

SP2 Deployment at Boston College—Aerodyne- Led Coated Black Carbon Study (BC4) Final Campaign Summary

TB Onasch
AJ Sedlacek

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SP2 Deployment at Boston College— Aerodyne-Led Coated Black Carbon Study (BC4) Final Campaign Summary

TB Onasch, Aerodyne Research, Inc.
AJ Sedlacek, Brookhaven National Laboratory
Principal Investigators

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Summary

The main objective of the Boston College-Aerodyne led laboratory study (BC4) was to measure the optical properties of black carbon (BC) particles from a diffusion flame directly and after being coated with secondary organic and inorganic material and to achieve optical closure with model predictions.

The measurements of single particle BC mass and population mixing states provided by a single particle soot photometer (SP2) was central to achieving the laboratory-based study's objective. Specifically, the DOE ARM SP2 instrument participated in the BC4 project to address the following scientific questions:

1. What is the mass-specific absorption coefficient as a function of secondary organic and inorganic material coatings?
2. What is the spread in the population mixing states within our carefully generated laboratory particles?
3. How does the SP2 instrument respond to well-characterized, internally mixed BC-containing particles?

Acronyms and Abbreviations

AAE	Absorption Ångstrom Exponent
AMS	Aerosol mass spectrometer commercial instrument developed and sold by ARI
ARI	Aerodyne Research, Inc.
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
BC	Black Carbon and/or Boston College
BC4	Fourth laboratory project in series of Boston College - Aerodyne led studies focusing on Black Carbon
BNL	Brookhaven National Laboratory
CAPS PMssa	Cavity Assisted Phase Shift Single Scattering Albedo monitor
CPMA	Centrifugal Particle Mass Analyzer
CRD	Cavity Ring-Down instrument
DDA	discrete dipole approximation
DMA	differential mobility analyzer
DMP	data management plan
DOE	U.S. Department of Energy
Eabs	Absorption enhancement
fg	Femtogram
HR-TEM	high resolution TEM
IOP	intensive operational periods
MAC	mass-specific absorption coefficient (m^2/g)
Mie	Mie theory for calculating scattering by spherical particles
MIT	Massachusetts Institute of Technology
PAM	potential aerosol mass flow reactor
PAS	photo-acoustic spectrometer
PI	Principal Investigator
rBC	refractory black carbon
RDG	Rayleigh–Debye–Gans theory for calculating the scattering matrix of soot aggregates
SEM	scanning electron microscopy
SMPS	scanning mobility particle sizer
SOA	secondary organic aerosol
SP2	Single Particle Soot Photometer
SP-AMS	soot particle aerosol mass spectrometer
SSA	single scattering albedo
TEM	transmission electron microscopy

T-matrix	Computational technique of light scattering by nonspherical particles
UC Davis	University of California Davis
UGA	University of Georgia Athens
UV-VIS	ultraviolet-visible
VAP	value-added products
VOC	volatile organic compounds

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1.0 Background

This purpose of this project was to deploy the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM)-owned Single Particle Soot Photometer (SP2) instrument at the Boston College-Aerodyne-led Coated Black Carbon Study (BC4). The measurements of single particle refractory black carbon (rBC) mass and population mixing states provided by the DOE ARM SP2 was central to the laboratory-based BC4 study. Specifically, we addressed the following scientific questions:

1. What is the mass-specific absorption coefficient (MAC) as a function of secondary organic and inorganic material coatings?
2. What is the spread in the population mixing states within our carefully generated laboratory particles?
3. How does the SP2 instrument respond to well-characterized, internally mixed BC-containing particles?

The main objective of the Boston College-Aerodyne led laboratory study (BC4) was to measure the optical properties of black carbon (BC) particles from a diffusion flame source directly and after being coated with secondary organic and inorganic material and to achieve optical closure with model predictions. The BC4 project was conducted in the aerosol laboratories at Boston College from March 23, 2015 to April 10, 2015.

