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Phase Dynamics of Wildland Fire Smoke Emissions and Their Secondary Organic Aerosols

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iii. **List of Abbreviations/Acronyms**

OA: organic aerosol
PM_{2.5}: particulate matter less than 2.5 microns in diameter
POA: primary organic aerosol
SOA: secondary organic aerosol
TOMAS: Two-Moment Aerosol Sectional model
VBS: Volatility Basis Set.

iv. **Keywords**

Biomass burning aerosol; primary organic aerosol; secondary organic aerosol; phase partitioning; smog chambers; wall losses; plume dilution; photooxidation

v. **Acknowledgements**

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Abstract

Biomass burning is an important source to the atmosphere of carbonaceous particulate matter that impacts air quality, climate, and human health. The semivolatile nature of directly-emitted organic particulate matter can result in particle evaporation as smoke plumes dilute. Further, oxidation of emitted and volatilized precursors can lead to additional formation of secondary organic aerosol (SOA) in the atmosphere. These processes are not fully understood, hindering efforts to quantify the impacts of prescribed and wildfires.

Experiments conducted in laboratory smog chambers are extensively used to study processes that drive gas and particle evolution in the atmosphere, with the findings then applied in air quality models. However, a limitation of smog chamber experiments is that particles and gas-phase species may be lost to chamber surfaces, biasing the conclusions. The objectives of this study, all of which were met, were: (1) To conduct detailed calculations of the phase partitioning behavior of fresh smoke emissions, including consideration of the evolving aerosol size distribution, with a view toward understanding conditions under which SOA precursors become available for oxidation; (2) To use the same framework to compute the potential phase partitioning behavior of oxidation products, to improve understanding of their potential impacts on $PM_{2.5}$ concentrations; and (3) To apply our findings to improve understanding of how phase partitioning and its timescales may lead to potential artifacts in smog chamber experiments that seek to quantify the SOA-formation potential of biomass burning emissions.

We conducted simulations to determine how particle and gas-phase wall losses contributed to the observed evolution of the aerosol during experiments in the third Fire Lab At Missoula Experiment (FLAME III), using a modified version of the Two-Moment Aerosol Sectional (TOMAS) microphysics algorithm coupled with the organic volatility basis set (VBS) and wall-loss formulations. By fitting to laboratory data, we could constrain many of the uncertain model parameters. Our first study was limited to simulating the dark periods in the chamber before photo-oxidation when only physical processes were active. Our model simulations suggested that over one-third of the initial particle-phase organic mass was lost during this portion of the experiments, and one-third of this loss arose from evaporation of the particles driven by vapor losses to the walls. Our second set of simulations considered the photo-oxidation stages of the FLAME III chamber experiments, and were able to reproduce the observed mean OA mass enhancement (the ratio of final to initial OA mass, corrected for particle-phase wall losses) of 1.7 across all experiments. The mean OA enhancement increased to over 3 when vapor wall losses were turned off, indicating that the presence of the chamber walls reduced SOA formation by almost a factor of 2. These results were robust across the ranges of uncertainties in the key model assumptions.

In ambient plumes, the plume dilution rate impacts partitioning between the gas and particle phases, which may impact the potential for SOA to form as well as the rate of SOA formation. Applying our model to plume evolution scenarios showed that the rapid dilution of smoke from small prescribed burns drives evaporation of organic vapors from the particle phase, leading to more effective SOA formation than in plumes emitted by large, intense wildfires. Emissions from the latter dilute more slowly, suppressing OA evaporation and subsequent SOA formation in the near field. Our results highlight that dilution and wall effects are likely contributors to past inconsistent observations and conclusions regarding the production of particulate matter from biomass burning emissions, and must be properly accounted for in future studies.

Objectives and Hypotheses

This project addressed **Task 3, *Contribution of smoke emissions to secondary organic aerosols***, advancing the state of knowledge of the impacts attributable to primary (direct) aerosol emissions vs. the impacts of particulate matter formed in the atmosphere (secondary organic aerosol, SOA) during the transport and evolution of fire emissions. For the first time, we modeled in detail the transfer of organic species between aerosol and gas phases under different lab and atmospheric conditions, showing how the formation of SOA depends upon those conditions. The key roles of meteorology and of fuel- and fire-specific data on gas and aerosol emissions were highlighted in our results.

Objective 1. To conduct detailed calculations of the phase partitioning behavior of fresh smoke emissions, including consideration of the evolving aerosol size distribution, with a view toward understanding conditions under which SOA precursors become available for oxidation.

This objective was met. We simulated phase partitioning for two scenarios. Our first scenario simulated laboratory chamber studies, in which smoke emissions are initially allowed to equilibrate with the chamber walls and then undergo oxidation, with additional re-partitioning as chemical reactions proceed. Our modeling was guided by laboratory data, providing confidence in the selection of the values for uncertain parameters. Our second scenario considered fires of different sizes emitting into atmospheres of different stabilities, affecting dilution rates, and used the physical partitioning model validated in the first scenario.

Objective 2. To use the same framework to compute the potential phase partitioning behavior of oxidation products, to improve understanding of their potential impacts on PM_{2.5} concentrations;

This objective was met. We developed very simple oxidation models that were grounded in best-estimates of reaction rates available to date, allowing the formation of species of lower volatility and simulating their phase partitioning in both the lab and free-atmosphere scenarios. Conditions optimizing the formation of SOA were identified from these studies. As new data identifying speciation of both emissions and oxidation products become available, our framework can be readily adapted to accept that information for updated simulations.

