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

Problem Set # 4, due Tues, 9 April, has been posted

Student Projects

• **Mandatory for 633 students**: project grade will count towards final grade in an amount equal to each exam
• Due Tuesday, 8 May 2013 … you’re welcome to complete sooner!
• ~8 pages single spaced (not including reference list or figures) on a topic related to class (your choice …we’re happy to discuss potential topics)
• Must be “new work” for this class but can be related to your dissertation or some other project in which you’ve had prior interest
• ~10 min presentations of project the evening of Wednesday, 9 May 2013 (everyone encouraged to attend)
• **433 students**: may complete a Student Project (same guidelines) and the grade on this project can take the place of a **single Problem Set**. This may be especially helpful for students who have not turned in a Problem Set.
• Request all students who will complete a project provide a **2 to 3 sentence project description** of a week from today: **Thursday, 4 April 2013**
• **We’re delighted to provide feedback on your project (paper & presentation) if given the opportunity prior to 8 May 2013**
Ozone Depletion at Mid-Latitudes

Ozone data from
http://www.bodekerscientific.com/data/ozone

Column Ozone Anomaly (DU) = 20.5 DU + 3.89 DU/W m⁻² × TSI + (-11.5 DU/ppb × Halogens) + (-11.4 DU/SOD × Strat τ) + (-1.27 DU/m s⁻¹ × QBO Index)

where SSA = Sulfate Surface Area

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Ozone Depletion at Mid-Latitudes

Column Ozone Anomaly (DU) =

\[ 20.5 \text{ DU} + 3.89 \text{ DU} / \text{W m}^{-2} \times \text{TSI} + (-11.5 \text{ DU} / \text{ppb} \times \text{Halogens}) + (-11.4 \text{ DU} / \text{SOD} \times \text{Strat } \tau) + (-1.27 \text{ DU} / \text{m s}^{-1} \times \text{QBO Index}) \]

where SSA = Sulfate Surface Area

Chlorine Source Gases

CFC usage, ~1986 percent of global release:

- Propellants: 28%
- Foam Blowing: 26%
- Refrigerants: 23%
- Cleaning Solvents: 21%
Total Organic Chlorine (CCl_y):
- Peaked at ~3.7 ppb around 1993
- Slowly declining
- Montreal Protocol and Amendments have banned production of CFCs

Table 5A-3, WMO/UNEP (2011)

Chapman Chemistry

\[
\left[ O_3 \right] = \left( \frac{J_1 \cdot k_2}{J_3 \cdot k_4} \right)^{1/2} \cdot f_{O_2} [M]^{3/2}
\]

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

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

Observed \([O_3] < \text{Chapman } [O_3] : \text{ why ??} \)

Lecture 9, Slide 5
**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.

Lecture 9, Slide 10

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**HO$_x$ : OH and HO$_2$**

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

**Production:**

- $O^1D + H_2O \rightarrow OH + OH$
- $O^1D + CH_4 \rightarrow OH + CH_3$

**Loss:**

- $OH + HO_2 \rightarrow H_2O + O_2$
- $OH + HNO_3 \rightarrow H_2O + NO_3$

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OH and HO2 are central to stratospheric and tropospheric photochemistry

Rapid inner cycle:

HO₂ formation:
\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \quad (1)
\]

HO₂ loss:
\[
\begin{align*}
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \quad (2) \\
\text{or} \quad \text{HO}_2 + \text{O} & \rightarrow \text{OH} + \text{O}_2 \quad (3) \\
\text{or} \quad \text{HO}_2 + \text{O}_3 & \rightarrow \text{OH} + \text{O}_2 + \text{O}_2 \quad (4)
\end{align*}
\]

Null cycle

\text{with respect to production & loss of odd oxygen}
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:**

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

**HO\textsubscript{2} loss:**

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (2)
\]

or

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

or

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

**HO\textsubscript{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\textsubscript{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 - HO\textsubscript{x}

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

The reactions:

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

are rate limiting steps for O\textsubscript{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, we consider HO\textsubscript{2} to be odd oxygen