The experimental plan for the BC4 laboratory-based project consisted of generating soot particles using an inverted diffusion flame source, selecting a well-defined particle distribution by size/mass, and coating the soot with secondary organic aerosol (SOA) using a range of atmospherically relevant precursor volatile organic compounds (VOC) (e.g., alpha pinene, isoprene, naphthalene) or secondary inorganic aerosol from sulfur dioxide. The optical properties were measured using state-of-the-art instrumentation as a function of wavelengths from the ultraviolet to the near infrared (300 to 700 nm). The per-particle mass of BC and coating was directly determined by Centrifugal Particle Mass Analyzer (CPMA) and SP2 measurements. The population mixing states were measured using the SP2 and Scanning/Transmission Electron Microscopy (SEM/TEM) images collected on filters.

The deployment of the DOE ARM SP2 as part of the BC4 laboratory study provided single-particle data that was crucial for quantifying the optical properties of internally mixed BC-containing aerosols, which, at present, are poorly represented in models. Furthermore, the SP2 was the only instrument with the sensitivity to quantify multiply-charged particles in the sample stream. In addition, as the DOE ARM SP2 is a field-based instrument, the calibrations and correlations with co-located measurements (e.g., SP-AMS, TEM, etc.) will help further characterize and refine the per-particle mixing state (and morphological) information that the SP2 measurements can provide to the greater DOE ARM/Atmospheric System Research (ASR) community during future field studies (Cross et al. 2010, Schwarz et al. 2010, Sedlacek et al. 2012, 2015).

BC4 study list of participants and instrumentation:

BC/Aerodyne Research, Inc. (ARI) group: Lindsay Wolff, Tim Onasch, Andy Lambe, Yatish Parmar, James Brogan, Andy Freedman, Leah Williams, and Paul Davidovits.

Instrumentation for aerosol generation, processing, and measuring:

Instrumentation for the production, processing, and coating of particles: Inverted diffusion flame (stable

soot source), Potential Aerosol Mass (PAM) reactor (providing controlled oxidative aging of such particles via OH and O₃ reactions over equivalent atmospheric lifetimes ranging from hours to multiple days), and Differential Mobility Analyzers (DMAs for selecting particles of a given mobility). Instrumentation for measuring and particle size, composition, and mass: Scanning Mobility Particle Sizer (SMPS; mobility diameter), Aerosol Mass Spectrometer (AMS; non-refractory composition and aerodynamic diameter), CPMA (particle mass), Soot Particle Aerosol Mass Spectrometer (SP-AMS; non-refractory and refractory composition and mass and aerodynamic diameter), and a Cavity Assisted Phase Shift Single Scattering Albedo (CAPS PMssa) monitor for measuring particle scattering and extinction (and absorption by difference).

UC Davis: Chris Cappa and Taylor Helgestad

Instrumentation:

Photo-acoustic Spectrometer (PAS)/Cavity Ring-down (CRD) instrument suite for simultaneously measuring light absorption and extinction at two distinct wavelengths (405 and 532 nm). This instrument suite provides concurrent and sensitive measures of light absorption (PAS) and light extinction due to scattering and absorption (CRD).

Massachusetts Institute of Technology: Jesse Kroll, Ellie Browne, and Gabriel Isaacman-Wertz

Instrumentation:

A CAPS PMssa single scattering albedo (SSA) monitor operating at 630 nm was provided by Massachusetts Institute of Technology (MIT)/ARI. The instrument is capable of measuring the extinction and scattering of light at a single wavelength. From this information, the particle absorption may be calculated. CPMA for particle mass selection.

U Georgia Athens: Geoff Smith and Al Fischer

Instrumentation:

UV-VIS PAS, capable of measuring gas -phase and aerosol absorption at eight distinct wavelengths ranging from 301 to 678 nm, and two broad-band cavity-enhanced extinction monitors that operates over 30 nm band widths in the UV (360-390 nm) and red (660- 690 nm) regions of the electromagnetic spectrum.

Michigan Technical University: Claudio Mazzoleni and Swarup China

Instrumentation:

Collection of particles on grids for analysis via SEM and Tunneling Electron Microscope (TEM). This data will be used to determine particle morphology.

Brookhaven National Laboratory: Art Sedlacek

Instrumentation:

An SP2 instrument owned by DOE ARM compares time evolution of the scattered and incandescent light. This data is used for determining the mass of the black carbon core, quantifying the number of multiply-charged particles, and providing information about the mixing state of the black carbon core with SOA coatings.

