ATM 507 – Meeting 5

Text reading – Chapter 5
Problem Set # 4 – due Oct 4
Today’s topic – Stratospheric Chemistry
As mentioned previously - An excellent web site for stratospheric chemistry:
http://www.ccpo.odu.edu/~lizsmith/SEES/ozone/oz_class.htm
Review

- Chapman ($O_x$) reactions
- $H_2O_x$, $NO_x$, $ClO_x$, and $BrO_x$ reactions
- Sources, radicals, reservoirs, sinks
- Catalytic cycles
- Null and Holding cycles
- Coupling between cycles

- Look at some examples …
How fast does the OH ↔ HO\textsubscript{2} catalytic cycle proceed?
What are the chemical lifetimes of the radicals?
What are the rates (and lifetimes) for removal to reservoir species?
What is the chain length of the catalytic cycle?

1. OH + O\textsubscript{3} \rightarrow HO\textsubscript{2} + O\textsubscript{2}; \quad R\textsubscript{1} = k\textsubscript{1}[OH][O\textsubscript{3}] \quad - \text{catalytic cycle}

2. HO\textsubscript{2} + O \rightarrow OH + O\textsubscript{2}; \quad R\textsubscript{2} = k\textsubscript{2}[HO\textsubscript{2}][O] \quad - \text{catalytic cycle}

3. OH + HO\textsubscript{2} \rightarrow H\textsubscript{2}O + O\textsubscript{2}; \quad R\textsubscript{3} = k\textsubscript{3}[OH][HO\textsubscript{2}] \quad - \text{termination}

4. OH + NO\textsubscript{2} + M \rightarrow HNO\textsubscript{3} + M; \quad R\textsubscript{4} = k\textsubscript{4}[OH][NO\textsubscript{2}][M] 
\quad = k\textsubscript{4}\textsubscript{eff}[OH][NO\textsubscript{2}] \quad - \text{termination}

5. O + O\textsubscript{3} \rightarrow 2 O\textsubscript{2}; \quad R\textsubscript{5} = k\textsubscript{5}[O][O\textsubscript{3}] \quad - \text{Chapman O}_x \text{ loss}
Consider the situation at 30 km (T = 225 K)

\[ k_1 = 2.45 \times 10^{-14} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}; \quad [O_3] = 3.1 \times 10^{12} \text{ molec cm}^{-3} \]

\[ k_2 = 7.3 \times 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}; \quad [O] = 3.5 \times 10^{8} \text{ molec cm}^{-3} \]

\[ k_3 = 1.2 \times 10^{-10} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}; \quad [OH] = 8.4 \times 10^{6} \text{ molec cm}^{-3} \]

\[ k_4^{\text{eff}} = 1.8 \times 10^{-12} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}; \quad [HO_2] = 1.6 \times 10^{7} \text{ molec cm}^{-3} \]

\[ k_5 = 8.45 \times 10^{-16} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}; \quad [NO_2] = 9.6 \times 10^{8} \text{ molec cm}^{-3} \]

Rates and Lifetimes

\[ R_1 = (2.45 \times 10^{-14} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}) \times (8.4 \times 10^{6} \text{ molec cm}^{-3}) \times (3.1 \times 10^{12} \text{ molec cm}^{-3}) \]
\[ = 6.4 \times 10^{5} \text{ molec cm}^{-3} \text{ s}^{-1} \]

\[ R_2 = (7.3 \times 10^{-11} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}) \times (1.6 \times 10^{7} \text{ molec cm}^{-3}) \times (3.5 \times 10^{8} \text{ molec cm}^{-3}) \]
\[ = 4.1 \times 10^{5} \text{ molec cm}^{-3} \text{ s}^{-1} \]

Rate constants from back of text; concentrations from Brasseur & Solomon, 3rd Ed (2005)
\[ \tau_{\text{OH} \rightarrow \text{HO}_2} = \frac{1}{(k_1[\text{O}_3])} = 13 \text{ s} \]

\[ \tau_{\text{HO}_2 \rightarrow \text{OH}} = \frac{1}{(k_2[\text{O}])} = 39 \text{ s} \]

