Development of Advanced Field Measurement Techniques for Sampling Atmospheric Particles

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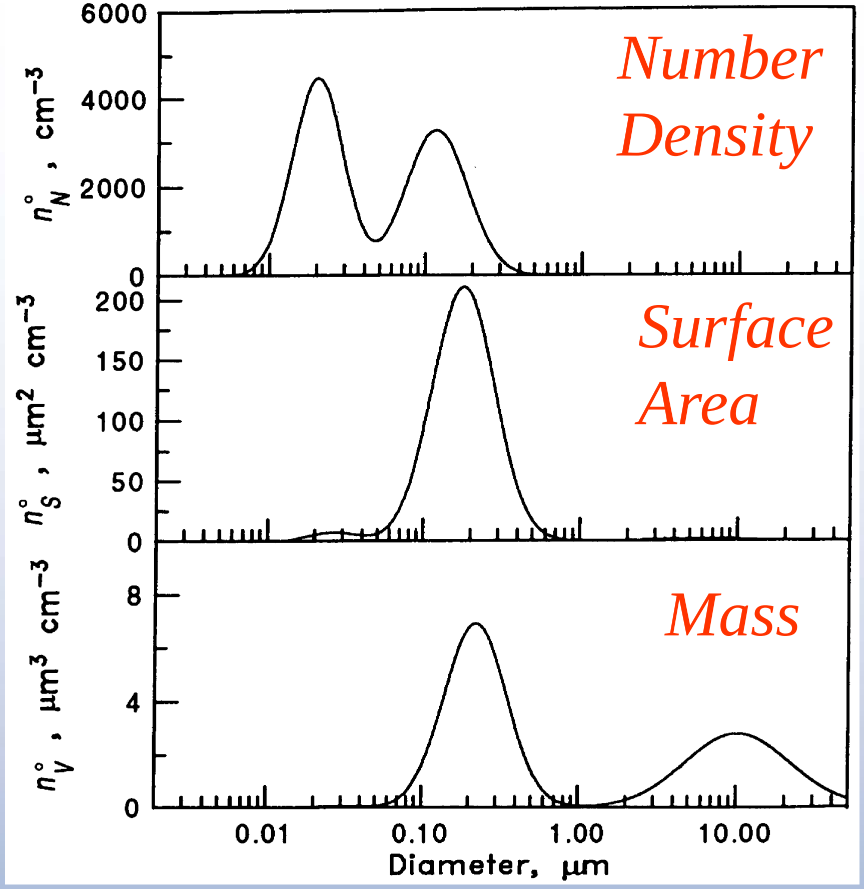
Ambient Aerosol Size Distribution



Ultrafine *Fine* *Coarse*

Aerosols can be complex

Variations in:

Size

Shape

Number

Chemical composition

$PM_{2.5} < 15\mu g/m^3$

$PM_{10} < 40\mu g/m^3$

"remote continental"

Pandis and Seinfeld, 1998

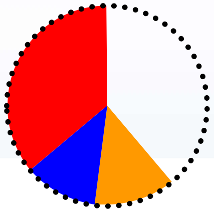
Key Atmospheric Fine PM Impacts

Chronic and Acute Impacts on Human Health
- $PM_{2.5}$ NAAQS

Climate Impacts from Scattering and Absorbing Solar Radiation and Cloud Nucleation
- Direct Radiative Forcing
- Indirect Radiative Forcing (Clouds)
- Precipitation (Clouds)

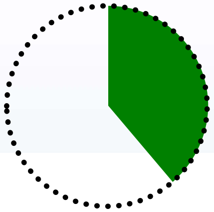
Impacts on Natural and Agricultural Ecosystems
- Acid Deposition
- Solar Radiation Diminution (PAR)
- Temperature and Precipitation Effects

Inorganic vs. organic aerosol PM components



Inorganics

- Few components (SO_4^{2-}, NO_3^-, NH_4^+…)
- Formed by well-established chemistry
- Well-characterized properties
- Relatively inert chemically



Organics

- 1,000's-10,000's of compounds (more?)
- Formation chemistry uncertain
- Properties highly variable
- Reactive (oxidation reactions)

Instrumentation for (Near) Real-Time Fine PM Chemical Characterization

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Recent Revolution in Development and Demonstrated Capability

Avoids Filter Analysis Artifacts and Delays

Higher Time Resolution Allows Mobil Mapping and Improved Source and Impact Analyses

Field and Lab Instrument Validations and Intercomparison Studies Available

Recent Fine PM Instrumentation Advances

Technique	Species	Cycle Times	Developers
Near Real-Time (Semi-Continuous)			
Denuder/PM Scavenging/Ion Chromatography (PILS-IC)	NO_3^-, $SO_4^=$, Cl^-, NO_2^-, NH_4^+ Organic acids	2.5-30 min	P. Dasgupta R. Weber J. Slanina
Denuder/PM Collector/Vaporization/Optical Vapor Detection (Fluorescence) (ICVC)	NO_3^-, $SO_4^=$, Organics	2-10 min	S. Hering P. Koutrakos
Denuder/Mo Mesh Converter/Optical Vapor Detector	NO_3^-	0.5 min	E. Edgerton
Growth Tube/Microschip/Electrophoresis (ACE)	NO_3^-, $SO_4^=$, CT	1-10 min	S. Hering J. Collett

Recent Fine PM Instrumentation Advances

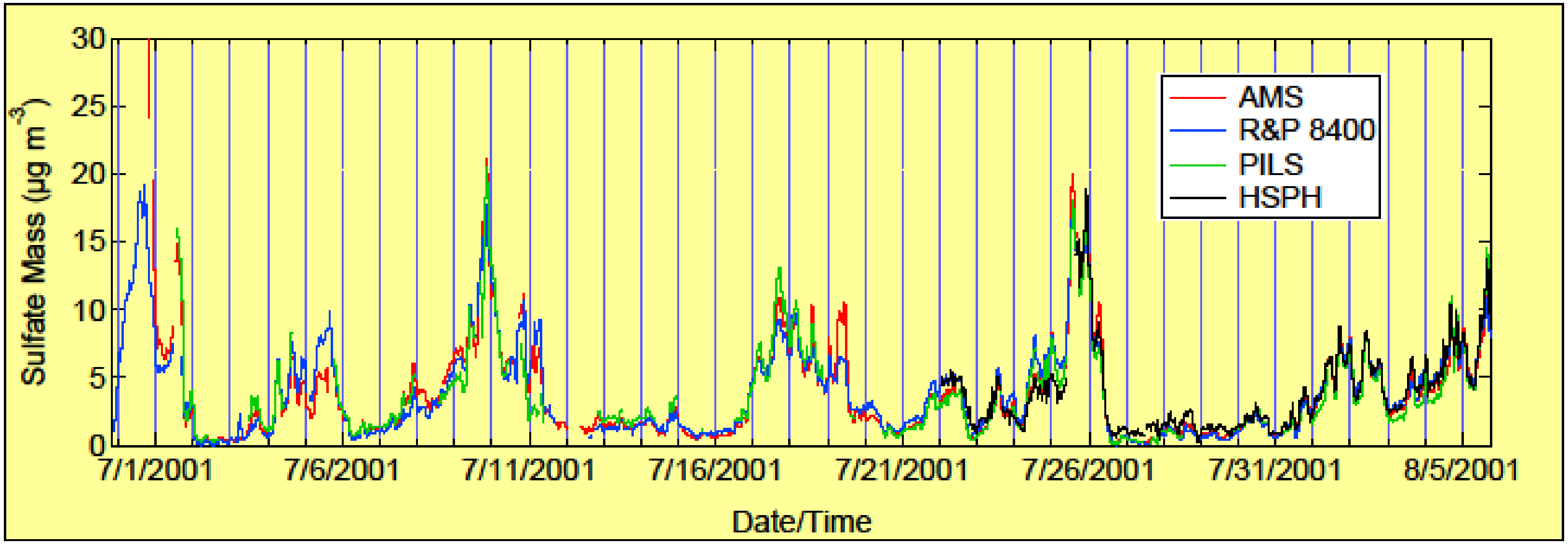
Technique	Species	Data Acquisition	Developers
Real-Time (Continuous)			
Laser Vaporization/Ionization Aerosol Mass Spectrometry (SPMS)	Metals, NO_3^-,$SO_4^=$,Cl^-, C/Organics	10 – 30 min	K. Prather M. Johnson/A. Wexler D. Murphy B. Spengler A. Zolenyuk A. Trimborn
Hot Surface Vaporization Aerosol Mass Spectrometry (AMS) (ACSM) (TDPBMS)	NO_3^-,SO_4^-,Cl^-,NH_4^-, Organics	2 s – 30 min	J. Jayne/D. Worsnop P. Ziemann
Laser Induced Incandescence (SP2)	C(soot)	10 s – 15 min	D. Baumgardner
Soot Photometry Mass Spectrometry (SP-AMS)	C(soot)	2s – 30 min	D. Worsnop/T. Onasch/G. Kok

Recent Organic PM Speciation Methods

Technique	Measurement	Time Response	Developers
Teflon Filter Collection/FTIR Absorption	Organic Functional Groups	~ 1 hr	L. Russel
Thermal Desorption Aerosol GG/MS (TAG)	Partial Organic Speciation (Marker Compounds)	~ 1 hr	A. Goldstein S. Hering

