Stratospheric Chemistry: Polar Ozone Depletion

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

Today:

- **Processes that govern the formation of the Antarctic ozone hole**
- **Compare & contrast Antarctic and Arctic ozone depletion**
- **Arctic Ozone 2020**

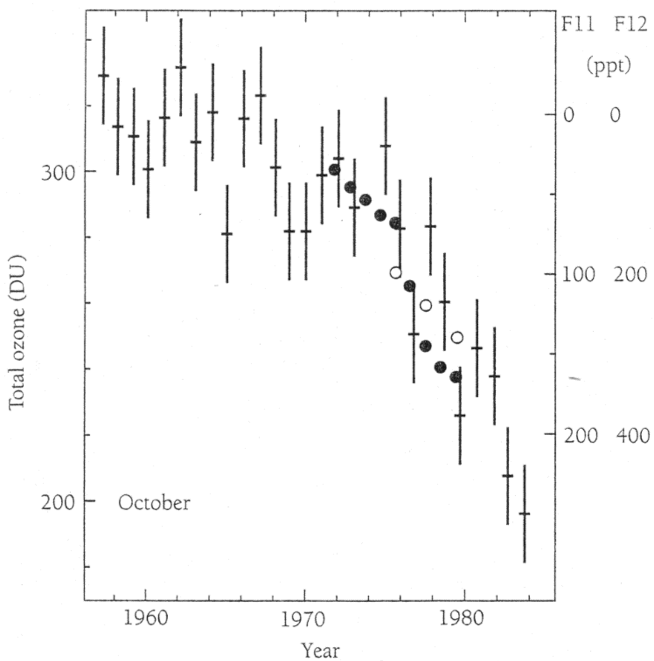
Lecture 16

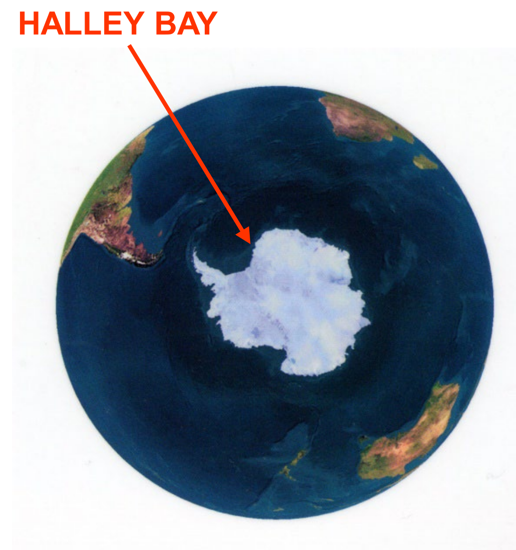
5 April 2022

Polar Ozone Depletion

Discovery of the ozone hole:

Halley Bay (76°S)
October Mean



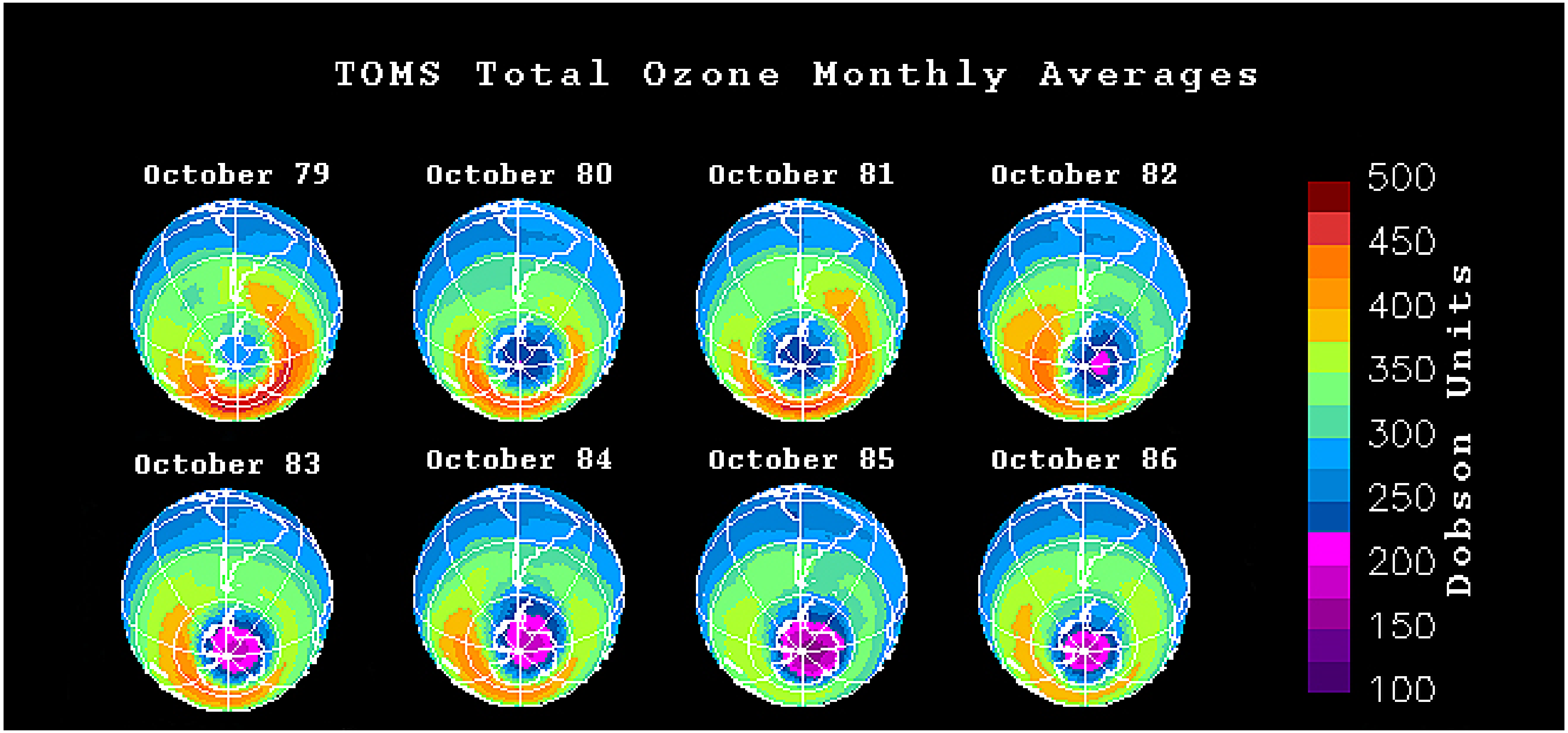


Southern Hemisphere

Farman *et al*., Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature, 315*, 207, 1985.

Polar Ozone Depletion

First view from space:



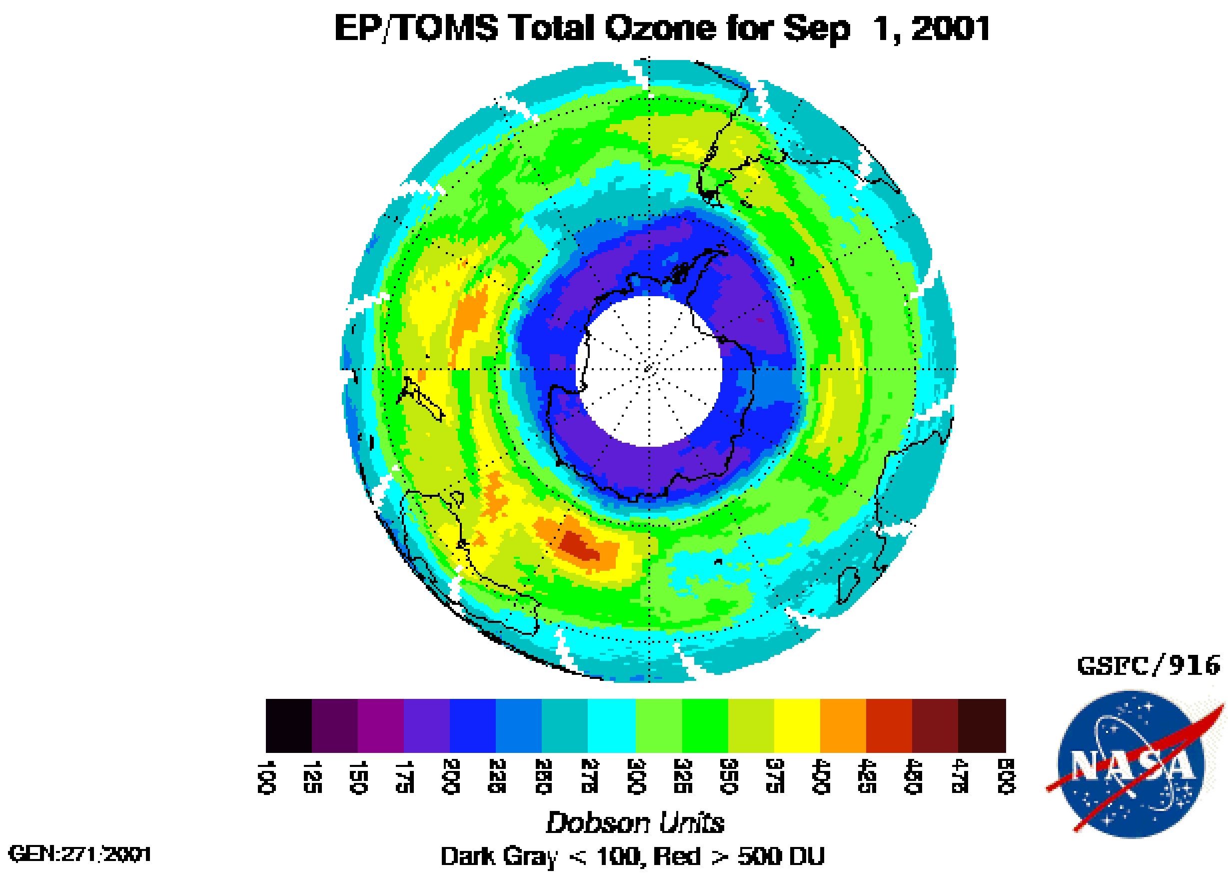
Stolarski *et al.*, *Nature*, 322, 808, 1986.

The paper showed data for Octobers of 1979 through 1985 in black & white contour diagrams. This image, produced soon after, showed color plots of total column ozone during Antarctic spring, including measurements for year 1986.

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



Polar Ozone Depletion Theories

Soon after the discovery of the ozone hole three theories emerged to explain the rapid springtime loss of ozone over Antarctica:

1. Chemistry due to **enhanced levels of ClO**, driven by heterogeneous reactions on the surface of polar stratospheric clouds (PSCs) [McElroy et al., *Nature*, 1986; Solomon et al., *Nature*, 1986]
   a) two new catalytic cycles, both involving halogen radicals and requiring ~1 ppb of ClO to be effective ($ClO + ClO + M \rightarrow ClOOCl + M$; $BrO + ClO \rightarrow Br + Cl + O_2$) [Molina and Molina, *JPC*, 1987; McElroy et al., *Nature*, 1986]
   b) suggestion that PSC particles might be composed of HNO_3 and upon sedimentation could appreciably lower NO_x (which would prevent conversion of ClO to $ClNO_3$) [Toon et al., *GRL*, 1986]
   c) decreasing ozone column driven by rising ClO, due to buildup of chlorine from CFCs

2. Chemistry due to **enhanced levels of NO_x**, driven by variations in solar UV [Callis and Natarajan, *Nature*, 1986]

3. Loss by transport due to **upwelling of ozone poor air** from the troposphere [Tung et al., *Nature*, 1986]

Polar Stratospheric Clouds

- Studies prior to the discovery of the ozone hole documented :
  - high altitude (~20 km) “mother of pearl” clouds over Norway
    [e.g., Carl Stormer, Remarkable clouds at high altitudes, Nature, *1929*]
  - greater prevalence of polar stratospheric clouds in SH compared to NH
    [e.g., McCormick et al., Polar Stratospheric Cloud Sightings by SAM II, *JAS*, 1982].

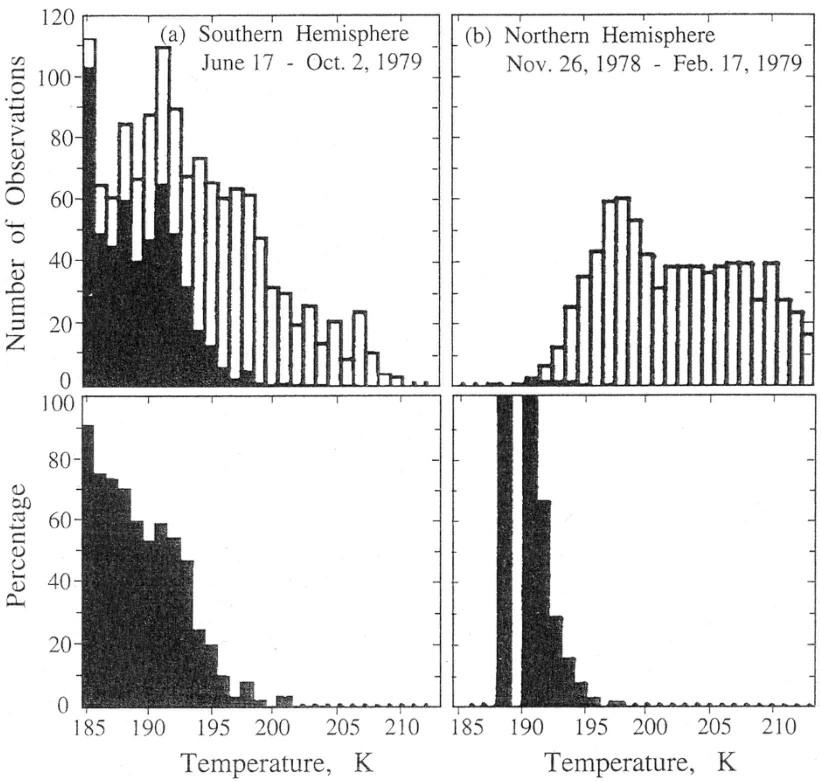
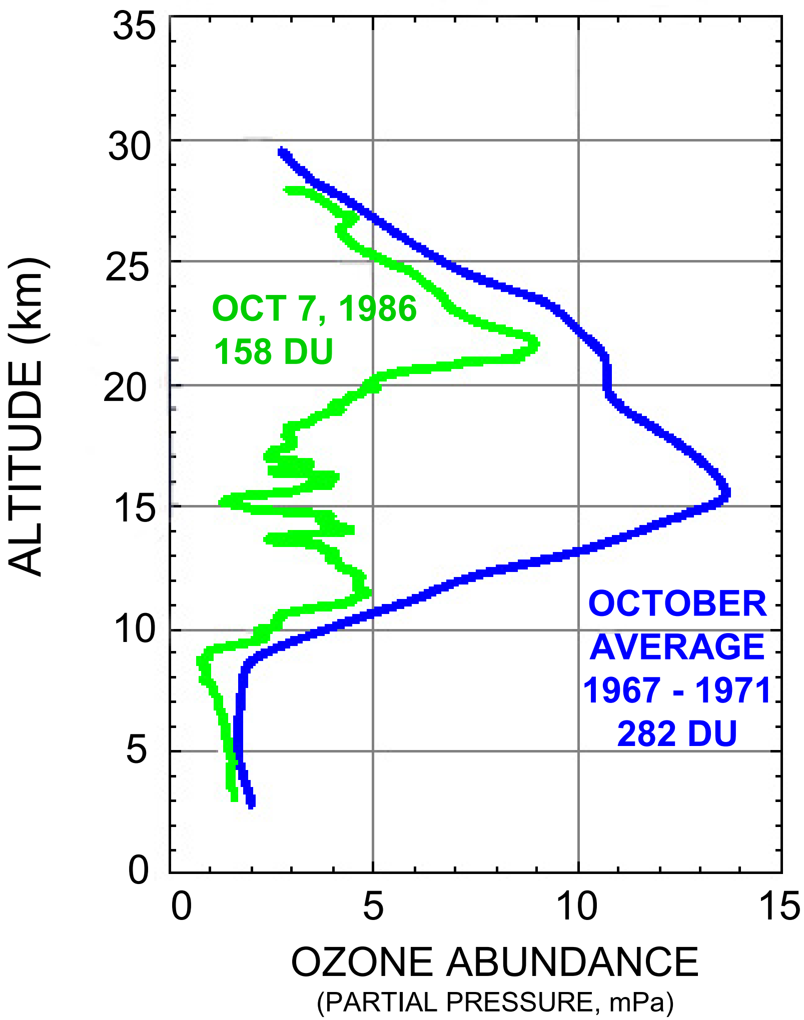


FIGURE 4.20 The top panels show a histogram of the total number of vertical temperature profiles having a given minimum temperature for the Antarctic and Arctic winters. The darkened bars represent observations of PSCs. The lower panel shows the frequency of PSC observations as a percentage of the total events with the same minimum temperature (McCormick et al., 1982). All events for temperatures ≤185 K are included in the 185 K bin.

