Review of Lectures 10 to 17

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

https://www.videoblocks.com/video/earth-sunset-spacewalk-view-from-space-station-r7dydlcsgjd23vml0

12 April 2022

Announcements

1. **Exam on Thursday**
    Conceptual questions only: <u>no calculators</u>
    Closed book; no notes
2. **Unless a prior arrangement has been made, everyone is expected to show up on time, in person, on Thursday, with a writing implement (pen or pencil)**
3. **For this exam, the 633 exam will differ only very slightly from the 433 exam and none of the 633 questions will be based on material covered only in the assigned auxiliary readings**
4. **Review of Problem Set #3 will occur quickly today, prior to completion of our grading, due to poor turnout (only 1 student) of our prior evening review**

Importance of Radicals

- With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical
- Radicals require significant energy to form: a bond must be broken
- Radical formation is tied to absorption of photons that “photodissociate” a compound, leading to radical formation

Initiation

$O_2 + \text{photon} \rightarrow O + O$

Propagation

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

$O_3 + \text{photon} \rightarrow O(^1D) + O_2$

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

$OH + O_3 \rightarrow HO_2 + O_2$

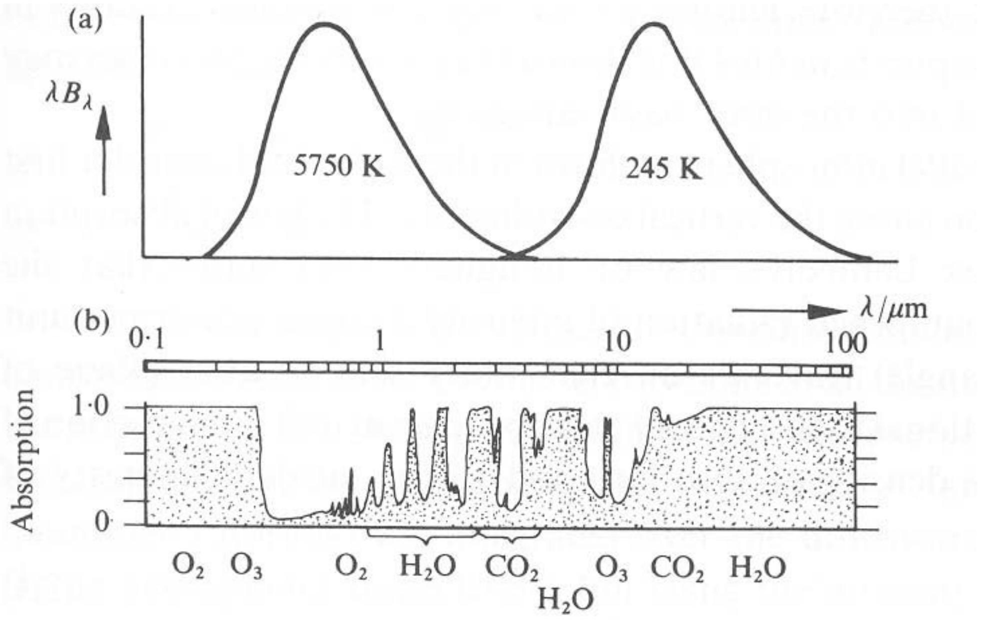
$HO_2 + O \rightarrow OH + O_2$

Termination

$OH + HO_2 \rightarrow H_2O + O_2$

Atmospheric Radiation

- Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K “black body” temperature)



Panel (a) : Curves of black-body energy versus wavelength for 5750 K (Sun’s approximate temperature) and for 245 K (Earth’s mean temperature).

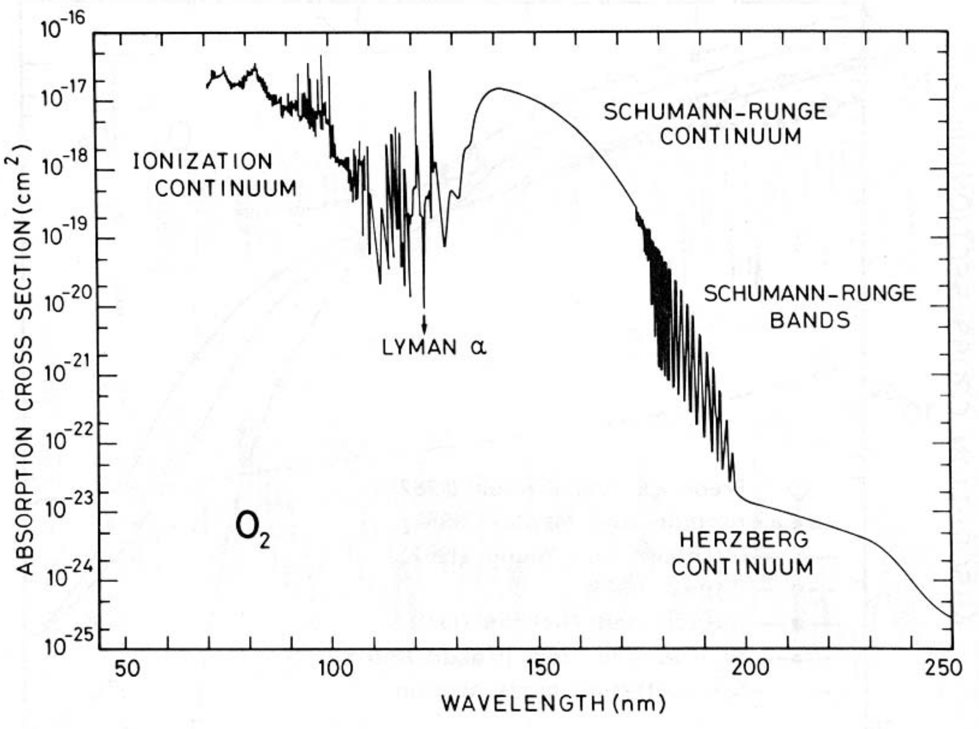
The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, *Physics of Atmospheres*, 1991

- Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules

Absorption Cross Section of O_2



From Brasseur & Solomon, *Aeronomy of the Middle Atmosphere*, 1986

- O_2 can not dissociate longward of ~250 nm
- All of the absorption shown above is dissociative (e.g., leads to production of two O atoms)
- Structure in the O_2 cross section is related to whether the initial transition involves an unbound electronic state (smooth) or involves a specific vibrational level of an electronic state (banded, due to requirement of specific quanta of energy)

Optical Depth of O_2 Absorption

Recall the *Beer-Lambert Law*:

$$F(z,\lambda) = F_{TOA}(\lambda)\, e^{-\tau(z,\,\lambda)}$$ (TOA : Top of Atmosphere)

where:

$$\tau(z,\lambda) = m \int_z^\infty \sigma_\lambda\,[C]\,dz'$$ (τ: optical depth)

Also:

$$\int_0^\infty [O_2]\,dz' \approx 4\times10^{24}\ \text{molecules/cm}^2$$

O_2 Optical Depth for $\theta = 0°$, $z = 0$ km			
	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\ \text{km})}$
Schumann-Runge Continuum	10^{-17}	4×10^7	0.
Schumann-Runge Bands	10^{-20}	4×10^4	0.
	3×10^{-23}	120	7.6×10^{-53}
Herzberg Continuum	10^{-23}	40	4.2×10^{-18}

Optical Depth of O_3 Absorption

A typical mid-latitude column abundance for O_3 is 300 Dobson units (DU):

$1\ \text{DU} = 2.687 \times 10^{16}$ molecules/cm^2; $300\ \text{DU} = 8 \times 10^{18}$ molecules/cm^2

Aside:

$$\frac{\text{Column } O_3}{\text{Column Air}} = \frac{8\times10^{18}}{2\times10^{25}} = 0.4 \text{ parts per million } \Rightarrow \text{Ozone is a trace species!}$$

O_3 Optical Depth for $\theta = 0°$, $z = 0$ km

	σ_{max} (cm^2)	τ (0 km)	$e^{-\tau\,(0\,\text{km})}$	O_3 Column, $\tau = 1.0$
Hartley (~220 to 280 nm)	10^{-17}	80	1.8×10^{-35}	3.7 DU
Huggins (~310 to 330 nm)	10^{-19}	0.8	0.45	372 DU
Chappuis (~500 to 700 nm)	3×10^{-21}	0 .024	~1.0	12,400 DU

Solar Spectral Actinic Flux

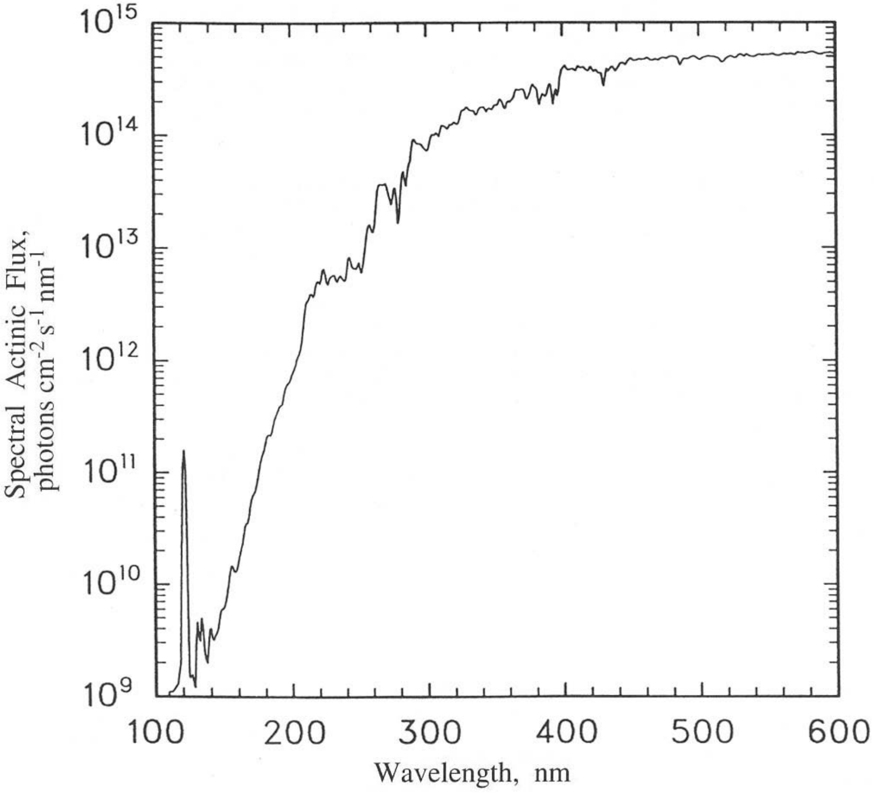
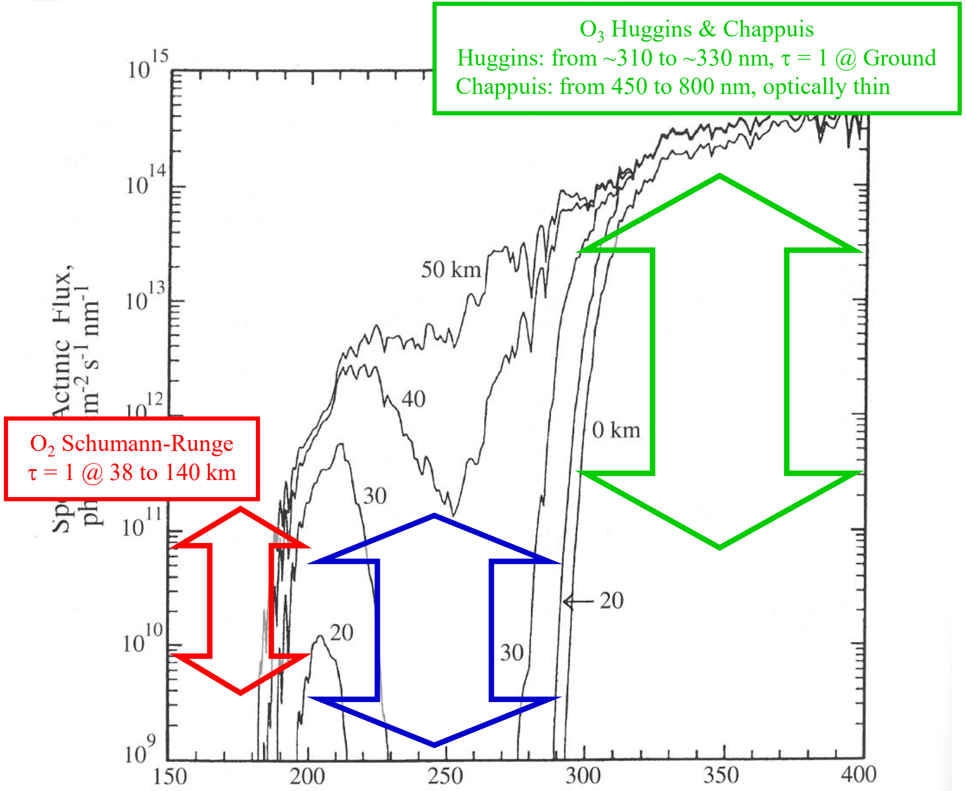


FIGURE 6. Solar spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}) at the top of Earth's atmosphere.

130 ATMOSPHERIC PHOTOCHEMISTRY AND CHEMICAL KINETICS



O_3 Huggins & Chappuis
Huggins: from ~310 to ~330 nm, $\tau = 1$ @ Ground
Chappuis: from 450 to 800 nm, optically thin

O_2 Schumann-Runge
$\tau = 1$ @ 38 to 140 km

O_2 Herzberg & O_3 Hartley
O_2: σ_λ peak @ 200 nm, $\tau = 1$ @ ~29 km
O_3: σ_λ peak @ 250 nm, $\tau = 1$ @ ~40 km

GURE 3.3 Solar s various altitudes and at the Earth's surface (DeMo

From DeMore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Evaluation No. 11, 1994.

From Seinfeld and Pandis, *Atmospheric Chemistry and Physics*, 1998.

