Atmospheric Chemistry
Stratospheric ozone

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Stratospheric ozone

Important concepts of this lecture:

- Chapman mechanism
  - $O_x$ – odd oxygen family
- Catalytic ozone destruction with
  - $HO_x, NO_x, ClO_x$ cycles
  - including initiation, propagation, null cycles and reservoirs
- The Antarctic ozone hole
  - ClO-ClO mechanism
  - $HNO_3$ and PSC heterogenous chemistry
Stratospheric ozone – Southern hemisphere

BUV & TOMS total ozone

Oct. 70          Oct. 71          Oct. 72          Oct. 79


Total Ozone (DU)
Why is the stratosphere?

Why T-inversion?!

1. Energy absorption by ozone lead to dissociation \((O_3->O+O_2)\) 280-315 nm
2. Recombination give heat release \((O+O_2->O_3)\)

As a result of T-inversion the stratosphere is stable, it has slow vertical mixing compared to the troposphere.
Stratospheric ozone

The stratospheric ozone layer

Ozone: \( \text{O}_3 \) ~ 3 mm thick if all ozone is concentrated to a layer at ground level (=300 Dobson Units, DU).

Protects life on Earth by absorbing UV radiation from the sun (\( \lambda < 320 \text{ nm} \), UVb).

The ozone layer is vital for life on Earth.

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**Spectrum of solar radiation vs. altitude**

Depletion of stratospheric ozone – Effects

A depleted ozone layer causes a number of negative effects:

- Increased risk of skin cancer (e.g. malignant melanoma)
- Increased risk of skin burns
- Increased risk of eye injuries such as cataract (grå starr)
- Suppression of the immune system
- Increased risk of damage to natural ecosystems
- Increased risk of damage to crops and forests

A 10% thinning of the ozone layer is expected to result in a 26% increase in the number of skin cancer cases.

The EU Environmental Agency (EEA) estimates that the levels of ozone depleting compounds reached their highest values in 1997, but the skin cancer prevalence will not reach its highest levels until 2055, with 78 million new cases globally per year!!
Stratospheric ozone - Effects

UVc (200 < $\lambda$ < 280 nm) does not reach Earth’s surface
UVb (280 < $\lambda$ < 320 nm) harmful
UVa (320 < $\lambda$ < 400 nm) less harmful

UV radiation can break the DNA molecules forming the genetic code, resulting in skin cancer (e.g. malignant melanoma).
The natural ozone layer

Figure is compilation of available measurements from 1960s

Region of largest production

- Theory predicts maximum $O_3$ production in the tropics
- But $[O_3]$ is not largest in the tropics
- To explain this (and low strat. $H_2O$) Brewer and Dobson suggested a circulation pattern
**Observation**
- O$_3$ columns are smallest in tropics despite this being the main stratospheric O$_3$ production region.

**Explanation**
- Rising tropospheric air with low ozone.
- B-D circulation transports O$_3$ from tropics to mid- and high latitudes.
- Recall that $\tau_{O_3}$ is quite long in the lower stratosphere.

**Other comments**
- O$_3$ maxima occur toward high latitudes in late winter/early spring - the result of the descending branch of the B-D circulation.
- Virtually no seasonal change in the tropics.
- More accurate data has led to improvements in our understanding of this simple circulation pattern.
Brewer – Dobson circulation

From the tropics to the mid- & high latitudes

Circulation stronger in the northern hemisphere

Highest UV in the tropics ⇒ highest ozone production

stratosphere
Chapman mechanism (1930)

The Chapman mechanism for stratospheric ozone

(R1) \( \text{O}_2 + h\nu \rightarrow \text{O}(^3P) + \text{O}(^3P) \) \hspace{1cm} (\lambda < 240 \text{ nm, UVC slower})

(R2) \( \text{O}(^3P) + \text{O}_2 + M \rightarrow \text{O}_3 + M \) \hspace{1cm} (2x, fast)

\( \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1D) \) \hspace{1cm} (\lambda < 320 \text{ nm, UVC+UVB})

O\(^1D\) + M \rightarrow O\(^3P\) + M

(R2)

(R3) net: \( \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^3P) \) \hspace{1cm} (fast)

(R4) \( \text{O}_3 + \text{O}(^3P) \rightarrow 2\text{O}_2 \) \hspace{1cm} (slower)

\( \text{O}_x \) family (odd oxygen molecules)
Check that the short-lived $O$ is in a steady state ($O=O^{(3P)}$), i.e. production and losses $\sim$ constant over its lifetime.

