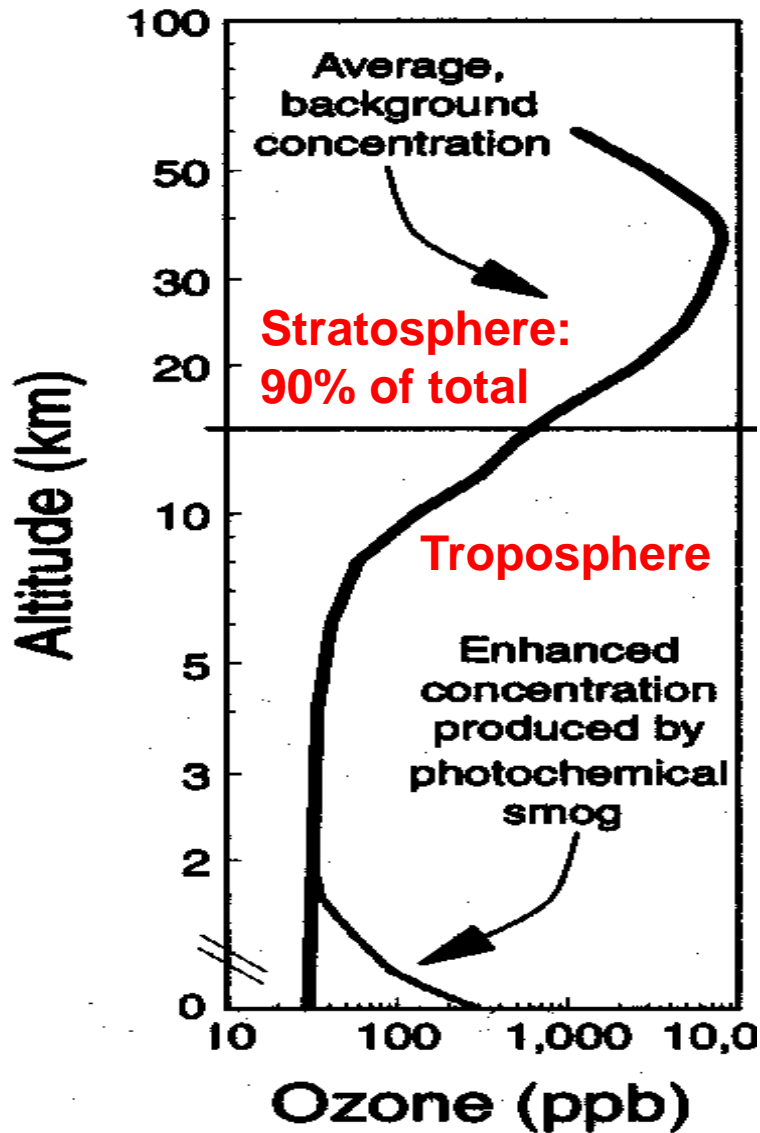


**EPS200: Atmospheric Chemistry and Physics**  
**Daniel J. Jacob, Harvard University**  
**Fall 2013**

**Tropospheric gas-phase chemistry: General**

# TROPOSPHERIC OZONE AND OXIDANT CHEMISTRY

The many faces of atmospheric ozone:



In stratosphere: UV shield

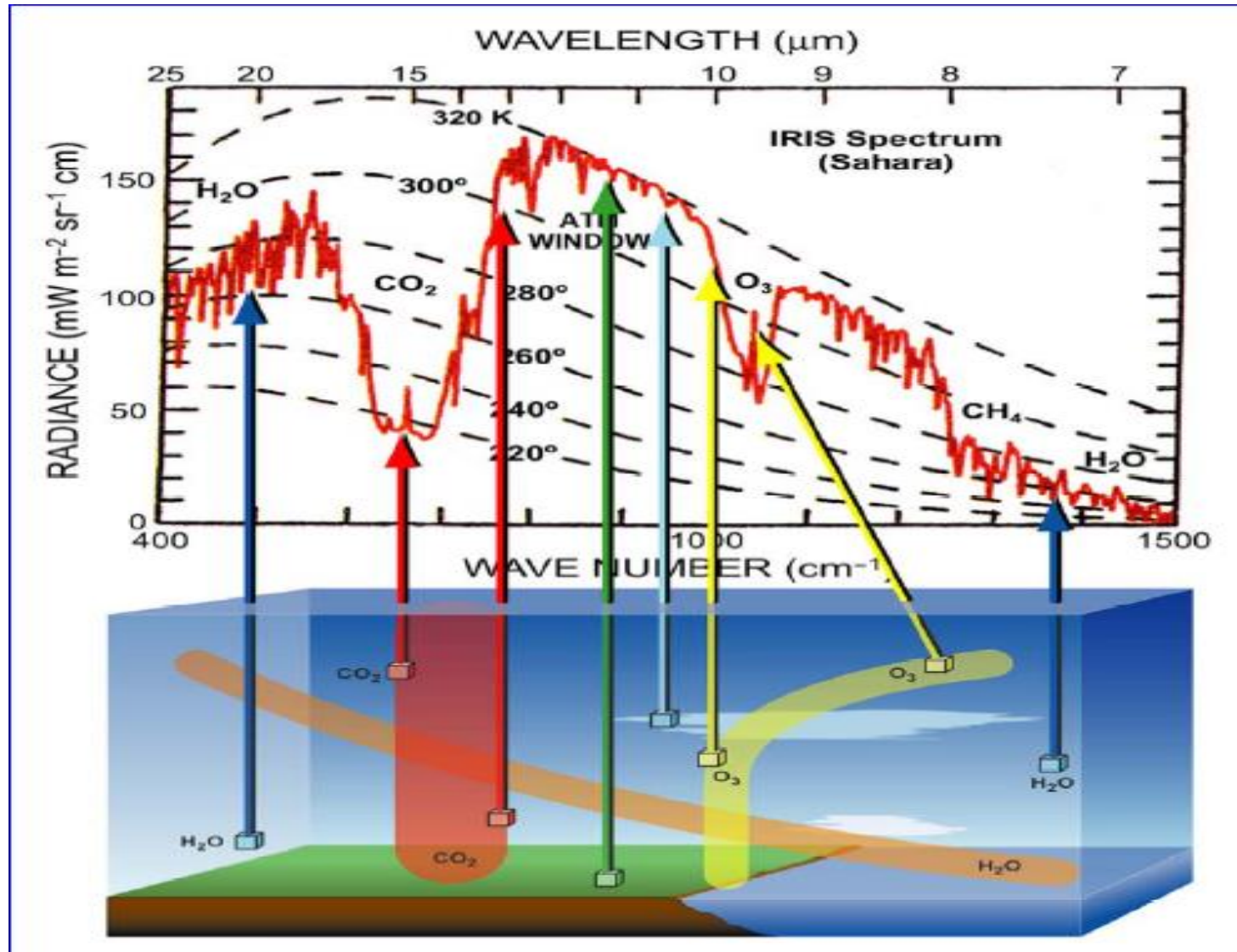
In middle/upper troposphere: greenhouse gas

