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physical
transformations of
organic aerosol**

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Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber

C. J. Hennigan¹, M. A. Miracolo¹, G. J. Engelhart¹, A. A. May¹, A. A. Presto¹, T. Lee², A. P. Sullivan², G. R. McMeeking², H. Coe³, C. E. Wold⁴, W.-M. Hao⁴, J. B. Gilman^{5,6}, W. C. Kuster^{5,6}, J. de Gouw^{5,6}, B. A. Schichtel⁷, J. L. Collett Jr.², S. M. Kreidenweis², and A. L. Robinson¹

¹Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, USA

²Department of Atmospheric Science, Colorado State University, Fort Collins, USA

³Centre for Atmospheric Science, University of Manchester, Manchester, UK

⁴Missoula Fire Sciences Laboratory, US Forest Service, Missoula, USA

⁵Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, USA

⁶Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Boulder, USA

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⁷National Park Service/CIRA, Colorado State University, Fort Collins, USA

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Correspondence to: C. J. Hennigan (hennigan@andrew.cmu.edu)

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Abstract

Smog chamber experiments were conducted to investigate chemical and physical transformations of organic aerosol (OA) during photo-oxidation of open biomass burning emissions. The experiments were carried out at the US Forest Service's Fire Science Laboratory as part of the third Fire Lab at Missoula Experiment (FLAME III). We investigated 12 different fuels commonly burned in North American wildfires. The experiments feature atmospheric and plume aerosol and oxidant concentrations; aging times ranged from 3–4.5 h. OA production, expressed as a mass enhancement ratio (ratio of OA to primary OA (POA) mass), was highly variable. OA mass enhancement ratios ranged from 2.9 in experiments where secondary OA (SOA) production nearly tripled the POA concentration, to 0.7 in experiments where photo-oxidation resulted in a 30% loss of the OA mass. The campaign-average OA mass enhancement ratio was 1.7 ± 0.7 (mean $\pm 1 \sigma$); therefore, on average, there was substantial SOA production. In every experiment, the OA was chemically transformed. Even in experiments with net loss of OA mass, the OA became increasingly oxygenated and less volatile with aging, indicating that photo-oxidation transformed the POA emissions. Levoglucosan concentrations were also substantially reduced with photo-oxidation. The transformations of POA were extensive; using levoglucosan as a tracer for POA, unreacted POA only contributed 17% of the campaign-average OA mass after 3.5 h of exposure to typical atmospheric hydroxyl radical (OH) levels. Heterogeneous reactions with OH could account for less than half of this transformation, implying that the coupled gas-particle partitioning and reaction of semi-volatile vapors is an important and potentially dominant mechanism for POA processing. Overall, the results illustrate that biomass burning emissions are subject to extensive chemical processing in the atmosphere, and the timescale for these transformations is rapid.

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substantial chemical and physical processing of the OA, suggesting a dynamic aging process for these systems. Both the variable nature of biomass emissions (e.g., Andreae and Merlet, 2001) and the large uncertainties in SOA formation demonstrate the need to empirically characterize SOA from biomass burning.

Environmental chambers provide an opportunity to investigate the OA chemistry under well characterized aging conditions, pollutant concentrations, fuel type and combustion conditions. Further, in the laboratory smoke can be aged in the absence of other emissions, such as dust or anthropogenic pollution. Laboratory data can then be used to develop predictions for the field that can be evaluated through direct measurements and models.

As part of the third Fire Lab at Missoula Experiment (FLAME III) study, we conducted a series of smog chamber experiments to investigate the effects of photo-oxidation on emissions from open biomass combustion. We investigated 12 different vegetation types commonly burned in North American wildfires (Table 1). The specific objectives of this paper include quantifying net SOA production and characterizing chemical transformations of POA.

2 Materials and methods

2.1 Methods

The FLAME III study was conducted at the US Forest Service's Fire Science Laboratory (FSL) in Missoula, MT during September–October 2009. To investigate the effects of photo-oxidation, primary emissions were sampled into an environmental or smog chamber after conducting a “chamber burn” in the FSL's main combustion chamber, a 12.4 × 12.4 × 19.6 m room (Fig. 1). The FSL facility is described in detail elsewhere (Yokelson et al., 1996; Christian et al., 2003; McMeeking et al., 2009). FLAME III investigated fuels representing different regions in North America commonly impacted by prescribed burning and wildfires (Table 1), including the Southeast (e.g., gallberry

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and pocosin), southern California (e.g., sagebrush and chamise) and forest regions of the western United States and Canada (e.g., ponderosa pine, lodgepole pine, and black spruce).

During a chamber burn, a small mass (0.3–1.0 kg) of fuel was placed on a ceramic plate atop a scale used to quantify the mass of fuel consumed during combustion. The fuel was ignited using electric heating coils that were pre-conditioned with a small amount of ethanol (~5 mL). The fuel bed was allowed to burn to completion, filling the FSL 3000 m³ combustion chamber with smoke from the entire burn event, including the flaming and smoldering phases. The FSL combustion chamber typically became well-mixed within 20 min after the burn was completed, as indicated by a suite of gas and aerosol measurements.

The schematic in Fig. 1 shows the experimental set up for the photo-oxidation experiments, which were performed in a 7.0 m³ Teflon smog chamber located outdoors, immediately adjacent to the western wall of the FSL burn chamber facility. Instrumentation for chamber experiments was housed in the Carnegie Mellon University (CMU) mobile air quality laboratory, which was parked adjacent to the smog chamber.

Two ejector dilutors (Dekati, Helsinki, Finland) and a heated, stainless steel transfer line were used to fill the smog chamber with smoke from the FSL combustion chamber. This inlet system pulled smoke from the FSL combustion chamber at a total flow rate of 15 L min⁻¹. The inlet to the transfer line inside the FSL combustion chamber was ~2 m from the wall and ~2 m off the ground to minimize wall or boundary effects. The transfer line was constructed of stainless steel tubing (1.07 cm ID) with a total length of approximately 12 m. The transfer line and ejector dilutors were electrically heated to 40 °C to reduce losses of semi-volatile components. The ejector dilutors were operated on conditioned (dried, HEPA- and activated-carbon filtered) air that had been heated to 40 °C. Prior to filling the smog chamber, the transfer line system was flushed with heated conditioned air for 1.5 h and then flushed with smoke from the FSL burn chamber for 30 min, venting the smoke through a bypass exhaust immediately upstream of the smog chamber. This was done to condition the transfer line, which should reduce

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losses of semi-volatile organic vapors. Particle losses in the transfer line system were characterized in separate experiments using dried atomized sodium chloride aerosol. The transmission efficiency was, on average, 0.94 across a particle electrical mobility diameter size range of 50–400 nm. No corrections were applied to account for losses in the transfer line.

Before each experiment, the portable smog chamber was flushed for at least 12 hours with conditioned air and then partially evacuated prior to smoke injection so that the final dilution ratio of the smoke inside the smog chamber was ~15:1 (relative to the FSL combustion chamber) after filling. Initial aerosol concentrations inside the smog chamber after filling ranged from 13–85 $\mu\text{g m}^{-3}$, which are representative of ambient and plume-like conditions. A blank experiment was performed in which the smog chamber was flushed with clean, dry air for 12 h, and then exposed to sunlight and UV lights to ensure that evolution of the OA in experiments was not affected by chamber or background conditions.

After filling the smog chamber, primary gas and particle concentrations were characterized for 75 min. Photo-oxidation was then initiated by turning on UV lights (GE model 10526 blacklights) and by removing the tarp to expose the smog chamber to natural sunlight, weather permitting (Table 2). The photo-chemical aging lasted for 3–4.5 h and during this phase of the experiment the temperature in the smog chamber increased $11.5 \pm 3.4^\circ\text{C}$ (average $\pm 1 \sigma$; see discussion in Sect. 3.2). Relative humidity (RH) inside the smog chamber was also variable, but was consistently low relative to ambient conditions. The maximum RH observed in each experiment was $30.0 \pm 6.1\%$ (mean $\pm 1 \sigma$) while the average RH observed across all of the experiments was 19.2%.

In 10 experiments, nitrous acid (HONO) was added to the smog chamber before adding smoke from the FSL burn chamber. The UV light photolyzed HONO to enhance hydroxyl radical (OH) levels (Table 2) and increase overall oxidant exposures. The addition of HONO also shifted the VOC:NO_x regime from low NO_x (experiments without HONO addition) to high NO_x (Table 2).

