# Stratospheric Ozone

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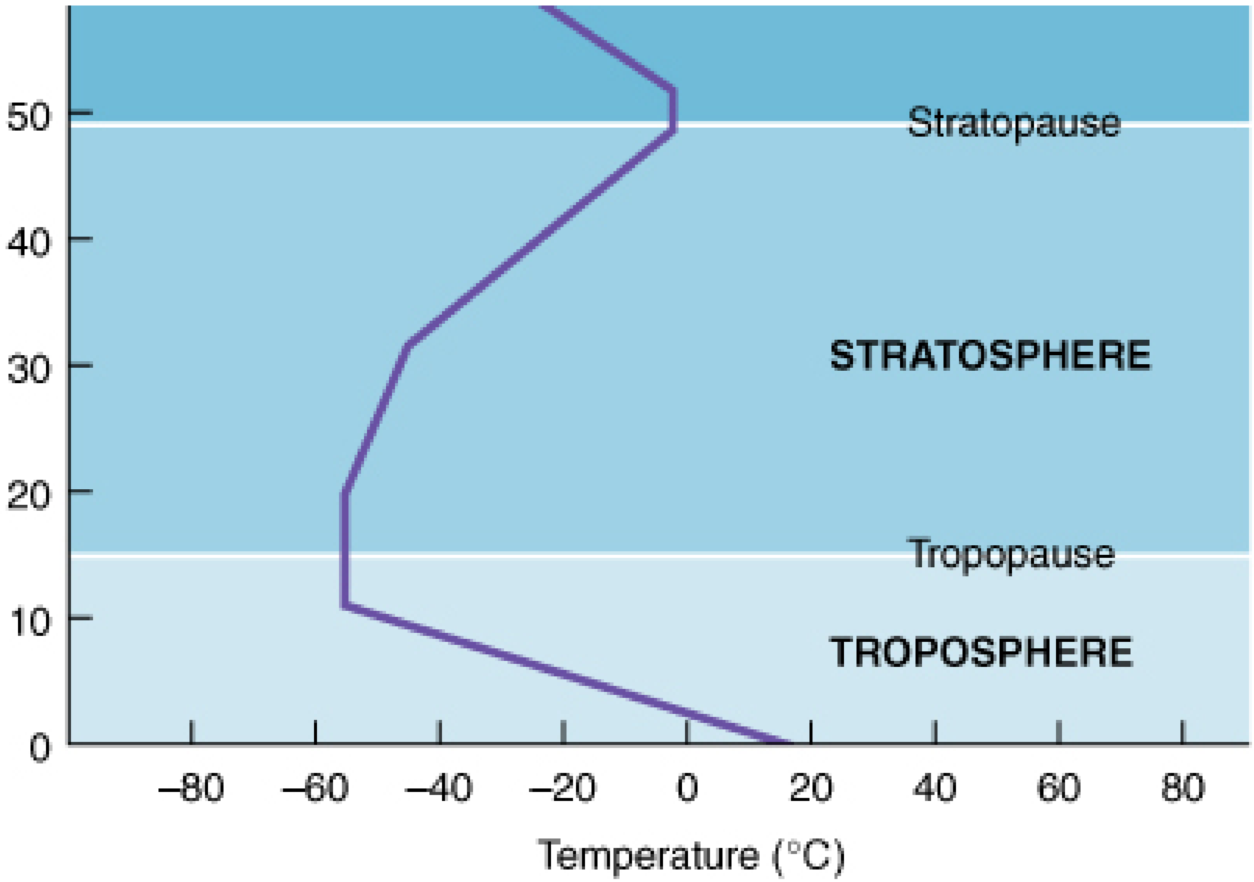
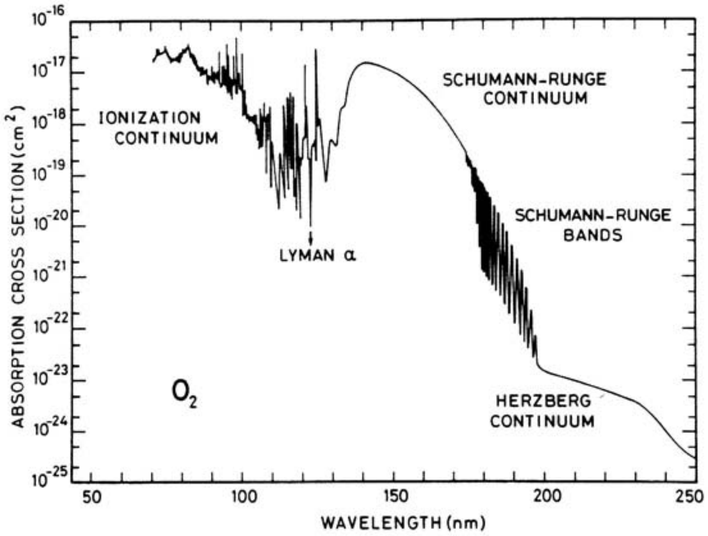
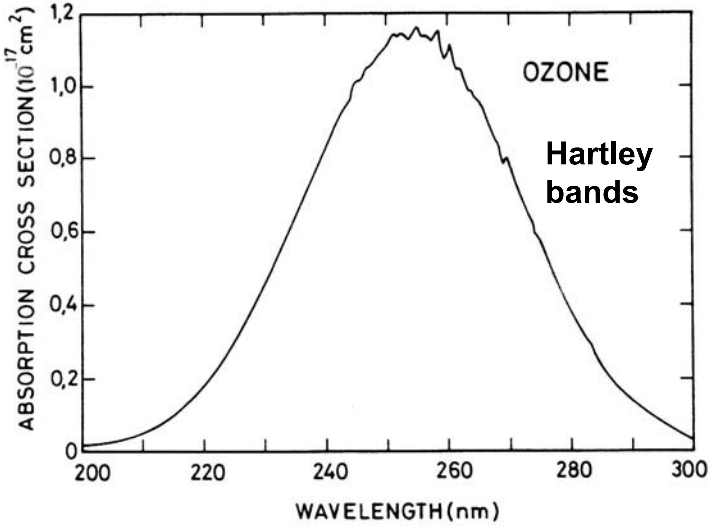


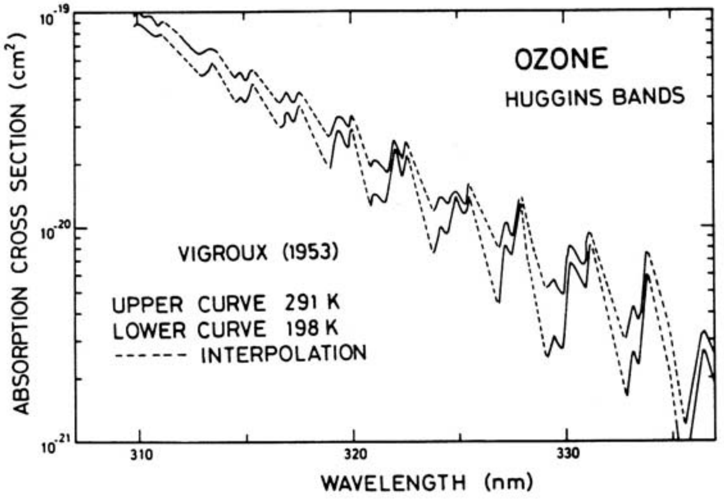
**Defining characteristic of the stratosphere: temperature increases with altitude ⇒ radiative heating**

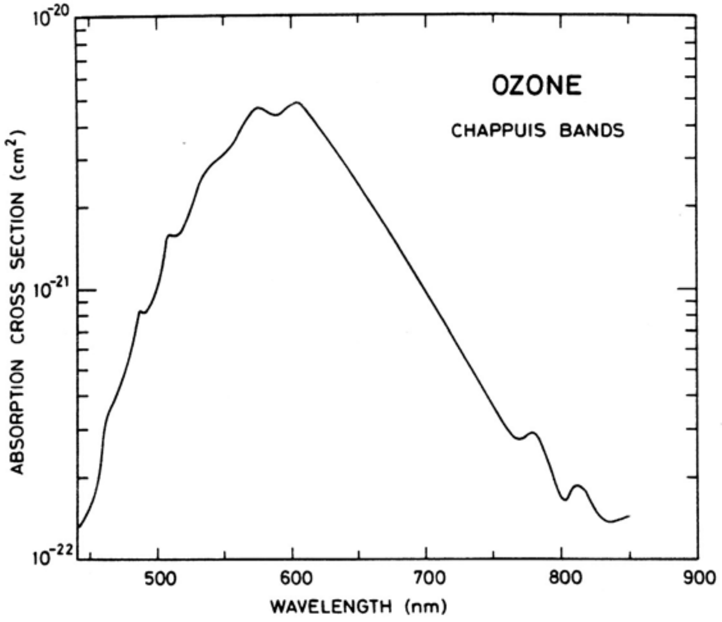
# $O_2$ and $O_3$ Absorption Cross Section





**Hartley bands**





[From Brasseur and Solomon, 1986]

# Spectrum of Solar Radiation vs. Altitude

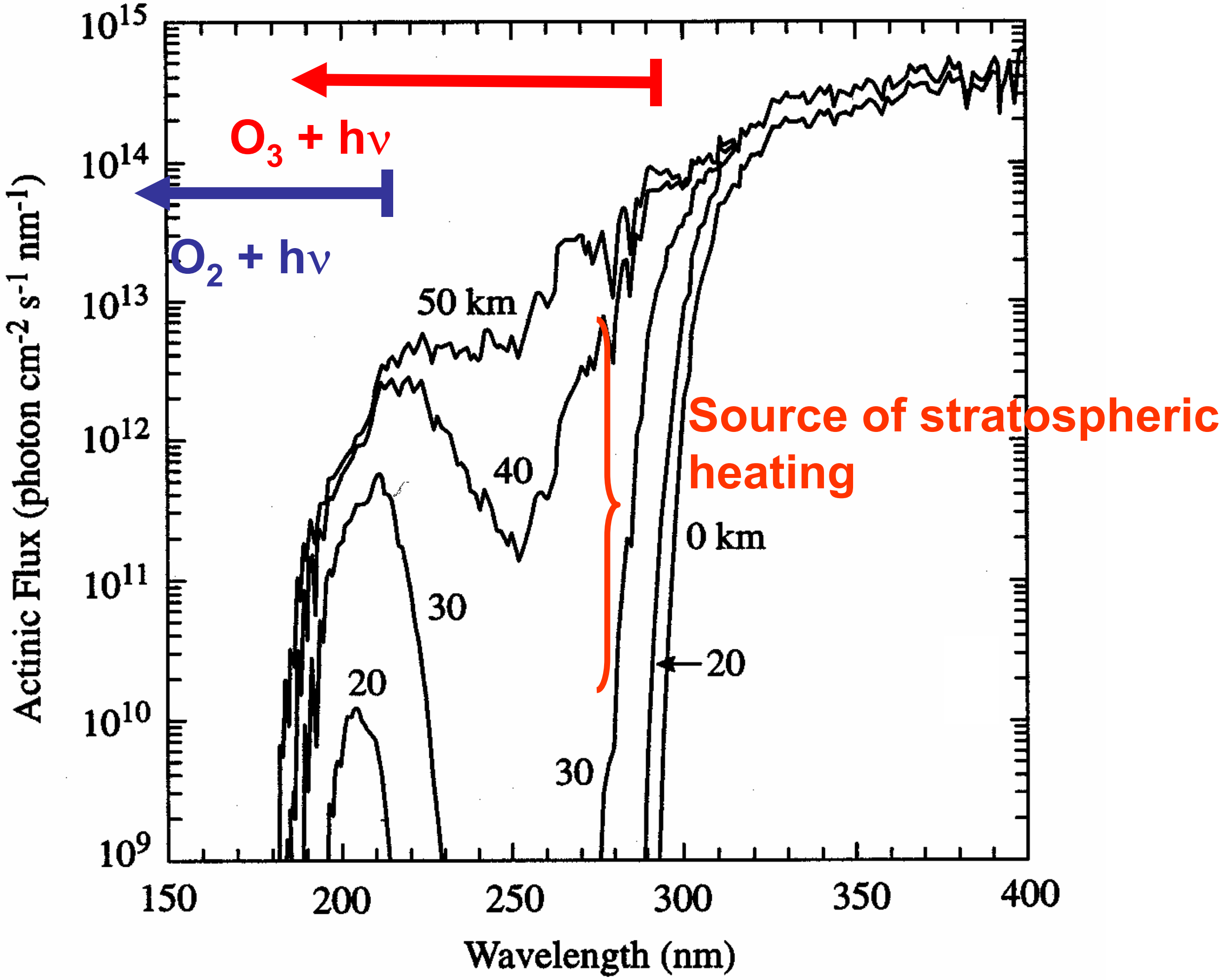


**Fig. 10-2** Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

# Stratospheric $O_3$

**Chapman mechanism:**

**Production:** $\boxed{O_2 + h\nu \rightarrow O + O}$ $(\lambda < 242\ \text{nm})$ (1)

$O + O_2 + M \rightarrow O_3 + M$ (2)

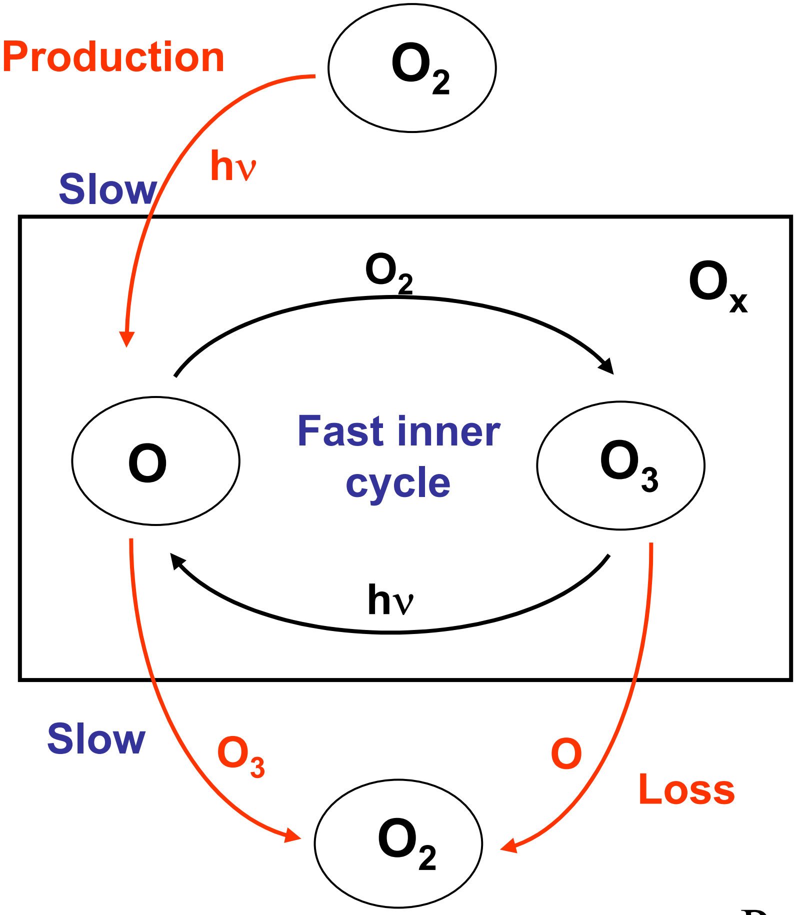
$O_3 + h\nu \rightarrow O_2 + O(^1D)$ $(\lambda < 325\ \text{nm})$

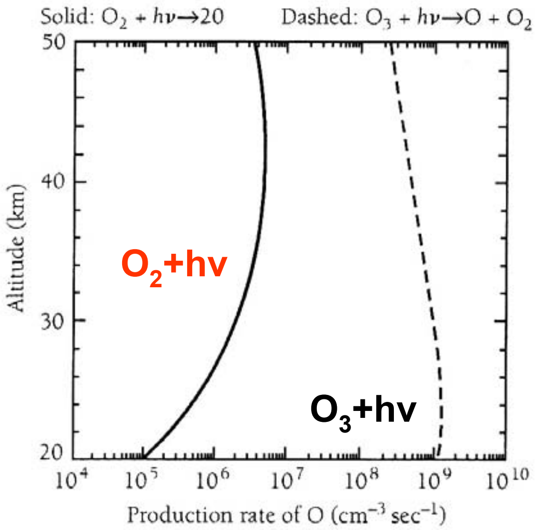
$O(^1D) + M \rightarrow O + M$

**Net:** $O_3 + h\nu \rightarrow O_2 + O$ (3)

**Loss:** $\boxed{O_3 + O \rightarrow 2O_2}$ (4)

# Odd-oxygen ($O_x$) Family





[From M. B. McElroy, 2002]

$$P_{O_x} = 2J[O_2]$$

$$L_{O_x} = 2k\,[O_3][O]$$

**Loss is quadratic with respect to $O_x$**

# $O_x$ Lifetime

$$O_2 + h\nu \rightarrow O + O \qquad (1)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (2)$$

$$O_3 + h\nu \rightarrow O_2 + O \qquad (3)$$

$$O_3 + O \rightarrow 2O_2 \qquad (4)$$

**Loss of O by reaction (2):**

$$-\frac{d[\mathrm{O}]}{dt} = k_2\,[\mathrm{O}_2][\mathrm{M}][\mathrm{O}]$$

$$\tau_{\mathrm{O}} = \frac{[\mathrm{O}]}{k_2\,[\mathrm{O}_2][\mathrm{M}][\mathrm{O}]} = \left(k_2\,[\mathrm{O}_2][\mathrm{M}]\right)^{-1}$$

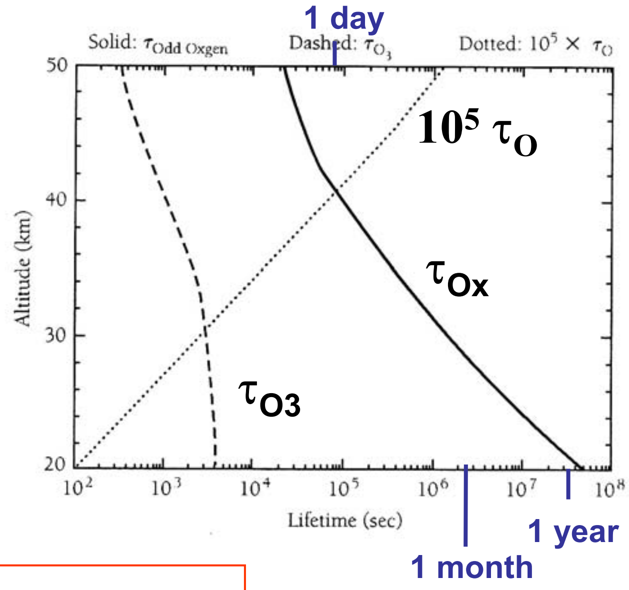
**Loss of $O_3$ by reaction (3):**

$$\tau_{\mathrm{O}_3} = \frac{[\mathrm{O}_3]}{J_3\,[\mathrm{O}_3]} = \left(J_3\right)^{-1}$$