Photolysis Frequency

For a specific spectral interval, the photolysis frequency (***partial J value***) of a gas is given by the product of its absorption cross section and the solar irradiance:

$$J_{gas}(z,\lambda) = \text{Quantum\_Yield}(\lambda)\ \sigma_{gas}(\lambda,T)\ F(z,\lambda)$$

Units: $s^{-1}\ nm^{-1}$

The total ***photolysis frequency*** (***J value***) is found by integrating $J_{gas}(z,\lambda)$ over all wavelengths for which the gas photodissociates:

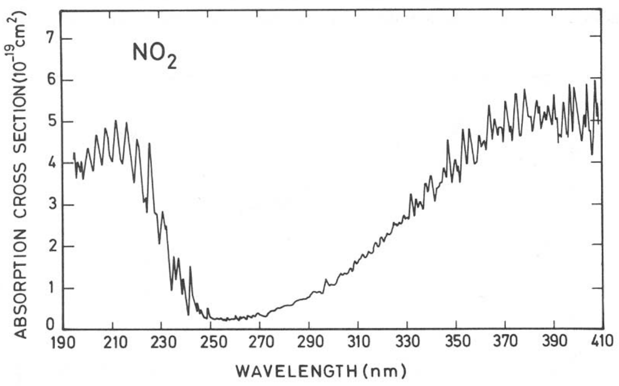
$$J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z,\lambda)\, d\lambda$$

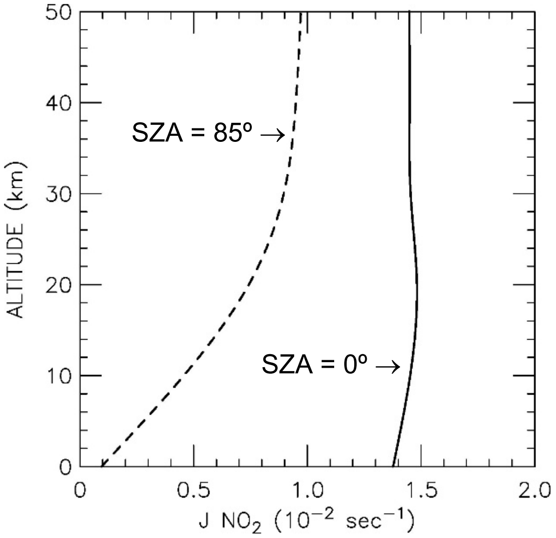
Units: s^{-1}

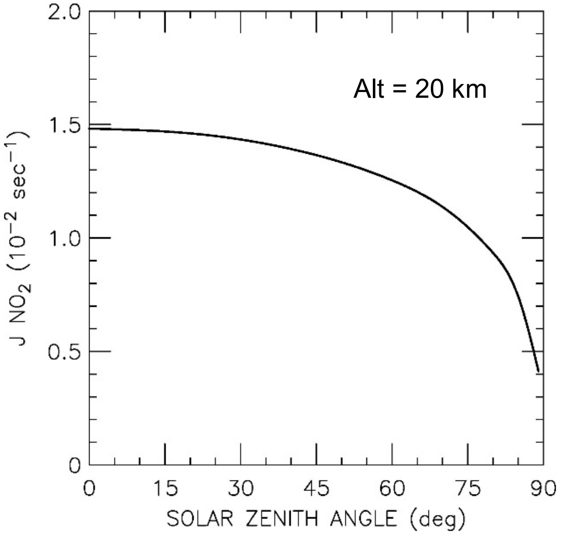
$$\boxed{\text{Rate of Reaction} = \frac{dO_3}{dt} = J\ [O_3];\quad \text{Units of } J \text{ are } s^{-1}}$$

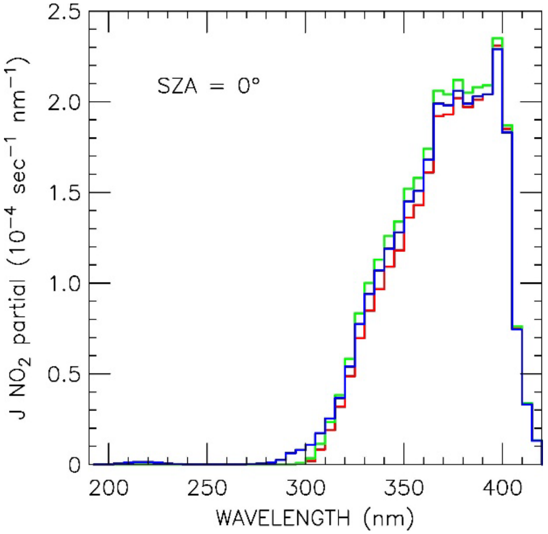
More precisely, calculations of photolysis frequencies consider the "spectral actinic flux", which represents the amount of available photons integrated over all angles, rather than "solar irradiance". These two quantities differ because of scattering of solar radiation by gases and aerosols, and reflection of radiation by clouds and the surface.

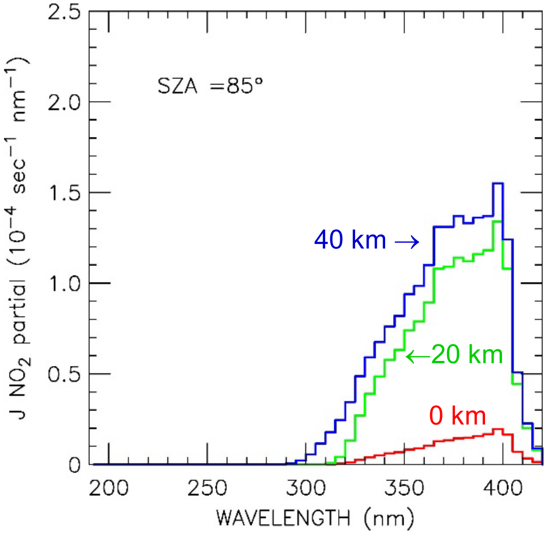
NO_2 Photolysis



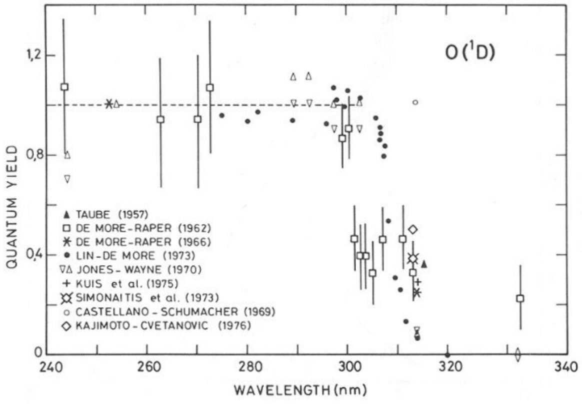


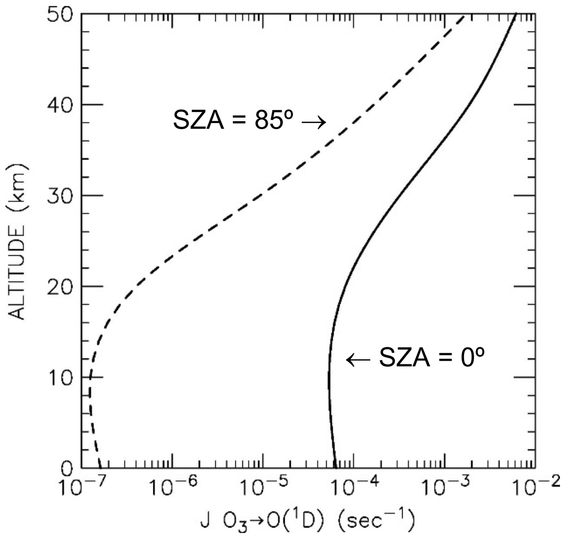


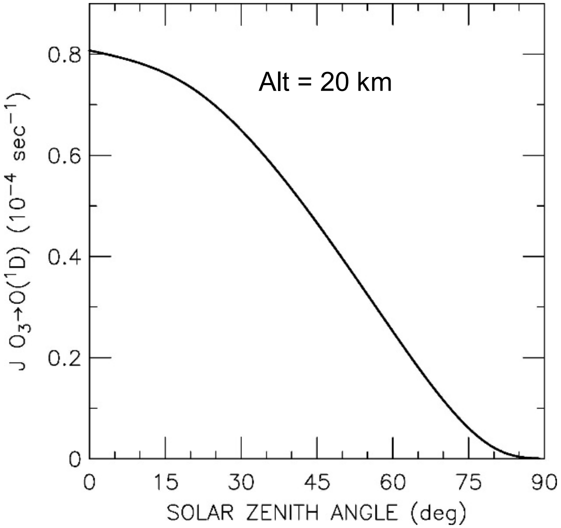


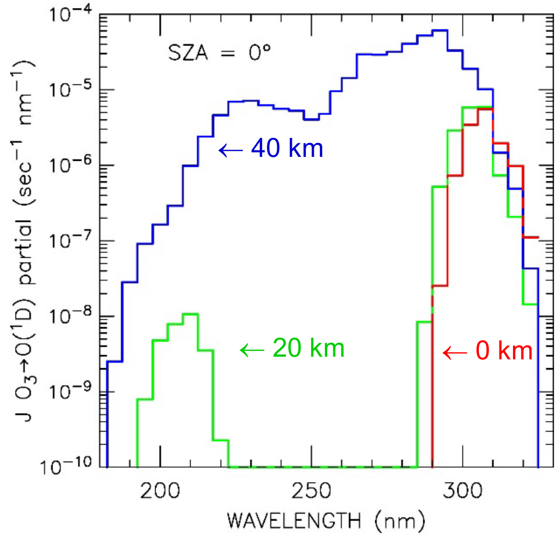


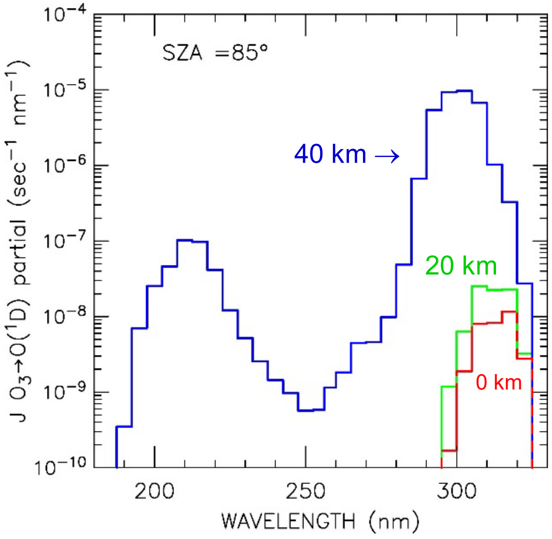
$O_3 \rightarrow O(^1D)$ Photolysis











Bimolecular Gas Phase Reactions

8.9 kcal/mole **–17.8 kcal/mole** **35.1 kcal/mole** **–57.8 kcal/mole**

$OH + CH_4 \rightarrow CH_3 + H_2O$

ΔEnthalpy = –13.8 kcal/mole

Exothermic !

$$\text{Rate of Reaction} = \frac{dCH_4}{dt} = k\,[OH][CH_4]$$

E_A / R ⇒ Activation Energy / Gas Constant

Arrhenius Expression for rate constant:

$$k = 1.85\times10^{-12} \times e^{-1690/T}\ \text{cm}^3\ \text{sec}^{-1}$$

Energy Term

R = 8.3143 × 10^7 erg / (K mole)
= 2.87 × 10^6 erg / (K gm) for air

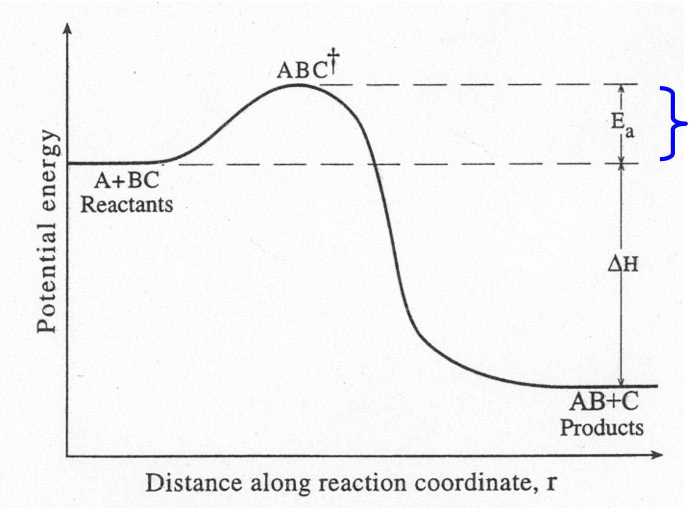


Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

Yung and DeMore, *Photochemistry of Planetary Atmospheres*, Oxford, 1999.

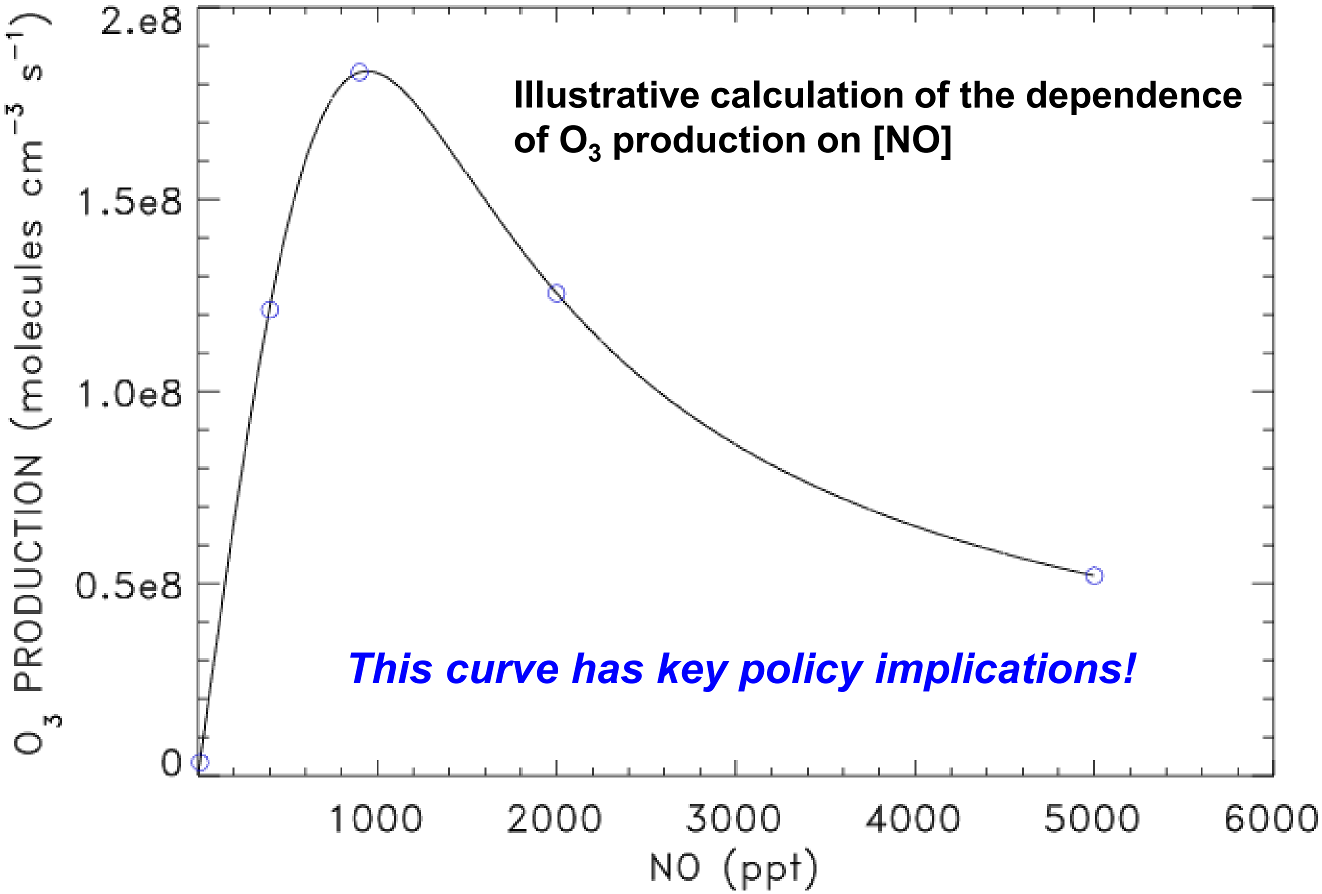
Tropospheric Ozone Production versus NO

Production of Tropospheric O_3 limited by: ____________ ?

