Smog

Livin’ ’n Dyin’ in L.A.

... and in London
Urban Smog

• History of Smog
• Smog Photochemistry
  ➔ Definitions
  ➔ Null Cycle
  ➔ Role of Volatile Organic Compounds
Smog in L.A.

- The South Coast Air Basin (SCAB)
- Regulation in the SCAB
- Alerts and Advisories
  - Health Effects from Exposure
  - Alert Stages
  - Air Quality Index (AQI)
- Control of Smog
  - Emission Control Technology
  - Air Quality Trends
From Wood to Coal to Gasoline

• Iron/Bronze Ages
  → Ore smelting requires source of heat: wood or charcoal fires

• Middle Ages (12th–13th c.)
  → Wood becoming scarce
  → Imported coal became primary fuel
“London by reason of the excessive coldness of the air, hindering the ascent of the smoke, was so filled with the fuliginous [sooty] steam of sea-coal, that hardly could one see across the street, and this filling the lungs with its gross particles exceedingly obstructed the breast, so as one would scarce breathe.” —Diary, 1684
“It goes so heavily with my disposition, that … this most excellent canopy, the air, look you, this brave o’er-hanging firmament this mystical roof fretted with golden fire—why, it appears no other thing to me but a foul and pestilent congregation of vapours.”

—*Hamlet* (Shakespeare)
Industrial Era

• Machines powered by steam engines—running on coal
  → “smog” = coal smoke + fog
  → 1840s: Legislation considered to regulate smoke emissions in England

• In U.S. (pre-1940), most coal smoke regulations done by individual cities
• 1948: Coal smog in Donora, PA killed 20

• 1952: Coal smog in London killed 4,000... led to legislation to reduce coal consumption
The “Gasoline Age”

- Early: invention of automobile and the internal combustion engine, running on gasoline or diesel fuel

→ Photochemical “smog” in Los Angeles
• 1947: Air Pollution Control District (APCD)
• 1954: Backyard trash incinerators banned
• 1952: Arie Haagen-Smit (CalTech) found how photochemical smog formed from automobile exhaust
London vs. LA. Smog

**Coal smoke + fog**

\[ \text{sm + og: Harold Des Voeux (1905)} \]

\[ \text{SO}_x + \text{H}_2\text{O} \rightarrow \cdots \rightarrow \text{H}_2\text{SO}_4 \]

- Cool, foggy weather
- From coal combustion

**Photochemical**

\[ \text{NO}_x + \text{sunlight} \rightarrow \cdots \rightarrow \text{O}_3 \]

- Warm, sunny weather
- From transportation exhaust, light industry
Definitions

**Primary Pollutant**
- Emitted directly into the air
  - Carbon monoxide (CO)
  - Oxide of nitrogen (NO\textsubscript{x})
  - Reactive Organic Gas (ROG)

**Secondary Pollutant**
- Produced by chemical reactions in the air
  - Ozone (O\textsubscript{3})
  - Nitrogen dioxide (NO\textsubscript{2})
  - Peroxyacetyl Nitrate (PAN)
Photodissociation

Chemical reaction where a reactant absorbs a photon of radiation and splits apart

Volatile Organic Compound (VOC)

Organic compound that evaporates at room temperature

Reactive Organic Gas (ROG)

A type of VOC that reacts easily in the atmosphere (ex.: gasoline, alcohol)
L.A. Smog Photochemistry

Preliminary—slow reaction: $\text{NO} + \text{O}_2 \rightarrow \cdots \rightarrow \text{NO}_2$

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

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

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

“Null Cycle”
Null Cycle

NO

O

O_2

O_3

NO_2
• Null cycle: ozone is destroyed about as fast as it is produced
  ➔ Small steady-state ozone concentration

• But: ozone builds up in concentration during the afternoon
  ➔ ??
ROGs in Smog

ROG made up of: reactive part ("radical") $R\cdot$ and hydrogen (H)

\[ \text{RH + \cdots} \rightarrow \cdots \rightarrow \text{RO}_2\cdot \]

Alkyl peroxy radical
\[
\text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O}
\]
\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

\[
\text{NO} + \text{RO}_2 \cdot \rightarrow \text{NO}_2 + \text{RO} \cdot
\]