National Ozone Expedition: McMurdo Station, 1986

Balloon-borne ozonesondes showed:

Region of nearly complete removal of ozone between ~12 and 20 km:

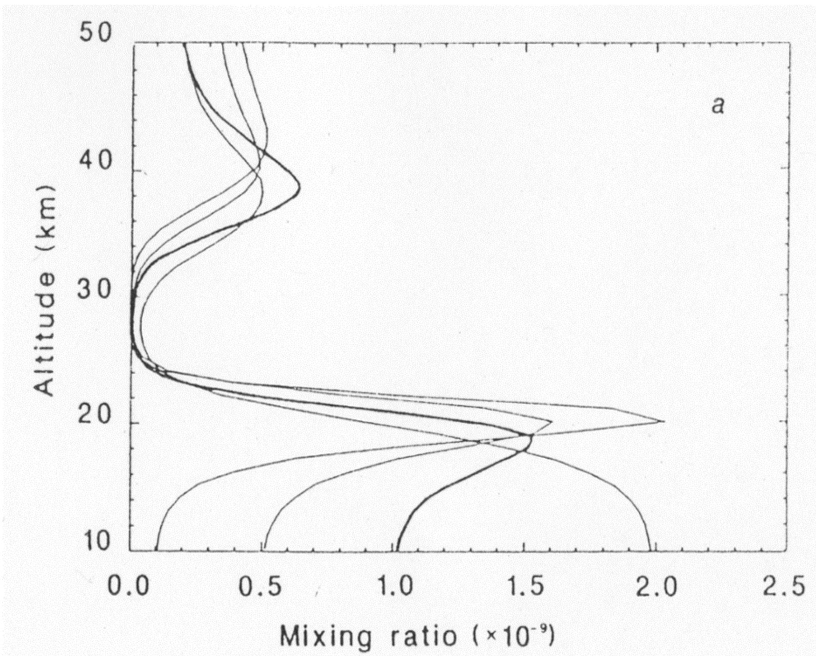


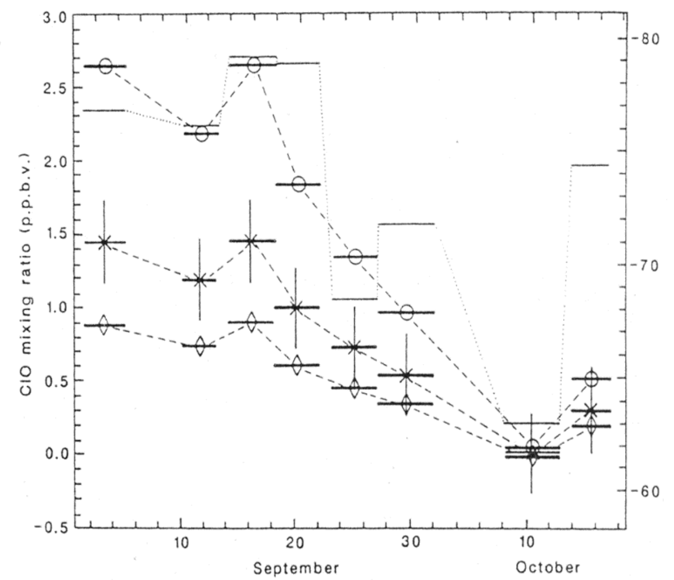
Hofmann et al., *Nature, 326*, 59, 1987.

National Ozone Expedition: McMurdo Station, 1986

Ground based measurements revealed:

- Presence of ~1 ppb of ClO over Antarctica
- Decreasing column HNO_3 throughout springtime and suppressed column HCl and $ClNO_3$, consistent with existence of large amounts of ClO [Farmer et al., *Nature*, 1987]

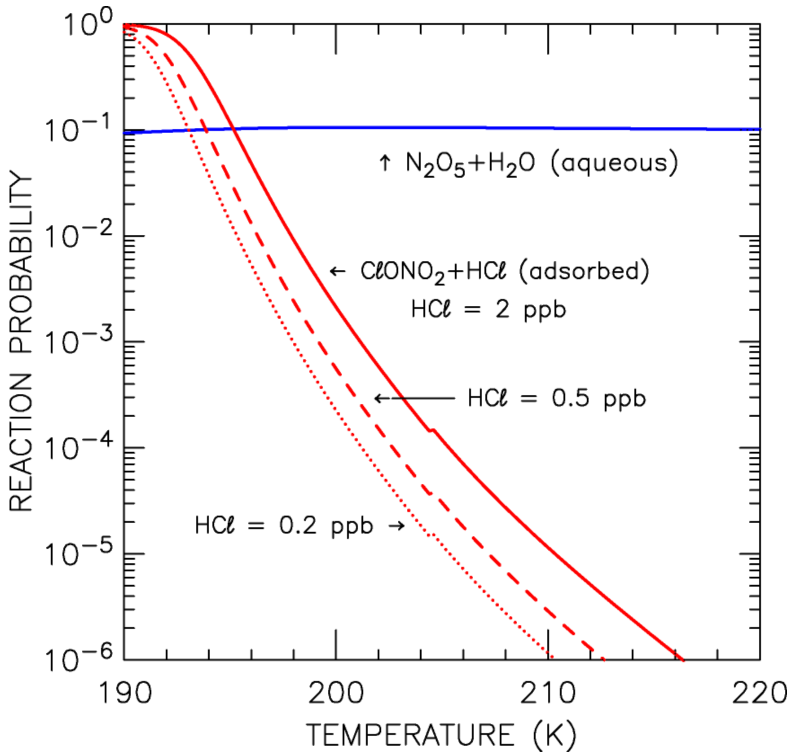




Left: ClO profiles retrieved over McMurdo Station based on ground based microwave spectra acquired 1-22 Sept 1986, for initial mixing ratio guesses of 0.1, 0.5, 1.0, and 2.0 ppb. Because pressure broadening > spectral bandwidth below ~15 km, the initial guess is unaltered by the retrieval algorithm below ~15 km. ***Right:*** Time series of ClO over McMurdo, assuming constant ClO mixing ratio vs altitude between 15-20 km (circles), 15-22 km (crosses), or 15-24 km (diamonds). Thin lines connected by dots are stratospheric temperature at 18 km. From *DeZafra et al*., *Nature*, 1987 and *P. Solomon et al*., *Nature,* 1987.

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.

Heterogeneous Chemistry, Mid-Latitude vs Polar Regions

a) What type of aerosol particles are present in the mid-latitude stratosphere (i.e., what is the chemical composition of these aerosols?)

b) What heterogeneous chemical reaction occurs on the aerosol particles present in the mid-latitude stratosphere and how is the abundance of ClO affected by this reaction?

c) What type of particles are present in the polar stratosphere during winter (i.e., what are these particles called and what is the chemical composition of a "common type" of these particles?)

d) What is the effect of these particles on the chemical composition of the polar stratosphere? Scientists have shown that chemical reactions occurring on the surface of these particles convert species such as and (that do not deplete ozone) and that, while reactive, do not not cause harm to the ozone layer during the darkness of winter.

e) Following the return of sunlight, significant levels of what radical compound builds up inside the Antarctic stratosphere, leading to rapid loss of ozone?

f) Why does the ozone hole occur only over Antarctica?

Polar Ozone Loss

- <u>Cold Temperatures</u> → Polar Stratospheric Clouds (**<u>PSCs</u>**)
- Reactions on PSC surfaces lead to elevated **<u>ClO</u>**

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

$ClNO_3 + H_2O \rightarrow HOCl + HNO_3$

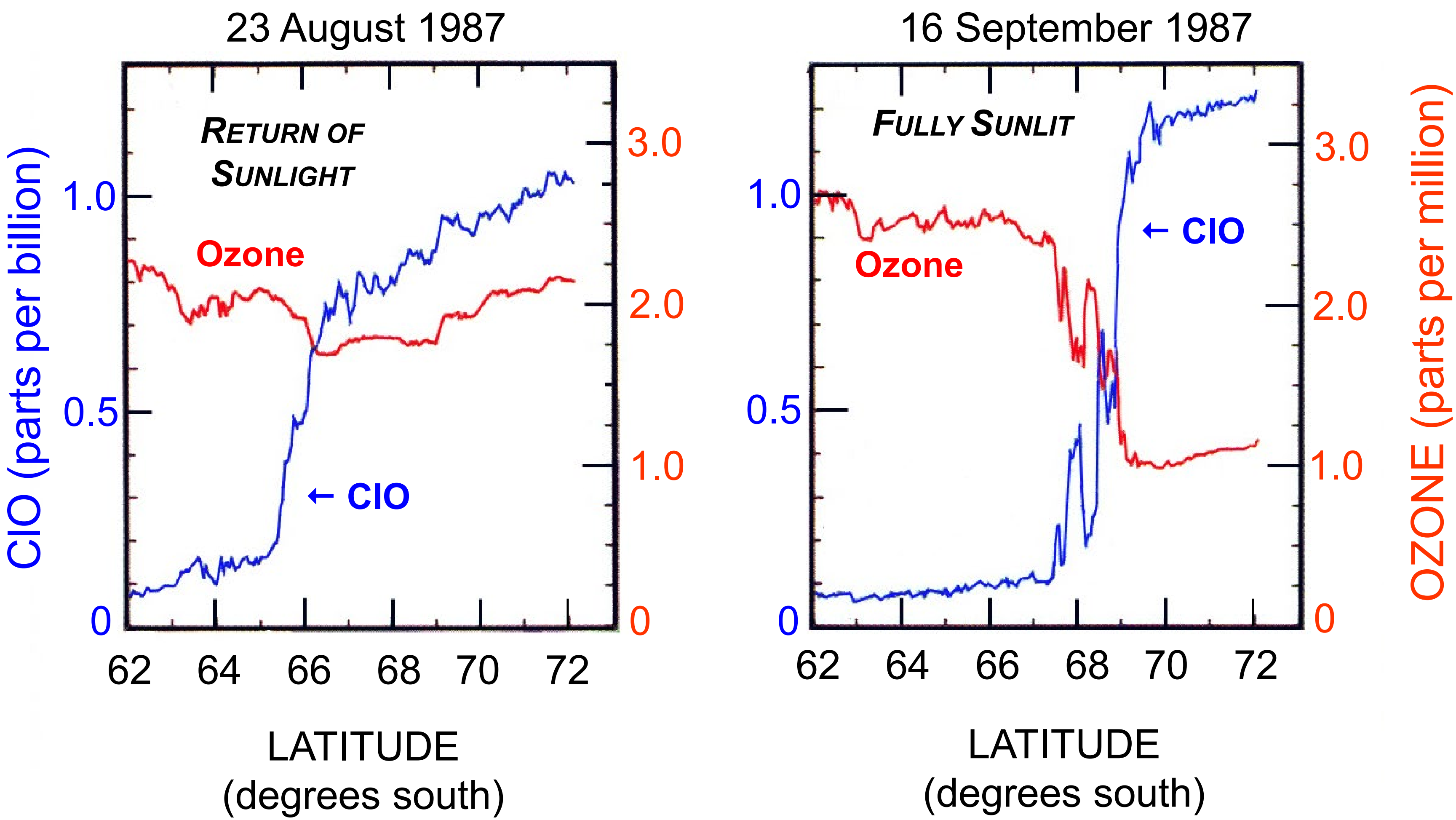
Cl_2 + SUNLIGHT + $O_3 \rightarrow ClO$

HOCl + SUNLIGHT + $O_3 \rightarrow ClO$

HNO_3 SEDIMENTS (PSCs fall due to gravity)

- Elevated **ClO** + <u>Sunlight</u> destroys O_3
- BrO : Reaction Partner For ClO ⇒ Additional O_3 Loss

Airborne Antarctic Ozone Expedition: Punta Arenas, Chile,1987



Anderson et al., *Science*, 1991

Polar Ozone Loss Cycles

Cycle (1a):

$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClOOCl + h\nu \rightarrow ClOO + Cl$$
$$ClOO + heat \rightarrow Cl + O_2$$
$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

Cycle (1b):

$$ClO + ClO + M \rightarrow ClOOCl + M$$
$$ClOOCl + heat \rightarrow ClO + ClO$$
$$\text{Net:} \quad M + heat \rightarrow M$$

Cycle (2a):

$$BrO + ClO \rightarrow BrCl + O_2$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$BrCl + h\nu \rightarrow Br + Cl$$
$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

Cycle (2b):

$$BrO + ClO \rightarrow ClOO + Br$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClOO + heat \rightarrow Cl + O_2$$
$$\text{Net:} \quad O_3 + O_3 \rightarrow 3\ O_2$$

Cycle (2c):

$$BrO + ClO \rightarrow OClO + Br$$
$$OClO + h\nu \rightarrow O + ClO$$
$$Br + O_3 \rightarrow BrO + O_2$$
$$\text{Net:} \quad O_3 \rightarrow O + O_2$$

Cycle (1) accounts for ~60% of polar ozone loss; Cycle (2) accounts for nearly all of the rest

Rate constants and products for these reactions worked out by many scientists:

- Molina and Molina, JPC, 1987
- Sander, Friedl, and Yung, *Science,* 1989
- Moore, Okumura *et al., Phys. Chem. A,* 1999
- Bloss, Nickolaisen, Sander *et al.*, JPC, 2001

Thermal Decomposition

30.5 kcal/mole **2 × 24.3 kcal/mole**

$ClOOCl + M \rightarrow ClO + ClO + M$ **ΔH = 18.1 kcal/mole**

$$\frac{k_{\text{THERMAL}}}{k_{\text{FORMATION}}} = e^{(G_{\text{REACTANTS}} - G_{\text{PRODUCTS}})/RT} = K^{\text{EQUILIBRIUM}}$$

JPL Data Evaluation gives values of $K^{\text{EQUILBRIUM}}$ and $k_{\text{FORMATION}}$

$$K^{EQ} = 1.27 \times 10^{-27}\, e^{(8744/T)}\, cm^{-3}$$

In equilibrium:

