Measurement of Ambient Aerosol Composition Using an Aerodyne Aerosol Mass Spectrometer in New York City: Winter 2004 Intensive Study

5PE4

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Introduction

In summer 2001 and winter 2004 field campaigns in Queens, NY were performed as part of the PM 2.5 Technology Assessment and Characterization Study in New York (PMTACS-NY), one of the EPA "Supersites".

During these studies several state–of–the–art aerosol instruments were deployed including an Aerodyne Aerosol Mass Spectrometer (AMS).

Primary objectives are characterization and evaluation of new atmospheric particle matter measurement technologies and investigation of similarities and differences in PM composition observed under summer and winter conditions.

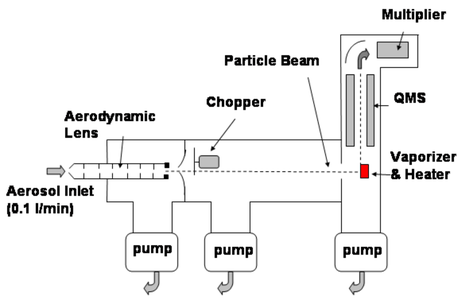
Here mass concentrations of Sulfate, Nitrate, Organics, Chloride and Ammonium are presented with specific attention to the behavior of primary and secondary organics for the winter campaign 2004.

Instrument Description and Sampling

PRINCIPLE of OPERATION of the AMS:

Particles are focused through an aerodynamic lens. The particle beam passes a skimmer, a chopper and the sizing chamber before impacting on a vaporizer (700 ºC). Volatile and semi-volatile components evaporate, are ionized by electron impact (70eV) and are analyzed using a quadrupole mass spectrometer (QMS).

The AMS is operated in two modes:
Time-of-Flight (ToF) mode: Measurement of species-resolved size distributions by chopping the particle beam and measuring the time-resolved ion signal for several selected masses (28, 15, 16, 18, 30, 46, 43, 44, 55, 57, 69, 71, 48, 64).
Mass Spec (MS) mode: Measurement of the aerosol composition by scanning the complete mass spectrum (1-300 amu) at 3 Hz. Chopper is completely removed from particle beam.



AMS Schematic

Sampling during PMTACS-NY 2004

Sampling Site: Queens College, Queens/New York (40.44° N, 73.49° W, ~25 m a.m.S.L.), parking field # 6
AMS Sampling Period Winter 2004:
January 9th – February 6th 2004
Instrument Performance:
- 10-min averages of volatile and semi-volatile Sulfate, Nitrate, Ammonium, Chloride, total non-refractory Organics Mass Concentrations
- 10-min averages of Sulfate, Nitrate, Ammonium and Organics Size Distributions
- More than 96% data coverage

AMS Particle Collection Efficiency

AMS Quantification:

Internal particle losses → empirically accounted for by collection efficiency factor (CEF)

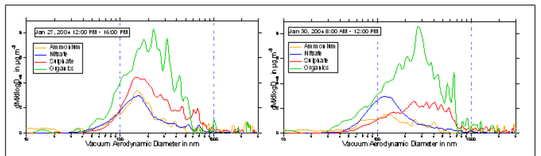
During Summer 2001:
CEF = 0.43 (for all species, internal mixture assumed based on size distributions; determined by comparison SO_4 AMS/PILS)

Here: Time intervals of internal as well as external mixture of NO_3/SO_4 (see size distribution plots); pure NH_4NO_3 has CEF = 1

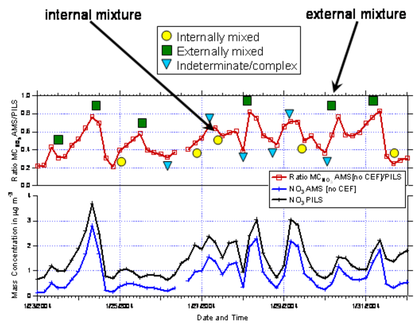
- Nitrate CEF not constant in time; dependent on externally mixed fraction of nitrate; calculated by comparison of AMS with PILS
- Sulfate, Organics and Chloride assumed to be internally mixed → constant CEF = 0.42 (from comparison of SO_4 AMS and PILS)
- Ammonium CEF calculated from CEF_{NO_3} and CEF_{SO_4}:

