# Understanding Thermal/Optical Analysis

Judith C. Chow (judy.chow@dri.edu)

John G. Watson

L.-W. Antony Chen

Desert Research Institute, Reno, NV

Presented at:

The Atmospheric Science Progress Review Meeting

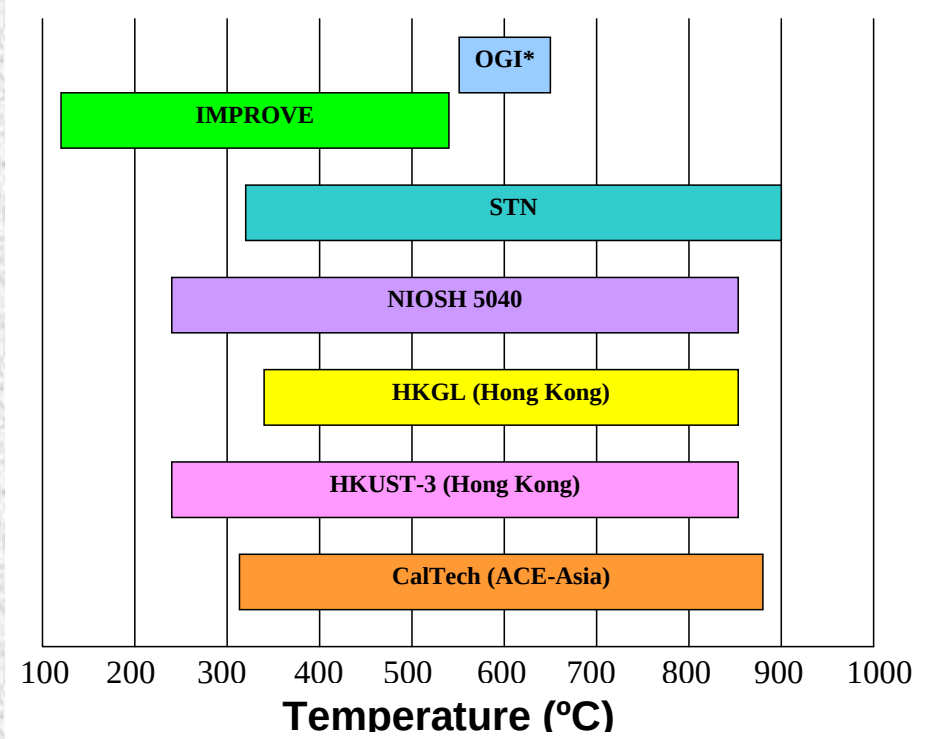
Research Triangle Park, NC

June 21, 2007

# Objectives

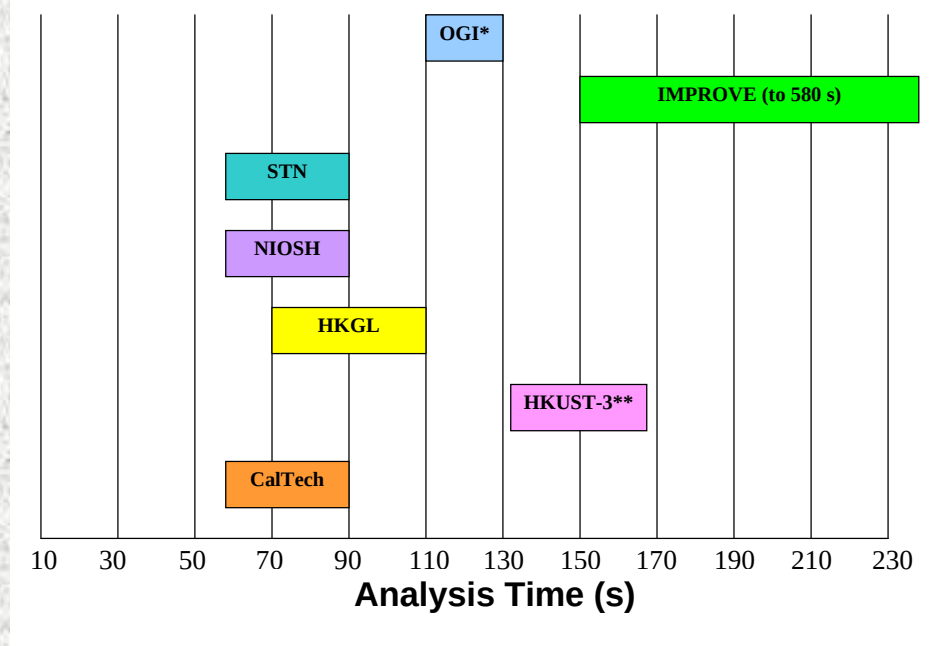
- Reconcile different thermal/optical methods by determining factors that influence OC/EC split
- Specify differences in optical properties between particles in the air, particles on a filter, and particles undergoing changes owing to thermal analysis
- Quantify differences in thermal carbon fractions determined by commonly used thermal/optical methods
- Optimize thermal/optical methods to meet multiple needs of health, visibility, global, and source apportionment

# Large Temperature and Analysis Time Variations in OC for Thermal/Optical Methods




(~120 to 900 °C)

*OGI OC performed at 600 °C only

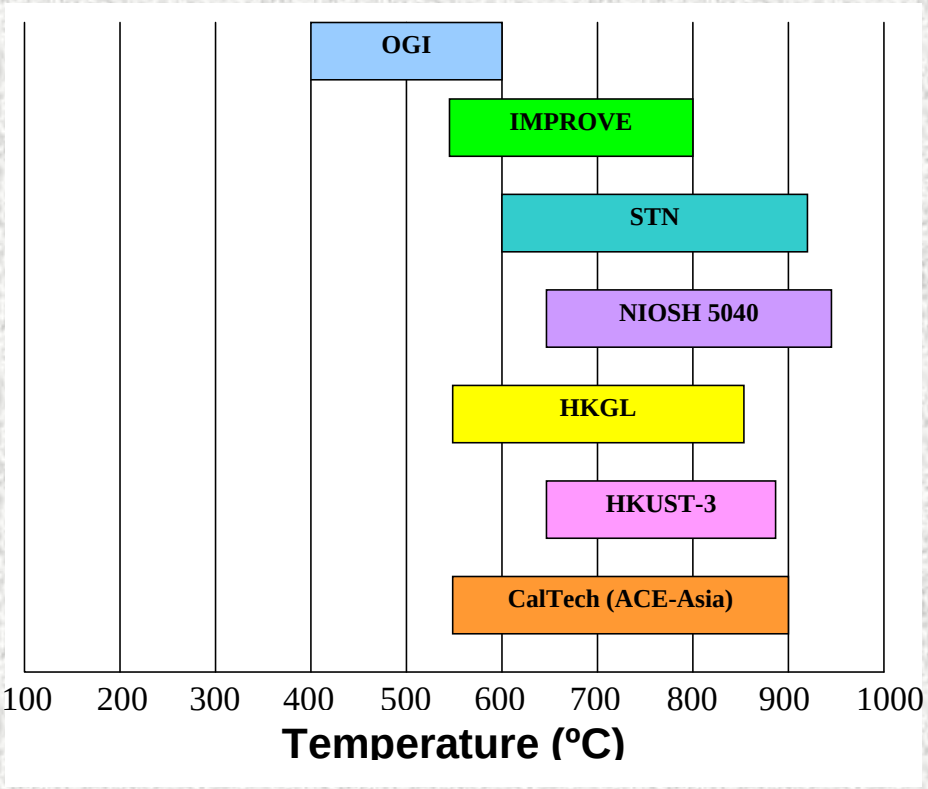



(~30 to 580 sec)

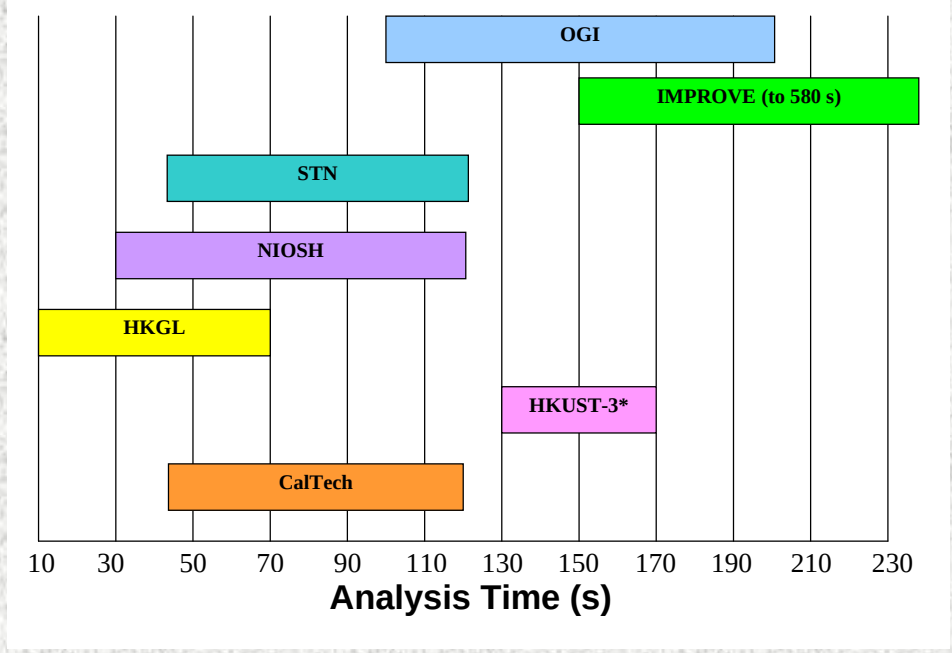
*OGI Time is variable
**HKUST-3 Time 150 s only

Watson et al. (2005)

# Large Temperature and Analysis Time Variations in EC for Thermal/Optical Methods




(400 to 920 °C)



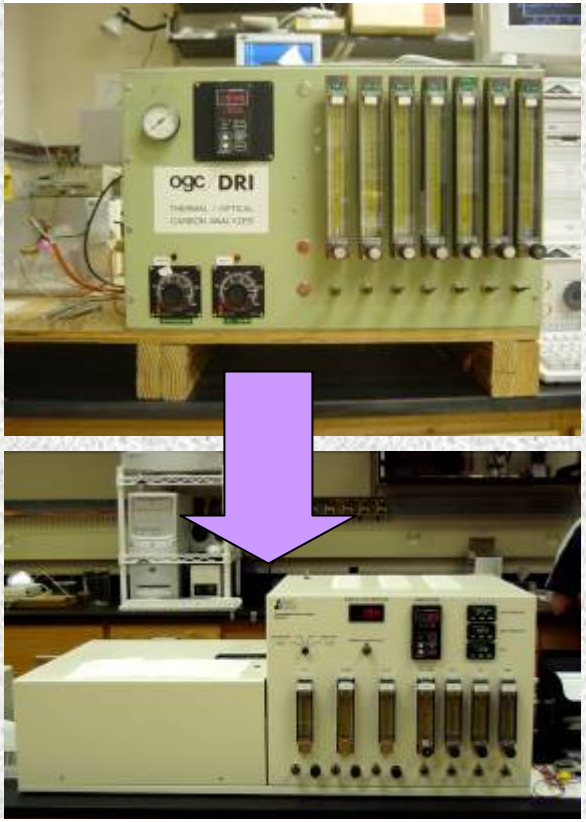

(60 to 580 sec)

*HKUST-3 Time 150 s only

Watson et al. (2005)

# IMPROVE vs. IMPROVE_A* Thermal Protocols

Original OGC/DRI Thermal Optical Analyzer (1986)

