Ozone Recovery?

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• 1928: start of CFC production

• 1971: 1st observation of CFC in the atmosphere (J. Lovelock)

• 1974: identification of O₃ destruction potential by CFC: Rowland & Molina


1990: 80% of stratospheric chlorine is of anthropogenic origin
Long term ozone depletion

- Increasing anthropogenic emissions, since industrial revolution, esp. CFCs since 1960
  - increasing concentrations of destructive radicals
  - steady decrease of O$_3$ on a global scale

- Recurrent spring-time ozone hole at the South pole

- Seasonal ozone depletion in the North pole, strongly modulated by dynamics
Large losses of total ozone in Antarctica reveal seasonal ClO$_x$/NO$_x$ interaction

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Recent attempts$^{1,2}$ to consolidate assessments of the effect of human activities on stratospheric ozone (O$_3$) using one-dimensional models for 30° N have suggested that perturbations of total O$_3$ will remain small for at least the next decade. Results from such models are often accepted by default as global estimates$^3$. The inadequacy of this approach is here made evident by observations that the spring values of total O$_3$ in Antarctica have now fallen considerably. The circulation in the lower stratosphere is apparently unchanged, and possible chemical causes must be considered. We suggest that the very low temperatures which prevail from midwinter until several weeks after the spring equinox make the Antarctic stratosphere uniquely sensitive to growth of inorganic chlorine, ClX, primarily by the effect of this growth on the NO$_2$/NO ratio. This, with the height distribution of UV irradiation peculiar to the polar stratosphere, could account for the O$_3$ losses observed.

- First alarming signs of O$_3$ degradation were given in 1982 and 1985 based on Dobson measurements at Syowa and Halley Bay (since 1957)

- Ozone layer thins dramatically in the local spring down to ~ 100 DU

This phenomenon was not expected!
Evolution of average (monthly) \( \text{O}_3 \) layer thickness between 1956 and 1986 in October.

In February.
Heterogeneous chemistry on PSCs

**In darkness**

1. Formation of polar stratospheric clouds:
   - ClO
   - ClO
   - ClO
   - ClO
   - ClO

2. Activation of Cl\(_x\):
   - ClO
   - ClO
   - ClO
   - ClO
   - ClO

**In the light of the rising spring sun**

3. Formation of ClO\(_x\):
   - Cl\(_2\) + hv \rightarrow 2Cl
   - HOCI + hv \rightarrow OH + Cl
   - Cl + O\(_3\) \rightarrow ClO + O\(_2\)

4. Catalytic ozone depletion:
   - ClO + ClO \rightarrow Cl\(_2\)O\(_2\)
   - Cl\(_2\)O\(_2\) + hv \rightarrow 2Cl + O\(_2\)
   - Cl + O\(_3\) \rightarrow ClO + O\(_2\)
Experimental evidence

Ozone and reactive chlorine measurements from a flight through the ozone hole in Antarctica, 1987.
Success of Montreal protocol

Used in Aerosols, Refrigeration, Air Conditioning and Manufacturing of Foams.
Effect of Montreal Protocol

Reduction of chlorine and bromine in the stratosphere follows decrease of concentrations of the surface with a delay of 3 to 5 years = time to reach from troposphere to stratosphere.

Courtesy: Univ. Liège

Courtesy: F. Hendrick, IASB
The impact of the Montreal Protocol on climate is of order 5-6 times larger than the objectives of the Kyoto Protocol 2008-2012!

Reduction by Montreal Protocol of ~12 GtCO$_2$-eq/yr
Monitoring of the ozone hole using satellites and models

Evolution of the Antarctic ozone hole from 2003-2011

MACC analyses of O3 at 475K (ppmv) by IFS-MOZART

http://www.gmes-stratosphere.eu

2003 2004 2005 2006 2007 2008 2009 2010

2011 01 Aug
Evolution of the Spring polar ozone over the North Pole from 1979 until 2011

MACC/MSR, KNMI
Ozone

MLS Chlorine Monoxide

Antarctic CIO in 2011 was outside the range of the 2005-2010 winter observations, and comparable to Antarctic CIO.

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Arctic Ozone in 2011 was outside the range of the 2005-2010 winter observations, as Antarctic ozone.
What would have happened if chlorofluorocarbons (CFCs) had not been regulated?

Newman et al., ACP, 2009
Current situation

• O_3 in the middle latitude:
  – 6% (3.5%) lower than average in 1964-1980 SH (NH)
  – UV has not increased since the late 1990s

• O_3 hole at the poles is still as in early 1990 (subject variability)
  i.e. in Antarctica in October, 40% lower than in 1980

• UV on Antarctic is higher by 55 to 85% than in 1963-1980

• Evidences for changes in SH tropospheric summertime circulation due to Antarctic ozone hole

• The stratosphere has cooled a few K between 1980 and 1995 due to ozone depletion; the cooling reinforced by increasing GHG esp. in recent years
Coupling between ozone and climate

- Concentrations of greenhouse gases (CO₂, CH₄, N₂O,...) rise
- T° rises at the surface; but decreases in the stratosphere
- Atmospheric transport changes, rate of chemical reactions changes
- Frequency of formation of clouds, aerosols and PSC change
- Radiation balance changes
- Ozone formation / degradation is influenced, in turn ozone affects UV, T° stratosphere ....
Future evolution of ODS

- EESC back to 1980 levels:
  - in ~2050
  - in ~2065 at the poles (older air)
Future evolution of mid-latitude ozone

Average total column ozone changes over the same period, from multiple model simulations compared with observations between 1965 and 2013.

Four possible greenhouse gas (CO$_2$, CH$_4$, and N$_2$O) futures are shown. The four scenarios correspond to +2.6 (purple), +4.5 (green), +6.0 (brown), and +8.5 (red) W m$^{-2}$ of global radiative forcing.
Impact of projected changes in GHGs on ozone

- Increased CO$_2$, CH$_4$ and N$_2$O cools the stratosphere, which tends to increase O$_3$ because of temperature-dependent chemistry (reduced efficiency of loss)
- Increased CH$_4$ and N$_2$O also have further chemical impact on O$_3$
  - CH$_4$ increases O$_3$ by mitigating the effect of halogen-driven O$_3$ destruction catalytic cycles
  - N$_2$O decreases O$_3$ through enhancing the efficiency of the NOx-driven catalytic cycles
Evidence for $\text{O}_3$ recovery in upper stratosphere

$\text{O}_3$ recovery at 45 km altitude is due to combination of reduction in ODS (Montreal protocol) reinforced by cooling due to GHG increase
Predicted reduction of the tropical ozone layer

Recent evidence for changes in tropical upwelling and higher latitudes downwelling due to climate change.
Summary

• O$_3$ on a global scale will return to state from 1980 by 2050, i.e. faster than ODS, namely:
  – Around 2030-2040 in middle latitudes of both hemispheres
  – Around 2045-2060 in Antarctica
  – The increase of ozone will be accelerated in a colder stratosphere under the impact of GHGs
• As result, at the end of the 21st century the stratospheric ozone concentration will be higher than in 1980
• Tropical ozone is expected to decrease due to climate-change induced changes in the Dobson-Brewer circulation
• The climate benefits of the Montreal Protocol could be significantly offset by projected emissions of HFCs used to replace ODSs
• Large uncertainties in future emission scenarios and resulting impacts
There are links between the stratospheric ozone evolution and climate change, and air pollution and atmospheric transport, and ... These effects make the scientific questions much more complicated, and make it very difficult to design the best mitigation policies.