Distribution and Variation of Trace Gases

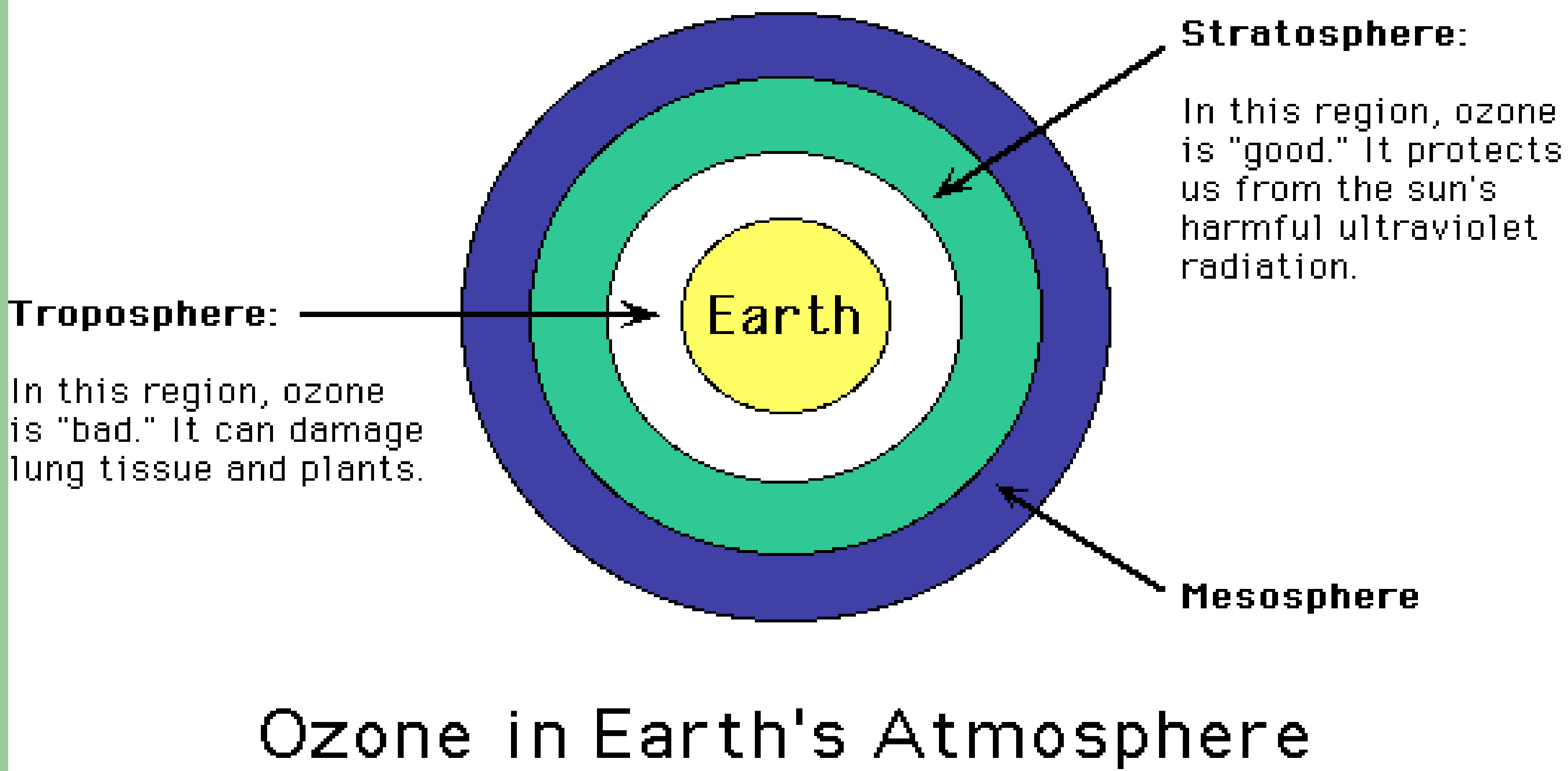
Part I: Brief introduction of trace gases and their chemistry (Jennifer)

Part II: Satellite retrievals of trace gases (Eric, Xiaozhen)

Part I

- Trace Gases
- O_3, CO, CO_2, H_2O, CH_4, HNO_3
- Major chemical reactions
- Distribution
- Lifetime
- Correlation

Is ozone good or bad?



Ozone Formation

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

- In Stratosphere:

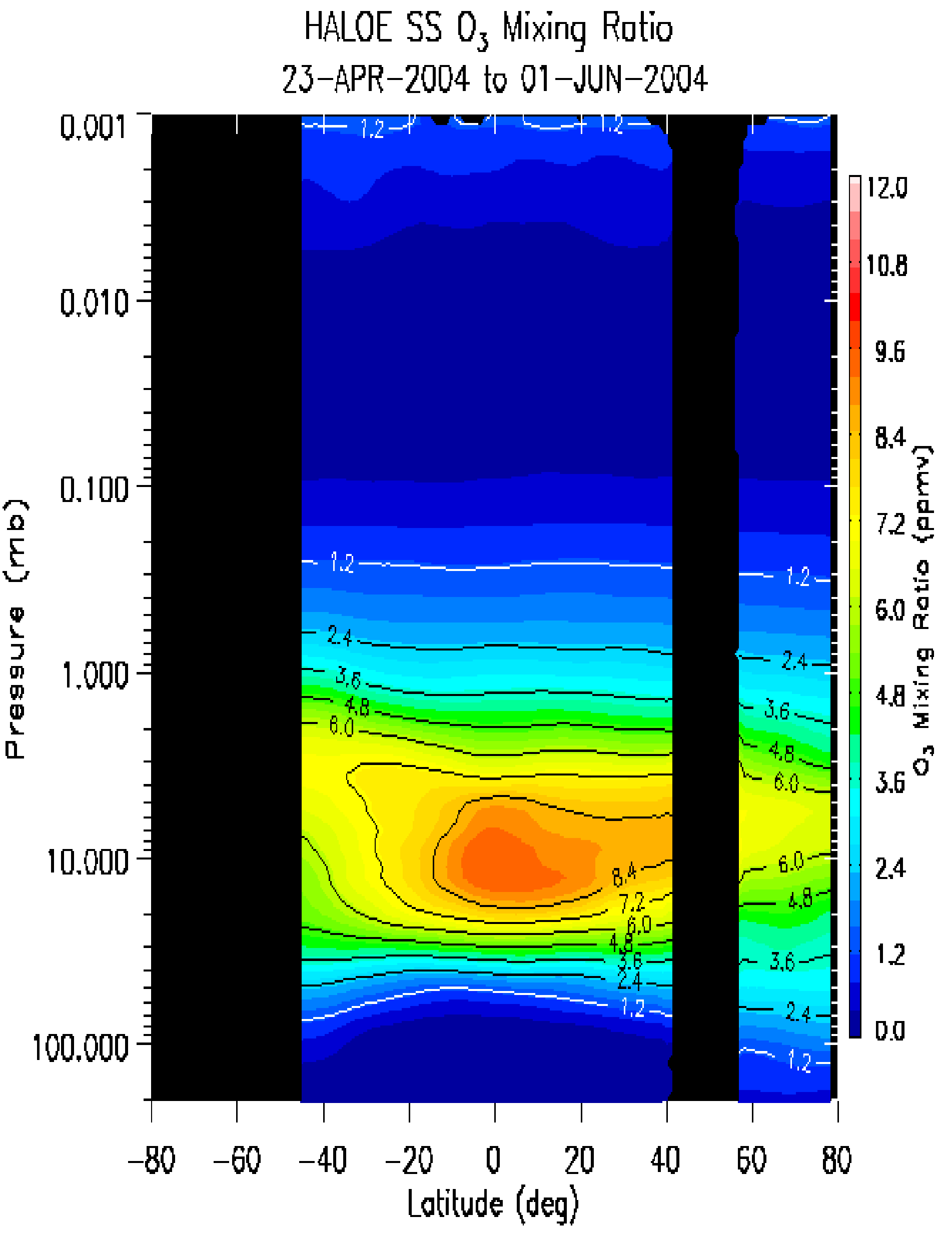
  $O_2 + h\nu$ ($\lambda < 242$nm)

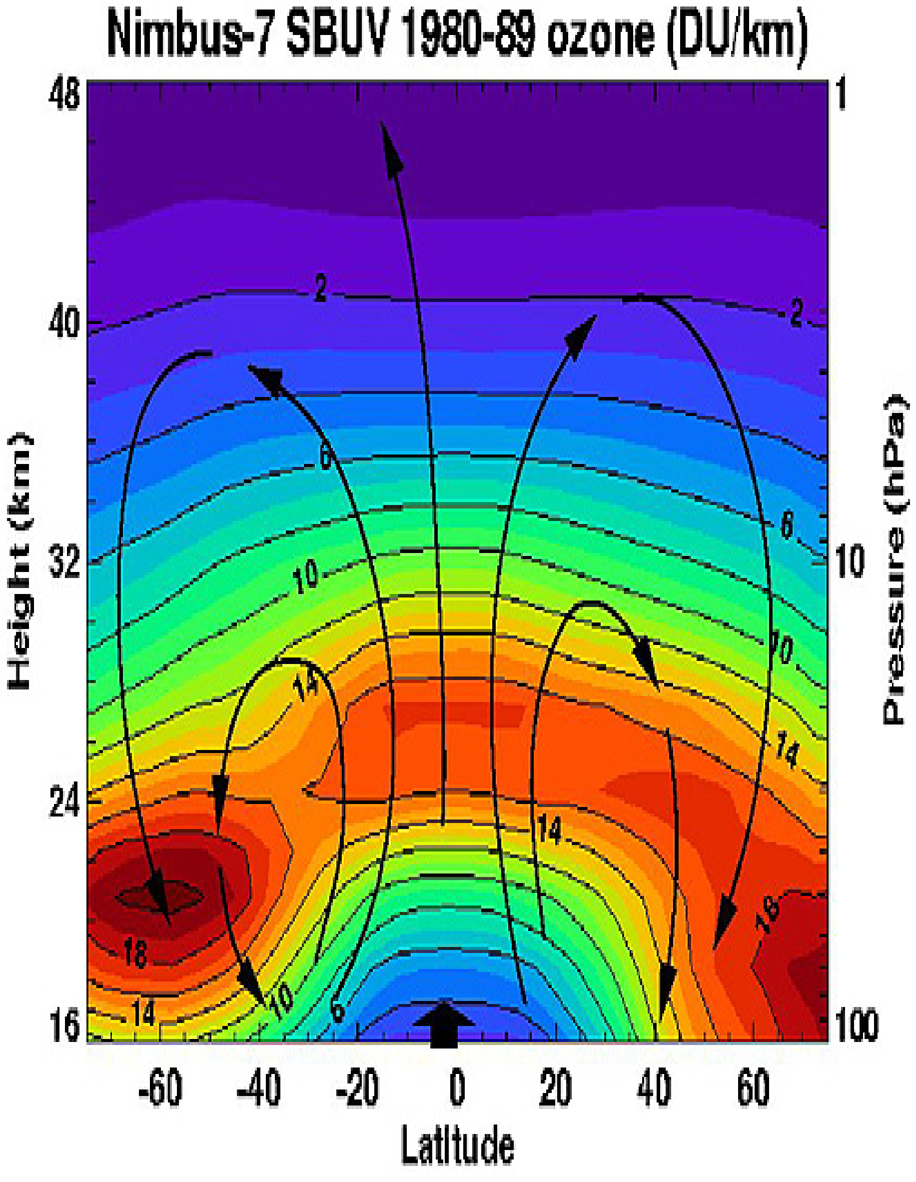
  $\rightarrow$ O + O

- In Troposphere:

