Contribution of Chemical Constituents to Visibility Reduction During the California Regional PM10/PM2.5 Air Quality Study

Steven Heisler, ENSR International
Camarillo, CA
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Approach

• Applied light extinction efficiencies to 24-hour average particulate matter chemical composition data to estimate constituent contributions to the light extinction coefficient

• Constituents included:
  Fine Soil = 1.89[Al] + 2.14[Si] +1.4[Ca] + 1.43[Fe]
  NH₄NO₃ = 1.29[NO₃⁻]
  (NH₄)₂SO₄ = 1.375[SO₄²⁻]
  Organic Compounds (OCM) = 1.4[OC]
  Elemental Carbon (EC) = measured EC
Light Extinction Efficiencies

- Used 10 m$^2$/g for light absorption by EC
- Evaluated light scattering efficiencies developed for IMS95 and for IMPROVE (Interagency Monitoring of Protected Visual Environments) with 24-hour average chemical composition, light scattering coefficient ($b_s$), and relative humidity (RH) data from Fresno First Street (FSF) site
- Chose FSF data because only site with open-air, unheated nephelometer (NGN-2)
IMS95 and IMPROVE Light Scattering Efficiencies

<table>
<thead>
<tr>
<th>Constituent</th>
<th>IMS95 $(m^2/g)$</th>
<th>IMPROVE $(m^2/g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine Soil</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>$2.1/(1-RH)^{0.7}$</td>
<td>$3f(RH)$</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>$2.1/(1-RH)^{0.7}$</td>
<td>$3f(RH)$</td>
</tr>
<tr>
<td>OC</td>
<td>$2.8/(1-RH)^{0.2}$</td>
<td>4</td>
</tr>
</tbody>
</table>
IMPROVE $f(RH)$
IMS95 and IMPROVE Efficiencies
Produced Essentially Identical Results

\[ \text{Calc.} = 1.00 \text{ Meas.} - 1.33 \text{ Mm}^{-1} \]
\[ R^2 = 0.9999 \]
\[ n = 54 \]
Measured $b_s$ is under-predicted, especially at high values.
Correlation is Good at Lower Values, but Measured $b_s$ is Under-Predicted
Calculated Seasonal Adjustments to IMPROVE Efficiencies

- Only adjusted efficiencies for NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$
- Seasonal adjustment calculated as average of:
  \[
  \frac{(\text{measured } b_s - \text{soil } b_s - \text{OCM } b_s)}{(\text{NH}_4\text{NO}_3 \ b_s + (\text{NH}_4\text{)}_2\text{SO}_4 \ b_s)}
  \]
- Also calculated adjustment factor for high light scattering (measured $b_s > 1000 \ \text{Mm}^{-1}$)
NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ Light Scattering Efficiency Adjustment Factors

<table>
<thead>
<tr>
<th>Season</th>
<th>Adjustment Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter (Dec. – Feb.)</td>
<td>2.17</td>
</tr>
<tr>
<td>Spring (Mar. – May)</td>
<td>0.74</td>
</tr>
<tr>
<td>Summer (Jun. – Aug.)</td>
<td>0.81</td>
</tr>
<tr>
<td>Fall (Sep. – Nov.)</td>
<td>1.51</td>
</tr>
<tr>
<td>High Measured $b_s$</td>
<td>5.09</td>
</tr>
</tbody>
</table>
Adjustment Improves Agreement

Adjusted IMPROVE Light Scattering Efficiencies

Calc. = 0.933 Meas. + 23.9 Mm$^{-1}$

$R^2 = 0.919$

$n = 54$
Agreement Is Best at Lower Values

Adjusted IMPROVE Light Scattering Efficiencies

- Calculated $b_s = 0.929 \times \text{Measured } b_s + 9.5 \text{ Mm}^{-1}$
- $R^2 = 0.983$
- $n = 48$
Application of Light Extinction Efficiencies

- Applied to 11 sites with annual relative humidity and PM2.5 chemical composition data
- Data available from 12/99 - 1/01
- Calculated $f(RH)$ for every hour and averaged over 24-hour filter sampling periods
- “Capped” $f(RH)$ at value for 95% relative humidity to avoid “instabilities”
- Did not apply adjustment for “high” values (i.e., only used seasonal adjustment)
Seasonal Average Total Calculated Light Extinction

Seasonal Average Calculated Light Extinction (Mm⁻¹)

Sacramento  Stockton  Modesto  Merced  Fresno-A  Fresno-B  Fresno-C  Selma  Visalia  Oildale  Bakersfield

Winter  Spring  Summer  Fall
Seasonal Average Total Calculated Light Extinction Coefficient

- Winter average values are higher than other seasons at all sites
- Fall average values are higher than spring or summer
- Values are highest at Visalia, Merced and Modesto
- Values are lowest at Sacramento and Stockton
Seasonal Average Constituent Contributions

- NH$_4$NO$_3$ is largest contributor at all sites during winter and fall, accounting for about 60% to about 80% during winter and about 40% to about 70% during fall.
- Organic compounds are largest contributor at most sites during spring, accounting for about 30% to about 40%, and at all sites during summer, accounting for about 30% to about 45%.
- Elemental carbon is a significant contributor at most sites during spring and summer, accounting for as much as 25%.
Why is Winter Calculated Light Extinction Higher at Visalia, Merced and Modesto than at Other Sites?
Winter Average NH$_4$NO$_3$ Concentrations are Higher at Other Sites
But Average $f(\text{RH})$ is Lower at Other Sites
Summary

• Previously developed light scattering efficiencies under-predicted measured light scattering, but seasonal adjustment factors improved agreement.
• Calculated total light extinction is highest during winter and lowest during summer.
• $\text{NH}_4\text{NO}_3$ is the largest contributor at all sites during winter and fall.
• Organic compounds are the highest contributor at most sites during spring and summer.
• Winter average light extinction was higher at Visalia, Merced and Modesto than at other sites because of higher reported relative humidity.