IMPROVE Fine Mass and $b_{\text{ext}}$
Reconstruction
Issues, Resolutions and Next Steps

Schichtel, Hand, Prenni, Malm,
Copeland, Vimont, White......
Fine Particulate Mass Composite Components

- Ammonium Sulfate = 1.375 * [SO₄]
- Ammonium Nitrate = 1.29 * [NO₃⁻]
- Organics = 1.8 [OC]
- Light Absorbing Carbon = [EC]
- Soil = 2.2[Al]+2.49[Si]+1.63[Ca]+2.42[Fe] +1.94[Ti]
- Sea Salt = 1.8 * [Cl⁻]
- Carbon multiplier (Roc = 1.8) found through empirical analysis

- RCFM = Sum of aerosol species
- FM = PM₂.₅ Gravimetric Fine Mass
- Residual = Other = Missing Mass = FM-RCFM
IMPROVE Reconstructed Extinction

\[ b_{\text{ext}} = 2.2 \times f_s(RH) \times [\text{Small Sulfate}] + 4.8 \times f_L(RH) \times [\text{Large Sulfate}] \\
+ 2.4 \times f_s(RH) \times [\text{Small Nitrate}] + 5.1 \times f_L(RH) \times [\text{Large Nitrate}] \\
+ 2.8 \times [\text{Small OMC}] + 6.1 \times [\text{Large OMC}] + 10 \times [EC] \\
+ 1 \times [\text{Fine Soil}] + 1.7 \times f_{ss}(RH) \times [\text{Sea Salt}] + 0.6 \times [\text{Coarse Mass}] + \text{Rayleigh} \]

- Aerosols are externally mixed
- Small and large refer to fine particle mass size distribution that have different light scattering properties.
- Assumed that aerosols shift to larger sizes for higher mass concentrations.
Sulfate, Nitrate and Organics Modes

\[
[\text{Large Sulfate Fraction}] = \frac{[\text{Total Sulfate}]}{20 \, \mu g/m^3}
\]

\[
[\text{Small Sulfate Fraction}] = 1 - [\text{Large Sulfate Fraction}]
\]

- MSE normalization factor = 20 $\mu$g/m$^3$
- The value of 20 was found through empirical analyses
25 Yrs of Seasonal PM2.5 Composition Budgets

1993

μg/m³

- Ammonium Sulfate
- Ammonium Nitrate
- Organics
- Elemental Carbon
- Fine Soil (Dust)
- Sea Salt
The fine mass residual (FM-RCFM) is increasing.

Annual residual increased ~ 0.5 µg m\(^{-3}\) from 2005-2016.
Reconstructed vs Measured $b_{sp}$

- Good comparison to the data used to developed the IMPROVE equation
- Systematic overestimation for 2005-2007
- Severe systematic underestimation for 2012 to today
### Potential causes of Increased Residual (FM – RCFM)

<table>
<thead>
<tr>
<th>Some biases known to affect PM$_{2.5}$ Gravimetric Mass and or RCFM*</th>
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</thead>
<tbody>
<tr>
<td>(+) (FM) Particle Bound Water (PBW: laboratory relative humidity)</td>
</tr>
<tr>
<td>(+/-) (RCFM) Organic multiplier ($R_{oc} = OM/OC$)</td>
</tr>
<tr>
<td>(+/-) (RCFM) Dust composition</td>
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<tr>
<td>(+) (RCFM) Sulfur vs sulfate (sulfate neutralization (~30%?); organosulfate)</td>
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<tr>
<td>(-) (FM) Nitrate is lost from Teflon filter (seasonal)</td>
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<tr>
<td>(RCFM) Changes in quartz carbon filter blanks</td>
</tr>
<tr>
<td>(FM &amp; RCFM) Semi-volatiles lost on quartz filter (underestimate OC by ~20%, Malm et al., 2011)</td>
</tr>
<tr>
<td>(FM &amp; RCFM) Other quartz filter artifacts: evaporation of OC during storage adsorption of VOC gases</td>
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</tbody>
</table>

*Possible known biases affecting PM$_{2.5}$ measurements (FM) or RCFM. The impact of the bias on FM is given in the parentheses (negative or positive).
Multiple Linear Regression (MLR):

\[ FM - EC - SS = a_0 + a_1 AS + a_2 AN + a_3 OC + a_4 dust \]

