IDENTIFICATION OF SOURCES OF ATMOSPHERIC PM AT THE PITTSBURGH SUPERSITE: RSMS III AND FILTER-BASED PMF

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INTRODUCTION

Three collocated samplers collected trace element and single particle composition data during the Pittsburgh Air Quality Study (PAQS). Datasets are compared and several hypotheses are discussed to further identify sources of $PM_{2.5}$.

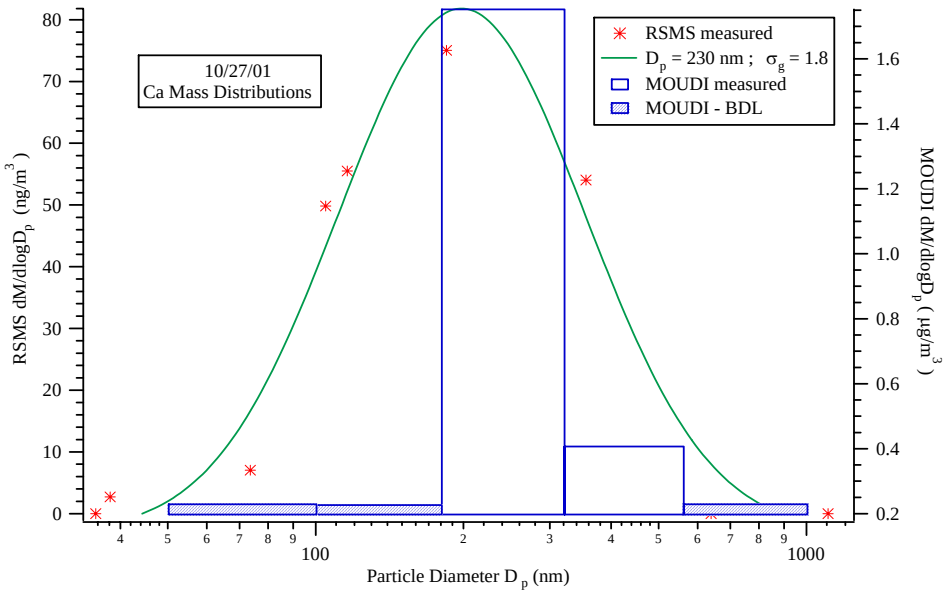
- RSMS III
  - Laser ablation time-of-flight mass spectrometer with 9 orifices corresponding to size bins between 30 and 1100 nm in diameter
  - Collected high time resolution data from Sept. 2001 – Sept. 2002
  - Provides composition and size distribution of single particles
- Filter-based samples collected using a $PM_{2.5}$ hi vol
  - Cellulose filters digested and analyzed by ICP-MS for trace element concentration
  - 24-hour samples collected from July 2001-July 2002
  - Trace element data used along with sulfate, nitrate, organic and elemental carbon data in PMF source-receptor model determined 11 factors or major sources of $PM_{2.5}$
- Filter-based samples collected using a MOUDI
  - Three dates of size-resolved samples analyzed by ICP-MS for size distributions of several elements

