# Lecture 1: Introduction to Atmospheric Chemistry

*Required Reading: FP Chapter 1 & 2*

*Additional Reading: SP Chapter 1 & 2*

Atmospheric Chemistry
CHEM-5151 / ATOC-5151
Spring 2005
Prof. Jose-Luis Jimenez

# Outline of Lecture 1

- Importance of atmospheric chemistry
- Atmospheric composition: big picture, units
- Atmospheric structure
  - Pressure profile
  - Temperature profile
  - Spatial and temporal scales
- Air Pollution:
  - historical origin: AP deaths
  - Overview of problems: smog, acid rain, stratospheric $O_3$, climate change, indoor pollution
    - Continue in Lecture 2

# Importance of Atmospheric Chemistry

- Atmosphere is very thin and fragile!
  - Earth diameter = 12,740 km
  - Earth mass ~ 6 * $10^{24}$ kg
  - Atmospheric mass ~ 5.1 * $10^{18}$ kg
  - 99% of atmospheric mass below ~ 50 km
  - Solve in class: order of magnitude of mass of the oceans? Mass of entire human population?
- Main driving forces to study Atm. Chem. are big practical problems:
  - Deaths from air pollution, smog, acid rain, stratospheric ozone depletion, climate change

# Structure of Course

- Introduction
- "Tools"
  - Atmospheric transport *(BT)*
  - Kinetics *(ED)* & Photochemistry
  - Aerosols *(QZ)*
  - Cloud and Fog chemistry
- "Problems"
  - Smog chemistry
  - Acid rain chemistry
  - *Aerosol effects*
  - Stratospheric Ozone
  - Climate change

# Interdisciplinarity of Atm. Chem.

- Very broad field of both fundamental and applied nature:
  - Reaction modeling → chemical reaction dynamics and kinetics
  - Photochemistry → atomic and molecular physics, quantum mechanics
  - Aerosols → surface chemistry, material science, colloids
  - Instrumentation → analytical chemistry, electronics, optics
  - Air pollution → toxicology, organic chemistry, biochemistry
  - Global modeling → meteorology, fluid dynamics, biogeochemistry
  - Global observations → aeronautics, space research
  - Air quality standards → environmental policies and regulations
- Comparatively new field:
  - First dedicated text book written in 1961 by P.A. Leighton ("Photochemistry of Air Pollution")
  - Ozone hole discovered in 1985 by British scientists, and later by NASA
  - 1995 Nobel prize awarded to Paul Crutzen, Mario Molina, Sherwood Rowland for predicting stratospheric ozone depletion

*Adapted from S. Nidkorodov, UCI*

# Atm. Composition: Big Picture I

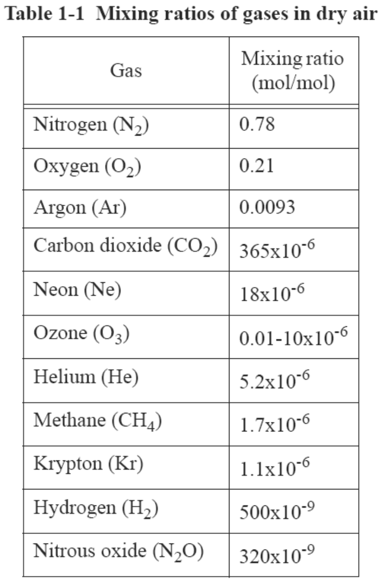


**Table 1-1 Mixing ratios of gases in dry air**

| Gas | Mixing ratio (mol/mol) |
|---|---|
| Nitrogen ($N_2$) | 0.78 |
| Oxygen ($O_2$) | 0.21 |
| Argon (Ar) | 0.0093 |
| Carbon dioxide ($CO_2$) | $365 \times 10^{-6}$ |
| Neon (Ne) | $18 \times 10^{-6}$ |
| Ozone ($O_3$) | $0.01\text{-}10 \times 10^{-6}$ |
| Helium (He) | $5.2 \times 10^{-6}$ |
| Methane ($CH_4$) | $1.7 \times 10^{-6}$ |
| Krypton (Kr) | $1.1 \times 10^{-6}$ |
| Hydrogen ($H_2$) | $500 \times 10^{-9}$ |
| Nitrous oxide ($N_2O$) | $320 \times 10^{-9}$ |

