Testing Assumptions of Mass Reconstruction Methods to Evaluate and Interpret PM Chemical Speciation Measurements

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Objectives

- Review the evolution and approaches for PM mass reconstruction

- Discuss the adequacy of each approach

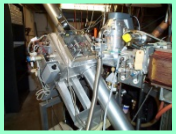
- Address major sampling and analysis issues that affect mass reconstruction

Purpose of Mass Reconstruction

(also termed mass closure or material balance)

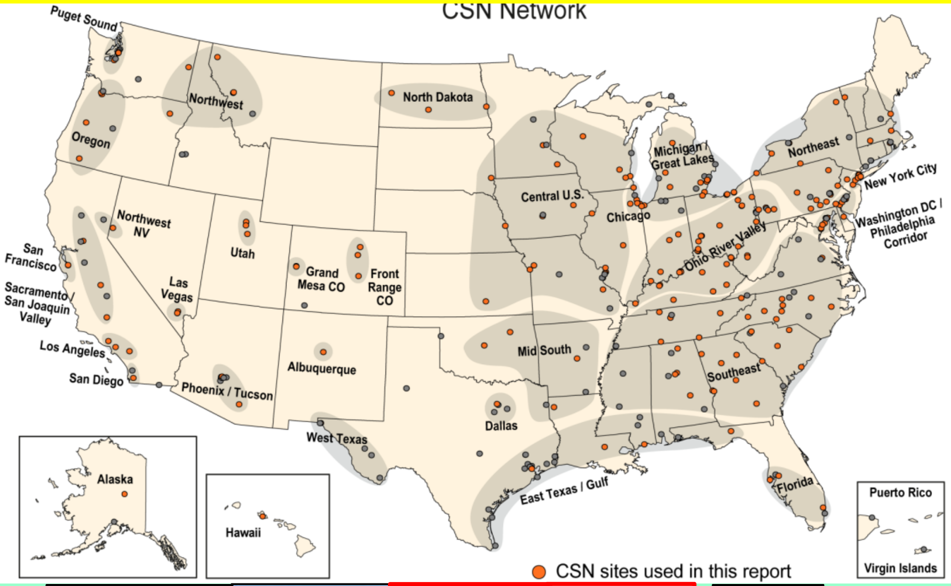
- Validate PM mass and chemical measurements (i.e., identify and correct measurement errors)
- Understand temporal and spatial variations of major chemical composition
- Estimate source contribution to PM and visibility impairment (i.e., light extinction)

Mass, elements, ions, and carbon measurements are needed for PM mass reconstruction

Measurement	**Method**	
PM Mass	Gravimetry	 Microbalance
Multi-elements (Na to U)	-X-ray Fluorescence (XRF) -Proton Induced X-ray Emission (PIXE) -Inductively Coupled Plasma (ICP)/Mass Spectrometry (MS)	 XRF  PIXE  ICP/MS
Anions and Cations	-Ion Chromatography (IC) -Automated Colorimetry (AC) -Atomic Absorption Spectroscopy (AAS)	IC  AC   AAS
Organic, Elemental, and Thermal Carbon Fractions	Thermal/Optical Reflectance Carbon Analysis (TOR)	 Model 2001  Model 2015

The urban CSN and non-urban IMPROVE network provide $PM_{2.5}$ chemical composition for source apportionment and tracking visibility impairment

Chemical Speciation Network (CSN)



URG MASS

Andersen RAAS

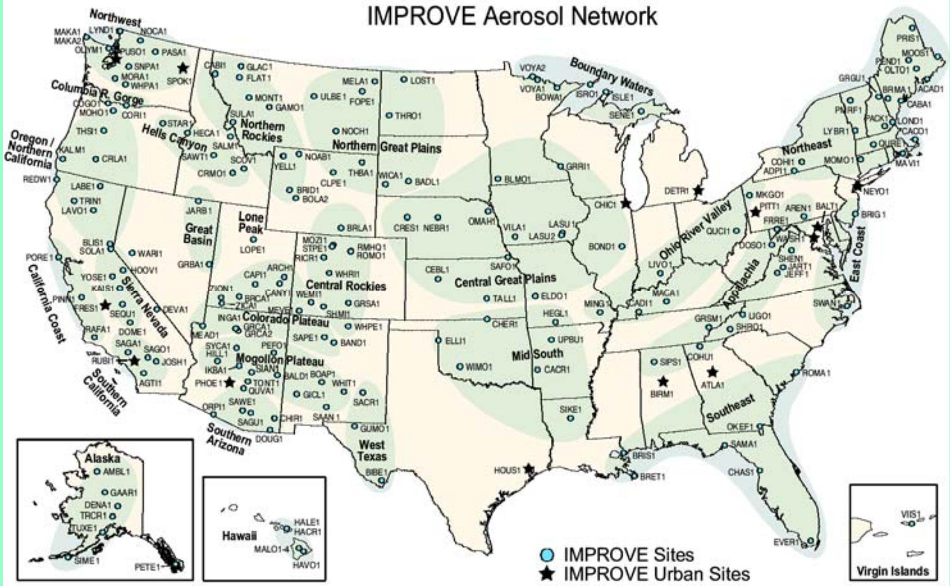
MetOne SASS

URG 3000N

R&P Partisol

CSN Samplers

Interagency Monitoring of PROtected Visual Environments (IMPROVE) Network

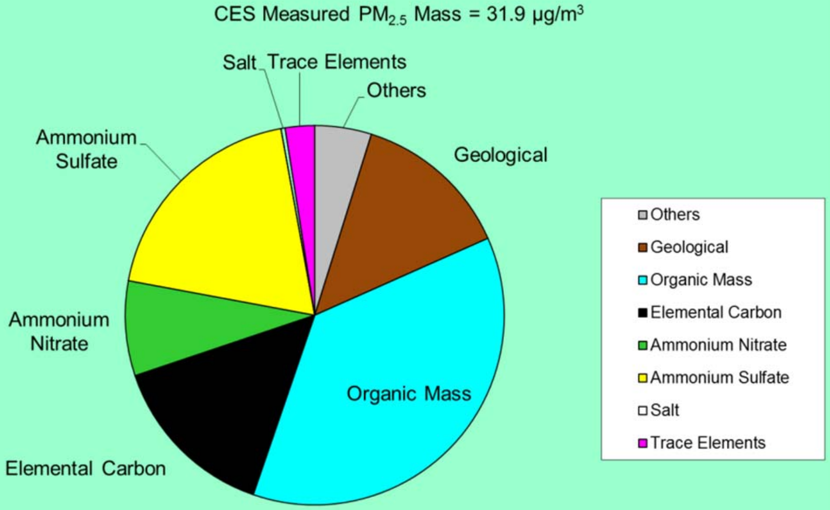


IMPROVE Samplers with Modules A, B, and C

http://vista.cira.colostate.edu/improve/Web/MetadataBrowser/metadatabrowser.aspx

There are 11 published mass reconstruction equations*

(RM = Inorganic Ions + OM + EC + Minerals + Salt + Trace Elements + Others)



I. Secondary inorganic ions
(i.e., sum of $SO_4^=$, NO_3^-, and NH_4^+ or sum of $(NH_4)_2SO_4$ and NH_4NO_3)

II. Organic mass (OM)
(i.e., OM=f×OC; f=1.2–1.8)

III. Elemental carbon

IV. Geological minerals (e.g., oxides of Al, Si, Ca, Ti, Fe, and sometimes K)

V. Salt (e.g., Na^++Cl^-, 1.4486×Na+Cl, or 1.8×Cl^-)

VI. Trace elements (e.g., sum of remaining measured species excluding double counting)

VII. Others (e.g., remaining mass, particle-bound water, non-crustal K as either (K–0.6×Fe) or 1.2×(K–0.6Fe), and non$SO_4^=$ S)

