Ozone

In the upper atmosphere

At the surface $\Rightarrow$ pollution (not discussed)
What is Ozone?

Oxygen molecule with 3 oxygen atoms ⇒ $O_3$
Normal form of oxygen: 2 oxygen atoms ⇒ $O_2$

Where does Ozone occur?

Stratosphere ⇒ “GOOD” $O_3$
Troposphere ⇒ “BAD” $O_3$

Pollutant associated with smog formation:
Concentration of $O_3$ measures severity of smog
Note: it NEVER reaches the stratosphere!
Units later. Ozone is a trace gas but critical for UV absorption
How is Ozone Created in the Stratosphere?

Prevalent O\textsubscript{2} molecules absorb ultraviolet radiation

⇒ Wavelengths less than 0.24 \( \mu \text{m} \)

Yields two O atoms which combine with O\textsubscript{2} molecules to form ozone

\[ \text{O} + \text{O}_2 \Rightarrow \text{O}_3 \]  in the upper stratosphere

Heating it up!
Ozone Production

SUN

UV
\[ \lambda < 240 \text{ nm} \]

\[ \text{O}_2 + \text{hv} \rightarrow 2 \text{O} \]

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]

Ozone is created by energetic UV radiation.
TEMPERATURE PROFILE (INVERSION)
How much ozone is where?

“mixing ratio” ppmv  parts per million per volume

Ozone at 35 km 8 ppmv ⇒ 8 out of every million molecules at 35 km will be ozone molecules

Ozone is a trace gas
How does the ozone layer work?

UV light with wavelengths between 0.24 and 0.32 µm is absorbed by ozone giving $O_2 + O$

The O atoms then recombine with an $O_2$ molecules to form $O_3$

So:
- ozone absorbs UV without being consumed
- net result: UV light $\Rightarrow$ heat
- check temperature profile of stratosphere
- ozone determines the properties of the stratosphere
- sink of $O_3$: it can recombine with O to form 2 $O_2$

Ozone absorbs:
- UVb partially (between 0.28 and 0.32 µm)
- UVc completely (between 0.24 and 0.28 µm)
- UVa not affected (larger than 0.32 µm)
BLACKBODIES AGAIN

(a) Energy distribution

Sun: 5750 K
Earth: 245 K

(b) Wavelength (μm)

Absorption spectrum:
- O₂
- O₃
- H₂O
- CO₂
- H₂O
OZONE PROFILE

[Diagram showing ozone profile with altitude (km) on the y-axis and ozone (DU/km) on the x-axis. Stratosphere and troposphere regions are indicated.]
OZONE DEPLETION CONSEQUENCE:

UVb and UVc are absorbed by DNA!

UVb increases as a result of O₃ depletion

Such a depletion was first observed in the seventies and is a serious concern in Australia, New Zealand, and Chili, since UVb is responsible for more than 90% of skin cancers.

Link to human health appears critical in fostering international agreements (global climate change appears less effective so far).
http://en.wikipedia.org/wiki/Macquarie_Island
NO OZONE LAYER?

NO LIFE AS WE KNOW IT!
- can seriously damage plant life
- generally harmful for marine life
- depletion perhaps linked to amphibian decline
- cataracts: each 1% total column ozone depletion leads to a worldwide increase of 100,000 blind people
- 180M new cases of skin cancer for unrestricted growth of CFCs plus 3.5M extra cancer deaths in the US alone (EPA study from 1987)
How much ozone is in the layer?

Dobson unit:
measures total amount of ozone in a column overhead

Example:
ozone layer above some place in the US compressed to
0 degrees C and 1 atmosphere pressure
⇒ 3 mm thick

1 DU (1 Dobson unit) = 0.01 mm at 0 degrees C and 1 atmosphere

Above the US typically 300 DU
OZONE COVER WITH THE "HOLE"
What Are CFC’s?

Chloro fluoro carbons volatile organic compounds

Used for
- refrigerants
- aerosol propellants
- foam blowing agents
- solvents (in electronics industry)

Discovered by Thomas Midgely in 1928 when asked by GM (sponsored by DuPont) to invent a new refrigerant to replace ammonia (gave headaches)

Relevant for ozone depletion: $\text{CFCl}_3$ (CFC-11)

$\text{CF}_2\text{Cl}_2$ (CFC-12) etc

replacement of Cl by Br (bromine)

They are chemically inert and eventually end up in the stratosphere where they hang out for hundreds of years!
CONCENTRATION OF CFC-11
HOW DO CFC’S DESTROY OZONE?

Molina & Rowland 1995 Chemistry Nobel prize

CFC’s in the upper atmosphere absorb UV light (.23µm) releasing Cl which acts as a catalyst able to destroy 1000’s of O$_3$

Br is an even more powerful catalyst
Ultraviolet radiation strikes a CFC molecule... and causes a chlorine atom to break away.

The chlorine atom collides with an ozone molecule... and steals an oxygen atom to form chlorine monoxide and leave a molecule of ordinary oxygen.

