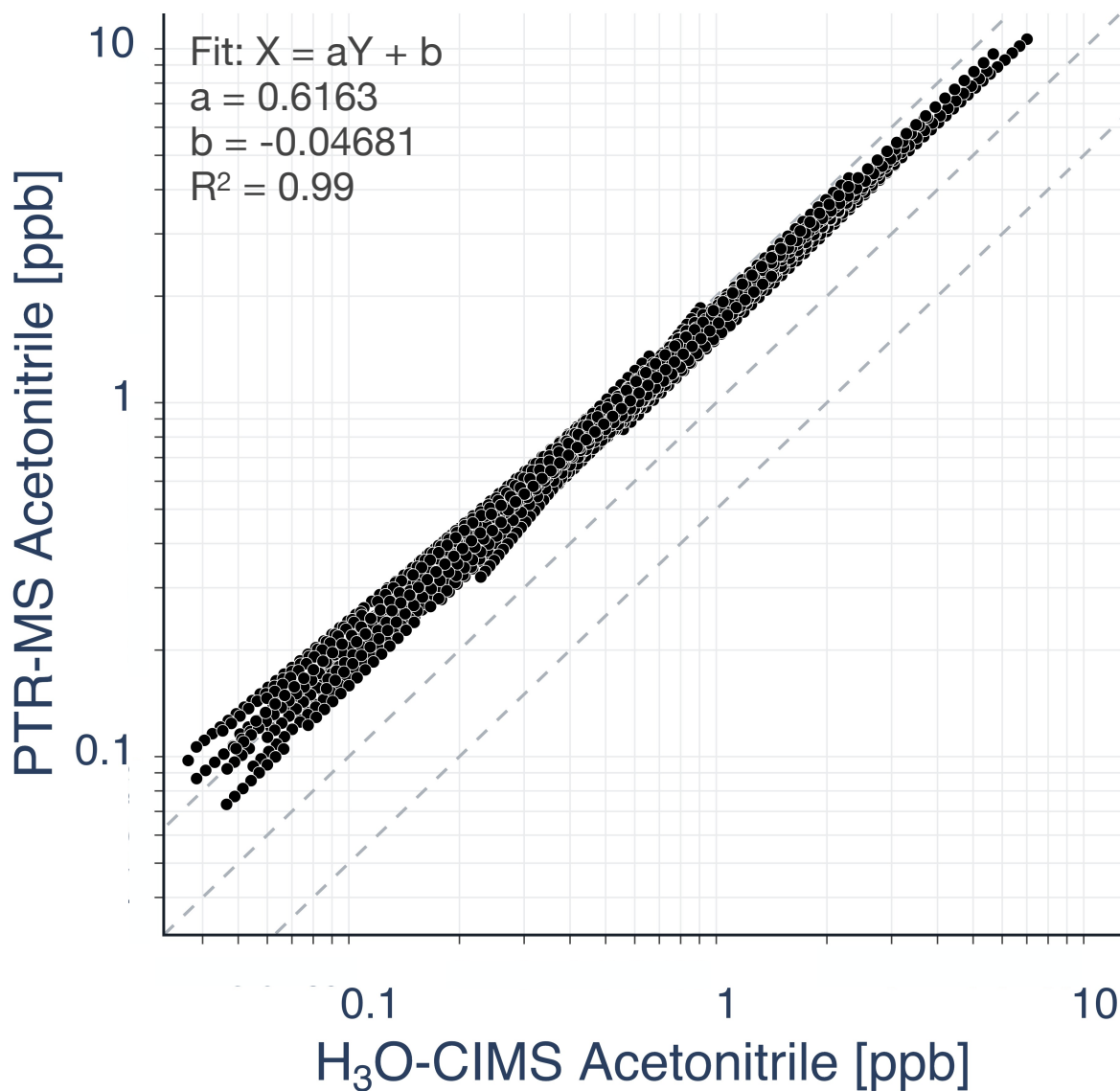


Figure B.2: Scatter plot comparing the acetonitrile concentration measured by the PTR-MS and PTR-ToF-MS in the MIT/UCD mini-chamber over 30 experiments (Tkacik et al., 2017). The slope was used to correct the acetonitrile concentrations in the CSU chamber before being used to determine the initial concentrations of SOA precursors.

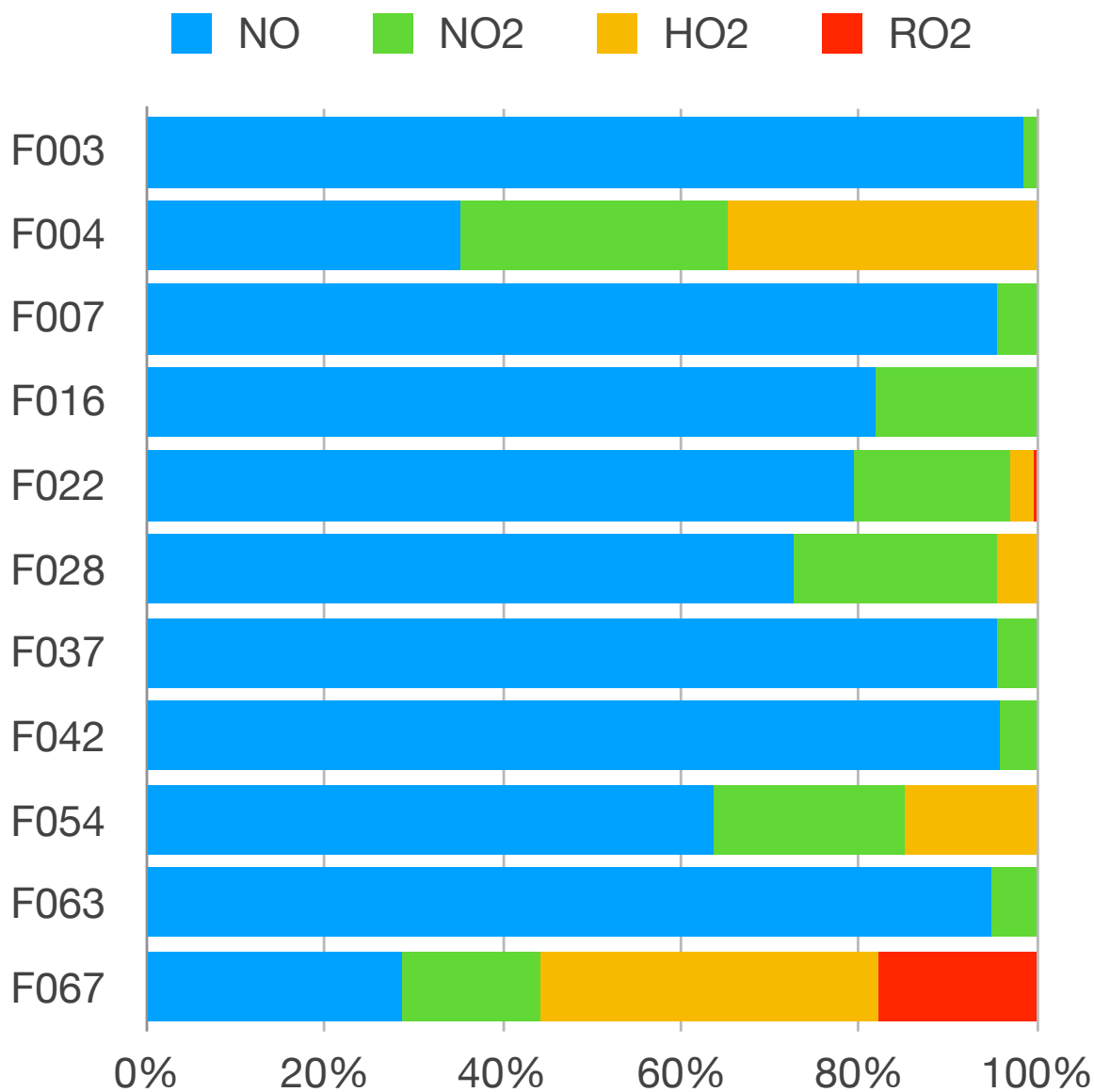


Figure B.3: Averaged fate of the RO₂ radical with reaction with NO, NO₂, HO₂, and RO₂, based on predictions from the Master Chemical Mechanism (MCM) over the entire duration of the chamber experiment (Coggon et al, 2019). Here, we only calculated the fate of RO₂ radicals with a carbon number larger than or equal to 4.

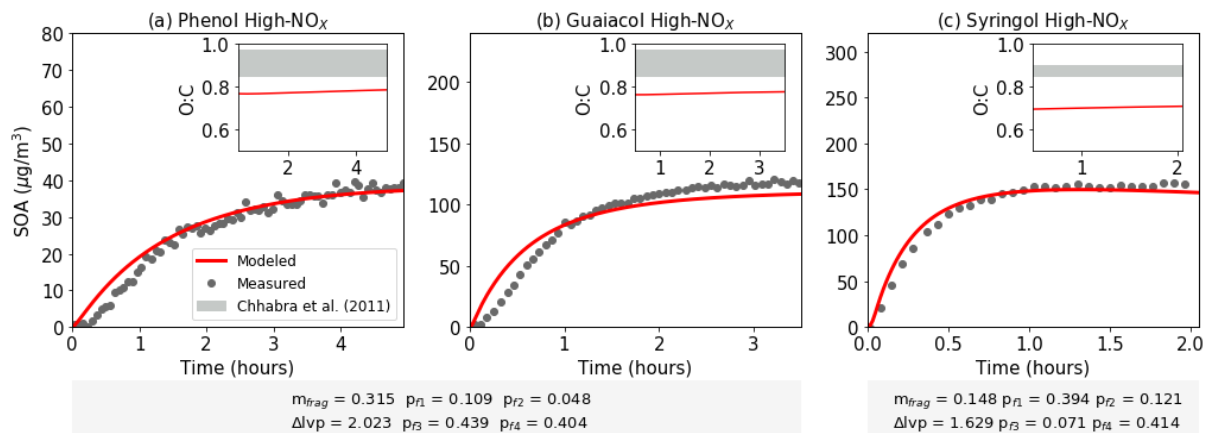


Figure B.4: Model predictions of SOA mass concentrations and O:C ratios for (a) phenol, (b) guaiacol, and (c) syringol compared against measurements from Yee et al. (2013) and Chhabra et al. (2011)

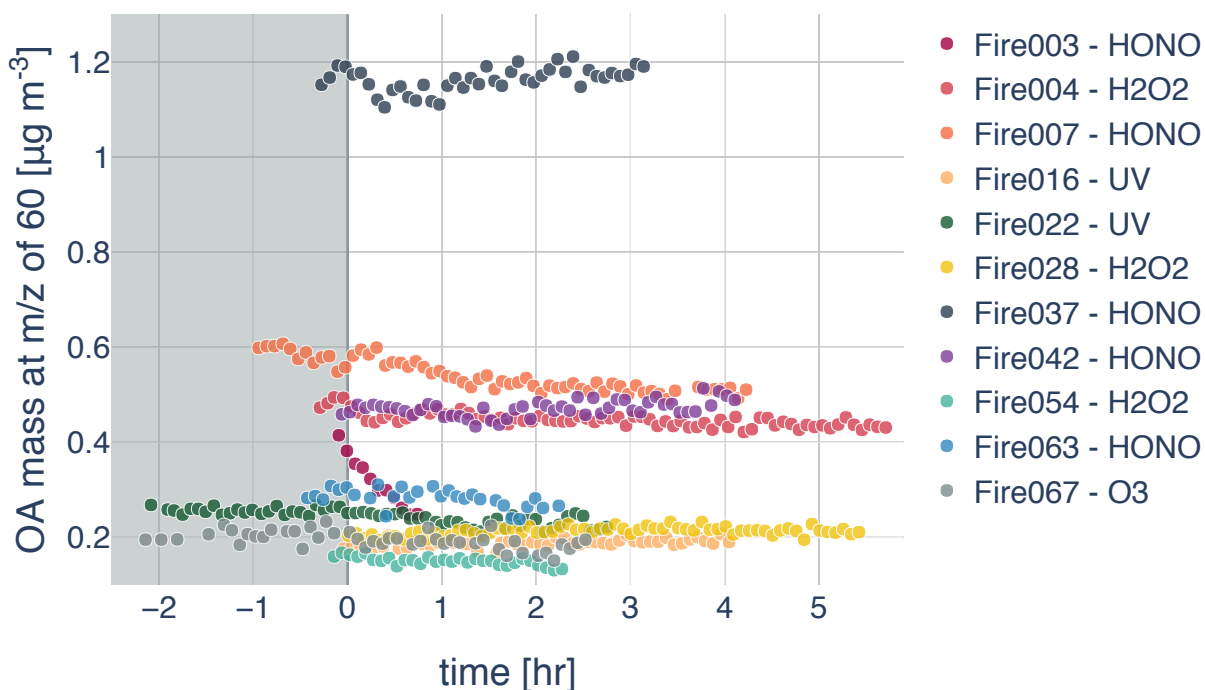


Figure B.5: Particle-wall-loss-corrected OA mass concentrations measured by the HR-AMS at a mass-to-charge ratio of 60.02113 for all eleven chamber experiments. Except for Fire003, the mass was found to be relatively constant during the lights-on period of the experiment, which we concluded as little indication of oxidation of POA

