IMPROVE Aerosol Measurements: Overview and Updates

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IMPROVE Network

• Interagency Monitoring of Protected Visual Environments
• Cooperative effort started in 1988 with ~30 sites
  – Expanded in 2000 to >170 sites
• Designed to monitor visibility-reducing particulate matter (PM) pollution in Class I areas
• Sponsors contribute ~$37k/year/site for
  – Sampler loan and repairs/upgrades, filter samples, lab analyses, data validation and delivery
Current Sponsors

- U.S. Environmental Protection Agency
- U.S. National Park Service
- U.S. Forest Service
- U.S. Fish & Wildlife Service
- Various State Governments & Tribes
- Environment Canada
- South Korea Ministry of Environment
Most samplers are located in National Parks & other remote areas.

A few samplers are collocated with urban network samplers.
The IMPROVE network maintains 156 sites. Sites collocated with CSN samplers circled in blue.
IMPROVE sampler

- Designed by UC-Davis for clean environments
  - High flow rate – 23 L/min
  - Small filter – 25 mm diameter concentrates the sample
- 4 samples collected every 3 days
  - PM$_{2.5}$ Teflo® PTFE filter analyzed by gravimetry, XRF, and laser absorption by UCD
- PM$_{2.5}$ nylon filter analyzed by ion chromatography at RTI
- PM$_{2.5}$ quartz filter analyzed for carbon by DRI
- PM$_{10}$ Teflo® PTFE filter analyzed by gravimetry by UCD
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Since the 1970s, the IMPROVE Air Quality Group has collected and analyzed particulate matter. The group routinely monitors visibility-impacting pollution in Schedule I areas as part of EPA’s Regional Haze Program and includes 150 national sampling sites, plus three international sites in Canada and South Korea.

Flow Control Valve Reconfiguration and Critical Orifice Deployment

- Previously, noisy transducer flow data was difficult to differentiate from non-flow data.
- Orifice area was previously determined empirically; with critical orifice the orifice area is known.
- New flow calibration equation is less sensitive to changes in valve needle.
- Obstructions in valve are easier to clean in new design.

PM10 Flow Data

- Modified CPC fitting and critical orifice installation tool.

CFLASH Memory Card Reader Redesign

- Before redesign, yearly average lost data due to memory card writing errors was 4.3%.
- New design transmits data over PCB traces rather than ribbon.
- After redesign, yearly average lost data due to memory cards is 1.9%.

Version III Controller Development

- New digital sensors and pressure transducers are less susceptible to analog noise.
- Open source Linux-based microcontroller (BeagleBone Black) for keeping software up to date and easily developed.
- Communication through Controller Area Network (CAN), Serial Peripheral Interface (SPI), Universal Serial Bus (USB), I2C, and RJ-45.
- Hardware supports networked data transfer for real-time instrument monitoring and remote control.
- Modern interface enables user instructions and troubleshooting guidance with high definition images and video.
- Modular card design will significantly reduce expensive shipping costs for replacement of components.
Data Validation and Analysis

• UC-Davis performs data validation for entire network
• Review flow rates immediately upon data receipt
• Review data from different perspectives (space, time) to identify contamination, interferences, patterns, and trends
Spatial Context Important for Validation

- Contour maps of annual average PM$_{2.5}$ Sr (right) and S (below) concentrations
- Dots represent sites
- Sometimes we discover unique sources of trace elements
Sometimes we identify contamination.
Data Validation Across Years

Sulfur by XRF

Sulfate by IC
Sometimes we find trends in atmosphere!

Vanadium

Nickel

- Nickel and vanadium are tracers for bunker fuel
Table 1

<table>
<thead>
<tr>
<th>Outside an ECA established to limit SOx and particulate matter emissions</th>
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<th>ARB’s California OGV Fuel Requirement Percent Sulfur Content Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.50% sulfur prior to January 1, 2012</td>
<td>1.50% sulfur prior to July 1, 2010</td>
<td>Phase I effective July 1, 2009: Marine gas oil (DMA) at or below 1.5% sulfur; or Marine diesel oil (DMB) at or below 0.5% sulfur</td>
</tr>
<tr>
<td>3.50% sulfur on and after January 1, 2012</td>
<td>1.00% sulfur on and after July 1, 2010</td>
<td>Phase I effective August 1, 2012: Marine gas oil (DMA) at or below 1.0% sulfur; or Marine diesel oil (DMB) at or below 0.5% sulfur</td>
</tr>
<tr>
<td>0.50% sulfur on and after January 1, 2020(^1,2)</td>
<td>0.10% sulfur on and after January 1, 2015</td>
<td>Phase II effective January 1, 2014: Both marine gas oil (DMA) and marine diesel oil (DMB) at or below 0.1% sulfur</td>
</tr>
</tbody>
</table>

\(^1\) depending on the outcome of a review, to be concluded by 2018, as to the availability of the required fuel oil, this date could be deferred to January 1, 2025.

\(^2\) European Union Directive 2012/33/EU mandates a maximum fuel sulfur content of 0.5% to be burned in ships in the European Economic Zone in areas outside of ECAs, beginning in 2020.
Where does the effect of the limits show up?

Near the big commercial ports!

