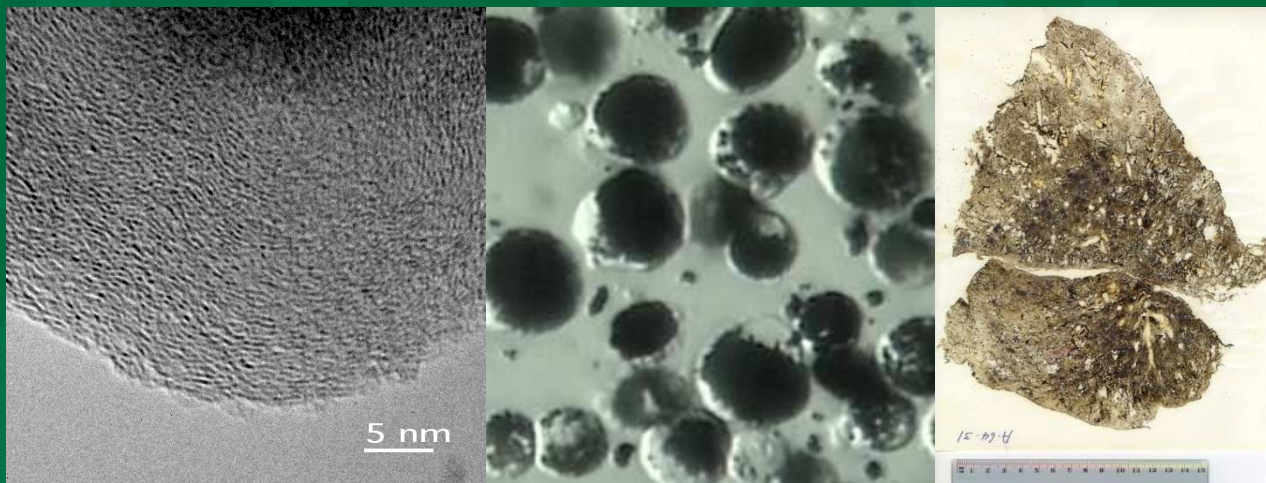


## BC measurement activities at the US EPA (ORD-RTP)

*Michael D. Hays*



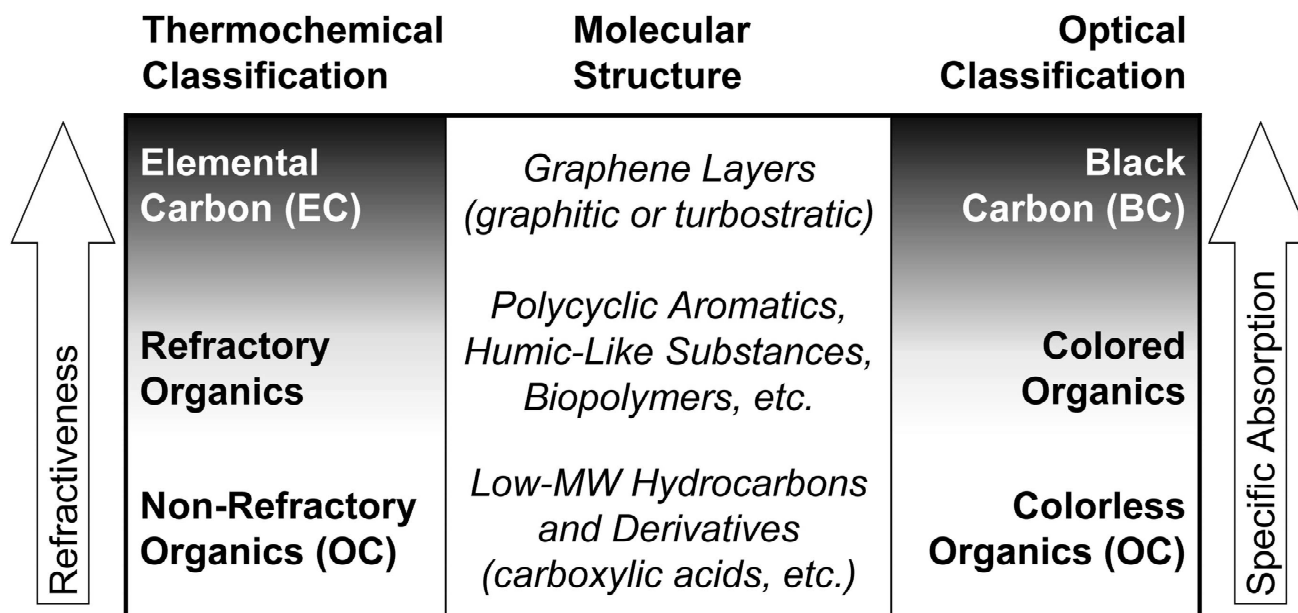
## Black carbon defined (and debated)

- **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<sub>2.5</sub> component
  - anthropogenic and biomass combustion sources

## Relevant terms

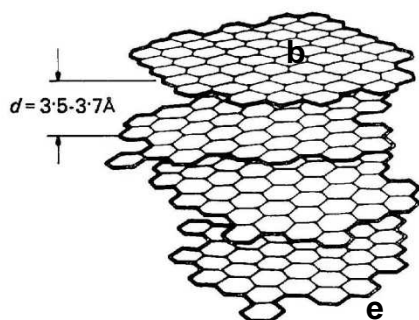
- **black carbon** (BC) – light absorption, optical properties
  - $sp^2$ -hybridized carbon
  - elemental carbon – thermal-optical properties
  - soot or char (combustion related aggregates)
  - light absorbing carbon – includes organic carbon
- 
- See Andreae and Gelencsér (2006) Atmos. Chem. Phys. 6, 3131-3148 for more definitions and proposed convention
    - $BC_e$  and  $EC_a$

## Carbon classification by analytical method



different sources emit these in different proportions

## Black carbon generation



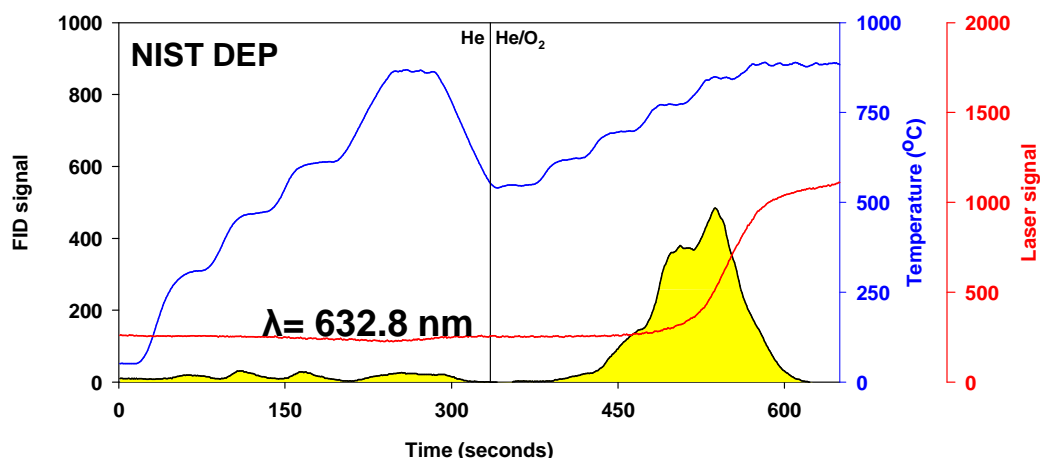
- BC forms in fuel-rich, poorly mixed hot (1600 °K+) flames
  - from fuel-nascent PAH; H abstraction; or other mechanisms (C5)
  - other factors include flame residence time, metal catalysis etc.
- 
- proportion of b/e can effect adsorption, soot reactivity, wettability
  - soot is oxygenated; not graphite per se