*From Jacob*

- Units of mixing ratio:
  - Mol fraction
    = Volume fraction
  - ppm: 1 molec in $10^6$
  - ppb: 1 molec in $10^9$
  - ppt: 1 molec in $10^{12}$
  - ppmv, ppbv, pptv
- Beware European billion ($10^{12}$), trillion ($10^{18}$) etc.
- ≠ mass fraction
- Q: approximate mass fraction of Kr in air?

# Atm. Comp: Unit Conversions

*From FP&P*

**TABLE 2.5 Conversion between Units of Concentration in ppm, pphm, ppb, ppt, and Molecules cm$^{-3}$, Assuming 1 atm Pressure and 25°C**[a]

| Parts per | Unit | Molecules, atoms, or radicals per cm$^3$ |
|---|---|---|
| $10^6$ | 1 ppm | $2.46 \times 10^{13}$ |
| $10^8$ | 1 pphm | $2.46 \times 10^{11}$ |
| $10^9$ | 1 ppb | $2.46 \times 10^{10}$ |
| $10^{12}$ | 1 ppt | $2.46 \times 10^{7}$ |

[a] 1 ppm in units of mass per cubic meter = $40.9 \times (\text{MW})$ $\mu$g m$^{-3}$.

- More complete tables on inside front cover of FP&P

# More on Units

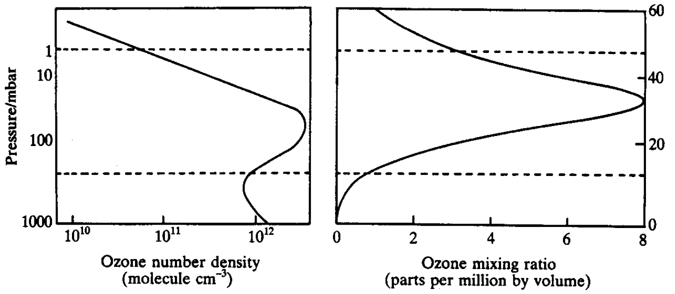


**Fig. 1.2.** Variation of atmospheric ozone concentration with altitude, expressed as an absolute number density and as a mixing ratio. From *Stratospheric Ozone 1988*, UK Stratospheric Ozone Research Group, HMSO, London, 1988.

- Units change the view very significantly
- Lack of / wrong units in your assignments or exams will be considered a serious a mistake.

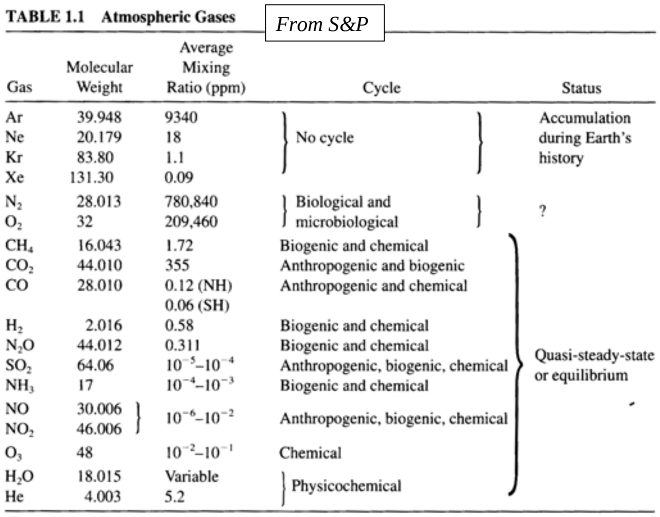
*Adapted from S. Nidkorodov, UCI*

# Example on Units

- Solve in class: Dr. Evil decides to poison humankind by spilling 100,000 55-gallon drums of tetrachloromethane in Nevada (MW = 154 g $mole^{-1}$; $\rho$ = 1.59 g $cm^{-3}$, 1 gallon = 3.785 liters).
- Assuming that all $CCl_4$ evaporated and that it does not react with anything, calculate its mixing ratio after it gets uniformly distributed through the entire atmosphere.
- Did he accomplish his objective given that the present day $CCl_4$ mixing ratio is roughly 100 ppt?
- How many drums could one fill with all the $CCl_4$ in the atmosphere?

