IMPROVE Carbon Analysis

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Objectives

- Report progress on IMPROVE carbon analysis
- Demonstrate OC/EC consistency between IMPROVE_A (DRI Model 2001) and IMPROVE (DRI/OGC) protocols
- Evaluate differences in carbon fractions among various laboratory-generated carbon sources
- Examine the effects of mixtures on carbon fractions

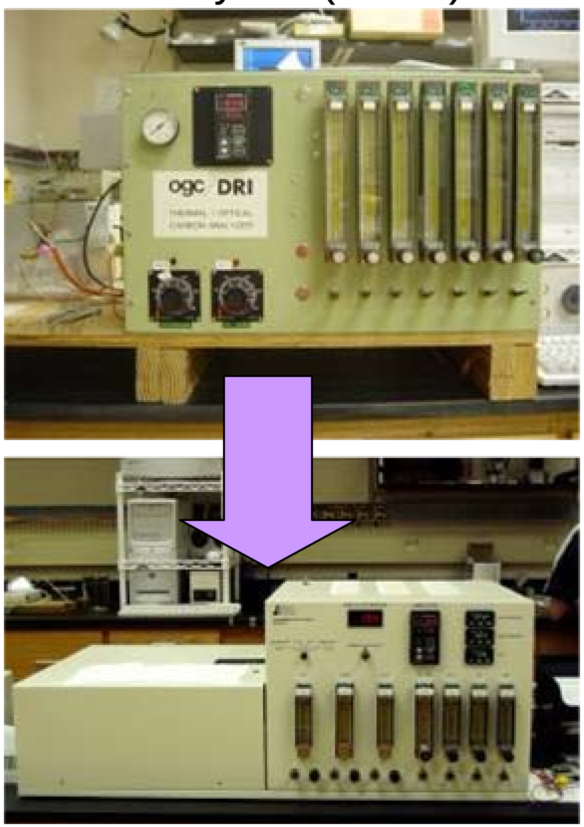
IMPROVE Samples for Carbon Analysis using the IMPROVE_A Protocol

Sampling Period	Samples Received	Analysis Completion Date
1/1/05-12/31/05	22,460	5/5/07
1/1/06-12/31/06	22,443	3/15/07
1/1/07-6/30/07	10,604	9/30/07*

* Expected completion date

IMPROVE vs. IMPROVE_A*
Thermal Protocols

Original OGC/DRI Thermal Optical Analyzer (1986)



