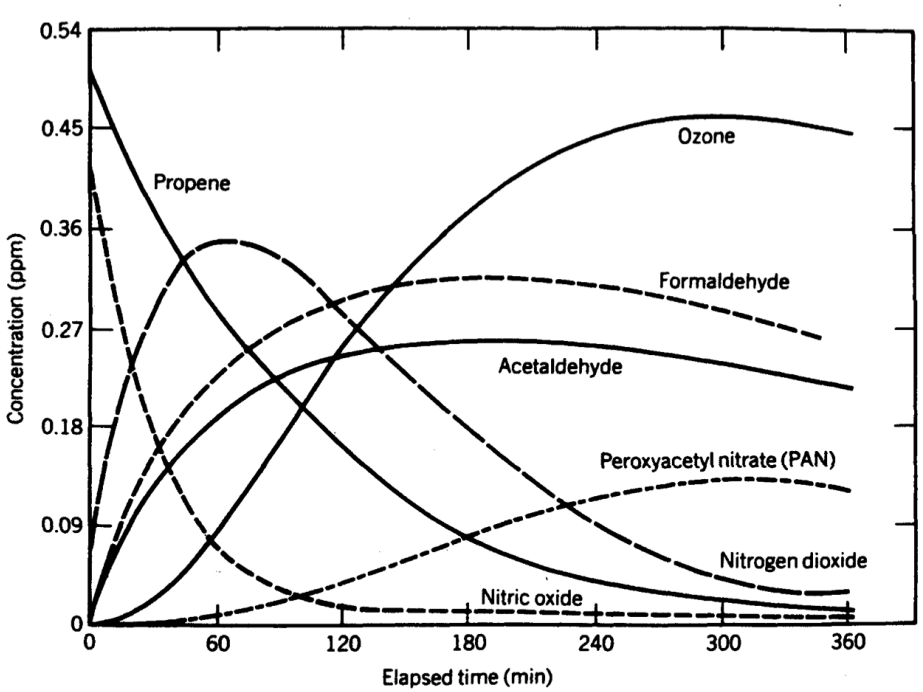
Tropospheric Air Quality

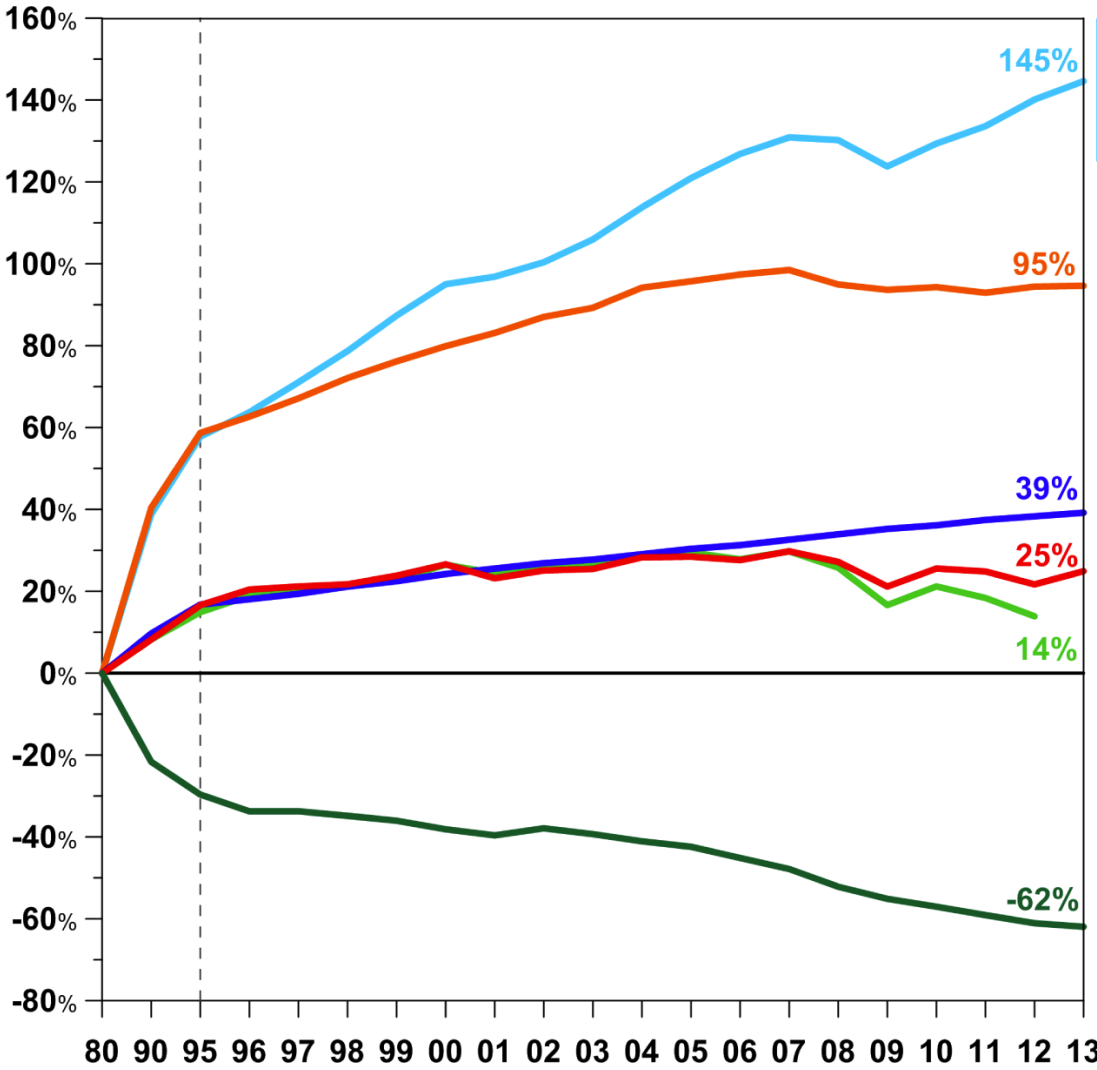
Smog, Particulate Matter, Acid Deposition



Outline of Topics

US Air Quality

Has the Clean Air Act improved air quality?




Gross Domestic Product


Vehicle Miles Traveled

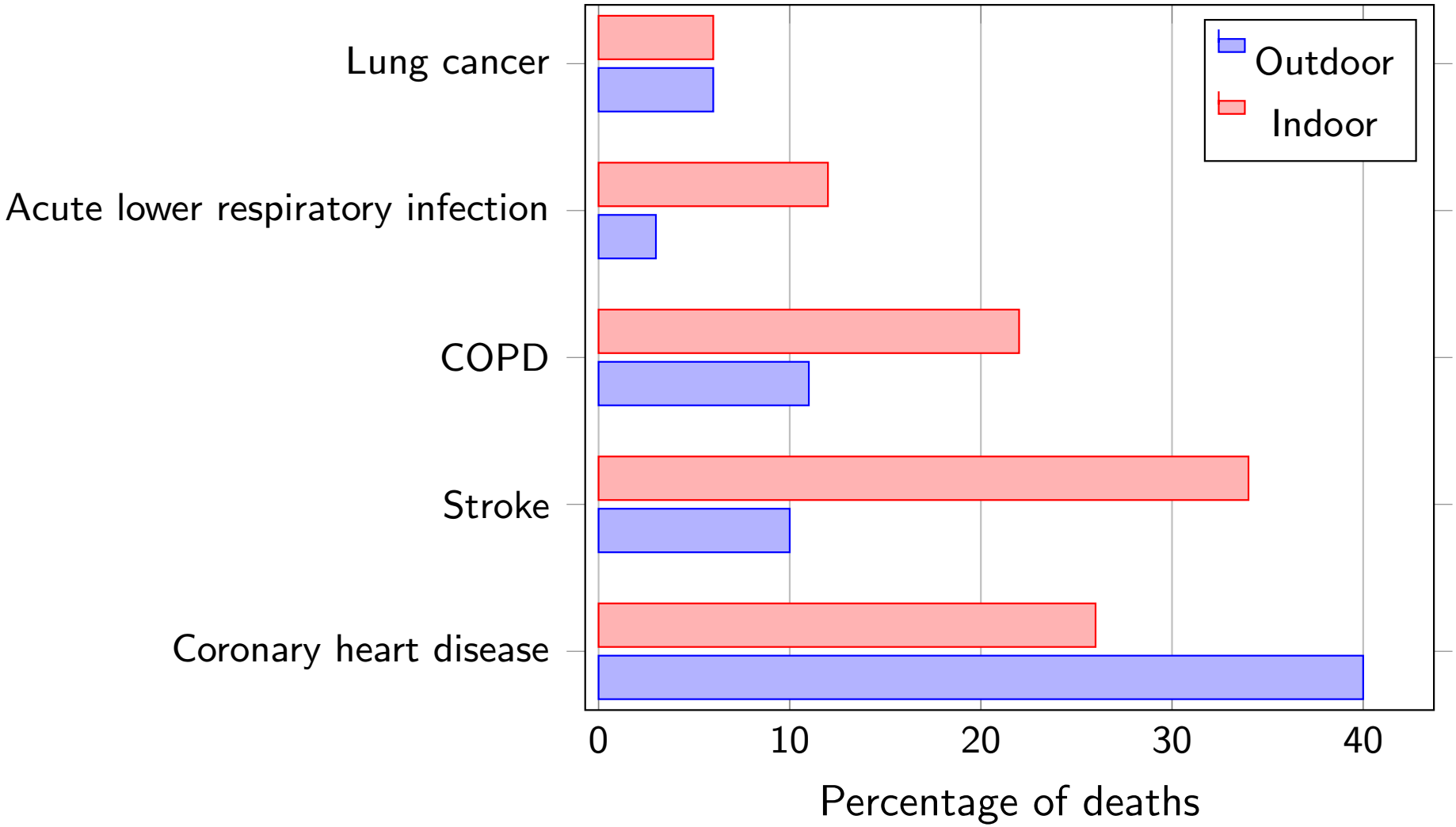

Population


Energy Consumption


CO_2 Emissions


Aggregate Emissions (Six Common Pollutants)

What kind of health problems are caused by air pollution?



