Pollution of Earth's Stratosphere: Ozone Recovery and Chemistry/Climate Coupling

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

Motivating questions:

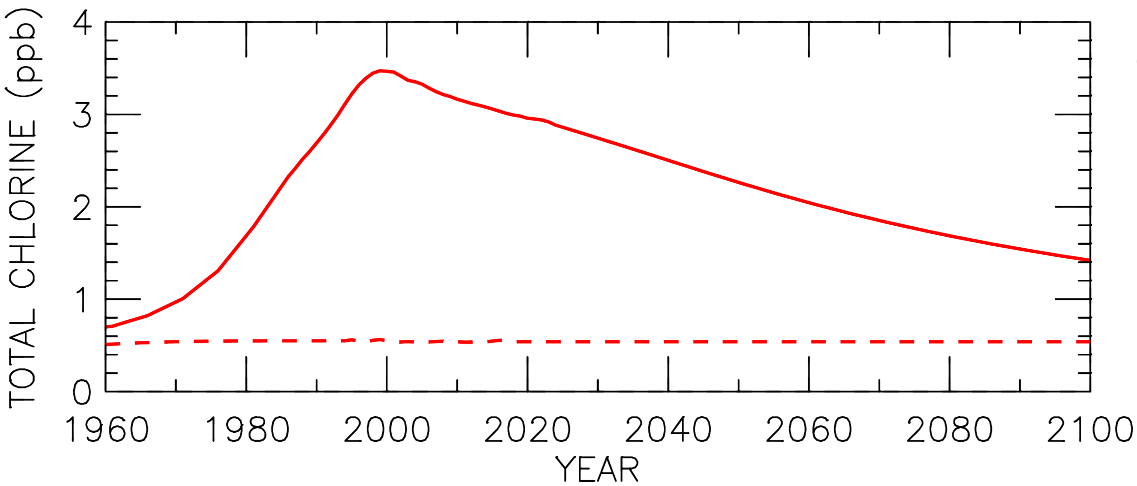
a) **How might climate change (future variations in temperature *and / or* circulation) driven by rising GHGs affect stratospheric ozone?**

b) **Might climate at the surface be affected by stratospheric ozone?**

Lecture 17

7 April 2022

Recovery of the Ozone Layer



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

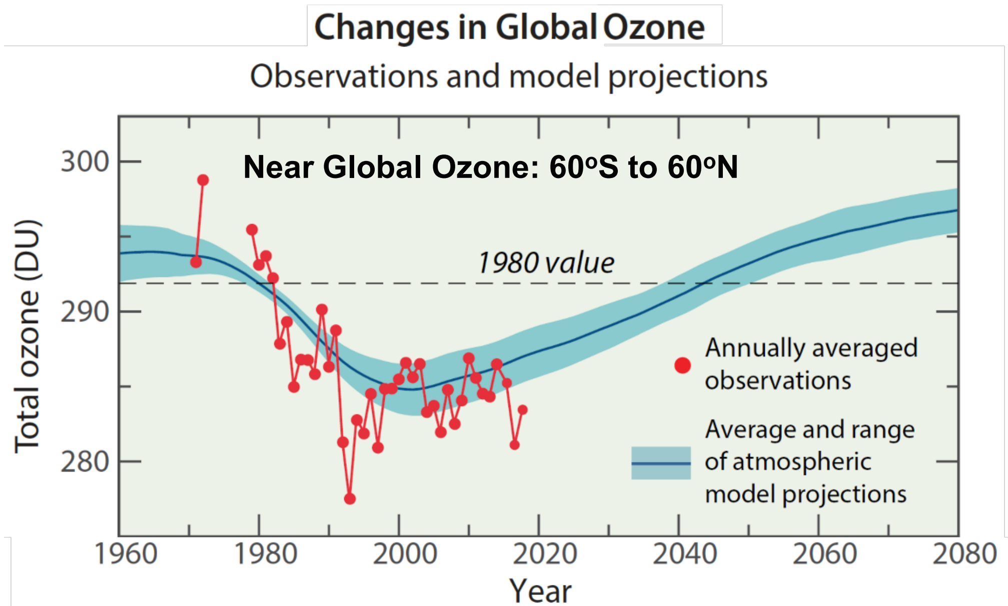
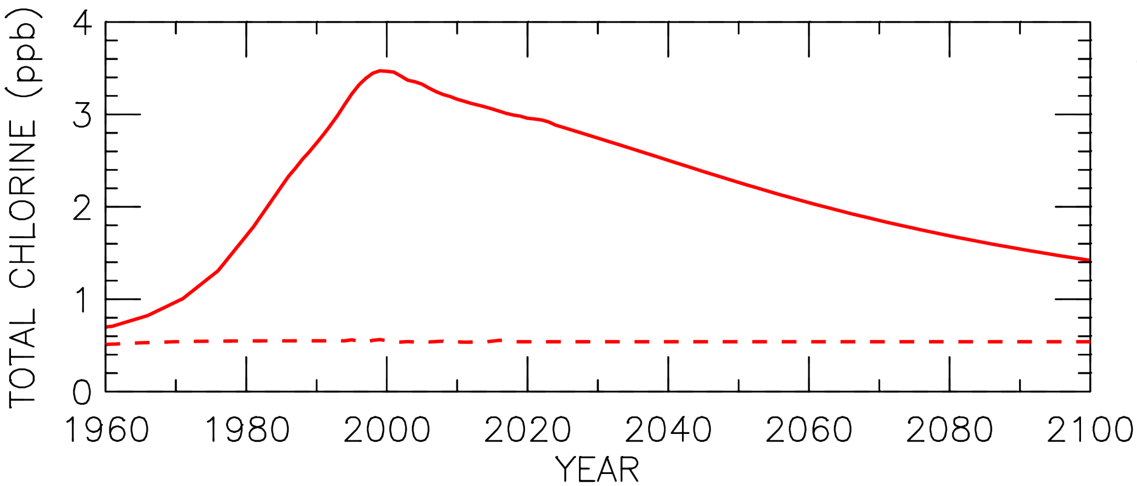


Fig Q20-1, *WMO/UNEP Twenty QAs Ozone*

Recovery of the Ozone Layer



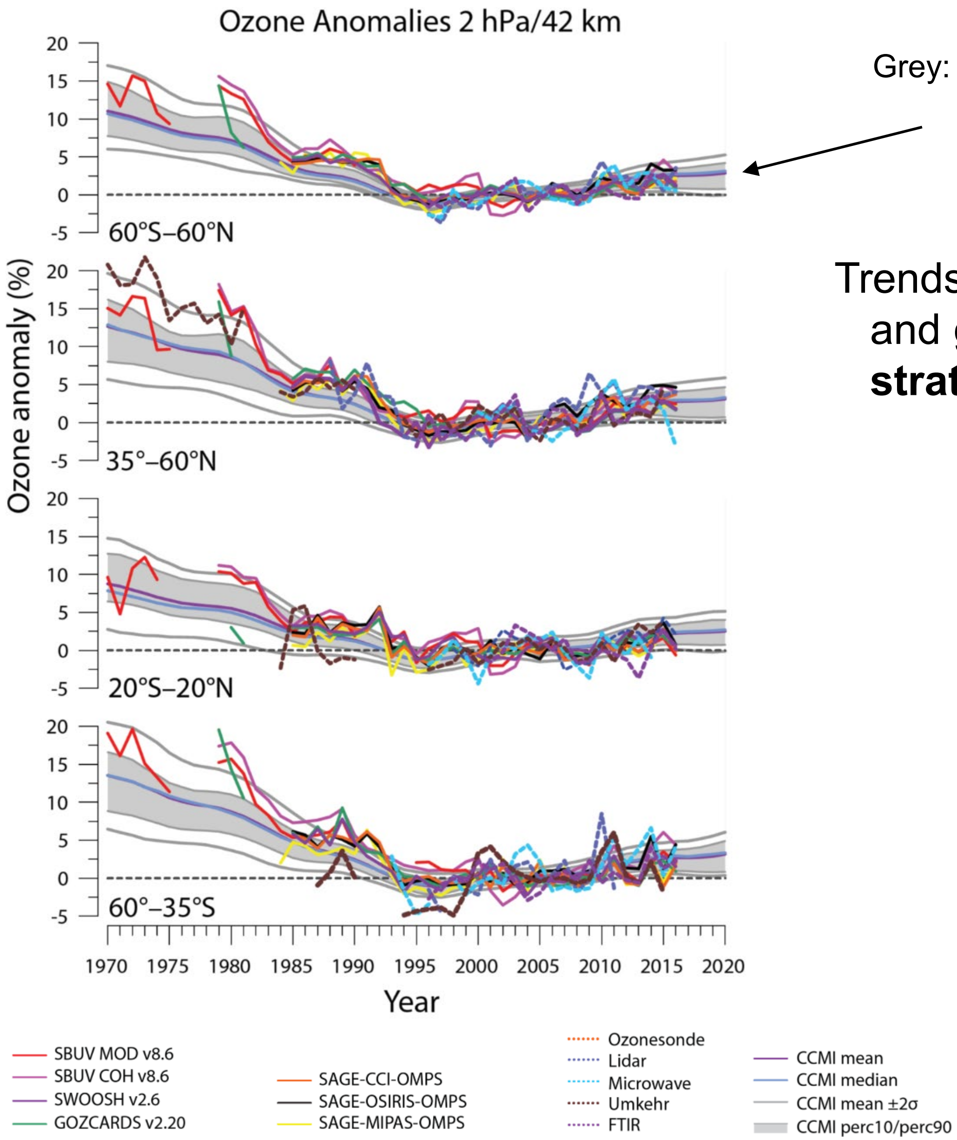
Time series of chlorine content of organic halocarbons that reach the stratosphere. Past values based on direct atmospheric observation. Future values based on projections that include the lifetime for removal of each halocarbon.

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

Lecture 15, Slides 11 to 16

Past Trends, Upper Stratospheric Ozone



Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

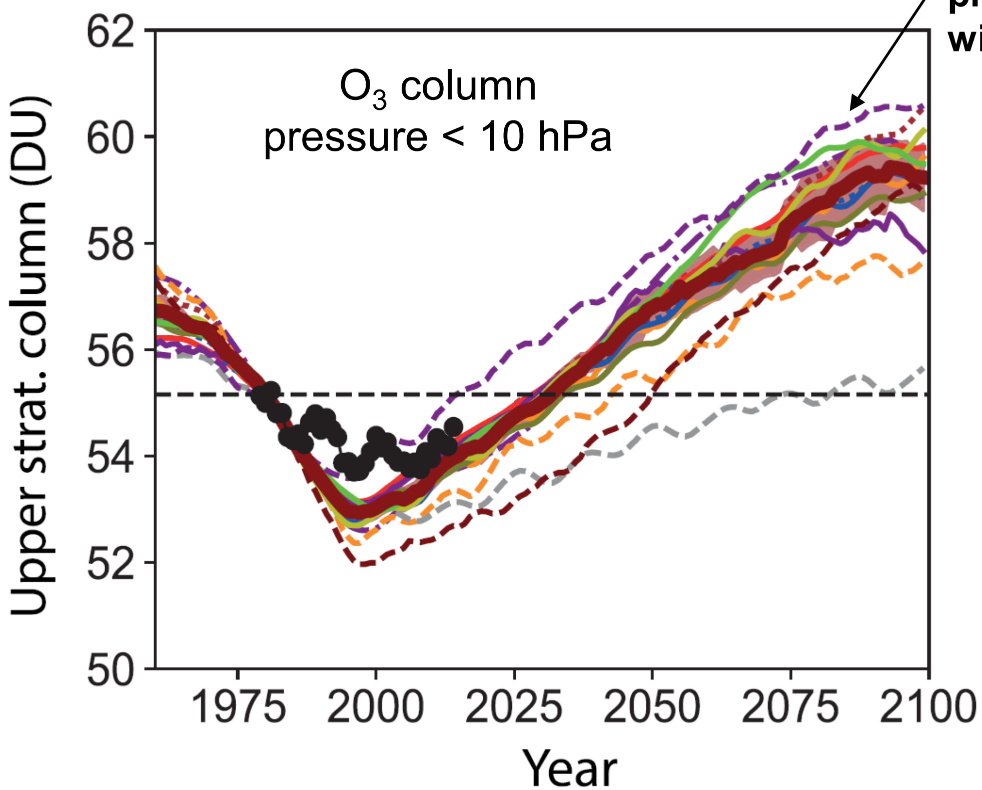
Trends in ozone at ~40 km are "well understood" and **generally follow track time history of stratospheric chlorine loading.**

