Update of IMPROVE
Carbon Analysis

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Objectives

• Report status of IMPROVE carbon analyses
• Discuss issues with new oven suppliers
• Update on minimum detection limits (MDLs)
• Explain the new calibration standard changes
Carbon Laboratory Operations
(July 2017 to June 2018 samples)

- Model 2015 produced over ~90,000 multiwavelength sample analyses since Jul 2015 (~50K IMPROVE and ~40K CSN samples)
- Received ~1,500 samples per month (~1,200 to 2,000 samples each month)
- Maintained 24 hours per day/5-7 days per week operation with 6-7 staff
- Analyzed ~25,200 IMPROVE samples (up to 4,123 per month)
  - 67% increase from previous year (15,100) to reduce the backlog
## IMPROVE_A Carbon Analyses

(July 2017 to June 2018 samples)

<table>
<thead>
<tr>
<th>Sampling Period</th>
<th>Samples Received</th>
<th>Analysis Completion Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/1/17-12/31/17</td>
<td>8,800</td>
<td>Jun 2018</td>
</tr>
<tr>
<td>1/1/18-6/30/18*</td>
<td>9,202</td>
<td>Nov 2018 (Estimate)</td>
</tr>
</tbody>
</table>

*Through July 2018, DRI reported sample data by sample month rather than by batch received in order to expedite final reporting.*
Daily injections* were added (March 2009) due to 24/7 operation (Prior to March 2009, only Autocalib was done daily)

*In addition to every 6 month multipoint calibration

### Daily Calibration Schedule

*Injections: Sucrose, KHP, and/or CO₂ (Based on 24/7 operation)*

<table>
<thead>
<tr>
<th></th>
<th>Sunday</th>
<th>Monday</th>
<th>Tuesday</th>
<th>Wednesday</th>
<th>Thursday</th>
<th>Friday</th>
<th>Saturday</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Morning</strong></td>
<td>System Blank, Lab Blank, Autocalib</td>
<td>Lab Blank, Sucrose</td>
<td>Lab Blank, Autocalib, KHP</td>
<td>Lab Blank, Sucrose</td>
<td>Lab Blank, Autocalib, KHP</td>
<td>Lab Blank, Sucrose</td>
<td>Lab Blank, Autocalib</td>
</tr>
<tr>
<td><strong>Evening</strong></td>
<td>CO₂ Injection</td>
<td>Autocalib</td>
<td>CO₂ Injection</td>
<td>Autocalib</td>
<td>CO₂ Injection</td>
<td>Autocalib</td>
<td>CO₂ Injection</td>
</tr>
</tbody>
</table>

*Retrieved from Model 2015 SOP #2-226r1*
Thirteen Model 2015 Multiwavelength Carbon Analyzers have been in operation since May 2017

(Magee Scientific, Berkeley, CA)
Various quality control (QC) checks are implemented (Oct 2017-Sep 2018)

n=28,502 QC runs (average 78 per day for all instruments)
IMPROVE carbon reporting time has decreased from \(~270\) (July 2017) to \(~160\) (Mar 2018) days (spiked during initial transition to Model 2015)

Days from Sample Receipt to Report
(Samples received between Jan 2014 and Mar 2018)

Begin analysis on Model 2015 (sample date starting 1/1/16)

Expedited GRSM1 & PINN1 analyses for special study
Carbon throughput averaged
~150 samples per day
(Jan 2017 – Sep 2018)

*Does not include calibration runs*
Continental Glass Company unexpectedly shut down in ~Feb 2018

(DRI Model 2015 oven is more complex than Model 2001 oven)

*The dorsal arm transports oxygen or helium to the MnO$_2$ during OC or EC stages, respectively, ensuring that carbon from the filter is completely oxidized to CO$_2$. 
New quartz oven suppliers show inconsistencies in production

General inconsistencies from product to product received*
(i.e., size of MnO₂ bulbs, lengths, heights, amount of support, misaligned cross arms, inner/outer diameter not to spec)

*After 5 months of testing, 3 out of 4 companies passed the acceptance testing (45 glass companies contacted)
Minimum Detection Limits (MDLs) varied by <0.027 µg/m³ with revised threshold.

1/13/16 – Based on 280 lab blank analyses on one analyzer with 2.00 threshold
7/25/18 – Based on 536 lab blank analyses on 13 analyzers with 0.72 threshold

MDL is calculated as three times the standard deviation of the blank filters.

\[ Unc_i = \sqrt{(CV \times c_i)^2 + (MDL/3)^2} \]

Where CV = coefficient of variance
N = number of samples
\( c_i \) = concentration of initial analysis
\( c_{ir} \) = concentration of sample “i” replicate analysis
MDL = minimum detection limit (3σ of laboratory blanks)
Unc = uncertainty
Proposed carbon calibration points will cover 10-90th percentiles to accommodate reducing OC trend. The table below illustrates the proposed calibration points:

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>10th Percentile</td>
<td>1.5</td>
<td>4.1</td>
<td>1.9</td>
<td>4</td>
<td>9</td>
<td>1.5, 3, 6, 12, and 24</td>
</tr>
<tr>
<td>25th Percentile</td>
<td>2.5</td>
<td>6.5</td>
<td>3.4</td>
<td>10</td>
<td>18</td>
<td>1200 ppmC solution</td>
</tr>
<tr>
<td>50th Percentile</td>
<td>4.3</td>
<td>10.0</td>
<td>6.4</td>
<td>15</td>
<td>27</td>
<td>• 20 µL -&gt; 24 µgC</td>
</tr>
<tr>
<td>75th Percentile</td>
<td>7.5</td>
<td>14.9</td>
<td>11.2</td>
<td>20</td>
<td>36</td>
<td>• 10 µL -&gt; 12 µgC</td>
</tr>
<tr>
<td>90th Percentile</td>
<td>12.4</td>
<td>21.6</td>
<td>17.6</td>
<td>(Keep)</td>
<td></td>
<td>• 5 µL -&gt; 6 µgC</td>
</tr>
<tr>
<td>Mean</td>
<td>7.2</td>
<td>12.2</td>
<td>9.3</td>
<td>4</td>
<td>9</td>
<td>150 ppmC solution</td>
</tr>
</tbody>
</table>
<pre><code>                                            |                            |                           |                                     | 10                          |                                  | • 20 µL -&gt; 3 µgC                 |
                                            |                            |                           |                                     | 15                          |                                  | • 10 µL -&gt; 1.5 µgC                |
</code></pre>

Old Sucrose and KHP (µgC/punch) calibration points
9   18   27   36
Proposed Sucrose and KHP (µgC/punch) calibration points
1.5  3    6    12  24
DRI publications and reports using the IMPROVE protocol (n=24)


DRI publications and reports using the IMPROVE protocol (continued)