IMPROVE TOR Analysis for Carbon – Assessment of Transition to a New Analyzer

Summary of DRI’s assessment report prepared by Marc Pitchford - 1/24/05
Motivation for replacing the IMPROVE carbon analyzer

- Current systems (DRI/OGC analyzers) built in the mid-1980s are antiquated
  - frequently breaking
  - some parts are no longer available
  - only 4 of 5 systems are currently operational
  - already affecting analysis schedules

- Proposed replacement system (Model 2001 carbon analyzers) are more capable
  - Generates both reflectance and transmission data
  - Has better precision because of better controlled sample temperatures & lower O₂ contamination of the Helium atmosphere
Desired characteristics of a replacement carbon analyzer

• Data comparable to the current IMPROVE system for total carbon (TC) and the organic carbon (OC) and elemental carbon (EC) splits
  – Critical because OC & EC are required to calculate light extinction for the regional haze rule

• As good or better analytical precision as the current system for OC, & EC
  – Important since OC & EC data have less precision than other components, though much of this is due to the uncertainty in field blank values used to adjust the OC data

• Data comparable to the current system for OC and EC subfraction data (OC1, OC2, OC3, OC4, OP, EC1, EC2, & EC3)
  – Desirable because subfraction data have been used in some receptor modeling source attribution
How does Thermal Optical Reflectance Analysis Work?

• Carbon released from a sample that is raised to specific temperatures in a helium atmosphere is measured and labeled organic carbon
  – The 4 OC subfractions correspond to the carbon measured at each of the 4 temperatures used during the OC phase of the analysis

• Then oxygen is added and the temperature is raised so that additional sample carbon is oxidized, released and measured as elemental carbon
  – The 3 EC subfractions correspond to the carbon measured at each of the 3 temperatures used during the EC phase of the analysis

• Changes in optical reflectance of the filter (how dark it looks) during the analysis process are used to adjust biases due to
  – charring of OC that could be mistaken for EC, or
  – oxidation of EC in the helium atmosphere that could be mistaken for OC
Example of an IMPROVE TOR Carbon Thermogram

a) IMPROVE Protocol

- Filter Transmittance
- Filter Reflectance
- Sample Temperature
- Carbon Response

**Temperature (°C), Reflectance & Transmittance (Relative Units) vs. Analysis Time (seconds)**

**Carbon Concentration (ng/second)**

- 100% He
- 2% O₂ / 98% He

Example of an IMPROVE TOR Carbon Thermogram

**IMPLOVE Protocol**

<table>
<thead>
<tr>
<th>Filter Transmittance</th>
<th>Filter Reflectance</th>
<th>Sample Temperature</th>
<th>Carbon Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>EC</td>
<td>OP</td>
<td>EC (TOT)</td>
</tr>
<tr>
<td>OC1</td>
<td>OC2</td>
<td>OC3</td>
<td>OC4</td>
</tr>
<tr>
<td>EC1</td>
<td>EC2</td>
<td>EC3</td>
<td>calib</td>
</tr>
</tbody>
</table>
Initial Comparability of the Current and New TOR Analyzers

- Model 2001 system was programmed to operate the same as the current system (i.e. same temperatures, gas atmosphere, timing, etc.)
- TC, OC,& EC data were comparable for a wide range of IMPROVE and other samples (~240 samples),
- But the subfraction where not comparable though they were correlated
- DRI initiated extensive assessments (~10 months) to understand the differences between the systems and to make adjustments where possible
DRI Assessments/Results

• Developed a method to calibrate analyzers’ thermocouple temperature to actual sample temperature – using temperature indicator liquids on the filter punches
  – DRI/OGC – samples are 10°C – 50°C hotter than thermocouple
  – Model 2001 – samples are 5°C – 20°C hotter than thermocouple
  – Model 2001 has much better temperature precision (between separate analyzers) than the DRI/OGC
  – Model 2001 has much faster heating response time than the DRI/OGC
DRI Assessments/Results (continued)

