Light Absorbing Carbon from Combustion Sources and Its Effect on Health and Climate

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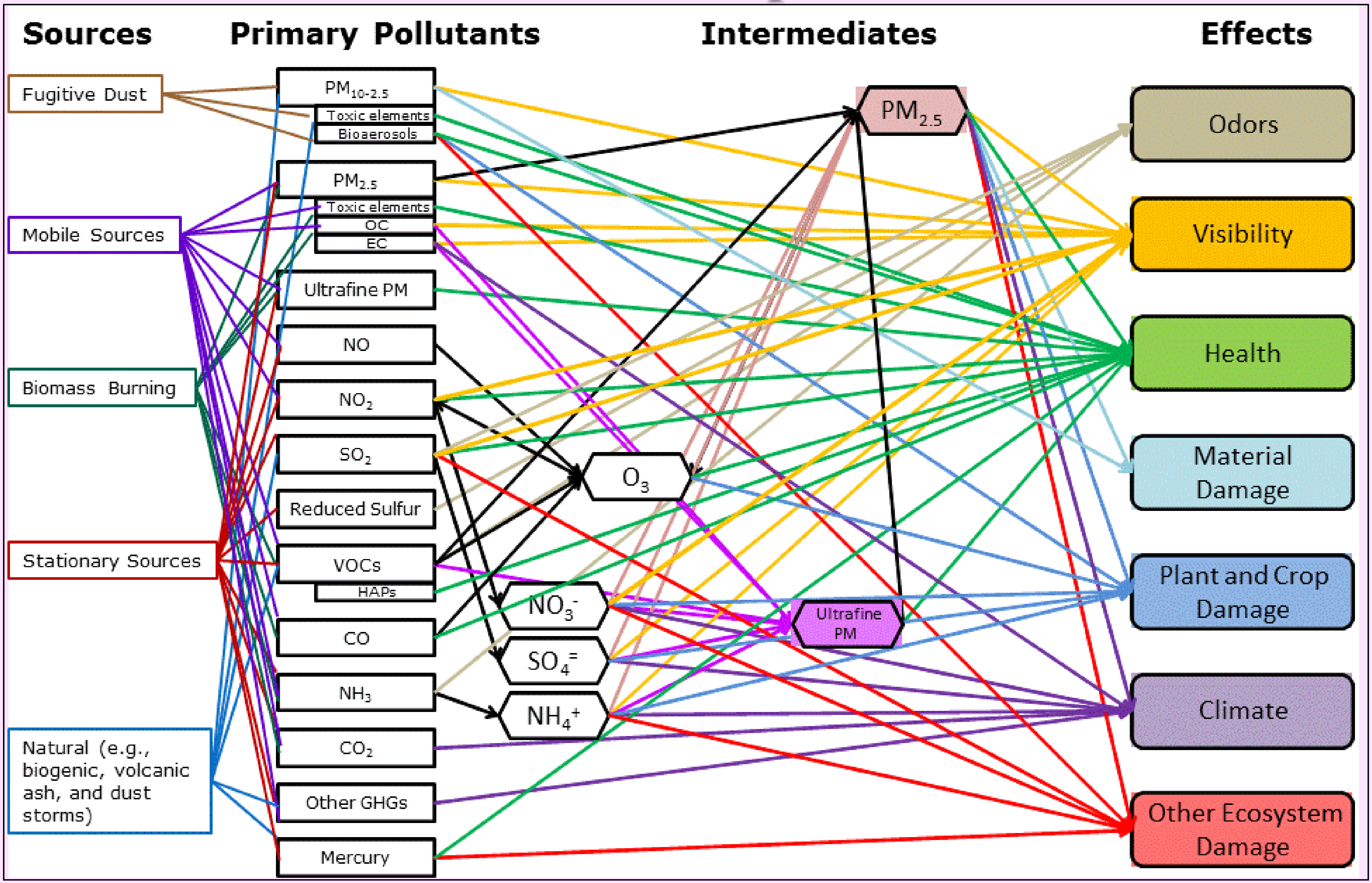
Objectives

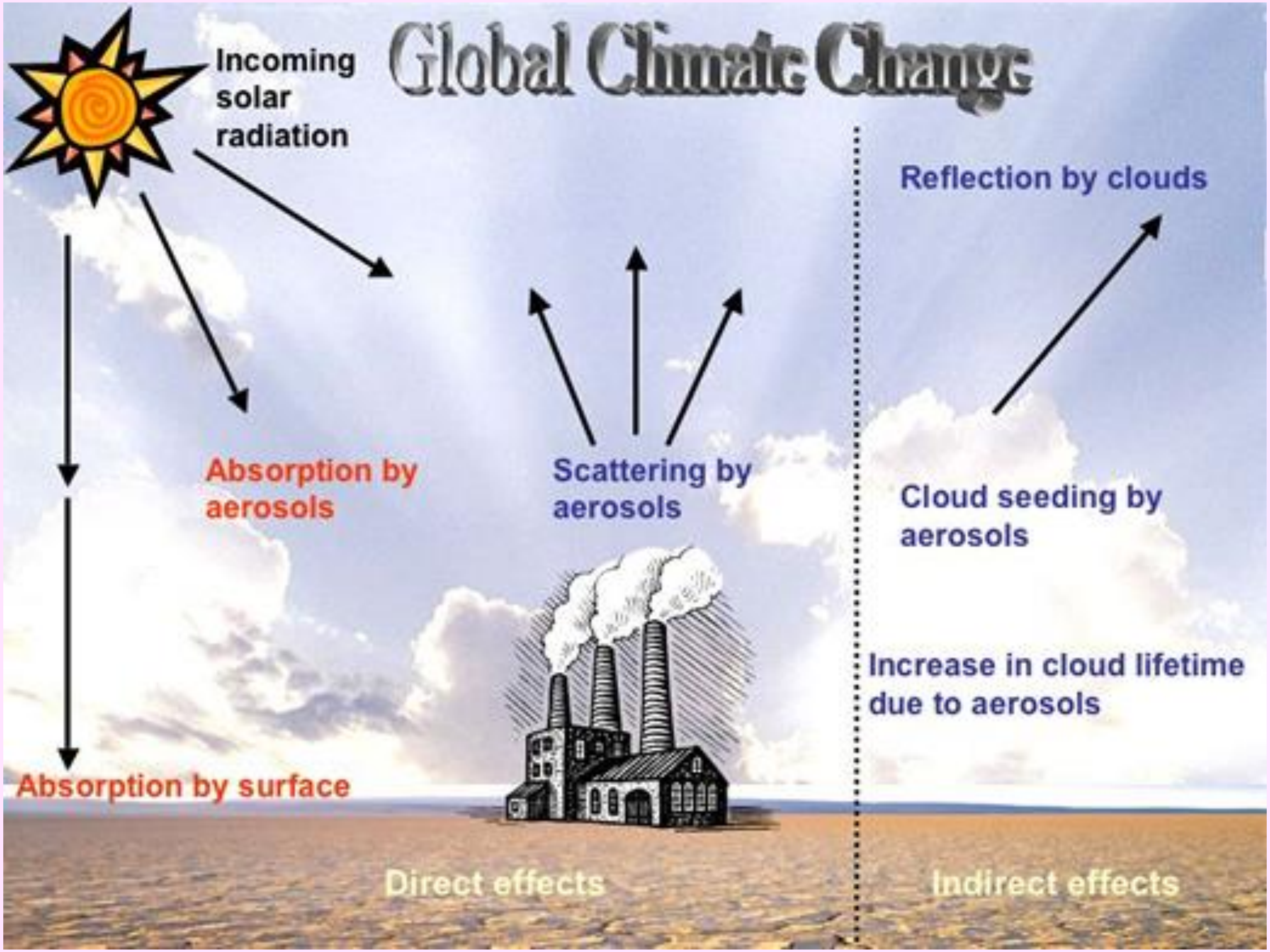
- Explain the effect of carbon on air pollution, health, visibility, and climate
- Introduce multiwavelength measurement of carbon to separate organic, elemental, and brown carbon (OC, EC, and BrC)
- Demonstrate how relative values of reflectance (R) and transmittance (T) can be related to separate brown carbon from black carbon.

Air pollution originates from multiple sources and cause multiple effects



Chow and Watson (2011) *Anal. Bioanal. Chem.*

Many aerosol effects are common for air pollution, visibility, and climate change



Carbonaceous aerosol plays a major role in air pollution, health, visibility, and climate

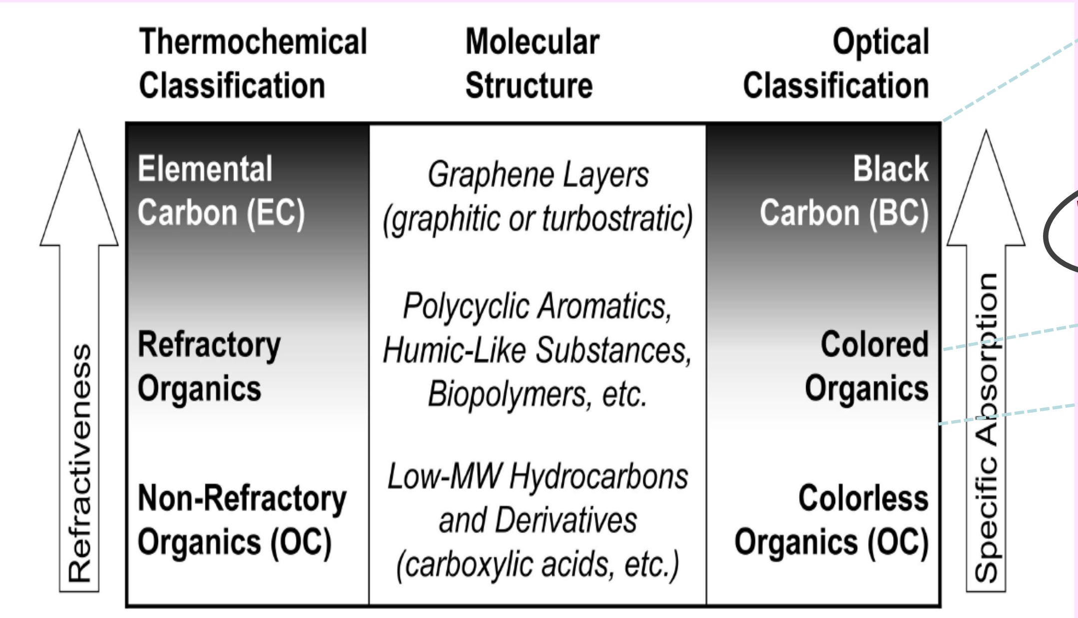
- **Biogenic Sources**
  - Viruses, bacteria, fungi, plant parts, pollens, and spores
  - Chemical conversion of terpenes and other biogenic volatile organic compounds (VOCs)
  - Wildfires

- **Anthropogenic Sources**
  - Fossil fuel combustion
  - Prescribed burns, woodstoves, and fireplaces
  - Cooking
  - Cigarette smoke
  - Roofing and tar pots
  - Geological material
  - Oxidation of man-made VOCs

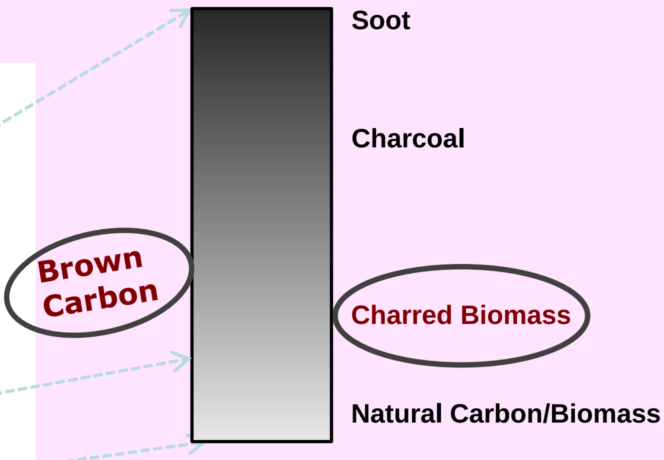
Mauderly and Chow (2008) *Inhal. Tox.*

Thermal, molecular, and optical properties of carbonaceous aerosol are complex

e.g., Biomass Combustion Products



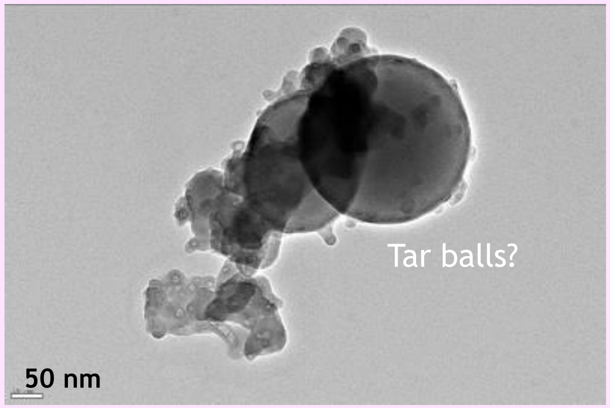
(Pöschl, 2003, *Anal. Bioanal. Chem.*)

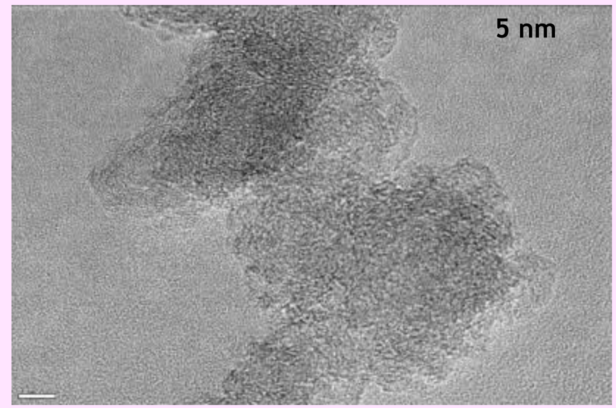


(Masiello and Druffel, 2003, *Geophys. Res. Lett.*)

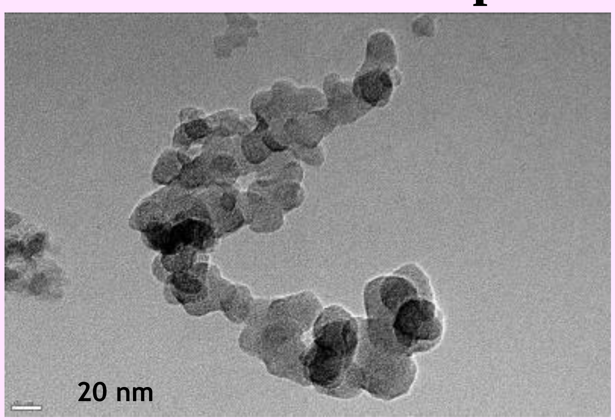
TEM[a] shows different morphologies between wood burning and diesel exhaust particles

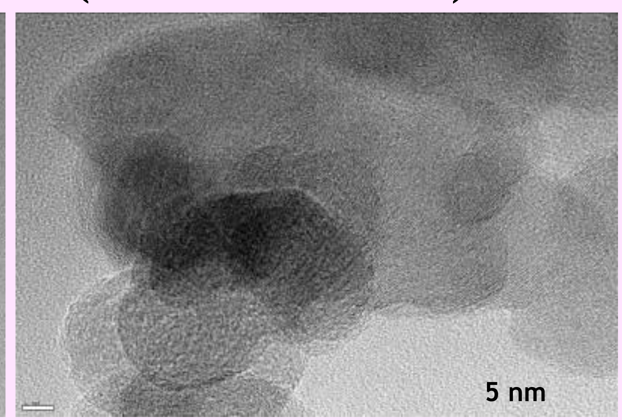
Wood Smoke Particles (OC mixed with char/soot)





Diesel exhaust particles (OC mixed with soot)