**In steady state:**

$$k_2\,[\mathrm{O}_2][\mathrm{M}][\mathrm{O}] = J_3[\mathrm{O}_3]$$

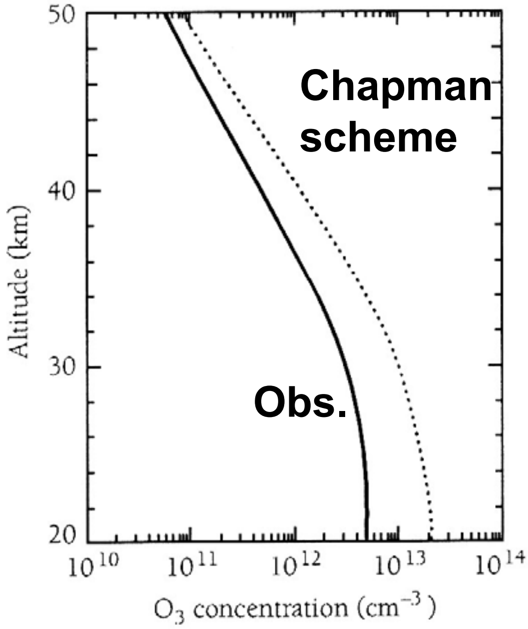
$$\frac{[\mathrm{O}]}{[\mathrm{O}_3]} = \frac{J_3}{k_2\,[\mathrm{O}_2][\mathrm{M}]} = \frac{\tau_{\mathrm{O}}}{\tau_{\mathrm{O}_3}} \ll 1$$



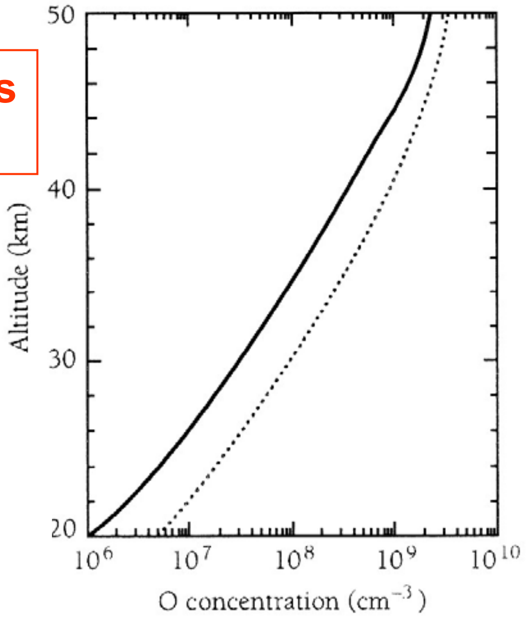
$$\boxed{[\mathrm{O}_x] = [\mathrm{O}] + [\mathrm{O}_3] \approx [\mathrm{O}_3]}$$

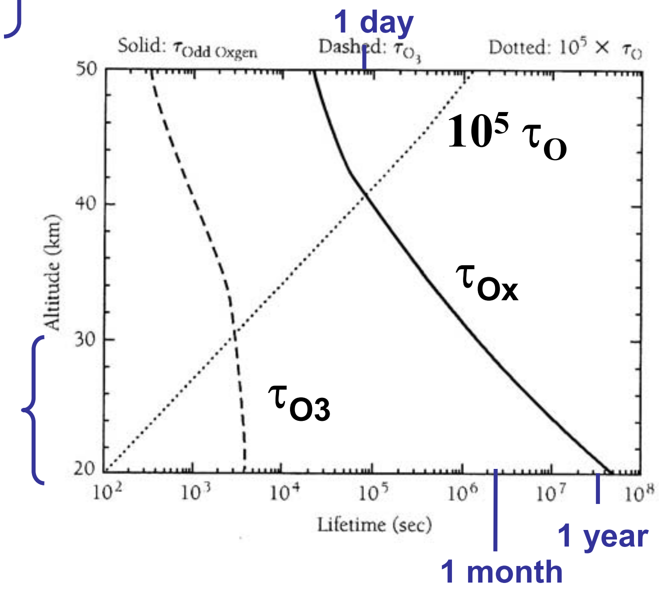
# Chapman Chemistry vs. Observations

**Box model calculation at 30ºN for equinox**



Chapman scheme overestimates $O_x$ abundances





In lower strat. long $\tau_{Ox}$
$\Rightarrow$ transport contributes to ozone distribution

[From M. B. McElroy, 2002]

# Catalytic Cycles For Ozone Loss: General Idea

$O_3 + X \rightarrow XO + O_2$

$O + XO \rightarrow X + O_2$

**Net:** $O_3 + O \rightarrow 2\ O_2$

**X is a catalyst**

***The catalyst is neither created nor destroyed…but the <u>rate</u> for the catalytic cycle [odd-o removal in this case] depends on catalyst concentrations***

# Hydrogen Oxide ($HO_x$) Radicals
# ($HO_x = H + OH + HO_2$)

Source from troposphere and the oxidation of $CH_4$

- **Initiation**:

  $H_2O + O(^1D) \rightarrow 2OH$

- **Propagation** through cycling of $HO_x$ radical family (example):

  $OH + O_3 \rightarrow HO_2 + O_2$
  $HO_2 + O_3 \rightarrow OH + 2O_2$
  Net: $2O_3 \rightarrow 3O_2$

  $OH + O_3 \rightarrow HO_2 + O_2$
  $HO_2 + O \rightarrow OH + O_2$
  Net: $O + O_3 \rightarrow 2O_2$

- **Termination** (example):

  $OH + HO_2 \rightarrow H_2O + O_2$

**$HO_x$ is a catalyst for $O_3$ loss**

# Nitrogen Oxide ($NO_x$) Radicals ($NO_x = NO + NO_2$)

- **Initiation** $N_2O + O(^1D) \rightarrow 2NO$
- **Propagation (example)**

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + h\nu \rightarrow NO + O$

$O + O_2 + M \rightarrow O_3 + M$

*Null cycle*

rate limiting step

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

Net $O_3 + O \rightarrow 2O_2$

**$O_3$ loss rate:**

$$-\frac{d[O_3]}{dt} = 2k\,[NO_2][O]$$

- **Termination**

$NO_2 + OH + M \rightarrow HNO_3 + M$

$NO_2 + O_3 \rightarrow NO_3 + O_2$

$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$

$N_2O_5 + H_2O \rightarrow 2HNO_3$

**Recycling**

$HNO_3 + h\nu \rightarrow NO_2 + OH$

$HNO_3 + OH \rightarrow NO_3 + H_2O$

$NO_3 + h\nu \rightarrow NO_2 + O$

$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$

# Catalytic Cycles For Ozone Loss:
# Chlorine ($ClO_x$ = Cl + ClO) radicals

- **Initiation :**

  (example) $CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$

- **Propagation (example):**

  $Cl + O_3 \rightarrow ClO + O_2$
  $ClO + O \rightarrow Cl + O_2$
  Net: $O_3 + O \rightarrow 2O_2$

  $Cl + O_3 \rightarrow ClO + O_2$
  $OH + O_3 \rightarrow HO_2 + O_2$
  $ClO + HO_2 \rightarrow HOCl + O_2$
  $HOCl + h\nu \rightarrow Cl + OH$
  Net: $O_3 + O_3 \rightarrow 3O_2$

reservoir species

- **Termination:**

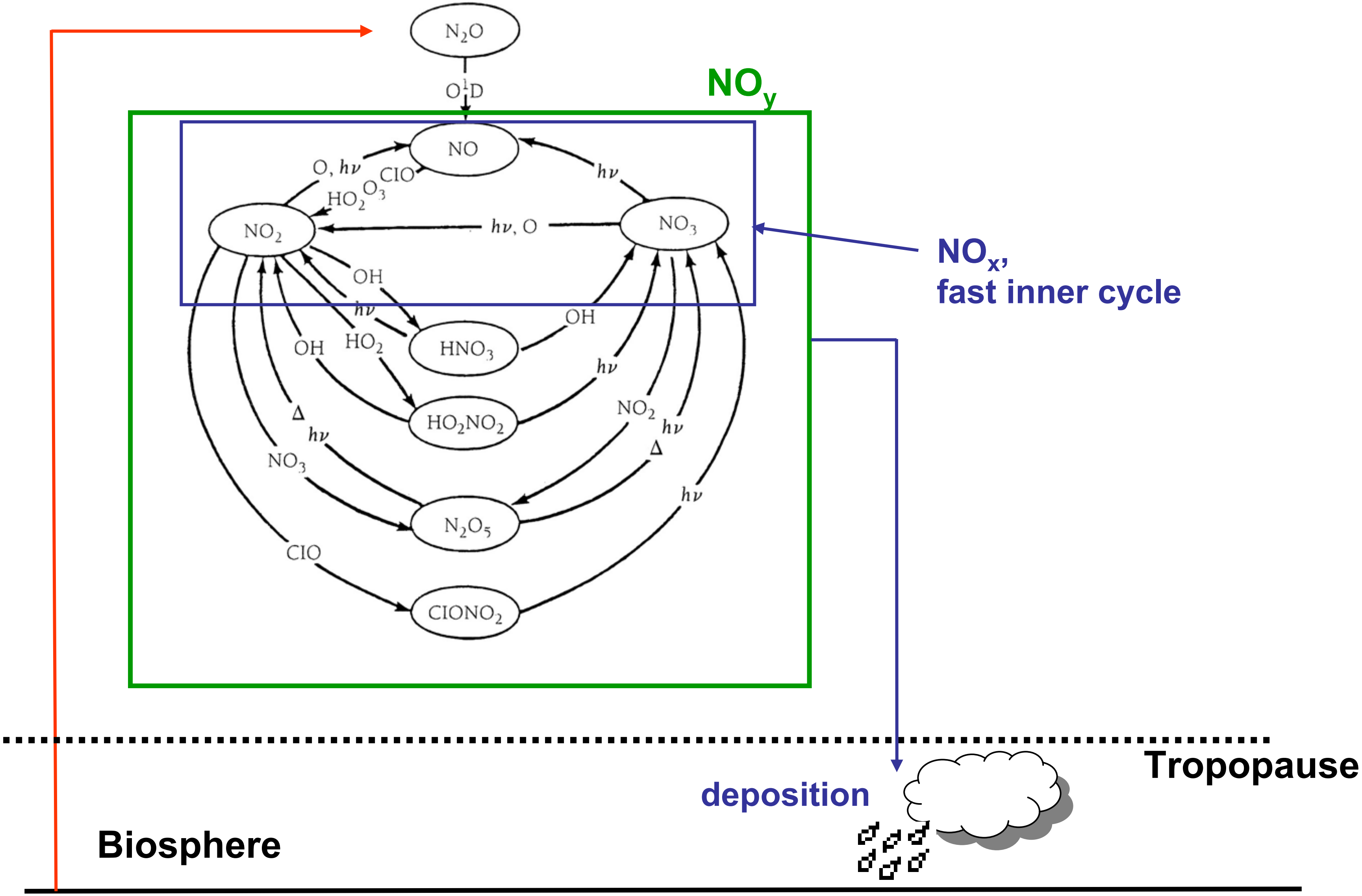
  $Cl + CH_4 \rightarrow HCl + CH_3$
  $ClO + NO_2 + M \rightarrow ClONO_2 + M$

**Recycling:**

$HCl + OH \rightarrow Cl + H_2O$
$ClONO_2 + h\nu \rightarrow ClO + NO_2$

couples $ClO_x$ and $NO_x$ cycles

# ATMOSPHERIC CYCLING OF $NO_x$ AND $NO_y$



**$NO_y$**

**$NO_x$, fast inner cycle**

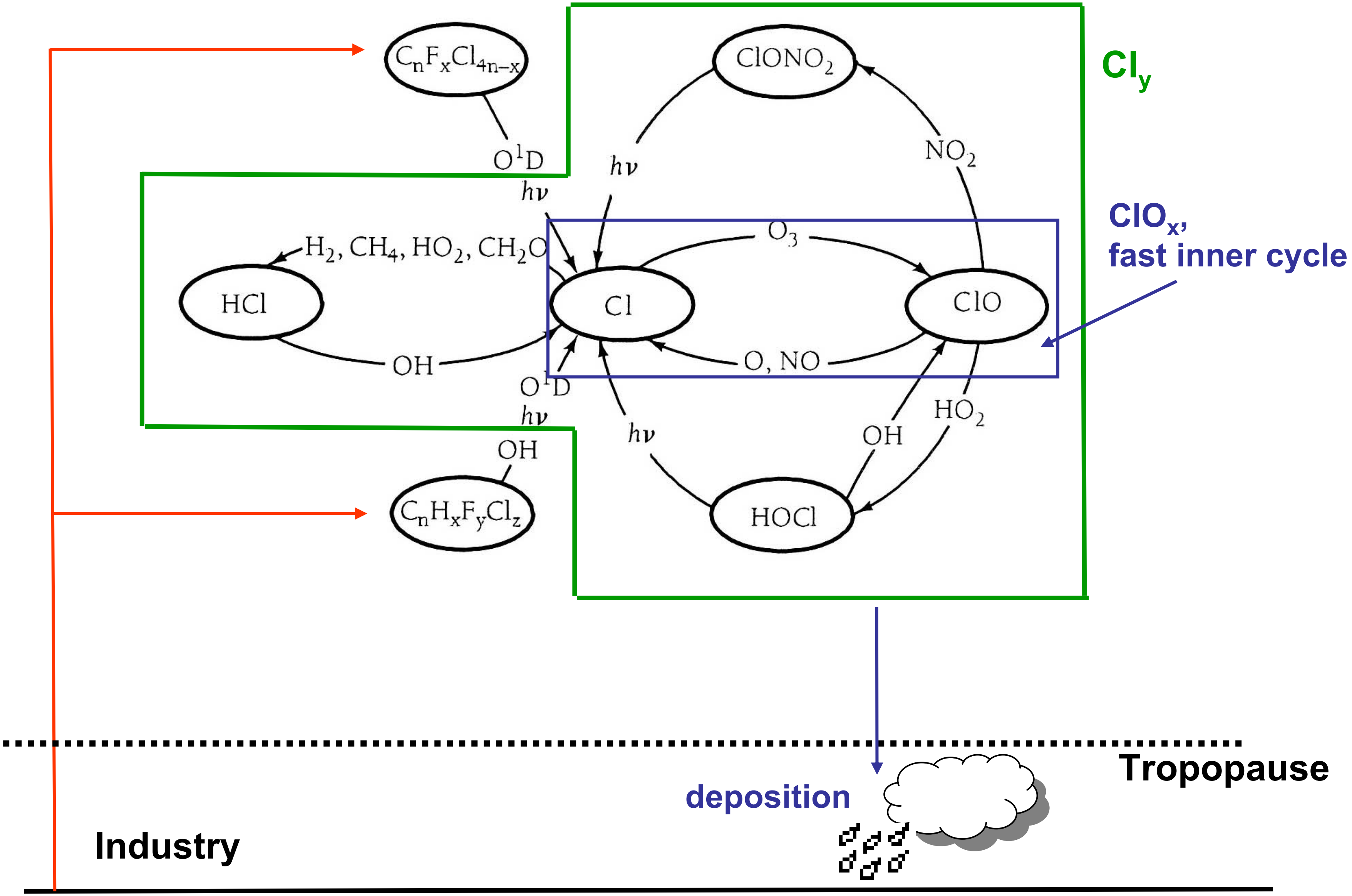
**deposition**

**Tropopause**

**Biosphere**

[Adapted from Jacob, 1999, and McElroy, 2002]

# Atmospheric Cycling Of $ClO_x$ AND $Cl_y$



[Adapted from Jacob, 1999, and McElroy, 2002]

# Catalytic Cycles For Ozone Loss:
# Bromine ($BrO_x = Br + BrO$) radicals

- **Initiation:**

  (example) $CH_3Br + h\nu \rightarrow Br + CH_3$

- **Propagation:**

  $Br + O_3 \rightarrow BrO + O_2$
  $BrO + O \rightarrow Br + O_2$
  Net: $O_3 + O \rightarrow 2O_2$

  $Br + O_3 \rightarrow BrO + O_2$
  $Cl + O_3 \rightarrow ClO + O_2$
  $ClO + BrO \rightarrow Br + Cl + O_2$
  Net: $O_3 + O_3 \rightarrow 3O_2$

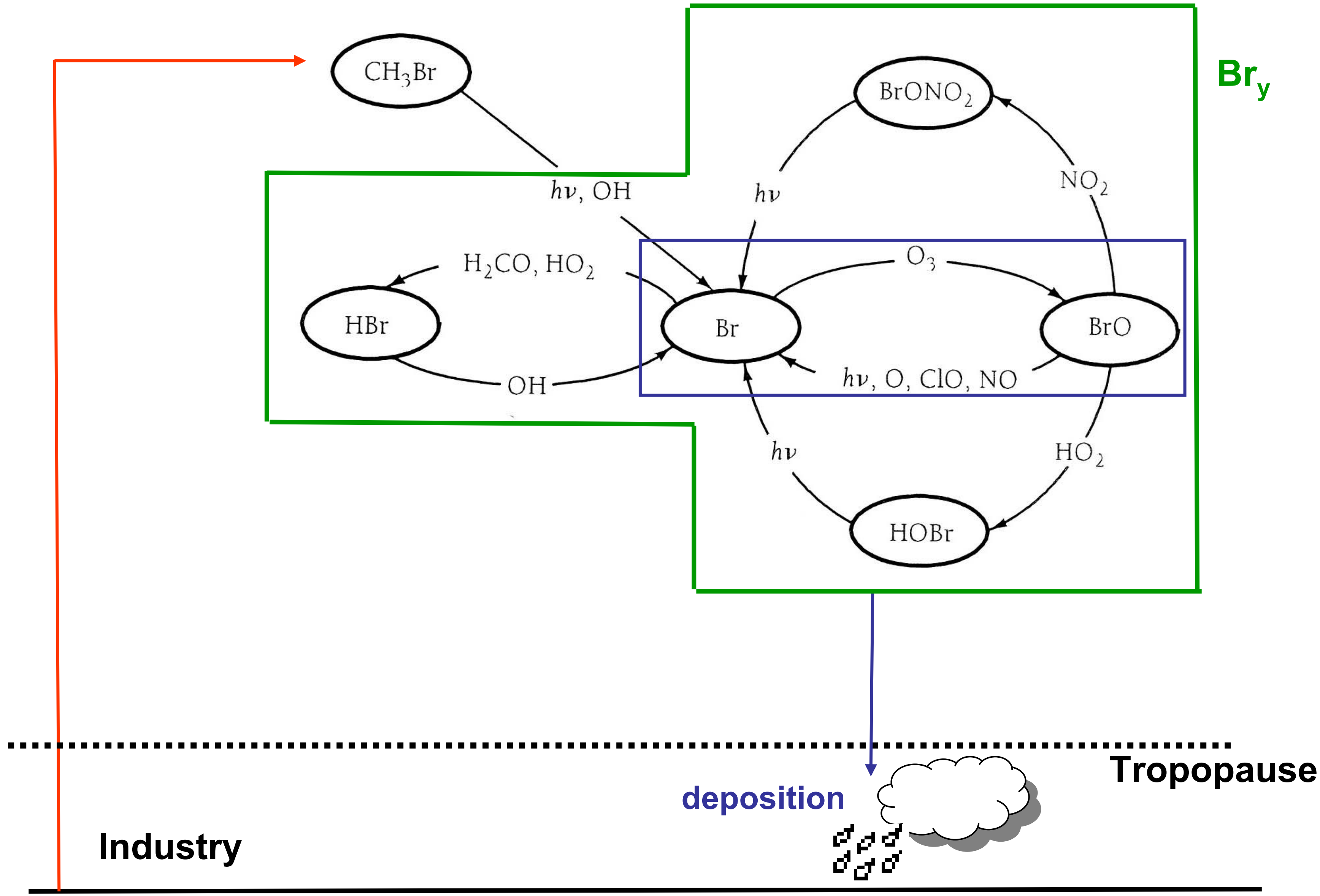
- **Termination:**

  $Br + HO_2 \rightarrow HBr + O_2$
  $BrO + NO_2 + M \rightarrow BrONO_2 + M$

**Recycling:**

$HBr + OH \rightarrow Br + H_2O$
$BrONO_2 + h\nu \rightarrow BrO + NO_2$

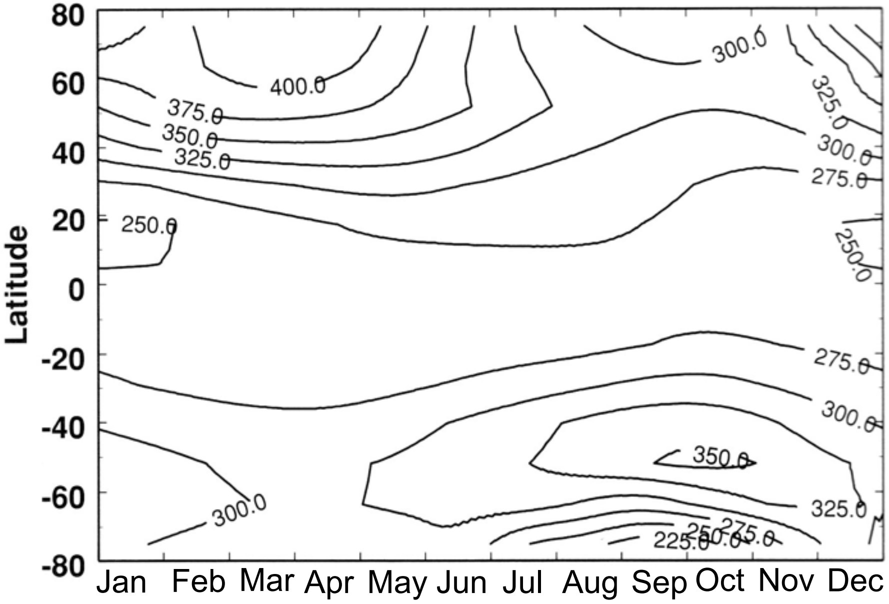
# Atmospheric Cycling Of $BrO_x$ And $Br_y$



