12.842
Climate Physics and Chemistry
Fall 2008

Atmospheric Chemistry I: Ozone, Chlorofluorocarbons, Nitrogen Oxides, and Dimethyl Sulfide
A brief history of the atmospheric chemistry of O$_3$, nitrogen oxides, and CFC's

- 1970: Paul Crutzen shows that destruction by NO$_x$ can account for discrepancy between factor of three excess of calculated ozone layer relative to observed ozone layer.
- 1971: Crutzen shows that dominant source of NO$_x$ in stratosphere is transport of N$_2$O released from biosphere.
- Harold Johnston suggests that nitrogen oxides released by supersonic transports might affect ozone layer (but US SST rejected on economic grounds rather than environmental concerns).
- 1973: James Lovelock, inventor of "electron capture" detector, shows that CFC concentrations in the atmosphere were increasing.
- 1974: Molina and Rowland suggest that CFCs would deplete ozone layer [at about same time, Ralph Cicerone and Johnston also suggest that Cl might deplete ozone, but focus on volcanism and the space shuttle as a source of Cl rather than CFC's].
- 1980: "Ozone hole" opens up in Antarctic, unbeknownst to the human race.
- 1985: Josephan Farman found that mean Antarctic ozone (column) had decreased by nearly half of what it had been in the early 1970's. This event was not predicted by Molina-Rowland model.
- Ozone hole intensity continues to increase, with Antarctic ozone virtually disappearing at 15-21 km altitude every spring. Late 1980's: Antarctic ozone hole linked to heterogeneous catalysis by polar stratospheric clouds.
Gas phase chemical kinetics I

- Elementary bimolecular reaction
  \[ A + B \rightarrow AB \]

- Probability of reaction depends on frequency of collision, orientation (random probability), and ability to overcome activation energy threshold

\[ \frac{d[AB]}{dt} = k[A][B] \]
Gas phase chemical kinetics II

\[
\frac{d \ln k}{dT} = \frac{E_a}{RT^2}
\]

If \( E_a \) is constant:

\[
k = Ae^{-E_a/RT} \quad \text{(Arrhenius equation)}
\]
Example: temperature dependence of rate constant for formation of hydrogen iodide

\[ \text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI} \]

\[ \frac{d \text{HI}}{dt} = [\text{H}_2][\text{I}_2] A e^{-E_a/RT} \]

Figure by MIT OpenCourseWare. Adapted from Moore. *Physical Chemistry*. 3rd ed. (1962): 274.
But things can get complicated: the example of hydrogen bromide

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \]

Reaction kinetics, as determined by Bedenstein (~1900):

\[
\frac{d[\text{HBr}]}{dt} = k[\text{H}_2][\sqrt{[\text{Br}_2]}] \\
M + \frac{[\text{HBr}]}{[\text{Br}_2]}
\]

The reaction actually proceeds by 5 separate reactions:

\[ \text{Br}_2 \rightarrow 2 \text{Br} \]

\[ \text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \]

\[ \text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br} \]

\[ \text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br} \]

\[ 2 \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M} \]
A. Ozone production

1. \( \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \)

2. \( \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \)

(M is some other molecule that acts as a catalyst)
Statospheric Ozone - key equations II

B. Ozone destruction

1. \( O_3 + h\nu \rightarrow O_2 + O \)
2. \( O + O_3 \rightarrow 2 \text{O}_2 \) (A1+A2+B1+B2 are sometimes referred to as the Chapman Cycle)
3a. \( O_3 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2 \)
3b. \( \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \) (3a and 3b involving OH are part of a more general class of reactions involving “\( O_X \)” where “\( O_X \)" = HO\(_x\), NO\(_x\), ClO\(_x\))
4a. \( \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O} \) (1D) (most N\(_2\)O destruction occurs this way; note that this reaction converts N\(_2\)O into forms which do not deplete ozone; O (1D) is an energetically excited oxygen atom)
4b. \( \text{N}_2\text{O} + \text{O} \) (1D) \( \rightarrow 2 \text{NO} \) (only 5% of N\(_2\)O is destroyed this way - but it leads to products that deplete ozone)
4c. \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \) (note: NO, NO\(_2\) and NO\(_3\) are collectively referred to as “\( \text{NO}_x \)”:
these plus all oxidized nitrogen species of NO\(_x\) on relatively short time scales (e.g. N\(_2\)O\(_5\), HNO\(_3\)) are referred to as “\( \text{NO}_y \)”
4d. \( \text{O}_3 \rightarrow \text{O} + \text{O}_2 \)
4e. \( \text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2 \)
5a. \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \)
5b. \( \text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2 \)
5c. \( \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \)
B. Ozone destruction (cont’d)

In the presence of ice clouds:

- 6a. \( \text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \)
- 6b. \( \text{Cl}_2 + h\nu \rightarrow 2 \text{Cl} \) (these are the reactions responsible for the ozone hole)

Source of stratospheric HCl:

- 7. \( \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \)
OZONE LAYER CHEMISTRY

(simplified!)