As NO_x rises:

$[HO_2]$ falls faster than [NO] rises,

leading to a decrease in the value ______________

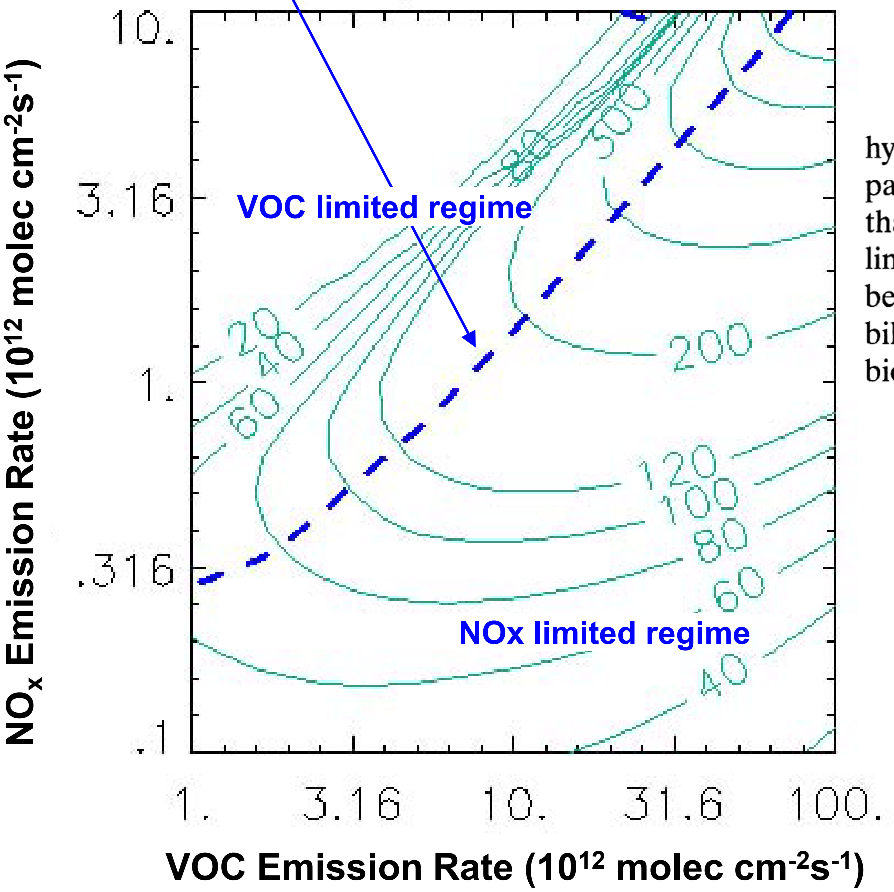


Illustrative calculation of the dependence of O_3 production on [NO]

This curve has key policy implications!

Tropospheric Ozone Production versus NO_x and VOCs

Ridge: local maximum for O_3 that separates the NOx-limited regime from and VOC limited regime



An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O_3 pollution may have been partly misdirected. Measurements and model calculations now show that O_3 production over most of the United States is primarily NO_x limited, not hydrocarbon limited. The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops.

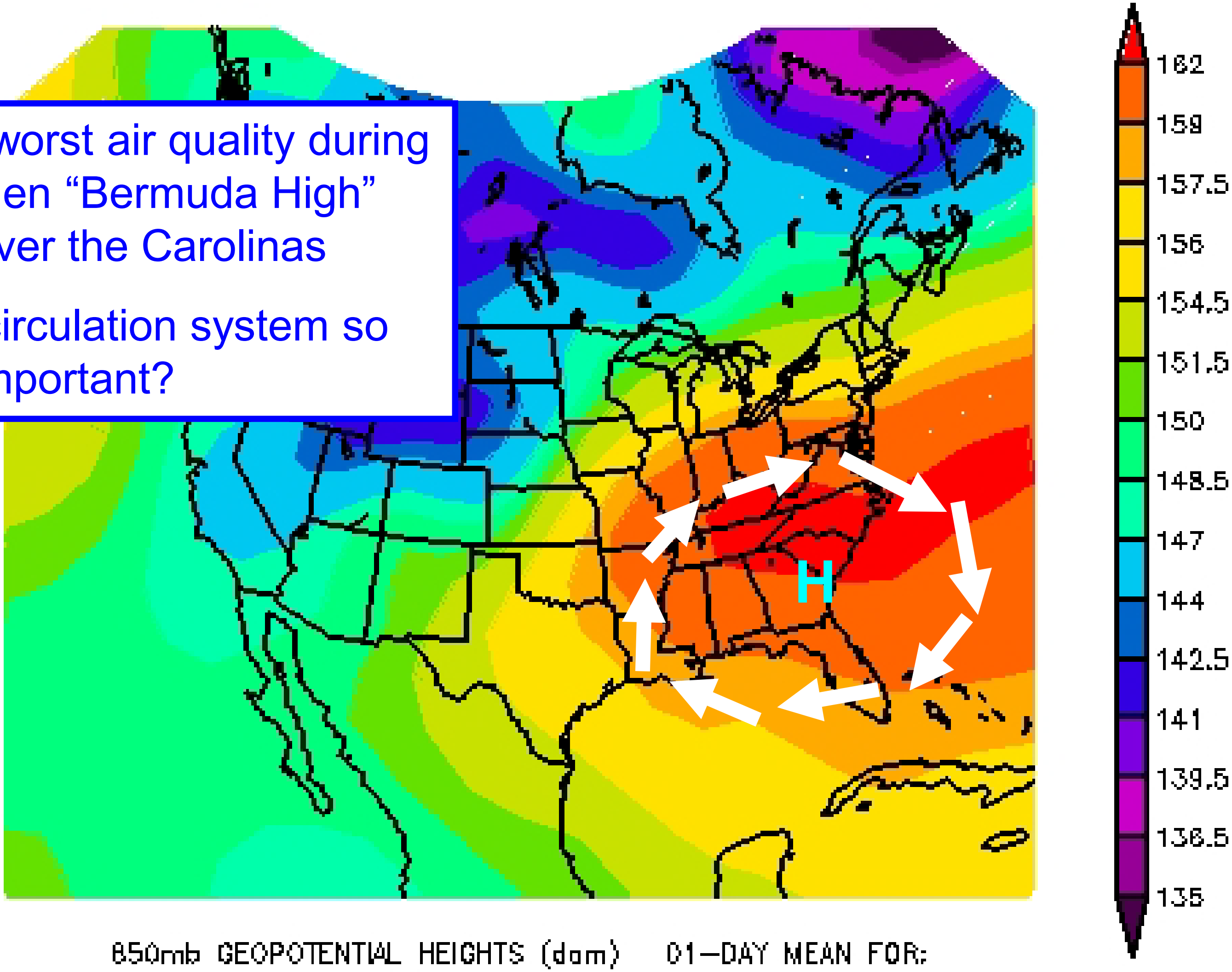
Jacob, Chapter 12, Introduction to Atmospheric Chemistry, 1999

Figure: http://www-personal.umich.edu/~sillman/ozone.htm

Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

Maryland has worst air quality during summer, when “Bermuda High” sets up over the Carolinas

Why is this circulation system so important?



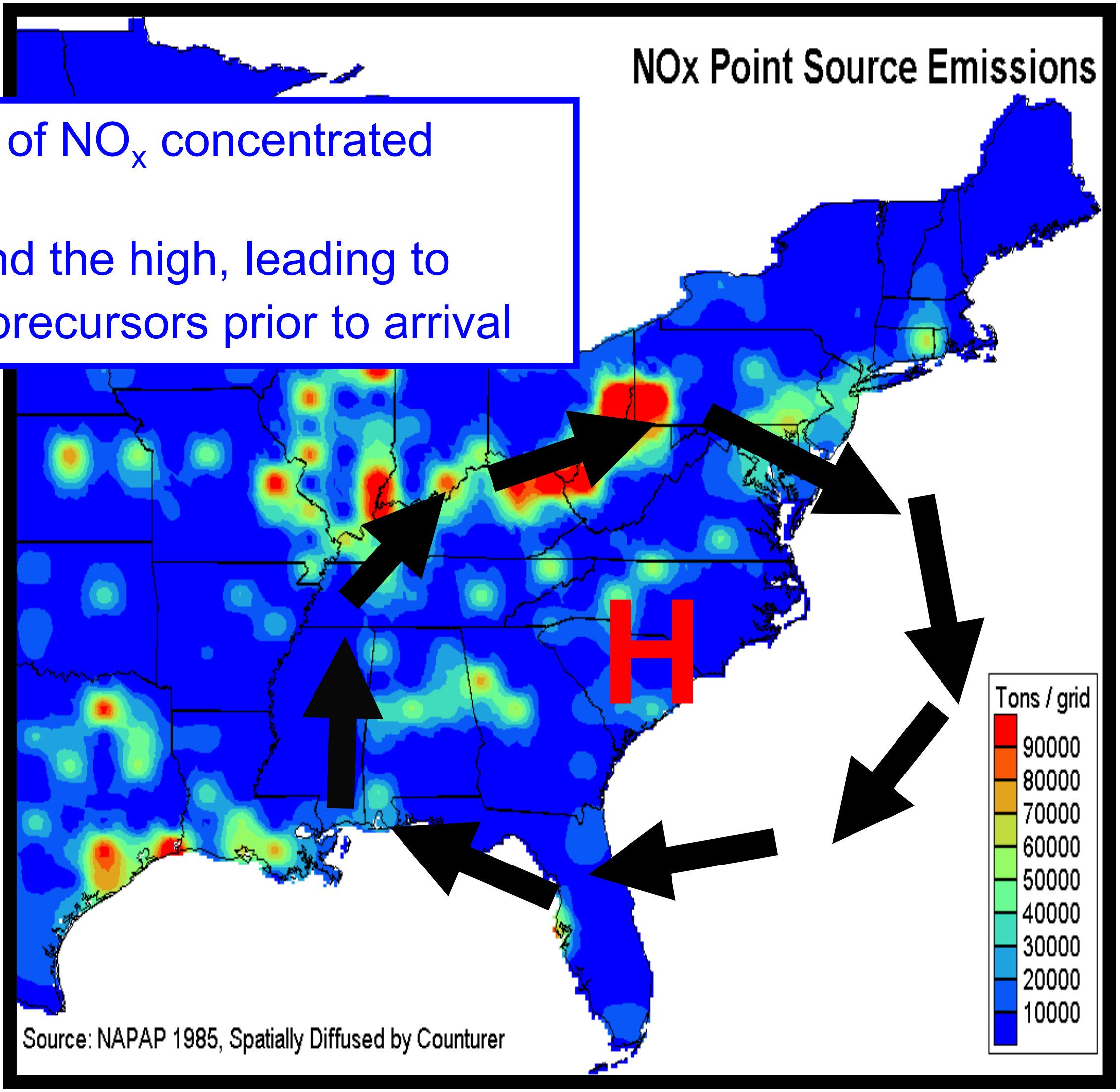
850mb GEOPOTENTIAL HEIGHTS (dam) 01–DAY MEAN FOR:
Sun JUL 04 1999

NCEP OPERATIONAL DATASET

http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt

Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

- Large power plant emissions of NO_x concentrated along the Ohio River valley
- Air circulates clockwise around the high, leading to significant build up of ozone precursors prior to arrival

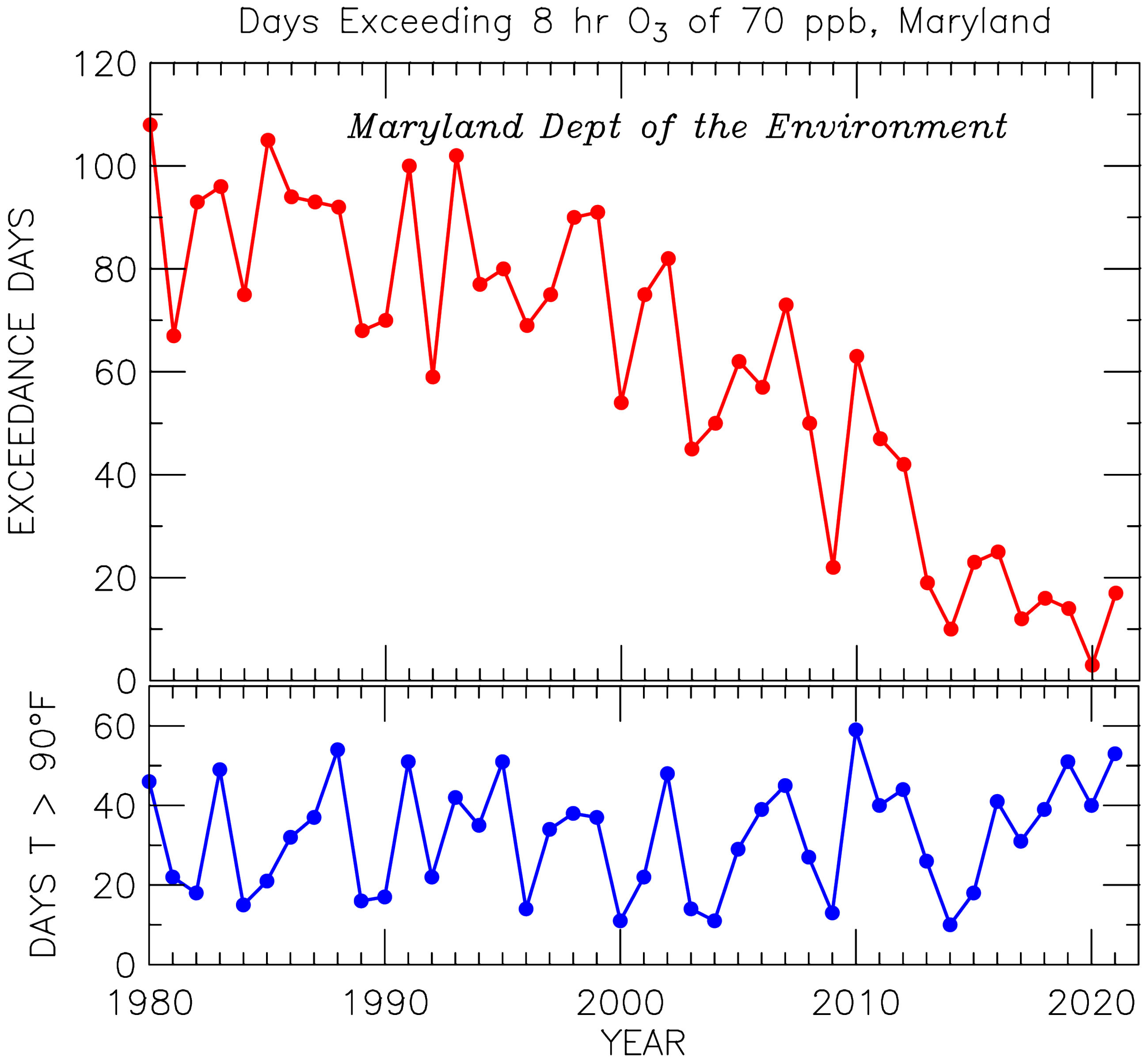


NOx Point Source Emissions

Source: NAPAP 1985, Spatially Diffused by Counturer

http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt

Significant Improvements in *Local* Air Quality since early 1980s

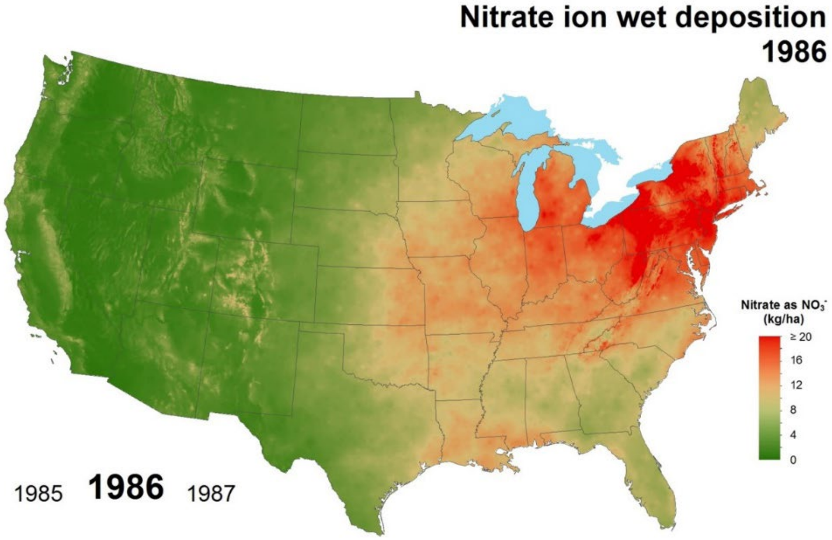


Number of days, each summer, for which T at BWI exceeded 90°F at some part of the day

http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/SeasonalReports.aspx

Nitrate Deposition (see Fig 6.12)

