Overview of Current AMS Issues and Developents

Doug Worsnop
Boulder AMS Users Mini Meeting
University of Colorado
March 9-10, 2003

Outline

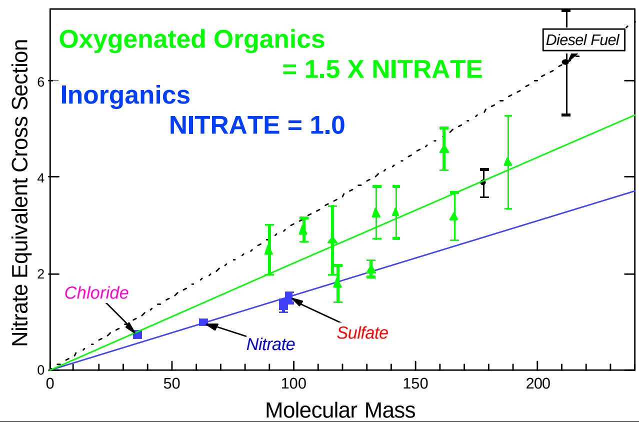
- Detection efficiency of diesel
- Explanation of delta series
- Sensitivity calculation
- Electronic noise reduction
- "DMA-less calibration"
- NaNO3 vaporization for calibrating heater temperature
- Diesel signature
- Chlorine in Tokyo
- PAHs
- New York mass balance and diurnal cycle
- (small) organics and sulfate
- Airplane sulfate / SO2

EI Ionization: A + e^- ----> A^+ ----> a_i^+

Mass Loading A µ (MW_A/IE_A) å **Ion Signal**
a_i

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

EI Ionization Cross Sections



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

Organic Mass Spectra

$$C_nH_m \xrightarrow{e^-} C_{n'}H_{m'}^+$$

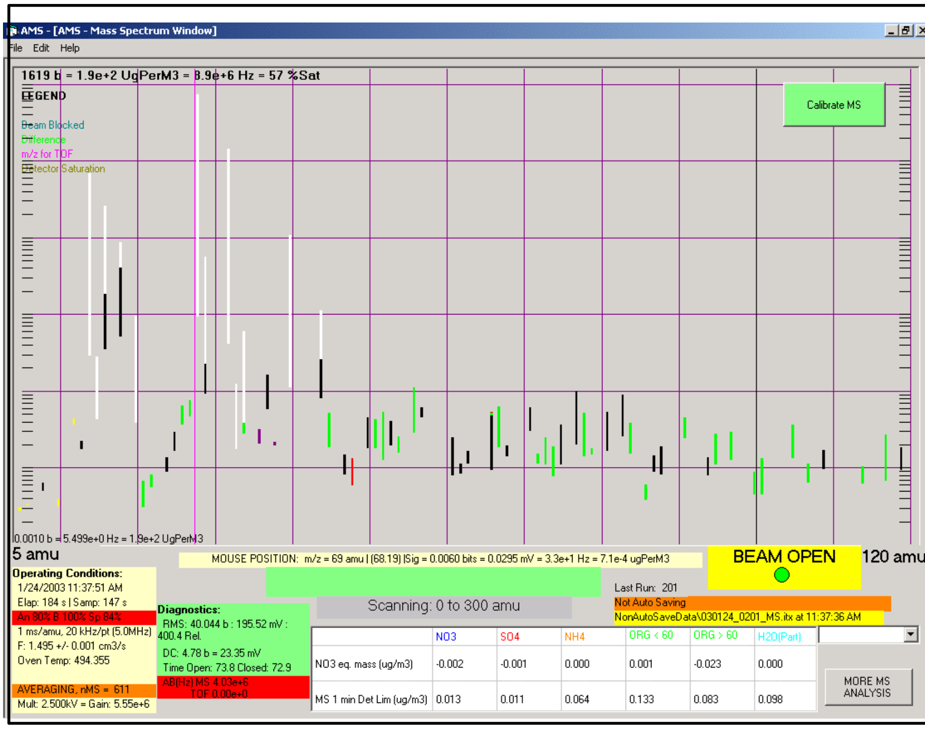
27, 29, ***41, 43, 55, 57,*** *69, 71, ...*

$$C_nH_mO_y \xrightarrow{e^-} CO_2^+ \quad HCO_2^+ \quad HC_2O^+ \quad C_{n'}H_{m'}^+$$

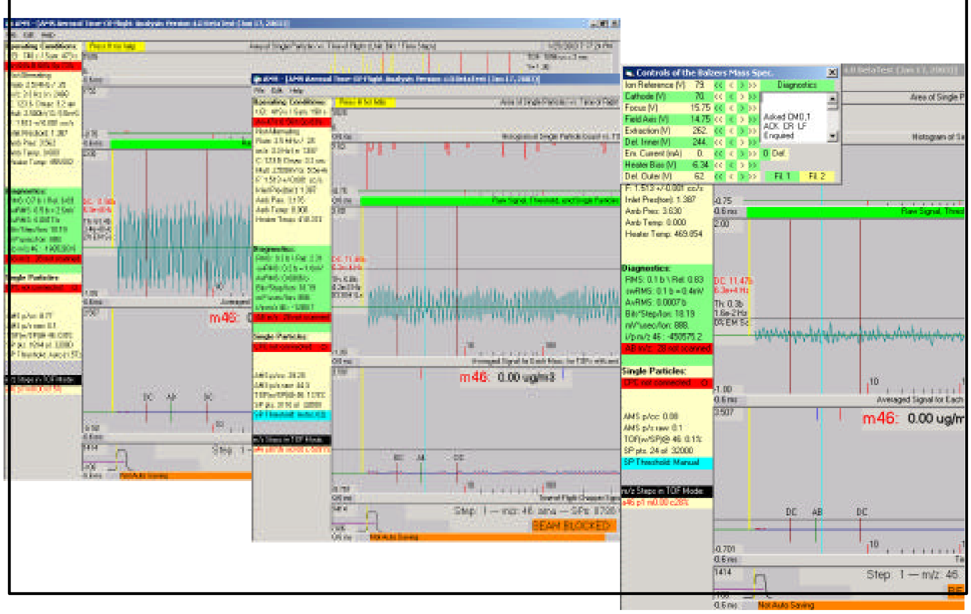
44   ***45***   ***43***   ***55, 57, ...***

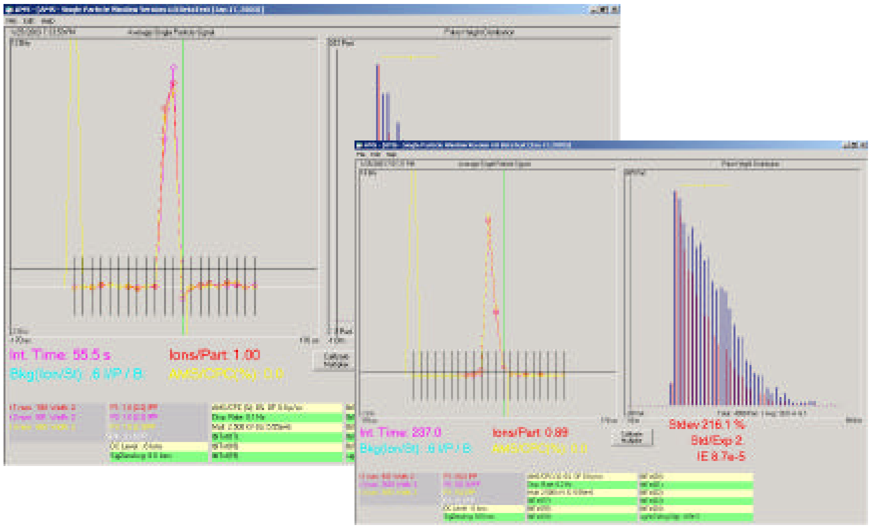
Following flash vaporization at ~550C

Di-Acid	$C_nH_{2n-4}O_4$	+ e- ---->	$C_nH_{2n-5}O_4^+$	6	87…
Di-Acid	$C_nH_{2n-4}O_4$	+ e- ---->	$C_nH_{2n-5}O_3^+$	4	73, …
Acid	$C_nH_{2n-0}O_2$	+ e- ---->	$C_nH_{2n-1}O_2^+$	4	45, 59, 73, …
Alcohol	$C_nH_{2n+2}O$	+ e- ---->	$C_nH_{2n+1}O^+$	4	31, 45, 59, 73, …
Acid	$C_nH_{2n-0}O_2$	+ e- ---->	$C_nH_{2n-1}O^+$	2	43, 57, 71, …
Carbonyl	$C_nH_{2n+0}O$	+ e- ---->	$C_nH_{2n-1}O^+$	2	29, 43, 57, 71, …
Alkane	C_nH_{2n+2}	+ e- ---->	$C_nH_{2n+1}^+$	2	15, 29, 43, 57, 71, …
Alkene	C_nH_{2n+0}	+ e- ---->	$C_nH_{2n-1}^+$	0	13, 27, 41, 55, 69, …
Di-ene	C_nH_{2n-2}	+ e- ---->	$C_nH_{2n-1}^+$	-2	25, 39, 53, 67, …
Tri-ene	C_nH_{2n-4}	+ e- ---->	$C_nH_{2n-3}^+$	-4	37, 51, 65, …
Phenyl	$C_6H_5C_nH_{2n-1}$	+ e- ---->	$C_6H_5C_nH_{2n}^+$	-6	77, 91, …



A 0.047microF capacitor in the output port at the preamp
Single ion threshold reduced from 1.2 bit to 0.2 bit.





Quality Control Protocol

Check Flowrate/Airbeam -→ EM Calibration — one-two days

Variable Airbeam -→ NH4NO4 Calibration — weekly

record filter / monitor sensitivity

plot in calibrations record

check 350nm sizing DMA and AMS-TOF

PSL size calibration — ?