  $NO_2 + h\nu$ ($\lambda = 290 \sim 400$ nm)

  $\rightarrow$ NO + O





http://haloedata.larc.nasa.gov/browse/index.php

Hydroxyl Radical (OH)

- produced from ozone photolysis

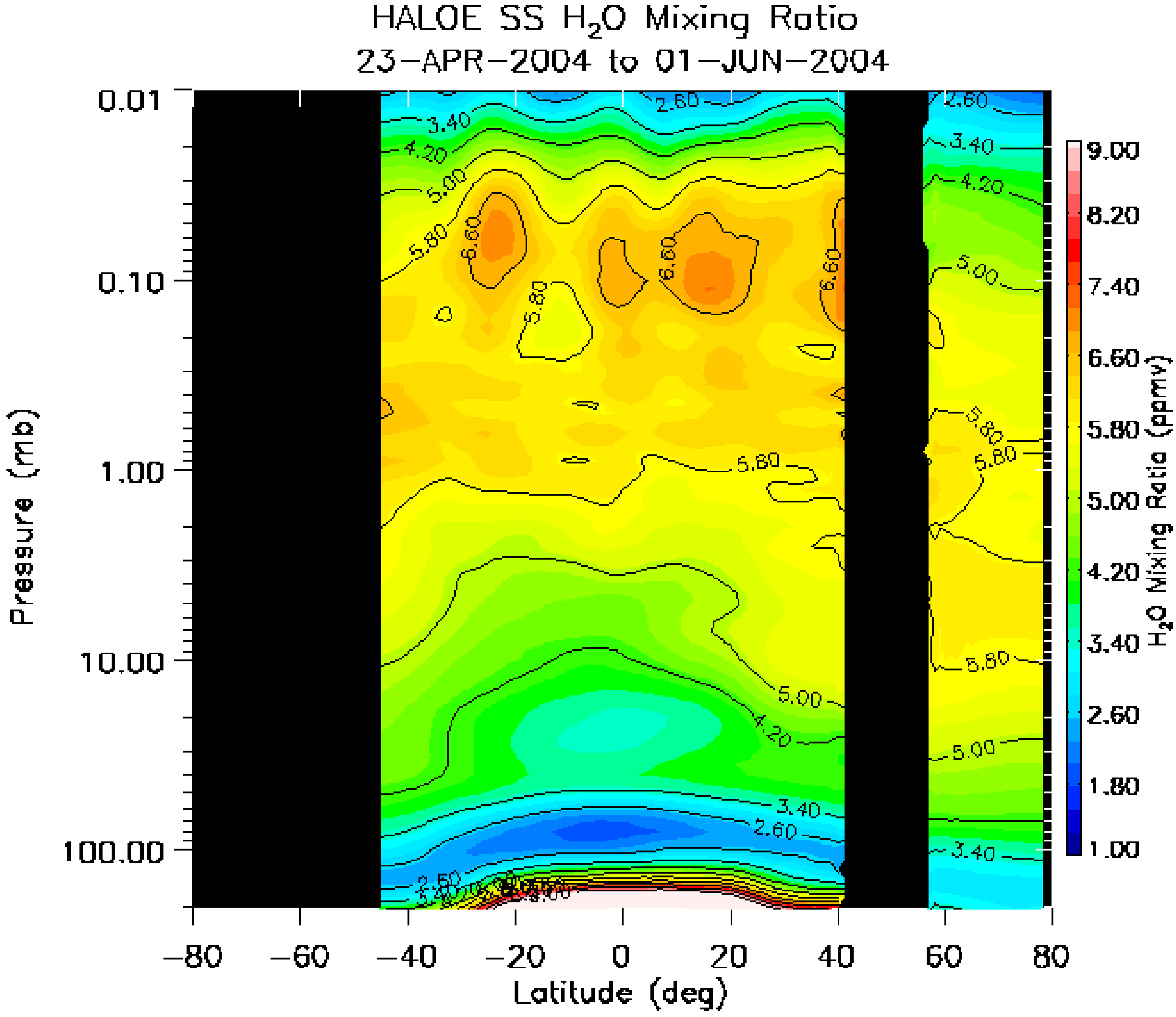
for radiation with wavelengths less than 320 nm:

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

followed by

$$O(^1D) + M \equiv O(3P) + M\ (+O_2 \equiv O_3) \qquad (\sim 90\%)$$
$$O(^1D) + H_2O \equiv 2\ OH\cdot \qquad (\sim 10\%)$$

•OH initiates the atmospheric oxidation of a wide range of compounds in the atmosphere
•referred to as 'detergent of the atmosphere'
•very reactive, effectively recycled



http://haloedata.larc.nasa.gov/browse/index.php

Oxidation of CO (O_3 production)

- Chemical lifetime of 30-90 days
- Primary natural source is oxidation of methane (20-50%), with the remainder from oxidation of other hydrocarbons and from oceans.
- Primary sink is OH radical attack:

$$\bullet OH + CO \rightarrow CO_2 + \bullet H \quad (1)$$

$$\bullet H + O_2 + M \rightarrow HOO\bullet + M \quad (2)$$ the hydroperoxyl radical

$$HOO\bullet + \mathbf{NO} \rightarrow \mathbf{NO_2} + \bullet OH \quad (3)$$

- If NOx concentrations are low, the following reaction competes with (3):

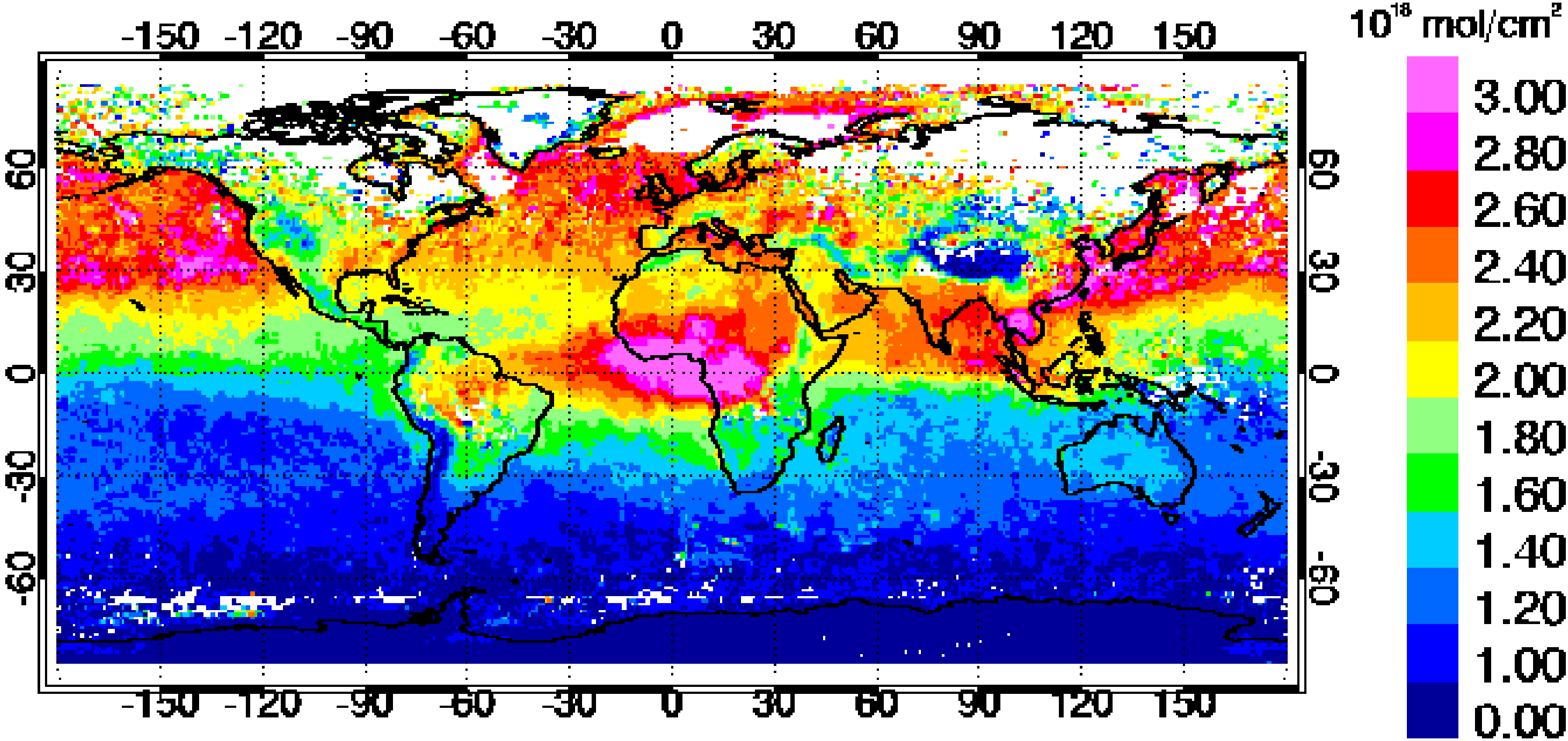
$$HOO\bullet + O_3 \rightarrow \bullet OH + 2O_2 \quad (4)$$

