Atmospheric Chemistry:
The Many Roles of Ozone in the Stratosphere and Troposphere

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MacMillan Group Meeting
4 March 2020
What is the atmosphere?

“...the gas and aerosol envelope that extends from the ocean, land and ice-covered surface of a planet outward into space”

Earth’s atmosphere: 78.08% $N_2$, 20.95% $O_2$, 0.93% $Ar$, 0.04% $CO_2$ + other minor components
The broad field of atmospheric chemistry

The broad field of atmospheric chemistry

homogeneous

heterogeneous

photochemical

The atmosphere of the Earth

- Troposphere
- Stratosphere
- Mesosphere
- Thermosphere
- Exosphere

- Troposphere:
  - Upper atmosphere: 10,000 km (6,200 miles)
  - Middle atmosphere: 604 km (375 miles)
  - Lower atmosphere: 85 km (53 miles)
- Stratosphere:
  - Upper atmosphere: 10 miles (10,000 km)
  - Middle atmosphere: 50 km (31 miles)
  - Lower atmosphere: 16 km (10 miles)
- Mesosphere:
  - Upper atmosphere: 53 miles (50 km)
- Thermosphere:
  - Upper atmosphere: 375 miles (310 km)
- Exosphere:
  - Upper atmosphere: 6,200 miles (10,000 km)

The atmosphere of the Earth with a more realistic scale

Exosphere

Thermosphere

Mesosphere

Stratosphere

Troposphere

99% of atmospheric mass is contained in the Stratosphere and Troposphere (50 km).

If the Earth were a basketball, this would be a 1 mm layer.
contains **nearly all water (99%)** and **majority of mass (75%)** in atmosphere

- location of weather and climate (including greenhouse effect and pollution)
- cools at a rate of 6.5 °C km\(^{-1}\) (reaches minimum of –51 °C)
- highly turbulent, well-mixed due to surface heating by Sun (convection)
The stratosphere - middle atmosphere

contains remaining mass (25%) and a 10 km wide ozone layer

- temperature increases with altitude (−3 °C at the stratopause)
- inverse temperature gradient prevents convection/mixing
- studied via weather balloons (air too thin for planes)
The mesosphere - middle atmosphere

referred to as the “ignorosphere” because difficult to study

- too high for planes and balloons, too low for satellites
- probed with sounding rockets (5-20 minute missions)
- temperature decreases to atmospheric minimum (−143 °C)
The thermosphere - upper atmosphere

contains 0.002% of mass and is the realm of satellites

- photoionization of N\textsubscript{2} and O\textsubscript{2} blocks UVC and x-rays from Sun
- temperature difficult to define (227–1725 °C depending on sun activity)
- anacoustic zone (no sound) starts at 160 km
- electrically charged, refracts radio waves over horizon

The exosphere - upper atmosphere

- maintains **constant temperature** and composed mainly of **H, He, and O**
- atoms rarely collide, follow ballistic trajectories
- atoms can escape the atmosphere
- extends as far as Earth’s gravitational pull
The ionosphere

region of atmosphere that contains charged species

ionization of gas molecules by Sun’s radiation

important filter of high energy light

*This portion of the atmosphere goes to sleep at night!*
Ozone: good up high but bad nearby

\[ \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \]

\[ \text{valuable shield against UV light} \]

\[ \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \quad \text{O}_3 \]

\[ \text{smog component and greenhouse gas} \]
The stratospheric ozone layer

Stratosphere

- Sits in a band 25 to 35 km above the Earth’s surface
- Existed for approximately 700 million years

What are the mechanisms regulating the ozone layer?

The Chapman mechanism for creation and destruction of ozone

The Chapman mechanism (1930) was the first atmospheric cycle discovered.

**ozone creation**

\[ \text{O}_2 \xrightarrow{h\nu} \text{O} + \text{O} \quad h\nu \leq 242 \text{ nm} \]

\[ \text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{What is M?} \]

**ozone destruction**

\[ \text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O} \quad h\nu \leq 336 \text{ nm} \]

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

Chapman, S. *Phil. Mag.* 1930, 10, 369.
Three-body reactions in the gas phase

where \( M = \text{inert molecule (N}_2\text{ in atmosphere, Ar in laboratory/computations)} \)

\( M^* \text{ dissipates excess energy as heat} \)

- Impact of third body on gas phase reaction rate

\[ \cdot \text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O}_2^* \]
\[ \text{CH}_3\text{O}_2^* + M \rightarrow \text{CH}_3\text{O}_2 + M^* \]

\( M = \text{neopentane} \)
\[ k_{\text{overall}} = 3.6 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1} \]

\( M = \text{N}_2 \)
\[ k_{\text{overall}} = 0.94 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1} \]
The “ozone isotopic anomaly”

Two surprising observations (over a contentious, high impact 18 years):

- 10% heavy ozone observed in the troposphere/stratosphere
- Equal $^{17}$O and $^{18}$O incorporation: mass-independent fractionation

Why are heavy O isotopes overrepresented in atmospheric ozone molecules?


