Mass Balance Closure and the Federal Reference Method for PM$_{2.5}$ in Pittsburgh

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Overview

- Compare FRM PM$_{2.5}$ mass to the sum of aerosol chemical components
- Mass balance discrepancy
  - Positive: FRM $>$ $\Sigma$ chemical components
  - Negative: FRM $<$ $\Sigma$ chemical components
- Water
- Volatilization of Organics and Nitrate
PM$_{2.5}$ Concentration (µg/m$^3$)

15.9 µg/m$^3$ (annual average)
OM = OC x 1.8
Mass Balance - February 2002

(b) PM$_{2.5}$ Concentration (µg/m$^3$)

- FRM PM$_{2.5}$
- Nitrate, NH$_4$, EC, & Crustal
- Sulfate
- OM

Date (February 2002)
Daily Mass Balance Discrepancy

- Negative Discrepancy
- Positive Discrepancy
- 95% Confidence Interval

FRM PM2.5 (µg/m³) vs. FRM Mass Sum Components

- Positive Discrepancy
- Negative Discrepancy
Monthly Mass Balance

PM$_{2.5}$ Concentration (µg/m$^3$)

- Missing
- Crustal
- EC
- Ammonium
- Nitrate
- Sulfate
- OM

Jul Aug Sept Oct Nov Dec Jan Feb Mar
Hypotheses to Explain Mass Discrepancy

- **Water**: Positive mass discrepancy (FRM > components)
- **Volatileization**: Negative mass discrepancy (FRM < sum of components)
  - Organic volatilization
  - Nitrate volatilization
Measurements of aerosol water content

Dry inlet

Particle Sizers
Nano-SMPS
SMPS
APS

Wet inlet

DAASS: Dry/Ambient Aerosol Size Spectrometer 12PD-14

Estimating Aerosol Water at 35% RH

\[
M_{H2O} = \left( V_{wet} - \frac{M_{dry}}{\rho_{dry}} \right) \rho_{H2O}
\]

\[
\frac{1}{RH} = 1 + B \frac{M_{dry}}{M_{water}}
\]

Where \( V_{wet} \) is PM\(_{2.5} \) volume, \( M_{dry} \) is dry mass – sum of components, \( \rho_{dry} \) is dry density, and \( B \) is f(RH, composition).
Hourly Mass Balance

![Graph showing PM2.5 (ug/m³) over time from 7/20/01 to 7/25/01. The graph includes various compounds such as Crustals, OC, EC, NH₄, SO₄, NO₃, and TEOM.](image)
Water content seems impacted by acidity; the more acidic the atmosphere, the greater the aerosol water.

Corresponds to presence of NH$_4$HSO$_4$, a species with hygroscopic properties.
Volatilization of Organics

\[ y = 0.809x - 0.3443 \]

\[ R^2 = 0.96 \]

19% volatilization
OC mass loss from Teflon filter
Mass loss from volatilization of Nitrates
Good mass balance was achieved for the winter months.
Mass Balance Closure Winter 2002

- PM$_{2.5}$ Concentration (µg/m$^3$)
  - Measured Mass
  - Adjusted Mass

- FRM PM$_{2.5}$ 11.6 µg/m$^3$

- Components:
  - Water
  - Nitrate
  - OM
  - EC
  - Crustal
  - Ammonium
  - Sulfate
Conclusions

- Accounting for water and volatilization we can account for FRM mass in Pittsburgh
  - Water retention significant on acidic high PM days
  - Volatilization losses in winter corresponding to higher nitrate

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