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/fall2020
https://myelms.umd.edu/courses/1291919

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

10 November 2020

Announcements: Class

- Problem Set #3:

  https://www2.atmos.umd.edu/~rjs/class/fall2020/problem_sets/ACC_2020_problem_set_03.pdf

  and is due on ~~Tuesday, 10 November~~ Thursday, 12 November.

- Due to "popular demand", this problem set will be completed outside of ELMS: prefer you mail me and Laura McBride (mcbridel@terpmail.umd.edu) either one PDF file (entire P Set) or two PDF files (one per question) when the problem set is complete, with an email subject such as:

  AOSC 433: Problem Set 3 *or* CHEM 633: Problem Set 3 , etc

- Please email me and Laura with questions

Problem Set #3 due date extended to Thursday, 12 Nov due to issues with the class website on 5 Nov 2020.

Announcements: Class

Next Exam:

- week from today (17 Nov), conducted in the same format as first exam:
  i.e., open book, open web, normal class time, via Zoom with camera on

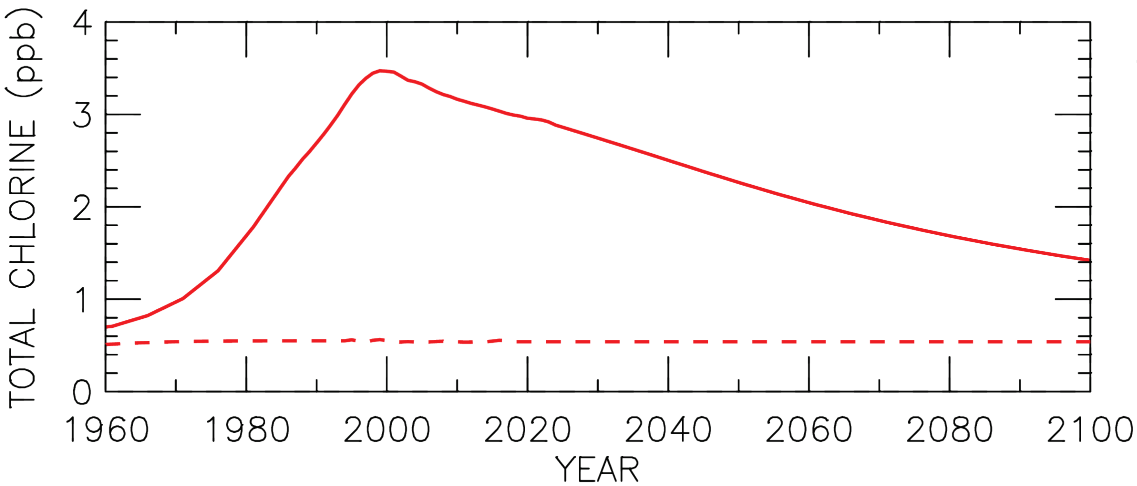
- conceptual focus mainly on material covered in Lectures 11 to 17

Thursday, 12 Nov:

- review of Lectures 11 to 17

- please hold off on questions about exam until Thursday

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

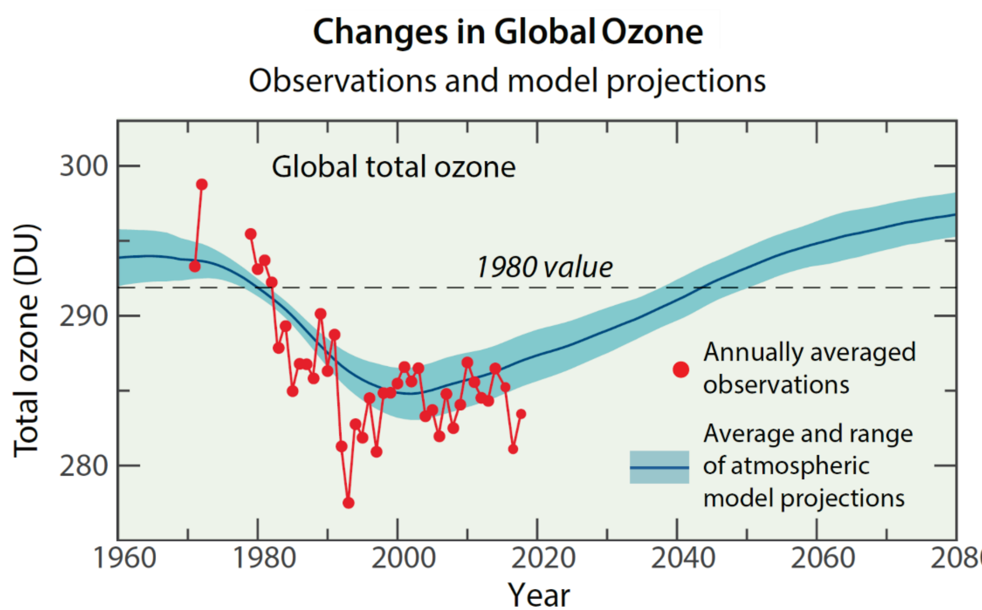


Fig Q20-1, *WMO/UNEP Twenty QAs Ozone*

Recovery of the Ozone Layer

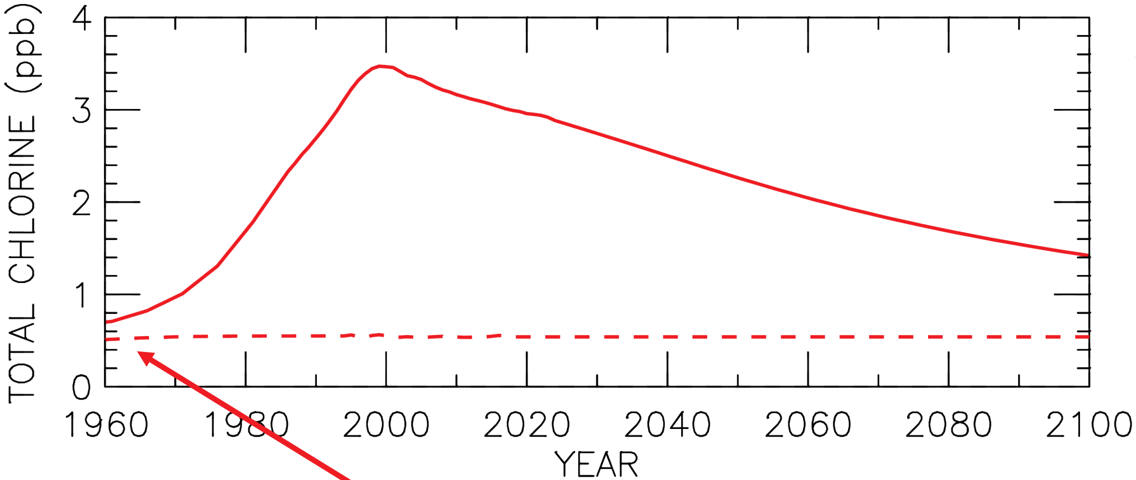


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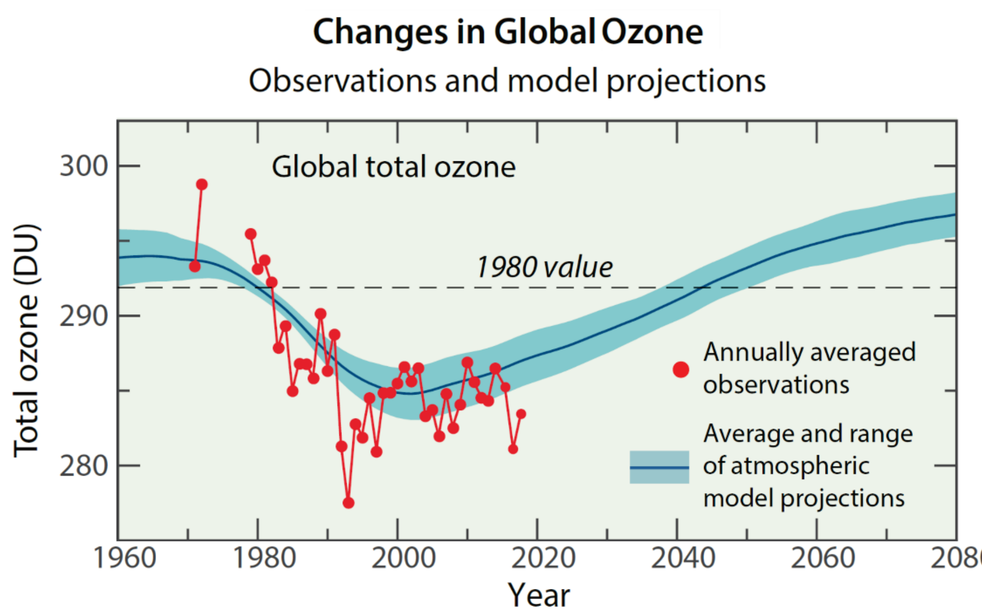
Table 6−4, WMO/UNEP 2018

Why was total chlorine ~0.6 ppb in 1960?



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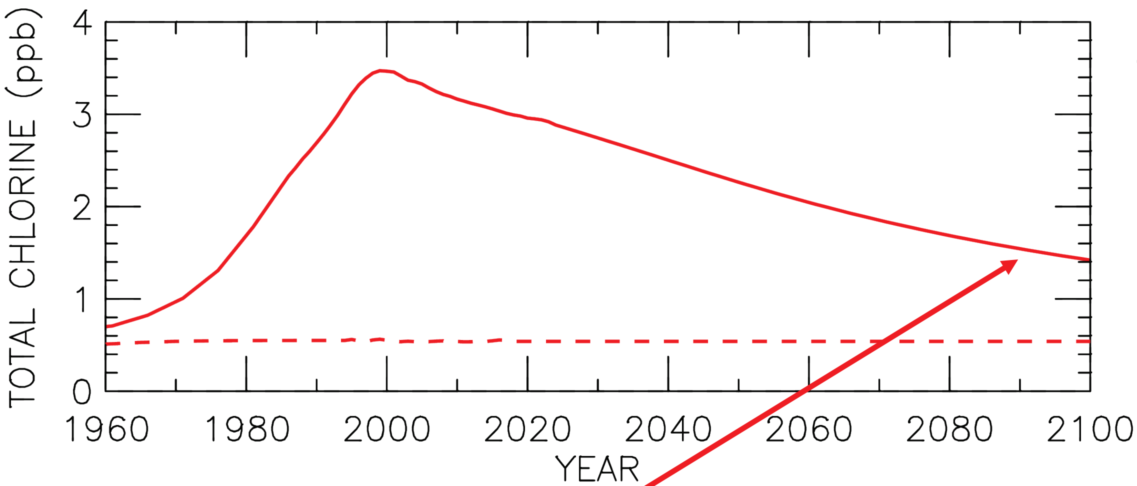


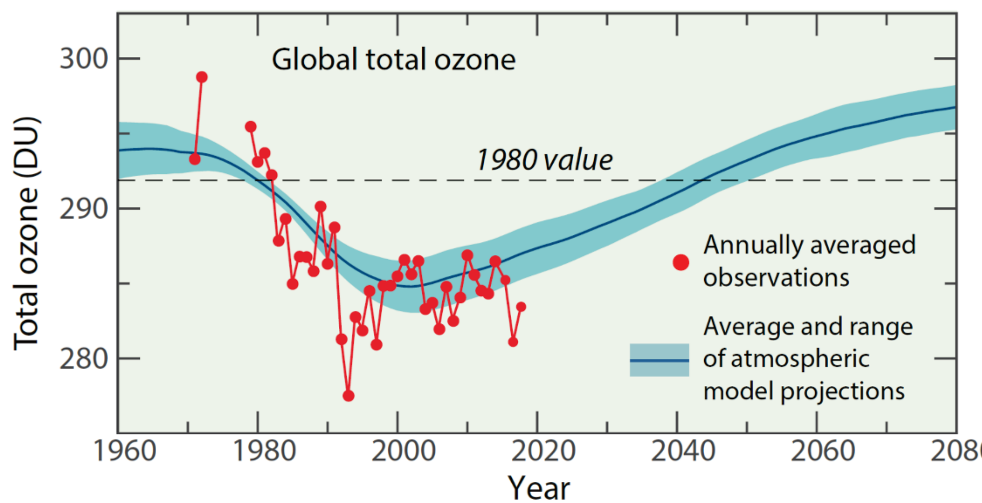
Time series of chlorine content of organic halocarbons that reach the stratosphere. Past values based on direct atmospheric observation. Future values based on projections that include the lifetime for removal of each halocarbon.

Table 6−4, WMO/UNEP 2018

What very long lived halocarbons are responsible for CCl_y in year 2100 exceeding CCl_y in year 1960 ?

Changes in Global Ozone

Observations and model projections



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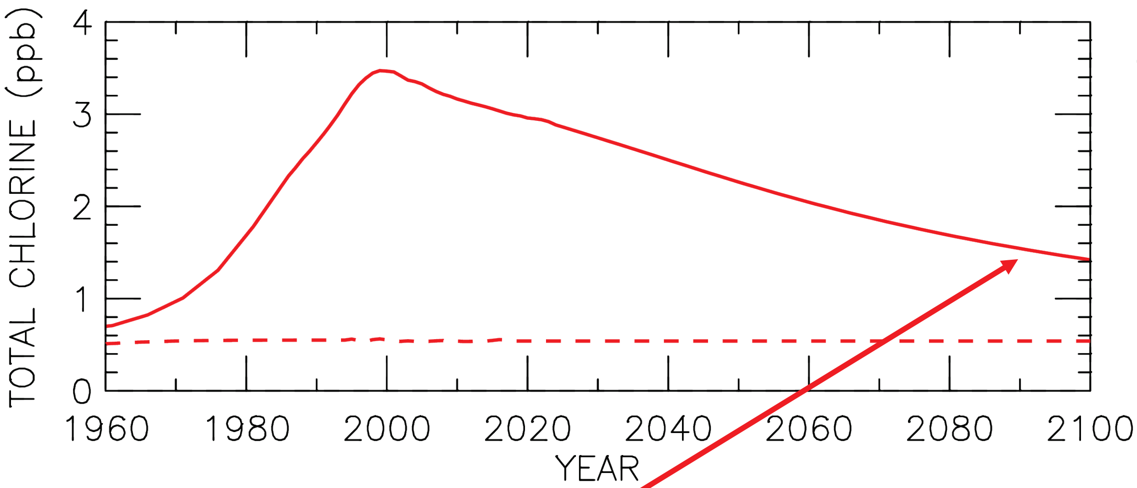
Recovery of the Ozone Layer



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.

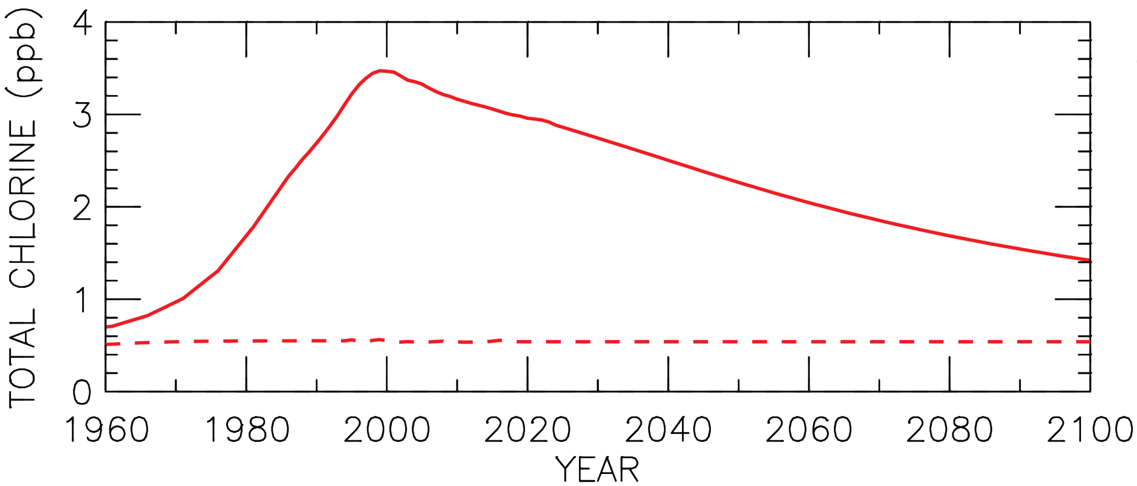
What very long lived halocarbons are responsible for CCl_y in year 2100 exceeding CCl_y in year 1960 ?

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

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

What is especially "odd" about these graphs when scrutinized in tandem ?