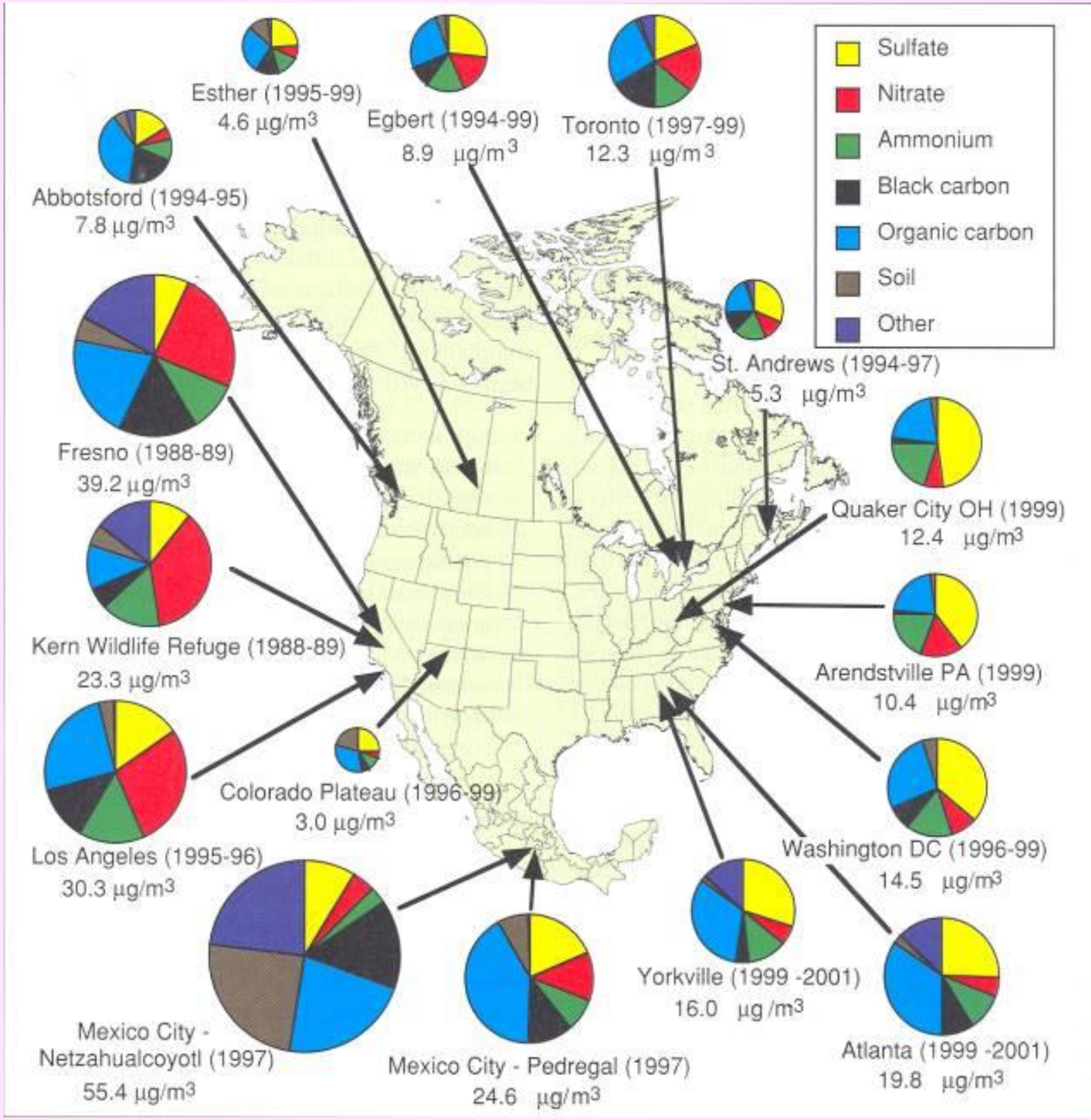




[a] Transmission electron microscopy

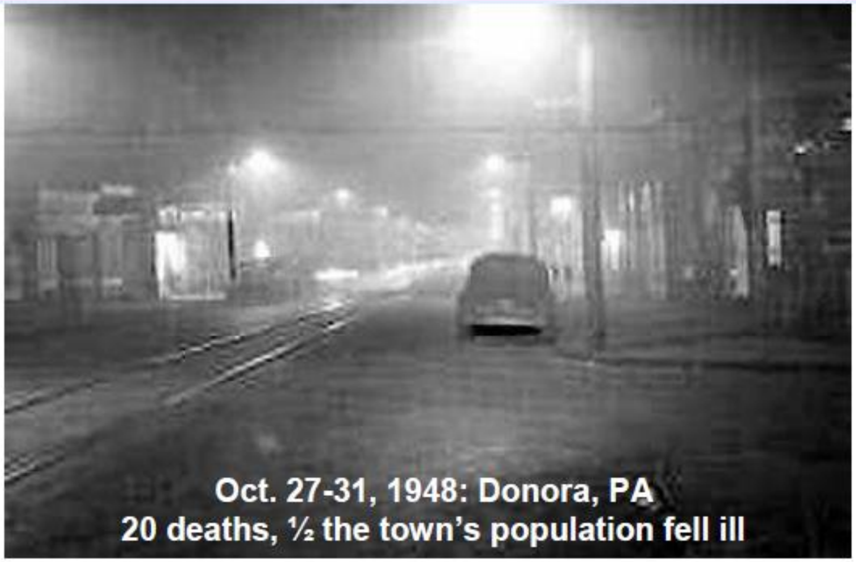
Carbon is a major component of atmospheric fine particles

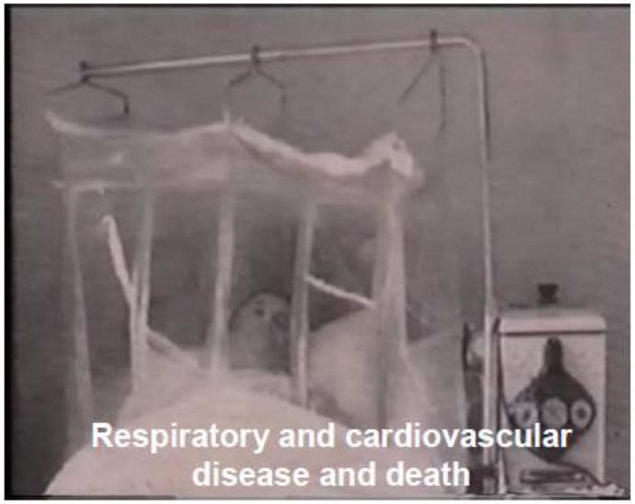
($PM_{2.5}$, EC, and OC absorb and scatter light)



NARSTO, 2004

Heavy smog has been associated with excess mortality rates since the 1930s (Killer Smog Episodes)





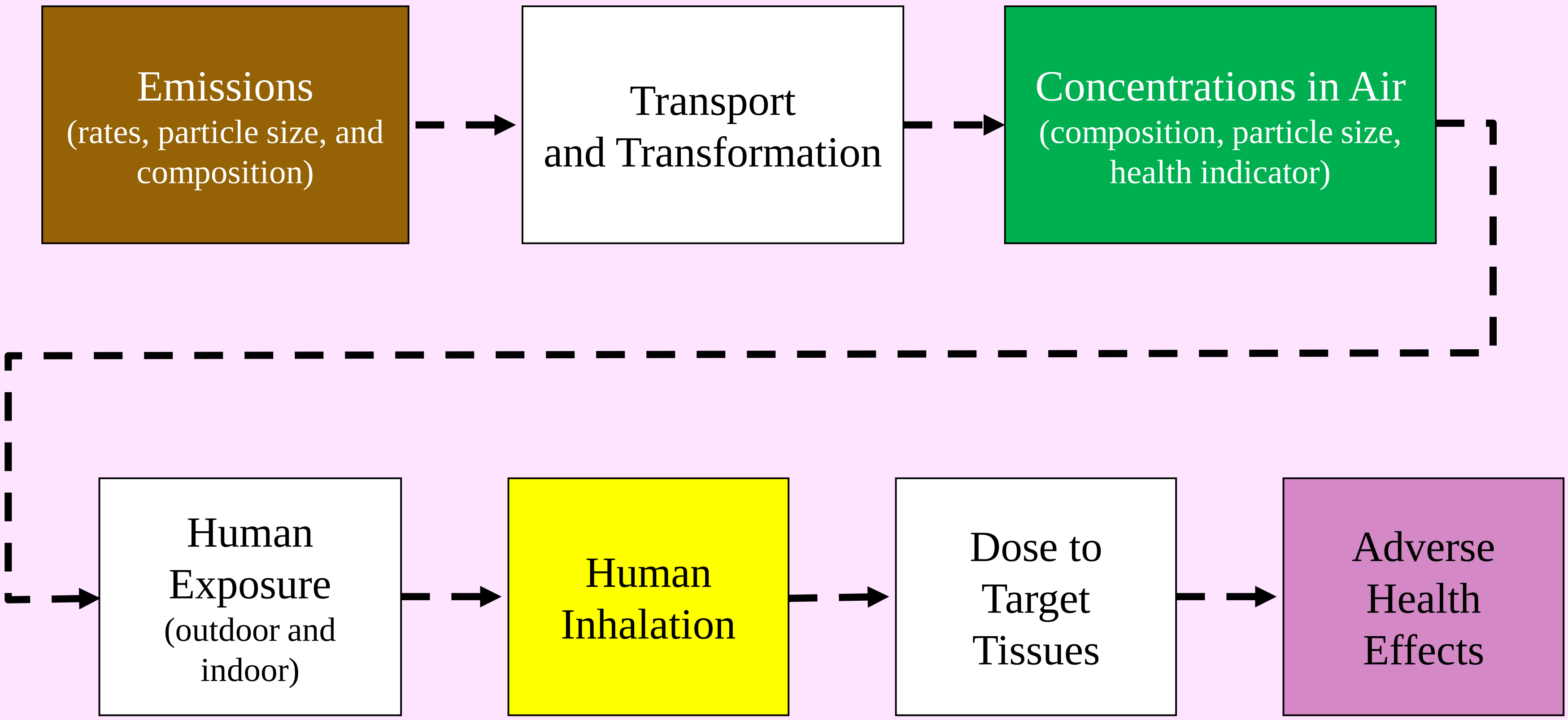
Courtesy of Pope, 2010

Pollution causes low visibility during daytime in London (December 1952)

Particle levels exceeded 3,000 µg/m^3

National Archives

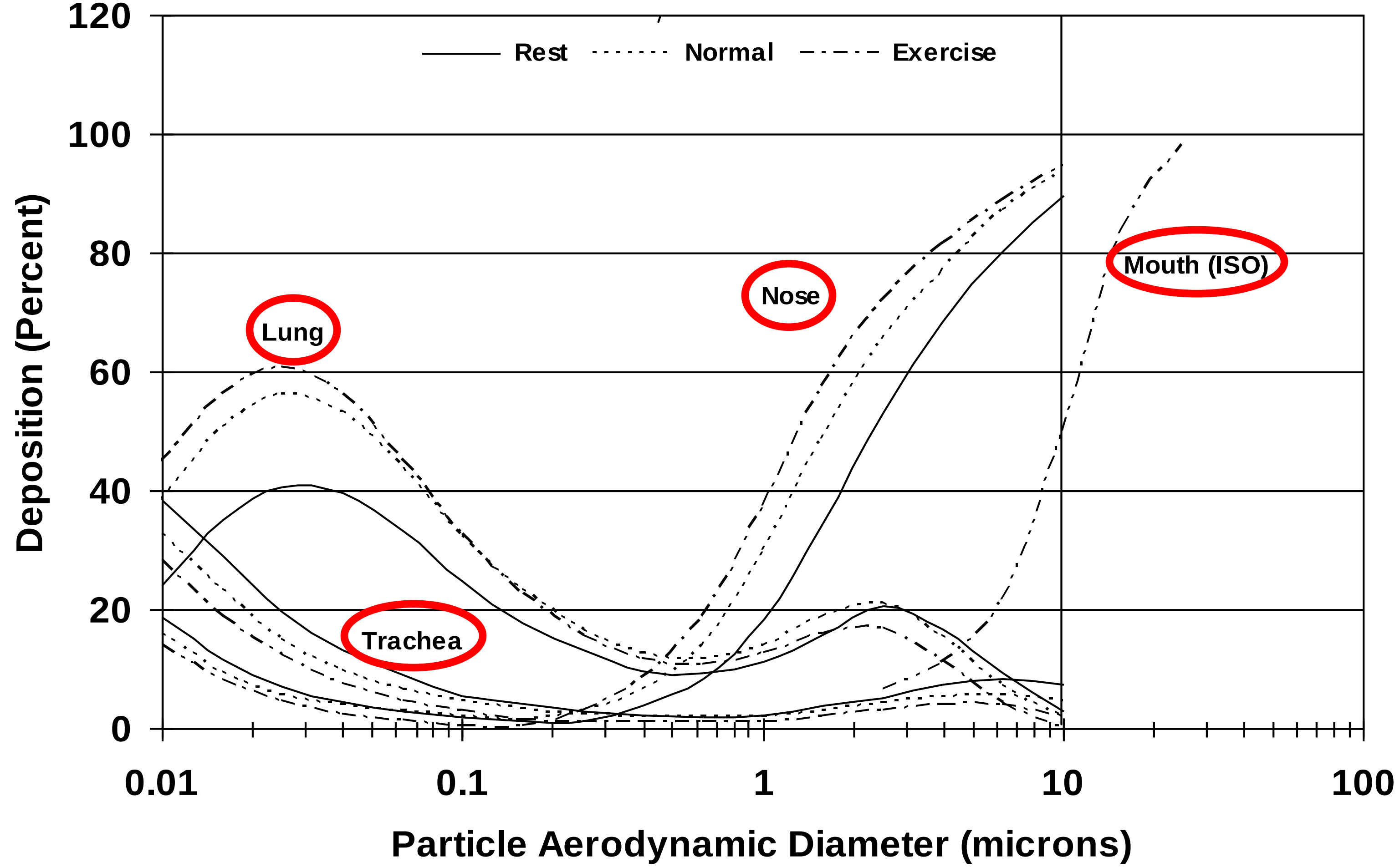
Emissions translate through several stages to health effects



National Research Council, 1998, *Research Priorities for Airborne Particulate Matter: I - Immediate Priorities and a Long-Range Research Portfolio*

Different-sized particles deposit in different parts of the respiratory tract

Lung deposition peaks at 40-60% for 30 nm UP*
Tracheal deposition is 20-40% for <10 nm UP*