Sulfate Intercomparison

PMTACS **Queens New York** July 2001



Good correlation between four separate measurement technologies

aerosol measurement technologies are developing

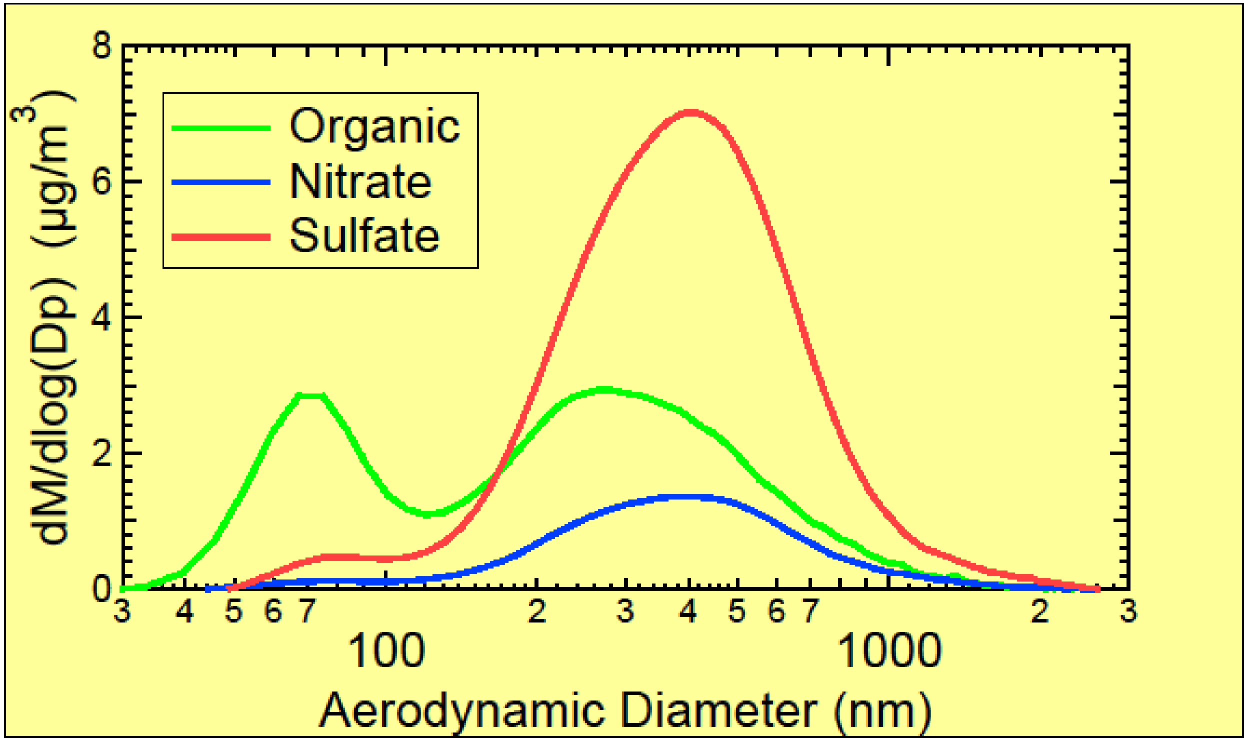
F. Drewnick et al., Atmos. Environ., 37, 3335-3350 (2005)

Queens, New York

PMTACS

Urban Site

Jul. 1-Aug. 5, 2001

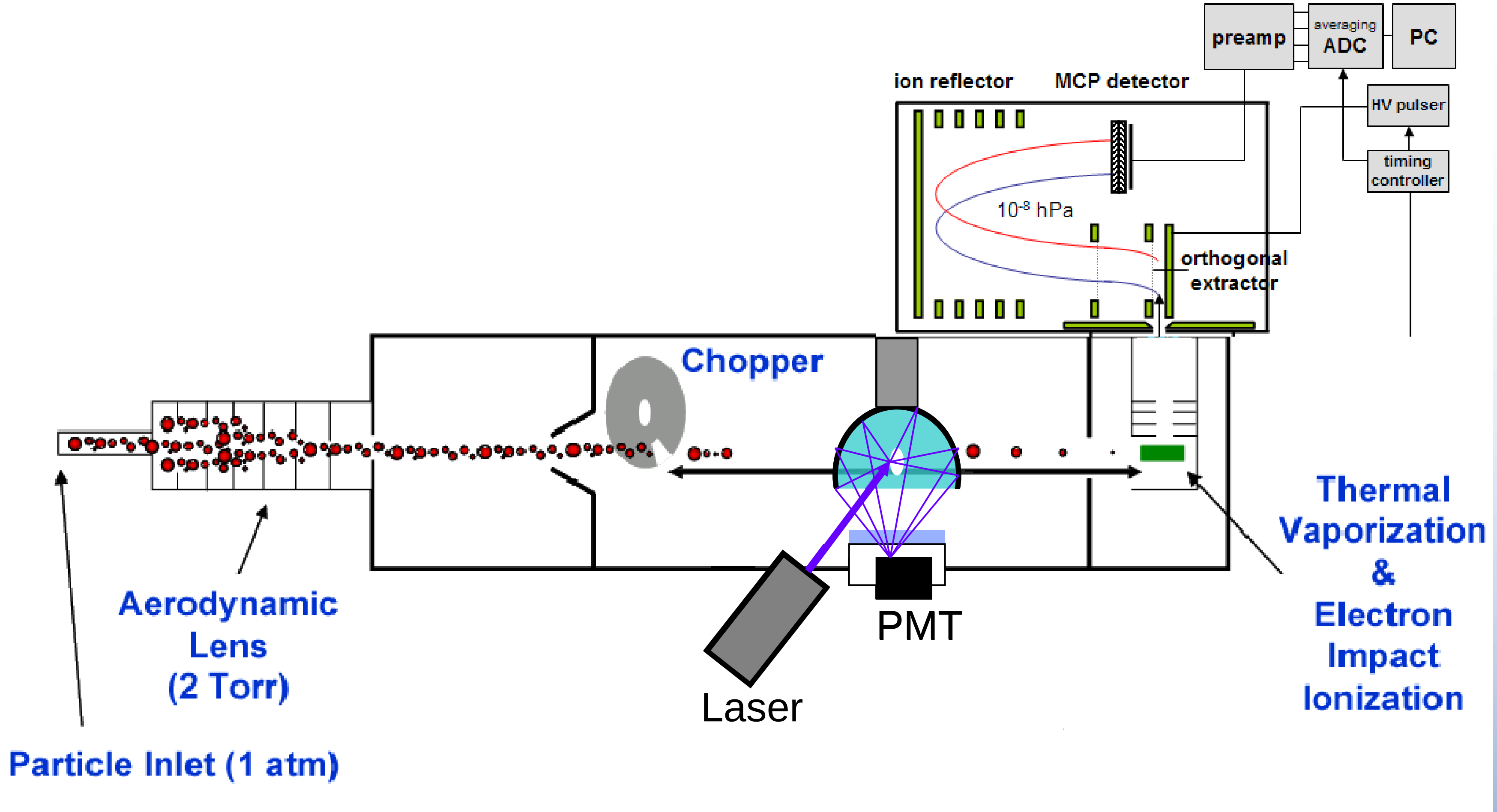


Characteristic Urban Bi-modal Size Distribution

Organic fraction dominates small size mode

F. Drewnick, K. Demerjian ASRC SUNY Albany

Aerodyne
Aerosol Mass Spectrometer



- Particles pass through laser beam before impacting vaporizer
- Correlated scattered light and chemical ion signals

FINE PARTICLE COMPOSITION

(Jimenez et al., Science 326, 1525-1529, 2009)

