Development of a Quantitative Accounting Framework for Black Carbon and Brown Carbon from Emissions Inventory to Impacts (Project End Date: 9/30/2015)

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Motivation

- Emissions inventories and air quality models of light absorbing carbon require parameterization of the radiative properties of emissions
- Current parameterizations of light absorbing carbon emissions do not address the range of variability within sources or control technologies
- Elemental carbon is not a good surrogate for light absorbing carbon for control strategy development nor assessment of control strategy implementation
  - May be OK if limited to absorption at 880 nm
- The light absorbing capacity of carbonaceous aerosol is not a conservative property from the point of emissions to atmosphere

Project Goals

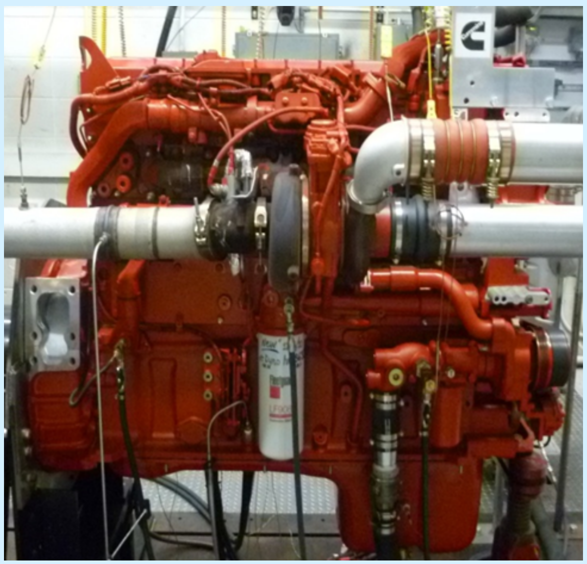
- Overall Goal
  - Development of a quantitative framework for source-receptor relationships for light absorbing carbon and their associated wavelength dependent light absorptivity
- Key Objectives
  - Deconstruct emissions from sources of light absorbing carbon to elucidate the contribution of different emissions components to wavelength dependent absorption
  - Elucidate how the evolution of emissions in plumes impact wavelength dependent absorption and the relative contributions for both BC and BrC
  - Integrate source apportionment models for aerosol components impacting light absorption with wavelength dependent light absorption closure calculations

Project Strategy

- Source Testing
- Mie theory calculations for closure of estimated and measured absorption
- Atmospheric measurements
- Mie theory calculations for atmospheric aerosols and light absorption closure
- Develop a source apportionment framework that can address the optical evolution of aerosols and precursors

Source Testing

- Examine key sources of light absorbing carbon:
  - Mobile sources
    - Conventional CI and SI and Emerging Technologies
  - Biomass and trash burning
    - Lab and Field Studies
  - Coal combustion
- Examine for each source
  - Role of process variables on emissions
  - Optical properties of the organic carbon
  - Optical properties of the elemental carbon
  - Impact of thermal stripping of organics
- Develop source specific light absorption closure models for measurement conditions and high dilution conditions



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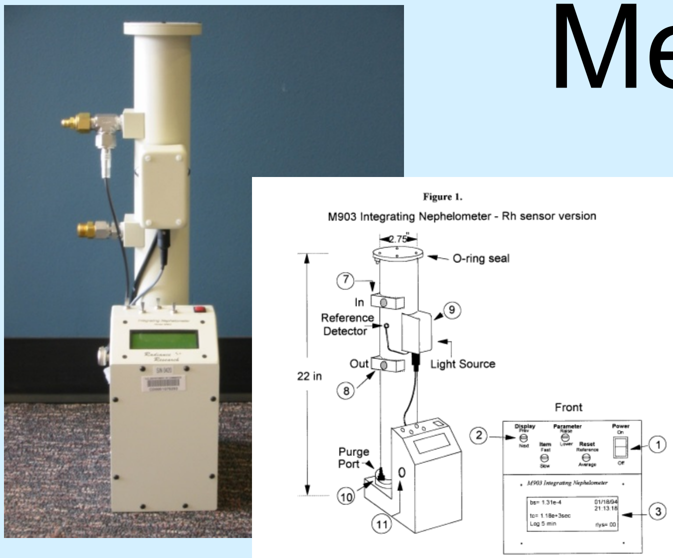
Atmospheric Measurements

- Use sites where we have conducted source apportionment studies in the past and where historical record and optical measurements
  - Atlanta, Georgia
    - Near Roadway
  - Rural Alabama and Northern Wisconsin
    - SOA
  - Kanpur, India
    - Trash and biomass burning impacted areas
  - Huairou (Beijing), China – Location of 2014 APEC
    - Before and during APEC air pollution control period
    - After APEC during heating season

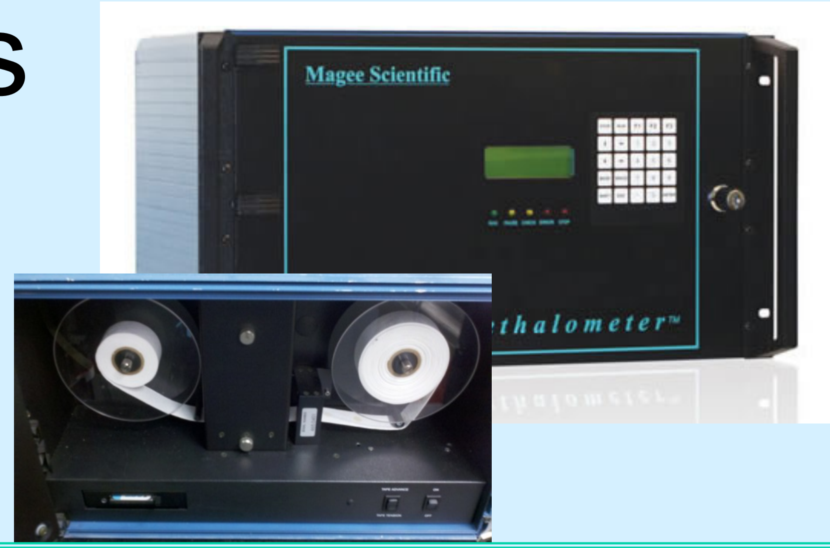
Measurement Approach

- Measure the optical properties under controlled conditions
  - Scattering and Absorption (multiple wavelengths)
- Measure physical-chemical properties
  - Size distribution, particle shape, chemical composition
- Segregate components of aerosols
  - Thermal Denuder, WS and Organic solvent atomization
- Correct absorption artifacts and compare optical properties of aerosol components

Methods

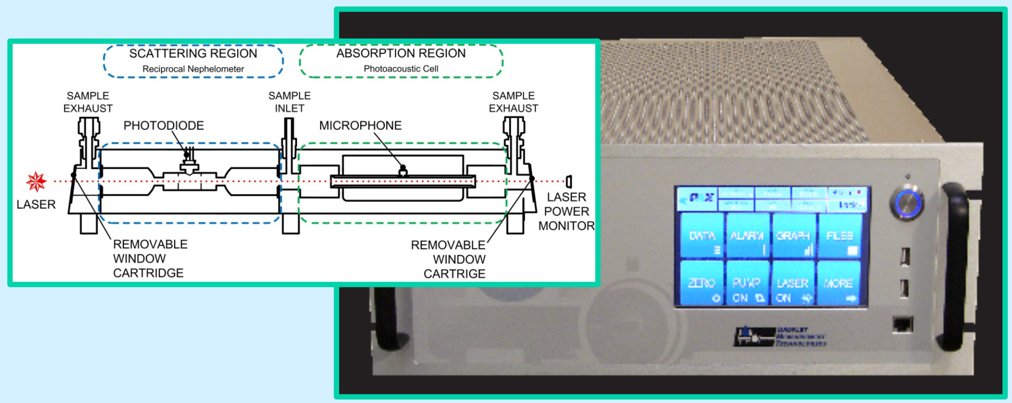


Radiance Research Nephelometer



Magee Scientific AE31 7-channel Aethalometer

TSI Scanning Mobility Particle Sizer/ Electrostatic classifier



DMT PAX 532: Photoacoustic Extictionometer

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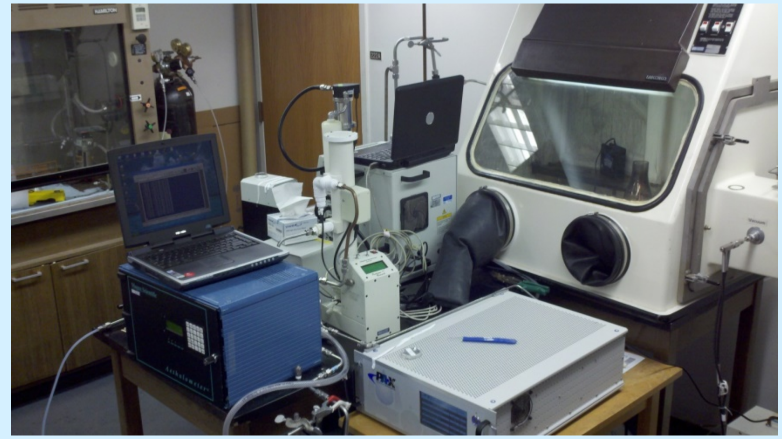
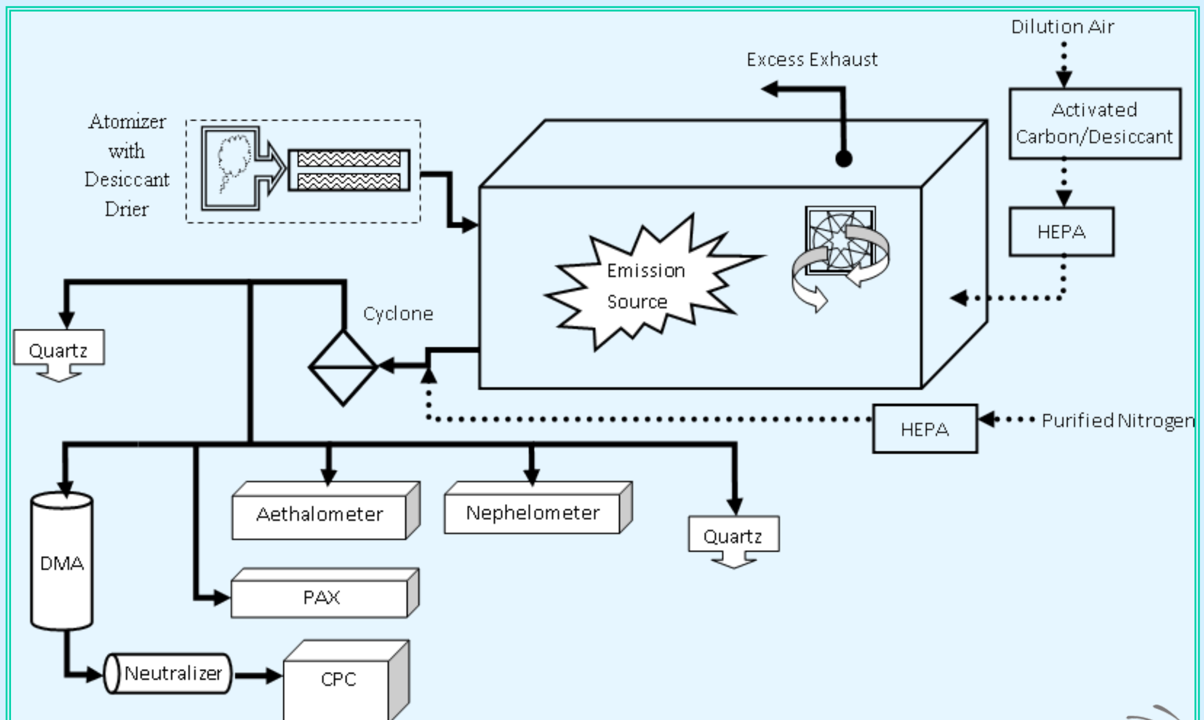
Methods





