Tropospheric Ozone and Air Quality
AOSC 433/633 & CHEM 433
Ross Salawitch

Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2017

Today:
• Tropospheric ozone production mechanism (CO, NO_x, and VOCs)
• Recent improvements of air quality
• Coupling of meteorology, and perhaps climate change, to air quality

Lecture 12
16 March 2017
Student Projects

• **Mandatory for 633 students**: project grade will count towards final grade in an amount equal to each exam

• Due Wednesday, 10 May 2017… 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 topic in which you’ve had prior interest

• ~10 min project presentations 6:30 pm, 10 May: everyone encouraged to attend

• Request all students who will complete a project to provide a 2 to 3 sentence description **2 weeks** from today: *Thurs, 30 March 2017*
  
  Please use next **2 weeks** to speak to me about a project topic

• Finally, I am delighted to provide feedback on your project (paper & presentation) if given the opportunity
Why do we care?

Many thousands of deaths attributed to London Smog of 1952:


http://www.ems.psu.edu/~lno/Meteo437/Smoglond.jpg

Why do we care?

Today, epidemiologists relate many thousands of deaths (annually) to air pollution.

Table 2. Decreases in ozone (the population-weighted annual average 8-h daily maximum) and premature mortalities when European emissions are removed, for eight NH regions.

<table>
<thead>
<tr>
<th>Region</th>
<th>Pop. (millions)</th>
<th>ΔO₃ (ppbv)</th>
<th>Premature mortalities (/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>688.9</td>
<td>6.0</td>
<td>18,800</td>
</tr>
<tr>
<td>Northern Africa</td>
<td>626.4</td>
<td>4.1</td>
<td>10,700</td>
</tr>
<tr>
<td>Near/Middle Eastᵇ</td>
<td>408.6</td>
<td>7.0</td>
<td>8,400</td>
</tr>
<tr>
<td>Former Soviet Unionᶜ</td>
<td>98.7</td>
<td>4.5</td>
<td>1,700</td>
</tr>
<tr>
<td>South Asiaᵈ</td>
<td>1,267.1</td>
<td>0.8</td>
<td>3,800</td>
</tr>
<tr>
<td>East Asiaᵉ</td>
<td>1,518.5</td>
<td>1.4</td>
<td>5,800</td>
</tr>
<tr>
<td>Southeast Asiaᶠ</td>
<td>361.9</td>
<td>0.4</td>
<td>300</td>
</tr>
<tr>
<td>America</td>
<td>578.7</td>
<td>0.9</td>
<td>1,400</td>
</tr>
<tr>
<td>Total Northern Hemisphere</td>
<td>5,548.8</td>
<td>2.5</td>
<td>51,000</td>
</tr>
</tbody>
</table>

ᵃ Regions are defined in only the Northern Hemisphere.
ᵇ Turkey, Cyprus, Israel, Jordan, Syria, Lebanon, countries on the Arabian Peninsula, Iraq, Iran, Afghanistan, and Pakistan.
ᶜ East of 60° E; west of 60° E and north of 44° N is considered part of the “Europe” region.
ᵈ India, Bangladesh, Sri Lanka, Nepal, and Bhutan.
ᵉ Japan, Mongolia, China, Taiwan, North Korea, and South Korea.

Duncan et al., Atmos. Chem. Phys., 2008
Air Quality Standards and Why We Care

<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>2015#</td>
<td>8 hr *</td>
<td>70 ppb</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 70 ppb

# On October 1, 2015 the EPA lowered the NAAQS for ground-level ozone to 70 ppb, based on extensive scientific evidence about the harmful effects of tropospheric ozone

Increased risk of premature mortality for even low levels of surface O₃; further reductions will benefit public health

Bell et al., 2006

http://www.ncbi.nlm.nih.gov/sites/pxmc/articles/PMC1440776
### Criteria Pollutants