Fig 3-15, *WMO/UNEP Ozone Report*

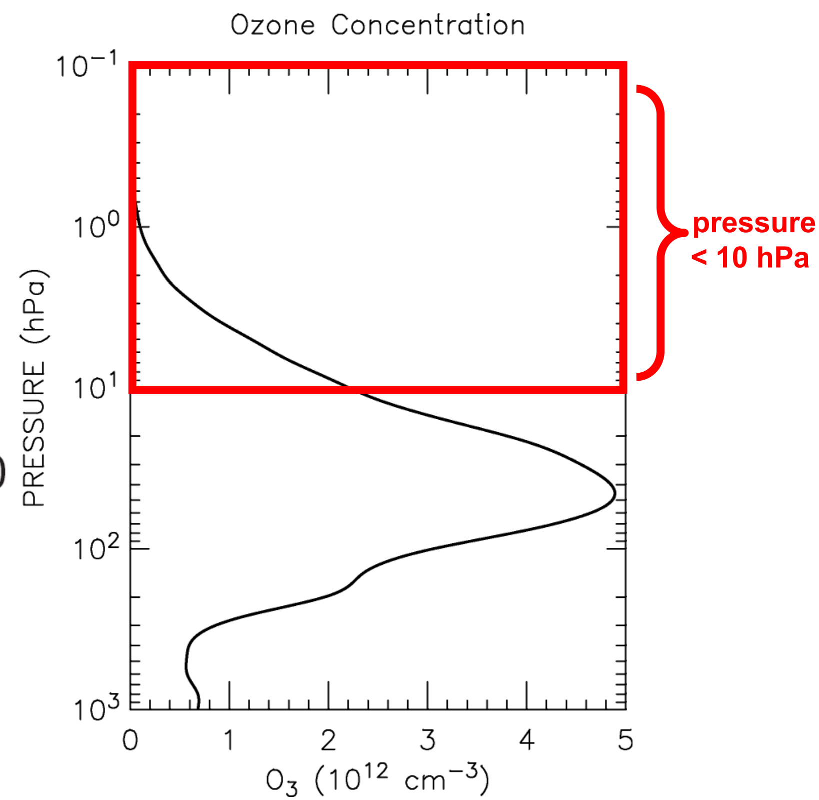
Lecture 15, Slide 52

Future Trends, Upper Stratospheric Ozone

14 coupled chemistry climate models (CCMs) predict upper stratospheric ozone in 2100 will exceed upper stratospheric ozone in 1960



Dhomse *et al.*, *ACP*, 2018



Climate and Chemistry Coupling

Scientists have long known that rising GHGs leads to cooling of the stratosphere, due to direct radiative effects

The stratosphere has been cooling past several decades in a manner quite consistent with theory:

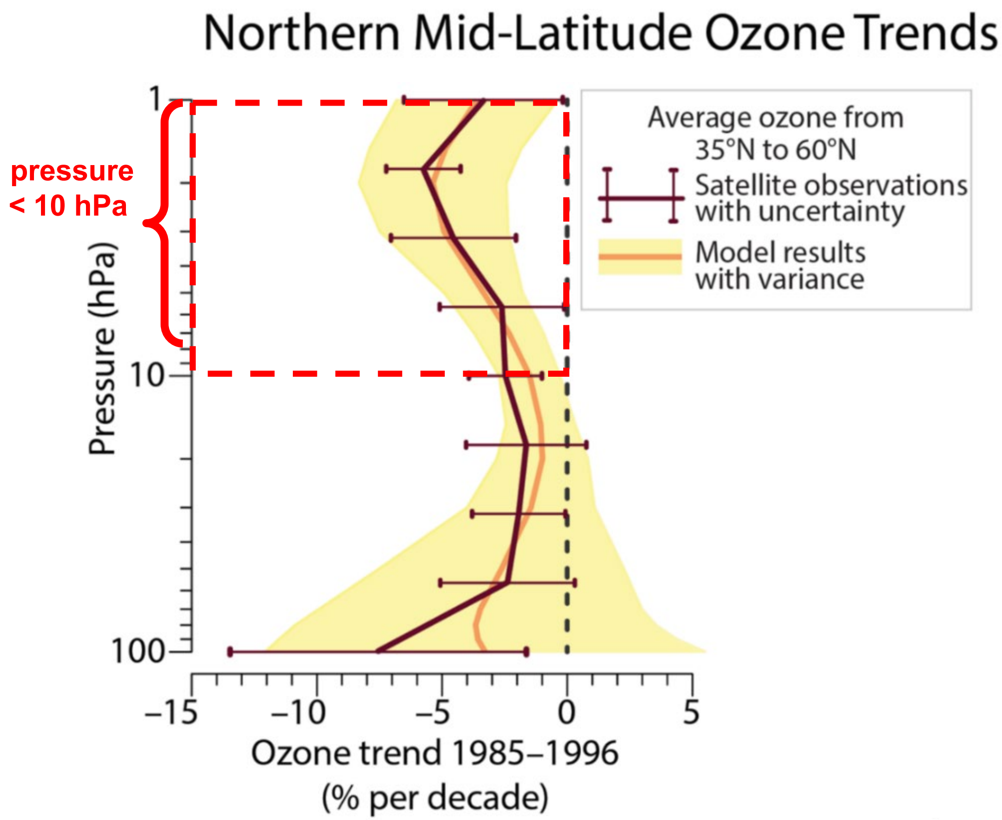
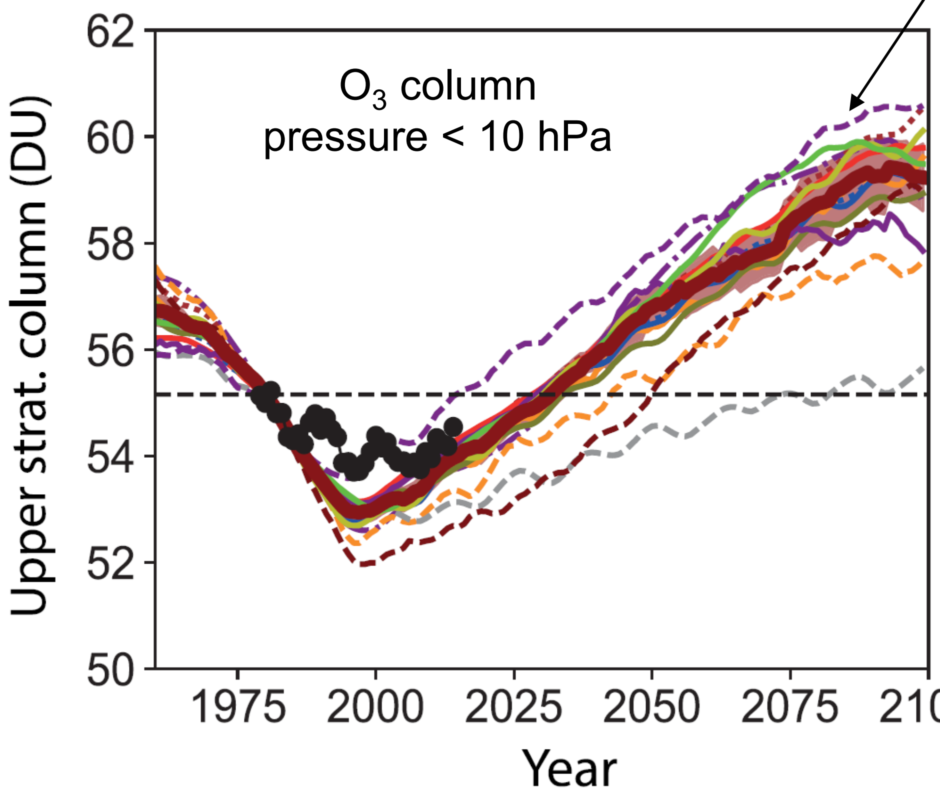


Fig ES-7, *WMO/UNEP Ozone Report Executive Summary*

Future Trends, Upper Stratospheric Ozone

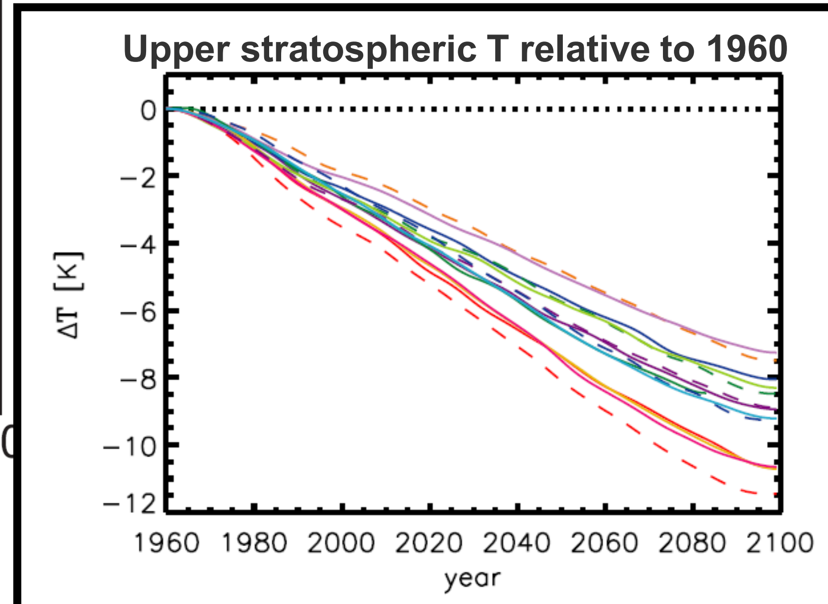


Dhomse *et al.*, *ACP*, 2018

14 coupled chemistry climate models (CCMs) predict upper stratospheric ozone in 2100 will exceed upper stratospheric ozone in 1960

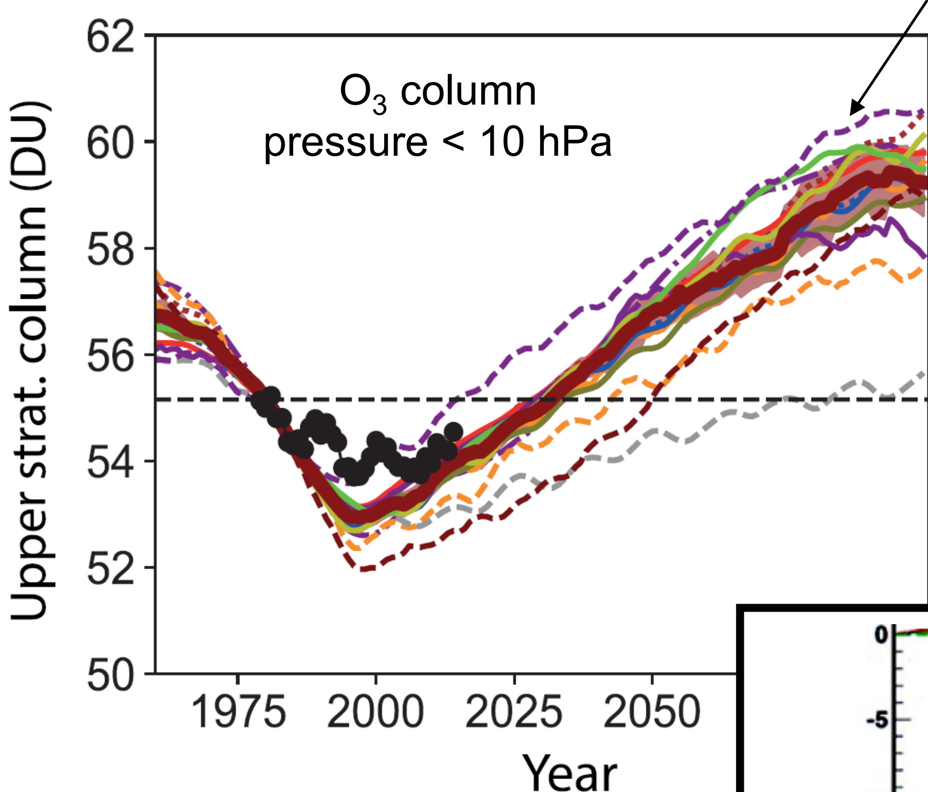
Due to stratospheric cooling !

Why this response of ozone to lower T ?



Oman *et al.*, *JGR*, 2010

Future Trends, Upper Stratospheric Ozone



Dhomse *et al.*, *ACP*, 2018

14 coupled chemistry climate models (CCMs) predict upper stratospheric ozone in 2100 will exceed upper stratospheric ozone in 1960

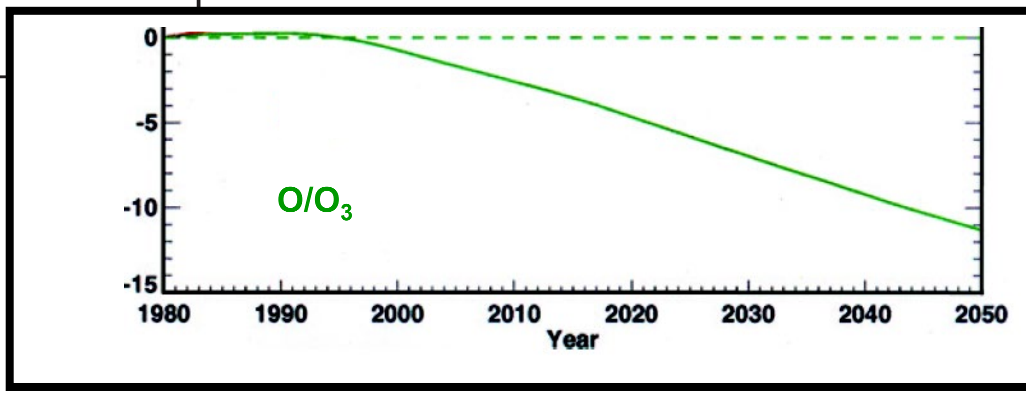
Due to stratospheric cooling !

Why this response of ozone to lower T ?

