Ozone and UV radiation

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Outline

1. Introduction: the role of ozone in the atmosphere
2. Stratospheric Ozone Chemistry
3. The time variability of ozone
4. Ozone and climate (change)?
5. Tropospheric ozone?

based on “Ozone” lecture of Physical Meteorology course at Postgraduate “Weather and Climate Modelling” at University of Gent, Belgium

Composition of the atmosphere

- major constituents (99.9%) are
  - ✓ N_2 (78% of the air by volume)
  - ✓ O_2 (21%)
  - ✓ Ar (0.9%)

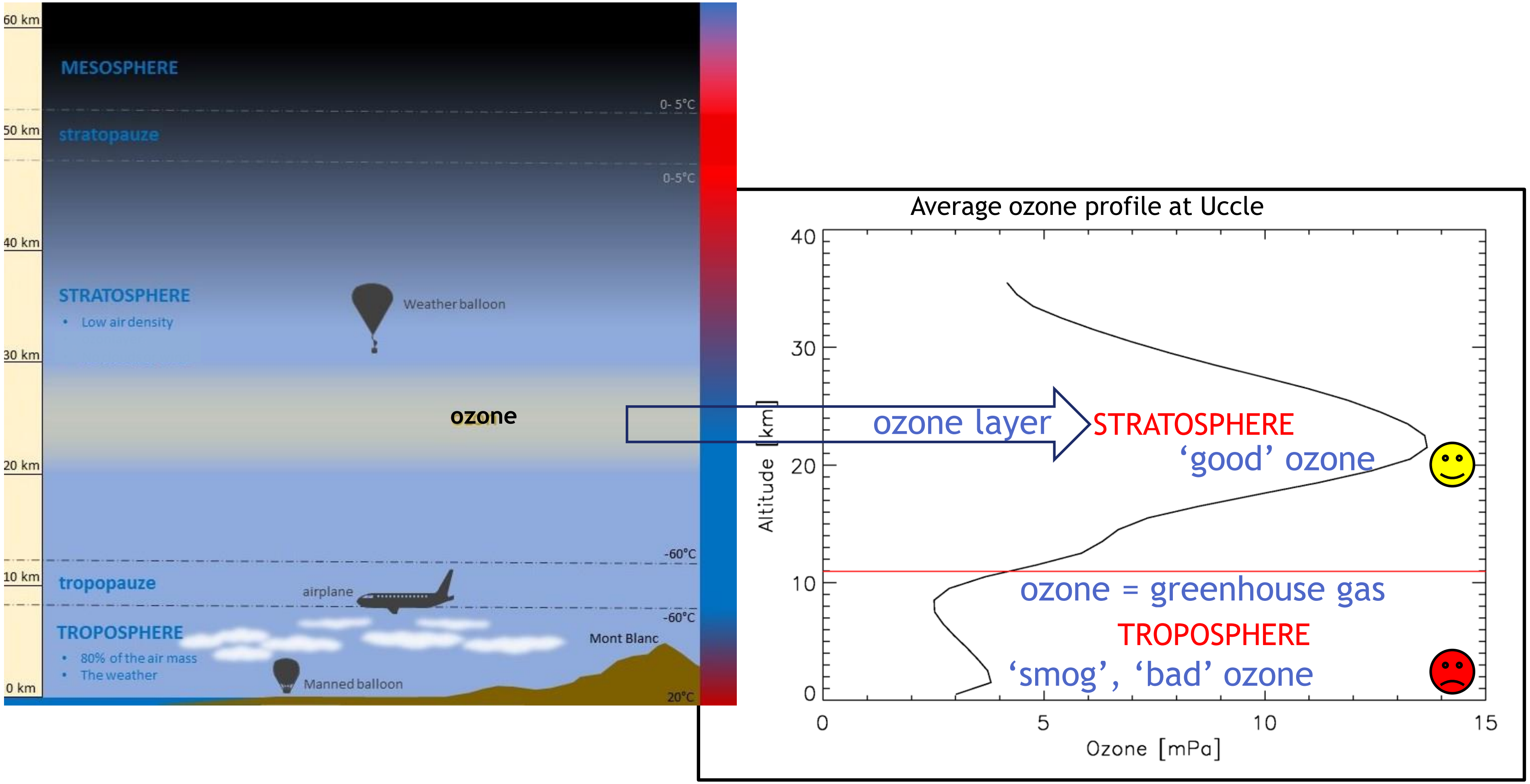
- the remaining 0.1% are “trace gases”:

greenhouse gases

  - ✓ Water vapour (H_2O) → can be 2-3% in warm ground fog, but only 4 to 6 ppmv or 0.0004 to 0.0006% in the stratosphere)
  - ✓ Carbon dioxide (CO_2) → 0.04% or 400 ppmv
  - ✓ Ozone (O_3) → 10 ppmv in stratosphere → **Why bother about ozone?**
  - ✓ Methane (CH_4) → 1.8 ppmv
  - ✓ various oxides of nitrogen
  - ✓ Neon → 0.002% or 20 ppmv
  - ✓ Helium → 5 ppmv

- additional atmospheric components: aerosols and ions

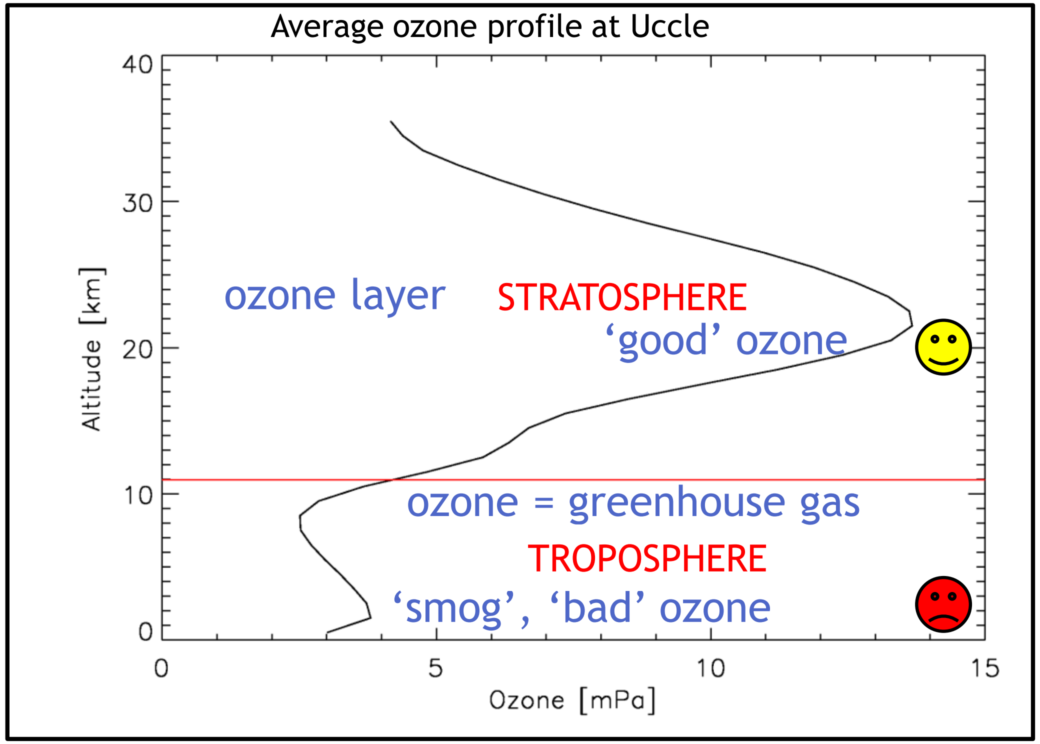
Ozone in the atmosphere



Ozone in the atmosphere

- 90 % of atmospheric ozone
- formed by a balance between sunlight that creates ozone and chemical reactions that destroy it
- beneficial role: acts as primary UV radiation shield

- 10 % of atmospheric ozone
- forms when nitrogen oxide gases from vehicle and industrial emissions react with volatile organic compounds (VOCs)
- harmful impact: toxic effects on humans, animals and vegetation



Effect of ozone on Earth

O_3 concentrations ↘ in stratosphere

⇩

UV radiation ↗

⇩

HUMAN BODY

- increase of eye diseases (cataract)
- more skin cancers

AGRICULTURE

- smaller crop yields
- less food (food shortage)

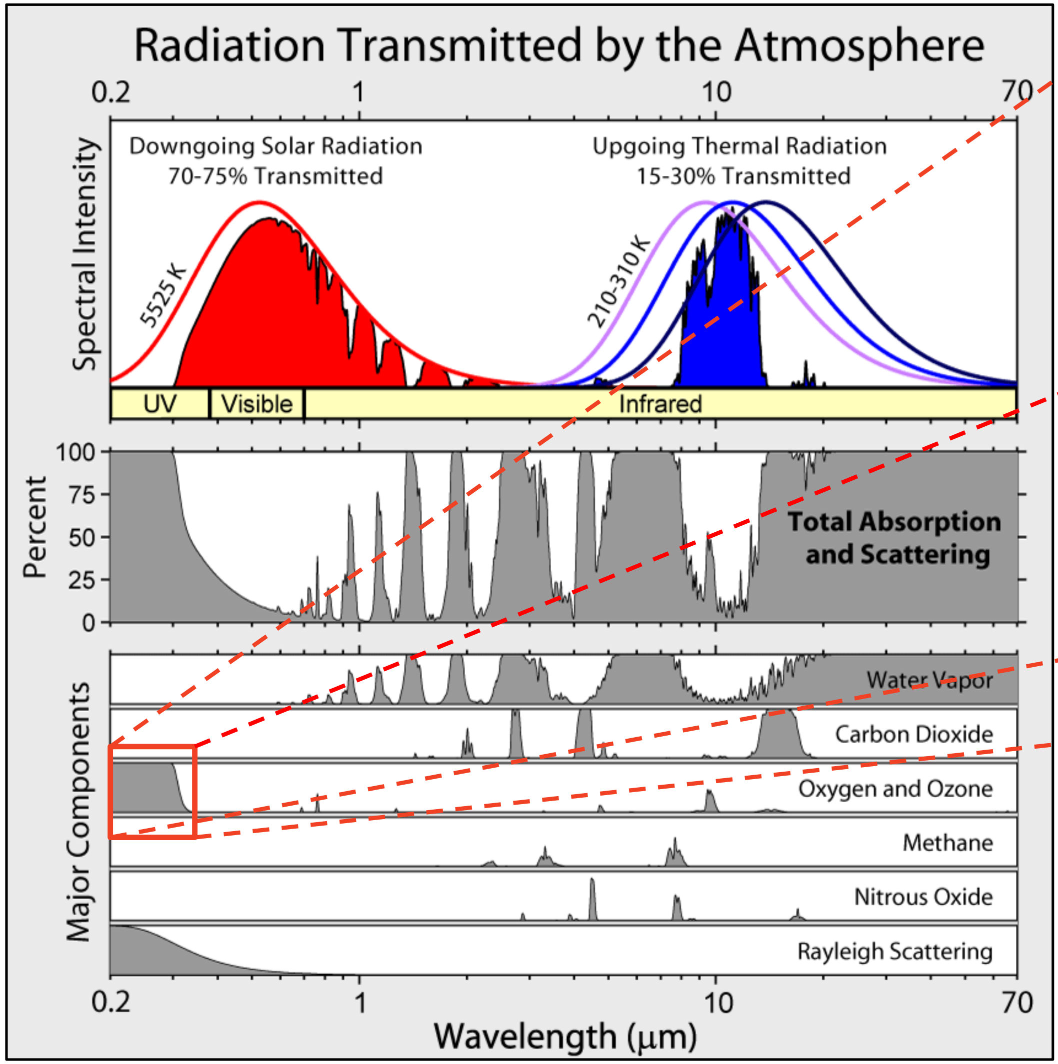
OCEANS

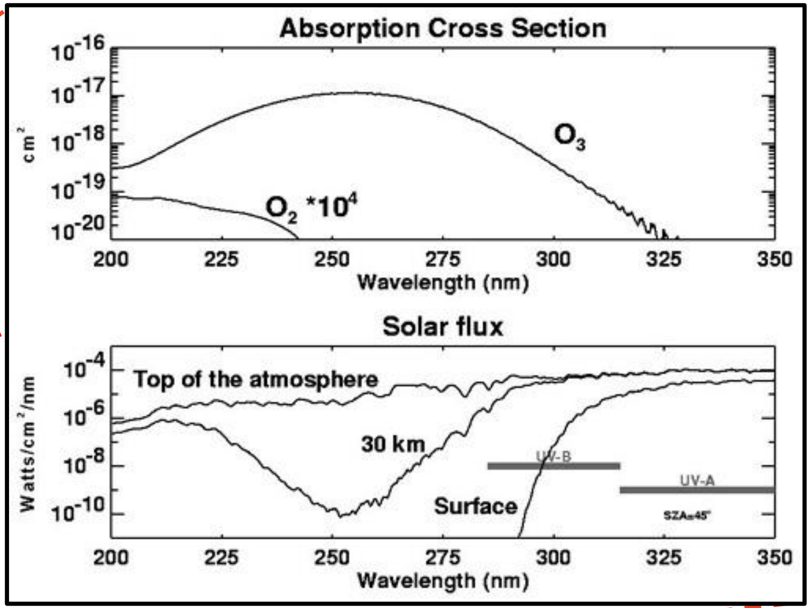
- plankton damage
- CO_2 ↗
- biodiversity disappearance

ECONOMY

- some materials (e.g. rubber) will break down faster
- faster and more replacement purchases

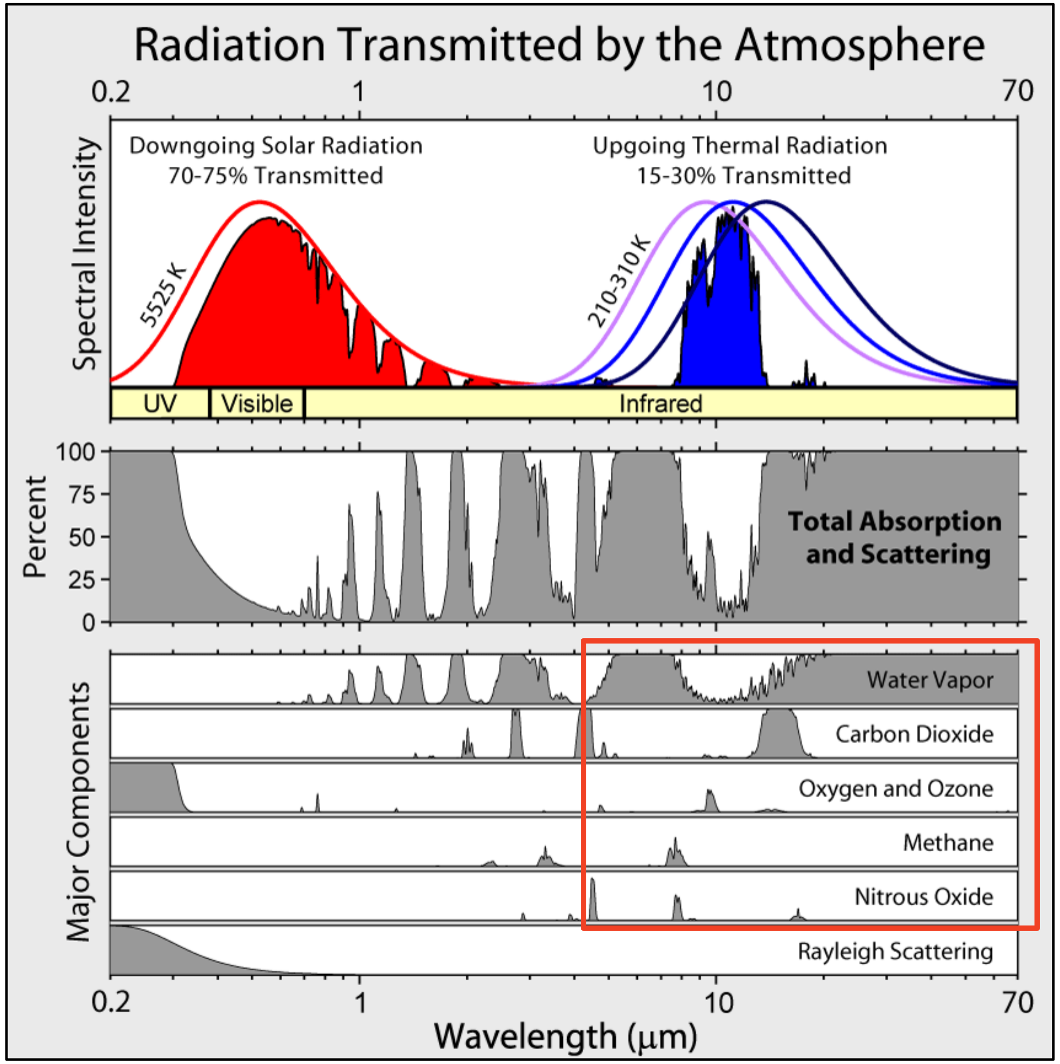
Ozone & radiation





- O_3 (and to a lesser extent: O_2): very efficient in absorbing the harmful solar UV-radiation (at the surface: UV-C: 100%, UV-B: 90%, UV-A: 50%)
- This property is important for its formation!

