Project Title: Experimental Determination of Secondary Organic Aerosol Production from Biomass Combustion

Final Report: JFSP Project Number 09-1-03-1

Principal Investigator:

Dr. Jeffrey Collett, Atmospheric Science Department, Colorado State University, Fort Collins, CO

Co-Principal Investigators:

Dr. Allen Robinson, Carnegie Mellon University, Pittsburgh, PA

Dr. Timothy Larson, University of Washington, Seattle, WA

Dr. Sonia Kreidenweis, Colorado State University, Fort Collins, CO

Federal Cooperator:

Dr. Bret Schichtel, National Park Service, Fort Collins, CO

I. Abstract

This project, a collaboration between Colorado State University (CSU), Carnegie Mellon University (CMU), the University of Washington (UW), and the National Park Service (NPS), investigated the atmospheric aging of biomass burning plumes in order to examine changes in both primary particle emissions and the production of additional, secondary organic aerosol (SOA). Included in the project were chamber studies to directly study smoke aging as well as analyses of ambient samples to look for evidence of smoke aging and SOA formation in the ambient atmosphere. CMU conducted smog chamber studies to investigate the atmospheric evolution of fine particle and organic aerosol emissions in fire plumes. The experiments were conducted at the USDA/FS Fire Science Laboratory (FSL) in Missoula, MT as part of the FLAME-3 campaign organized by CSU and FSL; similar experiments were also conducted in the Air Quality Laboratory at CMU. The experiments investigated emissions from laboratory fires from fuels representing different regions in North America commonly impacted by prescribed burning and wildfires, including the Southeast (e.g., gallberry 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). The results from the chamber experiments are described in six papers published in peer-reviewed archival literature on the atmospheric stability of the primary smoke marker levoglucosan (Hennigan et al., 2010), the secondary organic aerosol formation and primary organic aerosol emissions processing biomass burning plumes (Hennigan et al., 2011); the formation and growth of new particles in biomass burning plumes (Hennigan et al. 2012); the evolution of cloud condensation nuclei in biomass burning plumes (Engelhart et al. 2012); the evolution of organic aerosol optical properties in biomass burning plumes (Saleh et al. 2013); and the gas-particle partitioning and volatility distribution of primary organic aerosol emissions from fires (May et al. 2013).

Filter samples from the chamber experiments were analyzed by CSU. CSU also studied the chemical composition of ambient aerosol and smoke-impacted cloud water samples. This overall sample set was used to identify markers of secondary organic aerosol production: nitrocatechols. Detailed chemical analysis of aerosol samples collected at several different locations in the U.S., representing urban, rural, continental and coastal environments, showed good correlation between nitrocatechols and levoglucosan, a known marker of biomass burning. Primary smoke emissions; however, contain low levels of nitrocatechols; these compounds are formed during aging of smoke plumes during transport making them good markers of SOA formation. While the nitrocatechols were initially identified using liquid chromatography with time of flight mass spectrometric detection, a simpler, more practical analysis method using high-performance liquid chromatography with absorbance detection was developed and successfully used for analysis of nitrocatechols in aerosol samples collected using a Hi-Vol air sampler (Desyaterik et al., in prep). Nitrocatechols and other nitrogen-containing organic matter were also documented as important contributors to visible light absorption ("brown carbon") in

biomass burning aerosols and in smoke-impacted cloud water (Desyaterik et al., 2013), accounting for nearly half of the visible light absorption in clouds impacted by biomass burning.

UW and NPS collaborated on further developing source apportionment tools to apportion the contribution of biomass burning to fine particulate matter. The focus was on hybrid receptor models that incorporated source attribution estimates derived from a chemical transport model (CTM) into receptor-oriented frameworks based on measured air quality data. In this work, a simple semi-empirical, backward Lagrangian particle chemical transport model was refined, making an operational tool used by NPS to apportion biomass burning and other sources to fine particulate carbon measured at IMPROVE monitoring sites (Schichtel et al., 2012a). The model was used to apportion IMPROVE data from 2006-08 and these results were refined by incorporation into the hybrid model based on a synthesis inversion method (Schichtel et al., 2012b). A hybrid source apportionment modeling tool was also developed by incorporating CTM modeling results into the Positive Matrix Factorization (PMF) receptor model. This model was tested at two IMPROVE sites impacted by wildfires (Sturtz et al., 2013b). A user friendly version of this model was implemented in the Multilinear Engine (ME-2) optimization package and will be used by NPS personnel. Elements of this receptor model were used to apportionment coarse particulate matter in three cities (Sturtz et al., 2013a).

II. Background and Purpose

Smoke from wild and prescribed fires can be a significant contributor to regional haze (visibility impairment) and to urban and regional air pollution. Such contributions are often clear near fire sources, but can also be significant as smoke plumes are diluted during transport far downwind. The EPA Regional Haze Rule requires that states, through regional planning organizations (RPOs), develop emission reduction plans that make progress toward achieving natural visibility conditions by 2064. The Interagency Monitoring of Protected Visual Environments (IMPROVE) program, a federal land management agency/EPA monitoring program, was established to track progress toward this goal. However, current monitoring technology is not capable of apportioning or separating out classic anthropogenic emissions such as mobile sources or other industrial related activity from wild or prescribed fire emissions. Estimates suggest that a large fraction of the fine particle carbon present in Class I areas in the western US is associated with fire emissions. Because carbon comprises as much as half of $PM_{2.5}$ mass in parts of the western U.S., it is an important contributor to regional haze. Therefore RPOs and federal land managers working to meet the regional haze rule must understand its sources. Unraveling smoke contributions to visibility degradation in the eastern and southeastern U.S. is even more challenging, given the greater emissions of particulate organic matter from urban areas. Quantifying smoke impacts on fine particle concentrations is also important when classifying areas with respect to the $PM_{2.5}$ National Ambient Air Quality Standards (NAAQS). This is particularly true where EPA's implementation of the Exceptional Event Rule comes into play. This rule permits exclusion of periods impacted by uncontrollable events, such as wildfire smoke, in determining NAAQS violations.

The fine particle impacts of biomass burning include both the direct emission of particles from the combustion process and the formation of additional particulate matter, secondary organic aerosol (SOA), as the plume ages during downwind transport. Biomass burning (BB) is the most important source of primary organic aerosols in the global atmosphere. While considerable past work had been conducted to develop methods for identifying contributions of primary emissions from wild and prescribed fire, BB also emits large amounts of volatile organic compounds (VOC) which, after chemical transformation in the atmosphere, form SOA adding to the total aerosol load from BB. Production of SOA from biomass combustion has not been well understood or adequately studied.

Although challenging, air quality regulators need routine and cost-effective methodologies and tools capable of apportioning primary and secondary aerosols in measured PM2.5 to contributing sources, including different fire types and their source regions, with associated uncertainties, on a daily basis. Long-term results are also needed to assess the successes of smoke-management policies. These regulatory needs are post-fire events, separate and complementary to the operational smoke forecasting done collaboratively by smoke

managers and air quality agencies, and the methods and tools should be retrospective, taking advantage of all data and information generated during and after the events.