Radical lifetimes ~ seconds

Removal of Radicals to Reservoirs and/or Sinks

\[ R_3 = k_3[\text{OH}][\text{HO}_2] = 1.6 \times 10^4 \text{ molec cm}^{-3} \text{ s}^{-1} \]

\[ R_4 = k_{4\text{eff}}[\text{OH}][\text{NO}_2] = 1.45 \times 10^4 \text{ molec cm}^{-3} \text{ s}^{-1} \]

\[ \tau_{\text{OH} \rightarrow \text{H}_2\text{O}, \text{HNO}_3} = \frac{1}{(k_3[\text{HO}_2] + k_{4\text{eff}}[\text{NO}_2])} = 270 \text{ s or 4.5 min} \]

\[ \tau_{\text{HO}_2 \rightarrow \text{H}_2\text{O}} = \frac{1}{(k_3[\text{OH}])} = 1000 \text{ s or 16.5 min} \]
CHAIN LENGTH

\[ L_c = \frac{R(\text{propagation})}{R(\text{termination})} = \frac{R_2}{(R_3 + R_4)} \approx 13 \]

HOW DOES CATALYTIC DESTRUCTION DUE TO \( \text{OH} \leftrightarrow \text{HO}_2 \) CYCLING COMPARE TO CHAPMAN LOSS?

First – \( R_2 \) is slower than \( R_1 \), so it is the RDS (rate determining step)

\[ \frac{R(\text{O+HO}_2)}{R(\text{O+O}_3)} = \frac{R_2}{R_5} = \frac{(k_2[\text{HO}_2][\text{O}])}{(k_5[\text{O}_3][\text{O}])} = \frac{k_2[\text{HO}_2]}{k_5[\text{O}_3]} = 0.45 \]

AT 30 KM, FOR THE GIVEN CONDITIONS, THE CATALYTIC \( \text{HO}_X \) INDUCED OZONE LOSS (FROM THE COUPLETT OF REACTIONS 1 AND 2) ADDS AN ADDITIONAL 45% ONTO THE PURE \( \text{O}_X \) CHAPMAN LOSS.
Let’s explore a larger, mixed set of reactions involving ozone production and loss

1. \( O_2 + h\nu \rightarrow O + O; \quad k_1 \)
2. \( O + O_2 + M \rightarrow O_3 + M; \quad k_2 \)
3. \( O_3 + h\nu \rightarrow O + O_2; \quad k_3 \)
4. \( O + O_3 \rightarrow 2 O_2; \quad k_4 \)
5. \( NO + O_3 \rightarrow NO_2 + O_2; \quad k_5 \)
6. \( NO_2 + O \rightarrow NO + O_2; \quad k_6 \)
7. \( NO_2 + h\nu \rightarrow NO + O; \quad k_7 \)
8. \( Cl + O_3 \rightarrow ClO + O_2; \quad k_8 \)
9. \( ClO + O \rightarrow Cl + O_2; \quad k_9 \)
10. \( ClO + NO \rightarrow Cl + NO_2; \quad k_{10} \)

Chapman

\[ \begin{align*}
1. & \quad O_2 + h\nu \rightarrow O + O; \quad k_1 \\
2. & \quad O + O_2 + M \rightarrow O_3 + M; \quad k_2 \\
3. & \quad O_3 + h\nu \rightarrow O + O_2; \quad k_3 \\
4. & \quad O + O_3 \rightarrow 2 O_2; \quad k_4
\end{align*} \]

NO\(_X\) Catalytic

\[ \begin{align*}
5. & \quad NO + O_3 \rightarrow NO_2 + O_2; \quad k_5 \\
6. & \quad NO_2 + O \rightarrow NO + O_2; \quad k_6 \\
7. & \quad NO_2 + h\nu \rightarrow NO + O; \quad k_7
\end{align*} \]

Null

ClO\(_X\) Catalytic

\[ \begin{align*}
8. & \quad Cl + O_3 \rightarrow ClO + O_2; \quad k_8 \\
9. & \quad ClO + O \rightarrow Cl + O_2; \quad k_9 \\
10. & \quad ClO + NO \rightarrow Cl + NO_2; \quad k_{10}
\end{align*} \]