In lower/middle troposphere: precursor of OH, main atmospheric oxidant

In surface air: toxic to humans and vegetation

# TERRESTRIAL RADIATION SPECTRUM FROM SPACE:

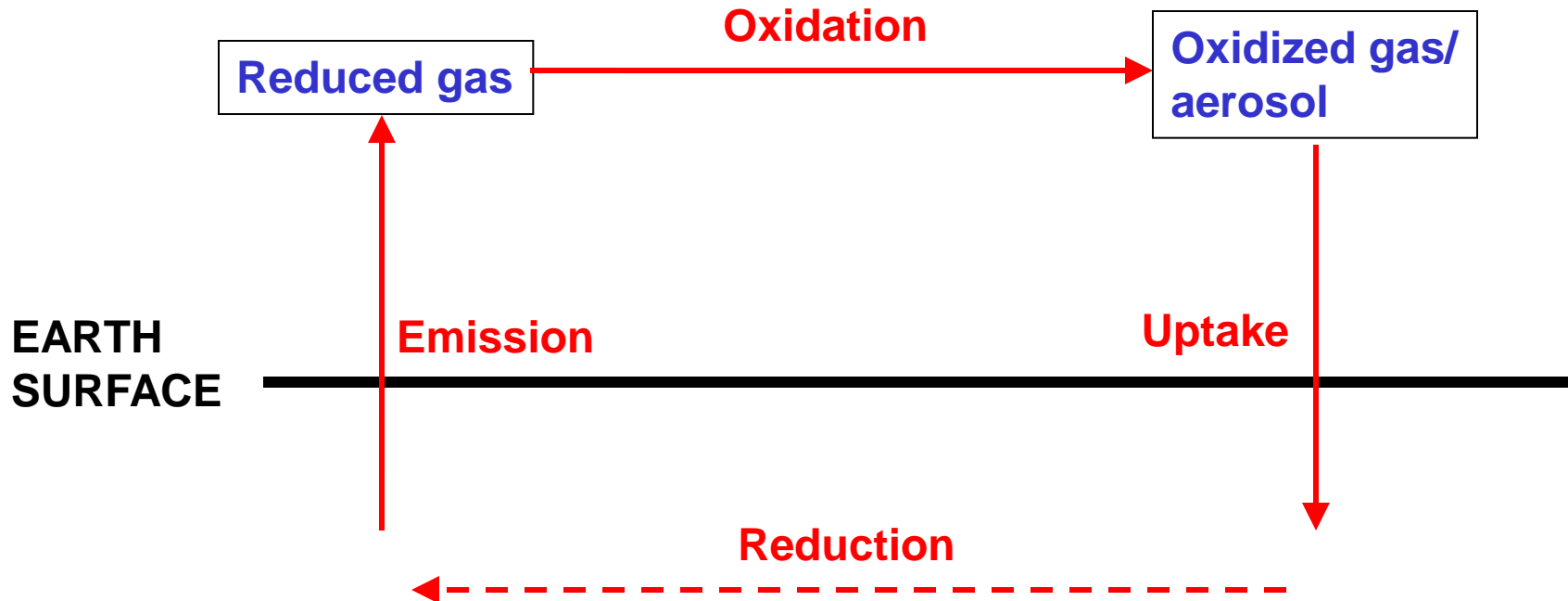
composite of blackbody radiation spectra emitted from different altitudes at different temperatures



