Black Carbon Emissions from Gasoline Vehicles are Underestimated in Canada: Insights Gained from LII and SP2

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Measurements of black carbon (BC) emissions with high sensitivity laser induced incandescence (HS-LII) and a single particle soot photometer (SP2) were conducted near-road and on-road for a highway dominated by light duty gasoline vehicles during a study conducted in a rural area north of Toronto, ON, Canada. HS-LII is a unique instrument recently developed by NRC, with support from Artium Technologies, which measures mass concentration to levels as low as 10 ng/m3 for an ensemble of BC particles. It also determines primary particle diameter and active surface area for BC particle sizes between 5 and 1000 nm. SP2 is a commercial instrument which measures the mass concentration and size of single BC particles with an effective diameter larger than 75 nm (the lower limit of detection for the instrument). Details about this study have been recently published [1].

Mobile Laboratory

Mobile measurements were made with the Canadian Regional and Urban Investigation System for Environmental Research (CRUISER) on a side road perpendicular to Highway 400, at a location north of Toronto, Canada. The site was dominated by agricultural fields and was not impacted by other primary PM sources. The mobile lab was used at this site to measure pollution concentration gradients along the upwind and downwind sides of the highway (45 – 1000 m from center); perpendicular to the north-south lanes of the highway. This was typically performed for several hours each day, spanning peak traffic volumes during the morning and/or the evening. A traffic camera (Miovision, Kitchener, ON, Canada) recorded traffic counts at the site and classified vehicles as passenger cars, medium sized, or heavy duty, with >95% accuracy. CRUISER was also driven on Highway 400 and 401 near Toronto for in-situ measurements behind HDDV.

Instrumentation

Black carbon measurements were performed onboard the mobile laboratory with a modified High Sensitivity Laser Induced Incandescence (HS-LII) instrument (NRC Canada and Artium Technologies Inc., CA, USA) and a Single Particle Soot Photometer (SP2, Droplet Measurement Technologies, Boulder, CO, USA.). These two real–time instruments are based on the principle of laser-induced incandescence.

HS-LII: High-Sensitivity Laser-Induced Incandescence

The principle of operation for the HS-LII, the calibration thereof, and its use during ambient studies have been described previously [2, 3]. Briefly, ambient particles are sampled at a flow of approximately 5 $Lmin^{-1}$ through a sample region with a depth of 0.2 cm and a cross-sectional area of 6.4 cm^2. The ambient particles containing BC within the sample volume are exposed to a pulsed laser beam (1064 nm; 7 ns FWHM) resulting in rapid heating to just below the soot sublimation temperature (approximately 4000 K). The absolute incandescence intensity from the BC particles is measured using collection optics and photomultipliers. Using an appropriate calibration and analysis of the absolute incandescence signal, information on the soot volume fraction is obtained without the need for a source of soot particles of known concentration [2].

To convert to a mass concentration, the required BC particle dependent parameters are the absorption function, *E(m)*, and the particle material density. Values for these parameters are well established and are robust over a wide range of sources of BC [4]. The largest uncertainty arises from *E(m)* for the particles (± 20%) [4], while the overall measurement of BC concentration has been determined to be within 25% [5]. In contrast to the SP2 (below), this instrument does not measure single BC particles, but rather determines the ensemble

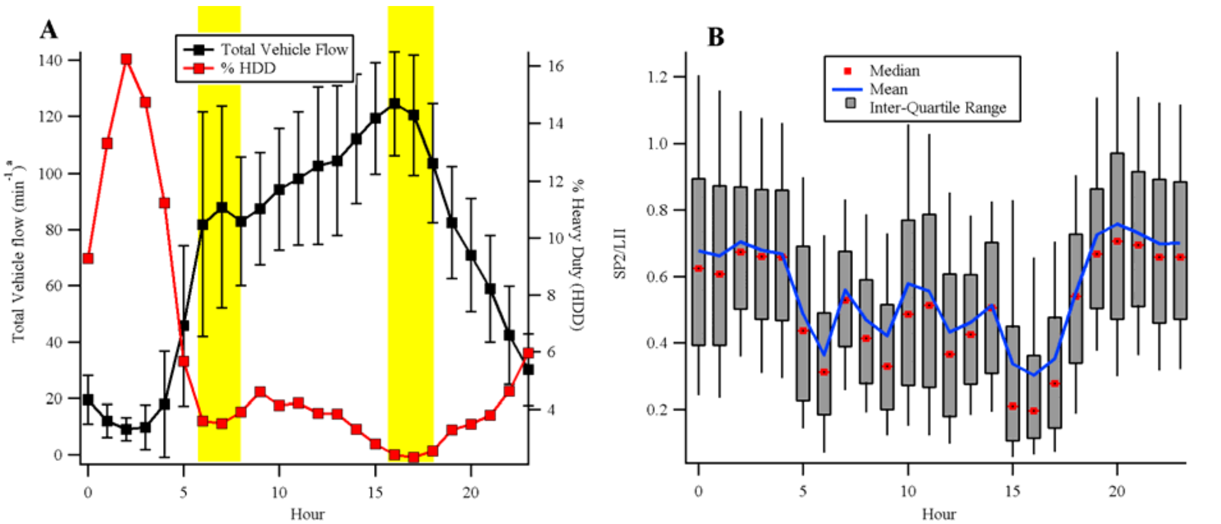

Figure 1. ***A.*** *Average diurnal traffic flow (vehicles min^{-1}) and fraction of the flow which was classified as heavy duty diesel (HDDV) during the 17 days of the study. HDDV fraction based on vehicle counts. Yellow vertical bars denote the times when perpendicular transects were driven, corresponding to the data utilized for emission factor calculations.* ***a****. Error bars denote the standard deviation of the mean.* ***B.*** *Ratio of measured BC concentration (SP2:HS-LII) as function of hour of day for 3 consecutive days during the study and within 100 m of HWY 400. Only data for distances less than 100 m from the highway during transects were utilized to be comparable with stationary situations during these days [1].*

properties for all particles in the measurement volume at the time of the laser pulse. As a result, there are no BC particle size constraints, provided that sufficient total mass is present in the detection volume. This method has been used to measure laboratory generated BC particles smaller than 7nm [6].

SP2: Single Particle Soot Photometer

The principle of operation of the SP2 and its use in ambient sampling have been described extensively [7, 8]. Individual BC particles sampled by the SP2 were irradiated with a continuous laser (1064 nm) resulting in BC incandescence which was monitored in the visible band (λ= 300-550 nm). The BC mass for each particle was estimated from the incandescence peak intensity. The BC mass concentration was calibrated with a mono-disperse aerosol stream selected with a scanning mobility particle sizer (SMPS, TSI inc.), from an atomized aqueous solution of graphitic black carbon (Aquadag; Acheson, USA). Given that the effective density of the BC calibration particle affects absolute mass measurement, the effective density of the mono-disperse Aquadag particles used for calibration was characterized prior to the study by simultaneous mobility sizing and mass selection using an SMPS and an Aerosol Particle Mass Analyzer (APM, Kanomax Inc., Japan) in a manner described previously [9]. The SP2 is able to detect single particles with effective diameter greater than about 90 nm with approximately 100% transmission efficiency [8]. An experimentally determined transmission efficiency correction was applied to the data to account for non-unity transmission of particles between 70 and 90 nm.

Uncertainties in the measurement of BC by the SP2 during the current study are primarily associated with the BC response linearity as determined by the mass calibration (± ~15%), and the ability to measure the effective density of the calibration material (± ~8%).

Results

The traffic volume and composition over the 17 days of the study are given in Figure 1A as a function of time of day. At the times of the highest traffic flow (yellow bars, Figure 1A) the mean HDDV fraction (on a vehicle count basis) is at a minimum and thus the flow is dominated by LDGV (light duty gasoline vehicles).

Differences between the HS-LII and SP2 emission factors [1] suggest a particle driven discrepancy between the instruments. We hypothesize that a cause of this discrepancy is a difference in the ability to measure particles ~ <90 nm between instruments. Such a difference could be critical given the size of the particles associated with gasoline exhaust (which dominate the LDGV emissions) and the predominance of these types of vehicles on the road. To investigate this hypothesis further Figure 1B shows the ratio of the SP2 to HS-LII measurements relative to the time of day, for 3 consecutive days (Sept 13th-16th). The mean and median of Fig 1B indicate that the SP2 is most significantly biased low relative to the HS-LII at times of peak traffic (6-8AM and 4-6PM), when the HDDV fraction is lowest

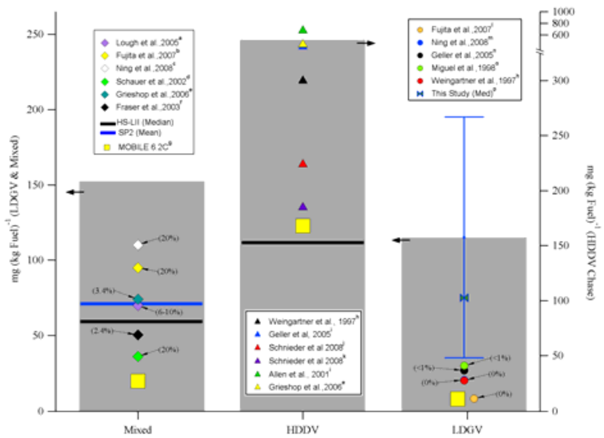

***Figure 2**. Average measured mixed fleet, HDDV and reconstructed LDGV fuel based BC emission factors from the present study (mixed fleet – left; HDDV – center; reconstructed LDGV – right,) compared with recent literature (reported means values), and the MOBILE 6.2C derived emission factors. The count based %HDDV during other studies is in brackets [1].*

***a.** Tunnel study, Milwaukee, WI. Converted to fuel based EF in Ning et al., 2008.*
***b.** Dynamometer study reconstructed by Ning et al., 2008 to compare with I-710 highway (20% HDDV).*
***c.** Highway study (I-710, CA).*
***d.** Dynamometer study; Converted to fuel based EF and reconstructed in Ning et al., 2008 to compare with I-710 highway.*
***e.** Tunnel study in Pittsburgh, PA.*
***f.** Tunnel study; Houston TX, 2.0-2.4% HDDV shown only.*
***g.** EF derived from MOBILE6.2C for mixed, HDDV and LDGV; Refer to text for details.*
***h.** Tunnel study, Zurich Switzerland.*
***i.** Tunnel study in CA with 4.2% uphill grade; HDDV EF reconstructed from mixed traffic tunnel and measured LDGV EF.*
***j.** mean reported value; HDDV vehicle chasing study, Germany.*
***k.** median reported value; HDDV vehicle chasing study, Germany.*
***l.** Dynamometer study for LDGV only as described by Ning et al., 2008.*
***m.** Highway study (CA-110).*
***n.** Tunnel study in CA with 0.25 – 0.54% HDDV assumed to ~100% LDGV and a 4.2% uphill grade.*
***o.** Same as (n) but 7 years earlier.*
***p.** Reconstructed median LDGV from current study.*

(i.e. gasoline dominated emissions). Conversely the mean SP2/LII ratio is highest overnight, early morning and during the middle of the day, when the HDDV fraction is higher.

