

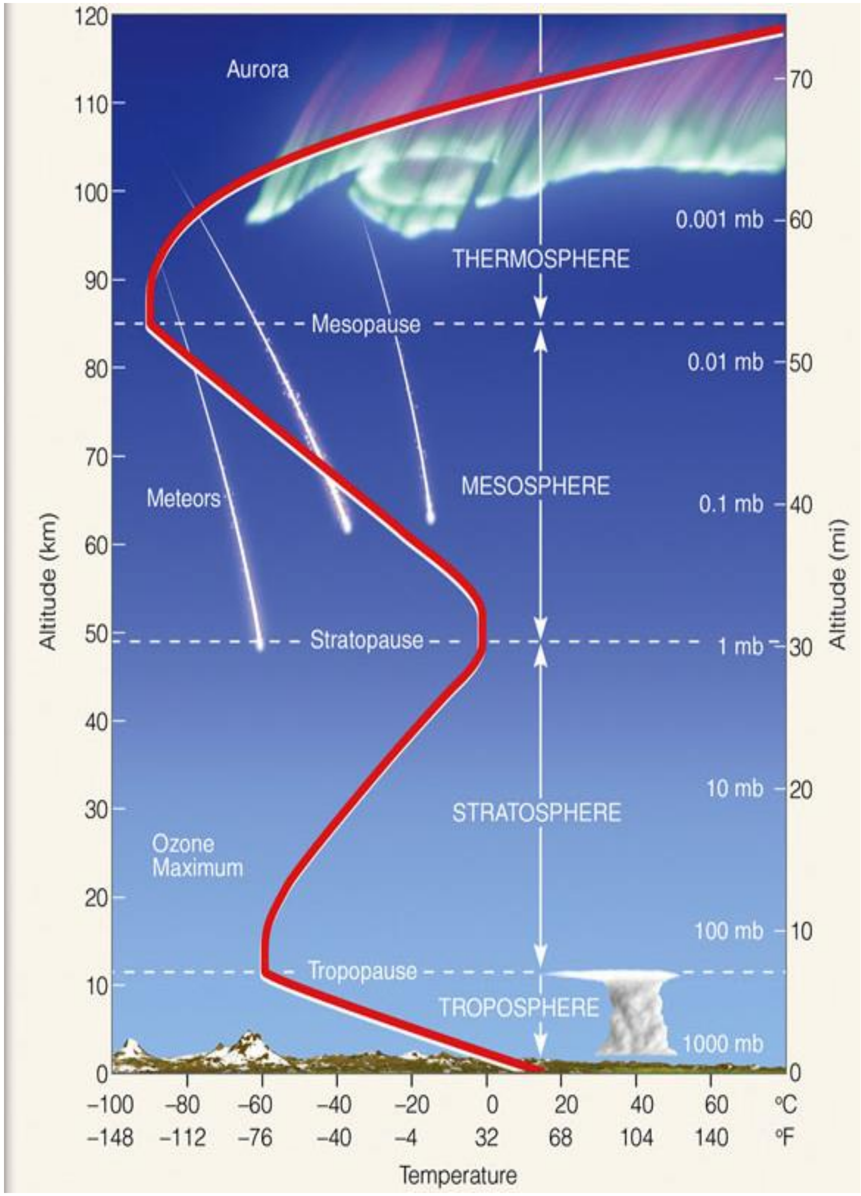
# Air Pollution-1

## - Introduction
## - Criteria Pollutants

*Changha Lee*

School of Chemical and Biological Engineering
Seoul National University

# The Earth Atmosphere and Composition




- ~100 km thick

(Karman Line = arbitrary boundary with Space)

- Weighs $5 \times 10^{18}$ kg

- Contains:
  - 78.08% nitrogen
  - 20.95% oxygen
  - 0.93% argon
  - Trace gases

  (0.039% $CO_2$, 0.000179% $CH_4$, $H_2O$ vapor, $O_3$, CO etc.)

# What is Air Pollution and its Effets?

√ **Air pollution**

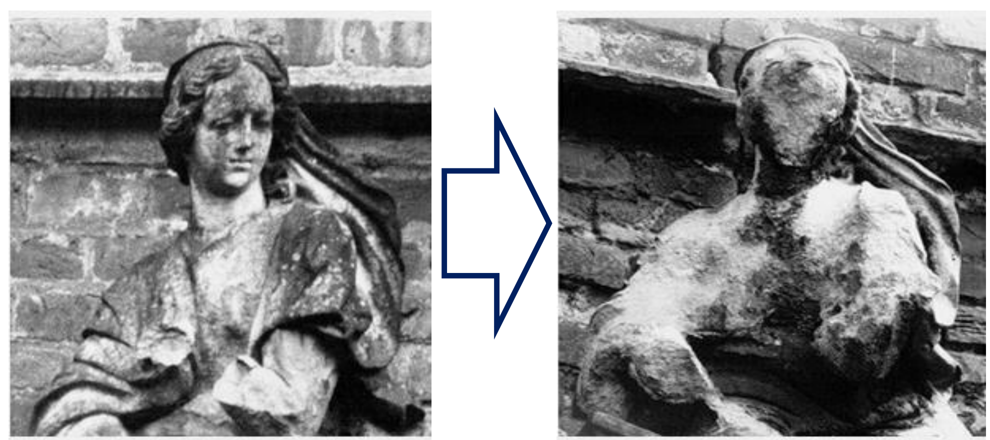
is the introduction (through direct emissions or transformation) of chemicals, particulate matter, or biological materials into the atmosphere that cause harm or discomfort to humans or other living organism, or damage the natural or built environment.– (modified from Wikipedia)

**Air pollution impact can be visible (visibility reduction).**

# What is Air Pollution and its Effects?

- **Air pollution can kill people!**
  - **PA 1948**: 20 people died, thousands ill
  - **London 1952**: 12,000 premature deaths
    (coal burning release sulfur dioxide and particulates)
  - **Bopal 1984**: 20,000 deaths by methyl isocyanate gas
  - So much more considering the chronic effects of air pollution

- **Acid rain problems**
  - Broad impacts on ecosystem, soil, vegetation, and architectures

