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

AOSC / CHEM 433 & AOSC 633

Ross Salawitch & Walt Tribett

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

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 16

9 April 2019

Announcements

Problem Set #3 due Thursday, 11 April, 2 pm

From Ross J. Salawitch | Reply | Reply All | Forward | Archive | Junk | Delete | More
Subject **AOSC / CHEM 433 & AOSC 633 : P Set #3 <- another important message** 4/7/2019, 10:45 AM
To atmospheric-chemistry-and-climate-2019@googlegroups.com, aosc433-0101-spr19@coursemail.umd.edu, chem433-0101-spr19@coursemail.un **1 more**

Hi Everyone,

Another important message for Problem Set #3.

I had inadvertently overlooked the need to add the data sheet for HOx reactions to the JPL Kinetic tables needed to complete Question 2, Part C.

Please use 2.4 x 10^{-13} cm^3 sec^{-1} as the value of the rate constant of HO2 + HO2 -> H2O2 + O2 at the temperature of interest, for this problem.

I apologize for this oversight.

I have updated the JPL link, to include the HOx reactions. When I review the problem set at the review session a week from Monday, I'll go over how the value of 2.4 x 10^{-13} cm^3 sec^{-1} is obtained for this reaction. The expression is a bit more complicated than those for other reactions, so just as well that I am emailing folks the numerical value to use for $k_{HO2+HO2}$ that should be used for Question 2.

Cheers,

Ross

From Ross J. Salawitch | Reply | Reply All | Forward | Archive | Junk | Delete | More
Subject **AOSC / CHEM 433 & AOSC 633 : P Set #3 <- can turn in Thursday without penalty** 4/8/2019, 1:20 PM
To atmospheric-chemistry-and-climate-2019@googlegroups.com, aosc433-0101-spr19@coursemail.umd.edu, chem433-0101-spr19@coursemail.um **1 more**

Hi Everyone,

I've decided to extend the due date for Problem Set #3 to Thurs, April 11, at 2 pm. At the start of class tomorrow, I'll review the content of the recent emails I had sent regarding this problem set and answer any general questions. I'll also be available after class tomorrow, and most of Wed, to help anyone who'd like to meet.

No penalty if turned in by 2 pm on Thursday. After this time, the late penalty goes into effect. Also, we can only guarantee return of graded Problem Sets on Mon, 15 April for those turned in by 2 pm on Thurs, April 11.

I'll also by in my office today from 2 to 3 pm, the Mon office hour.

Cheers,

Ross

Announcements

Problem Set #3 due Thursday, 11 April, 2 pm

Review of Problem Set #3 will be held Mon, 15 April, 5 pm in Room 2428

Second exam will be held Tues, 16 April, during normal class time

On Wed, 10 April, this hour long documentary will appear on PBS

Will show movie on Fri, 12 April, 6:30 pm for class if there is enough interest

Ozone Hole: How We Saved the Planet

OZONE HOLE: HOW WE SAVED THE PLANET
Courtesy of Windfall Films/NASA

Premieres Wednesday, April 10, 2019
10:00-11:00 p.m. ET on PBS

New Documentary Tells the Remarkable Story of How Scientists Discovered the Deadly Hole in the Ozone – and the Even More Remarkable Story of How the World's Leaders Came Together to Fix It

NASA DC-8

Figure 5. The NASA DC-8 showing the instruments used in TC4 and their placement on the aircraft.

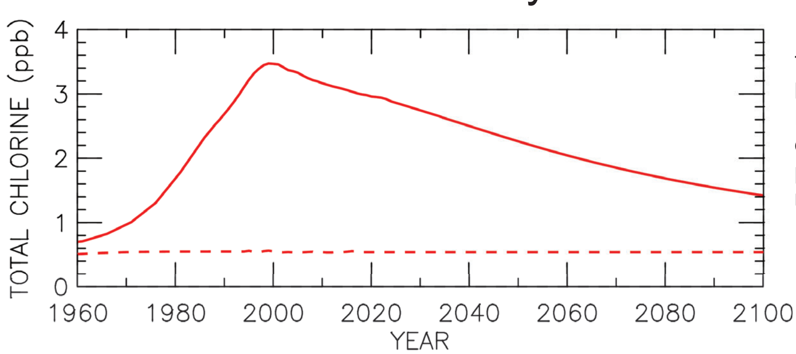
Table 6. DC-8 Instruments

Instrument	Name	Primary Investigator	Products
DLH	Open Path TDL	Glen Diskin, NASA LaRC	H_2O
2D-S, CPI	Cloud Probes	Paul Lawson, SPEC Inc.	Cloud particle size distribution and type (habit)
LARGE	Aerosol Spectrometers	Bruce Anderson, NASA LaRC	Particle size distribution, optical properties, CCN
PALMS	Particle Composition Mass Spectrometer	Dan Murphy, NOAA	Particle composition
CAPS, PIP	Cloud Probes	Andy Heymsfield, NCAR	Cloud particle size, images
CVI	Counterflow Virtual Impactor	Cynthia Twohy, Oregon State	Cloud water content
CIMS	Chemical Ion Mass Spectrometer	John Crounse, Caltech	Acids and organic peroxides, SO_2
DACOM	TDL (DACOM)	Glen Diskin, NASA LaRC	CO, CH_4, N_2O
FAST OZ	Chemiluminescence Ozone Probe	Melody Avery, NASA LaRC	Ozone mixing ratio
MACDON-NA	IR gas analyzer	Stephanie Vay, NASA LaRC	CO_2
SAGA	Mist Chamber	Jack Dibb, U. New Hampshire	NO_3^-, $SO_4^=$, aerosol composition
NO	Chemiluminescence Nitric Oxide	Ron Cohen, U. C., Berkley	NO
TD-LIF	Tunable Diode Laser	Ron Cohen, U. C., Berkley	NO_2, Alkylnitrates, PAN
WAS	Whole Air Sampler	Don Blake, U. C., Irvine	Many trace gases
Dropsondes	Atmospheric Probe	Errol Korn, NCAR	Temperature, pressure, winds, relative humidity
MMS	Pressure and Temperature Probe	Paul Bui, NASA ARC	Pressure, temperature, winds
APR-2	Precipitation Radar	Eric Smith, NASA MSFC	Reflectivity, precipitation
LASE	IR Lidar	Ed Browell, NASA LaRC	Water vapor, aerosol and cloud heights, aerosol type
DIAL	UV Lidar	Ed Browell, NASA LaRC	Ozone, aerosol and cloud heights, aerosol type
BB IR	Broadband Radiometer	Anthony Bucholtz NRL	IR radiative fluxes and layer heating rate
CAFS	UV-Vis Actinic Flux	Rick Shetter, NCAR	Ozone zenith column
SSFR	Solar Spectral Flux Radiometer	Peter Pilewskie, U. Colorado	Solar spectral fluxes and heating rate
DC-8 CAM	Video	Rick Shetter, U. N. Dakota	Nadir and forward video

