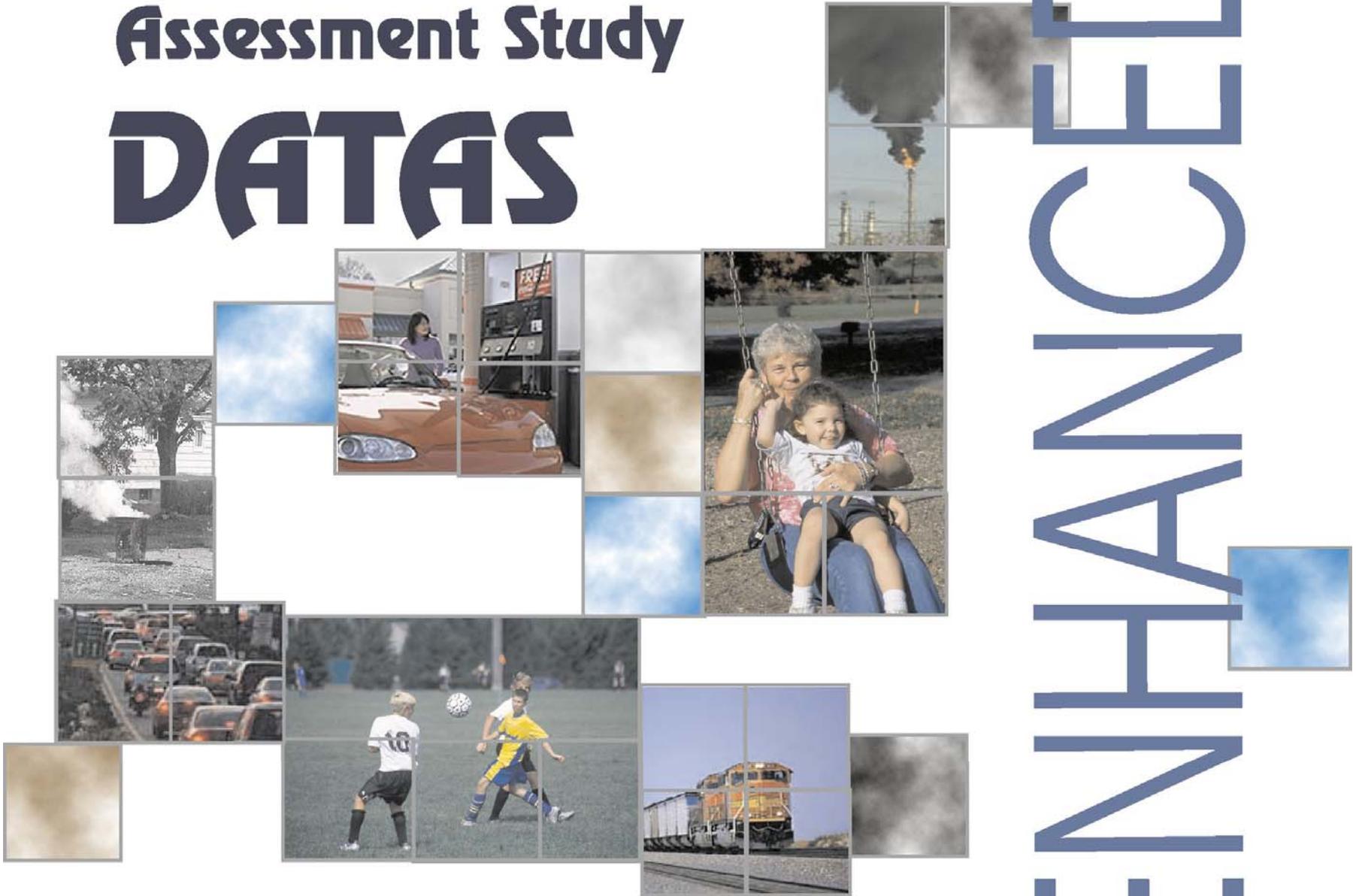


Delaware Air Toxics Assessment Study

DATAS



ENHANCED

Enhanced Delaware Air Toxics Assessment Study Project Partners

University of Delaware
✓ Murray Johnston PhD

Duke University
✓ Andrey Khylstov PhD

EPA
✓ Region III
✓ National Exposure Research Laboratory

Enhanced Delaware Air Toxics Assessment Study Goals

- To better understand, the micro-level air quality impacts of emission sources.
- To enhance the spatial resolution of the ambient toxics dataset by incorporating mobile measurements into the program.
- To define chromium measurements as CrIII and CrVI.

Enhanced Delaware Air Toxics Assessment Study

Historical Development

- ❑ The study was initiated in 2005 by DNREC.
- ❑ Add Aerosol and Mobile measurements to enhance temporal and spatial resolution of toxics monitoring network.
- ❑ Major components – Toxics Monitoring, Emissions inventory, Modeling (local and regional), Risk Assessment, Aerosol Characterization, and Mobile measurements.

Enhanced Delaware Air Toxics Assessment Study

Classes of Air Toxics Monitored

(Traditional Network)

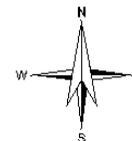
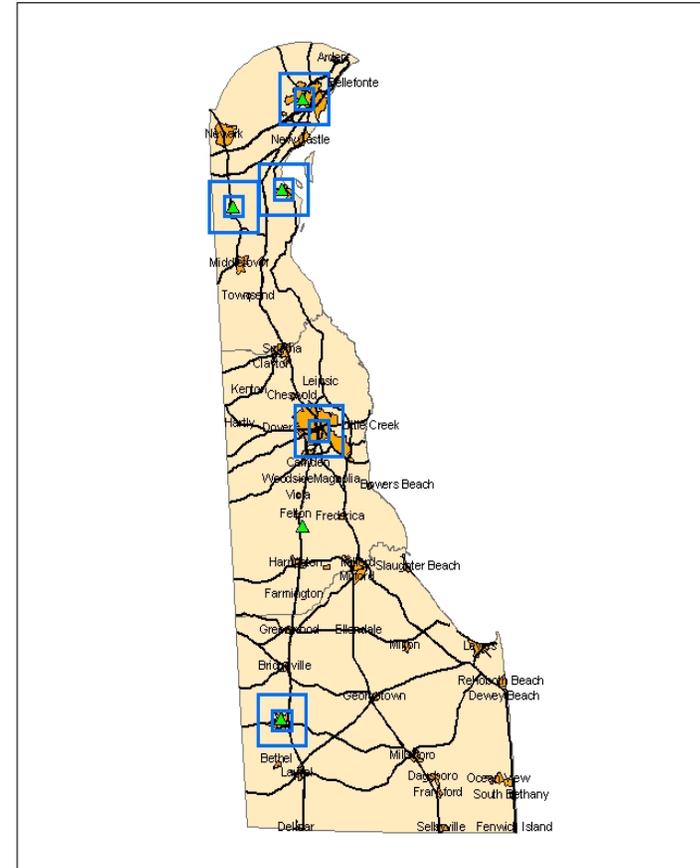
- Volatile Organic Compounds (VOC)
- Carbonyls
- Metals

Enhanced Delaware Air Toxics Assessment Study

Location of Monitoring Stations

- Martin Luther King Blvd.area (Urban)
- Lums Pond State Park and Summit Bridge area (Suburban/Rural)
- Delaware City area (Industrial)
- Felton / Killens Pond State Park area (Rural)
- Seaford area (Suburban/Urban)

Monitoring locations established throughout state to provide real data. Data collected approximately every 6 days.



