SOURCE SAMPLING AND CHARACTERIZATION USING A SINGLE PARTICLE MASS SPECTROMETER DURING THE PITTSBURGH SUPERSITE EXPERIMENT

Keith J. Bein, Yongjing Zhao, Anthony S. Wexler
University of California, Davis
Eric Lipsky, Allen L. Robinson
Carnegie Mellon University
Murray V. Johnston
University of Delaware
Source Sampling
Purpose

- Sample and characterize emissions from several air pollution sources in Pittsburgh, Pennsylvania, using a single particle mass spectrometer and a SMPS.
- Create source profiles of single particle size and composition and use profiles to isolate sources within the Pittsburgh Supersite ambient data set.
- Validate that ambient classes of particles correspond to specific sources or source categories.
- Use ambient single particle and SMPS data to obtain quantitative estimates of source contribution, for each source, on a particle number basis.
Experimental

- **Dilution Sampling – wood smoke and diesel exhaust**
  - Diesel Engine
    - Yanmar Single Cylinder 4500 kW Generator
    - Run at Steady Load
      - Low Load (25% Capacity)
      - Medium Load (55% Capacity)
  - Wood Stove
    - Blend of Oak, Cherry, and Ash
    - Sample during flaming period after initial start-up

- **Bag Sampling - USS Clairton Coke Works**
  - Samples were collected in a large Teflon bag
  - Teflon bag was transported to a lab where the samples were characterized using RSMS-2 and a SMPS
Data Analysis

- **Source Sampling**
  - Classification - single particle spectra were organized into particle classes based upon the distribution of their mass peaks
    - Each particle class represents a different type of particle and is used as a signature for that source
    - Multiple classes were isolated within the emissions of single sources

- **Ambient Data**
  - Subset of the Pittsburgh Supersites data – July, 2002
    - Single particle spectra were classified into particle classes
    - Source signatures were used to associate ambient classes with sources
    - Number distributions were constructed for ambient classes by combining single particle and SMPS data
      - Class distributions were compared to total distributions to obtain quantitative estimates of source contribution
    - Ambient classes were also correlated with wind direction measurements to identify the directions from which the ambient particles were most frequently observed
Wood Smoke Sampling

Wood Smoke Classification

- K (carbon ~ DL) 29.6%
- EC/OC/K 31.9%
- EC/OC (C1 - C3) 3.1%
- K/KCl (carbon ~ DL) 2.4%
- K/KCl/Na (carbon ~ DL) 0.4%

RSMS dN/dlogDp (#/cc)

K containing particles
- $D_p1 = 80$ nm, $\sigma_g1 = 1.5$
- $D_p2 = 300$ nm, $\sigma_g2 = 0.8$

EC/OC particles
- $D_p = 70$ nm, $\sigma_g = 1.4$

Dilution Sampling

Temporal distribution of EC/OC/K particles during the month of July, 2002

Quebec Wildfires (7PF-24)

Ambient Data

Missing data

Fractions of total number of EC/OC/K particles

Dilution Sampling Ambient Data

2.4x10^{-2}
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

Time (hours elapsed since July 1, 00 EST)

Fraction of total number of EC/OC/K particles

Temporal distribution of EC/OC/K particles during the month of July, 2002

Quebec Wildfires (7PF-24)
Wood Smoke Sampling – Ambient Data

- Large scale forest fire (July 7th): EC/OC/K particles account for ~ 30 – 80% of the total number distribution, depending on particle size
- Average day in July (17th): ~ 10 – 40%
- Low day in July (3rd): ~ 2 – 15%
Diesel Sampling

Spectral representation of EC/OC/Ca class isolated during diesel source sampling

C$^+$
C$^+$
C$^+$
Ca$^+$
CaO$^+$

Spectral representation of dominant EC/OC/Ca class isolated from July, 2002, ambient data

C$^+$
C$^+$
C$^+$
Ca$^+$
CaO$^+$

Dilution Sampling

Ambient Data

Temporal distribution of EC/OC-Ca particles during the month of July, 2002

Fraction of particles per sampling interval that are EC/OC-Ca

Missing data
Diego Sampling – Ambient Data

- Average day in July (3rd & 17th): EC/OC/Ca particles account for ~ 0.8 – 13% of the total number distribution, depending on particle size

- During dilution sampling, only 2 – 4% of the diesel particles sampled were EC/OC/Ca particles (12PF-29)
USS Clairton Coke Works Sampling

