• Read Chapter 17 (all)
• info on upcoming (extra-credit) talks now by email
Week 2

Chap 17: 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
Overview:

Stratospheric ozone illustrates:

- Earth-System couplings galore!
  human involvement
  unexpected consequences

- global environmental problem discovery
  explanation
  solution
Forms of oxygen in the atmosphere

Oxygen Atom (O)

Oxygen Molecule (O₂)

Ozone Molecule (O₃)

Which is most common?
Atmospheric ozone: vertical structure

Figure source: http://www.al.noaa.gov/WWWHD/pubdocs/Assessment02/Q&As.html
"stratosphere"
- atmospheric layer above the troposphere, where most ozone is found
- temperature increases with height

"troposphere"
- lowest atmospheric layer, where most "weather" occurs
- temperature decreases with height
DU: "Dobson Unit"

- measure of "ozone column depth"
  - literally: thickness of pure ozone atmosphere
  - measure of number of O$_3$ molecules overhead
  - 100 DU = 1 mm at surface
Geographical distribution of ozone column depth

- thin in the tropics
- thicker at high latitudes

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

Dobson Units: DU
If you moved from 60N (say, Sweden) to the equator (say, Kenya), how much of a change would you experience in the minimum ozone column depth in a typical year?

from ~300 to ~250 DU or 17% reduction (50/300 = 0.17)
Ozone Chemistry in the Stratosphere
Chapman Mechanism

(1) $\text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O}$ (slow)

(2) $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ (fast)

(3) $\text{O}_3 + \text{UV} \rightarrow \text{O} + \text{O}_2$ (fast)

(4) $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$ (slow)

production

reactants

products

KKC Table 17-2
(1)

(2)  \[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \] (fast)

(3)  \[ \text{O}_3 + \text{UV} \rightarrow \text{O} + \text{O}_2 \] (fast)

(4)

The symbol "M":

- see KKC Fig. 17-6 for explanation
- to simplify things, let's get rid of it

KKC Table 17-2
## Ozone Chemistry in the Stratosphere

### Fast Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td><strong>O + O₂ + → O₃</strong> (fast)</td>
</tr>
<tr>
<td>(3)</td>
<td><strong>O₃ + UV → O + O₂</strong> (fast)</td>
</tr>
<tr>
<td>(4)</td>
<td></td>
</tr>
</tbody>
</table>

**KKC Table 17-2**
Ozone Chemistry in the Stratosphere

Fast Reactions

production of ozone

\[ (2) \quad O + O_2 \rightarrow O_3 \quad \text{(fast)} \]

destruction of ozone (photolysis)

\[ (3) \quad O_3 + UV \rightarrow O + O_2 \quad \text{(fast)} \]

net reaction: add (2)+(3)

\[ \begin{align*}
\text{(net)} & \quad UV \\
\rightarrow & \quad \text{heat!}
\end{align*} \]

There is no net production or destruction of any chemical species. But, there is a net absorption of UV radiation, which warms the stratosphere.

"photo": light, "lysis": splitting
Ozone photolysis

"photo": light
"lysis": splitting
thus, "splitting apart by light" (actually, UV)

ultraviolet (UV) radiation
First consequence

- absorption of UV adds **heat**

> get max T at ~50 km altitude

(warm fluid on top is **stable**)

> creates "stratosphere"

("stratified" layer: little vertical motion; clouds are very rare)
Stratospheric ozone: Why we care

Ozone "photolysis"
\[ \text{O}_3 + \text{UV} \rightarrow \text{O} + \text{O}_2 + \text{heat} \]

Second consequence
- absorption of UV shields the Earth's surface from UV-B

> makes possible life on land
Role of ozone in Earth history

Tuesday April 4

Announcements
• Read Chapter 17 (all)
• Two talks today, 12:30 and 2:30
• HW #4

Today
• UV dose
• oxygen-only reactions
  dynamic equilibrium
  slow reactions control concentration
• CFC's and ozone
  catalyst
  atmospheric lifetime
  a very bad prediction (by a very smart man!)
Ultraviolet Radiation (UV)

• 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 reaches surface
  - B is the big concern
UV dose: the amount of UV-B radiation received at the surface