[Diagram showing chemical reactions involving ozone, oxygen, and various gases in the stratosphere and troposphere.]

CATALYSTS FOR OZONE DESTRUCTION!

NOX CYCLE

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

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

ClO\(_x\) CYCLE

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

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

HO\(_x\) CYCLE(S)

\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]
\[ \text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \]
\[ \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \]
N$_2$O (nitrous oxide): Greenhouse gas (and ozone sink)
(no laughing matter)

- N$_2$O is produced from dissolved nitrate by microbes in the earth surface environment:
  
  $2 \text{ "CH}_2\text{O"} + 2 \text{ NO}_3^- + 2 \text{ H}^+ \rightarrow \text{N}_2\text{O} + 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$

- Some microbes in the same environment will further reduce N$_2$O to N$_2$. However, gaseous N$_2$O can diffuse out of the environments where this sink reaction can occur, and once it enters the troposphere, it is relatively unreactive.

- The primary sink for tropospheric N$_2$O is the stratospheric photochemistry. It takes about a century for the troposphere to cycle through the stratosphere, so the residence time of N$_2$O in the atmosphere is about a century.
  
  $\text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O (}^{1}\text{D})$ (most N$_2$O destruction occurs this way; note that this reaction converts N$_2$O into forms which do not deplete ozone; O (}$^{1}\text{D}$) is an energetically excited oxygen atom)

  $\text{N}_2\text{O} + \text{O (}^{1}\text{D}) \rightarrow 2 \text{ NO}$ (only 5% of N$_2$O is destroyed this way - but it leads to products which deplete ozone)
$\text{N}_2\text{O}$ is increasing with time…

Figure by MIT OpenCourseWare.
Methane is a strong greenhouse gas and contributes to global warming.

Estimates of the globally and annually averaged anthropogenic radiative forcing (in Wm\(^{-2}\)) due to changes in concentrations of greenhouse gases and aerosols from pre-industrial times to the present day and to natural changes in solar output from 1850 to the present day.

Figure by MIT OpenCourseWare based on IPCC.
But it has also changed before large-scale human activities:

\[ \text{N}_2\text{O in a Greenland ice core} \]

Image removed due to copyright restrictions.
Citation: Figure 1. Sower, et al. Science 301 (August 15, 2003): 946.
The Nitrogen Cycle

\[ \text{nitrous oxide} \rightarrow \text{nitric oxide} \rightarrow \text{dissolved nitrite} \rightarrow \text{dissolved nitrate} \rightarrow \text{gaseous nitrogen} \]

\[ \text{nitrogen fixation} \rightarrow \text{proteins, ammonia} \]

\[ \text{denitification} \]

also: Anammox (anaerobic ammonia oxidation)
\[ (NH_4^+ + NO_2^- \rightarrow N_2) \]

\[ <- \text{anaerobic} \quad \text{aerobic} -> \]
The nitrogen cycle

Image removed due to copyright restrictions.

Image removed due to copyright restrictions.
Human perturbations of the nitrogen cycle:

- High temperature (and sometimes pressure) combustion converts $N_2$ into nitrogen oxides
- Production of nitrogen fertilizers, release into the environment
- Sewage inputs of fixed nitrogen
- High-nutrient environments lead to oxygen depletion (eutrophication), e.g. “dead zone” on Mississippi coast; this environment leads to denitrification.
Image removed due to copyright restrictions.
Citation: Figure 4. Ambio, J. *Galloway* 31 (March 2002): 2.
Fertilizer production

Figure by MIT OpenCourseWare based on Physics Today
Nitrate in a Greenland ice core

Concentrations of Nitrate Measured in the GISP2 Ice Core

Purple Line represents the 2000 year average

Parts/Billion (ppb)