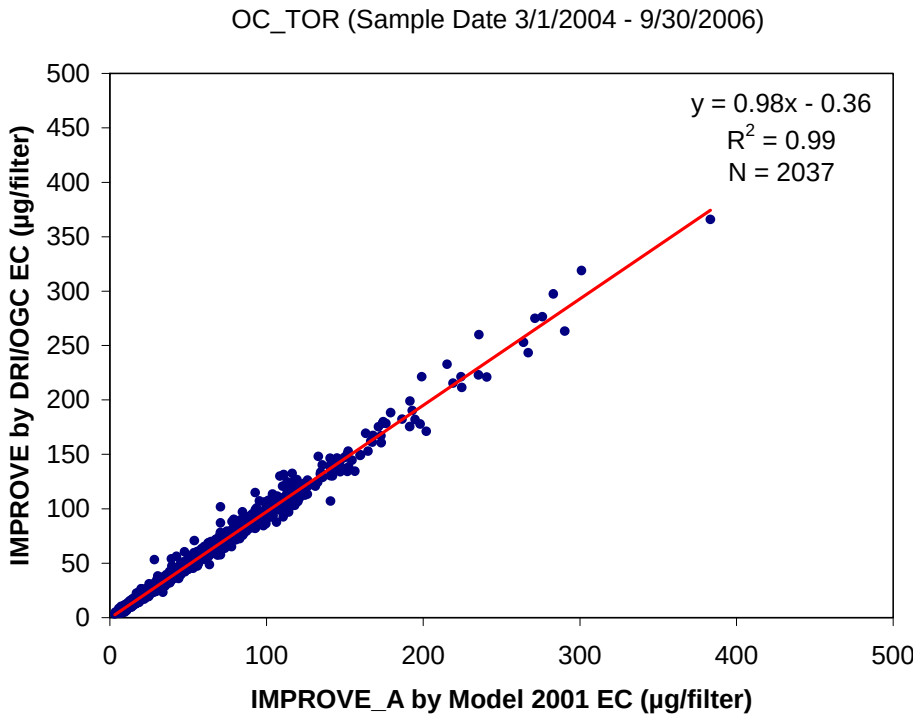


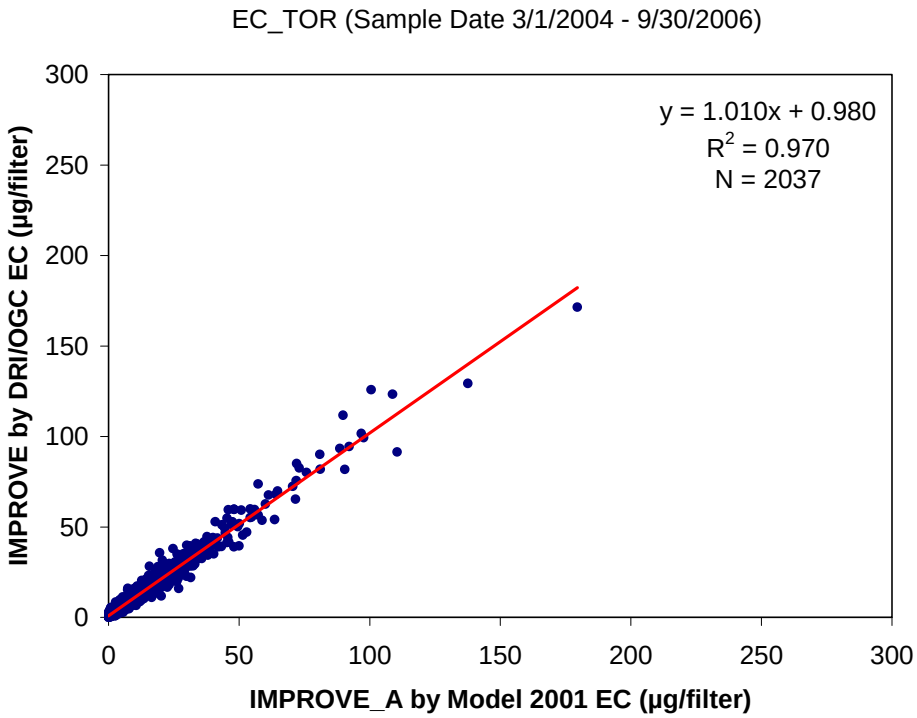

DRI Model 2001 Thermal/Optical Analyzer

| | IMPROVE_A* (DRI Model 2001) | IMPROVE (DRI/OGC) |
|---|---|---|
| OC1 | 140 ºC | 120 ºC |
| OC2 | 280 ºC | 250 ºC |
| OC3 | 480 ºC | 450 ºC |
| OC4 | 580 ºC | 550 ºC |
| OP (POC) | TOR/TOT | TOR |
| EC1 | 580 ºC | 550 ºC |
| EC2 | 740 ºC | 700 ºC |
| EC3 | 840 ºC | 800 ºC |

*After temperature and $O_2$ calibration. Implemented for samples acquired after January 1, 2005

# No difference in OC/EC split between IMPROVE by DRI/OGC and IMPROVE_A by Model 2001



# Effect on Carbon Fractions by Temperature and $O_2$ Level

- Low temperature OC1 (140 °C) and OC2 (280 °C) are sensitive to temperature independent of the oxidant level
- As $O_2$ > 100 ppmv in He atmosphere, changes in OC3 (480 °C), OP, and EC1 (580 °C) are found

# Laboratory Generated Carbon Sources

Diesel Generator

4 kW load
Dilution ratios (DR) of 18, 40, 80 and 150

sample time (T) of 20 or 60 min

Source, Source + NaCl

Acetylene Flame

2-inch flame

DR of 17

T of 20, 40, 70 min

Source, Source + NaCl

White Oak
DR of 18, 40, 105

T of 20 or 25 min

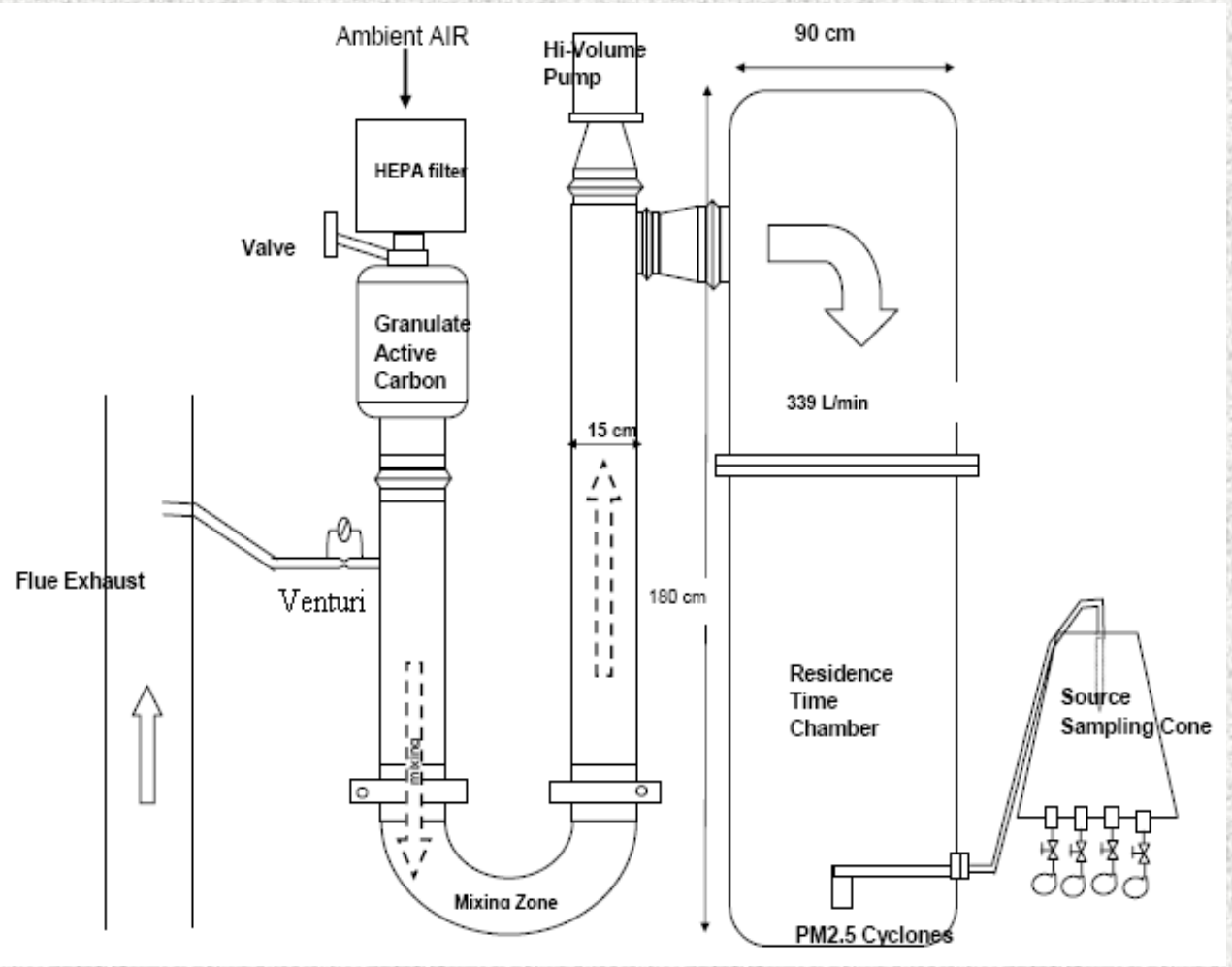
Source, Source + NaCl

Wood Stove

- Electric Arc Generator (PALAS) DR of 8; T = 20 or 40 min; Source, Source + NaCl

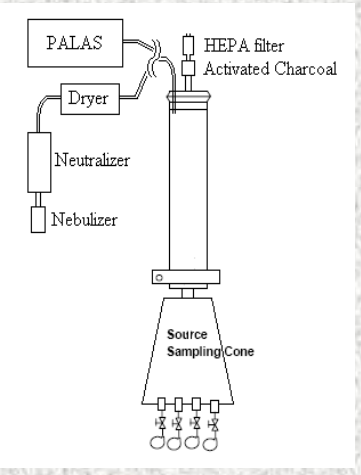
- Carbon Black and Graphite Powder

# Source Characterization Systems for Reference Samples



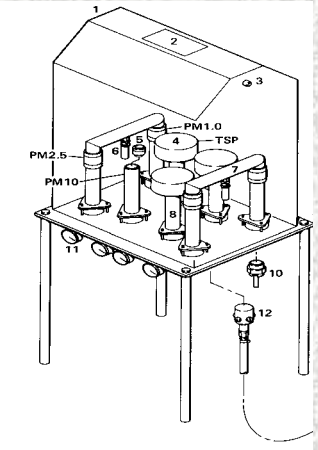

Dilution Sampling System

For
- Diesel Exhaust
- Acetylene Soot
- Wood Smoke




Miniature Dilution System

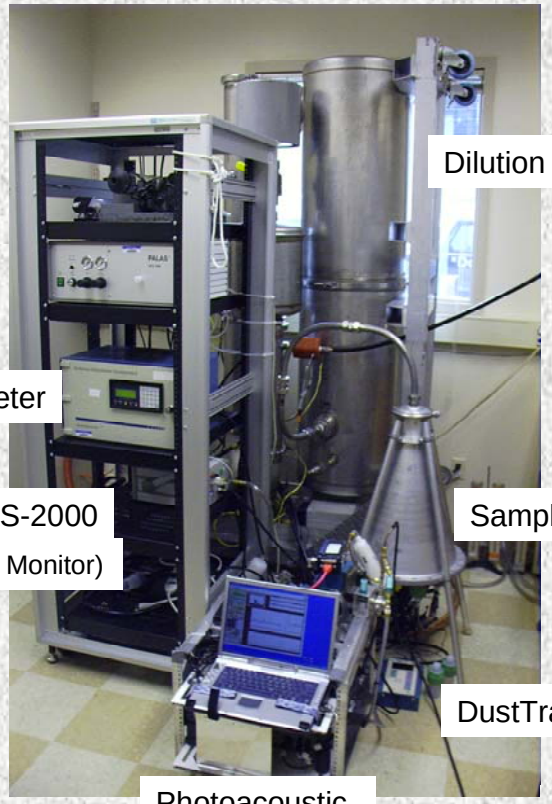
For Electric Arc Generator




Re-suspension Chamber

For Carbon Black

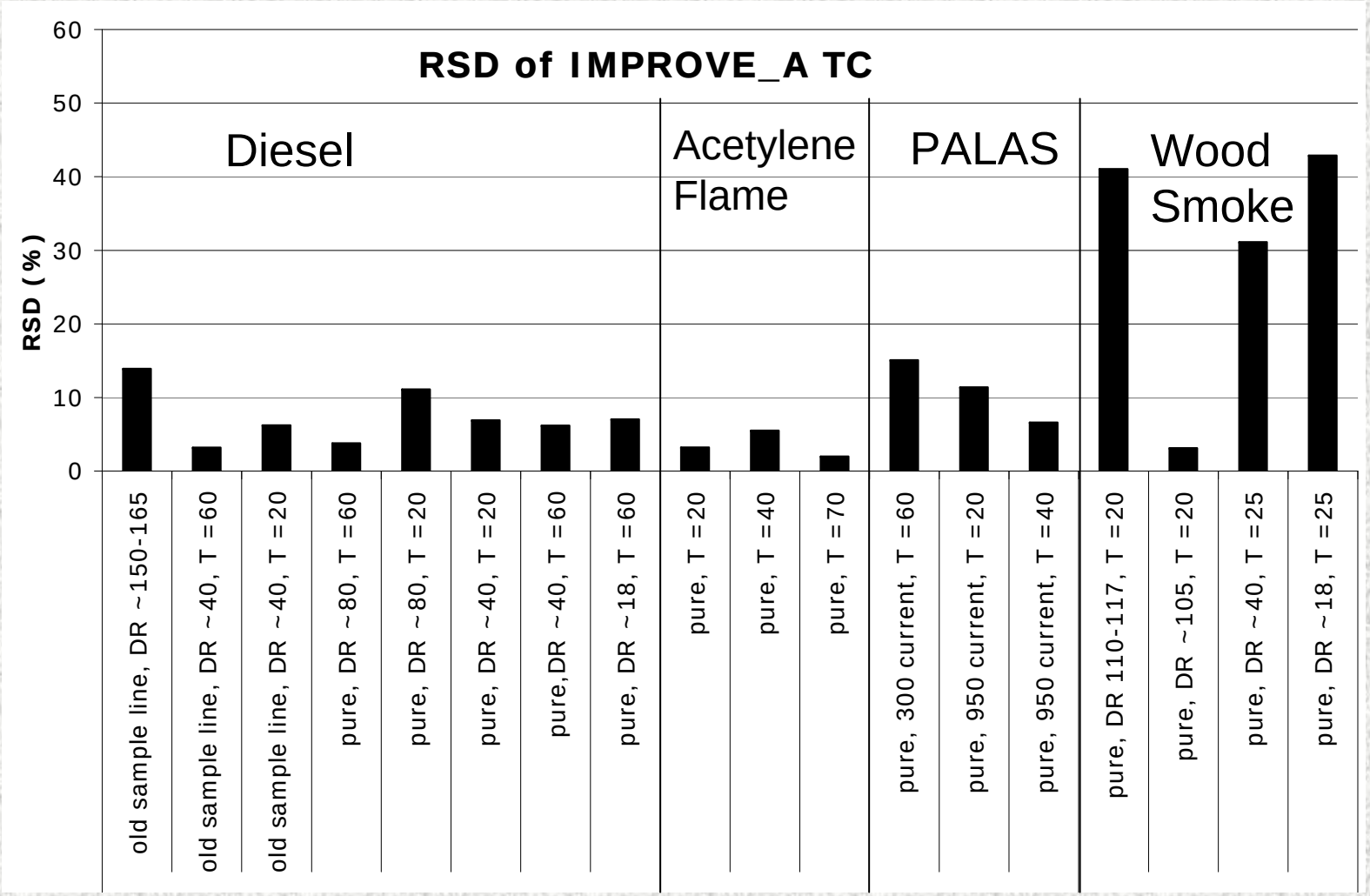
# Source Testing Instrumentation




Particle Sizing Instruments (3 nm to 10 µm)