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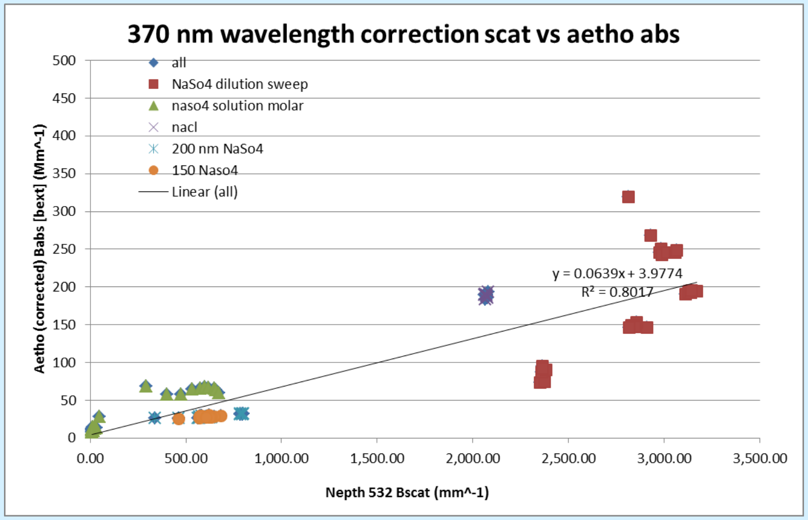
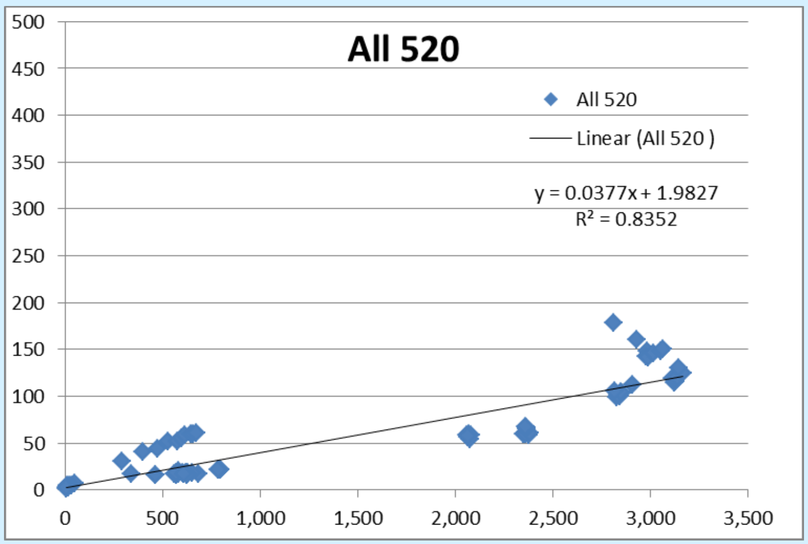
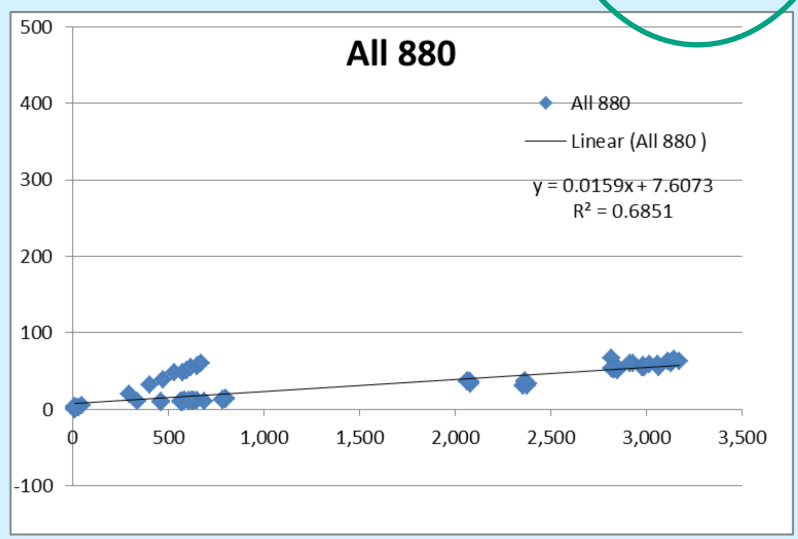
Attenuation by Non-Absorbing Aerosols



Absorption vs Scattering: Scattering Artifact correction

Wavelengths	slope (m)	Intercept (b)	R^2	slope forced through zero (m')
370	**0.064**	**3.977**	0.801747	**0.066**
470	**0.049**	**-0.909**	0.816126	**0.048**
520	**0.038**	**1.983**	0.835205	**0.039**
590	**0.030**	**2.919**	0.801001	**0.032**
660	**0.027**	**3.207**	0.84761	**0.028**
880	**0.016**	**7.607**	0.685092	**0.019**
950	**0.013**	**7.410**	0.651662	**0.016**





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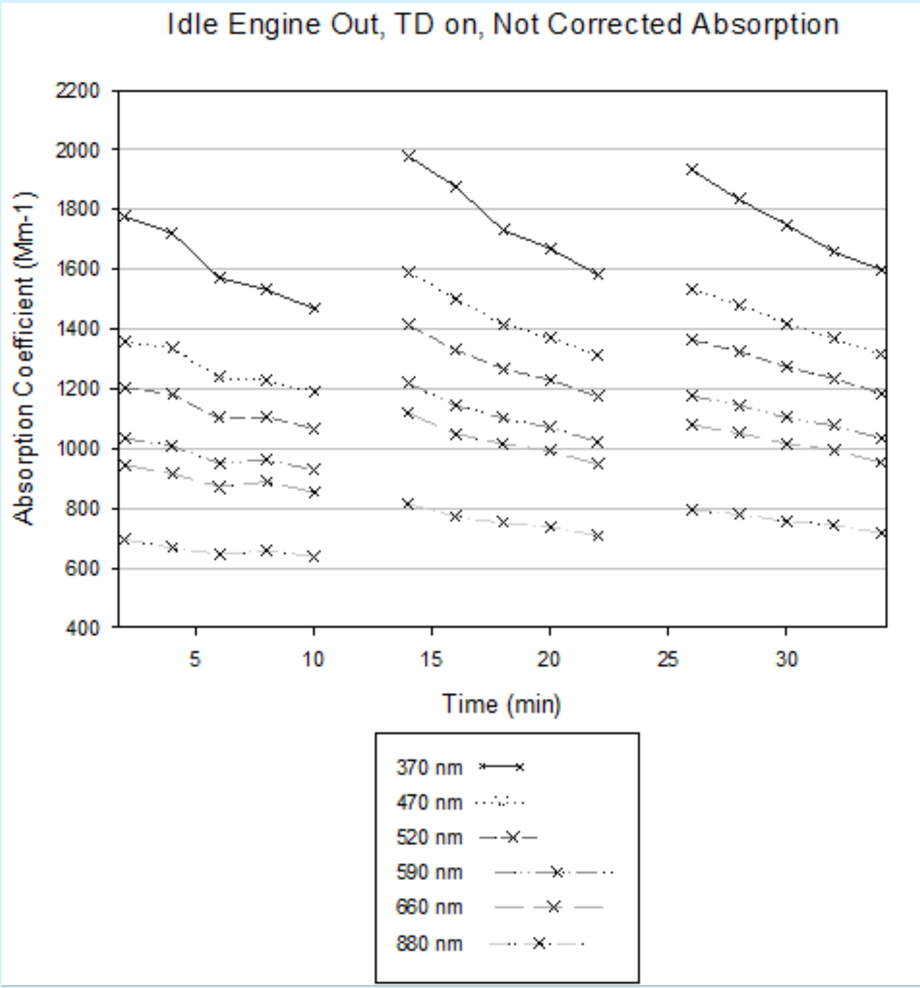
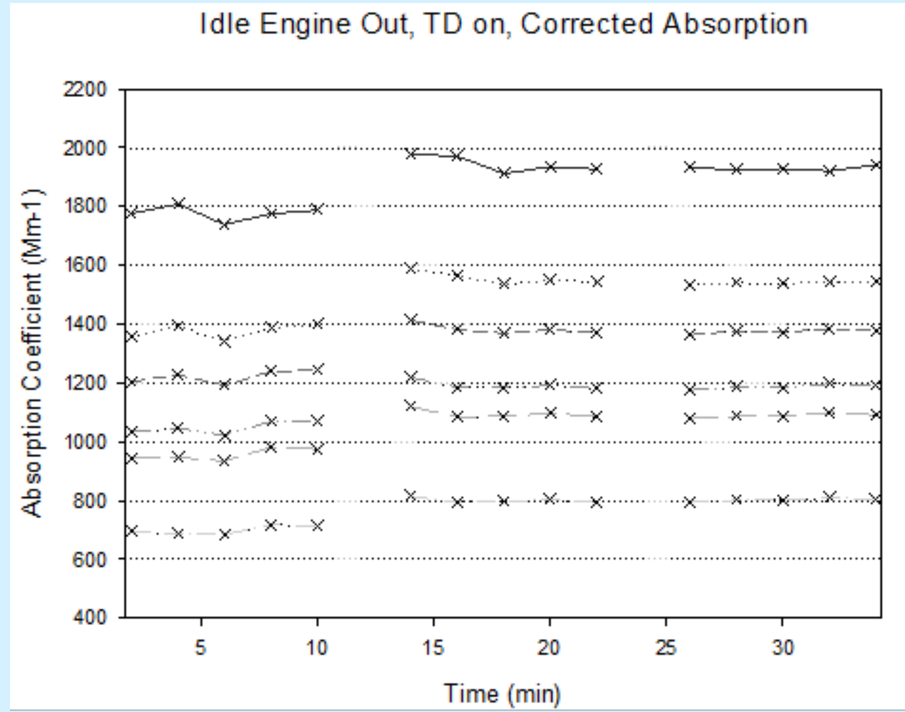
Multiple Wavelength Absorption Correction