## (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

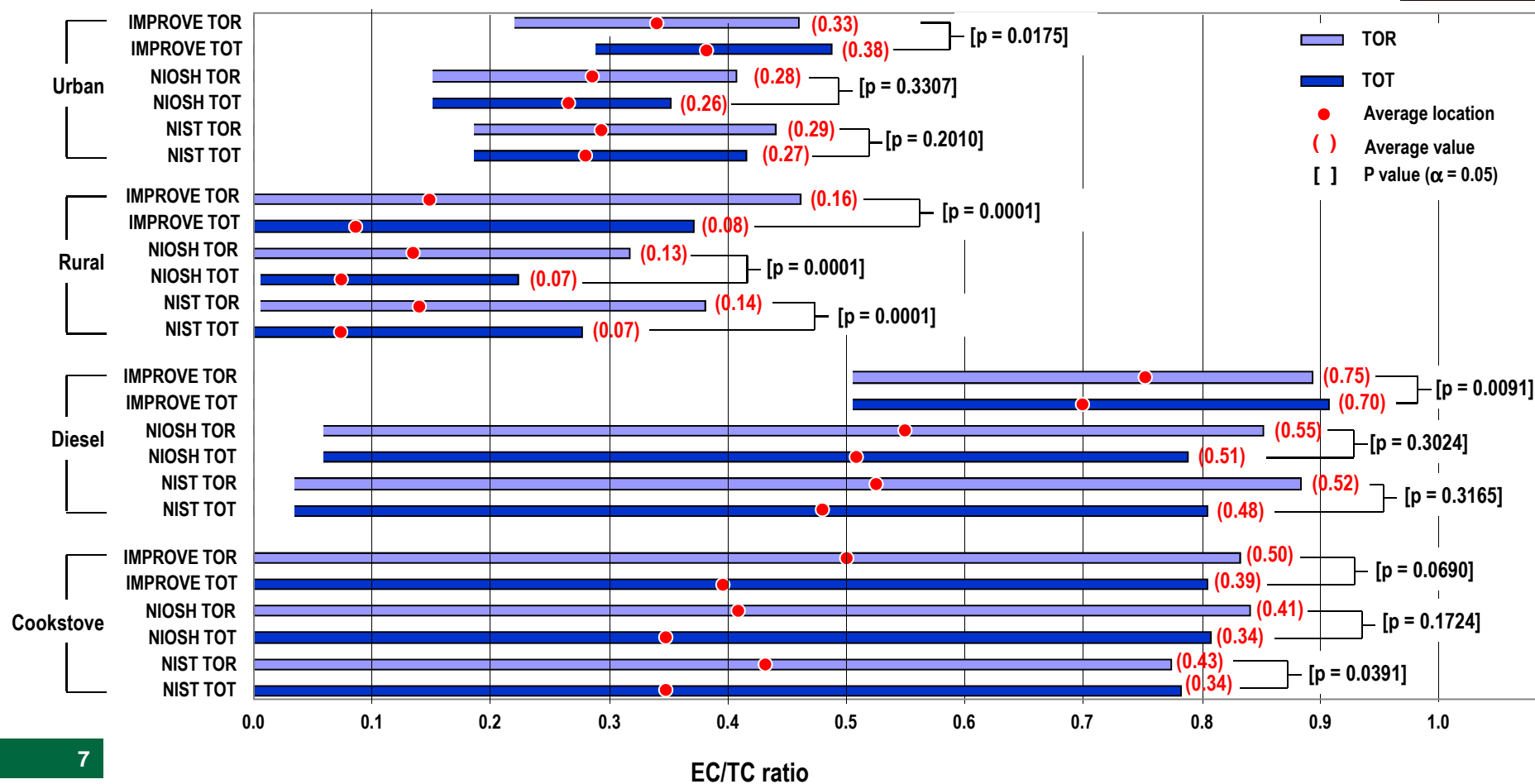
## Thermal and thermal-optical techniques

- semi-continuous (30 min,  $0.5 \mu\text{g}/\text{m}^3$ ) or integrated samples ( $0.2 \mu\text{g}/\text{cm}^2$ ) {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)

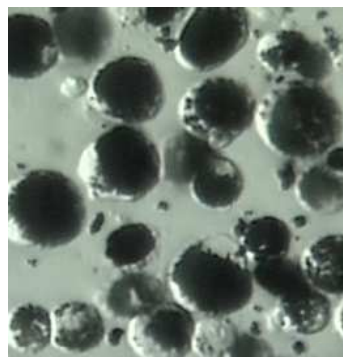
# Differences in the OC/EC Ratios that Characterize Ambient and Source Aerosols due to Thermal-Optical Analysis Bernine Khan, Michael D. Hays, Chris Geron & James Jetter (2012, 46: 127-137)



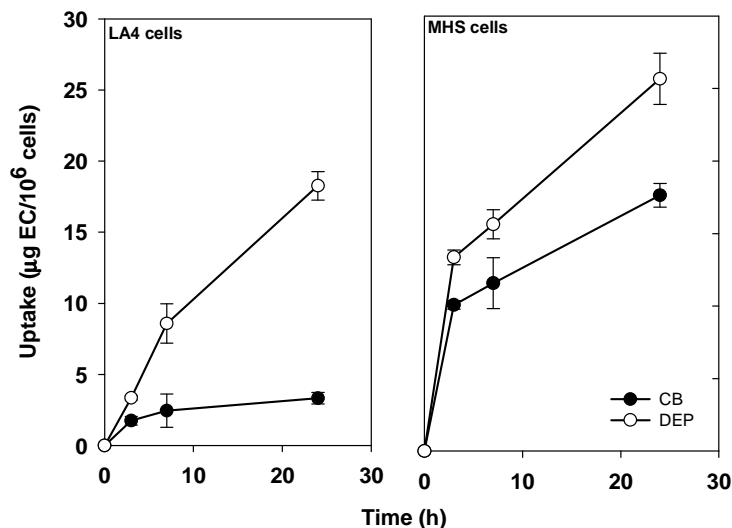


# Thermal-optical transmittance for EC in biological samples

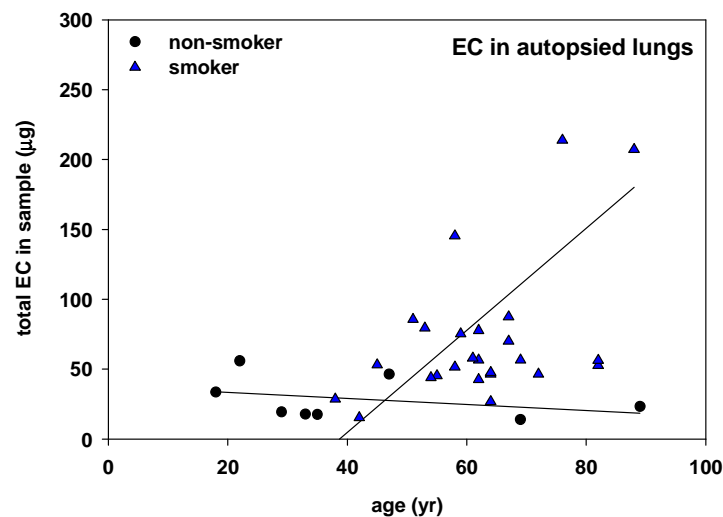
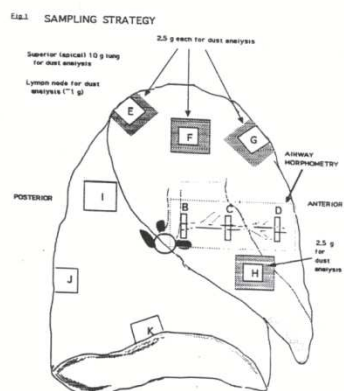
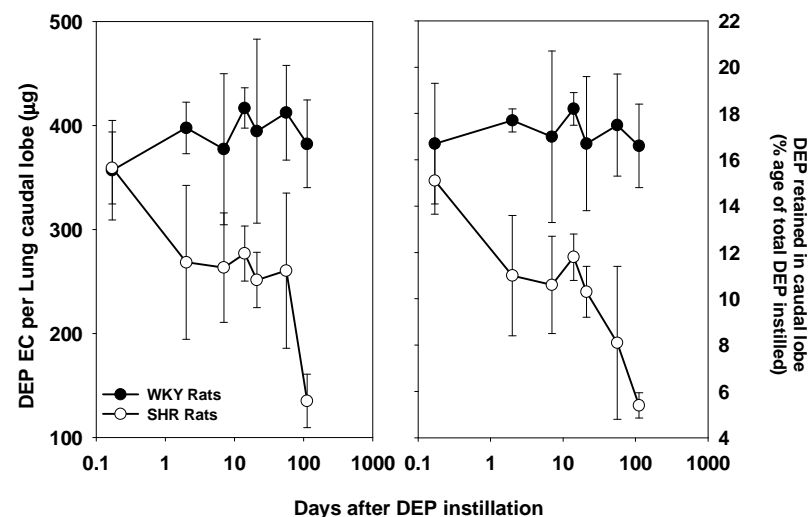
Saxena et. al., *Tox. Sci.* 111(2), p. 392 (2009); and *Biotechniques* 44, p. 799 (2008)



