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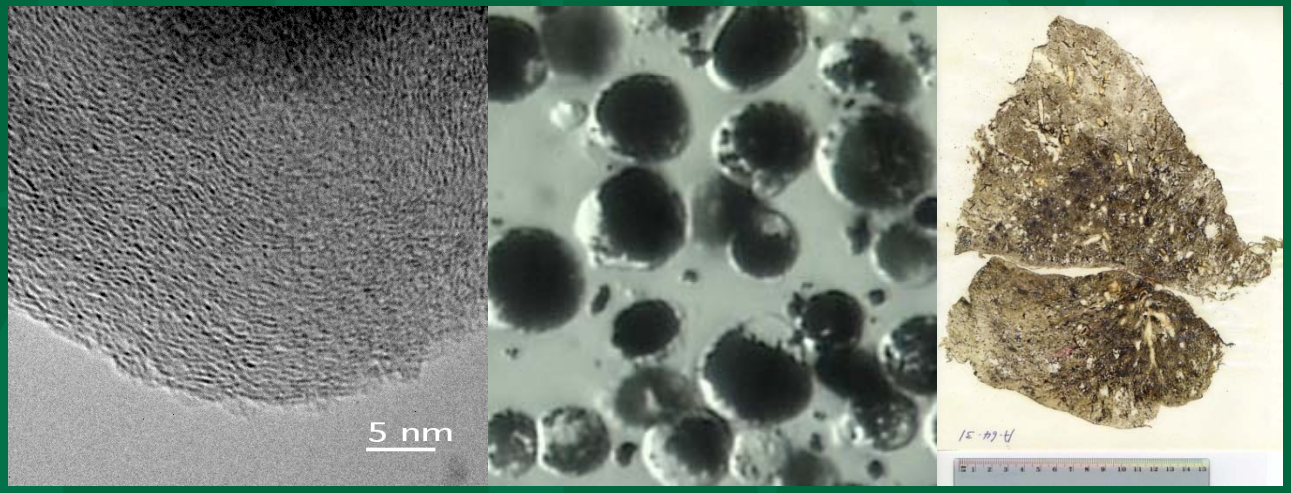
Environmental Protection
Agency

BC measurement activities at the US EPA (ORD-RTP)

Michael D. Hays



Office of Research and Development
National Health and Environmental Effects Research Laboratory and National Risk Management Research Laboratory

June 18, 2012

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Black carbon defined (and debated)

- **Black carbon** (BC)–sometimes referred to as soot, char, or elemental carbon–is a form of carbon produced from the incomplete combustion of fossil fuels and biomass. BC is usually in the fine aerosol mode, generally a component of particles smaller than 1 micrometer in diameter. It exists in atmospheric aerosols, sediments and soils, and snow and ice accumulations. Unlike long-lived greenhouse gases, the atmospheric lifetime of BC varies on the order of days to weeks. This lifetime allows for long-distance transport to occur, but also leads to ambient concentrations that vary orders-of-magnitude from urban to remote locations. Vertically, concentrations of BC tend to peak at approximately 2 km altitude. Although generally thought to be recalcitrant, there is evidence that BC may undergo oxidation in the atmosphere, which causes it to retain hydrophilic properties.

- A precise definition of BC has been elusive and subject to scientific debate for some time, and this has led to some confusion. When developing definition criteria, some scientists use its thermal and chemical stability, some its optical properties or light-absorbing characteristics, while others use its morphology or microstructure.

- Evolving term
  - major $PM_{2.5}$ component
  - anthropogenic and biomass combustion sources

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Relevant terms

- **black carbon** (BC) – light absorption, optical properties
- sp^2-hybridized carbon
- elemental carbon – thermal-optical properties
- soot or char (combustion related aggregates)
- light absorbing carbon – includes organic carbon

- See Andreae and Gelencsér (2006) Atmos. Chem. Phys. 6, 3131-3148 for more definitions and proposed convention
  - BC_e and EC_a

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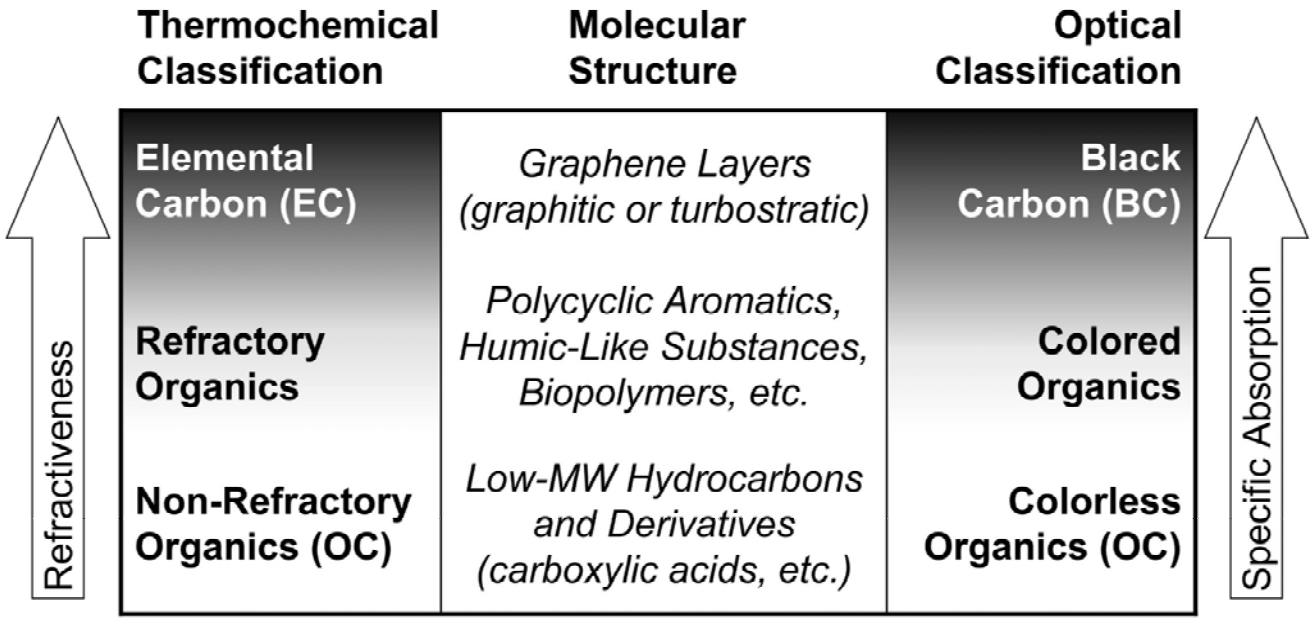
Carbon classification by analytical method



different sources emit these in different proportions

from Poschl, Anal. Bioanal. Chem 2003

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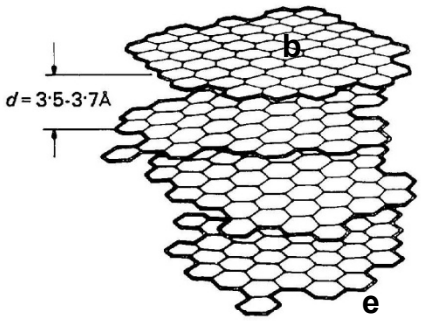
Black carbon generation



- BC forms in fuel-rich, poorly mixed hot (1600 °K+) flames
- from fuel-nascent PAH; H abstraction; or other mechanisms (C5)
- other factors include flame residence time, metal catalysis etc.

- proportion of b/e can effect adsorption, soot reactivity, wettability
- soot is oxygenated; not graphite per se

with help from Bond tutorial

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(Ground-based) Carbon measurement techniques

- current techniques
  - thermal-chemical or “evolved gas” analysis
  - thermal-optical analysis
    - NIOSH, 5040, EPA-NIST, and IMPROVE
  - light absorption measurements
    - filter-based – aethalometer, PSAP, MAAP [scattering correction])
    - direct on the aerosol – photoacoustics, incandescence (SP2)
  - Raman spectroscopy
    - molecular level, functional group concentration
    - poor for routine monitoring
  - HR-TEM
    - qualitative

- possible future techniques
  - high-resolution MS
    - chemical formulas
    - not always a matter of defining specific chemical structure
  - spectral absorption
  - fluorescence lidar
    - remote sensing technique
  - photophoretics
  - XPS

