PHOTOCHEMISTRY OF THE EARTH'S ATMOSPHERE

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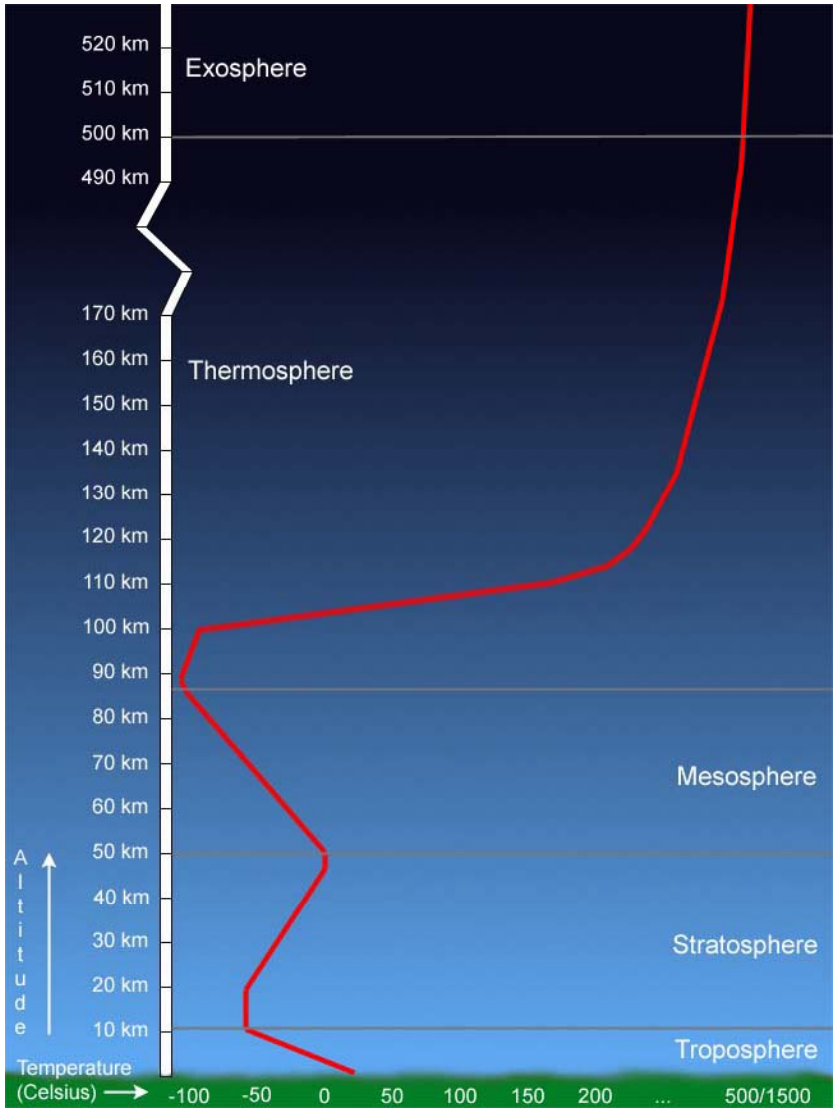
OUTLINE

- Regions of the Earth's Atmosphere – Energy sources
- What is "Photochemistry of Earth's Atmosphere" in Code 614
  - Present day
  - Ozone!!! (Biomarker)
  - Climate
  - Strong connection to observations
- Ozone photochemistry
- Atmospheric Observations (AURA)
- Ozone loss (Global)
  - Success of Montreal Protocol?
- Antarctic (Arctic?) Ozone Hole
- Ozone Recovery – Chemistry-Climate coupling
- Higher than the stratosphere – More appropriate to Earth-like exoplanets (no life)?



Note

Troposphere: Adiabatic cooling, other processes.

Stratosphere: Heating by ozone

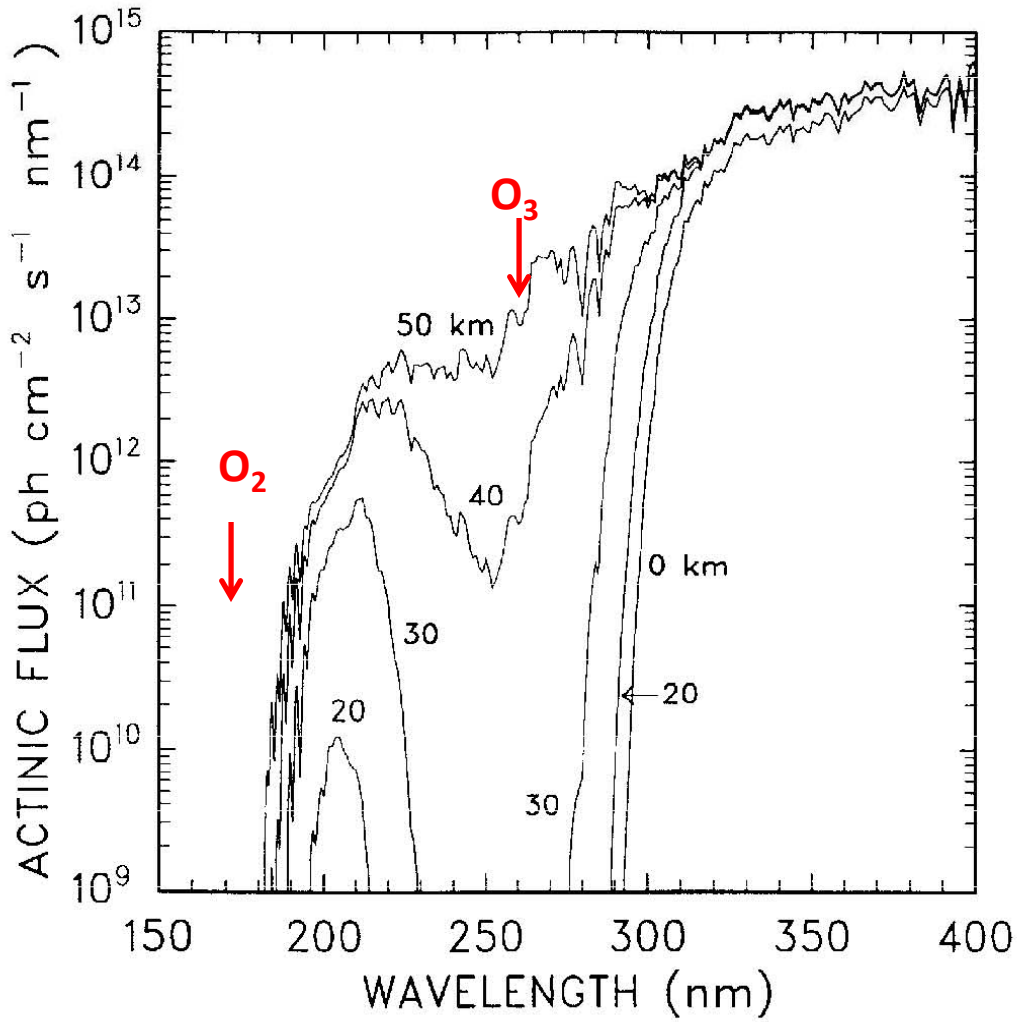
Mesosphere: No ozone heating, cooling by CO2, others.

Thermosphere: Ionization, ion-neutral reactions, energetic particles, absorption of short-wave radiation, other energy sources, ion chemistry

Exosphere: (> 500 km). Mean free path of molecules higher than scale height; molecules/atoms primarily in orbits.

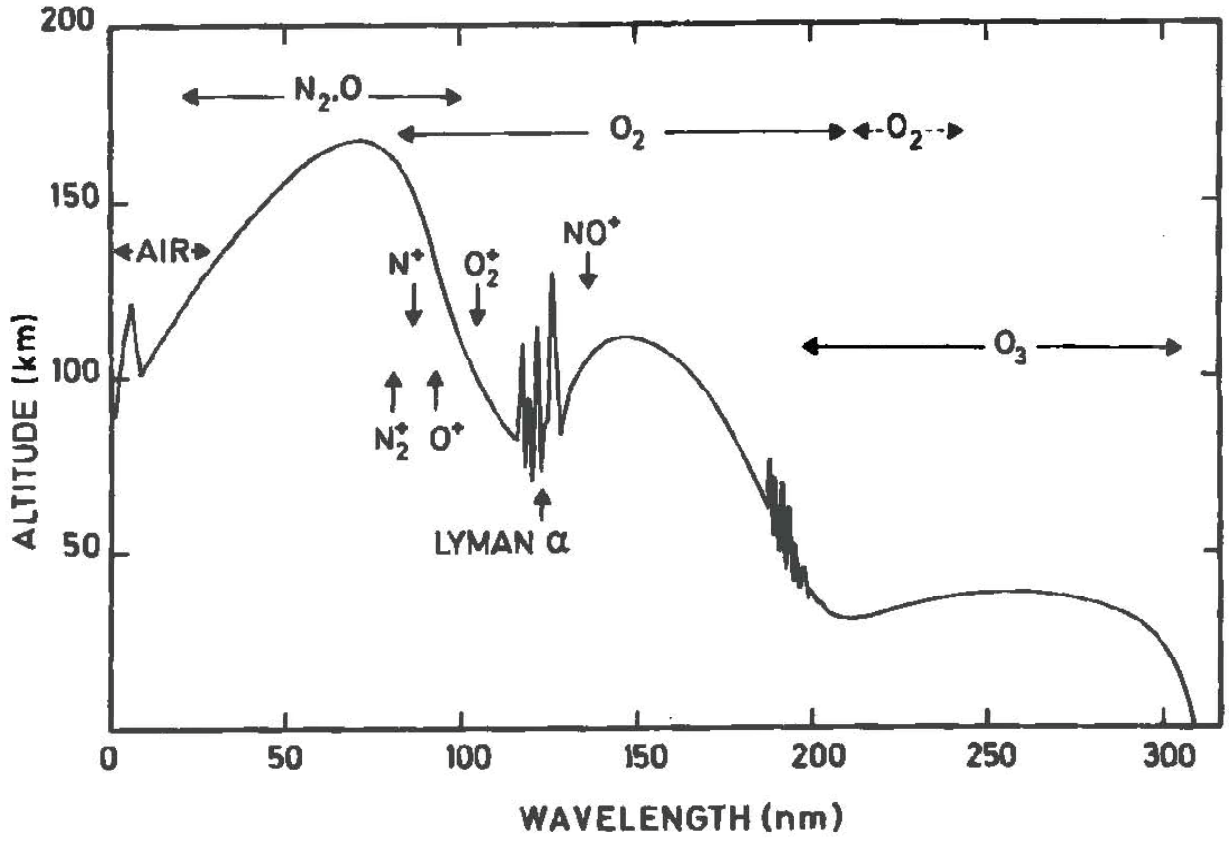
Homopause: Around 100 km. Molecular diffusion takes over.