Objective 3. To apply our findings to improve understanding of how phase partitioning and its timescales may lead to potential artifacts in smog chamber experiments that seek to quantify the SOA-formation potential of biomass burning emissions, with the goal of providing corrected yields for current emission inventories and suggestions for improved experimental design.

This objective was met. Our results clearly indicated large underestimates of SOA formation in smog chamber studies, due to significant losses of precursors to chamber walls. Subsequent work in the community has confirmed and built upon those findings.

Hypothesis 1 addressed the question posed in Task 3, *What atmospheric chemical processes transform fire emissions into SOA?*

- Hypothesis 1: SOA precursors must be moved into the gas phase in order for rapid oxidation to proceed. Thus, one of the most important processes in the transformation from emissions to SOA is the repartitioning of emissions during dilution and transport, yet the details of partitioning have been largely unexplored.

Confirmed. Our simulations showed that emissions from large fires that produce heavy smoke are not efficient at near-field SOA production, because evaporation of precursors is limited.

Hypotheses 2 and 3 addressed the question posed in Task 3, *Do the emission factors and the chemical transformation mechanisms used in current smoke emissions and modeling systems sufficiently account for the production and aging of SOAs?*

- Hypothesis 2: Current estimates of SOA formation mechanisms that derive from conventional “smog chamber” experiments have failed to adequately account for the interactions of reagents and products with the walls of the chamber.

Confirmed. Our simulations showed that a large fraction of precursors, as well as some oxidation products, are partitioned to the chamber walls and thus are unaccounted for in parameterizations that fail to recognize this artifact.

- Hypothesis 3: Observations of organic aerosol “aging” likely include effects of species repartitioning, and are not solely indicative of changes due to oxidation processes. We have observed, both in the lab and the field, apparent chemical changes in emissions that are clearly not undergoing active oxidation. We hypothesize that redistribution of species among particles of different sizes and between the gas and aerosol phases has in some cases been misinterpreted as oxidation, and thus incorrect mechanisms have been proposed to explain such observations.

Partially confirmed. The datasets we worked with had only limited information on speciation. The simulations are suggestive of a role of repartitioning in apparent shifts in the ratios of oxygen to carbon (O:C) in organic aerosol that may be due largely to volatilization of more-volatile species that have lower O:C. Our findings suggest the need for additional controlled studies that identify O:C in various volatility classes and consider the potential role of phase dynamics, separately from chemical reactions.

Hypothesis 4 addressed the question posed in Task 3, *To what extent do fire combustion phase, fire intensity, fuel characteristics, and type of fire (prescribed fire or a wildfire) influence the production of precursors to SOAs?*

- Hypothesis 4: Very little is known about how these factors affect SOA precursor emission rates. Well-documented studies are beginning to fill that gap.

Partially confirmed. The datasets we worked with had some limited information on fuel characteristics. Certainly, the composition of the aerosol emissions from various fuels in the lab studies varied widely, but we had almost no information on the variations in emissions of gaseous precursor compounds since techniques for their measurement were still in their infancy for the lab studies we simulated. We therefore addressed this question by varying the assumed volatility distributions of emissions from the global “best fit” through the extremes that fit the composited dataset, and report the resulting impacts on SOA formation. Our main conclusion that chamber studies have significantly underestimated SOA production remained unchanged, although the magnitude of the underestimation varied based on the assumed emissions. Subsequent lab studies by the community have been aimed at quantifying these key uncertainties.

Background

Biomass burning is increasingly being studied as a potentially major source of atmospheric particulate matter across the US, particularly in regions where prescribed burning (Southeastern US) and wildfires (California, Northern and Southern Rockies) are prevalent. Biomass burning emissions of particulate matter are strongly dependent on fuel type, fuel moisture, and burn phase. It is now understood that biomass burning emissions undergo further chemistry in the atmosphere, in both the gas and condensed phases, leading to the formation of secondary organic aerosol (SOA). In assessing the air quality, climate, and health impacts of wild and prescribed fires, managers are faced with the possibility that biomass-burning derived SOA has potentially larger impacts, and on a broader scale, than do the direct (primary organic aerosol, POA) emissions. However, three major difficulties exist at present in understanding the aerosol-related impacts from biomass burning. The first difficulty is that traditional methods that have measured emission factors for POA have not considered the fact that the OA species are semivolatile, meaning that their partitioning between the gas and aerosol phases, and hence the mass loading of particulate matter, is highly dependent on the degree of dilution. Second, the precursors to SOA formation are largely unknown. The third difficulty in improving models of fire-derived SOA relates to the representation of SOA formation rates using estimates derived from smog chamber studies. While smog chamber studies are highly useful and represent the state of the science with respect to developing understanding of SOA formation rates and pathways, the potential exists for serious biases due to the relatively small volume of air and the presence of the chamber walls. Standard chamber walls are generally constructed of Teflon and have been shown to readily absorb many compounds, biasing experimental results in previously unknown ways.