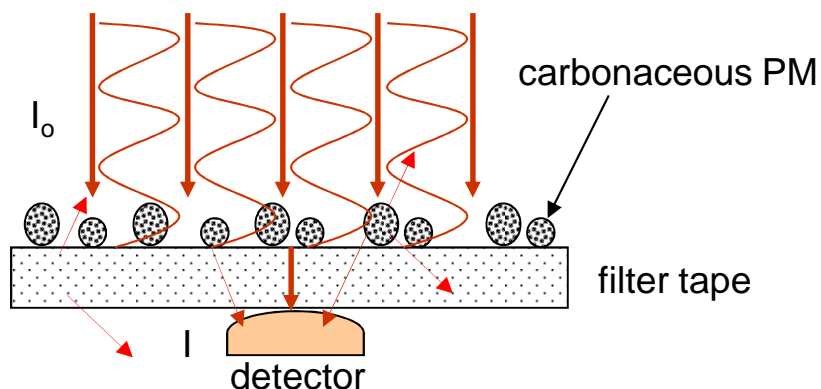
50 µg/mL DEP or CB



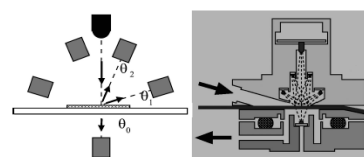
8 mg/mL NIST SRM 2975 (DEP)



## Light absorption techniques (filter-based)



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



Petzold et al. 2005

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

- on-line, semi-continuous methods
- $A = \ln(I_0/I)$  proportional  $\alpha_{\text{abs}} C$ 
  - $\alpha_{\text{ATN}} = \alpha_{\text{ABS}}/C_{\text{soot}} = 1\text{-}30 \text{ m}^2/\text{g}$
- dual or multiple wavelengths

### limits

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

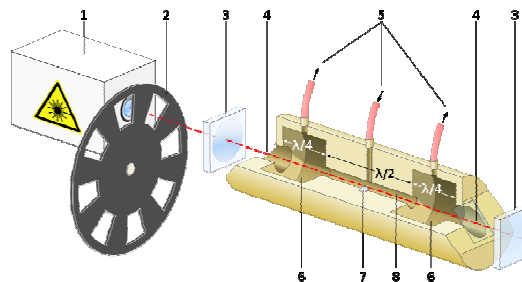
Technique	$\lambda$ (nm)	BC Sensitivity*	operation
Aethalometer	370, 470, 520, 590, 660, <b>880 (ir)</b> , 950	100 ng/m <sup>3</sup> at 1 min	transmission
PSAP	567	—	transmission, ref. filter, loading
MAAP	670	100-20 ng/m <sup>3</sup> at 2-30 min avg	sim. multi-angle, transmission, reflectance

\*depends on spot size

## 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  $\text{NO}_x$



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

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

### Droplet Measurements Technology [DRI]

- PASS-1 and -3
- one or three  $\lambda$  settings
- 50 ng/m<sup>3</sup> @ 1 sec integration

### AVL [TUM] (source emissions)

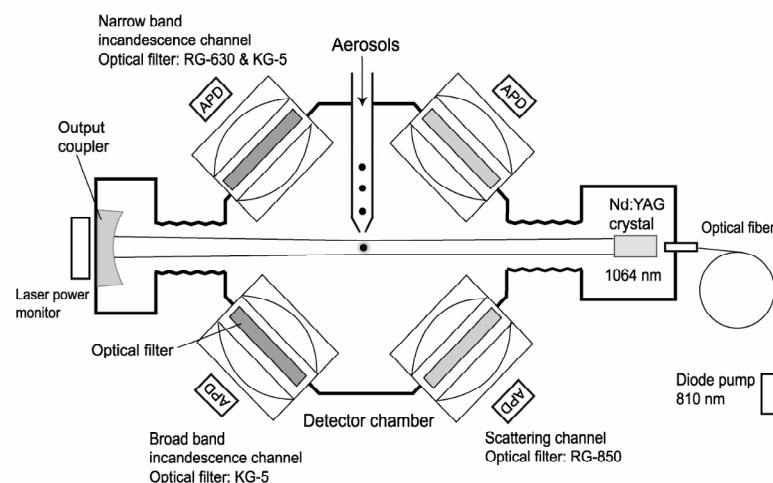
- $\lambda = 808 \text{ nm}$
- 5 µg/m<sup>3</sup> (up to 50 mg/m<sup>3</sup>)

## Laser-induced incandescence (LII)

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

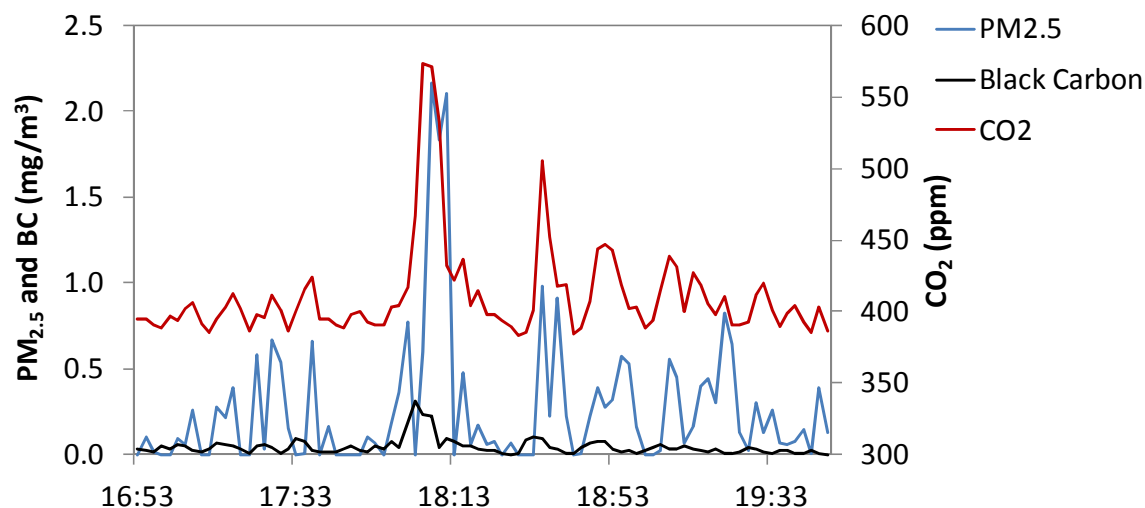
### Example: PS2 (Droplet Measurement Technologies)

- 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<sup>3</sup>



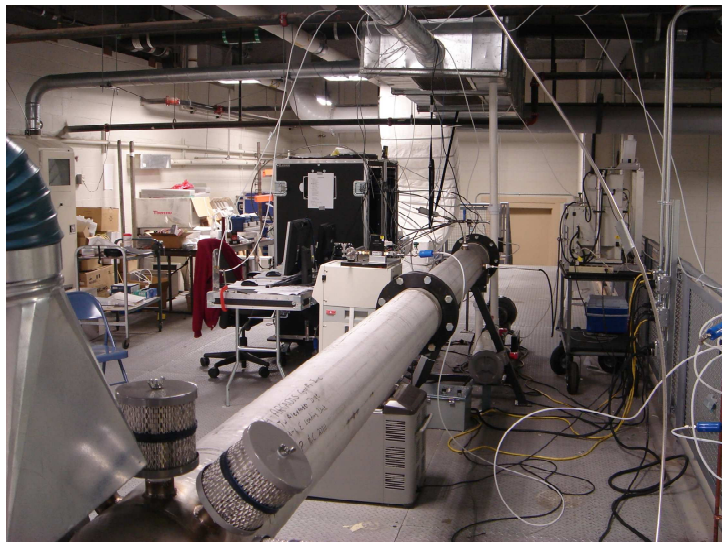
less widely used

## Aerostat sampling of PM<sub>2.5</sub>, BC, and CO<sub>2</sub> from prescribed forest fire – Eglin Air Force Base, FL (Brian Gullett)