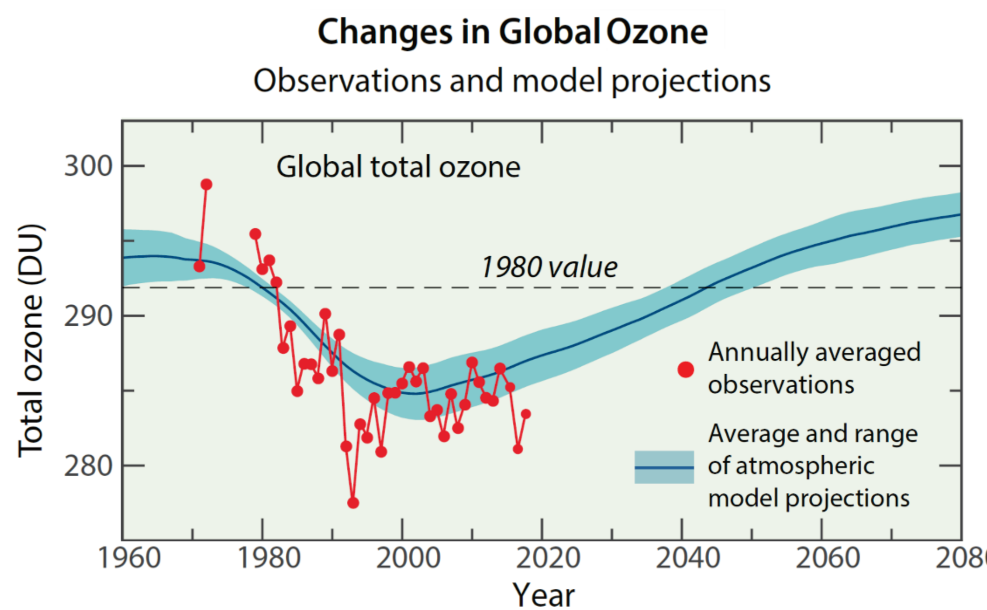
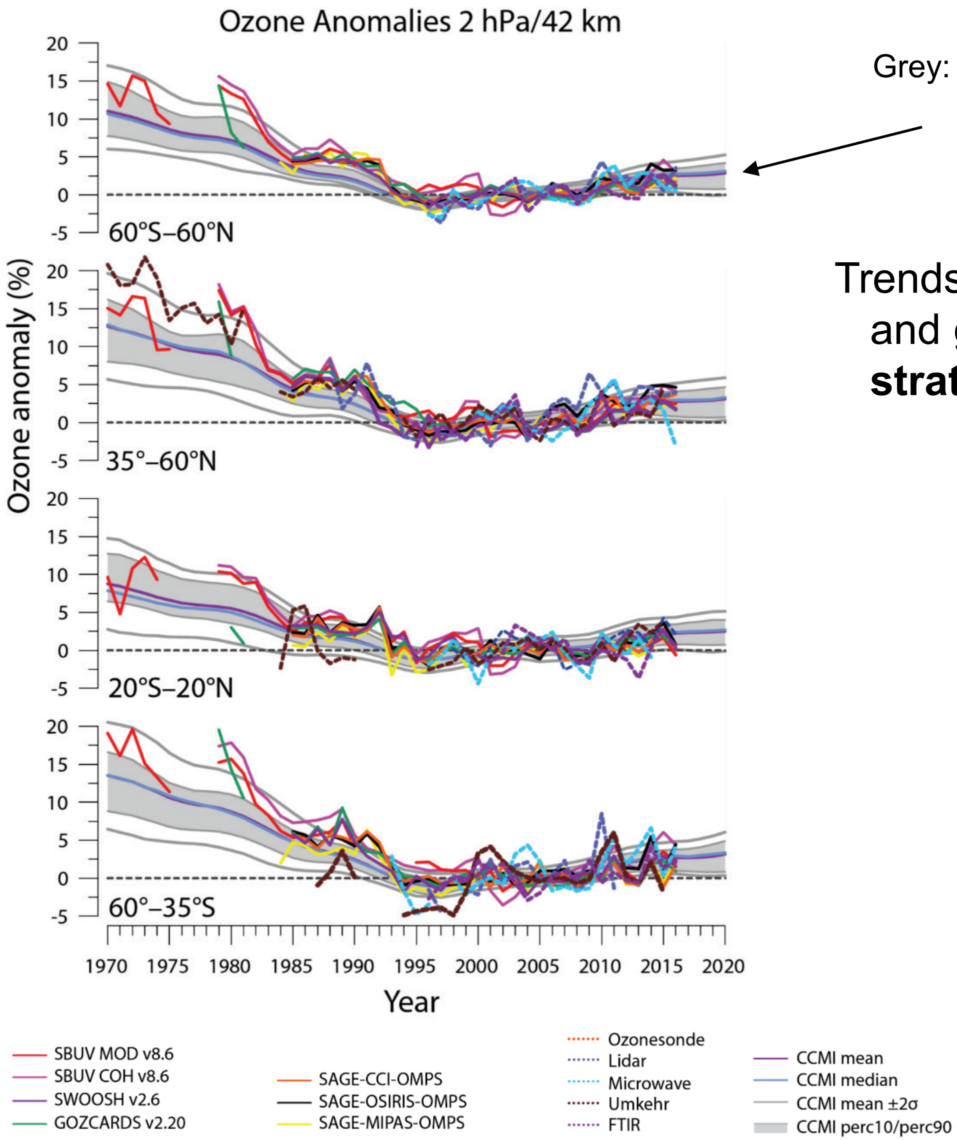


Fig Q20-1, *WMO/UNEP Twenty QAs Ozone*

Past Trends, Upper Stratospheric Ozone



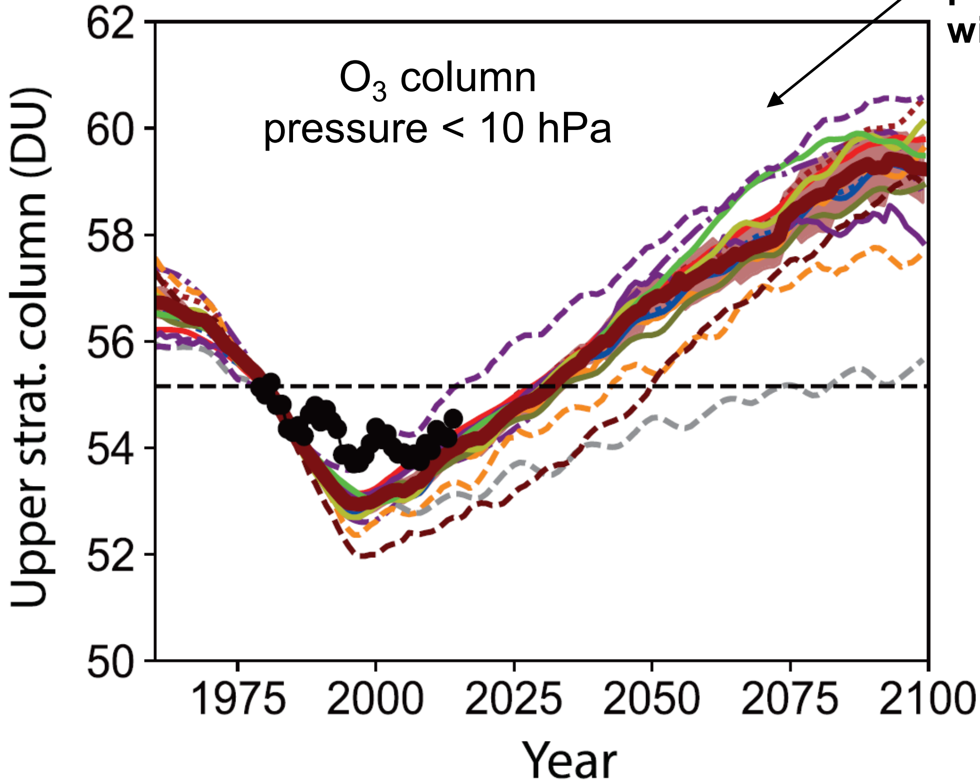
Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens

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, Slides 50 & 51

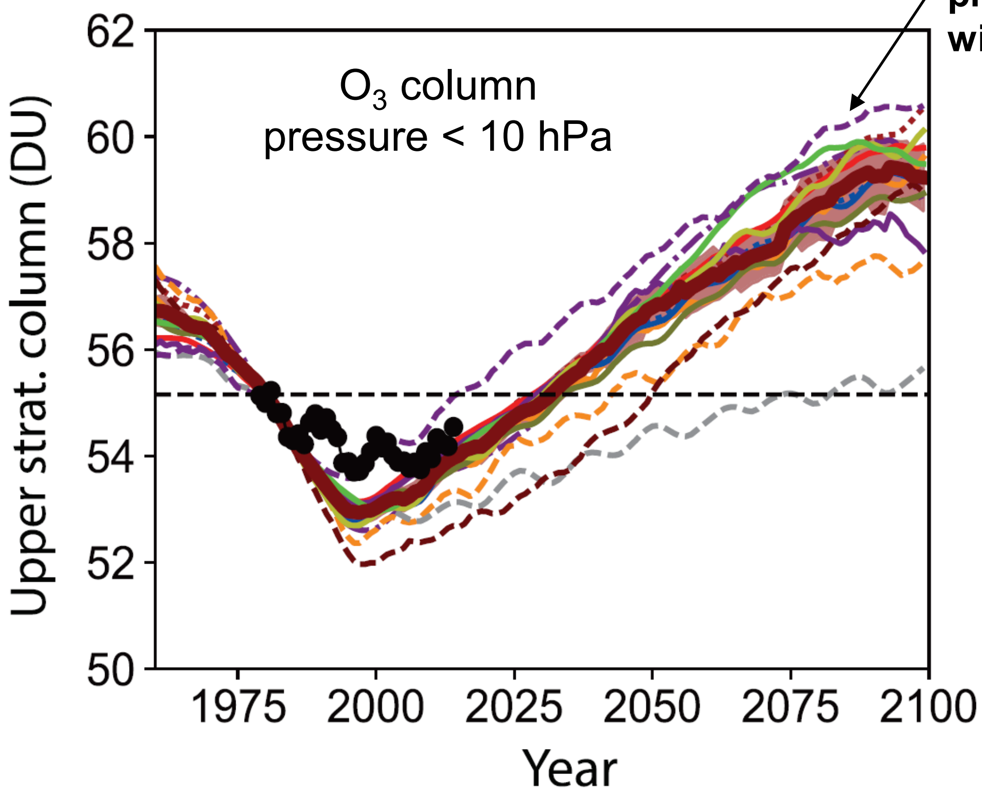
Future Trends, Upper Stratospheric Ozone



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

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

Future Trends, Upper Stratospheric Ozone



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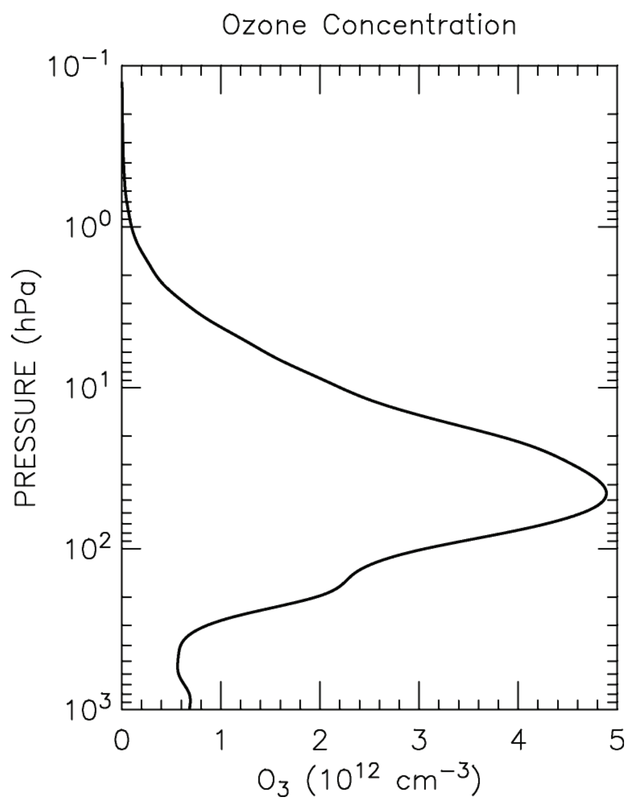

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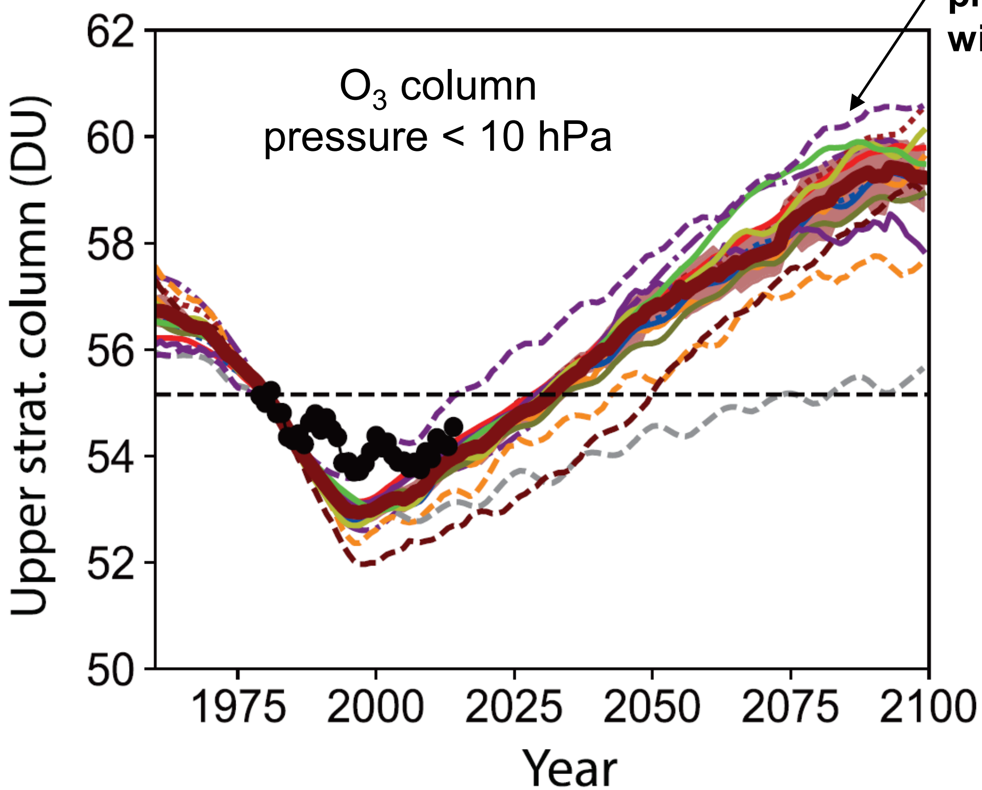

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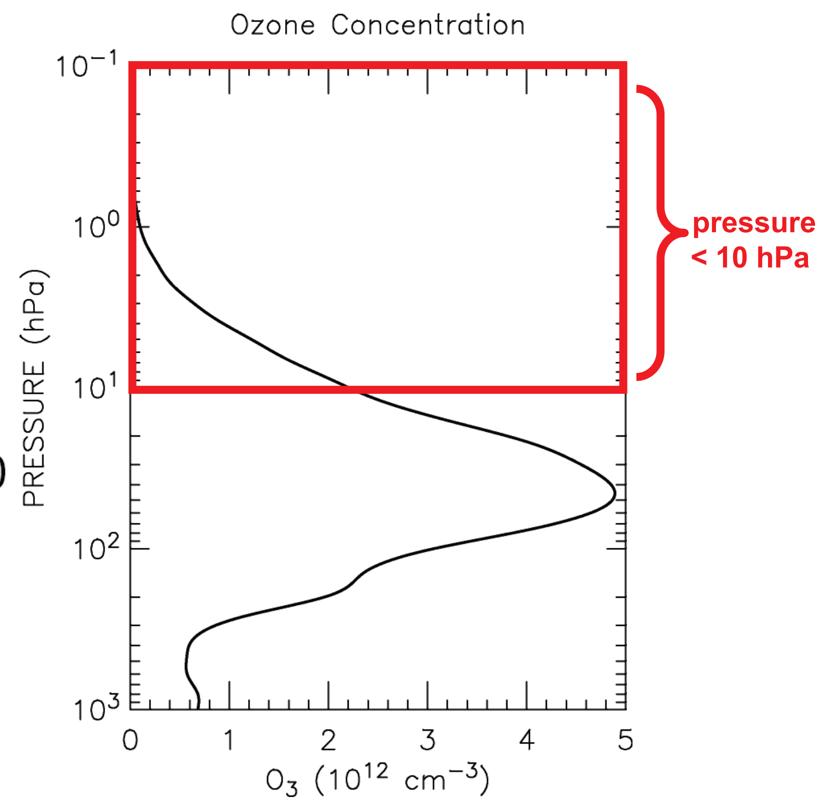


Climate and Chemistry Coupling

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 broadly consistent with theory:

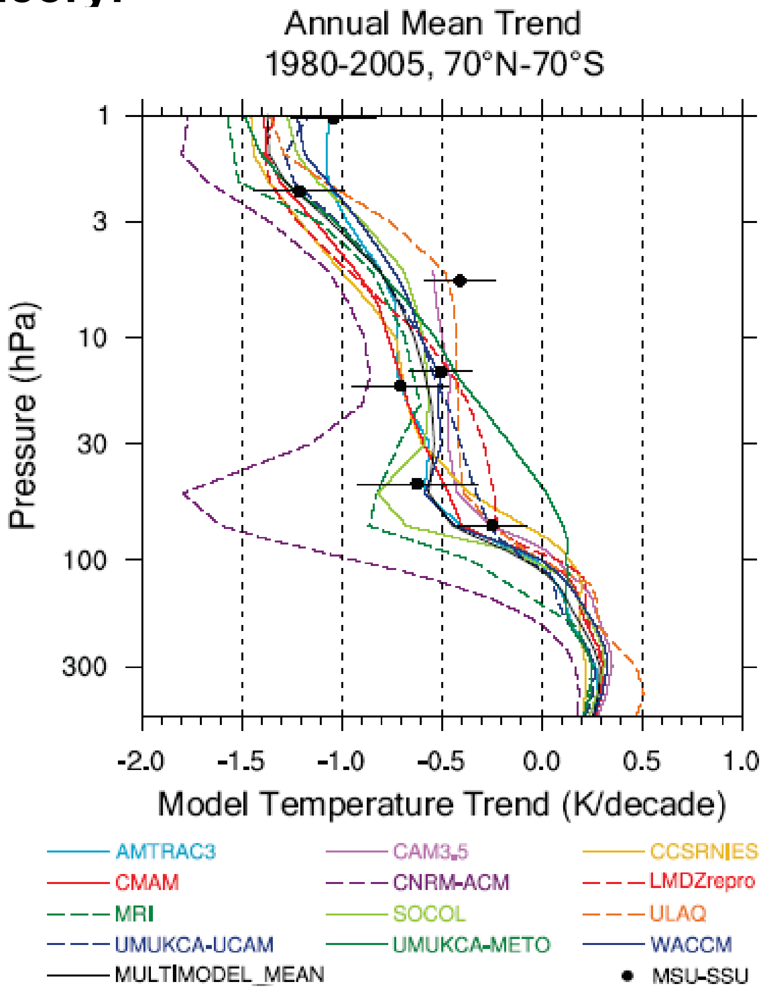
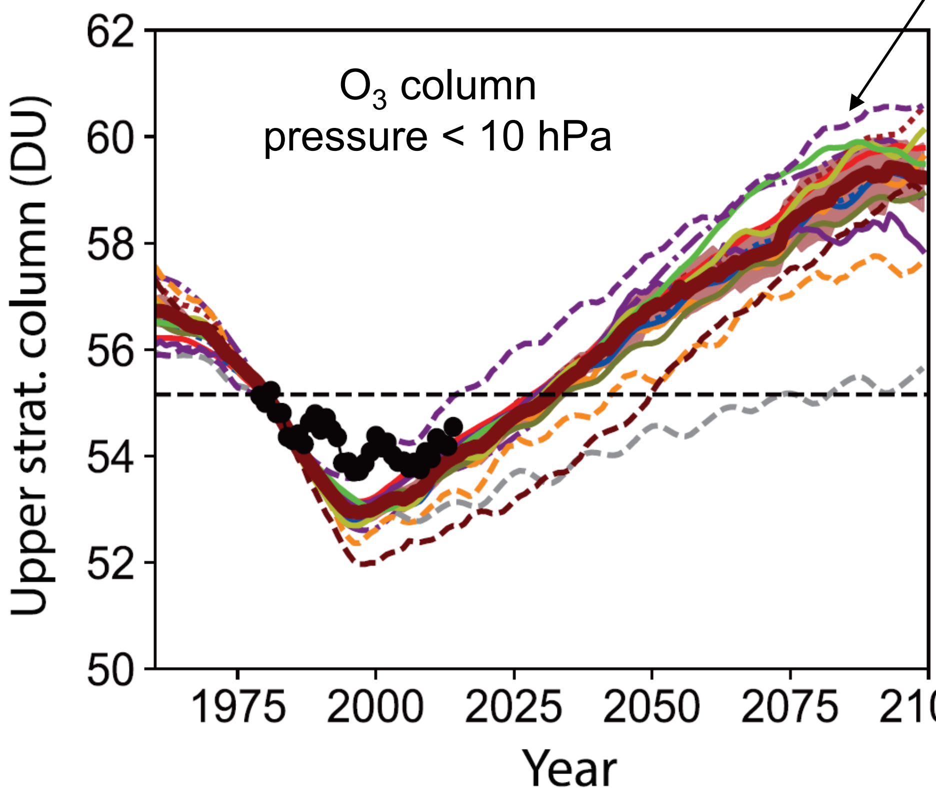


