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


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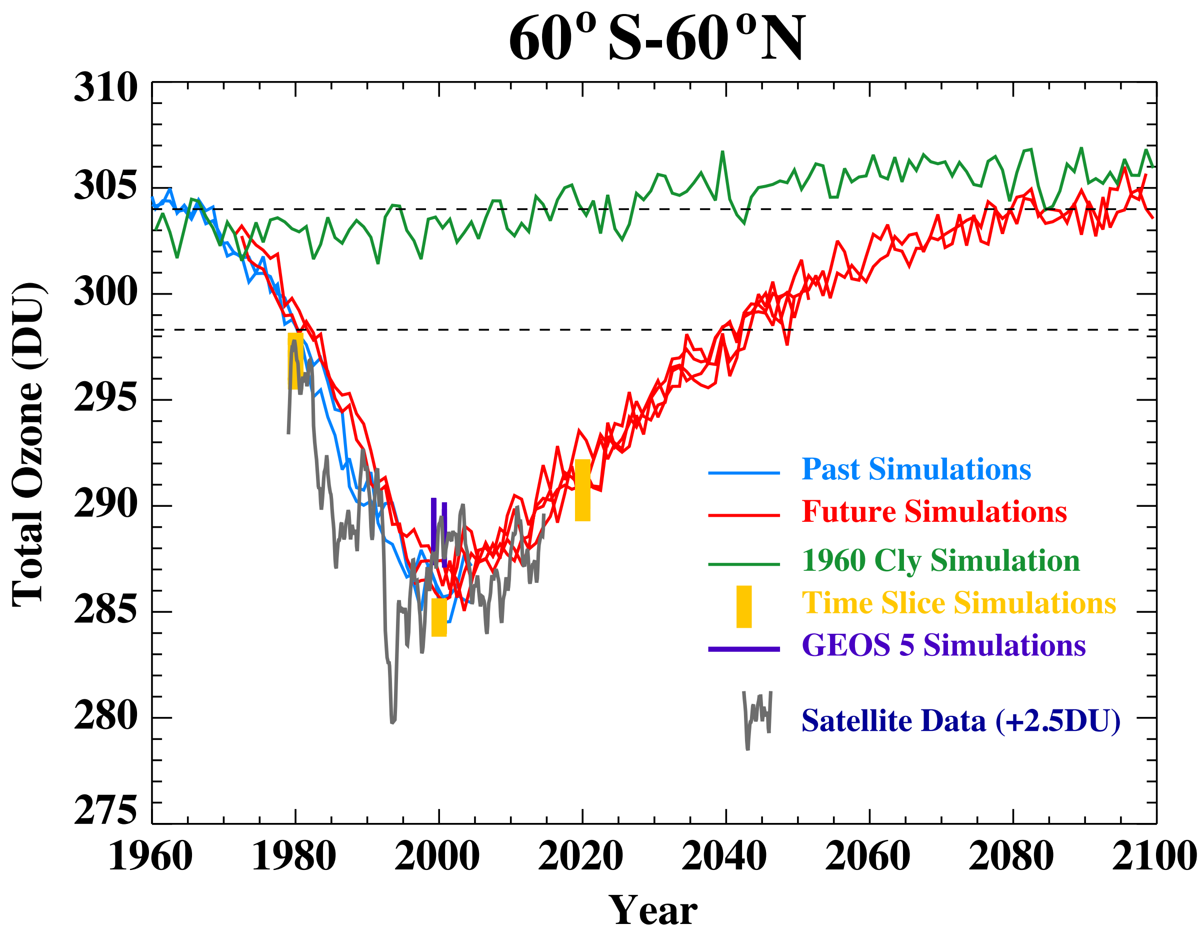
**and Emeritus at GSFC**

