Chlorofluorocarbons, Nitrous Oxide, and Carbon Dioxide:

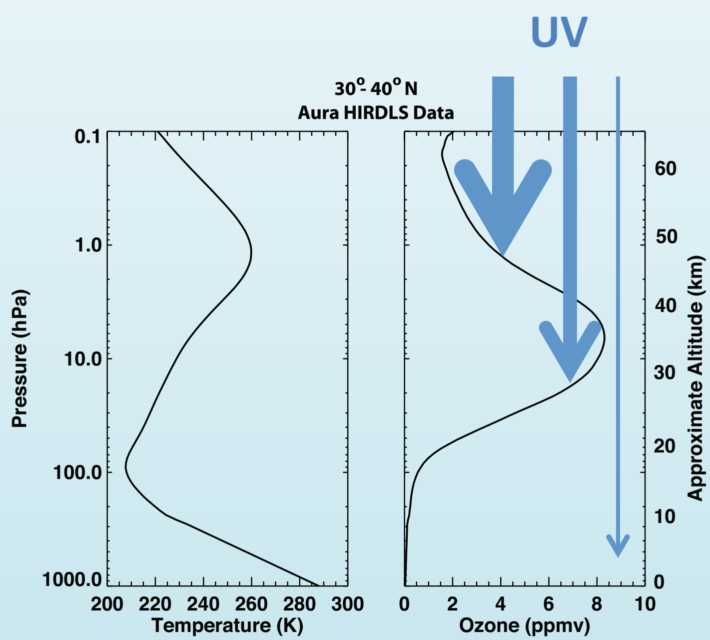
A Tale of Three Chemicals and Stratospheric Ozone

Richard S. Stolarski

Ocean-Atmosphere Seminar: 4 April 2012

Basic Background

- Ozone is produced from the photodissociation of atmospheric O_2 by solar ultraviolet (UV) radiation
- Ozone absorbs the UV radiation responsible for its own production leading to an ozone layer located in the stratosphere



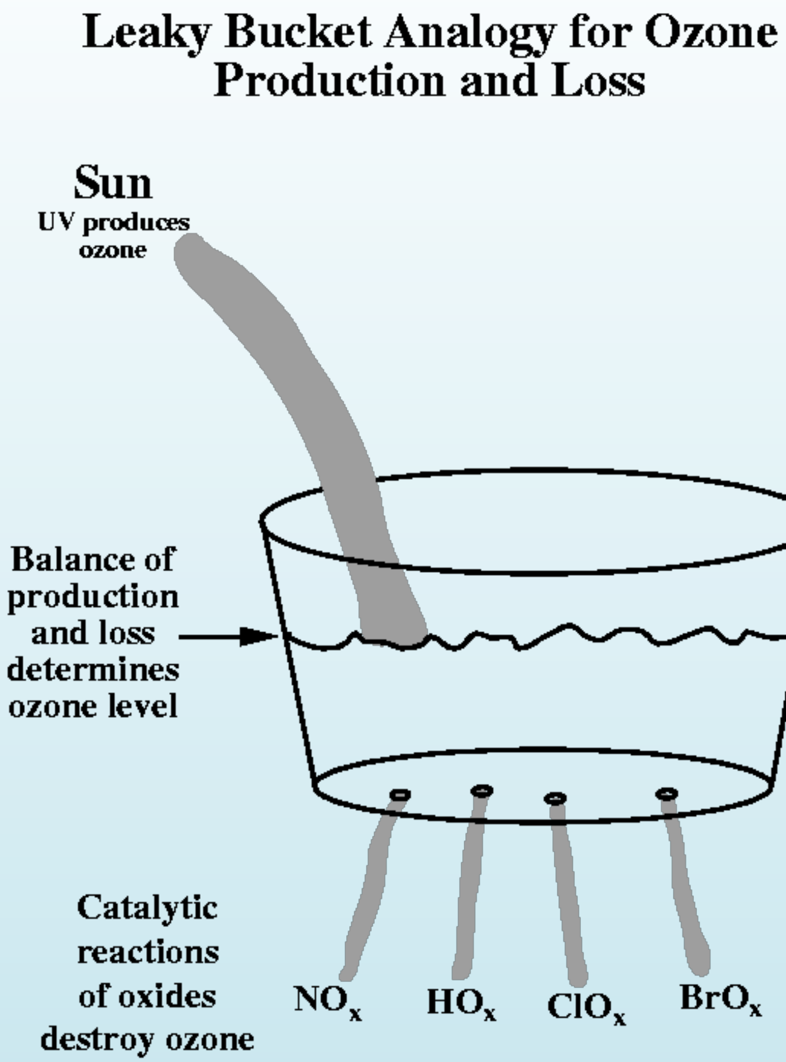
Simple Chemical Mechanism
Sydney Chapman (1930)

$$O_2 + h\nu \xrightarrow{\lambda < 240\text{nm}} O + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