* Starting with Countess et al. (1980, *JAPCA*) Denver Brown Cloud Study

IMPROVE equations are used for light extinction calculation

(part of the Regional Haze Rule)

b_{ext} (Mm^{-1}) = Σdry extinction efficiency (m^2/g) × humidity multiplier × species concentration $(\mu g/m^3)$

$$= 3f(RH) \times (NH_4)_2SO_4 + 3f(RH) \times NH_4NO_3 + 4 \times OM + 10 \times EC + Soil$$

$$+ 0.6 \times \text{Coarse Mass} + 10 \text{ (accounts for Clear Air Scattering)}$$

f(RH)=extinction efficiency increase with RH

OM = 1.4 × OC

OLD

b_{ext} (Mm^{-1}) = $2.2f_S(RH) \times$ [small sulfate] + $4.8f_L(RH) \times$ [large sulfate] +$2.4f_S(RH) \times$ [small nitrate] + $5.1f_L(RH) \times$ [large nitrate] + 2.8 × [small OM] + 6.1 × [large OM] + 10 × [EC] + 1 × [fine soil] + $\boxed{1.7f_{SS}(RH) \times \text{[sea salt]}}$ + 0.6 × [Coarse Mass] + Rayleigh Scattering (site specific) + $\boxed{0.33 \times [NO_2 \text{ (ppb)}]}$

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 ≥ 20 μg/m^3

OM = 1.8 × OC

NEW

I. Estimating contributions from Inorganic Ions is straight forward

- Without NH_4^+ measurements:

  --Sum of $(NH_4)_2SO_4$ and NH_4NO_3 (i.e., as 1.375×$SO_4^=$ and 1.29×NO_3^-; ion balance should be applied to verify the extent of neutralization)

  --Sum of 4.125xS (for $(NH_4)_2SO_4$ plus NO_3^- or 1.29×NO_3^- [excluding $NaNO_3$, $Ca(NO_3)_2$, and NH_4Cl])

- With NH_4^+ measurements:

  --Sum of $SO_4^=$*, NO_3, and NH_4^+ (excluding H_2SO_4, NH_4HSO_4, or levovicite [$(NH_4)_3H(SO_4)_2$])

*Non-sea salt $SO_4^=$ ($nssSO_4^=$) has been used to avoid overestimation of $SO_4^=$ in coastal environments

Uncertainties Associated with Using 3×S as $SO_4^=$

- Total sulfur (S) by XRF* may associate with insoluble organic compounds (e.g., methyl mercaptan, CH_4S)
- Not all S is water soluble (e.g., gypsum [$CaSO_4 \cdot 2H_2O$] and pyrite [FeS_2])
- Total S may consist of SO_2 adsorbed onto particles (e.g., soot)
- S standard deposited on thin-film filters for XRF is not as consistent as NIST rainwater standard for $SO_4^=$

*XRF: x-ray fluorescence

II. Different multipliers (f) are used to estimate Organic Mass (OM) for Organic Carbon (OC)

(not many measurements were made on OM/OC ratios)

(f=1.2-2.6; most commonly used is 1.4 for urban and 1.8 for non-urban aerosols)

- f=1.2 based on Countess et al., (1980) analysis of:

--carboxylic acid (C_{16} = (C+H+O)/C = 1.3)

--polynuclear aromatic ((C+H)/C=1.08)

--aliphatic compounds ((C+H)/C=1.17)

(average of 1.3, 1.08, and 1.17 is 1.18)

Countess et al., (1980). *JAPCA*

II. Different multipliers (f) are used to estimate Organic Mass (OM) for Organic Carbon (OC) (cont'd)

- f=1.4 derived from two Los Angeles TSP samples (White and Roberts, 1977):

-- (C+H+N+O)/C=1.5 for oxygen

-- (C+H)/C=1.17 or 1.2 for aliphatic compounds

-- (1.5 + 1.2)/2= 1.35, ~1.4

II. Different multipliers (f) are used to estimate Organic Mass (OM) for Organic Carbon (OC) (cont'd)

- f=1.5 was based on assumed organic composition proportional to $CH_2\ O_{0.25}$ (Macias et al., 1981)

- f=1.5 to 2.1 were used for biomass burning (Reid et al., 2005; Aiken et al., 2008)

- f=2.2 to 2.6 (Turpin and Lim, 2001)

Macias et al,. (1981). *Atmos. Environ*.; Reid et al., (2005) *Atmos. Chem. Phys.*;
Aiken et al., (2008) *Envi. Sci. Technol*.; Turpin and Lim (2001). *Aerosol Sci. Technol*.

III. Elemental Carbon is straightforward and does not require any multiplier

- Uncertainties derived from the use of different carbon analysis protocols:

--Thermal/optical reflectance

(e.g., IMPROVE_A protocol, Chow et al., 2007)

--Thermal/optical transmission

(e.g., STN, NIOSH-like, or EUSARR II protocol)

Chow et al., (2007). *JAWMA*

IV. There is no consistent formula to estimate geological minerals

(As geological minerals are not a major component of $PM_{2.5}$, variations in mineral oxide multipliers do not affect mass reconstruction)

	Multiplier for Crustal Elements*					
Equation	**Al**	**Si**	**Ca**	**K**	**Ti**	**Fe**
A	1.89	2.14	1.40	0	0	1.43
B	2.20	2.94	1.63	0	1.94	2.42
C	1.89	2.14	1.40	1.20	1.67	1.45
D	0	3.48	1.63	0	1.94	2.42

* Converted to common oxides: Al_2O_3, SiO_2, CaO, K_2O, TiO_2, and Fe_2O/FeO

A Chow et al., (1994, *Atmos. Environ.*), modified from Macias et al., (1981, *Atmos. Environ.*), by removing 1.21K

B IMPROVE "Soil" formulae, multiplied by 1.16.

C Andrews et al., (2000). *JAWMA*

D Simon et al., (2011). *Atmos. Chem. Phys.*

Single crustal elements are also used to estimate geological minerals

- 3.5×Si (Countess et al., 1980)
- 4.807×Si (assuming 20.8% Si in soil) (Scheff and Valiozis, 1990)
- 13.77×Al (Ho et al., 2006)
- 12.5×Al (Hsu et al., 2008)
- 14.29×Al (Zhang et al., 2013)
- 4.3×Ca + 9×Fe (for background)
  or 4.5×Ca + a^*×Fe (for roadside)
  (Harrison et al., 2003)

$a^* = 3.5$ to 5.5

Countess et al., (1980). *JAPCA*; Scheff and Valiozis (1990). *Atmos. Environ.*;
Ho et al., (2006). *Sci. Total Environ.*; Hsu et al., (2008). *J. Geophys. Res. -Atmospheres*;
Zhang et al., (2013). *Atmos. Chem. Phys.*; Harrison et al., (2003) *Atmos. Environ.*

Several methods are used to estimate salt contributions

(Sea salt may account for 40-80% of $PM_{2.5}$ in coastal areas, with non-coastal contributions from dry lake beds and de-icing material.)

- $Na^+ + Cl^-$ (Chow et al., 1996)
- $1.4486 \times Na + Cl$ (Maenhaut et al., 2002)
- $3.27 \times Na^+$ (Ohta and Okita, 1994)
- $2.54 \times Na^+$ (Chen et al., 1997)
- $1.65 \times Cl^-$ (Harrison et al., 2003)
- $1.8 \times Cl^-$ (Revised IMPROVE Eq., based on the abundance of Cl^- in sea water) (White, 2008)

Chow et al., (1996). *Atmos. Environ.*; Maenhaut et al., (2002). *Nuclear Instruments and Methods*; Ohta and Okita (1994). *Atmos. Environ.*; Chen et al., (1997). *J. Geophys. Res.*; Harrison et al., (2003). *Atmos. Environ.*; White (2008). *Atmos. Environ.*

Assumptions were made for IMPROVE salt calculation

(1.8×Cl^-)

- No depletion of Cl^- from reaction with H_2SO_4 or HNO_3
- HCl is retained on the nylon-membrane filter
  (i.e., preceding $NaCO_3$ denuder only removes HNO_3; Sciare et al., 2003; Zhang et al., 2013)
- HCl only originates from reactions of acids and salts

Several other methods are also used to estimate salt contribution

- $Na^+ + Cl^- + Mg^{++}$ (Hsu et al., 2010)
- $Na^+ + Cl^- + Mg^{++}$ + sea salt K^+ + sea salt Ca^{++} + sea salt $SO_4^=$ (Sciare et al., 2003; Zhang et al., 2013)
- Sum of elements (excluding Cl and Cl^-) to Na or Na^+ ratio in sea water (Riley and Chester, 1971)

Sciare et al., (2003). *Atmos. Chem. Phys.*; Zhang et al., (2013). *Atmos. Chem. Phys.*;
Hsu et al., (2010). *J. Geophys. Res. –Atmospheres*; Riley and Chester (1971). *Introduction to Marine Chemistry*

More complicated methods can be used to refine sea salt calculation

- substituted sea salt = depleted sea salt + substituted NO_3^- + substituted nss-$SO_4^=$

where:

