AMS Introduction

Doug Worsnop

AMS Users Meeting

~~Aerodyne~~

~~Caltech~~

~~Georgia Tech~~

~~FZ - Juelich~~

~~University of Minnesota~~

Desert Research Institute

~~October 2001/2002~~

~~October 24, 2003~~

~~October 8, 2004~~

~~25 August, 2005~~

~~16 September, 2006~~

29 September, 2007

AMS Introduction

AMS Users Meeting

~~**Aerodyne**~~	**Nitrate**
~~**Caltech**~~	**Sulfate**
~~**Georgia Tech**~~	**Ammonia**
~~**FZ - Juelich**~~	**Organics (44,57)**
~~**University of Minnesota**~~	**OOA, HOA**
Desert Research Institute	**OOA1, OOA2**

~~**October 13, 2002**~~

~~**October 24, 2003**~~

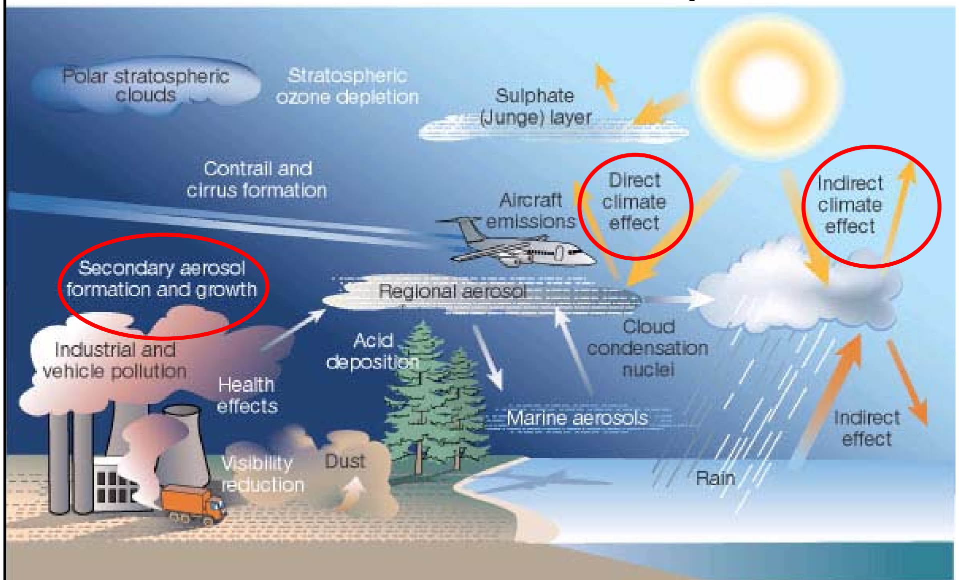
~~**October 8, 2004**~~

~~**25 August, 2005**~~

~~**16 September, 2006**~~

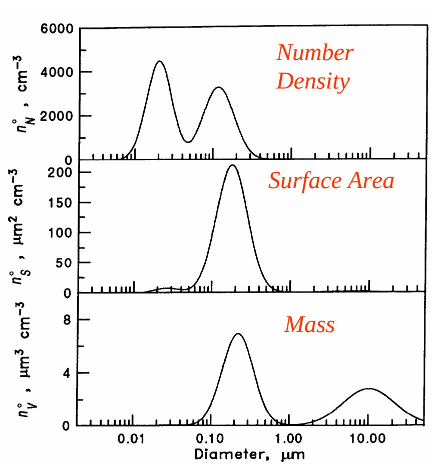
29 September, 2007

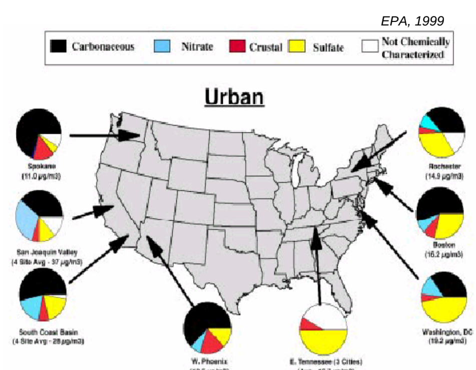
Aerosols in the Atmosphere



C.E. Kolb, Nature, 2002

Ambient Aerosol Size Distribution



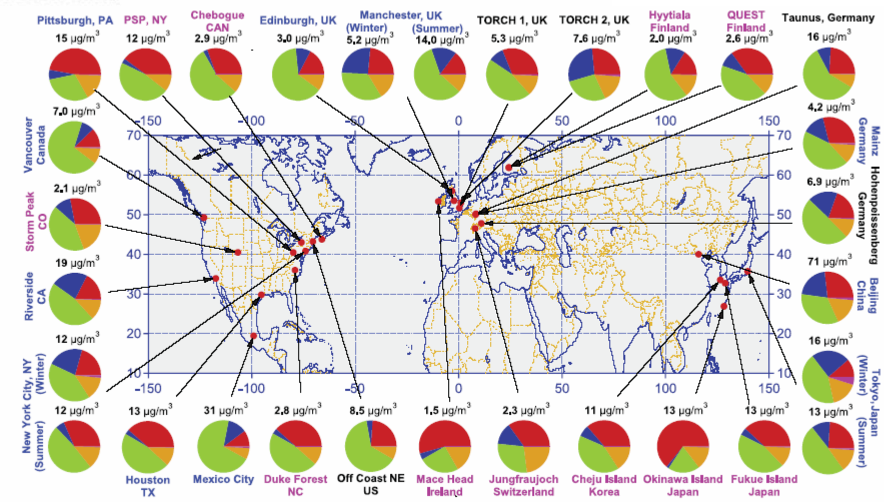


Ultrafine *Fine* *Coarse*

Goal: Size-Resolved Chemical Composition of Ambient Aerosol

Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes

Q. Zhang,[1] J. L. Jimenez,[2] M. R. Canagaratna,[3] J. D. Allan,[4] H. Coe,[4] I. Ulbrich,[2] M. R. Alfarra,[5] A. Takami,[6] A. M. Middlebrook,[7] Y. L. Sun,[1] K. Dzepina,[2] E. Dunlea,[2] K. Docherty,[2] P. F. DeCarlo,[2] D. Salcedo,[8] T. Onasch,[3] J. T. Jayne,[3] T. Miyoshi,[6] A. Shimono,[9] S. Hatakeyama,[6] N. Takegawa,[10] Y. Kondo,[10] J. Schneider,[11] F. Drewnick,[11] S. Borrmann,[11] S. Weimer,[1] K. Demerjian,[1] P. Williams,[4] K. Bower,[4] R. Bahreini,[2,7] L. Cottrell,[12] R. J. Griffin,[12] J. Rautiainen,[13] J. Y. Sun,[14] Y. M. Zhang,[14] and D. R. Worsnop[3]