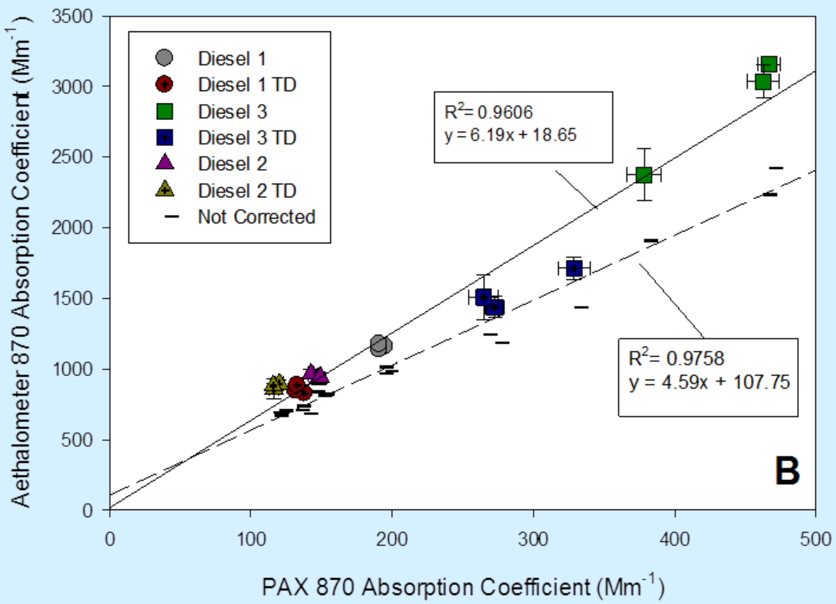


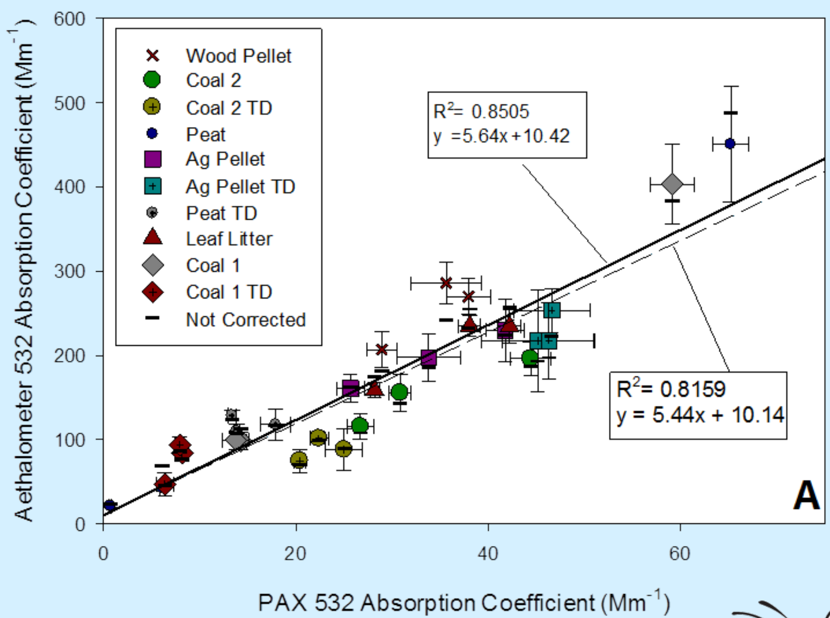


- Test run at steady-state
- Scattering correction is not significant for engine out emissions
- Loading correction is wavelength specific

Corrected Aethalometer and PAX

- Comparison at 532 and 870 nm
- Good agreement after filter loading and scattering artifact corrections





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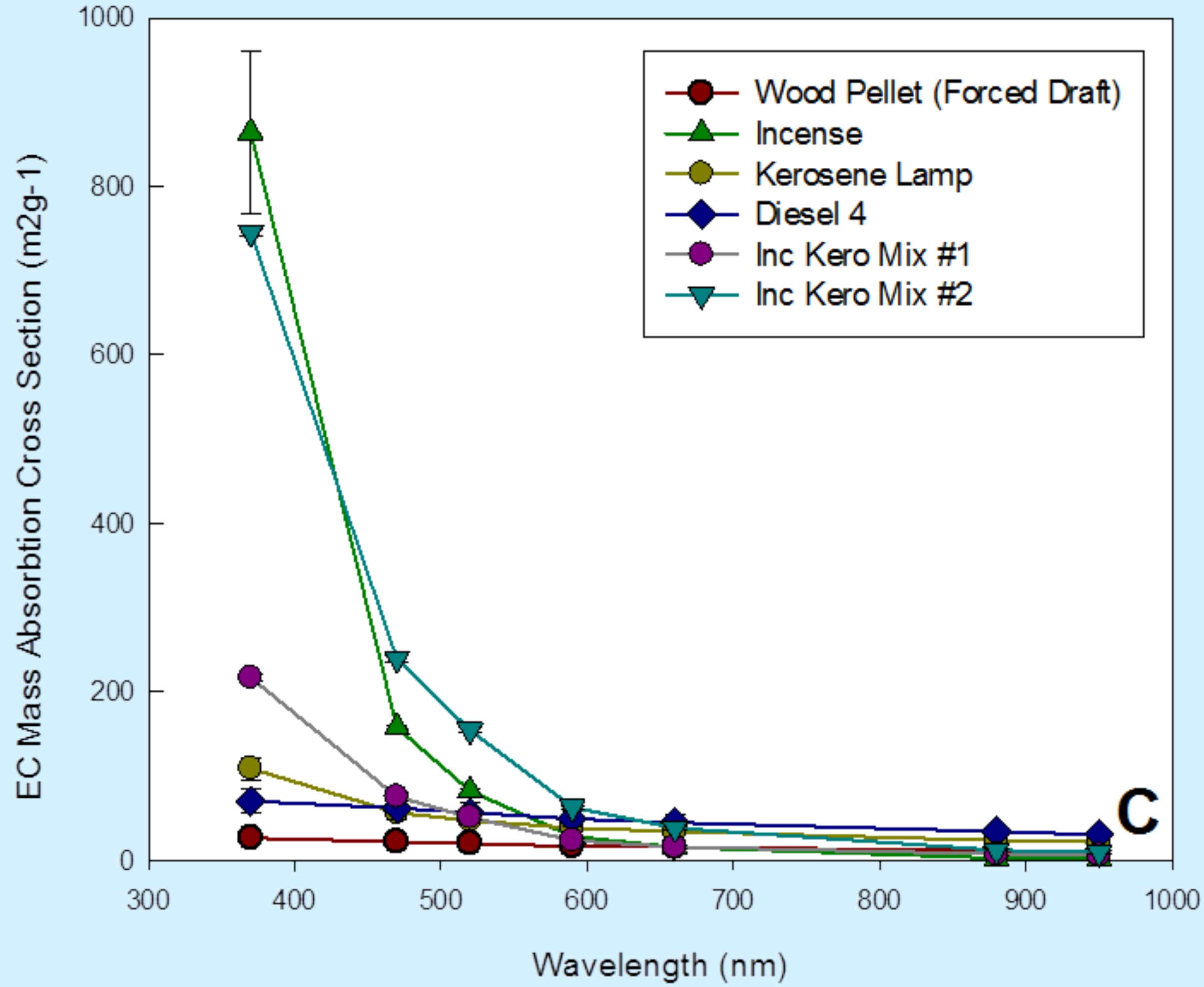
Example Bulk EC Mass Absorption Efficiency



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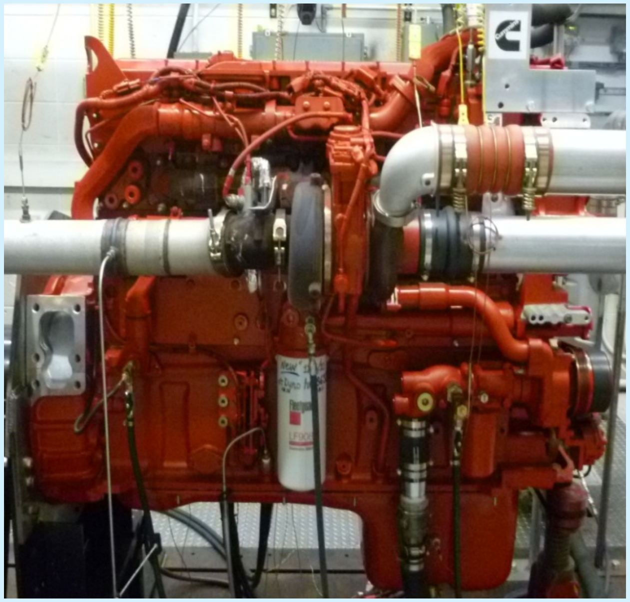
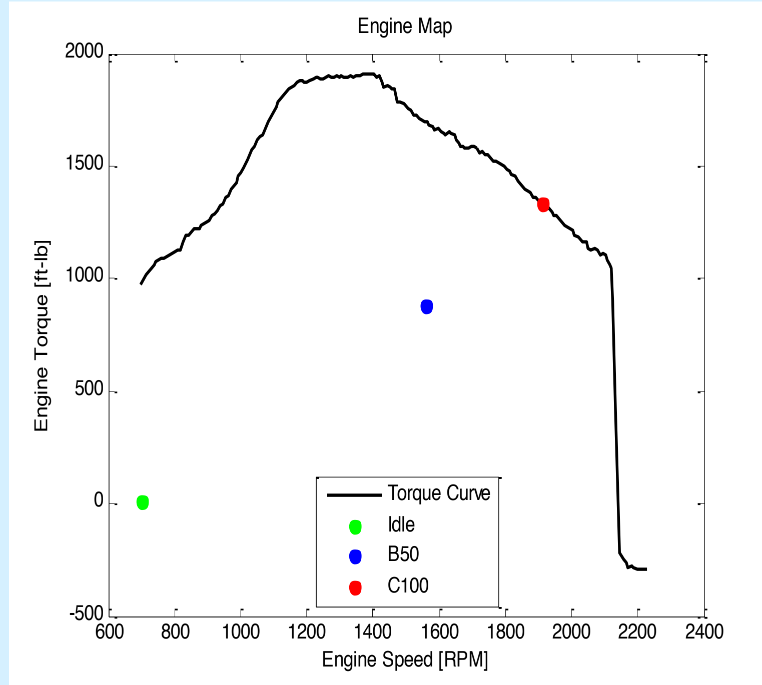
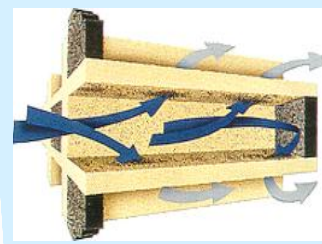
Experimental Setup



Model	2010, Cummins ISX15 – 500
Emission Certification	EPA 2010, CARB 2010
Type	4-stroke cycle
Cylinder Configuration	In-line 6
Bore and Stroke	137 mm x 169 mm
Compression Ratio	17.2:1
Aspiration	Turbocharged & Charge Air Cooled
Displacement	14.9 L
Rated Power & Rated Speed	373 kW & 1800 RPM
Peak Torque	2508 N-m at 1200 RPM
Fuel System	Cummins XPI
EGR System	Cooled High Pressure





