



## Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals

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[1] Experiments were carried out in a smog chamber to investigate the oxidation of levoglucosan in biomass burning particles exposed to gas-phase hydroxyl radicals (OH). The experiments featured atmospherically-relevant particle and oxidant concentrations and both high and low relative humidity conditions. In every experiment, we observed levoglucosan decay in particles exposed to OH. The extent of decay ranged from ~20% to ~90% and was strongly correlated to the integrated OH exposure. Increased relative humidity did not enhance or impede reaction. Relative kinetics indicate that levoglucosan has an atmospheric lifetime of 0.7–2.2 days when biomass burning particles are exposed to  $1 \times 10^6$  molecules  $\text{cm}^{-3}$  of OH (typical average summertime conditions). This implies that levoglucosan reacts with OH on a timescale similar to that of transport and deposition, which has important implications for the use of levoglucosan as a tracer for biomass burning emissions in source apportionment studies.

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### 1. Introduction

[2] Emissions from biomass combustion impact global climate and human health. It is the largest source of primary organic aerosol (POA) and black carbon (BC) on a global scale [Bond *et al.*, 2004]; it also represents a potentially large source of secondary organic aerosol (SOA) precursors [Grieshop *et al.*, 2009a, 2009b]. Thus, understanding the impacts of biomass burning on local, regional, and global aerosol budgets is important. Chemical receptor models are commonly employed to quantify the contribution of biomass burning emissions to ambient aerosol concentrations. These models often use individual organic compounds or molecular markers as chemical tracers; levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is an important marker for biomass burning [Simoneit *et al.*, 2004]. Although atmospheric particles are continuously bombarded by oxidants, and hydroxyl radicals (OH) can react with organic surfaces [Bertram *et al.*, 2001] and particles [Lambe *et al.*, 2007] at near unit efficiency, receptor models currently assume that organic

molecular marker compounds are chemically stable in the atmosphere [Schauer *et al.*, 1996].

[3] Few studies have examined the stability of levoglucosan in atmospheric particles. To characterize its potential to evaporate, Oja and Suuberg [1999] measured the saturation vapor pressure of levoglucosan above 70°C, but extrapolating their results to ambient conditions is highly uncertain. Several studies have examined the potential reactivity of levoglucosan, though not in biomass burning particles. No degradation of levoglucosan spiked onto filters was observed after eight hours of exposure to ambient air [Locker, 1988]. Levoglucosan was also stable when placed in an acidic solution for 10 days, suggesting that acid-catalyzed hydrolysis is unimportant [Fraser and Lakshmanan, 2000]. However, levoglucosan has been shown to react in aqueous media suggesting that oxidation in aerosol water and cloud droplets could potentially affect atmospheric concentrations [Holmes and Petrucci, 2006, 2007; Hoffmann *et al.*, 2010].

[4] In this study, we investigated levoglucosan stability by exposing particles to hydroxyl radicals (OH) in a smog chamber. To our knowledge, this is the first study to examine levoglucosan reactivity to gas-phase OH in complex, atmospherically relevant particles. We investigated three systems: pure levoglucosan particles, wood smoke extract particles, and particles emitted from wood combustion. Experiments were conducted at particle and oxidant concentrations relevant to biomass burning plumes and a relative rate approach was used to estimate levoglucosan-OH oxidation kinetics.

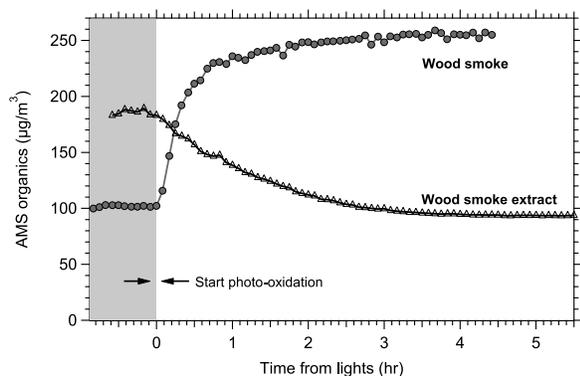
### 2. Methods

[5] The levoglucosan stability experiments were carried out in the Carnegie Mellon University smog chamber, a 12 m<sup>3</sup> Teflon bag suspended in a temperature-controlled room [Presto *et al.*, 2005]. Levoglucosan decay was investigated in three aerosol systems. First, gas and particle emissions from the combustion of hard wood logs (laurel oak) in a residential wood stove (602 CB, Jøtul, Norway) were directly injected into the smog chamber using a heated dilution system described by Grieshop *et al.* [2009a, 2009b]. After characterizing the primary emissions in the dark, photo-oxidation was initiated by turning on the chamber UV lights (GE model 10526 blacklights).

