An Overview of Chemical Speciation Fine Particle Monitoring Networks in the U.S.A.

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May 12, 2010

International Specialty Conference, Xi'an, China
Atmospheric Particles

- Small, discrete masses of solid or liquid matter.
- Examples: dust, smoke, mist, and fly ash.
- Defined and regulated by aerodynamic diameter $D_a$:
  - $\text{PM}_{2.5}$: $D_a < 2.5$ micrometers
  - $\text{PM}_{10}$: $D_a < 10$ micrometers
  - $\text{PM}_{\text{coarse}}$: $2.5 < D_a < 10$ micrometers
  - TSP: $D_a < 80$ to 100 micrometers (no size cut)
  - ultra-fine PM: $D_a < 0.1$ micrometers (not regulated)
Idealized Concentration Distribution of Particles in Ambient Air

- ULTRA-FINE
- WINDBLOWN DUST
- DROPLETS
- CONDENSATION
- Secondary Aerosols

Particle Aerodynamic Diameter, micrometers:
- TSP
- PM$_{10}$
- PM$_{2.5}$
- PM$_{COARSE}$

Relative Concentration
Reasons for Monitoring Fine Particulate Pollution

- Acid Precipitation – Nitrate and sulfate particles formed in the atmosphere deposit on land and water surfaces, causing acidification of water bodies.
- Visibility – Fine particles are responsible for much of the haze affecting national parks in the U.S.
- Health and ecological effects – Fine particles have been shown to have significant impact on human mortality and morbidity. Population exposure can come from both regional and local PM sources.
Three Major PM Speciation Networks

- **IMPROVE** - began in 1988 to monitor visibility degradation in National Parks.
  - [http://vista.cira.colostate.edu/views/](http://vista.cira.colostate.edu/views/)

- **CASTNET** – began in 1991 to monitor acid precipitation in the U.S.
  - [http://www.epa.gov/CASTNET](http://www.epa.gov/CASTNET)

- **CSN** – began in 1999 to monitor fine particulates based on health effects.
  - [http://www.epa.gov/ttn/amtic/speciepg.html](http://www.epa.gov/ttn/amtic/speciepg.html)
## Parameters Measured by Each Network

<table>
<thead>
<tr>
<th>Parameters</th>
<th>IMPROVE</th>
<th>CASTNET</th>
<th>CSN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass</td>
<td>PM$<em>{2.5}$, PM$</em>{10}$</td>
<td>PM*</td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Ions</td>
<td>PM$_{2.5}$</td>
<td>PM*</td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Trace elements by XRF</td>
<td>PM$_{2.5}$</td>
<td></td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>PM$_{2.5}$ carbon (OC/EC)</td>
<td>PM$_{2.5}$</td>
<td></td>
<td>PM$_{2.5}$</td>
</tr>
<tr>
<td>Visibility</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozone (hourly)</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>SO$_2$, HNO$_3$</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Meteorology</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

*CASTNET does not use a size-selective inlet for PM sampling.*
## Sampling Characteristics

<table>
<thead>
<tr>
<th></th>
<th>IMPROVE</th>
<th>CASTNET</th>
<th>CSN (MetOne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate</td>
<td>22.8 Lpm</td>
<td>1.5 Lpm</td>
<td>6.7 Lpm</td>
</tr>
<tr>
<td>Sampling Time</td>
<td>24 hours</td>
<td>168 hours</td>
<td>24 hours</td>
</tr>
<tr>
<td>Sample Volume</td>
<td>32.8 m³</td>
<td>15 m³</td>
<td>10 m³</td>
</tr>
<tr>
<td>Filter Diameter (total)</td>
<td>25 or 37 mm</td>
<td>47 mm</td>
<td>47 mm</td>
</tr>
<tr>
<td>Filter Area (sampled)</td>
<td>~3.5 cm² (for 25 mm filter)</td>
<td>~11.5 cm²</td>
<td>~11.5 cm²</td>
</tr>
<tr>
<td>Inlet</td>
<td>PM$<em>{10}$ head + PM$</em>{2.5}$ cyclone</td>
<td>Open face</td>
<td>PM$<em>{10}$ head + PM$</em>{2.5}$ cyclone</td>
</tr>
</tbody>
</table>
### Speciated PM by Filter Type

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>IMPROVE</th>
<th>CASTNET</th>
<th>CSN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon®</td>
<td>PM$_{2.5}$ mass, trace elements by EDXRF</td>
<td>PM (not sized) nitrate, ammonium, sodium, potassium</td>
<td>PM$_{2.5}$ mass, trace elements by EDXRF</td>
</tr>
<tr>
<td>2nd Teflon® (PM10)</td>
<td>PM$_{10}$ mass (not speciated)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nylon</td>
<td>Sulfate, nitrate, sodium, potassium, chloride (ammonium calculated)</td>
<td>Volatile nitrate Some gas-phase SO$_2$</td>
<td>Sulfate, nitrate, ammonium, sodium, potassium</td>
</tr>
<tr>
<td>Quartz</td>
<td>Organic and elemental carbon</td>
<td>--</td>
<td>Organic and elemental carbon</td>
</tr>
</tbody>
</table>
Gravimetric Mass

- Net mass is determined by difference: each filter is weighed twice, once before field sampling, and after the filter is returned from the field.