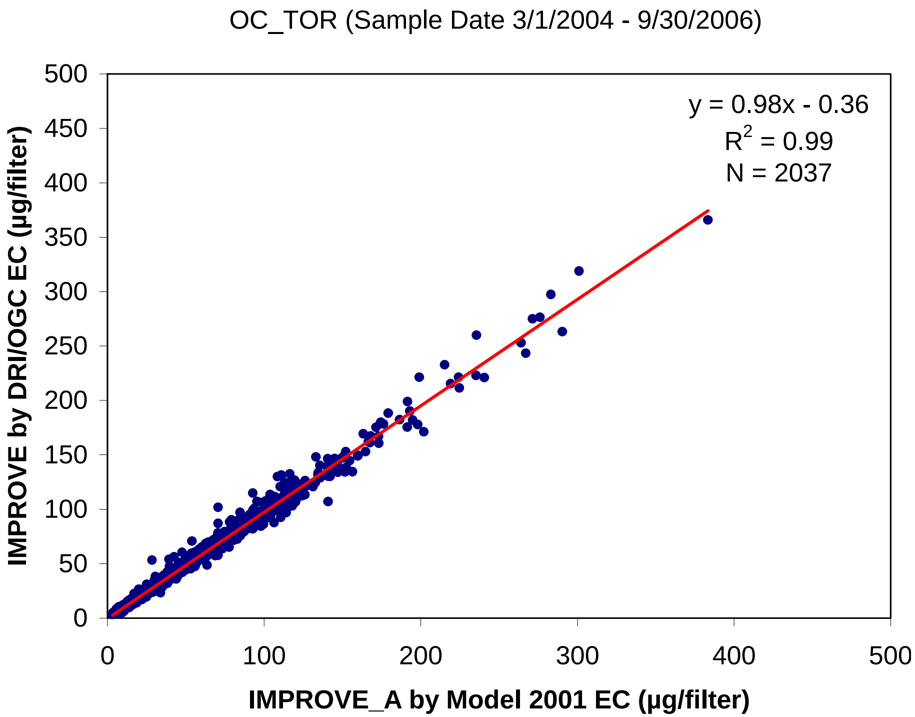
DRI Model 2001 Thermal/Optical Analyzer

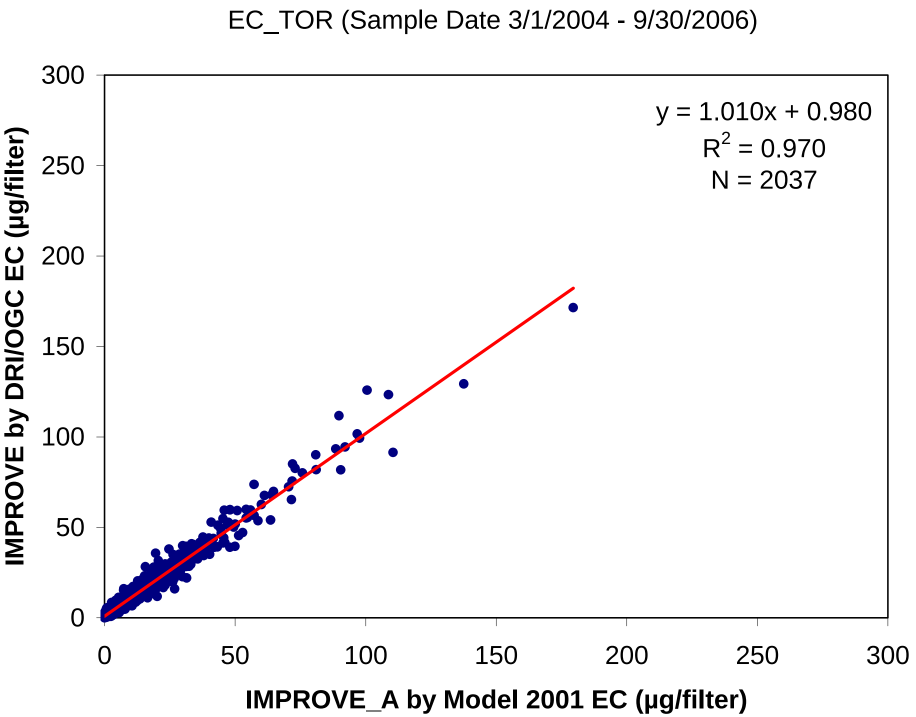
	IMPROVE_A* (DRI Model 2001)	IMPROVE (DRI/OGC)
OC1	140 ºC	120 ºC
OC2	280 ºC	250 ºC
OC3	480 ºC	450 ºC
OC4	580 ºC	550 ºC
OP (POC)	TOR/TOT	TOR
EC1	580 ºC	550 ºC
EC2	740 ºC	700 ºC
EC3	840 ºC	800 ºC