[6] We also investigated levoglucosan decay in a flash vaporized wood smoke extract and levoglucosan standard (99%, Sigma Aldrich). The extract was prepared by collecting emissions from laurel oak combustion onto a quartz filter, which was subsequently extracted by sonication in ultra-pure de-ionized water. The aqueous solution was

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**Figure 1.** Wall-loss corrected organic aerosol mass in typical wood smoke and wood smoke extract experiments.

filtered to remove insoluble particles and then concentrated using a gentle stream of  $N_2$ . This concentrated “wood smoke extract” was spiked with additional levoglucosan (99%, Sigma Aldrich) to create a solution in which levoglucosan comprised  $\sim 50\%$  of the total organic carbon on a mass basis. The wood smoke extract was injected into the smog chamber by flash vaporization, where the organic compounds in the extract volatilized and then rapidly re-condensed into accumulation-mode particles with mass-weighted median diameters between 300–450 nm. This method was also used to inject pure levoglucosan particles. Since neither VOCs nor  $NO_x$  were injected with the wood smoke extract or pure levoglucosan, an external source was needed to produce OH. This was done by introducing nitrous acid (HONO) into the chamber, which was subsequently photolyzed by turning on the UV lights. HONO is a high- $NO_x$  OH source, as its photolysis results in decomposition to  $OH + NO$  [Sander *et al.*, 2006]. NO concentrations typically reached several hundred ppb, similar to the levels observed during the wood smoke experiments. In a control experiment, wood smoke extract aerosol was injected and the UV lights were turned on without HONO addition.

[7] OH concentrations were inferred from the measured decay of toluene using a calibrated Proton Transfer Reaction Mass Spectrometer (Ionicon, Innsbruck, Austria). See Figure S2 of the auxiliary material for details on OH determination.<sup>1</sup> Toluene was naturally occurring in the wood smoke emissions, but was added at low levels ( $\sim 1\text{--}2 \mu\text{g m}^{-3}$ ) in the wood smoke extract and pure levoglucosan experiments.

[8] Total particle number and volume distributions were measured with a scanning mobility particle sizer (SMPS, TSI model 3080). Non-refractory aerosol chemical composition was monitored with an Aerodyne Quadrupole Aerosol Mass Spectrometer (AMS). Levoglucosan concentrations were determined by collecting quartz filter samples (sample collection times ranged from 5–12 min.), extracting them in water, and analyzing with high-performance anion exchange chromatography with pulsed amperometric detection [Engling *et al.*, 2006; Sullivan *et al.*, 2008]. An aethalometer (Magee Scientific, Model AE-31) quantified black carbon (BC) concentrations in the wood smoke experiments. The BC data were used to account for particle losses to the chamber walls. In the extract and pure levoglu-

cosan experiments, particle wall losses were estimated using both the SMPS and AMS measurements. Briefly, a first-order wall-loss rate constant was determined both at the beginning (before the lights were turned on) and the end (after the lights turned off) of each experiment [Weikamp *et al.*, 2007]. The wall-loss rates estimated by the BC measurement and the SMPS and AMS measurements agreed to within 11%, on average, in the wood smoke experiments (Figure S1). Unless otherwise noted, the chamber temperature was constant ( $20 \pm 2^\circ\text{C}$ ) and the relative humidity was low ( $<10\%$ ). In one wood smoke experiment, the RH was  $76 \pm 2\%$  (denoted ‘high RH’ in Figures 2 and 3).