This projected supported the needs of wildland fire managers and policy makers to determine the *total* contributions, including primary emissions and secondary organic aerosol (SOA) formation, from wild and prescribed fires to $PM_{2.5}$ and visibility on a regional basis. Through a series of controlled, coupled combustion-aging experiments and analysis of fire-impacted ambient aerosol samples, along with development of new modeling approaches, we pursued the following project objectives:

1. Quantify SOA production as a function of smoke age in emissions produced by combustion of a variety of important wildland and agricultural fuel types
2. Quantify emissions of SOA precursors (traditional and non-traditional) in biomass combustion smoke from wildland and agricultural fuels for incorporation into air quality models
3. Derive volatility distributions and an aging matrix required to simulate fire organic aerosol concentrations in chemical transport models using the volatility basis set approach
4. Identify compounds associated with smoke SOA production to complement use of existing primary smoke markers in determining total fire contributions to ambient $PM_{2.5}$ carbon
5. Identify the role of biomass burning primary and secondary aerosol formation as a source of "brown carbon", organic material with significant absorption of short wavelength visible light, and identify specific chemical compounds responsible for the absorbance
6. Examine the impacts of biomass burning emissions on climate-relevant aerosol properties, including aerosol particle number, aerosol hygroscopicity, and aerosol ability to act as cloud condensation nuclei (CCN)
7. Develop simple chemical analysis techniques for SOA markers suitable for use in routine air monitoring networks such as IMPROVE
8. Develop and refine a hybrid-receptor source apportionment model with the SOA markers as inputs to apportioning primary and secondary smoke to biomass burning types and their source regions on a daily timescale
9. Effectively disseminate project findings to those involved in fire management, air quality analysis, and modeling of smoke impacts

III. Study Description

The controlled aging portion of the project, led by CMU, involved conducting controlled smog chamber experiments with emissions from laboratory fires. These experiments were conducted as part of the FLAME III study at the U.S. Forest Service Fire Science Laboratory (FSL) in Missoula, MT during September-October 2009. The FLAME III experiment was led by Sonia Kreidenweis of CSU with primary funding provided by USEPA; the smoke aging

experiments were added on with support from JFSP. Additional experiments were conducted in the Air Quality Laboratory at Carnegie Mellon University. The goal of the experiments was to investigate the effects of photo-oxidation on aerosol emissions under plume-like conditions. The experiments investigated fuels representing different regions in North America commonly impacted by prescribed burning and wildfires, including the Southeast (e.g., gallberry 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).

The laboratory fires involved a small mass (0.3-1.0 kg) of fuel that was ignited using electric heating coils that were pre-conditioned with a small amount of ethanol (~5 mL). Dilute smoke was transferred from the fire into a Teflon smog chamber where it was photo-oxidized by turning on UV lights. In some cases, HONO was added to boost both hydroxyl radical and nitrogen oxide concentrations in the chamber. A suite of real time instrumentation and integrated samples were used to characterize the evolution of the emissions. Aerodyne High Resolution and Quadrupole Aerosol Mass Spectrometers were used to measure non-refractory aerosol mass, including OA as well as inorganic species sulfate, nitrate, chloride, potassium, and ammonium. A scanning mobility particle sizer measured aerosol number and volume distributions for particles in the size range 10.6-498 nm. Black carbon concentrations were measured with a Single Particle Soot Photometer (SP2) and a 7-channel Aethalometer. A thermodenuder was operated upstream of the SMPS and Q-AMS to investigate aerosol volatility. Total hydrocarbon concentrations were also measured using a Total Hydrocarbon Analyzer. Organic speciation was performed on whole air samples using gas chromatography mass spectrometry and a Proton Transfer Reaction-Mass Spectrometer. Additional gas-phase measurements included carbon dioxide, carbon monoxide, ozone, and oxides of nitrogen. Teflon membrane filter samples were collected for to characterize the chemical composition of primary and aged aerosol by CSU using offline techniques. Primary organic carbon (OC) and elemental carbon (EC) emission factors were determined using Hi-volume filter samples collected by CSU in the burn chamber. Aerosol number concentrations, hygroscopicity, cloud condensation nuclei (CCN) behavior, and light absorbance properties were also examined in order to better characterize potential climate-relevant impacts of biomass burning emissions.

Both chamber-aged biomass burning aerosol and ambient aerosol samples were chemically analyzed by CSU to characterize primary emissions and to identify candidate SOA marker species. Concentrations of levoglucosan, a commonly used primary smoke marker, were measured using high-performance anion-exchange chromatography with pulsed amperometric detection, an approach developed under prior JFSP support. Organic and elemental carbon were determined using a Sunset Labs EC/OC semi-continuous analyzer that quantifies OC and EC carbon mass by thermal/optical transmission. Initial screenings for candidate SOA markers were conducted on chamber and ambient samples using liquid chromatography with time-of-flight mass spectrometry (LC/ToF-MS).   Once nitrocatechols were identified as candidate SOA markers, a simpler, more practical method was developed for their routine analysis by LC with

absorbance detection. Unfortunately, limited aerosol mass available on chamber samples made measurement of the detailed organic composition in those experiments difficult by filter-based techniques. Nitrocatechol and levoglucosan concentrations were measured and compared in ambient aerosol samples collected at three different locations: Rocky Mountain National Park (RMNP), Yosemite National Park (YNP), and in a residential area in Chicago. Ratios of nitrocatechol (SOA marker) concentrations to levoglucosan (primary OA marker) concentrations measured in the field studies were compared with those emitted from 21 different burns in an experimental chamber.

With growing interest in the community in visible light absorption by organic aerosols, a phenomenon referred to as "brown carbon," along with knowledge that some of the nitrogen-containing compounds identified in SOA formation in biomass burning smoke plumes are strong absorbers, we also analyzed the detailed organic composition of several biomass burning impacted cloud samples collected in a previous experiment at the summit of Mt. Tai (1534 m), China. Cloud water collected at this mountain site in the China North Plain contained up to 200 ppmC, among the highest concentrations ever observed in clouds or fogs sampled around the world. The highest concentrations were observed when the clouds ingested regional emissions from extensive spring agricultural burning. The high total organic carbon (TOC) samples collected during these periods exhibited a strong yellow/brownish color, reflecting strong absorption of short visible wavelengths associated with the presence of brown carbon. We took advantage of these unique samples, collected by CSU under sponsorship of the National Science Foundation, to quantitatively determine the specific compounds active as brown carbon. The samples were analyzed with a liquid chromatograph coupled with a UV/Vis diode array detector followed by a time-of-flight mass spectrometer (ToF-MS) with an electrospray ionization source. The combination of on-line absorbance and MS detection permits us to identify sample compounds associated with strong absorbance in the near UV and visible. More than 90% of the time, absorbance peaks in sample chromatograms exhibited a corresponding ion current peak, in positive and/or negative mode, in the ToF-MS.

The development and refinement of tools to apportion the contribution of biomass burning to fine particulate matter and haze was conducted by UW and NPS. A dual tool development path was followed. First, a simple semi-empirical, backward Lagrangian particle chemical transport model was refined and made an operational tool used by NPS to apportion biomass burning and other sources to fine particulate carbon measured at IMPROVE monitoring locations. This built upon work from a previous JFSP project. The model was used to apportion the IMPROVE data from 2006-08. The simplistic treatment of atmospheric chemistry cannot reproduce the dynamics of real atmospheric processes. This likely resulted in biased source apportionment results. For example, the model appeared to overestimate biomass burning contributions from nearby fires and underestimate those from distant fires. Part of the bias is likely due to poor representation of SOA formation and highly uncertain biomass burning VOC emission rates. To refine these results two hybrid models were developed. One was a simple

method to adjust the model source apportionment results to fit measured fine particle carbon data. The second was a sophisticated receptor model that merged measured fine particle composition and smoke marker trace species and modeled source apportionment results. It is the second method in which SOA smoke marker species will ultimately be incorporated to further refine estimate of biomass burning to PM2.5 and haze.

