U.S. DEPARTMENT OF ENERGY | Office of Science

DOE/SC-ARM-17-011

FIREX-Related Biomass Burning Research Using ARM Single-Particle Soot Photometer Field Campaign Report

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March 2017

ARM CLIMATE RESEARCH FACILITY

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Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Acronyms and Abbreviations

AAE	absorption Angstrom exponent
AML	Aerodyne Mobile Laboratory
ARI	Aerodyne Research, Inc.
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
BBOP	Biomass Burning Observation Project
BC	black carbon
CSU	Colorado State University
DOE	U.S. Department of Energy
FIGAERO	filter inlet for gases and aerosols
FSL	Fire Sciences Laboratory
g	gram
G-1	Gulfstream-1 aircraft
I-CIMS	iodide chemical ionization mass spectrometer
IR	infrared
kg	kilogram
MAC	mass-specific absorption cross-section
MCPC	mixing condensation particle counter
NOAA	National Oceanic and Atmospheric Administration
NR-PM	non-refractory particulate matter
OPC	optical particle counter
PAM	potential aerosol mass
PTR-MS	proton transfer – mass spectrometer
QA	quality assurance
QC	quality control
QC – TILDAS	quantum cascade – tunable IR laser differential laser absorption spectroscopy
rBC	refractory black carbon
RH	relative humidity
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
SP2	single-particle soot photometer
SP-LTOF-AMS	soot particle – long time of flight – aerosol mass spectrometer
SSA	single scattering albedo
TD-CAPS	thermal dissociation – cavity-attenuated phase shift spectrometry
USFS	U.S. Forest Service
UV	ultraviolet
VOC	volatile organic compound

Contents

Figures

Tables

1.0 Summary

The scientific focus of this study was to investigate and quantify the mass loadings, chemical compositions, and optical properties of biomass burning particulate emissions generated in the laboratory from Western U.S. fuels using a similar instrument suite to the one deployed on the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility Gulfstream-1 (G-1) aircraft during the 2013 Biomass Burning Observation Project (BBOP) field study (Kleinman and Sedlacek, 2013).

We deployed the single-particle soot photometer (SP2) to make measurements of biomass burning refractory black carbon (rBC) mass loadings and size distributions to correlate with non-refractory particulate matter (NR-PM; i.e., HR-AMS) and rBC (SP-AMS) measurements as a function of photo-oxidation processes in an environmental chamber.

With these measurements, we will address the following scientific questions:

1. What are the emission indices (g/kg fuel) of rBC from various wildland fuels from the Pacific Northwest (i.e., relevant to BBOP analysis) as a function of combustion conditions and simulated atmospheric processing in an environmental chamber?
2. What are the optical properties (e.g., mass-specific absorption cross-section [MAC], single-scattering albedo [SSA], and absorption Angstrom exponent [AAE)] of rBC emitted from various wildland fuels and how are they impacted by atmospheric processing?
3. How does the mixing state of rBC in biomass-burning plumes relate to the optical properties?
4. How does the emitted rBC affect radiative forcing?

1.1 Relevancy to ARM Mission

This project fits squarely within the ARM Climate Research Facility mission as it provides better characterization of the SP2 instrument (and the G-1 BBOP payload in general) and thus more informed interpretation of data from past and future ARM deployments. The measurements will be used to improve the understanding and representation in models of biomass-burning aerosols and their impacts on climate.

1.2 Description

Aerodyne Research, Inc. (ARI) deployed the ARM SP2 instrument along with multiple measurement techniques onboard the Aerodyne Mobile Laboratory (AML) to participate in the U.S. Forest Service (USFS) Fire Sciences Laboratory (FSL) studies conducted from October 1 to November 15, 2016 as part of the U.S. National Oceanic and Atmospheric Administration (NOAA) FIREX project to investigate the emissions from fires of fuels collected in Western North America. Specifically, the Aerodyne-deployed instrument suite was connected to the Colorado State University (CSU) environmental chamber, deployed by Professor Shantanu Jathar, to study the atmospheric oxidation of biomass-burning emissions, using daytime radicals (O_3 and OH) and nighttime radicals (NO_3).