0 10 20 Kilometers

Legend

- ▲ Toxics Monitoring Sites
- Town Boundaries



Area of Martin Luther King Monitoring Station



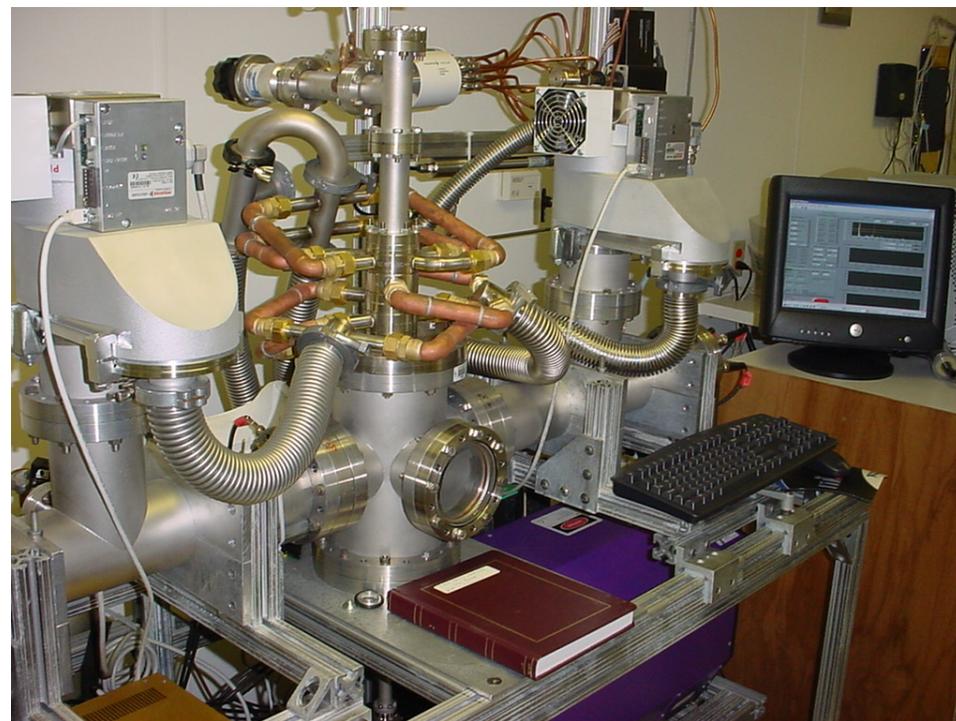
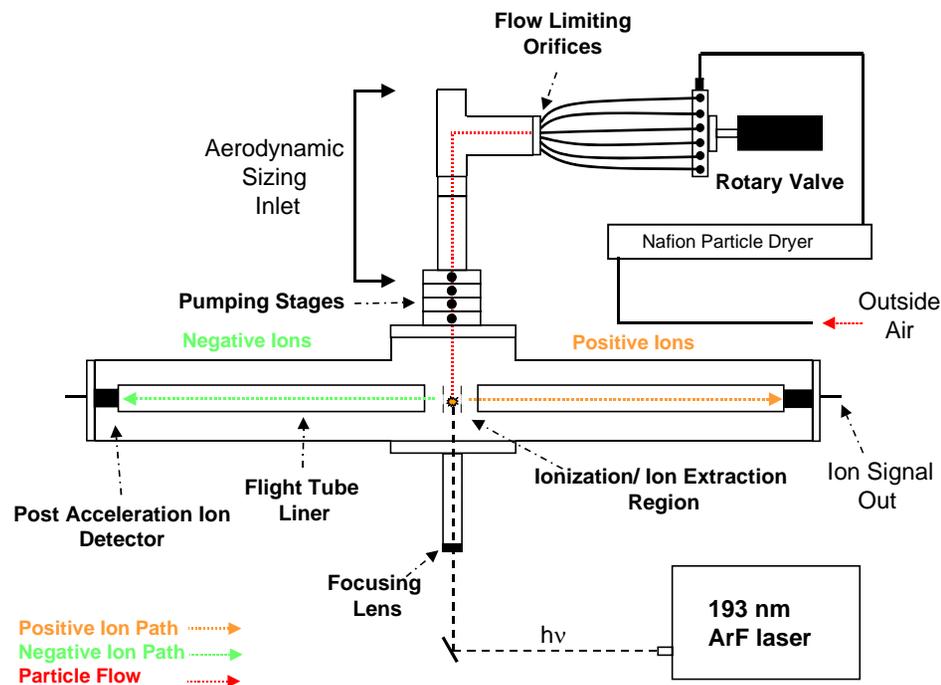
Martin Luther King Monitoring Station

Enhanced Delaware Air Toxics Assessment Study Partners

- ❑ Real-Time, Single Particle Mass Spectrometry - Murray Johnston, PhD, Department of Chemistry and Biochemistry University of Delaware.**

- ❑ Mobile Measurements for Formaldehyde and Chromium III, VI – Andrey Khylstov, PhD, Duke University.**

Real-Time Single Particle Mass Spectrometer V.3 (RSMS-3)



M.P. Tolocka, D.A. Lake, M.V. Johnston, A.S. Wexler, "Size-Resolved Fine and Ultrafine Particle Composition in Baltimore, Maryland", *Journal of Geophysical Research, Atmospheres* (2005) 110, D07S04, doi:10.1029/2004JD004573.

K.J. Bein, Y. Zhao, A.S. Wexler, M.V. Johnston, "Speciation of Size-Resolved Individual Ultrafine Particles in Pittsburgh, Pennsylvania", *Journal of Geophysical Research, Atmospheres* (2005) 110, D07S05, doi:10.1029/2004JD004708.

Real-Time Single Particle Mass Spectrometer Sampling Protocol

- ❑ Sampling interval – 1 hour

- ❑ Each sampling interval consists of:
 - 5 successive particle size bins (770, 440, 220, 110, 50 nm)
 - Acquire single particle spectra for 40 min (5-10 min per bin)

- ❑ Analysis modes:
 - Ambient aerosol sampled directly into RSMS-3; operate instrument up to 24 hr. per day (1000-2000 particles/day)
 - Ambient aerosol sent into a particle concentrator; concentrator output sampled into RSMS-3; operate ca. 7 hr. per day (up to 10,000 particles/day)

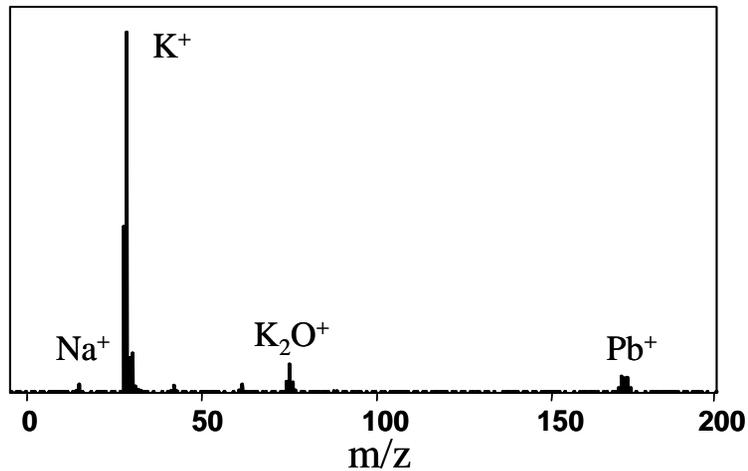
- ❑ Concurrent particle size distribution measurements with a scanning mobility particle sizer (SMPS; TSI, Inc.)