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A suite of instrumentation located in the CMU Mobile Air Quality Lab (Presto et al., 2011; Miracolo et al., 2011) was used to monitor gas and particle species in the photo-oxidation experiments. An Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS) was used to measure non-refractory aerosol mass, including OA as well as inorganic species sulfate, nitrate, chloride, potassium, and ammonium. Q-AMS data at m/z 44 were corrected for the measured CO_2 concentrations. A scanning mobility particle sizer (SMPS, TSI model 3080) and condensation particle counter (CPC, TSI model 3772) measured aerosol number and volume distributions for particles in the size range 10.6–498 nm. Black carbon (BC) concentrations were measured with the 880 nm channel of a 7-channel Aethalometer (Magee Scientific model AE-31) corrected for aerosol loadings according to the method of Kirchstetter and Novakov (2007).

A thermodenuder based on the design of Huffman et al. (2009) was operated upstream of the SMPS and Q-AMS to investigate aerosol volatility. These instruments alternately sampled between a heated “through thermodenuder” and ambient temperature “bypass” line. During the primary characterization period, the TD was run at temperatures of 40, 80, and 120 °C. The aerosol was sampled through the TD for 15 min at each temperature to quantify the extent of evaporation at two residence times (7 s and 19 s centerline at 25 °C). During the first two hours of photo-oxidation, the TD was held constant at 80 °C while the SMPS and Q-AMS measurements cycled between bypass and TD sampling (30 min per cycle). Finally, at the end of the photo-oxidation period, the primary TD program was repeated to investigate the volatility of the aged aerosol at 40, 80, and 120 °C.

For 15 min out of every hour, an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS) operated by Colorado State University sampled from the smog chamber. The HR-AMS was located in the FSL burn chamber control room.

The concentrations of select VOCs were measured with a Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon, Innsbruck, Austria). The PTR-MS was equipped with a quadrupole mass analyzer that achieved unit mass resolution, and hence was unable to resolve isobaric species such as m -, o -, and p -xylene. Along with

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ethylbenzene, these compounds were collectively quantified as “C-8 aromatics”. The measured decay of benzene, toluene, and C-8 aromatic concentrations were used to infer OH levels (see supplemental material of Hennigan et al., 2010). Additional gas-phase measurements included carbon dioxide (CO₂, Licor Biosciences model LI-820), carbon monoxide (CO, API model 300), ozone (O₃, API model 400A), and oxides of nitrogen (NO_x, Teledyne model 200EU). Gas-phase instruments, including the PTR-MS, were calibrated daily during the study. Similar gas-phase measurements were conducted in the FSL combustion chamber to characterize primary emission factors for each of the burns.

Teflon membrane filter samples (25 mm, Pall Corporation, P5PQ025) were collected from both the FSL combustion chamber and the CMU smog chamber to characterize primary and aged aerosol chemical composition using offline techniques. Filter samples were taken from the smog chamber after approximately 0.9, 2.1, and 3.3 h of photo-oxidation. The filters were extracted in deionized water and the extracts analyzed for cations and anions by ion chromatography (IC) with conductivity detection, and for anhydrosugars, including levoglucosan, by IC with pulsed amperometric detection (Sullivan et al., 2011). Primary organic carbon (OC) and elemental carbon (EC) emission factors were determined using Hi-volume filter samples collected in the burn chamber and analyzed by thermal/optical transmission using a Sunset Labs OC/EC analyzer. The Hi-volume sampling specifications and OC/EC analysis protocol are as described by Sullivan et al. (2008) and McMeeking et al. (2009).

2.2 Data analysis

2.2.1 Emissions data

Emission factors were calculated from the measured pollutant concentrations using the carbon mass balance approach (Ward and Radke, 1993):

$$EF_i = \frac{m_i \cdot x_C}{\Delta\text{CO}_2 + \Delta\text{CO} + \Delta\text{PM}_C + \Delta\text{HC}} \quad (1)$$

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where m_i is the concentration of species i , x_C is the mass fraction of carbon in the dry fuel determined by chemical analysis, ΔCO_2 is the background-corrected CO_2 concentration, ΔCO is the background-corrected CO concentration, ΔPM_C is the background-corrected carbon in the particle phase, and ΔHC is the background-corrected carbon concentration of hydrocarbons.

The modified combustion efficiency (MCE) was calculated to characterize burn conditions (Ward and Radke, 1993),

$$\text{MCE} = \frac{\Delta\text{CO}_2}{\Delta\text{CO}_2 + \Delta\text{CO}} \quad (2)$$

where ΔCO_2 and ΔCO are the background-corrected CO_2 and CO concentrations. During a chamber burn, fuels underwent multiple phases of combustion (see example FLAME II combustion timeline in Lee et al., 2010), thus the emission factors and MCE values in Table 1 are fire-integrated values.

2.2.2 Chamber data

To quantify the effects of photochemistry on aerosol mass concentrations, the data must be corrected for loss of particles and vapors to the chamber walls. Wall loss-corrected data were expressed as OA mass enhancement ratios. An OA mass enhancement ratio greater than 1 indicates net production of wall loss-corrected OA mass (i.e., SOA formation), while an OA enhancement ratio less than 1 indicates net loss of wall loss-corrected OA mass.

Following Grieshop et al. (2009a), an OA mass enhancement ratio was estimated using the OA concentration measured by the Q-AMS and the BC concentration:

$$\text{OA mass enhancement ratio} = \frac{\text{OA}_t/\text{BC}_t}{\text{OA}_0/\text{BC}_0} \quad (3)$$

where OA_t and BC_t are the OA and BC concentrations at some time t during the photo-oxidation phase of the experiment, respectively, while OA_0 and BC_0 are the

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OA and BC concentrations during the primary characterization period. This assumes that the aerosol on the chamber walls remains in equilibrium with semi-volatile vapors ($\omega = 1$ case described by Weitkamp et al., 2008).

An alternate estimate used a first order rate loss constant based on the measured decay in Q-AMS OA mass during the primary characterization period (before initiating oxidation). This rate constant was then used to correct for aerosol mass deposited on the chamber following the approach of Weitkamp et al. (2008) assuming that the particles on the walls remained in equilibrium with semi-volatile vapors ($\omega = 1$ case described by Weitkamp et al., 2008). The OA mass enhancement ratios reported here are the average of these two estimates (Table 2, Figs. 3 and 7). The lone exception was Burn 51 (Alaskan Duff, 28 September 2009), where BC concentrations were too low to calculate an OA/BC ratio. For this experiment, the first-order rate constant approach was the sole method used to calculate the OA enhancement ratio. OA enhancement ratios determined using the two methods agreed to within 17%, on average, demonstrating the robust estimates of the particle loss rate to the chamber walls (Fig. 2b and g).

To estimate loss of semi-volatile vapors to the chamber walls, we consider two limiting cases: condensable products only partition to the suspended particles ($\omega = 0$) and material lost to the walls remains completely in equilibrium with the gas phase ($\omega = 1$). The $\omega = 1$ assumption serves as an upper bound on the estimate of OA production for each experiment. The lower bound assumption, $\omega = 0$ (Weitkamp et al., 2008), is that only particle mass is lost to the walls (no vapor). The available evidence indicates that the $\omega = 1$ case better represents the actual behavior in the chamber (Weitkamp et al., 2008).

To quantify OA volatility, the OA mass fraction remaining (MFR) using the thermodenuder data was defined as:

$$\text{MFR} = \frac{\text{OA}_{\text{TD}}}{\text{OA}_{\text{bypass}}} \quad (4)$$

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where OA_{TD} and OA_{bypass} are the average OA concentrations measured downstream of the thermodenuder and bypass line with the Q-AMS, respectively. The TD data were corrected for minor particle losses within the thermodenuder, as determined by differences in the particle number concentration for samples through the thermodenuder compared with particle number concentrations measured in bypass. These losses were less than 10% for the temperatures used in this study.

3 Results

3.1 Primary emissions

Table 1 presents burn-average primary emission factors and MCE values for 18 chamber burns. These values were calculated from concentrations measured in the FSL combustion chamber. We briefly describe these data to provide context for the effects of photo-oxidation and to compare the primary emissions data with published laboratory and field data of biomass burning emissions. Future publications from the FLAME III study will focus on the primary emissions data.