The black carbon emissions factors from previous studies, this study, and emissions inventories are shown in Figure 2. The average LDGV emission factor is approximately 115 ± 80 mg kg^{-1}_{fuel}, and is considerably higher than the LDGV emission factors from previous chassis-dynamometer or road-way studies which range from 8 – 30 mg kg^{-1}_{fuel} (see refs. in [1]). Although our mean LDGV EF is more directly comparable to other reported values, which were stated as being mean values, using the median of our output values as a conservative estimate also yields a LDGV EF (~75 mg kg^{-1}_{fuel}, Fig 2), which is substantially larger than other reported values. Conversely, as demonstrated in Figure 2 (middle), BC EFs during HDDV chase events of the present study are similar to those reported in recent literature during other chase, tunnel or roadway studies (see refs. in [1]). All of those reported average values fall between the mean and median of the HDDV values measured here. The similarity between the HDDV values during these chase events and during other studies lends confidence to the mixed fleet values measured in the present study and to the inferred LDGV values.

Also shown in Figure 2 are the BC emission factors from the Canadian emissions inventory (Yellow squares), which are estimated with MOBILE 6.2C for the mixed fleet of this study, HDDV and LDGV. The reconstructed mixed fleet MOBILE 6.2C emission factor in Figure 2 (~19.7 mg kg^{-1}_{fuel}) is substantially below the average (152 mg kg^{-1}_{fuel}) and median (59.3 mg kg^{-1}_{fuel}) of the measured values in this study, while the MOBILE 6.2C emission factor for HDDV shows somewhat better agreement with measurements (middle, Figure 2). This suggests that much of this discrepancy is based in the LDGV emission factor. Considering the range of LDGV EFs for this study (Figure 2; Right side), the most conservative estimate for a LDGV emission factor (~75 mg kg^{-1}_{fuel}) is approximately a factor of two higher than other measurements, and a factor of nine higher than the LDGV EF derived from MOBILE 6.2C (~8 mg kg^{-1}_{fuel}). The MOBILE model does not include a vehicle speed or engine load input for BC emissions. A recent emission factor model (MOVES) accounts for such variables and thus may slightly increase the emissions factor for LDGV BC.

Summary

Fuel-based BC emission factors for real-world average light duty gasoline fleet and heavy duty diesel vehicles were derived separately with the use of simultaneous CO2 measurements. The derived emission factors from both instruments are compared, and a low SP2 bias (relative to the HS-LII) is found to be caused by a BC mass mode diameter less than 75 nm. This mode is most prominent with the gasoline fleet but is not present in the heavy duty diesel vehicle exhaust on the highway..Results from both the LII and the SP2 demonstrate that the BC emission factors from gasoline vehicles are at least a factor of two higher than previous North American measurements, and a factor of nine higher than currently used emission inventories in Canada, derived with the MOBILE 6.2C model. Conversely, the measured BC emission factor for heavy duty diesel vehicles is in reasonable agreement with previous measurements and the inventories. Greater attention must be paid to black carbon nanoparticle emissions 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.

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Measurement Science and Standards

Black Carbon Emissions from Gasoline Vehicles are Underestimated in Canada: Insights Gained from LII and SP2

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16th ETH-Conference on Combustion Generated Nanoparticles
24-27 June 2012 Zurich, Switzerland

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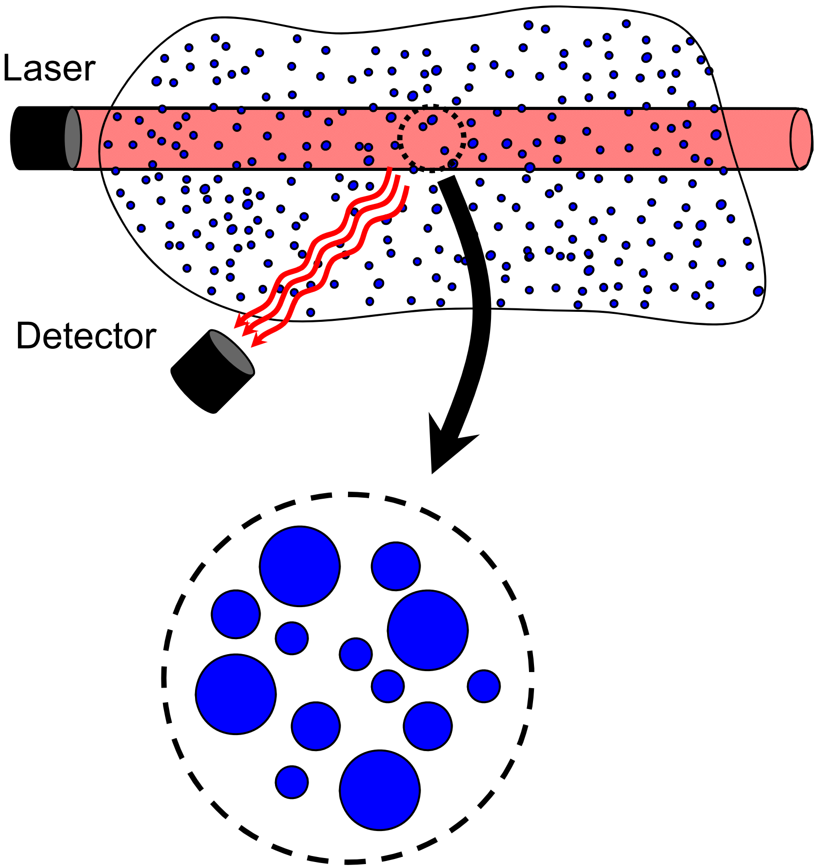
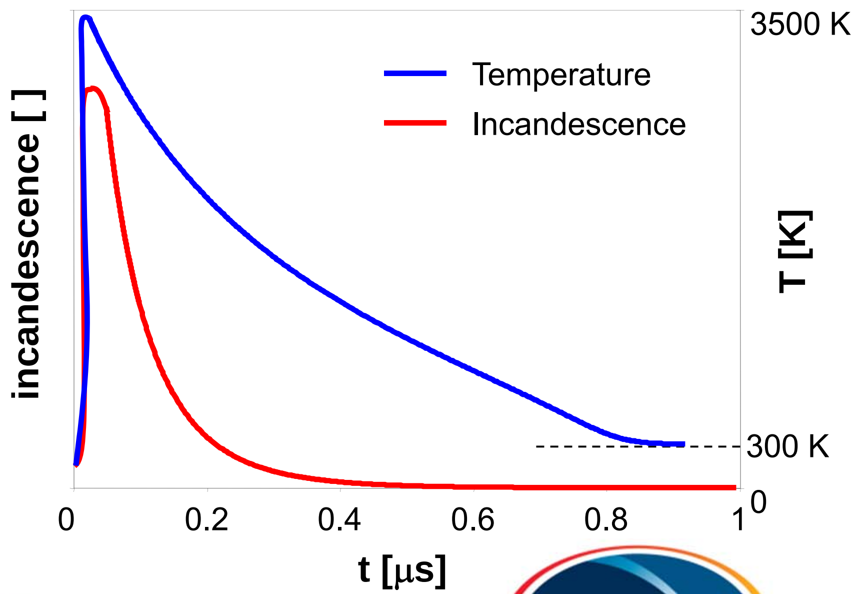
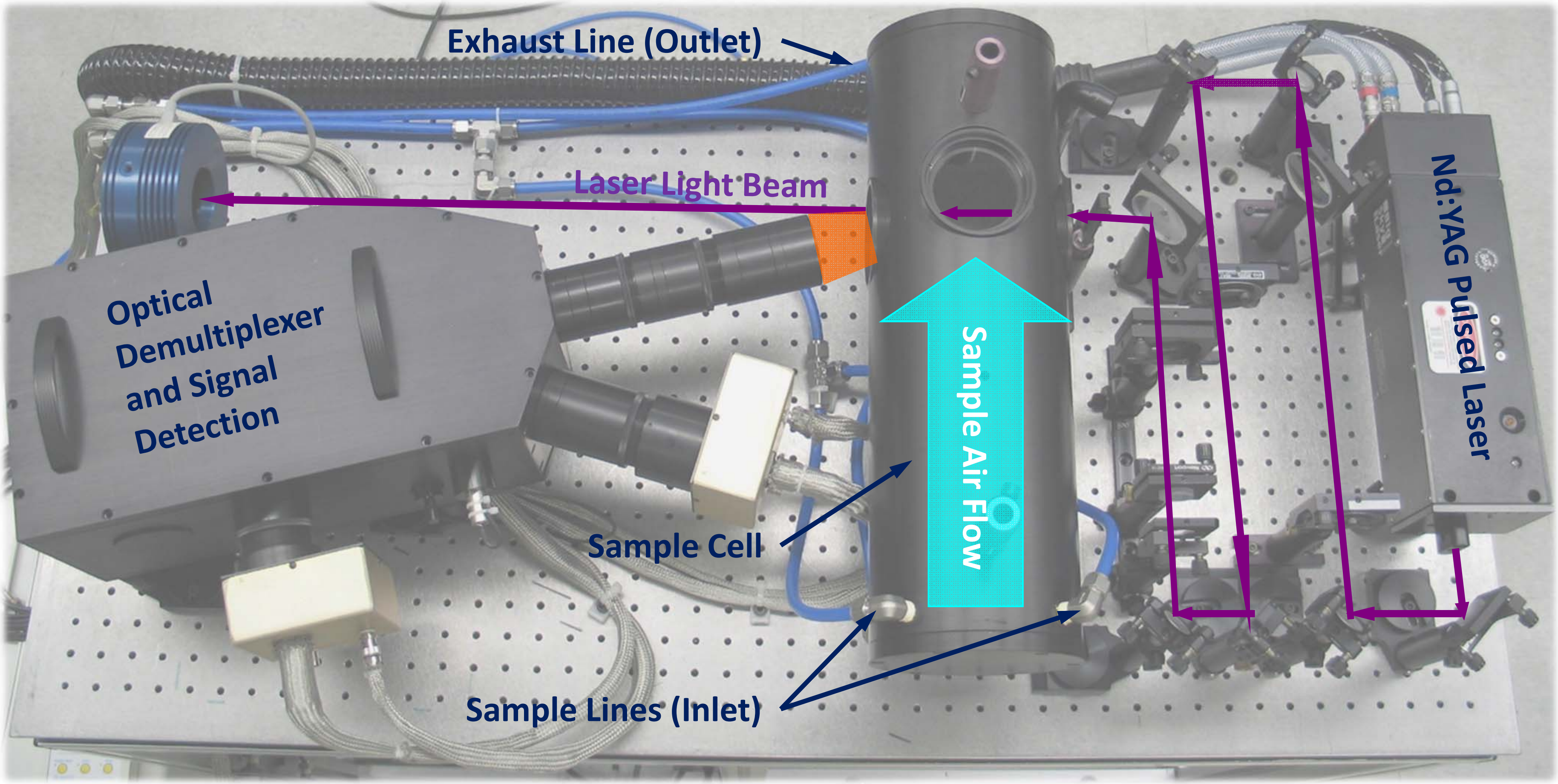
Canada