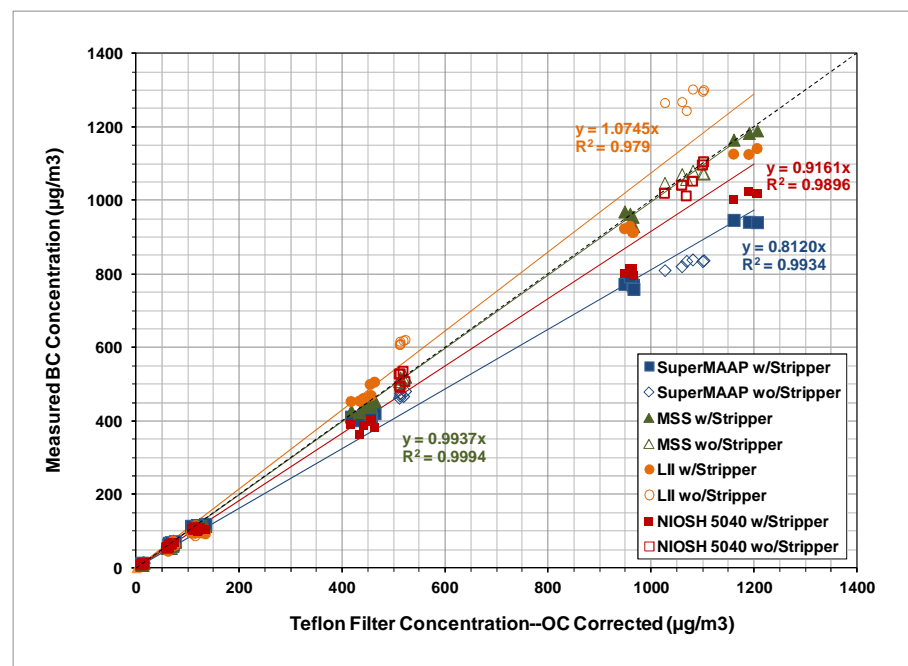


- 200-300 ft aloft
- vertical plume distribution
- 2-min average.
- ambient air CO<sub>2</sub> concentration: 390 ppm

## Characterizing PM emissions from commercial aircraft engines (John Kinsey)



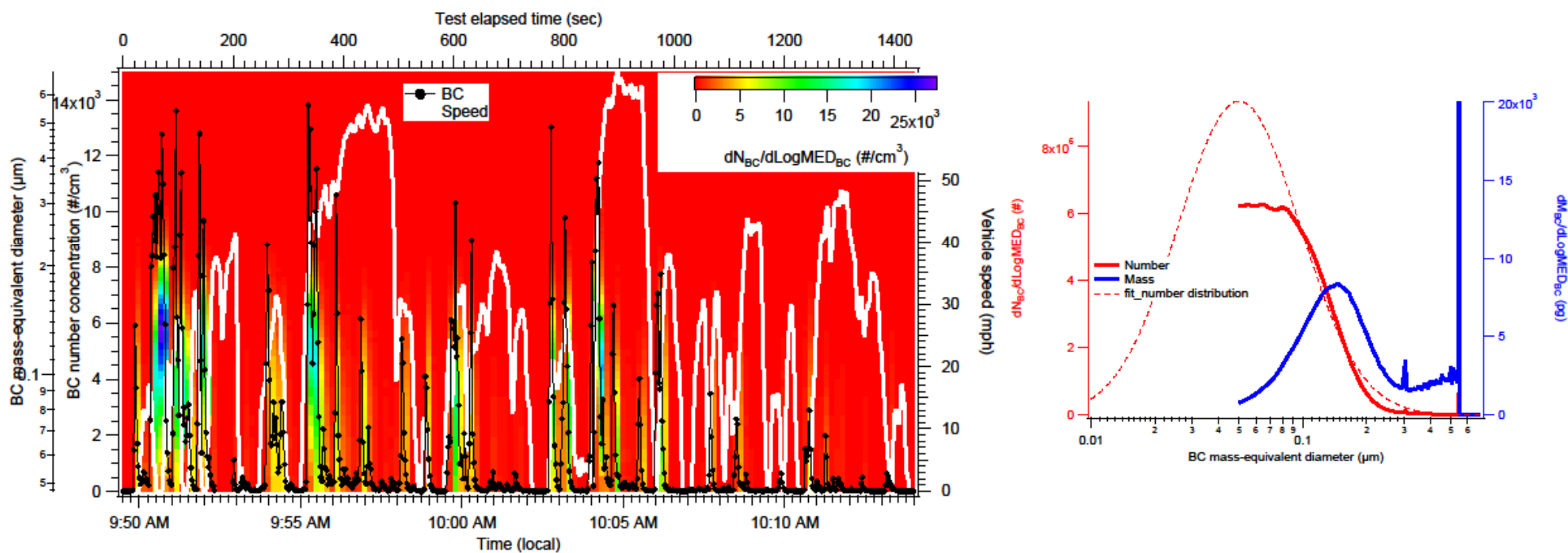
**Lab-scale flow tunnel system used for BC instrument evaluation.**



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



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



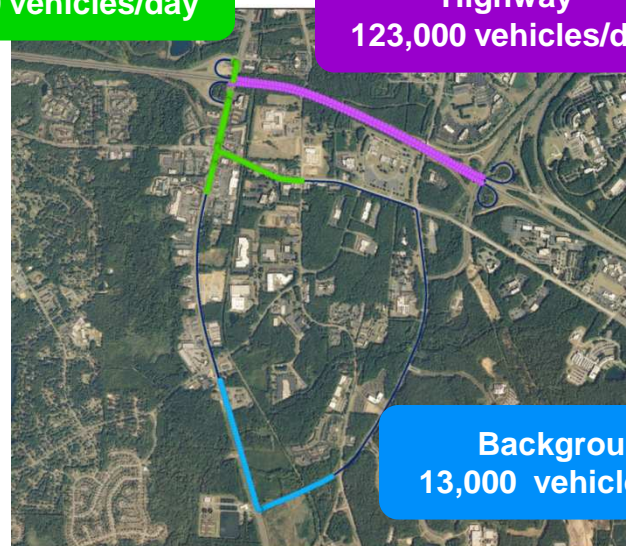


## On-road measurement of black carbon concentration and aerosol optical properties -- Amara Holder

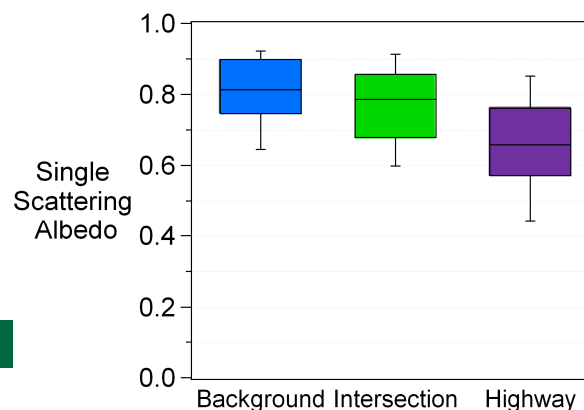
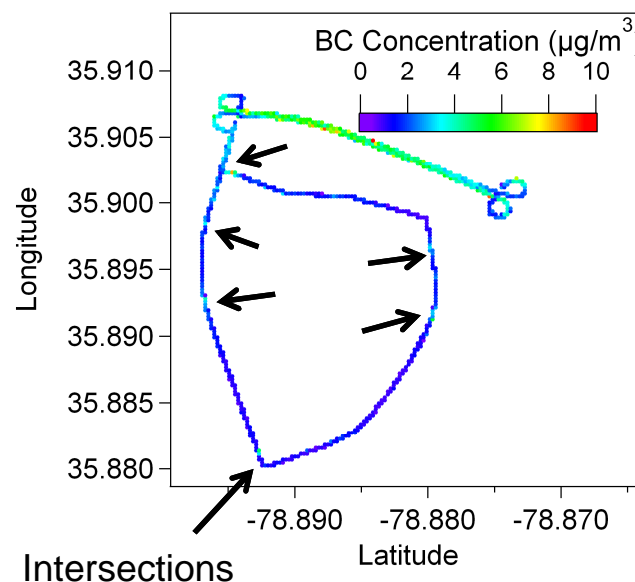
Intersection  
30,000 vehicles/day

Highway  
123,000 vehicles/day

Background  
13,000 vehicles/day



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.