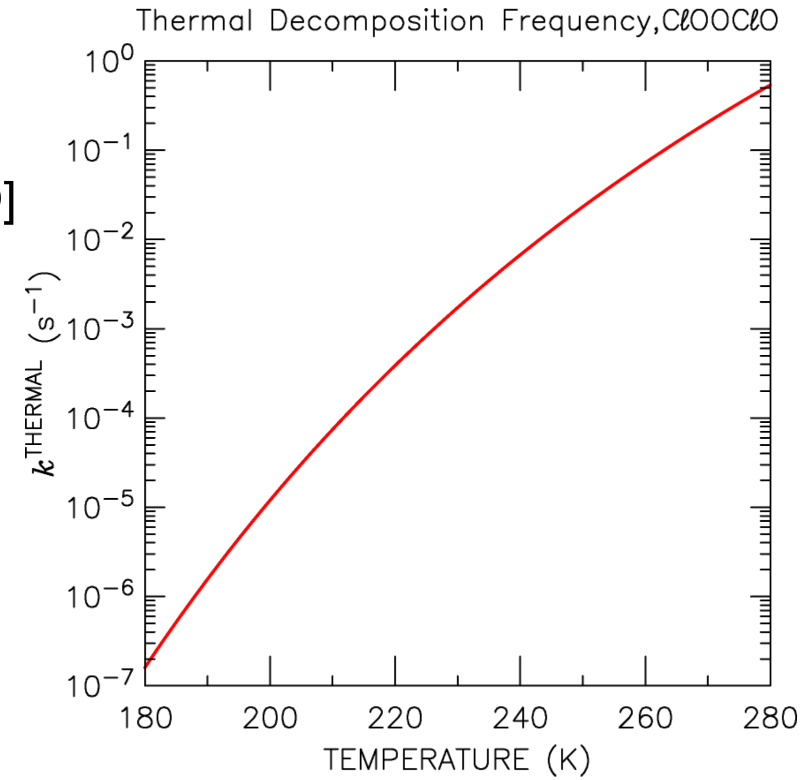
$$k^{\text{THERMAL}} [ClOOCl] = k^{\text{FORMATION}} [ClO]\,[ClO]$$

where $k^{\text{THERMAL}} = k^{\text{FORMATION}} \times K^{EQ}$

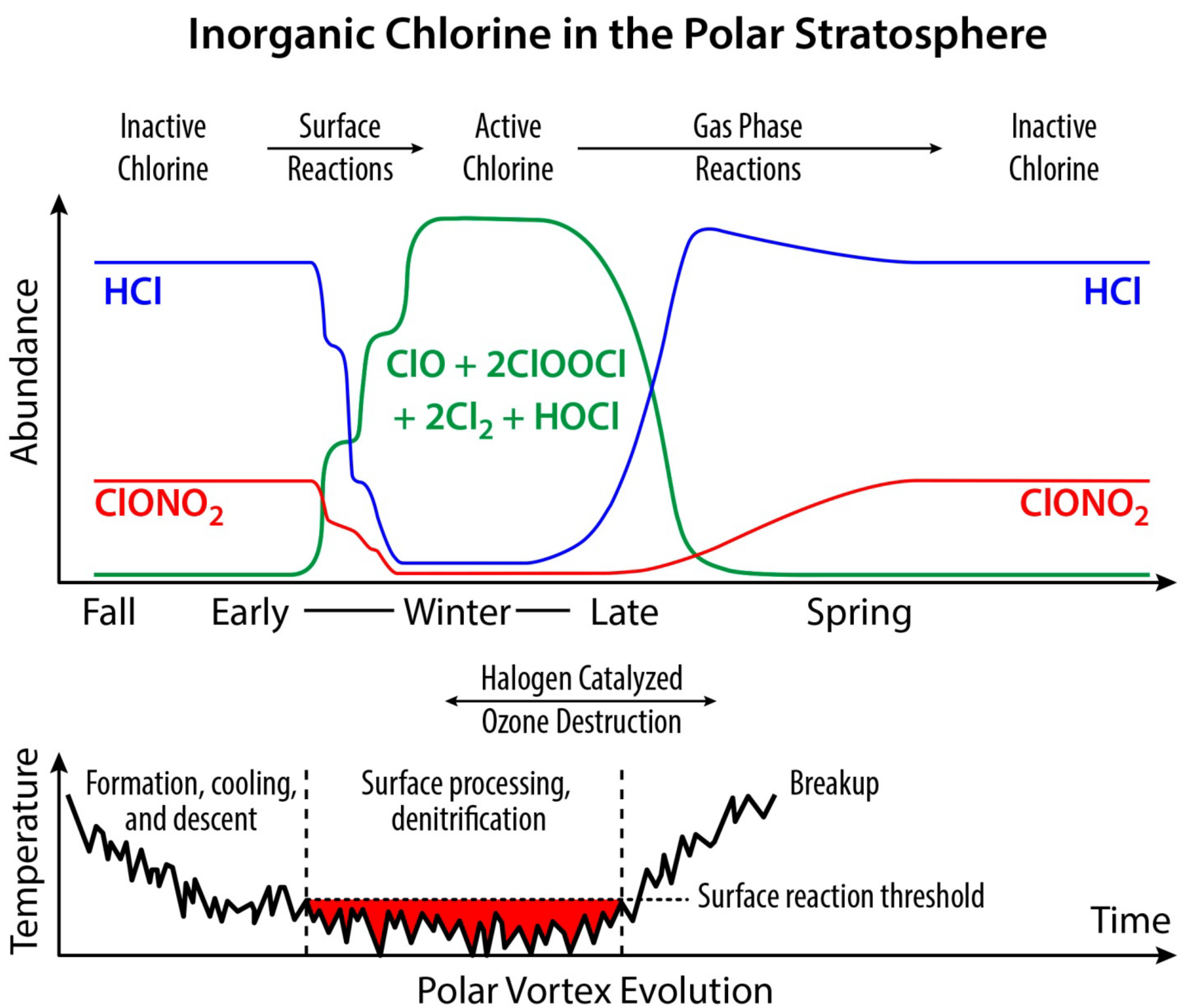
- **Energetically, system favors ClOOCl**
- **Entropically, system favors ClO & ClO**

at low T, ClOOCl stable: energy wins !
at high T, ClOOCl unstable: entropy rules !

Equilibrium constants given in **Section 3** of the JPL Data Evaluation.

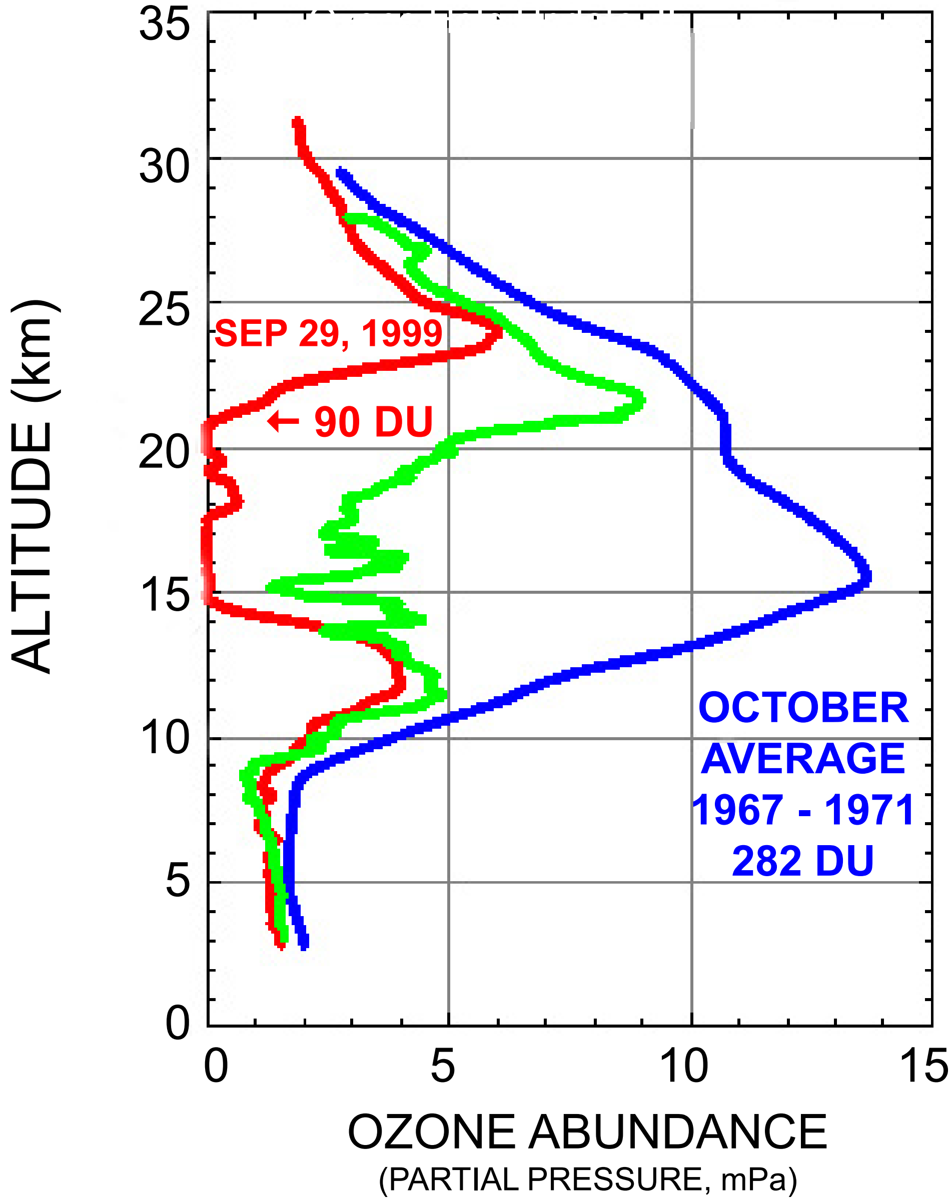


Polar Halogens, Seasonal Evolution



From Wilmouth, Salawitch & Canty, Stratospheric Ozone Depletion and Recovery, 2017

OZONE PROFILES, SOUTH POLE: UPDATE

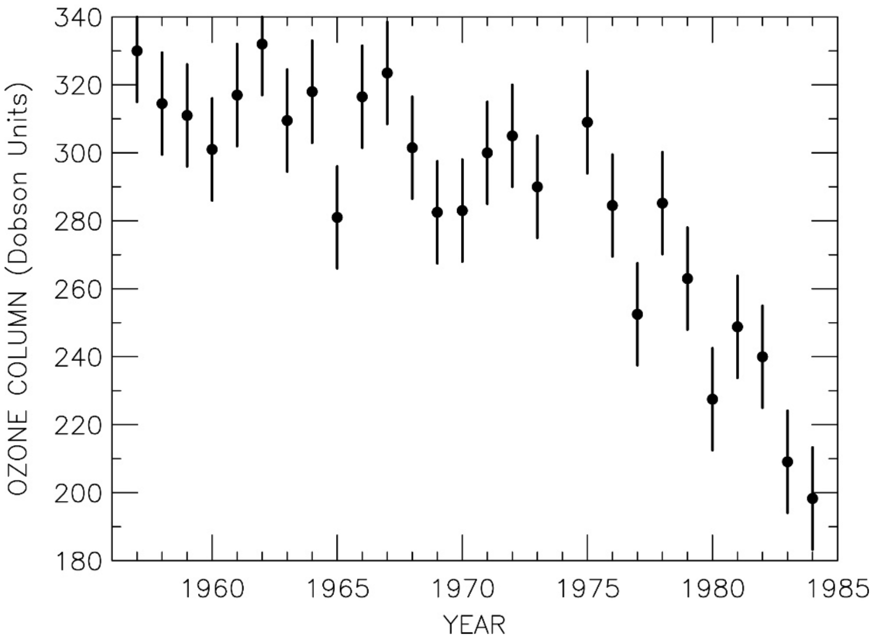


D. Hofmann, NOAA CMDL

Earth's Atmosphere – Effect of Humans

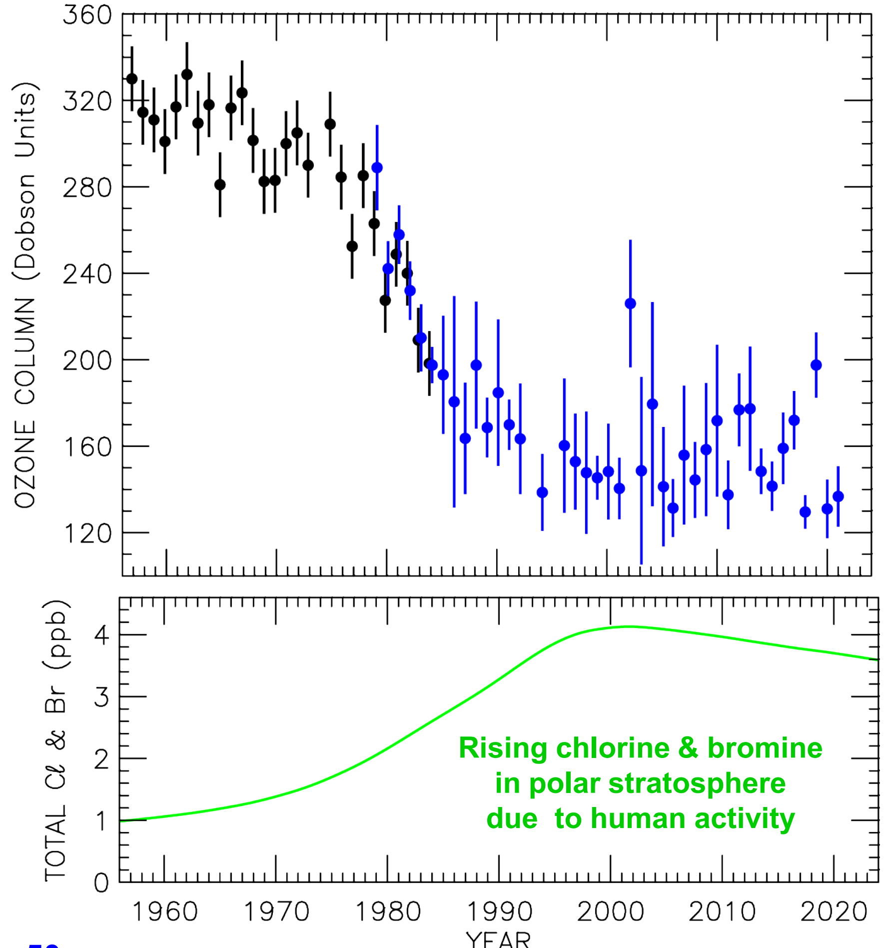
Stratospheric Ozone – shields surface from solar UV radiation

Total Ozone Over Halley Bay, Antarctica (76°S)
Average for October



Update

Total Ozone Over Halley Bay, Antarctica (76°S)
Average for October

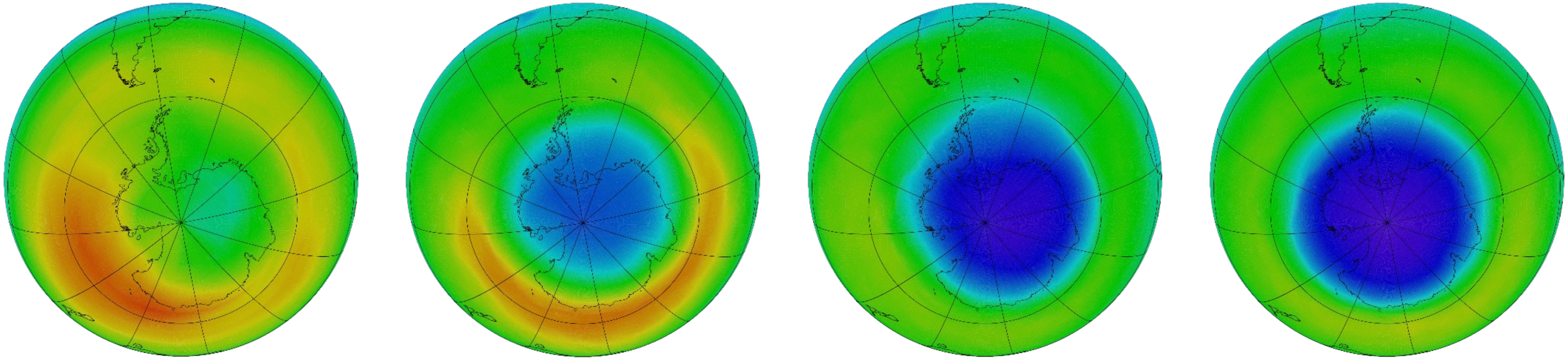


After Farman *et al*., Large losses of total ozone in Antarctica reveal Seasonal ClOx/NOx interaction, Nature, 315, 207, 1985.

