

Final Report: “The Influence of Organic-Aerosol Emissions and Aging on Regional and Global Aerosol Size Distributions and the CCN Number Budget” (**ER65296-1038624-0017484**). The PI attends ASR team meetings and is active in the Aerosol Lifecycle Working Group, focusing on organic-aerosol aging and new-particle formation. As part of our participation in FLAME-IV we have developed a collaboration with the optical properties group at Los Alamos National Laboratory led by M. K. Dubey.

We conducted laboratory experiments and analyzed data on aging of organic aerosol and analysis of field data on volatility and CCN activity. With supplemental ASR funding we participated in the FLAME-IV campaign in Missoula MT in the Fall of 2012, deploying a two-chamber photochemical aging system to enable experimental exploration of photochemical aging of biomass burning emissions. Results from that campaign will lead to numerous publications, including demonstration of photochemical production of Brown Carbon (BrC) from secondary organic aerosol associated with biomass burning emissions as well as extensive characterization of the effect of photochemical aging on the overall concentrations of biomass burning organic aerosol. Excluding publications arising from the FLAME-IV campaign, project research resulted in 8 papers: [11, 5, 3, 10, 12, 4, 8, 7], including one in *Nature Geoscience* addressing the role of organic compounds in nanoparticle growth [11]. The results from FLAME-IV lead to 4 additional publications: [14, 16, 1, 15] including one in *Nature Geoscience* on formation of brown carbon from biomass burning [14].

We made extensive progress in development of the two-dimensional volatility basis set (2D-VBS). We have developed a parameterization giving rate constants for reactions of organics with OH radicals within the 2D-VBS, including representation of heterogeneous aging [3]. In Fig. 1 we show a synopsis of this presented at Faraday Discussion on Atmospheric Chemistry in 2013 [10] showing that the average age of SOA in the Eastern US is roughly 1 day, but that the average lifetime of semivolatile organics associated with organic aerosols is generally much less than 1 day, indicating that organic aerosol will typically be heavily aged under most summertime conditions. We showed that during this organic aerosol aging, condensation of organic compounds to particles throughout the size distribution

A critical input to model calculations of SOA aging is the product distribution (the volatility distribution in VBS jargon) of the initial “fresh” SOA. Furthermore, the interactions of biogenic and anthropogenic SOA remain a topic of great interest. Therefore, we assessed the formation of first-generation SOA from α -pinene oxidation by different oxidants, finding that oxidation by OH radicals produces somewhat more SOA with on average a lower volatility than oxidation by ozone and suggesting model parameters to describe these different formation pathways [5].

To study organic-aerosol aging in the laboratory, we elected to work with the important toluene secondary organic aerosol system. In an earlier publication we had shown that toluene SOA levels are higher than previously estimated, but also that the degree of oxidation of the toluene SOA correlates with the amount of OH exposure during SOA formation [6]. Because model simulations have shown that aging of anthropogenic SOA can have an important role in both the level and degree of oxidation of simulated ambient organic aerosol, we decided to investigate this further. In collaboration with Thanos Nenes at Georgia Tech we conducted several experiments in which toluene was subjected to varying degrees of oxidation, measur-

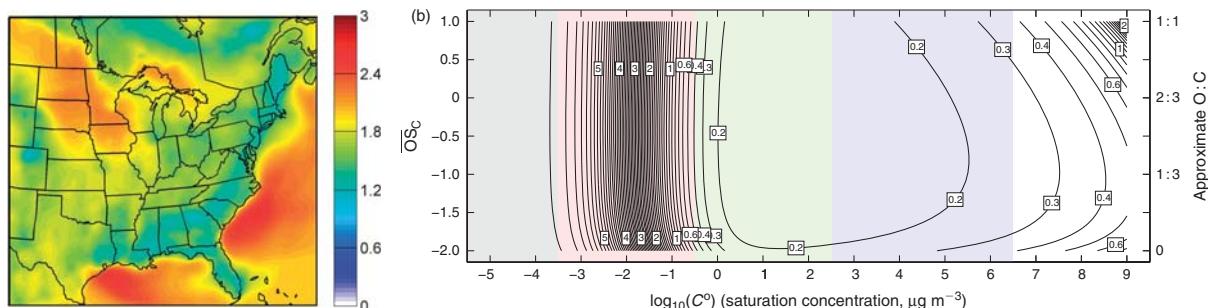


Figure 1: (a) Average age of organic aerosol in the Eastern United States in July using the Volatility Basis Set. (b) Average lifetime of organic species represented in the 2D-VBS in days.

ing the levels and composition of the SOA using a high-resolution Aerosol Mass Spectrometer, volatility using a thermodenuder, and CCN activity using a DMT CCN counter.

