

Mon Oct 6

Announcements:

- more on mechanics: Reports, Guest Speakers
- talks this week:
  - weather discussion, Tues 12:30, 310 ATG
  - Fri, Oct 10, 3:30pm, 15 OTB, "Identifying environmental and ecological controls on terrestrial carbon exchange"

Today:

- ozone and global warming in the news
- ozone basics:
  - photochemistry, UV radiation, vertical structure of the atmosphere, terrestrial life

Seattle Times Oct 4, 2003

# Ozone hole swells, matches record

## Implications of change worry experts

BY ERICA BULMAN  
The Associated Press

GENEVA — The ozone hole over the South Pole grew to record-tying size this year, reversing a downward trend of the past two years, and is lasting longer, heightening concern about harmful ultraviolet (UV) radiation reaching the Earth, the United Nations' weather organization said yesterday.

Compounding matters, the thinnest area is the largest ever measured, roughly two-thirds the hole's total size, the World Meteorological Organization said.

"The ozone hole is getting larger, deeper and is lasting longer," said Michael Proffitt, a leading U.N. expert on the ozone hole. "It has never stayed this large, this late."

The "hole" is a thinner-than-normal area in the protective layer of gas high in the earth's atmosphere. It has formed in August — the end of the Antarctic winter — every year since the mid-1980s, largely due to pollution.

In recent years, the hole has tended to reach maximum size around mid-September, after which it mostly gets refilled with surrounding ozone. But this year, the hole peaked twice, once in mid-September and again in late September, the U.N. agency said. Each time it measured 10.8 million square miles, matching the record size set in September 2000.

The meteorological agency also said the thinnest part — with the ozone level 50 percent below the pre-ozone hole period of 1964-76 — exceeded 5.7 million square miles for the first time. It peaked near 6.95 million square miles Sept. 26.

Reduction of the ozone layer can let harmful UV rays from the sun reach Earth's surface. Too much UV radiation can cause skin cancer and destroy tiny plants at the beginning of the food chain.

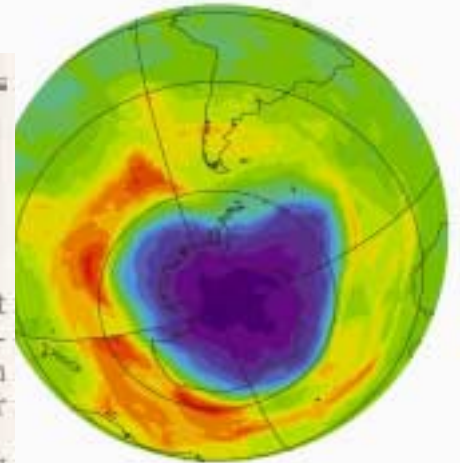
"There is certainly no indication it is getting smaller," Proffitt said. "It looks like it could be a while."

"The longer it lasts, the more effect you get from UV," he said. "When the sun is low, the UV rays slant through on an angle and have to go through a thicker layer. But as you go into the Antarctic's spring and the sun rises higher, more UV rays can get directly through the hole."

Proffitt said it was too soon to conclude what the significance of this year's larger weak spot would be.

One cause of ozone depletion is the chlorine and bromine released by human-made chemical compounds, such as chlorofluorocarbons, contained in some aerosols and refrigerants.

Emission of chlorofluorocarbons have been curbed under a global accord. As a result, measurements show they are decreasing in the lower atmosphere and have just peaked and stabilized in the important ozone layer in the stratosphere. Scientists predict it will take about 50 years for the ozone hole to stop forming.



# Putin criticizes Kyoto Protocol

*Pact wouldn't stop warming, he says*

BY VLADIMIR ISACHENKOV  
The Associated Press

MOSCOW — President Vladimir Putin cast new doubts yesterday on Moscow's willingness to ratify the Kyoto Protocol on curbing greenhouse-gas emissions, saying the pact will fail to achieve its goal of fighting global warming.



Vladimir Putin

"Even 100 percent compliance won't reverse climate change," he told a conference organized by the World Economic Forum in Moscow, citing disputes among scientists over the pact, which without Russia's backing will collapse.

The 1997 Kyoto Protocol calls for countries to reduce their

emissions, saying it would slow economic growth of European Union states.

He also said Russian approval of Kyoto would jeopardize Putin's goal of doubling gross domestic product in 10 years by forcing it to cut industrial emissions.

"The Kyoto Protocol will stymie economic growth," Ilarionov said. "It will doom Russia to poverty, weakness and backwardness."

He said that since the United States, China and other nations that rejected the protocol account for nearly 70 percent of global emissions, the pact would fail anyway.

Even so, Putin said yesterday that Moscow would "be reluctant to make decisions on just financial considerations."



Vladimir Putin

the pact will fail to achieve its goal of fighting global warming.

"Even 100 percent compliance won't reverse climate change," he told a conference organized by the World Economic Forum in Moscow, citing disputes among scientists over the pact, which without Russia's backing will collapse.

The 1997 Kyoto Protocol calls for countries to reduce their greenhouse-gas emissions to 1990 levels by 2012. If a country exceeds the standard, it could be forced to cut industrial production.

To be implemented, the protocol must be ratified by no fewer than 55 countries, accounting for at least 55 percent of global emissions in 1990. That minimum can be reached only with Russia, because the United States has rejected the treaty.

Earlier this week, Putin upset the opening of a U.N. World Climate Change Conference — held on the sidelines of the economic forum — by saying his Cabinet hadn't decided whether to sign off on Kyoto. He also said Russia might benefit in a warmer world with less-icy winters and higher farm output.

Throughout the conference, Putin's influential economic ad-

viser, Andrei Ilarionov, issued scathing attacks on Kyoto, saying it would slow economic growth of European Union states.

He said that since the United States, China and other nations that rejected the protocol account for nearly 70 percent of global emissions, the pact would fail anyway.

Even so, Putin said yesterday that Moscow would "be reluctant to make decisions on just financial considerations."

"We should be guided primarily by more noble ideas rather than the consideration of mundane, quick economic benefit," he said. Putin did not say how long Russia would take to decide.

Proponents said Kyoto was a vital first step in cutting emissions and warned failure to quickly put it into force would trigger a dangerous, steep rise in greenhouse-gas concentrations that would be far more difficult to control in the future.

Critics said that it has not been proved greenhouse-gas emissions were a top factor in global warming and that volcanic eruptions, the oceans' impact and solar activity needed to be more thoroughly analyzed.

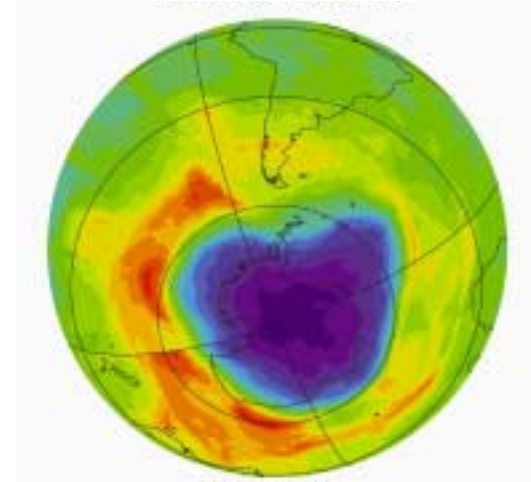
Material from Reuters is included in this report.



## Week 2

### Chap 14: stratospheric ozone

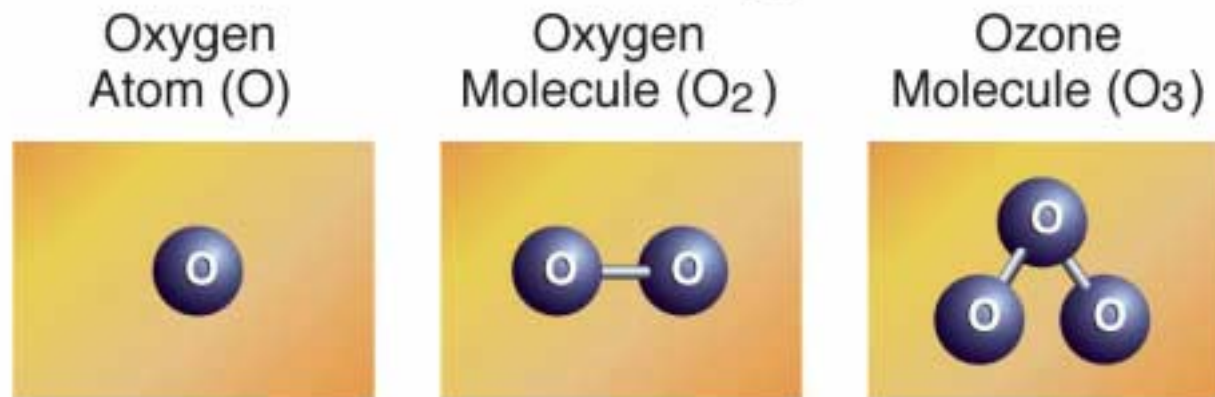
- Mon: ozone basics  
photochemistry  
UV radiation  
atmospheric structure  
terrestrial life
- Tues: CFC's and ozone  
catalytic reactions  
atmospheric cycles
- Wed: Antarctic ozone hole  
unexpected couplings
- Thurs: global ozone depletion  
ozone protection treaties  
ozone "skeptics"  
lessons from ozone
- Fri: *tutorial: math and chem*



### Goal / Motivation

- tidy example illustrating nature of the Earth-System (including humans)
- coupled system...
  - unbounded complexity
  - unexpected consequences
- global environmental problem
  - discovery
  - explanation
  - solution

## Molecular forms of oxygen



All three occur throughout the atmosphere.  
Which is most common?

# Atmospheric ozone: vertical structure

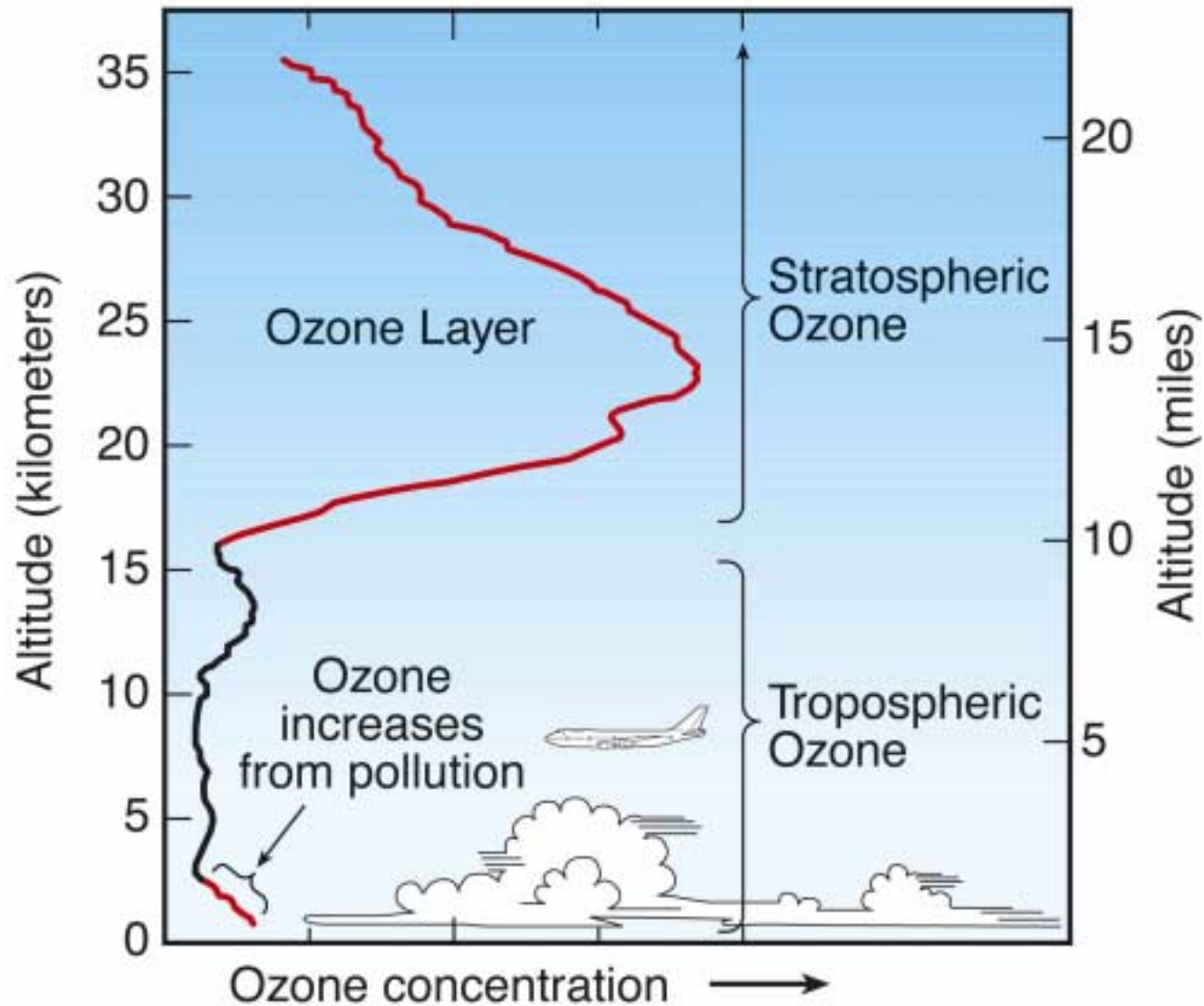
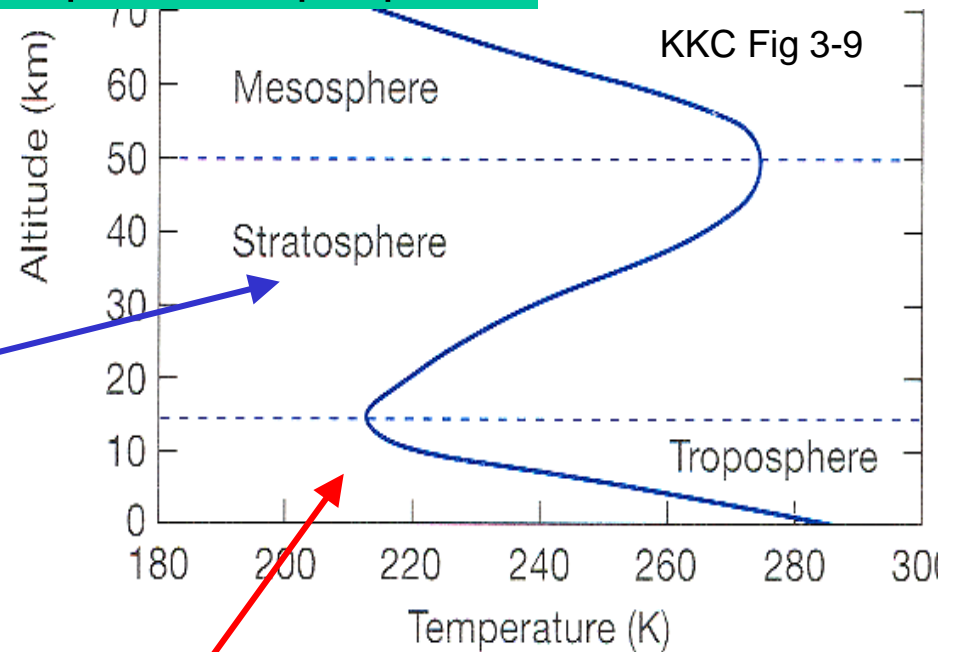


Figure source: <http://www.al.noaa.gov/WWWH/pubs/Assessment02/Q&As.html>

## Definitions: Stratosphere/Troposphere

### stratosphere

- atmospheric layer above the troposphere where most ozone is found
- temperature increases with height

