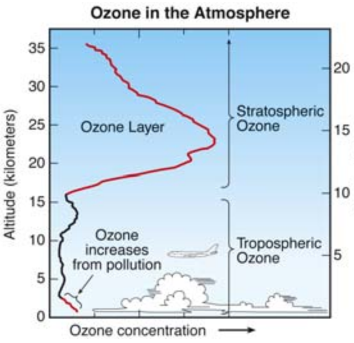
Stratospheric Chemistry

READING: Chapter 10 of text

- Mid-latitude Ozone Chemistry (and depletion)
- Polar Ozone Destruction (the Ozone Hole)

Stratospheric O_3: Overview



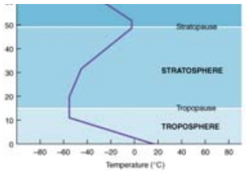
Most O_3 (90%) in stratosphere.

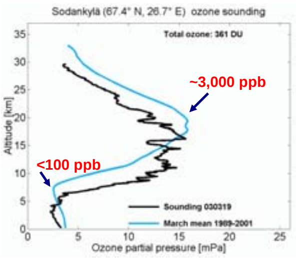
Remaining 10% in troposphere.

"Ozone layer" (15-30 km) is 3000 – 5000 ppb of O_3.

Surface O_3 ~ 40 – 100 ppb.

Stratospheric Ozone: Overview





~3,000 ppb

<100 ppb

- sustains terrestrial life by absorbing UV radiation
- impacts the atmospheric vertical temperature profile
- important role in Earth's overall radiative balance

Stratospheric Ozone: Motivating Questions

1. What are the natural production and loss mechanisms for stratospheric O_3?
2. What is the effect of anthropogenic emissions on stratospheric ozone, both past and future?
3. What are the mechanisms responsible for the drastic ozone decreases in the Antarctic?
4. What role, if any, does the stratospheric aerosol layer play in the gas-phase chemistry of the stratosphere?

Stratospheric Ozone—a brief history

1840's Ozone first discovered and measured in air by Schonbein who named it based on its smell.

1880-1900's: Hartley postulates the existence of a layer above the troposphere, where ozone is responsible for the absorption of solar UV between 200 and 300 nm.

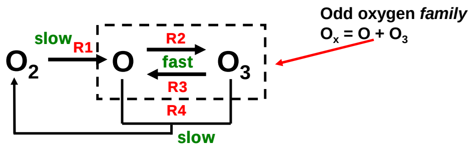
1913: Fabry and Buisson used UV measurements to estimate that if brought down to the surface at STP, O_3 would form a layer ~ 3 mm thick.

1920-25: Dobson first shows that T(z) in stratosphere not constant but increases with z and implicates O_3 absorption. Makes first extensive set of O_3 column measurements with his spectrophotometer

1930: Chapman proposed that O_3 continually produced in a cycle initiated by O_2 photolysis.

The Chapman mechanism

[R1] $O_2 + h\nu \rightarrow 2\,O$ $\lambda < 240$ nm
[R2] $O + O_2 + M \rightarrow O_3 + M$
[R3] $O_3 + h\nu \rightarrow O_2 + O$ $\lambda < 310$ nm
[R4] $O + O_3 \rightarrow 2O_2$



Mass balance for [O]:

$$\frac{d[O]}{dt} = 2\,j_{O2}\underset{\text{small}}{\cancel{[O_2]}} + j_{O3}[O_3] - k_2[O_2][O][M] - k_4\underset{\text{small}}{\cancel{[O_3]}}[O] \sim 0$$

Odd Oxygen Family: O_x

$[O_x] = [O] + [O_3] \cong [O_3]$

Mass balance for $[O_x]$: $\frac{d[O_x]}{dt} = 2j_{O2}[O_2] - 2k_4[O_3][O]$

- $[O_3]$ controlled by *slow net* production and loss via O_2 + hv (R1) and $O + O_3$ (R4)

NOT by fast production and loss of O_3 from $O + O_2$ (R2) and O_3 + hv (R3)

- Effective O_3 lifetime $\cong \tau_{Ox}$:

$$\tau_{Ox} = [O_x]/2k_4[O][O_3] \cong 1/\ 2k_4[O]$$

- In upper stratosphere τ_{Ox} short enough steady-state can be assumed: $2k_1[O_2] = 2k_4[O][O_3]$

$$\therefore [O_3] = (k_1k_2/k_3k_4)^{1/2}\ C_{O2}N_{air}^{3/2}$$

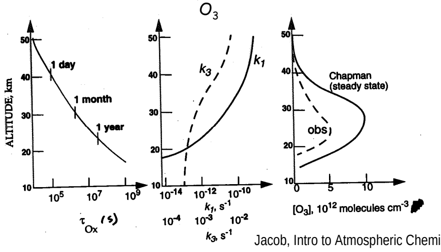
(where C_{O2} = [mole/mole] and N_{air} = air number density [cm^{-3}])

Vertical profiles

Reflects abundance of O atoms

Photolysis rate constants increase with altitude due to absorption of UV by O_2 and O_3

$[O_3]$ overestimated by a factor of 2



Jacob, Intro to Atmospheric Chemistry

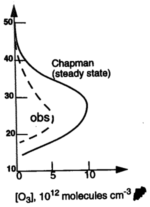
Questions

1. Why do ozone concentrations peak ~20 km altitude?
2. Where would you expect the highest ozone concentrations to be (equator vs. poles)?
3. The original Chapman mechanism included a fifth reaction:

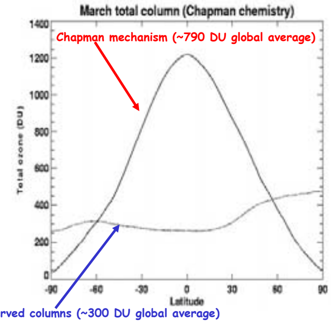
$$O + O + M \rightarrow O_2 + M$$

What would be the effect of this reaction on ozone? Where would it be most important?

What's missing from the Chapman mechanism?