- WHO 2012: air pollution caused 7 million premature deaths
- Outdoor 3.7 million, indoor 4.3 million (some overlap)
- Acute lower respiratory infection: children under 5
- MIT study: 90,000–362,000 premature deaths in US in 2005

Lecture Question

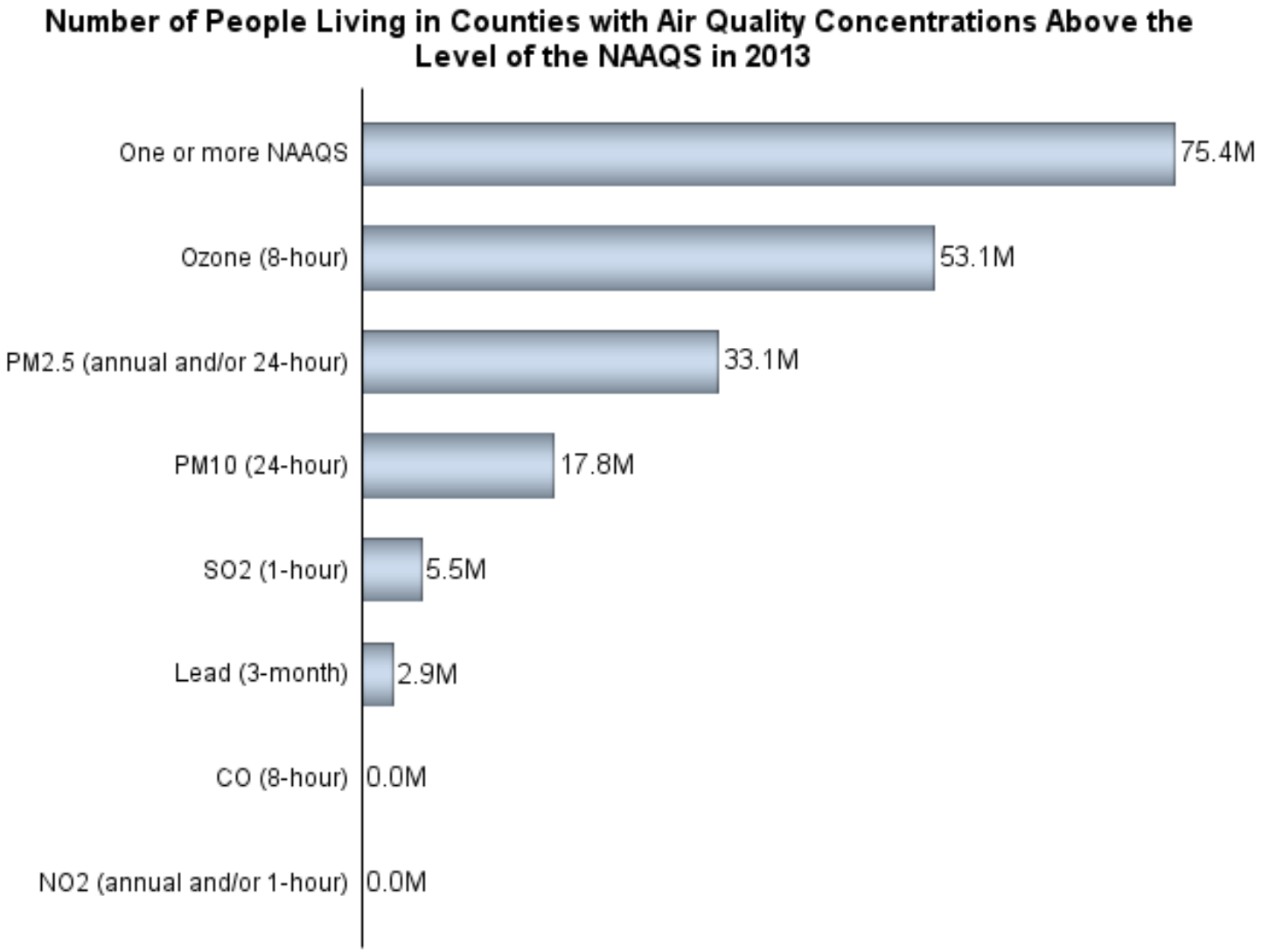
What are the US *National Ambient Air Quality Standards* (NAAQS)? How do they work?

Pollutant	Averaging Time	US NAAQS	WHO
O_3	8-hr	75 ppb	47 ppb
NO_2	1-hr	100 ppb	93 ppb
NO_2	annual	53 ppb	20 ppb
PM-2.5	annual	12 $\mu g/m^3$	10 $\mu g/m^3$
PM-2.5	24-hr	35 $\mu g/m^3$	25 $\mu g/m^3$
PM-10	annual	n/a	20 $\mu g/m^3$
PM-10	24-hr	150 $\mu g/m^3$	50 $\mu g/m^3$
SO_2	1-hr	75 ppb	n/a
SO_2	24-hr	n/a	7 ppb
SO_2	10-min	n/a	175 ppb
CO	8-hr	9 ppm	n/a
CO	1-hr	35 ppm	n/a
Pb	3-month	0.15 $\mu g/m^3$	n/a

- WHO stds converted from $\mu g/m^3$ when necessary
- EPA considering new O_3 std 65–70 ppb
- EPA has primary and secondary stds (primary shown here)
- What EPA considers a violation can be complicated

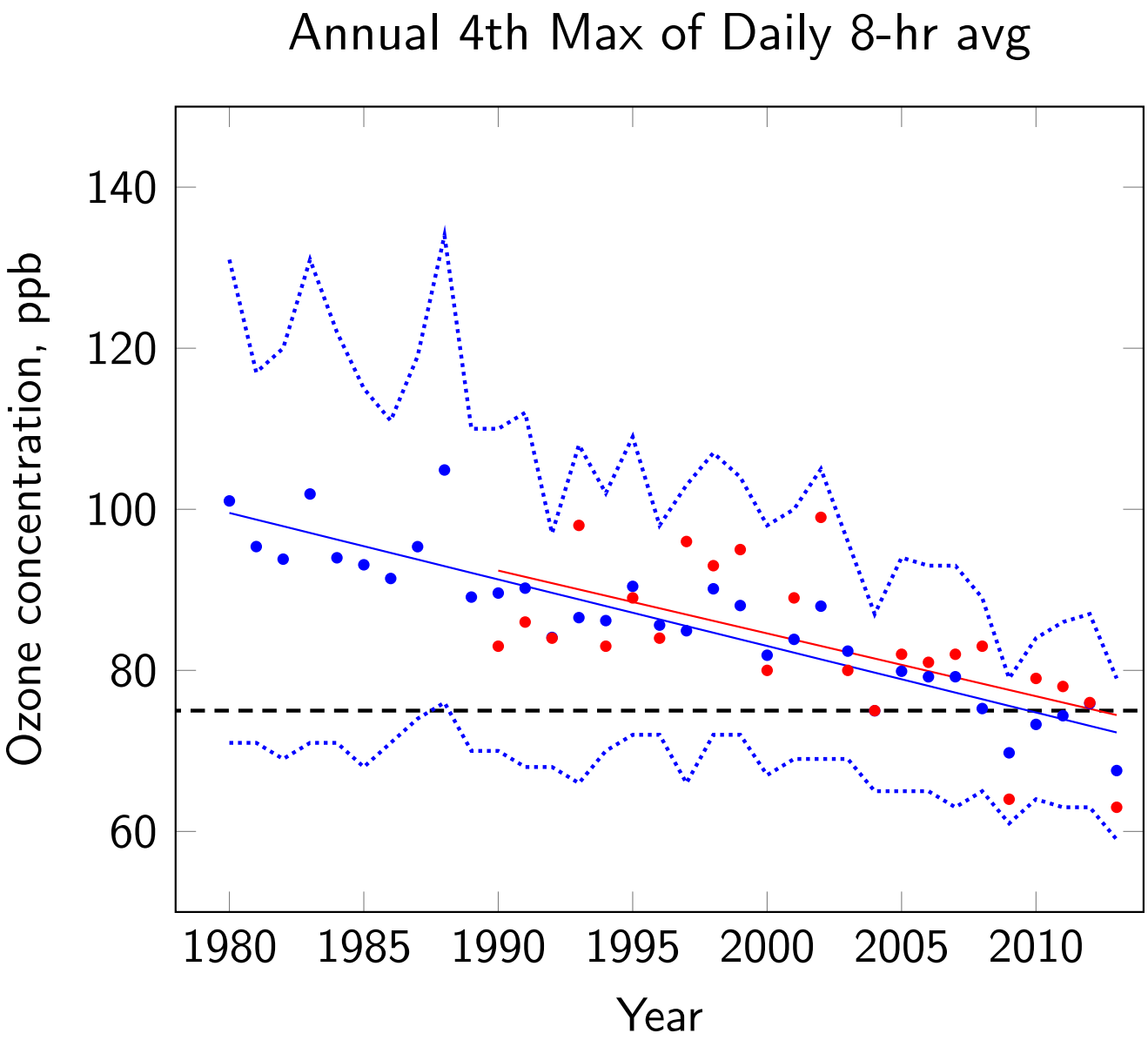
Lecture Question

Based on NAAQS violations, which air pollutants are the biggest health risk in the US?