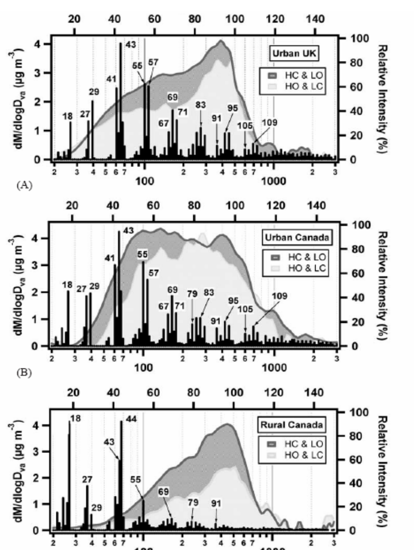
GEOPHYSICAL RESEARCH LETTERS, VOL. 34, L13801, doi:10.1029/2007GL029979, 2007

ATMOSPHERIC ENVIRONMENT

38 (2004) 5745–5758

Characterization of urban and rural organic particulate in the Lower Fraser Valley using two Aerodyne Aerosol Mass Spectrometers

M. Rami Alfarra[a,*], Hugh Coe[b], James D. Allan[b], Keith N. Bower[b], Hacene Boudries[c], Manjula R. Canagaratna[c], Jose L. Jimenez[d], John T. Jayne[c], Arthur A. Garforth[a], Shao-Meng Li[e], Douglas R. Worsnop[c]



Manchester center

Small particles <200nm

Hydrocarbon organics

Vancouver center

Rural (outside Vancouver)

Larger particles (>200 nm)

m/z 44 CO_2^+ dominates

Organic Mass Spectra

$C_nH_{2n+0,2}$ $\xrightarrow{e^-}$ $C_mH_{2m\pm1}^+$

27, 29, 41, 43, 55, 57, 69, 71, …

$C_3H_5^+$ $C_4H_7^+$ $C_5H_9^+$

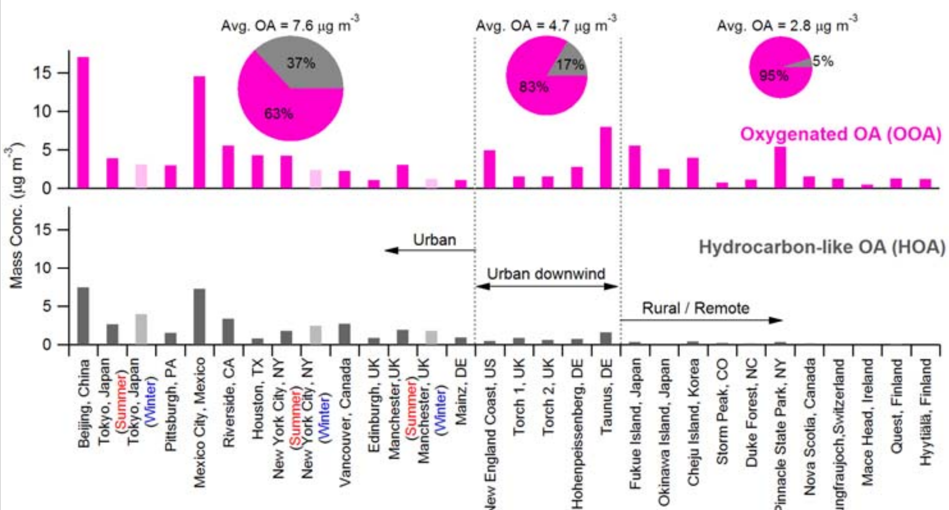
$C_nH_mO_y$ $\xrightarrow{e^-}$ H_2O^+, CO^+, CO_2^+, $C_2H_3O^+$

18 ***28*** ***44*** ***43***

29, 55, ….

Following flash vaporization at ~600^{o}C

Organic Aerosols: Urban vs. Rural/Remote



Zhang, Jimenez et al., *GRL*, 2007

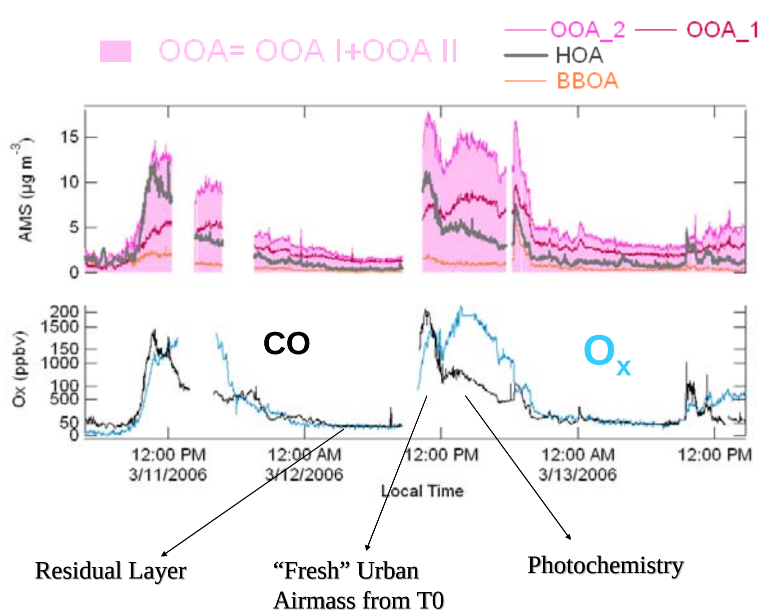
AMS (PMF) Factors

	600C, e-		m/z
HOA:	C_nH_m → $C_{n-x}H_{m-y}^+$		27,29,41,43,55,57,69,71,…
LESS OXIDZED OOA2	C_nH_mO → $C_2H_3O^+$, $C_3H_3O^+$, R'^+		43,55, …
MORE OXIDZED OOA1	$C_nH_mO_2$ → CO_2^+, HCO_2^+, R'^+		44,45, …
BBOA	R → R'^+, $C_2H_4O_2^+$, $C_3H_3O_2^+$		60,73, …. *levoglucosan*