Replaces \( \text{O}_3 \) as the NO oxidizer
“ROG Cycle”

\[
\begin{align*}
\text{NO}_2 & \rightarrow \text{O}_3 \\
\text{O}_3 & \rightarrow \text{RO}^+ \\
\text{RO}^+ & \rightarrow \text{RO}_2^+ \\
\text{RO}_2^+ & \rightarrow \text{NO} \\
\text{NO} & \rightarrow \text{O}_2 \\
\text{O}_2 & \rightarrow \text{NO}_2
\end{align*}
\]
Where does RO• Go?

\[
\text{RO}\cdot + \text{NO}_2 + \cdots \rightarrow \cdots \rightarrow \text{PAN}
\]

PAN = family of Peroxyacetyl Nitrate compounds

⇒ Mixing ratio \(\sim\) 10 ppbv causes lachrymation
The South Coast Air Basin

• “SCAB”

→ Includes parts of Los Angeles, Orange, Riverside, and San Bernardino Counties

→ Bounded by mountains along the north and east and ocean along the west and south
Regulation in the SCAB

• 1947: Los Angeles Air Pollution Control District (APCD) founded
• 1952: Haagen-Smit linked automotive emissions to photochemical smog
• 1959: California Motor Vehicle Pollution Control Board
  ➡ Positive Crankcase Ventilation (PCV) mandated for 1963
1960: Prototype NOx control via Exhaust Gas Recirculation (EGR)

• **Clean Air Act of 1963**
  - Federal government can regulate interstate pollution
  - Emission standards on stationary sources, but not automobiles
• 1966: California Motor Vehicle Pollution Control Board adopts first-in-nation tailpipe emission standards for hydrocarbons and carbon monoxide

• 1967: California Air Resources Board (CARB) established

  ➔ Merged CMVPCB and Bureau of Air Sanitation

• 1969: Emission standards criteria pollutants in California (nationally in 1970 by CAAA70)
Clean Air Act Amendments of 1970 (CAA70)

• Environmental Protection Agency (EPA) created
  ➔ National Ambient Air Quality Standards (NAAQS)
  ➔ Protects public health and welfare

• Criteria pollutants specified:
  • Carbon monoxide (CO)
  • Nitrogen dioxide (NO₂)
  • Sulfur dioxide (SO₂)
  • Total Suspended Particulate (TSP)
  • Hydrocarbons (HC)
  • Oxidants
• 1976: APCD upgraded to South Coast Air Quality Management District (SCAQMD)
  ➡ Mandatory participation by urban LA, San Bernardino, Riverside, and Orange Counties (i.e., the SCAB)

• 1990: Air Quality Management Plan (AQMP) implemented by SCAQMD
  ➡ 120+ control measures to limit total emissions of ROGs, CO, NOx
Clean Air Act Revision of 1997

• New NAAQS for ozone and particulate matter

➡ Eight-hour average concentration instead of one-hour average for ozone

➡ New PM2.5 standard (previous was only PM10)
Health Effects of Carbon Monoxide

% COHb (in blood)

1.5 10 ppmv CO exposure for 8 hours

2 Impaired ability to estimate time intervals

5 Night vision impaired, mental acuity reduced

10 Motor skills impaired

Cigarette smokers: typical blood COHb 5–15%
Health Effects of Ozone

ppmv

0.02  Odor threshold (acrid/sweet smell)

0.10  Nose/throat irritation in sensitive people

0.30  Nose/throat irritation in most people

1.0   Airway resistance; headache; sleep difficulties
SCAB Alert Levels for $O_3$

Stage 1  0.20 ppmv, 1 hr. average
Stage 2  0.35 ppmv, 1 hr. average
Stage 3  0.50 ppmv, 1 hr. average

NAAQS: 0.08 ppmv  (8 hr. average)

Calif. Clean Air Standard: 0.07 ppmv  (8 hr. average)
Air Quality Index (AQI)