- TSI Nano-SMPS (TSI, St. Paul, MN)
- Grimm SMPS+C (Grimm, Ainring, Germany)
- MSP Wide Range Spectrometer (MSP; St. Paul, MN)

# Most laboratory generated sources can reproduce TC (Relative Standard Deviation*, RSD < 15% typically, except for Wood Smoke)

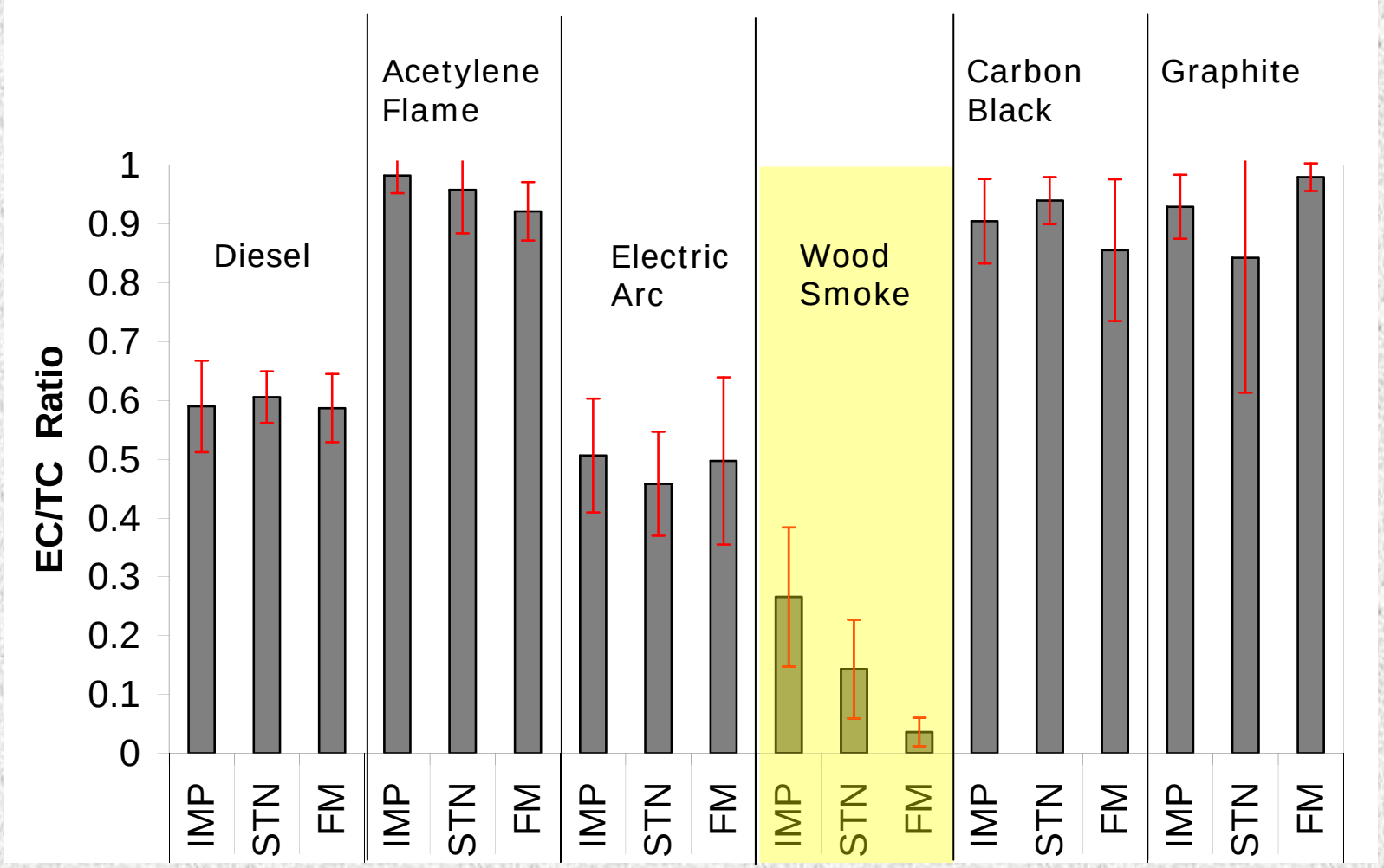



*standard deviation divided by the arithmetic mean, expressed in percentage

# IMPROVE, STN and French Protocols

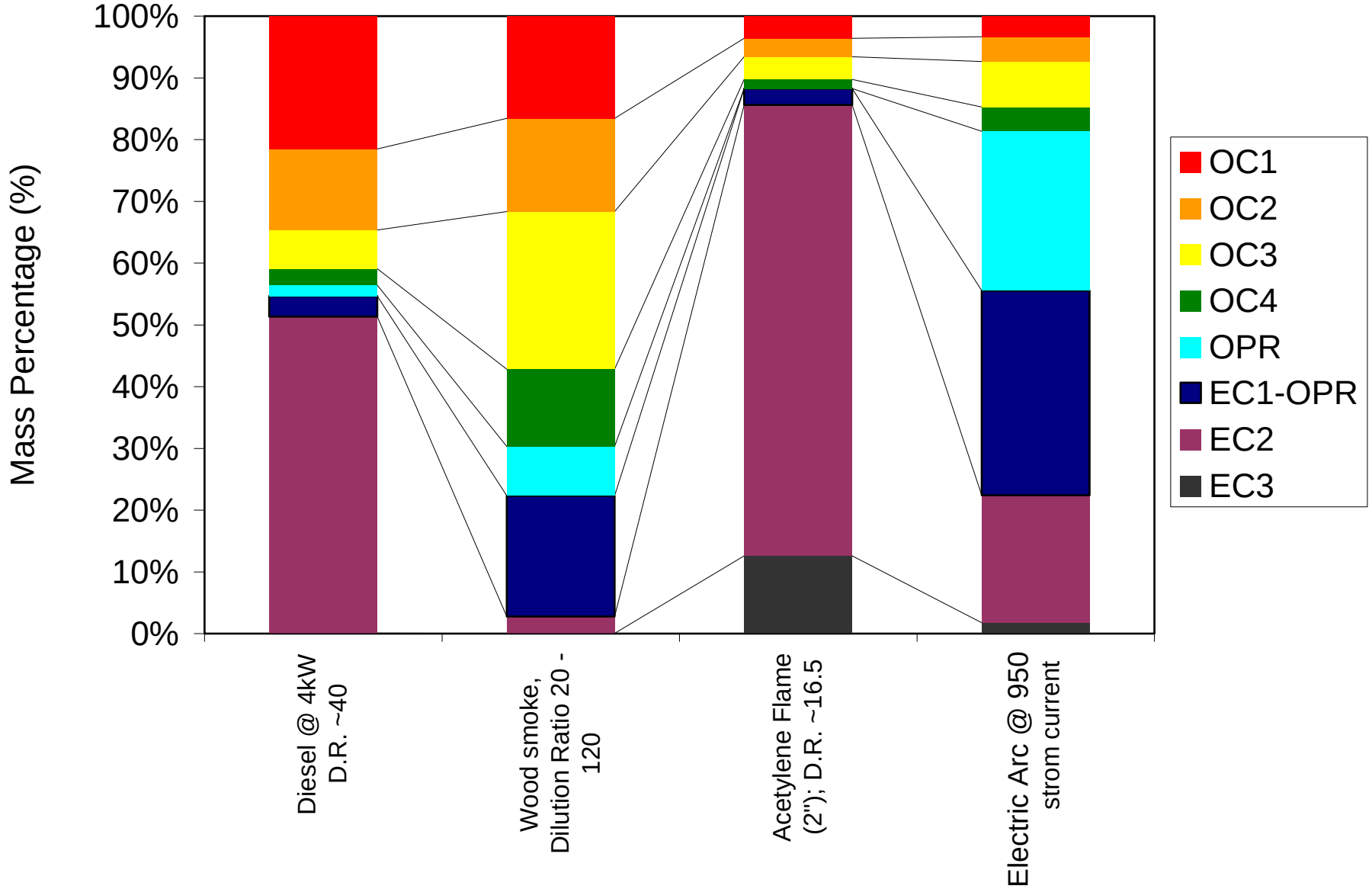
| | IMPROVE_A_TOR/TOT | | | STN_TOT | | | French 2-step | | |
|---|---|---|---|---|---|---|---|---|---|
| | Gas | Temp (°C) | Time (sec) | Gas | Temp (°C) | Time (sec) | Gas | Temp (°C) | Time (sec) |
| OC1 | He | 140 | 150 to 580 | He | 310 | 60 | | | |
| OC2 | He | 280 | 150 to 580 | He | 480 | 60 | | | |
| OC3 | He | 480 | 150 to 580 | He | 615 | 60 | $O_2$ | 340 | 7200 |
| OC4 | He | 580 | 150 to 580 | He | 900 | 90 | | | |
| | He | n/a | n/a | He | cool oven | - | | | |
| EC1 | $O_2$/He | 580 | 150 to 580 | $O_2$/He | 600 | 45 | | | |
| EC2 | $O_2$/He | 780 | 150 to 580 | $O_2$/He | 675 | 45 | | | |
| EC3 | $O_2$/He | 840 | 150 to 580 | $O_2$/He | 750 | 45 | $O_2$ | 1100 | ~600 |
| EC4 | $O_2$/He | n/a | n/a | $O_2$/He | 825 | 45 | | | |
| EC5 | $O_2$/He | n/a | n/a | $O_2$/He | 920 | 120 | | | |
| Detection | Methanator / FID | | | Methanator / FID | | | Coulometric titration of $CO_2$ for EC phase. TC from another punch. OC by difference. | | |
| Pyrolysis Correction | Reflectance & Transmittance | | | Transmittance | | | None | | |

# Source-to-source variations in EC are apparent (EC is similar between protocols, except for wood smoke)



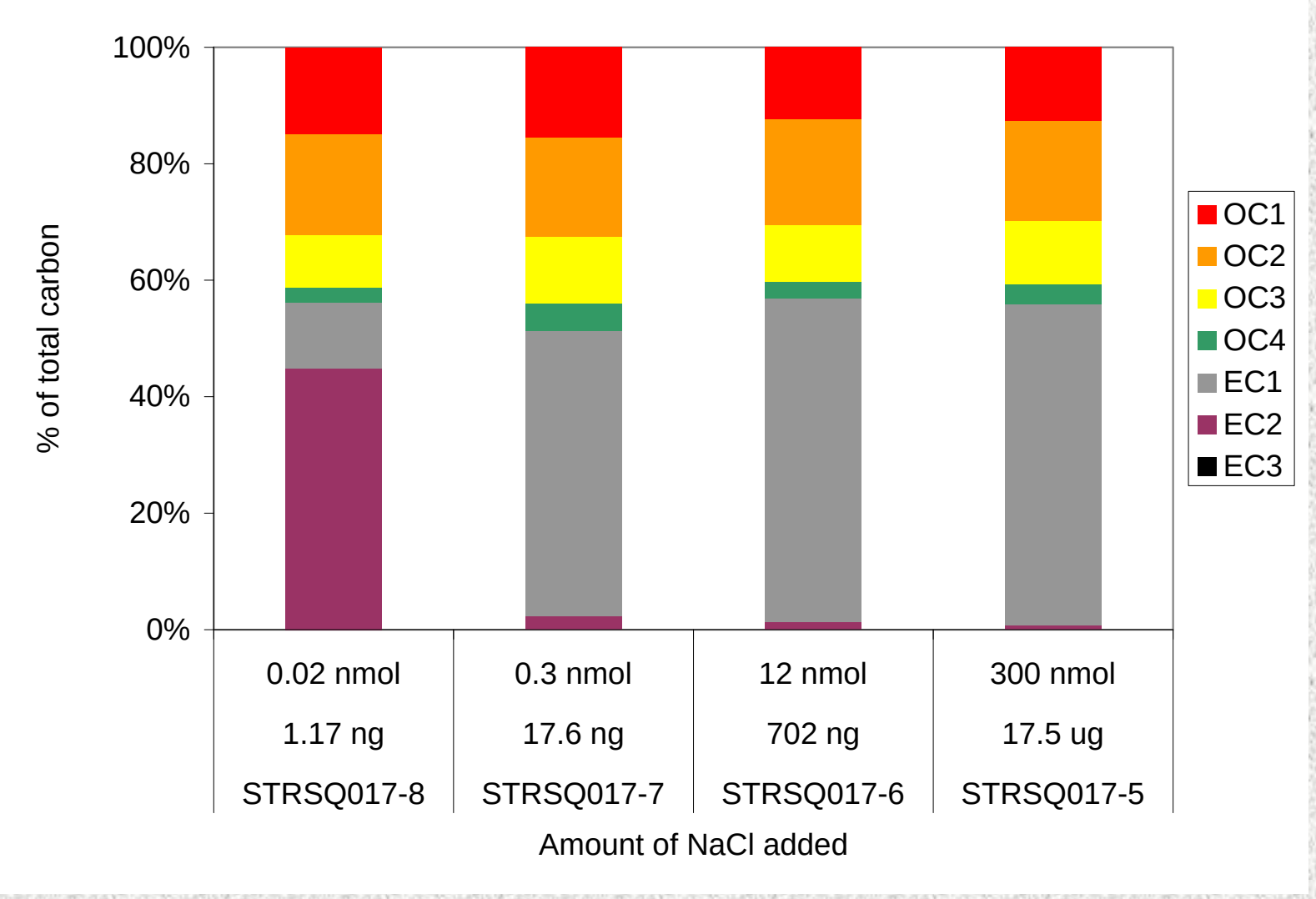

Doraiswamy (2007)

# Carbon fractions vary by source




Chow et al. (2007b)