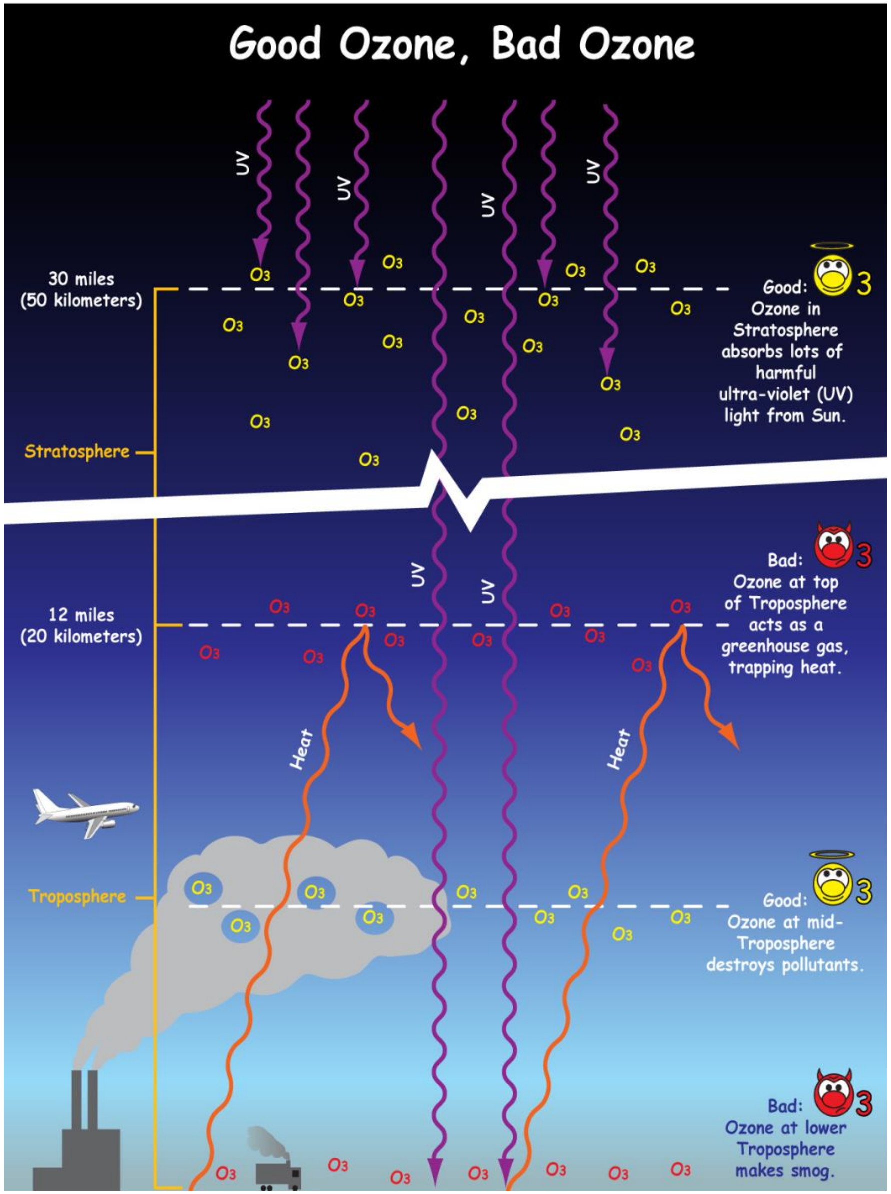


- **Ozone layer depletion**

# Ozone Layer Depletion

- **Ozone layer:**
  - refers to ozone in the stratosphere (12 – 24 km)
  - absorbs 97–99% of the Sun's high frequency UV light (**i.e. acts as the natural sunscreen**)
- $O_3$-depleting chemicals contain halogens (F, Cl, Br)
- Each Cl and Br radicals liberated by UV can catalyze a chain reaction capable of breaking down over 100,000 ozone molecules
- Based on Montreal Protocol 1989 to address the **ozone hole** (world ban on Chlorofluorocarbons, CFCs)

# Good Ozone, Bad Ozone




- **Stratospheric ozone :**
  - GOOD OZONE ☺
  - protects life on earth from harmful UV rays from sun
- **Tropospheric ozone :**
  - Urban ozone is smog. BAD OZONE ☹
  - Surface ozone affects lungs, plants and crop yields.
  - Produced from photochemical reactions involving CO, VOC & $NO_X$

# Urban Ozone is Smog

√ **Powerful oxidant, causes respiratory problems**

A study of 450,000 people living in U.S. cities showed a significant correlation between ozone levels and respiratory illness over the 18-year follow-up period. People living in cities with high ozone levels such as Houston or Los Angeles had an over 30% increased risk of dying from lung disease.

- Jerrett et al. "Long-Term Ozone Exposure and Mortality". *N. Engl. J. Med.* 2009

# Air Quality Regulation

- **Objective:**
  Set limits on ambient concentration of pollutants

- **To achieve the limits, two legislative approaches:**

  1) Set limits on the concentration of criteria pollutants that affects air quality

  2) Set limits on emission from industrial and transportation sectors

# Air Quality Regulation: NAAQS (US)

**National Ambient Air Quality Standards (NAAQS) and California Standards**

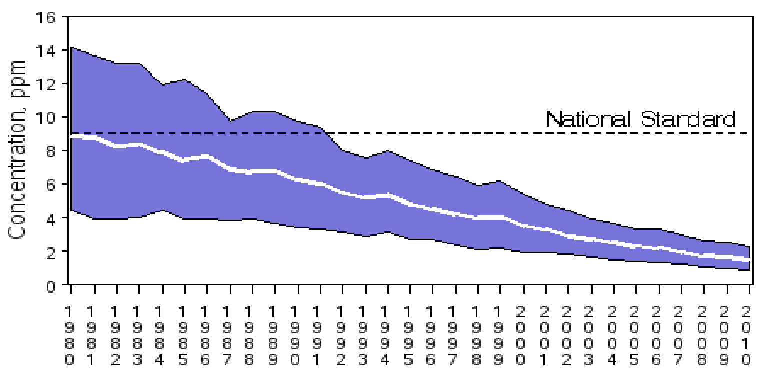
| Pollutant | Averaging Times | NAAQS Primary | California Standard | Most Relevant Health Effects |
|---|---|---|---|---|
| Carbon monoxide (CO) | 8-hour<br>1-hour | 9 ppm<br>35 ppm | 9 ppm<br>20 ppm | Aggravation of angina pectoris; decreased exercise tolerance; risk to fetuses |
| Lead | 3-months | 1.5 $\mu g/m^3$ | | Impaired blood formation; infant development effects |
| Nitrogen dioxide ($NO_2$) | Annual mean<br>1-hr | 0.053 ppm<br>— | <br>0.25 ppm, 1-hr | Aggravation of respiratory disease; atmospheric discoloration |
| Particulate matter ($PM_{10}$) | Annual mean<br>24-hour | —<br>150 $\mu g/m^3$ | 20 $\mu g/m^3$<br>50 $\mu g/m^3$ | Aggravated asthma; coughing; painful breathing; chronic bronchitis; decreased lung function; premature death in heart and lung patients |
| Particulate matter ($PM_{2.5}$) | Annual mean<br>24-hour | 15.0 $\mu g/m^3$<br>35 $\mu g/m^3$ | 12 $\mu g/m^3$ | |
| Ozone ($O_3$) | 8-hour<br>1-hour | 0.08 ppm | <br>0.09 ppm | Decreased pulmonary function; surrogate for eye irritation |
| Sulfur dioxide ($SO_2$) | Annual mean<br>24-hour<br>1-hour | 0.03 ppm<br>0.14 ppm<br>— | <br>0.04 ppm<br>0.25 ppm | Wheezing, shortness of breath, chest tightness; premature deaths |