- depleted sea salt = unreacted sea salt – depleted Cl
- unreacted sea salt = 3.267×Na
- $xNa = Na^+_{(ambient)} - Na^+_{(soil)}[Si_{(ambient)}/Si_{(soil)}]$
- depleted Cl = 1.798×Na – $Cl_{(ambient)}$
- substituted NO_3^- = depleted Cl(62/35)
- substituted non-sea-salt $SO_4^=$ = 0.25×Na

Watson and Chow (2015). *Introduction to Environmental Forensics*; Chen et al., (2015). *Atmos. Enivron*

VI. Trace elements are negligible in $PM_{2.5}$ (0.5-1.6% of $PM_{2.5}$ mass)

- Add CuO + ZnO + PbO in soil formula
- Sum of remaining elements by X-ray Fluorescence (XRF) (excluding S and geological minerals [Al, Si, K, Ca, Ti, and Fe])
- Add remaining oxides of trace elements (e.g., oxides of V, Mn, Ni, Cu, Zn, As, Se, Sr, and Cr) in soil formula

Macias et al., (1981). *Atmos. Environ.*; Chow et al., (1994). *Atmos. Environ.*; Landis et al., (2001). *Atmos. Environ.*

VII. The remaining mass (Others) could be negative or positive

- Measurement errors
- Particle-bound water
- Improper OM/OC multipliers
- Missing sources

Uncertainties in Mass Reconstruction

- Ammonium and nitrate volatilization
- Water uptake on Teflon-membrane filter deposits at different equilibration relative humidities (30-40% RH for gravimetric mass)
- Sampling and analysis of carbon (e.g., sampling artifacts, carbon analysis methods, and OC multiplier)

Chow et al., (2005). *JAWMA*

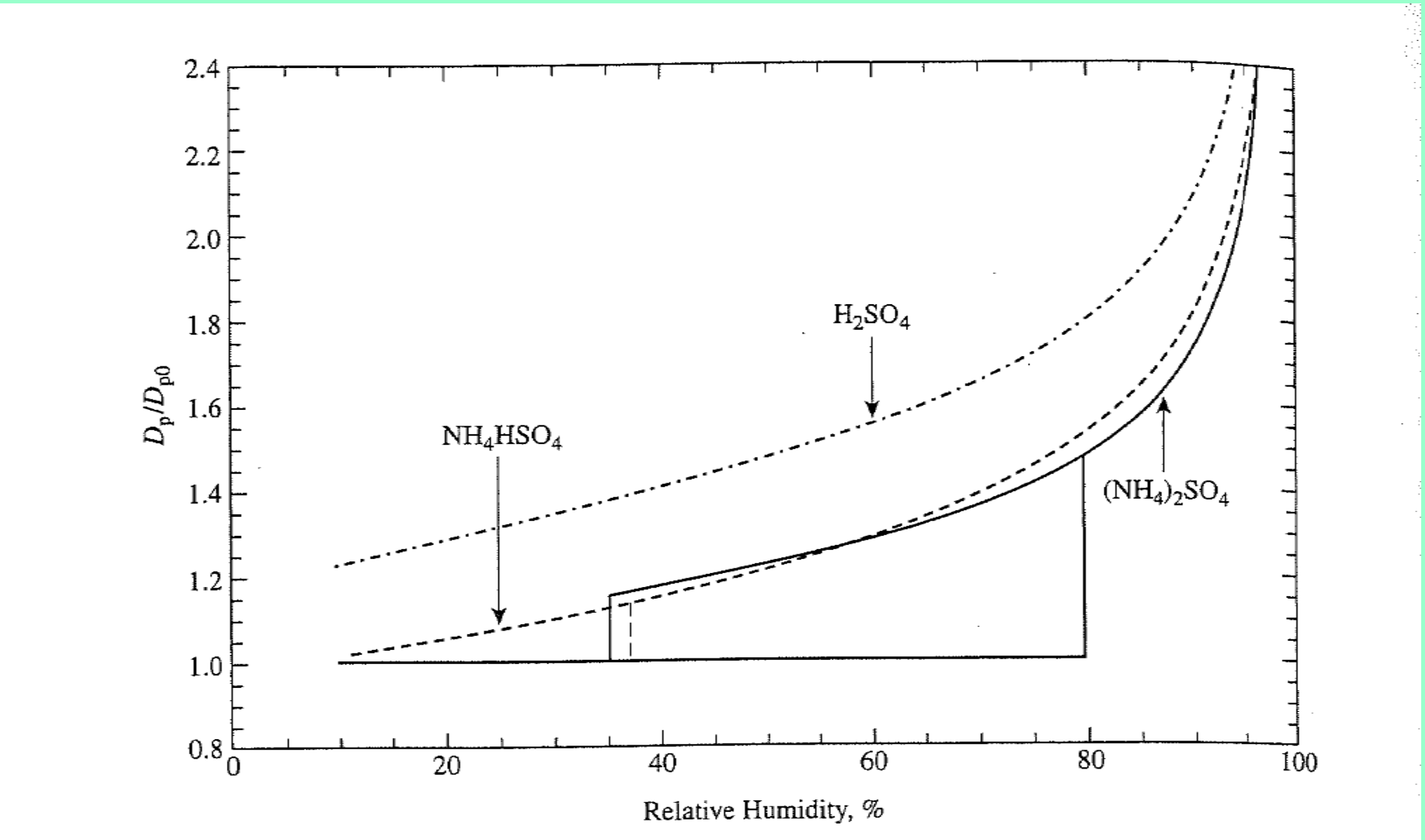
Both non-volatilized and volatilized NH_4^+ and NO_3^- should be measured

- Volatilized NO_3^- may account for ~80% of $PM_{2.5}$ during fall/winter (e.g., Central California, Chow et al., 2005)
- Volatilized NO_3^- is not considered in the U.S. EPA's $PM_{2.5}$ Federal Reference Method (FRM), but it needs to be included in evaluating light extinction and health effects
- Nylon-membrane filters (used in U.S. networks) retain volatilized NO_3^- but lose 1-65% of NH_4^+ (i.e., NH_3)

Chow et al., (2015). *Air Qual Atmos Health*

Water may constitute >50% of $PM_{2.5}$ mass at RH>80%

(($(NH)_4SO_4$, NH_4NO_3, NaCl, and organics absorb water)



From Seinfeld and Pandis, 2006

a. At deliquescence RH (DRH: ~80%), $(NH_4)_2SO_4$ starts to absorb H_2O
b. At efflorésence RH (ERH), the hydrated particle retains H_2O until it re-crystalizes at 30-40% RH