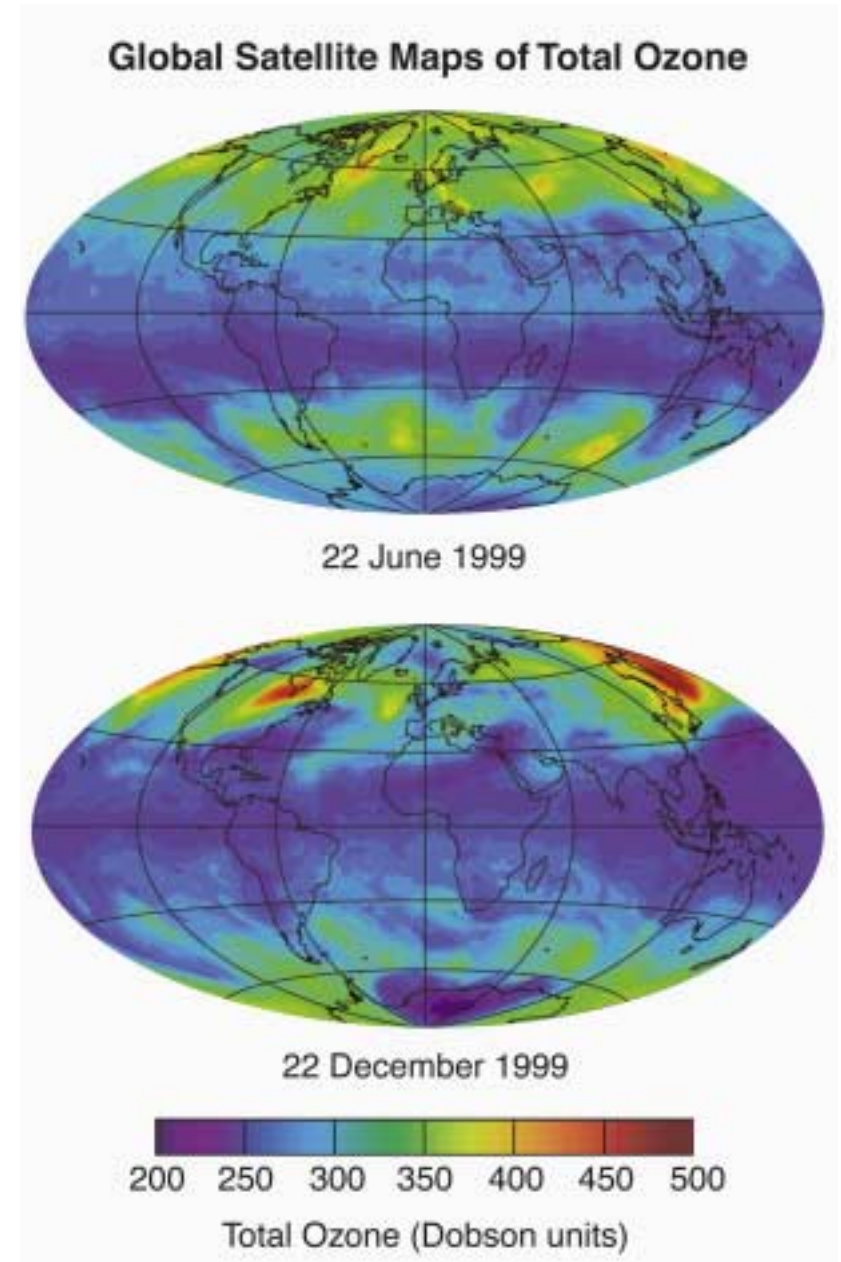


### troposphere

- the lower region of the atmosphere where "weather" occurs
- temperature decreases with height

## "DU" (Dobson Unit)

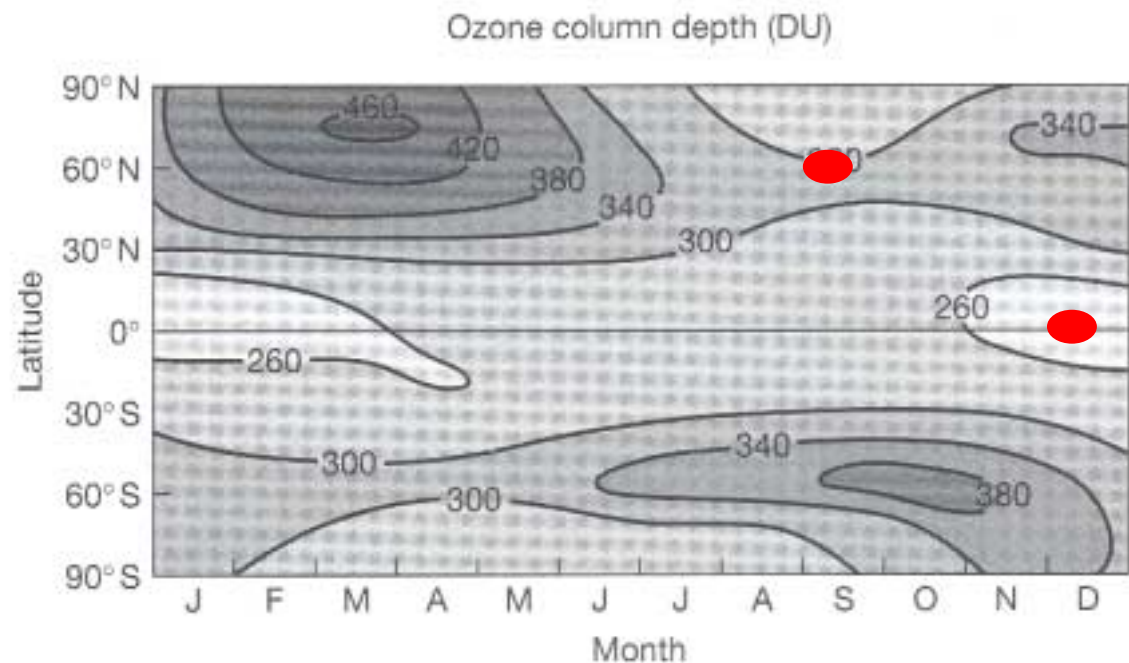
- measure of **"ozone column depth"**
  - > related to the number of  $O_3$  molecules overhead
  - > 1DU = 0.001 cm at surface pressure
- typical value is 300 DU  
= 0.3 cm layer (3 mm)
- geographical distribution ???
  - > thin in the tropics
  - > thicker at high latitudes
  - > thickest in NH high latitudes





## HW practice

If you were to move from 60°N (say, Stockholm, Sweden) to the equator (say, Nairobi, Kenya), how much of a change would you experience in minimum ozone column depth during a typical year?



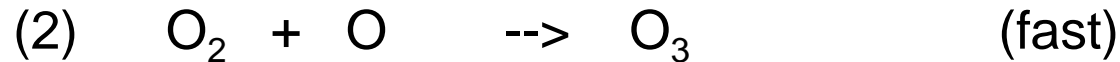
**FIGURE 14-5**

Latitudinal and seasonal distribution of ozone column depth as measured by satellite, composited over several years. Contours represent column depths in Dobson units.

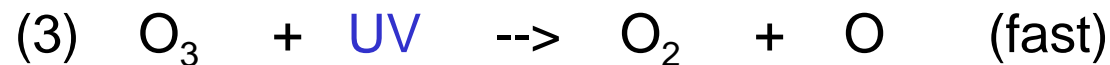
from ~300 DU to ~250 DU or ~17% reduction ( $50/300 = 0.17$ )

## ozone chemistry in stratosphere part I: fast reactions

### production of ozone



### destruction of ozone



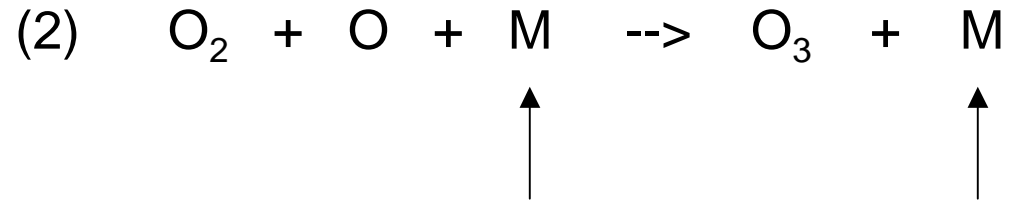
NET reaction: (2) + (3)



- There is no net production or destruction of any chemical species.
- This cycle of reactions results in the absorption of UV radiation, which warms the stratosphere

## note on production reaction

strictly speaking, the production reaction should be written:

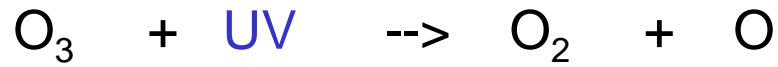


see KKC Figure 14-6 for explanation

I'm going to skip the "M" for simplicity

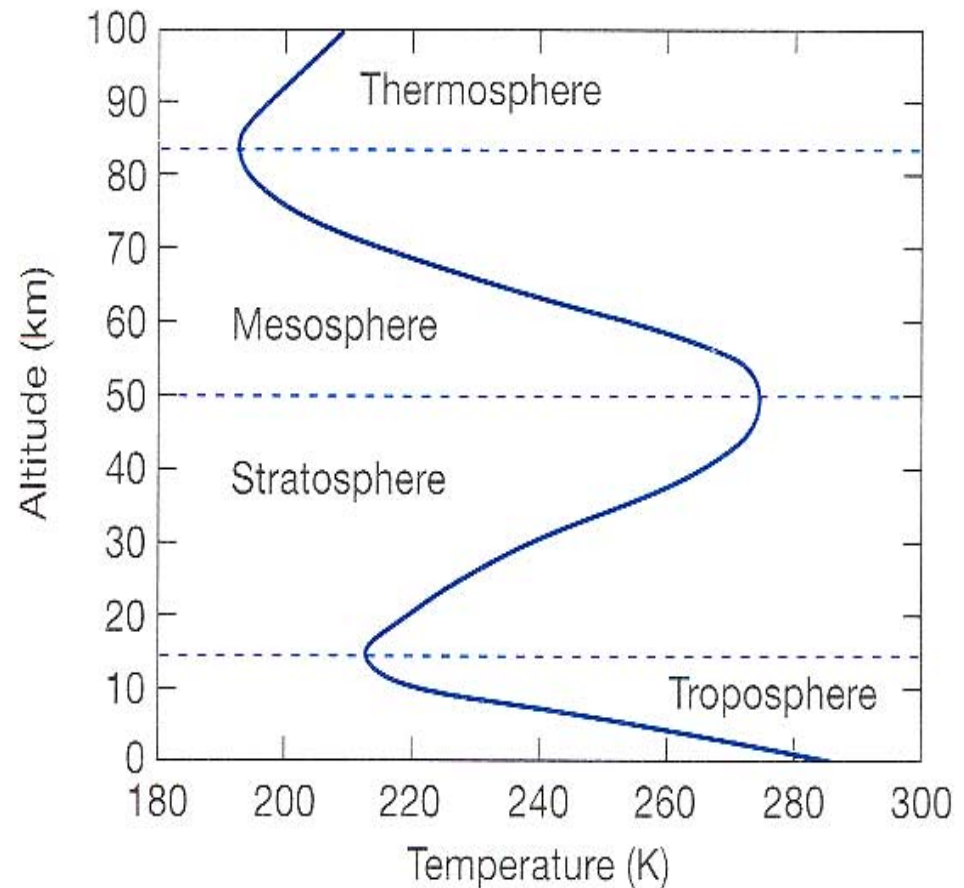
# Ozone and Atmospheric Structure

Photochemical reaction: Ozone Photolysis



## First Consequence:

- **energy** of UV radiation is added to the stratosphere
- stratosphere warms
- stratosphere becomes "stable" - resists vertical motions



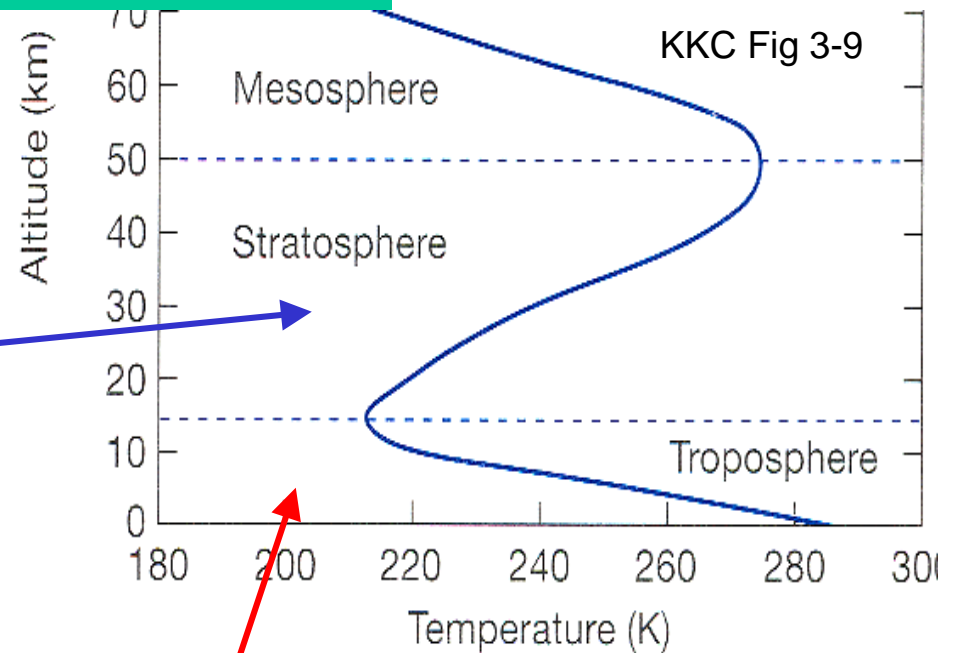
KKC Fig 3-9



## Vertical structure of atmosphere

### stratosphere

- atmospheric layer above the troposphere where most ozone is found
- heated from the within, especially at the top
- temperature increases with height
- (warm fluid on top is stable)
- little vertical motion, highly "stratified", clouds are extremely rare

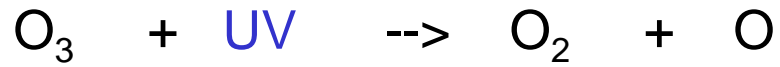


### troposphere

- the lower region of the atmosphere where "weather" occurs
- heated from the bottom
- temperature decreases with height
- (warm fluid on bottom is unstable)
- vertical motions, clouds, precipitation, hydrological cycle

# Stratospheric ozone: Why do we care?

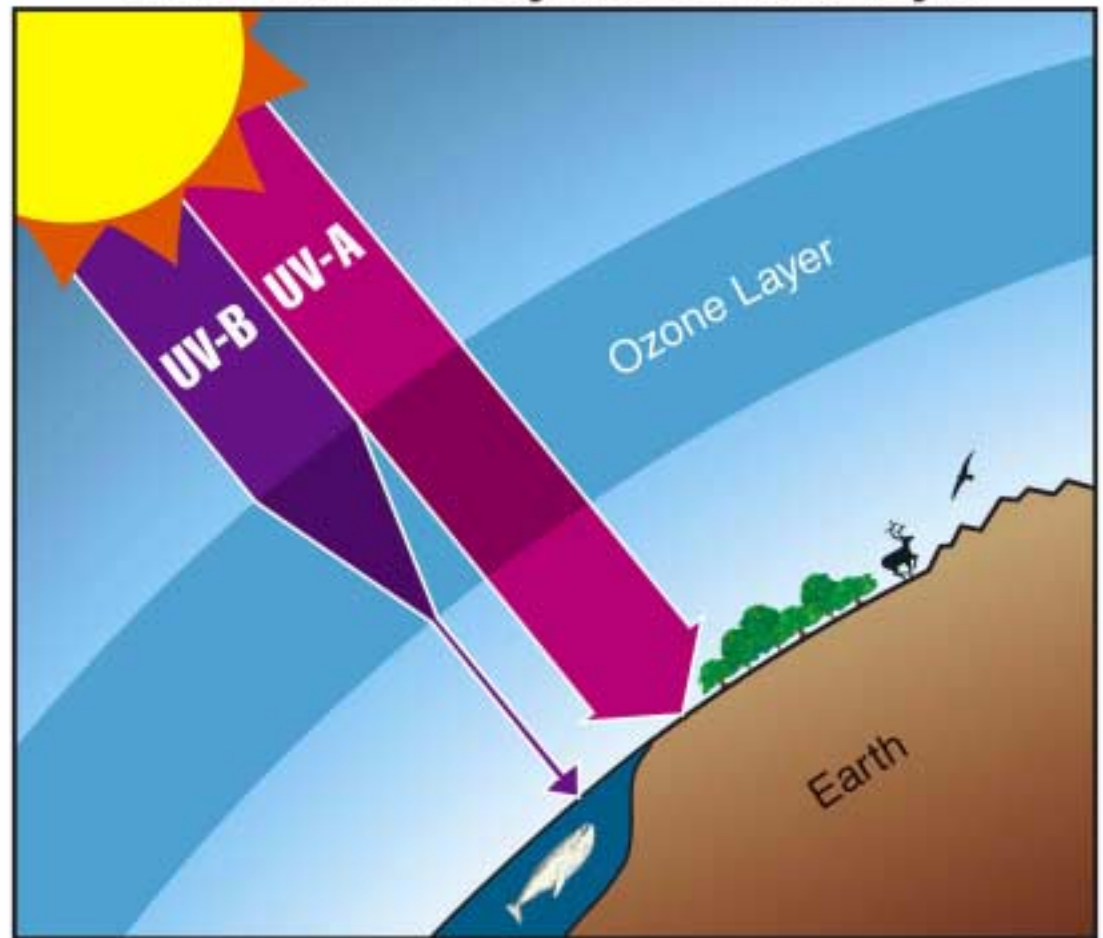
Photochemical reaction: Ozone Photolysis