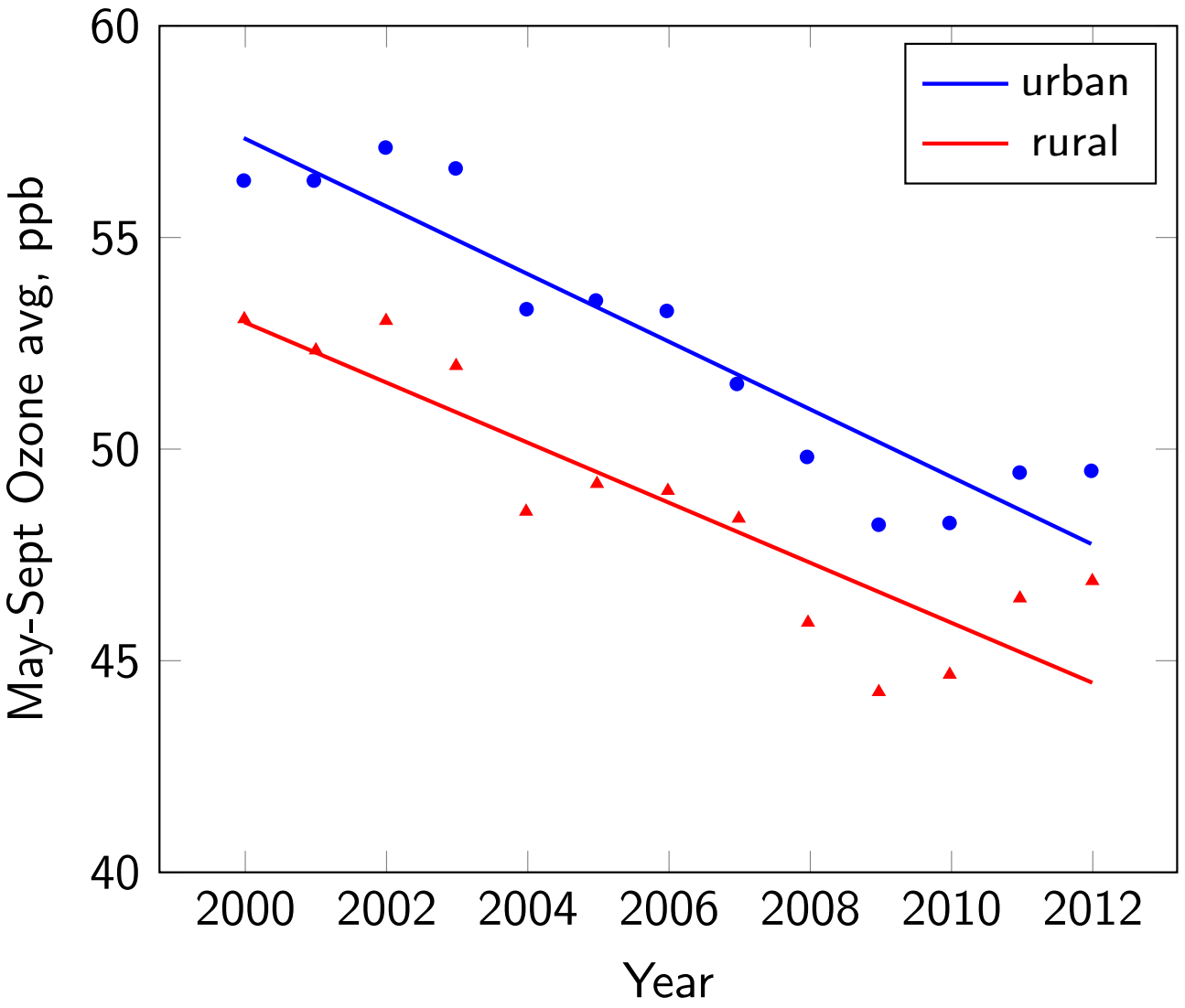
- US population was 316M in 2013
- 24% living in a county exceeding NAAQS

Compare trends in ground-level ozone to the NAAQS.



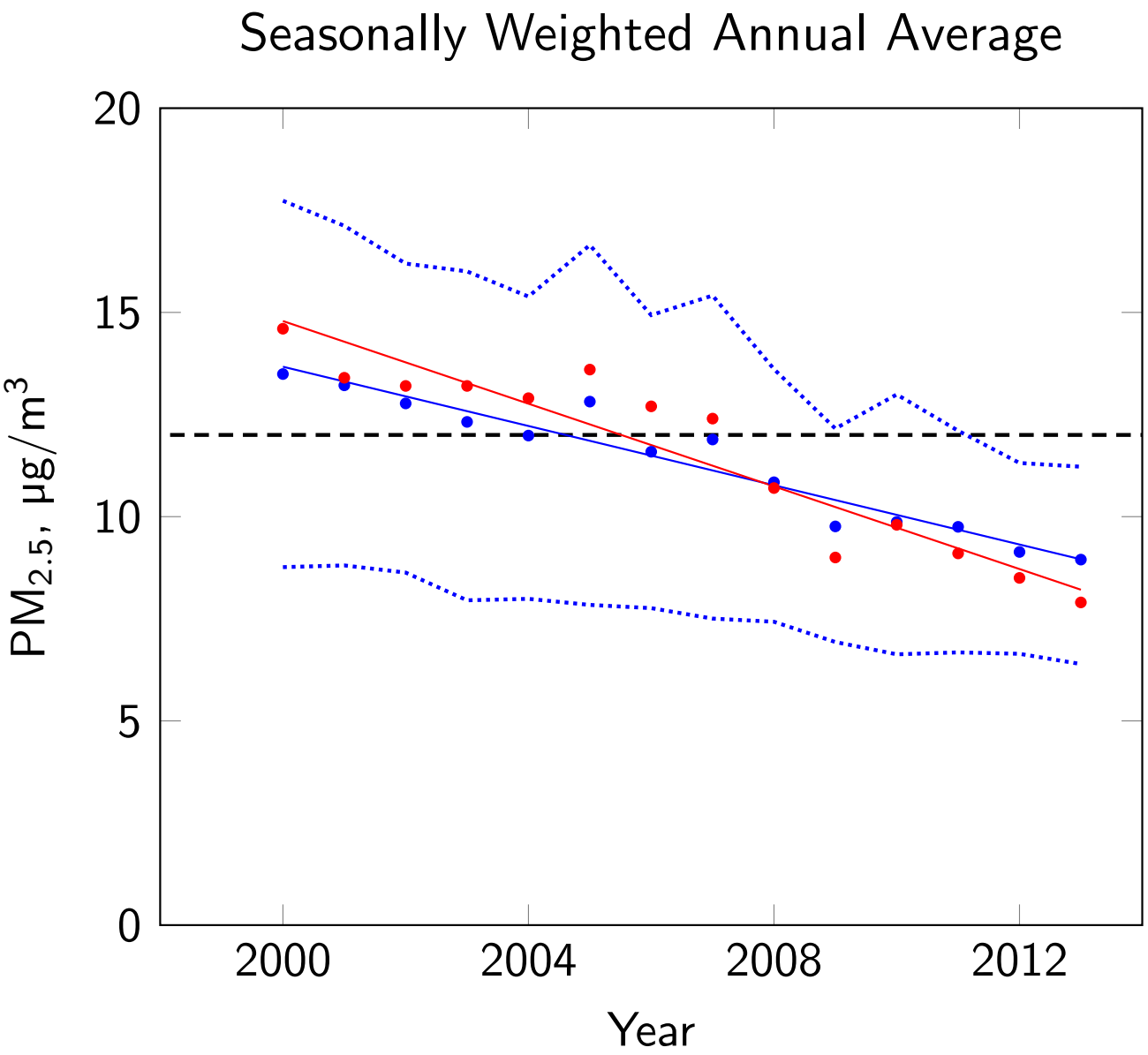
- Current daily NAAQS: 75 ppb 8-hr max avg
- 3 exceedances allowed
- Markers and trendlines: avg of the 4th highest max
- blue for national avg of 222 stations, trend under NAAQS in 2010
- red for 3 Richmond stations, trend under NAAQS in 2013
- Dashed blue lines are 10th and 90th percentiles

What is the trend in 'typical' (average) summer-time ozone concentration?



- Avg values, rather than 4th-highest
- Data adjusted to 'typical' weather conditions
- NAAQS is 75 ppb
- WHO guideline: 47 ppb
- Urban: −0.80 ppb/yr
- Rural: −0.71 ppb/yr

Compare trends in $PM_{2.5}$ to the NAAQS.



- Current NAAQS: $12\,\mu g/m^3$ (annual avg)
- WHO guideline: $10\,\mu g/m^3$
- Markers and trendlines: rolling 3-yr annual avgs
- Blue for national avg of 537 stations, trend under NAAQS in 2005
- Red for 4 Richmond stations, trend under NAAQS in 2006
- Dashed blue lines are 10th and 90th percentiles

Primary and Secondary Pollution

What is the difference between *primary* and *secondary* pollution? Give examples.