The average CO_2 emission factor across all of the burns used for smog chamber experiments was $1737 \pm 110 \text{ g kg}^{-1}$ (average $\pm 1 \sigma$), which agrees well with laboratory data for the same fuels burned under similar conditions (McMeeking et al., 2009). They are also comparable with emission factors from field studies of open biomass burning (Andreae and Merlet, 2001).

Average CO ($74.9 \pm 24.8 \text{ g kg}^{-1}$ – average $\pm 1 \sigma$) and NO_x ($3.5 \pm 1.8 \text{ g kg}^{-1}$ – average $\pm 1 \sigma$) emission factors were within the range of emission factors reported for previous laboratory-scale burns (e.g., Yokelson et al., 2008; McMeeking et al., 2009; Burling et al., 2010), and field data (Andreae and Merlet, 2001). MCE values in this study ranged from 0.89–0.97 with an average MCE of 0.94 ± 0.02 (average $\pm 1 \sigma$). In general, the MCE values demonstrate the influence from both flaming and smoldering fire conditions.

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In general, emissions of OC were more variable than emissions of EC or any of the gas-phase species discussed above. OC emission factors ranged from 0.4–22.6 g C kg⁻¹ with an average of 8.4 ± 10.6 g C kg⁻¹ (average ± 1 σ). EC emission factors ranged from 0.25–1.12 g C kg⁻¹, with an average of 0.51 ± 0.28 g C kg⁻¹ (average ± 1 σ). While variable, the range of OC and EC emission factors are consistent with laboratory (McMeeking et al., 2009) and field data (Andreae and Merlet, 2001). For example, average OC emission factors for the biomass burning classes Savannah and Grasslands, Tropical Forests, Extra Tropical Forests, and Agricultural Residues are 3.4, 5.2, 8.6–9.7, and 3.3 g C kg⁻¹, respectively (Andreae and Merlet, 2001).

3.2 Photo-oxidation and SOA production

To illustrate the effects of photo-oxidation on biomass smoke, Fig. 2 shows the time series data for gas- and particle-phase pollutants from two experiments, specifically chosen to represent the different behaviors observed in this study. Figure 2a–e show gas and particle concentrations in the smog chamber during a pocosin experiment (FLAME III burn 63, 5 October 2009), while Fig. 2f–j show concentrations during a gallberry experiment (burn 65, 6 October 2009).

Although pollutant concentrations inside the chamber varied from experiment to experiment, depending on emission rates and dilution levels, gas-phase species exhibited similar trends in every experiment. Concentrations of reactive hydrocarbons such as toluene, isoprene, and monoterpenes were stable during the primary characterization period, but decreased significantly with photo-oxidation (dashed vertical line in Fig. 2). Concentrations of oxygenated gas-phase species such as acetone and formic acid increased substantially during the aging period. Inert species such as CO₂ remained steady throughout the primary characterization and aging periods in every experiment.

Although gas-phase species behaved similarly in every experiment, there were dramatic differences in the evolution of wall loss-corrected OA concentrations. The two experiments shown in Fig. 2 were chosen to highlight these differences. There was significant SOA formation when the pocosin fire emissions were photo-oxidized (Fig. 2a).

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4.9×10^{10} molecules $\text{cm}^{-3} \text{s}^{-1}$ (Table 2). These values are representative of typical summertime OH concentrations and are similar to OH levels that have been observed in fresh biomass burning plumes (Hobbs et al., 2003; Yokelson et al., 2009).

One complication for interpreting the OA enhancement ratios is that the chamber temperature increased by an average of 11.5°C during the photo-oxidation period of the experiments. This will shift the equilibrium of semi-volatile organics towards the gas phase (Pankow, 1994), which will, in turn, reduce the OA enhancement ratios. However, we expect this to be, at most, a minor effect. For example, no correlation was observed between OA enhancement ratios and the magnitude of the temperature increase for each experiment (not shown: slope = 0.0, $R^2 = 0.0$). TD analysis of the aged OA suggests that a temperature increase of 11.5°C would cause, on average, only 7% of the OA to evaporate, which is similar to the temperature sensitivity of 1–2% of OA per $^\circ\text{C}$ observed by previous studies (Grieshop et al., 2009a; Huffman et al., 2009).

3.3 Chemical transformations of OA

Although the production of new OA mass was highly variable, photo-oxidation caused significant chemical and physical transformations of the OA in every experiment. In this section, we present multiple pieces of evidence to illustrate these changes, including changes in Q-AMS mass spectra, decreasing levoglucosan concentrations, and decreases in OA volatility with aging. These transformations occurred whether or not there was production of new OA mass, and appeared to be due to both SOA production (condensing organics) and to processing of POA.

3.3.1 Q-AMS OA MS

The Q-AMS provides a measure of the chemical composition of the OA. Figures 4 and 5 present a compilation of Q-AMS data to illustrate the evolution of OA emissions.

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Figure 4 plots time series of the coefficient of determination values (R^2) between each measured Q-AMS OA mass spectrum and different reference mass spectra, similar to Grieshop et al. (2009b) and Jimenez et al. (2009). The analysis was performed using several different reference spectra: the average POA spectrum measured during the primary characterization phase of the experiment, an oxygenated organic aerosol (OOA) factor derived from ambient data collected in Pittsburgh (Zhang et al., 2005), and low-volatility OOA (LV-OOA) and semi-volatile OOA (SV-OOA) factors derived from the Pittsburgh OOA (Ulbrich et al., 2009; Jimenez et al., 2009). Therefore, the time series shown in Fig. 4 illustrate how the composition of the OA inside the chamber changes relative to these reference spectra.

Separate time series are shown in Fig. 4 to compare results from low and high OA mass enhancement ratio experiments. One time series shows the average R^2 value from the four experiments with the highest OA mass enhancements (Burns 42, 43, 63, and 66; average OA mass enhancement ratio = 2.7) and the second shows the average value from the four experiments with the lowest OA mass enhancements (Burns 40, 55, 57, and 65; average OA mass enhancement ratio = 0.9). In both cases, photo-oxidation caused the OA mass spectra to become less similar to the POA mass spectrum and more similar to OOA (Zhang et al., 2005). Furthermore, the OA mass spectra in every experiment became more similar to LV-OOA than SV-OOA. Similar trends were reported by Grieshop et al. (2009b), who studied photo-oxidation of residential wood combustion emissions.

Figure 5 presents time series of key mass fragments measured using the Q-AMS: m/z 44 and m/z 60. m/z 44 (typically dominated by the CO_2^+ ion) is often used as a measure of the extent of oxygenation while m/z 60 (typically dominated by the $\text{C}_2\text{H}_4\text{O}_2^+$ ion) is often used as a marker for POA emissions from biomass burning (Alfarra et al., 2007; Lee et al., 2010). These mass fragments are presented as a fraction of total organic aerosol (f_{44} and f_{60}). Separate time series are shown to compare results from high and low OA enhancement ratio experiments.

Figure 5a and d show surprisingly similar evolution of f_{44} in experiments with high and low OA enhancement ratios. For the high OA mass enhancement experiments, the f_{44} increase is expected, since SOA is more oxygenated than the POA. However, the increase in f_{44} in experiments where the OA concentration decreased (Fig. 5d) was unexpected, and indicates significant chemical processing of the POA. Since the wall loss-corrected OA concentration decreased, on average, in these experiments, the addition of oxygen must be offset by the loss of carbon. A similar phenomenon has been observed in plume studies (Capes et al., 2008). These data imply that in some systems fragmentation reactions are important; these reactions break carbon-carbon bonds but add oxygen (Kroll et al., 2009).

Figure 5b and e show that photo-oxidation dramatically reduced f_{60} . This provides additional evidence for the substantial transformation of POA, especially in experiments with little or no SOA production (low OA mass enhancement ratio). If m/z 60 were an inert tracer for biomass burning emissions, then the f_{60} data in Fig. 5f would be expected to lie within the gray shaded region, which indicate the range of normalized and wall loss-corrected POA concentrations. Instead, f_{60} decreased rapidly in the first two hours of photo-oxidation, indicating that reactions took place depleting the compounds that contributed to the m/z 60 signal. This trend was also seen in experiments with substantial SOA formation (Fig. 5b). In these experiments, the rate of f_{60} decrease was much more rapid than the SOA production; therefore the data clearly indicate significant chemical processing of POA in experiments with substantial SOA production.

3.3.2 Levoglucosan

In addition to changes in AMS mass spectra with aging, photo-oxidation also reduced the concentration of levoglucosan (1,6-anhydro- β -D-glucopyranose), which is extensively used as a tracer for biomass burning emissions in source apportionment analysis (Simoneit et al., 1999).