NASA DC-8: Roll The Tape

https://www.youtube.com/watch?v=YnPfPkVhftQ

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

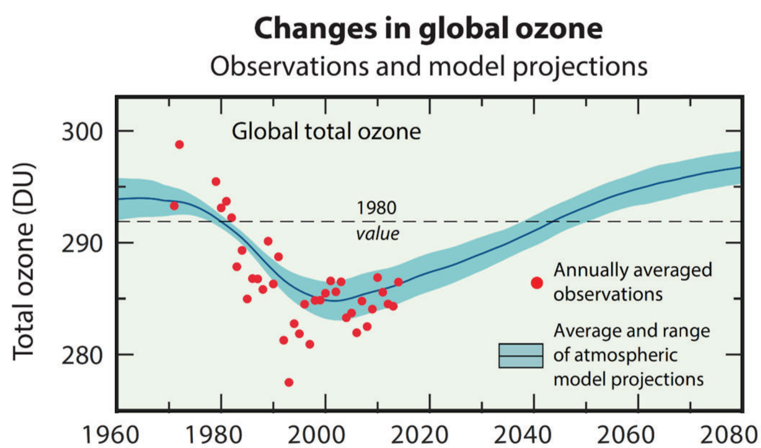
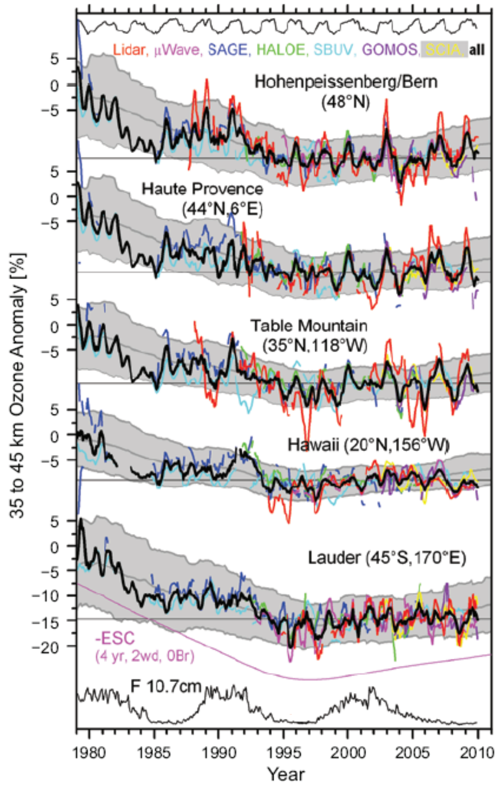


Fig Q20-1, 20 QAs, WMO (2019)

Past Trends, Upper Stratospheric Ozone



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

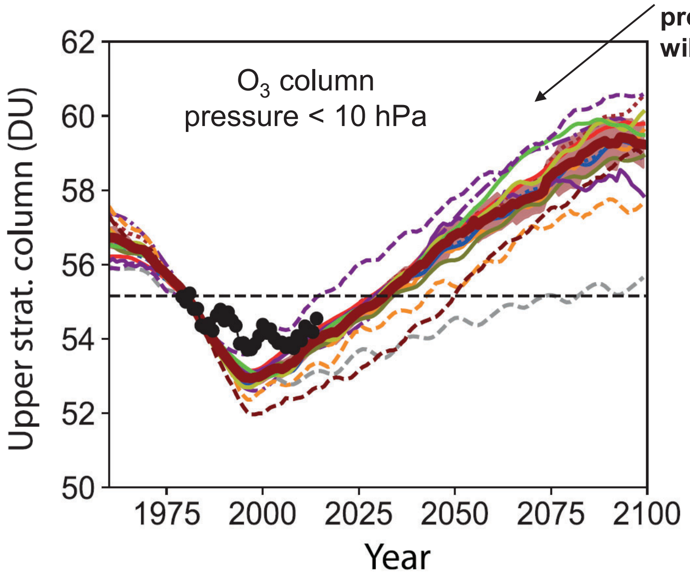
Trends in ozone at 40 km are "well understood" and **generally follow track time history of stratospheric chlorine loading.**

Lecture 14, Slide 32

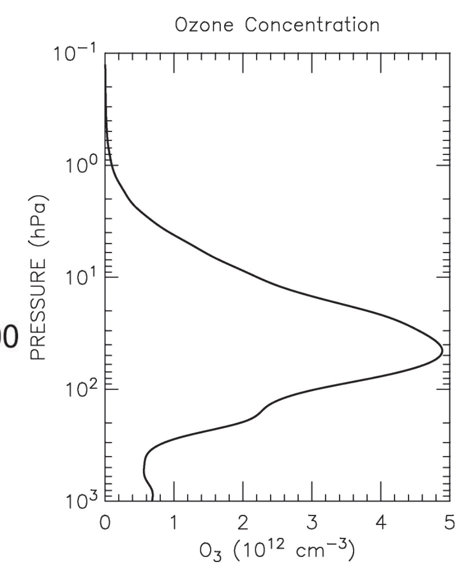
Figure 2-5, WMO/UNEP 2011

Future Trends, Upper Stratospheric Ozone

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



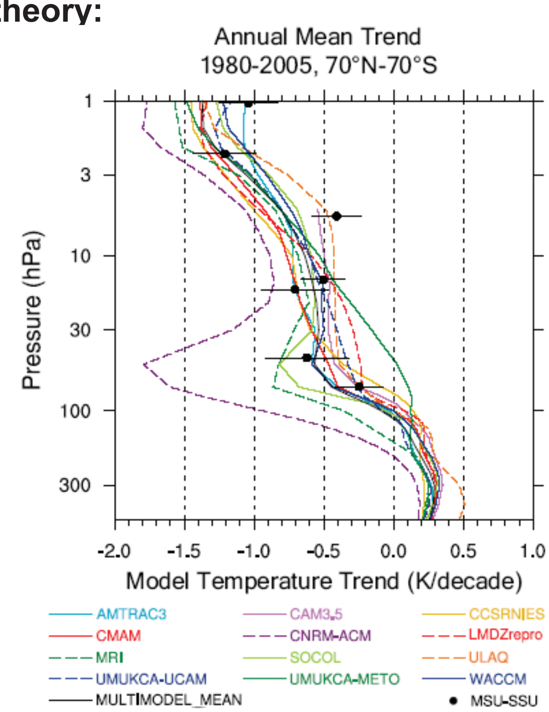
Dhomse *et al.*, *ACP*, 2018



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 broadly consistent with theory:



Lecture 15, Slide 36

Figure 4−11, WMO/UNEP (2011)

Future Trends, Upper Stratospheric Ozone

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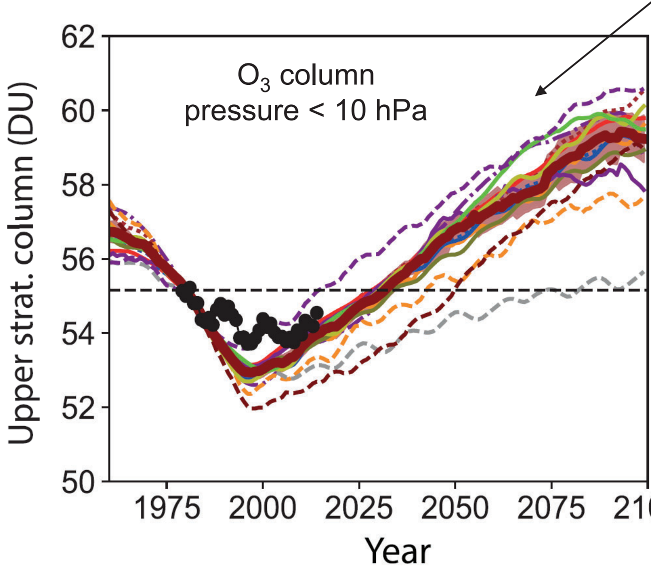
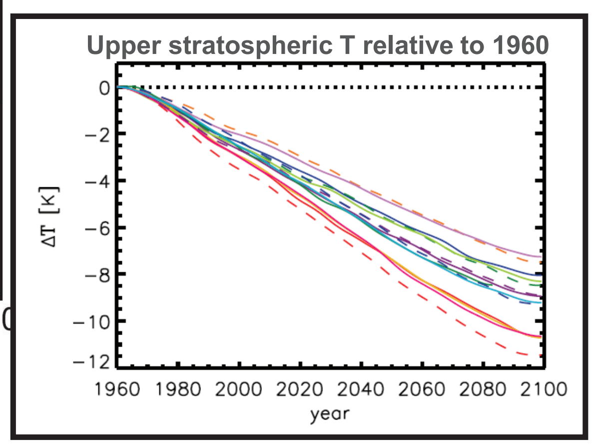