Thiemens Science 1999, 283, 341.
The “ozone isotopic anomaly”

Collisional cooling is key isotopic selectivity step:

\[
\text{O}_3^* + \text{M} \xrightarrow{k_{\text{cool}}} \text{O}_3 + \text{M}^*
\]

Breaking \(C_{2v}\) symmetry doubles allowed rovibrational states and increases probability of successful collisional cooling with \(\text{M}\)

Natural Abundance

\[
\begin{array}{ccc}
\text{Isotope} & \text{Abundance} \\
\text{16O} & 99.76\% \\
\text{17O} & 0.038\% \\
\text{18O} & 0.205\%
\end{array}
\]


Benefits of stratospheric ozone

Chapman cycle components (O$_2$ and O$_3$) absorb UV light

- Allows for life outside of oceans
- Prevents photoinduced DNA damage

<table>
<thead>
<tr>
<th>UV Band</th>
<th>Wavelength range</th>
<th>Absorption by O$_3$ layer</th>
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Benefits of stratospheric ozone

Chapman cycle components (O\textsubscript{2} and O\textsubscript{3}) absorb UV light

- Allows for life outside of oceans
- Prevents photoinduced DNA damage

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How did Earth develop an atmosphere with such a useful UV light filter?

The evolution of Earth’s atmosphere

4.5 billion years ago

high albedo (reflectance) and low surface temperatures

high energy radiation

hostile to life on land

principal components

\[\text{CO}_2, \text{N}_2\]

minor components

\[\text{NH}_3, \text{CH}_4\]

intense greenhouse effect led to evaporation

The evolution of Earth’s atmosphere

4.5 billion years ago

CaCO$_3$ + SiO$_2$ → CaSiO$_3$ via Urey reaction

CaCO$_3$ → H$_2$O, NH$_3$

principal components

CO$_2$, N$_2$

minor components

NH$_3$, CH$_4$

The evolution of Earth’s atmosphere

Irradiation of clouds led to the homolysis of water and the formation of O₂

\[ 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 2 \text{H}_2 \]

Principal components:
- \( \text{N}_2 \)
- \( \text{CH}_4 \)

Minor components:
- \( \text{NH}_3 \)

2 billion years ago

\( \text{CaCO}_3 + \text{SiO}_2 \)

\( \text{H}_2\text{O} \)

\( \text{NH}_3 \)

The evolution of Earth’s atmosphere

2 billion years ago

Principal components:
- N₂ (96%)

Minor components:
- O₂
- CH₄
- NH₃

CH₄ and NH₃ have been oxidized and greenhouse effect lessens.

CaCO₃ + SiO₂

H₂O

H₂O → O₂ + 2 H₂
The evolution of Earth’s atmosphere

Chapman cycle produces sufficient O$_3$ to protect life on land

420 million years ago

principal components

N$_2$ (96%)

minor components

O$_2$

H$_2$O

CaCO$_3$ + SiO$_2$
Why is the ozone layer in the stratosphere?

Mesosphere

insufficient gas density for three body reactions

Stratosphere

correct balance of light penetration and gas density

Troposphere

minimal light penetration at required $\lambda$

The Chapman mechanism overestimates ozone concentrations.

There must be additional mechanisms of ozone destruction.
**Mechanism of stratospheric ozone depletion**

Chapman cycle balances ozone *creation* with ozone *destruction*

\[ \text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O} \quad h\nu \leq 336 \text{ nm} \]

What if this step were catalyzed?

