Issues Concerning Natural Conditions Estimation
IMPROVE equation for estimating extinction

\[ b_{\text{ext}} = (e_{s\text{f}}) f_s (\text{RH}) [(\text{NH}_4)_2 \text{SO}_4] + (e_{n\text{f}}) f_n (\text{RH}) [\text{NH}_4 \text{NO}_3] \]
\[ + (e_{o\text{cmf}}) f_{o\text{cm}} (\text{RH}) [\text{OMC}] + (e_{\text{soilf}}) [\text{SOIL}] \]
\[ + (e_{c}) [\text{Coarse Mass}] + (e_{\text{lacf}}) [\text{lacf}] \]

\[ b_{\text{ext}} \text{ = extinction coefficient,} \]
\[ e = \text{extinction efficiencies,} \]
\[ f(\text{RH}) = \text{relative humidity enhancement factor } (b_{\text{wet}}(\text{RH})/b_{\text{dry}}), \]
\[ [\ldots\ldots] = \text{concentrations of species, and} \]
\[ \text{concentrations are 24 hr averages.} \]
Assumptions

- Sulfate as ammonium sulfate
- Nitrate as ammonium nitrate
- Organics as 1.4*OC
- Soil as oxides of crustal material
- Coarse mass as dust
- Efficiencies of 3.0, 4.0, 1.0, 0.6, and 10 m²/g for sulfate and nitrate, organics, fine soil, coarse mass, and lac respectively.
Equation for estimating the average Natural background of the 20% haziest days

\[
\text{group 10} \approx \bar{dv} - 1.28 \times s
\]
\[
\text{group 90} \approx \bar{dv} + 1.28 \times s
\]

where \(dv\) is deciview, 1.28 corresponds to 90\(^{th}\) percentile, and \(s\) is standard deviation,
Some technical issues

- Estimating extinction:
  - Species that are not included (sea salt?)
  - Internal vs external mixture?
  - Chemical form of species?
  - Constant mass scattering efficiencies?
  - What species are hygroscopic (and how hygroscopic) ?
  - Form of f(RH) curves (what RH values to use?)
  - Coarse mass composition?
  - Sampling issues?
Continued

- Estimating average of 20% haziest days
  - Is the distribution of dv normal?
  - 90\textsuperscript{th} percentile appropriate?
  - What standard deviation to use?
  - What are average natural conditions?
    - Seasonal?
    - Location specific?
    - Transboundary issues?
IMPROVE Sampling Issues

- Determine characteristics of ionic aerosol present at selected IMPROVE sites
  - Winter and summer
  - Ionic composition
  - Ion size distributions
  - Gas-particle distribution of N(-III) and N(V)
- Evaluate IMPROVE ion sampling and analysis approach
  - Utilize field and lab studies
  - Filter choice, Filter extraction method, and denuder protocol
- How might fine particle nitrate change if sulfate concentrations decline?
- Carbon measurement problems
How were the average of 20% haziest dv values estimated

- Comparison of Current Conditions to estimated natural levels
- Current deciview (dv) frequency distribution (FD) characteristics
- Inferences about natural conditions from current IMPROVE data
- Recommendations for natural conditions – ‘Default Approach’
- Application of default approach and sensitivity to reasonable changes in default parameters
- Refined estimation approaches
### Est. natural aerosol concentrations\(^a\)

<table>
<thead>
<tr>
<th>Component</th>
<th>East ((\mu g/m^3))</th>
<th>West ((\mu g/m^3))</th>
<th>Error Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate(^b)</td>
<td>0.23</td>
<td>0.12</td>
<td>2</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Organic carbon(^b)</td>
<td>1.4</td>
<td>0.47</td>
<td>2</td>
</tr>
<tr>
<td>Elemental carbon</td>
<td>0.02</td>
<td>0.02</td>
<td>2-3</td>
</tr>
<tr>
<td>Soil</td>
<td>0.5</td>
<td>0.5</td>
<td>1.5-2</td>
</tr>
<tr>
<td>Coarse Mass</td>
<td>3</td>
<td>3</td>
<td>1.5-2</td>
</tr>
</tbody>
</table>