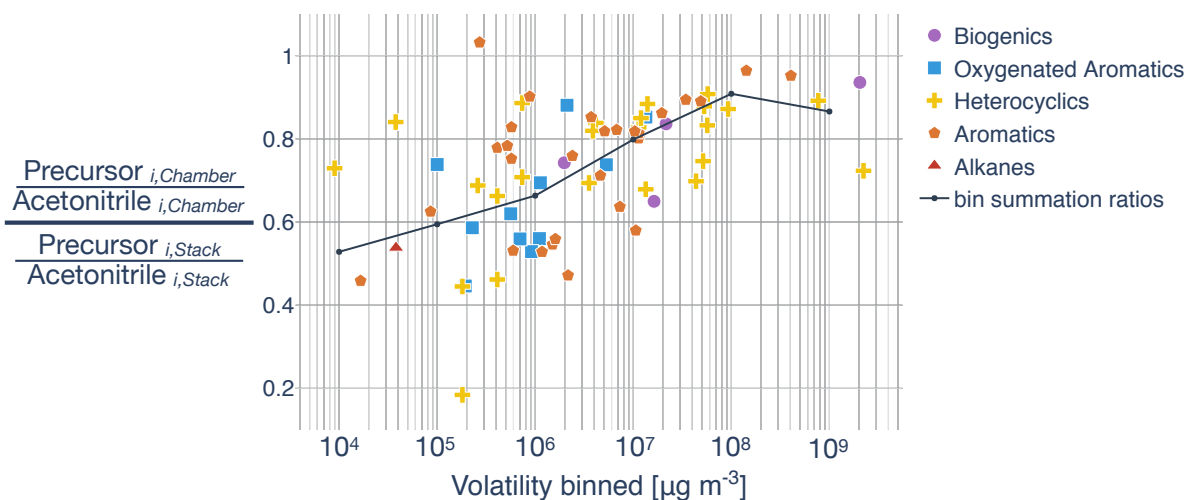


Figure B.6: Emissions ratios of individual SOA precursors to acetonitrile ratioed between those measured in the chamber to those measured in the stack for Fire007. The data are resolved by SOA precursor class. A ratio of 1 indicates no loss in the transfer duct and a ratio of 0 indicates a complete loss in the transfer duct. The time series of these species in the chamber were relatively flat during the dark period indicating that the losses were from those in the transfer duct and not to the walls of the chamber. The solid black line represents the chamber-to-stack ratio if the species were binned by volatility.

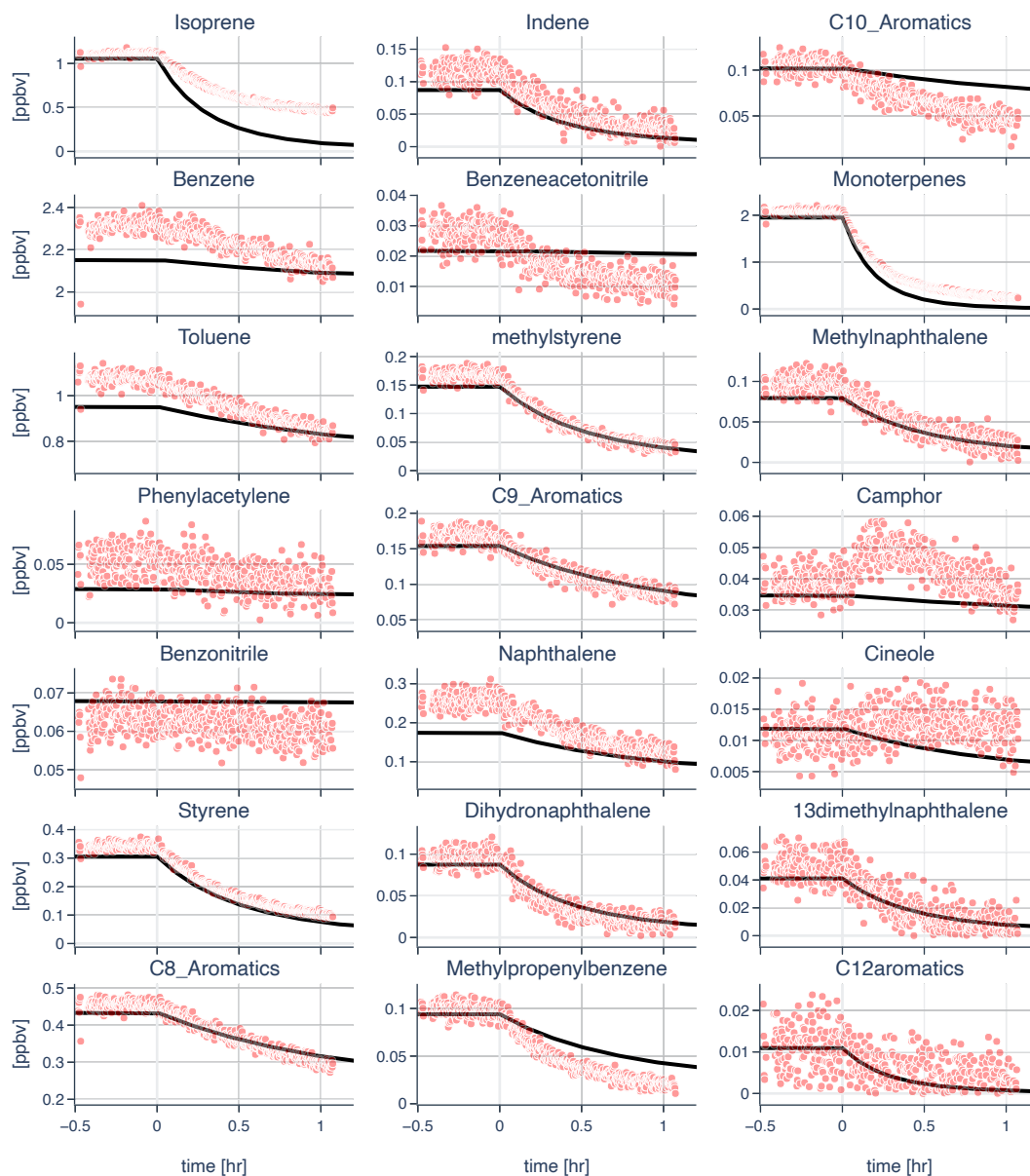


Figure B.7: Modeled (solid black line) and measured (peach circles) decay of reduced hydrocarbons identified by the PTR-ToF-MS for the chamber experiments performed on Fire007.

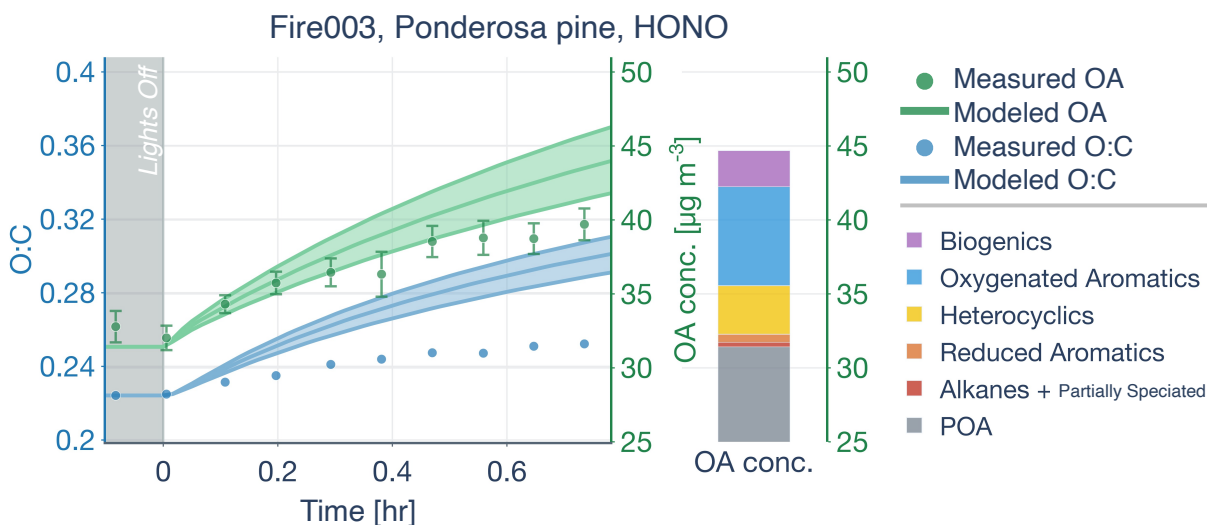


Figure B.8: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high NO_x conditions (Fire003). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

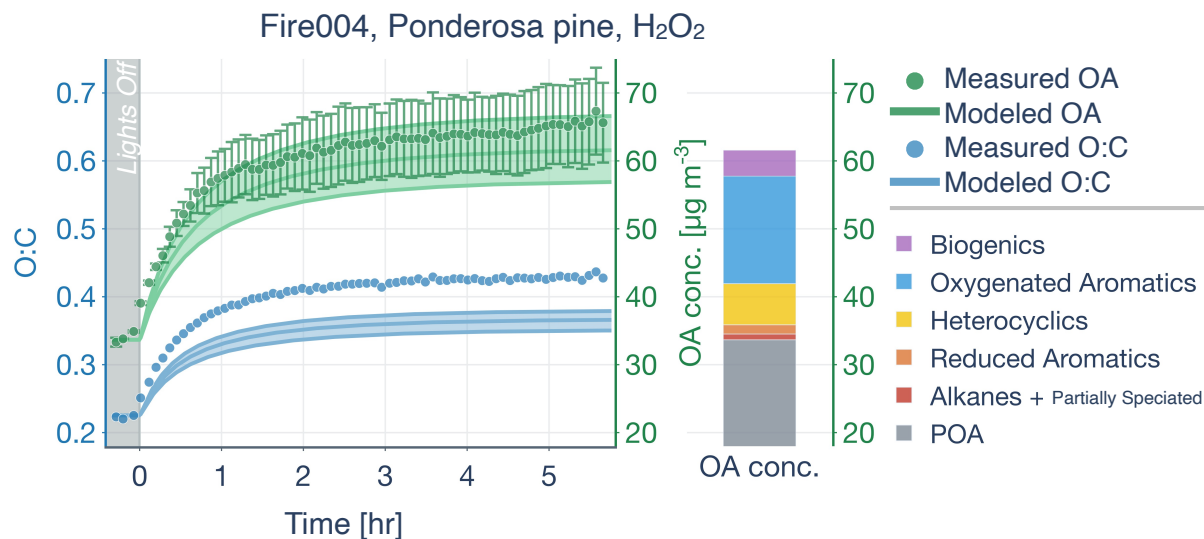


Figure B.9: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high NO_x conditions (Fire004). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

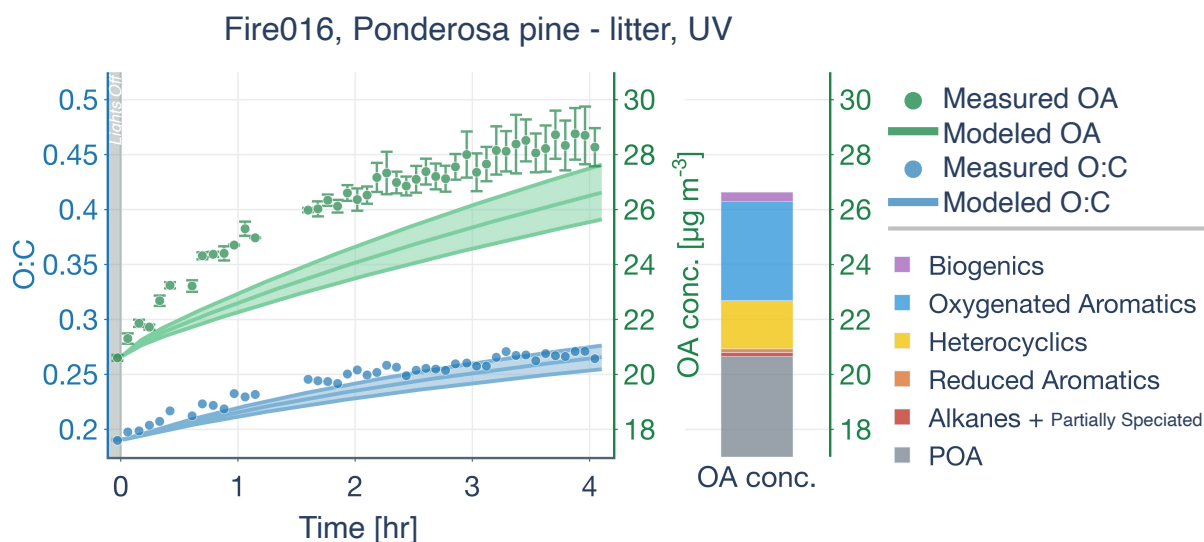


Figure B.10: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed without added oxidants (Fire016). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

