Laser-induced incandescence (LII) for the measurement of atmospheric black carbon

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Measurement Science and Standards

Laser-induced Incandescence (LII) for the Measurement of Atmospheric Black Carbon

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National Research Council Canada
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Canada

Acknowledgements

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- Dave Snelling, Kevin Thomson, Fengshan Liu, Bob Sawchuk, Dan Clavel, Daniel Gareau
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Atmospheric Measurements

- John Liggio, Mark Gordon, Jeffrey Brook, Shao-Meng Li, Craig Stroud, Ralf Staebler, Gang Lu, Patrick Lee
  - Environment Canada, Atmospheric Science and Technology Directorate

Atmospheric Inventory Data

- Brett Taylor
  - Environment Canada, Pollution Data Division

Outline

Background

Laser-induced Incandescence (LII)

High-Sensitivity Laser-induced Incandescence (HS-LII)

Comparison to other Instruments

Applications

Summary

Black Carbon (BC) and Particulate Matter (PM)

Black carbon (BC) is a major component of the particulate matter (PM) emissions from hydrocarbon-fuelled combustors

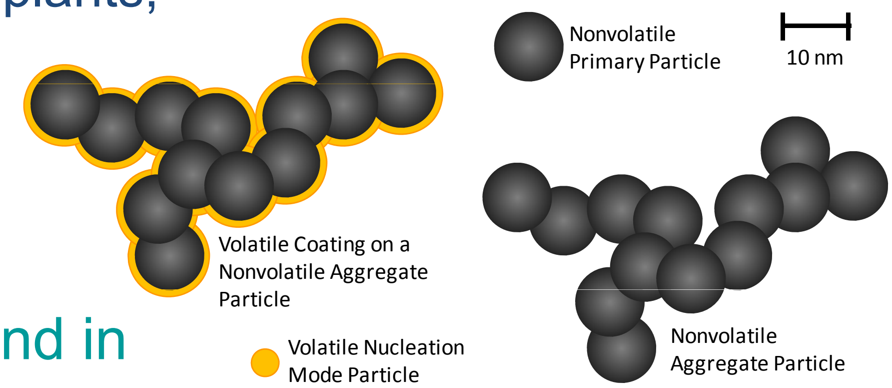
- diesel and gasoline internal combustion engines, gas turbine engines, powerplants, furnaces & boilers, etc.

Other PM components include

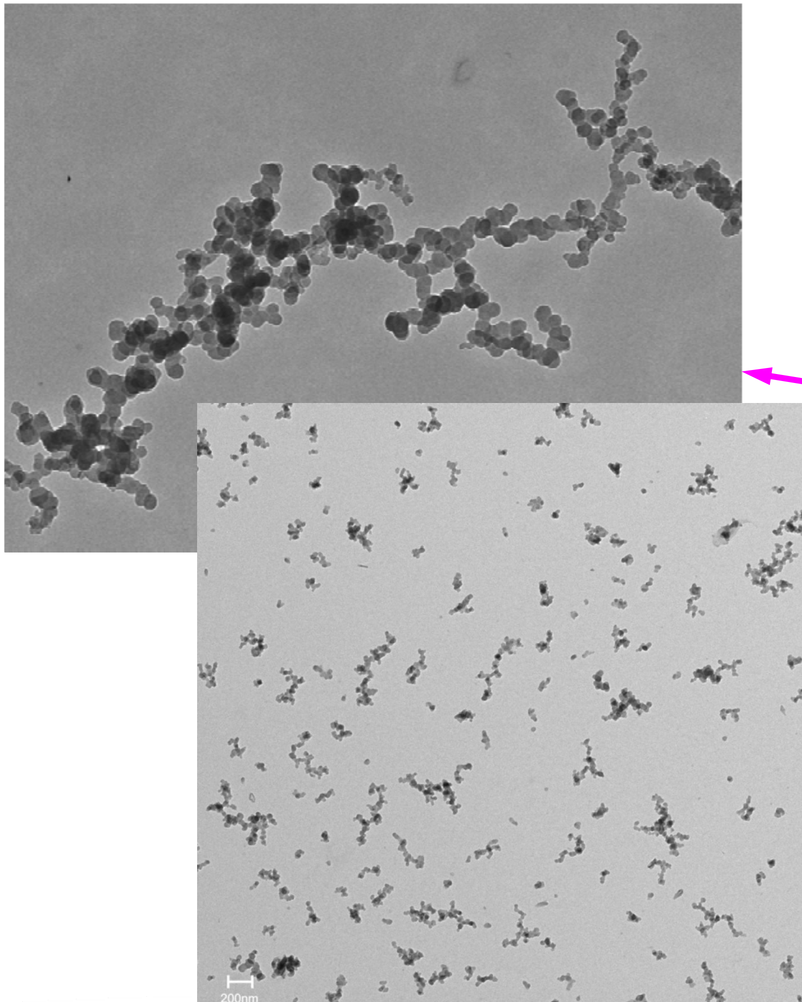
- condensed hydrocarbons
- sulphates, nitrates, and trace metals

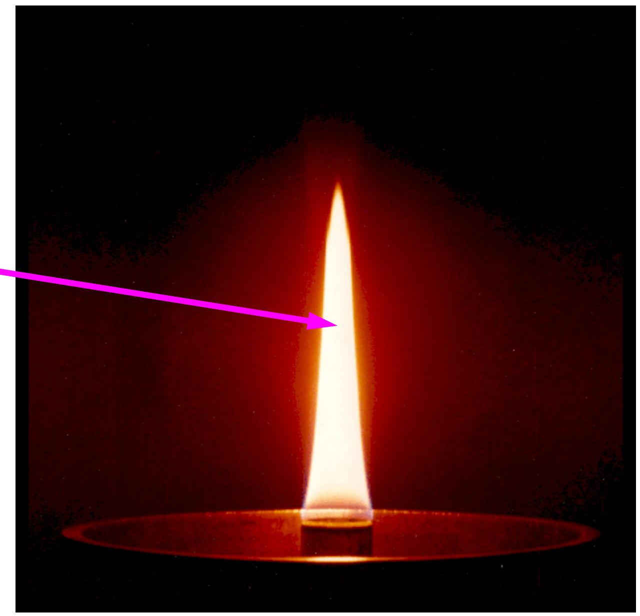
PM is implicated in health effects and in climate change

- cardiovascular, lung function, immune response, cancers
- black carbon warms the atmosphere



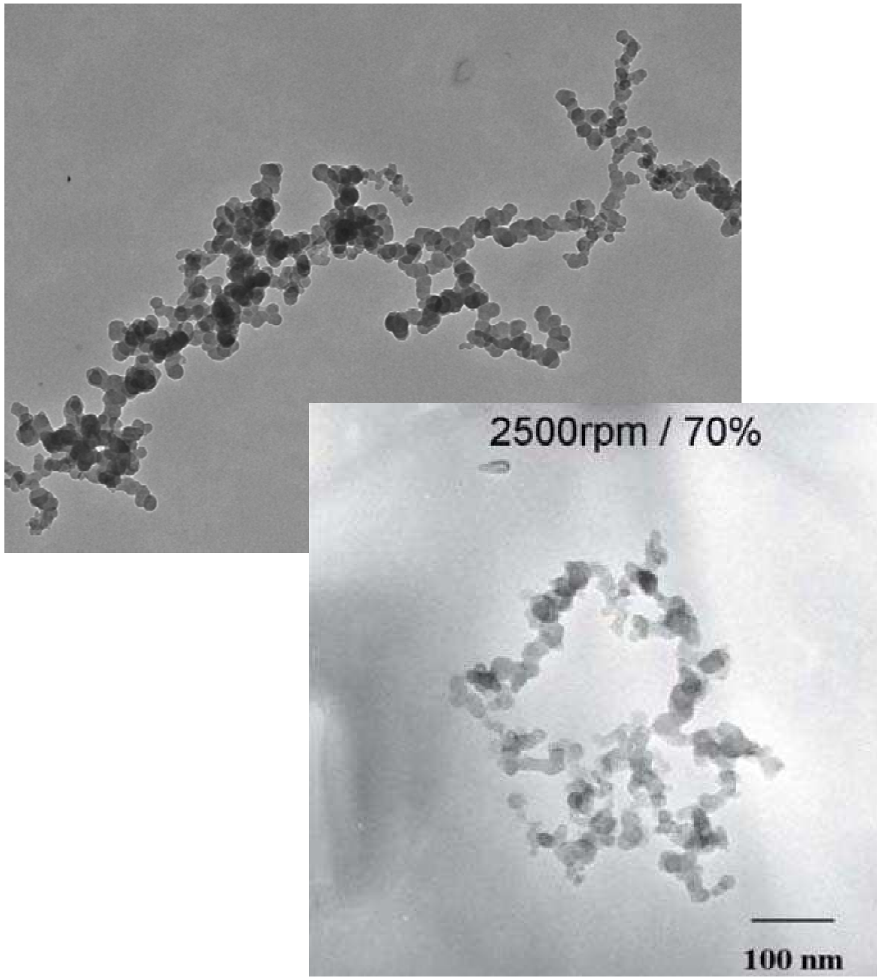
TEM Images of Black Carbon Sampled From a Flame





[Schulz *et al.*, Applied Physics B **83**, 2006]

TEM Images of Nanoparticles



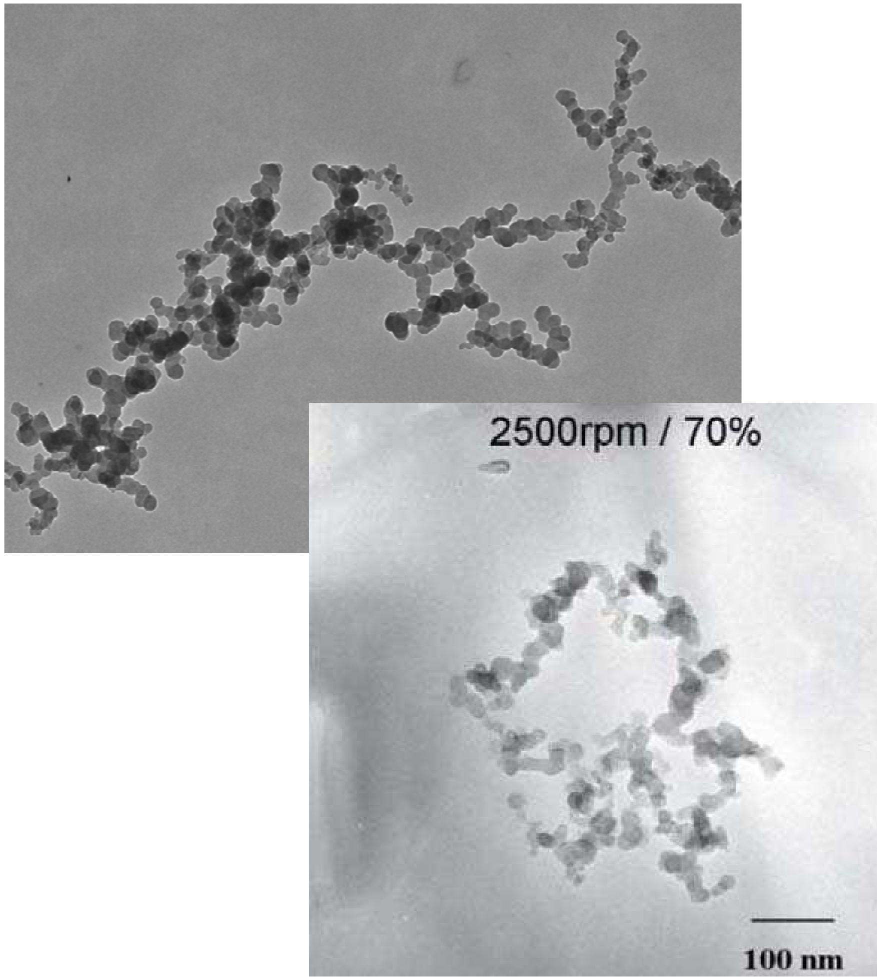
[Lee et al., SAE Paper No. 2003-01-3169, 2003]