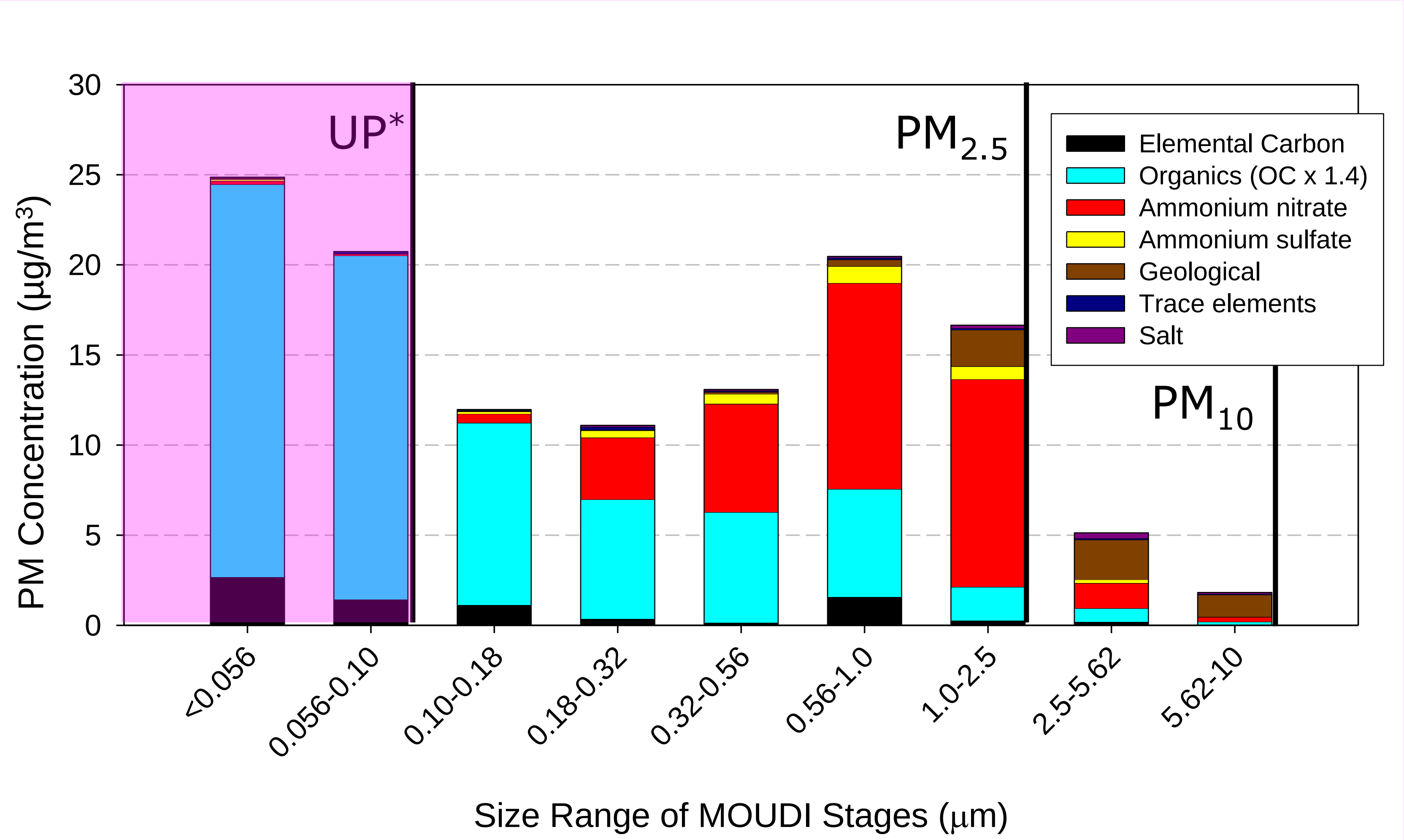


* Ultrafine Particles

Chow, 1995, *JAWMA*; Phalen et al., 1991, *Radiate. Protect. Dosim*

More abundant carbon is found in smaller particle sizes

(Fresno, CA, U.S.A.)



* Ultrafine Particles

Mauderly and Chow (2008) *Inhal. Tox.*

Laboratory and field study found association between carbonaceous aerosol and adverse health effects

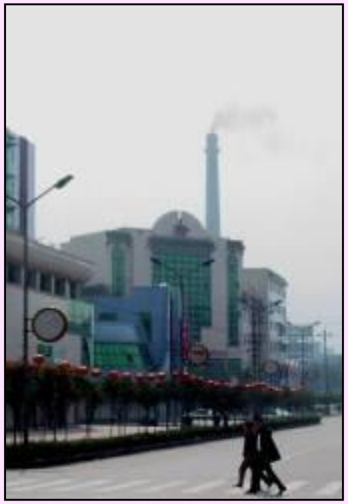
- Epidemiological evidence of exposure to carbonaceous aerosol (direct and indirect)
- Other evidence
  - Real-time exposure
  - Exposure to atmospheric carbonaceous materials
    - Estimating carcinogenic potential
    - Detecting the causal chemical species
    - Evaluating impact of different combustion materials
  - Exposure to laboratory-generated carbonaceous materials, components, and single or multiple organic compounds or classes

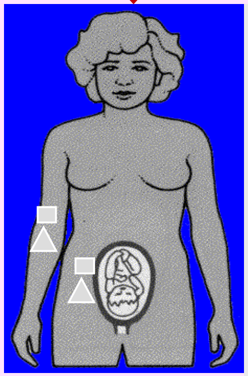
Mauderly and Chow (2008) *Inhal. Tox.*

PAHs and other organic compounds may cause long-term health effects

(Example from Tong Liang, Chongqing, China)

Exposures: $PM_{2.5}$, polycyclic aromatic hydrocarbons (PAHs), and heavy metals



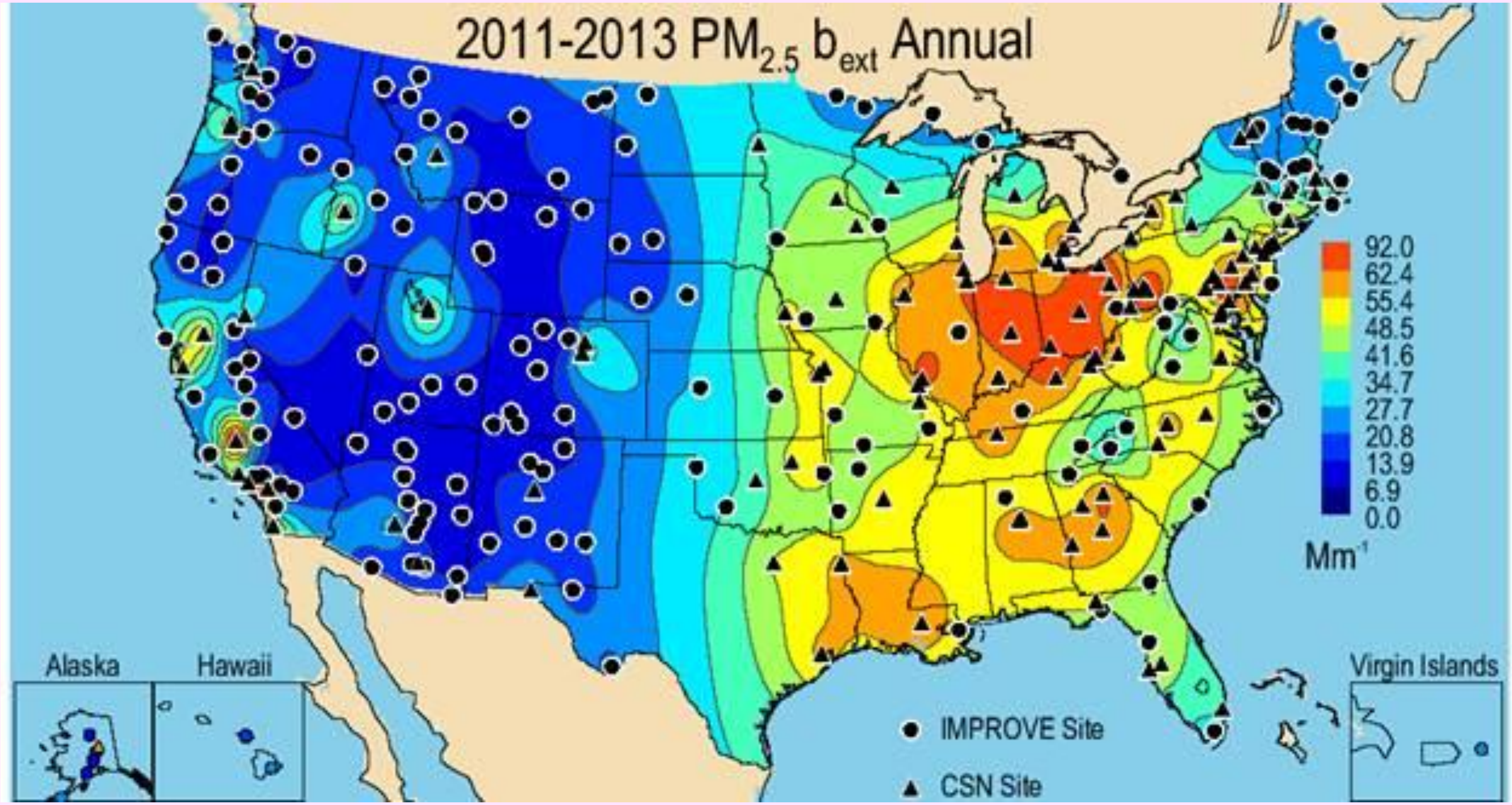


Biomarkers: PAH-DNA adducts and heavy metals

Child development, asthma, and cancer risk

Chow et al., 2006, *J. Envi. Sci. Health Part A*

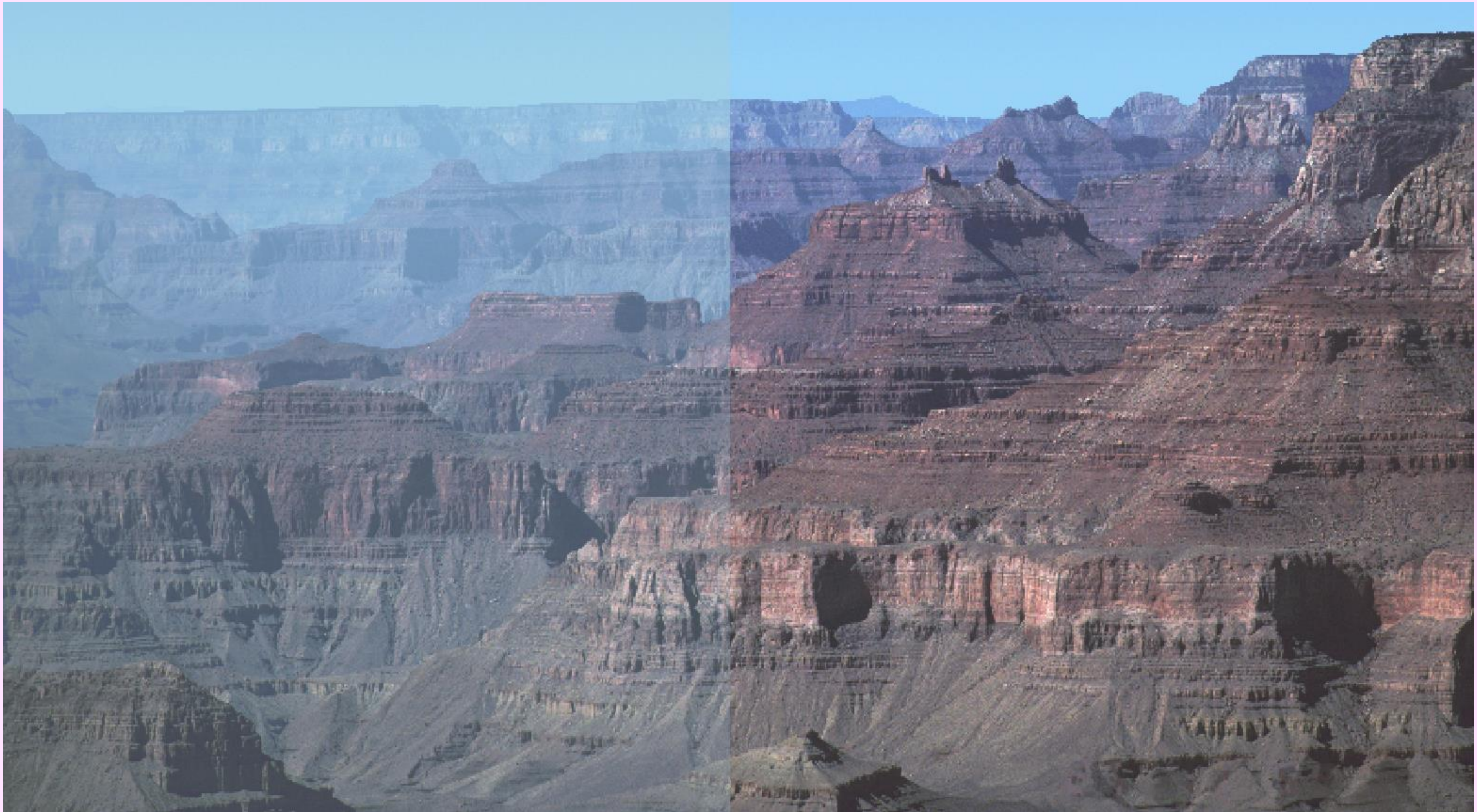
Haze is a regional issue in the USA
(100-1,000 km)



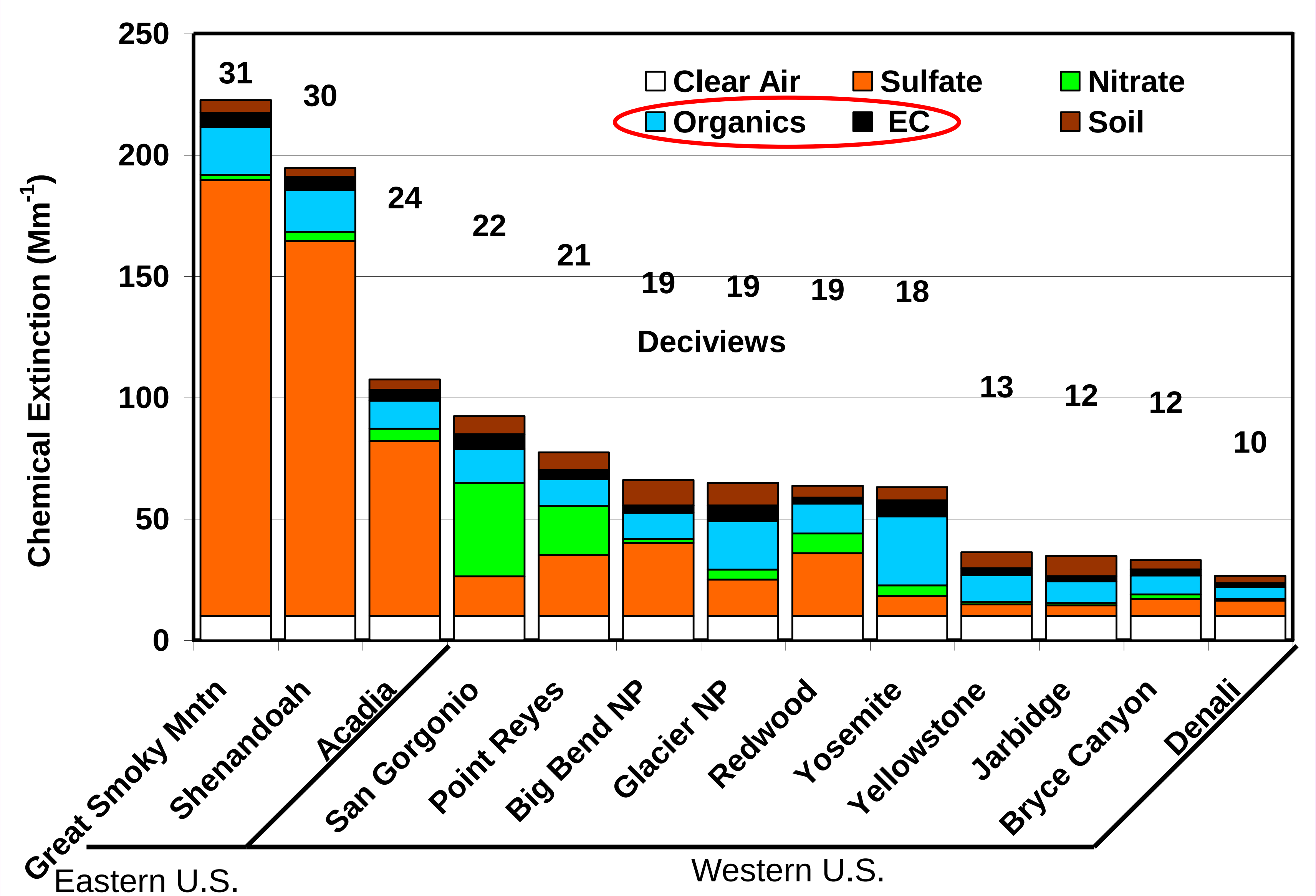
U.S. National Park Service

Poor and Natural Visibility at the Grand Canyon

WINHAZE (webcam.srs.fs.fed.us/winhaze.htm)