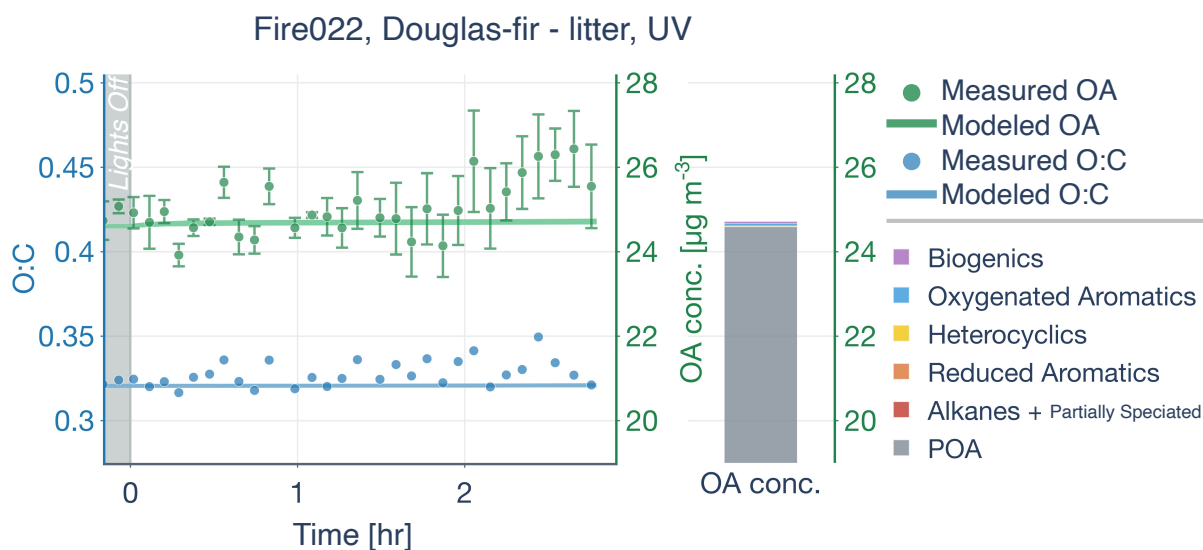


Figure B.11: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Douglas fir experiment performed without added oxidants (Fire022). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

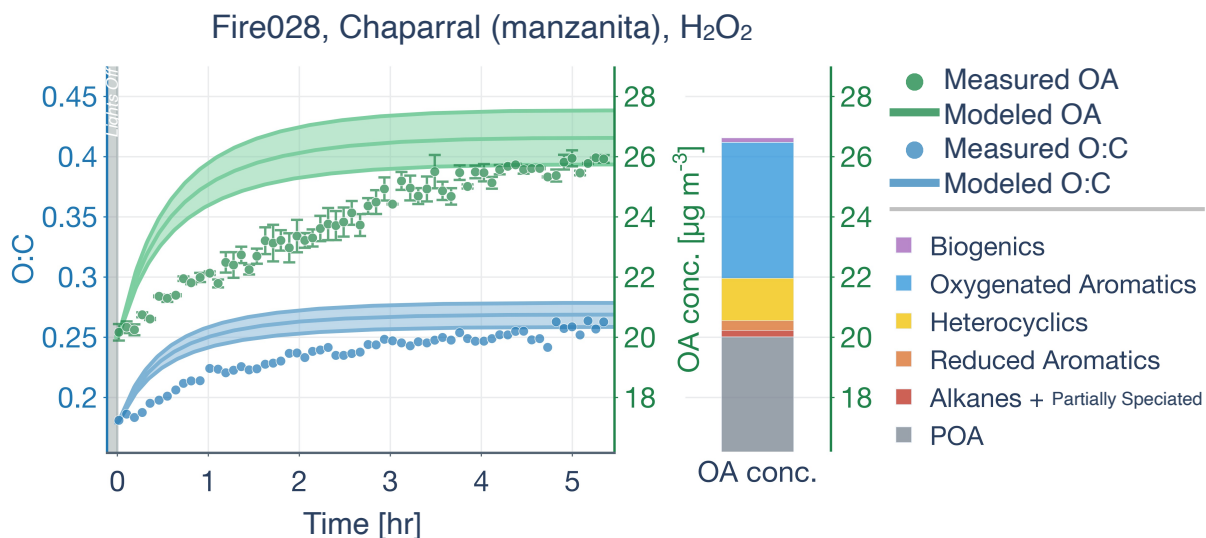


Figure B.12: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a chaparral (manzanita) experiment performed at high NO_x conditions (Fire028). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

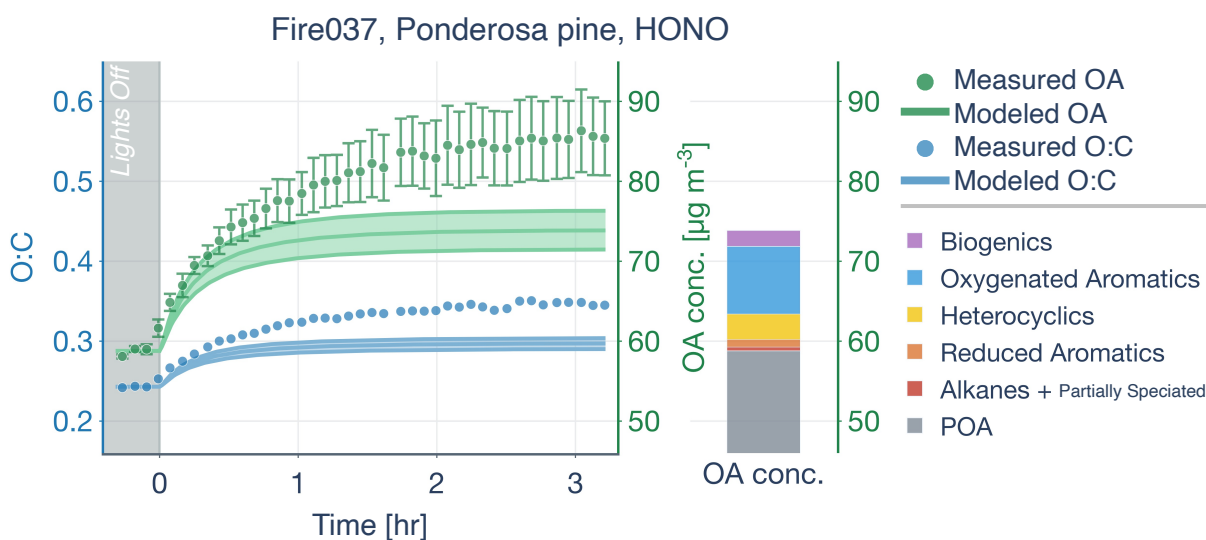


Figure B.13: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high NO_x conditions (Fire037). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

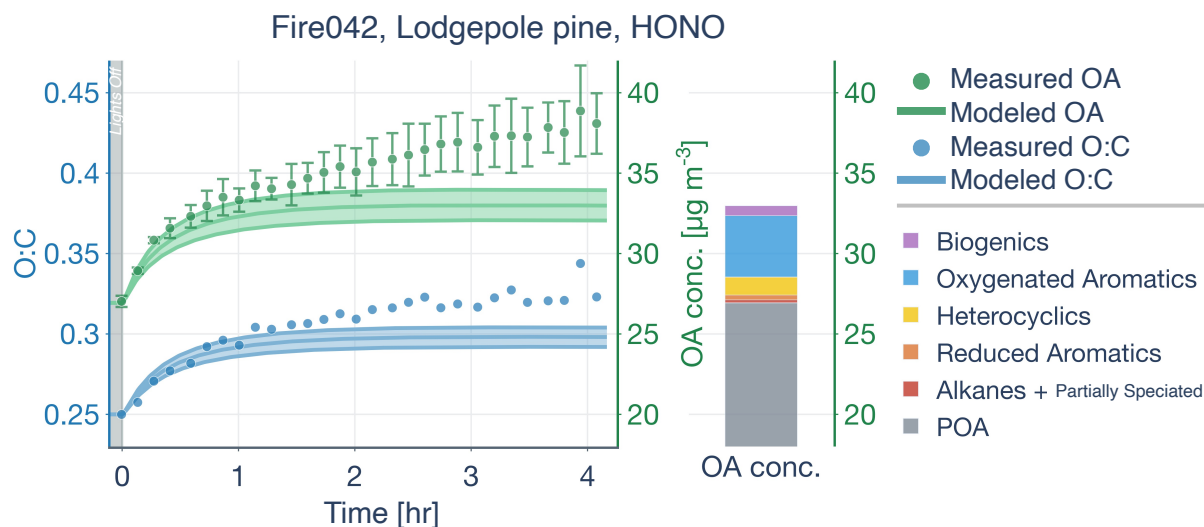


Figure B.14: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Lodgepole pine experiment performed at high NO_x conditions (Fire042). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

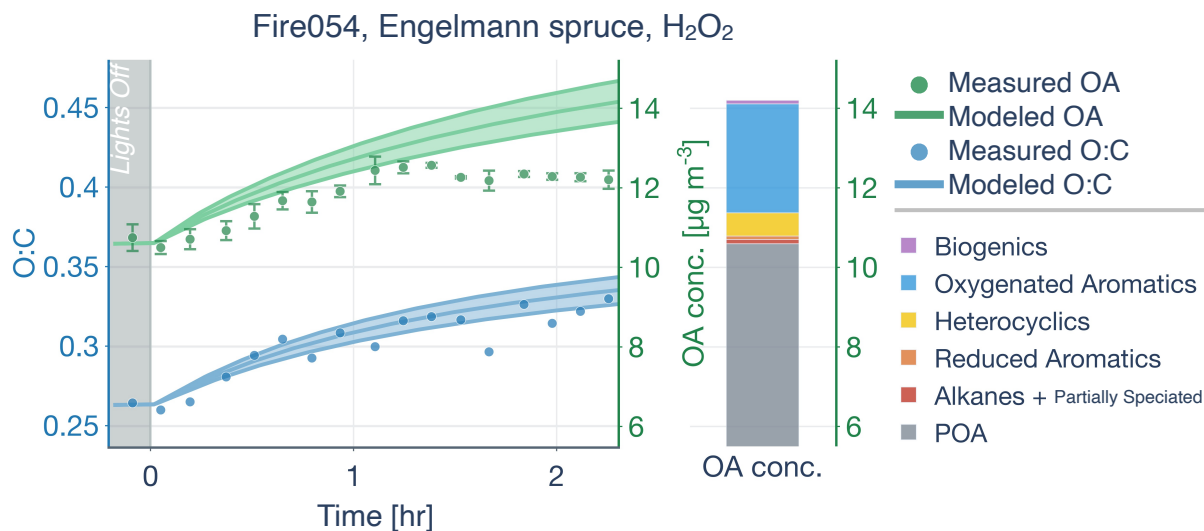


Figure B.15: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for an Engelmann spruce experiment performed at high NO_x conditions (Fire054). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

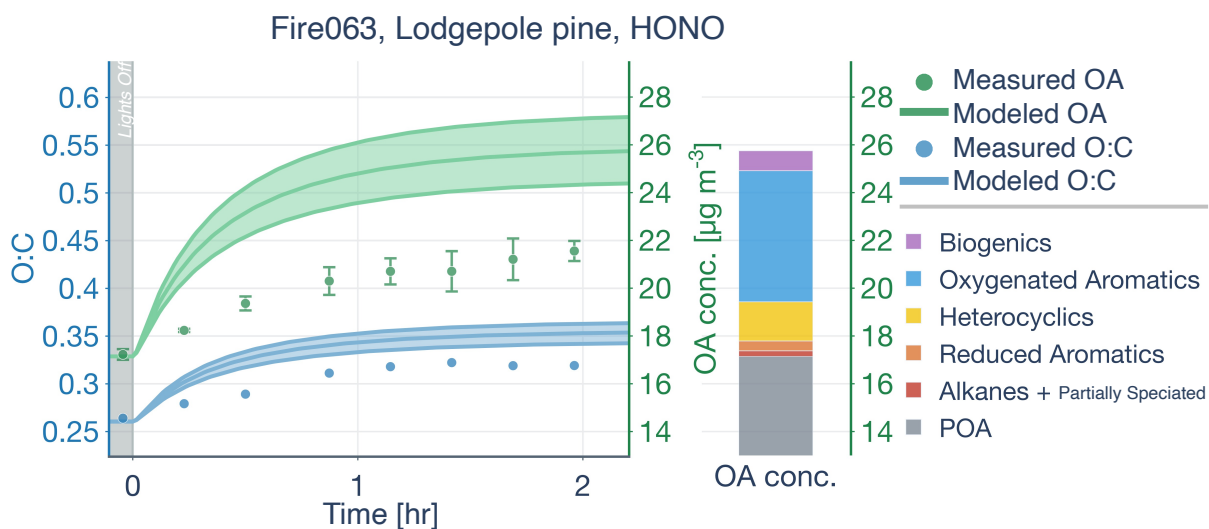


Figure B.16: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Lodgepole pine experiment performed at high NO_x conditions (Fire063). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