*Adapted from S. Nidkorodov, UCI*

# Atm. Composition: Big Picture II



*From S&P*

**TABLE 1.1 Atmospheric Gases**

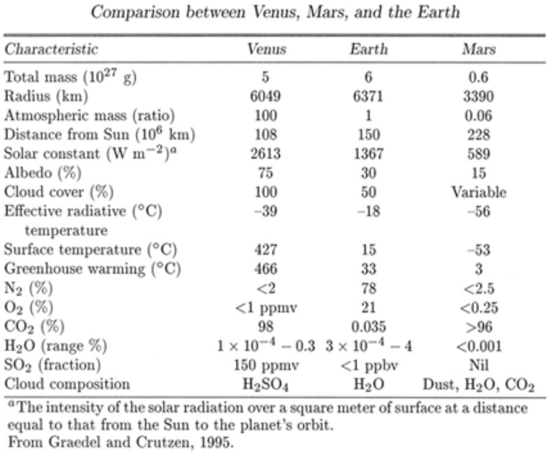
| Gas | Molecular Weight | Average Mixing Ratio (ppm) | Cycle | Status |
|---|---|---|---|---|
| Ar | 39.948 | 9340 | No cycle | Accumulation during Earth's history |
| Ne | 20.179 | 18 | | |
| Kr | 83.80 | 1.1 | | |
| Xe | 131.30 | 0.09 | | |
| $N_2$ | 28.013 | 780,840 | Biological and microbiological | ? |
| $O_2$ | 32 | 209,460 | | |
| $CH_4$ | 16.043 | 1.72 | Biogenic and chemical | Quasi-steady-state or equilibrium |
| $CO_2$ | 44.010 | 355 | Anthropogenic and biogenic | |
| CO | 28.010 | 0.12 (NH)<br>0.06 (SH) | Anthropogenic and chemical | |
| $H_2$ | 2.016 | 0.58 | Biogenic and chemical | |
| $N_2O$ | 44.012 | 0.311 | Biogenic and chemical | |
| $SO_2$ | 64.06 | $10^{-5}$–$10^{-4}$ | Anthropogenic, biogenic, chemical | |
| $NH_3$ | 17 | $10^{-4}$–$10^{-3}$ | Biogenic and chemical | |
| NO | 30.006 | $10^{-6}$–$10^{-2}$ | Anthropogenic, biogenic, chemical | |
| $NO_2$ | 46.006 | | | |
| $O_3$ | 48 | $10^{-2}$–$10^{-1}$ | Chemical | |
| $H_2O$ | 18.015 | Variable | Physicochemical | |
| He | 4.003 | 5.2 | | |

- Strongly oxidizing atmosphere
- Most atm. chemistry deals with “trace species”

# Earth’s Atmosphere in Perspective

- All major planets (except Pluto and Mercury) and some large satellites (Titan) have atmospheres.
- Properties of atmospheres on neighboring Mars, Venus, and Earth are amazingly different!
- Earth is unique in:
  - Very high $O_2$ content (close to spontaneous combustion limit)
  - High $H_2O$ content
  - Existence of graduate students and professors on the surface