Figure 6 shows the campaign-average of levoglucosan-to-potassium ion (K^+) ratios measured using the filter samples as a function of OH exposure. The data have been

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normalized to the initial levoglucosan:K⁺ ratio measured in the FSL burn chamber. If levoglucosan and K⁺ are internally mixed, then this ratio accounts for particle deposition to the chamber walls. Therefore, this ratio is expected to be constant if levoglucosan is inert.

Figure 6 shows that the levoglucosan:K⁺ ratio decreased dramatically in every experiment. On average, it decreased by 80% by the end of the photo-oxidation phase of the experiment. This decay rate is much more rapid than observed in previous studies (Hennigan et al., 2010; Kessler et al., 2010). A complication in interpreting these data is that initial filter samples were taken in the FSL combustion chamber but the aged samples were taken in the smog chamber. On average, the primary emissions were ~15 times more dilute in the smog chamber than in the combustion chamber. This dilution will cause semi-volatile compounds to evaporate. Therefore we hypothesize that some of the reduction in the levoglucosan:K⁺ is due to changes in partitioning caused by dilution; previous studies have also suggested that levoglucosan is semi-volatile (Huffman et al., 2009; Grieshop et al., 2009a; Hennigan et al., 2010).

We estimated the amount of levoglucosan that evaporated upon dilution using HR-AMS *m/z* 60-to-sulfate ratios measured inside the FSL combustion chamber and inside the smog chamber. On average, the *m/z* 60:sulfate ratio measured in the smog chamber during the primary characterization period was approximately half that measured in the FSL combustion chamber. We hypothesize that the difference in the *m/z* 60:sulfate ratio between the combustion and smog chamber was due to evaporation brought about by dilution when the smog chamber was filled with primary emissions.

Although multiple compounds contribute to the AMS *m/z* 60 signal, there is a strong correlation between levoglucosan and *m/z* 60 (Lee et al., 2010). Therefore, we used the *m/z* 60:sulfate ratio to estimate the initial levoglucosan:K⁺ of the primary emissions inside the smog chamber before photo-oxidation. This is represented in Fig. 6 by the open red symbol at OH exposure = 0, while solid red symbols in Fig. 6 are measurement values. This approach, while uncertain, should provide a conservative (lower bound) estimate of the amount of levoglucosan that reacted.

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With this correction, Fig. 6 indicates that the levoglucosan:K⁺ ratio decreased linearly with OH exposure during the photo-oxidation phase of the experiment. On average, levoglucosan concentrations decreased by approximately 60% during photo-oxidation. The effective rate constant (k_{OH}) for levoglucosan oxidation, averaged across the entire study, was $3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a range of 1.0 – $6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is within a factor of two of the average levoglucosan oxidation rate reported in a similar laboratory study conducted with residential wood smoke emissions (Hennigan et al., 2010 – hatched grey region in Fig. 6). Both studies showed variability in levoglucosan oxidation rates, which are likely due to factors such as aerosol matrix effects, and uncertainty in the levoglucosan evaporation estimate applied to the present study. However, the general agreement in levoglucosan oxidation rates between the two studies provides further evidence that levoglucosan is not an inert tracer for biomass burning emissions.

3.4 Rate of OA chemical transformations

Our discussion of Figs. 4–6 highlights the rapid chemical processing that occurred in every experiment. The OH concentrations inferred from the decay of aromatics inside the chamber (Table 2) were similar to, or lower than, those observed in aircraft studies of fresh biomass burning plumes (e.g., Hobbs et al., 2003; Yokelson et al., 2009). Therefore, the rate and extent of chemical transformations measured inside the smog chamber are likely to be similar to those that occur in actual fire plumes.

To quantify the processing rate and the potential contribution of heterogeneous reactions to POA transformations, Fig. 6 compares the measured decay of the wall loss-corrected levoglucosan concentration to the OH uptake coefficient (γ) according to Sage et al. (2009):

$$\gamma = -\frac{2}{3} \frac{\chi_{\text{levo}} \cdot \rho}{\bar{c}} \frac{D_V^3}{D_A^2} \frac{\delta \ln C_{\text{levo:K}^+}}{\delta t} \frac{1}{C_{\text{OH}}} \quad (5)$$

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where χ_{levo} is the measured mass fraction of levoglucosan relative to the total OA, ρ is the particle density ($\rho = 1.3 \text{ g cm}^{-3}$), \bar{c} is the mean speed of gas-phase OH molecules, D_V is the measured mean volume-weighted particle diameter, D_A is the measured mean surface area-weighted particle diameter, $C_{\text{levo:K}^+}$ is the measured levoglucosan:K⁺ ratio, and C_{OH} is the inferred OH concentration. In Eq. (5), γ is the ratio of the levoglucosan decay rate to the OH collision rate. By quantifying levoglucosan decay relative to an inert species (K⁺), γ accounts for the effects of wall losses (Sage et al., 2009). Therefore, γ represents the fraction of OH-particle collisions that result in the reaction of a levoglucosan molecule. This is weighted by the levoglucosan mass fraction of OA (χ_{levo}) since other condensed-phase compounds are also in competition with levoglucosan for reaction with OH. Since organic-OH reactions are likely to occur on the particle surface, Eq. (5) assumes that any mass transfer limitations within the particle are similar for all constituents of the OA.

Figure 6 shows that the campaign-average levoglucosan concentration decreased more rapidly than can be explained by uptake of OH to the particles. The $\gamma = 1$ line in Fig. 6 represents the expected levoglucosan decay assuming that each collision of an OH molecule with a particle resulted in the oxidation of one levoglucosan molecule. On average, only about 20% of the measured levoglucosan decrease can be explained by pure heterogeneous reactions. Using average experimental properties (levoglucosan decay, particle size distributions, OH levels, levoglucosan OA mass fraction), we calculate a campaign-average γ of 5.0, which means the levoglucosan decayed 5 times faster than the OH collision rate.

One possible explanation is secondary chemistry, but this chemistry is thought to, at most, double the extent of reaction (2 reactions with every OH collision or $\gamma = 2$) (Hearn and Smith, 2006; Hearn et al., 2007). An alternative explanation is that the gas phase reactions of OH with semi-volatile vapors contributed to the levoglucosan decrease. This hypothesis is consistent with the observations that levoglucosan is semi-volatile (Sect. 3.3.2). The oxidation of semi-volatile vapors, leading to the evaporation of condensed POA has been proposed to explain the rapid processing of motor vehicle POA

(Lambe et al., 2009; Miracolo et al., 2010).

3.5 OA volatility evolution

5 A final piece of evidence for the dramatic changes in OA properties is the changes in OA volatility measured using the thermodenuder. Figure 5c and f show that photo-oxidation decreased the volatility of the OA as indicated by an increase in OA MFR (Eq. 4). This change was observed in both experiments with and without significant SOA formation (Fig. 5c and f). Therefore, the aged aerosol was less volatile than the POA. The largest decreases in OA volatility occurred in the first hour of aging when OH levels were the highest, while relatively little change in volatility occurred after
10 that, despite continued evolution of the OA chemical composition (Figs. 4–6). Similar changes in volatility were measured during photo-oxidation of residential wood burning emissions (Grieshop et al., 2009a).

15 A possible explanation for the decrease in volatility in experiments with OA mass loss is the reaction of semi-volatile vapors. This would lead to evaporation of semi-volatile material from the particle phase to maintain thermodynamic equilibrium (Sect. 3.4), reducing the mass fraction of the most volatile aerosol phase compounds. The volatility changes in experiments with no OA mass enhancement were also likely affected by SOA formation because the PTR-MS data indicate that SOA precursors (Fig. 2) were present and were oxidized in these experiments. Heterogeneous reactions of POA
20 could also contribute to the decrease in OA volatility. It is likely that all of these factors contributed to the observed changes in OA volatility.

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4 Discussion and conclusions

Photo-oxidation of open biomass burning emissions in an environmental smog chamber produced a wide variability in OA mass enhancement ratios. The campaign-average OA mass enhancement ratio of 1.7 indicates that, on average, there was significant SOA production in these systems. The OA mass enhancement ratios observed in this study likely represent lower bounds for enhancements that would occur in the atmosphere due to the increase in chamber temperature during aging. In comparison, ambient fire plumes will be aged at lower temperatures brought about by convective lifting to higher altitudes. There was no correlation between OH exposure and production of new OA mass, suggesting that other factors were limiting here: a future manuscript will focus on explaining the variability in OA mass enhancements.