$$O_3 + h\nu \xrightarrow{\lambda < 310\text{nm}} O_2 + O$$

$$O_3 + O \longrightarrow O_2 + O_2$$



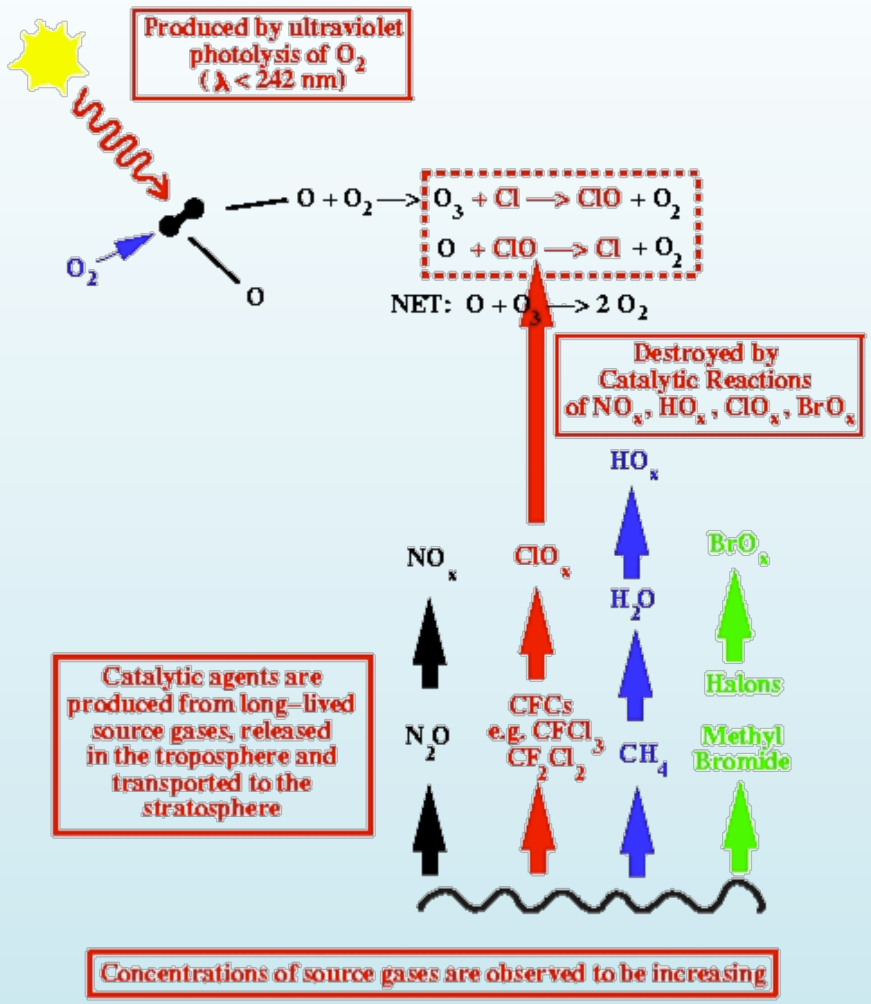
Ozone loss is enhanced by catalytic reactions of hydrogen, nitrogen, chlorine, and bromine oxides

Example is chlorine

- $Cl + O_3 \rightarrow ClO + O_2$
- $ClO + O \rightarrow Cl + O_2$

---

net: $O + O_3 \rightarrow O_2 + O_2$

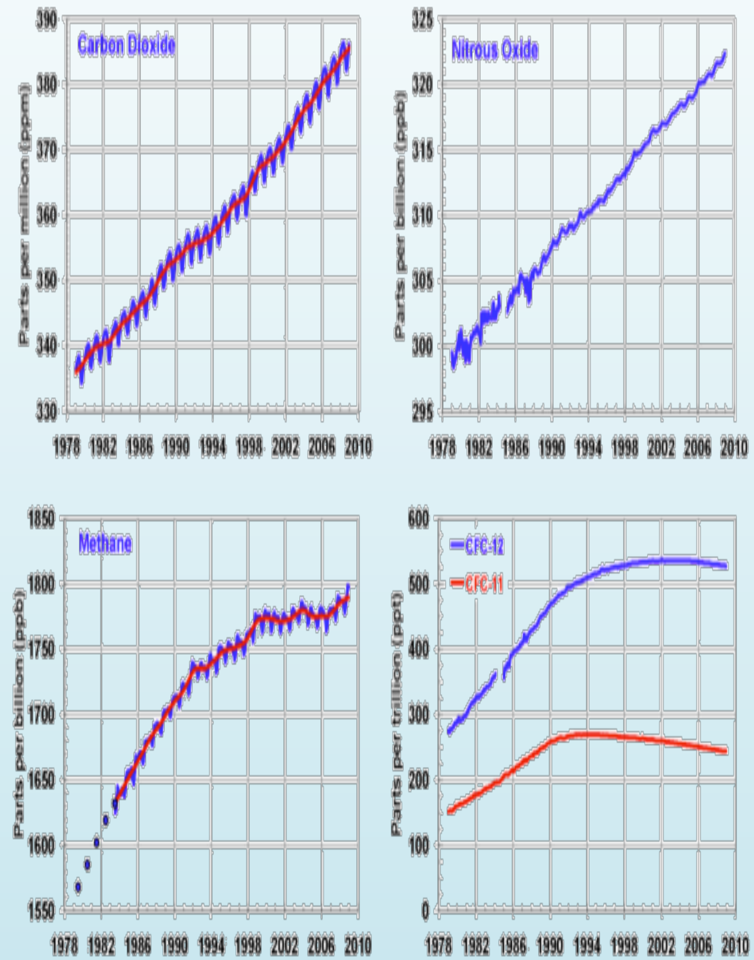


The Stratospheric Branch of the Biogeochemical Cycling of Elements

Critical factor is stability of compounds in the troposphere (insoluble, unreactive, nonabsorbent of visible and near uv radiation)