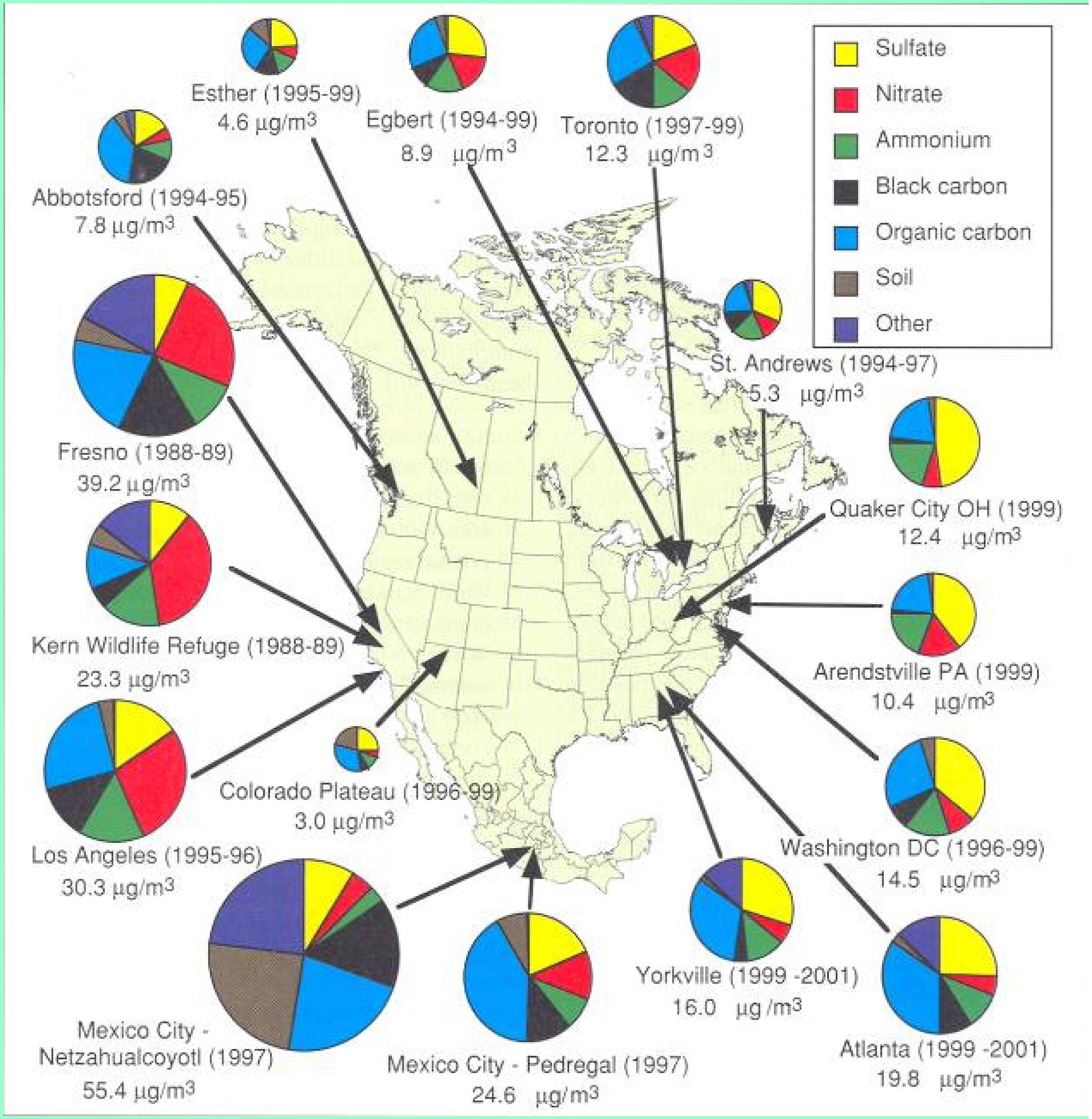
No standard methods to derive OM/OC ratios

(f = 1.2 - 2.6)

- Extraction (e.g., combination of water, solvent, and/or solid-state extraction) followed by organic speciation

- Direct analysis with different methods (e.g., elemental analysis [i.e., total C, H, N, S, and O]; Fourier-transform infrared [FTIR] spectroscopy [i.e., main functional groups]; and Quadrupole-Aerosol Mass Spectrometer [Q-AMS, i.e., molecular level quantification])

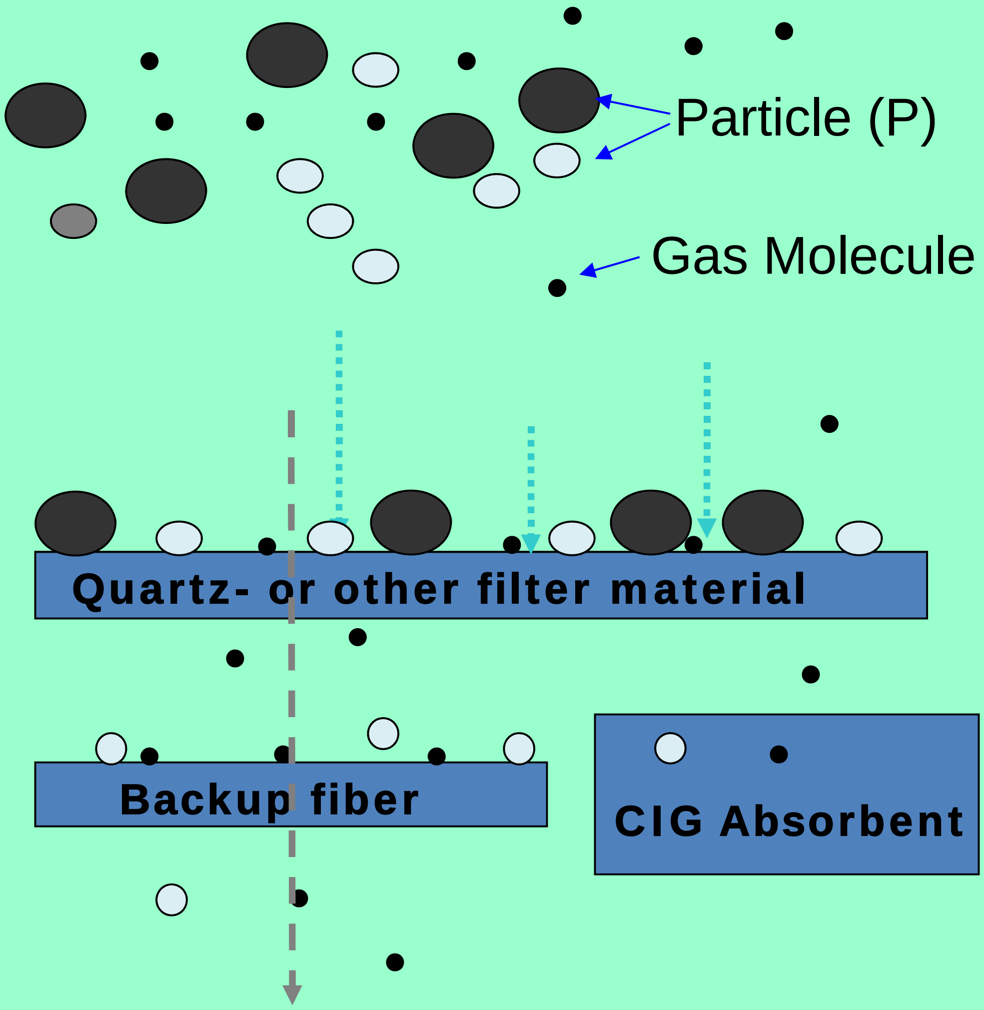
Carbon is a major component of atmospheric PM$_{2.5}$



NARSTO, 2004

There are positive and negative organic sampling artifacts

- **Positive** sampling artifact: SVOC is volatilized “*before*” captured by filters
- **Negative** sampling artifact: SVOC is volatilized “*after*” captured by filters

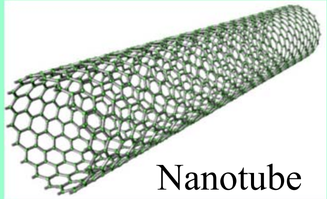


- Particle and gas are in a dynamic equilibrium!

CIG: Charcoal-impregnated glass-fiber filter
SVOC: semi-volatile organic compounds

Difficulties with OC and EC Sampling and Analysis

- No common definition or standard of EC for atmospheric applications
  - It's not graphite, diamond, or fullerenes (i.e., a molecular carbon)


Nanotube

- Light absorption efficiencies are not constant
  - They vary depending on particle shape and mixing with other substances
- OC and EC properties on a filter differ from those in the atmosphere
- OC gases are adsorbed onto the quartz-fiber filter while semi-volatile particles evaporate