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

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

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





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

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

Wood Stove

White Oak
DR of 18, 40, 105

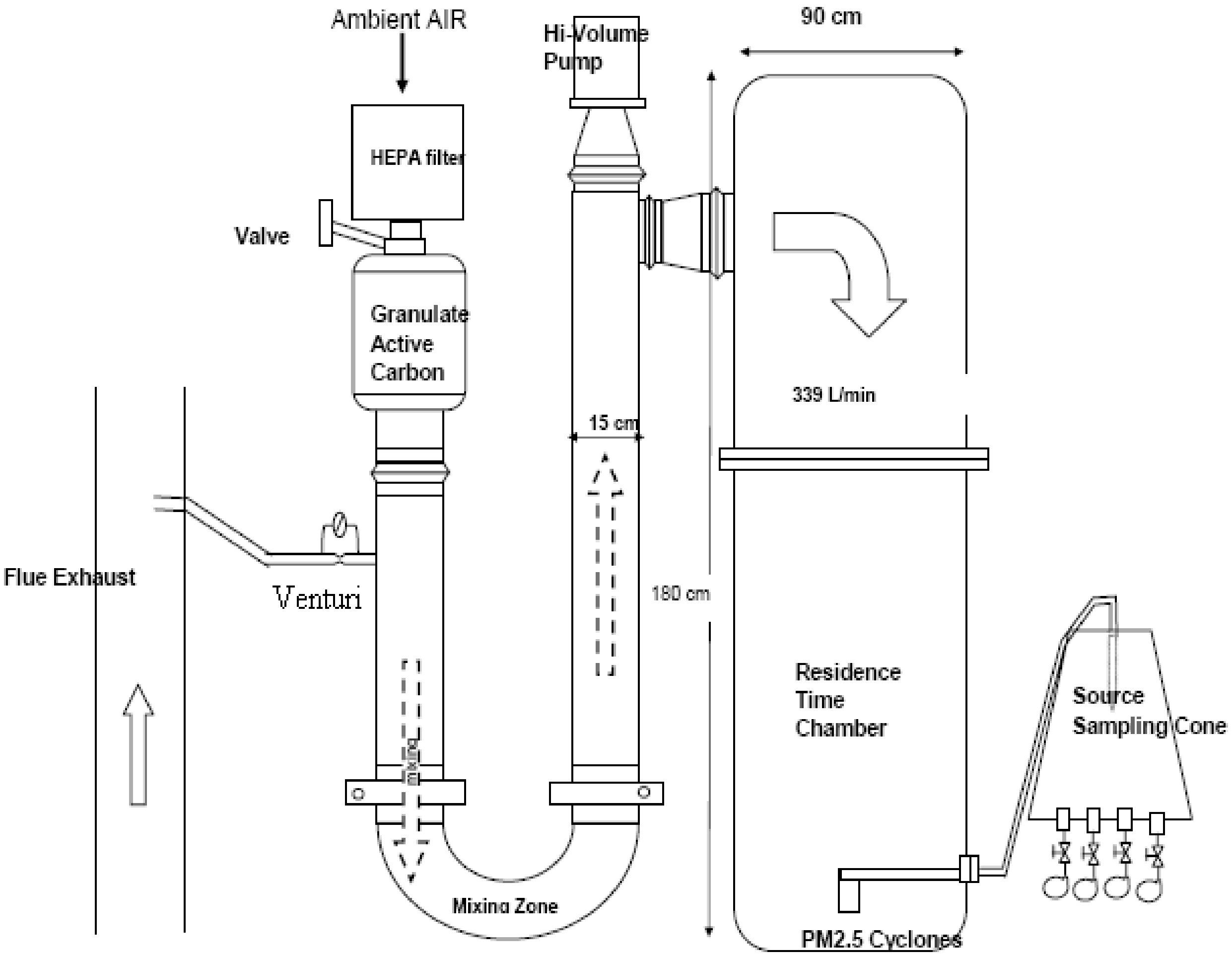