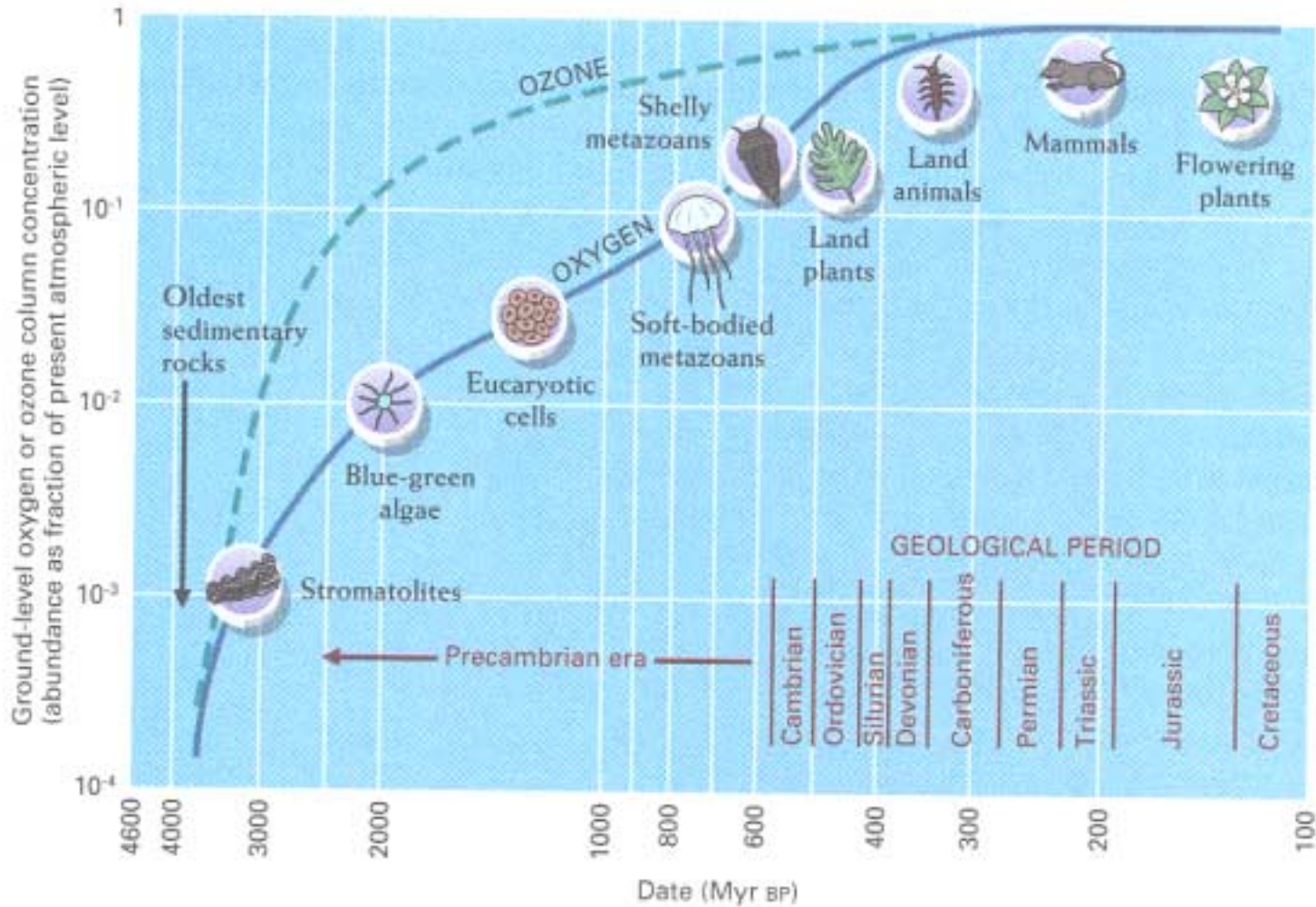
## Second Consequence:

- Earth surface shielded from UV-B radiation
- Makes possible life on land

UV Protection by the Ozone Layer



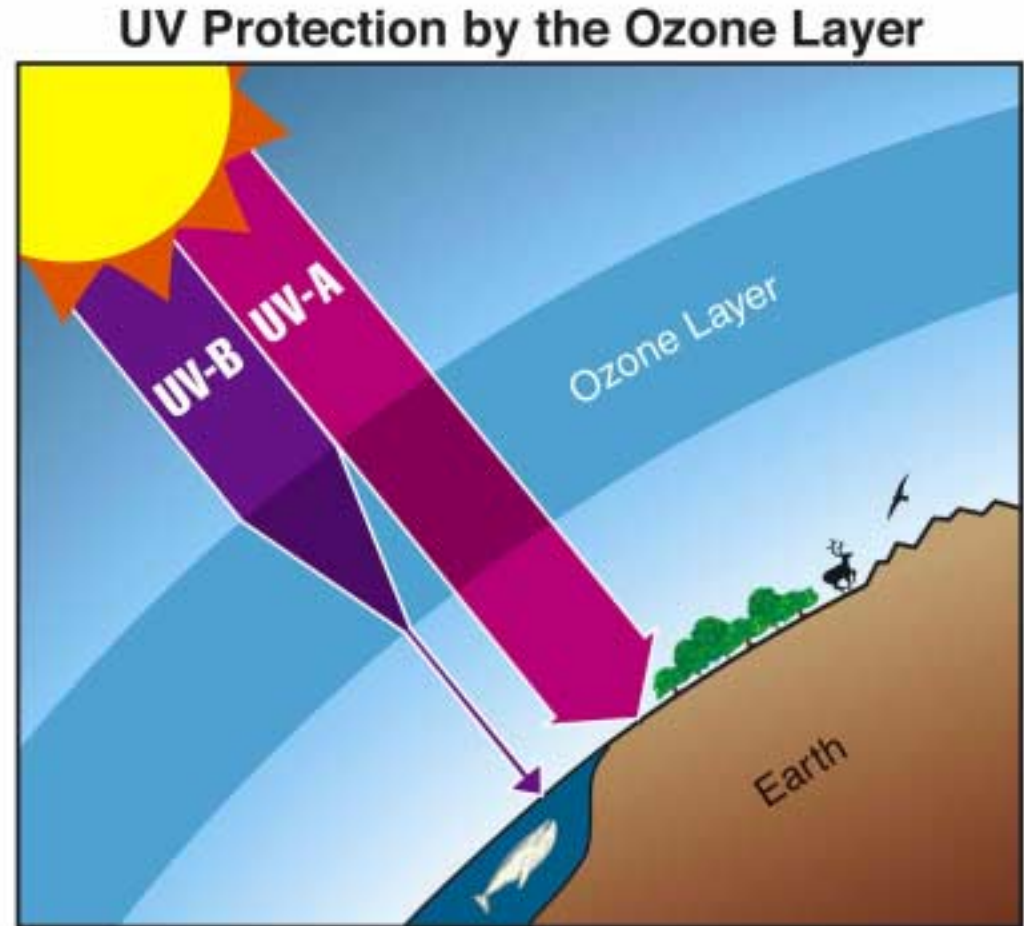
# Role of Ozone in Earth History



source: Graedel and Crutzen (1995) *Atmosphere, Climate, and Change*, p. 63

## "UV" (ultraviolet radiation)

- ultraviolet means "beyond violet"
  - shorter wavelength than violet
  - not visible to humans
- highly energetic
  - drives photochemical reactions
  - causes harm to life (sunburn, genetic damage, cancer)
- 3 classes: A, B, C
  - A not harmful
  - C extremely harmful, but none gets to surface
  - B is the big concern





Tues Oct 7

Announcements:

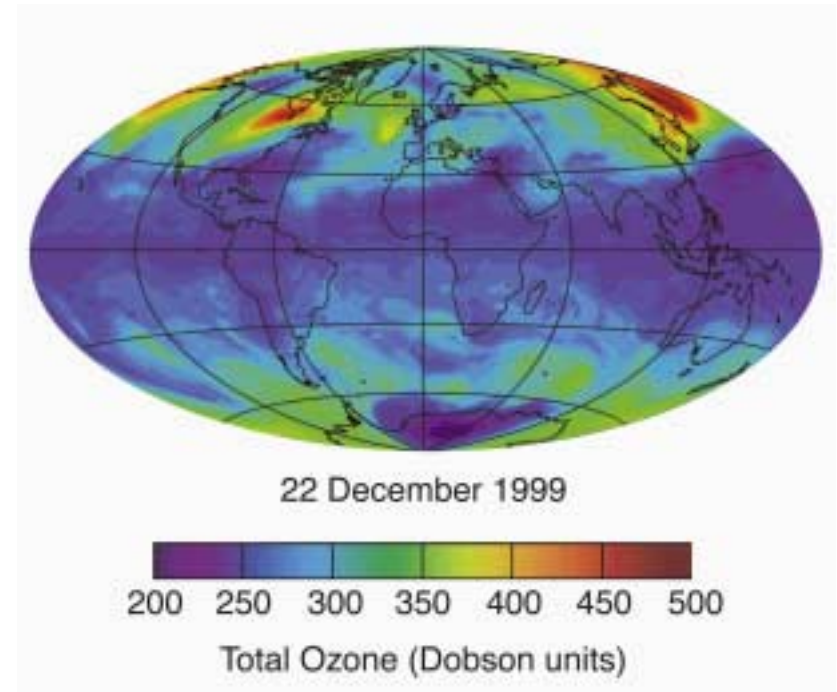
- ozone graphics and info posted to website
- talks this week:
  - weather discussion, Tues 12:30, 310 ATG
  - Fri, Oct 10, 3:30pm, 15 OTB, "Identifying environmental and ecological controls on terrestrial carbon exchange"

Today:

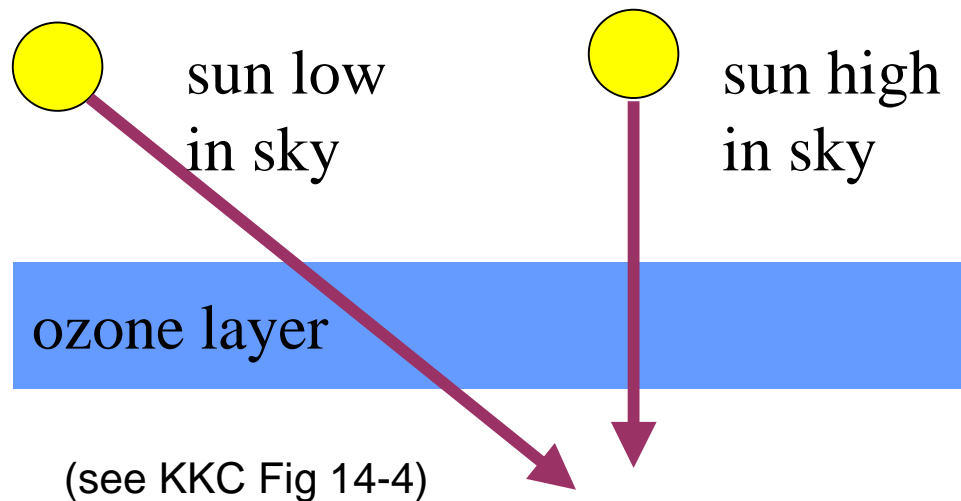
- UV dose
- ozone chemistry outline
- oxygen-only reactions
  - dynamic equilibrium
- CFC's and ozone
  - catalyst
  - atmospheric lifetime

## UV dose

- UV dose is the amount of UVB radiation received at the surface
- Give **two** reasons why UV dose is normally higher in the tropics (like Hawaii) than at high latitudes (like Seattle)?



(see KKC Fig 14-5)



### two factors control UV dose

- ozone column depth
- solar zenith angle

## Stratospheric Ozone Chemistry - Outline

- oxygen-only reactions
- catalytic destruction by halogens (Cl and Br)
- Antarctic ozone hole (Wednesday)
  - discovery
  - explanation: surface catalyzed reactions

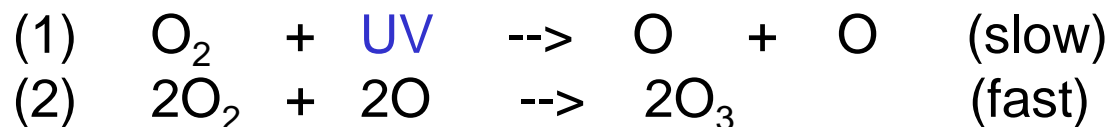
concepts:

- rate of reaction
- coupled reactions -> net reaction
- dynamic equilibrium
- catalyst (speeds up a reaction)

motto:

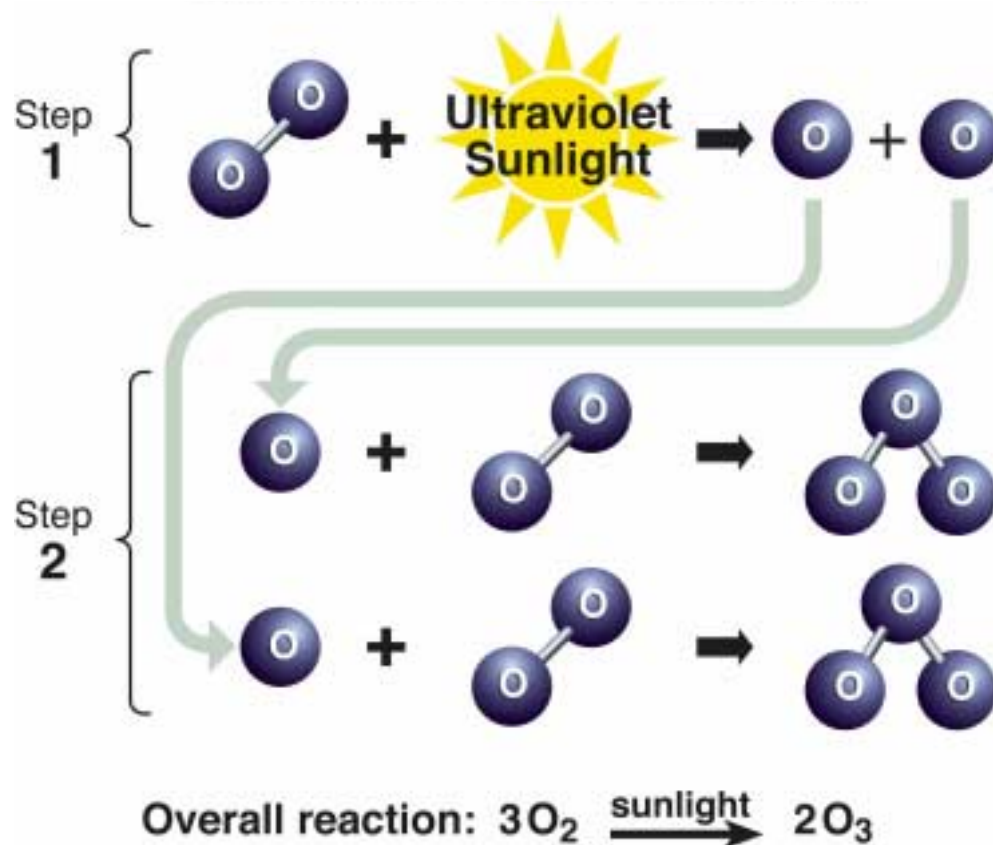
"No law says nature has to be simple!"

## Ozone Production in the stratosphere



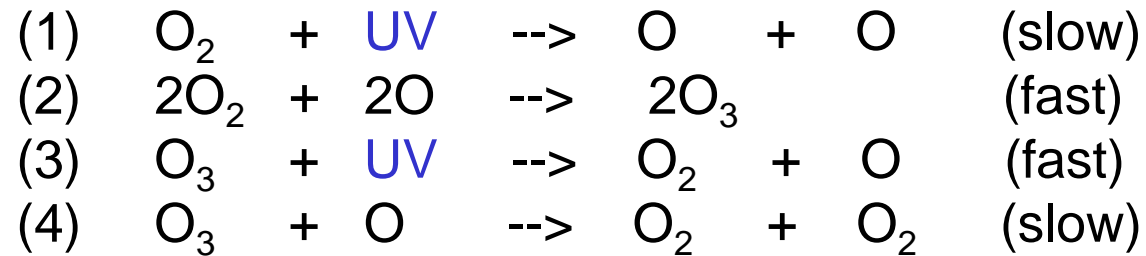
Step 1, the slow reaction, is the **rate-limiting** step.