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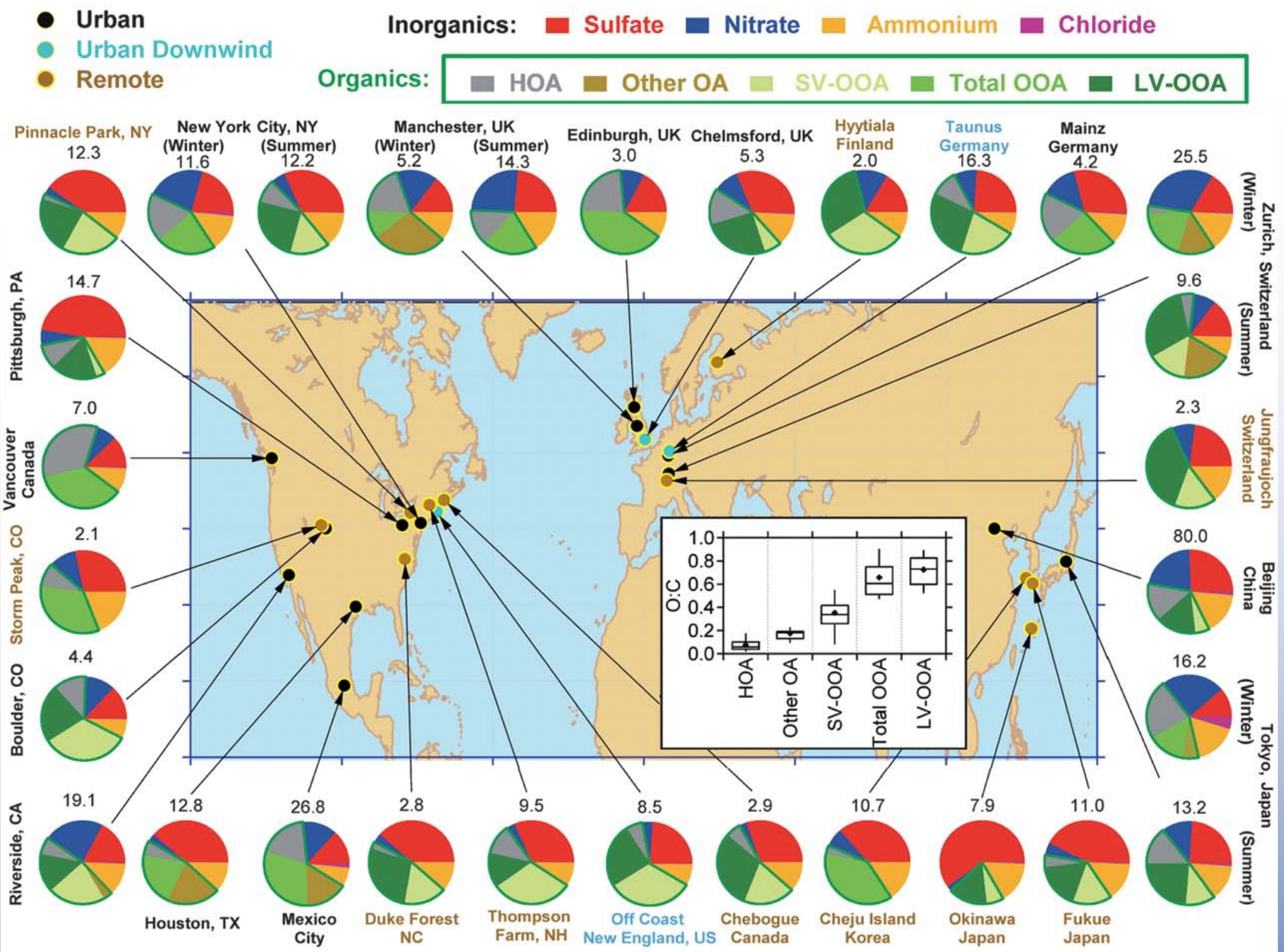
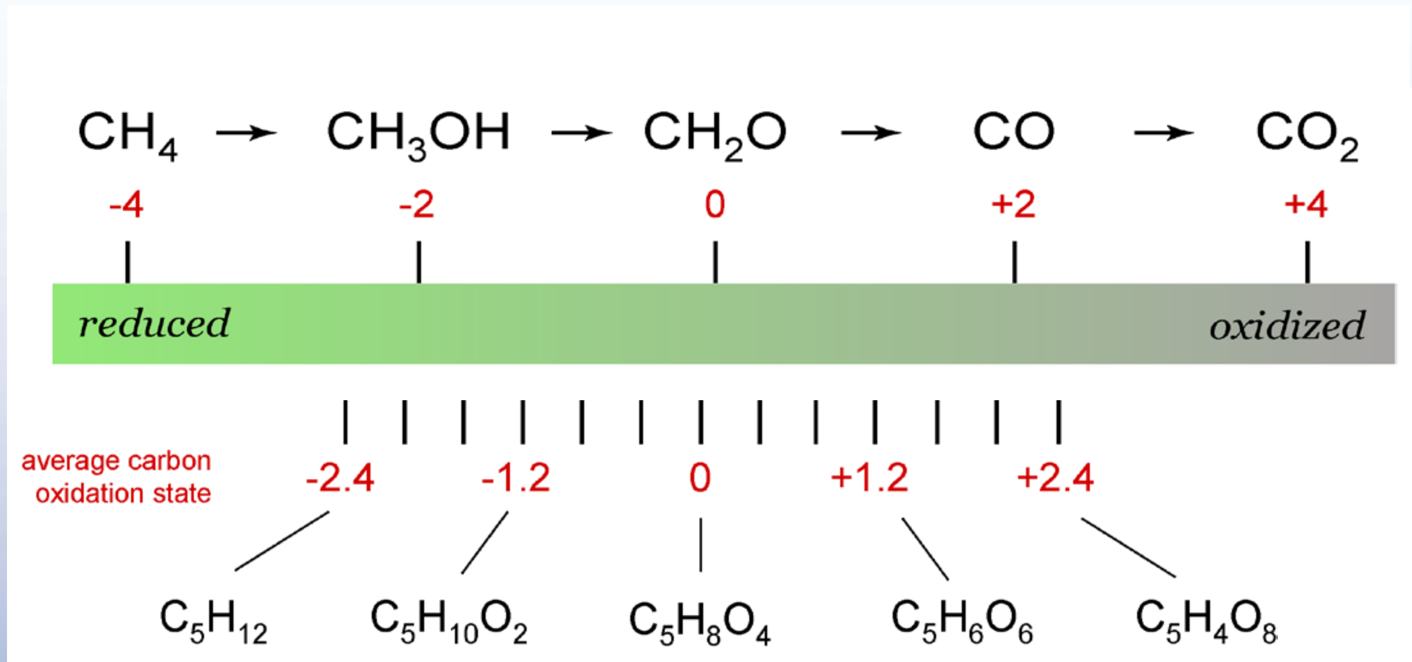


Oxidation of organic species

In an oxidizing atmosphere, the oxidation state of carbon increases:

methane oxidation



C_5 carbon chain

Oxidation state of organic aerosol

- Average carbon oxidation state can be determined from any analytical technique that measures elemental ratios (O/C, H/C) of organics (e.g., High-Resolution Aerosol Mass Spectrometer):

$$\text{Ox. State} \approx 2\,(O/C) - (H/C)$$

Averages from HR-AMS measurements in Mexico City:

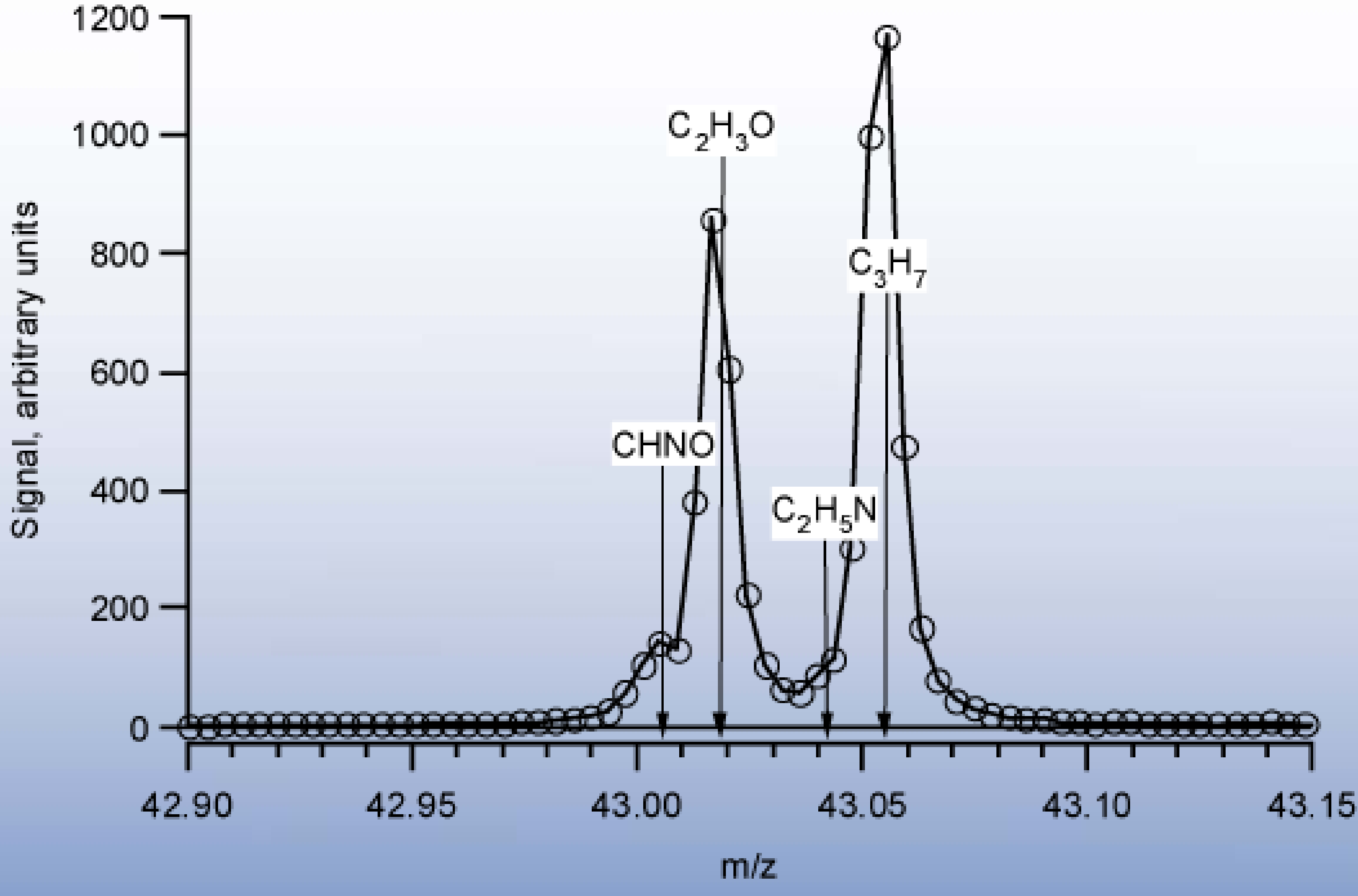
T0 (morning):	-1.0	C-130 (city):	-0.4
T0 (afternoon):	-0.5	C-130 (outflow):	-0.2
		C-130 (background):	+0.2

Factor analysis of Mexico City HR-AMS spectra:

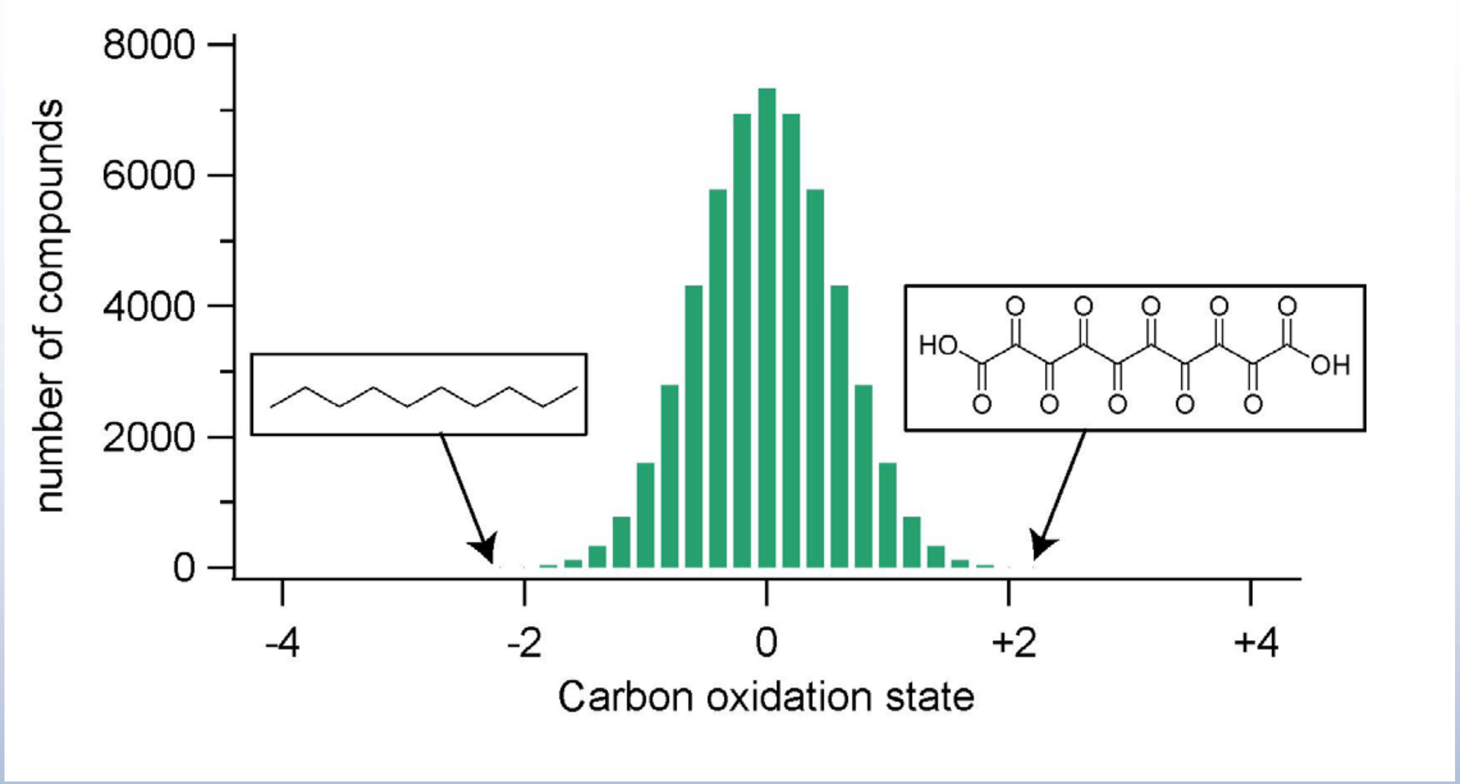
Hydrocarbon-like (HOA):	-1.7	Oxidized (“fresh”, OOA-2):	-0.4…0.0
Biomass burning (BBOA):	-1.0…-0.5	Oxidized (“aged”, OOA-1):	+0.5…+1.0