EESC = Total Chlorine + 65 × Total Bromine
(scientists use a multiplier of 65 for polar regions and 60 for extra-polar regions)

Lecture 1, Slide 50

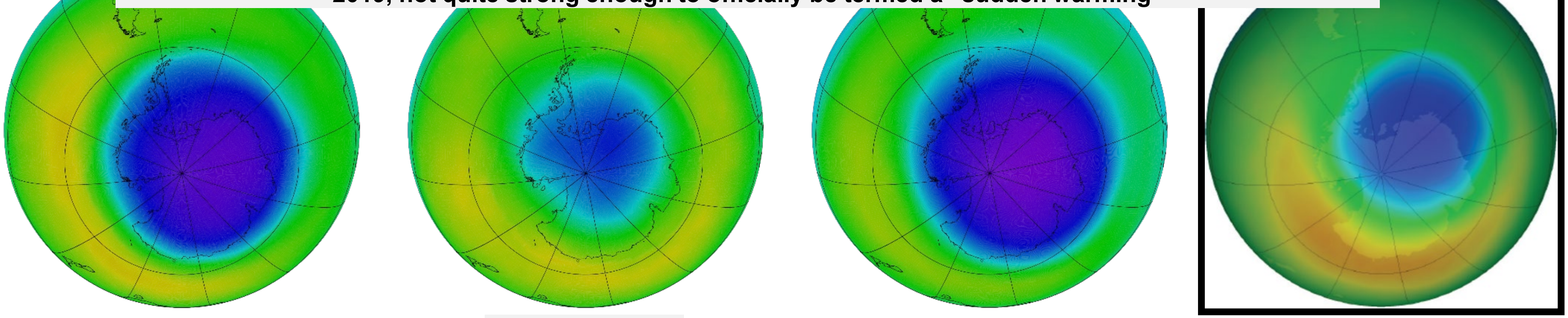
Antarctic Ozone versus Time



October 1972 | October 1980 | October 1985 | October 1990

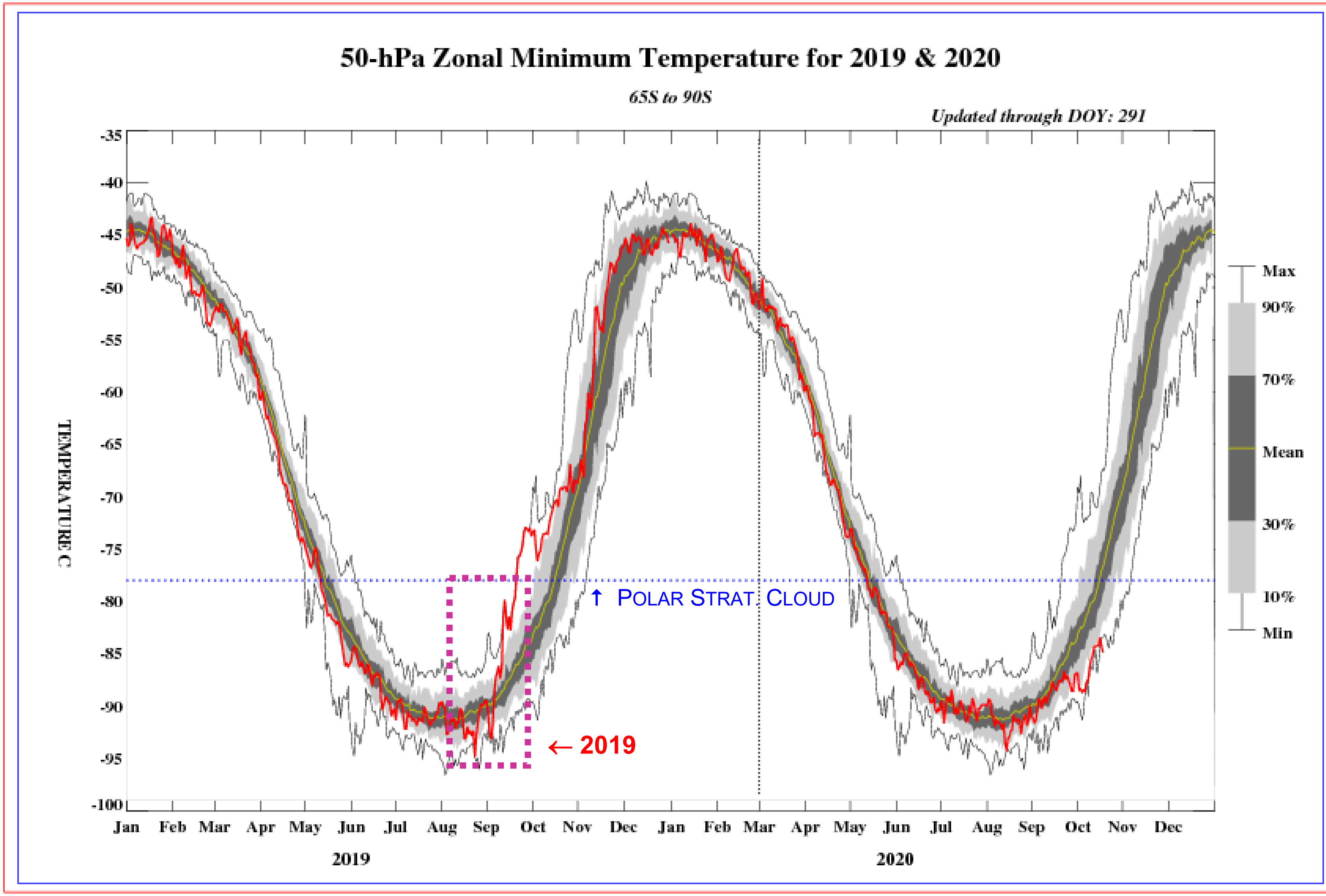
Much smaller Ozone Hole in October 2002 due to early “sudden warming” of Antarctic stratosphere polar vortex as explained in box entitled “The 2022 Antarctic Ozone Hole” within Question 10 of the 20 QAs document.

Similarly, smaller Ozone Hole in October 2019 due to dynamical disturbance of the Antarctic vortex in late Sept 2019, not quite strong enough to officially be termed a “sudden warming”



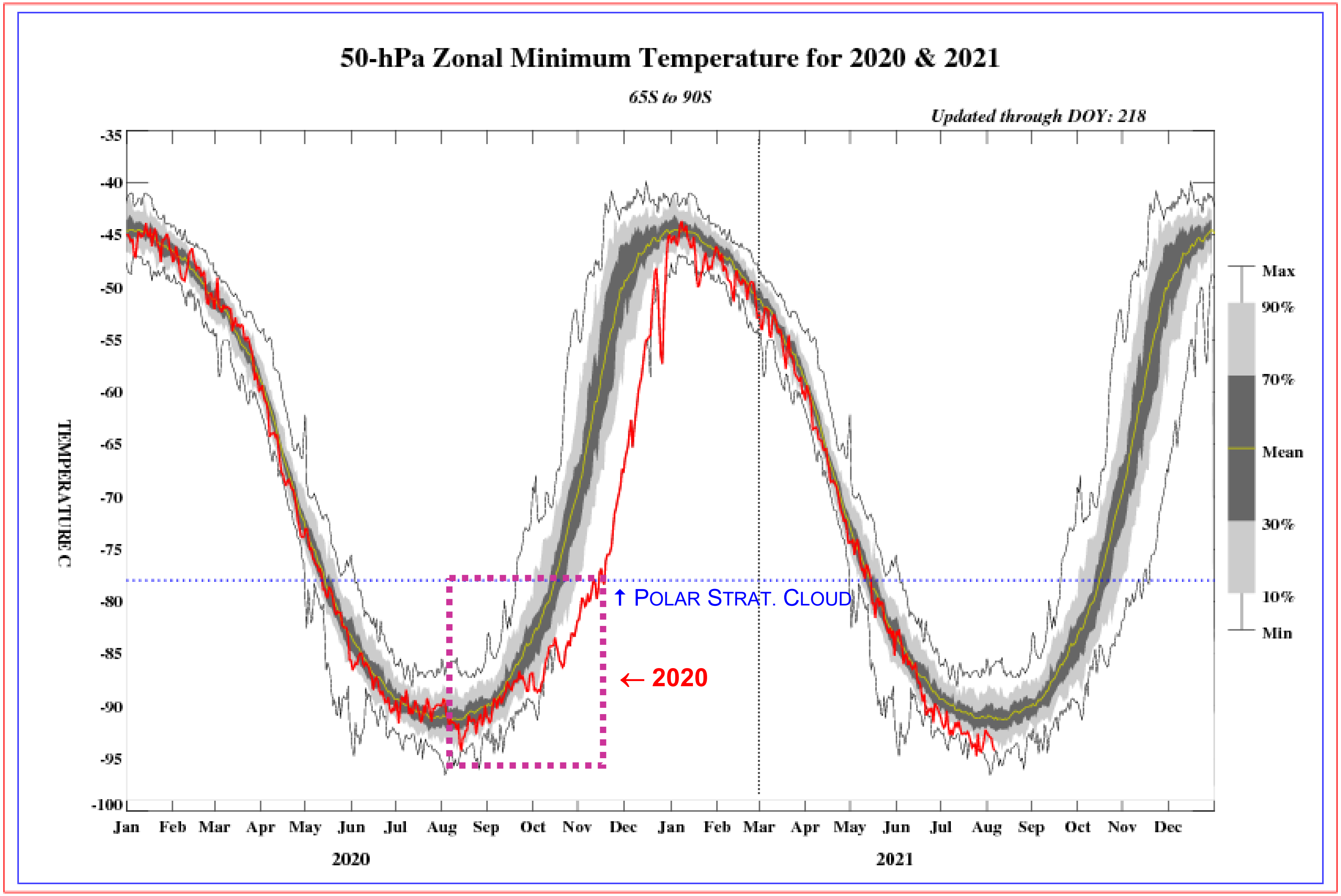
October 1996 | **October 2002** | October 2006 | **October 2019**

Antarctic Vortex Minimum Temperature: 2019-2020



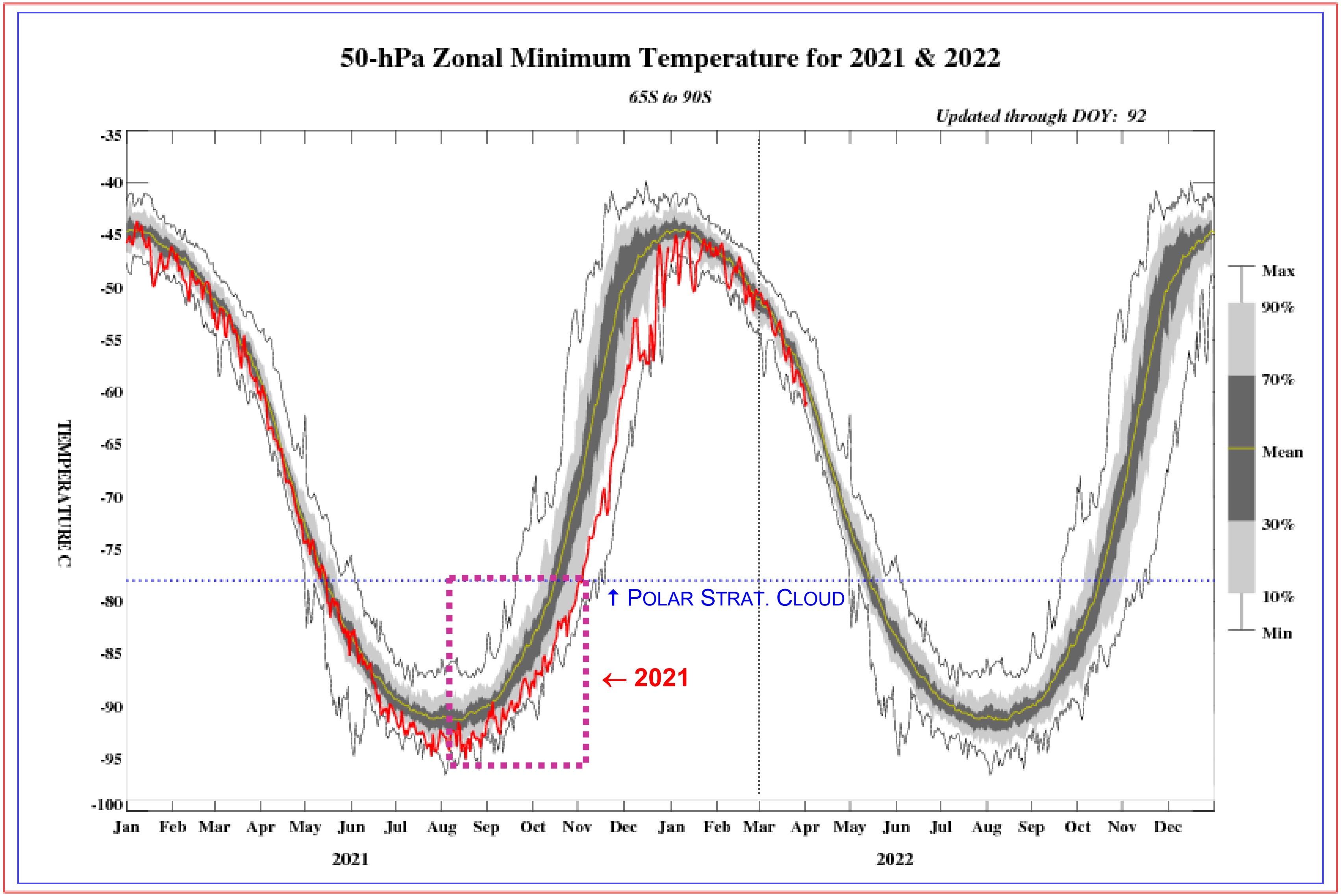
https://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbshlo.png