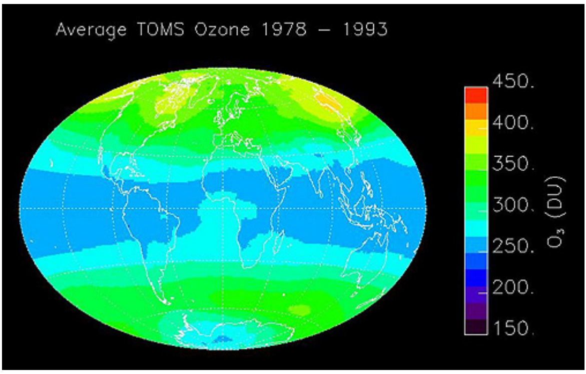
Jacob, Intro to Atmospheric Chemistry



Chapman mechanism (~790 DU global average)

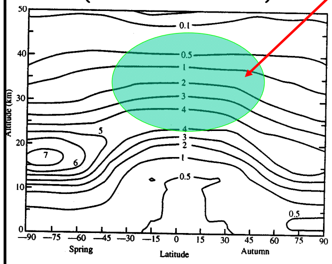
Observed columns (~300 DU global average)

Average Ozone Column (Dobson units)



Vertical and latitudinal distribution of ozone

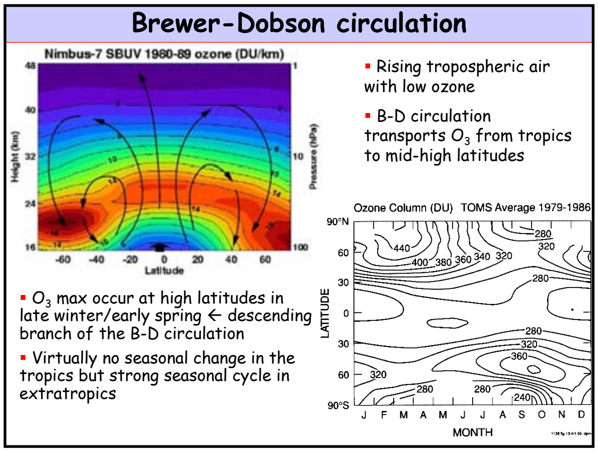
Ozone concentration
(10^{12} molecules cm^{-3})



Region of largest production

- **Theory predict maximum O_3 production in the tropics**
- **But $[O_3]$ is not largest in the tropics**
- **To explain this (and low strat. H_2O) Brewer and Dobson suggested a circulation pattern**

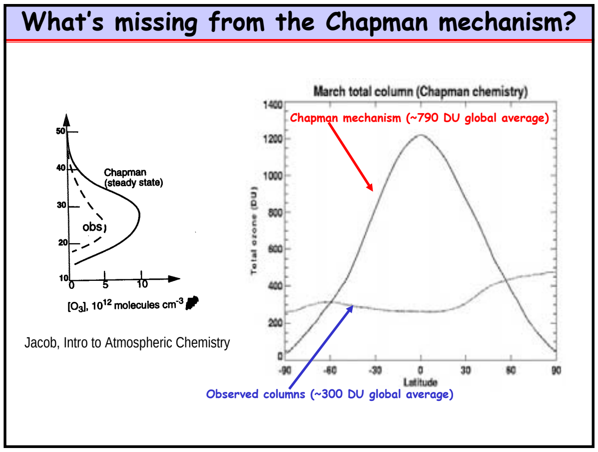
Figure is compilation of available measurements from 1960s



Brewer-Dobson circulation

- Rising tropospheric air with low ozone
- B-D circulation transports O_3 from tropics to mid-high latitudes

- O_3 max occur at high latitudes in late winter/early spring ← descending branch of the B-D circulation
- Virtually no seasonal change in the tropics but strong seasonal cycle in extratropics



What's missing from the Chapman mechanism?

Jacob, Intro to Atmospheric Chemistry

Chapman mechanism (~790 DU global average)

Observed columns (~300 DU global average)

Catalytic chemical cycles

Altitudes >30 km (need O)

$$\begin{aligned} X + O_3 &\rightarrow XO + O_2 \\ XO + O &\rightarrow X + O_2 \\ \hline \text{Net: } O + O_3 &\rightarrow 2O_2 \end{aligned}$$

Altitudes < 30 km

$$\begin{aligned} X + O_3 &\rightarrow XO + O_2 \\ XO + O_3 &\rightarrow X + 2\,O_2 \\ \hline \text{Net: } O_3 + O_3 &\rightarrow 3O_2 \end{aligned}$$

Catalysts:
X = OH, NO, Cl, Br

Hydrogen oxide (HO_x) radical family

$HO_x = H + OH + HO_2$

From troposphere and CH_4 oxidation

- Initiation: $H_2O + O(^1D) \rightarrow 2OH$
- Propagation through cycling of HO_x radical family (example):

$$OH + O_3 \rightarrow HO_2 + O_2$$
$$HO_2 + O_3 \rightarrow OH + 2O_2$$
$$\text{Net: } 2O_3 \rightarrow 3O_2$$

- Termination (example):

$$OH + HO_2 \rightarrow H_2O + O_2$$

HO_x is a catalyst for O_3 loss but not the only one…

HO_x sources in the stratosphere

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$
$$O(^1D) + M \rightarrow O + M$$
$$O + O_2 + M \rightarrow O_3 + M$$

Small fraction of $O(^1D)$ 1/15,000 (25 km) reacts with H_2O, CH_4, or H_2 to form HO_x:

$$H_2O + O(^1D) \rightarrow 2OH$$
$$CH_4 + O(^1D) \rightarrow OH + CH_3$$
$$H_2 + O(^1D) \rightarrow OH + H$$

H_2O ~ 3-6 ppmv; CH_4 ~1-1.5 ppmv; H_2 ~ 0.5 ppmv

Stratospheric OH Profile

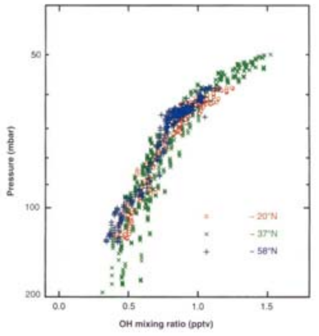
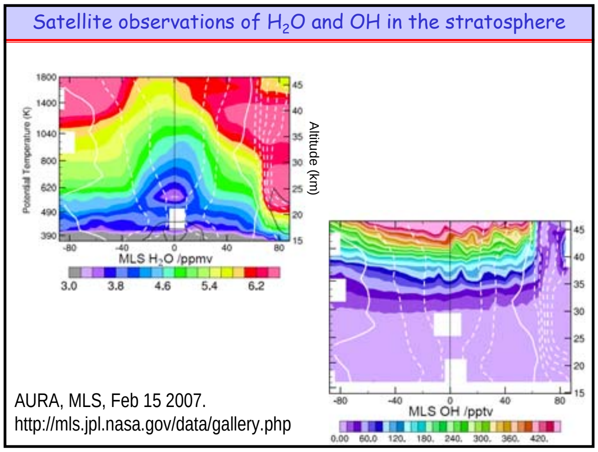