We leveraged the availability of data from a series of smog chamber experiments performed during the Fire Lab at Missoula Experiment series (specifically, FLAME-III in 2009), that included detailed information on aerosol size distributions, volatility distributions, and evolution with time during exposure to oxidants. We built a detailed aerosol microphysics model coupled to a phase partitioning model and a simple oxidation model, and simulated a series of experiments on different fuels, adjusting the model parameters in order to match the experimental data. We could then use the resulting validated model to simulate emissions released from a fire into the free atmosphere, to explore the relative roles of dilution and

chemistry in the evolution of the particulate emissions. Those simulations were compared to data from the JFSP-sponsored SCREAM Study in 2011 (South Carolina Fire Emissions and Ageing Measurements; May et al., 2015). The framework that we built can readily accommodate new information on speciation of emissions, oxidation rates, and speciation of secondary products, as the community actively works to develop better descriptions of the atmospheric impacts of biomass burning. Similarly, we can apply this model to upcoming studies of biomass burning plumes, separating the effects of dilution, volatilization, and chemistry to achieve a deeper understanding of the observational data. The interpretation of prior field measurements, especially from aircraft, did not explicitly consider how the degree and speed of dilution would impact deductions regarding primary and secondary emissions; we showed that misleading conclusions can be reached if these factors are not taken into account.

Materials and Methods

We developed a new version of the Two-Moment Aerosol Sectional (TOMAS) microphysics model (Adams and Seinfeld, 2002), expanded by Pierce et al. (2011) to include the organic-aerosol Volatility Basis Set (Donahue et al., 2006). This version of TOMAS that we will use tracks the number and composition of particles across 40 size sections spanning diameters of 1 nm to 10 μm . The previous model tracked 11 particulate species: black/elemental carbon and 10 organic species representing condensed matter in 10 organic volatility “bins” spanning equilibrium saturation concentrations (C^*) of 10^{-4} to $10^5 \mu\text{g m}^{-3}$ (component vapor pressures of $10^{-12} \sim 10^{-3}$ torr). For this application, we expanded the model to 15 volatility bins (C^* of 10^{-3} to $10^{11} \mu\text{g m}^{-3}$). We varied the effective Henry’s Law coefficient for dissolution into Teflon, using published estimates, as this sink is a key a parameter influencing the model results but is not yet well constrained. We also added 15 new variables that represent the condensed semivolatile organic species adsorbed into the smog chamber walls. The new version of TOMAS thus explicitly simulates the size-resolved evaporation/condensation of all particle sizes during cooling and dilution processes as well as estimating the amounts of each component residing in the particulate, gas, and chamber wall phases at any point in the time-dependent simulation. For application to ambient plumes, we remove the species that represent the chamber wall “phase”, and assumed that the box expanded according to simple Gaussian plume dispersion. For that application, we defined an initial plume width corresponding to the assumed size of the fire and provided initial mass concentrations consistent with observational data; the plume expansion rates were computed for different atmospheric stability classes.

Chamber experiment data were from the FLAME-III study as reported in Hennigan et al. (2011), May et al. (2013), and Bian et al. (2015).

Data for additional volatility bins beyond those characterized in FLAME-III were based on the study by Hatch et al. (2017) for FLAME-IV experiments.

Data for ambient plumes were from the compilations published by May et al. (2014) and May et al. (2015), both acknowledging support from (other) JFSP-sponsored projects.

Results and Discussion

In Bian et al. (2015), we conducted simulations to determine how particle- and gas-phase wall losses contributed to the observed evolution of the aerosol during chamber experiments in the third Fire Lab At Missoula Experiment (FLAME III). We simulated only the initial, 1-hour, dark (no photooxidation) equilibration period when the chamber was filled with emissions from the burns that were conducted in the Lab’s combustion facility. We restricted the simulations to this period in order to find best-fit parameters that accurately captured the evolution of the aerosol size distribution as it underwent only physical processes: evaporation as emissions were mixed with clean chamber air and further evaporation as gaseous species were lost into the Teflon walls, as well as direct particle deposition to chamber surfaces. By simulating both the number and mass distributions, which were directly measured, we were able to sufficiently constrain the simulations to develop a relatively narrow range of suitable parameters, which were not well constrained prior to our studies.

We stratified the experiments based on whether the emitted aerosol was largely organic in nature, or contained a large fraction of ionic and mineral species; each category contained half of the total 18 burn experiments. Figure 1, from Bian et al. (2015), shows the best-fit simulations for the subset of the experiments with high organic fraction in the aerosol phase. The blue symbols identified as “BS” are for the base case, best-fits. From Fig. 1a, the time history of the aerosol number concentrations, it is immediately evident that particle depositional wall losses were occurring in the chamber. However, it is not clear from this simulation alone whether losses of vapors to the walls should be taken into account. Figs. 1b,c clearly show that unless vapor losses were included in the simulations, we could not represent the evolution of the measured aerosol mass concentrations for either total aerosol (TA) or the organic fraction (OA). Hence, both evaporation and depositional losses were active in the chamber experiments.

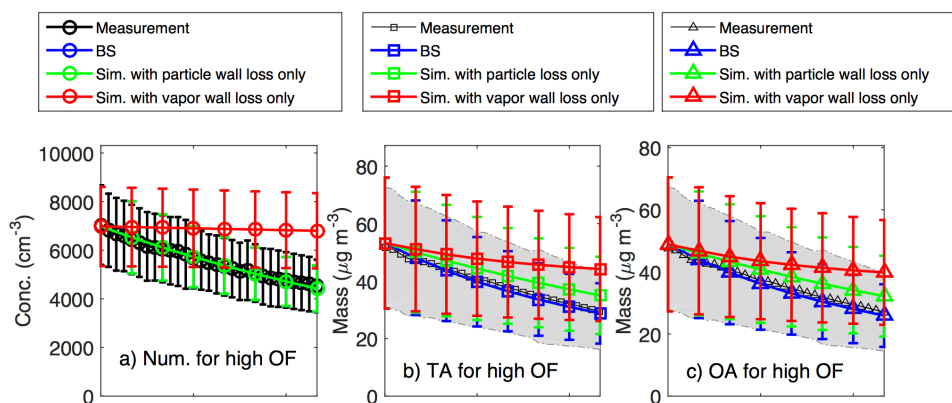


Figure 1. Measured and simulated time evolution of (a) aerosol number concentration, (b) total aerosol mass concentration, and (c) organic aerosol mass concentration. Data and simulations for the subset of experiments with high organic aerosol mass fractions are shown. From Bian et al. (2015).