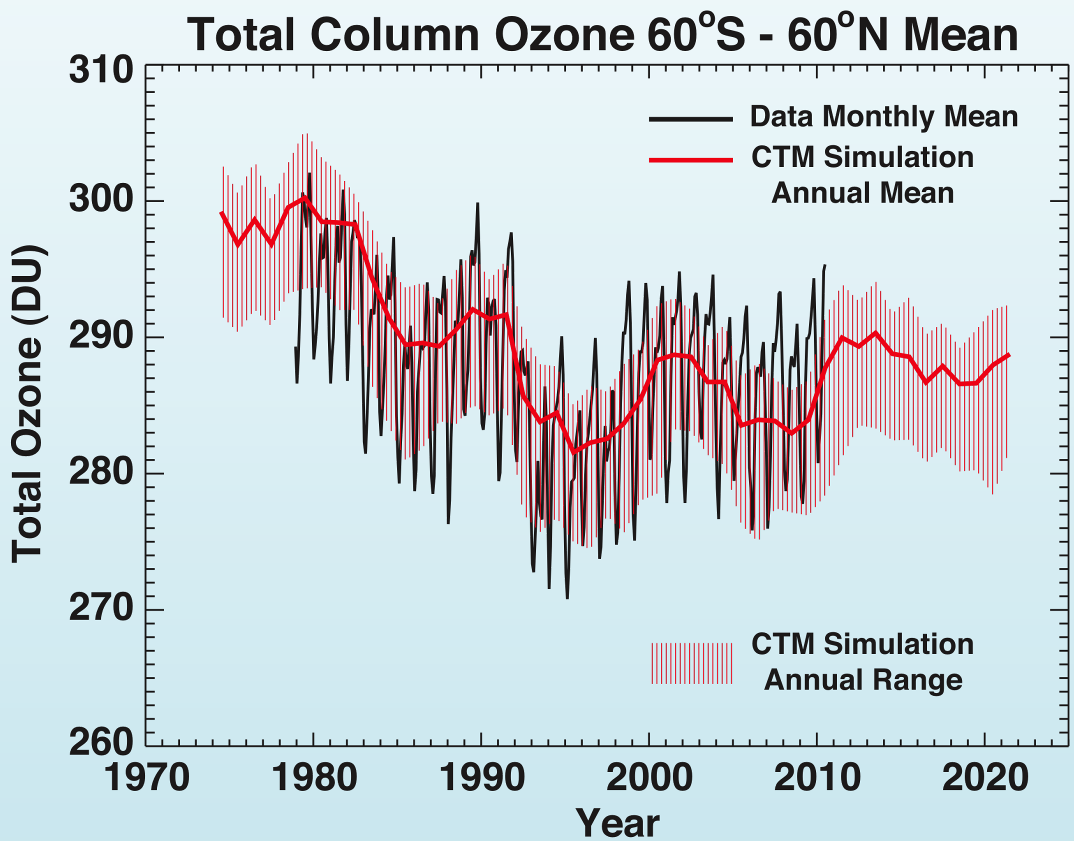
Long-Lived Source Gases: Where Do They Originate?

- **Chlorofluorocarbons ($CFCl_3$, CF_2Cl_2, CF_3CCl_3, etc.) – Almost exclusively industrially produced**
  - **Parts per billion**
  - **Increased at 3%/YEAR from 1970 to 1990**
  - **Now declining (Montreal Protocol)**
- **Nitrous Oxide (N_2O) – Part of global biogeochemical cycling of nutrient nitrogen; but enhanced by fertilizer usage and biomass burning**
  - **Hundreds of parts per billion**
  - **Increasing at about 2%/decade**
- **Carbon Dioxide (CO_2) – Part of global biogeochemical cycling but enhanced by fossil fuel burning**
  - **Hundreds of parts per million**
  - **Increasing at about 4%/decade**



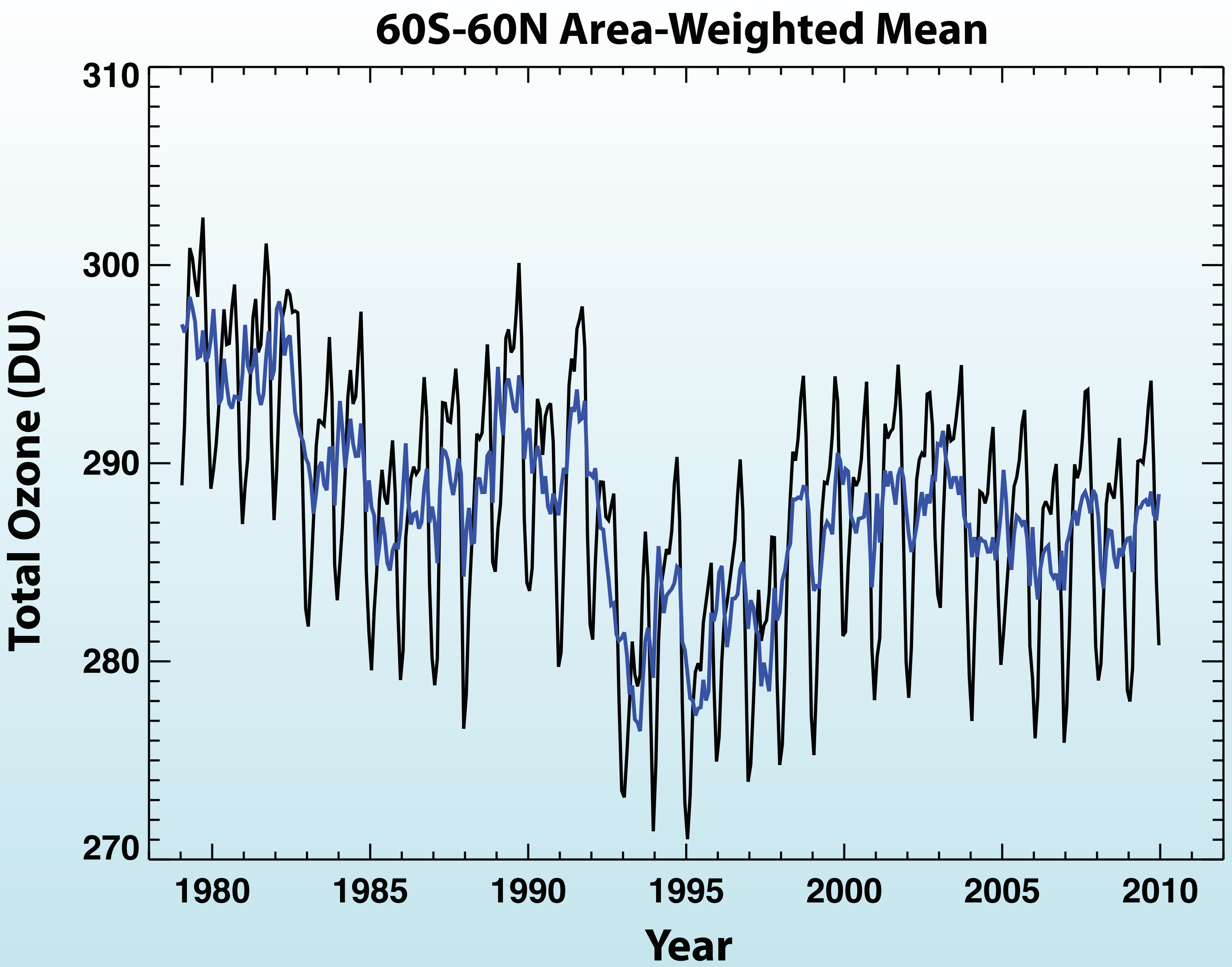
Recent Past Ozone Variation Dominated by Chlorine Change