The focus of further model development was on hybrid receptor models that incorporated source attribution estimates derived from a chemical transport model (CTM) into receptor-oriented frameworks based on measured air quality data. In this work, a simple semi-empirical, backward Lagrangian particle chemical transport model was refined and made an operational tool used by the NPS to apportion biomass burning and other sources to fine particulate carbon measured at IMPROVE monitoring sites (Schichtel et al., 2012a). The model was used to apportion the IMPROVE data from 2006-08 and these results were refined by incorporated into a hybrid model based on the synthesis inversion method (Schichtel et al., 2012b). A hybrid source apportionment modeling tool was also developed by incorporating CTM modeling results into the Positive Matrix Factorization (PMF) receptor model. This model was tested at two IMPROVE sites impacted by wildfires (Sturtz et al., 2013b). A user friendly version of this model was implemented in the Multilinear Engine (ME-2) optimization package and will be used by NPS personnel. Elements of this receptor model were used to apportionment coarse particulate matter in three cities (Sturtz et al,. 2013a).

IV. Key Findings

The key findings section provides a brief summary of the results for many of the project elements discussed above, and provides key citations for each; additional publications are in the listings in the next section. More detailed descriptions of the findings are available from the publications resulting from this work.

IV.I. The primary smoke marker levoglucosan decays during plume aging

Levoglucosan (1,6-anhydro-β-D-glucopyranose) is an important marker for source apportionment of biomass burning. Source apportionment analyses currently assume that levoglucosan is conserved in the atmosphere. 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 10^6 molec 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 primary biomass burning emissions in source apportionment studies. Atmospheric oxidation will cause receptor models that use levoglucosan as a marker for biomass smoke to underestimate the contribution of primary biomass smoke to ambient fine particulate matter.

Key publication:

Hennigan, C. J., A. P. Sullivan, J. L. Collett Jr., A. L. Robinson (2010) "Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals," *Geophysical Research Letters*, 37(L09806), doi:10.1029/2010GL043088.

IV.II. SOA production in aging smoke plumes can be substantial but varies with fuel type

In the atmosphere, emissions from fires are exposed to sunlight, other pollutants, and oxidants such as ozone (O_3), hydroxyl radicals (OH), and nitrate (NO_3) radicals, which cause the emissions to evolve chemically and physically. This processing can generate secondary particulate matter, such as SOA, which can increase the contribution of wild and prescribed fires to ambient fine particulate matter. Smog chamber experiments were conducted to investigate the chemical and physical transformations of organic aerosol (OA) during photo-oxidation of open biomass burning emissions. 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 SOA production nearly tripled the POA concentration to 0.7 in experiments where photo-oxidation resulted in a 30% loss of OA mass. OA mass can be lost when hydroxyl radical attack fragments POA constituents leaving behind more volatile components that escape to the gas phase. The campaign-average OA mass enhancement ratio was 1.7 ± 0.7 (mean $\pm$ 1σ); 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 POA emissions. 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 hours of exposure to typical 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. These atmospheric transformations must be accurately represented in chemical transport models to developing effective regulatory strategies for ambient fine particulate matter.

Key publication:

Hennigan, C. J.; Miracolo, M. A.; Engelhart, G. J.; May, A. A.; Presto, A. A.; Lee, T.; Sullivan, A. P.; McMeeking, G. R.; Coe, H.; Wold, C. E.; Hao, W. M.; Gilman, J. B.; Kuster, W. C.; de Gouw, J.; Schichtel, B. A.; Collett, J. L.; Kreidenweis, S. M.; and Robinson, A. L. (2011) Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber. *Atmospheric Chemistry & Physics,* 11, 7669-7686.

IV.III. The volatility of primary organic aerosol emitted by biomass burning needs to be accounted for when modeling the evolution of diluting smoke plumes

Atmospheric organic aerosol concentrations depend in part on the gas-particle partitioning of primary organic aerosol (POA) emissions. Heating and dilution were used to investigate the volatility of biomass burning smoke particles from combustion of common North American trees/shrubs/grasses. Fifty to eighty percent of the mass of biomass burning POA evaporated when isothermally diluted from plume (~1000 μg m^{-3}) to ambient-like (~10 μg m^{-3}) concentrations, while ~80% of the POA evaporated upon heating to 100 ^{o}C in a thermodenuder with a residence time of ~14 seconds. Therefore, the majority of the POA emissions were semi-volatile. A single volatility distribution can be used to successfully represent the measured gas-particle partitioning from the entire set of experiments, including different fuels, organic aerosol concentrations, and thermodenuder residence times. This volatility distribution and associated emission factors for each fuel studied can be used to update emission inventories and simulate the gas-particle partitioning of biomass burning POA emissions to improve predictions of ambient fine particulate matter concentrations using chemical transport models.

Key publication:

A.A. May, E.J.T. Levin, C.J. Hennigan, I. Riipinen, T. Lee, J.L. Collett, Jr., J.L. Jimenez, S.M. Kreidenweis, A.L. Robinson "Gas-particle partitioning of primary organic aerosol emissions 3. Biomass burning," *Journal of Geophysical Research: Atmospheres*, 118(19), 2013JD020286.

IV.IV. Fresh and aged biomass burning emissions exert an important influence on aerosol-related climate forcing

Biomass burning emits large amounts of trace gases and particles into the atmosphere, influencing climate and precipitation patterns. Fires also contribute a significant fraction of the global cloud condensation nuclei (CCN) burden. Fires also emit substantial amounts of light absorbing carbon. Smog chamber experiments were performed to study the effects of atmospheric processing of these and other climate relevant properties of fine particle emissions from fires.

Values of the hygroscopicity parameter, κ, were calculated from cloud condensation nuclei measurements of emissions from combustion of 12 biomass fuels commonly burned in North American wildfires. Prior to photochemical aging, κ for fresh primary aerosol varied widely,

between 0.06 (weakly hygroscopic) and 0.6 (highly hygroscopic). The hygroscopicity of the primary aerosol was positively correlated with the inorganic mass fraction of the particles. There was also a relationship between the hygroscopicity of the primary aerosol and the extent of oxygenation of POA, suggesting an influence of the POA composition on the primary aerosol hygroscopicity as well. Photochemical processing reduced the range of κ values to between 0.08 and 0.3. The changes in κ were driven by the photochemical production of SOA. Although initial CCN activity of biomass burning aerosol emissions are highly variable, after a few hours of photochemical processing κ converges to a value of 0.2±0.1. *Therefore, photochemical aging reduces the variability of biomass burning CCN, which should simplify analysis of the potential effects of biomass burning aerosol on climate.*

Photo-oxidation of dilute exhaust from combustion of 12 different North American fuels also induced significant new particle formation that increased the particle number concentration by a factor of four (median value). The production of secondary organic aerosol caused these new particles to grow rapidly, significantly enhancing CCN concentrations. Using inputs derived from these new data, global model simulations predict that nucleation in photo-chemically aging fire plumes produces dramatically higher CCN concentrations over widespread areas of the southern hemisphere during the dry, burning season (Sept.-Oct.), improving model predictions of surface CCN concentrations. *The annual indirect forcing from CCN resulting from nucleation and growth in biomass burning plumes is predicted to be -0.2 W m^{-2}, demonstrating that this effect has a significant impact on climate that has not been previously considered.*

We also investigated the effects of photochemical aging on the optical properties of carbonaceous aerosol emissions from biomass burning. We constrained the light-absorption properties of the organic using conservative limiting assumptions, and found that both POA in the fresh emissions and SOA produced by photochemical aging absorb light to a significant extent, and are categorized as brown carbon. This work presents the first direct evidence that SOA produced in aged biomass burning emissions is absorptive. For the investigated fuels, SOA is less absorptive than POA in the long visible, but exhibits steeper wavelength-dependence (larger Absorption Ångström Exponent) and is more absorptive in the short visible and near-UV. *Light absorption by SOA in biomass burning emissions might be an important contributor to the global radiative forcing budget.*

Key publications:

R. Saleh, C.J. Hennigan, G.R. McMeeking, W.K. Chuang, E.S. Robinson, H. Coe, N.M. Donahue, A.L. Robinson "Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions," *Atmospheric Chemistry and Physics*, 13, 7683-7693, 2013.