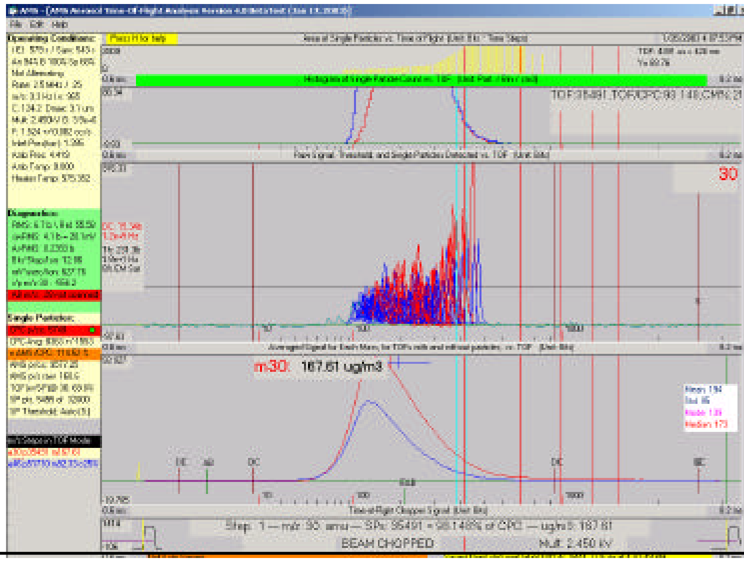
Variable IE/AB -→ Balzers MS tuning — little as possible

Data Analysis - check O^+, RH, CO_2, mass calibration

Operational Parameters: Oven Temperature - NaNO3 experiment

lens alignment – check after every move

Try to do the DMA-less calibration.
Find out that IE is very sensitive to the blue windows where you cou



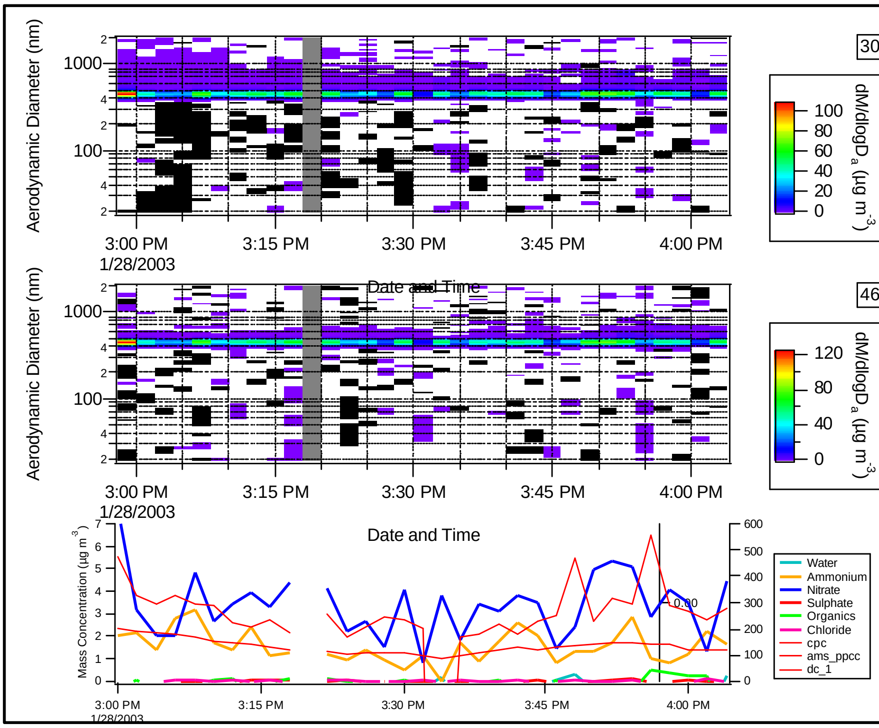
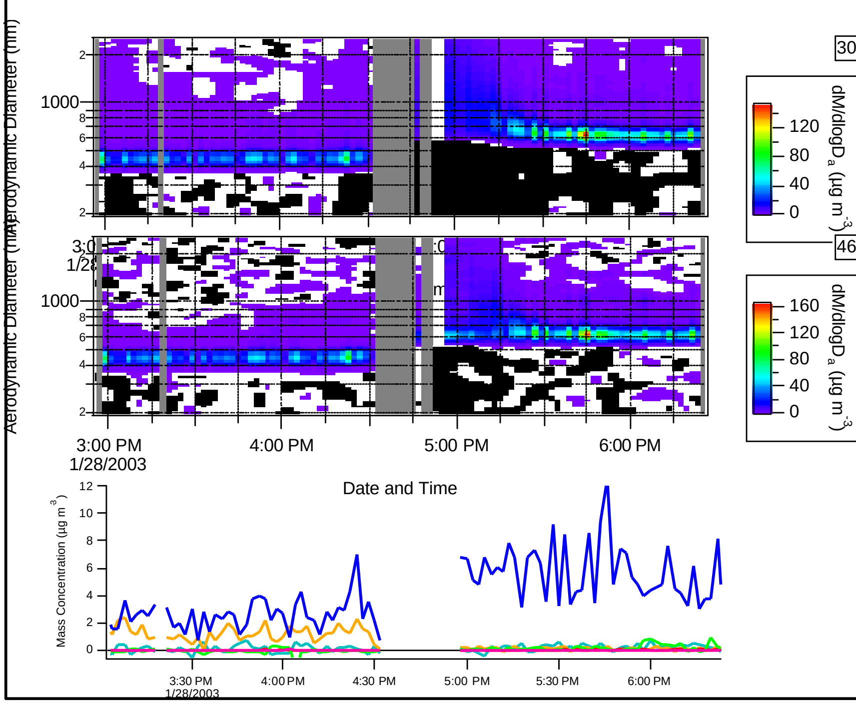


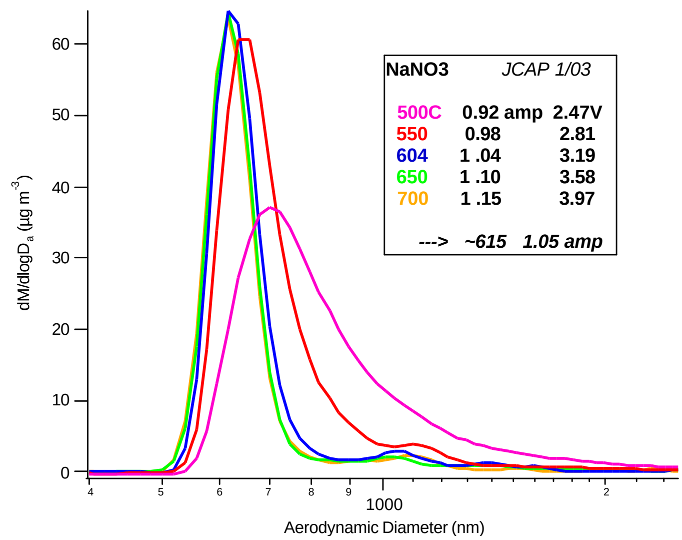
Table of oven T NH4NO3 3-4:30pm

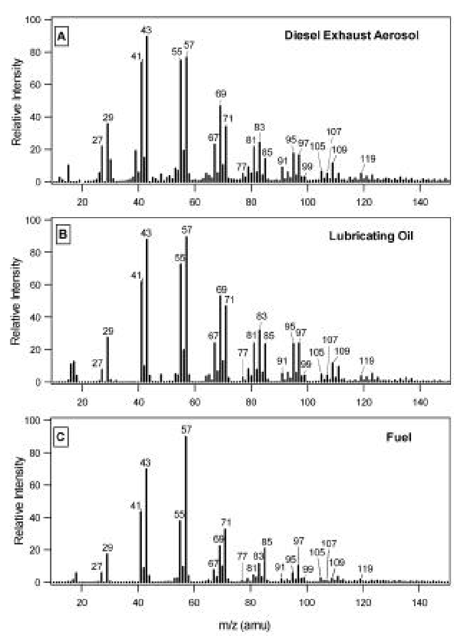
.93 amp	2.53V	516C	396
.98	2.85	558.3	400
1.04	3.21	608.1	406
1.10	3.61	658.0	415
1.16	4.02	704.0	419
1.23	4.50	754.8	424

Table of oven T NaNO3 5-6:30pm

.85 amp	2.10V	448C	447
.92 amp	2.47V	501.8C	453
.98 amp	2.81V	551C	457
1 .04 amp	3.19V	604C	461
1 .10 amp	3.58V	654.7C	466
1 .10 amp	3.58V	656.8C	472
1 .15 amp	3.97V	701.9C	485




NaNO3
JCAP 1/03
500C 0.92 amp 2.47V
550 0.98 2.81
604 1 .04 3.19
650 1 .10 3.58
700 1 .15 3.97
---> ~615 1.05 amp
dM/dlogD a (µg m-3)
Aerodynamic Diameter (nm)
1000


A
Diesel Exhaust Aerosol
B
Lubricating Oil
C
Fuel
Relative Intensity
m/z (amu)

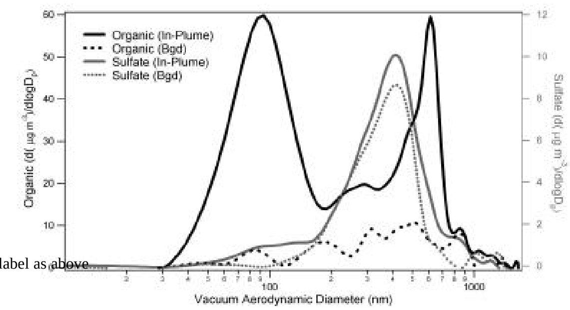
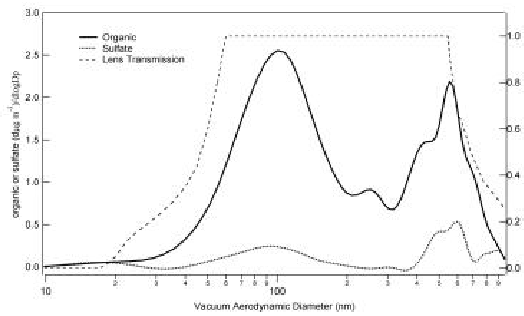
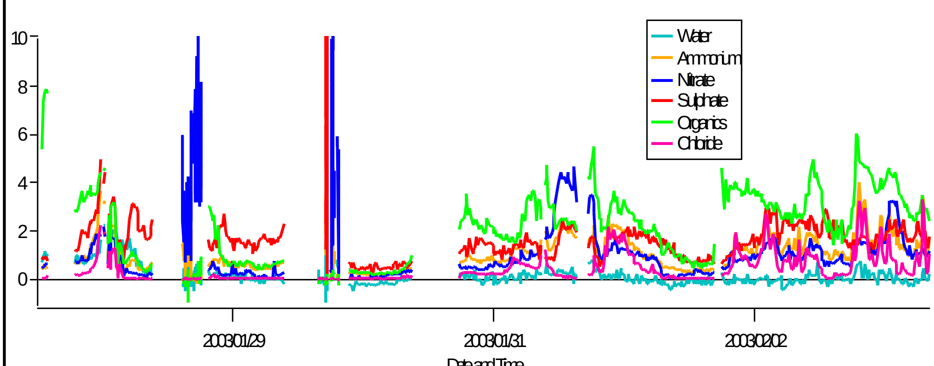


