WRAP Update
Projects

- Updated 1996 emissions
- QA procedures
- New evaluation tools
- Model updates
- CB-IV 2002

- 12 km MM5
- Fugitive dust
- NH₃ emissions
- Model comparisons
- Boundary Conditions
- Source Apportionment
IMPROVE Mean of Clearest 20% Non-Rayleigh Extinction
2001 Calendar Year - IMPROVE Methodology w/SAIC f(RH)s

Total non-rayleigh extinction is proportional to area of circles.
IMPROVE Mean of Hazziest 20% Non-Rayleigh Extinction

2001 Calendar Year - IMPROVE Methodology w/SA/C f(RH)s

Total non-rayleigh extinction is proportional to area of circles.
WRAP - CMAQ revisions

- v0301, released in early 2001
  - Used as the base case and all sensitivity cases for WRAP’s 309 simulations.
- v0602, released in June 2002
- v4.2.2, released in March 2003
The Classical Period: CMAQ v0301

CMAQ_Mean Normalized Bias

Month
1 2 3 4 5 6 7 8 9 10 11 12

NO3 SOIL RCFM SO4 PM25 EC OC PM10 CM

(%)
The Dark Ages: CMAQ v0602

• Included aero3
  – Added large heterogeneous N2O5 hydrolysis.
  – Improved SOA
  – ISORROPIA and updated SO4 nucleation
• Increased HNO3 production and increased nitrate over prediction.
The Renaissance: CMAQ v4.2.2

- v4.2.2, released in March 2003
  - Updated aero3 (reduced N2O5 hydrolysis)
- Full evaluation with all updates and corrections for CMAQ and input data sets discovered during the last two years
  - MCIP v2.2 corrected layer averaging bug
  - Monthly adjusted NH3 emissions
  - Corrected NH3 deposition velocity (0.95 V_HNO3)
  - Emission updates and corrections (baseh)
Modernity: CMAQ v4.3

• Released September 2003.
• Major revisions include:
  – Zeroed out gas N2O5 hydrolysis
  – Added reversible SOA
  – Updated cloud dynamics, time step algorithm
• Completed annual simulation.
• Implemented CB4_2002 (ran Jan & July)
Improvement from v.4.2.2 to v.4.3
Comparisons based on IMPROVE evaluation
Comparisons based on IMPROVE evaluation

Mean Normalized Error (Yearly)

- v0301
- v422
- v43

Bars represent different pollutants:
- SO4
- NO3
- NH4
- OC
- EC
- SOIL
- CM
- PM25
- RCFM
- PM10
- Bext
CB4 mechanism update

- Current regulatory version of CB4 (CB4_89, from Gery et al. 1989) is outdated.

- New updated CB4, CB4_2002, released by Jeffries et al. in 2002
  - Contains 100 principle reactions and 39 model species (excluding secondary organic aerosol precursor species and aqueous species)
  - Fully re-evaluated with smog chamber data
  - Better documentation; the old CB4 in which many of the changes since 1989 have not been well documented.
  - in “Morpho” language format, needs to be converted to CMAQ format
CB4 mechanism update (cont.)

- Major revisions made in CB4_2002 from old CB4
  - Updated photolysis rates; applying 12 photolysis rates, an expansion from 6 photolysis rates used in old CB4.
  - Reaction rates and product distributions are updated to reflect the most recent research findings; the most significant changes are:
    - Additional N2O5 hydrolysis reaction are added:
      - $N2O5 + H2O + H2O \rightarrow 2HNO3 + H2O$
    - New kinetic rate expression for HONO formation (1.5 times higher), and the use of new cross-sections for the HONO dissociations.
    - A 12% lower reaction rate of $OH + NO2 \rightarrow HNO3$, recommended by NASA is used (30% lower rate recommended by IUPAC).
    - Updated PAN formation and decay kinetics.
    - Revised rates and product yields for reactions of $OLE + O3 (NO3, O3P) \rightarrow$ to be consistent with current literature.