Assumption:

in-flame ethylene		in-flame methane		post-flame diesel		oxidized ambient	
BC	**=**	**BC**	**=**	**BC**	**=**	**BC**	**= …**

- particulate matter properties of interest:
  - concentration
  - active surface area
  - primary particle diameter distribution
  - aggregate size distribution
  - optical properties
  - volatile fraction
  - composition

TEM Images of Nanoparticles



[Lee et al., SAE Paper No. 2003-01-3169, 2003]

Reality:

in-flame ethylene		in-flame methane		post-flame diesel		oxidized ambient		
BC	≠	**BC**	≠	**BC**	≠	**BC**	≠	…

- particulate matter properties of interest:
  - concentration
  - active surface area
  - primary particle diameter distribution
  - aggregate size distribution
  - optical properties
  - volatile fraction
  - composition

Challenges for Optical Diagnostics of Black Carbon

Need to know the optical properties of the particles

- composition of particle
  - nascent soot (lower C/H ratio; potentially liquid)
  - mature soot/BC (high C/H ratio; solid)
  - mature soot/BC coated with condensed materials (organics, etc.)
- absorption enhancement
  - coatings
    - absorption by coating
    - focusing of light by coating
- changes induced by optical technique (not always non-intrusive)
  - sublimation/evaporation
  - internal structure changes that affect absorption/scattering properties
  - fragmentation of particles

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Laser-Induced Incandescence (LII)

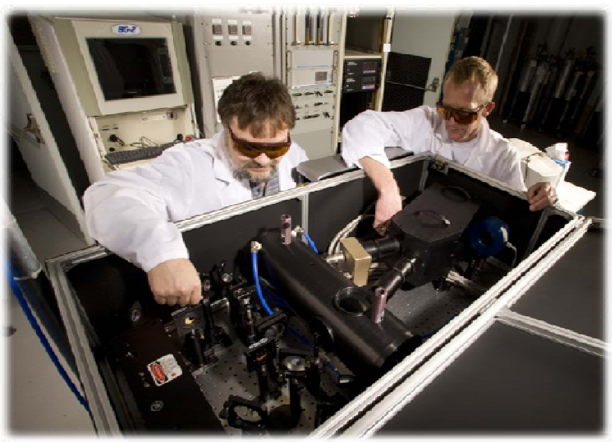
high selectivity technique for measuring black carbon

- soot, refractory carbon, elemental carbon, carbon black

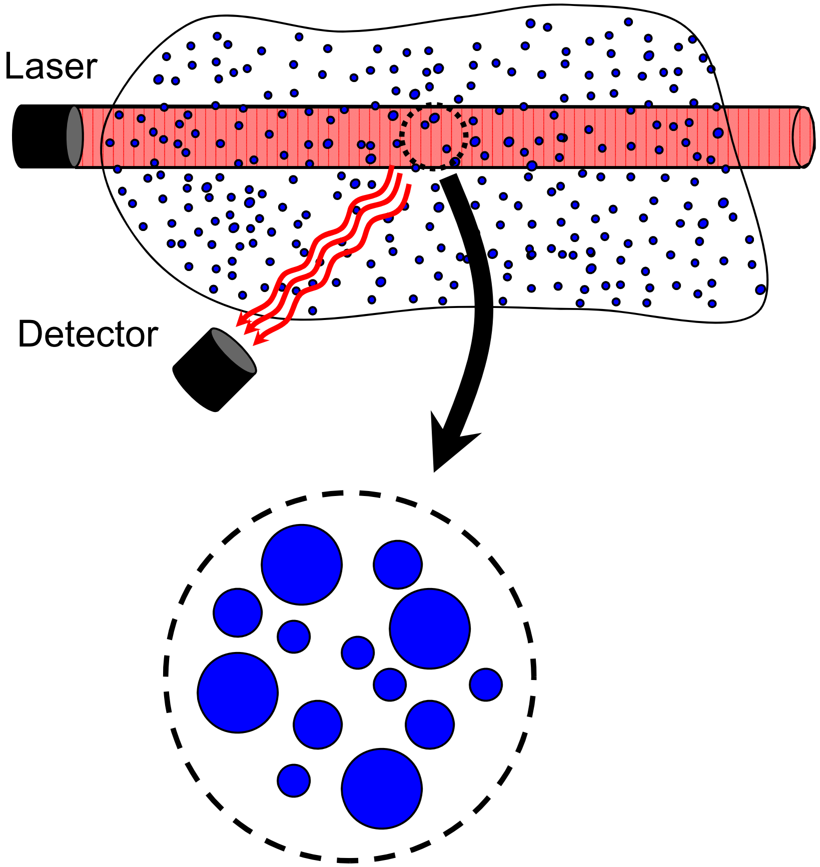
measures (for an ensemble of particles):

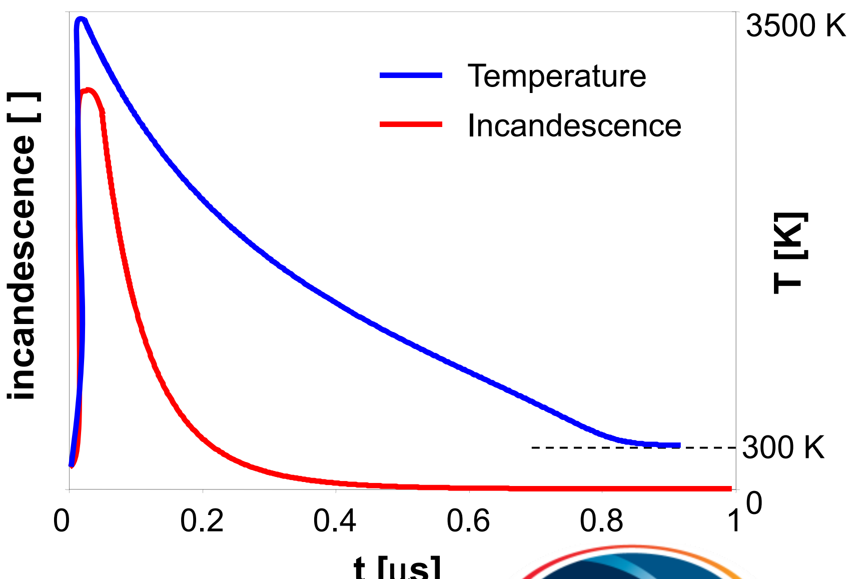
- mass concentration, volume concentration, active surface area, primary particle diameter
- broad measurement range (20ng/m^3 – 20g/m^3 mass; 50 – 200 m^2/g active surface area; 5-50 nm primary particle diameter)

real-time (20 Hz), instantaneous data analysis



Time-Resolved Laser-Induced Incandescence





Auto-Compensating LII (AC-LII)

Traceable physics-based calibration procedure

- using calibrated integrating sphere as a spectral radiance source
- not correlation against another aerosol instrument

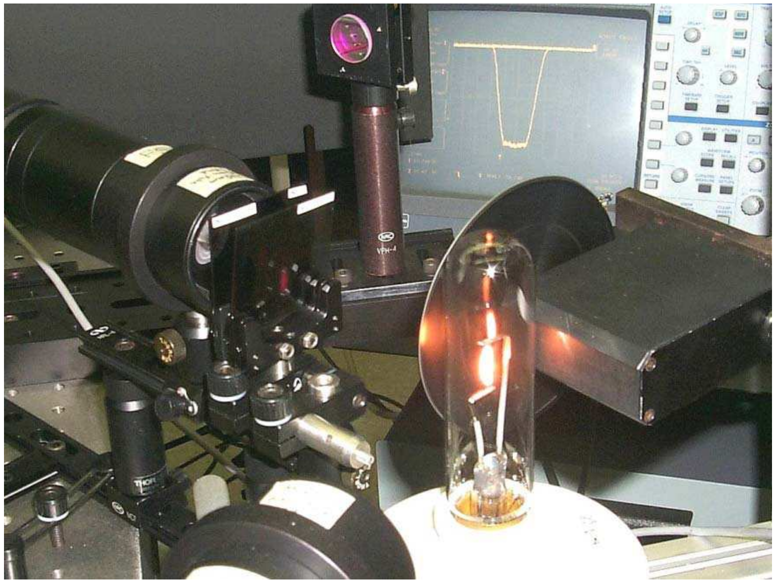
Two-color pyrometry coupled with LII to determine the time-resolved particle temperature

- permits use of low-fluence
- particles are kept below the sublimation temperature

This technique automatically compensates for any changes in the experimental conditions

- fluctuations in local ambient temperature
- variation in laser fluence
- laser beam attenuation by the particulate matter
- desorption of condensed volatile material

What Do We Need to Know in Advance?



calibration source

- radiance or irradiance calibration

electronics

- relative photodetector sensitivity
- photodetector gain
- amplifier gain

optics

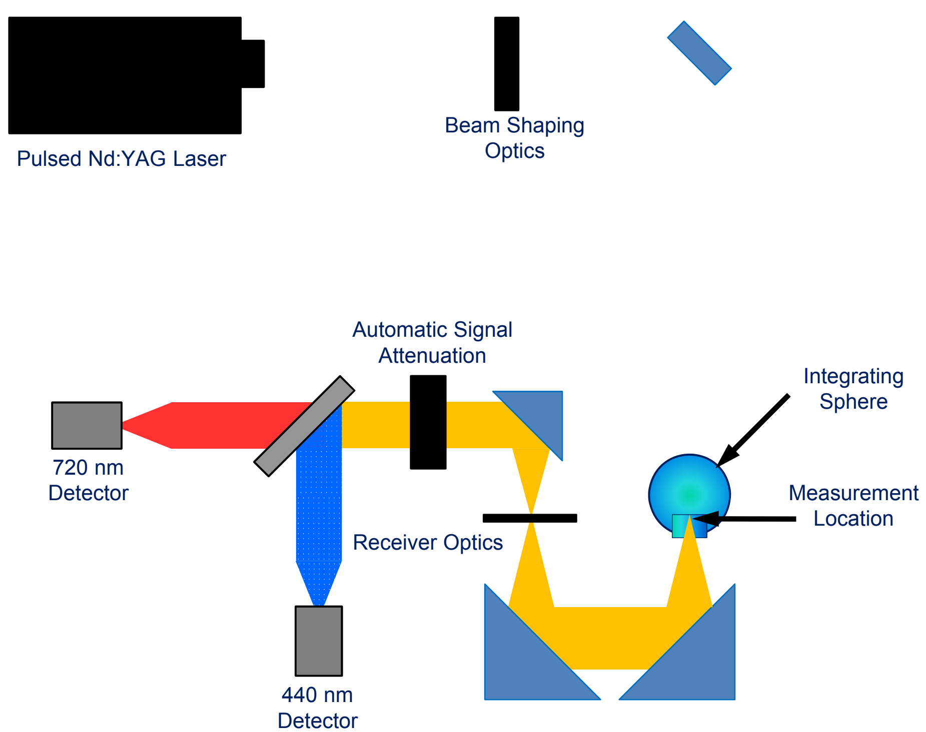
- absolute neutral density filter transmission
- relative dichroic mirror reflectivity and interference filter transmission

