Review of Lectures 9 to 13
AOSC 433/633 & CHEM 433/633
Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2013

Today:
• Health affects: i.e., why it is that so much research is funded in this area
• Photolysis and kinetics
• One atmosphere, one chemistry
• Non-linearity of tropospheric ozone production
• Recent improvements in air quality and future challenges

26 March 2013
Biological Effects of UV Radiation (Lecture 10)

Humans are:

- strongly affected by exposure to UV-C radiation (100 to 280 nm)
- moderately affected by exposure to UV-B radiation (280 to 315 nm)
- weakly affected by exposure to UV-A radiation (315 to 400 nm)

The “biologically active dose rate” maximizes in the UV-B region at \( \sim 305 \) nm, where \( \sigma_{O_3} = 3 \times 10^{-19} \) cm\(^2\) \( \Rightarrow \) \( \tau (0 \text{ km}) = 2.4 \) (for \( O_3 \) column= 300 DU)

Fig. 1. Biologically active UV radiation. The overlap between the spectral irradiance \( F(\lambda) \) and the erythemal action spectrum \( B(\lambda) \) gives the biologically active dose rate, \( \int F(\lambda) B(\lambda) \text{ d} \lambda \). The area under the product function \( F(\lambda) B(\lambda) \) is the biologically active dose rate. For a total ozone column of 348 DU.

From Mandronich et al., *J. Photochemistry and Photobiology*, vol. 46, pg. 5, 1998

Air Quality Standards and Why We Care (Lecture 12)

<table>
<thead>
<tr>
<th>Year</th>
<th>Averaging Period</th>
<th>EPA Surface Ozone Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979</td>
<td>1 hr</td>
<td>125 ppb</td>
</tr>
<tr>
<td>1997</td>
<td>8 hr</td>
<td>85 ppb</td>
</tr>
<tr>
<td>2008</td>
<td>8 hr *</td>
<td>75 ppb</td>
</tr>
<tr>
<td>2013 #</td>
<td>????</td>
<td>???</td>
</tr>
</tbody>
</table>

* The 8 hr standard is met when the 3-yr average of the annual 4th highest daily maximum 8 hr O₃ is less than 75 ppb.


Health Affects of Aerosols (Lecture 13)

Bronchi, Bronchial Tree, and Lungs

Alveoli radius ≈ 0.05-0.1 mm

PM10 may fill alveola
PM2.5 can inhibit oxygen exchange within alveola

Leads to increase risk of respiratory illnesses, cardiopulmonary disease, ischemic heart disease, heart attack, etc.

This is without even considering chemical effects
Long-term exposure to air pollution is associated with survival following acute coronary syndrome

Cathryn Tonne and Paul Wilkinson – Feb 19, 2013

"We found that for every 10\(\mu\)g/m\(^3\) increase in PM2.5 there was a 20% increase in the death rate. For example, over one year of follow-up after patients had been admitted to hospital with ACS, there would be 20% more deaths among patients exposed to PM2.5 levels of 20 \(\mu\)g/m\(^3\), compared to patients exposed to PM2.5 levels of 10\(\mu\)g/m\(^3\)."

http://eurheartj.oxfordjournals.org/content/early/2013/02/18/eurheartj.ehs480.full

Health Affects of Surface Ozone and Aerosols

Jerrett et al., 2009


There is biologic plausibility for a respiratory effect of ozone. In laboratory studies, ozone can increase airway inflammation\(^3\) and can worsen pulmonary function and gas exchange.\(^3\) In addition, exposure to elevated concentrations of tropospheric ozone has been associated with numerous adverse health effects, including the induction\(^4\) and exacerbation\(^5\) of asthma, pulmonary dysfunction,\(^6\)\(^8\) and hospitalization for respiratory causes.\(^8\)

In our two-pollutant models, the adjusted estimates of relative risk for the effect of ozone on the risk of death from cardiovascular causes were significantly less than 1.0, seemingly suggesting a protective effect. Such a beneficial influence of ozone, however, is unlikely from a biologic standpoint.

In summary, we investigated the effect of tropospheric ozone on the risk of death from any cause and cause-specific death in a large cohort, using data from 96 metropolitan statistical areas across the United States and controlling for the effect of particular air pollutants. We were unable to detect a significant effect of exposure to ozone on the risk of death from cardiovascular causes when particulates were taken into account, but we did demonstrate a significant effect of exposure to ozone on the risk of death from respiratory causes.
Typical Ozone Profile (Reading, Lecture 2)

Ozone column:
\[ \int_{z_1}^{z_2} [O_3(z)] \, dz \]

Figure Q1-2. Ozone in the atmosphere. Ozone is present throughout the troposphere and stratosphere... Increases in ozone occur near the surface as a result of pollution from human activities.