Problem	**Primary Pollutant**	**Secondary Pollutant**
Photochemical smog	NO_x, VOCs	O_3, partially oxidized organics, NO_2, HNO_3, nitrate PM, organic PM
Acid Deposition	NO_x, SO_2	HNO_3, H_2SO_4, acidic PM
Fine PM ($PM_{2.5}$)	NO_x, SO_2, VOCs	nitrate PM, sulfate PM, organic PM

- Primary (or *precursor*) pollutants are discharged into the air
- They react to form *secondary* pollutants
- A common theme in table above: photochemical oxidation of primary pollutants to form secondary pollutants
- PM also formed by reaction of NH_3 with acids to form (acidic) salts

Lecture Questions

How are NO_x and SO_2 pollutants generated?

- SO_2 formed by burning anything that has sulfur in it

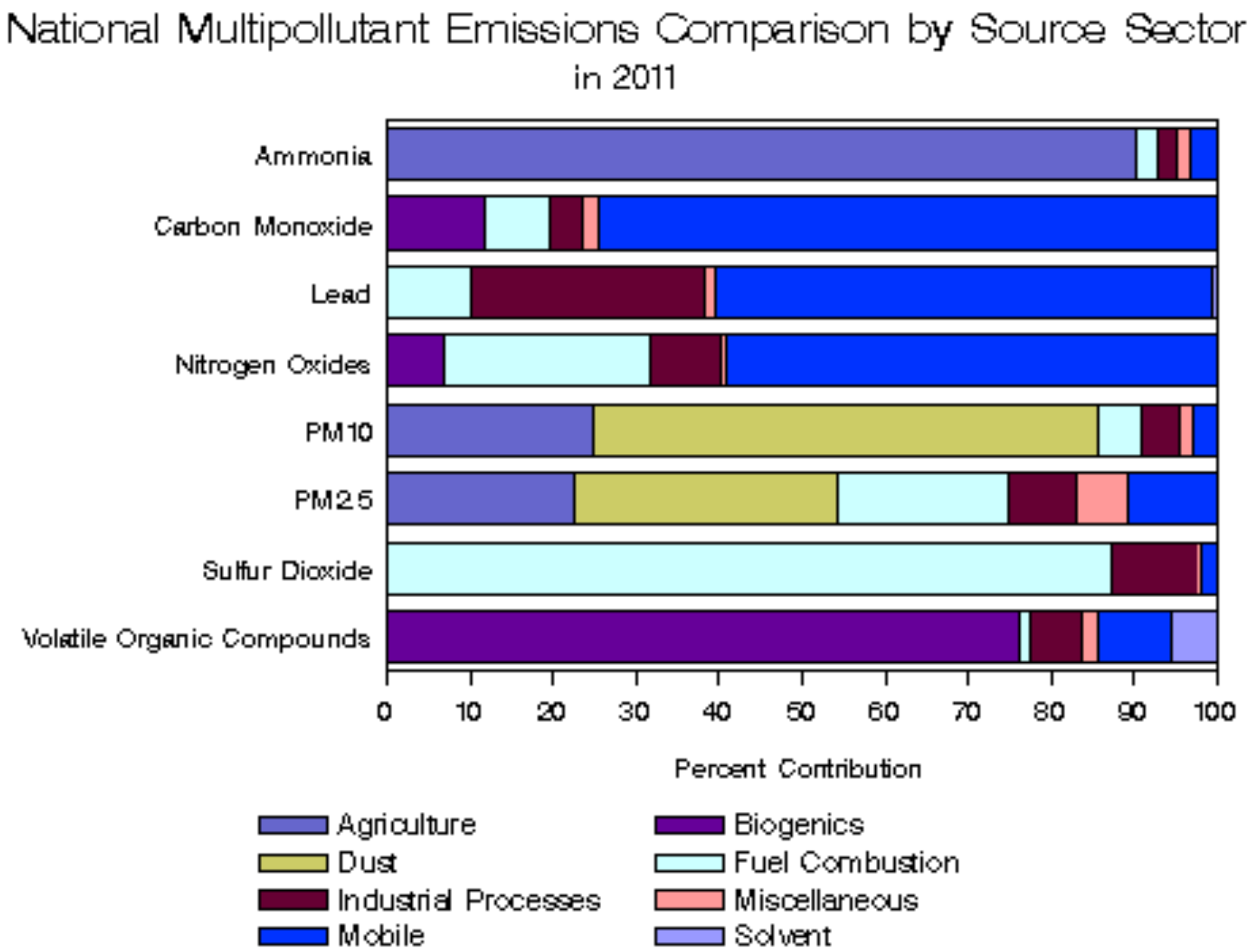
$$S + O_2 \longrightarrow SO_2$$

- Coal-fired power plants a common source
- NO_x formed by ANY combustion process hot enough to break the triple bond in atmospheric N_2
- Mostly formed as NO

$$N_2 + O_2 \longrightarrow 2\,NO$$

- NO and NO_2 are rapidly interconverted (draw this)

What activities generate the criteria pollutants and/or its precursors?



What activities generate the criteria pollutants and/or its precursors?

- **Agriculture**
  - Crops and livestock dust
  - Fertlizer application
  - Livestock waste
- **Dust**: fugitive emissions
  - Construction dust
  - Paved road dust
  - Unpaved road dust
- **Fuel combustion**, mostly for heat and electricity
  - Biomass, coal, natural gas, oil and other organic materials
- **Industrial processes**
  - Cement manufacturing
  - Chemical manufacturing
  - Ferrous and non-ferrous metal mills
  - Mining; oil and gas extraction
  - Petroleum refineries
  - Pulp and paper mills
- **Mobile** emission sources
  - Aircraft
  - Commercial maring vessels
  - Locomotives
  - Non-road equipment (diesel and gasoline)
- **Solvent** use
  - Consumer and commercial use
  - Degreasing
  - Dry cleaning
  - Graphics arts
  - Industrial surface coating and solvent use
  - Non-industrial surface coating
- **Miscellaneous** sources
  - Bulk gasoline terminals
  - Commercial cooking
  - Gas stations
  - Waste disposal

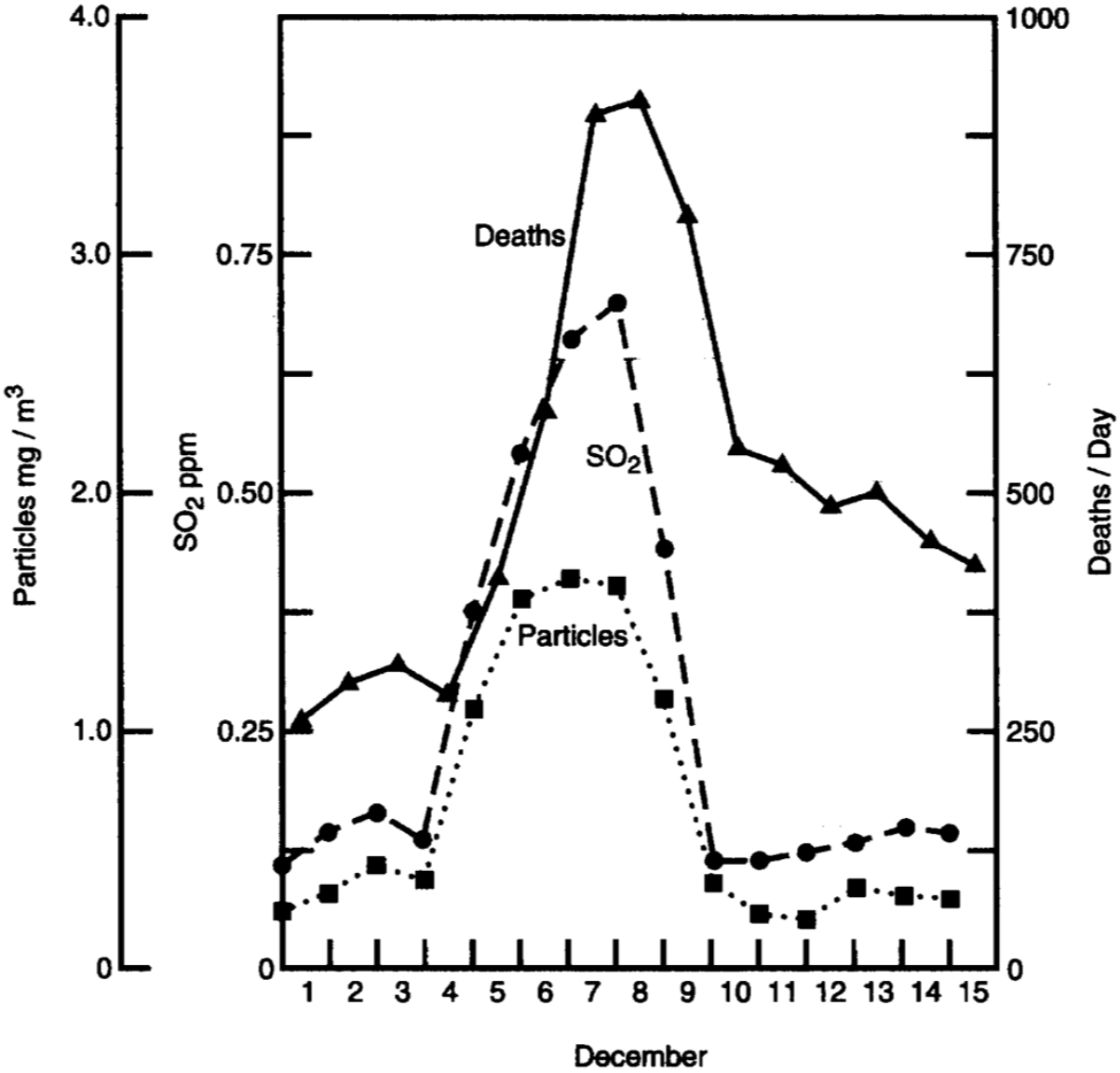
Killer Smog Episodes

So, smog: how bad can it be?