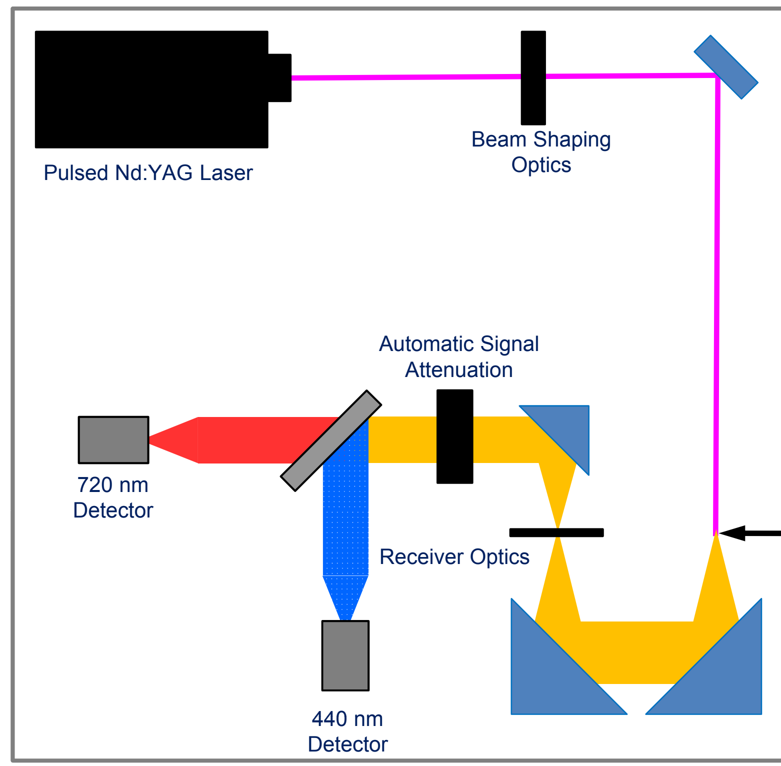
dimensions of probe volume

laser spatial fluence profile

optical and other properties of soot at high temperatures!

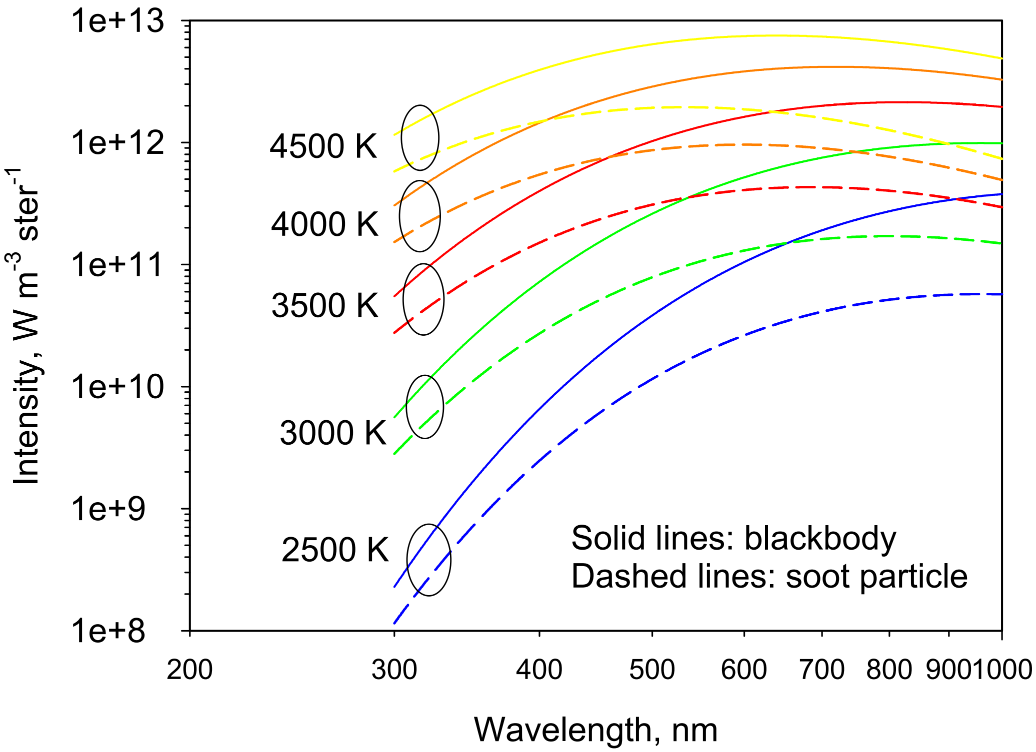
AC-LII Instrument Calibration





- integrating sphere with a traceable spectral radiance calibration
- incandescence from black carbon particles follows identical path as calibration source

Particle Emission Intensities



blackbody and soot particle emission intensity

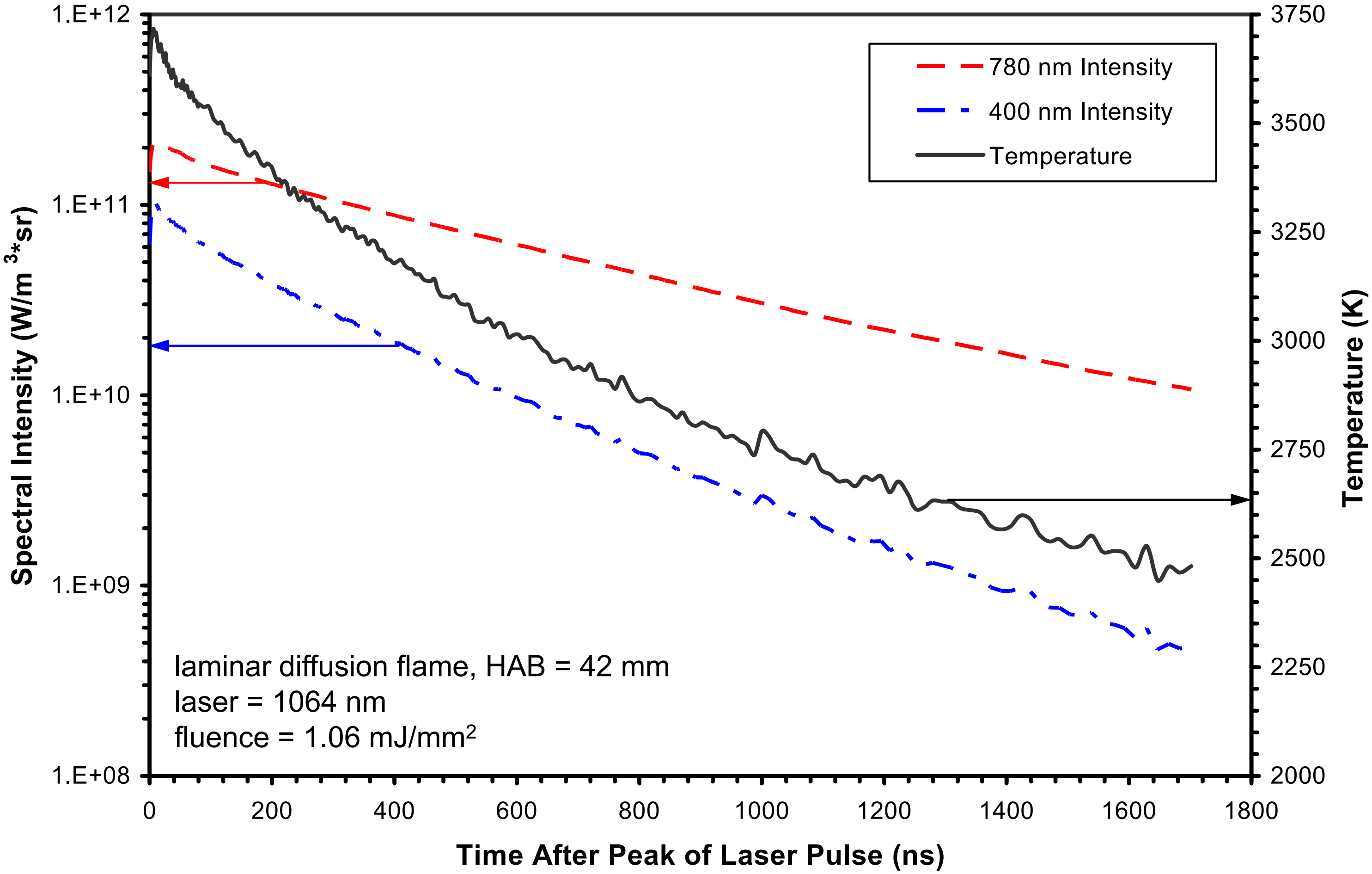
- over range of temperatures encountered in LII over the UV-VIS-NIR spectral range

emissivity

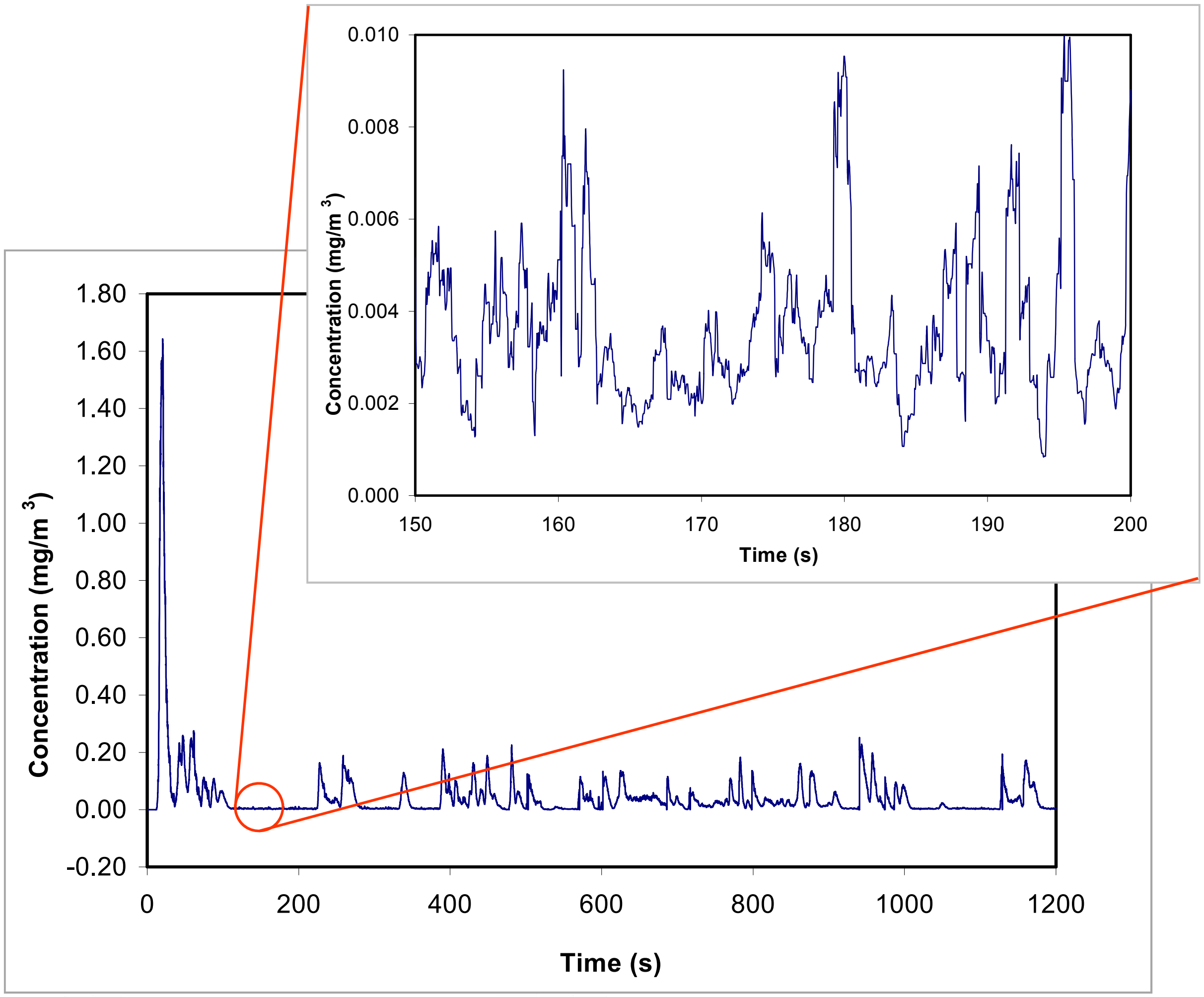
$$\varepsilon_p = \frac{4\pi d_p E(m)}{\lambda}$$