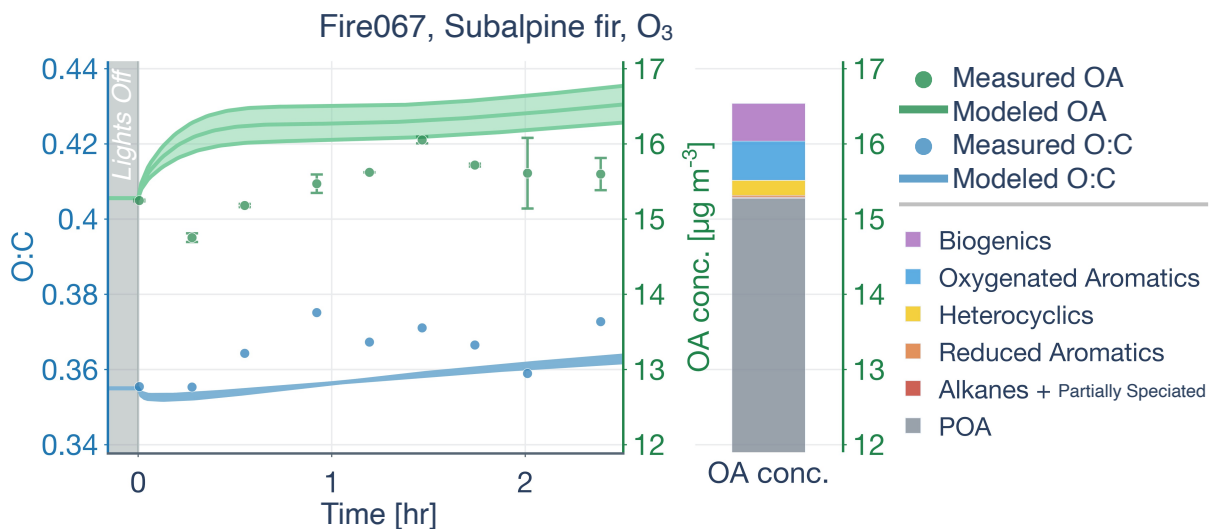


Figure B.17: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a subalpine fir experiment performed with additional ozone (Fire067). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

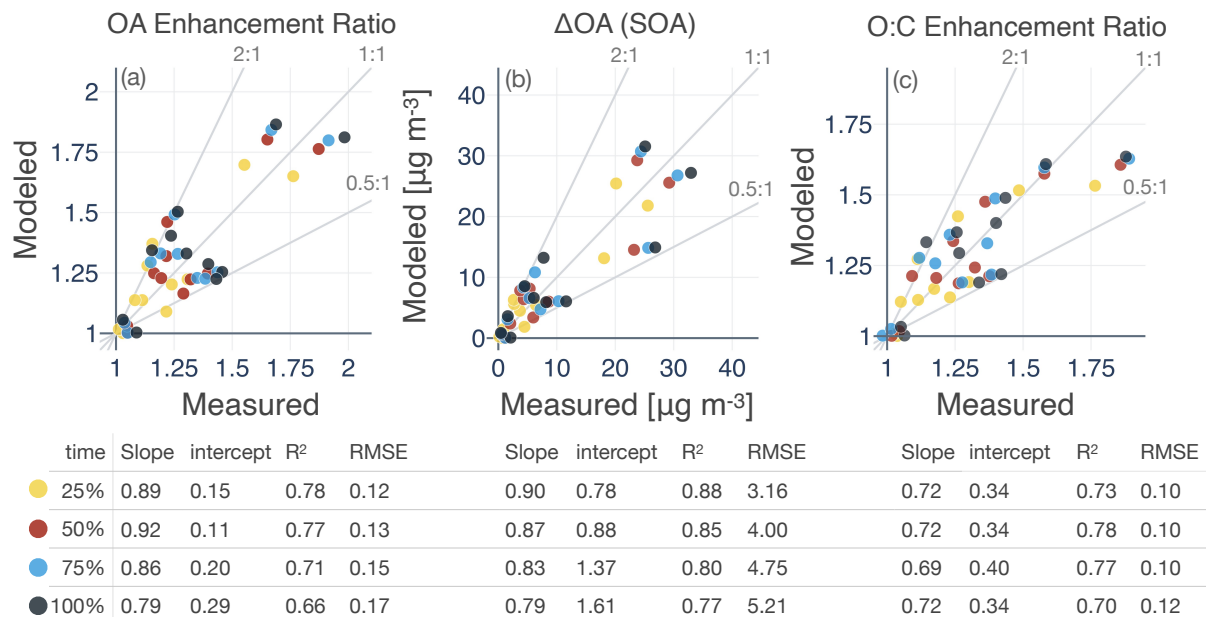


Figure B.18: Model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ($\mu\text{g m}^{-3}$), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments at four different time percentiles: 25%, 50%, 75%, and 100%.

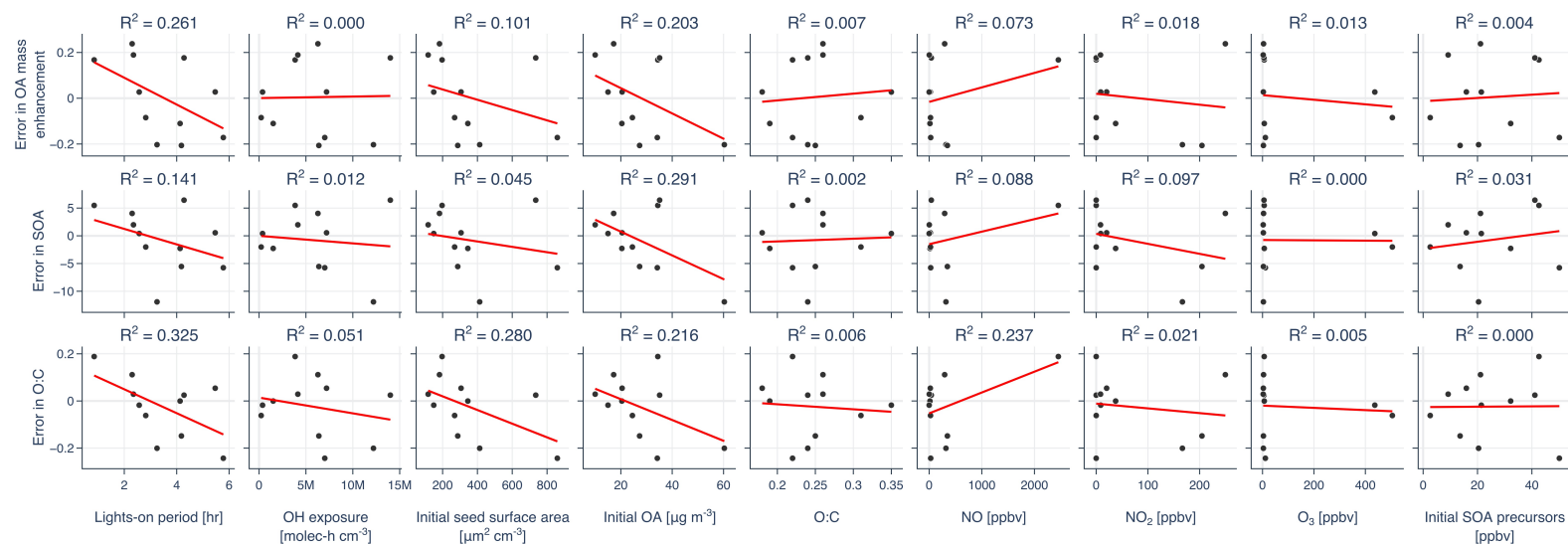


Figure B.19: Model error in OA mass enhancement ratio, SOA production, and OA O:C regressed against lights-on period, OH exposure, and initial concentrations of seed surface area, OA mass, O:C, NO, NO₂, O₃, and SOA precursors.

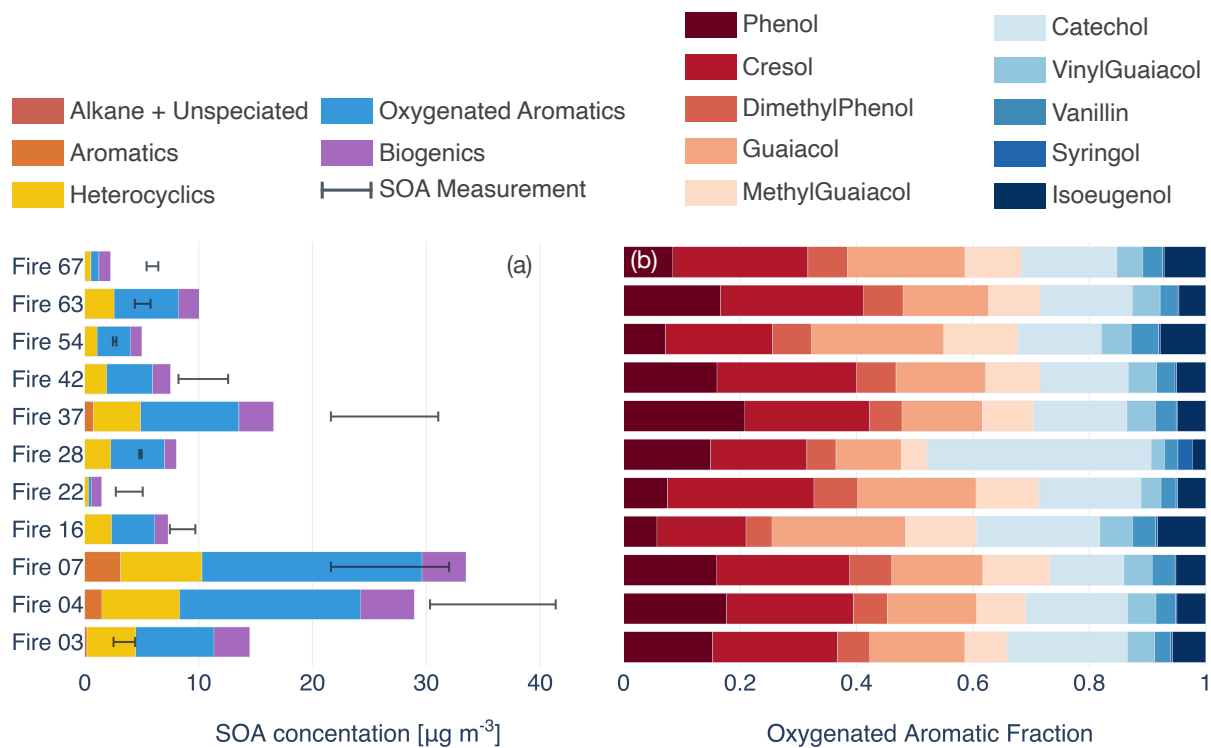


Figure B.20: (a) SOA mass concentrations apportioned by precursor class and (b) normalized precursor contributions to SOA arising from oxygenated aromatics. Data presented for all eleven chamber experiments.

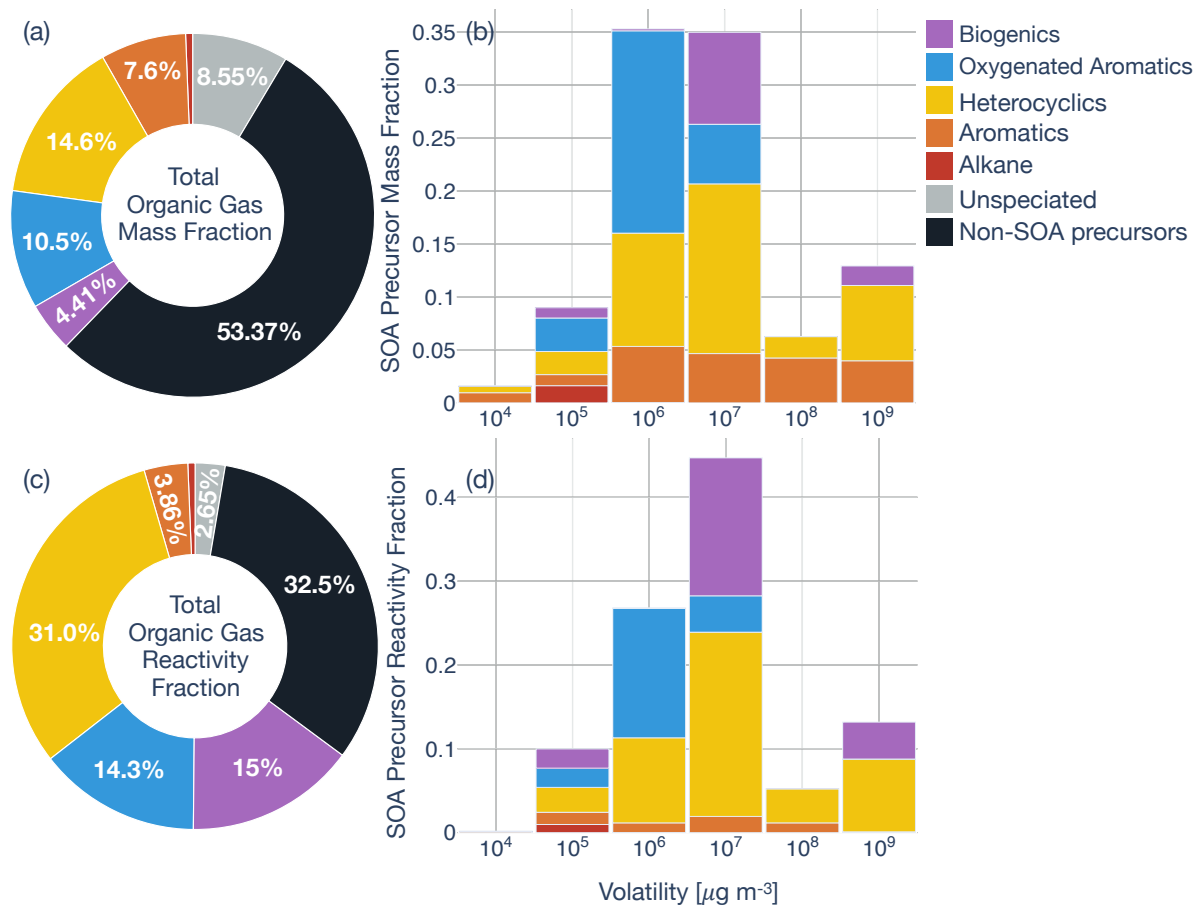


Figure B.21: (a) SOA precursor classes as a mass fraction of the total VOCs and (b) normalized distribution of SOA precursor emissions in volatility space. (c) SOA precursor classes as a fraction of the total VOC reactivity and (d) normalized distribution of SOA precursor reactivity in volatility space. Data are presented as an average of the emissions over the eleven chamber experiments.