SOLAR FLUX ATTENUATION

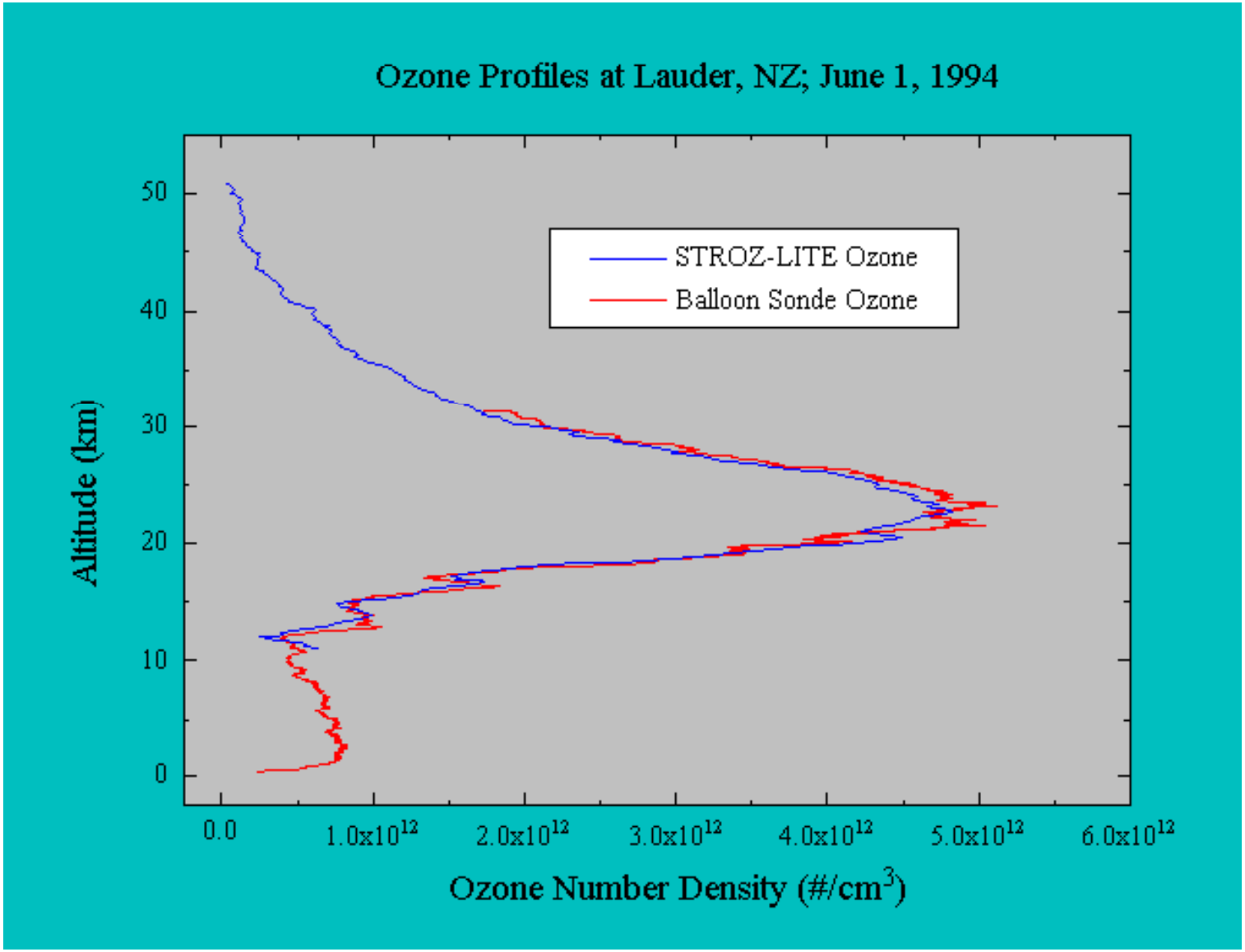


From DeMore et al., 1999

ALTITUDE OF UNIT OPTICAL DEPTH ABSORPTION AS A FUNCTION OF WAVELENGTH



From Brasseur and Solomon, 1984


Ozone Profiles at Lauder, NZ; June 1, 1994
STROZ-LITE Ozone
Balloon Sonde Ozone
Altitude (km)
0
10
20
30
40
50
0.0
1.0x10^12
2.0x10^12
3.0x10^12
4.0x10^12
5.0x10^12
6.0x10^12
Ozone Number Density (#/cm^3)

SIMPLE OZONE PHOTOCHEMISTRY

Stratospheric Ozone

- Production

$$O_2 + h\nu\ (\lambda < 240\ \mathrm{nm}) \rightarrow O + O$$

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

- Destruction by Catalytic Cycles
  - Chapman Cycle

$$O + O_3 \rightarrow 2\ O_2$$

Stratospheric Ozone (II)

- **HOx cycle**

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$2O_3 \rightarrow 3\,O_2$$

NOTE: OH, HO_2 (HOx) from H_2O (reaction with O^1D)

- **NOx cycle (anthropogenic influence, supersonic aircraft, N_2O)**

$$NO + O3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$

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

NOTE: NO, NO_2 (NOx) from N_2O, aircraft, lightning

Stratospheric Ozone (III)

- **Halogen Cycles (anthropogenic impact through emissions of CFCs, Halons, others).**

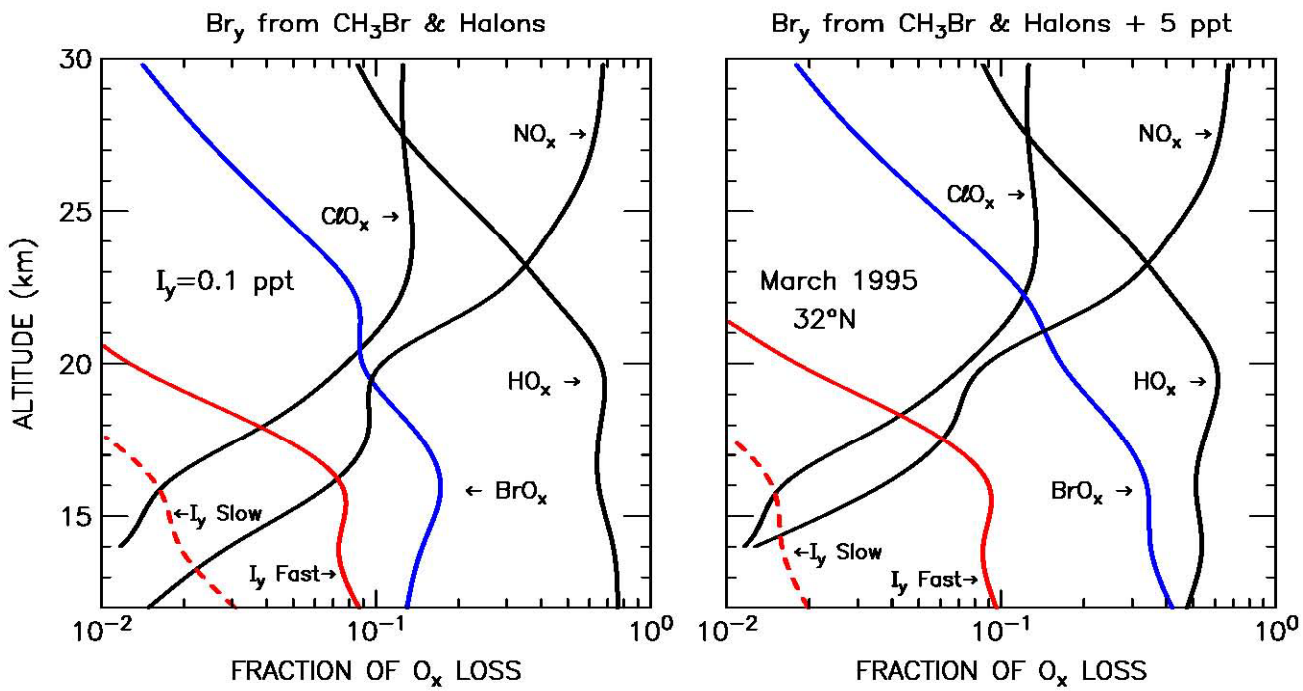
$$Cl\ (Br) + O_3 \rightarrow Cl\ (Br)O + O_2$$
$$Cl\ (Br)O + O \rightarrow Cl\ (Br) + O_2$$

$$O + O_3 \rightarrow 2\ O_2$$

$$Cl\ (Br) + O_3 \rightarrow Cl\ (Br)\ O + O_2$$
$$OH + O_3 \rightarrow HO_2 + O_2$$
$$Cl(Br)O + HO_2 \rightarrow HOCl(Br) + O_2$$
$$HOCl\ (Br) + h\nu \rightarrow Cl(Br) + OH$$

$$2\ O_3 \rightarrow 3\ O_2$$

NOTE: Chlorine from CFC, HCFC photolysis (CFC-11: $CFCl_3$, CFC-12: CF_2Cl_2
Bromine from methyl bromide (CH_3Br), Halons: Halon 1211 (CF_2ClBr)
Halon 1301 ($CBrF_3$)


Br$_y$ from CH$_3$Br & Halons
Br$_y$ from CH$_3$Br & Halons + 5 ppt
ALTITUDE (km)
30
25
20
15
I$_y$=0.1 ppt
March 1995
32°N
NO$_x$ →
ClO$_x$ →
HO$_x$ →
← BrO$_x$
BrO$_x$ →
←I$_y$ Slow
I$_y$ Fast→
10^{-2}
10^{-1}
10^{0}
FRACTION OF O$_x$ LOSS

WMO, 2006

MODELS

Photochemical Modeling: Chemical-Transport Model

Simple, just solve the mass continuity equation for all species of interest;

$$\frac{\partial n_i}{\partial t} = -\frac{\partial F_{x,i}}{\partial x} - \frac{\partial F_{y,i}}{\partial y} - \frac{\partial F_{z,i}}{\partial z} + P_i - L_i$$

$$= -\nabla \bullet (n_i U) + P_i - L_i - \nabla \bullet (F_{diff,i})$$

Subscript i denotes each species of interest. F_{diff} denotes all fluxes that are not represented by large-scale advection.

In a CTM, the large-scale fields, turbulent fluxes, convective fluxes, etc. are read from archived GCM calculation or data assimilation (GEOS-5). Current configuration (GMI CTM) has 72 (alt) x 91 (lat) x 144 (long) grid points

Note that the above represent, in principle, a large number of coupled equations, the occurring through chemical reactions, photolysis processes. GMI: 120 species, 341 chemical reactions, 81 photolysis processes.

Simplifications

- **Two-dimensional (for approximate symmetry around one of the dimensions? For example, longitude on Earth stratosphere. Tidally-locked planet?**

$$\frac{\partial f_i}{\partial t} + \bar{U} \bullet \nabla f_i = \frac{1}{n} \nabla \bullet (n\mathbf{K} \bullet \nabla f_i) + P_i - L_i$$

where f_i is the volume mixing ratio, U an "effective" advective velocity, n the Background density, and K an "eddy diffusion" tensor.

Note that derivation of "effective" velocity and eddy tensor requires careful averaging and consideration of dynamics

Simplifications (II)

- **If there is not sufficient multi-dimensional information, one can use a one-dimensional version:**

$$\frac{\partial n_i}{\partial t} = -\frac{\partial}{\partial z}(F_{turb,diff}) + P_i - L_i$$

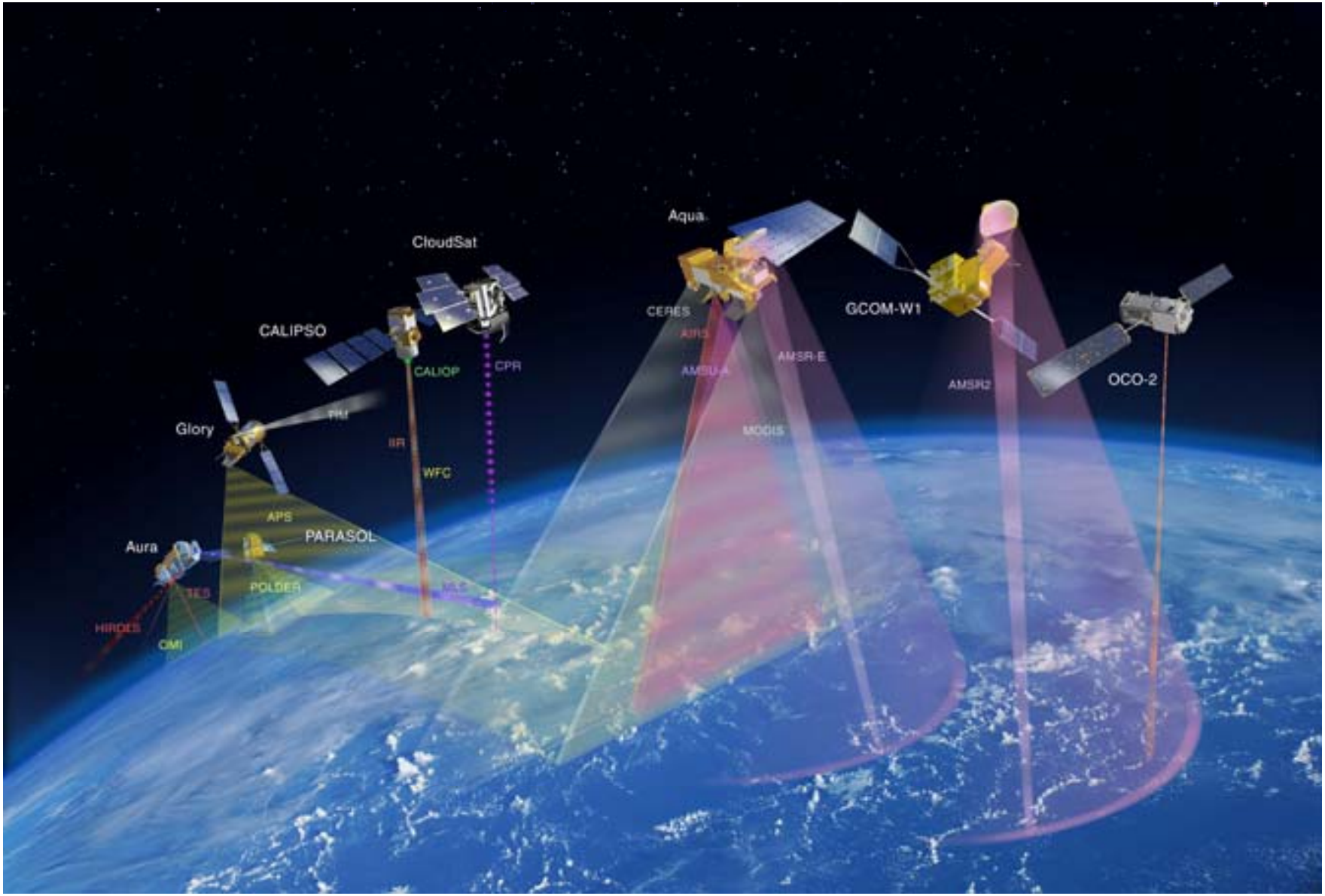
$$F_{turb,diff} = -D_i\left(\frac{\partial n_i}{\partial z} + \frac{n_i}{H_i} + \frac{1+\alpha_T}{T}\frac{dT}{dz}n\right) - K\left(\frac{\partial n_i}{\partial z} + \frac{n_i}{H_a} + \frac{1}{T}\frac{dT}{dz}n\right)$$

