Nitrous Oxide, Carbon Dioxide and the Future of the Ozone Layer

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Model Projections for Ozone Recovery

One of the original motivations of the GEOSCCM Project was “Ozone recovery into a changing stratosphere”
We put these together into an “Equivalent Effective Stratospheric Chlorine” or EESC
Model Projections for Ozone Recovery

![Graph showing model projections for ozone recovery from 1960 to 2100 for latitudes 60°S-60°N. The graph compares past simulations, future simulations, 1960 Cly Simulation, Time Slice Simulations, GEOS 5 Simulations, and Satellite Data (+2.5 DU).]
GHGs change ozone levels
Fixed ODS, increasing GHGs (2065-1980)

Stratosphere cools because of GHGs
T (K)

O$_3$ increases in upper stratosphere
O$_3$ (ppmv)

Troposphere warms because of GHGs

Feng Li, NASA/GSFC

Li, Stolarski, and Newman, Atmos. Chem. Phys., 9, 2207-2213, 2009

Stolarski, Goddard Branch Lunch, 14 May 2015
Greenhouse gas cooling leads to a clear “super-recovery” in the upper stratosphere (in model simulations)

So, what will control the amount of ozone in the stratosphere at the end of the century?
Nitrous oxide and methane?

Model did not calculate self-consistent temperature:
so no impact of carbon dioxide
A recent article has highlighted the impact of nitrous oxide on ozone

Ravishankara et al. Science 326, 123-125, 2009
The effects of nitrous oxide on ozone are impacted by cooling of the upper stratosphere due to greenhouse gases.
Odd Nitrogen (NO\textsubscript{\text{y}}) is produced by the reaction of O\textsuperscript{(1D)} with Nitrous Oxide (N\textsubscript{2}O) and destroyed by the reaction of N atoms with NO.

\[
\text{NO}_{\text{y}} = \text{N} + \text{NO} + \text{NO}_{2} + \text{NO}_{3} + 2*\text{N}_{2}\text{O}_{5} + \text{HNO}_{3} + \text{HO}_{2}\text{NO}_{2} + \text{ClNO}_{3} + \text{BrNO}_{3}
\]

- **Definition of NO\textsubscript{y}**

- **Production of NO\textsubscript{y}**

\[
\text{O(1D)} + \text{N}_{2}\text{O} \rightarrow \text{NO} + \text{NO}
\]

- **Production of N(\textsuperscript{4}S)**

\[
\text{hv} + \text{NO} \rightarrow \text{N(4S)} + \text{O}
\]

- **Loss of NO\textsubscript{y}**

\[
\text{N(4S)} + \text{NO} \rightarrow \text{N}_{2} + \text{O}
\]
NO$_y$ Production is balanced by loss and transport to the troposphere

Chemical Loss occurs in the upper stratosphere above ~10 hPa.

Chemical Loss is about 30-40% of total loss: transport to the troposphere is 60-70%.

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N atoms, formed by photolysis of NO, can either reform NO or can react with NO to remove NO$_y$.

$$K_{N+O_2} = 1.5 \times 10^{-11} \exp(-3600/T)$$

The branching ratio is strongly temperature dependent: low temperatures $\Rightarrow$ more NO$_y$ loss.
Climate change affects NO$_y$ impact on ozone

\[ \Delta O_3 = \frac{\partial O_3}{\partial NO_y} \Delta NO_y \]

\[ NO_y = NO_y (N_2O, T) \]

\[ \Delta NO_y = \frac{\partial NO_y}{\partial N_2O} \Delta N_2O + \frac{\partial NO_y}{\partial T} \Delta T \]

\[ \Delta O_3 = \frac{\partial O_3}{\partial NO_y} \frac{\partial NO_y}{\partial N_2O} \Delta N_2O + \frac{\partial O_3}{\partial NO_y} \frac{\partial NO_y}{\partial T} \Delta T \]

NO$_y$ leads to ozone loss

NO$_y$ is a function of both $N_2O$ and Temperature

The change in NO$_y$ (and ozone) thus depends on both $N_2O$ and Temperature

The ODP is the ratio of this term to the equivalent term for CFC-11
Simulation with 25% increase in N₂O yields 40% increase in NOₓ production and 70% increase in NOₓ loss.