Gas phase rate constants are sensitive to temperature

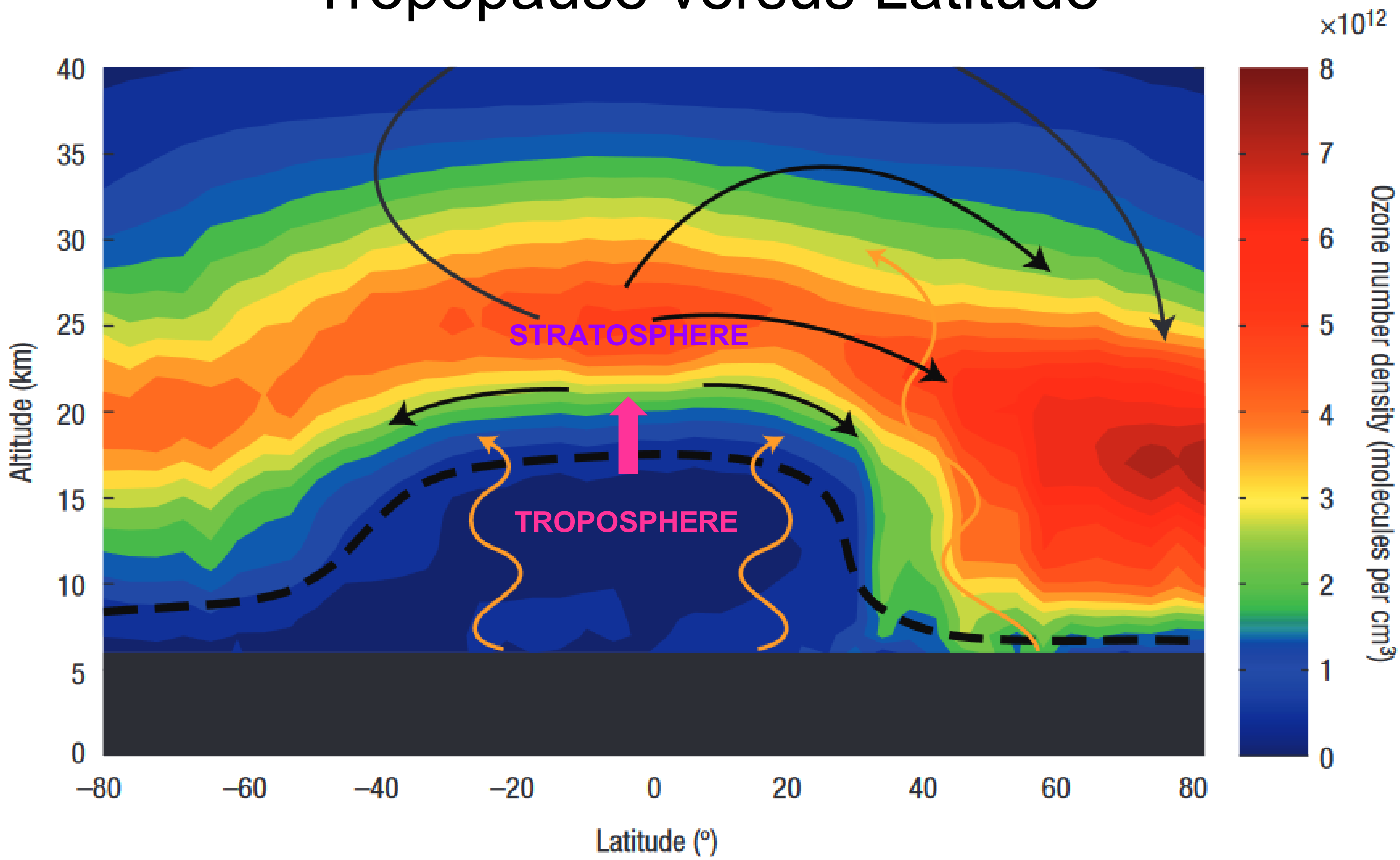
In particular, $O + O_2 + M \rightarrow O_3 + M$ ___________ as T drops

This cooling will alter the partitioning of O and O_3



Rosenfield *et al.*, *JGR*, 2002

Tropopause versus Latitude



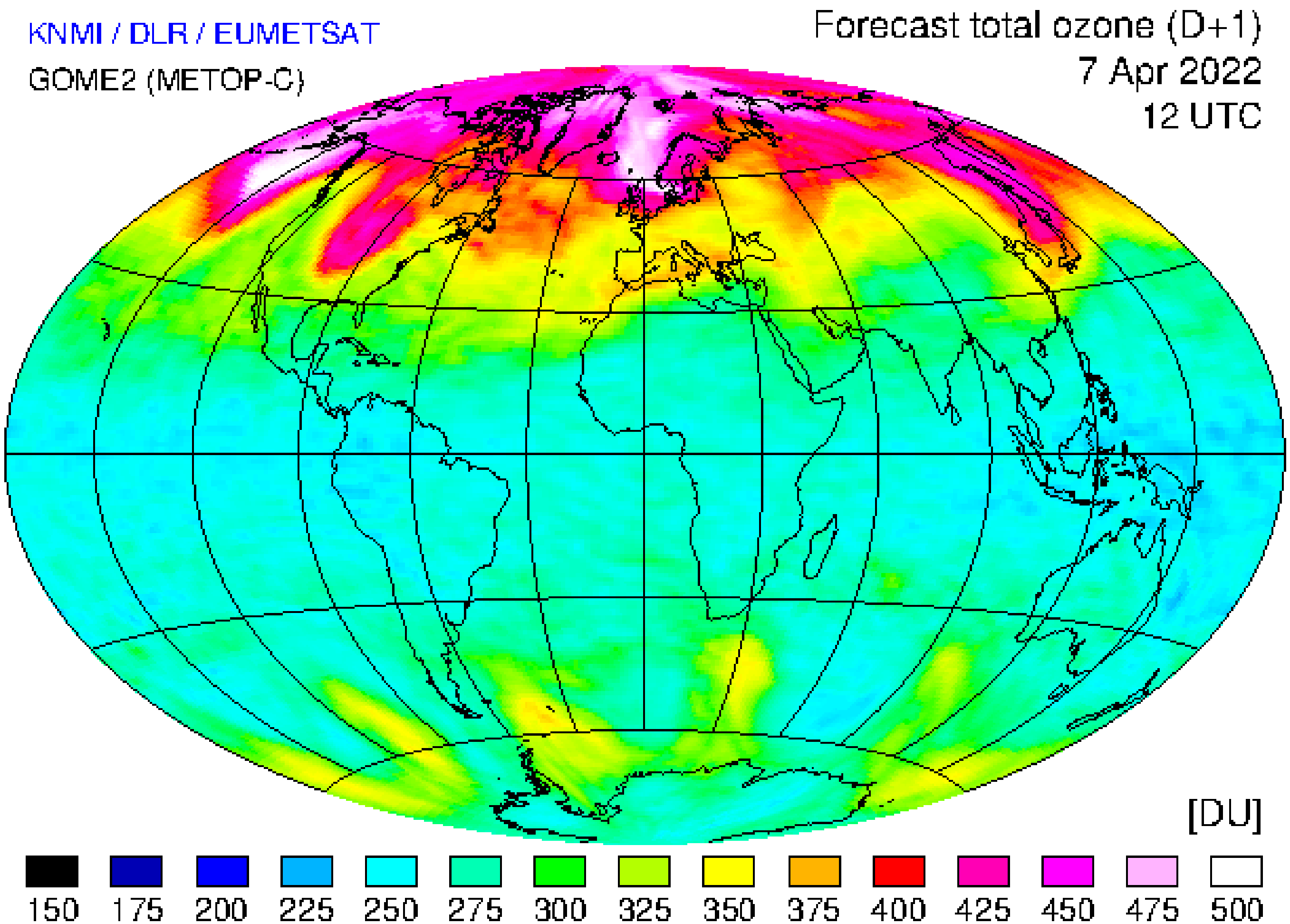
Brewer–Dobson circulation (arrows), ozone (colors), and tropopause (black dashed line).

Shaw and Shepherd, *Nature Geoscience*, 2008.

Brewer-Dobson Circulation is a model of atmospheric circulation, proposed by Alan Brewer in 1949 and Gordon Dobson in 1956, that attempts to explain why tropical air has less column ozone than polar air, even though the tropical stratosphere is where most atmospheric ozone is produced

Lecture 3, Slide 38
&
Lecture 12, Slides 46-50

Global Satellite Map of Total Ozone, 7 April 2022



https://www.temis.nl/protocols/O3global.php

More Chemistry and Climate Coupling

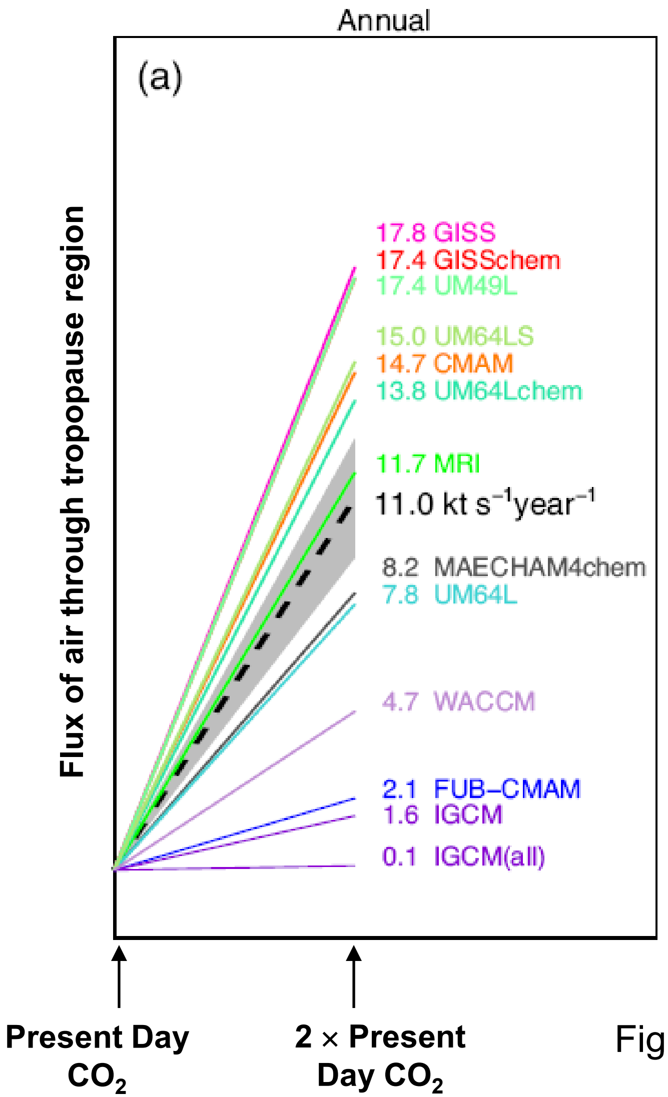


Figure 5-17. Trends in exchange of air from troposphere-to-stratosphere computed by 14 CCMs.

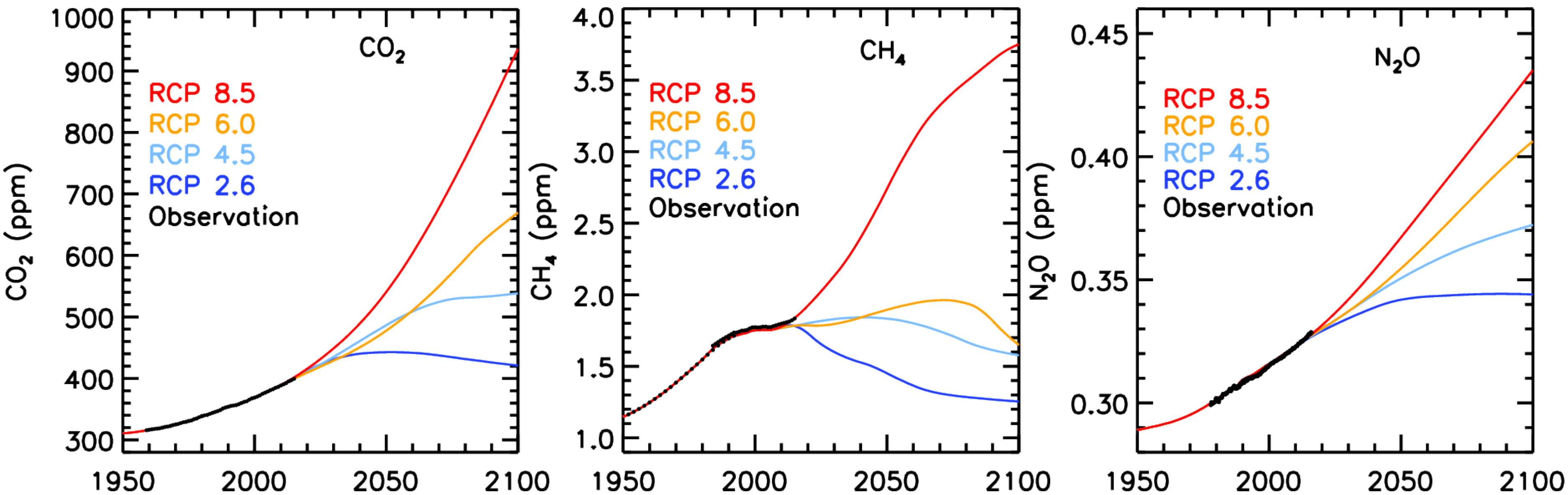
Trends (units of Gg s^{-1} $year^{-1}$) are represented by the slope of each line.

