Urban Air Pollution

• Smog- Complex mixture of hydrocarbon, nitrogen oxides, ozone, and submicrometer particles.
• A useful reference point for Smog $[O_3]>0.15$ ppm for one hour.
• The natural ambient air quality standard for ozone is 0.12 ppm (three times a year). Between 1983-85, 76 urban area were in VIOLATION.
• $O_3$ is the most difficult pollutant to control.
### Current standards

#### National Ambient Air Quality Standards

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Primary Standards</th>
<th>Secondary Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Level</td>
<td>Averaging Time</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>9 ppm (10 mg/m³)</td>
<td>8-hour&lt;sup&gt;(1)&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>35 ppm (40 mg/m³)</td>
<td>1-hour&lt;sup&gt;(1)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Lead</td>
<td>1.5 µg/m³</td>
<td>Quarterly Average</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>0.053 ppm (100 µg/m³)</td>
<td>Annual (Arithmetic Mean)</td>
</tr>
<tr>
<td>Particulate Matter (PM&lt;sub&gt;10&lt;/sub&gt;)</td>
<td>150 µg/m³</td>
<td>24-hour&lt;sup&gt;(2)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Particulate Matter (PM&lt;sub&gt;2.5&lt;/sub&gt;)</td>
<td>15.0 µg/m³</td>
<td>Annual (Arithmetic Mean)</td>
</tr>
<tr>
<td></td>
<td>35 µg/m³</td>
<td>24-hour&lt;sup&gt;(4)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.075 ppm (2008 std)</td>
<td>8-hour&lt;sup&gt;(5)&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.08 ppm (1997 std)</td>
<td>8-hour&lt;sup&gt;(6)&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>0.12 ppm</td>
<td>1-hour&lt;sup&gt;(7)&lt;/sup&gt; (Applies only in limited areas)</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>0.03 ppm</td>
<td>Annual (Arithmetic Mean)</td>
</tr>
<tr>
<td></td>
<td>0.14 ppm</td>
<td>24-hour&lt;sup&gt;(1)&lt;/sup&gt;</td>
</tr>
</tbody>
</table>
\[ \text{NO} \quad \rightarrow \quad \text{NO}_2 \quad \xrightarrow{\text{hv}} \quad \text{O}_3 \quad \xrightarrow{\text{fast}} \quad \text{O}_2 \quad \xrightarrow{\text{R}_2} \quad \text{O}\]
\[ R_1 = k_1[\text{NO}_2] \]
\[ R_2 = k_2[\text{O}_3][\text{NO}] \]

@ SS, \( R_1 = R_2 \)
\[ k_1[\text{NO}_2] = k_2[\text{O}_3][\text{NO}] \]
\[ [\text{O}_3] = \frac{k_1[\text{NO}_2]}{k_2[\text{NO}]} \]
Lets add organic carbon to the mix

- $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$
- $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{OO} + \text{M}$ (peroxy radical)
- $\text{CH}_3\text{OO} + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{O}$
- $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$
- $\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH}$ (NO$_2$ is a source of O$_3$)
- $\text{CH}_2\text{O} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HCO}$
- $\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}$ (HO$_2$, CO are sources of O$_3$)
\[ R_1 = k_1[\text{NO}_2] \]
\[ R_2 = k_2[\text{O}_3][\text{NO}] \]

\[ \text{at SS, } R_1 = R_2 \]

\[ k_1[\text{NO}_2] = k_2[\text{O}_3][\text{NO}] \]

\[ [\text{O}_3] = \frac{k_1[\text{NO}_2]}{k_2[\text{NO}]} \]
Let's put this chemistry into perspective
What do we need for SMOG?

- Sun
- Warm Temperature
- Hydrocarbons
- NOx - Combustion processes
1-5 hour
O_3, reactive organics, aldehydes, olefins

5-10 hour
other organics

NO_2 + OH \rightarrow HNO_3

1 hour
increase in OH, NO, NO_2, hydrocarbons

NOx + Hydrocarbons
General Diurnal Variation of Pollutants
Not all Hydrocarbons emissions have the same effect!