Time-Resolved Laser-Induced Incandescence

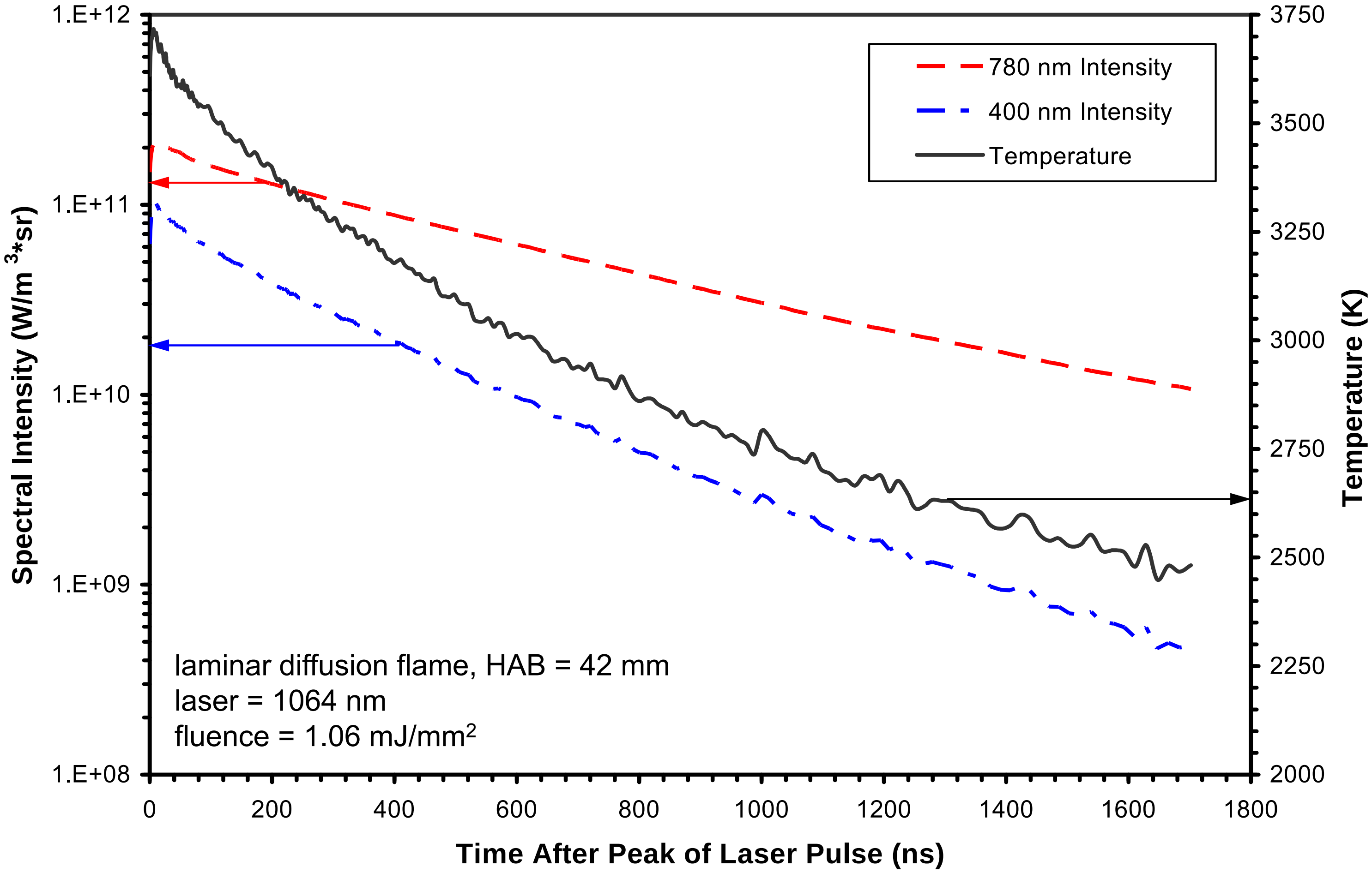




Optical layout of high sensitivity system (HS-LII)



Auto-Compensating LII (AC-LII) Absolute Signals



Mobile Platforms

CRUISER

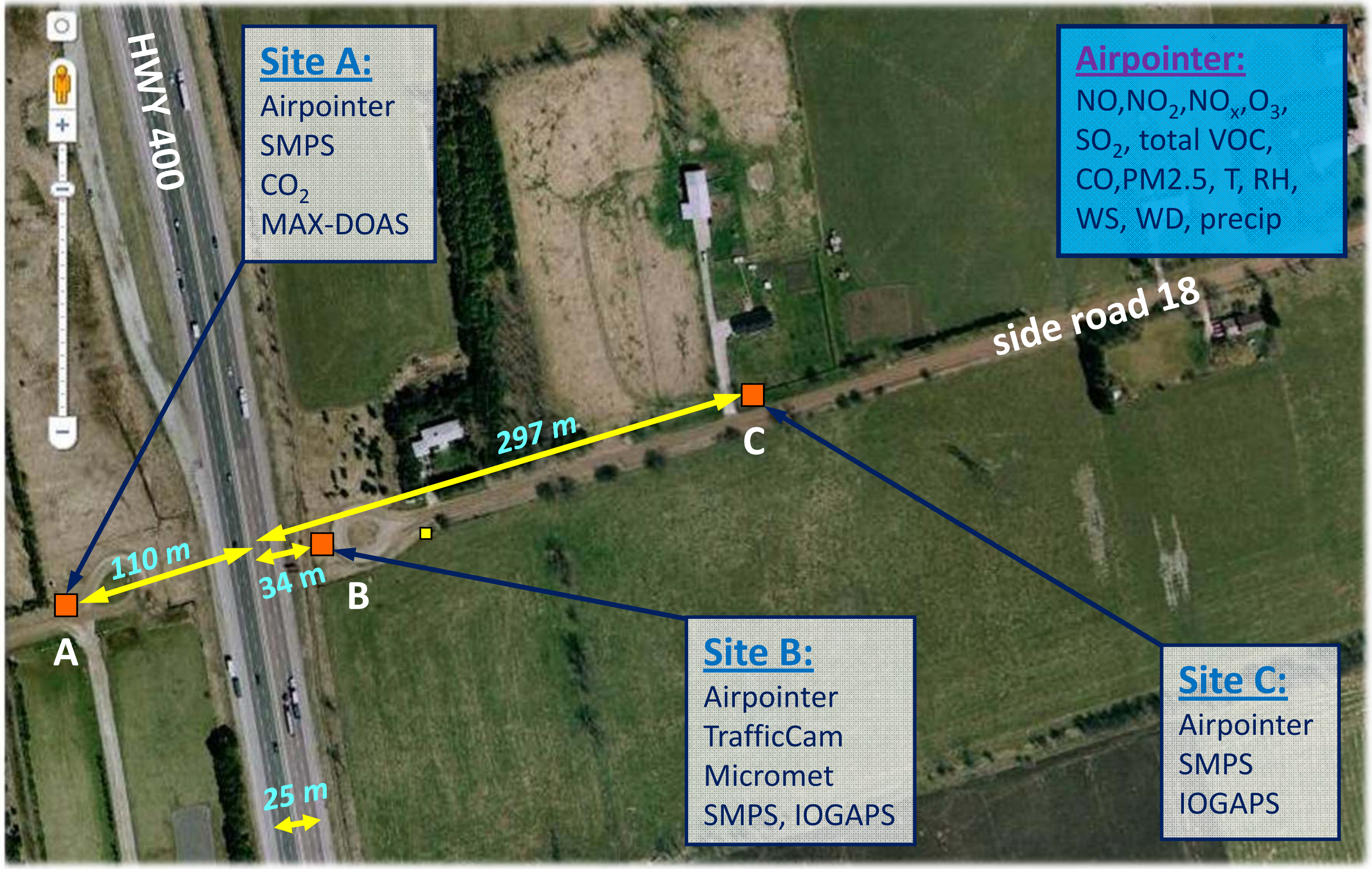
- 2 sonic anemometers
- 1 aircraft turbulence probe
- GPS, accelerometer, tilt-meter
- Aerosol Mass Spectrometer
- Single Particle Soot Photometer (SP2)
- High Sensitivity Laser-Induced Incandescence (HS-LII)
- PTR-MS
- CO2, CO, SO2, NO, NO2, Noy
- meteorology; webcam
- Fast Mobility Particle Sizer (FMPS)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

