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Black Carbon Absorption Enhancements (E_{abs}) from SOA Coatings

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ABSTRACT

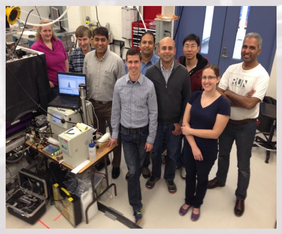
Absorbing aerosols (AA) represent a large uncertainty in climate models today. Before we can nail down their uncertainties in climate-relevant processes in the atmosphere, we need to improve our understanding of the uncertainties in their direct measurements and climate effects. While black carbon (BC) is historically the most studied AA, there are still a lot of unknowns related to absorption enhancements (E_{abs}) and the associated morphologies for those BC particles. When using core-shell Mie Theory, E_{abs} are expected to be as large as a factor of 2 for non-absorbing coatings on a BC core. Ambient measurements from large-scale field campaigns indicate that BC E_{abs} are not universal (Cappa et al., 2012, Liu et al., 2015). However, BC absorption is difficult to constrain in ambient data due to the presence of other absorbing species, e.g. brown carbon, absorbing dust species. For these reasons, the Soot Aerosol Aging Study (SAAS) was designed. SAAS was conducted at the Pacific Northwest National Laboratory's Environmental Chamber to investigate the relationship between internally-mixed BC with different morphologies and measured BC E_{abs}. By using the same BC (120 nm mobility-selected diesel emissions) and non-absorbing aerosol components SAAS can isolate the effect of morphology on diesel BC E_{abs}.

Three different types of experiments were conducted with 120 nm mobility diameter diesel BC and α–pinene secondary organic aerosol (SOA) formed in the chamber: (1) SOA coating BC, (2) BC coagulated with SOA, (3) BC coagulated then coated with SOA. Direct on-line measurements were made with the single particle soot photometer (SP2) from fresh and aged BC. BC measurements are coupled with photoactoustic measurements spanning the visible region to probe changes in BC light absorption when mixed with SOA. BC measurements from SPLAT-II confirm the presence of collapsed BC cores with SOA coatings. Here we focus on the BC E_{abs} at 781 nm for the SOA coating experiments that are tracked throughout SOA growth and quantified with SP2 coating thickness. Thermal denuder (TD) experiments are conducted and E_{abs} are calculated using two different methods that agree well, substantiating the measurements. E_{abs} are reported at varying temperatures: 100, 150, 250, and 300 ^{0}C for coatings of 50 nm and greater, which increase with temperature with more complete removal of the coatings, from 1.1 – 1.5. Loss rates are taken into account in the TD which by two methods and quantified at 14% - 30% for 100 - 300^{0}C.

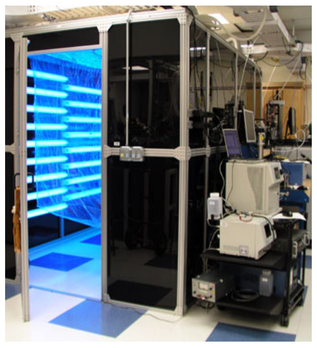
Introduction

Optical properties of BC are altered with Organic Aerosol (OA), e.g., coatings and coagulation with Secondary OA (SOA)

Soot Aerosol Aging Study (SAAS) at PNNL Environmental Chamber



- **18 experiments** simulating atmospheric aging of BC and SOA
- **"fresh" 120 nm d_m Diesel BC + α-pinene SOA**
- TD to remove SOA at 300^{0}C
  - 30% (± 3%) loss in the Thermal Denuder (TD) at 300^{0}C calculated from SP2 # and mass



3 Experiment Types:

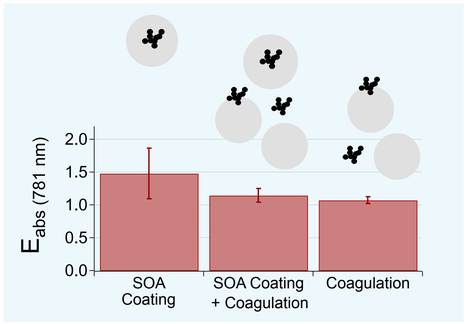
1) Coating: BC + SOA
2) Coagulation: BC + SOA
3) Coagulation then Coating: Type 2 Expt. + SOA

Absorption Enhancement (E_{abs})
2 Methods (TD and MAC)
- Liu, Aiken et al., 2015

- **TD: MAC/MAC$_{TD}$** or $B_{abs} \times (*TD_{loss}/B_{absTD})$ $*TD_{loss} = 0.7$
- **MAC: MAC/MAC$_{BCref}$**

(MAC$_{BCref}$ @781 nm= 5.3; Bond 2012 + α=1)

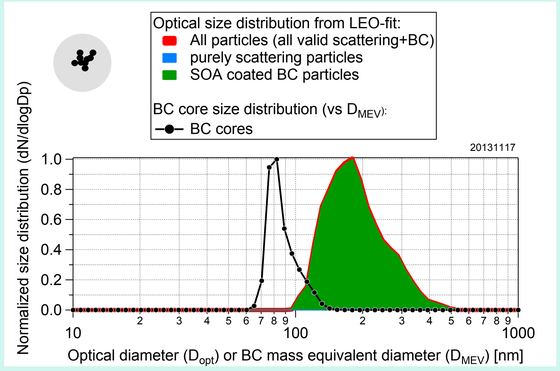
Summary of Experimental E_{abs}
TD method (SP2 + PASS)