A numerical scale vs. air quality criteria, normalized for different pollutants
<table>
<thead>
<tr>
<th>AQI</th>
<th>Criterion level</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–50</td>
<td>Good</td>
<td>Reference level; no harm</td>
</tr>
<tr>
<td>51–100</td>
<td>Moderate</td>
<td>Sensitive people affected</td>
</tr>
<tr>
<td>101–150</td>
<td>Unhealthy for sensitive groups</td>
<td>Sensitive people harmed</td>
</tr>
<tr>
<td>151–200</td>
<td>Unhealthy</td>
<td>All people harmed</td>
</tr>
<tr>
<td>201–300</td>
<td>Very unhealthy</td>
<td>Avoid outdoor activity</td>
</tr>
<tr>
<td>301–500</td>
<td>Hazardous</td>
<td>Everyone inside!</td>
</tr>
</tbody>
</table>
• Need to find where the primary pollutants come from, then devise strategic plan to control sources
Control Measures

• Carbon monoxide (CO)
  → Improve combustion of gasoline in automobiles (more CO₂ emissions, less CO): oxygenation additives
  • MTBE
  • Ethanol, methanol
  → Automotive emission control devices, such as the catalytic converter

• Oxides of nitrogen (NOₓ)
  → Automotive emission control devices, such as the catalytic converter
  → ZEV, PZEV, or SULEV (also reduces CO)
Control of ROGs

- Substantial stationary source, so must control both mobile and stationary

- Mobile controls
  - Vapor recovery nozzles at filling stations
  - Auto emission control devices
  - Switch to non-VOC fuel like compressed natural gas (CNG) or propane
  - ZEV, PZEV, or SULEV

- Stationary controls
  - Eliminate sources (BBQs, bakeries, dry cleaners, household chemicals, painting operations, ...)

- ZEV, PZEV, or SULEV

- Stationary controls
Control of PM

- Diesel exhaust is biggest mobile source
  - “Low emission” diesel engine and fuel
  - Compressed natural gas as a fuel
Control of PM

• Diesel exhaust is biggest mobile source
  ➔ “Low emission” diesel engine and fuel
  ➔ Compressed natural gas as a fuel

• Stationary sources: need better control of fugitive emissions
  ➔ Dust control
  ➔ Filtration, cyclone separators, electrostatic precipitators
SCAB Air Quality Trends

South Coast Air Basin Smog Trend

YEAR


Basin-Days Exceeding

Concentration, ppm

0.60

0.50

0.40

0.30

0.20

0.10

0.00

Days Over 1-Hour Federal Ozone Standard
Maximum 1-Hour Ozone Concentration (ppm)
SCAB Air Quality Trends

Figure 2
Maximum Pollutant Concentrations as Percent of Federal Standards
South Coast Air Basin Compared to U.S. Metropolitan Areas
Ozone Trends Summary: South Coast Air Basin
PM2.5 Trends Summary: South Coast Air Basin
Carbon Monoxide

Figure 6
Carbon Monoxide - 1996
Number of Days Exceeding the Federal Standard
Carbon Monoxide

CARBON MONOXIDE - 1998
Number of Days Exceeding Federal Standard
(8-Hour Average CO > 9.5 ppm)

NOT EXCEEDED  0-5  5-19  20 OR MORE

Los Angeles
Long Beach
San Bernardino
Riverside
Anaheim

[Map showing the number of days exceeding the federal standard for carbon monoxide in 1998, with symbols indicating the number of days exceeding the threshold.]
Ozone

Days exceeding Federal standard
- below 20
- 20 to 80
- 80 to 120
- 120 to 140
- above 140

1988

WLA
Azusa
Riverside
Ozone

OZONE – 1997
Number of Days Exceeding the Federal Standard

[Map showing the number of days exceeding the federal standard for ozone in 1997, with areas color-coded to indicate different ranges of exceedance.]
Particulate Matter

PM10 – 1999
Annual Arithmetic Mean, $\mu g/m^3$
(Federal Standard = 50 $\mu g/m^3$)

[Map showing air quality levels in Los Angeles and surrounding areas, with concentrations indicated by color coding: NOT EXCEEDED, 50 - 60, OVER 60 $\mu g/m^3$.]

52
Particulate Matter

PM2.5 – 1999
Annual Arithmetic Mean, μg/m³
(Federal Standard = 15 μg/m³)