Mid-Latitude Stratospheric Chemistry
AOSC 433/633 & CHEM 433
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Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2017

Today:
• Importance of how a chemical cycle is completed wrt odd-oxygen loss
• Role of halogens and aerosol loading on mid-latitude ozone
• Connection to recent research
Ozone Depletion and Halocarbons

Table Q7-1. Atmospheric Lifetimes and Ozone Depletion Potentials of some halogen source & HFC substitute gases.

<table>
<thead>
<tr>
<th>Halogen source gases</th>
<th>Atmospheric Lifetime (years)</th>
<th>Ozone Depletion Potential (ODP)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chlorine gases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFC-11</td>
<td>45</td>
<td>1</td>
</tr>
<tr>
<td>CFC-12</td>
<td>100</td>
<td>0.82</td>
</tr>
<tr>
<td>CFC-113</td>
<td>85</td>
<td>0.85</td>
</tr>
<tr>
<td>Carbon tetrachloride (CCL₄)</td>
<td>26</td>
<td>0.82</td>
</tr>
<tr>
<td><strong>HCFCs</strong></td>
<td>1–17</td>
<td>0.01–0.12</td>
</tr>
<tr>
<td>Methyl chloroform (CH₃CCl₂)</td>
<td>5</td>
<td>0.16</td>
</tr>
<tr>
<td>Methyl chloride (CH₃Cl)</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>Bromine gases</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halon-1301</td>
<td>65</td>
<td>15.9</td>
</tr>
<tr>
<td>Halon-1211</td>
<td>16</td>
<td>7.9</td>
</tr>
<tr>
<td>Methyl bromide (CH₃Br)</td>
<td>0.8</td>
<td>0.66</td>
</tr>
<tr>
<td><strong>Hydrofluorocarbons (HFCs)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HFC-134a</td>
<td>13.4</td>
<td>0</td>
</tr>
<tr>
<td>HFC-23</td>
<td>222</td>
<td>0</td>
</tr>
</tbody>
</table>

ODP (species "i") = \[
\frac{\text{global loss of } O_3 \text{ due to unit mass emission of } "i"}{\text{global loss of } O_3 \text{ due to unit mass emission of CFC-11}} \approx \frac{(\alpha n_{\text{Br}} + n_{\text{Cl}})}{3} \frac{\tau_i}{\tau_{\text{CFC-11}}} \frac{MW_{\text{CFC-11}}}{MW_i}
\]

where:
- \(\tau\) is the global atmospheric lifetime
- \(MW\) is the molecular weight
- \(n\) is the number of chlorine or bromine atoms
- \(\alpha\) is the effectiveness of ozone loss by bromine relative to ozone loss by chlorine

\[\alpha = 60\]

Halons (anthropogenic halocarbons containing bromine) much worse for ozone than CFCs (anthropogenic halocarbons containing chlorine)
Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons

Global Production of CFCs, Fig. 2.19, Chemistry in Context
Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons

Emissions of halogen source gases (ODSs + natural sources)
(Weighted by Ozone Depletion Potential (ODP))

- Based on atmospheric observations or industry data
- Future projections

Global Production of CFCs, Fig Q0-1, WMO 2014 QAs
Montreal Protocol and Various Amendments Have Banned Industrial Production of CFCs and Halons

Figure Q15-1, WMO 2010 QAs
Chlorine Source Gases

Fig Q7-1, WMO 2014 QAs
And Atmospheric Levels of these Pollutants are Declining
Ozone Depletion at Mid-Latitudes

Ozone data from http://acdb-ext.gsfc.nasa.gov/Data_services/merged

Column Ozone Anomaly (DU) =
19.6 DU +
2.38 DU/W m\(^{-2}\) × TSI +
−12.4 DU/ppb × Halogens +
−0.87 DU × ln (SSA) +
−0.02 DU/m s\(^{-1}\) × QBO

where
TSI = total solar irradiance
Halogens = stratospheric chlorine & bromine loading
SSA = Sulfate Surface Area
QBO = Quasi-biennial oscillation of the direction of winds in the tropical lower strat
\[ [O_3] = \left( \frac{J_1 k_2}{J_3 k_4} \right)^{1/2} f_{O_2} [M]^{3/2} \]

\[ [O_3] \text{ falls off with increasing altitude (high in stratosphere), at a rate determined by } [M]^{3/2}, \text{ because:} \]

\[ [O_3] \text{ falls off with decreasing altitude (low in stratosphere) due to a rapid drop in } J_1, \text{ reflecting:} \]

Stratospheric Photochemistry: Odd Oxygen Loss By Families

Fraction of $O_x$ Loss Due to Each Catalytic Family
JPL 2002 Kinetics
35°N, Sept

Calculated fraction of Ozone loss due to various family of radicals.

