

# **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

CH <sub>4</sub> (ppmv)	N <sub>2</sub> O (ppbv)	CO <sub>2</sub> (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**

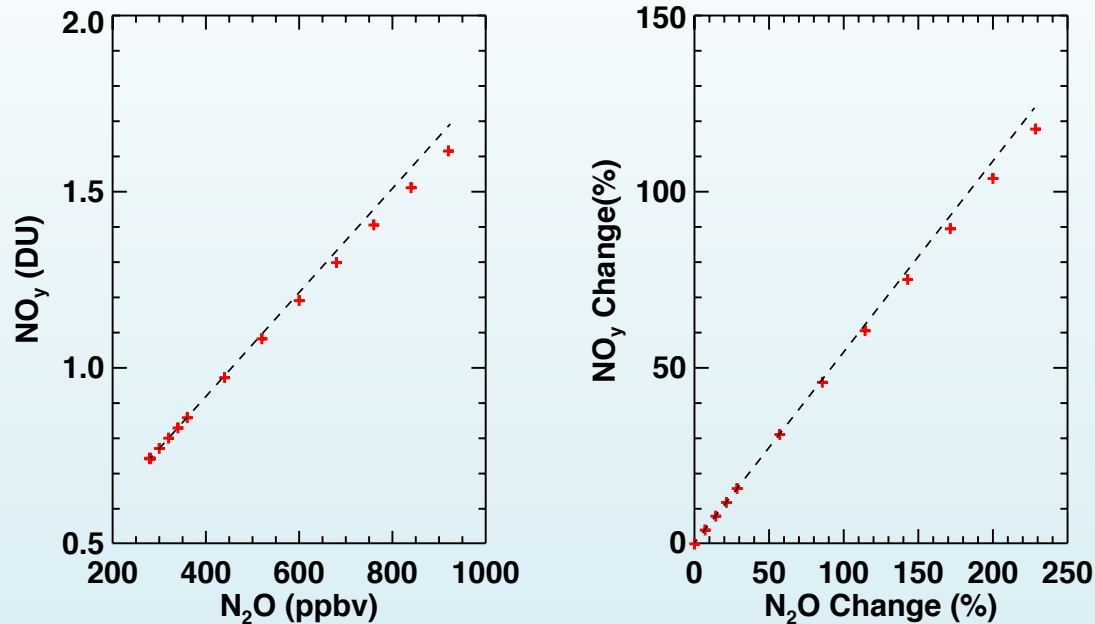
**Each run was 30 years from the same initial condition to reach steady state. Only last year used.**

**+17 more runs to elucidate difference between F11, F12, and CH<sub>3</sub>Br**

# Problem 1: Interaction of $\text{N}_2\text{O}$ and $\text{CO}_2$

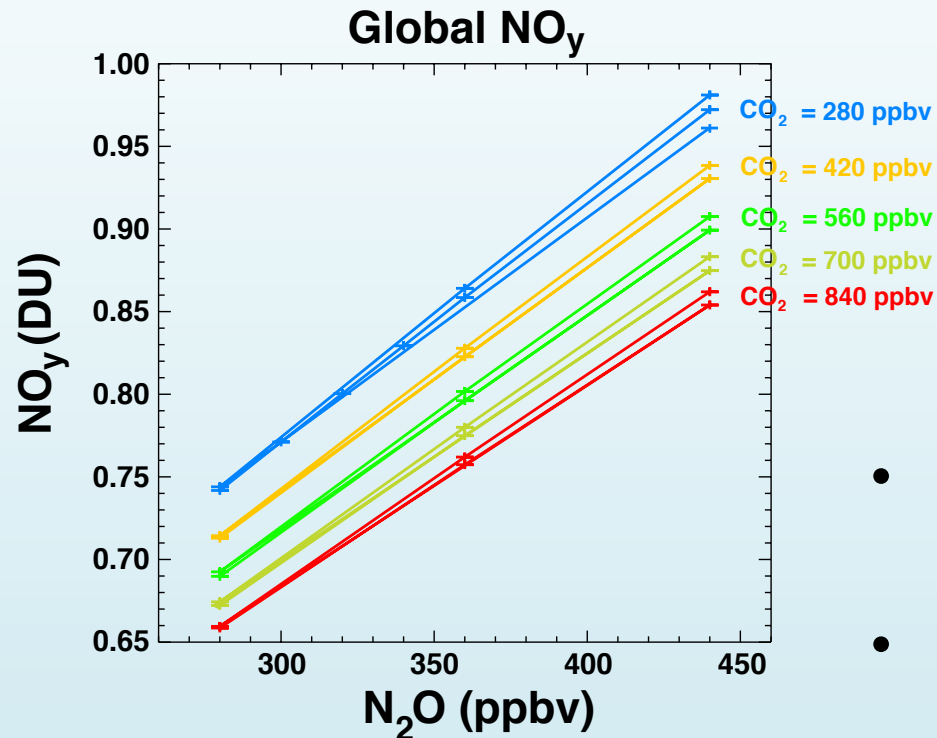
- $\text{N}_2\text{O}$  is the source of  $\text{NO}_y$  that can catalytically destroy ozone
- $\text{CO}_2$  cools the stratosphere slowing the ozone loss processes
- $\text{CO}_2$  cooling increases the loss of stratospheric  $\text{NO}_y$  by favoring  $\text{N} + \text{NO}$  reaction over  $\text{N} + \text{O}_2$