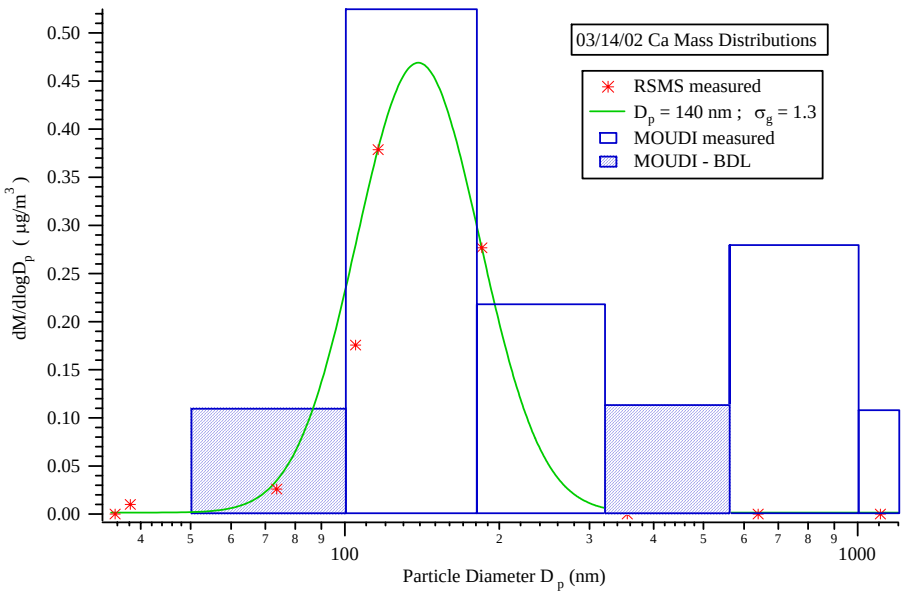
Hypothesis 1: Weighting RSMS data by D_p^3 compares with bulk elemental composition data from ICP-MS

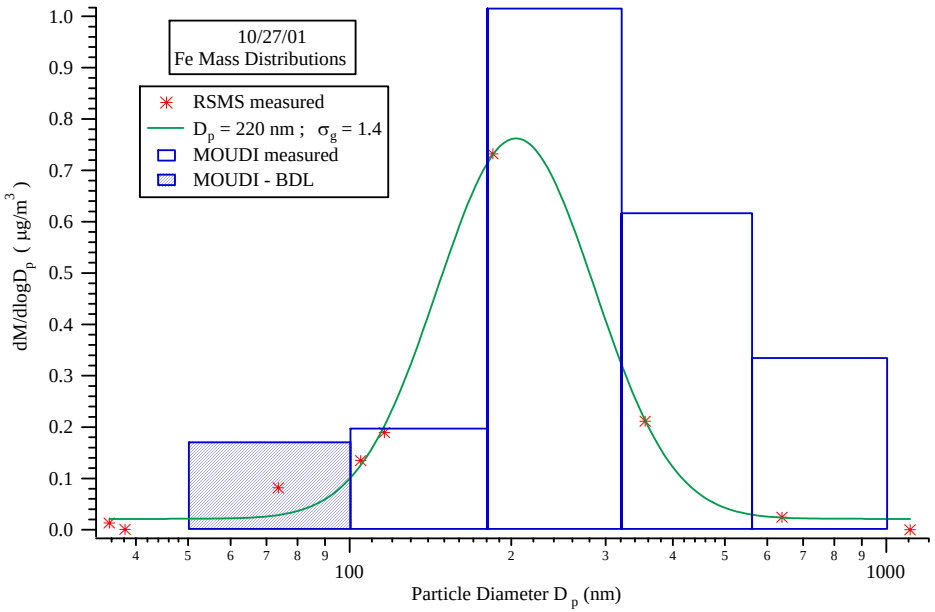
- Single particle data from the RSMS were converted from number distributions to mass distributions by weighting the number distributions by D_p^3, where D_p is particle diameter