**How about other planets?**



*Comparison between Venus, Mars, and the Earth*

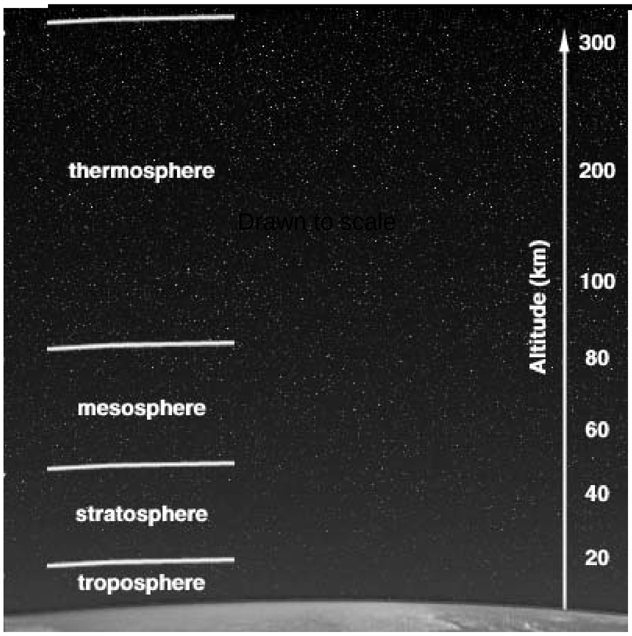
| *Characteristic* | *Venus* | *Earth* | *Mars* |
|---|---|---|---|
| Total mass ($10^{27}$ g) | 5 | 6 | 0.6 |
| Radius (km) | 6049 | 6371 | 3390 |
| Atmospheric mass (ratio) | 100 | 1 | 0.06 |
| Distance from Sun ($10^6$ km) | 108 | 150 | 228 |
| Solar constant (W $m^{-2}$)[a] | 2613 | 1367 | 589 |
| Albedo (%) | 75 | 30 | 15 |
| Cloud cover (%) | 100 | 50 | Variable |
| Effective radiative (°C) temperature | –39 | –18 | –56 |
| Surface temperature (°C) | 427 | 15 | –53 |
| Greenhouse warming (°C) | 466 | 33 | 3 |
| $N_2$ (%) | <2 | 78 | <2.5 |
| $O_2$ (%) | <1 ppmv | 21 | <0.25 |
| $CO_2$ (%) | 98 | 0.035 | >96 |
| $H_2O$ (range %) | $1 \times 10^{-4} - 0.3$ | $3 \times 10^{-4} - 4$ | <0.001 |
| $SO_2$ (fraction) | 150 ppmv | <1 ppbv | Nil |
| Cloud composition | $H_2SO_4$ | $H_2O$ | Dust, $H_2O$, $CO_2$ |

[a] The intensity of the solar radiation over a square meter of surface at a distance equal to that from the Sun to the planet’s orbit.

From Graedel and Crutzen, 1995.

*Slide from S. Nidkorodov, UCI*
*Table From Brasseur, 1999*

# Lower Atmosphere is “Flat”!



- For most practical purposes, lower atmosphere can be regarded as flat. Earth curvature only needs to be considered in very special cases.
- Earth does drag a veil of gas with itself (“exosphere”) with the size of approximately 10,000 km, however it is extremely dilute. For reference, space shuttle @ 300-600 km above the Earth surface

*From S. Nidkorodov, UCI*

# Atmospheric Structure I

*From FP&P*

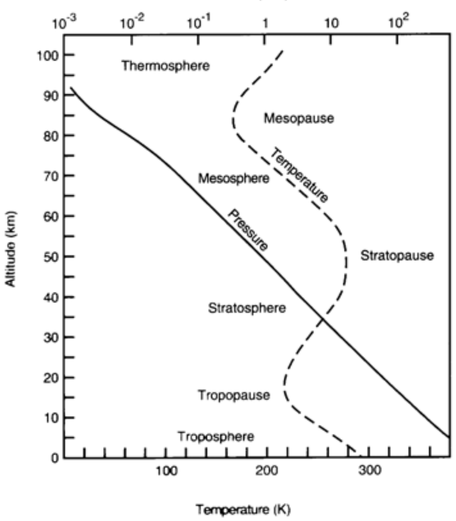
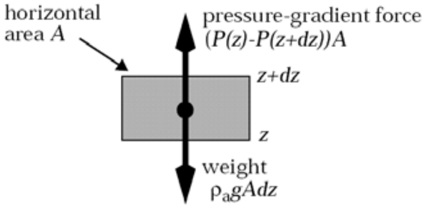


**FIGURE 1.1** Typical variation of temperature with altitude at mid-latitudes as a basis for the divisions of the atmosphere into various regions. Also shown is the variation of total pressure (in Torr) with altitude (top scale, base 10 logarithms) where 1 standard

- Questions:
  - – Physical basis for P variation?
  - – Physical basis for T variation?