Figure 4−11
WMO/UNEP (2011)

Lecture 16, Slide 54

Future Trends, Upper Stratospheric Ozone



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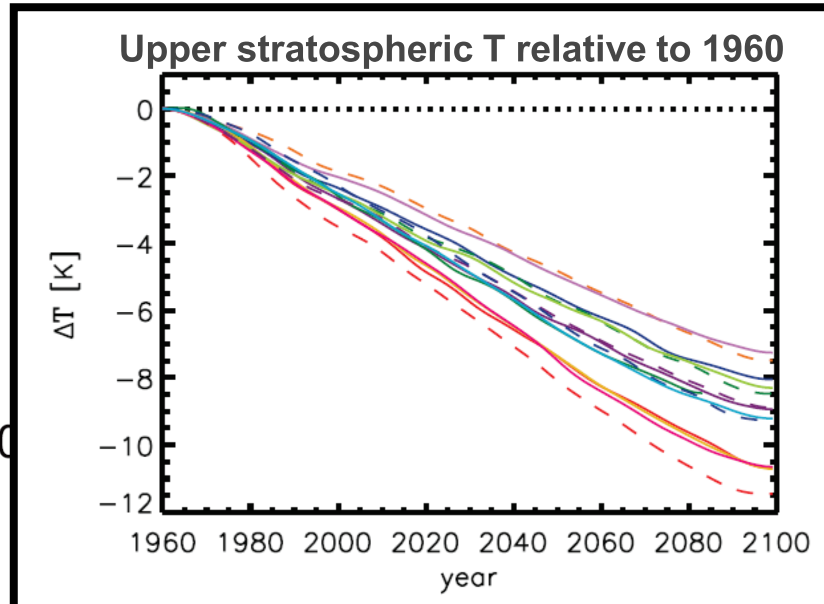
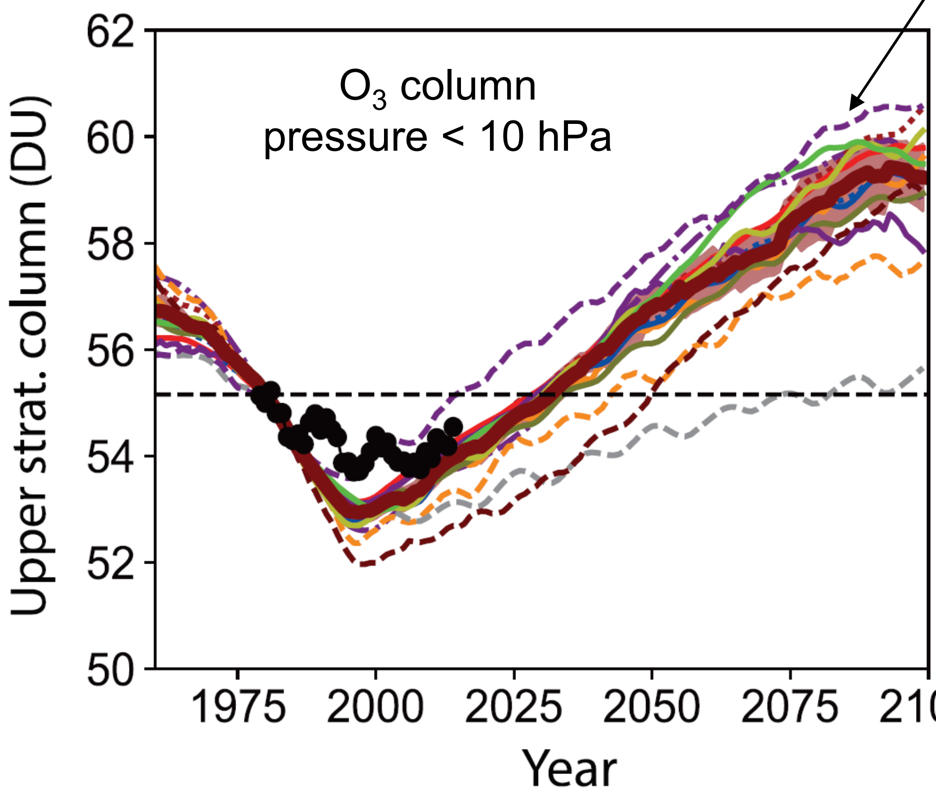
Dhomse *et al.*, *ACP*, 2018

Due to stratospheric cooling !



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

Future Trends, Upper Stratospheric Ozone



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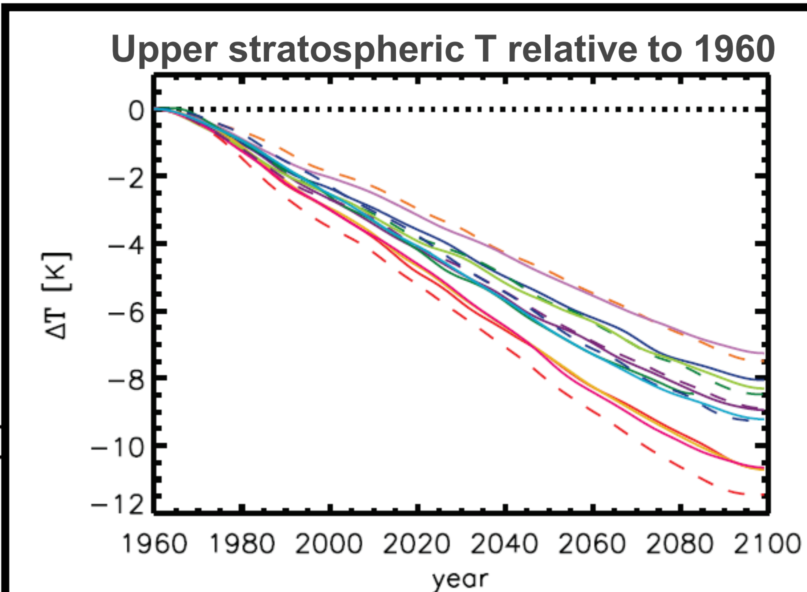
Why this response of ozone to lower T ?



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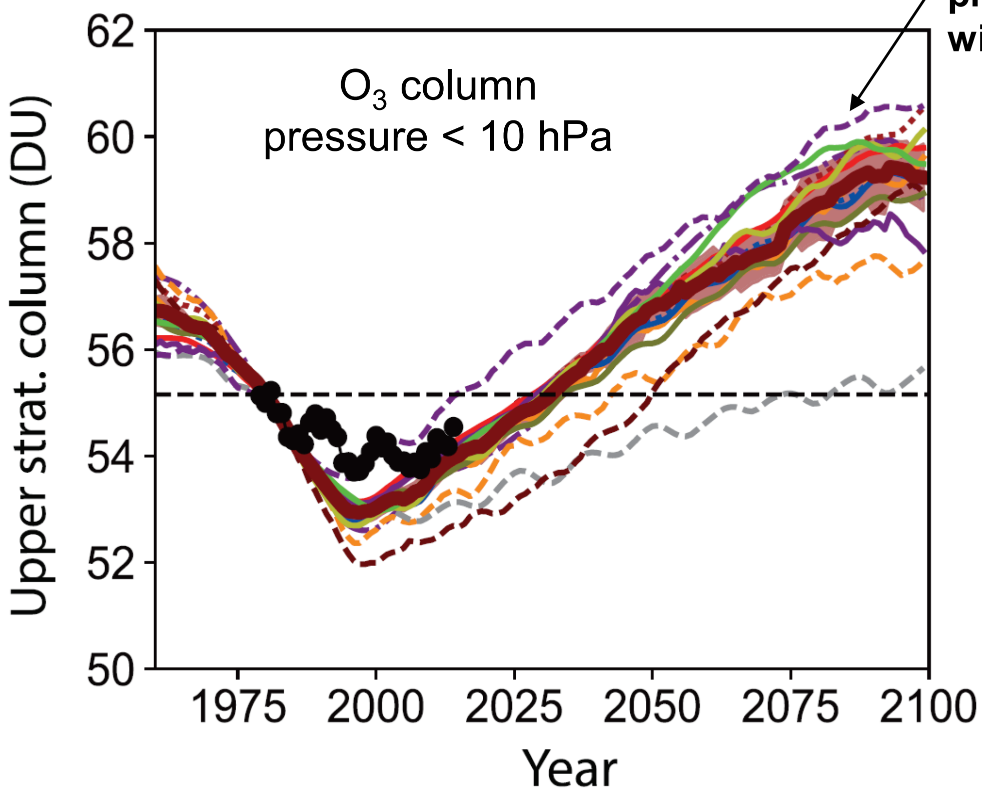

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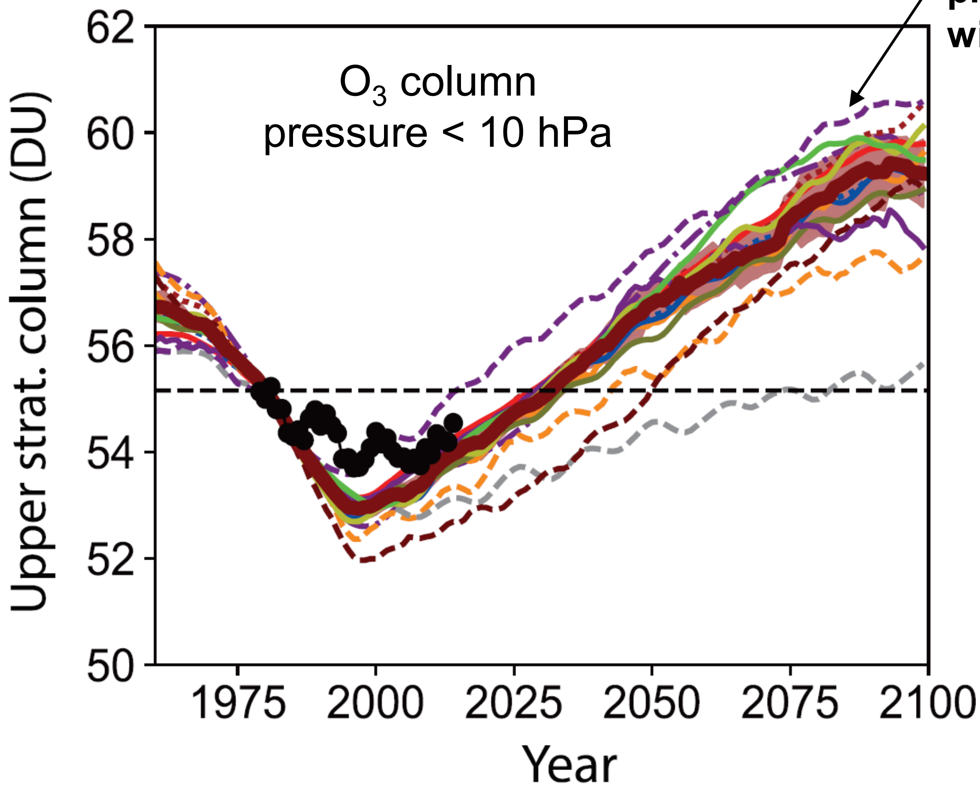
Future Trends, Upper Stratospheric Ozone



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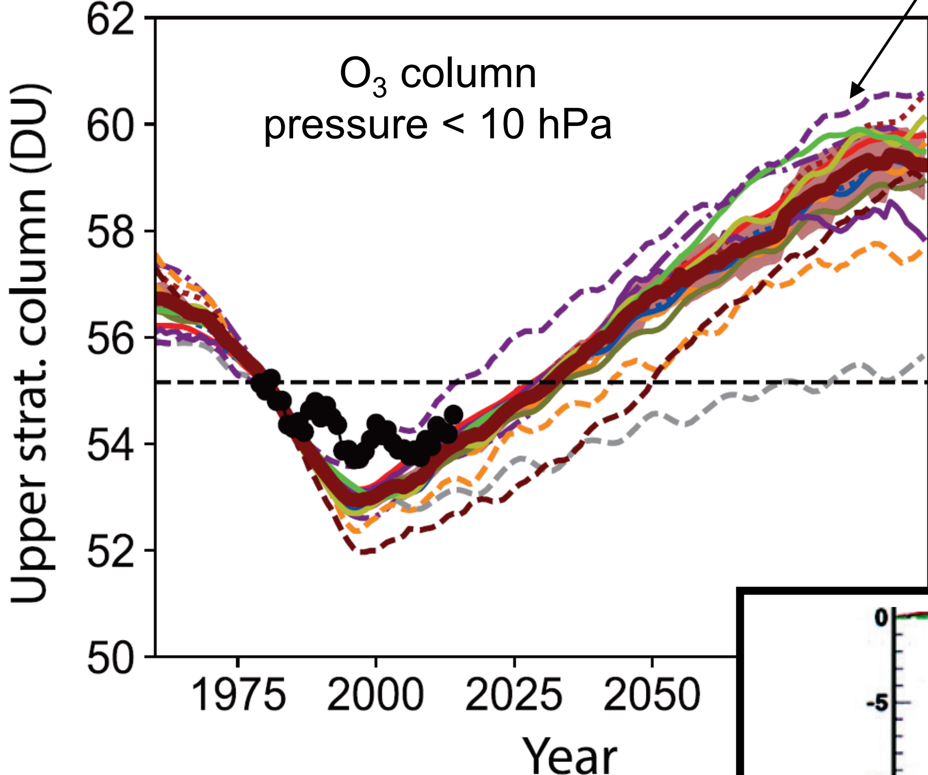
Future Trends, Upper Stratospheric Ozone



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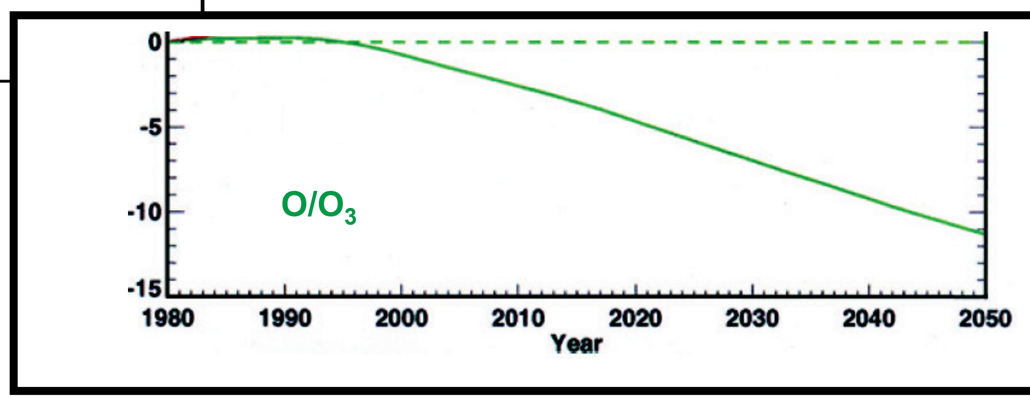
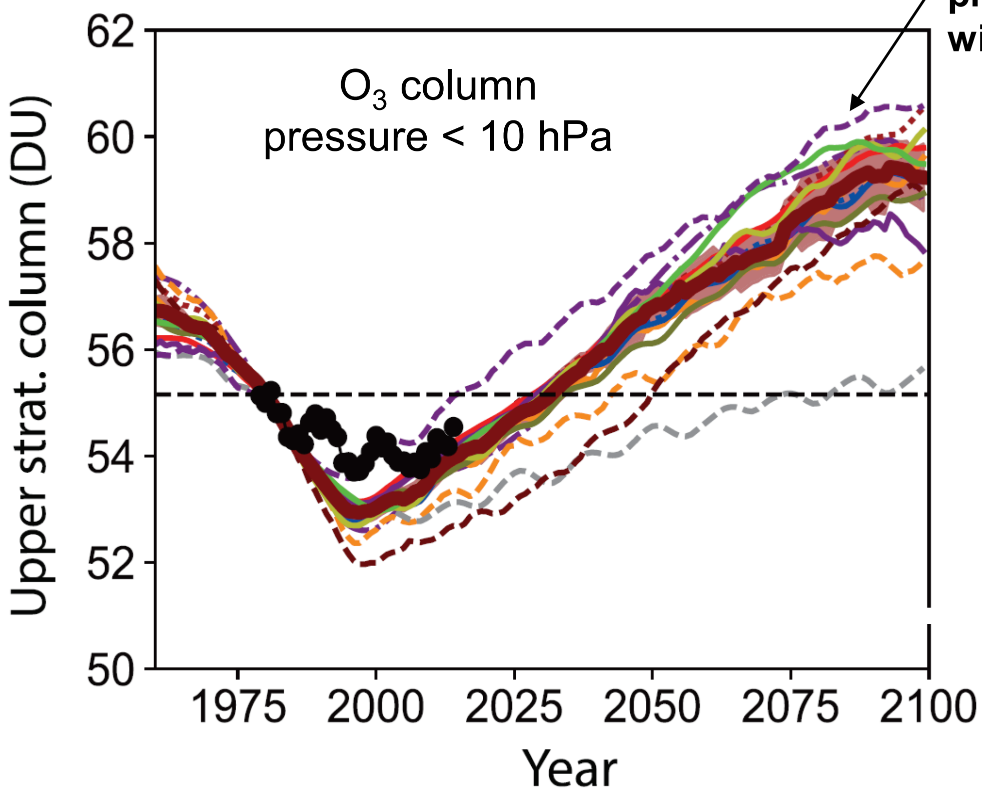
This cooling will alter the partitioning of O and O_3