(Production rate depends entirely on rate at which Step 1 occurs.)





## Ozone equilibrium from oxygen-only reactions

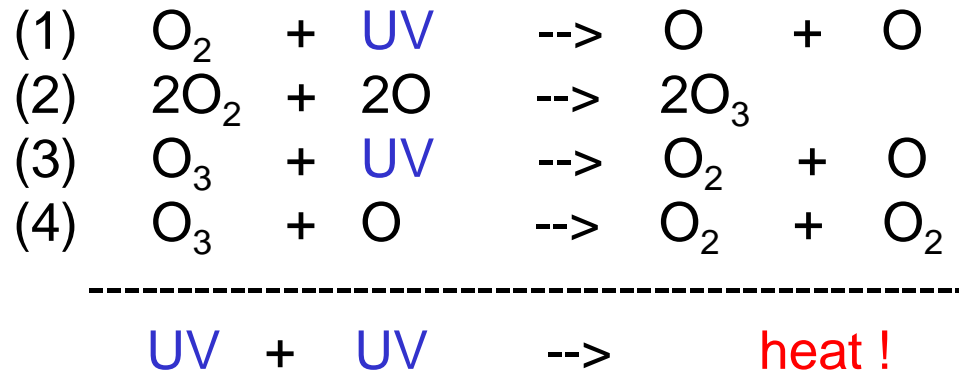


(KKC Tables 14-2, 14-3)

- Production: (1) and (2)
- Destruction: (3) and (4)
- Odd-oxygen: O &  $O_3$  (reactive, rare)
- Odd-oxygen cycling - (2) and (3) - is fast
- Real production: (1) convert  $O_2$  to odd-oxygen
- Real destruction: (4) convert odd-oxygen back to  $O_2$

## In-class activity (part 1)

Calculate the NET reaction...



- There is no net production or destruction of any chemical species.
- This cycle of reactions produces:
  - **heat** (warming the stratosphere)
  - an *equilibrium* concentration of  $\text{O}_3$  (also of  $\text{O}$ )
  - "dynamic equilibrium"

Given solar energy (UV flux) and  $\text{O}_2$  concentration...

- equilibrium concentration of  $\text{O}_3$  depends on rate of reaction (4).

## Catalyst definition

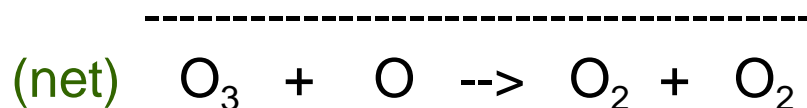
### catalyst

- a substance that accelerates the rate of a reaction without itself being consumed

## In-class activity (part 2)

Example catalytic reaction.

Calculate the NET reaction...



- Species X facilitates the destruction of ozone (and atomic oxygen) but is not itself consumed.
- Do you recognize the net reaction? Have you seen it before?

## Ozone Destruction Cycle 1

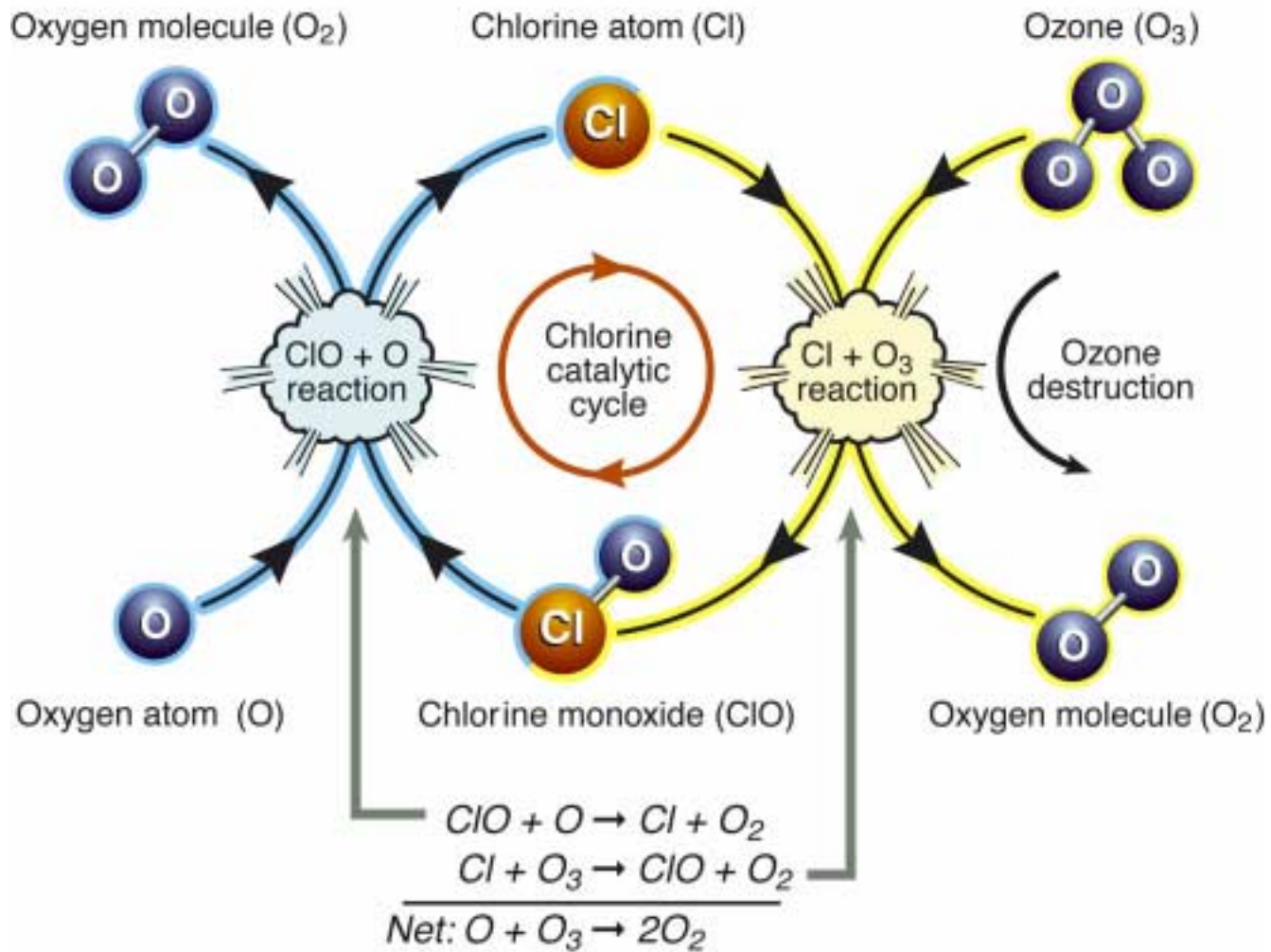
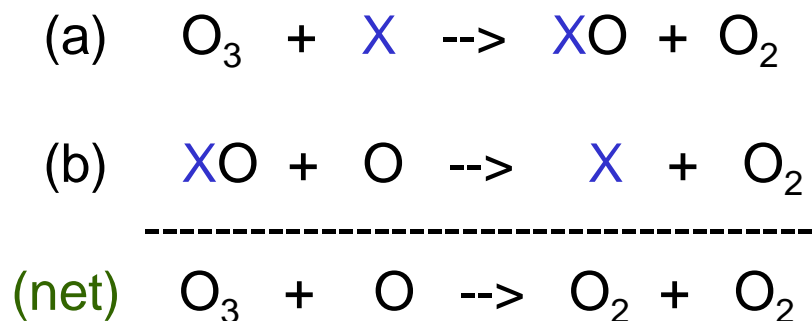


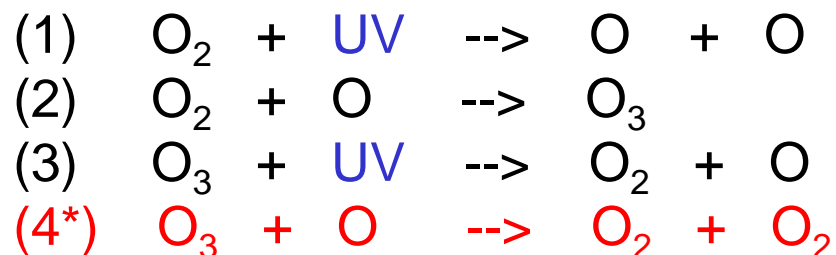
Figure source: <http://www.al.noaa.gov/WWWH/pubsdocs/Assessment02/Q&As.html>

## Catalytic Destruction

A catalyst accelerates the rate of a reaction without itself being consumed.



A new model of ozone equilibrium...



\*the 4th reaction from the oxygen-only cycle is catalyzed by species X.

Result will be a lower equilibrium concentration of  $\text{O}_3$  (due to more efficient removal).



## Catalytic Destruction

Species X can be:      NO (odd-nitrogen)  
                                 Cl (chlorine)  
                                 Br (bromine)

Reactions when X = chlorine...



NO, Cl, and Br have all been greatly enhanced in the stratosphere due to human activities.

## Origin of CFCs

In 1929, 100 people were killed in a hospital in Cleveland due to a leak in the refrigeration system.

Refrigeration systems require a "working gas" to transfer heat via compression and expansion cycle.

Traditional working gases - sulfur dioxide and ammonia - are highly toxic.

The invention of **chlorofluorocarbons (CFCs)** in the 1930s was a great step forward for public safety. These gases are totally "inert" - meaning totally non-toxic.

Soon, many other uses were found for CFCs and related bromine compounds known as halons.

Because CFCs are chemically inert, there is no mechanism by which they are removed from the atmosphere. They accumulate.

But don't be concerned. "The presence of these compounds constitutes no conceivable hazard" (Jim Lovelock, 1973).

## Vertical distribution of chlorine species

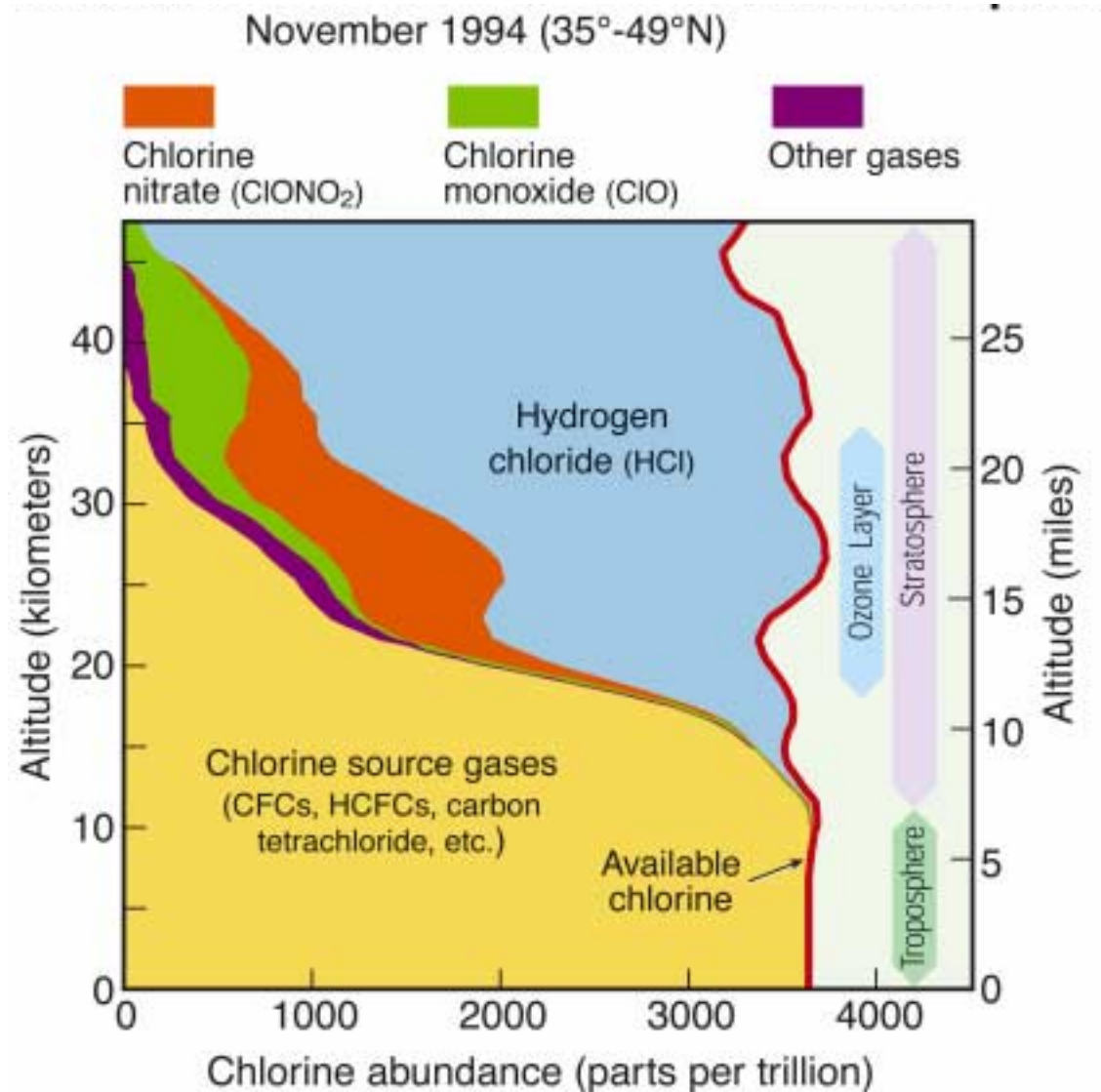
### CFC cycle in atmos:

- source in tropo; well-mixed
- sink in strato; decreases with height

### Three categories:

- **source gases (CFCs, etc)**
- **unreactive forms in strato**  
**HCl** and **ClONO<sub>2</sub>**
- **reactive form in strato: ClO**

**Only the reactive form is a catalyst and a danger to stratospheric ozone**



[Graph: Question 8 from WMO, Answers to Twenty Questions]

Wed Oct 8

Announcements:

- weather discussion anyone?
- review extra credit requirement (see website)
- upcoming talk:  
    Fri, Oct 10, 3:30pm, 15 OTB, "Identifying environmental  
    and ecological controls on terrestrial carbon exchange"

Today:

- atmospheric lifetime (exercise)
- ozone hole: discovery and explanation  
    chlorine cycle in the atmosphere  
    heterogeneous reactions (chemistry on surfaces)  
    science and policy (theory vs events)
- global trends

question from yesterday...



energy source for this catalytic cycle:

- odd-oxygen ( $\text{O}_3$  and  $\text{O}$ ) are high-energy forms.
- conversion to stable oxygen ( $\text{O}_2$ ) involves release of considerable energy.
- so energy comes from UV radiation (which creates the odd-oxygen in the first place.)