### 3. Results

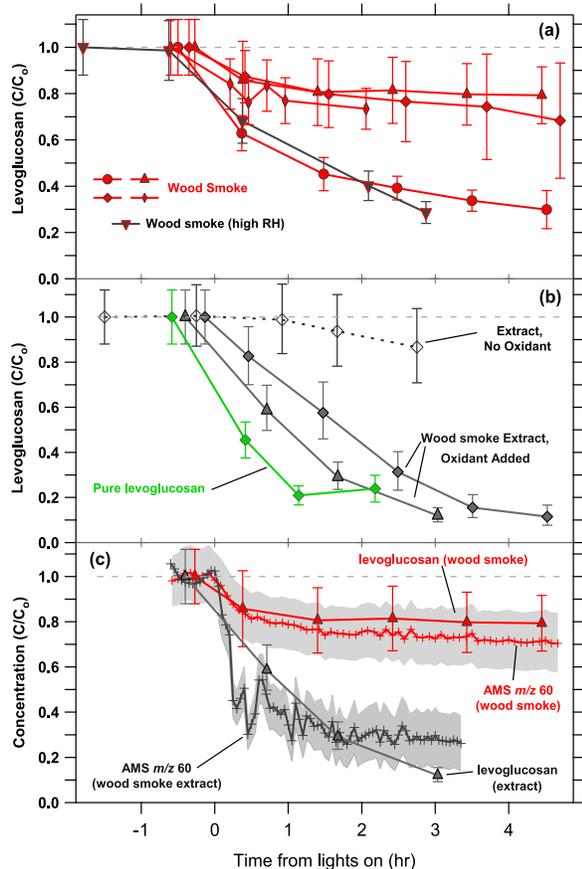
[9] Figure 1 shows wall-loss corrected organic aerosol concentrations measured by the AMS in typical wood smoke and wood smoke extract experiments. Across the set of experiments, the initial primary organic aerosol (POA) concentrations ranged from 10–230  $\mu\text{g m}^{-3}$  while initial levoglucosan concentrations ranged from 5–80  $\mu\text{g m}^{-3}$ . Therefore aerosol concentrations ranged from urban to plume-like conditions. For the biomass burning experiments, levoglucosan accounted for an average of 14.6% of POA mass. Oxidation of wood smoke generated significant SOA, more than doubling wall loss-corrected organic aerosol concentrations. In contrast, photo-oxidation of the wood smoke extract decreased the wall-loss corrected aerosol mass by almost 50%. Although an increase in aerosol mass was not expected in the extract experiments because of the lack of VOCs, the magnitude of the decrease was surprising and it indicates significant fragmentation and volatilization of the POA.

[10] Wall-loss corrected decay of levoglucosan in experiments with wood smoke, wood smoke extract, and pure levoglucosan is shown in Figure 2. In the wood smoke experiments (Figure 2a), wall-loss corrected levoglucosan concentrations decreased by 20–75% after 2–4.5 hours of exposure to OH. The average OH concentration was  $1 \times 10^7$  molecules  $\text{cm}^{-3}$  for the first hour of photo-oxidation; it then decreased by a factor of 3–5 for the remainder of the experiment. Significant levoglucosan decay was observed at both low ( $\sim 10\%$ ) and high RH conditions ( $\sim 76\%$ ) (Figure 2a). In the high RH wood smoke experiment, the two samples taken before initiating photo-oxidation demonstrate that levoglucosan is stable in the absence of OH.

[11] Significant levoglucosan decay was also observed in the experiments with wood smoke extract (Figure 2b). The wall loss-corrected concentrations of levoglucosan decreased by almost 90% in each extract experiment after  $\sim 3\text{--}4$  hours of exposure to OH (average OH concentration was  $3 \times 10^7$  molecules  $\text{cm}^{-3}$  for the first hour, followed by a decrease of a factor of 3–5 for remainder of experiment). Oxidation in pure levoglucosan particles was similar to that in the extract particles (Figure 2b). Figure 2b shows a modest decrease in levoglucosan in the control experiment ( $\sim 10\%$ ), the reason for this is unknown, but this decrease was minor compared to experiments with OH and was not significant given experimental uncertainty.

[12] The  $m/z$  60 ion is commonly used in AMS analysis as a marker of biomass burning aerosol and levoglucosan [Alfarra *et al.*, 2007]. The wall-loss corrected decay of  $m/z$  60 matched the decay of levoglucosan (Figure 2c), providing

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2010GL043088.