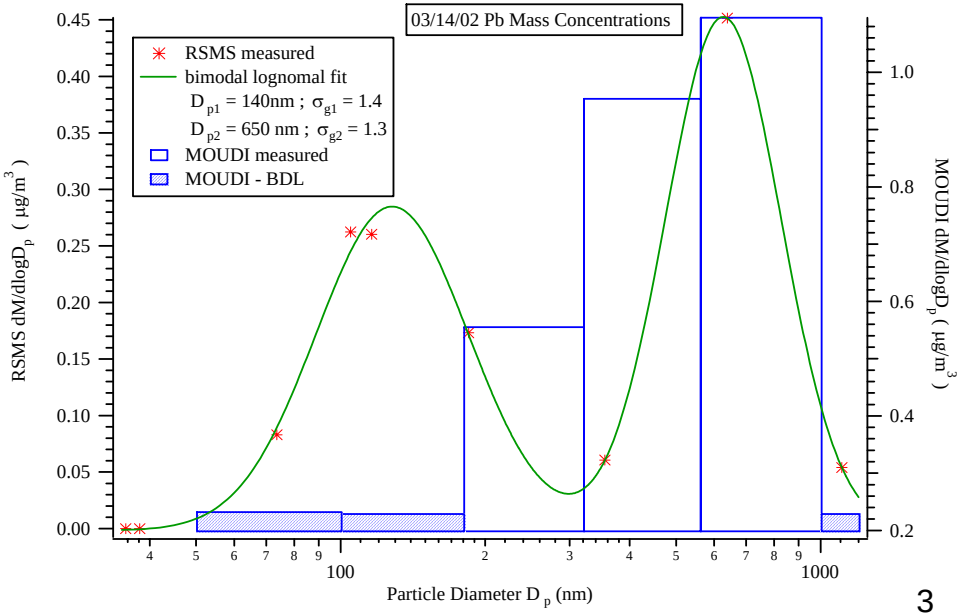
$$\left(\frac{dM}{d\log D_p}\right)_{i,g} = \rho\frac{\pi}{6}\left(D_p\right)^3_{RSMS,i}\left(\frac{dN}{d\log D_p}\right)_{i,g}$$

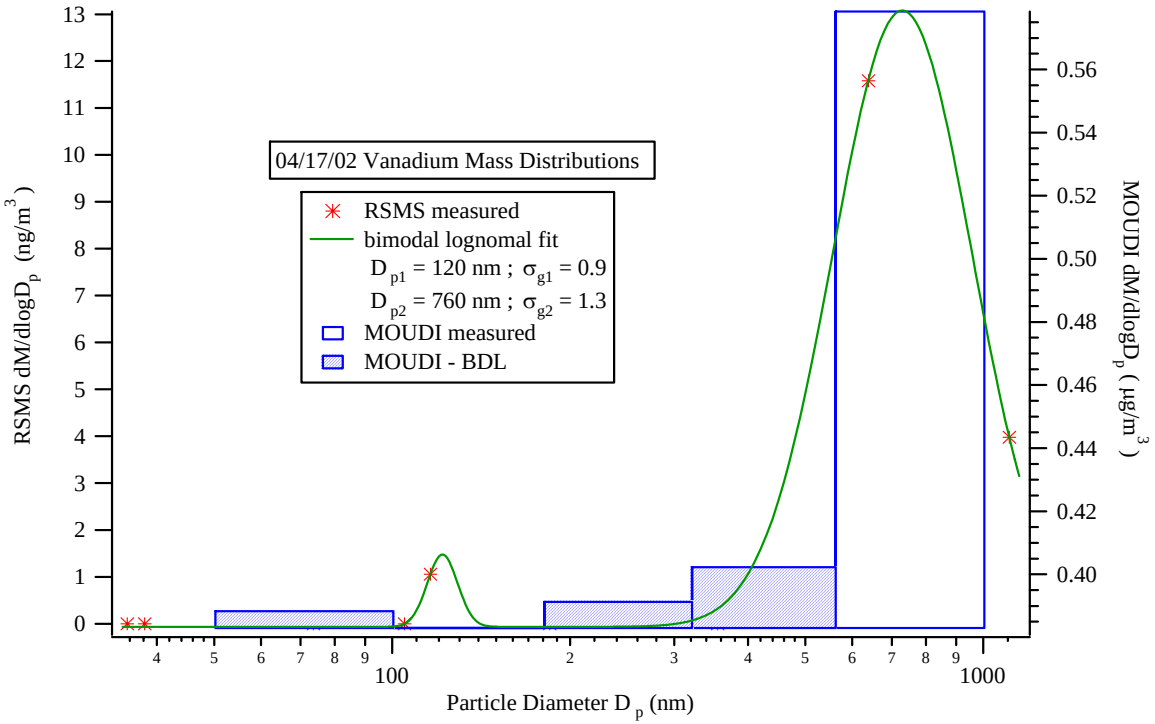
- $\left(\frac{dM}{d\log D_p}\right)$ and $\left(\frac{dN}{d\log D_p}\right)$ are the mass and number distribution function, respectively, of group of particles *g* measured at orifice *i*
- ρ is the assumed density of the particles
- Mass distributions derived from RSMS data are compared with mass distributions from MOUDI analysis