soot particles are calculated for d_p = 30 nm and $E(m)$ = 0.4

Auto-Compensating LII (AC-LII) Absolute Signals



LII: Post-DPF Sensitivity and Dynamic Range



- Post DPF (diesel particulate filter) BC emissions from a 2007-compliant heavy-duty diesel engine operating on the EPA FTP cycle
- Demonstrated range, sensitivity, and time response of Artium LII 300 instrument (<2 μg/m^3 at 20 Hz)

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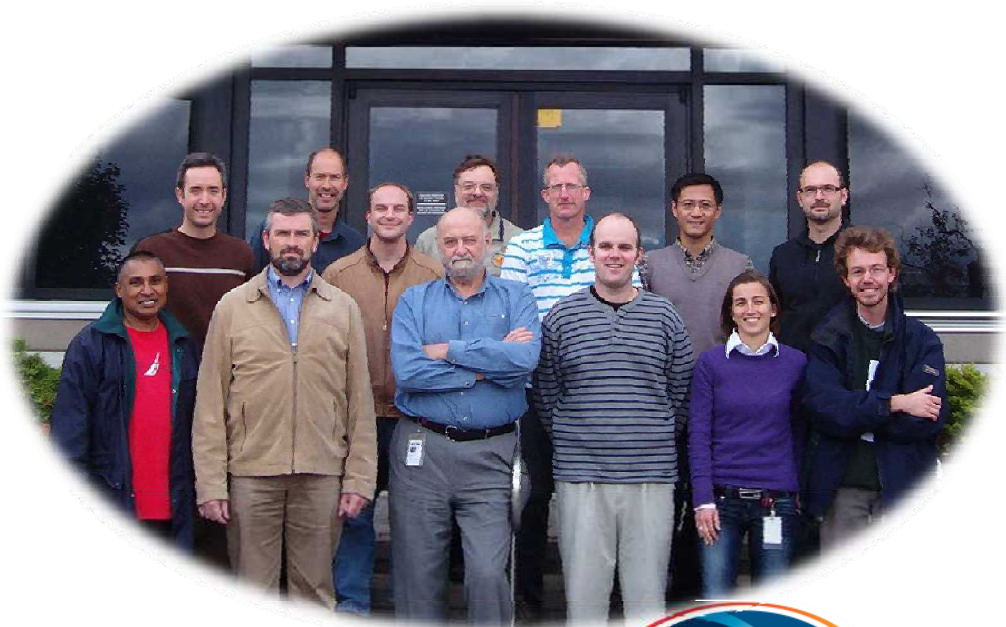
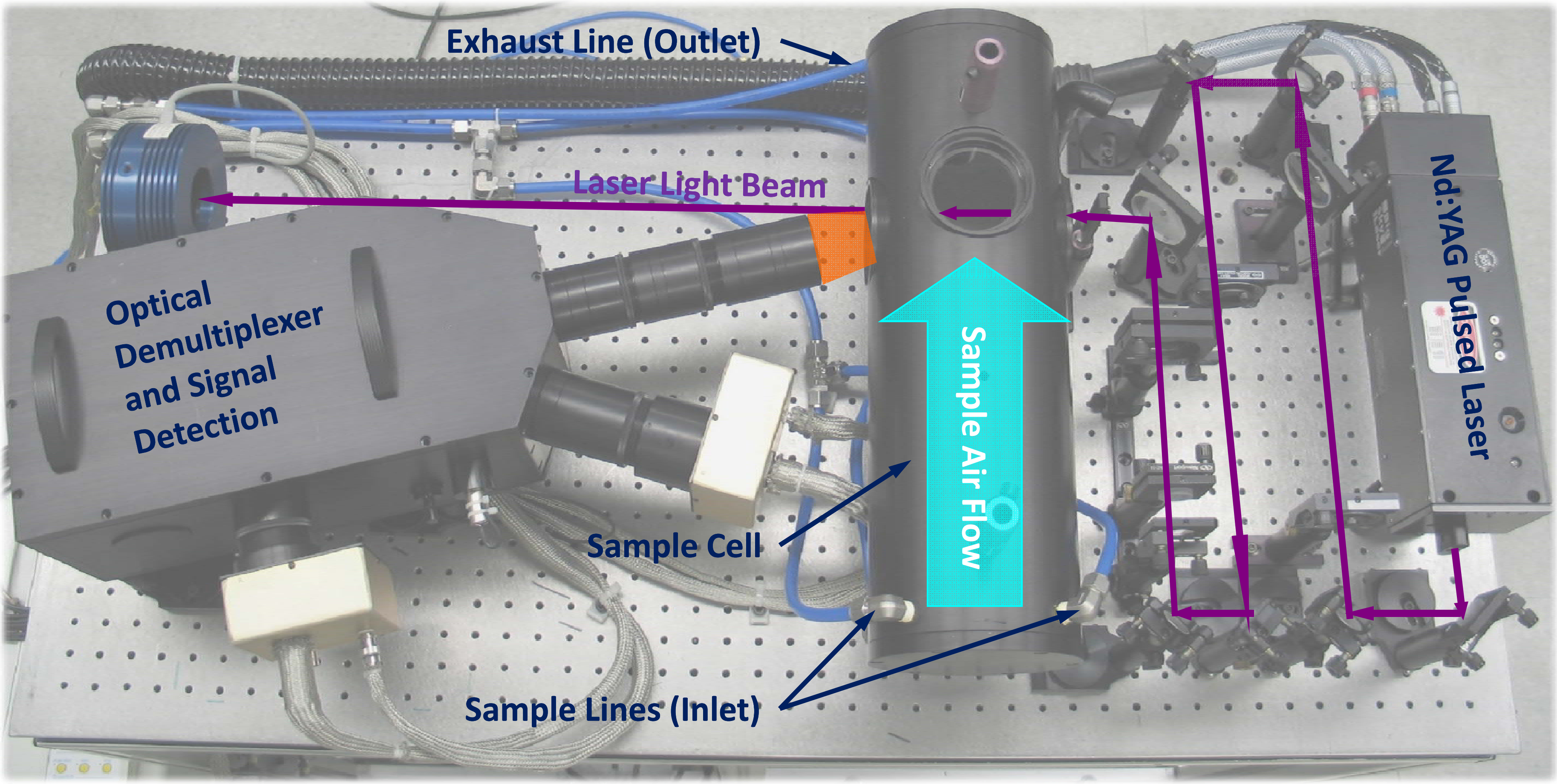
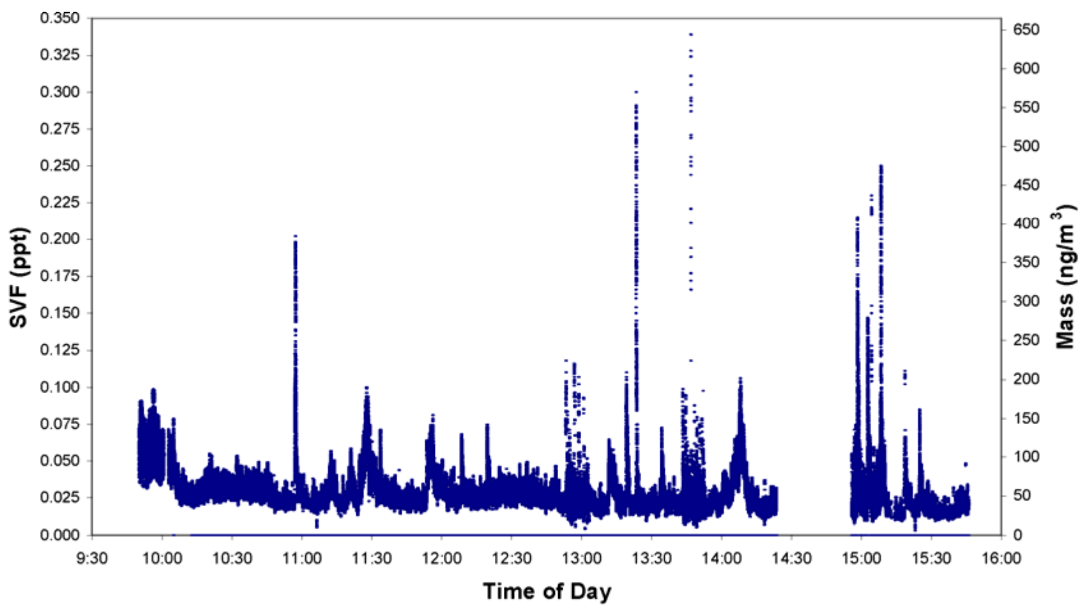


Optical layout of high sensitivity system (HS-LII)



Experiment: High Sensitivity LII

- optimize all aspects of the autocompensating laser-induced incandescence (AC-LII) method
- use Lagrangian invariant principle to constrain design of collection optics and receiver
- incorporate Artium Technologies electronics and software