Dhomse *et al.*, *ACP*, 2018



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

Future Trends, Upper Stratospheric Ozone

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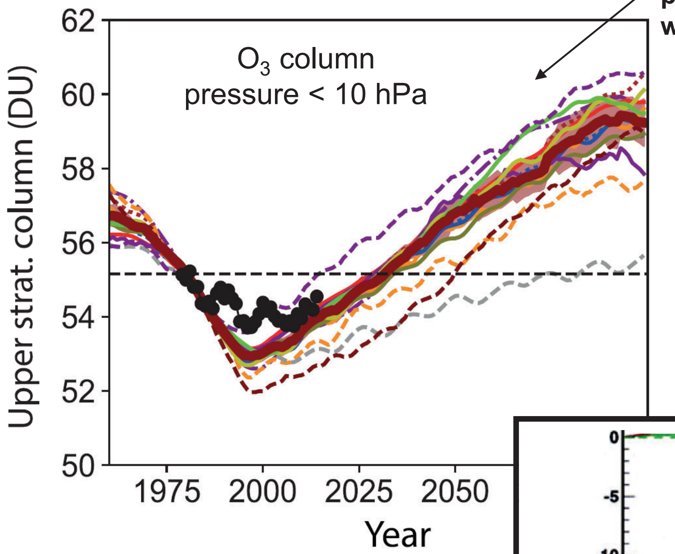
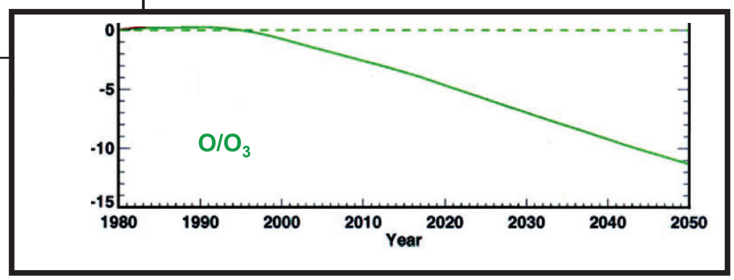