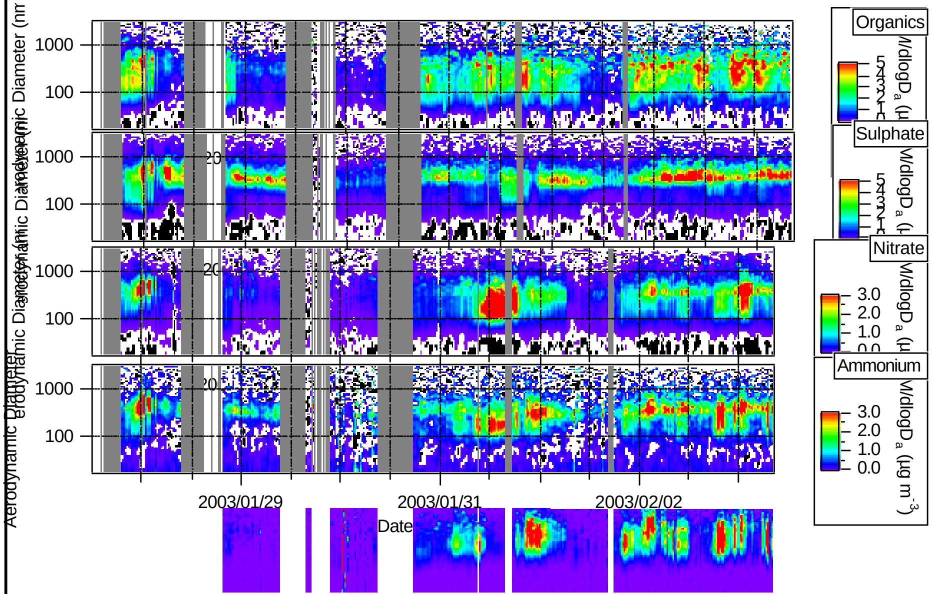
Figure 9 Same for left Y-axis label as above.



Trend of Mass and Diagnostics
27.01.2003 ~ 02.02.2003
JCAP Tokyo Region



Size Distribution Trend 27.01.2003 ~ 02.02.2003



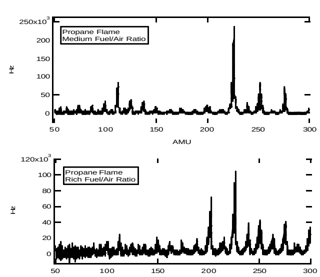
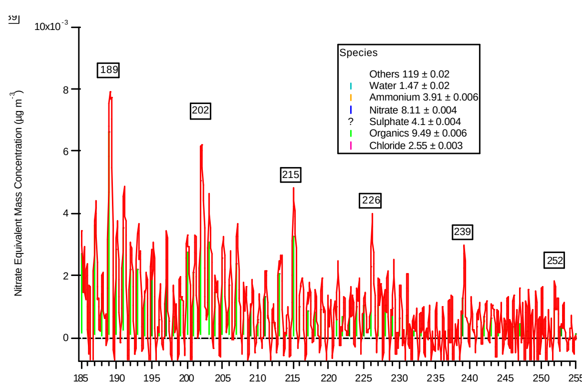
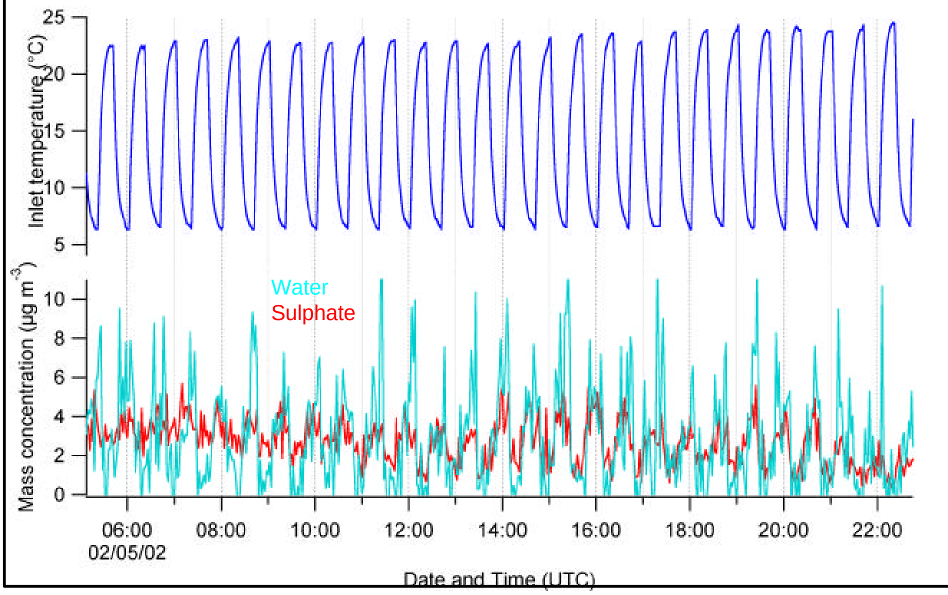
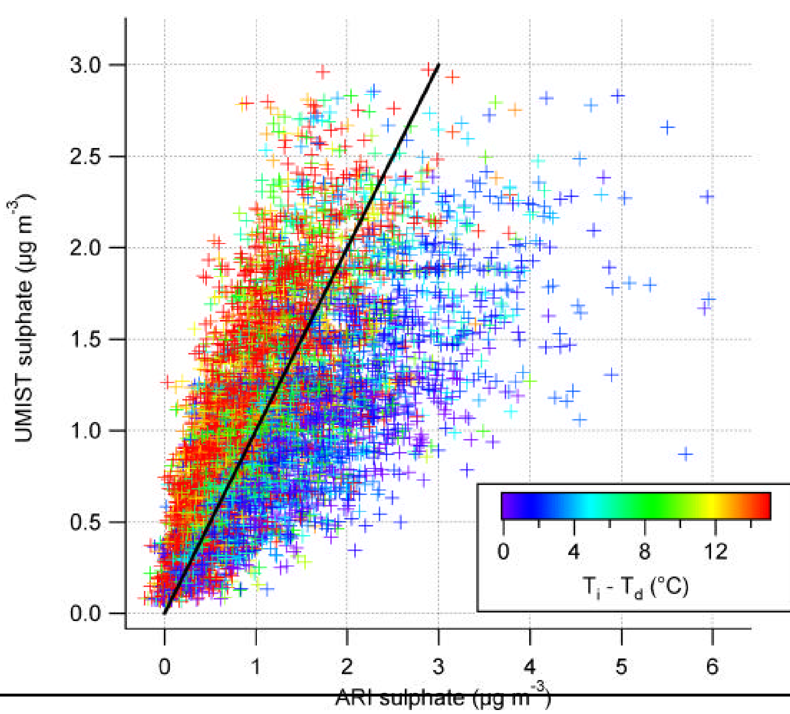


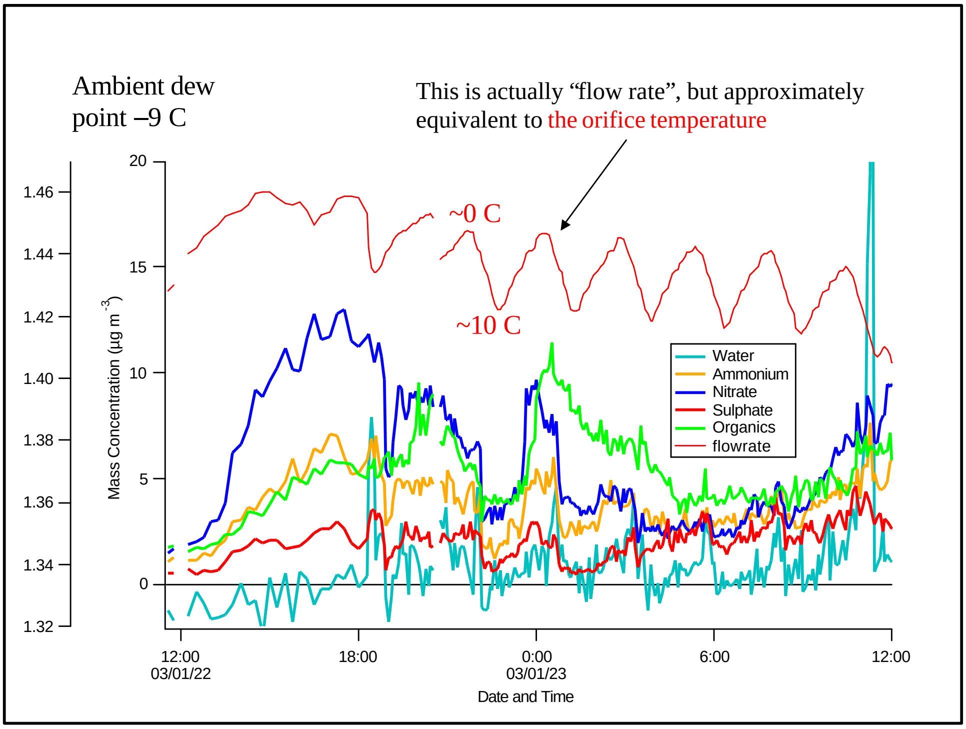
Figure 5. Top panel: Mass spectrum taken with Aerodyne AMS for a medium flame. Bottom panel: Mass spectrum taken with BC AMS for a rich flame.