\(^a\)Adopted from Trijonis et al., NAPAP SOS/T Report 24, 1990

\(^b\)Adjusted to current IMPROVE protocol
Annual Ammonium Sulfate

Annual Ammonium Sulfate Fine Mass

- 0.11
- 0.23
Annual Organic (1.4*OC)
Annual Ammonium Nitrate Fine Mass

Map showing the distribution of annual ammonium nitrate fine mass concentrations across the United States, with values ranging from 0.5 to 2.0 μg/m³.
How close are we now?

<table>
<thead>
<tr>
<th>SITE</th>
<th>YRS</th>
<th>Amm SO4</th>
<th>Amm. NO3</th>
<th>OC</th>
<th>EC</th>
<th>SOIL</th>
<th>CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>DENA</td>
<td>5</td>
<td>0.47</td>
<td>0.06</td>
<td>0.58</td>
<td>0.10</td>
<td>0.18</td>
<td>2.89</td>
</tr>
<tr>
<td>REDW</td>
<td>5</td>
<td>0.95</td>
<td>0.30</td>
<td>1.22</td>
<td>0.12</td>
<td>0.16</td>
<td>5.28</td>
</tr>
<tr>
<td>PORE</td>
<td>5</td>
<td>1.64</td>
<td>0.88</td>
<td>1.24</td>
<td>0.16</td>
<td>0.22</td>
<td>8.36</td>
</tr>
<tr>
<td>CRLA</td>
<td>5</td>
<td>0.42</td>
<td><strong>0.10</strong></td>
<td>1.08</td>
<td>0.21</td>
<td>0.37</td>
<td>3.21</td>
</tr>
<tr>
<td>MORA</td>
<td>5</td>
<td>1.18</td>
<td><strong>0.19</strong></td>
<td>2.01</td>
<td>0.32</td>
<td>0.22</td>
<td>2.95</td>
</tr>
<tr>
<td>THSI</td>
<td>5</td>
<td>0.69</td>
<td><strong>0.13</strong></td>
<td>1.49</td>
<td>0.19</td>
<td>0.28</td>
<td>3.52</td>
</tr>
</tbody>
</table>

5-year average aerosol mass concentrations (µg/m³)

- **0.58** Within error of NAPAP estimates
- **0.06** Less than NAPAP estimates
How close are we now - summary

<table>
<thead>
<tr>
<th>38 western sites</th>
<th>Amm. SO4</th>
<th>Amm. NO3</th>
<th>OC</th>
<th>EC</th>
<th>fSOIL</th>
<th>CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>≈</td>
<td>0</td>
<td>19</td>
<td>12</td>
<td>0</td>
<td>34</td>
<td>28</td>
</tr>
<tr>
<td>&lt;</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>11</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>17 eastern sites</th>
<th>≈</th>
<th></th>
<th>≈</th>
<th></th>
<th>&lt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>0</td>
<td>17 (all)</td>
<td>13</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>1</td>
</tr>
</tbody>
</table>

Number of sites with current (1995-1999) aerosol species mass concentrations close to estimated natural conditions

≈ sites within estimated error of natural estimates (includes <)
< sites currently (nominally) less than natural condition est.
Current dv frequency distributions

- \( dv = 10 \cdot \ln(\frac{b_{ext}}{10}) \)

- Examine dv FDs from current aerosol and optical data

- Trends in dv FD parameters
  - \(dv\) vs. dv mean
  - \(b_{ext}\) geometric standard deviation vs. geometric mean

- Inferences about dv FD shape under natural conditions

- Ability to predict RHR controlled metrics, 5-year mean of annual group 10, group 90 (mean of lowest and highest 20 percentile dv days annually) using probability statistics
dv frequency distributions
West – Denali and Three Sisters

