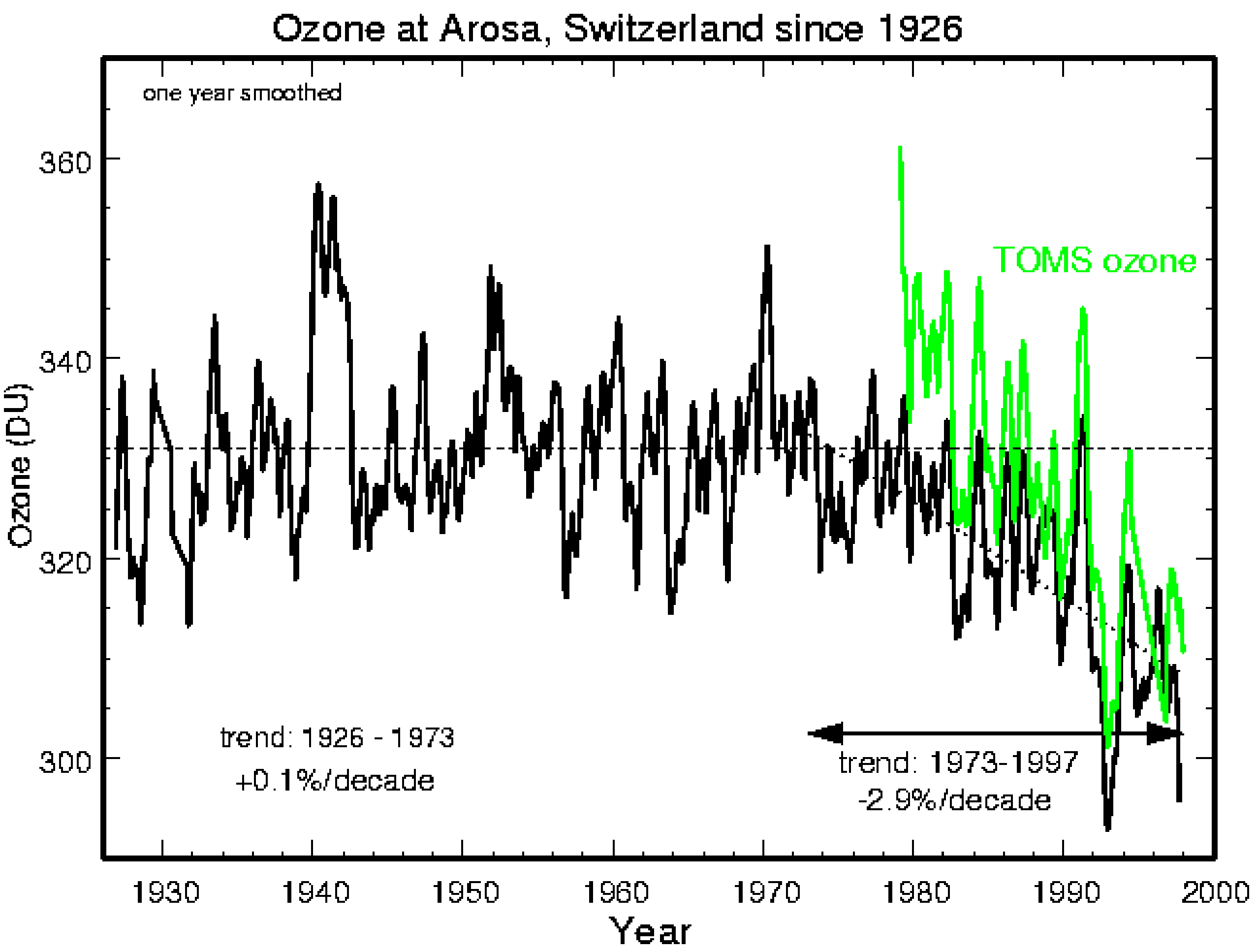
Chemistry of Ozone
in the Stratosphere

Levels of stratospheric ozone have been dropping



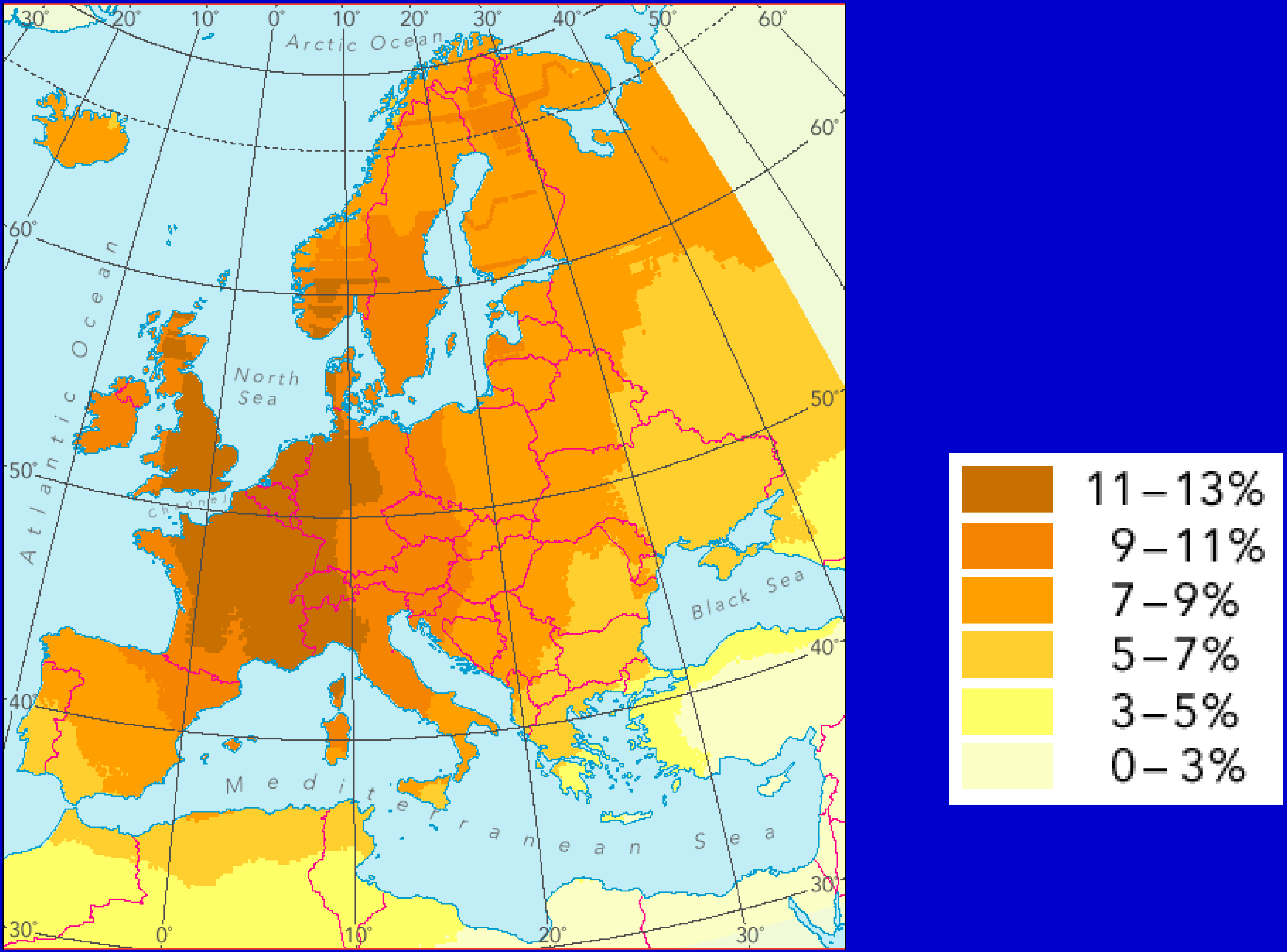
NASA - http://toms.gsfc.nasa.gov

Decreasing Levels of stratospheric ozone is harmful

There has been an increase in the number of cases of skin cancer and cataracts

Evidence of damage to plant and marine life

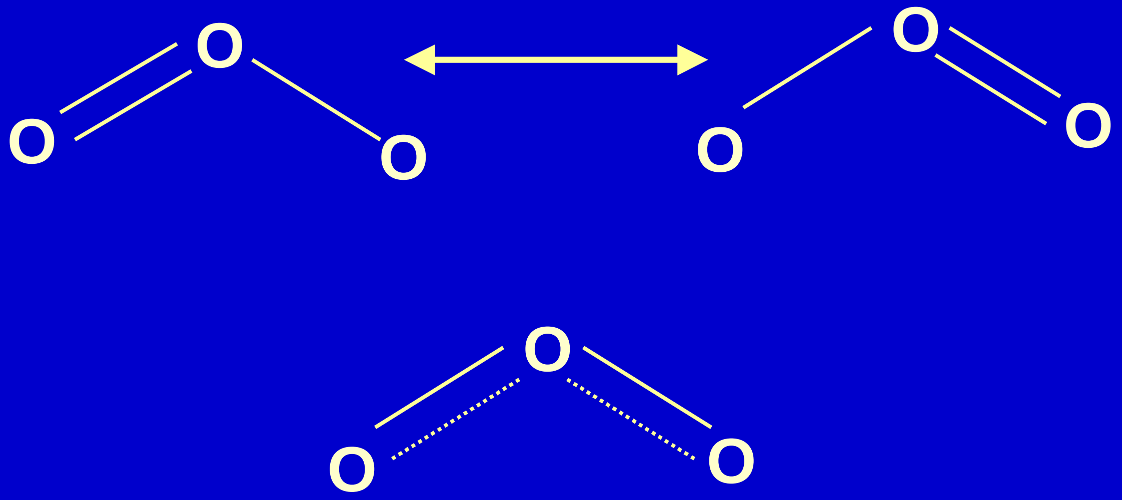
Note: tropospheric ozone is harmful, stratospheric ozone is beneficial.