Long-term data sets as a test of ozone photochemistry-transport model predictions

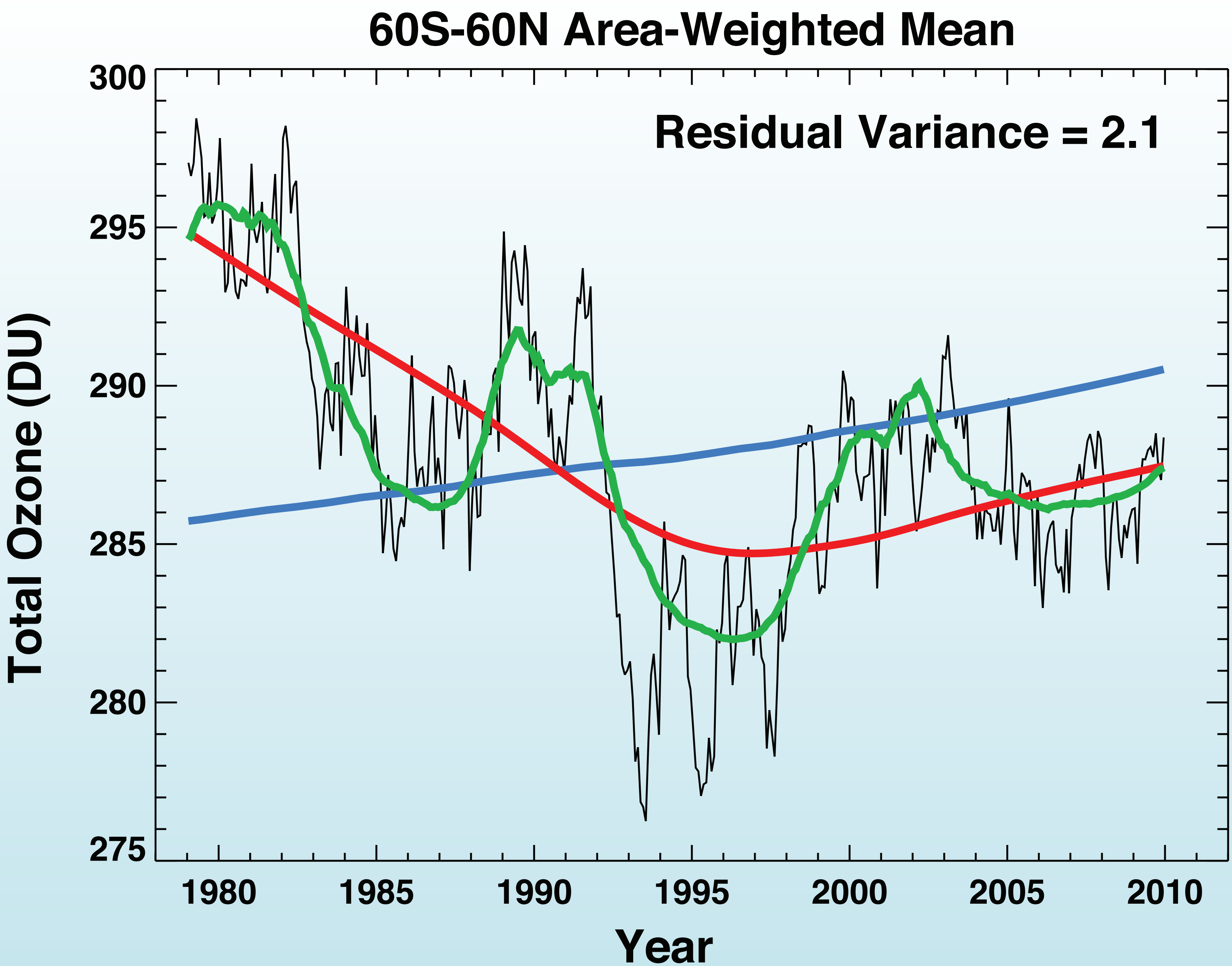


Model simulation using Goddard 3D CTM including CFCs, solar cycle, and volcanic aerosols.