- So the photolytic oxidation of CO to CO_2, catalyzed by OH, leads to a net production of ozone in the presence of NOx since:

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$

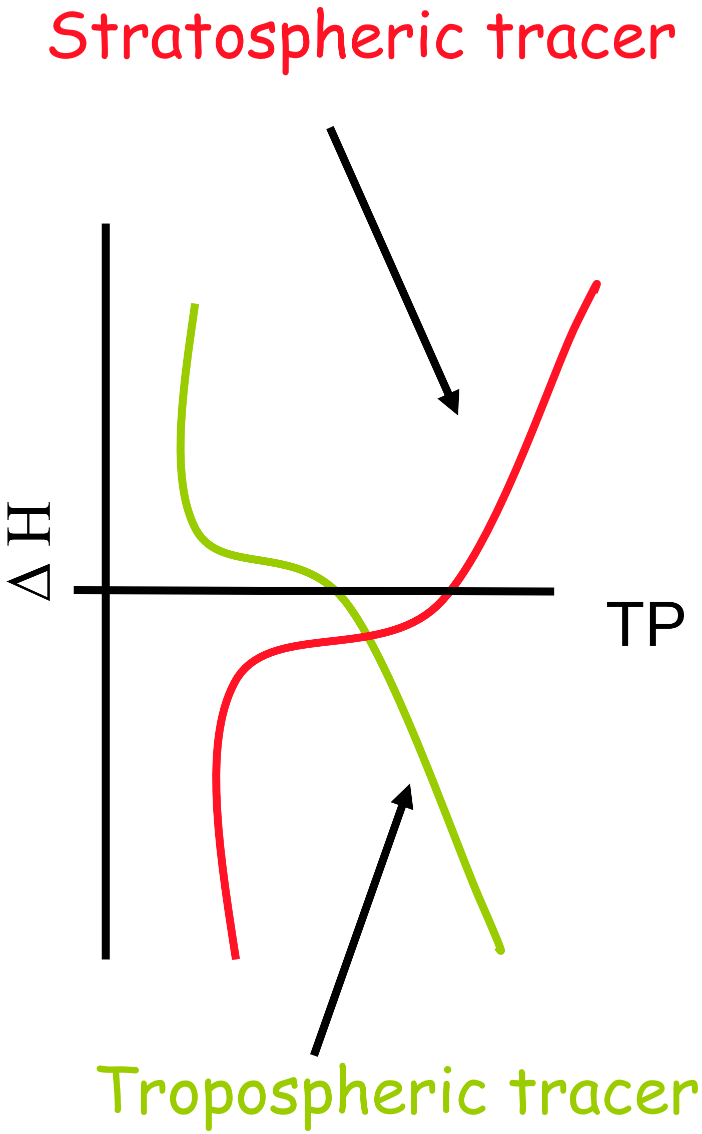
or to the net destruction of O_3 if NOx concentrations are low via (4)

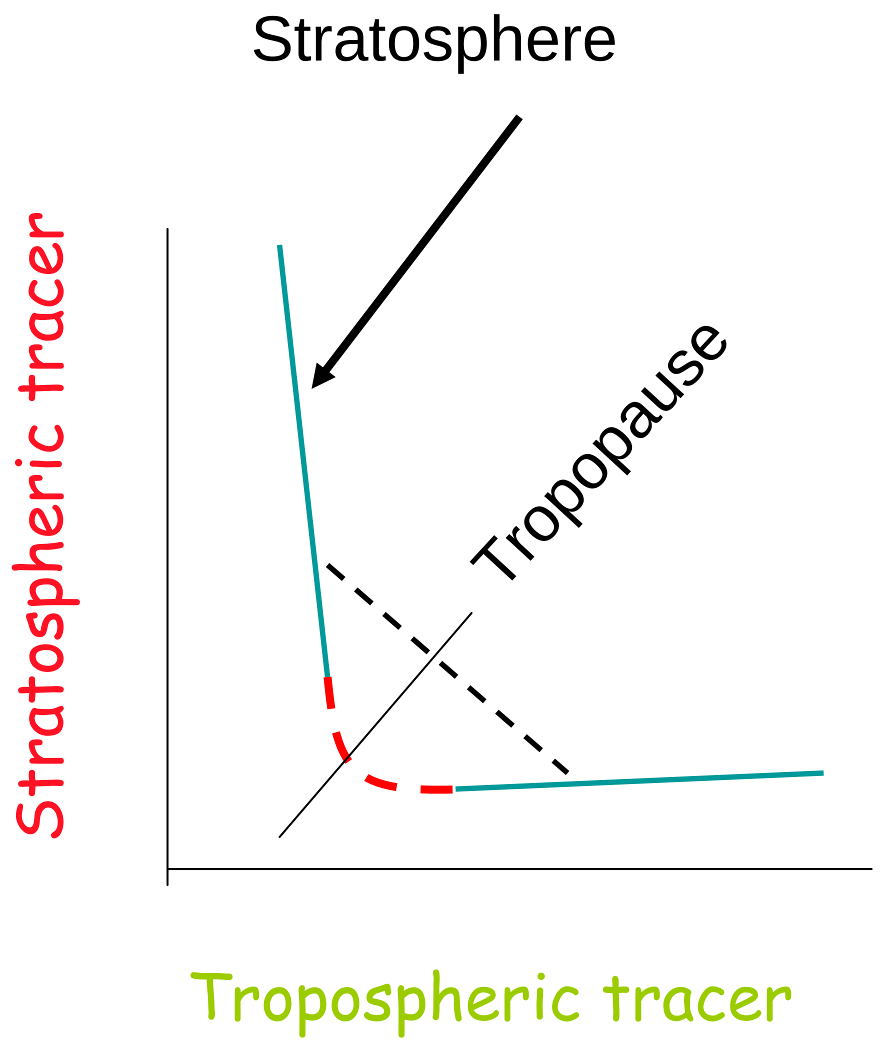
MOPITT CO (V3) Column Jan 1-31, 2005



Gridded at 1x1deg from MOP02-20050131-L2V5.9.4.val.hdf (apriori fraction < 50%)

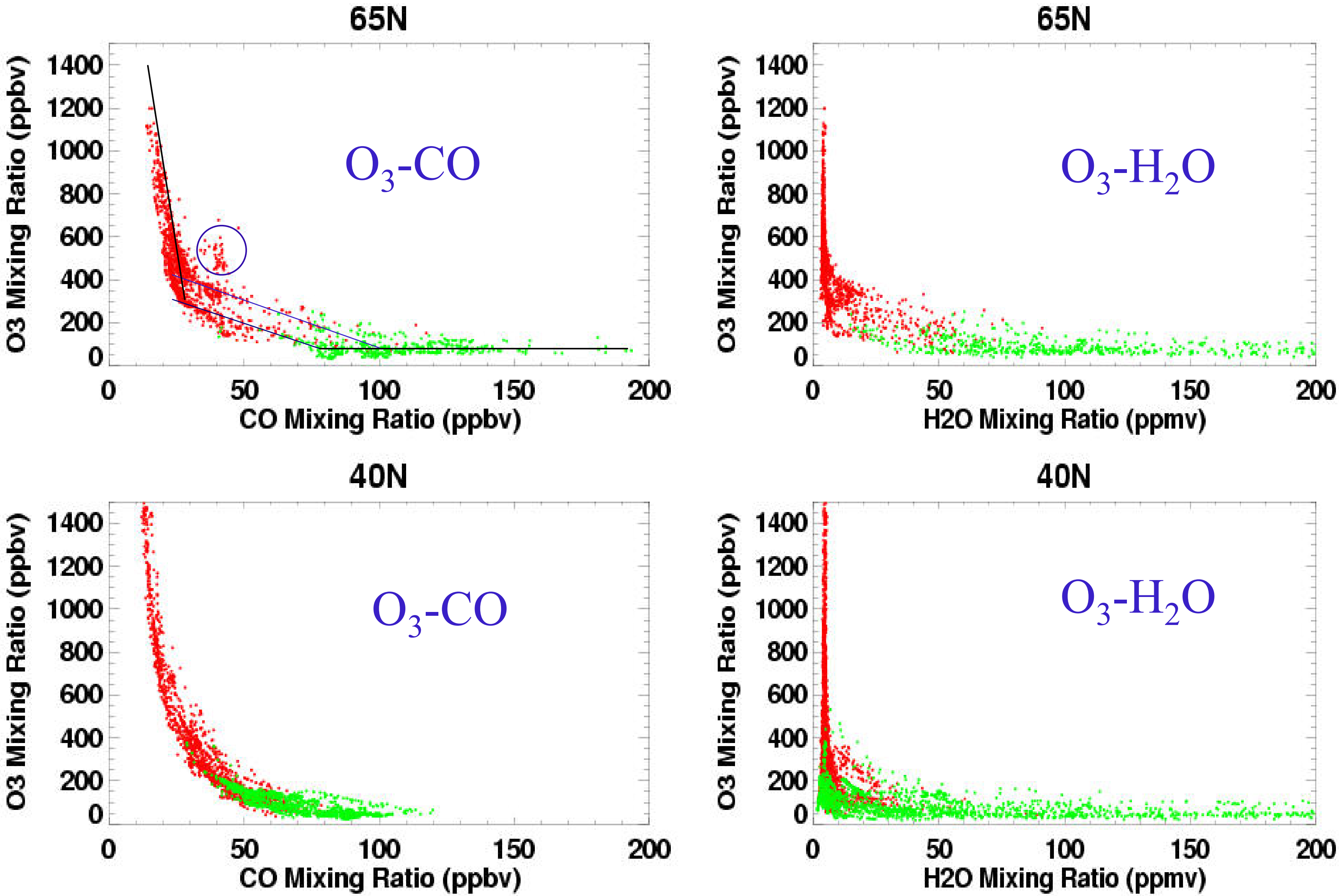
http://www.eos.ucar.edu/mopitt/data/plots/mapsv3_mon.html