Study Site

Hwy 400 & side road 18 (43.9936°N, 79.5832°W)



Laser-Induced Incandescence (LII)

high selectivity technique for measuring black carbon

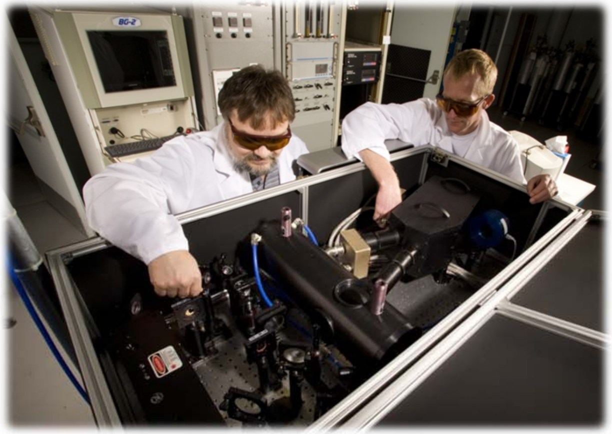
- soot, refractory carbon, elemental carbon, carbon black

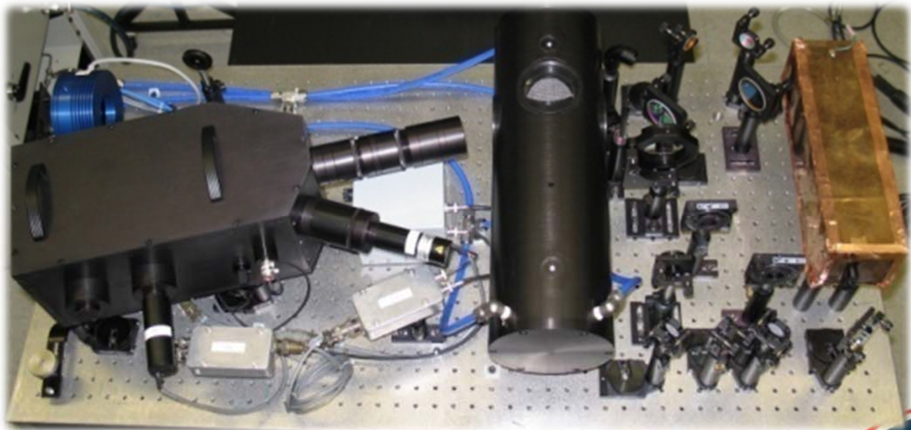
measures:

- mass concentration, volume concentration, active surface area, primary particle diameter