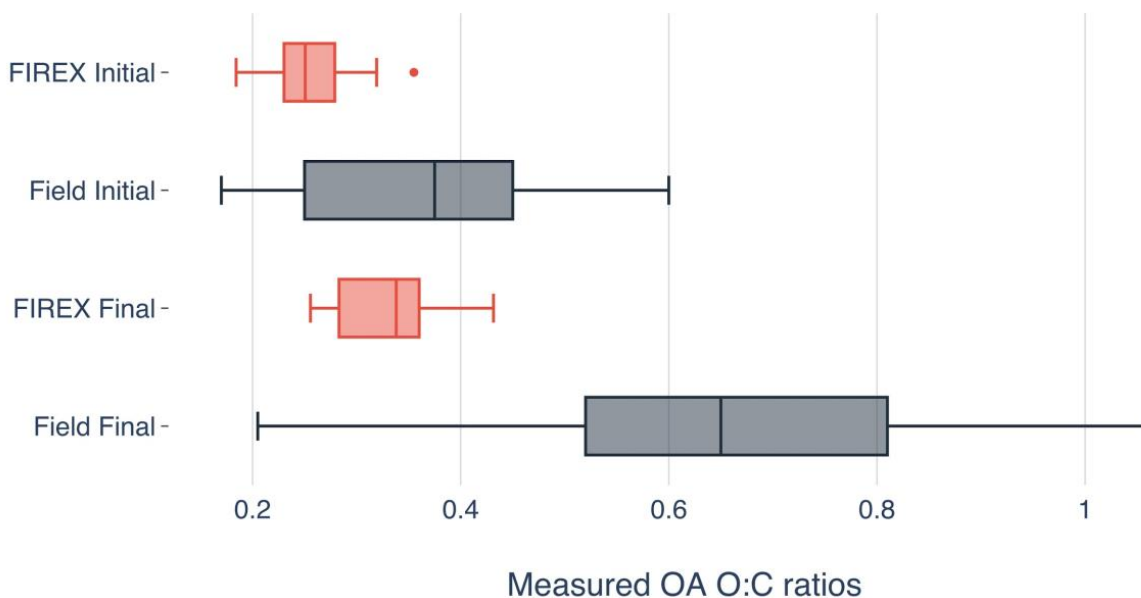


Figure B.22: Box plots for initial and final OA O:C ratios from the chamber experiments performed during FIREX and a host of field studies. The field studies are summarized in Hodshire et al (2019). The orange horizontal lines are medians and the dotted horizontal lines are means. Solid circles are outliers.

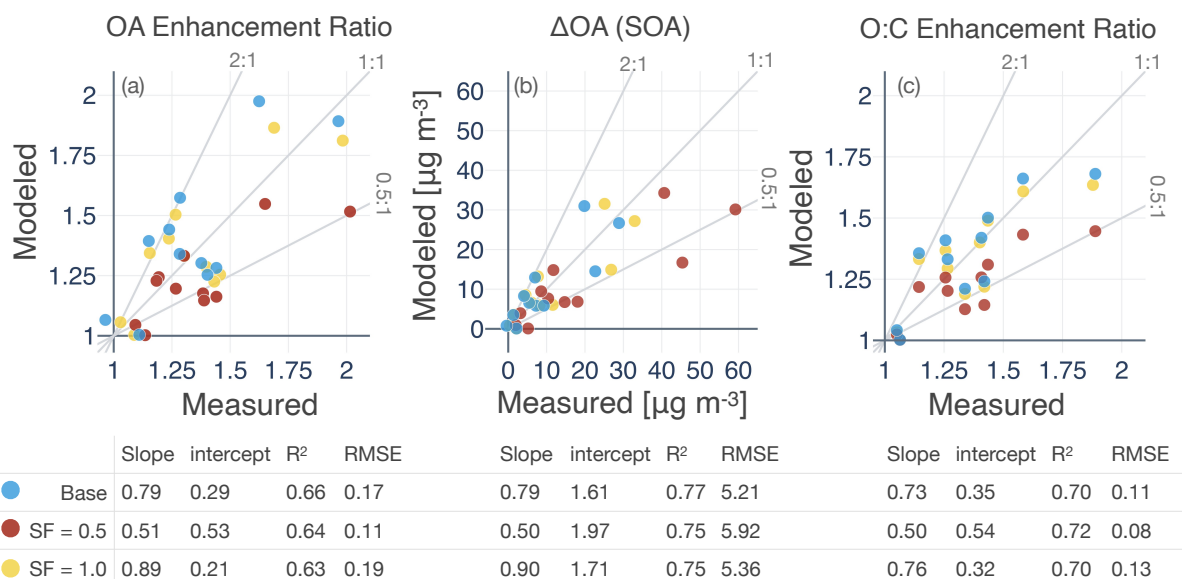


Figure B.23: End-of-experiment model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ($\mu\text{g m}^{-3}$), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments for three different assumptions about the scaling factor: constant scaling factor of 0.5 and 1 and a scaling factor as a function of the OA oxidation state.

Appendix C

Supplementary information for Chapter 4

Table C.1: Precursor classes, surrogates, and parameters used in this work.

Precursor Class	VOC Surrogate	ΔLVP	m_{frag}	p_{10}	p_{20}	p_{30}	p_{40}	Reference
SVOCs	naphthalene	1.4922	0.7673	0.8138	0.0072	0.0635	0.1155	Zhang et al. (2014)
Linear alkanes	<i>n</i> -dodecane	1.4629	0.2627	0.9657	0.0010	0.0020	0.0314	Loza et al. (2014)
Benzene*	benzene	1.5495	0.7895	0.0743	0.0213	0.8963	0.0081	Ng et al. (2007)
Toluene*	toluene	1.4169	1.3064	0.5634	0.3413	0.0016	0.0937	Zhang et al. (2014)
C ₈₊ single-ring aromatics*	<i>m</i> -xylene	1.4601	0.0736	0.1418	0.2971	0.4571	0.1040	Ng et al. (2007)
Multi-ring aromatics	naphthalene	1.4922	0.7673	0.8138	0.0072	0.0635	0.1155	Zhang et al. (2014)
Isoprene [#]	isoprene	1.8742	0.5207	0.9924	0.0003	0.0065	0.0009	Chhabra et al. (2011)
Terpene [#]	α -pinene	1.9139	0.1312	0.5991	0.2923	0.1079	0.0007	Chhabra et al. (2011)
Oxygenated aromatics	phenol, guaiacol	2.023	0.315	0.109	0.048	0.439	0.404	Yee et al.(2013)
Oxygenated aromatics	syringol	1.629	0.148	0.394	0.121	0.071	0.414	Yee et al. (2013)
Heterocyclics	2-methylfuran, dimethylfuran	1.459	0.449	0.0005	0.0014	0.998	0.0001	He et al. (2020)

*Together, reduced aromatics. [#]Together, biogenics

Table C.2: SOA precursors measured by the PTR-ToF-MS and included in the SOM-TOMAS model.

Species name	Species formula	k_{OH} ($\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$)	MW (g mol^{-1})	Surrogate
Pyrrole	$\text{C}_4\text{H}_5\text{N}$	1.45×10^{-10}	67.0892	Heterocyclics
Furan	$\text{C}_4\text{H}_4\text{O}$	4.00×10^{-11}	68.07356	Heterocyclics
Isoprene	C_5H_8	1.00×10^{-10}	68.11702	Biogenics
Dihydropyrrole	$\text{C}_4\text{H}_7\text{N}$	1.04×10^{-10}	69.10508	Heterocyclics
Tetrahydropyrrole	$\text{C}_4\text{H}_9\text{N}$	7.85×10^{-11}	71.12096	Heterocyclics
Benzene	C_6H_6	1.22×10^{-12}	78.11184	Aromatics
Pyridine	$\text{C}_5\text{H}_5\text{N}$	3.70×10^{-13}	79.0999	Heterocyclics
Methylpyrrole	$\text{C}_5\text{H}_7\text{N}$	1.10×10^{-10}	81.11578	Heterocyclics
MethylFuran	$\text{C}_5\text{H}_6\text{O}$	7.80×10^{-11}	82.10014	Heterocyclics
Furanone	$\text{C}_4\text{H}_4\text{O}_2$	5.66×10^{-11}	84.07256	Heterocyclics
Toluene	C_7H_8	5.63×10^{-12}	92.13842	Aromatics
2-Furancarbonitrile	$\text{C}_5\text{H}_3\text{NO}$	7.15×10^{-12}	93.08302	Heterocyclics
MethylPyridine	$\text{C}_6\text{H}_7\text{N}$	1.10×10^{-12}	93.12648	Heterocyclics
Phenol	$\text{C}_6\text{H}_6\text{O}$	2.80×10^{-11}	94.11084	Oxygenated Aromatics
Furfural	$\text{C}_5\text{H}_4\text{Ov2}$	3.56×10^{-11}	96.08326	Heterocyclics
Dimethylfuran	$\text{C}_6\text{H}_8\text{O}$	2.00×10^{-10}	96.12672	Heterocyclics
2-Methanolfuran	$\text{C}_5\text{H}_6\text{O}_2$	1.04×10^{-10}	98.09914	Heterocyclics
Dihydrofurandione	$\text{C}_4\text{H}_4\text{O}_3$	8.56×10^{-13}	100.0716	Heterocyclics
Benzonitrile	$\text{C}_7\text{H}_5\text{N}$	3.44×10^{-13}	103.1213	Aromatics
Styrene	C_8H_8	5.80×10^{-11}	104.1491	Aromatics
Vinylpyridine	$\text{C}_7\text{H}_7\text{N}$	2.66×10^{-11}	105.1372	Heterocyclics
Benzaldehyde	$\text{C}_7\text{H}_6\text{O}$	1.20×10^{-11}	106.1215	Aromatics

C8_Aromatics	C ₈ H ₁₀	1.32×10^{-11}	106.165	Aromatics
Benzoquinone	C ₆ H ₄ O ₂	4.51×10^{-12}	108.094	Aromatics
Cresol	C ₇ H ₈ O	5.30×10^{-11}	108.1374	Oxygenated Aromatics
Benzenediol	C ₆ H ₆ O ₂	1.04×10^{-10}	110.1098	Oxygenated Aromatics
Trimethylfuran	C ₇ H ₁₀ O	1.59×10^{-10}	110.1533	Heterocyclics
Dihydroxypyridine	C ₅ H ₅ NO ₂	4.55×10^{-11}	111.0979	Heterocyclics
5-Hydroxy 2-furfural	C ₅ H ₄ O ₃	4.90×10^{-11}	112.0823	Heterocyclics
Nitrofuran	C ₄ H ₃ NO ₃	5.06×10^{-12}	113.0703	Heterocyclics
5-hydroxymethyl- -2[3H]-furanone	C ₅ H ₆ O ₃	1.00×10^{-10}	114.0981	Heterocyclics
5-hydroxy tetrahydro 2-furfural	C ₅ H ₈ O ₃	5.00×10^{-12}	116.114	Heterocyclics
Benzeneacetonitrile	C ₈ H ₇ N	2.07×10^{-12}	117.1479	Aromatics
Benzofuran	C ₈ H ₆ O	3.70×10^{-11}	118.1322	Aromatics
Methylstyrene	C ₉ H ₁₀	5.40×10^{-11}	118.1757	Aromatics
Tolualdehyde	C ₈ H ₈ O	1.60×10^{-11}	120.1481	Aromatics
C9_Aromatics	C ₉ H ₁₂	2.20×10^{-11}	120.1916	Aromatics
Salicylaldehyde	C ₇ H ₆ O ₂	2.80×10^{-11}	122.1205	Aromatics
Dimethylphenol	C ₈ H ₁₀ O	5.05×10^{-11}	122.164	Oxygenated Aromatics
Hydroxy benzoquinone	C ₆ H ₄ O ₃	1.30×10^{-11}	124.093	Aromatics
Guaiacol	C ₇ H ₈ O ₂	7.53×10^{-11}	124.1364	Oxygenated Aromatics
Hydroxymethylfurfural	C ₆ H ₆ O ₃	1.00×10^{-10}	126.1088	Heterocyclics