- 1930: 63 die in Meuse Valley, Belgium
- 1948: 20 die in Donora, PA
- The Great Smog of 1952: 4000 die in London
- 1962: 700 die in London
- These are sulfurous ("London") Smogs

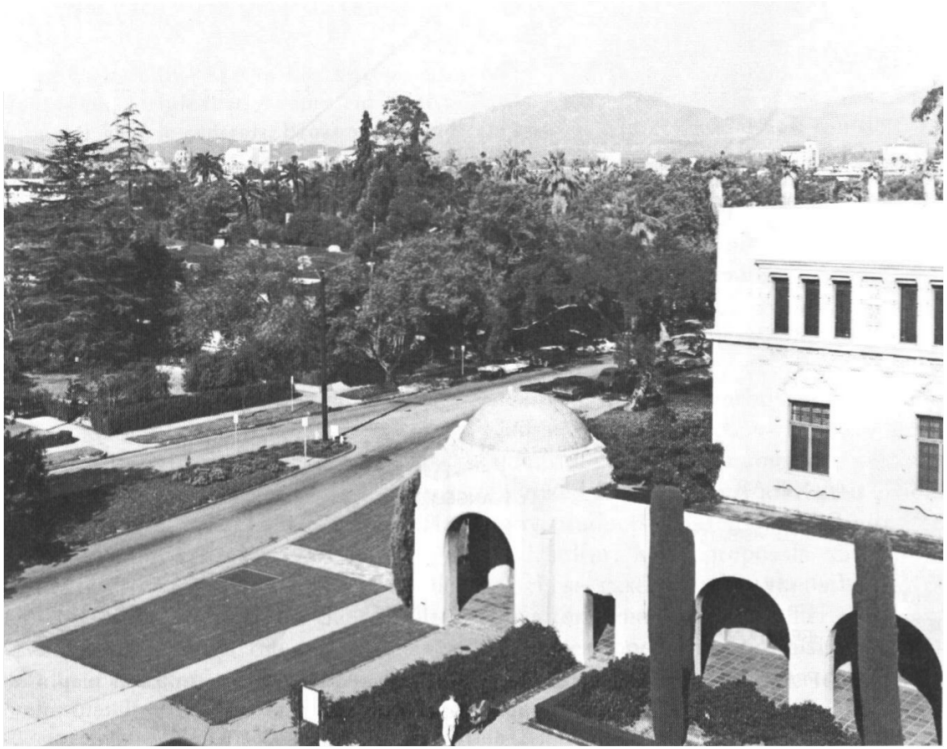
The Great Smog and Environmental Epidemiology

How do we know that 4000 died due to the 1952 smog in London?



- Examine correlation between pollutant level and some health-based indicator
- Expect to see a lag
- Should be supported by biological plausibility and other toxicological studies (animal, clinical, biochemical)

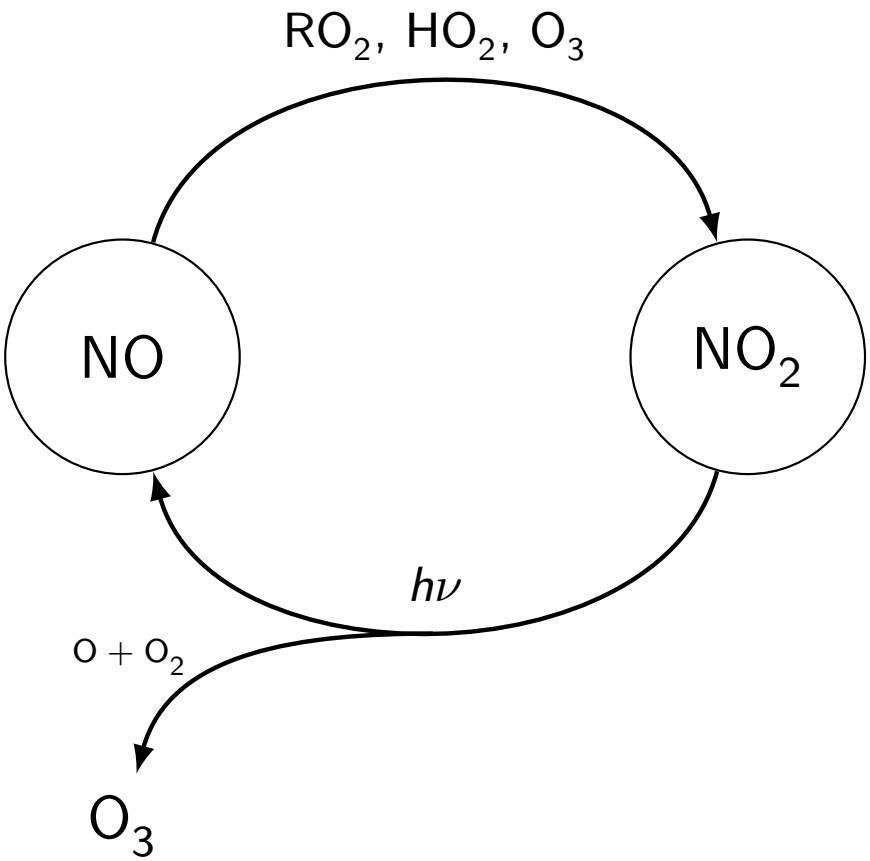
How does photochemical smog manifest?



- Left: morning view; right: afternoon view (same day)
- Different from sulfurous (London) smog:
  - favored by sunny, warm days
  - strongly oxidizing, eye-watering
  - air pollution peaks in the afternoon

Oxidation of Hydrocarbons

Explain how hydrocarbon oxidation in the presence of NO can lead to smog formation.



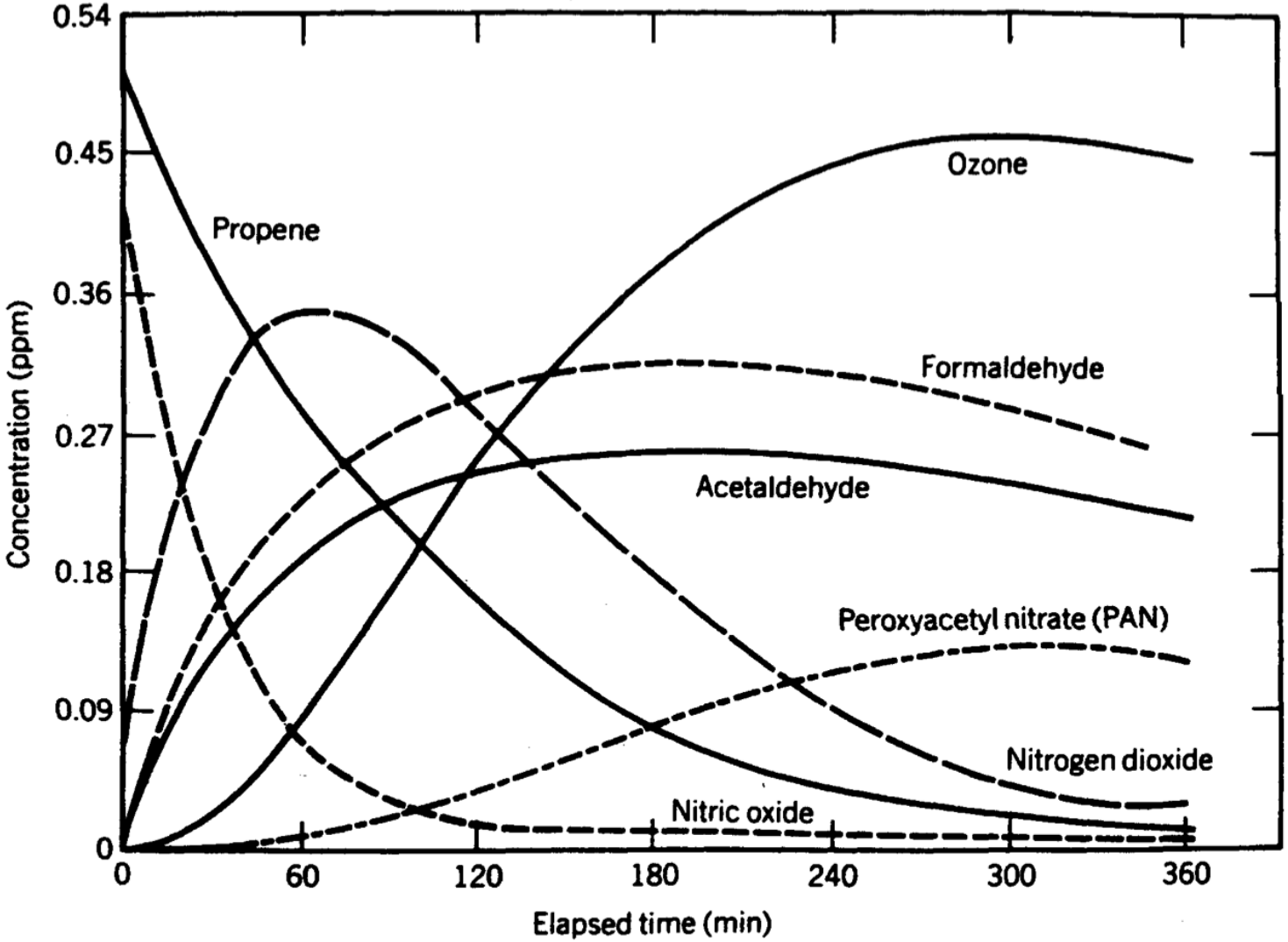
- Each cycle produces ozone by NO_2 photodissociation