Aiken et al., ES&T, 2008

ORGANIC PM ATOMIC RATIOS FROM HIGH RESOLUTION AMS

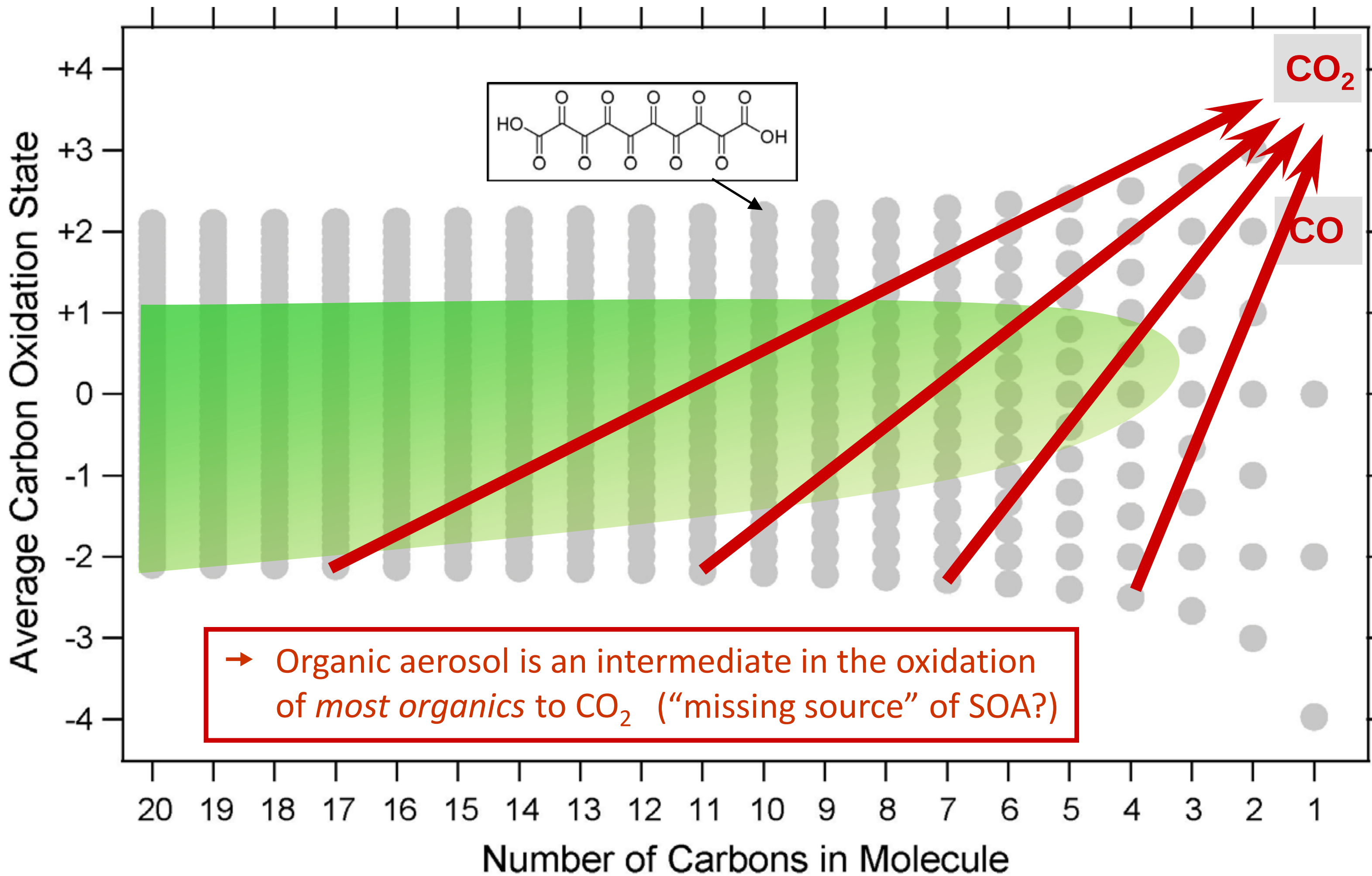


Products: *n*-decane ($C_{10}H_{22}$) oxidation



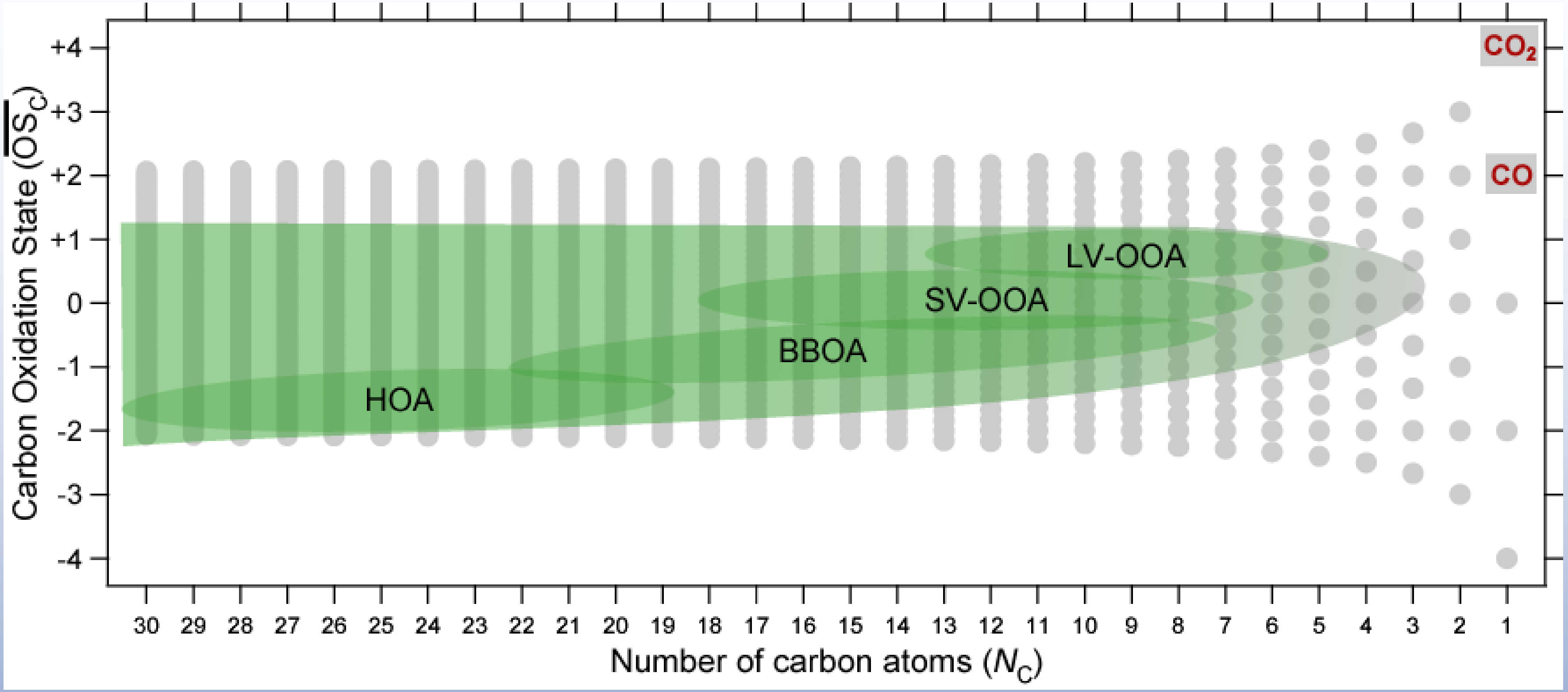
carbonyls, alcohols, acids only

Oxidation states of organic aerosol

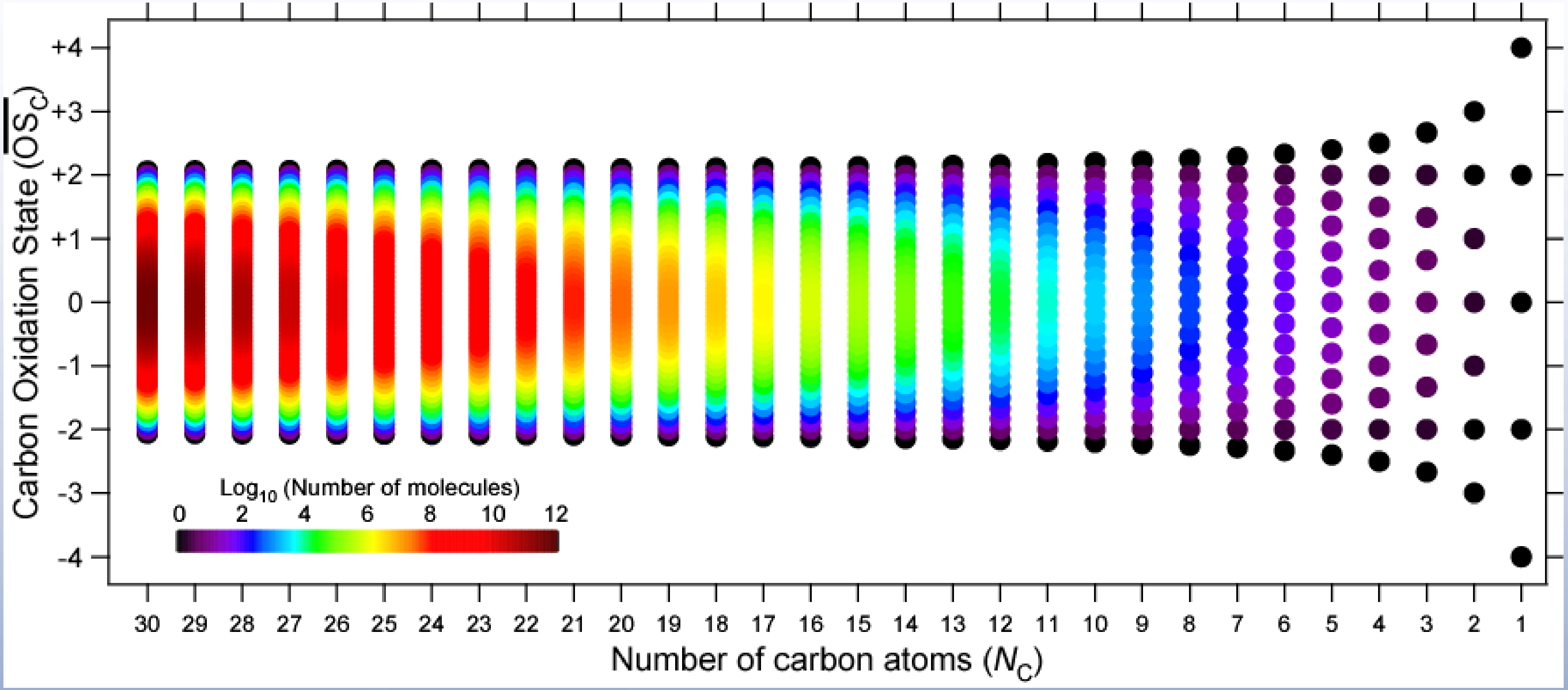


[e.g. Heald et al. 2005; de Gouw et al 2005; Volkamer et al 2006]