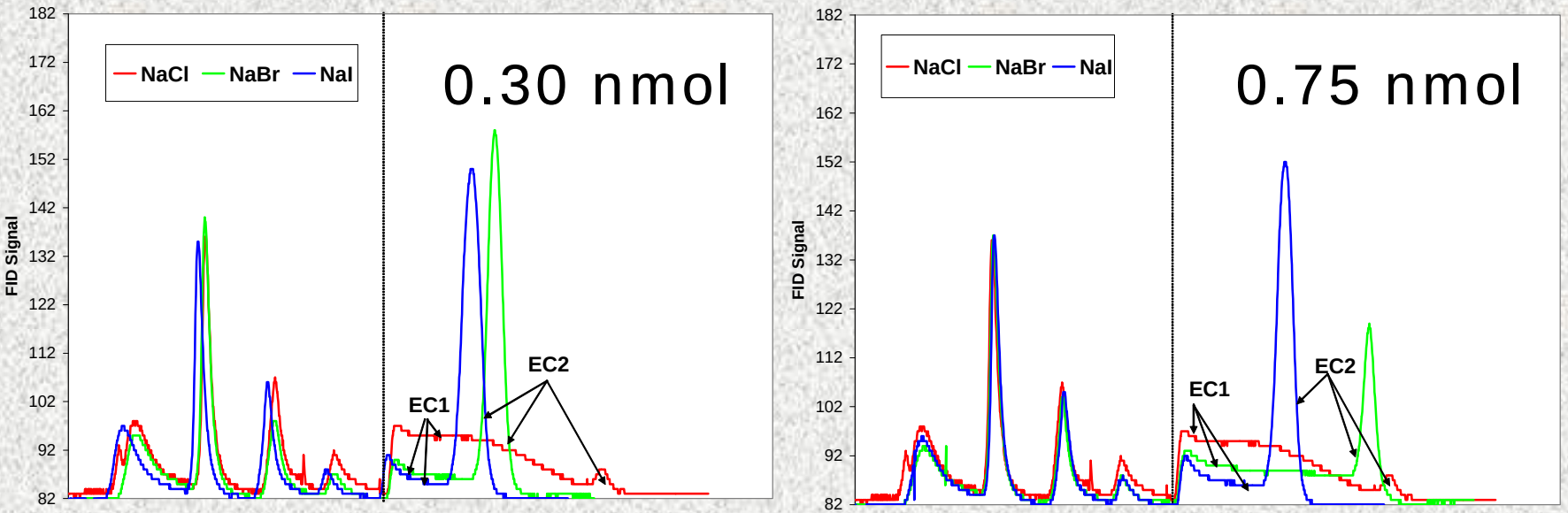
# Presence of NaCl shifts EC to lower temperature fractions*




* Higher NaCl -> greater shift from EC2 to EC1

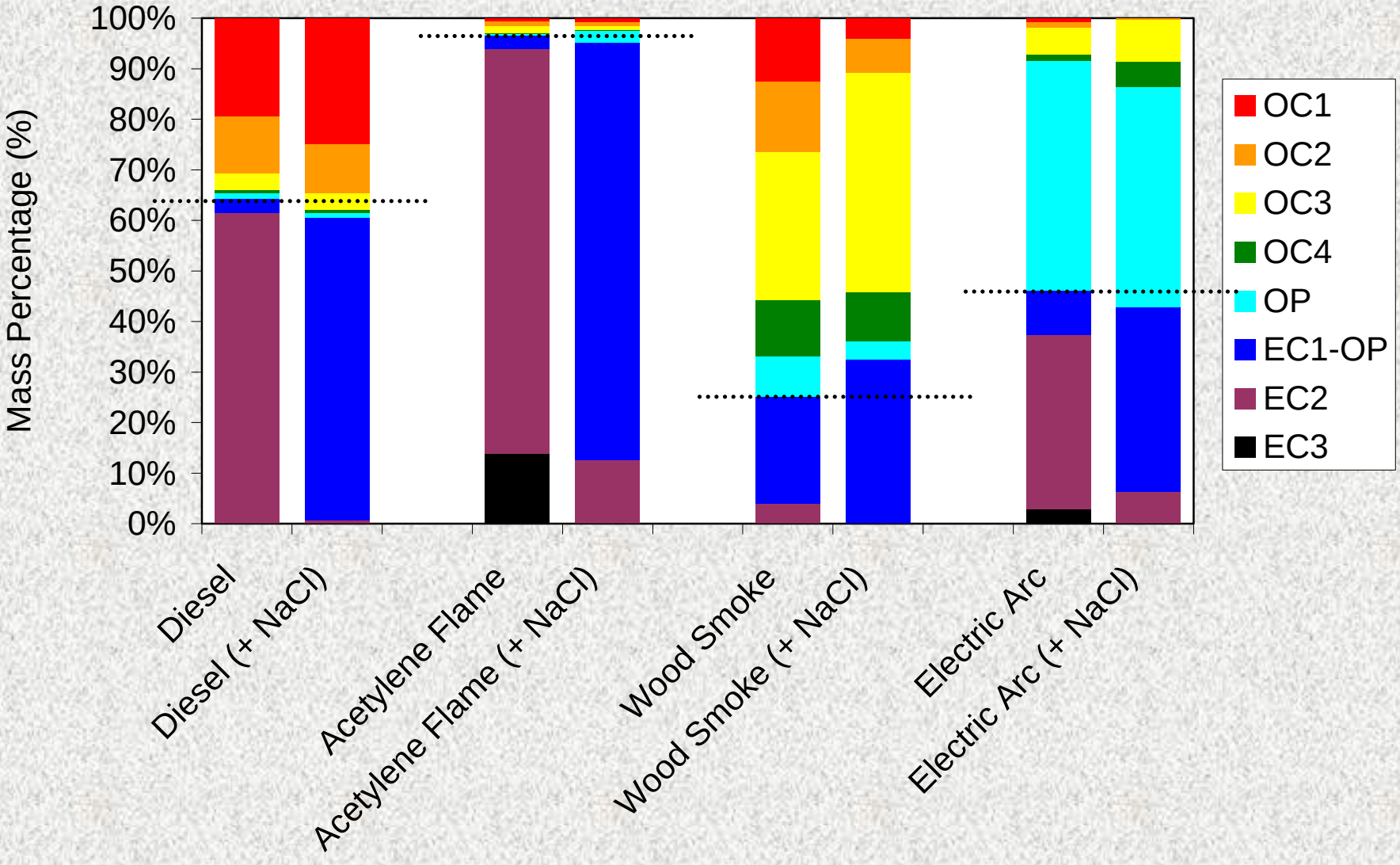
# NaCl has the largest effect among halogen salts on EC fractions

- For NaCl, shift of EC2 to EC1.
- For NaBr, no shift at 0.3 nmol but shift at 0.75 nmol
- For NaI, no shift for both 0.3 and 0.75 nmol



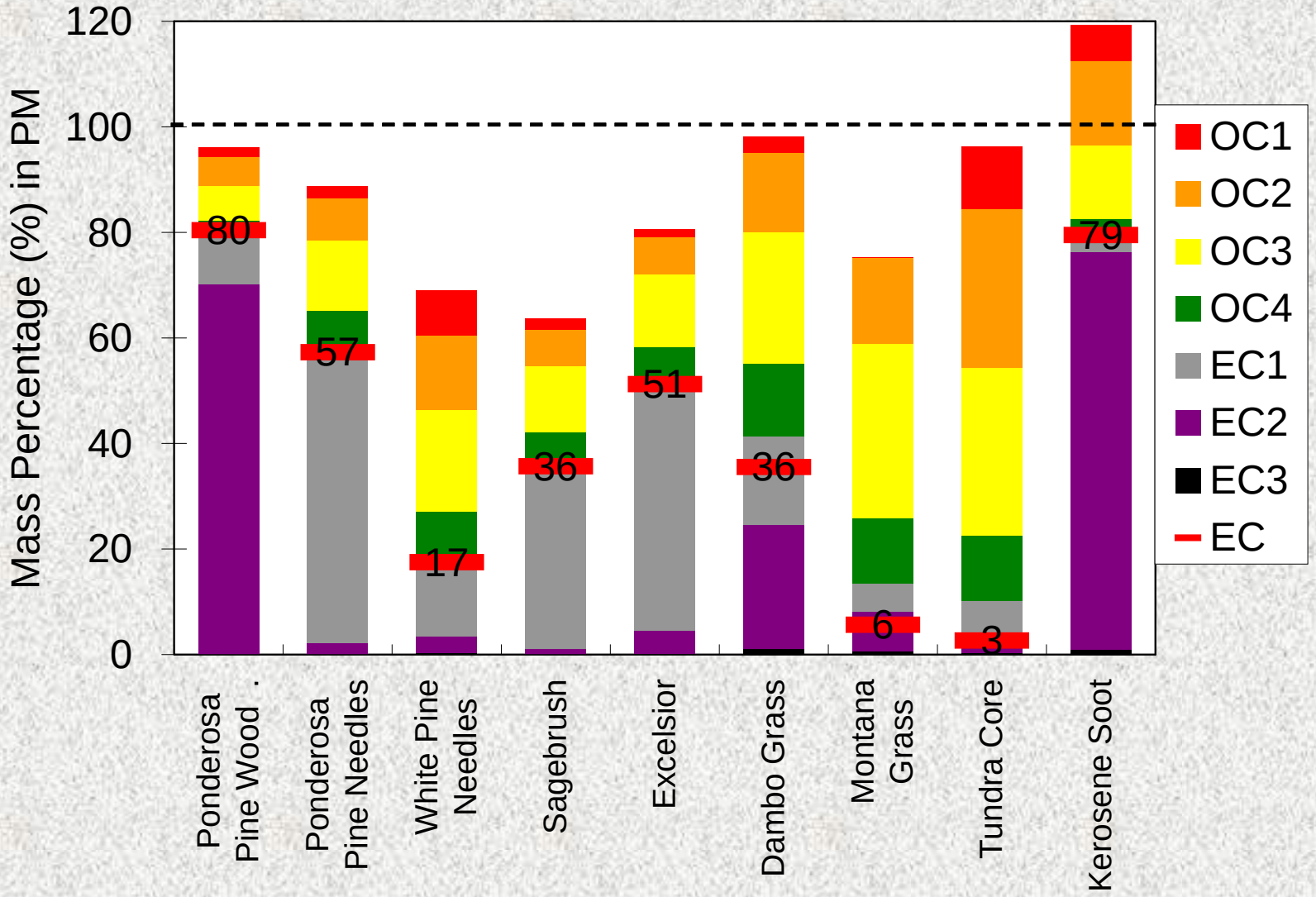

Catalytic reactivity: NaCl > NaBr > NaI

# Addition of NaCl shifts EC to lower temperature fractions




Chow et al. (2007b)

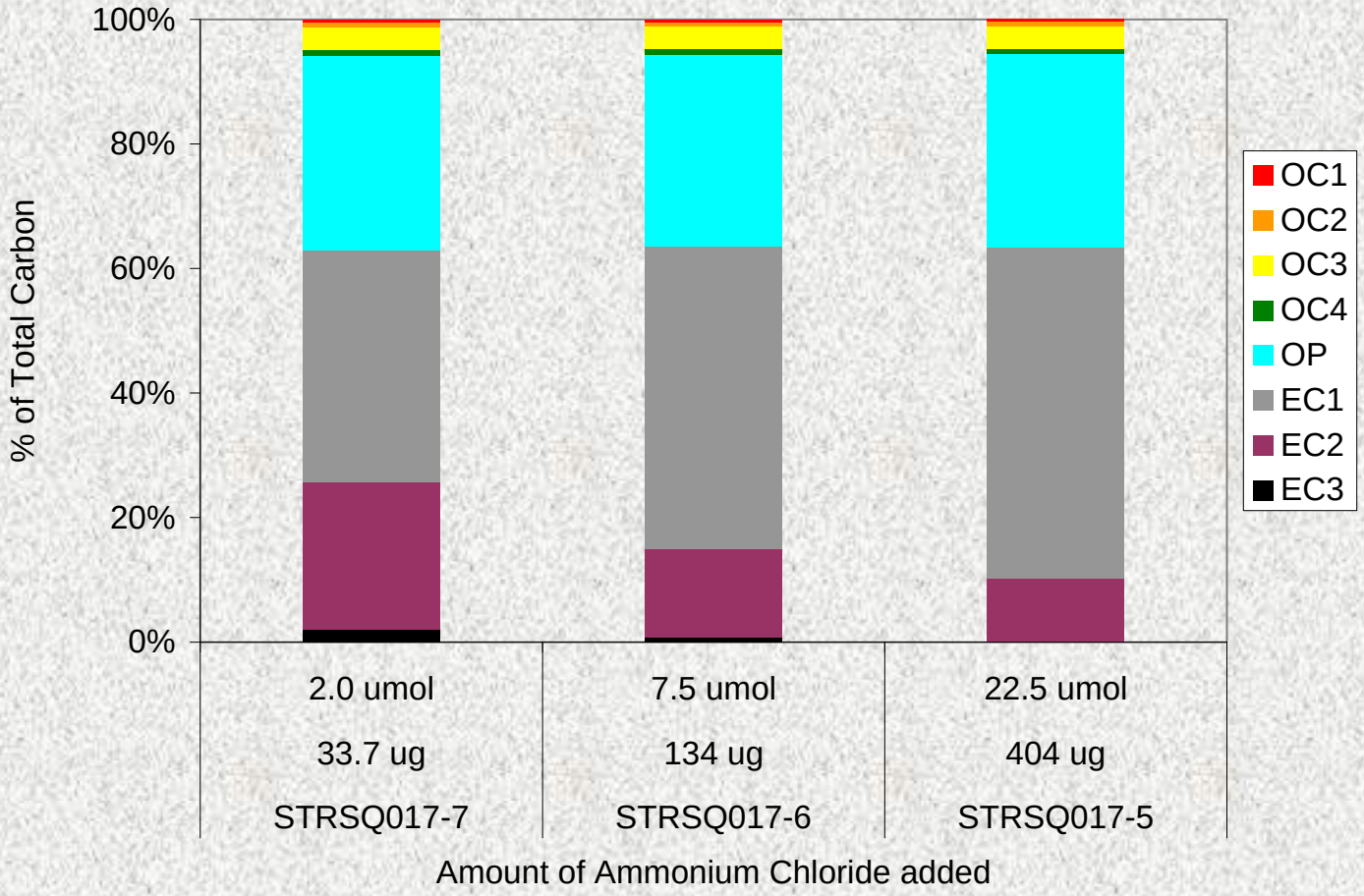
# Carbon fractions in biomass burning varied by fuel and combustion conditions