Dashed line is the multi-model mean, which indicates a 30% rise in the exchange of air between the troposphere and stratosphere at the time CO_2 doubles relative to pre-industrial.

After Butchart *et al*., *Clim. Dyn*., 2006.

Fig 5.17, WMO/UNEP (2006)

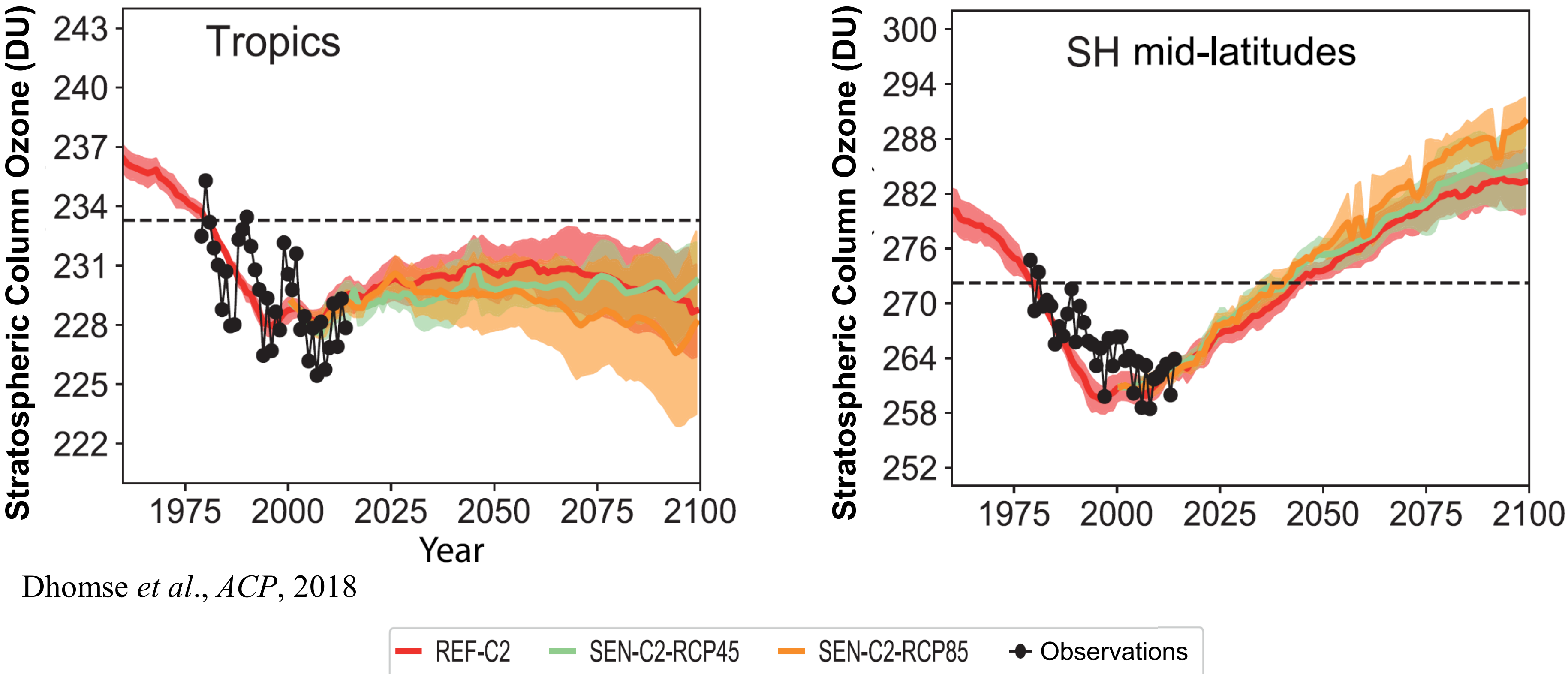
RCP Scenarios Forecast Wide Range of Possible Futures



- RCP: Representative Concentration Pathway
  Number represents ΔRF of climate (W m^{-2}) at the end of this century
- GHG mixing ratio time series for CO_2, CH_4, N_2O, as well as CFCs, HCFCs, and HFCs that are provided to climate model groups

Figure 2-1, from *Paris Climate Agreement: Beacon of Hope*: https://link.springer.com/content/pdf/10.1007%2F978-3-319-46939-3_2.pdf

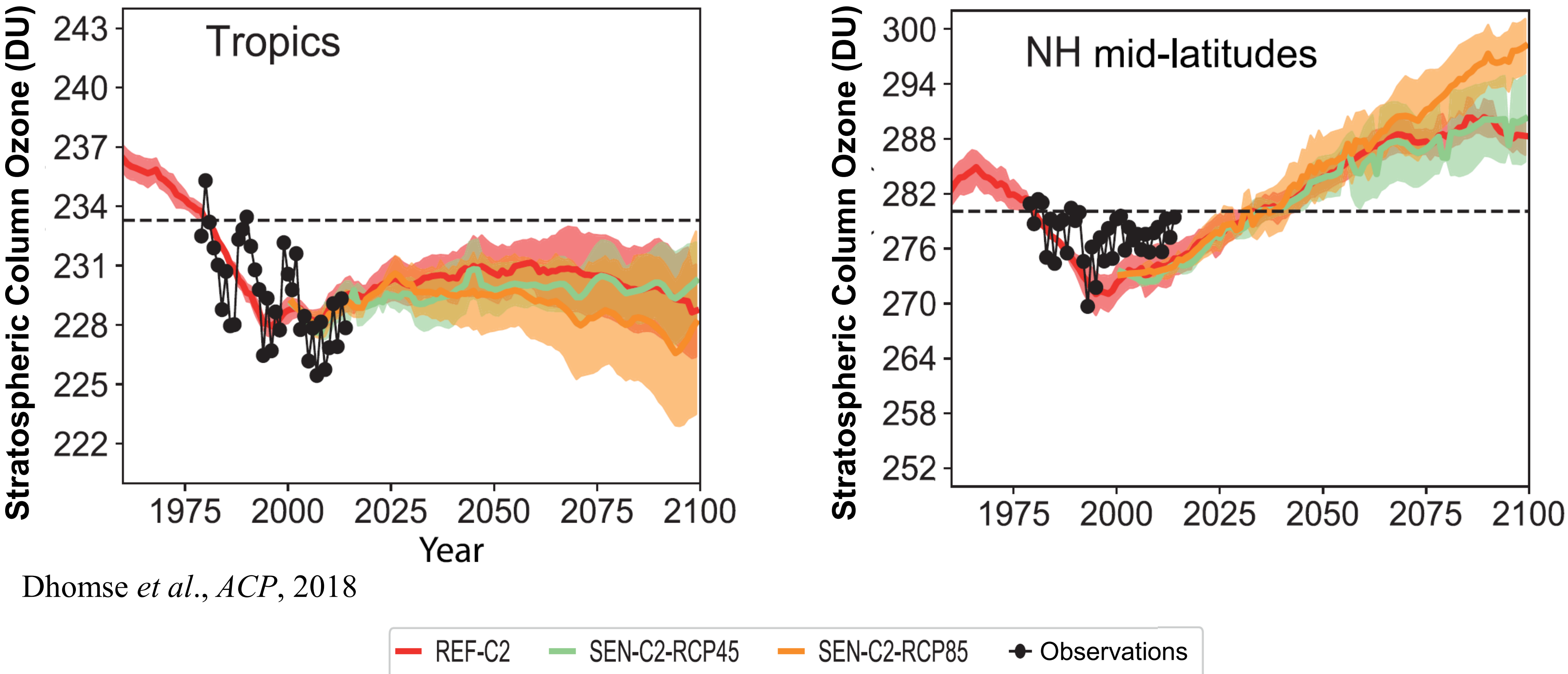
More Chemistry and Climate Coupling



Dhomse *et al.*, *ACP*, 2018

Acceleration of the *Brewer-Dobson Circulation* causes modeled total ozone column in the tropics to exhibit a sustained, long term decline and modeled total ozone column at mid-latitudes to experience a “super recovery”

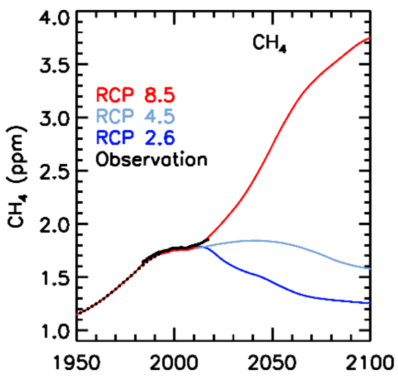
More Chemistry and Climate Coupling

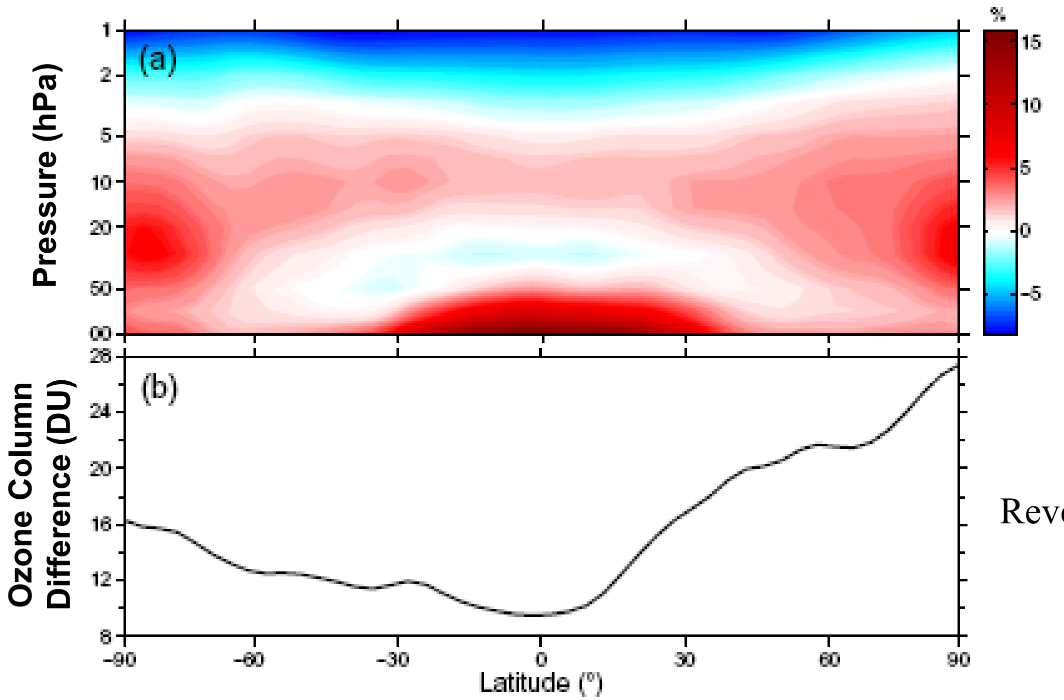


Dhomse *et al*., *ACP*, 2018

Acceleration of the *Brewer-Dobson Circulation* causes modeled total ozone column in the tropics to exhibit a sustained, long term decline and modeled total ozone column at mid-latitudes to experience a "super recovery"

CH_4 and Stratospheric Ozone





Revell *et al.*, *ACP*, 2012

Stratospheric O_3 difference in the 2090s found for a computer simulation run using CH_4 from RCP 8.5 minus that of a simulation using CH_4 from RCP 2.6

Rising CH_4 leads to:

a) ozone loss in the upper stratosphere by increasing the speed of OH and HO_2 (HO_x) mediated loss cycles.

b) a cooler stratosphere, slowing the rate of all ozone loss cycles

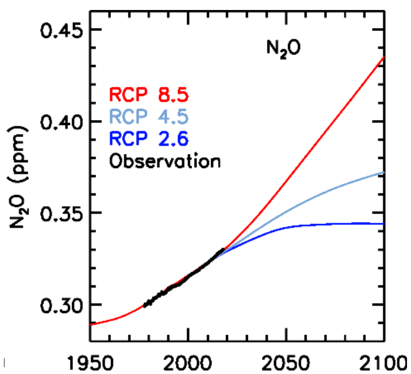
c) speeds up the rate of Cl+CH_4, shifting chlorine from ClO into HCl (i.e., deactivates chlorine)

