Causes of Haze for Hawaii’s Two Class I Areas

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for the USDA AAQTF meeting
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Uses of IMPROVE Monitoring Data in the Regional Haze Rule

- IMPROVE Network has 110 particle speciation monitoring sites that nominally represent 155 visibility-protected class I areas.
- Each site collects every-third-day samples of PM$_{2.5}$ for gravimetric and compositional analysis and PM$_{10}$ for gravimetric analysis.
- Major particle components are used to estimate current haze levels (used to establish baseline conditions and to track trends).
- All components are used to help identify the sources (or source types & regions) that contribute to haze.
Haleakula and **Hawaii Volcano** National Park Monitoring Sites
Haze Indices

- **Light extinction (Mm\(^{-1}\))** – loss of light per unit distance due to scattering & absorption (*directly related to aerosol concentration*)

- **Visual range (km)** – largest distance that a suitable object can be seen (*inversely proportional to light extinction*)

- **Deciview haziness index (dv)** – uniform with respect to perceived haze changes (*logarithmic transformation of light extinction*)
Haze Levels from IMPROVE Network Particle Speciation Data

• Light extinction associated with each of the major particle components is the component concentration times an extinction efficiency (efficiency depends on the component and the relative humidity)

• Total light extinction is the sum of the particle component extinction values plus about $10\text{Mm}^{-1}$ for molecular scattering of clean air

• The six major particle components – typical extinction efficiencies are:
  – Fine ($\text{PM}_{2.5}$) ammonium sulfate – $3\text{m}^2/\text{g}$ (grows with humidity)
  – Fine ammonium nitrate – $3\text{m}^2/\text{g}$ (grows with humidity)
  – Fine organic compounds – $4\text{m}^2/\text{g}$
  – Fine elemental carbon – $10\text{m}^2/\text{g}$
  – Fine crustal compounds – $1\text{m}^2/\text{g}$
  – Coarse ($\text{PM}_{(10-2.5)}$) mass – $0.6\text{m}^2/\text{g}$
Growth curve used for ammonium sulfate and ammonium nitrate make them much more efficient at high relative humidity. (growth for relative humidity greater than 95% is held constant)
Hawaii IMPROVE Monitoring Site

Haleakula

Hawaii Volcano
Haze & Ammonium Sulfate on Worst Haze Days for 2003 Hawaii Compared to Lower 48

- Hawaii Volcano – 77Mm⁻¹
- Haleakula – 36Mm⁻¹
- Hawaii Volcano – 8.1µg/m³
- Haleakula – 3.4µg/m³
Hawaii Volcano IMPROVE Aerosol Extinction (2001 -2002)

Worst Day Monthly Frequency

Worst Day Monthly Averaged Composition

Legend:
- CM
- Soil
- LAC
- OMC
- Nitrate
- Sulfate
- Rayleigh
SO$_2$ Pollution Rose & Wind Frequency for Visitor Center/IMPROVE Site for 2002

Hawaii Volcano Map
from NPS Alert web site for 9:00am 4/7/05
Hawaii Volcano Particulate vs Gaseous Sulfur

\[ y = 0.014x + 0.187 \]

\[ R^2 = 0.6452 \]
Haleakula IMPROVE Monitoring Site on Maui

Site is about 3 miles NW of the Park boundary at an elevation of 3800’

Park elevation range is 0’ to 10,023’

Worst Day Monthly Frequency

Worst Day Monthly Averaged Composition
Hawaii Volcano Plume is Still Intense Hundreds of Miles from its Source – Satellite Image
Sulfate Concentrations at the Two Hawaii IMPROVE Sites

Consistent trade winds

Interesting period
24-hour Forward Trajectories from the Volcano (starting mid-day Hawaii time)

Low sulfate at both sites for 10/15 sample period
Low at HALE but high at HAVO for 10/18 sample period.

Low for both sites for Oct. 21 sample period.
High for both sites for Oct. 24 sample period.
Highest at both sites for Oct. 27 sample period
High at both sites for Oct. 30 sample period.

Typical trade winds produce trajectories like these for many of the following days when sulfate levels are low at both monitoring sites.

- This analysis demonstrates that volcanic sulfate is likely impacting haze on at least some of the worst haze days for Haleakula.
- How much of the Haleakula sulfate is caused by the volcano?
Positive Matrix Factorization

• PMF is a statistical method that identifies a user specified number of source profiles (i.e. relative composition particle species for each source) and source strengths for each sample period that reduce the difference between measured and PMF fitted PM$_{2.5}$ mass concentration.