Ozone & radiation



Greenhouse gases!
→ especially ozone in the UT acts as a greenhouse gas

1. The Chapman cycle for ozone production

- Chapman (1930) hypothesized that UV radiation was responsible for ozone production and proceeded to lay the foundation of stratospheric photochemistry: the Chapman reactions
- atomic oxygen is formed by the splitting (dissociation) of O_2 by high energy ultraviolet photons ($\lambda < 240$ nm) via (“O_2 photolysis”)

$$O_2 + hc/\lambda \rightarrow O + O \quad (1)$$

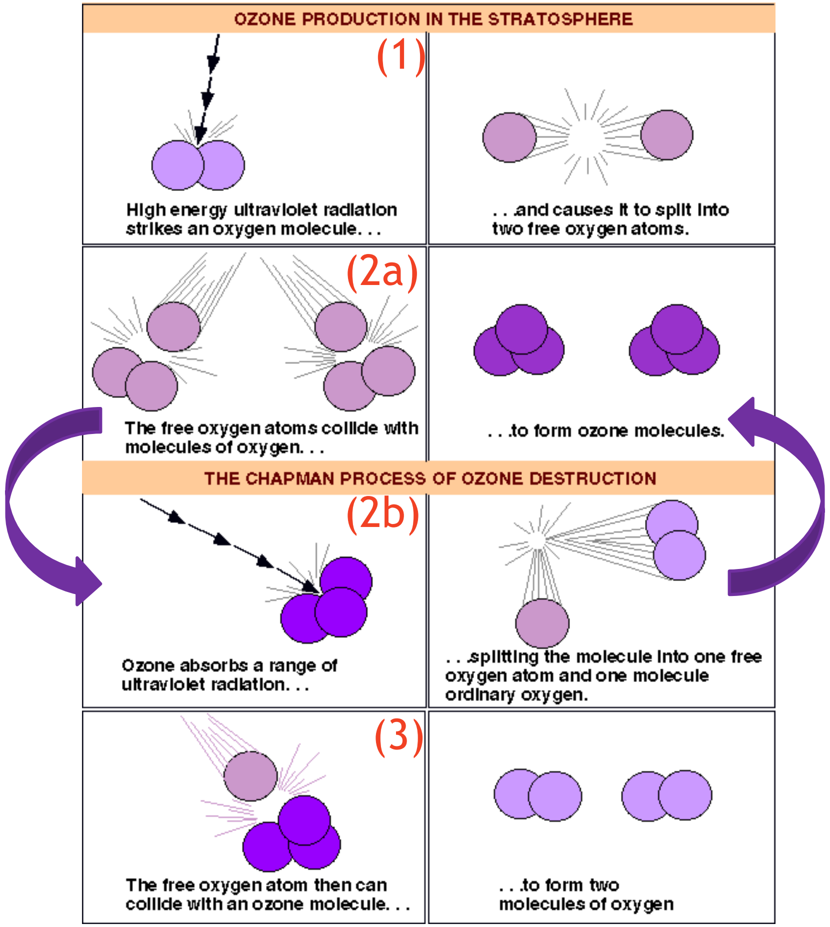
- atomic oxygen is highly reactive (very short lifetime, <1s in stratosphere):

$$O_2 + O + M \rightarrow O_3 + M^* \text{ (exothermic) } (2a)$$

  with M any other molecule (most likely N_2 or O_2)
- The ozone photolysis reaction ($220 < \lambda < 320$ nm)

$$O_3 + hc/\lambda \rightarrow O_2 + O \quad (2b)$$

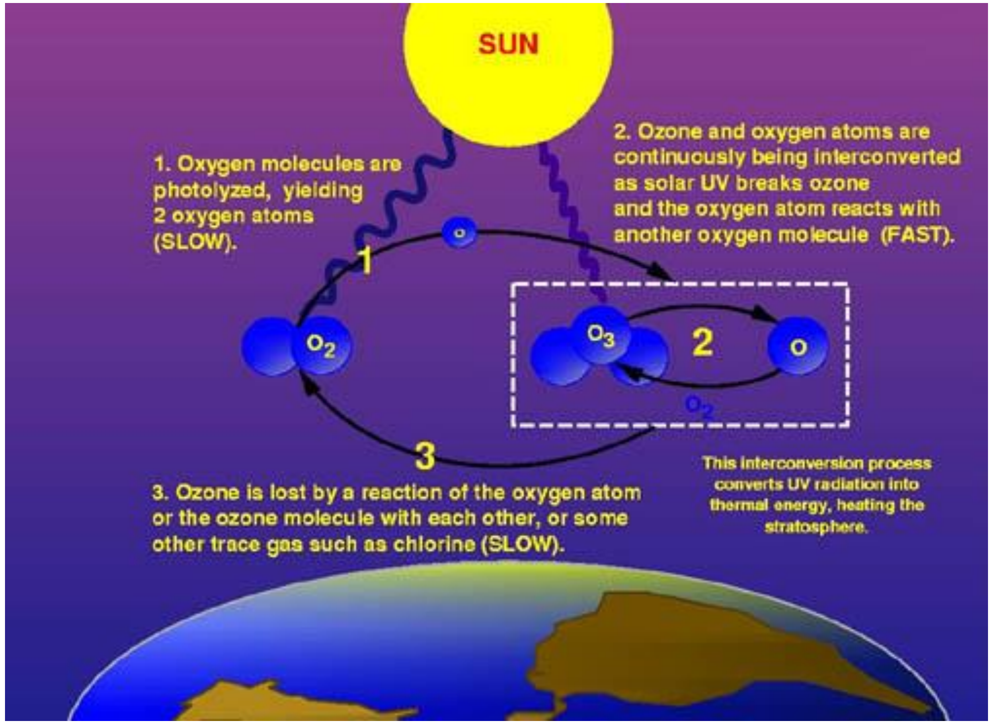
  cycles with (2a), leading to
  - a continuous interconversion of O_3 and O
  - heating of the stratosphere due to conversion of UV in thermal energy

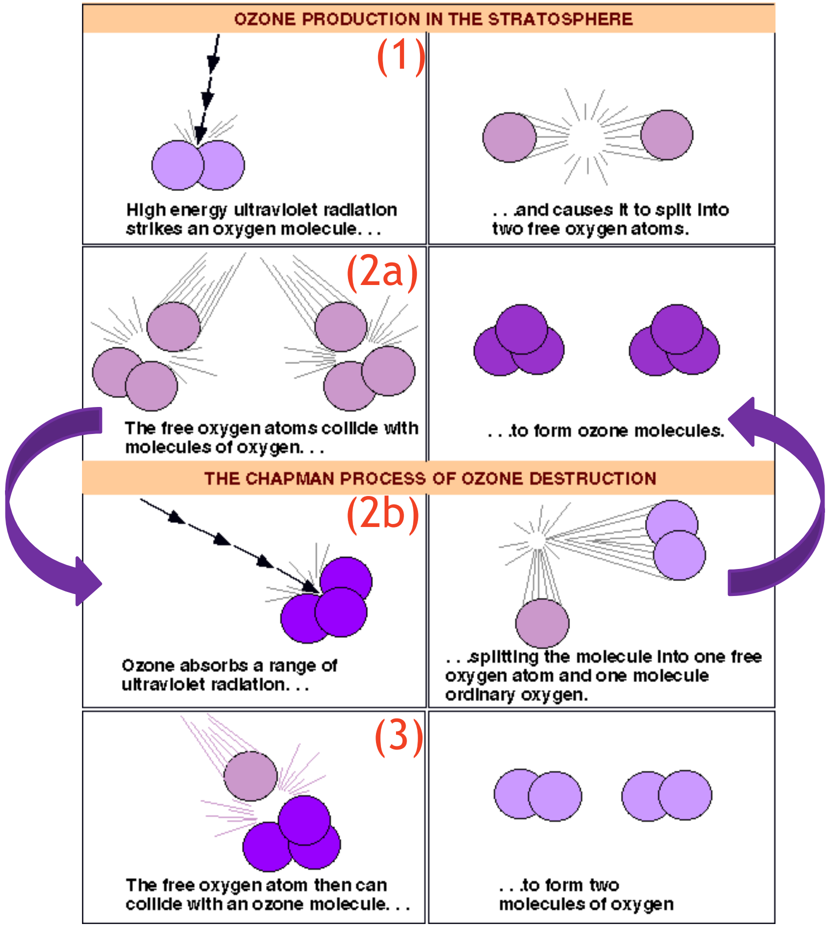


2. The Chapman cycle for ozone loss

- Chapman also hypothesized that ozone is lost by a reaction with the free oxygen atoms. This ozone loss balances production:

$$O_3 + O \rightarrow O_2 + O_2 \quad (3)$$

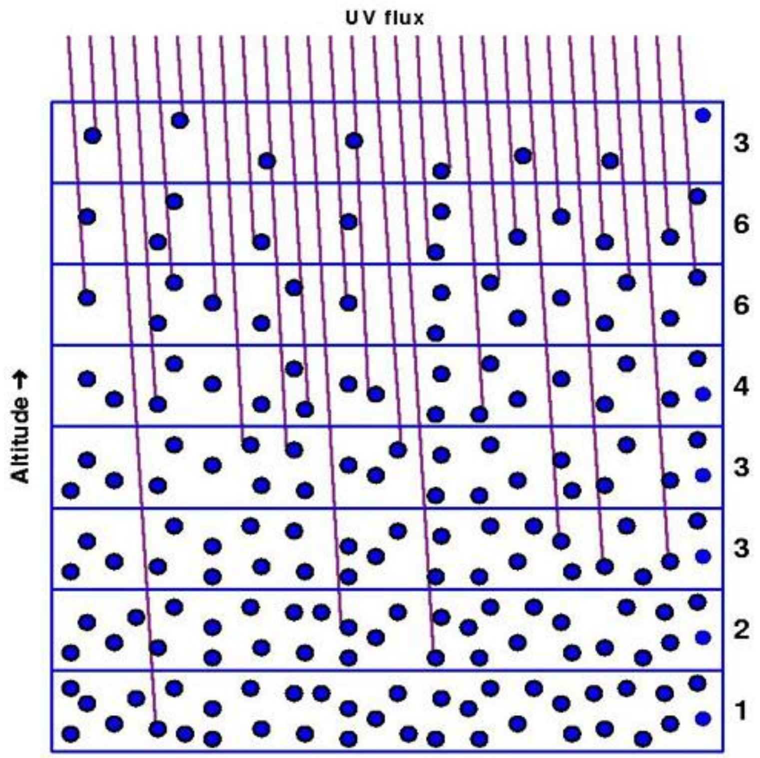




BUT: different reaction rates due to wavelength of light, relative concentrations ($[O_3]/[O_2]$= 1/100000), lifetimes (O: 10^{-4} – 10 s, O_3: 3-60 min), photon flux (↗ with h ↗), oxygen density (↘ with h ↗), etc.

3. Example: Ozone photolysis

We illustrate how the ozone photolysis rate (← absorption cross-section + # of incident photons + # O_3) depends on altitude, latitude, season and has some diurnal variation.



- Density of molecules decreases with higher altitude, and abosorption is proportional to the density of the molecules and the cross- section.
- Greatest absorption occurs in the middle layers where the density- cross section product has become large enough for significant absorption.

Dependence on altitude

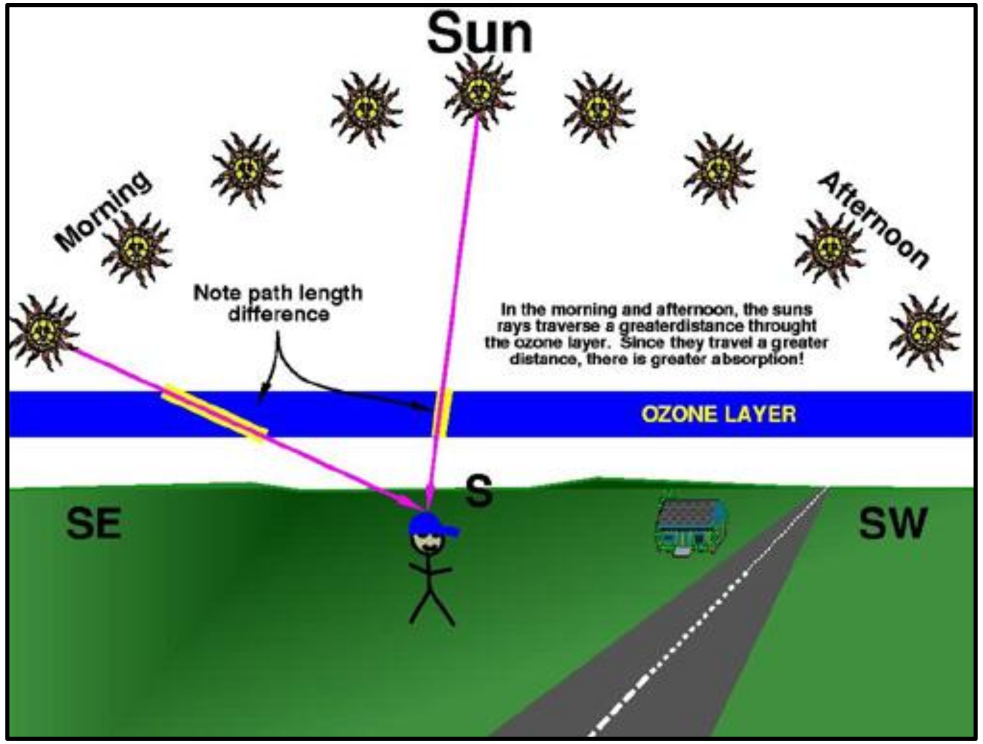
- steady flux of photons at the top of the atmosphere
- As they travel down through the atmosphere, these photons are intercepted by ozone and other molecules (→ less photons at lower altitudes)
- In the low density region at the top of the atmosphere, there are very few molecules to absorb photons, hence little absorption occurs at the highest altitudes.
- At lower altitudes, the density of molecules increases, hence the absorption becomes quite strong.