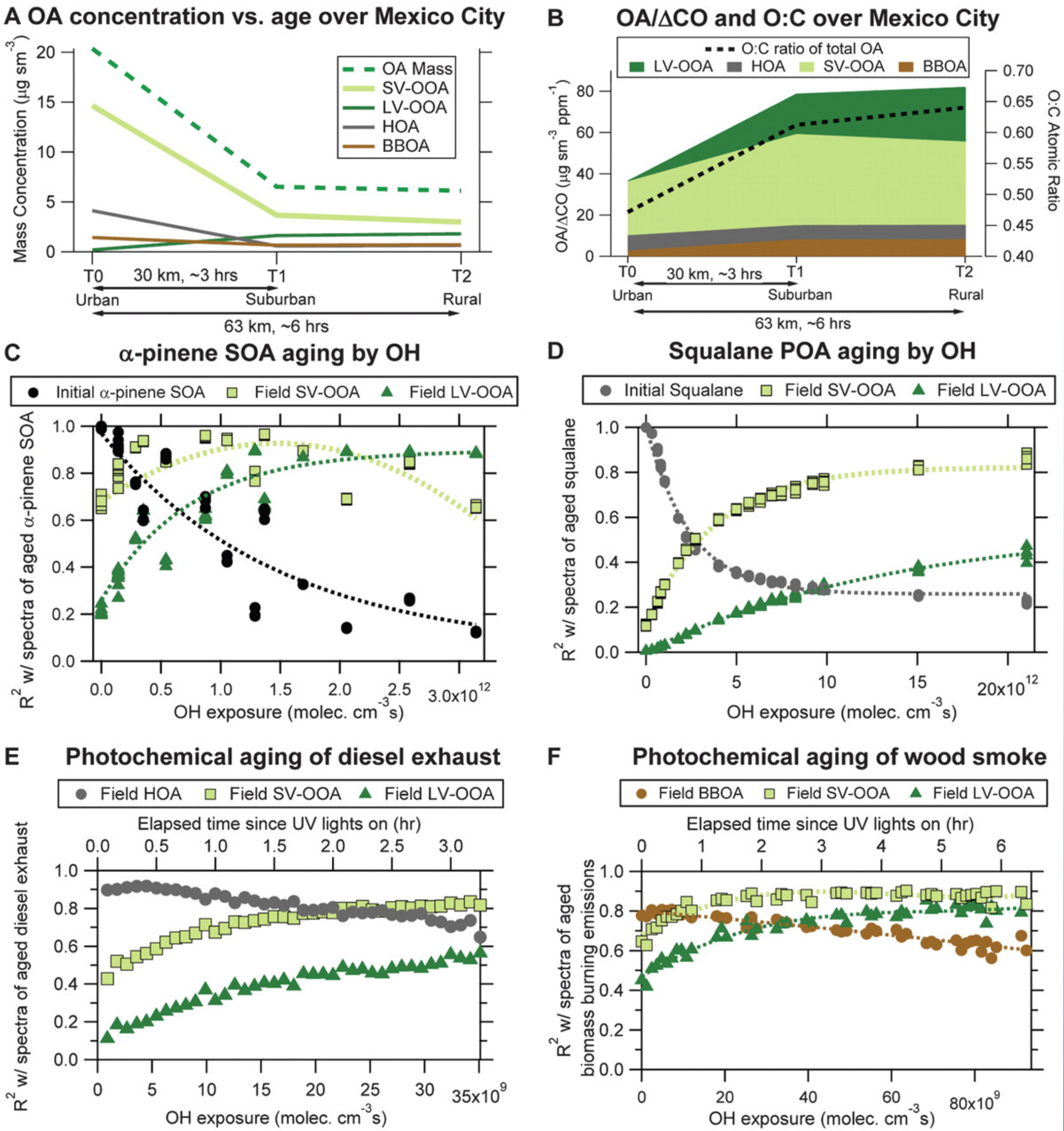
OXIDATION STATES OF ORGANIC AEROSOL PM



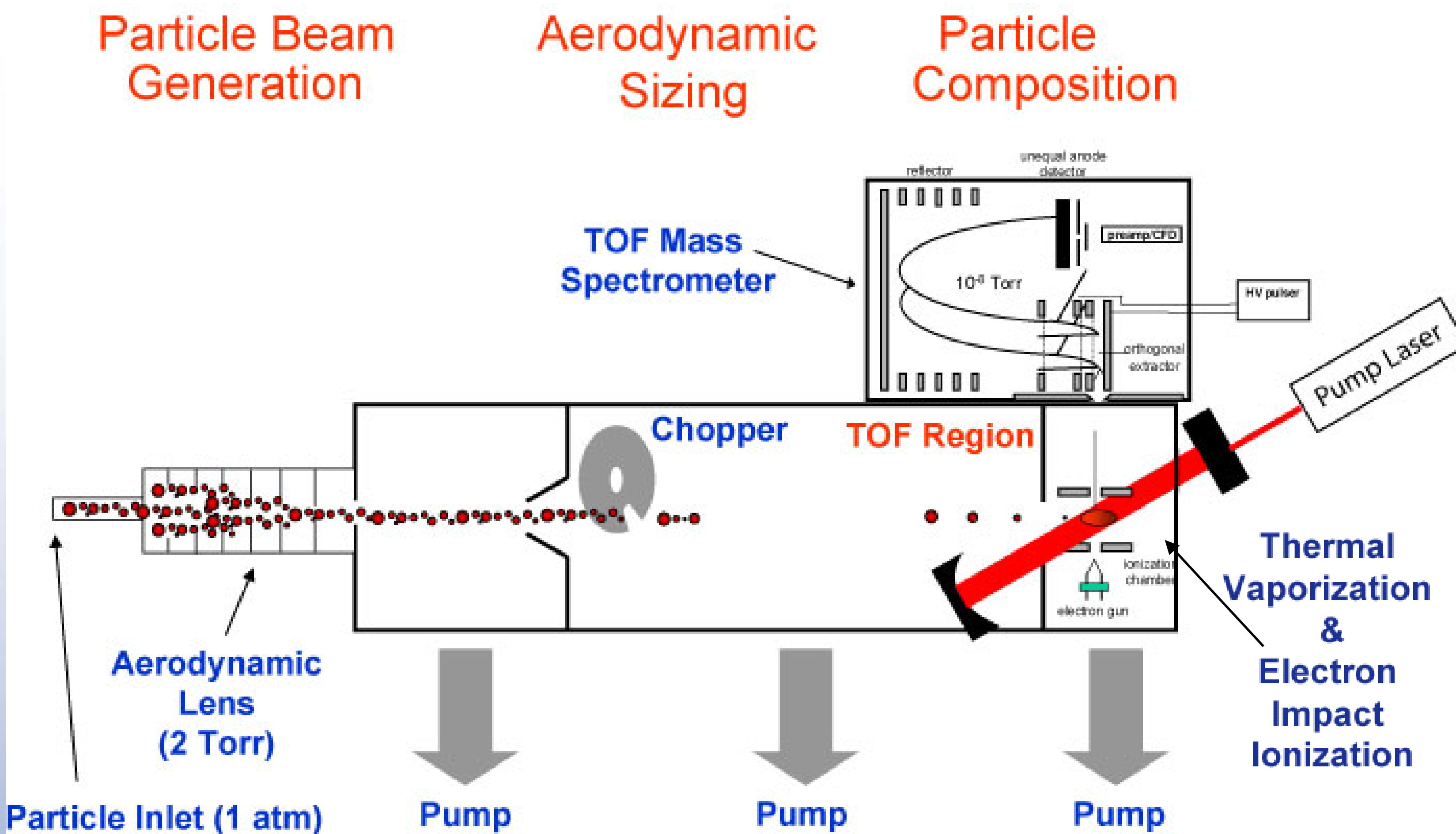
CHEMICAL COMPLEXITY OF AEROSOL PM



FINE ORGANIC PM CHARACTERISTICS

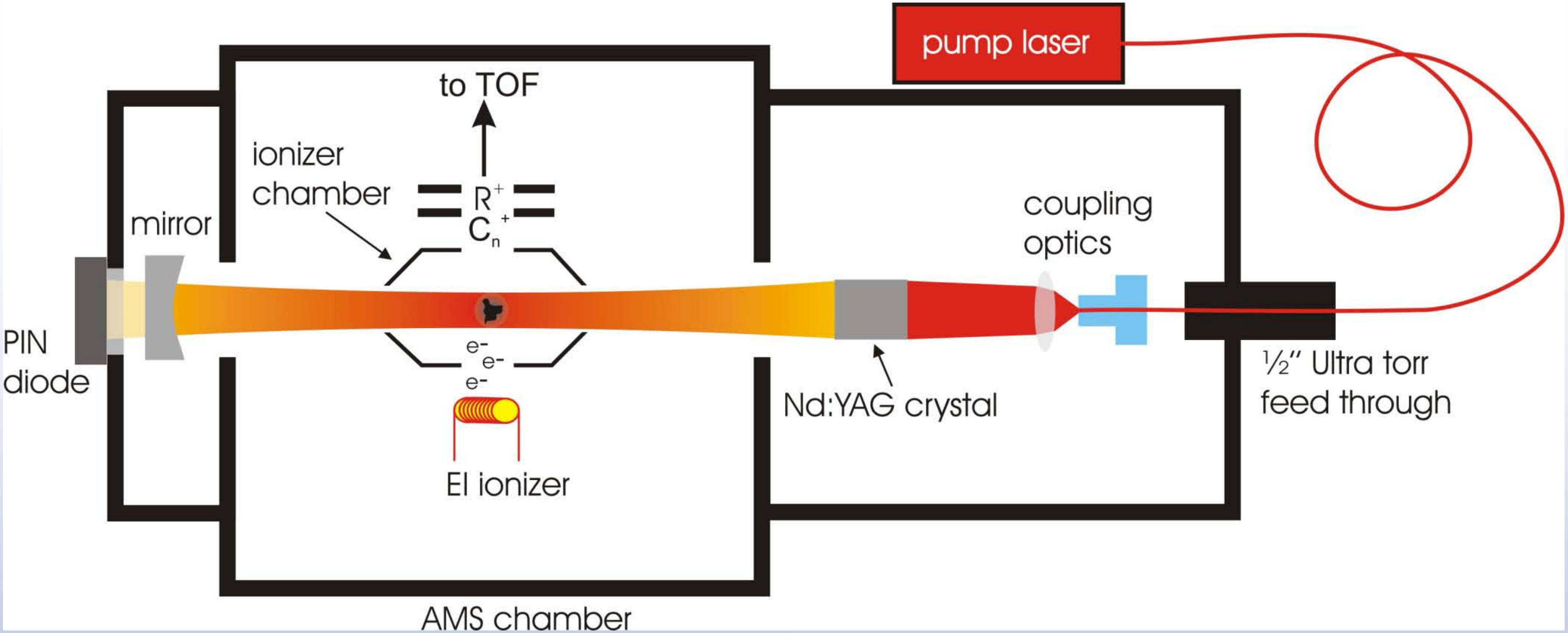


SP-AMS schematic



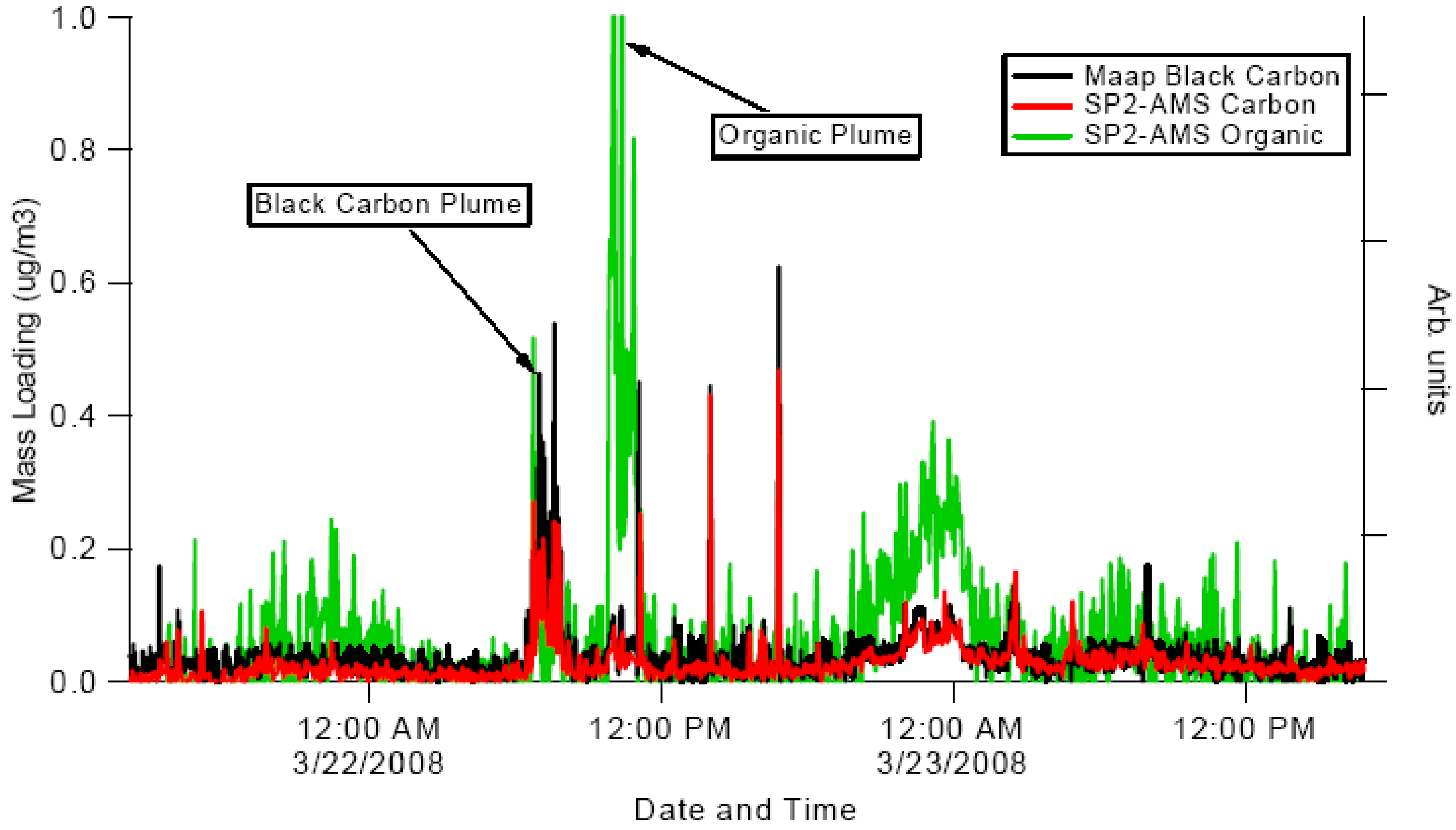
- Install SP2 module

Schematic of the SP-AMS module



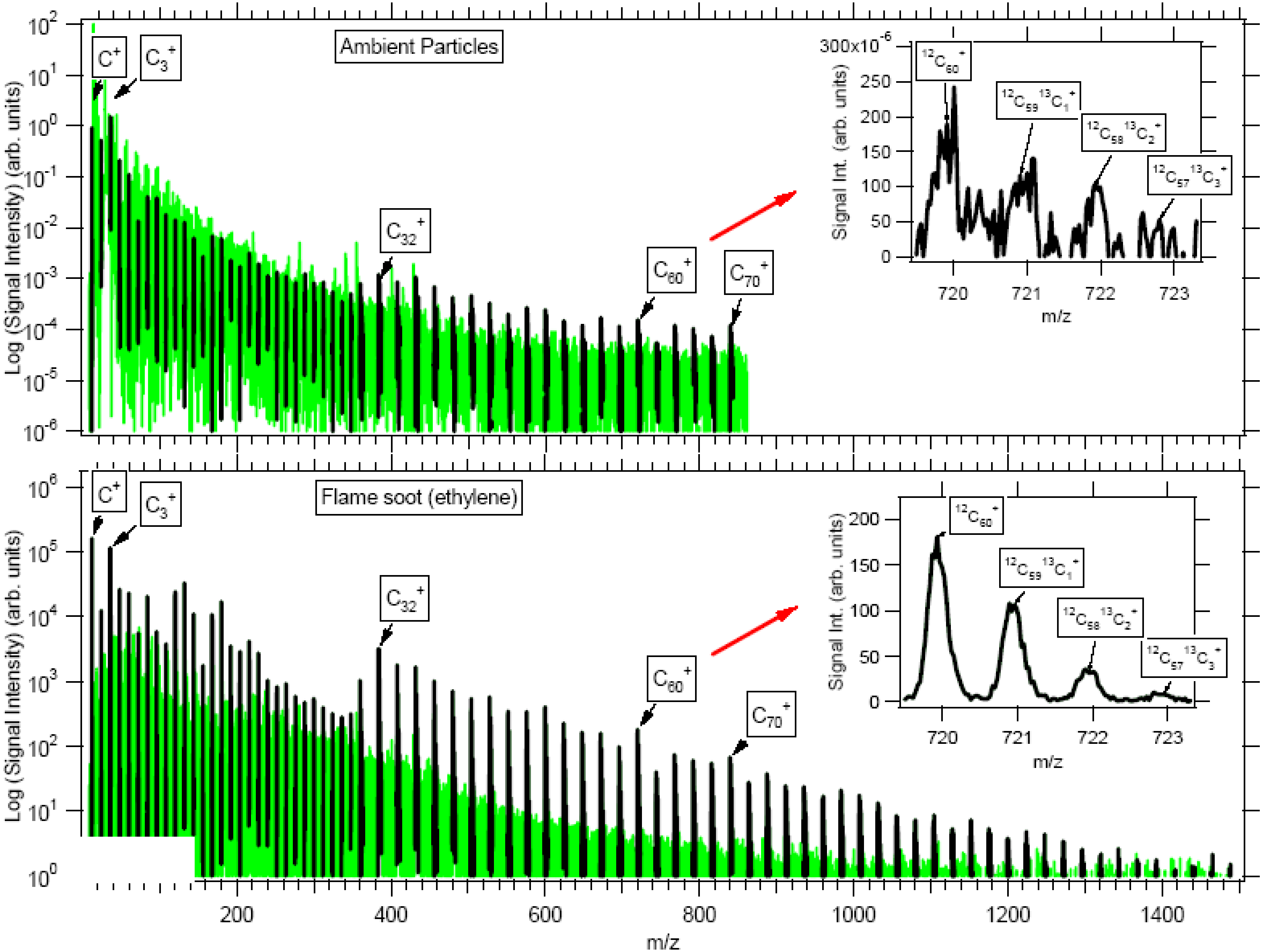
- Absorbing particles (coating and core) vaporize in laser
- Vapor is ionized by electron impact ionization
- Detection of the ions by Time-of-Flight mass spectrometry