Stratospheric tracer
Δ H
TP
Tropospheric tracer


Stratosphere
Stratospheric tracer
Tropopause
Tropospheric tracer

Tracer relationship

(Pan et al., 2004, JGR)



CH_4 Chemistry

- Chemical lifetime of 8-10 years
- Primary natural source is biogenic (swamps, tropical rainforests, livestock)
- In urban air, methane oxidation is slower than other hydrocarbons
- Primary sink is OH radical attack:

$$\bullet OH + CH_4 \rightarrow \bullet CH_3 + H_2O$$

$$\bullet CH3 + O_2 + M \rightarrow CH_3OO\bullet + M \qquad \text{methylperoxy radical}$$

$$CH_3OO\bullet + \mathbf{NO} \rightarrow \mathbf{NO_2} + CH_3O\bullet \qquad \text{methoxy radical}$$

$$CH_3O\bullet + O_2 \rightarrow HCHO + HOO\bullet \qquad \text{formaldehyde}$$

$$(HOO\bullet + \mathbf{NO} \rightarrow \mathbf{NO_2} + \bullet OH)$$

- HCHO is further attacked by OH to form CO:

$$HCHO + \bullet OH \rightarrow HCO\bullet + H_2O$$

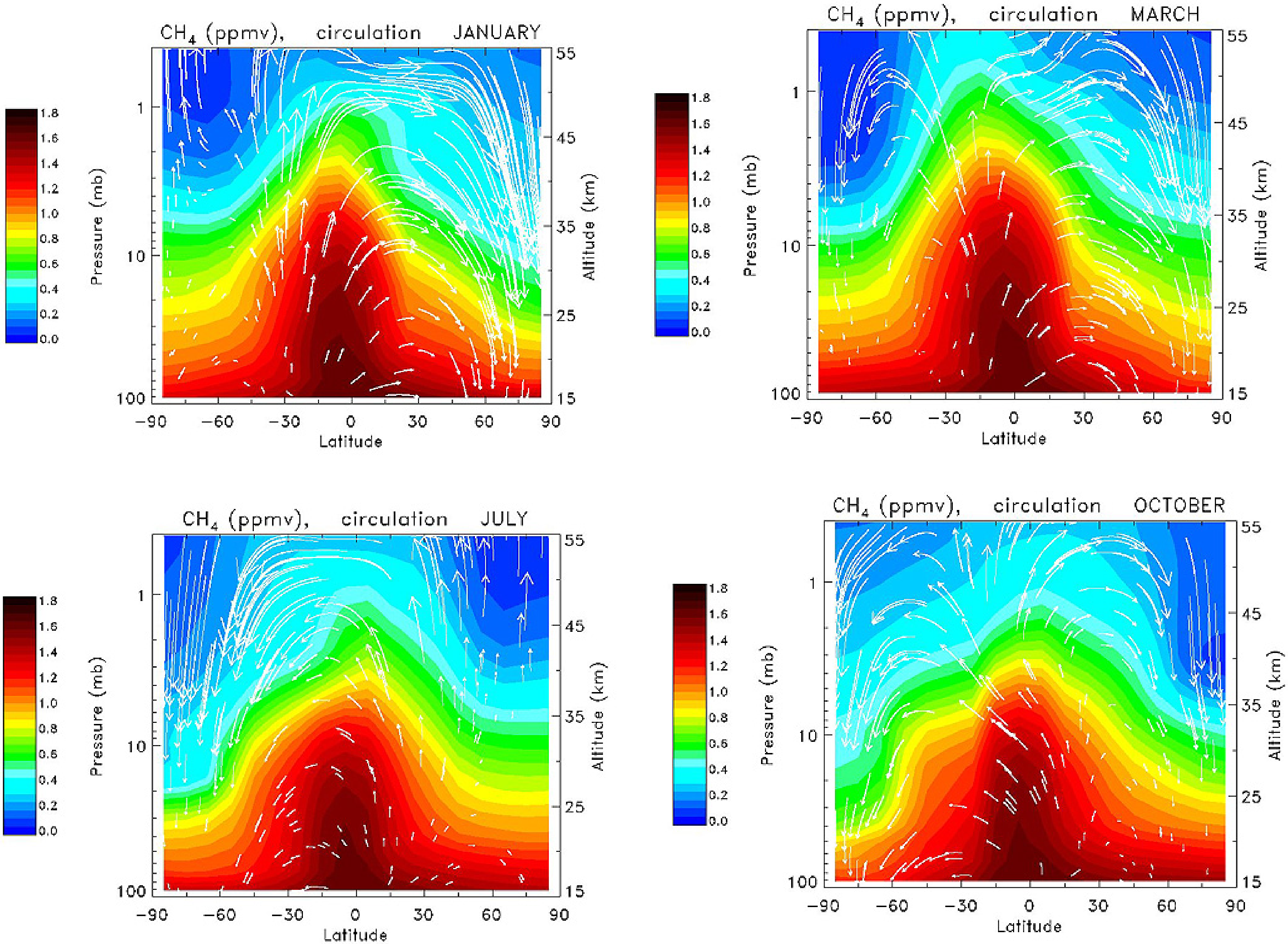
$$HCO\bullet + O_2 \rightarrow HOO\bullet + CO$$

$$(HOO\bullet + \mathbf{NO} \rightarrow \mathbf{NO_2} + \bullet OH)$$

- As we saw before, CO is oxidized to CO_2:

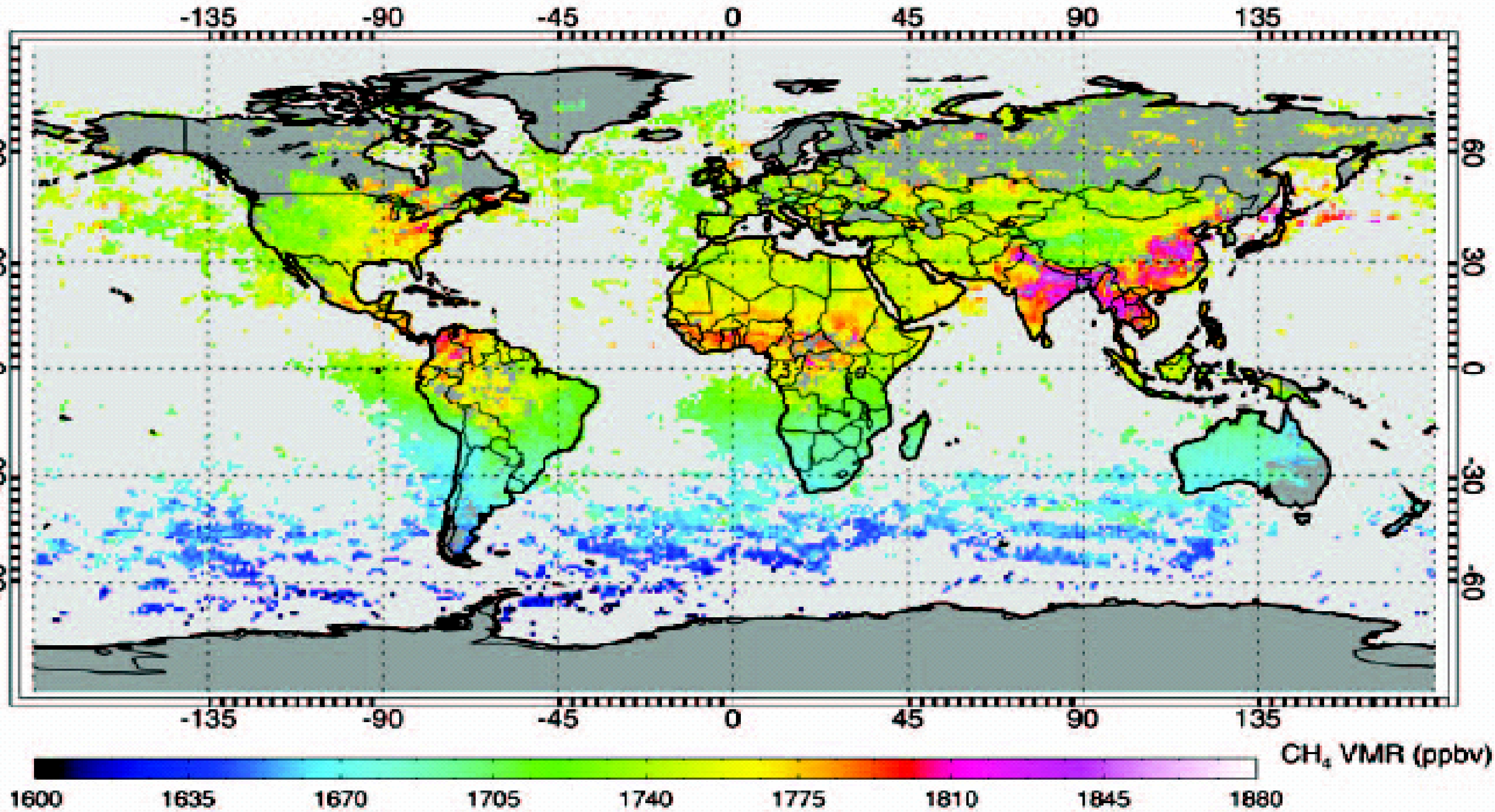
$$CO + 2O_2 + h\nu \rightarrow CO_2 + O_2$$

- So methane is oxidized photolytically to CO_2 via OH attack, with formaldehyde and CO as intermediates and net production of ozone.