$$CEF(NH_4) = \frac{CEF(NO_3)\cdot\frac{MC(NO_3)}{MW(NO_3)} + CEF(SO_4)\cdot 2\cdot\frac{MC(SO_4)}{MW(SO_4)}}{\frac{MC(NO_3)}{MW(NO_3)} + 2\cdot\frac{MC(SO_4)}{MW(SO_4)}} = \frac{MC(NO_3)}{MW(NO_3)} + 2\cdot\frac{MC(SO_4)}{MW(SO_4)}$$

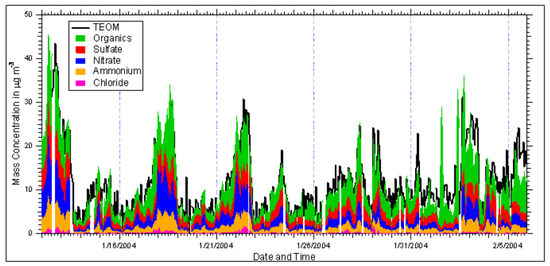
(MW = Molecular Weight; MC = Mass Concentration)



4-hour size distributions (examples)



Upper panel: Ratio of AMS NO_3 / PILS NO_3 for 01/23 – 01/31 ; times of internal/external mixture of NO_3/SO_4 are marked
Lower panel: Mass concentrations of AMS NO_3 without CEF (blue) and PILS NO_3 (black) for the same period



Mass Concentration Time Series: AMS and TEOM

AMS mass concentration time series:

Events with mass concentration up to 30 µg m-3 (Jan 12th, Jan 18th and Feb 3rd)

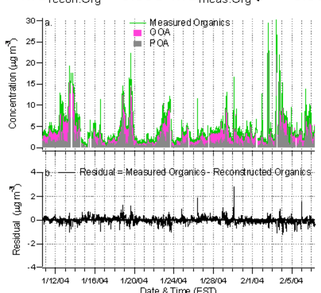
During events nitrate mass concentrations increased more than sulfate

Good comparison of total AMS with FDMS TEOM:

Correlation
$MC_{AMS} = 0.94\ MC_{TEOM} + 0.89\ \mu gm^{-3}$
($r^2 = 0.78$)
Missing 5%: Metals, EC

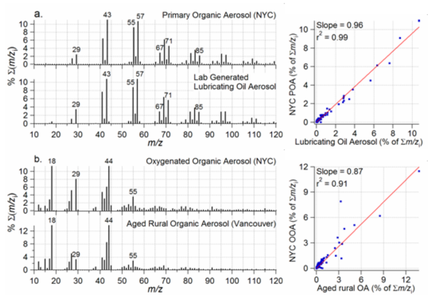
Primary and Oxygenated Organic Aerosol

Organic mass concentration (MC) was estimated and mass spectra (MS) of primary and oxygenated organic aerosols (POA and OOA) were extracted using recently developed technique (Presentation 1C2 in this conference)
- Below: Very good agreement between measured and reconstructed organic MC (= POA + OOA)
- $MC_{recon.Org} = 0.998*MC_{meas.Org}$ ($r^2 = 0.994$)



a) Time series of the measured organic MC and POA and OOA estimates (OOA is stacked on top of POA); b) variations of the residual of the fit (= measured – POA – OOA) as a function of time.

- Extracted MS of POA almost identical to AMS MS of lab measured lubricating oil aerosols[1] ($r^2 = 0.99$) while MS of OOA closely resembles that of aged organic aerosol sampled from a rural area in Vancouver[2] ($r^2 = 0.91$)
- Extracted MS of POA shows high similarity to that of diesel aerosol sampled during a chase study in NYC[1] ($r^2 = 0.95$)



Comparisons between the MS of a) derived "POA" from NYC and that of lab generated lubricating oil aerosols [1]; 2) "OOA" and aged rural organic aerosols [2].