# AS II: Pressure Variation



*From Jacob*

**Figure 2-3 Vertical forces acting on an elementary slab of atmosphere**

- Write differential mass balance for slab

- Solution: $p(z)/P_0 = e^{-z/H}$
- 99.9% of mass below stratopause

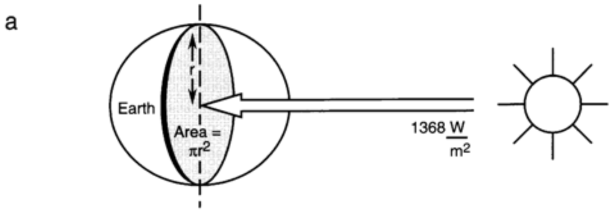
*See S&P p.9*

# AS III: Species Variation?

- $H(z) = RT(z)/(MW_{air} * g)$
- Dalton's law: each component behaves as if it was alone in the atmosphere
- $H_i(z) = RT(z)/(MW_i * g)$
  - $O_2$ at lower altitudes than $N_2$?
  - Some scientists: CFCs could not cause stratospheric $O_3$ depletion; too heavy to rise to stratosphere
- But gravitational separation due to molecular diffusion, much slower than turbulent diffusion
  - Only > 100 km enriched in lighter gases

# AS IV: T Variation

*From FP&P Fig. 1.9*



- First order approximation:
  - Atmosphere is transparent, only surface is heated
  - Loss by convection + re-radiation
  - Shape of atmospheric temperature profile?

# AS V: T Variation

- In the absence of local heating, T decreases with height
- Exceptions: Stratosphere: Chapman Cycle (1930s)

  $O_2 + h\nu \rightarrow 2O$

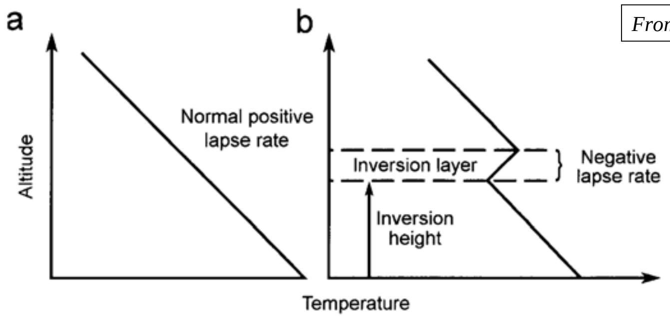
  $O + O_2 + M \rightarrow O_3$ (+ heat)

  $O + O_3 \rightarrow 2O_2$

  $O_3 + h\nu \rightarrow O + O_2$ (+ heat)

  – Q: what is heat at the molecular level?
- Mesosphere: absorption by $N_2$, $O_2$, atoms…

# Temperature Inversions



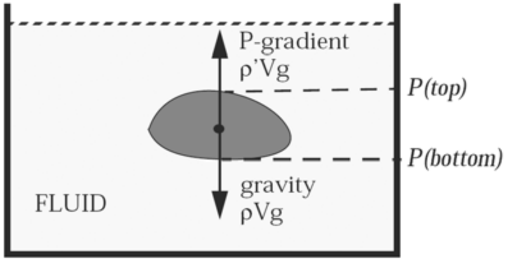
*From FP & P*

**FIGURE 2.18** Variation of temperature with altitude within the troposphere: (a) normal lapse rate; (b) change in lapse rate from positive to negative, characteristic of a thermal inversion.

- “Inversion layer”: temperature increases with height
- Supresses mixing. Why?