2.0 Notable Events or Highlights

The participation of the DOE ARM SP2 instrument in the BC4 study went very smoothly. The BC4 study benefitted tremendously from having both the DOE ARM SP2 instrument and the participation of Dr. Arthur Sedlacek. Given DOE ARM's objectives and consent, we will definitely plan on requesting DOE ARM instrumentation again in the future to augment and enhance our DOE-funded laboratory and field research programs.

3.0 Lessons Learned

DOE ARM equipment (and facilities) represent a powerful suite of instrumentation that when properly operated can be a significant benefit to augment and enhance measurement capabilities for DOE-funded laboratory and field projects. The ability to request individual instruments from the ARM inventory for highly targeted laboratory studies as BC4 enables ASR scientists to contribute cutting-edge scientific discoveries to the community that would otherwise happen elsewhere.

4.0 Results

The participation of the DOE ARM SP2 instrument in the BC4 study went very smoothly. Dr. Sedlacek (BNL) brought the instrument to Boston College, set it up, connected it to our aerosol sampling lines, calibrated the instrument, and showed us how to collect data. During the study, a graduate student from Dr. Claudio Mazzoleni's research group (Swarup China) operated the SP2. Sedlacek processed the data, providing us with near-real-time output and subsequent follow-up data quality assurance and control.

The SP2 instrument is a single-particle instrument that provides a measure of the number concentration and per-particle mass of refractory black carbon (rBC)-containing particles, independent of the amount of non-refractory particulate material on the particles. The per-particle mass measurement is an important measure when characterizing coated soot particles, as the CPMA measures the total particle mass (refractory and non-refractory). The single-particle number concentration measurements of rBC-containing particles is important for determining the small number of multiply-charged particles that pass through our size and mass (DMA/CPMA) selection. While the number fraction of these multiply-charged particles to the total is very small (less than 10%), the mass fraction can be significant. Thus, when attempting to measure the optical properties of size/mass-selected particles, we must know how many larger, multiply-charged particles were in the sampled aerosol stream. Currently, the SP2 instrument is the only one available that can make these measurements with the sensitivity required for our BC4 study.

Some preliminary results from the SP2 data set are presented here, followed by some preliminary absorption results we are currently analyzing, which rely upon the SP2 for determining the number fraction of larger, multiply-charged particles.

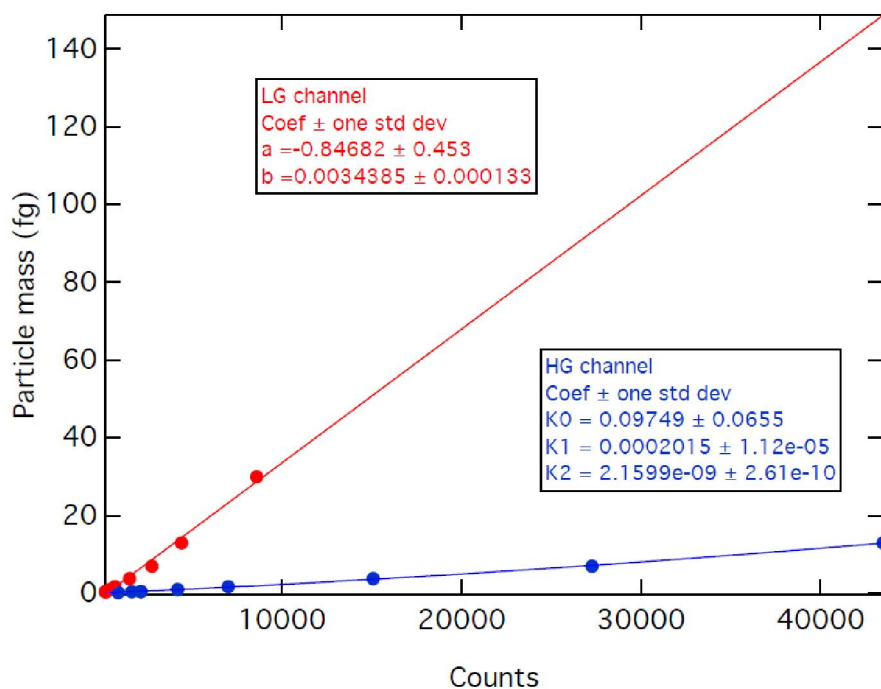


Figure 1. SP2 calibration to carbon black at the start of the BC4 study.