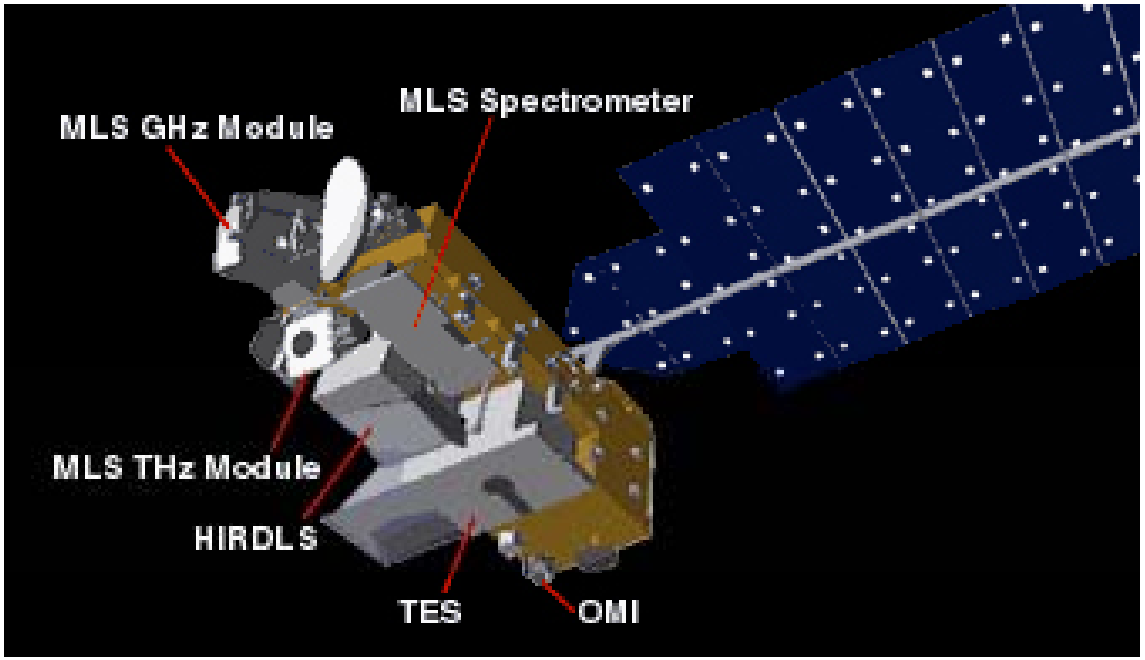
Where D_i = molecular diffusion coefficient for species I
H_i, H_a = scale heights for species i and background atmosphere
α_T = thermal diffusivity coefficient
K = Eddy diffusion coefficient (mostly parameterized)

ATMOSPHERIC OBSERVATIONS

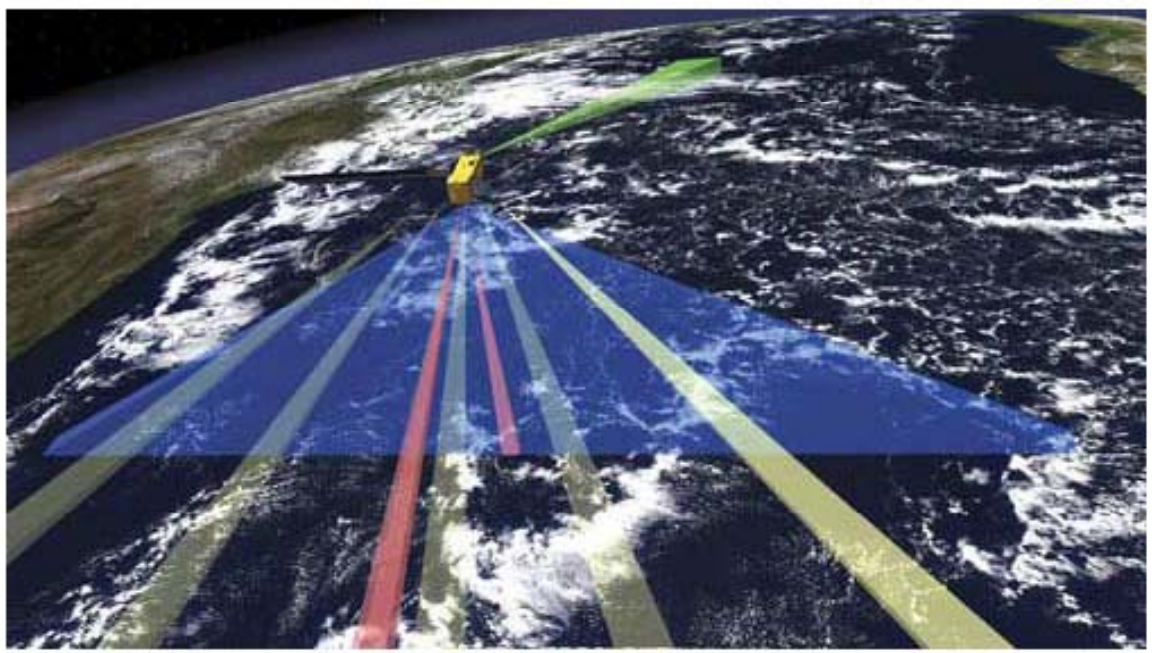
- GROUND BASED
  - IN-SITU
  - LIDAR
- BALLOONS
- AIRCRAFT
- SATELLITE

THE NASA A-TRAIN





AURA



Green: MLS
Blue: OMI swath
Pink: TES (nadir, limb)
HIRDLS: yellow

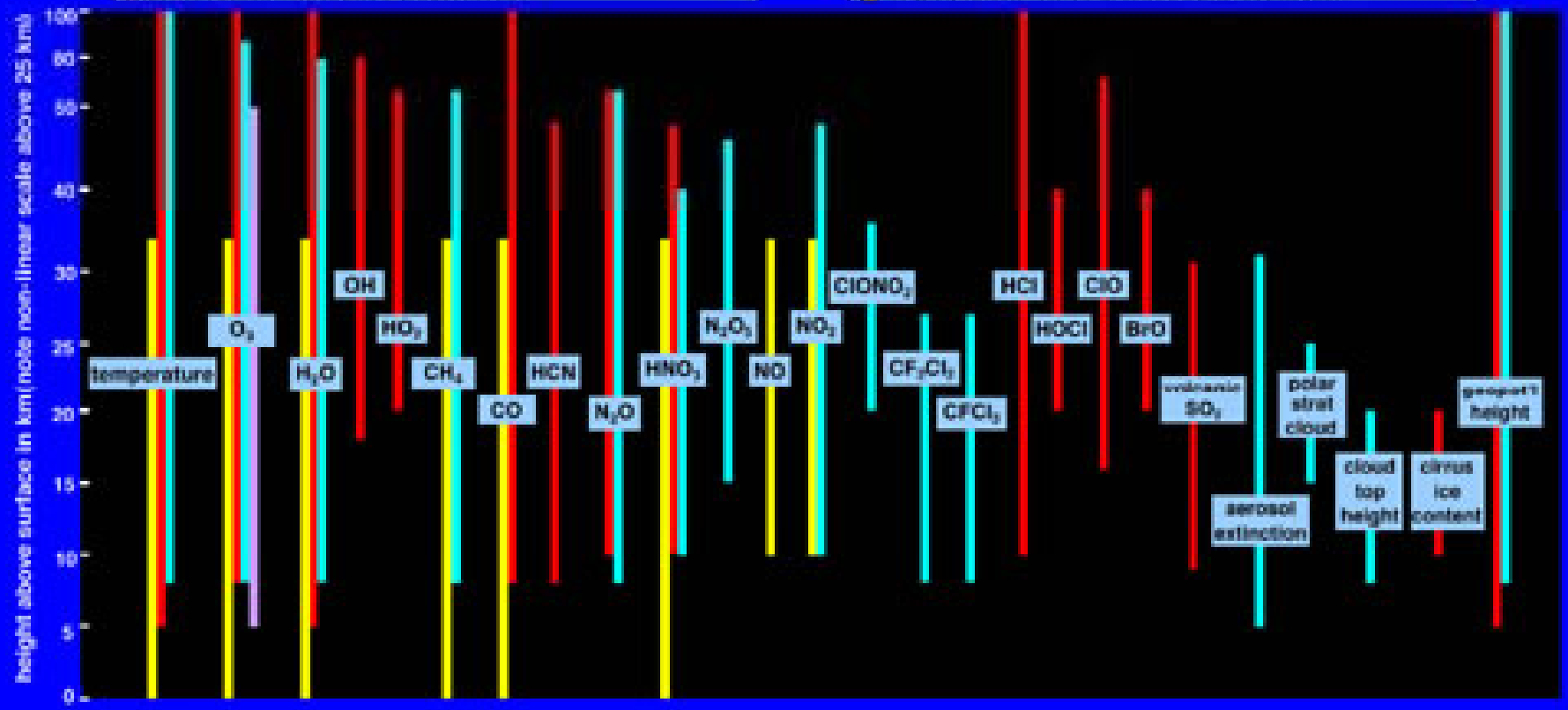
TABLE I
AURA INSTRUMENTS AND MEASUREMENTS

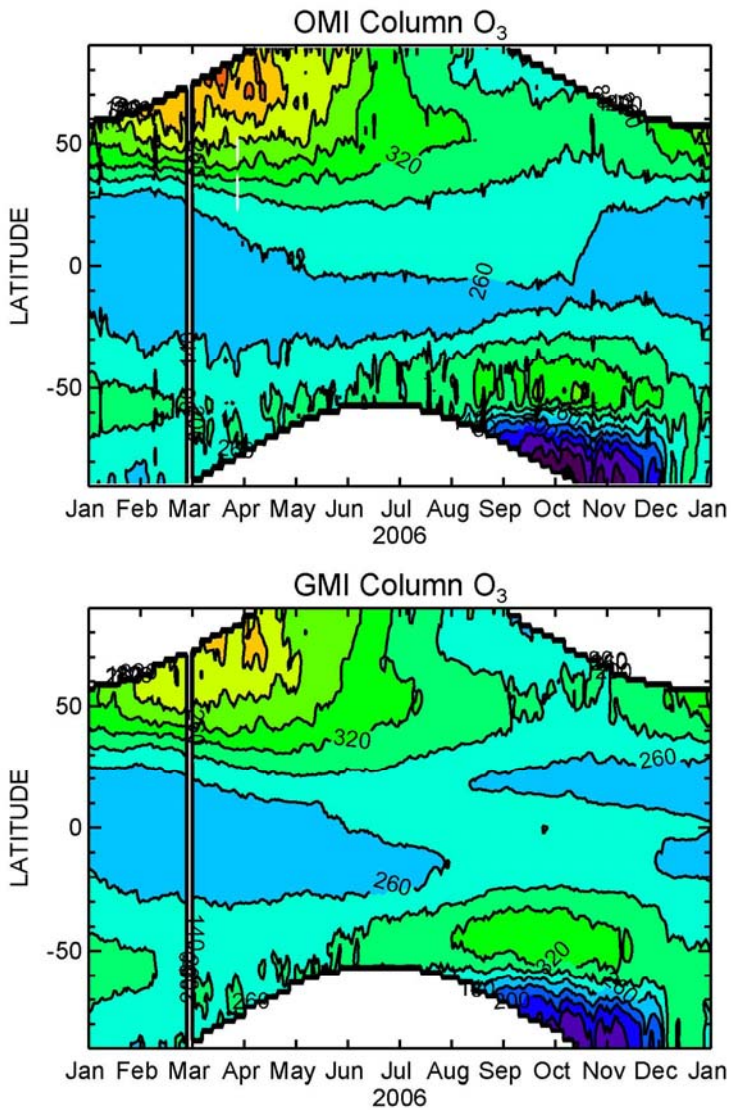
Acronym	Name	Instrument PI	Constituent	Instrument Description
HIRDLS	High Resolution Dynamics Limb Sounder	John Gille, National Center for Atmospheric Research & U. of Colorado; John Barnett, Oxford University	Profiles of T , O_3, H_2O, CH_4, N_2O, NO_2, HNO_3, N_2O_5, CF_3Cl, CF_2Cl_2, $ClONO_2$, Aerosols	Limb IR filter radiometer from 6.2μ to 17.76μ 1.2 km vertical resolution up to 50 km.
MLS	Microwave Limb Sounder	Joe Waters, Jet Propulsion Laboratory	Profiles of T, H_2O, O_3, ClO, BrO, HCl, OH, HO_2, HNO_3, HCN, N_2O, CO, cloud ice.	Microwave limb sounder 118 GHz to 2.5 THz 1.5-3 km vertical resolution
OMI	Ozone Monitoring Instrument	Pieternel Levelt, KNMI, Netherlands	Column O_3, SO_2, aerosols, NO_2, BrO, OClO. HCHO, cloud top pressure, O_3 profiles, UV-B.	Hyperspectral nadir imager, 114° FOV, 270-500 nm, 13x24 km footprint for ozone and aerosols
TES	Tropospheric Emission Spectrometer	Reinhard Beer, Mike Gunson, Jet Propulsion Laboratory	Profiles of T, O_3, NO_2, CO, HNO_3, CH_4, H_2O.	Limb (to 34 km) and nadir IR Fourier transform spectrometer 3.2-15.4μ Nadir footprint 5.3x8.5 km, limb 2.3 km