# What controls $\text{NO}_y$ in the stratosphere?



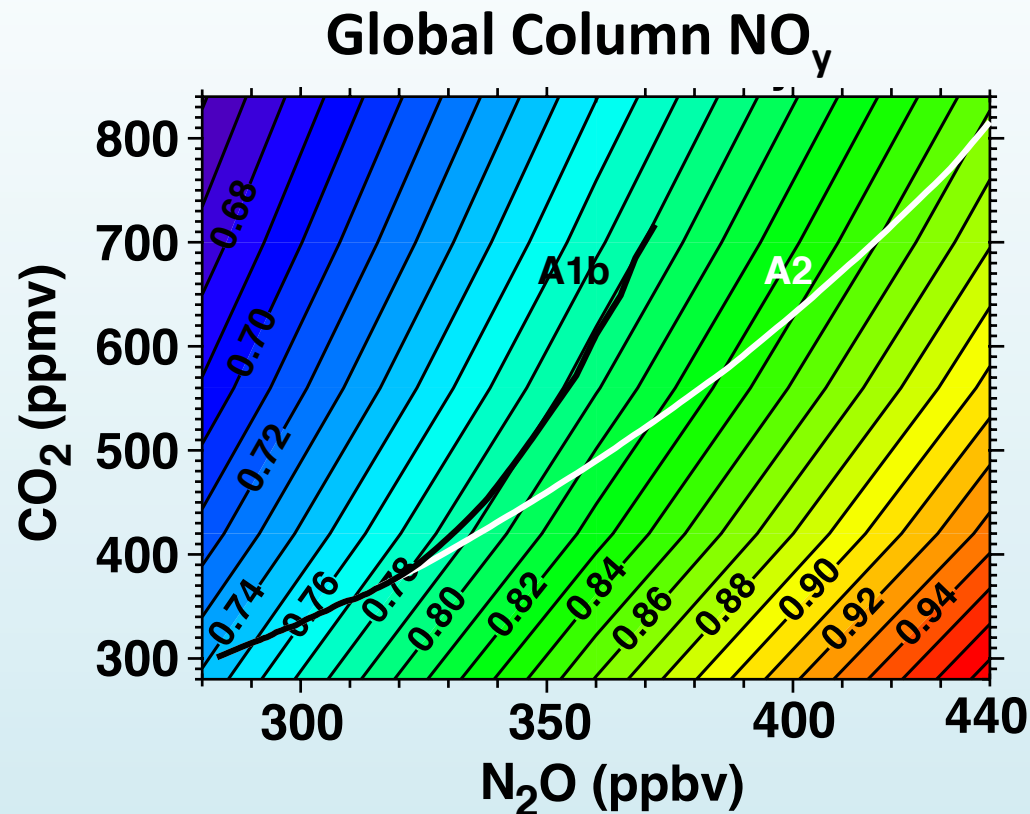
- $\text{N}_2\text{O}$  is the primary source of  $\text{NO}_y$  ( $\text{N} + \text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \cdot \text{N}_2\text{O}_5 + \text{HNO}_3 + \text{ClONO}_2 + \text{BrONO}_2$ )
- Doubling of  $\text{N}_2\text{O}$  leads to 50% increase in  $\text{NO}_y$  ( $\text{NO}_y$  chemical loss term proportional to  $[\text{NO}_y]^2$ )