Classification of 09/03/02 Clairton Coke Works Sampling

- Amines/EC/OC
- Unidentified Organics
- Li/Na/K
- Na/Al/Si/K/Fe/Ga
- EC/OC
- Na/K/Pb
- Amines/Na/K

Bag Sampling

09/03/02 Clairton Coke Works Sampling: Number Distributions - RSMS and SMPS

- RSMS measured - EC/OC/Amine particles
  - \( D_{p1} = 60 \text{ nm}, \sigma_{p1} = 1.6 \)
  - \( D_{p2} = 190 \text{ nm}, \sigma_{p2} = 1.3 \)
- SMPS measured - all particles

Ambient Data

Temporal distribution of amine containing particles during the month of July, 2002

Shenango
(297°, ~ 13 km)

USS Clairton
(160°, ~ 16 km)
USS Clairton Coke Works Sampling - continued

**July 3rd, 2002**

- Average number distribution of EC/OC/Amine particles (24hr)
  - $D_{p1} = 100 \text{nm}$, $\sigma_{g1} = 1.3$
  - $D_{p2} = 170 \text{nm}$, $\sigma_{g2} = 1.6$
- Contribution of EC/OC/Amine particles to the total number distribution (SMPS)

---

**July 18th, 2002**

- Average number distribution of EC/OC/Amine particles (24hr)
  - $D_{p1} = 70 \text{nm}$, $\sigma_{g1} = 1.2$
  - $D_{p2} = 220 \text{nm}$, $\sigma_{g2} = 1.6$
- Contribution of EC/OC/Amine particles to the total number distribution (SMPS)

---

**Bag Sampling**

- Spectral representation of Na/Al/Si/K/Fe/Ga particles detected during Clairton sampling

---

**Ambient Data**

- Spectral representation of Na/Al/Si/K/Fe/Ga class isolated from July, 2002, ambient data
USS Clairton Coke Works – Ambient Data

Fraction of Na/Al/Si/K/Fe particles containing each element

Day of the month (July, 2002)

Zn  Cr  Sr  Ti  Mn  V  Ba  Ca  Li  Pb  Ga  Na  Al  K  Si  Fe

0.03 0.06 0.09 0.12 0.15

dN/dlogDp (#/cc)

4 5 6 7 8 9

100

Particle Diameter Dp (nm)

0.14 0.12 0.10 0.08 0.06 0.04 0.02

July 4th, 2002

Average number distribution of Na/Al/Si/K/Fe/Ga particles

Dp1 = 40 nm, σg1 = 1.3

Dp2 = 140 nm, σg2 = 1.4

Contribution of Na/Al/Si/K/Fe/Ga particles to the total number distribution

July 19th, 2002

Average number distribution of Na/Al/Si/K/Fe/Ga particles

Dp1 = 110 nm, σg1 = 1.5

Dp2 = 340 nm, σg2 = 1.3

Contribution of Na/Al/Si/K/Fe/Ga particles to the total number distribution (SMPS)

3 major CFPP
(301°, 298°, 280°)
Conclusions

- Wood smoke, diesel exhaust and emissions from USS Clairton Coke Works were characterized on the basis of size and composition using a single particle mass spectrometer and a SMPS.

- Multiple particle classes were identified from each source and used in conjunction with size data to construct source profiles.

- Several of these particle classes were isolated within a subset of the ambient data collected during the Pittsburgh Supersite experiment indicating that ambient classes of particles correspond to specific sources or source categories.

- This was further validated by correlating the ambient particles with the wind directions from which they were most frequently observed and matching those directions to the locations of the sources.

- Particle number distributions within the ambient classes were constructed from a combination of single particle and SMPS data and were used to obtain quantitative estimates of source contribution.

- Road dust and emissions collected from the ventilation shaft of a roadway tunnel were also sampled and characterized during this series of experiments but were omitted from this presentation due to time constraints. For more details on these two experiments please see posters 12PF-29 and 12PF-34, respectively.
Acknowledgements

- This research was conducted as part of the Pittsburgh Air Quality Study which was supported by the US Environmental Protection Agency under contract R82806101 and the US Department of Energy National Energy Technology Laboratory under contract DE-FC26-01NT41017. This paper has not been subject to EPA's peer and policy review, and therefore does not necessarily reflect the views of the Agency. No official endorsement should be inferred.