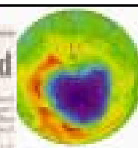
Mon Oct 6

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

---

Ozone hole swells, matches record



Putin criticizes Kyoto Protocol

Week 2

Chap 14: stratospheric ozone

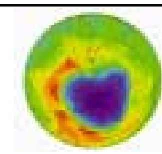
Mon: ozone basics
- photochemistry
- UV radiation
- atmospheric structure
- terrestrial life

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

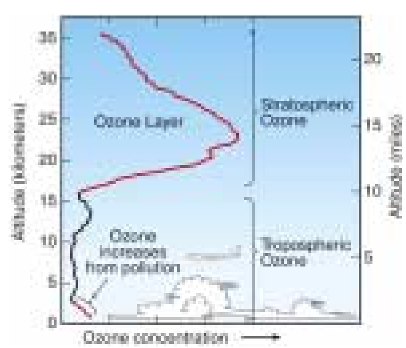
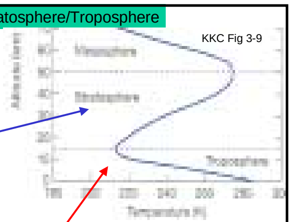


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

Definitions: Stratosphere/Troposphere



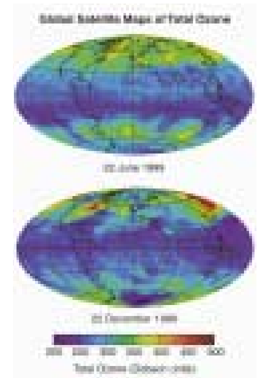
KKC Fig 3-9

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

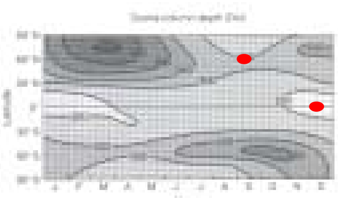
"DU" (Dobson Unit)

- 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 60N (say, Stockholm, Sweden) to the equator (say, Nairobe, Kenya), how much of a change would you experience in minimum ozone column depth during a typical year?



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

ozone chemistry in stratosphere
part I: fast reactions

production of ozone

(2) O_2 + O --> O_3 (fast)

destruction of ozone

(3) O_3 + UV --> O_2 + O (fast)

NET reaction: (2) + (3)

UV --> heat !

- There is no net production or destruction or 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:

(2) O_2 + O + M --> O_3 + M

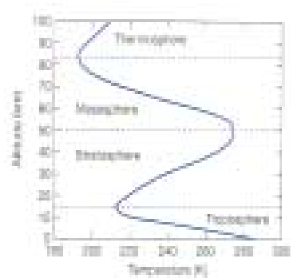
see KKC Figure 14-6 for explanation

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

Ozone and Atmospheric Structure

Photochemical reaction: Ozone Photolysis
O_3 + UV --> O_2 + O

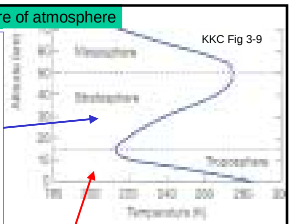
First Consequence:
- energy of UV radiation is added to the stratosphere
- stratosphere warms
- stratosphere becomes "stable" - resists vertical motions



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



KKC Fig 3-9

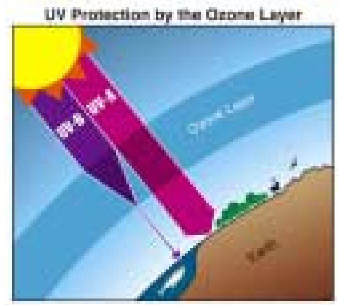
troposphere
- the lower region of the atmosphere where "weather" occurs
- heated from the bottom
- temperature decreases with height
- (warm fluid on bottom is unstable)
- vertical motions, clouds, precipitation, hydrological cycle

Stratospheric ozone: Why do we care?