Null
Rate equations for the reactive species

\[
\begin{align*}
\frac{d[O]}{dt} &= 2k_1 \left[O_2\right] + k_3 \left[O_3\right] + k_7 \left[NO_2\right] - k_2 \left[O\right]\left[O_2\right]\left[M\right] - k_4 \left[O\right]\left[O_3\right] \\
&\quad - k_6 \left[NO_2\right]\left[O\right] - k_9 \left[ClO\right]\left[O\right] \\
\frac{d[O_3]}{dt} &= k_2 \left[O\right]\left[O_2\right]\left[M\right] - k_3 \left[O_3\right] - k_4 \left[O\right]\left[O_3\right] - k_5 \left[NO\right]\left[O_3\right] - k_8 \left[Cl\right]\left[O_3\right] \\
\frac{d[Cl]}{dt} &= k_9 \left[ClO\right]\left[O\right] + k_{10} \left[ClO\right]\left[NO\right] - k_8 \left[Cl\right]\left[O_3\right] \\
\frac{d[ClO]}{dt} &= k_8 \left[Cl\right]\left[O_3\right] - k_9 \left[ClO\right]\left[O\right] - k_{10} \left[ClO\right]\left[NO\right] \quad (= \frac{-d[Cl]}{dt} ) \\
\frac{d[NO]}{dt} &= k_7 \left[NO_2\right] + k_6 \left[NO_2\right]\left[O\right] - k_5 \left[NO\right]\left[O_3\right] - k_{10} \left[ClO\right]\left[NO\right] \\
\frac{d[NO_2]}{dt} &= k_5 \left[NO\right]\left[O_3\right] + k_{10} \left[ClO\right]\left[NO\right] - k_7 \left[NO_2\right] - k_6 \left[NO_2\right]\left[O\right] \quad (= \frac{-d[NO]}{dt} )
\end{align*}
\]
How do we solve this set of equations?

1. Use (or “invoke”) **Photochemical Steady State** – this method is applicable whenever the time constants for the production and loss of any “steady state species” are small (short) compared to other time constants capable of affecting the concentration and distribution of this species.

2. Use our definition of ODD OXYGEN – \( O_X = O + O_3 \)

The rate equation for ODD OXYGEN is then

\[
d[O_X]/dt = 2 k_1 [O_2] + k_7 [NO_2] - 2 k_4 [O][O_3] - k_5 [NO][O_3] \\
- k_6 [NO_2][O] - k_8 [Cl][O_3] - k_9 [ClO][O]
\]
Use steady state to simplify – in this case we will invoke steady state for NO \((d[\text{NO}]/dt = 0)\) and Cl \((d[\text{Cl}]/dt = 0)\)

**Steady state for NO** ⇒

\[
k_7 [\text{NO}_2] + k_6 [\text{NO}_2][\text{O}] = k_5 [\text{NO}][\text{O}_3] + k_{10} [\text{ClO}][\text{NO}] \text{ or }\]
\[
k_7 [\text{NO}_2] = k_5 [\text{NO}][\text{O}_3] + k_{10} [\text{ClO}][\text{NO}] - k_6 [\text{NO}_2][\text{O}]\]

**Steady state for Cl** ⇒

\[
k_8 [\text{Cl}][\text{O}_3] = k_9 [\text{ClO}][\text{O}] + k_{10} [\text{ClO}][\text{NO}]\]

Substitute these expressions for \(k_7 [\text{NO}_2]\) and \(k_8 [\text{Cl}][\text{O}_3]\) into our equation for \(d[\text{O}_X]/dt\) (from the last slide)

\[
d[\text{O}_X]/dt = 2k_1 [\text{O}_2] - 2k_4 [\text{O}][\text{O}_3] - 2k_6 [\text{NO}_2][\text{O}] - 2k_9 [\text{ClO}][\text{O}]\]

**Real odd oxygen production term**

**Ozone Destruction Terms**

Last two terms are rates of the “Rate Determining Step” of each catalytic cycle
Key Concept

- **Rate Determining Step** or **RDS** – The slowest reaction rate in a set of catalytic cycle reactions defines the rate of the catalytic cycle – and that reaction is the RDS.