# Air Quality Regulation (대기환경기준, Korea)

| 항 목 | 기 준 | 측정방법 |
|---|---|---|
| 아황산가스($SO_2$) | 연간평균치 0.02ppm 이하<br>24시간평균치 0.05ppm 이하<br>1시간평균치 0.15ppm 이하 | 자외선형광법<br>(Pulse U.V. Fluorescence Method) |
| 일산화탄소(CO) | 8시간평균치 9ppm 이하<br>1시간평균치 25ppm 이하 | 비분산적외선분석법<br>(Non-Dispersive Infrared Method) |
| 이산화질소($NO_2$) | 연간평균치 0.03ppm 이하<br>24시간평균치 0.06ppm 이하<br>1시간평균치 0.10ppm 이하 | 화학발광법<br>(Chemiluminescent Method) |
| 미세먼지($PM_{10}$) | 연간평균치 50㎍/㎥ 이하<br>24시간평균치 100㎍/㎥ 이하 | 베타선흡수법<br>(β-Ray Absorption Method) |
| 초미세먼지($PM_{2.5}$) | 연간평균치 15㎍/㎥ 이하<br>24시간평균치 35㎍/㎥ 이하 | 중량농도법 또는 이에 준하는<br>자동측정법 |
| 오존($O_3$) | 8시간평균치 0.06ppm 이하<br>1시간평균치 0.1ppm 이하 | 자외선광도법<br>(U.V Photometric Method) |
| 납(Pb) | 연간평균치 0.5㎍/㎥ 이하 | 원자흡광광도법<br>(Atomic Absorption Spectrophotometry) |
| 벤젠(Benzene) | 연간평균치 5㎍/㎥ 이하 | 가스크로마토그래프법<br>(Gas Chromatography) |

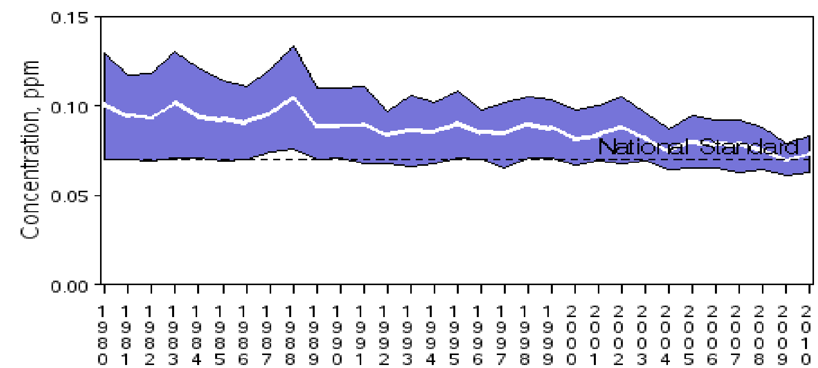
# Benefit of Air Quality Legislation

CO Air Quality, 1980 - 2010
(Based on Annual 2nd Maximum 8-hour Average)
National Trend based on 104 Sites



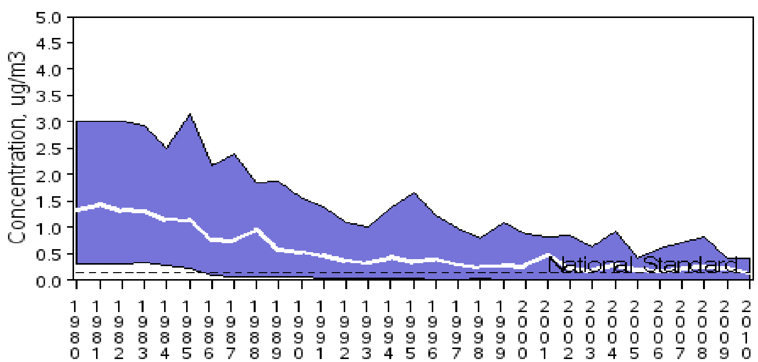

1980 to 2010 : 82% decrease in National Average

Ozone Air Quality, 1980 - 2010
(Based on Annual 4th Maximum 8-Hour Average)
National Trend based on 247 Sites



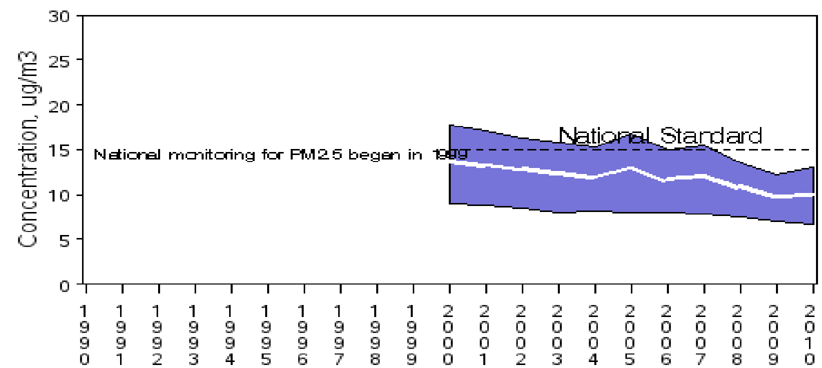

1980 to 2010 : 28% decrease in National Average

Lead Air Quality, 1980 - 2010
(Based on Annual Maximum 3-Month Average)
National Trend based on 31 Sites