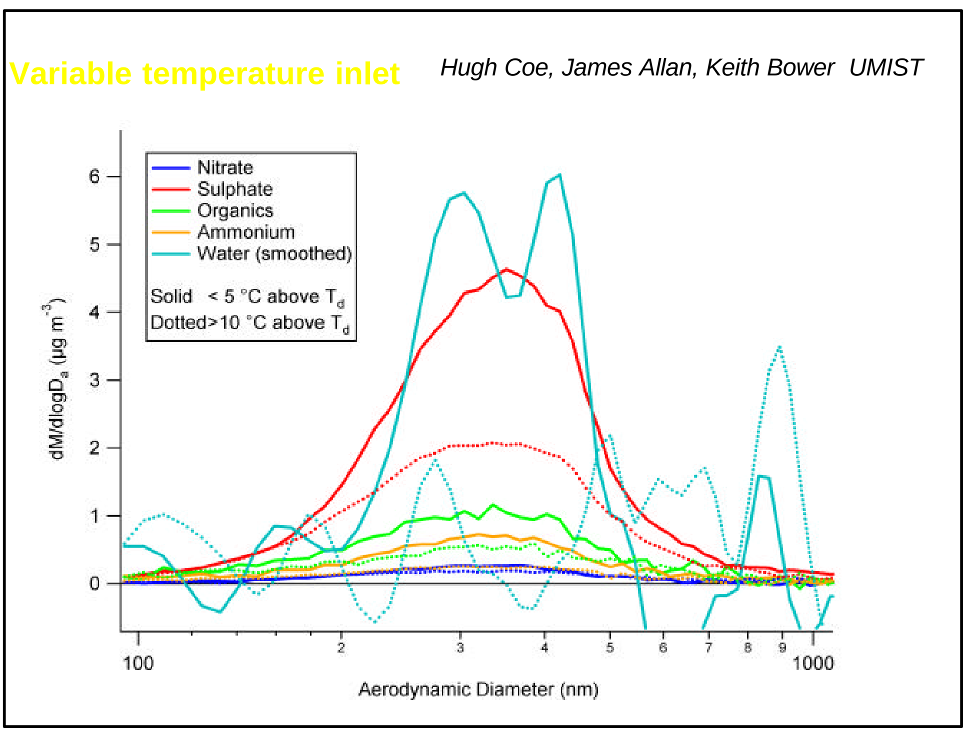


Temperature Cycling

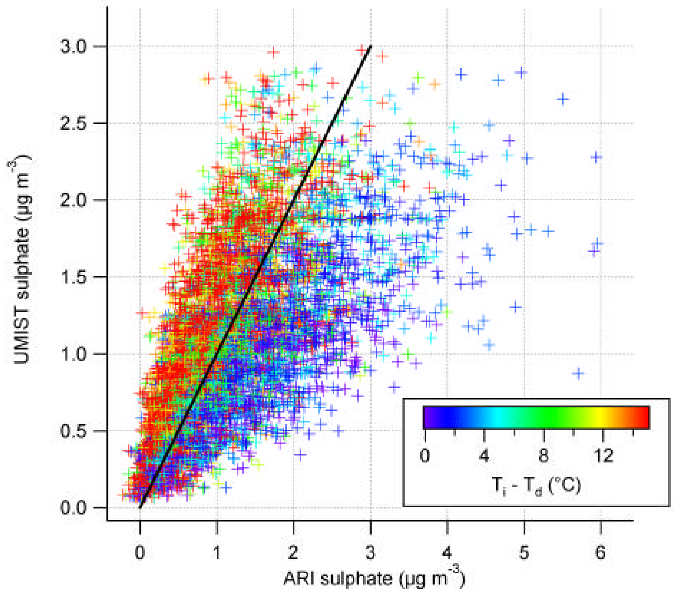





Ambient dew point –9 C
This is actually "flow rate", but approximately equivalent to the orifice temperature
~0 C
~10 C
1.46
1.44
1.42
1.40
1.38
1.36
1.34
1.32
20
15
10
5
0
Mass Concentration (µg m-3)
Water
Ammonium
Nitrate
Sulphate
Organics
flowrate
12:00 03/01/22
18:00
0:00 03/01/23
6:00
12:00
Date and Time


Variable temperature inlet
Hugh Coe, James Allan, Keith Bower UMIST
Nitrate
Sulphate
Organics
Ammonium
Water (smoothed)
Solid < 5 °C above Td
Dotted>10 °C above Td
dM/dlogDa (µg m-3)
6
5
4
3
2
1
0
100
2
3
4
5
6
7
8
9
1000
Aerodynamic Diameter (nm)