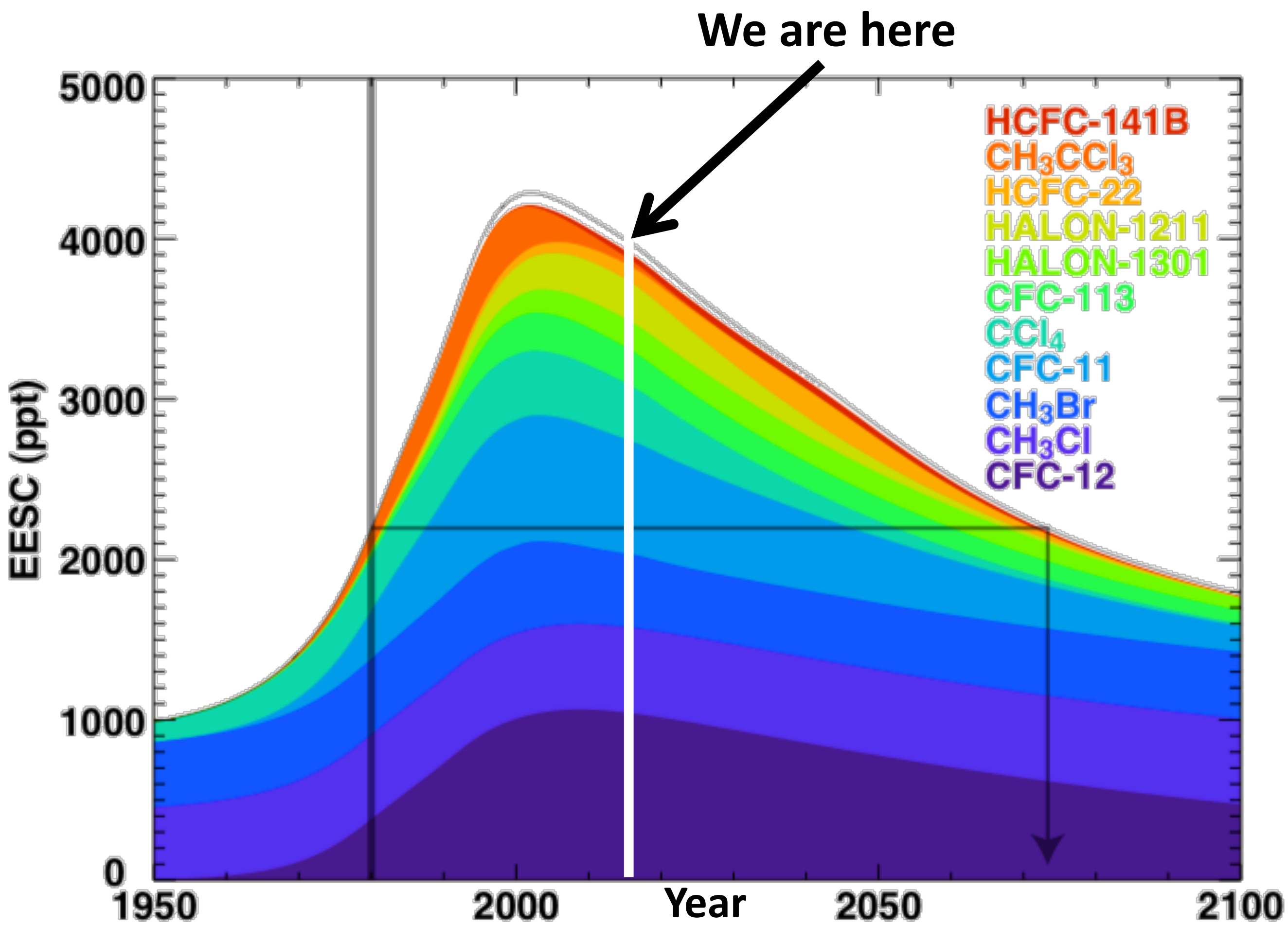
# Model Projections for Ozone Recovery

Early results from GEOSCCM




*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



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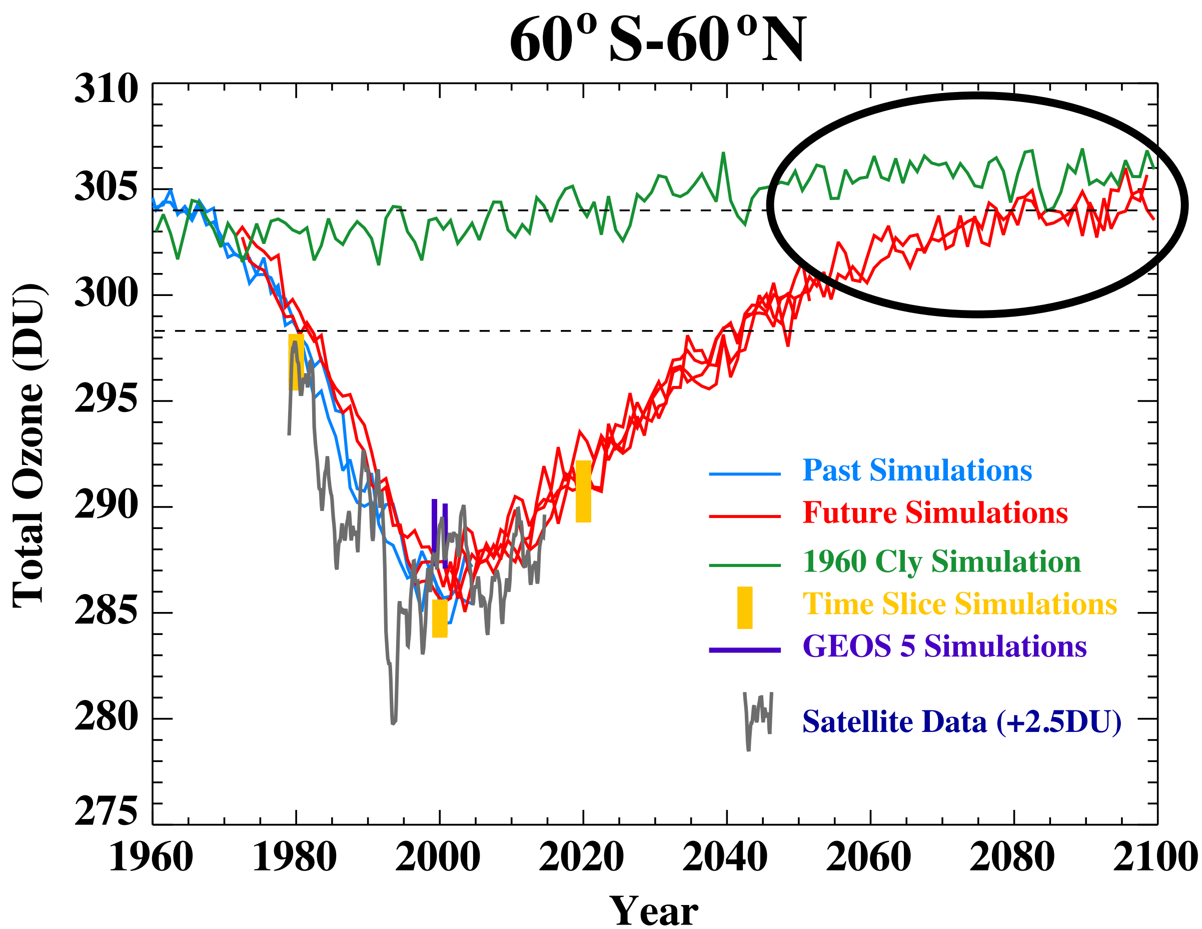
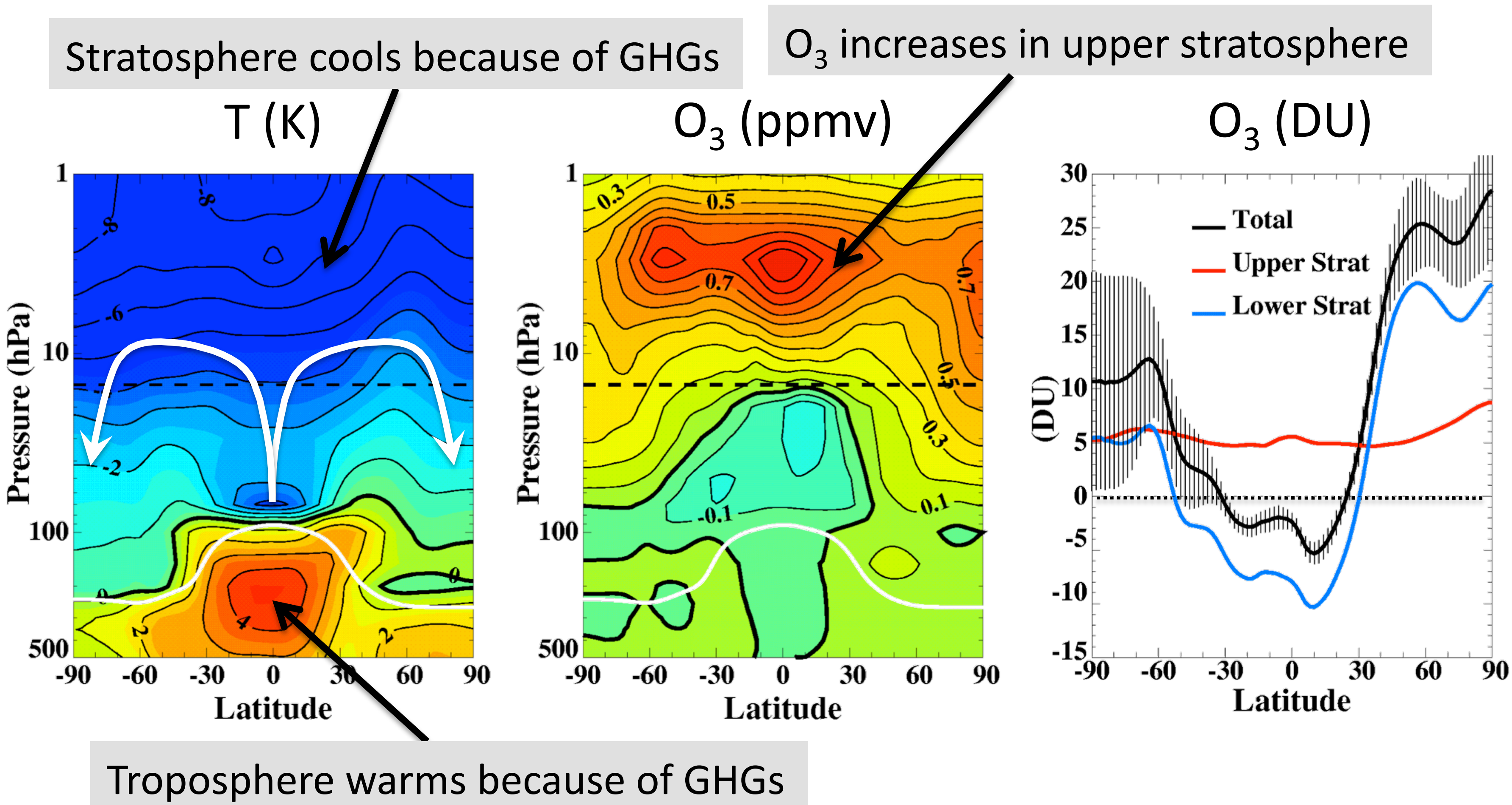