We made a significant contribution to the practice of AMS data analysis [2]. The most chemically sound metric for oxidation is the mean oxidation state of carbon: $\overline{OS}_C = 2O:C - H:C$, as described by Kroll *et al.* [9]. \overline{OS}_C is a “good” metric for oxidation and thus tends to increase monotonically during oxidation processes. In addition, non-oxidative phenomena such as dehydration (eliminating H_2O) will change O:C but not \overline{OS}_C . This means that \overline{OS}_C should also be a “better” metric for AMS data analysis because it eliminates the need to accurately estimate the organic contribution to various water signals in the aerosol mass spectrum, which can come from myriad sources. In the process of analyzing data from these campaigns, we realized that the currently accepted data analysis procedures for AMS data did not properly conserve water. Specifically, signal of protons at $m/z = 1$ was ignored. Some water signal exists at $m/z = 18$, but some at $m/z = 17$ (OH), which should have a companion signal at $m/z = 1$. The omission of this signal has a negligible effect on the total organic mass, but a nontrivial effect on the \overline{OS}_C calculation. In addition, we were able to work out an appropriate way to account for organic nitrates ($RO-NO_2$) by treating the NO_2 moiety as an independent group and ignoring it for calculations of O:C and \overline{OS}_C .

In a succession of aging experiments on the toluene SOA system we showed that OA produced under more highly oxidizing conditions was significantly more oxidized, less volatile, and more hygroscopic (acting as a better CCN) than OA produced under less highly oxidizing conditions. Significant signals from organic nitrates observed at high NO_x levels are also relatively volatile, as expected based on volatility predictions [7]. We observed a modest inverse relationship between hygroscopicity and \overline{OS}_C , as shown in Fig. 2, suggesting that the less volatile, more oxidized material remaining after thermal denuding may well consist of higher molecular weight products (oligomers), which have reduced hygroscopicity [7]. We developed a methodology to better constrain the volatility distribution of organic aerosol before and after aging by combining thermodenuder measurements with dilution experiments [8].

Using data from the FLAME-III campaign at the Missoula Fire Sciences Laboratory, we found that both fresh and aged organics in wood smoke (BBOA) are significantly light absorbing (brown), though the aged (SOA) from BBOA has a lower molar absorptivity (k_{OA}) [12]. These observations were part of the foundation for the FLAME-IV campaign.

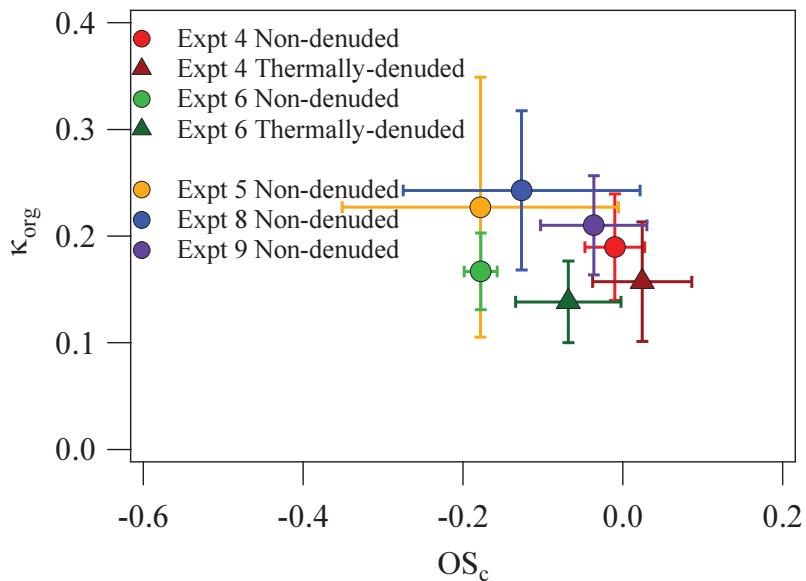


Figure 2: (a) Relationship between hygroscopicity (κ) and oxidation state of carbon (\overline{OS}_C) during aging of SOA formed from toluene photooxidation.