In Figure 2, we show the budgets computed for losses of organic species in our simulations. About 40% of the initial organic aerosol mass is lost during the initial step of filling and equilibrating the chamber, with about one-third of this loss due to evaporation. A very large fraction, about 80%, of the initial vapor is transferred into the chamber walls and hence unavailable for oxidation.

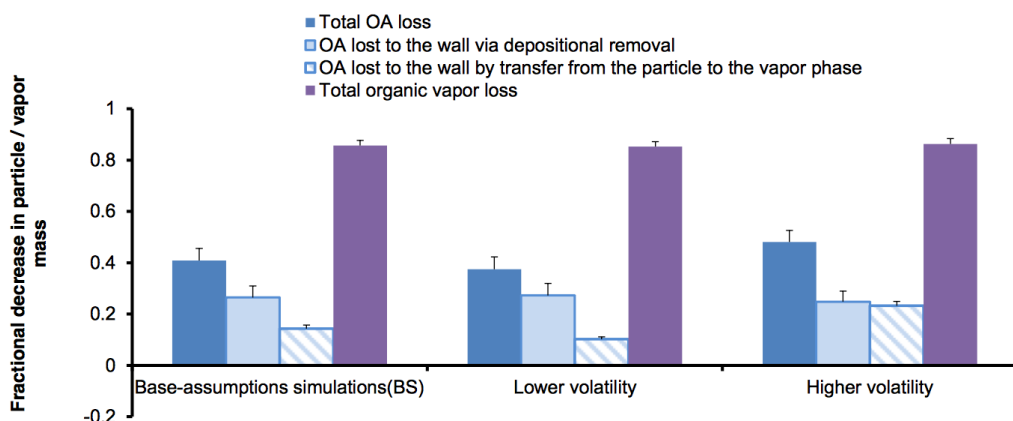


Figure 2. Fractional decreases in organic aerosol and organic vapor, as simulated in our study. Organic vapor loss is via absorption into the Teflon chamber walls. From Bian et al. (2015).

Figure 3 shows the range of volatility distributions of emissions that matched existing data, as fit by May et al. (2013). Panel (a) is the recommended best-fit distribution that was used in our base case, but clearly, the total amount of emitted vapor and its distribution with respect to vapor pressure (volatility, expressed here as the saturation concentration, C^*) is poorly constrained. Further, insufficient data exist to create such distributions for different fuels, and hence these represent an average for a large number of fuels and burn conditions. Somewhat surprisingly, however, as shown in Figure 2, these large differences in assumed volatility distributions translated into a less than 20% change in the calculated budgets of organic species. This is an encouraging result, suggesting the robustness of our findings. Nevertheless, better information on the volatility distributions for emissions from various fuels burned under varying conditions, and information on the speciation within each bin and which compounds can serve as SOA precursors, remain urgent needs.

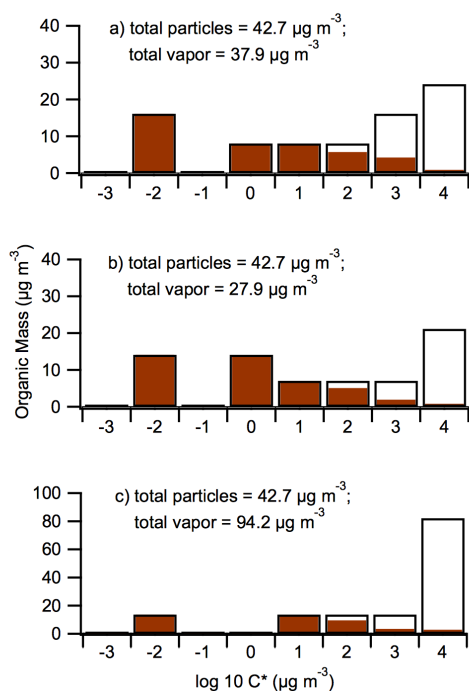


Figure 3. The range of volatility distributions used in our simulations. Panel (a) is the best-fit distribution from May et al. (2013). Panels (b) and (c) envelop the range of distributions that fit May et al.'s data within uncertainties.

We report on additional sensitivity simulations in Bian et al. (2015). Our results after 1 hour of “dark”, physics-only simulation represent the initial conditions for the subsequent FLAME-III photooxidation experiments, which we simulated in Bian et al. (2017).

To include photochemistry in the simulations, we needed to couple the TOMAS model to a gas-phase chemical oxidation mechanism. Unfortunately, since most of the semi-volatile species that are likely to oxidize to condensable products remain unspecified, we had to turn to a simplified model that had been tested in earlier studies, and conducted sensitivity tests varying that scheme to quantify the impacts on our simulations. In the simplified model, we allowed all gas-phase organics to react according to an assumed rate constant (that is a function of volatility), and the products were assigned volatilities either two or four bins lower than the precursor. We ignored fragmentation reactions, which would create higher-volatility products, and thus our assumptions may overestimate the formation of SOA. Of course, partitioning to existing particles and to the walls was computed at every time step, and thus the oxidation products did not necessarily end up in the particle phase, depending on the evolving chamber conditions.