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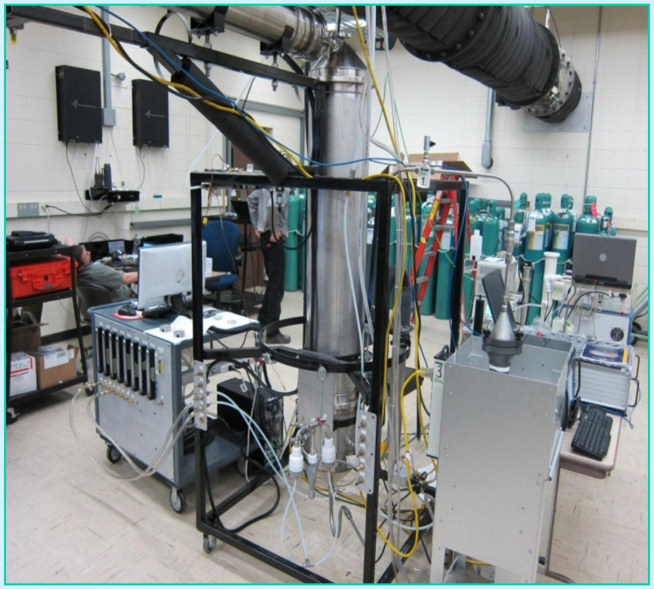
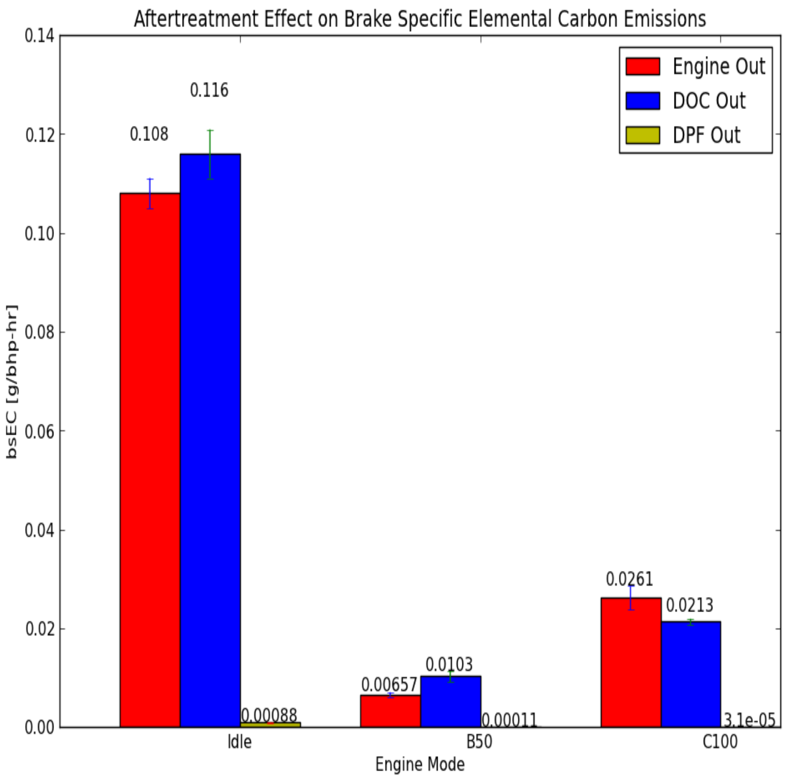
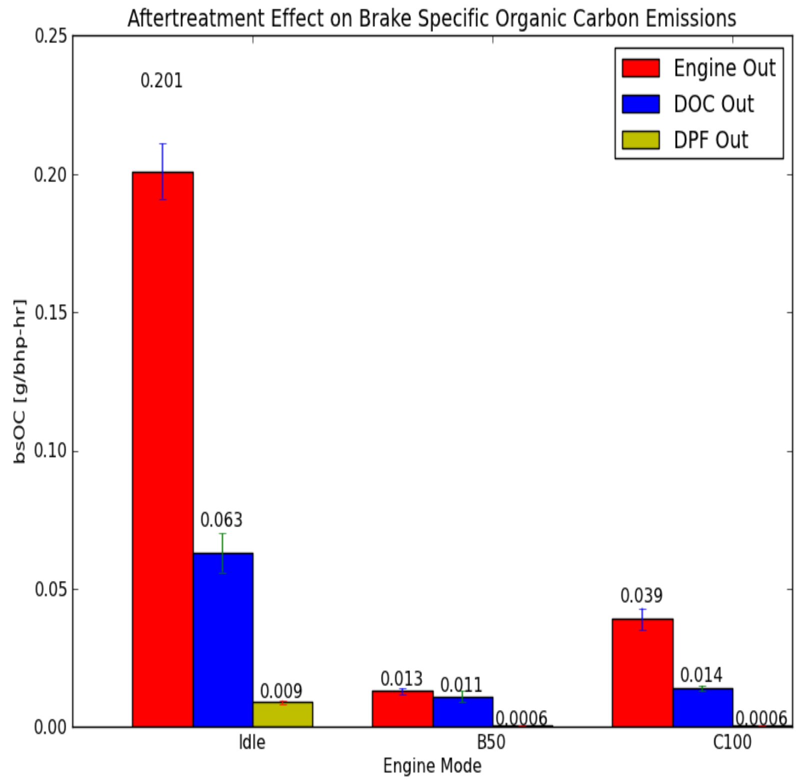
Emissions Testing Lab



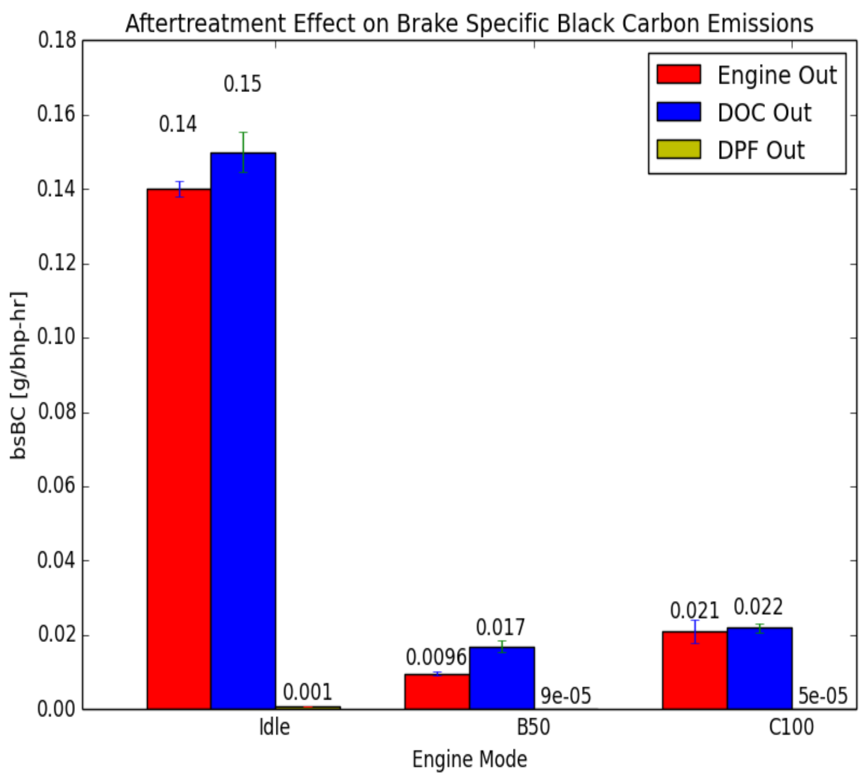
Effect of Aftertreatment on EC/OC emissions

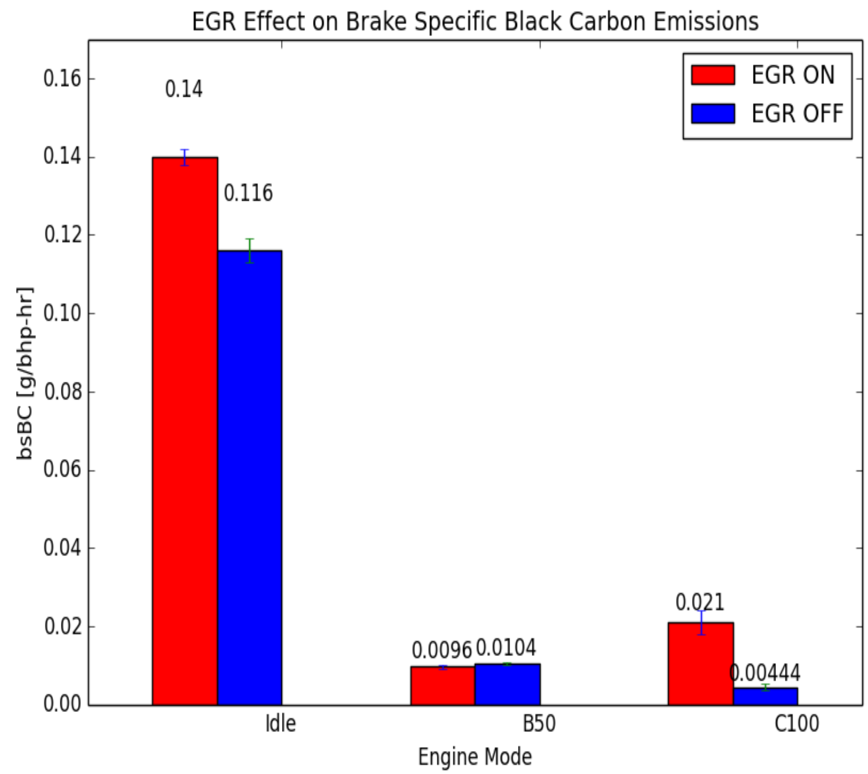




- Excellent reduction of EC emissions due to DPF
- OC emissions are significant at Idle even with a DPF present (which may contribute to BrC light absorption)

Emission Control effect on bsBC





- Excellent reduction of BC with DPF.
- EGR increases BC due to poor in-cylinder oxidation of primary BC particles

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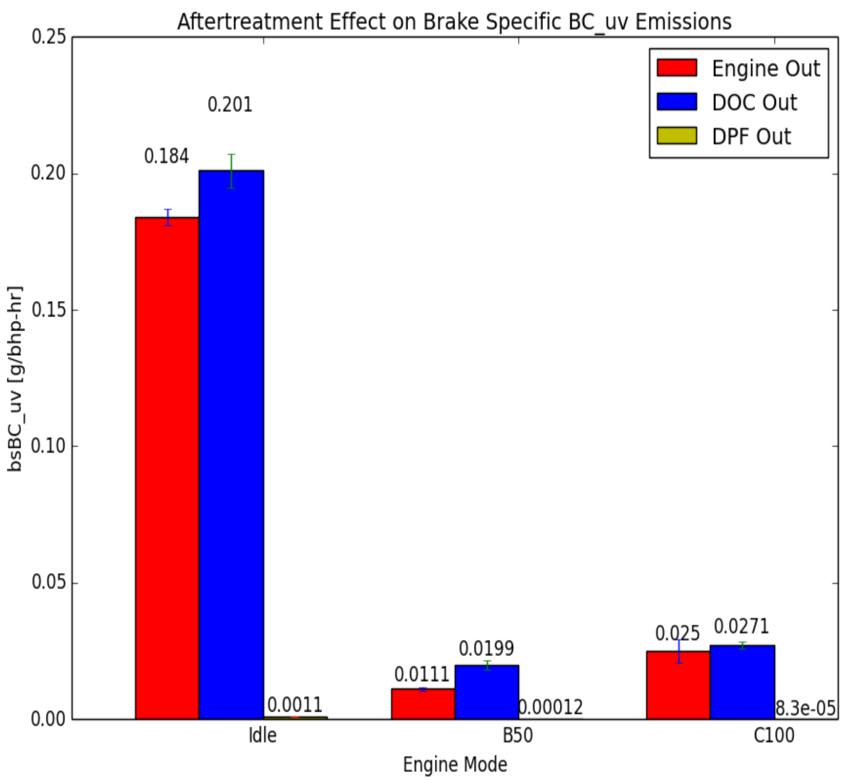
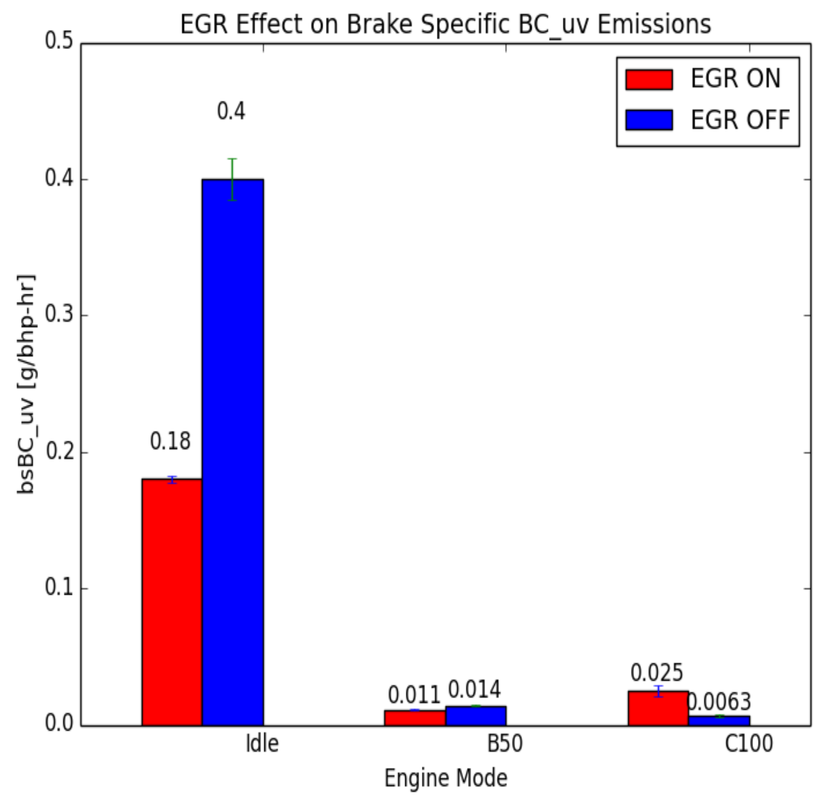
Emission Control effect on $bsBC_{UV}$