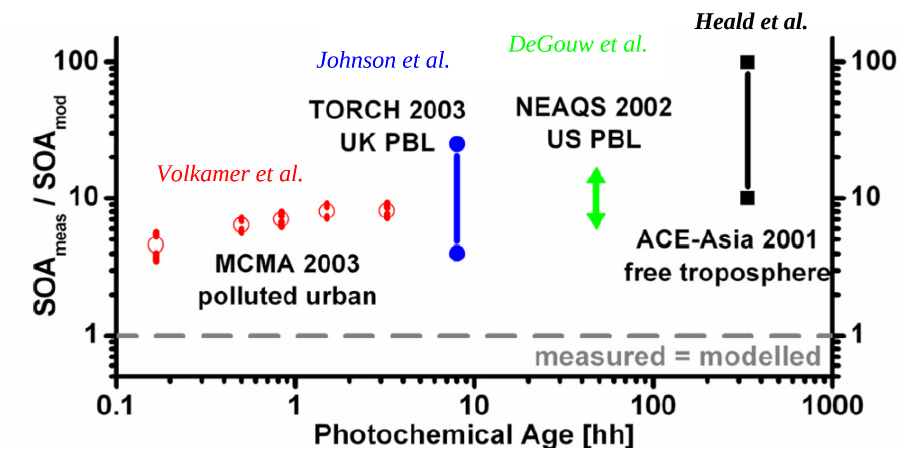
O:C ratio: HOA << OOA2 ~ BBOA < OOA1

Factors are not unique or identical among campaigns, platforms

CONSISTENT TRENDS



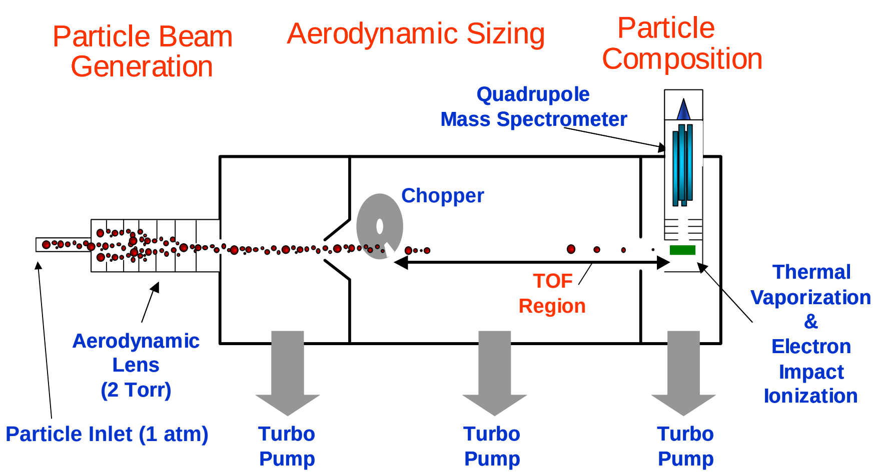
SOA: measurements vs. models



- ***SOA correlates with photochemistry: O_x***

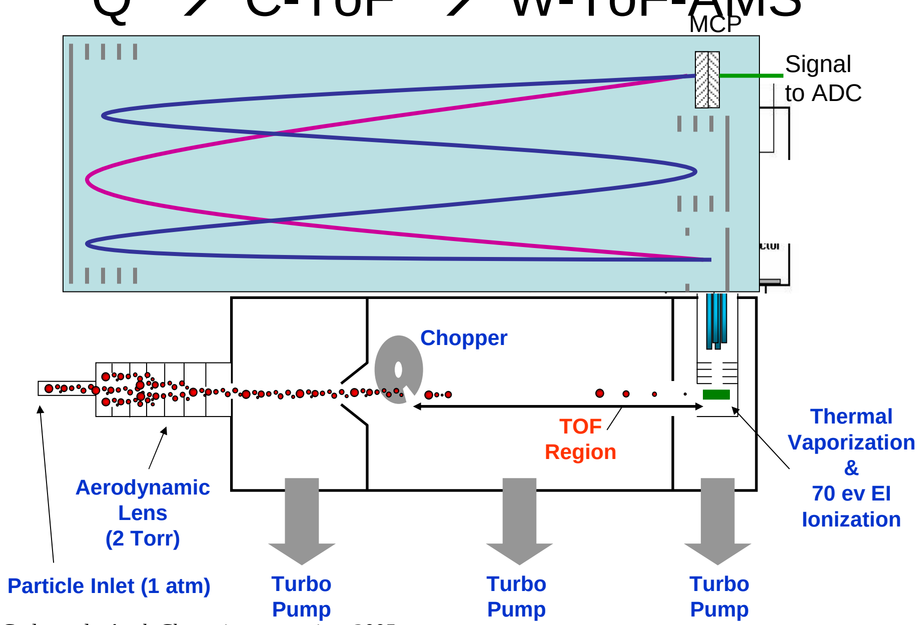
Volkamer, Jimenez, et al GRL, 2006

Aerosol Mass Spectrometer (AMS)



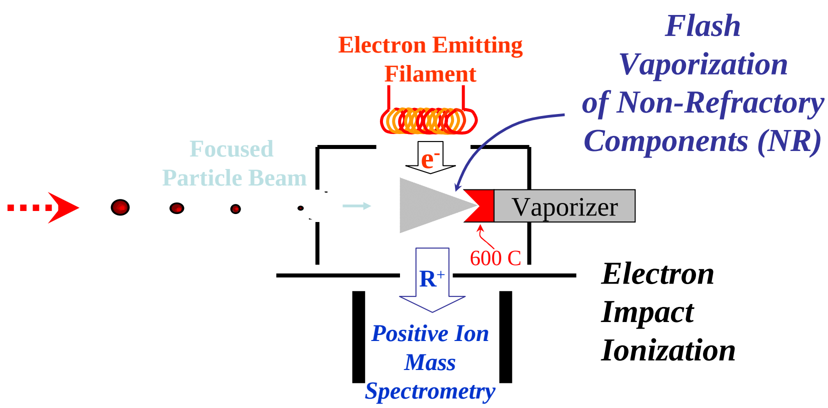
- **Efficient transmission (40-1000 nm), aerodynamic sizing, linear mass signal**
- **Non-refractory PM1.0 mass loadings and chemically-speciated mass distributions**

Q → C-ToF → W-ToF-AMS



DeCarlo et al., *Anal. Chem.*, in preparation, 2005.