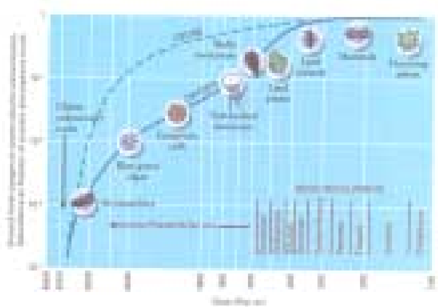
Photochemical reaction: Ozone Photolysis

O_3 + UV --> O_2 + O

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



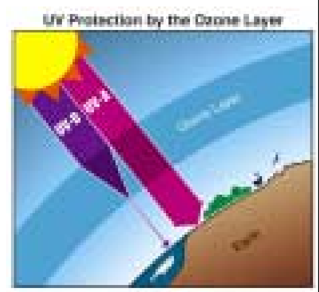
Role of Ozone in Earth History



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



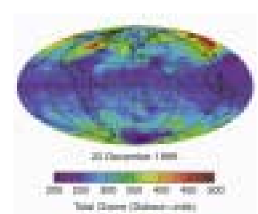
Tues Oct 7

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"

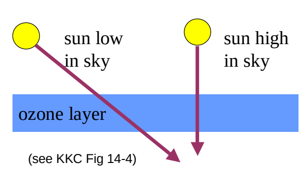
Today:
- UV dose
- ozone chemistry outline
- oxygen-only reactions
  - dynamic equilibrium
- CFC's and ozone
  - catalyst
  - atmospheric lifetime

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)



(see KKC Fig 14-4)

two factors control UV dose
- ozone column depth
- solar zenith angle

X

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

(1)	O_2	+	UV	-->	O	+	O		(slow)
(2)	$2O_2$	+	2O	-->	$2O_3$				(fast)

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

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

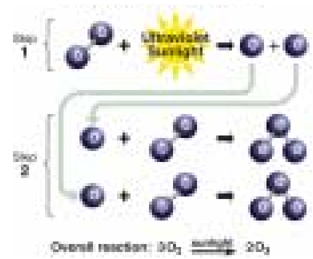


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

Ozone equilibrium from oxygen-only reactions

(1)	O_2	+	UV	-->	O	+	O	(slow)
(2)	$2O_2$	+	2O	-->	$2O_3$			(fast)
(3)	O_3	+	UV	-->	O_2	+	O	(fast)
(4)	O_3	+	O	-->	O_2	+	O_2	(slow)

(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…

(1)	O_2	+	UV	-->	O	+	O
(2)	$2O_2$	+	2O	-->	$2O_3$		
(3)	O_3	+	UV	-->	O_2	+	O
(4)	O_3	+	O	-->	O_2	+	O_2
	UV	+	UV	-->	heat !		

- There is no net production or destruction of any chemical species.
- This cycle of reactions produces:
  - heat (warming the stratosphere)
  - an *equilibrium* concentration of O_3 (also of O)
  - "dynamic equilibrium"

Given solar energy (UV flux) and O_2 concentration…

- equilibrium concentration of 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…

(a) O_3 + X --> XO + O_2

(b) XO + O --> X + O_2

(net) O_3 + O --> O_2 + O_2

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

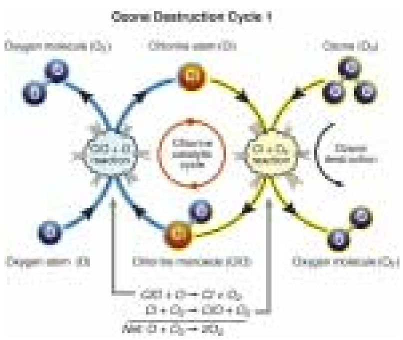


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

Catalytic Destruction

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

(a) $O_3 + X \rightarrow XO + O_2$

(b) $XO + O \rightarrow X + O_2$

(net) $O_3 + O \rightarrow O_2 + O_2$

A new model of ozone equilibrium...

(1) $O_2 + UV \rightarrow O + O$
(2) $O_2 + O \rightarrow O_3$
(3) $O_3 + UV \rightarrow O_2 + O$
(4*) $O_3 + O \rightarrow O_2 + O_2$

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

Result will be a lower equilibrium concentration of O_3 (due to more efficient removal).