Fig. 1. Altitude profiles of [OH] measured during the SPADE campaign. The data have been normalized to 30° SZA by using the measured diurnal behavior. Despite the large increase in the concentrations of O_3 and NO_y observed between 20 and 60°N latitude, little variation in [OH] is observed at a given altitude.

Wennberg, et al Science 1994



Satellite observations of H_2O and OH in the stratosphere

AURA, MLS, Feb 15 2007.
http://mls.jpl.nasa.gov/data/gallery.php

Nitrogen oxide (NO_x) radical family

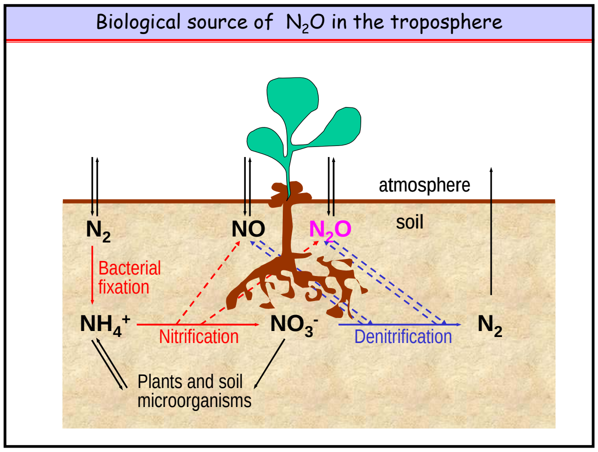
NO_x = NO + NO_2

- Initiation $N_2O + O(^1D) \rightarrow 2NO$
- Propagation

$NO + O_3 \rightarrow NO_2 + O_2$	$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + h\nu \rightarrow NO + O$	$NO_2 + O \rightarrow NO + O_2$
$O + O_2 + M \rightarrow O_3 + M$	
Null cycle	Net $O_3 + O \rightarrow 2O_2$

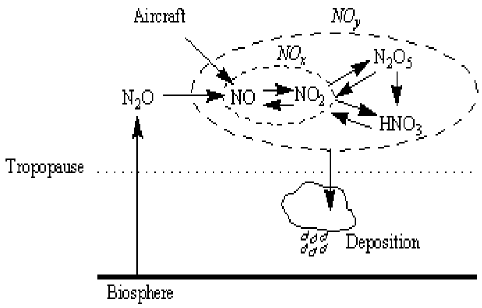
- Termination

Termination	Recycling
$NO_2 + OH + M \rightarrow HNO_3 + M$	$HNO_3 + h\nu \rightarrow NO_2 + OH$
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$	$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$



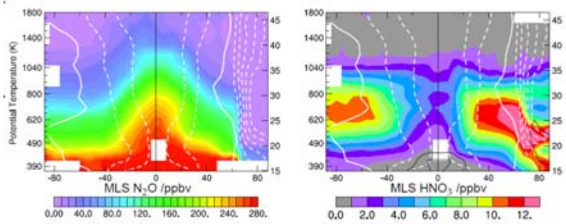
Biological source of N_2O in the troposphere

Cycling of NO_x and NO_y



N_2O and HNO_3 distribution in the stratosphere

(AURA satellite observations – MLS instrument)



Feb 15 2007
http://mls.jpl.nasa.gov/data/gallery.php

What have we learned about NO_y?

- **Production:**

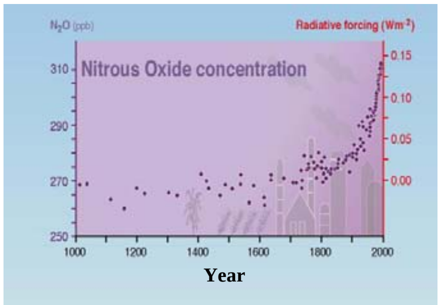
  $N_2O + O(^1D)$ - well understood natural source

- **Loss:** *via transport from stratosphere to troposphere.* Residence time for air in stratosphere is 1-2 years. Loss rate well constrained

- ***Cycling:*** O_3 loss related to NO_x/NO_y ratio.

NO_x catalytic cycle reconciled Chapman theory with observations…1995 Nobel Prize

Human Influence on Stratospheric NO_x



IPCC SYR Figure 2-1

Questions

1. Of the ozone loss mechanisms we have examined so far, can any operate at night?

2. A minor oxidation pathway for NO is

$HO_2 + NO \rightarrow OH + NO_2$

What is the net effect of this reaction on ozone?

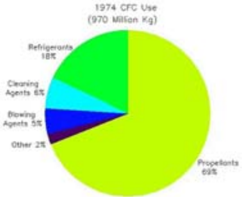
Anthropogenic perturbations to stratospheric ozone

$$\begin{array}{c} X + O_3 \rightarrow XO + O_2 \\ XO + O \rightarrow X + O_2 \\ \hline \text{Net: } O + O_3 \rightarrow 2O_2 \end{array}$$

Catalysts:

X = OH ← increasing CH_4 from troposphere
X = NO ← increasing N_2O from troposphere, supersonic fleet
X = Cl, Br ← Chlorofluorocarbons (CFCs) - Freons

"wonder gas" CFCs were invented in 1928



Use of CFCs increases rapidly

Chlorofluorocarbons (CFCs)

Used as refrigerants and as propellants in spray cans

Non-toxic, non-flammable, stable gases that are easily compressed.

Thought to be ideal…due to safety and durability.