T of 20 or 25 min

Source, Source + NaCl

- 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

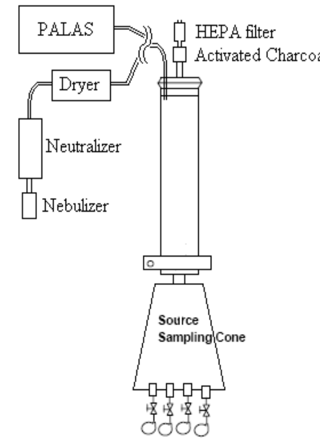


Dilution Sampling System

For Diesel Exhaust

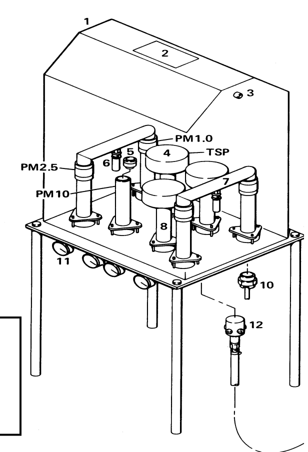
Acetylene Soot

Wood Smoke



Miniature Dilution System

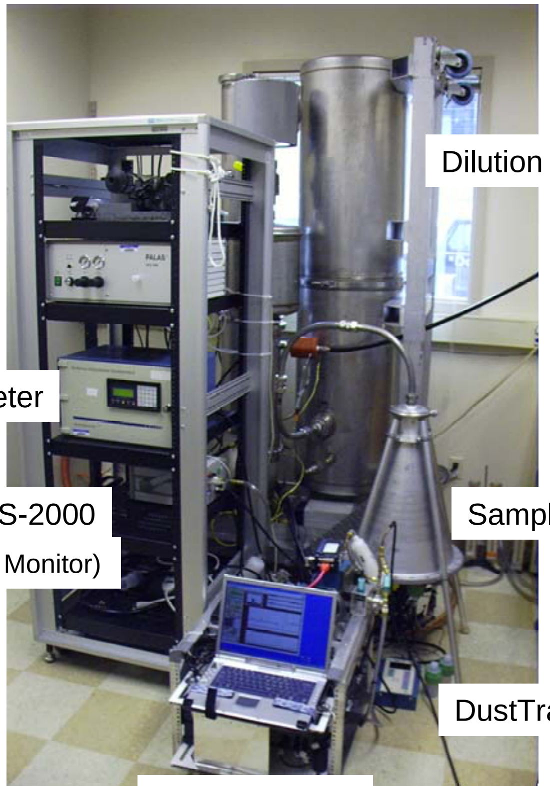
For Electric Arc Generator