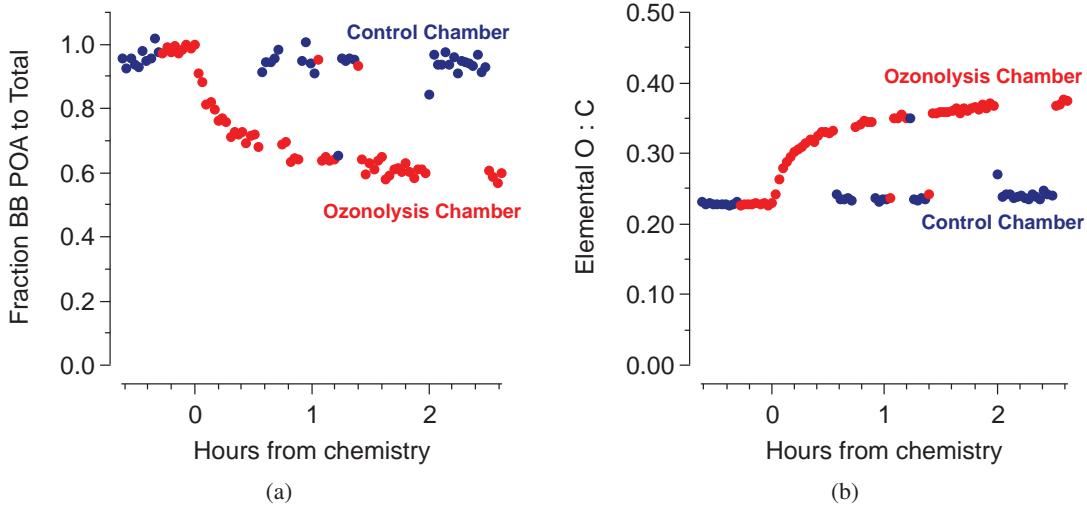


Figure 3: (a) Fraction of POA to total OA as a function of time of oxidation. Control chamber was left unperturbed for the course of the experiment. After 3 hours of oxidation, half of the suspended OA was SOA, the other half POA. (b) Time series of elemental O:C calculated from high-resolution AMS data. Little oxidative change was seen in the POA measured from the control chamber, while oxidation caused a doubling of O:C in the suspended OA.

FLAME-IV: The FLAME-IV experiment made use of a dual smog chamber setup [16], which allowed for more precise understanding of biomass burning organic aerosol (BBOA) composition changes, mass enhancements, and other physical properties than the single-chamber design used in FLAME-III (also with CMU participation) [12]. During FLAME-IV we developed a significant collaboration with Los Alamos National Lab (Manvendra Dubey) focused on experimental constraints of biomass burning optical properties. When using one chamber as a control and the other as a photochemical reactor, we can more accurately characterize chemical evolution of the primary smoke emissions, and constrain any changes in our aerosol due to wall losses. The “control” is sometimes no action and sometimes some form of aging for comparison; we calculate dual-chamber enhancements (DUCE) in each case. This eliminates the burn-to-burn variability of smoke as a source of variability.

Methods:

- Aerosol non-refractory chemical composition analysis using the HR-ToF-AMS.
- BC quantification in biomass-burning emissions using the Single- Particle Soot Photometer (SP2)
- Collection efficiency estimation and change with BBOA chemical evolution measured using the light scattering single particle (LSSP) module from the HR-ToF-AMS.