Catalytic Destruction

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

Reactions when X = chlorine…

(a) $O_3 + Cl \rightarrow ClO + O_2$

(b) $ClO + O \rightarrow Cl + O_2$

(net) $O_3 + O \rightarrow O_2 + O_2$

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 **chlororfluorocarbons (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.

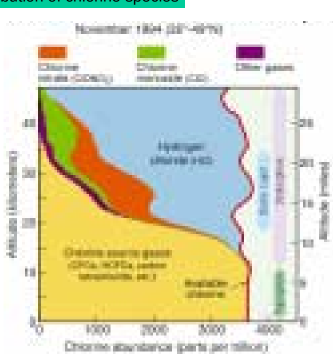
But don't be concerned. "The presence of these compounds constitutes no conceivable hazard" (Jim Lovelock, 1973).

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 ClONO2**
- **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...

(a) O_3 + Cl --> ClO + O_2

(b) ClO + O --> Cl + O_2

(net) O_3 + O --> O_2 + O_2

energy source for this catalytic cycle:

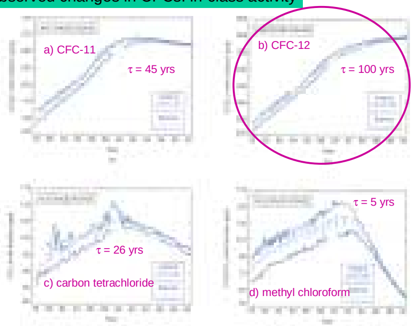
- odd-oxygen (O3 and O) are high-energy forms.
- conversion to stable oxygen (O2) involves release of considerable energy.
- so energy comes from UV radiation (which creates the odd-oxygen in the first place.)

Atmospheric lifetimes of CFCs

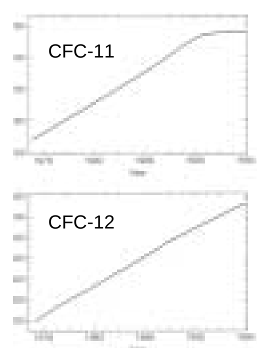
atmospheric lifetime (or "residence time"):
The average length of time a substance spends in the atmosphere.

name	other name	chemical formula	atmospheric lifetime
CFC-12	Freon-12	CCl_2F_2	100 yrs
CFC-11	Freon-11	CCl_3F	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.

(1) O_2 + UV --> O + O
(2) O_2 + O --> O_3
(3) O_3 + UV --> O_2 + O
(4) O_3 + O --> O_2 + O_2

Understanding in 1970's:
- Cl can **catalyze** reaction (4)
- Cl in stratosphere is increasing due to CFCs

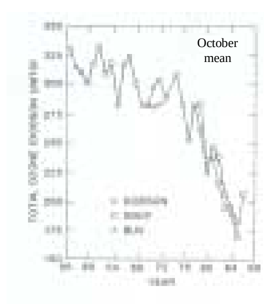
but
- most Cl is stratosphere is locked up in **unreactive forms**

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.

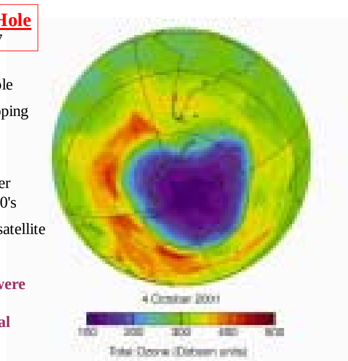
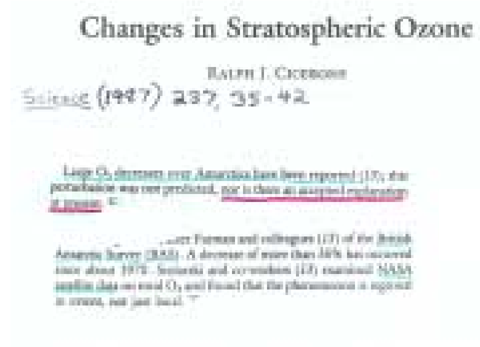


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

1987: State of Knowledge


Changes in Stratospheric Ozone

Ralph J. Cicerone

Science (1987) 237, 35-42

Large O_3 decreases over Antarctica have been reported (17); this perturbation was not predicted, nor is there an accepted explanation at present.