Our simulations were able to reproduce the average OA enhancement ratio of 1.7 that was observed in the series of FLAME-III experiments, as shown in Figure 4. This agreement with the observations held over the range of sensitivity simulations we tested (hatched bars in Figure 4), and spanned the variability in the dataset of Hennigan et al. (2011). Here, the enhancement of OA indicates the additional OA mass observed, relative to an experimental tracer, selected as black carbon; this additional OA mass is assumed to be produced via chemical reactions. In other words, although the mass concentrations of aerosol are continuously decaying during the chamber experiments due to losses by deposition and possibly evaporation, the decay rate of OA is less than the decay rate of black carbon particles. Since their depositional losses should be approximately similar, it is concluded that production of OA must have occurred.

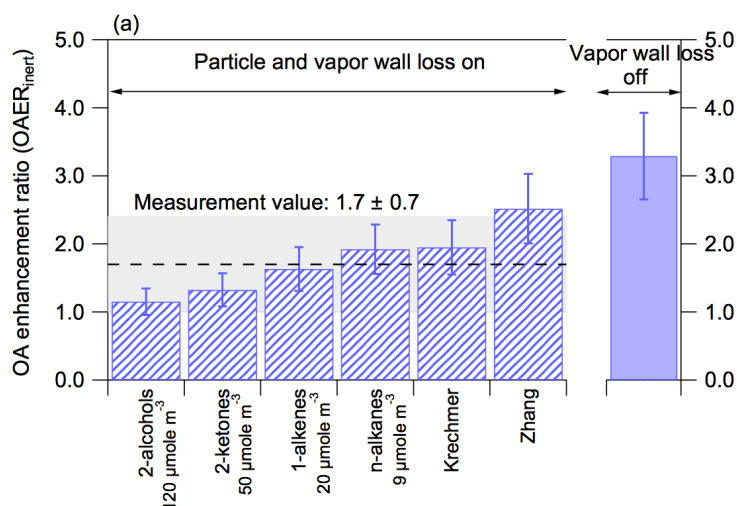


Figure 4. Comparison of the measured OA enhancement ratio reported by Hennigan et al (2011) with those simulated in our study. The hatched bars represent various sets of sensitivity simulations, as described more fully in Bian et al. (2017), all with particle and vapor wall losses simulated. The solid, right-most bar represents the simulated enhancement in the absence of losses of vapors to the chamber walls.

The solid, right-most bar in Figure 4 represents the simulated OA enhancement in the absence of losses of vapors to the chamber walls, and indicates that the presence of the chamber walls serves to significantly suppress observed OA concentrations. In fact, if the chamber walls were not absorbing, we would expect the observed OA enhancement ratio to approximately double, due to the increased availability of vapors for conversion to SOA.

In the chamber experiments, the measured OA is not speciated, and thus it is impossible to ascertain how much of the observed “excess” OA is due to SOA, since evaporation of POA may continue to occur throughout the photooxidation experiments. Indeed, some of the experiments reported in Hennigan et al (2011) have OA enhancement ratios less than 1, indicating that, while SOA formation may have occurred, it was more than offset by evaporation. In our modeling study, we have the advantage of being able to separate these effects, since we can run simulations with and without active oxidation. We added this feature to our modeling and conducted a series of experiments that simulated dilution and oxidation in a smoke plume evolving freely in the atmosphere over a 4-hour period, according to simple Gaussian dispersion under various meteorological regimes.

In Figure 5, we show the simulated time evolution of two “enhancement ratios”, for a range of fire sizes selected to represent small prescribed burns (blue and green lines) through large wildfires (red and yellow lines). In Figure 5a we show the apparent OA enhancement, calculated relative to a conserved tracer. This enhancement ratio is that which would be observed in an airborne field study that sampled a plume near its source and followed it downwind. Depending on fire size and distance downwind, enhancement ratios from 0.6 to 1.2 would be observed. For

the smallest fires, only after 4 hours does the OA recover, via addition of SOA, to close to its emitted concentrations. One might conclude from such observations that formation of SOA was relatively inefficient, since evaporation appeared to dominate over the 4-hour history of the emissions. Interestingly, the opposite is in fact the case, as shown in Figure 5b. For this figure, the enhancement ratio was calculated by conducting dual simulations of the plume, one with the SOA formation chemistry turned “on” and the other with chemistry turned “off”, and forming the ratio:

$$\text{OAER}_{\text{chem}} = (\text{OA}_{\text{chem on},t} - \text{OA}_{\text{background}}) / (\text{OA}_{\text{chem off},t} - \text{OA}_{\text{background}}).$$

As seen in Figure 5b, the smallest fires dilute faster, evaporating POA which oxidizes to SOA, more than doubling the amount of OA after 4 hours relative to the OA expected in the absence of chemistry. In contrast, larger fires produce more concentrated plumes that dilute more slowly, limiting the formation of SOA; overall, an increase of only about 20% in total OA was calculated for the larger fires, although the enhancement ratio relative to a tracer (Figure 5a) is always larger than 1, implying vigorous oxidation chemistry.