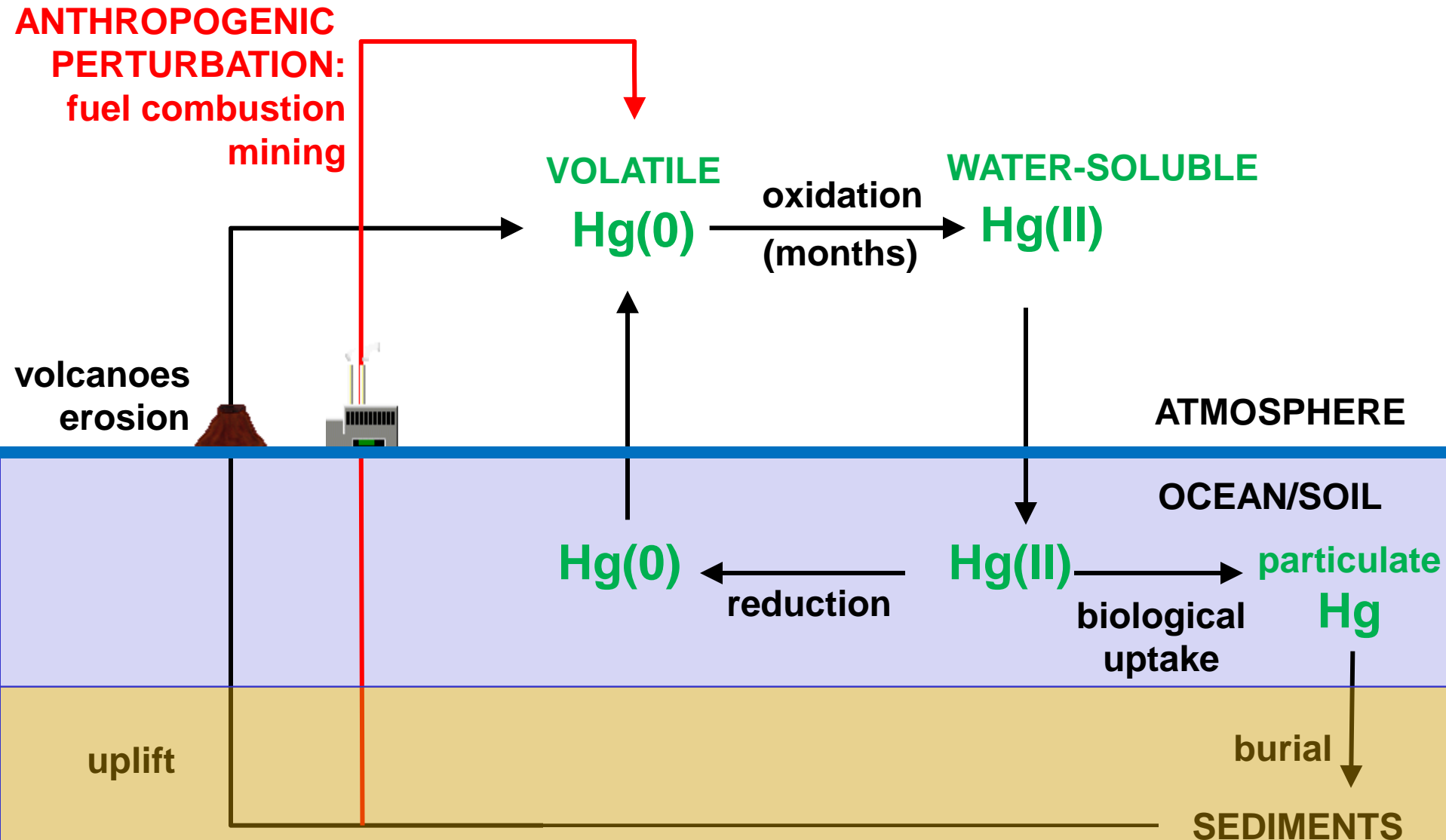
# THE ATMOSPHERE: OXIDIZING MEDIUM IN GLOBAL BIOGEOCHEMICAL CYCLES

Atmospheric oxidation is critical for removal of many pollutants, e.g.

- methane (major greenhouse gas)
- Toxic gases such as CO, benzene, mercury...
- Gases affecting the stratosphere

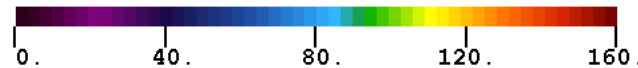
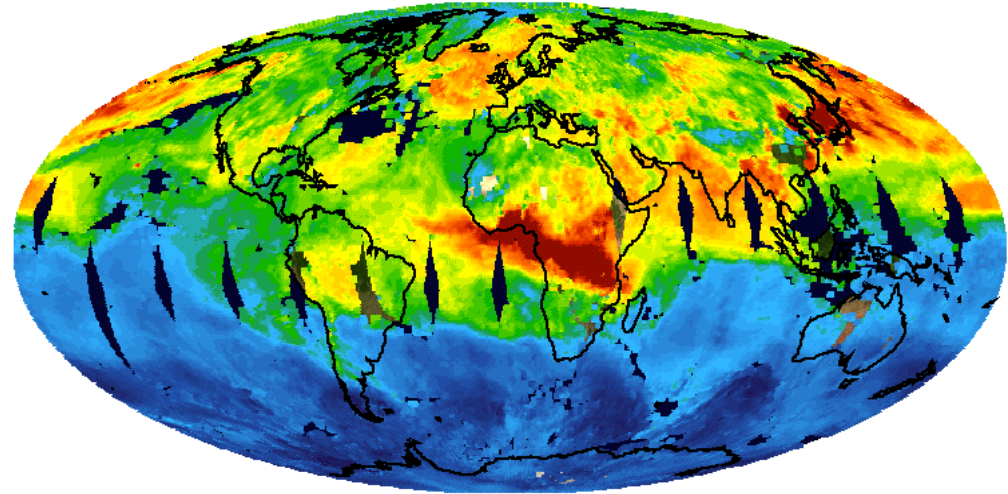


# Example: Biogeochemical cycle of mercury



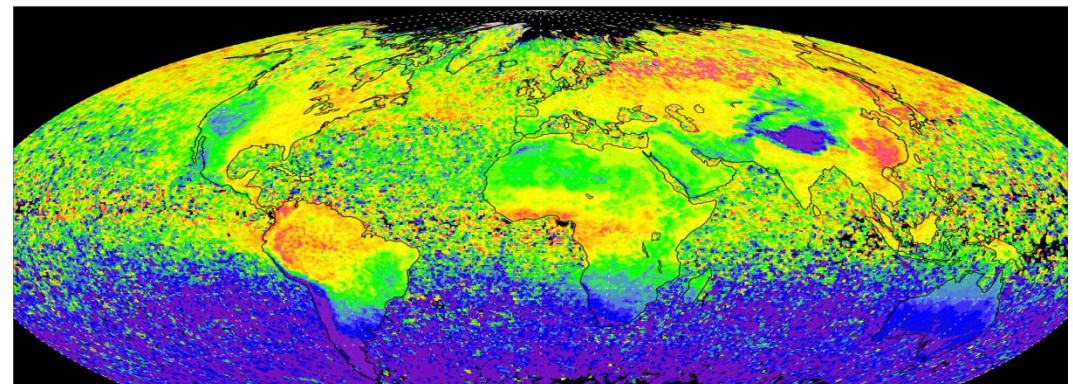
# CO and methane account for most of reduced gas flux to atmosphere

- CO observed from space: 50-200 ppb



- Methane observed from space: 1650-1800 ppb

Methane SCIAMACHY/ENVISAT 2003-2005



CH<sub>4</sub> column-averaged mole fraction [ppb]



# THE TROPOSPHERE WAS VIEWED AS CHEMICALLY INERT UNTIL 1970

- “*The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen...Methane and CO are chemically quite inert in the troposphere*”  
[Cadle and Allen, *Atmospheric Photochemistry, Science, 1970*]
- Lifetime of CO estimated at 2.7 years (removal by soil) leads to concern about global CO pollution from increasing car emissions [Robbins and Robbins, *Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants, SRI report, 1967*]

## FIRST BREAKTHROUGH:

- Measurements of cosmogenic  $^{14}\text{CO}$  place a constraint of  $\sim 0.1$  yr on the tropospheric lifetime of CO [Weinstock, *Science, 1969*]

## SECOND BREAKTHROUGH:

- Tropospheric OH  $\sim 1 \times 10^6 \text{ cm}^{-3}$  predicted from  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$ , results in tropospheric lifetimes of  $\sim 0.1$  yr for CO and  $\sim 2$  yr for  $\text{CH}_4$  [Levy, *J. Geophys. Res. 1973*]