Different carbon analysis methods can result in a factor of 7 variations in EC

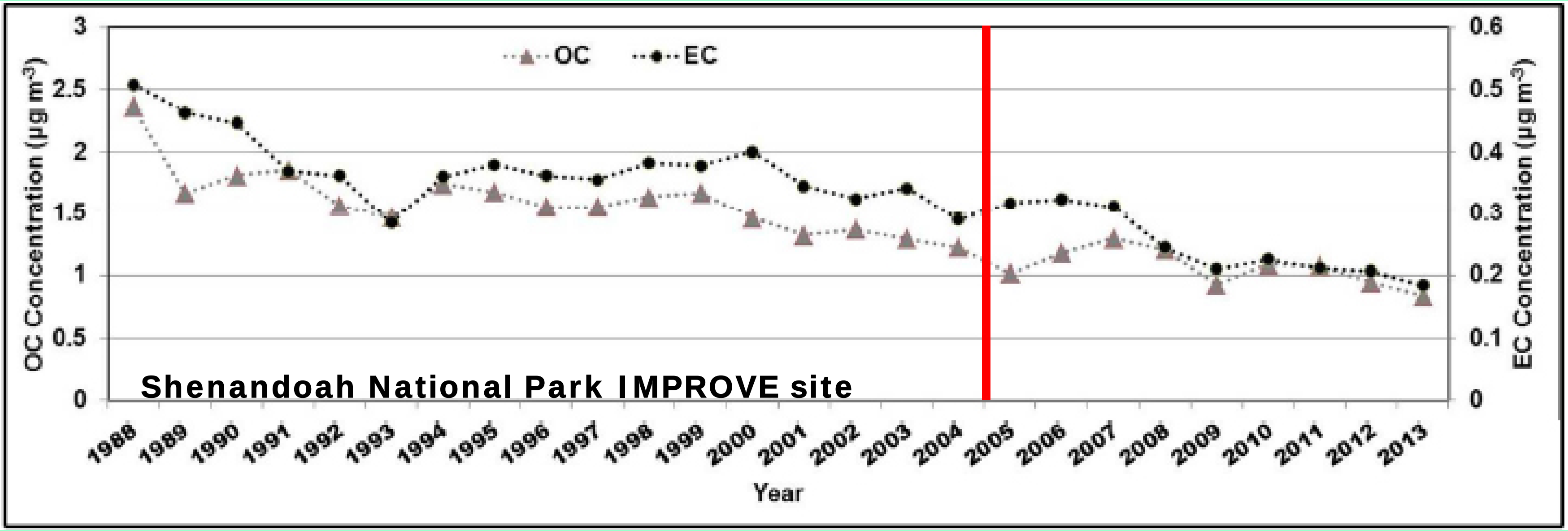
		IMPROVE_A*_TOR		**STN_TOT**		**EUSAAR_II_TOT**	
Carbon Fraction	Atmosphere[d]	Temp. (°C)	Residence Time (sec)	Temp. (°C)	Residence Time (sec)	Temp. (°C)	Residence Time (sec)
OC1	Inert	140	80–580	310	60	200	120
OC2	Inert	280	80–580	480	60	300	150
OC3	Inert	480	80–580	615	60	450	180
OC4	Inert	580	80–580	900	90	650	180
	Oven cooling	NA	NA	NA	30	NA	30
EC1	Oxidizing	580	80–580	600	45	500	120
EC2	Oxidizing	740	80–580	675	45	550	120
EC3	Oxidizing	840	80–580	750	45	700	70
EC4	Oxidizing	NA	NA	825	45	850	80
EC5	Oxidizing	NA	NA	920	120	NA	NA

*U.S. long-term network applied IMPROVE_A thermal/optical reflectance protocol

[Chow et al., (2007). *JAWMA*; Watson et al., (2005). *AAQR*]

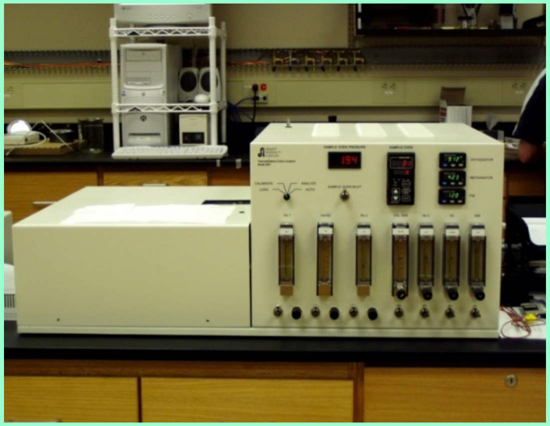
Long-term trends require consistent measurements

(1987/88-Present)



DRI/OGC (1987-2004)

DRI Model 2001 (2005-2015)



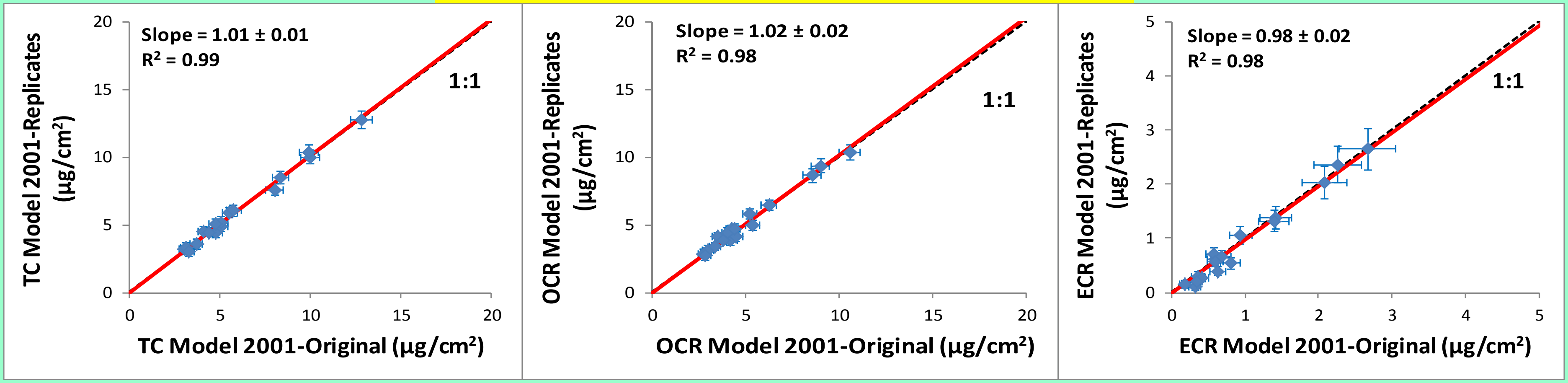
DRI Model 2015 (2016-onward)

Chow et al., (2015). *AAQR*

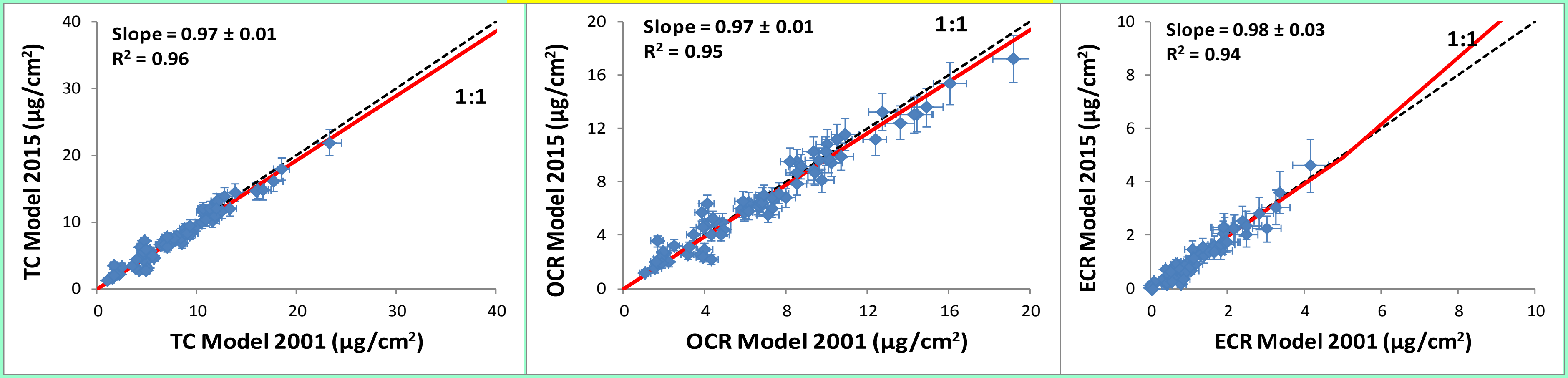
Equivalent OC and EC are obtained for single- and multi-wavelength systems

(633 nm vs 635 nm)

Model 2001 (A) vs Model 2001 (B)



Model 2015 vs Model 2001



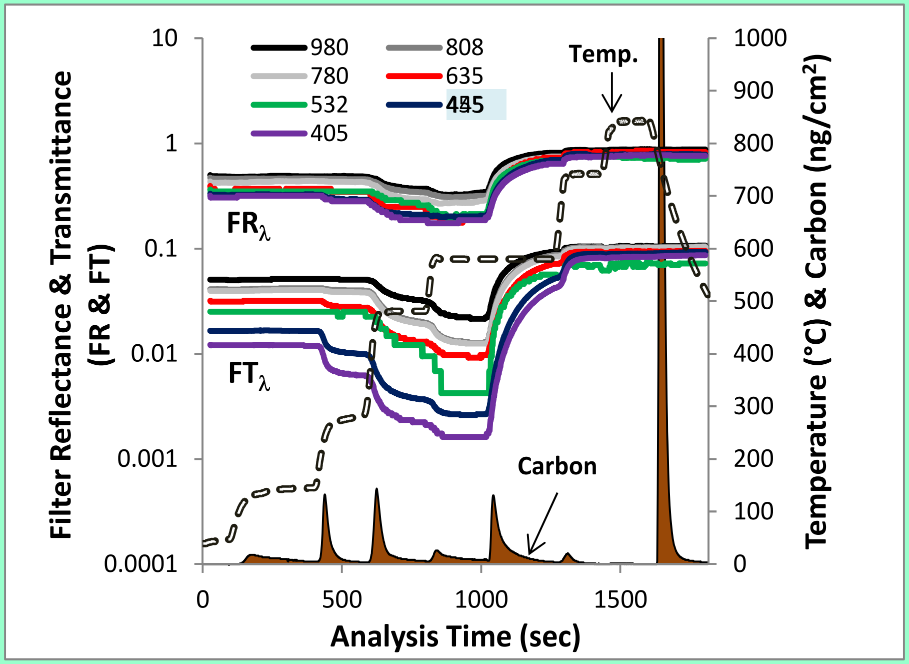
OCR and ECR are OC and EC by reflectance.