EOS Aura Atmospheric Profile Measurements

OMI also measures UVB flux, cloud top/cover, and column abundances of O_3, NO_2, BrO, aerosol and volcanic SO_2

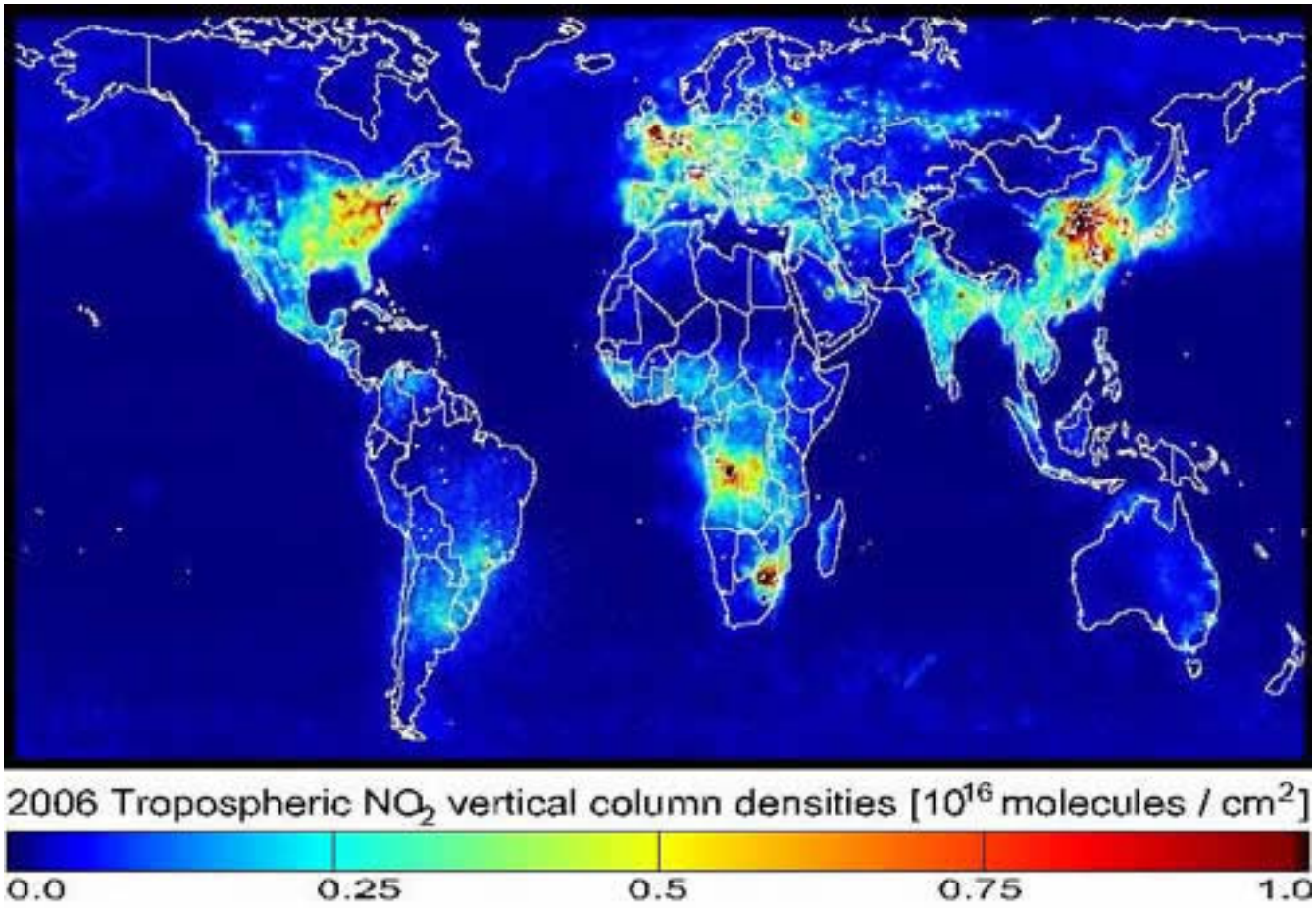
TES also measures several additional 'special products' such as $ClONO_2$, CF_2Cl_2, $CFCl_3$, N_2O and volcanic SO_2



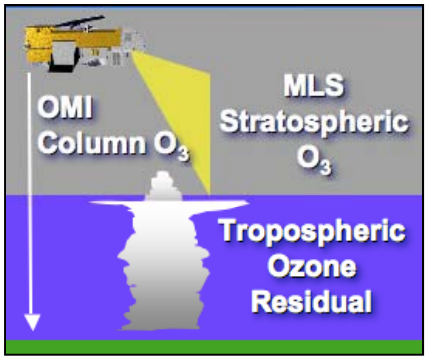


GMI: CTM driven by GEOS-5 assimilated meteorology for 2006; (Rodriguez, Strahan)

OMI NO2 TROPOSPHERIC VERTICAL COLUMN



Tropospheric Ozone from OMI-MLS



Tropospheric (lower atmosphere) ozone is a toxic pollutant and an EPA criteria pollutant. As industrialization increases, pollutants flow from one country to another and from one continent to another.

For the first time we are getting a clear picture of this ozone transport by combining ozone measurements of the stratosphere and the total column to produce the tropospheric amount.

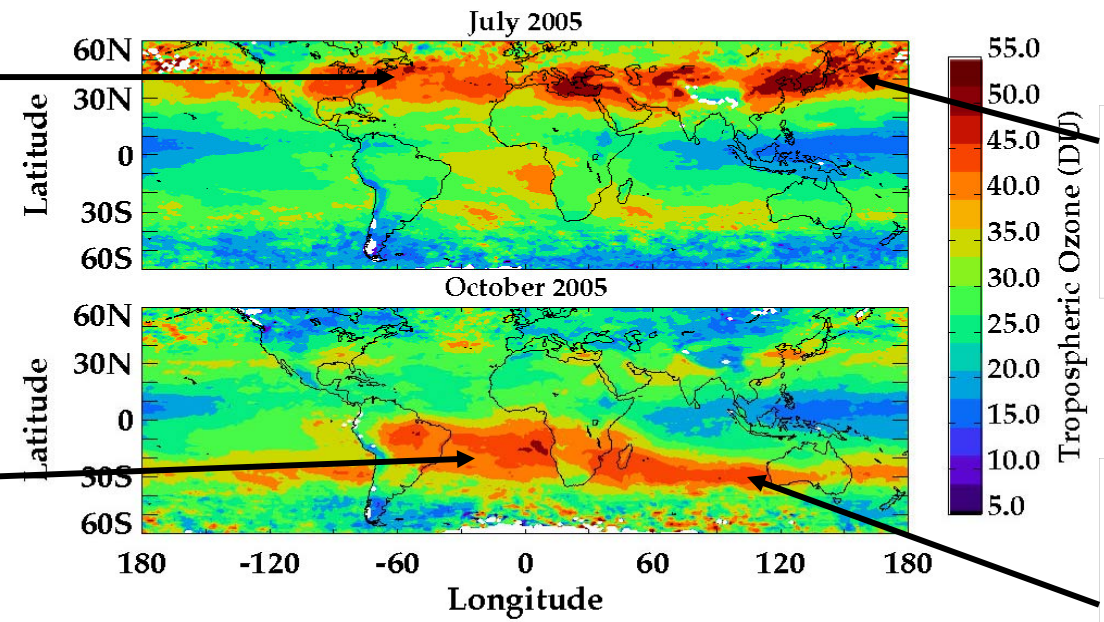
Monthly average July and October 2005

Pollution from North America reaches Europe

Pollution from China reaches North America

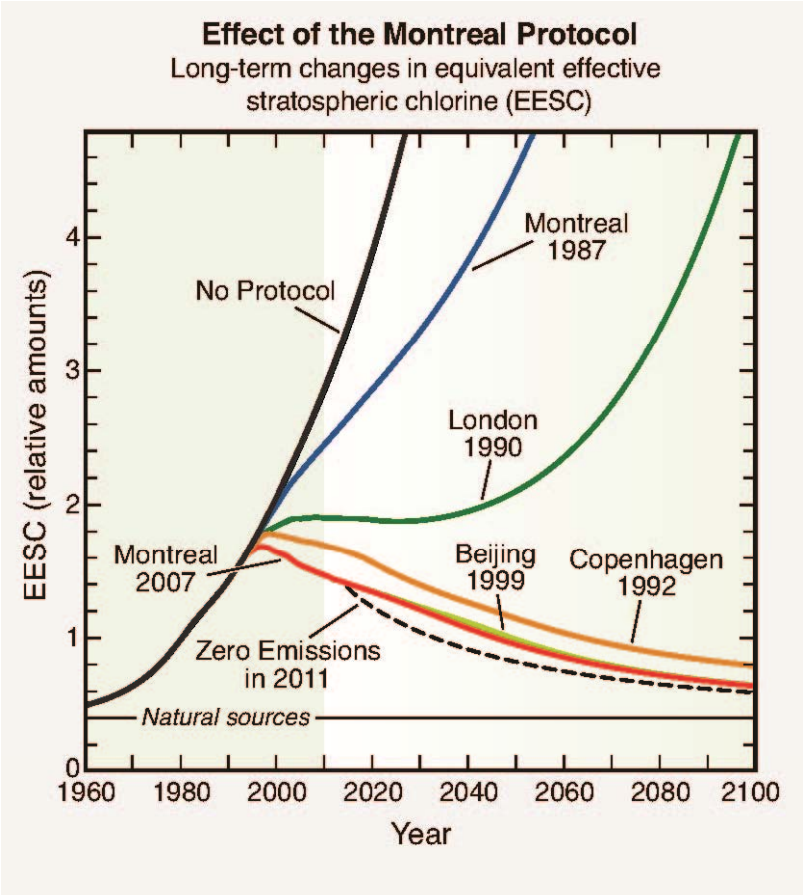
Pollution from Africa and South America fills the South Atlantic

Pollution from Africa spreads to Australia

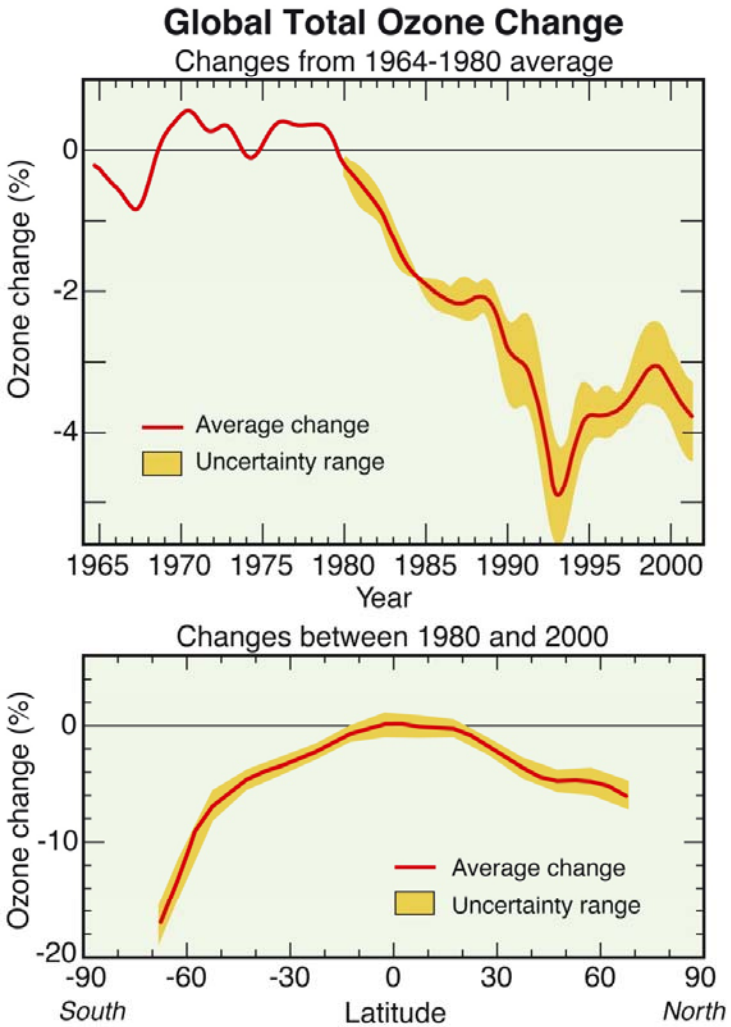


Global maps of tropospheric ozone showing effects of pollution in the Northern Hemisphere in summer and biomass burning in Southern Hemisphere in spring