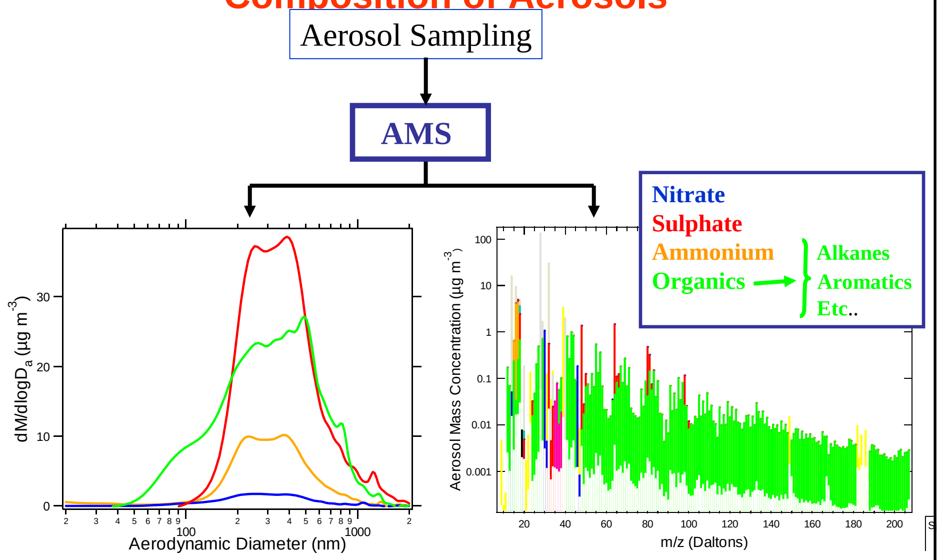
AMS Particle Detection Process



Universal and quantitative chemical analysis: 0.01μg/m^3 sensitivity.

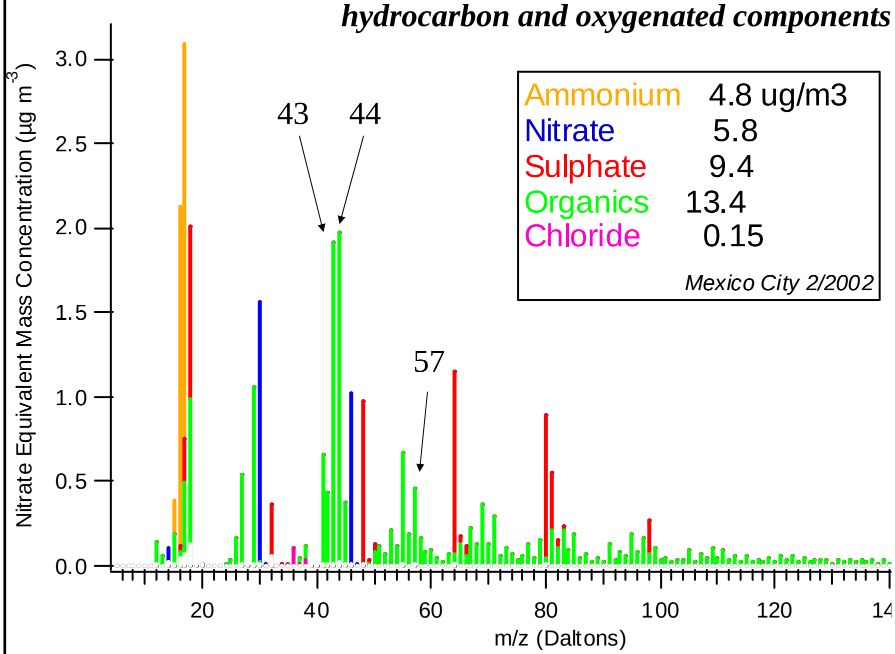
Vaporization and analysis of most aerosol chemical constituents
- *with primary exception of* ***crustal oxides*** *and* ***elemental carbon***.

Real Time Chemical and Physical Composition of Aerosols



Mass distribution **Chemical composition**

Urban organic aerosol is a mixture of hydrocarbon and oxygenated components



Same AMS, same issues, new issues

"CE" collection efficiency

particle bounce ***CE ~ 0.5, except …***

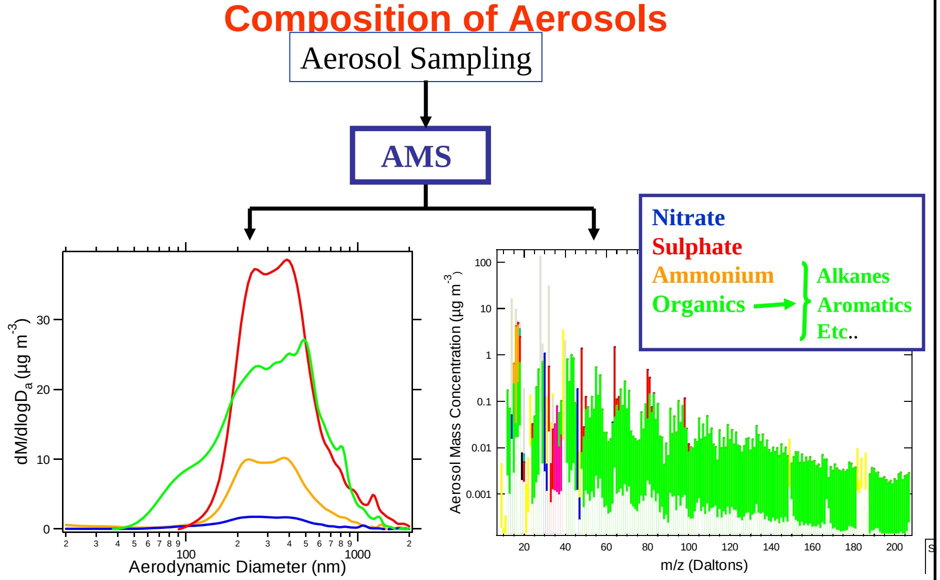
"RIE" relative ionization efficiency

- particularly **RIE_org ~ 1.4**

"ToF threshold & baseline" - single ion determination

linearity of large and small signals (**dynamic range**)