WMO/UNEP 2010 Ozone Twenty Questions

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Chapman Chemistry (Lecture 9)

• Production of stratospheric \( O_3 \) initiated when \( O_2 \) is photo-dissociated by UV sunlight

• \( O_3 \) formed when resulting \( O \) atom reacts with \( O_2 \):

\[
\begin{align*}
\text{hv} + O_2 & \rightarrow O + O \quad (1) \\
O + O_2 + M & \rightarrow O_3 + M \quad (2)
\end{align*}
\]

• \( O_3 \) removed by photo-dissociation (UV sunlight) or by reaction with \( O \):

\[
\begin{align*}
\text{hv} + O_3 & \rightarrow O + O_2 \quad (3) \\
O + O_3 & \rightarrow O_2 + O_2 \quad (4)
\end{align*}
\]

This reaction sequence was first worked out in the 1930s by Sydney Chapman, an English mathematician and geophysicist.
• The cycling between O and O₂ (rxns 2 and 3) occurs *much* more rapidly than leakage into (rxn 1) or out of the system (rxn 4)

• The sum O + O₃ is commonly called “odd oxygen”

Rxn (1) produces two *odd oxygen* molecules
Rxn (4) consumes two *odd oxygen* molecules
and reactions 2 and 3 recycle *odd oxygen* molecules

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

*O₃* falls off with increasing altitude (high in stratosphere), at a rate determined by \([M]^{3/2}\), because:

*O₃* falls off with decreasing altitude (low in stratosphere) due to a rapid drop in \(J_1\), reflecting:

Observed \([O_3]\) < Chapman \([O_3]\) : why ?!!?
Calculated fraction of odd oxygen loss due to various families of radicals

After Osterman et al., GRL, 24, 1107, 1997;
Sen et al., JGR, 103, 3571. 1998;
Sen et al., JGR, 104, 26653, 1999.

**One Atmosphere – One Photochemistry (Lecture 9)**

**Stratosphere**

HO₂ formation:

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

HO₂ loss:

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

Net:

\[ \text{O}_3 + \text{O}_3 \rightarrow 3\ \text{O}_2 \]

**Troposphere**

HO₂ formation:

\[ \text{OH} + \text{CO} \rightarrow \text{HO}_2 + \text{CO}_2 \]

HO₂ loss:

\[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]

Followed by:

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

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

Net:

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

Above Tropopause:

Lots of \text{O}_3, little \text{CO}

Below Tropopause:

Lots of \text{CO}, little \text{O}_3

Courtesy of Laura Pan, NCAR
Importance of Radicals (Lectures 9 & 10)

• With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical

• Radicals require significant energy to form: a bond must be broken

• Radical formation is tied to absorption of photons that “photodissociate” a compound, leading to radical formation

\[
\text{Initiation} \\
\text{O}_2 + \text{photon} \rightarrow \text{O} + \text{O}
\]

\[
\text{Propagation} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \\
\text{O}_3 + \text{photon} \rightarrow \text{O}(^1\text{D}) + \text{O}_2 \\
\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \\
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2
\]

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

Atmospheric Radiation (Lecture 10)

• Solar irradiance (downwelling) at top of atmosphere occurs at wavelengths between ~200 and 2000 nm (~5750 K “black body” temperature)

Panel (a): Curves of black-body energy versus wavelength for 5750 K (Sun’s approximate temperature) and for 245 K (Earth’s mean temperature). The curves are drawn with equal area since, integrated over the entire Earth at the top of the atmosphere, the solar (downwelling) and terrestrial (upwelling) fluxes must be equal.

Panel (b): absorption by atmospheric gases for a clear vertical column of the atmosphere (1.0 represents complete absorption).