Stolarski, Goddard Branch Lunch, 14 May 2015

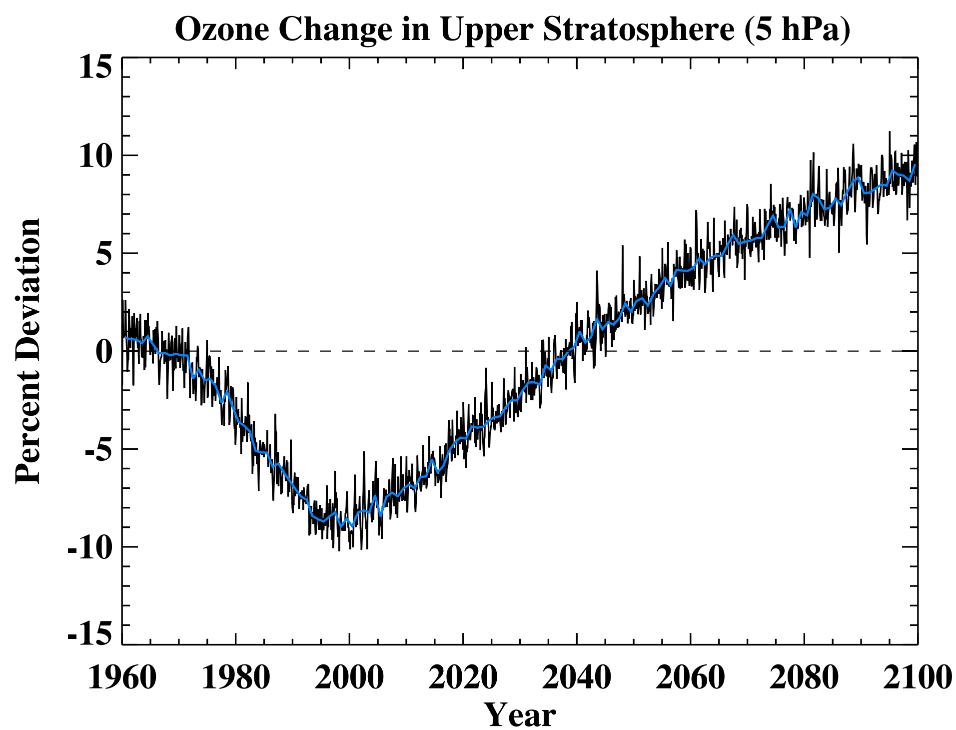
# GHGs change ozone levels
# Fixed ODS, increasing GHGs (2065-1980)




Feng Li, NASA/GSFC

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

# 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?

GEOPHYSICAL RESEARCH LETTERS, VOL. 29, NO. 4, 1051, 10.1029/2001GL014295, 2002

## Stratospheric ozone depletion at northern mid latitudes in the 21st century: The importance of future concentrations of greenhouse gases nitrous oxide and methane

L. K. Randeniya, P. F. Vohralik, and I. C. Plumb
CSIRO Telecommunications and Industrial Physics, PO Box 218, Lindfield, NSW 2070, Australia

Received 29 October 2001; revised 10 January 2002; accepted 11 January 2002; published 28 February 2002.

**Model did not calculate self-consistent temperature:**
**so no impact of carbon dioxide**

now, not so recent

# A ~~recent~~ article has highlighted the impact of nitrous oxide on ozone

Ravishankara et al.
*Science* **326,** 123-125, 2009

Sciencexpress Report

**Nitrous Oxide ($N_2O$): The Dominant Ozone-Depleting Substance Emitted in the 21st Century**

A. R. Ravishankara,* John S. Daniel, Robert W. Portmann

Chemical Sciences Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder CO 80305 USA.

*To whom correspondence should be addressed. E-mail: A.R.Ravishankara@noaa.gov

**By comparing the ozone depletion potential-weighted anthropogenic emissions of $N_2O$ with those of other ozone depleting substances, ODSs, we show that $N_2O$ emission currently is the single most important ODS emission and is expected to remain the largest throughout the 21st century. $N_2O$ is unregulated by the Montreal Protocol. Limiting future $N_2O$ emissions would enhance the recovery of the ozone layer from its depleted state, and would also reduce the anthropogenic forcing of the climate system, representing a 'win-win' for both ozone and climate.**

of as primarily a natural atmospheric constituent but the influence of its changes on long-term changes in ozone levels has also been examined (*8-10*).

Nitrous oxide shares many similarities with the CFCs, historically the dominant ODSs. The CFCs and $N_2O$ are very stable in the troposphere, where they are emitted, and transported to the stratosphere where they release active chemicals that destroy stratospheric ozone through chlorine- or nitrogen oxide-catalyzed processes. They both have significant anthropogenic sources. Unlike CFCs, $N_2O$ also has natural sources, akin to methyl bromide, which is another

U.S.News & WORLD REPORT Wednesday, September 2, 2009

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**Nitrous Oxide Fingered as Monster Ozone Slayer**

Posted August 28, 2009

*By Janet Raloff, for Science News' Science & the Public Blog*

ScienceNews

Most people know nitrous oxide as the laughing gas that dentists reserve for drill-phobic patients. But once it enters the atmosphere, N2O is no laughing matter. New calculations indicate that it has risen to become the leading threat to the future integrity of stratospheric ozone, Earth's protective shield against the sun's harmful ultraviolet rays.

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**Farmers take another blow: Nitrous oxide linked to ozone**

SEPTEMBER 1, 2009

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Nitrous oxide, a gas emitted by the application of nitrogen fertilizer to cornfields, already has been blamed for making the Earth hotter by contributing to greenhouse gas emissions.

# The effects of nitrous oxide on ozone are impacted by cooling of the upper stratosphere due to greenhouse gases

GEOPHYSICAL RESEARCH LETTERS, VOL. 25, NO. 23, PAGES 4381-4384, DECEMBER 1, 1998

## Doubled $CO_2$ Effects on $NO_y$ in a Coupled 2D Model

Joan E. Rosenfield
General Sciences Corporation, Laurel, MD

Anne R. Douglass
Laboratory for Atmospheres, NASA Goddard Space Flight Center, Greenbelt, MD

**Abstract.** Stratospheric $NO_y$ fields calculated using a zonally averaged interactive chemistry-radiation-dynamics model show significant sensitivity to the model $CO_2$. Modeled upper stratospheric $NO_y$ decreases by about 15% in response to $CO_2$ doubling, mainly due to the temperature decrease calculated to result from increased $CO_2$ cooling. The abundance of atomic nitrogen, N, increases because the rate of the strongly temperature dependent reaction $N + O_2 \rightarrow NO + O$ decreases at lower temperatures. Increased N leads to an increase in the loss of $NO_y$ which is controlled by the reaction $N + NO \rightarrow N_2 + O$. The decrease in $NO_y$ due to the lowered temperatures is partially compensated by changes in the residual circulation. In addition, the $NO_y$ reduction is shown to be sensitive to the NO photolysis rate.

article, the dominant form of $NO_y$ is NO. $NO_y$ is destroyed photochemically via $N + NO \rightarrow N_2 + O$. The efficiency of this reaction is controlled by photolysis of NO, which produces N atoms, and the competition between two reactions which remove N atoms, N + NO and $N + O_2 \rightarrow NO + O$. Note that the latter reaction is sensitive to temperature. Since the local concentration of $N_2O$ is a function of circulation, the production of $NO_y$ is also a function of circulation. Models tend to overestimate the maximum $NO_y$ compared with observations [*Nevison et al.*, 1997]. These authors have discussed the sensitivity of modeled $NO_y$ to photolysis and kinetic input, and have explored possible explanations for this overestimate.