Real Time Chemical and Physical Composition of Aerosols



Mass distribution **Chemical composition**

MS Signatures for Aerosol Species Identification

color coded to match spectra

Group	Molecule/Species		Ion Fragments	Mass Fragments
Water	H_2O	$\xrightarrow{e^-}$	H_2O^+ , HO^+ , O^+	18, 17, 16
Ammonium	NH_3	$\xrightarrow{e^-}$	NH_3^+, NH_2^+, NH^+	17, 16, 15
Nitrate	HNO_3	$\xrightarrow{e^-}$	HNO_3^+, NO_2^+, NO^+	63, 46, 30
Sulfate	H_2SO_4	$\xrightarrow{e^-}$	$H_2SO_4^+$, HSO_3^+, SO_3+ SO_2^+, SO^+	98, 81, 80 64, 48
Organic *(Oxygenated)*	$C_nH_mO_y$	$\xrightarrow{e^-}$	H_2O^+, CO^+, CO_2^+ $H_3C_2O^+$, HCO_2^+, $C_{n'}H_{m'}^+$	18, 28, 44 43, 45, ...
Organic *(hydrocarbon)*	C_nH_m	$\xrightarrow{e^-}$	$C_{n'}H_{m'}^+$	27,29,41,43,55,57,69,71...

Standard electron impact ionization @ 70 eV

- ***Easy to quantify: ca. NIST MS library***
- ***Easy to separate inorganic and organic components***
- ***Speciation of organic composition is challenging***

ELECTRON IMPACT (EI) IONIZATION

$$R + e^- \xrightarrow{\sigma} R^+ + e^- + e^-$$

$$R^+ \downarrow \; R_i^+ + R_j$$

Measure all ions:

Ion Rate $= \Sigma R_i^+$

EI Cross Section (σ) $\propto$ electrons/molecule

$\propto$ mass/molecule

Ion Rate = *2*[ndary] electrons/sec $\propto$ $\sigma \cdot$ molecules/sec

Ion Rate = ΣR_i^+ $\propto$ total mass/sec

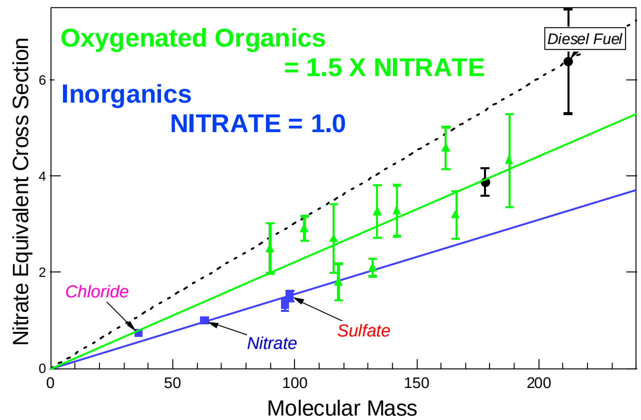
independent of parent or fragment (neutral or ion) molecular mass

EI Ionization: $A + e^- \longrightarrow A^+ \longrightarrow a_i^+$

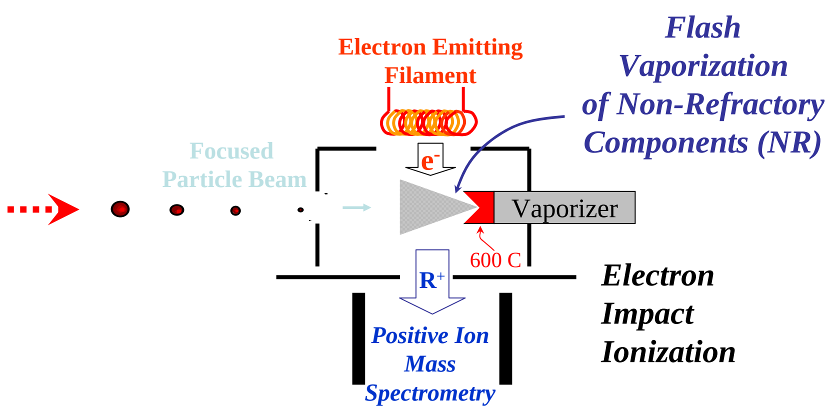
Mass Loading A $\propto$ $(MW_A/IE_A)\ \Sigma$ Ion Signal

Calibration Factor * (MW_{NO3}/IE_{NO3})

EI Ionization Cross Sections



AMS Particle Detection



Universal / quantitative chemical analysis: 0.01$\mu g/m^3$ sensitivity.

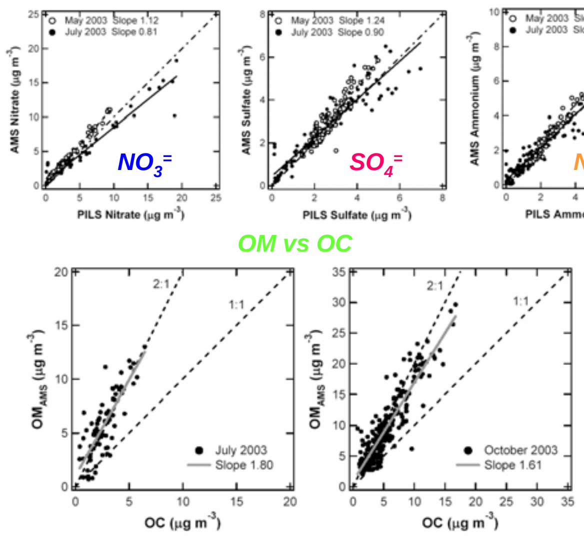
"EVERTYHING AT THE SAME TIME"

No Separation - bulk analysis

[no dust (oxides)** or **elemental (black) carbon]

Characterization of an Aerodyne Aerosol Mass Spectrometer (AMS): Intercomparison with Other Aerosol Instruments

N. Takegawa,[1] Y. Miyazaki,[1] Y. Kondo,[1] Y. Komazaki,[1] T. Miyakawa,[1] J. L. Jimenez,[2] J. T. Jayne,[3] D. R. Worsnop,[3] J. D. Allan,[4] and R. J. Weber[5]