• Measured trace O$_2$ concentrations diffused into the helium atmosphere in the sample oven
  – O$_2$ concentration in ultra-pure helium gas used is <1ppmv
  – DRI/OGC O$_2$ – 150 to 320ppmv with an average among analyzers of ~250ppmv
  – Model 2001 O$_2$ – ~25ppmv
DRI Assessments/Results (continued)

• Measured the sensitivity of OC and EC and subfractions to sample temperature and O_2 levels in the helium in the ranges seen in the DRI/OGC analyzers using Fresno samples
  – OC & EC are insensitive to temperature or O_2
  – OC1, OC2, OC3, OP, & EC2 are temperature dependent
  – OC3, OP, and EC1 are O_2 level dependent
Impact of temperature and atmospheric environment (O2) on carbon fractions (OC1 and OC2)
Impact of temperature and atmospheric environment (O2) on carbon fractions (OC3 and OC4)
Impact of temperature and atmospheric environment (O2) on carbon fractions (OP and EC1)
Impact of temperature and atmospheric environment (O2) on carbon fractions (EC2 and ECR)
Alternate Model 2001 Operational Protocols

- IMPROVE Protocol – uses the nominal temperatures for the DRI/OGC analyzer
  - Use linear adjustment to relate new carbon subfraction measurements to historic data
- IMPROVE-A Protocol – uses the same sample temperatures (rounded to nearest 10°C) as in the DRI/OGC analyzer
  - Attempt to better reproduce carbon subfraction of “typical” DRI/OGC without having to add O₂
- IMPROVE(250) – 250ppmv O₂ in the helium during the OC analysis phase and temperatures optimize for best agreement with DRI/OGC on Fresno samples
  - Attempt to better match the “typical” DRI/OGC carbon subfractions
Temperature Protocols

<table>
<thead>
<tr>
<th></th>
<th>IMPROVE (°C)</th>
<th>IMPROVE-A (°C)</th>
<th>IMPROVE (250) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC1</td>
<td>120</td>
<td>140</td>
<td>142</td>
</tr>
<tr>
<td>OC2</td>
<td>250</td>
<td>280</td>
<td>238</td>
</tr>
<tr>
<td>OC3</td>
<td>450</td>
<td>480</td>
<td>468</td>
</tr>
<tr>
<td>OC4</td>
<td>550</td>
<td>580</td>
<td>579</td>
</tr>
<tr>
<td>EC1</td>
<td>550</td>
<td>580</td>
<td>591</td>
</tr>
<tr>
<td>EC2</td>
<td>700</td>
<td>740</td>
<td>738</td>
</tr>
<tr>
<td>EC3</td>
<td>800</td>
<td>840</td>
<td>841</td>
</tr>
</tbody>
</table>
Assessment of Alternate Model 2001 Protocols

- DRI/OGC data for IMPROVE samples are compared to Model 2001 IMPROVE (n=243) and IMPROVE-A (n=160) protocols
- DRI/OGC data for IMPROVE samples (n=110) are compared to Model 2001 IMPROVE protocol
- DRI/OGC data are the historic analyses, not recent re-analyses; the Model 2001 analyses are done on the archived portions of the quartz filters
Summary of DRI/OGC and DRI Model 2001