Then:

clear now that reactions (3) and (4) each consume two odd oxygens at rates determined by $2k_3 \left[\text{HO}_2\right]\left[\text{O}\right]$ and $2k_4 \left[\text{HO}_2\right]\left[\text{O}_3\right]$
Odd Oxygen Loss - HO\textsubscript{x}

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

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

One dominates at low altitude, the other at high altitude ⇒ which is which ?!!
NO\(_x\): NO and NO\(_2\)

NO and NO\(_2\) are central to stratospheric and tropospheric photochemistry

**Stratospheric Production**: O\(^1\)D + N\(_2\)O → NO + NO

Final sinks: N + NO → N\(_2\) + O (uppermost stratosphere)
HNO\(_3\) solubility & rainout (lowermost stratosphere)

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NO\(_x\): NO and NO\(_2\)

NO and NO\(_2\) are central to stratospheric and tropospheric photochemistry

**Rapid inner cycle:**

NO\(_2\) formation:

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

NO\(_2\) 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)

**NO\(_2\) 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:

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

**NO\(_2\) 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:

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

Can show:

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

As a convenient short hand, we consider NO\(_2\) to be odd oxygen
NOy versus N2O

Figure 6-8, WMO (1999)

\[ \text{NOy} = \text{NO} + \text{NO}_2 + \text{NO}_3 + 2 \times \text{N}_2\text{O}_5 + \text{HONO} + \text{HONO}_2 + \text{HO}_2\text{NO}_2 + \text{ClNO}_3 + \text{BrNO}_3 \]

ClOx : ClO and Cl

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

Production : CFCs + hv \rightarrow \text{Inorganic chlorine}

Final sinks : HCl solubility & rainout (lowermost stratosphere)
ClO: ClO and Cl

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

Rapid inner cycle:

ClO formation:
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]  \hspace{1cm} (1)

ClO loss:
\[ \text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \]  \hspace{1cm} (2)

or
\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]  \hspace{1cm} (3)

Followed by:
\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \]

Final net:
\[ \text{O}_3 + h\nu \rightarrow \text{O} + \text{O}_2 \]

ClO loss step (2):
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]
\[ \text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \]

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

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, we consider ClO to be odd oxygen

Proof Halocarbons Reach The Stratosphere

Zander et al., GRL, 1996
Trends in Ozone, \(\sim 40 \text{ km}\)

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**

But: ozone at 40 km has little effect on surface UV radiation.

**Figure 2-5, WMO/UNEP 2010**
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.

Figure 2-4, WMO/UNEP 2010

Ozone loss due to halogens at low altitude sensitive to:
- a) aerosol loading
- b) how much bromine is present

After Osterman et al., GRL, 1997.
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 aerosol surface (heterogeneous chemistry) couples NO\textsubscript{2} and HNO\textsubscript{3}

• As sulfate aerosol rises, NO\textsubscript{x} (NO and NO\textsubscript{2}) falls

\[ \text{NO} \quad \text{NO}_2 \quad \text{O} \quad \text{hv} \quad \text{NO}\textsubscript{2} + \text{M} \quad \text{O}_3 \quad \text{O}_3 \quad \text{Sulfate Aerosol} \quad \text{N}_2\text{O}_5 + \text{H}_2\text{O} \text{ (aerosol)} \rightarrow 2 \text{HNO}_3 \]

Chemical reaction on aerosol surface (heterogeneous chemistry) couples NO\textsubscript{2} and HNO\textsubscript{3}, which in turn affects ClO

• As NO\textsubscript{2} drops, ClO will rise

\[ \text{HCl} \quad \text{O, OH, hv} \quad \text{CH}_4 \quad \text{CINO}_3 \quad \text{NO}_2 \quad \text{hv, OH} \quad \text{Cl} \quad \text{NO} \quad \text{ClO} \quad \text{O} \]
Ozone responds to:

a) rise and fall of chlorine

b) volcanic perturbations to aerosol loading

c) amount of bromine in lowermost stratosphere

After Salawitch et al., GRL, 2004.
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.

See also WMO (2007), Question 15