G. J. Engelhart, C. J. Hennigan, M. A. Miracolo, A. L. Robinson, and S. N. Pandis "Cloud condensation nuclei activity of fresh primary and aged biomass burning aerosol," *Atmospheric Chemistry and Physics*, 12, 7285-7293, 2012.

C. J. Hennigan, D. M. Westervelt, I. Riipinen, G. J. Engelhart, T. Lee, J. L. Collett Jr., S. N. Pandis, P. J. Adams, and A. L. Robinson "New particle formation and growth in biomass burning

plumes: An important source of cloud condensation nuclei," *Geophysical Research Letters*, 39, L09805, doi:10.1029/2012GL050930, 2012.

IV.V. Nitrocatechols are good markers for SOA production from biomass burning emissions

Analysis of aerosol samples collected in different locations of the U.S. under different environments (urban and rural) revealed that nitrocatechol concentrations correlate well with the concentration of levoglucosan, a marker of BB emission, indicating a common biomass burning source for levoglucosan (primary smoke marker) and nitrocatechols. Nitrocatechols can also be formed by oxidation of toluene, and have been observed in the emissions of gasoline-powered engines; however, such contributions to nitrocatechols measured in our samples indicate that such urban sources are minor. Measurements of nitrocatechols in fresh emissions from the burning of 21 biomass fuels at FSL demonstrated that primary emissions are low. Together, these observations indicate that the major source of nitrocatechols in the atmosphere is from the oxidation of volatile organic compounds VOCs emitted from biomass burning.

Key publication:

Desyaterik, Y., A. P. Sullivan, B. A. Schichtel, and J. L. Collett, Jr. (2013), Tracer Compounds for Secondary Organic Aerosols from Biomass Burning, in preparation for submission to *Atmos. Environ.*

IV.VI. A simple, practical method has been developed for routine analysis of nitrocatechols in filter samples

While initial screenings for biomass burning SOA markers in the study were conducted using a complex and expensive research grade instrument, LC/ToF-MS, the strong absorptivity of these compounds makes them suitable for identification by other techniques. A much simpler, practical technique was developed and successfully applied for quantitative nitrocatechol analysis of PM2.5 aerosol collected on quartz filters. This technique involves aqueous extraction of the filter sample followed by analysis using high performance liquid chromatography (HPLC) with absorbance detection. The development of this simple and sensitive analytical approach makes the analysis of nitrocatechols practical for filter samples collected in routine monitoring efforts.

Key publication:

Desyaterik, Y., A. P. Sullivan, B. A. Schichtel, and J. L. Collett, Jr. (2013), Tracer Compounds for Secondary Organic Aerosols from Biomass Burning, in preparation for submission to *Atmos. Environ.*

IV.VII. Nitrocatechols and other nitro-aromatic compounds account for a large fraction of brown carbon absorption

It is well accepted that biomass burning is one important source of "brown" carbon in the atmosphere. In finding IV above we report that both POA and SOA from biomass burning emissions are important absorbers of visible light. Analysis of the chemical composition of light absorbing compounds present both in biomass burning aerosol and in cloud water strongly impacted by biomass burning reveals the importance of nitrocatechols and other nitro-aromatic compounds as sources of the yellow/brown color associated with biomass burning aerosol. Quantitative analysis was conducted on cloud water strongly impacted by agricultural burning using high performance liquid chromatography equipped with a UV/Vis absorbance detector immediately followed by electrospray ionization and analysis using a time-of-flight (ToF) mass spectrometer. Using this approach, the elemental compositions of 16 major light-absorbing compounds, which together accounted for approximately half of measured sample absorption between 300 and 400 nm, were determined. The most important classes of light-absorbing compounds were found to be nitrophenols (including nitrocatechols) and aromatic carbonyls. Total sample absorbance and concentrations of nitrated organics were considerably lower in the absence of biomass burning. Nitrocatechols and other nitro-aromatic compounds formed through atmospheric oxidation of biomass burning emissions are major contributors to atmospheric brown carbon.

Key publication:

Desyaterik, Y., Y. Sun, X. Shen, T. Lee, X. Wang, T. Wang, and J. L. Collett Jr. (2013), Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China, *J. Geophys. Res. Atmos.*, 118, 7389–7399, doi:10.1002/jgrd.50561.

IV.VIII. Simulated 2006-2008 fine particle carbon concentrations at rural IMPROVE monitoring sites reveal seasonal prescribed, wild, and agricultural fire impacts

A receptor-oriented, Lagrangian particle dispersion model was used to simulate the total particulate carbon at rural IMPROVE monitoring sites from 2006-2008. Modeling evaluation revealed potential spatial and temporal biases in the model results. To reduce these biases and refine the source attribution results, an inverse modeling approach was used that regressed the source attribution results against the measured total carbon (TC) data using a Bayesian regression method. It was found that during the summer months, TC was predominantly due to biomass burning and SOA from vegetation. Smaller contributions from area and mobile sources also occurred. During the winter months, vegetation and biomass burning had smaller contributions, while the relative contributions from mobile sources increased, and area sources were the largest contributor, accounting for about half of the TC. Different fire seasons were also evident, with large contributions during the summer months due to wildfires and smaller

contributions during the spring and fall when prescribed and agricultural fires regularly occur.

Key publications:

Schichtel, B. A., M. A. Rodriguez, M. G. Barna, K. A. Gebhart, M. L. Pitchford and W. C. Malm, A semi-empirical, receptor-oriented Lagrangian model for simulating fine particulate carbon at rural sites, *Atmospheric Environment*, 61, 361-370, 2012.

Schichtel, B. A., M. A. Rodriguez, M. G. Barna, K. A. Gebhart, L. A. Patterson, J. L. Collett, Jr. and W. C. Malm, Contributions of biomass burning and other sources to fine particulate carbon at rural locations throughout the United States, Proceedings of the Air & Waste Management Association specialty conference, Aerosol and Atmospheric Optics: Visibility and Air Pollution, Whitefish, Montana, September 24-28, 2012.

IV.VIII. A new, receptor-oriented hybrid model approach improves modeled PM concentrations and associated source apportionment estimates

Source contributions to total fine particle carbon predicted by a chemical transport model (CTM) were incorporated into the positive matrix factorization (PMF) receptor model to form a receptor-oriented hybrid model. The level of influence of the CTM versus traditional PMF was varied using a weighting parameter applied to an object function as implemented in the Multilinear Engine (ME-2). The resulting hybrid model was used to quantify the contributions of total carbon from both wildfires and biogenic sources at two IMPROVE monitoring sites, Monture and Sula Peak, Montana, from 2006 through 2008. CTM source impacts were used to aid in the separation of biogenic sources from biomass combustion due to wildfires. Two additional features were identified at each site, a soil derived feature with elevated contributions in the summer and a feature enriched in both sulfate and nitrate with significant, but sporadic contributions across the sampling period. The fit of the hybrid model was improved compared to the fit of either independent model alone. Therefore, the hybrid approach provides an important technique for tying together emission estimates and downwind measurements to better understand the sources impacting the modeled airshed.

A "front-end" to the model was developed using the platform independent python scripting language to allow easier use by experts. The model will be delivered to the NPS-ARD and training provided in January 2014.

Key publications:

Sturtz, T. M., B. A. Schichtel, and T. V. Larson (2013) Coupling Chemical Transport Model Source Attributions with Positive Matrix Factorization: Application to two IMPROVE sites impacted by wildfires. In preparation for submission to *Environ. Sci. Tech.*

IV.IX. Outreach

As part of this project there was extensive outreach conducted to the federal, state, and

private scientific and regulatory communities. This outreach was conducted by means of the participation and sharing of results at a number of conferences, workshops, and meetings; see list below.