**Table 1.2** U.S. National Ambient Air Quality Standards

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Standard (ppm)</th>
<th>Approximate Equivalent Concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon monoxide</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8-hr average</td>
<td>9</td>
<td>10,000</td>
</tr>
<tr>
<td>1-hr average</td>
<td>35</td>
<td>40,000</td>
</tr>
<tr>
<td><strong>Nitrogen dioxide</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual average</td>
<td>0.053</td>
<td>100</td>
</tr>
<tr>
<td><strong>Ozone</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8-hr average</td>
<td>0.075</td>
<td>147</td>
</tr>
<tr>
<td>1-hr average</td>
<td>0.12</td>
<td>235</td>
</tr>
<tr>
<td><strong>Particulates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM₁₀, annual average</td>
<td>—</td>
<td>50</td>
</tr>
<tr>
<td>PM₁₀, 24-hr average</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td>PM₂.₅, annual average</td>
<td>—</td>
<td>15</td>
</tr>
<tr>
<td>PM₂.₅, 24-hr average†</td>
<td>—</td>
<td>35</td>
</tr>
<tr>
<td><strong>Sulfur dioxide</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual average</td>
<td>0.03</td>
<td>80</td>
</tr>
<tr>
<td>24-hr average</td>
<td>0.14</td>
<td>365</td>
</tr>
<tr>
<td>3-hr average</td>
<td>0.50</td>
<td>1,300</td>
</tr>
</tbody>
</table>

*PM₁₀ refers to all airborne particles 10 µm in diameter or less. PM₂.₅ refers to particles 2.5 µm in diameter or less.
—The unit of ppm is not applicable to particulates.
†PM₂.₅ standards are likely to be revised after 2011.

Source: U.S. Environmental Protection Agency. Standards also exist for lead, but are not included here.

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**Chemistry in Context**

**Criteria pollutant:** common-place and detrimental to human welfare

**U.S. NAAQS frequently updated**

http://www.epa.gov/air/criteria.html

← 1 hr 100 ppb is primary standard, Feb 2010

← 8 hr 70 ppb is standard, Oct 2015

← No annual average standard, Dec 2012

← Lowered to 12 µg/m³, Dec 2012

← 1 hr, 75 ppb is primary standard, Jun 2010
Tropospheric Ozone Production

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{NO} + \text{HO}_2 & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

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

**NO & NO\textsubscript{2}:** Emitted by fossil fuel combustion & biomass burning

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

**CO:** Emitted by fossil fuel combustion & biomass burning

Complete combustion:

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

**Extreme, incomplete combustion:**

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

**OH & HO\textsubscript{2}:** ?????
Suppose NO is converted to NO$_2$ by reaction with O$_3$:

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

Net:
Tropospheric Ozone Production

\[
\begin{align*}
OH + CO &\rightarrow CO_2 + H \\
H + O_2 + M &\rightarrow HO_2 + M \\
HO_2 + NO &\rightarrow OH + NO_2 \\
NO_2 + h\nu &\rightarrow NO + O \\
O + O_2 + M &\rightarrow O_3 + M \\
\text{Net:} &\quad CO + 2 O_2 \rightarrow CO_2 + O_3
\end{align*}
\]

Chain Mechanism for production of ozone

Chemical Initiation: \( H_2O+O(1D) \rightarrow 2OH \) & human emission of NO, CO

Since method for conversion of NO to NO\(_2\) is crucial for whether \( O_3 \) is produced by this chain mechanism, chemists consider production of tropospheric ozone to be “limited” by \( k[HO_2][NO] \)
Tropospheric Ozone Production

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

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

\[
\begin{align*}
\text{RH} + \text{OH} & \rightarrow \text{R} + \text{H}_2\text{O} \\
\text{R} + \text{O}_2 + \text{M} & \rightarrow \text{RO}_2 + \text{M} \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \\
\text{RO} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{R’CHO} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{OH} + \text{NO}_2 \\
2\times \text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
2\times \text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

\[
\text{Net: } \text{RH} + 4\text{O}_2 \rightarrow \text{R’CHO} + \text{H}_2\text{O} + 2\text{O}_3
\]