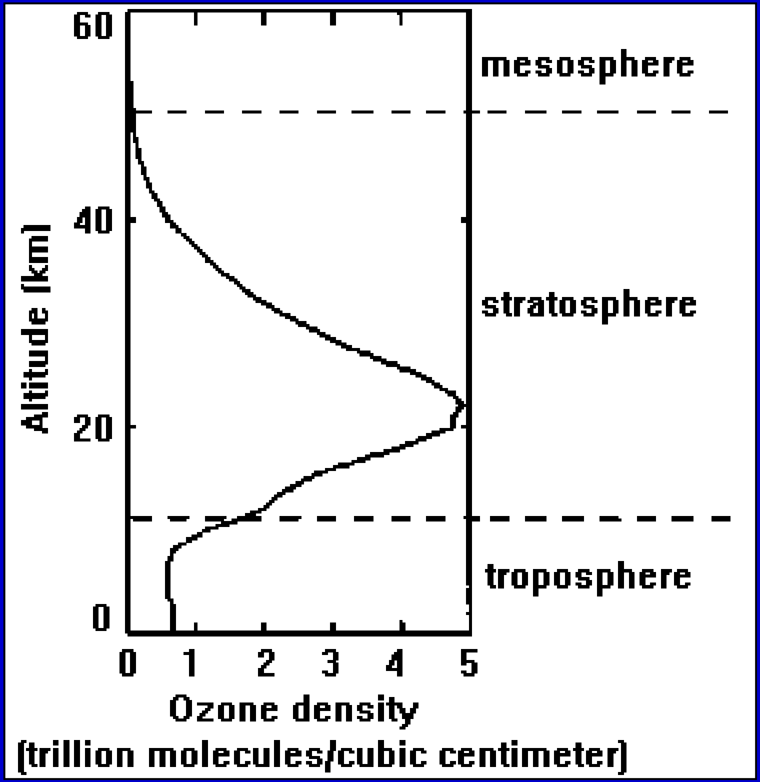
Increase in yearly ultraviolet radiation: The % increase from 1980 to 1997 in UV radiation (causing the skin to turn red) is calculated using observed total ozone values from the TOMS satellite instruments and assuming clear sky conditions.

Environment in the European Union at the turn of the century, European Environment Agency, Chapter 3.2. Ozone-depleting substances

Structure of Ozone, O_3



Where is ozone found in the atmosphere ?

