Lecture 7: The Ozone Hole

Ozone layer in the news: Nov 23, 2003

“[The US] administration is insisting on a sharp increase in spraying of the most dangerous ozone-destroying chemical still in use, the pesticide methyl bromide, even though it is due to be phased out under the Montreal Protocol in little more than a year. …the United States could withdraw from the treaty’s provisions altogether if its demand is not met… US delegates…even rejected a European Union proposal that would have allowed farmers to use the same amount of the pesticide as at present, even though this, itself, would violate the spirit of the protocol.”

The Independent (London-based UK national newspaper)
1987: State of Knowledge

Changes in Stratospheric Ozone

Ralph J. Cicerone

Large O3 decreases over Antarctica have been reported (1); this perturbation was not predicted, nor is there an accepted explanation at present.

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1987: State of Knowledge

Science and Policy

NORMAL TIMES (theory-driven)
1974 Mario Molina and Sherwood Rowland propose catalytic destruction of stratospheric ozone by CFCs. 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. (Reagan administration).
1987 Cause of ozone hole is still in question. The leading theories are:
- dynamics and natural variability
- nitric oxide (NO) and sunspots
- CFCs and polar stratospheric clouds

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Stratospheric "Ozone Hole": Explanation

Four years (1985-1988) of frantic research

Led to scientific consensus that the CFC/PSC explanation was correct (as given in Kump textbook, p.353-357):

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

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Polar Stratospheric Clouds (PSCs) in twilight
Recall vertical distribution of chlorine species:

Only the reactive forms of chlorine, Cl and ClO, are catalysts and a danger to stratospheric ozone.

Almost all Cl, esp. in lower stratosphere, is bound up in unreactive forms (recall earlier vertical distribution diagram) mainly HCl (hydrogen chloride) and ClONO₂ (chlorine nitrate).

Reactions on crystal surfaces of polar stratospheric clouds (PSCs) do two things: (1) sequester NO₂ and (2) liberate molecular chlorine.

The second of these is:

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3
\]

chlorine nitrate + hydrogen chloride = chlorine molecules + nitric acid.

The chlorine gas molecules are photolyzed to make Cl atoms.

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

"Smoking gun": Correlation with ClO from aircraft

Question: What is the ratio of ClO to O₃ within the ozone hole?

O₃ in ppb ClO in ppt

1100 ppt ClO

1000 ppb O₃

~ 1 ppt 1 ppb

1 ppt 1000 ppt

= 1/1000

Not much ClO, but it has big effect.

Nowadays, we can see the same correlation from satellite.
Polar vortex: An added twist?

Stratospheric winds from west to east

Cold at pole: air sinks

Like a whirlpool

Sinking air removes NO2 in ice particles (which otherwise inactivates ClO)

Vortex isolates air over Antarctica: Little new O3 brought in.

Kump Fig 17-10
Global trends

Natural variability:
1) Stratosphere winds cycle annually and every 27 months - affects seasonal ozone levels
2) 11-year sunspot cycle causes changes of 2-3% (solar max - more UV and more O$_3$)

Subtract these out to get global trend

International Treaties and Scientific Assessments

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