Elemental and organic carbon are important components of light absorption and scattering



IMPROVE Chemical Extinction Algorithm is used to evaluate visibility impairment

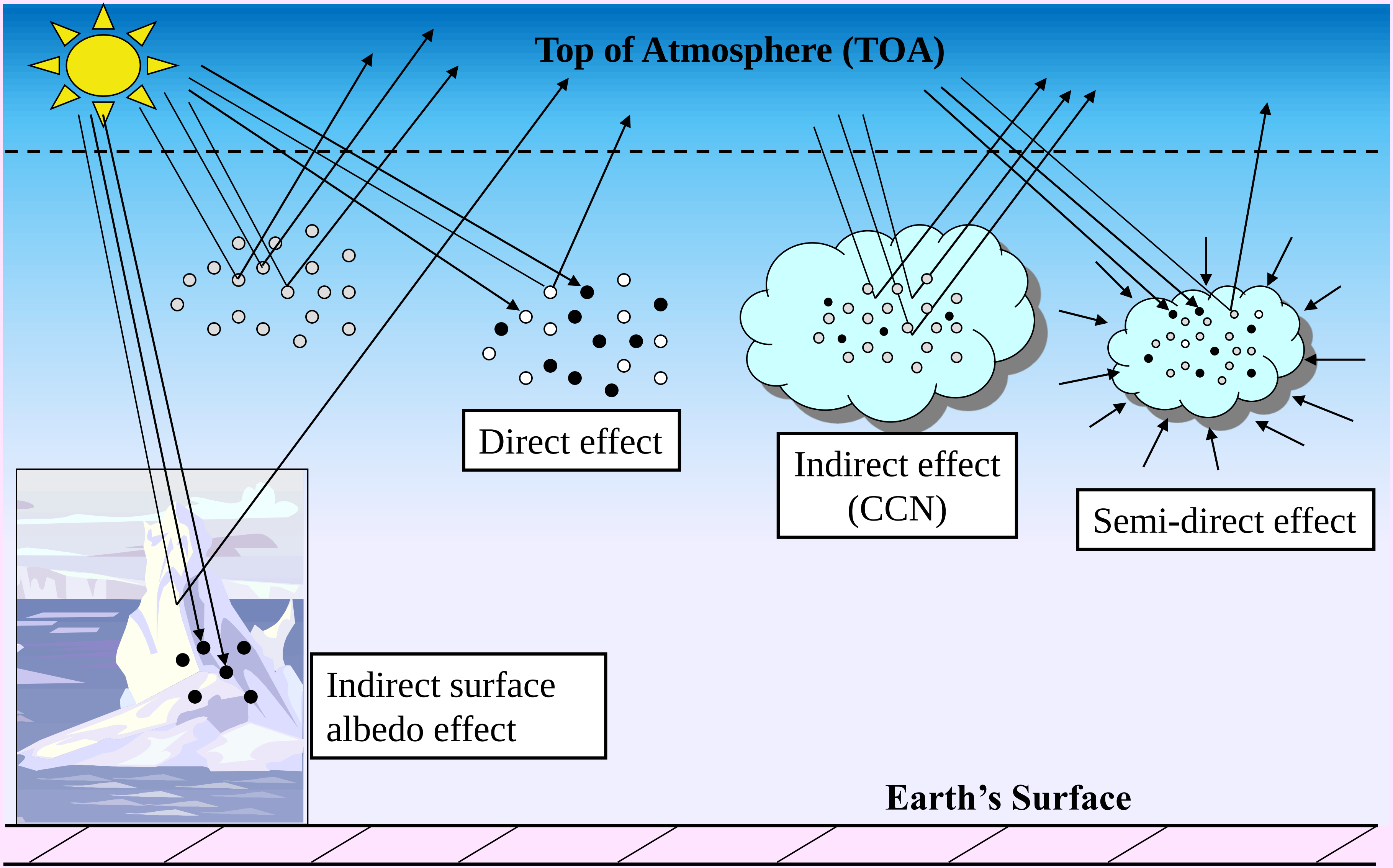
b_{ext} (Mm^{-1}) = 2.2 × f_S(RH) × [small sulfate]
+ 4.8 × f_L(RH) × [large sulfate]
+2.4 × f_S(RH) × [small nitrate]
+ 5.1 × f_L(RH) × [large nitrate]
+ 2.8 × [small organic mass]
+ 6.1 × [large organic mass]
+ 10 × [elemental carbon]
+ 1 × [fine soil]
+ 1.7 × f_{SS}(RH) × [sea salt]
+ 0.6 × [coarse mass]
+ Rayleigh Scattering (site specific)
+ 0.33 × [NO_2 (ppb)]

Small sulfate = total sulfate–large sulfate;
Large sulfate = total sulfate/(20 μg/m^3 × total sulfate) if total sulfate < 20 μg/m^3
Large sulfate = total sulfate if total sulfate $\geq$ 20 μg/m^3
OM = 1.8 * OC

Pitchford

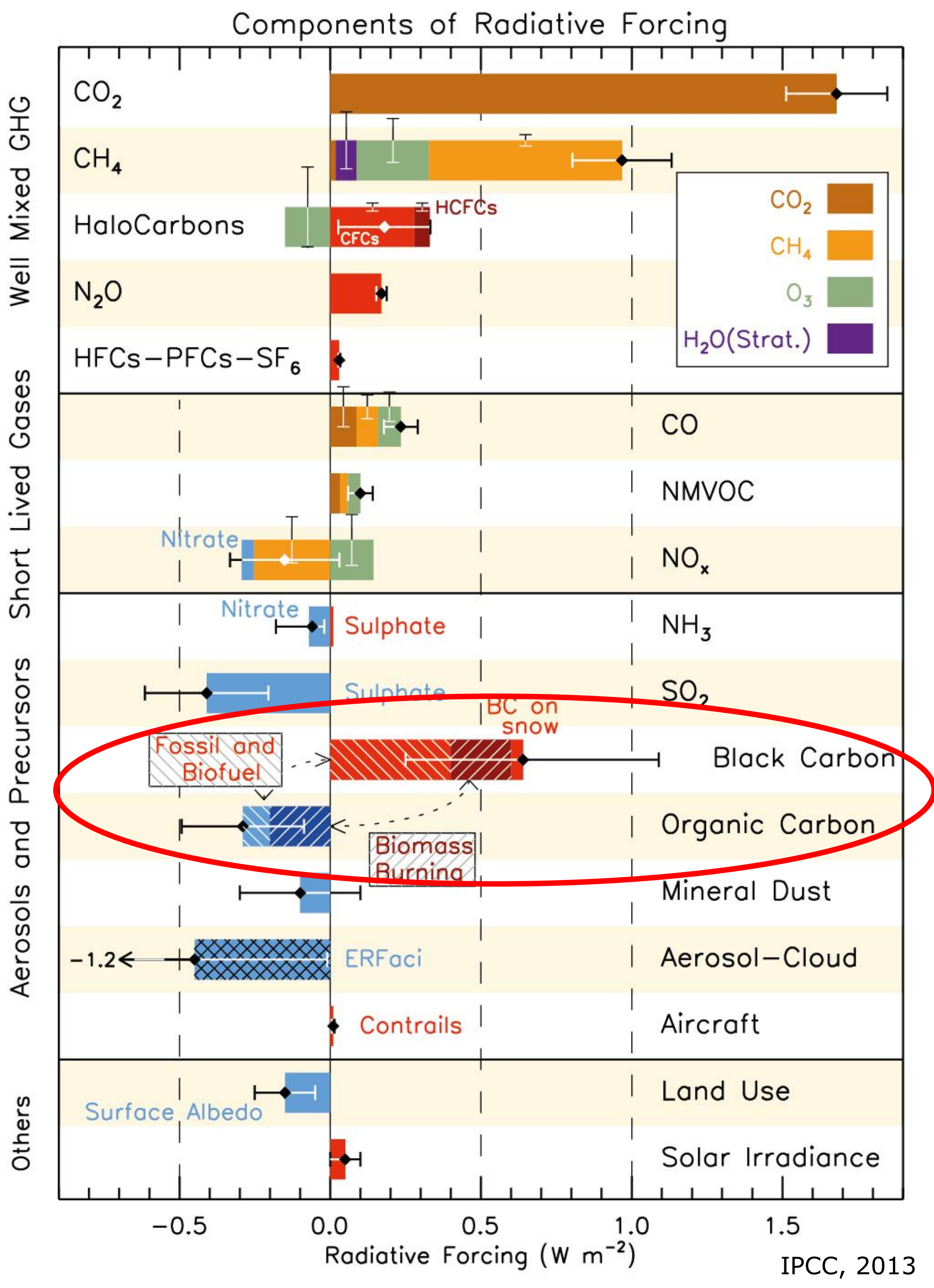
Black carbon deposit also destroys cultural heritage

How does black carbon impact climate?



Husain, 2011

High uncertainties found for carbonaceous aerosol effects on global radiation balance



While the focus has been on "black carbon," PM comes in many colors that are not black. All of these affect the Earth's radiation balance.

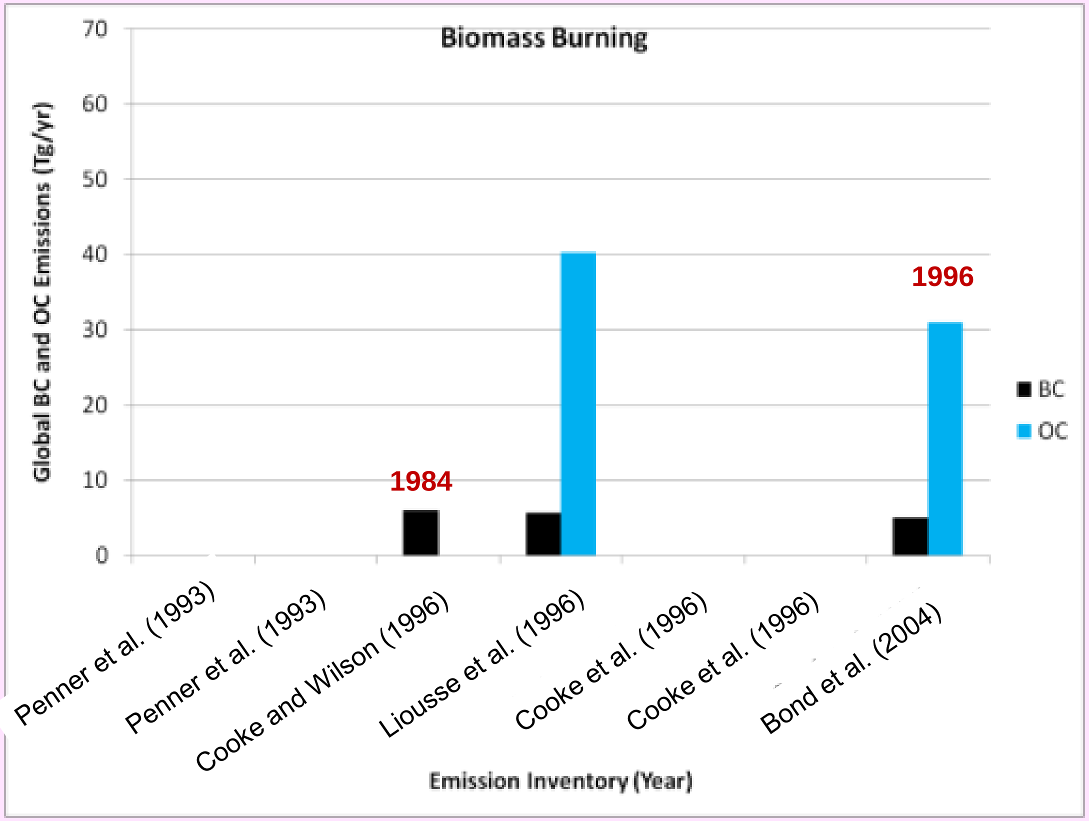
There is no consistent terminology for light absorbing carbon (LAC) and light absorbing aerosol (LAA)

- Thermal/optical analysis (TOA) on filter substrate quantifies OC and EC at 633 nm (i.e., $LAC_{633} = EC_{633}$)
- Continuous BC instruments (e.g., Aethalometer, PSAP, MAAP, and PA) convert light absorption (Mm^{-1}) to BC ($\mu g/m^3$) with manufacturer stated MAC (m^2/g)
- BC is commonly used in Emission Inventories and by the IPCC, along with soot and/or refractory carbon
- The concept of light absorbing OC at shorter wavelengths (300-400 nm) is not new, but the introduction of BrC terminology (~10 years ago) requires redefining LAC (i.e., $LAC_\lambda = BC_\lambda + BrC_\lambda$)

- OC = Organic Carbon
- EC = Elemental Carbon
- BC = Black Carbon
- IPCC = Intergovernmental Panel on Climate Change (http://www.ipcc.ch/)
- Aethalometer (14625/λ; 22.16 m^2/g at 660 nm)
- PSAP = Particle Soot Absorption Photometer (2.7 m^2/g at 467 nm, 2.5 m^2/g at 530 nm, and 1.9 m^2/g at 660 nm)
- MAAP = Multiangle Absorption Photometer (6.6 m^2/g at 670 nm)
- PA = Photoacoustic Spectrometer (10 m^2/g at 532 nm and 5 m^2/g at 1047 nm)
- MAC = Mass Absorption Cross section (m^2/g)

Global emission inventories do not distinguish BrC from BC

(Biomass burning is one of the major global sources or carbon emissions.)



Tg/yr = teragrams/year

BrC originates mostly from smoldering of biomass burning

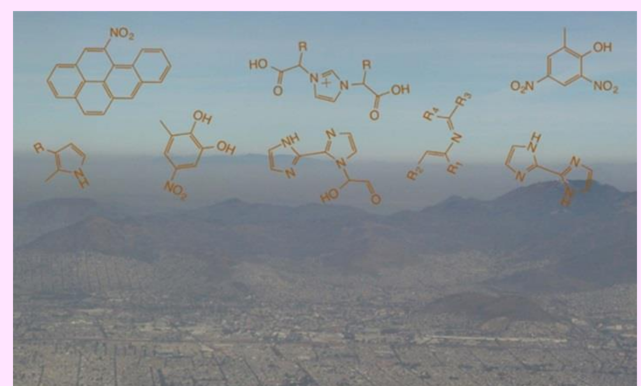
- Smoldering forest fires/biomass burning

(crop residual burn)