**General mechanism of catalytic ozone destruction**

\[ \text{O}_3 + \text{Z} \rightarrow \text{ZO} + \text{O}_2 \]

\[ \text{ZO} + \text{O} \rightarrow \text{Z} + \text{O}_2 \]

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

catalysts (Z)

\[ \text{HO}_x \]

\[ \text{NO}_x \]

\[ \text{ClO}_x \]

---


**The HO$_x$ cycle**

In the HO$_x$ cycle, the OH radical serves as a catalyst

\[
\begin{align*}
O_3 + \text{OH} & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \\
O_3 + \text{O} & \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

*Major source of OH in the stratosphere is reaction of atomic oxygen and water vapor*

\[
\begin{align*}
\text{O} + \text{H}_2\text{O} & \rightarrow \text{OH} + \text{OH}
\end{align*}
\]

*with minor contributions from hydrogen and methane*

\[
\begin{align*}
\text{O} + \text{H}_2 & \rightarrow \text{OH} + \text{H} \\
\text{O} + \text{CH}_4 & \rightarrow \text{OH} + \text{CH}_3
\end{align*}
\]

The $\text{NO}_x$ cycle

In the $\text{NO}_x$ cycle, the NO radical serves as a catalyst.

\[
\begin{align*}
\text{O}_3 & + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 & + \text{O} \rightarrow \text{NO} + \text{O}_2 \\
\text{O}_3 & + \text{O} \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

Sources of NO:

- In upper atmosphere:
  \[\text{O}_2 + \text{N}_2 + h\nu \ (< 220 \text{ nm}) \rightarrow \text{NO} + \text{NO}\]

- In stratosphere:
  \[\text{NO}_2 \text{ (fertilizers)} + h\nu \ (< 398 \text{ nm}) \rightarrow \text{NO} + \text{O}\]

The HO$_x$ and NO$_x$ cycles are dependent

interplay of HO$_x$ and NO$_x$ cycles

\[
\text{HO}_2 + \text{NO} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \\
\text{reservoir}
\]

**mechanism of reactivation:**

\[
\text{HNO}_3 + h\nu (< 546 \text{ nm}) \rightarrow \text{OH} + \text{NO}_2
\]

\[
\text{NO}_2 + h\nu (< 398 \text{ nm}) \rightarrow \text{NO} + \text{O}
\]

anthropogenic HNO$_3$ also adds to the concentration of HO$_x$ and NO$_x$ catalysts

The ClO\textsubscript{x} cycle

In the ClO\textsubscript{x} cycle, the Cl radical is the catalyst

\[
\begin{align*}
O_3 + Cl & \rightarrow ClO + O_2 \\
ClO + O & \rightarrow Cl + O_2
\end{align*}
\]

10x faster than NO\textsubscript{x} cycle

1 Cl atom can destroy 100,000 O\textsubscript{3}

Generation of odd Cl from Cl\textsubscript{2} and HCl

\[
\begin{align*}
Cl_2 \text{ + h\nu} & \rightarrow Cl + Cl \\
HCl \text{ + OH} & \rightarrow Cl + H_2O
\end{align*}
\]


Chlorofluorocarbons (CFCs). Earth System Research Laboratory. NOAA. http://www.esrl.noaa.gov/gmd/hats/publictn/elkins/cfcs.html
Sources of Cl

natural sources of atmospheric Cl

oceans

2 x 10^8 tons/yr

volcanoes

9 x 10^6 tons/yr

anthropogenic sources

industry (pre-Montreal Protocol)

~1 x 10^7 tons/yr

Atmospheric cycles involve many elementary steps

The comprehensive HO\textsubscript{x}, NO\textsubscript{x}, and ClO\textsubscript{x} cycles involve many more elementary steps and reservoir species.

The kinetic relevance of each step depends on the altitude, latitude, season, etc.

Also worth noting, these cycles go to sleep at night!