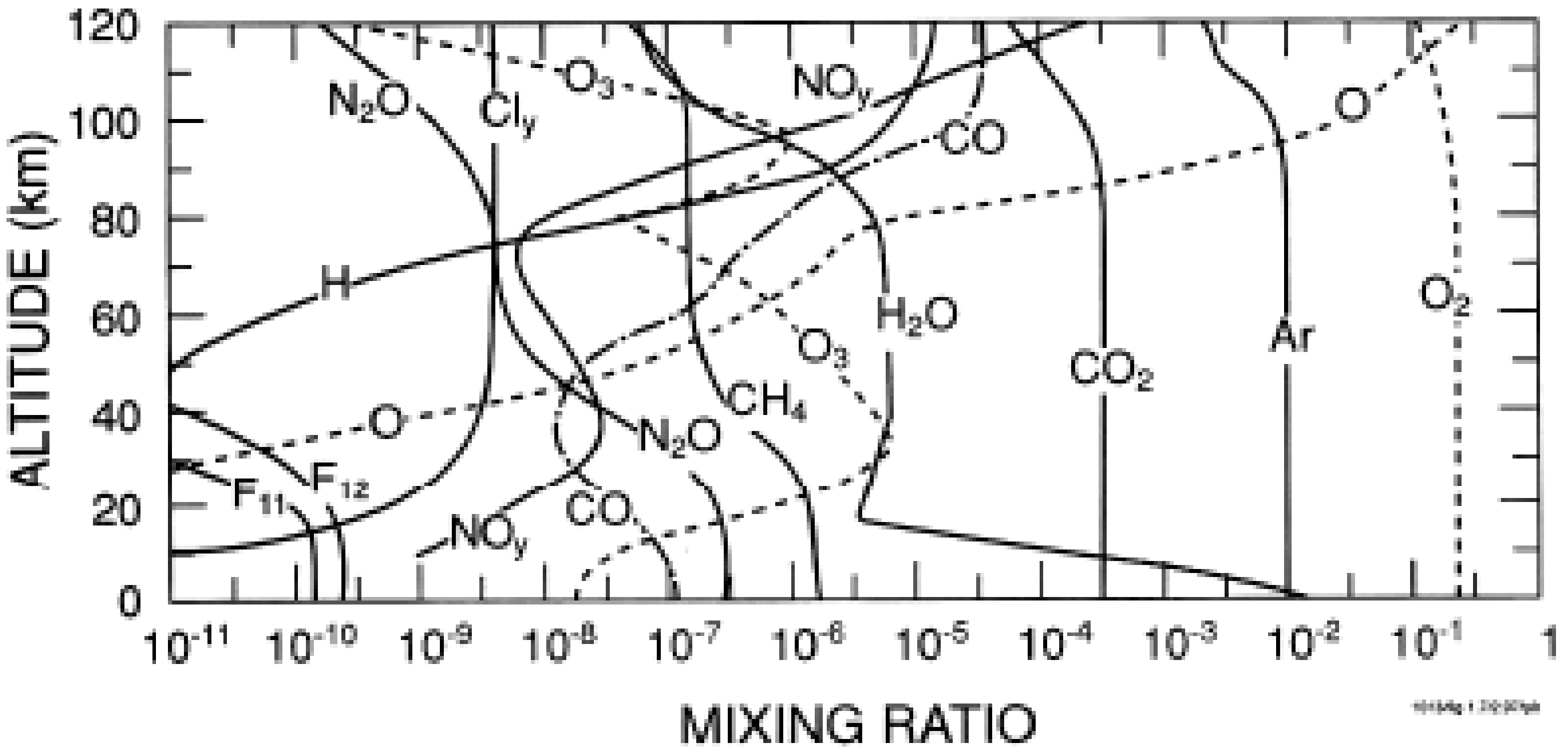


CH$_4$ (ppmv), circulation JANUARY
CH$_4$ (ppmv), circulation MARCH
CH$_4$ (ppmv), circulation JULY
CH$_4$ (ppmv), circulation OCTOBER
Pressure (mb)
Altitude (km)
Latitude
1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0
1 10 100
55 45 35 25 15
−90 −60 −30 0 30 60 90

SCIAMACHY Column Averaged of CH_4 over Aug-Nov (Frankenberg et al., 2005)

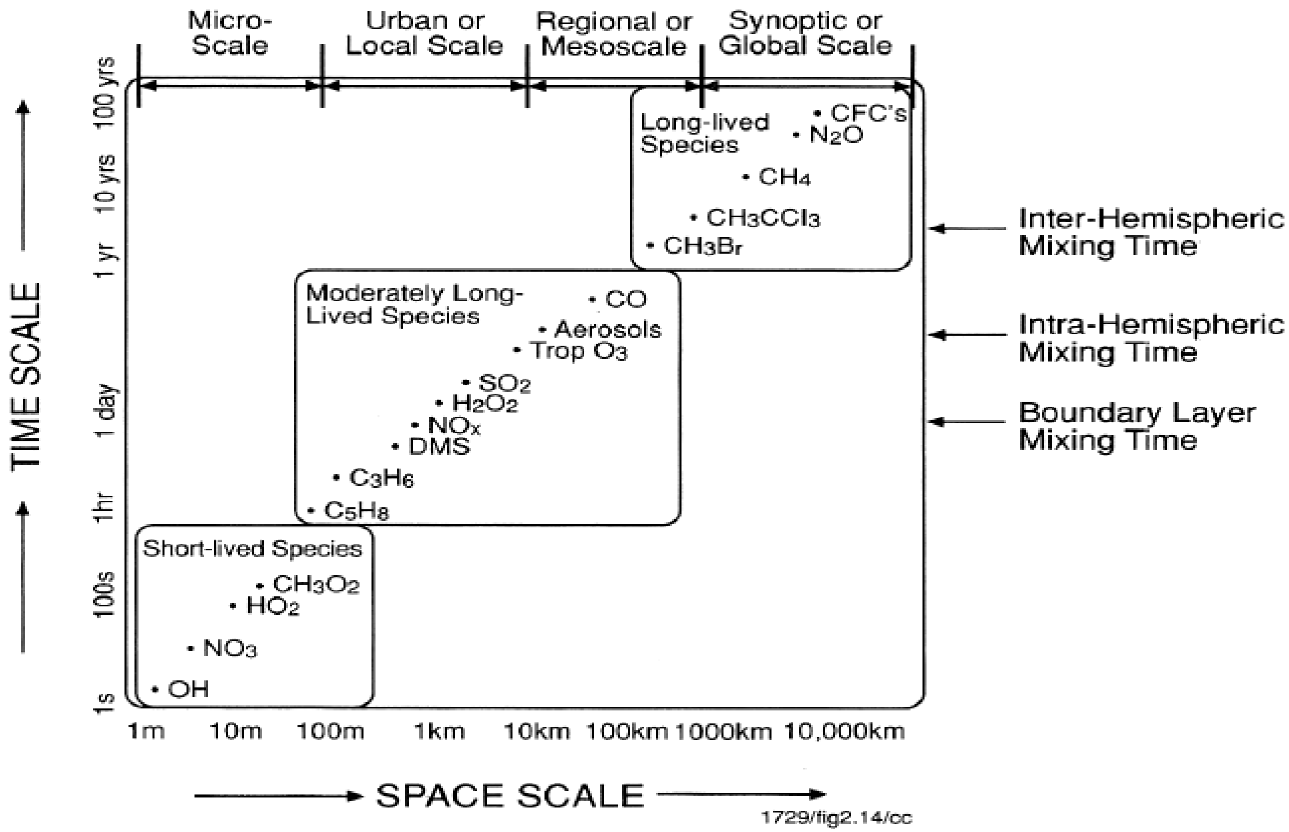


Vertical Distribution of Trace Gases



Brasseur and Solomon, 1988

Chemical Lifetime



HNO_3 Chemistry (NOx reservoir)

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

Nighttime:

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

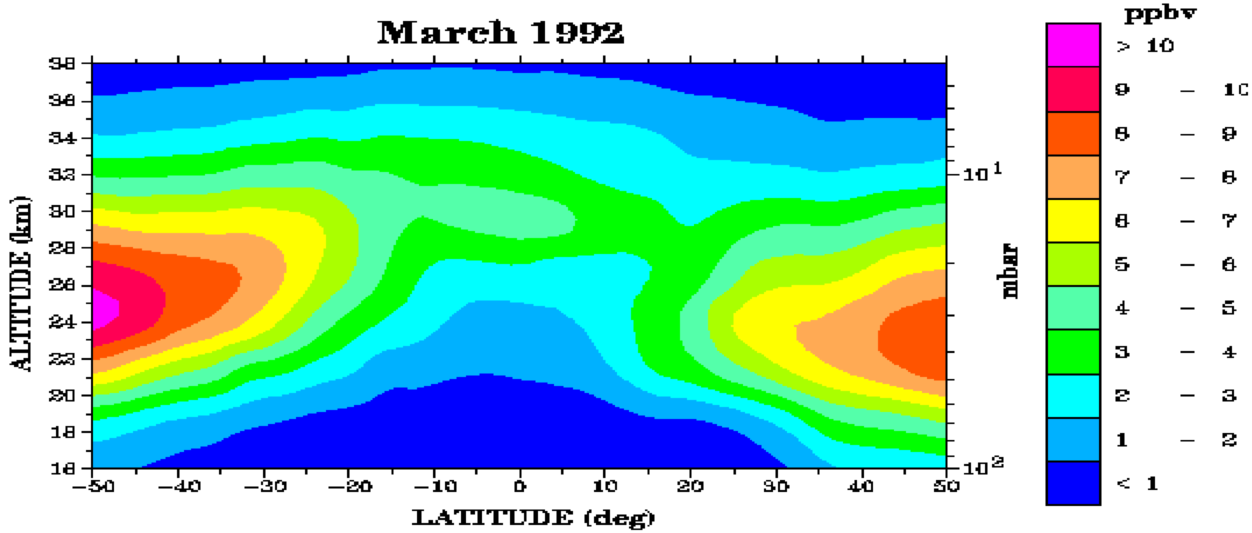
$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$$