## THIRD BREAKTHROUGH:

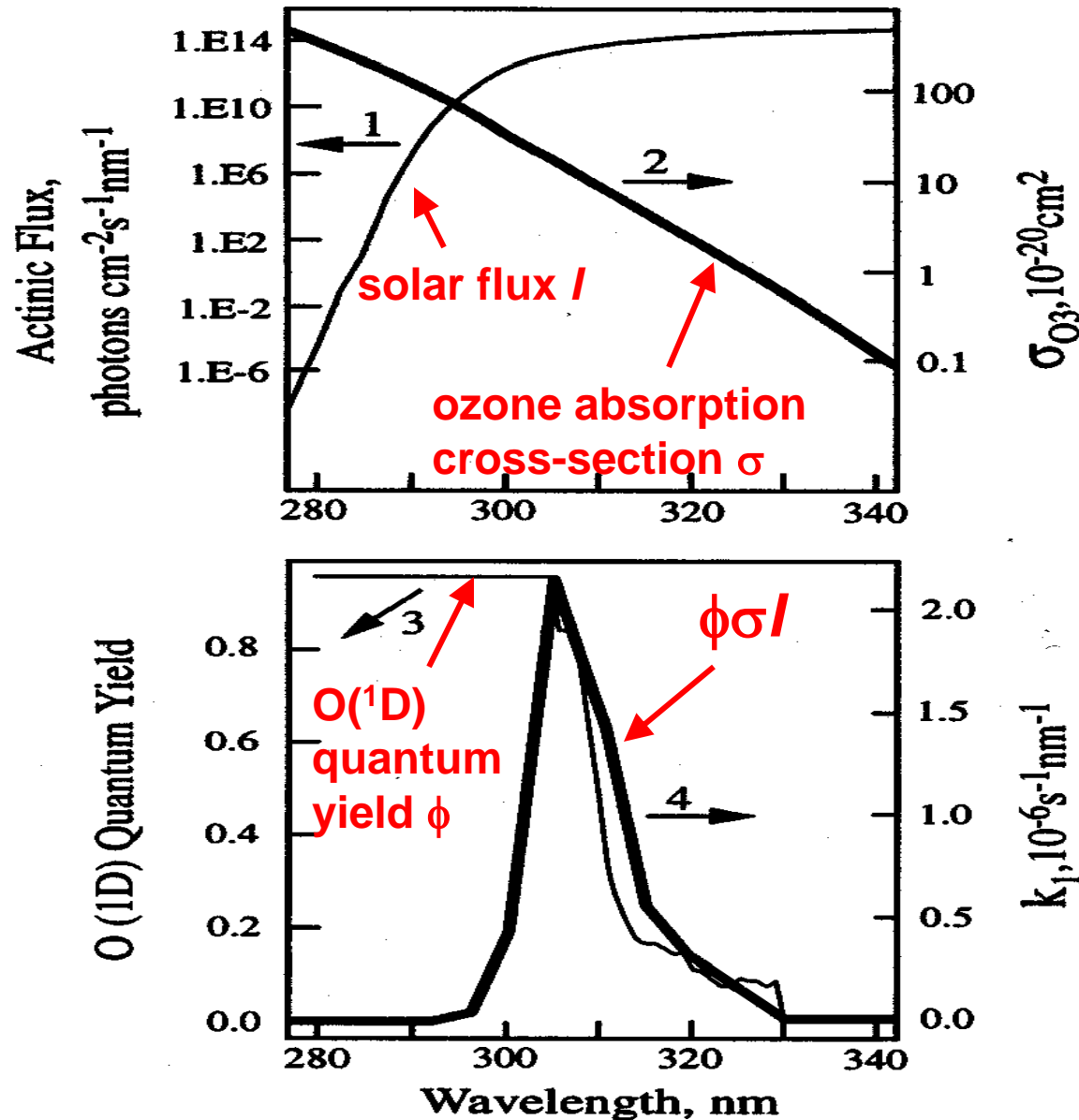
- Methylchloroform observations provide indirect evidence for OH at levels of  $2\text{-}5 \times 10^5 \text{ cm}^{-3}$  [Singh, *Geophys. Res. Lett. 1977*]

...but direct measurements of tropospheric OH had to wait until the 1990s



# WHY WAS TROPOSPHERIC OH SO DIFFICULT TO FIGURE OUT?

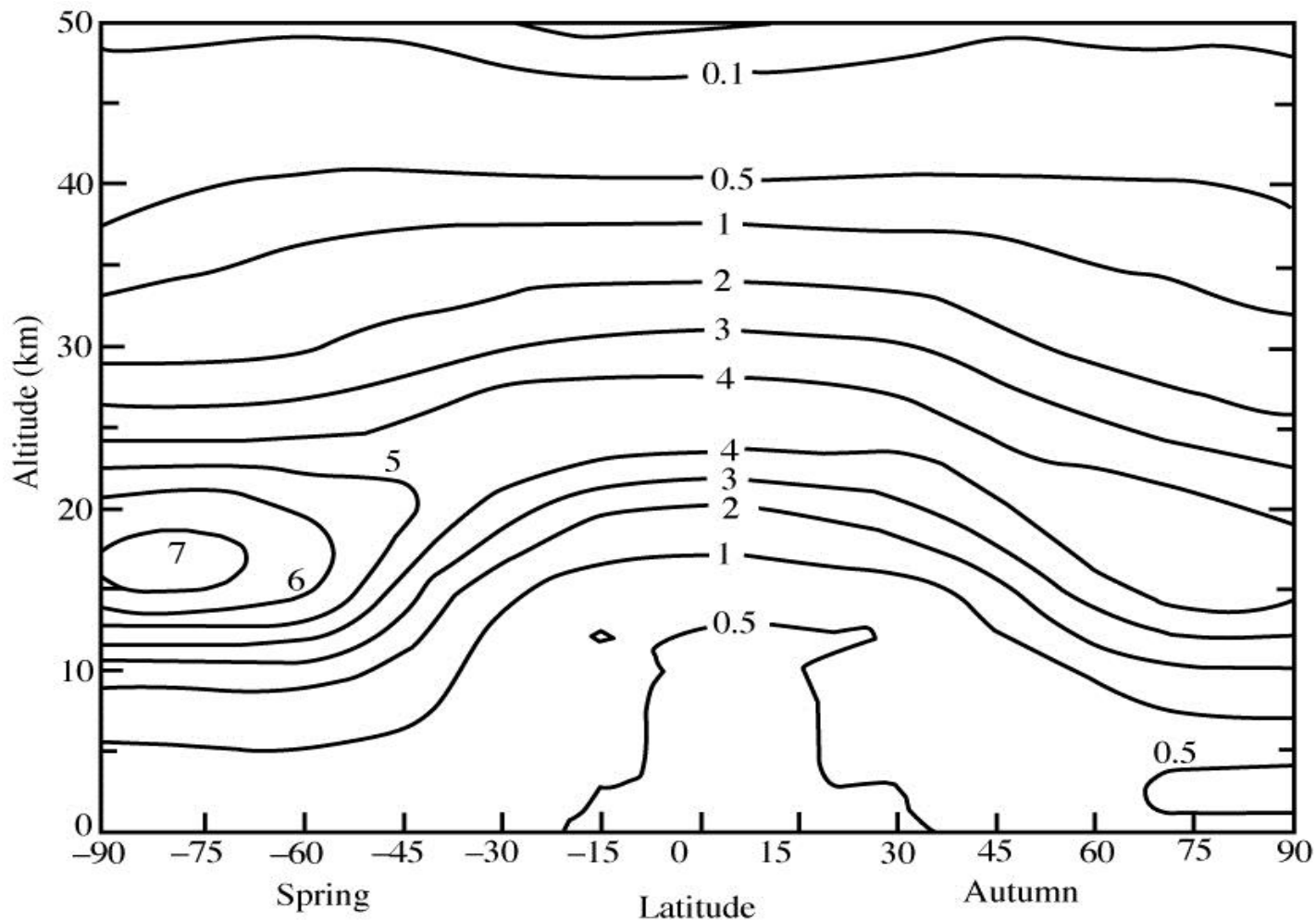
Production of  $O(^1D)$  in troposphere takes place in narrow band [290-320 nm]