Chow et al., (2015). *AAQR*

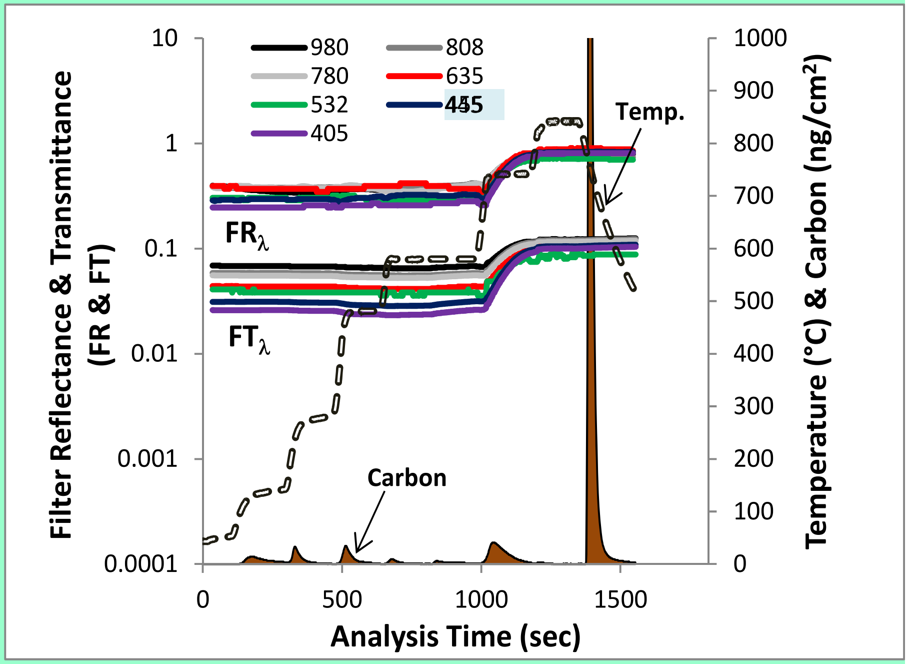
U.S. long-term CSN and IMPROVE network has transitioned to report OC and EC in seven wavelengths*

(starting 1/1/2016)

After Optical Calibration



Fresno Ambient Sample



Diesel Exhaust

- FR = Filter reflectance
- FT = Filter transmittance

*The seven wavelengths (i.e., 405, 445, 532, 635, 780, 808, and 980 nm) to separate brown carbon (BrC) from BC and EC

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, 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
- BrC = Brown 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)

BrC originates mostly from smoldering of biomass burning

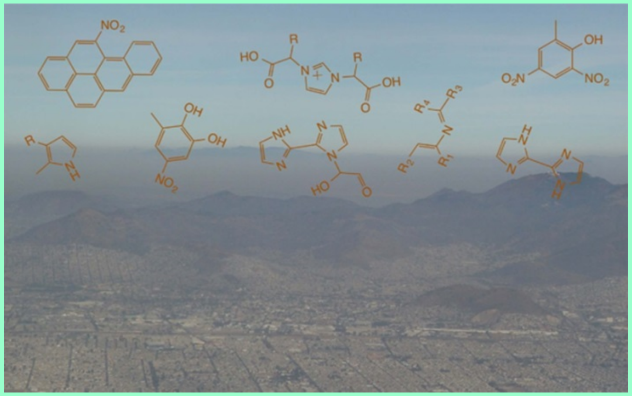
- Smoldering forest fires/biomass burning

(crop residual burn)

- Residential wood/coal cooking/heating

Andreae and Gelencser, 2006, *ACP*

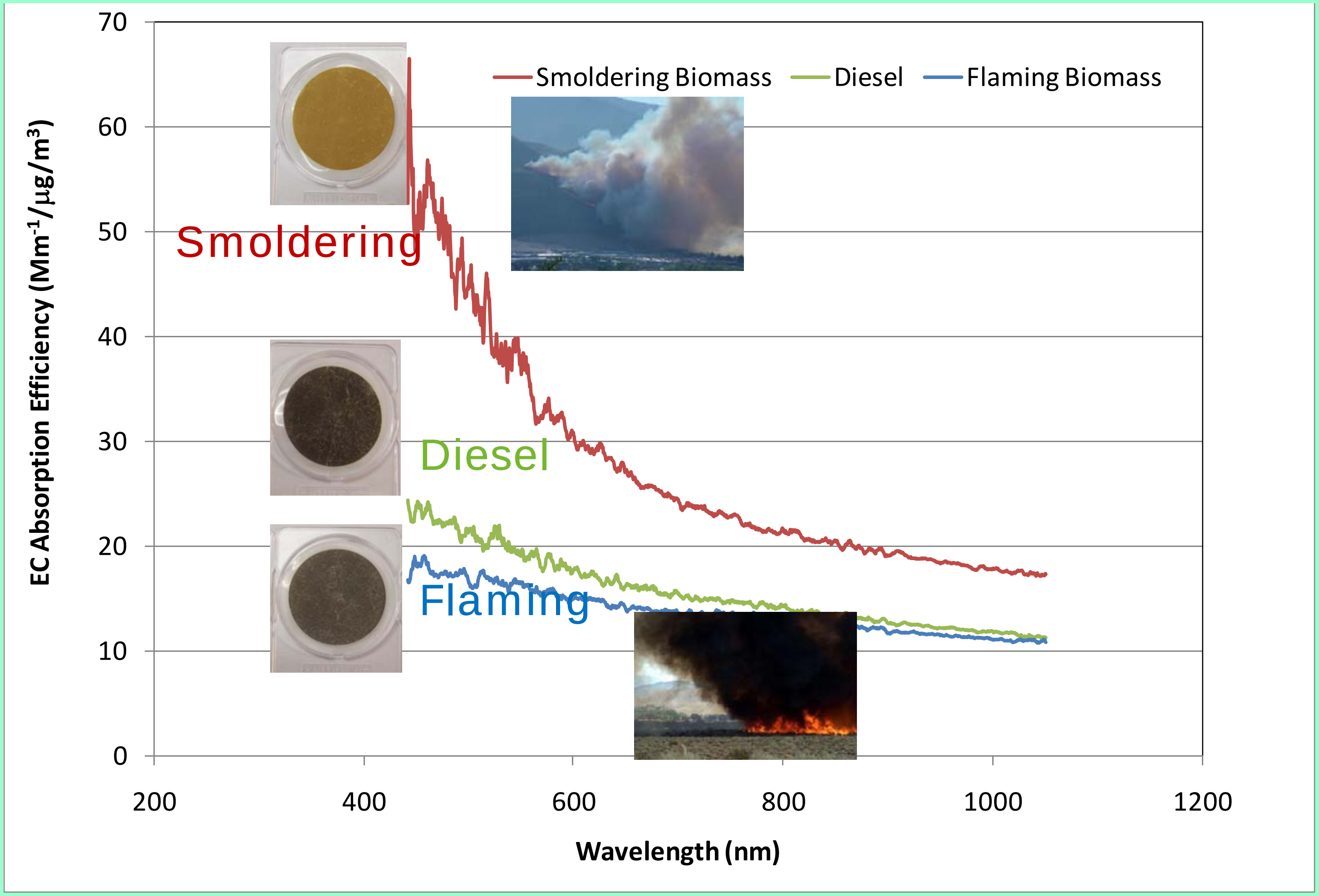
- Bioaerosol, soil humus, and humic-like substances (HULIS)