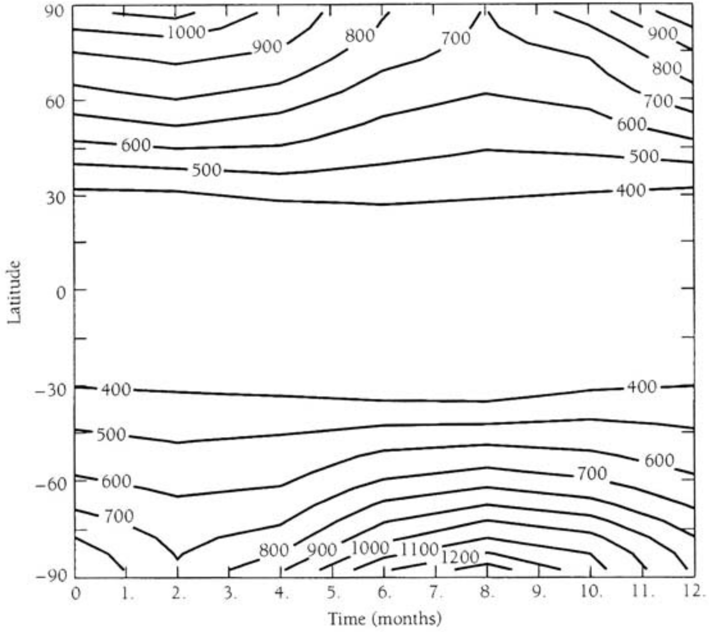
[Adapted from Jacob, 1999, and McElroy, 2002]

# Influence of Catalytic Cycles in Column $O_3$

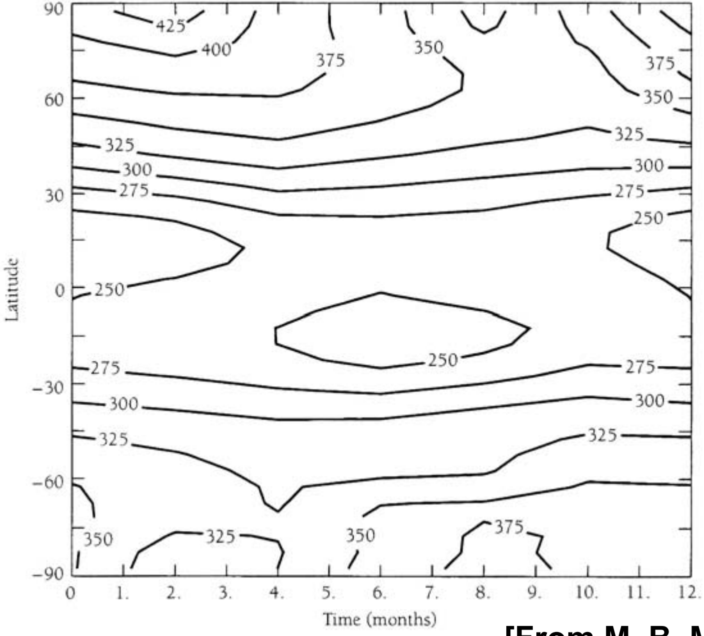
**Observed $O_3$ column from TOMS (1988-1996)**



**Harvard 2-D model with Chapman chemistry**



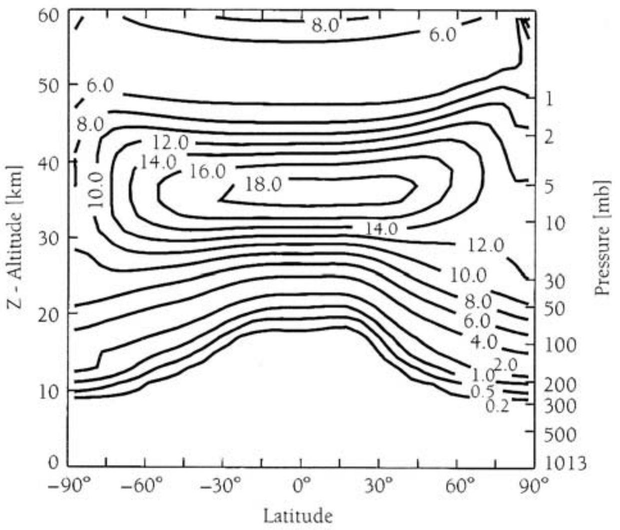
**Including $HO_x$, $NO_x$, and $ClO_x$**

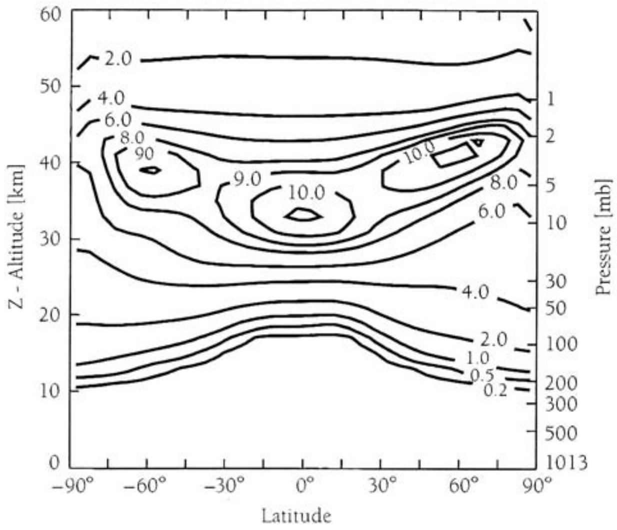


[From M. B. McElroy, 2002]

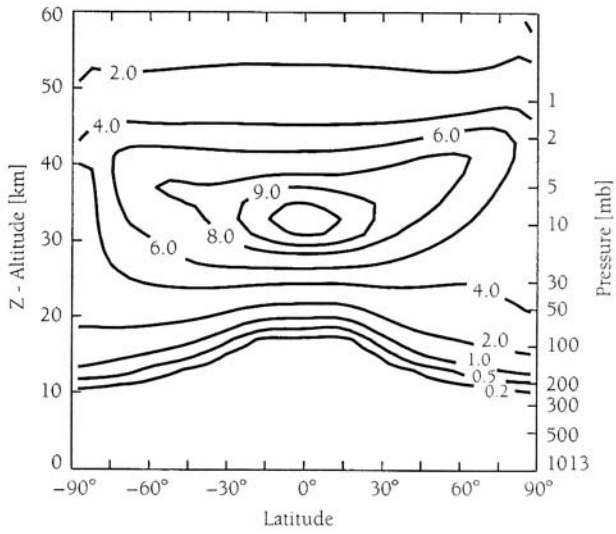
# Vertical Distribution of $O_3$

**Harvard 2-D model with Chapman chemistry**





**Including $HO_x$ and $NO_x$**



**Altitude region of $ClO_x$ impact**

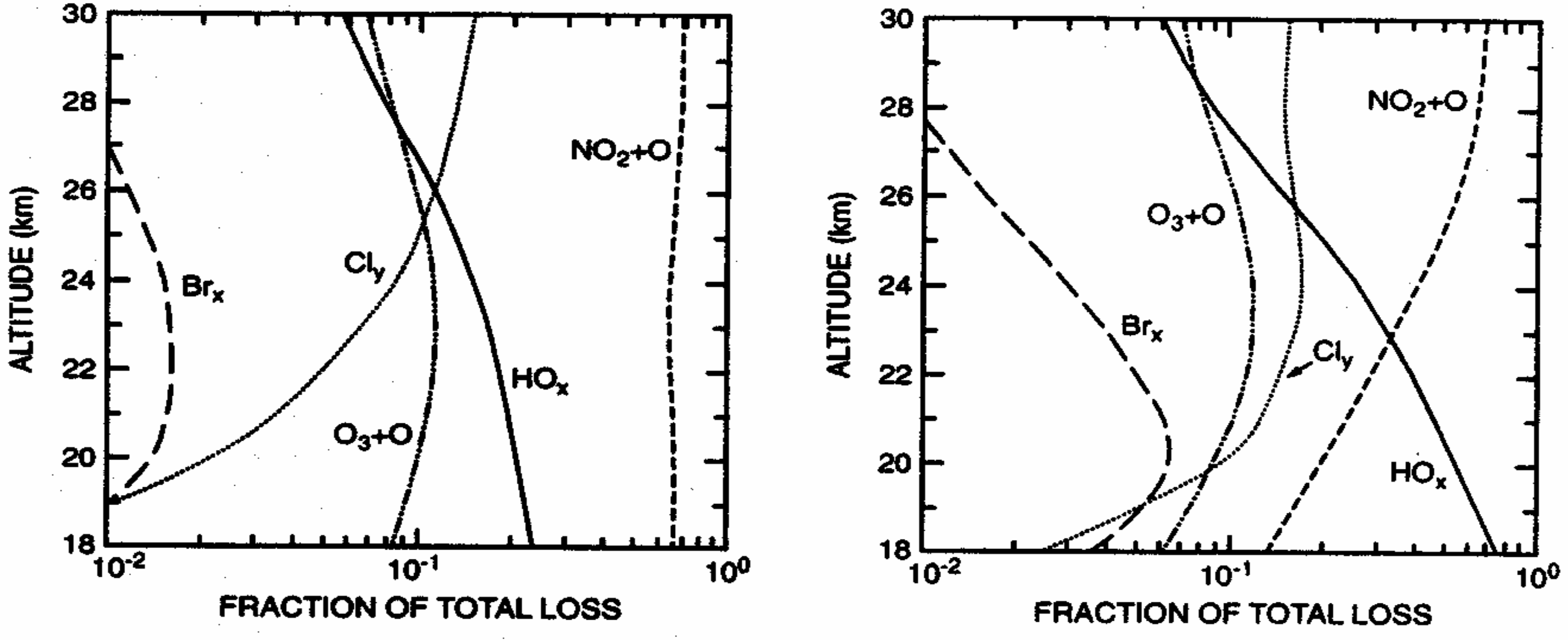
**Including $HO_x$, $NO_x$, and $ClO_x$**

**[From M. B. McElroy, 2002]**

# Hydrolysis of $N_2O_5$ in Aerosols Increases the Sensitivity to Cl in the Lower Stratosphere

$N_2O_5 + H_2O_{(l)} \rightarrow 2\ HNO_3$

**Box model Calculations**



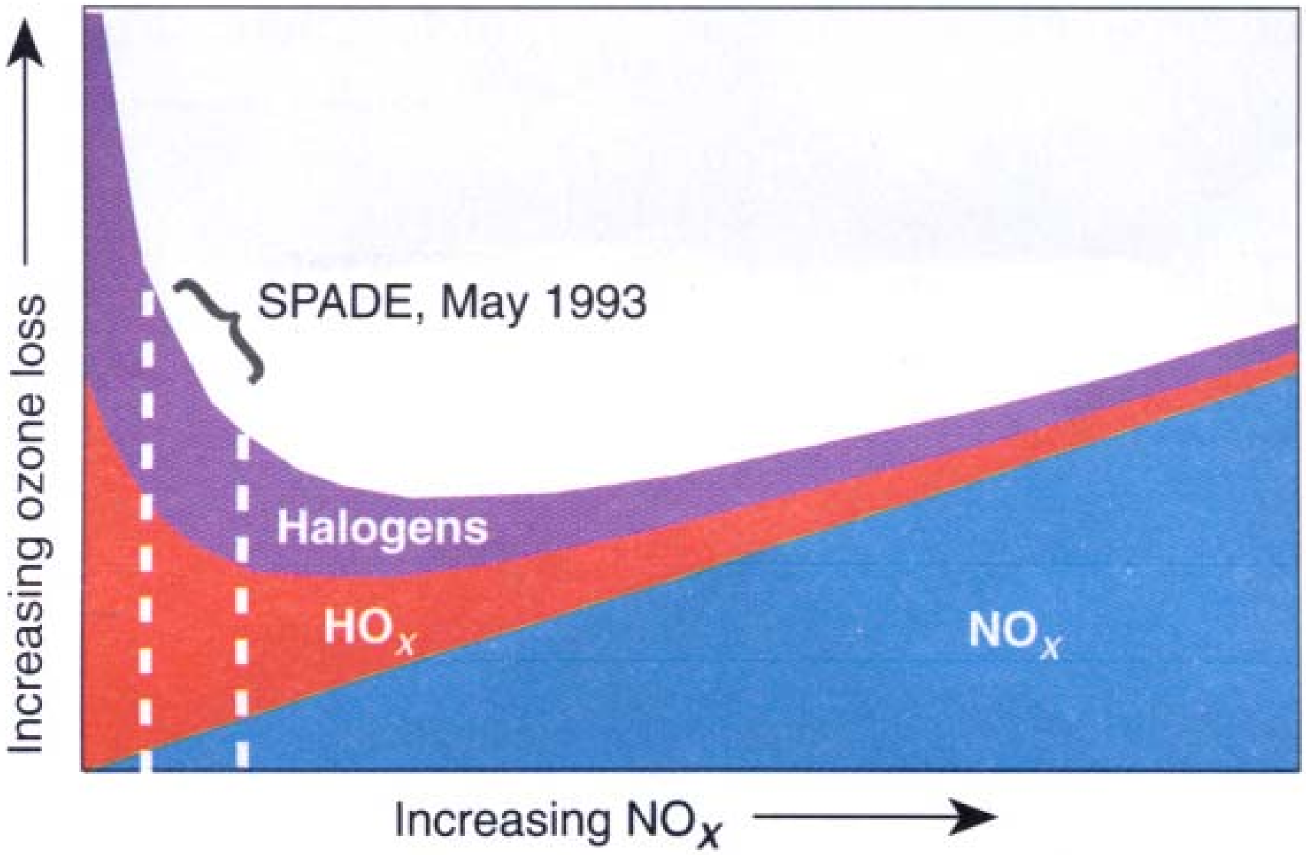
Without $N_2O_5$ hydrolysis

With $N_2O_5$ hydrolysis

$N_2O_5$ hydrolysis decreases $NO_x$ and increases $ClO_x$ and $BrO_x$

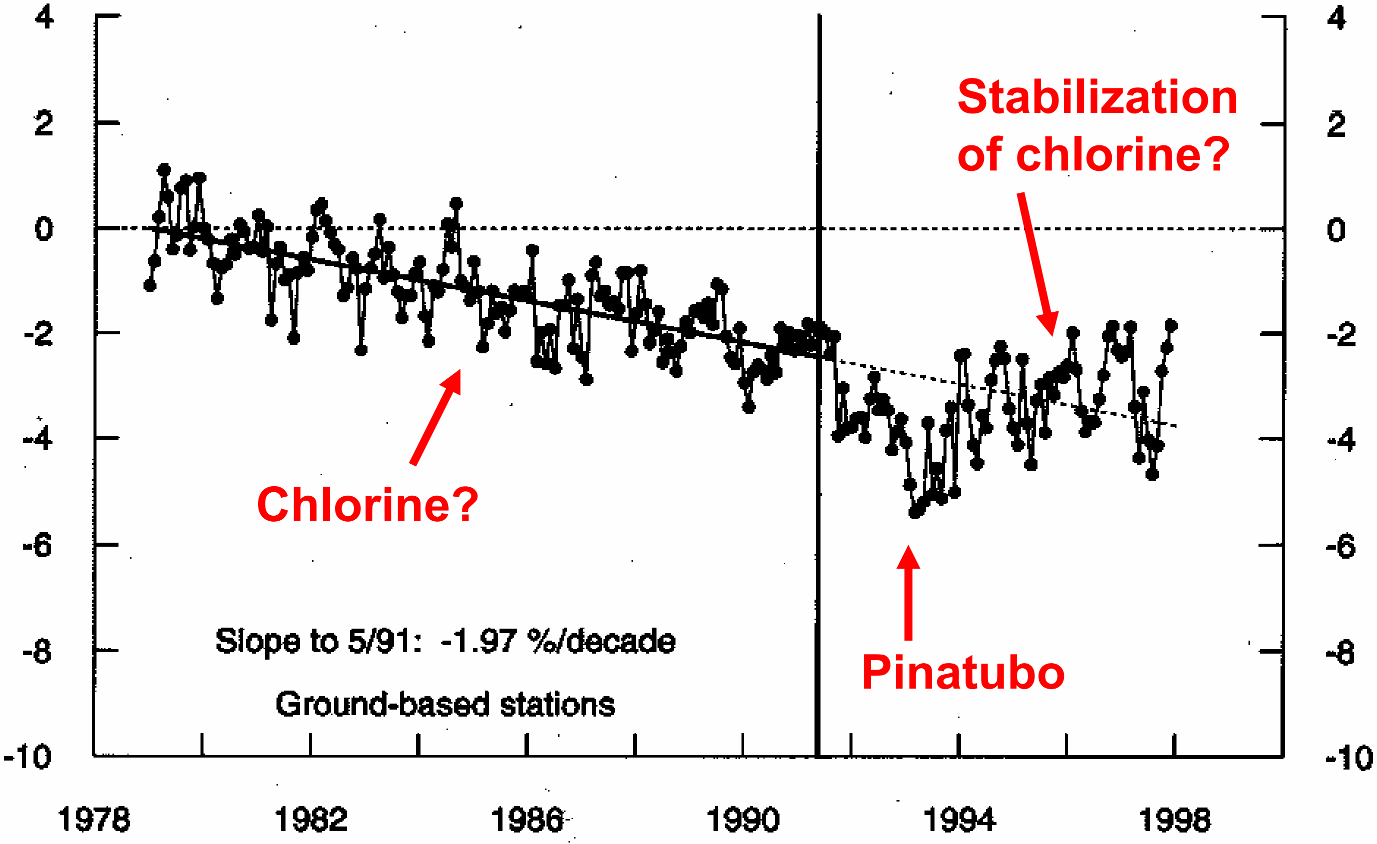
[From McElroy et al., 1992]