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

Future Trends, Upper Stratospheric Ozone



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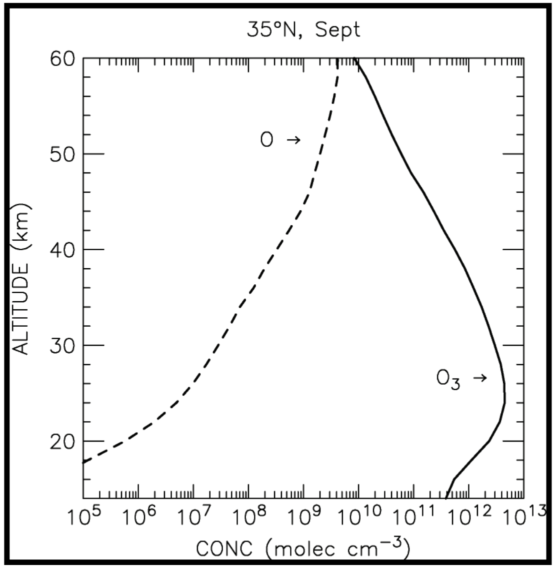
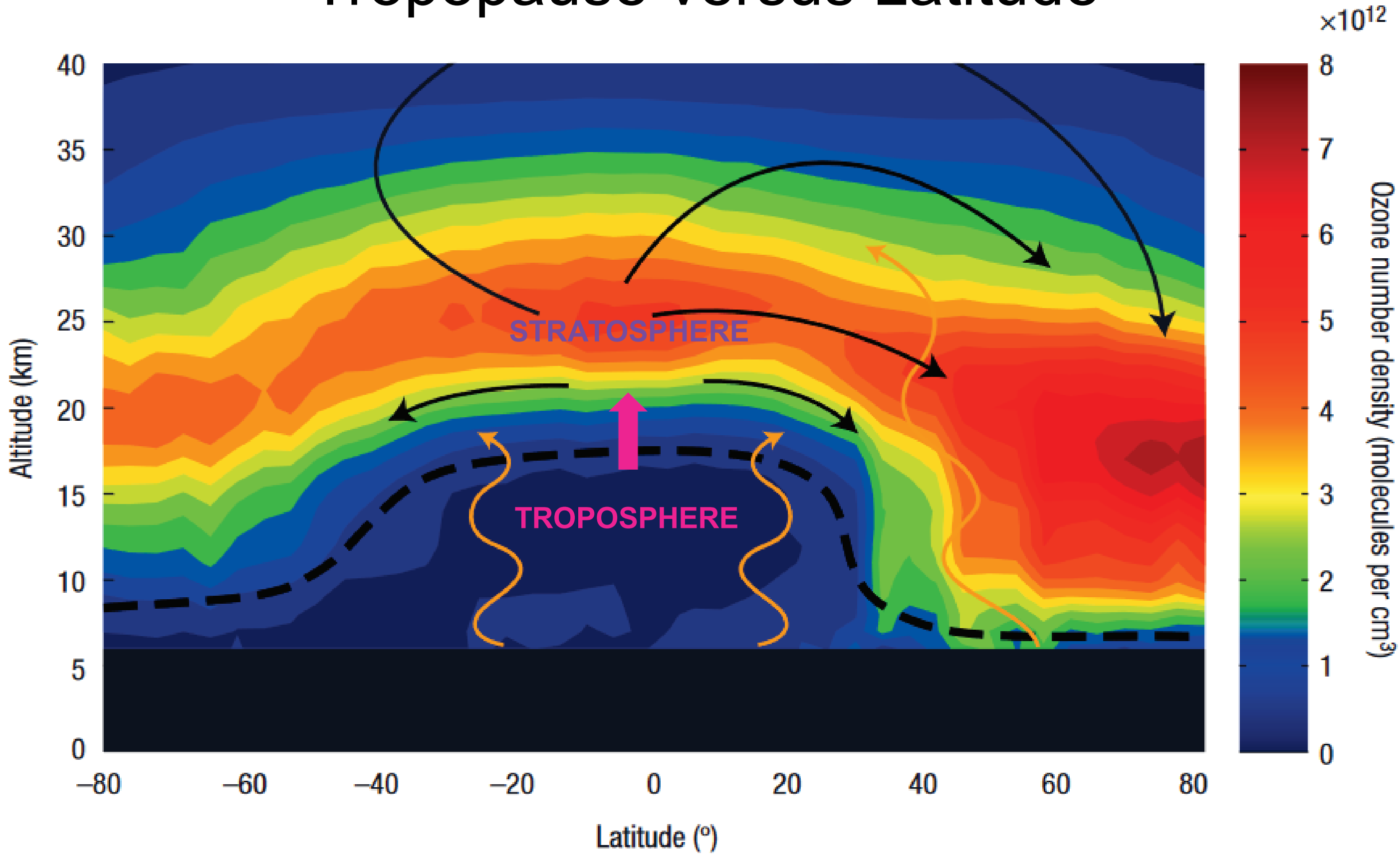


Tropopause versus Latitude



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

Shaw and Shepherd, Nature Geoscience, 2008.

<u>Brewer-Dobson Circulation</u> 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 43
&
Lecture 12, Slides 46-50

Global Satellite Maps of Total Ozone in 2009

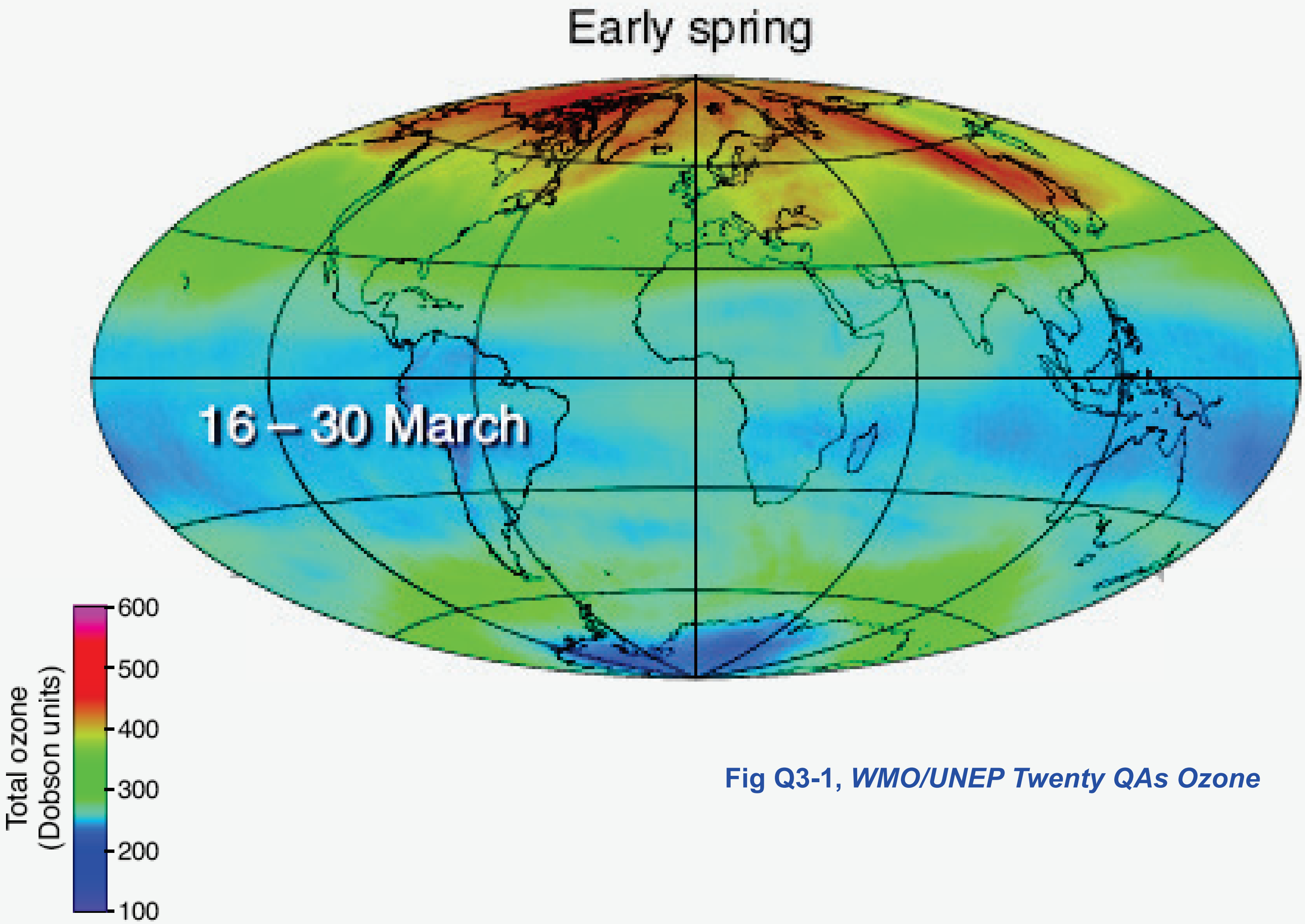
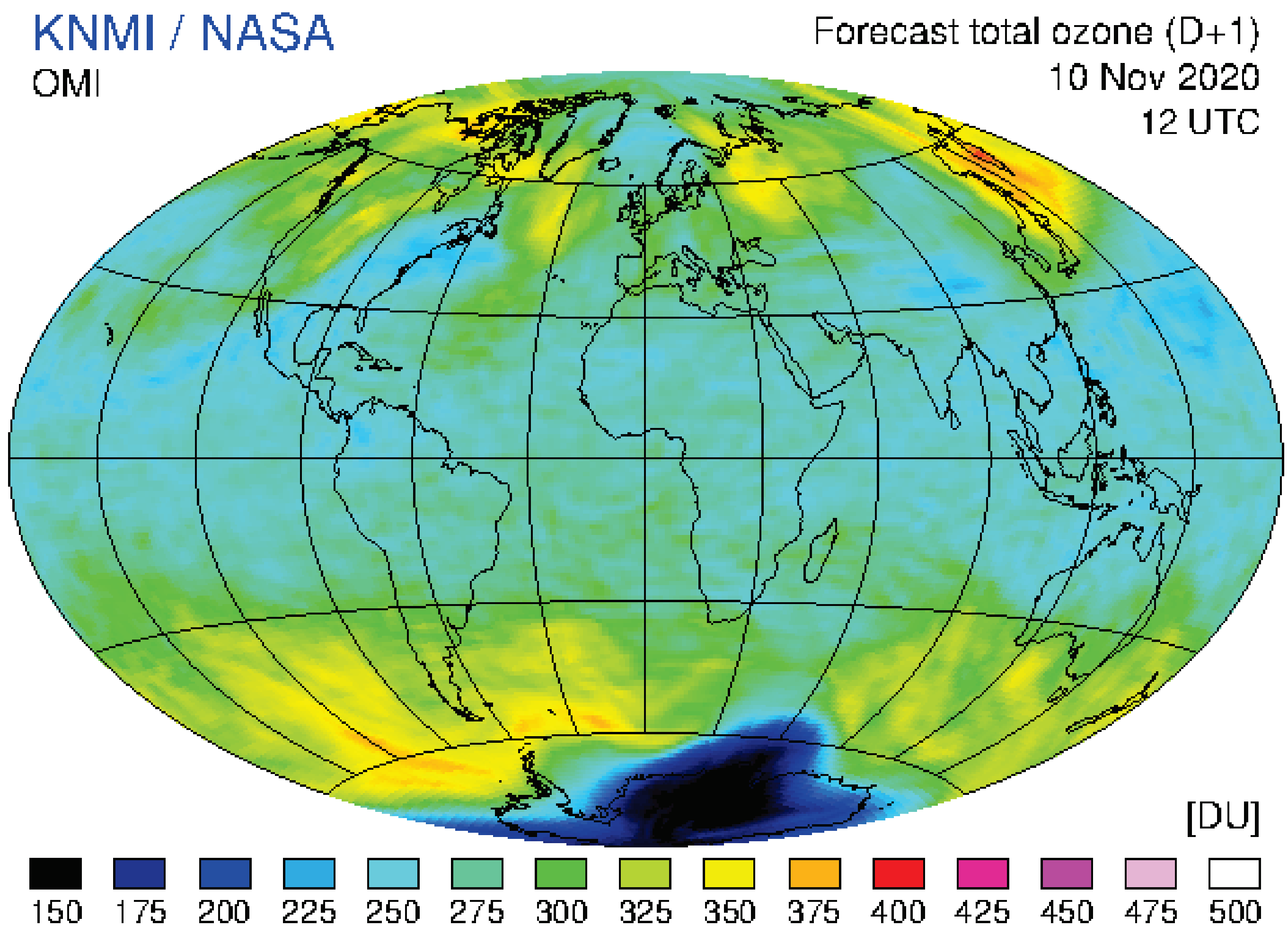


Fig Q3-1, *WMO/UNEP Twenty QAs Ozone*

Global Satellite Maps of Total Ozone in 2009



http://www.temis.nl/protocols/o3field/data/omi/forecast/today_wd.gif

More Chemistry and Climate Coupling

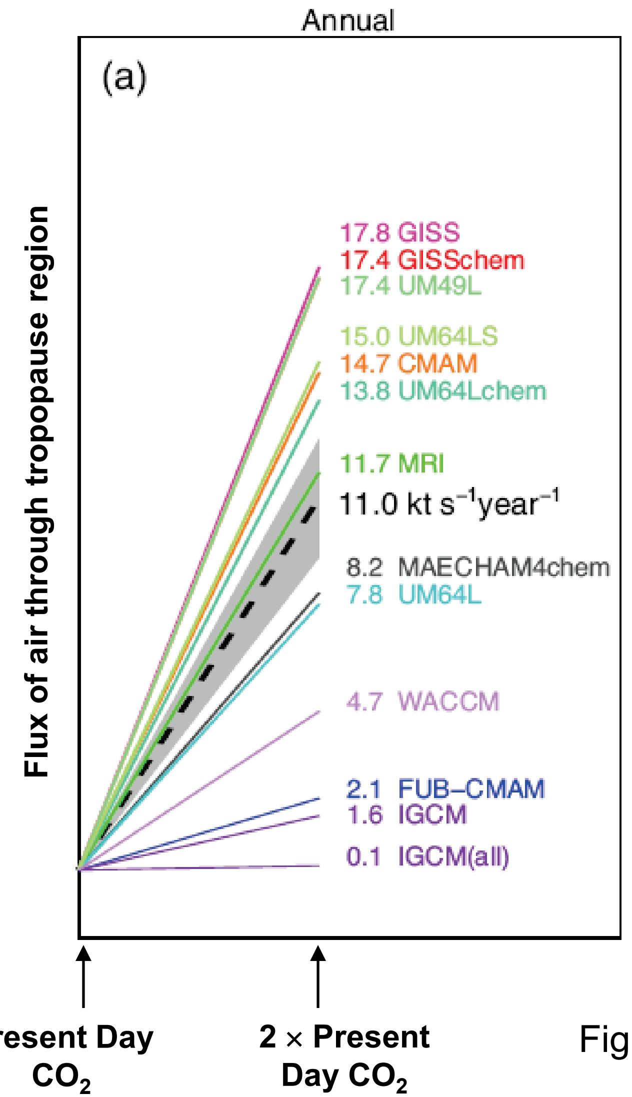


Figure 5-17. Trends in exchange of air from troposphere-to-stratosphere computed by 14 CCMs.

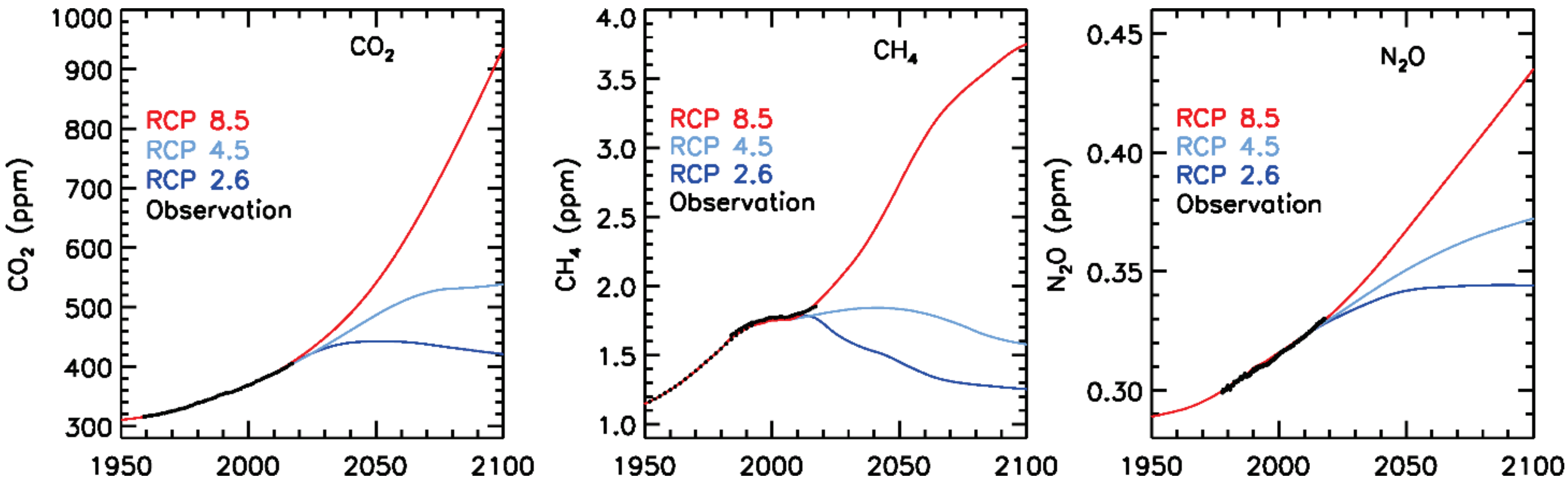
Trends (units of Gg s^{-1} year $^{-1}$) are represented by the slope of each line.