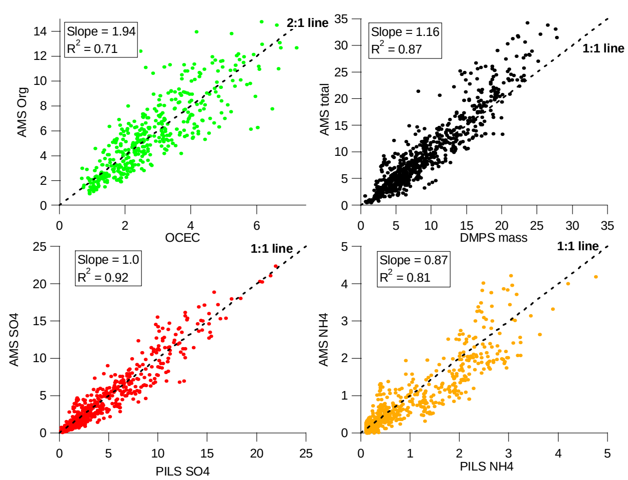


Takegawa et al., 2005

Assumed CE = 0.5

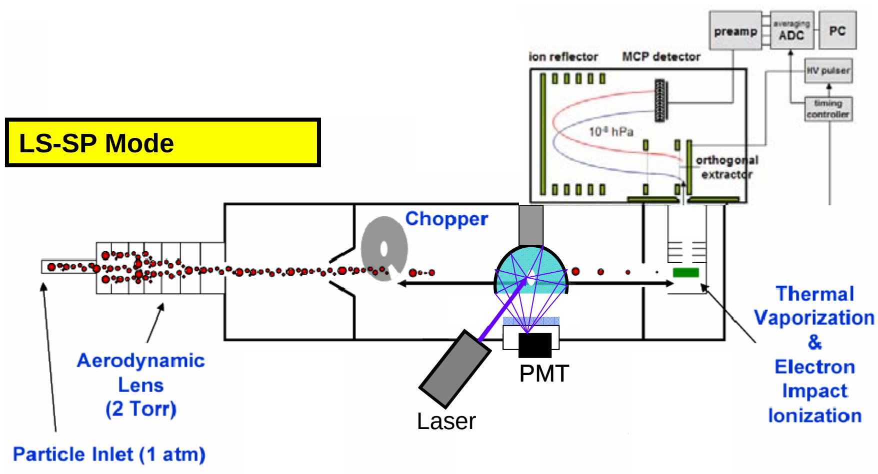
$$\frac{OM}{OC} = \frac{C_nH_mO_p}{C_n}$$

AMS (NR-PM_1) quantification

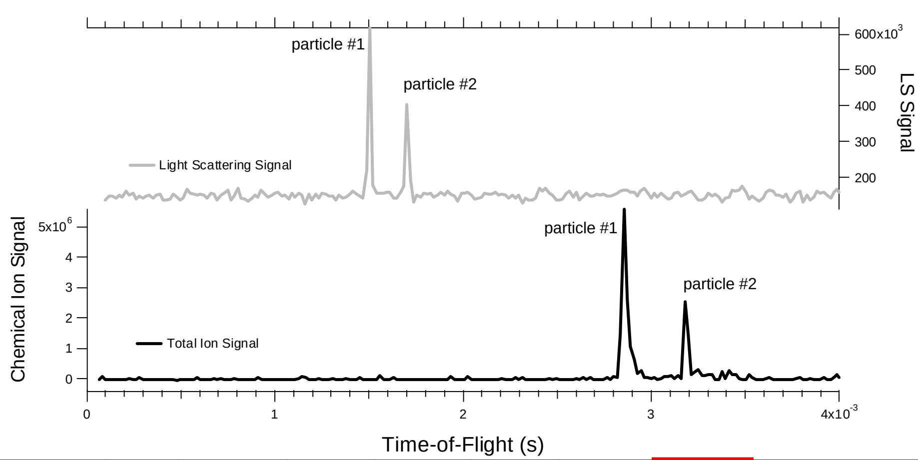


- Composition/phase-dependent collection efficiency (CE) applied
- Correction for smaller cut diameter in AMS lens compared to PM_1 impactors