IV.IX.I. Publications: Peer-Reviewed Journal Articles

1. Hennigan, C. J., A. P. Sullivan, J. L. Collett Jr., A. L. Robinson (2010) Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, *Geophysical Research Letters*, **37**(L09806), doi:10.1029/2010GL043088.

2. Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett, J. L., Kreidenweis, S. M., and Robinson, A. L. (2011) Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber. *Atmospheric Chemistry & Physics* **11**, 7669-7686.

3. Engelhart, G. J., C. J. Hennigan, M. A. Miracolo, A. L. Robinson, and S. N. Pandis (2012) Cloud condensation nuclei activity of fresh primary and aged biomass burning aerosol, *Atmospheric Chemistry and Physics*, **12**, 7285-7293.

4. Hennigan, C. J., D. M. Westervelt, I. Riipinen, G. J. Engelhart, T. Lee, J. L. Collett Jr., S. N. Pandis, P. J. Adams, and A. L. Robinson (2012) New particle formation and growth in biomass burning plumes: An important source of cloud condensation nuclei, *Geophysical Research Letters*, **39**, L09805, doi:10.1029/2012GL050930.

5. Schichtel, B. A., M. A. Rodriguez, M. G. Barna, K. A. Gebhart, M. L. Pitchford and W. C. Malm (2012) A semi-empirical, receptor-oriented Lagrangian model for simulating fine particulate carbon at rural sites, *Atmospheric Environment*, 61, 361-370.

6. May, A.A., E.J.T. Levin, C.J. Hennigan, I. Riipinen, T. Lee, J.L. Collett, Jr., J.L. Jimenez, S.M. Kreidenweis, A.L. Robinson (2013) Gas-particle partitioning of primary organic aerosol emissions 3. Biomass burning, *Journal of Geophysical Research: Atmospheres*, **118**(19), 2013JD020286.

7. Saleh, R., C.J. Hennigan, G.R. McMeeking, W.K. Chuang, E.S. Robinson, H. Coe, N.M. Donahue, and A.L. Robinson (2013) Absorptivity of brown carbon in fresh and photo-chemically aged biomass-burning emissions, *Atmospheric Chemistry and Physics*, **13**, 7683-7693.

8. Desyaterik, Y., Y. Sun, X. Shen, T. Lee, X. Wang, T. Wang, and J. L. Collett Jr. (2013), Speciation of "brown" carbon in cloud water impacted by agricultural biomass burning in eastern China, *Journal of Geophysical Research: Atmospheres*, 118, 7389–7399, doi:10.1002/jgrd.50561.

9. Desyaterik, Y., A. P. Sullivan, B. A. Schichtel, and J. L. Collett, Jr. (2013) Tracer Compounds for Secondary Organic Aerosols from Biomass Burning, in preparation for submission to *Atmos. Environ.*

10. Sturtz, T. M., S. D. Adar, T. Gould, T. V. Larson (2013a) Constrained Source Apportionment of Coarse Particulate Matter and Selected Trace Elements in Three Cities from the Multi-Ethnic Study of Atherosclerosis, *Atmospheric Environment*, Available online 21 November 2013, http://dx.doi.org/10.1016/j.atmosenv.2013.11.031.

11. Sturtz, T. M., B. A. Schichtel, and T. V. Larson (2013b) Coupling Chemical Transport Model Source Attributions with Positive Matrix Factorization: Application to two IMPROVE sites impacted by wildfires, in preparation for submission to *Environ. Sci. Tech.*

IV.IX.II. Other Articles

Balcerak, E. *(2013),* Identifying the chemical composition of "brown carbon" in the atmosphere*, Eos Trans. AGU,* 94*(30),* 268*.*

IV.IX.III. Theses Partially Supported by This Project

- Andrew May, PhD, Department of Mechanical Engineering, Carnegie Mellon University, 2012.

- Gabriel Engelhart, PhD, Department of Chemical Engineering, Carnegie Mellon University, 2010.

- Timothy M. Sturtz, PhD, Department of Civil & Environmental Engineering, University of Washington, 2013.

IV.IX.IV. Conference Proceeding and Presentations

1. Sturtz, T., Schichtel, B., Larson, T.V., Development of an Air Quality Forensics Model, May 2013, American Society of Civil Engineers Seattle Chapter Meeting, Invited Speaker.

2. C. J. Hennigan*, D. Westervelt, I. Riipinen, G. Engelhart, T. Lee, J. L. Collett, S. N. Pandis, P. J. Adams, A. L. Robinson "New Particle Formation and Growth in Biomass Burning Plumes: an Important Source of Cloud Condensation Nuclei," American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, December 3-7, 2012.

3. J. L. Collett*, Y. Desyaterik, A. P. Sullivan, C. Hennigan, A.L. Robinson, A. Holden, S. Kreidenweis, B. Schichtel "Aging of Biomass Burning Aerosols: Comparison of Smog Chamber Experiments with Ambient Aerosols," American Association of Aerosol Research 31st Annual Conference (AAAR 2012), Minneapolis, MN, October 8-12, 2012.

4. R. Saleh*, C. Hennigan, G. McMeeking, W. Chuang, H. Coe, N.M. Donahue, A.L. Robinson "Light Absorption Properties of Brown Carbon from Fresh and Photo-chemically Aged Biomass Burning Emissions," American Association of Aerosol Research 31st Annual Conference (AAAR 2012), Minneapolis, MN, October 8-12, 2012.

5. A. A. Presto*, T. Gordon, C. Hennigan, M. Miracolo, A. L. Robinson "Primary to Secondary Organic Aerosol: Evolution of Emissions from Combustion Sources," American Association of Aerosol Research 31st Annual Conference (AAAR 2012), Minneapolis, MN, October 8-12, 2012.

6. A.L. Robinson*, R. Saleh, C. Hennigan, G. McMeeking, W. Chuang, H. Coe, N.M. Donahue, A.L. Robinson "Light Absorption Properties of Brown Carbon from Fresh and Photo-chemically Aged Biomass Burning Emissions," Aerosol and Atmospheric Optics Visibility & Air Pollution, Whitefish, MT, September 24-28, 2012.

7. Jeffrey L. Collett, Jr.*, Yury Desyaterik, and Yele Sun, Speciation of Atmospheric "Brown" Carbon, Air and Waste Management Association Annual Conference, Whitefish, Montana, 25-28 September 2012.

8. Sturtz, T. M., T. V. Larson and B. A. Schichtel, Source apportionment of primary and secondary fine particles: A hybrid model, Proceedings of the Air & Waste Management Association specialty conference, Aerosol and Atmospheric Optics: Visibility and Air Pollution, Whitefish, Montana, September 24-28, 2012.

9. Schichtel, B. A., M. A. Rodriguez, M. G. Barna, K. A. Gebhart, L. A. Patterson, J. L. Collett, Jr. and W. C. Malm, Contributions of biomass burning and other sources to fine particulate carbon at rural locations throughout the United States, Proceedings of the Air & Waste Management Association specialty conference, Aerosol and Atmospheric Optics: Visibility and Air Pollution, Whitefish, Montana, September 24-28, 2012.

10. Schichtel, B. A., M. A. Rodriguez, M. G. Barna, K. A. Gebhart, L. A. Patterson, J. L. Collett, Jr. and W. C. Malm, Contributions of biomass burning and other sources to fine particulate carbon at rural locations throughout the United States, AMS annual meeting, New Orleans, LA, January 22-26, 2012.

11. Jeffrey L. Collett, Jr.*, Yury Desyaterik, Yele Sun, Xinhua Shen, Taehyoung Lee, Xinfeng Wang, Wenxing Wang, and Tao Wang, Speciation of "Brown" Carbon in Cloud Water Affected by Biomass Burning, *AGU Fall Meeting,* San Francisco, California, 5–9 December, 2011.