# Sensitivity of Halogen Loss to $NO_x$



[From Wennberg et al. 1994]

# Ozone Column Trend, 60ºS-60ºN [WMO, 1998]

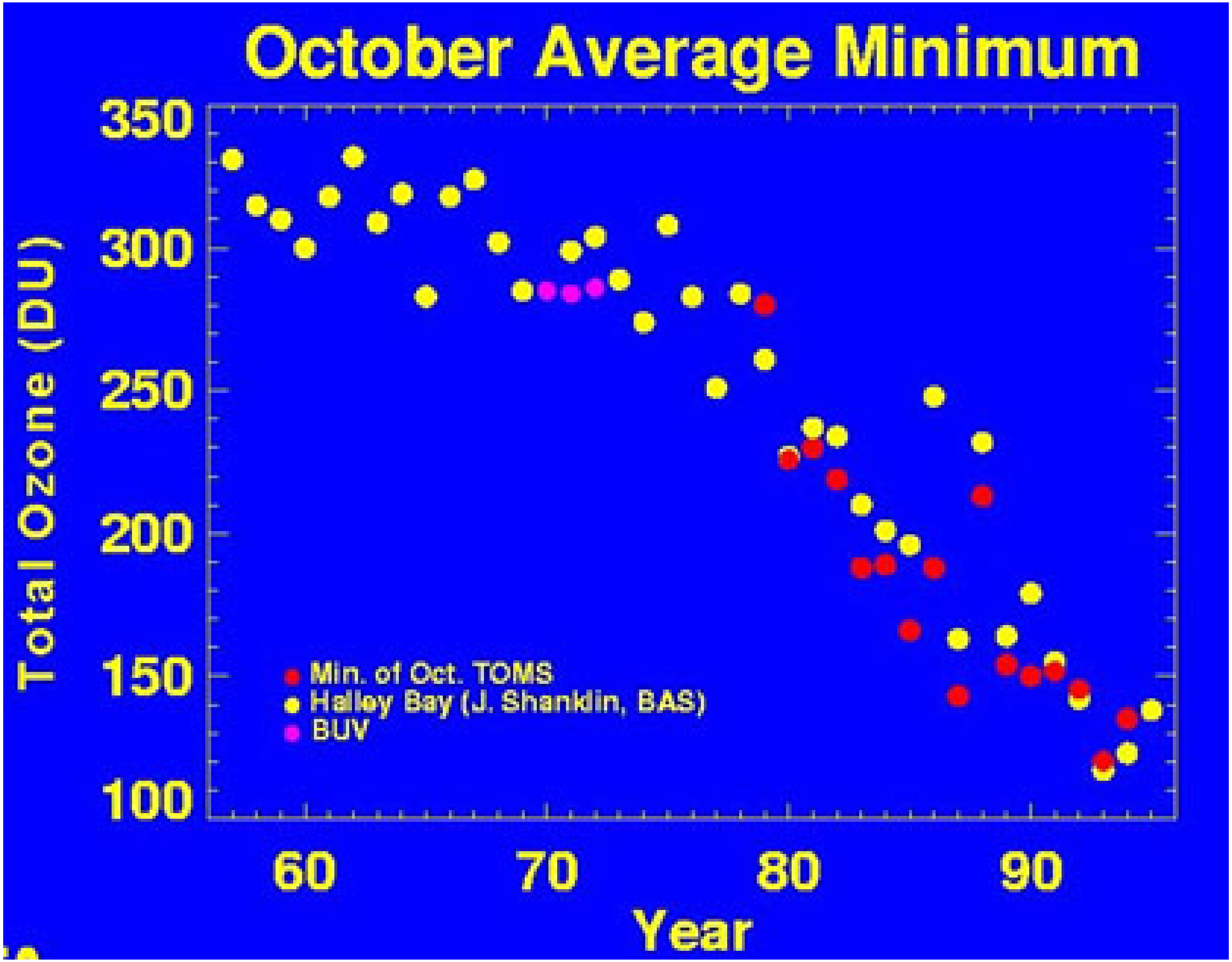


Stabilization of chlorine?

Chlorine?

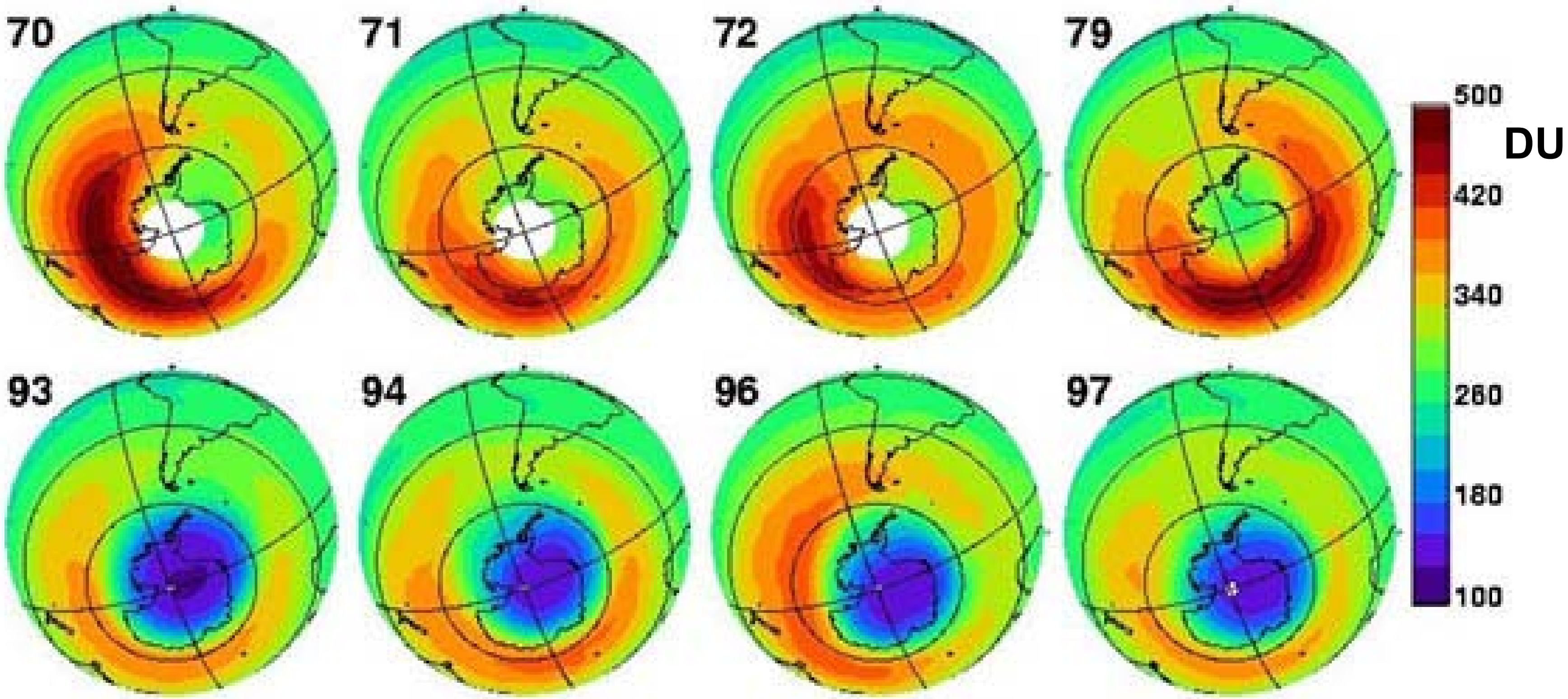
Pinatubo

# Ozone Trend at Halley Bay, Antarctica



# The Antarctic Ozone Hole

## Southern hemisphere ozone column seen from TOMS, October



1 Dobson Unit (DU) = 0.01 mm $O_3$ STP = $2.69 \times 10^{16}$ molecules $cm^{-2}$

# Polar Ozone loss: Heterogeneous Chemistry

- $N_2O_5(g) + HCl(s) \rightarrow ClNO_2(g) + HNO_3(s)$
- $N_2O_5(g) + H_2O(s) \rightarrow 2\ HNO_3(s)$
- $ClONO_2(g) + H_2O(s) \rightarrow HOCl(g) + HNO_3(s)$
- $ClONO_2(g) + HCl(s) \rightarrow Cl_2(g) + HNO_3(s)$
- $HOCl(g) + HCl(s) \rightarrow Cl_2(g) + H_2O(s)$
- $BrONO_2(g) + H_2O(s) \rightarrow HOBr(g) + HNO_3(s)$
- $HOBr(g) + HCl(s) \rightarrow BrCl(g) + H_2O(s)$

Converts chlorine and bromine from stable forms ($ClONO_2$, HCl, and $BrONO_2$) to species that are rapidly photolyzed to yield reactive Cl and Br atoms

**Reactions occur on surface of Polar Stratospheric clouds (PSC)**

**Type 1 PSC:**

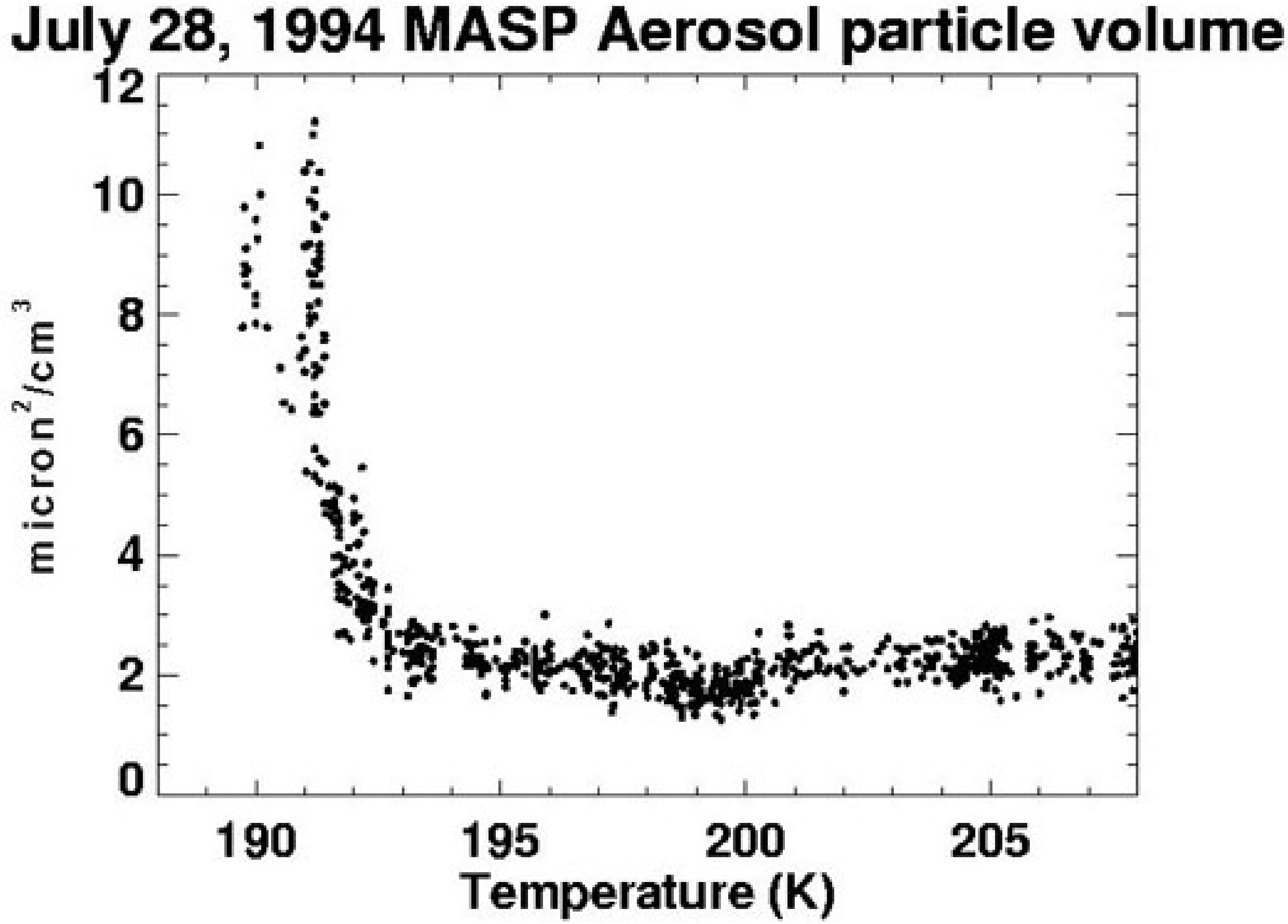
- composed of nitric acid trihydrate and a ternary solution of $HNO_3$, $H_2SO_4$, $H_2O$
- Formation temperature: 195K
- Particle size < 10 µm

**Type 2 PSC:**

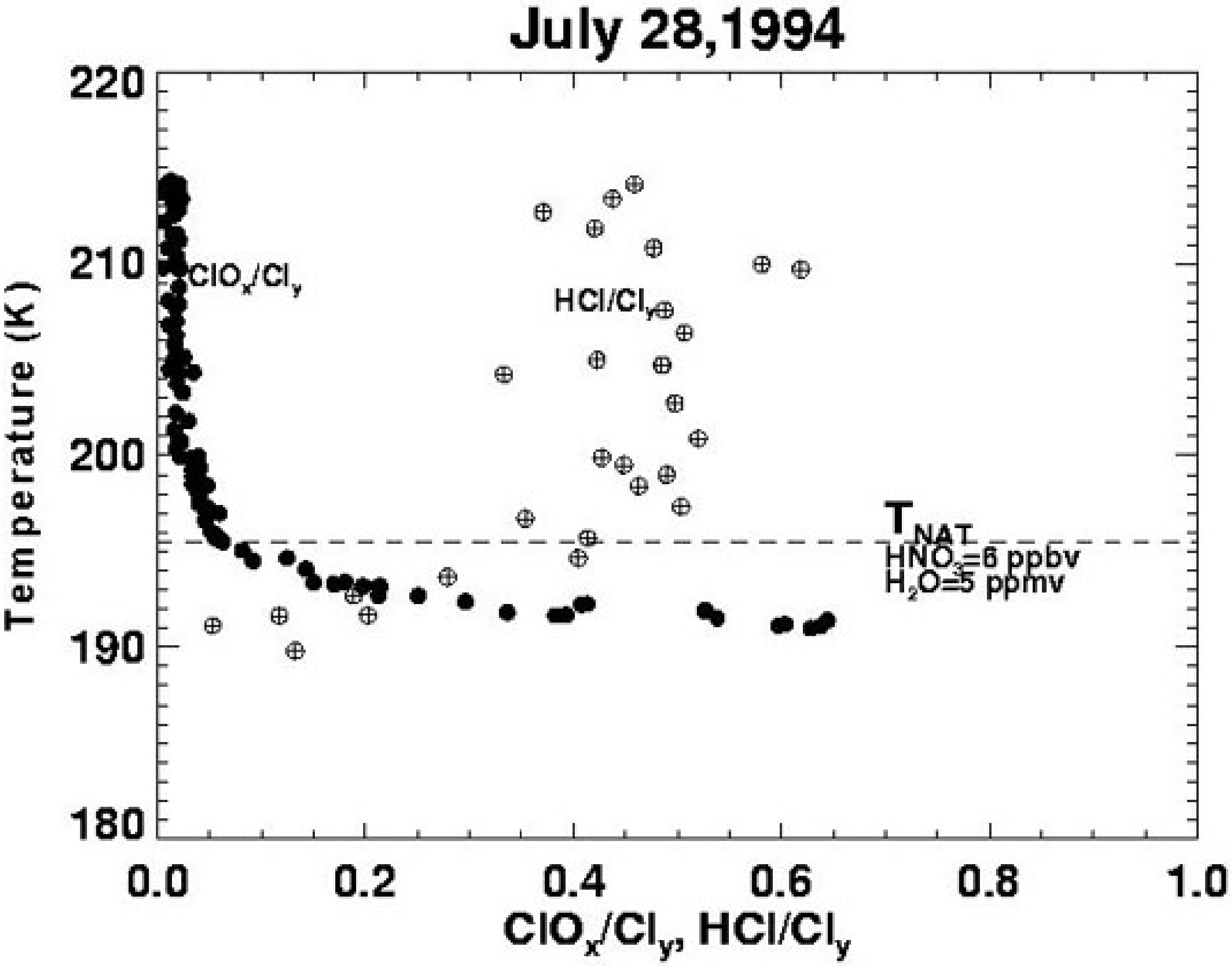
- Water ice particles
- Formation temperature: 188K
- Particle size > 10 µm

Sedimentation of PSC particles removes $NO_y$ from polar stratosphere (denitrification)

# PSC Formation vs. Temperature



# Activation of Chlorine in The Antarctic Vortex



[From Kawa et al. 1997]