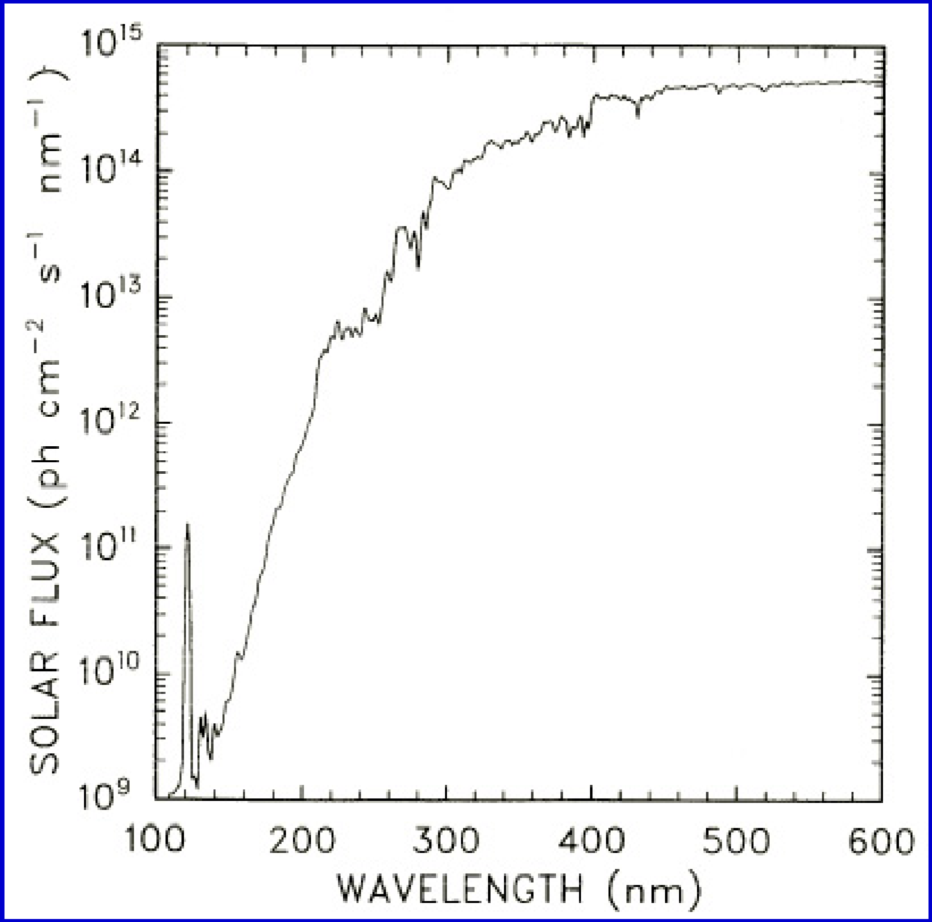


NASA Goddard Space Flight Center

Note, higher concentration in stratosphere, compared with troposphere

Role of Ozone in the Stratosphere

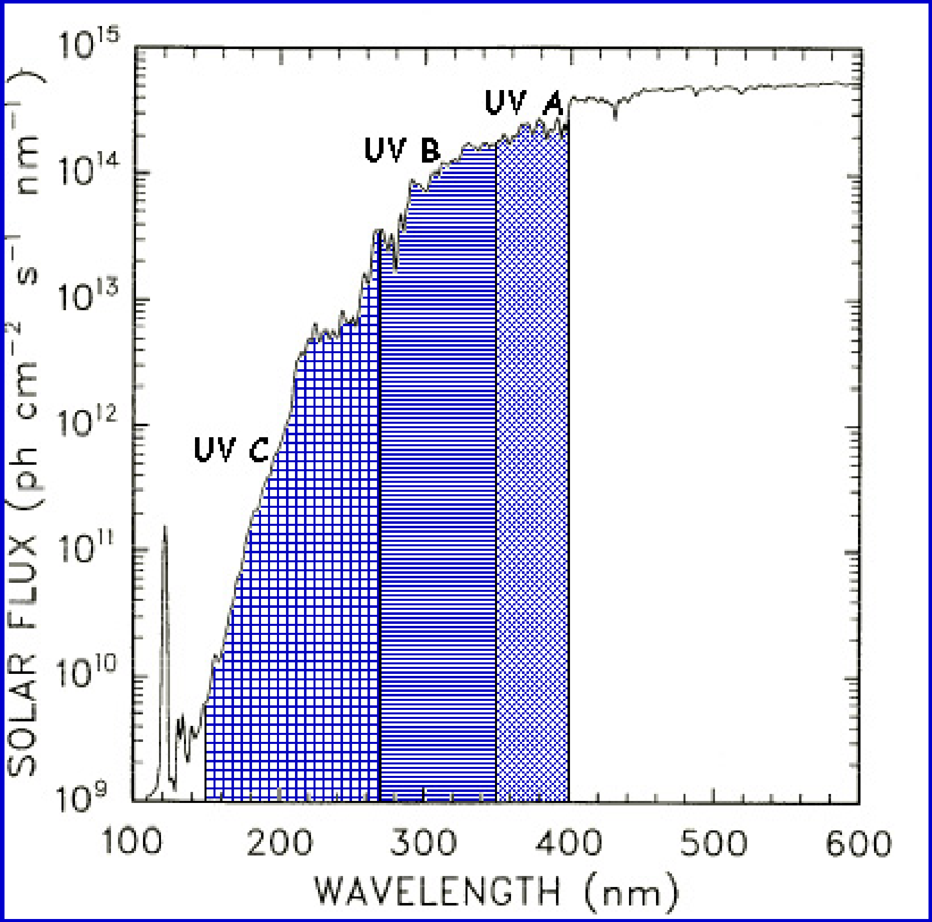
Solar Flux



Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling - JPL Publication97-4

Role of Ozone in the Stratosphere

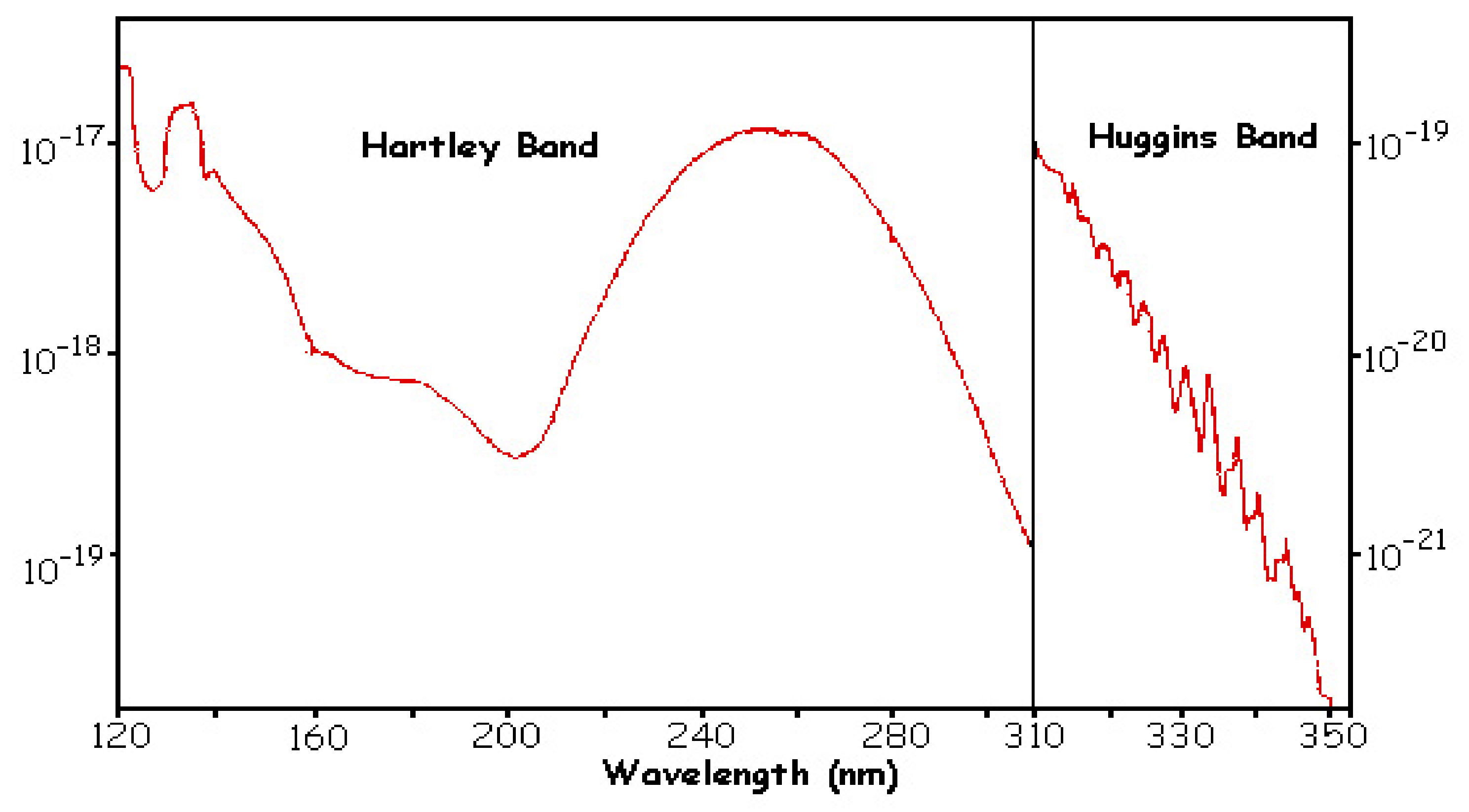
Solar Flux



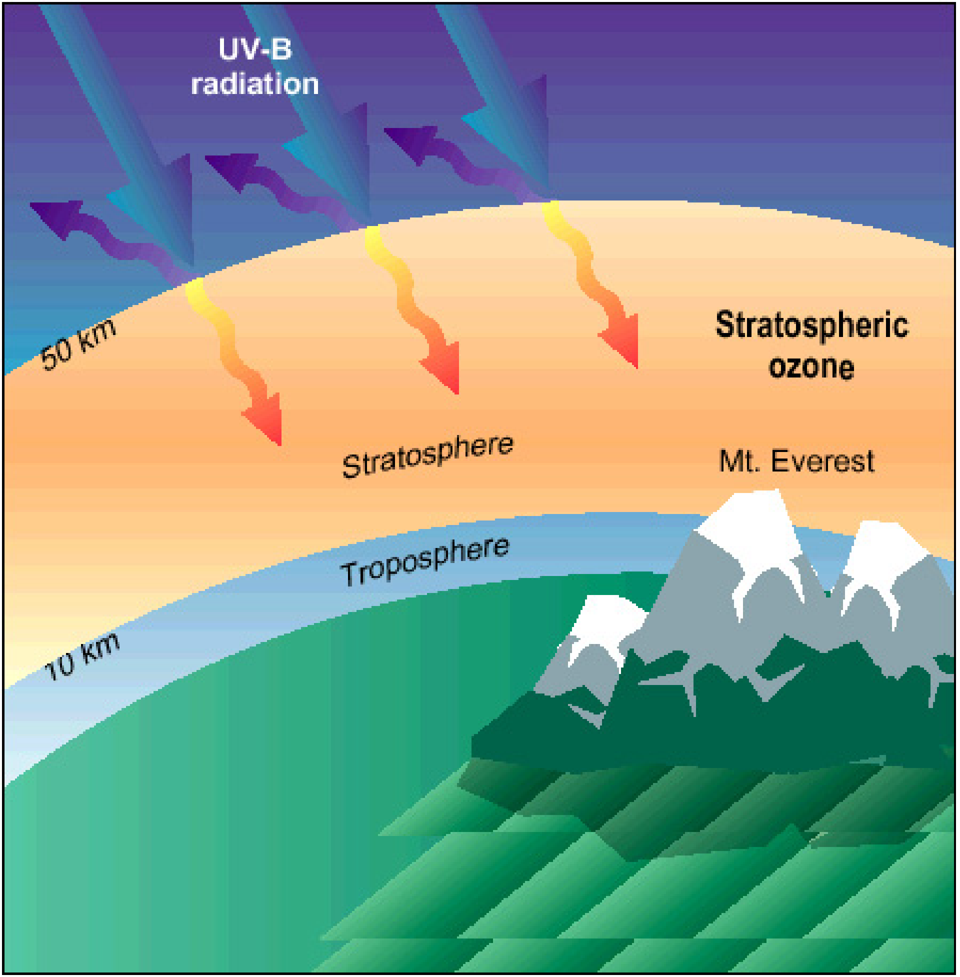
Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling - JPL Publication97-4