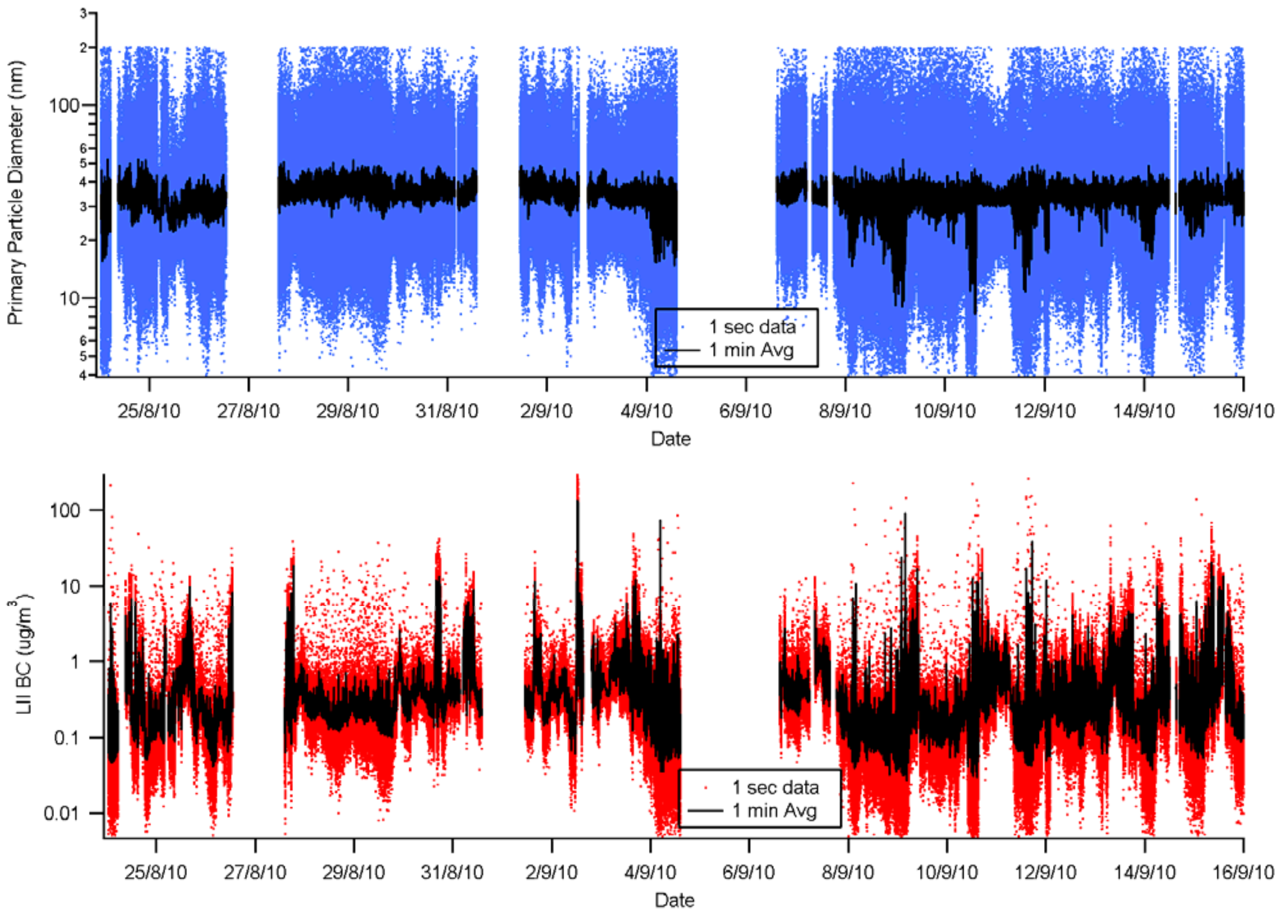
broad measurement range

real-time (20 Hz), instantaneous data analysis



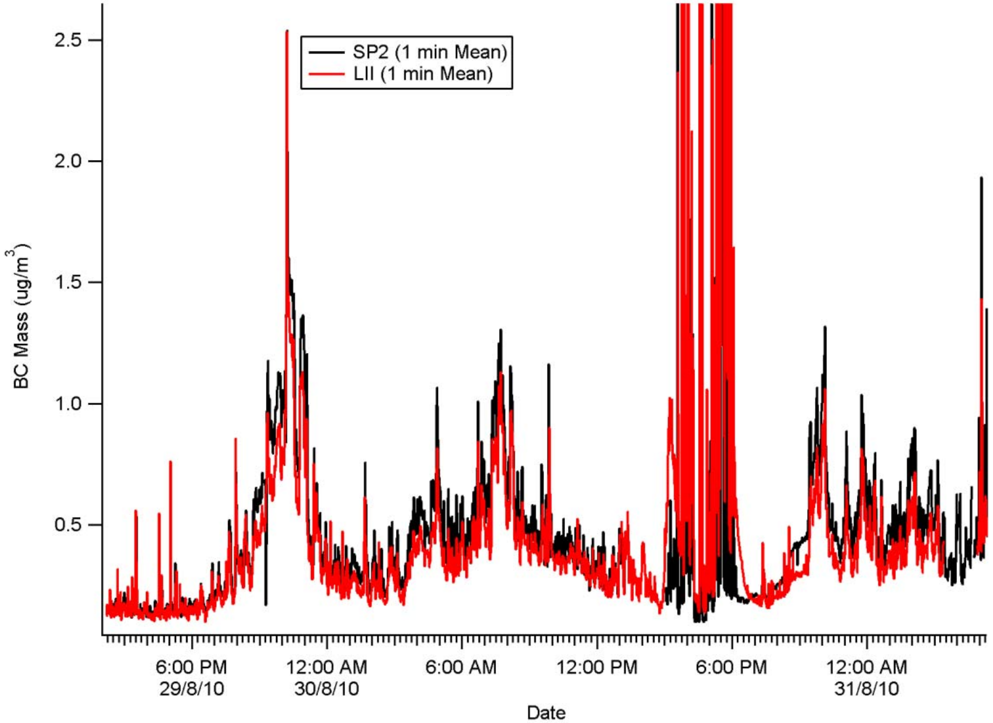


One Month of HS-LII Data



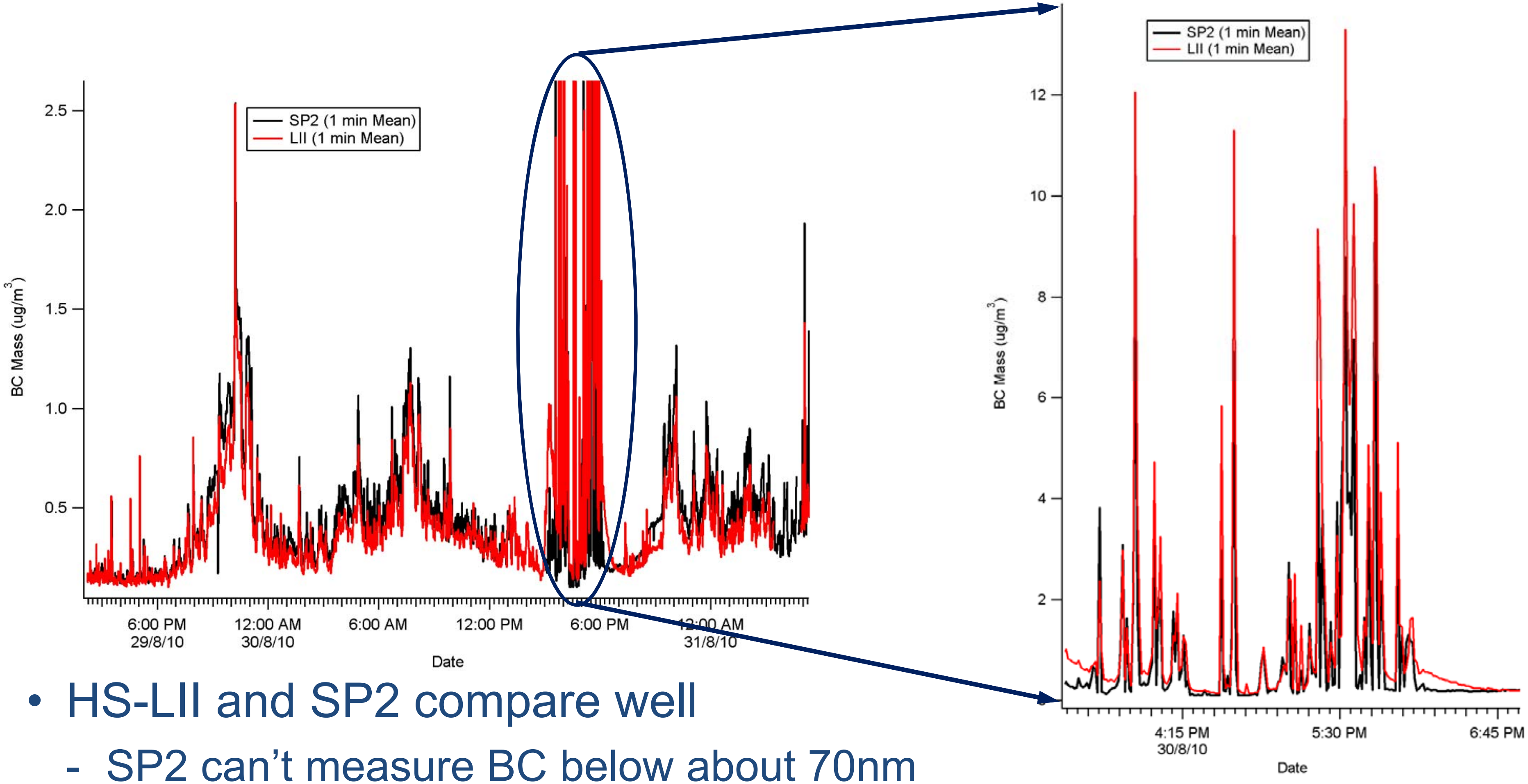
- 30 days
- 2 Hz
- 5,000,000 individual measurements

Time-resolved HS-LII and SP2



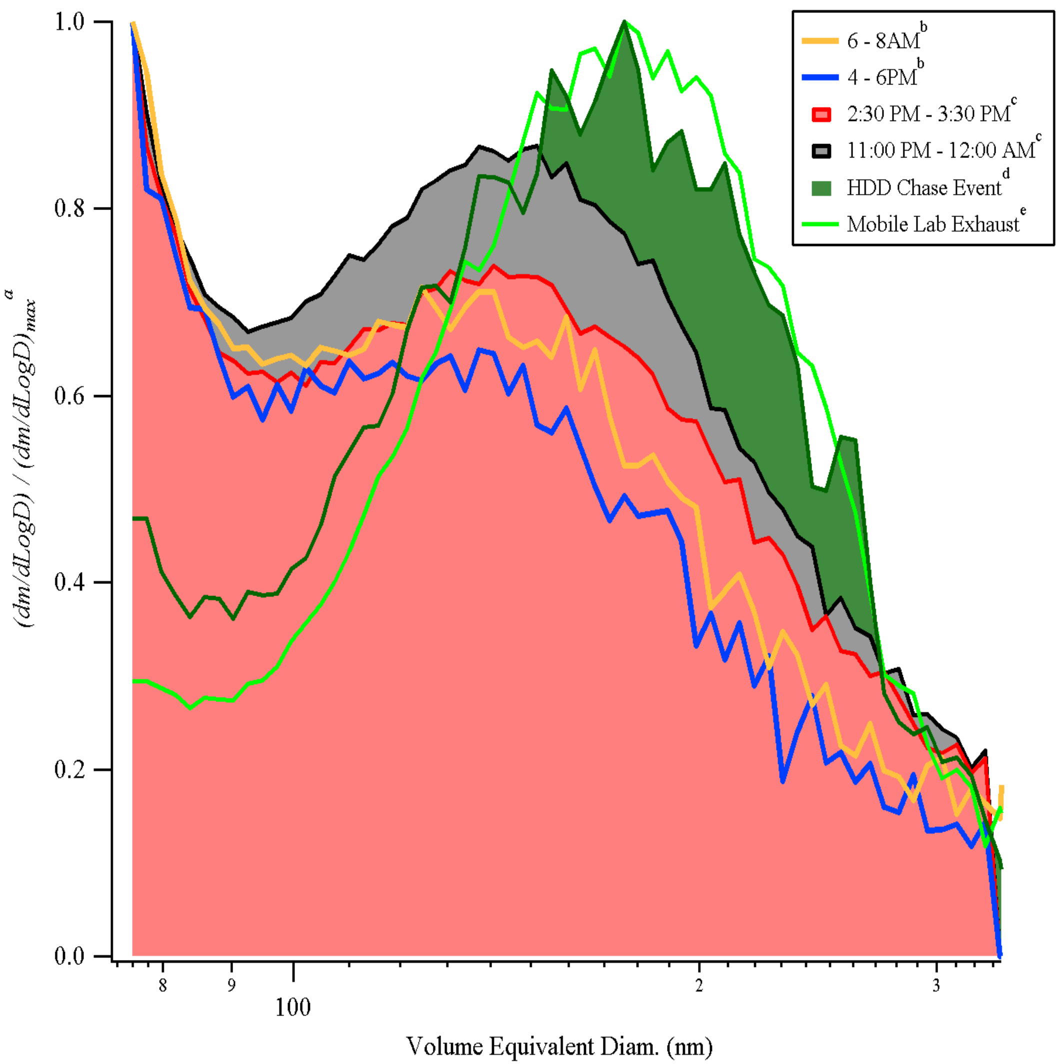
- HS-LII and SP2 compare well
  - best agreement at concentrations below 2.0 μg/m^3
  - SP2 can't measure BC below about 70nm
    - may be better for processed than freshly emitted particles

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?

Black Carbon Size Distributions – SP2



- Two BC size modes are measured by SP2
- Smaller mode dominates the **mass** during high LDGV traffic
- Larger mode clearly from diesel trucks
- **Suggests the single BC mode in current models may need to be updated**

Validating vehicle emission estimates for Black Carbon

- Using latest BC incandescence technology (LII & SP2)
- Emissions factors derived from HWY measurements (Heavy Duty Diesel; HDD) and from perpendicular to HWY transects