Data Overview

Data overview for Jan 9th until Feb 6th AMS data:

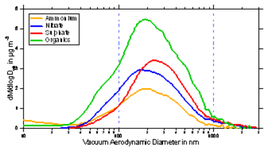
Mass Concentration: particle composition dominated by organics; about equal amounts of nitrate and sulfate

Average size distributions: Nitrate particles smaller than others (partial external mixture), sulfate particle mode larger than others; small particle mode (dva ~ 70 nm) for nitrate and organics

Diurnal patterns: Clear pattern for organics, sulfate, nitrate and ammonium found:

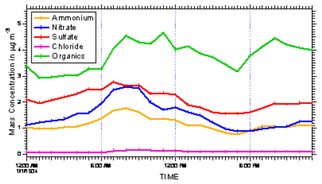
(µg/m³)	Nitrate	Ammonium	Sulfate	Organics
Minimum	< LOD	< LOD	< LOD	< LOD
Median	1.38	1.10	1.99	3.72
Mean	2.19	1.51	2.41	4.80
Maximum	15.72	7.96	9.74	33.75

Mass Concentration Data



Mode diameters:	
Nitrate	170 nm
Sulfate	240 nm
Ammonium	200 nm
Organics	200 nm

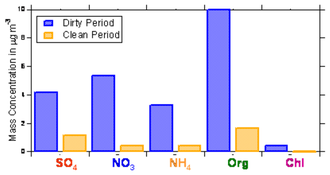
Average Size Distributions



Diurnal patterns

Org.: maxima during times of intensive traffic (7:00–10:00 AM; 2:00–6:00 PM; 7:00–11:00 PM)
NO_3, NH_4: short maximum ~ 8:00 AM (after sunrise)
SO_4: long maximum from 5:00 – 11:00 AM

Clean and Dirty Periods



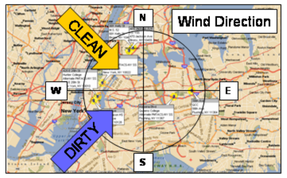
Relative aerosol composition

Independent analysis of clean ($PM_{2.5}$ < 5 µg m-3) and dirty ($PM_{2.5}$ > 15 µg m-3) periods:

Aerosol Composition: During dirty periods ratio of nitrate and sulfate is reversed compared to clean periods

Size Distributions: During clean periods nitrate has an additional small particle mode around 70 nm; during all times sulfate mode diameter larger than others

Correlation of wind direction with clean (NW) and dirty (SW) periods



Wind directions associated with clean and dirty periods

Mode / nm	Dirty Period	Clean Period
Ammonium	200	200
Nitrate	200	70 and 200
Sulfate	240	240
Organics	200	200

Size distribution data

Summary

- Externally mixed fraction of nitrate occurred in winter time 2004
- Constant CEF for sulfate, organics, chloride; different CEF for nitrate and ammonium
- Good agreement between corrected Total AMS data and FDMS TEOM data
- Clear diurnal patterns for sulfate, nitrate, organics and ammonium
- Reversed ratio of NO_3 to SO_4 for clean and dirty periods
- Small particle mode around 70 nm for nitrate for clean period
- Wind direction correlates with clean (NW) and dirty (SW) periods
- Good agreement between extracted mass spectrum (MS) of POA and the lab-measured AMS MS of lubricating oil
- Good agreement between extracted MS of OOA and the AMS MS of organic aerosol sampled from rural areas

Acknowledgements

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References

[1] Canagaratna, M.R., J.T. Jayne, D.A. Ghertner, S. Herndon, Q. Shi, J.L. Jimenez, P.J. Silva, P. Williams, T. Lanni, F. Drewnick, K.L. Demerjian, C.E. Kolb, and D.R. Worsnop: Chase studies of particulate emissions from in-use New York city vehicles, *Aerosol Science & Technology*, *38*, 555-573, 10.1080/02786820490465504, 2004.

[2] Alfarra, M.R., H. Coe, J.D. Allan, K.N. Bower, H. Boudries, M.R. Canagaratna, J.L. Jimenez, J.T. Jayne, A. Garforth, S.-M. Li, and D.R. Worsnop: Characterization of urban and regional organic aerosols in the lower Fraser Valley using two Aerodyne Aerosol Mass Spectrometers, *Atmospheric Environment (in press)*, 2004.