<table>
<thead>
<tr>
<th>Carbon Fraction</th>
<th>DRI/OGC (Y) to DRI Model 2001 with IMPROVE (Y), n=243</th>
<th>DRI/OGC (Y) to DRI Model 2001 with IMPROVE_A (Y), n=160</th>
<th>DRI/OGC (Y) to DRI Model 2001 with IMPROVE(250) (Y), n=110</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>slope Y/X R</td>
<td>slope Y/X R</td>
<td>slope Y/X R</td>
</tr>
<tr>
<td>Total Carbon</td>
<td>1.05±0.005 1.03±0.10 0.99</td>
<td>1.02±0.007 1.00±0.13 0.99</td>
<td>0.98±0.00 0.96±0.12 1.00</td>
</tr>
<tr>
<td>Organic Carbon</td>
<td>1.08±0.006 1.05±0.10 0.98</td>
<td>1.01±0.008 1.00±0.13 0.99</td>
<td>0.92±0.01 0.93±0.13 1.00</td>
</tr>
<tr>
<td>Elemental Carbon</td>
<td>0.89±0.009 0.96±0.28 0.97</td>
<td>1.02±0.010 1.08±0.32 0.98</td>
<td>1.38±0.05 1.60±1.69 0.90</td>
</tr>
<tr>
<td>OC1</td>
<td>1.83±0.09 4.85±16.60 0.45</td>
<td>1.12±0.05 1.89±2.81 0.80</td>
<td>0.85±0.03 1.22±0.89 0.95</td>
</tr>
<tr>
<td>OC2</td>
<td>0.85±0.01 0.85±0.14 0.94</td>
<td>0.74±0.01 0.73±0.14 0.97</td>
<td>1.21±0.02 0.92±0.21 0.98</td>
</tr>
<tr>
<td>OC3</td>
<td>1.55±0.02 1.48±0.30 0.94</td>
<td>1.12±0.02 1.19±0.29 0.93</td>
<td>0.74±0.02 0.87±0.19 0.97</td>
</tr>
<tr>
<td>OC4</td>
<td>1.26±0.02 1.30±0.31 0.89</td>
<td>1.09±0.02 1.16±0.86 0.96</td>
<td>0.87±0.02 1.13±0.37 0.95</td>
</tr>
<tr>
<td>OP</td>
<td>0.37±0.01 0.44±0.21 0.49</td>
<td>0.78±0.03 0.86±0.35 0.76</td>
<td>1.03±0.18 3.07±9.35 0.29</td>
</tr>
<tr>
<td>EC1</td>
<td>0.59±0.01 0.68±0.21 0.88</td>
<td>0.95±0.02 0.95±0.27 0.92</td>
<td>1.45±0.10 1.29±1.16 0.76</td>
</tr>
<tr>
<td>EC2</td>
<td>0.57±0.01 0.63±0.23 0.72</td>
<td>0.84±0.02 0.96±0.35 0.80</td>
<td>1.24±0.04 1.28±0.47 0.79</td>
</tr>
<tr>
<td>EC3</td>
<td>0.30±0.02 0.88±4.86 0.45</td>
<td>0.89±0.11 1.97±2.76 0.43</td>
<td>7.78±1.54 7.33±9.64 0.33</td>
</tr>
</tbody>
</table>

- IMPROVE-A is more comparable to DRI/OGC for all carbon components except for OC2 which is moderately less comparable
- IMPROVE(250) is not comparable to DRI/OGC for EC and has a poor correlation for OP & EC3
Comparisons DRI/OGC to IMPROVE(250) for OC & EC

- Good correlation at low concentrations degrades at higher concentrations
Comparisons of TC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

**IMPROVE**

\[ y = (1.05 \pm 0.005)x, \quad r^2 = 0.99 \]

\[ y/x = 1.05 \pm 0.10 \]

**IMPROVE_A**

\[ y = (1.02 \pm 0.01)x, \quad r = 0.99 \]

\[ y/x = 1.00 \pm 0.13 \]
Comparisons of OC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

**IMPROVE**

- $y = (1.08 \pm 0.006)x$, $r = 0.98$
- $y/x = 1.05 \pm 0.10$

**IMPROVE_A**

- $y = (1.01 \pm 0.01)x$, $r = 0.99$
- $y/x = 1.00 \pm 0.13$
Comparisons of EC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

for IMPROVE:

\[ y = (0.89 \pm 0.009)x, \ r = 0.97 \]
\[ y/x = 0.96 \pm 0.28 \]

N = 243

for IMPROVE_A:

\[ y = (1.02 \pm 0.01)x, \ r = 0.98 \]
\[ y/x = 1.08 \pm 0.32 \]

N = 160
Comparisons of OC1 from DRI/OGC with DRI
Model 2001 IMPROVE and IMPROVE_A

N=243
y=(1.83±0.09)x, r=0.45
y/x=4.85±16.60

N=160
y=(1.12±0.05)x, r=0.80
y/x=1.89±2.81
Comparisons of OC2 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

N=243
\[ y = (0.85 \pm 0.01)x, \quad r = 0.94 \]
\[ y/x = 0.85 \pm 0.14 \]