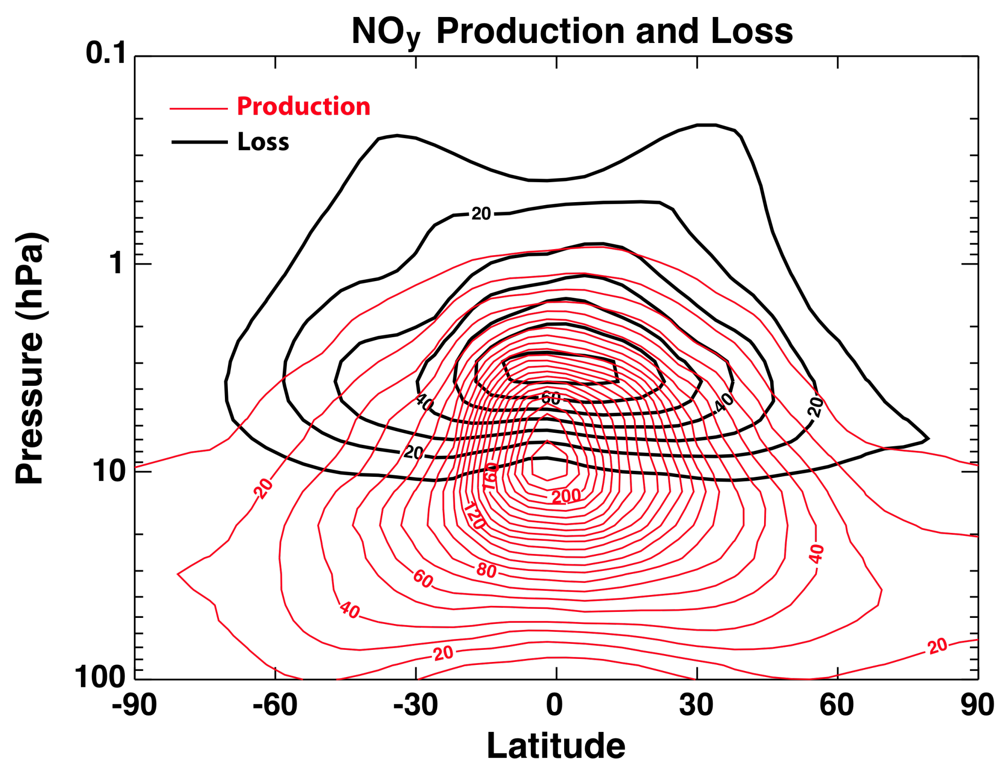
# Odd Nitrogen ($NO_y$) is produced by the reaction of $O(^1D)$ with Nitrous Oxide ($N_2O$) and destroyed by the reaction of N atoms with NO.

| | |
|---|---|
| **Definition of $NO_y$** | $NO_y = N + NO + NO_2 + NO_3 + 2{*}N_2O_5 + HNO_3 + HO_2NO_2 + ClNO_3 + BrNO_3$ |
| **Production of $NO_y$** | $O(^1D) + N_2O \rightarrow NO + NO$ |
| **Production of $N(^4S)$** | $h\nu + NO \rightarrow N(^4S) + O$ |
| **Loss of $NO_y$** | $N(^4S) + NO \rightarrow N_2 + O$ |

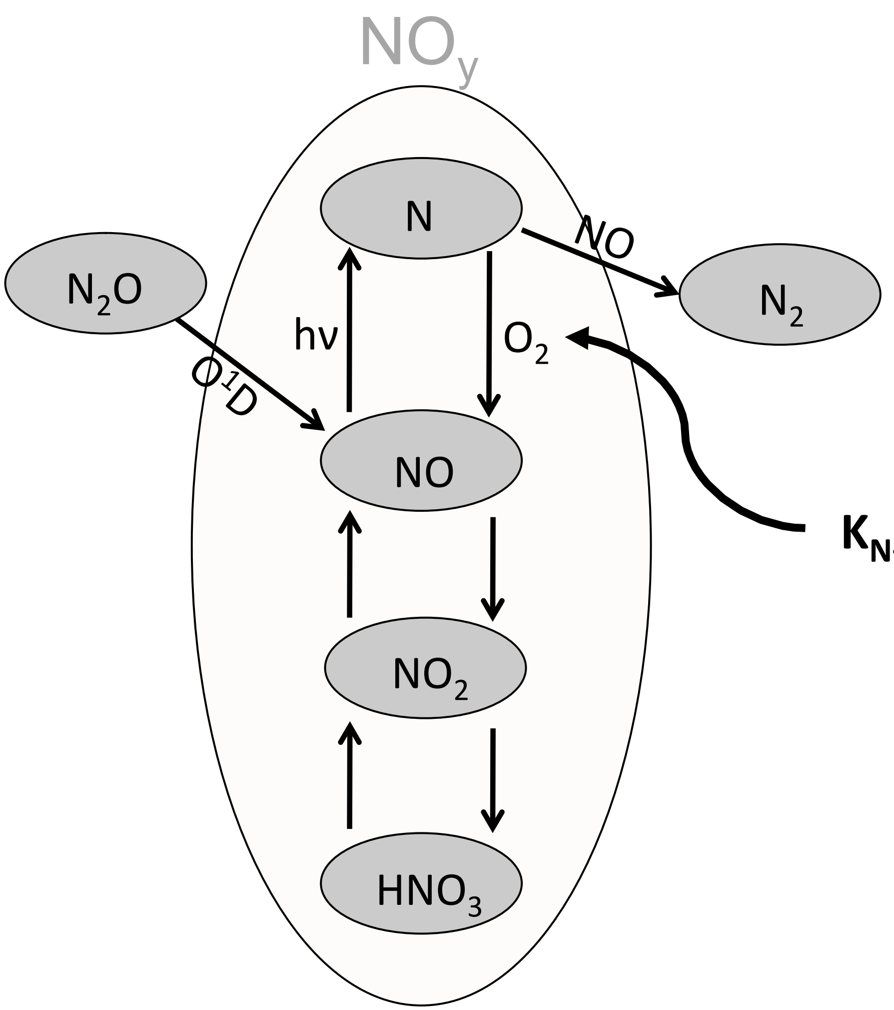
# $NO_y$ Production is balanced by loss and transport to the troposphere

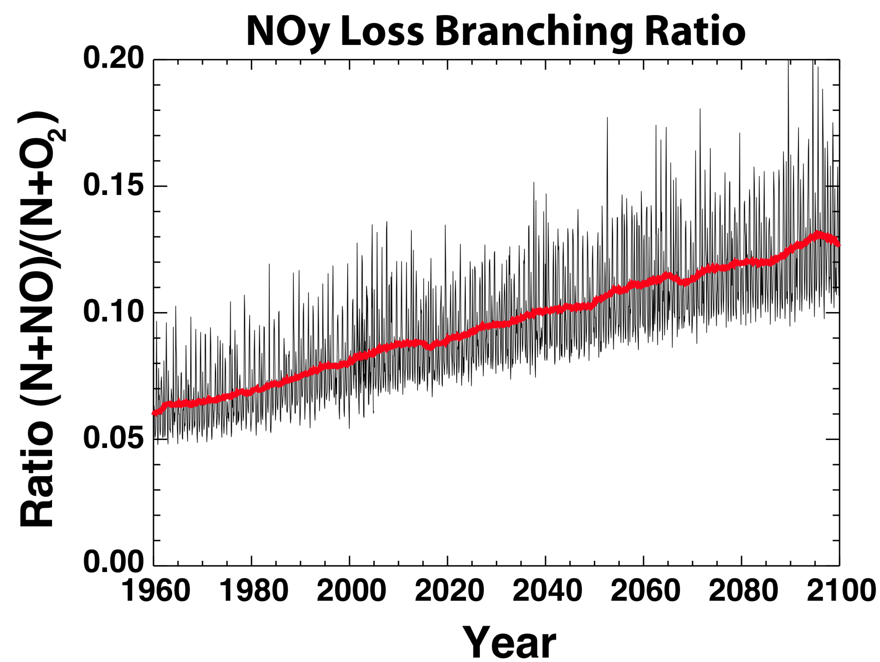
Chemical Loss occurs in the upper stratosphere above ~10 hPa.