RESULTS

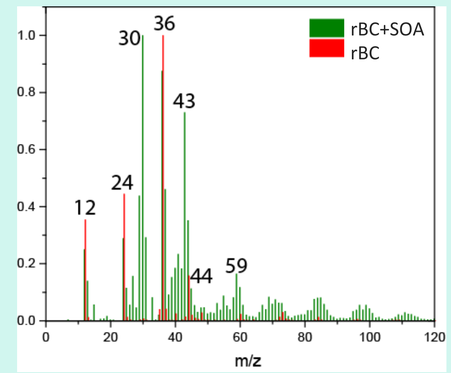
Type 1 Expt. (SOA Coating): rBC + SOA grown to 270 nm d_m avg

SP2 Size Distributions

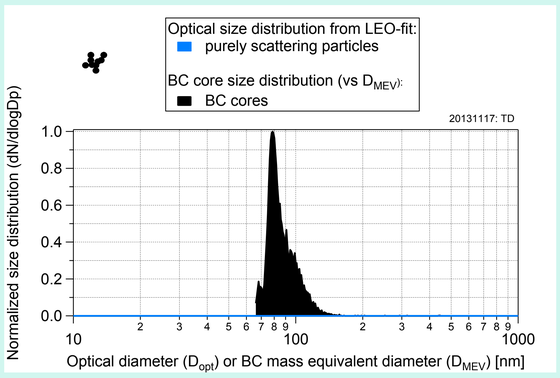


rBC core (84 d_{me}) + SOA coating

SPLAT-II Mass Spectra

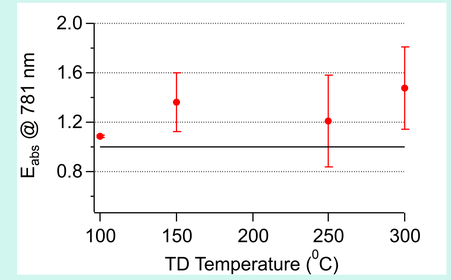


Coated rBC and TD at 300^{0}C



SOA removed at 300^{0}C

TD Method : E_{abs} @ 781 nm



E_{abs} increases w/TD temp. (more complete SOA removal)

Coating Experiment Measured Averages (λ = 781 nm)

rBC	MAC$_{rBC}$:	5.1	SSA$_{rBC}$:	0.03	E_{abs}: 1.0
rBC+SOA	MAC$_{rBC+SOA}$:	7.5	SSA$_{rBC+SOA}$:	0.67	E_{abs}: 1.5

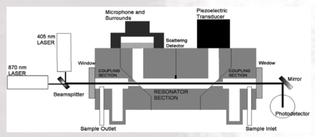
Core-Shell Mie Calculations (λ = 781 nm)
Core RI = 1.82 – 0.74*i;* Shell RI = 1.45 – 0*i*

Core Dia. (nm)	Total Dia. (nm)	BC MAC	SSA	E_{abs}
84	84	4.0	0.03	1.0
84	270	8.1	0.75	2.1

Instrumentation

PhotoAcoustic Soot Spectrometry (PASS):

- Direct online measurement of aerosol absorption and scattering (nephelometry) on the same air mass
- 4 wavelengths spanning the visible range: 375, 405, 532, 781 nm
- Absorption coefficient (B_{abs}) and Scattering coefficient (B_{sca})

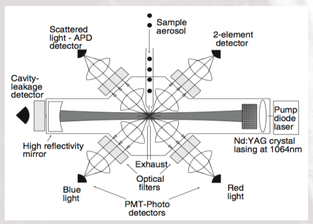


- Lack '06; Lewis '08

Single Particle Soot Photometer (SP2)

- Single particle refractory BC (rBC) mass and number
- Scattering detection and coating thickness of rBC

- Schwarz 2006



Absorption Enhancement (E_{abs}) measured by TD at 300^{0}C
Mass Absorption Coefficient (MAC) measured by PASS and SP2 (ratio of B_{abs} to rBC mass)

Conclusions

- SOA coating experiments produced thickly-coated rBC
- Agreement between SP2 and SPLAT-II rBC and Coating Information
  - 84 nm d_{me} rBC cores (measured by SP2; 86 nm by SPLAT-II)
  - 270 nm d_m rBC + SOA particles (measured by SP2/SPLAT-II/SMPS)
  - 90-95 nm SOA coatings (measured by SP2 and SPLAT-II)
- rBC Absorption Enhancement (E_{abs}) at 781 nm
  - E_{abs} (1.5 ± 0.3) for 270 nm d_m total diameter particles (rBC+SOA)
- Comparison of measured MAC, SSA, and E_{abs} with first-order Core-Shell Mie Theory Calculations at 781 nm
- Future work: MAC and E_{abs} plotted as a function of rBC coating thickness and Improved Core-Shell calculations using measured size distributions