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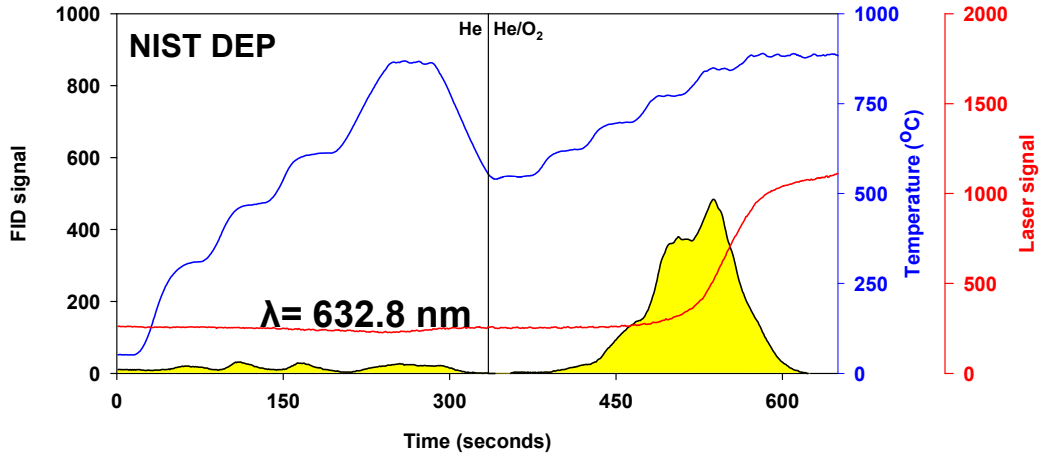
Thermal and thermal-optical techniques

- semi-continuous (30 min, 0.5 µg/m^3) or integrated samples (0.2 µg/cm^2) {field and lab}
- multitude of thermal programs, reflectance, transmittance
- ambient monitoring networks rely on these methods



- thermal technique issues (French method)
  - filter-sample interactions and oxidant composition varies
  - charring (possibly avoided with extractions, more temp. steps = tedious)

- thermal-optical techniques correct for charring but….
  - carbon with OC- and EC-like properties (“brown carbon” [likely invisible])
    - EC not a proxy for LAC
  - light extinction of char varies with that of native BC
  - methods disagree for some sources (in-filter charring)

widely used; EPA

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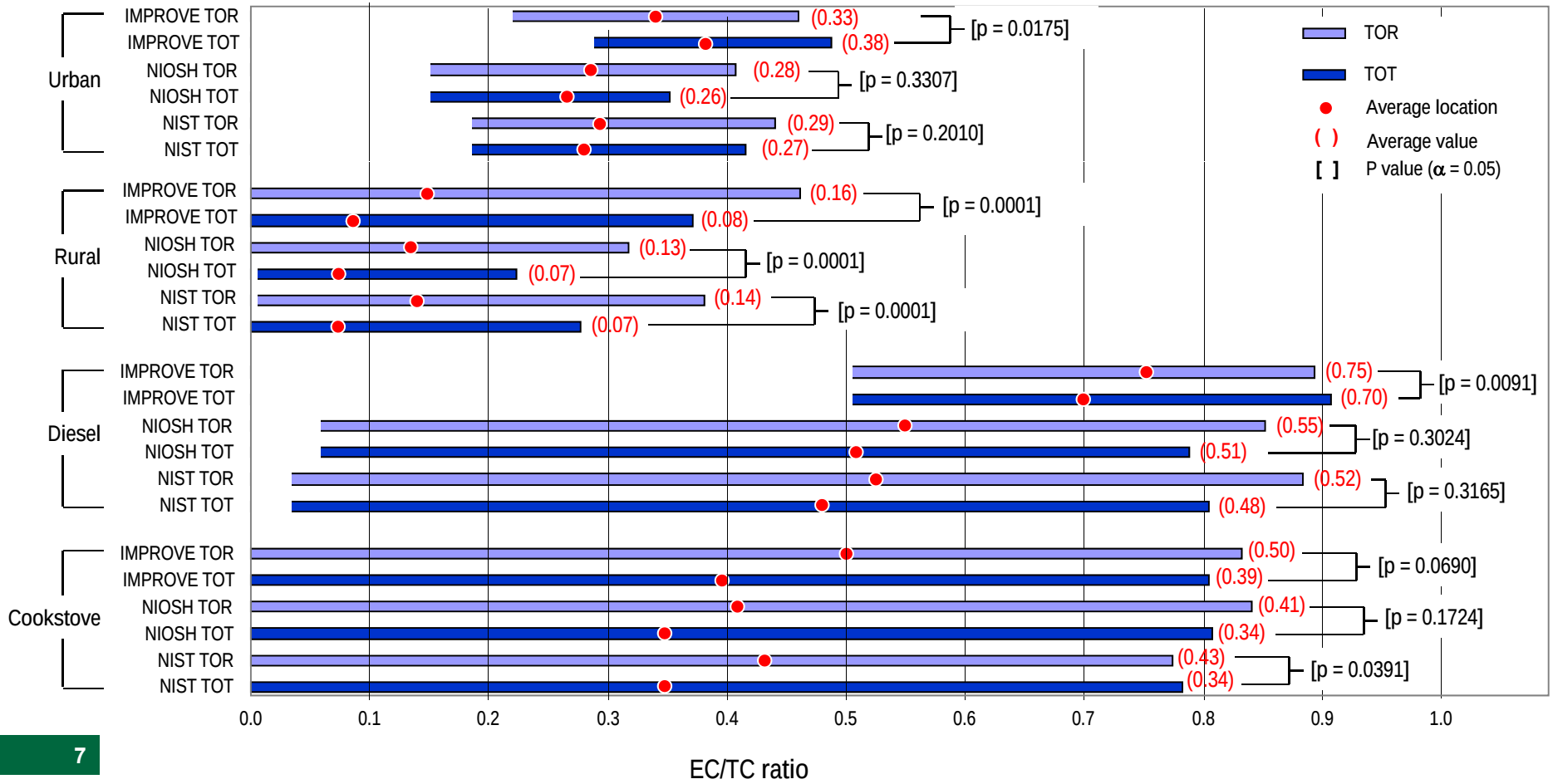
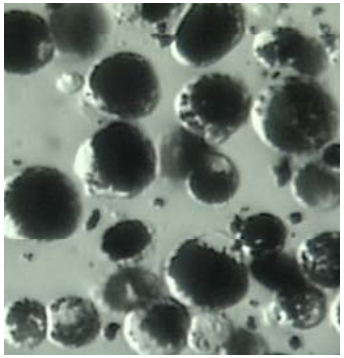
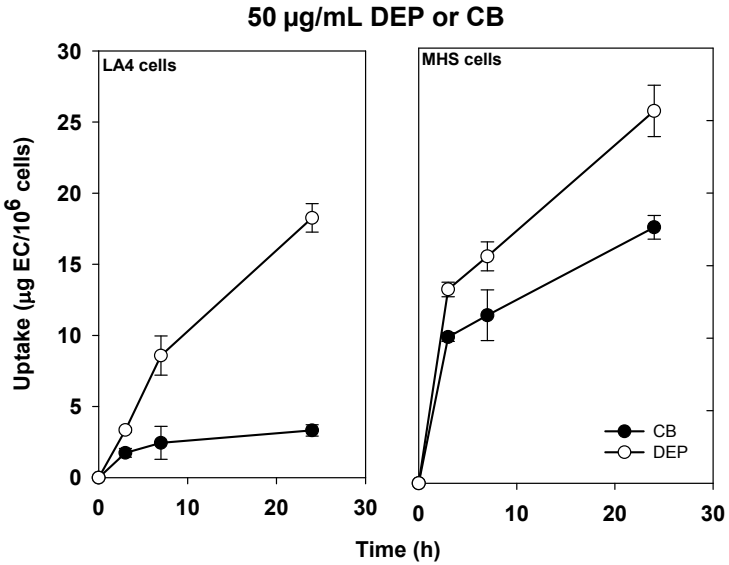
Differences in the OC/EC Ratios that Characterize Ambient and Source Aerosols due to Thermal-Optical Analysis Bernine Khan, Michael D. Hays, Chris Geron & James Jetter (2012, 46: 127-137)

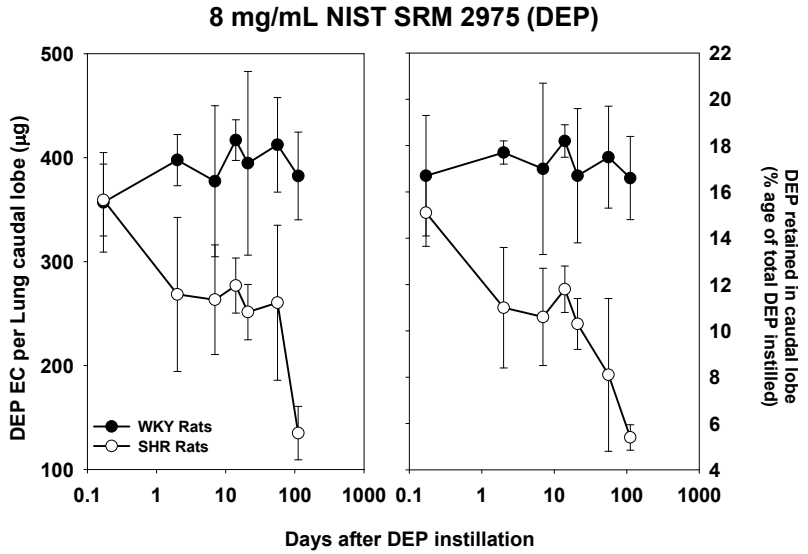


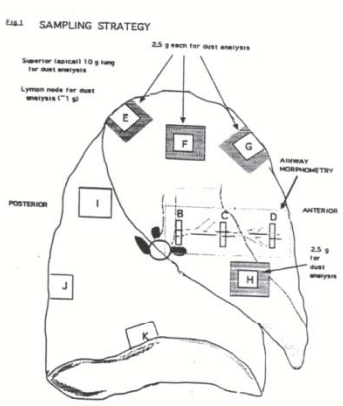
Thermal-optical transmittance for EC in biological samples