• In matrix notation,

$$X = GF + E$$

where $X$ is the matrix of measured composition for each sample period, $F$ is the source profile, $G$ is the source strength or factor scores for each sample period, and $E$ is the residual or error matrix.
PMF application to Hawaii IMPROVE Particle Speciation Data

- All available PM$_{2.5}$ speciation data for both sites (>2 years each) are used together in the PMF to explain measured PM$_{2.5}$ mass
- Six factors seemed to separate reasonably explained source factors
- Multiple linear regression was used to explain coarse mass using the six PMF factors
Six Source Profiles from Hawaii PMF Analysis

#1, Sea salt

#2, Volcano sulfate

#3, Dust

#4, Smoke

#5, Secondary Nitrate

#6, Secondary Sulfate & Nitrate
Coarse Mass to PM$_{2.5}$ Ratios
(Based on Multiple Linear Regression of Coarse Mass on the Factor Scores)
This shows that the 6 PMF factors provide a good fit to the PM$_{2.5}$ measurements.
<table>
<thead>
<tr>
<th>Source Factors</th>
<th>All Days</th>
<th>Worst 20% Haze Days</th>
<th>Site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfate &amp; Nitrate</td>
<td>6</td>
<td>1</td>
<td>Haleakula</td>
</tr>
<tr>
<td></td>
<td>16%</td>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14%</td>
<td>33%</td>
<td></td>
</tr>
<tr>
<td>Smoke</td>
<td>4</td>
<td>3</td>
<td>Hawaii Volcano</td>
</tr>
<tr>
<td></td>
<td>22%</td>
<td>19%</td>
<td></td>
</tr>
<tr>
<td>Dust</td>
<td>3</td>
<td>19%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8%</td>
<td>7%</td>
<td></td>
</tr>
<tr>
<td>Sea salt</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7%</td>
<td>1%</td>
<td></td>
</tr>
</tbody>
</table>

For Haleakula Site:
- **Haleakula**: 88%
- **Hawaii Volcano**: 70%

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- **Haleakula**: 88%
- **Hawaii Volcano**: 70%
Contributions of Source Factors to PM2.5 in 20% Worst Days of 2003

At Haleakula, about half of worst haze days are associated with volcano emissions, while the others are associated with different factors (e.g. smoke, secondary sulfate and nitrate).

Note that October 24, 27, & 30 had trajectories from the volcano to Haleakula.

At Hawaii Volcano, all worst haze days are dominated by the volcano sulfate factor.
PMF Next Steps

• Assess credibility of the non-volcano factors for Haleakula
  – Is the smoke factor elevated during known burning events?
  – Is the dust factor primarily local emission activities &/or high winds, or global dust impacts?
  – What sources are associated with the nitrate (#5) and the sulfate/nitrate (#6) factors?

• Incorporate coarse mass & convert factors to contribution to light extinction for both monitoring sites
  – Want to separate coarse mass from local man-made activities from Asian dust, sea salt, & other natural sources
  – Need to weigh emissions control priorities based on haze contributions
Local verses Global OC/EC Impacts  
(a proposed conceptual model)

• Because Hawaii is on islands in the middle of the Pacific Ocean
  – All the fine OC and EC is either local or global (there is some small amount of oceanic OC)
  – Global OC/EC probably from large biogenic fires should affect both Hawaii sites to the same extent, most of the time
  – Local OC/EC can affect one site but probably not the other site

• Differences between the two sites for fine soil and coarse mass should be an indicator of local impact

• When both sites measure relatively high levels global dust is a likely explanation
The ratio of elemental carbon to organic carbon at Haleakula is larger than at Hawaii Volcano.

Also the correlation is much stronger at Haleakula than at Hawaii Volcano.

Haleakula is expected to have smoke and other combustion source impacts that would provide both organic and elemental carbon.

It seems that Hawaii Volcano must have some local source contributing organic carbon with little or no elemental carbon (e.g. secondary organics).
Summary

• The volcanic emissions of sulfate dominates the haze measured at Hawaii Volcano National Park.
• It is also the single largest source of worst haze conditions at Haleakula National Park.
• There are other sources of haze that are significantly contributing on worst haze days at Haleakula.
  – PMF analysis indicates that smoke, dust and non-volcanic sulfur and nitrate sources are important.
  – These need to be better understood and tied to specific sources or source activities to be useful.
• More assessment work is needed and suggestions are welcome.
Causes of Haze Assessment --Nation-Wide--

- Data analysis similar to that done for Hawaii’s two visibility-protected areas and regional scale air quality modeling is being conducted by Regional Planning Organizations for all such areas to support development of Regional Haze State Implementation Plans due in 2007