- Near zero BC_{UV} emissions post DPF
- EGR effect on UV spectrum absorbing aerosols is significant and counter to the traditional NOx-PM tradeoff

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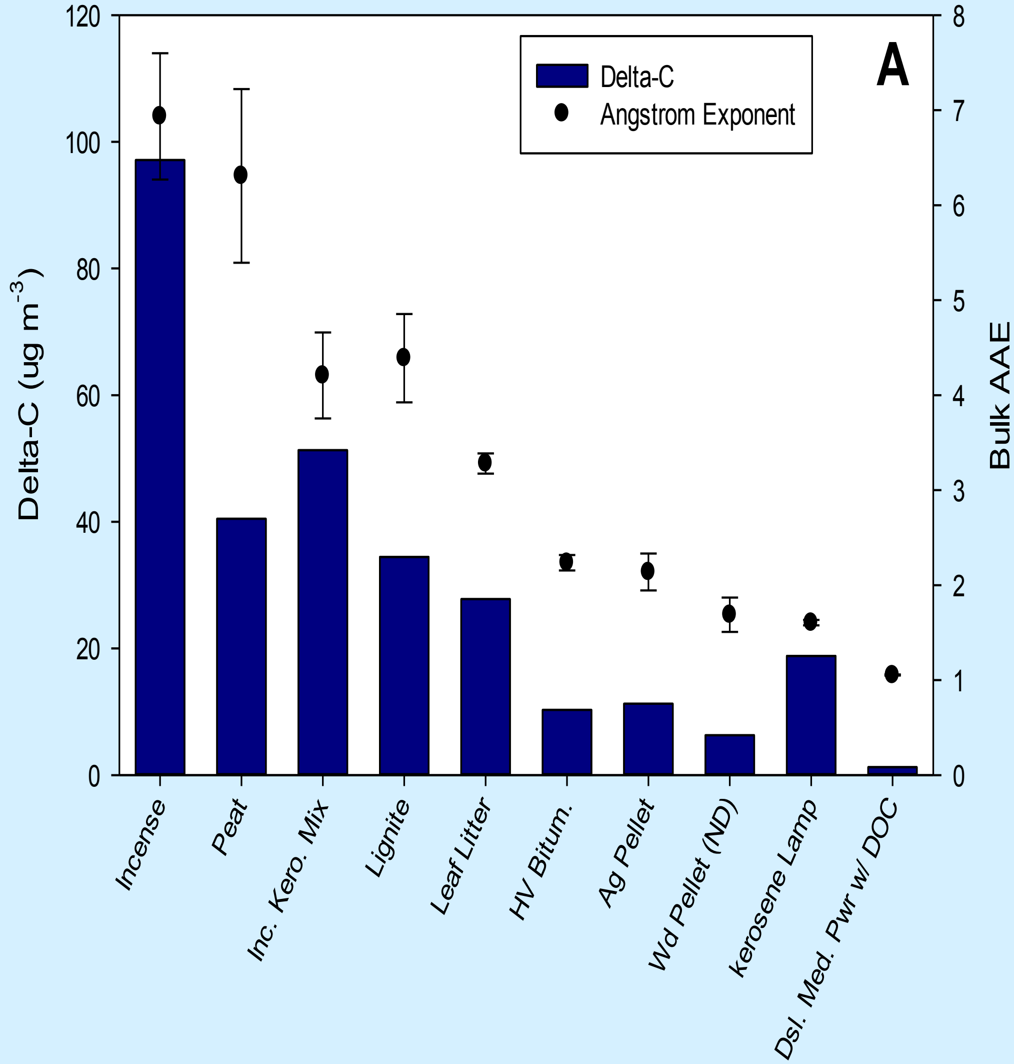
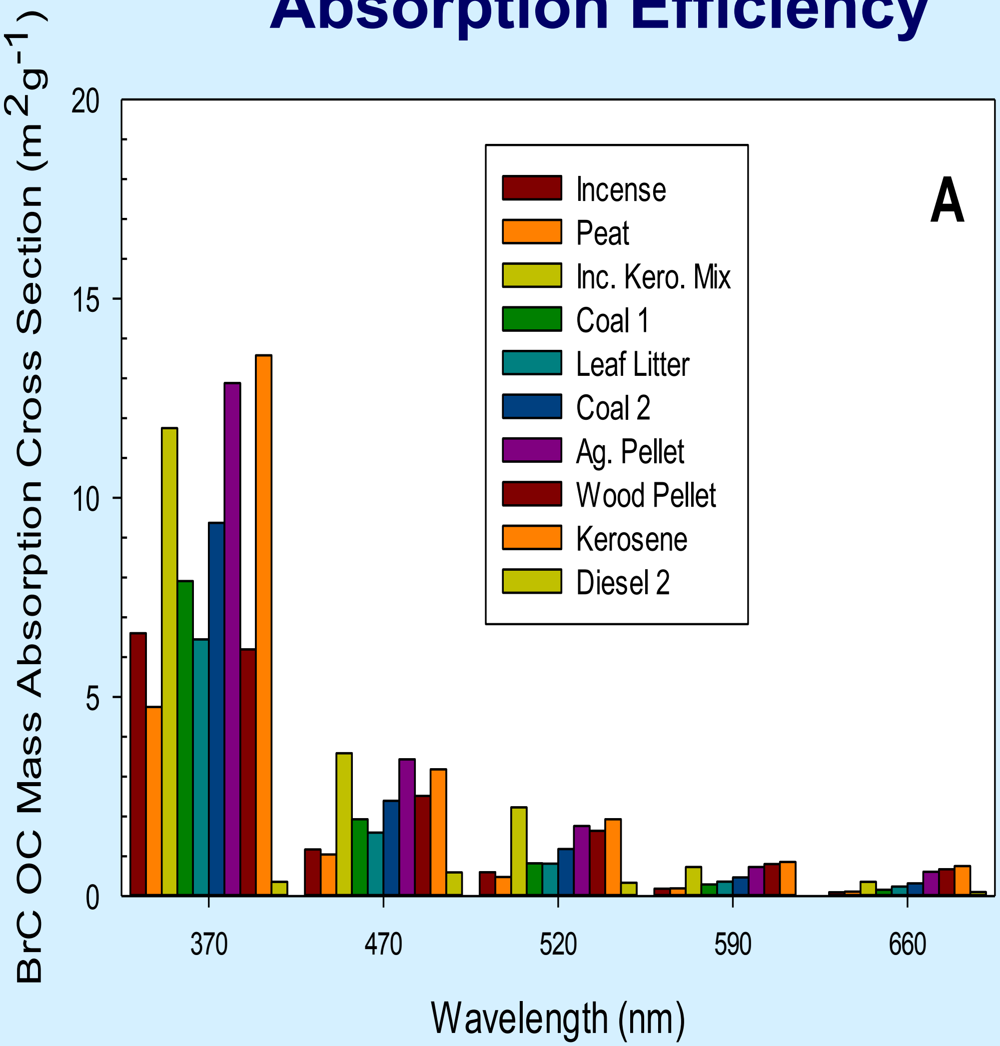
- Calculation of brown carbon indicators: Delta-C (mass concentration difference at 370 and 880 nm wavelength) and AAE (power law regression fit all wavelengths)
- High variability across sources
- Coal and Kerosene can show relatively high values for these indicators
- Driven by OC content of the sample



- Normalize the brown carbon component to OC concentration to get OC Mass Absorption Efficiency
- UV light absorption is more variable across source emissions
- Visible light absorption shows variability across sources, not as extreme as the UV