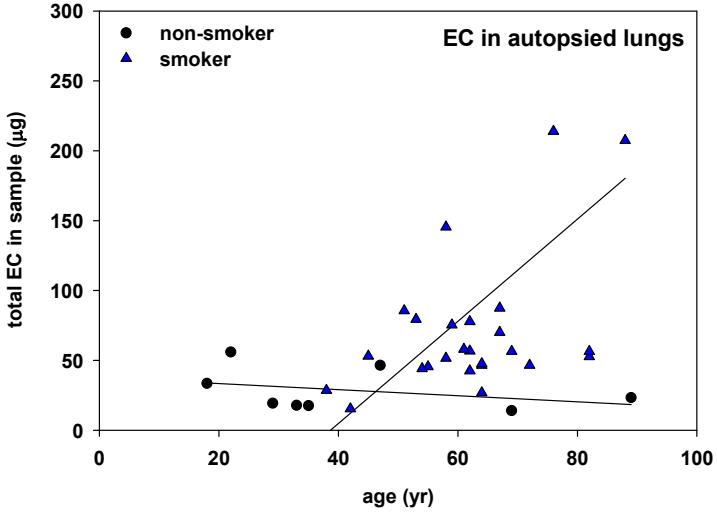
Saxena et. al., *Tox. Sci.* 111(2), p. 392 (**2009**); and *Biotechniques* 44, p. 799 (**2008**)



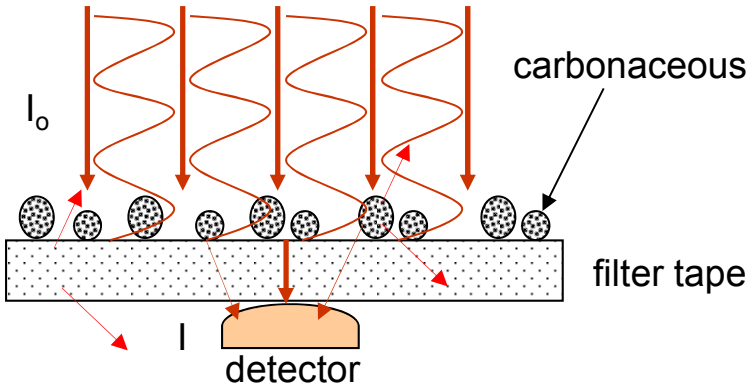








Light absorption techniques (filter-based)



- on-line, semi-continuous methods
- A = $\ln(I_o/I)$ proportional $\alpha_{abs}C$
  - $\alpha_{ATN} = \alpha_{ABS}/C_{soot}$ = 1-30 m^2/g
- dual or multiple wavelengths

limits
- lack of reference standards
- no unique α_{abs} for conversion
- PM aging
- filter-aerosol interactions
  - scattering
  - shadowing
- systematic errors up to 2

- Aethalometer
- Particle Soot Absorption Photometer (PSAP)
- Multi-Angle Absorption Photometer (MAAP)
- Difference method (loading issue)

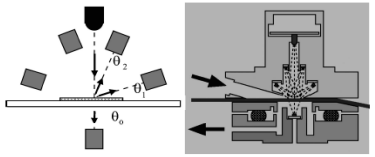


Figure 1. Optical sensor of the MAAP. Left: position of the photodetectors at detection angles $\theta_0 = 0°$, $\theta_1 = 130°$, and $\theta_2 = 165°$ with respect to the incident light beam (λ_{MAAP} = 670 nm). Right: layout of the MAAP sensor unit, arrows indicate the airflow through the sensor unit across the filter tape.

Petzold et al. 2005

Technique	λ (nm)	BC Sensitivity*	operation
Aethalometer	**370**, 470, 520, 590, 660, **880 (ir)**, 950	100 ng/m^3 at 1 min	transmission
PSAP	567	—	transmission, ref. filter, loading
MAAP	670	100-20 ng/m^3 at 2-30 min avg	sim. multi-angle, transmission, reflectance

*depends on spot size

α – mass-specific absorption coefficient

widely used; EPA

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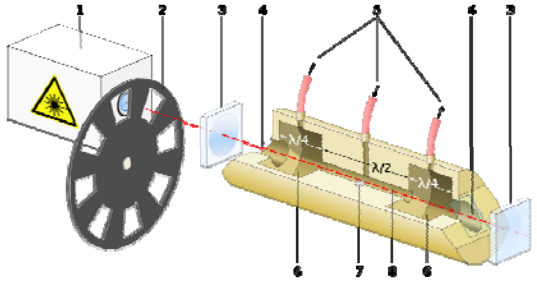
Light absorption techniques (direct)

Photoacoustics spectrometry (PAS)

- continuous, suspended state
- absorbed energy → acoustic pressure wave
- no response to light scattering
- issues
  - drifting
  - expensive
  - used less
  - cross-sensitive to NO_x



$b_{PAS} = Pm\ \pi 2 A_{res}\ f_0 / PLQ\ (\gamma - 1) = \alpha_{ABS} * C_{soot}$

cell cross sectional area, resonator quality, laser power
carrier gas specific heats

Droplet Measurements Technology [DRI]
- PASS-1 and -3
- one or three λ settings
- 50 ng/m^3 @ 1 sec integration

AVL [TUM] (source emissions)
- λ = 808 nm
- 5 µg/m^3 (up to 50 mg/m^3)

BECOMING widely used

Laser-induced incandescence (LII)

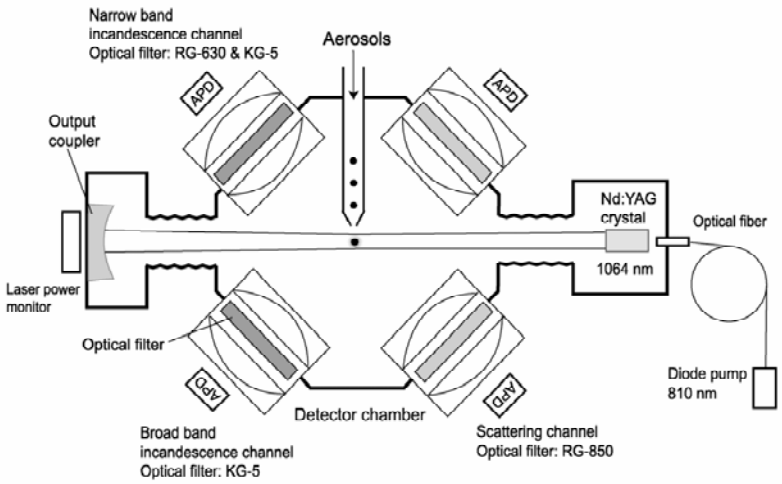
- in-house designs
  - combustion and flame experiments
- not routine

Example: PS2 (Droplet Measurement Technologies)

- real-time single particle technique
  - sub-femtogram (d_a = 70 nm)

- 4 optical axis measure scattering and LII emissions
  - non-absorbers sized (d = 250-1000 nm)
  - heated (1000 K) to incandesce – vaporize organics
    - sensitive to soot f_v
    - image output
  - LII peak can be used for BC particle sizing
    - d_a = 50-500 nm (mass equivalent diameter)