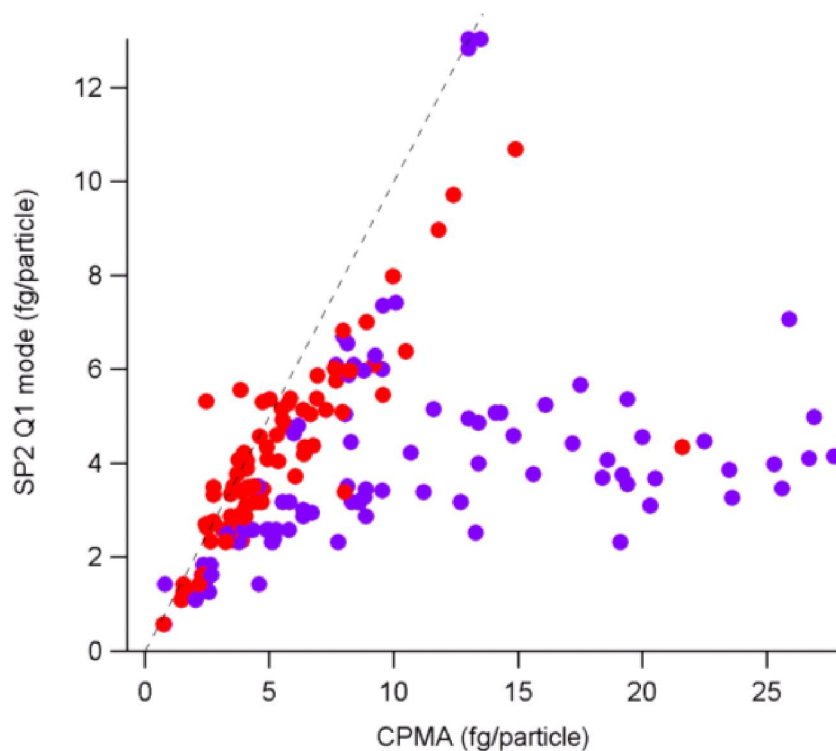


Figure 2. Comparison between the SP2 and CPMA for per-particle mass measurements. The red points are for nascent soot (i.e., direct from diffusion flame) and the purple points show coated soot particles.

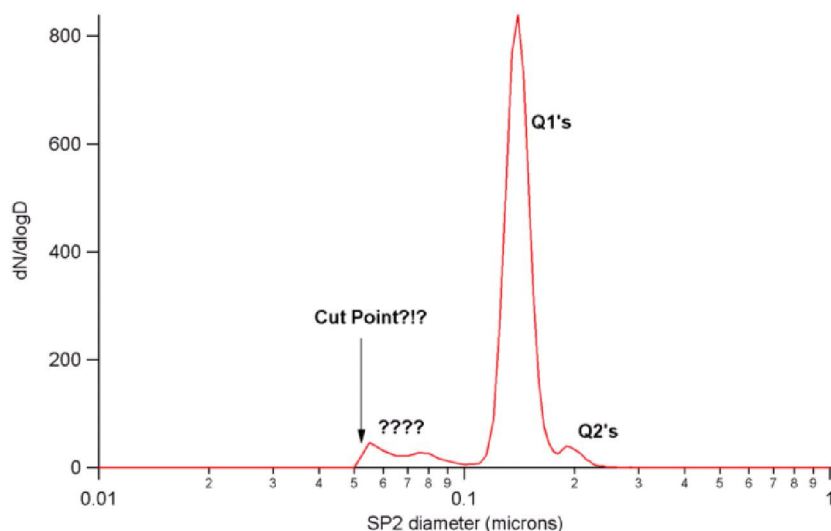


Figure 3. Number-based size distribution of rBC-containing soot particles measured by the SP2, showing the instrument's noise levels at small particle sizes and the measured singly-charged (Q1) and doubly-charged (Q2) fractions.