➢Ozone photolysis reaches a maximum in the middle layers of the atmosphere.

3. Example: Ozone photolysis

We illustrate how the ozone photolysis rate (← absorption cross-section + # of incident photons + # O_3) depends on altitude, latitude, season and has some diurnal variation.

Diurnal dependence



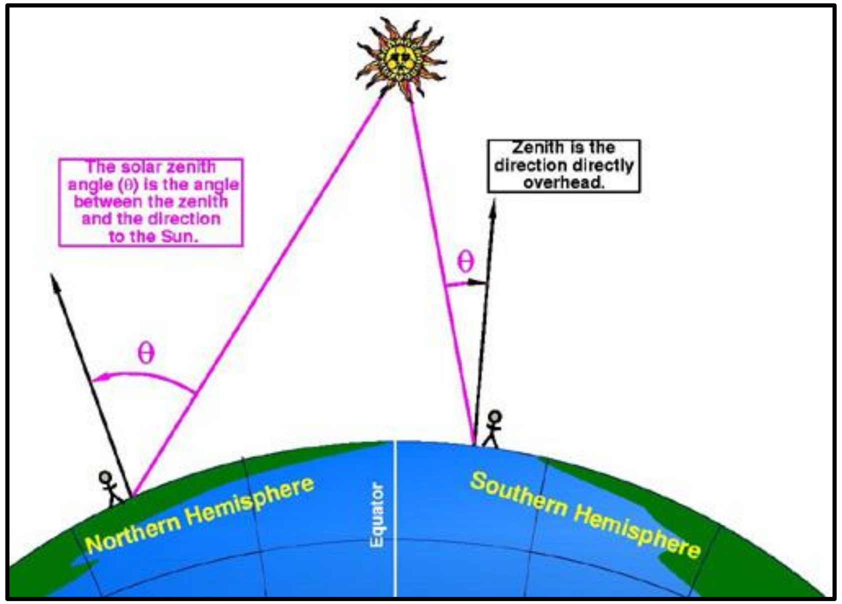
- at night: no sunlight → photolysis rate =0
- longest path lengths at sunrise and sunset, shortest at noon
- The longer the path that light must travel through the atmosphere, the more molecules the light will encounter, the more photons that get absorbed.

➢ Ozone photolysis rates for a given altitude are higher at noontime (more remaining photons) than at sunrise and sunset

3. Example: Ozone photolysis

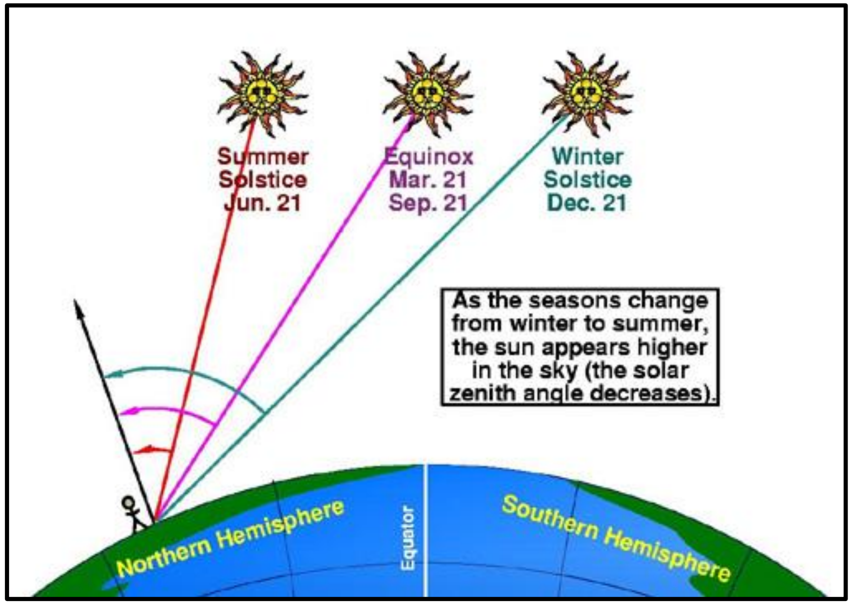
We illustrate how the ozone photolysis rate (← absorption cross-section + # of incident photons + # O_3) depends on altitude, latitude, season and has some diurnal variation.

Dependence on latitude



highest photolysis rates at tropics

Dependence on season

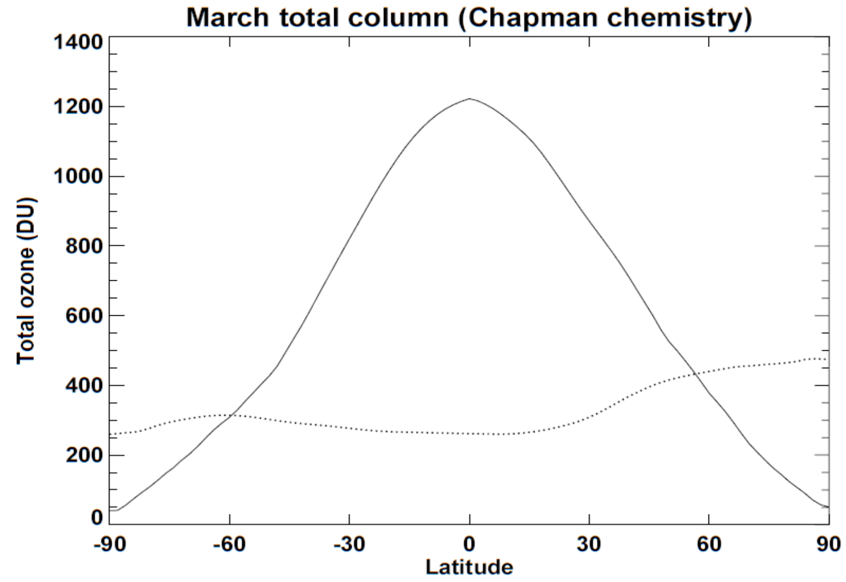


highest photolysis rates in summer

4. Total ozone column for the Chapman chemistry

Chapman chemistry

- Ozone is created in the middle to upper stratosphere of the tropics.
  - ☺ @ tropics: availability of the necessary extreme ultraviolet (EUV) light
  - @ these altitudes: the creation of ozone is maximized owing to two effects: a sufficient supply of oxygen and a sufficient amount of incoming UV light
- ☹ too much global average for column ozone (790 DU vs. 300 DU in measurements)
- ☹ Chapman estimates are much too high in the tropics, and too low in the polar regions



March total ozone column for Chapman chemistry (solid line) and measured by satellite instrument (dotted line)

1. reactions of O_X with other trace gases alter the ozone budget (**catalytic loss**)
2. Atmospheric circulation transports ozone from its tropical source region into the extratropics (**Brewer-Dobson**)

5. Catalytic loss

- Nobel Price in Chemistry in 1995 awarded to Paul Crutzen, Mario Molina and Sherwood Rowland “for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone”

- A catalyst is a substance, usually present in small amounts, that facilitates chemical reactions without itself being consumed by those reactions.

- In this catalytic process, the ozone molecule is lost while the catalyst is reformed to potentially destroy another ozone molecule.

- Most important catalysts for ozone loss: chlorine, nitrogen, bromine or hydrogen:
    - Cl_x ($Cl+ClO$)
    - NO_x ($NO+NO_2$)
    - Br_x ($Br+BrO$)
    - HO_x ($OH+HO_2$)

} catalytic cycles

5. Catalytic loss: a Cl_x catalytic cycle

- The catalyst is ClO, which reacts with an ozone atom to form Cl and O2

  $O_3 + hc/\lambda \rightarrow O + O_2$

  $ClO + O \rightarrow O_2 + Cl$

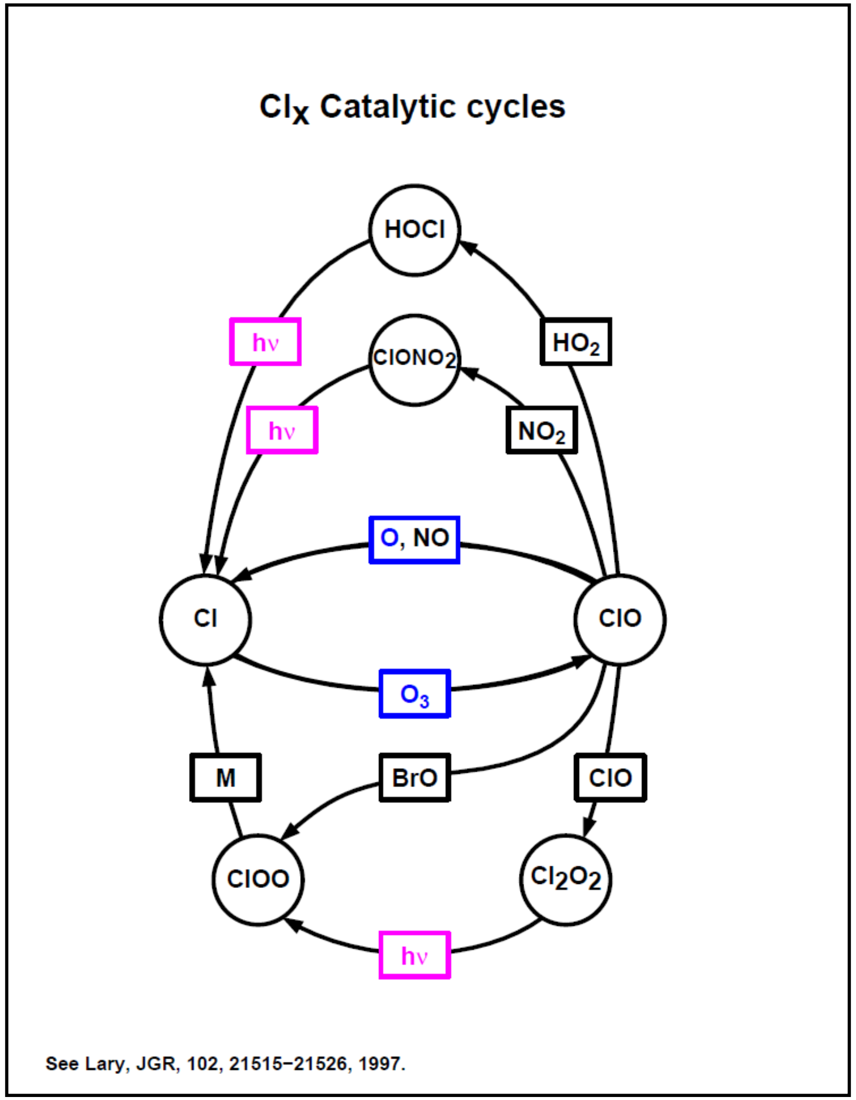
  $Cl + O_3 \rightarrow O_2 + ClO$

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

- At 40 km, this Cl-ClO catalytic chain can destroy nearly 1000 ozone molecules before the Cl or ClO is converted to a benign chlorine form (“reservoir species”) such as HCl, $ClONO_2$, and, to a lesser extent HOCl.

- HCl/$ClONO_2$ and HOCl typically last for days and hours respectively, and are photolyzed by UV radiation. This again frees the chlorine to destroy more ozone.

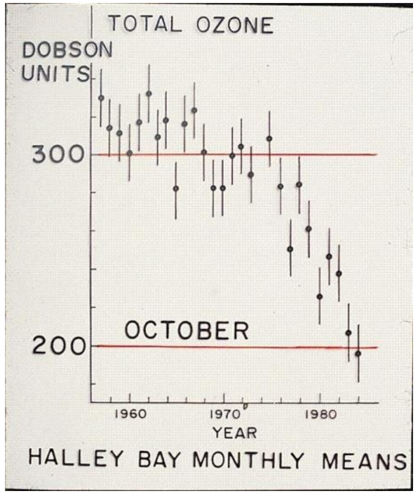
- Eventually, the Cl atom is carried out of the stratosphere. Over its lifetime in the stratosphere, an individual Cl atom can destroy about 100000 ozone molecules.



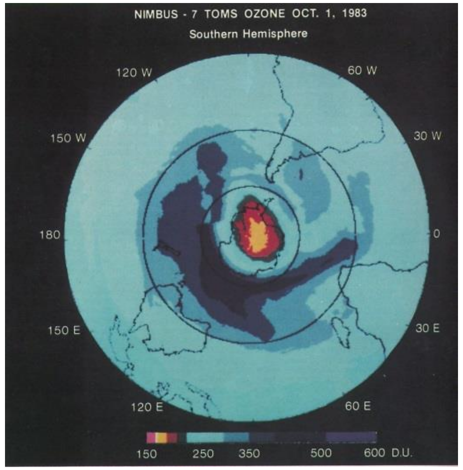
See Lary, JGR, 102, 21515–21526, 1997.

Discovery of the ozone hole

- In 1985, **Joseph Farman** and colleagues noted a drastic depletion of the ozone layer over the Antarctic, the "ozone hole“.
- The surprisingly rapid depletion of the ozone layer over Antarctica could not be explained by transport processes or by gas phase chemical reactions. **Crutzen** and colleagues identified the alternative mechanism as chemical reactions on the surface of cloud particles in the stratosphere.



Farman et al., *Nature*, 1985



Barthia et al., August 1985

6. Heterogeneous chemistry

- A heterogeneous reaction is a **chemical process that involves solid, liquid, and gaseous phases** (hence, it is a multiphase process). Heterogeneous chemistry occurs on or in condensed particles (such as liquid water droplets or solid ice particles) that are in contact with gaseous molecules.