Chen et al. (2007a)

# Higher $NH_4Cl$ results in lower EC2

- Higher $NH_4Cl$ shifts more EC2 to EC1
- Effects at micro-mole/micro-gram level
- No effect on OC speciation

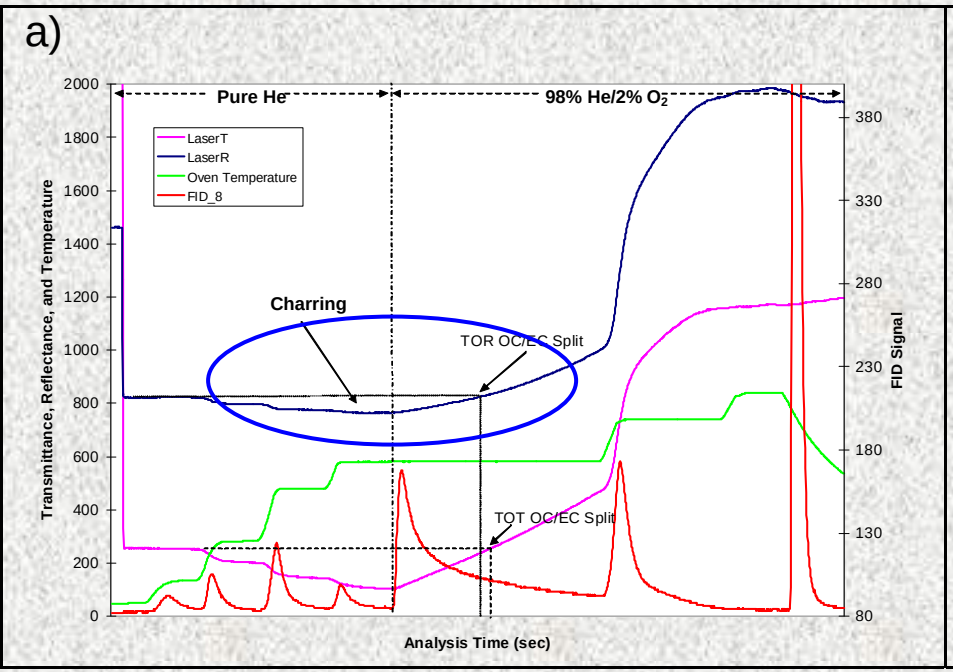


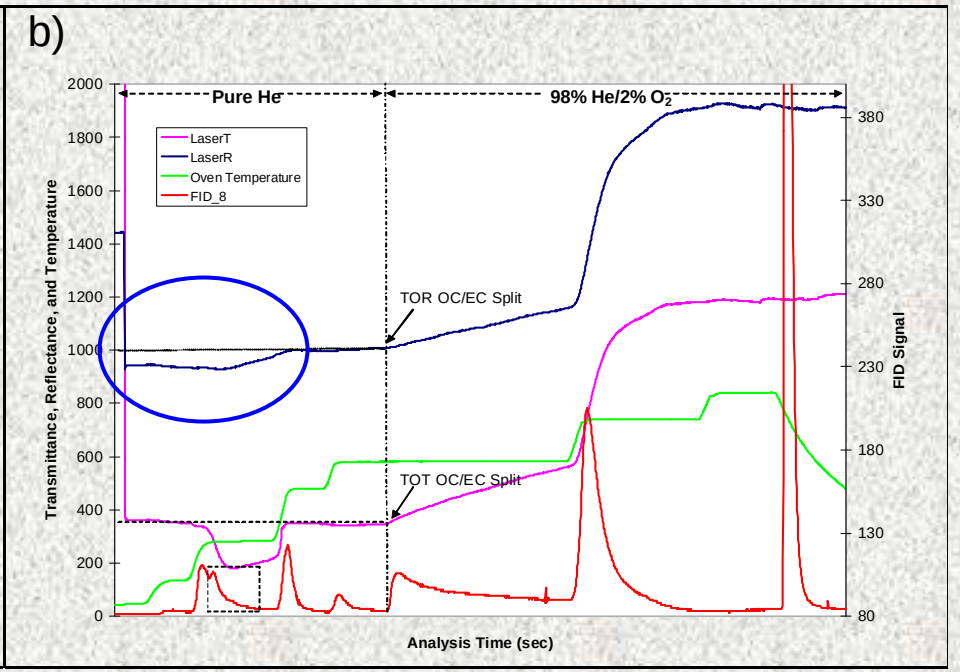
# Presence of $(NH_4)_2SO_4$ minimizes pyrolysis

- Melting point = 280°C
- Suppression of pyrolyzed carbon formed
- No EC shift was observed

Original Filter

Spiked with 3.0 µmol of ammonium sulfate

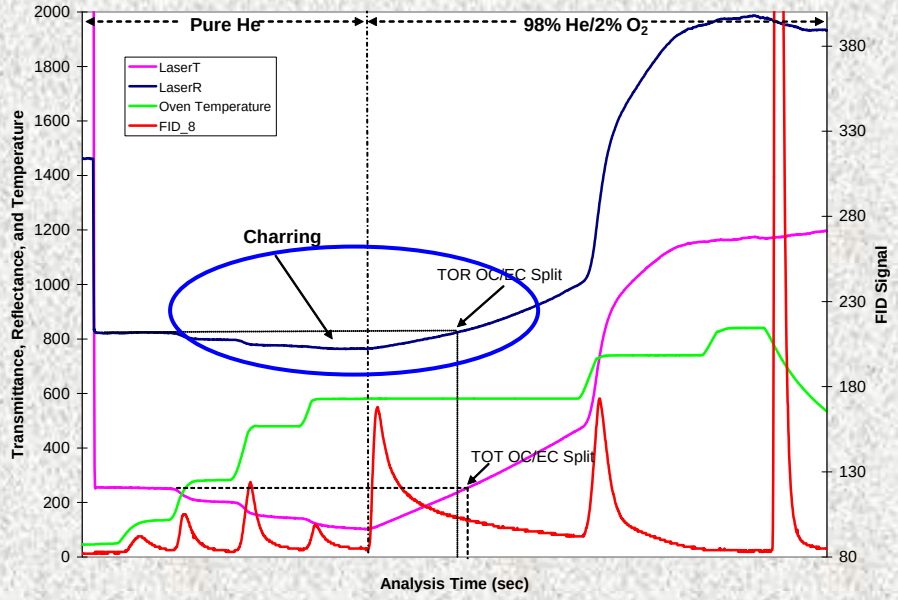


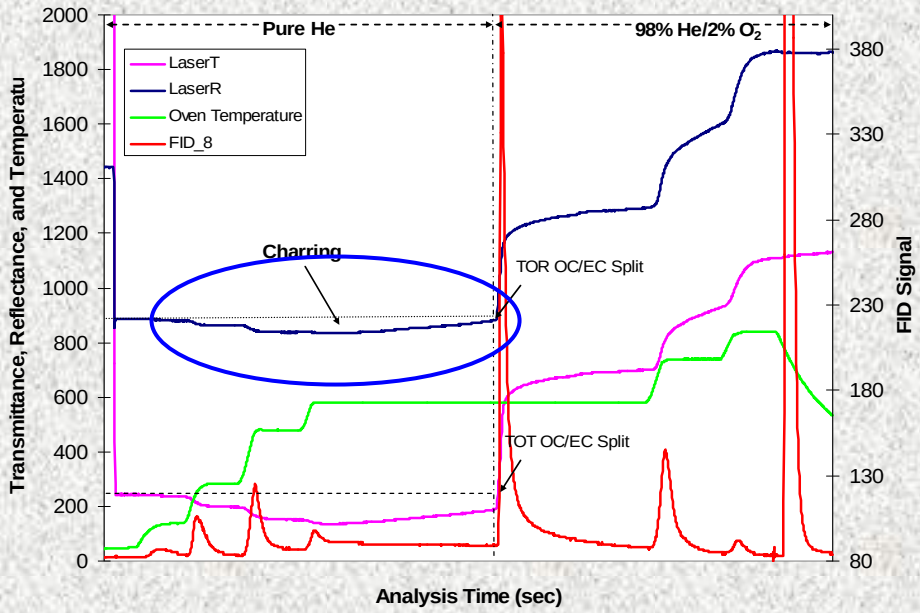
# $Na_2SO_4$ does not suppress pyrolysis

- Melting point = 884 ºC.
- Shift of EC 2 to EC1 but no suppression of charring.

