Updated: 11 December 2019

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CEE 370 Environmental Engineering Principles

Lecture #37

Air Pollution II:

Air Pollution & Modeling

Reading: Mihelcic & Zimmerman, Chapt 11

Reading: Davis & Cornwall, Chapt 7-6 to 7-9

Reading: Davis & Masten, Chapter 12-6 to 12-9

Nitrogen dioxide

- Natural Sources
  - Nitrous oxide (N_2O) is produced by soil bacteria
  - This reacts with atomic oxygen (from ozone) to form nitric oxide (NO)

$$N_2O + O \leftrightarrow 2NO$$

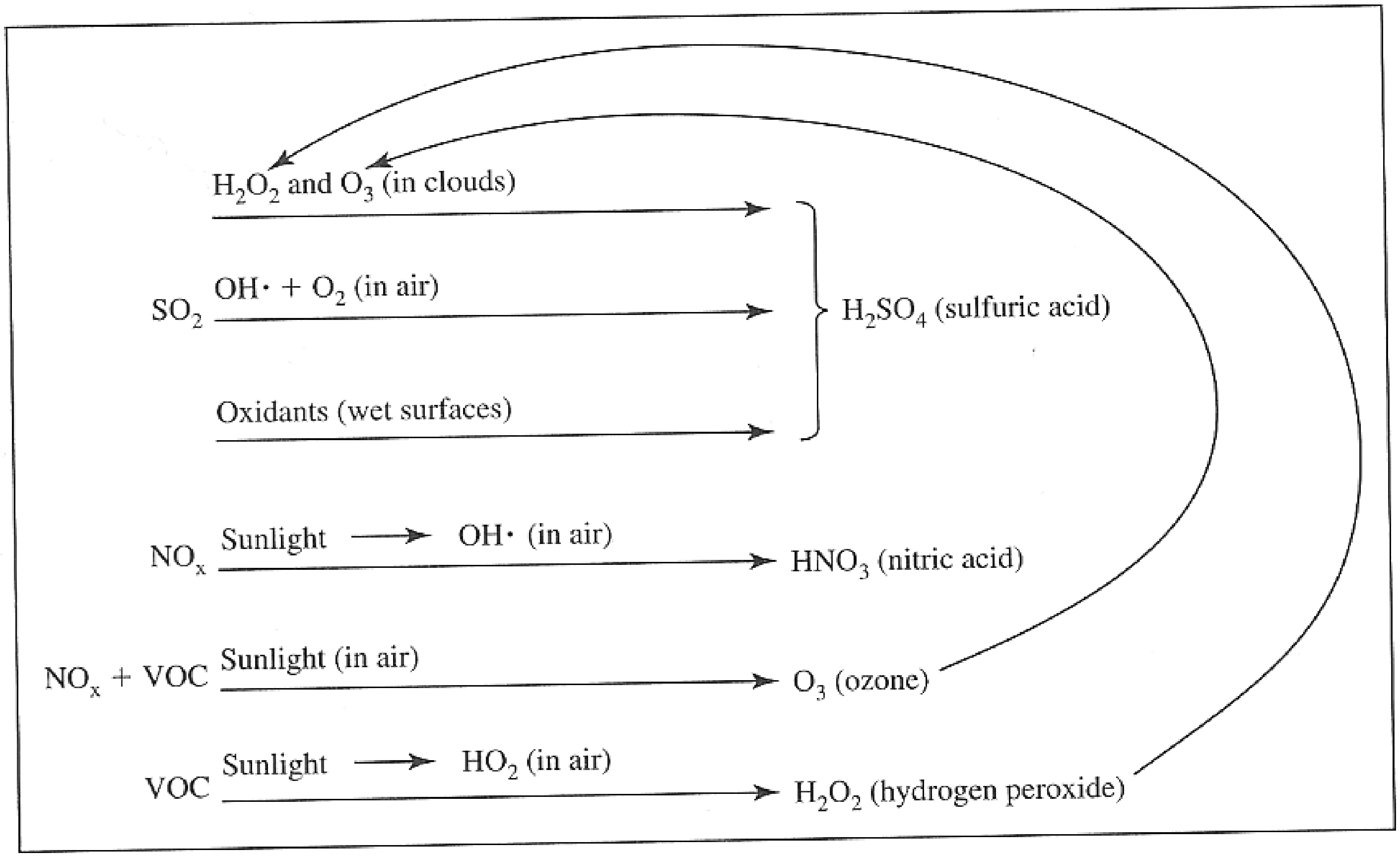
  - NO then reacts with ozone to form nitrogen dioxide (NO_2)