Re-suspension Chamber

For Carbon Black and graphite powder

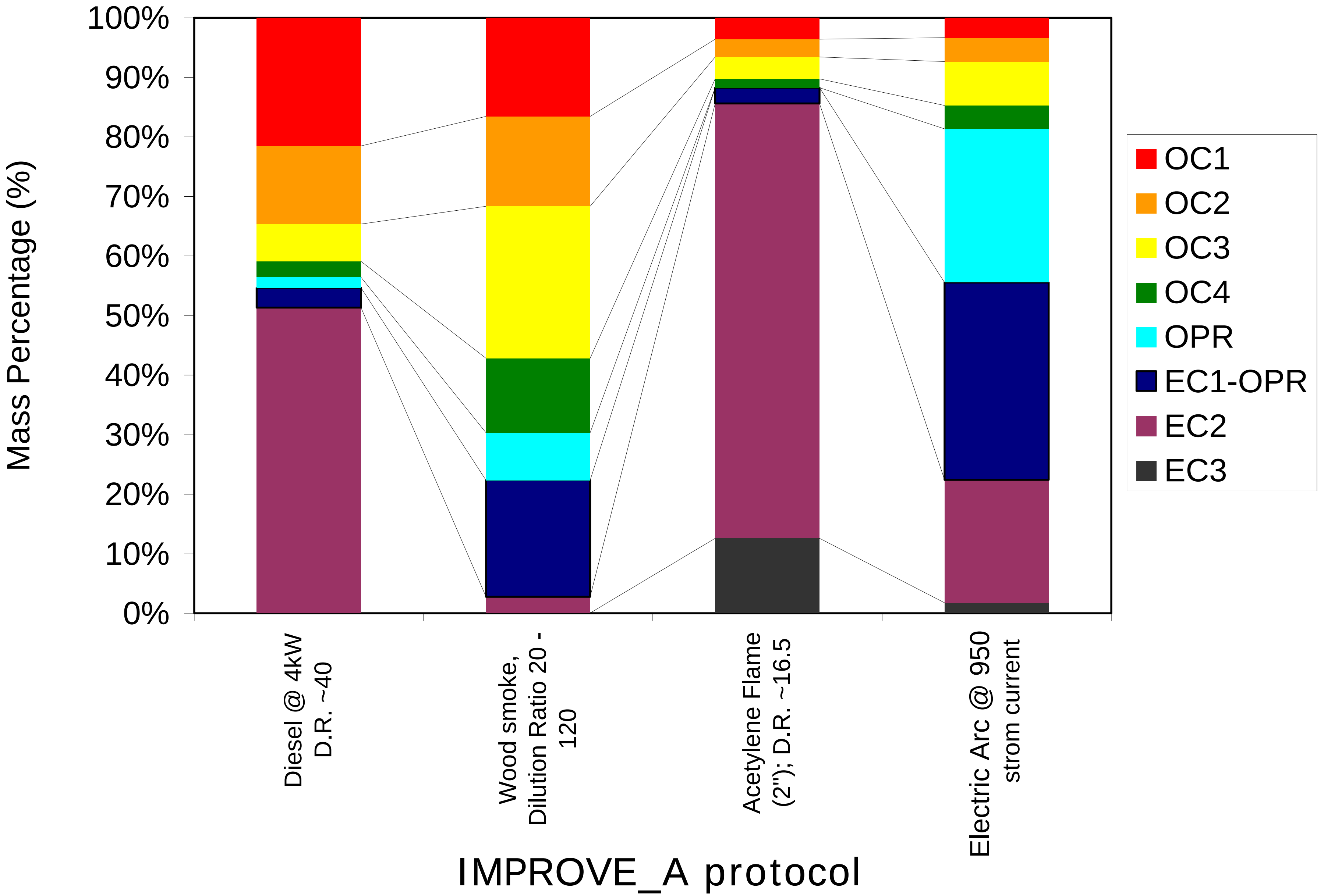
Source Testing Instrumentation



Particle Sizing Instruments (3 nm to 10 µm)

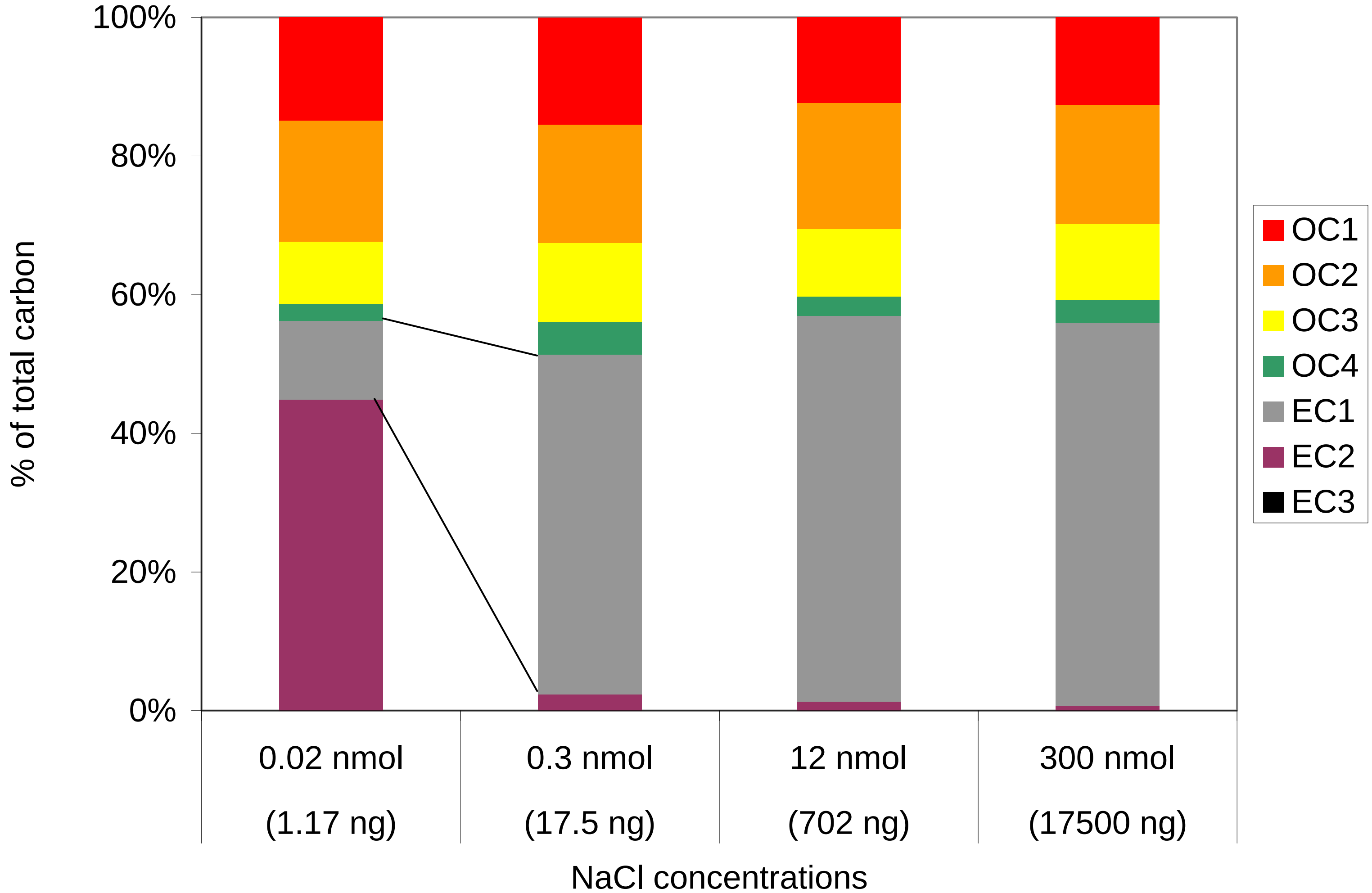
- TSI Nano-SMPS (TSI, St. Paul, MN)
- Grimm SMPS+C (Grimm, Ainring, Germany)
- MSP Wide Range Spectrometer (MSP; St. Paul, MN)

