Chemical Loss of Polar Ozone: Present Understanding and Remaining Uncertainties

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1. Introduction and Overview
2. Is Antarctic Ozone Recovering ?
3. Do We Understand Chemical Ozone Loss Rates ?
4. Arctic Ozone Loss and Climate Change ?
DISCOVERY OF ANTARCTIC OZONE HOLE

Total Ozone Over Halley Bay, Antarctica (76°S)
Average for October

Farman et al., Nature, 1986

Southern Hemisphere
ANTARCTIC OZONE HOLE FROM SPACE

TOMS Total Ozone Monthly Averages

October 79  October 80  October 81  October 82

October 83  October 84  October 85  October 86

Stolarski et al., Nature, 1986
OCTOBER-AVERAGE 1967-1971: 282 DU

OZONE ABUNDANCE (PARTIAL PRESSURE, mPa)

OCTOBER AVERAGE 1967-1971: 282 DU

OCT 7, 1986: 158 DU

D. Hofmann, NOAA CMDL
**Chemical Hypothesis**

- **Cold Temperatures** $\rightarrow$ **Polar Stratospheric Clouds (PSCs)**
- **Reactions on PSC Surfaces Lead to Elevated CIO**:  
  
  \[
  \text{HCl} + \text{ClNO}_3 \rightarrow \text{Cl}_2 \text{ (gas)} + \text{HNO}_3 \text{ (solid)} \\
  \text{Cl}_2 + \text{SUNLIGHT} + \text{O}_3 \rightarrow \text{CIO} \\
  \text{HNO}_3 \text{ SEDIMENTS on PSCs}
  \]

- **Elevated CIO + Sunlight Destroys O}_3

- **BrO : Reaction Partner For CIO $\Rightarrow$ Additional O}_3 Loss
Ozone Loss Details

\[ \text{ClO} + \text{ClO} \rightarrow \text{ClOOCI} \]

\[ \text{ClOOCI} + \text{Sunlight} \rightarrow \text{Cl} + \text{Cl} + \text{O}_2 \]

\[ 2 \left[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \right] \]
Ozone Loss Details

\[ \text{ClO} + \text{ClO} \rightarrow \text{ClOOC1} \]

\[ \text{ClOOCI} + \text{Sunlight} \rightarrow \text{Cl} + \text{Cl} + \text{O}_2 \]

2 \[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]
Ozone Loss Details

\[
\text{CIO} + \text{CIO} \rightarrow \text{CIOOCI}
\]

\[
\text{CIOOCI} + \text{Sunlight} \rightarrow \text{Cl} + \text{Cl} + \text{O}_2
\]

\[
2 \left[ \text{Cl} + \text{O}_3 \rightarrow \text{CIO} + \text{O}_2 \right]
\]

Net: \(2 \text{O}_3 + \text{Sunlight} \rightarrow 3 \text{O}_2\)

Kinetics Studies:
~1 part per billion needed to match observed loss rates
Ozone Loss Details

\[ \text{Net: } 2 \text{O}_3 + \text{Sunlight} \rightarrow 3 \text{O}_2 \]
McMurdo Station, Antarctic, 1986

P. Solomon et al., *Nature*, 1987
Anderson et al., *Science*, 1991
MICROWAVE LIMB SOUNDER (MLS)
SATellite MEASUREMENTS OF THE
ANTARCTIC OZONE HOLE

Waters et al., Nature, 1993
Santee et al., Science, 1995
MONTREAL PROTOCOL
and AMENDMENTS
ESSENTIALLY BANNED CFCs

Figure 15
20 Questions and Answers About the Ozone Layer
WMO/UNEP 2003 (Fahey et al.)
Total Ozone Over Halley Bay, Antarctica (76°S)
Average for October
OZONE ABUNDANCE

OZONE PROFILES, SOUTH POLE:
UPDATE

ALITUDE (km)

OZONE ABBUNDANCE
(PARTIAL PRESSURE, mPa)

SEP 29, 1999
90 DU

OCTOBER
AVERAGE
1967 - 1971
282 DU

D. Hofmann,
NOAA CMDL
"Recipe" for an Ozone Hole:
- Total Chlorine (> ~2 parts per billion)
- Cold Temperatures (→ PSCs)
- Sunlight

What about the Arctic?
ANTARCTIC (S.H.) POLAR VORTEX
MINIMUM TEMPERATURE, 20 km

ARCTIC (N.H.) POLAR VORTEX
MINIMUM TEMPERATURE, 20 km

Data Courtesy
P. Newman,
E. Nash,
&
R. Nagatani
Figure 12
20 Questions and Answers About the Ozone Layer
WMO/UNEP 2003 (Fahey et al.)

After Newman et al., GRL, 1997
Is Antarctic Ozone Recovering?