10/27/01
Ca Mass Distributions
RSMS measured
D_p = 230 nm ; σ_g = 1.8
MOUDI measured
MOUDI - BDL
RSMS dM/dlogD_p (ng/m^3)
MOUDI dM/dlogD_p (μg/m^3)
Particle Diameter D_p (nm)


03/14/02 Ca Mass Distributions
RSMS measured
D_p = 140 nm ; σ_g = 1.3
MOUDI measured
MOUDI - BDL
dM/dlogD_p (μg/m^3)
Particle Diameter D_p (nm)


10/27/01
Fe Mass Distributions
RSMS measured
D_p = 220 nm ; σ_g = 1.4
MOUDI measured
MOUDI - BDL
dM/dlogD_p (μg/m^3)
Particle Diameter D_p (nm)

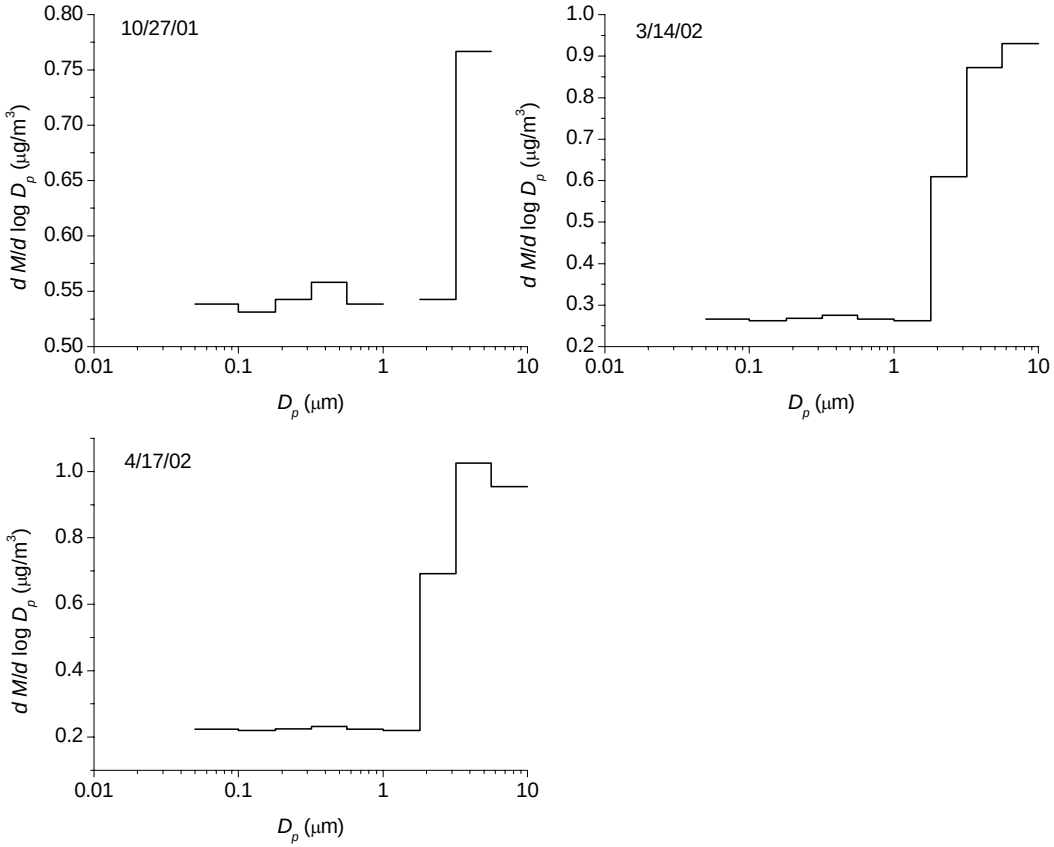

03/14/02 Pb Mass Concentrations
RSMS measured
bimodal lognomal fit
D_p1 = 140nm ; σ_g1 = 1.4
D_p2 = 650 nm ; σ_g2 = 1.3
MOUDI measured
MOUDI - BDL
RSMS dM/dlogD_p (μg/m^3)
MOUDI dM/dlogD_p (μg/m^3)