Carbon fractions vary by source



Chow et al. (2006), Report to ARB

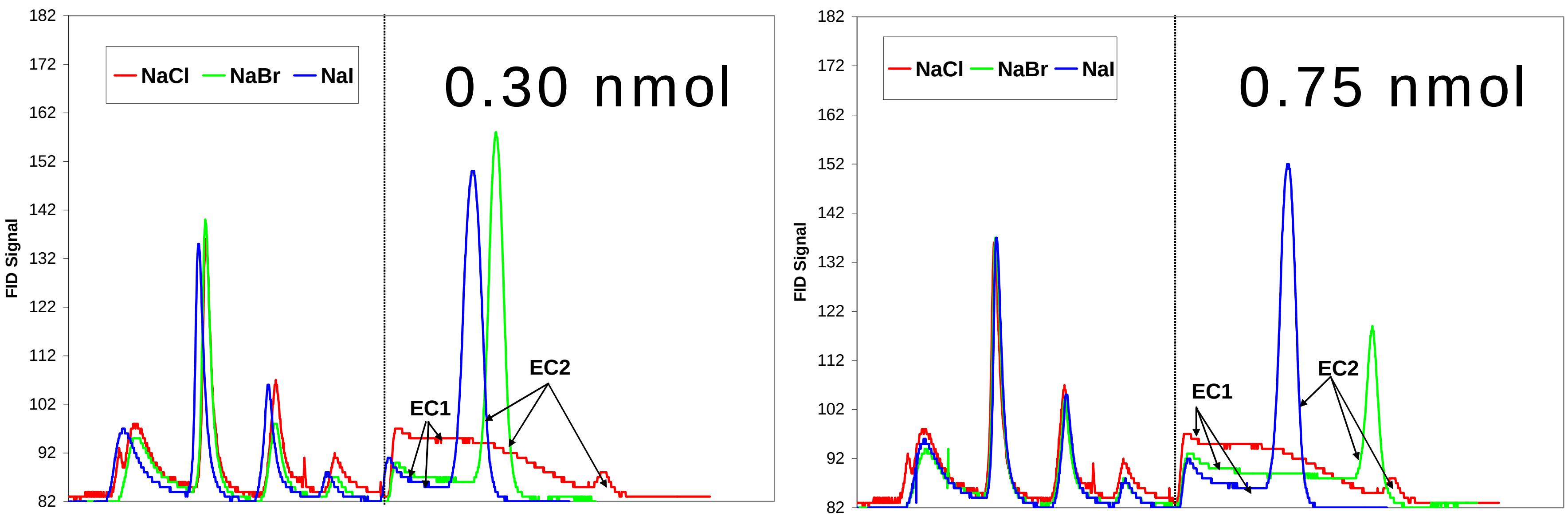
Presence of NaCl shifts EC to lower temperature fractions*



* Higher NaCl -> greater shift from EC2 to EC1

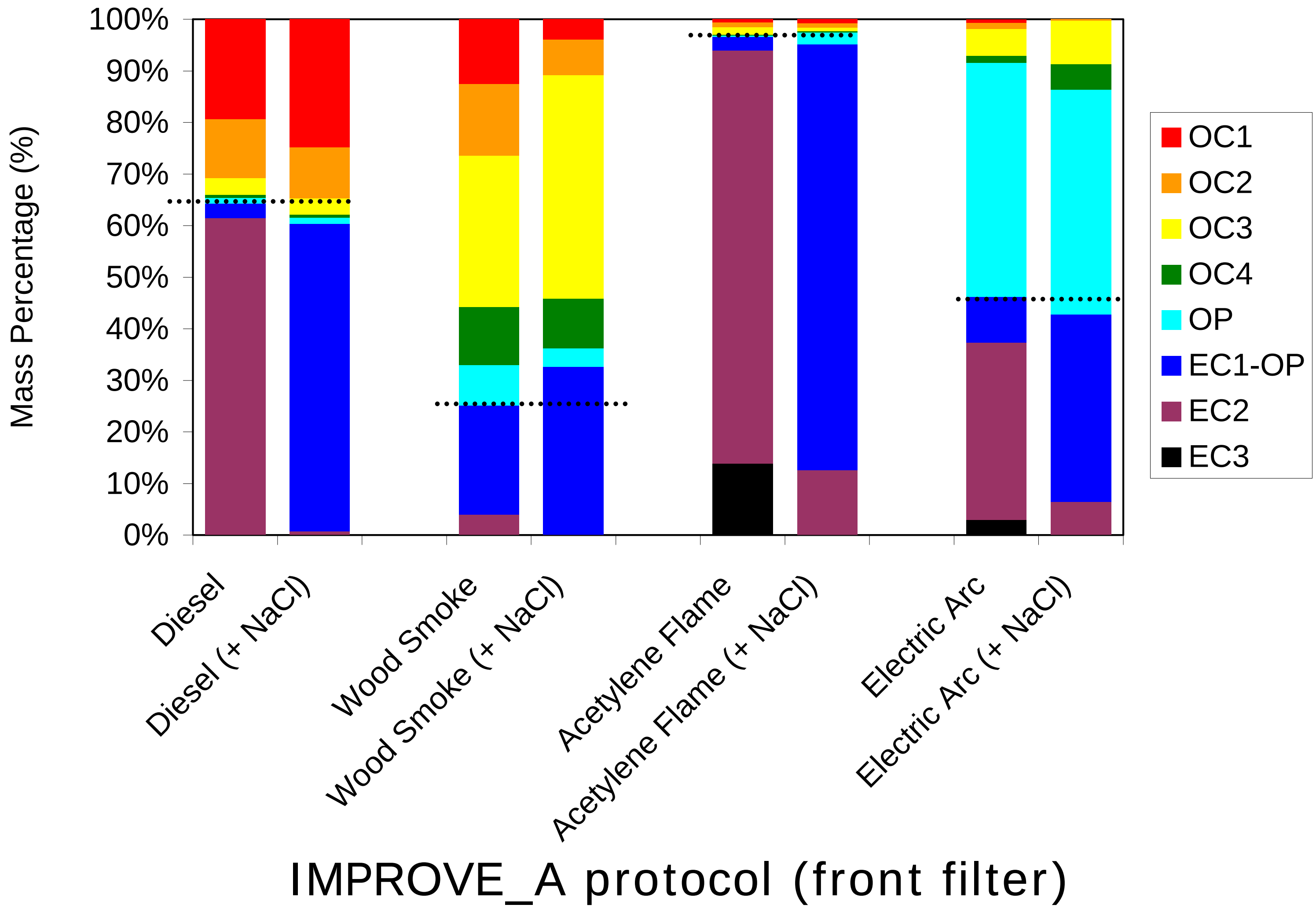
NaCl has the largest effect among halogen salts on EC fractions