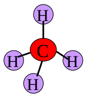
"Aerosol" Spray Cans: NOT SAME AS ATMOSPHERIC AEROSOL PARTICLES

Chlorofluorocarbons (CFCs)

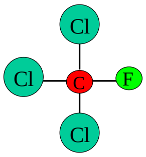
organic molecules where the H atoms have been completely replaced by fluorine and chlorine (synthetic molecules- entirely artificial)

Examples:

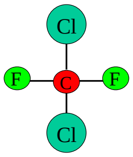
Methane



CFC11



CFC12



Chlorofluorocarbons and Halons

Halocarbon= halogen-containing organic compounds

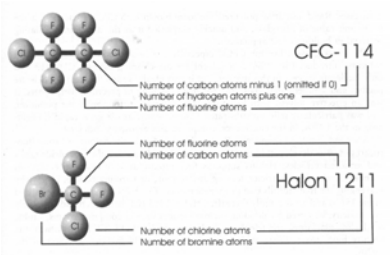


Figure 2.4 Names of CFCs and Halons. CFCs and halons are identified by numbering systems in which each digit is related to the number of one type of atom in the molecule. Source: UNEP Division of Technology, Industry, and Economics.

Halocarbon containing C, Cl and F

Br containing halocarbon

CATALYTIC CYCLES FOR OZONE LOSS:

Chlorine (ClOx = Cl + ClO) radicals

- Initiation:

$CCl_3F + h\nu \rightarrow CCl_2F + Cl$ wavelengths<230 nm

$CCl_2F + h\nu \rightarrow CFCl + Cl$

- Propagation:

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net: $O_3 + O \rightarrow 2O_2$

O_3 loss rate:

$$\frac{d[O_x]}{dt} = -2k[ClO][O]$$

Chain length > 10 (10^3 in upper stratosphere)

- Termination:

$Cl + CH_4 \rightarrow HCl + CH_3$

$ClO + NO_2 + M \rightarrow ClONO_2 + M$

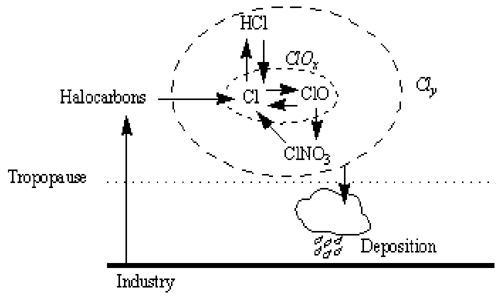
Recycling:

$HCl + OH \rightarrow Cl + H_2O$

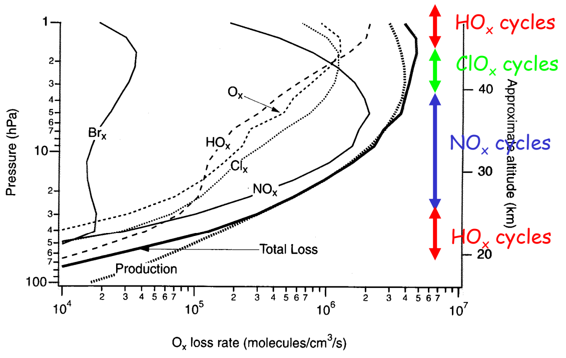
$ClONO_2 + h\nu \rightarrow ClO + NO_2$

Molina & Rowland, 1974 …1995 Nobel Prize

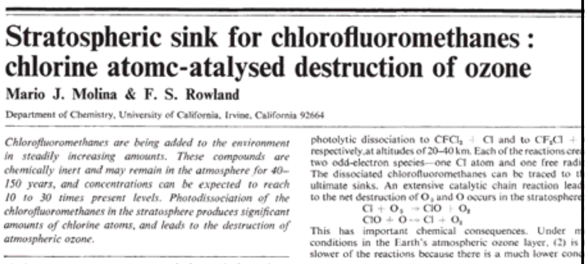
Cycling of ClO_x and Cl_y



Vertical distribution of O_x catalytic loss cycles



Early Warning Signs



Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

photolytic dissociation to $CFCl_2$ + Cl and to CF_2Cl +
respectively at altitudes of 20–40 km. Each of the reactions cre
two odd-electron species—one Cl atom and one free radi
The dissociated chlorofluoromethanes can be traced to t
ultimate sinks. An extensive catalytic chain reaction lead
to the net destruction of O_3 and O occurs in the stratosphere

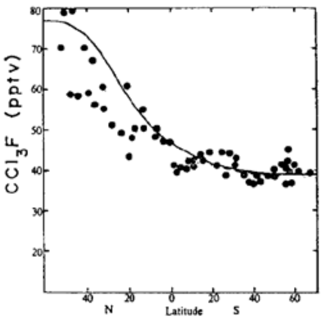
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

This has important chemical consequences. Under m
conditions in the Earth's atmospheric ozone layer, (2) is
slower of the reactions because there is a much lower conc

Nature, June 28, 1974

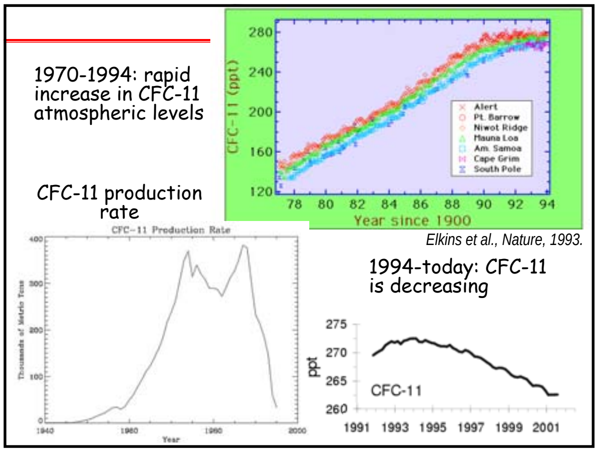
Molina, Rowland, and Crutzen win Nobel Prize in 1994

CCl_3F measurements in 1971: cruise from England to Antactica



CFC-11

J. E. Lovelock, R. J. Maggs and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, Nature, 241, 194-196 (1973)



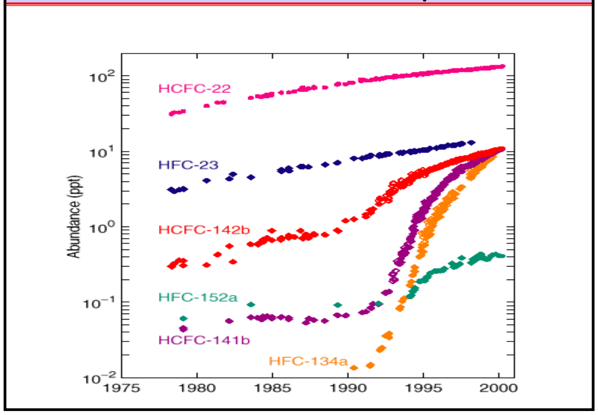
1970-1994: rapid increase in CFC-11 atmospheric levels

CFC-11 production rate

Elkins et al., Nature, 1993.