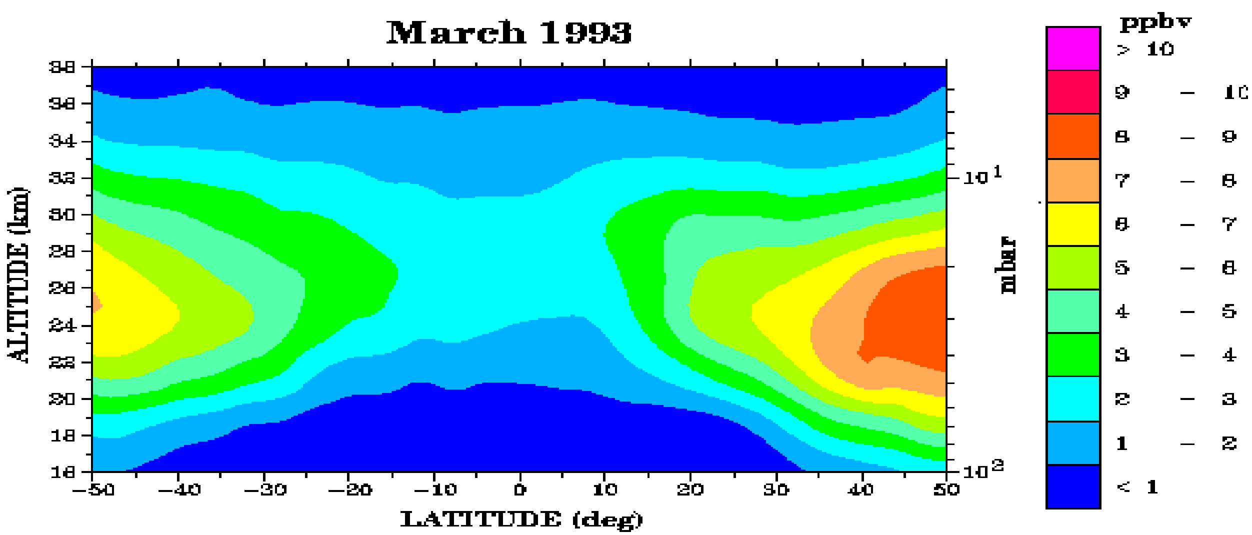
$$N_2O_5 + H_2O \xrightarrow{aerosol} 2HNO_3$$

HNO3 is effectively scavenged by precipitation in the troposphere.

Lifetime: < 1 day in boundary layer
~ 1 month in upper troposphere

CLAES HNO_3 ZONAL MEAN MAPS



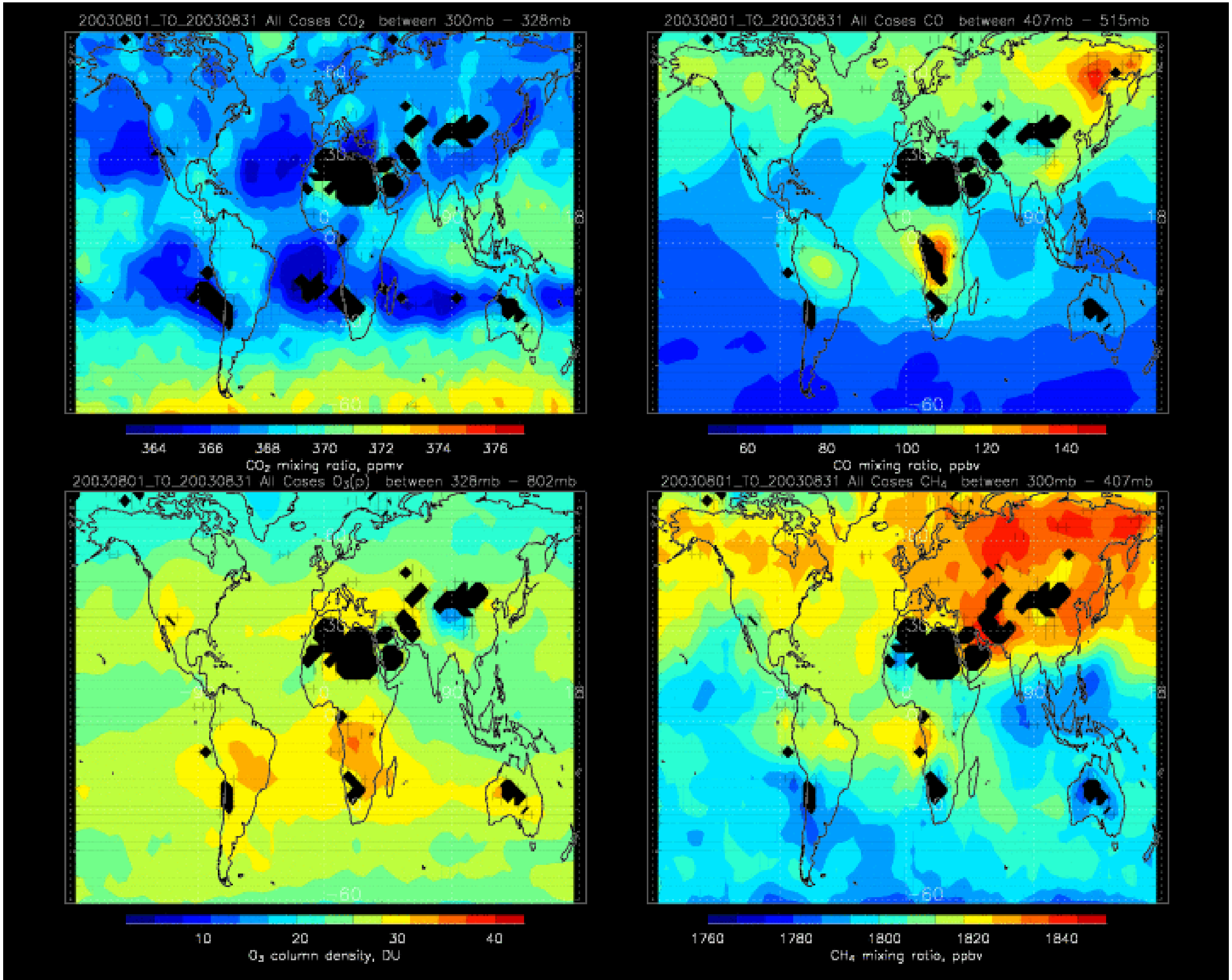


Part II Satellite Retrievals

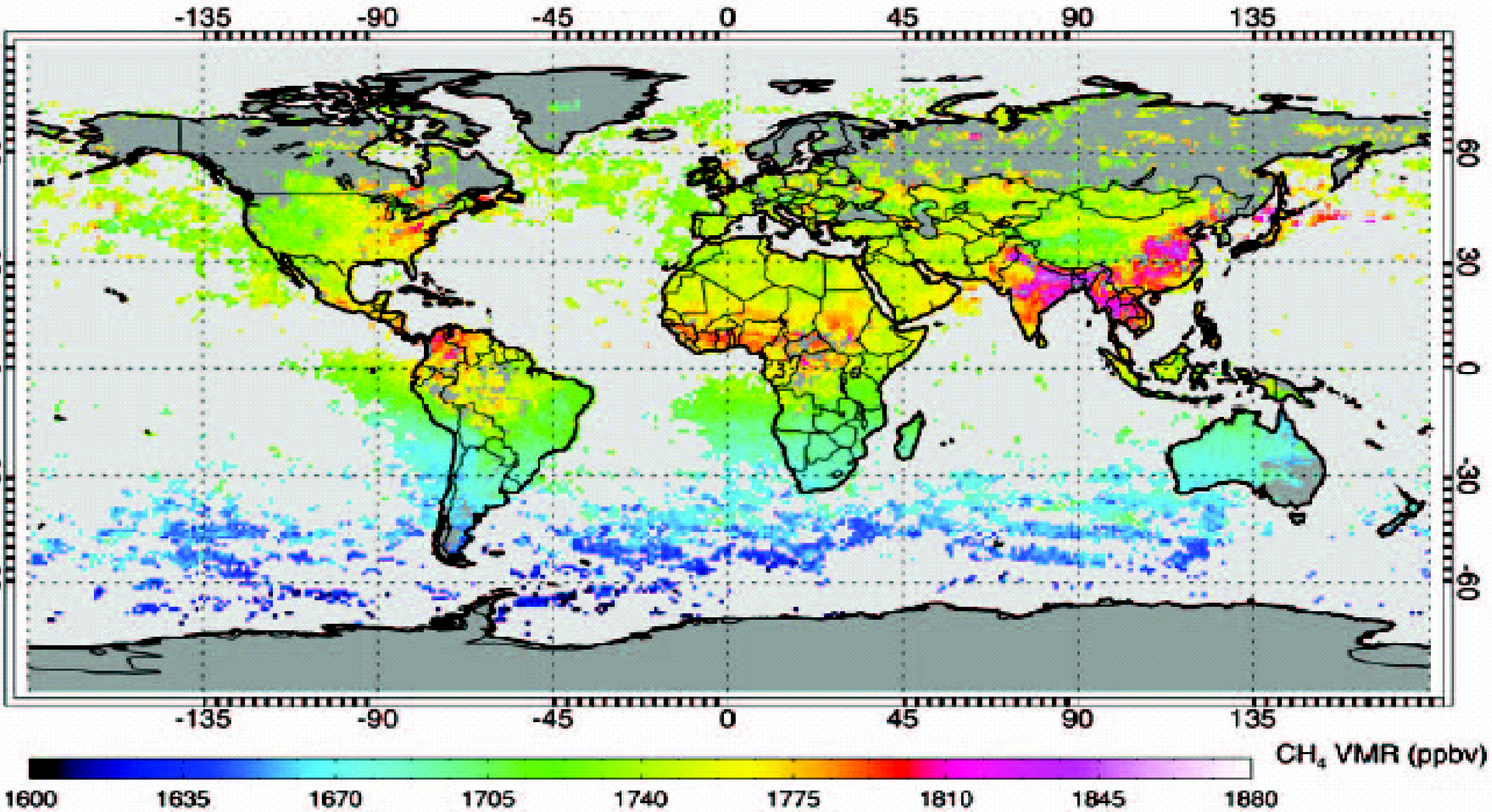
Q: How to convert radiances to trace gases? (level 1 to level 2)