Lifetime ($\tau_O$) for $O$ can be written

$$\tau_O = \frac{\text{mass in the reservoir}}{\text{loss rate}}$$

Lifetime ($\tau_O$) $\sim$ seconds or less.

Production of $O$ varies on longer time scales.

$\Rightarrow$ Steady state for $[O]$. 
$O_x$ according to the Chapman mechanism


$[O_x] = [O_3] + [O] \approx [O_3]$

$O_3$ production and loss determined by the slow reactions (1) and (4).
$O_x$ lifetime

$O_3$ production determined by (1)
$O_3$ loss determined by (4)
$O_3$ lifetime determined by (4)

Steady-state conditions valid for $O_x$ in large parts of the stratosphere, but maybe not in the lower part.
Chapman mechanism – Ozone levels

Stratospheric O₃ levels (Chapman):

\[
[O_3]^2 = \frac{k_1k_2}{k_3k_4} C_{O_2}^2 n_a^3
\]

\[\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}\] (Odd oxygen molecules)

\[\lambda < 320 \text{ nm}\]

\[\text{O}_2 + h\nu \rightarrow \text{O} + \text{O}\] (Odd oxygen molecules)

\[\lambda < 240 \text{ nm}\]
Chapman mechanism – Results

The Chapman mechanism can explain qualitatively the O$_3$ maximum at 20-30 km altitude.

O$_x$ production = $2k_1[O_2]$ via reaction (1) depends strongly on altitude.

Photolysis rate ($k_1$) increases with altitude while $[O_2]$ decreases due to the pressure drop.

Observed natural ozone levels are significantly lower than predicted by the Chapman mechanism. ⇒

Additional sinks needed!
Catalytic ozone loss

Ozone can be consumed, meaning that the component causing ozone destruction is not consumed.

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]

Net reaction:
\[ 2\text{O}_3 \rightarrow 3\text{O}_2 \quad (\text{OH} \text{ conserved}) \]

Or:
\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]

Net reaction:
\[ \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \quad (\text{OH} \text{ conserved}) \]
Catalytic ozone loss

Ozone can be consumed, meaning that the component causing ozone destruction is not consumed.

How does the cycle look for Br and Cl?
Catalytic ozone loss

\[ \text{Cl} + O_3 \rightarrow \text{ClO} + O_2 \]
\[ \text{ClO} + O \rightarrow \text{Cl} + O_2 \]
**Net:** \[ O_3 + O \rightarrow 2O_2 \]

\[ \text{Br} + O_3 \rightarrow \text{BrO} + O_2 \]
\[ \text{BrO} + O \rightarrow \text{Br} + O_2 \]
**Net:** \[ O_3 + O \rightarrow 2O_2 \]

\[ \text{Br} + O_3 \rightarrow \text{BrO} + O_2 \]
\[ \text{BrO} + O_3 \rightarrow \text{Br} + 2O_2 \]
**Net:** \[ 2O_3 \rightarrow 3O_2 \]
Catalytic ozone loss - $\text{HO}_x$

From troposphere

\[ H_2O + O(^1D) \rightarrow 2\text{OH} \quad \text{(initiation step)} \]
\[ \text{CH}_4 + O(^1D) \rightarrow \text{OH} + \text{CH}_3 \quad \text{(initiation step)} \]

\[ \begin{align*}
(1) \quad & \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad \text{(propagation step)} \\
(2a) \quad & \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \quad \text{(propagation step, >20 km)} \\
(2b) \quad & \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \quad \text{(propagation step, <40 km)}
\end{align*} \]

These catalytic ozone loss cycles (1+2a, or 1+2b) are broken by

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{(termination step)} \]
Catalytic ozone loss - HOx

HOx is an important O3 sink, but it is not enough as only complement to the Chapman mechanism to fully account for the observed natural ozone levels (1960-ies).