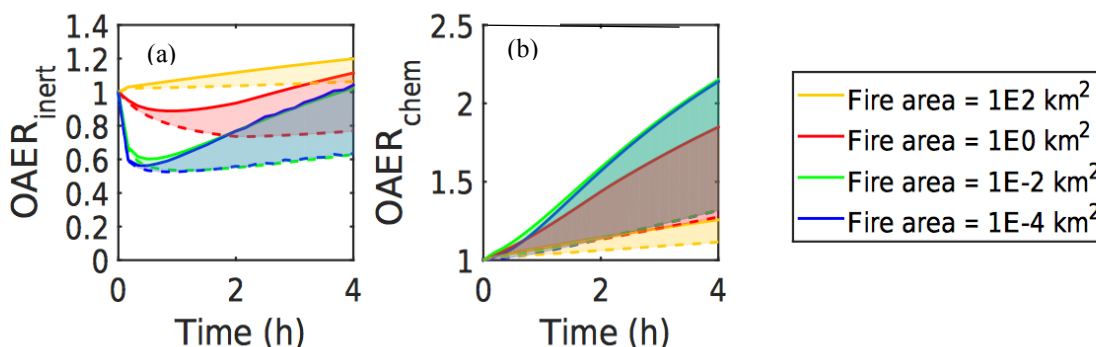


Figure 5. Calculated OA enhancement ratios: (a) in simulations with SOA production allowed to proceed, but computed for the resulting OA concentrations relative to concentrations of an inert (nonvolatile) tracer, as typically done for field observations; (b) computed by differencing simulations with oxidation chemistry turned on and off. From Bian et al. (2017).

Implications and Relevance: Our simulations are among the first to explore in detail the physical processing of smoke – the effects of dilution and deposition on the repartitioning of semivolatile species and hence on mass loadings of primary emissions. In chamber studies, because the walls are active sinks with large capacities, this repartitioning leads to losses of vapors to the walls and drives strong evaporation of emissions. In essence, semivolatile compounds are readily distilled off the particulate matter, and are absorbed into the walls, where they cannot participate in oxidation chemistry. Hence, prior work using chamber studies to quantify SOA formation from combustion emissions is likely to have a low bias in the estimated SOA formation. On average, our calculations suggest that accounting for SOA formation from these lost vapors would approximately double the estimated SOA yields, a correction that would have large impacts on predicted PM_{2.5} concentrations in regions affected by biomass burning.

In ambient plumes, since absorbing walls are not a factor, the relative rates of dilution/evaporation and chemical production control the observed evolution of OA. Although thick smoke plumes have higher OA concentrations, production of SOA is limited by the rate at which evaporation of precursors occurs and hence SOA formation represents a relatively small fractional enhancement of total OA. In contrast, the emissions from smaller fires dilute more rapidly and engage in more vigorous production of SOA – that is, more of the mass of precursor vapors is converted to SOA. These simulations imply that observational field studies should report absolute mass concentrations as well as estimates of fire size and dilution rates, in order to put observed emission ratios into proper context. Further, the simulations suggest that prescribed and wild fires have different types of impacts on air quality.

Science Delivery Activities:

Published papers in refereed journals:

Bian, Q., May, A. A., Kreidenweis, S. M., Pierce, J. R.: Investigation of particle and vapor wall-loss effects on controlled wood-smoke smog-chamber experiments, *Atmos. Chem. Phys.*, 15, 11027-11045, doi:10.5194/acp-15-11027-2015, 2015.

Article and supplement are available for download at: <https://www.atmos-chem-phys.net/15/11027/2015/>

Bian, Q., Jathar, S. H., Kodros, J. K., Barsanti, K. C., Hatch, L. E., May, A. A., Kreidenweis, S. M., and Pierce, J. R.: Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies and ambient plumes, *Atmos. Chem. Phys.*, 17, 5459-5475, doi:10.5194/acp-2016-949, 2017.

Article and supplement are available for download at: <https://www.atmos-chem-phys.net/17/5459/2017/>

Presentations at conferences:

Qijing Bian, Andrew May, Sonia Kreidenweis, Jeffrey Pierce, “Investigation of Particle and Vapor Wall-loss Effects on Controlled Wood-smoke Smog-chamber Experiments”, Abstract 181, presented at the American Association of Aerosol Research Annual Meeting, Minneapolis, MN, October 12-16, 2015. Abstract available for download at

<http://aarabstracts.com/2015/viewabstract.php?pid=181>

Pierce, J. R., Bian, Q.-j., Kreidenweis, S. M., Kodros, J. K., Jathar, S., May, A., Hatch, L., Barsanti, K., "Investigation of particle and vapor wall-loss effects on controlled wood-smoke smog-chamber experiments", Paper SS3.4, Presented at the International Association of Wildland Fire, 5th International Fire Behavior and Fuels Conference, *Wicked Problem, New Solutions: Our Fire, Our Problem*, Portland, Oregon and Melbourne, Australia, April 11-15, 2016. Abstract available for download at

<http://portland.firebehaviorandfuelsconference.com/wp-content/uploads/sites/2/2015/06/Special-Session-Abstracts-Portland.pdf>

Qijing Bian, Shantanu Jathar, John Kodros, Kelley Barsanti, Lindsay Hatch, Andrew May, Sonia Kreidenweis, Jeffrey R. Pierce, "Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies", Abstract 10, presented at the American Association of Aerosol Research Annual Meeting Portland, OR, October 17-21, 2016. Abstract available for download at <http://aarabstracts.com/2016/viewabstract.php?pid=10>

Bian, Q., Pierce, J. R., Kodros, J. K., Kreidenweis, S. M., Jathar, S., May, A., Barsanti, K., Hatch, L., "Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies", International Smoke Symposium, IAWF, Long Beach, CA, November 14-17, 2016. Abstract available for download at <http://www.iawfonline.org/ISS2%20Oral%20Presentation%20Abstracts.pdf>

Other presentations:

Pierce, J. R., Bian, Q.-j., May, A., Jathar, S., Kodros, J. K., Barsanti, K., Hatch, L., Kreidenweis S. M., "Exploring the evolution of biomass-burning aerosol in chambers and the atmosphere", University of Colorado (Invited Seminar), Chemistry, October 2016.