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

Samples from the fire plume are identified by the CO<sub>2</sub> concentration and the combustion regime is identified by the angstrom exponent ( $\alpha$ ).

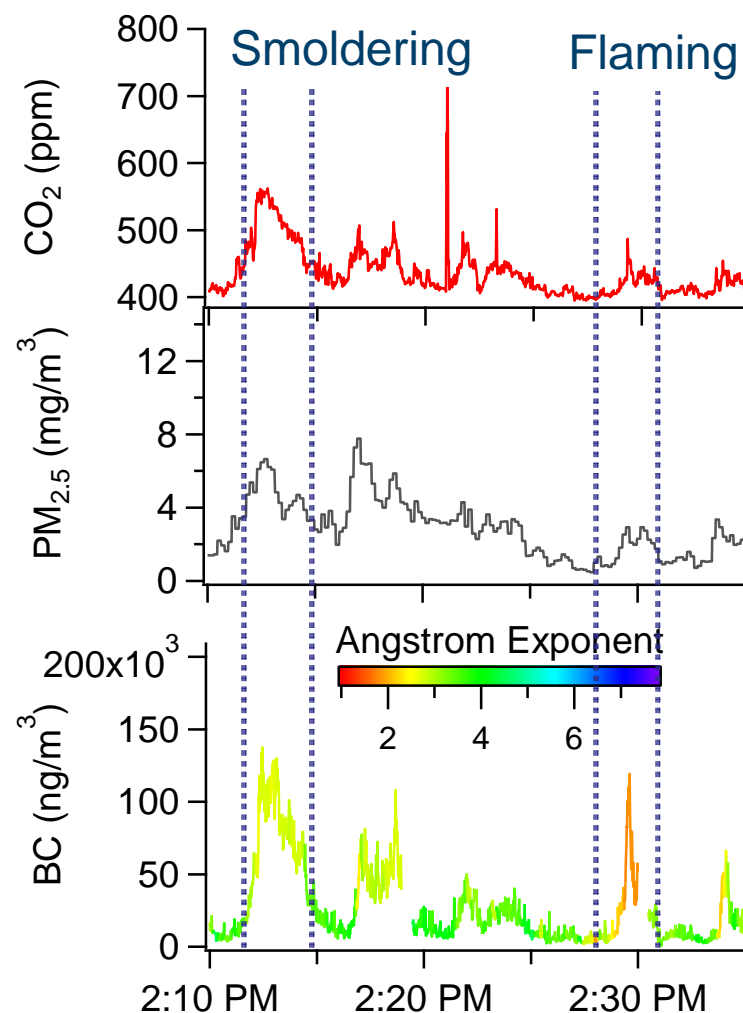
Flaming

$\alpha \sim 1$

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

Smoldering

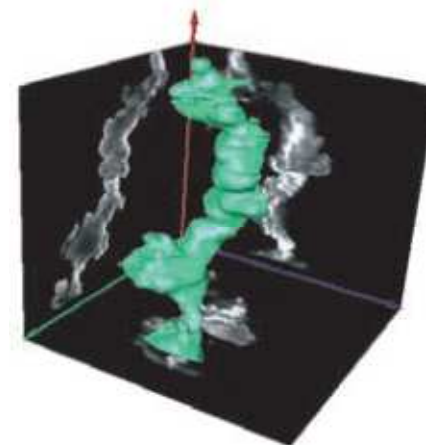
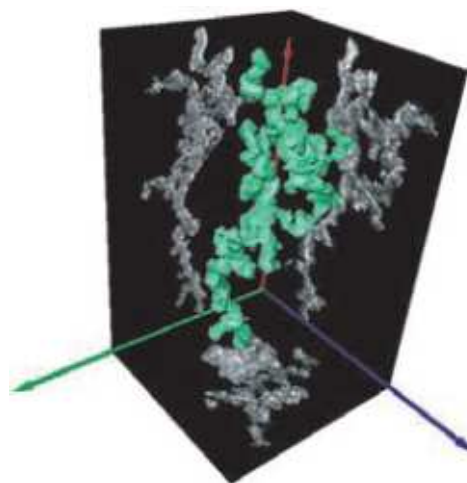
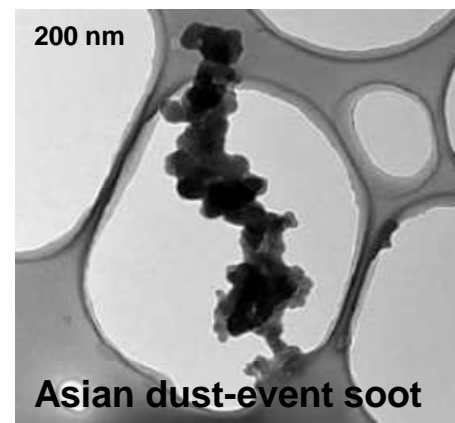
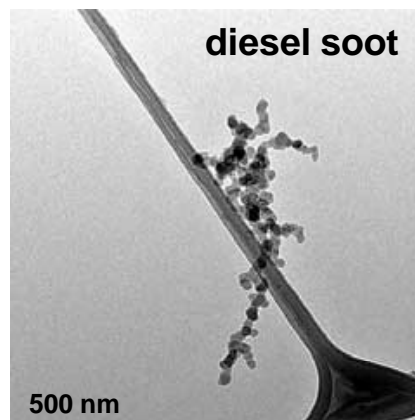
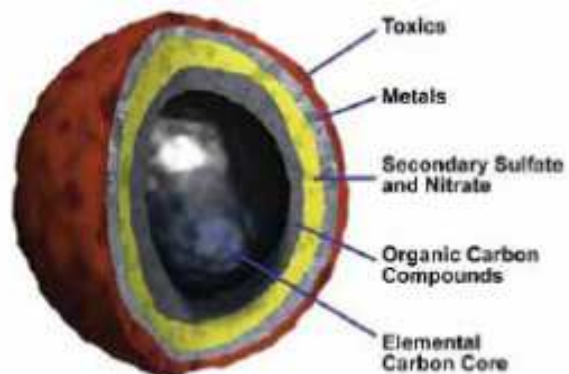
$\alpha > 1$



## Visualizing soot

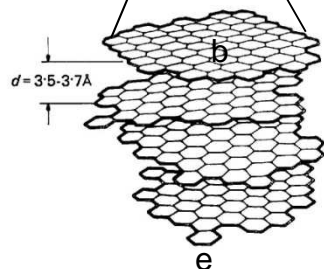
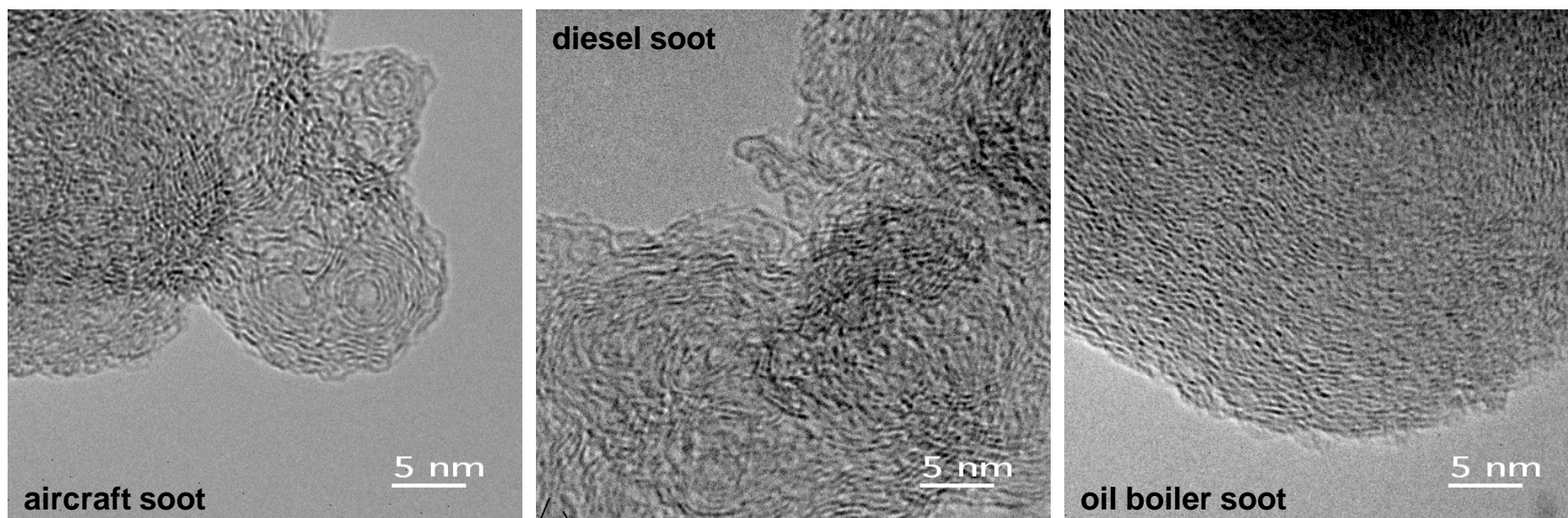
Electron tomography with TEM images  
Adachi et al. 2007, JGR