From Houghton, Physics of Atmospheres, 1991

• Absorption and photodissociation in the UV occurs due to changes in the electronic state (orbital configuration) of molecules
Beer-Lambert Law (Lecture 10)

\[ F(z, \lambda) = F_{TOA}(\lambda) e^{-\tau(z, \lambda)} \quad (TOA : \text{Top of Atmosphere}) \]

where:

\[ \tau(z, \lambda) = m \int_z^\infty \sigma_\lambda [C] \, dz' \quad (\tau: \text{optical depth}) \]

- \( F \): solar irradiance (photons/cm\(^2\)/sec)
- \( \sigma_\lambda \): absorption cross section
- \( C \): concentration of absorbing gas (molecules/cm\(^3\))
- \( m \): ratio of slant path to vertical path, equal to \(1/\cos(\theta)\) for \(\theta < \sim 75^\circ\)
- \( \theta \): solar zenith angle

Governs basics of radiative transfer in the UV and near IR regions

Photolysis Frequency (Lecture 10)

For a specific spectral interval, the photolysis frequency (partial \( J \) value) of a gas is given by the product of its absorption cross section and the solar irradiance:

\[ J_{gas}(z, \lambda) = \text{Quantum Yield}(\lambda) \sigma_{gas}(\lambda, T) F(z, \lambda) \]

Units: s\(^{-1}\) nm\(^{-1}\)

The total photolysis frequency (\( J \) value) is found by integrating \( J_{gas}(z, \lambda) \) over all wavelengths for which the gas photodissociates:

\[ J_{gas}(z) = \int_{\lambda_{min}}^{\lambda_{max}} J_{gas}(z, \lambda) \, d\lambda \]

Units: s\(^{-1}\)

Rate of Reaction = \( \frac{dO_3}{dt} = J \, [O_3] \); Units of \( J \) are s\(^{-1}\)

More precisely, calculations of photolysis frequencies consider the “spectral actinic flux”, which represents the amount of available photons integrated over all angles, rather than “solar irradiance”. These two quantities differ because of scattering of solar radiation by gases and aerosols, and reflection of radiation by clouds and the surface.
Admission Ticket Lecture 11

Gibbs Free energy involves both enthalpy and entropy. Briefly describe the relative roles of the change in enthalpy and entropy in affecting the rate of a chemical reaction.

Under what conditions will each term tend to dominate the rate of a chemical reaction.

Briefly: why is kinetic information needed, in addition to thermodynamic information, to quantity our understanding of atmospheric chemistry?
CH$_4$ is lost by reaction with OH (Lecture 6)

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

\[ \frac{d\text{CH}_4}{dt} = \text{Production} - \text{Loss} = \text{Production} - k \left[ \text{OH} \right] \left[ \text{CH}_4 \right] \]

Arrhenius Expression for rate constant:

\[ k = 2.45 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ sec}^{-1} \]

Lifetime of CH$_4$ = \frac{\text{Abundance}}{\text{Loss}} = \frac{[\text{CH}_4]}{k[\text{OH}][\text{CH}_4]} = \frac{1}{k[\text{OH}]} \]

Commonly $T = 272 K$ and $[\text{OH}] = 1 \times 10^6$ molec cm$^{-3}$ are used (see Box 1-3 of http://www.unep.ch/ozone/Assessment_Panels/SAP/Scientific_Assessment_2010/03-Chapter_1.pdf) yielding:

\[ \text{Lifetime of CH}_4 = \frac{1}{3.59 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \cdot 1 \times 10^6 \text{ molecules cm}^{-3}} = \frac{1}{3.59 \times 10^{-9} \text{ s}^{-1}} = 8.9 \text{ yr} \]

Bimolecular Gas Phase Reactions

\[ \begin{align*}
8.9 \text{ kcal/mole} & \quad 35.1 \text{ kcal/mole} \\
-17.8 \text{ kcal/mole} & \quad -57.8 \text{ kcal/mole} \\
\text{OH} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
\Delta \text{Enthalpy} = & \quad -13.8 \text{ kcal/mole} \\
\text{Exothermic!} \\
\end{align*} \]

Rate of Reaction = \frac{d\text{CH}_4}{dt} = k[\text{OH}][\text{CH}_4]

Arrhenius Expression for rate constant:

\[ k = \frac{E_A}{R} \Rightarrow \text{Activation Energy / Gas Constant} \]

\[ k = 2.45 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ sec}^{-1} \]

A factor
Tropospheric Ozone Production (Lecture 12)

\[
\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \\
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

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

\text{NO} \text{ & NO}_2 : \text{Emitted by fossil fuel combustion \& biomass burning}

\[
\text{N}_2 + \text{O}_2 \xrightarrow{\text{High T}} 2 \text{NO}
\]

\text{CO: Emitted by fossil fuel combustion \& biomass burning}

\text{Complete combustion:}

\[
2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O}
\]

\text{Extreme, incomplete combustion:}

\[
2 \text{C}_8\text{H}_{18} + 17 \text{O}_2 \rightarrow 16 \text{CO} + 18 \text{H}_2\text{O}
\]

\text{OH \& HO}_2: ???