12. C.J. Hennigan*, I. Riipinen, G.J. Engelhart, A.A. May, D. Westervelt, P.J. Adams, S.N. Pandis, A.L. Robinson "New Particle Formation in Aging Biomass Burning Plumes and Implications for Global CCN Budgets," AAAR 30th Annual Conference, Orlando, FL October 3-7, 2011.

13. J. L. Jimenez*, A.M. Ortega, M. Cubison, D.A. Day, W.H. Brune, C.J. Hennigan, A.L. Robinson, H. Coe, D. Bon, J. A. De Gouw, S.M. Kreidenweis, C. Warneke "Organic Aerosol Evolution with Photochemical Processing of Open Biomass Burning Smoke: Field vs. Lab Observations and Implications for the Global OA Budget," Abstract A22A-04 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13-17 Dec 2010.

14. G. R. McMeeking*, J. W. Taylor, A.P. Sullivan, M.J. Flynn, S.K. Akagi, C.M. Carrico, J.L. Collett, E. Fortner, T. B. Onasch, S.M. Kreidenweis, R.J. Yokelson, C. J. Hennigan, A.L. Robinson, H Coe "Black carbon aerosol properties measured by a single particle soot photometer in emissions from biomass burning in the laboratory and field," Abstract A23C-02 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13-17 Dec 2010.

15. C.J. Hennigan*, M.A. Miracolo, G.J. Engelhart, A.A. May, C.E. Wold, W. M. Hao, T. Lee, A.P. Sullivan, J.B. Gilman, W.C. Kuster, J. A. De Gouw, J. L. Collett "Oxidative Aging and Secondary Organic Aerosol Formation from Simulated Wildfire Emissions," Abstract A22A-05 presented at 2010 Fall Meeting, AGU, San Francisco, Calif., 13-17 Dec 2010.

16. C. J. Hennigan*, M. A. Miracolo, G. J. Engelhart Farnham, A. P. Sullivan, J. L. Collett Jr., S. M. Kreidenweis, C. E. Wold, A. L. Robinson "Secondary Organic Aerosol Formation from the Photo-oxidation of Biomass Burning Emissions," American Association of Aerosol Research 29th Annual Conference, Portland, OR, October 25-29, 2010.

17. J. L. Collett Jr.*, Y. Desyaterik, A. Sullivan, C. Hennigan, A.L. Robinson, A. S. Holden, S. M. Kreidenweis, B. Schichtel "Organic Nitrogen in Fresh and Aged Aerosols Produced by Biomass Burning," American Association of Aerosol Research 29th Annual Conference, Portland, OR, October 25-29, 2010.

18. A. A May*, C. J. Hennigan, I. Riipinen, A. A. Presto, A.L. Robinson "Volatility of Primary Organic Aerosol Emissions from Combustion Sources: A Comparison of Thermodenuder Measurements to an Aerosol Dynamics Model,"American Association of Aerosol Research 29th Annual Conference, Portland, OR, October 25-29, 2010.

19. Schichtel, B. A., J. L. Hand, W. White, W. C. Malm, M. Pitchford, D. Murphy, J. Chow, N. Frank. Spatial and Temporal Patterns in Urban and Rural Fine Particulate Organic and Elemental Carbon in the United States, American Association for Aerosol Research, Portland, OR, October 2010.

20. G. J. Engelhart*, C. J. Hennigan, A. Sullivan, M. A. Miracolo, J.L. Collett, S. Kreidenweis, A.L. Robinosn, S.N. Pandis, CCN Activity of Primary and Photo-oxidized Biomass Burning Aerosol," 2010 International Aerosol Conference, Helsinki Finland, August 29-September 3, 2010.

21. A. Presto*, N.T. Nguyen, M. Ranjan, C.J. Hennigan, A. May, T. Gordon, M. A. Miracolo, A. L. Robinson, "Volatility and gas-particle partitioning of organic aerosol emissions from combustion sources," 2010 International Aerosol Conference, Helsinki Finland, August 29-September 3, 2010.

22. C.J. Hennigan*, M.A. Miracolo, G. Engelhart, A.A. Presto, A. Sullivan, J.L. Collett Jr, S. Kreidenweis, C. Wold, B. Schichtel, A.L. Robinson, "Oxidative Aging and Secondary Organic Aerosol Formation from Biomass Burning Emissions," 2010 International Aerosol Conference, Helsinki Finland, August 29-September 3, 2010.

23. A.M. Ortega*, W.H. Brune, M.J. Cubison, D. Welsh-Bon, J. de Gouw, T. Lee, S. Kreidenweis, A. L. Robinson, C. J. Hennigan, J.L. Jimenez, "Variability of Secondary Organic Aerosol Production and Aerosol Oxidation from Rapid and Intense Photochemical Processing of Biomass Burning Smokes," 2010 International Aerosol Conference, Helsinki Finland, August 29-September 3, 2010.

24. A.L. Robinson*, A. A. Presto, M. A. Miracolo, C. J. Hennigan, N. T. Nguyen, N. M. Donahue, "Atmospheric Transformations of Fine Particle Emissions from Combustion Systems," Air Pollution and Health: Bridging the Gap From Sources to Health Outcomes, San Diego, CA March 22-26, 2010.

25. C. J. Hennigan*, A. Sullivan, J. L. Collett, A. L. Robinson, "Laboratory Studies of the Heterogeneous Oxidation of Levoglucosan in Biomass Burning Particles," American Geophysical Union (AGU) Fall Meeting, December 14-18, 2009.

26. Y. Desyaterik*, A. Sullivan, C. J. Hennigan, A. L. Robinson, J. L. Collett "Composition of Secondary Organic Aerosols Produced by Photo-Oxidation of Biomass Burning Emissions in a Smog Chamber," American Geophysical Union (AGU) Fall Meeting, December 14-18, 2009.

27. Collett, Jr., J.L.*, Sullivan, A.P., Holden, A.S., Patterson, L., Schichtel, B., Kreidenweis, S., Malm, W.C., Wold, C., and Hao, W.M., Identifying chemical markers for quantifying smoke impacts on particulate matter concentrations and regional haze, Platform presentation at the 4th International Congress, Fire, Ecology and Management, November 30 -- December 4, 2009, Savannah, GA.

28. Kreidenweis, S.M., McMeeking, G.R., Arnott, W.P., Baker, S., Carrico, C.M., Chow, J.C., Collett, Jr., J.L.*, Hao, W.M., Holden, A.S., Kirchstetter, T.W., Levin, E.J., Lewis, K., Mack, L., Malm, W.C., Moosmuller, H., Sullivan, A.P., and Wold, C.E., The Fire Lab at Missoula Experiment (FLAME): Measurements of trace gases and aerosols during the open combustion of biomass in the laboratory, poster presentation at the 4th International Congress, Fire, Ecology and Management, November 30 -- December 4, 2009, Savannah, GA.

29. Amanda S. Holden*, Yury Desyaterik, Jeffrey L. Collett, Jr., Sonia M. Kreidenweis, and William Malm, Analysis of Fresh and Aged Aerosols Produced by Biomass Combustion, AAAR 28th Annual Conference, Minneapolis, Minnesota, October 26-30, 2009.

IV.IX.V. Workshops and Meetings

- Schichtel, B.A., J. L. Hand, W. White, W. C. Malm, M. Pitchford, D. Murphy, J. Chow, N. Frank. Exploration of IMPROVE and CSN Fine Particulate Carbon Spatial and Temporal Patterns, IMPROVE Carbon Issues and Trends Workshop, Skamania Lodge, Stevenson, WA, October 20, 2010.

