Stratospheric Ozone: Production, Destruction, & Trends

Antarctic Ozone Hole: Sept. 12, 2012

http://ozonewatch.gsfc.nasa.gov/
Take away concepts

1. Why is the Ozone layer important?
2. Atmospheric thermal structure
3. UV radiation and stratospheric $O_2$ and $O_3$.
4. Natural ozone production and destruction
5. The life cycle of CFCs, and their role in ozone destruction.
6. Why the Antarctic ozone hole is larger than the arctic, and why there is no "hole" over the tropics.
7. How large is the ozone hole now?
8. Future trends
Ozone ($O_3$)

Triatomic oxygen molecule
Max concentration is $\sim$10 ppm, occurring in Stratosphere (15-30 km).
Stratosphere contains 90% of all ozone.
Tropospheric ozone from auto emissions (bad)
What does the ozone layer do for us?

Ozone absorbs UV radiation (between 210 and 290 nm).

Radiation at these wavelengths harm biomolecules (DNA).

The ozone layer is a consequence of oxygen-only chemistry.

Significant oxygen appeared on earth about 2 billion years ago due to rise of cyanobacteria.
Why it matters …

UV damages DNA
Observations: (i) $O_3$ is **not** the most concentrated gas in the ozone layer (not even close!) (ii) maximum concentration is in the middle stratosphere.

Why does the ozone layer exist in the stratosphere?

What processes are responsible for its formation and maintenance?
Radiation and Matter

Also dependent upon the frequency of radiation!
Emission Spectra: Sun and Earth

BLACK BODY CURVES

SUN

EARTH

Range of wavelengths of solar and Earth spectra.
## INCOMING Solar Radiation budget

<table>
<thead>
<tr>
<th>Incoming Solar energy...</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflected</td>
<td>35%</td>
</tr>
<tr>
<td>Absorbed by atm (ozone)</td>
<td>18%</td>
</tr>
<tr>
<td>Scattered to Earth from blue sky</td>
<td>10%</td>
</tr>
<tr>
<td>Scattered to Earth from clouds</td>
<td>15%</td>
</tr>
<tr>
<td>Radiation going directly to Earth surface</td>
<td>22%</td>
</tr>
<tr>
<td></td>
<td>100%</td>
</tr>
</tbody>
</table>
Composition of the atmosphere

Nitrogen: 78%
Oxygen: 21%
Argon: 1%

CO$_2$: 380 ppm
Plus: CH$_4$, H$_2$O, He,
Atmospheric layers

60 km

15 km
Why is the Sky blue?

Ozone scatters short-wavelength (blue) incoming radiation from the sun.

Rayleigh scattering of incoming, short wavelength radiation (photons with specific energy)

Radiation scattered by O$_3$, O$_2$ in stratosphere (10-50 km)
Why are sunsets red?

Blue wavelengths are scattered/absorbed

Red and orange pass through to surface
Blackbody emission curves and absorption bands
Photon Absorption: Vibration, Dissociation, and Ionization

<table>
<thead>
<tr>
<th>A molecule plus a photon of wavelength less than</th>
<th>can</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cm</td>
<td>excite rotation</td>
</tr>
<tr>
<td>20 μ</td>
<td>excite vibration</td>
</tr>
<tr>
<td>1 μ</td>
<td>photodissociate</td>
</tr>
</tbody>
</table>

or an atom

| 1 μ                                              | excite outer shell |
| 1000 A                                           | photoionize outer shell |
| 100 A                                            | photoionize inner shell |

Figure 2-1: Possible interactions between a molecule or atom and a photon. The longer wavelength events, which involve less energy, are at the top.
Absorption of incoming solar radiation

Thermal Structure of the Atmosphere
Why are the Thermosphere and Stratosphere so “hot”?

**Thermosphere**:
Photodissociation of $\text{O}_2$
$\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}$ ionization
$\lambda \ 120$-$210 \text{ nm}$

**Stratosphere**:
Ozone production and destruction is **exothermic**.
$\text{O}_2 + \text{O} \rightarrow \text{O}_3$ (production)
$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$ (destruction)
produces heat
$\lambda < 310 \text{ nm}$
Photodissociation of Oxygen

\[ \text{O}_2 + \text{UV light (120-210 nm)} \rightarrow \text{O} + \text{O} \]

Makes “free O” for making ozone (O$_3$)

Occurs above 50 km in atmosphere
(Upper Stratosphere)
“Good” and “Bad” Ozone

Now

Polar Ozone Depletion

Antarctic Ozone
South Pole (90°S)

Arctic Ozone
Sodankyla, Finland (67°N)

October averages
1962 - 1971
1992 - 2001
2 October 2001

March average
1988 - 1997
30 March 1996
The Chapman Profile: balancing density and photon flux
Factors controlling the rate of photodissociation

1. **The wavelength of light.**
   The wavelength must be short enough so the wave has sufficient energy to break the bond between the two atoms in the oxygen molecule. The most efficient wave lengths for photodissociation occur in the ultraviolet (0.15\(\mu\)m).