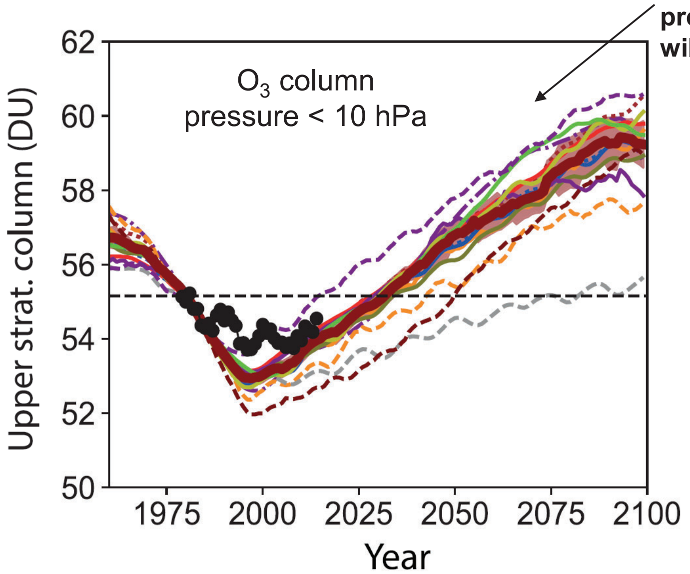
Dhomse *et al.*, *ACP*, 2018



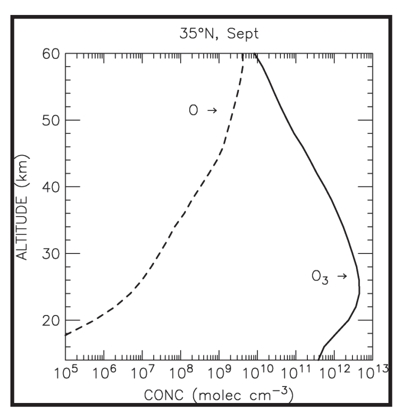
Rosenfield *et al.*, *JGR*, 2002

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



Brewer-Dobson Circulation

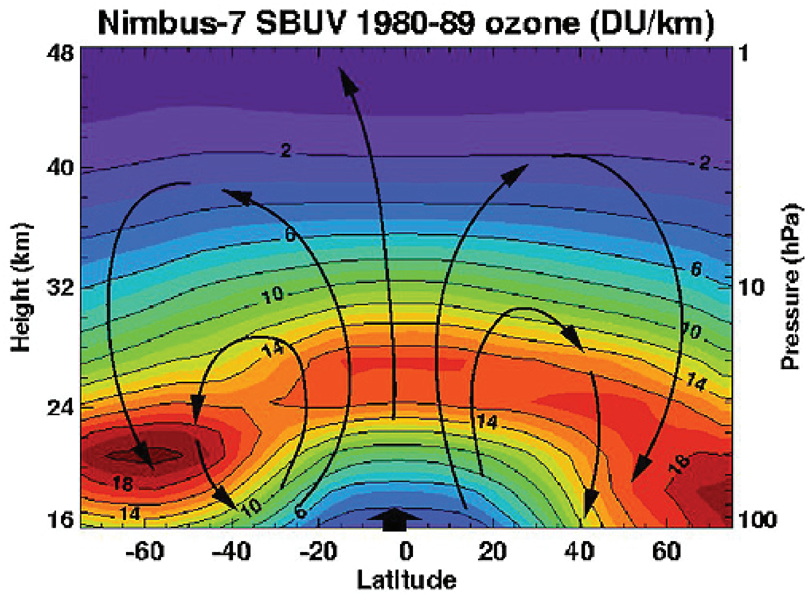
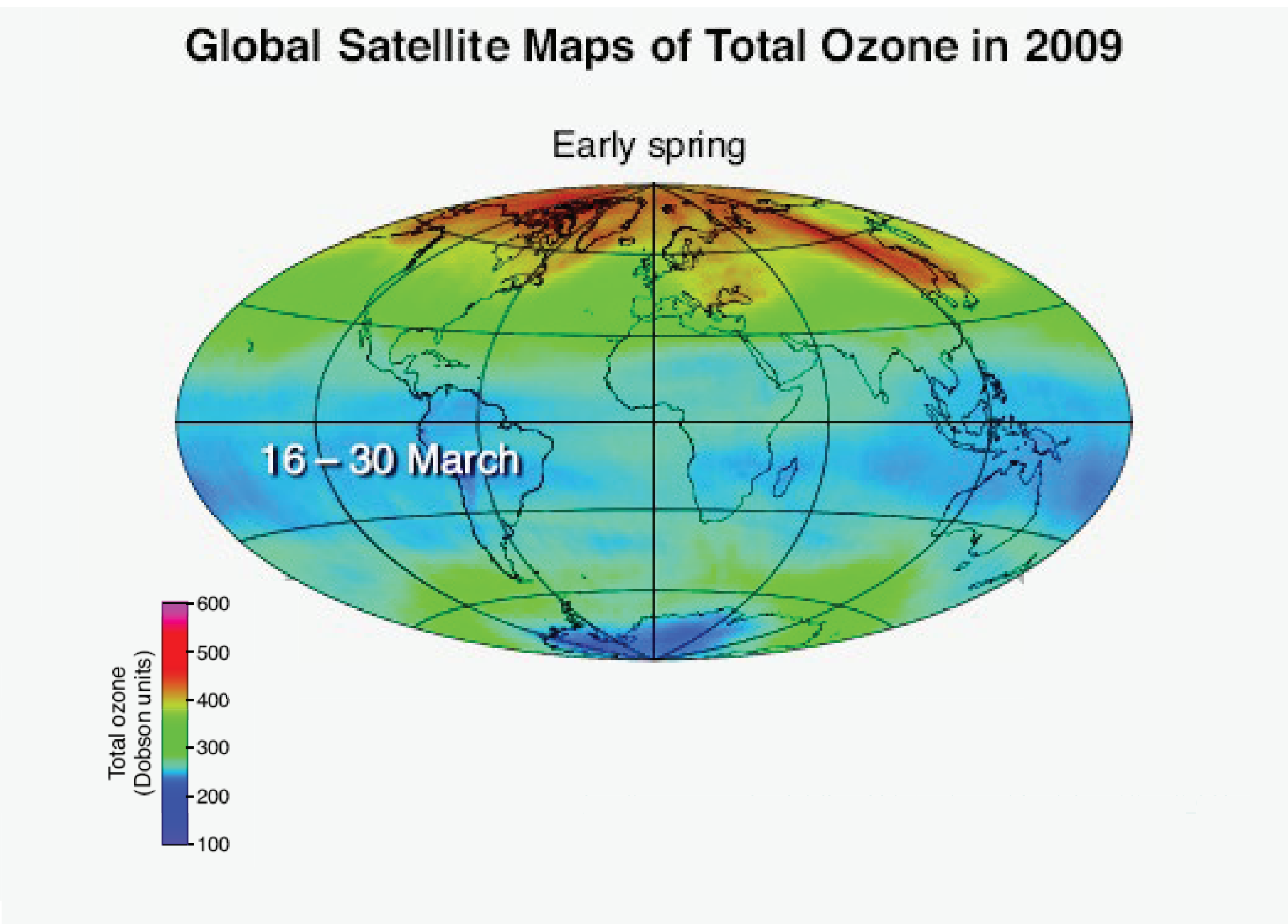


Figure 6.03 Schematic diagram of Brewer-Dobson circulation with seasonally averaged ozone concentration

http://www.ccpo.odu.edu/~lizsmith/SEES/ozone/class/Chap_1/1_Js/1-06.jpg

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



More Chemistry and Climate Coupling

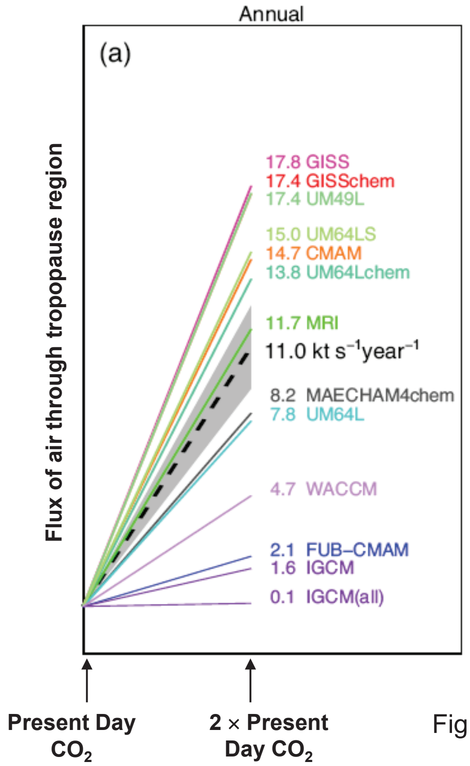


Figure 5-17. Trends in exchange of air from troposphere-to-stratosphere computed by 14 CCMs.

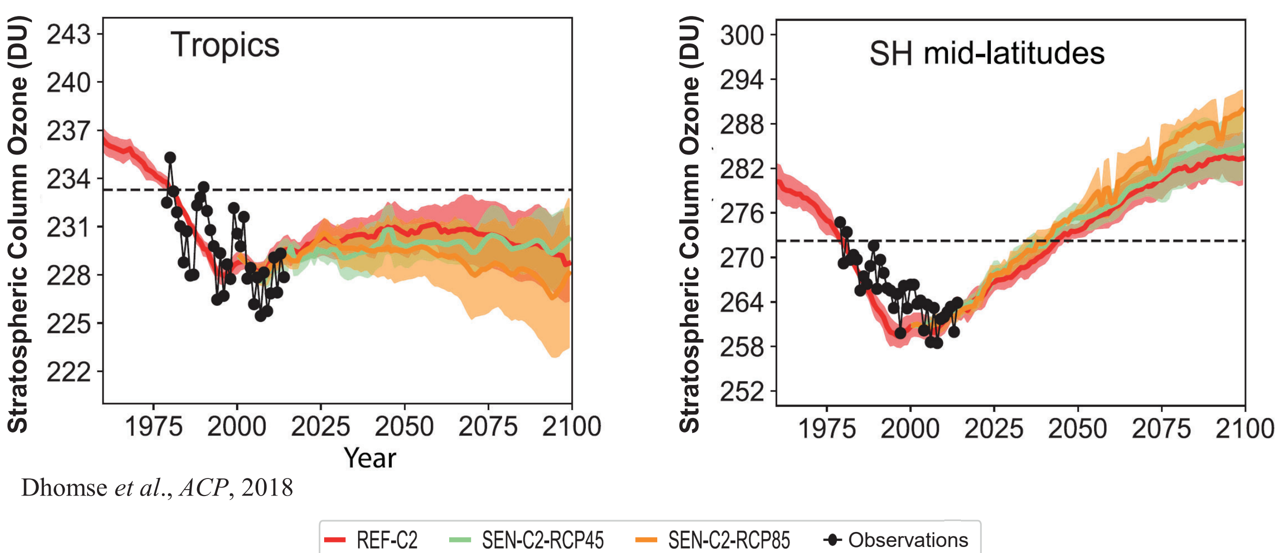
Trends (units of Gg s^{-1} $year^{-1}$) are represented by the slope of each line.

Dashed line is the multi-model mean.