**Figure 2.** Wall loss-corrected decay of levoglucosan in experiments with (a) real wood smoke particles and (b) wood smoke extract and pure levoglucosan particles. (c) Wall-loss corrected decay of levoglucosan and AMS  $m/z$  60 ion in selected wood smoke and wood smoke extract experiments. The grey shaded regions represent uncertainty in the  $m/z$  60 concentration associated with the wall loss correction. Data are normalized by initial concentration ( $C/C_0$ ). Different symbols represent data for different experiments. Error bars indicate uncertainty associated with both wall loss correction and levoglucosan measurements.

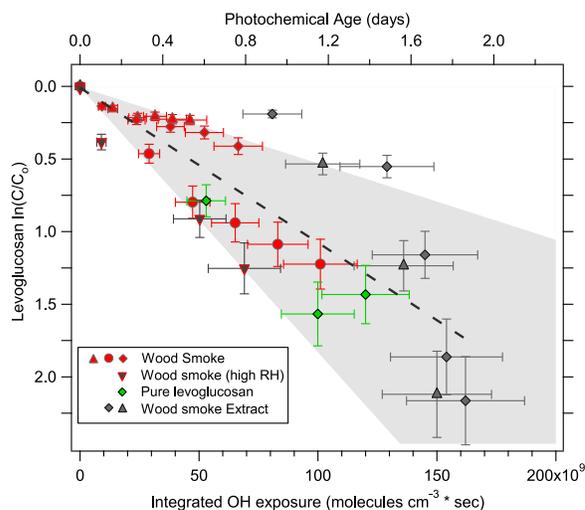
additional evidence that exposure to OH chemically transforms biomass burning POA. The minor differences in the decay of  $m/z$  60 signal and levoglucosan shown in Figure 2c could be due to differences in time resolution between the filter and the AMS measurements or the fact that compounds other than levoglucosan also contribute to the AMS  $m/z$  60 signal. Overall, the results in Figure 2 provide compelling evidence that levoglucosan is not inert in biomass burning particles, but reacts with OH at atmospherically-relevant particle and oxidant concentrations.

[13] Figure 2 shows the extent of levoglucosan oxidation varied widely between experiments. To account for experiment-to-experiment differences in OH levels, Figure 3 plots wall-loss corrected levoglucosan levels as a function of integrated OH exposure (OH concentration  $\times$  time). The levoglucosan decay as a function of OH exposure was similar in the various aerosol systems. Except for the wood smoke extract experiments, the levoglucosan decay varied linearly with increasing exposure in each experiment; however, the slope of this relationship varied by about a factor

of three across the set of experiments. The cause of this variation is not known, but likely is due to the complex interplay between mass transfer and chemistry that determines the overall reaction rate.

[14] The linear fit to all of the experimental data indicates an effective levoglucosan-OH rate constant of  $1.1 \pm 0.5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1}$  (black dotted line in Figure 3). This value implies an average levoglucosan lifetime of 1.1 days (the time for its decay to  $1/e$  of the initial concentration) when biomass burning particles are exposed to a constant OH concentration of  $1 \times 10^6 \text{ molecules cm}^{-3}$  (typical average summertime conditions). The experiment-to-experiment variability indicates a range of lifetimes of 0.7–2.2 days, which means that 30–75% of the levoglucosan will react within one day at typical atmospheric OH levels. Therefore, reactions with OH occur on a comparable time-scale to transport and deposition and these effects on ambient concentrations must be considered. It is important to note that the lifetime is dependent upon the OH concentration, and thus will vary depending on atmospheric conditions. Figure 3 also indicates that the prominent SOA formation observed in wood smoke experiments did not significantly alter levoglucosan reaction.

[15] The measured oxidation rate of levoglucosan is similar to that of motor vehicle molecular markers [Weitkamp et al., 2008; Lambe et al., 2009]. In addition, the effective uptake coefficient was greater than one (see Text S1 for details), which suggests that gas-phase reactions may contribute to the measured decay of levoglucosan [Lambe et al., 2009]. Though more research is needed to characterize the volatility of levoglucosan, the results of *Oja*



**Figure 3.** Wall-loss corrected levoglucosan decay as a function of integrated OH exposure for all experiments. The photochemical lifetime (top x-axis) assumes a constant OH concentration of  $1 \times 10^6 \text{ molecules cm}^{-3}$ , a typical average summertime OH concentration. The aerosol system is denoted by different colors with the different shaped symbols denoting data for individual experiments. The black dotted line represents a linear fit to all data, while the gray shaded region represents the range of slopes observed. Data are normalized by the initial levoglucosan concentration. Error bars indicate uncertainty associated with both wall loss correction and levoglucosan measurements.

and Suuberg [1999] suggest that levoglucosan is semi-volatile at 20°C. Thermogravimetric measurements also suggest that levoglucosan may be semi-volatile [Grieshop et al., 2009a; Huffman et al., 2009].