Role of Ozone in the Stratosphere

Absorption Spectrum of Ozone



Role of Ozone in the Stratosphere



"The Ozone Depletion Phenomenon", Beyond Discovery, National Academy of Sciences

Role of Ozone in the Stratosphere

UV A (~400 to 350 nm) not absorbed by earth’s atmosphere

UV B (~ 350 to 270 nm) partially absorbed by earth’s atmosphere

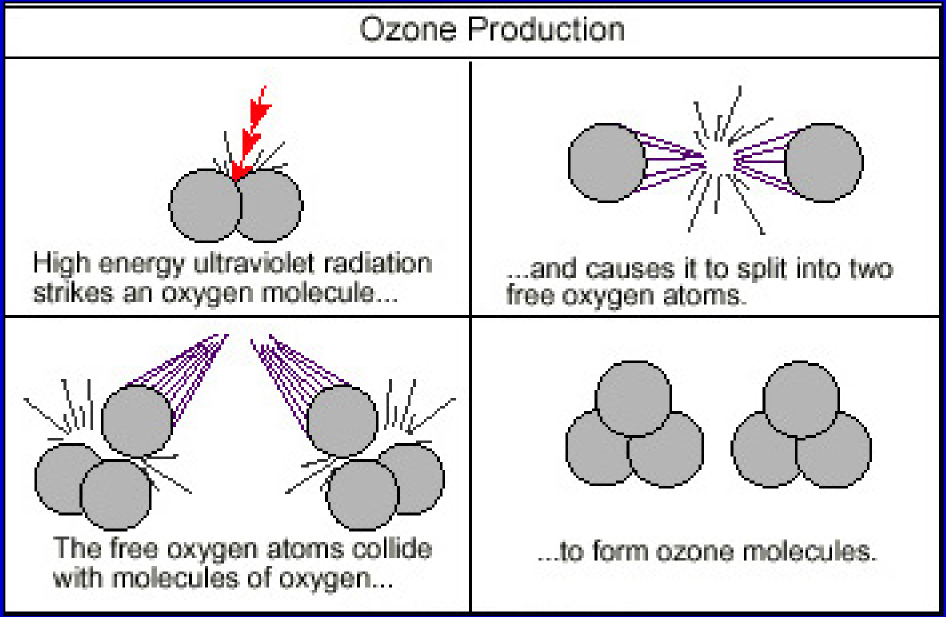
UV C (~270 to 150 nm) completely absorbed by earth’s atmosphere

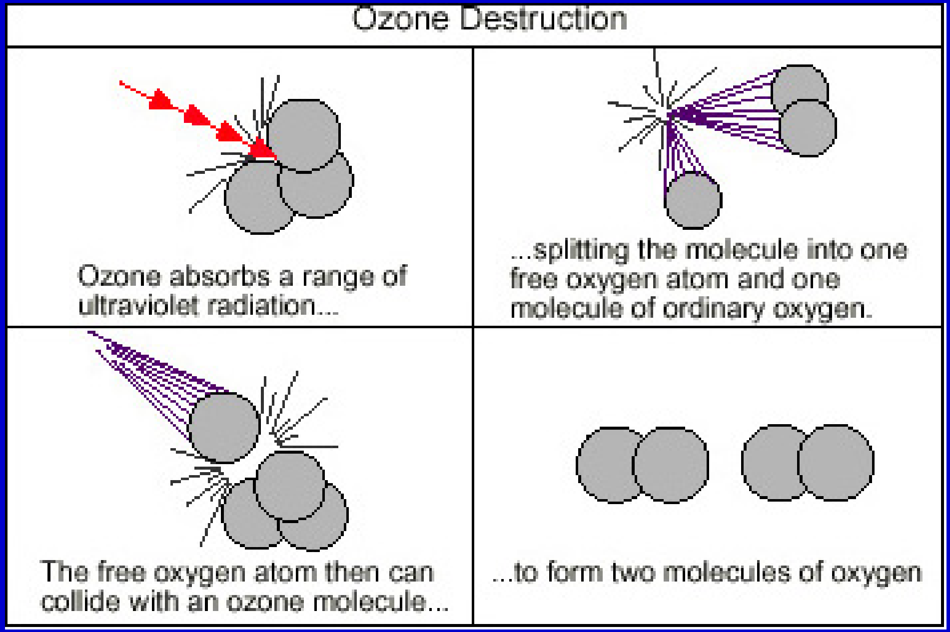
How is ozone formed in the stratosphere?