$$NO_2 \xrightarrow{h\nu} NO + O$$
$$O + O_2 \longrightarrow O_3$$

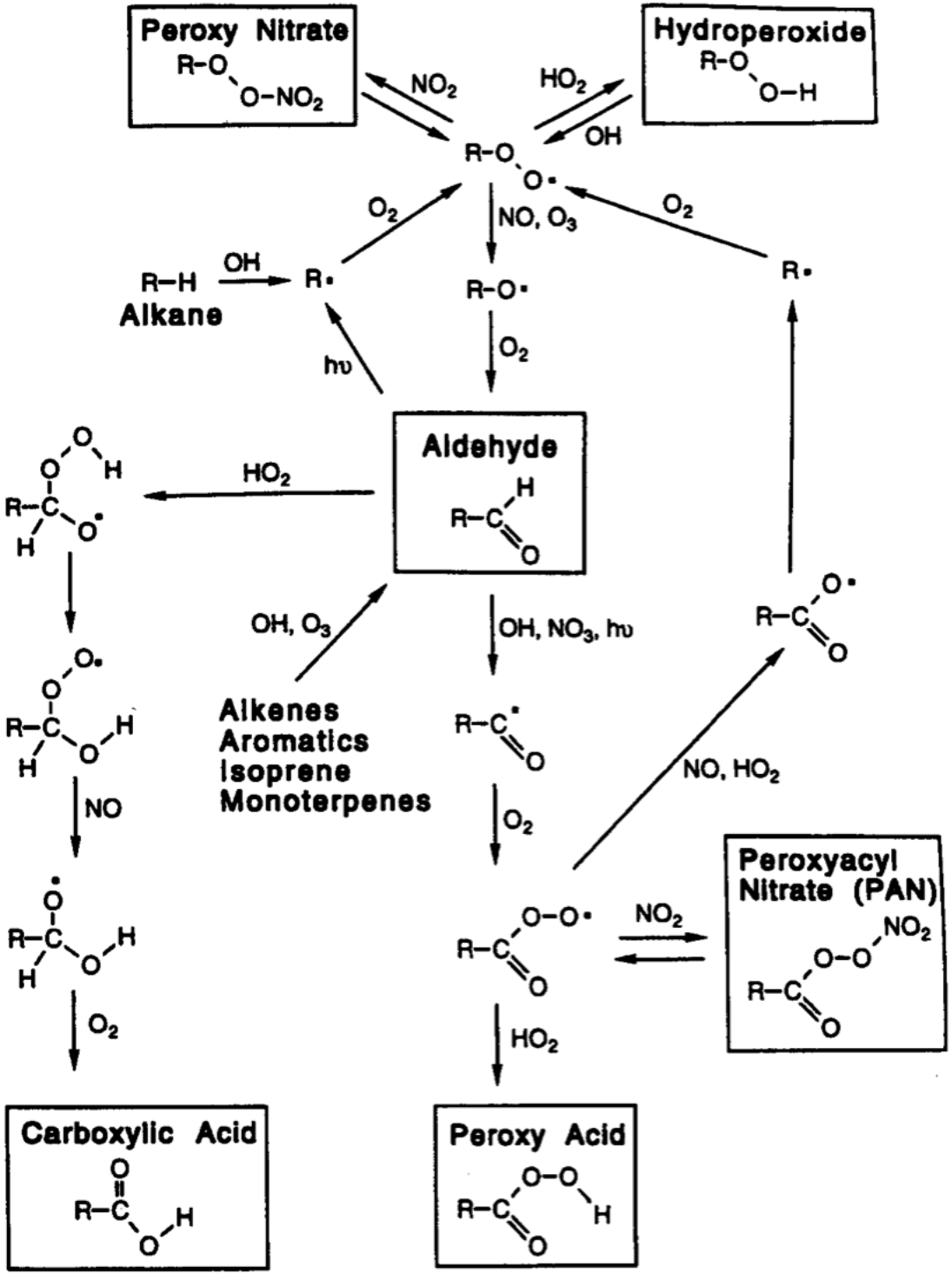
- Cycling rate (ie, O_3 production) accelerated by O_3, RO_2 and HO_2
- Cycling via $NO + O_3 \longrightarrow NO_2 + O_2$ produces no net O_3
- Oxidation of hydrocarbons (RH) produces RO_2
- Oxidation of CO produces HO_2

Evolution of Photochemical Smog

Why does ground-level ozone peak in the afternoon?



- Precursors: propene (a reactive HC) and NO, generated in morning traffic
- O_3 peaks after about 6 h
- One reason: reactive VOCs are emitted in rush hour traffic
- Another: OH generation starts when sun rises



How complicated is smog formation?

- Boxed molecules are non-radical: more stable
- They are semi-volatile, can condense to form organic PM
- PAN is characteristic of smog, releases NO_x downwind
- Oxidation of HCs in presence of NO_x is somewhat self-catalytic
- There is an NO_x 'switch' of about 10 pptr

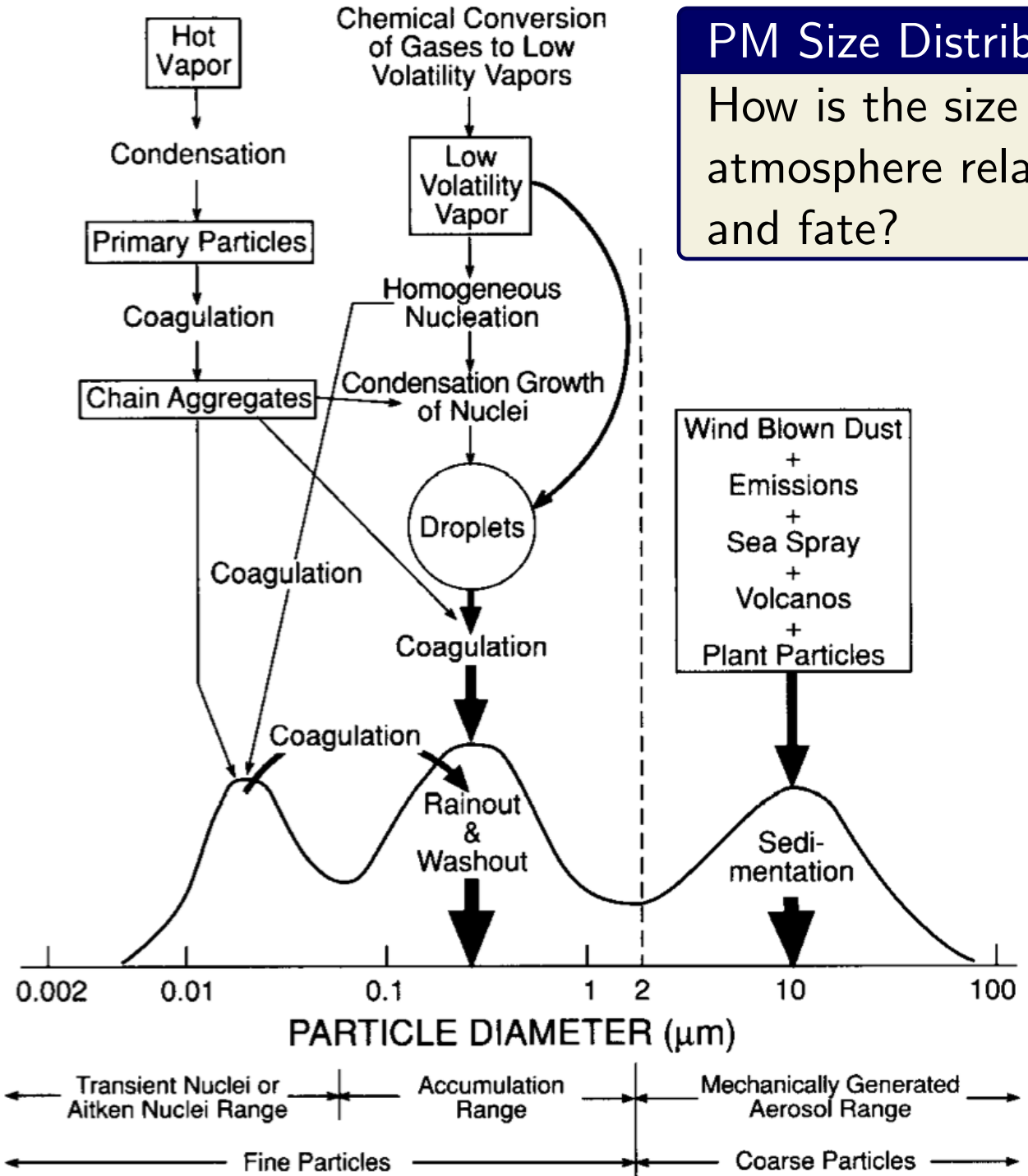
Significance of Atmopsheric Aerosol (PM)

What is the atmospheric aerosol (PM) and why is it an important part of the atmosphere?