Variable temperature inlet

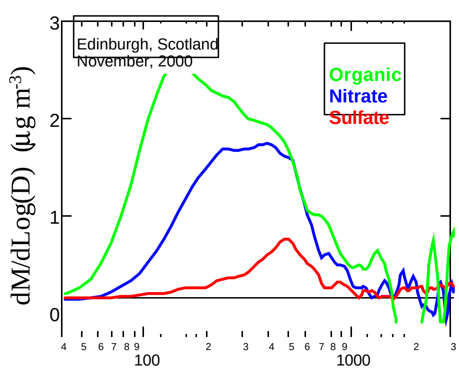


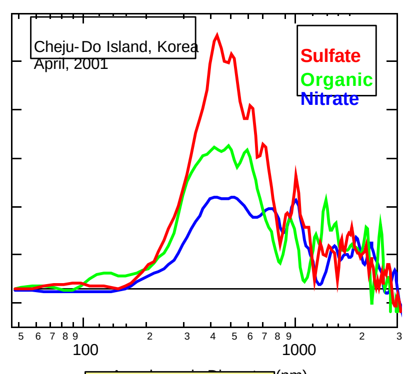
Urban Site *Bi-modal*

Local Sources

Remote Site *Mono-modal*

Aged-Transported



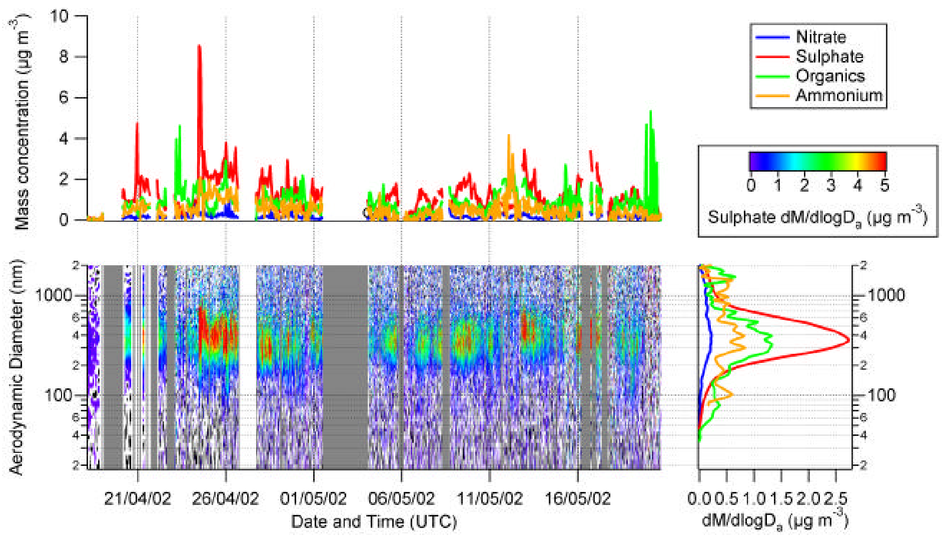


Scotland *SASUA-3*

ACE ASIA

Overview of AMS Data

ITCT, Trinidad Head, May 2002



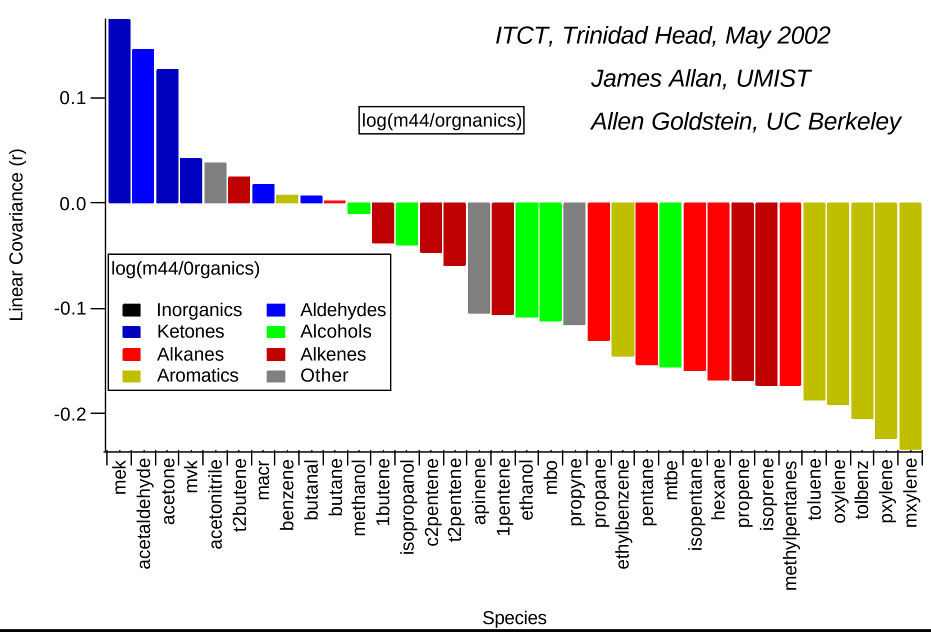
Hugh Coe, James Allan et al, UMIST

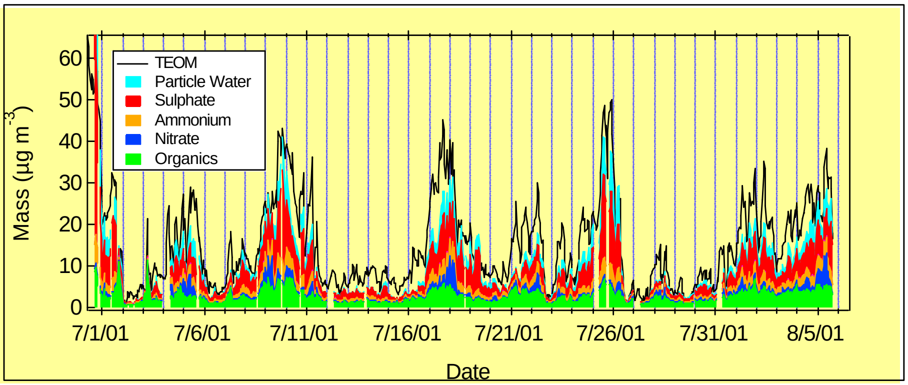
AMS Oxy-Organic / Covariance with VOCs

ITCT, Trinidad Head, May 2002

James Allan, UMIST

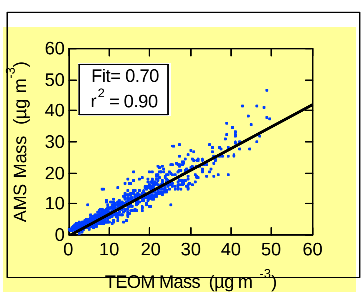
Allen Goldstein, UC Berkeley

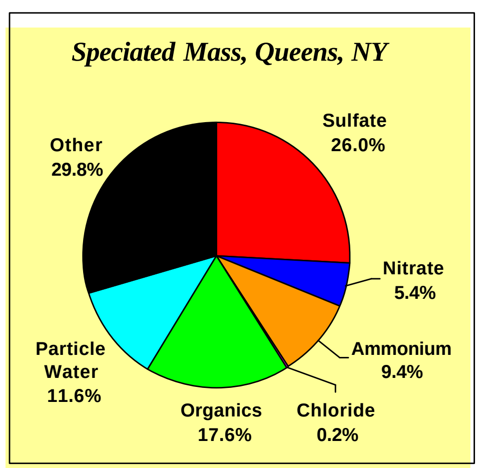




High Mass Loading Events Extending Over Several Days

Regional Transport of Sulfate





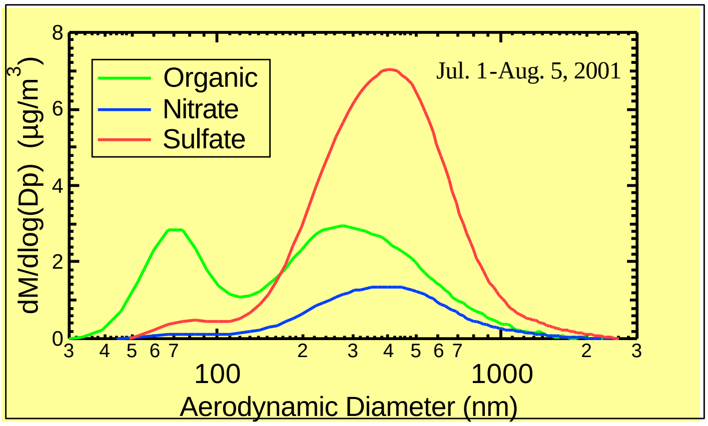
The "Other" Category

-PM1 vs PM2.5

-elemental carbon

-crustal oxides

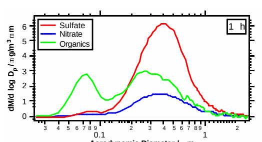
Urban Site



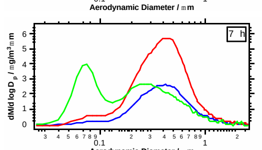
Characteristic Urban Bi-modal Size Distribution
Organic fraction dominates small size mode

Diurnal Cycles in NYC Mass Distributions

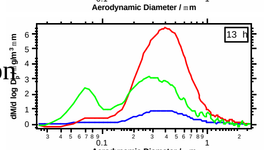
Night



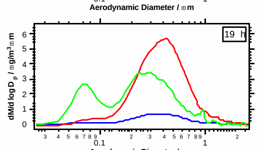
Morning



Afternoon



Evening

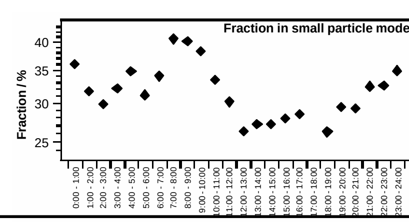


morning: peak in small organics and nitrate
rush hour, low T

afternoon: large SO_4 and oxygenated organic
photochemical processing

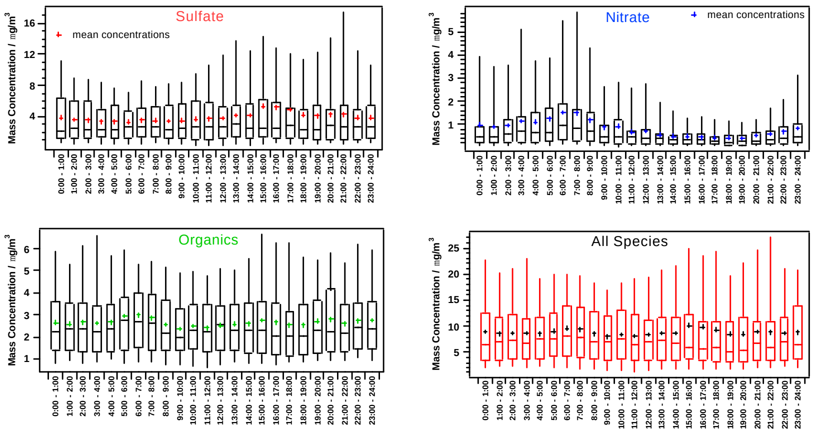
night: all aerosol increase
lower boundary layer

Small mode fraction of OC:



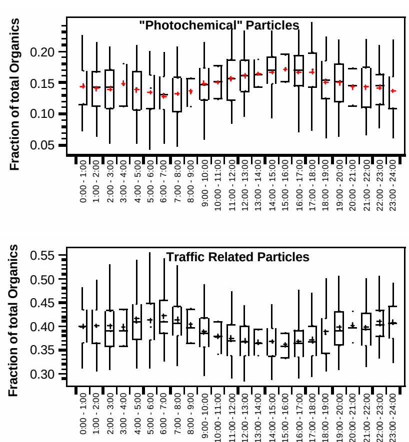
Diurnal Cylcles

Mass Concentrations



Diurnal Cylcles

Organic Aerosol Composition



Ion-series analysis

(McLafferty, Turecek)

Δ = peak mass – 14n + 1

Markers:

Δ-group 0, 2: Traffic-related aerosol

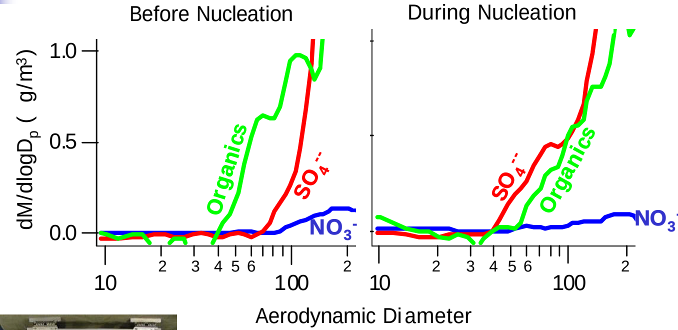
Δ-group 3: Photochemically generated aerosol

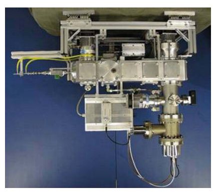
→Major fraction of the organic aerosol in New York City is related to traffic

Pandis group, Carnegie Mellon, Pittsburgh

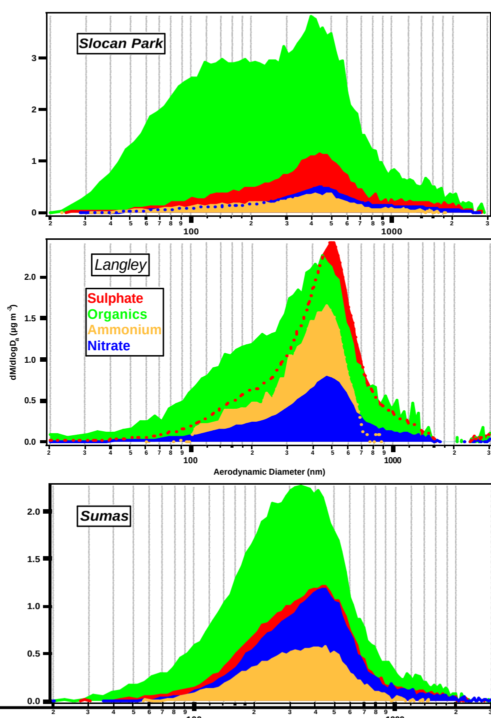
In-Situ Formation of Ultrafine Aerosols In an Urban Area – C. Stanier et al.

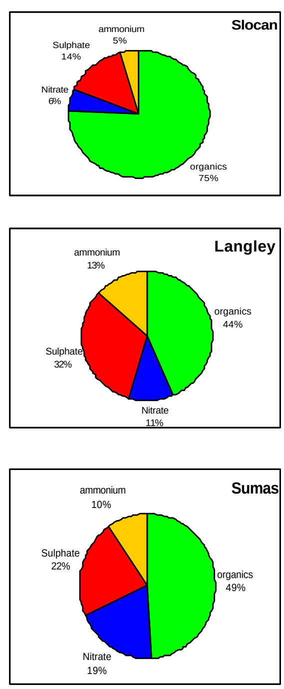
Indication of Sulfate Involvement in Growth





Aerosol Mass Spectrometer
Sept 12, 2002
Zhang, Q.; Jimenez, J.L.;
Caragaratna, M.; Worsnop, D. 20



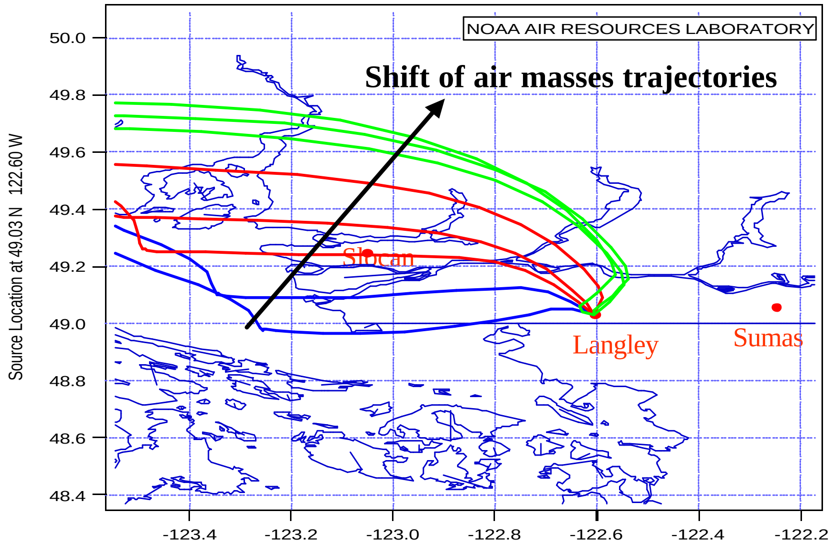


4.8 $\mu g m^{-3}$

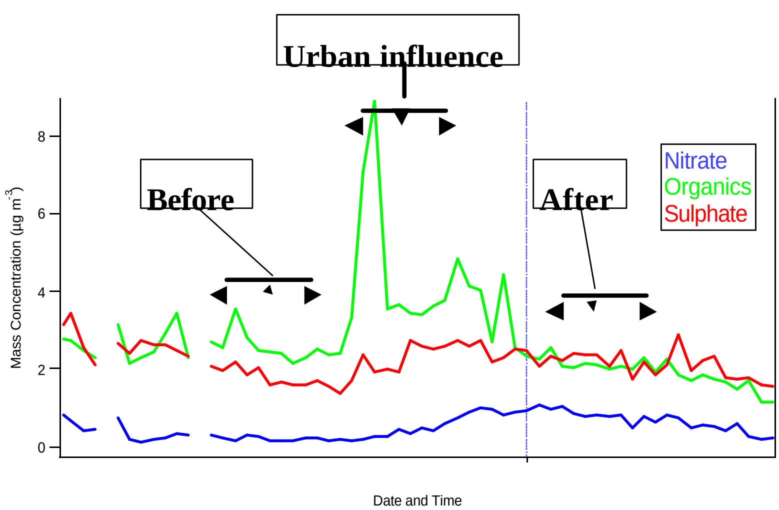
3.3 $\mu g m^{-3}$

3.2 $\mu g m^{-3}$

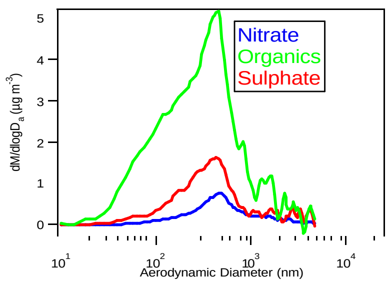
Typical air mass passing Slocan site before reaching Langley site (August 15, 2002)



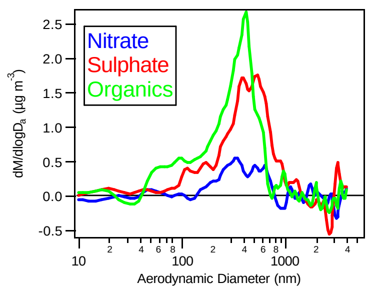
Size distribution variation before, after and during urban influence measured at Langley site.