2. **Variation of oxygen density.**
   As altitude increases oxygen density decreases (Chapman Profile). The higher the oxygen density the greater the likelihood of having an interaction between an oxygen molecule and a photon.

3. **Variation of photon flux**
   Photon flux decreases with decreasing altitude because of photon absorption by the atmosphere. Rate of photodissociation of oxygen is greatest at an altitude of about 100 km:
1930s, Sydney Chapman proposed a series of reactions to account for the ozone layer: *the Chapman Cycle*

The *Chapman Cycle* explains how the ozone layer is formed and maintained. Describe this process in some detail.

Four chemical reactions:

- **Initiation** \( O_2 + \text{light} \rightarrow 2O \) (120 – 210 nm)

- **Propagation** (cycling) \( O + O_2 + M \rightarrow O_3 + M^* \) (exothermic)
  \( O_3 + \text{light} \rightarrow O_2 + O \) (220 – 320 nm)

- **Termination** \( O_3 + O \rightarrow 2O_2 \) (exothermic)
The Chapman Cycle
Oxygen-only Chemistry

“odd-oxygen” species \((O_x)\) are rapidly interconverted

\[ O_x = O + O_3 \]
Ozone Production
(>50km)

Ozone Destruction
(50-15 km)

Ozone Production in the Stratosphere:
- High energy ultraviolet radiation strikes an oxygen molecule.
- It causes it to split into two free oxygen atoms.
- The free oxygen atoms collide with molecules of oxygen.
- They form ozone molecules.

The Chapman Process of Ozone Destruction:
- Ozone absorbs a range of ultraviolet radiation.
- It splits the molecule into one free oxygen atom and one molecule of ordinary oxygen.
- The free oxygen atom then can collide with an ozone molecule.
- It forms two molecules of oxygen.
$O_3$ production & destruction
DU: Ozone measurement unit

Dobson Unit (100 DU = 1 mm $O_3$ at STP)
Rowland & Molina & Crutzen (1974)

Discovered that CFCs can last 10-100s of years in atmosphere.
CFCs susceptible to break down by UV
Predicted that CFCs will reduce ozone inventories.
Proof that this was occurring came in 1985.
Montreal Protocol 1987

Nobel Prize (1995)
A Brief History

- June 28, 1974, Drs. Sherry Rowland and Mario Molina published the first study warning that CFCs could harm the ozone layer (Molina and Rowland, 1974).
- They calculated that if CFC production continued to increase it would cause a global ozone loss of 30-50% loss by 2050. (current number is 70%!).
- They warned that the loss of ozone would significantly increase the amount of UV-B light reaching the surface, increasing incidences of skin cancer.
- Although no stratospheric ozone loss had been observed yet, CFCs should be banned.
- At the time, the CFC industry was worth about $8 billion in the U.S., employed over 600,000 people directly, and 1.4 million people indirectly (Roan, 1989).
Key ingredients to make an Ozone Hole:

- **Chlorine**: supplied by manmade CFCs
- **Cold**: Antarctic Polar Vortex
- **Seasons**: Dark and Light seasons
- **Clouds**: Polar Stratospheric Clouds
- **UV radiation**: Springtime sunlight
CFCs: Chlorofluorocarbons

CFCs introduced 1950s

“Miracle compounds”: inert, cheap, many applications.

Uses:
- Foam & Insulation
- Propellants
- Air conditioning
- Electronics
## CFC Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>ODP</th>
<th>Atmospheric lifetime (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>CFCl₃</td>
<td>1.0</td>
<td>60</td>
</tr>
<tr>
<td>CFC-12</td>
<td>CF₂Cl₂</td>
<td>1.0</td>
<td>120</td>
</tr>
<tr>
<td>CFC-113</td>
<td>CF₂CICF₂Cl</td>
<td>0.8</td>
<td>90</td>
</tr>
<tr>
<td>CFC-114</td>
<td>CF₂CIF₂Cl</td>
<td>0.6-0.8</td>
<td>200</td>
</tr>
<tr>
<td>Halon-1211</td>
<td>CF₂Br₂Cl</td>
<td>2.2-3.5</td>
<td>25</td>
</tr>
<tr>
<td>Halon-1301</td>
<td>CBrF₃</td>
<td>7.8-16</td>
<td>80-110</td>
</tr>
<tr>
<td>Halon-2402</td>
<td>C₂F₄Br₂</td>
<td>5.0-6.2</td>
<td>23-28</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>CHF₃Cl</td>
<td>0.04-0.06</td>
<td>15-20</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>CF₂CHCl₂</td>
<td>0.02-0.16</td>
<td>1-2</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>CH₃CFCl₂</td>
<td>0.03-0.11</td>
<td>6-11</td>
</tr>
<tr>
<td>HCFC-124</td>
<td>CF₃CHFCl</td>
<td>0.016-0.024</td>
<td>5-10</td>
</tr>
</tbody>
</table>
Antarctic Polar Vortex