# CO<sub>2</sub> also impacts NO<sub>y</sub> in the stratosphere



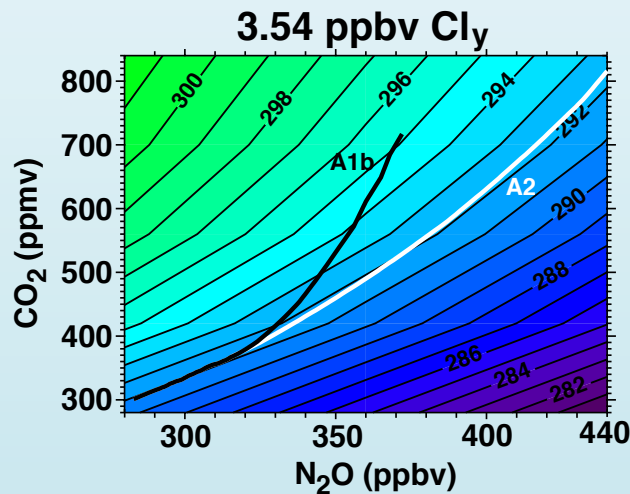
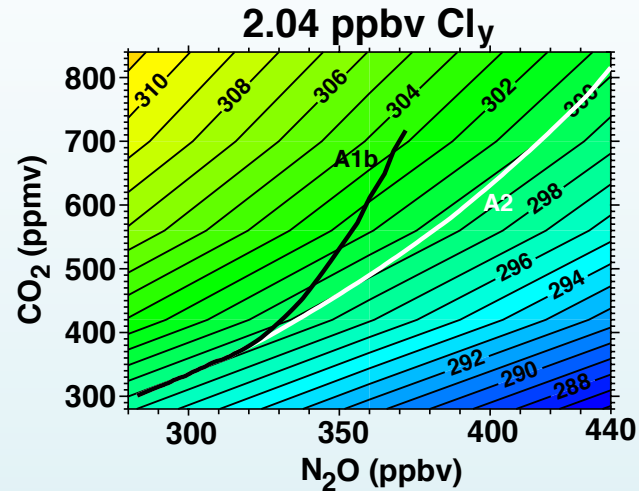
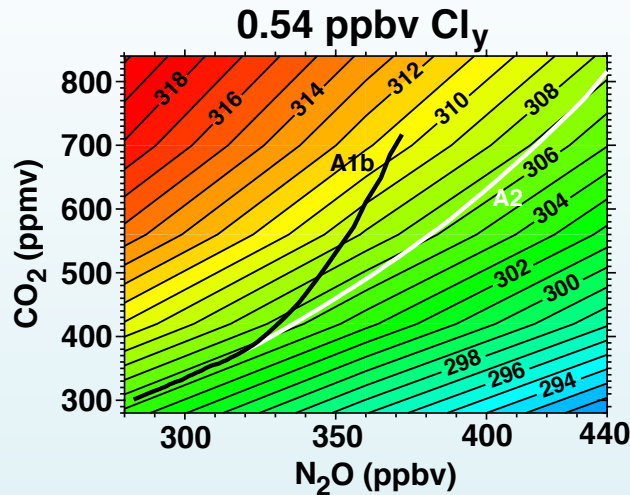
- 3 x CO<sub>2</sub> → 10-15% decrease in NO<sub>y</sub>
- Cooling of stratosphere changes balance of
  - $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$
  - $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$

# The evolution of stratospheric $\text{NO}_y$



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

# Ozone Scenarios



- Chlorine dominates ozone change
- Amount of global “super-recovery” depends on relative scenario for N<sub>2</sub>O and CO<sub>2</sub> change