Brown Carbon OC Mass Absorption Efficiency



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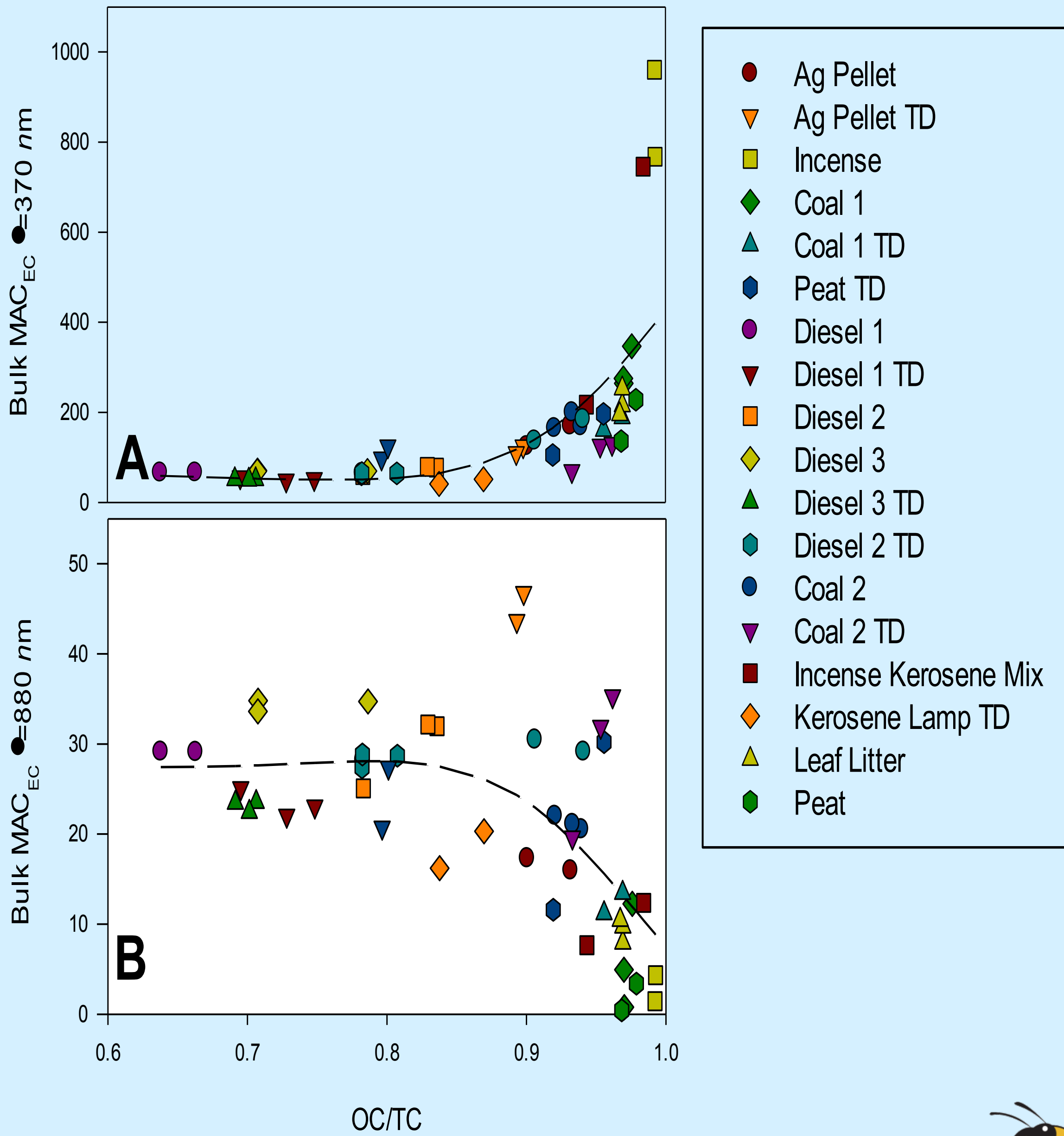
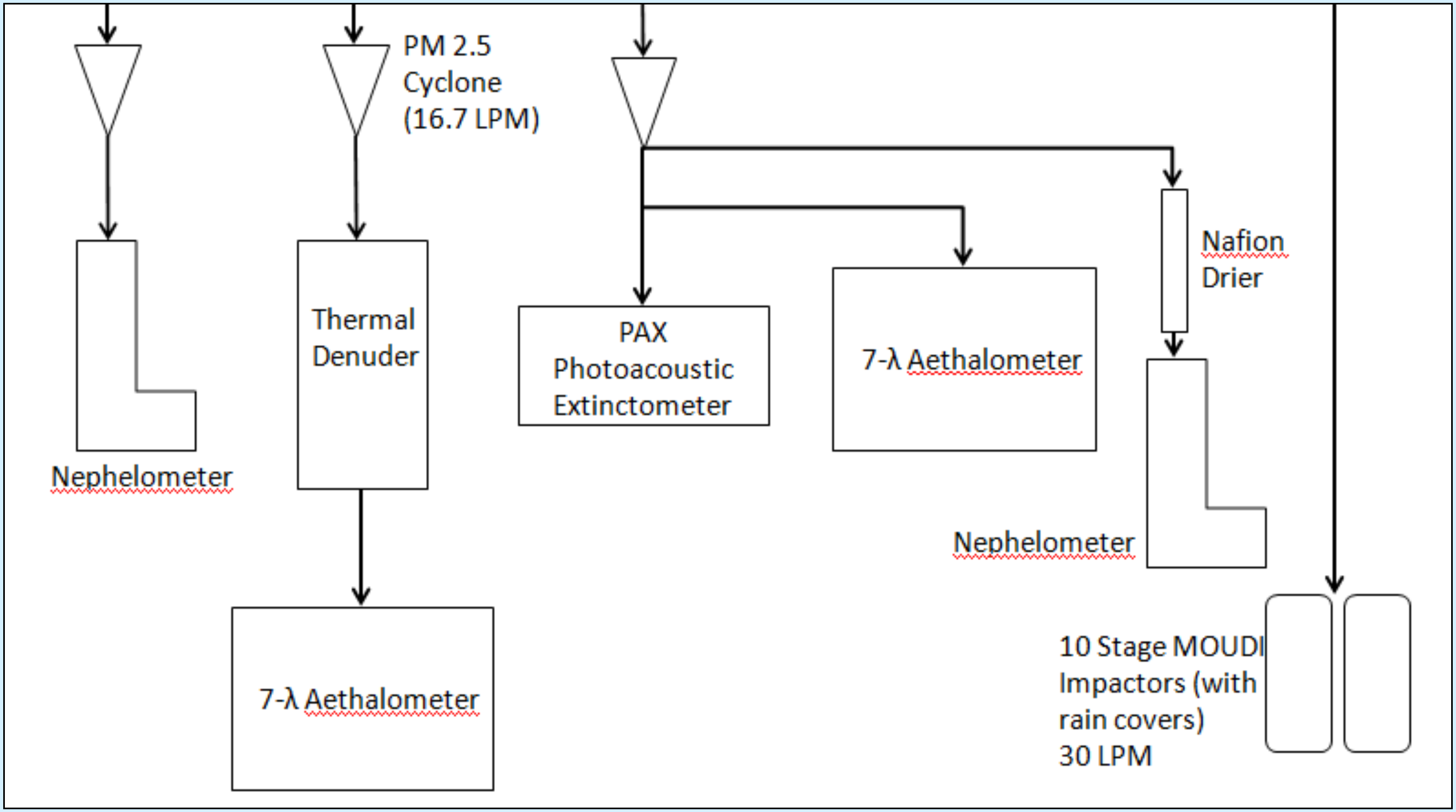
- OC content effects the measured EC Mass absorption efficiency for source samples and is independent of source type
- Brown carbon increase with OC content
- BC absorption efficiency decreases at high OC content



Atmospheric Sampling Approach



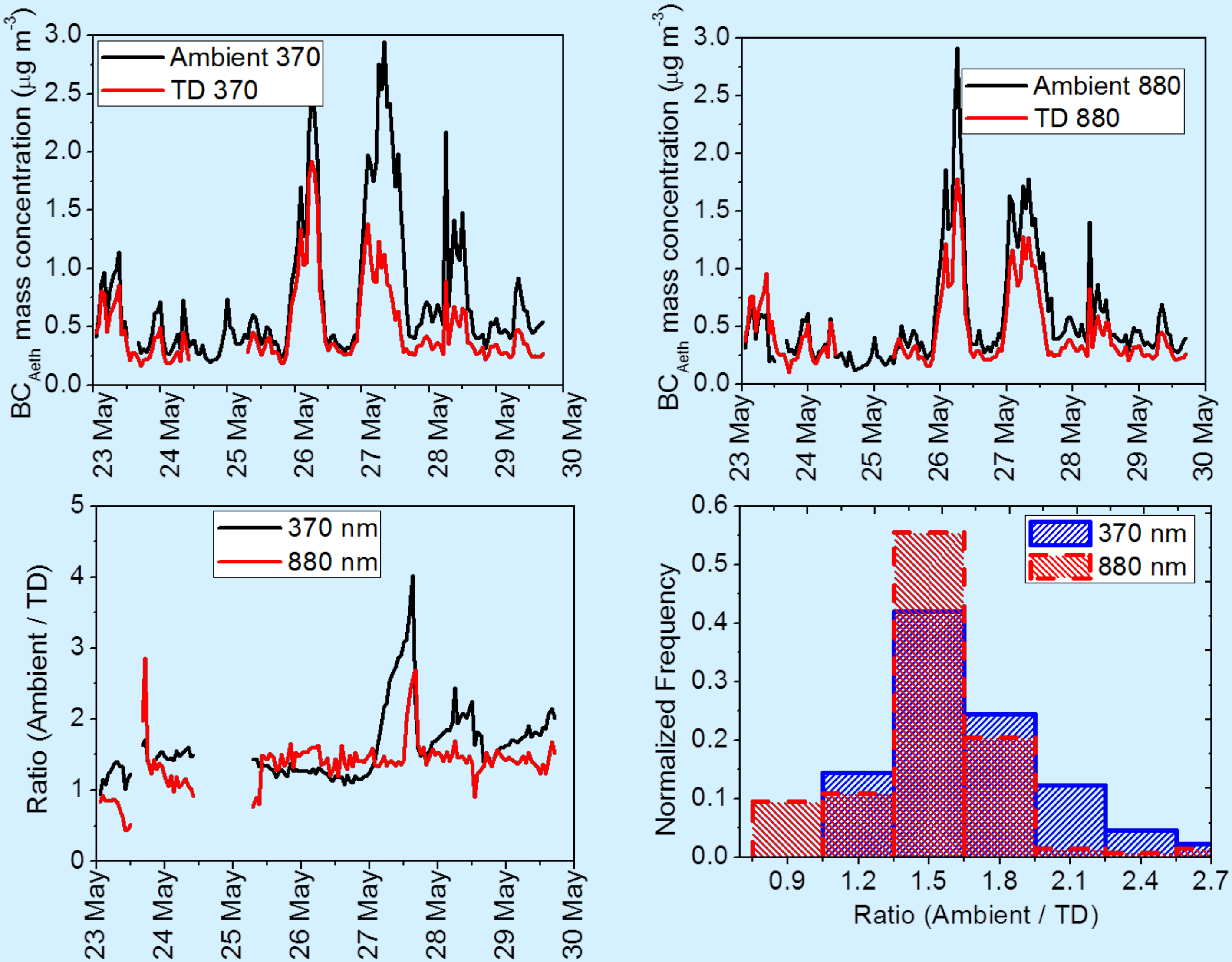
Size-Resolved Chemical Analyses

- Elemental (EC) and Organic Carbon (OC)
- Water Soluble Organic Carbon (WSOC)
- Light absorption coefficients in water and methanol extracts (200 – 700 nm)

Estimating Light Absorption Coefficients

- External mixtures of BrC and BC components
- Refractive index calculations based on water and methanol extract light absorption
- Mie theory calculations as a function of size to get wavelength dependent light absorption

Atlanta Thermal Denuder Results (200^{o}C)