- Aromatic chemistry left unchanged.
## Additional reactions added to CB4_2002

<table>
<thead>
<tr>
<th>ADDED RXNS</th>
<th>CB4_2002, k</th>
<th>Rxn ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2O5 + H2O + H2O = 2*HNO3 + H2O</td>
<td>1.8E-39</td>
<td>[IB7]</td>
</tr>
<tr>
<td>NO3 + OH = NO2 + HO2</td>
<td>2.2E-11</td>
<td>[IB8]</td>
</tr>
<tr>
<td>NO3 + HO2 = HNO3 + O2</td>
<td>9.2E-13</td>
<td>[IB9]</td>
</tr>
<tr>
<td>NO3 + NO3 = 2*NO2 + O2</td>
<td>8.5E-13 @ 2450</td>
<td>[IB10]</td>
</tr>
<tr>
<td>O3 + O(3P) = 2*O2</td>
<td>8E-12 @ 2058</td>
<td>[IC7]</td>
</tr>
<tr>
<td>HONO = HO2 + NO2</td>
<td>J[HONO_NO2]</td>
<td>[ID6]</td>
</tr>
<tr>
<td>OH + HO2 = O2 + H2O</td>
<td>4.8E-11 @ -250</td>
<td>[IF6]</td>
</tr>
</tbody>
</table>
Implementation of *CB4_2002* with aerosol and aqueous extensions in CMAQ v.4.3

**CB4_02_AE3_AQ**

- *Followed the changes made in cb4 for new version of CMAQ*
  - New deposition velocity surrogates
  - New cloud scavenging surrogates
  - Changed names of aero3/SOA NR species
  - Eliminated advection and diffusion of fast-reacting species (e.g. OH, HO2)
  - Modified gas-phase Monoterpene reaction rates (to be consistent with those in SAPRC mechanism): higher rate for OH rxn, lower rate for NO3 and O3 rxns.

- *Except changes in ...*
  - Zeroing reaction rate constant for N2O5+H2O→2HNO3
Evaluation of **CB4_2002**

- CMAQ v.4.3 with CB4_02_ae3_aq; smvgear option
- WRAP 1996 January and July episodes
- Area differences between CB4_02 vs. CB4 (pave plots)
- Comparisons against ambient data: (statistics: \( MFB\% \), \( NMB\% \))
  - AQS (31 sites in Jan., 439 sites in July)
  - IMPROVE, (44 sites in Jan., 49 sites in July)
  - CASTNet (3 sites in Jan., 25 sites in July)
  - NADP (87 sites in Jan., 103 sites in July)
IMPROVE
## IMPROVE, January, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>SO4</th>
<th></th>
<th>NO3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>17</td>
<td>21</td>
<td>41</td>
<td>57</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>25</td>
<td>28</td>
<td>5</td>
<td>11</td>
</tr>
</tbody>
</table>

### SO4 vs. CB4/4 CB4 at 48 stations for all days
- **Model Equation:** $y = 0.52454x + 0.32670$
- **R²:** 0.617976
- **Normalized Mean Bias (%):** 17.4018%
- **Fractional Bias (%):** 25.5366%

### NO3 vs. CB4/4 CB4 at 48 stations for all days
- **Model Equation:** $y = 0.528244x + 0.029150$
- **R²:** 0.124719
- **Normalized Mean Bias (%):** 41.2884%
- **Fractional Bias (%):** 5.11328%

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**Notes:**
- The tables and graphs illustrate the comparison of SO4 and NO3 concentrations between CB4 and CB4_02.
- The model equations and statistical metrics provide insights into the performance of the model in predicting the observed concentrations.
### IMPROVE, January, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>NH4</th>
<th>OC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>15</td>
<td>23</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>14</td>
<td>18</td>
</tr>
</tbody>
</table>

**Observed vs. cb4/cb4_02 NH4 at 48 stations for all days**

- CB4: $y = 0.463409x + 0.170547$
- CB4_02: $y = 0.227547$
- Normalized Mean Bias (%) = 15.0128
- Fractional Bias (%) = 14.1846