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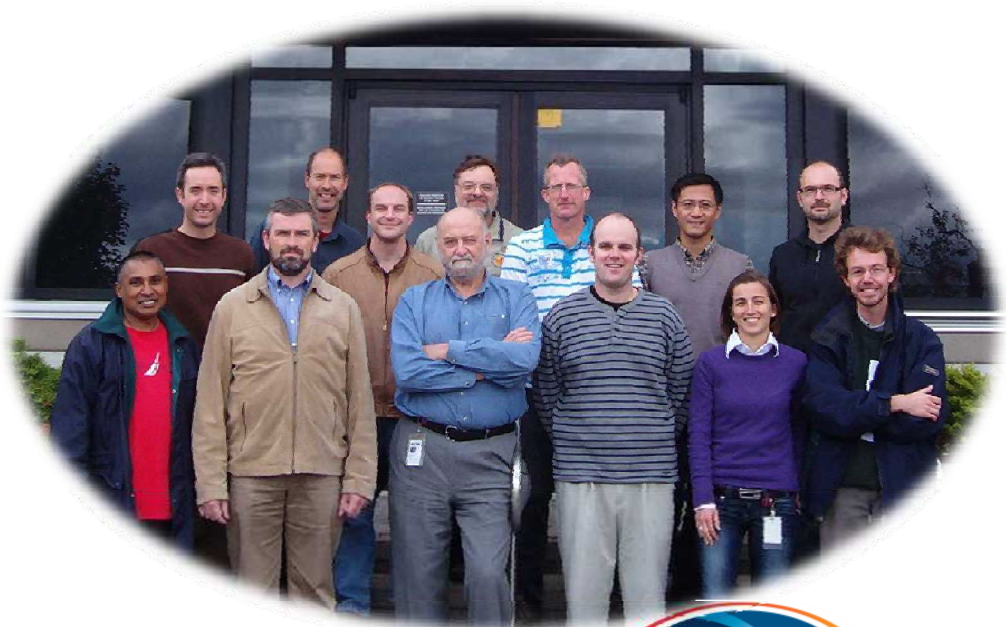
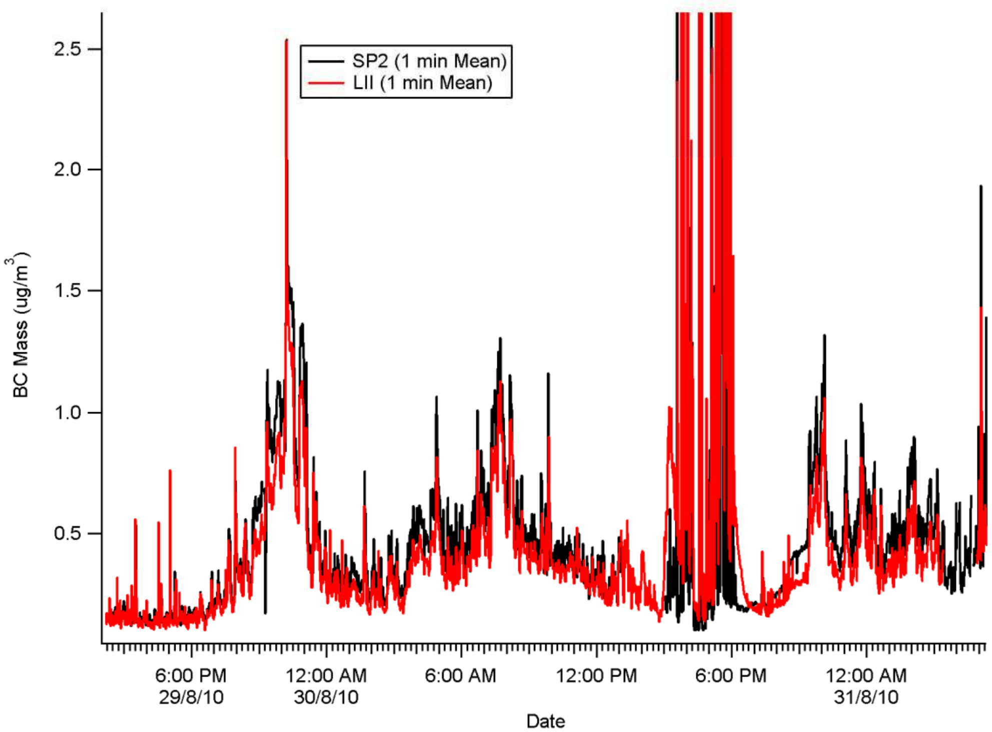
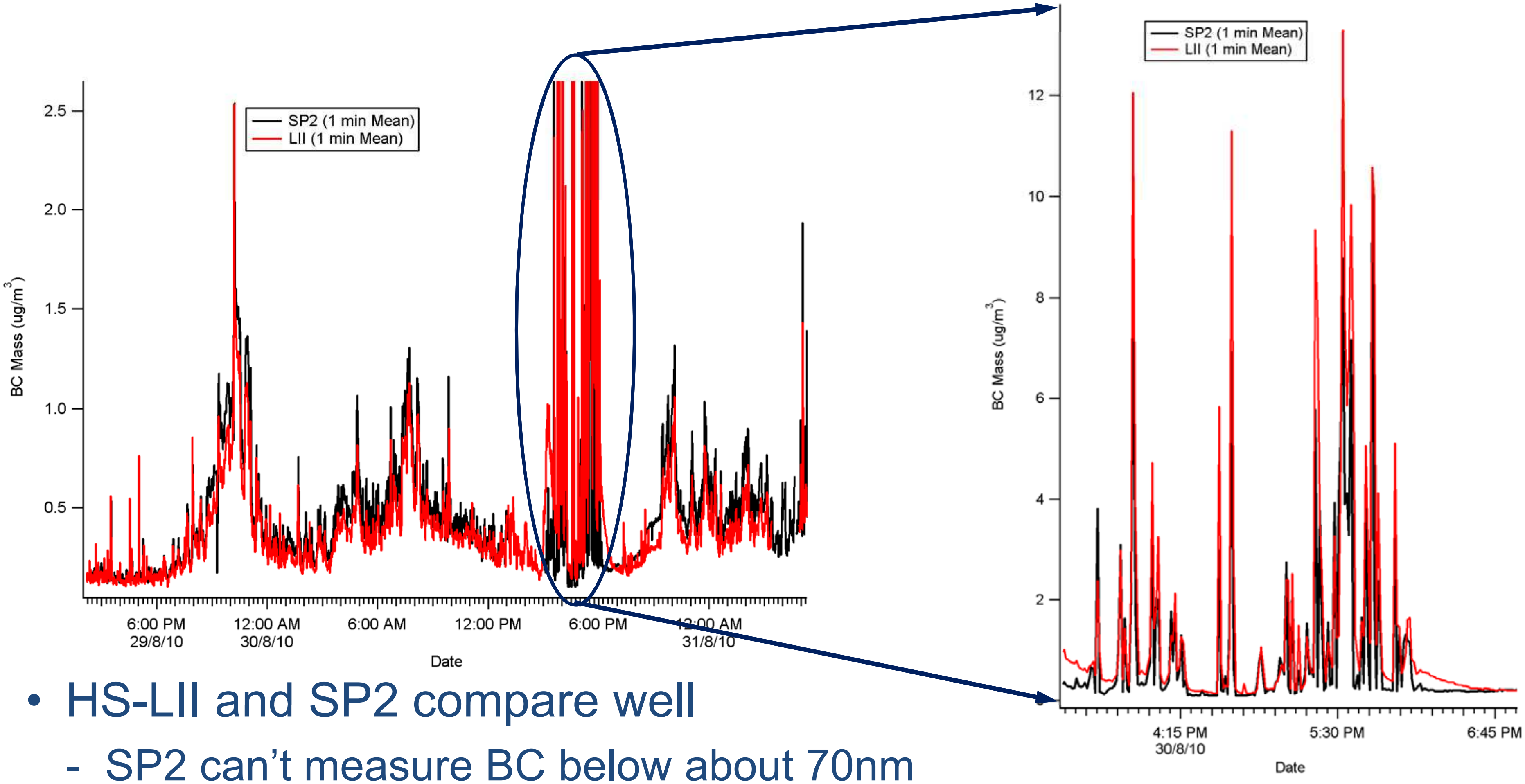


Time-resolved HS-LII and SP2



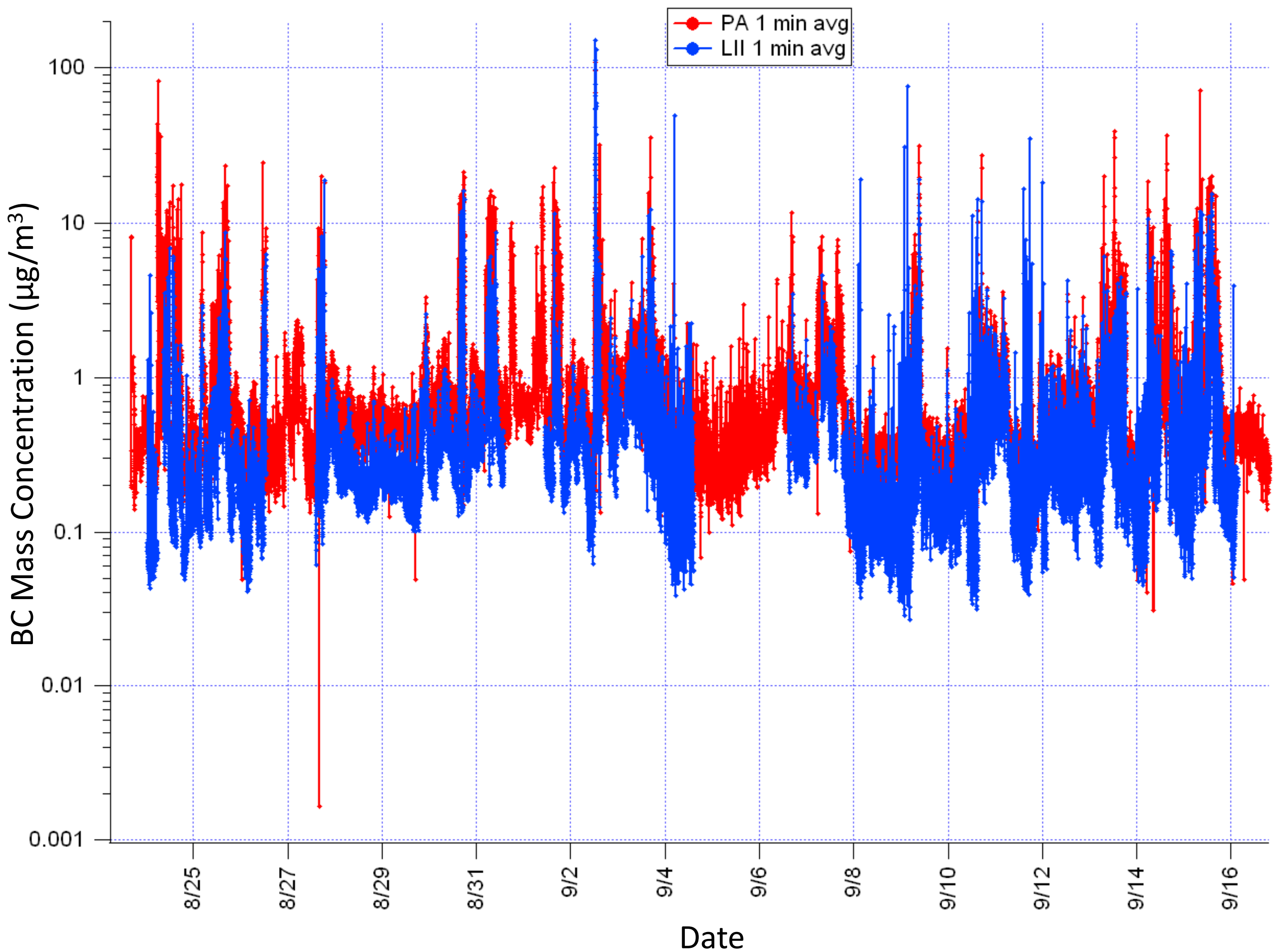
- HS-LII and SP2 compare well
  - best agreement at concentrations below 2.0 µg/m^3
  - SP2 can't measure BC below about 70nm
    - may be better for processed than freshly emitted particles

