Atmospheric Aerosol Source-Receptor Relationships: The Role of Coal-Fired Power Plants

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Atmospheric Particulate Matter

PM-2.5 Standard Promulgated in 1997

Design of efficient and effective control strategies requires understanding:

- What PM component(s) cause adverse health effects
- The contribution of various sources to current PM levels
- How PM concentrations respond to emission changes of a given source or sources
Sources of Fine PM and Their Precursors

PM-2.5 Composition during the Winter of 1999 in Philadelphia
Coal-Fired Power Plants and PM-2.5

PM-2.5 Composition during the Winter of 1999 in Philadelphia
Objectives of the Pittsburgh Air Quality Study

- Characterize PM and its sources in the Pittsburgh area
- Quantify the impact of the various sources (transportation, power plants, biogenic, etc.) to the PM concentrations in the area
- Improve our understanding of the responses of PM to changes in emissions
- Develop and evaluate the next generation of atmospheric PM monitoring techniques (real time single particle measurements, ultrafine PM, organics, continuous, etc.)
- Elucidate the links between PM and health
- Quantify the relationship between indoor and outdoor concentrations

See homer.cheme.cmu.edu
The Pittsburgh Air Quality Study (PAQS)

OBJECTIVES & HYPOTHESES

- Ambient Measurements
- Instrument Development
- Health Effects
- Source Apportionment
- Source Characterization

DOE

EPA
Current Team Members

- S. Pandis, C. Davidson, A. Robinson, N. Donahue [CMU] (NSM distributions, ions, metals, ozone, NOx, HNO₃, NH₃, VOCs, size-resolved measurements)
- A. Wexler, [U.C. Davis] (Single particle mass spectrometry, organic aerosols)
- M. Johnston [U. Delaware] (Single particle mass spectrometry, organic aerosols)
- W. Rogge [Florida Int.] (Organic speciation)
- B. Turpin [Rutgers] (OC/EC, FTIR, organic characterization)
- S. Hering [Aerosol Dynamics] (Semi-continuous nitrate, sulfate, carbon)
- D. Eatough [BYU] (Organic/Inorganic sampling)
- J. Ondov [U. Maryland] (Semi-continuous metals)
- S. Buckley [U. Maryland] (Single-Particle metals metals)
- M. Hernandez [U. Colorado] (Bioaerosols)
- J. Collett [Colorado State] (Peroxides, fogwater)
- U. Baltensperger [Paul Sherrer Inst.] (Surface area)
- K. Christ [Ohio U.] (Satellite sites, data management)
- G. Cassucio [RJ Lee Group] (Morphology, coarse single particle analysis)
- J. Kahl [U. Wisconsin] (Meteorology)
- P. Hopke [Clarkson] (Source-receptor relationships)
- L. Barrie [PNNL] (Organics)
- C. White [DOE-NETL] (Organics)
Support

**Direct:**
- DOE (45%)
- EPA (45%)
- Carnegie Mellon University and others (10%)

**Indirect:**
- EPA speciation network
- Allegheny County Health Department
- Pennsylvania DEP
- Ohio EPA
- West Virginia EPA
Why Pittsburgh?

Predicted PM$_{2.5}$ Aerosol for the Eastern US  *(July 10, 1995)*
Ambient Measurements

Objectives:

- Examine Atmospheric Process
- Evaluate Deterministic Air Quality Models
- Statistical Source-Apportionment
- Examine Health Effects
- Indoor-outdoor relationships
Baseline Ambient Measurements

May 01–Oct 02 (18 months)

Almost continuous:
- Number distribution (3 nm - 10 μm)
- Surface area
- TEOM PM mass
- OC/EC
- Sulfate/nitrate/carbon
- Single particle size composition
- Gases (O₃, NOₓ, CO, SO₂)
- Meteorology, Visibility

Daily averages:
- PMₓ Mass
- PM₂.₅ Composition
- PM₁₀ Composition
- Gases (VOCs, HNO₃, NH₃)
- Bioaerosols
- Hydrogen and organic peroxides

Other:
- Organic speciation (2 weeks)
- Cloud-fog composition
**Intensive Ambient Measurements**

**Three Intensive Sampling Periods**
- July 2001
- January 2002
- October 2002

**Increased frequency of all measurements**
- **PLUS:** Size-resolved composition, PC-BOSS, FTIR, Organic Partitioning, Semi-continuous metals, LIBS, TDMA-RSMSII, CCN measurements, etc.

**Coordination with Other Studies**
- DOE
- EPA Supersite
- Other
Sites in the City of Pittsburgh

- Lawrenceville
- CMU Supersite
- Hazelwood
Remote Satellite Sites

- Steubenville
- Wheeling
- Florence
- Greensburg
- Holbrook
- Athens
Supersite Location: Carnegie Mellon University

Location of Central Supersite
Advanced Ambient Measurements

- Continuous Size Distributions
- Single Particle Characterization
  - Single Particle Mass Spectrometry
  - Laser Induced Breakdown Spectroscopy
- Semi-Continuous Metals
- Semi-Continuous OC/EC
- Semi-Continuous Nitrate, Sulfate, and Carbon
- Continuous Particle Surface Area
- Organics Speciation
Continuous Measurements of Particle Size Distributions

![Graph showing particle size distribution over time]

- **$D_p$ (nm)**
- **Log$_{10}(dN/d\log D_p)$**

**Total #**

**Volume**
On-Line Single Particle Measurement
(size and composition)

Three Instruments:
- RSMS-III - Wexler (UC Davis)
- APS-IMS - Johnston (U. Del.)
- LIBS – Buckley (U. Maryland)

Applications:
- Ambient measurements
- Source characterization
- Advanced source apportionment

RSMS – Single Particle Mass Spectrometer
PI: Wexler
Single Particle Classification

Class 1 - 74.0%

Normalized Peak Area

Mass to charge ratio (m/z)

Fraction Total Particles in Size Bin

Fraction Total Particles in Wind Dir. Bin

Most prevalent particle class in Atlanta August 1999. (Pl Wexler)
Semi-continuous metals measurements allow identification of individual sources.