Slocan Site



Langley site

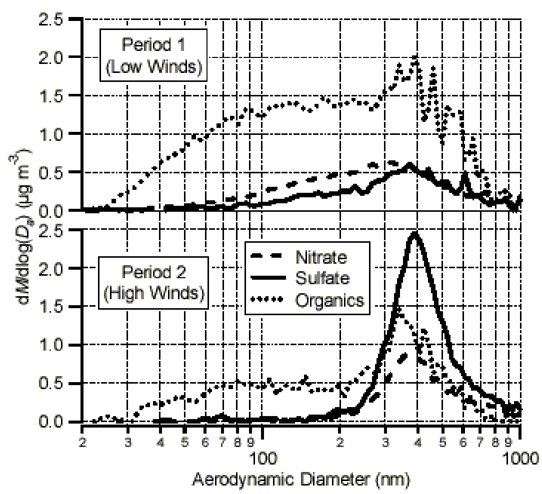


Organics =5 mg m^{-3}
Sulphate = 1 mg m^{-3}
Nitrate = 0.5 mg m^{-3}

Transport → **photochemistry**

Organics =3-5 mg m^{-3}
Sulphate = 2 mg m^{-3}
Nitrate = 0.5 mg m^{-3}

Local vs Regional



"low wind"

high organic

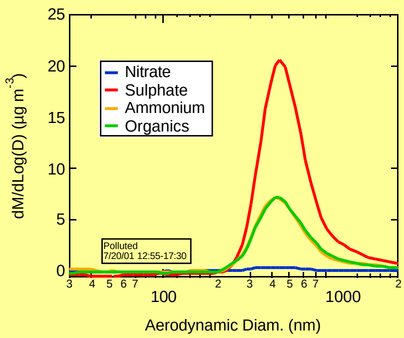
(and nitrate)

"high wind"

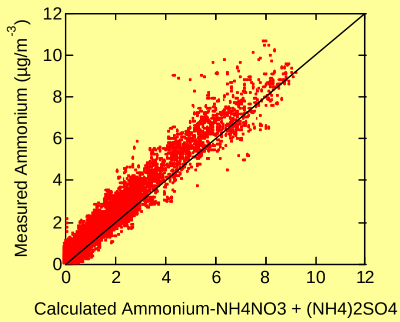
high sulfate

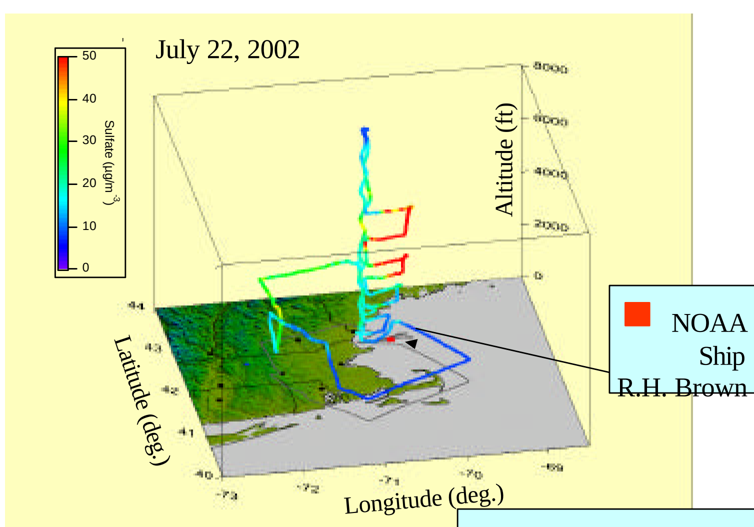
Manchester, January, 2002 *Allan et al, 2002*

“Narrow” Mass Distribution



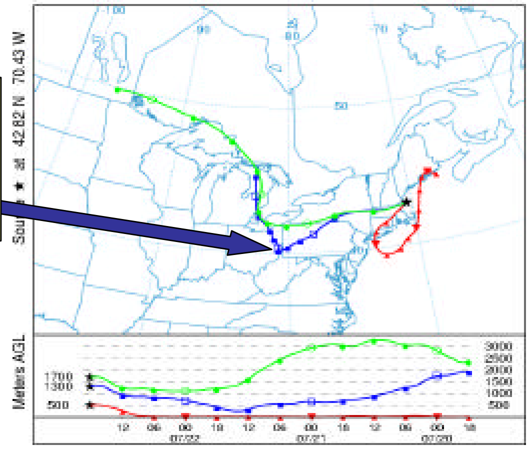
Acids are neutralized

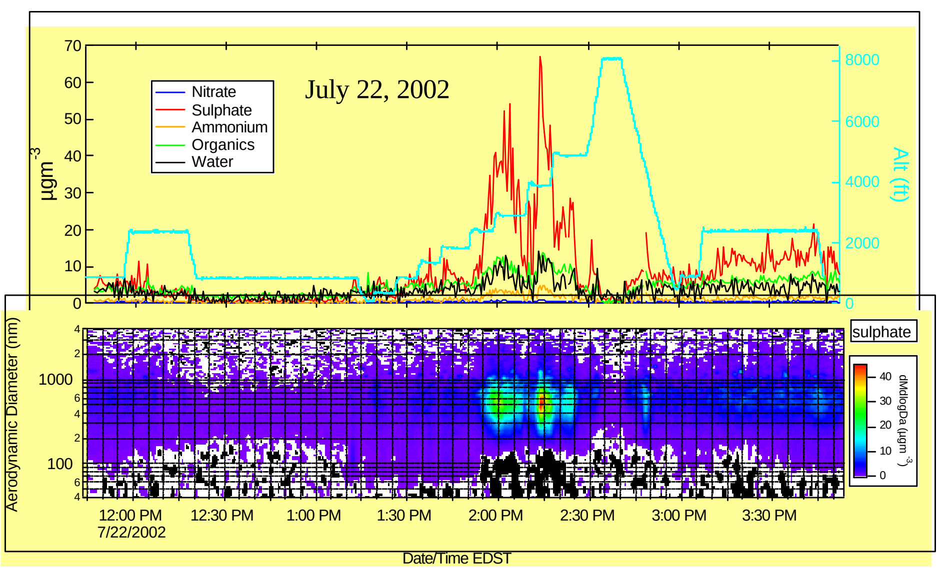


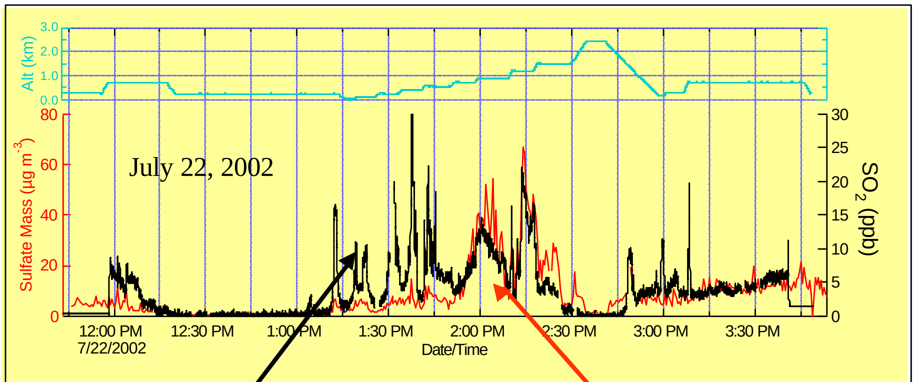


Air masses are “layered”

Back Trajectory Shows High Sulfate Air Mass at 1.3 km Originating from Ohio Valley

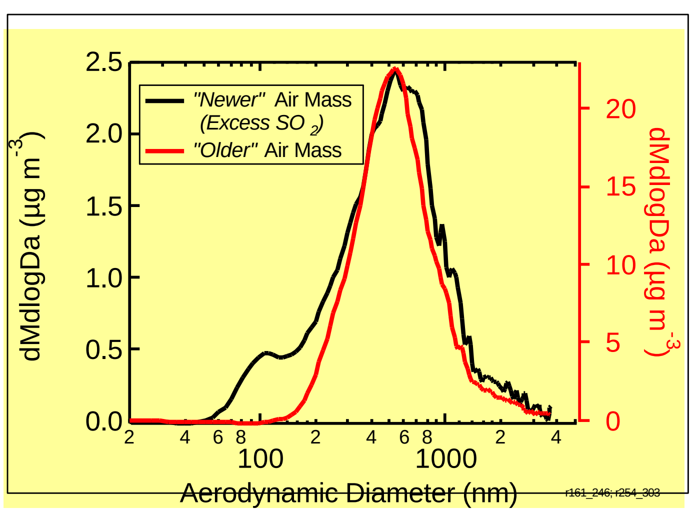






"*Newer/less-processed*"
Air Mass

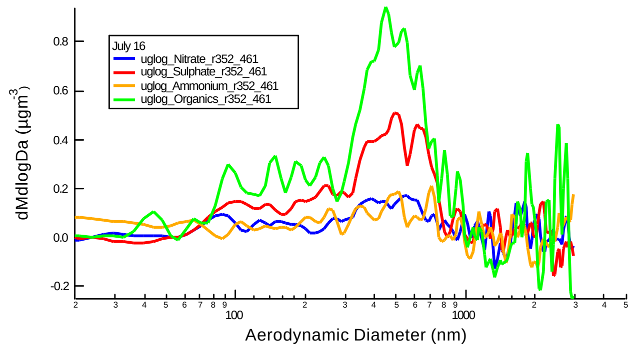
"*Older/more-processed*"
Air Mass



July 22, 2002

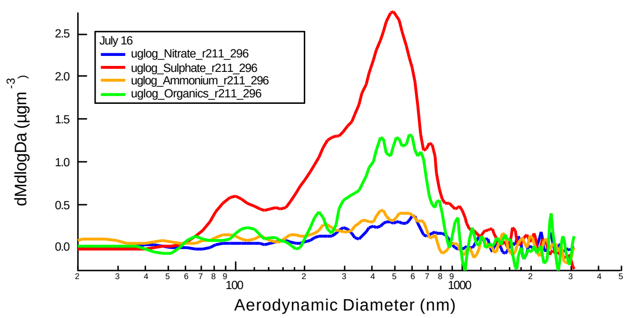
“Organic”