# Catalytic Cycles of Polar $O_3$ Loss

**Chlorine**

$2[Cl + O_3 \rightarrow ClO + O_2]$

$ClO + ClO + M \rightarrow ClOOCl + M$

$ClOOCl + h\nu \rightarrow Cl + ClOO$

$ClOO + M \rightarrow Cl + O_2 + M$

Net: $O_3 + O_3 \rightarrow 3O_2$

**$O_3$ loss rate:**

$$-\frac{d[O_3]}{dt} = 2k\,[ClO]^2[M]$$

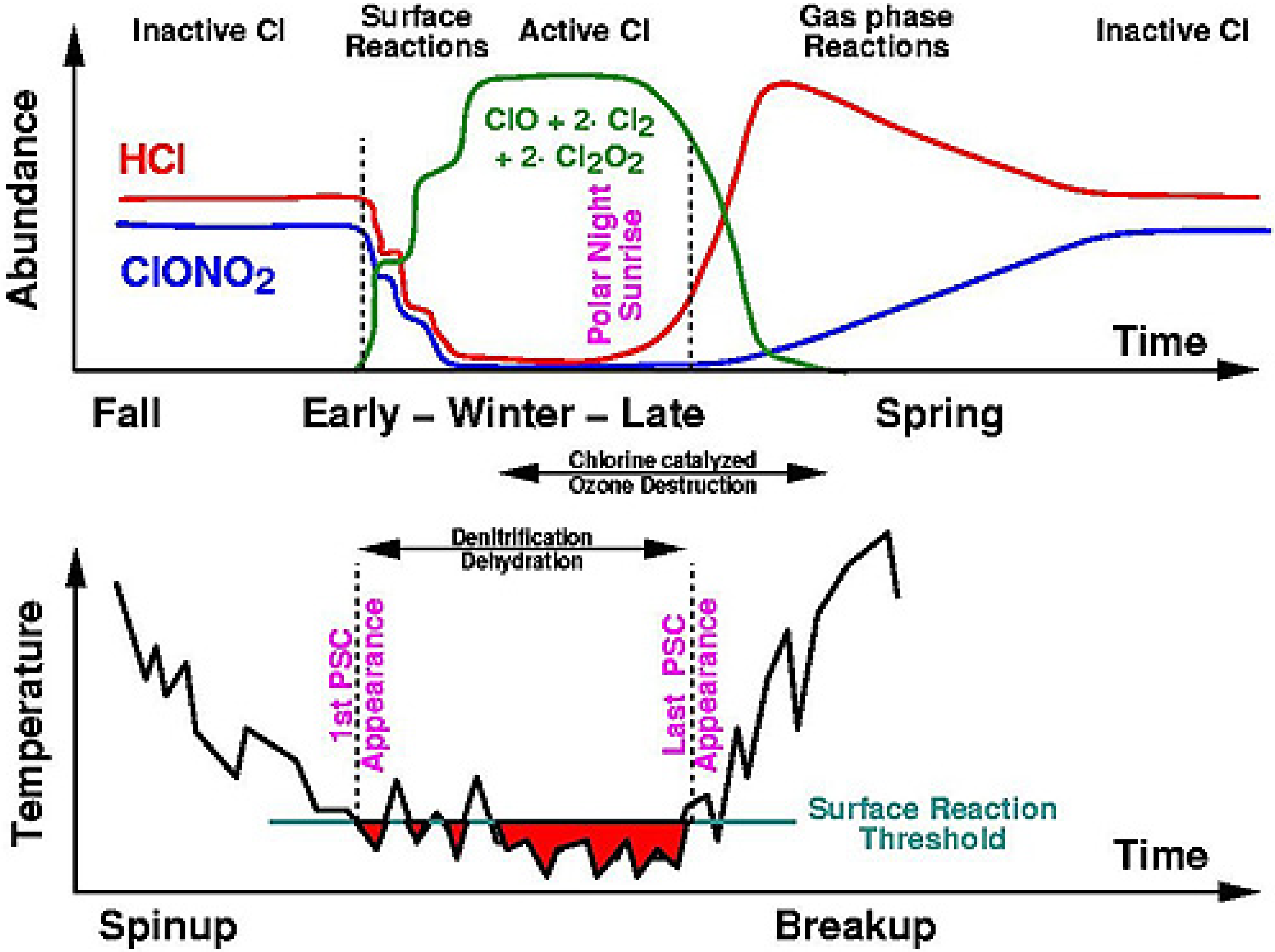
$O_3$ loss proportional to the square of the ClO concentration

**Bromine**

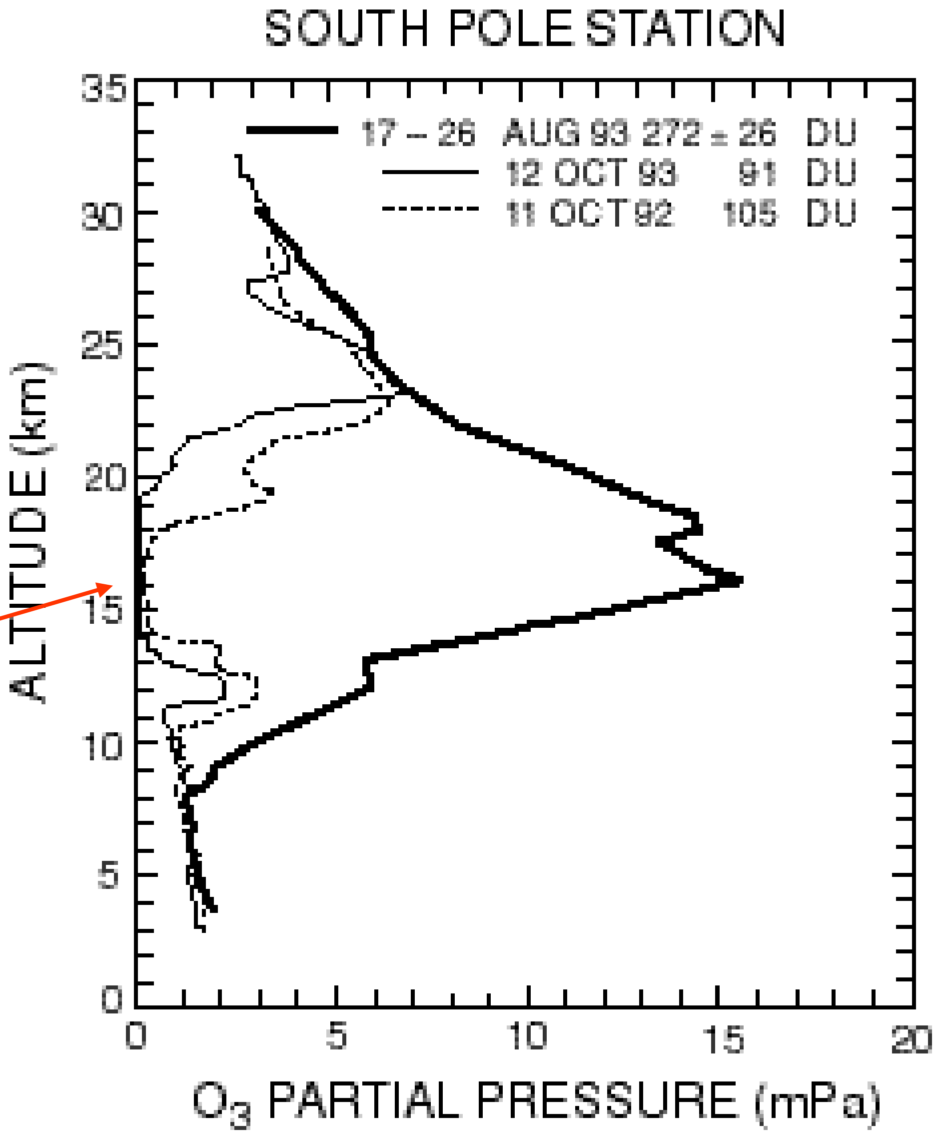
| | | |
|---|---|---|
| $Br + O_3 \rightarrow BrO + O_2$ | | $Br + O_3 \rightarrow BrO + O_2$ |
| $Cl + O_3 \rightarrow ClO + O_2$ | | $Cl + O_3 \rightarrow ClO + O_2$ |
| $ClO + BrO \rightarrow BrCl + O_2$ | or | $ClO + BrO \rightarrow ClOO + Br$ |
| $BrCl + h\nu \rightarrow Cl + Br$ | | $ClOO + M \rightarrow Cl + O_2 + M$ |
| Net: $O_3 + O_3 \rightarrow 3O_2$ | | Net: $O_3 + O_3 \rightarrow 3O_2$ |

Denitrification removes $NO_y$ (and thus $NO_x$), delaying the conversion of Cl and Br to $ClONO_2$ and $BrONO_2$

# Chronology of Antarctic Ozone Hole



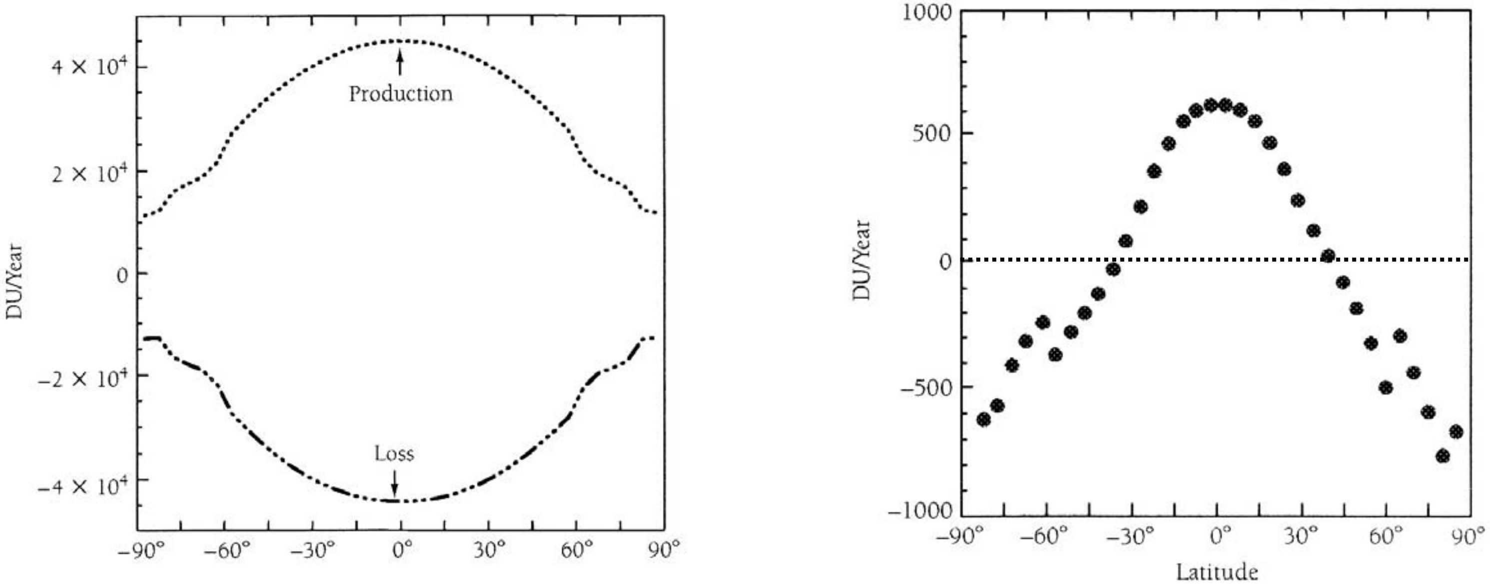
# Vertical Structure of The Ozone Hole



100% ozone loss

# Influence of Transport on Stratospheric $O_3$

**Column $O_3$ P and L from Harvard 2-D model (for equinox)**

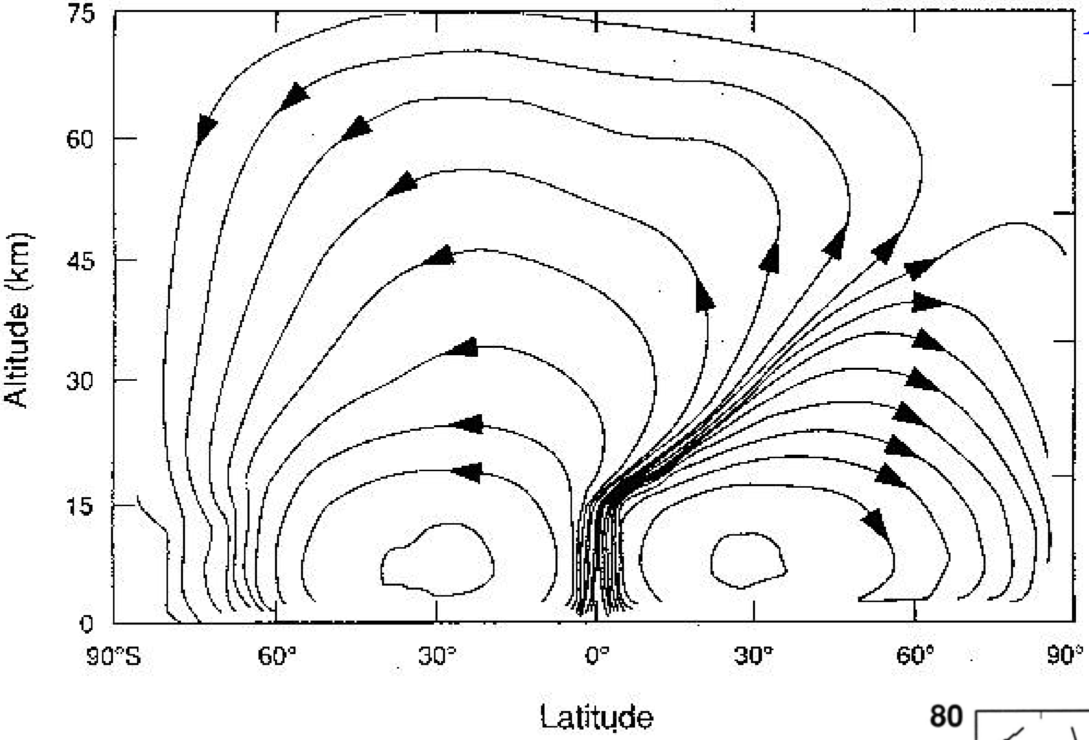


- Net $O_3$ production in tropics
- Net $O_3$ loss in mid- and high-latitudes

**⇒ Net transport of $O_3$ from tropics to high-latitudes**

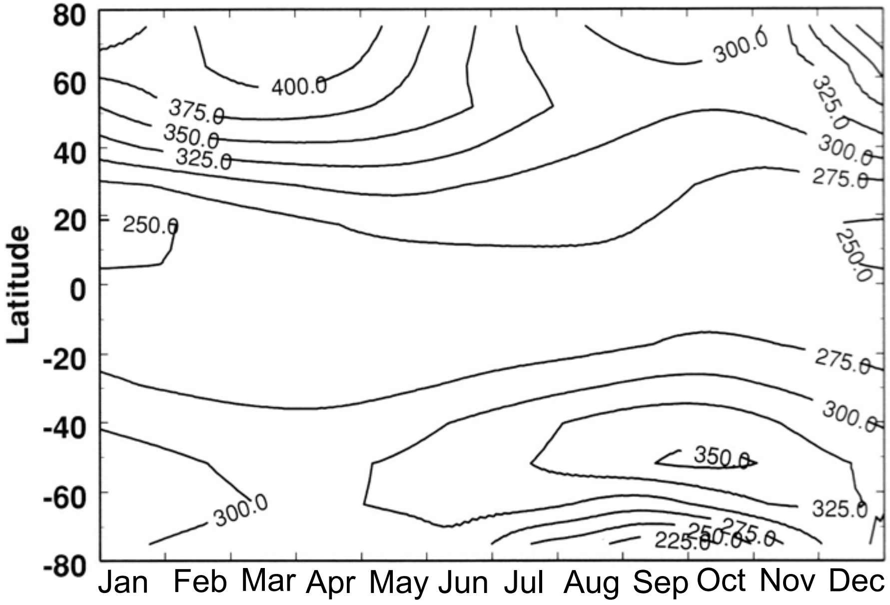
[From M. B. McElroy, 2002]

# Brewer-Dobson Circulation



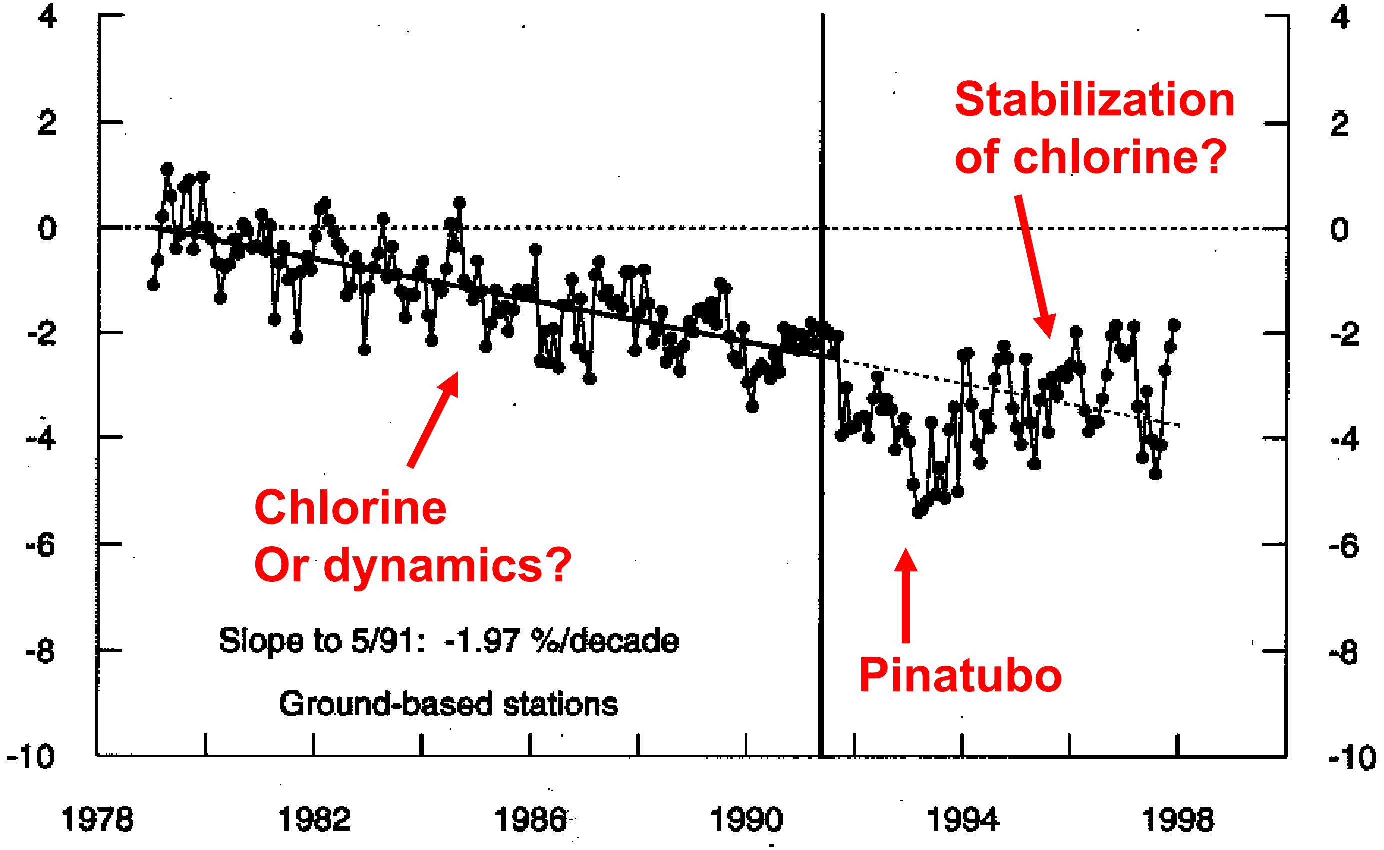
- B-D circulation transports $O_3$ from tropics to mid-high latitudes
- Rising tropospheric air with low ozone ⇒ $O_3$ columns are smallest in tropics despite this being the main stratospheric $O_3$ production region

**TOMS $O_3$ column (1988-1996)**



- $O_3$ maxima occur toward high latitudes in late winter/early spring - the result of the descending branch of the B-D circulation
- Virtually no seasonal change in the tropics