- Such multiphase processes include adsorption (i.e. adhesion of a thin layer of molecules to a surface) or **absorption of molecules onto particles. This is followed by chemical reactions on the particle surfaces or within the particles themselves.**

- Stratospheric particles of interest:
  - ✓ sulfate aerosols, typically composed of a solution of sulfuric acid (H_2SO_4) and water. The sulfuric acid comes from carbonyl sulfide (COS) and sulfur dioxide (SO_2) carried into the stratosphere via tropical lifting, or by direct injection of SO_2 into the stratosphere from very explosive volcanic eruptions, such as El Chichon in 1982 or Mount Pinatubo in 1991.
  - ✓ polar stratospheric clouds (PSCs): clouds in the winter polar stratosphere.
    - ○ at very high altitudes, between 15 and 25 km
    - ○ at temperatures of around -80ºC (192 K), colder than average lower stratosphere temperatures
    - ○ at those extremely low temperatures, water and nitric acid (HNO_3) condense to form clouds
    - ○ associated with the polar vortex: during the long dark Antarctic winter, stratospheric winds move in a circular pattern over the polar region, isolating the air above the Antarctic land mass.

6. Heterogeneous chemistry

- The reservoir species (HCl, $ClONO_2$) are mostly nonreactive in their gaseous state.
- However, dissolved in liquid sulfate aerosol particles or on the surfaces of PSCs, they become highly reactive with one another:

  $ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

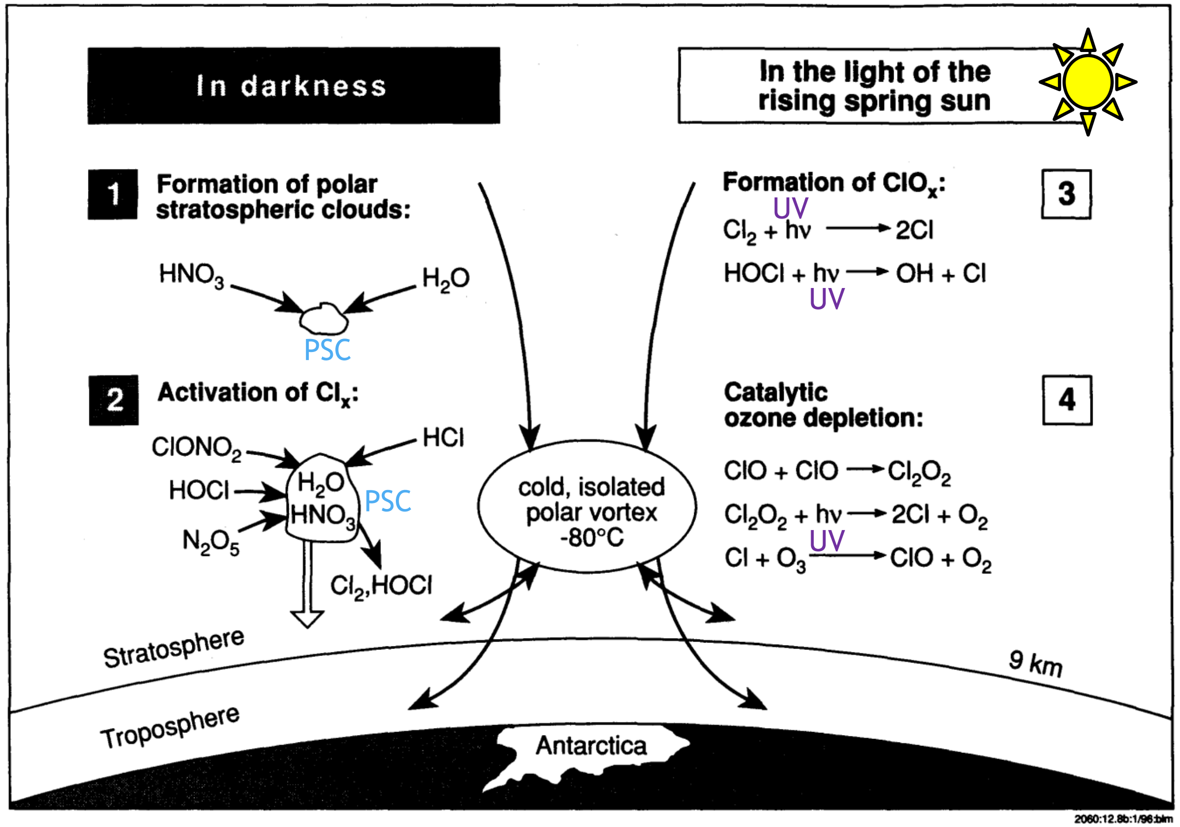
  $ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

  $HOCl + HCl \rightarrow Cl_2 + H_2O$

  2

- The formed nonreactive HNO_3 remains in a solid (frozen) state on the surfaces of the PSC (type 2). As those PSCs undergo sedimentation, the HNO_3 is carried out of the stratosphere ("denitrification") 2

- The formed chlorine species Cl_2 and HOCl are short lived. They are quickly photolyzed by sunlight (even in visible wavelengths!) when the sun returns to the Antarctic in the early Spring. 3

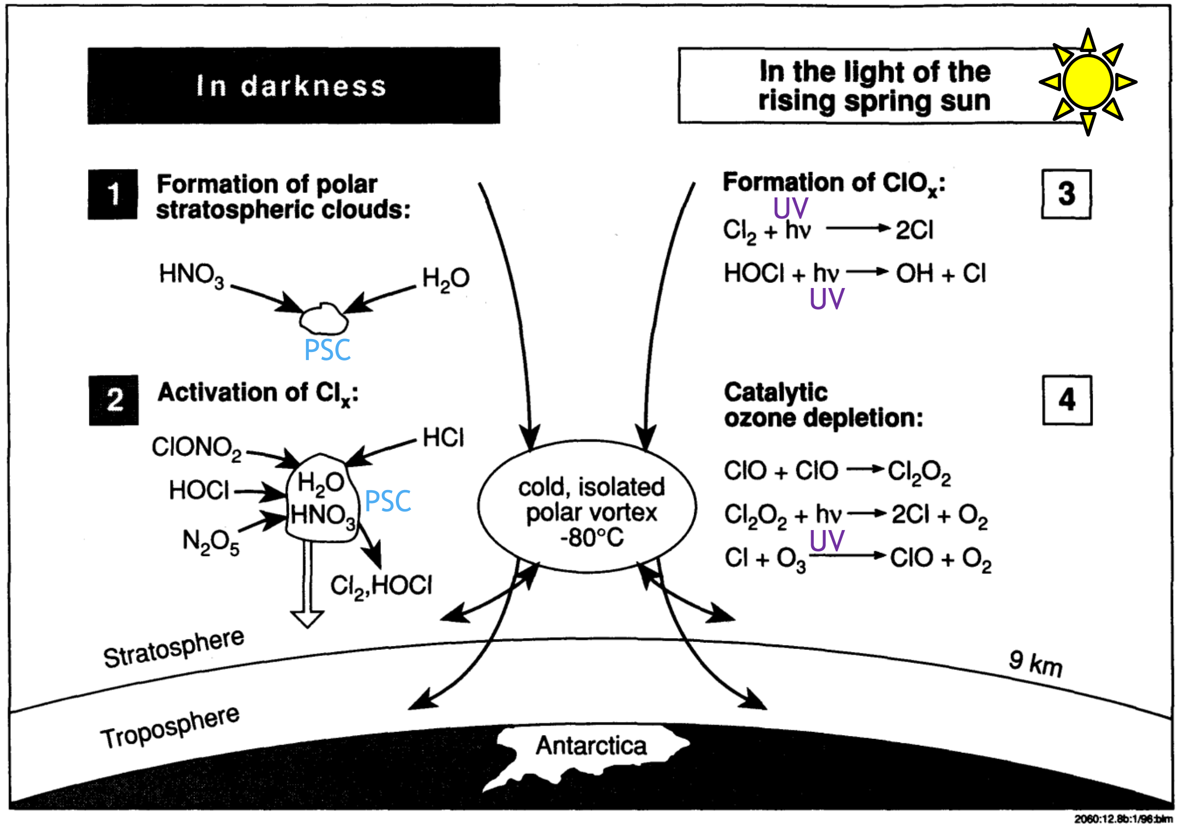


6. Heterogeneous chemistry

- As a result, via the Cl-ClO catalytic chain, ozone can be destroyed over this area in the spring season. 4

- Moreover, as NO_2 is locked up as nonreactive HNO_3 in the ice crystals, it cannot deactivate chlorine ($ClO + NO_2 \rightarrow ClONO_2$) and helps to maintain high levels of active chlorine!

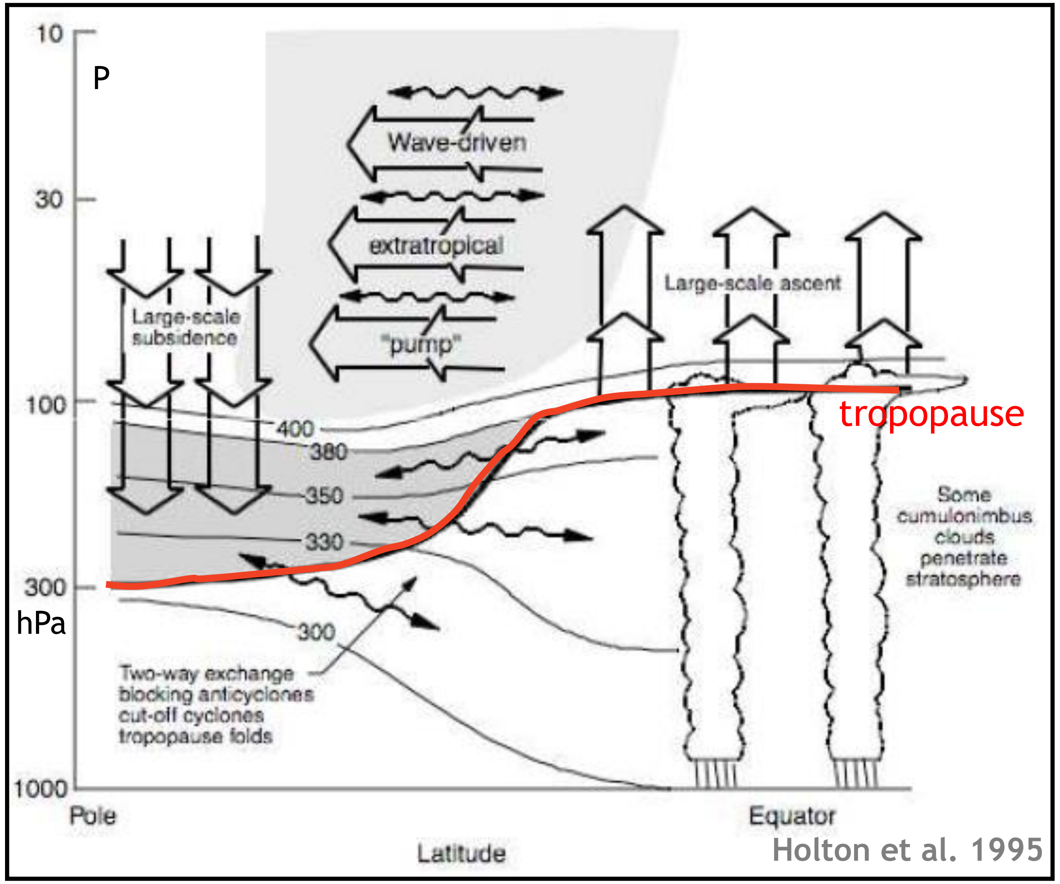
- Key ingredients to have ozone loss at the poles
  - ✓Chlorine: ClO catalytic cycle
  - ✓Cold: polar vortex
  - ✓Seasons: dark and light
  - ✓Clouds: PSCs
  - ✓UV radiation: springtime sunlight



7. Brewer-Dobson circulation

General principle

- The Brewer-Dobson circulation consists of 3 parts:
  - ✓rising tropical motion from the troposphere into the stratosphere
  - ✓poleward transport in the stratosphere
  - ✓descending motion in both the stratospheric middle and polar latitudes
    - ❖The middle latitude descending air is transported back into the troposphere
    - ❖the polar latitude descending air is transported into the polar lower stratosphere, where it accumulates.



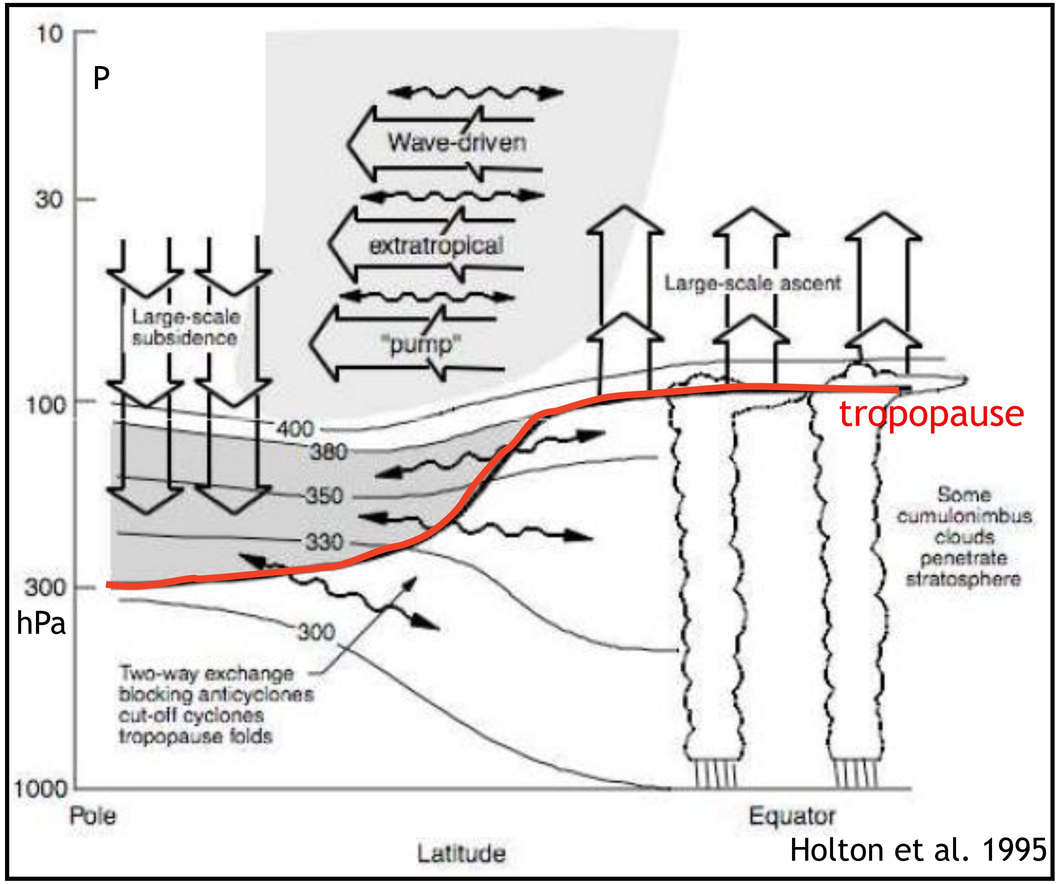
Holton et al. 1995

7. Brewer-Dobson circulation

Implications for ozone

- Tropics:
  - “ozone clean” air moves slowly upward in the tropical stratosphere, where ozone is being created by the slow photochemical production caused by the interaction of solar UV radiation (most intense there) and molecular oxygen.
  - even though ozone production is small and slow in the lower tropical stratosphere, the slow lifting circulation (6 months to raise air from 16 to 27 km) allows enough time for ozone to build-up.