classic particle model



improved  $D_f$ ,  $R_g$ ,  $A_s/V$ ,  $k_a$

## 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



## Experimental setup

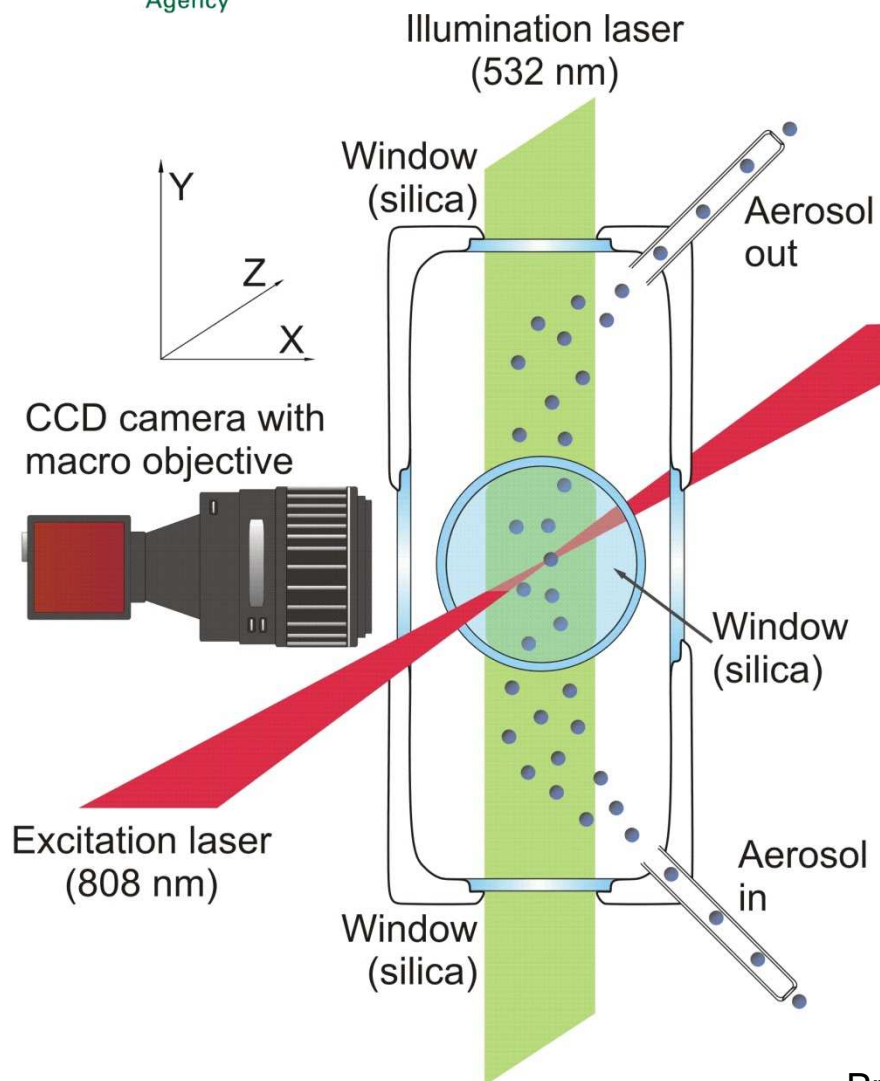
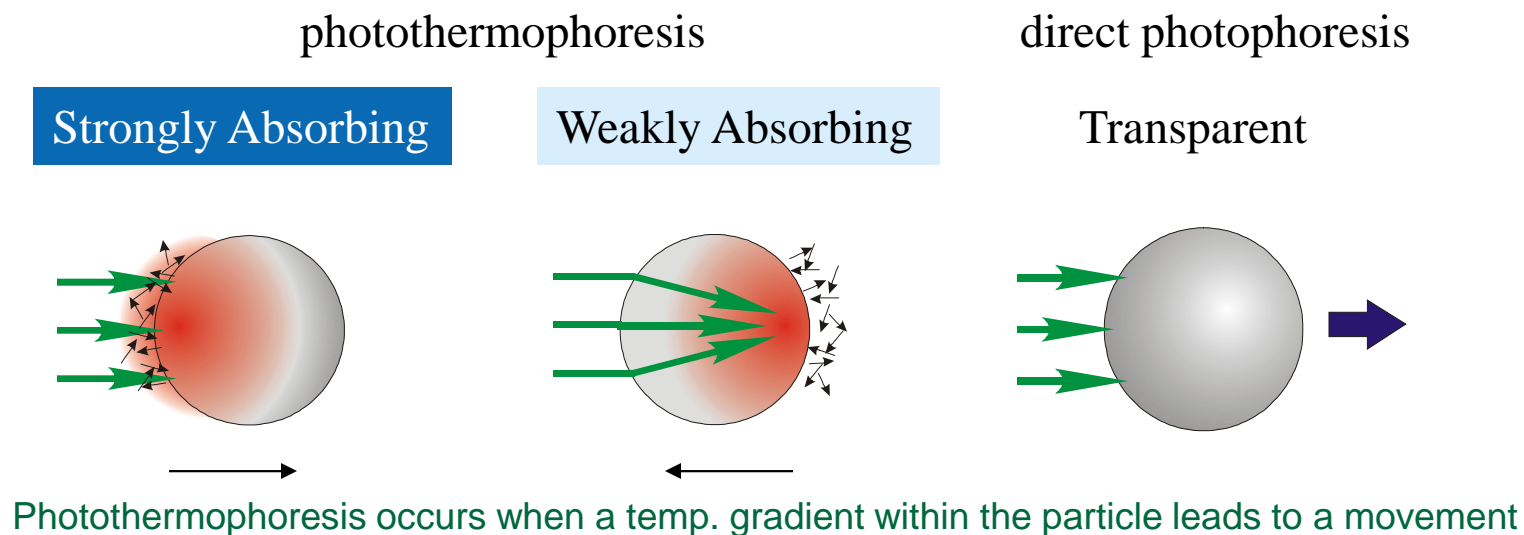


Photo of the Setup  
(phototonics spectra 4/2008)