- issues
  - relatively new (can be linked to AMS)
  - expensive
  - max no. conc = 5000 particles/cm^3



less widely used

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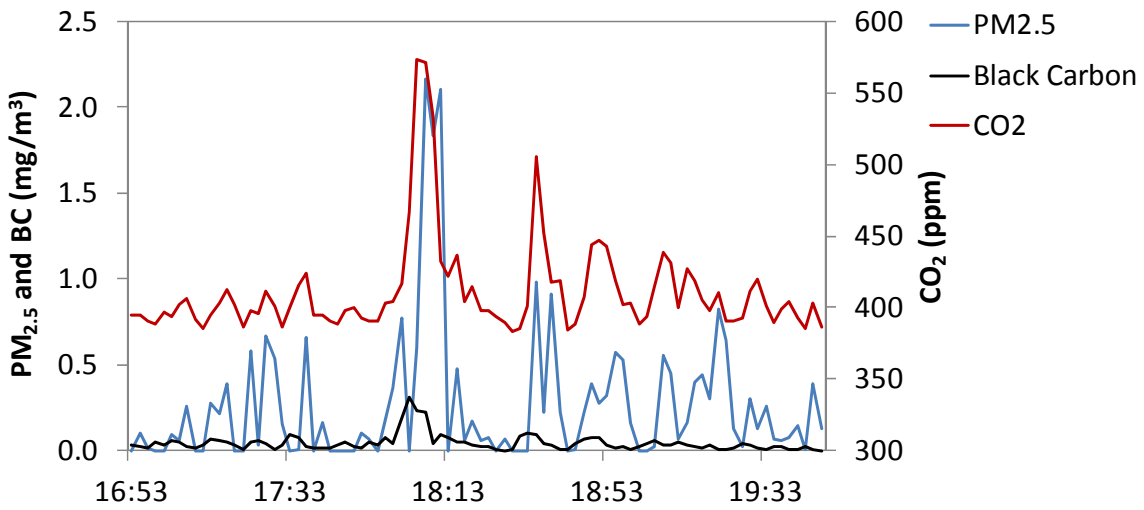
Aerostat sampling of $PM_{2.5}$, BC, and CO_2 from prescribed forest fire – Eglin Air Force Base, FL (Brian Gullett)



- 200-300 ft aloft
- vertical plume distribution
- 2-min average.
- ambient air CO_2 concentration: 390 ppm

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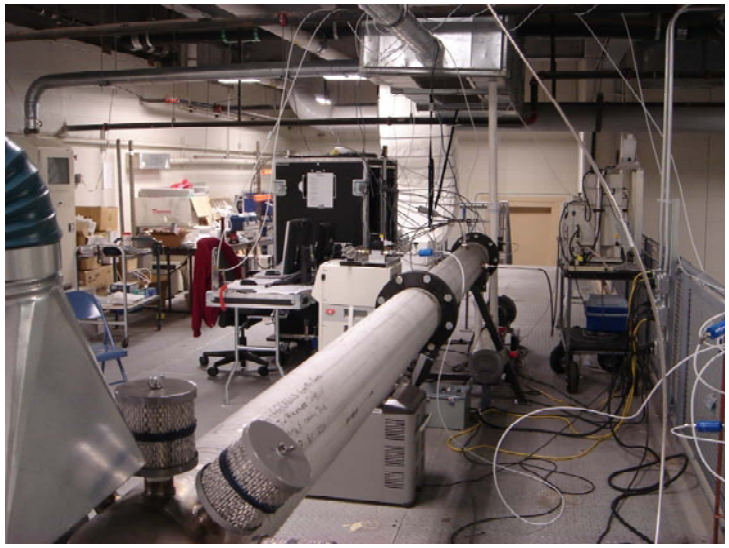
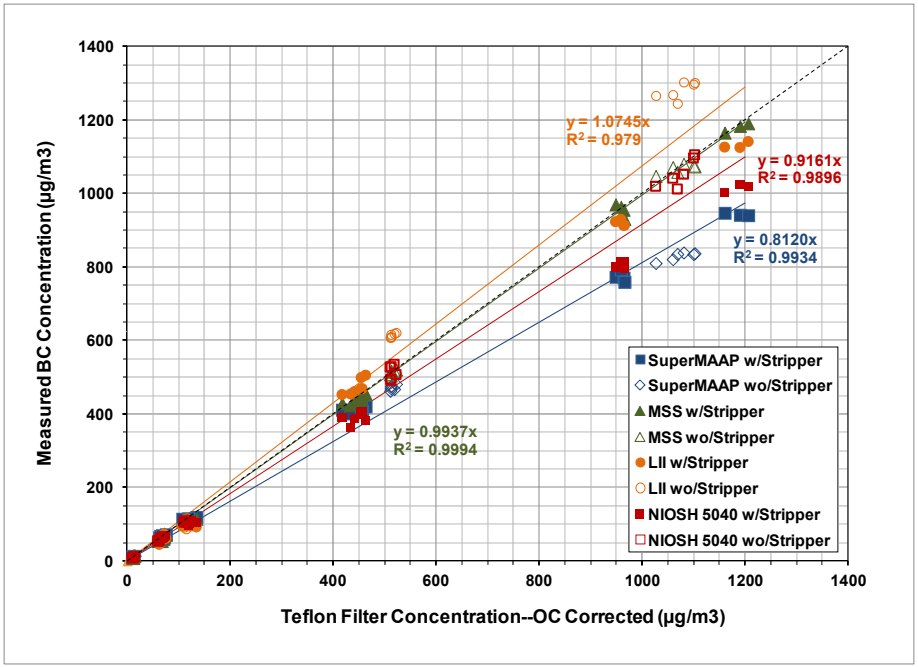
Characterizing PM emissions from commercial aircraft engines (John Kinsey)



Lab-scale flow tunnel system used for BC instrument evaluation.



Can a standardized test method be developed for measuring non-volatile PM emissions for use in aircraft engine certification world-wide?

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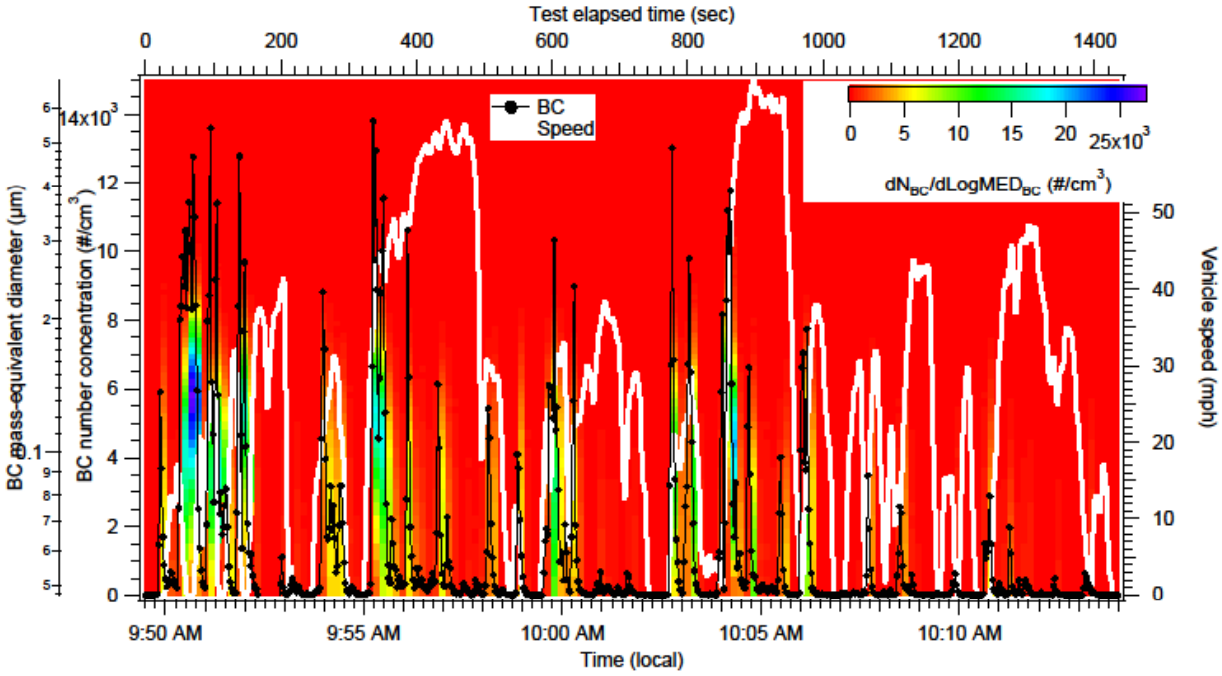
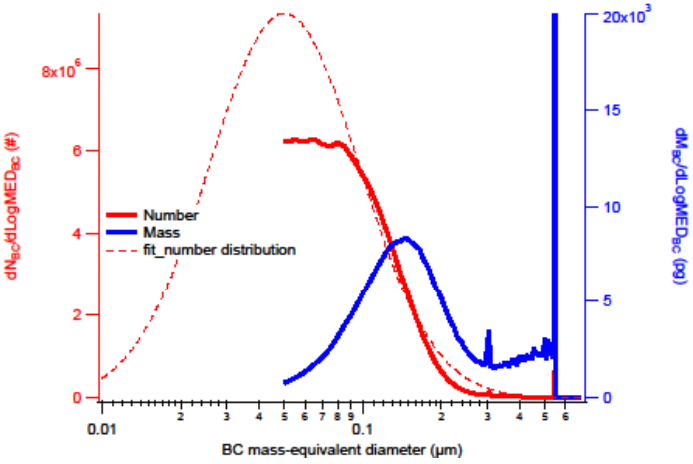
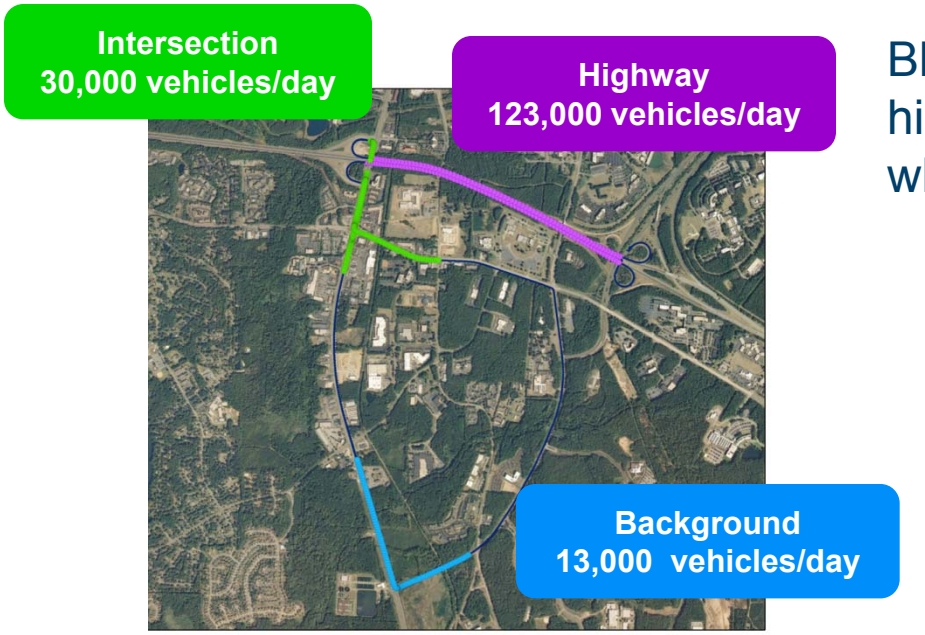
EPActs LDV Dynamometer/LII studies – E10 at 23 °C