1994-today: CFC-11 is decreasing

Recent Rise in HCFC's (CFC Replacements)



Coupling Between HO_x, NO_x, and ClO_x Cycles

What is the effect of increasing stratospheric NO_x on the rate of ClO_x-catalyzed ozone loss?

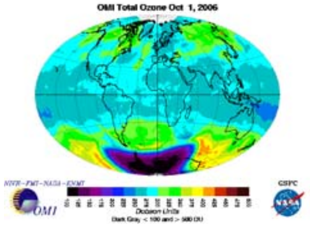
Give an example of how HO_x and NO_x are coupled.

How might an increase in OH affect ClO_x cycles?

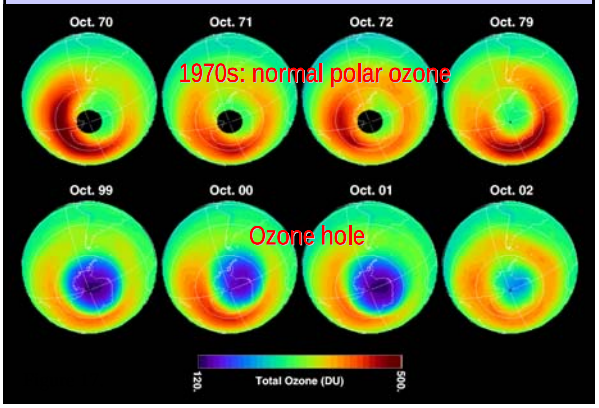
Polar Ozone Loss

Severe depletion of stratospheric O_3 occurs every spring (since 1980's) over the poles (especially South Pole).

Example of:
- far reach of human activities
- environmental catastrophe and political blame game
- scientific process and ability of humans to correct



The Antarctic ozone hole viewed from space



Discovery of the Antarctic ozone hole: 1985

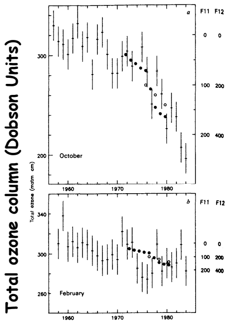


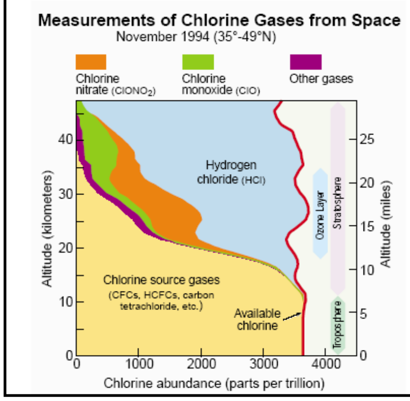
Fig. 2 Monthly means of total O_3 at Halley Bay, and Southern Hemisphere measurements of F-11 (●, p.p.t.v. (parts per thousand by volume) $CFCl_3$) and F-12 (○, p.p.t.v. CF_2Cl_2). *a*, October, 1957–84. *b*, February, 1958–84. Note that F-11 and F-12 amounts increase down the figure.

┼ Ozone column
● CFC-11
○ CFC-12

Total ozone observations at Halley Bay (76°S, 27°W), Antarctica: 1956-1985

Farman et al., Nature, 315, May 1985
"Large losses of ozone in Antarctic reveal seasonal ClO_x/NO_x interactions"

Chlorine Partitioning in Stratosphere

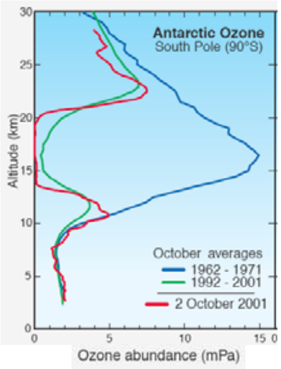


Most Cl is in its reservoir form (HCl, $ClONO_2$), not active form (Cl_x).

Gas-phase processes deplete strat. O_3, but are not capable of creating the O_3 "hole".

Why is there an ozone "hole" over polar regions?

Vertical distribution of ozone at the South Pole



Chlorine from CFCs predicted to be most effective ~ 40 km.

So why is depletion at 15 – 20 km?

Discovery of Antarctic Ozone Hole

The Conundrum:

- Known catalytic reactions with chlorine not fast enough to explain near complete depletion in couple months.
- Why only in spring?
- Why only between 15 – 25 km?
- Why only in polar region?

Debate Over Causes of Ozone Hole

Sun

How Joan Van Ark beats agonizing feelings of guilt

UFO ALIENS FOUND AT SOUTH POLE

ETs are burning up our ozone

Rub pineapple on your face to

Psychic's touch removes 20 lbs

There was also a real scientific debate over the relative roles of chemistry and meteorology.

Turns out to be both (of course!)

Chlorine: The Smoking Gun?

ClO and O_3 certainly anti-correlated.

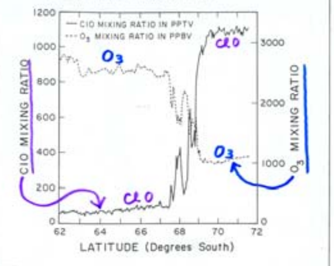
But how is there so much ClO?

What is the mechanism for ClO to destroy ozone so fast?

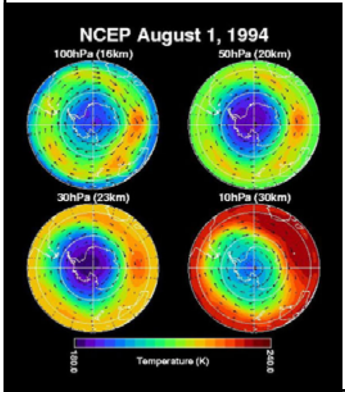
Can't be ClO + O…

Figure 7. Chlorine oxide and total ozone measured with instruments on ER-2 aircraft flight, September 16, 1987, from 53°S (Punta Arenas, Chile) to 72°S (Antarctica).