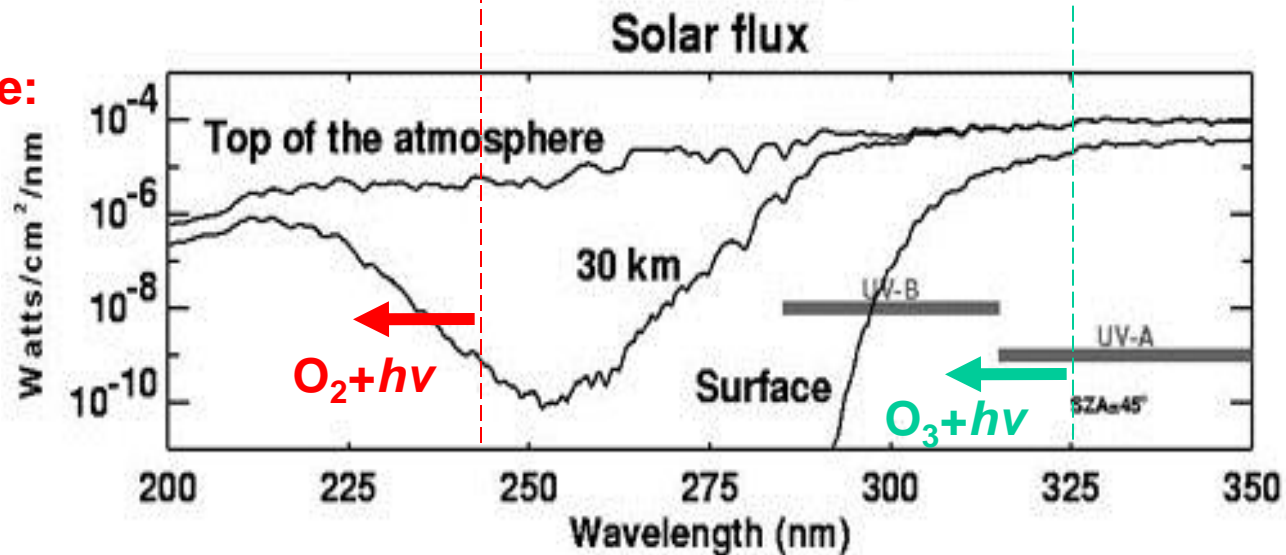
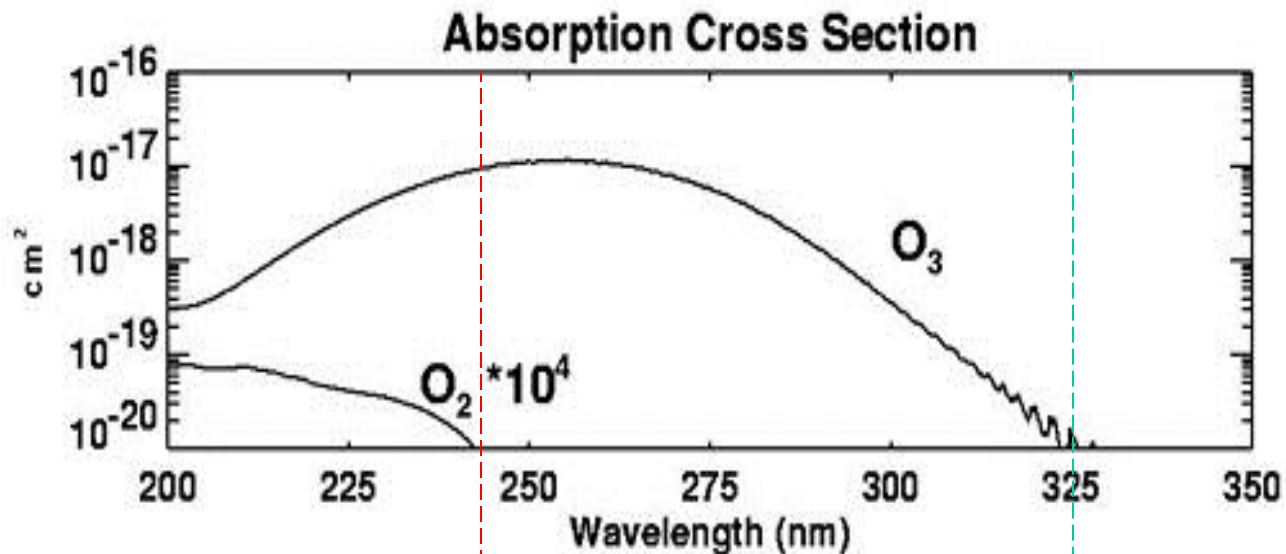
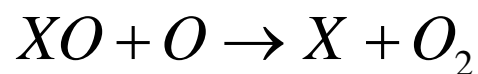
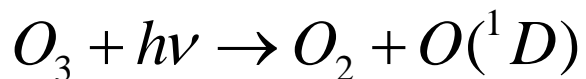
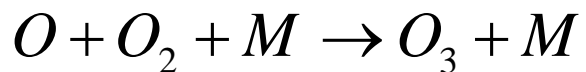
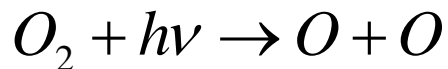