Satellite data record is constructed from Nimbus 7 TOMS, Earth Probe TOMS, Nimbus 7 SBUV, NOAA 9, 11, 14, 16, 17, 18 SBUV/2, and OMI instruments.



Stolarski 4/4/2012 JHU Ocean-Atmosphere Seminar



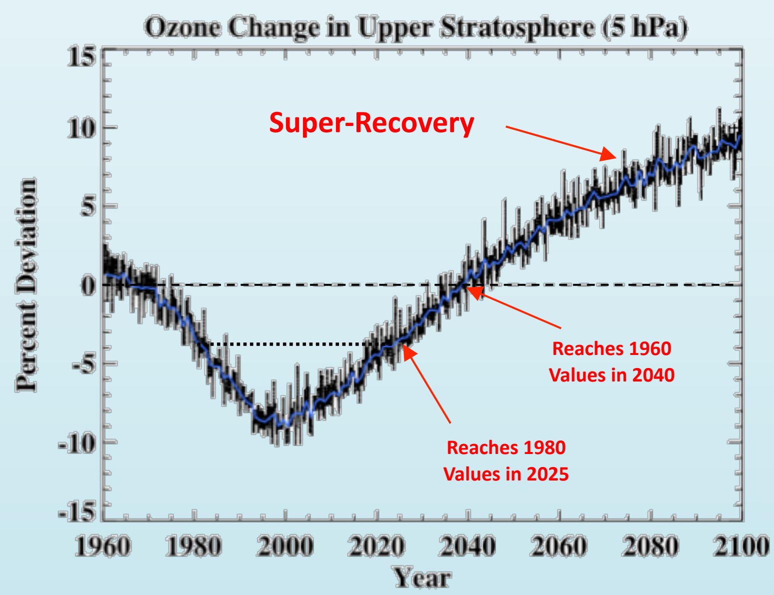
Stolarski 4/4/2012 JHU Ocean-Atmosphere Seminar

Future Ozone Change Expected to Be Dominated by CO_2

Super-Recovery of Ozone in the Upper Stratosphere

- **Ozone is expected to recover to its pre-1980 concentrations as CFCs are removed from the atmosphere in accordance with the Montreal Protocol**
- **Continued increases in greenhouse gases (esp. CO_2) will continue to cool the stratosphere**
- **Temperature decreases will slow natural ozone loss rates and lead to an increase in ozone**
- **This effect is know as "super-recovery"**

Results from simulations by the Goddard Chemistry Climate model (GEOS CCM)

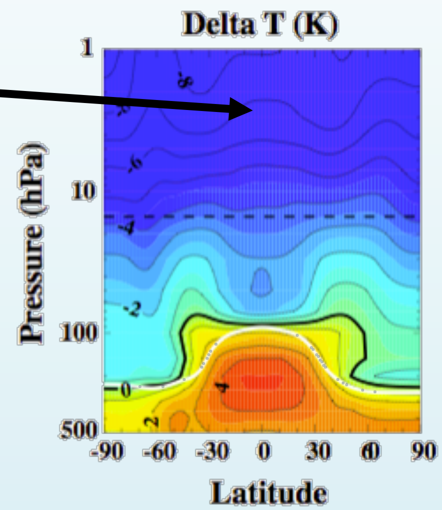


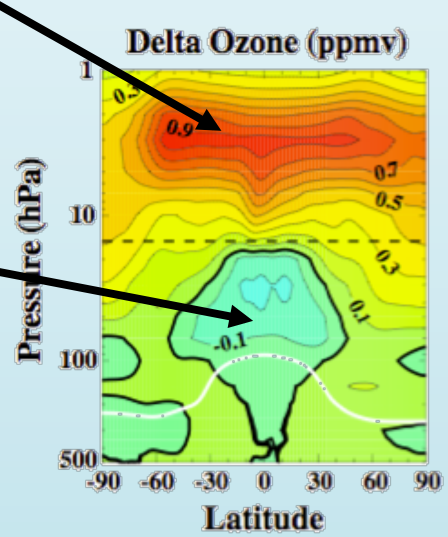
The Post-CFC Ozone Layer

What will the stratospheric ozone layer look like after CFCs have been removed?

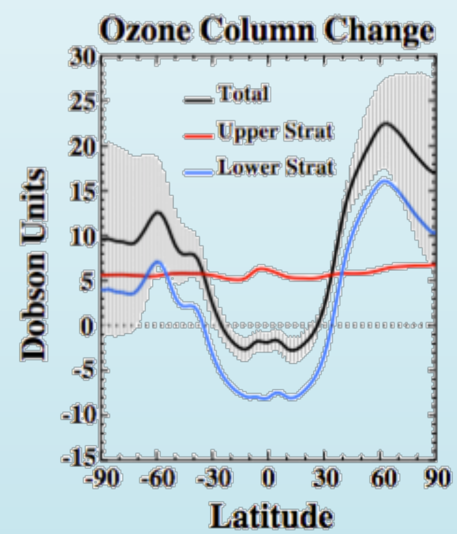
Results from the GEOS CCM 2065-1980

- **Greenhouse gases cool the stratosphere**
- **Cooling slows ozone loss in upper stratosphere leading to ozone increase**
- **Lower stratospheric circulation speeds up leading to tropical ozone decrease and mid-latitude ozone increase**