Large polar land mass
Ice covered, large temperature gradients
Circular airflow around Antarctica

APV effectively creates an atmospheric “fence” impeding air exchange with other regions

(this is arctic polar vortex)
Polar Stratospheric Clouds (PSCs)

Ice clouds during Austral winter (no light, very cold)
PSCs concentrate, activate Cl (as Cl- and CLO)
Ice crystals act as reaction sites for O$_3$ destruction
CFCs accumulate in stratosphere
O$_3$ loss by UV photolysis

**Austral spring:** sunlight appears, UV

1. UV radiation splits off Cl atom from CFC molecule
2. Ozone destroying reactions:
   - Cl + O$_3$ $\rightarrow$ ClO + O$_2$
   - ClO + O $\rightarrow$ Cl + O$_2$
     
     (Cl is free to react with another O$_3$ again)

Net: O$_3$ + O $\rightarrow$ O$_2$ + O$_2$
UV radiation and CFCs
CFC and $O_3$
1. Formation of polar stratospheric clouds:
   - $\text{HNO}_3$
   - $\text{H}_2\text{O}$

2. Activation of $\text{Cl}_x$:
   - $\text{ClONO}_2$
   - $\text{HOCl}$
   - $\text{N}_2\text{O}_5$
   - $\text{Cl}_2\text{HOCl}$

3. Formation of $\text{ClO}_x$:
   - $\text{Cl}_2 + \text{hv} \rightarrow 2\text{Cl}$
   - $\text{HOCl} + \text{hv} \rightarrow \text{OH} + \text{Cl}$

4. Catalytic ozone depletion:
   - $\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2\text{O}_2$
   - $\text{Cl}_2\text{O}_2 + \text{hv} \rightarrow 2\text{Cl} + \text{O}_2$
   - $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
Discovery of the Ozone Hole
British Antarctic Survey (Farman et al 1985)

Figure 3. Mean October atmospheric ozone levels over Antarctica. Open boxes: British Antarctic Survey data. Closed boxes: NASA data (redrawn from Stolarski 1988).
Antarctic Ozone Hole in Dobson Units
Area of the Ozone Hole

http://jwocky.gsfc.nasa.gov/eptoms/dataqual/oz_hole_avg_area_v8.jpg
The Ozone Hole right now

Antarctic Ozone Hole:
Sept. 12, 2012

http://ozonewatch.gsfc.nasa.gov/
The Ozone Hole in 2007

Blue = low ozone levels
Current Status (2012)

Ozone Hole Area

SH Dobson units

http://jwocky.gsfc.nasa.gov/epptoms/dataqual/ozone_v8.html
Future projections

![Graph showing future projections of ozone-damaging stratospheric chlorine/bromine abundance with three scenarios: No Protocol, Montreal Protocol, and Copenhagen Amendments. The graph plots year on the x-axis from 1950 to 2100 and abundance in parts per trillion on the y-axis, with lines representing different protocols and their impact over time.]
Changes In Surface Ultraviolet Radiation

- Trend (Percent per Decade)
- Average
- Uncertainty Range

South to North of Latitude
-80 to 80
Recovery Stages of Global Ozone

- **Stage 1:** Initial slowing of ozone decline
- **Stage 2:** Onset of ozone increases
- **Stage 3:** Full recovery of ozone from ozone-depleting gases

Expected return of ozone-depleting gases to 1980 levels

Range of model projections

Pre-1980 ozone amounts

Global ozone change from pre-1980 values
Full recovery takes a long time (50 years)
Tactics of the Ozone Hole Skeptics (1970s - 90s)

1. Launch a public relations campaign.
2. Predict dire economic consequences.
3. Find and pay a respected scientist to argue your point.
4. Elevate discredited scientific studies.
5. Emphasize scientific uncertainty.
6. “Cherry-pick” data to support your view.
7. Disparage and impugn specific scientists.
8. Compliance puts the nation at an economic disadvantage.
9. More research is needed before action should be taken.
10. Argue that it is less expensive to live with the effects.

A great link to Jeffrey Masters’ article on this