...ver Farman and colleagues (17) of the British Antarctic Survey (BAS). A decrease of more than 40% has occurred since about 1975. Stolarski and co-workers (13) examined NASA satellite data on total O_3 and found that the phenomenon is regional in extent, not just local.

Science and Policy

NORMAL TIMES (theory-driven)

1974 Molina and Rowland propose catalytic destruction of stratosphereic 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 NO_2 and H
5. liberation of Cl (normally tied up via bonding with NO_2 and H)
6. massive, catalytic destruction of 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 NO2 and H and liberate Cl.

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

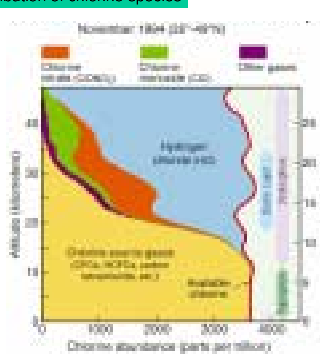
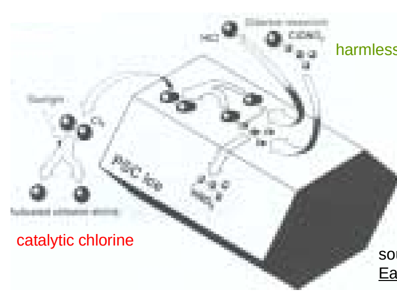


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

Heterogeneous Reactions
Key to catastrophic ozone destruction

harmless chlorine



catalytic chlorine

source: Turco (1987) Earth Under Seige

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_3 within the ozone hole?

$\frac{1100 \text{ ppt ClO}}{1000 \text{ ppb } O_3}$

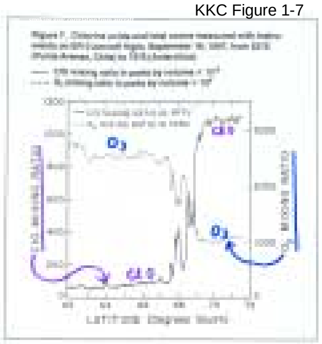
$\frac{\sim 1 \text{ ppt}}{1 \text{ ppb}}$

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

= 1/1000

Not much ClO, but it has big effect.

KKC Figure 1-7



Nowadays, we can see the same correlation from satellite

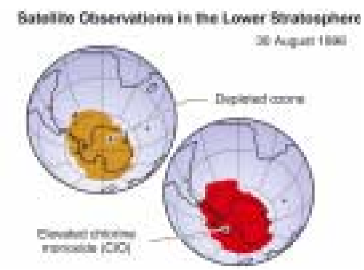


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

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 Soloman 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 (CCl_4):
non-flammable, heavy liquid (boils 77C)
uses: fire extinguisher, solvent, cleaning agent, industrial processes

Methyl chloroform (CH_3CCl_3):
non-flammable liquid (boils 74C)
uses: solvent, cleaning agent, industrial processes

Global trends

1991: Mt Pinatubo eruption

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

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."

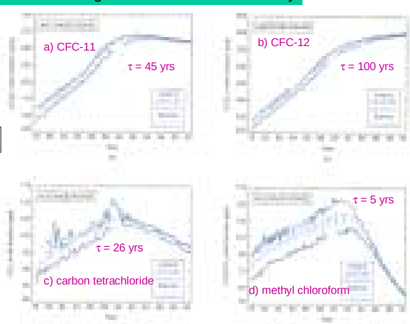
• "Analyses of air trapped in snow since the late 19th century have confirmed that non-industrial sources of the CFCs, halons, and major chlorocarbons were insignificant."