- Extra-tropical latitudes:
  - poleward of about 30°N and 30°S, the Brewer-Dobson circulation becomes downward as well as poleward, hereby transporting the ozone-rich air to the lower stratosphere and increasing the ozone concentrations there.
  - As the lifetime of ozone in lower stratosphere is long (very few O atoms there), it is not easily destroyed and can accumulate.



Holton et al. 1995

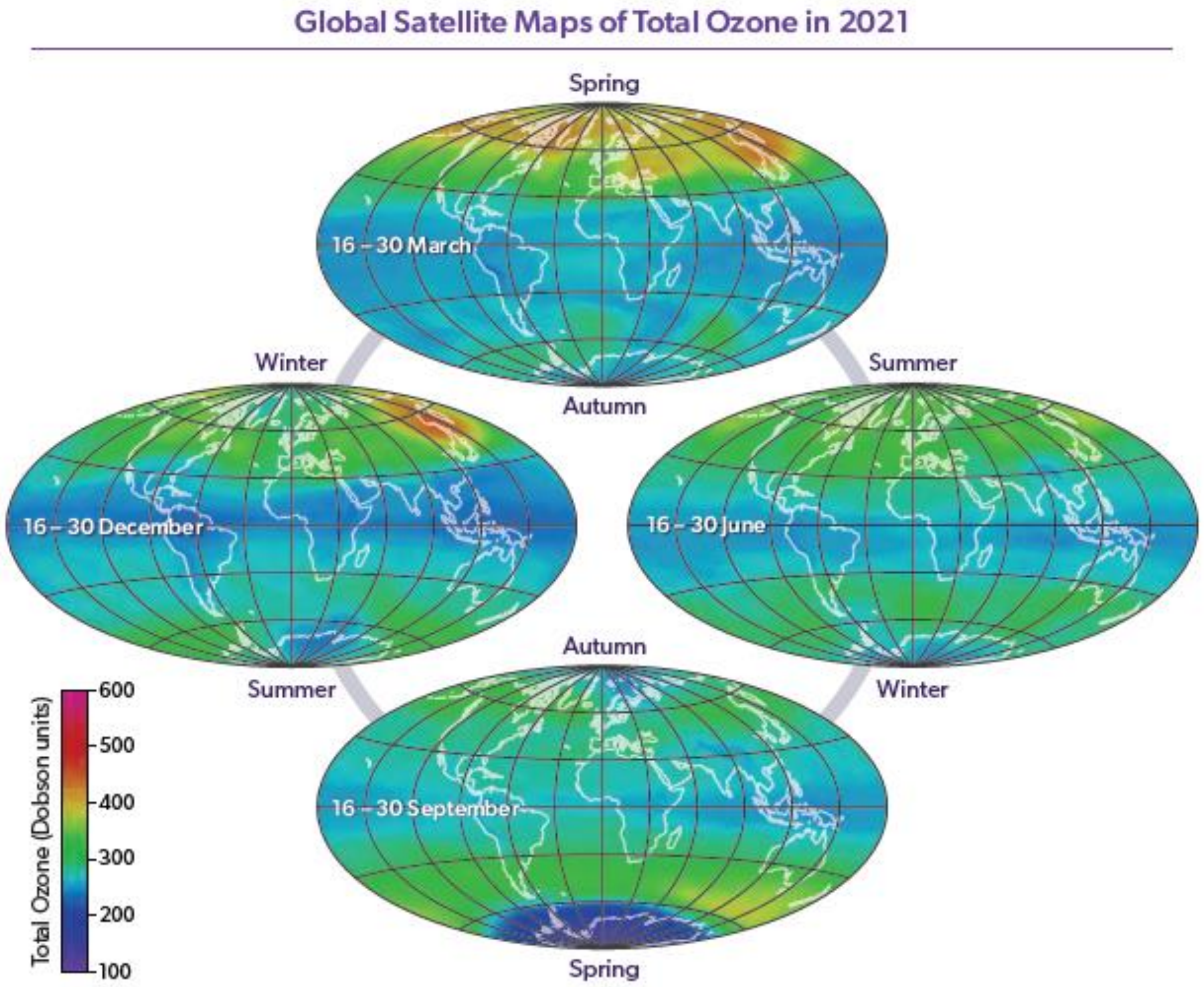
7. Brewer-Dobson circulation

Global total ozone distribution

- total ozone is generally lowest at the equator and highest in polar regions, due to the Brewer-Dobson transport

- this transport of ozone is strongest during late fall and winter and in NH (because of the prominent topography and more pronounced land-ocean contrasts in the northern hemisphere) ➔ highest ozone amounts late winter and early spring

- very small ozone amounts in the Antarctic in September-October: “ozone hole”



1. Ozone Depleting Substances (ODS)

- In the stratosphere, natural ozone creation and natural ozone destruction are in equilibrium.

- Stratospheric ozone is destroyed when it reacts with molecules containing nitrogen, hydrogen, chlorine or bromine.

- In the 1950s, CFCs (chlorofluorocarbons) or “Freon” were introduced in the industry as “miracle compounds”: inert, non-toxic, non-flammable, long-living, cheap, safe, many applications:
  - ✓ foam blowing
  - ✓ aerosol propellants
  - ✓ refrigeration and air conditioning
  - ✓ industrial cleaning of metals and electronic components

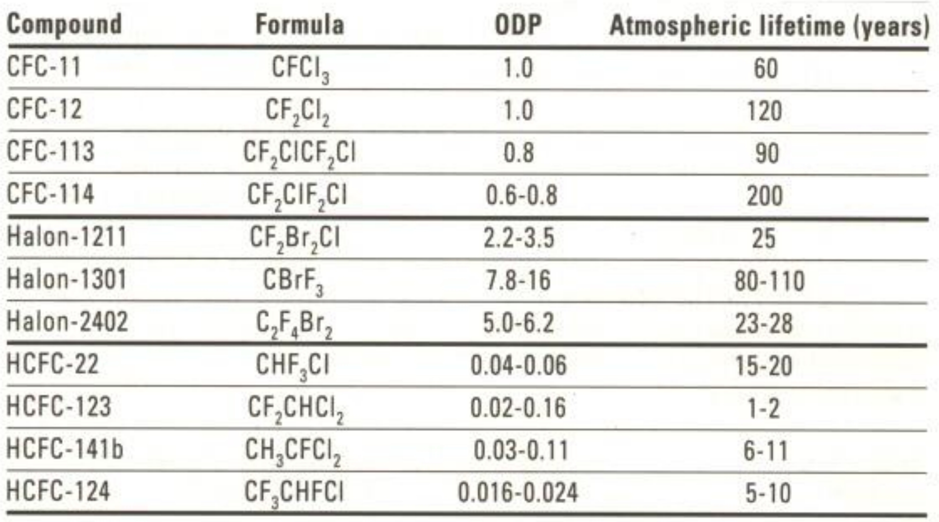
- Other halons (halogeneted hydrocarbons) contain also Br and have been used in fire extinguishing systems.

- These CFCs and other halons are transported to the stratosphere (e.g. by tropical lifting).

- In the stratosphere, Cl and Br are freed from CFCs and halons by UV photolysis, and they are converted to reactive gases containing chlorine and bromine that lead to ozone depletion through the Cl_x and Br_x catalytic cycles.

2. The Montréal Protocol

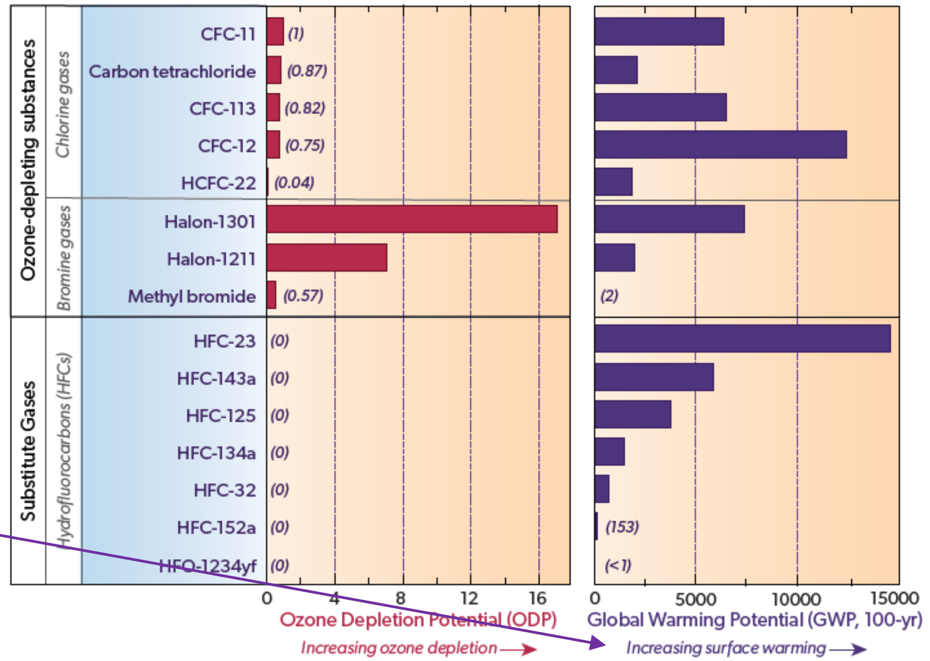
- Due to the discovery of the ozone hole, the global production and consumption of ODS (mainly CFCs and halons) was regulated by the Montréal Protocol (signed in 1987).
- A phase-out of the production of CFCs and Halons was foreseen, and they were replaced by HCFCs (also containing H) and HFCs (hydrofluorocarbons) for many applications.
- HCFCs have smaller ozone depleting potentials (reference = CFC-11) and shorter atmospheric lifetimes; HFCs are not ODS.
- In Oct 2016, a Protocol amendment that controls HFCs has been signed in Kigali, Rwanda.
- all these substances are greenhouse gases (global warming potential)!



Compound	Formula	ODP	Atmospheric lifetime (years)
CFC-11	$CFCl_3$	1.0	60
CFC-12	CF_2Cl_2	1.0	120
CFC-113	CF_2ClCF_2Cl	0.8	90
CFC-114	CF_2ClF_2Cl	0.6-0.8	200
Halon-1211	CF_2Br_2Cl	2.2-3.5	25
Halon-1301	$CBrF_3$	7.8-16	80-110
Halon-2402	$C_2F_4Br_2$	5.0-6.2	23-28
HCFC-22	CHF_3Cl	0.04-0.06	15-20
HCFC-123	CF_2CHCl_2	0.02-0.16	1-2
HCFC-141b	CH_3CFCl_2	0.03-0.11	6-11
HCFC-124	CF_3CHFCl	0.016-0.024	5-10

Evaluation of Selected Ozone-Depleting Substances and Substitute Gases

Relative importance of equal mass emissions for ozone depletion and climate change



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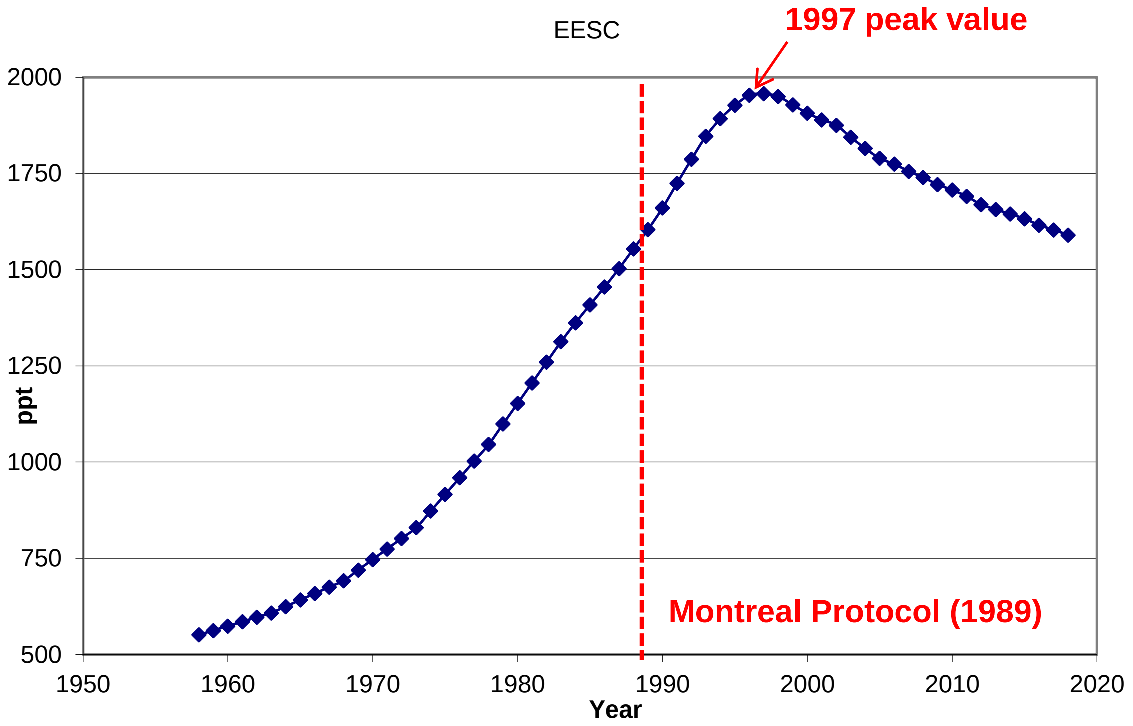