# MEAN VERTICAL DISTRIBUTION OF ATMOSPHERIC OZONE: only 10% is in the troposphere

Natural ozone levels from sonde measurements in the 1960s ( $10^{12}$  molecules  $\text{cm}^{-3}$ )



# OZONE CHEMISTRY IN STRATOSPHERE



**By contrast, in troposphere:**

- no photons < 240 nm  
→ no oxygen photolysis;
- negligible O atom conc.  
→ no XO + O loss

# UNTIL ~1990, PREVAILING VIEW WAS THAT TROPOSPHERIC OZONE ORIGINATED MAINLY FROM STRATOSPHERE...but that cannot work.

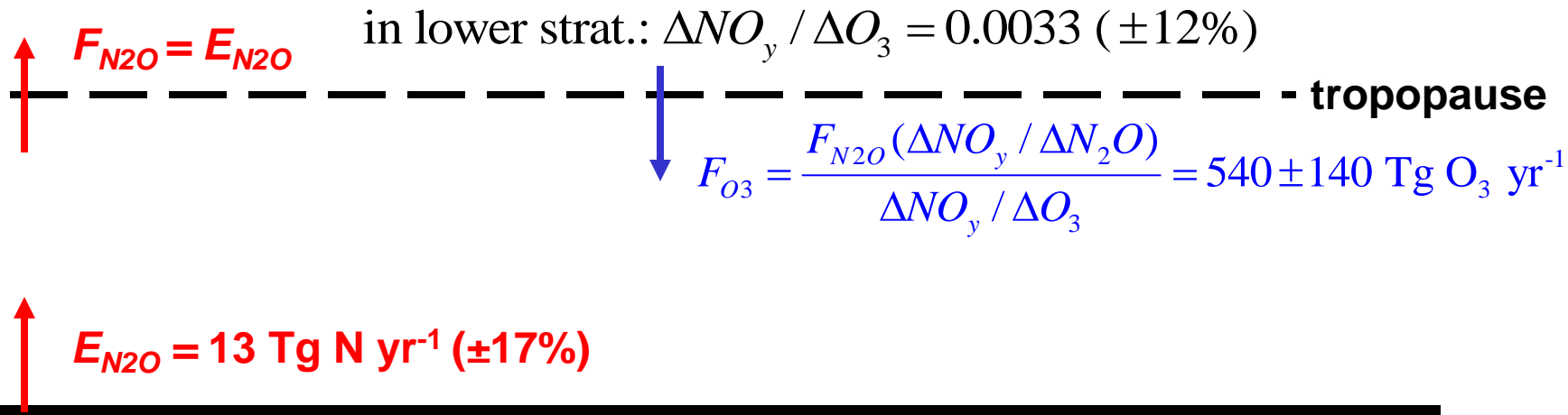
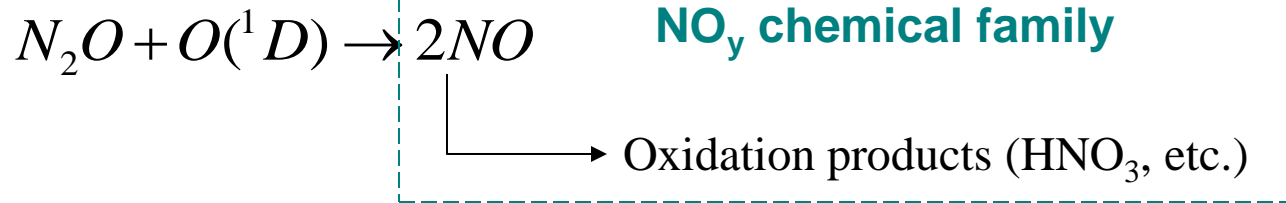
- Estimate ozone flux  $F_{O_3}$  across tropopause (strat-trop exchange)
  - Total  $O_3$  col =  $5 \times 10^{13}$  moles
  - 10% of that is in troposphere
  - Res. time of air in strat = 1.4 yr
$$F_{O_3} = 3 \times 10^{13} \text{ moles yr}^{-1}$$
- Estimate  $CH_4$  source  $S_{CH_4}$ :
  - Mean concentration = 1.7 ppmv
  - Lifetime = 9 years
$$S_{CH_4} = 3 \times 10^{13} \text{ moles yr}^{-1}$$
- Estimate CO source  $S_{CO}$ :
  - Mean concentration = 100 ppbv
  - Lifetime = 2 months
$$S_{CO} = 9.7 \times 10^{13} \text{ moles yr}^{-1}$$

$S_{CO} + S_{CH_4} > 2F_{O_3} \Rightarrow$  OH would be titrated!

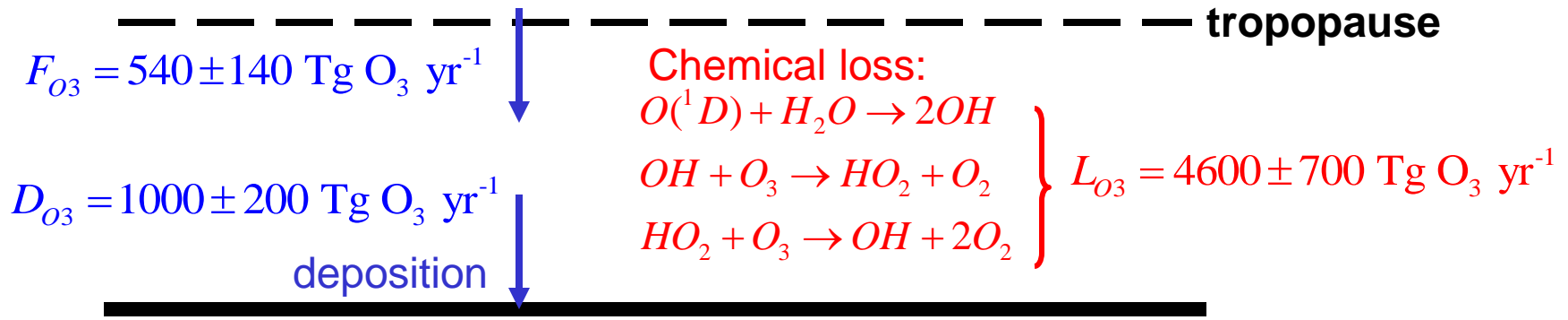
We need a much larger source of tropospheric ozone