LS-C-ToF-AMS

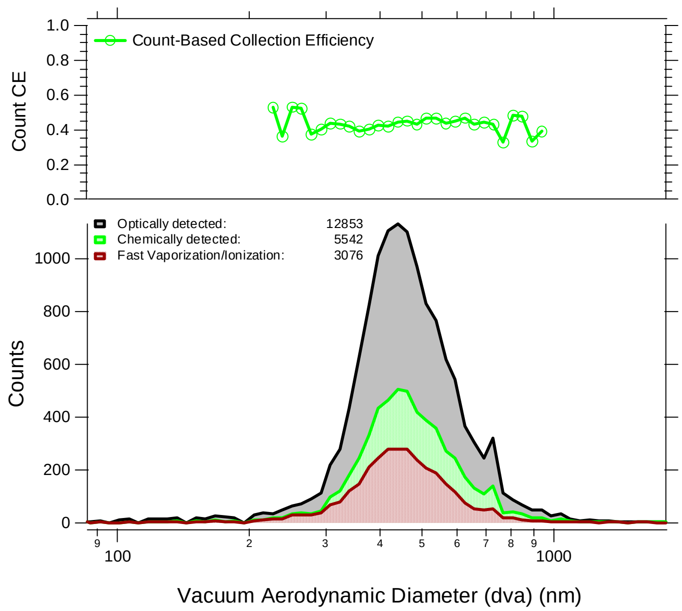


Coincident Particles: Evidence of External Mixing

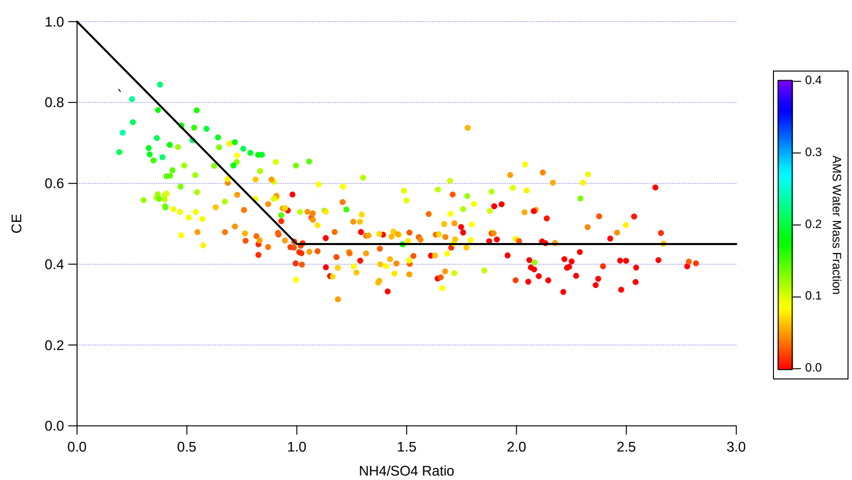


PARTICLE PROPERTY	Velocity (m/s)	Vacuum Aerodynamic Diameter (nm)	Optical Diameter (nm)	Predicted Physical Diameter (nm)	Chemical Density (g/cc)	Optical Density (g/cc) [dva/dopt]	Measured Total Mass (fg)	Predicted Total Mass (fg) [Chemical Density]	Predicted Total Mass (fg) [Optical Density]
Particle #1							18.2	26.3	29.0
Particle #2							13.0	8.8	15.8

Collection Efficiency: Particle Counting



Apparent CE depends on NH4/SO4 ratio



Onasch et al, Ron Brown, 2004

QUARTERLY JOURNAL OF THE ROYAL METEOROLOGICAL SOCIETY
Q. J. R. Meteorol. Soc. 133: (S1) 61–75 (2007)
Published online in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/qj.88

RMetS
ROYAL METEOROLOGICAL SOCIETY

Chemical composition of summertime aerosol in the Po Valley (Italy), northern Adriatic and Black Sea

J. Crosier,[a*] J. D. Allan,[a] H. Coe,[a] K. N. Bower,[a] P. Formenti[b] and P. I. Williams[a]
[a] Centre for Atmospheric Science, SEAES, University of Manchester, UK
[b] LISA, Creteil, France

$$CE = 0.975 - \frac{SO_4^{-2}}{SO_4^{-2} + NO_3^-} 0.582.$$

NH4/SO4 → 0

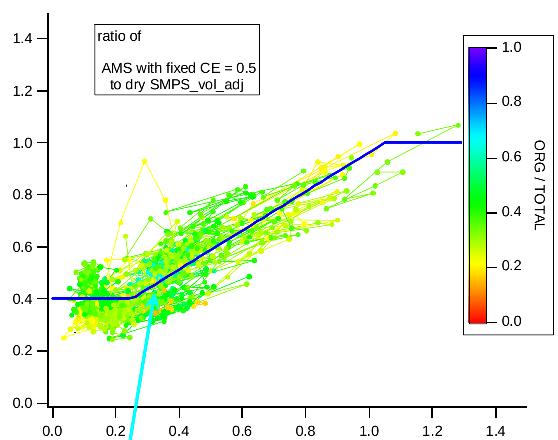
NO3/SO4 → >>1 **CE = 0.4 → 1**

H2O/Total → 1

Tim Onasch, Ann Middlebrook: ***particle phase***

Junying Sun, Yangmei Zhang Beijing July 2006

AMS Mass / SMPS Mass



AMS H2O / AMS Total

Note: cluster of highest org fraction have low H2O and CE

Lens Transmission issues

Reasonable understanding of current lenses

Peter Liu, Leah Williams, John Jayne

Ann Middlebrook, Brendan Matthew, Ken Docherty

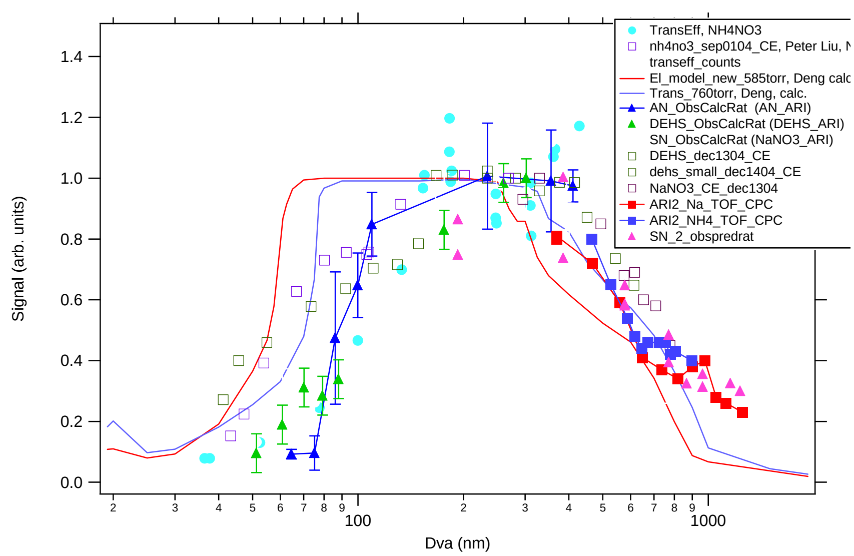
"standard" vs ~~"high throughput"~~

some variability

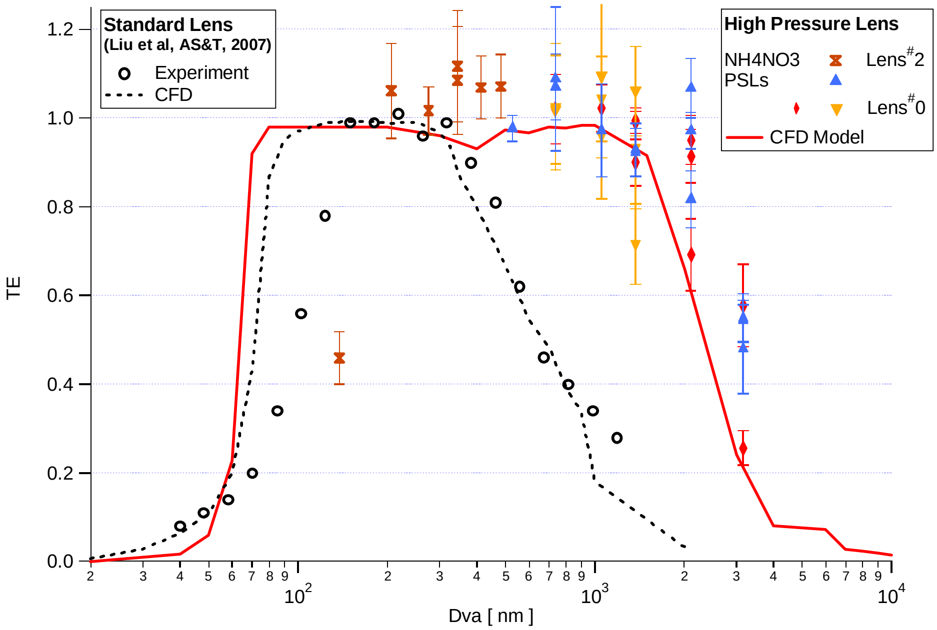
New "high pressure" lens – modification of Schreiner lens