DENA1

THSI1

1995 dv N = 90
1996 dv N = 95
1997 dv N = 88
1998 dv N = 80
1999 dv N = 71

1995 dv N = 95
1996 dv N = 91
1997 dv N = 100
1998 dv N = 85
1999 dv N = 83
dv frequency distributions
West – Bridger Teton and Yellowstone
dv frequency distributions
West – Rocky Mountain and Mount Zirkel
dv frequency distributions
West - Redwood and Lassen Volcanic

REDW1

1995 dv N = 85
1996 dv N = 87
1997 dv N = 90
1998 dv N = 89
1999 dv N = 95

LAVO1

1995 dv N = 78
1996 dv N = 79
1997 dv N = 82
1998 dv N = 79
1999 dv N = 85

Fraction less than observed
dv frequency distributions
West – Big Bend and Great Basin

[BIBE1 Diagram]
- 1995 dv N = 90
- 1996 dv N = 69
- 1997 dv N = 100
- 1998 dv N = 65
- 1999 dv N = 87

[CRBA1 Diagram]
- 1995 dv N = 101
- 1996 dv N = 100
- 1997 dv N = 68
- 1998 dv N = 56
- 1999 dv N = 54

Fraction less than observed

dv
Z

Z
0
1
2
3
0
1
2
3

dv

0
5
10
15
20
25
0
5
10
15
20

0
.01
.05
.1
.5
.9
.95
.99

0
.01
.05
.1
.5
.9
.95
.99

dv frequency distributions
East - Great Smoky Mountains & Shenandoah
Cumulative frequency distributions of \textit{bsp} at Shenandoah and Jarbridge (left). Cumulative frequency distributions of \textit{bext} at Acadia and Canyonlands (right).

Black diamonds are reconstructed and green triangles are measured (observed) parameters.

Plot axes are the standard variable $Z$ and fraction less than the stated value vs. Mm$^{-1}$.
Ability of normal normal probability statistics to predict RHR controlled metrics

- Observed 90th percentile dv and the 90th percentile dv predicted from a normal distribution agree to within 2% on average with a median difference of 2% and range from 0 to 6%.
- Observed 90th percentile dv is lower than the observed group 90 dv value by 3% on average, with a median difference of 2% and range from 0 to 8%.

Normal FDs observed in optical data when converted to dv

- 10th percentile and group 10 dv are predicted with similar accuracy by a normal distribution.
Inferences from current data

dv s vs mean

annual mean dv

dv standard deviation

West
Interior West
Pac. Coast
East
SE Coast

SHRO

DENA
Inferences from current data

- Little information from polluted sites
- Trend where dv frequency distribution narrows as dv magnitude deceases
  - Rayleigh contribution
  - Is trend characteristic of natural condition FDs?
- Missing data?
Natural conditions scenario

- Reduce current sulfate and nitrate aerosol mass concentrations so that regional averages match NAPAP values.
- Daily sulfate reduced by 96% in the East, 90% in the West.
- Nitrates reduced to a constant level.
- Current magnitude and variability of other chemical species (carbon, fine soil, and coarse mass) retained.
Natural conditions scenario

dv s vs mean

YOSE, SEQU, SOLA

annual mean dv

dv standard deviation

West
Interior West
Pac. Coast
East
SE Coast
Recommendations for natural condition dv variability

- East, dv FD standard deviation of 3
- West, dv FD standard deviation of 2
  - Recommendations for two regions conforms to geographic NAPAP aerosol estimates.
  - Possible need for regional &/ or site specific refinement of annual average aerosol species mass concentrations (dv magnitude), dv FD variability.
Default Approach

Calculate annual average $dv$ using NAPAP aerosol mass concentrations and site specific climatological annual average $f(RH)$.

- Assume normal $dv$ frequency distributions.
- Approximate worst 20 percentile mean (group 90) from 90th percentile value and two free parameters, $dv$ mean and standard deviation, $s$.

\[
group{10} \cong dv - 1.28 \times s \\
group{90} \cong dv + 1.28 \times s
\]
Default dv values - 20% worst days

7-9 dv in the west, 10-12 dv in the east
Default dv values – 20 % best days
2-4 in the west, 3.5-4.5 in the east
How close are we now?