Time-resolved HS-LII and SP2

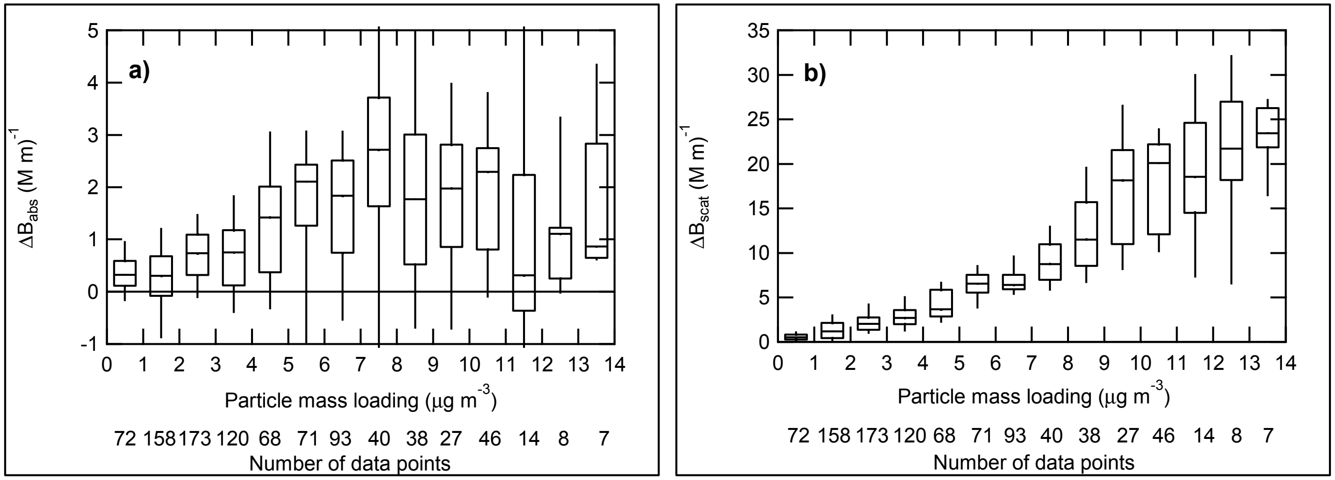


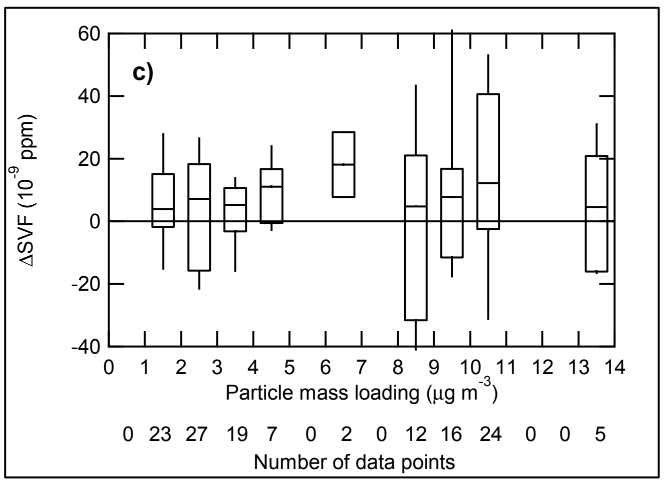
- HS-LII and SP2 compare well
  - SP2 can't measure BC below about 70nm
  - SP2 shows less response at higher concentrations
    - smaller particles when measuring closer to highway?

Time-resolved HS-LII and PA



Atmospheric Black Carbon: HS-LII vs. Photoacoustic

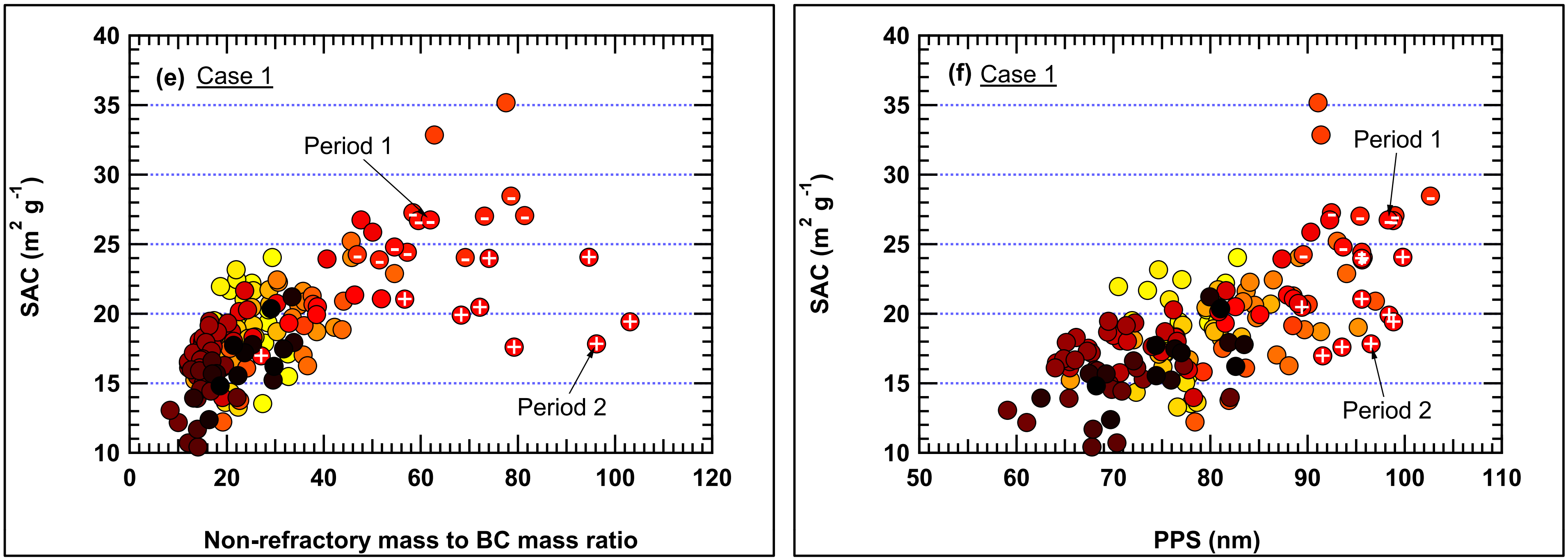




- The variations of (a) the particle light absorption (PA), (b) particle light scattering (PA), and (c) the soot volume fraction (LII), as a function of particle volatile coating mass
- The photoacoustic results are significantly affected by the presence of a volatile coating
- LII shows no significant effect

[Chan *et al.*, Atmospheric Chemistry and Physics, 11, 10407–10432, 2011]

Use of Simultaneous LII and PA to Determine Specific Absorption Coefficient



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Mobile Platforms

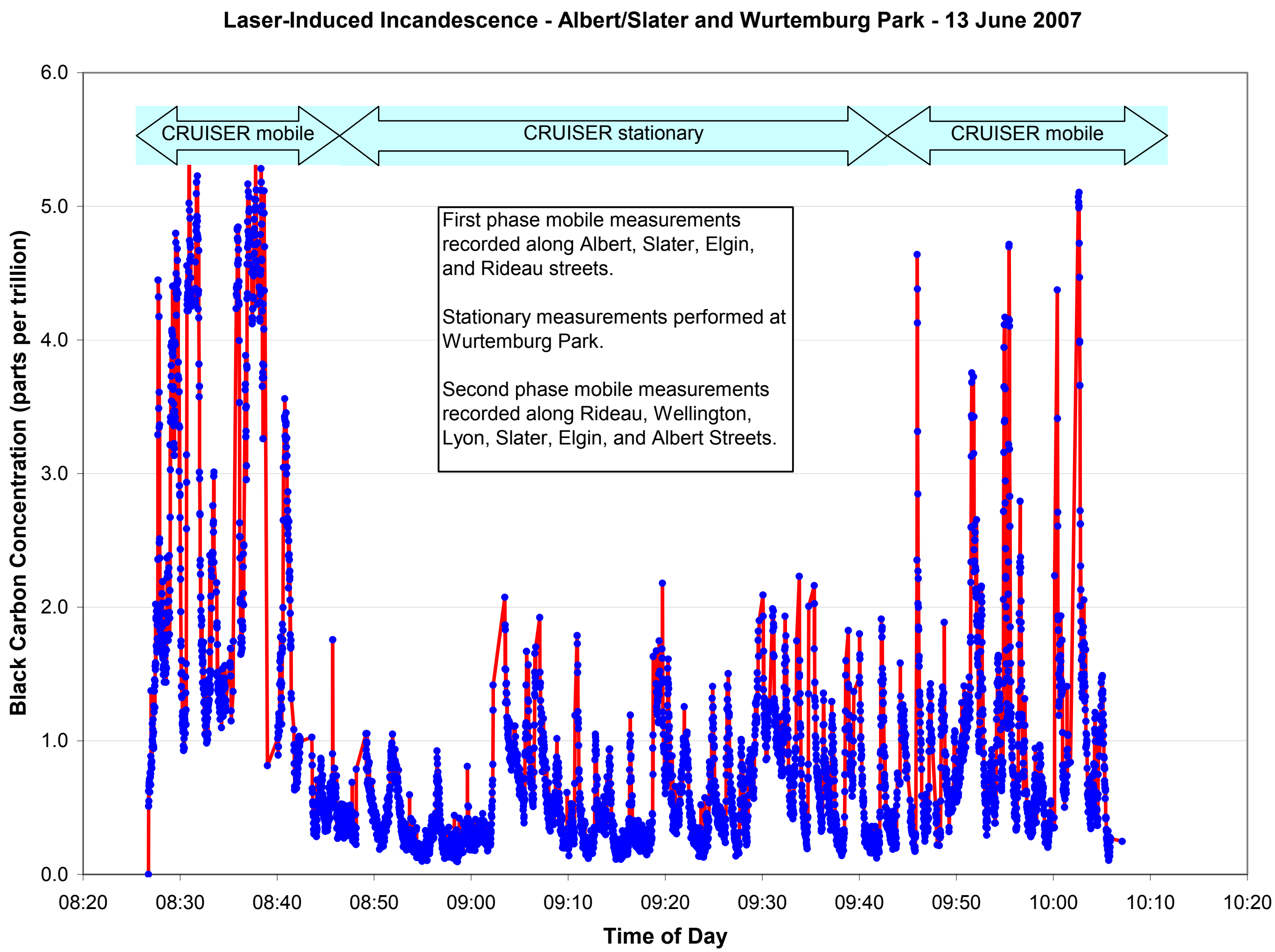
CRUISER

- 2 sonic anemometers
- 1 aircraft turbulence probe
- GPS, accelerometer, tilt-meter
- Aerosol Mass Spectrometer
- Single Particle Soot Photometer (SP2)
- High Sensitivity Laser-Induced Incandescence (HS-LII)
- PTR-MS
- CO2, CO, SO2, NO, NO2, Noy
- meteorology; webcam
- Fast Mobility Particle Sizer (FMPS)
- CPC

