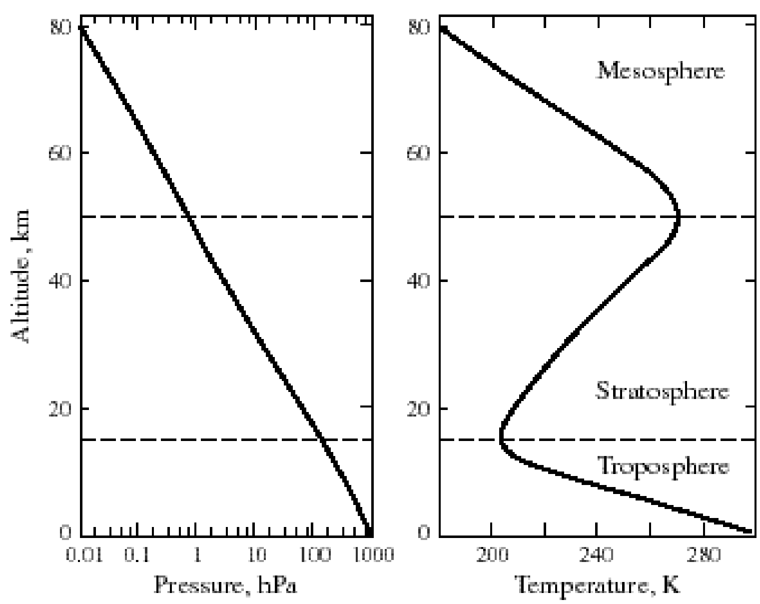
ATMS 558 Apr 13 2008

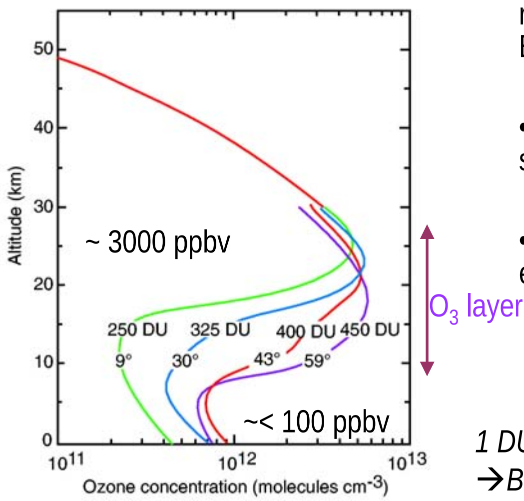
STRATOSPHERIC CHEMISTRY

1. **Stratospheric ozone: distribution**
2. **Chapman mechanism**
3. **Catalytic loss cycles**
   - **Hydrogen oxide radicals (HO_x)**
   - **Nitrogen oxide radicals (NO_x)**
   - **Chlorine oxide and bromine oxide radicals (ClO_x, BrO_x)**
4. **Polar ozone loss**
5. **Role of aerosol chemistry in the stratosphere**

The stratosphere



Stratospheric ozone



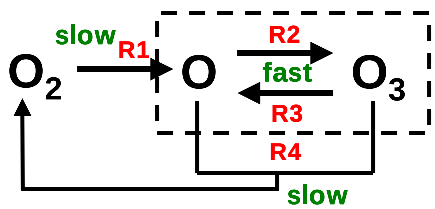
- Protective shield reducing UV radiation (230-320 nm) reaching Earth's surface
- Vertical profile of temperature in stratosphere
- Vulnerable to anthropogenic emissions

1 DU = 2.6 x 10^{16} molecules O_3 cm^{-2}
→Bring all ozone to the ground (0°C 1 atm) 300 DU = 3 mm thick layer

Wallace & Hobbs

The Chapman mechanism

[R1] $O_2 + h\nu \rightarrow 2\,O$ $\lambda < 240$ nm
[R2] $O + O_2 + M \rightarrow O_3 + M$
[R3] $O_3 + h\nu \rightarrow O_2 + O$ $\lambda < 310$ nm
[R4] $O + O_3 \rightarrow 2O_2$



Odd oxygen *family*
$O_x = O + O_3$

Steady state solution

Chemical steady-state assumed for species if production and loss rate constant over lifetime

Shortest-lived species:

$\tau_O = [O] / k_2[O][O_2][M] = 1 / k_2[O_2][M] \cong$ secs

→ Steady-state valid (& neglecting slow R1 and R4) for [O] between R3 and R2

$[O]/[O_3] = k_3/ k_2[M][O_2]$

$[O]/[O_3] << 1$

$[O_x] = [O] + [O_3] \cong [O_3]$

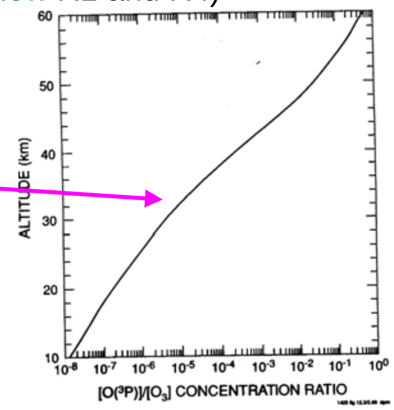
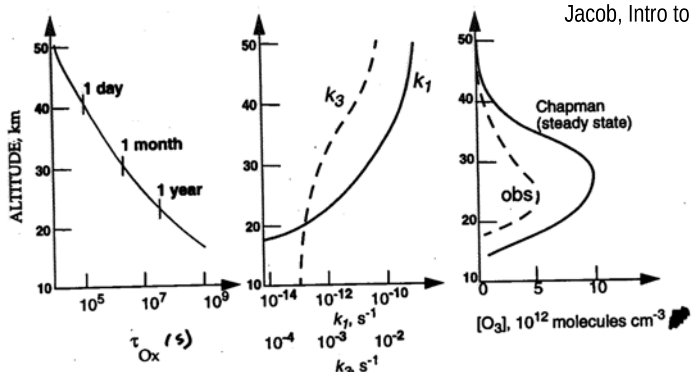


Figure 14.6. Calculated daytime ratio of the concentration of $[O(^3P)]$ to $[O_3]$ in the stratosphere.

Jacob, Intro to Atmospheric Chemistry



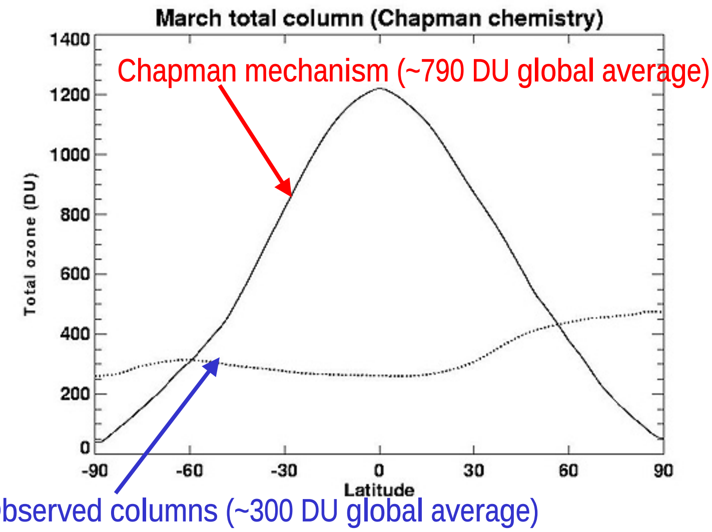
- $[O_3]$ controlled by slow reactions R1 and R4
- Effective O_3 lifetime $\cong \tau_{Ox}$:

$$\tau_{Ox} = [O_x]/2k_4[O][O_3] \cong 1/ 2k_4[O]$$

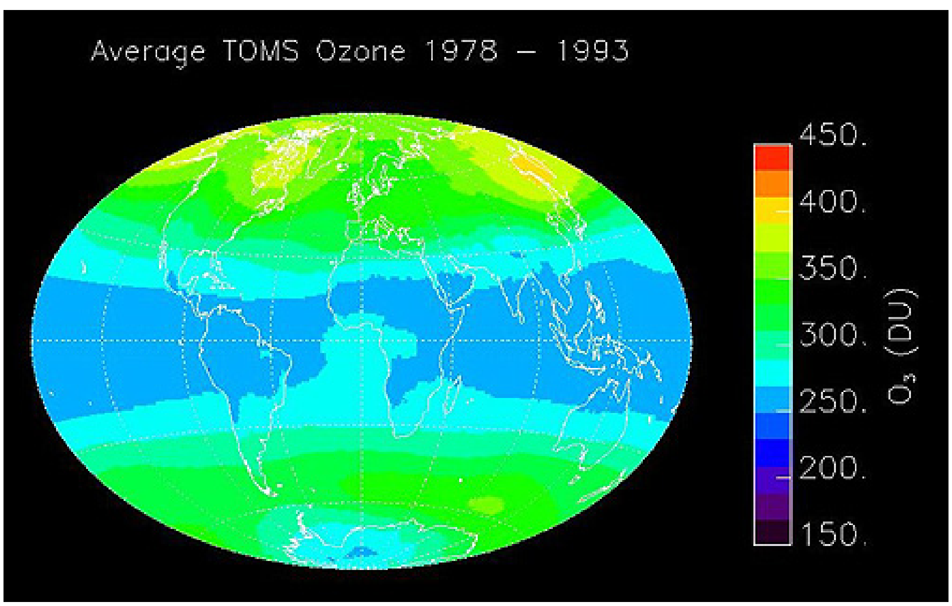
• In upper stratosphere τ_{Ox} short enough steady-state can be assumed: $2k_1[O_2] = 2k_4[O][O_3]$

$$\therefore [O_3] = (k_1k_2/k_3k_4)^{1/2} C_{O2} n_a^{3/2}$$

Latitudinal morphology of ozone columns (March)



What's missing from the Chapman mechanism?

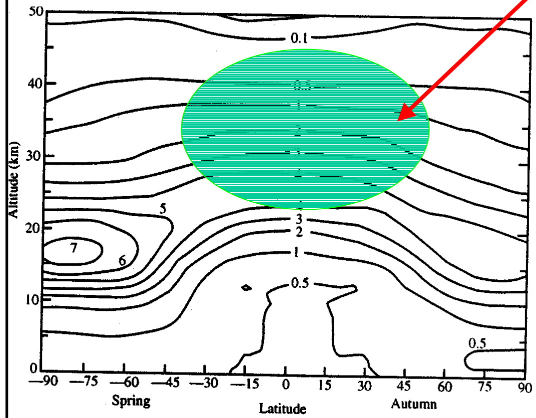


Average ozone column (Dobson units)

Vertical and latitudinal distribution of ozone

Figure is compilation of available measurements from 1960s

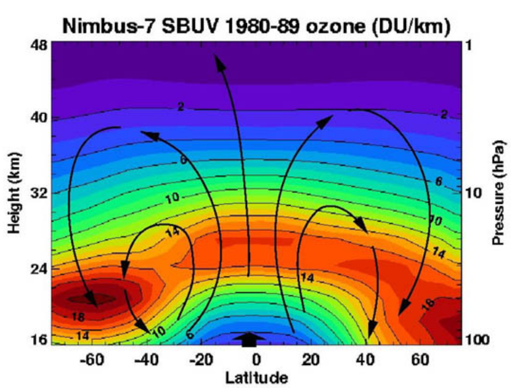
Region of largest production



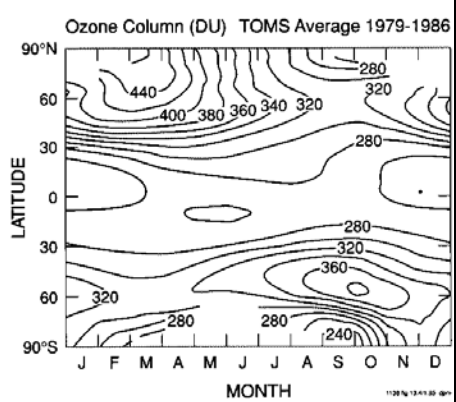
Ozone concentration (10^{12} molecules cm^{-3})

- **Theory predict maximum O_3 production in the tropics**
- **But $[O_3]$ is not largest in the tropics**
- **To explain this (and low strat. H_2O) Brewer and Dobson suggested a circulation pattern**

Brewer-Dobson circulation



- Rising tropospheric air with low ozone
- B-D circulation transports O_3 from tropics to mid-high latitudes



- O_3 max occur at high latitudes in late winter/early spring ← descending branch of the B-D circulation
- Virtually no seasonal change in the tropics but strong seasonal cycle in extratropics

Catalytic chemical cycles

Altitudes >30 km (need O)

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$\text{Net: } O + O_3 \rightarrow 2O_2$$

Altitudes < 30 km

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O_3 \rightarrow X + 2\,O_2$$
$$\text{Net: } O_3 + O_3 \rightarrow 3O_2$$

Catalysts:

X = OH, NO, Cl, Br

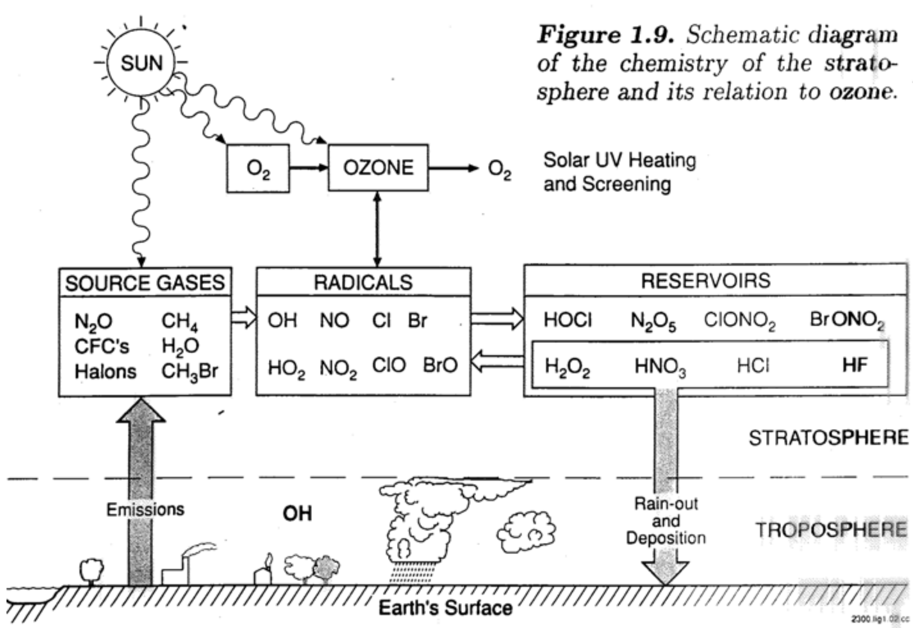


Figure 1.9. *Schematic diagram of the chemistry of the stratosphere and its relation to ozone.*

BOT

Hydrogen oxide (HO_x) radicals ($HO_x = H + OH + HO_2$)

Source from troposphere

- Initiation: $H_2O + O(^1D) \rightarrow 2OH$
- Propagation through cycling of HO_x radical family (example):

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O \rightarrow OH + O_2$$

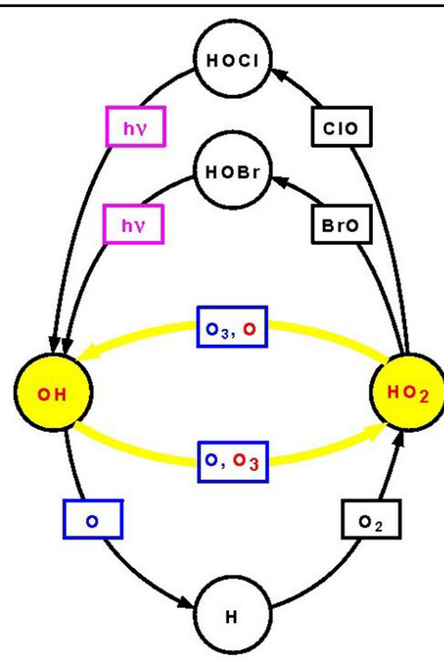
Net: $O_3 + O \rightarrow 2\,O_2$

- Termination (example):

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

HO_x catalytic cycles

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



See Lary, JGR, 102, 21515-21526, 1997.

HOx sources in the stratosphere

$O_3 + h\nu \rightarrow O(^1D) + O_2$

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

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

Small fraction of $O(^1D)$ 1/15,000 (25 km) reacts with H_2O, CH_4, or H_2 to form HO_x:

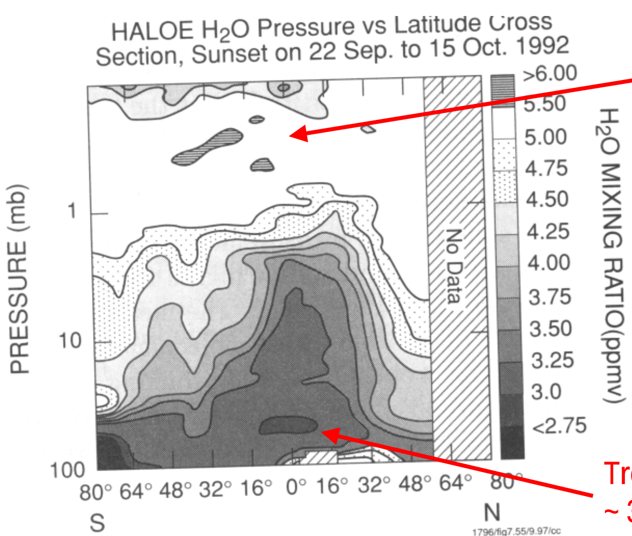
$H_2O + O(^1D) \rightarrow 2OH$

$CH_4 + O(^1D) \rightarrow OH + CH_3$

$H_2 + O(^1D) \rightarrow OH + H$

H_2O ~ 3-6 ppmv; CH_4 ~1-1.5 ppmv; H_2 ~ 0.5 ppmv

Water vapor in the stratosphere



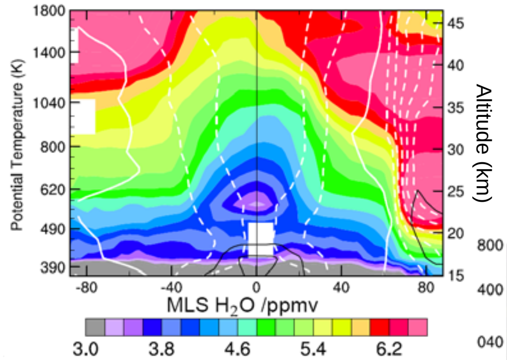
Upper stratosphere ~ 5 ppmv

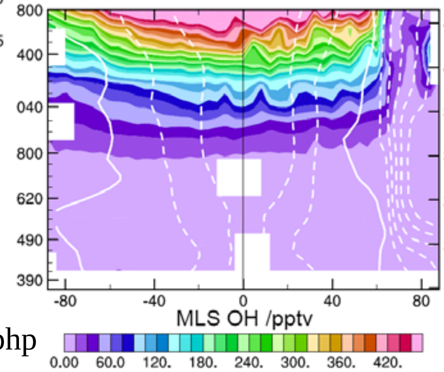
Additional H_2O from CH_4 oxidation: $CH_4 + OH \rightarrow \ldots 2\, H_2O$

Tropical tropopause ~ 3-4 ppmv "freeze-dried" air

BOT, Fig 6.4

Satellite observations of H_2O and OH in the stratosphere





AURA, MLS, Feb 15 2007.
http://mls.jpl.nasa.gov/data/gallery.php

Nitrogen oxide (NO_x)radicals
($NO_x = NO + NO_2$)

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

$NO + O_3 \rightarrow NO_2 + O_2$	$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + h\nu \rightarrow NO + O$	$NO_2 + O \rightarrow NO + O_2$
$O + O_2 + M \rightarrow O_3 + M$	
Null cycle	Net $O_3 + O \rightarrow 2O_2$

O_3 loss rate:

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

- Termination

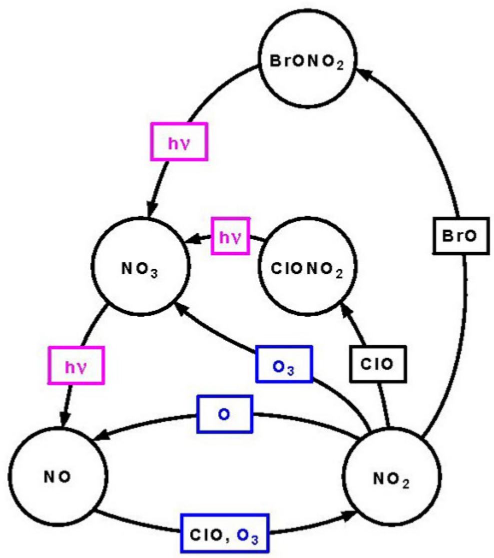
day $NO_2 + OH + M \rightarrow HNO_3 + M$

night:
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$
$N_2O_5 + H_2O \rightarrow 2HNO_3$

Recycling

$HNO_3 + h\nu \rightarrow NO_2 + OH$
$HNO_3 + OH \rightarrow NO_3 + H_2O$
$NO_3 + h\nu \rightarrow NO_2 + O$
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$

NO_x Catalytic cycles



See Lary, JGR, 102, 21515-21526, 1997.