[16] Data from recent field studies also indicate that levoglucosan may react in the atmosphere. For example, in Helsinki, Finland, there was a strong seasonal trend observed in the levoglucosan:potassium ion ( $K^+$ ) ratio with significantly larger ratios in the winter than in the summer [Saarikoski et al., 2008]. A similar trend was also observed in the southeastern U.S. [Zhang et al., 2010]. Although this pattern could be due to seasonal variations in biomass burning emissions ( $K^+$  is also not always a strong tracer for biomass burning emissions [Sullivan et al., 2008]), it is consistent with oxidation with higher OH levels in the summer depleting molecular marker concentrations relative to winter time [Robinson et al., 2006]. This hypothesis is supported by the significant levoglucosan decay in wood smoke particles reported here. Furthermore, many laboratory studies have shown significant transformations of organic aerosol by reaction with gas-phase oxidants [Rudich et al., 2007], including the reaction of particle phase molecular markers for motor vehicle emissions [e.g., Weitkamp et al., 2008; Lambe et al., 2009].

[17] These findings have important implications for the use of levoglucosan as a molecular marker for biomass smoke in receptor models, which currently assume that levoglucosan is inert. Our results suggest that one day of exposure to typical summertime OH levels will cause these models to underestimate the biomass burning contribution to ambient aerosol concentrations by ~30–75%. Additional transport time or elevated OH levels (e.g., within biomass burning plumes) could lead to even greater under-predictions. This underscores the need to use levoglucosan in combination with other chemical indicators, such as acetonitrile ( $CH_3CN$ ) [de Gouw et al., 2006], to apportion biomass smoke. More broadly, it also reinforces the emerging understanding of the dynamic nature of POA, which evolves continuously in the atmosphere due to changes in partitioning and oxidative processing [Robinson et al., 2007; Jimenez et al., 2009].