BC fuel based emission factor

Above background measured BC concentration

$$EF_{BC} = 10^6 \left(\frac{\Delta[BC]}{\Delta[CO_2]} \right) \omega_c$$

Above background measured CO_2 concentration

Fuel carbon mass fraction

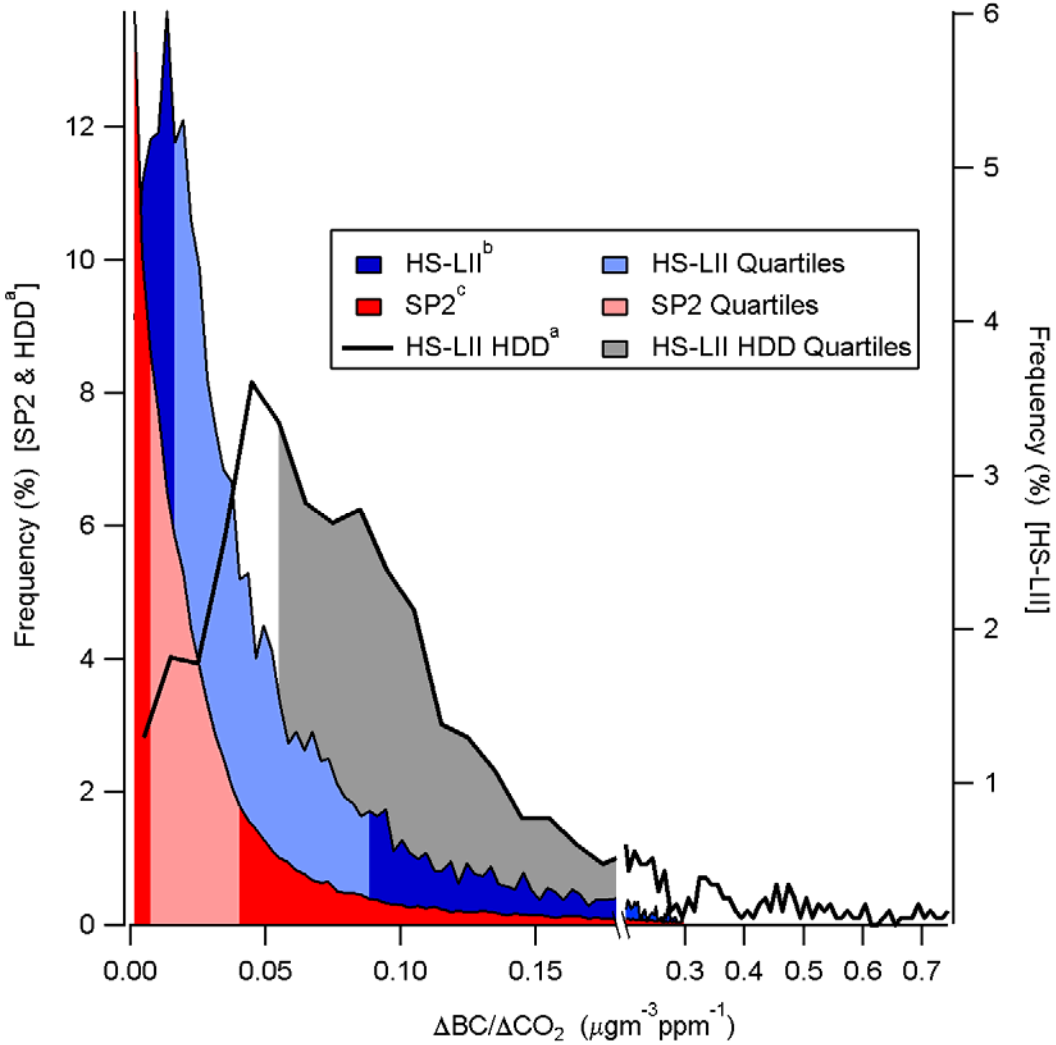
Light Duty BC emission factor

Fuel use fraction

$$EF_{meas} = ff_{HDD} EF_{HDD} + ff_{LDV} EF_{LDGV}$$

Emission factor measured during HWY driving

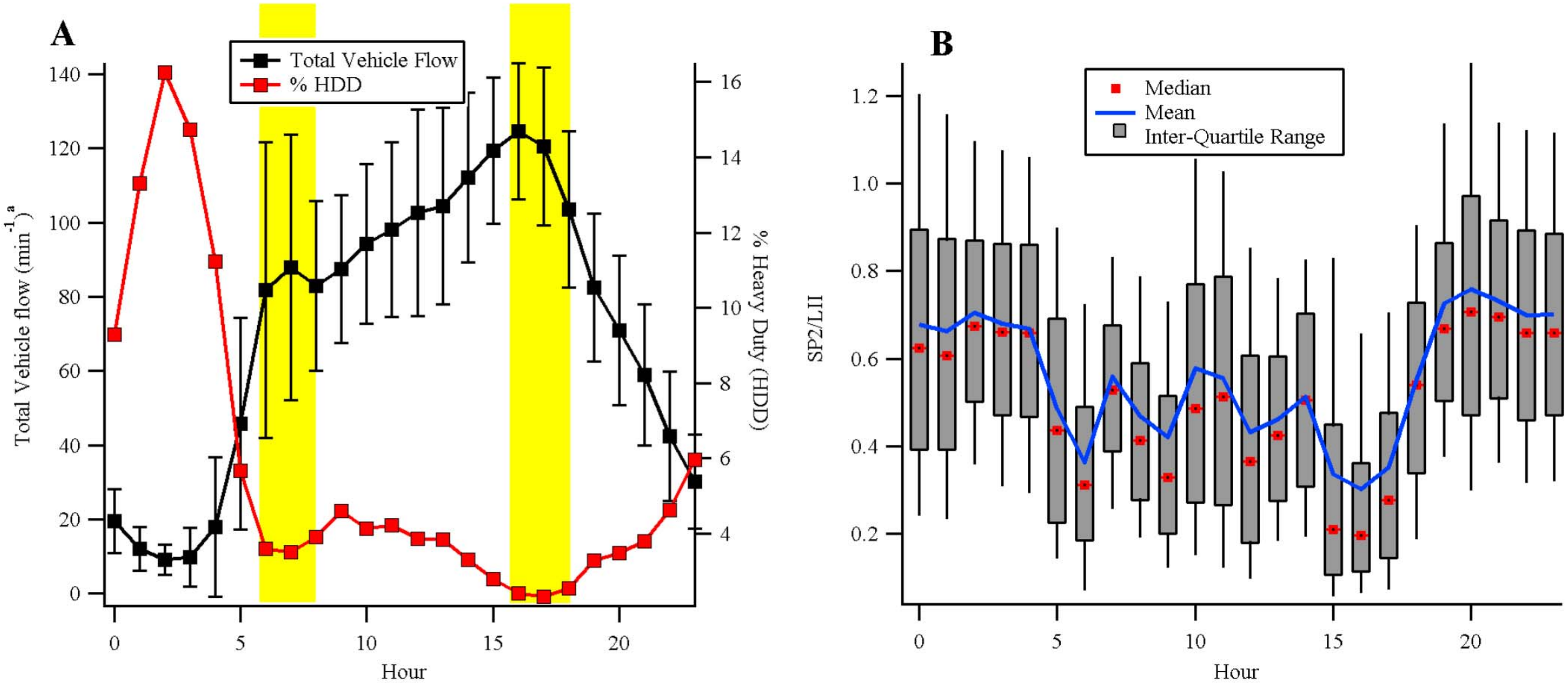
FEVER: BC from Gasoline Vehicles is Substantial



above background BC/CO_2 measurements

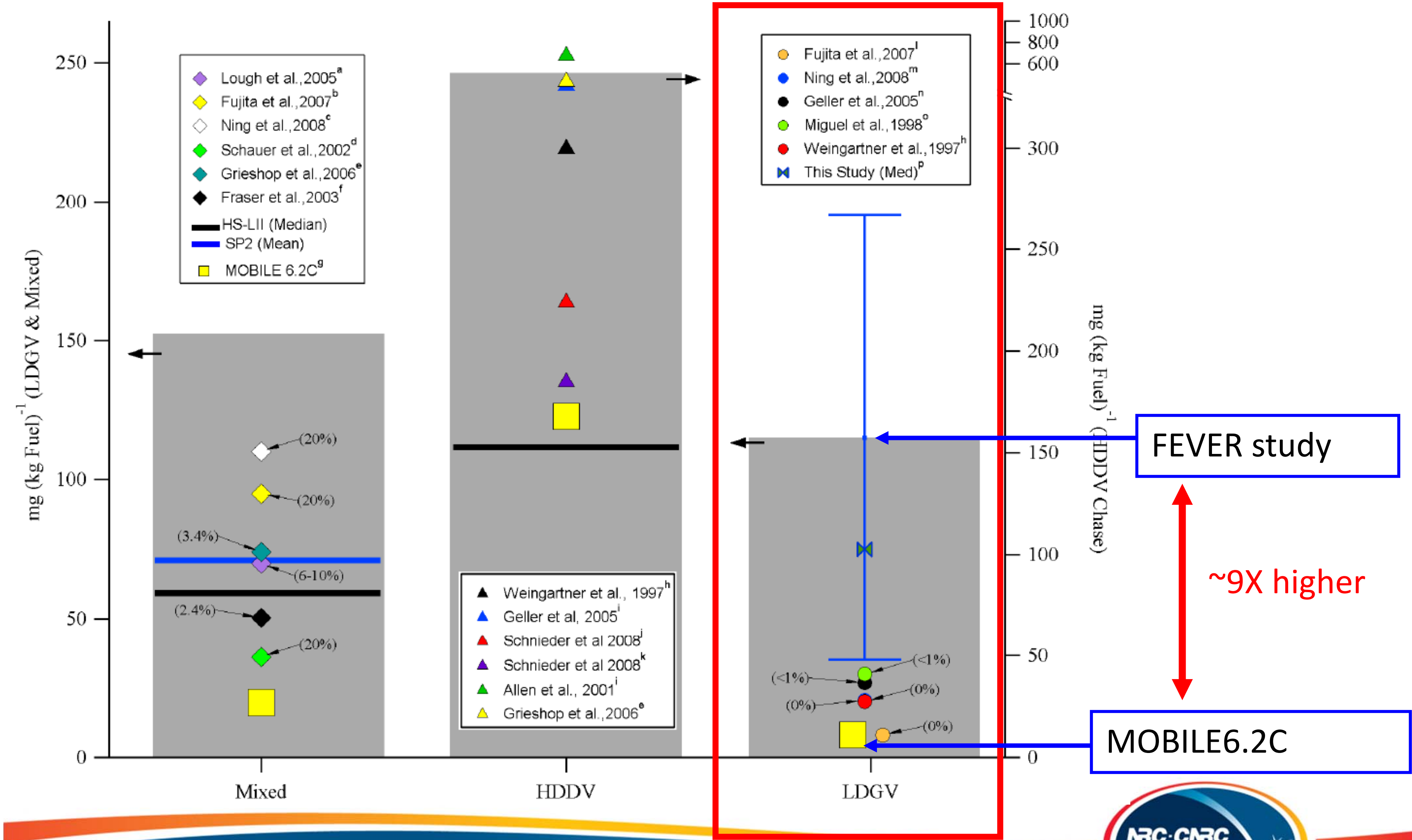
a. measured ratio using HS-LII during Heavy Duty Diesel (HDDV) chasing
b. HS-LII during transect driving
c. SP2 during transect driving

FEVER: HDD 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)