## Atmospheric lifetimes of CFCs

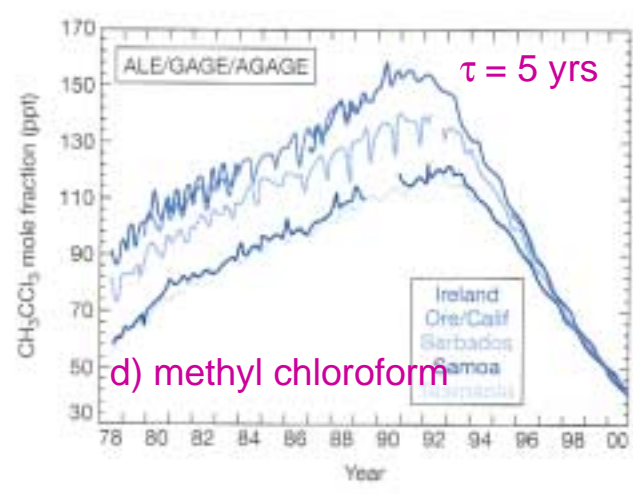
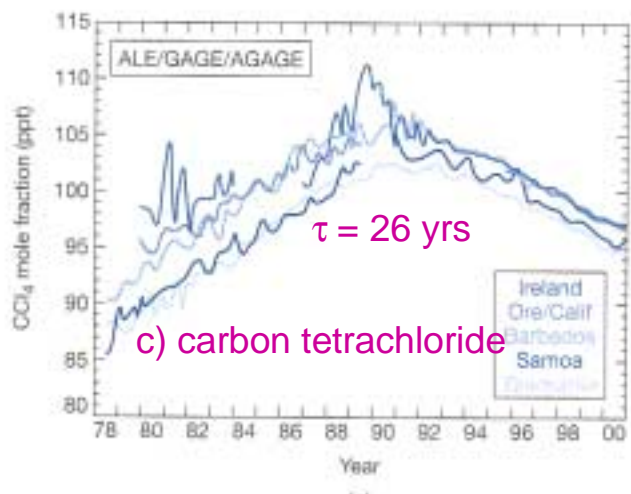
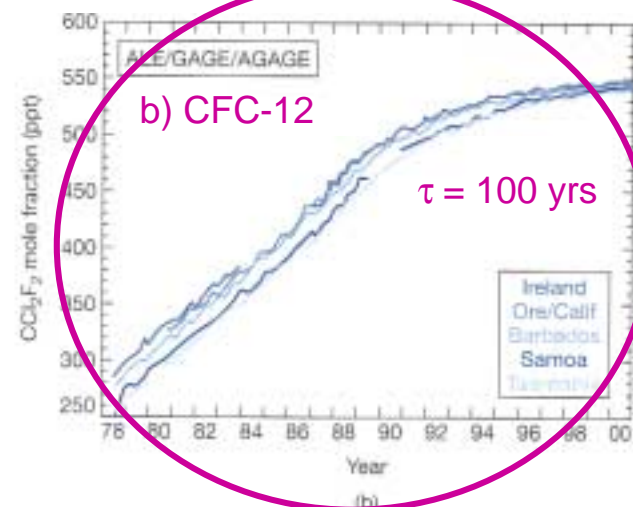
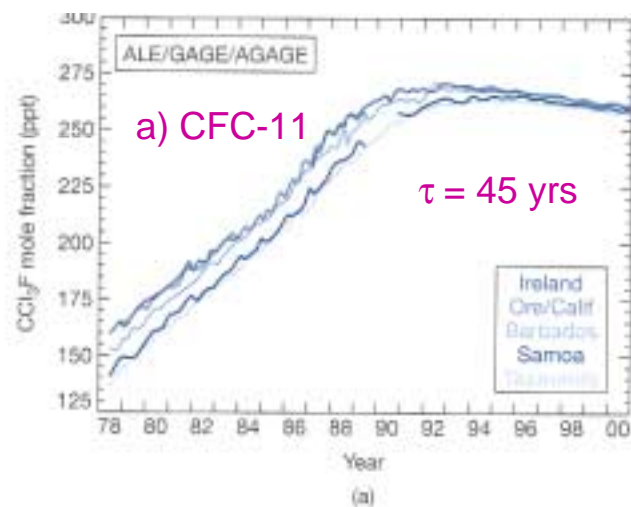
atmospheric lifetime (or "residence time"):

The average length of time a substance spends in the atmosphere.

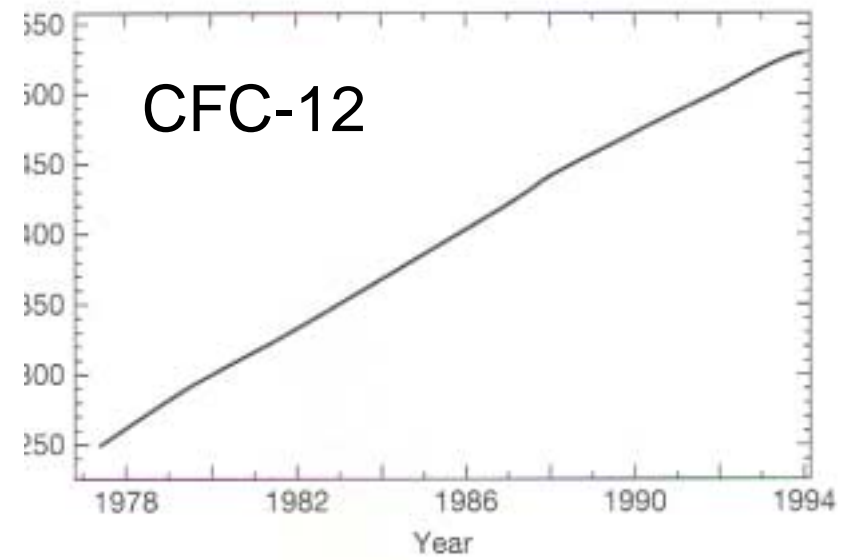
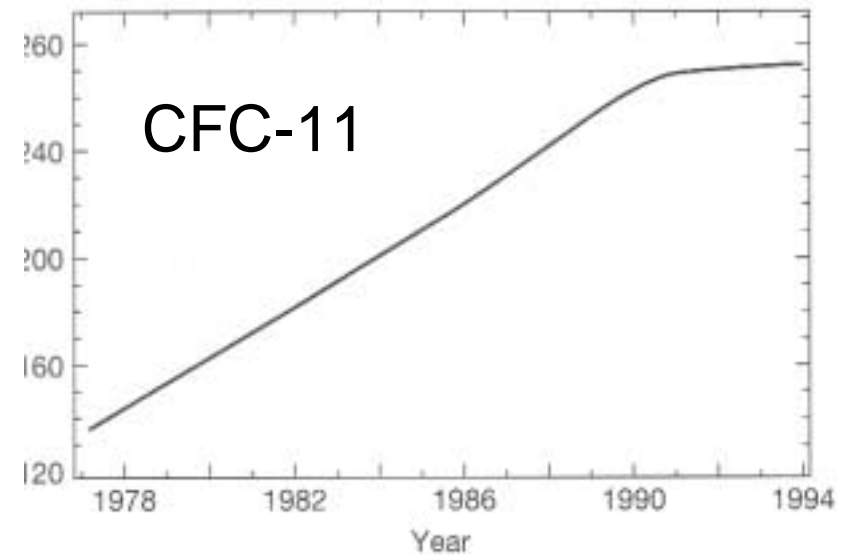
name	other name	chemical formula	atmospheric lifetime
CFC-12	Freon-12	$\text{CCl}_2\text{F}_2$	100 yrs
CFC-11	Freon-11	$\text{CCl}_3\text{F}$	45 yrs



## Observed changes in CFCs: in-class activity



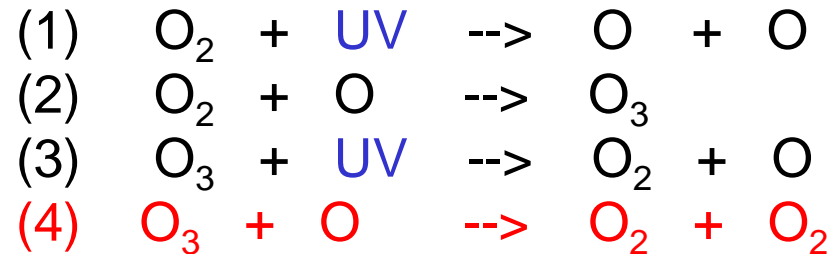
Emissions of all these compounds were greatly reduced in about 1990.  
Which compound has the longest atmospheric lifetime? Explain.



KKC Fig 14-8

## ozone and CFC recap...

Ozone level governed by **dynamic equilibrium**. Loss rate via step (4) is key.



Understanding in 1970's:

- Cl can **catalyze** reaction (4)
- Cl in stratosphere is increasing due to CFCs

but

- most Cl in stratosphere is locked up in **unreactive forms**

thus,

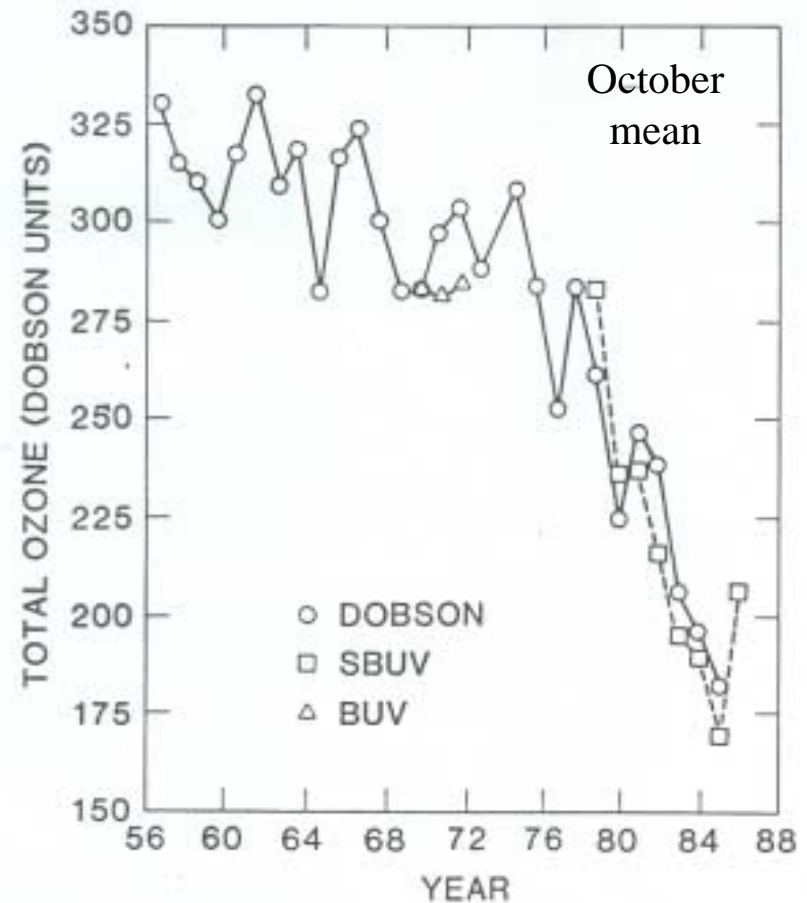
- CFCs should cause only modest losses of ozone  
(predicted 7% loss by 2100)

**then came Farman et al., 1985...**

## **1985: Ozone Hole Discovery**

see also KKC Fig 1-6

- Total ozone over Halley Bay, Antarctica in October.
- Farman et al., (1985) long-term, ground-based measurements (circles)
- later confirmed by TOMS satellite measurements (squares)



## Antarctic Ozone Hole

see also KKC Fig 1-7

- Satellite view of ozone hole
- TOMS: Total Ozone Mapping Spectrometer
- TOMS launched in 1979
- Ozone hole developed over Antarctica in the early 1980's
- So, naturally, the TOMS satellite discovered it, right?

**WRONG! Low values were rejected by the TOMS computer as instrumental error.**

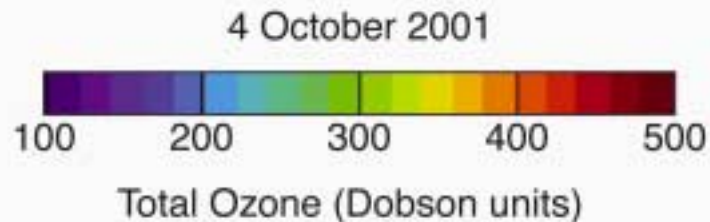
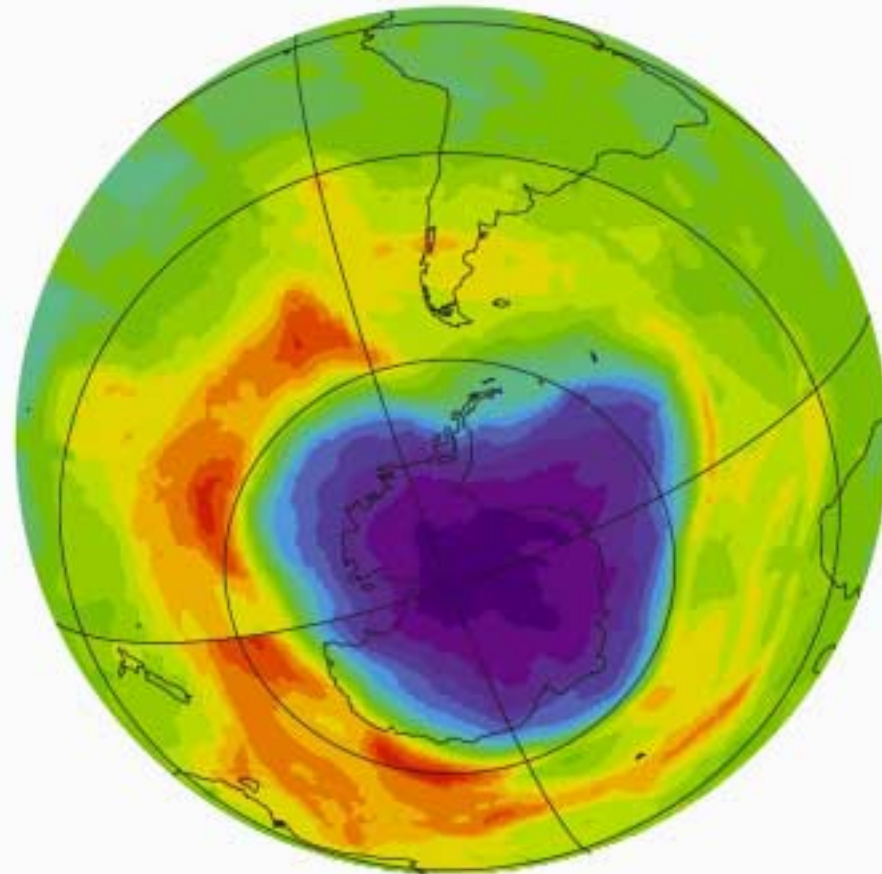


Figure source: <http://www.al.noaa.gov/WWWH/pubdocs/Assessment02/Q&As.html>

## 1987: State of Knowledge

# Changes in Stratospheric Ozone

RALPH J. CICERONE

Science (1987) 237, 35-42

Large O<sub>3</sub> decreases over Antarctica have been reported (13); this perturbation was not predicted, nor is there an accepted explanation at present. E:-

, after Farman and colleagues (13) of the British Antarctic Survey (BAS). A decrease of more than 35% has occurred since about 1970. Stolarski and co-workers (13) examined NASA satellite data on total O<sub>3</sub> and found that the phenomenon is regional in extent, not just local. "T"



## Science and Policy

### NORMAL TIMES (theory-driven)

- 1974 Molina and Rowland propose catalytic destruction of stratospheric ozone by CFC's. They predict 7% loss over the next 50-100 years (Nature, 249, 194-196).
- 1978 US bans CFC use in aerosol sprays.
- 1979 NASA launches TOMS satellite to monitor global ozone.

### UNUSUAL TIMES (event-driven)

- 1985 Springtime "ozone hole" discovered over Antarctica (Farman et al., Nature, 315, 207-210).
- 1987 Montreal Protocol calling for strict limits on CFC emissions is signed by 59 nations, including U.S. (under Reagan).
- 1987 Cause of ozone hole is still in question. The leading theories are:
  - dynamics and natural variability
  - nitric oxide (NO) and sunspots
  - CFC's and polar stratospheric clouds

## Stratospheric "Ozone Hole": Explanation

Four years (1985-1988) of frantic research and debate led to definitive consensus that the CFC/PSC explanation was correct (KKC 14:287-290). Outline of that explanation:

1. polar vortex (extremely cold conditions)
2. formation of polar stratospheric clouds (PSCs)
3. heterogeneous reactions (reactions on surfaces)
4. removal of  $\text{NO}_2$  and H
5. liberation of Cl (normally tied up via bonding with  $\text{NO}_2$  and H)
6. massive, catalytic destruction of  $\text{O}_3$

## Vertical distribution of chlorine species

Only the **reactive form** of Cl is a catalyst and a danger to stratospheric ozone.

Almost all Cl, esp. in lower stratosphere, is bound up in **unreactive forms**.

Reactions on crystal surfaces of **polar stratospheric clouds** (PSCs) sequester NO<sub>2</sub> and H and liberate Cl.

These **heterogeneous reactions** were left out of the early models that calculated modest ozone destruction from CFCs.