---

Chapman Chemistry

\[
\begin{align*}
O_2 + h\nu & \rightarrow 2O \\
O + O_2 + M & \rightarrow O_3 + M \\
O_3 + h\nu & \rightarrow O_3 + O(1D) \\
O(1D) + M & \rightarrow O + M \\
O_3 + h\nu & \rightarrow O_2 + O \\
O + O + M & \rightarrow O_2 + M \\
O + O_3 & \rightarrow 2O_2 \\
O + OH & \rightarrow O_2 + H \\
H + O_2 + M & \rightarrow HO_2 + M \\
O + HO_2 & \rightarrow O_2 + OH \\
\text{Net Cycle 1: } O + O + M & \rightarrow O_2 + M \\
OH + O_3 & \rightarrow HO_2 + O_2 \\
HO_2 + O_3 & \rightarrow OH + 2O_2 \\
\text{Net Cycle 2: } 2O_3 & \rightarrow 3O_2 \\
NO + O_3 & \rightarrow NO_2 + O_2 \\
O + NO_2 & \rightarrow NO + O_2 \\
\text{Net Cycle 3: } O + O_3 & \rightarrow O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + O & \rightarrow Cl + O_2 \\
\text{Net Cycle 4: } O + O_3 & \rightarrow O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + ClO & \rightarrow Cl_2 + O_2 + M \\
ClO + ClO + M & \rightarrow ClO_2 + M \\
ClO_2 + ClO & \rightarrow Cl_2 + O_2 + M \\
\text{Net Cycle 5: } 2O_3 & \rightarrow 3O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
Br + O_3 & \rightarrow BrO + O_2 \\
BrO + ClO & \rightarrow Br + ClO_2 \\
ClO_2 + M & \rightarrow Cl + O_2 + M \\
\text{Net Cycle 6: } 2O_3 & \rightarrow 3O_2 \\
ClO + NO & \rightarrow Cl + NO_2 \\
Cl + CH_4 & \rightarrow HCl + CH_3 \\
HO_2 + ClO & \rightarrow HClO + O_2 \\
CIO + NO_2 + M & \rightarrow ClONO_3 + M \\
OH + NO_2 + M & \rightarrow HNO_3 + M \\
\text{Some Important Coupling and Reservoir Reactions} \\
HCl + ClONO_2 & \rightarrow HNO_3 + Cl_2 \\
N_2O_5 + H_2O & \rightarrow 2HNO_3 \\
ClO(NO_2) + H_2O & \rightarrow HNO_3 + HOCIC \\
HCl + HOCIC & \rightarrow H_2O + Cl_2 \\
BrO_2 + H_2O & \rightarrow HNO_3 + HOBre \\
HCl + BrONO_2 & \rightarrow HNO_3 + BrCl \\
HCl + HOBre & \rightarrow H_2O + BrCl \\
\text{Key Heterogeneous Reactions} \\
\end{align*}
\]
Atmospheric cycles involve many elementary steps

Chapman Chemistry

\[
\begin{align*}
O_2 + h\nu & \rightarrow 2O \\
O + O_2 + M & \rightarrow O_3 + M \\
O_3 + h\nu & \rightarrow O_2 + O_3(D) \\
O_3(D) + M & \rightarrow O + M \\
O_3 + h\nu & \rightarrow O_2 + O \\
O + O_3 & \rightarrow O_2 + M \\
O + O_3 & \rightarrow 2O_2 \\
O + OH & \rightarrow O_2 + H \\
H + O_3 + M & \rightarrow HO_3 + M \\
O + HO_2 & \rightarrow O_2 + OH \\
\text{Net Cycle 1:} & \ O + O + M \rightarrow O_2 + M \\
OH + O_3 & \rightarrow HO_2 + O_2 \\
HO_2 + O_3 & \rightarrow OH + 2O_2 \\
\text{Net Cycle 2:} & \ 2O_3 \rightarrow 3O_2 \\
NO + O_3 & \rightarrow NO_2 + O_2 \\
O + NO_2 & \rightarrow NO + O_2 \\
\text{Net Cycle 3:} & \ O + O_3 \rightarrow O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + O & \rightarrow Cl + O_2 \\
\text{Net Cycle 4:} & \ O + O_3 \rightarrow O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
ClO + ClO + M & \rightarrow Cl_2O_2 + M \\
ClO_2 + h\nu & \rightarrow Cl + ClO_2 \\
ClO_2 + M & \rightarrow Cl + O_2 + M \\
\text{Net Cycle 5:} & \ 2O_3 \rightarrow 3O_2 \\
Cl + O_3 & \rightarrow ClO + O_2 \\
Br + O_3 & \rightarrow BrO + O_2 \\
BrO + ClO & \rightarrow Br + ClO_2 \\
ClO_2 + M & \rightarrow Cl + O_2 + M \\
\text{Net Cycle 6:} & \ 2O_3 \rightarrow 3O_2 \\
ClO + NO & \rightarrow Cl + NO_2 \\
Cl + CH_4 & \rightarrow HCl + CH_3 \\
HO_2 + ClO & \rightarrow HOCl + O_2 \\
ClO + NO_2 + M & \rightarrow ClONO_2 + M \\
OH + NO_2 + M & \rightarrow HNO_3 + M \\
\text{Some Important Coupling and Reservoir Reactions} \\
HCl + ClONO_2 & \rightarrow HNO_3 + Cl_2 \\
N_2O_4 + H_2O & \rightarrow 2HNO_3 \\
ClO(NO_2) + H_2O & \rightarrow HNO_3 + HOC1 \\
HCl + HOCI & \rightarrow H_2O + Cl_2 \\
BrONO_2 + H_2O & \rightarrow HNO_3 + HOB r \\
HCl + BrONO_2 & \rightarrow HNO_3 + BrCl \\
HCl + HOBr & \rightarrow H_2O + BrCl \\
\text{Key Heterogeneous Reactions} \\
\end{align*}
\]

Illustrative Odd Hydrogen Catalytic Cycles

Illustrative Odd Nitrogen Catalytic Cycles

Illustrative Odd Chlorine Catalytic Cycles

Illustrative Cl-Br Catalytic Cycle

The comprehensive HOx NOx and ClOx cycles involve many more elementary steps and reservoir species.