ORPI, at the top of the Gulf of California
IMPROVE Reinvestment and Data Analysis

Investigations can lead to better understanding and improvements of the measurements
Aerosol generation system

- Dilution Air
- Atomizer
- Particle Dryer
- Mixing Chamber
- IMPROVE PM2.5 Module
- RH Monitor
- Analyte Solution
- Dilution Air Dryer
Creating XRF Calibration Reference Filters

- Reference filters prepared using IMPROVE or Partisol® sampler
- Provides reference filters at relevant concentrations
- XRF benchmark independent of Micromatter Inc. (commercially available) standards
- Single-compound reference filters for S, Na, Cl, Pb, and K are used in current UC-Davis XRF calibrations
- Multi-element reference filters are also under development
  - used to check stability of XRF measurements
Sulfur Reference Filters

Multi-Element Reference Filters Analyzed by 12 Labs
• Eventually plan to use ME reference filter to explore interferences, matrix effects, and calibrate the instrument
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Objective: To generate single and multi-element reference materials (RMs) on Polytetrafluoroethylene (PTFE, Teflon) filters using aerosol chamber at CNL-UC Davis (Fig.1), and utilize them in calibration and quality control (QC) of EDXRF analyzers in order to address the limitations of available resources.

Materials & Method: High purity salts and nanoparticles for single compound RMs (SE-RMs)
Certified multi-elemental solutions containing 28 elements for multi-element RMs (ME-RMs).

Certified or Reference loadings of RMs:
- The loadings of SE-RMs (C_{ref}) are certified gravimetrically using a balance with 0.1 μg sensitivity
- The ME-RMs reference loading of element i (C_{ref,i}) was assigned assuming:
  1. The elemental ratios in solutions are preserved onto ME-RMs
  2. The potassium (K) measurement by UCD-EDXRF C_{k,UCD-EDXRF} (Epsilon S, Panalytical Inc, the Netherlands) is accurate to be <10%. These assumptions resulted in estimated uncertainties below 10%.

Data Evaluation:
1. Agreement between certified loadings of SE-RMs and EDXRF: Linear regression, bias and En number (ISO/IEC 17043, 2010):
   \[ U = \frac{|C_{EDXRF} - C_{cer}|}{\sqrt{U^2_{C(EDXRF)} + U^2_{C(cer)}}} \]
   When En ≤1, C_{EDXRF} and C_{cer} are equivalent

   For good interlaboratory comparability, |z| ≤3

2. Linear regression between reference loading of ME-RMs (x) and lab (y),

3. z-score (ISO 13528:2005): Loadings in μg/cm² converted to μg/g for 12 ME-RMs in interlaboratory comparison
   \[ z = \frac{C_{lab} - \bar{C}}{\delta} \]
   δ: outlier-excluded standard deviation

Results and Discussion
- The SE-RMs could be generated successfully for Na, Al, Si, S, Cl, K, Ti, Fe, Zn and Pb with loadings almost spanning the range of two large US atmospheric PM monitoring networks, namely IMPROVE (Interagency Monitoring of PROtected Visual Environments) and CSN (Chemical Speciation Network) (Fig.2.-Left) while the loadings of ME-RMs span the range of both networks (Fig.2.-Right).

Interlaboratory Comparison of ME-RMs
- An interlaboratory comparison study of ME-RMs were conducted with participation of 9 XRF and 3 ICP-MS laboratories
- The slopes of reference vs. labs are mostly within 20% of unity (R²>0.95) (Fig.6)
- Participating labs are mostly in good agreement (|z| ≤3) (Fig.7)
Different views, same data
Collocated IMPROVE PM$_{2.5}$ Data

Scaled Arithmetic Difference $= \frac{C_1 - C_2}{\sqrt{2}}$

Scaled Relative Difference $= \frac{(C_1 - C_2)/\sqrt{2}}{(C_1 + C_2)/2}$
Additive and Multiplicative Errors

S Scaled Arithmetic Diff. (ug m-3)

S Average Concentration (ug m-3)

V Scaled Arithmetic Diff. (ug m-3)

V Average Concentration (ug m-3)
Distribution of Differences and Precision Estimates

As Scaled Relative Difference

Count of Collocated Pairs

RMS
Mean Absolute
Percentiles
Errors: often not normally distributed

Precision Estimation Approaches
- RMS
- Mean Absolute
- Percentiles
Updated Uncertainty Estimates

Notable Improvements in Some Elements

- **Ni Concentration/Detection**
- **Zn Concentration/Detection**

○ Existing Uncertainty Estimate
× Updated Uncertainty Estimate
## Limits of Detection

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<th>Analyte is not measured</th>
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<tr>
<td>Analyte is measured</td>
<td>Type I error, $L_C$</td>
<td>Correct decision</td>
</tr>
<tr>
<td>Analyte is not measured</td>
<td>Correct decision</td>
<td>Type II error, $L_D$</td>
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Illustration of Type I & II Errors

Probability Density Function (PDF)

Distribution of Blank Measurements

Distribution of Measurements at a value of $L_D$

(Blank Mean) $L_C$ $L_D$

Measured Value or Concentration

(Blank Mean)

$(Currie, 1995)$
Estimating Detection limits from duplicate measurements

- **As**: Counts per Bin ~ 57
- **Cl**: Counts per Bin ~ 15
- **Se**: Counts per Bin ~ 63

Probabilities of detection on both filters vary with filter loading (ng cm\(^{-2}\)).
Reanalysis of 15 years of Archived Filters

- Great Smoky Mountains, Mount Rainier, Point Reyes
- Reanalysis under stable conditions and calibration
- Long-term uncertainties not reflected in our precision or collocated measurements
Original Measured Concentrations
Great Smoky Mountains National Park
Ratios of Original and Reanalysis Concentrations
Great Smoky Mountains National Park
Trends based on Reanalysis versus Original Results
IMPROVE: Our legacy is clear skies