Antarctic Vortex Minimum Temperature: 2020-2021



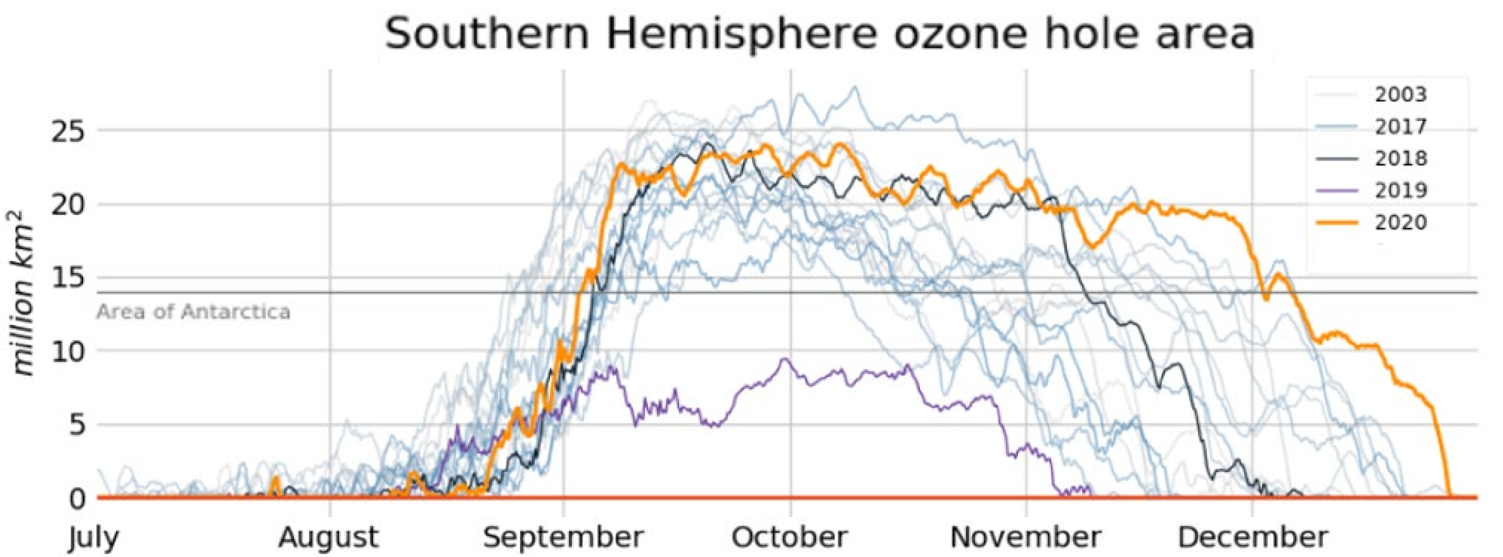
https://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbshlo.png

Antarctic Vortex Minimum Temperature: 2020-2021



https://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbshlo.png

Antarctic Ozone, 2020



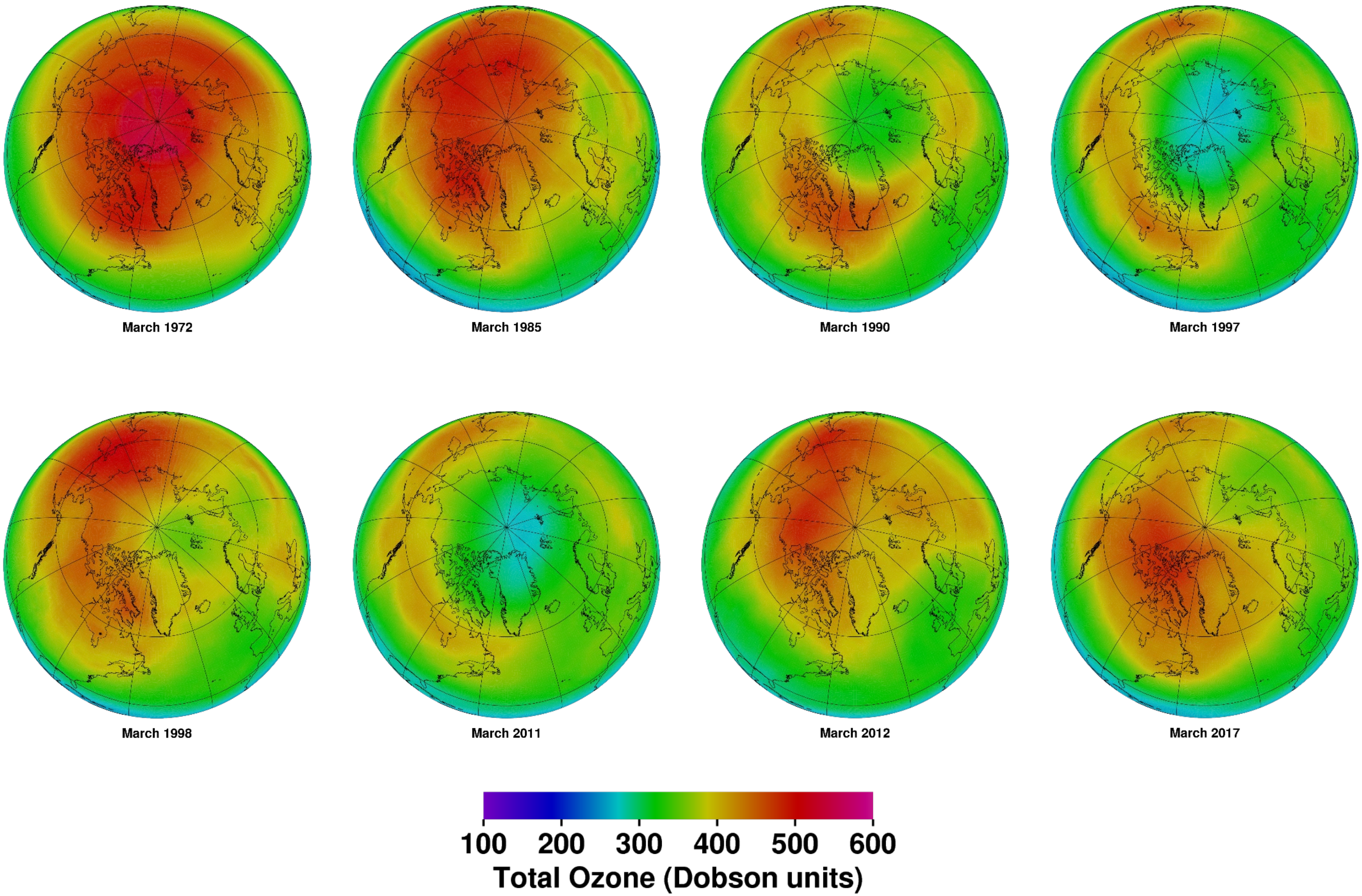
The record-breaking 2020 Antarctic ozone hole finally closed at the end of December after an exceptional season. The 2020 Antarctic ozone hole grew rapidly from mid-August and peaked at around 24.8 million km^2 on 20 September 2020, spreading over most of the Antarctic continent. It was the longest-lasting and one of the largest and deepest holes since the monitoring began 40 years ago. It was driven by a strong, stable and cold polar vortex and very cold temperatures in the stratosphere. The same meteorological factors also contributed to the record 2020 Arctic ozone hole.

This is in contrast to the unusually small and short-lived Antarctic ozone hole in 2019.

“The last two ozone hole seasons demonstrate the year-to-year variability of the ozone hole and improve our understanding of the factors responsible for its formation, extent and severity,” said Oksana Tarasova, head of WMO Atmospheric Environment Research Division, which oversees WMO Global Atmosphere Watch network of monitoring stations. “We need continued international action to enforce the Montreal Protocol on ozone depleting chemicals. There is still enough ozone depleting substances in the atmosphere to cause ozone depletion on an annual basis,” said Dr Tarasova.

https://public.wmo.int/en/media/news/record-breaking-2020-ozone-hole-closes

Arctic Ozone versus Time



Polar Ozone Depletion: NH and SH

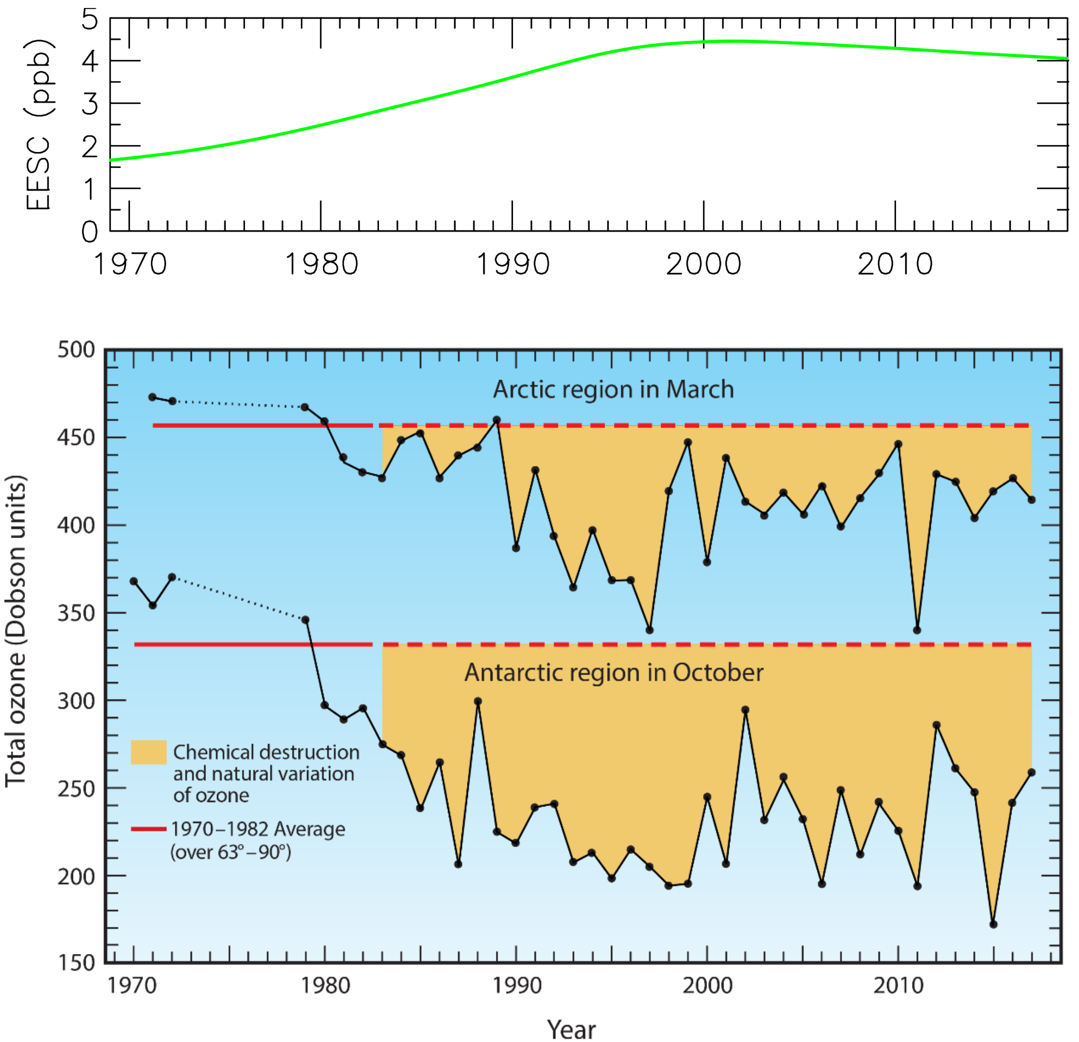


Fig Q11-1, *WMO/UNEP Twenty QAs Ozone*

Arctic Overview

Arctic vortex (polar stratosphere):

- Always warmer than typical Antarctic winter
- Tremendous year to year variability in temperature
- Chemical ozone loss occurs *only* during cold winters
- Enough HNO_3 usually remains so that ClO recovers to $ClNO_3$:
  faster ClO de-activation (less ozone depletion) compared to Antarctic

All of this is due to hemispheric differences in atmospheric dynamics:

- More vigorous circulation in NH due to much more land-sea contrast, which
  triggers poleward transport of heat by atmospheric motions
  (Antarctic ice sheet suppresses poleward transport of heat by atmosphere)
- Stronger circulation in NH leads to more disturbed vortex (warmer, less PSCs)

Minimum Temperature: NH and SH

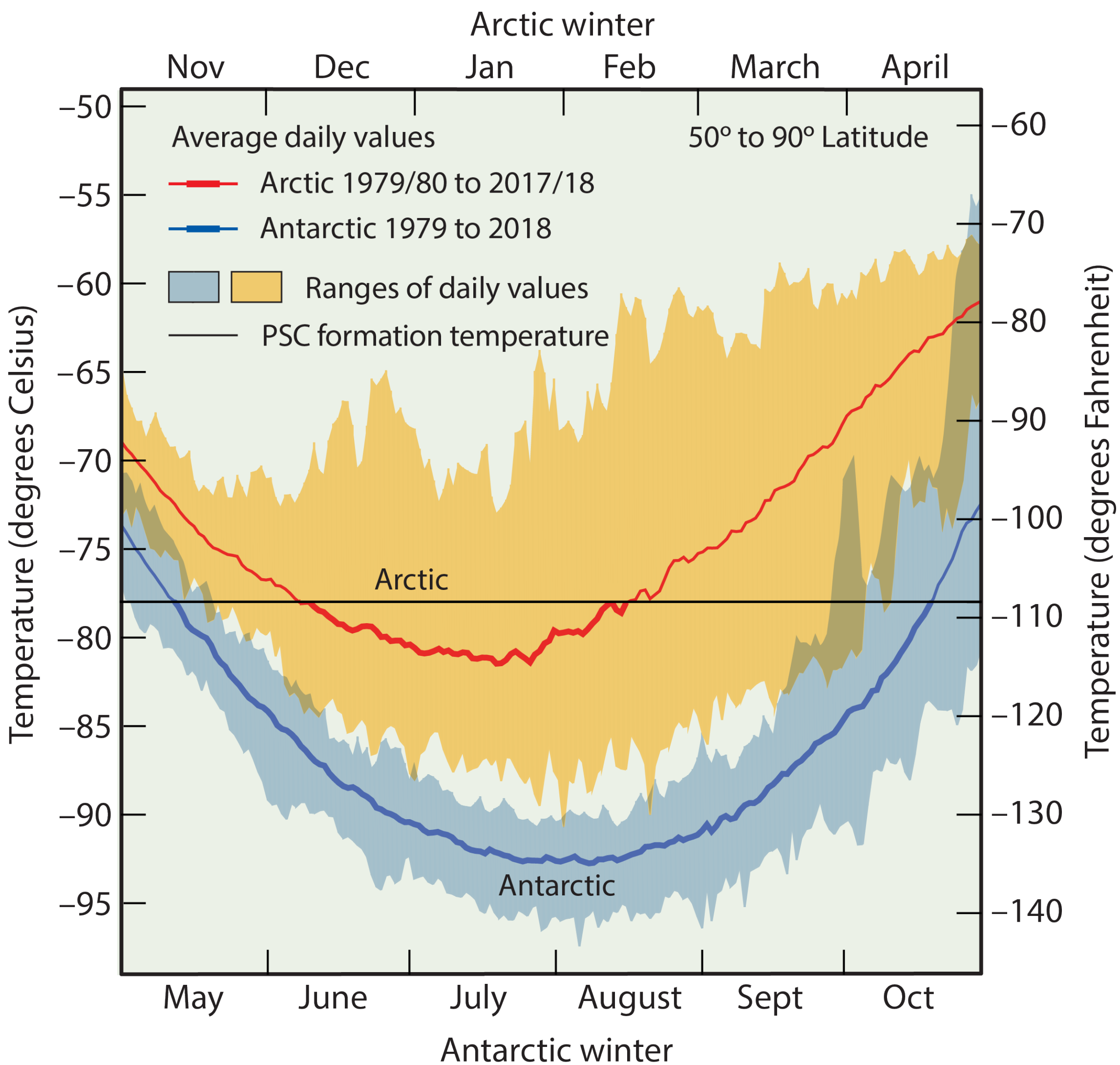
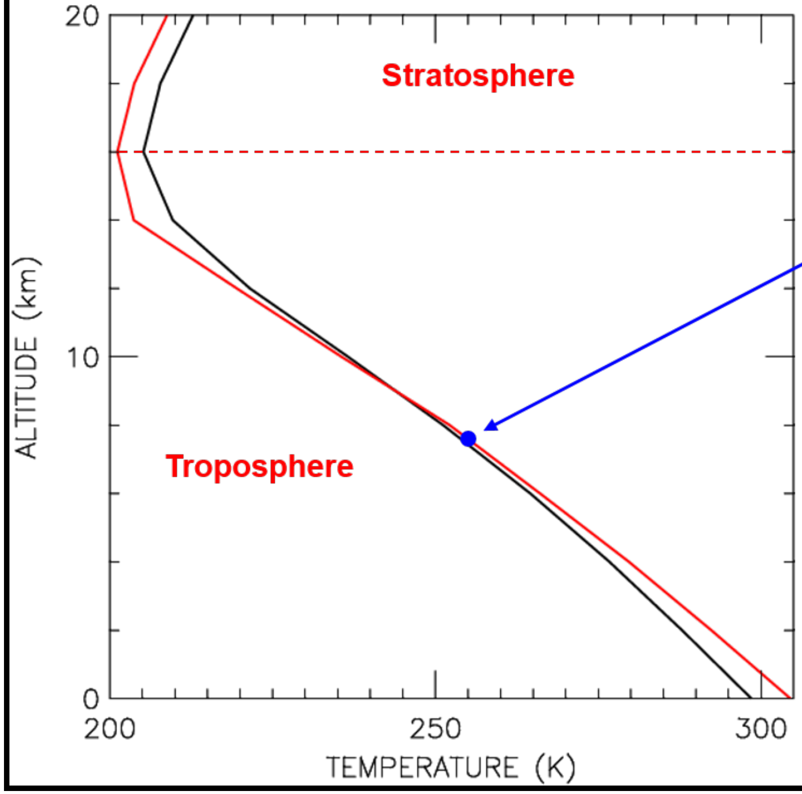