- Atmospheric composition and reactions
- Cloud formation and properties
- Absorption and light scattering (radiative energy balance)
- Climate
- Human and ecosystem health
- Visibility

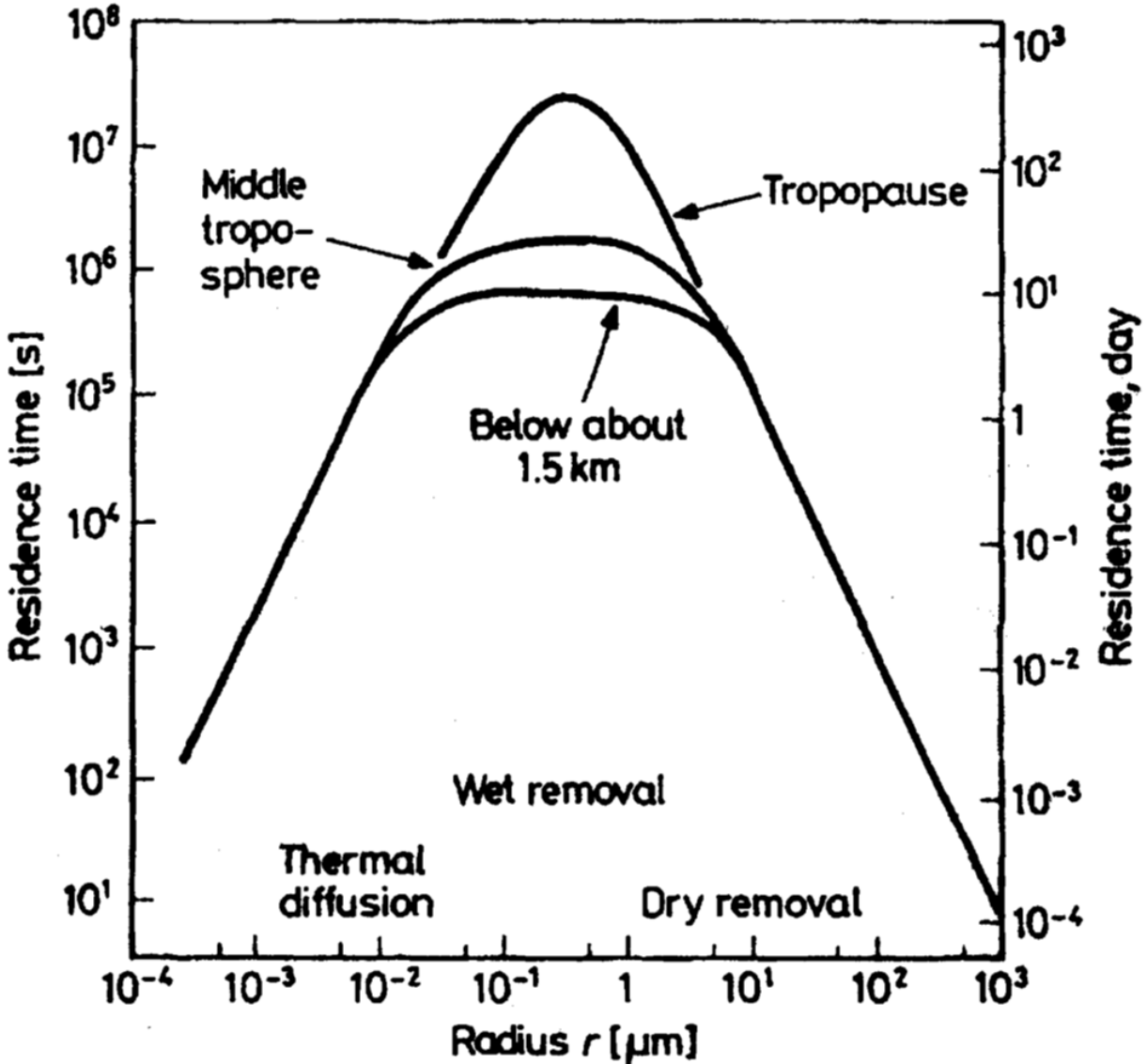
PM Size Distribution

How is the size of a particle in the atmosphere related to its formation and fate?



PM Removal Processes

How long does a particle last in the atmosphere?



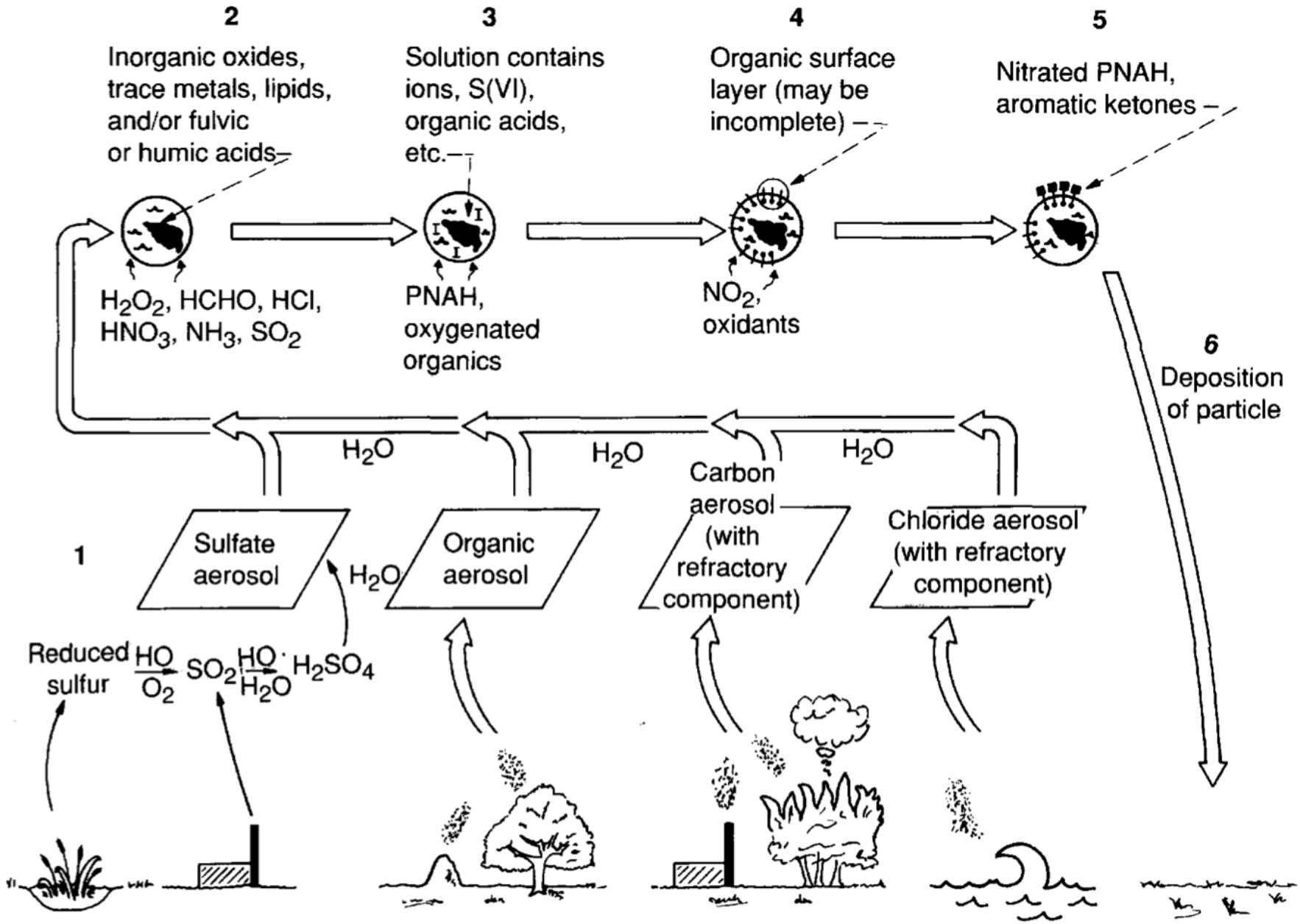
- Ultrafine PM (Aitken nuclei) are rapidly removed by coagulation
- Coarse PM are rapidly removed by sedimentation
- PM in accumulation range last the longest (weeks to months)

PM Composition

Chemically, what are the types of (non-biological) PM?

- Carbonaceous aerosol
  - Elemental carbon (soot) directly emitted by combustion processes
  - Organic aerosol: direct emission of condensed phase organic material (combustion, biogenic), and some condensation of secondary organic formed by atmospheric oxidation
- Nitrate aerosol
  - Formed from dissolution/neutralization of atmospheric HNO_3
- Sulfate aerosol
  - Formed from dissolution of gaseous SO_3 or aqueous-phase oxidation of dissolved SO_2
- Crustal material
  - Mechanical formation (wind erosion)
  - Consists of Si, O, Al, Fe, Mn, etc
- Chloride aerosol (sea-spray)
  - Mechanical formation in oceans (waves, bubbles)
  - Consists of Cl, Na, K, Mg, SO_4^{2-}, others

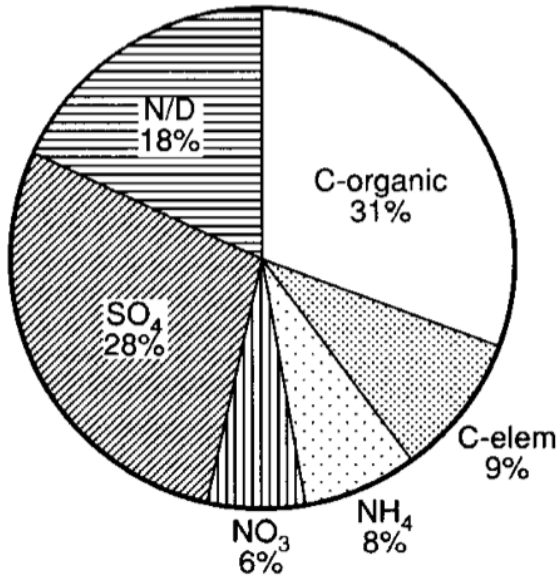
Describe a 'day in the life' of a fine particulate.