Particle Diameter D_p (nm)



The particle diameters for the concentration peaks are generally in agreement with some exceptions.

Hypothesis 2: Lack of Titanium in RSMS data compared with appreciable amounts measured by ICP-MS reflects a significant amount of Ti between 1.1 and 2.5 μm

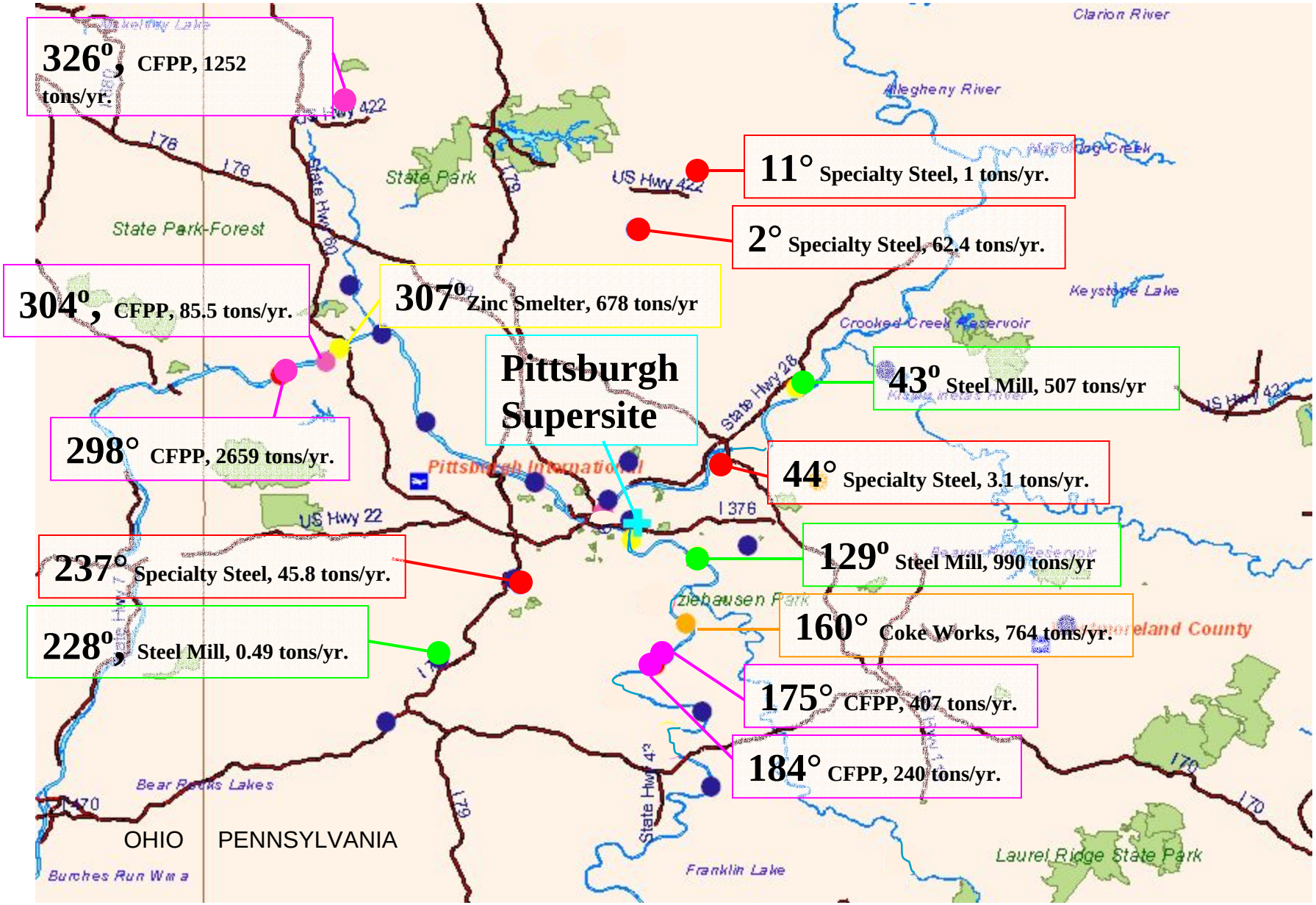
- Three dates of MOUDI filters analyzed by ICP-MS for Ti size distribution
- RSMS III maximum size measured is 1.1 μm
- All Ti concentrations on MOUDI stages less than 1.8 μm are below detection
- Ti size distributions show that Ti exists almost completely in particles of sizes greater than 1.8 μm in diameter, which is larger than the cutoff of the RSMS III