Methyl benzofuran	C ₉ H ₈ O	9.75×10^{-11}	132.1588	Heterocyclics
Methyl propenyl benzene	C ₁₀ H ₁₂	3.30×10^{-11}	132.2023	Aromatics
3-methylacetophenone	C ₉ H ₁₀ O	2.42×10^{-12}	134.1747	Aromatics
C10_Aromatics	C ₁₀ H ₁₄	9.50×10^{-12}	134.2182	Aromatics
Methylbenzoicacid	C ₈ H ₈ O ₂	1.20×10^{-11}	136.1471	Aromatics
Monoterpenes	C ₁₀ H ₁₆	1.63×10^{-10}	136.234	Biogenics
Nitrotoluene	C ₇ H ₇ NO ₂	7.72×10^{-13}	137.1352	Aromatics
MethylGuaiacol	C ₈ H ₁₀ O ₂	3.98×10^{-11}	138.163	Oxygenated Aromatics
Methylnaphthalene	C ₁₁ H ₁₀	5.65×10^{-11}	142.1971	Aromatics
Product of levoglucosan dehydration (pyrolysis)	C ₆ H ₈ O ₄	5.28×10^{-11}	144.1237	Alkanes
Dimethylbenzofuran	C ₁₀ H ₁₀ O	1.20×10^{-10}	146.1854	Aromatics
Methylchavicol	C ₁₀ H ₁₂ O	5.43×10^{-11}	148.2013	Oxygenated Aromatics
C11_aromatics	C ₁₁ H ₁₆	5.00×10^{-11}	148.2447	Aromatics
VinylGuaiacol	C ₉ H ₁₀ O ₂	5.44×10^{-11}	150.1737	Oxygenated Aromatics
Vanillin	C ₈ H ₈ O ₃	2.73×10^{-11}	152.1461	Oxygenated Aromatics
Camphor	C ₁₀ H ₁₆ O	4.30×10^{-12}	152.233	Biogenics
Syringol	C ₈ H ₁₀ O ₃	9.66×10^{-11}	154.162	Oxygenated Aromatics
Cineole	C ₁₀ H ₁₈ O	2.26×10^{-11}	154.2489	Biogenics
1,3-dimethylnaphthalene	C ₁₂ H ₁₂	6.94×10^{-11}	156.2237	Aromatics
Decanal	C ₁₀ H ₂₀ O	3.45×10^{-11}	156.2648	Alkanes

C12_aromatics	$C_{12}H_{18}$	1.13×10^{-10}	162.2713	Aromatics
Isoeugenol	$C_{10}H_{12}O_2$	8.84×10^{-11}	188.2217	Aromatics Aromatics
C13_aromatics	$C_{13}H_{20}$	1.13×10^{-10}	176.2979	Aromatics
Sesquiterpenes	$C_{15}H_{24}$	3.00×10^{-10}	204.3511	Biogenics
5-Methyl furfural	$C_6H_6O_2$	5.18×10^{-11}	110.1098	Heterocyclics

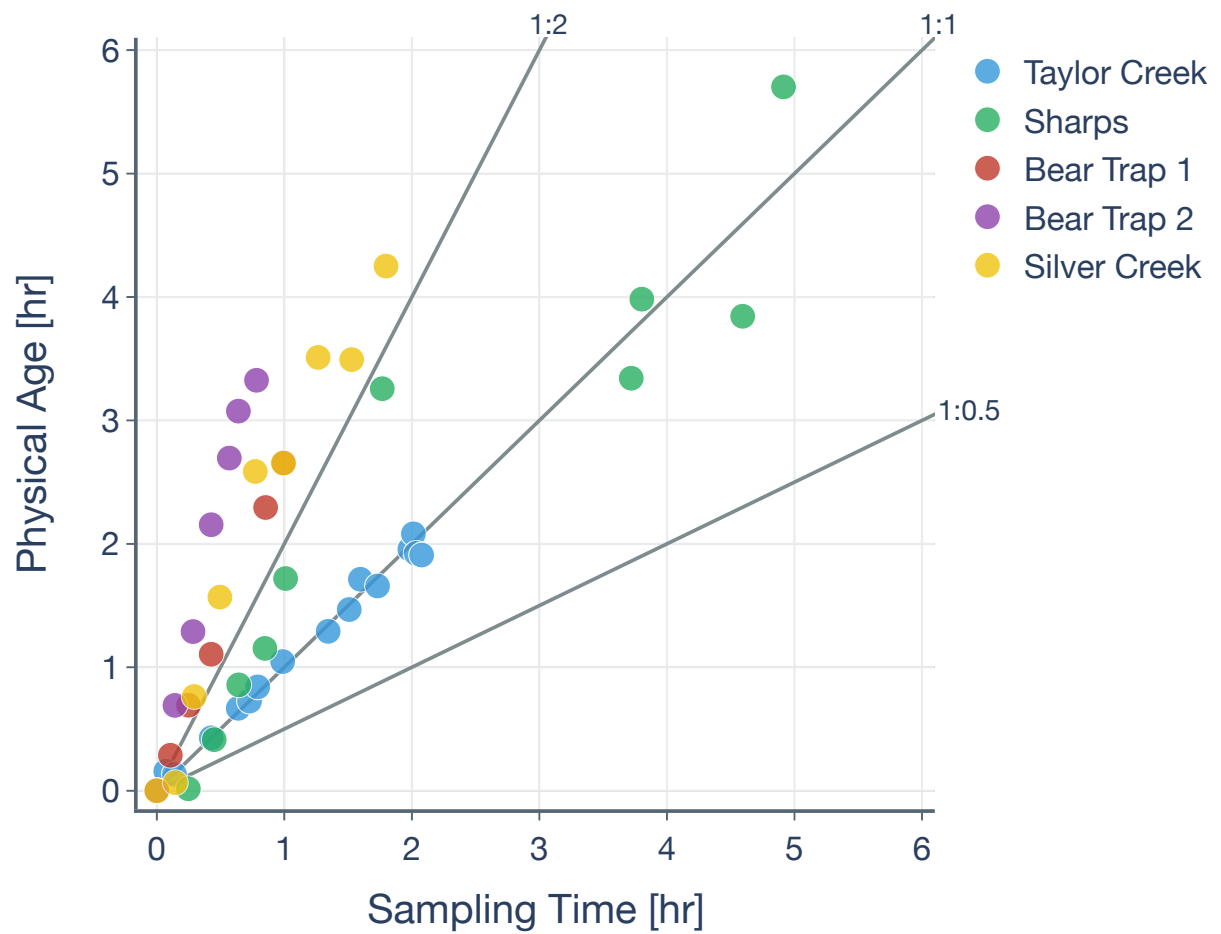


Figure C.1: Physical age plotted against the sampling time for the five transect sets and four wildfire plumes.

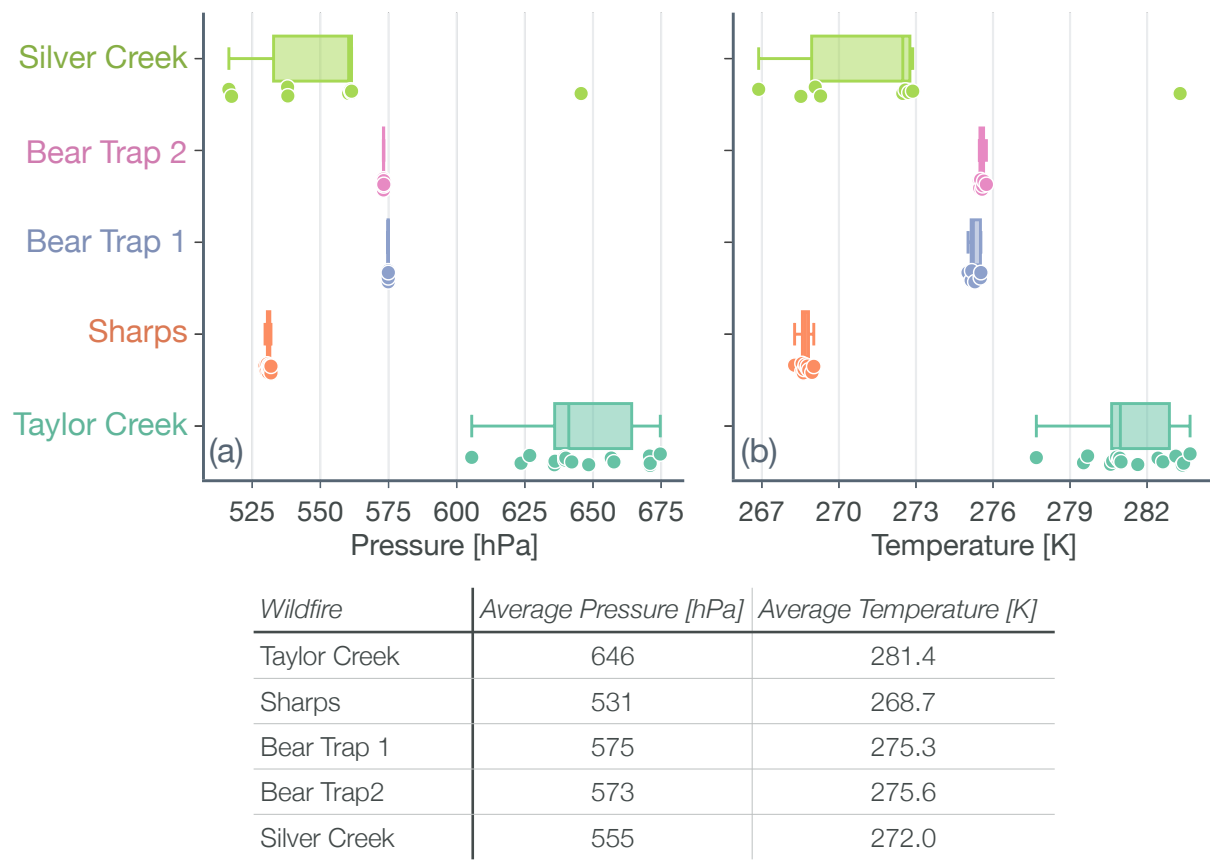


Figure C.2: Box plots for (a) pressures and (b) temperatures encountered during the pseudo-Lagrangian evolution of smoke in the five transect sets and four wildfire plumes.

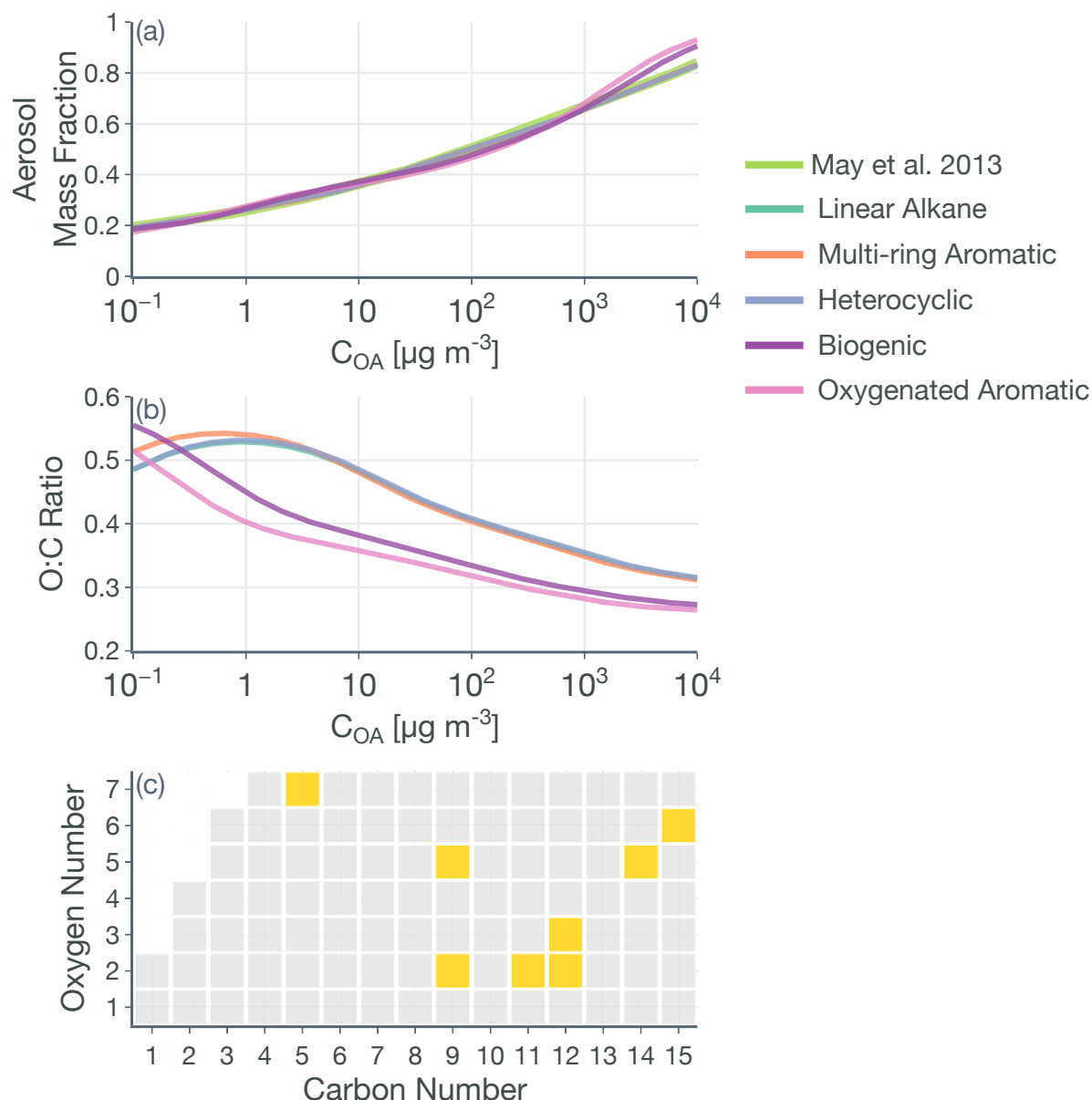


Figure C.3: (a) POA volatility from May et al. (2013) and that used in this work expressed as the aerosol mass fraction against the OA mass concentration. The POA volatility based on the use of multi-ring aromatics was used with the base configuration of the SOM-TOMAS model while the POA volatility based on the use of other organic classes was used to perform sensitivity simulations. (b) Dependence of the OA O:C ratio as a function of the OA mass concentration. (c) Model species, shown in yellow, in the SOM grid used to represent the POA and SVOC mass. This distribution was informed based on the Monte-Carlo simulations performed and discussed in Section 3.2.