FEVER: BC from Gasoline Vehicles is Underestimated



Summary

Laser-induced incandescence

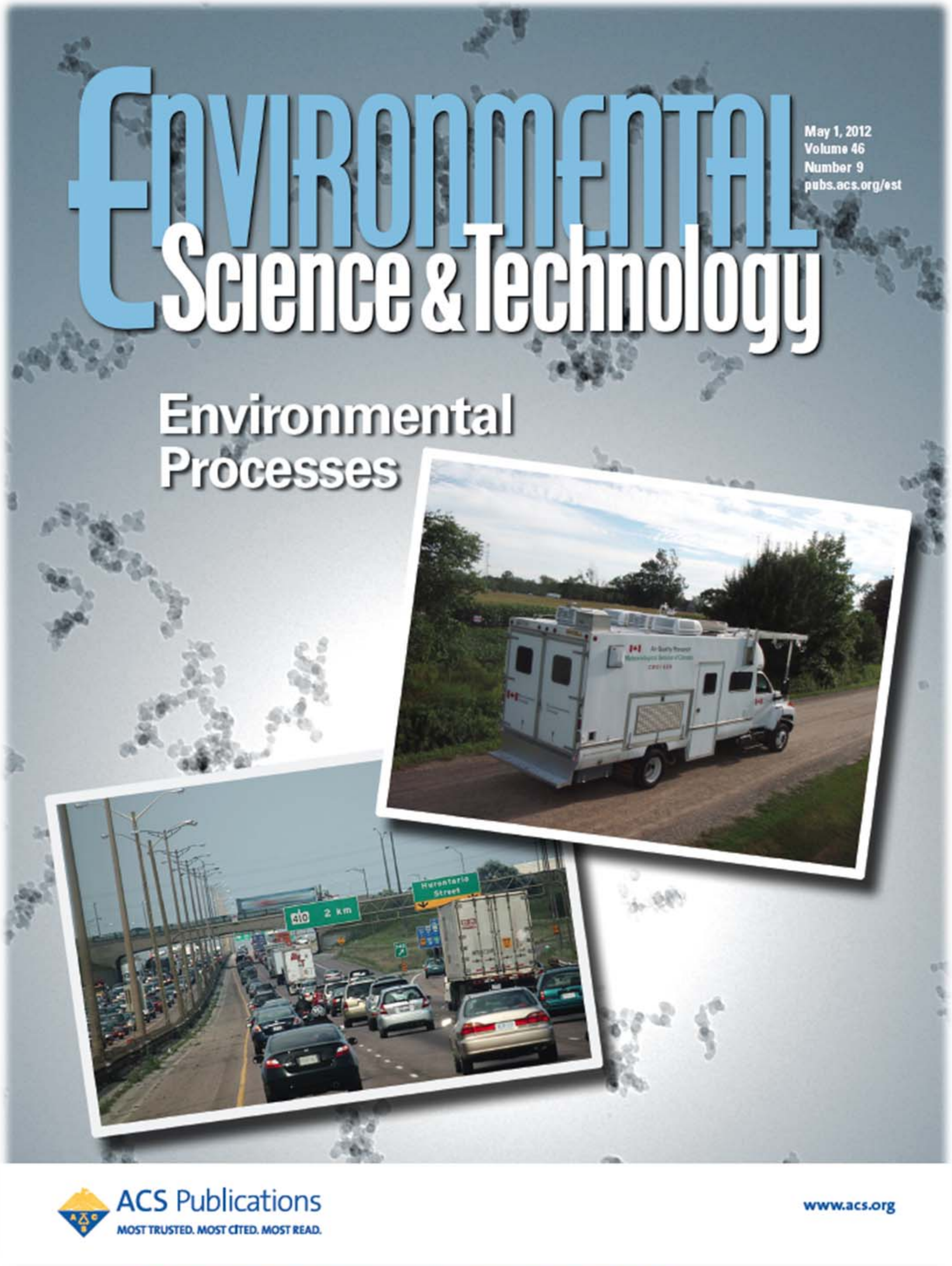
- HS-LII has the sensitivity to measure atmospheric levels of BC

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

- LII+SP2 to assess the source of BC emissions (gasoline vs. diesel)

Black Carbon (BC) Emission Factors

- BC from gasoline vehicles at least a factor of two higher than previous North American measurements, and **a factor of nine higher** than currently used emission inventories in Canada (MOBILE 6.2C)
- BC from heavy duty diesel vehicles is in reasonable agreement with previous measurements and the current inventory
- 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
  - increased popularity of GDI engines in the future could further shrink the gap between gasoline and diesel BC emissions
  - 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.

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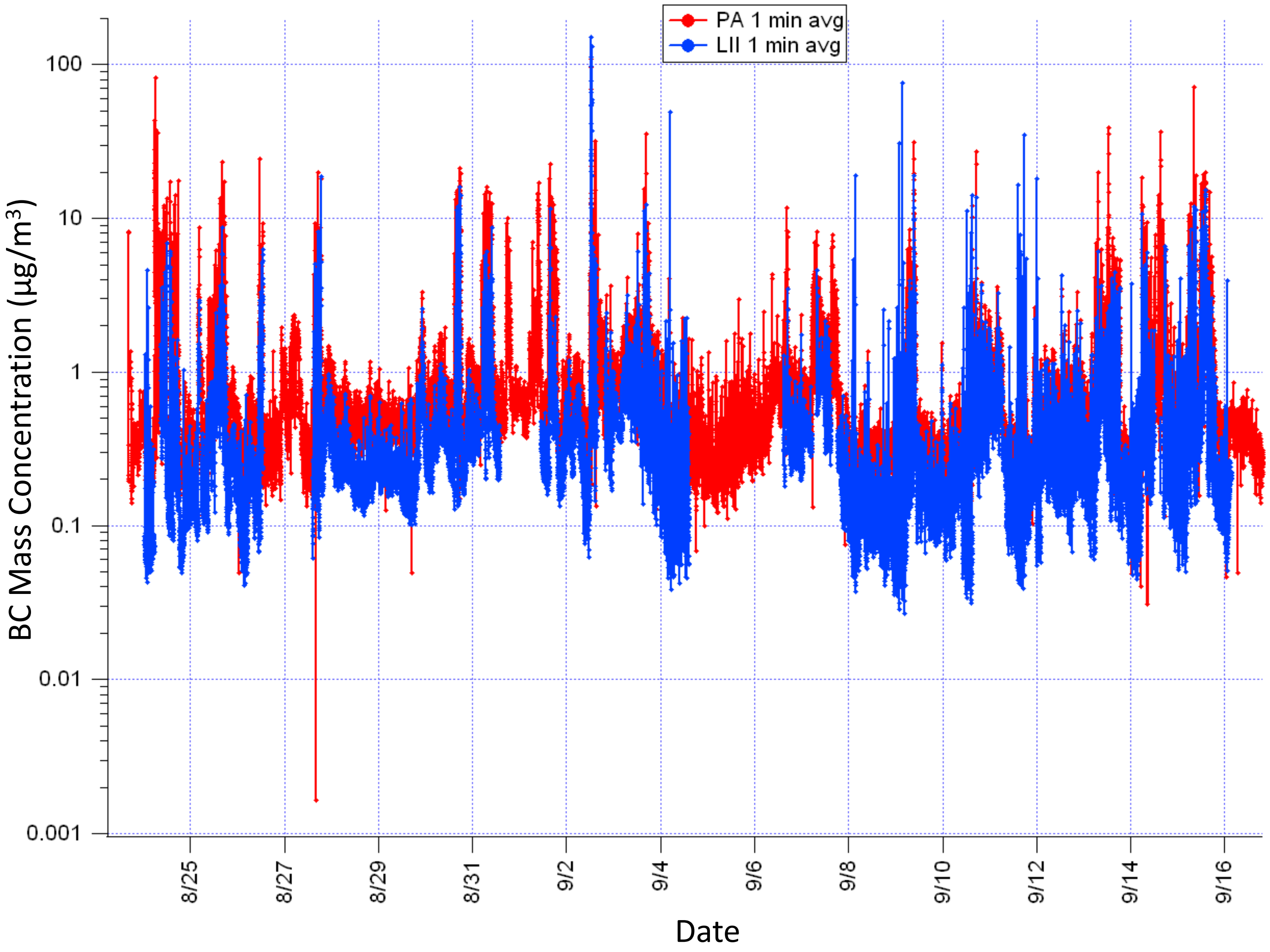
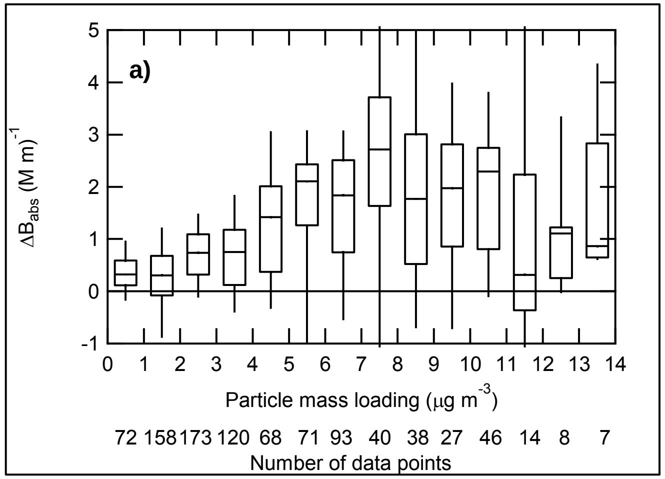
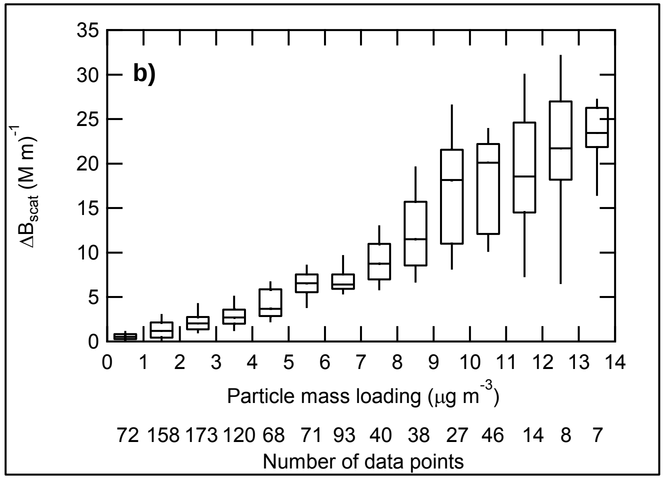
Ontario Ministry of the Environment
National Research Council (Dan Clavel, Bob Sawchuk)