Additional catalytic sinks are needed!
Catalytic ozone loss - NOx

From troposphere

\[ N_2O + O(1D) \rightarrow 2 \text{NO} \]  \hspace{1cm} \text{(initiation step)}

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  \hspace{1cm} \text{(propagation)}

\[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]  \hspace{1cm} \text{(propagation, >20 km)}

From aircraft

NO and NO\(_2\) are held up as reservoirs owing to:

\[ \text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]  \hspace{1cm} \text{(daytime termination)}

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]  \hspace{1cm} \text{(propagation)}

\[ \text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \]  \hspace{1cm} \text{(nighttime termination)}

\( \text{N}_2\text{O}_5 \) and \( \text{HNO}_3 \) can be converted back to NO and NO\(_2\), however they temporarily halt the catalytic cycle.
Catalytic ozone loss - $\text{NO}_x$

$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (propagation)

$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ (photolysis, radical production)

$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$

**Null cycle!** No net effect on ozone, and competes with the NOx catalytic ozone destruction. Especially efficient during daytime.
Catalytic ozone loss – NO\textsubscript{x}

The O\textsubscript{3} sinks attributable to NO\textsubscript{x} and HO\textsubscript{x} are sufficient as complement to the Chapman mechanism to account for the observed natural ozone levels (1970-ies).

Before the discovery of the ozone hole!

Paul Crutzen shared the Nobel prize in Chemistry 1995
Other important types of cycles

O + O catalytic cycle (example)
OH + O → H + O₂
H + O₂ + M → HO₂ + M
HO₂ + O → OH + O₂
Net: O + O + M → O₂ + M
• Important at high altitudes where [O]/[O₃] is higher

O₃ + O₃ catalytic cycle (example)
OH + O₃ → HO₂ + O₂
HO₂ + O₃ → OH + O₂ + O₂
Net: O₃ + O₃ → O₂ + O₂ + O₂
• Important at low altitudes where [O]/[O₃] is low

Null cycle (example)
NO + O₃ → NO₂ + O₂
NO₂ + hν → NO + O
Net: O₃ + hν → O₂ + O
• No Oₓ loss. Important because the NOₓ tied up in null cycle is not removing Oₓ in catalytic cycles.

Holding cycle (example)
Cl + CH₄ → HCl + CH₃
OH + HCl → H₂O + Cl
Net: CH₄ + OH → CH₃ + H₂O
• Does not involve Oₓ directly, but Cl atoms "tied up" as HCl are not participating in catalytic cycles.

Holding cycles involve reservoir species.
Other processes of ozone loss

*HOX, CLOX and NOX cycles not the only way to destruct ozon.*

*Members of one family can react with members of another!*

All reaction rates are still not fully estimated. Some question marks remain in the ozone chemistry in the stratosphere.
Bromine – the most effective ozone killer

- Br – BrO catalytic cycle similar to Cl – ClO cycle.
- However, Br is **almost 60 times as effective** as Cl in destroying ozone. Why?
- 1) BrONO₂ is much less stable than ClONO₂:
  - BrONO₂ + hν → BrO + NO₂ Effective also for long λ (visible light)
  - BrONO₂ + hν → Br + NO₃ No such channel available for Cl
- 2) HBr formation thermodynamically unfavourable (unlike HCl formation)
  - Br + CH₄ → HBr + CH₃ endothermic reaction
- Mixed bromine – chlorine cycle also strengthens ozone depletion:
  - BrO + ClO → Br + Cl + O₂
  - Br + O₃ → BrO + O₂
  - Cl + O₃ → ClO + O₂
  - Net: O₃ + O₃ → O₂ + O₂ + O₂
- **Fortunately, atmospheric bromine levels are quite low.**
  - The decision to use chlorine instead of bromine in CFCs is one of the luckiest decisions ever made. If bromine had been used instead, the ozone layer would probably have been gone before anyone noticed.
Stratospheric ozone – Antarctica

The ozone hole was first observed 1981 at Halley Bay, Antarctica.

The results were so astonishing that the scientists first would not believe their own data, and waited to publish them until 1985.