- **IMPORTANT** – The rate of O$_3$ destruction by a catalytic cycle is given by (the rate of) the RDS of that cycle.
Ozone Balance in the Mid- and Low-Latitude Stratosphere

- The following equation includes the most important, but not all, ozone loss processes:

\[
\frac{d[O_X]}{dt} = 2k_{O_2}[O_2] - 2k_{O+O_3}[O][O_3] - 2k_{O+NO_2}[O][NO_2] - 2k_{O+ClO}[O][ClO] - 2k_{O+HO_2}[O][HO_2] - 2k_{O+BrO}[O][BrO] - 2k_{O_3+HO_2}[O_3][HO_2]
\]
Ozone Balance in the Mid-Latitude Stratosphere (cont.)

• The ozone balance equation from the last slide can be checked using measurements or model calculations. Measurements are difficult and few – particularly for the radicals that can’t be measured from satellites. The measurements that we do have constrain the models and our picture of ozone balance (chemical production and loss) is taken primarily from the model calculations.

• Also, recall that production is due (almost) entirely to $\text{O}_2$ photolysis. The calculations we will look at involve the various loss processes.
Ozone loss processes expressed in terms of reaction set RDS's (and rates for HO$_x$)

This figure is from model calculations done in the early 1980's.

Note NO$_x$ is "dominant" through most of stratosphere, but HO$_x$ has important contributions higher and lower.
Loss to production ratio from a 1-D model

L/P is the percent of ozone destruction due to the labeled process as a function of altitude.

Note that this figure starts at the middle stratosphere and goes up.

This model calculation was done in the late 1980's.

Both this figure and the previous one show that near 45 km, the contributions from NO$_x$, HOx, and ClOx are nearly equal.
Lower and middle stratosphere – mid-1990’s.

This calculation brings in the ClO-BrO cycle and the BrO$_x$ cycle.

It illustrates that NO$_x$ related ozone loss is not dominant below 20 km.

Also check out Figures 5.28 and 5.29 in the text for similar figures.
These plots summarize our understanding of mid-latitude stratospheric ozone chemistry – make sure you understand them!
Ozone Balance in the Mid- and Low-Latitude Stratosphere

• The following equation includes the most important, but not all, ozone loss processes:

\[
d[O_X]/dt = \begin{align*}
2 & \ k_{O_2} \ [O_2] \\
-2 & \ k_{O+O_3} \ [O][O_3] \\
-2 & \ k_{O+NO_2} \ [O][NO_2] \\
-2 & \ k_{O+ClO} \ [O][ClO] \\
-2 & \ k_{O+HO_2} \ [O][HO_2] \\
-2 & \ k_{O+BrO} \ [O][BrO] \\
-2 & \ k_{O_3+HO_2} \ [O_3][HO_2]
\end{align*}
\]
Verifying this understanding.

• How can one use measurements to check the theory (and the models)?
• Recall the $O_3$ balance equation

$$d[O_X]/dt = 2 k_{O2} [O_2] - 2 k_{O+O3} [O][O_3] - 2 k_{O+NO2} [O][NO_2]$$
$$- 2 k_{O+ClO} [O][ClO] - 2 k_{O+HO2} [O][HO_2]$$
$$- 2 k_{O+BrO} [O][BrO] - 2 k_{O3+HO2} [O_3][HO_2]$$

• To check this would require simultaneous measurements of $O_2$, $O_3$, $O$, $NO_2$, $HO_2$, $ClO$ and $BrO$ (at least).
• These are difficult measurements to make, and $HO_x$ measurements have proven to be the hardest.
• In 1993 a series of airplane flights made the simultaneous measurements that allowed this full test of the theory for the lower stratosphere (Wennberg et al., Science 1994)
Lower Stratosphere Catalytic Cycles

Of these 7 most commonly considered catalytic cycles for this region, 5 have a net reaction that is $O_3 + O_3$ instead of $O + O_3$. WHY?