**Observed vs. cb4/cb4_02 OC at 48 stations for all days**

- CB4: $y = 0.343058x + 0.407389$
- CB4_02: $y = 0.154829$
- Normalized Mean Bias (%) = 14.8072
- Fractional Bias (%) = 14.8072
# IMPROVE, January, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>PM25</th>
<th>RCFM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>19</td>
<td>23</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>10</td>
<td>12</td>
</tr>
</tbody>
</table>

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**Observed vs. CB4/CB4_02 PM2.5 at 48 stations for all days**

- CB4: \( y = 0.327513x + 1.50213 \)  
  - \( r^2 \approx 0.63 \)  
  - Normalized Mean Bias (NMB) (%) = 19.1255  
  - Fractional Bias (FB) (%) = 9.99599

- CB4_02: \( y = 0.358656x + 1.33678 \)  
  - \( r^2 \approx 0.68 \)  
  - Normalized Mean Bias (NMB) (%) = 20.2745  
  - Fractional Bias (FB) (%) = 11.8754

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**Observed vs. CB4/CB4_02 RCFM at 48 stations for all days**

- CB4: \( y = 0.544633x + 1.70320 \)  
  - \( r^2 \approx 0.60 \)  
  - Normalized Mean Bias (NMB) (%) = 29.4590  
  - Fractional Bias (FB) (%) = 18.4801

- CB4_02: \( y = 0.565535x + 1.78652 \)  
  - \( r^2 \approx 0.63 \)  
  - Normalized Mean Bias (NMB) (%) = 30.0790  
  - Fractional Bias (FB) (%) = 28.3889
IMPROVE, January, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>PM10</th>
<th>BEXT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>-40</td>
<td>-38</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>-44</td>
<td>-43</td>
</tr>
</tbody>
</table>

Observed vs. cb4/cb4_02 PM10 1 at 48 stations for all days

- CB4 Model
- CB4_02 Model
- Normalized Mean Bias (%) = -29.54
- Fractional Bias (%) = -44.01%
- Observed vs. cb4/cb4_02 BEXT Recon 1 at 48 stations for all days
- CB4 Model
- CB4_02 Model
- Normalized Mean Bias (%) = 18.82
- Fractional Bias (%) = 5.45%
## IMPROVE, July, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>SO4</th>
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<th>NO3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CB4</td>
<td></td>
<td>CB4_02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NMB(%)</td>
<td>-30</td>
<td>-28</td>
<td>-50</td>
<td>-44</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>-35</td>
<td>-33</td>
<td>-103</td>
<td>-99</td>
</tr>
</tbody>
</table>

**Graphs:**

- **SO4 vs. cb4/cb4 02 SO4 at 49 stations for all days**
  - \( y = 0.470032x + 0.202200 \)
  - \( r^2 = 0.362022 \)
  - Normalized Mean Bias (%) = -29.4454
  - Fractional Bias (%) = -50.9743

- **NO3 vs. cb4/cb4 02 NO3 at 49 stations for all days**
  - \( y = 0.256061x + 0.071067 \)
  - \( r^2 = 0.171623 \)
  - Normalized Mean Bias (%) = -45.2861
  - Fractional Bias (%) = -103.172
**IMPROVE, July, CB4 vs. CB4_02**

<table>
<thead>
<tr>
<th></th>
<th>NH4</th>
<th>OC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>-37</td>
<td>-35</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>-42</td>
<td>-40</td>
</tr>
</tbody>
</table>

**NH4**: Observed vs. cb4/cb4 02 NH4 at 49 stations for all days

- cb4: $y = 0.07091 x + 0.14046$
- cb4 02: $y = 0.07016 x + 0.14380$
- r² = 0.61204
- Normalized Mean Bias (%) = -37.2024
- Fractional Bias (%) = -41.6693