Andreae and Gelencser, 2006, *ACP*

- Residential wood/coal cooking/heating

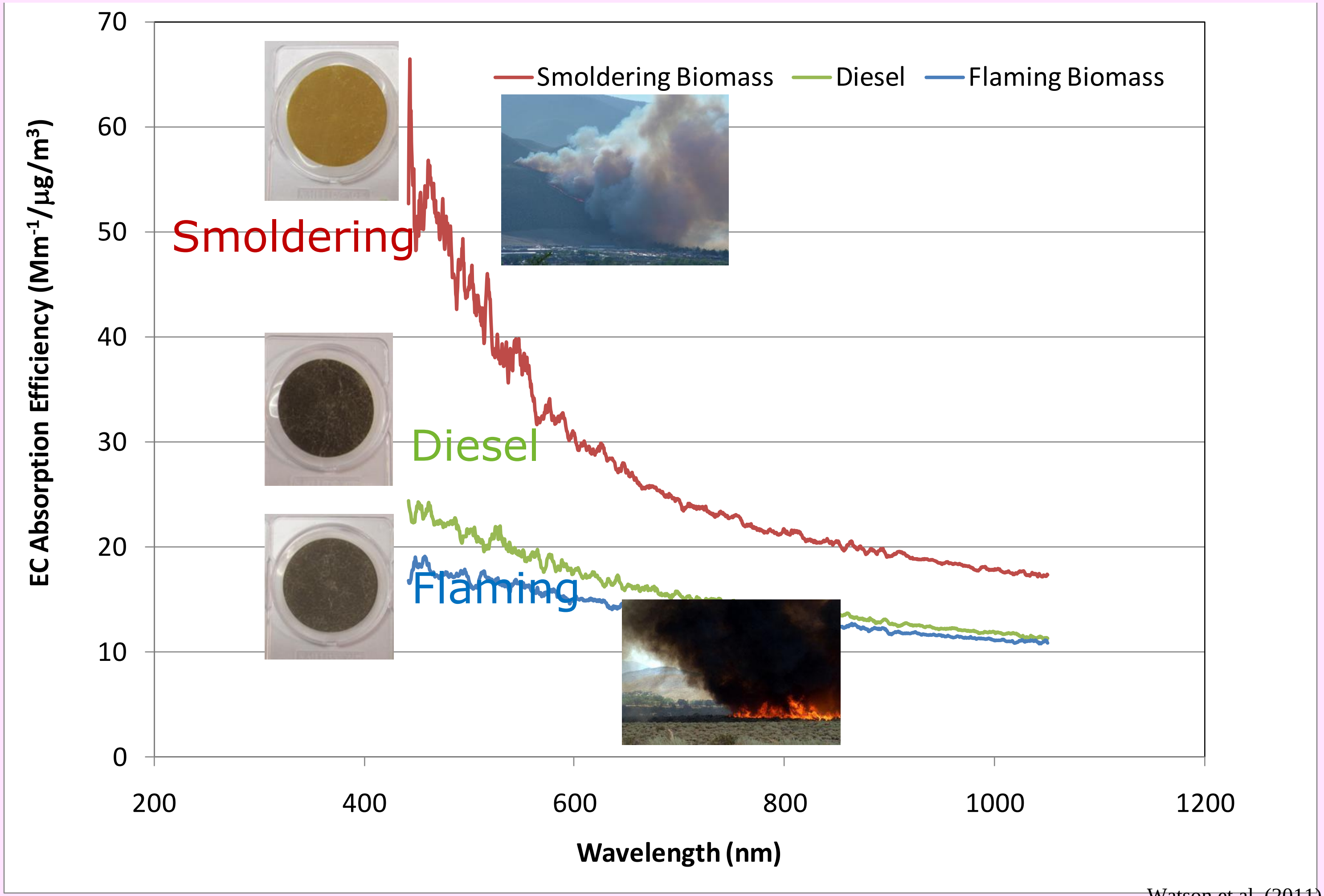
- Bioaerosol, soil humus, and humic-like substances (HULIS)



Laskin et al., 2015, *Chem. Reviews*

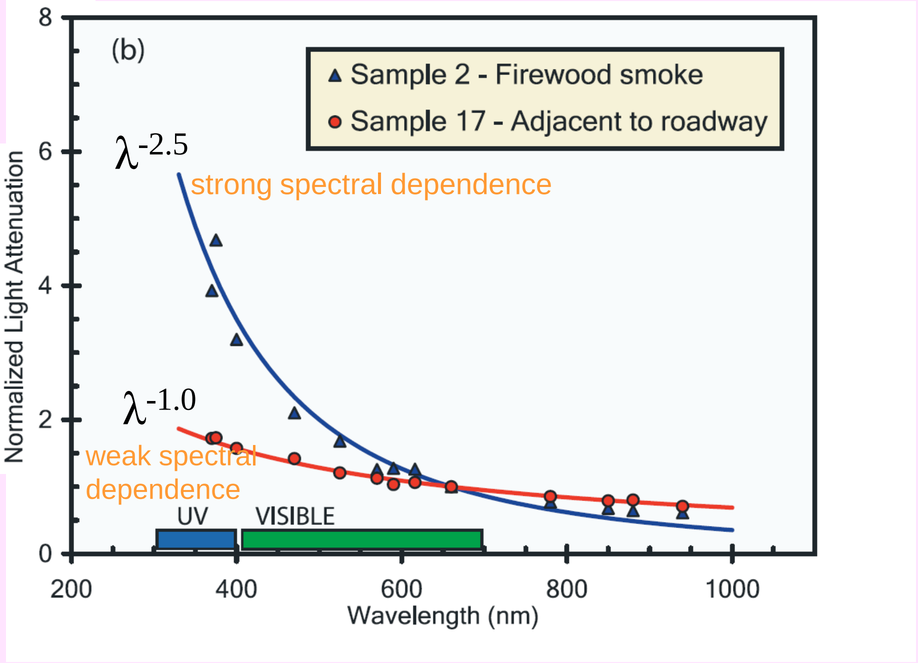
The smoldering and flaming phases of biomass burning show the largest differences between brown and black carbon

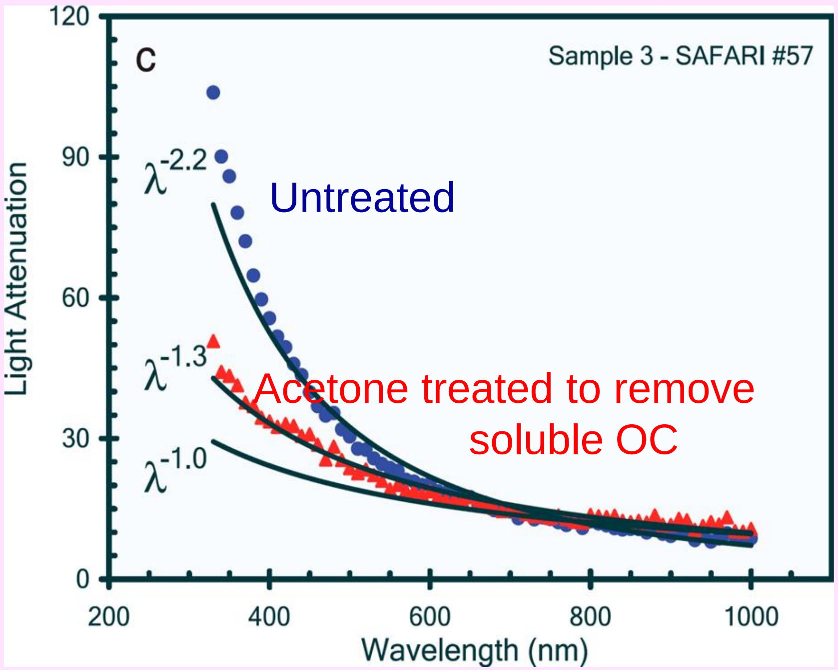
(EC absorption efficiency varies by source and wavelength)



Watson et al. (2011) *Sci. Total Environ.*

BrC absorbs more light at shorter (300-400 nm) wavelengths





- AAE* and magnitude of ATN are reduced for $\lambda < 600$ nm after acetone extraction

$$ATN(\lambda) = \ln\left(\frac{FT_{\lambda,F}}{FT_{\lambda,I}}\right)$$

$$b_{ATN(\lambda)} = ATN(\lambda) \times \frac{\text{Area}}{\text{Volume}}$$

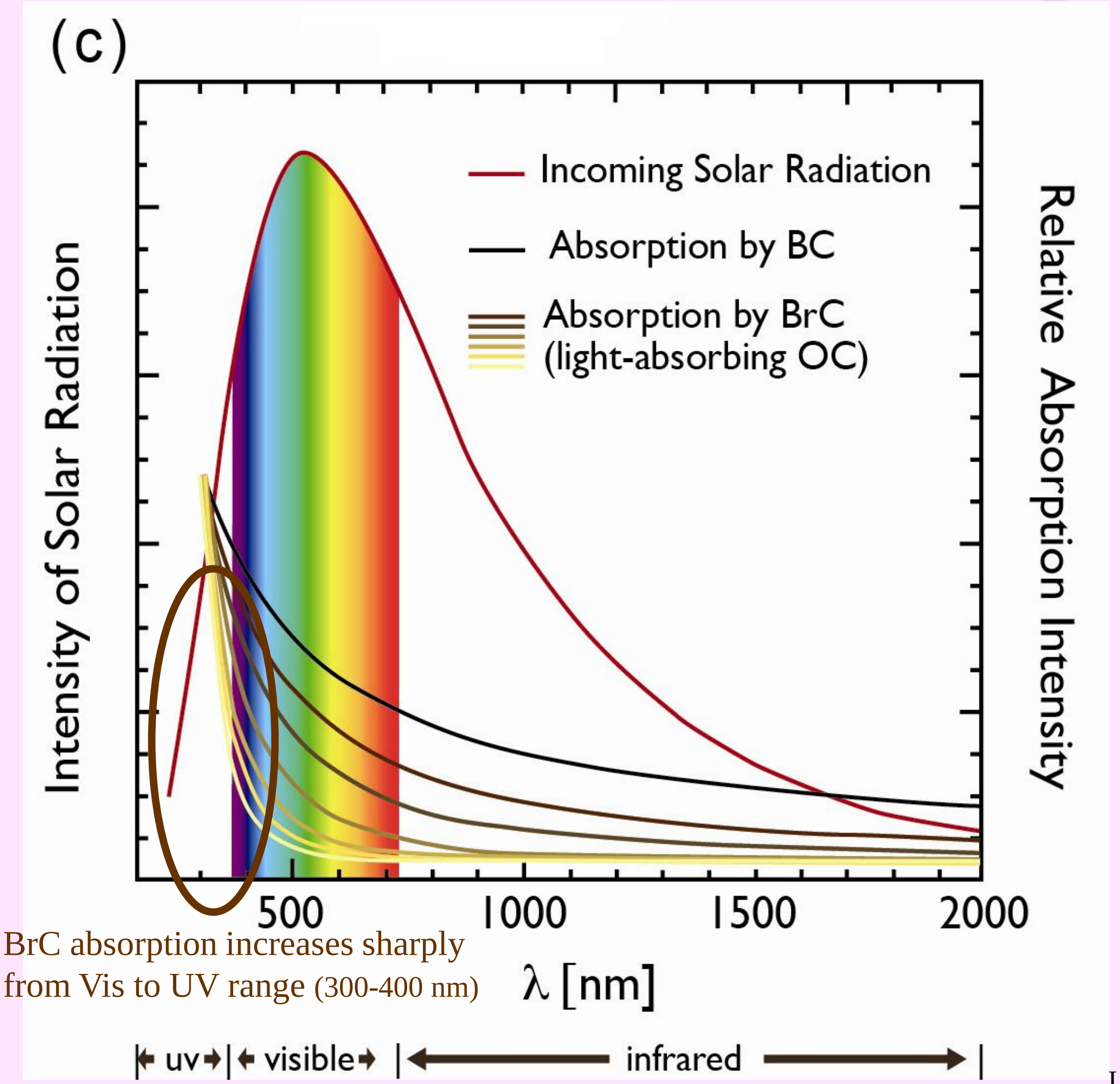
MAC (Mass Absorption Cross section, m^2/g) $= k \times \lambda^{-AAE}$

(Power Law relationship) where $MAC = \frac{b_{ATN(\lambda)}}{EC}$

Kirchstetter et al., 2004, *J. Geophys. Res.*

* AAE: Absorption Ångström Exponent

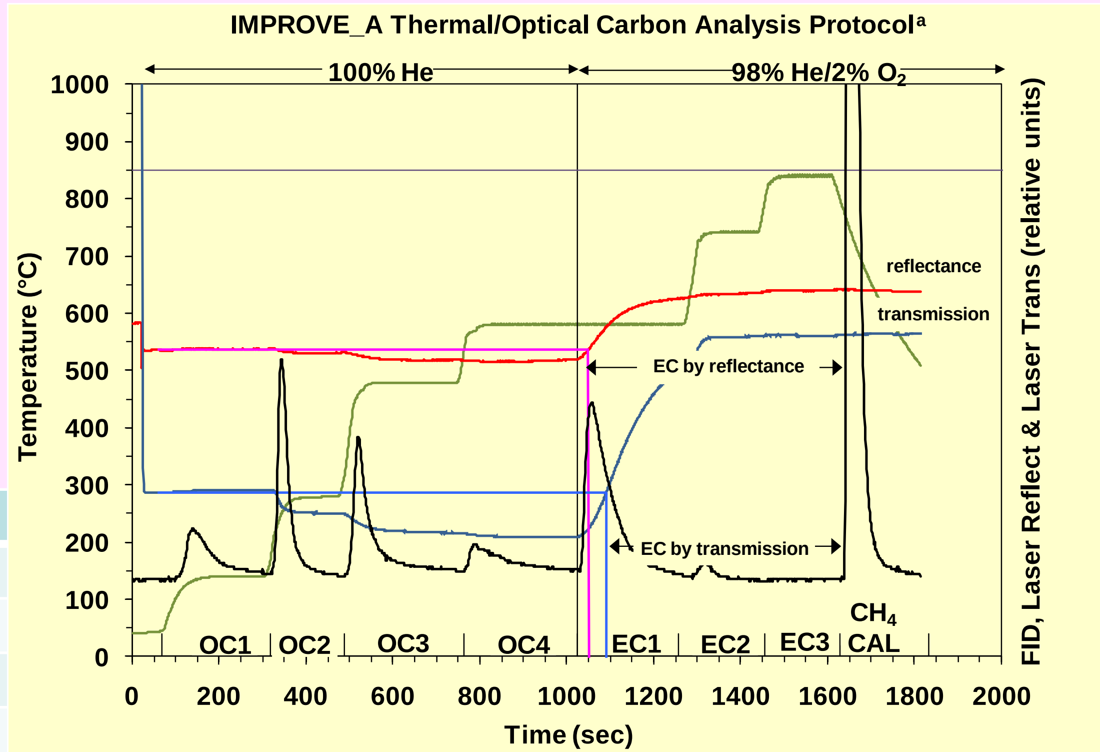
Brown Carbon (BrC) and BC absorb solar radiation over a broad spectrum range



U.S. EPA, Report to Congress on Black Carbon, 2012

U.S. long-term non-urban and urban networks have used the IMPROVE_A Thermal/Optical Reflectance protocol to separate OC and EC carbon fractions

DRI Model 2001 Thermal/Optical Analyzer



	°C	Analysis Atmosphere
OC1	140	100% He (99.99% Purity)
OC2	280	100% He (99.99% Purity)
OC3	480	100% He (99.99% Purity)
OC4	580	100% He (99.99% Purity)
OP	Return to original reflectance/transmittance value	
EC1	580	98% He/2% O_2
EC2	740	98% He/2% O_2
EC3	840	98% He/2% O_2
TC	OC (OC1+OC2+OC3+OC4+OP) + EC (EC1+EC2+EC3-OP)	