The kinetic relevance of each step depends on the altitude, latitude, season, etc.

Also worth noting, these cycles go to sleep at night!
Br is an even more potent $O_3$ depletor

A concentration of $1 \times 10^{-11}$ (v/v) Br was tied to a 0.3% loss of $O_3$ in the stratosphere

~20% of atmospheric Br could be traced to human activity in 1975

10% leaded gasoline
10% MeBr (agricultural fumigant)
80% marine salts

total input $1.1 \times 10^6$ tons/yr

Bromine emissions are brought under control

- From 1970 to 1995 leaded gasoline usage plummets

- MeBr is phased out as a fumigant in the Montreal Protocol (discussed later in detail)
The chlorofluorocarbons (CFCs)

Small organic molecules consisting of chlorine, fluorine, and carbon

characterized by low toxicity and non-flammability

Developed by Thomas Midgley, Jr. and Albert Henne (General Motors) in 1928

- General Motors-Frigidaire-DuPont collaboration
- safer refrigerant (vs. ammonia, methyl chloride, sulfur dioxide)

main uses of CFCs are as refrigerants and propellants (spray foam insulation and rescue inhalers)

Chlorofluorocarbons (CFCs). Earth System Research Laboratory. NOAA. http://www.esrl.noaa.gov/gmd/hats/publictn/elkins/cfcs.html
CFC Nomenclature

“CFC” is a systematic acronym, “Freon” is a proprietary name

CFC-12
“Freon-12”

- back-calculate composition from number

Step 1: add 90

Step 2: examine three-digit number

12 + 90 = 102

1  C
0  H
2  F
2  Cl (satisfy octet rule)

CFC-12 Example

Chlorofluorocarbons (CFCs). Earth System Research Laboratory. NOAA. http://www.esrl.noaa.gov/gmd/hats/publictn/elkins/cfcs.html
CFCs and the destruction of ozone

CFCs are unreactive in the troposphere and survive into the stratosphere

CFCs and the destruction of ozone

CFCs are unreactive in the troposphere and survive into the stratosphere.

CFCs and the destruction of ozone

CFCs are unreactive in the troposphere and survive into the stratosphere.

CFC-11 (CFCl₃) undergoes photodissociation at wavelengths of 175–220 nm.

CFC-12 (CF₂Cl₂) also undergoes photodissociation at wavelengths of 175–220 nm.

CFCs and the destruction of ozone

CFCs are unreactive in the troposphere and survive into the stratosphere

\[
\text{CFCl}_3 \quad \text{h} \nu = 175-220 \text{ nm} \quad \rightarrow \quad \text{CFCl}_2 + \text{Cl}
\]

\[
\text{CF}_2\text{Cl}_2 \quad \text{h} \nu = 175-220 \text{ nm} \quad \rightarrow \quad \text{CF}_2\text{Cl} + \text{Cl}
\]

CFCs and the destruction of ozone

CFCs are unreactive in the troposphere and survive into the stratosphere.

\[
\begin{align*}
\text{CFCl}_3 & \xrightarrow{h\nu = 175–220\,\text{nm}} \text{CFCl}_2 + \text{Cl} \\
\text{CFCl}_2 & \xrightarrow{h\nu = 175–220\,\text{nm}} \text{CF}_2\text{Cl} + \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{O}_3 + \text{Cl} & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \\
\text{O}_3 + \text{O} & \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

Stratospheric sink for chlorofluoromethanes: chlorine atomic-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

Photolytic dissociation to \( \text{CFC}_3 + \text{Cl} \) and to \( \text{CF}_2\text{Cl} + \text{Cl} \), respectively, at altitudes of 20–40 km. Each of the reactions creates two odd-electron species—one Cl atom and one free radical.