Kreidenweis, S. M., Pierce, J. R., Bian, Q.-j., May, A., Jathar, S., Kodros, J. K., Barsanti, K., Hatch, L., "Biomass burning aerosol: Emissions, evolution, and atmospheric impacts," seminar to be presented in the William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, September 7, 2017.

Data Archive:

<https://www.fs.usda.gov/rds/archive/Product/RDS-2017-0019/>

Key Findings. Our simulations confirmed that reliance on laboratory smog chamber experiments to quantify the potential for biomass burning emissions to create secondary organic aerosol (SOA) is problematic. Even considering the range of uncertainties in some of the key parameters, we find that large losses of aerosol precursors occur in all cases, and thus SOA formation is generally underpredicted. Reasons for large fuel-to-fuel / experiment-to-experiment differences in SOA formation remain uncertain, and additional studies are urgently needed to identify important aerosol precursors and their product compounds. Such data would help refine the model and provide more granularity on how larger-scale air quality models should be adapted to more accurately represent SOA formation from this source.

In a similar vein, using field observations in diluting plumes to quantify SOA formation is also problematic. Our model clearly shows the competition between evaporation of emissions and formation of new condensable compounds, which vary with fire size and with plume dilution

rates. The result is that a plume that appears to be nearly unchanging in mass concentration may actually be quite photochemically active. It is important that additional data be taken and reported in field studies, including absolute mass concentrations and plume dilution rates, so that the modeling studies can be used to place observations in a proper context.

Implications of the results to management/policy. One of the issues faced by wildland managers is selecting between multiple prescribed burns and a single larger burn to treat targeted areas. Our work shows that impacts on regional scales, where SOA formation plays a large role, can be quite different. To our knowledge, this factor has heretofore not been taken into account in management decisions.

Air quality models clearly require modification of current assumptions regarding SOA formation from biomass burning emissions. Our results suggest the SOA formation has been underestimated by at least a factor of 2, if it has been determined from smog chamber data. We do note, however, that we did not investigate the fate of oxidation products, and it is possible these are broken down and volatilized on short enough time scales that a factor of 2 impact on mass loadings is not realized in practice.

Opportunities for direct implementation by end users. Modeling teams can test our parameterized reactions and other model parameters in air quality models, reactive plume models used to analyze field observation, or other model systems. Teams engaged in field studies should consider additional measurements and/or additional methods for analyzing data in order to more accurately determine the atmospheric impacts of emissions based on observational data. It is likely that a combination of observations and models is required for all such applications.

Implications for future research. Some uncertainties that should be addressed by the modeling community include: refinement of smoke volatility distributions, especially as a function of fuel type; identification of aerosol precursors and their properties; and improved chemical mechanisms leading to the formation of SOA. The observational community should consider revised strategies and new analysis procedures to enable further progress in the interpretation of field data.

Literature Cited

Adams, P. J. and Seinfeld, J. H.: Predicting global aerosol size distributions in general circulation models, *J. Geophys. Res.*, 107, 4370, doi:10.1029/2001JD001010, 2002.

Bian, Q., May, A. A., Kreidenweis, S. M., Pierce, J. R.: Investigation of particle and vapor wall-loss effects on controlled wood-smoke smog-chamber experiments, *Atmos. Chem. Phys.*, 15, 11027-11045, doi:10.5194/acp-15-11027-2015, 2015.

Bian, Q., Jathar, S. H., Kodros, J. K., Barsanti, K. C., Hatch, L. E., May, A. A., Kreidenweis, S. M., and Pierce, J. R.: Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies and ambient plumes, *Atmos. Chem. Phys.*, 17, 5459-5475, doi:10.5194/acp-2016-949, 2017.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40, 2635–2643, doi:10.1021/es052297c, 2006.

Hatch, L. E., Yokelson, R. J., Stockwell, C. E., Veres, P. R., Simpson, I. J., Blake, D. R., Orlando, J. J., and Barsanti, K. C.: Multi-instrument comparison and compilation of non-methane organic gas emissions from biomass burning and implications for smoke-derived secondary organic aerosol precursors, *Atmos. Chem. Phys.*, 17, 1471–1489, doi:10.5194/acp-17-1471-2017, 2017.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W.-M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett Jr., J. L., Kreidenweis, S. M., and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, *Atmos. Chem. Phys.*, 11, 7669–7686, doi:10.5194/acp-11-7669-2011, 2011.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L., Kreidenweis, S. M., and Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, *J. Geophys. Res.-Atmos.*, 118, 11327–11338, doi:10.1002/jgrd.50828, 2013.

May, A. A., et al., Aerosol emissions from prescribed fires in the United States: A synthesis of laboratory and aircraft measurements, *J. Geophys. Res. Atmos.*, 119, doi:10.1002/2014JD021848, 2014.