Net result is a column ozone increase at mid to high latitudes and almost no change near the equator



Li et al. *Atmos. Chem. Phys.*, **9,** 2207-2213, 2009

Nitrous Oxide is Source of NO_x in the Stratosphere

- **Present: Chlorine/N_2O Interaction**
- **Future: N_2O/CO_2 Interaction**

Example: Volcanic Eruption Impacts on Stratospheric Ozone

- Eruptions release SO_2 into stratosphere
- Oxidizes to small sulfate aerosols
- Surface reactions convert NO_x to nitric acid (HNO_3)
- Reduces NO_x catalytic loss → increased ozone
- Reduced NO_x decreases interference with chlorine catalytic loss → decreased ozone
- Net effect depends on chlorine amount

→ Pinatubo – 1991 decreased ozone
→ El Chichon – 1982 had little impact on ozone
→ Agung – 1963 increased?? ozone
→ Future volcano – little impact? increase in ozone?

Nitrous Oxide is Source of NO_x in the Stratosphere

- Present: Chlorine/N_2O Interaction
- Future: N_2O/CO_2 Interaction

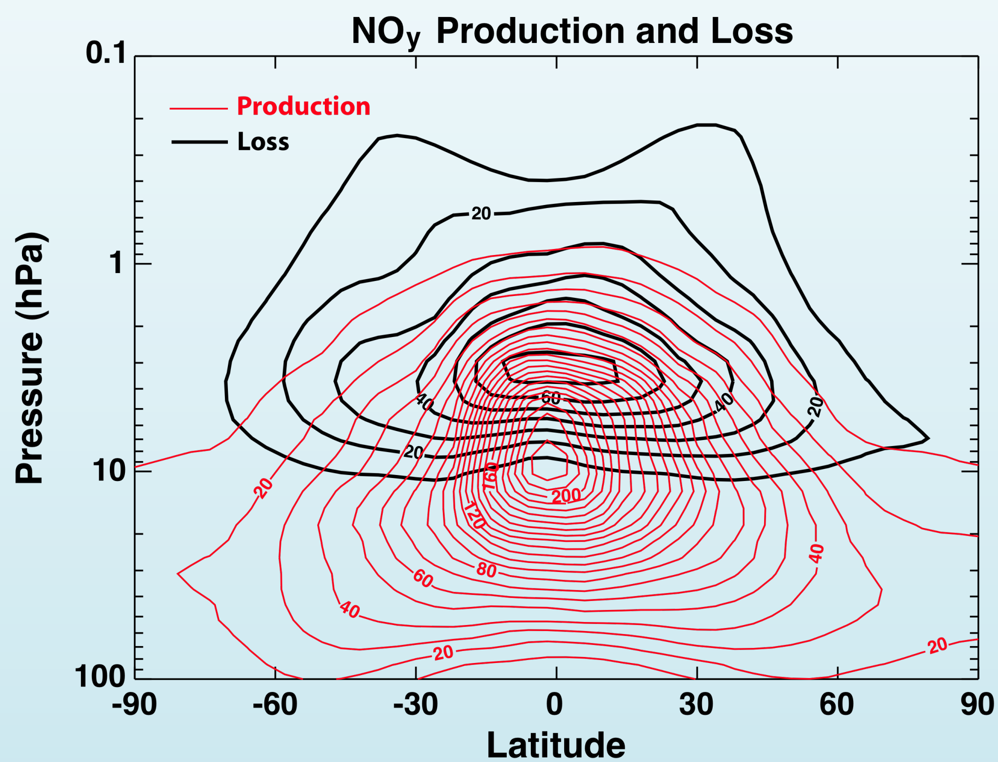
Odd Nitrogen (NO_y) is produced by the reaction of $O(^1D)$ with Nitrous Oxide (N_2O) and destroyed by the reaction of N atoms with NO.

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	$O(^1D) + N_2O \rightarrow NO + NO$
Loss of NO_y	$N(^4S) + NO \rightarrow N_2 + O$

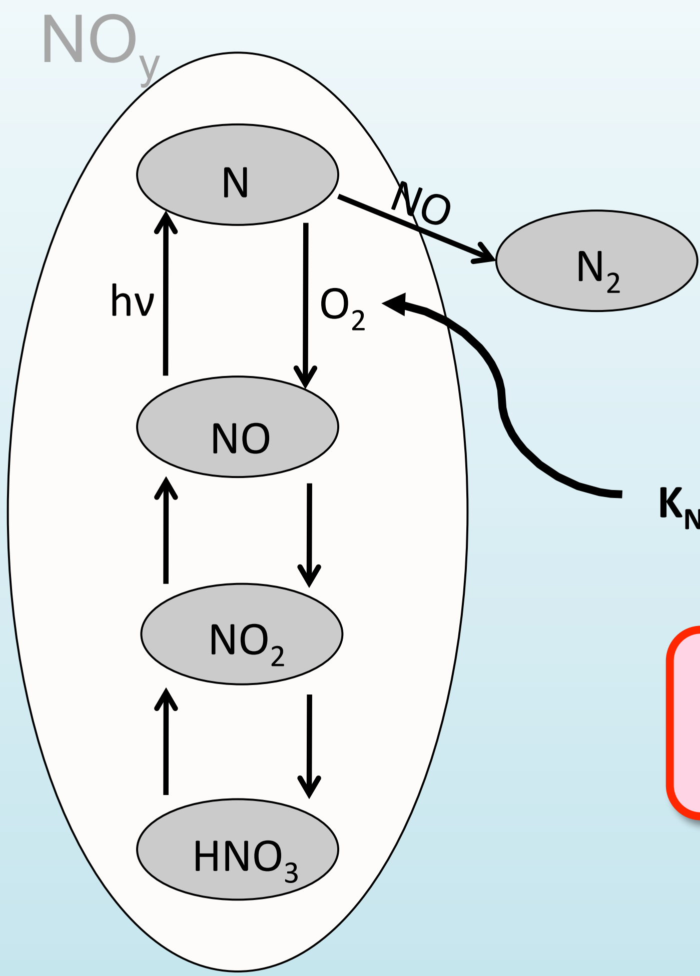
NO_y Production is balanced by loss and transport to the troposphere