Semi-volatile light absorption at 370 nm responsible for 60% of absorption

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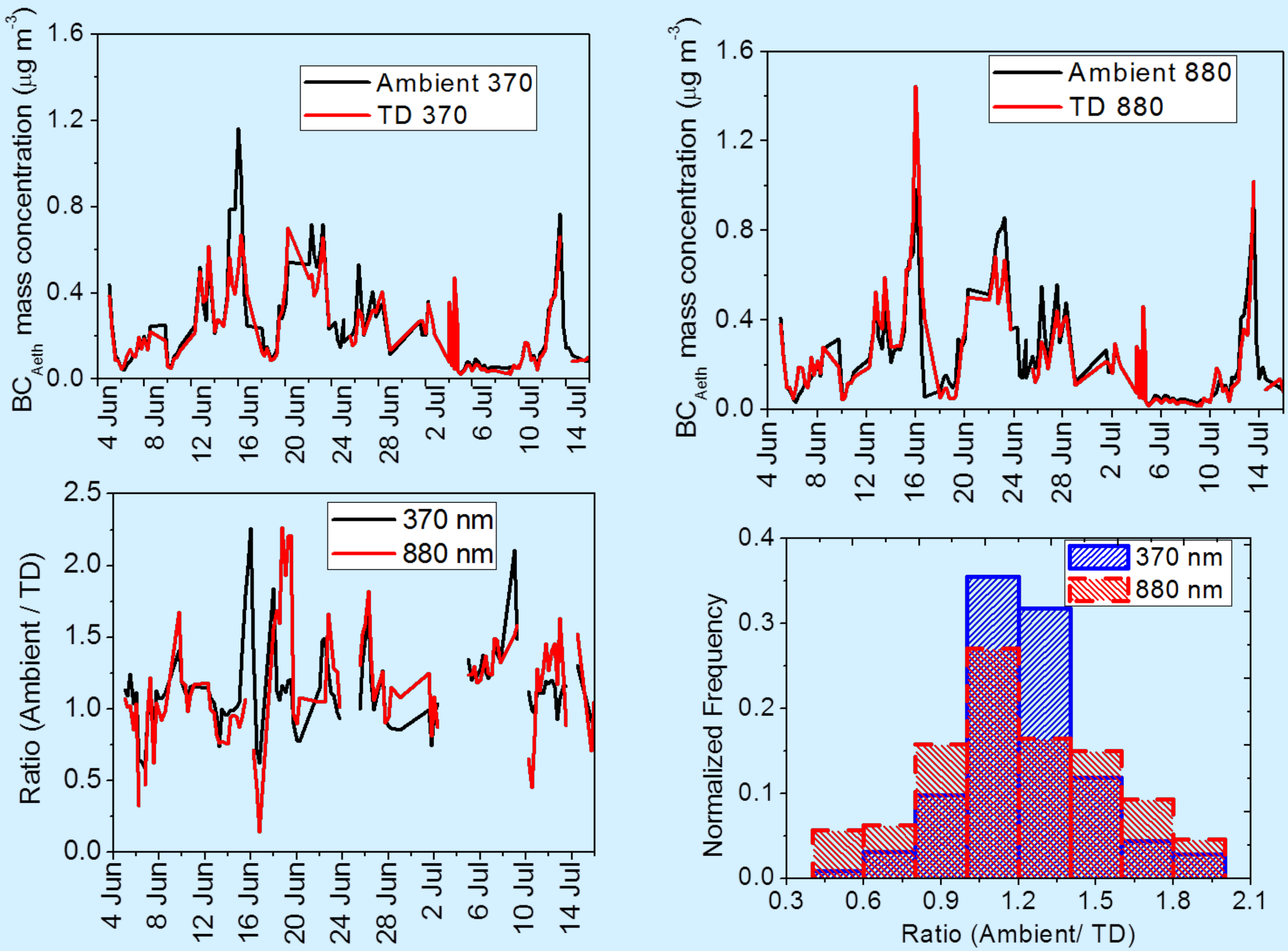
Centreville Thermal Denuder Results (200^{o}C)



The rural site has much less absorption by semi-volatiles (~15% at 370 nm)

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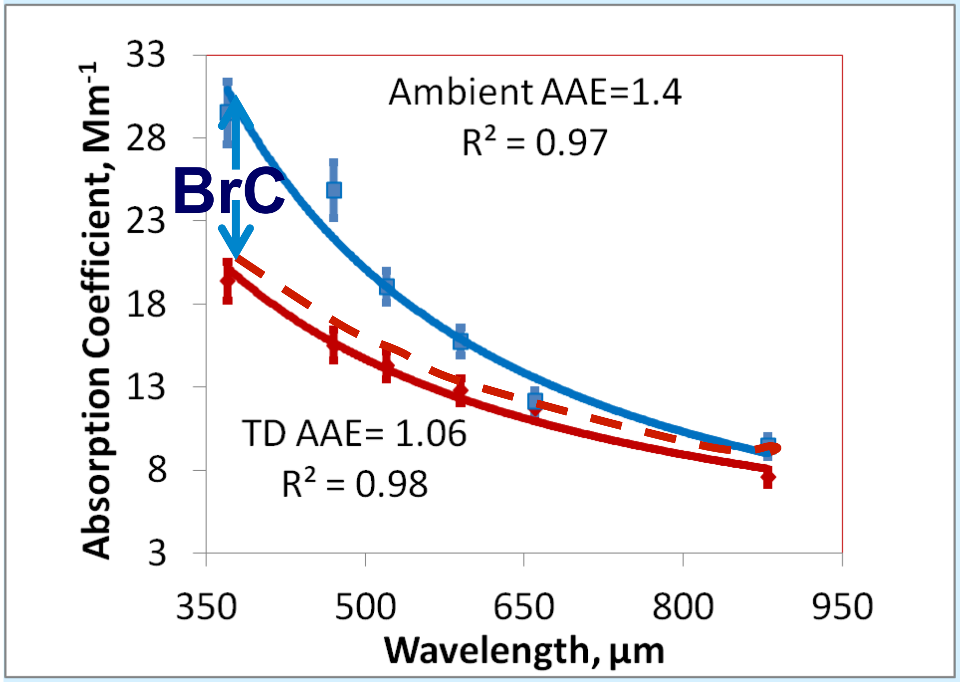
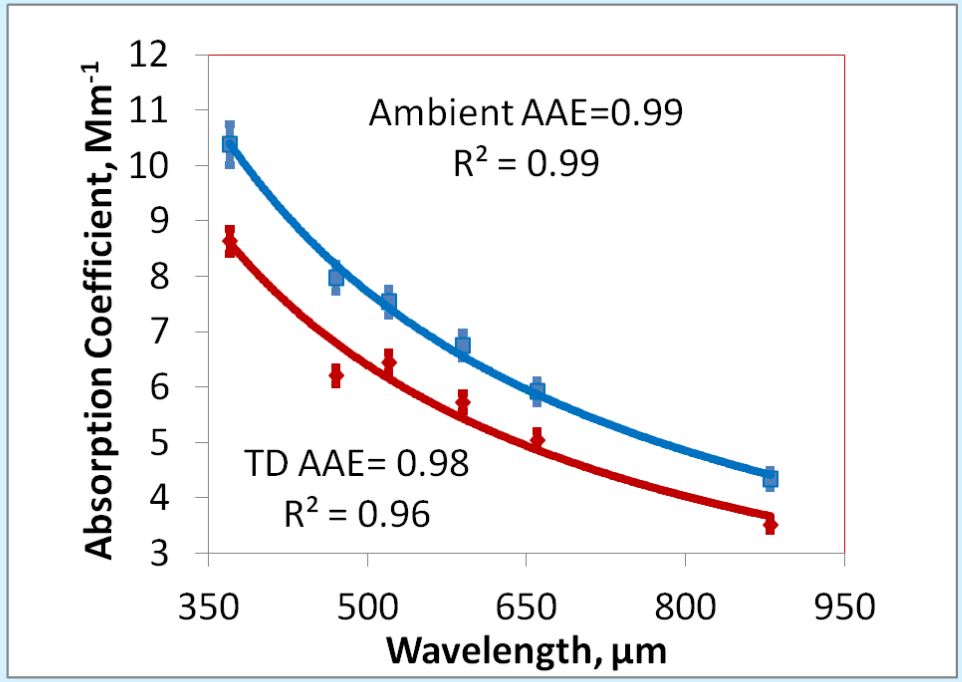
BrC Contribution to Light Absorption: Urban vs. Rural

Atlanta



Centerville



- **Semi-volatile contribution to light absorption apparent in AAE curves for Atlanta, not Centreville**

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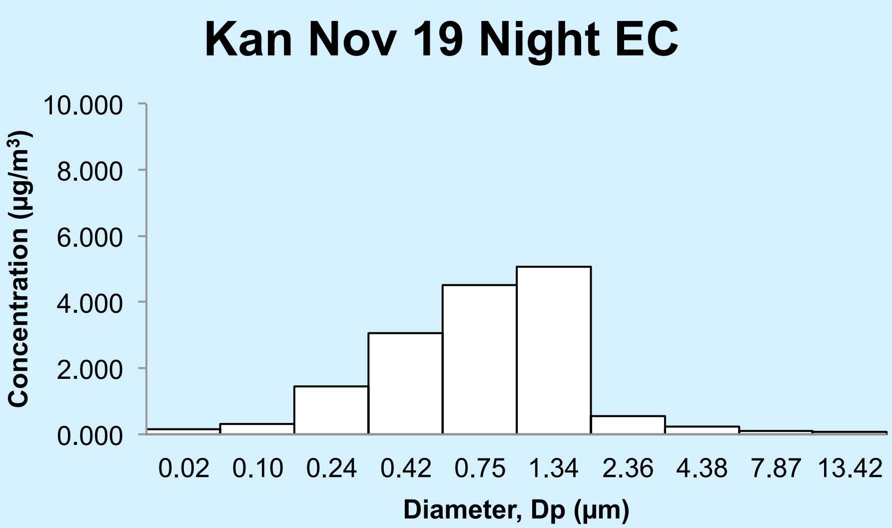
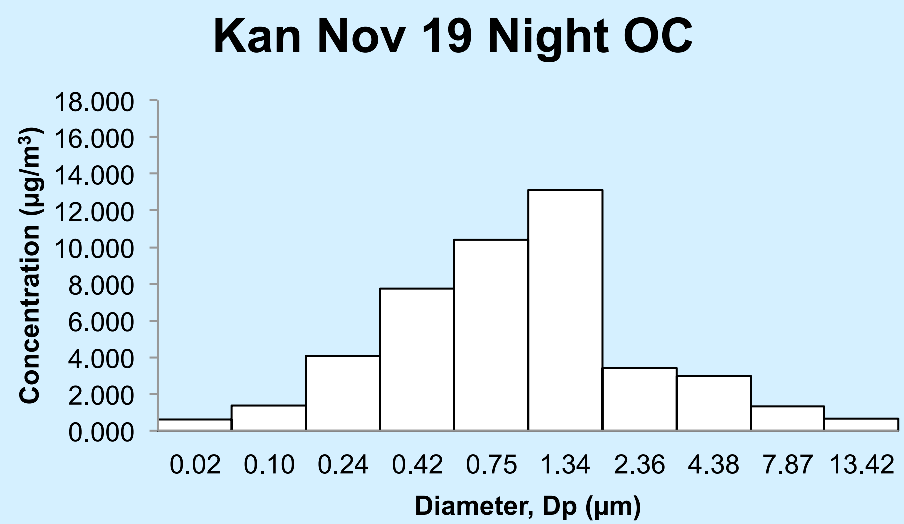
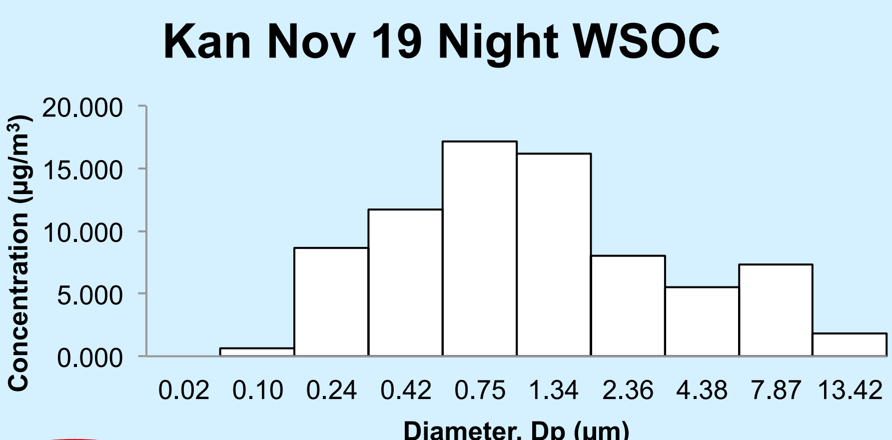
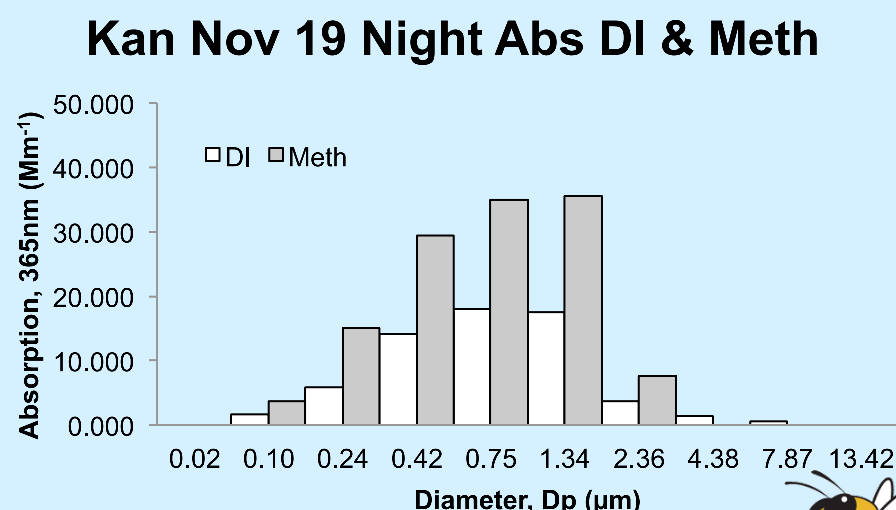
Size-resolved Chemical Composition Related to Light Absorption