The four primary objectives of Aerodyne's participation in the FIREX study with NOAA and DOE support in terms of this project include: (1) characterize the initial and evolving chemical, physical, and optical properties of biomass-burning aerosol, including BC and BrC particles; (2) characterize the daytime radical chemistry that controls the daytime evolution of biomass-burning plumes; (3) characterize the radical chemistry that controls the nocturnal evolution of biomass-burning plumes; and (4) identify source-specific gas- and particle-phase chemical markers in biomass-burning plumes. These four goals are closely aligned with DOE Atmospheric System Research (ASR)'s long-term interest in absorbing aerosols and its goal of improved scientific understanding of the changing climate system and its impacts. The matrix of measurements and sampling strategies will provide a rich, unique data set for regional and global climate models.

The results, including those from the ARM SP2, will be used in studies to test, build, and compare biomass-burning atmospheric evolution in models developed by Professor Jathar of CSU, with direct ties in many cases between the related DOE and NOAA programs focused on modeling biomass-burning emissions.

1.3 ARM Resources Used

An ARM SP2 was deployed for October 1 to November 15, 2016 for participation in laboratory studies of wildland biomass burning in the Federal Fire Sciences Laboratory in Missoula, Montana. All SP2 data collected as part of this project are archived in the ARM external archive in accordance with established protocols. The ARM SP2 mentor, Dr. Arthur Sedlacek, was responsible for data reduction, QA/QC, and data analysis.

2.0 Results

The results from this project are summarized as follows:

1. The ARM SP2 instrument was successfully installed in the Aerodyne Mobile Laboratory, along with an extensive suite of gas and particle instruments, and participated in the first NOAA FIREX laboratory study at the Montana FSL;

2. We collected three weeks of data consisting of almost daily experiments where biomass-burning smoke was sampled into the CSU environmental chamber and oxidized over hours (4-8 hours) with various daytime and nighttime oxidants;

3. We collected one week of data consisting of daily experiments where biomass-burning smoke was sampled into the Aerodyne Potential Aerosol Mass (PAM) oxidation flow tube and oxidized with nighttime oxidants (O_3 and NO_3);

4. The SP2 data set has been reduced and QA/QCed by Dr. Arthur Sedlacek;

5. We identified and fixed a bug in the ARM SP2 processing code, where the user-selected duty cycle was not being applied to the size distribution information;

6. The SP2 data set has been submitted, in full, to the ARM Data Archive, following protocol;

7. The SP2 data set is currently being used in the preliminary analyses of the environmental chamber and flow tube studies, including analysis of particle wall loss and the varying chemical compositions of the particles as a function of oxidation, and will be a critical measurement for the project as we continue to analyze the rich biomass-burning data set collected during FIREX.

The ARM SP2 instrument was incorporated into the Aerodyne Mobile Laboratory (AML) at Aerodyne and the AML was driven to Missoula, Montana to participate in the FIREX first FSL project. Table 1 shows the instrument suite in the AML during this FIREX project and Figure 1 shows the AML located at the FSL site in Montana. The SP2 was calibrated with fullerene soot samples from Dr. Shuka Schwarz (NOAA) and Prof. Chris Cappa (University of California, Davis). The calibration is shown in Figure 2.

The ARM SP2 operated for the full study without significant issues. We found and fixed a bug in the SP2 processing code where the user-selected duty cycle was not applied to the size distribution data. Figure 3 shows the complete time series of measured black carbon mass loadings during FIREX. Samples prior to October 24 were from the CSU environmental chamber and those after October 24 were from the Aerodyne PAM flow tube.