Outflow from NYC



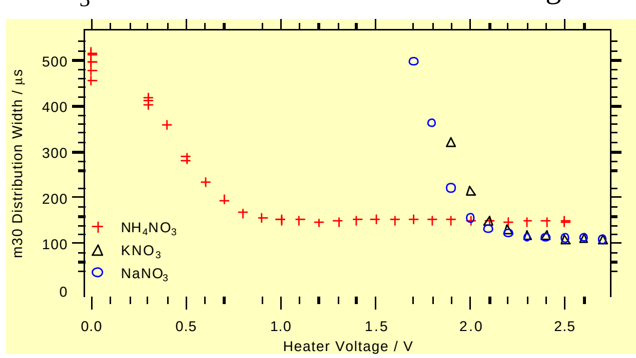
“Sulfate”

Regional aerosol



Heater Experiments

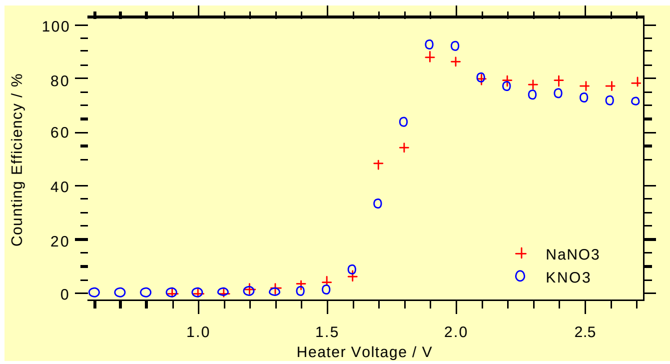
Size Distribution Width for 200 nm NH_4NO_3, $NaNO_3$ and KNO_3 Particles for different Heater Voltages :



- Above Threshold Heater Temperature instantaneous Evaporation
- Threshold Heater Temp. depends on Boiling Point

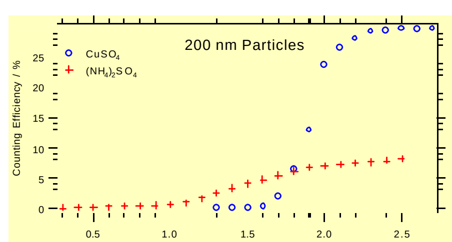
Heater Experiments (IV)

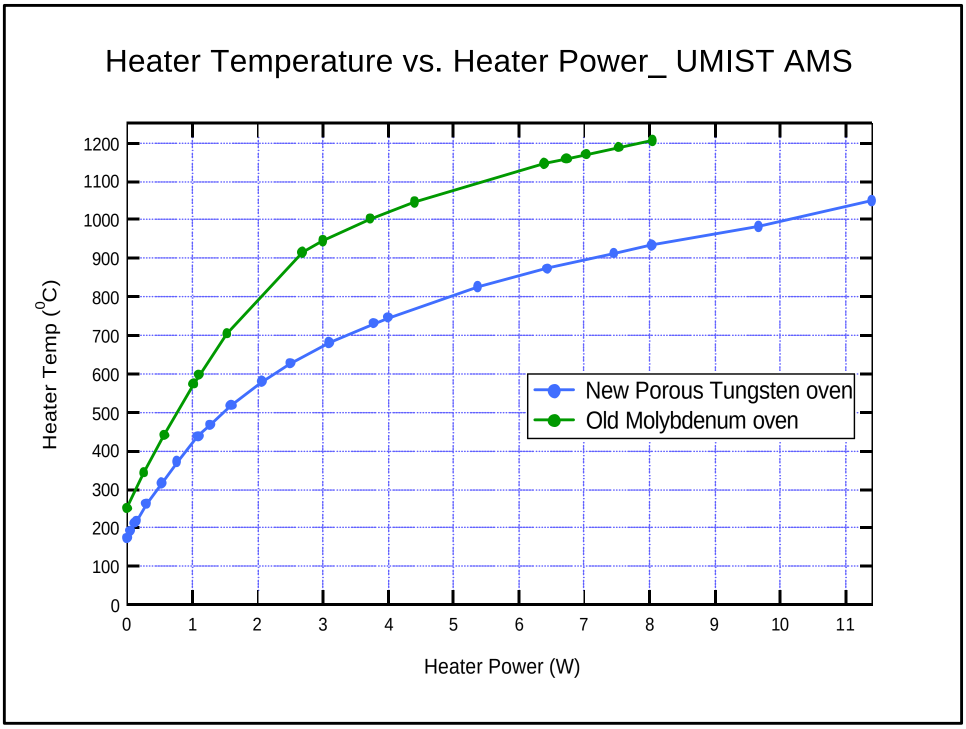
Counting Efficiency for m30, 200 nm Particles, for $NaNO_3$ and KNO_3:



Heater Experiments (VII)

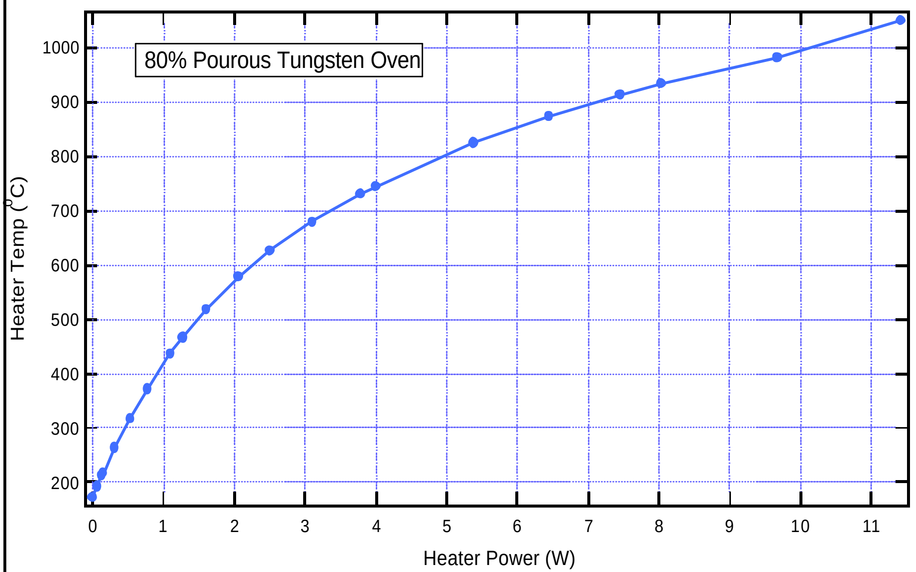
- ➢ No Counting Efficiency Increase above sufficient Heater Temperature
- ➢ Count. Eff. Significantly larger for $CuSO_4$ than for $(NH_4)_2SO_4$



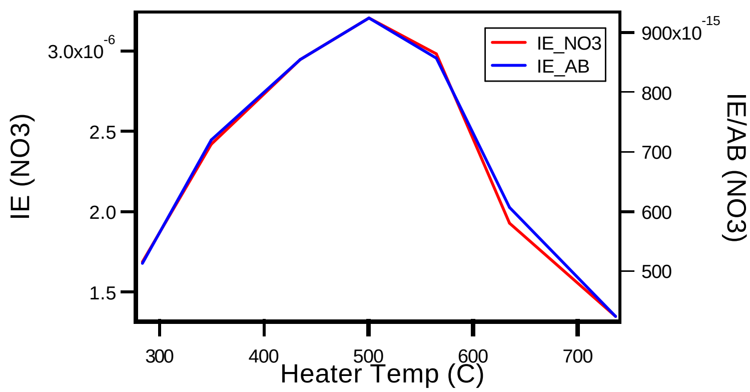


Investigation of the heater temperature Effect on the detection of organic compounds

Rami Alfarra
UMIST
February 2002



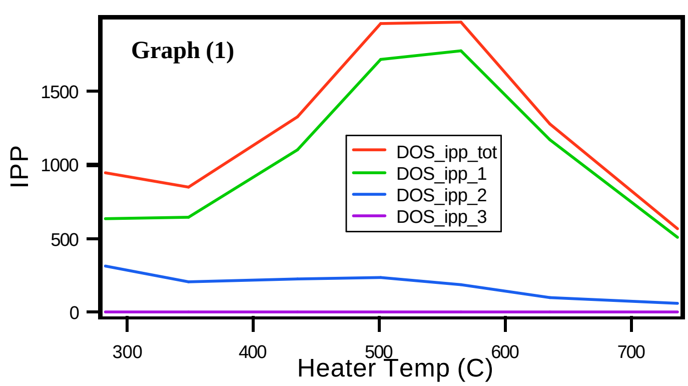
The same old heater temperature/ power curve.. Useful to relate heater Temperatures in this experiment to heater powers..



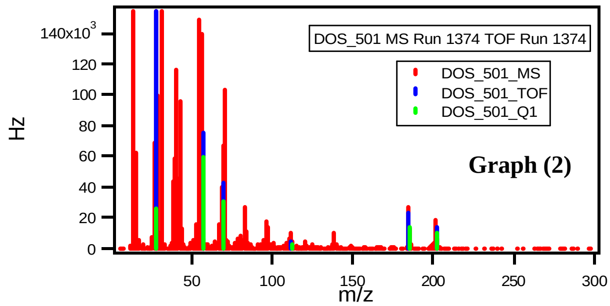
This graph shows that IE (NO3) depends on the heater temperature setting, while the air beam strength is, obviously, not.

IPP (NO3) was as high as 700 at 500 ^{0}C, and fall down above and below this temperature despite many re-tuning attempts, indicating That this trend is a result of the heater temperature not tuning.