Real-Time Single Particle Mass Spectrometer Urban Aerosol Measurements with RSMS-3

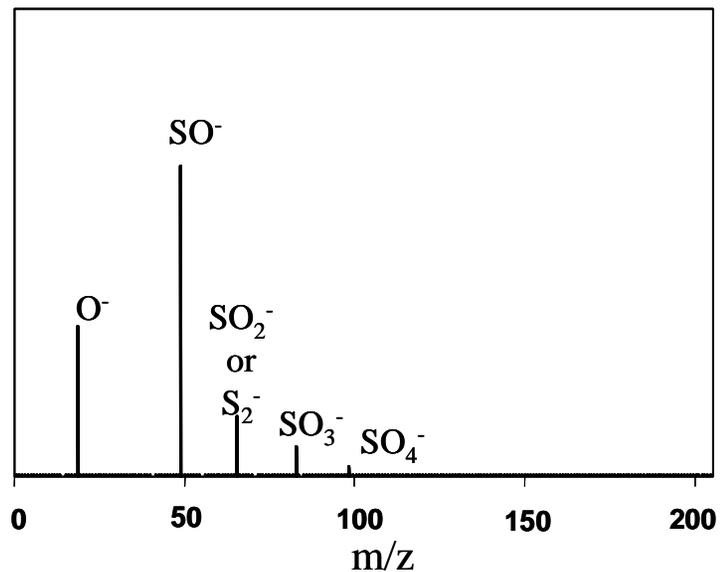
Location	Dates	Particles Analyzed
Atlanta	Aug 1999	18,000
Houston	Aug-Sept 2000	23,000
Pittsburgh	Aug 2001 - Aug 2002	236,000
Baltimore	Mar 2002 - Dec 2002	365,000
Wilmington	Apr 2005 - Jan 2006	107,000 (through 8/05)

Real-Time Single Particle Mass Spectrometer Mass Spectra of a Single 50 nm Diameter Particle Baltimore, MD (17:20 EST, 7/20/02)

Positive
Ions



Negative
Ions

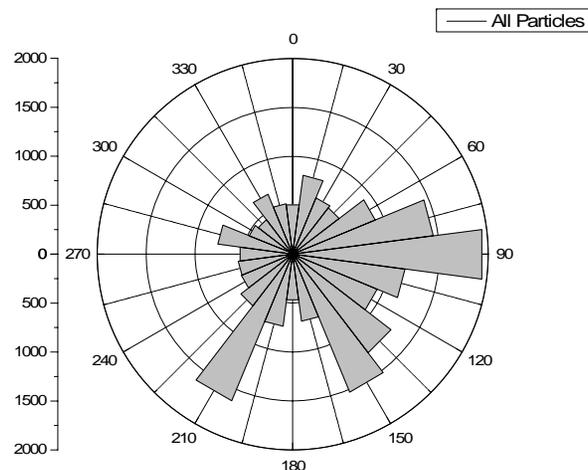


Real-Time Single Particle Mass Spectrometer Summary of Single Particle Measurements in Wilmington, Delaware (April-August 2005)

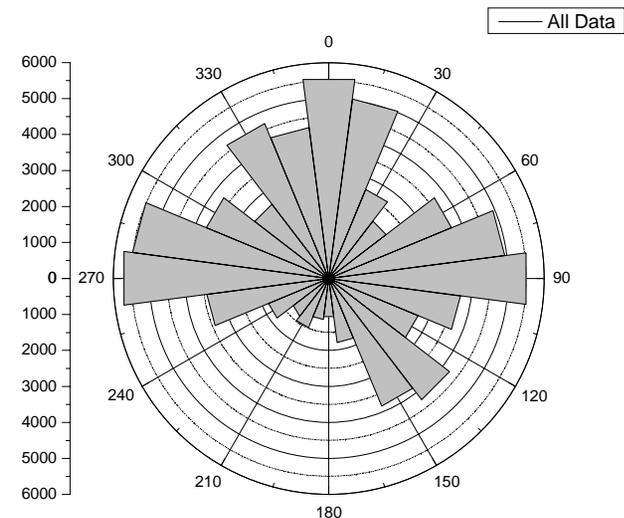
Time Period	Particle Hits
April 3-22	4,941
May 4 - June 3	20,479
July 13 – Aug 25	82,401

Particle Hits vs. Wind Direction

May-June



July-Aug



Mobile Sampling

Objective:

To provide information on the spatial distribution of pollutants throughout the city as well as variability within neighborhoods with the spatial scale of the order of 100 meters.



Methodology:

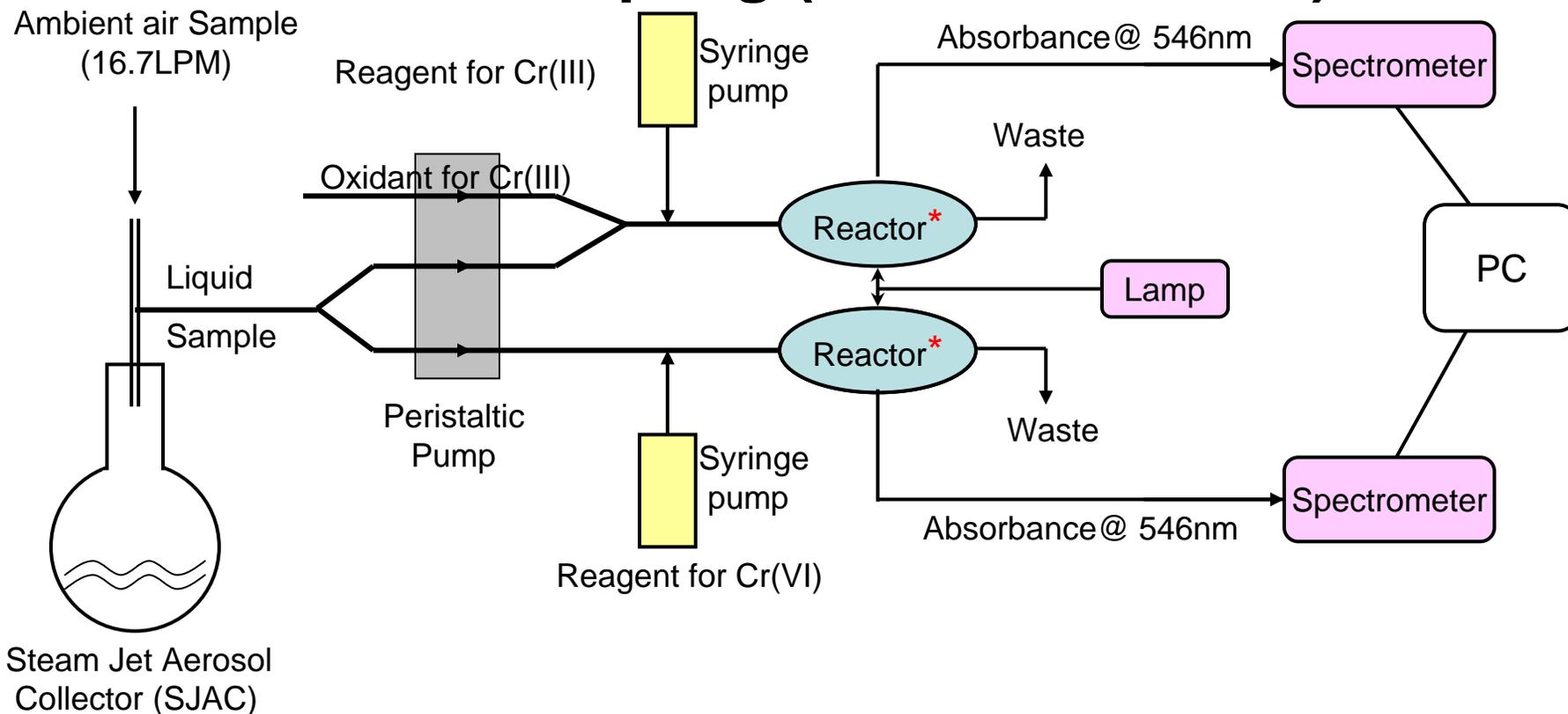
Mobile measurements of:

- PM water-soluble chromium species,
- gas-phase formaldehyde, and
- aerosol number size distribution
- ozone (possible)

Time resolution: 10 – 40 sec

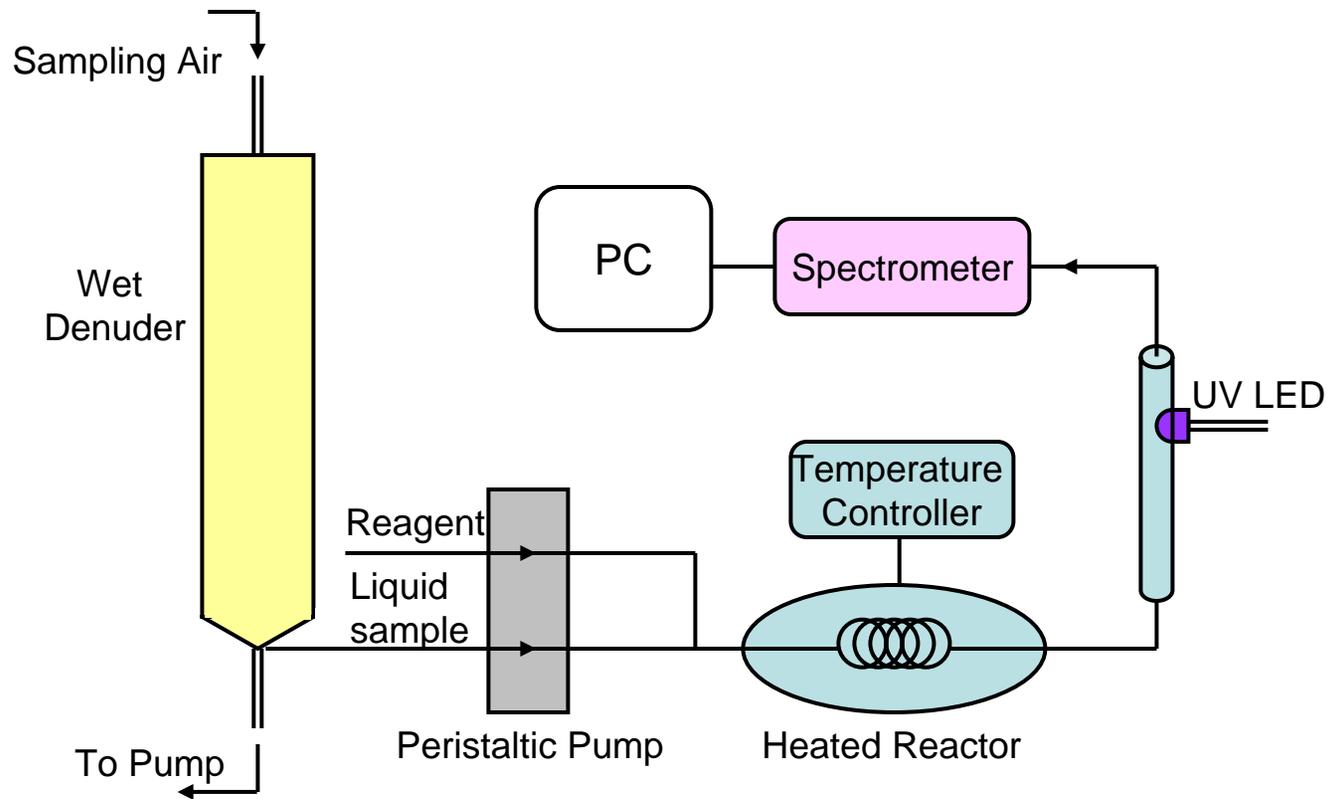
Spatial resolution: ~ 100 m

Mobile Sampling (Chromium III, VI)



- Liquid sample containing collected aerosols is used for Cr(VI) and Cr(III) analysis.
- Cr(VI) is analyzed using the diphenycarbazide colorimetric method. Absorbance at 546nm is used for concentration determination.
- The analytical method for Cr(III) is similar to that of Cr (VI), except that Cr (III) needs to be oxidized to Cr(VI) before analysis.
- *Teflon AF-2400 tubing Liquid core waveguide is used inside the reactor for lower detection limit.

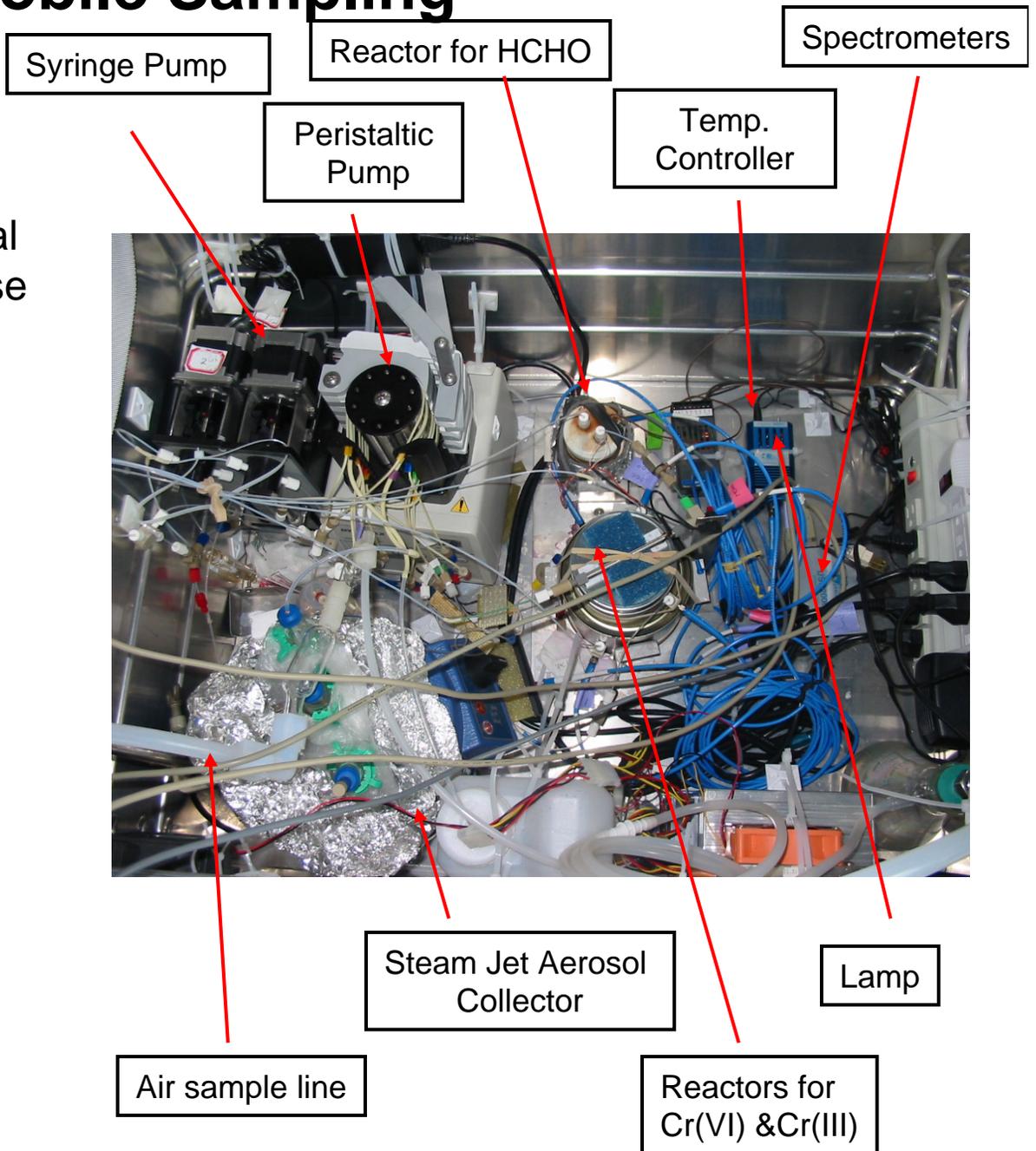
Mobile Sampling (Formaldehyde)