• "... 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

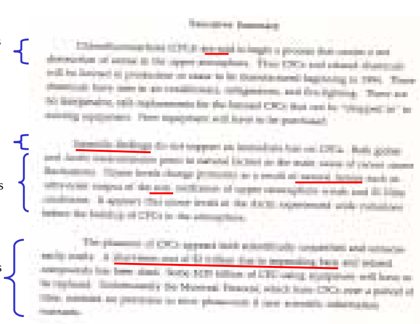
example arguments of a "skeptic"

summary of consensus science is presented as an allegation

author claims to speak for "science"

human cause is disputed; changes are natural

proposed protections are the real danger



[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]

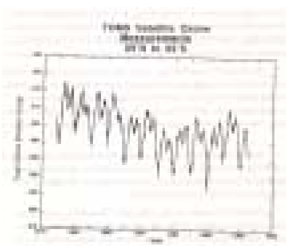
1. World production of CFCs is ~750,000 tons of Cl per year, but...
   1a. seawater evaporation puts ~600,000,000 tons of Cl into the atmosphere per year, and
   1b. volcanic eruptions put millions of tons of Cl into the atmosphere.

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.

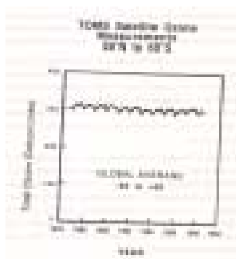
Question: Why are 1a and 1c absurd?
Answers: 1a: Neither particulate NaCl nor gaseous HCl mix into the upper troposphere much less the stratosphere, in significant amounts.
2: Turbulent motions mix all gases throughout the atmosphere regardless of molecular weight. Heavy gases have no tendency to "fall 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

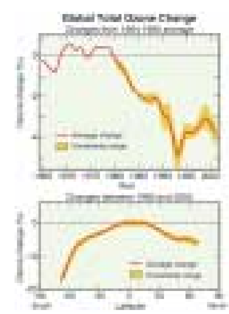


Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

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.

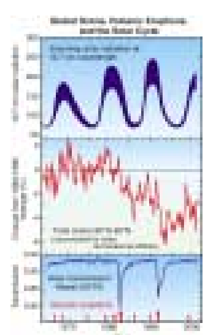


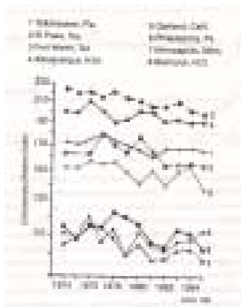
Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html

Sallie Baliunas: no evidence of predicted consequences

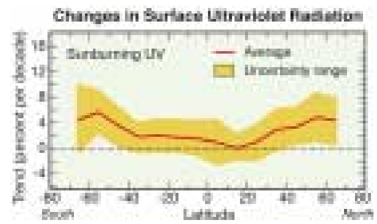
Predicted increase in UVB is not supported by the data, which actually shows a <u>decrease</u> in UVB at all stations

<u>Note:</u>
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?)



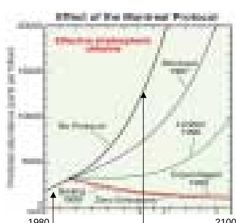
WMO: barely detectable effect on UVB



<u>Note:</u> 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.

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

The ozone problem in perspective: where we might have gone



unanticipated ozone "hole" develops over Antarctica

?

Stratospheric ozone recap

Ozone <u>absorbs UV-B</u> radiation, thereby
- <u>warming</u> the upper atmosphere and creating a stable layer known as the "stratosphere"
- <u>shielding</u> the surface from UV-B and making terrestrial life possible

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

Since the production rate is essentially fixed, the <u>destruction rate controls the concentration</u>.

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

Stratospheric ozone recap

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

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

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

Stratospheric ozone recap

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

The <u>Montreal Protocol (1987)</u> 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 <u>50-100 years</u>.

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

Due to international regulation, <u>stratospheric chlorine has probably peaked</u> and will decline over the coming decades. Without these treaties (assuming business as usual), it would have reached levels <u>5-10 times higher</u> 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] instread 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 O3, NOx, and other YZOxs, Les Pris 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.