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

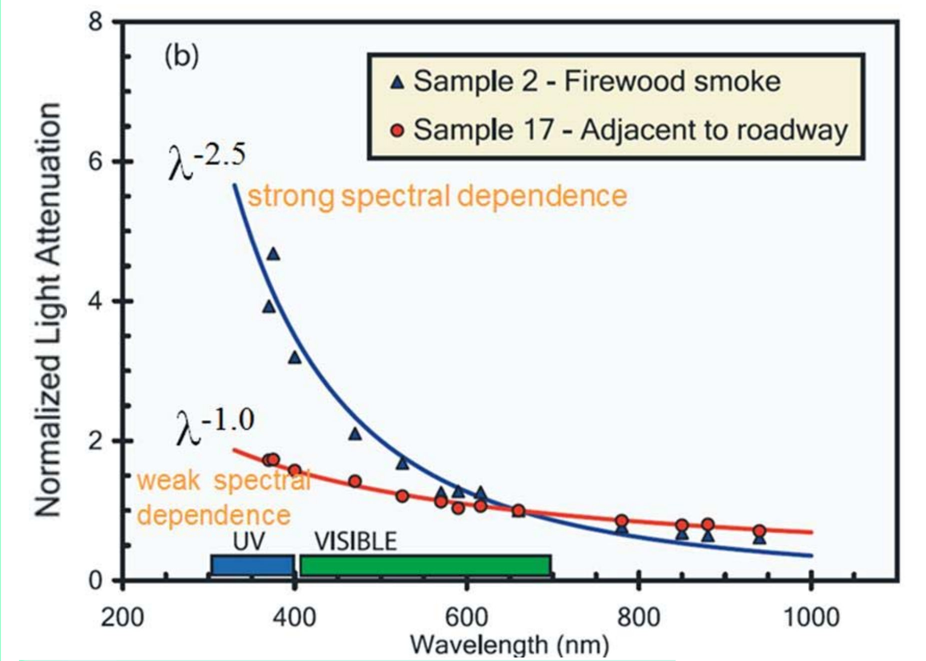
The smoldering and flaming phases of biomass burning show the largest differences between brown and black carbon

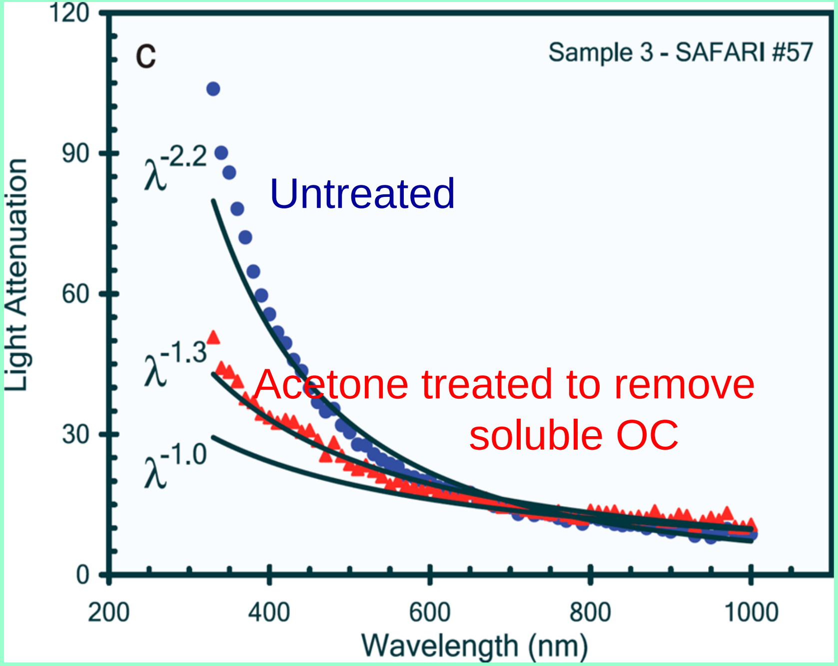
(EC absorption efficiency varies by source and wavelength)



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

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





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

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

MAC (Mass Absorption Cross section, m^2/g) = k x λ^{-AAE}

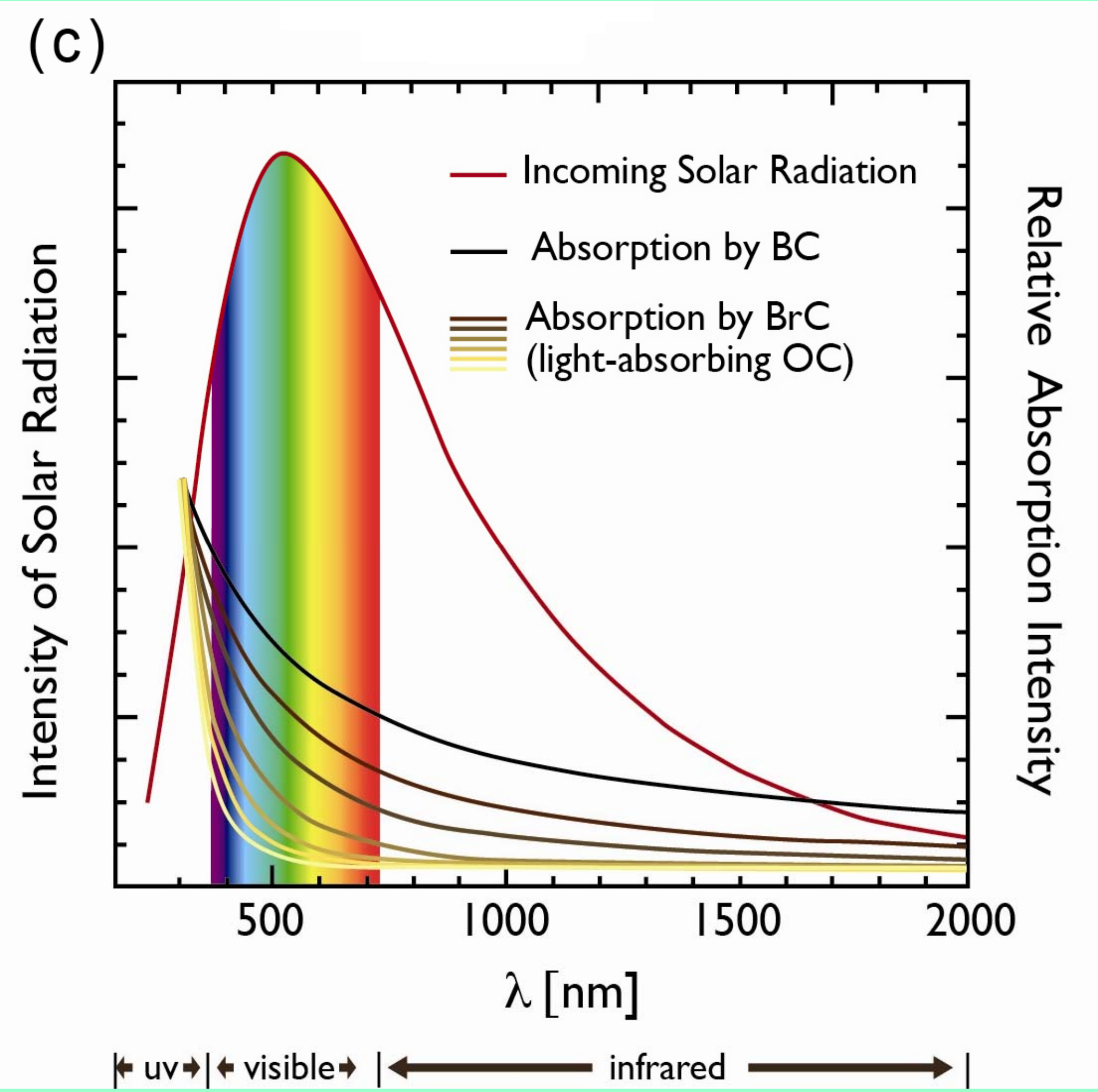
(Power Law relationship) where $MAC = \frac{b_{ATN(\lambda)}}{EC}$