Dashed line is the multi-model mean.

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

Fig 5.17, WMO/UNEP (2006)

RCP Scenarios Forecast Wide Range of Possible Futures

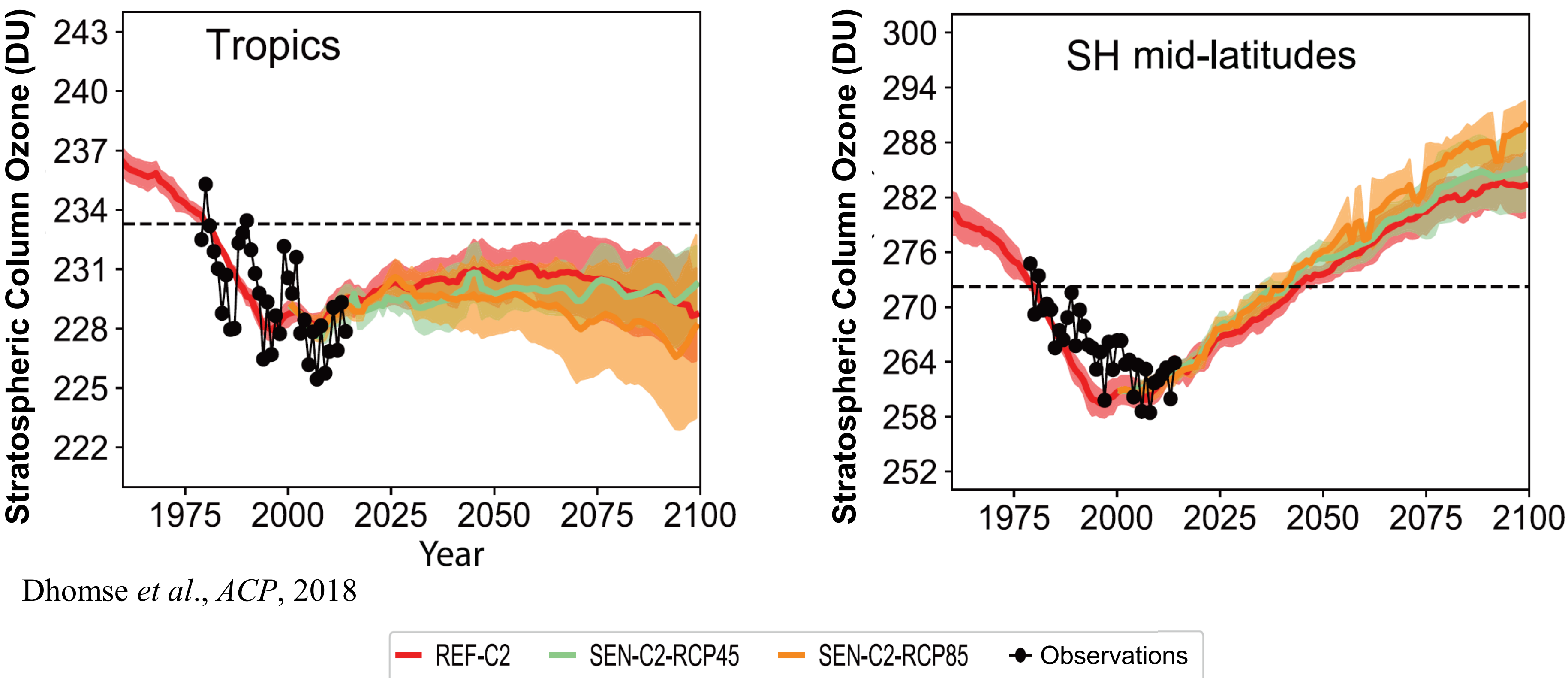


- RCP: Representative Concentration Pathway
  Number represents ΔRF of climate (W m^{-2}) at the end of this century
- GHG mixing ratio time series for CO_2, CH_4, N_2O, as well as CFCs, HCFCs, and HFCs that are provided to climate model groups

Figure from *Hope et al*., 2020: https://www.essoar.org/pdfjs/10.1002/essoar.10504179.1

Lecture 6, Slide 7

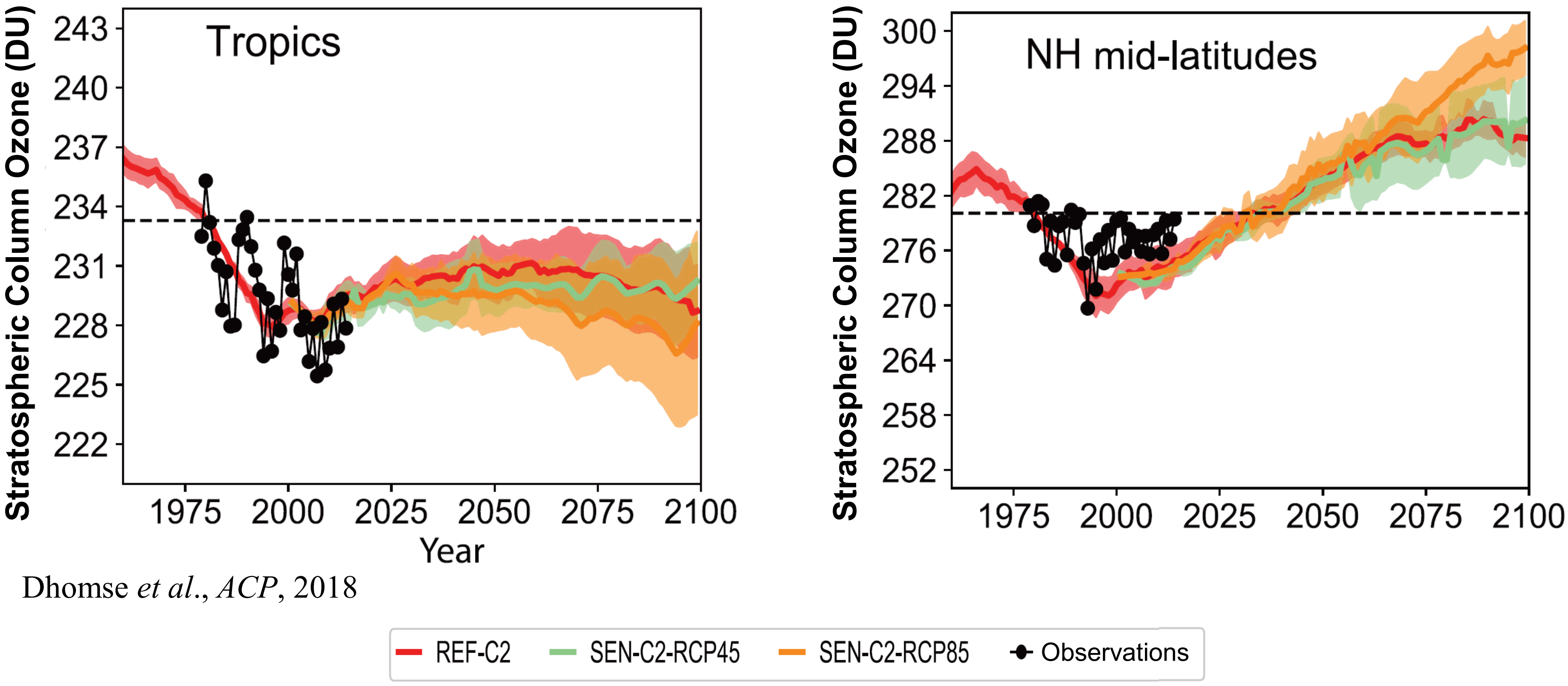
More Chemistry and Climate Coupling



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



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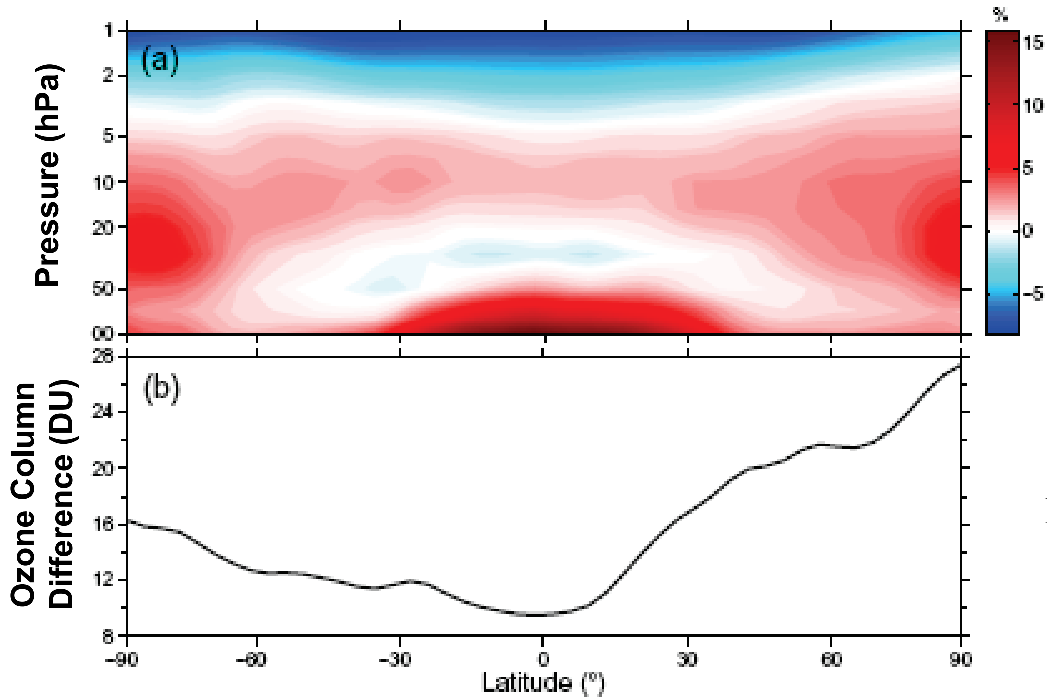
CH_4 and Stratospheric Ozone



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

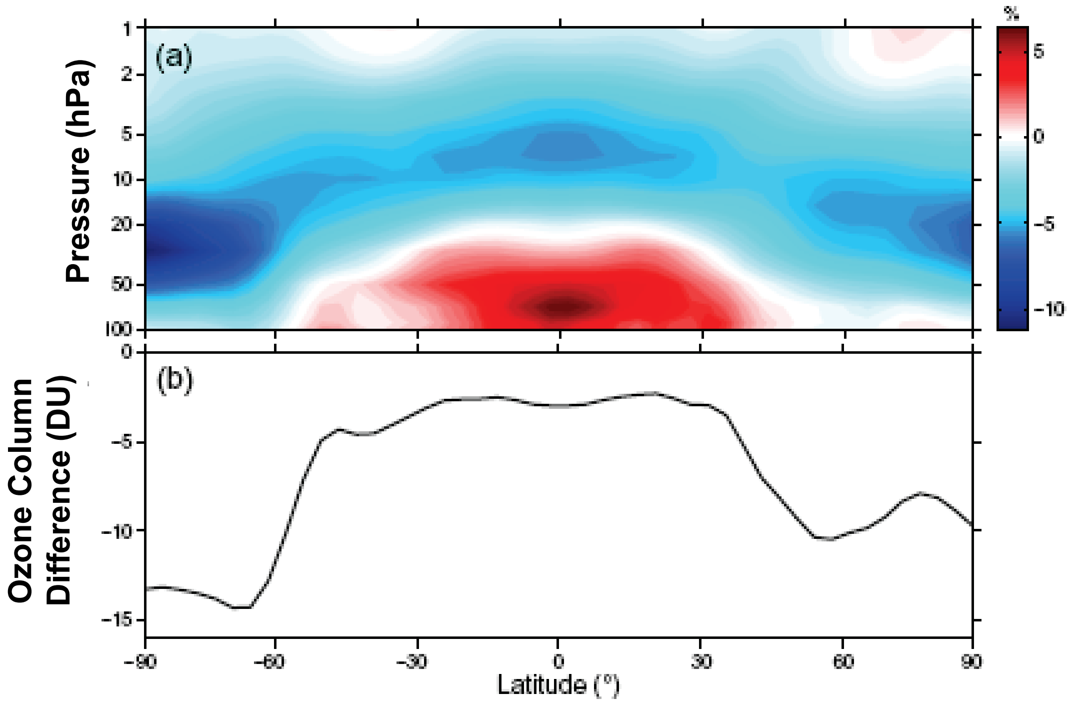
b) a cooler stratosphere, slowing the rate of all ozone loss cycles

c) speeding up of the the rate of $Cl+CH_4$, shifting chlorine from ClO into HCl

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

Computer models project stratospheric column O_3 will increase as CH_4 rises

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 69

Future Ozone: ODSs, CO_2, CH_4 and N_2O

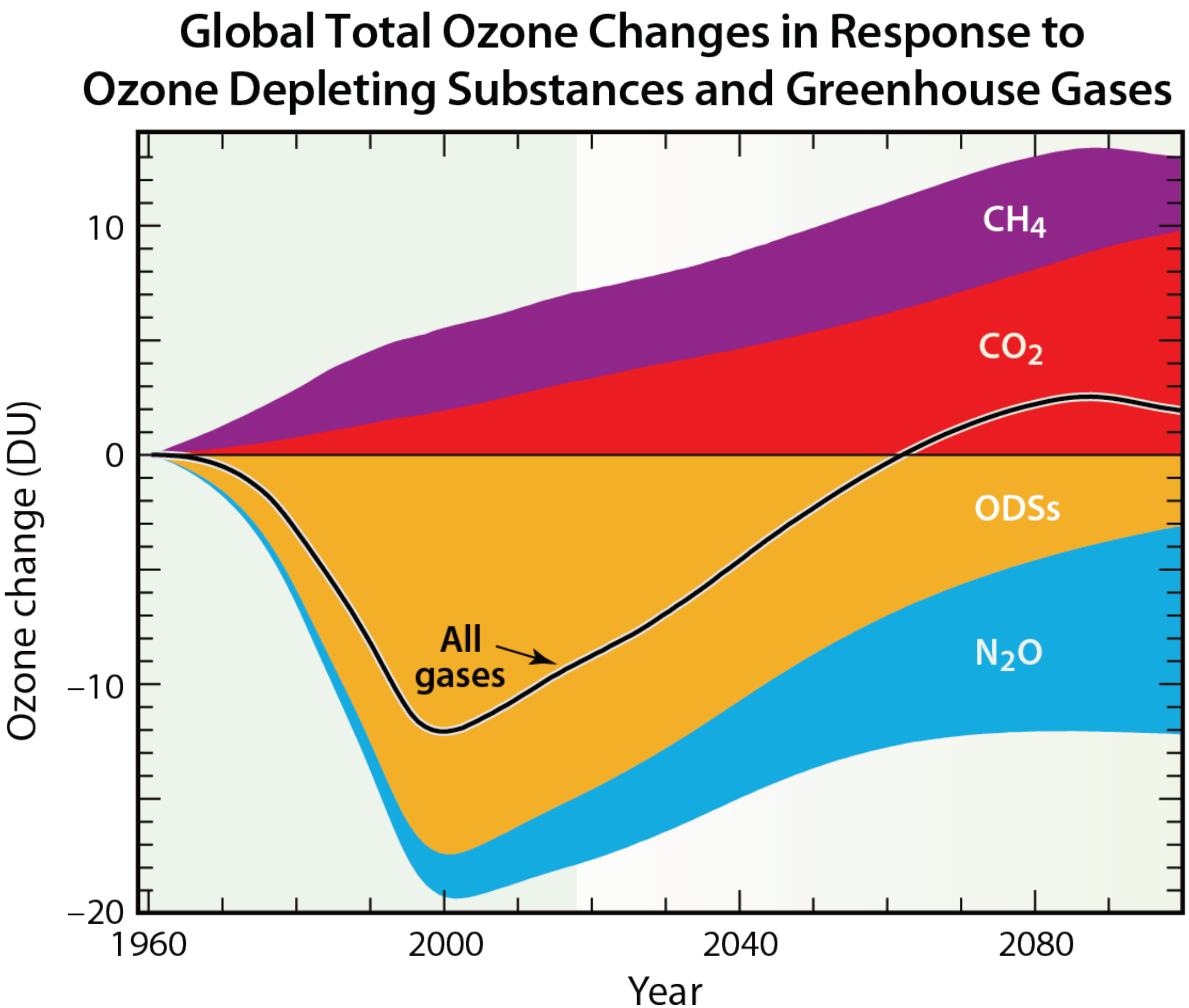
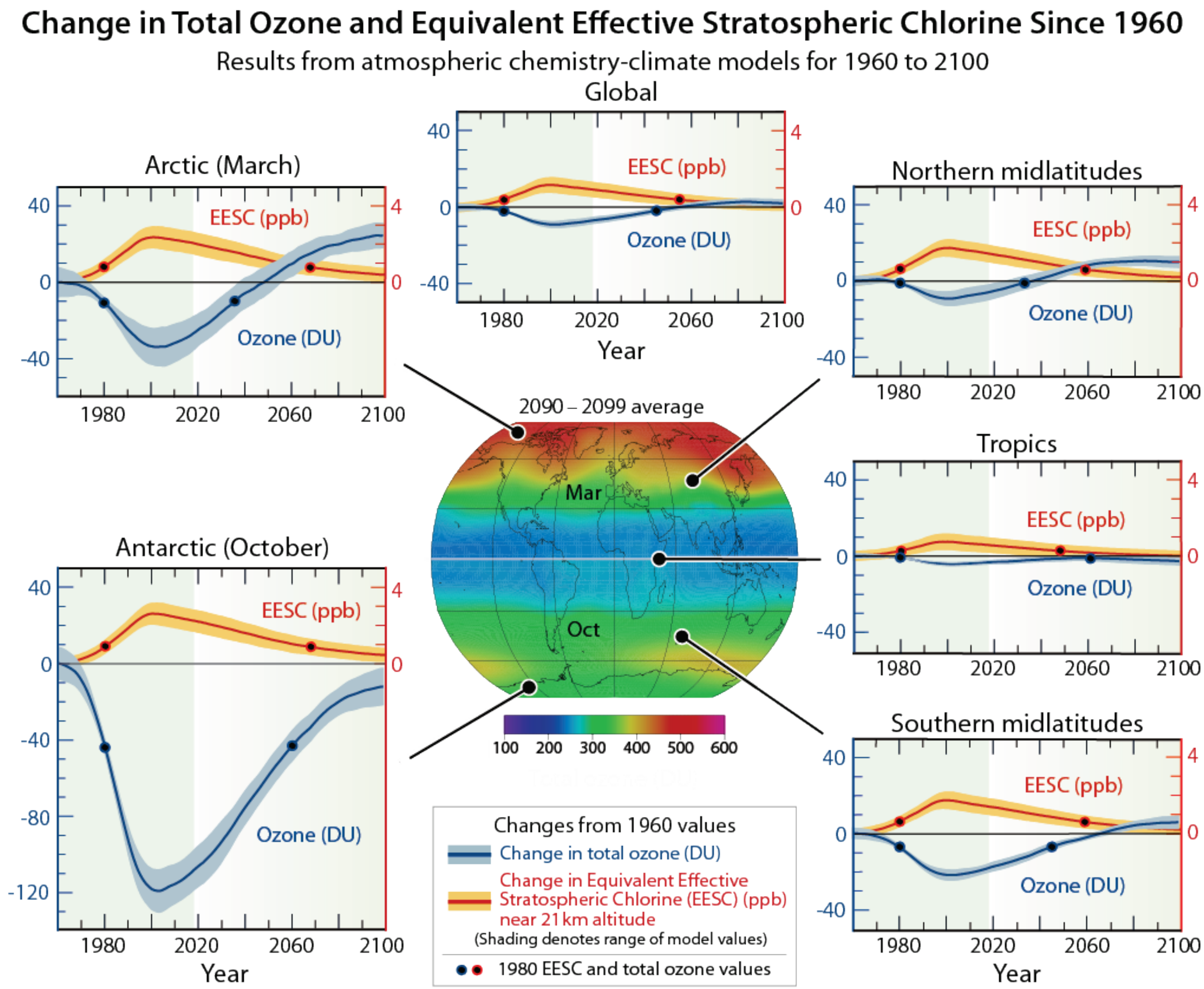