Hypothesis 3: Molybdenum and chromium are found together in RSMS individual particles and the PMF results. Combining datasets allows identification of sources.

- RSMS particle class: Cr/Mo/MoO/W
  - 0.13% of total particle hits (a minor class)
  - Few negative ions associated with these particles (8.9% of the positive spectra also had a negative spectrum), indicative of a local source
  - Most frequent directions were SW at 235° and SE at 129°
    - SE source: existing steel mill at 129°, 8.7 km from site
    - SW sources: steel mill 228°, 32 km; specialty steel plant 237°, 16 km
- PMF Factor: specialty steel (with Mo and Cr tracers)
  - CPF analysis shows most probable direction of this source SE at 105° and NNE at 15°
  - PSCF analysis indicates influence from local sources SE and NNE
    - NNE sources: specialty steel plants at 43° and 26 km away, 2° and 45 km, 11° and 51 km, 10° and 112 km, 44° and 11 km
- Presence of Cr and Mo, dominant wind direction (SE), and proximity of the source to the monitoring station are in agreement between the RSMS and ICP-MS/PMF data, and most probable directions point to existing specialty steel sources

Map of major $PM_{2.5}$ sources in the Pittsburgh region. Degrees from Supersite, facility type, and tons/year of $PM_{2.5}$ emitted in 1999 are given for sources described elsewhere on this poster. (CFPP = coal-fired power plant)



Hypothesis 4: Iron, Manganese, and Zinc mark a PMF factor but RSMS data suggest that these elements are not associated with the same particles. This suggests external mixing of the particles, possibly from steel production.

- Two RSMS particle classes associated with steel production: Li/Na/K and Fe
  - Li/Na/K class: 2.3% of total particle hits, and predominant wind direction was SE at 120°
  - Fe class: 1.2% of total particle hits, and predominant wind direction was SE at 125°
    - SE source: existing steel mill at 129°, 8.7 km from site
- PMF Factor: Fe, Mn, and Zn (likely from steel production industry)
  - Mass of K in this factor is significant (39%) but ambient concentrations of K did not correlate strongly with the factor source contributions so it is not considered a tracer for this source
  - CPF analysis shows most probable direction of this source SE 115° - 145° in the direction of the steel mill at 129° and 8.7 km from the site
- The presence of Fe and K along with the SE most probable direction are in agreement for the RSMS data and ICP-MS/PMF results, suggesting this source of particles is the local steel mill SE of the site.

