

Biomass Burning Research Using DOE ARM Single-Particle Soot Photometer (SP2) Field Campaign Report

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This project was funded primarily by the DOE Atmospheric System Research (ASR) program, and the DOE Atmospheric Radiation Measurement (ARM) Climate Research Facility made their Single-Particle Soot Photometer (SP2) available for September 1-September 31, 2016 in the Aerodyne laboratories. The DOE ARM mentor (Dr. Sedlacek) requested no funds for mentorship or data reduction. All DOE ARM SP2 data collected as part of this project are archived in the DOE-ARM external archive in accordance with established protocols.

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement Climate Research Facility
ASR	Atmospheric System Research
ASU	Arizona State University
BBOP	Biomass Burning Observation Project
CE	collection efficiency
DOE	U.S. Department of Energy
EDS	energy-dispersive X-ray spectrometry
G-1	Gulfstream-1 aircraft
rBC	refractory black carbon
SMPS	scanning mobility particle sizer
SP2	single-particle soot photometer
SP-AMS	Aerodyne Soot Particle Aerosol Mass Spectrometer
TEM	transmission electron microscope
UM	University of Michigan

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1.0 Summary

The focus of this laboratory study was to investigate the chemical and optical properties, and the detection efficiencies, of tar balls generated in the laboratory using the same instruments 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, during which tar balls were observed in wildland biomass burning particulate emissions. Key goals of this laboratory study were: (a) measuring the chemical composition of tar balls to provide insights into the atmospheric processes that form (evaporation/oxidation) and modify them in biomass burning plumes, (b) identifying whether tar balls contain refractory black carbon, (c) determining the collection efficiencies of tar balls impacting on the 600°C heated tungsten vaporizer in the Aerodyne Soot Particle Aerosol Mass Spectrometer (SP-AMS) (i.e., given the observed low volatilities, AMS measurements might underestimate organic biomass burning plume loadings), and (d) measuring the wavelength-dependent, mass-specific absorption cross-sections of brown carbon components of tar balls.

This project was funded primarily by the DOE Atmospheric System Research (ASR) program, and the ARM Facility made their single-particle soot photometer (SP2) available for September 1-September 31, 2016 in the Aerodyne laboratories. The ARM mentor (Dr. Sedlacek) requested no funds for mentorship or data reduction. All ARM SP2 data collected as part of this project are archived in the ARM Data Archive in accordance with established protocols.

The main objectives of the ARM Biomass Burning Observation Period (BBOP, July-October, 2013) field campaign were to (1) assess the impact of wildland fires in the Pacific Northwest on climate, through near-field and regional intensive measurement campaigns, and (2) investigate agricultural burns to determine how those biomass burn plumes differ from those from wildland fires. During BBOP, tar balls, small solid particles of organic substances, were observed downwind from wildland fires (at plume ages of 0-3 hours), but not agricultural burns. Observations of the tar balls on transmission electron microscope (TEM) grids suggest that they formed during atmospheric transport, likely due to the same atmospheric processes that increased the oxidation levels of the organic aerosol. Preliminary analyses suggest that tar balls may account for almost 50% of the total particle number, and 30% of the total organic particle mass, of the aerosol emitted from the burning events. These BBOP observations are described in detail in a manuscript in preparation (Sedlacek *et al.*, 2017).

The current laboratory study lasted four weeks and was conducted in the aerosol laboratories located at Aerodyne Research, Inc. in Billerica, Massachusetts. Tar balls were generated from several different biomass fuels, including samples from BBOP-related field sites, following literature procedures (Hoffer, Tóth, Nyirő-Kósa, Pósfai, and Gelencsér, 2016; Tóth, Hoffer, Nyirő-Kósa, Pósfai, and Gelencsér, 2014), and they were characterized using the same equipment used during the 2013 BBOP study, specifically the SP-AMS, SP2 and TEM. This study determined that laboratory-generated tar balls (1) are refractory with respect to TEM analysis in a similar manner to those collected during BBOP from wildland fires, (2) are composed of organic material with some refractory carbon components, (3) can be measured quantitatively by the SP-AMS, strengthening observations during BBOP, (4) absorb visible light, and (4) are dominated by unsaturated hydrocarbons that may be responsible for their light-absorbing properties. The results from this project are already being incorporated into our analysis of the formation processes and emission rates of tar balls as a function of fuel and combustion conditions from wildland fires.

2.0 Results

The results from this project are summarized as follows. Laboratory-generated tar balls are:

1. Refractory with respect to TEM analysis in a similar manner to those collected during BBOP from wildland fires;
2. Composed of organic material with some refractory carbon components;
3. Measured quantitatively by the SP-AMS;
4. Absorb visible light;
5. Dominated by unsaturated hydrocarbons that may be responsible for their light-absorbing properties.

These results directly address the questions we originally proposed for this project. Furthermore, results from this project are currently being incorporated into the various BBOP-related analyses, including the direct observations of the formation of tar balls as secondary aerosol in ambient wildland fires (Sedlacek *et al.*, 2017).