Results: For all experiments performed at FLAME-IV, we measured the chemical evolution of the non-refractory aerosol. In the Ponderosa Pine and Black Spruce burning experiments, the BC mass measured by the SP2 was low compared to the organic mass measured by the AMS. Inorganics measured by the AMS were negligible. For a series of fuels selected as potential high emitters of ice nuclei (IN), BC and inorganics comprised a much higher fraction of the total particulate mass, including very high levels of chlorine for two of the fuels. Regardless of the chemical perturbation (UV lights, O₃, OH from HONO+UV), we see chemical changes in the BBOA in our reaction chamber, indicating that secondary organic aerosol (SOA) formation is important for the fuel types and burn conditions of these experiments. Using a residual method, we have estimated the amount of primary organic aerosol (POA) versus SOA as a function of time from chemical perturbation. Interestingly, even when there is no measured mass enhancement, which was the case for some of the experiments, there is oxidation of the aerosol. Fig. 3a shows this, as the fraction of POA decreases when ozone is added to the reaction chamber in the 121101 Ponderosa Pine experiment. Fig. 3b

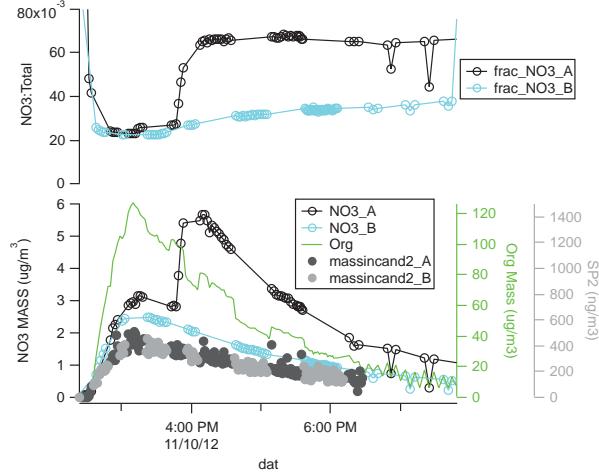


Figure 4: Time series identifying the presence of organonitrates for 121110 Black Spruce burn. Top panel shows the fraction of measured nitrate to total organic mass, with a dramatic increase prior to 4:00PM in the chamber where OH was added from HONO+UV (black markers), and a more gradual increase in the chamber where only UV lights were applied (blue markers). Bottom panel shows measured nitrate and organic masses from the AMS and BC mass from SP2 used for wall corrections.

shows the evolution of oxidation in the particles as a function of time from the ozone injection, as well as the lack of chemical change in the non-perturbed control chamber.

As Fig. 4 shows, we also see indications of the formation of organic nitrates with oxidation. We observe strong signals of $m/z = 30$ (NO^+) and $m/z = 46$ (NO_2^+) in the POA for almost all experiments, with an increase (relative to total measured organic mass) after the chemical perturbation. The fragmentation ratio between NO^+ and NO_2^+ is of order 10 for all experiments, consistent with organic nitrates.

Optical Closure: In collaboration with LANL, we perform optical closure analysis to determine the imaginary part of the refractive indices (absorptivity) of organic aerosol (OA) in fresh and aged biomass burning emissions. The derived imaginary part of the refractive indices (k_{OA}) can be used in chemical transport models employing Mie-theory to predict light absorption for different atmospheric conditions. Optical closure combines Mie theory model calculations with light absorption and aerosol size distribution measurements to determine optical properties of the aerosol [12]. The procedure includes the following steps:

1. Measure black carbon (BC) and total size distributions using a Single Particle Soot Photometer (SP2) and a Scanning Mobility Particle Sizer (SMPS), respectively.
2. Infer the mixing state of BC and OA from the SP2 and SMPS measurements [12].
3. Measure absorption coefficients as a function of wavelength of the aerosol ensemble using a 7-wavelength Aethalometer and a 3-wavelength Photo Acoustic Soot Spectrometer (PASS-3, LANL).
4. Optimize the Mie-theory model using BC and OA size distributions as inputs in order to match the observed absorption coefficients, with the free parameter being the wavelength-dependent k_{OA} .