- Ambient HCHO is collected by the wet denuder with collection efficiency ~70%.
- Collected HCHO liquid sample is analyzed with fluorometric method with UV LED emission at 375nm, and excitation measured at 465nm.

Mobile Sampling

- Time resolution for Cr (VI), Cr(III) and HCHO
 - As low as 1 second
 - Normally run at several seconds for lower noise level
- Limit of Detection of Cr (VI)
 - 0.190 ng/m³ Cr(VI)
- Limit of Detection of Cr (III)
 - 1.935 ng/m³ Cr(III)
- Limit of Detection of HCHO
 - 0.026 umol/m³



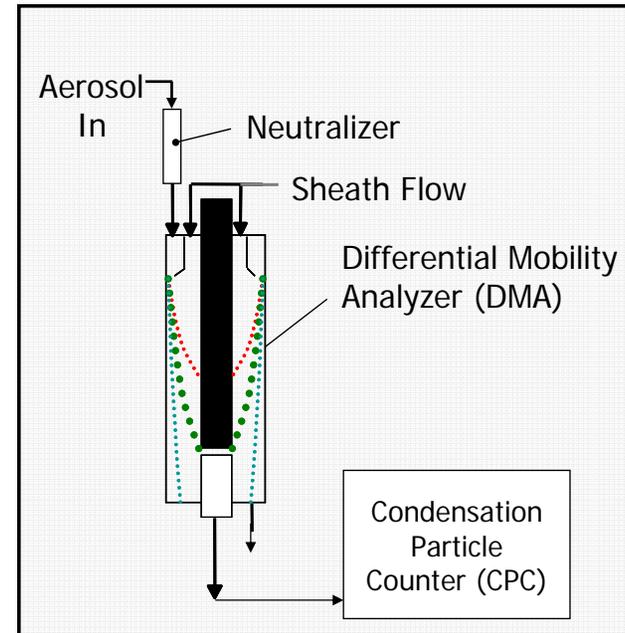
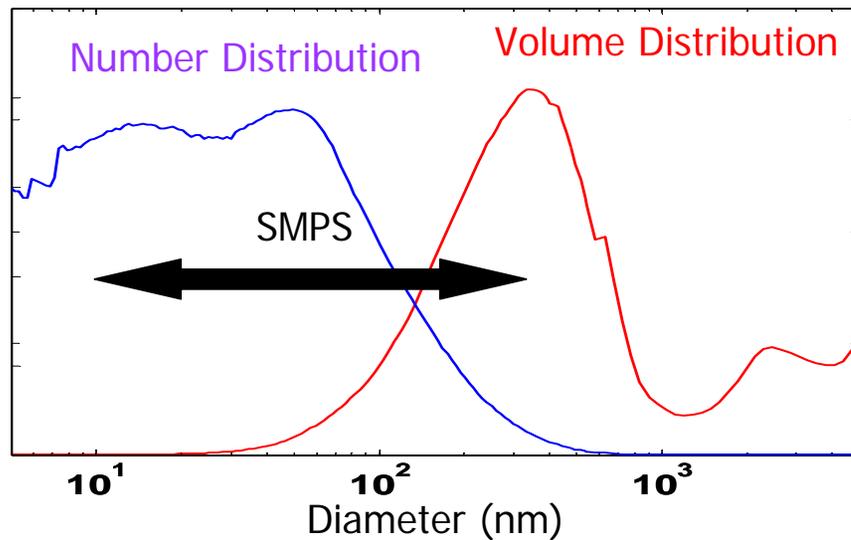
Mobile Sampling Scanning Mobility Particle Sizer (SMPS)

Measures :

- Number size distribution
- Volume size distribution
- Number concentration
- Volume concentration below 350 nm

Size range: 12 nm – 350 nm

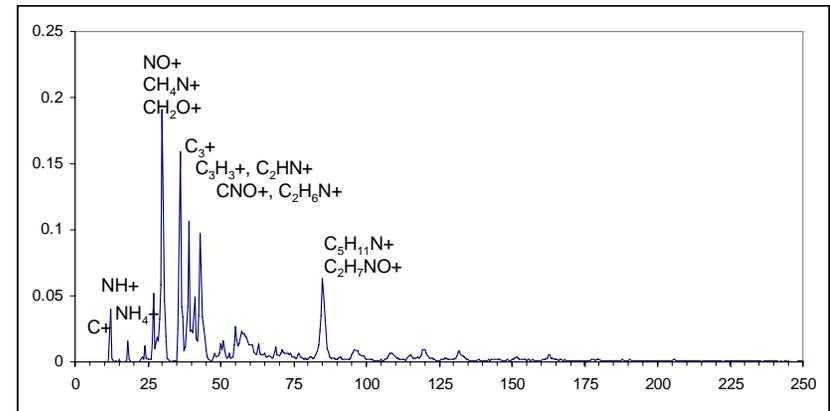
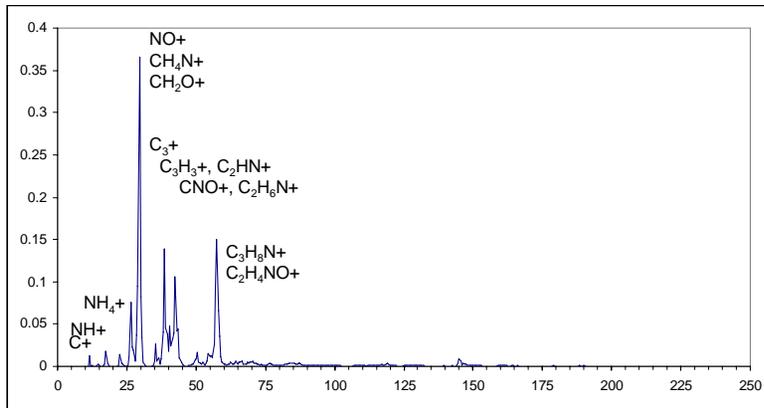
Time resolution: 40 s