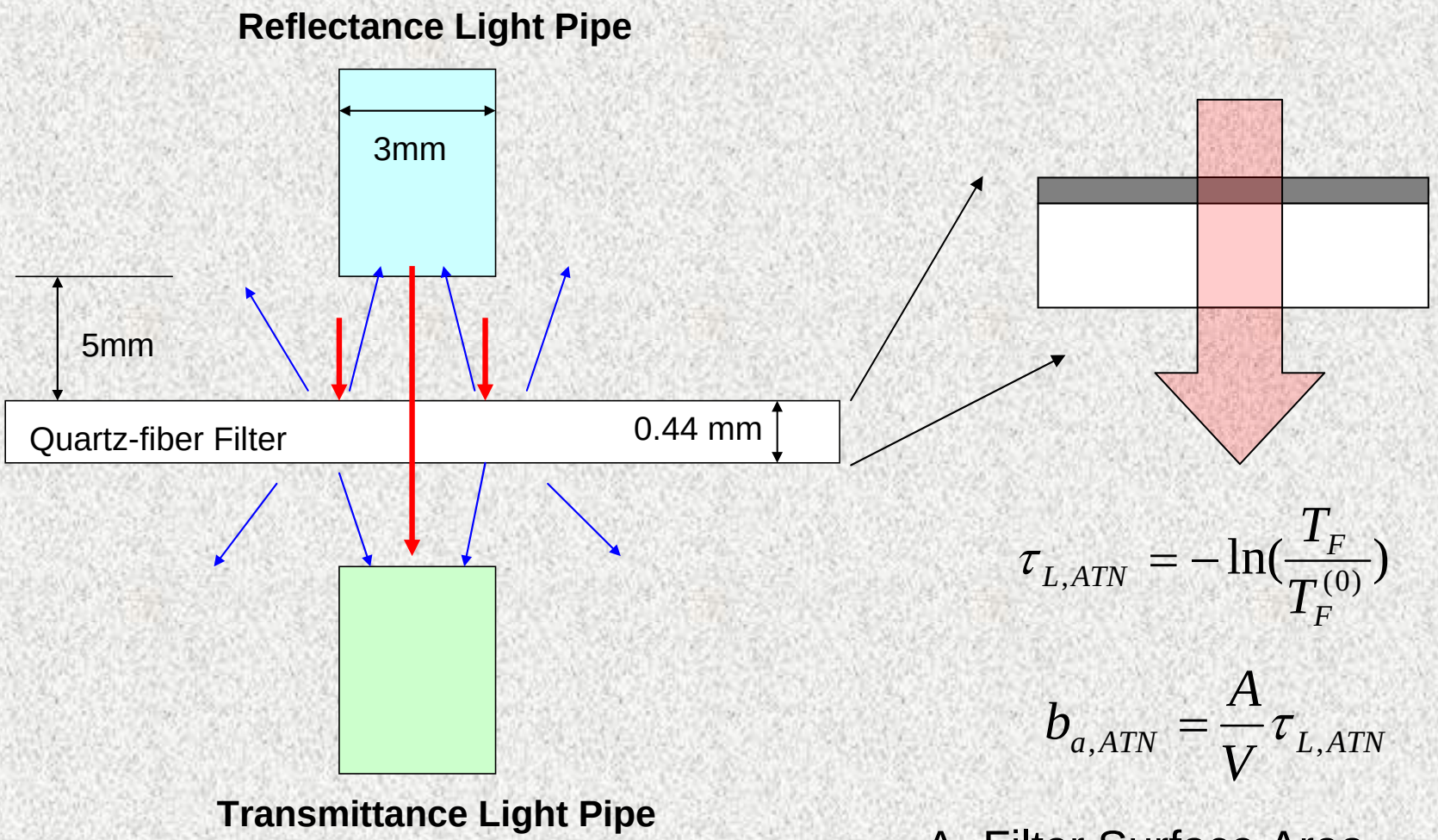
Original Filter




Spiked with 3.0 µmol of sodium sulfate



# Optical Modeling of Filter Reflectance and Transmittance




$$\tau_{L,ATN} = -\ln\left(\frac{T_F}{T_F^{(0)}}\right)$$

$$b_{a,ATN} = \frac{A}{V}\tau_{L,ATN}$$

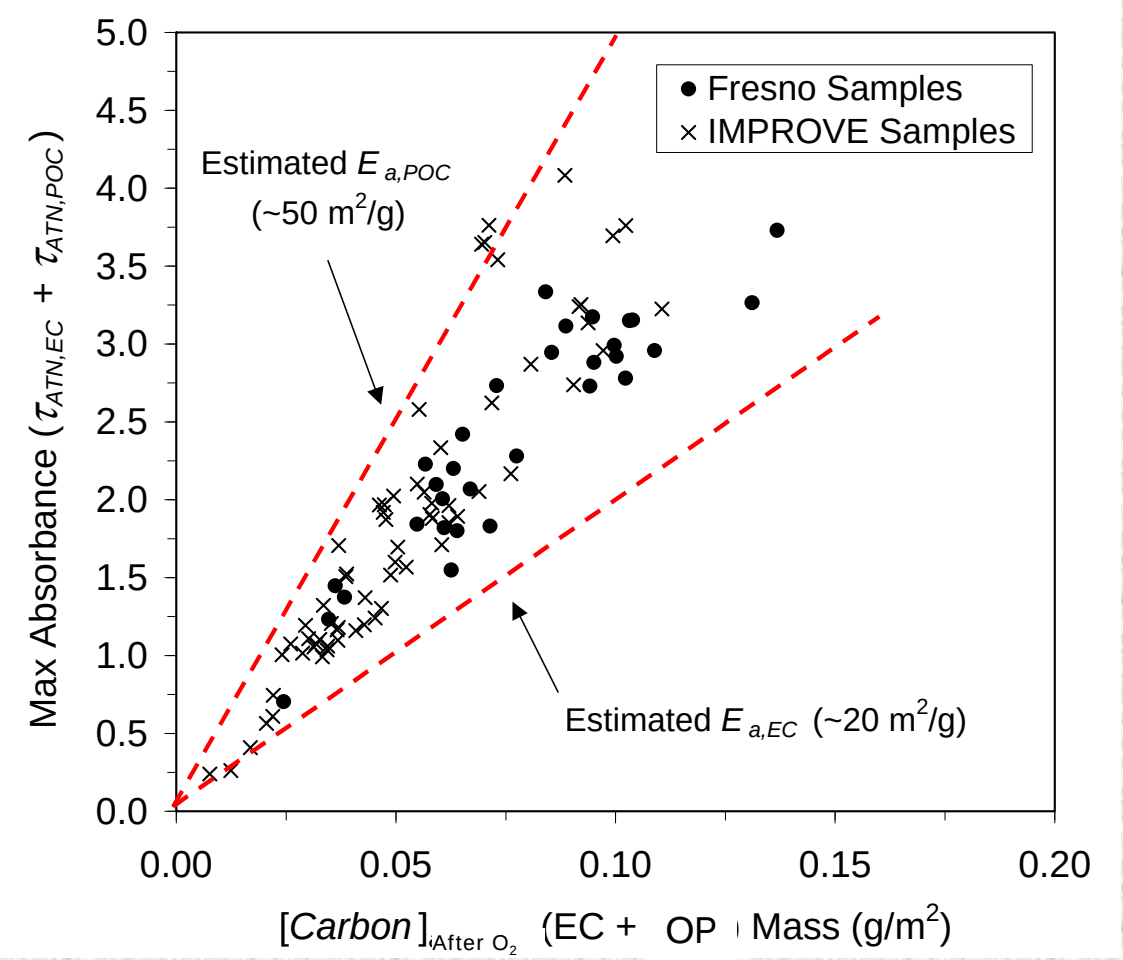
A=Filter Surface Area

V=Sample Volume

- Multiple scattering?
- Effect of loading?

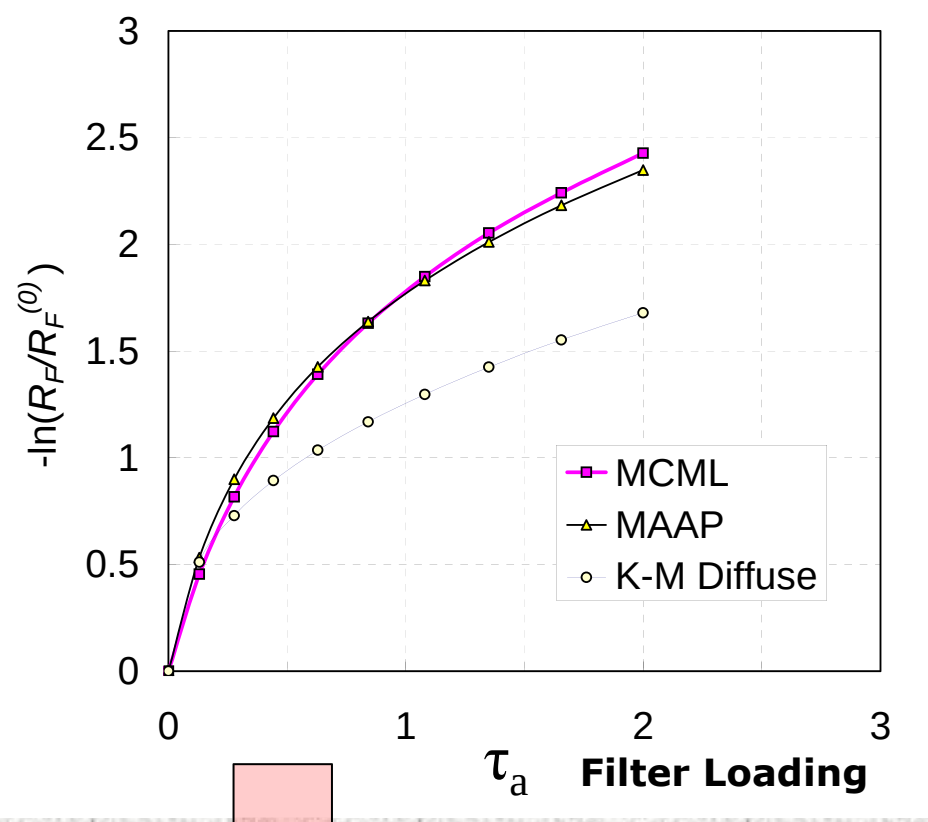
# (Apparent) Absorption Efficiency Varies between EC and OP

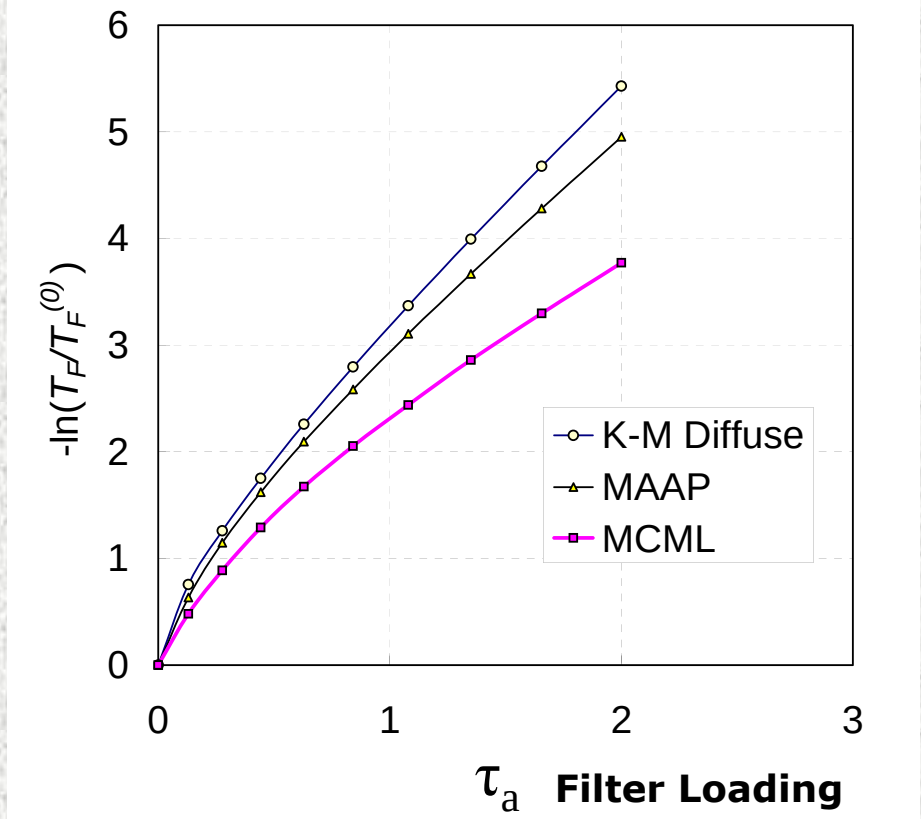
$$[Carbon]_{after\_O_2} = [EC] + [OP] = \frac{\tau_{ATN,EC}}{E_{a,EC}} + \frac{\tau_{ATN,OP}}{E_{a,OP}}$$

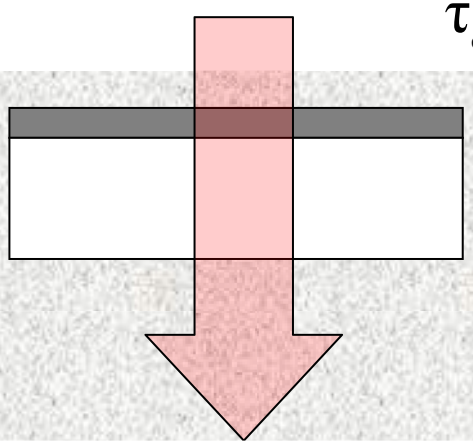



Chow et al. (2004)

# Monte Carlo Model Estimation of Reflectance (R) and Transmittance (T)



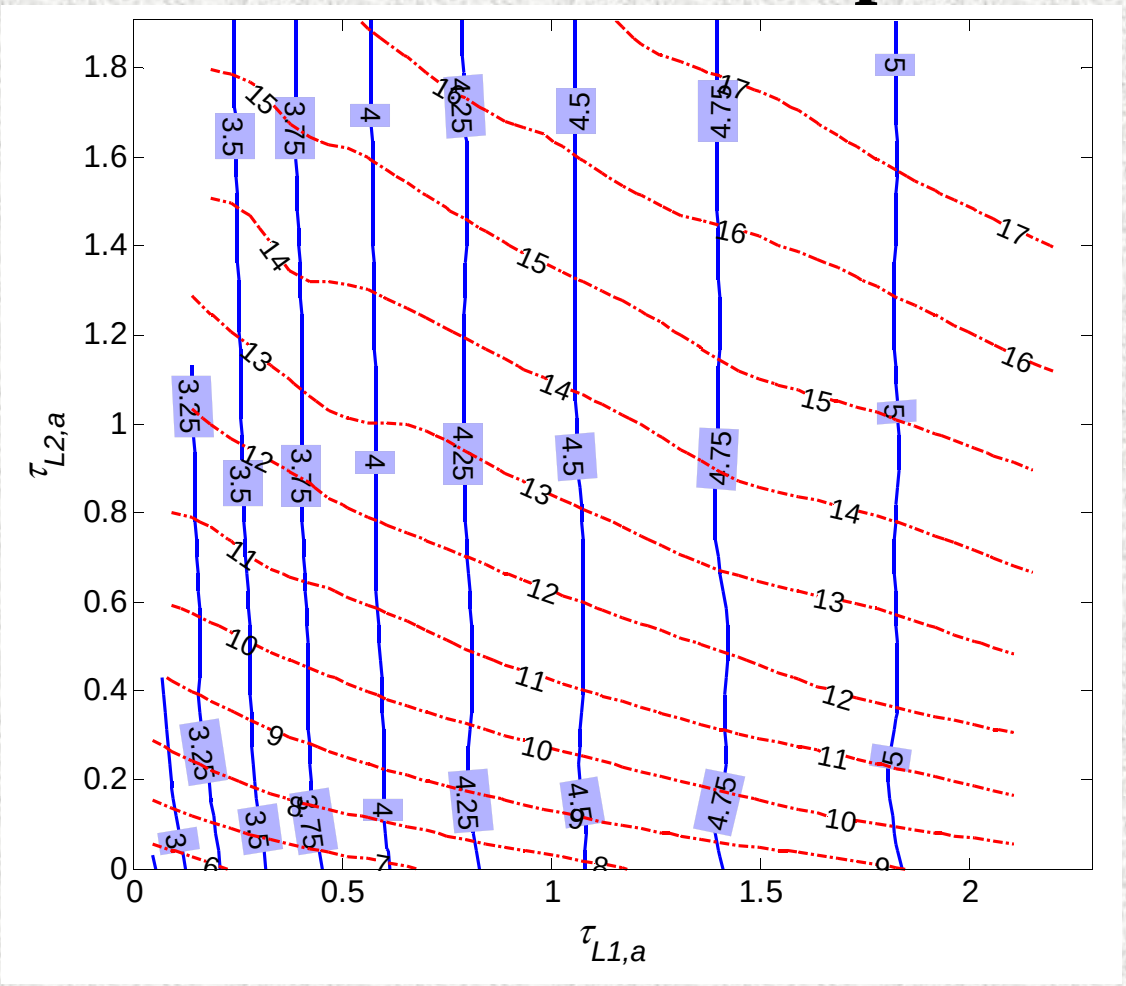



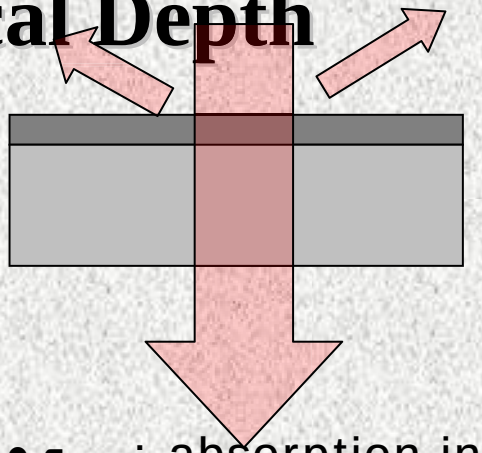



- MCML: Monte Carlo Simulation (reference method for two-layer model)
- MAAP: Code used by Multiple Angle Absorption Photometer
- K-M: Kubelka-Munk theory

Chen et al. (2007b)