Calender Years

Figure by MIT OpenCourseWare based on Mauerski et al., 1990 and Zielinski et al., 1994.
NH$_4^+$ (ammonium) in an Alpine ice core

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## Tropospheric N\textsubscript{2}O Budget

### ESTIMATED SOURCES AND SINKS OF N\textsubscript{2}O TYPICAL OF THE LAST DECADE (Tg(N)/yr)

<table>
<thead>
<tr>
<th></th>
<th>Range of Estimates</th>
<th>Most Likely Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Increase in Atmosphere</strong></td>
<td>3.1 - 4.7</td>
<td>3.9#</td>
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<tr>
<td><strong>Sinks</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stratosphere (N\textsubscript{2}O + h \rightarrow N\textsubscript{2} + O)</td>
<td>9 - 16</td>
<td>12.3</td>
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<tr>
<td>Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total Sinks</strong></td>
<td>9 - 16</td>
<td>12.3</td>
</tr>
<tr>
<td><strong>Implied Total Sources</strong></td>
<td>13 - 20</td>
<td>16.2</td>
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</tbody>
</table>

Table: Known Sources

<table>
<thead>
<tr>
<th>Known Sources</th>
<th>Range of estimates</th>
<th>Most Likely Value</th>
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</thead>
<tbody>
<tr>
<td><strong>Natural</strong></td>
<td></td>
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<tr>
<td>Oceans</td>
<td>1 - 5</td>
<td>3</td>
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<tr>
<td>Tropical Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet Forests</td>
<td>2.2 - 3.7</td>
<td>3</td>
</tr>
<tr>
<td>Dry Savannas</td>
<td>0.5 - 2.0</td>
<td>1</td>
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<tr>
<td>Temperate Soils</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forests</td>
<td>0.1 - 2.0</td>
<td>1</td>
</tr>
<tr>
<td>Grasslands</td>
<td>0.5 - 2.0</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total Known Natural Sources</strong></td>
<td>6 - 12</td>
<td>9</td>
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<tr>
<td><strong>Anthropogenic</strong></td>
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<tr>
<td>Cultivated Soils</td>
<td>1.8 - 5.3</td>
<td>3.5</td>
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<tr>
<td>Biomass Burning</td>
<td>0.2 - 1.0</td>
<td>0.5</td>
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<tr>
<td>Industrial Sources</td>
<td>0.7 - 1.8</td>
<td>1.3</td>
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<tr>
<td>Cattle and Feed Lots</td>
<td>0.2 - 0.5</td>
<td>0.4</td>
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<tr>
<td><strong>Total Known Anthropogenic</strong></td>
<td>3.7 - 7.7</td>
<td>5.7</td>
</tr>
<tr>
<td><strong>KNOWN SOURCE TOTALS</strong></td>
<td>10 - 17</td>
<td>14.7</td>
</tr>
</tbody>
</table>

\# The observed atmospheric increase implies that sources exceed sinks by 3.9 Tg(N)/yr.
Dimethyl sulfide and climate

- A. Marine organisms (e.g. coccolithophorids, single-celled plants) produce DMSP (dimethylsulfoniopropionate):

\[
\begin{array}{c}
\text{CH}_3 \\
\text{S}^+ \text{-CH}_2 \text{-CH}_2 \text{-COO}^- \quad \text{DMSP} \\
\text{CH}_3 \\
\end{array}
\]

This compound is converted to DMS [(CH₃)₂S] when the cell is destroyed and the cell contents are degraded.

- B. DMS is volatile and moves into the atmosphere by gas exchange.

- C. DMS is oxidized in the atmosphere to two byproducts with a "branch ratio": sulfuric acid (H₂SO₄) and methanesulfonic acid (MSA: CH₃SO₃H). Cycle is complex with many intermediates; branch ratio appears to depend mainly on temperature (low MSA:nssSO₄⁻ at warmer temperatures)

- D. The products are transported to ice cores and recorded there as non-sea-salt sulfate (nss SO₄⁻) and MSA.

- E. The non-sea-salt sulfate, (initially sulfuric acid but later reacted with sea salt particles and mineral aerosols) forms particles that act as cloud condensation nuclei (CCN). In areas that are far from land, these CCN can be an important factor regulating cloud formation and rainfall. Some people have hypothesized a feedback between DMS and climate.
Image removed due to copyright restrictions.
Citation: See the image about concentration of DMS in seawater published on Woods Hole Notes by John W. H. Dacey, Woods Hole Oceanographic Institution.