A summary of the experiments conducted by Aerodyne is given in Table 2. In total, the SP2 participated in 24 experiments and 4 blanks. The focus of these studies was the chemical and physical properties of biomass-burning particles as they undergo atmospherically relevant oxidation in a controlled laboratory experiment using the CSU's large "standard" environmental chamber. Studies of daytime oxidation included irradiating the biomass-burning emissions with ultraviolet (UV) light to induce photochemistry within the smoke: UV light with H_2O_2 addition to increase the OH radical concentrations compared with UV alone, and UV light with HOHNO addition to generate high OH radical concentrations under high NOx conditions. In some studies, butanol was added as a measure of OH radical concentrations. Studies of nighttime chemistry included studies with O_3 and NO_3, where the NO_3 was generated via O_3 + HONO in the CSU chamber (the HONO source also generated significant amounts of NOx) and via N_2O_5 dissociation in the PAM.

The SP2 data has been QA/QCed and submitted to the ARM Data Archive following the appropriate guidelines. The data are being incorporated with the other aerosol particle data. Initially, the SP2 data will provide a measure of the particle wall loss rates in the CSU environmental chamber and as a measure of the particle chemical composition; both of these aspects are critical for modeling the CSU environmental chamber results. Specifically, the wall-loss information provides a direct method for determining the amount of secondary organic matter that has formed due to the oxidation processes within the CSU chamber.

An example of the type of information derived from the ARM SP2 measurements is illustrated in the experiment that was carried out on October 8, 2016 where smoke from burning Douglas fir was injected into the CSU chamber that was pre-filled with O_3 and NOx. Under dark conditions, the O_3 + NOx forms significant quantities of the NO_3 radical. When the Douglas fir smoke was injected into the chamber, the O_3 molecules and NO_3 radicals started to oxidize the volatile organic compounds (VOCs) in the smoke. After three hours of processing by the O_3 molecules and NO_3 radicals, the UV lights were turned on (representing daytime conditions) and the oxidant mix changed from O_3/NO_3 dominated to OH dominated. Figure 4a shows a time series of the chemical composition of the smoke aerosol during this experiment. Measurements include the refractory black carbon [rBC] mass loadings from the SP2 and the non-refractory organic [Org], nitrate [NO_3], sulfate [SO4], ammonium [NH_4], and chloride [Chl] chemical

composition from the Aerodyne AMS instrument. Figure 4b shows the same time series, but with the black carbon mass loadings increased by a factor of 5 and the nitrate mass loadings increased by a factor of 7.5. The [rBC] reached its maximum early in the experiment during the smoke sampling period and then decreased exponentially due to wall loss effects. Comparing the decrease in the [rBC] with the simultaneous [Org] and [NO_3] loadings show that there were different rates of secondary organic aerosol (SOA) formation during the dark (nighttime chemistry) and the light (daytime chemistry) segments of the experiment, where the SOA mass loading can be estimated by the ratio of the [Org] or [NO_3] to the [rBC].

As we continue to analyze these data sets collected during the 2016 FIREX laboratory project, we will learn more about how biomass-burning emissions evolve in the atmosphere under both daytime and nighttime chemistries. These insights will help us while we continue to analyze the 2013 ARM-funded Biomass Burning Observation Project (BBOP), where we sampled wildland and agricultural fire plumes in a quasi-Lagrangian manner downwind from the fires.

Table 1. Analytical instruments on the Aerodyne Mobile Laboratories (AML and MinAML) during the FIREX laboratory project at FSL.