- Briefed the National Park Service Air Resource Division on project results, Denver CO, March 2013

- IMPROVE Steering Committee Meeting, Tahoe Environmental Research Center, Incline Village, NV, October, 2012

- Colorado Smoke Modeling Workshop, Golden CO, March, 2013

IV.IX.VI. Other Outreach

A variety of discussions and consultations were held with scientists with the IMPROVE program concerning the composition of fresh and aged biomass burning aerosol and techniques for analyzing biomass burning-derived fine particles on filters collected by the network. Findings from research conducted as part of this project were also presented in invited presentations at leading research institutions in the U.S. and abroad:

- Robinson, A. (2010) Atmospheric Transformations of Organic Aerosol Emissions from Biomass Combustion: Preliminary Results from FLAME 3, invited presentation to the NOAA Chemical Science Division, Boulder CO, March 3, 2010.
- Collett, J. L., Jr. (2010) Characterizing impacts of wild and prescribed fires on ambient fine particle concentrations. Invited lecture at the University of California at Davis, April 14, 2010.
- Collett, J. L., Jr. (2013) Clouds, Fog, and Haze. Invited lecture at Peking University, Beijing, China, November 14, 2013.
- Collett, J. L., Jr. (2013) Clouds, Fog, and Haze. Invited lecture at the Institute for Atmospheric Physics of the Chinese Academy of Sciences, Beijing, China, November 13, 2013.
- Collett, J. L., Jr. (2013) Clouds, Fog, and Haze. Invited lecture at the Institute for Nanjing University of Information Science and Technology, Nanjing, China, November 19, 2013.

V. Management Implications

Findings from this project reveal the importance of atmospheric aging to fine particle concentrations and composition in biomass burning plumes. Key management implications of findings include the following:

- Emission inventories for primary particles and secondary particle precursors developed as part of this study will greatly improve the ability of air quality modelers to assess the overall impacts of wild and prescribed fires on fine particle concentrations. These findings can be used in models by air quality regulators in developing regional haze and PM2.5 State Implementation Plans (SIPs) to reduce the haze and PM2.5 below regulated thresholds.

- Photochemical aging of biomass burning emissions reveal that fine particle mass in wild and prescribed firms is likely to increase as a result of oxidation of gas phase compounds emitted by the fire. In a series of studies investigating the open combustion of numerous fuel types commonly involved in North American fires, the average increase in particle mass from plume aging was approximately 70%. This is a substantial increase in fine particle mass and in the effect of fire-derived particles on human health and regional haze and needs to be weighed when considering air quality impacts of fire management strategies.

- The volatile nature of primary particles emitted by biomass burning observed in this study reveals that air quality models attempting to represent near-field concentrations of fine particles in a diluting plume need to actively treat gas-particle partitioning. Considerable organic matter present in fine particles in a highly concentrated plume near the source will volatilize and repartition to the gas phase as the plume dilutes.

- Emissions from biomass burning have important effects on climate-forcing in addition to air quality. These include:

    - Increases in particle number and condensed phase mass which together can increase the abundance of cloud condensation nuclei (CCN). Increases in CCN can alter the microphysical properties of clouds. Larger numbers of smaller cloud droplets make clouds more reflective (a cooling effect) and also inhibit precipitation.

    - Increases in atmospheric concentrations of both black carbon and brown carbon can increase atmospheric absorption of solar radiation, a warming effect. Deposition of light absorbing particles to snow surfaces are suspected of accelerating snowpack melting which can feedback on fire activity through a lengthened fire season.

- The development of effective, practical techniques for measuring concentrations of chemical species that are tracers of primary particle emissions (levoglucosan) and

21

secondary particle formation (nitrocatechols) from biomass burning offers the air quality and fire management communities important new capabilities for identifying the total effect of wild and prescribed fires on regional fine particle concentrations. These approaches, developed with JFSP support under this and prior projects, are specifically designed to provide low-cost options for analysis of filters collected by routine air quality monitoring networks (e.g., IMPROVE or EPA's Chemical Speciation Network (CSN)) to document fire impacts. Application of these new capabilities promises to greatly improve our ability to document fire impacts on human health and regional haze.

- The source apportionment tools developed as part of this project have improved upon past options. The models have been made operational for expert use and transferred to the National Park Service Air Resource Division. It is planned that these models will be used for regional haze rule planning purposes. These tools will also be used by NPS to better understand the contributions of biomass burning to reactive nitrogen deposition in sensitive ecosystems, which will be used by NPS for air quality management and planning purposes.

VI. Relationship to Other Recent Findings and Ongoing Work on This Topic

Prior work funded by JFSP, USEPA, and NPS has focused on improved understanding of primary emissions from biomass burning. Through a series of Fire Lab at Missoula Experiments (FLAME), a wide range of biomass fuel types have been conducted and their emissions characterized. Special emphasis has been placed on emission of levoglucosan and other smoke marker species, the size distribution of emitted particles, black carbon emissions, emissions of trace gas species, the hygroscopicity of emitted particles, the ability of primary biomass burning particles to act as CCN and ice nuclei, and other matters. Much of this work involved collaborations between CSU, NPS, the Desert Research Institute, USFS, Aerodyne Research, and others.

The work presented here represents a next phase in this long-term effort to better understand smoke formation and impacts from wild and prescribed fires, with the focus shifted to aging of emitted species and the formation of SOA. SOA formation from a variety of biogenic and anthropogenic precursor species has received considerable attention in recent years. Several studies have found that air quality models grossly underestimate atmospheric concentrations of organic aerosol, with the gap being often attributed to poor representation of SOA formation mechanisms and the lack of full understanding of source emissions.

The effort reported here to determine the quantities and properties of SOA formed during aging of biomass burning emissions is consistent with findings from a recent study by Ortega et al. (2013), who also participated in the FLAME III experiment with support from USEPA.

Ortega et al. used a flow-through reactor, known as the Potential Aerosol Monitor (PAM), to rapidly and aggressively oxidize biomass burning emissions in an online experiment. While actual experimental oxidation times were of the order of seconds, the equivalent atmospheric oxidation times were on the order of several days. Despite the more aggressive oxidation method used by Ortega et al., their findings were broadly consistent with our findings from this study. While aged aerosol always showed evidence of increased oxidation, amounts of SOA formed strongly varied across fuel type. The average mass enhancement reported by Ortega et al. (1.4) was similar to the average value (1.7) reported in this study. Taking a more fundamental chemical approach, Yee et al. (2013) also recently reported SOA formation yields from smog chamber studies of the oxidation of a variety of individual biomass burning intermediates including phenols and methoxyphenols. Aerosol yields varied between precursor species and as a function of chamber aerosol mass concentration.

The work here to identify suitable candidate species to act as SOA markers was paralleled by similar efforts in Europe led by Iinuma et al. (2010). As observed in this work for North America, Iinuma et al. identified and reported nitrocatechols as good markers of SOA formation from European biomass burning emissions, including residential wood combustion.

The importance of visible light absorption by organic aerosols, so-called "brown carbon," has drawn considerable attention in recent years. Feng et al. (2013) recently concluded that visible light absorption by atmospheric brown carbon exerts a substantial radiative forcing in Earth's atmosphere. Many investigators have examined ambient aerosol to determine visible light absorption while others have hypothesized important mechanisms for brown carbon formation. A paper by Lukacs et al. (2007) examined brown carbon concentrations at several high and low elevation sites in Europe. They concluded that biomass burning, including fall/winter residential wood combustion and summer agricultural burning were major sources of observed brown carbon concentration levels.