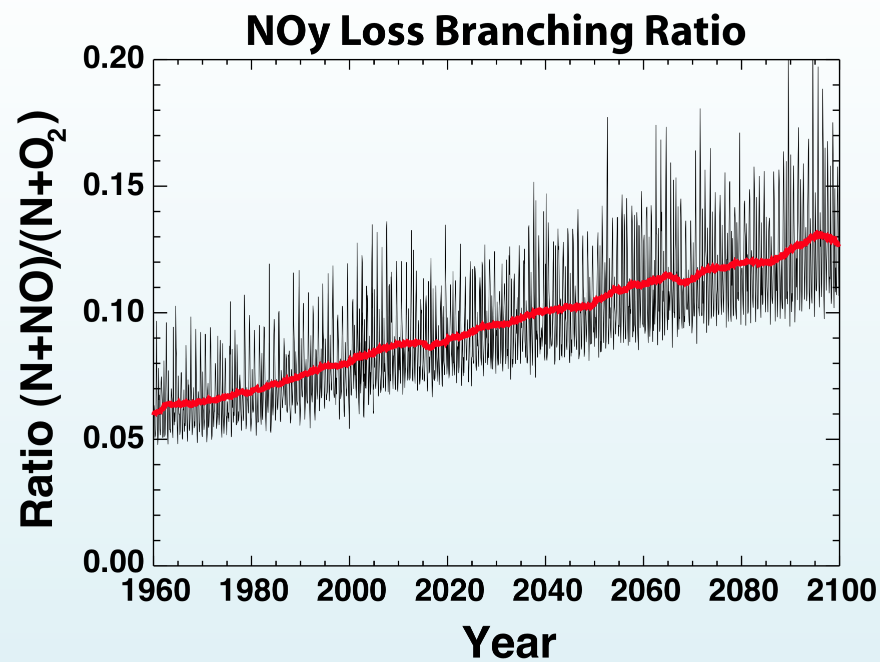
Chemical Loss occurs in the upper stratosphere above ~10 hPa.

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

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

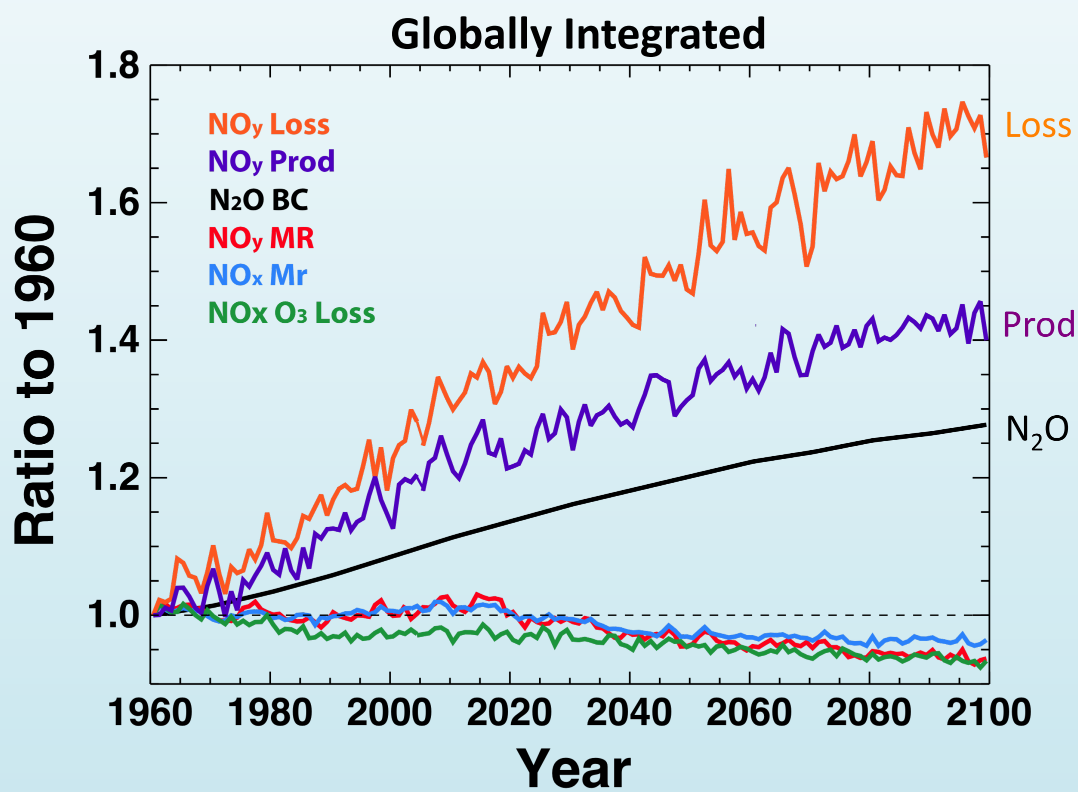
The ODP is the ratio of this term to the equivalent term for CFC-11