*Where:*
- FM = PM\(_{2.5}\) (gravimetric)
- AS = ammonium sulfate (1.375*SO\(_4\)\(^{-2}\))
- AN = ammonium nitrate (1.29*NO\(_3\)\(^{-}\))
- OC = organic carbon
- Dust = sum of oxides
- SS = sea salt (1.8*Cl\(^{-}\))

**Interpretation:**
- \(a_1, a_2, a_4 \approx 1\)
- \(a_3 = R_{oc}\) (e.g. OM/OC ratio)
Excess water on filters after 2011

Ammonium Sulfate Network Median MLR

• AS coefficients > 1 indicating associated water
• The bias was most acute in summer and fall after 2011 when lab RH increased

Dry FM: Adjusted FM for PBW

Ammonium bisulfate

• Using dry FM in the regression reduced AS coeff. to 1 or less
• Coefficients increased in time
  – more neutralized aerosol
  – error in the drying method
Network Median MLR Results (Dry FM) by Season

- Regression analysis suggests
  - Roc factor is increasing with time
  - Roc is seasonal with high summer values ~2 and lower winter values ~1.6
  - Soil is underestimated by 15-20%
Network Median MLR Results (Dry FM) by Region

- Regression analysis suggests
  - Sulfate maybe more acidic in the east than the west
  - Roc is larger in the east than west
  - Soil composition regionality is smaller than noise

Regions split at 40°N and -100°W
IMPROVE Reconstructed Extinction

\[ b_{\text{ext}} = 2.2 \times f_s(RH) \times [\text{Small Sulfate}] + 4.8 \times f_L(RH) \times [\text{Large Sulfate}] + 2.4 \times f_s(RH) \times [\text{Small Nitrate}] + 5.1 \times f_L(RH) \times [\text{Large Nitrate}] + 2.8 \times [\text{Small OMC}] + 6.1 \times [\text{Large OMC}] + 10 \times [\text{EC}] + 1 \times [\text{Fine Soil}] + 1.7 \times f_{SS}(RH) \times [\text{Sea Salt}] + 0.6 \times [\text{Coarse Mass}] + \text{Rayleigh} \]

- Assumes that fraction of large particles is proportional to the species mass
- The proportionality constant (MSE normalization factor) = 1/20

Large Sulfate Frac = \( \frac{\text{Sulfate}}{20 \ \mu g/m^3} \)
Sulfate scattering: GRSM and GRCA

- IMPROVE Equation predicts sulfate scattering efficiencies trending down in the eastern US due to decreased sulfate.
- Constant in the west where sulfate has been more constant.
- Assumption is that lower masses ➔ less aged aerosol ➔ more aerosol is in smaller mode, which is less efficient at scattering visible light.
Is scattering efficiency proportion to mass?

- Many studies have shown a relationship between scattering efficiency and mass over short periods (not space).
- No study has looked at the dependence over years with trending aerosol concentrations, but we can:
  - Great Smoky Mountains aerosol size measurements
    - Lowenthal et al. 2006-2008. SMPS.
    - SOAS (Russell). 2013. SMPS.
  - Analysis
    - Lognormal distributions were fit to aerosol volume data.
    - Distributions fit with a single mode.
    - Data were limited to identical size range (120 – 750 nm).
GRSM size distribution fits

- No long term trend in size.
- Size distributions NOT dependent on long term trends in aerosol mass.
- Some correlation of aerosol mass and diameter in 2006-2008.
  - Could be seasonal effect
Focus on the MSE Normalization Factor of 20

\[
\text{[Large Sulfate]} = \frac{\text{[Total Sulfate]}}{20} \times \text{[Total Sulfate]}
\]

- A constant normalization factor implies that changes in size distribution are caused by changes in concentrations
- Concentrations and size distribution are more likely correlated and driven by aging processes
  - Less aged aerosol \(\rightarrow\) smaller concentrations and size distributions
  - More aged / cloud processed aerosol \(\rightarrow\) larger conc. and size distributions
- The size distributions and scattering efficiency's should be dependent on the relative concentrations at a given site/year
Focus on the MSE Normalization Factor of 20

\[
[\text{Large Sulfate}] = \frac{[\text{Total Sulfate}]}{\text{MSE Norm Frac}} \times [\text{Total Sulfate}]
\]

- The size distributions and scattering efficiency's should be dependent on the relative NOT absolute concentrations at a given site/year.