Compound/parameter	Technique	Typical averaging time	Operator
CO, N_2O, CH_4, H_2O, C_2H_2, C_2H_6, C_3H_8, H_2O_2, HCHO, HONO	Quantum cascade – tunable IR laser differential absorption spectroscopy (QC-TILDAS)	1 s	Aerodyne
Aromatic VOCs, OVOCs	Proton TRansfer – Mass Spectrometer (PTR-MS)	1 s	Montana State University
NO_2, total organic nitrates	CDTD - Thermal Dissociation - Cavity Attenuated Phase Shift Spectrometry (TD-CAPS)	1 s – 30 s	Drexel University
$HO_2 + RO_2$, $O_3 + NO_2$ (Ox)	ECHAMPS - C_2H_6/NO chemical amplification – CAPS (UMass)	5 - 60 s (XO_2) 1 s (Ox)	Drexel University
C5-C10 VOCs	GC-FID	10 min	Aerodyne
NO, NOx, NO_2	Chemiluminescence sensor (Thermo 42i) and Aerodyne CAPS-NO2	1 s	Aerodyne
CO_2	Licor IR sensor	1 s	Aerodyne
O_3	UV sensor (2B Tech)	2 s	Aerodyne
VOCs and SVOCs, HONO, HO_2, $CH_3C(O)O_2$	Iodide Chemical Ionization Mass Spectrometer (I^- CIMS)	1 to 30 s	Aerodyne
Oxidized, low volatility particle phase organic compounds	Filter Inlet for Gases and AEROsols collector module (FIGAERO) I^- CIMS (via thermal desorption)	30 to 60 s	Aerodyne
Size-resolved chemical speciation of particles, including black carbon	Soot Particle – Long Time of Flight - Aerosol Mass Spectrometer (SP-LTOF-AMS)	20 s	Aerodyne
Size-resolved black carbon	Single Particle Soot Photometer (SP2)	10 s	Brookhaven
Size distributions and total number concentrations	Scanning Mobility Particle Sizer (SMPS), GRIMM Optical Particle Counter (OPC), and BMI Mixing Condensation Particle Counter (MCPC)	120 s	Aerodyne
Potential Aerosol Mass	PAM	varies	Aerodyne
RH, temperature	RH and Temp probes	1 s	Aerodyne

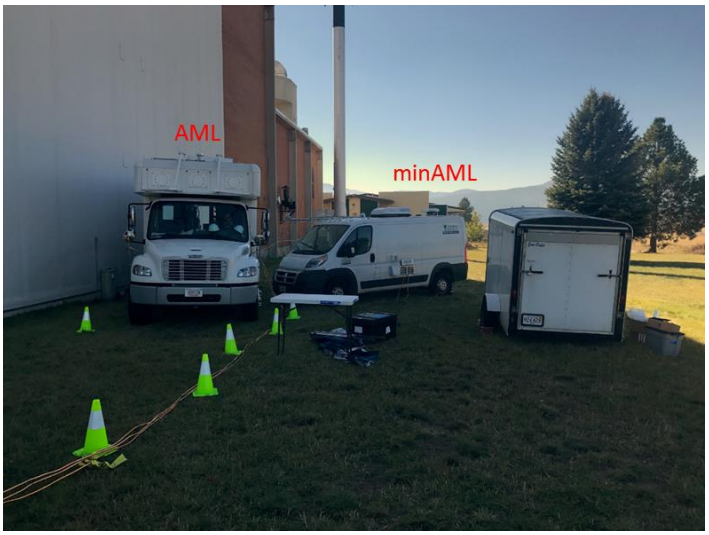


Figure 1. Aerodyne instrumentation situated for sampling biomass burning emissions from within the Fire Science Laboratory in Missoula, Montana during the FIREX laboratory project, October-November, 2016.