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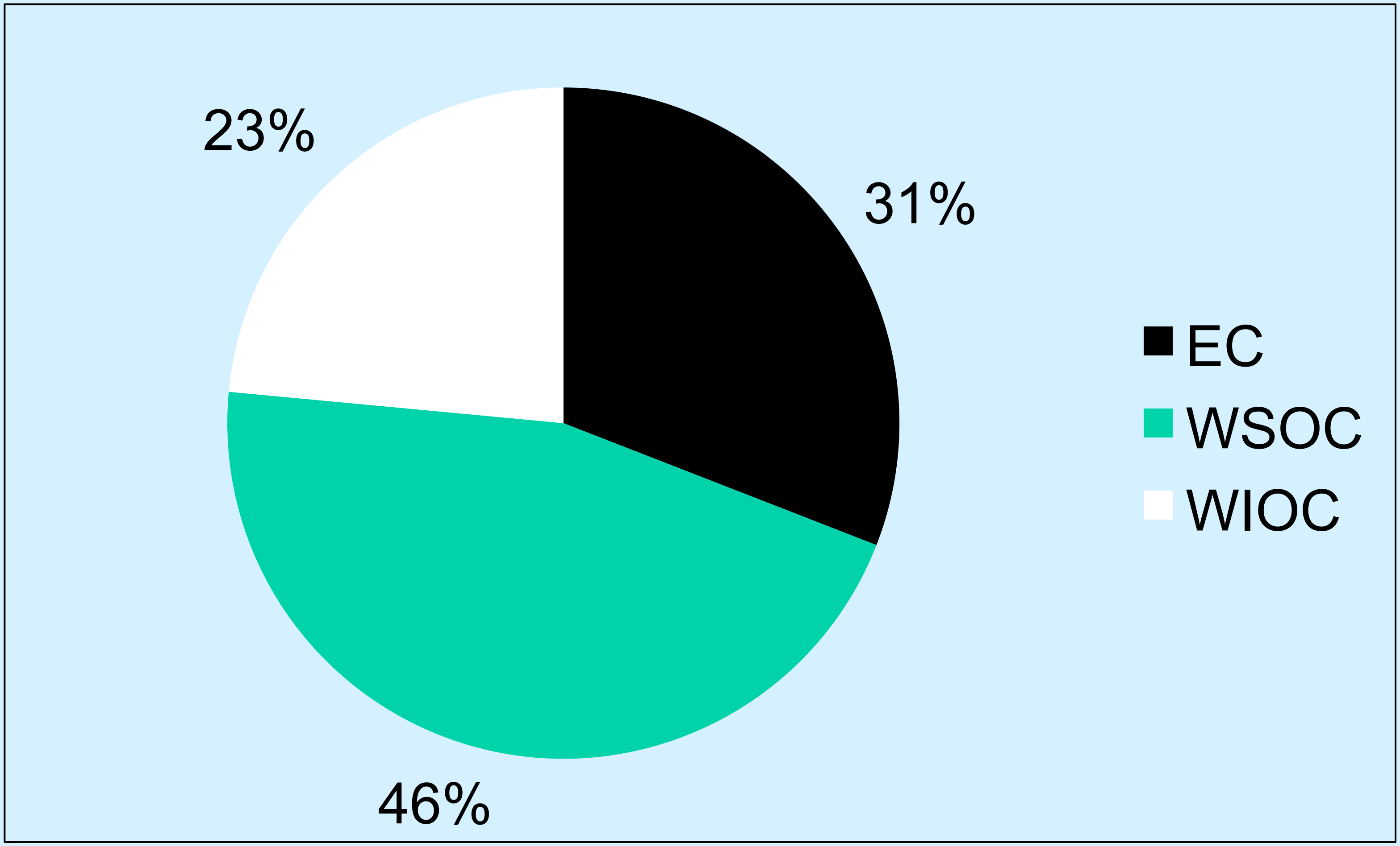
Average Estimated Contribution of Carbonaceous Compounds to Light Absorption at 365 nm



- **BrC is responsible for on average 50-80% of the light absorption**

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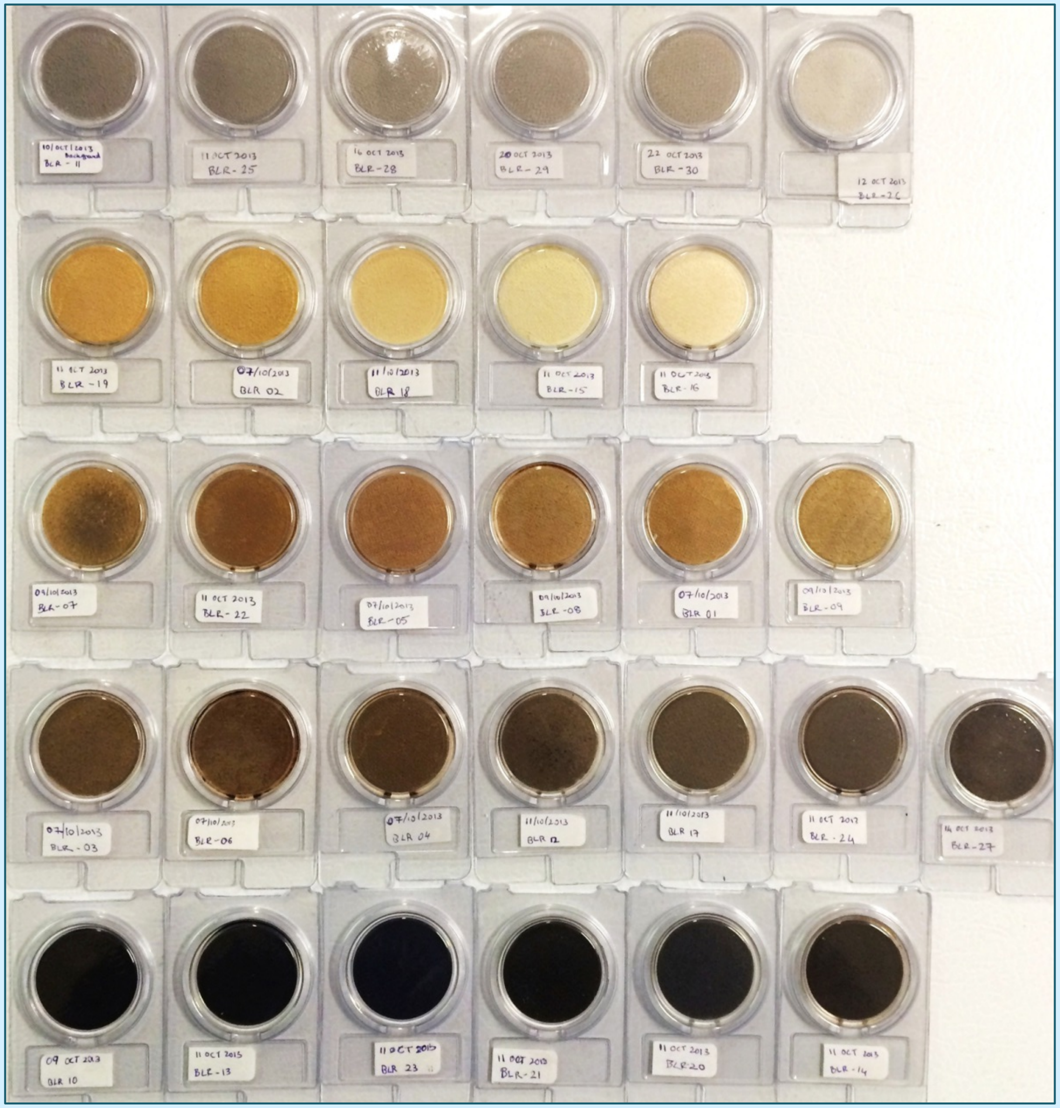
Trash/Refuse Burning Source Sampling



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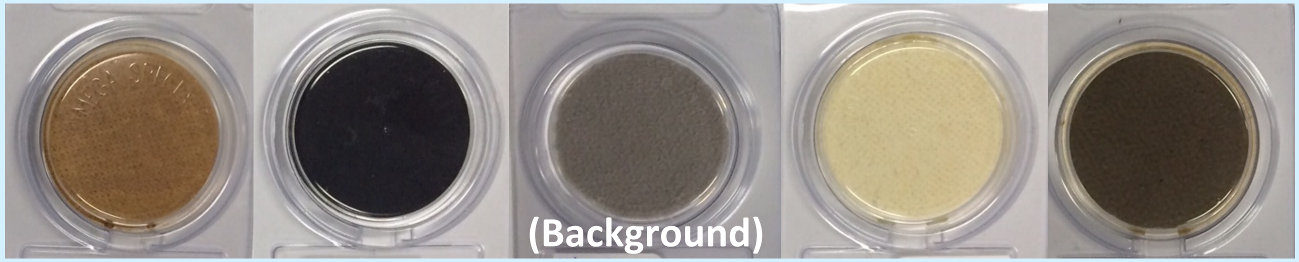
BrC as a Function of Burning Conditions and Aging



OC/EC	487.75	0.80	4.26	--	291.63
WSOC/OC	0.84	0.65	**1.27**	--	0.70
Abs365$_{H2O}$ /OC	10.62	22.12	0.05	--	4.51
Abs365$_{MeOH}$ /OC	6.90	11.15	0.01	--	1.91
DTT/OC (pmol/min/ug OC)	0.54	3.46	35.99	--	0.72

- **Does BrC quickly (~hours) disappear from sources?**

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Key Observations

- Large variability in mass absorption efficiencies for sources of BC/EC linked with OC carbon fraction
- DPM-diesel emissions work well for BC, can generate BrC under certain conditions
- Other diesel control methodologies may emit relatively large amounts of BrC (i.e. EGR)
- Field measurements suggests BrC/EC ratio decreases quickly due to atmospheric aging (~hours to days)
-

Ongoing Efforts

- Beijing APEC and Heating Season Sampling
- Organic Carbon Re-Aerosolization Experiments with a few more source samples and the Beijing Samplers

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