1980 to 2010 : 89% decrease in National Average

PM2.5 Air Quality, 2000 - 2010
(Based on Seasonally-Weighted Annual Average)
National Trend based on 646 Sites




2000 to 2010 : 27% decrease in National Average

http://www.epa.gov/airtrends/index.html

# AQI: Air Quality Index (US)

- Air pollution index to report information to public
- Combines info about 5 pollutants into one number
- Used to be PSI – Pollutant Standard Index
- Highest subindex determines overall AQI
- Index from 0 – 500
- Also color coded:

| 0-50 | 51-100 | 101-150 | 151-200 | 201-300 | 301 - 500 |
|---|---|---|---|---|---|
| Good | Moderate | Unhealthy for sensitive groups | Unhealthy | Very unhealthy | Hazardous |

# AQI: Air Quality Index (US)

**Air Quality Index (AQI) Categories and Ranges**

| Category | AQI | 8-hr $O_3$ (ppm) | 1-hr $O_3$ (ppm) | 24-hr $PM_{2.5}$ ($\mu g/m^3$) |
|---|---|---|---|---|
| Good | 0–50 | 0.000–0.064 | — | 0.0–15.4 |
| Moderate | 51–100 | 0.065–0.084 | — | 15.5–40.4 |
| Unhealthy for Sensitive Groups | 101–150 | 0.085–0.104 | 0.125–0.164 | 40.5–65.4 |
| Unhealthy | 151–200 | 0.105–0.124 | 0.165–0.204 | 65.5–150.4 |
| Very Unhealthy | 201–300 | 0.125–0.374 | 0.205–0.404 | 150.5–250.4 |
| Hazardous | 301–400 | use 1-hr | 0.405–0.504 | 250.5–350.4 |
| | 401–500 | use 1-hr | 0.505–0.604 | 350.5–500.4 |

| AQI | 24-hr $PM_{10}$ ($\mu g/m^3$) | 8-hr CO (ppm) | 24-hr $SO_2$ (ppm) | 1-hr $NO_2$ (ppm) |
|---|---|---|---|---|
| 0–50 | 0–54 | 0.0–4.4 | 0.000–0.034 | — |
| 51–100 | 55–154 | 4.5–9.4 | 0.035–0.144 | — |
| 101–150 | 155–254 | 9.5–12.4 | 0.145–0.224 | — |
| 151–200 | 255–354 | 12.5–15.4 | 0.225–0.304 | — |
| 201–300 | 355–424 | 15.5–30.4 | 0.305–0.604 | 0.65–1.24 |
| 301–400 | 425–504 | 30.5–40.4 | 0.605–0.804 | 1.25–1.64 |
| 401–500 | 505–604 | 40.5–50.4 | 0.805–1.004 | 1.65–2.04 |

# Example

- **Suppose on a given day, the maximum concentrations are measured:**

| | |
|---|---|
| **1 hr $O_3$** | 0.18 $ppm_v$ |
| **8 hr CO** | 9 $ppm_v$ |
| **24 hr PM2.5** | 35 $\mu g/m^3$ |
| **24 hr PM10** | 130 $\mu g/m^3$ |
| **24 hr $SO_2$** | 0.12 $ppm_v$ |
| **1 hr $NO_2$** | 0.3 $ppm_v$ |

- **Find AQI and descriptor characterizing air quality**

# Example (solution)

- Determine pollutant with highest subindex

| | |
|---|---|
| **1 hr $O_3$** | Unhealthy |
| **8 hr CO** | Moderate |
| **24 hr PM2.5** | Moderate |
| **24 hr PM10** | Moderate |
| **24 hr $SO_2$** | Moderate |
| **1 hr $NO_2$** | None |

- Ozone concentrations determines AQI here

# Example (solution)

- **Ozone 1 hr**
  - At 0.18 ppm
- **Range of AQI**
  - 151 – 200
- **Range of $O_3$ concentration at this category**
  - 0.165 – 0.204
- **By linear interpolation,**

$$151 + \frac{0.18 - 0.165}{0.204 - 0.165} \times (200 - 151) \approx 170$$

$$\therefore AQI \text{ is } \underline{170} \text{ and the category is } \underline{\text{Unhealthy}}$$

# CAI: Comprehensive Air Quality Index (Korea)
## 통합대기환경지수

| 지수 | | A | | B | | C | | D | E |
|---|---|---|---|---|---|---|---|---|---|
| 지수구분 | | 좋음 | | 보통 | | 나쁨 | | 매우나쁨 | |
| 점수구분값 | $I_{LO}$ | 0 | | 51 | | 101 | | 251이상 | |
| | $I_{HI}$ | 50 | | 100 | | 250 | | | |
| 오염도 | | $BP_{LO}$ | $BP_{HI}$ | $BP_{LO}$ | $BP_{HI}$ | $BP_{LO}$ | $BP_{HI}$ | $BP_{LO}$ | $BP_{HI}$ |
| $SO_2$(ppm) | 1hr | 0 | 0.020 | 0.021 | 0.050 | 0.051 | 0.150 | 0.151 | 1 |
| $NO_2$(ppm) | 1hr | 0 | 0.030 | 0.031 | 0.060 | 0.061 | 0.200 | 0.201 | 2 |
| CO(ppm) | 1hr | 0 | 2 | 2.01 | 9 | 9.01 | 15 | 15.01 | 50 |
| $O_3$(ppm) | 1hr | 0 | 0.030 | 0.031 | 0.090 | 0.091 | 0.150 | 0.151 | 0.6 |
| PM-2.5(㎍/㎥) | 24hr | 0 | 15 | 16 | 35 | 36 | 75 | 76 | 500 |
| PM-10(㎍/㎥) | 24hr | 0 | 30 | 31 | 80 | 81 | 150 | 151 | 600 |

| 등급(CAI) | 좋음 (0~50) | 보통 (51~100) | 나쁨 (101~250) | 매우나쁨 (251~) |
|---|---|---|---|---|
| 상징색 | 파랑 | 초록 | 노랑 | 빨강 |
| RGB Code | 0000FF | 00FF00 | FFFF00 | FF0000 |
| 픽토그램 |  |  |  |  |

※ 캐릭터 출처: 에어코리아(한국환경공단) 하랑이

# Criteria Pollutants

√ Presently six air pollutants are regulated to protect human health:

- CO
- $SO_2$
- Pb
- $NO_x$
- $O_3$
- Particulates (PM10/PM2.5)

# Carbon Monoxide (CO)

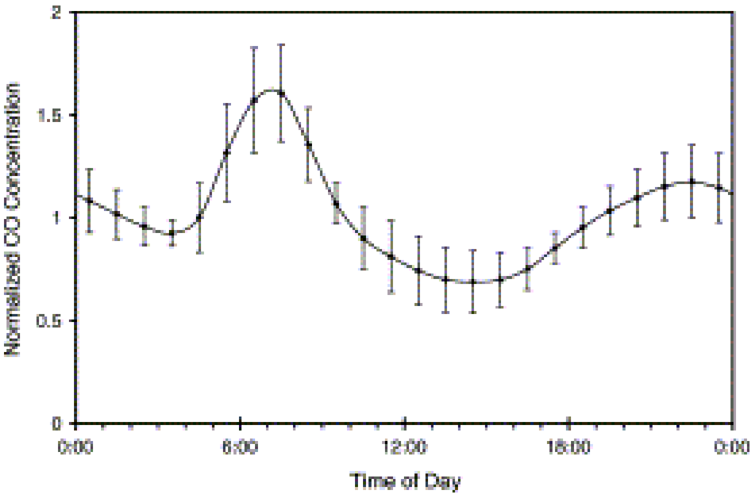
- Gaseous, no odor, no color

- **Result of incomplete combustion of C-fuels**
  - Insufficient oxygen supply
  - Low combustion temperature
  - Insufficient contact time
  - Chamber turbulence

- 70% of CO from vehicles

- Diurnal profile –

  peaks with rush hours




- **CO binds to hemoglobin in place of $O_2$ (asphyxiant)**

- **Reduces $O_2$ availability in human body**
  - Decreases brain function
  - Increases heart rate

# Oxides of Nitrogen

- NO and $NO_2$ are referred to as $NO_x$
- Mainly from fuel combustion

  - Thermal $NO_x$

    when air ($N_2$ and $O_2$) is heated to high temps (>1000 $^{o}$C)

  - Fuel $NO_x$

    From N present in the fuel (like $SO_x$)

- $NO_x$ emissions are primarily NO
- NO reacts and form $NO_2$ = light absorber
- $NO_2 + hv + O_2 \rightarrow NO + O_3$ (smog)
- $NO_2$ + hydrocarbons $\rightarrow$ more smog
- $NO_2 + {}^{\bullet}OH \rightarrow HNO_3$ (acid rain)

# Oxides of Nitrogen

- Control:
  - Stationary fuel combustion, motor vehicles
  - Reduce combustion temperature
  - Find low-N fuels

- **However, higher temperatures represent a tradeoff**
  - lower CO but
  - increase $NO_x$

- NOx Emissions have been relatively constant since the 1970s

# Oxides of Sulfur

- $SO_2$ and $SO_3$ referred to as $SO_x$

- Sources
  - Combustion of fuels containing sulfur
    85% of total emissions from this source

  - Some from industrial smelting, refining
    Much of industry is now well controlled

- Products of $SO_2$ are also problematic:

  - $SO_2 + {}^{\bullet}OH \rightarrow HOSO_2{\bullet}$ (hydroxysulfonyl radical)

  - $HOSO_2^{\bullet} + O_2 \rightarrow SO_3 + HO_2^{\bullet}$

  - $SO_3 + H_2O \rightarrow H_2SO_4 \rightarrow$ acid rain

# Oxides of Sulfur and Health Effects

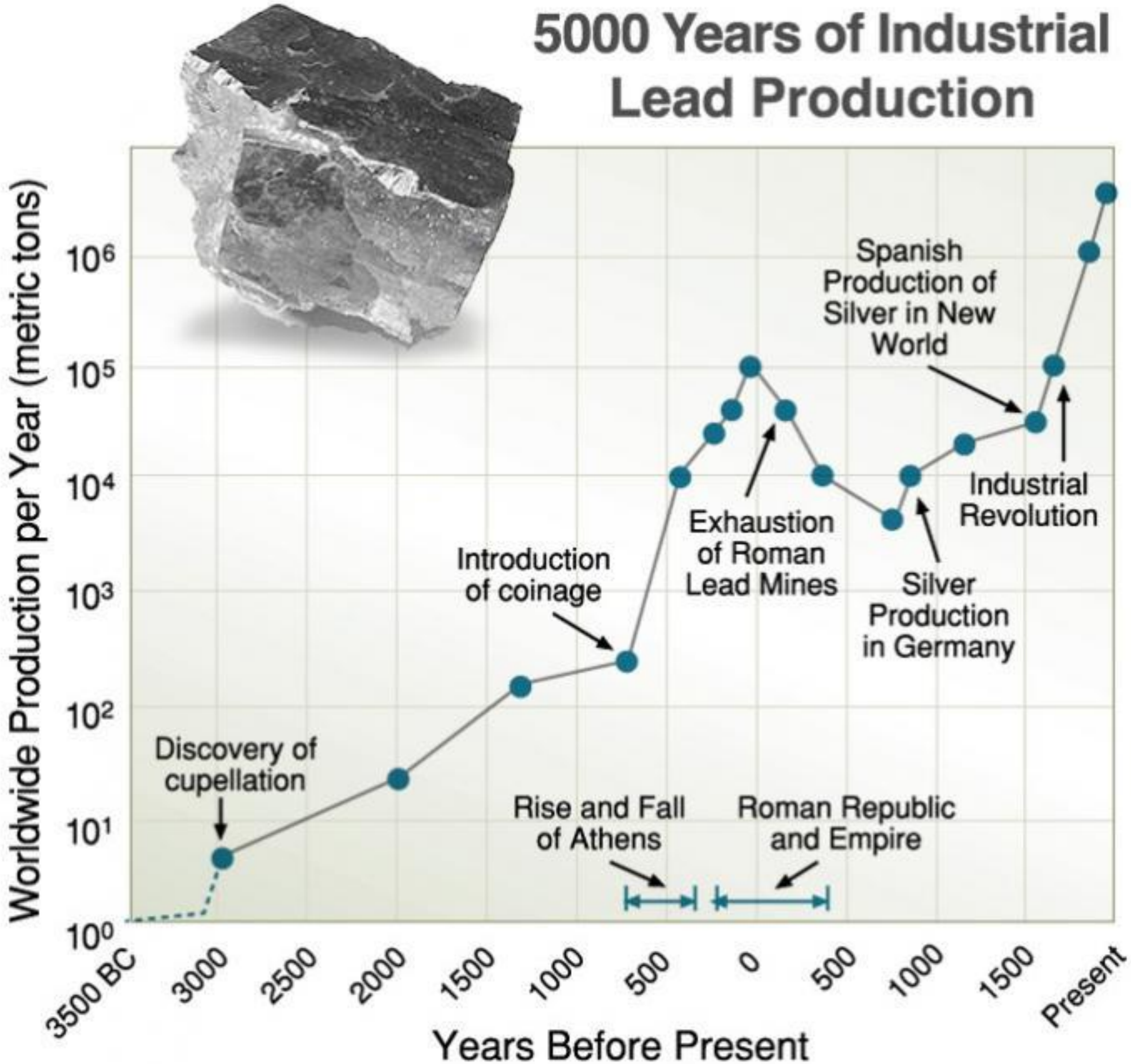
- **$SO_2$ can eventually form sulfate aerosols**