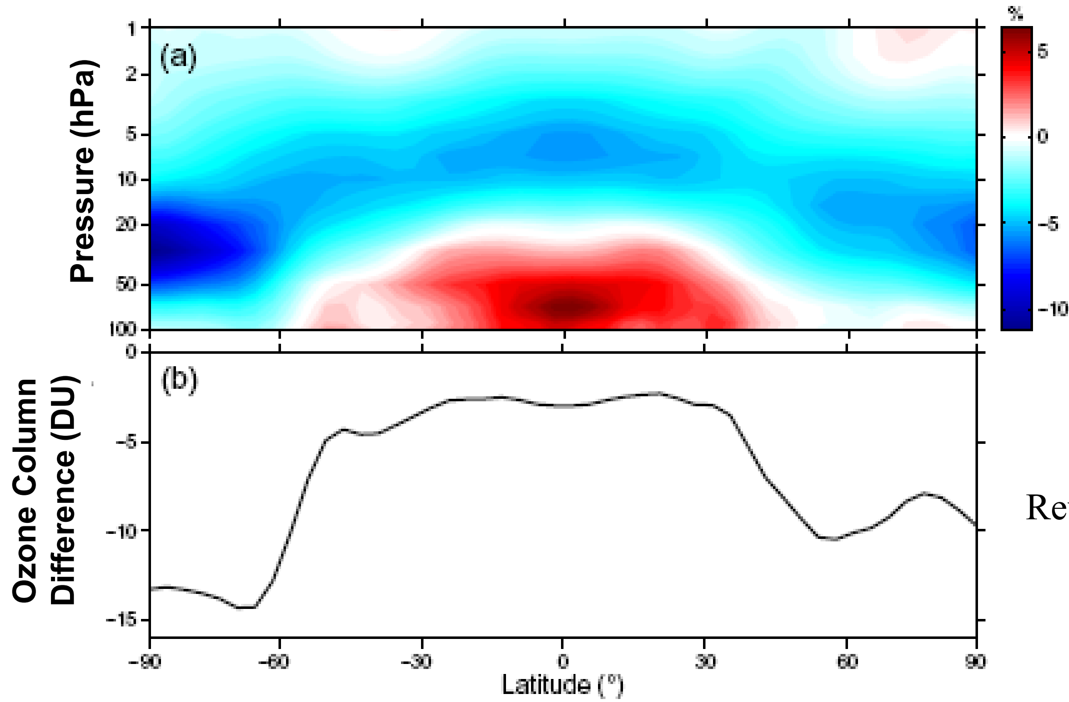
d) more HO_2 in the lowermost stratosphere where there is sufficient CO to result in O_3 production by "smog chemistry"

Computer models project stratospheric column O_3 will increase as CH_4 rises

Lecture 15, Slide 39

N_2O and Stratospheric Ozone





Revell *et al.*, *ACP*, 2012

Difference of stratospheric O_3 in the 2090s for a computer simulation run using N_2O from RCP 8.5 minus that of a simulation using N_2O from RCP 2.6

Rising N_2O leads to:

a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO_2 mediated loss cycles.

b) speeds up the rate of $OH+NO_2+M \rightarrow HNO_3$ & $ClO+NO_2+M \rightarrow ClNO_3+M$ in the lowermost stratosphere, leading to slower ozone loss by these cycles & less O_3 where these cycles dominate total loss of O_3

Computer models project stratospheric column O_3 will decline as N_2O rises

Lecture 6, Slide 74

Future Ozone: ODSs, CO_2, CH_4 and N_2O

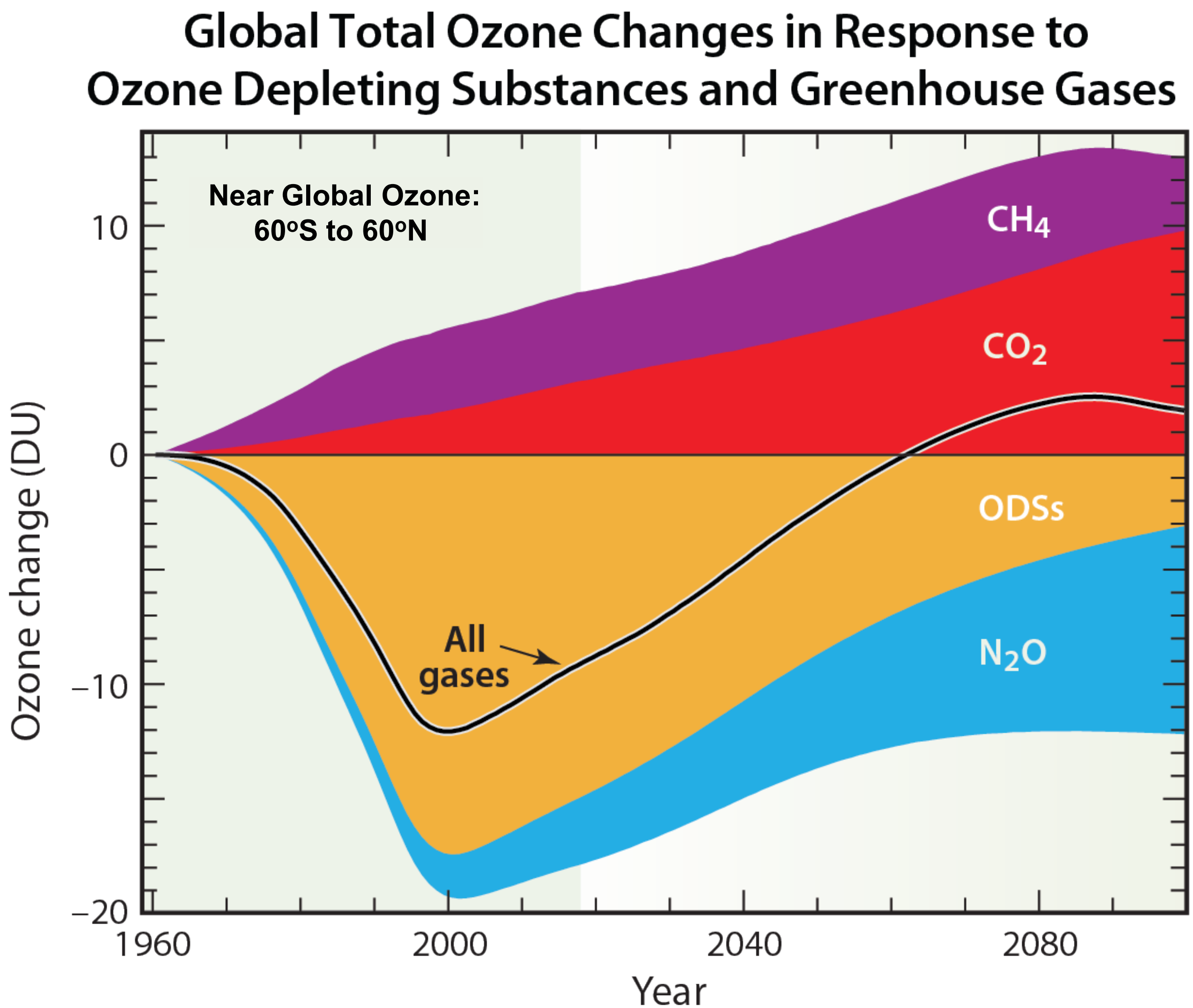
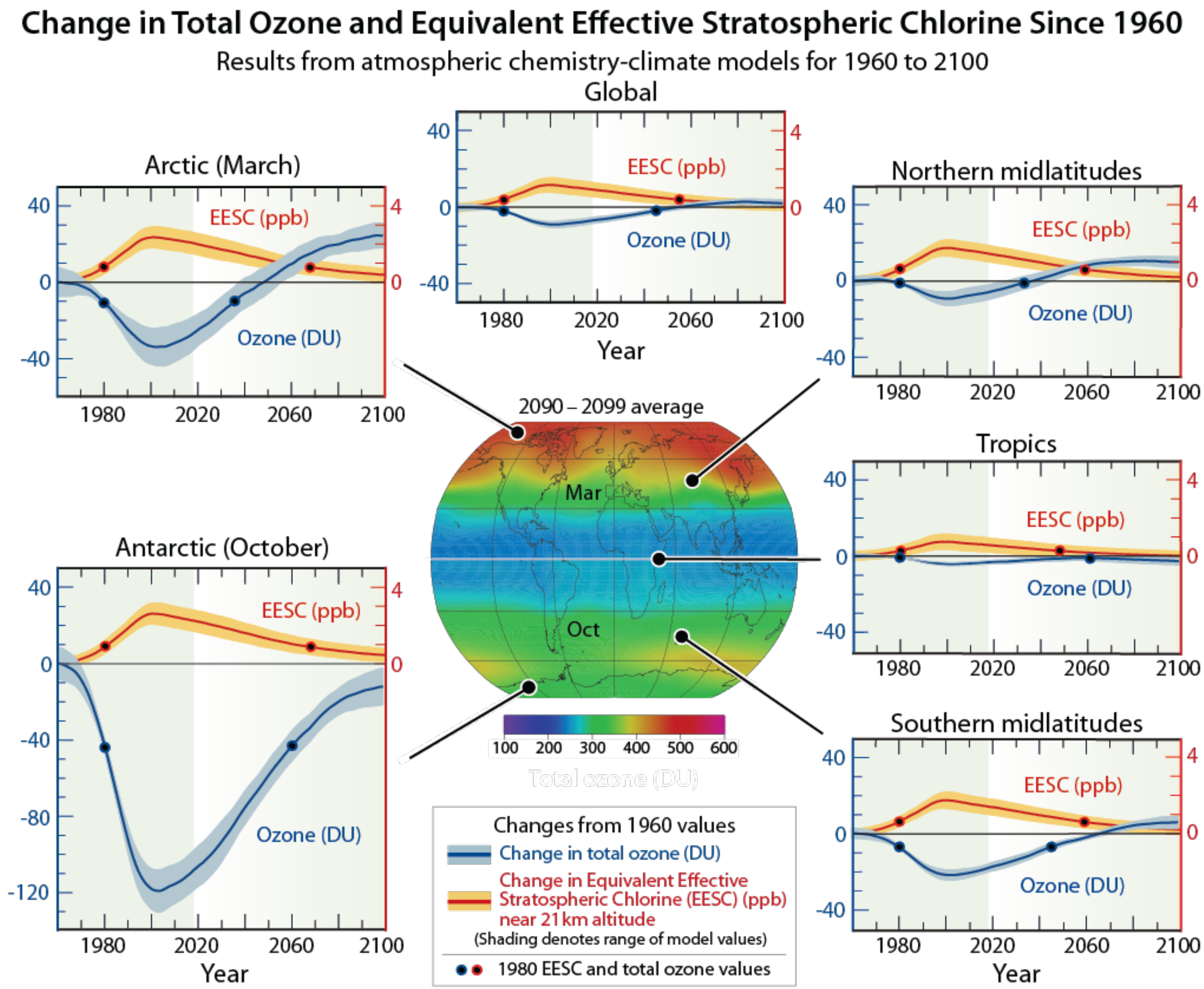


Fig Q20-3, *WMO/UNEP Twenty QAs Ozone*

Future Ozone: Regional Variations



EESC: Equivalent Effective Stratospheric Chlorine

$Cl_y + 60 \times Br_y$ (tropics & mid-latitudes)

$Cl_y + 65 \times Br_y$ (polar)