120 mm

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

## Experimental phase optical and BC particle measurements

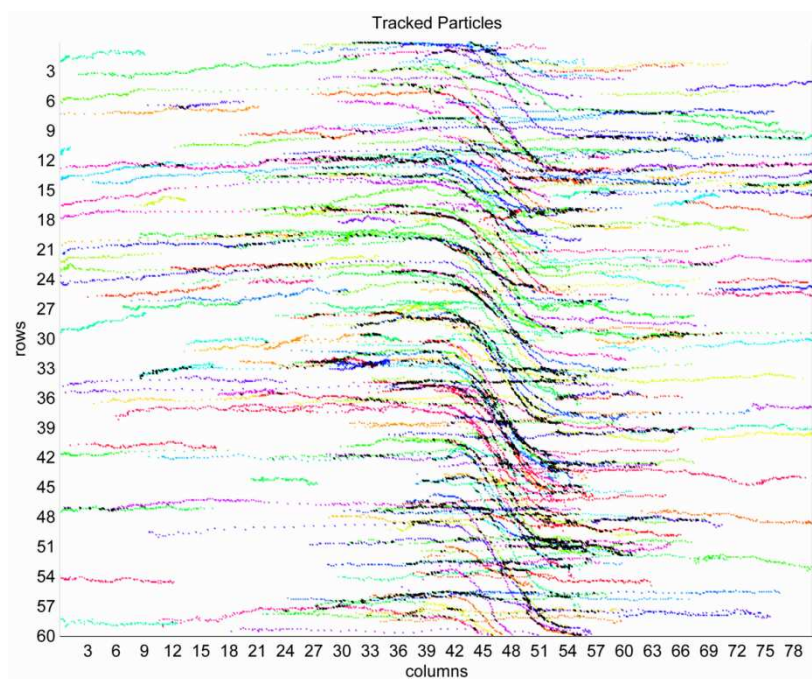


### Photophoretic Velocimetry for the Characterization of Aerosols

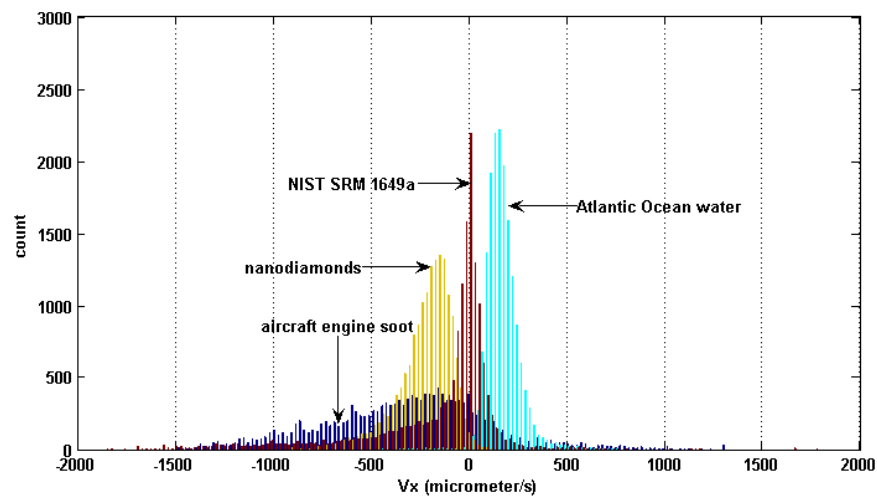
Christoph Haisch,, Carsten Kykal, and, Reinhard Niessner

*Analytical Chemistry* **2008** 80 (5), 1546-1551

## Results



tracking results (single experiment)

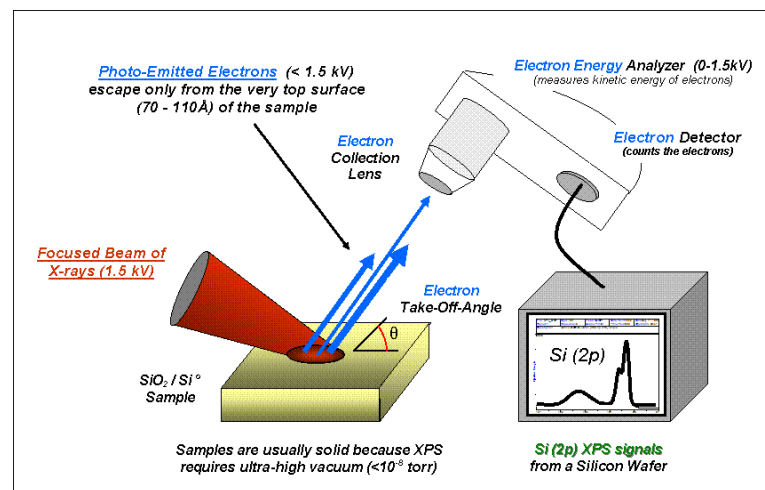


### Photo-thermophoresis as a new tool for aerosol characterization.

Haisch, C., Opilik, L., Hays, M., and Niessner, R.. (2009) Journal of Physics: Conference Series, in review.

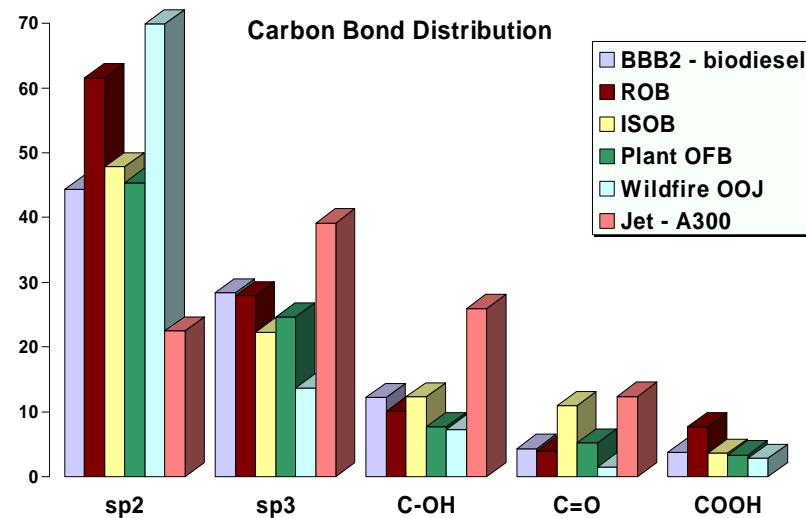
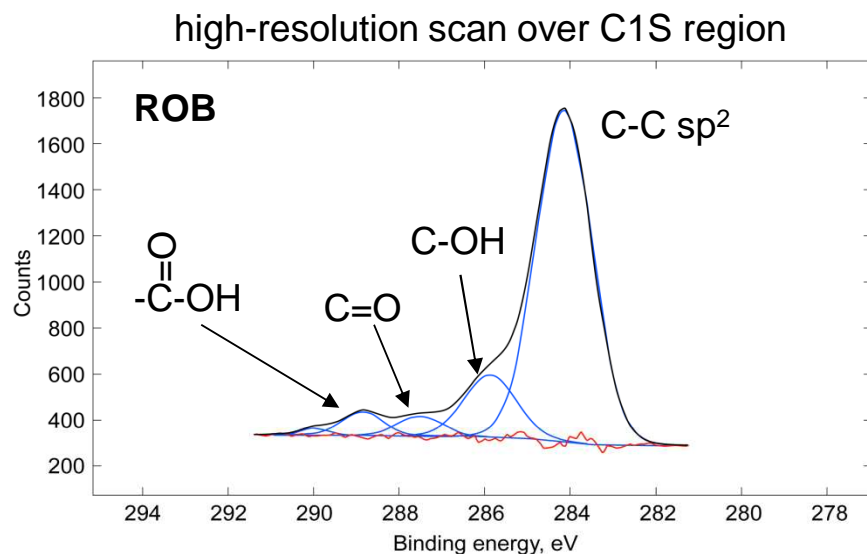
## XPS technique and experimental details

- 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  $\pm 0.1\%$  (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

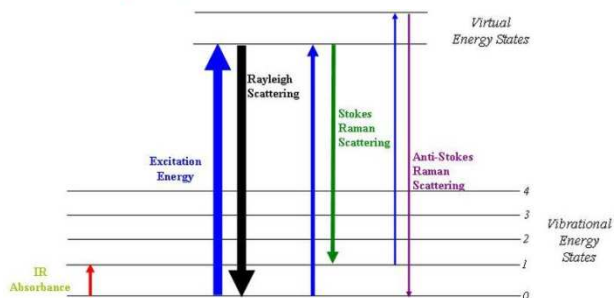
## XPS (ESCA) for aerosol surface chemistry