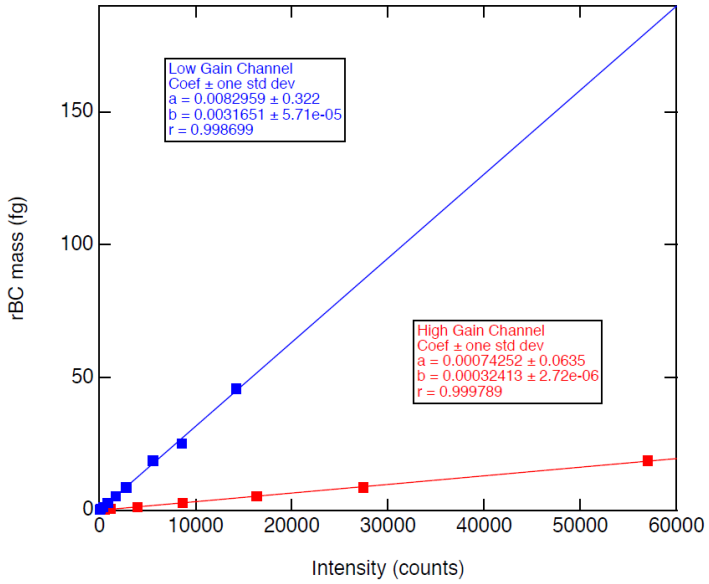


Figure 2. Calibration of the low- and high-gain channels of the SP2 for fullerene soot samples during the FIREX study.

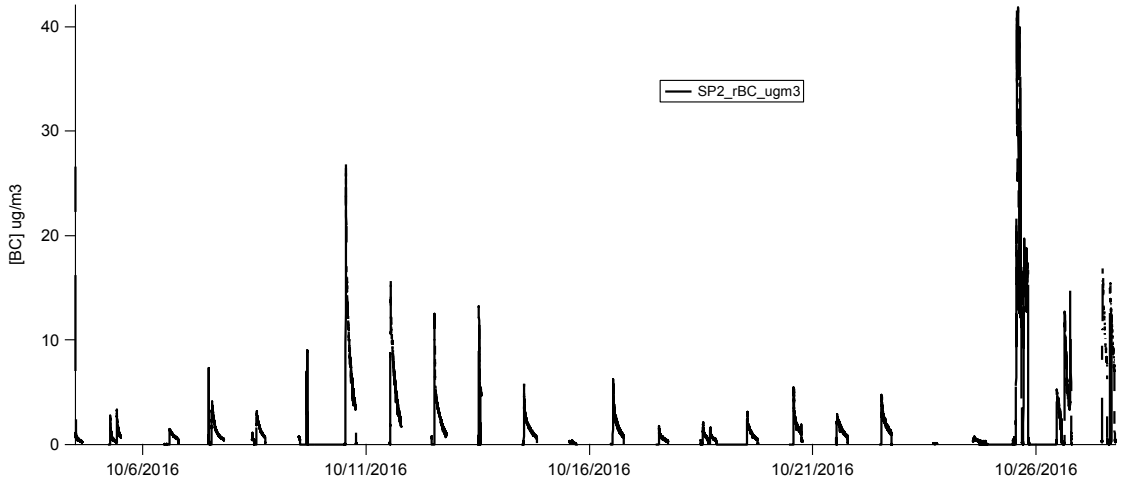
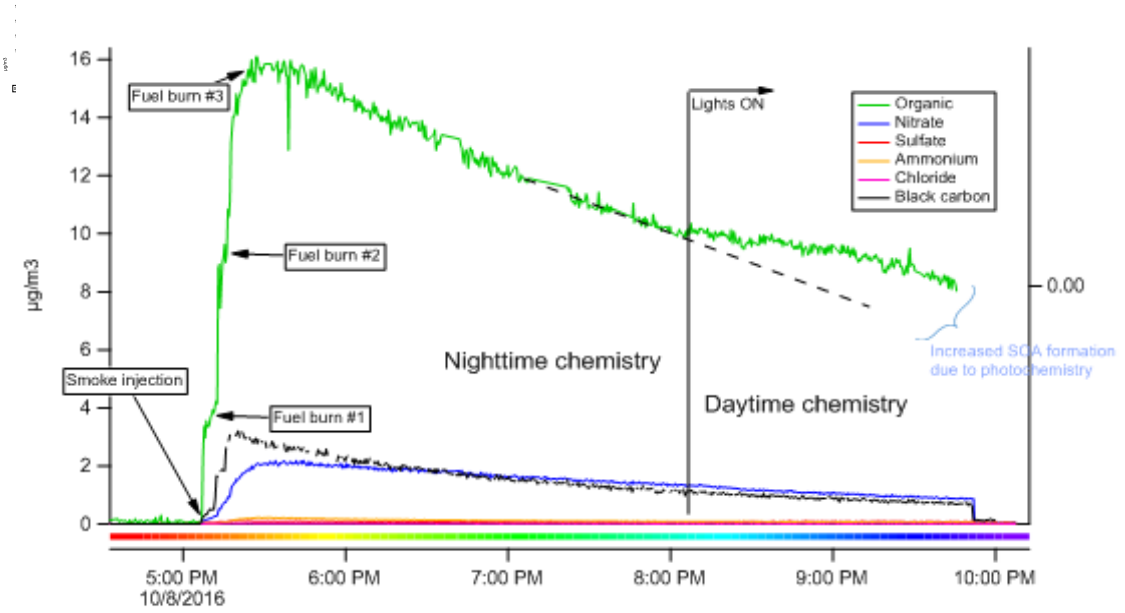