Fig. 5a shows an example of optical closure analysis, for fresh black spruce emissions. The red symbols are the absorption coefficient data points used to constrain the Mie theory model (black solid line). The Aethalometer measurements are prone to artifacts related to organic loadings on the filter, which can lead to bias in the magnitude of the absorption coefficients; however, the Aethalometer is reliable in determining the wavelength-dependence of the absorption curve [12]. PASS-3 provides more accurate absorption coefficient measurements. In this work, we use the PASS-3 data to scale the Aethalometer data, and then the data points from the two instruments are used in the optical closure analysis, as shown in Fig. 5a. The advantage of

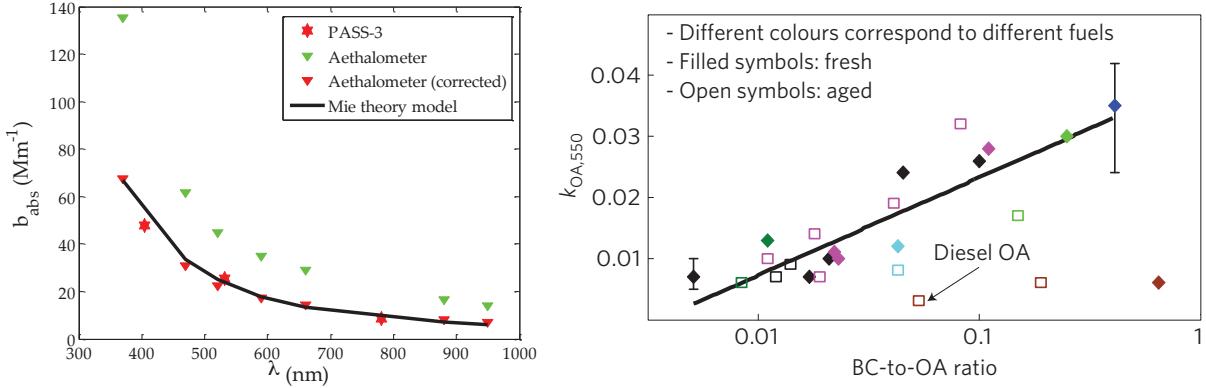


Figure 5: (a) Optical closure analysis for fresh black spruce emissions to obtain molecular absorption coefficient (kOA) for one burn condition. (b) Overall relationship between absorptivity (brownness) of BrC and black-carbon content (BC:OA) of the emissions.

this over relying solely on PASS-3, is to obtain more data points over a wider range of wavelengths, which constitutes a better constraint.

Analyzing the optical properties of the complete set of burns, with and without aging chemistry, we observed a relationship between the molecular absorptivity (kOA) of the brown carbon and the amount of black carbon in the BBOA (BC:OA). This relationship is mechanistically plausible, as it suggests that the chromophores in BBOA brown carbon are “frustrated black carbon” formed by the same pyrolysis mechanism in fuel rich combustion conditions. These findings do not suggest that the overall absorptivity (b_{abs}) of high-BC biomass-burning emissions is higher than smoky high-OA emissions, because the mildly absorbing BrC in emissions with high OA content can still lead to more overall absorption. It does show, however, that on a molecule by molecule basis the high BC brown carbon is far more efficient at absorbing light.

The implications of this finding are substantial, and thus we were able to publish the work in *Nature Geoscience* [14]. First, the relatively refractory brown carbon does not evaporate in most thermodenuders, and it exists both as a coating on BC cores as well as independently in an external mixture (as part of “tarballs”). This means that analysis of optical properties – specifically lensing – in experiments where thermodenuders are used to strip OA off of BC cores must be undertaken with great care to consider both the (absorbing and lensing) BrC residual after thermal denuding as well as the externally mixed (absorbing) BrC that remains after thermal denuding. This can significantly affect data interpretation. Second, the findings suggest an easily implementable parameterization that could and does explain variability in absorptivity for various biomass burning environments around the globe. We have in fact developed and implemented such a parameterization in the global model GEOS-Chem and shown that it has high skill in predicting absorptivity in biomass-burning emissions. We also showed that proper treatment of both the mixing state and coupled absorption and refraction in lensing BrC material has a large effect on the predicted optical properties [13].

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