Chapman mechanism - Sidney Champman, 1930

$O_2 + h\nu\ (\lambda < 242\ \text{nm}) \rightarrow O + O$	$k_1 \sim 5 \times 10^{-11}\ s^{-1}$
$2[O + O_2 + M \rightarrow O_3 + M]$	$k_2 \sim 5.6 \times 10^{-34}\ cm^6\ mol^{-2}\ s^{-1}$
$O_3 + h\nu \rightarrow O + O_2$	$k_3 \sim 9.5 \times 10^{-4}\ s^{-1}$
$O + O_3 \rightarrow 2\ O_2$	$k_4 \sim 1 \times 10^{-15}\ cm^3\ mol^{-1}\ s^{-1}$

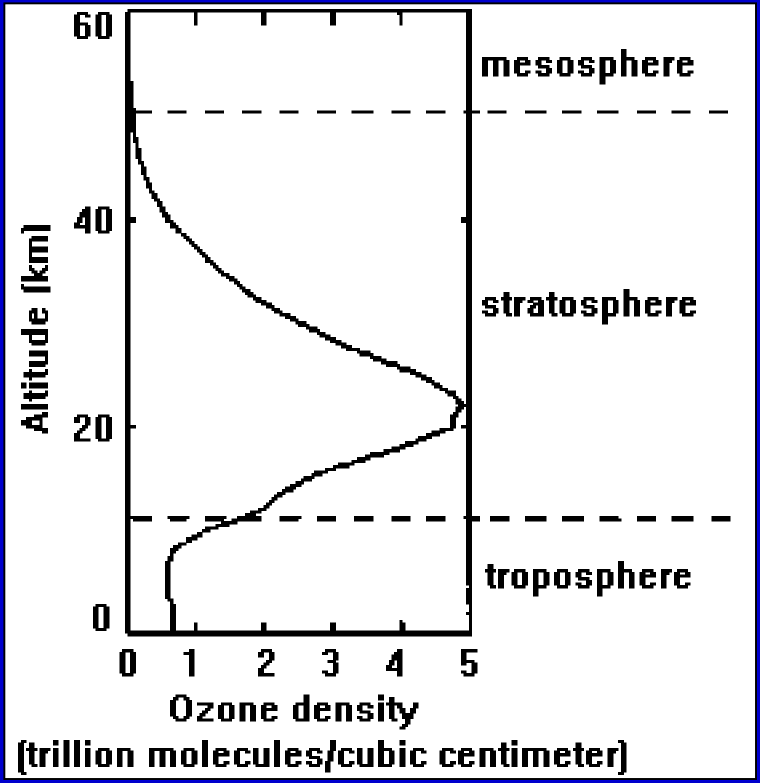
Note: k_1 and k_3 depend on intensity of light; above values are for mid day





"Ozone: What is it and why do we care about it?", NASA Facts, Goddard Space Flight Center

This mechanism, which describes how sunlight converts the various forms of oxygen from one to another, explains why the highest contents of ozone occur in the layer between 15 and 50 km - the ozone layer



Kinetics of Chapman Mechanism

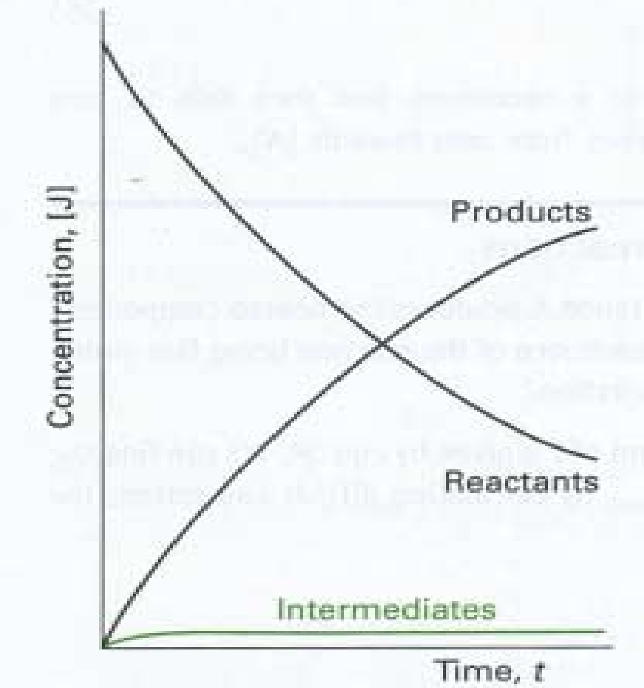
Rate of formation of O and O_3

$$d[O]/dt = 2k_1[O_2] - k_2[O][O_2][M] + k_3[O_3] - k_4[O][O_3]$$

$$d[O_3]/dt = k_2[O][O_2][M] - k_3[O_3] - k_4[O][O_3]$$

Steady-State Approximation

$$d[O]/dt = d[O_3]/dt = 0$$



Kinetics of Chapman Mechanism

Can re-write $[O_3]$ as:

$$[O_3] = \frac{k_2[O_2][M]/k_4}{k_3/(k_4[O]) + 1}$$

Since the rate constants and concentration of species are known, can shown that:

$$\frac{k_3}{k_4[O]} >> 1$$

Hence,

$$[O_3] \approx \frac{k_2[O_2][M][O]}{k_3}$$

Kinetics of Chapman Mechanism

$$[O_3] \approx \frac{k_2 [O_2][M][O]}{k_3}$$

$[O_3]$ depends on rate of reaction 2 and the intensity of light

$2[O + O_2 + M \rightarrow O_3 + M]$ k_2

$O_3 + h\nu \rightarrow O + O_2$ k_3

Reaction 2 is slow (termolecular); makes ozone "vulnerable" to ozone-depleting reactions

Later measurements showed appreciable deviations from Chapman's theory.

Calculations of ozone concentration based on the Chapman mechanism were considerably higher than observed ones.

Must be other chemical reactions contributing to the reduction of the ozone content.

Competing Reactions

Marcel Nicolet: HO_x cycle

H, OH and HO_2 species formed by reaction of excited O atoms with H-containing atmospheric species like H_2O and CH_4

$O_3 + h\nu\ (\lambda < 310\ nm) \rightarrow O + O_2$

$O + H_2O \rightarrow OH + OH$

$O + CH_4 \rightarrow CH_3 + OH$

$H_2O + h\nu \rightarrow H + OH$

Reactions of HO_x species with O_3

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

Net Reaction

$$O + O_3 \rightarrow 2O_2$$

“Ozone Depletion”

Competing Reactions

Paul Crutzen: NO_x Cycle

NOx species are produced during the reaction of O atoms with N_2O (produced in the soil by bacteria)

$$O + N_2O \rightarrow 2\ NO$$

Reactions of NO_x species with O_3

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

Paul Crutzen, ~ 1970

Net Reaction

$O + O_3 \rightarrow 2O_2$ “Ozone Depletion”

The first “man-made” threat to the ozone layer was noted by Harold Johnston (1971): supersonic aircrafts

These aircraft would be capable of releasing nitrogen oxides right in the middle of the ozone layer at altitudes of 20 km.

This was also the start of intensive research into the chemistry of the atmosphere.

Competing Reactions

Mario Molina, Sherwood Rowland (1974): ClO_x cycle

ClO_x species are produced from chlorofluorocarbons (CFC's) and methyl chloride

CFC's are artificially produced; methyl chloride is a naturally occuring chemical.

Examples of CFC's : Freons ($CFCl_3$, CF_2Cl_2)

$CCl_2F_2 + h\nu \rightarrow CF_2Cl + Cl$

$CCl_2F_2 + O \rightarrow CF_2Cl + ClO$

Reactions of ClO_x species with O_3

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net Reaction

$$O + O_3 \rightarrow 2O_2$$

“Ozone Depletion”