Ratio of current to ‘default’ natural dv group 90
Climatological monthly average RH
January
What Corrections Have Been Proposed (Tombach)

1. Fix Ames and Malm statistical procedure to reflect 20% haziest days -- adds 0.42 dv
2. Change carbon mass multiplier from 1.4 (urban) to 2.1 (rural) to better represent natural conditions
3. Include fine sea salt
4. Salt is hygroscopic, so extinction impact is greater than for same amount of (non-hygroscopic) soil, although size distributions are similar
5. Oceanic organic particle concentration ~0.3 µg/m3
6. Review default soil concentrations
7. Consider biogenic organic carbon (and, perhaps, sulfur) from forests
8. Consider carbon (EC and OC) impacts from natural fires
9. Consider episodic impact of intercontinental dust transport
   - Episodic African dust impacts are frequently greater than 3 µg/m³
     Episodic Asian dust impacts are greater than 1 µg/m³ from spring through fall
   - These episodic concentrations exceed the average soil default value of 0.5 µg/m³
10. Consider impact of intercontinental sulfate and nitrate transport (mostly anthropogenic)
    - Global modeling suggests mean transported sulfate and nitrate concentrations are ~2-3 times the default concentrations
What Corrections Have Been Proposed (Kumar)

a) Use of global chemistry model predicts that “natural conditions” estimates of PM components used in the RHR are too low.
b) There is a significant transboundary impact on background concentrations of ammonium sulfate at Class I sites.
c) IMPROVE reconstruction equation overpredicts measured light scattering at low levels and underpredicts at high levels.
d) Adopting OCM/OC factor of 2.0 and ammonium sulfate and nitrate scattering efficiency increasing with concentration predicts least amount of bias when comparing to measured light scattering.
e) Climatological f(RH) are biased high compared to those calculated using actual f(RH), particularly at low RH.
1. Correct 1.28 factor – could but in many cases the 90th percentile is closer to the mean of the top 20% because of distribution aren’t exactly normal. Value of $\sigma$ was not addressed – if OC were corrected as sulfate was $\sigma$ would decrease significantly.

2. Carbon multiplier should be changed to 1.8 – no measurement evidence for higher values.

3. Inclusion of sea salt in background and current conditions should not change amount each species is reduced.

4. Oceanic organics would be in both current and natural conditions – same issue.

5. Carbon background is an issue –

6. Many current levels of soil are already below background estimates – leave as is.

7. Policy call for transboundary issues – little doubt there are impacts from areas outside the boundary of US.
a) Ultimately only way of estimating spatial and temporally varying or average background conditions will be through the use of transport and diffusion models.

b) Could adjust mass scattering efficiencies but need more information.

c) Climatological RH is ok – any measured RH at one location is not representative the many and varied sight paths in view shed.
Some Issues Not Addressed

- Sulfate ammoniation
- Nitrate as sodium nitrate – nitric acid interaction with soil and sea salt – hygroscopic properties and nitric acid for the most part is anthropogenic.
- Coarse mass speciation and associated efficiencies and $f(RH)$.
- OC hygroscopicity – what are the appropriate growth curves for any species – effect in low RH environments significant.
- Sampling issues – especially OC bias.
Yosemite special study

- Aerosol dominated by OC

**Study average PM$_{2.5}$ composition**

- POM: 73%
- Black C: 2%
- Soil: 6%
- Ions: 19%
- Oxalate: 1%
- Na+: 1%
- NH$_4$+: 4%
- K+: 0%
- Mg$:^{2+}$: 0%
- Ca$:^{2+}$: 0%
- NO$_3$-: 3%
- NO$_2$-: 0%
- Cl$:^{-}$: 0%
- SO$_4^{2-}$: 10%
- NO$_3$-: 10%
- NO$_2$-: 0%
• Nitrate in coarse mode
• 2.5 um cutpoint issue
• Organics about 1/2
Semi Continuous Ion Data

- Carbon-dominated aerosol
- \((\text{NH}_4)_2\text{SO}_4\) dominant salt
- \(\text{NO}_3^-\) replaced \(\text{Cl}^-\) in sea salt

![Graph showing Na+ vs. Cl- and Na+ vs. ((NO3-)+(Cl-)) with a slope for sea water (1.164).]