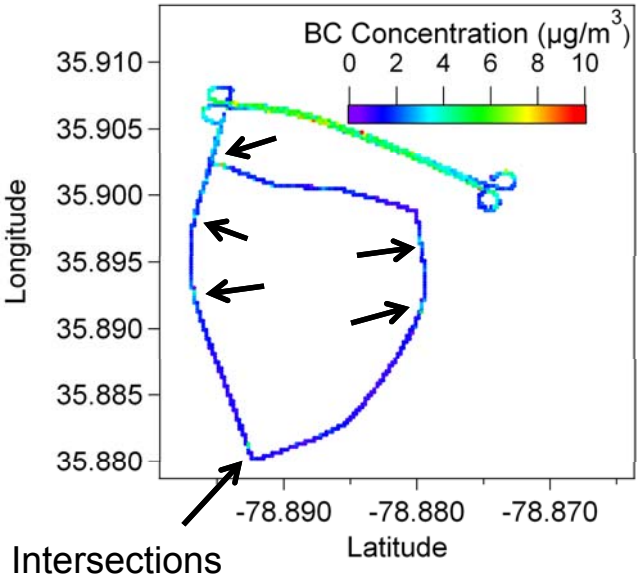


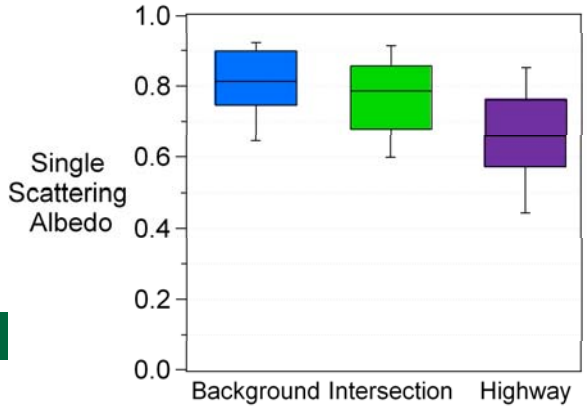
Done with DMT (Subu)

On-road measurement of black carbon concentration and aerosol optical properties -- Amara Holder



Black carbon concentrations are highest on the highway, but are also elevated at intersections where vehicles accelerate from a stop.





Similarly, particle optical properties vary by location. Strongly absorbing particles dominate on the highway leading to low SSA values.

Done with DMT (Subu)

Ground level particle emissions from a prescribed fire at Ft. Jackson, SC – Amara Holder

Samples from the fire plume are identified by the CO_2 concentration and the combustion regime is identified by the angstrom exponent (α).

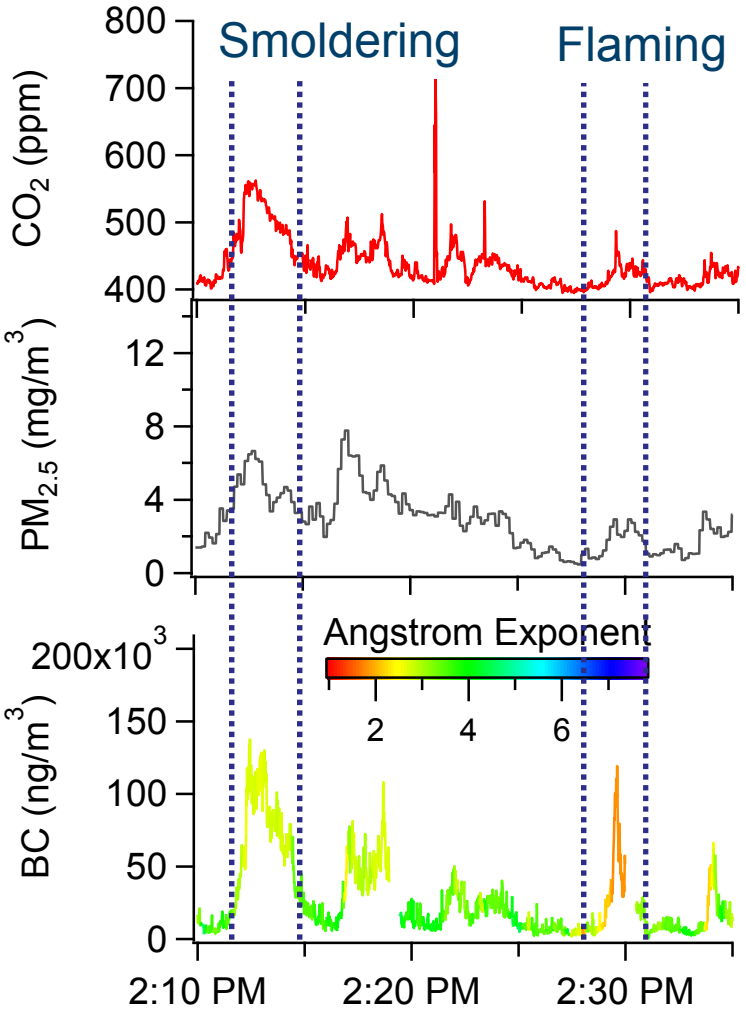
Flaming

$\alpha \sim 1$

$$B_{abs} = \lambda^{-\alpha}$$

Smoldering

$\alpha > 1$



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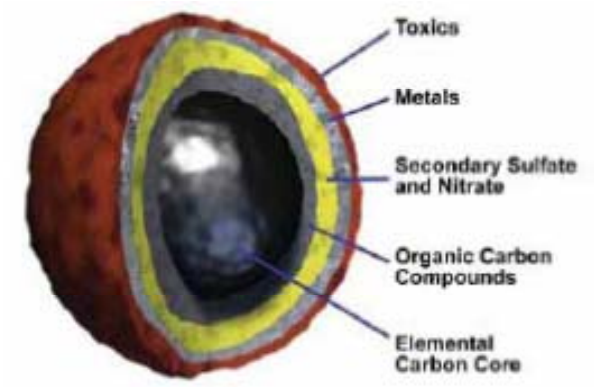
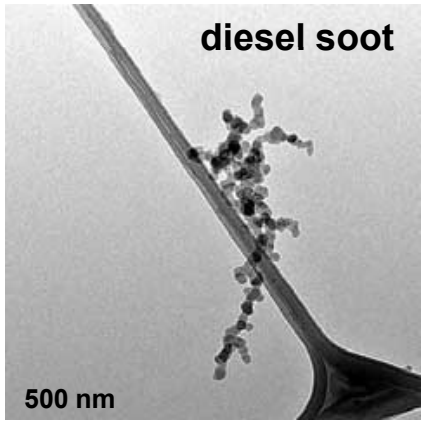
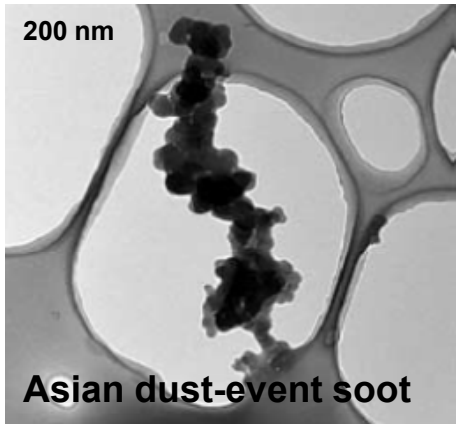
Visualizing soot