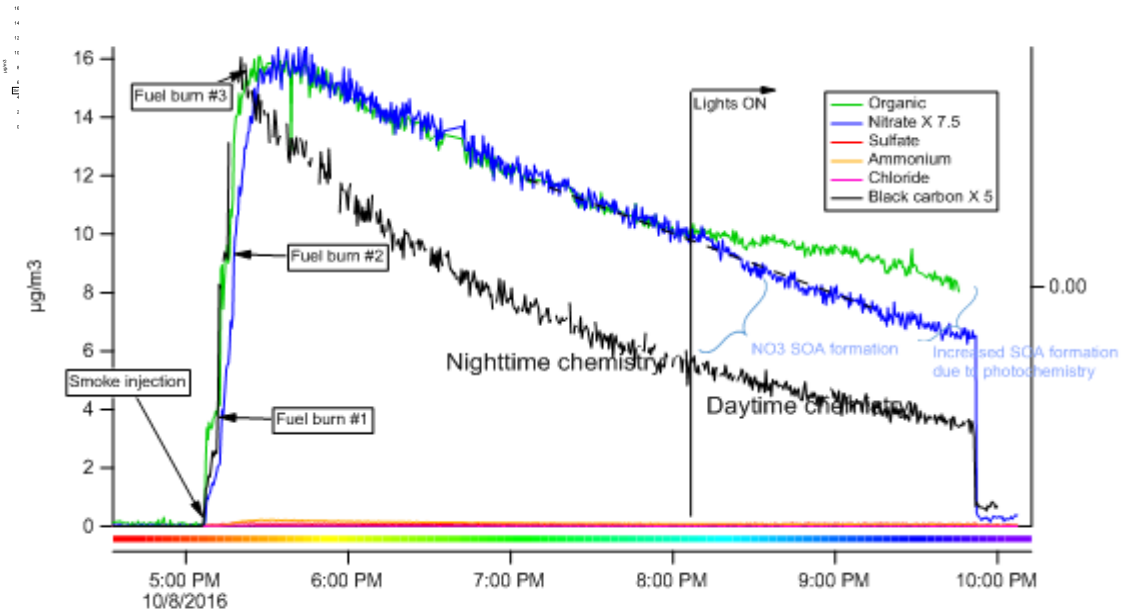
Figure 3. Refractory black carbon mass loading measurements by the SP2 during the FIREX study.

Table 2. Summary of experiments conducted by Aerodyne during the 2016 FIREX laboratory project.