After Osterman et al., GRL, 1997.
OH and HO\textsubscript{2} are central to stratospheric and tropospheric photochemistry.

**Production:**

\[ \text{O}^1\text{D} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]
\[ \text{O}^1\text{D} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3 \]

**Loss:**

\[ \text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \]
\[ \text{OH} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3 \]
OH and HO\textsubscript{2} are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO\textsubscript{2} formation:
\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]  \hspace{1cm} (1)

HO\textsubscript{2} loss:
\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  \hspace{1cm} (2)
\[ \text{or} \quad \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]  \hspace{1cm} (3)
\[ \text{or} \quad \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 \]  \hspace{1cm} (4)
**HO\textsubscript{x} : OH and HO\textsubscript{2}**

OH and HO\textsubscript{2} are central to stratospheric and tropospheric photochemistry

**Rapid inner cycle:**

- **HO\textsubscript{2} formation:**
  \[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]  

- **HO\textsubscript{2} loss:**
  - \[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]  
  - or \[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]  
  - or \[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 \]  

**HO\textsubscript{2} loss step (2):**

\[
\begin{array}{c}
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \\
\text{Net: } \text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2
\end{array}
\]

This is followed quickly by:

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

Yielding final “net”:

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

**Null cycle**

with respect to production & loss of odd oxygen
HO$_x$ : OH and HO$_2$

OH and HO$_2$ are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO$_2$ formation:

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad (1) \]

HO$_2$ loss:

- \[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (2) \]
- \[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \quad (3) \]
- \[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 \quad (4) \]

HO$_2$ loss step (3):

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \\
\text{Net:} & \quad \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2
\end{align*}
\]

HO$_2$ loss step (4):

\[
\begin{align*}
\text{OH} + \text{O}_3 & \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 \\
\text{Net:} & \quad \text{O}_3 + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}_2
\end{align*}
\]

Catalytic Ozone (Odd Oxygen) Loss Cycles
Odd Oxygen Loss - $\text{HO}_x$

\[
\frac{d \text{(Odd Oxygen)}}{dt} = -2k_4[\text{HO}_2][\text{O}_3] - 2k_3[\text{HO}_2][\text{O}] \quad \text{Eq (7)}
\]

The reactions:

\[
\begin{align*}
\text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 & (3) \\
\text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 & (4)
\end{align*}
\]

are rate limiting steps for $\text{O}_3$ loss by two catalytic cycles:

Cycle (1) Net :
\[
\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2
\]

Cycle (2) Net :
\[
\text{O}_3 + \text{O}_3 \rightarrow 3 \text{O}_2
\]

As a convenient short hand, \textit{we consider HO}_2 \textit{to be odd oxygen}

Then:

clear now that reactions (3) and (4) each consume two odd oxygens at rates determined by $2k_3[\text{HO}_2][\text{O}]$ and $2k_4[\text{HO}_2][\text{O}_3]$
OH, HO$_2$, H$_2$O, and CH$_4$

JPL 2002 Kinetics, 35°N, Sept
Odd Oxygen Loss - $\text{HO}_x$

At what altitudes will loss of ozone by these rate limiting steps be dominant?

$$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \quad (3)$$

$$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 \quad (4)$$

One dominates at low altitude, the other at high altitude $\Rightarrow$ which is which?!!?
NO and NO$_2$ are central to stratospheric and tropospheric photochemistry.

**Stratospheric Production**: $O^1D + N_2O \rightarrow NO + NO$

Final sinks: $N + NO \rightarrow N_2 + O$ (uppermost stratosphere)

$HNO_3$ solubility & rainout (lowermost stratosphere)
NOx : NO and NO₂

NO and NO₂ are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

NO₂ formation:

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

NO₂ loss:

\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \]  (2)

or \[ \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \]  (3)

\[ \frac{\text{dO}_3}{\text{dt}} + \frac{\text{dO}}{\text{dt}} = \frac{\text{d(Odd Oxygen)}}{\text{dt}} = -2k_3[\text{NO}_2][\text{O}] \]

As a convenient short hand, we consider NO₂ to be odd oxygen

NO₂ loss step (2):

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

Net: \[ \text{O}_3 + \text{hv} \rightarrow \text{O} + \text{O}_2 \]