Fig Q20-3, *WMO/UNEP Twenty QAs Ozone*

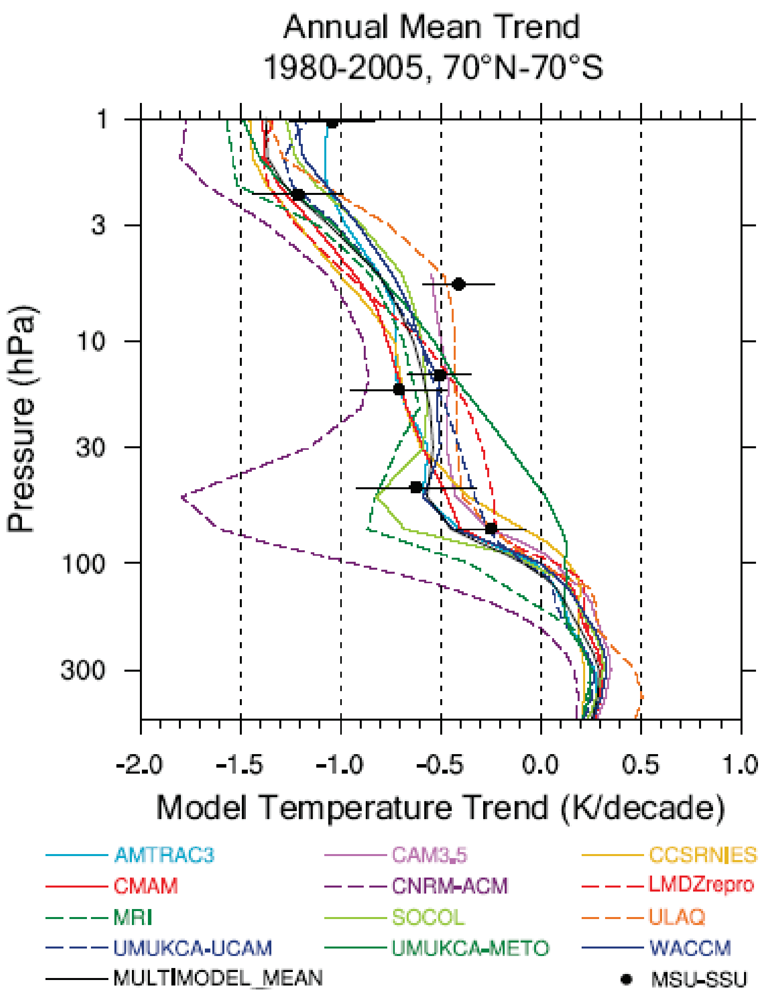
Future Ozone: Regional Variations



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



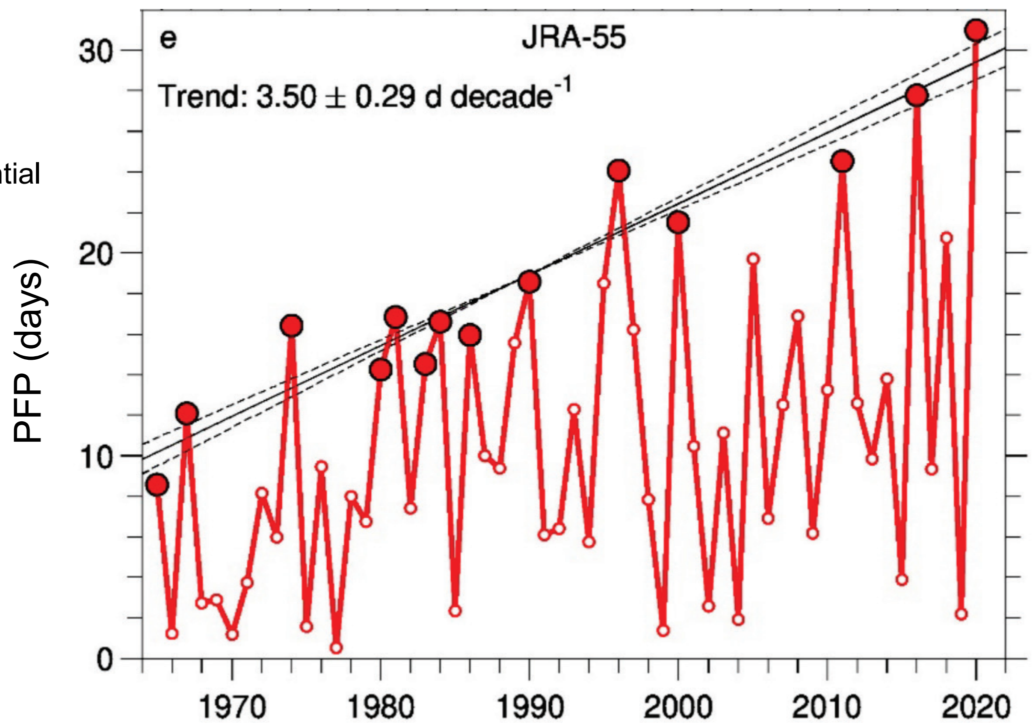
If the stratosphere *continues to cool*, for which region of the stratosphere is ozone "most vulnerable"?

Figure 4−11, WMO/UNEP (2011)

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

Data:

PFP is PSC Formation Potential



von der Gathen, *Nature Communications*, submitted, 2020

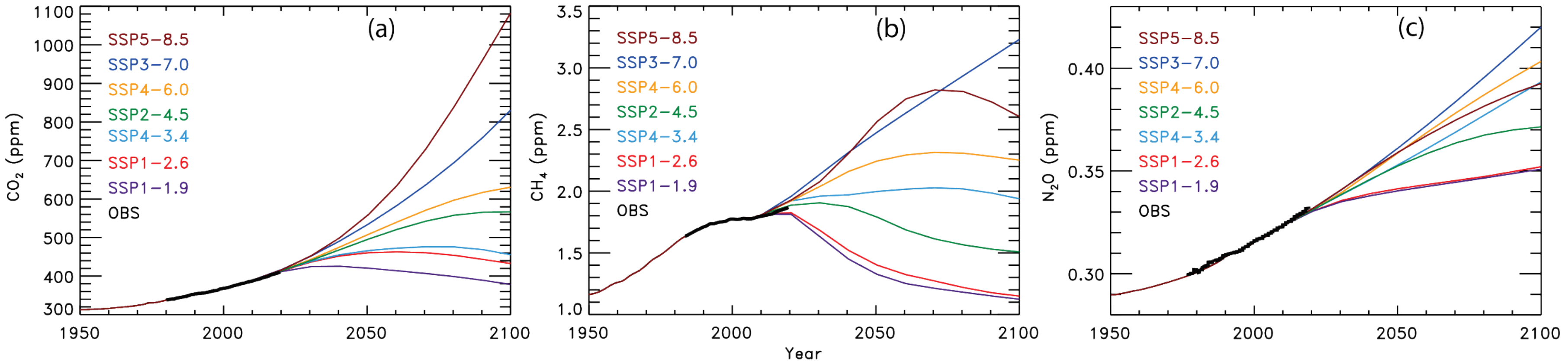
PSC Formation Potential in Arctic Vortex
based on data from the Japanese 55 year re-analysis project
https://jra.kishou.go.jp/JRA-55/index_en.html

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

Lecture 16, Slide 76

SSP: Shared Socioeconomic Pathway Scenarios Will Drive Upcoming IPCC Report

Climate Model Input



McBride et al., *Earth System Dynamics*, submitted, 2020

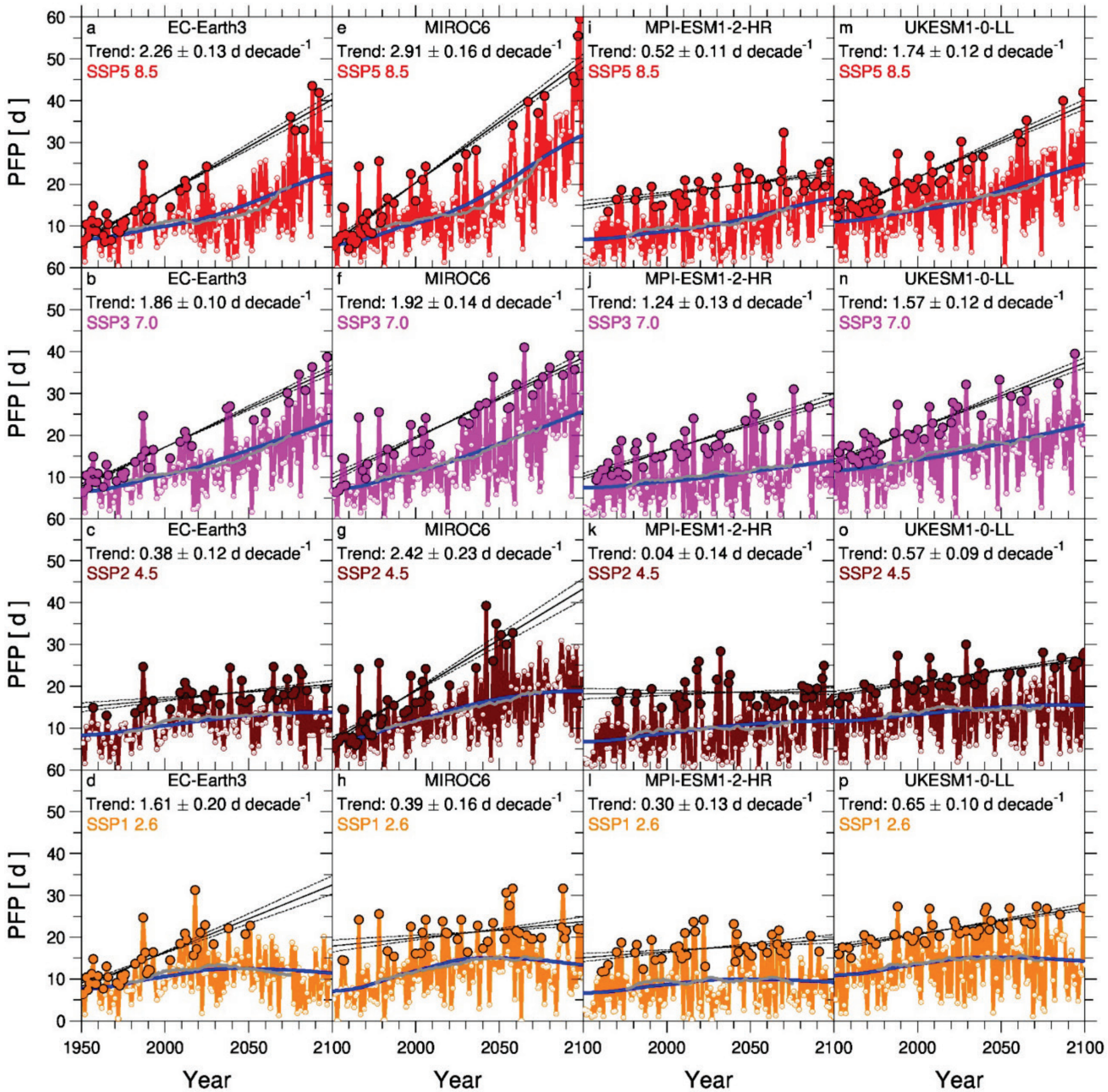
Number before dash represents base narrative and number after dash represents W m^{-2} RF of climate at end of century

Lecture 16, Slide 77

Tendency for Colder Arctic Winters Getting Colder Drive by Rising GHGs

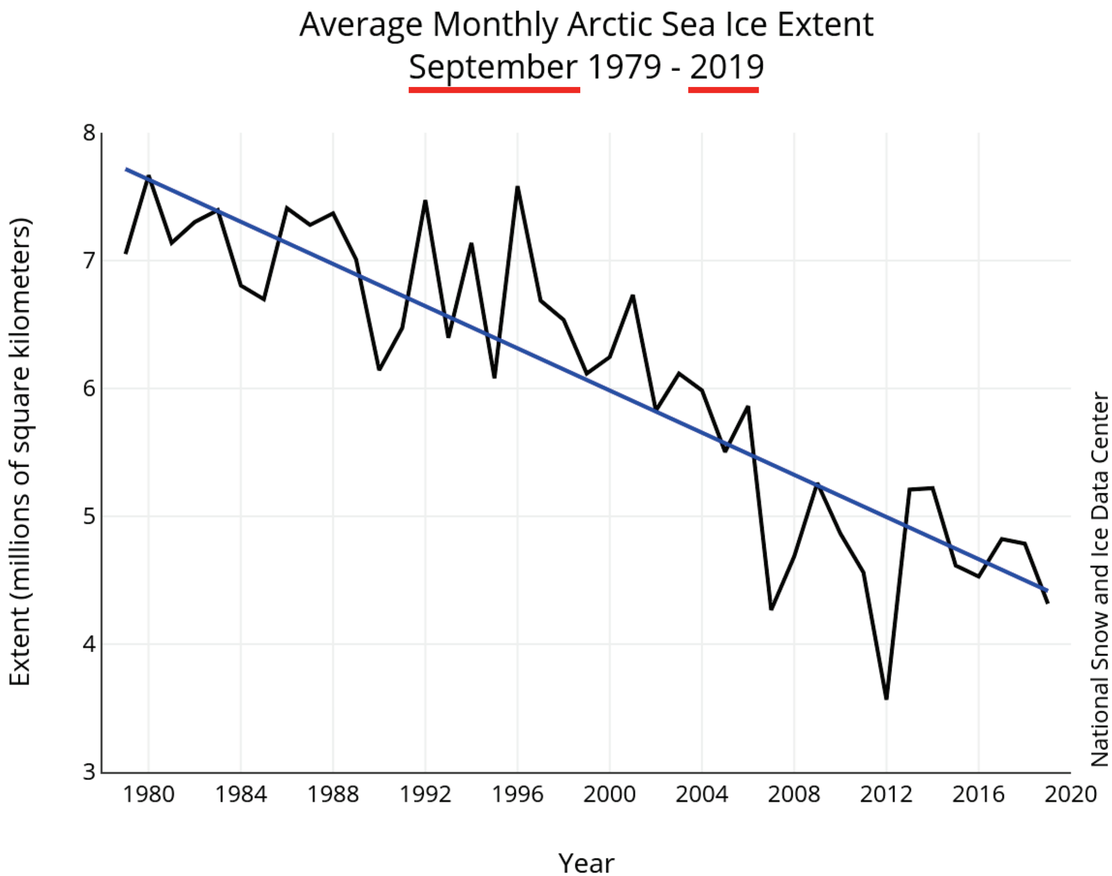
Climate Model Output

PFP is PSC Formation Potential



von der Gathen, *Nature Communications*, submitted, 2020

Arctic Sea-Ice: Canary of Climate Change



- Sea ice: ice overlying ocean
- Annual minimum occurs each September
- Decline of ~13% / decade over satellite era