The high variability in SOA production reported here is consistent with data from other field and laboratory studies. For example, significant OA production was observed in the aging of residential wood smoke emissions in laboratory studies (Grieshop et al., 2009a; Heringa et al., 2011) and in aircraft measurements of an aging fire plume (Yokelson et al., 2009). However, other aircraft studies report more modest increases in OA concentrations (Reid et al., 1998; DeCarlo et al., 2010) or no increase in OA concentrations at all downwind of fires (Capes et al., 2008; Hecobian et al., 2011; Cubison et al., 2011).

Our results suggest that SOA production from biomass burning could be a significant source of OA globally. Based on primary emissions reported by Bond et al. (2004) the campaign-average OA enhancement factor of 1.7 indicates that global SOA production from biomass burning is on the order of 20 Tg yr^{-1} (comparable to primary biomass burning emissions). A complication is that some of this SOA may be embodied in the POA emission factors used by Bond et al. (2004) because of either sampling artifact or gas-particle partitioning biases in the emission measurements (Robinson et al., 2010). Twenty Tg yr^{-1} is a factor of 6–7 greater than the global POA emissions from all non-biomass burning sources. Better constraining this first-order estimate would require a

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more rigorous analysis using detailed emissions inventories and 3-D chemical transport models. Our results suggest that SOA from biomass burning emissions will vary greatly by region according to specific fire and plume aging conditions. However, the scale of global biomass burning emissions and high SOA formation we observed from a variety of fuels demonstrate that aging of biomass burning is likely an important component of the global OA burden.

Even though it did not always produce new OA mass, photo-oxidation chemically and physically transformed the OA in every experiment. A unique feature of the smog chamber experiments is our ability to quantify the rate of these transformations. The OA transformations were significantly faster than could be explained by heterogeneous reactions (Fig. 6), suggesting that reactions of semi-volatile vapors contributed to the observed chemical and physical processing. In some of the experiments, there was even a net loss of OA mass during photo-oxidation. Molina et al. (2004) proposed that chemistry could be a significant loss mechanism for OA mass, focusing on heterogeneous oxidation. However, the OA mass loss observed in our experiments occurred with much less oxidant exposure than that used in most heterogeneous oxidation experiments (e.g., Molina et al., 2004; Knopf et al., 2006; George et al., 2007; Hearn et al., 2007; Kroll et al., 2009). We hypothesize that oxidation of semi-volatile vapors in these systems played an important role in the OA mass loss in our experiments.

The extensive transformations of OA blur the traditional definitions of SOA and POA. Traditionally, POA is defined as OA emitted directly into the atmosphere in the particle phase while SOA is comprised of semivolatile products from reactions of gas-phase organics (Robinson et al., 2010). Most chemical transport models and emission inventories assume that POA is non-volatile and non-reactive.

To illustrate the definitional challenges created by photo-oxidation, Fig. 7 compares different estimates of POA and SOA from the FLAME III experiments. One approach uses physical definitions to define POA and SOA-POA is the amount of OA in the chamber before photo-oxidation while SOA is the net production of new OA mass due to photo-chemistry. The physical definition corresponds to the traditional definition of

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non-volatile and non-reactive POA. The second approach uses a chemical definition of SOA and POA using levoglucosan as a tracer for POA. Levoglucosan is widely used as tracer for biomass burning POA in receptor models.

We use data from a wire grass experiment (burn 42) to illustrate the two different approaches for defining SOA and POA. In this experiment, the OA mass enhancement ratio was 2.6 ± 0.3 after 3.5 h of aging. Thus, based on the physical definition, the SOA mass fraction of the wall loss-corrected OA at the end of the experiment was 0.6 ($\text{SOA} = (2.6 - 1)/2.6$) and the POA contribution was 0.4. However, in this experiment, the levoglucosan: K^+ ratio decreased by 64% between the initial measurement in the FSL combustion chamber and the final aged sample. This indicates that there was significant chemical processing of the POA. Using levoglucosan to define POA, the mass fraction of unreacted POA at the end of the experiment was only 14% of the aged OA mass ($\text{POA} = (1 - 0.64)/2.6$). Thus, the contribution of POA to the aged OA mass was much less than if POA is assumed to be inert. We define the difference between the new OA mass and the unreacted POA as oxygenated POA (O-POA), which contributed 25% of the aged OA mass ($\text{O-POA} = 0.64/2.6$). Our definition of O-POA assumes that all POA reacts at the same rate as levoglucosan. This likely is not true because levoglucosan appears to be semi-volatile and the reaction of vapors likely contributed to its depletion in the particle phase. However, receptor models often use levoglucosan as a tracer for biomass burning POA; therefore, it is a widely applied assumption. Chemical receptor models currently assume that levoglucosan is non-volatile and non-reactive in the atmosphere (Schauer and Cass, 2000); however, the decrease in levoglucosan concentrations due to reactions measured here is in agreement with recent laboratory and field studies that suggest levoglucosan is not inert (Hoffmann et al., 2010; Hennigan et al., 2010; Kessler et al., 2010; Saarikoski et al., 2008; Zhang et al., 2010; Mochida et al., 2010; Holden et al., 2011). Figure 7 indicates that, on average, using levoglucosan as a tracer for biomass burning emissions underestimates the contribution of biomass burning to the chamber aerosol by a factor of 7. This illustrates the dramatic biases created by changing partitioning and reaction of levoglucosan.

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Figure 7 plots the OA mass enhancement ratios for all burns (the same as Fig. 3) and quantifies the contributions of SOA, POA, and O-POA to the aged OA mass based on previously discussed definitions. Replacing the traditional definition of POA with one that accounts for oxidation reactions and changes in partitioning dramatically alters our understanding of the contribution of oxidation versus direct emissions to OA mass. Assuming a traditional definition (non-volatile and non-reactive), POA accounted for 60% of the campaign-average OA at the end of the aging experiment while SOA accounted for 40%. However, using levoglucosan as a tracer for the POA, then POA accounted for only 17% of campaign-averaged aged OA while O-POA accounted for the largest fraction at 43%. SOA accounted for 40% of aged OA mass in both cases. This distinction is not precise since some of the O-POA may be SOA formed from the oxidation of semivolatile vapors that is offset by evaporation of POA. The contribution of O-POA was variable, though it was observed in every experiment and was not dependent on the net change in OA mass. The extent of oxidation estimated by this method qualitatively agrees with the other metrics of chemical transformation of the POA, including Q-AMS analysis (e.g. using m/z 60 as a marker for biomass POA, Figs. 4 and 5) and evolution of OA volatility (Fig. 5).

The large contribution of O-POA demonstrates that the physical and chemical transformations of OA were extensive, which is in agreement with results from multiple field studies (e.g., Capes et al., 2008; Mochida et al., 2010; Holden et al., 2011). Our results indicate that the OA in biomass burning emissions are altered on timescales of hours at typical atmospheric and plume conditions. Therefore, this dynamic behavior needs to be accounted for in models which are used to evaluate the impact of these emissions on air quality, atmospheric chemistry, and climate.

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Table 1. Primary emission factors for burns that were sampled to conduct aging experiments.

Burn Number ¹	Burn Date	Fuel	Name	Material	CO ₂ *
37	19 Sep 2009	Lodgepole Pine	<i>Pinus contorta</i>	branches, leaves	1551
38	20 Sep 2009	Lodgepole Pine	<i>Pinus contorta</i>	branches, leaves	1716
40	21 Sep 2009	Ponderosa Pine	<i>Pinus ponderosa</i>	branches, leaves	
42	22 Sep 2009	Wire Grass	<i>Aristida beyrichiana</i>	grass	1784
43	23 Sep 2009	Saw Grass	<i>Cladium mariscus</i>	leaves (grass-like)	1765
45	24 Sep 2009	Turkey Oak	<i>Quercus laevis</i>	leaves	1793
47	25 Sep 2009	Gallberry	<i>Ilex glabra</i>	branches, leaves	1827
49	26 Sep 2009	Sage	<i>Artemisia tridentata</i>	branches, leaves	1714
51	28 Sep 2009	Alaskan Duff	<i>Hylocomium splendens</i> , <i>Sphagnum spp.</i>	decayed vegetation matter	1501
53	29 Sep 2009	Sage	<i>Artemisia tridentata</i>	branches, leaves	1733
55	30 Sep 2009	White Spruce	<i>Picea glauca</i>	branches, leaves	1704
57	1 Oct 2009	Ponderosa Pine	<i>Pinus ponderosa</i>	branches, leaves	1603
59	2 Oct 2009	Chamise	<i>Adenostoma fasciculatum</i>	branches, leaves	1876
61	4 Oct 2009	Lodgepole Pine	<i>Pinus contorta</i>	branches, leaves	1656
63	5 Oct 2009	Pocosin	<i>Lyonia lucida</i> , <i>Pinus serotina</i>	shrub branches, leaves; dried pine litter	1903
65	6 Oct 2009	Gallberry	<i>Ilex glabra</i>	branches, leaves	1766
66	7 Oct 2009	Black Spruce	<i>Picea mariana</i>	branches, leaves	1847
67	8 Oct 2009	Wire Grass	<i>Aristida beyrichiana</i>	grass	1794

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Table 1. Continued.