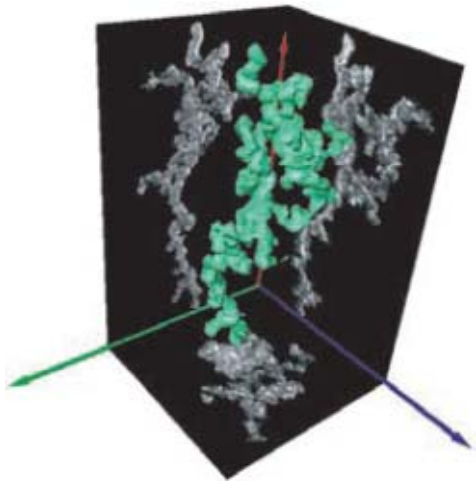
classic particle model

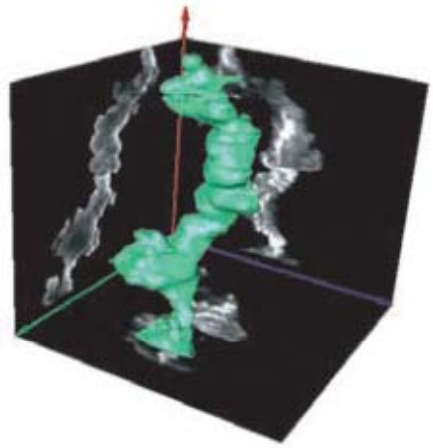


Electron tomography with TEM images
Adachi et al. 2007, JGR









improved D_f, R_g, A_s/V, k_a

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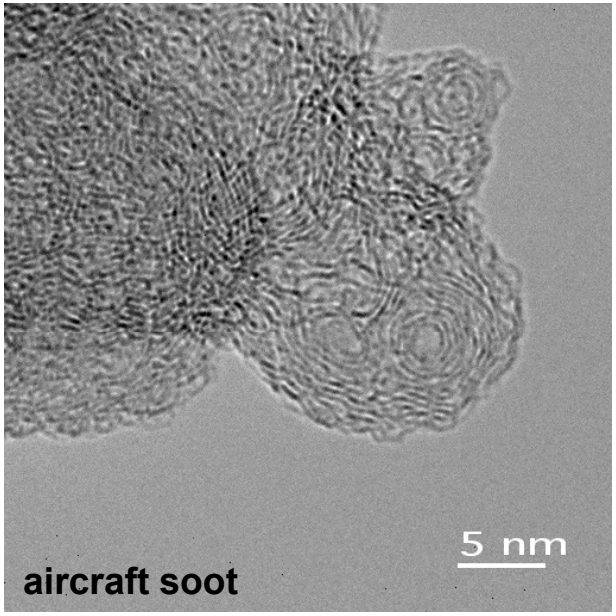
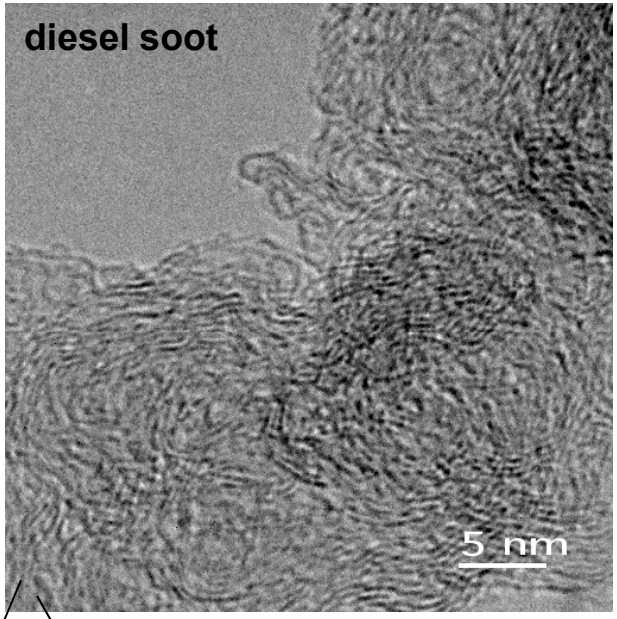
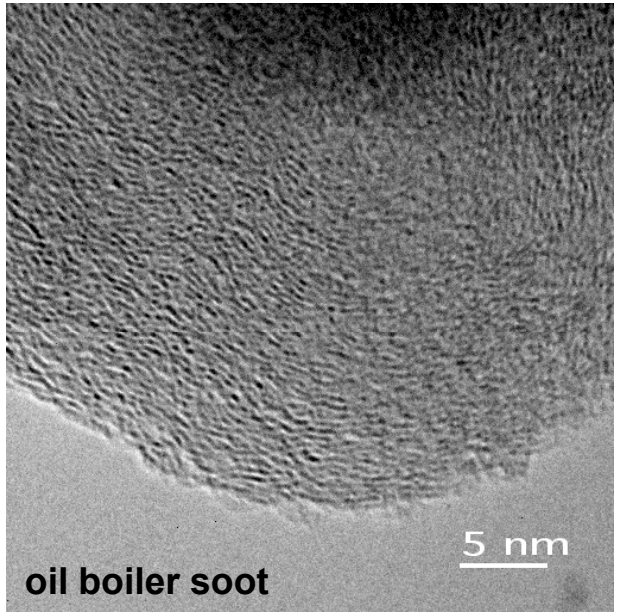
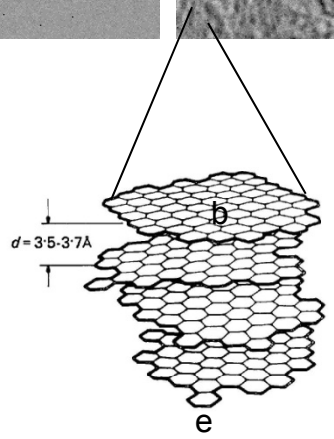
Visualizing black carbon









- BC is nanoheterogeneous
- internal and external mixture
- interior-perimeter effects
- fullerenic structure – anthropogenic emissions
- fringe analysis confirmed subtle differences
- variety of soot types in atmospheric aerosols