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$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 + M \rightarrow O_3 + M$
Null cycle

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$

Net $O_3 + O \rightarrow 2O_2$

O_3 loss rate:

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

- Termination

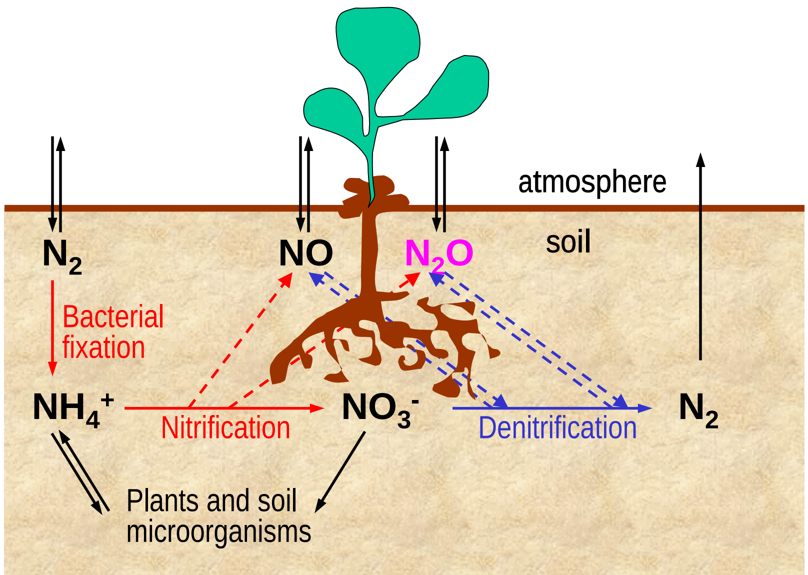
day $NO_2 + OH + M \rightarrow HNO_3 + M$

night:
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$
$N_2O_5 + H_2O \rightarrow 2HNO_3$

Recycling

$HNO_3 + h\nu \rightarrow NO_2 + OH$
$HNO_3 + OH \rightarrow NO_3 + H_2O$
$NO_3 + h\nu \rightarrow NO_2 + O$
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$

Biological source of N_2O in the troposphere



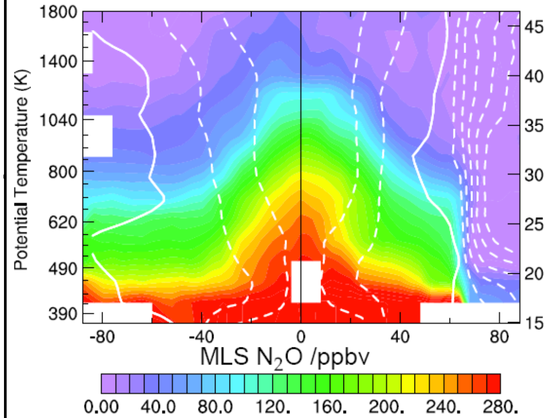
IPCC, 2001

Global budget of N_2O (TgN/yr)

Reference:	Mosier *et al.* (1998b) Kroeze *et al.* (1999)		Olivier *et al.* (1998)	
Base year:	1994	range	1990	range
Sources				
Ocean	3.0	1 – 5	3.6	2.8 – 5.7
Atmosphere (NH_3 oxidation)	0.6	0.3 – 1.2	0.6	0.3 – 1.2
Tropical soils				
Wet forest	3.0	2.2 – 3.7		
Dry savannas	1.0	0.5 – 2.0		
Temperate soils				
Forests	1.0	0.1 – 2.0		
Grasslands	1.0	0.5 – 2.0		
All soils			6.6	3.3 – 9.9
Natural sub-total	9.6	4.6 – 15.9	10.8	6.4 – 16.8
Agricultural soils	4.2	0.6 – 14.8	1.9	0.7 – 4.3
Biomass burning	0.5	0.2 – 1.0	0.5	0.2 – 0.8
Industrial sources	1.3	0.7 – 1.8	0.7	0.2 – 1.1
Cattle and feedlots	2.1	0.6 – 3.1	1.0	0.2 – 2.0
Anthropogenic Sub-total	8.1	2.1 – 20.7	4.1	1.3 – 7.7
Total sources	**17.7**	**6.7 – 36.6**	**14.9**	**7.7 – 24.5**
Imbalance (trend)	3.9	3.1 – 4.7		
Total sinks (stratospheric)	**12.3**	**9 – 16**		
Implied total source	16.2			