— ClO mixing ratio in parts by volume × 10^{12}
--- O_3 mixing ratio in parts by volume × 10^9



The Antarctic Polar Vortex: Wind and temperature



- Lack of sunlight between June and September → **cooling** of Antarctic stratosphere and adiabatic **downwelling**
- Large latitudinal temperature gradient (sunlight/polar night) →strong zonal winds = Polar night jet (150 km/h at 20 km)
- Antarctic polar vortex: region poleward of polar night jet
- **Isolation** of polar vortex: little mixing of warmer air from lower latitudes occurs
- **Sustained cold temperatures** over Antarctica during winter (~183K at 20km in early August).

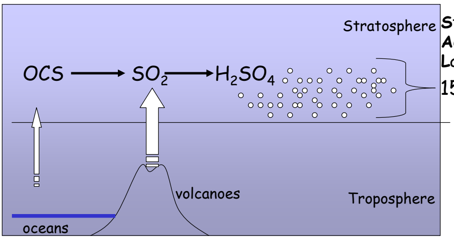
Polar Stratospheric Clouds (PSC)

http://earthobservatory.nasa.gov/

Temperatures as low as 183K can exist at 15-20 km altitude, where even small amounts of water can condense to produce PSCs.

	Type I PSC	Type II PSC
Composition:	Nitric Acid Trihydrate (HNO_3-3 H_2O) Ternary solution (H_2O, H_2SO_4, HNO_3)	Water Ice
Formation Temp.:	195 K	188 K
Particle diameter:	1 μm	>10 μm
Altitudes:	10-24 km	10-24 km
Settling rates:	1 km/30 days	> 1.5 km/day

PSC Formation Starts on S.A.L



Stratosphere

$OCS \longrightarrow SO_2 \longrightarrow H_2SO_4$

volcanoes

Troposphere

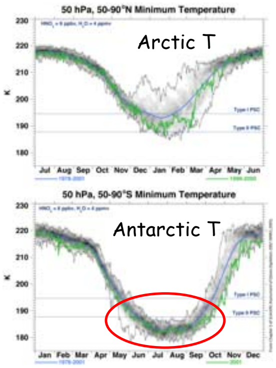
oceans

Stratospheric **A**erosol (Jung) **L**ayer

15-35 km

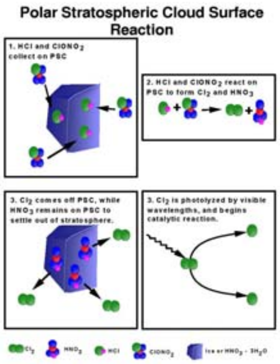
- Extends vertically from 15 to 35 km
- Aerosol composition primarily H_2SO_4-H_2O
- Typical particle radius ~ 700 nm
- Typical particle number density ~ 10 cm^{-3}

PSC Formation Requires Very Low T



Polar Vortex cuts off warm, ozone/NO_x rich mid-latitude air

Chlorine activation on polar stratospheric clouds



$$HCl + ClONO_2 \xrightarrow{PSCs} Cl_2 + HNO_3$$

Conversion of chlorine reservoirs HCl and $ClONO_2$ to Cl_2 and HNO_3 on PSCs

→Cl_2 photolyzes in sunlight (spring) releasing Cl and catalytic ozone loss begins

→HNO_3 remains on PSCs and settles out of stratosphere suppressing NO_x levels: $ClO+NO_2+M \rightarrow ClONO_2 + M$ cannot deactivate ClO radicals.

Chlorine activation on PSCs

Reactions taking place on polar stratospheric clouds:

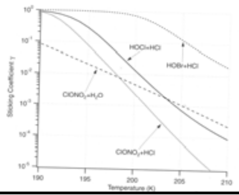
$$HCl + ClONO_2 \rightarrow Cl_2 + HNO_3$$
$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$$
$$HOCl + HCl \rightarrow Cl_2 + H_2O$$
$$BrONO_2 + H_2O \rightarrow HNO_3 + HOBr$$
$$HCl + BrONO_2 \rightarrow HNO_3 + BrCl$$
$$HCl + HOBr \rightarrow H_2O + BrCl$$

Chlorine/Bromine activation + sequestration of HNO_3 in PSCs

Low temperature heterogeneous reactions

$$ClONO_2 + H_2O \xrightarrow{aerosol} HOCl + HNO_3$$
$$ClONO_2 + HCl \xrightarrow{aerosol} Cl_2 + HNO_3$$
$$HOCl + HCl \xrightarrow{aerosol} Cl_2 + H_2O$$
$$HOBr + HCl \xrightarrow{aerosol} BrCl + H_2O$$
$$BrONO_2 + H_2O \xrightarrow{aerosol} HOBr + HNO_3$$

Reactions converting chlorine from the long-lived reservoirs HCl and $ClONO_2$ to Cl_2, HOCl, BrCl which readily photolyze and release Cl_x. Similarly $BrONO_2$, and HOBr are converted to BrCl and HOBr.



Rapid ozone destruction mechanisms after sunrise

Polar sunrise: $Cl_2 + h\nu \rightarrow Cl + Cl$, $BrCl + h\nu \rightarrow Br + Cl$

Molina and Molina (1987): ClO dimer catalytic cycle

$2(Cl + O_3 \rightarrow ClO + O_2)$
$ClO + ClO + M \rightarrow Cl_2O_2 + M$
$Cl_2O_2 + h\nu \rightarrow ClOO + Cl$
$ClOO + M \rightarrow Cl + O_2 + M$
Net: $2O_3 \rightarrow 3O_2$

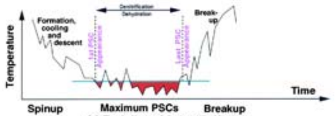
~75 % of ozone removal in ozone hole

McElroy et al. (1986) and Tung et al. (1986): Bromine/chlorine coupling

$Cl + O_3 \rightarrow ClO + O_2$
$Br + O_3 \rightarrow BrO + O_2$
$BrO + ClO \rightarrow Br + ClOO$
$ClOO + M \rightarrow Cl + O_2 + M$
Net: $2O_3 \rightarrow 3O_2$