  - $SO_4^{2-}$ in water droplets
  - Condensing in other existing particles

- What are the effects of these particles?

  - Particles in atmosphere lead to light scattering.
  - Particles may be breathed deep into lungs.
  - Combination of $SO_2$ and particles is quite unhealthy.

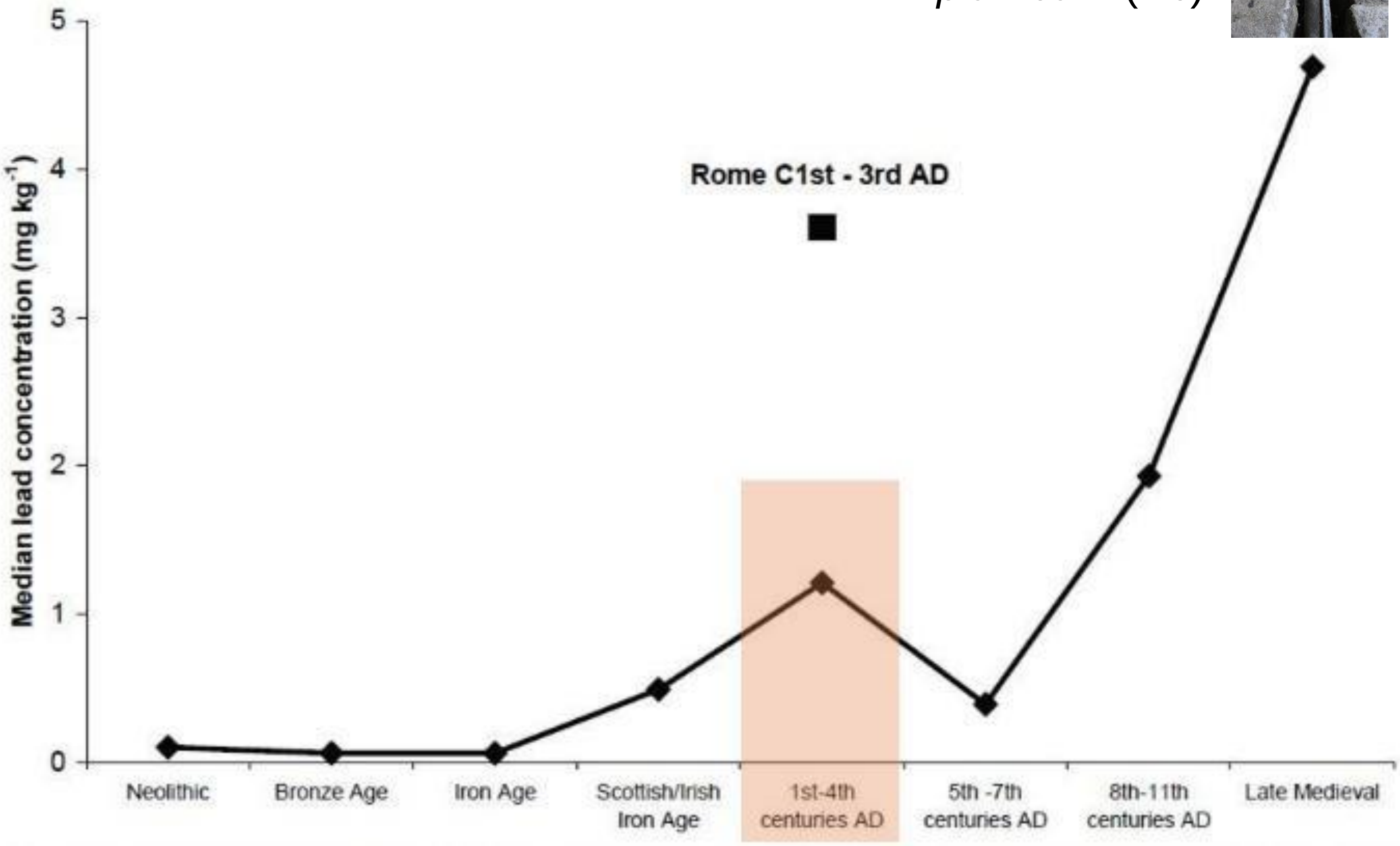
# Lead


5000 Years of Industrial Lead Production
Worldwide Production per Year (metric tons)
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
Spanish Production of Silver in New World
Industrial Revolution
Exhaustion of Roman Lead Mines
Silver Production in Germany
Introduction of coinage
Discovery of cupellation
Rise and Fall of Athens
Roman Republic and Empire
3500 BC
3000
2500
2000
1500
1000
500
0
500
1000
1500
Present
Years Before Present

# Lead

√ **Lead in human bones (Britain)**

"plumbing" is derived from *plumbum* (Pb)



# Lead

- Until 1980, most lead in air came from motor vehicles
  - Gas contained $(C_2H_5)_4Pb$ – tetraethyl lead
  - Had 1.1 g per gallon

- When motor vehicle emission restrictions forced catalytic converters
  Lead was phased out
  - Lead would ruin or poison the catalytic converter
  - Catalytic converter: CO, HC, NOx $\rightarrow$ $CO_2$, $H_2O$, $N_2$

- 1984 lead content lowered to 0.1 g per gallon

# Lead

- **Exposure route:**
  - Lead is emitted as lead salts
  - Deposited close to roadways
  - Particles are tracked into houses, resuspended, and inhaled

  Other routes:
  - Lead in water from lead pipes or lead solder
  - Lead ingested through paint chips or soil

- **Health effects:**
  - Lead gets into blood and replaces iron
  - Children can result in learning disabilities or severe brain damage
  - 25 to 50 μg lead in a deciliter of blood can result in health effects
  - Emissions have been reduced dramatically by removing leaded gasoline from the market

# Ozone ($O_3$)

- **Ozone is not directly emitted into the atmosphere**

  - **Produced by a series of reactions involving**

    Oxides of Nitrogen ($NO_x$) + Hydrocarbons (HC) + Sunlight ($h\nu$)

  - Material effects

    Reduce the life of rubber and tires

    Can damage vegetation (reduce crop production)

  - Human health effects

    Eye irritation

    Chest constriction, sore throat

    High concentration aggravates respiratory diseases.