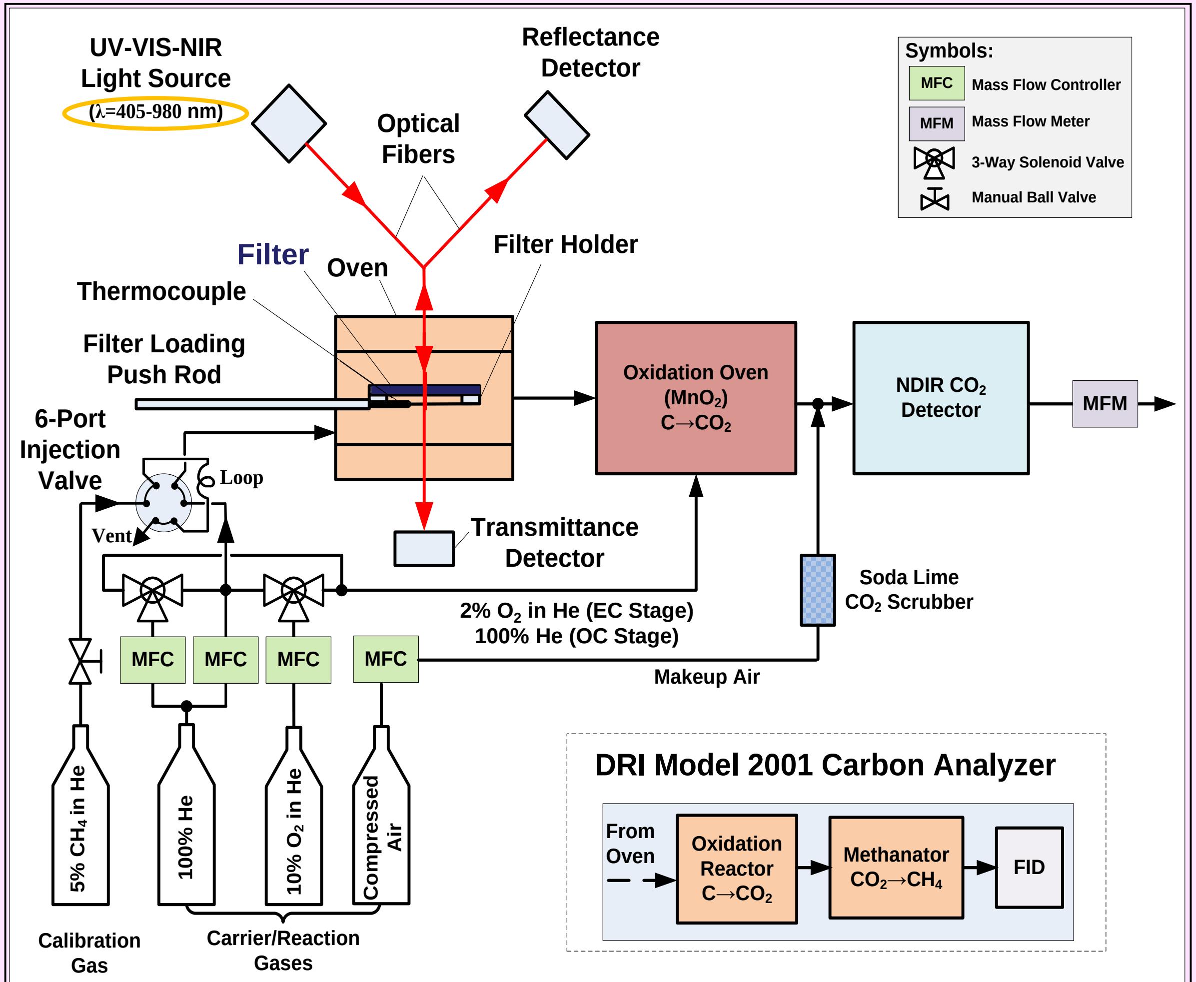
← IMPROVE_A Thermal/Optical Protocol

Chow et al. (2007) *JAWMA*

There are good reasons for upgrading to multiwavelength carbon analysis

- Thermal/optical analyses are widely used for OC/EC measurement using reflectance (R) or transmittance (T) for pyrolysis correction (λ = 633 nm)
- Modern components are available for better performance
- Spectral measurements can optimize temperature protocols for light-absorbing organic compounds
- Calibrated R and T can be used to separate BrC and BC and estimate $b_{ATN}(\lambda)$ for radiation transfer (e.g., Beer's Law, Kubelka-Munk Theory, or Monte Carlo Ray Tracing, etc.), along with OC/EC measurements, at no additional cost

Reflectance and transmittance are continuously recorded at 405, 445, 532, 635, 780, 808, and 980 nm



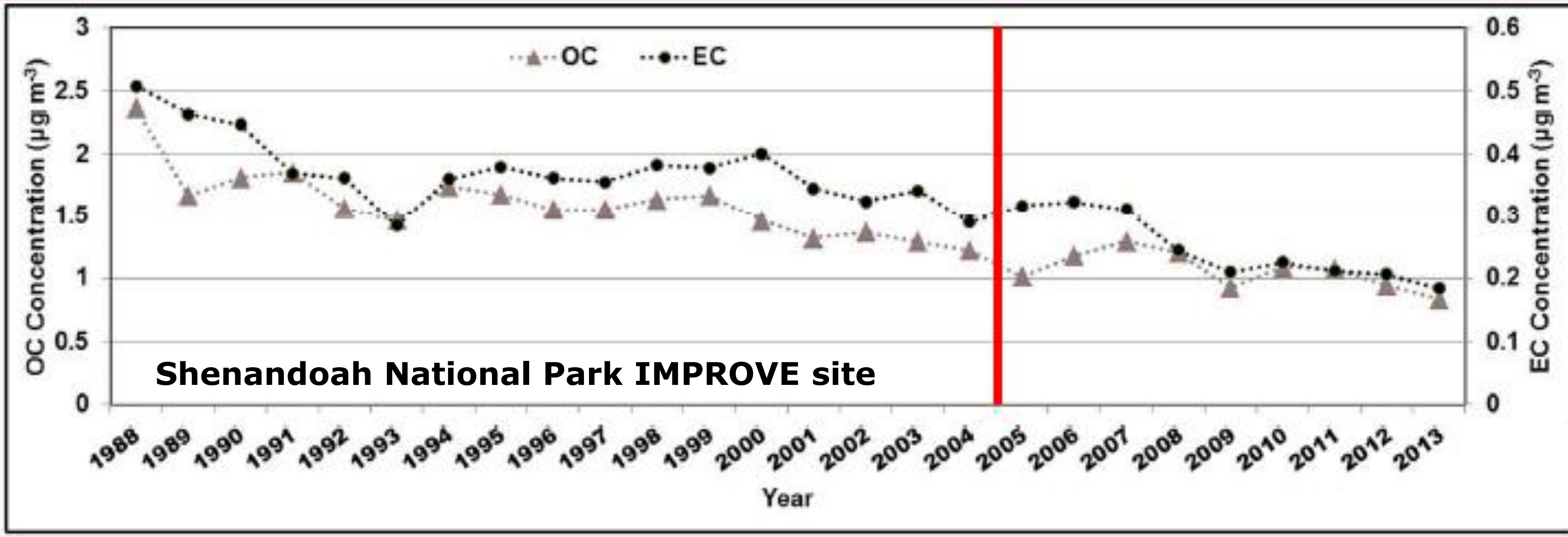
(Magee Scientific, Berkeley, CA)

DRI Model 2015 configuration

Long-term trends require consistent measurements

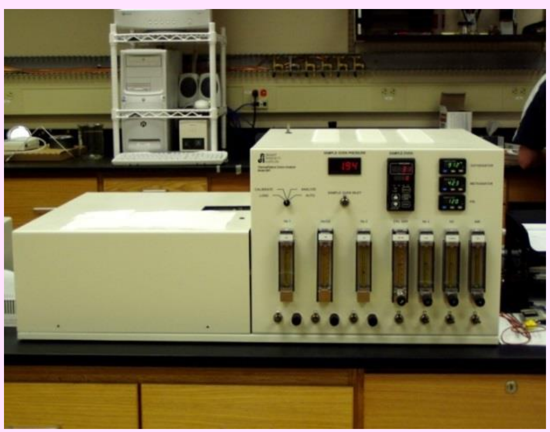
(1987-Present)

Chow et al., 2015, AAQR



DRI/OGC (1987-2004)

DRI Model 2001 (2005-2015)

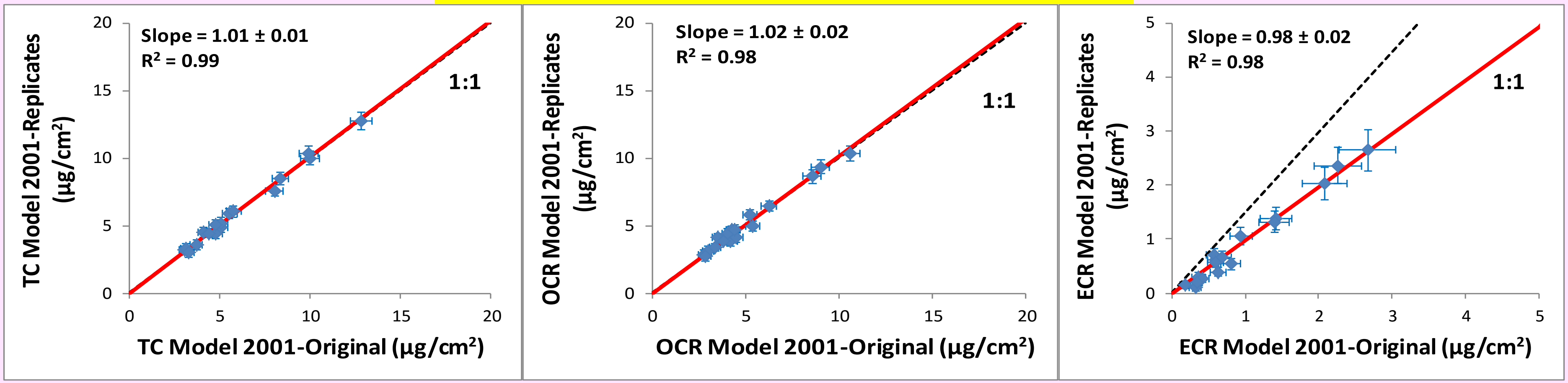


DRI Model 2015 (2016-onward)

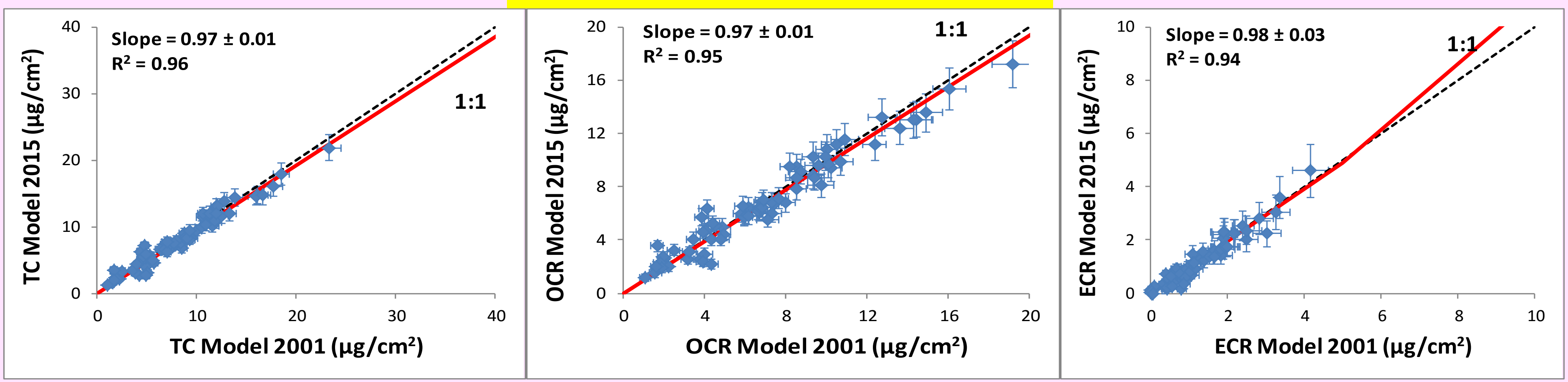
Equivalent OC and EC are obtained for single- and multi-wavelength systems

(633 nm vs 635 nm)

Model 2001 (A) vs Model 2001 (B)



Model 2015 vs Model 2001

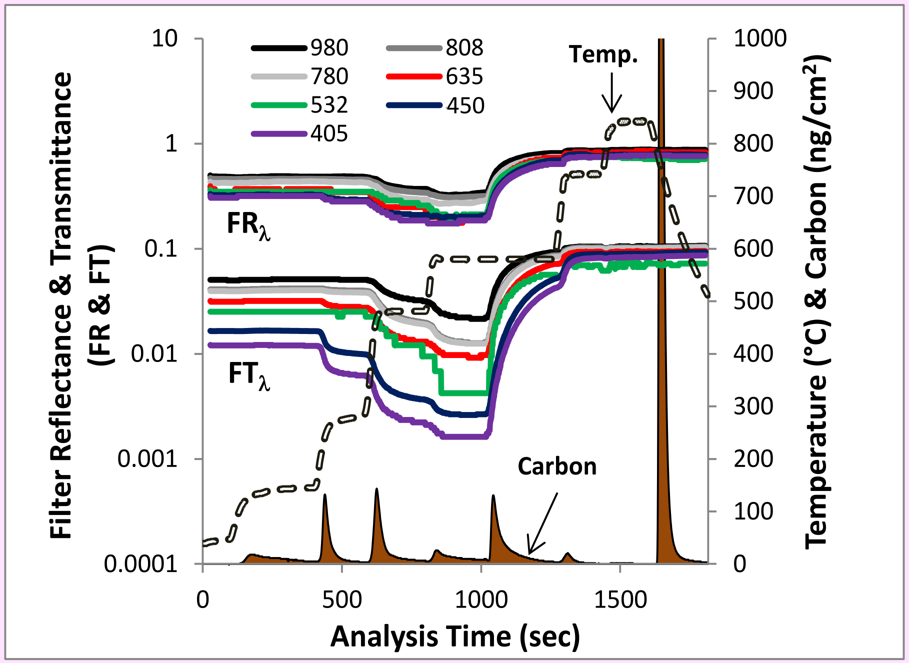


OCR and ECR are OC and EC by reflectance.