# CONSTRAINT ON CROSS-TROPOPAUSE OZONE FLUX FROM OBSERVED OZONE-NO<sub>y</sub> CORRELATION IN LOWER STRATOSPHERE

$$\Delta NO_y / \Delta N_2O = -0.073 (\pm 14\%)$$



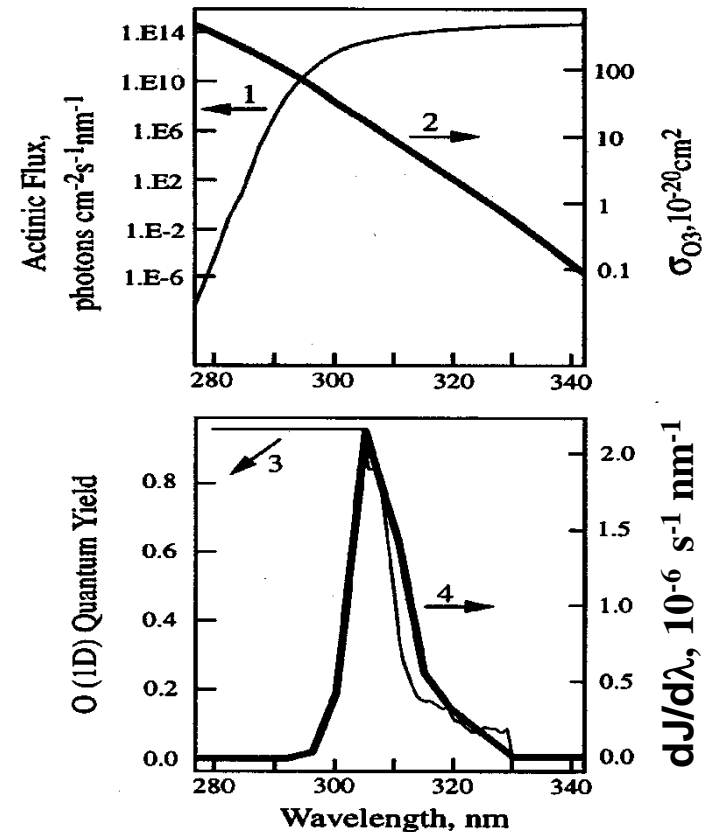
# OZONE LOSS IN TROPOSPHERE



Ozone chemical loss is driven by photolysis frequency  $J(O_3 \rightarrow O(^1D))$  at 300-320 nm:

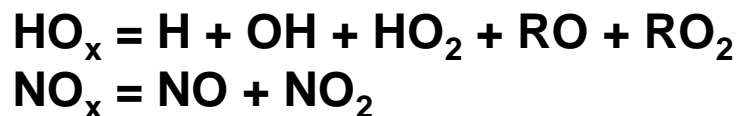
$$J = \int_0^{\infty} q(\lambda) \sigma(\lambda) I(\lambda) d\lambda$$

Closing the tropospheric ozone budget requires a tropospheric chemical source  $\gg F_{O_3}$

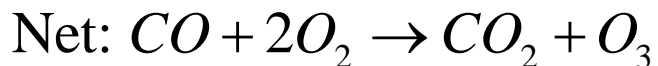
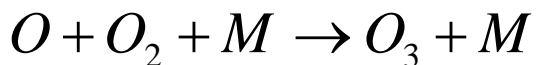
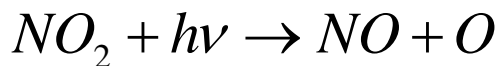
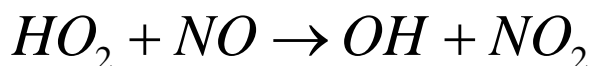
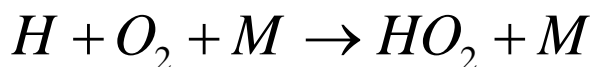
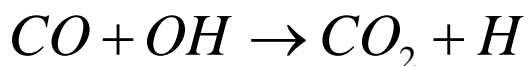


# OZONE PRODUCTION IN TROPOSPHERE

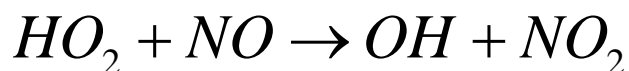
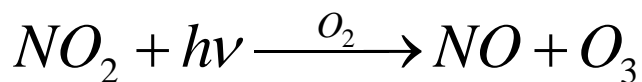
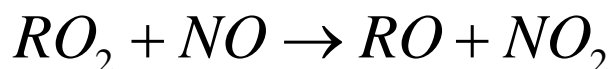
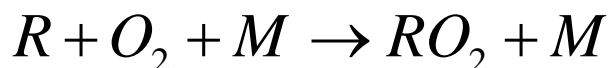
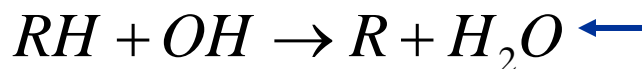
Photochemical oxidation of CO and volatile organic compounds (VOCs) catalyzed by hydrogen oxide radicals ( $\text{HO}_x$ ) and nitrogen oxide radicals ( $\text{NO}_x$ )



