Atmospheric Chemistry

Lecture 11
Stratospheric Ozone

Produced by ultraviolet photolysis of $O_2$ ($\lambda < 242$ nm)

$O_3 + Cl \rightarrow ClO + O_2$

$O + ClO \rightarrow Cl + O_2$

NET: $O + O_3 \rightarrow 2O_2$

Destroyed by Catalytic Reactions of NOx, HOx, ClOx, BrOx

Catalytic agents are produced from long-lived source gases, released in the troposphere and transported to the stratosphere

Concentrations of source gases are observed to be increasing

Biogeochemical Cycling of Elements and Stratospheric Ozone

Leaky Bucket Analogy for Ozone Production and Loss

Sun UV produces ozone

Balance of production and loss determines ozone level

Catalytic reactions of oxides destroy ozone

Atmospheric Chemistry Lecture 11
Continuity Equation Including Catalytic Losses

\[
\frac{d[O_x]}{dt} = P_{Ox} - (l_{Ox} + l_{HOx} + l_{NOx} + l_{ClOx}) \cdot [O_3]
\]

In steady state \(d[O_x]/dt = 0\)

\[
[O_3] = \frac{P_{Ox}}{(l_{Ox} + l_{HOx} + l_{NOx} + l_{ClOx})}
\]

where \(l_{ClOx}\) is

\[
l_{ClOx} = k_{O,ClO} \cdot \frac{[O]}{[O_3]} \cdot \frac{[ClO]}{[Cl_y]} \cdot [Cl_y]
\]
Total Column Thickness of the Ozone Layer

How is Ozone Measured?

Total Ozone – Dobson Unit (milli–atmosphere centimeter)

- Bring all ozone above a certain location down to the ground
- Measure the thickness of the layer
- 300 D. U. (approximately the global average) = 3 millimeters (~ 0.1 inch). About the thickness of two stacked pennies.
- 100 D. U. (approximate thickness of the ozone hole) = 1 millimeter. About the thickness of one dime.

Ground–based instruments measure the intensity of two wavelengths of ultraviolet solar radiation; one absorbed by ozone, the other not absorbed.

Atmospheric Chemistry Lecture 11
Discovery of the Ozone Hole: Long-Term Ozone Measurements from Halley Bay, Antarctica

Halley Bay Station set up during the IGY (1957)

"Annual Variation of Ozone in Antarctica" by G. M. B. Dobson
Quart. J. Royal Met. Soc. 92, 549–552 (1966)

Atmospheric Chemistry Lecture 11
Discovery of the Ozone Hole: Long-Term Ozone Measurements from Halley Bay, Antarctica

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**Timeline: < 3 yrs**

1985: Antarctic ozone hole discovered by British Antarctic Survey

1986: Antarctic ozone hole mapped by TOMS/SBUV satellite instruments

1986: Three theories of ozone hole published

1986: NOZE ground-based expedition to McMurdo, Antarctica

1987: Balloon measurements at McMurdo show vertical structure of ozone hole

1987: Airborne Antarctic Ozone Expedition (AAOE) flown out of Punta Arenas, Chile – produces “smoking gun” graph clearly showing ozone loss in response to chlorine increase
Figures from our 1986 Nature paper on the ozone hole

Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease


NASA/Goddard Space Flight Center, Laboratory for Atmospheres, Greenbelt, Maryland 20771, USA
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What about the theory of the ozone hole?
Atmospheric Chemistry Lecture 11
Variety of Initial Theories of the Ozone Hole

- Chlorine chemistry

- Dynamics – was ozone just moved around by wave motions but conserved over the entire polar region? No, there was a net decrease.

- Solar Cycle – NOx chemistry variations induced by solar cycle- required N2O change that was not observed.

- Other?
There were alternative theories
Basic Mechanism for Antarctic/Antarctic Ozone Loss

Active Chlorine Catalytic Cycle for Ozone Loss

Reservoir Chlorine Temporary Storage (~days to weeks)

Cl → ClO

ClO → HCl

HCl → ClNO

ClNO → Cl

“Normal” Atmosphere (<1%)

“Normal” Atmosphere (>99%)

Atmospheric Chemistry Lecture 11
Basic Mechanism for Antarctic/Arctic Ozone Loss

Active Chlorine Catalytic Cycle for Ozone Loss

- Cl → ClO
- ClO → Cl

Reservoir Chlorine Temporary Storage (~days to weeks)

- HCl
- CINO₃

Reactions on PSCs

Polar Winter Atmosphere (>50%)

Polar Winter Atmosphere (<50%)
Polar Stratospheric Clouds (PSCs)

Primary Condensables

- Background sulfate aerosols
- $\text{H}_2\text{O}$ (3–5 ppmv)
- $\text{HNO}_3$ (5–10 ppbv)

At temperatures below $\sim 195K$

- Ternary solutions form which eventually become nitric acid trihydrate (NAT)
- Particle size $\sim 0.5 \mu$
- Negligible fall velocity

At temperatures below $\sim 188K$

- Water ice forms
- Several $\mu$ size, significant fall velocity
- Dehydration and denitrification
Why Do PSCs Matter?