http://nsidc.org/arcticseaicenews/2019/10/

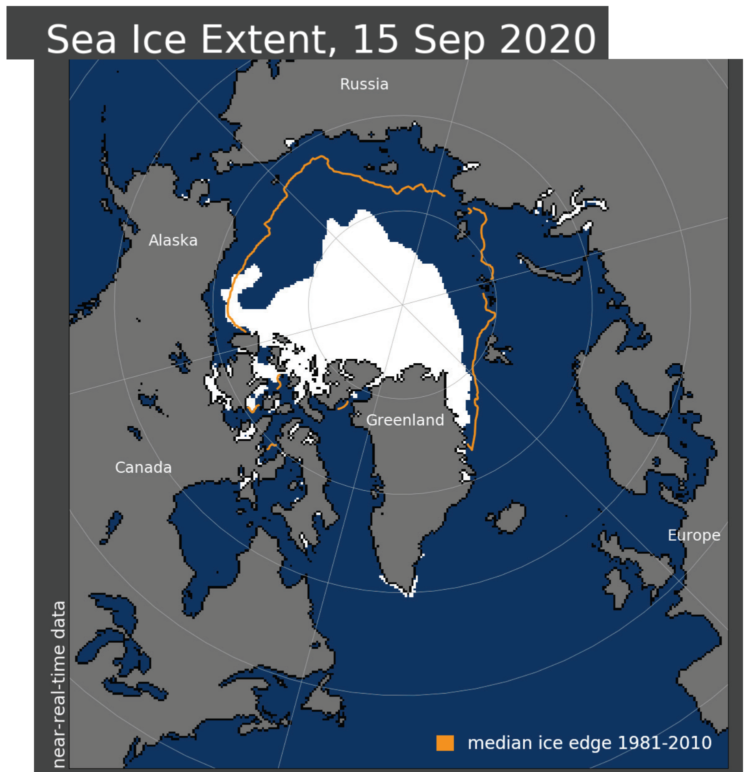
Lecture 8, Slide 28

Arctic Sea Ice News & Analysis

September 21, 2020

Arctic sea ice decline stalls out at second lowest minimum

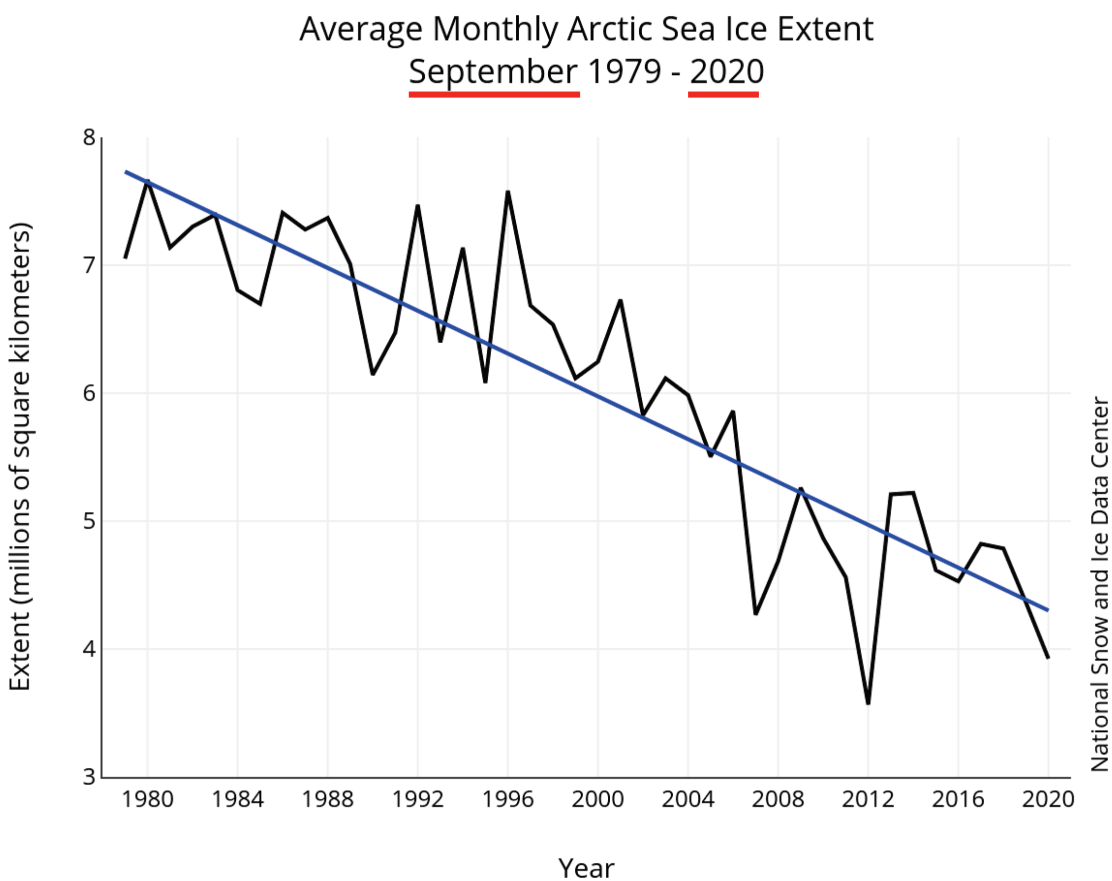
On September 15, Arctic sea ice likely reached its annual minimum extent of 3.74 million square kilometers (1.44 million square miles). The minimum ice extent is the second lowest in the 42-year-old satellite record, reinforcing the long-term downward trend in Arctic ice extent. Sea ice extent will now begin its seasonal increase through autumn and winter. In the Antarctic, sea ice extent is now well above average and within the range of the ten largest ice extents on record, underscoring its high year-to-year variability. The annual maximum for Antarctic sea ice typically occurs in late September or early October.



Lecture 8, Slide 29

https://nsidc.org/arcticseaicenews/2020/09/arctic-sea-ice-decline-stalls-out-at-second-lowest-minimum/

Arctic Sea-Ice: Canary of Climate Change

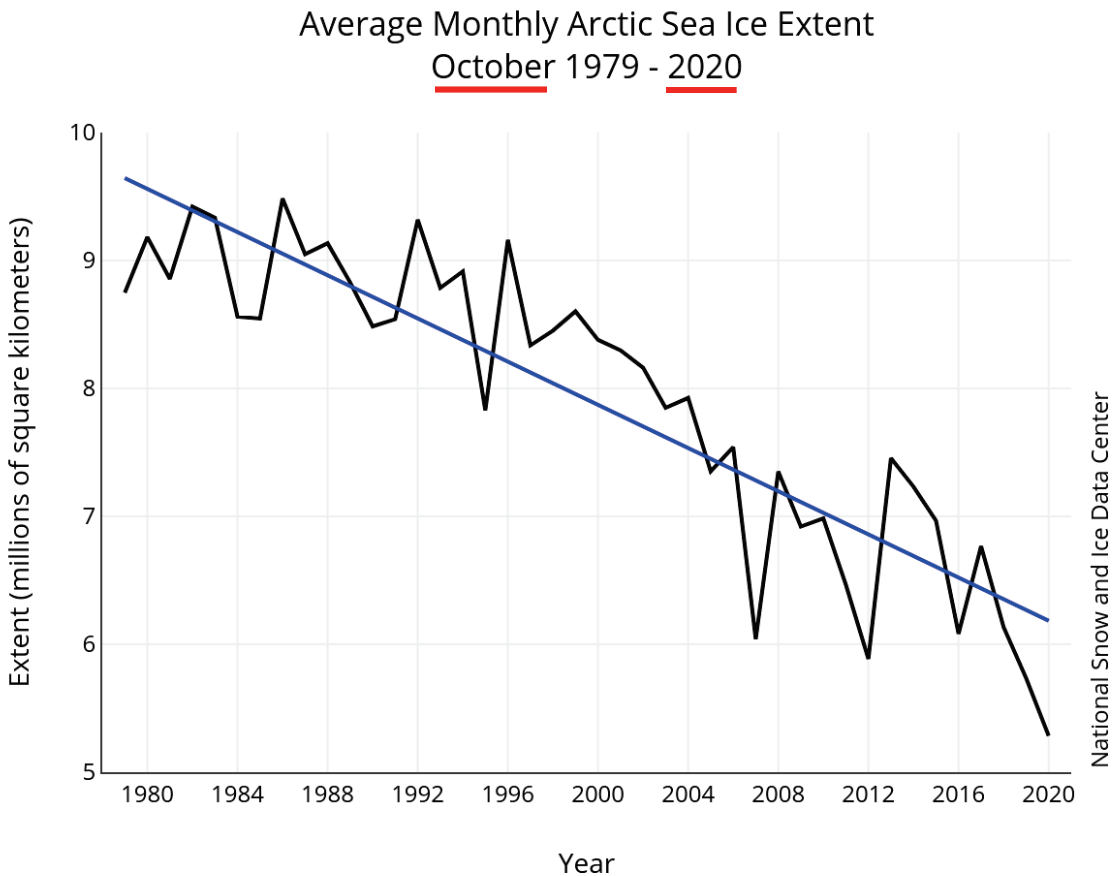


- Sea ice: ice overlying ocean
- Annual minimum occurs each September
- Decline of ~13% / decade over satellite era

http://nsidc.org/arcticseaicenews/2020/10/

Update to Lecture 8, Slide 28

Arctic Sea-Ice: Canary of Climate Change



- Sea ice: ice overlying ocean
- Annual minimum occurs each September
- Decline of ~13% / decade over satellite era

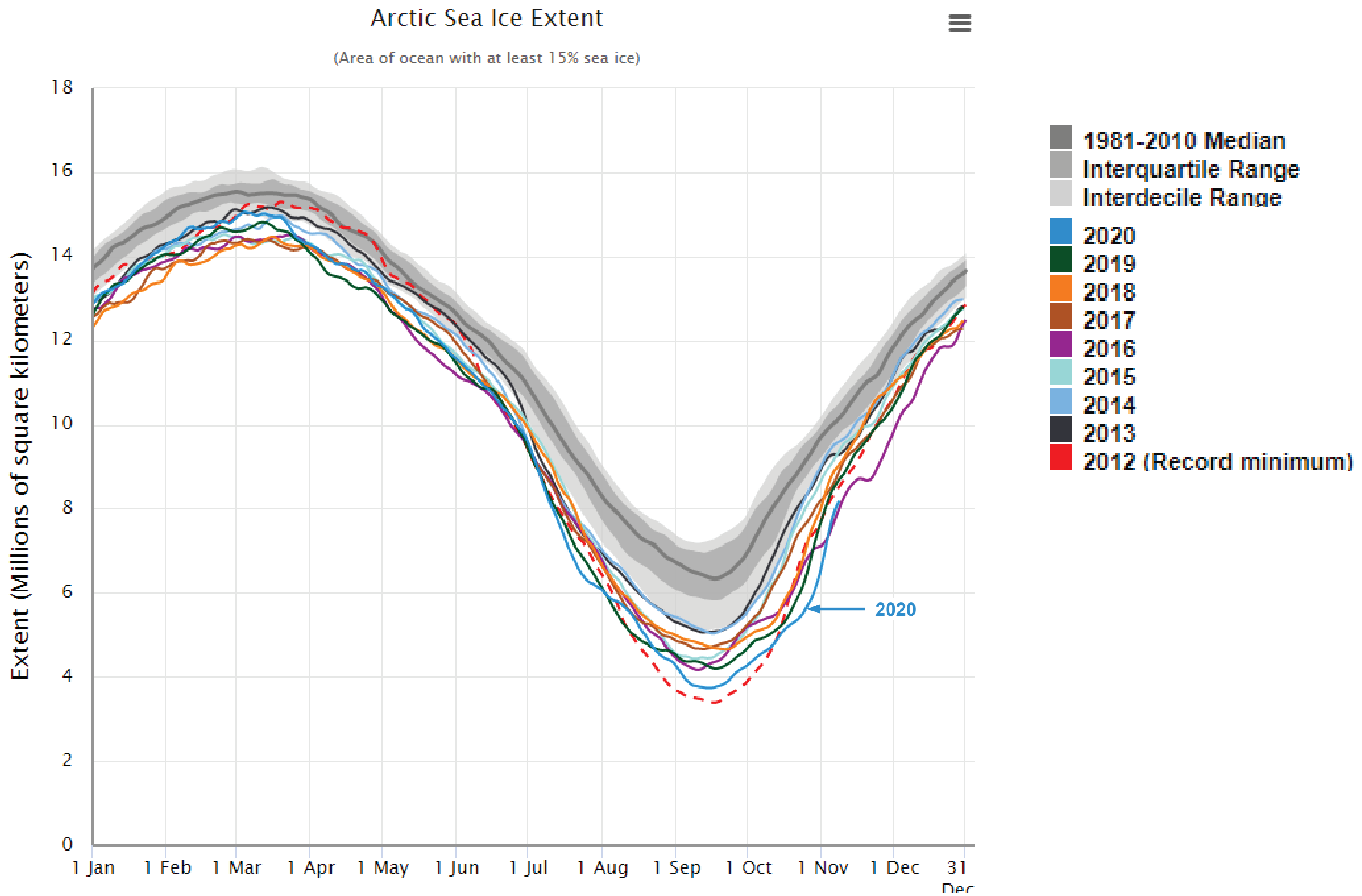
http://nsidc.org/arcticseaicenews/files/2020/11/Figure3.png

Declining Arctic Sea Ice: Canary of Climate Change?

Arctic sea ice extent for October 2020 was 5.3 million square kilometers, <u>the largest departure from average conditions seen in any month thus far in the satellite record.</u>

http://nsidc.org/arcticseaicenews

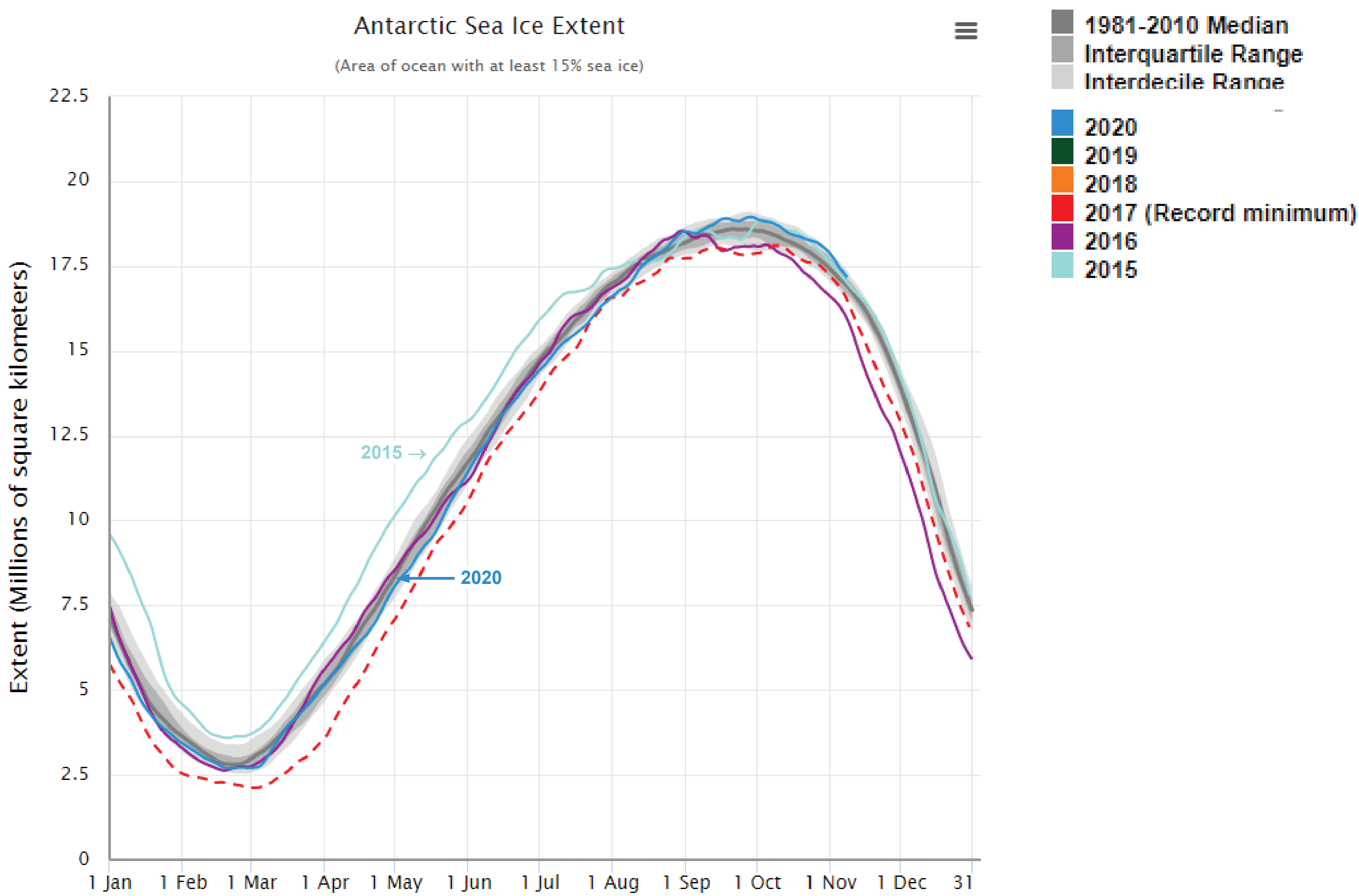
Declining Arctic Sea Ice: Canary of Climate Change?



Don't need to use any heavy duty statistics to see the trend!