with help from Bond tutorial

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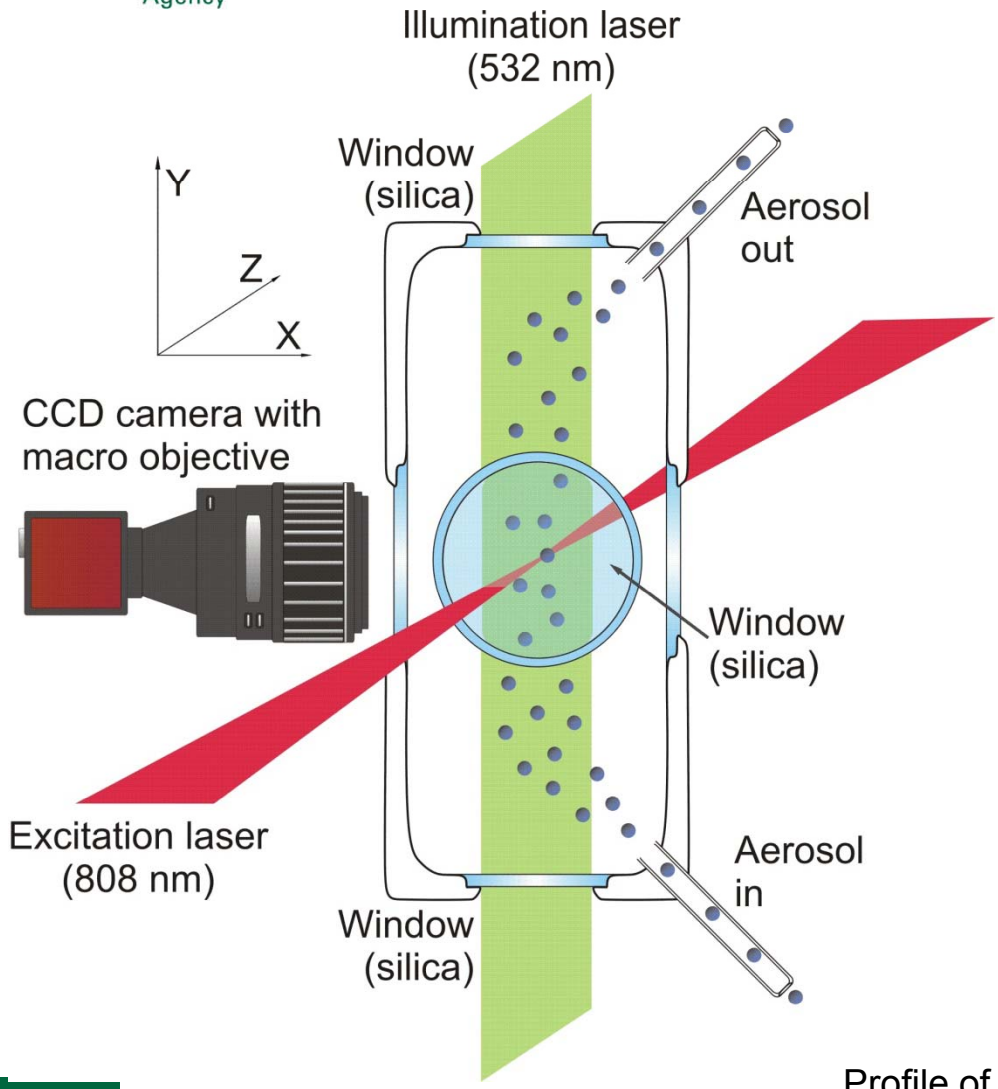
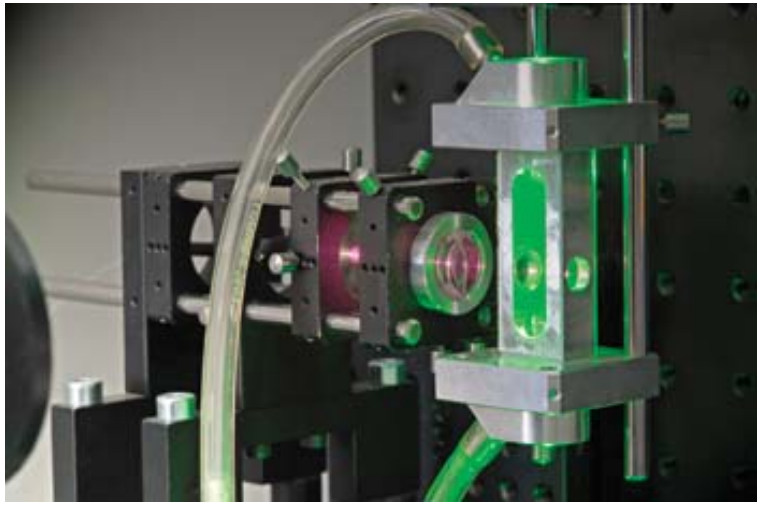
Experimental setup





120 mm

Photo of the Setup
(phototonics spectra 4/2008)

Profile of the illuminaton laser is modified to a thin layer
to observe only the by the excitation laser affected particles

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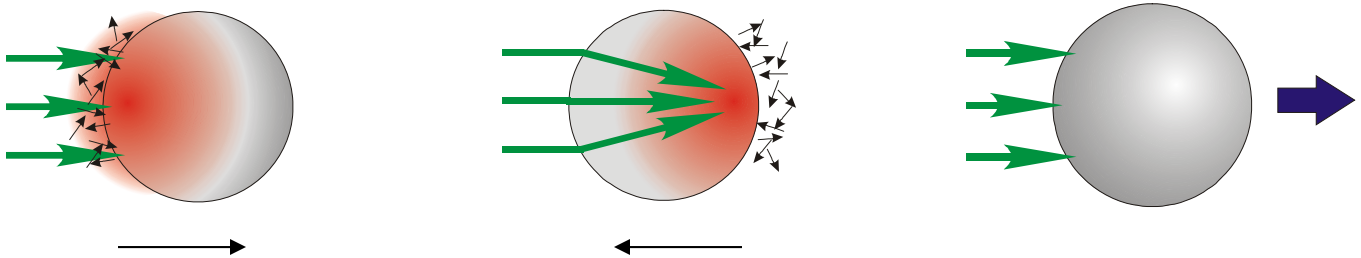
Experimental phase optical and BC particle measurements

photothermophoresis | direct photophoresis

Strongly Absorbing | Weakly Absorbing | Transparent



Photothermophoresis occurs when a temp. gradient within the particle leads to a movement

Photophoretic Velocimetry for the Characterization of Aerosols
Christoph Haisch,, Carsten Kykal, and, Reinhard Niessner
Analytical Chemistry **2008** *80* (5), 1546-1551

in development at TUM

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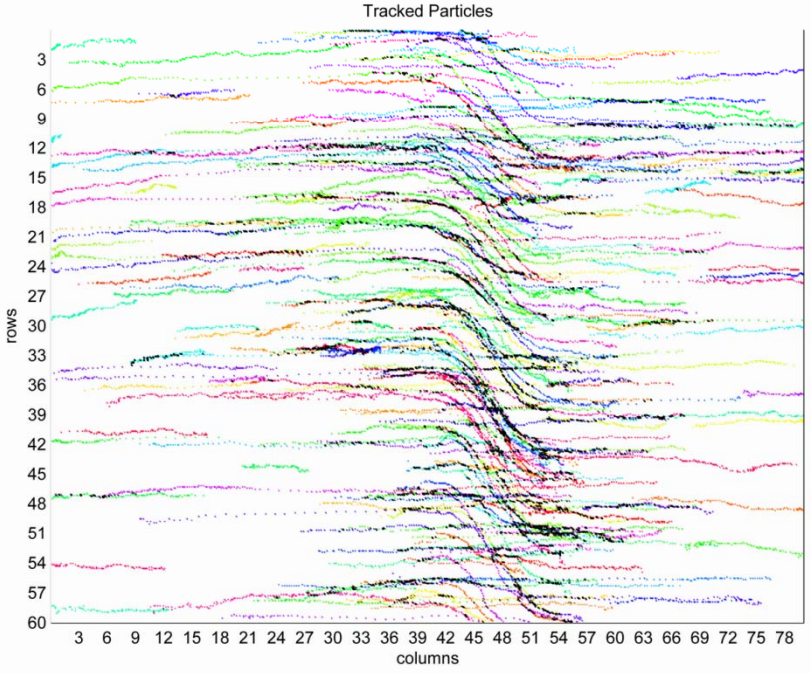
Results



tracking results (single experiment)

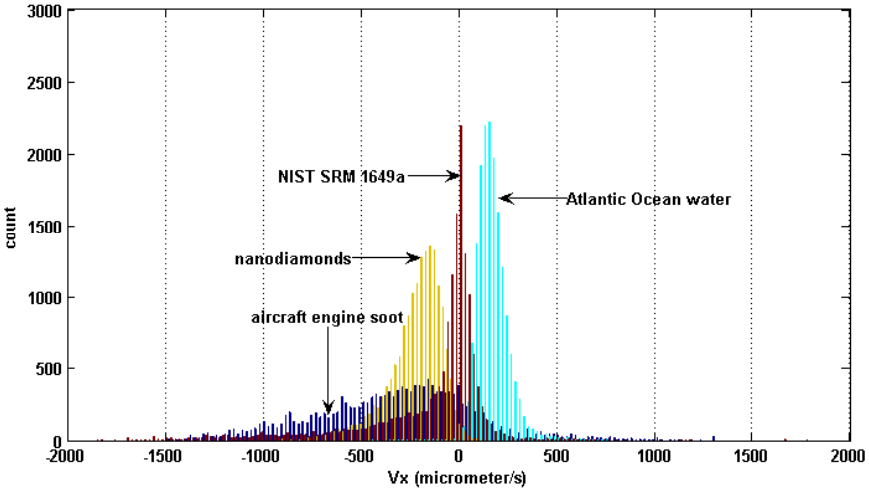


Photo-thermophoresis as a new tool for aerosol characterization. Haisch, C., Opilik, L., Hays, M., and Niessner, R.. (2009) Journal of Physics: Conference Series, in review.