Fig Q9-1, *WMO/UNEP Twenty QAs Ozone*

The Stratosphere Cools as the Surface Warms !

Let's take a closer look at T_{EFF} = 255 K



Altitude in troposphere where T = 255 K

Termed Earth's mean radiating altitude to space

As Earth warms in response to rising GHGs, the lower troposphere will warm, the stratosphere will cool, and the mean radiating level will likely rise slightly higher in altitude

Regardless, the temperature of the mean radiating altitude will not change unless Earth's overall reflectivity varies *OR* the output of the Sun varies

Lecture 3, Slides 54 & 55

The Stratosphere Cools as the Surface Warms !

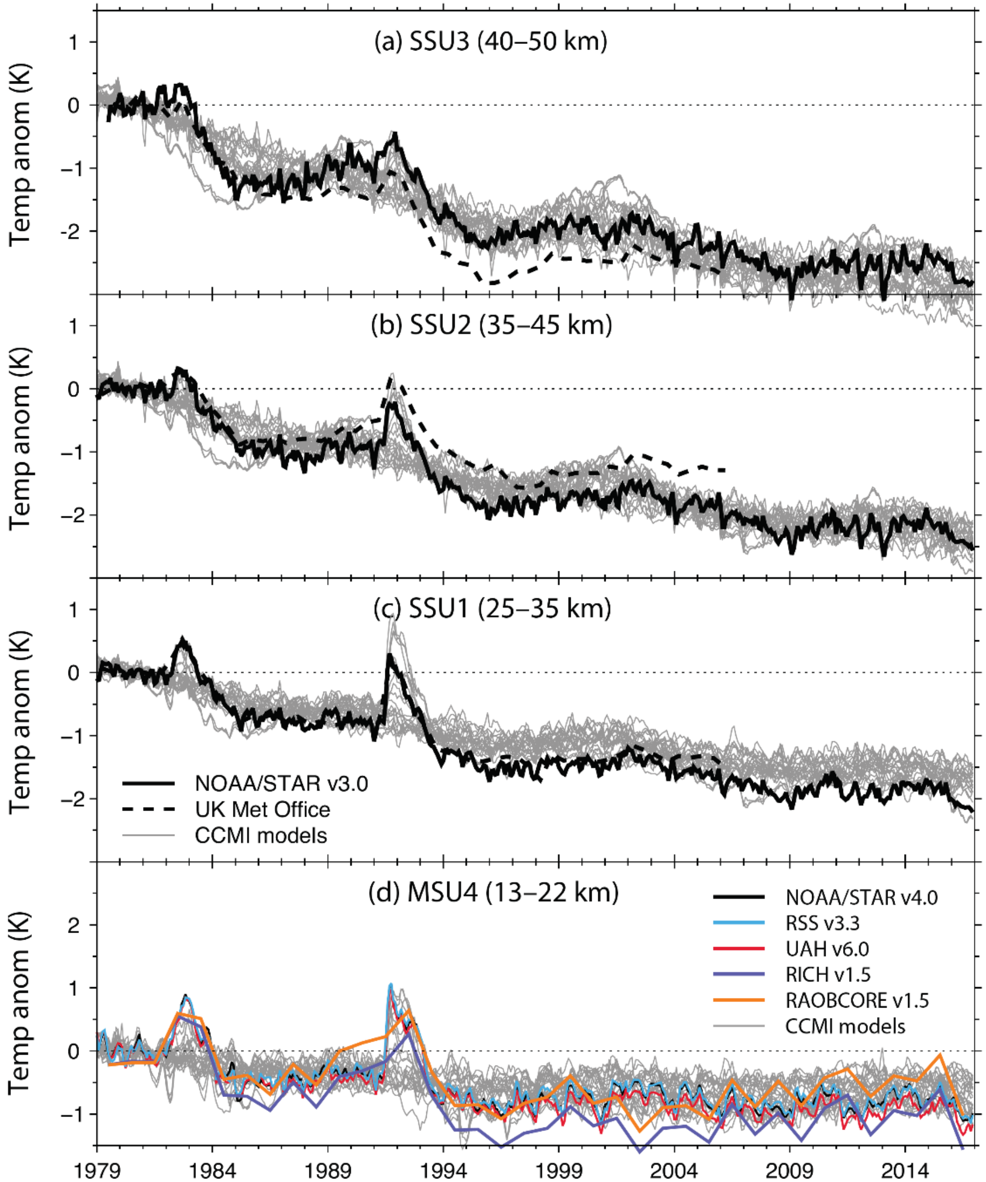
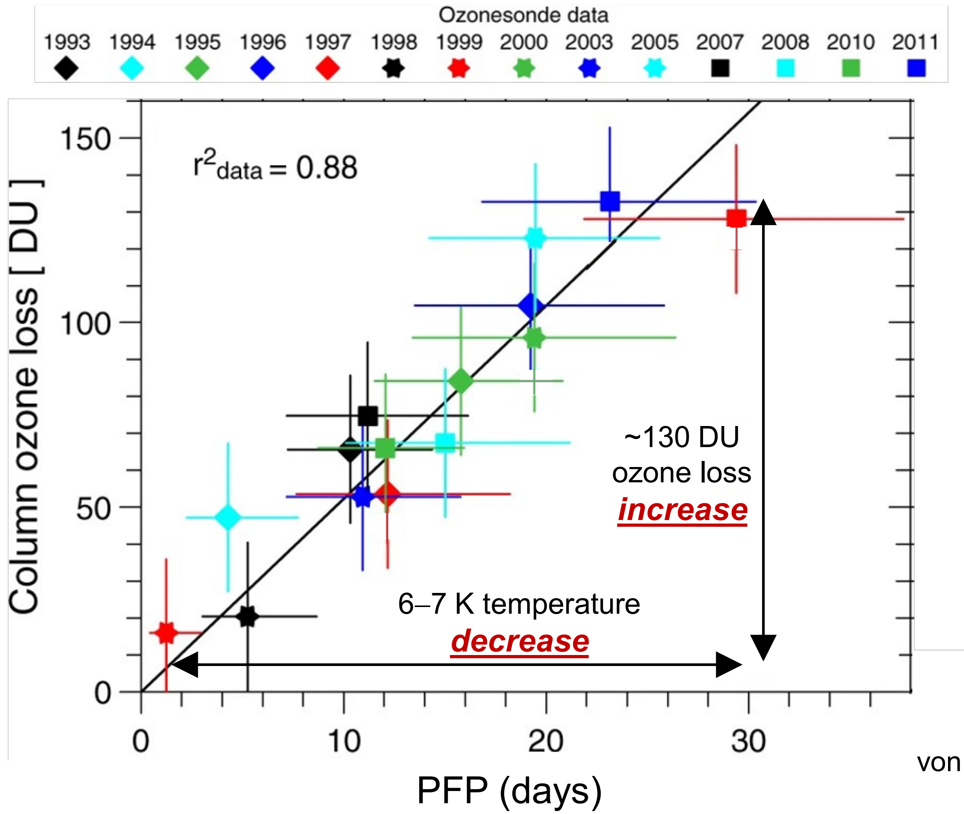


Figure 5-4. Time series of global mean stratospheric temperature anomalies from 1979 to 2016. Panels show SSU Channels 3, 2, 1 (SSU3, SSU2, SSU1; a, b, c) and MSU channel 4 (MSU4; d) for the altitude ranges, datasets, and model outputs indicated in the legends. Gray lines indicate results from a total of 23 ensemble members across 14 Chemistry-Climate Model Initiative (CCMI) models for the REF-C2 experiment, weighted by the appropriate satellite weighting function for comparison with observations. All data in panel d are shown as monthly averages except the UK Met Office dataset, which uses 6-month averages, and the two radiosonde datasets, which are annual means. The radiosonde data are as in Figure 2.8 of Blunden and Arndt (2017). Anomalies are shown relative to 1979–1981. Adapted from Maycock et al. (2018).

Figure 5-4, WMO/UNEP (2018)

Arctic Ozone Loss Varies as a function of PSC Formation Potential

Data:



von der Gathen, *Nature Communications*, 2021

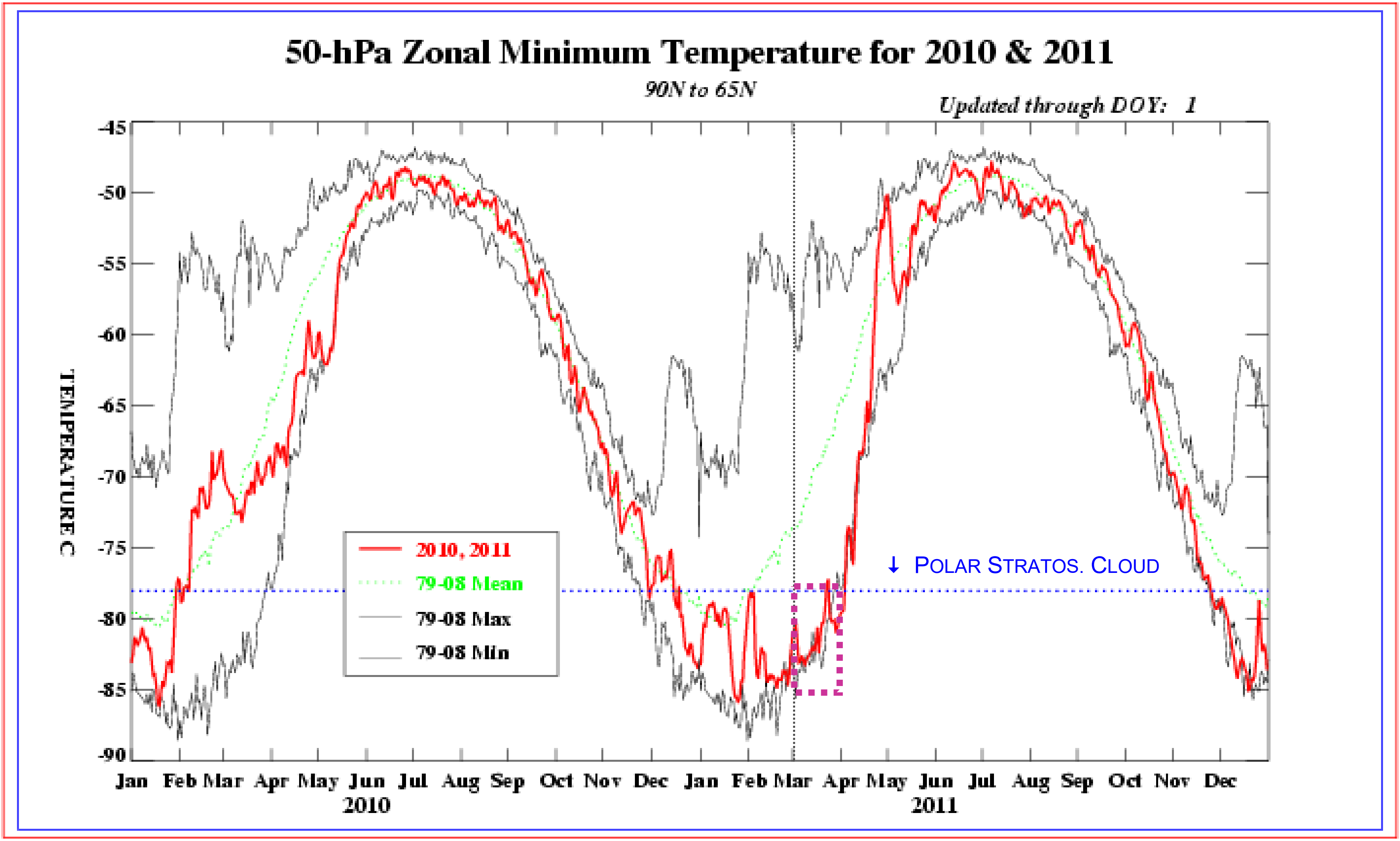
- Surprisingly simple relationship between chemical loss of column ozone and volume of air exposed to PSC formation potential over winter, where