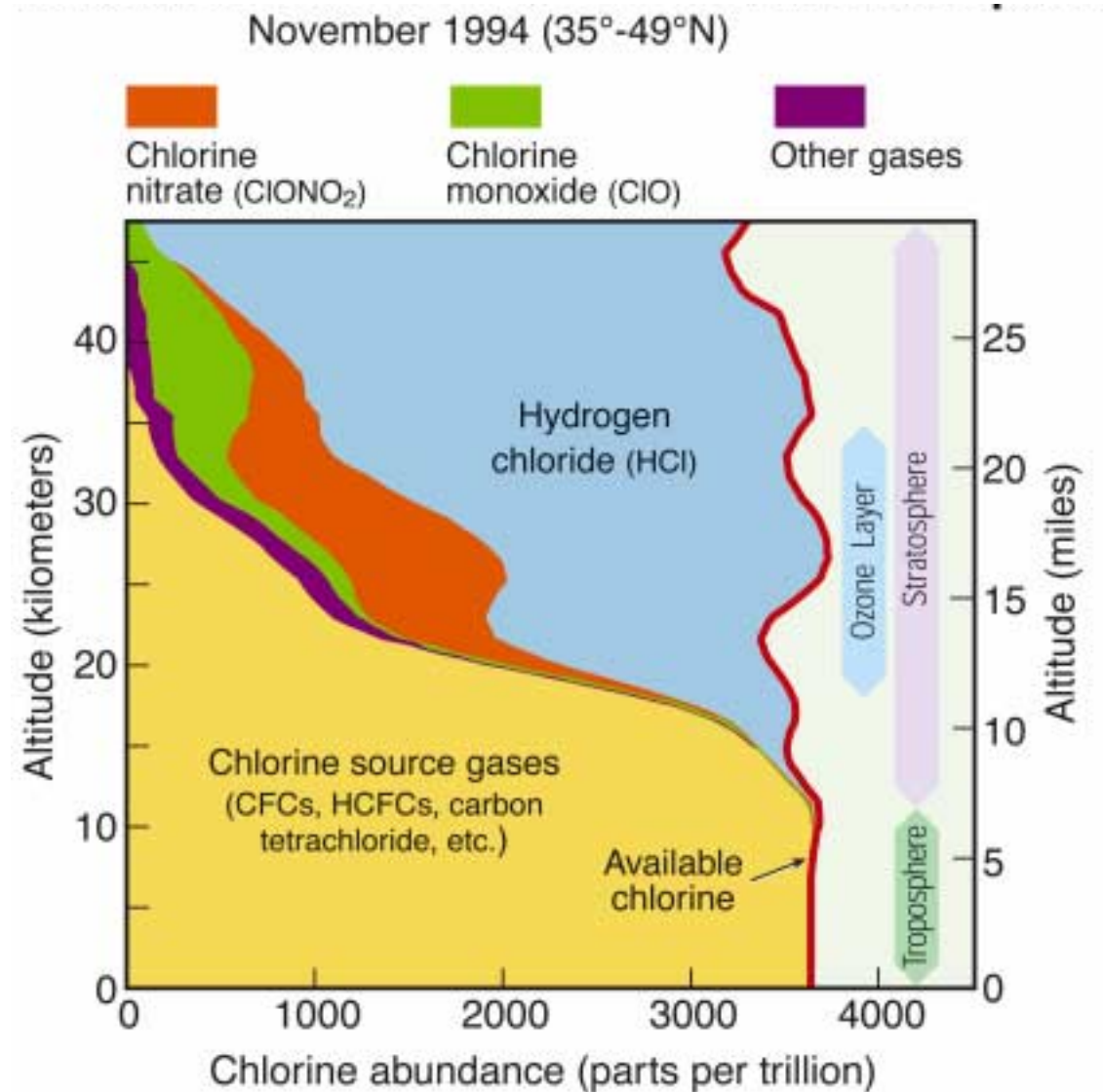
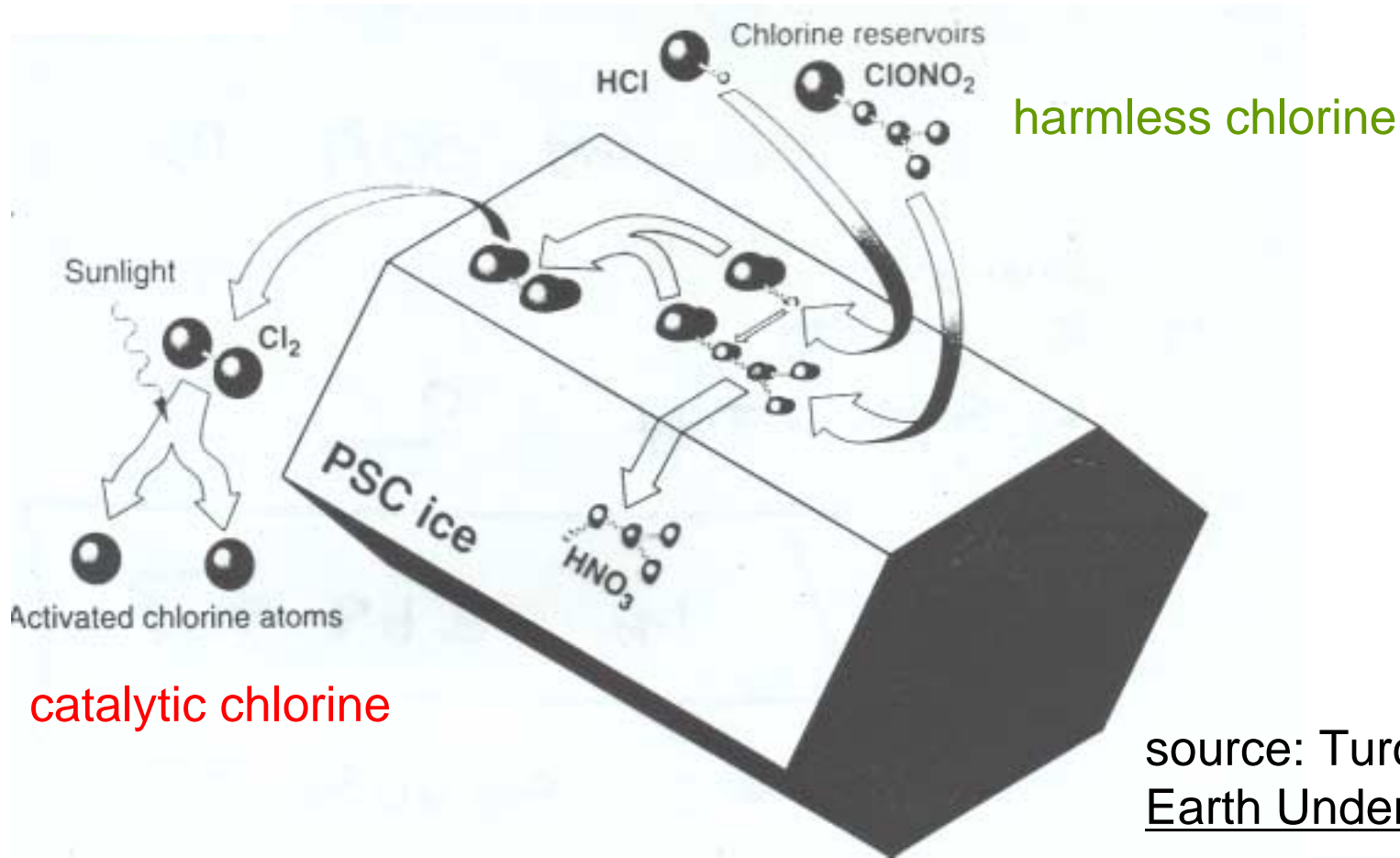


Figure source: <http://www.al.noaa.gov/WWHD/pubdocs/Assessment02/Q&As.html>

## Heterogeneous Reactions Key to catastrophic ozone destruction



source: Turco (1987)  
Earth Under Siege

Prediction: Ozone destruction should correlate with regions with high concentrations of activated chlorine (Cl and ClO)

## "Smoking gun": Correlation with ClO from aircraft

Question:

What is the ratio of  
ClO to O<sub>3</sub> within  
the ozone hole?

KKC Figure 1-7

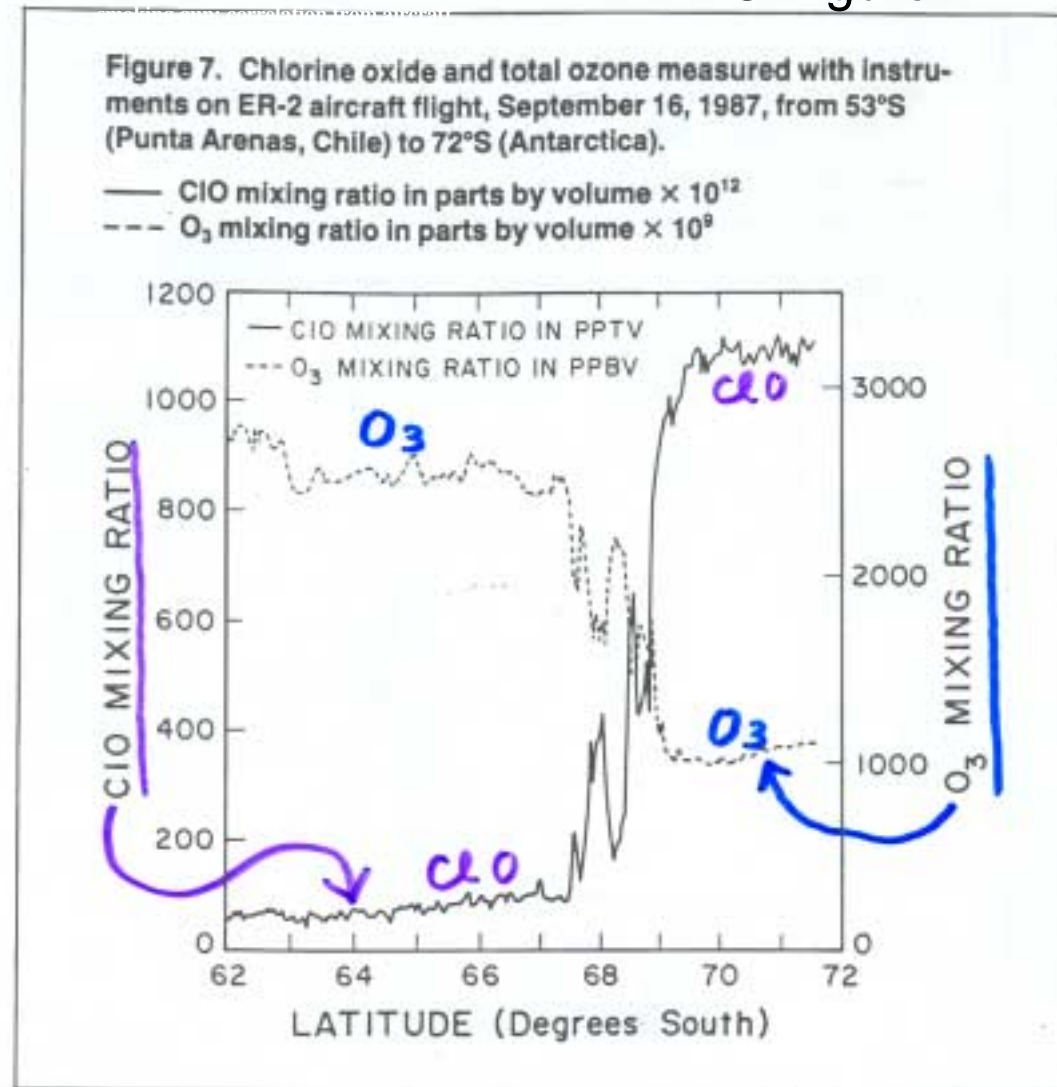
$\frac{1100 \text{ ppt ClO}}{1000 \text{ ppb O}_3}$

$\frac{\sim 1 \text{ ppt}}{1 \text{ ppb}}$

$\frac{1 \text{ ppt}}{1000 \text{ ppt}}$

= 1/1000

Not much ClO, but  
it has big effect.



**Nowadays, we can see the same correlation from satellite**

## Satellite Observations in the Lower Stratosphere

30 August 1996

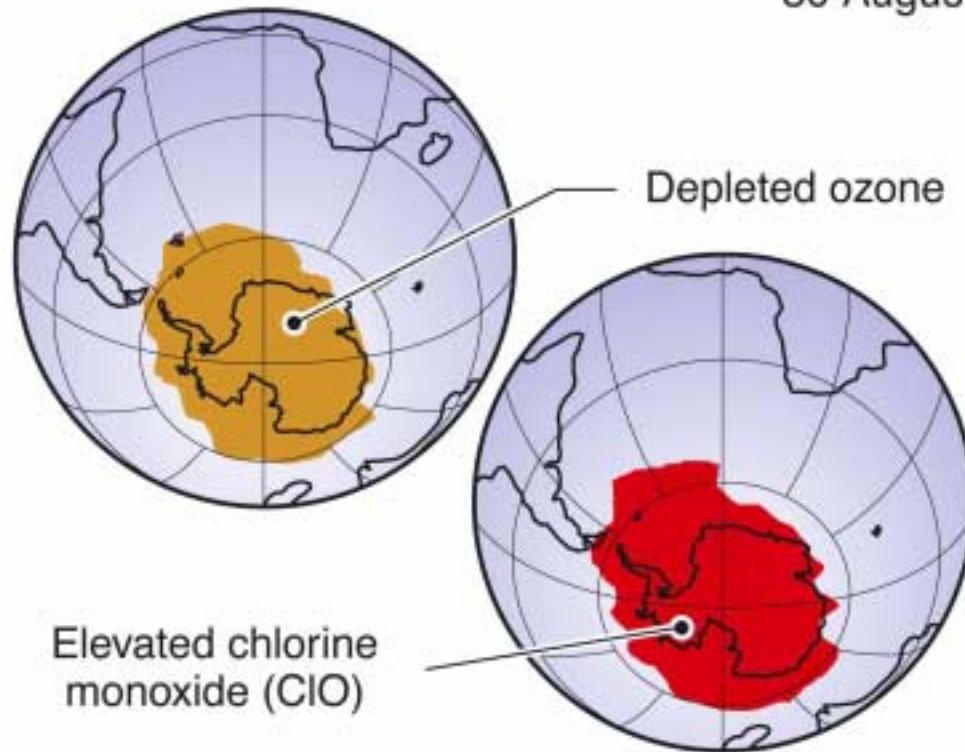


Figure source: <http://www.al.noaa.gov/WWWH/pubdocs/Assessment02/Q&As.html>



## Global trends

Very hard to determine trends at high latitudes because of large seasonal variability (Figure 14-11).

Global ozone concentrations show some response to solar cycle variations (Figure 14-12) and to volcanoes (Figure 14-13), along with a significant, overall downward trend (Figure 14-13).

1991: Mt Pinatubo eruption

1992: Susan Solomon demonstrates vulnerability of global ozone to volcanic eruptions. Involves heterogeneous reactions. Explain.

As long as chlorine levels in the stratosphere are elevated, we are vulnerable to adding particulate surface area to the stratosphere. (Heterogeneous reactions convert unreactive Cl to reactive Cl.)

When will stratospheric chlorine return to pre-industrial level?

Proposed "geoengineering" solution to global warming problem: add particles to stratosphere to reflect sunlight!

Thurs Oct 9

Announcements:

- HW due Monday (at beginning of class)

Today:

- global trends
- ozone control (Sci Assessments and Int'l Treaties)
- ozone skeptics
- ozone lessons

Friday: math/chem review

Next week: Daisyworld and the science of systems  
(Chapter 2)

question from yesterday...

Carbon tetrachloride ( $\text{CCl}_4$ ):

non-flammable, heavy liquid (boils 77C)

uses: fire extinguisher, solvent, cleaning agent,  
industrial processes

Methyl chloroform ( $\text{CH}_3\text{CCl}_3$ ):

non-flammable liquid (boils 74C)

uses: solvent, cleaning agent, industrial processes

## Global trends

1991: Mt Pinatubo eruption

1992: Susan Solomon demonstrates vulnerability of global ozone to volcanic eruptions. Involves heterogeneous reactions. Explain.

