The role of chemistry in upper troposphere NO$_2$ under-predictions

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CMAQ compared with SCIAMACHY: worst in rural areas.

Figure 1: NO$_2$ columns ($10^{15}$ molec/cm$^2$) from Napelenok ACP 2008

Figure 2: Vertical profiles of background and polluted conditions from Singh 2007.
Which model processes lead to under-prediction?

- Potential sources of error:
  - chemistry, photolysis, aerosols, advection, convection, diffusion, wet deposition, dry deposition, emissions, the stratosphere, the ocean, ...

- Modeled chemistry has been questioned (Olson 2006, Bertram 2007, Ren 2008)
  - typically: evaluate a model against a chamber study (i.e. a controlled timeseries of measurements)
  - problem: does anyone have a chamber at 236K and 0.298 atm?

- What to do?
  1. We need a timeseries of observations
  2. We need a timeseries of model results
Bertram results can derive air parcel ages

Deep convection sends a plug of surface air to upper troposphere
- wet scavenging removes HNO$_3$ and lightning adds NO$_x$
- Air parcels are mostly stable for up to 5 days
- Freshly convected: NO$_x$:HNO$_3$ $>>$ 1
- Aged air parcel: NO$_x$:HNO$_3$ $<<$ 1

Figure 3: Deep convection from Bertram et al. Science 2007
Figure 4: NO$_x$:HNO$_3$ is used to categorize days since convection. O$_3$ shows a monotonic increase with time. CO shows a monotonic decrease with time. NO$_2$ shows a gradual increase with time.
Observation timeseries: classified by “derived age”

Figure 4: NO_x:HNO_3 is used to categorize days since convection. O_3 shows a monotonic increase with time. CO shows a monotonic decrease with time. NO_2 shows a gradual increase with time.
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Simulating aging of freshly convected air parcels

- Box modeling air parcels using LEEDS DSMACC box model
- Physical and initial conditions from “freshly convected” observations

**Table 1**: Overview of 7 chemical mechanisms in this study.

<table>
<thead>
<tr>
<th>Model (abbreviation)</th>
<th># Rxns</th>
<th># Spcs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Bond '05 (CB05)</td>
<td>176</td>
<td>62</td>
</tr>
<tr>
<td>State Air Pollution Research Center ‘99 (SAPRC99)</td>
<td>222</td>
<td>77</td>
</tr>
<tr>
<td>SAPRC ‘07 (SAPRC07)</td>
<td>&lt;700</td>
<td>153</td>
</tr>
<tr>
<td>Model for OZone And Related chemical Tracers “Standard” (MZ4)</td>
<td>290</td>
<td>88</td>
</tr>
<tr>
<td>GEOS-Chem “full” (GEOS)</td>
<td>290</td>
<td>88</td>
</tr>
<tr>
<td>Regional Atmospheric Chemistry Mech v.2 (RACM2)</td>
<td>341</td>
<td>117</td>
</tr>
<tr>
<td>Master Chemical Mechanism (MCM)</td>
<td>&gt;4500</td>
<td>&gt;1700</td>
</tr>
</tbody>
</table>

Barron Henderson, MS, ORISE Research Fellow
Upper troposphere NO₂ under-predictions 6/16
Figure 5: Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).
### Figures

#### Figure 5

Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).
Figure 5: Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations ($p < 0.0001$).
Figure 5: Model predictions compared to observations with the Mann-Whitney U test. Model medians are displayed circles that are filled when consistent with observations (p < 0.0001).
Models over-predict NO$_2$/NO$_x$, PAN, and HNO$_3$

Figure 6: Nitrogen species 24 hours since convection: observed (back) and modeled (front). Filled circles are consistent with observations (p < 0.0001).
Conclusions: Model performance

- Semi-explicit, regional, and global models all
  - under-predict $\text{NO}_x$:HNO$_3$
  - under-prediction $\text{NO}_x$
  - over-predict $\text{NO}_x$, esp. CH$_3$C(O)ONO$_2$ and HNO$_3$
  - over-prediction $\text{NO}_2$/NO$_x$

- All problems point to too many radical reactions
Figure 7: GEOS-Chem tested with old acetone quantum yield, with 2×CO, and with constrained acetaldehyde. Model medians are displayed circles that are filled when consistent with observations (p < 0.0001).
Figure 8: HOx by solar zenith angle 24 hours since convection: observed (back) and modeled (front). Filled circles are consistent with observations (p < 0.0001).
Potential issues

- Over-predicting radical source (i.e. photolysis)
- Over-predicting radical amplification
  - **CH₂O**
    - \( \text{OH} + \text{CH}_2\text{O} \rightarrow \text{CO} + \text{HO}_2 \)
    - \( \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}^\cdot \)
  - **CH₃CHO**
    - \( \text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{C(O)OO}^\cdot \)
    - \( \text{CH}_3\text{C(O)OO}^\cdot + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{OO}^\cdot \)
    - \( \text{CH}_3\text{OO}^\cdot + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{HO}_2 \)
    - \( \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}^\cdot \)
- Over-predicting radical cycling efficiency
  - ratio of radical propagating to radical terminating reactions
  - propagation (i.e. \( \text{RO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{RO}^\cdot \))
  - termination (i.e. \( \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \))
Radicals sources in the first 4 hours