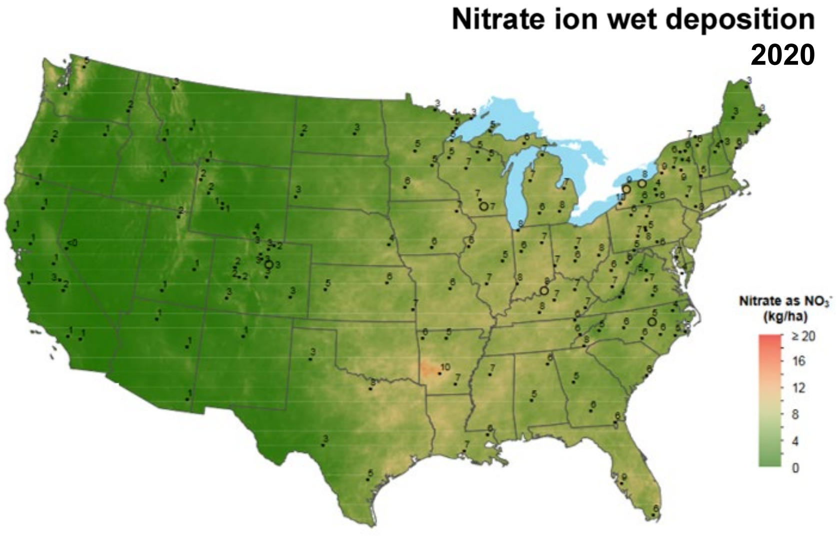
1986



Nitrate ion wet deposition
1986

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

2020



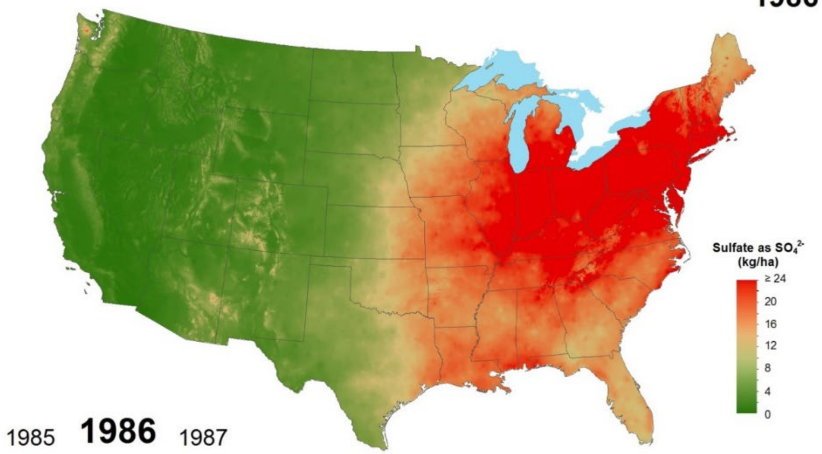
Nitrate ion wet deposition
2020

National Atmospheric Deposition Program/National Trends Network
http://nadp.slh.wisc.edu

http://nadp.slh.wisc.edu

Sulfate Deposition (see Fig 6.12)

1986



Sulfate ion wet deposition
1986

National Atmospheric Deposition Program/National Trends Network
http://nadp.isws.illinois.edu

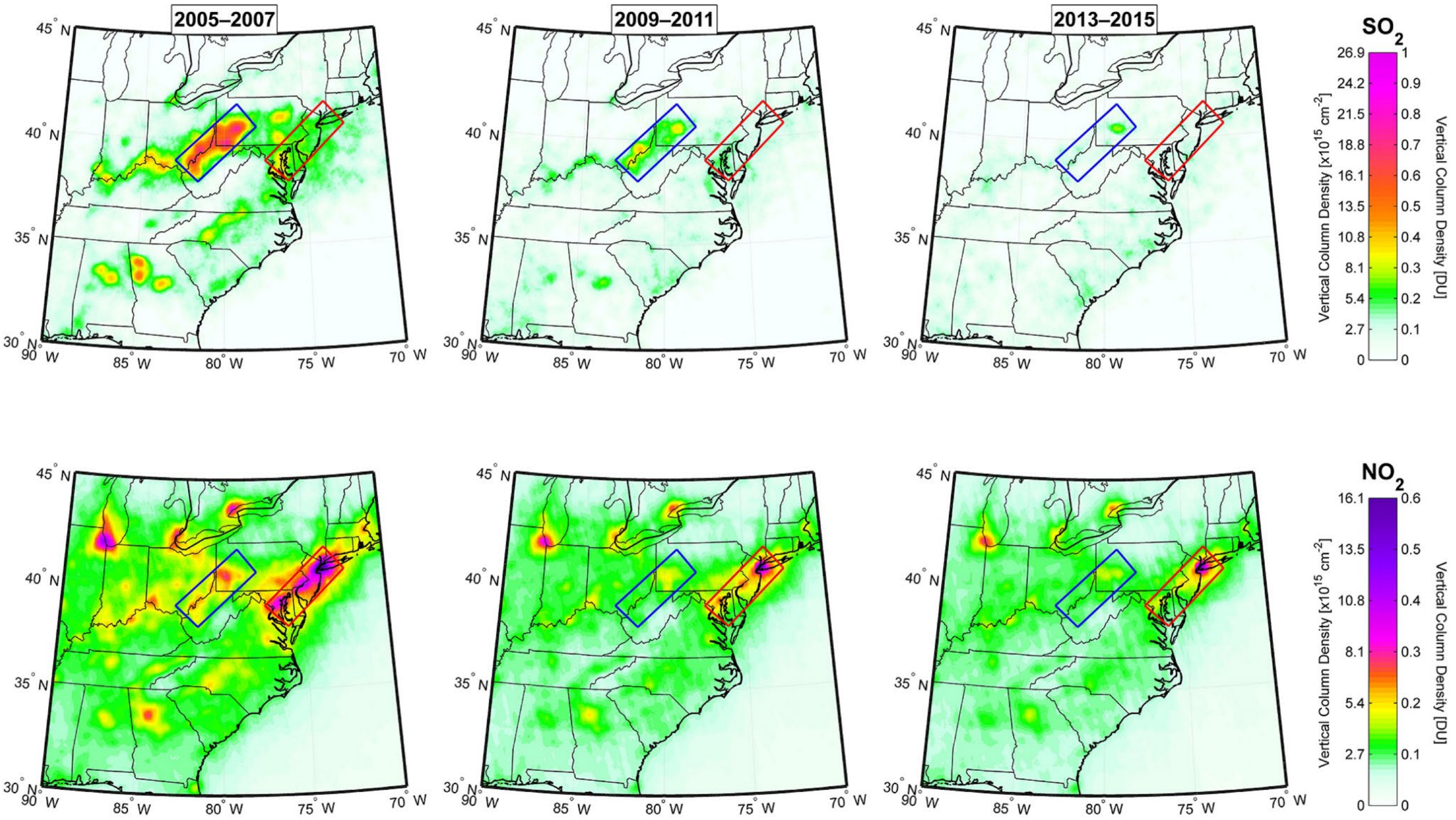
2020

Sulfate ion wet deposition
2020

National Atmospheric Deposition Program/National Trends Network
http://nadp.slh.wisc.edu

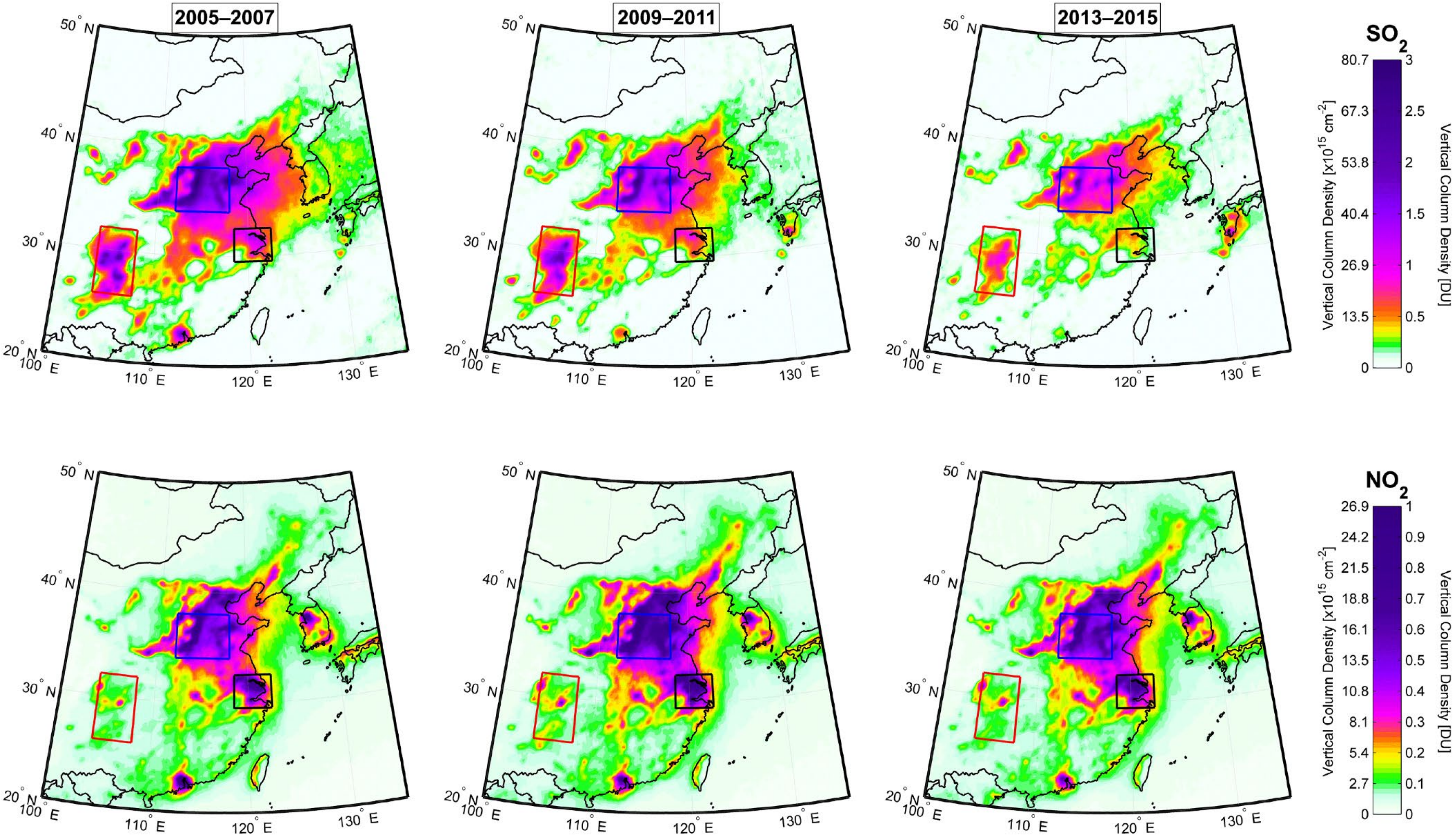
http://nadp.slh.wisc.edu

US Trends: NO$_2$ and SO$_2$



Krotkov *et al.*, *ACP*, 2016

China Trends: NO_2 and SO_2



Krotkov *et al.*, *ACP*, 2016

Stratospheric Ozone: Chapman Chemistry

- Production of O_3 initiated when O_2 is photodissociated by UV sunlight

- O_3 formed when resulting O atom reacts with O_2 :

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

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

- O_3 removed by photodissociation (UV sunlight) or by reaction with O :

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

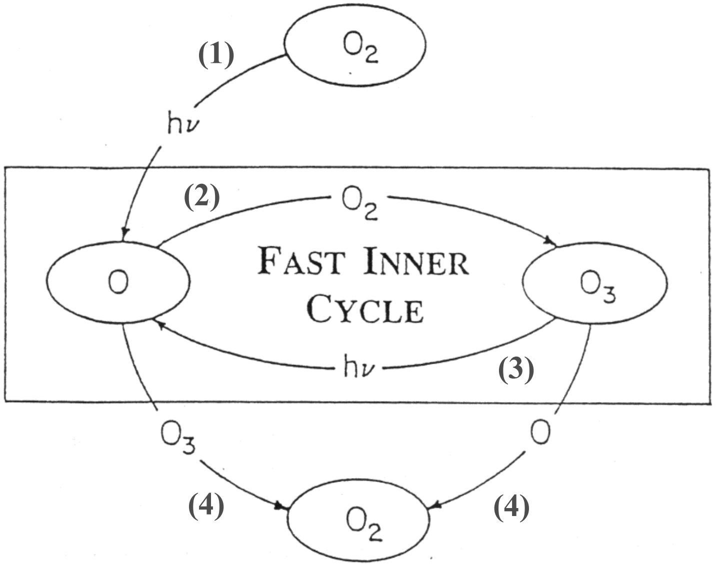
$$O + O_3 \rightarrow O_2 + O_2 \qquad (4)$$

This reaction sequence was first worked out in the 1930s by Sidney Chapman, an English mathematician and geophysicist

Chapman Chemistry

- The cycling between O and O_2 (rxns 2 and 3) occurs *much* more rapidly than leakage into (rxn 1) or out of the system (rxn 4)