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

Fig 5.17, WMO/UNEP (2006)

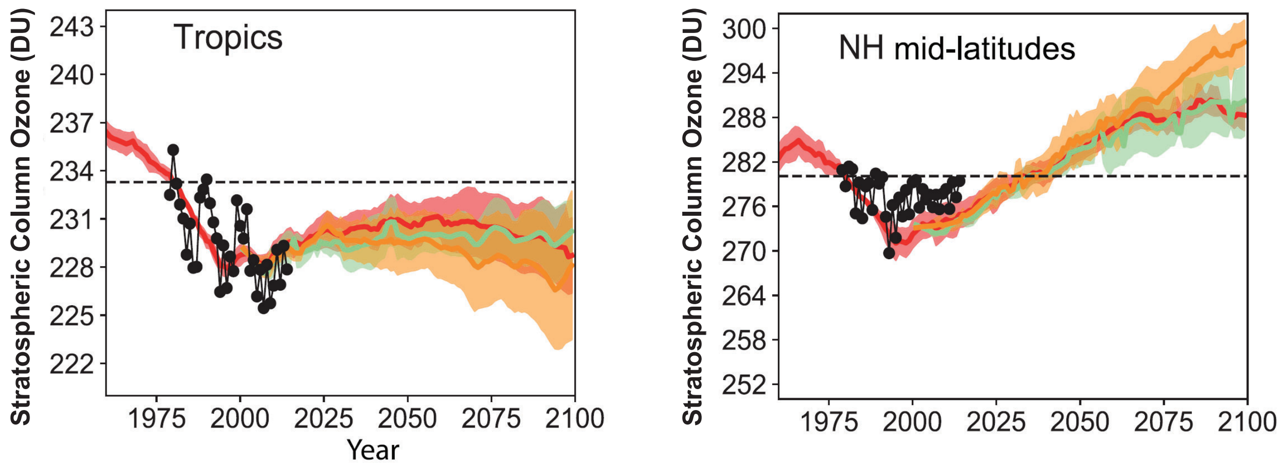
More Chemistry and Climate Coupling



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"

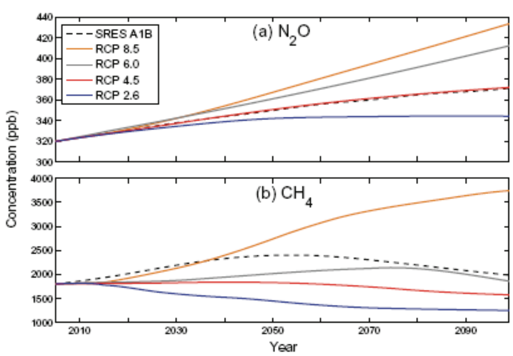
More Chemistry and Climate Coupling



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

Acceleration of the <u>*Brewer-Dobson Circulation*</u> 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"

Future Mid-Latitude Ozone: CH_4



Rising CH_4 leads to ozone loss in the upper & lower stratosphere by increasing the speed of HO_x mediated loss cycles (blue regions, Fig 6b).

However, there are other processes that result in more ozone (red regions, Fig 6b):

- Rising CH_4 leads to more stratospheric H_2O, cooling this region of the atmosphere, which slows the rate of all ozone loss cycles
- Rising CH_4 speeds up the rate of Cl+CH_4, shifting chlorine from ClO into HCl
- Rising CH_4 leads to more HO_2 in the lowermost stratosphere, where there is sufficient CO to result in production of O_3 by photochemical smog chemistry

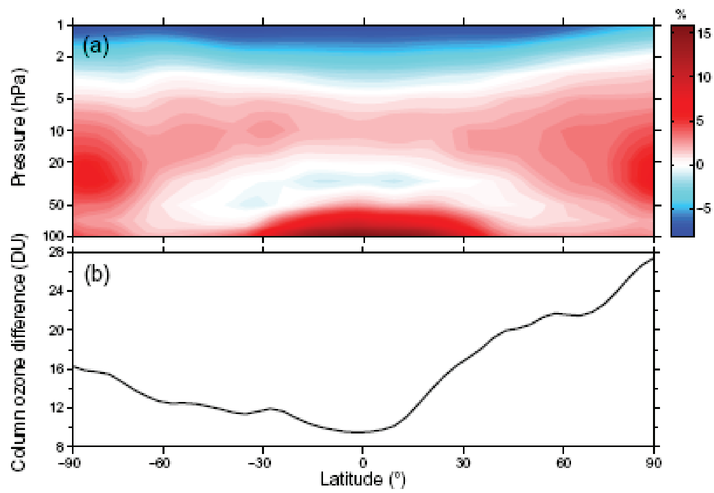
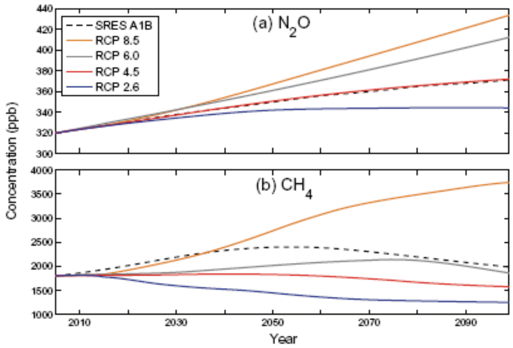


Fig. 6. (a) CH_4-8.5 ozone minus CH_4-2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the CH_4-2.6 simulation. **(b)** 2090s-decade CH_4-8.5 total column ozone minus CH_4-2.6 total column ozone.

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

Future Mid-Latitude Ozone: N_2O



Ozone depleting NO_x cycles speed up with increasing N_2O throughout the middle stratosphere, where these cycles make the largest relative contribution to odd oxygen loss (blue region, Fig 5a).

• As NO_2 increases due to rising N_2O, the abundance of ClO declines, particularly in the lower stratosphere, leading to reduced rates in the total speed of all ozone depleting cycles (red region, Fig 5a); small contrib. to the red region due to production of O_3 by photochemical smog chemistry.