International Ozone Commission Definition, 1\textsuperscript{st} of 3 Stages of Recovery:

“A statistically significant slowing of the downward trend”


BLACK Points:
Ozone data adjusted to account for dynamic variability

RED Curve:
Fits of Equiv Eff. Strat Cl to ozone data

BLACK Line:
Trend to data, 1979 – 1996, forecast linearly thereafter

60 – 70°S: Antarctic Vortex “Collar Region”

BLACK:
Cumulative sun of ozone residuals from linear trend

BLUE:
95% confidence envelope of departure from natural variability (including trend model uncertainty)

Note:
Yang et al. show this result not driven by “saturation” of chemical ozone loss

E-S. Yang et al., GRL, 2005
Do We Understand the Rate of Chemical Ozone Loss?

- Photochemical model run along 10-day back trajectories
- Observations of ClO+ClOOCl used to initialize model
- Observed ozone loss rate based on temporal evolution of the $O_3$ vs $N_2O$ relation:

Model accounts for 72% of observed ozone loss
Do We Understand the Rate of Chemical Ozone Loss?

Stimpfle et al., JGR, 2004 show:
- Measured ClO/ClOOCl ratio agrees best with Burkholder cross section, given present understanding of ClO+ClO rate constant

Model accounts for 83% of observed ozone loss
Do We Understand the Rate of Chemical Ozone Loss?

\[ \text{BrO}_x = \text{BrO} + \text{BrCl} \]

**BLACK Line:** BrO\(_x\) based on measured BrO

---

**Why is empirical BrO\(_x\) ~factor of 2 > Model BrO\(_x\)?**

- Models consider supply of stratospheric bromine from only "long-lived" CH\(_3\)Br + halons
- A suite of VSL (very short lived) bromocarbons may supply significant levels of stratospheric bromine
  
  \[ \implies \text{e.g., Salawitch et al., GRL, 2005; Poster A23A-0914 (Tues Afternoon)} \]
Frieler et al., GRL, submitted:

- Consistency between observed Arctic loss rates (Match method) & meas. ClO, ClOOCI, and BrO assuming Burkholder et al. cross section for ClOOCI

- Bromine catalysed O₃ loss may be more important, relative to chlorine catalysed loss, than previously thought:
  
  Reference Run (1st bar): bromine 17 to 33 % of total
  
  Final Run (4 th bar) : 32 to 55% of total
Arctic Ozone Loss and Climate Change

- $V_{PSC}$: Volume of air in Arctic vortex exposed to Polar Stratospheric Clouds (PSCs)
- Factor of three increase in the maximum of $V_{PSC}$ over the past four decades
- The coldest Arctic winters are getting colder !!!
- Cause uncertain: may be due to climate change
- Arctic winter of 2004-2005: new record for maximum $V_{PSC}$

Several talks Wed morning, this session, about Arctic ozone loss 2004-2005 winter

Rex et al., GRL, 2004 (updated)
Arctic Ozone Loss and Climate Change

Rex et al., GRL, 2004

Rex et al., GRL, 2004
Arctic Ozone Loss and Climate Change

\[ V_{PSC} \times 10^6 \text{ km}^3 \]

\[ \text{Ozone column loss [DU]} \]

(14-25 km, mid-Jan to late March)

\[ 5-6 \text{ K temperature change} \]

\[ 80 \text{ DU ozone loss} \]

\[ \sim 15 \text{ DU additional ozone loss} \]

per Kelvin cooling of the Arctic stratosphere

Rex et al., *GRL*, 2004
SLIMCAT "Old" underestimates sensitivity of Arctic ozone loss to climate change by nearly factor of three

Rex et al., *GRL*, 2004
Arctic Ozone Loss and Climate Change

New SLIMCAT run reproduces observed data quite well.

New SLIMCAT: JPL 2002 + Burkholder Cross Section + NAT-based Denit. Scheme + Improved Radiation (More Realistic Polar Descent & Cl₂)
Summary

Is Antarctic Ozone Recovering?
- Collar region (area near edge of vortex) showing “first signs” of recovery
- Lots of debate about meaning of “recovery”
- Considerable uncertainty regarding when “Pre Ozone Hole” levels will be attained

Do We Understand Chemical Ozone Loss Rates?
- Perhaps!
  - Long standing model underestimation of ozone loss rate may be resolved by:
    a) Faster photolysis of ClOOCI \( \Leftrightarrow \text{requires better lab confirmation of cross section} \)
    b) Factor of 2 more bromine \( \Leftrightarrow \text{subject of active research} \)

Arctic Ozone Loss and Climate Change?
- Recent ozone loss proportional to volume of polar vortex exposed to PSC temperatures
- 15 DU (~4% of total column) additional ozone loss per Kelvin cooling \( \Leftrightarrow \text{reproduced by model} \)
- Coldest Arctic winters, in terms of \( V_{\text{PSC}} \), are getting colder

Climate change?
\[ \downarrow \text{PWD (planetary wave drag) due to stronger vertical shear of the zonal wind at high latitudes (Limpasuvan and Hartmann, J. Climate, 2000)} \]
\[ \downarrow \text{PWD due to increased westerly winds in the subtropics (Shindell et al., Nature, 1998)} \]
\[ \downarrow \text{PWD} \Rightarrow \uparrow \text{Arctic Vortex Strength} \Rightarrow \text{lower } T \Rightarrow \text{Higher } V_{\text{PSC}} \]

Natural Variability?