The dissociated chlorofluoromethanes can be traced to their ultimate sinks. An extensive catalytic chain reaction leading to the net destruction of \( \text{O}_3 \) and \( \text{O} \) occurs in the stratosphere:

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (1)
\]

\[
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \quad (2)
\]

This has important chemical consequences. Under most conditions in the Earth’s atmospheric ozone layer, (2) is the slower of the reactions because there is a much lower concen-
CFCs are a global problem

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- Troposphere is turbulent and well-mixed
- Exchange with stratosphere is slow
  (10% of the troposphere mixes every 5 years)

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- troposphere is turbulent and well-mixed
- exchange with stratosphere is slow
  (10% of the troposphere mixes every 5 years)
- uniform distribution of CFCs in stratosphere, regardless of source

CFCs are a global problem

- troposphere is turbulent and well-mixed
- exchange with stratosphere is slow
  (10% of the troposphere mixes every 5 years)
- long stratospheric lifetimes
  50-100’s of years
  rained out as HCl in troposphere

Two kinds of ozone depletion

I. Continual loss of ozone throughout the atmosphere and around the globe

II. Formation every winter/spring of an “ozone hole” over Antarctica
Questions about the Antarctic ozone hole

1. Why over Antarctica?

extended cold periods (–78 °C) and isolated stratosphere (polar vortex)

2. How big is it?

typically 8 million mi² (16.4 million km²)
Questions about the Antarctic ozone hole

1. Why over Antarctica?

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3. Why is a cold environment accelerating a chemical reaction?

   polar stratospheric clouds (PSCs) act as catalysts
Questions about the Antarctic ozone hole

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2. How big is it?

   typically 8 million mi² (16.4 million km²)

3. Why is a cold environment accelerating a chemical reaction?

   polar stratospheric clouds (PSCs) act as catalysts

4. Why not the Arctic?

   higher temperatures, only form PSCs for 10-60 days (5 months in Antarctica)
First reported in 1985, data from Halley Bay (Antarctica) revealed a seasonal pattern of ozone depletion. Decline in both [CFC] and [O₃] suggests transformation of CFCs into O₃-destroying species. Massive drop in spring O₃ levels.
The growth of the Antarctic ozone hole

The ozone hole increased in severity until reaching a minimum in 1994.
A change in the seasonal cycle of ozone depletion

Antarctic ozone levels decrease overall and decrease sharply into a lower spring minimum.

Cold season persists longer because stratospheric warmth provided by O$_3$ UV absorption.

Measuring ozone concentrations

Ozone is measured as a “total” or “column” amount between instrument and Sun

Common Undergraduate Experiment

1. measure absorbance at multiple characteristic λ.

2. apply modified Beer-Lambert Law (no $I_o$).

$$\frac{I}{I_o} = e^{-\varepsilon \ell \text{[ozone]}}$$

3. account for scattering by air (Mie) and aerosols (Rayleigh)

Dobson units (DU)

The thickness of the layer of pure ozone that would over the Earth (in units of 10 μm) at STP

Example: 300 DU would correspond to a 3 mm layer of ozone on the Earth surface.
Polar Stratospheric clouds (PSCs) have long been a feature of the Antarctic sky.

The light was especially good today; the sun was directly reflected by a single twisted iridescent cloud in the North, a brilliant and most beautiful object.

Robert Falcon Scott, diary entry for August 1, 1911
[Scott, 1996, p. 264]

---

**Type 1 PSCs**

clouds of nitric acid and water crystallizing below -78 °C
key component is nitric acid trihydrate (NAT)
catalytically active in ozone depletion

---

**Type 2 PSCs**

brightly-colored clouds composed mainly of water

---

Ozone-destroying clouds?

1. PSCs catalyze activation of Cl from inert precursors
2. PSCs sequester NO₂ (key Cl-deactivating species)


Ozone-destroying clouds?

Ozone depletion is fastest in antarctic spring (Sep-Dec):

- **cold enough** to generate PSCs
- **sufficient sunlight** to initiate photochemical reactions

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“The Parties to this protocol [are]…determined to protect the ozone layer by…control[ling] equitably total global emissions of substances that deplete it, with the ultimate objective of their elimination on the basis of developments in scientific knowledge…”

- deadlines for stop in production and consumption of ODS
- established scientific committees to evaluate progress and modify protocol
- delegated funds to assist developing countries in meeting standards

The only United Nations environmental agreement ratified by every country in the world (as of 2009)
# Ozone depleting substances and timelines for phaseout

<table>
<thead>
<tr>
<th>Article A, Group I: <strong>CFCs</strong></th>
<th>Article A Group II: <strong>Halon</strong></th>
<th>Article C Group I/II: <strong>HCFCs/HBFCs</strong></th>
</tr>
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<tbody>
<tr>
<td><img src="image" alt="CFC-11" /></td>
<td><img src="image" alt="Halon-1301" /></td>
<td><img src="image" alt="HCFC-22" /></td>
</tr>
<tr>
<td><img src="image" alt="CFC-12" /></td>
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<td>1.0</td>
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</tr>
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<td>developing countries 2010</td>
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<td>developing countries 2030</td>
</tr>
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</table>
The Ozone Secretariat