## Atmospheric (Vertical) Stability I

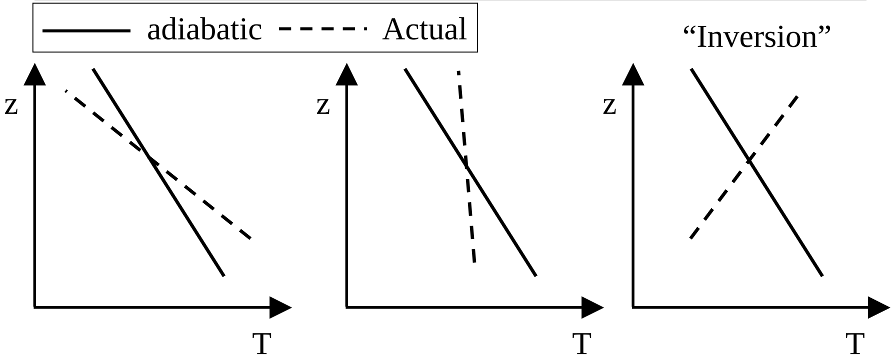
- Adiabatic Lapse Rate ($\Gamma$)
  - vertical temperature profile when air ascends or descends adiabatically, i.e. w/o giving or receiving heat
  - For Earth, $\Gamma = 9.8$ K km$^{-1}$
  - Will deduce it from first principles later in the course
- Buoyancy force $F_b = \rho' g - \rho g$



*From Jacob*

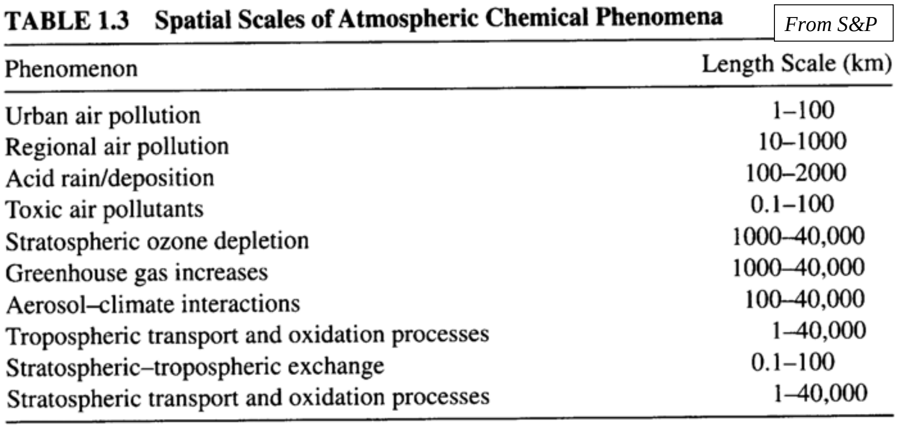
**Figure 4-13 Gravity and pressure-gradient forces applied on an object (density ρ) immersed in a fluid (density ρ')**

## Atmospheric (Vertical) Stability II



- Q: which of the following profiles are stable and unstable
  - Stable: a small perturbation is damped
  - Unstable: a small perturbation is amplified

# Spatial Scales of Atm. Chemistry



*From S&P*

**TABLE 1.3 Spatial Scales of Atmospheric Chemical Phenomena**

| Phenomenon | Length Scale (km) |
|---|---|
| Urban air pollution | 1–100 |
| Regional air pollution | 10–1000 |
| Acid rain/deposition | 100–2000 |
| Toxic air pollutants | 0.1–100 |
| Stratospheric ozone depletion | 1000–40,000 |
| Greenhouse gas increases | 1000–40,000 |
| Aerosol–climate interactions | 100–40,000 |
| Tropospheric transport and oxidation processes | 1–40,000 |
| Stratospheric–tropospheric exchange | 0.1–100 |
| Stratospheric transport and oxidation processes | 1–40,000 |

- Enormous range of variation
  - Typically separate research communities, don’t talk much to each other