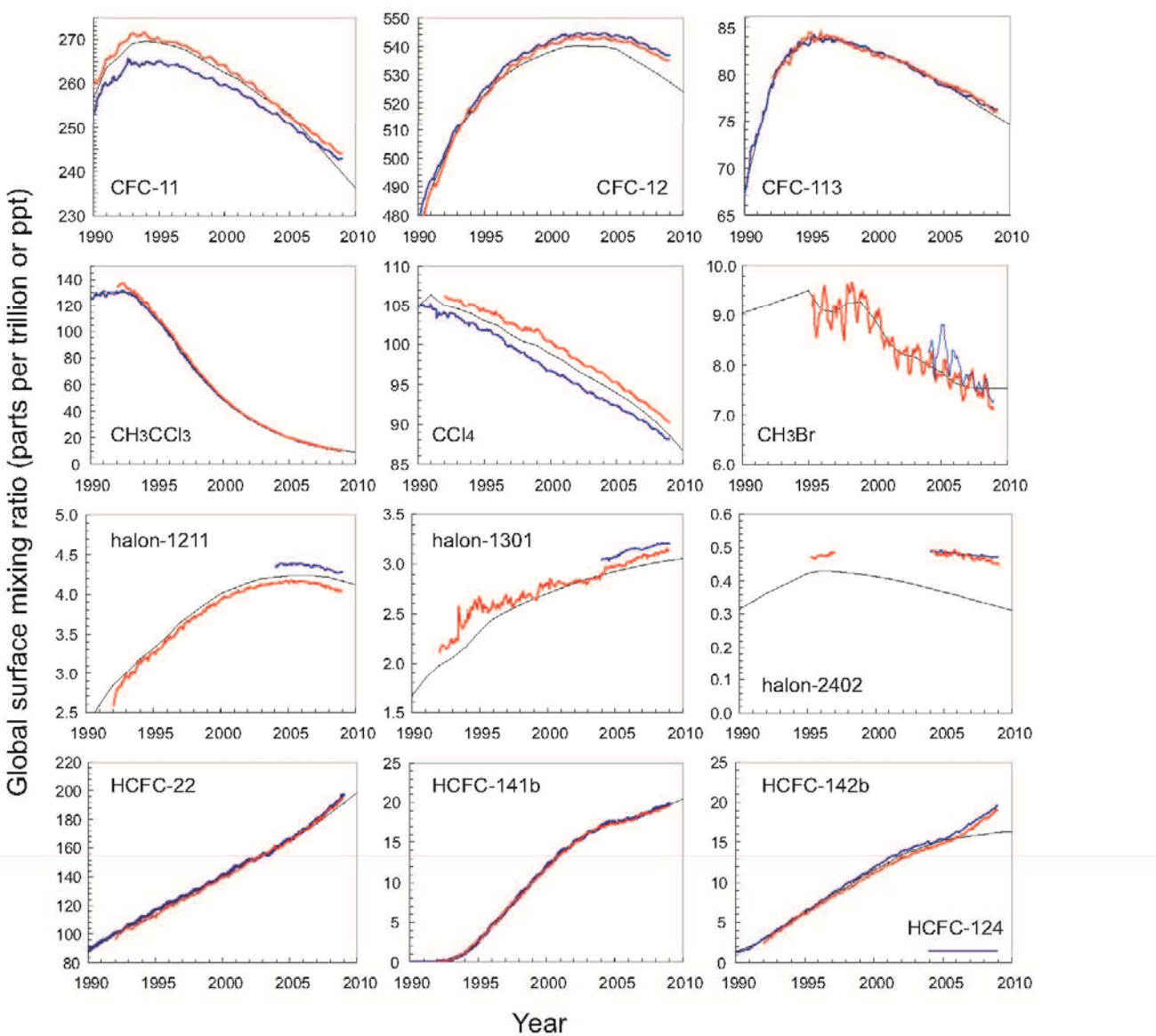
STRATOSPHERIC OZONE LOSS: GLOBAL


Effect of the Montreal Protocol
Long-term changes in equivalent effective stratospheric chlorine (EESC)
EESC (relative amounts)
0
1
2
3
4
1960
1980
2000
2020
2040
2060
2080
2100
Year
No Protocol
Montreal 1987
London 1990
Montreal 2007
Beijing 1999
Copenhagen 1992
Zero Emissions in 2011
Natural sources

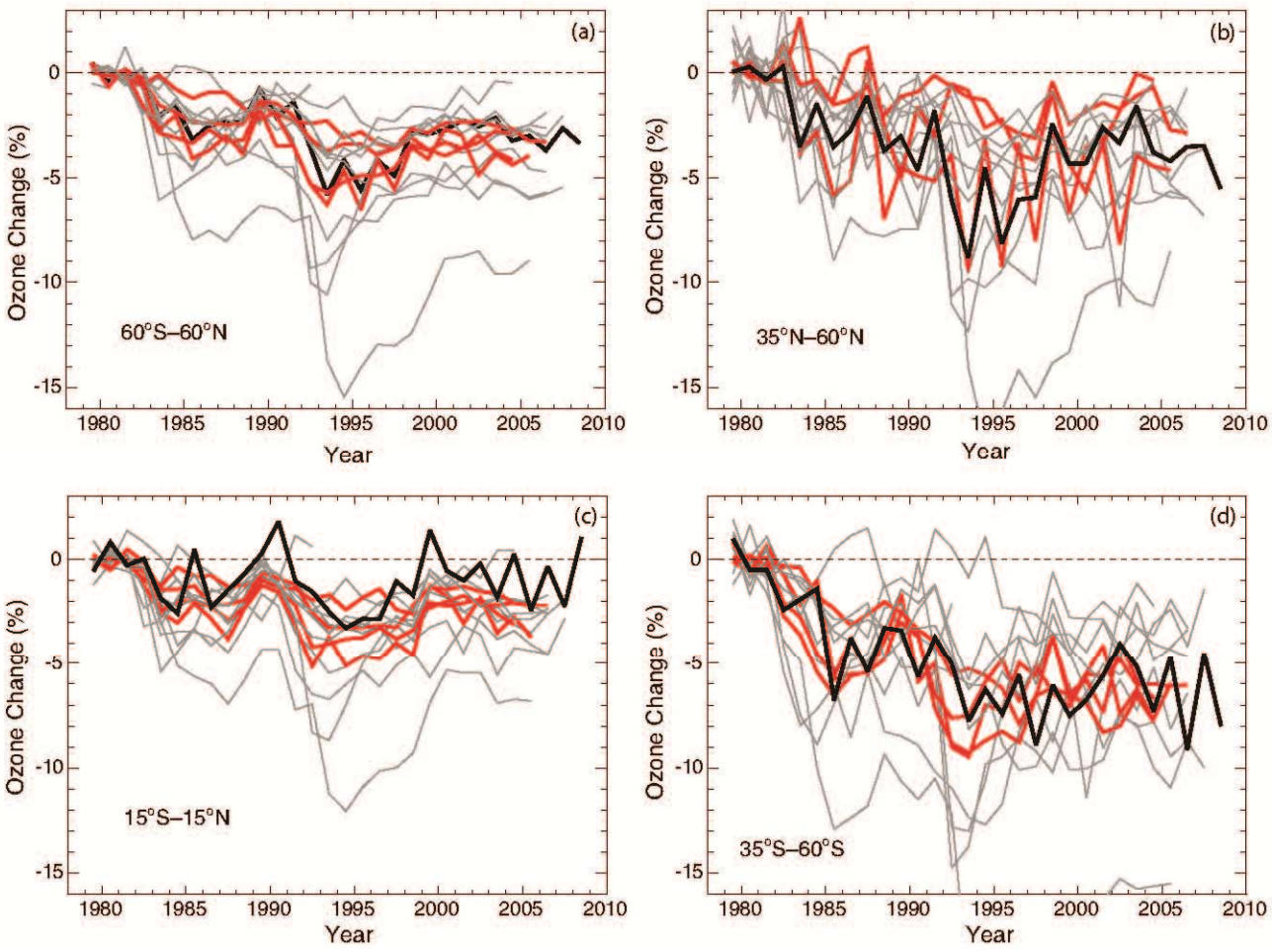
WMO, 2010


Global Total Ozone Change
Changes from 1964-1980 average
Ozone change (%)
0
-2
-4
Average change
Uncertainty range
1965 1970 1975 1980 1985 1990 1995 2000
Year
Changes between 1980 and 2000
Ozone change (%)
0
-10
-20
Average change
Uncertainty range
-90 -60 -30 0 30 60 90
South
Latitude
North

WMO, 2010



Ground-based measurements from NOAA network (red), AGAGE (blue). Historical scenario in black (WMO, 2012)



WMO, 2010; Measurements in black. “Best models” in red.

STRATOSPHERIC OZONE LOSS: ANTARCTIC OZONE HOLE (ARCTIC)

THE OZONE HOLE "NATURAL" CONSPIRACY

- Temperature gradients between Antarctica and mid-latitudes set up a circumpolar vortex starting in Antarctic winter. Vortex isolates Antarctica, making it colder.
- Cold temperatures facilitate formation of Polar Stratospheric Clouds
  - Some are water ice, but mostly Nitric Acid Trihydrate (NAT; crystal) and supercooled sulfate ternary solutions (STS, liquid).
- Heterogeneous reactions take place on PSCs which radically alter the partitioning of chlorine species towards more active chlorine.
- Fast catalytic cycles for O_3 destruction ensue
- As an extra, PSCs containing nitric acid grow very large and sediment out of stratosphere – This "denitrification" prevents formation of NOx from photolysis of HNO_3, which keeps active chlorine for a longer period.
- Same processes in Arctic, but vortex more unstable.

PSCs photographed from Kiruna, Sweden, February (Salawitch?)

Heterogeneous Reactions

- $ClNO_3 + HCl\ (psc) \longrightarrow Cl_2 + HNO_3\ (psc)$
- $ClNO_3 + H_2O\ (psc) \longrightarrow HOCl + HNO_3\ (psc)$
- $HOCl + HCl\ (psc) \longrightarrow Cl_2 + H_2O\ (psc)$

Ozone Destruction Cycles

Cycle 2

$$ClO + ClO \rightarrow (ClO)_2$$

$$(ClO)_2 + \text{sunlight} \rightarrow ClOO + Cl$$

$$ClOO \rightarrow Cl + O_2$$

$$2(Cl + O_3 \rightarrow ClO + O_2)$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

Cycle 3

$$ClO + BrO \rightarrow Cl + Br + O_2$$

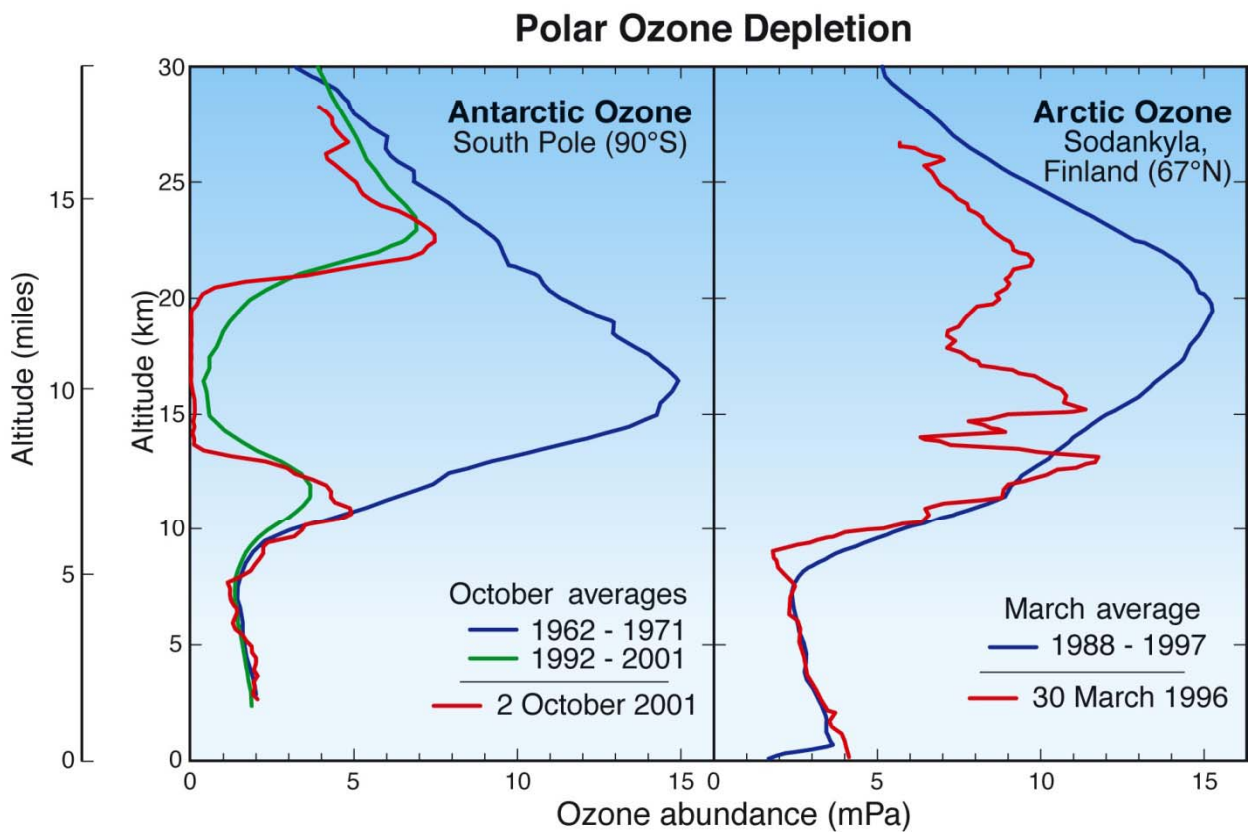
or

$$\left(\begin{array}{r} ClO + BrO \rightarrow BrCl + O_2 \\ BrCl + \text{sunlight} \rightarrow Cl + Br \end{array}\right)$$