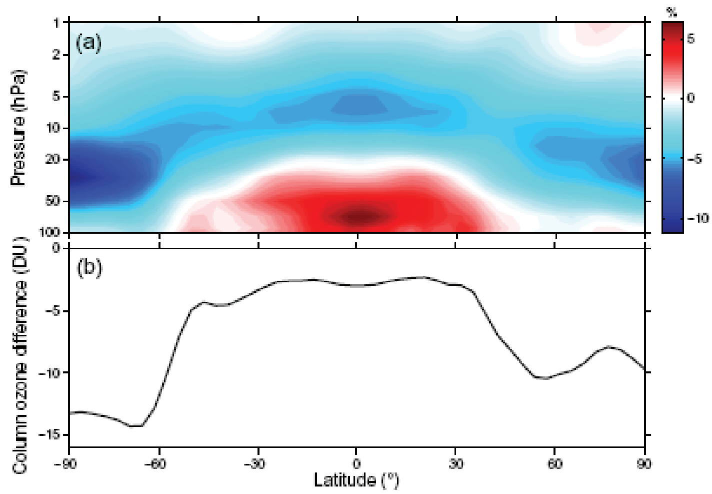
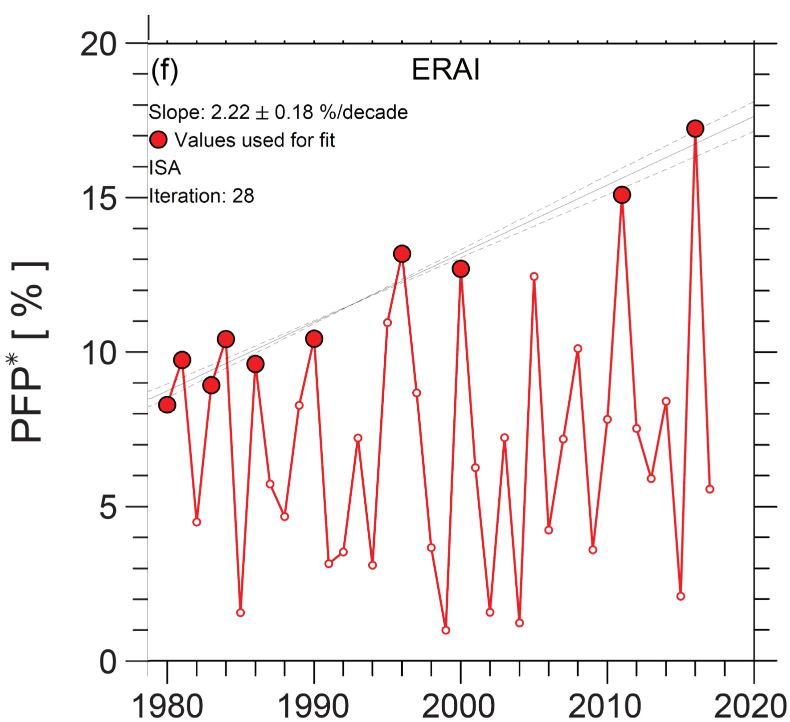


Fig. 5. **(a)** N_2O-8.5 ozone minus N_2O-2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the N_2O-2.6 simulation. **(b)** 2090s-decade N_2O-8.5 total column ozone minus N_2O-2.6 total column ozone.

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

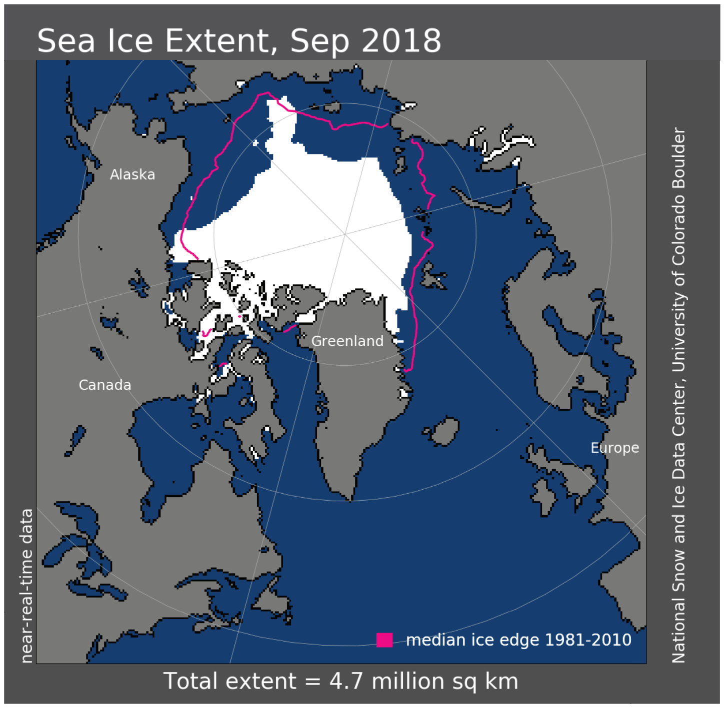
Future Trends, Stratospheric Ozone



PFP: Potential of vortex cold enough for PSC formation

Lecture 15, Slide 51

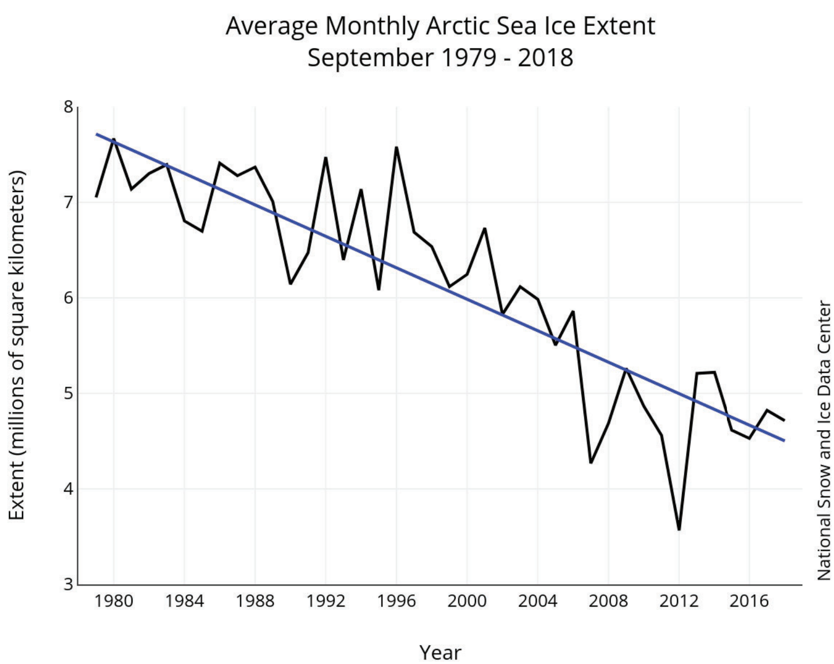
Declining Arctic Sea Ice: Canary of Climate Change?



Arctic sea ice extent for September 2018 was 4.71 million square kilometers, which is 1.70 million square kilometers below the 1981 to 2010 average.

http://nsidc.org/arcticseaicenews/files/2018/10/Figure1.png

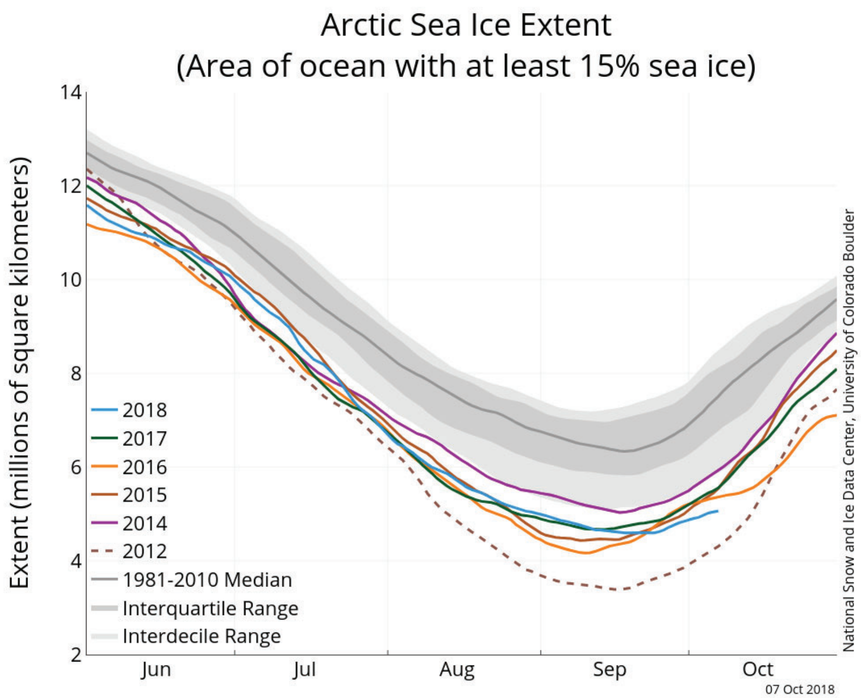
Declining Arctic Sea Ice: Canary of Climate Change?