N=160
\[ y = (0.74 \pm 0.01)x, \quad r = 0.97 \]
\[ y/x = 0.73 \pm 0.14 \]
Comparisons of OC3 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

IMPROVE

\[ y = (1.55 \pm 0.02)x, \quad r = 0.94 \]
\[ y/x = 1.48 \pm 0.30 \]

N=243

IMPROVE_A

\[ y = (1.12 \pm 0.02)x, \quad r = 0.93 \]
\[ y/x = 1.19 \pm 0.29 \]

N=160
Comparisons of OC4 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

- **IMPROVE**
  - N=243
  - \( y = (1.26 \pm 0.02)x \), \( r = 0.89 \)
  - \( y/x = 1.48 \pm 0.30 \)

- **IMPROVE_A**
  - N=160
  - \( y = (1.09 \pm 0.02)x \), \( r = 0.96 \)
  - \( y/x = 1.16 \pm 0.33 \)
Comparisons of OPC from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

**IMPROVE**

- N=243
- \( y = (0.37 \pm 0.01)x \), \( r = 0.49 \)
- \( y/x = 0.44 \pm 0.21 \)

**IMPROVE_A**

- N=160
- \( y = (0.78 \pm 0.03)x \), \( r = 0.76 \)
- \( y/x = 0.86 \pm 0.35 \)
Comparisons of EC1 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

**IMPROVE**

- N=243
- y=(0.59±0.01)x, r=0.88
- y/x=0.68±0.21

**IMPROVE_A**

- N=160
- y=(0.95±0.02)x, r=0.92
- y/x=0.95±0.27
Comparisons of EC2 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

\[
y = (0.57 \pm 0.01)x, \quad r = 0.72
\]

\[
y/x = 0.63 \pm 0.23
\]

\[
y = (0.84 \pm 0.02)x, \quad r = 0.80
\]

\[
y/x = 0.96 \pm 0.35
\]
Comparisons of EC3 from DRI/OGC with DRI Model 2001 IMPROVE and IMPROVE_A

**IMPROVE**

- N=243
- \( y = (0.30 \pm 0.02)x, \ r = 0.45 \)
- \( y/x = 0.88 \pm 4.86 \)

**IMPROVE_A**

- N=160
- \( y = (0.89 \pm 0.11)x, \ r = 0.43 \)
- \( y/x = 1.97 \pm 2.76 \)
Summary/Recommendations

- Model 2001 analyzer using IMPROVE(250) protocol does not reproduce EC data from the currently used DRI/OGC very well for high carbon concentration IMPROVE samples
- IMPROVE & IMPROVE-A produces comparable OC & EC data to the DRI/OGC analyzer data
- IMPROVE-A protocol produces more comparable carbon subfraction data to the DRI/OGC analyzer data than the IMPROVE protocol
- Temperature profiles for all Thermal/Optical Carbon (TOC) analyzers should to be calibrated to actual sample temperatures to aid in understanding their operation
- $O_2$ levels in the helium of the organic phase of the TOC analyzers should be periodically monitored & kept low
IMPROVE Carbon Analysis Decision

- IMPROVE Steering Committee will
  - review the information,
  - discuss it as needed via emails & conference calls and
  - make the decision concerning the use of IMPROVE or IMPROVE-A, or “back to the drawing board”

- If the decision to use IMPROVE or IMPROVE-A is made by the end of February, all samples collected during calendar year 2005 can be analyzed by the same new protocol

- A “back to the drawing board” decision could affect carbon analysis backlogs and slow data turn-around
Additional Assessment Results
Included in the DRI Report

• The OP values that are sometimes negative (<5% of IMPROVE samples) should not be set to zero, but should be applied as a negative correction to the OC (increasing the EC value)

• TOR produces more comparable OC & EC results among the different temperature profiles than TOT (specifically useful for relating IMPROVE to STN OC & EC data)
57 Fresno Samples

18 Hong Kong Samples
Comparison of STN_TOT and STN_TOR with IMPROVE_TOR

IMPROVE III Samples

Fresno Samples
Comparison of STN_TOT and STN_TOR with IMPROVE_TOR (cont’d)

Hong Kong Samples (Road Side)

Montana Fire Samples