Advancing the understanding of ground-level ozone pollution

by Tom Ryerson, Aeronomy Laboratory

Research led by scientists at the NOAA Aeronomy Laboratory has illustrated two major factors that could be used to help guide future programs designed to clean up the air downwind of the Nation's fossil-fuel burning electric power plants: the size of the power plant, and the location of the power plant.

These power plants emit about one-quarter of the total U.S. human-made contribution of nitrogen oxides, or NOx, to the atmosphere.
many steps

\[ R_1 = k_1[NO_2] \]
\[ R_2 = k_2[O_3][NO] \]

@ SS, \( R_1 = R_2 \)

\[ k_1[NO_2] = k_2[O_3][NO] \]

\[ [O_3] = \frac{k_1[NO_2]}{k_2[NO]} \]
**Fig. 4.7** Peak ozone isopleths generated under controlled conditions as calculated using an EKMA (empirical kinetic modelling approach). (Redrawn from Finlayson-Pitts, B. J. and J. N. Pitts Jr; see note 6.)
Thomas Hill, MO
Megan L. Melamed ‘00

- MIDAS: miniature differential absorption spectroscopy
- Background spectrum from clear air in the stratosphere.
- Foreground spectrum measures NO₂ concentrations in polluted air
- By knowing angle between the flight direction and the wind direction and the wind and flight velocities, they can determine the point source of NO₂

\[ \text{MIDAS}_{-\text{NO}_2}_{-\text{Flux}} = v(\text{flightspeed}) \cos \alpha \int_{t_1}^{t_2} (\text{NO}_2 \text{vertical}_\text{column}) dt \]

Figure 4. Diagram representing the slant column measurements taken by MIDAS from aircraft.

Melamed, M.L., et. al. “Measuring reactive nitrogen emissions from point sources using visible spectroscopy from aircraft.” 

Rose Becker, Lauren Brown, Danny Lin, Megan Watts
Tim Bertram’s Work with Laser-Induced Fluorescence (LIF) Instrument

Evan Kaplan, Morgan Davies, Rachel Terry, Carolyn Litty
(left) Example of flight track (blue line) which sampled plumes from power plants of different NOx emission rates. Measurements (black and red lines) superimposed on the track show where the plumes were encountered.

(right) Ozone is formed more slowly and in lower yield when NOx concentrations are very high or when reactive VOC concentrations are very low, as shown here by contrasting data from three different power plant plumes.

http://www.oar.noaa.gov/spotlite/archive/spot_ozone.html
Fig. 4.7 Peak ozone isopleths generated under controlled conditions as calculated using an EKMA (empirical kinetic modelling approach). (Redrawn from Finlayson-Pitts, B. J. and J. N. Pitts Jr; see note 6.)
Implications for air quality in the U.S.

The U.S. is considering a policy to reduce ozone pollution that would require reductions in NOx emissions from power plants, whereby the overall amount of NOx emitted is decreased, but individual power plants could freely trade emission credits to minimize costs. This NOAA research suggests that emission trading strategies that value all NOx emissions equally might not be optimal with respect to air quality. *There could be* "good-for-air-quality" *trades that result in less ozone pollution, such as trades that move NOx emissions away from high-VOC forested regions, or trades that shift emissions from smaller power plants to larger ones. However, there could also be* "bad-for-air-quality" *trades that actually result in more ozone pollution being produced*, despite a reduction in the overall amount of NOx emitted. In addition, this new NOAA information is also important input into considerations of the location and size of planned new fossil-fuel electric power plants.

http://www.oar.noaa.gov/spotlite/archive/spot_ozone.html
Traditional and High Risk Air Quality Measurements

Traditional Measurements:
- Ambient air measurements – measured in ppm (0.12 ppm+ considered unhealthy for anyone)
- Measurement of trends – higher concentration in summer and downwind of cities.