![Graph showing 2-week excerpt, PILS 15-min data with Cl-, NO3-, and Na+ concentrations.]
Yosemite size distributions

- Size distributions measured with Differential Mobility Analyzer (DMA)
- Two submicron modes present during some time periods

"CLEAN"

Sometimes smoke had a bimodal distribution
Measured vs Reconstructed Dry Scattering Using IMPROVE Assumptions

Assume an externally mixed model

\[ b_{s,f} = (3)[(NH_4)_2SO_4] + (3)[NH_4NO_3] + (4)[OMC] + (1)[SOIL] \]

Scattering underestimated by about 30% at high scattering values using the above equation.
Mass scattering efficiency is considerably higher than 4.0 m²/g based on DMA size measurements.
Different size distributions have different efficiencies and f(RH) curves.
At RH=85% f(RH) may be about 0.1 for OCM – Generally (RH) is underpredicted for high OCM/SO4 but over predicted for low OCM/SO4.
Measured $f(RH=85\%)$ and difference between measured and predicted $f(RH=85\%)$ as a function of OCM/SO$_4$

24 hr ratios

OCM/SO$_4$ ratios during humidograph scan ($\approx 2$ hrs)
What is carbon natural background?

- Good correlation between water soluble potassium and OC
- Large changes in OC
  - EC remained small
- “Contemporary” carbon dominant
  - Wood smoke
  - Biogenic production
- Molecular markers indicate presence of wood smoke and secondary biogenic particles
  - Vehicle contribution appears small
IMPROVE Seasonal EC and OC

Winter 2001, Dec, Jan, Feb

Elemental Carbon, Winter 2001

Summer 2001, Jun, Jul, Aug

Elemental Carbon, Summer 2001

Organic Carbon, Winter 2001

Organic Carbon, Summer 2001
Great Smoky
Jarbidge
OC/EC Ratio

Winter 2001, Dec, Jan, Feb

- OC/EC ratio varies between 3 - 5, indicative of more primary urban emissions

Summer 2001, Jun, Jul, Aug

- OC/EC > 7 throughout upper West and Texas, Fires?
- OC/EC ~ 3 in Industrial Midwest, primary urban?
- OC/EC > 4-6 in southeast, increased secondary organics?
Simulation

- Gridded fire occurrence data serve as surrogates for fire emissions
- IMPROVE data provide known receptor aerosol mass concentrations
- ATAD back trajectories select fires that impact IMPROVE sites
Wildland fire contribution to IMPROVE OC for 2000
Some Recommendations

- Evaluate each species background and standard deviation – then estimate natural background dv levels. (Higher than current estimates)
- Track each species individually to avoid “trade off” between species when some species estimates are more uncertain than others
Sulfate median values and geometric Standard Deviations

Sulfates

IMPROVE Network by Agency

Sulfates

median Sulfate

sigma
Organics median values and geometric Standard Deviations
Nitrates median values and geometric Standard Deviations
LAC median values and geometric Standard Deviations
Soil median values and geometric Standard Deviations
More Recommendations

- Change OC multiplier from 1.4 to 1.8.
- Leave other variables as is until further information is developed.
- Focus should be on role of organics
  - Mass scattering efficiencies
  - Hygroscopicity
  - Apportionment
  - Measurement
  - Model development (SOA probably play a BIG role) – ?
Washington
SO₂ AND SO₄ COMPARISON

Western US

North Eastern US

South Middle US

South Eastern US