**OC**: Observed vs. cb4/cb4 02 OC at 49 stations for all days

- cb4: $y = 0.71860 x - 0.007613$
- cb4 02: $y = 0.71827 x - 0.20767$
- r² = 0.81220
- Normalized Mean Bias (%) = -29.2876
- Fractional Bias (%) = -33.81
### IMPROVE, July, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>PM25</th>
<th>RCFM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>-38</td>
<td>-37</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>-49</td>
<td>-49</td>
</tr>
</tbody>
</table>

**Observed vs. cb4/cb4_02 PM25**
- $y = 0.240039x + 1.66227$
- $r^2 = 0.109747$
- Normalized Mean Bias (NMB) = -37.3515$
- Fractional Bias (FB) = -48.0946$

**Observed vs. cb4/cb4_02 RCFM**
- $y = 0.70309x + 0.006006$
- $r^2 = 0.374594$
- Normalized Mean Bias (NMB) = -20.3928$
- Fractional Bias (FB) = -32.8879$

**Observed vs. cb4/cb4_02 PM25**
- $y = 0.35951+ 1.65147$
- $r^2 = 0.157446$
- Normalized Mean Bias (NMB) = -37.3893$
- Fractional Bias (FB) = -48.0941$

**Observed vs. cb4/cb4_02 RCFM**
- $y = 0.560056x - 0.306295$
- $r^2 = 0.309035$
- Normalized Mean Bias (NMB) = -20.0126$
- Fractional Bias (FB) = -32.7005
## IMPROVE, July, CB4 vs. CB4_02

<table>
<thead>
<tr>
<th></th>
<th>PM10</th>
<th>BEXT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CB4</td>
<td>CB4_02</td>
</tr>
<tr>
<td>NMB(%)</td>
<td>-64</td>
<td>-64</td>
</tr>
<tr>
<td>MFB(%)</td>
<td>-89</td>
<td>-89</td>
</tr>
</tbody>
</table>

---

### Observed vs. cb4/cb4_02 PM10

<table>
<thead>
<tr>
<th>cb4</th>
<th>y = 0.126491x + 2.34207</th>
</tr>
</thead>
<tbody>
<tr>
<td>r^2</td>
<td>0.112859</td>
</tr>
<tr>
<td>Normalized Mean Bias (%)</td>
<td>-62.7179</td>
</tr>
<tr>
<td>Fractional Bias (%)</td>
<td>-89.2821</td>
</tr>
<tr>
<td>cb4_02 Model</td>
<td>y = 0.511058x + 5.54176</td>
</tr>
<tr>
<td>r^2</td>
<td>0.511058</td>
</tr>
<tr>
<td>Normalized Mean Bias (%)</td>
<td>-25.9886</td>
</tr>
<tr>
<td>Fractional Bias (%)</td>
<td>-30.5861</td>
</tr>
</tbody>
</table>

### Observed vs. cb4/cb4_02 BEXT Recon1

<table>
<thead>
<tr>
<th>cb4</th>
<th>y = 0.608497x + 5.14231</th>
</tr>
</thead>
<tbody>
<tr>
<td>r^2</td>
<td>0.510621</td>
</tr>
<tr>
<td>Normalized Mean Bias (%)</td>
<td>-25.9286</td>
</tr>
<tr>
<td>Fractional Bias (%)</td>
<td>-30.5861</td>
</tr>
<tr>
<td>cb4_02 Model</td>
<td>y = 0.613590x + 4.74911</td>
</tr>
<tr>
<td>r^2</td>
<td>0.519022</td>
</tr>
<tr>
<td>Normalized Mean Bias (%)</td>
<td>-25.57</td>
</tr>
<tr>
<td>Fractional Bias (%)</td>
<td>-29.2055</td>
</tr>
</tbody>
</table>
IMPROVE, January, Mean Fractionalized Bias

![Bar chart showing fractionalized bias for various components.](chart.png)
IMPROVE, July, Mean Fractionalized Bias

![Bar chart showing the mean fractionalized bias for various pollutants including SO4, NO3, NH4, OC, EC, SOIL, CM, PM25, RCFM, PM10, and BEXT. The chart compares CB4 and CB4_02 models.]