May, A. A., Lee, T., McMeeking, G. R., Akagi, S., Sullivan, A. P., Urbanski, S., Yokelson, R. J., and Kreidenweis, S. M.: Observations and analysis of organic aerosol evolution in some prescribed fire smoke plumes, *Atmos. Chem. Phys.*, 15, 6323-6335, <https://doi.org/10.5194/acp-15-6323-2015>, 2015.

Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petäjä, T., Junninen, H., Worsnop, D. R., and Donahue, N. M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, *Atmos. Chem. Phys.*, 11, 9019– 9036, doi:10.5194/acp-11-9019-2011, 2011.

Appendices

Appendix A: Contact Information for Key Project Personnel

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Appendix B: List of Completed/Planned Scientific/Technical Publications/Science Delivery Products:

1. Articles in peer-reviewed journals:

Bian, Q., May, A. A., Kreidenweis, S. M., Pierce, J. R.: Investigation of particle and vapor wall-loss effects on controlled wood-smoke smog-chamber experiments, *Atmos. Chem. Phys.*, 15, 11027-11045, doi:10.5194/acp-15-11027-2015, 2015.

Article and supplement are available for download at: <https://www.atmos-chem-phys.net/15/11027/2015/>

Bian, Q., Jathar, S. H., Kodros, J. K., Barsanti, K. C., Hatch, L. E., May, A. A., Kreidenweis, S. M., and Pierce, J. R.: Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies and ambient plumes, *Atmos. Chem. Phys.*, 17, 5459-5475, doi:10.5194/acp-2016-949, 2017.

Article and supplement are available for download at: <https://www.atmos-chem-phys.net/17/5459/2017/>

2. Technical reports: N/A.

3. Text books or book chapters: N/A

4. Graduate thesis: N/A

5. Conference or symposium proceedings scientifically recognized and referenced (other than abstracts): N/A

6. Conference or symposium abstracts:

Qijing Bian, Andrew May, Sonia Kreidenweis, Jeffrey Pierce, "Investigation of Particle and Vapor Wall-loss Effects on Controlled Wood-smoke Smog-chamber Experiments", Abstract 181, presented at the American Association of Aerosol Research Annual Meeting, Minneapolis, MN, October 12-16, 2015. Abstract available for download at

<http://aaarabstracts.com/2015/viewabstract.php?pid=181>

Pierce, J. R., Bian, Q.-j., Kreidenweis, S. M., Kodros, J. K., Jathar, S., May, A., Hatch, L., Barsanti, K., "Investigation of particle and vapor wall-loss effects on controlled wood-smoke smog-chamber experiments", Paper SS3.4, Presented at the International Association of Wildland Fire, 5th International Fire Behavior and Fuels Conference, *Wicked Problem, New Solutions: Our Fire, Our Problem*, Portland, Oregon and Melbourne, Australia, April 11-15, 2016. Abstract available for download at

<http://portland.firebehaviorandfuelsconference.com/wp-content/uploads/sites/2/2015/06/Special-Session-Abstracts-Portland.pdf>

Qijing Bian, Shantanu Jathar, John Kodros, Kelley Barsanti, Lindsay Hatch, Andrew May, Sonia Kreidenweis, Jeffrey R. Pierce, "Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies", Abstract 10, presented at the American Association of Aerosol Research Annual Meeting Portland, OR, October 17-21, 2016. Abstract available for download at <http://aarabstracts.com/2016/viewabstract.php?pid=10>

Bian, Q., Pierce, J. R., Kodros, J. K., Kreidenweis, S. M., Jathar, S., May, A., Barsanti, K., Hatch, L., "Secondary organic aerosol formation in biomass-burning plumes: Theoretical analysis of lab studies", International Smoke Symposium, IAWF, Long Beach, CA, November 14-17, 2016. Abstract available for download at <http://www.iawfonline.org/ISS2%20Oral%20Presentation%20Abstracts.pdf>

7. Posters: N/A

8. Workshop materials and outcome reports: N/A

9. Field demonstration/tour summaries: N/A

10. Website development: N/A

11. Presentations/webinars/other outreach/science delivery materials:

Pierce, J. R., Bian, Q.-j., May, A., Jathar, S., Kodros, J. K., Barsanti, K., Hatch, L., Kreidenweis S. M., "Exploring the evolution of biomass-burning aerosol in chambers and the atmosphere", University of Colorado (Invited Seminar), Chemistry, October 2016.

Kreidenweis, S. M., Pierce, J. R., Bian, Q.-j., May, A., Jathar, S., Kodros, J. K., Barsanti, K., Hatch, L., "Biomass burning aerosol: Emissions, evolution, and atmospheric impacts," seminar to be presented in the William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, September 7, 2017.

Notes: (1) Do not append copies of the preceding publications or unpublished materials to your report; rather, upload these to the **Other Products tab** or if a required deliverable to the **Deliverables tab**. (2) For published materials subject to licensing agreement requirements, please note the JFSP policy posted on the **Other Products tab** and flag the uploaded material appropriately (i.e., publicly releasable or not). If materials are not by copyright publicly releasable via a public website but you still want the JFSP to have access to them, select **Draft** (under the **Product Status field**). This will preclude the materials from being publicly accessible. (3) JFSP encourages PIs to periodically update materials on the **Other Products tab** after the project is complete.

Appendix C: Metadata

We have followed the proposed Data Management Plan. The data archived include the output from our simulations, and are referenced to the corresponding figure numbers in our two publications.

Metadata can be found at:

https://www.fs.usda.gov/rds/archive/products/RDS-2017-0019/_metadata_RDS-2017-0019.html

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