Because reactions such as:

\[ \text{HCl} + \text{ClNO}_2 \rightarrow \text{Cl}_2 \text{ (g)} + \text{HNO}_3 \text{ (s)} \]

convert chlorine from unreactive (towards ozone) reservoirs to Cl\(_2\) which is rapidly photolyzed in springtime sunlight to form chlorine atoms

\[ \text{Cl}_2 + \text{h}_\text{v} \rightarrow \text{Cl} + \text{Cl} \]

This is followed by conversion to ClO

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

When concentrations are large (~1ppbv), ClO reacts with itself to form the dimer

\[ \text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M} \]

The dimer photolyzes asymmetrically to form Cl atoms

\[ \text{Cl}_2\text{O}_2 + \text{h}_\text{v} \rightarrow \text{Cl} + \text{ClOO} \]

This forms a catalytic cycle destroying ozone without the need for atomic oxygen.
Antarctic Ozone Hole
Sequence of Events

- Winter vortex isolation
- Cold temperatures
- NAT/ice/ternary solution particle formation
- Surface reactions
  \[ \text{HCl} + \text{CINO}_3 \rightarrow \text{Cl}_2 + \text{HNO}_3 \]
- Dehydration and denitrification
- Springtime sunlight
  \[ \text{Cl}_2 \rightarrow 2\text{ClO} \]
- Ozone destruction
- Vortex breakdown
Arctic Sequence of Events

- Winter vortex
  - Not as isolated
  - Not as cold
  - NAT formation (little ice)
  - Little dehydration or denitrification
  - Surface reactions
    \[ \text{HCl} + \text{CINO}_3 \rightarrow \text{Cl}_2 + \text{HNO}_3 \]
- Vortex breakdown (?)
- Springtime sunlight
  \[ \text{Cl}_2 \rightarrow 2\text{ClO} \]
- Ozone destruction competes with ClO recovery back to CINO$_3$
- Vortex breakdown (?)
Arctic/Antarctic Contrast

Narrow range of year-to-year minimum temperatures

Antarctic

October 15 2011

50-90°S Minimum Temperature
50 hPa MERRA

Min 10%
Mean 70%
Max 90%

Note wide range of year-to-year minimum temperatures

Arctic

March 15 2011

50-90°N Minimum Temperature
50 hPa MERRA

Min 10%
Mean 70%
Max 90%

P. Newman (NASA), E. Nash (SSAI), S. Pawson (NASA)

HNO$_3$ = 6 ppbv, H$_2$O = 4.5 ppmv

Type I PSC

Type II PSC

50-90°S Minimum Temperature
50 hPa MERRA

Min 10%
Mean 70%
Max 90%

Note wide range of year-to-year minimum temperatures

Type I PSC

HNO$_3$ = 6 ppbv, H$_2$O = 4.5 ppmv

Type II PSC

1979-2017
2011
2012

Note wide range of year-to-year minimum temperatures

Atmospheric Chemistry Lecture 11
Cold Arctic Winters → Low Springtime Ozone
Warm Arctic Winters → High Springtime Ozone

Winter 2010-2011
Very cold → Low ozone

Winter 1996-1997
Also cold → Low ozone

Winter 1987-1988
Warm → High ozone

March 15 2011
March 15 1997
March 15 1988

http://acdb-ext.gsfc.nasa.gov/
Data_services/met/ann_data.html

http://ozoneaq.gsfc.nasa.gov
We now measure ozone and the chemicals that affect ozone
Summary

• Antarctic Ozone Hole:
  – Cooling during polar night, stable vortex
  – Conversion of chlorine on polar stratospheric clouds
  – Rapid ozone loss when sun comes up

• Arctic Ozone
  – More disturbed vortex because of land mass distribution
  – Same chemical processes occurring
  – Ozone loss limited by vortex breakup

• Arctic variability
  – Large year-to-year variability
  – Cannot predict year-to-year variability
  – Coupling to stratospheric and tropospheric climate uncertain