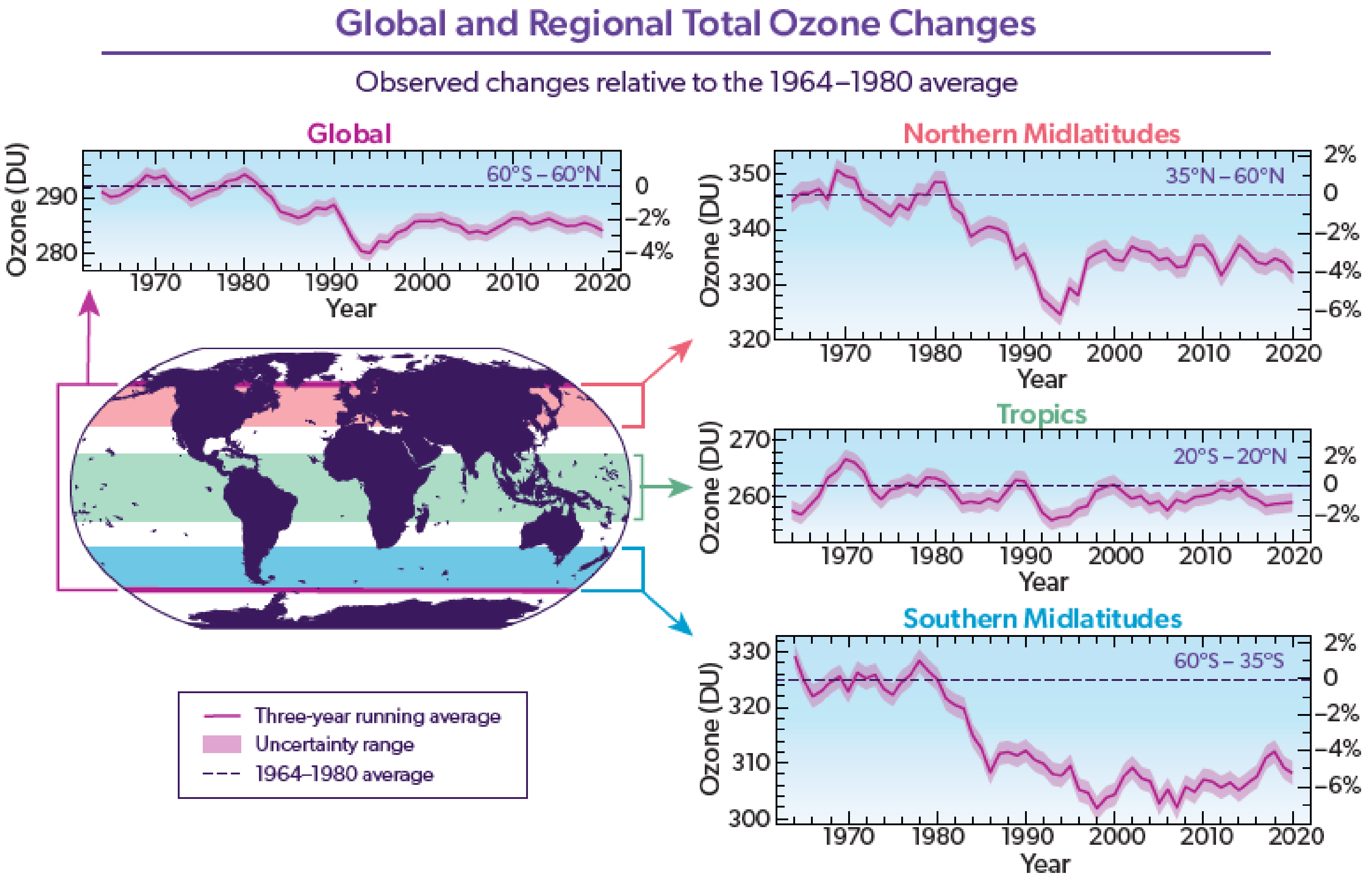
EESC

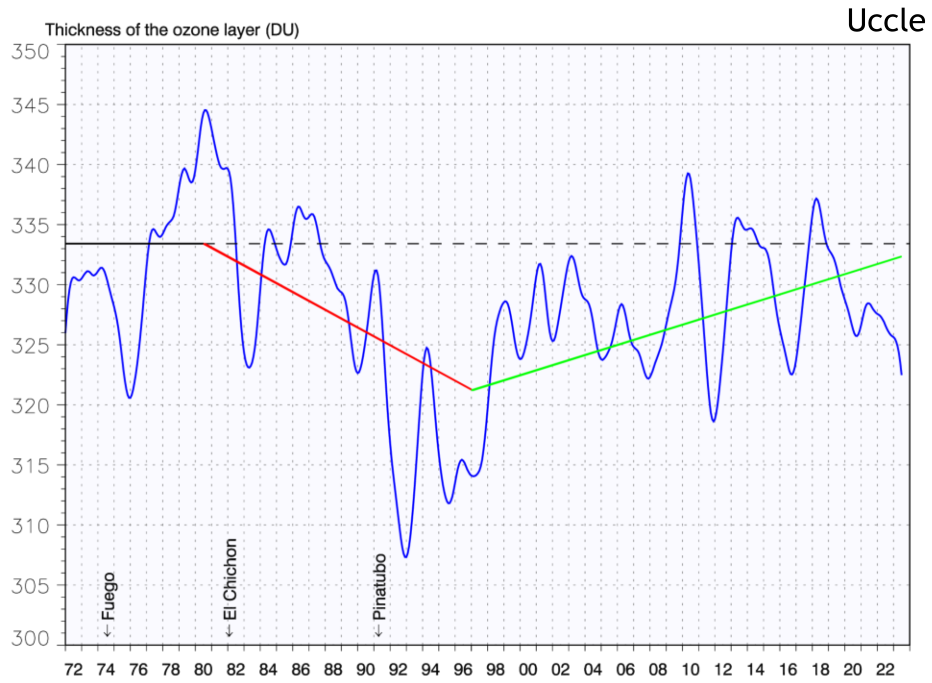
= equivalent effective stratospheric chlorine

= a relative measure of the potential for stratospheric ozone depletion that combines the contributions of chlorine and bromine from surface observations from Ozone Depleting Substances (ODS)

- due to the long lifetimes of some CFCs and halons (50-100 years) in the stratosphere, the decline is rather slow.

3. Ozone variability: Global (total ozone)

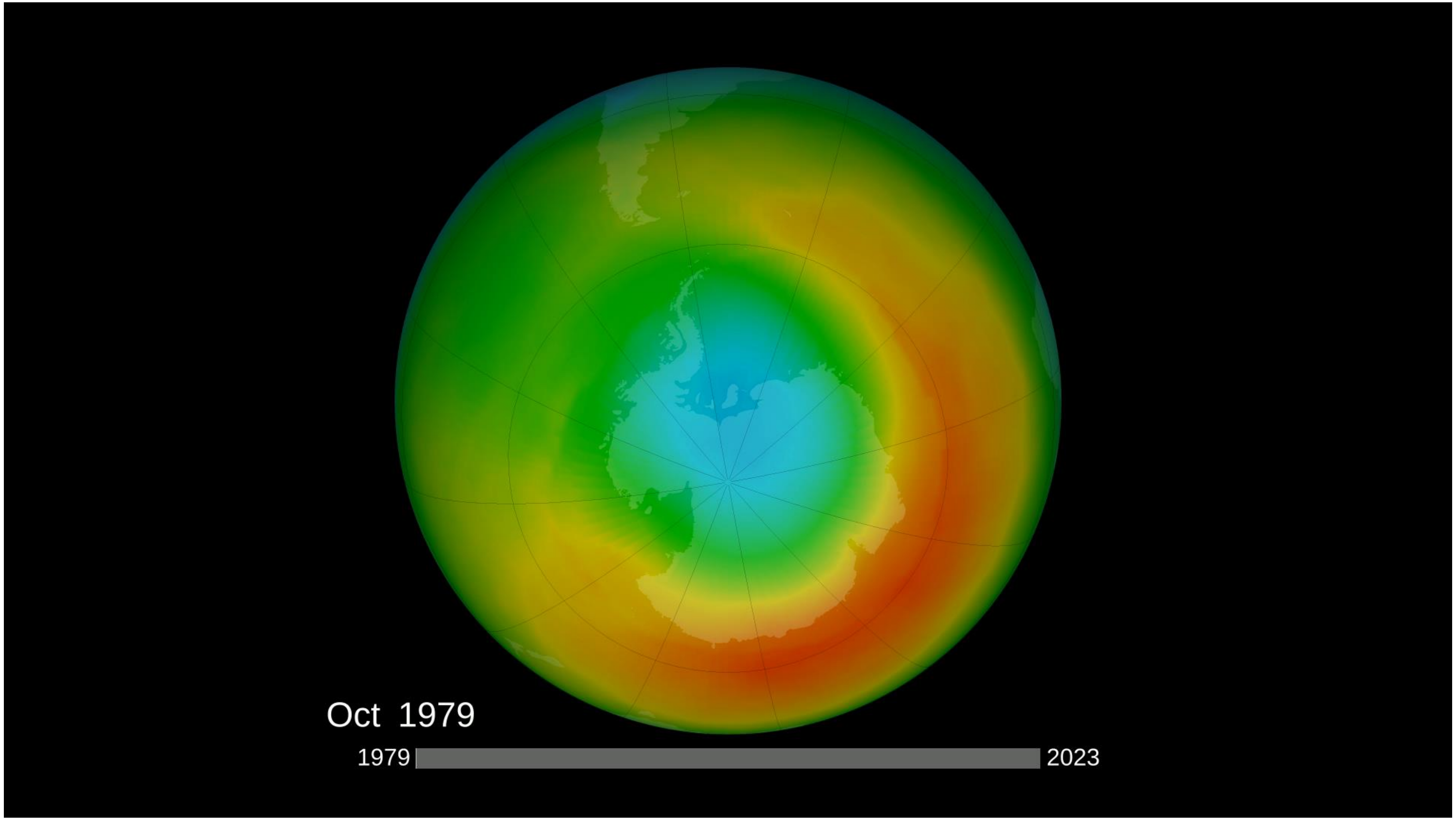




- onset of total ozone recovery?
- highly uncertain due to large year to year variability in most recent year (→ dynamics, impact of volcanic eruptions)
- latitude dependent!

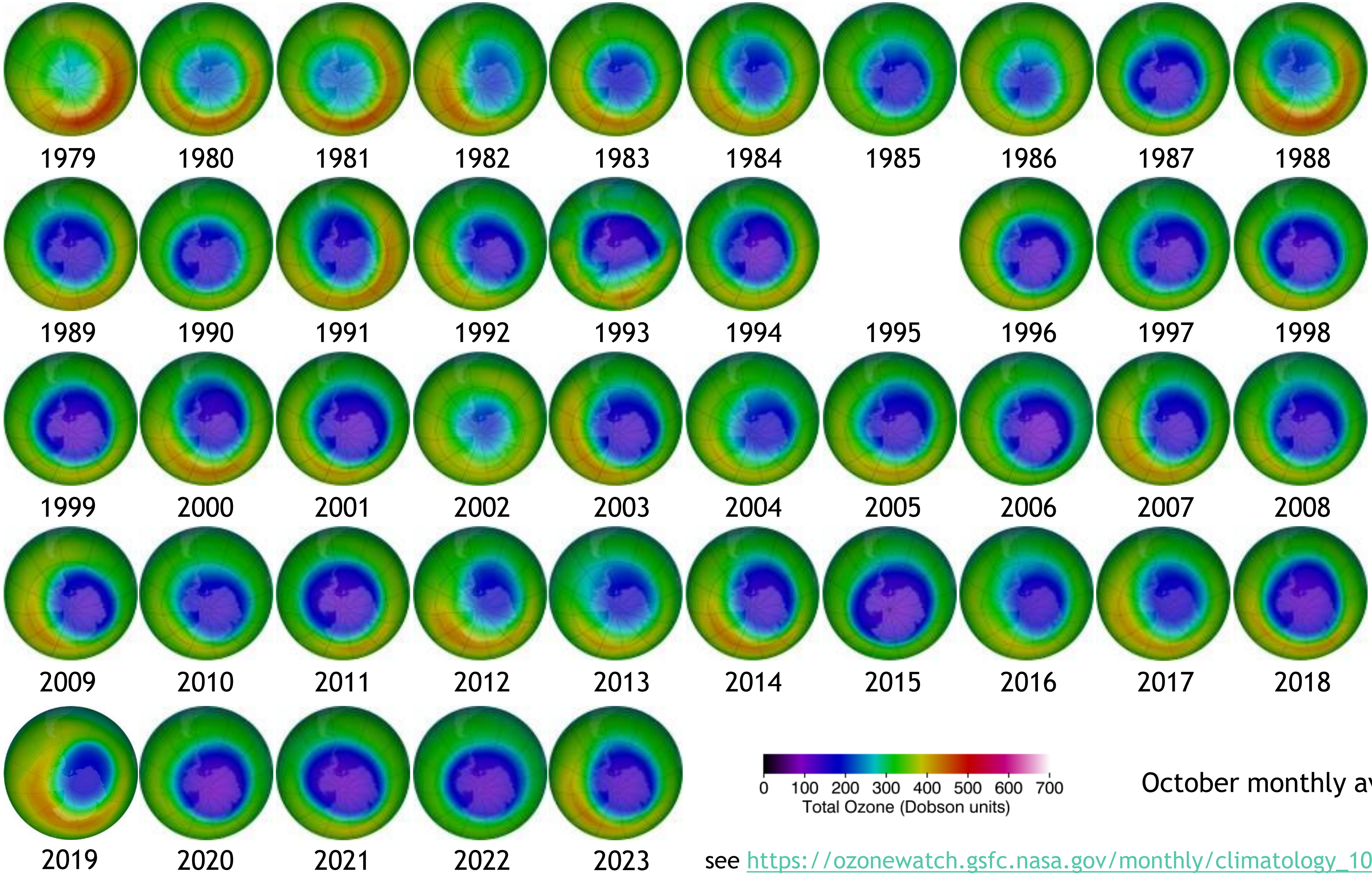
WMO Scientific Assessment of Ozone Depletion, 2022

3. Ozone variability: Antarctic



https://ozonewatch.gsfc.nasa.gov/ozone_maps/movies/OZONE_D1979-10%25P1Y_G%5e1920X1080.IOMPS_PNPP_V21_MMERRA2_LSH.mp4