- Regression and data analysis showed that the best fit between reconstructed and measured light scatter occurred with
  
  MSE Norm Factor = 95\textsuperscript{th} percentile concentration at each site, year and species.
Measured vs Calculated for all Parks

- MSE normalization factor = 95th %-ile
- At all parks, overall better agreement.
- Temporal trend still apparent.
  - Did not account for findings from the RCFM analysis
Uncontrolled laboratory RH since 2011 has likely increased the relative water on the filters resulting in increased bias
  • The new RH controlled weighting chamber will fix this

Ammoniated sulfate appears to be moving from ammonium bisulfate in early 2000’s to ammonium sulfate today
  • East is more acid than west
  • Current assumption of ammonium sulfate is good, but the ammoniated sulfate mass and scatter likely overestimated in early years

Fine soil maybe underestimated by 15-20%
  • Any revised IMPROVE equation should include the increased soil
  • This should have minimal impacts on RHR metrics
RCFM - Carbonaceous Conclusions

• Roc appears to vary by season and region
  • Higher Roc in the summer ~2, than winter ~1.6
  • Higher Roc in the East ~2 than West ~1.8
• Some indication that Roc has increased since 2011, especially in summer (varies regionally), Why?
  • Emissions/chemistry changes? (See Bill’s presentation)
  • Analytical issues?

• Any revised IMPROVE equation should account for
  • Roc Seasonal variations
  • Roc Long-term trends
  • Possibly Roc regional variations
Reconstructed $b_{\text{ext}}$ - Summary

- Associated with large decreases in FM (especially sulfate), the reconstructed $b_{\text{ext}}$ is now significantly underestimated in the eastern US
- Size distributions are correlated to mass concentrations but not caused by mass concentrations
- The mass scattering efficiency (MSE) should be dependent on the relative concentration not the absolute concentration, e.g. the 95th %-ile for a given site, species
• Next steps
  – Publish reconstructed FM and bext findings
  – Develop potential IMPROVE equation III that incorporates new findings
    • Evaluate impact of the revised equation on RHR metrics and trends
      – Will increase reconstructed $b_{ext}$ thus remove some “current” progress
      – May shift some days that are considered most impaired
      – May increase perceived benefit from future source reductions
    • Any new equation should incorporate any changes to carbonaceous aerosol measurements
• Questions?
Multiple Linear Regression

\[ b_{sp}^* = bsp_{Meas} - [SOIL] - 1.7 \times fRH_{SS} \times [SS] - 0.6 \times 0.5 \times [CM] \]

\[ AS = 2.2 \times fRH_s \times [ammSO_4]_s + 4.8 \times fRH_l \times [ammSO_4]_l \]

\[ = 2.2 \times fRH_s \times \left(1 - \frac{[ammSO_4]}{x}\right) \times [ammSO_4] + 4.8 \times fRH_l \times \frac{[ammSO_4]}{x} \times [ammSO_4] \]

\[ = 2.2 \times fRH_s \times [ammSO_4] + \frac{1}{x} \times [ammSO_4]^2 \times (4.8 \times fRH_l - 2.2 \times fRH_s) \]

Move to \( b_{sp}^* \) term.  \hspace{2cm} AS

Repeat for ammNO_3 and OMC.

Regression: \[ b_{sp}^* = c_1 \times AS + c_2 \times AN + c_3 \times OMC \]

Normalization Factors: \[ ammSO_4 = \frac{1}{c_1}; \quad ammNO_3 = \frac{1}{c_2}; \quad OMC = \frac{1}{c_3} \]
Regression Results: MSE normalization factor decreasing, especially for ammonium sulfate

Best fit MLR coefficients are ~ 95th percentile conc for each species each year.
Extinction

- Study Sheds New **Light** on **Extinction** of Dinosaurs
Changes in Fine Particulate Matter in the Rural US over the past 22 years

3 year annual average 1994
Changes in Fine Particulate Matter in the Rural US over the past 22 years

3 year annual average 1994
Interagency Monitoring of Protected Visual Environments (IMPROVE)

- Objectives
  - Support Regional Haze Rule by providing haze monitoring representing all visibility-protected CIA
  - Establish current visibility and aerosol conditions;
  - Document long-term trends for assessing progress towards the national visibility goal for CIA & as required by the Regional Haze Rule
  - Identify chemical species and emission sources responsible for existing man-made visibility impairment