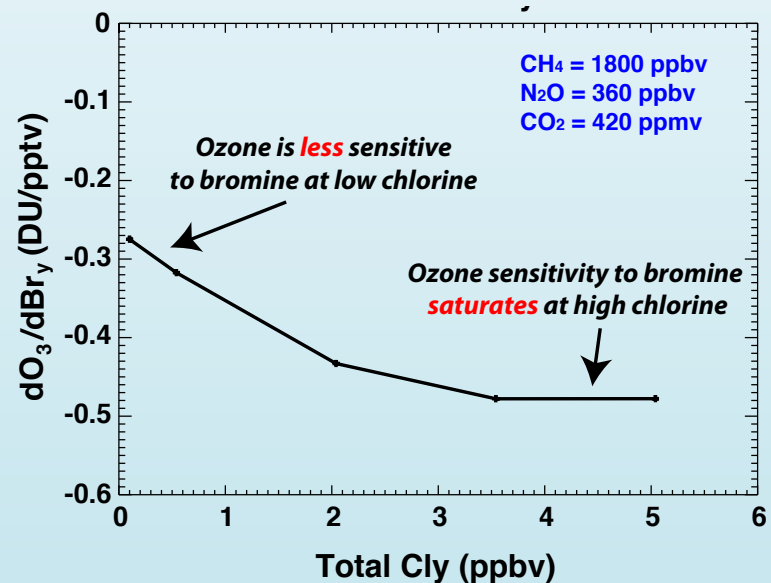
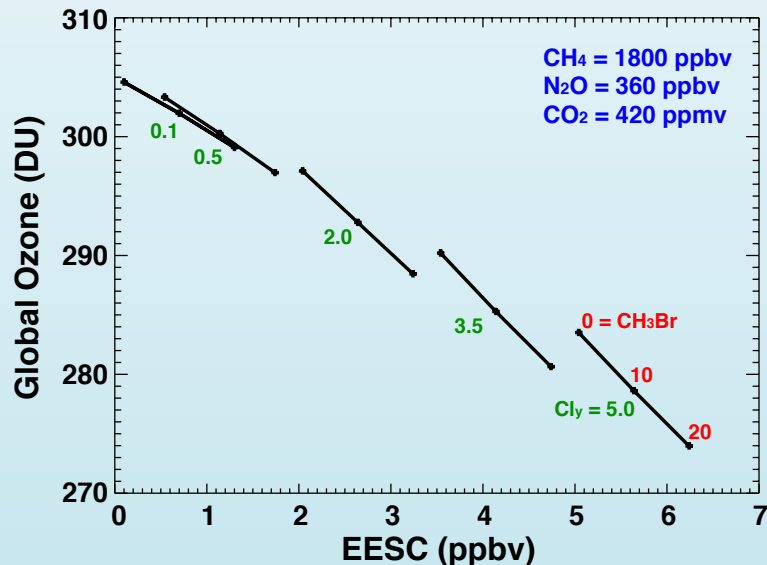
# Problem 2: Relative impact of halogens

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

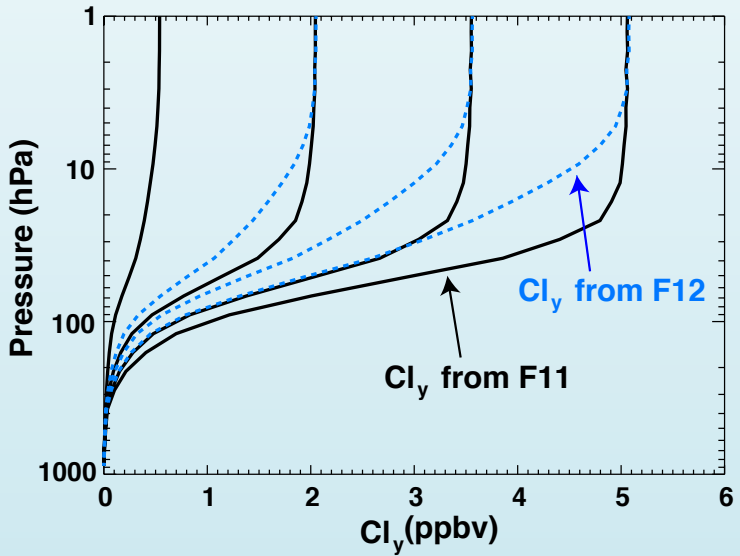
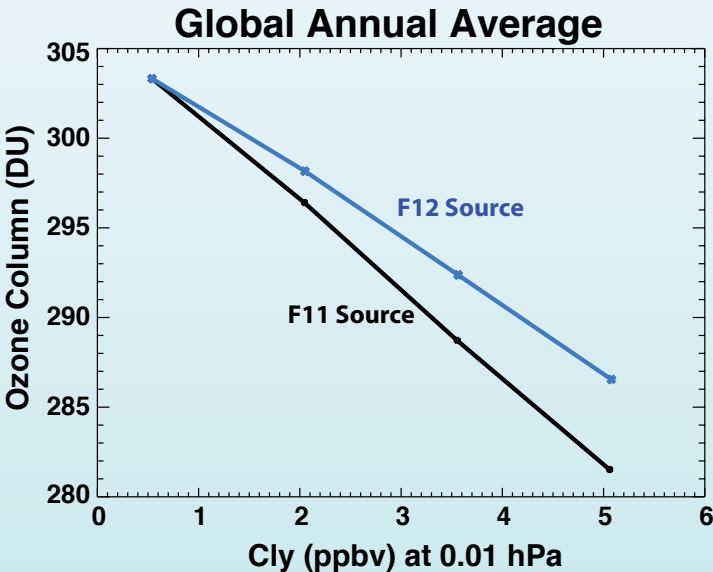