High risk:
- Measured in terms of exposure risk
- Groups such as children, people with respiratory diseases and highly active people are more susceptible to ozone exposure – concentrations as low as 0.065 may affect some sensitive people
- Cities (pop 350,000+) must report when AQI is above standard levels
- Time spent outdoors or active when AQI is above certain levels should be limited

Air Quality Index (AQI)
- Color-coded index representing levels of ozone and other pollutants
- AQI value of 100 (0.084 ppm pollutants) represents NAAQS standard

- [EPA’s AIRNow map](#)
- [UNH AirMap](#)
Air Mass Modeling in the Troposphere

Main pollutants modeled
- Tropospheric Ozone
- Nitrous Oxides
- Carbon Monoxide
- VOC
- Particulate Matter

Policy/Regulation
- Health Concerns
- Emissions Control
- Industrial Certification
- Accuracy

Why is modeling important?
- Modeling forecasts the direction and rates that pollution will travel given weather, distance, and emission rates.
- Potential industrial/chemical disasters and environmental effects
- Natural disasters (volcanic activity)
What else is needed?

http://www.arl.noaa.gov/ready/hysplit4.html
How to read the trajectory maps

The HYSPLIT trajectory map shows an aerial (plan) view of the path(s) an air parcel(s) took, and a vertical view of its movement at different altitudes. Symbols are used along each trajectory to indicate the position of the air parcel over the calculational period, the interval of which can be defined by the user.

The vertical view at the bottom of the map shows the height of the air parcel measured at these corresponding tick marks. The height of the air parcel is measured in meters above model ground level (AGL).

http://www.arl.noaa.gov/ready/hyp_info.html#INFO
http://www.arl.noaa.gov/ready/open/hysplit4.html
Particulate Matter (PM)

DEFINITION
• The term for particles found in the air, including dust, dirt, soot, smoke, and liquid droplets. The size, length of time in the atmosphere, and sources of these particles vary.

CONCERNS
• PM is the cause of many health problems, especially among people with lung and heart problems.
• Harms the environment by settling on land and soil and changing the chemical balance. (ex. Making lakes acidic, stripping soil of nutrients)

REGULATIONS MADE BY EPA
• Passed new emission standards for diesel engines in 1994, reducing PM emissions by 90 percent.
• Issued visibility protection regulations in 1999 to reduce haze and erosion, which involved cooperative efforts by states to reduce the amount of PM produced.
• The EPA is currently collecting data from various areas and plans to release final PM$_{2.5}$ designations in December of this year. (PM$_{2.5}$ is particle matter 2.5 microns or smaller in diameter.)

• [http://www.epa.gov/pmdesignations/documents/Mar07/factsheet.htm](http://www.epa.gov/pmdesignations/documents/Mar07/factsheet.htm)

Source: www.epa.gov
Particles in the Atmosphere

- Aerosols: solids and liquids 100 µm ---> 0.5 mm (sand)
- Particles: 1 nm (cluster) ---> 100 µm.
- Particulate material make up most of the visible form of pollution.
- Important in cloud formation, fog formation, heat balance
Atmospheric Chemical Processes involving particles

This is a particle!

Condensation

H₂O
Atmospheric Chemical Processes
involving particles

Solution phase reactions
HCl + NH₃ --> NH₄Cl

Photochemical processes (R*)

Condensation

H₂O
Atmospheric Chemical Processes involving particles

Evolution of volatile species (hydrocarbons)

Solution phase reactions
\[ \text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl} \]

Gas/solid reactions
\[ \text{CaO}(s) + \text{SO}_2(g) \rightarrow \text{CaSO}_3(s) \]

Condensation

Photochemical processes (R*)

Catalytic surface reactions
\[ \text{A} + \text{B} \]

AB

\[ \text{H}_2\text{O} \]
Types of particles

- Transient nuclei (AIKEN) particles 2 nm ---> 0.1 µm
  - formed from gas phase condensation (hot vapor)
  - removed by accumulation

- Accumulation range particles 0.1 µm ----> 1 µm
  - formed from low volatility gases and accumulation processes
  - removed by rain
  - these particles do not “settle out of the atmosphere”

\[
\begin{align*}
CaCO_3 + \text{heat} & \Rightarrow CaO + CO_2 \\
Pb(C_2H_5)_4 + O_2 + \text{halogens} & \Rightarrow CO_2 + H_2O + PbCl_2 \\
2SO_2 + O_2 + 2H_2O & \Rightarrow 2H_2SO_4
\end{align*}
\]
• **Course or Mechanically generated particles 1-100 μm.**
  - dust, sea spray, industrial grinding
  - removed by sedimentation
Particles in the atmosphere
FIGURE 12.8. Number, surface, and volume distributions for a typical urban model aerosol (from Whitby and Sverdrup, 1980).
Why do we care about particle size

- Health implications
- Transport
- Reactivity
- Information on source functions

- How do we measure particle sizes
Cascade Impactor Design
Where do the particles GO?