Separate work, sponsored by NPS and underway at CSU, reveals that wild and prescribed fires are major sources of atmospheric reactive nitrogen. This includes compounds such as the nitrophenols reported here and other forms of organic nitrogen (Benedict et al., 2013). Substantially elevated concentrations of ammonia are also observed in smoke plumes (Chen et al., 2013; Prenni et al., 2013). Prenni et al. (2013) also report substantial quantities of organic, reduced reactive nitrogen species. Together, measurements of these many forms of reactive nitrogen in smoke plumes indicate suggest that wild and prescribed fires may be a major source of nitrogen deposition, especially to sensitive, alpine ecosystems in the Rocky Mountain region and elsewhere in the western U.S. where natural deposition levels of reactive nitrogen are very low.

References

Benedict, K.B., Kreidenweis, S.M., Schichtel, B., Malm, W.C., Carrico, C. and Collett, Jr., J. L. (2013) A seasonal nitrogen deposition budget for Rocky Mountain National Park, *Ecol. Appl.*, 23, 1156-1169.

Chen, X., D. Day, B. Schichtel, W. Malm, A. K. Matzoll, J. Mojica, C. E. McDade, E. D. Hardison, D. L. Hardison, S. Walters, M. Van De Water, and J. L. Collett, Jr. (2013) Seasonal ambient ammonia and ammonium concentrations in the western United States determined in a pilot IMPROVE NHx monitoring network, *Atmos. Environ.*, in review.

Feng, Y., V. Ramanathan, and V. R. Kotamarthi (2013) Brown carbon: a significant atmospheric absorber of solar radiation? Atmos. Chem. Phys., 13, 8607–8621

Iinuma, Y., Böge, O., Gräfe, R., and Herrmann, H. (2010) Methyl-Nitrocatechols: Atmospheric tracer compounds for biomass burning secondary organic aerosols, *Environ. Sci. Technol.*, 44, 8453–8459, doi:10.1021/es102938a.

Lukacs, H., A. Gelencser, S. Hammer, H. Puxbaum, C. Pio, M. Legrand, A. Kasper-Giebl, M. Handler, A. Limbeck, D. Simpson, and S. Preunkert (2007) Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe, J. Geophys. Res., 112, D23S18, doi:10.1029/2006JD008151.

Prenni, A. J., E. J. T. Levin, K. B. Benedict, A. P. Sullivan, M. I. Schurman, K. A. Gebhart, D. E. Day, C. M. Carrico, W. C. Malm, B. A. Schichtel, J. L. Collett, Jr., and S. M. Kreidenweis (2013) Gas-phase reactive nitrogen near Grand Teton National Park: Impacts of transport, anthropogenic emissions, and biomass burning, *Atmos. Environ.*, in review.

Yee, L.D., K. E. Kautzman, C. L. Loza, K. A. Schilling, M. M. Coggon, P. S. Chhabra, M. N. Chan, A.W. H. Chan, S. P. Hersey, J. D. Crounse, P. O. Wennberg, R. C. Flagan, and J. H. Seinfeld (2013) Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols. *Atmos Chem. Phys.* 13, 8019–8043.

VII. Future Work Needed

To improve confidence in our ability to determine the effects of biomass burning on U.S. air quality, future work that still needs to be addressed includes the following:

- Chamber aging studies revealed significant loss of the primary smoke marker levoglucosan over a period of 1-2 days. This important finding needs to be further explored in order to better assess limits on the utility of levoglucosan as a primary source marker for source apportionment studies. This should include additional chamber studies, under a variety of conditions, as well as field studies of plume aging during long range transport.

- Considerable information was gained from this project about emissions of a wide range of compounds from volatile organic compounds to organic compounds with low volatility. The effect of aging of compounds with intermediate volatility (IVOC) needs to be further explored by utilizing model simulations incorporating the more comprehensive set of emissions measured in this project and other similar, recent efforts.

- Plume aging by nighttime chemical processing needs to be investigated. Results from chamber studies conducted as part of this project reveal the importance of secondary organic aerosol production for the addition of fine particle mass during aging of fire

24

emissions under daytime conditions. The abundance of nitroaromatic compounds observed in aged, ambient smoke samples suggests the likely importance of nighttime chemistry involving VOC attack by nitrate radicals.

- Aging of biomass burning emissions via cloud processing needs to be investigated. While SOA production has long been considered primarily as a gas phase phenomenon, numerous recent investigations have indicated that aqueous SOA production, especially in clouds, can be an important contributor to atmospheric organic aerosols. Most current chemical transport models severely underestimate ambient PM2.5 organic carbon levels; many scientists hypothesize that long-ignored aqueous VOC oxidation pathways may be a critical, overlooked source of atmospheric organic aerosol production. The many polar VOCs emitted in abundance by biomass burning will readily partition to cloud droplets where they can be oxidized to lower volatility products that remain behind as aqueous SOA when droplets evaporate. The abundance of clouds in the summertime atmosphere and the ability of intense fires to generate their own pyrocumulus clouds render the probability of cloud processing of fire emissions high.

- A large-scale effort is recommended to conduct routine monitoring of concentrations of both primary and secondary markers of fine particles produced by wild and prescribed fires. Measurements of both levoglucosan (primary marker) and nitrocatechols (secondary marker) across several fire seasons at a number of sites across the country would provide considerable new insight into the primary and secondary contributions of wild and prescribed fires to PM2.5 concentrations and regional haze. Use of a subset of the IMPROVE network's existing ~170 one-in-three day monitoring sites would provide an ideal platform for this study as samples could be analyzed from filters collected at existing sites in fire-prone regions of the U.S. where sample collection costs are already funded.

- Additional effort is needed to incorporate both degrading primary tracer compound (e.g., levoglucosan) concentrations and secondary marker species (e.g., nitrocatechols) into source apportionment models. Inadequate mass collected on filter samples from the chamber experiments conducted in this project and the unexpectedly rapid decay of levoglucosan concentrations complicate a direct approach to implementing SOA marker source profiles in a traditional chemical mass balance receptor model. Availability of tracer concentrations from ambient observations should be exploited in a PMF or hybrid modeling approach to help identify POA and SOA contributions to ambient PM in smoke-impacted environments.

VIII. Deliverables Cross-Walk

Deliverable	Description	Status
Annual reports	Annual reports	Complete
Final report	Project final report, summarizing results and deliverables	Complete
Project website	Project website reporting SOA results	With increased public availability of project information posted on the JFSP website, we did not create a separate website specifically for this project.
Dataset	Dataset documenting SOA production vs. smoke age and SOA marker/SOA ratios for source apportionment. Parameters (volatility distributions and aging matrix) needed to simulate SOA production from fire emissions in chemical transport models using the volatility basis set approach.	Complete
Peer-reviewed journal articles	3-4 journal manuscripts describing SOA production, SOA marker profiles, SOA marker measurement methods	Complete; 9 articles have been published from this study in leading peer-reviewed journals including Atmospheric Chemistry and Physics, Geophysical Research Letters, and Journal of Geophysical Research – Atmospheres. 2 additional articles are currently in preparation and more articles are anticipated.
Conference presentations	Invited and contributed presentations at various national and international scientific conferences (e.g., AAAR, AGU)	Numerous invited and contributed presentations have been made at national and international scientific conferences and leading research institutions.
Hybrid model	Develop synthetic dataset and gather measured and modeled data for development and testing; Refine hybrid model to incorporate a priori source profiles and estimate uncertainties; Incorporate SOA marker species and apportion smoke to fire types and source regions	Items 1 and 2 are complete. Item 3 was more difficult than anticipated due to sensitivity issues in detecting SOA candidate markers in chamber experiments and is not yet complete.
Workshop	Presentation of project findings to local, state, and federal user communities at IMPROVE and Blue Sky meetings (exact dates per meeting schedule)	Complete. Project findings were presented in several venues including the IMPROVE steering committee meeting, at NPS Air Resources Division, at a Smoke Modeling Meeting, and at the AWMA Visibility conference in Whitefish, MT, in 2012 in order to reach a broad group of smoke/air quality scientists and federal land managers.