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

(see KKC Fig 17-4)
Stratospheric Ozone Chemistry: Outline

1. Oxygen-only reactions
2. Catalytic destruction by halogens (Cl and Br)
3. Antarctic ozone hole (Wednesday)
   - discovery
   - explanation (surface catalyzed reactions)

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

Motto
"No law that says nature has to be simple!"
Oxygen-only reactions

(1) \( \text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O}_2 \) (slow)
(2) \( 2\text{O} + 2\text{O}_2 \rightarrow 2\text{O}_3 \) (fast)
(3) \( \text{O}_3 + \text{UV} \rightarrow \text{O} + \text{O}_2 \) (fast)
(4) \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \) (slow)

KKC Table 17-2

- Production (1) and (2)
- Destruction (3) and (4)
- "Odd-oxygen" \( \text{O} \) & \( \text{O}_3 \) (reactive, rare)
- Odd-oxygen cycling is fast: (2) and (3)
Slow reactions: rate-limiting

(1) $\text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O}$ (slow)

(4) $\text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2$ (slow)

KKC Table 17-2

- **Real production is (1):**
  convert $\text{O}_2$ to odd-oxygen

- **Real destruction is (4):**
  convert odd-oxygen back to $\text{O}_2$
Ozone production in the stratosphere

(1) \( O_2 + \text{UV} \rightarrow O + O \) (slow)
(2) \( 2O + 2O_2 \rightarrow 2O_3 \) (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 production in the stratosphere

Production depends entirely on rate of Step 1...

What controls the rate of Step 1?

- Concentration of $O_2$ (molecular oxygen)
- Solar luminosity

Consequence:
Average rate of ozone production for current climate on Earth is pretty much fixed (i.e. essentially constant).
### Oxygen-only reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical Equation</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$O_2 + \text{UV} \rightarrow O + O$</td>
<td>slow</td>
</tr>
<tr>
<td>(2)</td>
<td>$2O + 2O_2 \rightarrow 2O_3$</td>
<td>fast</td>
</tr>
<tr>
<td>(3)</td>
<td>$O_3 + \text{UV} \rightarrow O + O_2$</td>
<td>fast</td>
</tr>
<tr>
<td>(4)</td>
<td>$O_3 + O \rightarrow O_2 + O_2$</td>
<td>slow</td>
</tr>
<tr>
<td>(net)</td>
<td>$\text{UV} + \text{UV} \rightarrow \text{heat}$</td>
<td></td>
</tr>
</tbody>
</table>

"Dynamic equilibrium"

- lots of activity, but no net production or destruction

Since production rate is essentially fixed, equilibrium concentration of $O_3$ depends on (4)
catalyst

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

(a) \( \text{O}_3 + X \rightarrow \text{XO} + \text{O}_2 \)
(b) \( \text{XO} + \text{O} \rightarrow X + \text{O}_2 \)

--------------------------------------

(\text{net}) \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \)

• 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?
Catalytic ozone destruction

Ozone Destruction Cycle 1

- Oxygen molecule ($O_2$)
- Chlorine atom ($Cl$)
- Ozone ($O_3$)
- Oxygen atom ($O$)
- Chlorine monoxide ($ClO$)

$ClO + O \rightarrow Cl + O_2$

$Cl + O_3 \rightarrow ClO + O_2$

Net: $O + O_3 \rightarrow 2O_2$

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

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

(a) \[ \text{O}_3 + \text{X} \rightarrow \text{XO} + \text{O}_2 \]

(b) \[ \text{XO} + \text{O} \rightarrow \text{X} + \text{O}_2 \]

----------

(1) \[ \text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O} \]
(2) \[ 2\text{O}_2 + 2\text{O} \rightarrow 2\text{O}_3 \]
(3) \[ \text{O}_3 + \text{UV} \rightarrow \text{O}_2 + \text{O} \]
(4*) \[ \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \]

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 ozone 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.
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.
Origin of CFC's

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

1970: Jim Lovelock invents electron capture device, allowing CFC's in open atmosphere to be measured.

1973: Lovelock deduces that essentially all CFC's ever produced are still in the atmosphere.