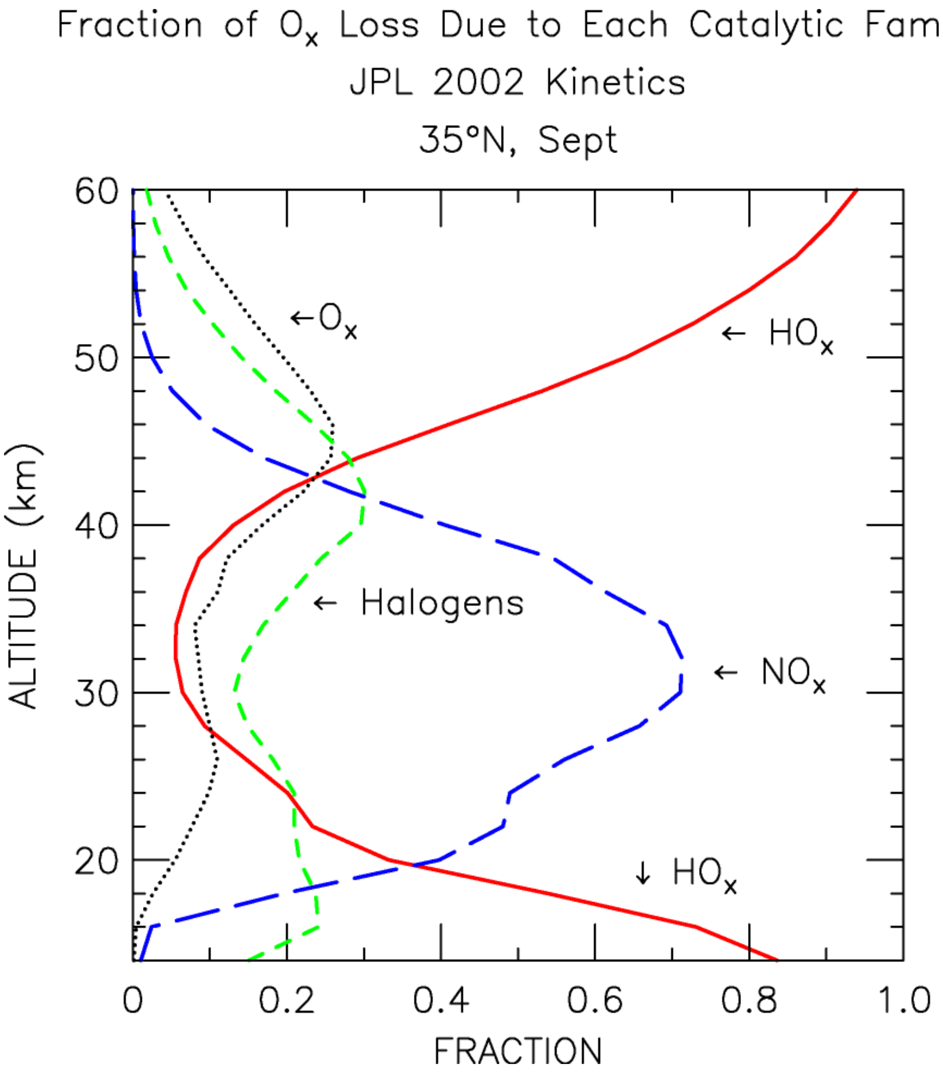
- The sum O + O_3 is commonly called *"odd oxygen"*



Rxn (1) produces two *odd oxygen* molecules
Rxn (4) consumes two *odd oxygen* molecules

and reactions 2 and 3 recycle *odd oxygen* molecules

Stratospheric Photochemistry: Odd Oxygen Loss By Families



Calculated fraction of odd oxygen loss due to various families of radicals

After Osterman *et al*., *GRL*, 24, 1107, 1997;
Sen *et al*., *JGR*, 103, 3571. 1998;
Sen *et al*., *JGR*, 104, 26653, 1999.

One Atmosphere – One Photochemistry

Stratosphere

HO$_2$ formation:

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

HO$_2$ loss:

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

Net: $O_3 + O_3 \rightarrow 3\,O_2$

Rate HO$_2$ Formation = k_{OH+O3}×[OH][O$_3$] + k_{OH+CO}×[OH][CO]

Rate HO$_2$ Loss = k_{HO2+O3}×[HO$_2$][O$_3$] + k_{HO2+NO}×[HO$_2$][NO]

Troposphere

HO$_2$ formation:

$$OH + CO \xrightarrow{O_2} HO_2 + CO_2$$

HO$_2$ loss:

$$HO_2 + NO \rightarrow OH + NO_2$$

Followed by:

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

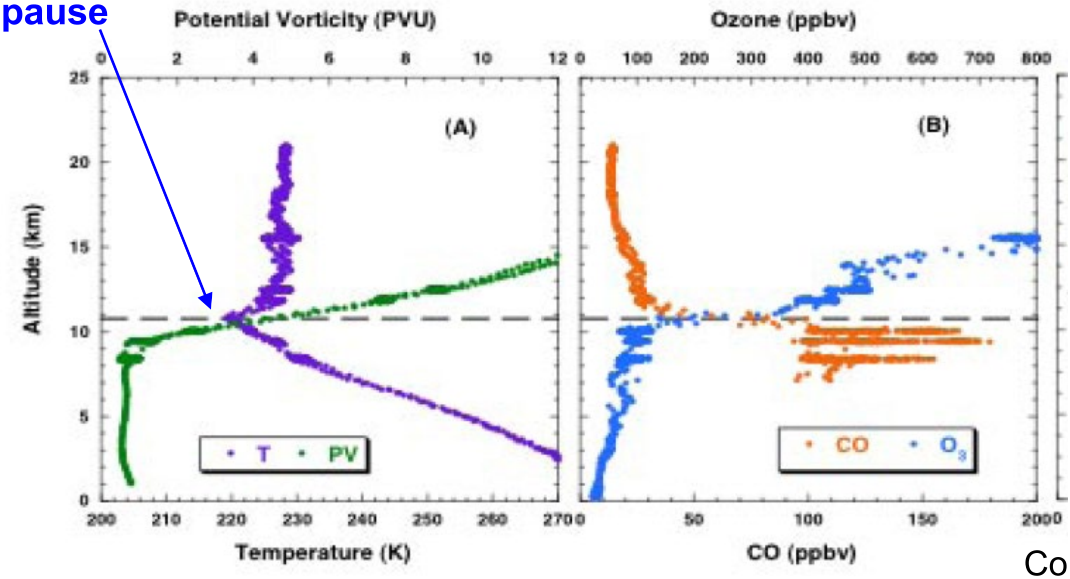
$$O + O_2 + M \rightarrow O_3 + M$$

Net: $CO + 2\,O_2 \rightarrow CO_2 + O_3$

Rate HO$_2$ Formation = k_{OH+O3}×[OH][O$_3$] + **k_{OH+CO}×[OH][CO]**

Rate HO$_2$ Loss = k_{HO2+O3}×[HO$_2$][O$_3$] + **k_{HO2+NO}×[HO$_2$][NO]**

Tropopause



Above Tropopause:

Lots of O$_3$, little CO

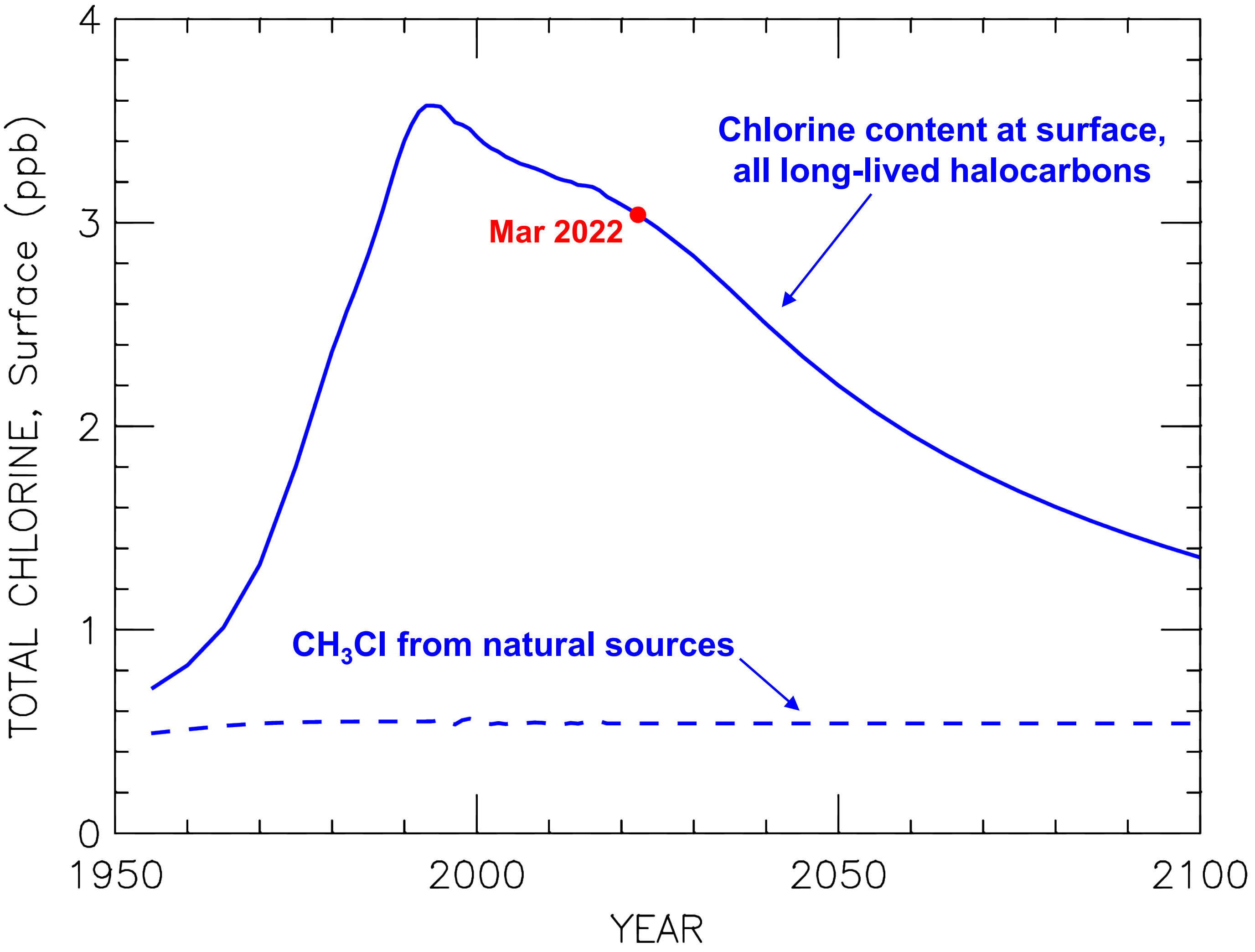
Below Tropopause:

Lots of CO, little O$_3$

Courtesy of Laura Pan, NCAR

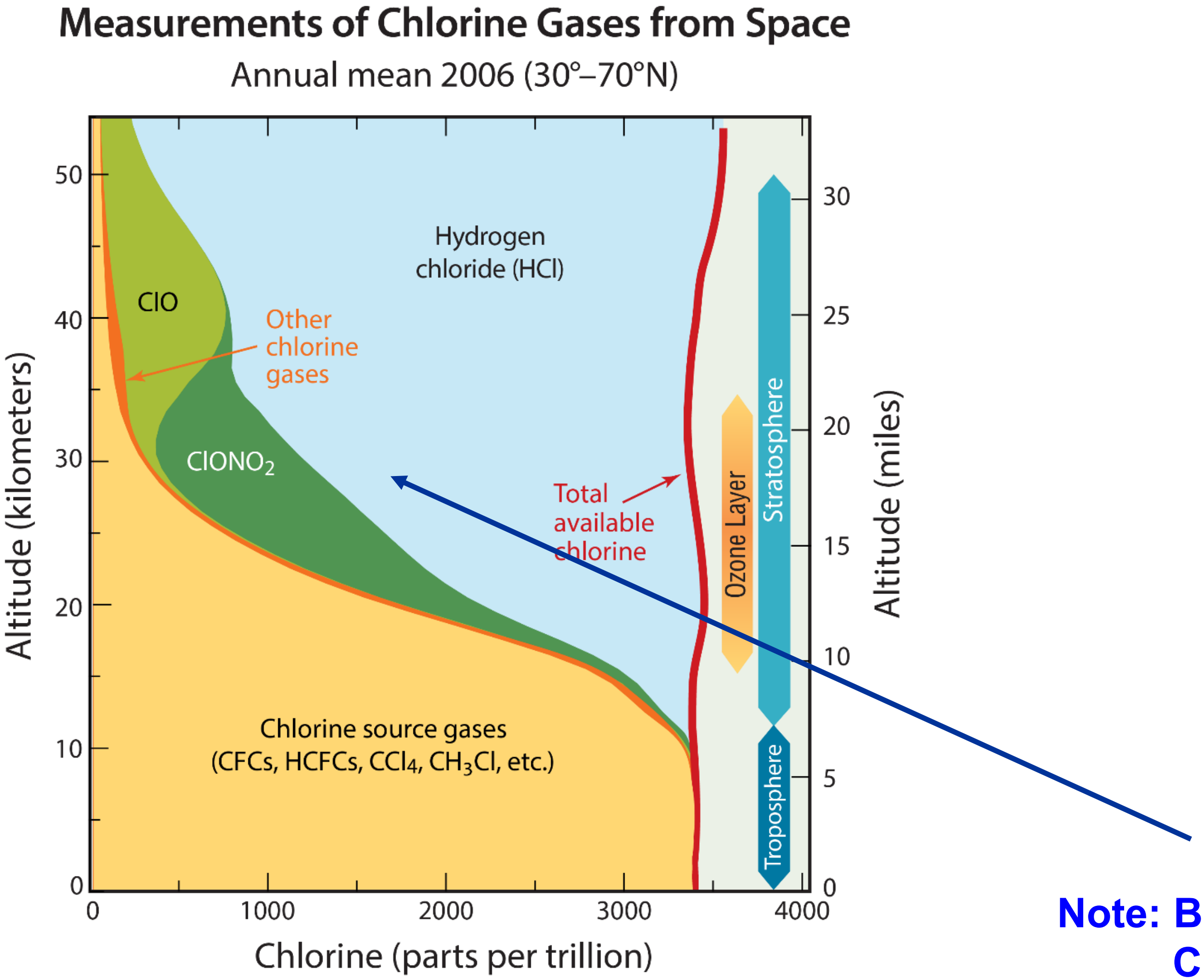
Montreal Protocol Has Banned Industrial Production of CFCs & Other ODS

Projections Based on 2018 World Meteorological Organization Scientific Assessment of Ozone Depletion Report