NO₂ loss step (3):

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

Net: \[ \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \]
Figure 6-8, WMO (1999)

\[
\text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \times \text{N}_2\text{O}_5 + \text{HONO} + \text{HONO}_2 + \text{HO}_2\text{NO}_2 + \text{ClNO}_3 + \text{BrNO}_3
\]
Rising $\text{N}_2\text{O}$ leads to:

a) ozone loss in the middle & upper stratosphere by increasing the speed of NO and NO$_2$ (NO$_x$) mediated loss cycles.

b) speeds up the rate of $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ & $\text{ClO} + \text{NO}_2 + \text{M} \rightarrow \text{ClNO}_3 + \text{M}$ in the lowermost stratosphere, leading to slower ozone loss by these cycles & therefore more O$_3$ where these cycles dominate total loss of O$_3$.

Computer models project stratospheric column O$_3$ will decline as $\text{N}_2\text{O}$ rises
Future ODP of N$_2$O depends on CH$_4$ & CO$_2$

ODP of N$_2$O in year 2100 found by a Swiss three dimensional, chemistry climate model called SOCOL (Solar Climate Ozone Links)

Revell et al., GRL, 2015
**ClO\(_x\) : ClO and Cl**

ClO is central to stratospheric photochemistry, at mid-latitudes and polar regions.

**Production:** CFCs +hv → Inorganic chlorine

**Final sinks:** HCl solubility & rainout (lowermost stratosphere)

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\( \text{ClO}_x : \text{ClO} \text{ and Cl} \)

\( \text{ClO} \) is central to \textit{stratospheric} photochemistry, at mid-latitudes and polar regions:

**Rapid inner cycle:**

- **ClO formation:** \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \) (1)
- **ClO loss:**
  - \( \text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \) (2)
  - or \( \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \) (3)

Can show:

\[
\frac{d\text{O}_3}{dt} + \frac{d\text{O}}{dt} = \frac{d(\text{Odd Oxygen})}{dt} = -2k_3[\text{ClO}][\text{O}]
\]

As a convenient short hand, \textit{we consider ClO to be odd oxygen}
Proof Halocarbons Reach The Stratosphere

Zander et al., GRL, 1996
Trends in Ozone, ~40 km

Grey: range of model calculations, where models are forced by rising levels of stratospheric halogens.

Trends in ozone at 40 km are “well understood” ozone generally anti-correlates with time history of stratospheric chlorine loading.

Figure 2-5, WMO/UNEP 2010

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Trends in Ozone vs Altitude

Trends in ozone as a function of latitude and altitude, for the time period 1979 to 2005, from the NASA SAGE I & SAGE II instruments. Shaded region indicates significance at the 2σ level.

Units: % per decade

Two complications to understanding ozone trends in the lower stratosphere: aerosol surface area and bromine.

Figure 2-4, WMO/UNEP 2010
Bromine Source Gases

Halons:
• fire extinguishing agents
• production in developed world halted by Montreal Protocol
• present emissions primarily from “banks”

CH$_3$Br:
• fumigant; released by biomass burning
• production halted by Montreal Protocol
• significant natural & human sources

VSL Gases (e.g., CHBr$_3$, CH$_2$Br$_2$):
• emitted mainly by ocean biology
• not considered in most ozone calcs
• chemistry of decomposition products subject of active research
Total Column Ozone Time Series, NH

Stratospheric aerosol loading, Deshler et al., 2003.

Stratospheric chlorine

Change in ozone column relative to 1980, 35 to 60°N

WMO/UNEP 2006 Ozone Report
Chemical reaction on surface of volcanic aerosol couples NO$_2$ and HNO$_3$

- As sulfate aerosol rises, NO$_x$ (NO and NO$_2$) falls
- As NO$_2$ drops, CINO2 falls and ClO rises
Ozone responds to:

a) rise and fall of chlorine
b) volcanic perturbations to aerosol loading
c) amount of bromine in lowermost stratosphere

Salawitch et al., GRL, 2005
EXCESS SKIN CANCER CASES IN THE UNITED STATES, PER YEAR, DUE TO OZONE DEPLETION FOR VARIOUS CFC SCENARIOS


See also Slaper et al., Estimates of ozone depletion and skin cancer incidence to examine the Vienna Convention achievements, Nature, 384, 256–258, 1996, who state:

The no-restrictions and Montreal Protocol scenarios produce a runaway increase in skin cancer incidence, up to a quadrupling and doubling, respectively, by year 2100.