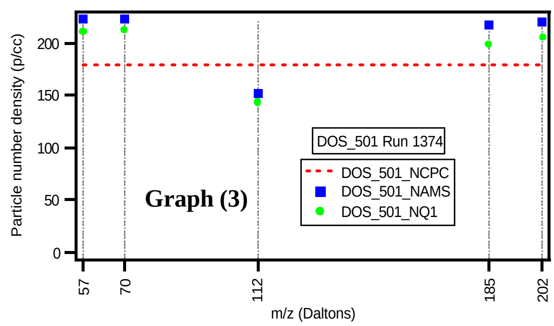
(1) 350nm Dioctyl-Sebacate (DOS) in Methanol



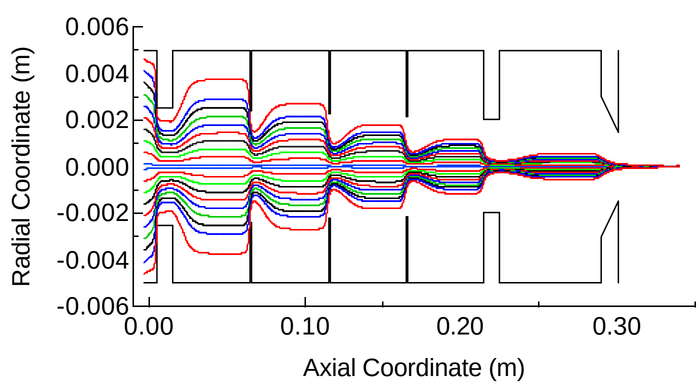
- Most of signal is at the first 100 amus "green line"
- Below 500 C, it appears that there isn't enough thermal energy to vaporize the whole particle. While at 500 – 550 C, maximum vaporization and therefore IPP can be obtained.
- As found before, IPP starts to decrease above a certain temperature, 550 in this case.



I don't know exactly the reason why the AMS detects more particles than the CPC. The CPC was suspected to be undercounting, but this was ruled out as it was compared to another CPC and were in a relatively good agreement.
It could be due to the sampling method.



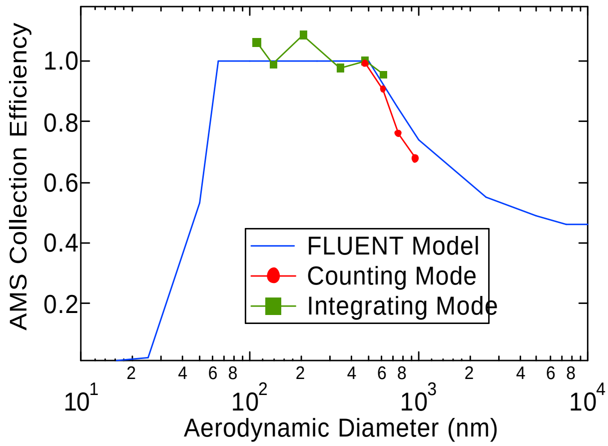
Aerodynamic Particle Focusing



2.4 Torr inlet

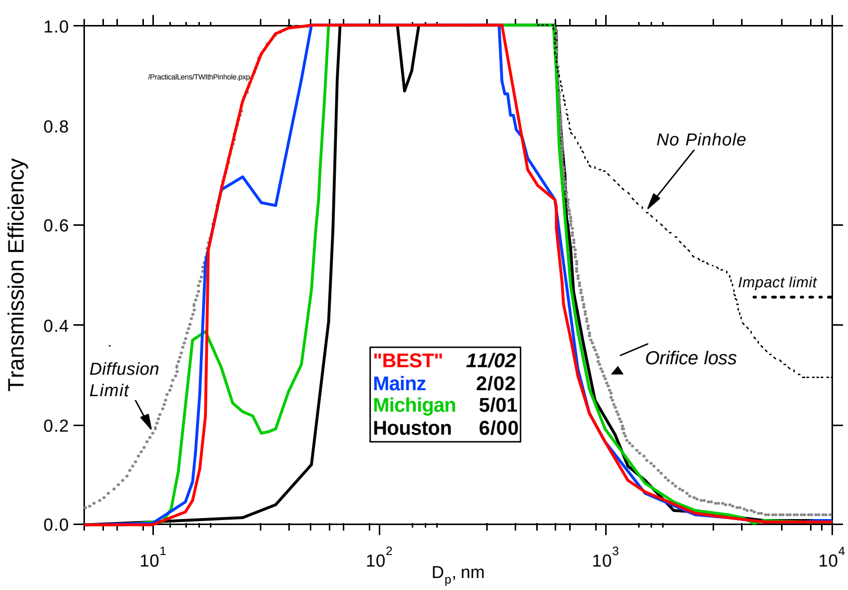
10^{-3} torr Exit

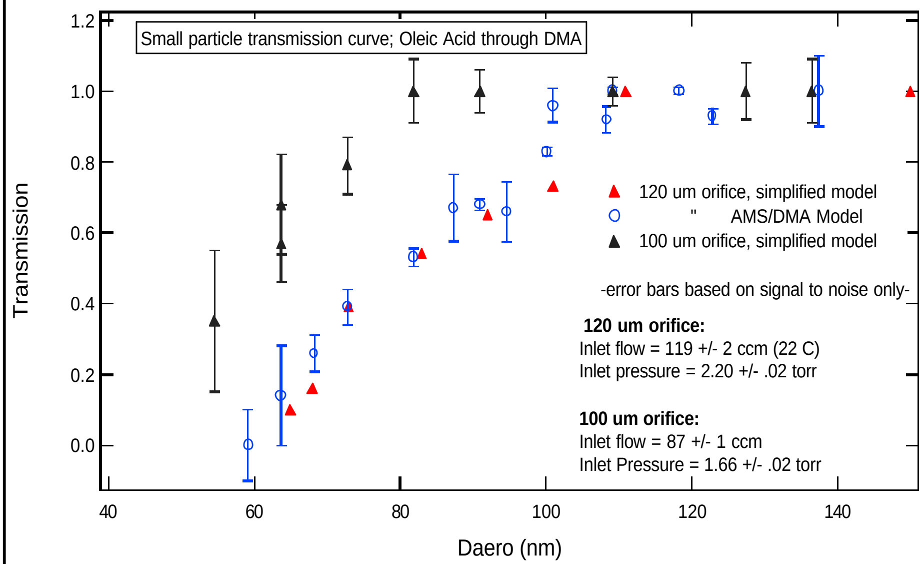
Calculated Particle Trajectories
100 nm Diameter Unit Density Spheres
(Fluent ver 4.47)



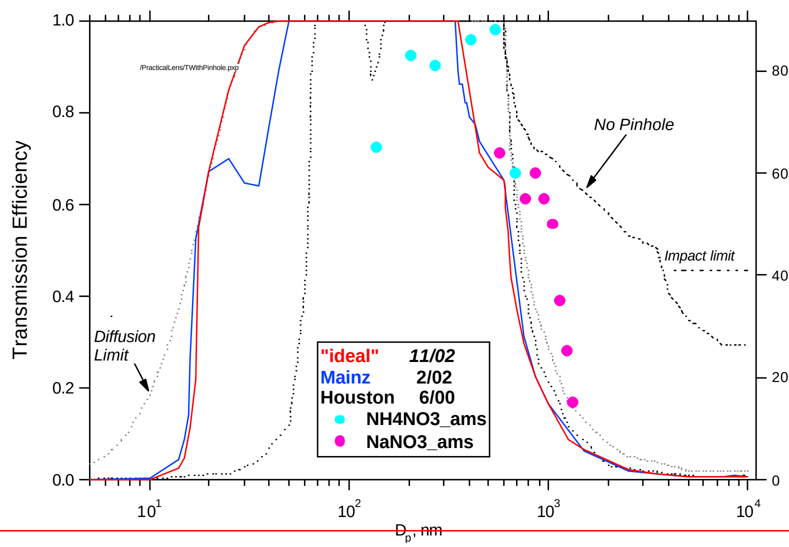
Jayne et al, 2000

Lens Transmission Curves *(Zhang et al)*



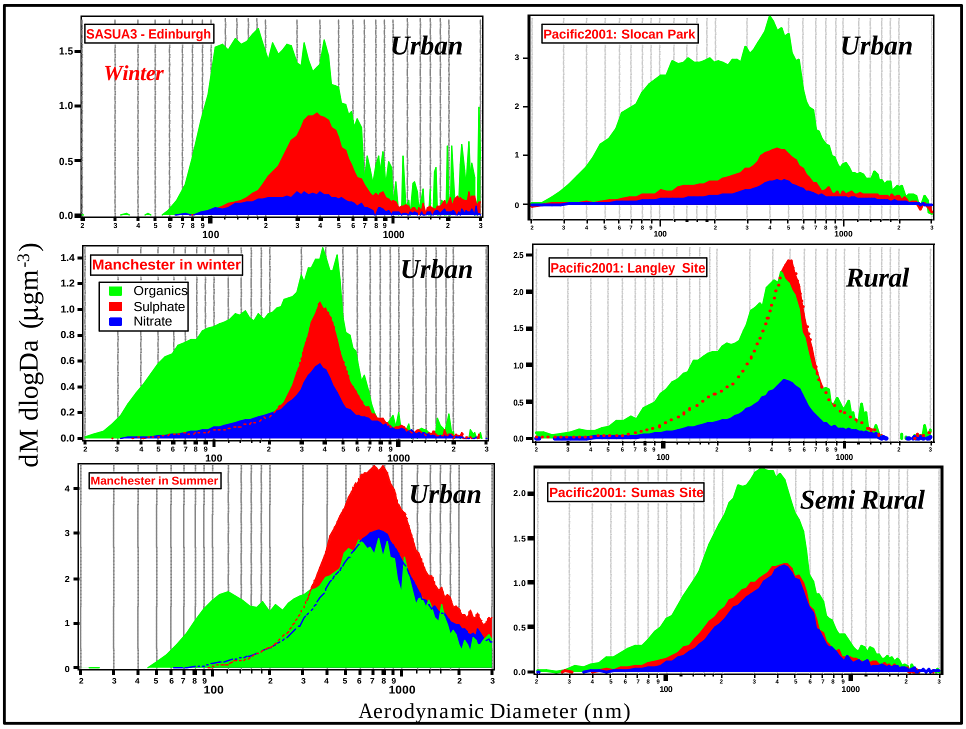


Including measurements made at JCAP



Note that data points likely should be scaled from 85% and 65% to 100% for NH4NO3 and NaNO3, respectively

And the 120nm NH4NO3 point is low because of AMS undercounting at high number density



SASUA3 - Edinburgh
Winter
Urban
Pacific2001: Slocan Park
Urban
Manchester in winter
Organics
Sulphate
Nitrate
Urban
Pacific2001: Langley Site
Rural
Manchester in Summer
Urban
Pacific2001: Sumas Site
Semi Rural
dM dlogDa (µgm-3)
Aerodynamic Diameter (nm)