2018 WMO Scientific Assessment of Ozone Depletion Report:
https://www.esrl.noaa.gov/csd/assessments/ozone/2018

Chlorine Abundance, Mid-Latitude Stratosphere



Note: Below ~30 km,
ClO << ClNO$_3$ and HCl

Fig Q7-2, *WMO/UNEP Twenty QAs Ozone*

Chlorine Source Gases

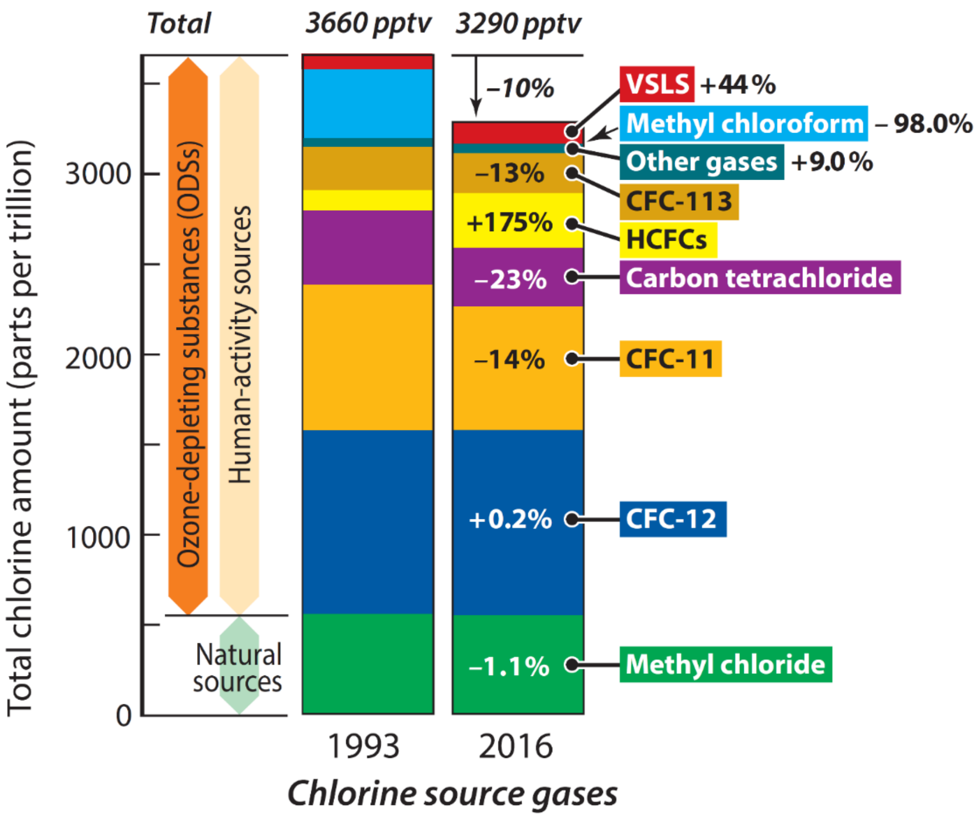
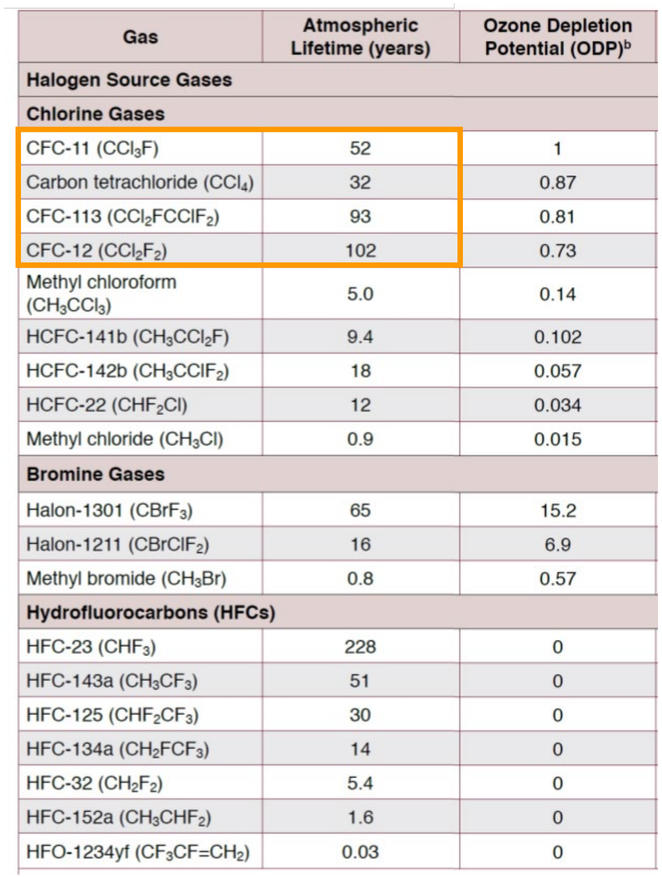


Fig Q6-1, *WMO/UNEP Twenty QAs Ozone*

Time series of chlorine content of organic halocarbons that reach the stratosphere. Past values based on direct atmospheric observation. Future values based on projections that include the lifetime for removal of each halocarbon.

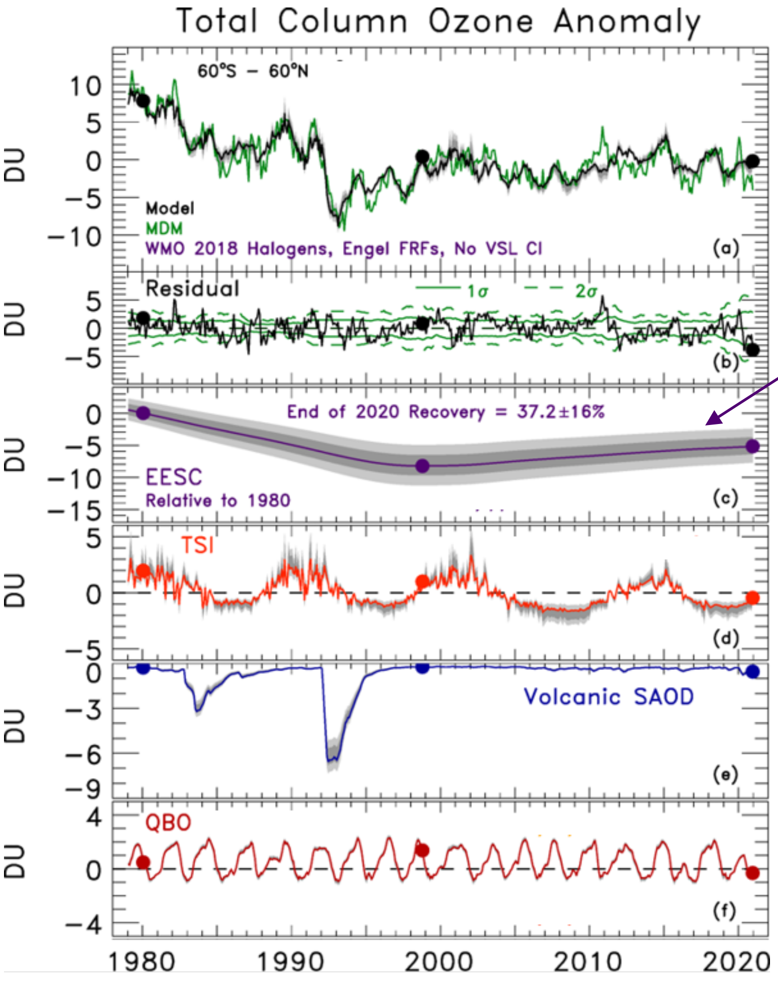
Table 6−4, WMO/UNEP 2018



Gas	Atmospheric Lifetime (years)	Ozone Depletion Potential (ODP)[b]
Halogen Source Gases		
Chlorine Gases		
CFC-11 (CCl_3F)	52	1
Carbon tetrachloride (CCl_4)	32	0.87
CFC-113 (CCl_2FCClF_2)	93	0.81
CFC-12 (CCl_2F_2)	102	0.73
Methyl chloroform (CH_3CCl_3)	5.0	0.14
HCFC-141b (CH_3CCl_2F)	9.4	0.102
HCFC-142b (CH_3CClF_2)	18	0.057
HCFC-22 (CHF_2Cl)	12	0.034
Methyl chloride (CH_3Cl)	0.9	0.015
Bromine Gases		
Halon-1301 ($CBrF_3$)	65	15.2
Halon-1211 ($CBrClF_2$)	16	6.9
Methyl bromide (CH_3Br)	0.8	0.57
Hydrofluorocarbons (HFCs)		
HFC-23 (CHF_3)	228	0
HFC-143a (CH_3CF_3)	51	0
HFC-125 (CHF_2CF_3)	30	0
HFC-134a (CH_2FCF_3)	14	0
HFC-32 (CH_2F_2)	5.4	0
HFC-152a (CH_3CHF_2)	1.6	0
HFO-1234yf ($CF_3CF{=}CH_2$)	0.03	0

Mid-Latitude Ozone Depletion

Total column ozone anomaly is deseasonalized, cosine latitude weighted average of total column ozone collected between 60°S and 60°N, relative to the mean total column abundance over the entire time period.



"Expected" recovery of near global ozone layer for end of 2019 relative to maximum depletion since 1980, driven by atmospheric halogens

Circles (•) placed at 1980, column minimum due to EESC, & end of 2020

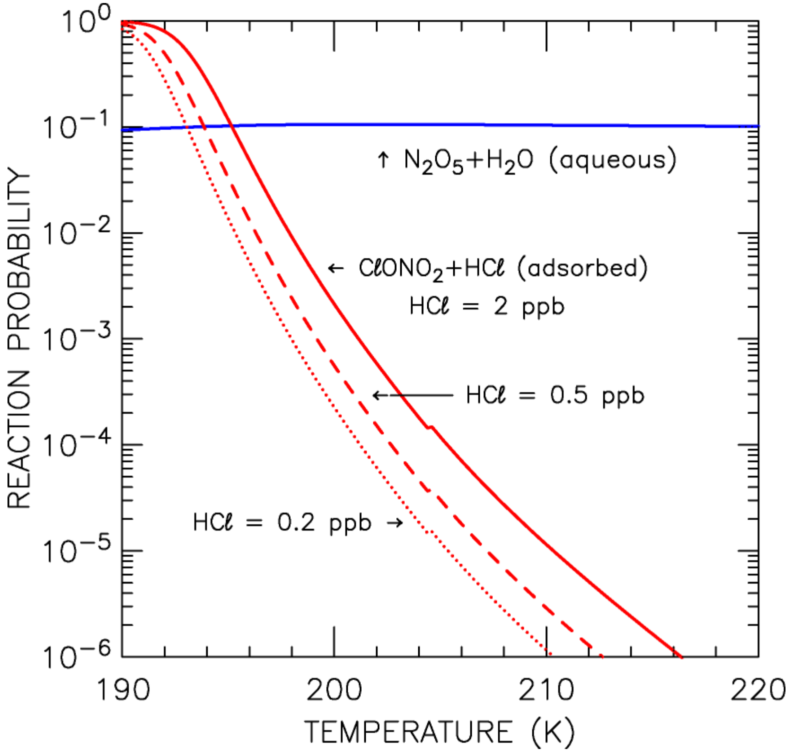
Multiple linear regression of <u>total ozone column</u> anomaly as a function of <u>equivalent effective stratospheric chlorine</u> (**EESC**), total solar irradiance (**TSI**), stratospheric aerosol optical depth (**SAOD**), and the quasi-biennial oscillation (**QBO**) has long been used to quantitatively assess factors that drive variations in the thickness of the ozone layer.

Note: EESC = Inorganic Stratospheric Chlorine +
60× Inorganic Stratospheric Bromine

McBride *et al.*, In Prep, 2022

Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

In all cases, γ must be measured in the laboratory



Reaction probabilities given for various surface types, with formulations of various degrees of complexity, in **Section 5** of the JPL Data Evaluation.

Atmospheric Chemistry and Physics by Seinfeld and Pandis provides extensive treatment of aqueous phase chemistry, properties of atmospheric aerosol, organic aerosols, etc.

POLAR OZONE LOSS

- COLD TEMPERATURES → POLAR STRATOSPHERIC CLOUDS (**PSCs**)
- REACTIONS ON PSC SURFACES LEAD TO ELEVATED **ClO**

$HCl + ClNO_3 \rightarrow Cl_2$ (gas) + HNO_3 (solid)

$ClNO_3 + H_2O \rightarrow HOCl + HNO_3$

Cl_2 + SUNLIGHT + $O_3 \rightarrow ClO$

HOCl + SUNLIGHT + $O_3 \rightarrow ClO$

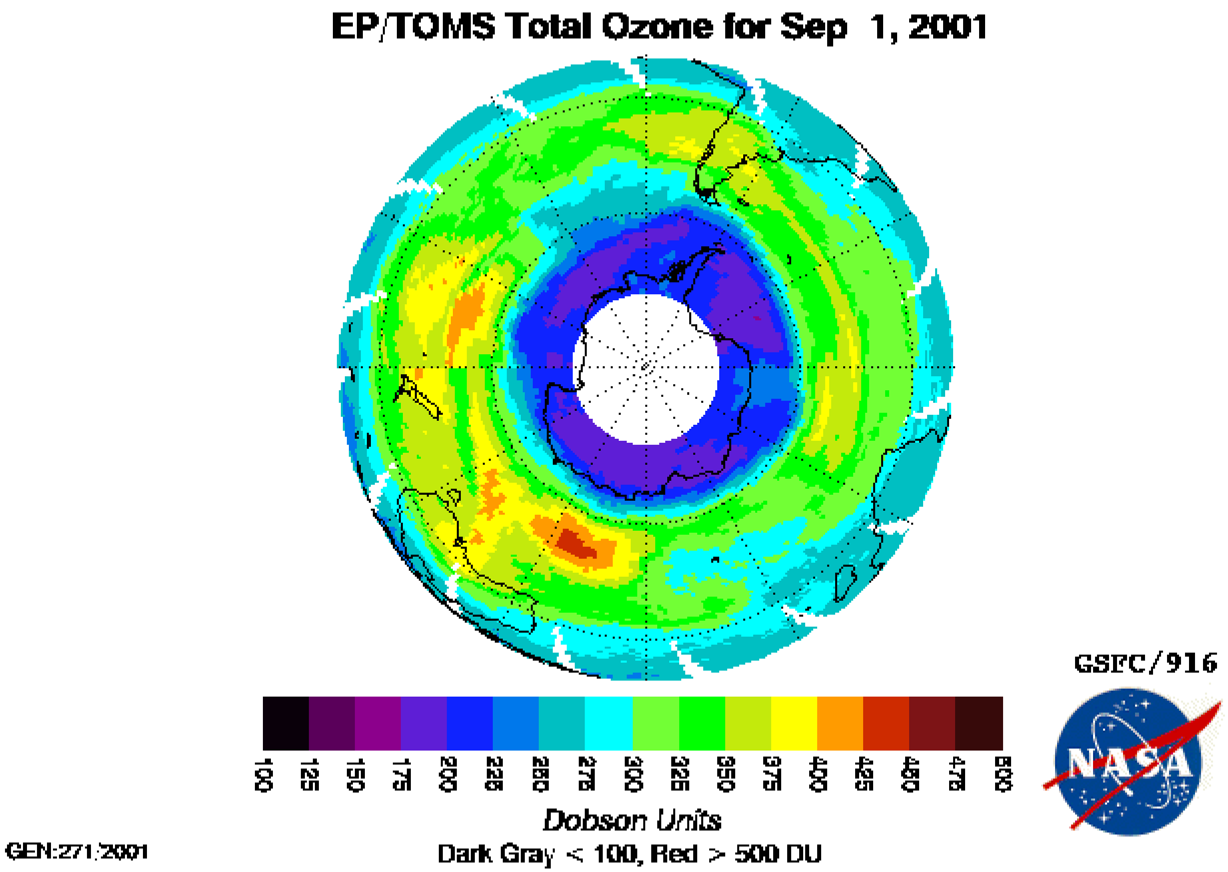
HNO_3 SEDIMENTS (PSCs fall due to gravity)