Table 2: Comparison of new radicals (ppt) by chemical mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>GEOS</th>
<th>CB05</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_2\text{O} \rightarrow \text{CO} + 2 \cdot \text{HO}^\cdot$</td>
<td>488</td>
<td>346</td>
</tr>
<tr>
<td>$\text{O}_3 \rightarrow \text{O}^1\text{D}; \text{O}^1\text{D} + \text{H}_2\text{O} \rightarrow 2 \cdot \text{HO}^\cdot$</td>
<td>215</td>
<td>246</td>
</tr>
<tr>
<td>$\text{HNO}_2 \rightarrow \text{NO} + \text{HO}^\cdot$</td>
<td>226</td>
<td>186</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 \rightarrow 2 \cdot \text{HO}^\cdot$</td>
<td>100</td>
<td>103</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C(O)OOH} \rightarrow \text{CH}_3\text{OO}^\cdot + \text{HO}^\cdot$</td>
<td>38</td>
<td>59</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CHO} \rightarrow \text{CO} + \text{HO}^\cdot_2 + \text{CH}_3\text{OO}^\cdot$</td>
<td>31</td>
<td>37</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C(O)CH}_3 \rightarrow \text{CH}_3\text{C(O)OO}^\cdot + \text{CH}_3\text{OO}^\cdot$</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>$\text{HNO}_4 \rightarrow \text{HO}^\cdot_2 + \text{NO}_2$</td>
<td>23</td>
<td>13</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OOH} \rightarrow \text{CH}_2\text{O} + \text{HO}^\cdot_2 + \text{HO}^\cdot$</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td><strong>Total new Radicals</strong></td>
<td><strong>1199</strong></td>
<td><strong>1035</strong></td>
</tr>
<tr>
<td>$\text{CH}_3\text{OOH} + \text{HO}^\cdot \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{HO}^\cdot$</td>
<td>0</td>
<td>26</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OOH} + \text{HO}^\cdot \rightarrow \text{HO}_2 + \text{XO}_2 + \text{CH}_3\text{OO}^\cdot$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Radicals sinks in the first 4 hours

Table 3: Comparison of radical removals (ppt) by chemical mechanism.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>GEOS</th>
<th>CB05</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO$^\cdot$ + HO$^\cdot$ $\rightarrow$ H$_2$O + O$_2$</td>
<td>363</td>
<td>266</td>
</tr>
<tr>
<td>HO$^\cdot$ + NO $\rightarrow$ HNO$_2$</td>
<td>234</td>
<td>192</td>
</tr>
<tr>
<td>NO$_2$ + HO$^\cdot$ $\rightarrow$ HNO$_4$</td>
<td>176</td>
<td>154</td>
</tr>
<tr>
<td>HO$^\cdot$ + NO$_2$ $\rightarrow$ HNO$_3$</td>
<td>131</td>
<td>104</td>
</tr>
<tr>
<td>HO$^\cdot$ + HO$^\cdot$ $\rightarrow$ H$_2$O$_2$</td>
<td>92</td>
<td>88</td>
</tr>
<tr>
<td>HO$^\cdot$ + HNO$_4$ $\rightarrow$ H$_2$O + NO$_2$ + O$_2$</td>
<td>83</td>
<td>71</td>
</tr>
<tr>
<td>CH$_3$OO$^\cdot$ + HO$^\cdot$ $\rightarrow$ CH$_3$OOH + O$_2$</td>
<td>43</td>
<td>29</td>
</tr>
<tr>
<td>HO$_2$ + CH$_3$C(O)OO$^\cdot$ $\rightarrow$ CH$_3$C(O)OOH</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
<td><strong>Total Radical Sink</strong></td>
<td><strong>1219</strong></td>
<td><strong>1025</strong></td>
</tr>
</tbody>
</table>
Conclusions

Model performance
- models under-predict NO\textsubscript{2} particularly after 1 day old
- over-predict rate of “aging” in the first 24 hours (improves subsequently)
- best O\textsubscript{3} came from worst HO\textsubscript{x}·
- HO\textsubscript{x}·
  - Like other studies HO\textsubscript{·model} = 2 \times HO\textsubscript{·obs}
  - Unlike other studies HO\textsubscript{2model} > HO\textsubscript{2obs}

Best practices
- check model photolysis for pressure/temperature sensitivity
- use detailed photolysis in the upper troposphere
- use Blitz et al. 2004 CH\textsubscript{3}C(O)CH\textsubscript{3} quantum yield

Next steps
- Investigate HO\textsubscript{2model} improvement compared to other studies
- Attribute radical production to initial species (not immediate precursor)
- Assess uncertainty in major radical source species
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