J.C. Farman, B.G. Gardiner and J.D. Shanklin.
Large losses of total ozone in Antarctica reveal seasonal ClO$_x$/NO$_x$ interaction
*Nature*, 1985
Stratospheric ozone hole – Antarctica

Ozone Hole Area
(<220 DU; 40°-90°S)

- North American Area
- Antarctic Area

Ozone Hole Altitude Profile
- August 7, 1997
- September 9, 1997
- October 10, 1997

Source: NASA

Ozone Partial Pressure (mPa)

Million Square Kilometers

0 5 10 15 20 25

July Aug Sep Oct Nov Dec
Stratospheric ozone – CFCs

Ozone depleting substances:

CFC: ChloroFluoroCarbons ("hard CFC")
HCFC: HydroChloroFluoroCarbons ("soft CFC")
Halons, methyl bromide, certain solvents

Volatile compounds containing chlorine and bromine.

Extremely stable in the troposphere ➔ They can be transported up to the stratosphere.

Use of these substances:

• Cooling medium
• Blower for plastics
• Dry cleaning fluid
• Cleaning detergent
• Solvents
• Propellant gas in spray cans
Catalytic ozone loss – CFC

CFCs and HCFC are not found in nature. Industrial-scale production started in the 1930-ies. CFC has a lifetime in the atmosphere of 50-300 years.

Cl-levels in the atmosphere:
- 1980 level: 2 ppb (reached again 2050?)
- Natural level: ~0.7 ppb (reached earliest 2100)

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**N₂O**

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**CFC11**
Catalytic ozone loss - $\text{ClO}_x$

CFCs are photolysed by UV radiation in the stratosphere.

$$\text{CF}_2\text{Cl}_2 + h\nu \rightarrow \text{CF}_2\text{Cl} + \text{Cl} \quad \text{(initiation)}$$

$\text{ClO}_x$ family: $\text{Cl}$ and $\text{ClO}$ (radicals)

(*) $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$

(**) $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$

Net reaction:

$$\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$$

Reaction (*) and (**) destroys $\text{O}_x$ (=ozone) without consuming $\text{ClO}_x$ radicals (=catalysts).

http://www.ucar.edu/learn/images/o3split.gif
Catalytic ozone loss - $\text{ClO}_x$

The catalytic cycle is broken when $\text{ClO}_x$ radicals are consumed.

\[
\begin{align*}
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3 \\
\text{ClO} + \text{NO}_2 + M & \rightarrow \text{ClNO}_3 + M \quad \text{(termination)}
\end{align*}
\]

Both $\text{HCl}$ ($\tau=$weeks) and $\text{ClNO}_3$ ($\tau\approx1$ day) are non-radicals.

Together, $\text{HCl}$ and $\text{ClNO}_3$ form a $\text{ClO}_x$ reservoir.

$\text{Cl}_y$ family: $\text{ClO}_x$+ its $\text{ClO}_x$ reservoirs

$\text{Cl}$ and $\text{ClO}$ (radicals), $\text{HCl}$ and $\text{ClNO}_3$ (non-radicals)

The reservoirs return to $\text{ClO}_x$

\[
\begin{align*}
\text{HCl} + \text{OH} & \rightarrow \text{Cl} + \text{H}_2\text{O} \\
\text{ClNO}_3 + h\nu & \rightarrow \text{Cl} + \text{NO}_3 \quad \text{(photolysis)}
\end{align*}
\]
Catalytic ozone loss – ClO$_x$

1980-ies: The evidence that CFCs can seriously damage the stratospheric ozone layer led to the signing of the Montreal protocol in 1987. CFC production stopped in 1996.

Mario Molina, Sherwood Rowland shared the Nobel prize in Chemistry in 1995
Catalytic ozone loss
The catalytic cycle with $CIO_x$ radicals was rewarded the Nobel prize but could not explain the ozone hole!!
Stratosfäriskt ozon

CFC

\( \text{ClO}_x^- \) cykel

\( \text{ClO}_x^- \) reservoar

Antarktiskt vortex

PSC

\( \text{HNO}_3 \)

Kloriner

\( h_v \) (svag)

\( \text{ClO-ClO-} \) cykel

\( O_3^- \) förlust

\( h_v \) (starkare)

\( O_3^- \) produktion

\( O_3 \)

sedimentering

höst

vinter

vår

sommar

Källor: Jacob, D. J., 1999. Introduction to Atmospheric Chemistry.