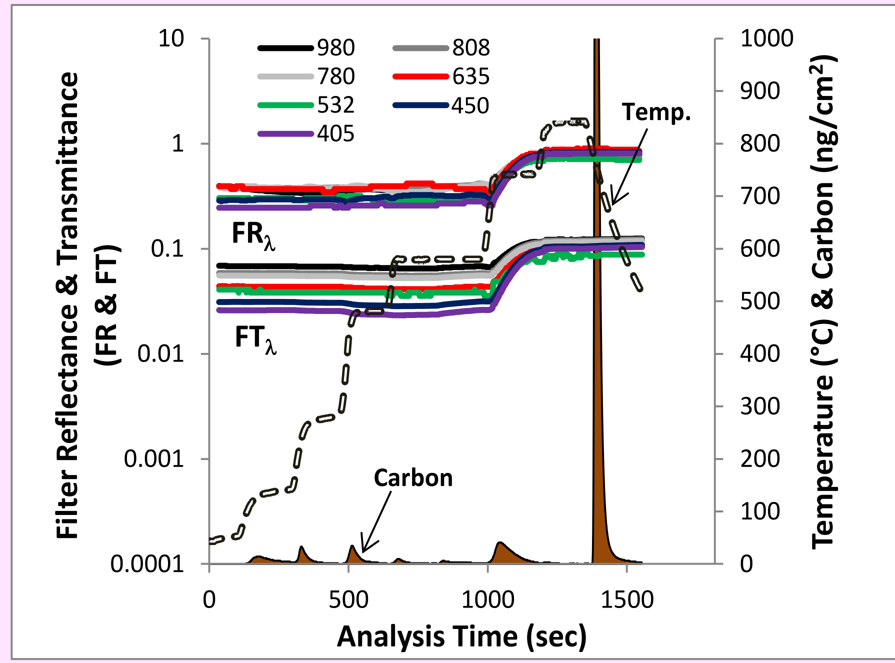
Chow et al., 2015, *AAQR*

OC and EC can be reported as a function of wavelength

After Optical Calibration



Fresno Ambient Sample

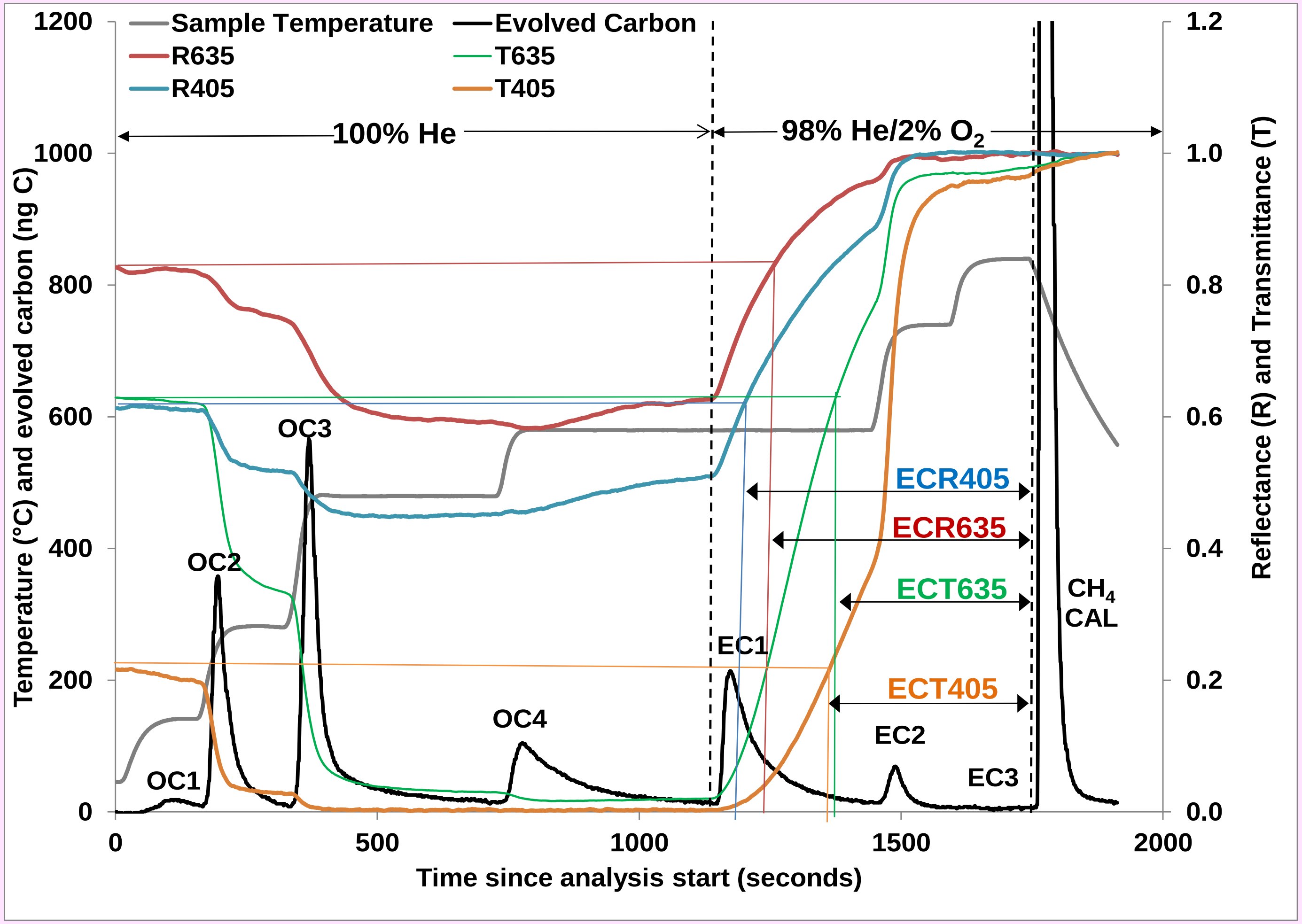


Diesel Exhaust

- FR = Filter reflectance
- FT = Filter transmittance

For wood smoke dominated samples*

EC_{405} (i.e., ECR and ECT at 405 nm) exceeds EC_{635}



* IMPROVE samples from Buffalo Pass, CO, USA, using multiwavelength IMPROVE_A protocol

Filter transfer standards with variable deposits can be standardized against traceable Spectralon* primary standards

(diffusive reflectance)

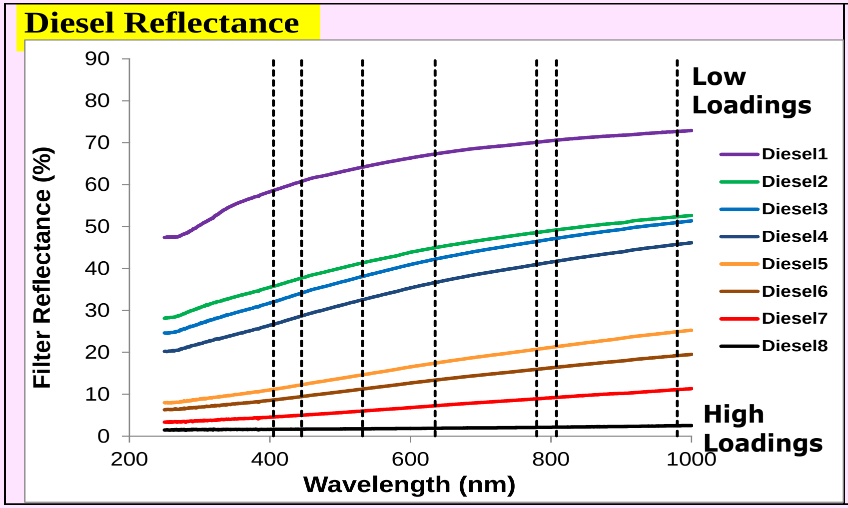
(Lambda 35 UV/VIS Spectrometer, Perkin Elmer, Waltham, MA; an Integrating-Sphere Spectrometer; measures R and T at 0 and 100%, 300-1000 nm)

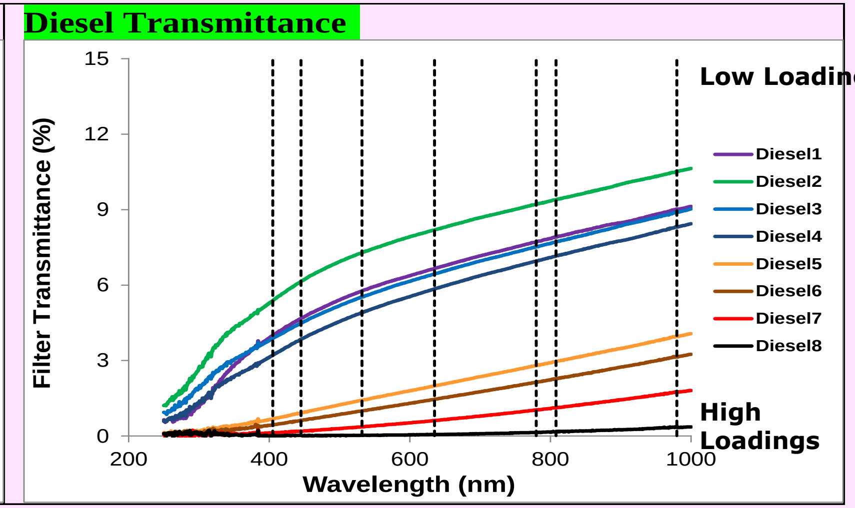
* NIST Certified Labsphere Spectralon® Diffusive Reflectance Standards

R and T are lower for shorter wavelengths

(Vertical lines designate the seven wavelengths in Model 2015)

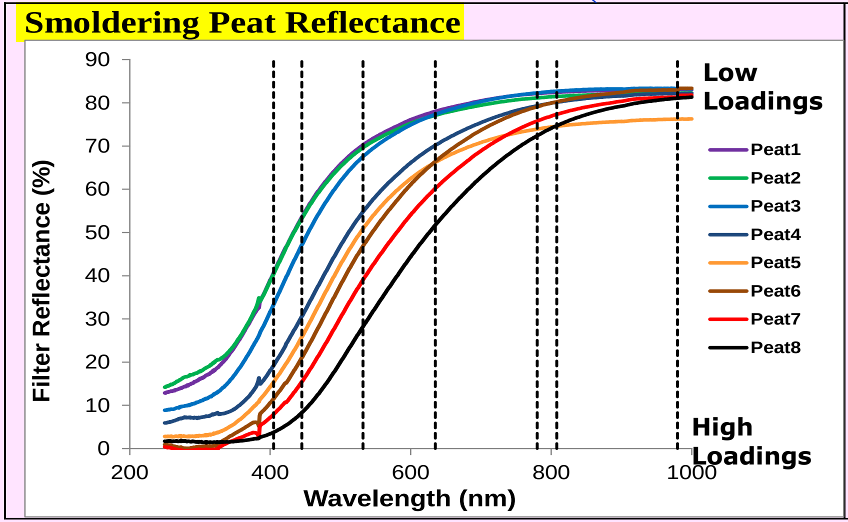
R and T in diesel samples are lower with increasing loadings.

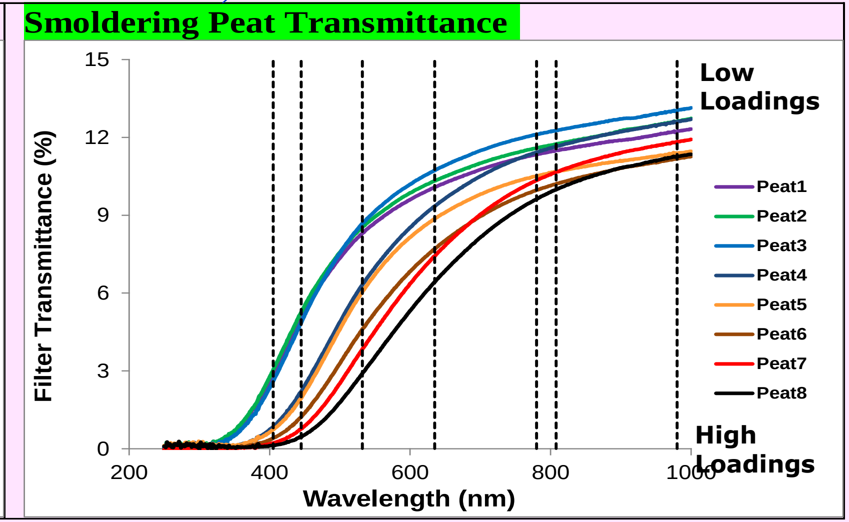




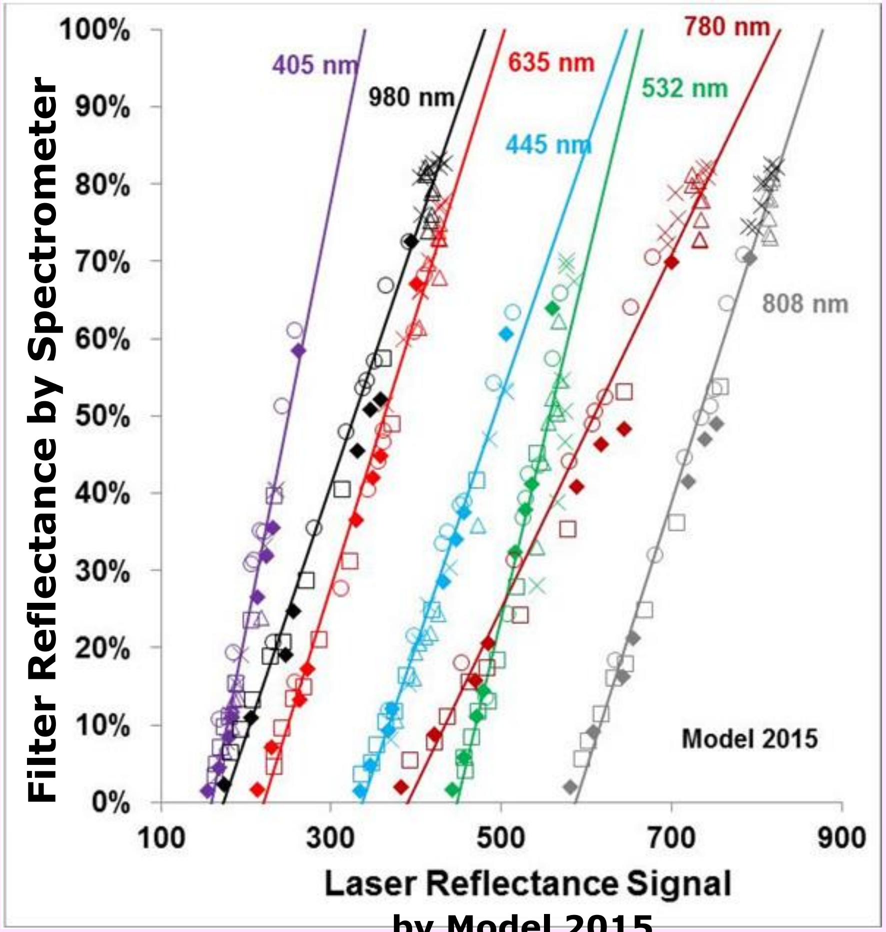
R and T in smoldering samples show minor changes with loading and clustered at high wavelengths

(less useful than the blacker standard).

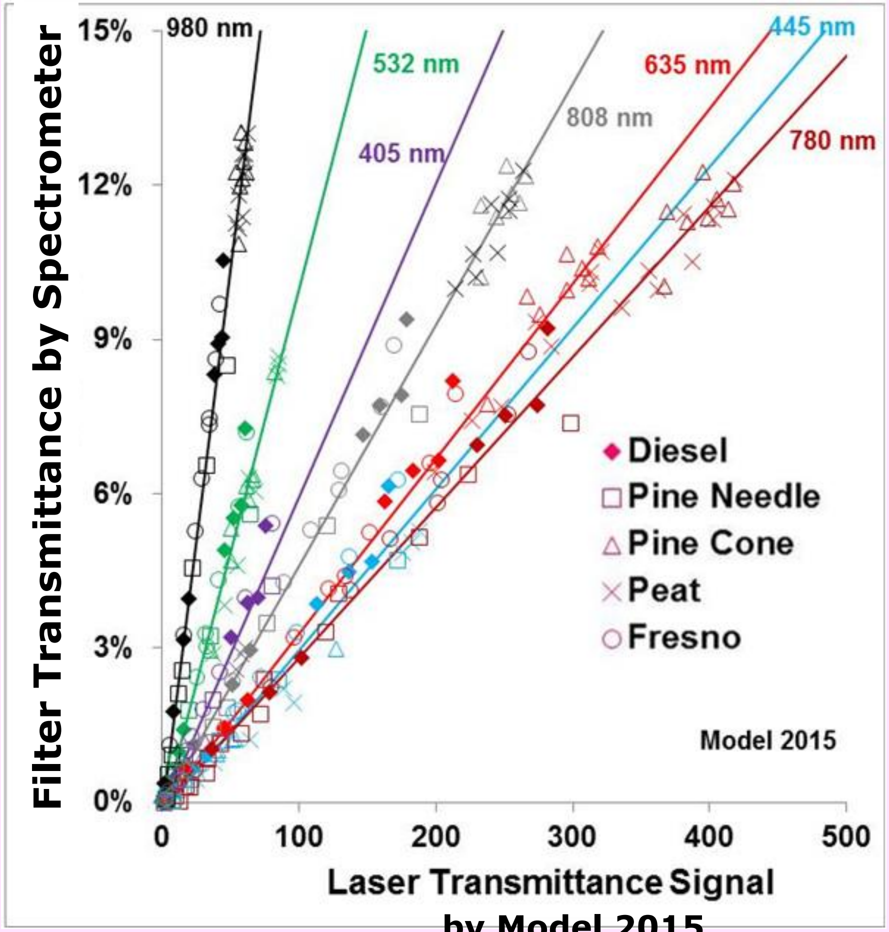




Calibration curves using transfer standards show linear responses independent of sample type or loading