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

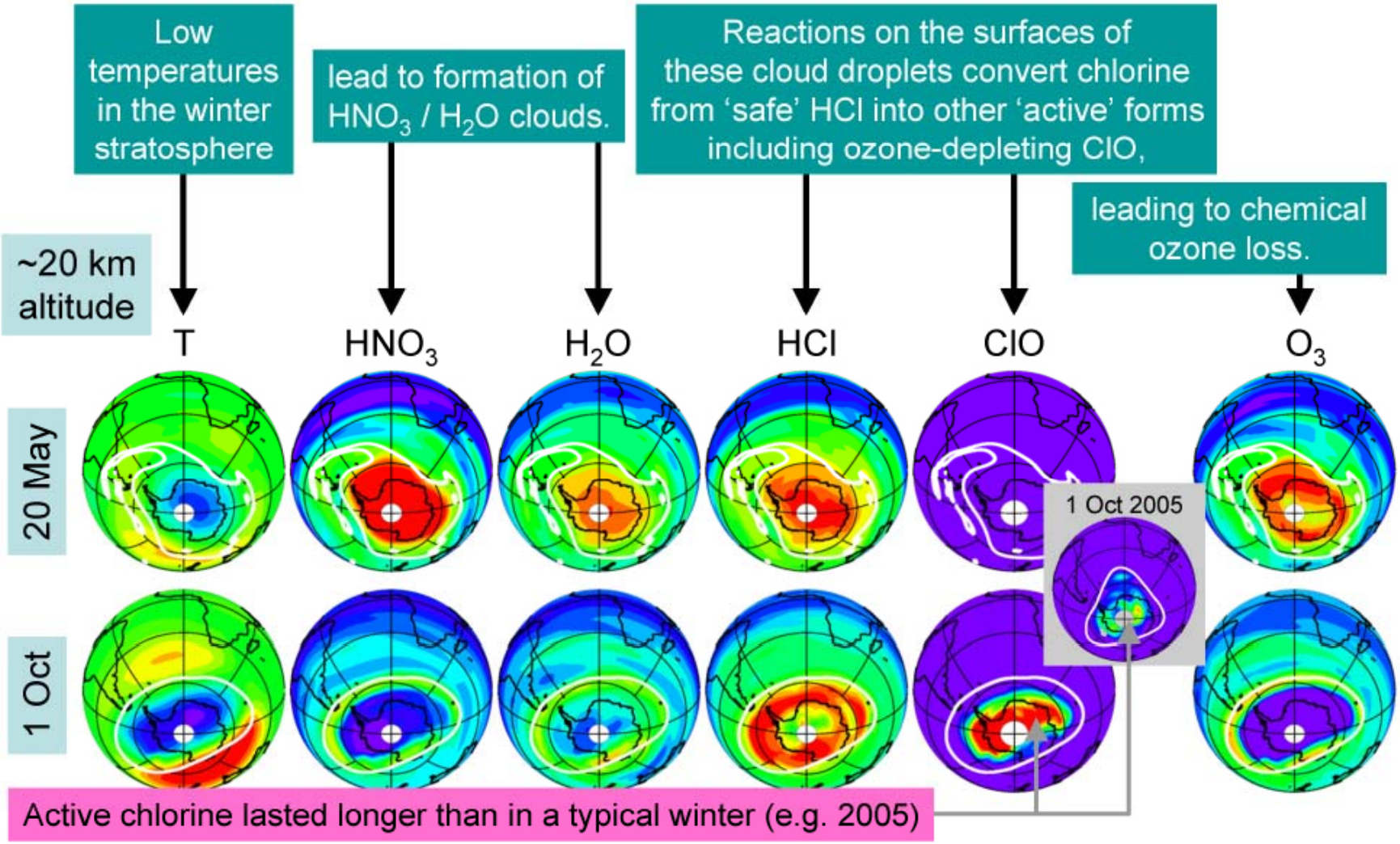
$$Br + O_3 \rightarrow BrO + O_2$$

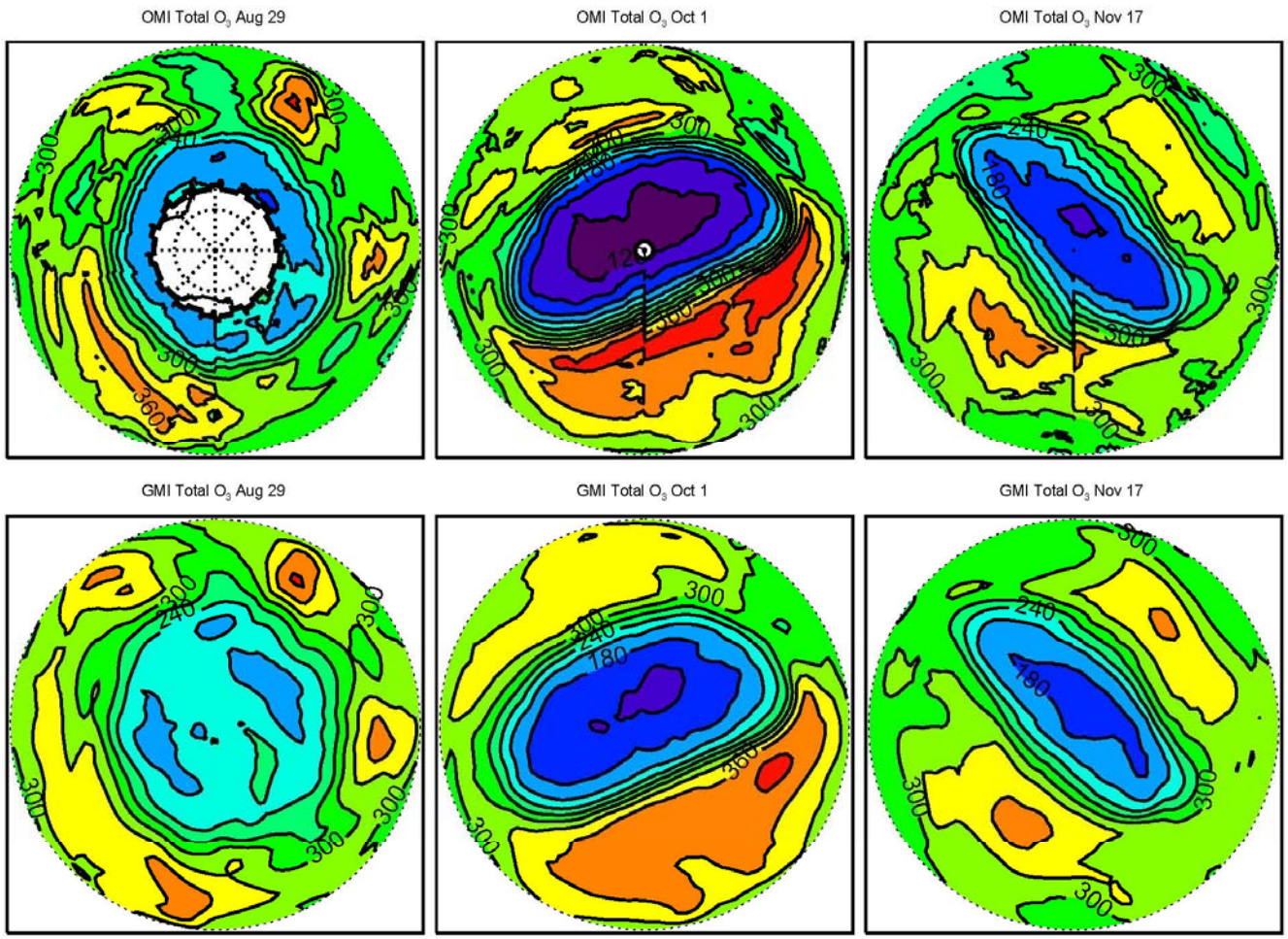
$$\text{Net: } 2O_3 \rightarrow 3O_2$$


Polar Ozone Depletion
Antarctic Ozone
South Pole (90°S)
Arctic Ozone
Sodankyla,
Finland (67°N)
October averages
1962 - 1971
1992 - 2001
2 October 2001
March average
1988 - 1997
30 March 1996
Altitude (miles)
Altitude (km)
Ozone abundance (mPa)