- founded in 1991 in Nairobi, Kenya
- collects reporting data from government agencies
- supervises the Assessment Panels

An administrative body within the United Nations Environment Programme (UNEP) that implements the Montreal Protocol

Scientific Assessment Panel (SAP)

assesses status of ozone layer depletion and current atmospheric science

Technology and Economic Assistance Panel (TEAP)

investigates new alternative technologies

Environmental Effects Assessment Panel (EEAP)

assesses effects of ozone depletion and remediation efforts
Amendments to the Montreal Protocol

**London (1990)** accelerated CFCs/halons/CCl₄ phaseout (2000), extended to CCl₃CH₃

**Copenhagen (1992)** accelerated CFCs/halons/CCl₄ phaseout (1996), extended to hydrochlorofluorocarbons (HCFC)

**Montreal (1997)** established phaseout of MeBr to 2005 (developed)/ 2015 (developing countries)

**Beijing (1999)** restricted trade/production of HCFCs, extended to BrClCH₂ (2004)

**Kigali (2016)** extended to hydrofluorocarbons (HFC, weak ODS, strong greenhouse gas)
Amendments to the Montreal Protocol

International Treaties and Cooperation about the Protection of the Stratospheric Ozone Layer

http://EPA.gov


Annual meeting of the parties (MOP)

London (1990) accelerated CFCs/halons/CCl₄ phaseout (2000), extended to CCl₃CH₃

Copenhagen (1992) accelerated CFCs/halons/CCl₄ phaseout (1996), extended to hydrochlorofluorocarbons (HCFC)

Annual meetings involve documenting compliance, reevaluating the state of the ozone layer, and proposing amendments

Beijing (1999) restricted trade/production of HCFC

Kigali (2016) extended to hydrofluorocarbons (HFC, weak ODS, strong greenhouse gas)
Has the Montreal Protocol proven effective?

The ozone layer is recovering!

Full recovery expected by 2050

(Antarctic ozone hole expected to recover by 2060)

**Concentrations of Ozone-Depleting Substances. Exhibits 1 and 2. United States EPA.**

ODS levels in the atmosphere have **decreased or leveled off** in accordance with Montreal Protocol.

Compliance through the mid-2010’s appears promising.

Total amount of global atmospheric chlorine is **decreasing steadily**.

Source: Concentrations of Ozone-Depleting Substances. Exhibits 1 and 2. United States EPA. [https://cfpub.epa.gov/roe/indicator.cfm?i=11#1](https://cfpub.epa.gov/roe/indicator.cfm?i=11#1)
An unexpected rise in CFC-11 emissions

- CFC-11 levels start to plateau.

- Promising CFC-11 reduction trends are threatening to reverse.
- Production reported as nearly zero since 2006, but emissions consistent with new production.
- Measurements confirmed in both hemispheres (not an artifact of measurement devices).

Fig. 1 | Observations of atmospheric CFC-11 over time.

A call to action

40th Open-Ended Working Group of the Montreal Protocol (OEWP) reviewed scientific data and provided recommendation to 30th Annual Meeting of the Parties (MOP) to call for thorough investigation of new CFC-11 production sources.

Multinational research collaboration locates CFC-11 emission source

Chinese provinces of Shandong and Hebei identified as two sites of emission

- at least 40-60% of observed increase in CFC-11 emissions
- emissions are observed at site of use (e.g., spray foam insulation) *not production*

The world responded quickly to the ozone crisis

Crutzen and others describe mechanisms of ClO_x cycle

1974
Molina and Rowland propose CFCs as source of Cl

1985
Vienna Convention signed

1985
Shanklin reports formation of the Antarctic ozone hole

1987
Montreal Protocol signed

1995
Nobel Prize awarded
The 1995 Nobel Prize in Chemistry

Paul J. Crutzen  
Mario J. Molina  
F. Sherwood Rowland

The Nobel Prize in Chemistry 1995 was awarded jointly to Paul J. Crutzen, Mario J. Molina and F. Sherwood Rowland

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone."
Ozone: good up high but bad nearby

\[ \begin{align*}
\text{O}_3 & \quad \text{valuable shield against UV light} \\
\text{smog component and greenhouse gas} & \quad \text{Tropopause} \\
\text{Stratosphere} & \quad \text{stratopause} \quad \text{50 km} \\
\text{Troposphere} & \quad \text{tropopause} \quad \text{16 km}
\end{align*} \]
The cross-state effects of tropospheric ozone pollution

Ozone and fine particulate matter are deadliest components responsible for 90% of total air pollution-related mortality.