- Production increases due to speed up of circulation pushing N₂O to higher altitude.
- Loss increases due to cooling of upper stratosphere.
- Net result is slight decrease in NOₓ, NOₓ, and ozone loss despite the increase in N₂O.
Cautionary Note:
Quantitative model results may vary because of treatment of NO absorption that leads to photolysis to N atoms

![Graph showing ratio of concentration to 2010](image1.png)

- NO absorption lines are interspersed among the Schumann-Runge Bands of O$_2$ that determine the penetration of solar UV into the upper stratosphere.

- Consideration of the N$_2$O/NO$_y$ relationship provides some constraint on NO photolysis and should narrow the model range.


All models in the CCMVal2 exercise found a significant temperature feedback on NO$_y$ concentrations. GEOS CCM had one of the larger impacts.

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What would happen if we could limit \( \text{N}_2\text{O} \)?

Reducing \( \text{N}_2\text{O} \) in 2100 would lead to greater super-recovery in the extra-tropics and perhaps a full recovery (or more) in the tropics (but we have no quantitative estimates!)

Models (e.g. Li et al. *Atmos. Chem. Phys.*, 9, 2207-2213, 2009) simulate a “super-recovery” of ozone at mid and high latitudes and a slight under recovery in the tropics.

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Nearly 6 years later, we have finally managed to publish these results!

Environmental Research Letters

LETTER

Impact of future nitrous oxide and carbon dioxide emissions on the stratospheric ozone layer

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Keywords: ozone layer, nitrous oxide, carbon dioxide
### 2D Model Run Boundary Conditions

<table>
<thead>
<tr>
<th>CH&lt;sub&gt;4&lt;/sub&gt; (ppmv)</th>
<th>N&lt;sub&gt;2&lt;/sub&gt;O (ppbv)</th>
<th>CO&lt;sub&gt;2&lt;/sub&gt; (ppmv)</th>
<th>F11/F12 (ppmv)</th>
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<tr>
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Ran all combinations of boundary conditions in table
\[ 5 \times 3 \times 5 \times 4 = 300 \text{ model runs} \]

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 CH<sub>3</sub>Br

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Global Average NO$_y$ Column vs CO$_2$ and N$_2$O Boundary Conditions (at 2 ppbv Cl$_y$, 1.8 ppmv CH$_4$)
Global Average Ozone Column vs CO₂ and N₂O Boundary Conditions (at 2 ppbv Cl₂, 1.8 ppmv CH₄)
2D Model Run Boundary Conditions

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Problem 1: Interaction of N$_2$O and CO$_2$

• N$_2$O is the source of NO$_y$ that can catalytically destroy ozone
• CO$_2$ cools the stratosphere slowing the ozone loss processes
• CO$_2$ cooling increases the loss of stratospheric NO$_y$ by favoring N + NO reaction over N + O$_2$
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.
Conversion to ODP

- F12 (303.5-286.7)/4.5Cl(ppbv)=3.73DU O3 change/Cl ppbv
- F11 (303.5-281.5)/4.5Cl(ppbv)=4.89DU O3 change/Cl ppbv

Multiply by # Cl atoms/CFC
- F12 x2 = 7.46DU O3 change/CFC ppbv
- F11 x3 = 14.7DU O3 change/CFC ppbv

Multiply by lifetime to convert to flux necessary
- F12 x103.7 = 774 DU O3 change /CFC flux
- F11 x 58.6 = 861 DU O3 change /CFC flux

Divide by molecular mass to convert flux to lbs
- F12/121 = 5.98 DU O3 change /CFC lb
- F11/137.7= 6.25 DU O3 change /CFC lb

ODP of F12 should be about 0.96 (0.90 if done per molecule)(0.76 if done by Cl atom)
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 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 CH$_4$ and CO$_2$ on Tropospheric OH

Caveat: Model has a simple tropospheric chemistry with CH$_4$ as the only significant hydrocarbon
Summary and Conclusions

• Stratospheric NO\textsubscript{y} (or NO\textsubscript{x}) depends on both N\textsubscript{2}O and CO\textsubscript{2}

• As CFCs decrease, N\textsubscript{2}O and CO\textsubscript{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\textsubscript{y})

• Tropospheric OH responds to changes in both CH\textsubscript{4} and CO\textsubscript{2}
  – Decreases in lower to middle troposphere
  – Increases in upper troposphere and stratosphere