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



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




$K_{N+O2} = 1.5 \times 10^{-11} \, EXP(-3600/T)$

**The branching ratio is strongly temperature dependent: low temperatures → more $NO_y$ loss**

# Climate change affects $NO_y$ impact on ozone

$$\Delta O_3 = \frac{\partial O_3}{\partial NO_y} \Delta NO_y$$

**$NO_y$ leads to ozone loss**

$$NO_y = NO_y(N_2O, T)$$

**$NO_y$ is a function of both $N_2O$ and Temperature**

$$\Delta NO_y = \frac{\partial NO_y}{\partial N_2O} \Delta N_2O + \frac{\partial NO_y}{\partial T} \Delta T$$

**The change in $NO_y$ (and ozone) thus depends on both $N_2O$ and Temperature**

$$\Delta O_3 = \underline{\frac{\partial O_3}{\partial NO_y} \frac{\partial NO_y}{\partial N_2O}} \Delta N_2O + \frac{\partial O_3}{\partial NO_y} \frac{\partial NO_y}{\partial T} \Delta T$$

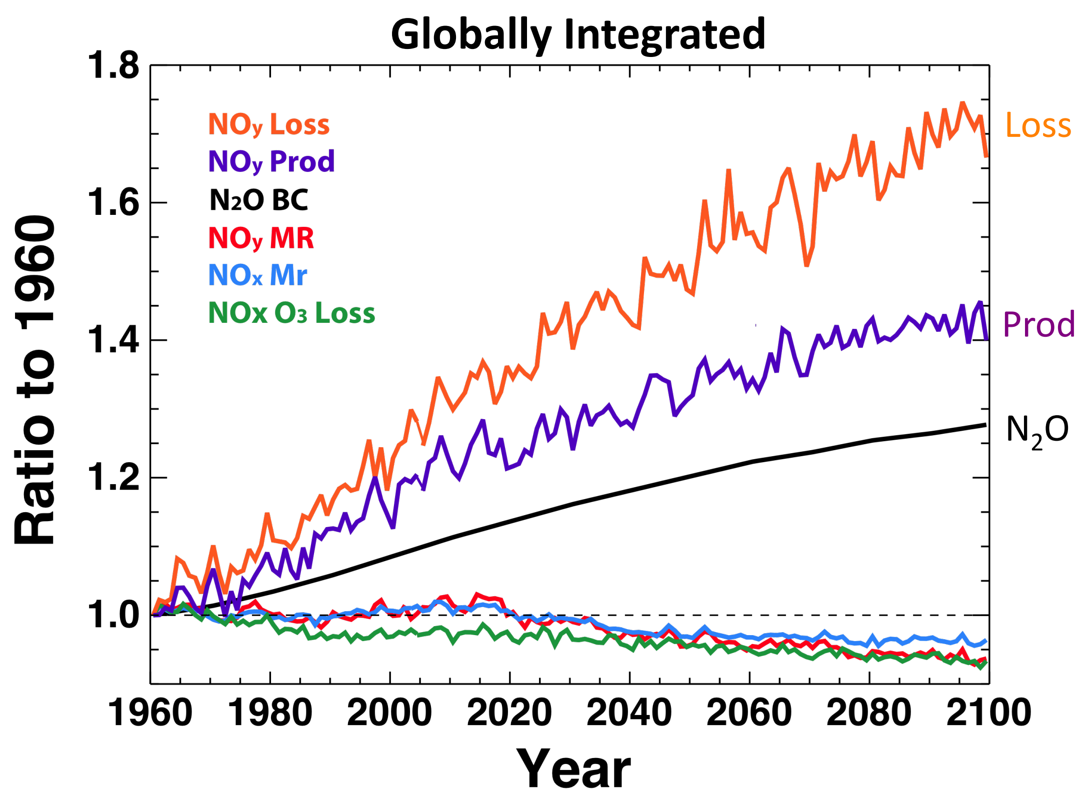
**The ODP is the ratio of this term to the equivalent term for CFC-11**

# Simulation with 25% increase in $N_2O$ yields 40% increase in $NO_y$ production and 70% increase in $NO_y$ loss

Production increases due to speed up of circulation pushing $N_2O$ to higher altitude

Loss increases due to cooling of upper stratosphere

Net result is slight decrease in $NO_y$, $NO_x$, and ozone loss despite the increase in $N_2O$.



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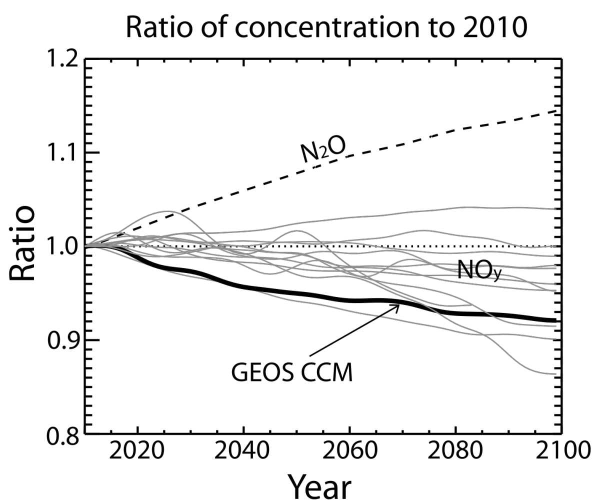
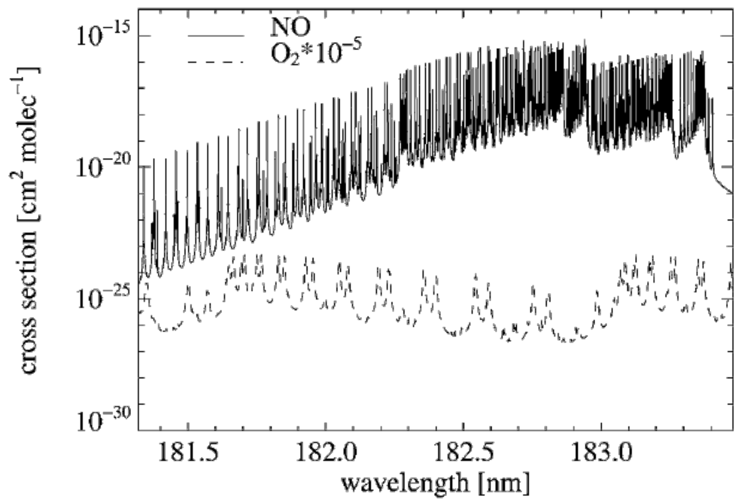
# Cautionary Note:

## Quantitative model results may vary because of treatment of NO absorption that leads to photolysis to N atoms




**All models in the CCMVal2 exercise found a significant temperature feedback on NOy concentrations. GEOS CCM had one of the larger impacts.**