WMO, 2010

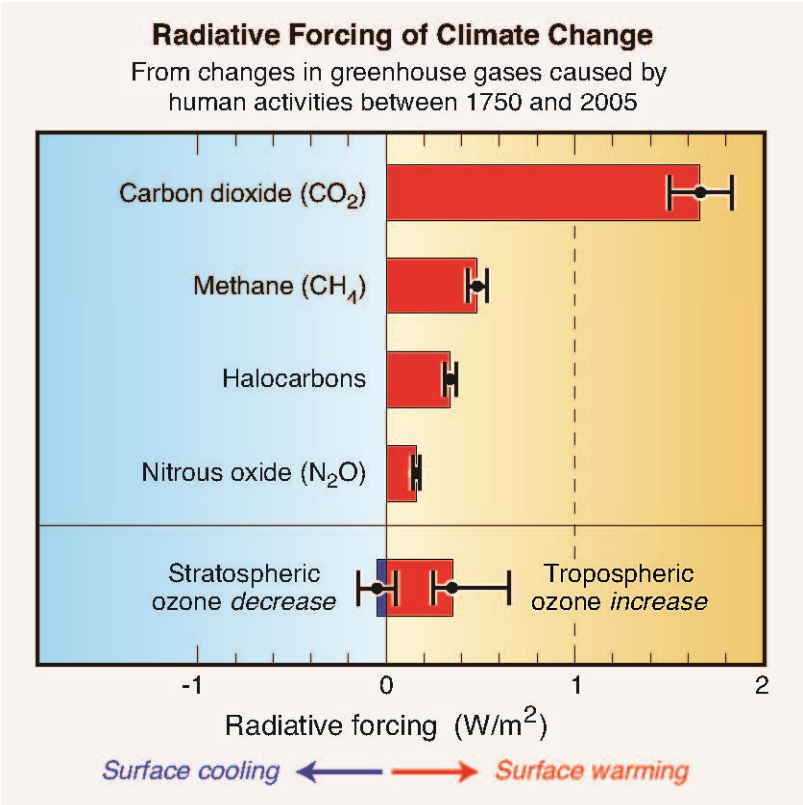
MLS VIEW OF 2006 OZONE HOLE

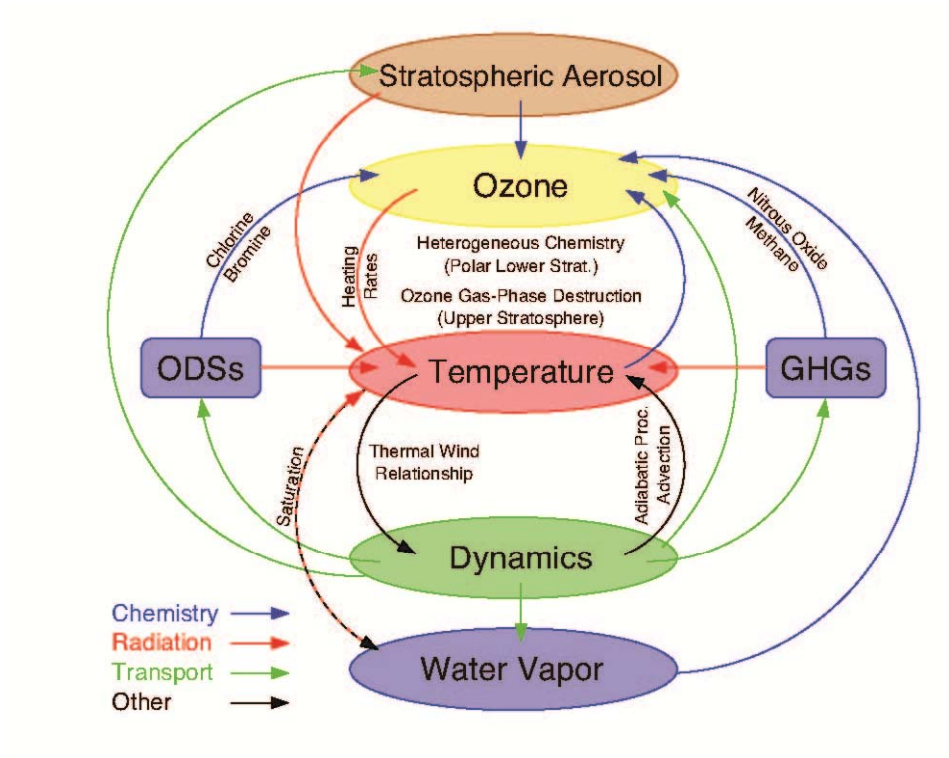




GMI driven by GEOS-5 assimilated meteorology, 2006; Strahan

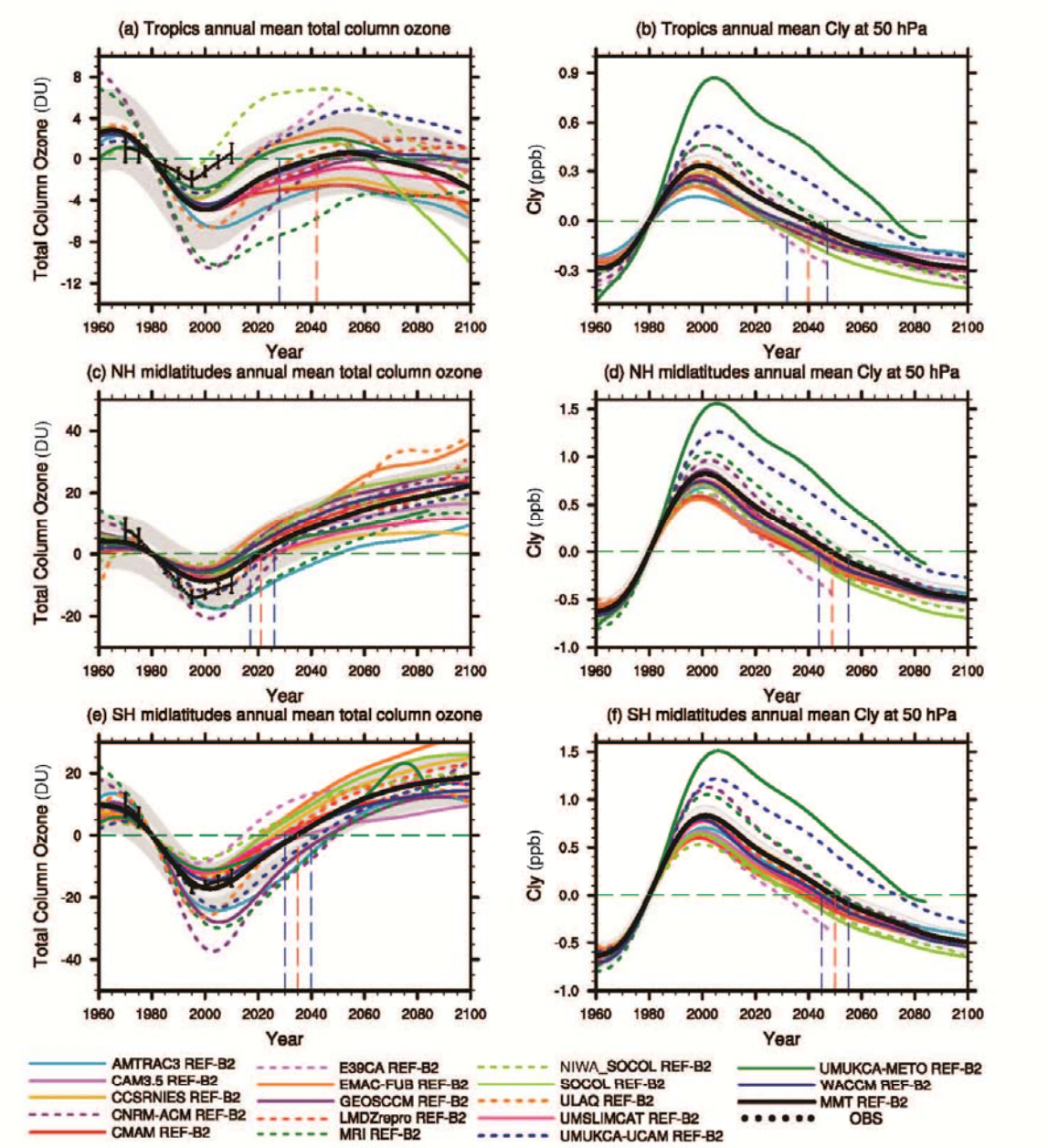
CHEMISTRY-CLIMATE COUPLING: OZONE RECOVERY


Radiative Forcing of Climate Change
From changes in greenhouse gases caused by human activities between 1750 and 2005
Carbon dioxide (CO_2)
Methane (CH_4)
Halocarbons
Nitrous oxide (N_2O)
Stratospheric ozone *decrease*
Tropospheric ozone *increase*
-1
0
1
2
Radiative forcing (W/m^2)
Surface cooling
Surface warming

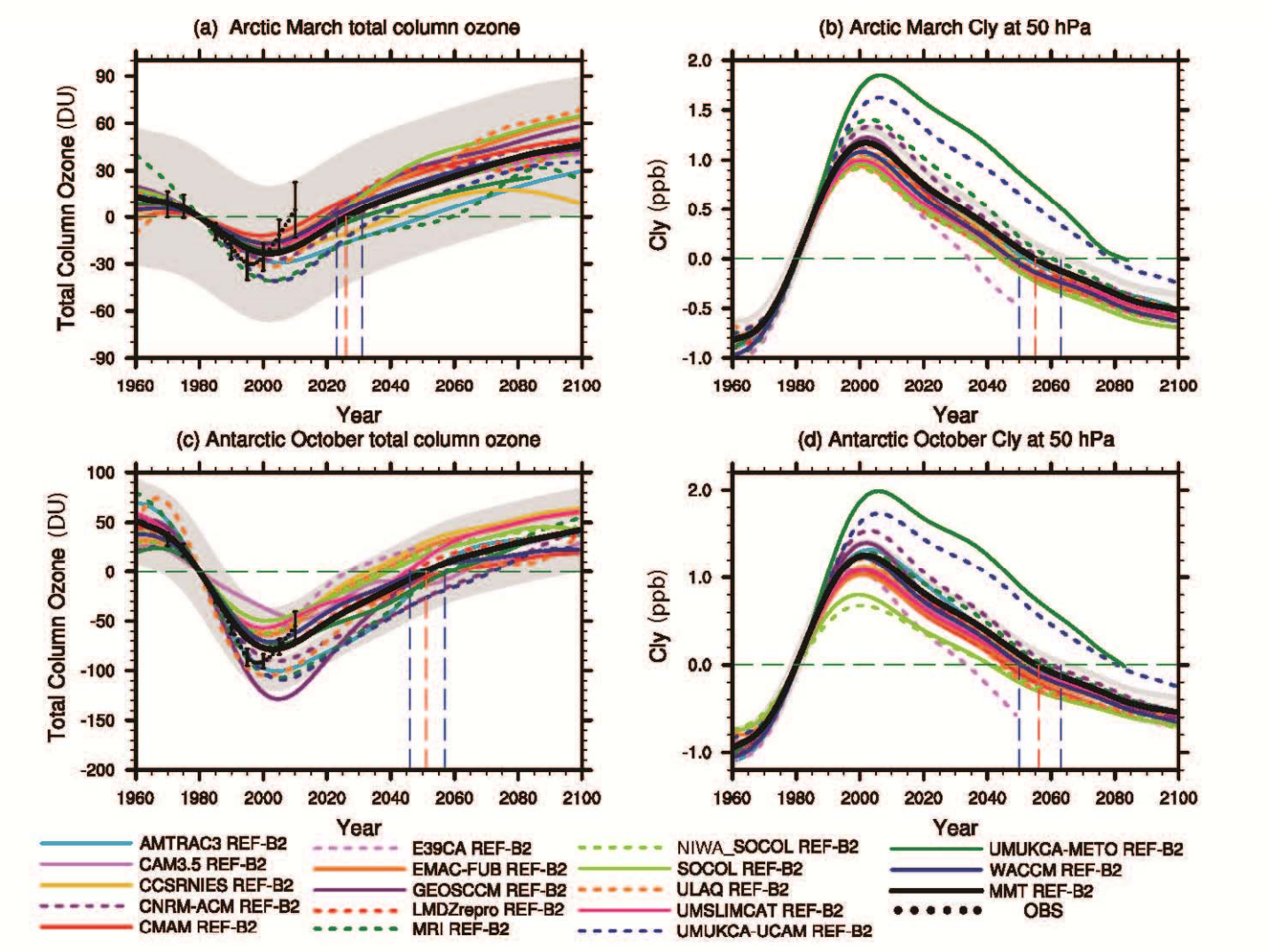


Need to solve momentum, energy equations also, coupled to chemistry (GCM with chemistry)

WMO, 2010


(a) Tropics annual mean total column ozone
Total Column Ozone (DU)
Year
(b) Tropics annual mean Cly at 50 hPa
Cly (ppb)
Year
(c) NH midlatitudes annual mean total column ozone
Total Column Ozone (DU)
Year
(d) NH midlatitudes annual mean Cly at 50 hPa
Cly (ppb)
Year
(e) SH midlatitudes annual mean total column ozone
Total Column Ozone (DU)
Year
(f) SH midlatitudes annual mean Cly at 50 hPa
Cly (ppb)
Year
AMTRAC3 REF-B2
CAM3.5 REF-B2
CCSRNIES REF-B2
CNRM-ACM REF-B2
CMAM REF-B2
E39CA REF-B2
EMAC-FUB REF-B2
GEOSCCM REF-B2
LMDZrepro REF-B2
MRI REF-B2
NIWA_SOCOL REF-B2
SOCOL REF-B2
ULAQ REF-B2
UMSLIMCAT REF-B2
UMUKCA-UCAM REF-B2
UMUKCA-METO REF-B2
WACCM REF-B2
MMT REF-B2
OBS

WMO, 2010


(a) Arctic March total column ozone
Total Column Ozone (DU)
Year
(b) Arctic March Cly at 50 hPa
Cly (ppb)
Year
(c) Antarctic October total column ozone
Total Column Ozone (DU)
Year
(d) Antarctic October Cly at 50 hPa
Cly (ppb)
Year
AMTRAC3 REF-B2
CAM3.5 REF-B2
CCSRNIES REF-B2
CNRM-ACM REF-B2
CMAM REF-B2
E39CA REF-B2
EMAC-FUB REF-B2
GEOSCCM REF-B2
LMDZrepro REF-B2
MRI REF-B2
NIWA_SOCOL REF-B2
SOCOL REF-B2
ULAQ REF-B2
UMSLIMCAT REF-B2
UMUKCA-UCAM REF-B2
UMUKCA-METO REF-B2
WACCM REF-B2
MMT REF-B2
OBS

WMO, 2010

HIGHER UP: MESOSPHERE, THERMOSPHERE

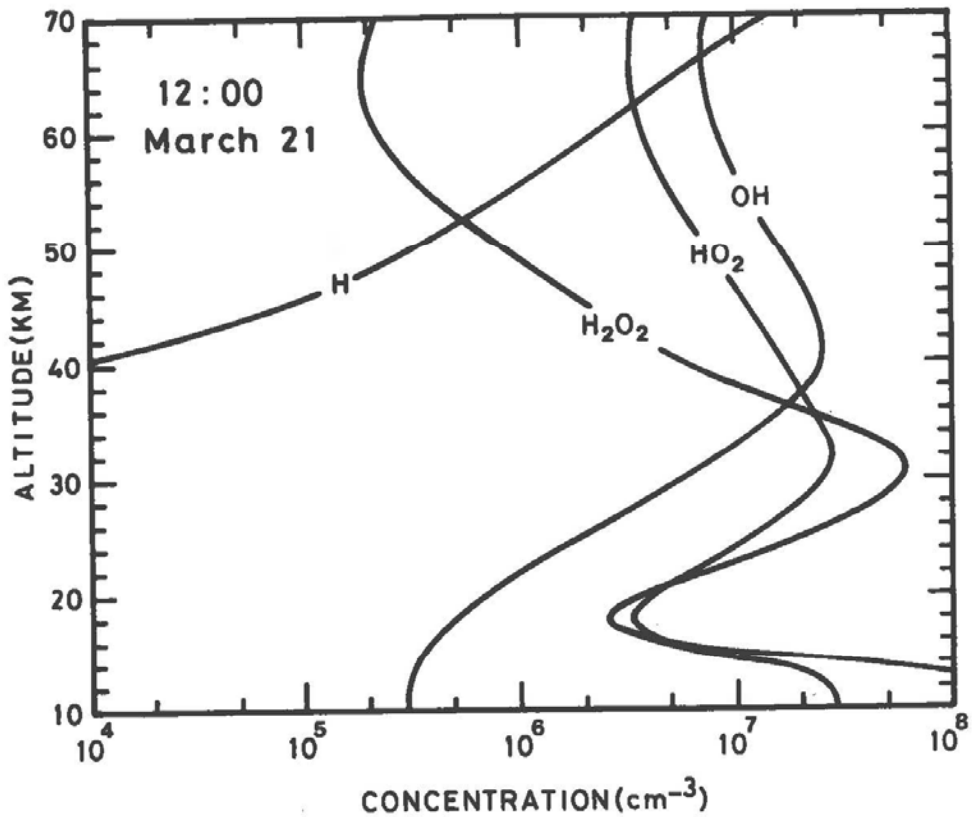


Fig. 5.31. Calculated distributions of some hydrogen compounds (noon, equinox). From the model of Brasseur et al. (1983).