# Global Total Ozone Sensitivity to Bromine

- Used added 2D model runs for 0, 10, 20 pptv of  $\text{CH}_3\text{Br}$  at 0.1, 0.5, 2.0, 3.5, and 5.0 ppbv of chlorine for single values of  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{CO}_2$
- Sensitivity increased with increasing chlorine (because of  $\text{ClO} + \text{BrO}$  reaction)



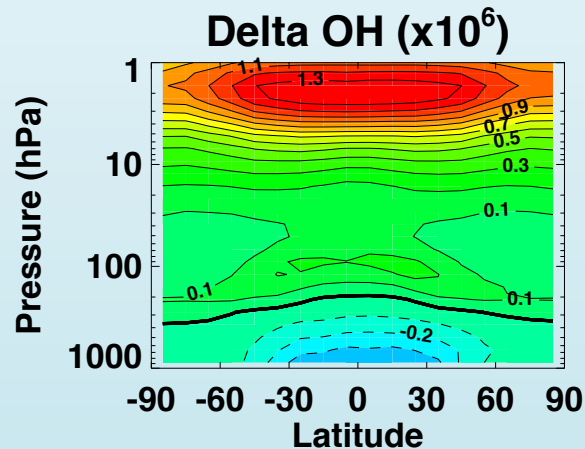
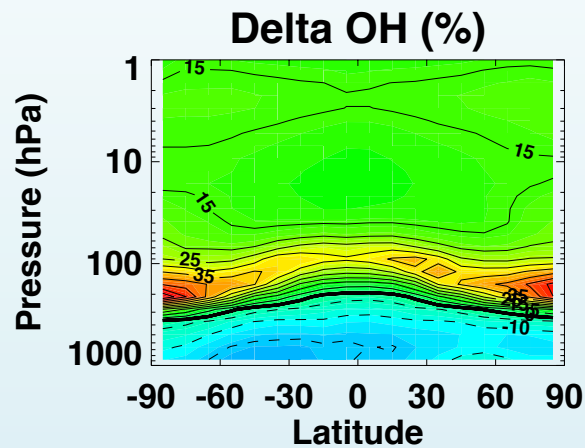
# Chlorine from F11 is more effective in reducing ozone than is the same amount of chlorine from F12