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

The Antarctic

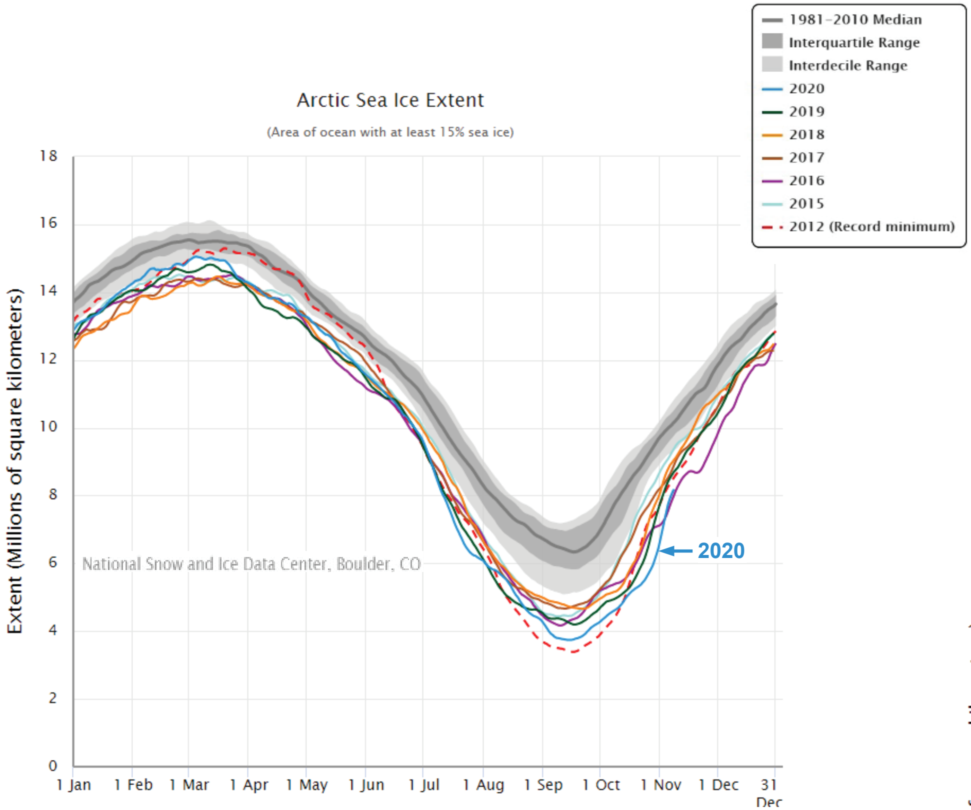


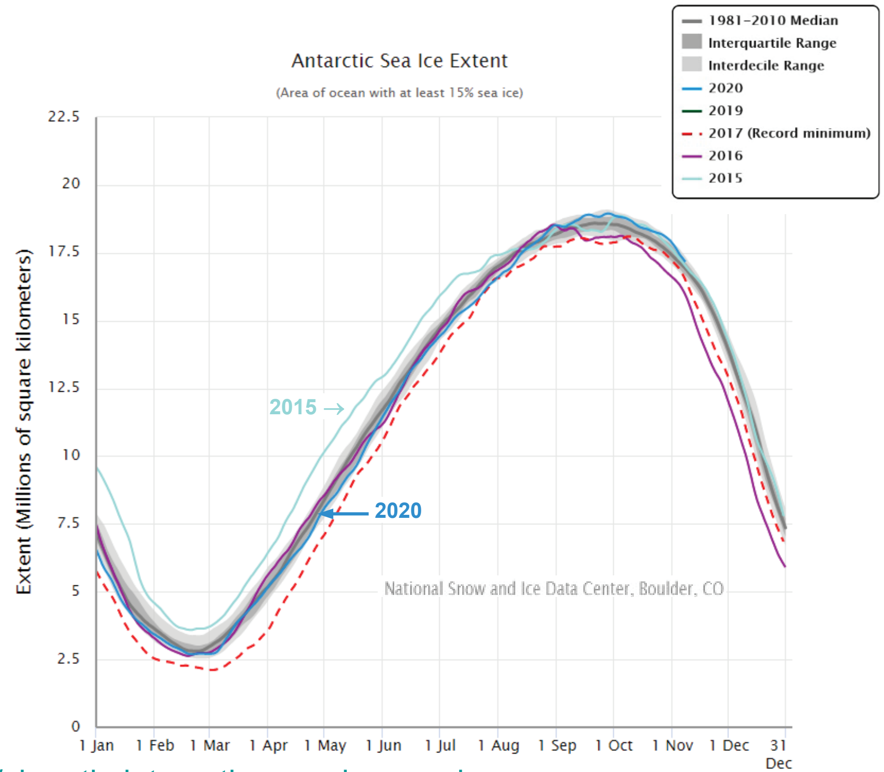
https://nsidc.org/arcticseaicenews/charctic-interactive-sea-ice-graph

The Arctic and the Antarctic

Shaded region: 1981 to 2010 mean ± 2σ

Colors: Individual years since 2017 (plus 2012 for Arctic, since this was year of record minimum in NH)





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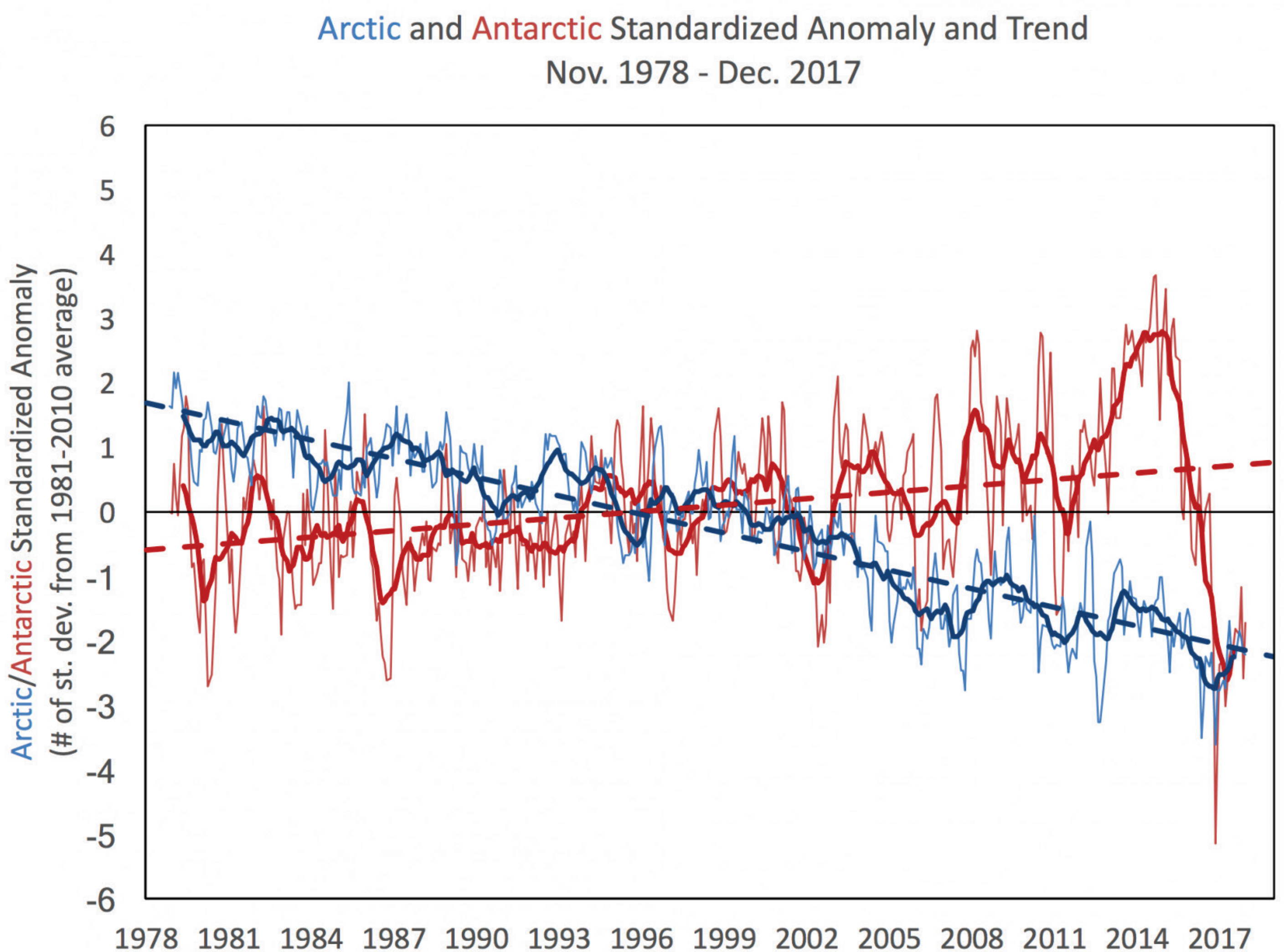
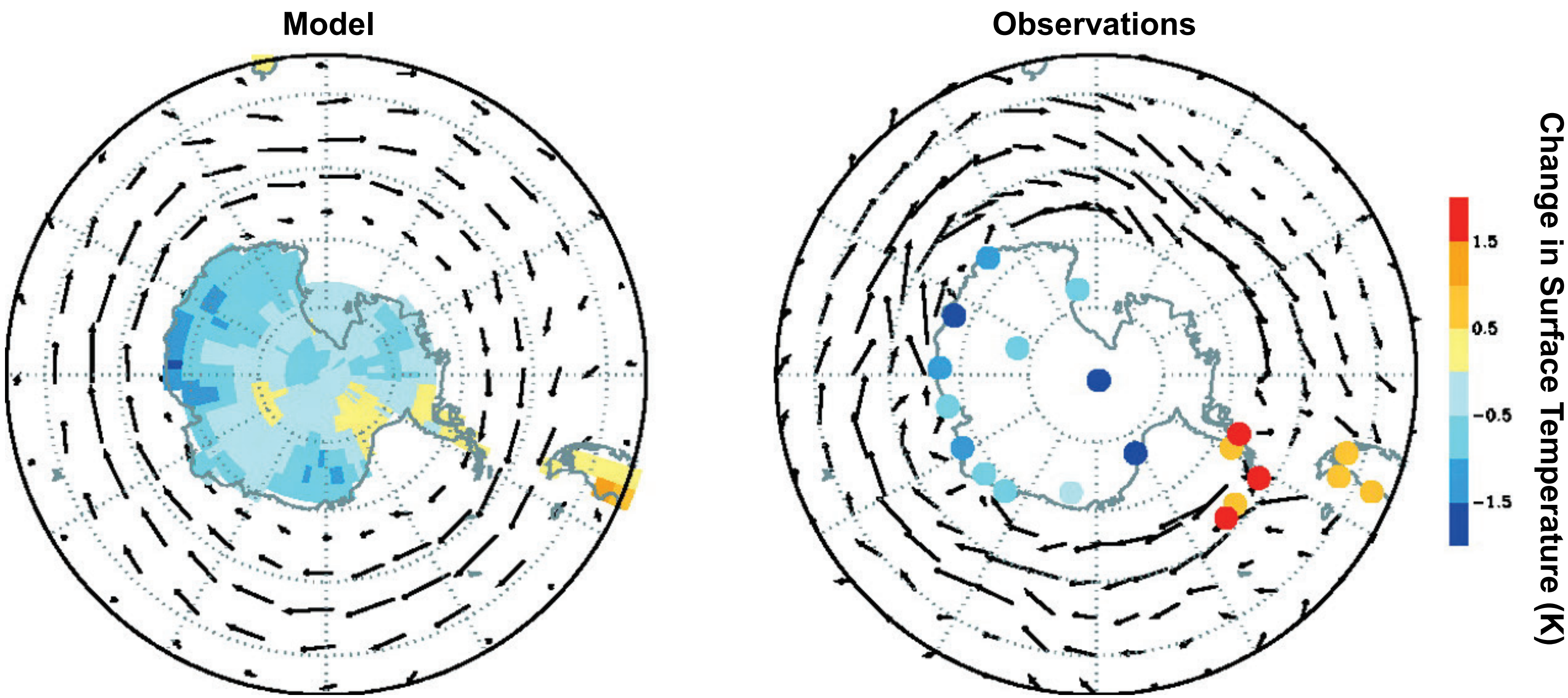


Changes in the extent of Arctic (blue) and Antarctic sea ice (red) from November 1978 to December 2017, relative to a 1981-2010 baseline. Thick lines show changes to the yearly average and thin lines show changes to the monthly anomalies. Source: [National Snow and Ice Data Center, University of Colorado, Boulder]

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

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



Simulated and observed changes in surface temperature (K) and wind speed,1969 to 2000, averaged over December to May. The longest wind vector corresponds to 4 m/s.

Gillett and Thompson, *Science*, 2003

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

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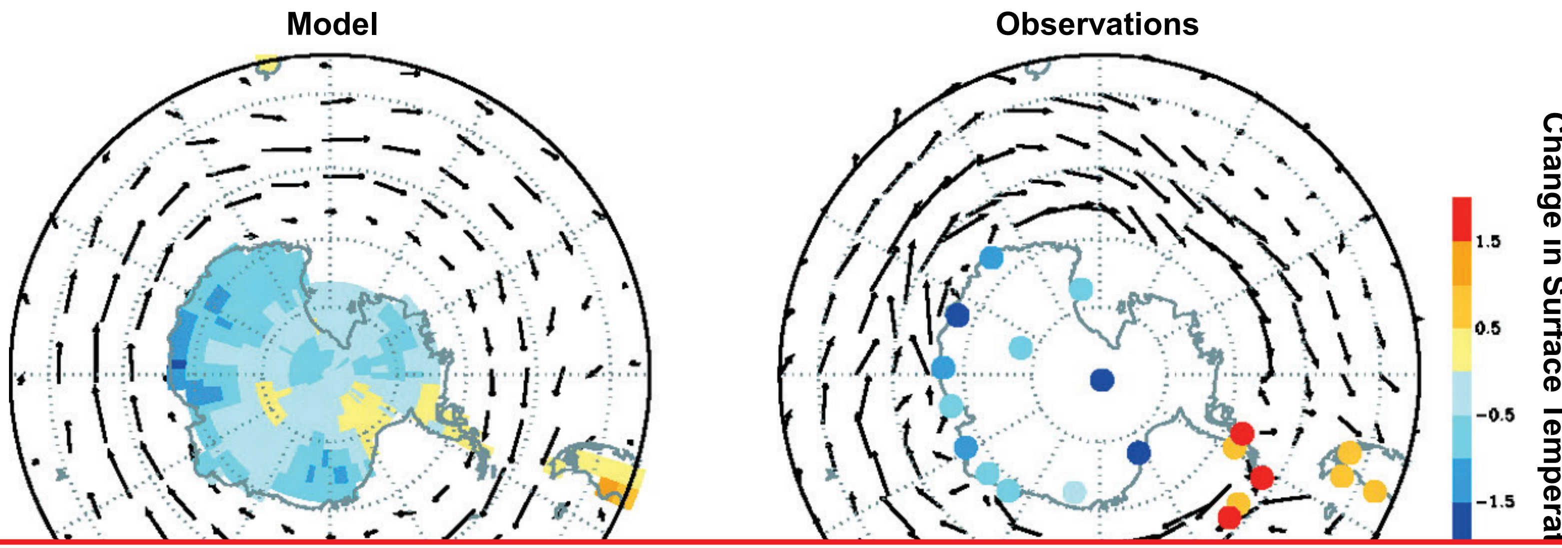


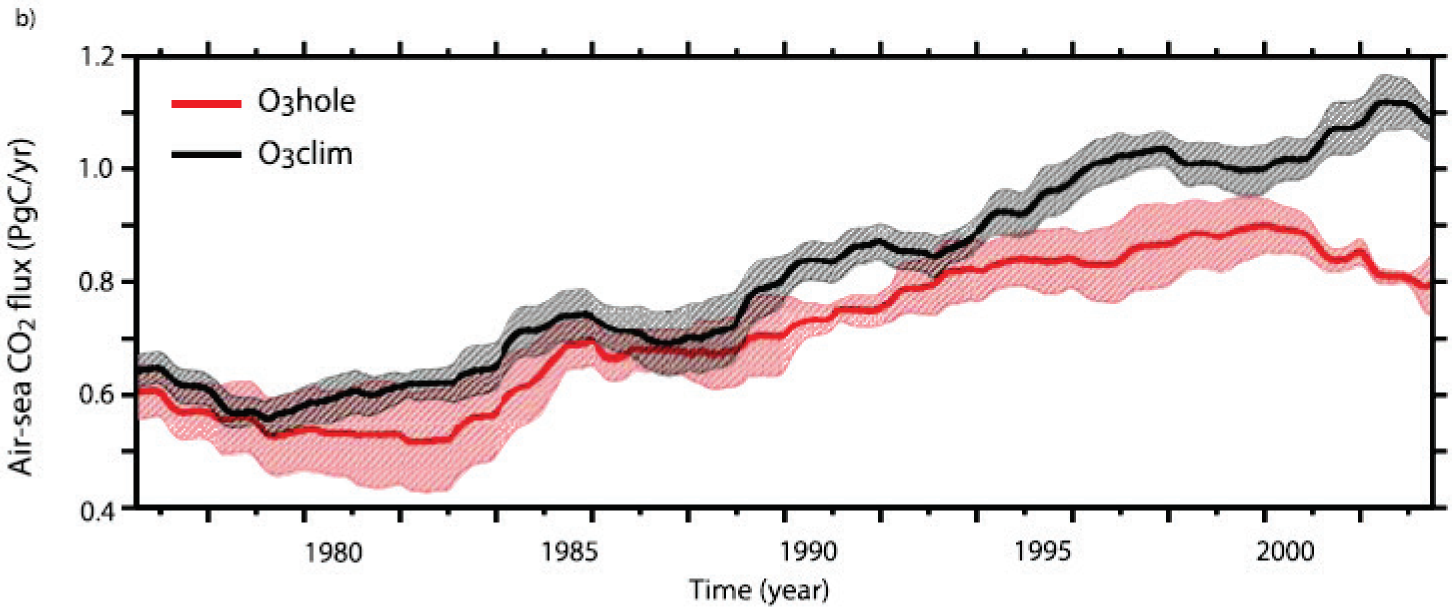
SAM: difference in zonal mean sea-level pressure between 40°S and 65°S. The pattern associated with SAM is a nearly annular pattern with a large low pressure anomaly centered on the South Pole and a ring of high pressure anomalies at mid-latitudes. The SAM effects storm tracks, precipitation patterns,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

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Uptake of Atmospheric CO_2 by Oceans

– Solubility Pump:

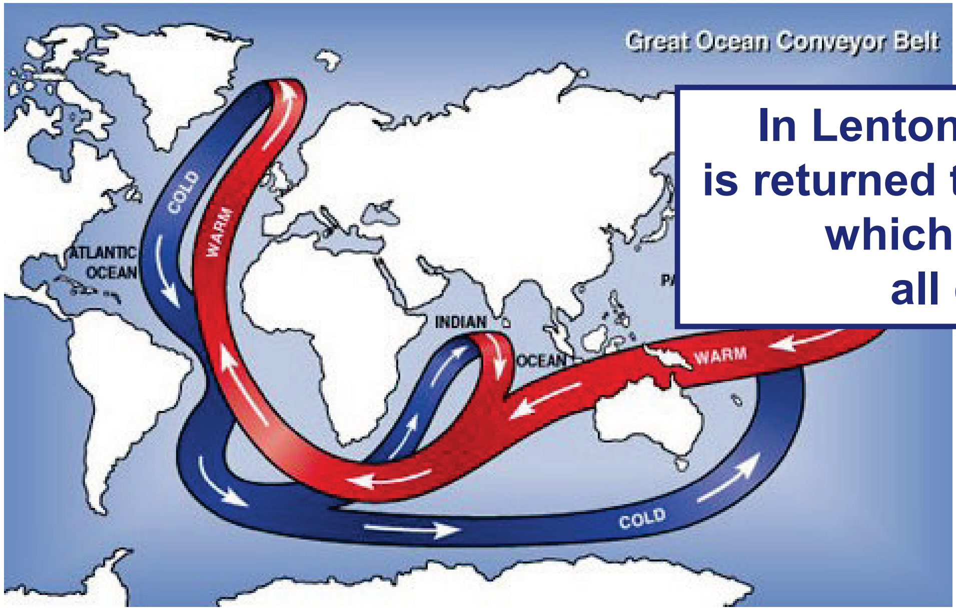
a) More CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

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. 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 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)**

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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)**