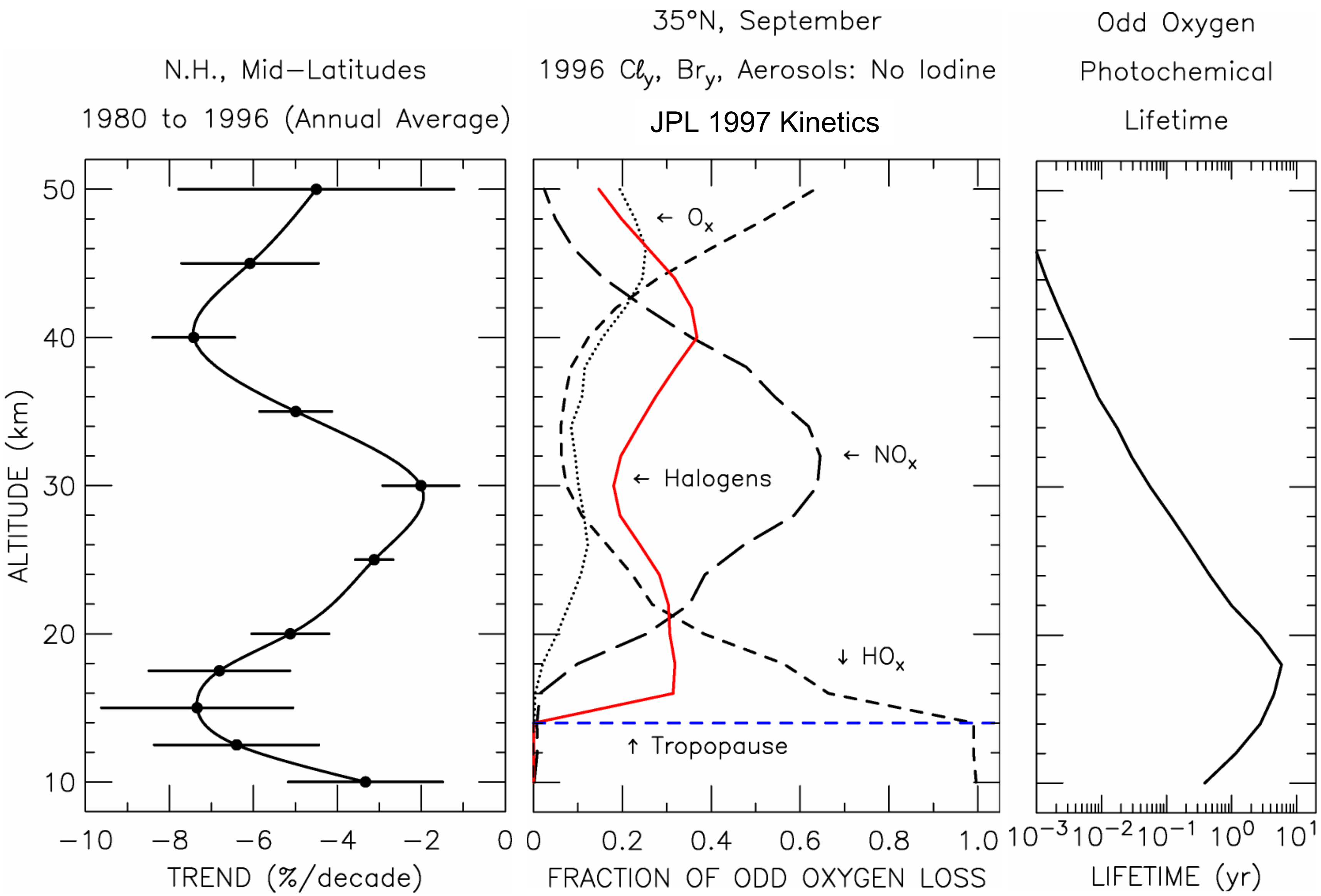
# Ozone Column Trend, 60ºS-60ºN [WMO, 1998]



Stabilization of chlorine?

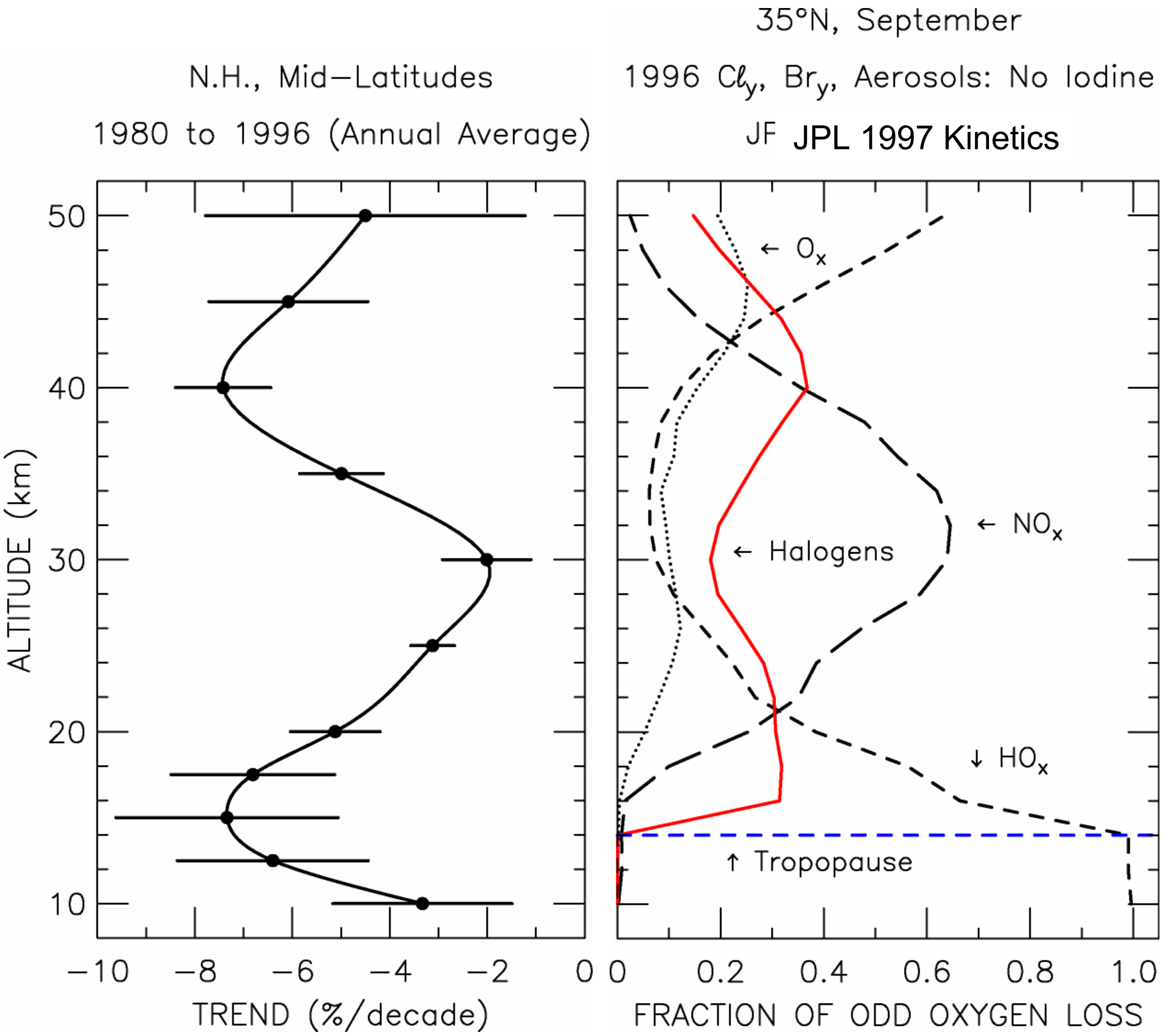
Chlorine Or dynamics?

Pinatubo



Ozone "forcing" and lifetime found using a photochemical model constrained by balloon-borne observations of $O_3$, $Cl_y$, $NO_y$, $H_2O$, $CH_4$, etc (e.g., Osterman *et al., GRL, 24*, 1107, 1997)

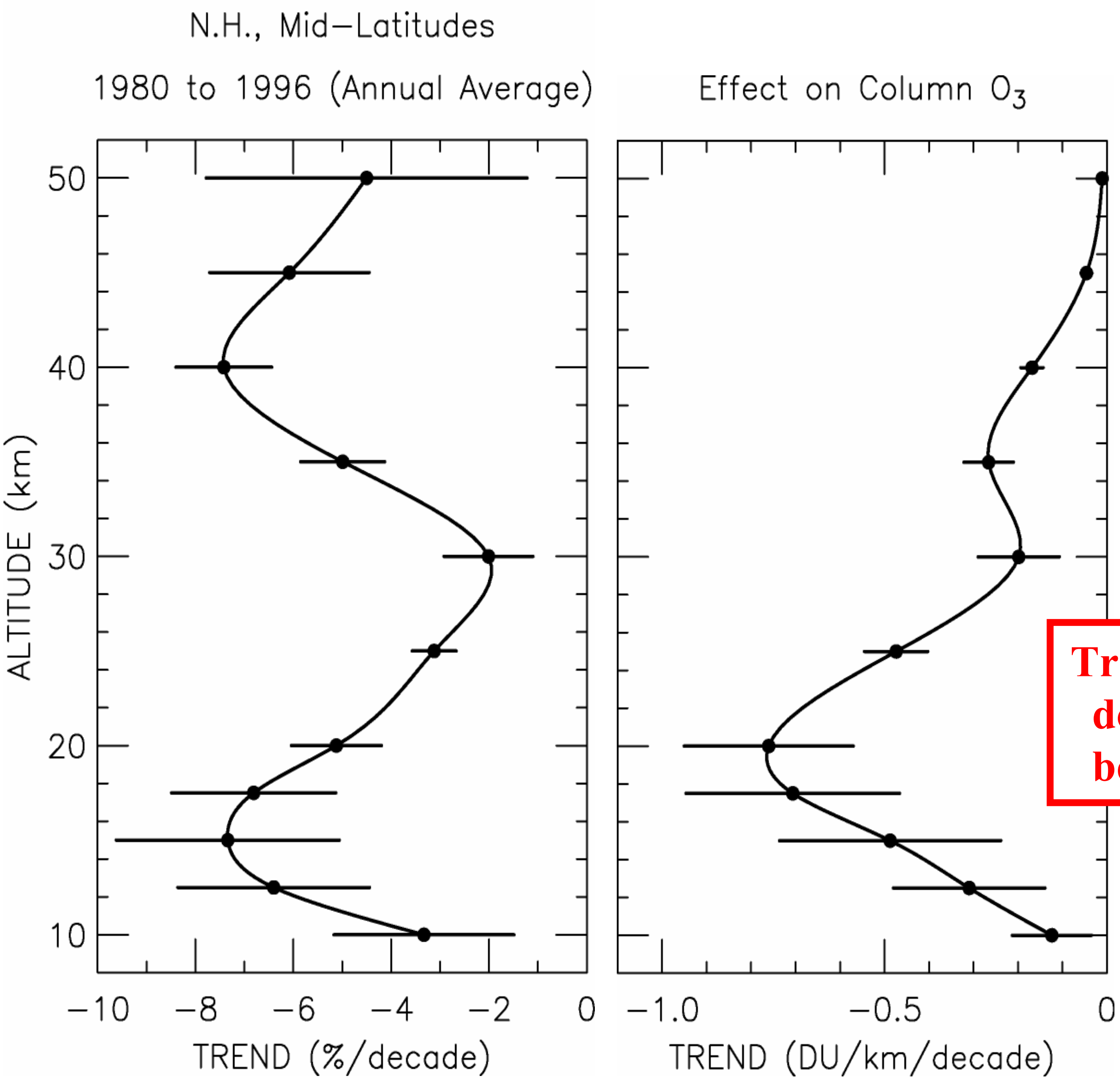
**[courtesy of R. J. Salawitch]**



**Upper Stratospheric Ozone: Newchurch *et al., JGR, 108*, 4507, 2003:**

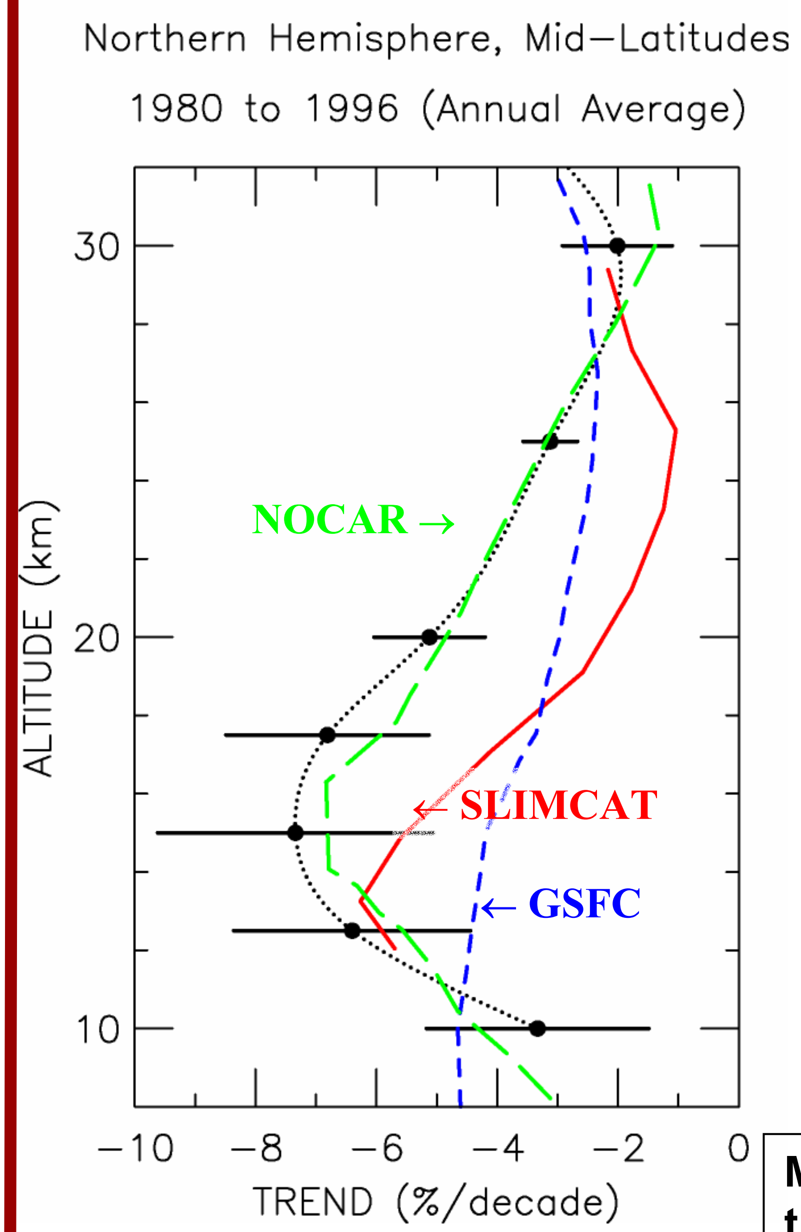
- **Calculated change in trend between 35-45 km from 1997 – 2003**
- **Consistent with slowdown of Cl loading**
- ***"First stage of ozone recovery"***

**[courtesy of R. J. Salawitch]**



**Trend in column ozone dominated by changes below 30 km**

**[courtesy of R. J. Salawitch]**



**Solomon et al. (1998)**

- NCAR/NOAA (NOCAR) 2-D model
  ⇒ climatological transport
- Enhancement in ClO due to longitudinal variations in temperature (wavenumbers 1,2,3)
- JPL 1997 kinetics, sulfate aerosol loading based on satellite obs.

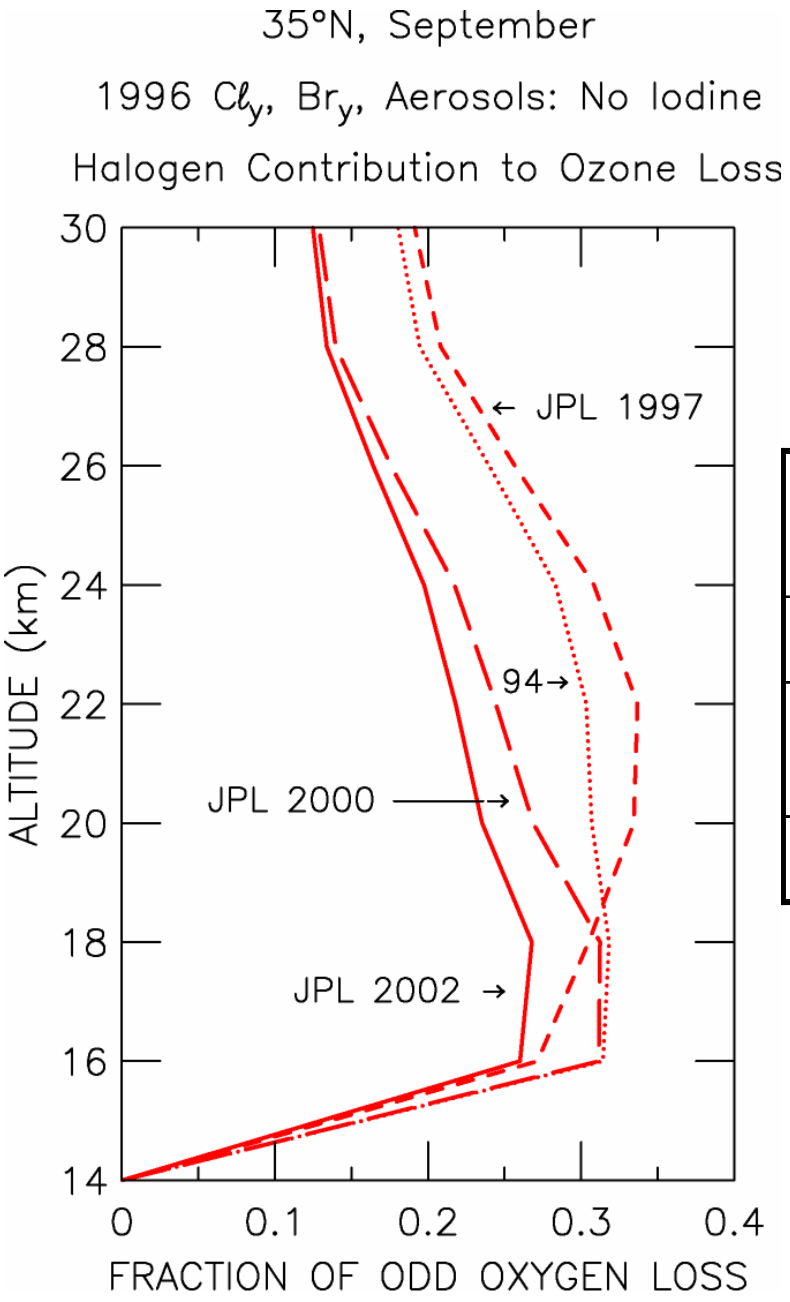
**Jackman et al. (1996)**

- GSFC 2-D model ⇒ climatological transport
- JPL 1997 kinetics, sulfate aerosol loading based on satellite obs.