- Readily installed in any exiting AMS instrument

SP-AMS Ambient Measurements

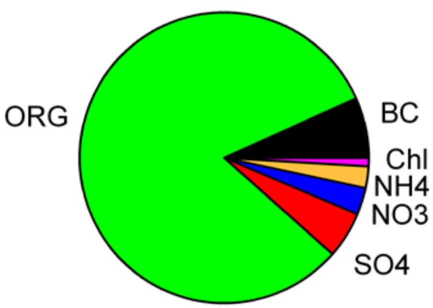
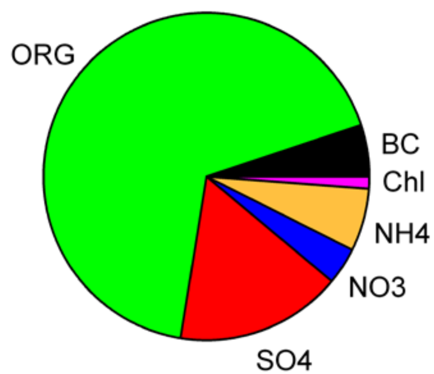
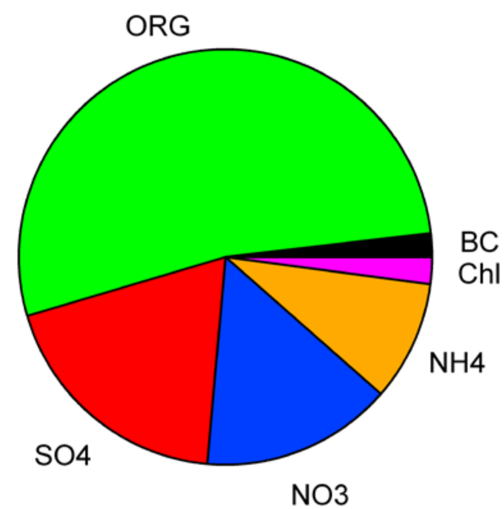


Ambient aerosol particles sampled by the SP2-AMS (red=carbon, green=organics, left axis) and the MAAP (black, right axis) in Chestnut Hill, MA.

SP-AMS Mass Spectra for Ambient Particles and Ethylene Flame Soot

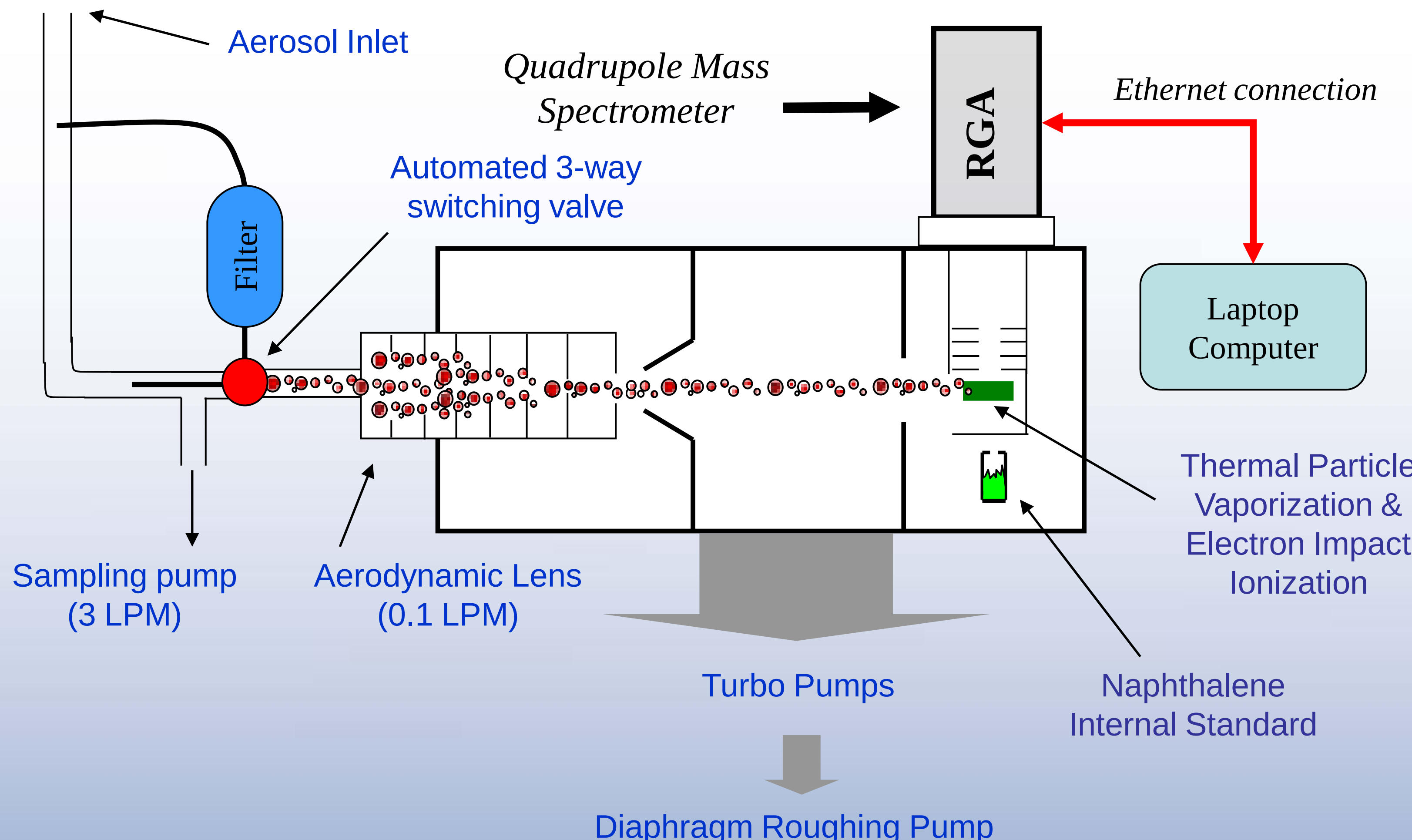


Composition and Size Distribution of BC Coating and Ageing of BC Containing Particles