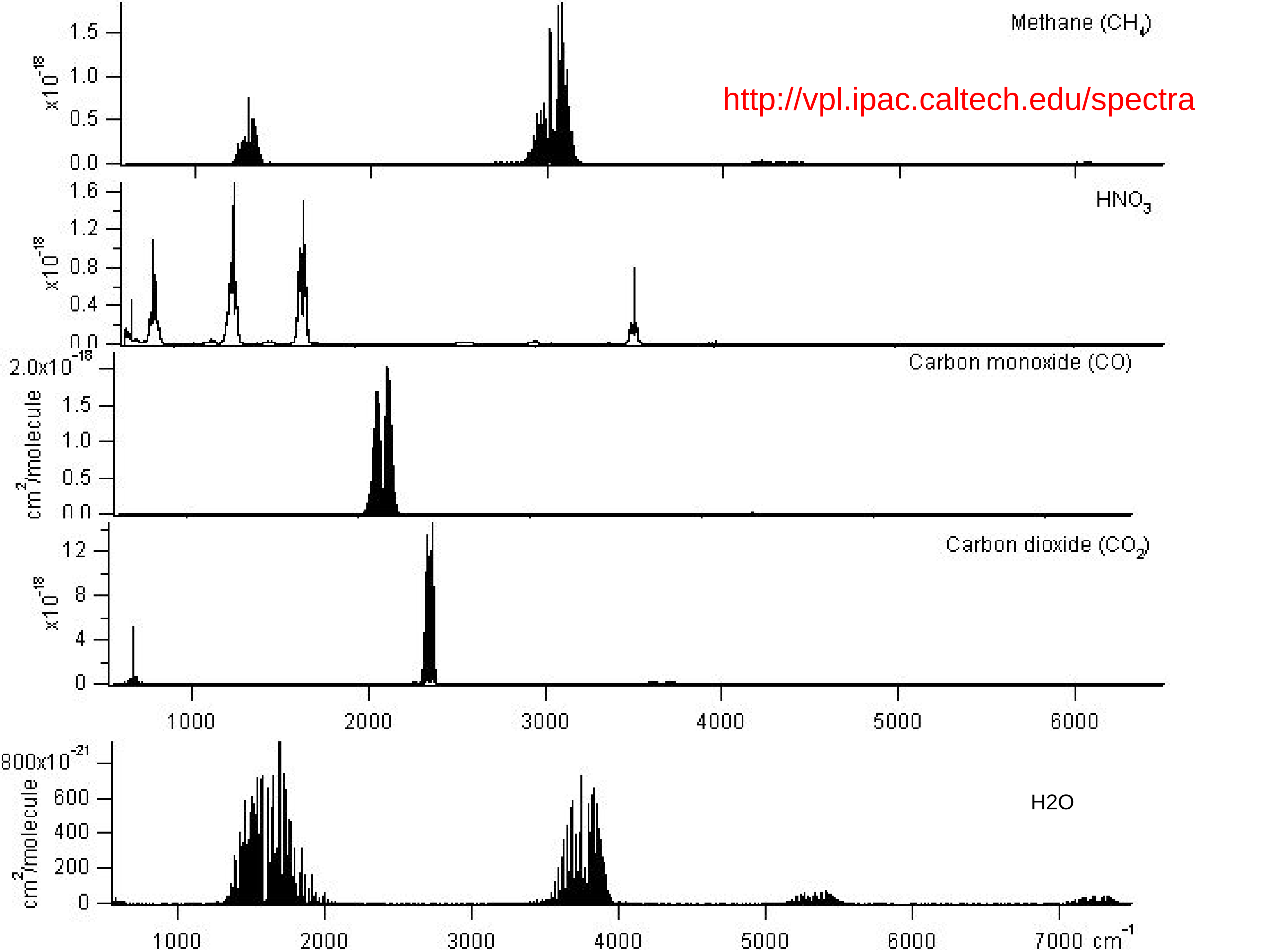
- Trace gas spectra
- Instrument type
- Interference by other species
- Contamination (clouds, aerosols...etc)
- Validation

AIRS Retrievals of Trace Gases
3ºx3º Monthly Average



SCIAMACHY Column Averaged of CH_4 over Aug-Nov (Frankenberg et al., 2005)

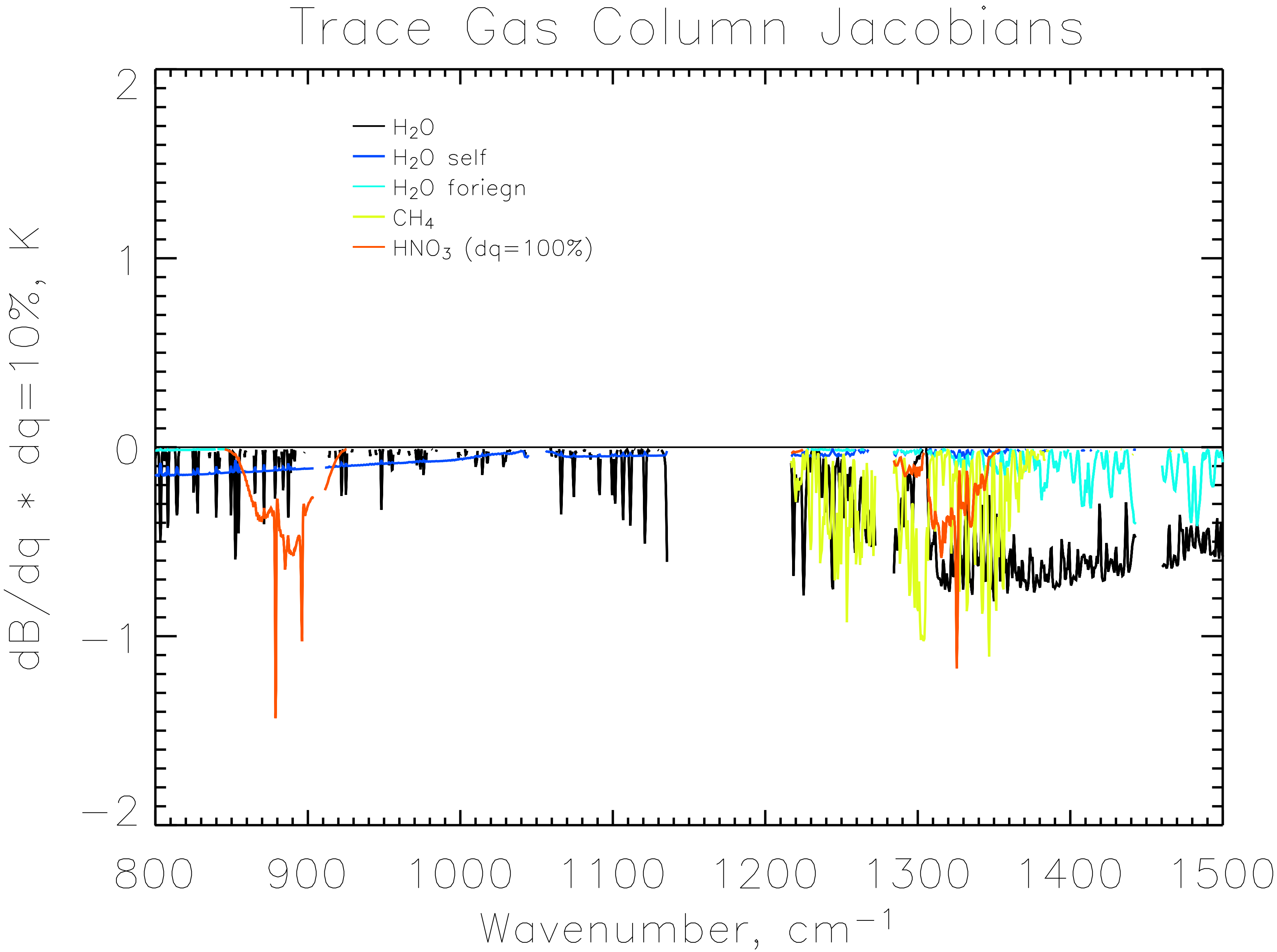




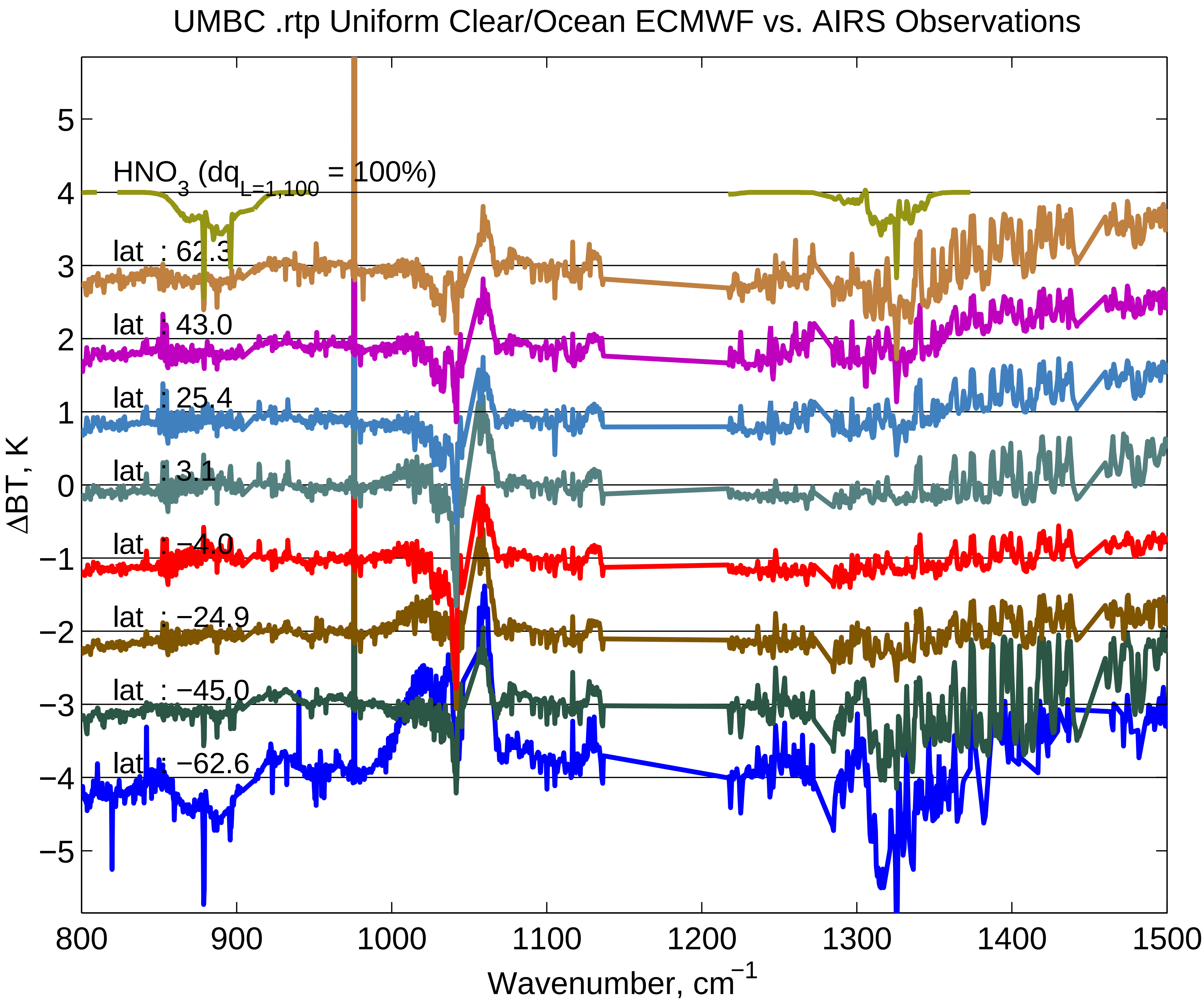
Methane (CH_4)
http://vpl.ipac.caltech.edu/spectra
HNO_3
Carbon monoxide (CO)
Carbon dioxide (CO_2)
H2O
cm^2/molecule
$x10^{-18}$
$2.0x10^{-18}$
$800x10^{-21}$
1000
2000
3000
4000
5000
6000
7000 cm^{-1}