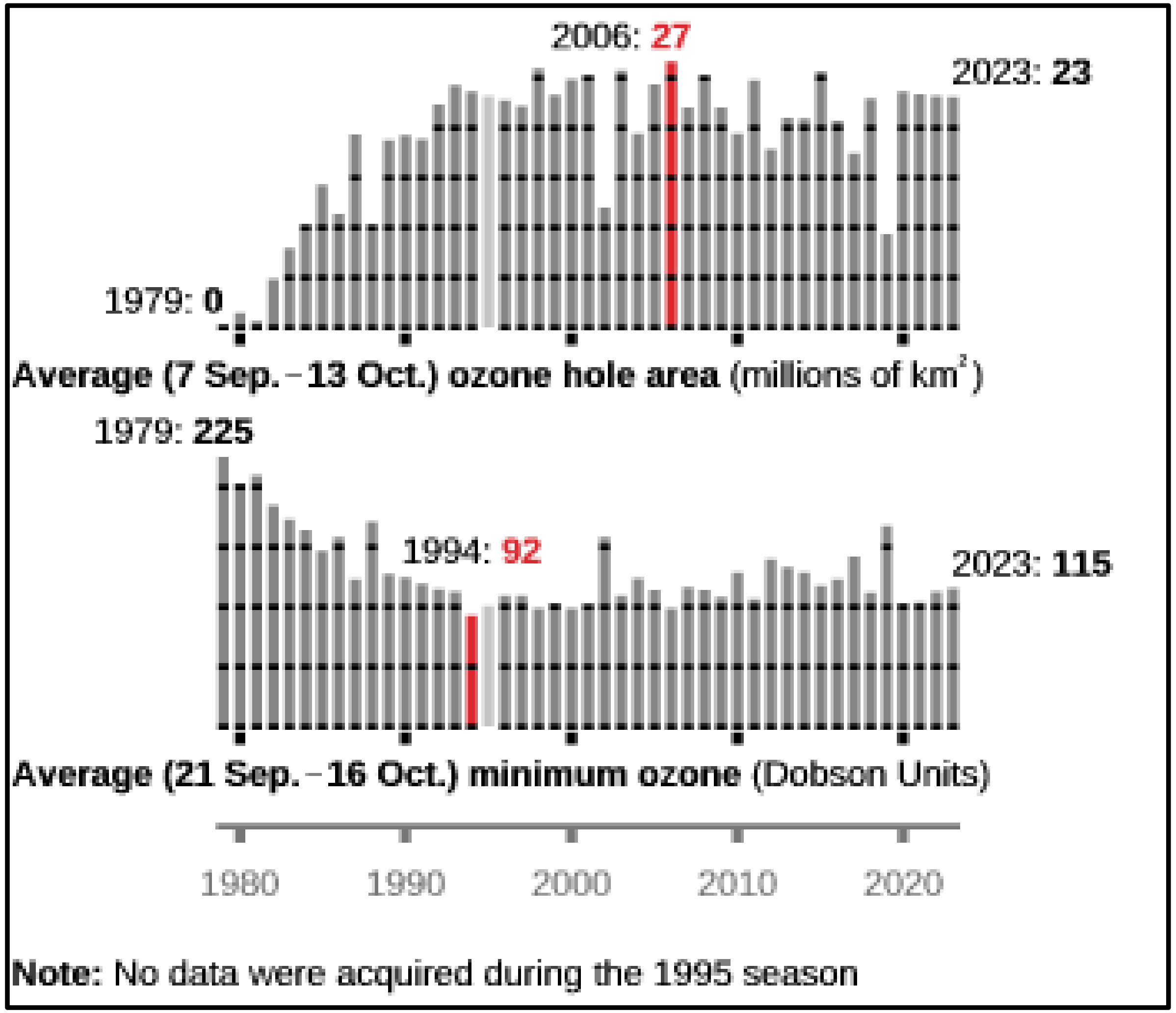
3. Ozone variability: Antarctic



October monthly averages

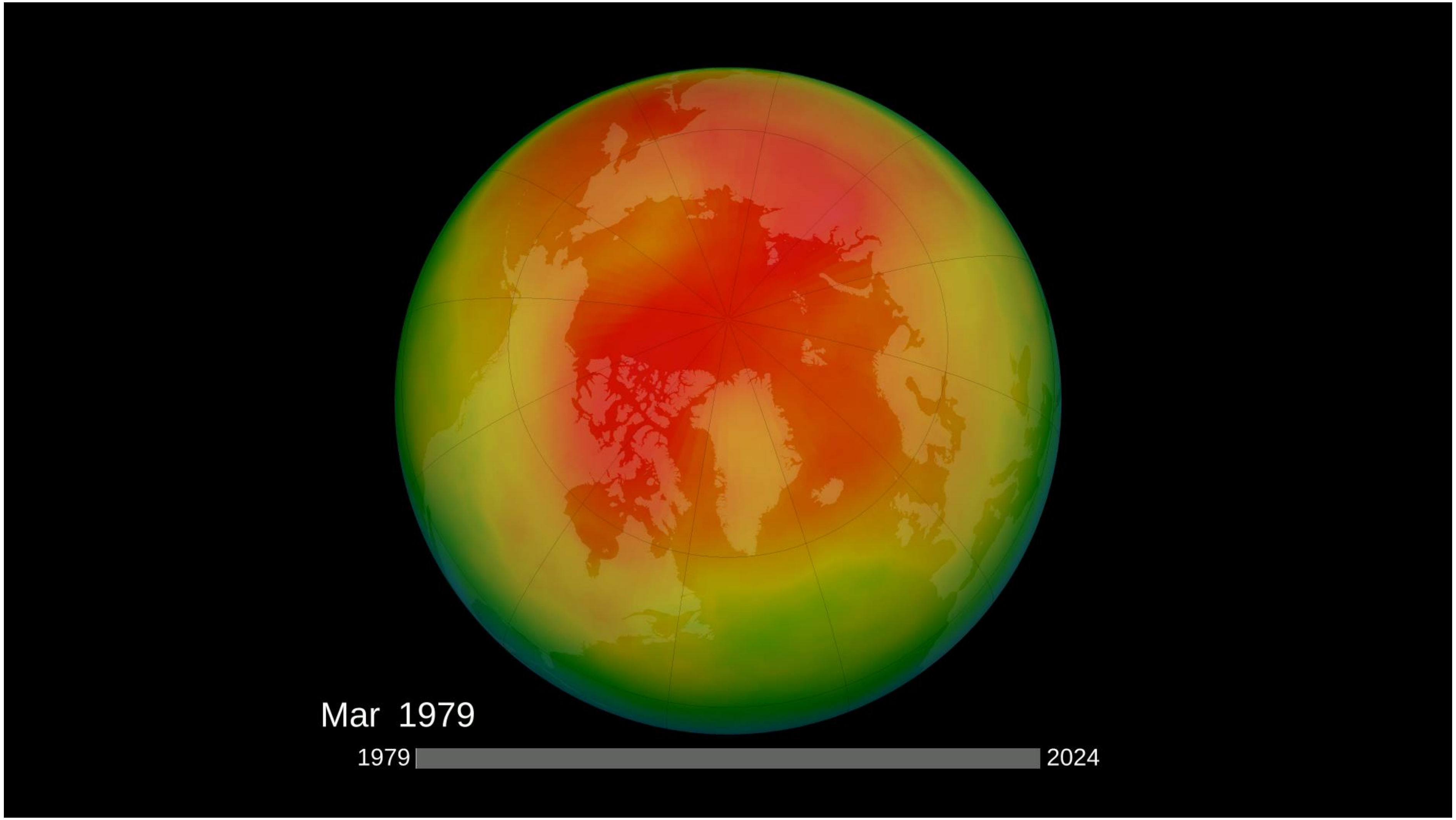
see https://ozonewatch.gsfc.nasa.gov/monthly/climatology_10_SH.html

3. Ozone variability: Antarctic



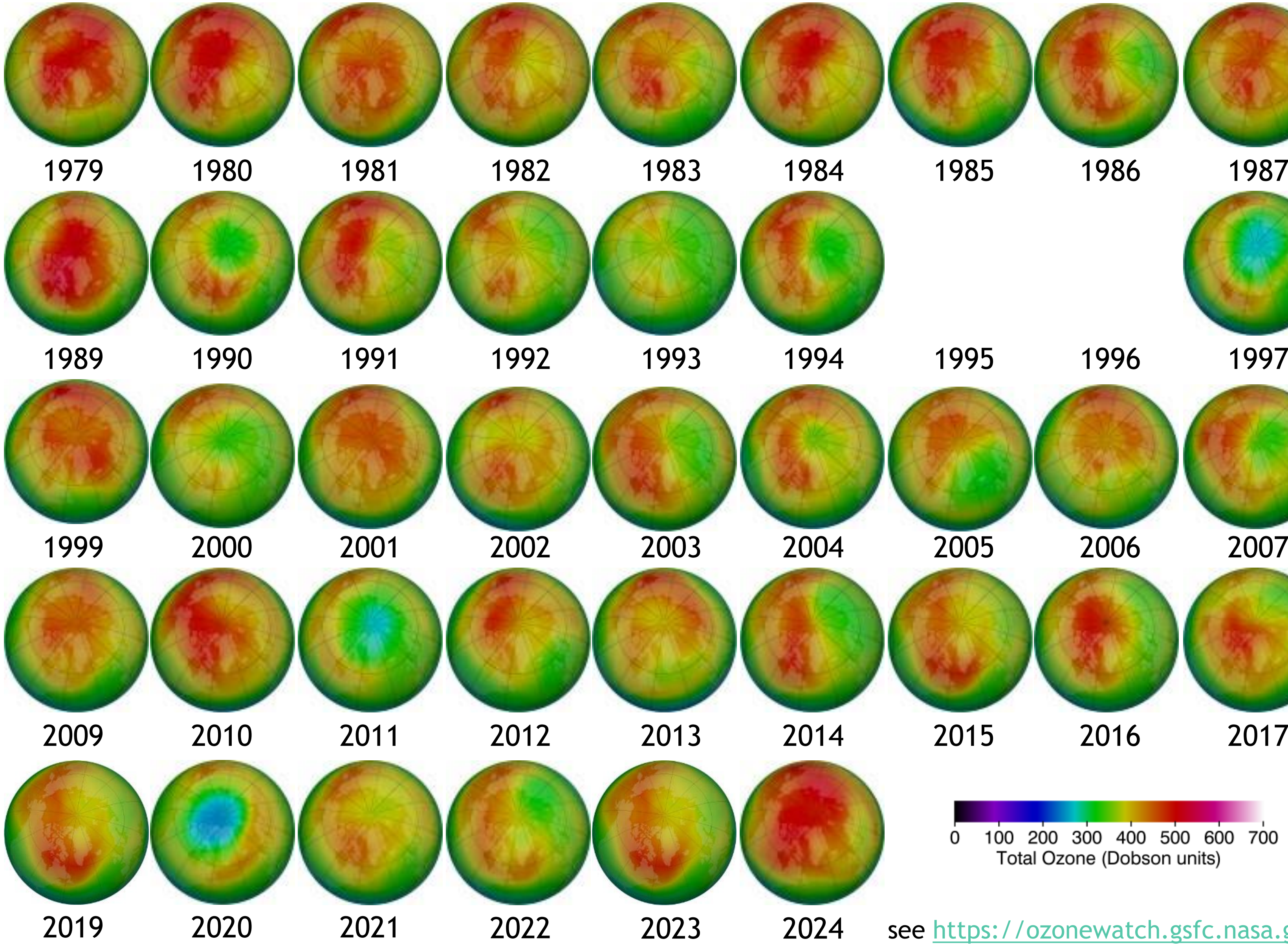
Note: No data were acquired during the 1995 season

3. Ozone variability: Arctic



https://ozonewatch.gsfc.nasa.gov/ozone_maps/movies/OZONE_D1979-03%25P1Y_G%5e1920X1080.IOMPS_PNPP_V21_MMERRA2_LNH.mp4

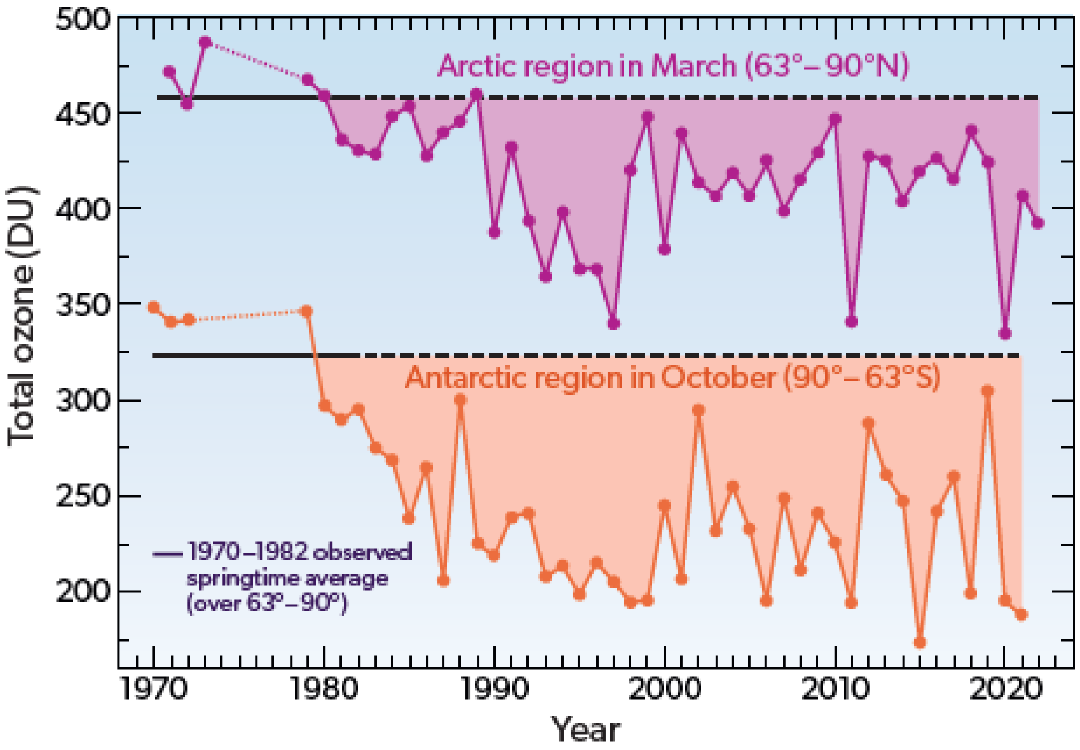
3. Ozone variability: Arctic



March monthly averages

see https://ozonewatch.gsfc.nasa.gov/monthly/climatology_03_NH.html

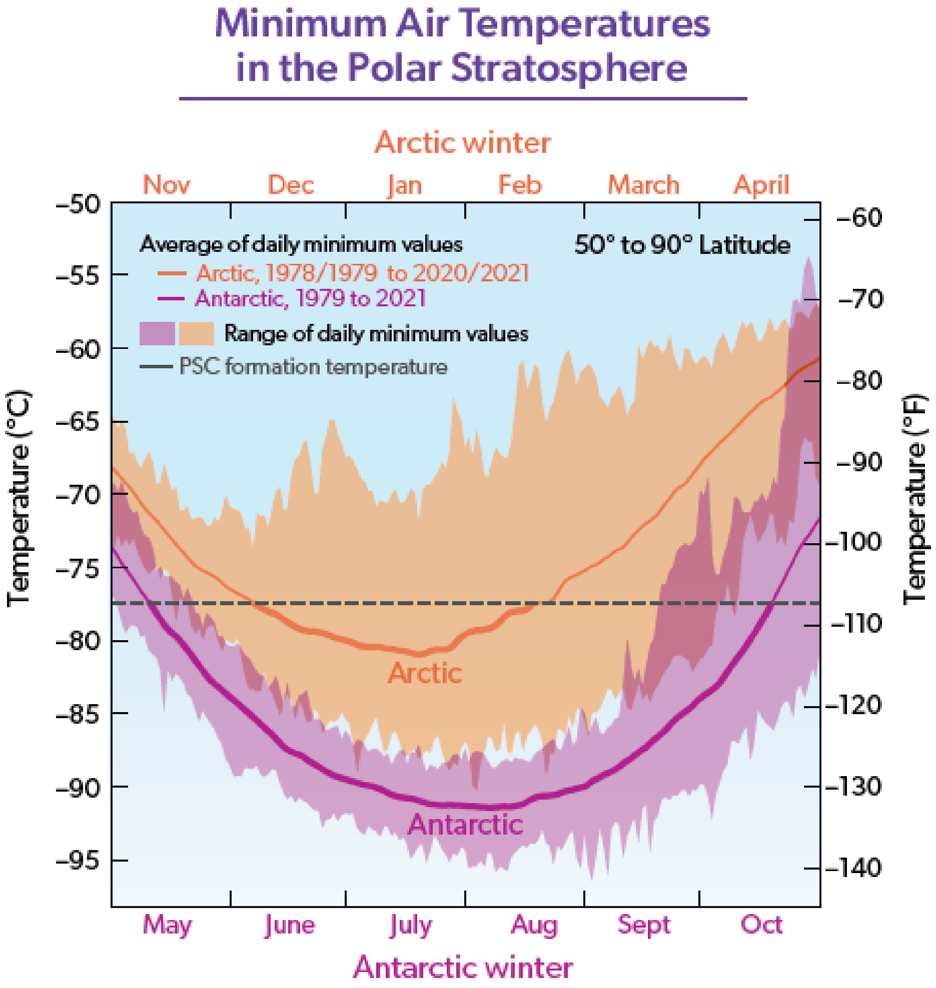
3. Ozone variability: Arctic vs. Antarctic


Average Total Ozone in Polar Regions

- consistently lower springtime ozone amounts above the Antarctic region compared to Arctic.
- Arctic ozone holes in 1997, 2011, 2020
- presence/absence of (polar) vortex is essential for facilitating the creation of ozone holes!