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

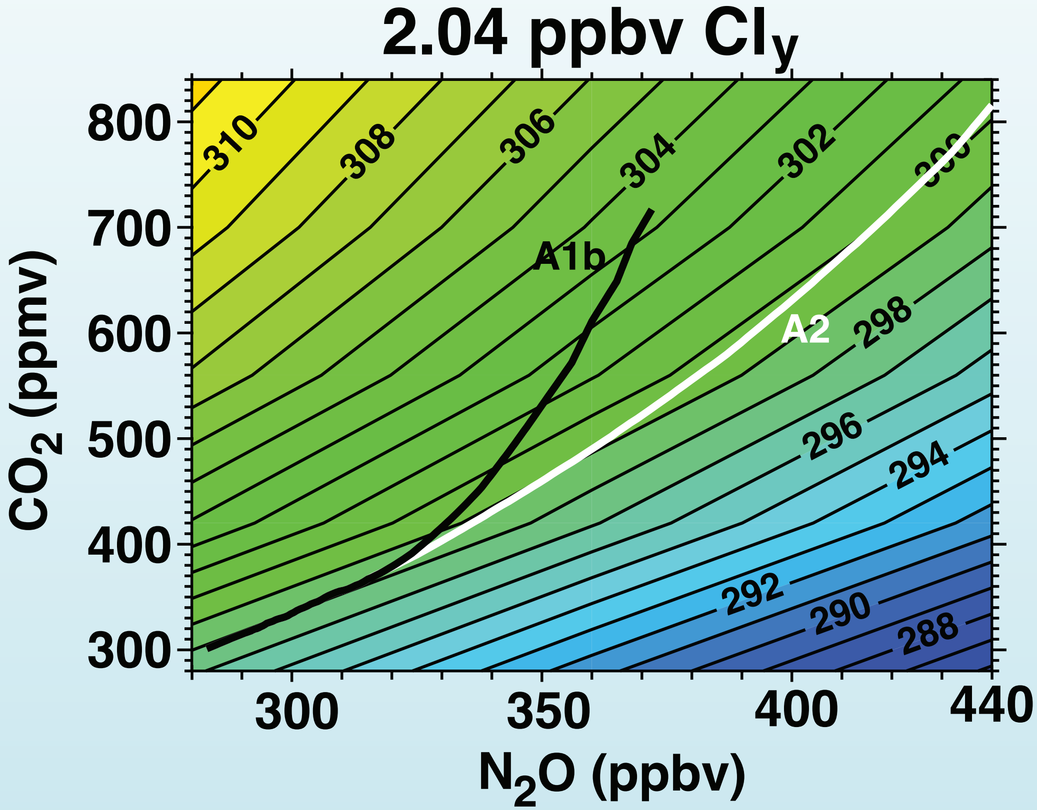
Production increases due to speed up of circulation pushing N_2O to higher altitude

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.

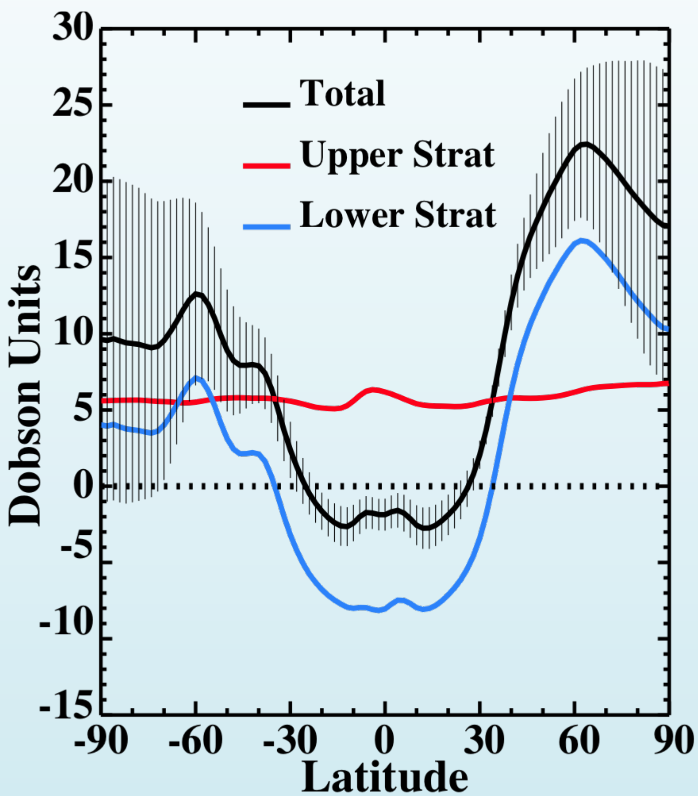


Future course of ozone dependent on the combined future for CO_2 and N_2O concentrations



Global Average
Total Ozone

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.

Conclusions

- Chlorine from CFCs have reduced ozone concentrations
  - Regulated by Montreal Protocol
  - Chlorine and its impact recovering
  - Will not recover to pre-CFC atmosphere
- Carbon dioxide cools stratosphere
  - Should lead to increased ozone at middle and high latitudes
  - Will govern properties of ozone layer post-CFCs
- Nitrogen oxides from nitrous oxide lead to ozone loss
  - Cooling from increased carbon dioxide limits impact of nitrous oxide
  - Future volcanoes, at times of low chlorine content, may not cause much ozone loss
  - It is not clear whether preventing ozone loss after "super-recovery" is the best thing to do