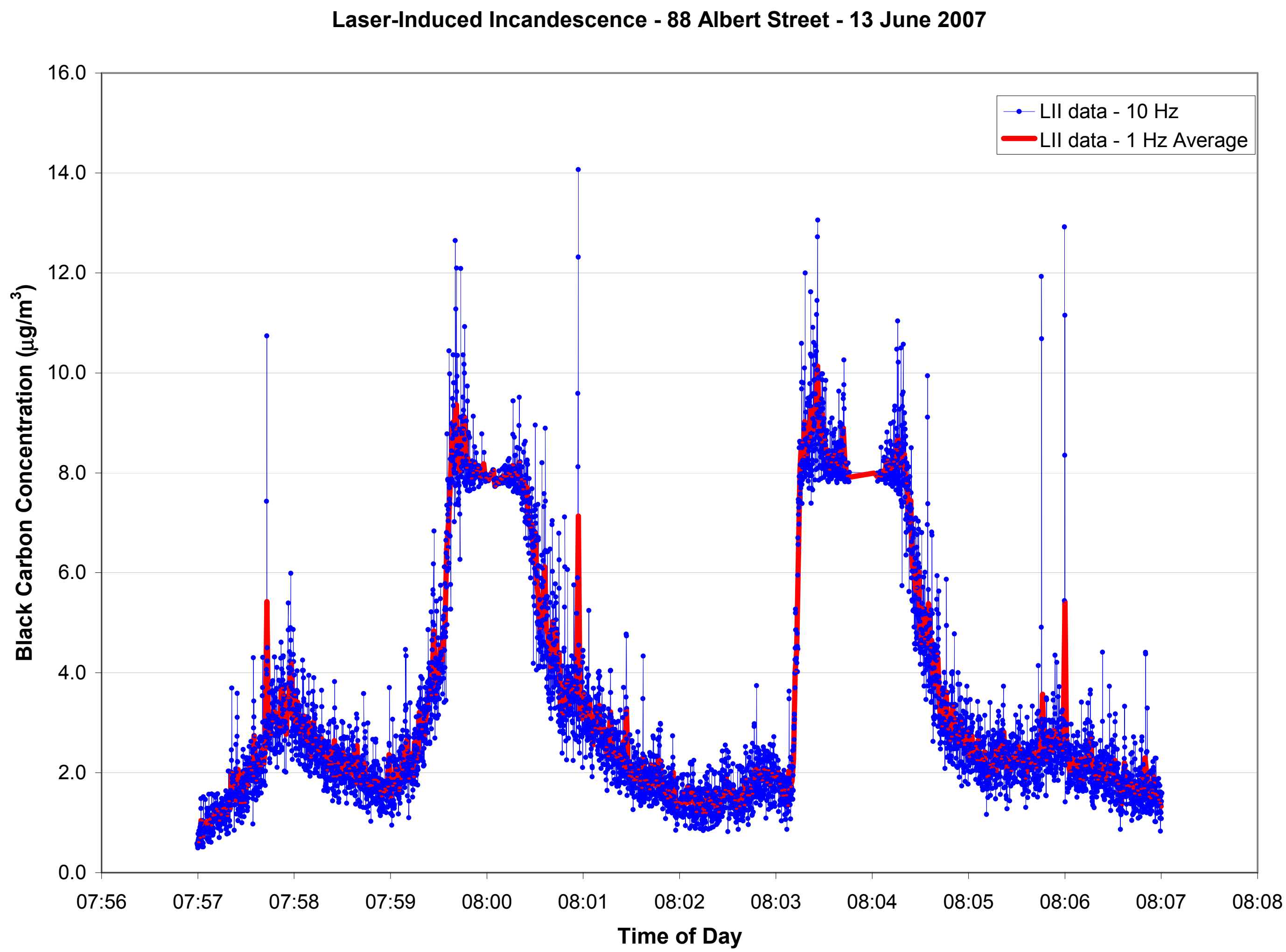
MAPLE

- Aerosol Time of Flight Mass spectrometer (ATOF-MS)
- Heated/cooled inlet system
- High-resolution Aerodyne Aerosol Mass Spectrometer (HR-ToF-MS)
- Fast Mobility Particle Sizer-Thermal Denuder (FMPS-TD)