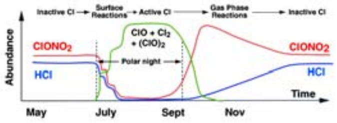
~20% of ozone removal in ozone hole

Evolution of Antarctic Vortex



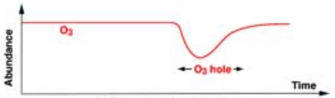
(a) Evolution of Antarctic Vortex

Reactive chlorine and chlorine reservoirs



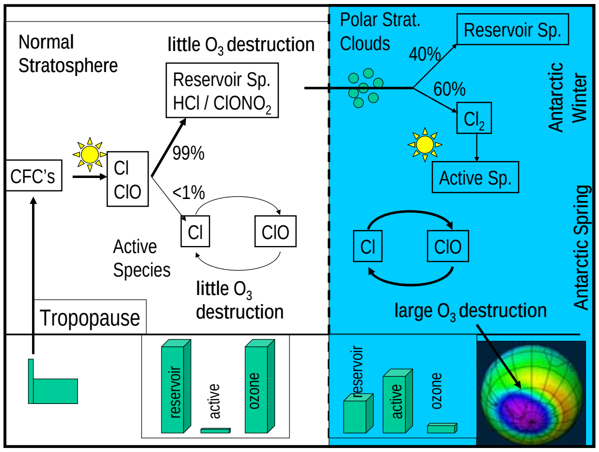
(b) Chlorine Reservoirs in Antarctic Vortex

Ozone levels



(c) Ozone in Antarctic Vortex

Wallace & Hobbs



Normal Stratosphere

little O_3 destruction

Reservoir Sp.
HCl / $ClONO_2$

CFC's

Cl
ClO

99%

<1%

Cl
ClO

Active Species

little O_3 destruction

Tropopause

Polar Strat. Clouds

40%

60%

Reservoir Sp.

Cl_2

Active Sp.

Antarctic Winter

Cl
ClO

large O_3 destruction

Antarctic Spring

Antarctic Ozone Hole Today

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

Antarctic Ozone Hole: Key Points

- Why only in spring?

Wintertime processing on PSCs needed for active chlorine production and denitrification. Sunlight required to generate Cl atoms from Cl_2 and ClOOCl.

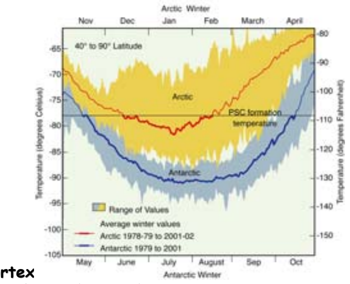
- Why only between 15 – 25 km?

Where PSCs form (on aerosol layer), and where the ClOOCl mechanism is fastest.

- Why only in (south) polar region?

PSCs are required and only form under cold conditions achieved during polar winter (and mainly only Antarctic winter).

An Arctic ozone hole?

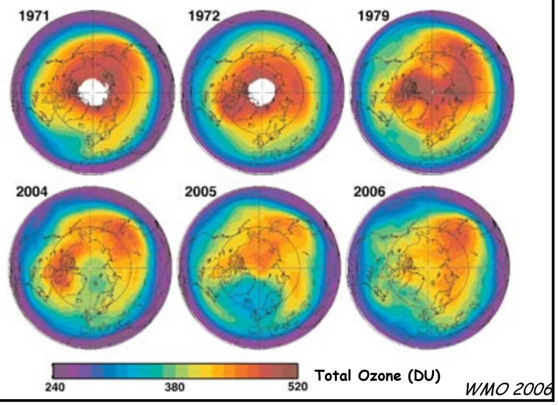


Arctic vortex

- No land mass (warmer)
- Less symmetric
- Planetary wave activity (Tibet, North America…)

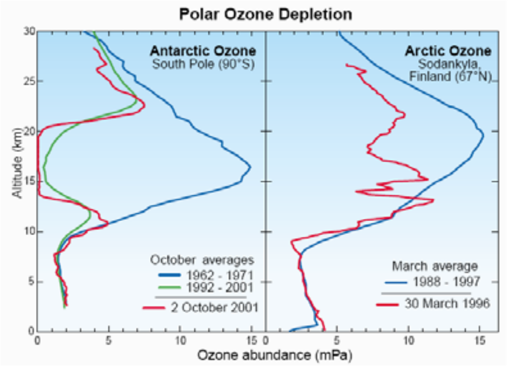
→ **Overlap between cold temperatures and sunlight are limited in the Arctic and ozone depletion episodic and minor**

Arctic Ozone depletion: March



WMO 2006

Comparison: Arctic, Antarctic lower stratosphere



Aerosol chemistry on sulfate aerosols

Role of N_2O_5 hydrolysis:

$$N_2O_5 + H_2O \xrightarrow{aerosol} 2\ HNO_3$$

→ Converts active nitrogen (NO_x) to long-lived reservoir (HNO_3) [NO_x/NO_y ratio decreases], and slows down O_x loss through NO_x cycles.

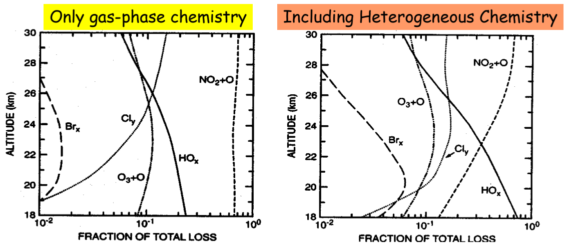
But at the same time it enhances O_x loss through ClO_x, BrO_x, and HO_x cycles. Lower NO_x result in:

- Slower deactivation of ClO_x through $ClO + NO_2 + M \rightarrow ClONO_2 + M$
- Slower deactivation of BrO_x through $BrO + NO_2 + M \rightarrow BrONO_2 + M$
- Slower deactivation of HO_x through $OH + NO_2 + M \rightarrow HNO_3 + M$

➔ Concentrations of ClO_x, BrO_x, and HO_x increase!