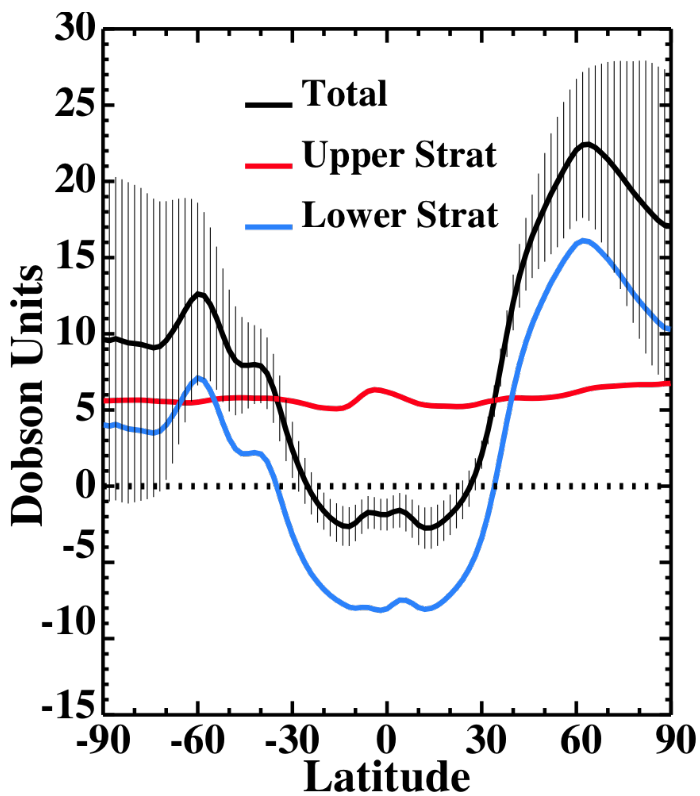
From Minschwanner, 1992 as reproduced by Trentmann et al. 2003.




**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 $N_2O/NO_y$ relationship provides some constraint on NO photolysis and should narrow the model range.**

# What would happen if we could limit $N_2O$?




Reducing $N_2O$ 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.**

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

Environmental Research Letters

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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

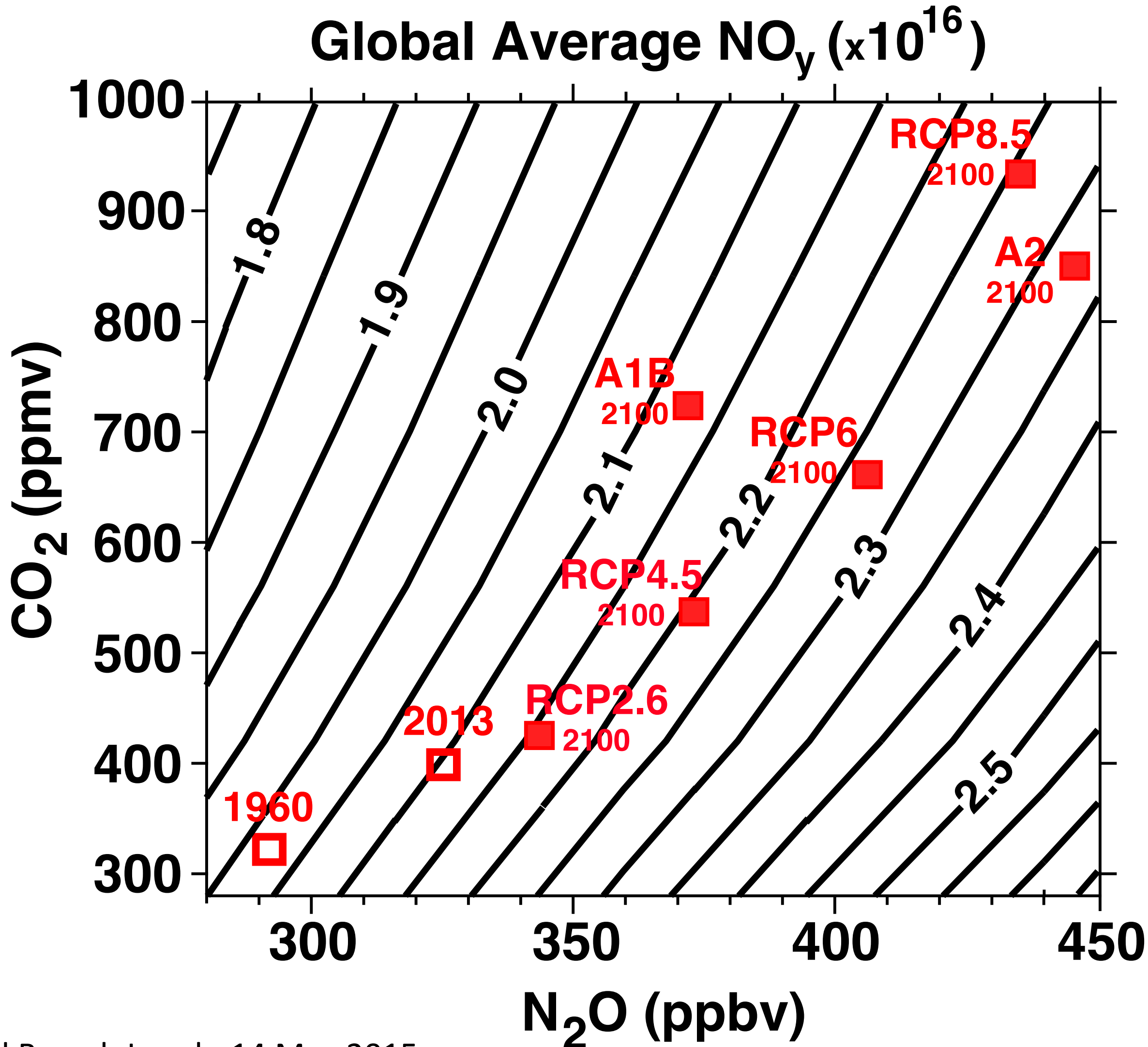
| $CH_4$ (ppmv) | $N_2O$ (ppbv) | $CO_2$ (ppmv) | F11/F12 (ppmv) |
|---|---|---|---|
| 1.2 | 280 | 280 | 0 |
| 1.8 | 360 | 420 | 0.3 |
| 2.4 | 440 | 560 | 0.6 |
| 3.0 | | 700 | 0.9 |
| 3.6 | | 840 | |