1974 - Mario Molina, Sherwood Rowland

Paul Crutzen, Mario Molina, Sherwood Rowland

1995 Nobel Prize in Chemistry - for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"

http://www.nobel.se/chemistry/laureates/1995/press.html

Consequences of Competing Reactions

Catalytic Reactions

catalyst intermediate

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

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

intermediate catalyst

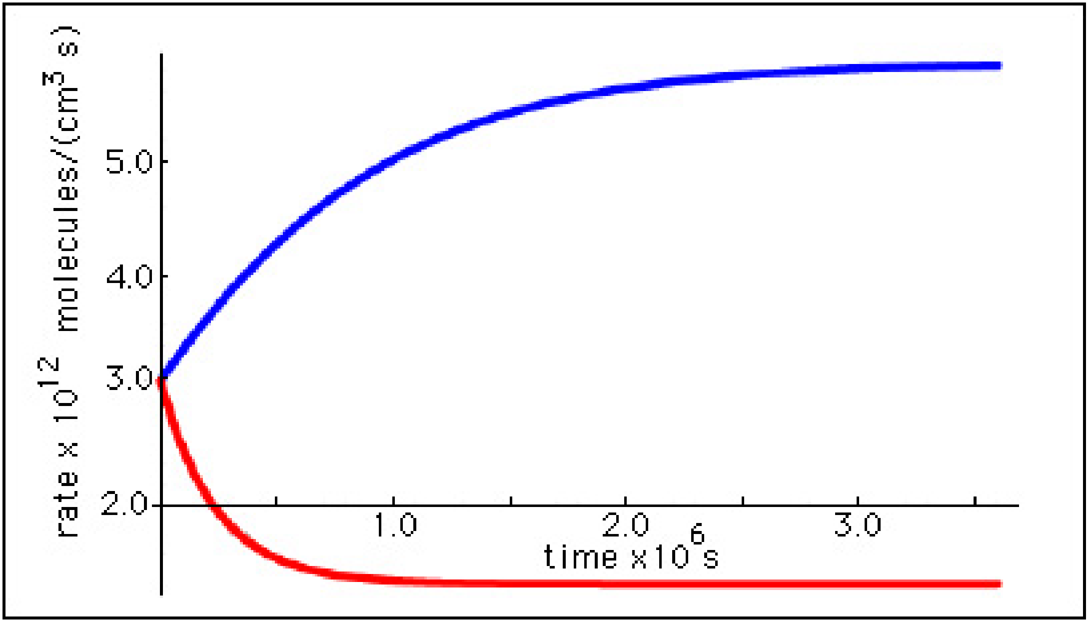
- lower activation energy

E_a for Chapman mechanism = 17.1 kJ/mol

E_a for ClO_x reaction = 2.1 kJ/mol

Consequences of Competing Reactions

Effect of competing reaction on rate of ozone formation



Depleting reactions are NOT independent of each other; all occur simultaneously

NET LOSS OF OZONE

Sources of ozone depleting molecules in the stratosphere

Naturally occuring species (H_2O, N_2O, CH_4)

Artificial, “man-made” species

- CFC’s (CCl_3F,CCl_2F_2, etc.)
- CCl_4, $CHCl_3$
- HBFC ($CHFBr_2$,CHF_2Br)
- CH_3Br
- NO from supersonic aircrafts

The artificial compounds have the most severe effect

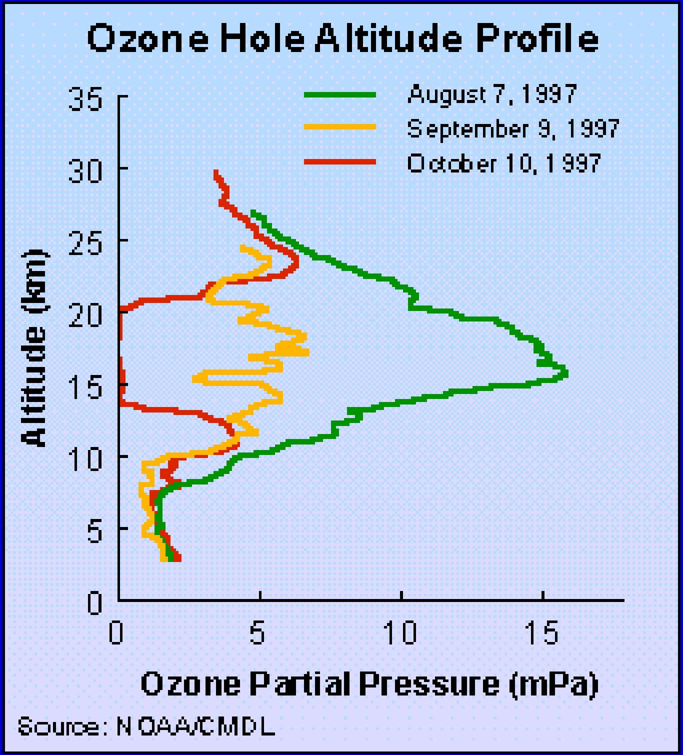
What is the “Ozone Hole”?

First observed in 1985 by the British Antarctic Survey - “realization” of ozone depleting reactions

Every spring, a huge “hole” in atmospheric levels of ozone is observed over the Antarctic.

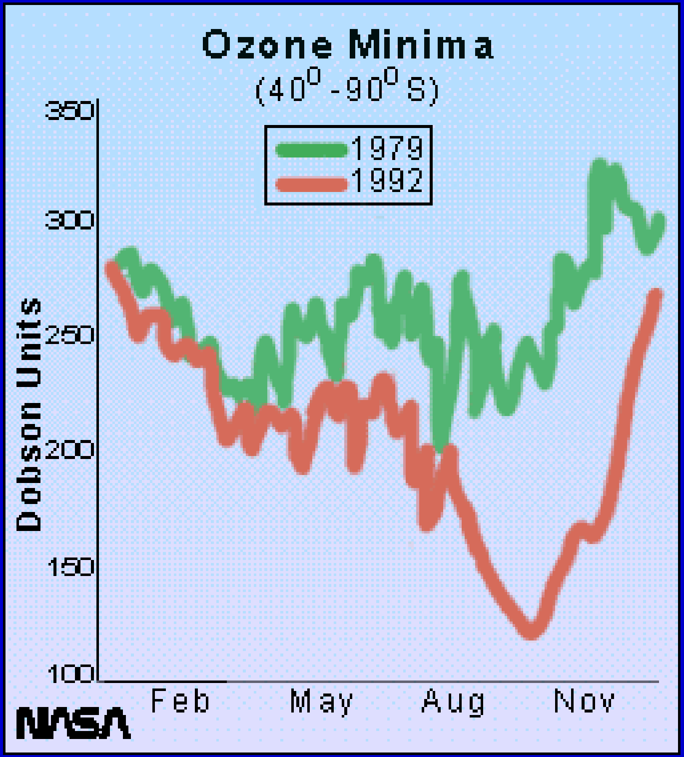
July - Sept 2001

Variation of Partial Pressure of Ozone over the Antarctic for 3 months in 1997



http://www.epa.gov/ozone/science/hole/size.html

Comparison of Ozone Levels over the Antarctic



http://www.epa.gov/ozone/science/hole/size.html

Why does the Ozone Hole form over the Antarctic and why in spring?

The Antarctic Vortex

Polar Stratospheric Clouds

Concentrations of Active Chlorine

The Antarctic Vortex

In the winter, the air around the S. Pole cools and circulates west creating a “vortex”

Cold air containing ozone depleting species is trapped in the vortex

Heat from outside is “shut off”, prolonging the duration of low stratospheric temperatures.