The largest fraction of energy/time spent during this project was in the process of generating tar balls in the laboratory. We designated four weeks for the project, but were limited by the fact that the only unambiguous method for identifying and verifying that tar balls were successfully generated was via external TEM analysis, which required shipping TEM grids and performing offline analyses on them. Thus, there was no direct, real-time feedback. During the study, we collected multiple TEM grids for analysis by Professor Buseck (Arizona State University; ASU) and Dr. Adachi (Meteorological Research Institute, Japan) and Professor Andrew Ault (University of Michigan; UM).

We followed literature methodologies for generating tar balls in a laboratory (Hoffer *et al.*, 2016; Tóth *et al.*, 2014). These methods consist of three stages: (1) distillation via pyrolysis of biomass material, (2) atomization of the distillate in water or methanol solvent via nebulization or atomization techniques, and (3) heating the particles to remove volatile components. Figure 1 shows the generation process. There were many variables in this process, including (1) different biomass material, (2) varying sizes of the biomass material, (3) different temperatures or temperature ramps used for pyrolysis of the biomass material, (4) different atmospheres (e.g., air or nitrogen) for pyrolyzing the biomass materials, (5) solvating the distillate in water or methanol or mixtures and with or without mechanical/ultra-sound aid, (6) nebulizing or atomizing the solutions using ultra-sound or Collision methods, and (7) varying the particle heating temperatures after aerosolization, but we were able to investigate only a small number of these. We conducted 33 different experiments during this project and found that varying these generation conditions can have substantial effects on the properties of the particles generated. Thus there is much additional research that can be done on generating and characterizing laboratory generated tar balls.

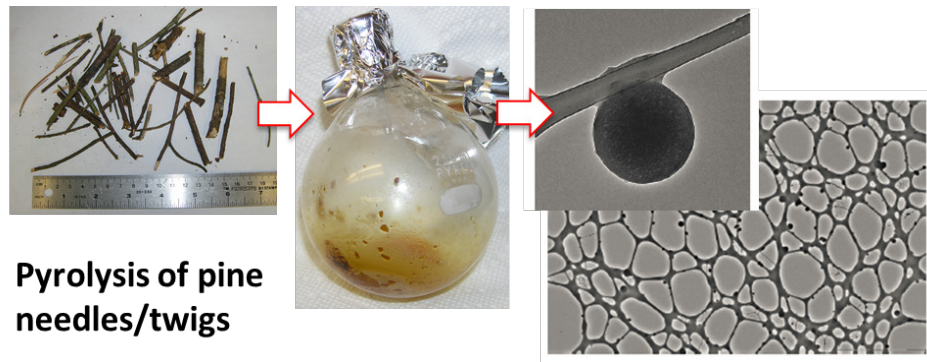


Figure 1. Tar ball generation in the laboratory was done via a three-stage process: (a) pyrolysis, (b) aerosolization, and (c) heating. The pyrolysis distillate was brown-to-black due to the light-absorbing properties of the predominately organic material. TEM images confirmed that tar balls were formed from this process.

Laboratory-generated tar balls are generated by a different mechanism than ambient ones, although the general characteristics of both were very similar. In particular, (1) the distillate was always colored brown to black, indicating that it absorbs visible light (Alexander, Crozier, and Anderson, 2008; Chakrabarty *et al.*, 2010), (2) analysis by TEM indicated that these laboratory-generated tar balls did not evaporate under a strong electron beam (Adachi and Buseck, 2011; Posfai *et al.*, 2004), and (3) analysis by energy-dispersive X-ray spectrometry (EDS) indicated that the laboratory-generated tar balls were composed mainly of C, N, and O but contained some inorganic elements such as Na, Mg, S, K, Ca, and Zn. Inorganic elements, such as Na, K, and S, have been observed in ambient tar balls, but Zn has not (Adachi and Buseck, 2011; Hand *et al.*, 2005).

In addition to the off-line analyses, we performed on-line sampling with the Aerodyne Soot Particle Aerosol Mass Spectrometer (SP-AMS), a TSI scanning mobility particle sizer (SMPS), and a Droplet Measurement Technologies single particle soot photometer (SP2). Figure 2 shows a time series of the measured volume and mass loadings from the SMPS and the mass loadings from the SP-AMS and the SP2. These real-time measurements are overlapped by the TEM grid samples obtained during this time period for UM and ASU analyses. The TEM analyses indicate that during this time frame, we generated tar balls successfully.

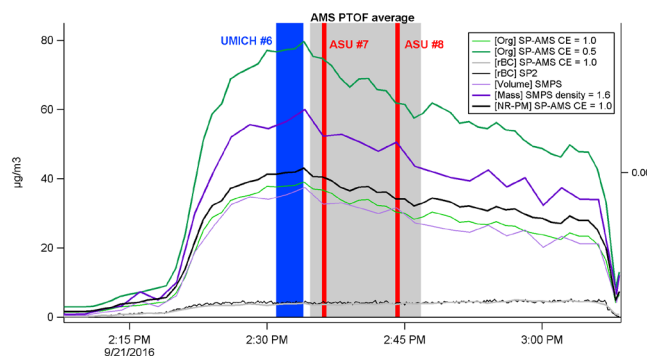


Figure 2. Real-time sampling of laboratory generated tar balls sampled using the SMPS, SP-AMS, and SP2, overlapped with TEM grids collected for UM and ASU.