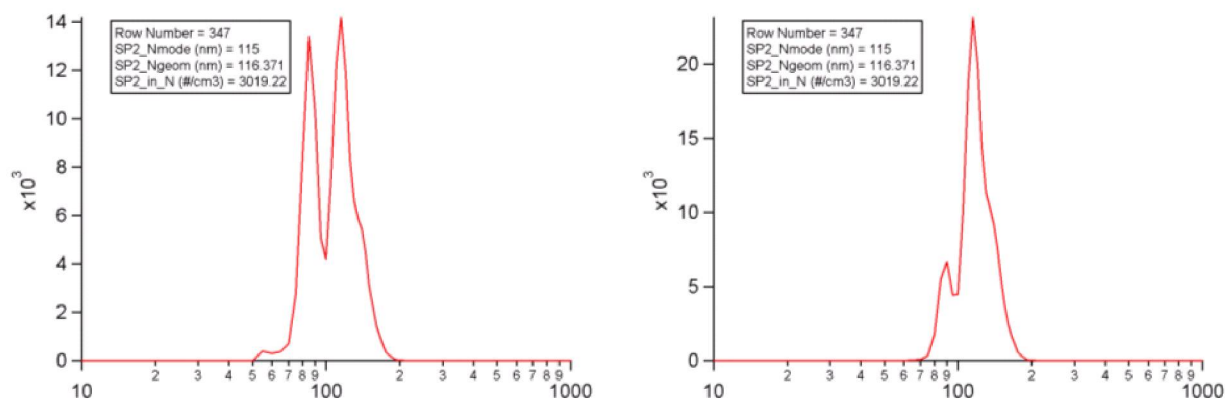


Figure 4. Two plots showing the number-based size distributions of rBC-containing soot particles (dN/dlogD) versus particle mass-weighted rBC size (nm). Data Quality Assurance/Quality Control processing includes removing the noise peaks, to ensure accurate accountability of the Q1 and Q2 fractions. The left plot shows the raw data collected by the SP2 instrument, whereas the right plot shows the final results after the noise has been rejected. The first peak on the small particle side in both plots represented the Q1 number fraction, whereas the peak on the large particle side represents the Q2 number fraction.

As one example of how we will use the SP2 measurements, we believe that we have measured the MAC of nascent diffusion flame soot with the highest level of accuracy to date by using the SP2's measurements to quantify the per-particle mass distributions (i.e., Q1 and Q2 fractions). As almost all atmospheric black carbon mass measurements rely on measuring the absorption of black carbon (either on filters or in situ), understanding and measuring the relationship between black carbon mass and absorption is important. The MAC is not a physico-chemical property that can be derived from fundamental physics, due to the complex chemical nature of black carbon material and, thus, must be measured as a function of wavelength and black carbon material. Recent literature indicates that black

carbon generated by most controlled anthropogenic combustion (i.e., diesel engines) can be considered mature soot with a relatively high MAC. A laboratory representative source for mature soot is diffusion flames, similar to the one we operated during BC4. The other important optical property with respect to black carbon particles is a measure of the SSA, which is the fraction of the total light extinction due to scattering ($SSA = \text{scattering}/\text{extinction}$). Using our recently developed CAPS PMssa instrument, we are preparing a manuscript detailing our measurements of laboratory diffusion flame soot.