**VOC: Volatile Organic Compounds**

Produced by trees and fossil fuel vapor

Strong source of HO\textsubscript{x} (OH & HO\textsubscript{2}) & O\textsubscript{3} (depending on NO\textsubscript{x} levels)

Examples of RH and R’CHO:
- CH\textsubscript{4} (methane) $\rightarrow$ CH\textsubscript{2}O (formaldehyde)
- C\textsubscript{2}H\textsubscript{6} (ethane) $\rightarrow$ CH\textsubscript{3}CHO (acetaldehyde)
- C\textsubscript{3}H\textsubscript{8} (propane) $\rightarrow$ CH\textsubscript{3}COCH\textsubscript{3} (acetone)

Ozone Production “limited” by $k[\text{HO}_2][\text{NO}] + \sum k_i [\text{RO}_2]_i [\text{NO}]$
Tropospheric Ozone Production

\[
\begin{align*}
CO + OH & \rightarrow CO_2 + H \\
H + O_2 + M & \rightarrow HO_2 + M \\
HO_2 + NO & \rightarrow OH + NO_2 \\
NO_2 + hv & \rightarrow NO + O \\
O+ O_2 + M & \rightarrow O_3 + M \\
\text{Net: } CO + 2 O_2 & \rightarrow CO_2 + O_3
\end{align*}
\]

\[
\begin{align*}
RH + OH & \rightarrow R + H_2O \\
R + O_2 + M & \rightarrow RO_2 + M \\
RO_2 + NO & \rightarrow RO + NO_2 \\
RO + O_2 & \rightarrow HO_2 + R’CHO \\
HO_2 + NO & \rightarrow OH + NO_2 \\
2 \times NO_2 + hv & \rightarrow NO + O \\
2 \times O+ O_2 + M & \rightarrow O_3 + M \\
\text{Net: } RH + 4O_2 & \rightarrow R’CHO + H_2O + 2 O_3
\end{align*}
\]

Chain Mechanism for production of ozone

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

Ozone production: \( k[HO_2][NO] \)

Termination: can occur via either:

\[
\begin{align*}
HO_2 + HO_2 & \rightarrow H_2O_2 + O_2 \\
\text{or} \\
OH + NO_2 + M & \rightarrow HNO_3 + M
\end{align*}
\]
Tropospheric Ozone Production versus NO

As NO\textsubscript{x} rises:

\([\text{HO}_2]\) falls faster than [NO] rises,
leading to a decrease in the value of the product of k [HO\textsubscript{2}] [NO],
and hence the production rate of O\textsubscript{3}.

![Illustrative calculation of the dependence of O\textsubscript{3} production on [NO]](image)

\textit{This curve has key policy implications!}
An important discovery in the past decade is that the focus on hydrocarbon emission controls to combat O$_3$ pollution may have been partly misdirected. Measurements and model calculations now show that O$_3$ production over most of the United States is primarily NO$_x$ 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

Figure: http://www-personal.umich.edu/~sillman/ozone.htm
Temperature Inversions and Air Quality

Temperature inversion: increase in temperature with height

Inversions important for Air Quality because they inhibit vertical mixing of air

Air pollutants can accumulate in cities ringed by mountains, such as Los Angeles, Mexico City, and Salt Lake City.
Temperature Inversions and Air Quality

Temperature inversion: increase in temperature with height

Inversions important for Air Quality because they inhibit vertical mixing of air

Air pollutants can accumulate in cities ringed by mountains, such as Los Angeles, Mexico City, and Salt Lake City

Figure 1.10, Chemistry in Context

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

Probability of ozone exceedance vs. daily max. temperature

Why does probability of high ozone rise with increasing temperature?