Figure 6.19 The time evolution of the principal chemical components of photochemical smog: carbon monoxide (CO), reactive hydrocarbons (HC), nitrogen oxide (NO), nitrogen dioxide (NO₂), peroxyacetyl nitrate (PAN), and ozone (O₃). This behavior of the pollutants is observed during a day in a smoggy city. The sequential appearance of the pollutants is related to the timing of the emissions and rates at which CO, NO, and reactive hydrocarbons are transformed into secondary pollutants by photochemical reactions, as explained in the text.

Turco, Earth Under Siege, 1997
Tropospheric Ozone Production (Lecture 12)

Chain Mechanism for production of ozone

Chemical Initiation: Human emission of NO, CO and either human (RO2) or natural (HO2) hydrogen radicals

Ozone production: $k[\text{HO}_2][\text{NO}]$

Termination: refers to “loss of radicals” in the chain mechanism

Tropospheric Ozone Production versus NO (Lecture 12)

As NOx rises:

$[\text{HO}_2]$ falls faster than [NO] rises,
leading to a decrease in the value of the product of $k \times [\text{HO}_2] \times [\text{NO}]$,
and hence the production rate of O3.

Illustrative calculation of the dependence of O3 production on [NO]

This curve has key policy implications!
Tropospheric Ozone Production versus NO\textsubscript{x} and VOCs (Lecture 12)

Ridge: local maximum for O\textsubscript{3} that separates the NO\textsubscript{x}-limited regime from and VOC limited regime

An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O\textsubscript{3} pollution may have been partly misdirected. Measurements and model calculations now show that O\textsubscript{3} production over most of the United States is primarily NO\textsubscript{x} limited, not hydrocarbon limited. The early models were in error in part because they underestimated emissions of hydrocarbons from automobiles, and in part because they did not account for natural emission of biogenic hydrocarbons from trees and crops.

Jacob, Chapter 12, Introduction to Atmospheric Chemistry, 1999

Day-to-day meteorology (weather!) affects severity and duration of pollution episodes

Maryland has worst air quality during summer, when “Bermuda High” sets up over the Carolinas

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t.
Significant Improvements in *Local* Air Quality since early 1980s

http://www.mde.state.md.us/programs/Air/AirQualityMonitoring/Pages/HistoricalData.aspx

**Probability of Surface O₃ Exceedance:**
**DC, MD, and Northern VA**

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Probability of Surface $O_3$ Exceedance: DC, MD, and Northern VA

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Analysis in this framework motivated by Pusede and Cohen, ACP, 2012
http://www.atmos-chem-phys.net/12/8323/2012/acp-12-8323-2012.html

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Subtropical Jet

Subtropical Jet: area where poleward descending branch of the Hadley Circulation meets the equatorward descending of the Ferrel Cell (see Lecture 3)

Semi-permanent area of high pressure, fair weather, low rainfall:
conditions conducive to high ozone

Climate Change and Air Pollution

Poleward expansion of the sub-tropical jet:

- Surface ozone highs occur along Subtropical Jet
- Number of days Subtropical Jet within 150 miles of Baltimore has increased by ~50% between 1979 and 2003, due to “frontal movement” (expansion of the Hadley Cell)
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics
- As a consequence, models predict increase in severity and duration of surface O$_3$ episodes in the Mid-Atlantic, even for constant emissions
Tropospheric NO$_2$ columns derived from SCIAMACHY measurements, 2004.
The NO$_2$ hot-spots coincide with the locations of the labeled cities.

Herman et al., NCAR Air Quality Remote Sensing from Space, 2006

http://www.doas-bremen.de/lectures/richter_nox_erca_100126.ppt
Change in tropospheric NO$_2$, 2002 minus 1996
GOME: Global Ozone Monitoring Instrument

A. Richter et al., Increase in tropospheric NO$_2$ over China observed from space, *Nature*, 2005

http://www-iup.physik.uni-bremen.de/gome

http://www.doas-bremen.de/lectures/richter_nox_erca_120203.ppt

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Surface O$_3$: Temporal Transition from Local to Regional

Timeseries of top & bottom third monthly average o$_3$ weekend & weekday, hours: 10–19, months: apr to sep

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