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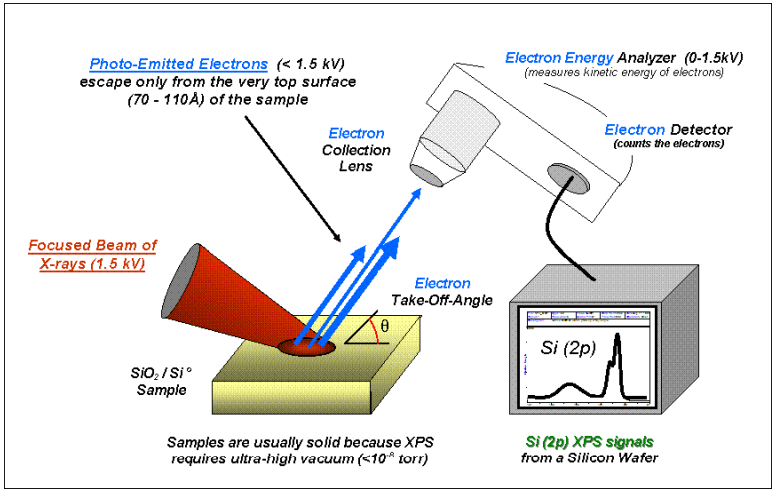
XPS technique and experimental details

- measured difference between ejected electron energy and incident beam = binding energy
- 1-10 nm sample depth
- survey scan and high resolution scan
  - elements determined to within ±0.1% (atomic)
  - HR scan for carbon bonding states and functional groups (10 sweeps 7 cycles)
  - curve fit C1s binding region
  - Lorentzian and Shirley fit



- examined emissions from plant-, institutional-, and residential-scale oil boilers, diesel and bio-diesel engine exhaust, wildfire, and aircraft engines

rarely used

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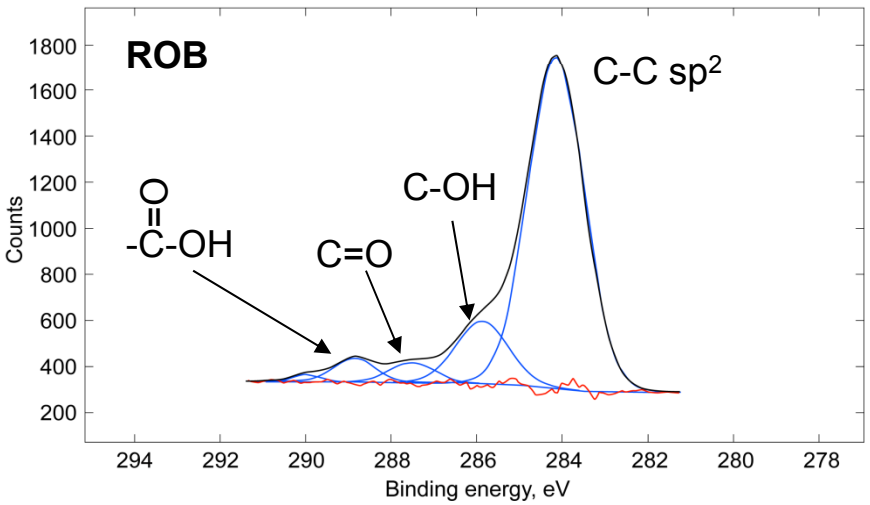
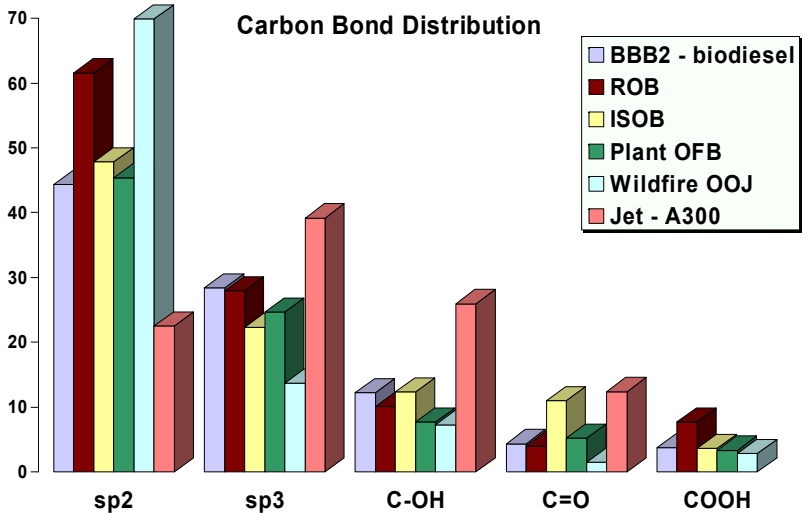
XPS (ESCA) for aerosol surface chemistry

high-resolution scan over C1S region





- percentages of carbon atoms apportioned to oxygen functional groups
- slight shift in C1s binding energy indicate different oxygen functional groups
- different carbon bonding states at the particle surface

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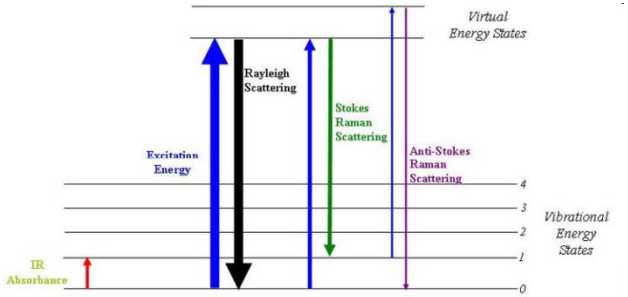
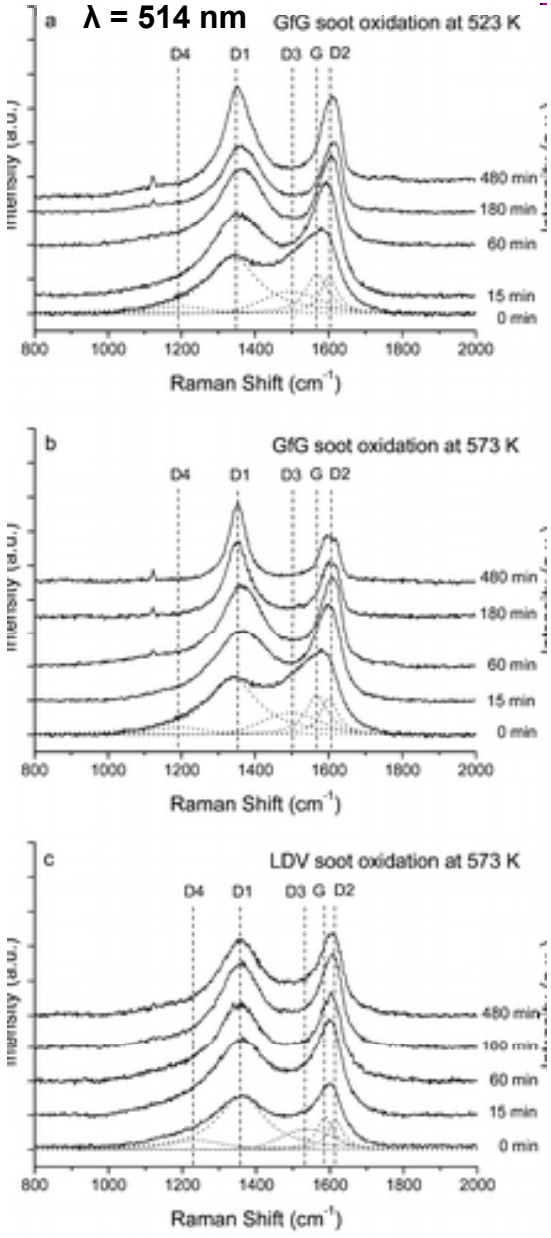
Raman spectroscopy



- specific to vibrational and rotational modes
- sensitive to electron clouds and bonds
- ground state >>> vibrational energy state

- chemical structure and soot reactivity



- defect (D) and graphite (G) peaks
  - G – ideal graphite
  - D1 – vibration mode graphene e
  - D2 – vibration surface graphene
  - D3 – amorphous, organics
  - D4 – disordered graphite and sp^3

Ivleva et al. EST **2007**

with help from Wikipedia

rarely used

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Upcoming BC Investigation: Stationary Diesel Generators

- Three different generators will be tested with and without after-market, post-combustion emissions controls for emissions factors
  - o ~300hp, 500hp, and 700hp diesel generators
  - oPost-combustion controls will vary but will fall within the categories of:
    - ➢ Active DPF
    - ➢ Ceramic
    - ➢ Oxidative catalyst
- Instrumentation/Methodology to be used:
  - oAethlometer
  - oPhotoacoustic
  - oLII
  - oThermal-optical (NIOSH5040 or IMPROVE)
  - o CEM benches to monitor combustion gases
  - o PM mass via teflon filter collection

After-market active DPF installed on diesel generator (photo courtesy of Rypos)

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Refine thinking to climate-relevant properties of PM

- likely interlaced with metals and organic matter over a strongly adsorbing matrix
  - i.e., BC is not alone
- organic matter on PM is light absorbing
  - nitrated and aromatic aerosols
- uneven surface coverage of chemical groups
  - very poor knowledge of surface chemistry in general
- atomic order gives rise to nano- and micro-structure which changes conformation and binding properties of soot
- photophoretics suggests physical and chemical properties impacts optical properties

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Conclusions

- Selection of BC instrument depend on aerosol sample being taken and information needed
- Instruments can be designed, modified, and outfitted to solve specific problems
- Advancements are being made
  - Newer instrumentation will be available
- Source aerosol emissions are studied relatively less than atmospheric aerosols