# Ozone ($O_3$)

- Basic ingredients
  $HC + NO_x + h\nu \rightarrow$ smog

- **NOx atmospheric reactions produce ozone**
  - $\mathbf{NO_2} + h\nu \rightarrow \mathbf{NO} + O$
  - $O + O_2 + \rightarrow O_3$

- **Ozone is also consumed when it reacts with NO**
  - $O_3 + \mathbf{NO} \rightarrow \mathbf{NO_2} + O_2$

- **Another important radical: $^{\bullet}OH$**
  - $O + H_2O \rightarrow 2\ ^{\bullet}OH$
  - Extremely reactive in the atmosphere

# Ozone ($O_3$)

- **Hydrocarbons increase ozone formation**

  - $RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O$
  - $R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$
  - $\underline{RO_2^{\bullet} + \mathbf{NO} \rightarrow RO^{\bullet} + \mathbf{NO_2}}$

  - No ozone formed, but this influences $O_3$ concentration

  - Ozone formation increases with $\mathbf{NO_2}$ availability (**source**)
  - Ozone destruction depends on **NO** availability (**sink**)
  - Above reactions remove an $O_3$ sink and creates an $O_3$ source

# Ozone ($O_3$)

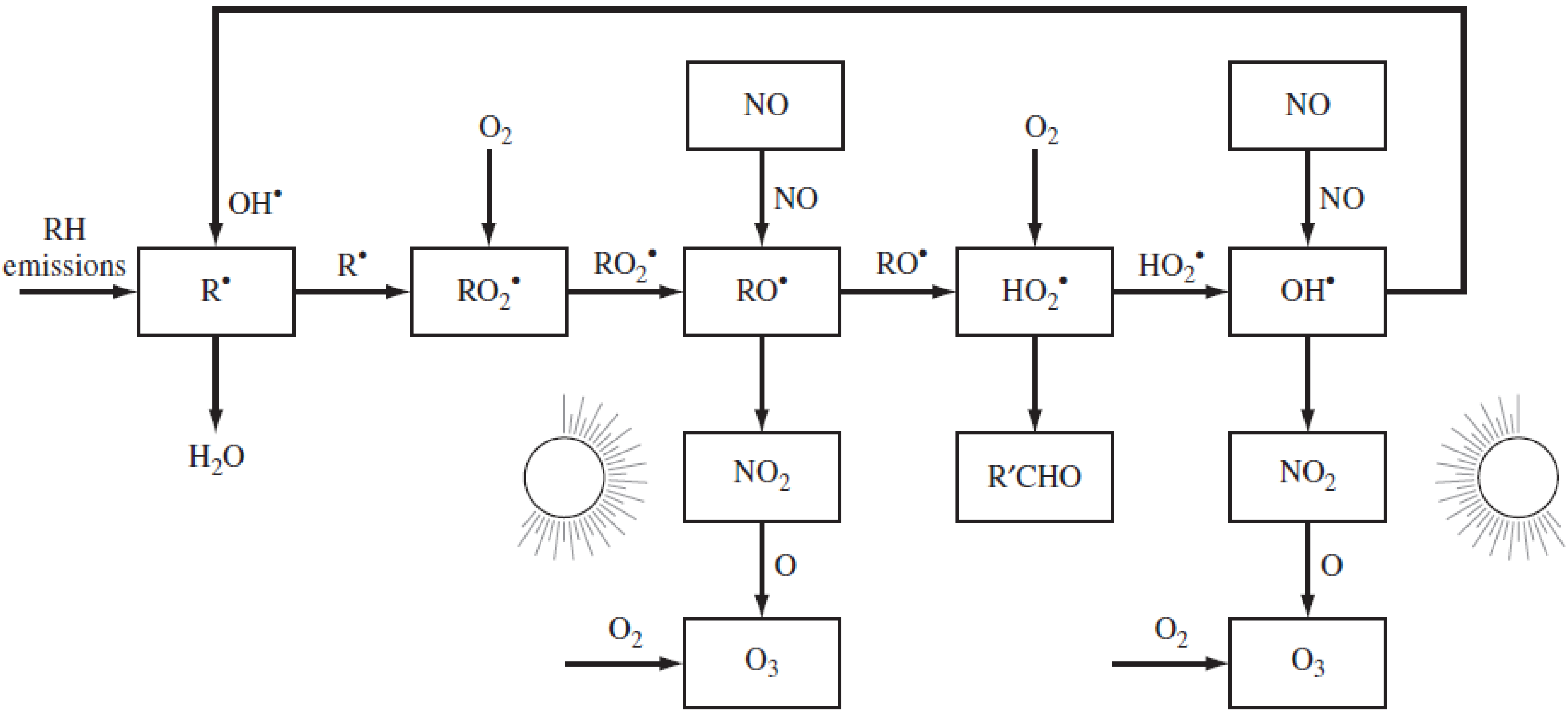



**FIGURE** Showing one way that hydrocarbons can cause NO to convert to $NO_2$. Reducing NO slows the removal of $O_3$, while increasing $NO_2$ increases the production of $O_3$, so this cycle helps account for elevated atmospheric $O_3$ levels.