**Chipperfield, APC, 3, 1253, 2003**

- SLIMCAT: 3-D CTM
- Transport based on ECMWF winds for 1979 to 1992
- JPL 2000 chemistry
- Sulfate aerosol loading based on observations
- Difference in $O_3$ found by comparing two long-term simulations of ozone:
  - one with fixed halogen loading and
  - other with variable halogen loading

**Most models can not fully account for observed trend in lower stratosphere based solely on rising levels of halogens**



# Major Kinetics Changes Affecting Ozone Loss by Halogens

(since JPL 1997 Evaluation)

| | | |
|---|---|---|
| $OH+NO_2+M$ ↓<br>$OH+HNO_3$ ↑ | JPL00 | Halogen Loss ↓ |
| $NO_2+O$ ↑ | JPL00 | Halogen Loss ↓ |
| $ClO+OH \rightarrow HCl$ (~3%) | JPL00 | Halogen Loss ↓ |
| $ClO+HO_2$ ↓ | JPL02 | Halogen Loss ↓ |

**Kinetics changes since JPL 1997 have led to reduced effects of halogens on ozone**

**[courtesy of R. J. Salawitch]**

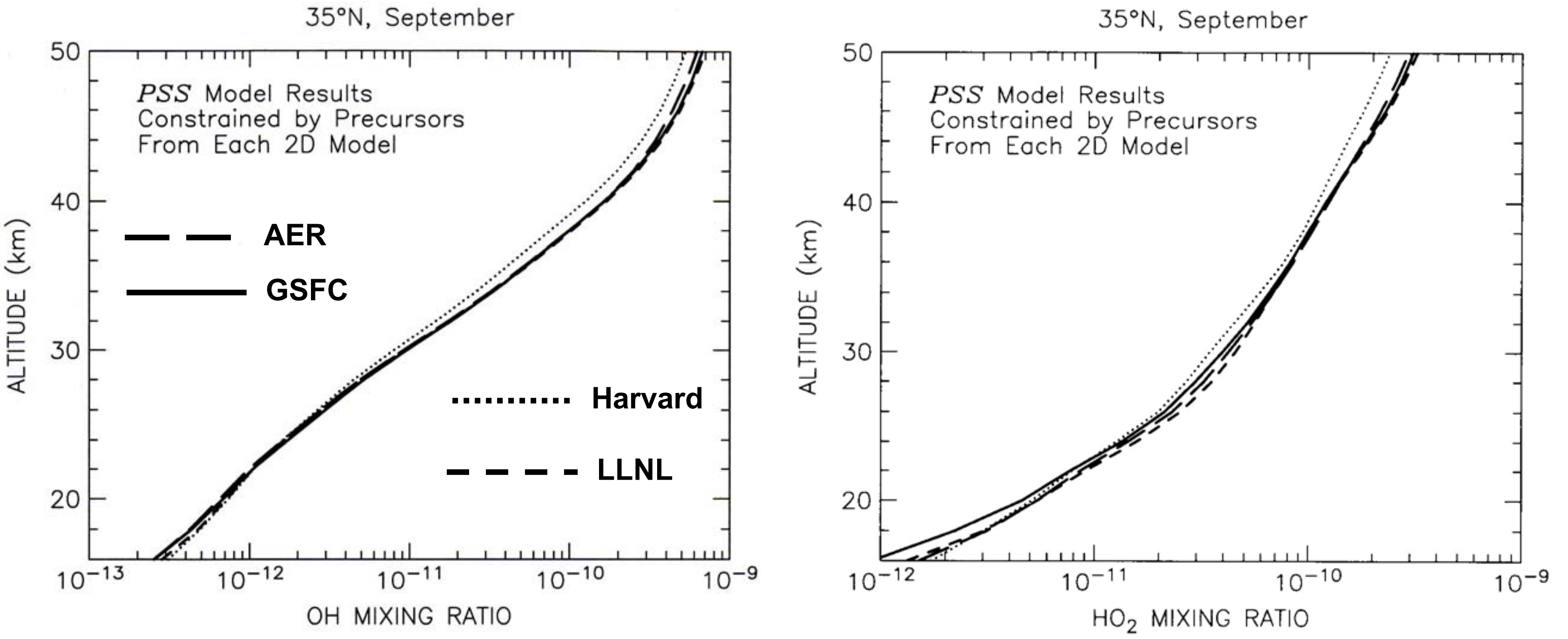
# Reconciling Modelled and Observed Mid-latitude $O_3$ trends

- **Missing source of reactive Cl or Br :**
  **- in most models it is assumed that $Br_y$ is supplied mainly from the decomposition of $CH_3Br$ and Halons. But short lived bromocarbons (e.g. $CHBr_3$, $CH_2Br_2$, $CHBr_2Cl$, $CH_2BrCl$, $CHBrCl_2$) could provided an important source of Br to the stratosphere**

- **Changes in atmospheric dynamics not captured by models**

# Model-Model Intercomparison: Short-lived Species ($HO_x$)

**Testing the chemical mechanism in models: constrain short-lived species in photo-stationary-state box model with long-lived tracers from 2-D model [NASA Models and Measurements Inter. II, 1999]**

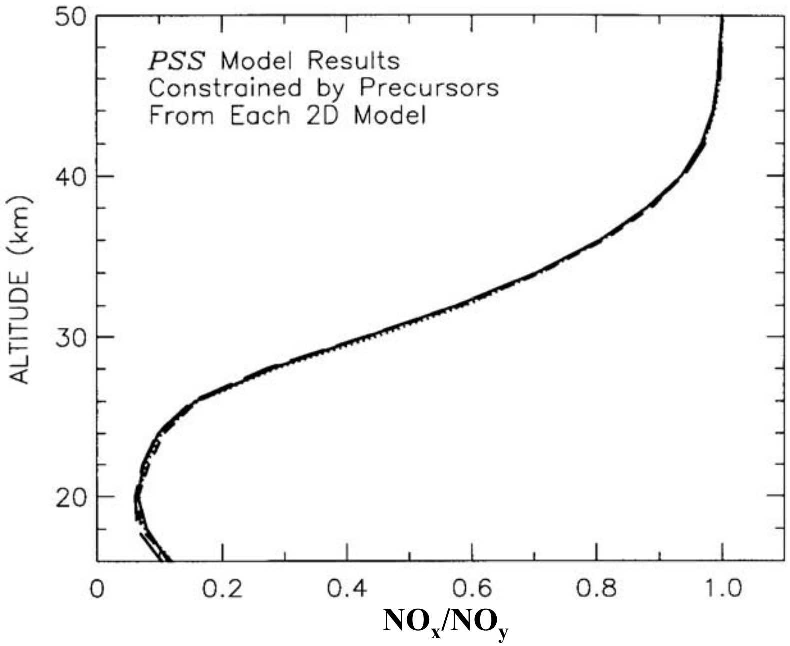


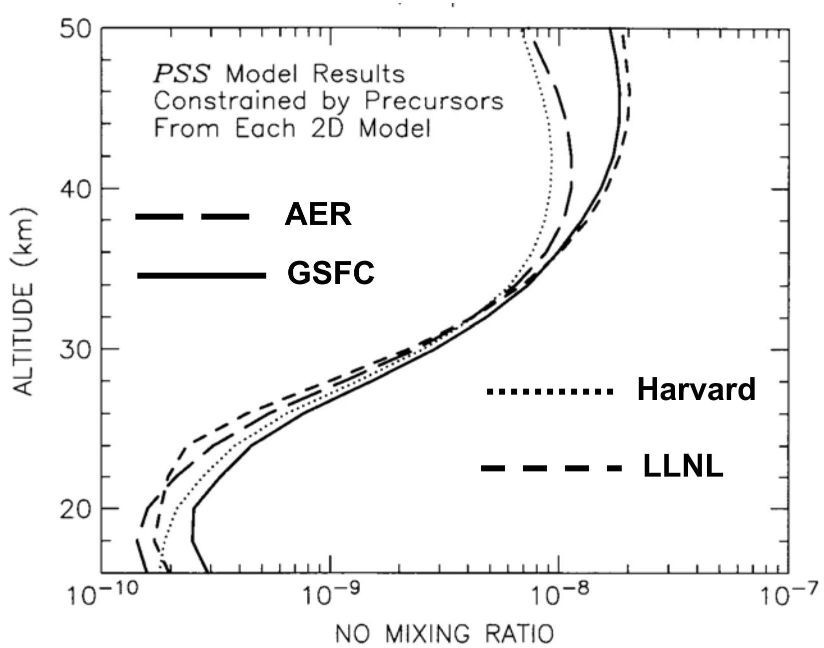
- **PSS model calculated abundances are similar using individual model precursors**
- **Radical concentration calculated by the individual models agree with the PSS calculation (not shown) ⇒ gas phase chemistry consistent between models**

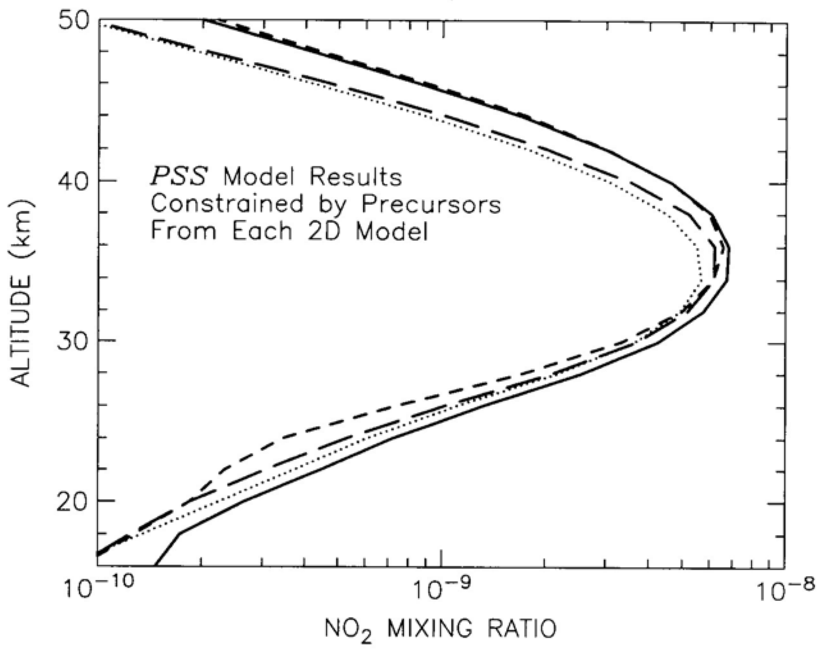
**[courtesy of R. J. Salawitch]**

# $NO_x$ & $NO_y$, 35ºN, September

- $NO_x/NO_y$ ratios are similar
- Differences in $NO_x$ reflect differences in $NO_y$ (most likely due to transport)



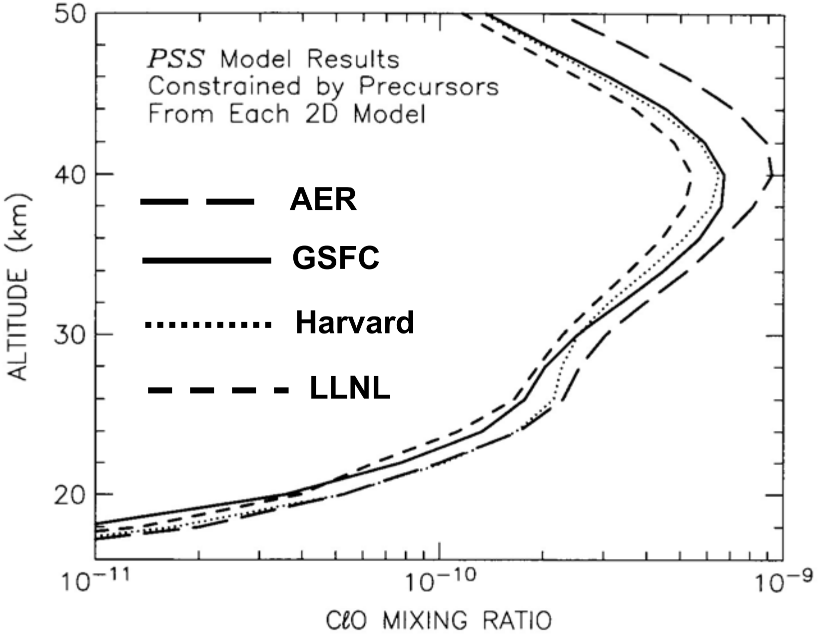


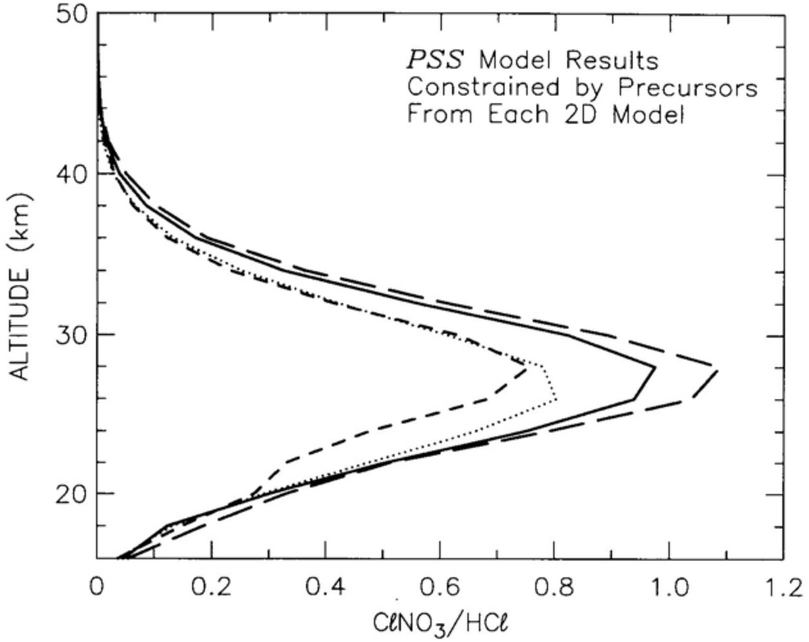


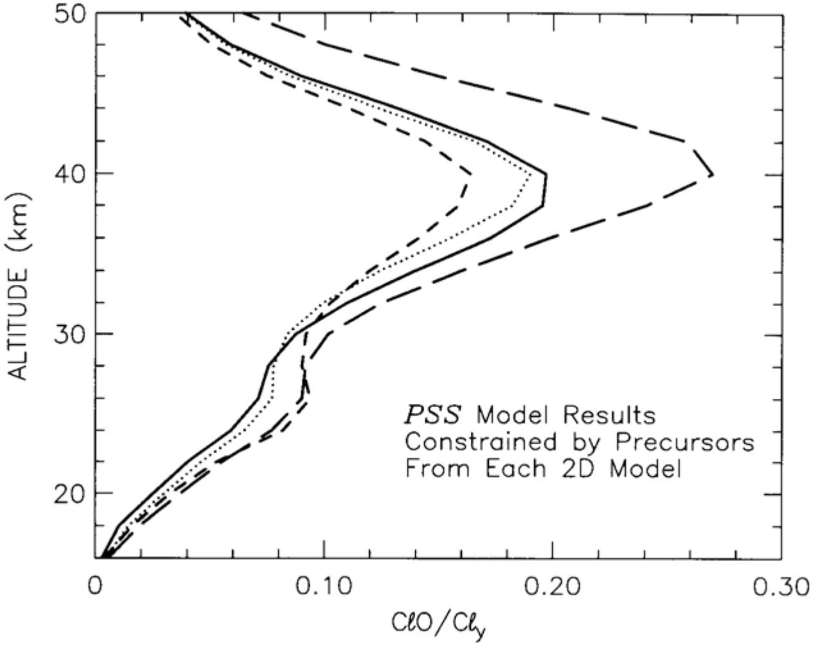
[courtesy of R. J. Salawitch]

# $ClO_x$ & $Cl_y$, 35ºN, September

- Large differences in ClO, reflecting variations in precursors
- Differences in $ClO/Cl_y$ are due in part to differences in $NO_x$



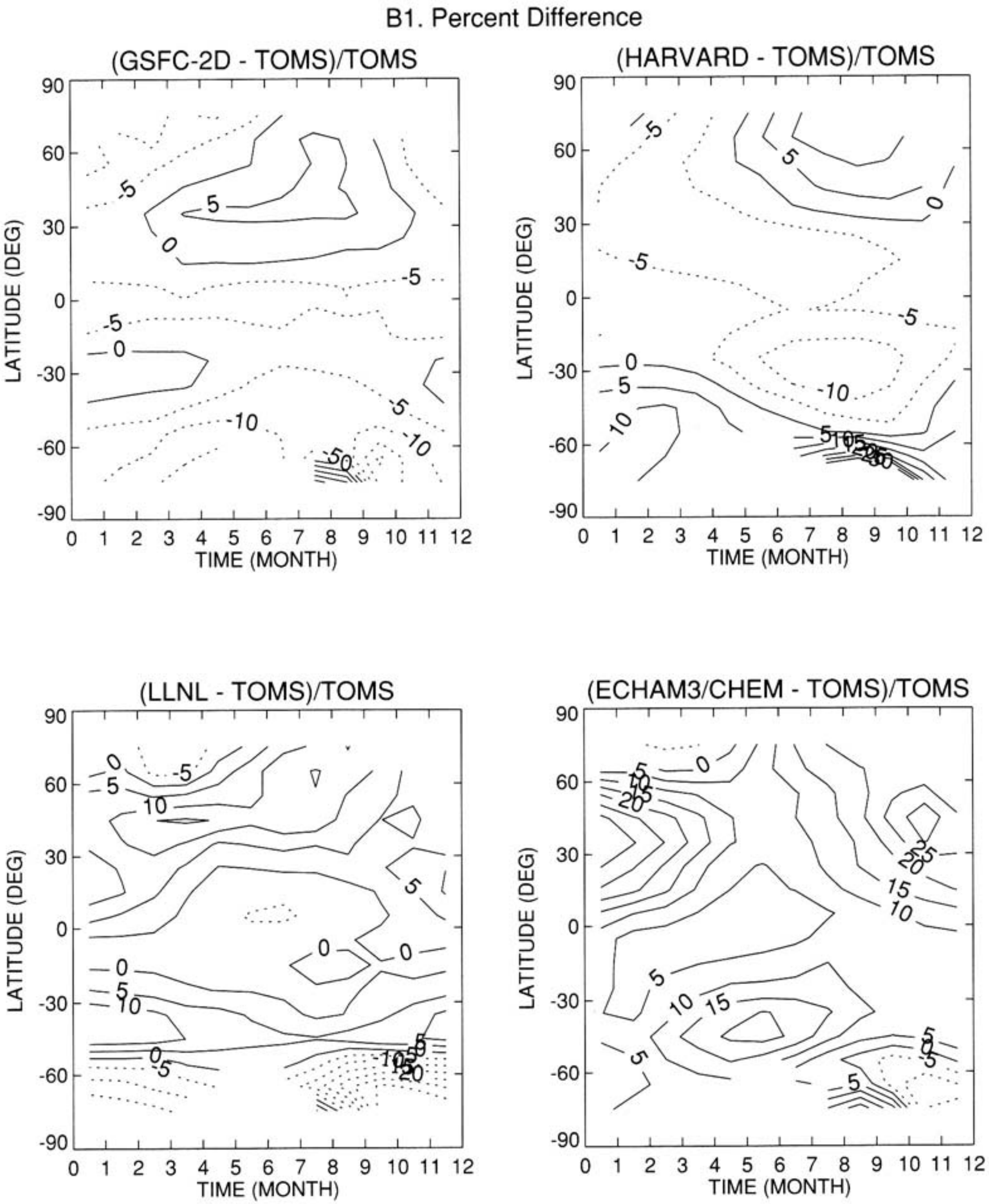




[courtesy of R. J. Salawitch]