Burn Number ¹	Burn Date	CO ²	NO _x ²	MCE	OC ³	EC ³
37	19 Sep 2009	113.0	7.6	0.90	32.6	0.54
38	20 Sep 2009	82.9	3.0	0.93	11.4	0.41
40	21 Sep 2009					
42	22 Sep 2009	38.1	3.1	0.97	1.51	0.39
43	23 Sep 2009	49.4	3.9	0.96	1.57	0.69
45	24 Sep 2009	62.1	3.1	0.95	1.04	0.25
47	25 Sep 2009	59.8	2.7	0.95	8.72	0.41
49	26 Sep 2009	89.4	4.6	0.92	2.12	1.12
51	28 Sep 2009	89.2	1.7	0.91	4.96	
53	29 Sep 2009	88.2	5.8	0.93	0.78	0.66
55	30 Sep 2009	69.3	2.3	0.94	6.55	1.01
57	1 Oct 2009	96.9	1.8	0.91	27.7	0.25
59	2 Oct 2009	71.1	3.3	0.94	0.52	0.86
61	4 Oct 2009	128.4	3.0	0.89	28.1	0.37
63	5 Oct 2009	54.7	2.8	0.96	1.44	0.29
65	6 Oct 2009	81.4	3.9	0.93	10.0	0.35
66	7 Oct 2009	60.2	3.5	0.95	2.79	0.25
67	8 Oct 2009	38.9	3.6	0.97	1.62	0.37

¹Numbering convention used during the FLAME-III study.

²Emission factors in units of g kg⁻¹ dry fuel.

³Emission factors in units of gC kg⁻¹ dry fuel.

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Table 2. Characteristics of aging experiments. Blank value indicates data not available.

Burn Number ¹	Fuel	Smog Chamber POA ²	Smog Chamber BC ²	VOC:NO _x ³
37	Lodgepole Pine	36	1.7	44.5
38	Lodgepole Pine	34	2.3	94.4
40	Ponderosa Pine	58	1.5	–
42	Wire Grass	9.3	7.1	–
43	Saw Grass	6.6	10.1	19.1
45	Turkey Oak	8.2	6.4	26.6
47	Gallberry	35	4.2	39.1
49	Sage	5.4	8.3	26.4
51	Alaskan Duff	16	–	2.5
53	Sage	5.3	9.5	0.22
55	White Spruce	21	11.0	0.82
57	Ponderosa Pine	71	1.8	1.41
59	Chamise	5.9	16.7	0.29
61	Lodgepole Pine	53	1.2	0.76
63	Pocosin	16	10.0	0.19
65	Gallberry	79	7.0	0.40
66	Black Spruce	31	4.7	0.10
67	Wire Grass	23	6.1	0.05

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Table 2. Continued.

Burn Number ¹	HONO Added?	UV source	OH Exposure ⁴	OA Mass Enhancement Ratio
37	N	Sunlight	1.56E + 10	1.5 ± 0.2
38	N	UV lights	1.40E + 10	2.3 ± 0.7
40	N	Both	2.71E + 10	0.9 ± 0.1
42	N	Both	3.50E + 10	2.6 ± 0.3
43	N	Both	3.10E + 10	2.6 ± 0.3
45	N	Both	2.09E + 10	1.8 ± 0.3
47	N	Both	6.12E + 10	2.0 ± 0.5
49	N	Both	1.84E + 10	1.3 ± 0.1
51	Y	Both	–	1.2 ± 0.1
53	Y	UV lights	–	1.4 ± 0.1
55	Y	UV lights	6.59E + 10	1.1 ± 0.1
57	Y	UV lights	7.99E + 10	0.9 ± 0.1
59	Y	UV lights	4.95E + 10	1.9 ± 0.2
61	Y	UV lights	7.89E + 10	1.4 ± 0.2
63	Y	Both	8.22E + 10	2.8 ± 0.4
65	Y	Both	4.94E + 10	0.7 ± 0.1
66	Y	UV lights	2.63E + 10	2.9 ± 1.0
67	Y	Both	3.06E + 10	1.4 ± 0.1

¹Numbering convention used during the FLAME-III study.

²Concentration in units of $\mu\text{g m}^{-3}$.

³Units are ppbC ppb^{-1} .

⁴Units are $\text{molecules cm}^{-3} \text{s}^{-1}$.

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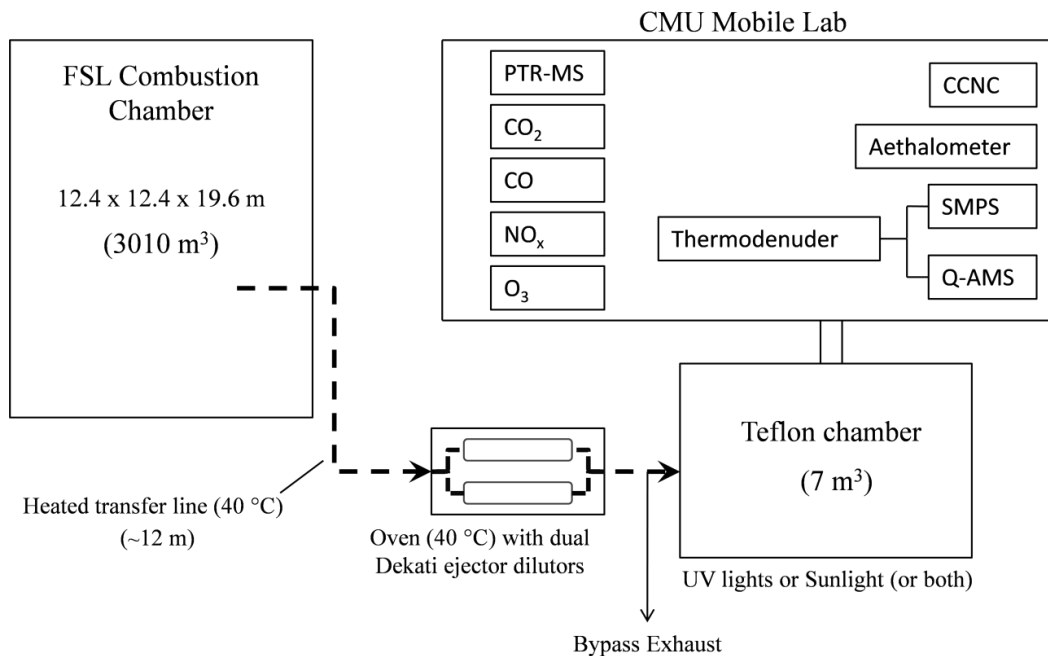


Fig. 1. Schematic showing experimental setup used for the photo-oxidation experiments (not drawn to scale). Primary emissions from the Fire Science Lab combustion chamber were sampled into the Carnegie Mellon 7 m³ Teflon smog chamber and then aged.