Fig Q20-2, *WMO/UNEP Twenty QAs Ozone*

Future Trends, Stratospheric Ozone

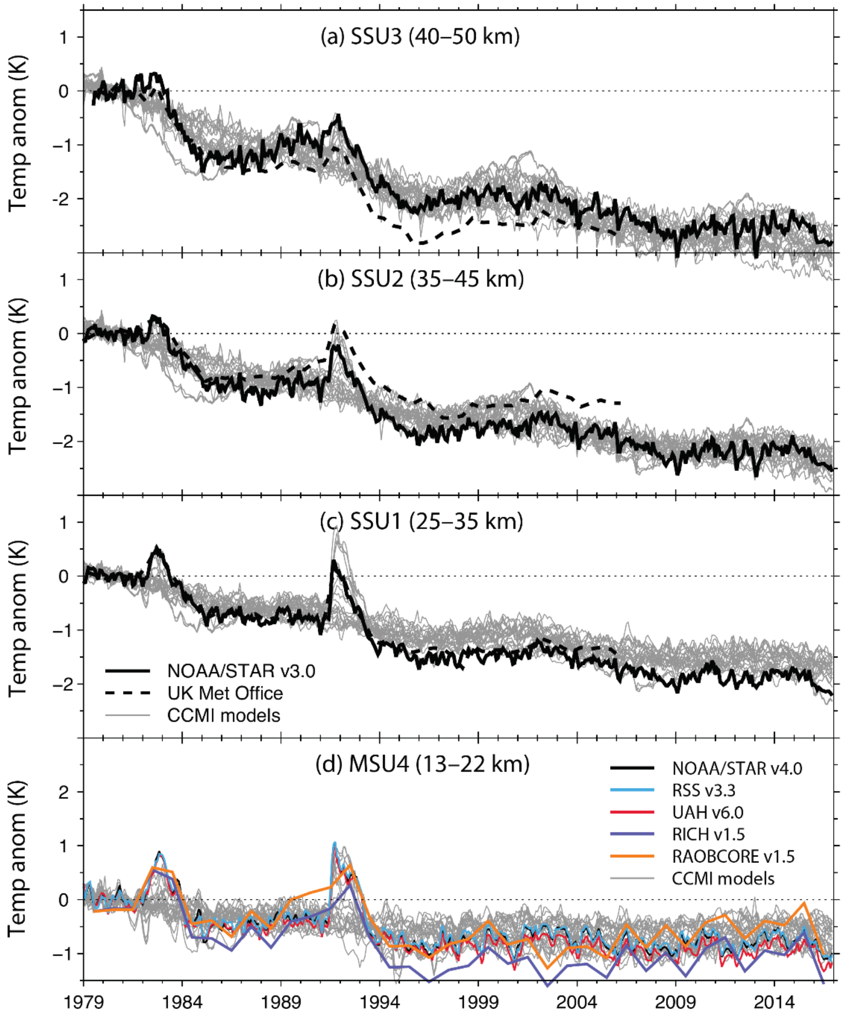
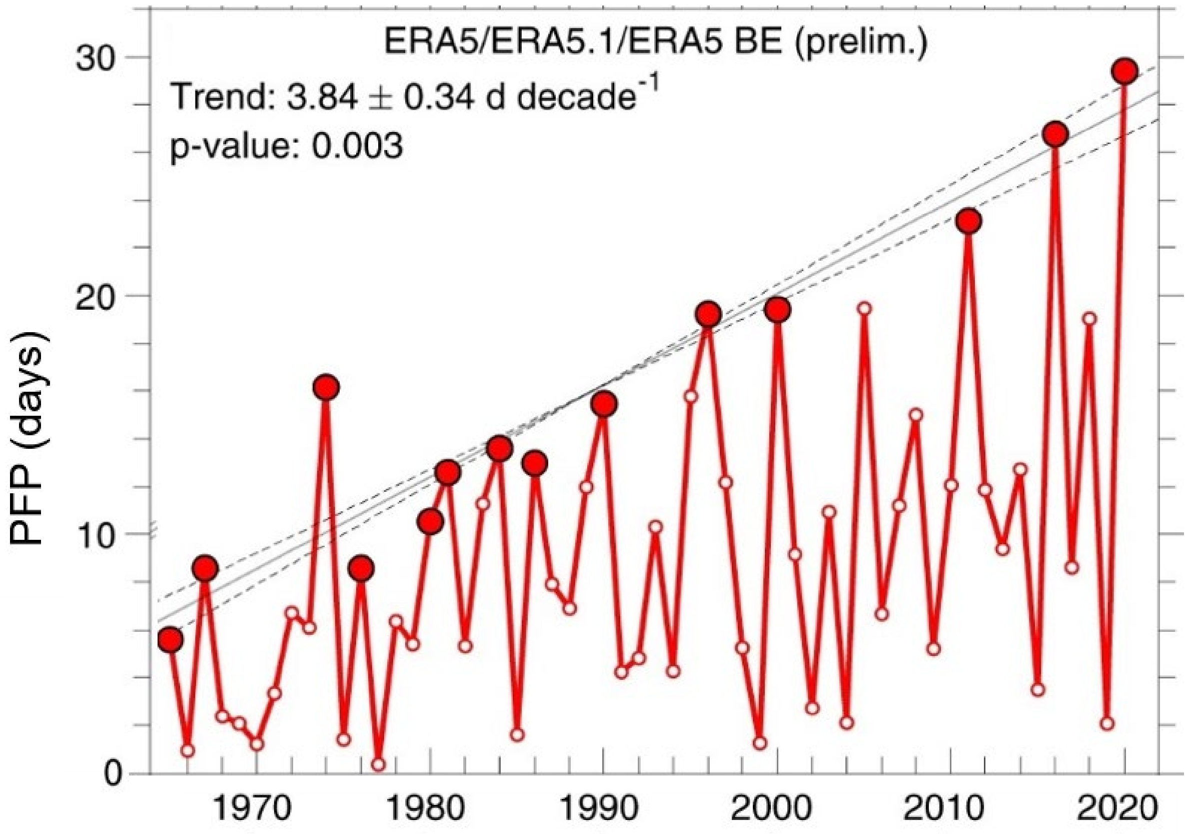


Figure 5-4, WMO/UNEP (2018)

If the stratosphere *continues to cool*, for which region of the stratosphere is ozone "most vulnerable"?

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

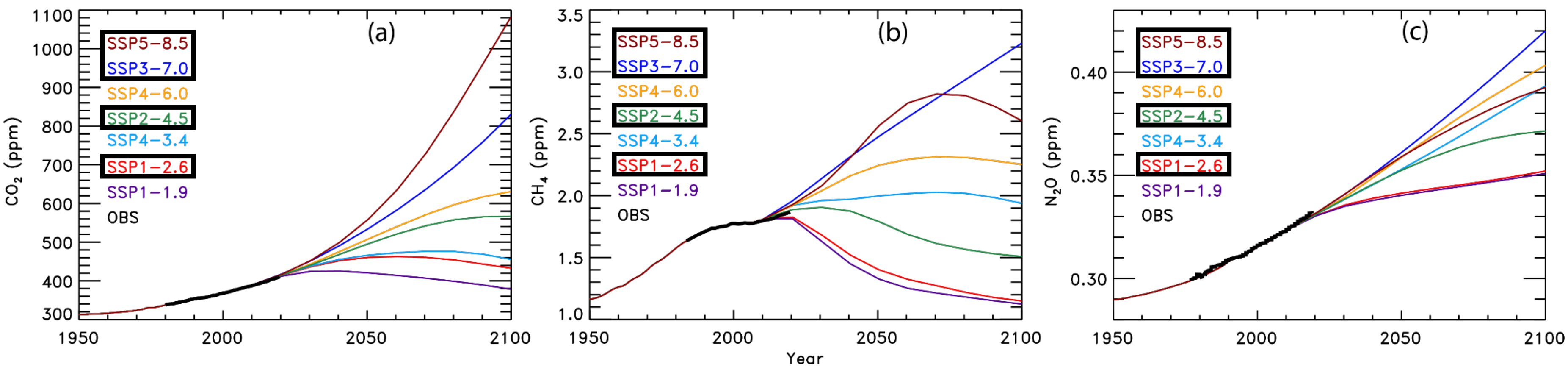
based on 55 years of data from the European Centre for Medium-Range Weather Forecasts (ECMWF)

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

Lecture 16, Slide 79

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

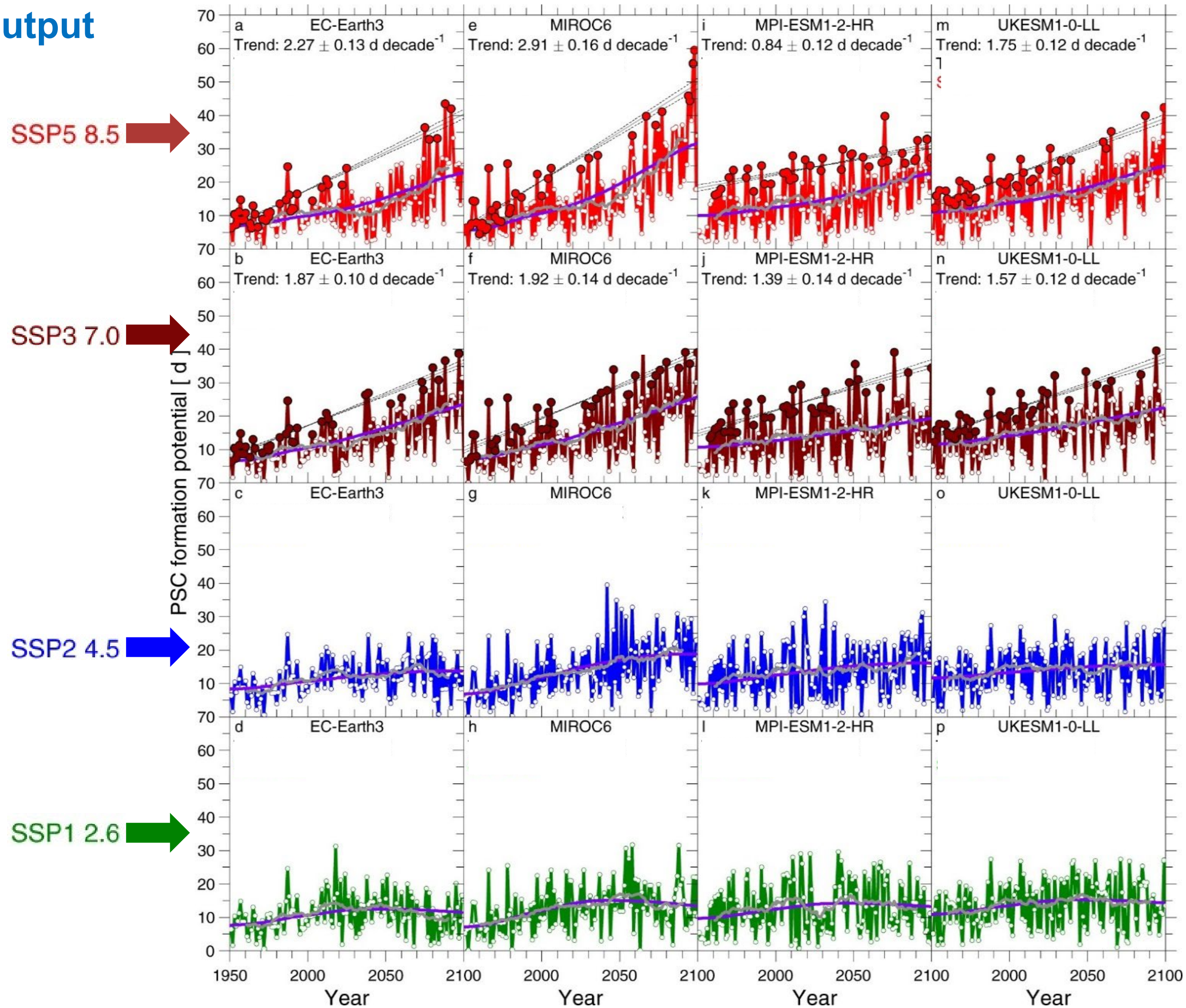
McBride et al., *Earth System Dynamics*, 2021

Lecture 16, Slide 80

Tendency for Colder Arctic Winters Getting Colder Driven by Rising GHGs

Climate Model Output

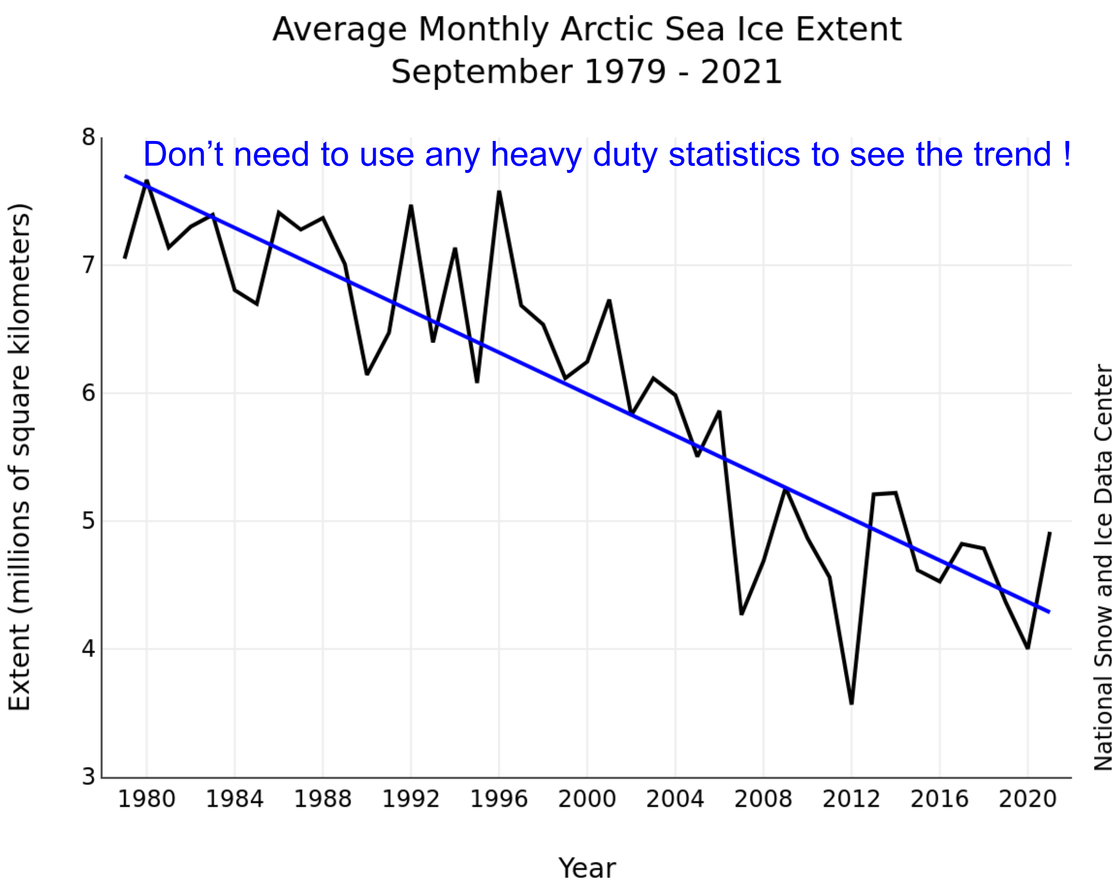
PFP is PSC Formation Potential



von der Gathen, *Nature Communications*, 2021

Lecture 16, Slide 81

Arctic Sea-Ice: Canary of Climate Change



- Sea ice: ice overlying ocean
- Annual minimum occurs each September
- Decline of ~12.7% / decade over satellite era

http://nsidc.org/arcticseaicenews/2021/10/

Lecture 8, Slide 24

NSIDC National Snow & Ice Data Center | DATA | RESEARCH | NEWS | ABOUT | SEARCH | Web pages

Arctic Sea Ice News & Analysis

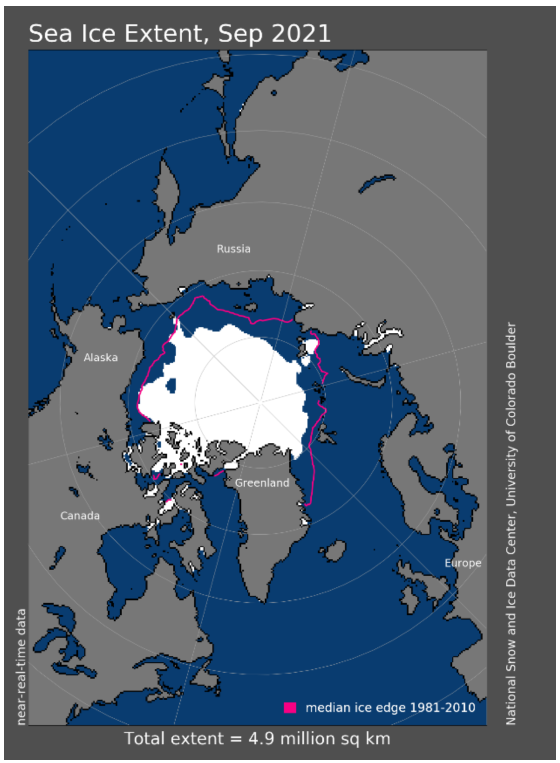
← Previous Next →

October 5, 2021

September turning

Search

The summer melt season has come to a modest end. The summer of 2021 was relatively cool compared to the most recent years and September extent was the highest since 2014. It was nevertheless an eventful summer, with many twists and turns.