Stage 1 (5-9)
Stage 2 (5-6)
Stage 3 (4-5)
Stage 4 (2-3)
Stage 5 (1-2)
Stage 6 (0.5-1)

(Diameter in µM)
Natural versus anthropogenic emissions of trace metals to the atmosphere

<table>
<thead>
<tr>
<th>Trace Metal</th>
<th>Anthropogenic</th>
<th>Natural</th>
<th>Natural/total</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>19</td>
<td>12</td>
<td>0.39</td>
</tr>
<tr>
<td>Cd</td>
<td>7.6</td>
<td>1.3</td>
<td>0.15</td>
</tr>
<tr>
<td>Cr</td>
<td>30</td>
<td>44</td>
<td>0.59</td>
</tr>
<tr>
<td>Hg</td>
<td>3.6</td>
<td>2.5</td>
<td>0.41</td>
</tr>
<tr>
<td>Pb</td>
<td>332</td>
<td>12</td>
<td>0.04</td>
</tr>
<tr>
<td>V</td>
<td>86</td>
<td>28</td>
<td>0.25</td>
</tr>
</tbody>
</table>

(units 10⁹ g/yr)
Organics on Particles (PAH)

benzo[a]pyrene

benzo[a]pyrene-7,8-dihydrodiol-9,10-dihydroepoxide
Asbestos - Fear and Panic

• What is asbestos?

• Two major types:
  – Serpentine(90%) - fiber bundles (Chrysotile Mg₆Si₄O₁₀(OH)₈
  – Amphiboles(10%) - rods (Crocidolite Na₂(Fe³⁺)₂(Fe²⁺)₂Si₈O₂₂(OH)₂)

• Proven carcinogen since 1900’s based on lung tumors in asbestos mine workers

• QUESTION: Does the carcinogenicity apply to the general population? POLICY <-> SCIENCE
Asbestos

• Why do we use asbestos?
  – fireproofing
  – insulation
  – cement construction
  – friction materials
  – sealants

• Different types of fibers differ in chemical composition, morphology, durability!

• -each fiber type must be considered independently
Does it Kill You?

• Yes...but, many questions are unanswered.
• The relationship between exposure and lung cancer is approximately linear, but the slope is a function of type and industrial usage!
• Chrysotite at current occupational levels may not be dangerous (90% of asbestos).
• The US does not differentiate between fibers, Europe does!
• Cost! EPA expects asbestos removal in 733,000 buildings in the next 30 years
  • $53 - $150 billion dollars!
Risk: What are the concentrations?

<table>
<thead>
<tr>
<th>Statistic</th>
<th>Schools</th>
<th>Outdoor air</th>
<th>Public Buildings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>0.00000</td>
<td>0.00040</td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>0.00024</td>
<td>0.00039</td>
<td>0.00059</td>
</tr>
<tr>
<td>SD</td>
<td>0.00053</td>
<td>0.00198</td>
<td>0.00052</td>
</tr>
</tbody>
</table>

(fibers/cm\(^3\) air)

The current EPA Limit is 0.2-2 fibers/cm\(^3\)!
# Risk: How bad is the problem?

<table>
<thead>
<tr>
<th>Cause</th>
<th>Annual rate (death/10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whooping cough vaccination (1970-1980)</td>
<td>1-6</td>
</tr>
<tr>
<td>Aircraft accidents</td>
<td>6</td>
</tr>
<tr>
<td>High School football</td>
<td>10</td>
</tr>
<tr>
<td>Drowning (age 5 to 14)</td>
<td>27</td>
</tr>
<tr>
<td>Hit by car (age 5 to 14)</td>
<td>32</td>
</tr>
<tr>
<td>Long-term smoking</td>
<td>1200</td>
</tr>
<tr>
<td>Asbestos exposure in schools</td>
<td>0.005-0.093</td>
</tr>
</tbody>
</table>