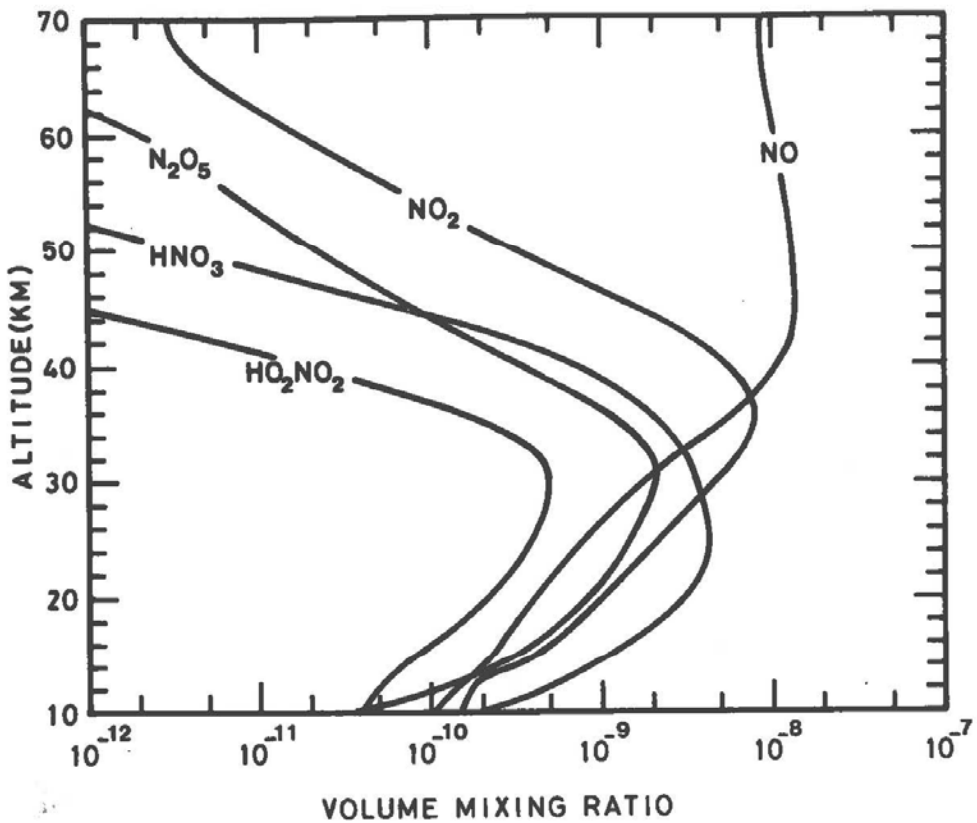


Fig. 5.39. Calculated vertical distributions of nitrogen species. From the model of Brasseur et al. (1983).

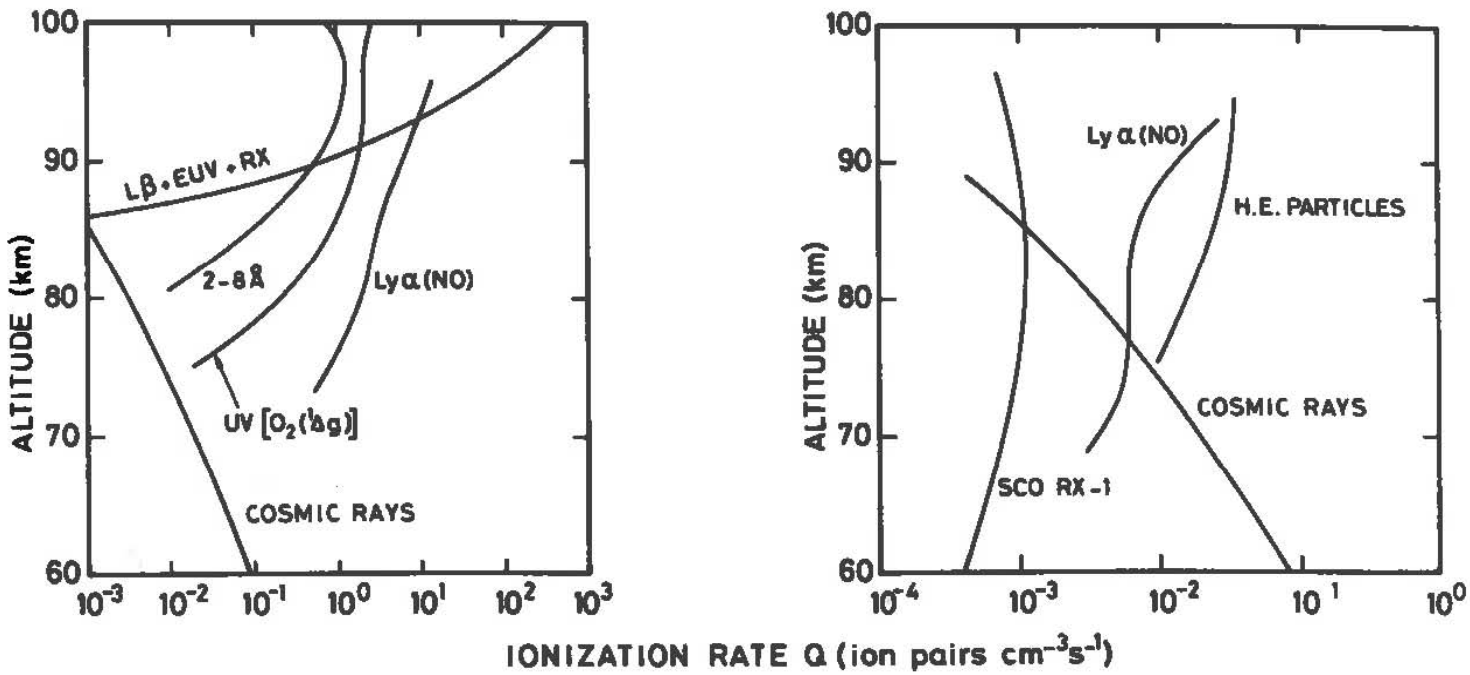


Fig. 6.10a and 6.10b. Ionization rates produced by various sources in the region from 60 to 100 km, during the day and at night. From Thomas, (1974). (Copyright by the American Geophysical Union).

Aura MLS Measurements of Atmospheric Effects Caused by the Solar Proton Events in January 2005

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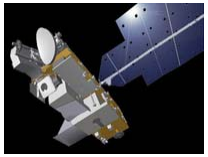

EOS Aura

Solar eruptions in early 2005 led to a substantial barrage of charged particles on the Earth's polar atmosphere during the January 16-21 period. Most of these charged particles were protons, thus the term "Solar Proton Event (SPE)" has been used to describe this phenomenon. The solar protons created hydrogen- containing compounds, which led to the polar ozone destruction. We have used the Aura Microwave Limb Sounder (MLS) observations to quantify the changes in the hydroxyl radical (OH), hydrogen dioxide (HO_2), and ozone due to these SPEs.

The atmospheric changes in OH, HO_2, and ozone for the latitude band 60-82.5ºN shown in Figure 1 are all relative to the quiet January 1-14, 2005 time period, which contained no SPEs. Fairly substantial OH enhancements (up to 4 ppbv) and HO_2 enhancements (up to 0.8 ppbv) were caused by the SPEs. *To the best of our knowledge, this is the first time that SPE-caused HO_2 measured increases have been reported.* The SPE-caused ozone decreases (up to 80%, area outlined by the 'yellow' line) are confined to pressures <0.5 hPa. The ozone changes below these large decreases are mostly seasonal variations, not connected to the SPEs.

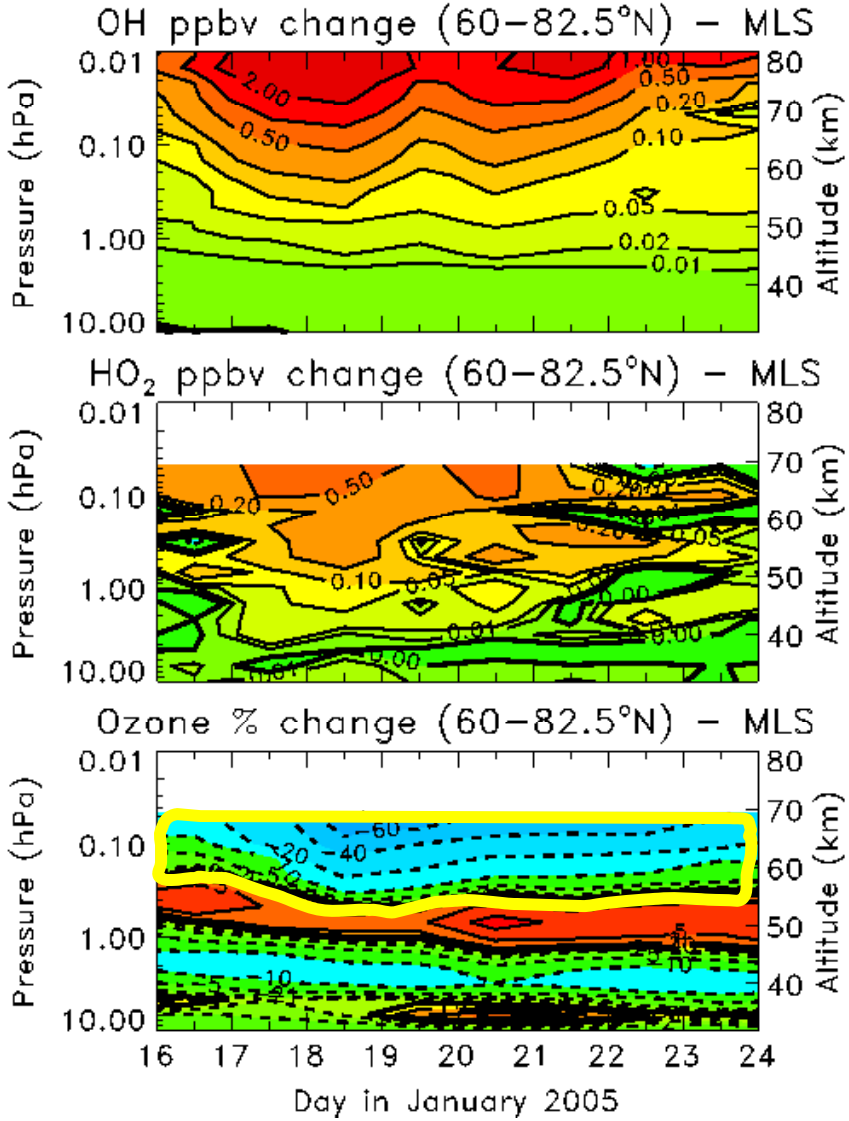

Figure 1. Daily averaged OH (Top), HO_2 (Middle), and ozone (Bottom) change from an average of the observations for the period January 1-14, The contour intervals for the three constituents are: OH (0.0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 ppbv); HO_2 (-0.1, 0.0, 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 ppbv); Ozone (-80, -60, -40, -20, -10, -5, -2, -1, 0, 1,2,5, and 10%). The region of ozone decrease caused by the SPEs is roughly outlined by the 'yellow' line in the Bottom plot.

SUMMARY

- We understand the processes controlling stratospheric ozone (???!!!)
- Where are we going?
  - Chemistry/climate coupling
  - Tropospheric chemistry/dynamics (an order of magnitude more complicated).
  - Aerosols!!!
  - Testing model processes, model improvement; uncertainty analysis
- What tools do we have for other planets?
  - Solving systems of coupled (chemical) equations and calculation of photolysis rates (Ion chemistry?)
  - Three and two-dimensional models (a fair amount of work to look at the underlying assumptions, approximations, to adapt to another atmosphere).
  - One dimensional models? (Maybe most appropriate for exoplanets with small day-night or latitudinal gradients in temperature).