# Ozone ($O_3$)

**To control $O_3$ we must control the precursors, $NO_X$ and VOCs.**

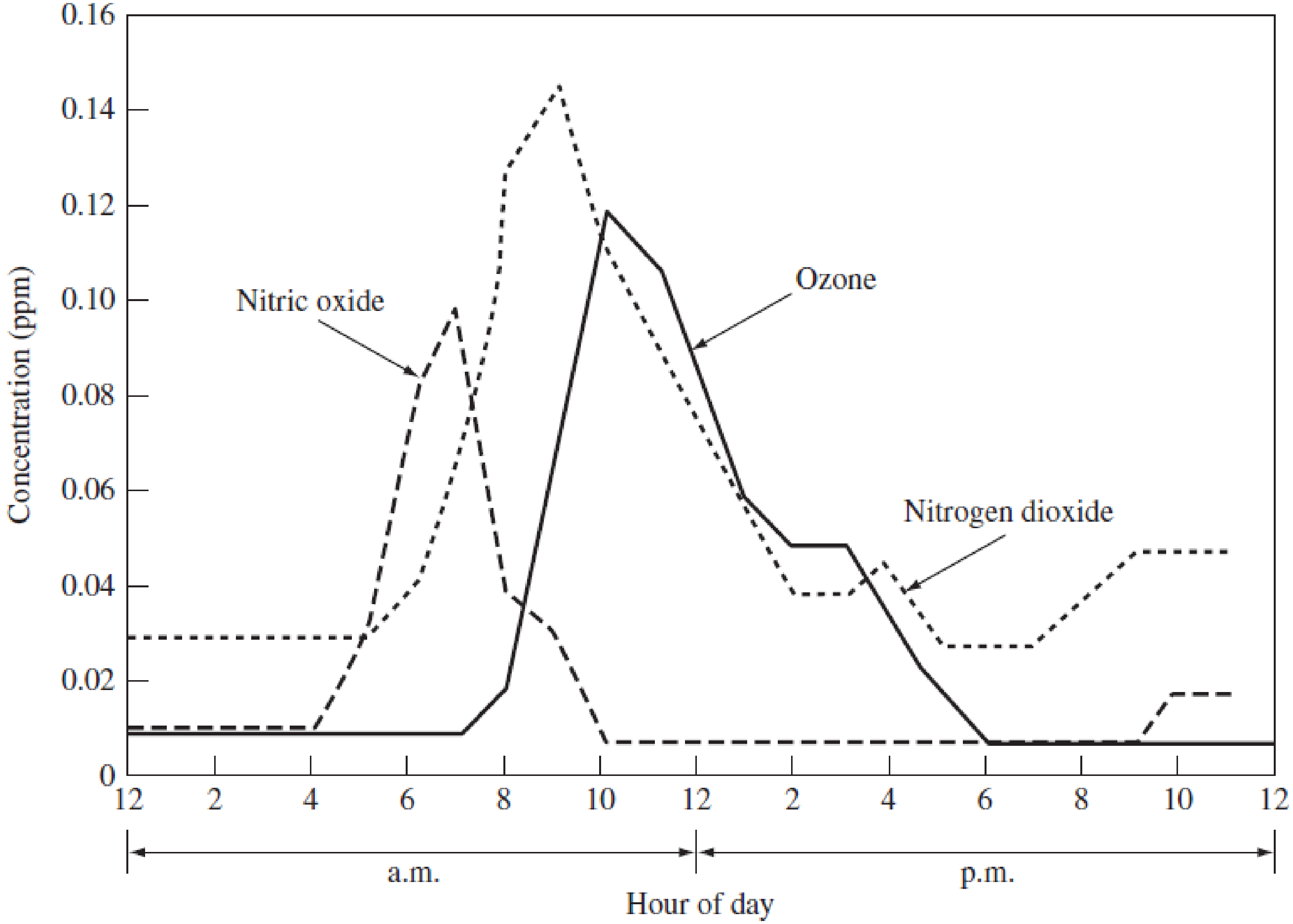



**FIGURE** Diurnal variation of NO, $NO_2$, and $O_3$ concentrations in Los Angeles on July 19, 1965.
(*Source:* U.S. HEW, 1970.)

# Gasoline reformulation (MTBE) and catalytic converters improved air quality in urban areas

~10 years

# Particulate Matter

- **Particulate matter (PM)** refers to any dispersed matter, solid or liquid, in which the individual particles are larger than single molecules but generally smaller than 100 μm
- Very small particles (<0.1 μm) move randomly (Brownian motion)
- Grows to larger particle sizes through condensation and coagulation
- Larger particles (>5 μm) fall out of atmosphere quickly
- Particles in between stay in the atmosphere longer

# Particulate Matter

√ **Types of PM:**

- **Aerosols** – tiny solid or liquid particles dispersed in the atmosphere
- **Dust** – solid particles caused by grinding or crushing
- **Fumes** – solid particles caused by condensing vapors
- **Fog or Mist** – liquid particles dispersed in atmosphere
- **Smoke or Soot** – refers to combustion emissions (uncombusted carbon)
- **Smog** – smoke + fog, now used to describe air pollution in general

# Particulate Matter

√ **Composition depends on emissions and transport**

- Emissions may be natural or anthropogenic:
  Natural sources – windblown dust, sea salt spray
  Anthropogenic – road dust, industrial emissions, tilling

- Particle may contain:
  - Sulfate (from $SO_2$)
  - Carbon
  - Ammonium
  - Organic material
  - Nitrate
  - Crystal
  - Water
  - Dirt

- Smaller particles more likely to be products of atmospheric reactions

# Particulate Matter

**√ Health effects of PM depends on how it interacts with respiratory system**

- Nose – hair in nose and mucous trap large particles
- Trachea (from mouth cavity to lungs) – smaller particles captured in mucous and coughed up or swallowed
- Bronchi and Lungs – smallest particles arrive
  - Some settle onto lung
  - Really small particles are exhaled

# Particulate Matter

✓**Radiation effectively scattered by objects of similar size to radiation wavelength**

- Visible light has wavelengths of 0.4 to 0.7 μm

- Particles in atmosphere of this size will scatter light and cause a reduction in visibility

# Particulate Matter

√ **The first NAAQS for particulate matter was written for total suspended particulates or TSP**

- But one large particle could weight as much as thousands or hundred of thousand of smaller particle
  (Very large particles pose a lower health risk)

- 1987 standard changed to **PM10** - particulate matter with an aerodynamic diameter of less than 10 µm

- The EPA adopted in 1999 a new standard: the **PM2.5**
  15 $mg/m_3$ three-year average
  65 $mg/m_3$ 24-hour maximum

- Expected benefits: reduction in premature deaths by 15,000/yr and in serious respiratory diseases by 250,000/year