Date	Fire ID	Fuel	Experiment Notes	Chamber
4-Oct	Fire001	Ponderosa pine (PIPO)	Smoke + UV	CSU
5-Oct	Fire002	Ponderosa pine(PIPO)	Smoke + HONO + UV	CSU
6-Oct	Fire004	Ponderosa pine (PIPO)	Smoke + H2O2 + UV	CSU
7-Oct	Fire007	Lodgepole (PICO)	Smoke + kiss of HONO + UV	CSU
8-Oct	Fire011	Douglas-fir (PSME)	Smoke + HONO + O3 +UV	CSU
9-Oct	Blank001	None	Seed + H202 + Butanol + UV	CSU
10-Oct	Fire016	Ponderosa pine (PIPO) - Litter	Smoke + Butanol + UV	CSU
11-Oct	Fire022	Douglas-fir (PSME) - Litter	Smoke + Butanol + UV after first 2 hrs	CSU
12-Oct	Fire028	Chaparral (manzanita) - Uncontaminated (M-NM), Canopy	Smoke + Butanol + H2O2 + UV	CSU
13-Oct	Fire033	Chaparral (manzanita) - Contaminated (M-SD), Canopy	HONO + Ozone+ Smoke + Butanol + UV after first x hours	CSU
14-Oct	Fire038	Ponderosa pine (PIPO) - Litter	HONO + Smoke+ Butanol + UV	CSU
15-Oct	Blank002	None	Seed + H2O + NOx + UV + inject room air	CSU
16-Oct	Fire042	Lodgepole (PICO)	HONO + Smoke + Butanol + UV	CSU
17-Oct	Fire047	Subalpine fir (ABLA), Fish Lake	HONO + Ozone+ Smoke + Butanol + UV after first x hours	CSU
18-Oct	Fire052	Engelmann spruce (PIEN)	BAD experiment. Community inlet failure	CSU
18-Oct	Fire054	Engelmann spruce (PIEN)	H2O2 + Smoke + Butanol + UV	CSU
19-Oct	Fire058	Lodgepole (PICO)	HONO + Ozone+ Smoke + Butanol + UV after first x hours	CSU
20-Oct	Fire063	Lodgepole (PICO)	High Hono + low(ish) NOx + Smoke + Butanol + UV	CSU
21-Oct	Fire067	Subalpine fir (ABLA)	High O3 + Smoke + Butanol + UV after 2 hrs	CSU
22-Oct	Fire072	Ponderosa pine (PIPO)	HONO+O3+Butanol+UV	CSU
23-Oct	Blank003	None	Blank on CSU Reaction Chamber	CSU
25-Oct	Blank004	None	PAM limonene injection	PAM
25-Oct	Fire076	Chaparral (manzanita) - Uncontaminated (M-NM), Canopy	PAM bypass and NO2 and O3	PAM
25-Oct	Fire077	Chaparral (chamise) - Uncontaminated (C-NM), Canopy	PAM NO2 and O3	PAM
26-Oct	Fire078	Ponderosa pine (PIPO)	PAM NO2 and O3, varying concentrations	PAM
26-Oct	Fire079	Lodgepole (PICO)	PAM N2O5	PAM
27-Oct	Fire080	Douglas-fir (PSME)	PAM NO2 and primary NO3- formation tests	PAM
27-Oct	Fire081	Subalpine fir (ABLA)	PAM N2O5	PAM



(a)



(b)

Figure 4. (a) The particulate mass loadings during the October 8, 2016 experiment in the CSU environmental chamber. (b) Same as (a), but with the [rBC] increased by a factor of 5 and [NO_3] increased by a factor of 7.5 to show how the [Org] and [NO_3] decrease more slowly with time (i.e., SOA formation) compared with the wall losses of the [rBC] and how they differ depending upon the oxidants.

3.0 Publications and References

Kleinman, LI, and AJ Sedlacek. 2013. Biomass Burning Observation Project Science Plan. Department of Energy, Report No. DOE/SC-ARM-13-014. Available at http:// www.arm.gov/publications/programdocs/doe-sc-arm-15-083.pdf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