Polar Stratospheric Clouds

Low stratospheric temperatures result in “ice clouds” called Polar Stratospheric Clouds (Crutzen, et. al)

The surface of the ice clouds serve as reaction sites for heterogeneous gas-surface reactions

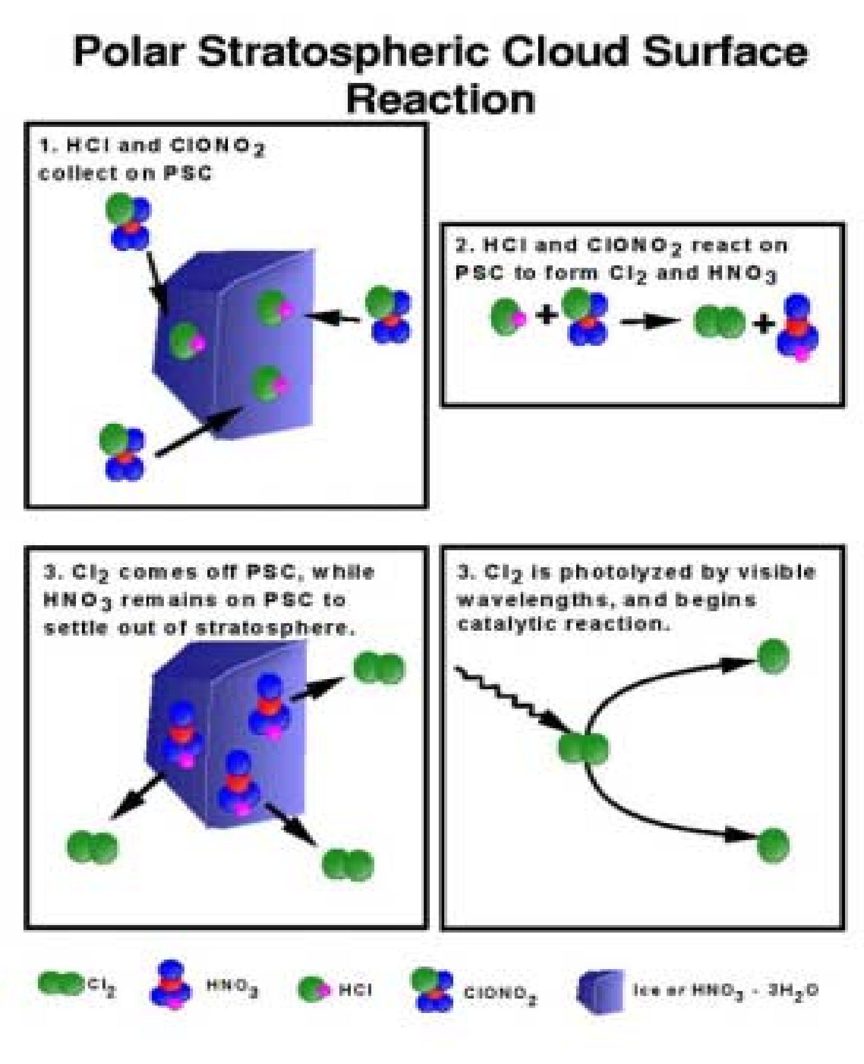
$ClO + NO_2 + M \rightarrow ClONO_2 + M$ (gas phase)

$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2$ (ice surface)

$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$ (ice surface)

Cl_2 and HOCl are “Cl reservoirs”

Heterogenous reactions



Polar Stratospheric Cloud Surface Reaction

1. HCl and $ClONO_2$ collect on PSC

2. HCl and $ClONO_2$ react on PSC to form Cl_2 and HNO_3

3. Cl_2 comes off PSC, while HNO_3 remains on PSC to settle out of stratosphere.

3. Cl_2 is photolyzed by visible wavelengths, and begins catalytic reaction.

(NASA's Goddard Space Flight Center Atmospheric Chemistry and Dynamics Branch)

The same reactions in the gas phase have much higher activation energies. High E_a and low temperatures result in very slow rates.

Concentrations of Active Chlorine

The Cl_2 and HOCl formed photodissociate to yield reactive Cl atoms

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$HOCl + h\nu \rightarrow Cl + OH$$

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

OZONE DEPLETION

“Ingredients” for the formation of the Ozone Hole

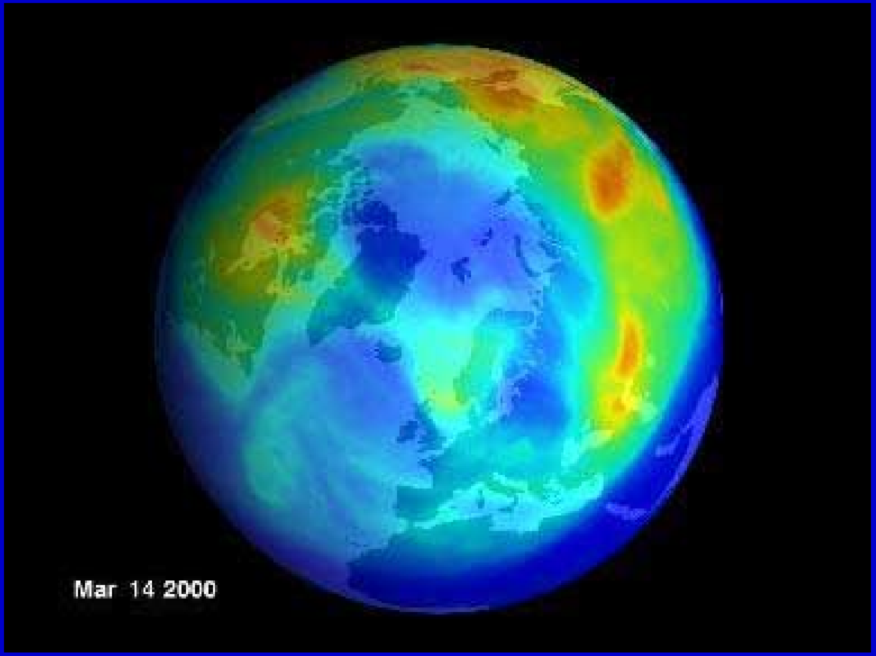
The Antarctic vortex traps CFC’s

The low polar temperatures results in ice particles on which gas-solid reactions can occur efficiently

The onset of spring corresponds to higher light intensities and hence photolysis of Cl containing species (Cl_2, HOCl)

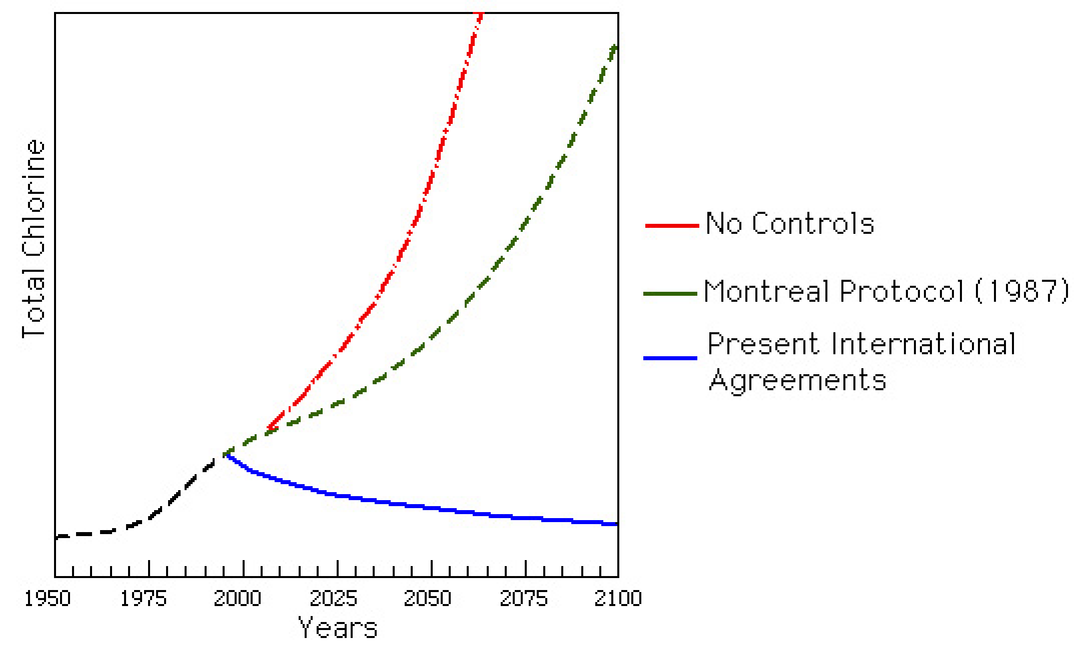
Arctic Ozone Hole

Unlike the Antarctic where it is cold every winter, the winter in the Arctic stratosphere is highly variable, NASA satellite and airborne observations show that significant Arctic ozone loss occurs only following very cold winters.