- ELEVATED **ClO** + SUNLIGHT DESTROYS O_3
- BrO : REACTION PARTNER FOR ClO ⇒ ADDITIONAL O_3 LOSS

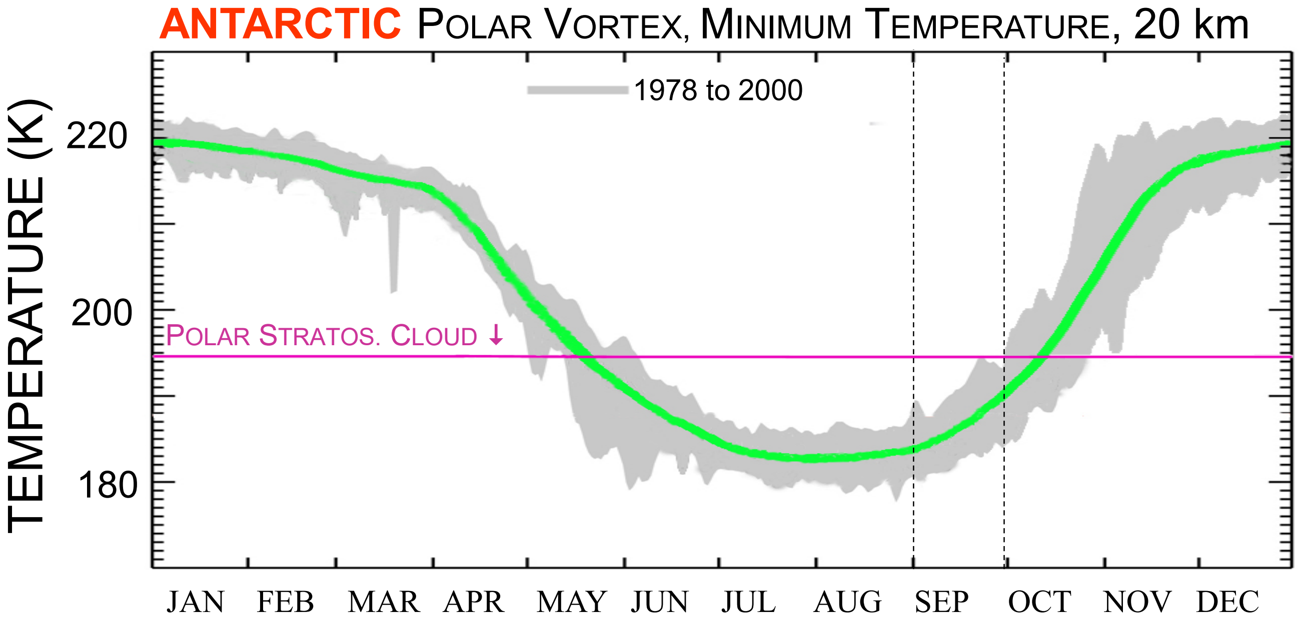
Polar Vortex Circulation

During winter:

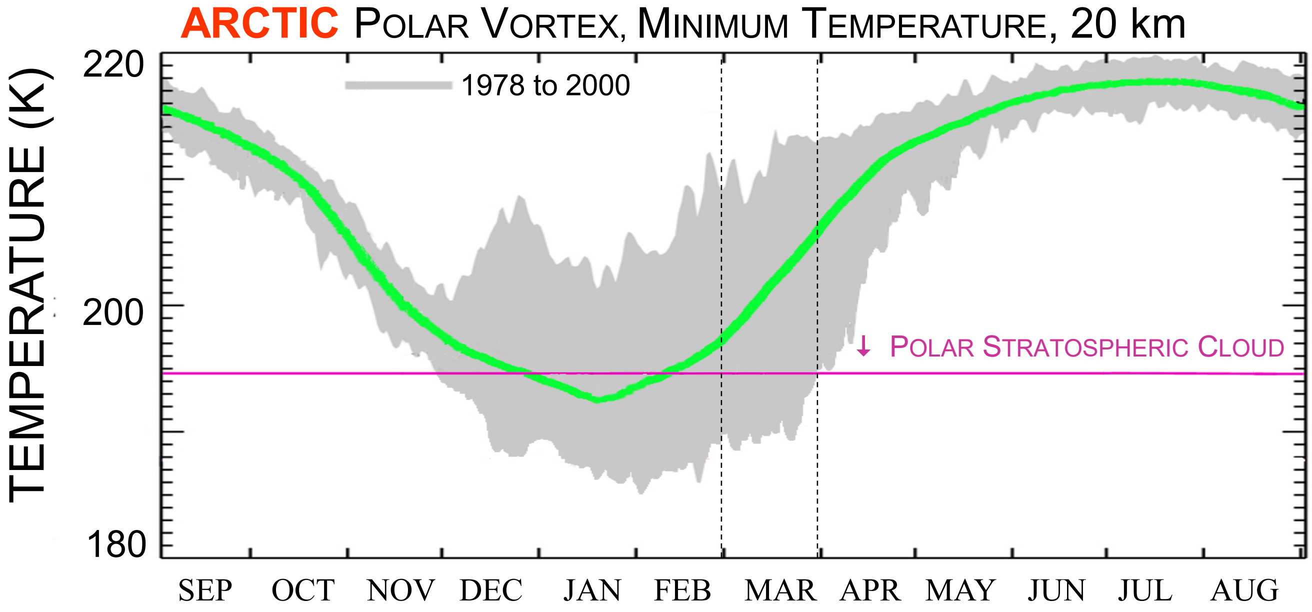
- radiative cooling leads to cold air in polar stratosphere
- large scale low pressure region develops over pole
- strong “polar night jet” develops, isolating air at high latitudes from air at low latitudes
- T continues to fall in the “vortex like” circulation near the pole



EP/TOMS Total Ozone for Sep 1, 2001



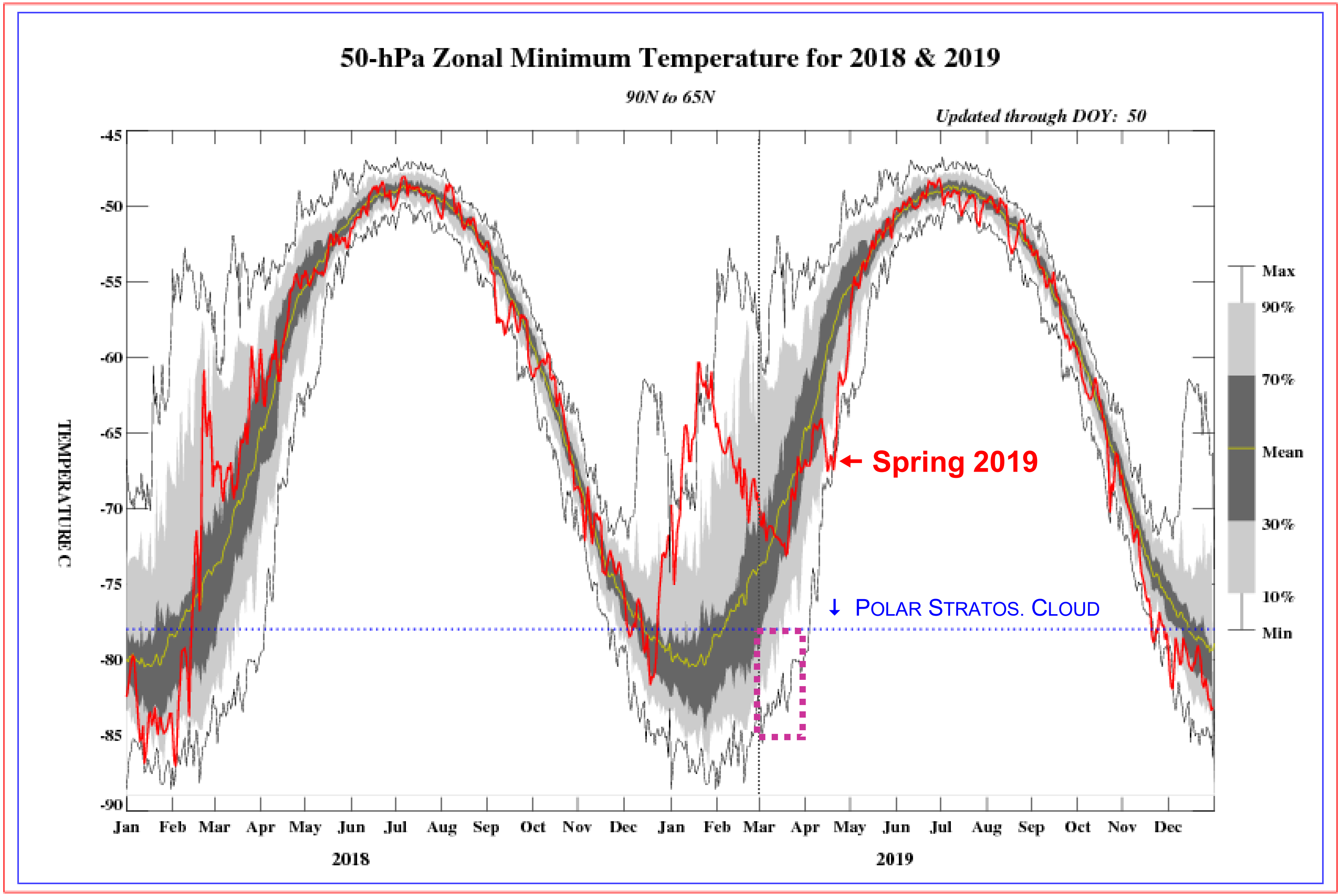
ANTARCTIC POLAR VORTEX, MINIMUM TEMPERATURE, 20 km



ARCTIC POLAR VORTEX, MINIMUM TEMPERATURE, 20 km

Data Courtesy P. Newman,
NASA/GSFC

Arctic Temperature: Mar 2019

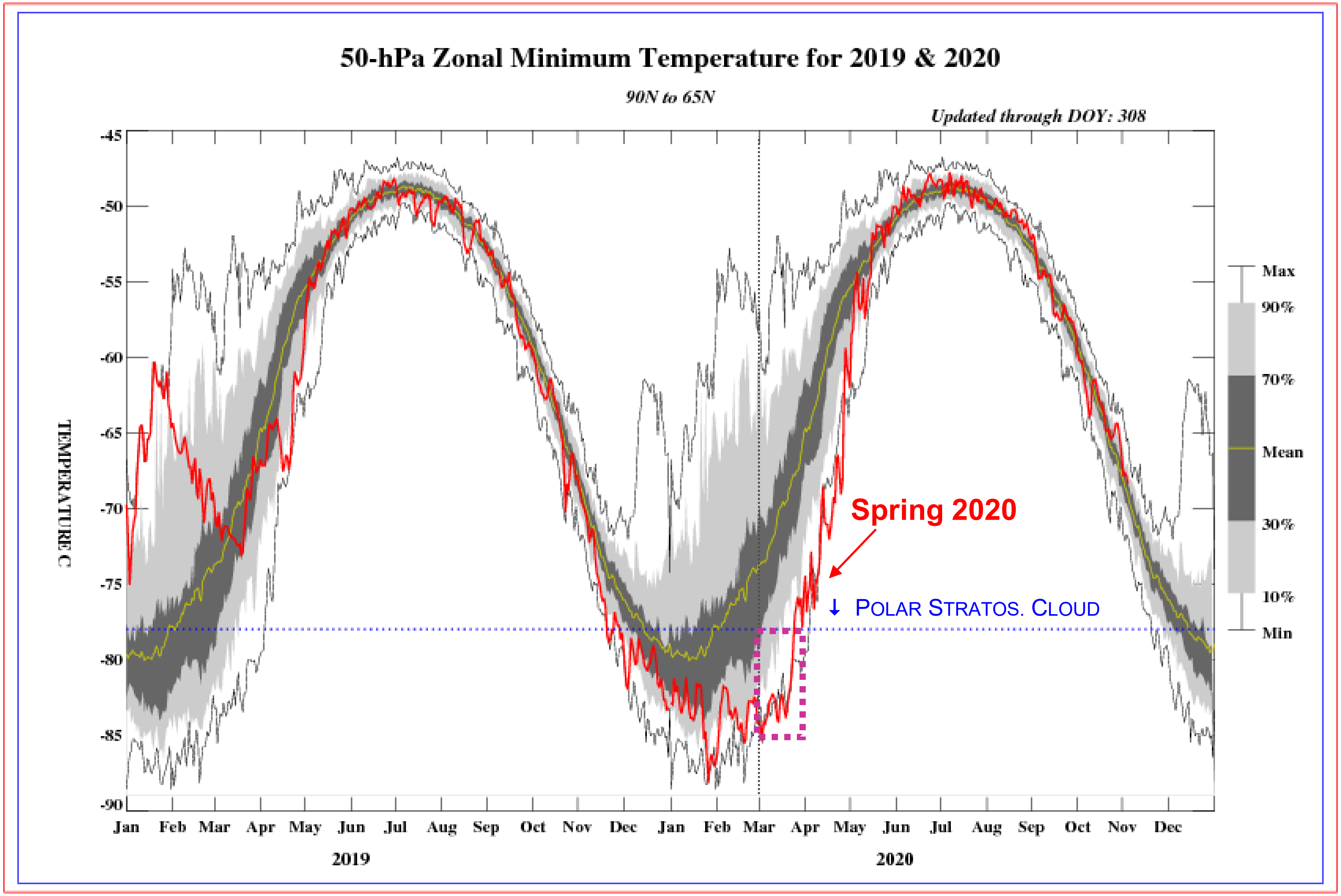


← Spring 2019

↓ POLAR STRATOS. CLOUD

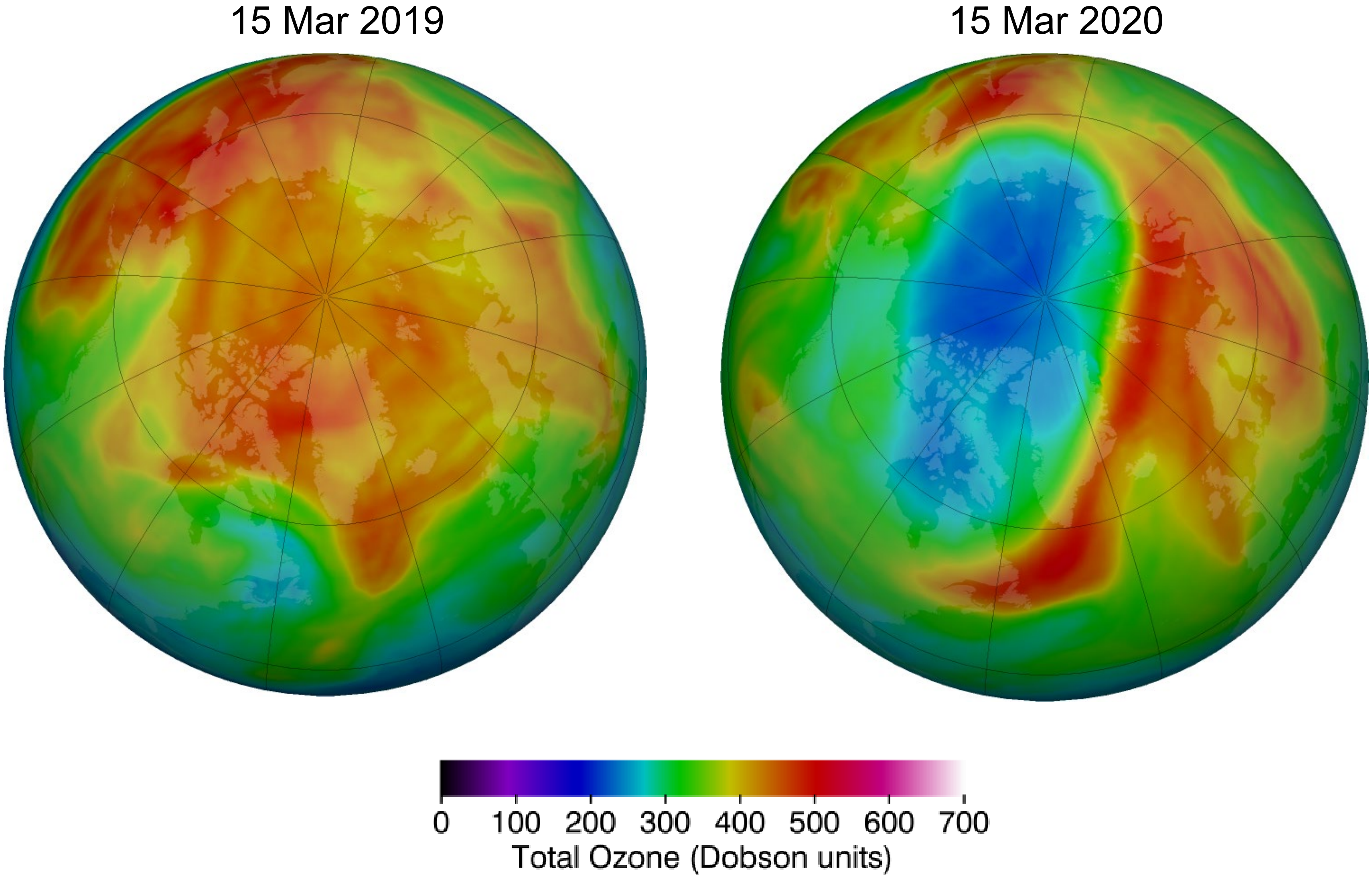
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png