# Spatial and Temporal Scales

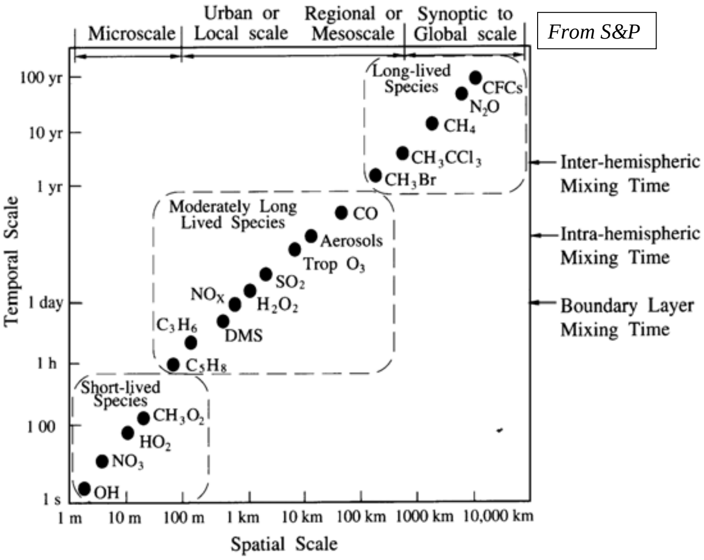


**FIGURE 1.17** Spatial and temporal scales of variability for atmospheric constituents.

- Tight link between spatial & temporal scales

# A flavor about the main problems

- London smog
  - Primary pollutants
- Photochemical (“LA”) smog
- Global tropospheric pollution
- Particles
  - Health
  - Visibility
- Acid deposition
- Stratospheric ozone depletion
- Global climate change

# Air Pollution & Excess Deaths

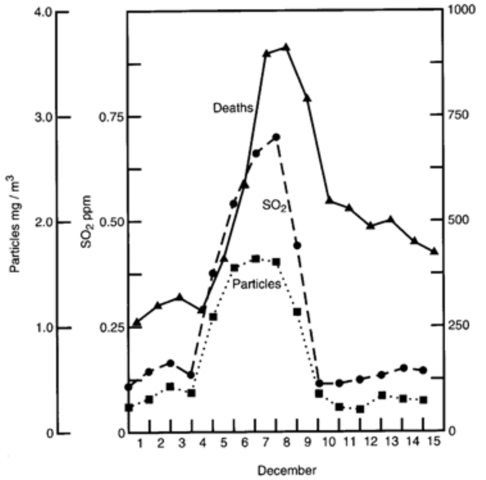


**FIGURE 1.2** Concentrations of $SO_2$ and “smoke” as well as the death rate during the 1952 smog episode (adapted from Wilkins, 1954).

*From FP & P*

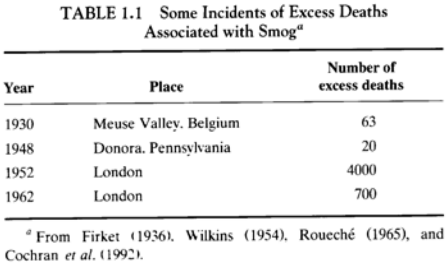


TABLE 1.1 Some Incidents of Excess Deaths Associated with Smog[a]

| Year | Place | Number of excess deaths |
|---|---|---|
| 1930 | Meuse Valley, Belgium | 63 |
| 1948 | Donora, Pennsylvania | 20 |
| 1952 | London | 4000 |
| 1962 | London | 700 |

[a] From Firket (1936), Wilkins (1954), Roueché (1965), and Cochran *et al.* (1992).

- Cold days, strong inversions, foggy
- Smoke + Fog = “Smog”
- Governments, industry & scientists start to recognize importance of *AP*

*From FP & P*

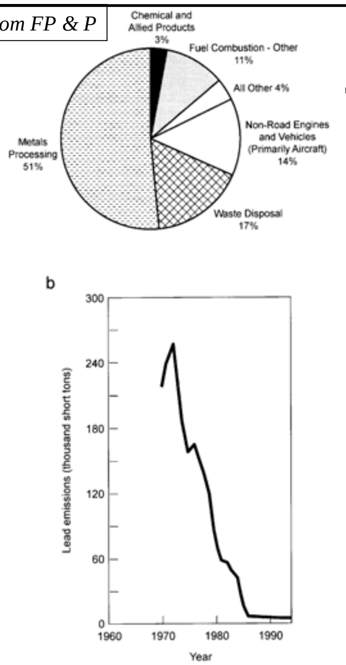


**FIGURE 2.16** (a) Contribution of various sources to total anthropogenic Pb emissions in the United States in 1996. (b) Trend in lead emissions in the United States (from EPA, 1995, 1997).