\[
\begin{align*}
\text{OH} + O_3 & \rightarrow \text{HO}_2 + O_2 \\
\text{HO}_2 + O_3 & \rightarrow \text{OH} + 2O_2 \\
\text{NET}: \quad O_3 + O_3 & \rightarrow 3O_2
\end{align*}
\]

\[
\begin{align*}
\text{Cl} + O_3 & \rightarrow \text{ClO} + O_2 \\
\text{ClO} + O & \rightarrow \text{Cl} + O_2 \\
\text{NET}: \quad O_3 + O & \rightarrow 2O_2
\end{align*}
\]

\[
\begin{align*}
\text{NO} + O_3 & \rightarrow \text{NO}_2 + O_2 \\
\text{NO}_2 + O & \rightarrow \text{NO} + O_2 \\
\text{NET}: \quad O_3 + O & \rightarrow 2O_2
\end{align*}
\]

\[
\begin{align*}
\text{BrO} + \text{ClO} & \rightarrow \text{Br} + \text{Cl} + O_2 \\
\text{Cl} + O_3 & \rightarrow \text{ClO} + O_2 \\
\text{Br} + O_3 & \rightarrow \text{BrO} + O_2 \\
\text{NET}: \quad O_3 + O_3 & \rightarrow 3O_2
\end{align*}
\]

\[
\begin{align*}
\text{NO} + O_3 & \rightarrow \text{NO}_2 + O_2 \\
\text{NO}_2 + O_3 & \rightarrow \text{NO}_3 + O_2 \\
\text{NO}_3 + \text{hv} & \rightarrow \text{NO} + O_2 \\
\text{NET}: \quad O_3 + O_3 & \rightarrow 3O_2
\end{align*}
\]

\[
\begin{align*}
\text{Cl} + O_3 & \rightarrow \text{ClO} + O_2 \\
\text{OH} + O_3 & \rightarrow \text{HO}_2 + O_2 \\
\text{ClO} + \text{HO}_2 & \rightarrow \text{HOCI} + O_2 \\
\text{HOCI} + \text{hv} & \rightarrow \text{Cl} + \text{OH} \\
\text{NET}: \quad O_3 + O_3 & \rightarrow 3O_2
\end{align*}
\]

(Also this last cycle with Br.)
Consider \( \text{HO}_2 + \text{O} \) vs. \( \text{HO}_2 + \text{O}_3 \)

- Which reaction has the faster rate?
- Consider \( \frac{R_O}{R_{O3}} = \frac{k_O[O]}{k_{O3}[O_3]} \) since the \( \text{HO}_2 \)'s cancel
- \( \frac{k_O}{k_{O3}} \approx 4700 \)
- From figure at right, \( \frac{[O]}{[O_3]} = \frac{1}{4700} \) at about 32 km
- To first approximation, \( R_O \) more impt above, \( R_{O3} \) more impt below

Figure 14.6. Calculated daytime ratio of the concentration of \([\text{O}^{3P}]\) to \([\text{O}_3]\) in the stratosphere.
Lower stratosphere measurements
Straight from the journal

Fig. 4. Photochemical loss and production rates for O₃. Measurements of the concentrations of OH, HO₂, ClO, NO, and O₃ obtained during three altitude profiles on 1 May 1993 are used to infer the O₃ removal rates. The in situ measurements are scaled according to the observed diurnal profiles to obtain the integrated loss rates. The odd-hydrogen radicals were responsible for >40% of the photochemical loss in the lower stratosphere. The catalytic action of the halogen radicals accounted for nearly one-third of the total. Net removal of O₃ at the northernmost latitudes approached 10% per month.

Full citation: Wennberg et al. (1994) Removal of Stratospheric O₃ by Radicals: In Situ Measurements of OH, HO₂, NO, NO₂, ClO, and BrO. 266, 398-404
Ozone removal as a function of NO$_X$

Fig. 7. The O$_3$ removal rate is shown versus [NO$_x$]. Because of the coupling that exists between the radical families, the response of the total O$_3$ removal rate to changes in [NO$_x$] is highly nonlinear. At sufficiently low [NO$_x$], such as observed during the SPADE campaign, the removal rates are inversely correlated with [NO$_x$].
Key Findings for SPADE Mission –
lower stratosphere (15-20 km); mid-latitudes