**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 $CH_3Br$**

# Global Average $NO_y$ Column vs $CO_2$ and $N_2O$ Boundary Conditions (at 2 ppbv $Cl_y$, 1.8 ppmv $CH_4$)

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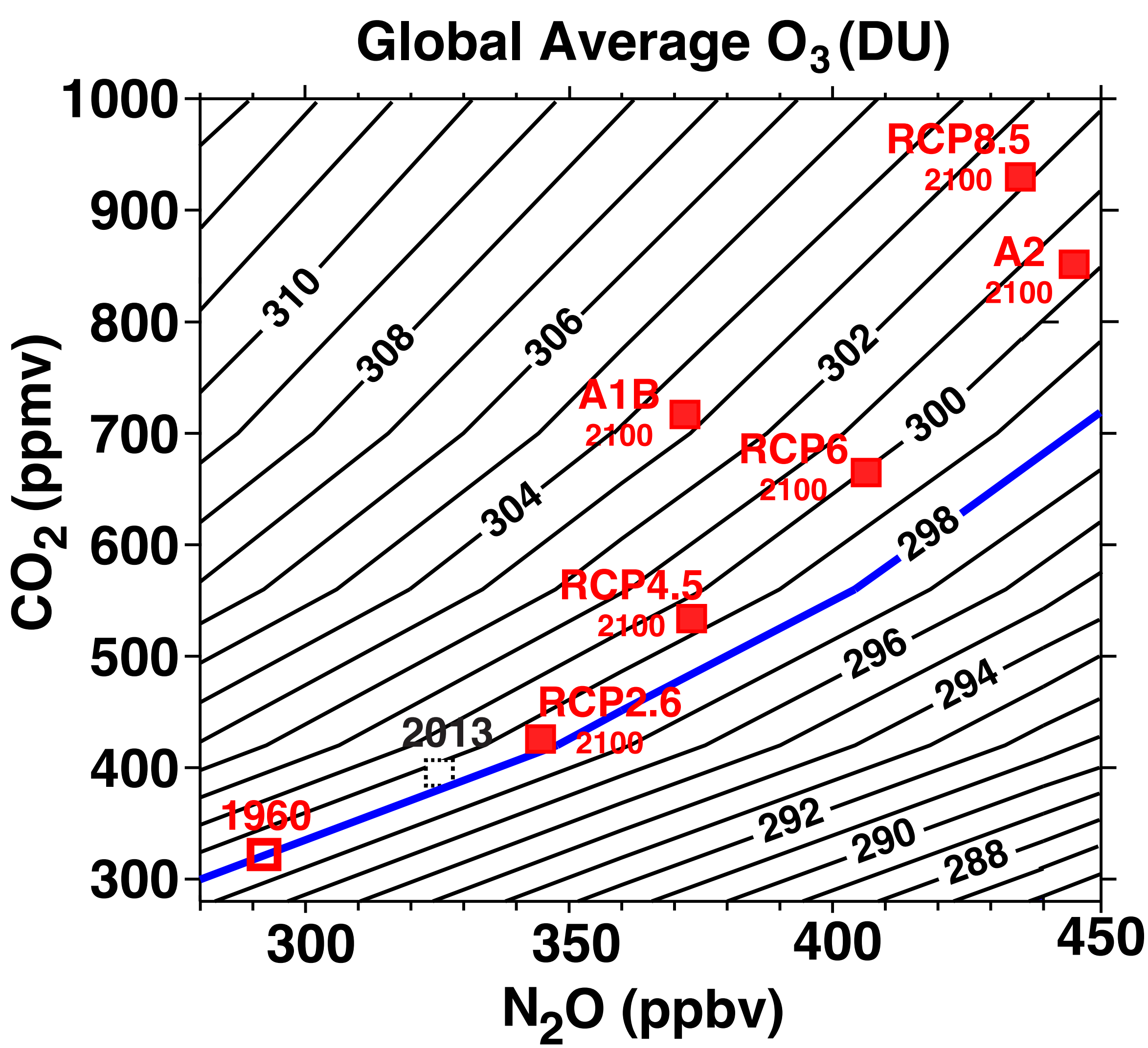




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# Problem 1: Interaction of $N_2O$ and $CO_2$

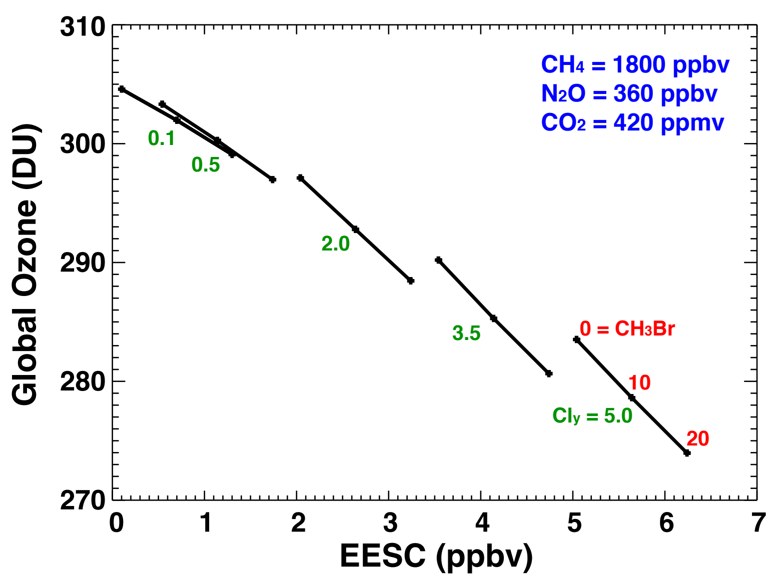
- **$N_2O$ is the source of $NO_y$ that can catalytically destroy ozone**
- **$CO_2$ cools the stratosphere slowing the ozone loss processes**
- **$CO_2$ cooling increases the loss of stratospheric $NO_y$ by favoring N + NO reaction over N + $O_2$**

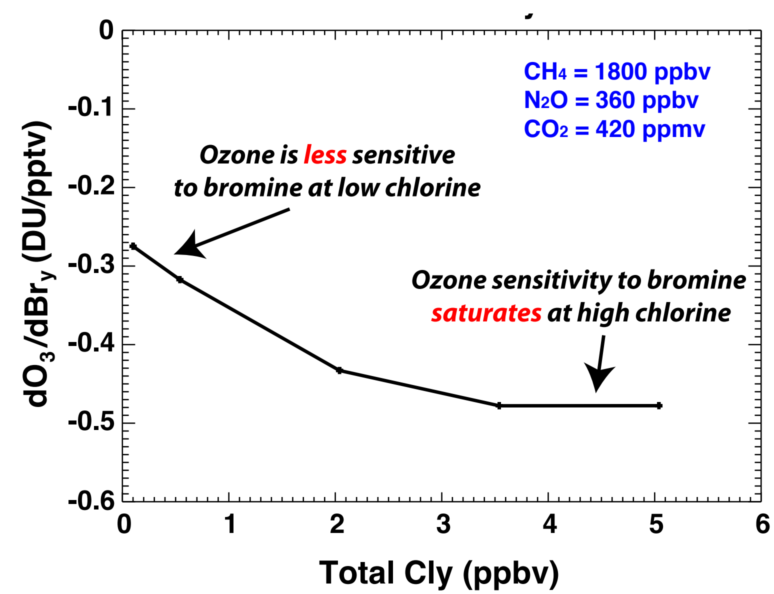
# Problem 2: Relative impact of halogens

- **Bromine impact on ozone depends on chlorine amount**
- **F11 is more effective than F12 because it is photolyzed at lower altitude.**

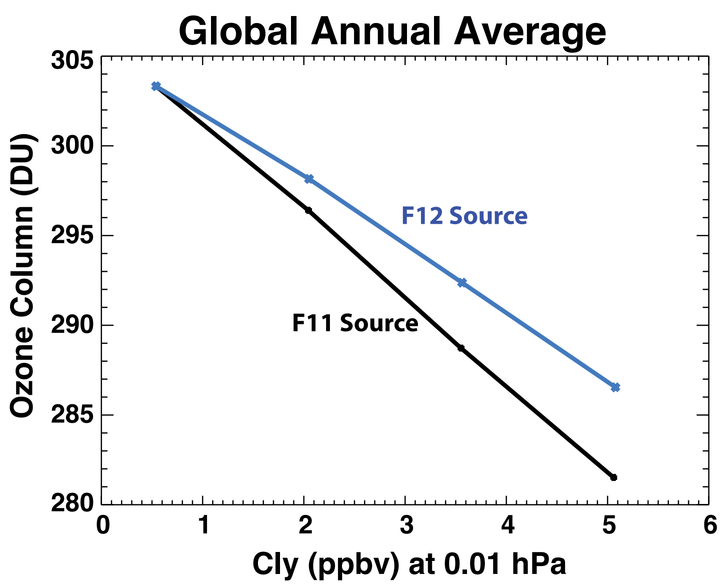
# Global Total Ozone Sensitivity to Bromine