# Concurrent R and T Measurements Allow Estimation of Absorption Optical Depth

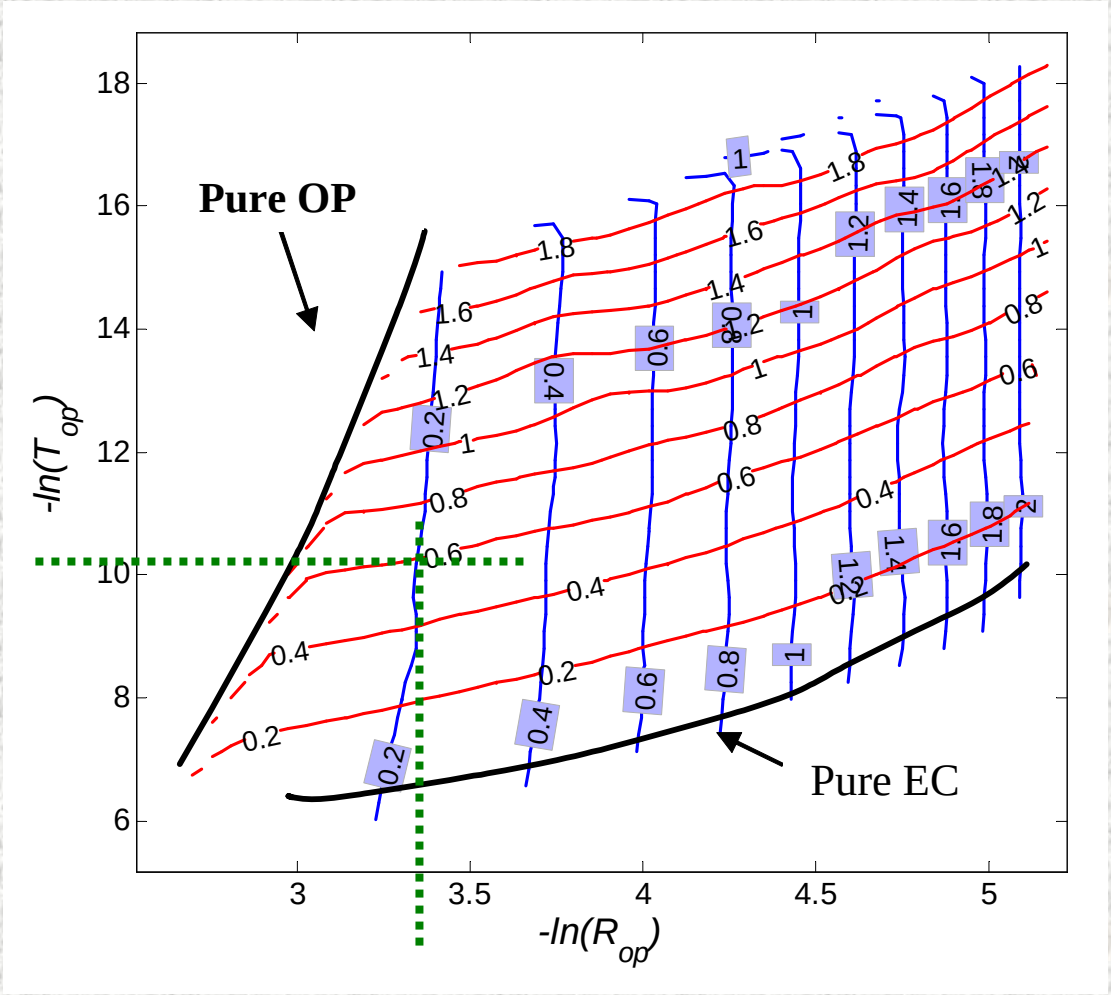


- $\tau_{L1,a}$: absorption in the first layer
- $\tau_{L2,a}$ : absorption in the second layer
- Blue line: reflectance measure
- Red line: transmittance measure

- Absorption in the second layer has no impact on the reflectance
- Absorption in the first layer does not affect transmittance as much as absorption in the second layer

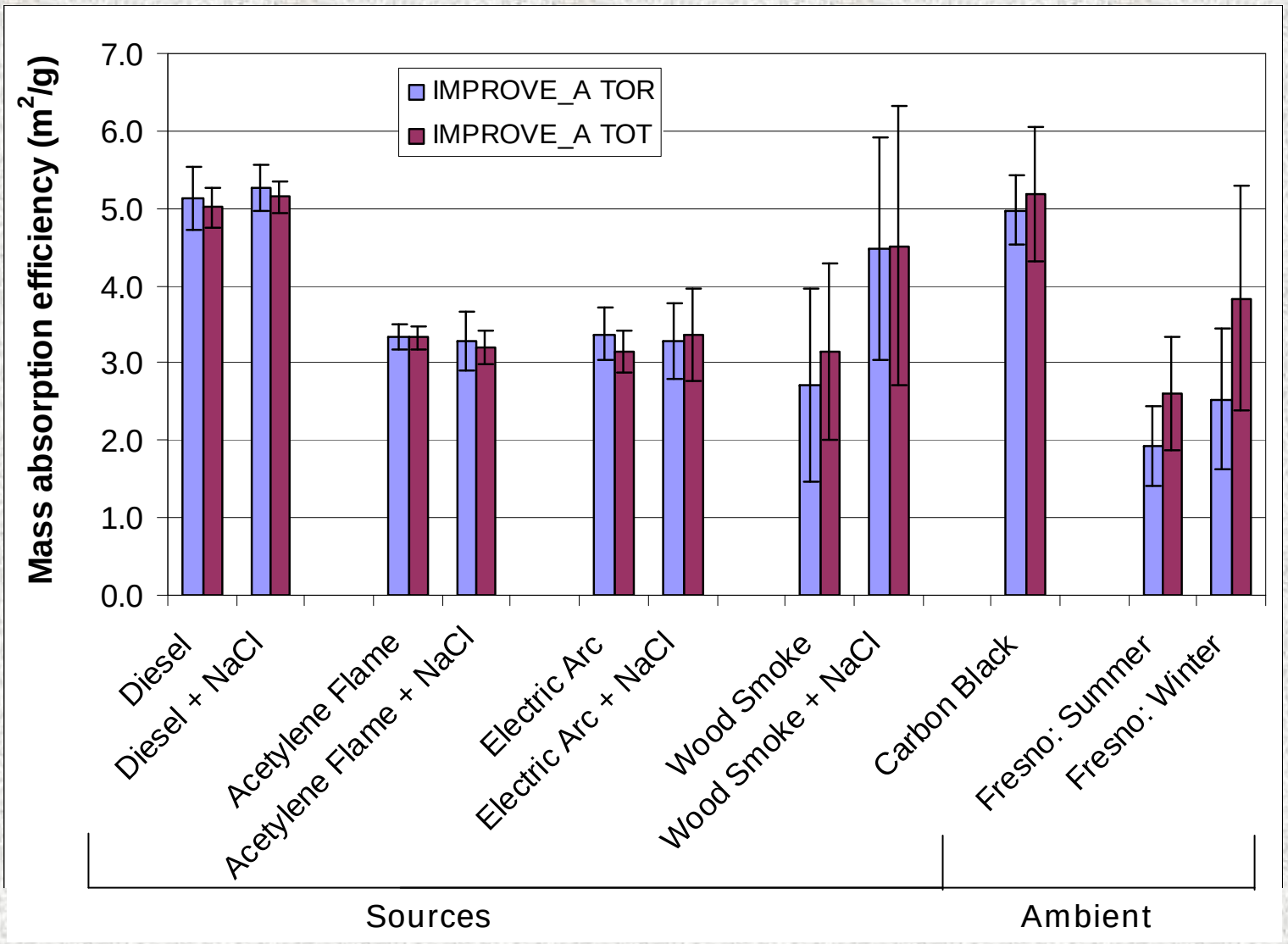
# Retrieve OP and EC Absorption based on R and T Measurements



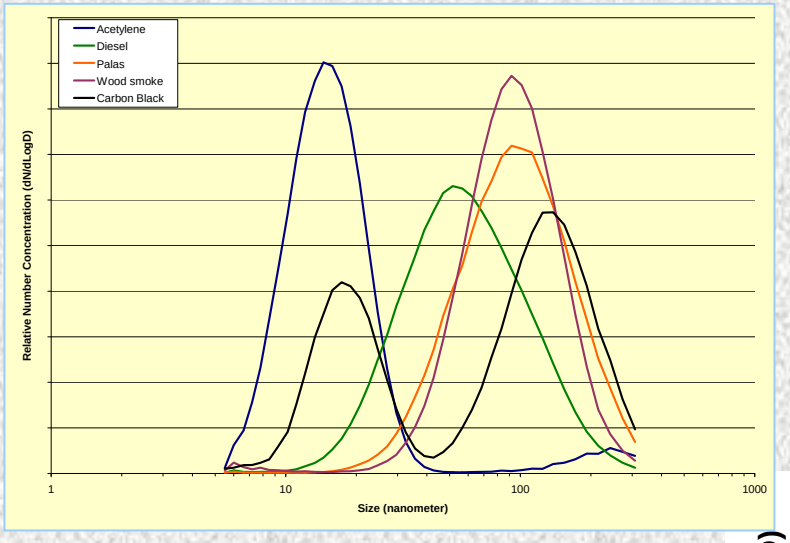

- Blue line: absorption in the first layer
- Red line: absorption in the second layer

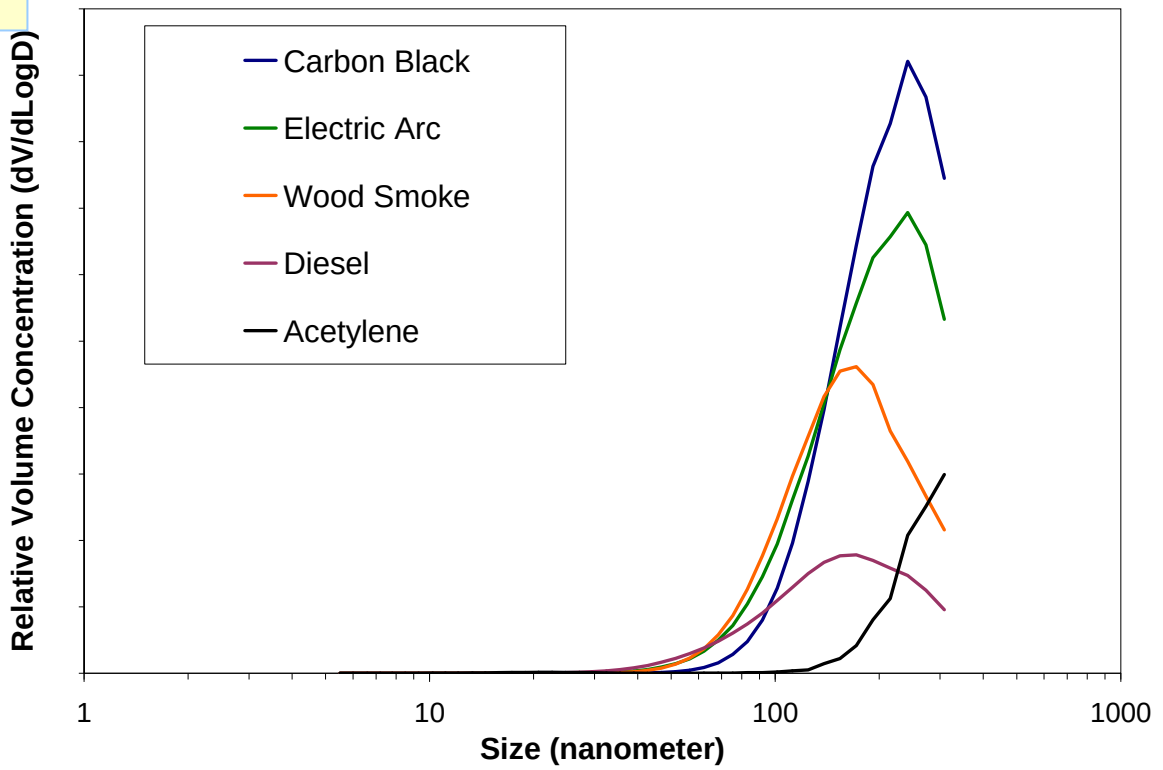
Chen et al. (2007b)