- Odd hydrogen radicals were responsible for the largest fraction (> 40%) of odd oxygen loss at all latitudes.
- Halogen radicals fairly consistently account for about 1/3 of the odd oxygen loss for these altitude/latitude conditions.
- The ratio of production to loss changes dramatically with latitude – P/L << 1 at 60 deg N; but P/L > 1 at 38 deg N.
- These flights sampled relatively “low NO$_x$” regimes – as NO$_x$ changes, the partitioning of odd oxygen removal changes dramatically.
- Our theory is fairly straightforward and largely correct – but the atmosphere is complex and there can be dramatic differences with altitude, latitude, and “chemical regime”. (and season!)
Polar Stratospheric Chemistry

• In the 60’s, 70’s, and early 80’s, nearly all work on stratospheric chemistry centered on the midlatitudes, and the worries that unchecked emissions of chlorine (from CFC’s) or NO\textsubscript{X} (from aircraft, fertilizer, or other sources) would perturb the ozone balance and reduce ozone levels significantly. (Actually, the attention was focused on the 40 km region. WHY?) Reduced stratospheric ozone leads to increased levels of harmful UV radiation (UVA and UVB), and to increases in skin cancer and related diseases.

• Note that balanced emissions of nitrogen and chlorine tend to offset each other somewhat (by forming the CINO\textsubscript{3} reservoir). This buffering capacity is a good thing, but does tend to make the situation less stable, since there is lots of both chlorine and nitrogen “sitting around” in the CINO\textsubscript{3}.
“Chlorine Catastrophe”

• In 1984, Prather et al. published a purely speculative paper describing a scenario they called the “chlorine catastrophe”.

• Consider the present condition of the stratosphere, where the total chlorine abundance is roughly 3 ppb, and the total NO\textsubscript{X} abundance is 15-20 ppb.

• Under these conditions, the NO\textsubscript{X} “buffers” the ClO\textsubscript{X} by forming ClNO\textsubscript{3}:

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

• At very high levels of total chlorine (> 15-20 ppb), all the NO\textsubscript{X} gets converted to ClNO\textsubscript{3}.

• Since there is no more NO\textsubscript{X} to buffer the ClO\textsubscript{X}, chlorine catalyzed ozone removal proceeds essentially unchecked. (At least much more efficiently!)
Lessons from the “Chlorine Catastrophe” Study

1. The atmosphere frequently has ways to keep in balance (i.e., ClNO$_3$ as a buffer).
2. Significant perturbations to emissions can disrupt the balance.
3. As atmospheric loadings of source gases increase, so does the potential for large scale perturbations to ozone.
Excitement in the 80’s

• In the early 1980’s a team of scientists at the British Antarctic Station noticed a dramatic recurring phenomenon during the austral spring (September/October).
• They measured ozone levels much lower than observed before and/or expected. The values were so low they waited a few years to publish! (Farman et al., 1985)
• The popular press labeled the seasonal phenomenon the “Ozone Hole” and the name stuck.
• The paper unleashed a flurry of activity, including re-examination of satellite data, head-scratching and speculation, and numerous measurement campaigns.
Ozone hole observations

• Web sites:
  – http://ozonewatch.gsfc.nasa.gov/
Antarctic Ozone Minimum Values – 1979 - 2005

Antarctic ozone minimum (60° - 90° S)

- 1979-1992 Nimbus 7 TOMS
- 1993-1994 Meteor 3 TOMS
- 1995 (no TOMS in orbit)
- 1996-2004 Earth Probe TOMS
- 2005 OMI
Average (Sep. 7 - Oct. 13) ozone hole area (millions of km²)

1979: 0
1979: 225
2007: 22
2006: 26

Average (Sep. 21 - Oct. 16) minimum ozone (Dobson Units)

1980
1990
2000
1998: 96
2007: 114

Note: No data were acquired during the 1995 season
This year – 2011 – from http://ozonewatch.gsfc.nasa.gov/
Time Series of minimum ozone
Area covered by ozone hole

Average area of ozone hole

Area of North America

Area of Antarctica

Size (million Sq km)

Year

Area of ozone < 220 DU
Average over 30 days
Vertical line = minimum and maximum area
Daily Ozone Hole Area

Ozone Hole Area (40°S - 90°S)

- 1990-2001
- 2002
- 2003
- 2004
- 2005 (OMI)