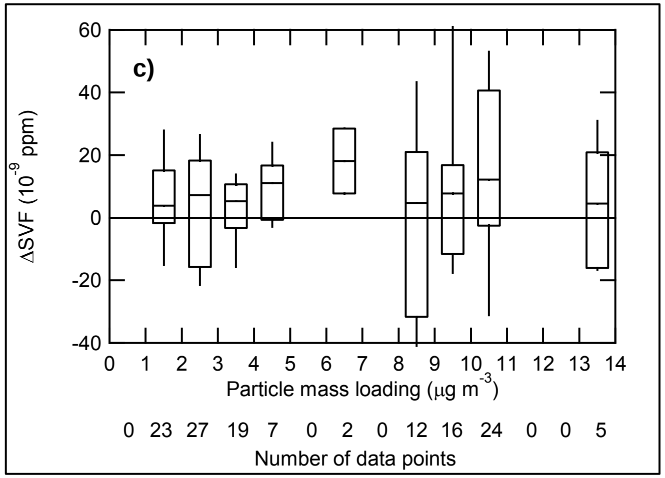
FEVER: Time-resolved HS-LII and PA



Atmospheric Black Carbon: HS-LII vs. Photoacoustic



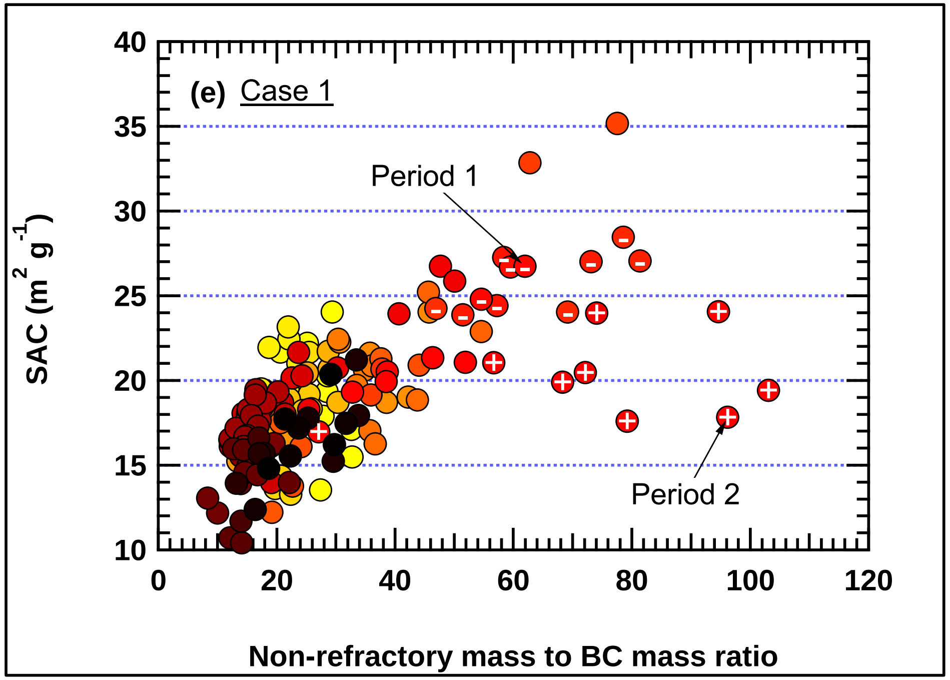


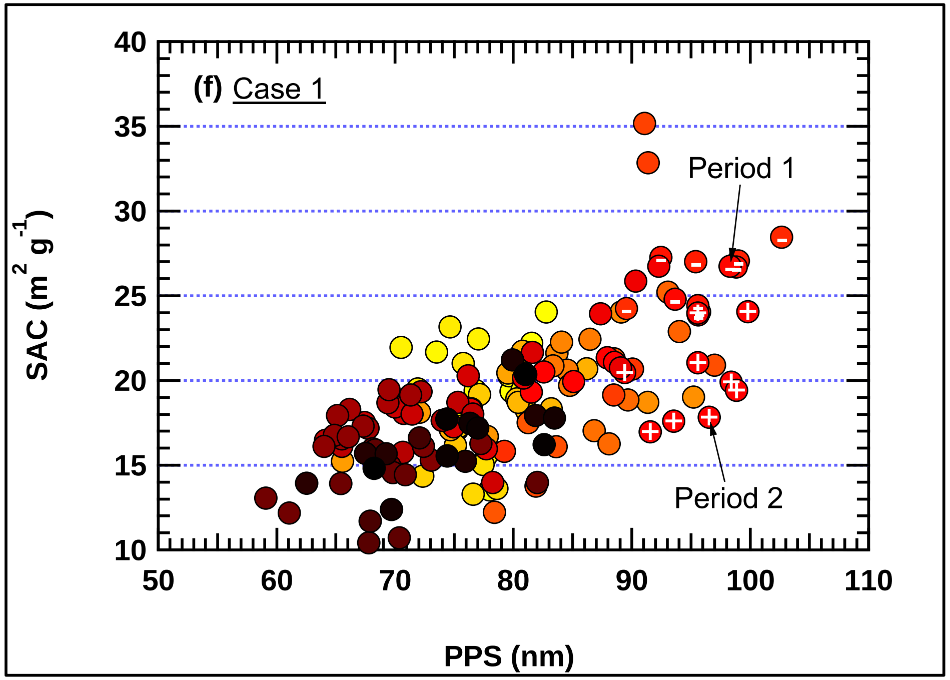


- The variations of (a) the particle light absorption (PA), (b) particle light scattering (PA), and (c) the soot volume fraction (LII), as a function of particle volatile coating mass
- The photoacoustic results are significantly affected by the presence of a volatile coating
- LII shows no significant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

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

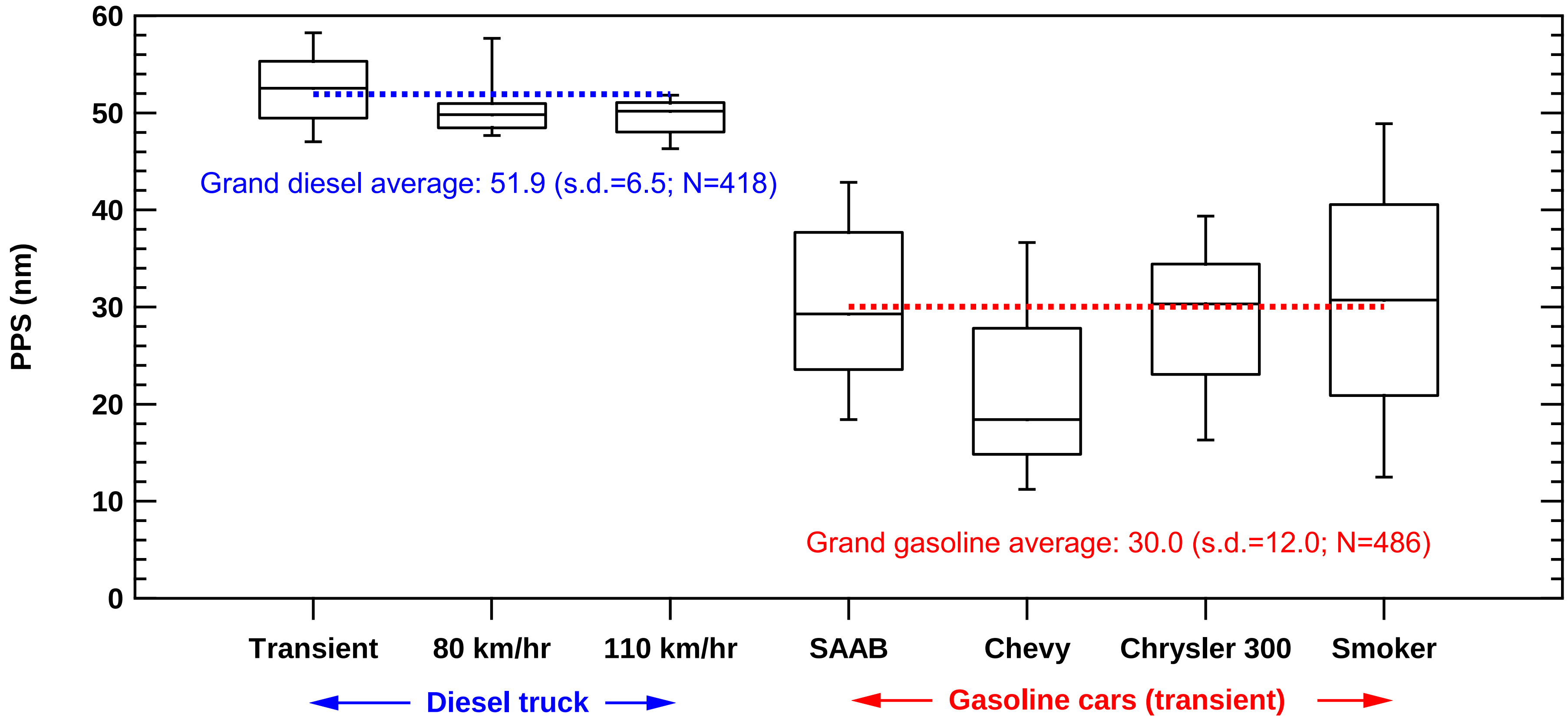
Use of Simultaneous LII and PA to Determine Specific Absorption Coefficient





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

LII May Identify BC Source



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