# Model & Measurement Intercomparison: $O_3$ Column

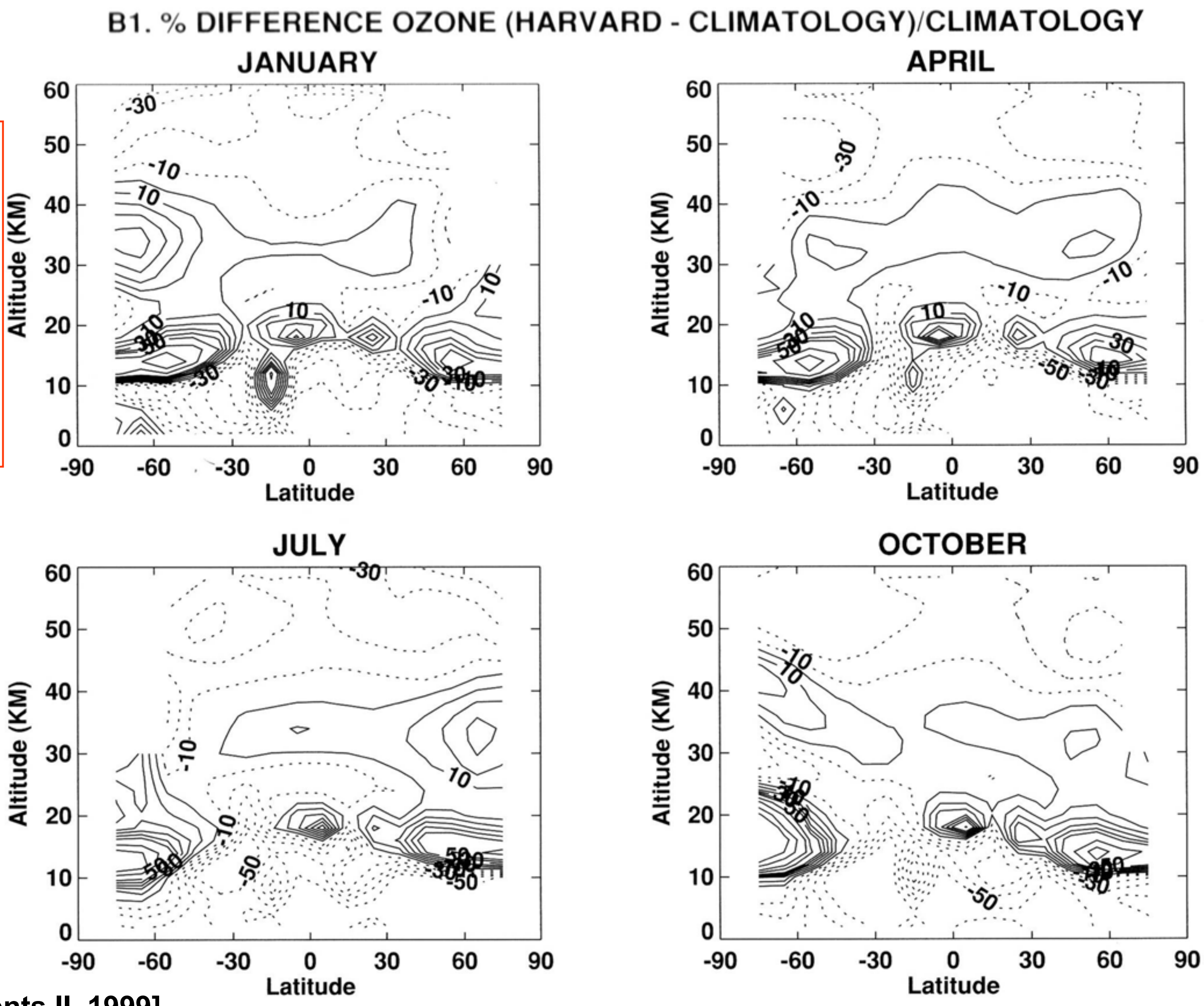
Generally good agreement with observed $O_3$ columns (typically within 10% in mid-latitudes)



[NASA Models and Measurements II, 1999]

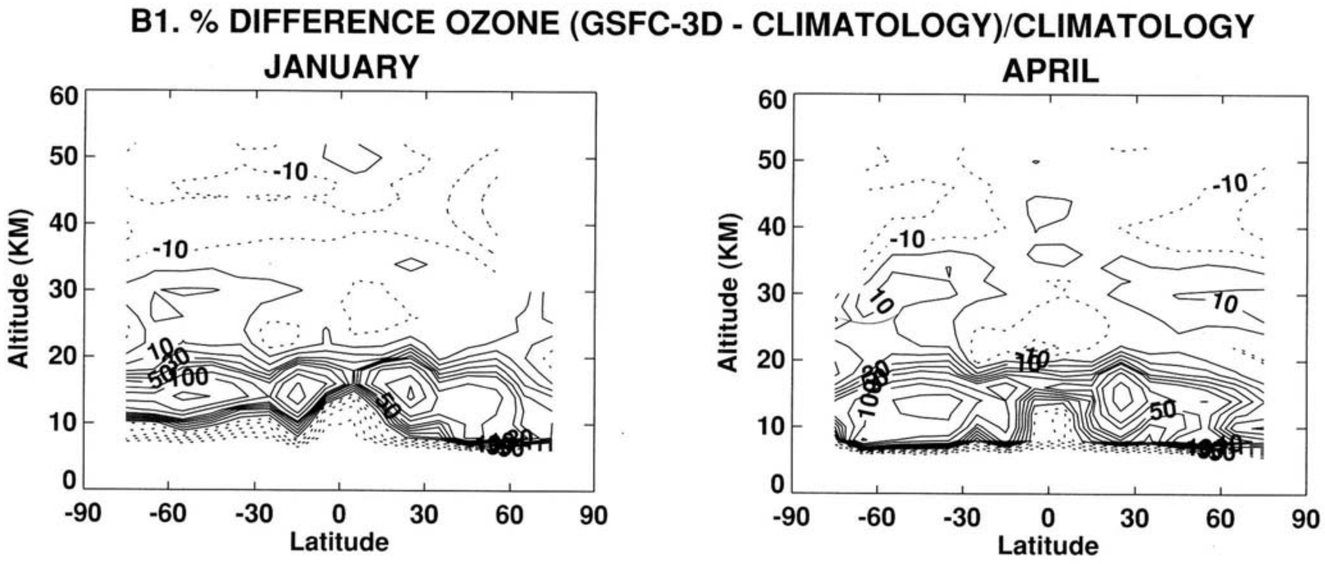
# Model & Measurement Intercomparison: Vertical Distribution

Despite good agreement with observed $O_3$ columns, the Harvard model has large differences (>50%) below 20 km



[NASA Models and Measurements II, 1999]

# Model & Measurement Intercomparison: Vertical Distribution



Fiogure 4.7. Continued.

- **Both 2-D and 3-D models have difficulties in reproducing the $O_3$ distribution in the lower stratosphere**

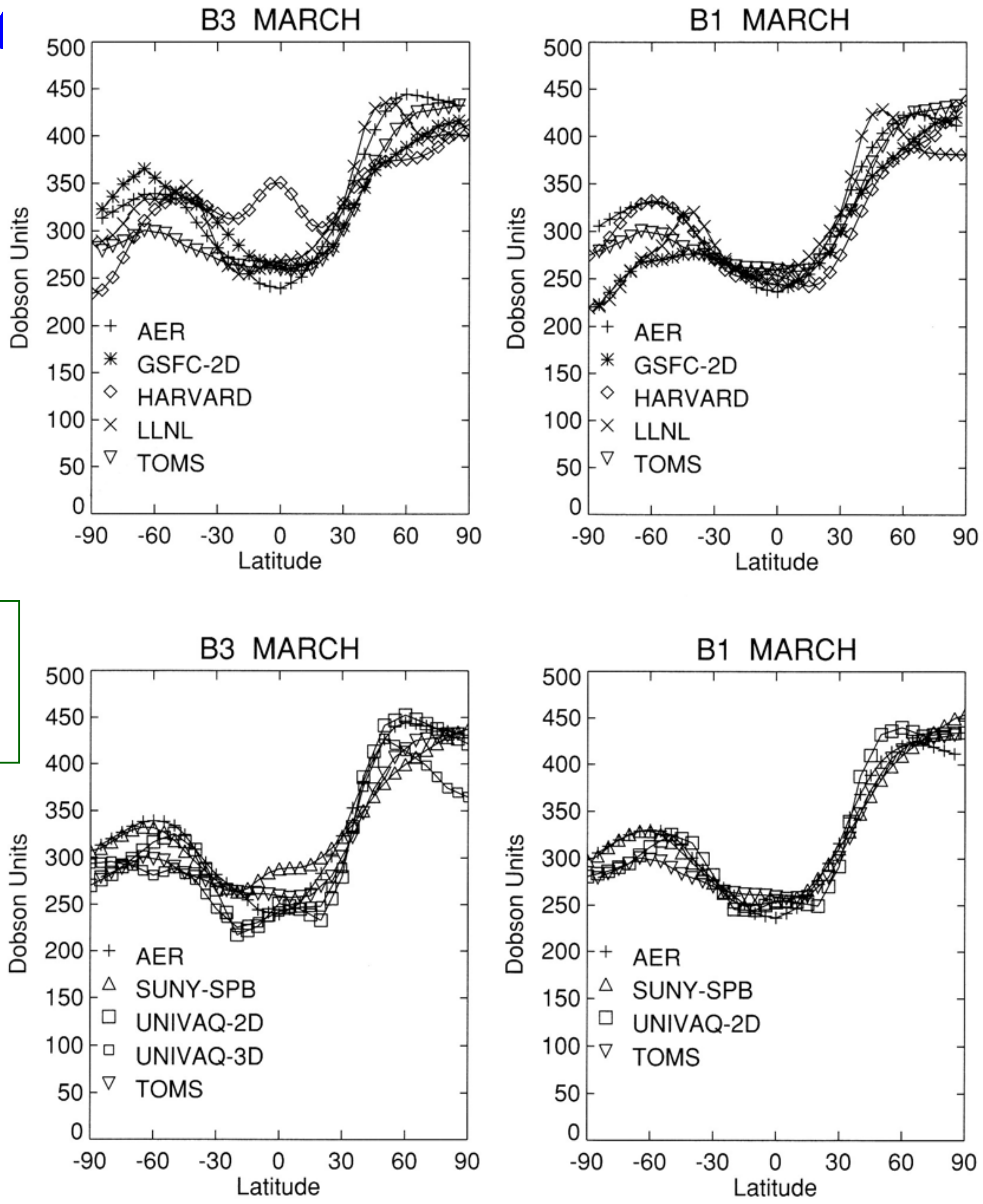
**[NASA Models and Measurements II, 1999]**

# Impact of Model Transport on $O_3$ Column

**Run B1**: specified surface boundary conditions for source gases

**Run B3**: specified O3 production rates and loss frequencies in the models

Isolates variations in $O_3$ column due to transport differences in the models

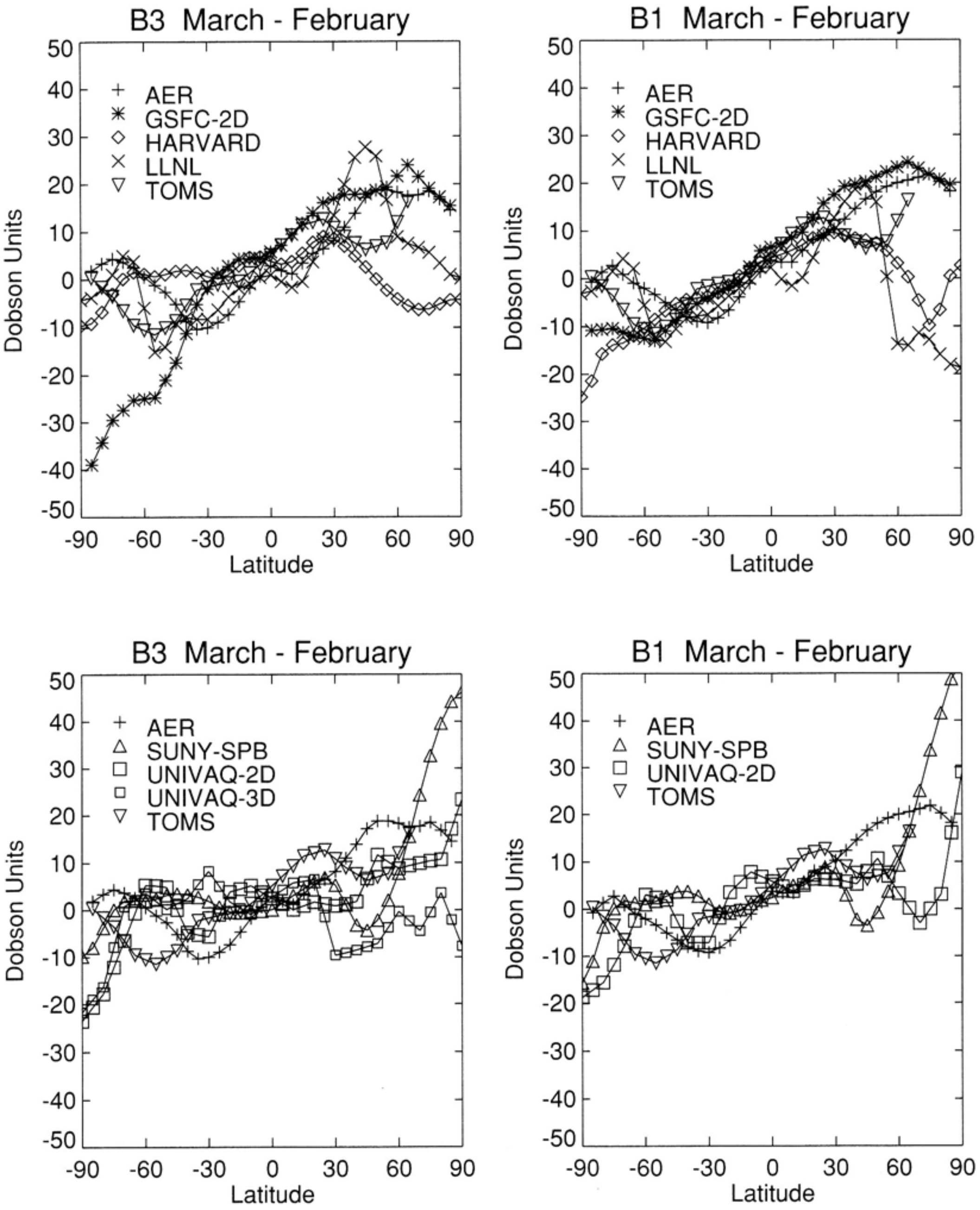


[NASA Models and Measurements II, 1999]

# Changes in $O_3$ Column from Mar.-Feb.

**Run B1**: specified surface boundary conditions for source gases

**Run B3**: specified O3 production rates and loss frequencies in the models



Modelled $O_3$ columns with constrained chemistry are similar to those calculated with individual model chemistry

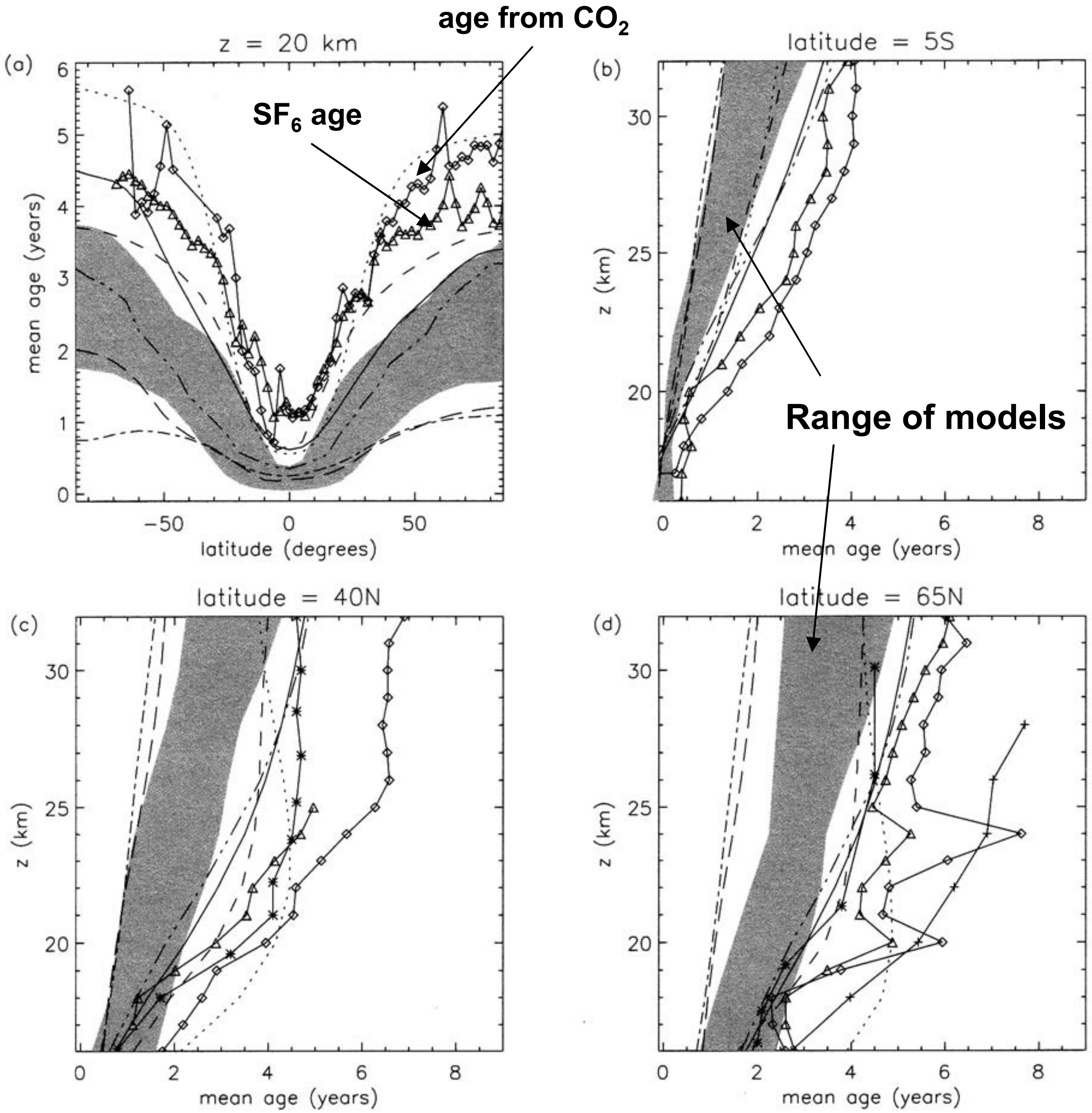
⇒ variations between models are driven mainly by transport differences

[NASA Models and Measurements II, 1999]

# Mean age of air in the Stratosphere

**Models significantly underestimate the mean age of air**

**$\Rightarrow$ will result in errors in the distribution of long-lived tracers e.g. $NO_y$, $Cl_y$, etc…**



[NASA Models and Measurements II, 1999]

# Main Points of Lecture

- The abundance of stratospheric $O_3$ represents a balance between chemistry and transport (especially in the lower stratosphere)
- Radical-catalyzed loss represents the dominant sink for $O_3$ in the lower and middle stratosphere
- Model cannot fully account for observed trend in lower stratosphere based solely on rising levels of halogens
- Differences in transport is the main source of variations in $O_3$ between models
- In 2-D and 3-D models there are significant deficiencies in transport in the lower stratosphere $\Rightarrow$ large errors in modelled $O_3$ in the lower stratosphere