Lund University / Department of Physics / Division of Nuclear Physics / Adam Kristensson
**Antarctic polar vortex**

The vortex forms in winter conditions. The air over the antarctic is "trapped" in the vortex, little exchange with rest of the atmosphere $\Rightarrow$ no transport of new ozone from the mid-latitude or tropics via the B-D circulation.
Stratospheric ozone

Polar stratospheric clouds (PSC) are formed at temperatures lower than \( \sim 197 \) K, which is more frequent at the South Pole than at the North Pole.

![Graph showing temperature distribution for South and North Pole]
Polar stratospheric clouds
(pärlemormoln)
Not to be confused with:
Aurora borealis (norrsken)
Catalytic ozone loss - ClO

Early spring in Antarctica is relatively dark (low photochemistry) and levels of $O$ are low.

\[
\begin{align*}
\text{NO}_2 + O & \rightarrow NO + O_2 \\
\text{ClO} + O & \rightarrow Cl + O_2 \\
\end{align*}
\]

\(\text{(*)}\)

...are not efficient!

Since there is for example no photolysis of $\text{NO}_2$

\[
\left(\text{NO}_2 + h\nu \rightarrow NO + O\right)
\]

Yet another cycle involving ClO is needed (CLO-CLO cycle):

\[
\begin{align*}
\text{ClO} + \text{ClO} + M & \rightarrow \text{ClOOCl} + M \quad (\text{ClO dimer}) \\
\text{ClOOCl} + h\nu & \rightarrow + \text{ClOO} + Cl \quad \text{(split in "wrong" place)} \\
\text{ClOO} + M & \rightarrow Cl + O_2 + M \\
Cl + O_3 & \rightarrow \text{ClO} + O_2 \ (2x)
\end{align*}
\]

Net reaction:

\[
2O_3 \rightarrow 3O_2
\]

Loss rate proportional to $[\text{ClO}]^2$, as opposed to the ClO\(_x\) mechanism (\(\ast\)), which depends on abundance of O atoms ($=2k_{22}[\text{ClO}][O]$).
Catalytic ozone loss - ClO

Why are levels of ClO-radicals so high during Antarctic spring?

Heterogeneous chemical processes (multiple phases involved) constitute an efficient sink for the ClO\textsubscript{x} reservoir. Polar stratospheric clouds (PSC) provide a surface.

\begin{align*}
\text{PSC} \\
(*) & \quad \text{ClNO}_3 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \\
& \quad \text{Cl}_2 + h\nu \rightarrow 2\text{Cl} \\
& \quad \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2
\end{align*}

Reaction (*) is so fast that either all ClNO\textsubscript{3} or HCl is titrated out.

The ratio ClO\textsubscript{x}/Cl\textsubscript{y} is normally ~0.1, but can reach 1 during early spring.
Catalytic ozone loss - ClO

But isn’t it possible that HNO$_3$ is photolyzed again and continue to supress ozone destruction?

(*)  \[ \text{HNO}_3 + \text{hv} \rightarrow \text{NO}_2 + \text{OH} \]

(**)  \[ \text{ClO} + \text{NO}_2 + M \rightarrow \text{ClNO}_3 + M \]

where ClO is consumed.

The answer is no! HNO$_3$-containing PSC have been sedimented to the troposphere.
Stratosfäriskt ozon

Källor: Jacob, D. J., 1999. Introduction to Atmospheric Chemistry.
Without emission reductions, stratospheric chlorine levels would have grown catastrophically.

- Free growth of CFCs
- Montreal Protocol (freezes production of 85% emissions)
- London Amendments (CFC phaseout begins in 1995)
- Copenhagen (Complete phaseout by 96)
  - CI recovers to 1975 levels in 2041
Stratospheric ozone - Recovery

Recovery Stages of Global Ozone

Stage 1: Initial slowing of ozone decline
Stage 2: Onset of ozone increases
Stage 3: Full recovery of ozone from ozone-depleting gases

Expected return of ozone-depleting gases to 1980 levels
Range of model projections

Global ozone change from pre-1980 values

Time increases
Ozone trend at Halley bay, Antarctica

Mean October ozone at Halley

Total ozone (Dobson units)

Year

Faraday total ozone

Dobson Units

British Antarctic Survey, 2005
Figure 3. Anomalous springtime ozone that is independent of dynamically-induced changes (solid). The positive trend after 1996 is significant at the 99.5% level. EEASC, corresponding to a mean age of air of 5 yr and a bromine scale factor of 60 (dotted).