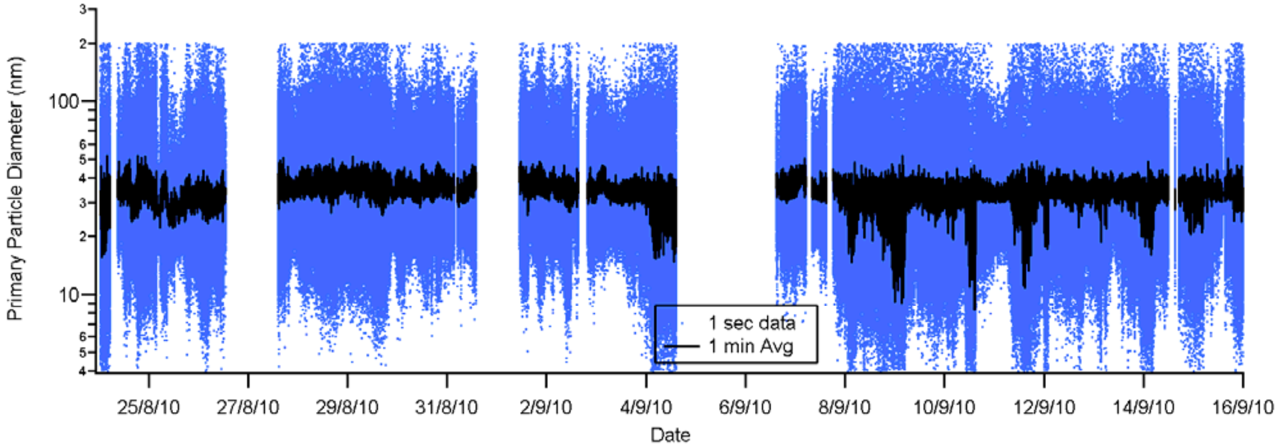
Urban Air Quality – High Sensitivity

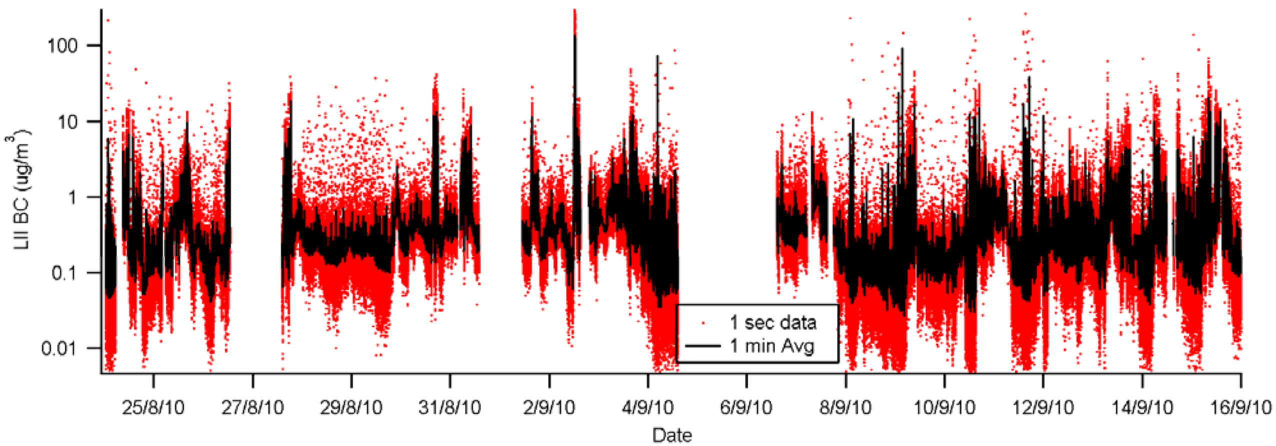


Urban Air Quality – High Sensitivity



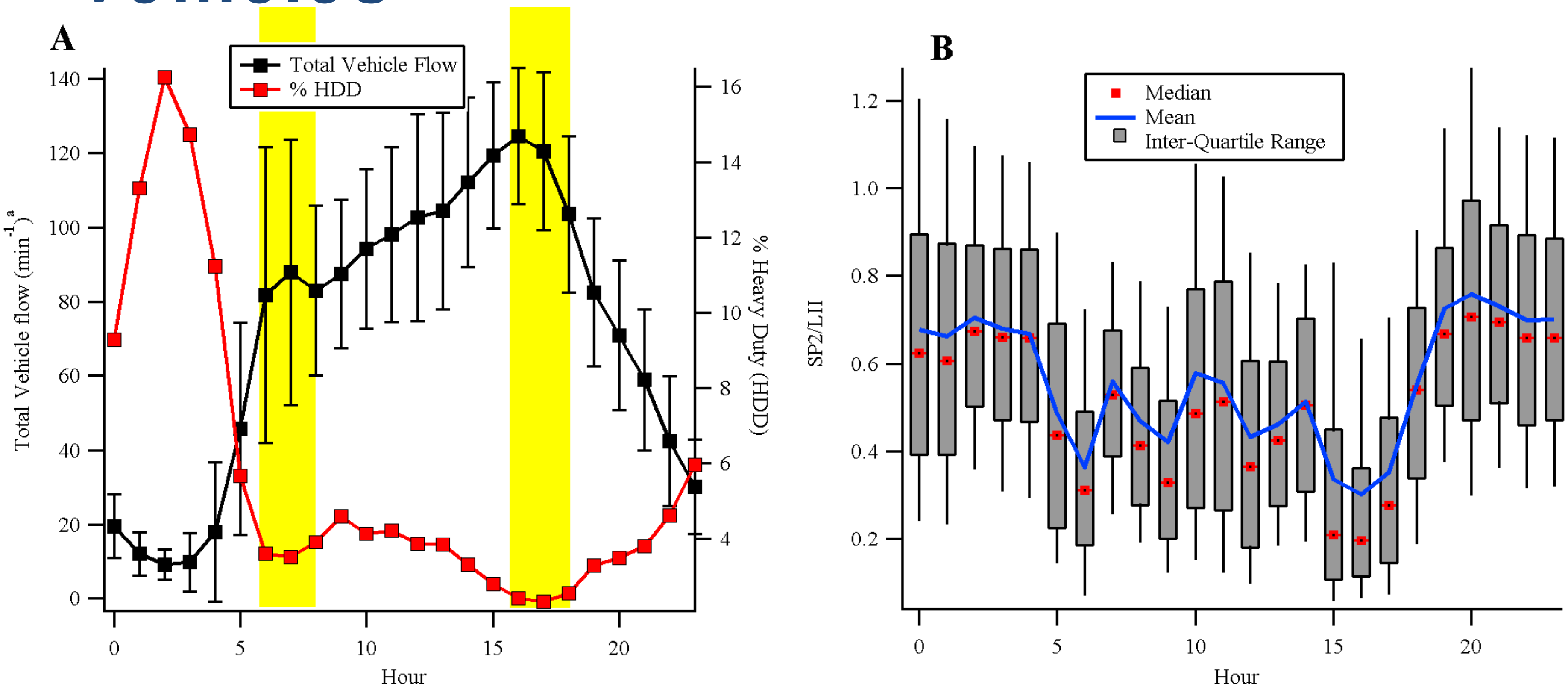
One Month of HS-LII BC Data





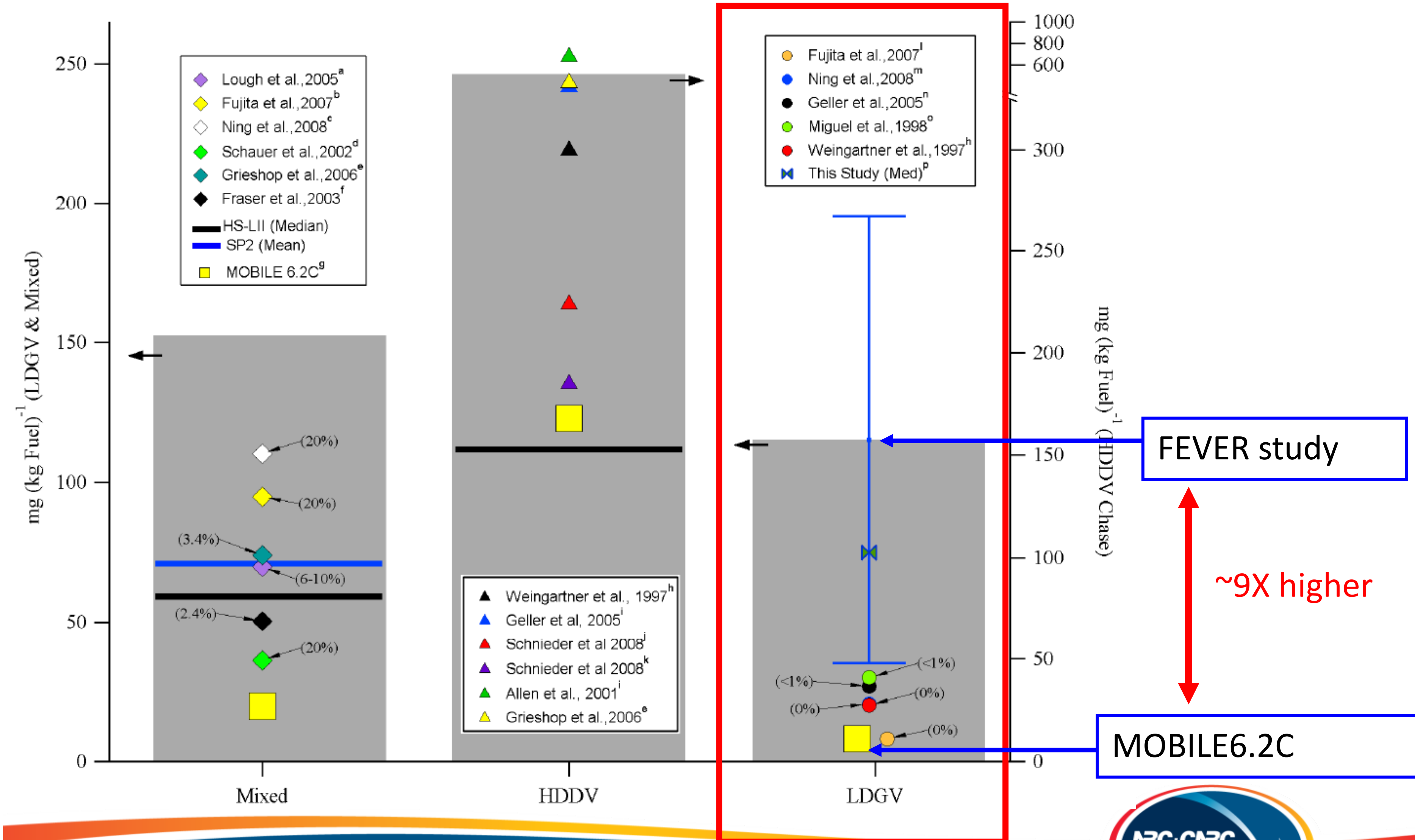
- 30 days
- 2 Hz
- 5,000,000 individual measurements

Heavy Duty Diesel vs. Gasoline Vehicles



- SP2/LII ratio is highest during periods when there is an increase in HDD; lowest during rush hours (LDGV)
  - suggests BC particles from LDGV are smaller (below SP2 threshold)

BC from Gasoline Vehicles is Underestimated



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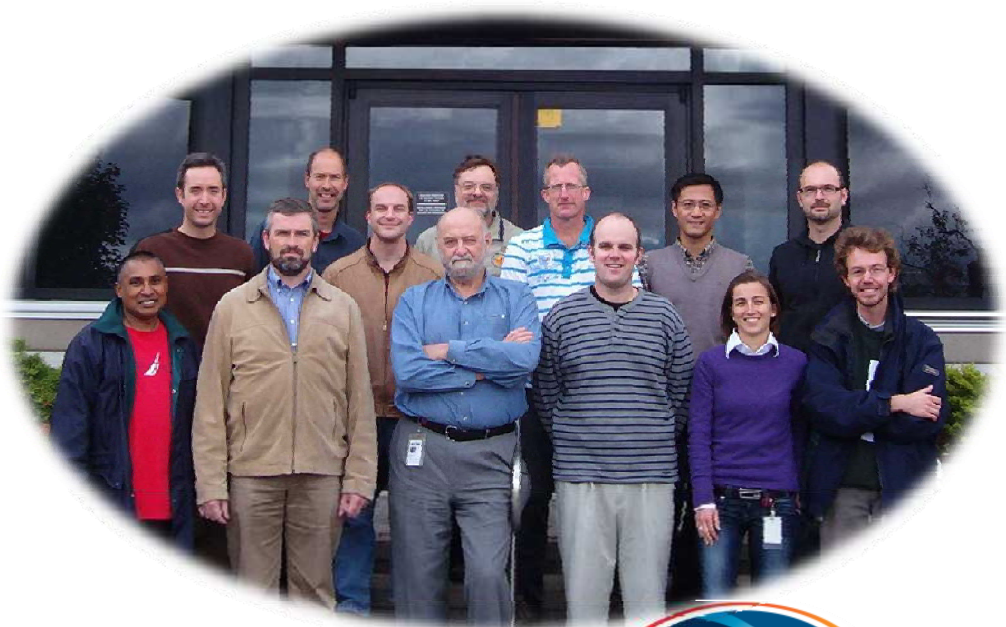


Summary

Laser-induced incandescence

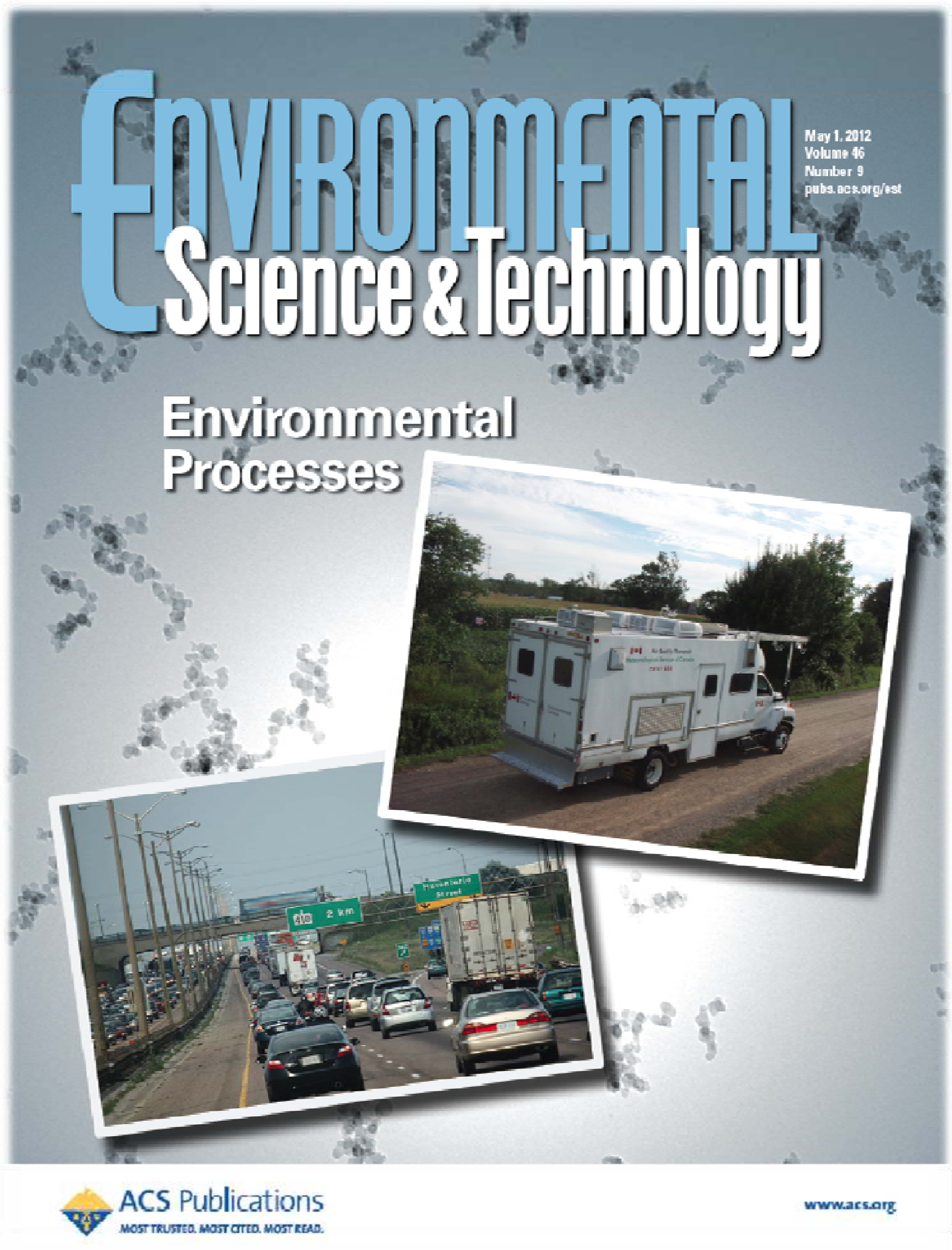
- technique with high specificity to the measurement of black carbon
- HS-LII has the sensitivity to measure atmospheric levels of BC

The combination of LII with other techniques used to measure BC provides additional and valuable insights

- LII+PA to determine specific absorption coefficient
- LII+SP2 to assess the source of BC emissions (gasoline vs. diesel)

Example insights

- the specific absorption coefficient, which is the ability of BC to absorb solar radiation and affects the impact of BC on climate change, is greatly enhanced by the degree of volatile coating on the surface of the BC particles
- results suggest that **greater attention must be paid to black carbon from gasoline engines** to obtain a full understanding of the impact of black carbon on air quality and climate and to devise appropriate mitigation strategies
  - significant implications for climate by BC, a short lived climate forcer (SLCF)



Questions?

John Liggio, Mark Gordon, Jeffrey R. Brook, Gregory Smallwood, Shao-Meng Li, Craig Stroud, Ralf Staebler, Gang Lu, Patrick Lee, Brett Taylor, (2012). "Are emissions of black carbon from gasoline vehicles underestimated? Insights from near and on-road measurements," *Environmental Science and Technology*, 46, 4819-4828, 2012.

- DOI: 10.1021/es2033845

Soot Concentration from Two-Color Pyrometry

temperature is determined from the spectral radiance signals at two wavelengths

- varies with relative *E*(*m*) at the two wavelengths

$$T = \frac{hc}{k}\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)\left[\ln\left(\frac{V_{\exp_1}\lambda_1^{\,6}}{\eta_1 E(m_{\lambda_1})}\right) - \ln\left(\frac{V_{\exp_2}\lambda_2^{\,6}}{\eta_2 E(m_{\lambda_2})}\right)\right]^{-1}$$

soot volume fraction is determined from the temperature and the spectral radiance signal at either one of the wavelengths

- depends upon absolute value of *E*(*m*) at the selected wavelength

$$f_V = \frac{V_{EXP_\lambda}\,\rho}{\eta_\lambda w_b}\,\frac{\lambda^6\left(e^{\frac{hc}{k\lambda T}} - 1\right)}{12\pi c^2 h\,E(m_\lambda)} = V_{EXP_\lambda}\,\frac{K_1}{E(m_\lambda)}\left(e^{\frac{K_2}{T}} - 1\right)$$