N_2O distribution in the stratosphere

(AURA satellite observations – MLS instrument)



Feb 15 2007

http://mls.jpl.nasa.gov/data/gallery.php

$N_2O + h\nu \rightarrow N_2 + O$

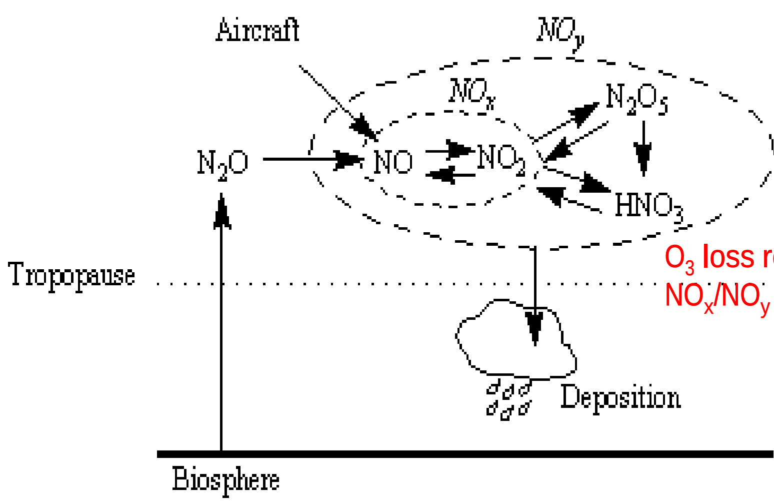
$N_2O + h\nu \rightarrow NO + N$ (minor branch)

$N_2O + O(^1D) \rightarrow N_2 + O_2$

$N_2O + O(^1D) \rightarrow NO + NO$

~ 120 year lifetime

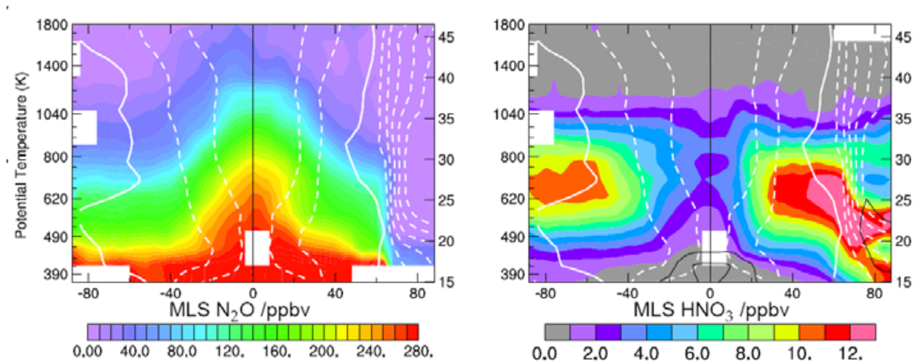
ATMOSPHERIC CYCLING OF NO_x AND NO_y



O_3 loss related to NO_x/NO_y ratio

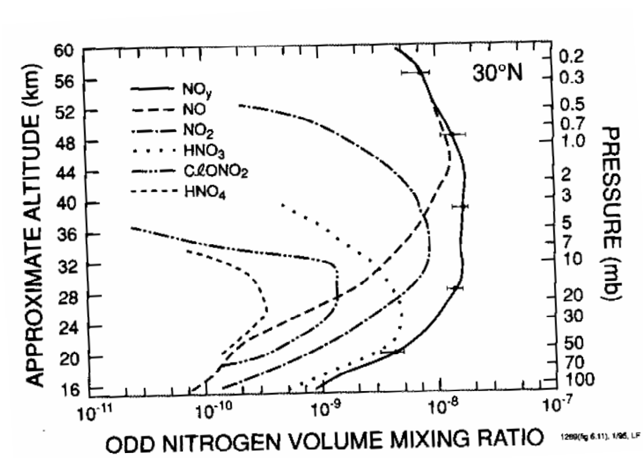
NO_x catalytic cycle reconciled Chapman theory with observations (Paul Crutzen)…1995 Nobel Prize

N_2O and HNO_3 distribution in the stratosphere
(AURA satellite observations – MLS instrument)



Feb 15 2007
http://mls.jpl.nasa.gov/data/gallery.php

Vertical distribution of NOy



BOT, figure 7.6