HNO_3 interference
(Spectral overlap with H_2O and CH_4)

- Impact on surface emissivity retrieval: mainly a high latitude issue
- Affects regression (surface emissivity? over desert area?)
- CH_4/H_2O interference at poles

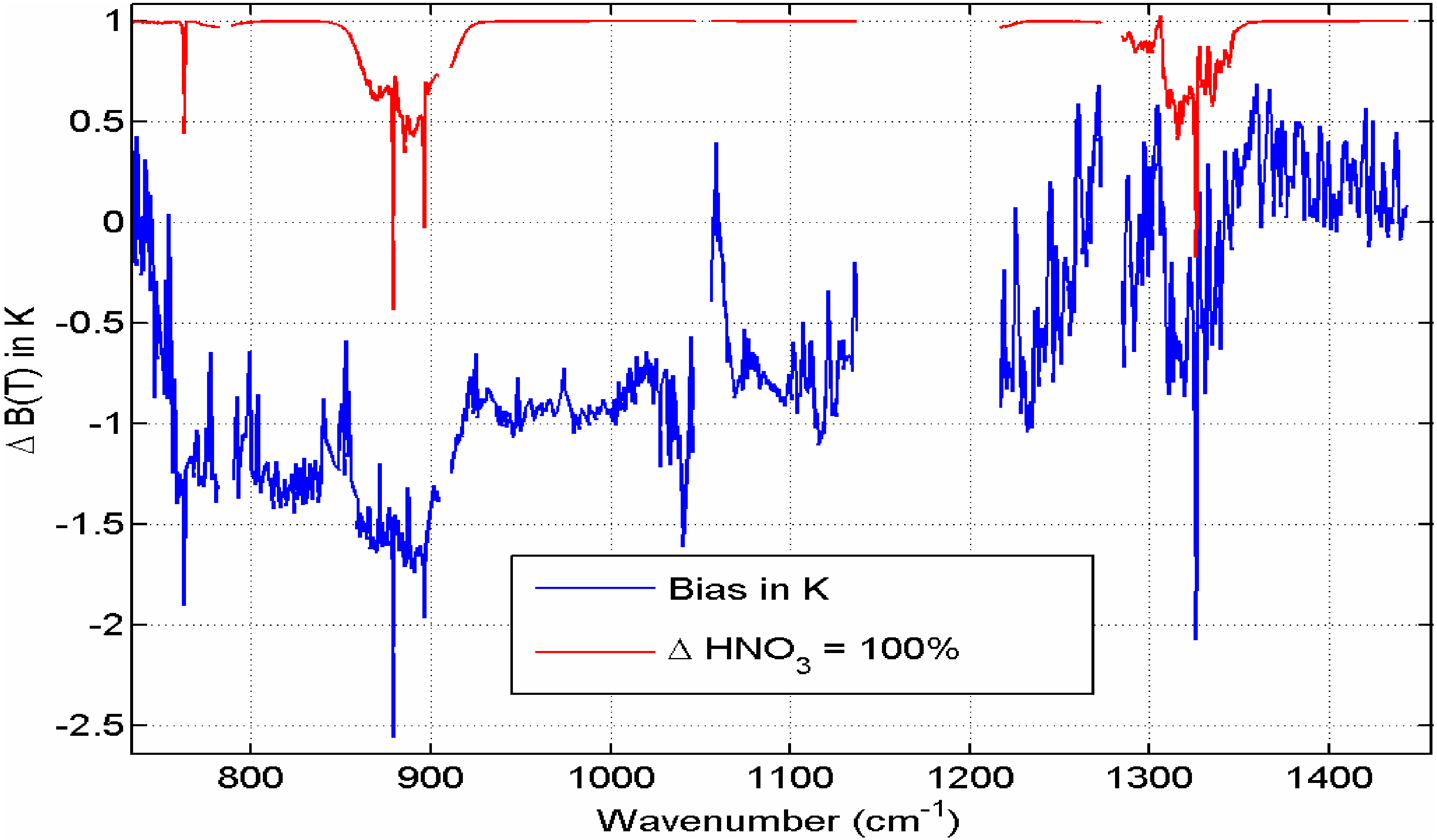


Trace Gas Column Jacobians
H_2O
H_2O self
H_2O foriegn
CH_4
HNO_3 (dq=100%)
dB/dq * dq=10%, K
2
1
0
−1
−2
800
900
1000
1100
1200
1300
1400
1500
Wavenumber, cm^{-1}

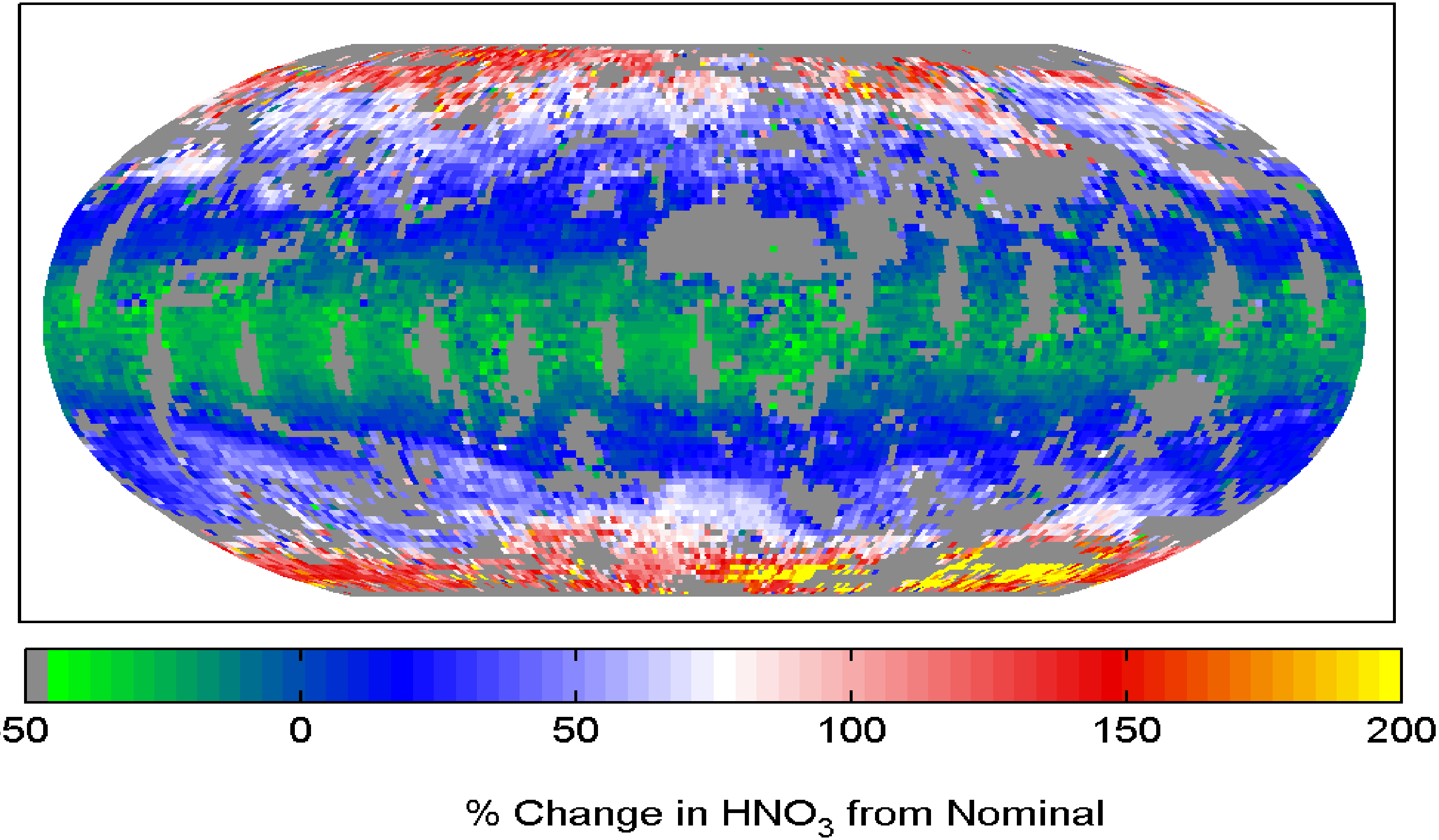


UMBC .rtp Uniform Clear/Ocean ECMWF vs. AIRS Observations
HNO$_3$ (dq$_{L=1,100}$ = 100%)
lat : 62.3
lat : 43.0
lat : 25.4
lat : 3.1
lat : −4.0
lat : −24.9
lat : −45.0
lat : −62.6
ΔBT, K
Wavenumber, cm^{-1}
5
4
3
2
1
0
−1
−2
−3
−4
−5
800
900
1000
1100
1200
1300
1400
1500

HNO_3 interference



L. L. Strow (AIRS Science Team Meeting)



L. L. Strow (AIRS Science Team Meeting)

Polar Stratospheric Clouds

The End