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## References

- Alfarra, M. R., et al. (2007), Identification of the mass spectral signature of organic aerosols from wood burning emissions, *Environ. Sci. Technol.*, *41*, 5770–5777, doi:10.1021/es062289b.
- Bertram, A. K., et al. (2001), The reaction probability of OH on organic surfaces of tropospheric interest, *J. Phys. Chem.*, *105*, 9415–9421.
- Bond, T. C., et al. (2004), A technology-based global inventory of black and organic carbon emissions from combustion, *J. Geophys. Res.*, *109*, D14203, doi:10.1029/2003JD003697.
- de Gouw, J. A., et al. (2006), Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada, *J. Geophys. Res.*, *111*, D10303, doi:10.1029/2005JD006175.
- Engling, G., et al. (2006), Determination of levoglucosan in biomass combustion aerosol by high-performance anion-exchange chromatography with pulsed amperometric detection, *Atmos. Environ.*, *40*, 299–311, doi:10.1016/j.atmosenv.2005.12.069.
- Fraser, M. P., and K. Lakshmanan (2000), Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols, *Environ. Sci. Technol.*, *34*, 4560–4564, doi:10.1021/es991229l.
- Grieshop, A. P., et al. (2009a), Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 2: analysis of aerosol mass spectrometer data, *Atmos. Chem. Phys.*, *9*(6), 2227–2240.
- Grieshop, A. P., et al. (2009b), Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution, *Atmos. Chem. Phys.*, *9*(4), 1263–1277.
- Hoffmann, D., et al. (2010), Atmospheric stability of levoglucosan: A detailed laboratory and modeling study, *Environ. Sci. Technol.*, *44*, 694–699, doi:10.1021/es902476f.
- Holmes, B. J., and G. A. Petrucci (2006), Water-soluble oligomer formation from acid-catalyzed reactions of levoglucosan in proxies of atmospheric aqueous aerosols, *Environ. Sci. Technol.*, *40*, 4983–4989, doi:10.1021/es060646c.
- Holmes, B. J., and G. A. Petrucci (2007), Oligomerization of levoglucosan by Fenton chemistry in proxies of biomass burning aerosols, *J. Atmos. Chem.*, *58*(2), 151–166, doi:10.1007/s10874-007-9084-8.
- Huffman, J. A., et al. (2009), Chemically-resolved volatility measurements of organic aerosol from different sources, *Environ. Sci. Technol.*, *43*, 5351–5357, doi:10.1021/es803539d.
- Jimenez, J. L., et al. (2009), Evolution of organic aerosols in the atmosphere, *Science*, *326*(5959), 1525–1529, doi:10.1126/science.1180353.
- Lambe, A. T., et al. (2007), Controlled OH radical production via ozone-alkene reactions for use in aerosol aging studies, *Environ. Sci. Technol.*, *41*, 2357–2363, doi:10.1021/es061878e.
- Lambe, A. T., et al. (2009), Effective rate constants and uptake coefficients for the reactions of organic molecular markers (n-alkanes, hopanes, and steranes) in motor oil and diesel primary organic aerosols with hydroxyl radicals, *Environ. Sci. Technol.*, *43*, 8794–8800, doi:10.1021/es901745h.
- Locker, H. B. (1988), The use of levoglucosan to assess the environmental impact of residential wood burning on air quality, Ph.D. thesis, Dartmouth College, Hanover, N. H.
- Oja, V., and E. M. Suuberg (1999), Vapor pressures and enthalpies of sublimation of D-glucose, D-xylose, cellobiose, and levoglucosan, *J. Chem. Eng. Data*, *44*(1), 26–29, doi:10.1021/jc980119b.
- Presto, A. A., et al. (2005), Secondary organic aerosol production from terpene ozonolysis. 1. Effect of UV radiation, *Environ. Sci. Technol.*, *39*, 7036–7045, doi:10.1021/es050174m.
- Robinson, A. L., et al. (2006), Photochemical oxidation and changes in molecular composition of organic aerosol in the regional context, *J. Geophys. Res.*, *111*, D03302, doi:10.1029/2005JD006265.
- Robinson, A. L., et al. (2007), Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, *315*(5816), 1259–1262, doi:10.1126/science.1133061.
- Rudich, Y., et al. (2007), Aging of organic aerosol: Bridging the gap between laboratory and field studies, *Annu. Rev. Phys. Chem.*, *58*, 321–352, doi:10.1146/annurev.physchem.58.032806.104432.
- Saarikoski, S., et al. (2008), Sources of organic carbon in fine particulate matter in northern European urban air, *Atmos. Chem. Phys.*, *8*(20), 6281–6295.
- Sander, S. P., et al. (2006), Chemical kinetics and photochemical data for use in atmospheric studies, *Eval. 15*, JPL Publ. 06-2, Jet Propul. Lab., Pasadena, Calif.
- Schauer, J. J., et al. (1996), Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, *30*(22), 3837–3855, doi:10.1016/1352-2310(96)00085-4.
- Simoneit, B. R. T., et al. (2004), Sugars: Dominant water-soluble organic compounds in soils and characterization as tracers in atmospheric particulate matter, *Environ. Sci. Technol.*, *38*, 5939–5949, doi:10.1021/es0403099.
- Sullivan, A. P., et al. (2008), A method for smoke marker measurements and its potential application for determining the contribution of biomass burning from wildfires and prescribed fires to ambient PM<sub>2.5</sub> organic carbon, *J. Geophys. Res.*, *113*, D22302, doi:10.1029/2008JD010216.
- Weitkamp, E. A., et al. (2007), Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber, *Environ. Sci. Technol.*, *41*, 6969–6975, doi:10.1021/es070193r.
- Weitkamp, E. A., et al. (2008), Laboratory measurements of the heterogeneous oxidation of condensed-phase organic molecular markers for motor vehicle exhaust, *Environ. Sci. Technol.*, *42*, 7950–7956, doi:10.1021/es800745x.
- Zhang, X., et al. (2010), Biomass burning impact on PM<sub>2.5</sub> over the southeastern US during 2007: integrating chemically speciated FRM filter measurements, MODIS fire counts and PMF analysis, *Atmos. Chem. Phys. Discuss.*, *10*, 7037–7077.

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