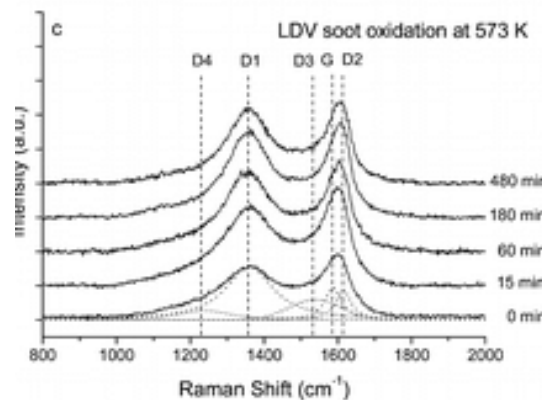
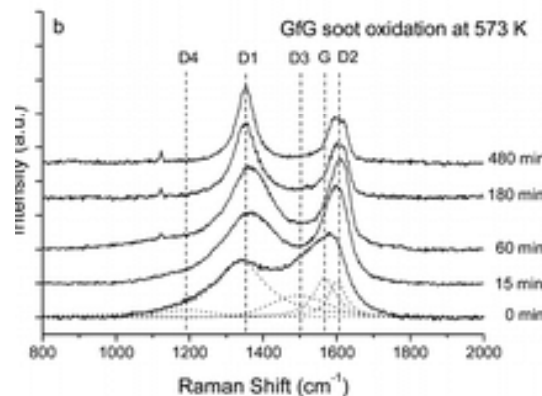
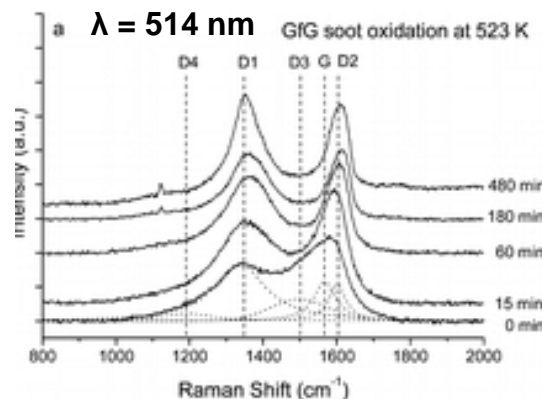
- percentages of carbon atoms apportioned to oxygen functional groups
- slight shift in C1s binding energy indicate different oxygen functional groups
- different carbon bonding states at the particle surface



## 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  $sp^3$





# Upcoming BC Investigation: Stationary Diesel Generators

- Three different generators will be tested with and without after-market, post-combustion emissions controls for emissions factors

- ~300hp, 500hp, and 700hp diesel generators
- Post-combustion controls will vary but will fall within the categories of:

- Active DPF
- Ceramic
- Oxidative catalyst

- Instrumentation/Methodology to be used:

- Aethlometer
- Photoacoustic
- LII
- Thermal-optical (NIOSH5040 or IMPROVE)
- CEM benches to monitor combustion gases
- PM mass via teflon filter collection



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

## Refine thinking to climate-relevant properties of PM

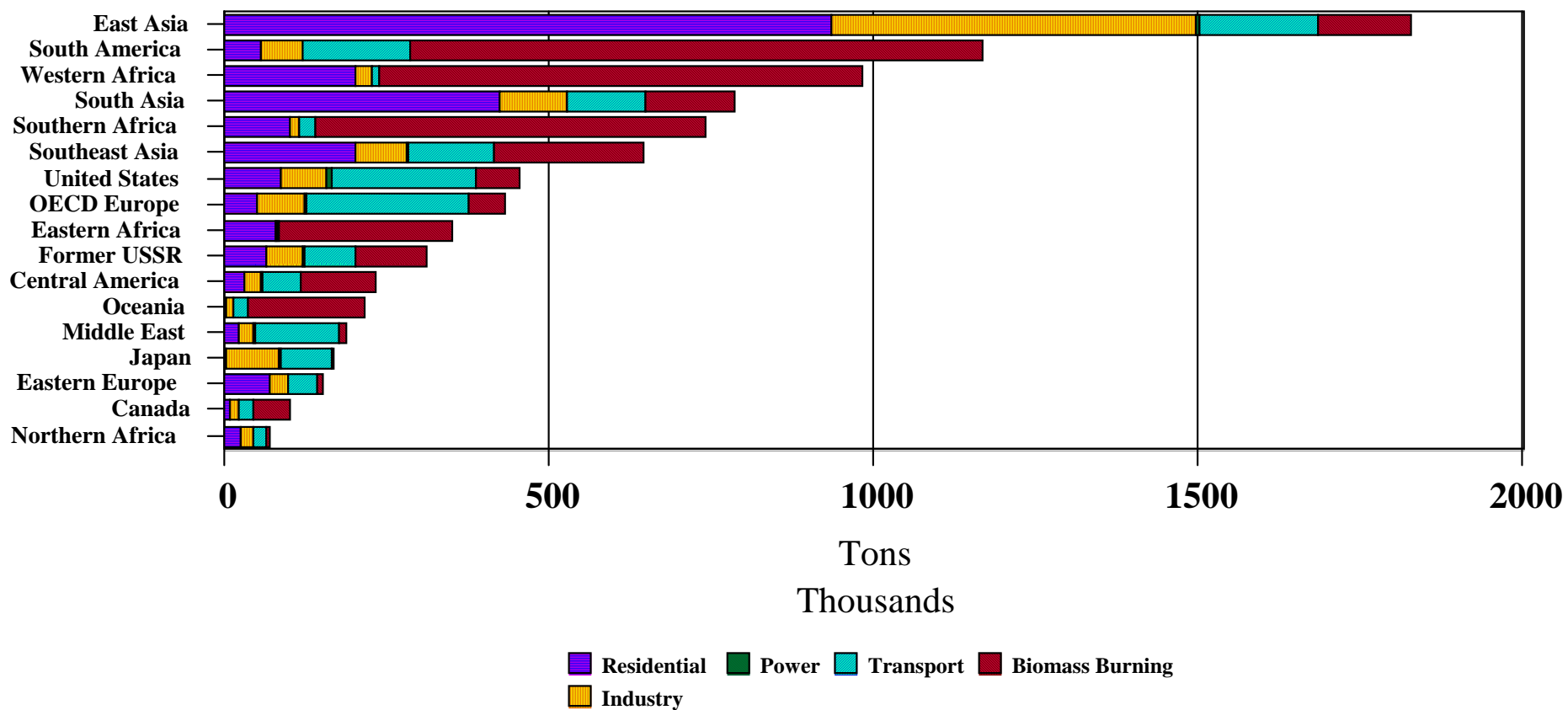
- likely interlaced with metals and organic matter over a strongly adsorbing matrix
  - i.e., BC is not alone
- organic matter on PM is light absorbing
  - nitrated and aromatic aerosols
- uneven surface coverage of chemical groups
  - very poor knowledge of surface chemistry in general
- atomic order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



## Conclusions

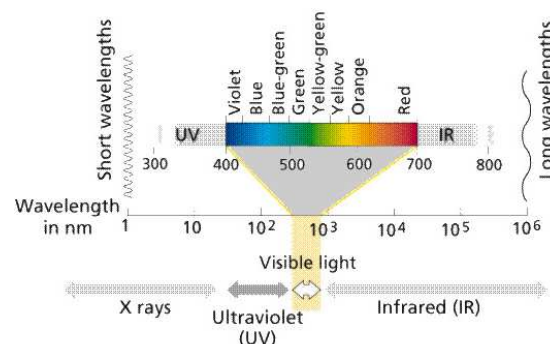
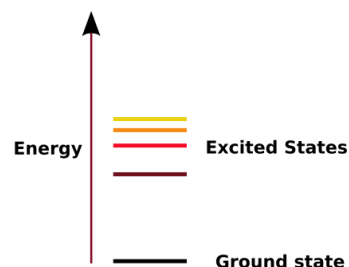
- Selection of BC instrument depend on aerosol sample being taken and information needed
- Instruments can be designed, modified, and outfitted to solve specific problems
- Advancements are being made
  - Newer instrumentation will be available
- Source aerosol emissions are studied relatively less than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

## ~ Year 2000 Global EC Emissions



## Optical properties of PM (terms)

- **light absorption** – photon energy taken up by e- and re-released as heat or light
  - spacing of electronic energy states depend on molecular structure (i.e., resonance state)
  - increasing conjugation of double bonds – aromatic ring systems – energy level spacing's decrease



- **refractive index** (n) – real and imaginary (i) parts that account for the effect of the bulk material on radiation
  - $\lambda$  dependent - dispersion and absorption loss [extinction coefficient {related to  $\alpha$ }]
- **extinction** = scattering + absorption
- **scattering albedo** = scattering/extinction
- **specific mass absorption coefficient or efficiency** ( $\alpha_{\text{ABS}}$ ) – directly related to BC mass
  - Depends on n,  $\rho$ , mixing state,  $\lambda$ , and particle size distribution