# Mass absorption efficiency varied by source (1047 nm)



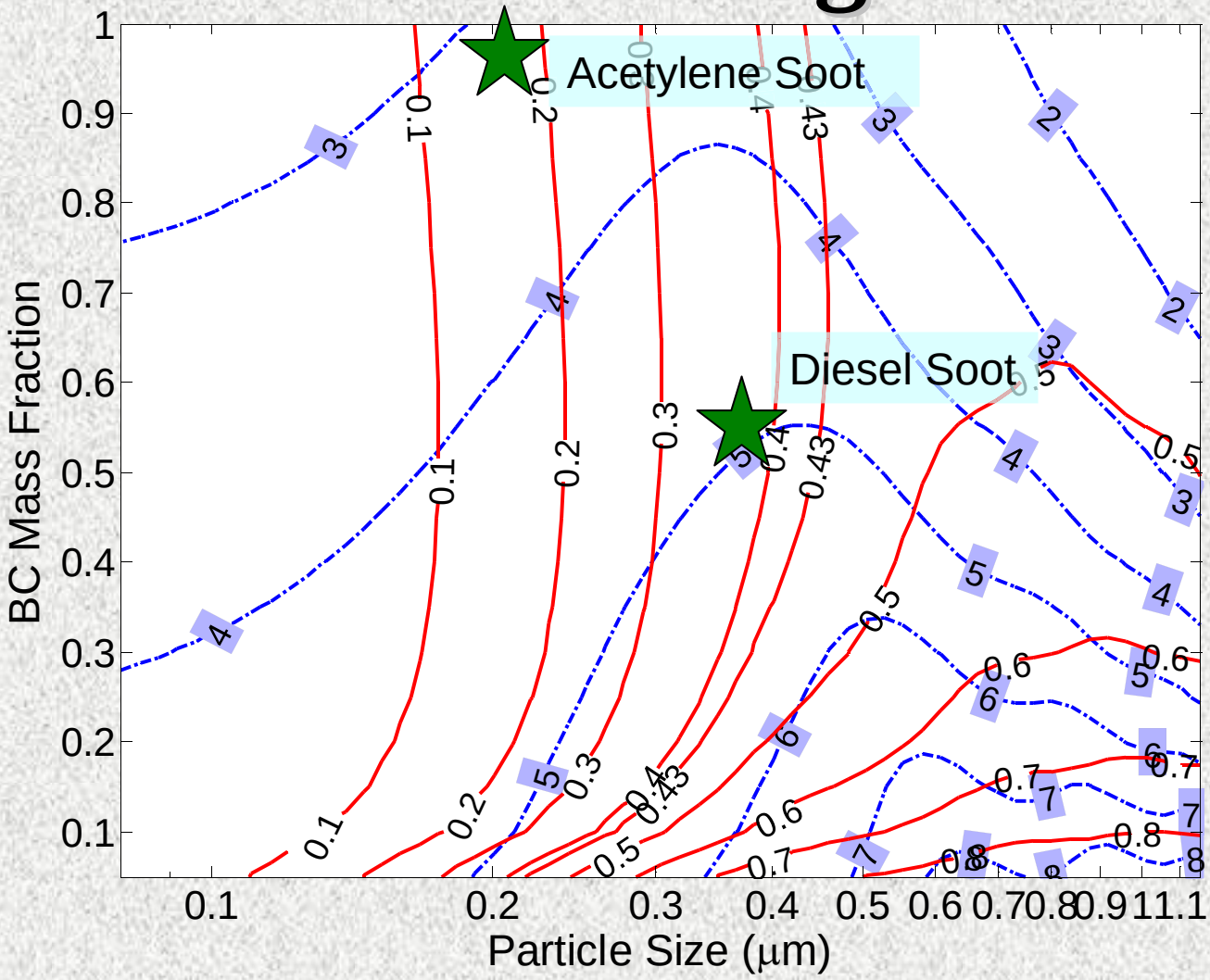
# Size distribution varies by source



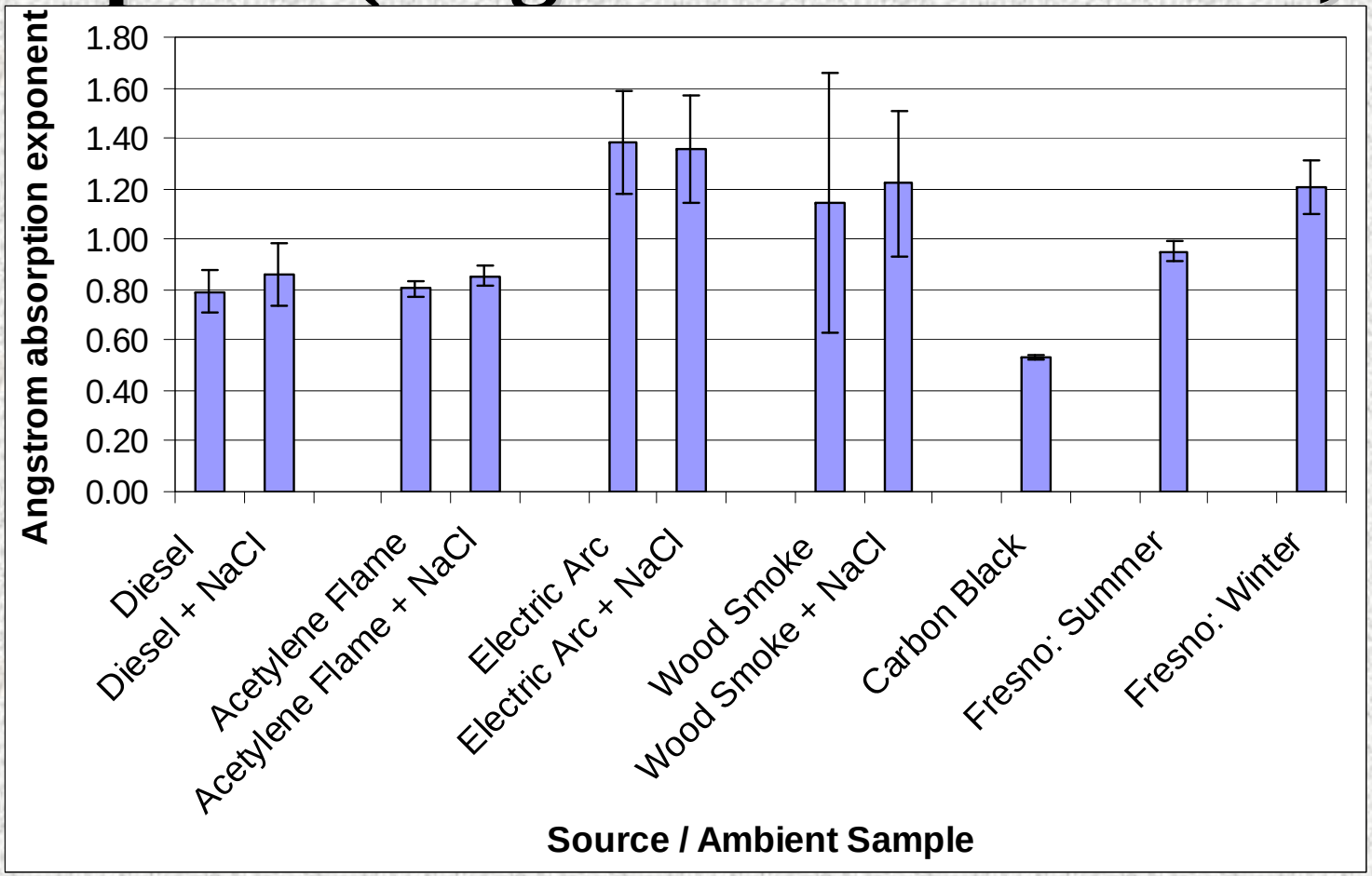

By WPS (Chow et al. 2007b)

# Mie-Scattering Model




The blue lines indicate BC $\sigma_{abs}$ at 1047 nm in $m^2/g$ and the red lines indicate the single scattering albedo, $\omega$. The refractive index and density for EC/BC are assumed to be 1.96 – 0.66i and 1.7 $g/cm^3$, respectively (Chen et al., 2006). OM is modeled with a refractive index of 1.42 – 0.001i and density of 1.2 $g/cm^3$.

# Spectral Dependence of Light Absorption (Angstrom Power Law; $\lambda^{-\alpha}$)




Estimate of the Angstrom absorption exponent, $\alpha$, using 7-AE (seven wavelength aethalometer) measurements for different source and ambient samples. Error bars shown are one standard deviation from the mean.

# Conclusions

- The IMPROVE_A protocol was developed to represent actual sample temperature and to maintain consistency in OC/EC measurements for IMPROVE and other networks.
- Temperature calibration and $O_2$ <100 ppb auditing is necessary for thermal/optical methods.
- Small (20 to 40 °C) temperature differences do not affect the OC/EC split in TOR, but they do affect the TOT split and the carbon fractions.
- OC/EC split is insensitive to analytical conditions as long as reflectance correction is used.

# Conclusions (continued)

- The presence of salts in samples increases EC oxidation rate at lower temperatures, thereby shifting thermal carbon fractions to lower temperature plateaus.
- Charring is minimized in the presence of $(NH_4)_2SO_4$, but not $Na_2SO_4$.
- Due to the formation of char and EC decomposition at high temperatures w/o $O_2$, optical correction is necessary in thermal methods to separate OC from EC.
- EC and OP have different absorption efficiencies. Optical correction should minimize the effects of the OP char.

# Conclusions (continued)

- Pyrolyzed carbon (OP) is more abundant in ambient and wood smoke samples than in diesel and acetylene flame soot. This results in less consistent OC/EC splits for vegetative burning than for other EC sources.
- Low-temperature OC and high-temperature EC are relatively abundant in diesel soot but low in wood smoke PM.
- Under laboratory-controlled conditions, source samples can be reproduced within ±10-15% for diesel, acetylene flame, and electric arc soot, and within ±40-50% for wood combustion.
- Biomass fuel and combustion conditions (e.g., temperature) result in EC/TC abundances of 3 to 80%.

# Conclusions (continued)

- Absorption efficiencies at 1047 nm from photoacoustic instruments yield 3 – 5 $m^2/g$ for EC from the IMPROVE, but are different for different sources.
- The absorption exponent is smaller for diesel and acetylene soot (~0.8) and larger for electric arc (PALAS) and wood smoke PM (>1).
- Optical properties cannot be fully explained by Mie theory (especially for wood smoke and electric arc PM) due to uncertain refractive indeces and irregular particle shapes.
- Filter characteristics condition (thickness, refractive indices, particle penetration depth) need to be better specified to model OC/EC splits.

# STAR Grant-Related Publications

## 2003 - 2004


- Chen, L.-W. A., Chow, J.C., Watson, J.G., Moosmüller, H., Arnott, W.P. (2004). Modeling reflectance and transmittance of quartz-fiber filter samples containing elemental carbon particles: Implications for thermal/optical analysis. *J. Aerosol Sci.* 35, 765-780, doi: 10.1016/j.jaerosci.2003.12.005.
- Chow, J.C., Watson, J.G., Chen, L.W., Arnott, W.P., Moosmüller, H., Fung, K.K. (2004). Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. *Environ. Sci. Technol.* 38 (16), 4414-4422.
- Ho, K.F., S.C. Lee, C.K. Chan, J.C. Yu, J.C. Chow, and X.H. Yao (2003). Characterization of chemical species in $PM_{2.5}$ and $PM_{10}$ aerosols in Hong Kong. *Atmos. Environ.*, 37(1), 31-39.
- Ho, K.F., J.J. Cao, S.C. Lee, Y.S. Lee, J.C. Chow, J.G. Watson, and K. Fung (2004). Variability of levels, water soluble and isotopic composition of organic and elemental carbon in Hong Kong urban atmosphere. *Environ. Sci. Technol.,* submitted.
- Sin, D.W.M., W.H. Fung, Y.Y. Choi, C.H. Lam, P.K.K. Louie, J.G. Watson, and J.C. Chow (2004). Seasonal and spatial variation of solvent extractable organic compounds in fine suspended particulate matter in Hong Kong. *JAWMA*, 55(3):291-301.

# STAR Grant-Related Publications

## 2005


- Arnott, W.P., B. Zielinska, C.F. Rogers, J. Sagebiel, K. Park, J.C. Chow, H. Moosmüller, J.G. Watson, K. Kelly, D. Wagner, A. Sarofim, J. Lighty, and G. Palmer (2005). Evaluation of 1047-nm Photoacoustic Instruments and Photoelectric Aerosol Sensors in Source-Sampling of Black Carbon Aerosol and Particle-Bound PAHs from Gasoline and Diesel Powered Vehicles. *Environ. Sci. Technol.*, **39**(14):5398-5406.
- Chow, J.C., J.G. Watson, P.K.K. Louie, L-W.A. Chen, and D. Sin (2005). Comparison of PM2.5 Carbon Measurement Methods in Hong Kong, China. *Environ. Poll.*, **137**(2):334-344.
- Chow, J.C., J.G. Watson, L.W.A. Chen, G. Paredes-Miranda, M.C.O. Chang, D. Trimble, K. Fung, H. Zhang, and J.Z. Yu (2005). Refining Temperature Measures in Thermal/Optical Carbon Analysis. *Atmos. Chem. And Physics Discuss.*, **5**:4477-4505.
- El-Zanan, H.S., D.H. Lowenthal, B. Zielinska, J.C. Chow, and N. Kumar (2005). Determination of the organic aerosol mass to organic carbon ratio in IMPROVE samples. *Chemosphere*, **60**(4):485-496.
- Watson, J.G., J.C. Chow, and L.W.A. Chen (2005). Summary of Organic and Elemental Carbon/Black Carbon Analysis Methods and Intercomparisons. *AAQR*, **5**(1):65-102.

# STAR Grant-Related Publications

## 2006


- Chen, L.-W.A.; Moosmüller, H.; Arnott, W.P.; Chow, J.C.; Watson, J.G.; Susott, R.A.; Babbitt, R.E.; Wold, C.; Lincoln, E.; and Hao, W.M. (2006). Particle emissions from laboratory combustion of wildland fuels: In situ optical and mass measurements. *Geophys. Res. Lett.*, 33(L04804):1-4.
- Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Chen, L.-W.A.; and Magliano, K. (2006). Particulate Carbon Measurements in California's San Joaquin Valley. *Chemosphere*, 62(3):337-348.
- Chow, J.C.; Watson, J.G.; Park, K.; Lowenthal, D.H.; Robinson, N.F.; and Magliano, K. (2006). Comparison of Particle Light Scattering and Fine Particulate Matter Mass in Central California. *JAWMA,* 56(4)398-410.
- Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; Chen, L.-W.A.; Zielinska, B.; Rinehart, L.R.; and Magliano, K. (2006). Evaluation of organic markers for chemical mass balance source apportionment at the Fresno Supersite. *Atmos. Chem. Phys.,* http://www.atmos-chem-phys.net/7/1741/2007/acp-7-1741-2007.pdf.
- Chow, J.C., J.G. Watson, D.H. Lowenthal, L.-W.A. Chen, and K. Magliano (2006). Particulate Carbon Measurements in California's San Joaquin Valley. *Chemosphere*, in press.
- Park, K.; Chow, J.C.; Watson, J.G.; Trimble, D.L.; Doraiswamy, P.; Arnott, W.P.; Stroud, K.R.; Bowers, K.; Bode, R.; Petzold, A.; and Hansen, A.D.A. (2006). Comparison of continuous and filter-based carbon measurements at the Fresno Supersite. *J. Air Waste Manage. Assoc.*, 56(4):474-491.
- Park, K., J.C. Chow, J.G. Watson, W.P. Arnott, D. Trimble, K. Stroud, K. Bowers, R. Bode, A. Petzold, and A.D.A. Hansen (2006). Comparison of Continuous and Filter-Based Carbon Measurements at the Fresno Supersite. *JAWMA*, in revision.

# STAR Grant-Related Publications

**2007**

- Chen, L.-W.A.; Chow, J.C.; Watson, J.G.; Lowenthal, D.H.; and Chang, M.C. (2007). Particle emissions from laboratory combustion of wildland fuels: Emission factors and source profiles. *Environ. Sci. Technol.*, in press.
- Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Chang, M.C.O.; Robinson, N.F.; Trimble, D.L.; and Kohl, S.D. (2007). The *IMPROVE_A* temperature protocol for thermal/optical carbon analysis: Maintaining consistency with a long-term data base. *J. Air Waste Manage. Assoc.*, 57:accepted.