- Heterogeneous reactions (on surfaces) convert unreactive Cl to reactive Cl.
  - As long as chlorine levels in the stratosphere are elevated, we are vulnerable to adding particulate surface area to the stratosphere.
  - When will stratospheric chlorine return to pre-industrial levels?
- 
- Note: One proposed "geoengineering" solution to global warming problem: add particles to stratosphere to reflect sunlight.  
*Do you think this is a good idea?*

## International Treaties and Scientific Assessments

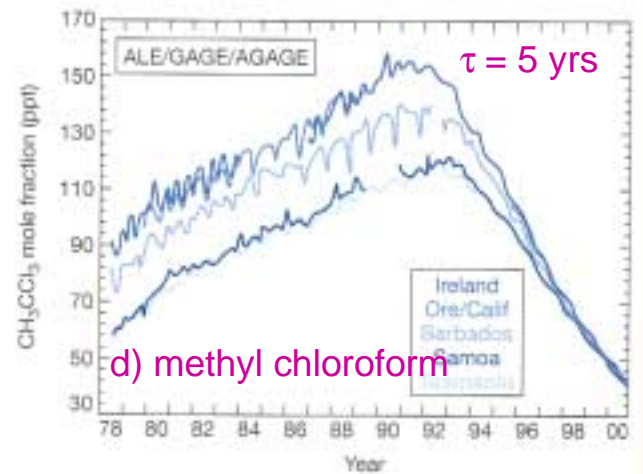
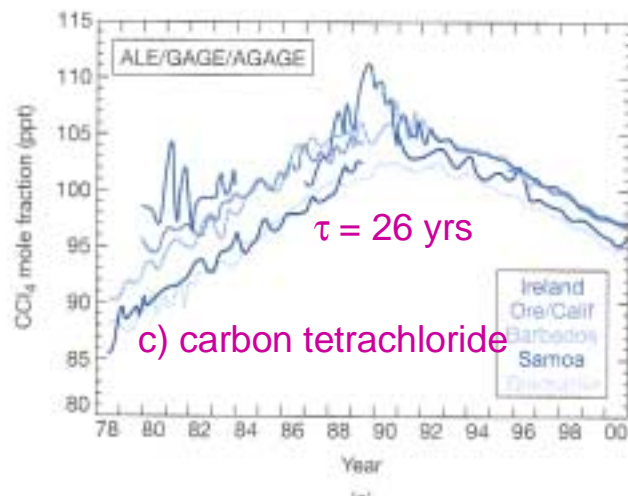
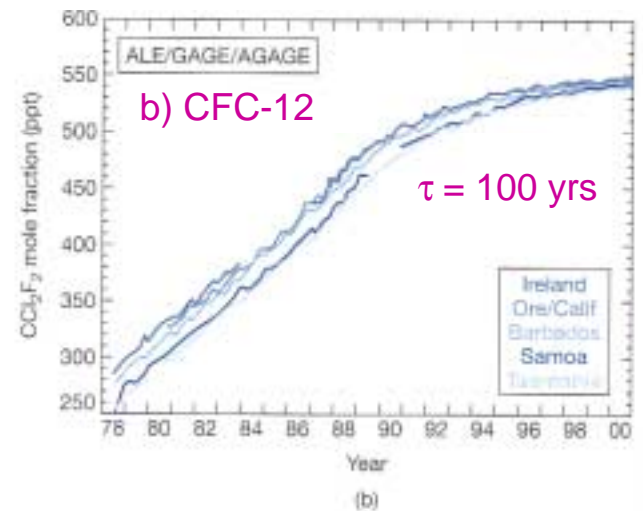
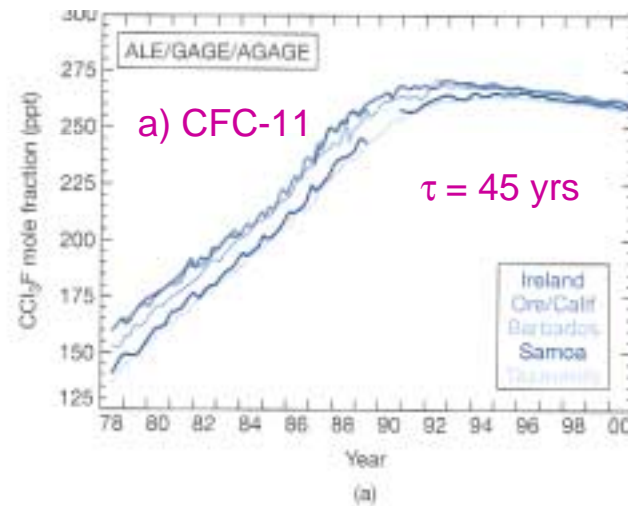
Year	Policy Process	Scientific Assessment
1981		<i>The Stratosphere 1981. Theory and Measurements.</i> WMO No. 11.
1985	Vienna Convention	<i>Atmospheric Ozone 1985.</i> Three volumes. WMO No. 16.  Farman et al., ozone hole discovery
1987	Montreal Protocol	
1988		<i>International Ozone Trends Panel Report 1988.</i> Two volumes. WMO No. 18.
1989		<i>Scientific Assessment of Stratospheric Ozone: 1989.</i> Two volumes. WMO No. 20.
1990	London Adjustments	
1991		<i>Scientific Assessment of Ozone Depletion: 1991.</i> WMO No. 25.
1992	Copenhagen Adjustments	
1994		<i>Scientific Assessment of Ozone Depletion: 1994.</i> WMO No. 37.
1995	Vienna Adjustment	
1997	Montreal Adjustment	
1998		<i>Scientific Assessment of Ozone Depletion: 1998.</i> WMO No. 44
2002		<i>Scientific Assessment of Ozone Depletion: 2002.</i>

## Example statements from 2002 Scientific Assessment

- "In the troposphere, observations show that the total combined effective abundance of ozone-depleting compounds continues to decline slowly from the peak that occurred in 1992-1994."
- "Analyses of air trapped in snow since the late 19th century have confirmed that non-industrial sources of the CFCs, halons, and major chlorocarbons were insignificant."
- "... a future Arctic polar ozone hole similar to that of Antarctica appears unlikely."
- "Additional measurements continue to confirm that decreases in ozone column amounts lead to increases in UV radiation."
- "The ozone layer will remain particularly vulnerable during the next decade or so, even with full compliance [to the Montreal Protocol and its amendments]."

## Observed changes in CFCs: in-class activity

Answer: ~zero



cf KKC Fig 14-8

Question: What is the natural, or pre-industrial, concentration of these compounds?



## typical arguments of the "skeptics"

### typical arguments of the "skeptics"

- 1) Natural variations are much more important than human impacts.
  - > historical record shows more extreme conditions than today
  - > effects of sun and volcanoes dwarf effects of humans
- 2) Changes observed to date are small; larger changes predicted for the future are based on flawed theoretical models.
- 3) Observed changes are not due to humans (see 1).
- 4) Even if humans are changing the environment, the consequences are not serious and may even be good.
- 5) On the other hand, regulations designed to reduce human impacts will cause severe economic damage.

### NOTE:

Every one of these arguments was made in regard to the ozone problem.

## "skeptics" of human-induced ozone depletion

two examples (available for reports):

Dixy Lee Ray and Louis R. Guzzo (1993) Environmental Overkill: Whatever happened to common sense?, Regnery Gateway, Washington, D.C. [book, 260 pages; see Chapters 3 and 4]

Sallie Baliunas (1994) The Ozone Crisis, Washington Roundtable on Science and Public Policy, Washington, D. C. [pamphlet published by the George C. Marshall Institute, 22 pages]

### **Dixy Lee Ray:**

Ph.D. zoologist, University of Washington  
Washington State Governor  
Chairman of Atomic Energy Commission

### **Sallie Baliunas:**

Ph.D. Astrophysicist, Harvard-Smithsonian Center  
Deputy Director of Mt. Wilson Institute

## example arguments of a "skeptic"

### Executive Summary

summary of consensus  
science is presented as  
an allegation



Chlorofluorocarbons (CFCs) are said to begin a process that causes a net destruction of ozone in the upper atmosphere. Thus CFCs and related chemicals will be limited in production or cease to be manufactured beginning in 1994. These chemicals have uses in air conditioners, refrigerators, and fire-fighting. There are no inexpensive, safe replacements for the banned CFCs that can be "dropped in" to existing equipment. New equipment will have to be purchased.

author claims to  
speak for "science"  
human cause is  
disputed; changes  
are natural



Scientific findings do not support an immediate ban on CFCs. Both global and Arctic measurements point to natural factors as the main cause of recent ozone fluctuations. Ozone levels change primarily as a result of natural factors such as ultraviolet output of the sun, oscillation of upper stratosphere winds and El Niño conditions. It appears that ozone levels in the Arctic experienced wide variations before the buildup of CFCs in the atmosphere.

proposed protections  
are the real danger



The phaseout of CFCs appears both scientifically unjustified and unnecessarily costly. A short-term cost of \$2 trillion due to impending bans and related compounds has been cited. Some \$135 billion of CFC-using equipment will have to be replaced. Unfortunately the Montreal Protocol, which bans CFCs over a period of time, contains no provision to slow phase-outs if new scientific information warrants.

[source: Baliunas, S. (1994) The Ozone Crisis, George C. Marshall Institute, Washington, D. C., 22 pp.]

## Dixy's advice...

from Environmental Overkill (1993) by Dixy Lee Ray:

"The Ozone Vanishes" cover story, Time Magazine, Feb 17, 1992

VS

"The Ozone Scare," Insight Magazine, April 6, 1992

"The Hole Story - The Science Behind the Scare", Reason magazine, June, 1992

"No wonder thoughtful people ask, 'Who should we believe?' My only advice is this: Look for evidence, not for arguments; discount any unsupported assertions, even if they come from an eminent authority, and then make up your own mind based on what facts you can assemble and on your own common sense." [p.29]

from Environmental Overkill (1993) by Dixy Lee Ray:

"Although the presence of chloride appears to be directly involved in ozone breakdown, the origin of that chloride is open to question." [p.34]

1. World production of CFCs is ~750,000 tons of Cl per year, but...

1a. seawater evaporation puts ~600,000,000 tons of Cl into the atmosphere per year, and

1b. volcanic eruptions put millions of tons of Cl into the atmosphere.

2. Besides, there are some "obvious" problems with the theory of CFCs being responsible for Cl in the stratosphere. "How does CFC rise when its molecules are four to eight times heavier than air?" [p.35]

Question: Which of these three points (1a, 1b, or 2) has merit? Why?

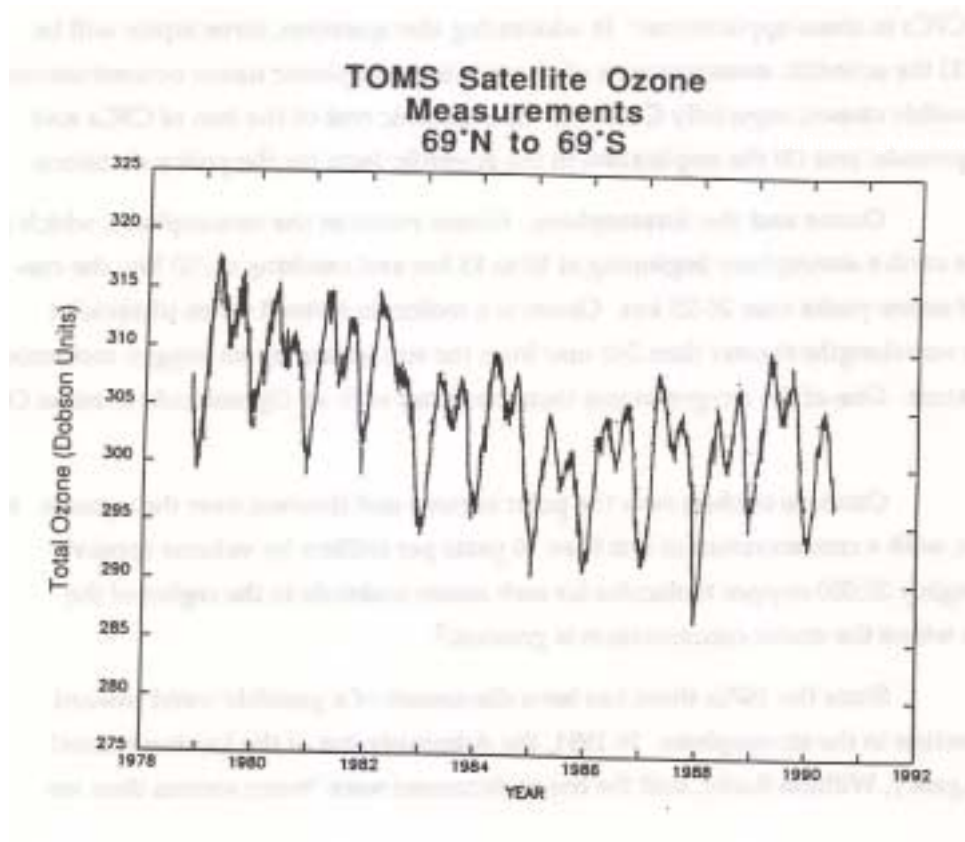
Answer: 1b. Volcanoes are indeed a potential source of Cl to the stratosphere. As a result, this has been extensively studied. The Pinatubo eruption in 1991 provided an ideal test. The volcanic source had already been ruled out by 1993.

Question: Why are 1a and 1c absurd?

Answers: 1a: Neither particulate NaCl nor gaseous HCl mix into the upper troposphere much less the stratosphere, in significant amounts.

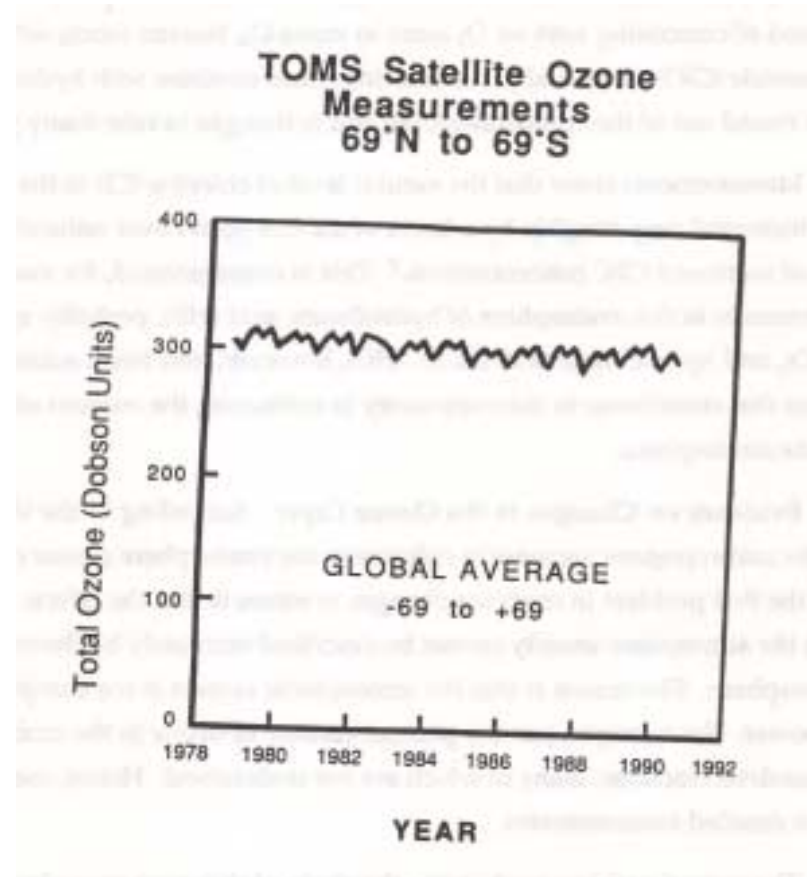
2: Turbulent motions mix all gases throughout the atmosphere regardless of molecular weight. Heavy gases have no tendency to "fall out".