Lack of symmetry about the diagonal indicates that some states are "exporters of early death" and some are "importers of early death".

The cross-state effects of tropospheric ozone pollution

Biggest exporters: Wyoming, North Dakota, West Virginia

Biggest importers: New York and Massachusetts

fine particulate matter 8x more deadly, ozone travels farther

40% of combustion-emission-related early deaths cross state lines

Tropospheric ozone decreases crop yields

- Reactive oxygen species (ROS) trigger antioxidant defense system

- Resultant decrease in CO$_2$ consumption lowers biomass production

Calculated economic loss of $6.3-12.0$ billion globally in 2000

Wheat, rice, maize, soybean

Bulk of losses occurred in India (22%) and China (21%)


Tropospheric ozone cycles

Topospheric ozone is not from the stratosphere (slow mixing, hence the long lifetimes of CFCs)

\[
\text{tropospheric ozone creation}
\]

\[
\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O} \quad h\nu \leq 420 \text{ nm}
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

fossil fuel combustion is a major source of NO\(_x\) compounds

\[
\text{tropospheric ozone destruction}
\]

\[
\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2
\]

This cycle does not lead to the buildup of ozone, so what does?

Tropospheric ozone cycles

Topospheric ozone is not from the stratosphere (slow mixing, hence the long lifetimes of CFCs)

**tropospheric ozone creation**

\[ \text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O} \quad h\nu \leq 420 \text{ nm} \]

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**fossil fuel combustion is a major source of NO\textsubscript{x} compounds**

**tropospheric ozone destruction**

\[ \text{O}_3 + \text{NO} \xrightarrow{\times} \text{O}_2 + \text{NO}_2 \]

\[ \text{NO}_2 \text{ via alternative pathways} \]

$HO_x$ and $NO_x$ cycles are also relevant in the troposphere

$HO_x$, $NO_x$, and volatile organic compound (VOC) pollution create positive feedback loop

For net $O_3$ destruction, need to lower [NO] to 10 ppt (atmosphere of 30 ppb $O_3$)

Ozone: good up high but bad nearby

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Stratosphere

valuable shield against UV light

Tropopause \hspace{2cm} 50 km

Troposphere

smog component and greenhouse gas

The greenhouse effect (in a nutshell)

visible light from Sun warms the Earth

The greenhouse effect (in a nutshell)

Greenhouse gases absorb and emit IR, warming troposphere.

Visible light from Sun warms the Earth.

Warm Earth emits IR.

What makes a molecule a greenhouse gas?

Greenhouse gases must absorb and emit infrared radiation

- need IR-active vibrational modes
- permanent or transient dipoles

Ozone has a permanent dipole

\[ \text{O}_3 \]

\[ \delta^+ \]

\[ \delta^- \delta^- \]

\[ \text{CH}_4 \] has a transient dipole

\[ \text{CH}_4 \]

\[ \text{CH}_4 \]
Factors determining the strength of a greenhouse gas

1. Global Warming Potential (GWP)

*radiative effect of a unit of gas over a specified time, defined relative to CO₂*

2. Atmospheric Lifetime

*how long a gas survives in the troposphere (tie-breaker between equal GWP substances)*
Is ozone the greenhouse gas we are worried about?

<table>
<thead>
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**Source**
Fourth Assessment Report (Intergovernmental Panel on Climate Change IPCC, 2007).

No, although the GWP is high (~1000), the short lifetime of 22 days mitigates the concern.
Is ozone the greenhouse gas we are worried about?

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ODS are much more worrisome greenhouse gases


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An atmospheric crisis in the troposphere

The world was told 25 years ago that CO₂ levels are rising anomalously...

An atmospheric crisis in the troposphere

...and CO₂ levels have been allowed to rise essentially unchecked

Ozone: good up high but bad nearby

\[ \text{O}_3 \text{O}_3 \text{O}_3 \text{O}_3 \equiv \text{O}_3 \text{O}_3 \text{O}_3 \text{O}_3 \]

---

**Stratosphere**

50 km

valuable shield against UV light

---

**Troposphere**

16 km

smog component and greenhouse gas

The interconnected cycles of atmospheric chemistry

2019 Antarctic ozone hole was the smallest recorded since 1982

An unusually warm Antarctic winter limited polar stratospheric cloud formation

2019 Antarctic ozone hole smallest on record.

UN Ozone Secretariat. Published October 22, 2019. https://ozone.unep.org/2019-antarctic-ozone-hole-