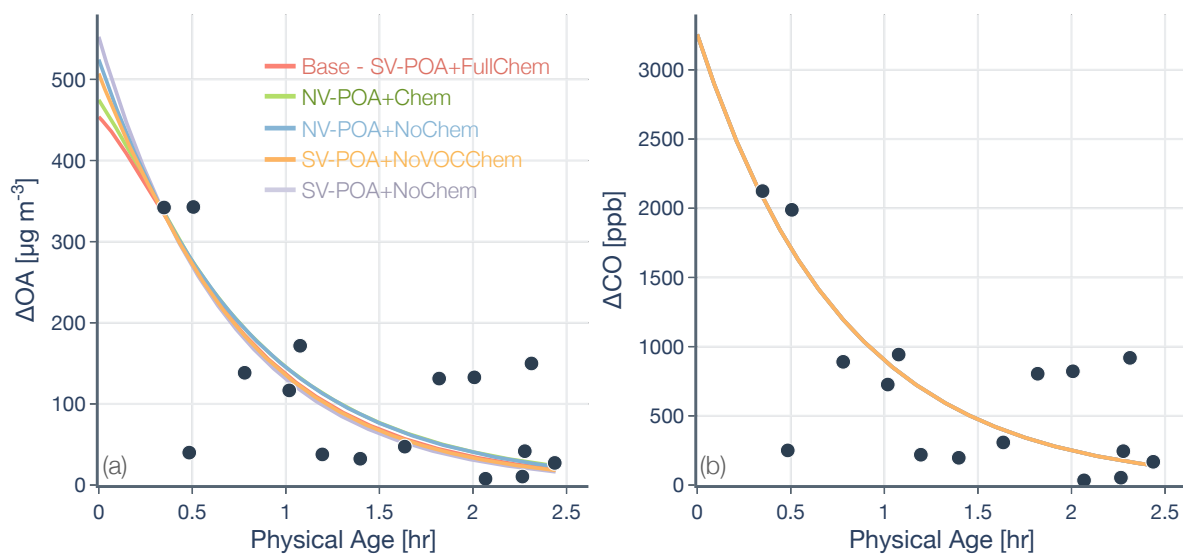


Figure C.4: Predictions of the (a) OA and (b) CO concentrations from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. Model predictions are shown for five different simulations that vary in their assumptions about POA volatility and oxidation chemistry.

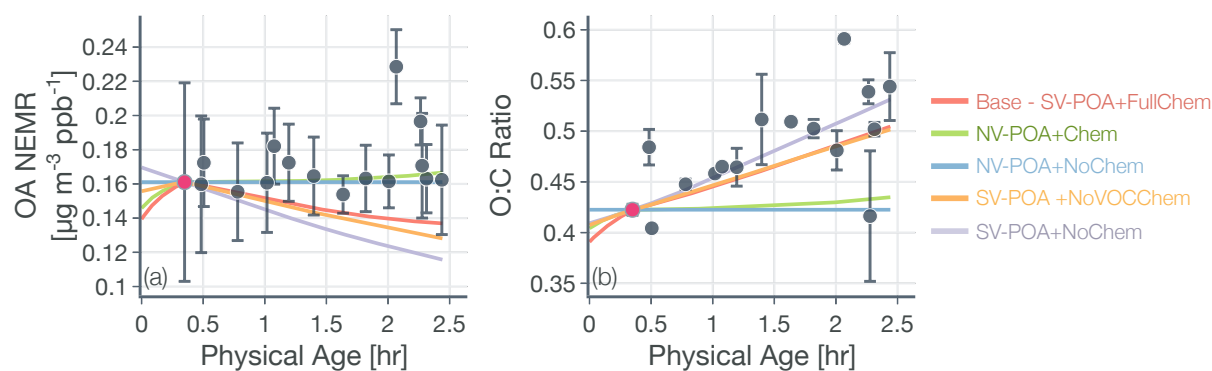


Figure C.5: Same as Figure 4.4 but with the standard error in the mean for the observations.

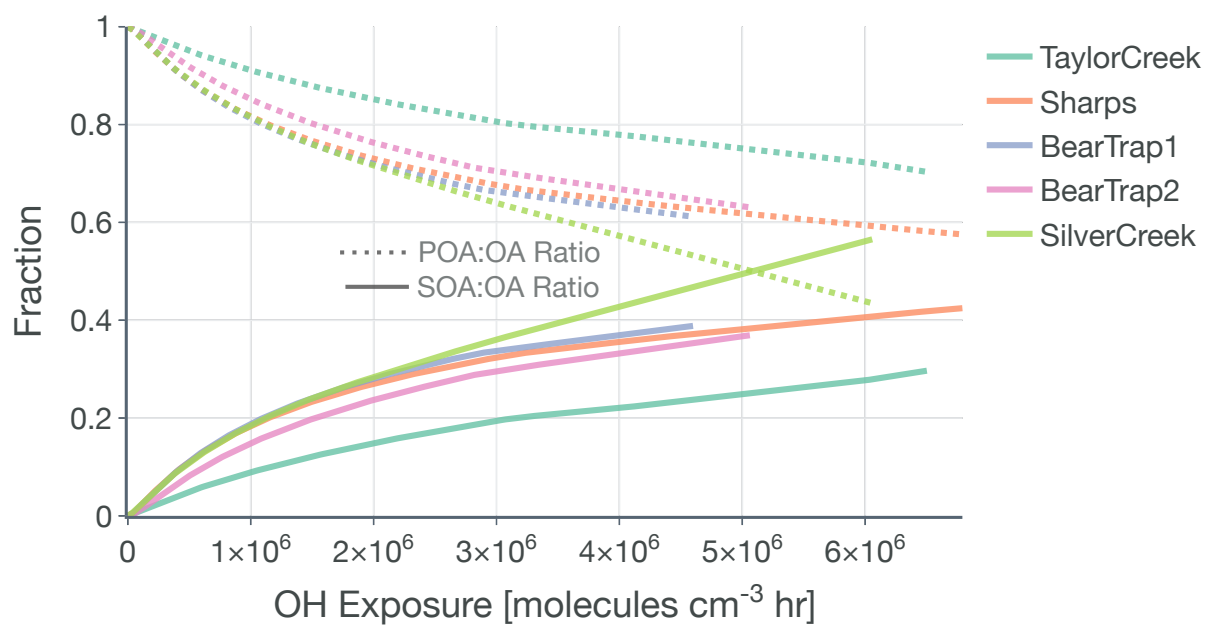


Figure C.6: Predicted POA (dotted lines) and SOA (solid lines) ratios with OA for the base simulation results presented in Figures 4 and 5.

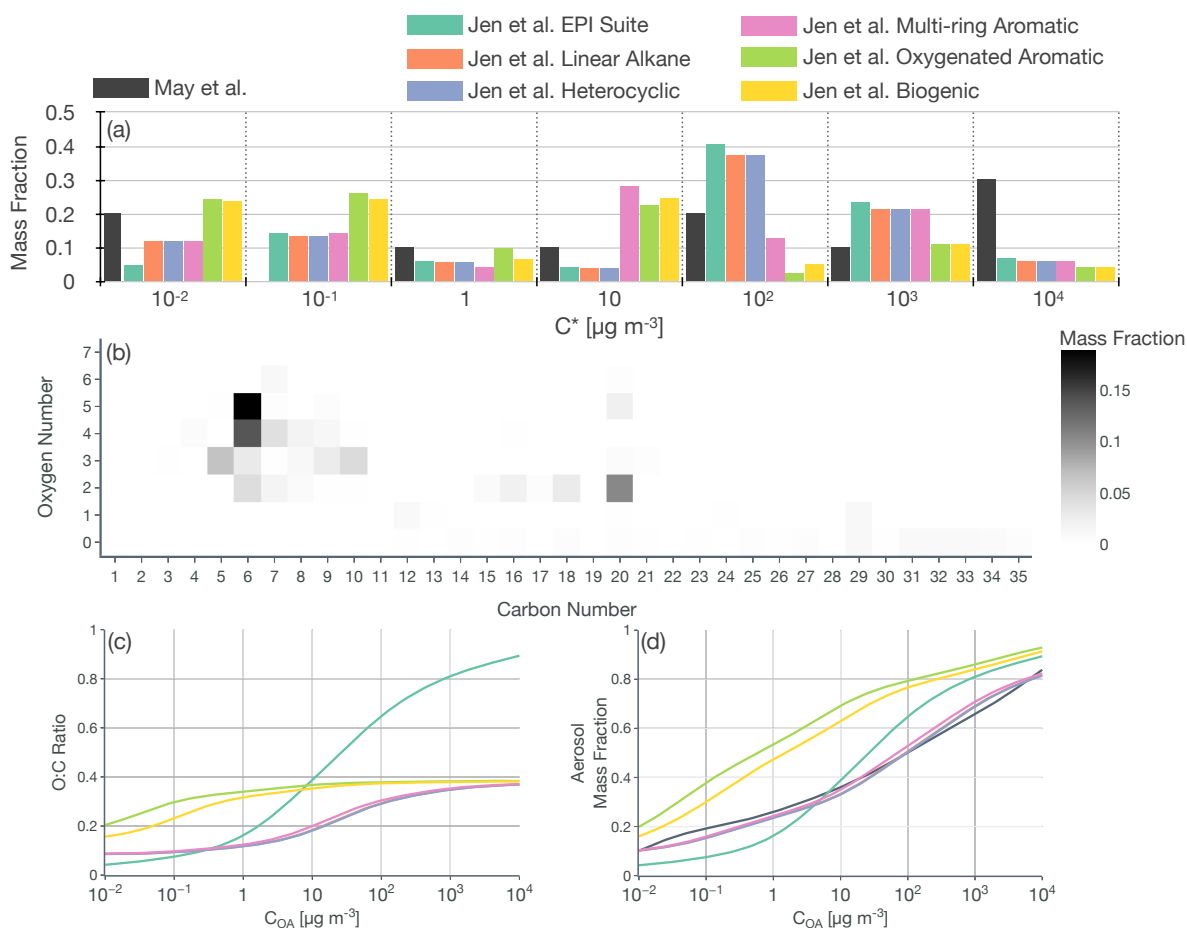


Figure C.7: Averaged and normalized, (a) volatility distribution and (b) mass distribution in carbon-oxygen space for the POA and SVOC emissions and (c) O:C ratio behavior with respect to total organic aerosol concentration quantified by Jen et al. (2019). Jen et al. (2019) only quantified 10 to 65% of the POA and SVOC mass collected on quartz filters. The volatility (c^*) was calculated for the POA and SVOC species using EPISuite v4.11 (EPA, 2021), and the Statistical Oxidation Model (SOM) parameterizations based on different surrogate (Cappa and Wilson, 2012; Jathar et al., 2015).

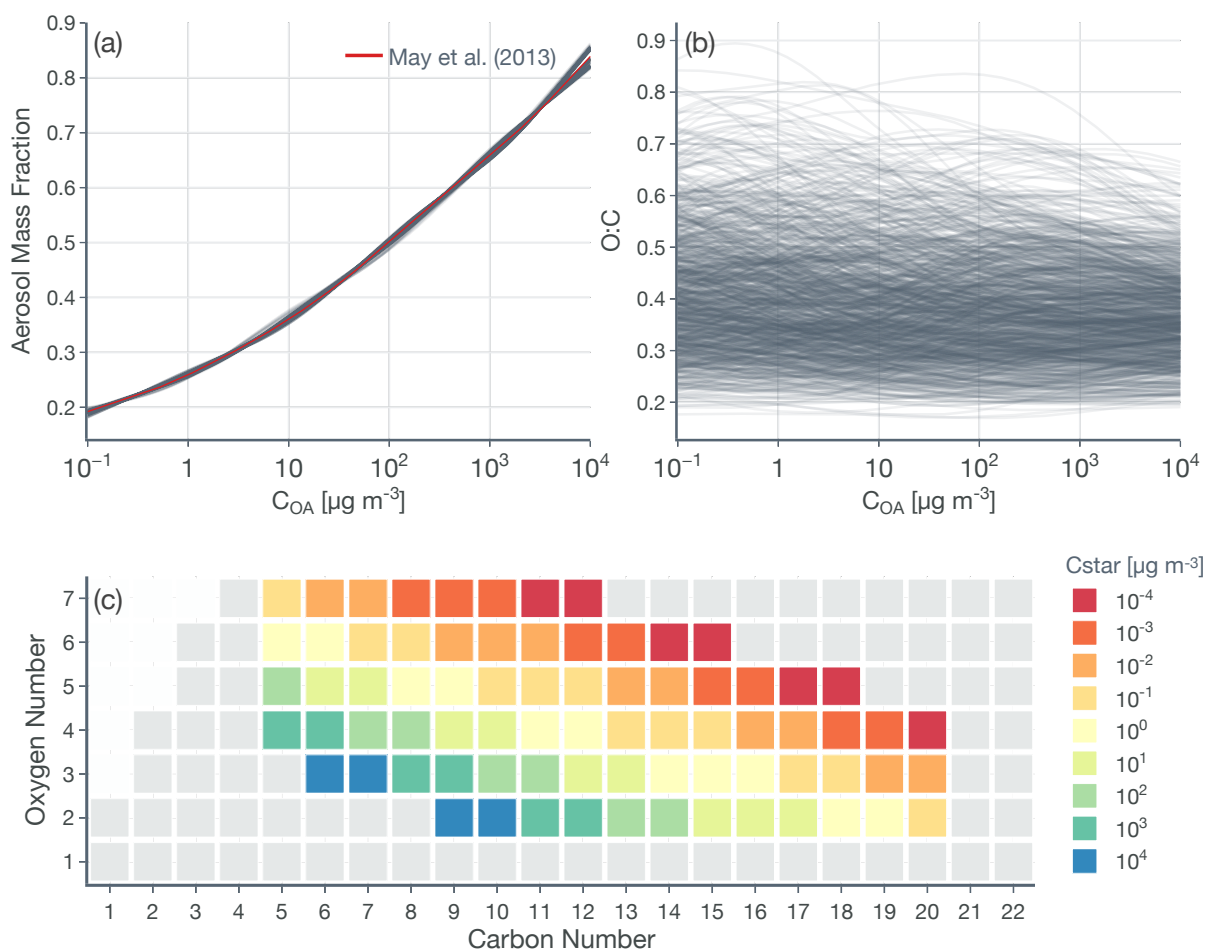


Figure C.8: (a) POA volatility from May et al. (2013) and 1000 Monte Carlo simulations. The POA volatility based on the use of linear alkanes was used to perform Monte Carlo sensitivity simulations. (b) Dependence of the OA O:C ratio as a function of the OA mass concentration for all simulations. (c) Model volatility class from which one species was chosen randomly to perform Monte Carlo simulations.