When a free atom of oxygen collides with the chlorine monoxide... the two oxygen atoms form a molecule of oxygen. The chlorine atom is released and free to destroy more ozone.
Ozone levels over Antarctica have fallen to abnormally low levels between late August (starts at 300 DU) & late November.

Instead of rising, a drop to 150 DU and below is observed.

Overall losses reaching 50%.
MORE OF THE MINIMUM

Mean October ozone at Halley

- Total ozone (Dobson units)
- Year

- Data points showing a downward trend from the 1950s to the 2010s.
Maximum Ozone Hole Area

![Graph showing the increase in TOMS O₃ hole area (10⁶ km²) from 1975 to 2005. The graph indicates a significant increase in hole area over time, with error bars indicating variability in the measurements.](image-url)
SIZE OF THE HOLE

2002 Southern Hemisphere Ozone Hole Area
NOAA SBUV/2
Current Year Compared Against Past 10 Years

Million Sq Km

Updated through Nov 6, 2002

Ozone Hole Area

August  September  October  November  December

2002  2001  92-01 Mean  92-01 Max  92-01 Min
2003 Southern Hemisphere Ozone Hole Area
NOAA SBUV/2
Current Year Compared Against Past 10 Years

2003

Updated through Nov 10, 2003

Million Sq Km

August September October November Dec

2003 2002 93-02 Mean 93-02 Max 93-02 Min
2007

2007 Southern Hemisphere Ozone Hole Area
NOAA SBUV/2
Current Year Compared Against Past 10 Years

Updated through Dec 12, 2007

August | September | October | November | December

Why is the hole in the Antarctic?

Everywhere similar amounts of Cl

- unusual physics & chemistry creates a Cl reservoir
- polar vertex (cooling of antarctic stratosphere in winter decouples the antarctic from the rest of circulation)
- polar stratospheric clouds where the chemical reactions take place
- theory developed by Crutzen in 85-87 (also 95 Nobel prize)
- manmade Chlorine responsible for hole

No longer an issue for debate
FIG. 1. Total ozone observations above Halley Bay\textsuperscript{6} and the South Pole\textsuperscript{8,9}, showing the development of the ozone hole. Total chlorine abundances in the troposphere and stratosphere are also indicated, based on an assumed 3.5-year lag time between the two atmospheric regimes (ref. 5 and A. F. Tuck, personal communication). Natural chlorine abundances are believed to be \( \sim 0.6 \) p.p.b.v., with man-made chlorine making up the remainder of the stratospheric chlorine budget\textsuperscript{6}. 

Typical Data
VARIATION OF THE HOLE WITH TIME
What has been done?

Scientific insight into future conditions has had enormous impact leading to

Global international agreements

1974-85 Industry extremely skeptical (as usual)
1985 Hole discovered acted like shock therapy
1987 Montreal protocol CFC’s reduced by 50% by 2000
1990 London 100%
1992 Copenhagen 4 years accelerated

See next slide
REAL SUCCESS!

Montreal Protocol versus London Revisions
Atmospheric Chlorine Loading

Note: Although the London revisions do not control HCFCs, the graph assumes that HCFCs, with an atmospheric lifetime of eight years, replace 30 percent of the CFC market and that HCFC production is frozen in 2020 and phased out in 2040.

Table 5.5. Summary of 1992 Adjustments and Amendments

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<td>Halons</td>
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<td>Methyl chloroform</td>
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<td>HBFCs</td>
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<td>Methyl bromide</td>
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</table>

*All dates are January 1.

Source: UNEP/OzL.Pro.4/15.
OUTLOOK

Halogen Loading as Equivalent Effective Stratospheric Chlorine

- Carbon Tetrachloride
- Methyl Chloroform
- Controlled part of methyl bromide
- Halons
- HCFCs
- CFCs

Natural Part of Methyl Bromide
Methyl Chloride (Natural)

Parts per trillion

Year
1940 1960 1980 2000 2020 2040 2060 2080 2100
http://www.esrl.noaa.gov/gmd/index.html
CLOSING THE HOLE
Nevertheless ...

7 September 2003 - The Ozone hole reached land and population areas in Argentina, Chile and The Falkland Islands.
The area and population affected including the Argentinean city of Ushaia which has a population of 30,000 and Punta Arenas, Chile which has a population of 120,000 are all at risk during this time period. The public should avoid going outside during the peak hours of 11:00 a.m. and 3:00 p.m. to avoid exposure to the UV rays. If people do go outside during these hours they should wear protective sunscreen and if possible a hat or head covering and sunglasses with a uv rating. The Ozone hole has reached land and population areas in Argentina, Chile and The Falkland Islands since the early 1990's. Ozone levels drop down as much as 70% in some areas. The protective level of ozone has dropped below 150 dobson units in some areas. It has reached further north at times affecting the towns of Rio Gallegos, Puerto Santa Cruz, and Rio Grande affecting an additional 200,000 people.
The ozone layer has protected life for a billion years until …