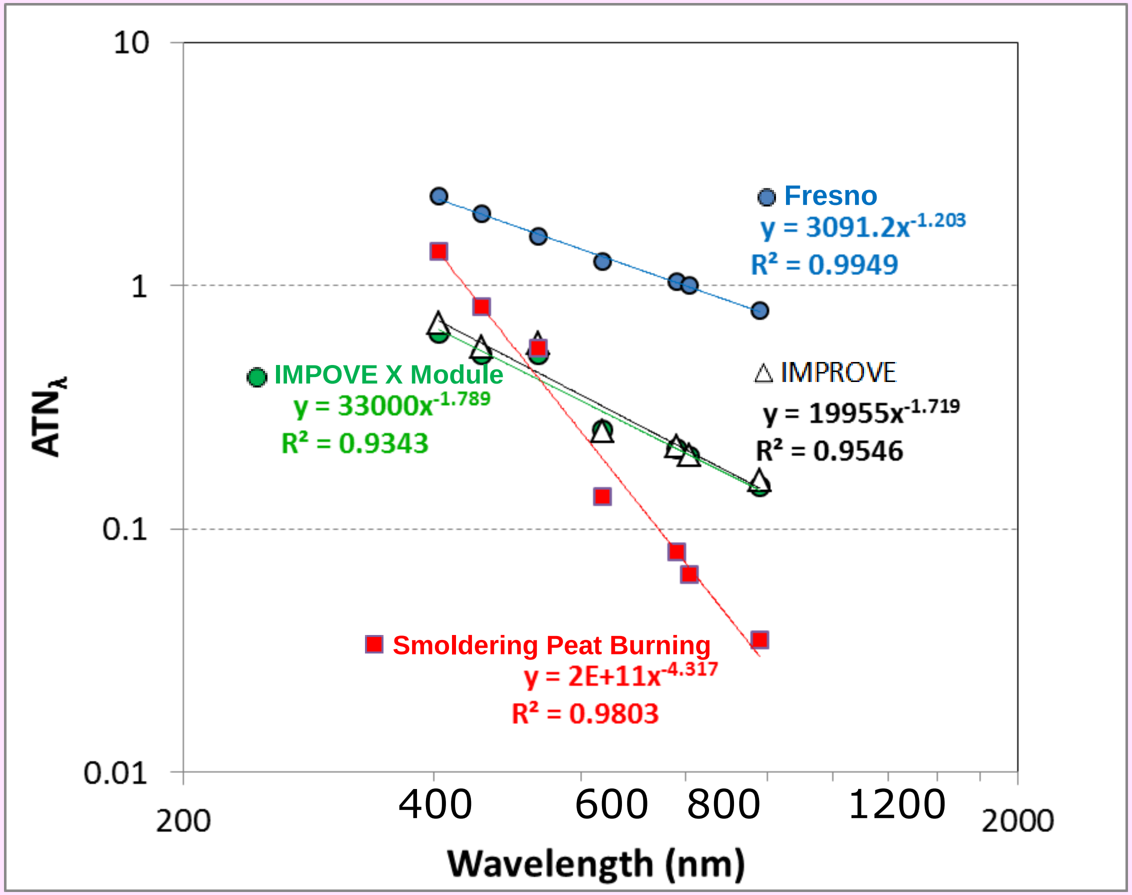
by Model 2015



by Model 2015

Spectral absorption inferred from initial and final filter transmittance vary by sample type

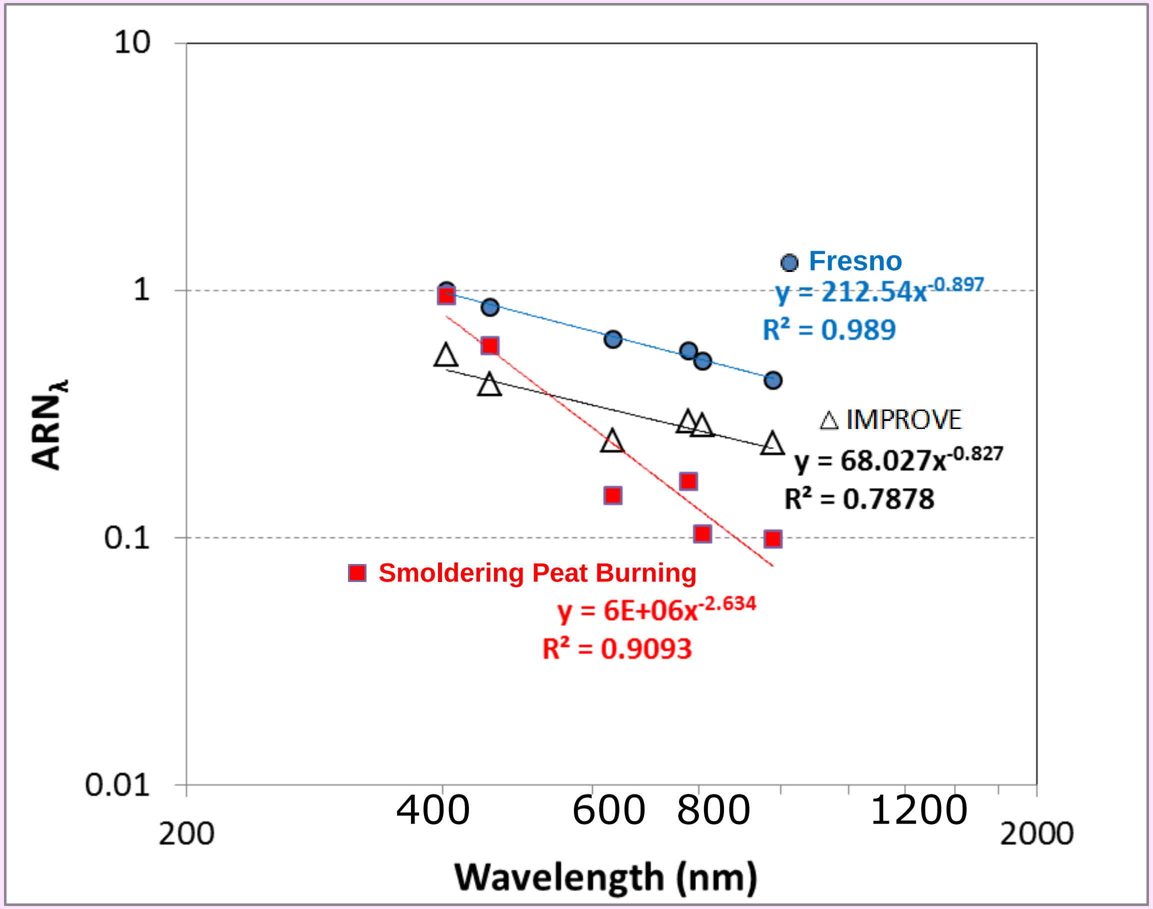
$$ATN_\lambda = -\ln\left(\frac{FT_{\lambda,i}}{FT_{\lambda,f}}\right)$$



- Spectral absorption averaged by sample type
- Smoldering samples acquired in DRI combustion chamber

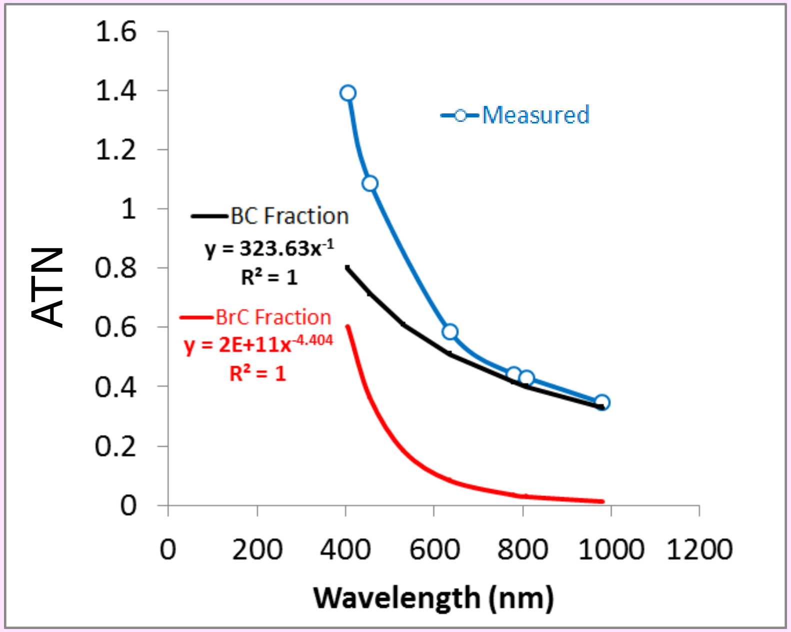
Spectral absorption inferred from initial and final filter reflectance also varies

$$ARN_{\lambda} = -\ln\left(\frac{FR_{\lambda,i}}{FR_{\lambda,f}}\right)$$

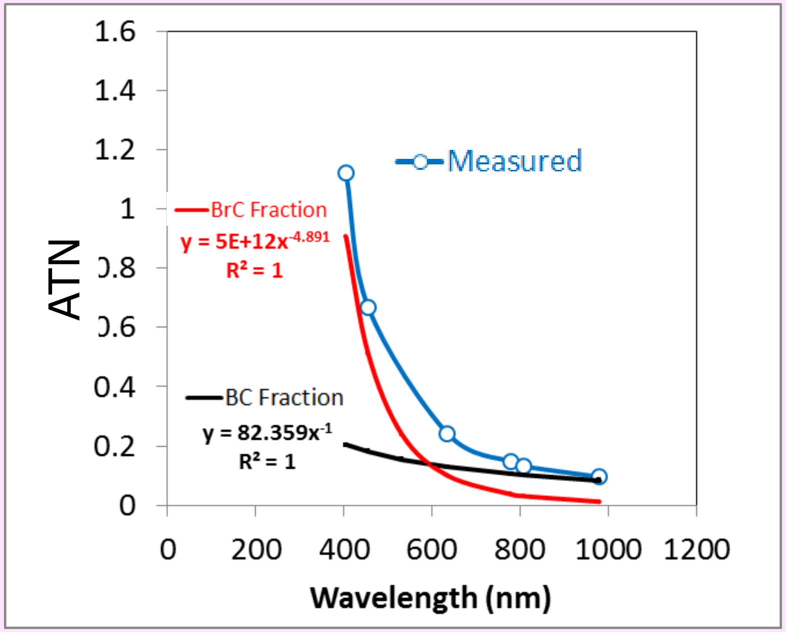


- Reflectance usually has lower signal to noise ratios than transmittance
- R and T can be combined for better quantification of light absorption as indicated by Petzold and Schönlinner (2004)

Absorption Angström Exponent (AAE) model can be used to decouple BrC and BC



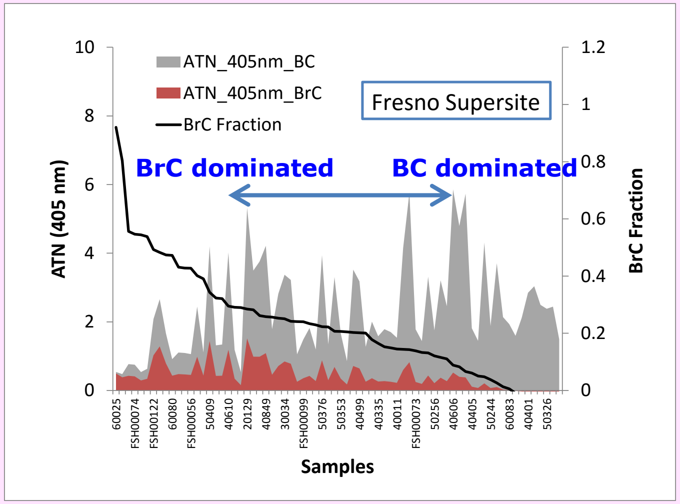
Ambient Fresno, CA

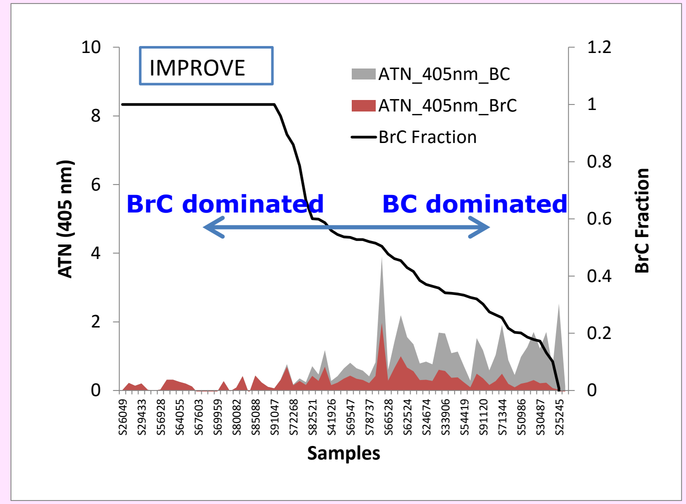


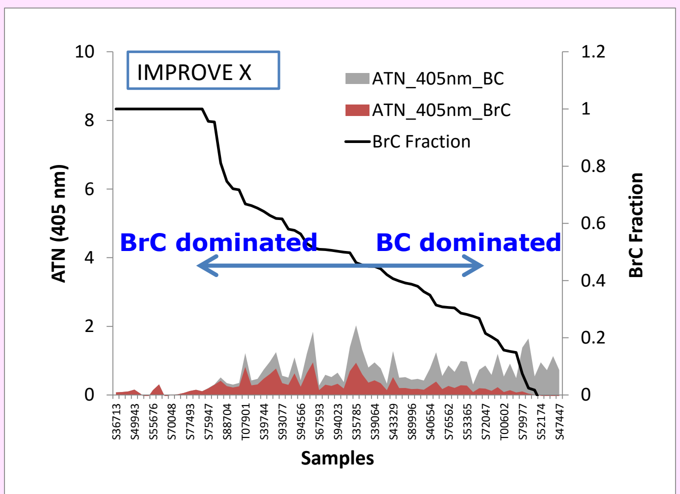
Smoldering Biomass Burning

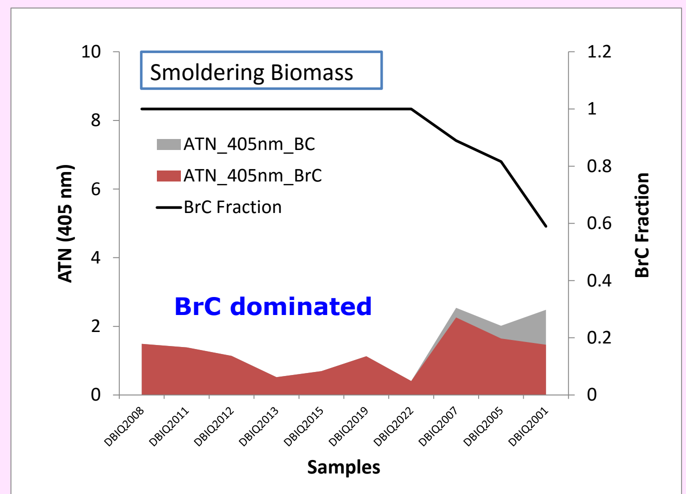
- $\mathrm{ATN}_\lambda = q_{\mathrm{BC}} \times \lambda^{-\alpha_{\mathrm{BC}}} + q_{\mathrm{BrC}} \times \lambda^{-\alpha_{\mathrm{BrC}}}$
- $\mathrm{ATN}_\lambda \times \lambda = q_{\mathrm{BC}} + q_{\mathrm{BrC}} \times \lambda^{-(\alpha_{\mathrm{BrC}}-1)}$

BrC and BC contributions to light attenuation (ATN_{405}) can be estimated









- Assuming only BC absorbs at 980 nm and an AAE_BC of 1 to extrapolate BC absorption to 405 nm
- Samples sorted by BrC fraction (0 to 100%) in ATN_405 nm

Potential future uses of calibrated multiwavelength reflectance and transmittance on thousands of samples

- Identifying light absorbing compounds
- Separating artifact OC from aerosol OC
- Ground-truthing remotely-sensed BrC
- Improving radiation transfer estimates
- Conducting source apportionment for BrC and BC

More information in online articles

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Optical Calibration and Equivalence of a Multiwavelength Thermal/Optical Carbon Analyzer

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Atmospheric Measurement Techniques

Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol

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Conclusions

- Reflectance (R) and Transmittance (T) can be traceable to primary standards and be made consistent among wavelengths and instruments
- The absorption spectrum is used to separate brown carbon (BrC) from black carbon (BC)
- Incorporation of BrC in the global emission inventory can reduce uncertainties in biomass burning emission estimates

Research Needs

- Increase understanding of carbon-containing chemicals, sources, and formation mechanisms
- Standardize compounds, terminology, and naming conventions
- Establish standard reference materials for OC, EC, and BrC

Team Effort at DRI

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