Lin et al. 2001
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

http://www.mde.state.md.us/assets/document/BJH%20-%20Basics%20on%20Ozone%20Transport.ppt
Day-to-day meteorology (weather!) affects severity and duration of pollution episodes.
Significant Improvements in U.S. Air Quality, Past 3 Decades

Figure 1.8, Chemistry in Context
Significant Improvements in U.S. Air Quality, Past 3 Decades

CO Air Quality, 1980 - 2015
(Annual 2nd Maximum 8-hour Average)
National Trend based on 69 Sites

NO2 Air Quality, 1980 - 2015
(Annual 98th Percentile of Daily Max 1-Hour Average)
National Trend based on 26 Sites

SO2 Air Quality, 1980 - 2015
(Annual 99th Percentile of Daily Max 1-Hour Average)
National Trend based on 45 Sites

Ozone Air Quality, 1980 - 2015
(Annual 4th Maximum of Daily Max 8-Hour Average)
National Trend based on 212 Sites

http://www.epa.gov/airtrends

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Significant Improvements in U.S. Air Quality, Past 3.5 Decades

https://www.epa.gov/air-trends/air-quality-national-summary
Removal of NO\textsubscript{x} from Power Plants

**NO\textsubscript{x} Control:**

- **SCR Selective Catalytic Reduction**

  \[
  4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
  6\text{NO}_2 + 8\text{NH}_3 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}
  \]

  **Catalyst**
  - Maximize NO\textsubscript{x} \rightarrow N\textsubscript{2}
  - Minimize SO\textsubscript{2} \rightarrow SO\textsubscript{3}

  Slide courtesy John Sherwell, Md Dept of Natural Resources
Removal of $\text{NO}_x$ from Power Plants

Figure 2. The trends in summertime (June–August) mean $\text{NO}_2$ columns from the GOME and SCIAMACHY satellites and the bottom-up $\text{NO}_x$ emission rates in the Ohio River Valley and the northeast U.S. urban corridor during 1997–2005. SCIAMACHY data are used for 2003–2005, while GOME data are utilized for the earlier period. Data are normalized to 1999 values.

Kim et al., GRL, 2006
Dramatic Improvements California Air Quality, Past 4 Decades

Southern California

Data from http://www.aqmd.gov

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Dramatic Improvements Local Air Quality, Past 4 Decades
Dramatic Improvements Local Air Quality, Past 4 Decades

Days Exceeding 2008 EPA Std (8 hr $O_3 > 75$ ppb)

Maryland Dept of the Environment

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Dramatic Improvements Local Air Quality, Past 4 Decades

Days Exceeding 2015 EPA Std (8 hr O₃ > 70 ppb)

Maryland Dept of the Environment

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

Figures above research product of UMCP Graduate Student Sandra Roberts
Reformulated Gasoline 1990 CAAA Phase 1

Catalytic Converters Mandatory

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

Figures above research product of UMCP Graduate Student Sandra Roberts
Probability of Surface $O_3$ Exceedance (DC, MD, No. VA) vs Daytime NO$_2$
Hot Summer Days ($T_{BWl} > 90^\circ F$)

Figure above research product of UMCP Graduate Student Sandra Roberts

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

Figures above research product of UMCP Graduate Student Sandra Roberts
Nitrogen Dioxide (NO₂): Combustion product that leads to formation of tropospheric ozone

Value in 2011 minus value in 2006

Δ VCD\textsubscript{trop} NO₂ [10\textsuperscript{14} molec cm\textsuperscript{-2} yr\textsuperscript{-1}]

-12 -9 -6 -3 0 3 6 9 12

Value in 2011 minus value in 2006

Δ VCD\textsubscript{trop} NO₂ [10\textsuperscript{14} molec cm\textsuperscript{-2} yr\textsuperscript{-1}]

-6.0 -4.5 -3.5 -2.5 -1.5 -0.5 0.5 1.5 2.5 3.5 4.5 6.0

Hilboll et al., ACP, 2013
US Trends: NO$_2$ and SO$_2$

Krotkov et al., ACP, 2016
China Trends: NO$_2$ and SO$_2$

Krotkov et al., ACP, 2016
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”
- Driving force: weakening of the equator to pole temperature gradient, caused by more rapid warming at high latitudes compared to tropics

Seidel et al., *Nature Geoscience*, 2008

- Computer models predict increase in severity and duration of pollution episodes over Midwest, Mid-Atlantic, and Northeast U.S. in 2050, even for constant emissions