Measurements of Se & Ni in College Park, MD

PI: John Ondov
Source Apportionment of Primary vs. Secondary PM

PM-2.5 Composition during the Winter of 1999 in Philadelphia
Statistical Source-Measurement for Primary PM-2.5 Composition during the Winter of 1999 in Philadelphia

PM-2.5 Composition during the Winter of 1999 in Philadelphia
Traditional Statistical Source Apportionment

Ambient Data + Source Fingerprints

- Power plant
- Trucks
- Smelter
- Cars
- Wood smoke
Advanced Statistical Source Apportionment

Combining PM and meteorology data allows identification of source regions.

PI: P. Hopke

Source regions for As in Underhill, VT
Source Characterization

Objectives:

- Update source fingerprints for CMB
  - Steel industry
  - Coal fired boilers
  - Mobile sources
  - Wood burning

- Advanced source characterization
  - Organics
  - Single Particle
Dilution Sampling: Organic PM Emissions From Combustion Systems

- Plume processes effect volatile PM emissions
- Organic fingerprints for source apportionment
- Characterization of sources with single particle instruments

Schematic of Portable Dilution Sampler
Dilution Effects Emissions

Dilution sampling on a pilot-scale combustor

Dilution Stack Sampler

Organic Aerosol Emissions

µg Organics

Dilution Ratio

0x  27x  36x  46x  49x  95x
Single Particle Source Characterization

Objective: Combining single particle ambient and source data may allow source apportionment on a particle by particle basis.

Two Systems:
- APS-IMS - Johnston (U. Del.)
- LIBS – Buckley (U. Maryland)

LIBS: Single Particle Metals Data
LIBS system deployed at Gallo Glass Furnace #1.
Single Particle Source Apportionment

LIBS provides elemental composition of particle. Associations between elementals potentially allow source identification on a single particle basis. **PI: Buckley**
Deterministic Modeling to Apportion Secondary PM

PM-2.5 Composition during the Winter of 1999 in Philadelphia

Secondary PM:
- Deterministic Models
Atmospheric processes and PM-2.5

Primary Pollutants

Dispersion

Reactions

Secondary Pollutants

Aqueous-phase chemistry

Atmospheric aerosol

Acid Rain

EMISSIONS

Atmospheric processes and PM-2.5
Grid to model PM in the Eastern US
Predicted Ozone and Sulfate
July 15, 1995 (2:00 p.m.)

OZONE

SULFATE
Model Evaluation

Los Angeles Air Basin
Model Performance in Los Angeles, CA

Observed Concentration, µg m⁻³

Predicted Concentration, µg m⁻³

Nitrate
Sulfate
Ammonium
Organic Carbon

UAM-AERO
Southern California
October 17-20, 1995
Multiple sites
The Source-Receptor Challenge: Interactions between Fine PM and Their Precursors

PM-2.5 Composition during the Winter of 1999 in Philadelphia
Nonlinear interactions determine effect of Sulfur controls on PM levels.

- **Reduced S emissions**
- **HNO$_3$ Present**
- **No HNO$_3$**

Conditions:
- Temp = 278 K
- RH = 70%
- $\text{NH}_3$ = 3 $\mu$g m$^{-3}$
Response of Ozone and PM$_{2.5}$ Concentrations to VOC and NO$_x$ controls in L.A.

Fine PM can increase for significant reductions of VOC emissions if NO$_x$ is not reduced too (formation of additional nitric acid)
Results and Expected Benefits

- Comprehensive characterization of PM in Pittsburgh region
- Development of database for evaluation of air quality models
- Updated fingerprints for critical sources
- Development of next generation of source apportionment techniques
- Quantify the contribution of coal-fired power plants to primary and secondary PM
- Evaluation of emission control strategies
PM Characteristics and Health

- Total number (N)
- Total surface area (S)
- PM$_x$, PM$_{2.5}$, PM$_{10}$, PM$_{x-y}$
- Metals (Fe, Mn, etc.)
- Sulfate (PM$_{2.5}$, PM$_{10}$)
- Nitrate (PM$_{2.5}$, PM$_{10}$)
- OC (PM$_{2.5}$, PM$_{10}$)
- EC (PM$_{2.5}$, PM$_{10}$)
- Acidity
- Bioaerosols
- Polar Organics
- Non-polar organics
- Specific organic classes
- Hydrogen and organic peroxides
- Total soluble PM$_{2.5}$, PM$_{10}$
- Specific sources (diesel or gasoline combustion, power plants, ...)
- Gas-phase co-pollutants (CO, O$_3$, NO$_x$, SO$_2$, etc.)
- Combinations of the above
Epidemiology-Indoor Pollution

**EPIDEMIOLOGY** (Samet, Johns Hopkins)
- Collection of mortality and morbidity data from emergency rooms in Oakland
- Use of time-series analysis relating the PM measurements to the health effects
- Coordination with Baltimore Supersite using common measurements
- Complimentary panel study of susceptible populations (children with asthma, chronic obstructive pulmonary disease, and ischemic heart disease).

**INDOOR POLLUTION** (Sextro, LBNL)
- Indoor measurements in Pittsburgh houses
- Testing of models