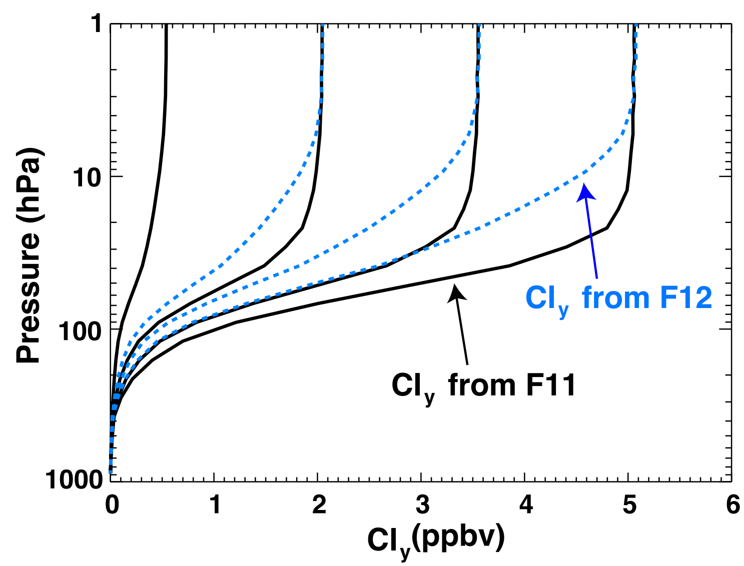
- Used added 2D model runs for 0, 10, 20 pptv of $CH_3Br$ at 0.1,0.5,2.0,3.5, and 5.0 ppbv of chlorine for single values of $CH_4$, $N_2O$, and $CO_2$
- Sensitivity increased with increasing chlorine (because of ClO + BrO reaction)



# Chlorine from F11 is more effective in reducing ozone than is the same amount of chlorine from F12



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# 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

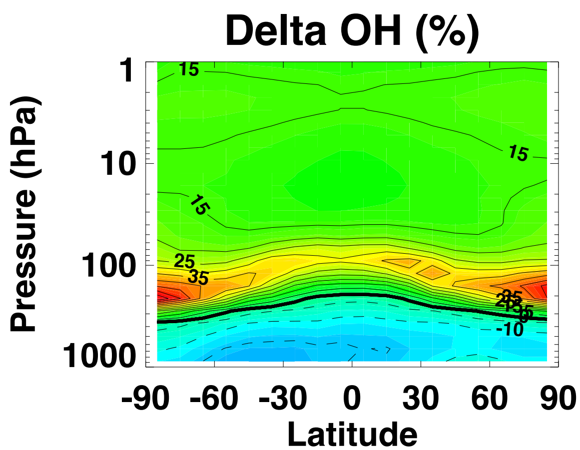
- F12/121 = 5.98 DU O3 change /CFC lb
- F11/137.7= 6.25 DU O3 change /CFC lb

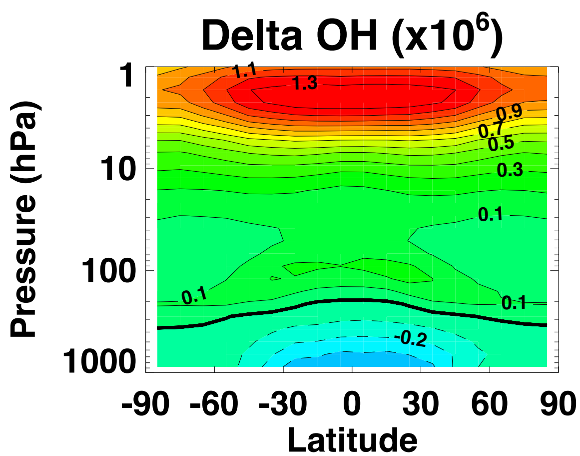
ODP of F12 should be about 0.96 (0.90 if done per molecule)(0.76 if done by Cl atom)

# 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**

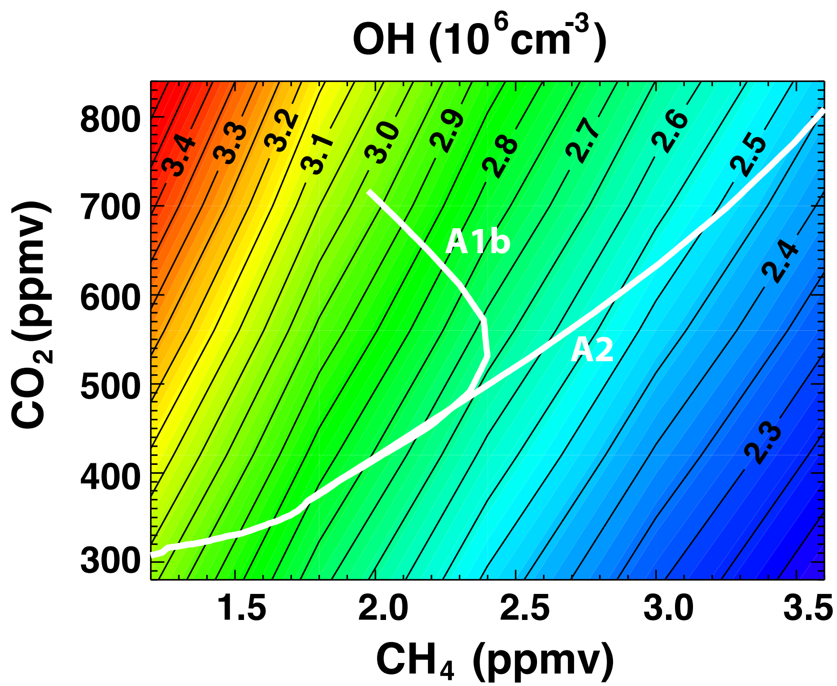
# Impact of Doubling $CH_4$ on OH



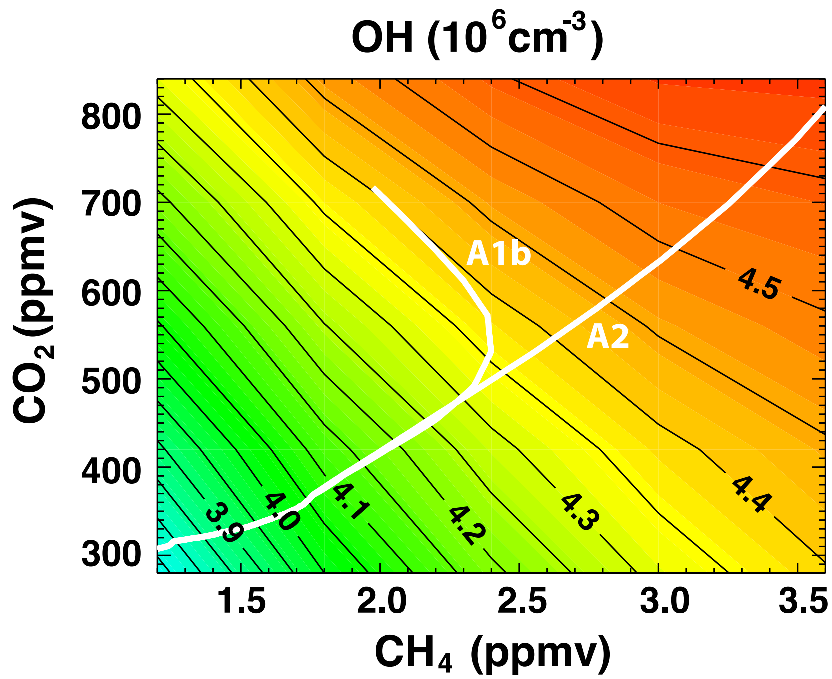




- OH decreases in lower to middle troposphere
- OH percentage increase maximizes in upper troposphere and lower stratosphere
- OH absolute increase maximizes in upper stratosphere

# Combined Effect of $CH_4$ and $CO_2$ on Tropospheric OH




**Near Surface**




**Upper Troposphere**

***Caveat: Model has a simple tropospheric chemistry with $CH_4$ as the only significant hydrocarbon***

# Summary and Conclusions

- Stratospheric $NO_y$ (or $NO_x$) depends on both $N_2O$ and $CO_2$
- As CFCs decrease, $N_2O$ 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