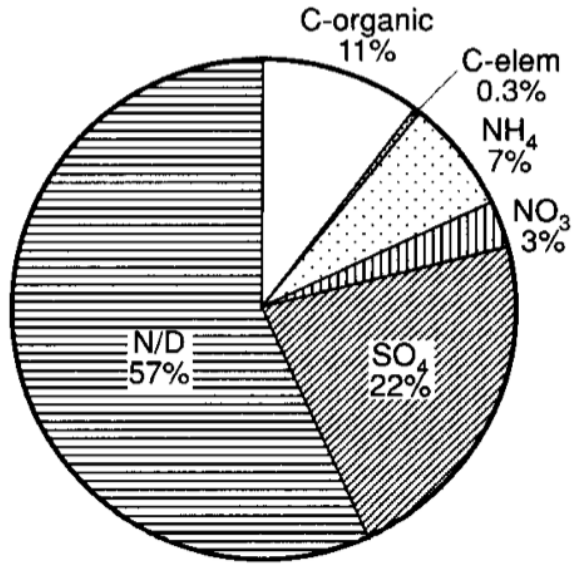
Effect of Pollution on Fine PM

How does pollution affect the concentration and composition of fine PM?

Average Urban Fine Particle Composition (by mass)
Total Suspended Mass: 33 $\mu g\ m^{-3}$



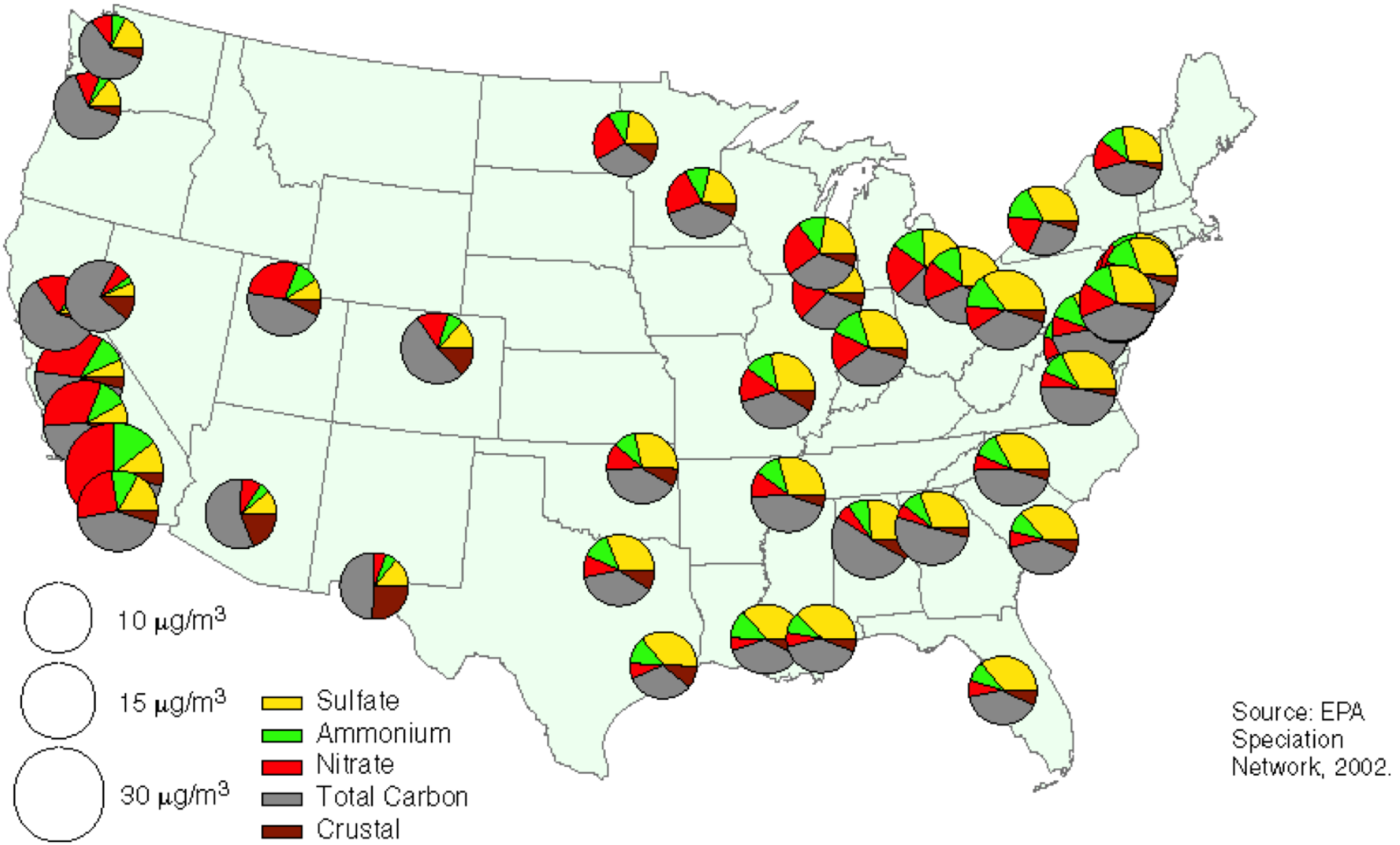
Average Remote Fine Particle Composition (by mass)
Total Suspended Mass: 4.8 $\mu g\ m^{-3}$



Note that more polluted urban air has (a) more PM (7-fold) and (b) greatly increased sulfate and carbon PM fractions.

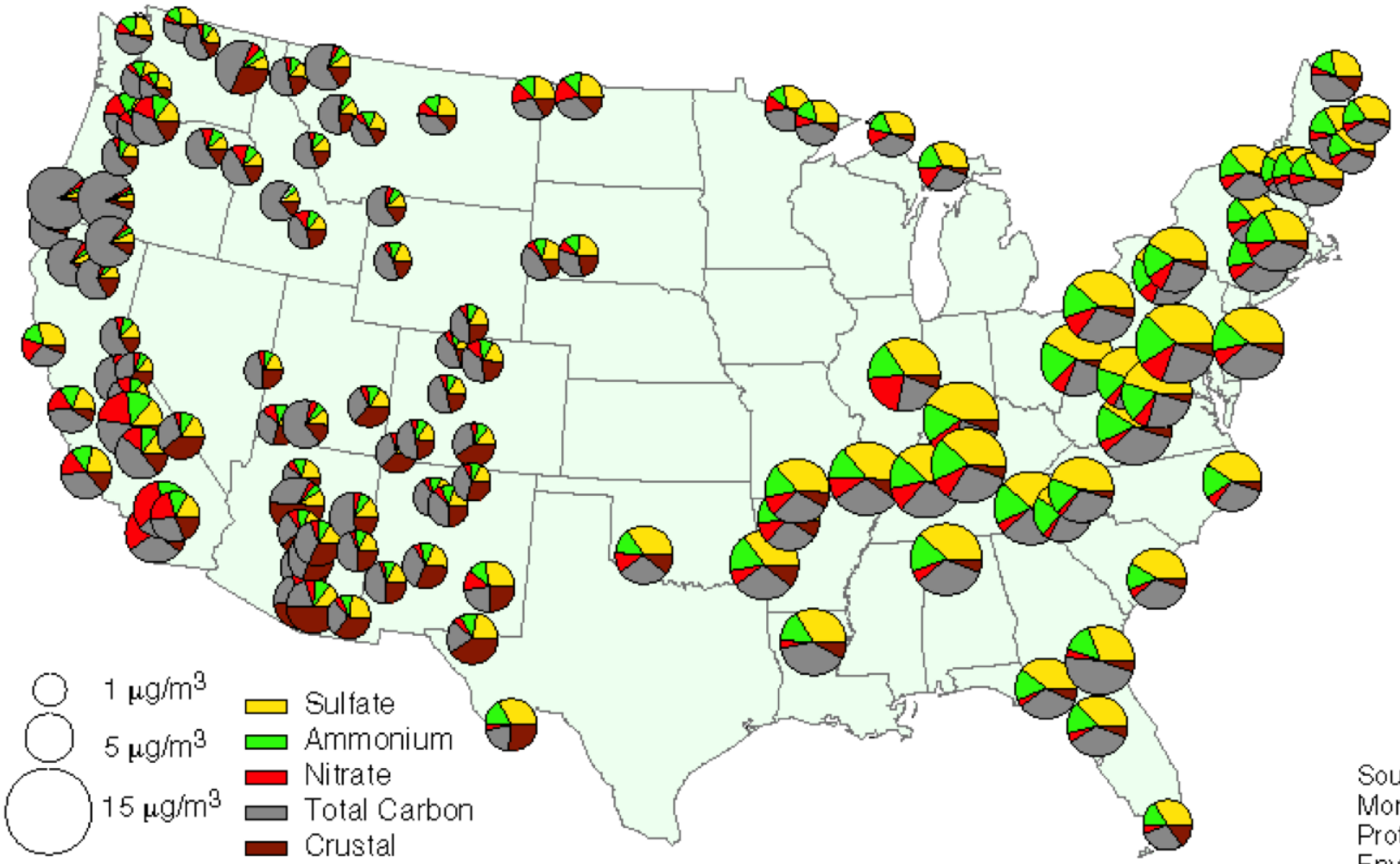
Urban Fine PM

Describe the geographic distribution of the concentration and composition of urban fine PM.



Rural Fine PM

Describe the geographic distribution of the concentration and composition of rural fine PM.



Source: Interagency Monitoring of Protected Visual Environments Network, 2002.