## Oxidation of CO:



## Oxidation of VOC:



OH can also add to double bonds of unsaturated VOCs

RO can also decompose or isomerize; range of carbonyl products

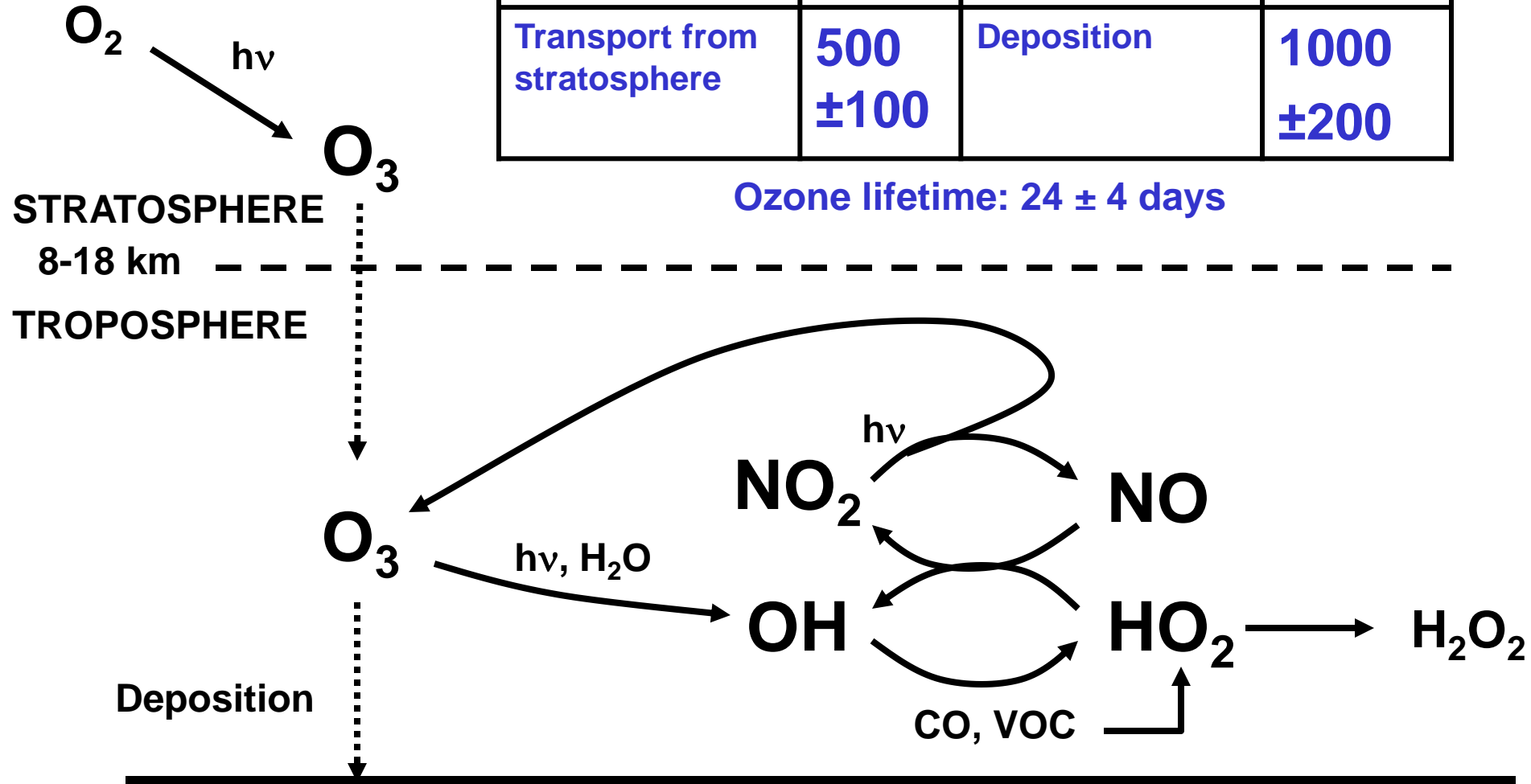
**Carbonyl products can react with OH to produce additional ozone, or photolyze to generate more  $\text{HO}_x$  radicals (branching reaction)**

# GLOBAL BUDGET OF TROPOSPHERIC OZONE ( $\text{Tg O}_3 \text{ yr}^{-1}$ )

IPCC (2007) average of 12 models

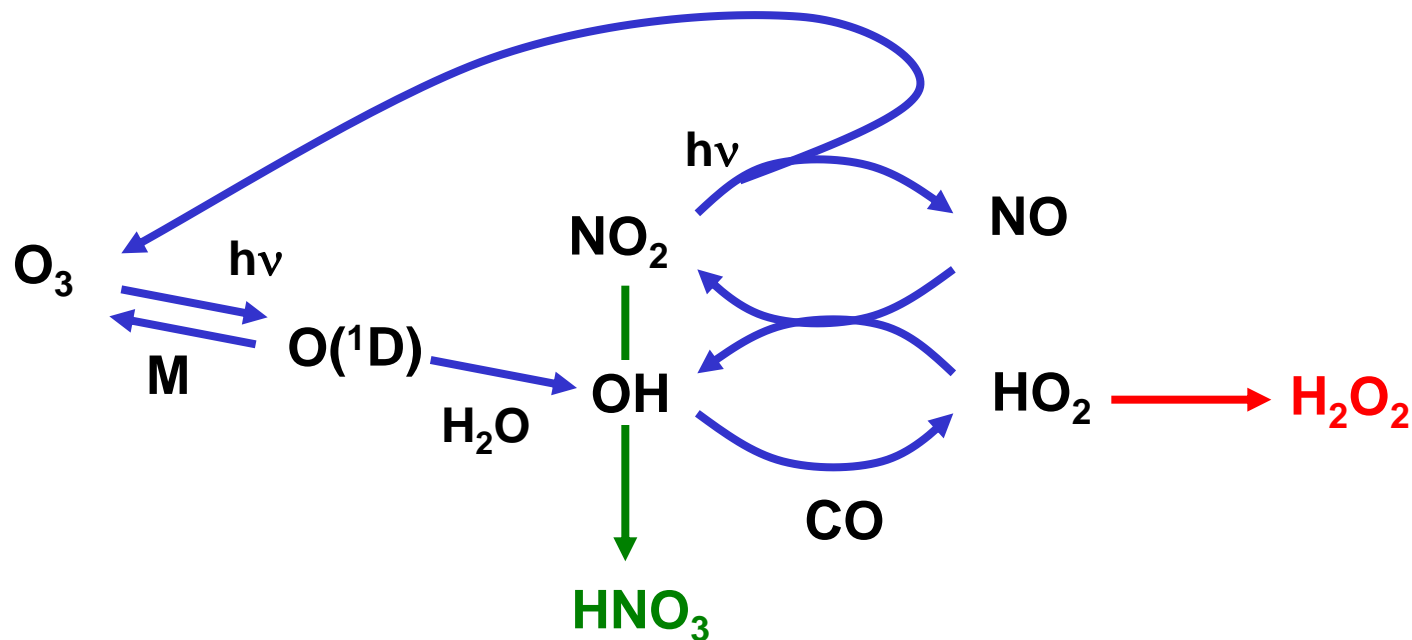
Chem prod in troposphere	4700 $\pm 700$	Chem loss in troposphere	4200 $\pm 500$
Transport from stratosphere	500 $\pm 100$	Deposition	1000 $\pm 200$

Ozone lifetime:  $24 \pm 4$  days





# Factors controlling tropospheric ozone and OH



$P(O_3)$

$[OH]$

**NO<sub>x</sub>-limited regime:**

$\sim [O_3]^{1/2}[H_2O]^{1/2}[NO]$

$\sim [O_3]^{1/2}[H_2O]^{1/2}[NO]/[CO]$

**NO<sub>x</sub>-saturated regime:**

$\sim [O_3][H_2O][CO]/[NO_2]$

$\sim [O_3][H_2O]/[NO_2]$

# OZONE CONCENTRATIONS vs. NO<sub>x</sub> AND VOC EMISSIONS

## Box model calculation