Quote from Lovelock's 1973 article:
"The presence of these compounds constitutes no conceivable hazard" (Jim Lovelock, 1973).
CFC lifetimes

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

<table>
<thead>
<tr>
<th>name</th>
<th>other name</th>
<th>chemical formula</th>
<th>atmospheric lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-12</td>
<td>Freon-12</td>
<td>CCl$_2$F$_2$</td>
<td>100 yrs</td>
</tr>
<tr>
<td>CFC-11</td>
<td>Freon-11</td>
<td>CCl$_3$F</td>
<td>45 yrs</td>
</tr>
</tbody>
</table>
Emissions of all these compounds were greatly reduced in about 1990. Which compound has the longest atmospheric lifetime? Which has the shortest? Explain.

\[ \tau = 45 \text{ yrs} \]
\[ \tau = 100 \text{ yrs} \]
\[ \tau = 5 \text{ yrs} \]
\[ \tau = 26 \text{ yrs} \]

Longest (responds most slowly)

Shortest (responds most quickly)

KKC Fig 17-8
CFC destruction

CFC lifetime's in atmosphere are long, but not infinite.

How do you think they (eventually) get destroyed?

**Answer:**
Slowly diffuse into the stratosphere.
There, they encounter UV radiation.
Photolysis breaks off chlorine atoms.
Wednesday April 5

Announcements
• Novak, Hansen, Science

Today
Antarctic ozone hole
  - "reactive" vs "unreactive" chlorine
  - role of theory vs discovery in science
  - high-tech embarrassment
  - weighing the evidence for CFC (i.e. human) causation
  - science (and policy) in normal times vs unusual times
Global trends in stratospheric ozone
Startling amounts of ice slipping into the sea have taken glaciologists by surprise; now they fear that this century’s greenhouse emissions could be committing the world to a catastrophic sea-level rise.

A Worrying Trend of Less Ice, Higher Seas
All things considered, it seems clear that “Greenland has been shifting to a negative mass balance the last few years,” says glaciologist Richard Alley of Pennsylvania State University in State College. The same can be said for the West Antarctic Ice Sheet. All recent surveys have the far more massive East Antarctic Ice Sheet slowly gaining mass from increased snowfall. But that gain falls far

*Going under?* Global warming might trigger a 6-meter rise in sea level that would inundate coasts (red) worldwide. Southern Louisiana (left) and South Florida (lower right) would be hard hit.

textbook, you’ll see an ice sheet response time of 1000 years or more.” That’s because models “treat ice sheets as a big lump of ice,” he says. They melt, or they don’t melt.

In the case of West Antarctica, there is tentative agreement about what is triggering the acceleration of the glaciers. Around the
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]
Ozone level governed by **dynamic equilibrium**. Loss rate via step (4) is key.

Understanding in 1970's and early '80'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 1-5

- 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 1-6

- 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
Large O₃ decreases over Antarctica have been reported (13); this perturbation was not predicted, nor is there an accepted explanation at present.

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 O₃ and found that the phenomenon is regional in extent, not just local.
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)
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
Four years (1985-1988) of frantic research and debate led to definitive consensus that the CFC/PSC explanation was correct (KKC 17:353-356). 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 NO₂ and H
5. liberation of Cl (normally tied up via bonding with NO₂ and H)
6. massive, catalytic destruction of O₃
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.
Prediction: Ozone destruction should correlate with regions with high concentrations of activated chlorine (Cl and ClO)
Question: What is the ratio of ClO to O₃ within the ozone hole?

\[
\frac{1100 \text{ ppt ClO}}{1000 \text{ ppb O}_3} \\
\approx 1 \text{ ppt} \\
1 \text{ ppb} \\
\approx \frac{1 \text{ ppt}}{1000 \text{ ppt}} \\
= 1/1000
\]

Not much ClO, but it has big effect.
Nowadays we can see the same correlation from satellites

Satellite Observations in the Lower Stratosphere
30 August 1996

Depleted ozone

Elevated chlorine monoxide (ClO)

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

The "ozone hole is serious, but very limited in extent
- mainly in October
- mainly over Antarctica

Have CFC's caused a reduction in stratospheric ozone at the global scale?
Global trends in ozone

Global ozone correlates with solar luminosity.

*Change (%) in mean ozone column depth, 40N-40S, after removal of seasonal cycle, QBO, and long-term trend.

KKC Fig 17-12

*Change (%) in mean ozone column depth, 40N-40S, after removal of seasonal cycle, QBO, and long-term trend.
Correlation with sun...