➔ Ozone becomes more sensitive to human-induced increases in chlorine and bromine species in the lower stratosphere.

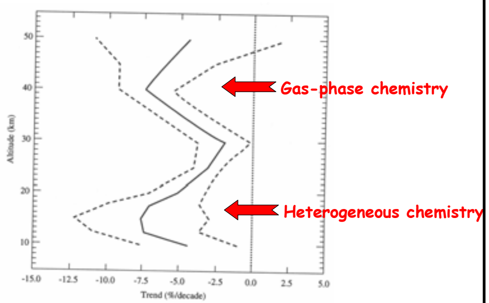
Effect of N_2O_5 + Aerosols→ $2HNO_3$


Only gas-phase chemistry

Including Heterogeneous Chemistry

HO_x becomes most important catalyst in aerosol layer!

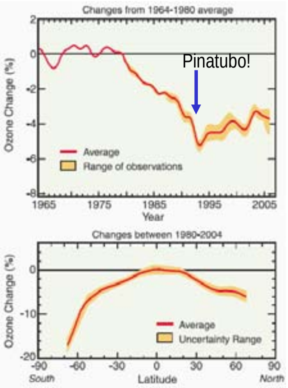
Vertical distribution of ozone trends at midlatudes


Gas-phase chemistry

Heterogeneous chemistry

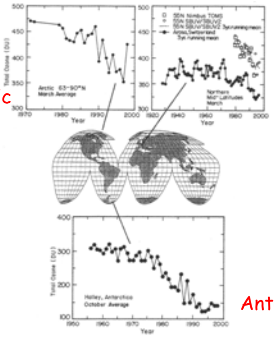
Fig. 10-15 Vertical distribution of the O_3 trend at northern midlatitudes for the period 1980–1996: best estimate (solid line) and uncertainties (dashed lines). Adapted from *Scientific Assessment of Ozone Depletion: 1998*. Geneva: WMO, 1999.

Global total ozone change:1964-2005


Pinatubo!

WMO, 2006

Stratospheric Ozone Depletion



Arctic

Mid-latitudes

Antarctic

→ Downward trends in ozone column on a global scale

Regulations on the production of CFCs

- **Vienna convention (1985):** "Convention for the Protection of the ozone layer" signed by 20 nations (research, future protocols)
- **Montreal Protocol (1987):** "Protocol on substances that deplete the ozone layer" ratified in 1989. Legally binding controls freezing production to 1985 levels.
- **London Amendment (1990):** phaseout of production by 2000 for developed nations and by 2010 for developing nations.
- **Copenhagen Agreement (1992):** Phaseout for developed nations by 1996.
- HCFC production allowed as short-term substitutes for CFCs. HCFC production to be phased out by 2030 (developed nations), 2040 (developing nations).

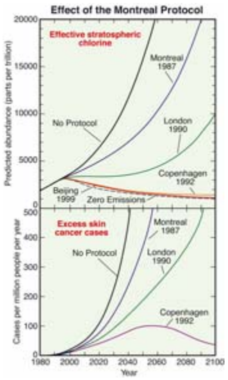
First environmental problem solved on an international basis!

The Solution: Montreal Protocol

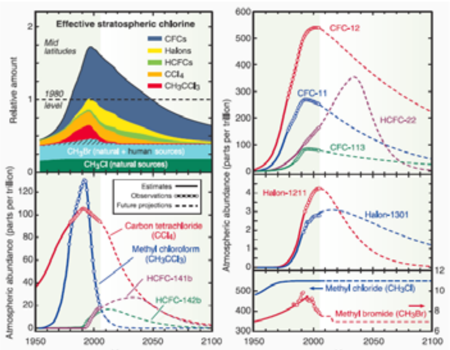
The persistent observations of the ozone hole from 1984 – 1987 led to legally binding international agreements.

The Montreal Protocol and its amendments eventually called for a near complete ban on the production and use of CFCs.

A suitable and easy replacement for CFCs, known as HCFCs, made these acts easier to swallow.



Past and expected future abundances of halogen source gases

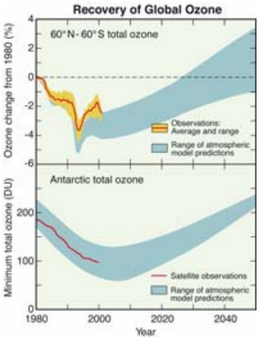


WMO, 2006

Ozone Recovery

Computer model predictions:
- Antarctic ozone will recover to pre-1980 values by ~2040.
- Extra-polar ozone should recover by 2020-2040.

Predictions assume strict adherence to Montreal Protocol.



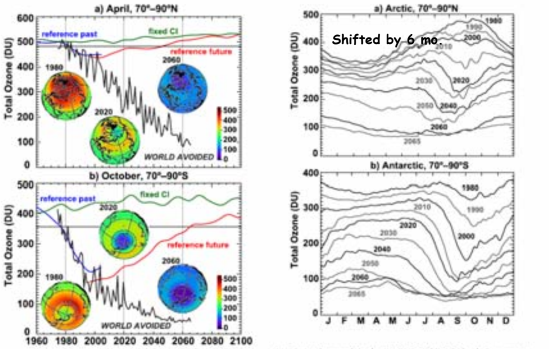
Questions

1. One "geo-engineering" scheme to reduce global warming is to inject sulfur into the stratosphere to enhance the stratospheric aerosol layer – which reflects incoming solar radiation. How would that affect stratospheric ozone at present?

2. How might volcanic eruptions in the distant past (before CFCs) affect stratospheric ozone?

What would have happened?

Newman, et al. *ACP* 2009



Shifted by 6 mo.

Fig. 5. Total ozone from the *WORLD AVOIDED* simulation over (a)

Positive Feedback: O_3 Destruction and T

Less O_3 → less heating

Less heating → colder strat

Colder stratosphere → ??

Newman, et al. *ACP* 2009

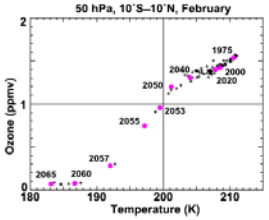


Fig. 8. The February *WORLD AVOIDED* ozone versus temperature (also at 50 hPa and 10° S–10° N, as in Fig. 7). Certain years are highlighted in magenta.