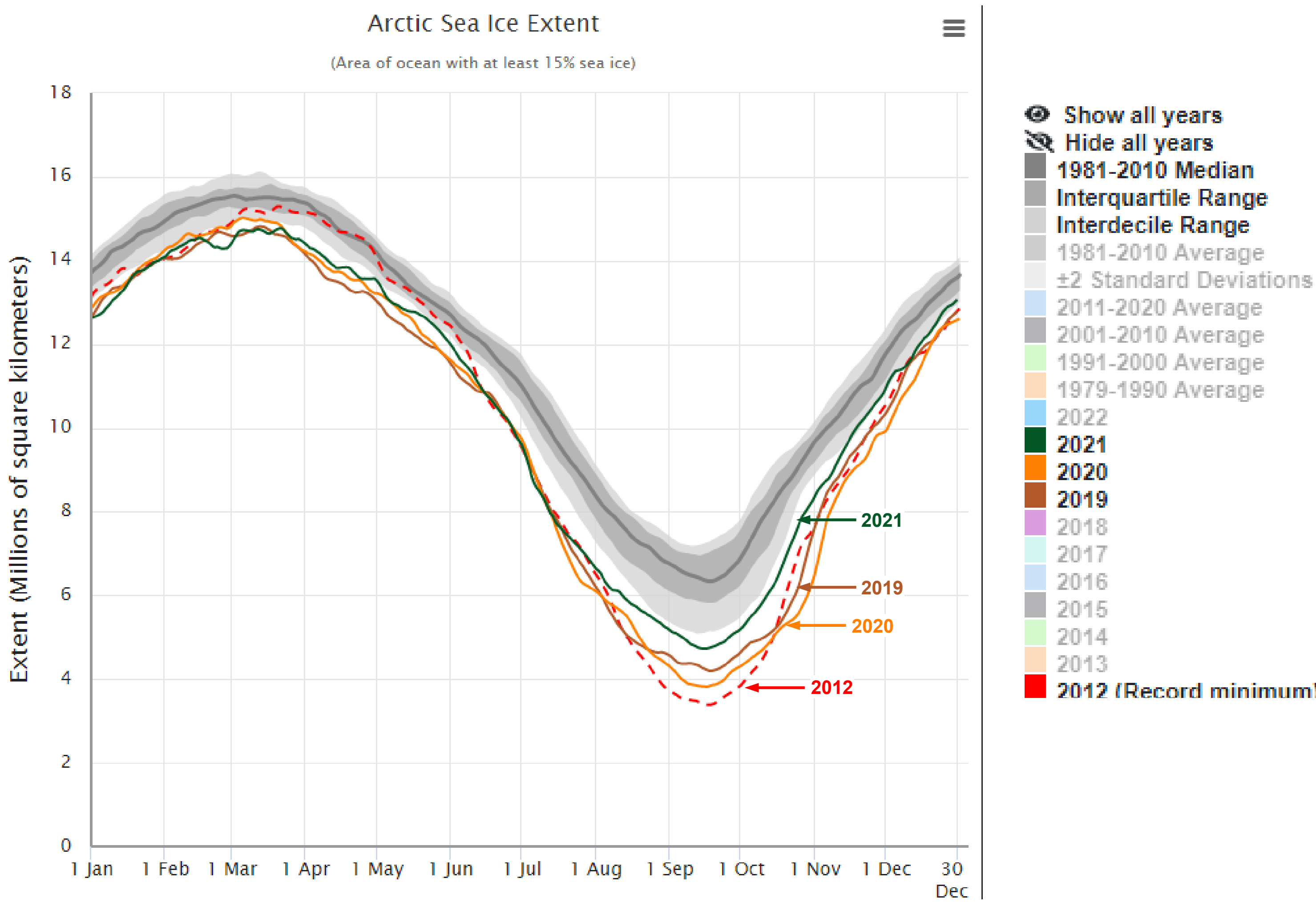


Arctic sea ice extent for September averaged 4.92 million square kilometers (1.90 million square miles), the twelfth lowest in the 43-year satellite record. This is 1.35 million square kilometers (521,000 square miles) above the record low set in September 2012, and 1.49 million square kilometers (575,000 square miles) below the 1981 to 2010 average. The last 15 years (2007 to 2021) have had the 15 lowest September extents in the record.

Figure 1a. Arctic sea ice extent for September 2021 was 4.92 million square kilometers (1.90 million square miles). The magenta line shows the 1981 to 2010 average extent for that month. Sea Ice Index data. About the data

http://nsidc.org/arcticseaicenews/2021/10/september-turning/

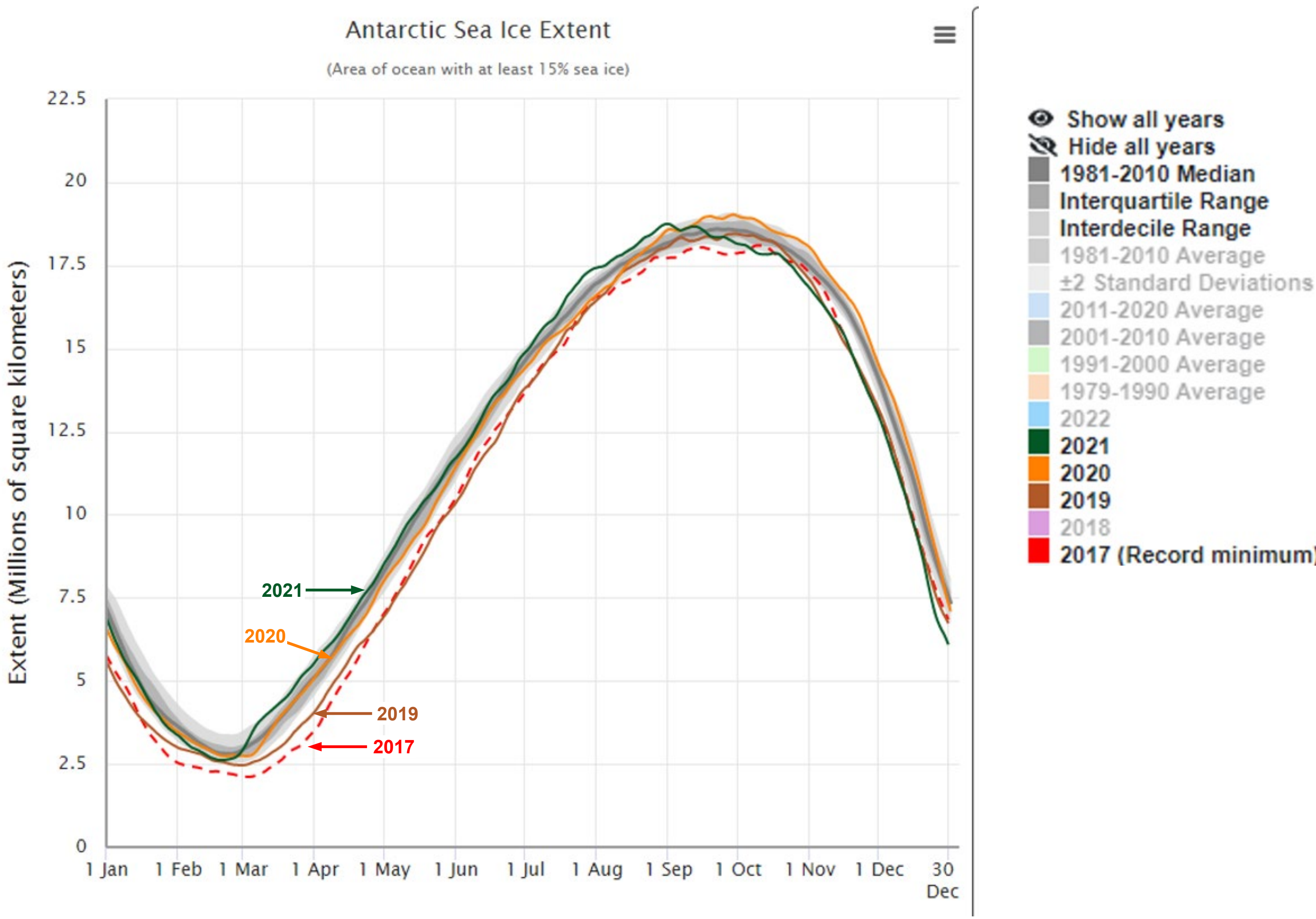
Declining Arctic Sea Ice: Canary of Climate Change?



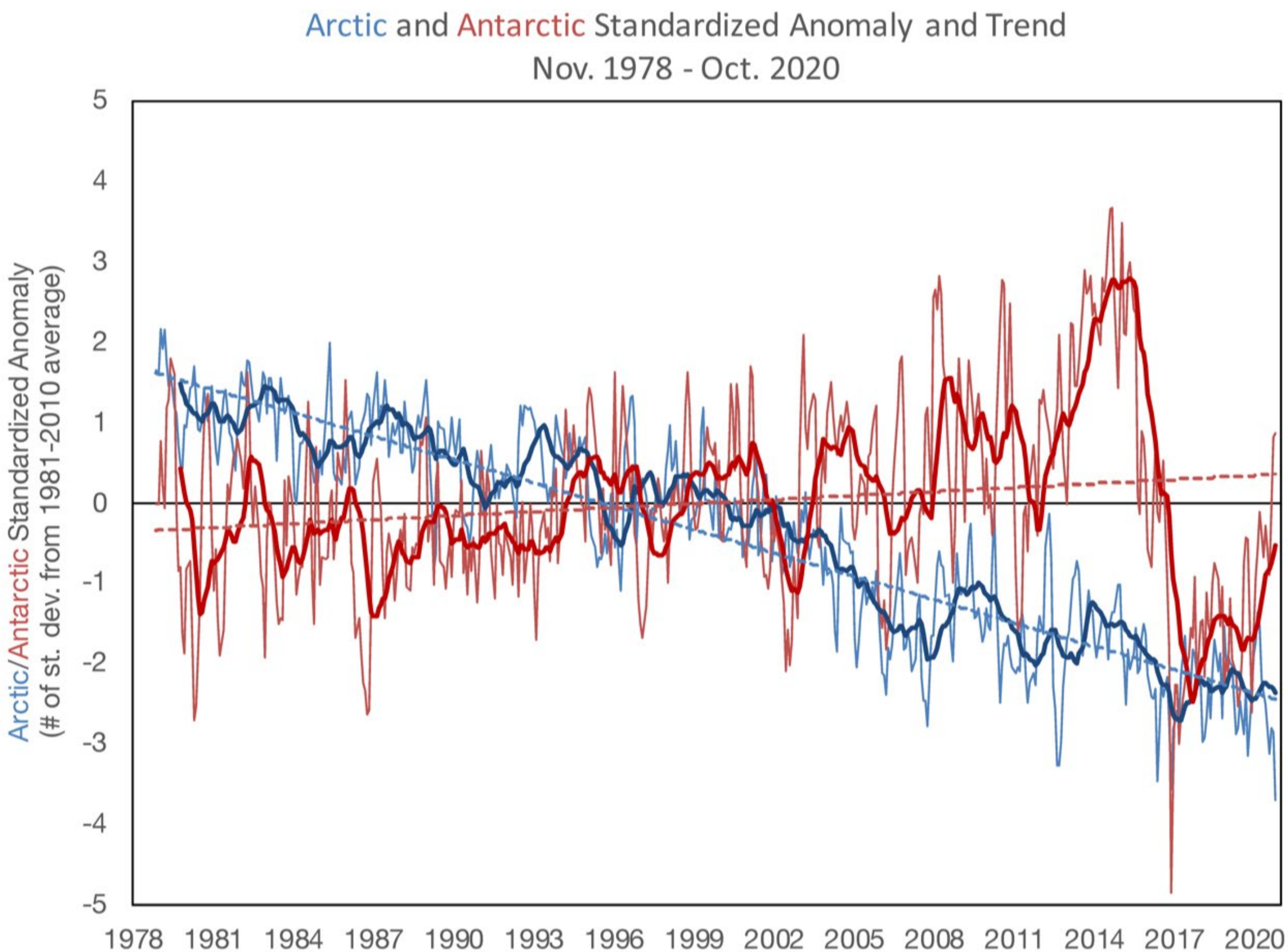
Again, don't need to use any heavy duty statistics to see the trend !