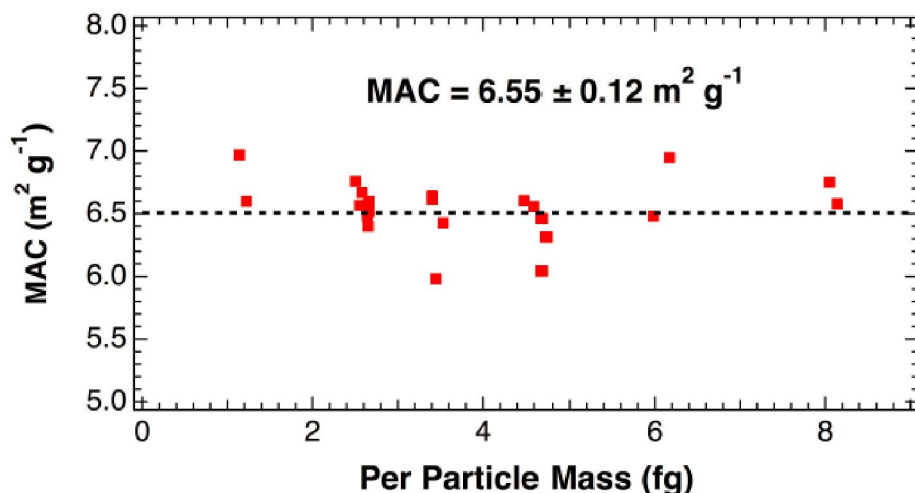


Figure 5. CAPS PMssa (630 nm wavelength) measurements of the MAC of diffusion flame soot as a function of particle mass (size), showing the lack of particle size dependence for the absorption.

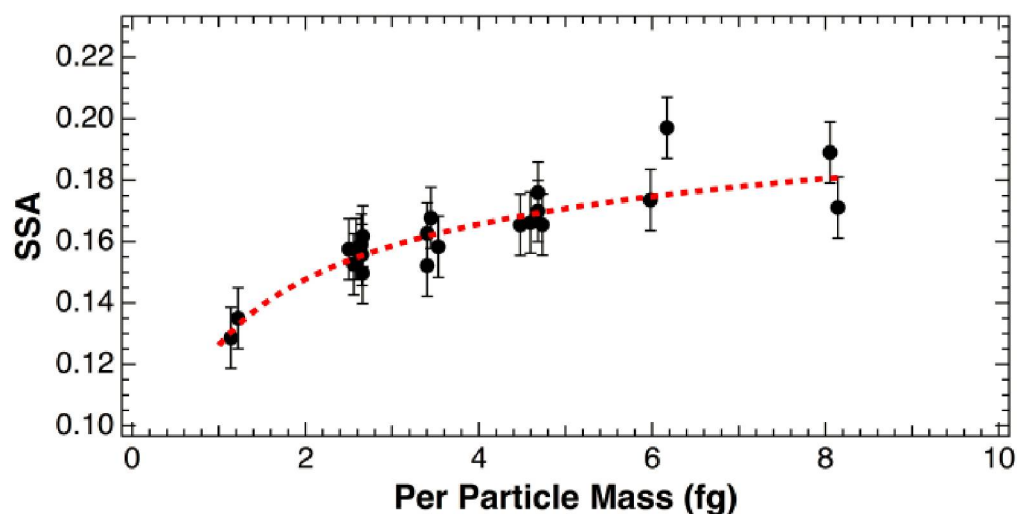


Figure 6. CAPS PMssa (630 nm wavelength) measurements of the SSA of diffusion flame soot as a function of particle mass (size), showing the strong dependence of the SSA on the particle size.

5.0 Public Outreach

We have already presented results from the BC4 study at three different research meetings (see next section) and we have plans to present this work at others in the coming year. We also have plans on submitting six manuscripts for publication in peer-reviewed journals (see next section) in the next year or two. In all cases, we acknowledge and thank DOE ARM for the use of the SP2 instrument, and DOE ASR for direct funding and the indirect support of Dr. Art. Sedlacek for his participation in BC4.

6.0 BC4 Publications

6.1 Journal Articles/Manuscripts in Preparation

1. Soot-only papers

1.1. Accuracy of absorption measurements using CAPS-SSA monitor.

Suggested lead groups: BC/ARI (Onasch lead)

Having the ability to size and mass select minimizes multiply-charged particles without having to change the flame conditions and thus the soot “maturity” or chemical composition. With the SP2 data, we also have the ability to correct for multiply-charged particles. This paper will focus on nascent soot generated under constant flame conditions and include information on absorption and extinction properties (e.g., MAC, Absorption Ångstrom Exponent [AAE], etc.). The accuracy of our absorption measurement approach with the CAPS-SSA monitor will be discussed in detail. Preliminary data analysis suggests a mass independence to the absorption coefficients and a linear increase of the SSA with mass across the range of masses from 0.8-8 fg.