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

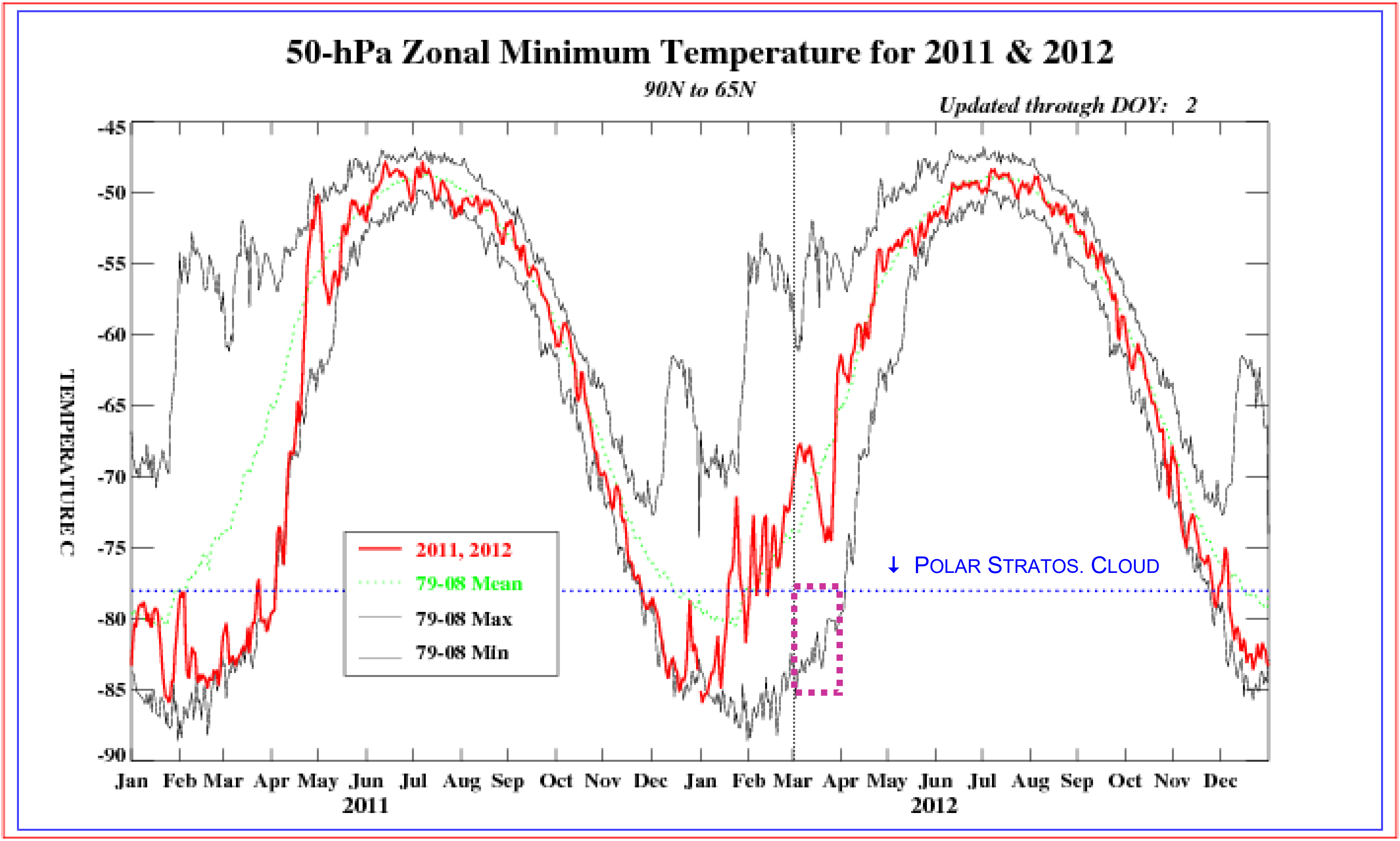
- Relation leads to estimate of ~20 DU additional loss of ozone per degree Kelvin cooling of *Arctic* stratosphere

Arctic Temperature: Mar 2011



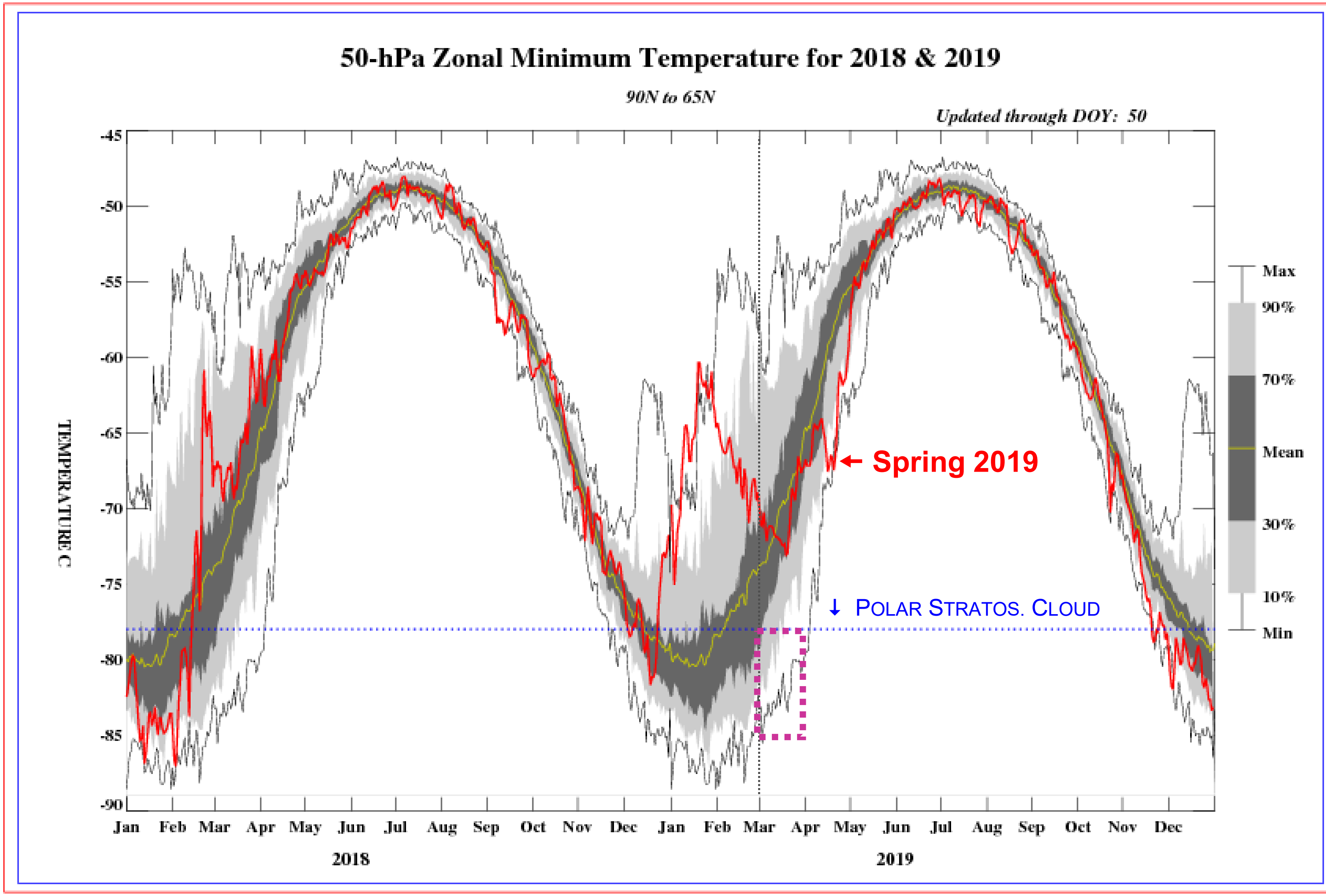
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2011.gif

Arctic Temperature: Mar 2012



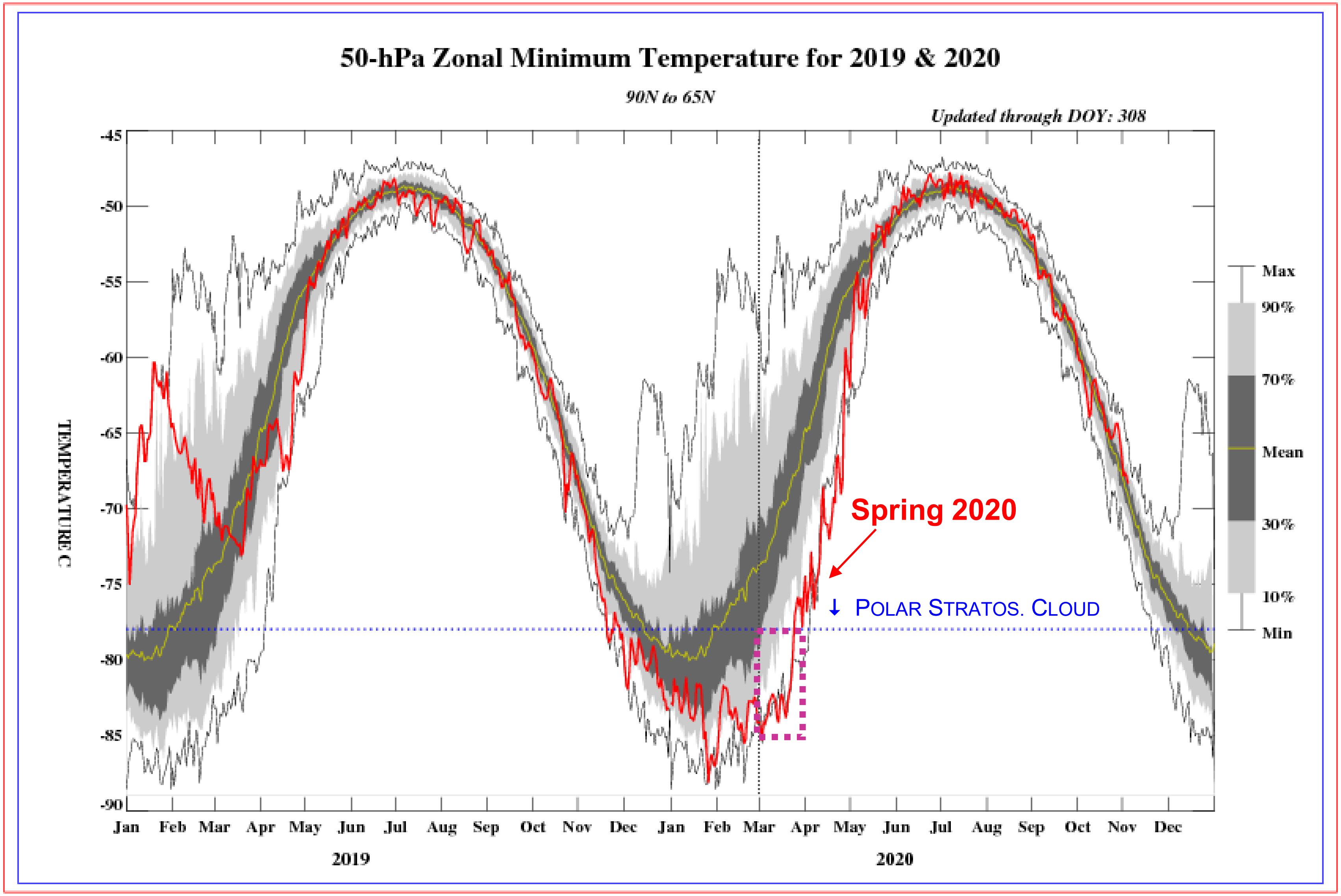
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/archive/50mbnhlo_2012.gif

Arctic Temperature: Mar 2019



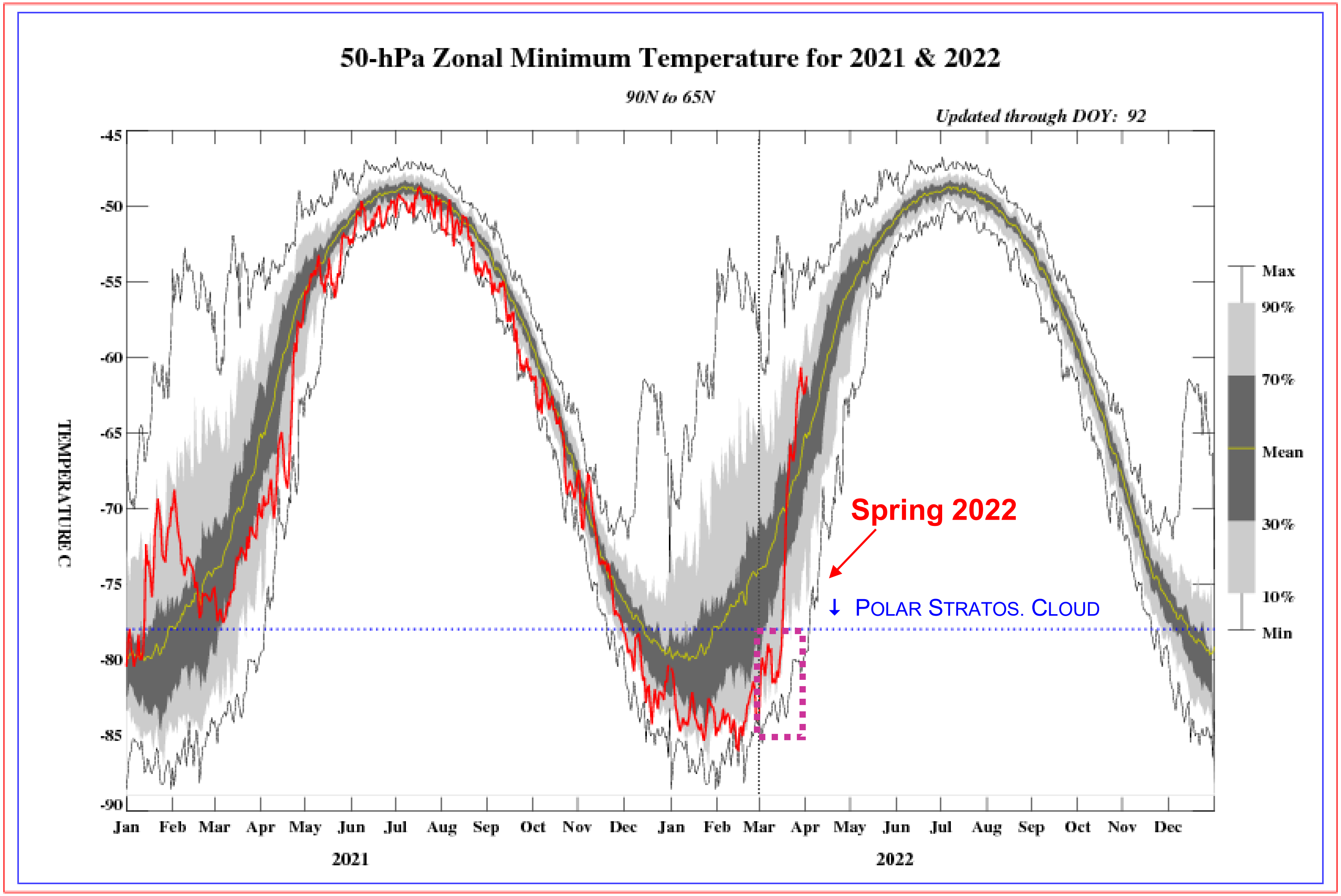
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png