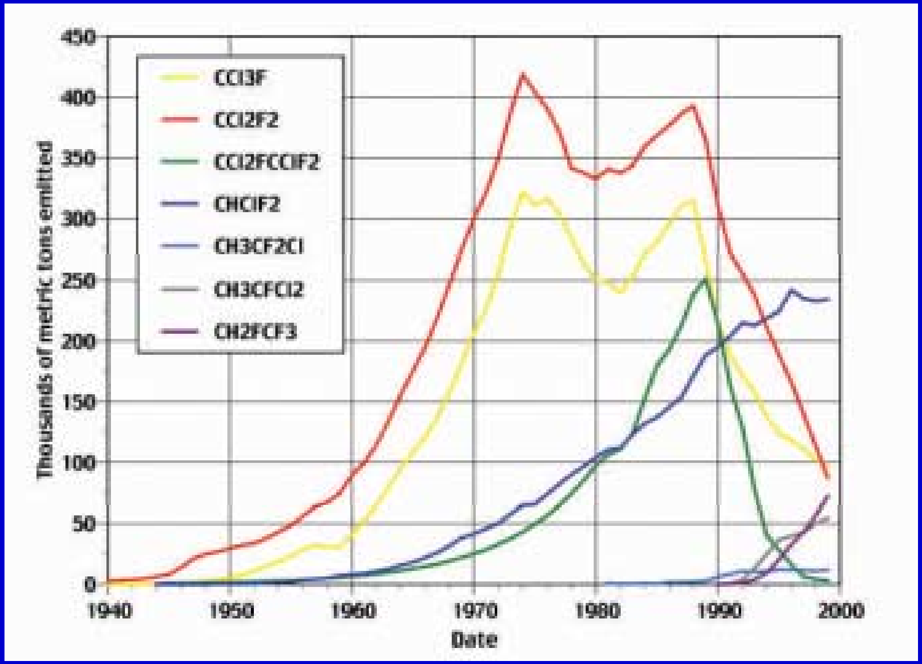
What is being done to reduce ozone depletion?

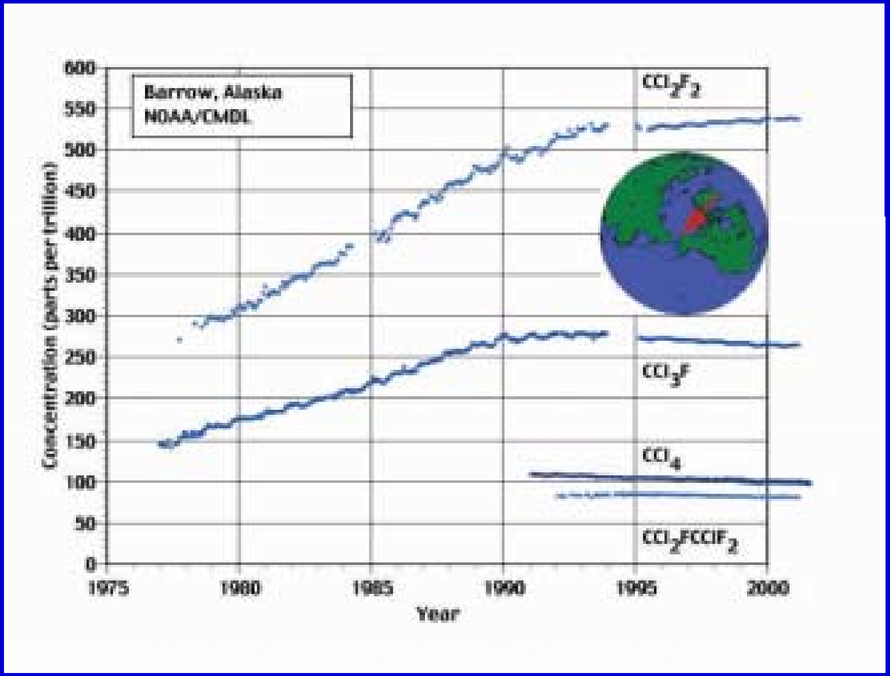
Montreal Protocol (1987) and subsequent treaties ban world-wide usage of ozone depleting substances



http://www.nobel.se/chemistry/laureates/1995/press.html

Given compliance with the prohibitions, the ozone layer should gradually begin to heal. It will take at least 100 years before it has fully recovered.

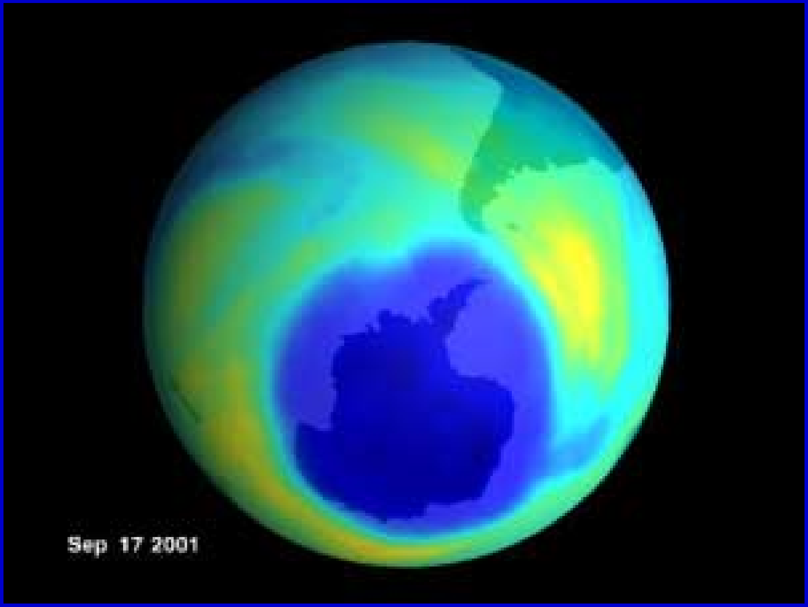

CCl3F
CCl2F2
CCl2FCClF2
CHClF2
CH3CF2Cl
CH3CFCl2
CH2FCF3
Thousands of metric tons emitted
450
400
350
300
250
200
150
100
50
0
1940
1950
1960
1970
1980
1990
2000
Date


Barrow, Alaska
NOAA/CMDL
CCl_2F_2
CCl_3F
CCl_4
CCl_2FCClF_2
Concentration (parts per trillion)
600
550
500
450
400
350
300
250
200
150
100
50
0
1975
1980
1985
1990
1995
2000
Year

2001 OZONE HOLE ABOUT THE SAME SIZE AS PAST THREE YEARS -

"This is consistent with human-produced chlorine compounds that destroy ozone reaching their peak concentrations in the atmosphere, leveling off, and now beginning a very slow decline”

http://www.gsfc.nasa.gov/topstory/20011016ozonelayer.html



References

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(www.atm.ch.cam.ac.uk/tour/index.html)

British Antarctic Survey http://www.antarctica.ac.uk/

Chemical Kinetics and Dynamics,Ch 15, J. Steinfeld,
J. Francisco, W. Hase