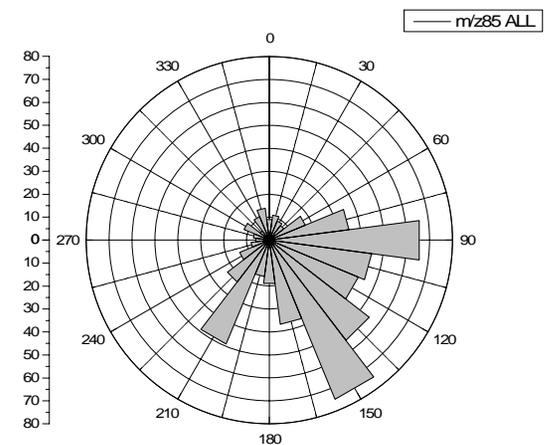
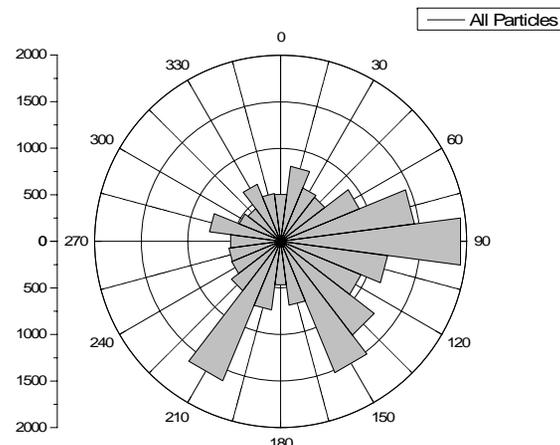
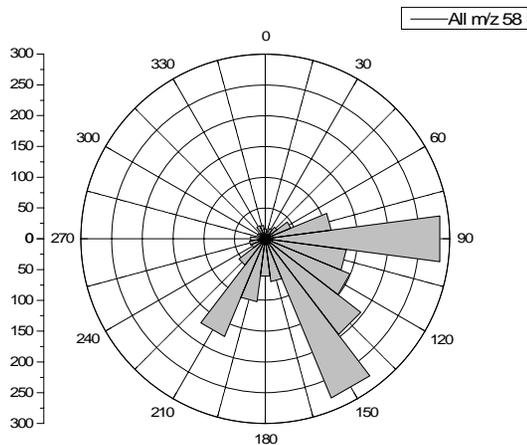
Volume of particles smaller than $0.3 \mu\text{m}$ is proxy for traffic-related $\text{PM}_{2.5}$

Customer Focus

Example of Aliphatic Amine Particle Classes: 12% by Number (PM 0.5) during May-June 2005



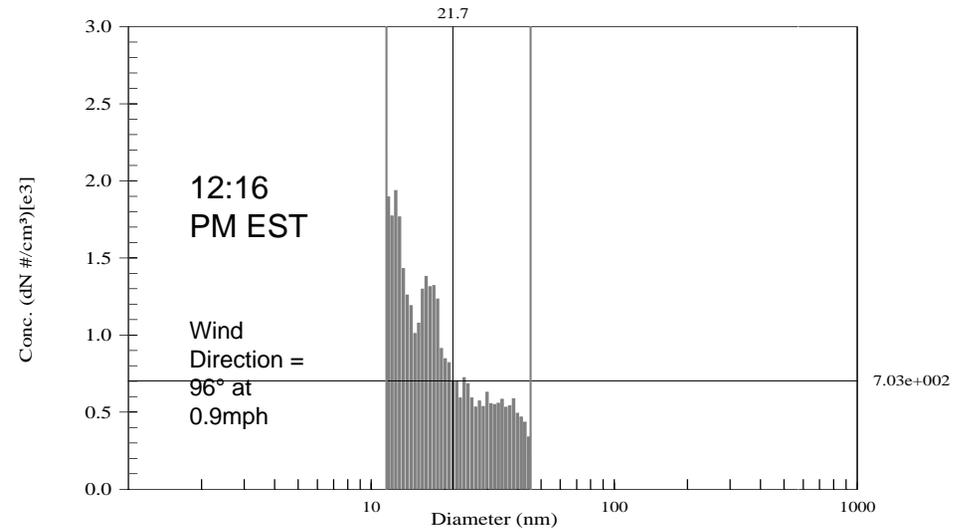
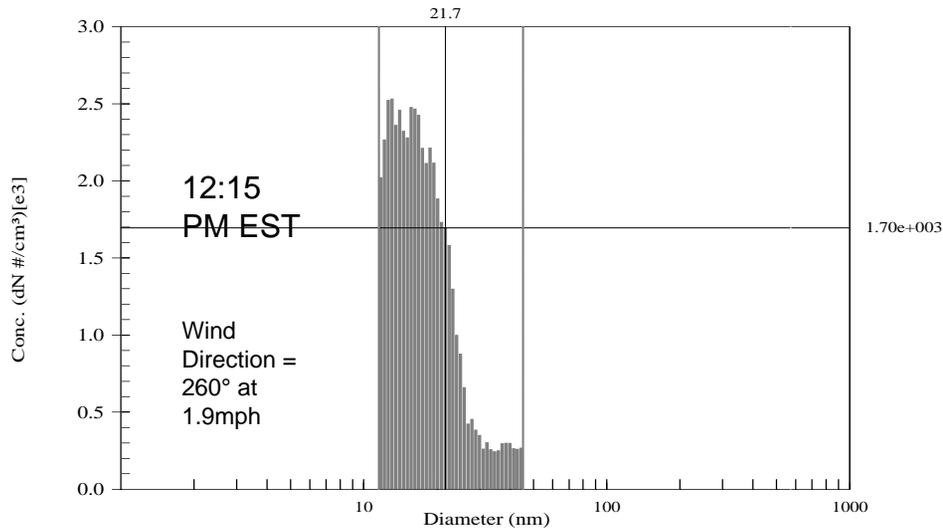
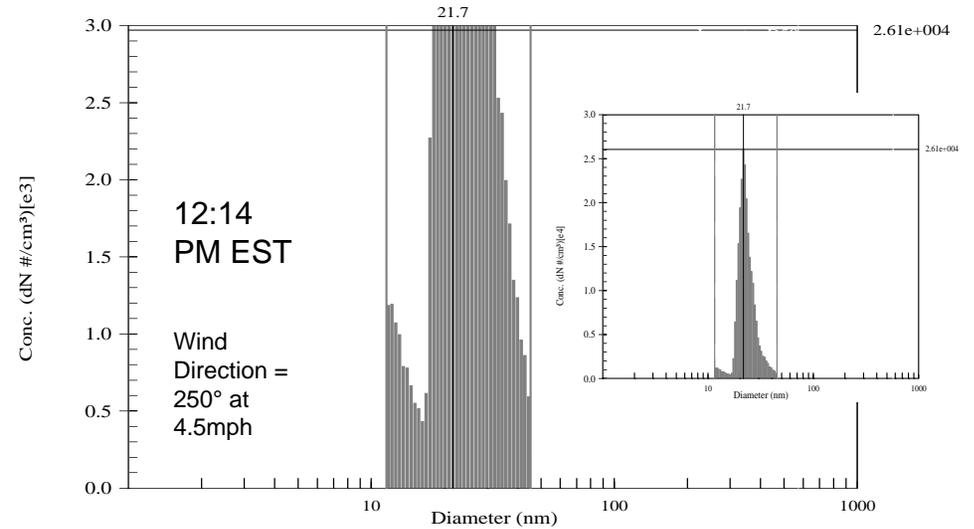
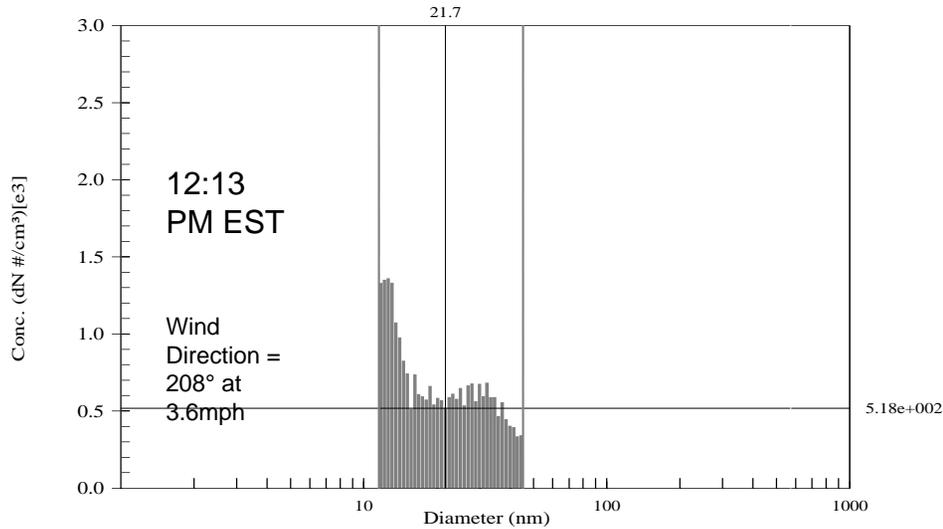
Few amine particles from the north and west relative to the total particle hits