Hypothesis 5: Lead is common in many RSMS particle classes, including a Na/K/Zn/Pb class. Pb is found in its own source category in the PMF results. A variety of Pb sources is most likely responsible for ambient Pb concentrations.

- RSMS particle class: Na/K/Zn/Pb
  - 2.9% of total particle hits, and predominant wind direction was NW at 300°
    - Zinc smelter in this direction, 307°
- PMF Factor: Lead source
  - There are many point sources of lead in the Pittsburgh area in all directions from the supersite
  - CPF analysis shows most probable direction of this source NNW 330° - 360°
- The Na/K/Zn/Pb particle class and the PMF Pb factor are most closely correlated; however, direction of the source differs by 30° and the importance of K and Zn in the particles is not reflected in the PMF Pb factor.
- Due to the presence of Pb in many particle classes detected by RSMS and the multitude of Pb point sources in the Pittsburgh region, it is clear that ambient Pb concentrations do not solely originate from one point source.

Hypothesis 6: The ICP-MS shows and abundance of selenium, although this is not seen in the RSMS data. Coal combustion is most likely the responsible source.

- RSMS did not detect particles containing a significant amount of Se
  - Se is contained in fine particulate ($PM_{2.5}$:PM_{10} = 0.97) so detection is not an issue of size
  - Mass-to-charge ratio, *m/z*, of Se is similar to that of several organic carbon compounds which could swamp the Se signal
  - Se is semivolatile and may spread in small amounts over several particles, making it difficult to detect in single particles by RSMS
- PMF Factor: Selenium source
  - PSCF analysis shows that the Ohio River Valley, SW of the site, is the most probable location
  - Se is typically associated with coal combustion, and there are several large coal-fired power plants in the Ohio River Valley
- Lack of detection of Se by RSMS could be due to the low ablation efficiencies and low instrument sensitivities for this element.

Hypothesis 7: Both RSMS and PMF analyses detect a source of gallium-containing particles NW of the site. Gallium could be from coal combustion but direction suggests possibly another, unknown source.

- RSMS particle class: Si/K/Fe/Ga
  - Largest class of metal-containing particles in the dataset
  - Majority of particles fall in 100-300 nm size range, suggesting high temperature combustion
  - Dominant wind direction at 305°
- PMF Factor: Gallium-rich (with significant amounts of Ni, Cu, V, and As)
  - CPF and PSCF analyses show most probable location NW of site in NW Pennsylvania or NE Ohio
    - Coal-fired power plants in this direction: 298° and 45.5 km from the site, 304° and 42 km, 326° and 66 km
- This source to the NW could be a coal combustion source(s) with distinctly different source profile from the more dominant S and SW sources, or an as yet unidentified source of gallium.

CONCLUSIONS

Comparison of RSMS, ICP-MS/PMF, and MOUDI data shows converging conclusions in several of the hypotheses presented here, increasing confidence in the different techniques' identification of sources of $PM_{2.5}$.

- Convergent conclusions:
  - Identification of several local specialty steel sources
  - Iron- and potassium-containing particles attributed to the steel mill SE of the monitoring station
  - Sources of lead particles to the NW
  - Source(s) of gallium-containing particles to the NW
- Divergent conclusions:
  - Lack of manganese and zinc in the particles from steel mills that was reflected in the PMF analysis
  - Lack of zinc and potassium in the PMF-modeled lead factor that otherwise compared well with the RSMS Zn/K/Na/Pb particle class
  - Lack of selenium in RSMS data, while selenium was detected in abundance by ICP-MS
- Examination of converging and diverging results from comparative studies such as this will hopefully result in improved understanding of each technique.

Acknowledgements

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