## Sallie Baliunas: global ozone changes are small



measurements showing  
change in global ozone

replotted to reveal small  
magnitude of change



## WMO: global ozone changes are small

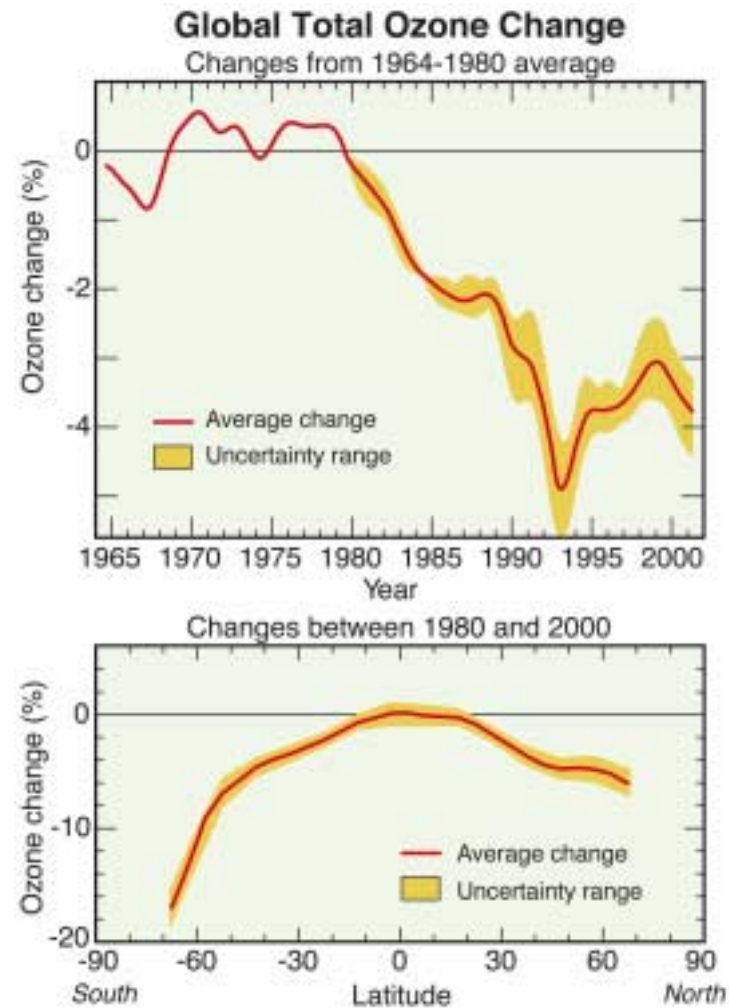
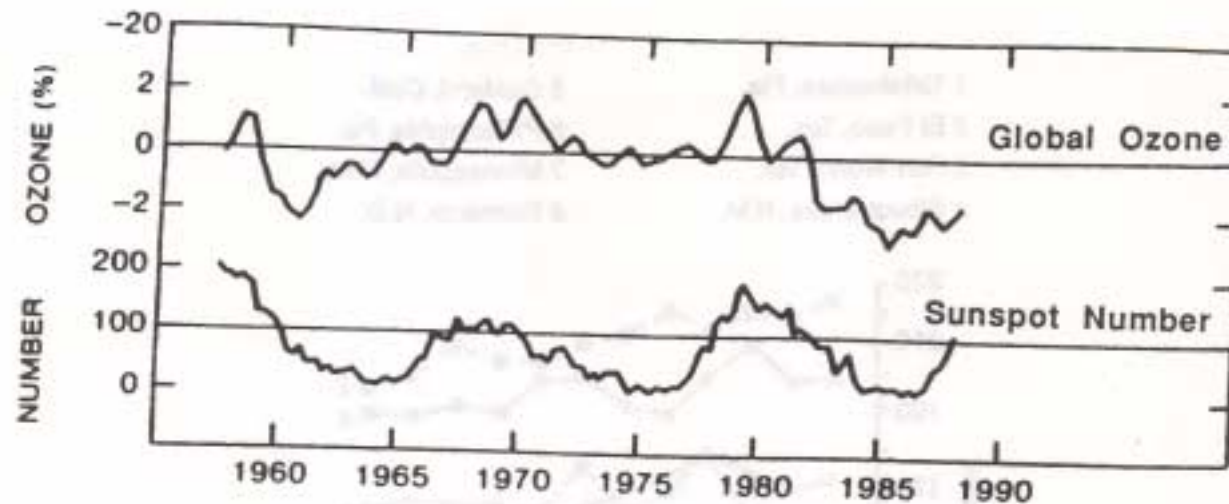


Figure source: <http://www.al.noaa.gov/WWWH/pbdocs/Assessment02/Q&As.html>



## Sallie Baliunas: global ozone and the sun

correlation of ozone changes with the solar changes  
(implying cause is natural)



## WMO: ozone, sun, and volcanoes

Note: correlations with sun and volcanoes appear to be real, but do not explain the downward trend from 1980-2000.

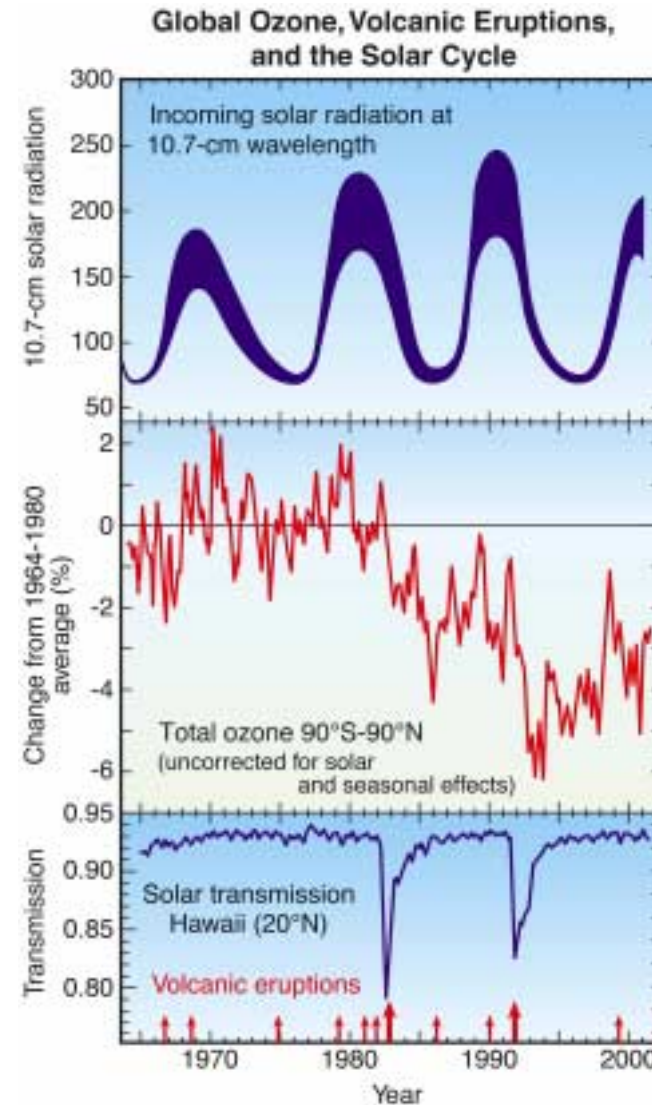


Figure source: <http://www.al.noaa.gov/WWVHD/pubdocs/Assessment02/Q&As.html>

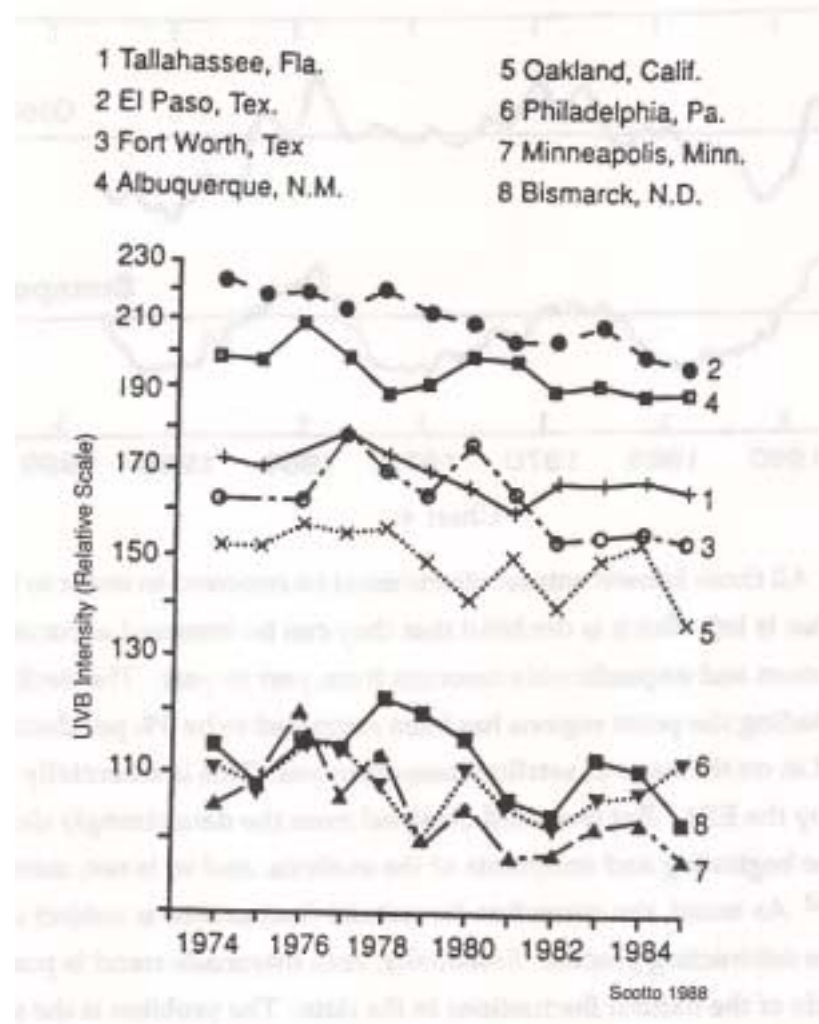
## Sallie Baliunas: no evidence of predicted consequences

Predicted increase in UVB is not supported by the data, which actually shows a decrease in UVB at all stations

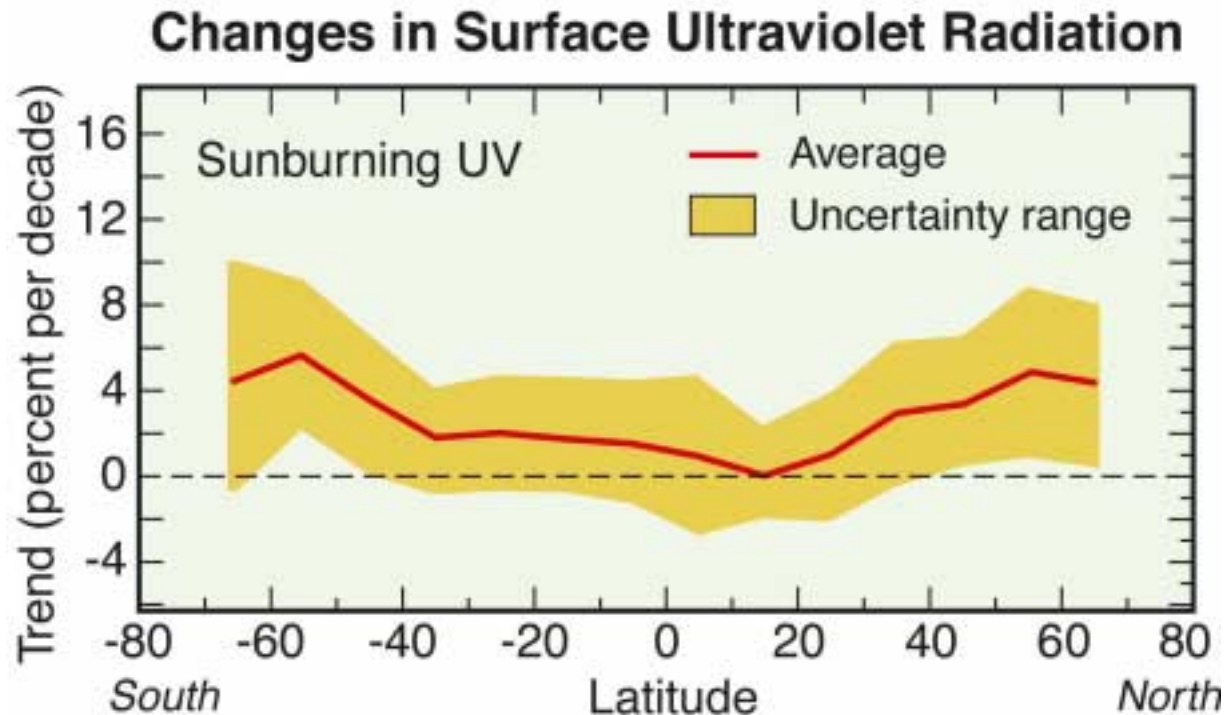
### Note:

Report date is 1995 but data only runs to 1985 (?).

Are these stations correctly located to see the predicted UVB increase? (Did ozone actually thin over these locations?)

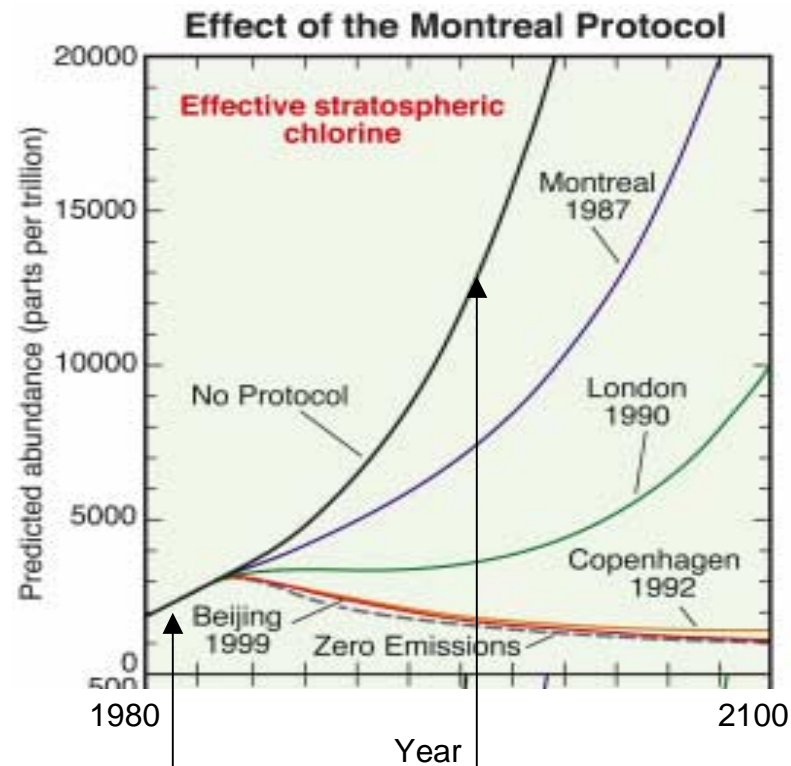


## WMO: barely detectable effect on UVB



Note: This was a serious weakness with the ozone assessment science (identified from the beginning in the WMO reports). As a result, very careful studies were done. These revealed the expected effect. The measurement is quite difficult.

## The ozone problem in perspective: where we might have gone



unanticipated  
ozone "hole"  
develops over  
Antarctica

?

## Stratospheric ozone recap

Ozone absorbs UV-B radiation, thereby

- warming the upper atmosphere and creating a stable layer known as the "stratosphere"
- shielding the surface from UV-B and making terrestrial life possible

Ozone exists in a state of "dynamic equilibrium", a balance between the production and destruction of "odd-oxygen".

Since the production rate is essentially fixed, the destruction rate controls the concentration.

Chlorine and other compounds catalyze the destruction of odd-oxygen and thus the depletion of stratospheric ozone.

## Stratospheric ozone recap

CFCs accumulate in the troposphere (long atmospheric lifetimes) and undergo photolysis in the stratosphere to release chlorine atoms. This has already caused a modest (few percent) decrease in global-mean ozone column amount.

Most chlorine from CFCs is locked up in unreactive forms that do not threaten ozone.

BUT heterogeneous reactions on PSC's (and volcanic particles) can sequester the compounds that normally bond to Cl and, thereby, release it to the active, ozone-destroying form. This process caused an "ozone-hole" to develop over Antarctica in the springtime starting about 1980 and growing worse ever since.



## Stratospheric ozone recap

Global ozone depletion has been modest (a few percent). The expected increase in UV-B radiation at the surface has been detected. Both these measurements are difficult because the changes are small with respect to natural variability.

The Montreal Protocol (1987) and subsequent amendments have put the world on a course to eliminating CFCs (and halons) from the atmosphere, thereby protecting the ozone layer. This will take 50-100 years.

Meanwhile, high chlorine levels make stratospheric ozone vulnerable to volcanic eruptions or other sources of particulate matter.

Due to international regulation, stratospheric chlorine has probably peaked and will decline over the coming decades. Without these treaties (assuming business as usual), it would have reached levels 5-10 times higher during this century.

## A lucky escape?

We have seen that both chlorine, Cl (from CFCs) and bromine, Br (from halons) can catalytically destroy ozone.

CFCs are far more common, largely due to their use as refrigerants and blowing agents.

In fact, halons also make great refrigerants and blowing agents.

But Br is **10 times** more efficient than Cl at destroying ozone.

It just happens that freons are cheaper and easier to manufacture.

But what if halons had been cheaper?

Upon accepting the Nobel Prize for his work on stratospheric ozone, Paul Crutzen considered this "nightmarish thought"...

## A lucky escape?

"... if the chemical industry had developed organobromine compounds [halons] instead of CFC's... then without any preparedness, we would have been faced with a catastrophic ozone hole everywhere and in all seasons during the 1970's"

[Recall: Jim Lovelock's CFC measurements were not made until 1973. At the time, he concluded they posed "no conceivable hazard".]

"Noting that nobody had given any thought to the atmospheric consequences of the release of Cl or Br before 1974, I can only conclude that mankind has been extremely lucky."

(Source: P. Crutzen (1995) My life with O<sub>3</sub>, NO<sub>x</sub>, and other YZO<sub>x</sub>s, Les Prix Nobel (The Nobel Prizes) 1995. Stockholm: Almqvist & Wiksell International, pp. 123-157).

## Lessons from the ozone experience

- Earth is a coupled system:
  - >> actions can have unanticipated consequences
  - >> these can be sudden and dramatic
- Be careful of anything that has a long atmospheric lifetime
- Vigilant monitoring is good. We caught the ozone hole almost as soon as it appeared.
- High-tech monitoring systems can screw up. Good to have someone actually looking at the data.
- Dramatic events drive public policy far more effectively than theoretical predictions.
- A successful model for coping with global change: International scientific assessments and international treaties based on them.