Arctic sea ice is declining at a rate of about12.8 percent per decade, relative to the 1981 to 2010 average.

http://nsidc.org/arcticseaicenews/files/2018/10/Figure3.png

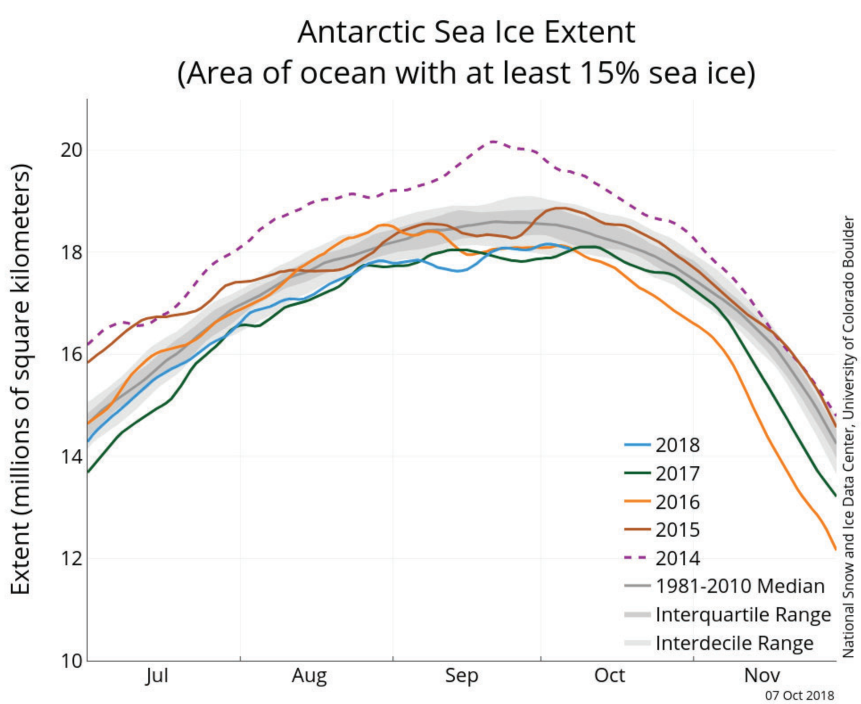
Declining Arctic Sea Ice: Canary of Climate Change?



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

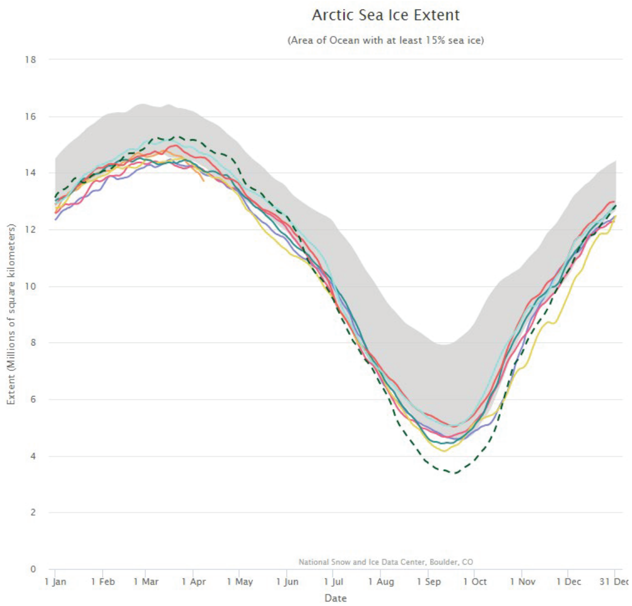
http://nsidc.org/arcticseaicenews/files/1999/10/Figure2_10072018.png