# Primary Pollutants

- “Primary”: emitted directly, e.g. Pb
  - You reduce emission to reduce concentrations
- “Secondary”: formed in the atmosphere, e.g. $O_3$
- Pb was “easy”
  - Almost all from gasoline vehicles
  - Added to gasoline as anti-knock agent
  - Did without it after regulation required its removal
- Many countries still use leaded gasoline (~1/4 of gasoline in Spain, most in Africa)

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# Phothochemical (“LA”) Smog

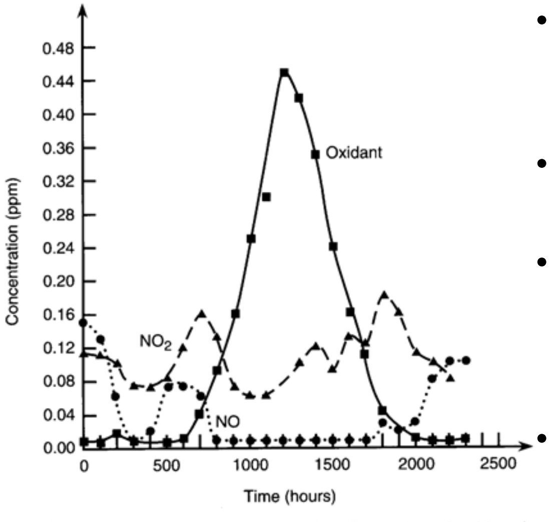


**FIGURE 1.3** Diurnal variation of NO, $NO_2$, and total oxidant in Pasadena, California, on July 25, 1973 (adapted from Finlayson-Pitts and Pitts, 1977).

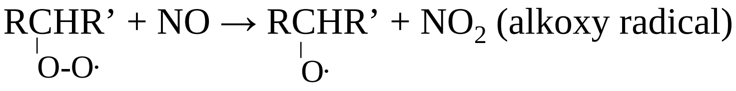
*From FP & P*

- Sharp contrast to London: sunny, hot days
- Eye irritation, plant damage
- 1950’s: Haagen-Smit:
  - Organics + $NO_x$ + sunlight → $O_3$ + “other products”
- Now widespread problem throughout the world

# What causes photochemical smog?

- Observation: NO emitted first, then forms $NO_2$, then $O_3$ peaking in afternoon
- Can Chapman mechanism produce $O_3$ in LA?
  - – Requires $O_2 + h\nu \rightarrow 2O$
  - – Needs hard UV that does not reach surface
  - – Need another route
- Blacet, 1952: photodissociation of $NO_2$
  - – $NO_2 + h\nu$ ($\lambda < 430$ nm) $\rightarrow NO + O$
  - – $O + O_2 + M \rightarrow O_3$
  - – Also $NO + O_3 \rightarrow NO_2 + O_2$ (rapid)

# What causes smog II

- How does NO form $NO_2$? (w/o $O_3$)
- Thermal reaction $2NO + O_2 \rightarrow 2NO_2$ very slow
- Answer: organic oxidation
  - – RCH2R' + OH → RC·HR' + $H_2O$
  - – 
    $RC\cdot HR' + O_2 \rightarrow \underset{|\atop O\text{-}O\cdot}{RCHR'}$ (peroxy radical)
  - – 
    $\underset{|\atop O\text{-}O\cdot}{RCHR'} + NO \rightarrow \underset{|\atop O\cdot}{RCHR'} + NO_2$ (alkoxy radical)
  - – Every step in organic oxidation creates $NO_2$, then $O_3$