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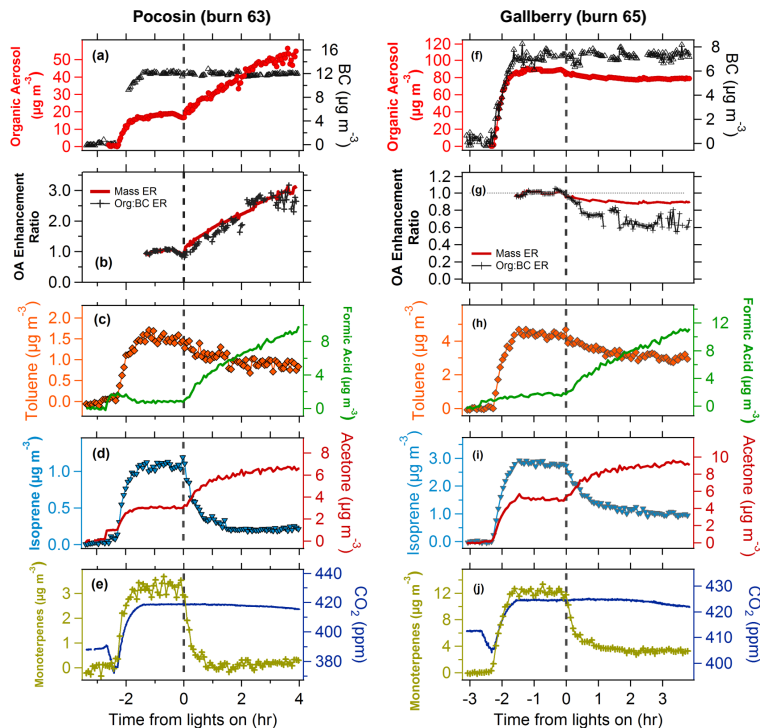


Fig. 2. Measured time series of gas and particle species in experiments where significant OA production was observed – Burn 63, pocosin, (a–e) – and where a net loss of OA mass with aging was observed – Burn 65, gallberry, (f–j). (a, f) Wall loss-corrected OA and BC concentrations. (b, g) OA mass enhancement ratios calculated using the OA:BC ratio and the first-order wall loss rate constant. (c, h) Toluene and formic acid concentrations measured by the PTR-MS. (d, i) Isoprene and acetone concentrations measured by the PTR-MS. (e, j) Monoterpene concentrations determined by the m/z 81 signal in the PTR-MS and CO_2 levels. Note, isoprene concentrations were likely influenced by furan, which is also detected in the PTR-MS at m/z 69 (Warneke et al., 2011).

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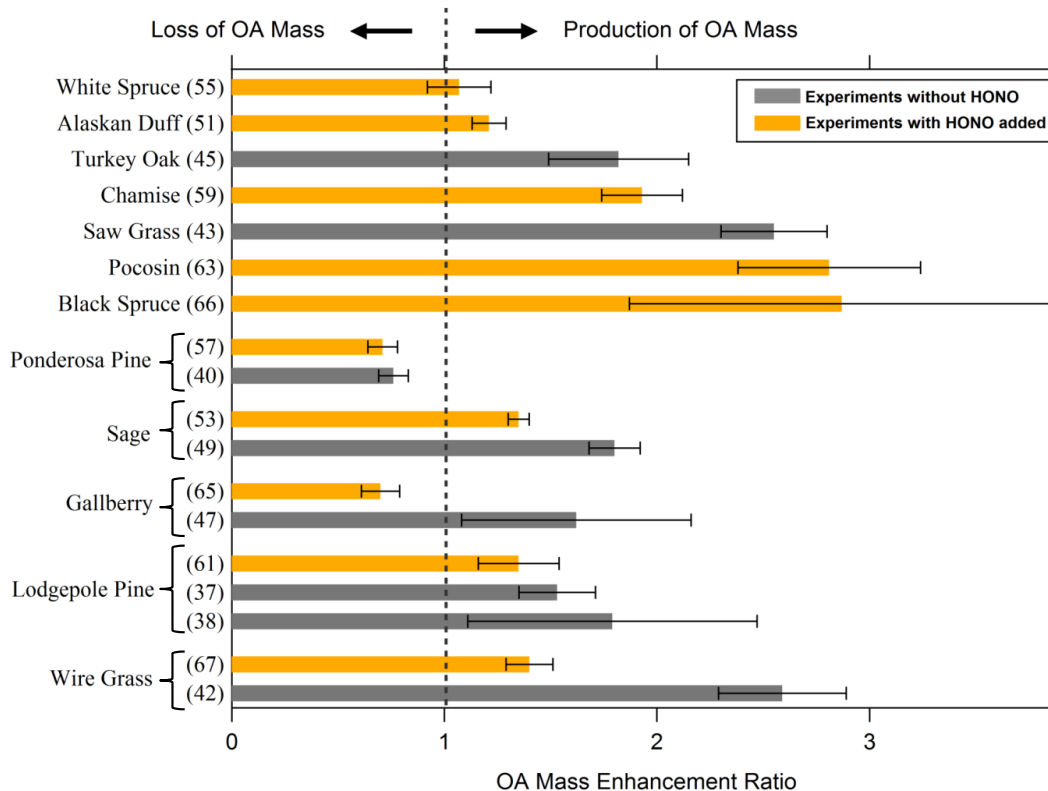


Fig. 3. Organic aerosol mass enhancement ratios measured at the end of the photo-oxidation phase of each experiment (labeled by fuel name, with burn number in parenthesis) conducted during the FLAME-III study. Gray color indicates experiments with no HONO addition, while orange color indicates experiments where HONO was added to increase OH levels (see Table 2).

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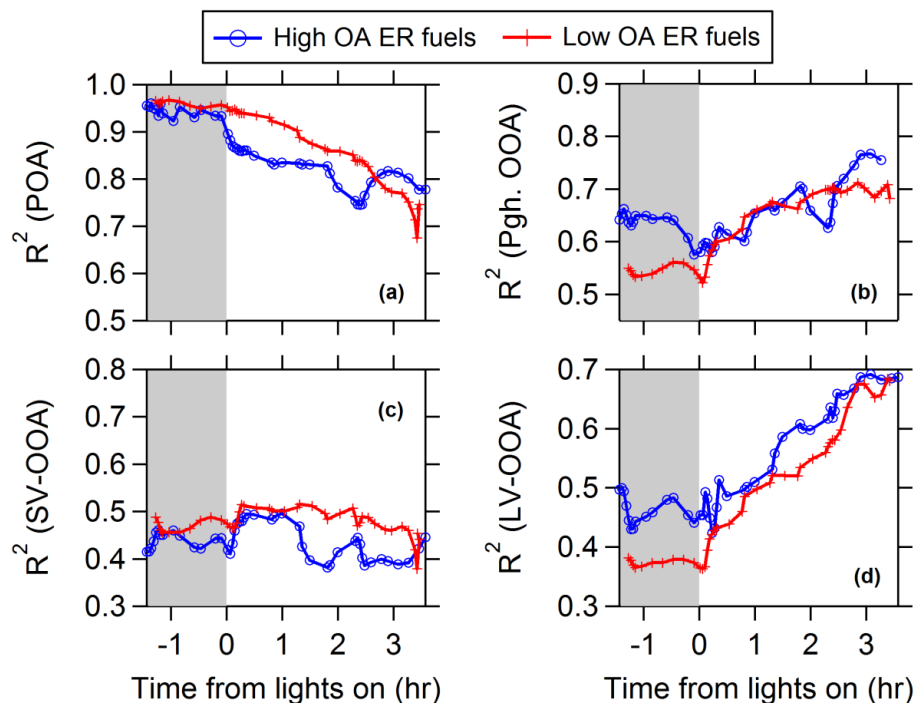


Fig. 4. Evolution of Q-AMS mass spectra with photo-oxidation measured in the four experiments with the highest OA mass enhancement ratios (Burns 42, 43, 63, and 66) and the four experiments with the lowest OA mass enhancement ratios (Burns 40, 55, 57, and 65). Average coefficient of determination (R^2) values for spectra at each Q-AMS time step (2.5 min resolution, with thermodenuder measurements removed) compared to **(a)** POA in each experiment, **(b)** Pittsburgh OOA spectrum (Zhang et al., 2005), **(c)** unit-mass-resolution semi-volatile OOA spectrum (Ulbrich et al., 2009), and **(d)** low-volatility OOA spectrum (Ulbrich et al., 2009). Grey shaded regions represent primary characterization period before photo-oxidation was initiated.