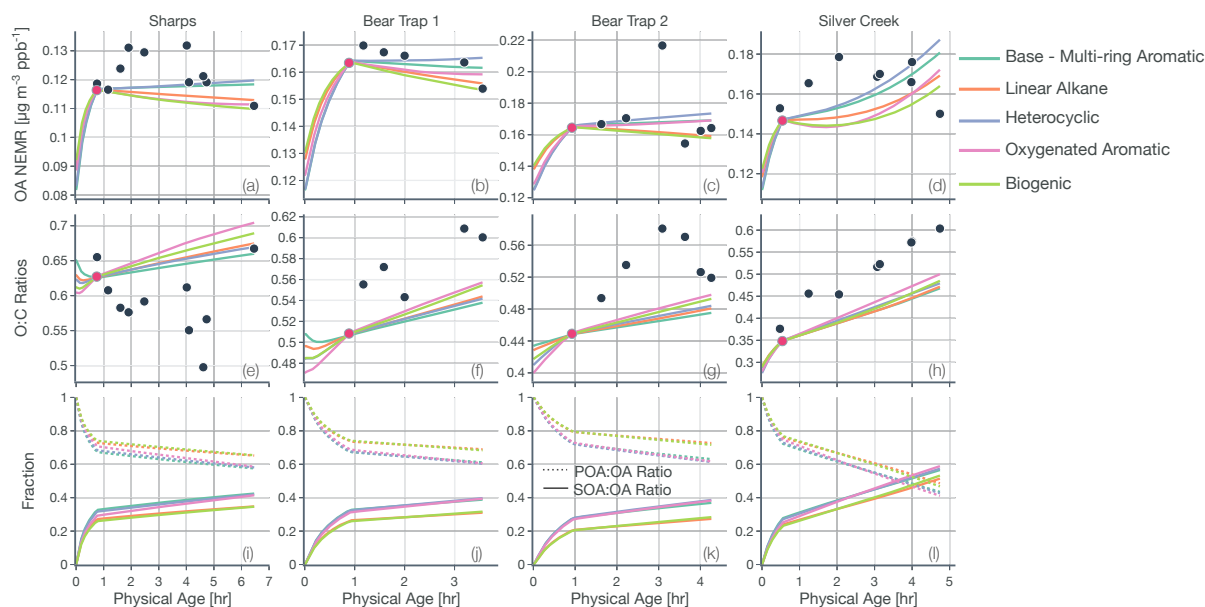


Figure C.9: Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the four different fires. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for the SVOC oxidation chemistry.

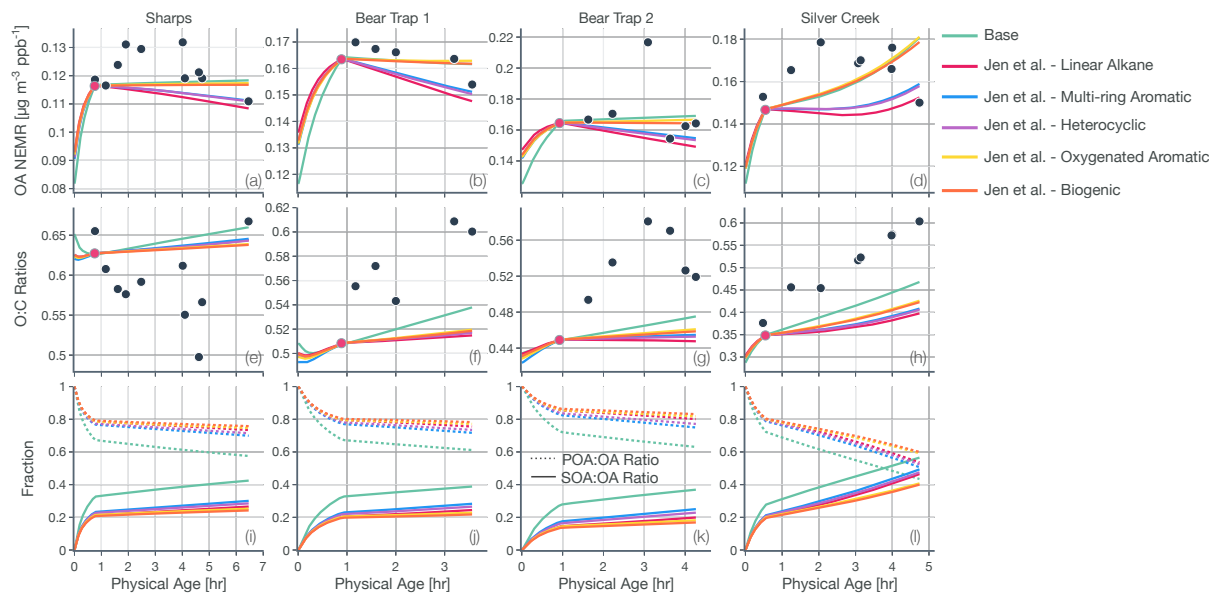


Figure C.10: Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the four different fires. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for the POA volatility and SVOC oxidation chemistry.

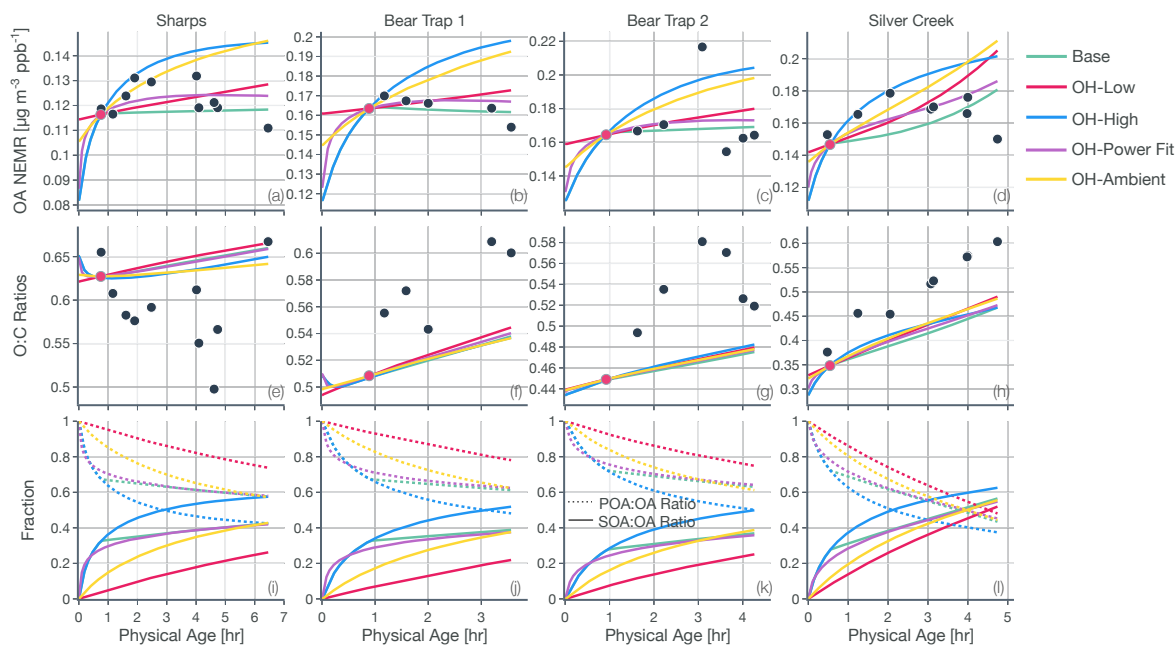


Figure C.11: Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying assumptions for OH.

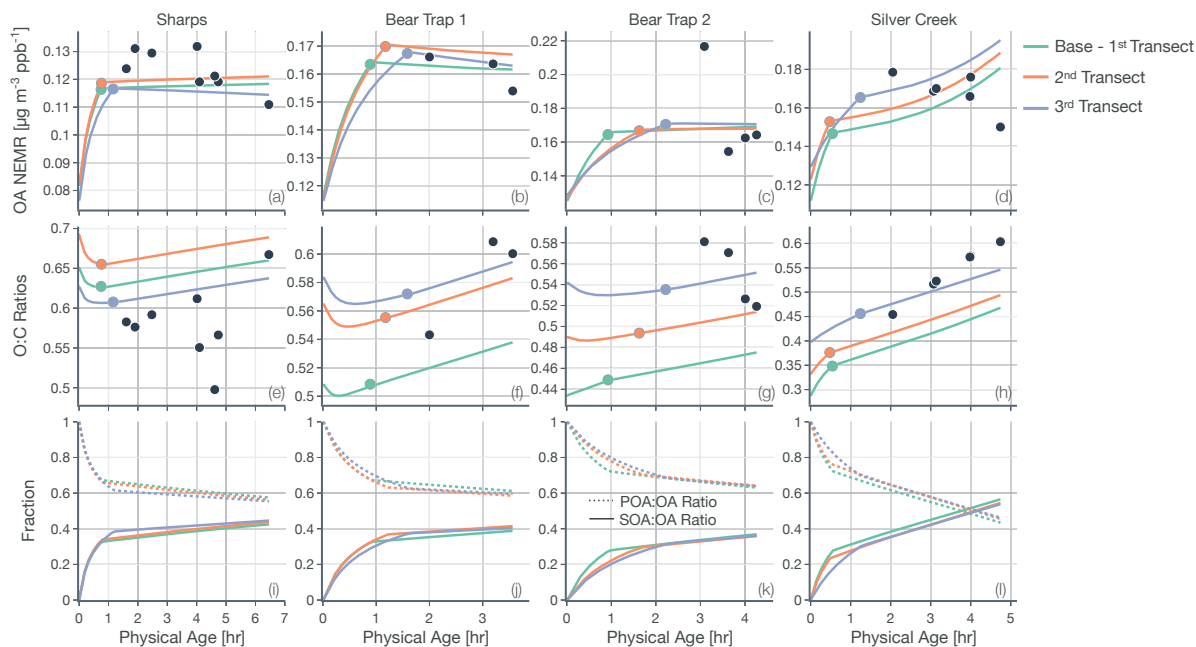


Figure C.12: Predictions of (a,b,c,d) OA NEMR and (e,f,g,h) OA O:C from the SOM-TOMAS model (solid colored lines) compared against measurements (solid black circles) from the Taylor Creek fire. (i,j,k,l) Predictions of the fractional contributions of POA and SOA to OA. Model predictions are shown for sensitivity simulations performed with varying 'first' transect.

Glossary

aI-SOA Anthropogenic SOA formed from IVOC oxidation.

ARO1 Aromatic Compounds Similar to Toluene.

ARO2 Aromatic Compounds Similar to Xylene.

aS-SOA Anthropogenic SOA formed from SVOC oxidation.

aV-SOA Anthropogenic SOA formed from VOC oxidation.

bV-SOA Biogenic SOA formed from VOC oxidation.

CIMS chemical Ionization Mass Spectrometry.

CTM Chemical Transport Model.

Gas Chromatography Mass spectrometry Hydroxyl radical.

HOA Hydrocarbon-like organic aerosol measured by the aerosol mass spectrometer.

IVOC Intermediate-volatility organic compound.

NMOG Non-methane organic gas.

OA Organic Aerosol.

OOA Oxygenated organic aerosol measured by the aerosol mass spectrometer.

POA Primary organic aerosol or direct emissions of organic aerosol.

PTR-MS Hydroxyl radical.

PTR-MS Proton Transfer Reaction - Mass Spectrometry.

PWL Particle Wall Loss.

SOA Secondary organic aerosol or organic aerosol formed in the atmosphere.

SOM Statistical Oxidation Model.

SVOC Semi-volatile organic compound.

TOMAS Two Moment Aerosol Sectional.

VOC Volatile organic compound.

VWL Vapor Wall Loss.