1.2. Soot Maturity Paper.

Suggested lead groups: BC/ARI (Wolff lead)

With ability to precisely and accurately measure the absorption of rBC as well as our ability to characterize rBC composition and morphology (SP-AMS, SP2, TEM, HRTEM), we are nicely geared to track the maturity of soot from “less mature” nascent soot, through “more mature” nascent soot, to oxidized soot and regal black carbon. Combined optical measurements (MAC, AAE, etc.), chemical composition, most specifically H:C (SP-AMS), graphitization/morphology (TEM) all provide proxies for soot maturity. Optimally, we will map out the maturity of soot on an axis similar to Bond and Bergstrom (2006) showing how “maturity” affects the optical properties of rBC. Potential to be combined with theoretical calculations (T-matrix, Mie, RDG, DDA).

2. Coated soot papers

2.1. Mie closure paper.

Suggested lead groups: UCDavis/BC

Use coatings with alpha-pinene SOA, naphthalene SOA, and H₂SO₄ and compare to Mie Theory predictions to determine whether Eabs is predicted reasonably well by core-shell Mie Theory. Use complex refractive indices from methane diffusion flame bare soot data (use coated-denuded extinctions for Mie fitting?) Implications for modeling direct effect with Mie Theory.

2.2. Coating comparison paper.

Suggested lead groups: BC/UCDavis

May be included with previous paper depending on results. If morphologically different, would be of great importance to state whether this is related to the observed absorption enhancement. Can use TEM/SEM as well as the SP2 data to get morphological information about the coatings. How might the chemical composition affect the observed Eabs (SP-AMS data)? Do H₂SO₄ and/or mixed organic- H₂SO₄ particles have similar morphology to organic only? All show roughly the same degree of enhancement. Also possible inclusion of the ambient data into this paper. Can we explain the absorption enhancement (or lack thereof) observed in ambient samples by the particle morphology?

3. Overview Papers

3.1. Optical instrument wavelength dependence paper.

Suggested lead groups: UGA/BC

Comparison of optical instruments for the study of nascent, oxidized, and coated soot. MAC, AAE, etc. comparisons between different optical instruments. Some instruments (PAS) measure absorption while others rely on scattering-extinction. How do the extinction measurements compare between CRD and CAPS when AAE is assumed? If instruments are in pretty good agreement, we can present the most comprehensive study of the wavelength dependence of optical properties for soot and coated soot.

3.2. Particle chemistry/mass measurements.

Suggested lead groups: MIT/BNL/BC

Comparison of SP-AMS to per-particle mass determination by CPMA for various types of particles (nascent, oxidized, coated, coated+denuded). What can we learn about the particle chemistry (and/or our ability to detect) based on these comparisons? How do the SP-AMS and SP2 compare for different particle chemistries (nascent, oxidized, coated, coated+denuded). Can we learn anything new about the particle morphology?

6.2 Meeting Abstracts/Presentations/Posters

1. 2015 ICCPA (International Conference on Carbonaceous Particles in the Atmosphere), Oral presentation, "Measuring Absorption of Primary Emissions by Difference Using a Single Scattering Albedo Monitor", Timothy B. Onasch, Lindsay R. Wolff, Paola Massoli, Paul L. Keabian, Andrew Lambe, Paul Davidovits, Andrew Freedman

2. 2015 EAC (European Aerosol Conference), Poster presentation, “Measurement of Particle Optical Properties Using the CAPS PMssa Monitor”, Timothy B. Onasch, Lindsay R. Wolff, Andrew Lambe, Paola Massoli, Paul L. Kebebian, Paul Davidovits, Andrew Freedman
3. 2015 AAAR (American Association for Aerosol Research), Oral presentation, “New Optical Experiments “Shed Light” on Role of Particle Morphology and Chemical Composition in the Absorption Enhancement of Coated Soot Particles”, Lindsay R. Wolff, Andrew Lambe, Timothy Onasch, Andrew Freedman, Leah Williams, Taylor Helgestad, Christopher Cappa, Al Fischer, Geoff Smith, Swarup China, Claudio Mazzoleni, Arthur J. Sedlacek, Eleanor Browne, Gabriel Isaacman-VanWertz, Jesse Kroll, James Brogan, Yatish Parmar, Andrew Lee, Noopur Sharma, Janarjan Bhandari, John Jayne, Douglas Worsnop, Paul Davidovits

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