Customer Focus

Emission Profile of a Diesel Locomotive using SMPS

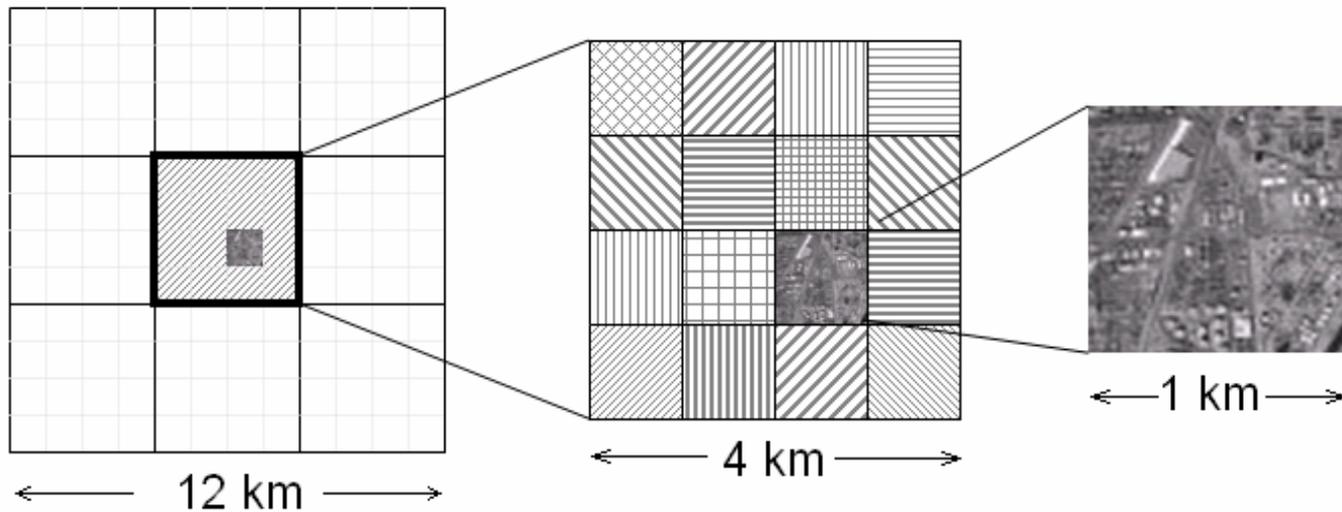
Two Amtrak Diesel Engines Attached to One Another (No Freight Cars) Passing the MLK Site at 12:14 PM EST (6/08/05)



Customer Focus

Analyzing Sub-Grid Variability

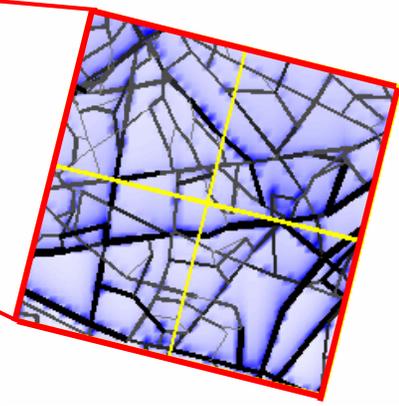
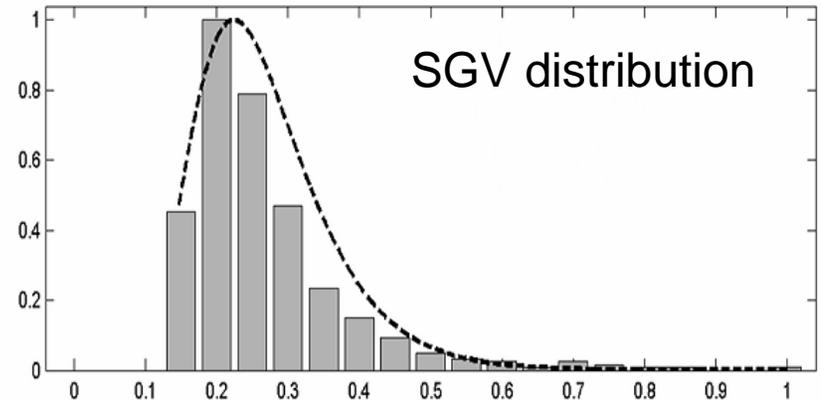
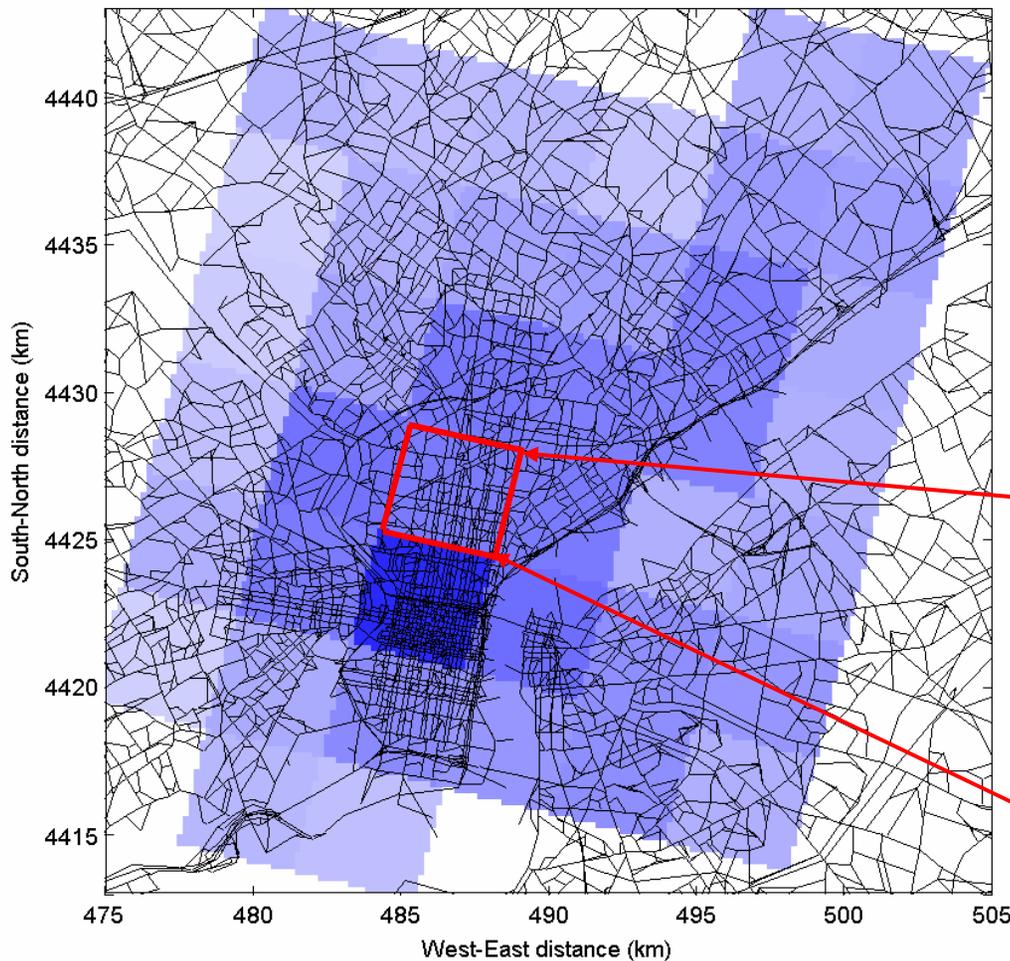
Typically, photochemical models provide results at a coarse grid resolution
For every grid resolution, there are sub-grid features:



Customer Focus

Analyzing Sub-Grid Variability

CMAQ 4x4 km grid



Local details within a grid cell

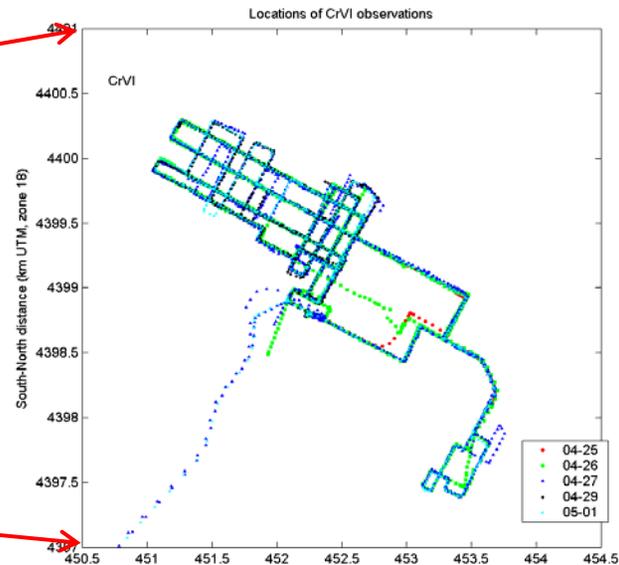
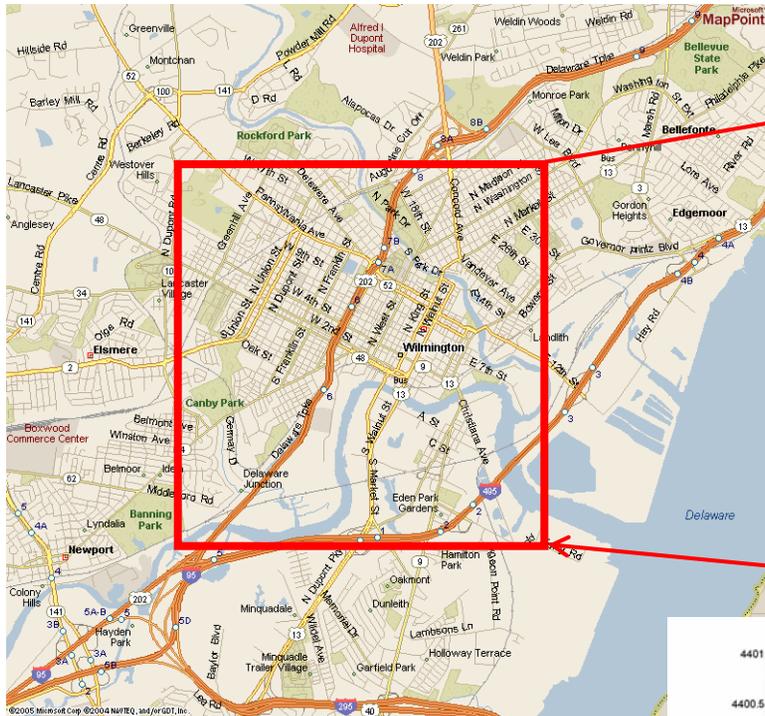
Detailed fine-scale measurements are needed for model evaluation

Customer Focus

Analyzing Sub-Grid Variability

Using Fine-Scale Mobile Measurements to Analyze SGV

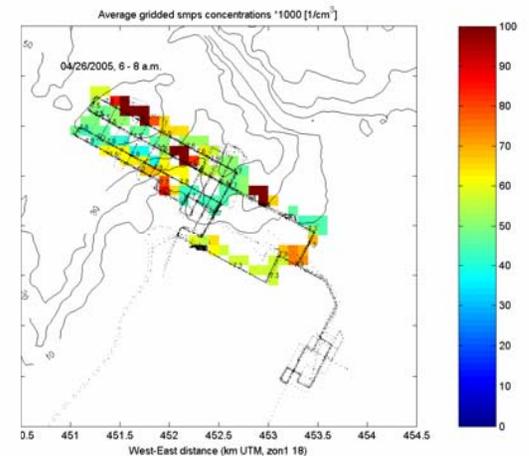
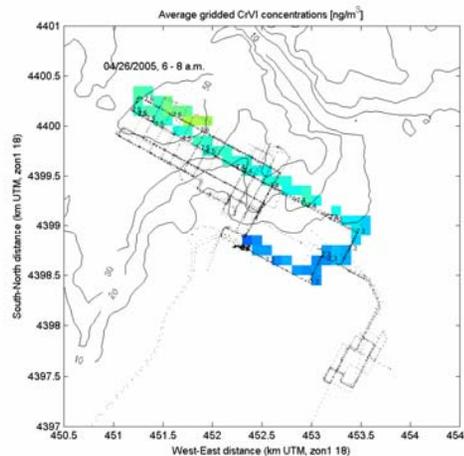
Locations of mobile measurements in Wilmington, DE



4 km x 4 km
area
represents
one CMAQ
grid cell

Examples:

3-hour average concentrations
of CrVI and fine particulates
from mobile measurements
in Wilmington, DE



Conclusions

- ❑ Real-Time Mass Spectrometry will enable DNREC to better define potential source impacts at the MLK site. This information will be helpful in defining control strategies.
- ❑ Mobile Monitoring will help with the evaluation of the modeling exercises that are being performed as part of this toxics project.
- ❑ A lot still needs to be done.

Progress Report

- Spring and Summer Sampling intensives are complete.
- Need to complete the Fall and Winter intensives.
- Data analysis to meet project objectives.

Questions