Arctic Temperature: Mar 2020



http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png

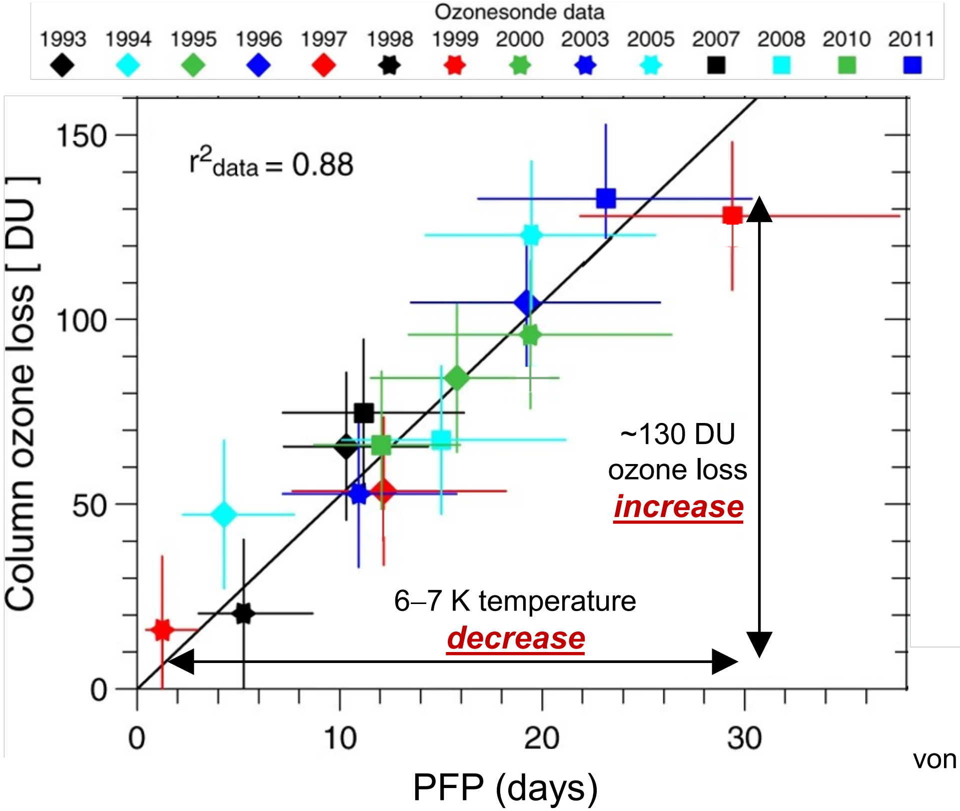
Arctic Ozone: 2019 and 2020



http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png

Arctic Ozone Loss Varies as a function of PSC Formation Potential

Data:



von der Gathen, *Nature Communications*, 2021

- Surprisingly simple relationship between chemical loss of column ozone and volume of air exposed to PSC formation potential over winter, where

$$\text{PFP} = \int_{1\,\text{Nov}}^{30\text{Apr}} \frac{V_{PSC}(t)}{V_{VORTEX}(t)}\, dt\ ;$$

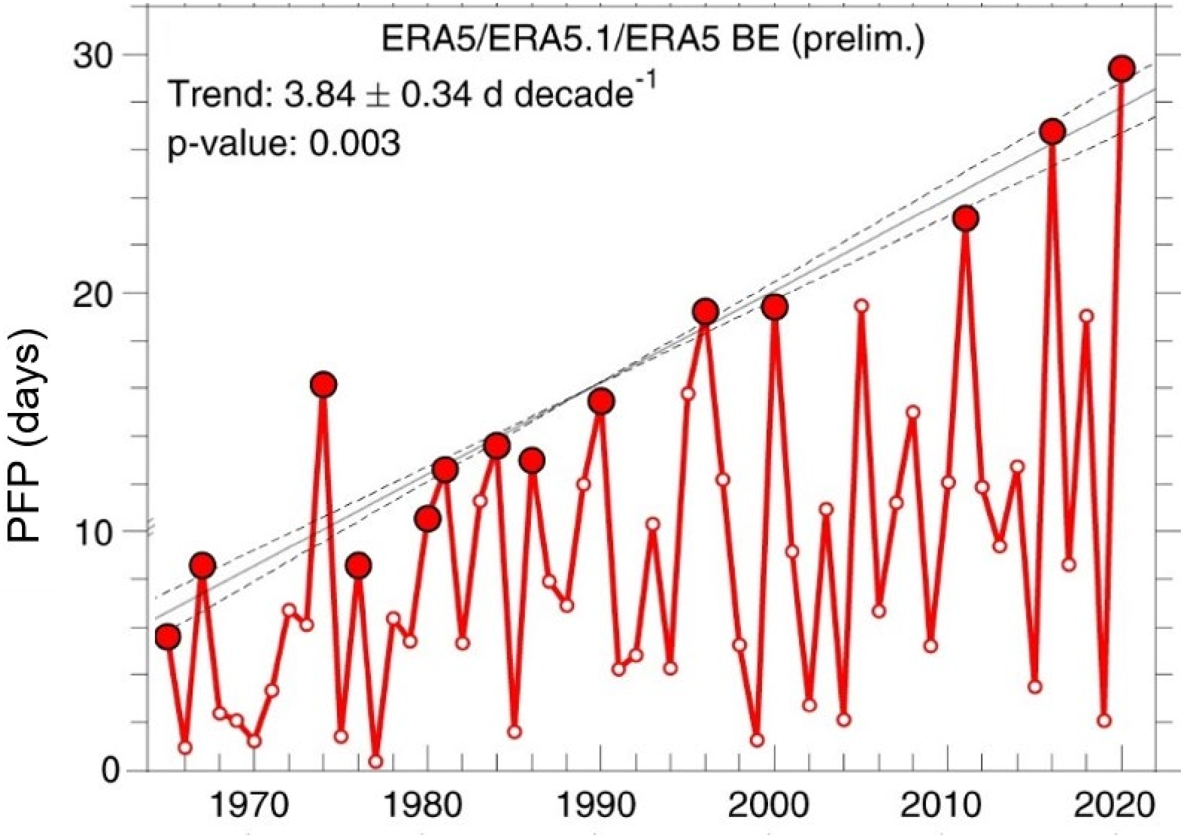
PFP stands for PSC Formation Potential

and V_{PSC} is the volume of the vortex where T is cold enough to allow for formation of PSCs, and V_{VORTEX} is the volume of the Arctic vortex

- Relation leads to estimate of ~20 DU additional loss of ozone per degree Kelvin cooling of *Arctic* stratosphere

Cold Arctic Winters Tend to Exhibit Larger PFP as a Function of Time

More Data: **PFP is PSC Formation Potential**



von der Gathen, *Nature Communications*, 2021

PSC Formation Potential in Arctic Vortex

based on 55 years of data from the European Centre for Medium-Range Weather Forecasts (ECMWF)

SOLID CIRCLES denote local maxima in PFP relative to a trend line

Future Ozone: ODSs, CO_2, CH_4 and N_2O

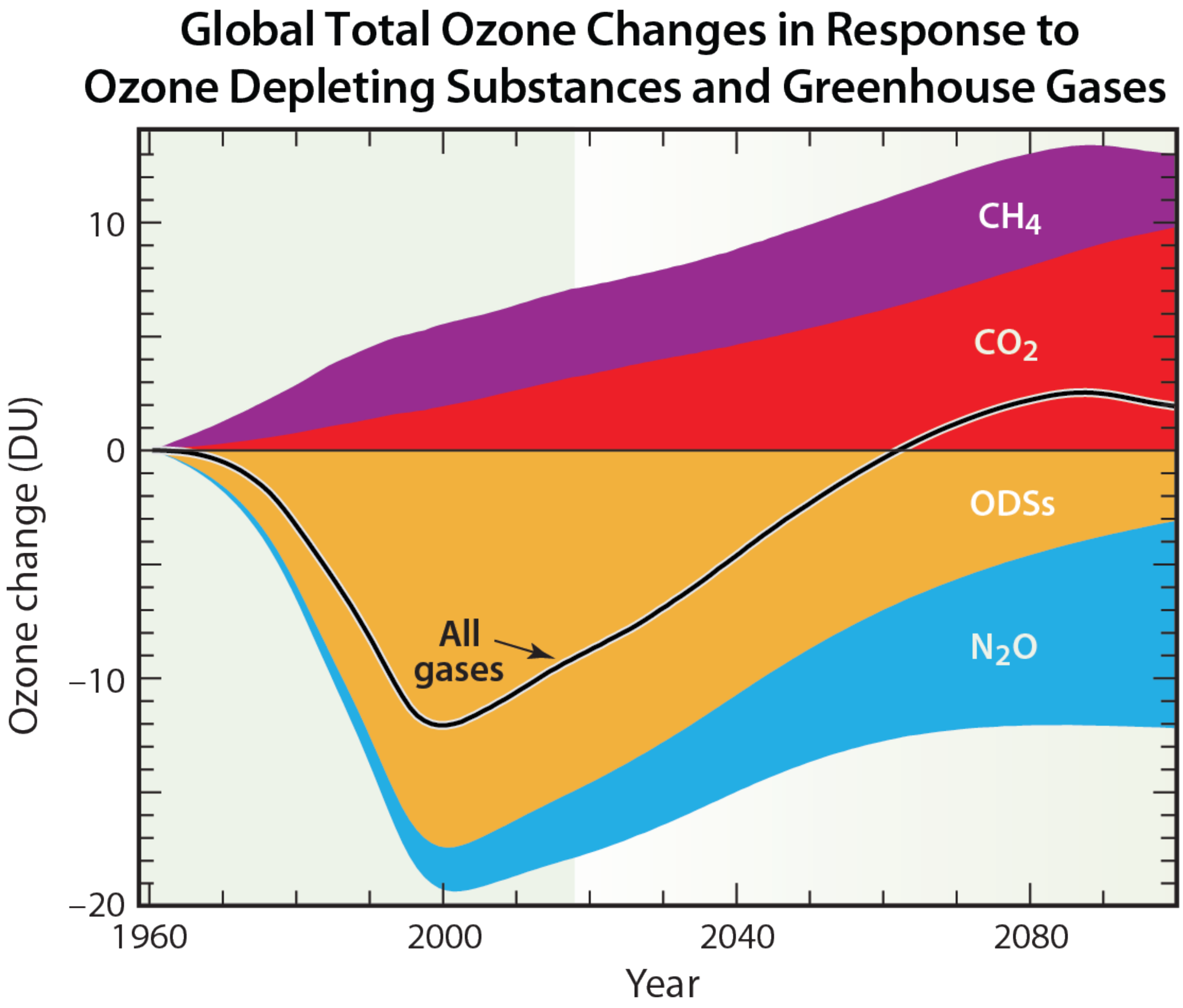
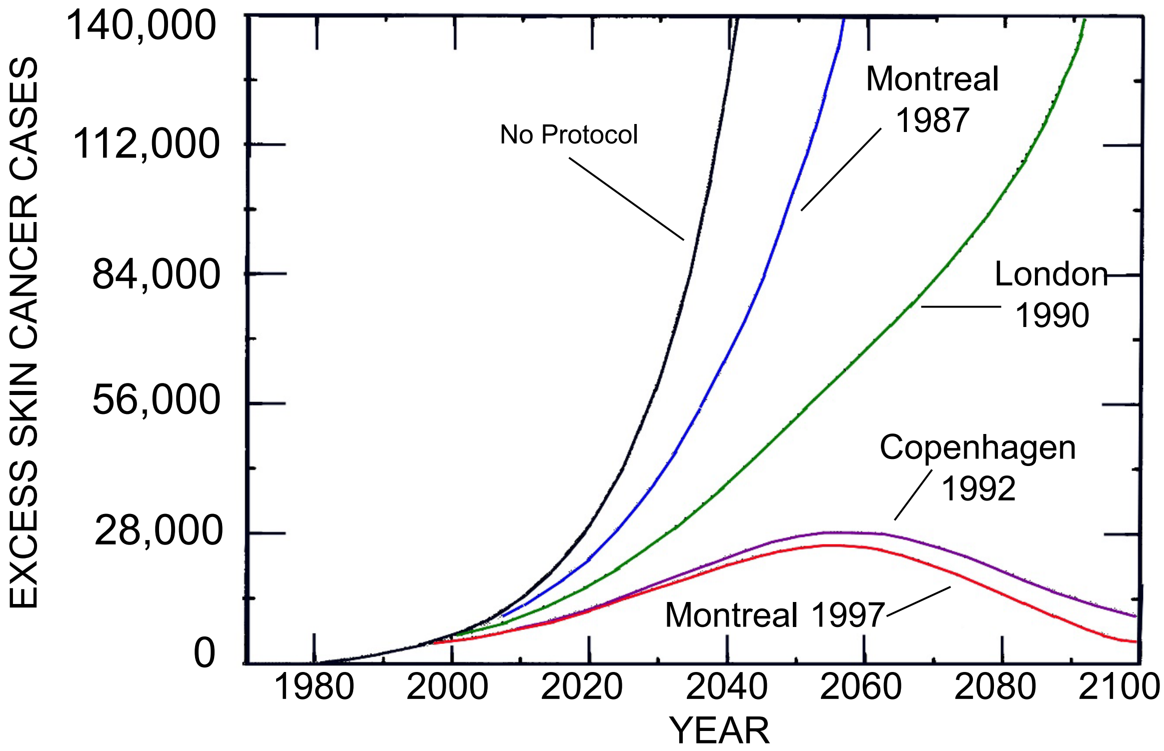


Fig Q20-3, 20 QAs, WMO (2019)

EXCESS SKIN CANCER CASES IN THE UNITED STATES, PER YEAR, DUE TO OZONE DEPLETION FOR VARIOUS CFC EMISSION SCENARIOS



Longstreth *et al.*, *J. of Photochemistry and Photobiology B*, 46, 20–39, 1998.

See also Slaper *et al.*, Estimates of ozone depletion and skin cancer incidence to examine the Vienna Convention achievements, *Nature*, *384*, 256–258, 1996, who state:

> The no-restrictions and Montreal Protocol scenarios produce a runaway increase in skin cancer incidence, up to a quadrupling and doubling, respectively, by year 2100.