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

* AAE: Absorption Ångström Exponent

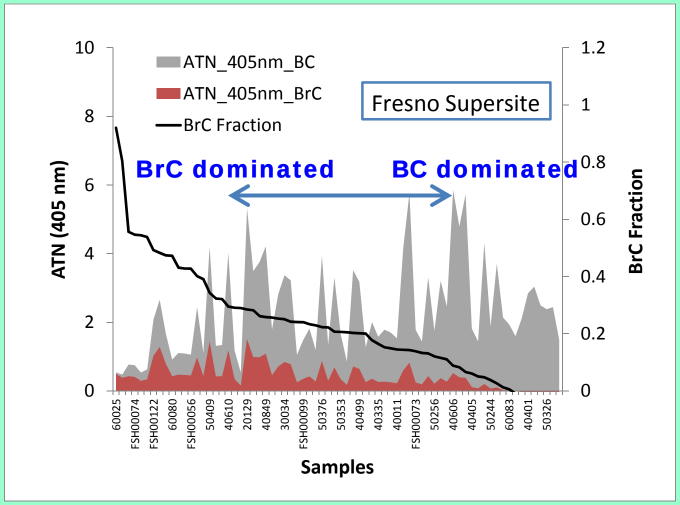
Kirchstetter et al., (2004). *J. Geophys. Res.*

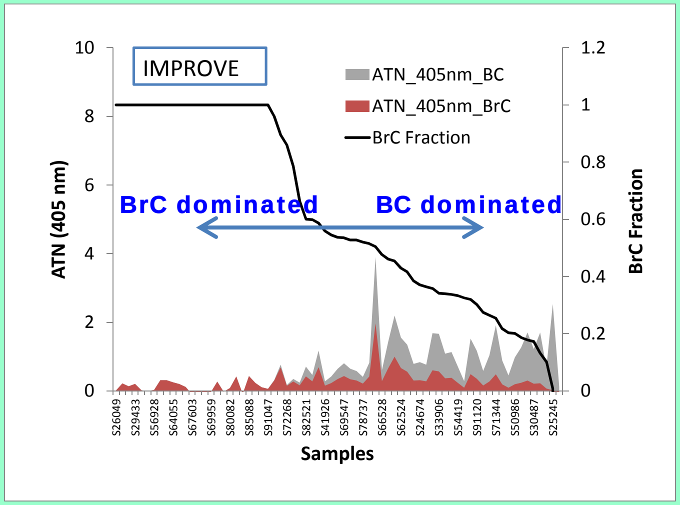
Brown Carbon (BrC) and BC absorb solar radiation over a broad spectrum range

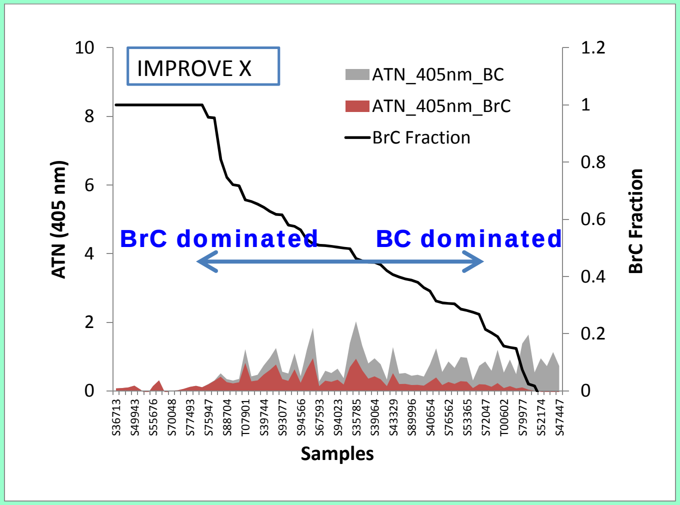


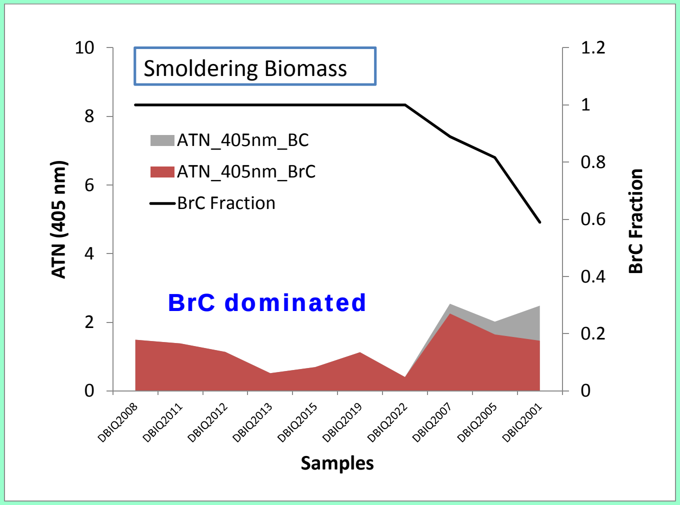
U.S. EPA, Report to Congress on Black Carbon, 2012

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

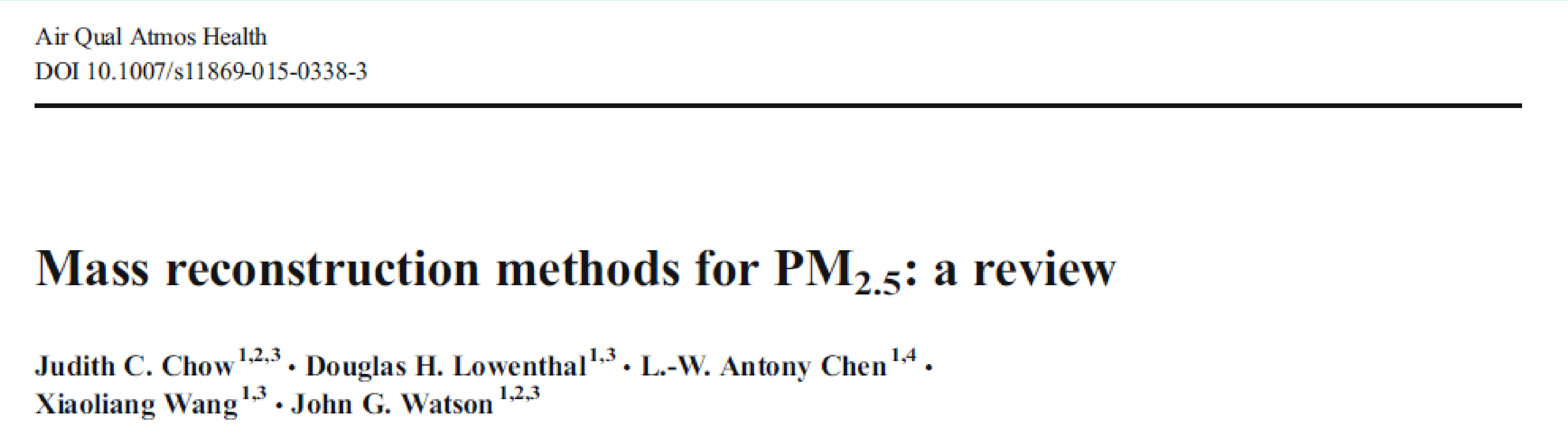
Summary and Conclusion

- Mass reconstruction is a simple and useful tool for validating the consistencies and addressing the uncertainties among mass and chemical measurements.
- Major PM can be summed with seven components:
  - -- major inorganic ions (e.g., $SO_4^=$, NO_3^-, and NH_4^+);
  - -- OC and its multiplier [f] to estimate OM;
  - -- EC;
  - -- geological minerals (based on estimated metal oxides of aluminum, silicon, calcium, potassium, titanium, and iron);
  - -- salt;
  - -- trace elements (excluding double counting of ions and crustal elements in geological minerals); and
  - -- others (as remaining mass, including particle-bound water and measurement errors).

Summary and Conclusion (cont.)

- Most commonly applied geological minerals are assumed as Al_2O_3, SiO_2, CaO, and Fe_2O_3/FeO (the assumption of oxide forms is more important for $PM_{10-2.5}$ and PM_{10} than for $PM_{2.5}$ [i.e., not a major component]).
- OC multiplier ranges 1.2-2.6, depending on the extent of OM oxidation (e.g., 1.4 for urban fresh aerosol and 1.8 for non-urban aged aerosol). Site specific OM/OC ratios (e.g., by month or season) need to be measured.
- Multi-wavelength carbon analysis may separate brown carbon from black carbon.
- Reasonably accurate mass reconstruction can be achieved by minimizing sampling artifact and conducting chemical analysis for ions, carbon, and elements.

More detailed information can be found in the following review:



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Mass reconstruction methods for $PM_{2.5}$: a review

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