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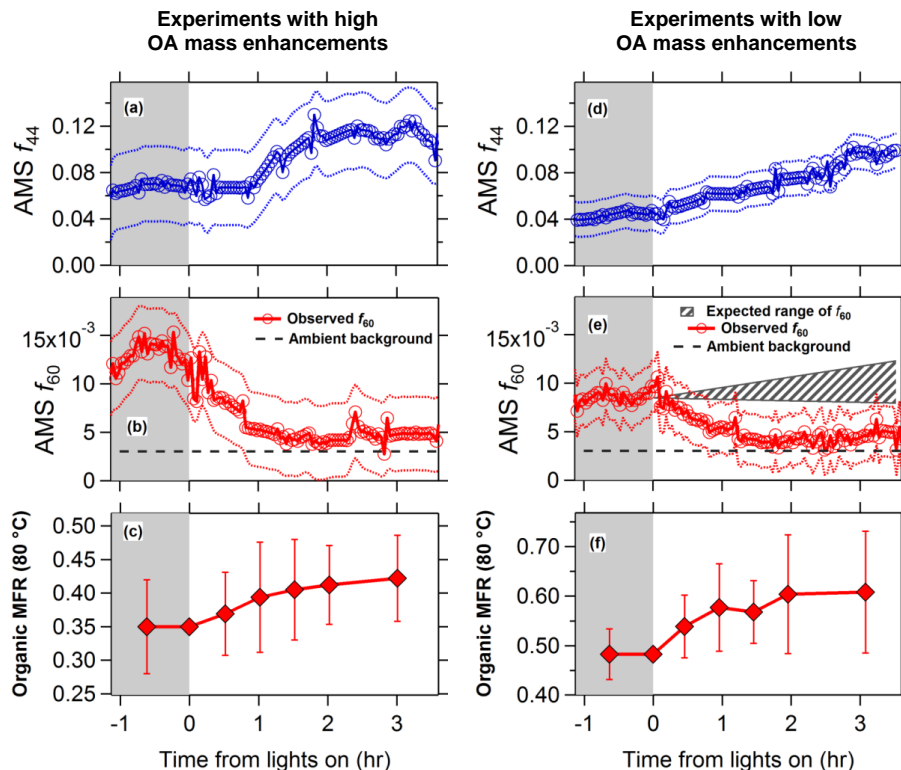


Fig. 5. Changes in chemical and physical properties of organic aerosol for the four experiments with the highest OA mass enhancement ratios – (a–c): Burns 42, 43, 63, and 66 – and the four experiments with the lowest OA mass enhancement ratios – (d–f): Burns 40, 55, 57, and 65. (a, d) Changes in the fraction of the total OA mass at m/z 44 – f_{44} (dotted lines represent $\pm 1 \sigma$ from mean). (b, e) Changes in the fraction of the total OA mass at m/z 60 – f_{60} (dotted lines represent $\pm 1 \sigma$ from mean). (c, f) Evolution of OA volatility with time. Error bars represent $\pm 1 \sigma$ from mean.

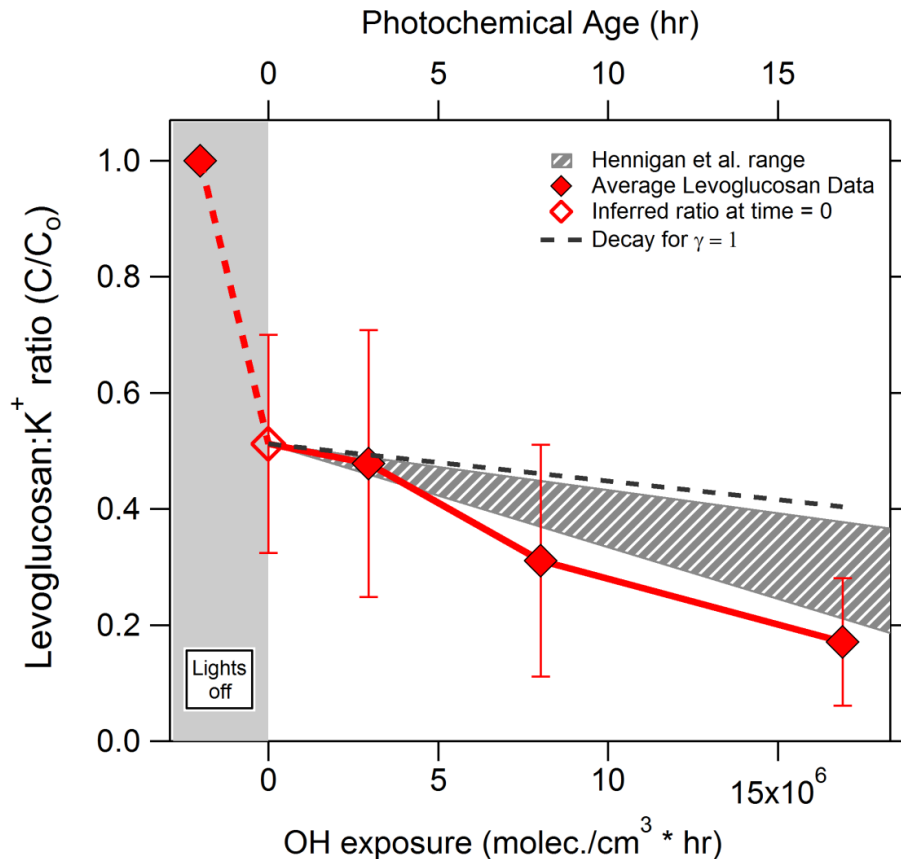


Fig. 6. Evolution of the normalized levoglucosan:K⁺ concentration with OH exposure. Solid red symbols represent campaign-average values, while the open red symbol at OH exposure = 0 was inferred based upon dilution of primary emissions. Error bars represent ± 1 standard deviation. Photochemical age (top axis) assumes an OH concentration of 1×10^6 molecules cm^{-3} . Solid grey region before OH exposure = 0 indicates period prior to photo-oxidation.

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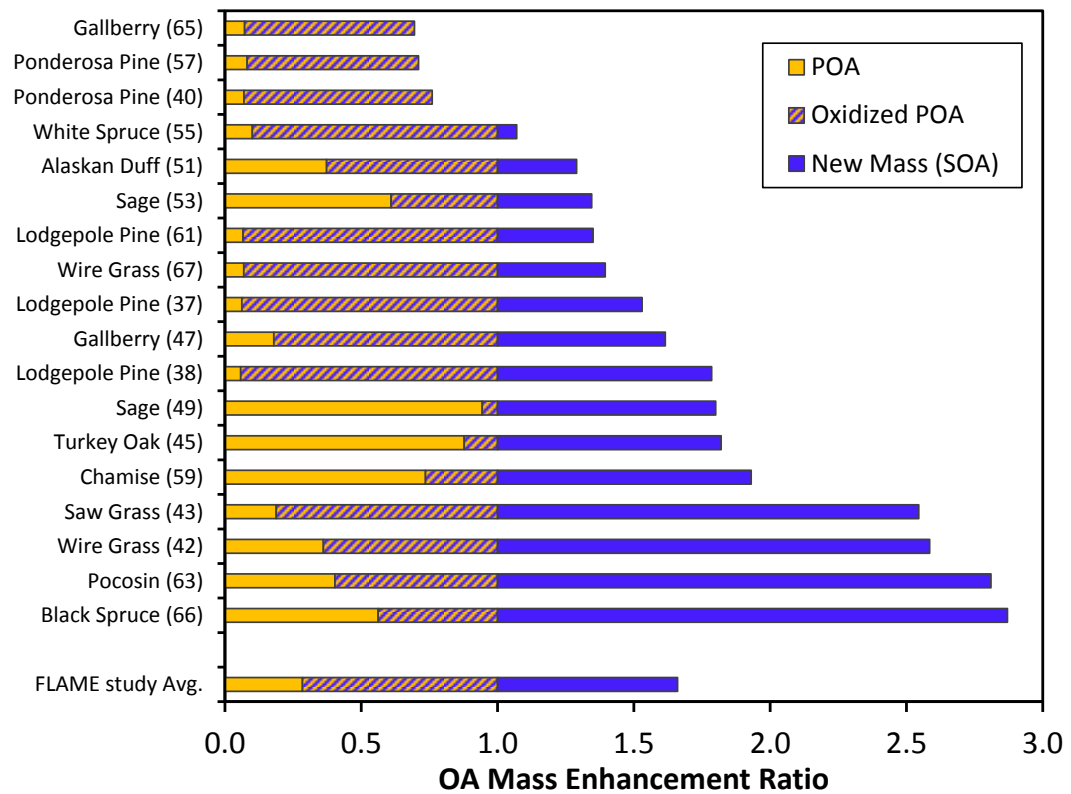


Fig. 7. OA mass enhancement ratios measured at the end of each experiment (Burn number in parentheses), as in Fig. 3. Colored portions of each bar represent the chemical composition of the aged OA. SOA was defined as new mass, O-POA was determined based on levoglucosan decay, and POA was taken as 1 minus O-POA.

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