- 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



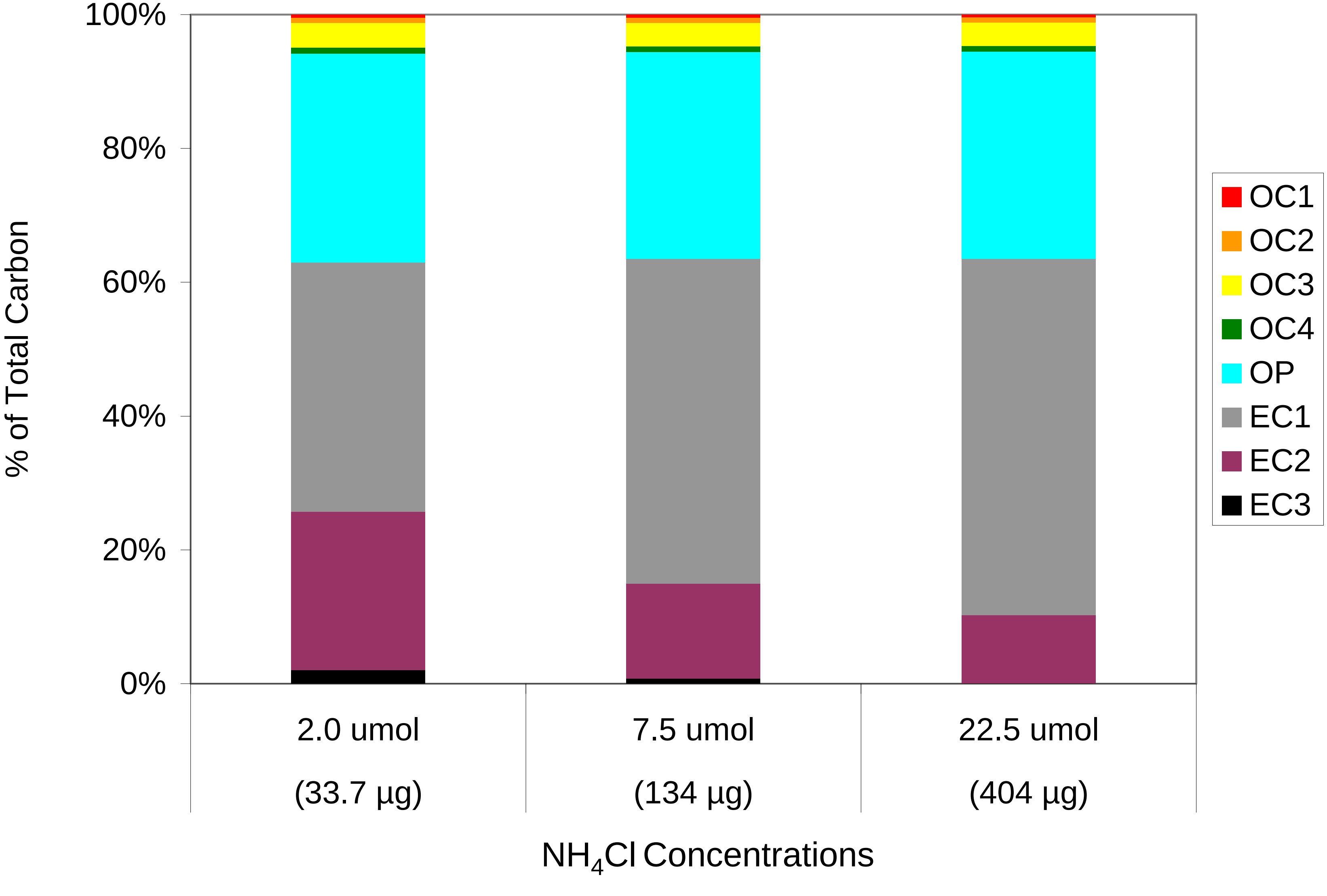
Catalytic reactivity: NaCl > NaBr > NaI

Addition of NaCl shifts EC to lower temperature fractions

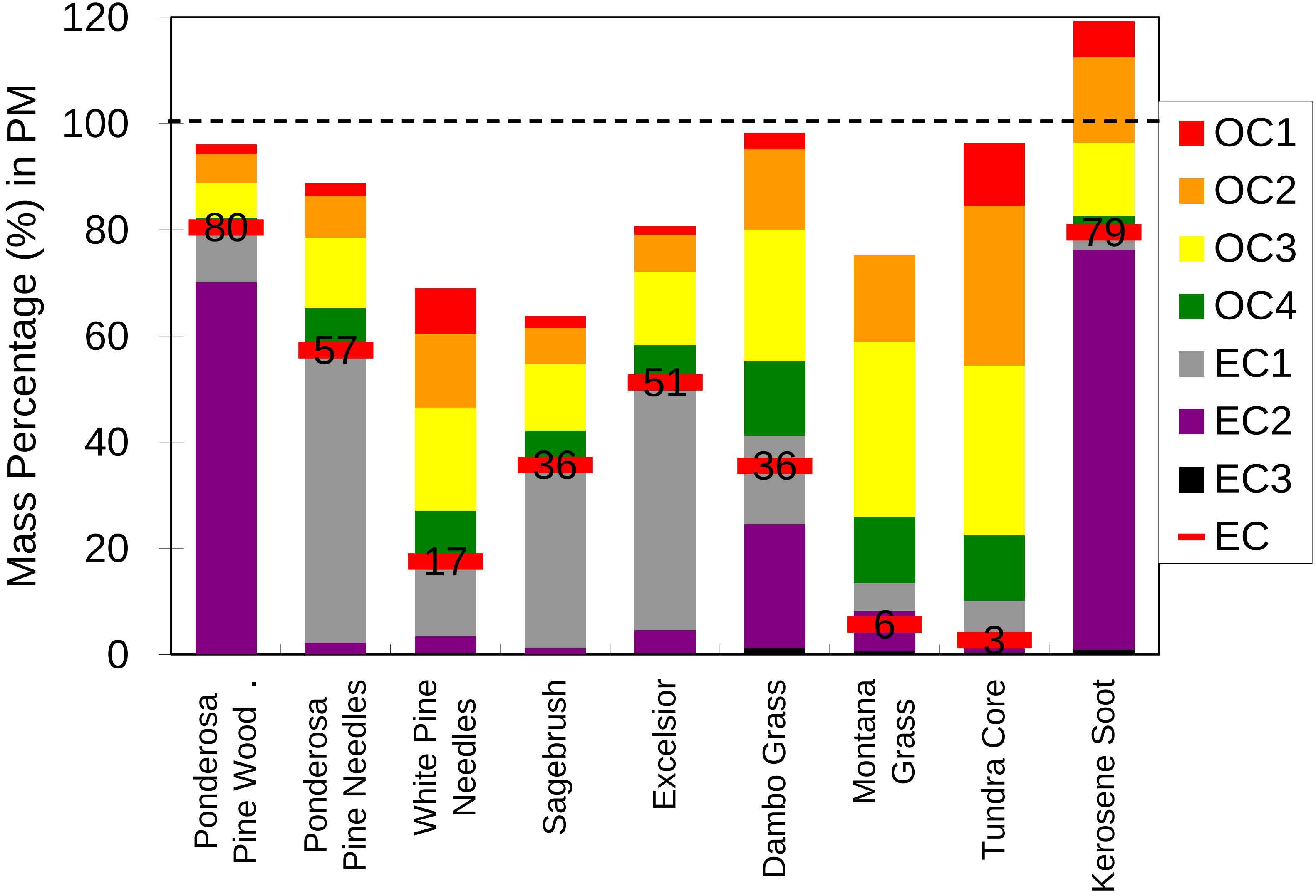


Chow et al. (2006), Report to ARB

Higher NH_4Cl shifts EC2 to EC1
(No OC shift)