WMO Scientific Assessment of Ozone Depletion, 2022

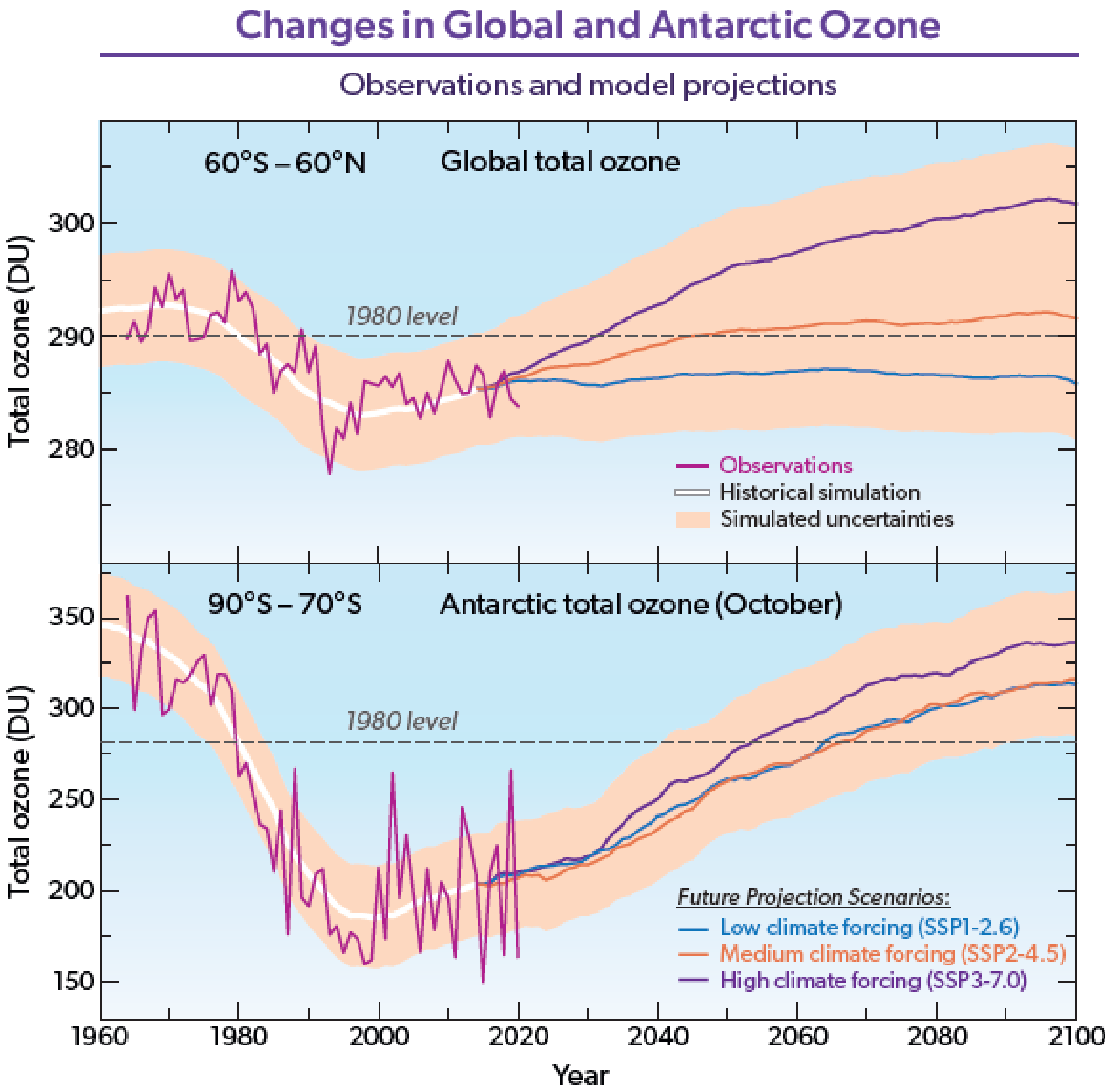
3. Ozone variability: Arctic vs. Antarctic



WMO Scientific Assessment of Ozone Depletion, 2022

- much lower stratospheric temperatures in Antarctic vs. Arctic
- the PSC areas are much smaller in the Arctic than in the Antarctic

1. Ozone-climate is a 2-way interaction: climate → ozone



models show differing amounts of ozone changes for different greenhouse gas scenarios: **ozone layer recovery is influenced by climate change** (and acting differently at different locations on Earth)

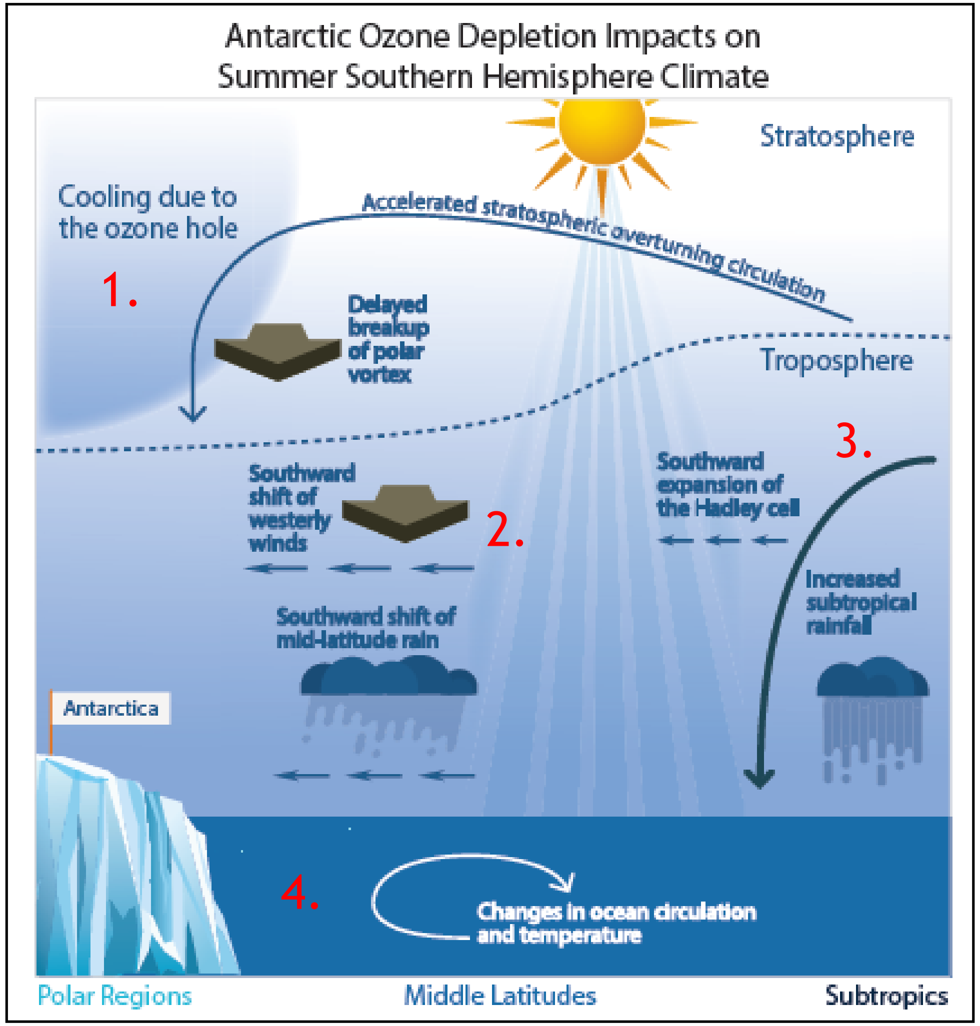
- GHGs cool the stratosphere
  - * slow down of gas phase ozone destruction: O_3 up
  - * in colder conditions more PSCs can be formed for a longer time: O_3 down at the poles
- GHGs strengthen Brewer-Dobson circulation
- GHGs interact chemically with ozone

From WMO Scientific Assessment of Ozone Depletion, 2022

2. Ozone-climate is a 2-way interaction: ozone → climate

- climate has been affected by ozone loss and will be influenced by the trajectory of ozone recovery
  - ✓ tropospheric ozone is a greenhouse gas!
  - ✓ stratospheric temperatures
  - ✓ tropospheric circulation, temperatures and precipitation

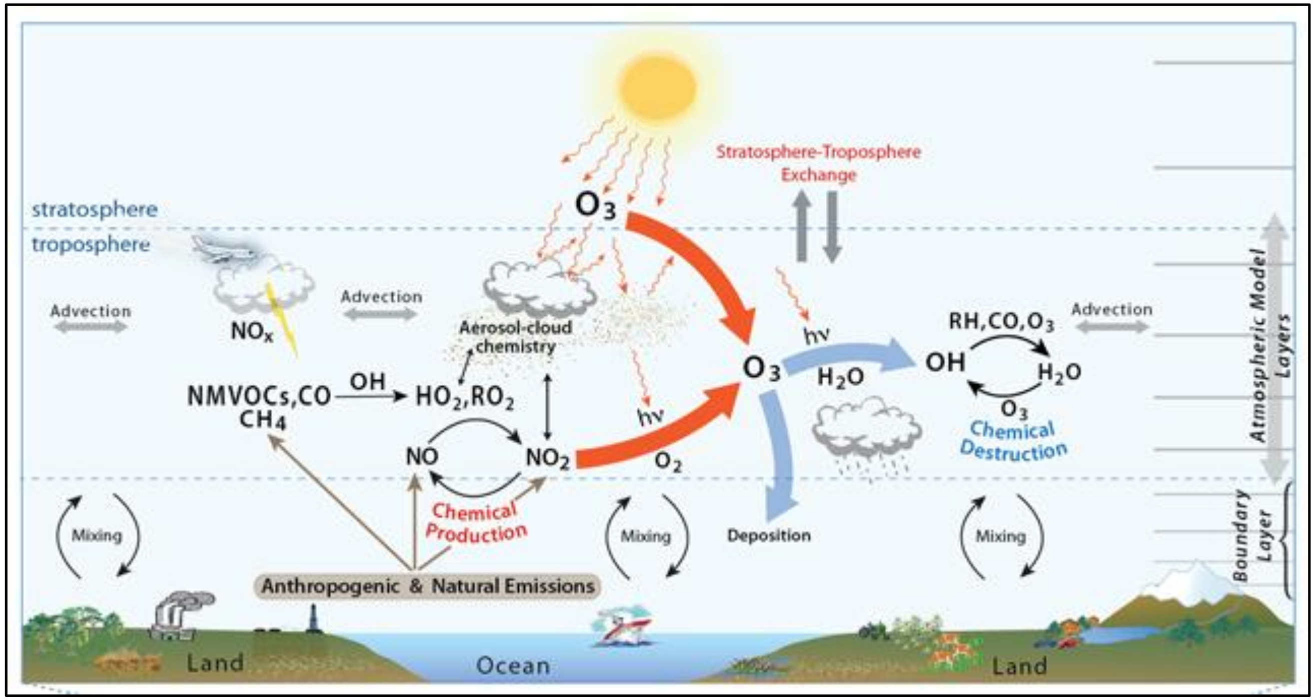
1. The O_3 hole cools the lower stratosphere during the Austral spring and summer.
2. The cooling is very likely the dominant cause of the Southern Hemisphere tropospheric midlatitude jet to strengthen and shift poleward in summer.
3. The hole contributes to a Hadley circulation expansion, with an associated increase of summer subtropical precipitation.
4. The increased tropospheric jet increases surface wind stress, thereby changing the ocean's circulation
5. No robust link between stratospheric ozone changes and Northern Hemisphere tropospheric climate has been found.


Antarctic Ozone Depletion Impacts on Summer Southern Hemisphere Climate

WMO Scientific Assessment of Ozone Depletion, 2018

Tropospheric ozone

- 10 % of atmospheric ozone
- strong oxidant detrimental to human health (smog!), crops and ecosystems
- important for tropospheric chemistry as the primary source of the OH radical, the so-called “detergent” of the atmosphere (O_3 + hv → O + O_2, O + H_2O → 2 OH), converting trace gases (like CO, CH_4) into water-soluble products that are washed out by rain and snow
- greenhouse gas: contributes to global warming
- formation/destruction of tropospheric ozone by
  - ✓ stratosphere-troposphere exchange
  - ✓ photochemical formation: sun + precursors (NO_x, CO and VOC)
  - ✓ photochemical destruction in low NO_x conditions (OH-HO_2 cycle)
  - ✓ dry deposition on the ground



From Young et al., *Elementa*, 2018

Take home messages

- The role of ozone in the atmosphere: the story of “the good” (stratosphere) and “the bad” (troposphere).
- Ozone is formed by photolysis with UV light, hereby heating up the stratosphere.
- Ozone is destroyed by reactions involving Cl, Br, N, and H atoms.
- Stratospheric ozone is lowest in its tropical source region due to global circulation!
- However, the record holder of the lowest ozone amounts is the Antarctic ozone hole, formed in spring.
- The detection of this ozone hole led to the reduction of the emission of Ozone Depleting Substances (ODS) through the Montreal Protocol.
- Since those ODS have long lifetimes, the pending question now is if ozone is recovering or not.
- Climate change interacts with ozone recovery, making predictions about full ozone recovery difficult (and uncertain).

Further interesting reading

- WMO Scientific Assessment of Ozone Depletion, 2014 (https://www.wmo.int/pages/prog/arep/gaw/ozone_2014/full_report_TOC.html)
- WMO Scientific Assessment of Ozone Depletion, 2018 (https://ozone.unep.org/sites/default/files/2019-05/SAP-2018-Assessment-report.pdf)
- WMO Scientific Assessment of Ozone Depletion, 2022 (https://ozone.unep.org/system/files/documents/Scientific-Assessment-of-Ozone-Depletion-2022.pdf)

- http://www.ozonedepletion.info/education/ozone.html

- http://www.ccpo.odu.edu/SEES/ozone/oz_class.htm

- http://www.theozonehole.com/

- http://ozonewatch.gsfc.nasa.gov/

- https://atmosphere.copernicus.eu/monitoring-ozone-layer

- http://ozone.meteo.be

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