Area of North America

Area of ozone < 220
Shaded area gives range

Ozone hole area (million km²)

Month
October Monthly Averages – 1979 - 1997

TOMS Total Ozone Monthly Averages

October 79 - October 88

October 89 - October 93

October 94 - October 97

Dobson Units

100 150 200 250 300 450 500
Circumstances surrounding the ozone hole phenomenon

1. “Sets up” during polar night (i.e., hole occurs as region comes out of polar night.
2. Confined to the Polar Vortex (i.e., very cold)
3. Return of the sun in spring triggers ozone loss.
4. Break-up of the polar vortex, and mixing in of non-vortex air restores normal levels of ozone.
Why were we “caught by surprise”?

• The large observed ozone depletions were inconsistent with the \( \text{O}_3 \) chemistry as it had been formulated until then (i.e., with the \( \text{O}_3 \) chemistry we have learned until now).

• The ozone loss rate was very large and dramatic – on the order of 1+\% per day for about six weeks

• Satellite measurements confirmed the phenomenon (as we have seen).

• An extensive ground-based observation campaign was stage in 1986 from McMurdo station in Antarctica. These measurements ruled out some of the proposed explanations. Three were “left standing”.
Ozone Hole Theories

• Chemical Theory I (requires low NO$_X$)
  • ClO dimer mechanism (Molina & Molina, 1987)
    \[
    \text{ClO} + \text{ClO} + \text{M} \rightarrow \text{ClOOCl} + \text{M} \\
    \text{ClOOCl} + \text{hv} \rightarrow \text{Cl} + \text{ClOO} \\
    \text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M} \\
    2[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 ]
    \]
    NET: $2\text{O}_3 + \text{hv} \rightarrow 3\text{O}_2$

• Chemical Theory II (also requires low NO$_X$)
  • ClO-BrO mechanism (McElroy et al., 1986)
    \[
    \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \\
    \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \\
    \text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2 \\
    \]
    NET: $2\text{O}_3 \rightarrow 3\text{O}_2$

* There are three channels for the BrO + ClO reaction. This is the one that is most efficient at destroying ozone.
Ozone Hole Theories (cont.)

• **Dynamical Theories** In these theories, rising motions import air (from the troposphere) with low mixing ratios of ozone into the lower and middle stratosphere. (This could possibly be accompanied by a diminished supply of ozone transported from the equatorial regions.)

• Since the loss rates were so much higher than anything conceived of before, many leading atmospheric chemists believe the dynamical theories were more likely to be correct.
What do the observations show?

• Balloon sondes in 1986 and 1987 showed that the depletion was not uniform, nor was it “from the bottom up”.

• Ozone was being destroyed most dramatically in the 12-22 km range, with little change above and below.

• At some altitudes in this range, there were periods when nearly all of the ozone was “chewed up”.

• Microwave ground-based measurements observed very large levels of ClO in the Antarctic stratosphere.
Balloon Sondes

Hoffmann et al., 1987

Harder et al., 1988
Ozone Depletion over South Pole

Balloon borne ozone profiles measured at South Pole: blue is the average of several profiles measured in September and October during 1967-1971 before the Antarctic ozone hole; red is on the day of the maximum ozone loss in 2001; green is the lowest total ozone recorded in 1986, the first year of CMDL's sounding program at the South Pole. Total column ozone is given in Dobson Units (DU) for each of the profiles.
The animation shows the development of stratospheric temperatures and the Antarctic ozone hole at the South Pole in 2001, starting in January and continuing to the current profile. The measurements were made with balloon-borne ozone instruments launched at regular intervals at the Amundsen-Scott South Pole Station. The animation clearly will show ozone depletion in the September to October period, following sunrise, when ozone in the 6 - 14 mile altitude region is destroyed by chemical reactions involving chlorine and bromine from human-produced chlorofluorocarbons (CFCs). The thermometer gives a measure of the total column of ozone, which is related to the area of the colored portion of the ozone profile, nearly two-thirds of which will be lost. Source: NOAA [http://www.cmdl.noaa.gov/info/ozoneAnim.html](http://www.cmdl.noaa.gov/info/ozoneAnim.html)