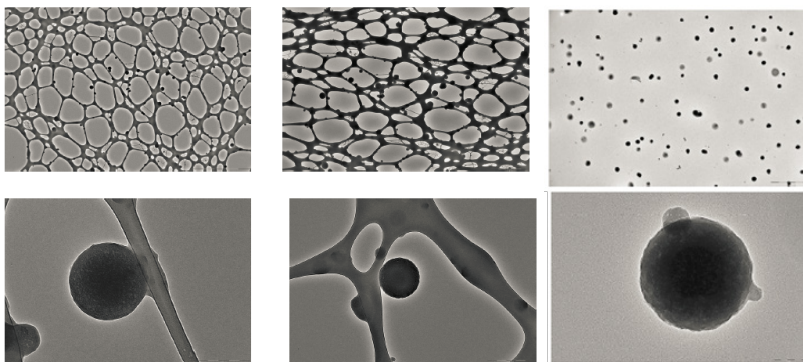


Figure 3. TEM images from ASU #7 (lacy carbon grid) and #8 (formvar substrate) showing the predominance of tar balls in both samples.

The grey region in Figure 2 shows the times where we can directly compare the size distributions measured by the SMPS and AMS. This comparison is shown in Figure 3. Using the observations that the tar balls are spherical (Figure 2), we can apply a density to the SMPS mobility diameter measurements to convert directly to AMS vacuum aerodynamic diameters. This comparison, using the modes of the distributions as the guide, yields a density for the tar balls of 1.6 g/cm^3 , very close to literature values of 1.5 g/cm^3 . With this applied density, Figure 3 also shows that the measured SP-AMS organic mass loadings are quite close to the measured SMPS mass distribution. Thus, the SP-AMS Collection Efficiency (CE) is between 0.5 (which is standard for ambient biomass burning measurements) and 1.0, indicating that the SP-AMS can provide quantitative measurements of tar balls in ambient measurements (Collier *et al.*, 2016).

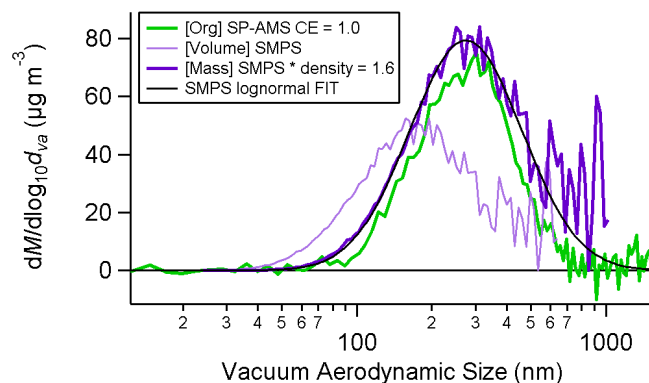


Figure 4. Comparison of measured size distributions between the SMPS ($dN/d\log D$) and AMS PTOF ($dM/d\log D_{va}$).

A very interesting observation from Figure 2 is that both the SP-AMS and the SP2 measure refractory black carbon (rBC) mass loadings for these laboratory-generated tar balls. Although it has typically been assumed that ambient tar balls contain little to no rBC, the laboratory-generated tar balls did contain rBC, although less than 10% by mass. It is not known whether the rBC was located in only a few of the particles, or if each particle contained a small amount of rBC, but further investigations will address this topic, which has important implications for the light absorbing properties of tar balls as well as their formation mechanisms.

The initial chemical analysis by the SP-AMS of the tar balls generated during this study (Figure 5) indicates a mass spectrum that is dominated by several large C_xH_y unsaturated hydrocarbon peaks. While we know the molecular formulae, we do not yet know the structures of these species, but they may be the organic components that give tar balls their ability to absorb visible light. Future work on the chemistry of these tar balls and how the chemical composition relates to their optical properties is required.

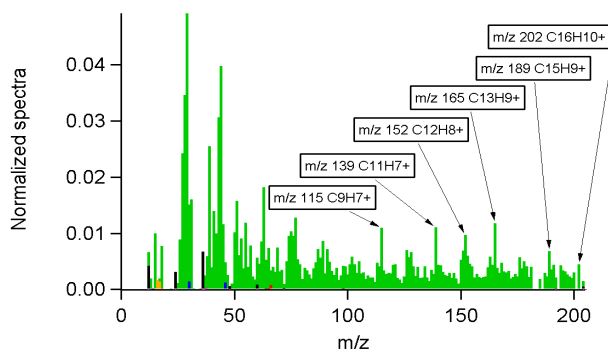


Figure 5. The SP-AMS average mass spectrum for the tar balls generated in the laboratory showing specific unsaturated hydrocarbon (i.e., composed of C and H) ion signals.

Finally, a second version of these laboratory experiments is planned which will build upon these results and focus specifically on (1) measuring the mass-specific absorption cross sections for these tar balls, and (2) correlating the absorption properties with chemical analyses.

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