Carbon fractions in biomass burning varied by fuel and combustion conditions

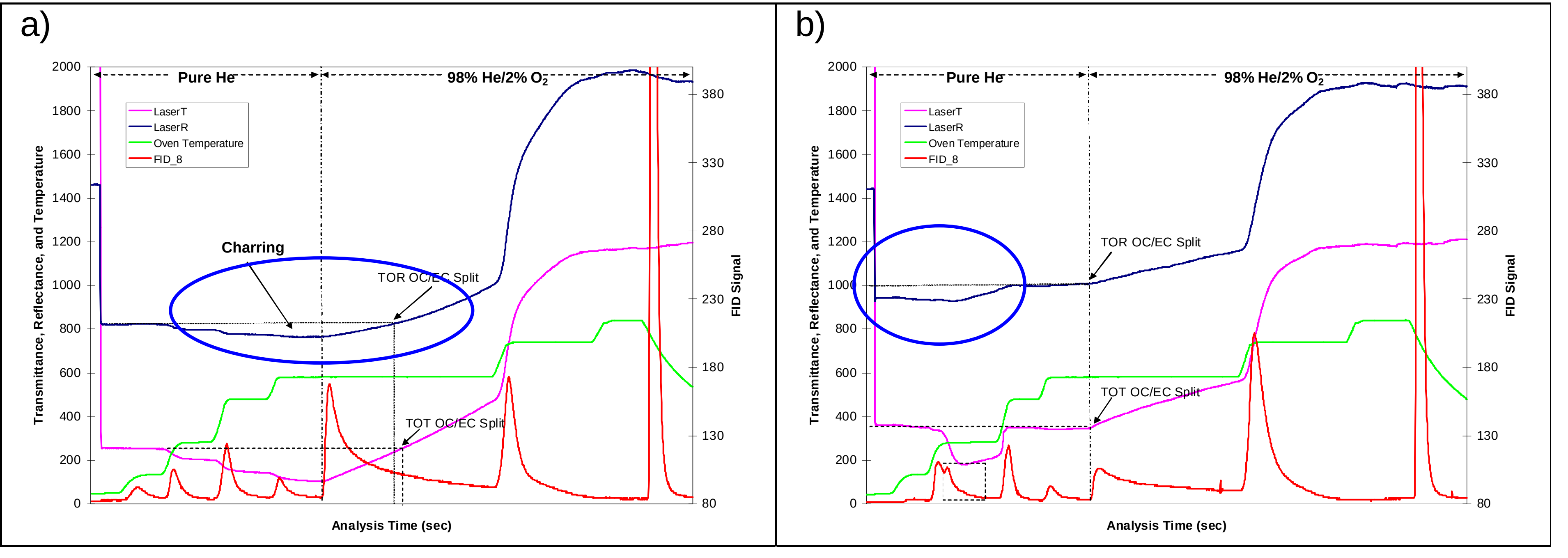


Chen et al. (2007), *Environ.Sci.Tech.*, in press

Presence of $(NH_4)_2SO_4$* minimizes pyrolysis (No EC shift)

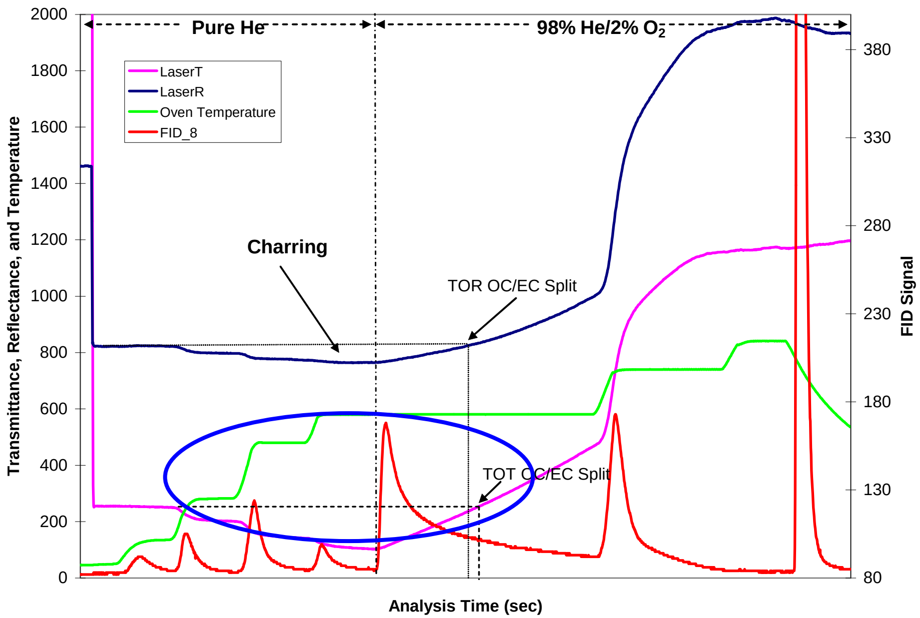
Original Filter

Spiked with 3.0 µmol of ammonium sulfate

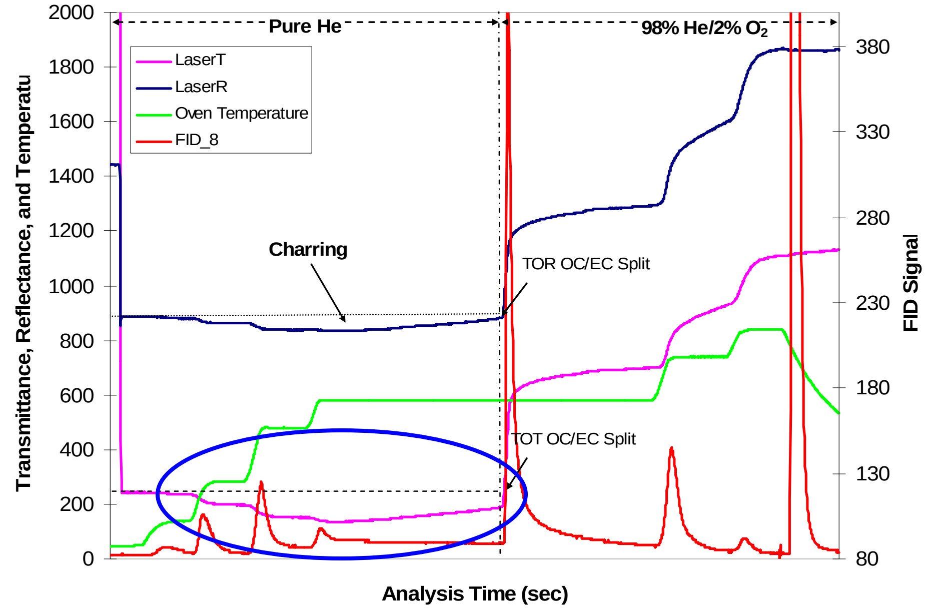


Na_2SO_4* does not suppress pyrolysis
(Shift EC1 to EC2)

Original Filter



Spiked with 3.0 µmol of Na_2SO_4



* Melting point = 884 °C

Conclusions

- 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 to separate OC from EC.