- Teflon filters received from the manufacturer are checked for defects and conditioned in a weighing chamber prior to the first weighing.

- Laboratory quality checks include lot stability checks, and trip and field blanks.
For CSN and IMPROVE, energy dispersive x-ray fluorescence (XRF) is used for the determination of up to 48 elements (sodium through lead).

XRF is nondestructive, and Teflon filters are being archived for many years by CSN and IMPROVE.

The detection limits vary by element, and range from 0.04 to 0.40 µg/filter. More sensitive methods, such as ICP/MS are also available for selected filters.
Water-extractable ions are measured using ion-chromatography.
The detection limits are low (~0.1 µg/filter).

Common cations:
- Ammonium - mainly associated with sulfate and nitrate
- Sodium - often from crustal sources and sea water
- Potassium - from crustal minerals, woodsmoke, fireworks

Common anions:
- Sulfate - produced by secondary reactions of sulfur dioxide
- Nitrate - mainly ammonium nitrate in fine fraction; can be volatile, so filter samples should be cooled to prevent loss
- Chloride - mainly from evaporation of water droplets
For the CSN and IMPROVE OC/EC methods, carbon species are operationally defined by a thermal-optical analysis method.

Individual compounds are not identified; only aggregate “organic” and “elemental” fractions are reported.

- **Organic carbon**
  - Includes many semi-volatile compounds (>C$_{20}$)

- **Elemental carbon (soot, black carbon)**
  - Graphitic carbon structures from sources such as diesel engines
  - May include high molecular weight non-volatile organics such as tar, biogenics, and coke.

- **Carbonate (optional analysis)**
  - Found in certain desert areas
  - Seldom found in most parts of the U.S.
OC/EC Thermograms

Thermogram - STN/CSN Method

Thermogram - Improve Method
Network Intercomparisons

The IMPROVE, CASTNET, and CSN networks differ significantly in several ways:

- site locations (rural vs. urban)
- species measured/reported
- sensitivity
- sampler technology
- filter sampling time
  - 24 hours (CSN & IMPROVE)
  - 169 hours (CASTNET)
CASTNET vs. IMPROVE and CSN

- CASTNET sampling differs in three important ways from CSN and IMPROVE:
  - Open-faced inlet does not exclude coarse PM
  - 7-day (CASTNET) vs. 24 hour (CSN and IMPROVE) sampling periods
  - CASTNET includes gaseous air pollutants and meteorological parameters
  - CASTNET currently does not measure trace elements
An EPA-sponsored study to compare CSN and IMPROVE monitoring results was carried out at six locations in the US, 2001 – 2004.

Three urban/rural site pairs were chosen in different areas of the U.S.

Three different CSN sampler types were used in the study (only MetOne SASS is currently in use)

Speciated PM$_{2.5}$ concentrations determined by the CSN and IMPROVE sampling and analysis protocols were statistically analyzed.
CSN vs. IMPROVE
Gravimetric Mass Intercomparison

Data from Phoenix, AZ, and Tonto National Monument monitoring sites, 2001 - 2004
CSN vs. IMPROVE
Sulfur and Sulfate Intercomparisons

Sulfur by XRF

Sulfate by Ion Chromatography

Data from Phoenix, AZ, and Tonto National Monument monitoring sites, 2001 - 2004
CSN vs. IMPROVE
Organic Carbon Intercomparison

Phoenix & Tonto monitoring sites
2001 - 2004

OC differences

IMPROVE Conc. (µg/m³)

CSN Conc. (µg/m³)

1:1 line
Regression

www.rti.org
CSN vs. IMPROVE
Nitrate Intercomparison

Phoenix & Tonto monitoring sites 2001 - 2004

No Evidence of differences in nitrate capture at Arizona sites.

1:1 line Regression
Many important species agree well. Slopes are near 1.00 for mass, sulfur, nitrate and sulfate.

Significant differences are found for organic carbon:

- EPA has decided to make the organic carbon measurements more similar by replacement of CSN's sampling and analysis methods for carbon.
Ames and Malm (2001) found concentration differences for nitrate measured by nearby CASTNET and IMPROVE sites:

- At western sites, CASTNET nitrate was significantly lower than IMPROVE nitrate. This was attributed to volatilization of sample from the Teflon filter used by CASTNET.
- At eastern sites, CASTNET nitrate concentrations were slightly higher than those from IMPROVE. This is possibly due to the open-face CASTNET sampler sampling additional coarse PM.
Each network has been optimized for its specific objectives, but PM data from the three networks for the same chemical species are not totally comparable:

- Agreement is good between CSN and IMPROVE for most chemical species, except for organic carbon.

- CASTNET inlet is not selective for PM$_{2.5}$, unlike CSN and IMPROVE; therefore, sulfate and nitrate PM results may not be comparable between CASTNET and the other two networks.
Lessons Learned

- Side-by-side sampling is very valuable to compare results between monitoring networks and establish comparability.
- Within-network collocation of samplers is important for assessing precision.
- Round-robin filter exchanges with other monitoring programs help establish comparability and identify problems.
- Blanks and other QC data should be monitored continuously to identify problems and minimize data loss.