Summary of Lab Transmission Experiments

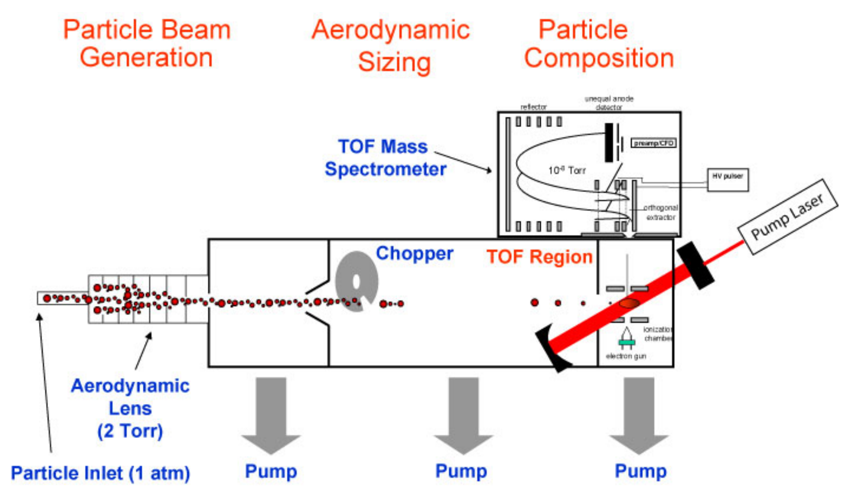
"Standard Lens" Williams et al



Comparison of “Standard” and “High Pressure Lenses” August, 2007

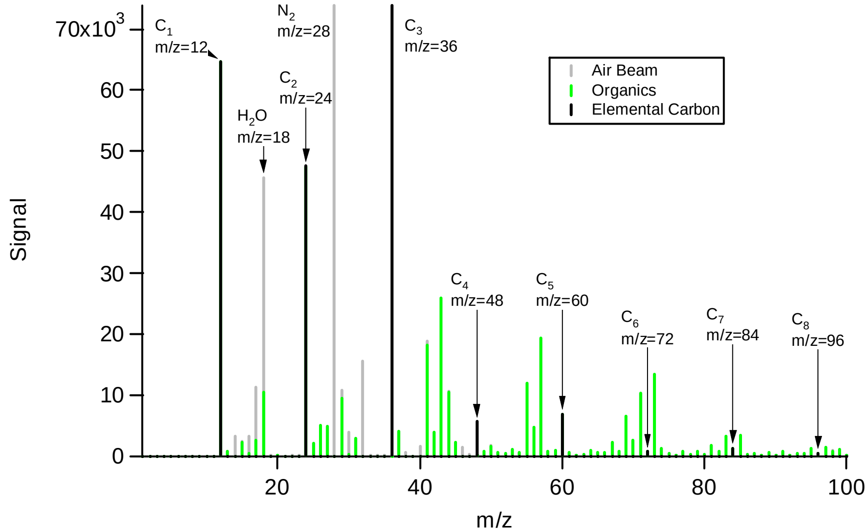


How to build a SP2-AMS



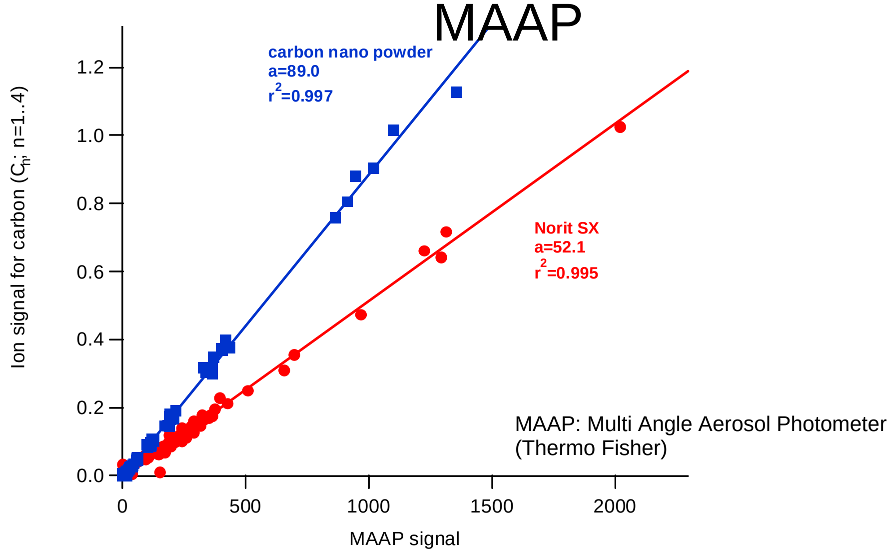
- Install SP2 module

Oil Lamp Soot Particles



Obtain chemical information on BC and Organics

Comparison SP2-AMS and MAAP



Strong correlation between SP2-AMS carbon signals and the MAAP absorption measurement

		600C, e-	m/z
HOA:	C_nH_m	→ $C_{n-x}H_{m-y}^+$	27,29,41,43,55,57,69,71,…
OOA2	C_nH_mO	→ $C_2H_3O^+$, $C_3H_3O^+$, R'^+	43,55, …
OOA1	$C_nH_mO_2$	→ CO_2^+, HCO_2^+, R'^+	44,45, …
BBOA	R	→ R'^+, $C_2H_4O_2^+$, $C_3H_3O_2^+$	60,73, …. *levoglucosan*

SP2 + e-

Graphitic C → C_n^+

ORGANIC FACTORS ↔ **BETTER CHEMICAL (MOLECULAR) ANALYSIS**