Step 1 (ozone production) is controlled by...

- Concentration of $O_2$ (molecular oxygen)
- Solar luminosity
Global trends in ozone

Trends at mid-latitudes are small and hard to pick out due to large seasonal variability.

Hohenpeissenberg, Germany (KKC Fig 17-11)
Global trends in ozone

Despite all this, a modest downward trend in global ozone is apparent.

Schematic of the North-to-South Ozone Depletion: 1979–1997

KKC Fig 17-13
Global trends in ozone

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?*
Announcements:
• HW due Monday (at beginning of class)
• late homework: 10% per day

Today:
• your feedback
• ozone control (Sci Assessments, Int'l Treaties)
• ozone skeptics
• ozone lessons

Friday: math/chem review

Next week: Daisyworld and the science of systems (Chapter 2)
The fundamental theory behind global-warming research is the "energy balance theory of climate change":

\[ \Delta T = \lambda \Delta F \]

Questions: Exactly what is \( \Delta T \)? How is it measured? How well is it known?

**GAAST:** Global-Annual Average Surface Temperature

\( \Delta T \): change in GAAST

Actually, there are two different meanings/roles:

- \( \Delta T_{\text{pred}} \): predicted response to a forcing (theory)
- \( \Delta T_{\text{meas}} \): measured temperature change (evidence)
<table>
<thead>
<tr>
<th>Year</th>
<th>Policy Process</th>
<th>Scientific Assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1987</td>
<td>Montreal Protocol</td>
<td><em>Farman et al., ozone hole discovery</em></td>
</tr>
<tr>
<td>1990</td>
<td>London Adjustments</td>
<td></td>
</tr>
<tr>
<td>1995</td>
<td>Vienna Adjustment</td>
<td></td>
</tr>
</tbody>
</table>
Effect of Int'l Treaties

Freon-12

serious controls begin
1. "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."

2. "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."

3. "... a future Arctic polar ozone hole similar to that of Antarctica appears unlikely."

4. "Additional measurements continue to confirm that decreases in ozone column amounts lead to increases in UV radiation."

What scientific question is being addressed by each of these statements? How do those scientific questions relate to policy choices?
1. "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."

Science:
How are CFC concentrations changing with time? Do we understand what controls the atmospheric lifetime of these substances?

Policy:
Are the Int'l Agreements having the intended effect of reducing CFC concentrations?
2. "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."

Science:
Were these species already present before the modern chemical industry?
Are humans responsible for the presence of CFCs and halons in the atmosphere?

Policy:
Cutting emissions would be a waste of effort if our emissions are not in fact the cause of CFCs and halons in the atmosphere.
3. "... a future Arctic polar ozone hole similar to that of Antarctica appears unlikely."

Science:
(self-evident) Could an "ozone hole" develop in the Arctic? Would it be as dramatic as the one in the Antarctic?

Policy:
How serious is this problem? What is the level of danger for the citizens and ecosystems of the far North?
4. "Additional measurements continue to confirm that decreases in ozone column amounts lead to increases in UV radiation."

Science:
Theory predicts that UV radiation at the surface should increase as stratospheric ozone decreases. Does the evidence support this prediction? Is it possible that factors other than stratospheric ozone control how much UV radiation gets to the surface?

Policy:
Increased UV-B is the real danger. If reduced stratospheric ozone does not actually cause UV-B to go up, then there is little or no cause for alarm or action.
typical arguments of the "skeptics"

1) Natural variations are much more important than human impacts.
2) Observed changes may be real, but not due to humans (see 1).
3) Predicted harm based on flawed theoretical models.
4) Regulations designed to reduce human impacts will cause severe economic damage.
"skeptics" of human-induced ozone depletion

two examples (available for reports):


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

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/WWHD/pubdocs/Assessment02/Q&As.html
correlation of ozone changes with the solar changes (implying cause is natural)
Note: correlations with sun and volcanoes appear to be real, but do not explain the downward trend from 1980-2000.
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

KKC-Fig 17-14
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 through the 1990's.
**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.
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."

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.
"Is glacier acceleration the 'ozone hole' of sea level rise?" Science, Mar 24, 2006, p1701

A Worrying Trend of Less Ice, Higher Seas