Sensitivity of Stratospheric and Tropospheric Chemistry to Perturbations of Methane, Carbon Dioxide, Nitrous Oxide, and Chlorofluorocarbons

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2D Model Run Boundary Conditions

<table>
<thead>
<tr>
<th>CH₄ (ppmv)</th>
<th>N₂O (ppbv)</th>
<th>CO₂ (ppmv)</th>
<th>F11/F12 (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>280</td>
<td>280</td>
<td>0</td>
</tr>
<tr>
<td>1.8</td>
<td>360</td>
<td>420</td>
<td>0.3</td>
</tr>
<tr>
<td>2.4</td>
<td>440</td>
<td>560</td>
<td>0.6</td>
</tr>
<tr>
<td>3.0</td>
<td>700</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>840</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ran all combinations of boundary conditions in table
→ 5 x 3 x 5 x 4 = 300 model runs

Each run was 30 years from the same initial condition to reach steady state. Only last year used.

+17 more runs to elucidate difference between F11, F12, and CH₃Br

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Problem 1: Interaction of $N_2O$ and $CO_2$

- $N_2O$ is the source of $NO_\gamma$ that can catalytically destroy ozone
- $CO_2$ cools the stratosphere slowing the ozone loss processes
- $CO_2$ cooling increases the loss of stratospheric $NO_\gamma$ by favoring $N + NO$ reaction over $N + O_2$
What controls $NO_y$ in the stratosphere?

- $N_2O$ is the primary source of $NO_y$ ($N + NO + NO_2 + NO_3 + 2*N_2O_5 + HNO_3 + ClONO_2 + BrONO_2$)

- Doubling of $N_2O$ leads to 50% increase in $NO_y$ ($NO_y$ chemical loss term proportional to $[NO_y]^2$)
CO$_2$ also impacts NO$_y$ in the stratosphere

- 3 x CO$_2$ $\rightarrow$ 10-15% decrease in NO$_y$
- Cooling of stratosphere changes balance of
  - N + NO $\rightarrow$ N$_2$ + O
  - N + O$_2$ $\rightarrow$ NO + O
The evolution of stratospheric NO$_y$

- Depends on the relative change of N$_2$O and CO$_2$ in the future
- A1b scenario leads to constant future NO$_y$
- A2 scenario leads to increasing NO$_y$

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Ozone Scenarios

- Chlorine dominates ozone change
- Amount of global “super-recovery” depends on relative scenario for N₂O and CO₂ change
Problem 2: Relative impact of halogens

- Bromine impact on ozone depends on chlorine amount
- F11 is more effective than F12 because it is photolyzed at lower altitude.
Global Total Ozone Sensitivity to Bromine

- Used added 2D model runs for 0, 10, 20 pptv of CH$_3$Br at 0.1, 0.5, 2.0, 3.5, and 5.0 ppbv of chlorine for single values of CH$_4$, N$_2$O, and CO$_2$

- Sensitivity increased with increasing chlorine (because of ClO + BrO reaction)
Chlorine from F11 is more effective in reducing ozone than is the same amount of chlorine from F12.
Problem 3: Impact on tropospheric and stratospheric OH

- Increasing methane increases stratospheric OH
- Percent positive OH change maximizes in UTLS
- Increasing methane decreases lower and middle tropospheric OH
- Increasing $\text{CO}_2$ increases tropospheric OH
- Future direction depends on scenario
Impact of Doubling CH$_4$ on OH

- OH decreases in lower to middle troposphere
- OH percentage increase maximizes in upper troposphere and lower stratosphere
- OH absolute increase maximizes in upper stratosphere
Combined Effect of CH₄ and CO₂ on Tropospheric OH

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Summary and Conclusions

• Stratospheric NO\(_y\) (or NO\(_x\)) depends on both N\(_2\)O and CO\(_2\)

• As CFCs decrease, N\(_2\)O and CO\(_2\) will control the ozone depending on the future scenario for growth of each

• Bromine is more effective in reducing ozone at high chlorine amounts (increased efficiency saturates at about 3.5 ppbv Cl\(_y\))

• Tropospheric OH responds to changes in both CH\(_4\) and CO\(_2\)
  – Decreases in lower to middle troposphere
  – Increases in upper troposphere and stratosphere