https://nsidc.org/arcticseaicenews/charctic-interactive-sea-ice-graph

The Antarctic



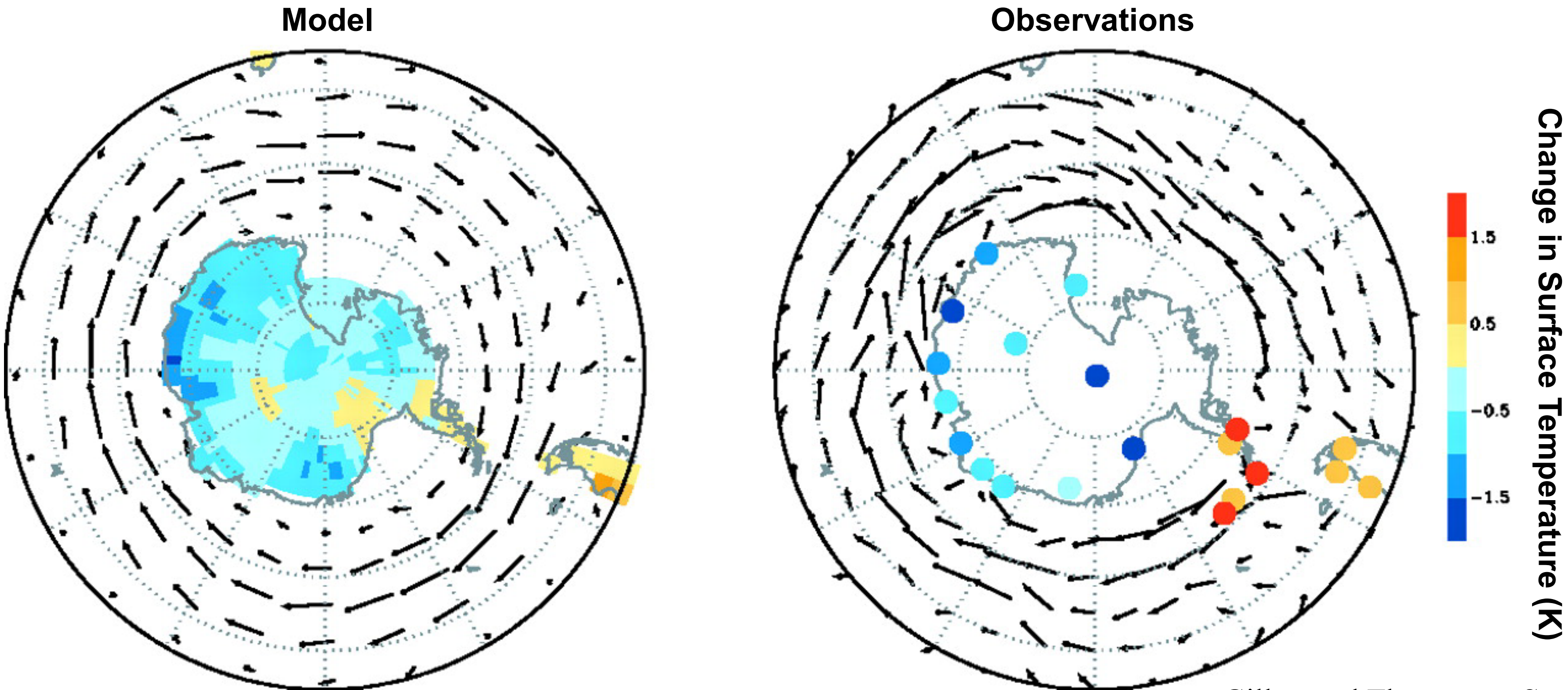
https://nsidc.org/arcticseaicenews/charctic-interactive-sea-ice-graph



Arctic and Antarctic Sea Ice Extent Anomalies, 1979-2020: Arctic sea ice extent underwent a strong decline over the course of the satellite record, but Antarctic sea ice underwent a slight increase, although some regions of the Antarctic experienced strong declining trends in sea ice extent. Thick lines indicate 12-month running means, and thin lines indicate monthly anomalies. See the Arctic Sea Ice FAQ for more information. Image provided by National Snow and Ice Data Center, University of Colorado, Boulder.

https://nsidc.org/cryosphere/sotc/sea_ice.html

The Ozone Hole may have shielded the Antarctic surface from warming!



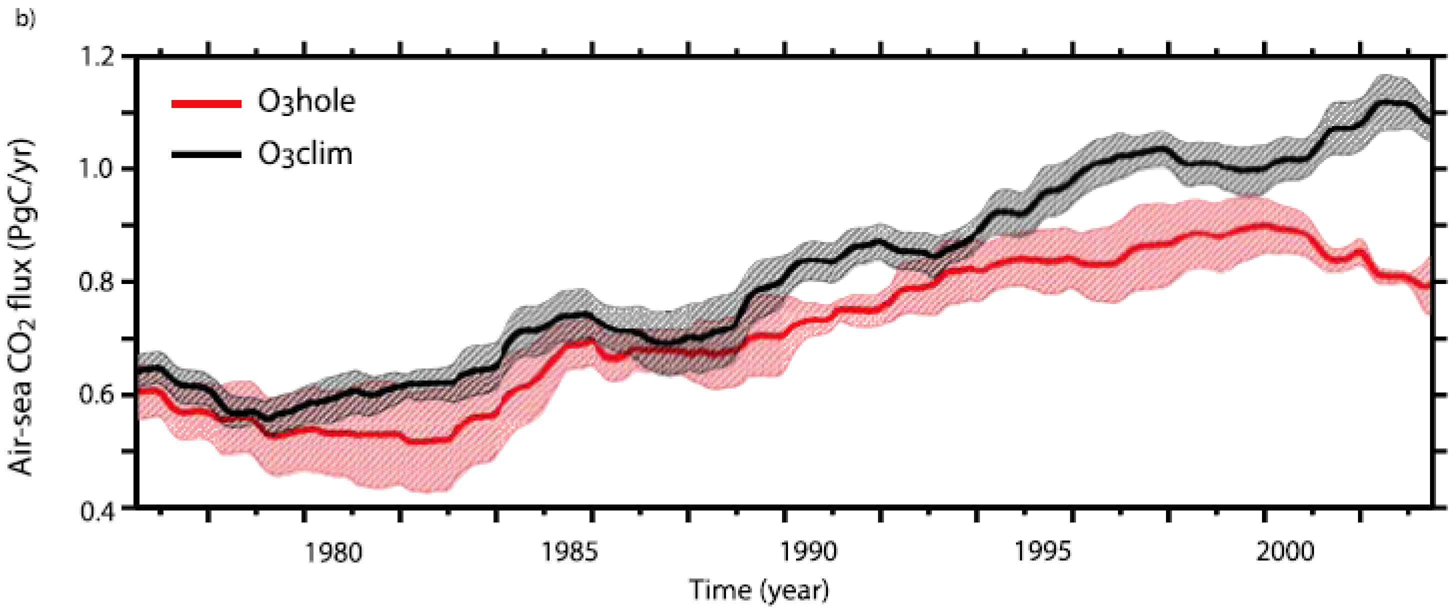
Gillett and Thompson, *Science*, 2003

SAM: difference in zonal mean sea-level pressure between 40°S and 65°S. The pattern associated with SAM is a nearly annular pattern with a large low pressure anomaly centered on the South Pole and a ring of high pressure anomalies at mid-latitudes. The SAM effects storm tracks, precipitation patterns, etc. http://www.climate.be/textbook/chapter5_node6.html

As ozone depletion occurs:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to intensify, resulting in cooling of Antarctic continent

The Ozone Hole may have lead to increased ventilation of CO_2 from southern ocean



(b) Integrated air to sea CO_2 flux (south of 40°S) showing stratospheric ozone depletion (O_3hole) significantly reduces CO_2 uptake (relative to O_3clim), and is strongly correlated with changes in ΔpCO_2.

Lenton *et al.*,*GRL*, 2009

As ozone depletion occurs:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to intensify, resulting in increased ventilation of CO_2 from southern ocean

Uptake of Atmospheric CO_2 by Oceans

– Solubility Pump:

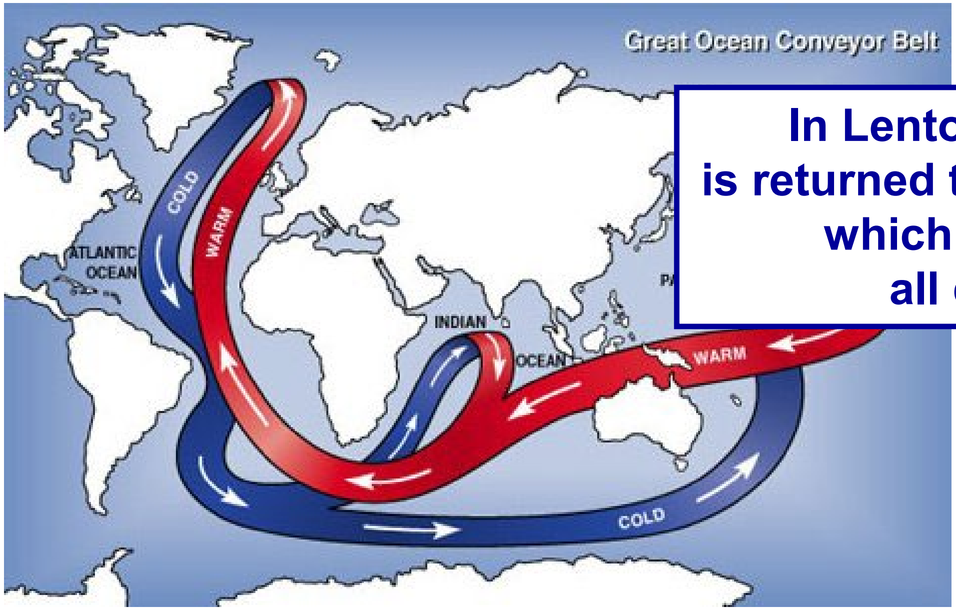
a) More CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

b) Deep water forms at high latitude. ***As deep water sinks, ocean carbon (ΣCO_2) accumulated at the surface is moved to the deep ocean interior***.

– Biological Pump:

a) Ocean biology limited by availability of nutrients such as NO_3^-, PO_4^-, and Fe^{2+} & Fe^{3+} . Ocean biology is never carbon limited.

b) Detrital material "rains" from surface to deep waters, ***contributing to higher CO_2 in intermediate and deep waters***



In Lenton *et al*. model, elevated oceanic CO_2 is returned to the atmosphere due to stronger winds, which leads to more ocean turbulence … all due to the Antarctic ozone hole !

http://science.nasa.gov/headlines/y2004/05mar_arctic.htm

Chemistry Climate Coupling

CCMs (chemistry climate models): developed to quantify impacts of climate change on stratospheric ozone *and* impacts of ozone depletion/recovery on climate:

As GHGs rise:

1. **Brewer-Dobson circulation predicted to accelerate leading to:**
   a) **less ozone in tropical lower stratosphere ("permanent depletion")**
   b) **more ozone in mid-latitude lower stratosphere ("super recovery")**
2. **Upper stratosphere cools, slowing down rate limiting steps for ozone loss and therefore leading to "super recovery"**
3. **Eventually, CH_4 and N_2O will drive future levels of ozone**

Data analysis suggests "coldest Arctic winters getting colder":

1. **Possibly due to rising GHGs**
2. **Not represented well by some Chemistry Climate Model (CCMs)**

As Antarctic ozone depletion *had occurred*:

The positive phase of the southern annular mode (SAM) increases, causing Antarctic surface westerlies to *intensify*, resulting in:

1. **Cooling of Antarctic continent (good for sea-level)**
2. **Increased ventilation of CO_2 from southern ocean (bad for climate)**

Chemistry Climate Coupling

CCMs (chemistry climate models): developed to quantify impacts of climate change on stratospheric ozone *and* impacts of ozone depletion/recovery on climate:

As GHGs rise:

1. **Brewer-Dobson circulation predicted to accelerate leading to:**
   - **a) less ozone in tropical lower stratosphere ("permanent depletion")**
   - **b) more ozone in mid-latitude lower stratosphere ("super recovery")**
2. **Upper stratosphere cools, slowing down rate limiting steps for ozone loss and therefore leading to "super recovery"**
3. **Eventually, CH_4 and N_2O will drive future levels of ozone**

Data analysis suggests "coldest Arctic winters getting colder":

1. **Possibly due to rising GHGs**
2. **Not represented well by some Chemistry Climate Model (CCMs)**

As Antarctic ozone recovery *occurs*:

The positive phase of the southern annular mode (SAM) may decline, causing Antarctic surface westerlies to *weaken*, resulting in:

1. **Warming of Antarctic continent (bad for sea-level)**
2. **Decreased ventilation of CO_2 from southern ocean (good for climate)**