## **Problem 3: Impact on tropospheric and stratospheric OH**

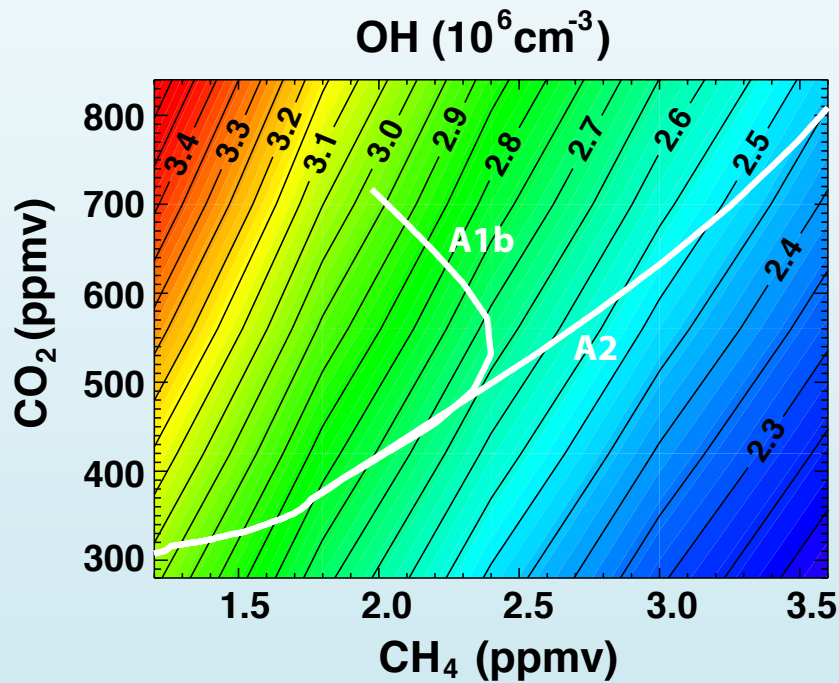
- **Increasing methane increases stratospheric OH**
- **Percent positive OH change maximizes in UTLS**
- **Increasing methane decreases lower and middle tropospheric OH**
- **Increasing CO<sub>2</sub> increases tropospheric OH**
- **Future direction depends on scenario**

# Impact of Doubling CH<sub>4</sub> on OH

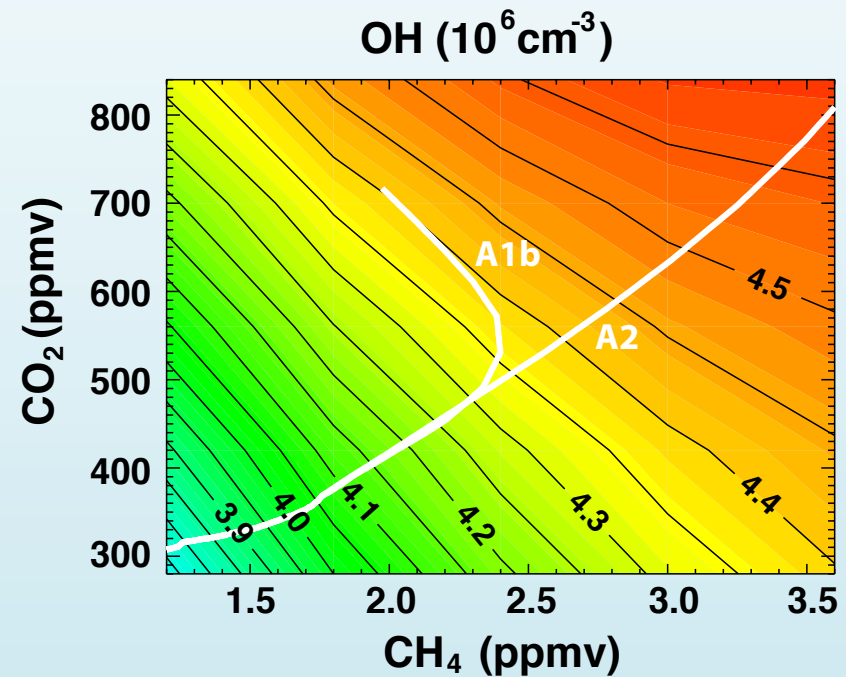


- OH decreases in lower to middle troposphere
- OH percentage increase maximizes in upper troposphere and lower stratosphere
- OH absolute increase maximizes in upper stratosphere

# Combined Effect of CH<sub>4</sub> and CO<sub>2</sub> on Tropospheric OH



Near Surface



Upper Troposphere

# Summary and Conclusions

- **Stratospheric  $\text{NO}_y$  (or  $\text{NO}_x$ ) depends on both  $\text{N}_2\text{O}$  and  $\text{CO}_2$**
- **As CFCs decrease,  $\text{N}_2\text{O}$  and  $\text{CO}_2$  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  $\text{Cl}_y$ )**
- **Tropospheric OH responds to changes in both  $\text{CH}_4$  and  $\text{CO}_2$** 
  - **Decreases in lower to middle troposphere**
  - **Increases in upper troposphere and stratosphere**