Fresh (downwind LA 0529)	Moderately Aged (downwind Santa Barbara, 0531)	Aged (downwind Santa Monica 0515)
		

increasing of total coating mass →

Aerosol Chemical Speciation Monitor



Aerodyne Research, Inc.
Aerosol Chemical Speciation Monitor

Size: 19”D x 21”W x 32”H

Weight: 140 lbs

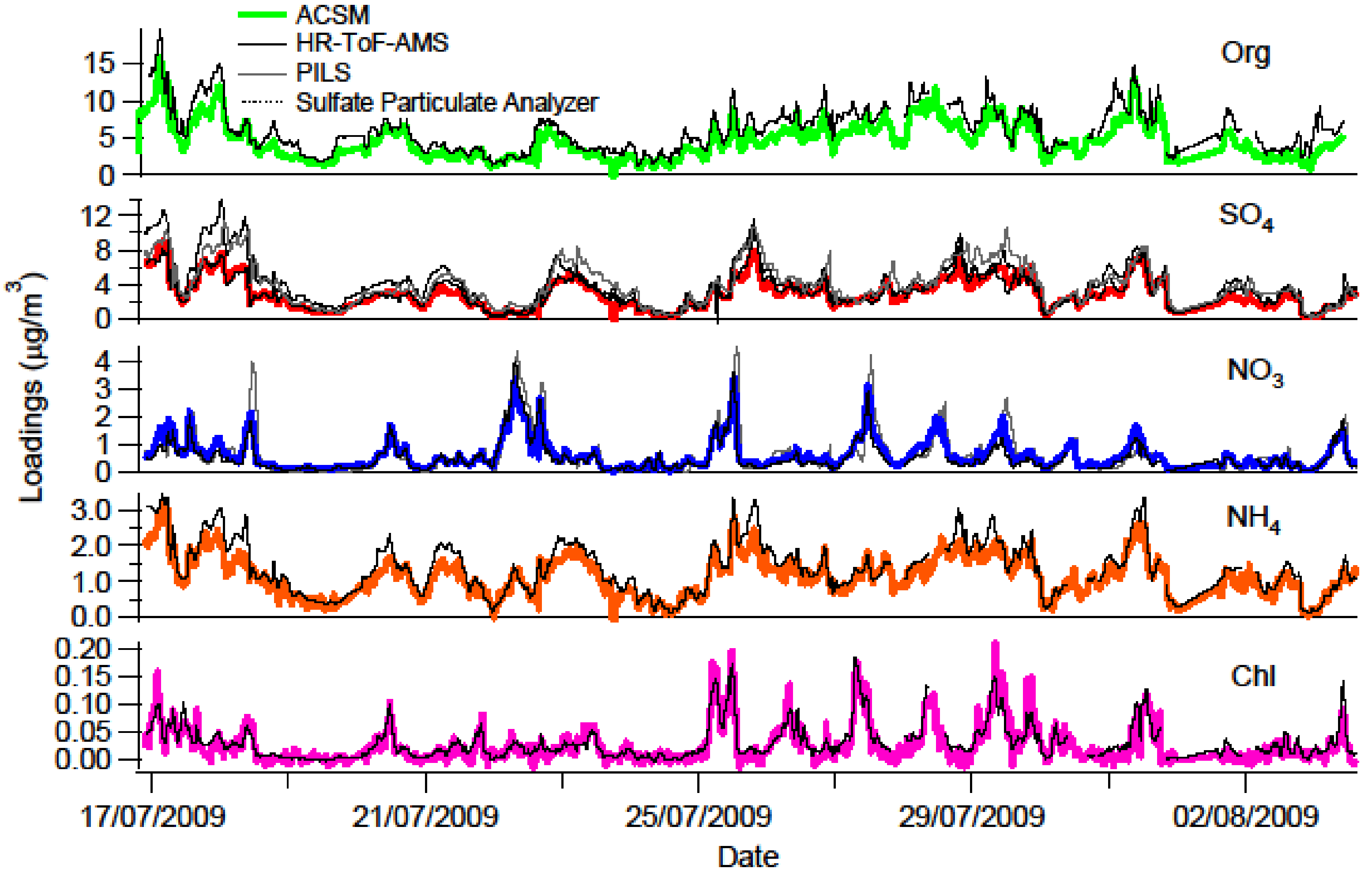
Power: 300W

universal AC power; 85-264 VAC, 47-63 Hz

ACSM-002 SN 140-100

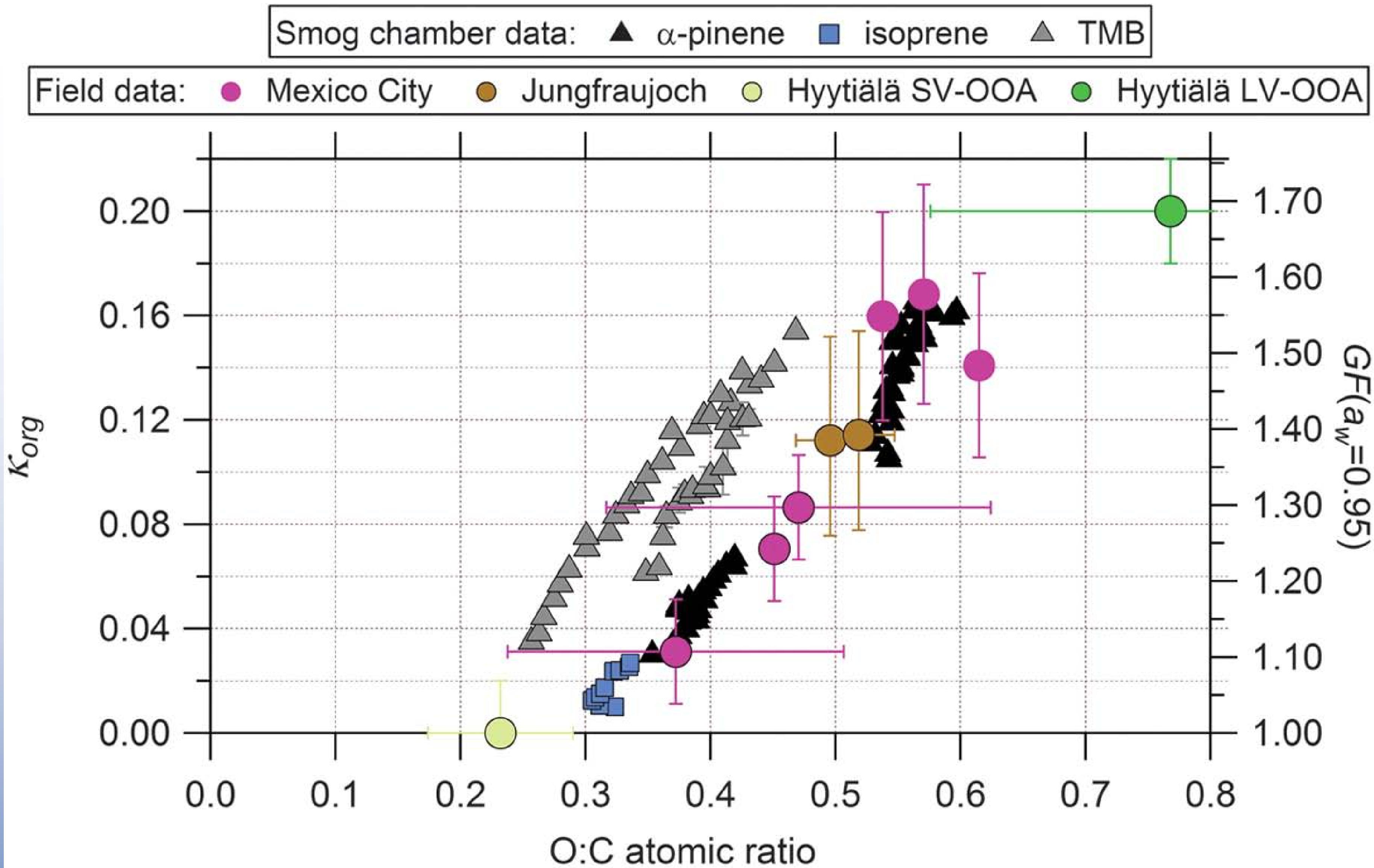
Shown with Pfeiffer Pumps and Integrated Power Supply

Instrument Intercomparisons



Ng et al., 2011b

FINE ORGANIC PM – HYGROSCOPICITY VS O/C RATIO



Prompt Fine PM Chemical Speciation Measurements

-SUMMARY-

Real-Time/ Near Real-Time Quantification of Fine PM Necessary to Understand Climate Impact

Great Advances in Robust, Research Grade, Field Instruments Since 2000

Several Instruments Quantify Major Inorganic Components ($SO_4^=$, NO_3^-, Cl^-, NH_4^+)

Quantification and General Chemical Characterization of Organic Fraction Now Routine

Direct, Real-time Quantification of Elemental Carbon Fraction Now Available

More Compact, Less Expensive, Automated Instruments for Routine Monitoring Being Developed

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People

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D. M. T.

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