Arctic Temperature: Mar 2020



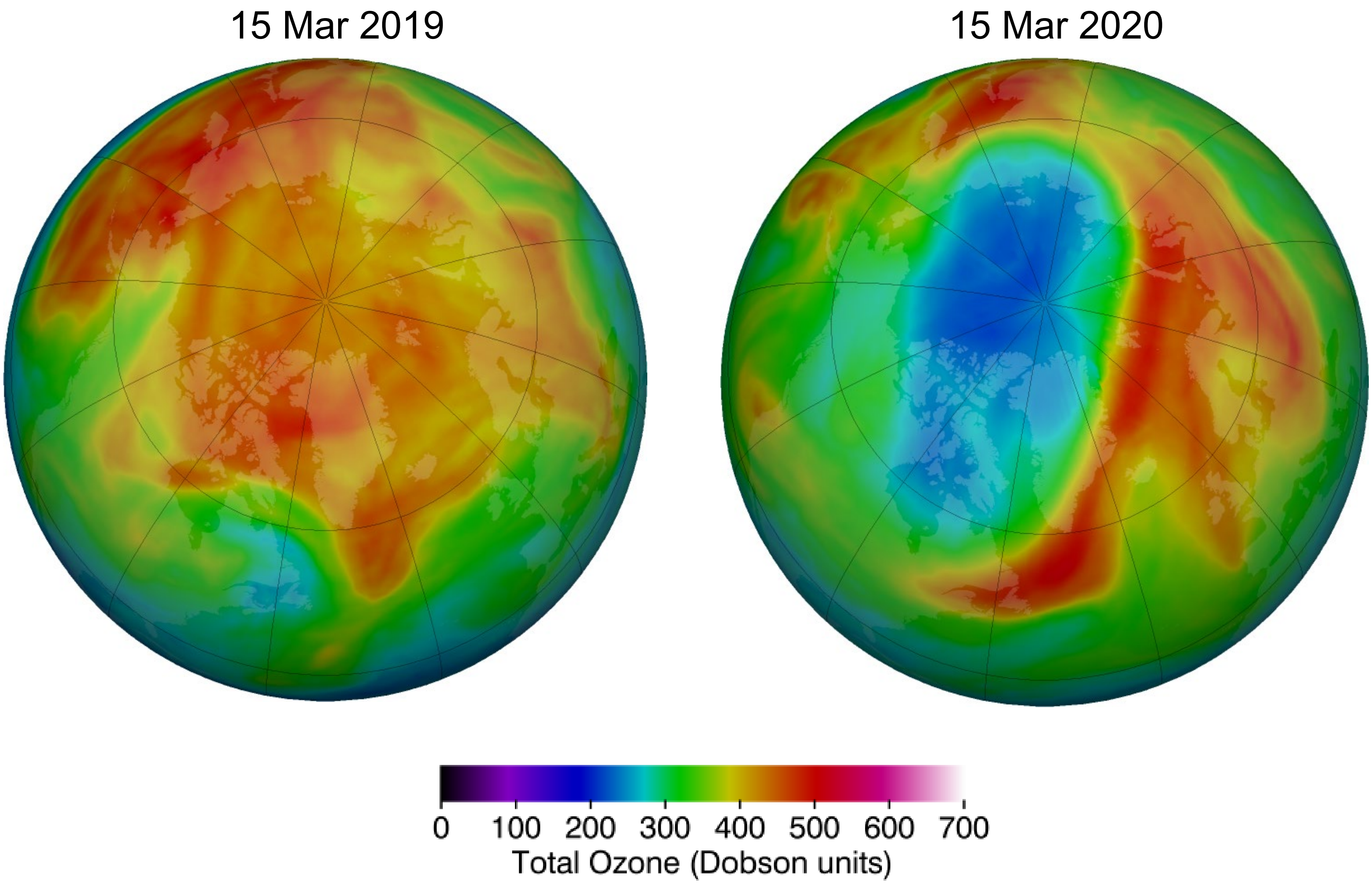
http://www.cpc.ncep.noaa.gov/products/stratosphere/temperature/50mbnhlo.png

Arctic Temperature: Mar 2022



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

Arctic Ozone: 2019 and 2020



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Arctic Ozone Loss Varies as a function of PSC Formation Potential

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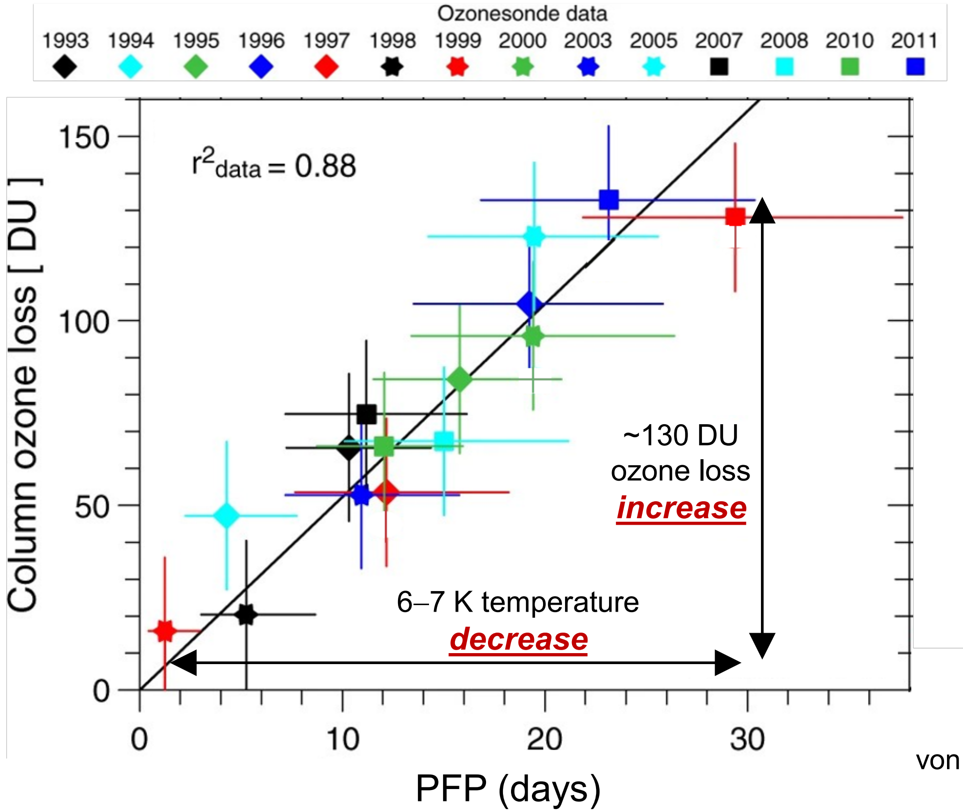

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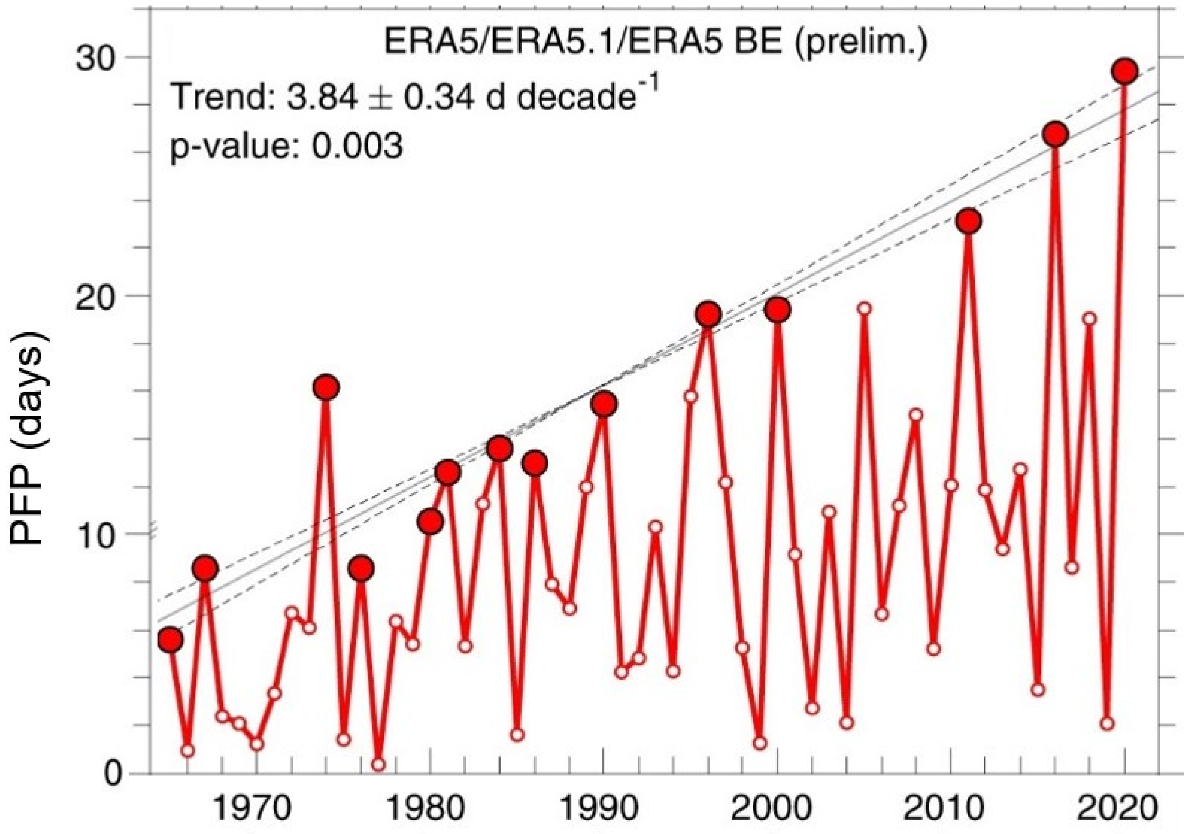
and V_{PSC} is the volume of the vortex where T is cold enough to allow for formation of PSCs, and V_{VORTEX} is the volume of the Arctic vortex

- 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

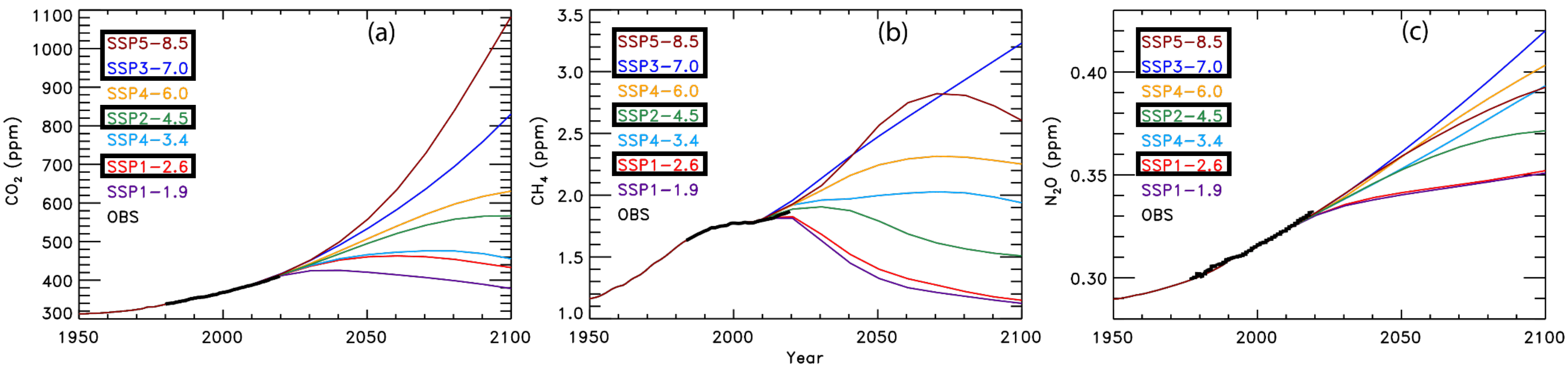
PSC Formation Potential in Arctic Vortex

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

SSP: Shared Socioeconomic Pathway Scenarios Will Drive Upcoming IPCC Report

Climate Model Input



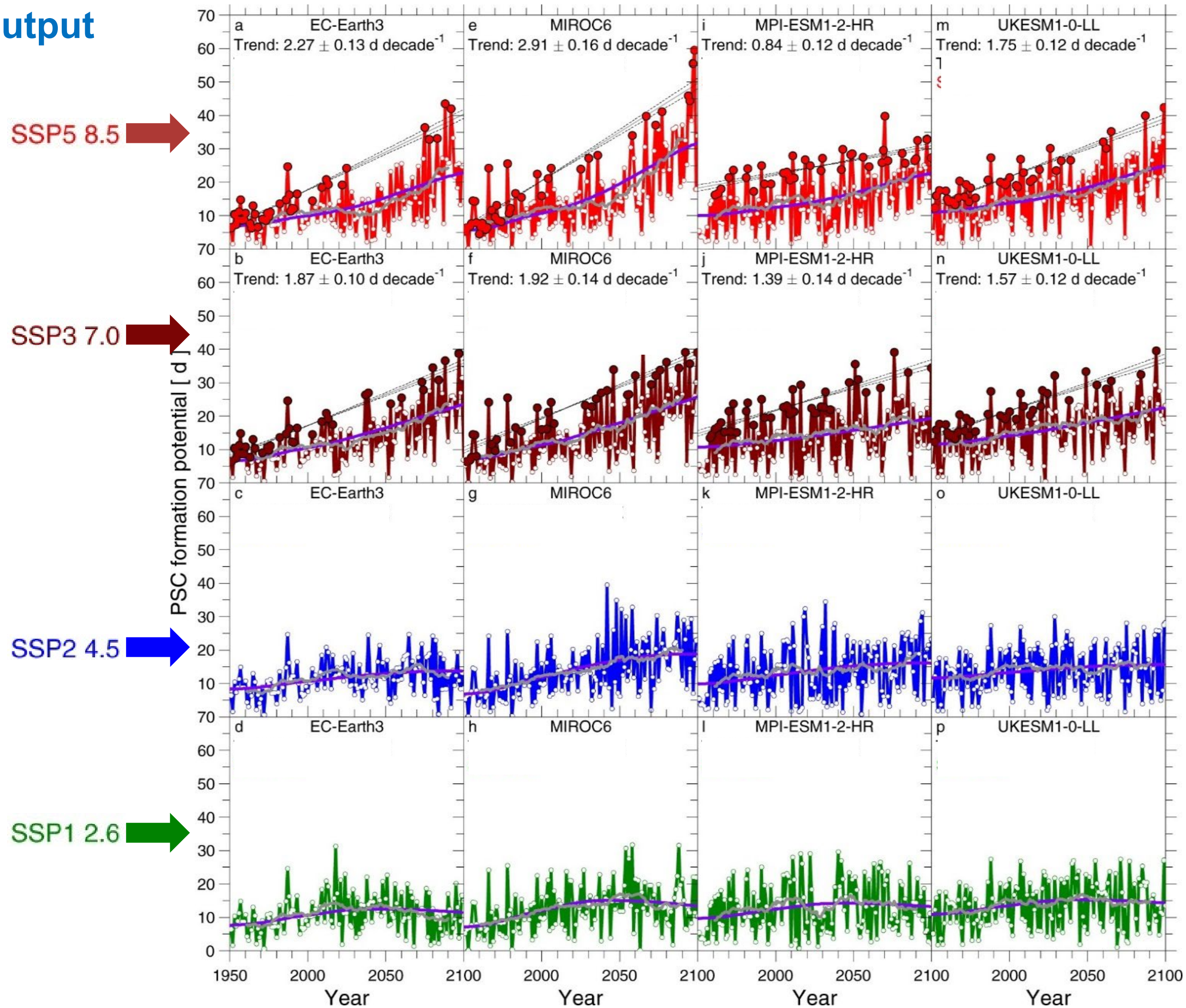
Number before dash represents base narrative and number after dash represents W m^{-2} RF of climate at end of century

McBride et al., *Earth System Dynamics*, 2021

Tendency for Colder Arctic Winters Getting Colder Driven by Rising GHGs

Climate Model Output

PFP is PSC Formation Potential



von der Gathen, *Nature Communications*, 2021

Next Two Classes

Thursday

- **No AT, because reading is "light" & Problem Set #3 is due on Friday**
- **Please get started on Problem Set 3 prior to Thurs evening**

Next Tuesday

- **Will hold review of Lectures 10 to 17 in preparation for second exam to be held on Thursday, 14 April**