The Antarctic

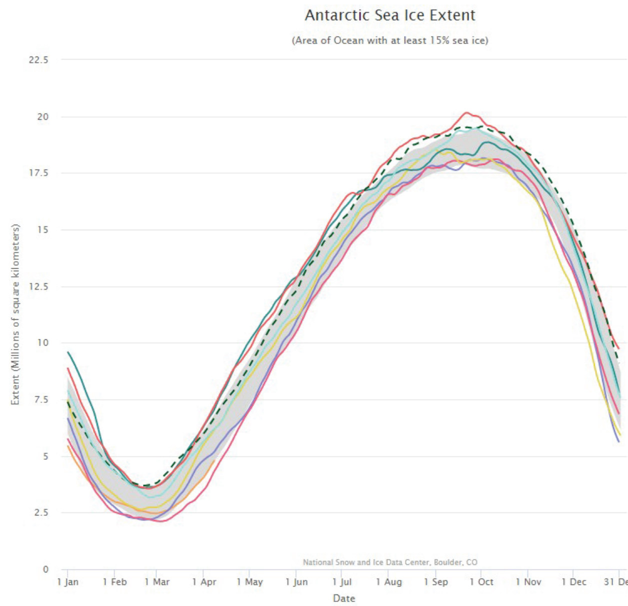


http://nsidc.org/arcticseaicenews/files/1999/10/Figure6_10072018.png

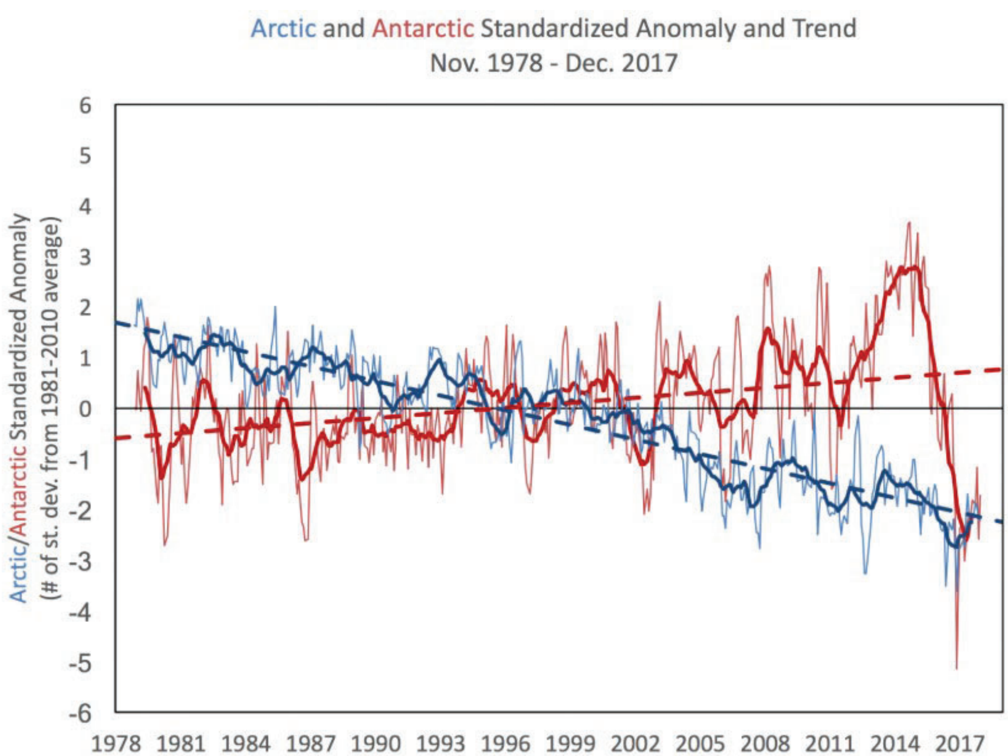
The Arctic and the Antarctic



Shaded region: 1981 to 2010 mean ± 2σ
Colors: Individual years since 2012



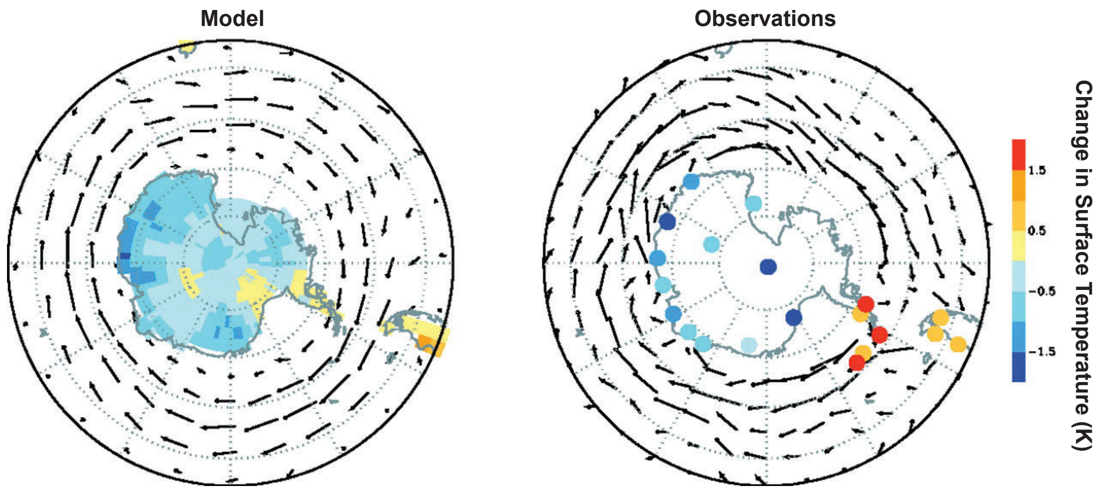
http://nsidc.org/arcticseaicenews/charctic-interactive-sea-ice-graph/



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://www.carbonbrief.org/natural-ocean-fluctuations-help-explain-antarctic-sea-ice-changes

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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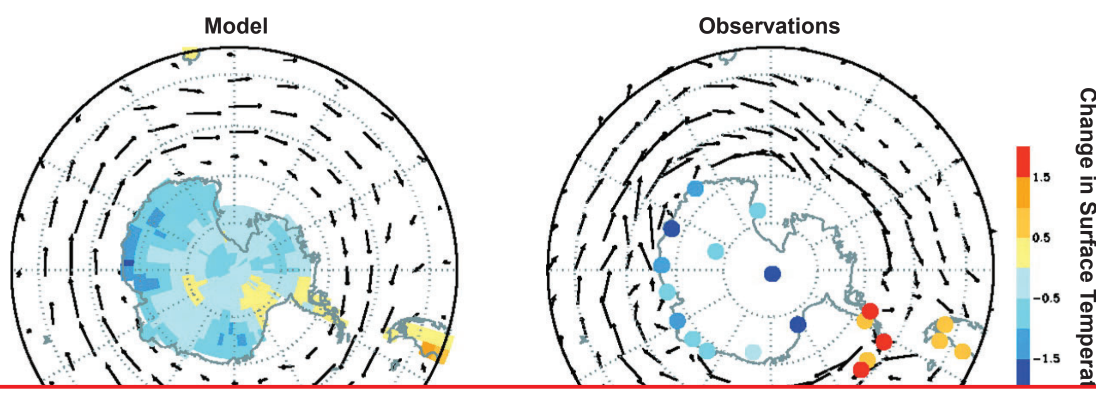


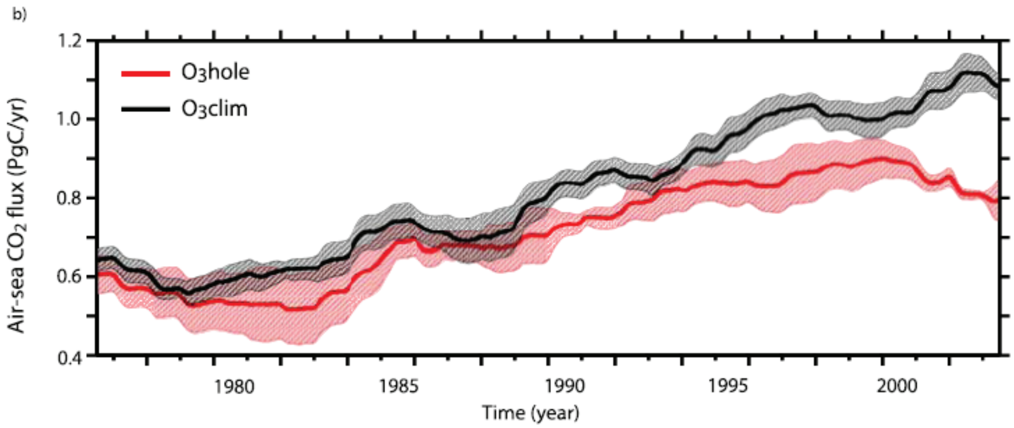
SAM: difference in zonal mean sea-level pressure between 40°S and 65°S. The pattern associated with SAM is a nearly annular pattern with a large low pressure anomaly centered on the South Pole and a ring of high pressure anomalies at mid-latitudes. The SAM effects storm tracks, precipitation patterns,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

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:

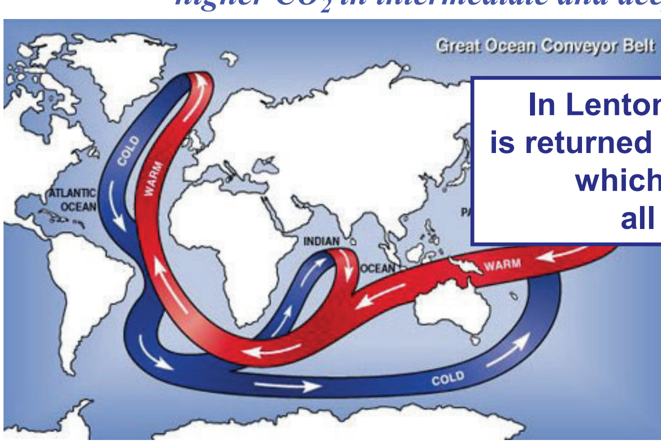
a) More CO_2 can dissolve in cold polar waters than in warm equatorial waters. As major ocean currents (e.g. the Gulf Stream) move waters from tropics to the poles, they are cooled and take up atmospheric CO_2

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. 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)**

Chemistry Climate Coupling

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Data analysis suggests “coldest Arctic winters getting colder”:

1. **Possibly due to rising GHGs**
2. **Not represented well by CCMs**

As Antarctic ozone recovery _will occur_:

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)**