$$NO + O_3 \leftrightarrow NO_2 + O_2$$

- Anthropogenic Sources
  - Combustion processes account for 74% of anthropogenic sources

NO_X/SO_X Atmospheric chemistry

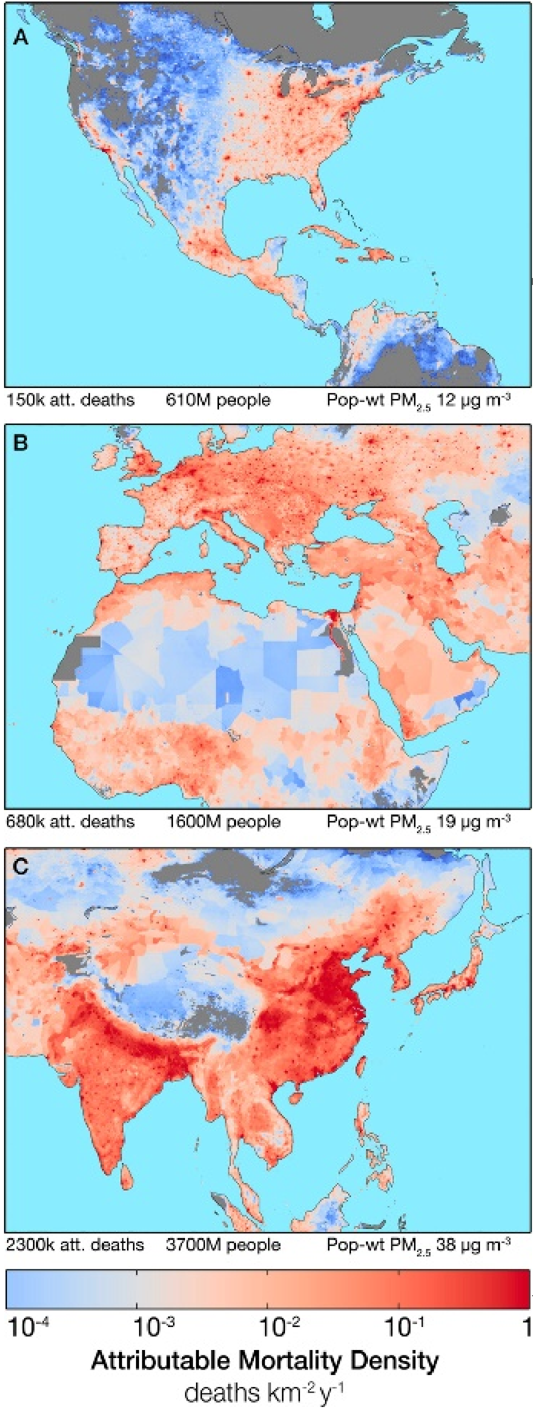
- Acid Rain precursors and products



Particulate Pollutants

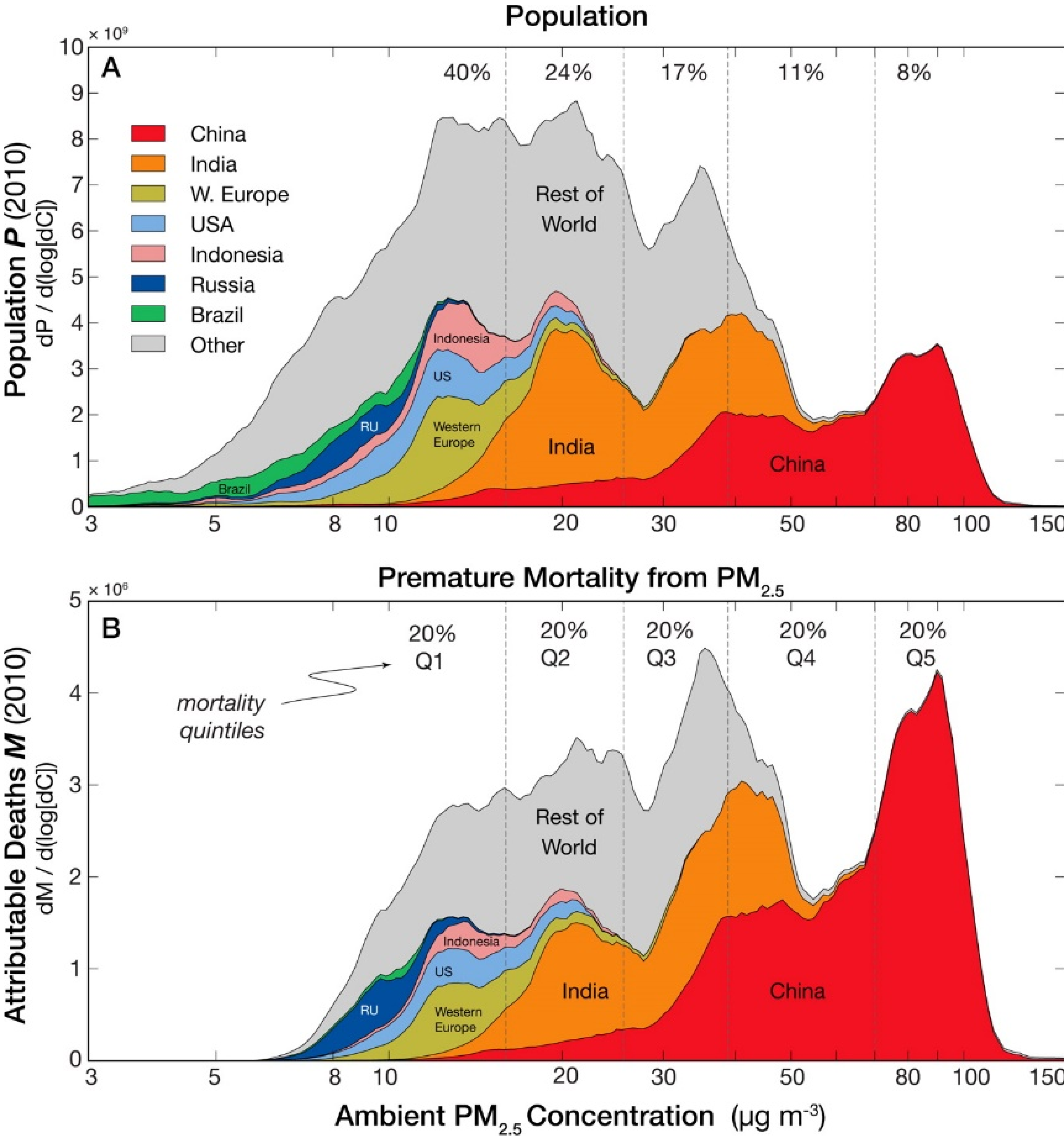
- Sources:
  - combustion processes (0.05-200μm)
    - power generation, motor vehicles, forest fires
  - entrained matter
    - sea salt (0.05-0.5μm), soil dust (0.5-50μm)
  - dust from mechanical abrasion (1-30μm)
- Sinks
  - Smaller particles: accretion to water droplets & ppt.
  - Larger particles are washed out by falling ppt.
  - Dry deposition
- Human Impact
  - small particles enter lungs, may be permanently retained

Apte et al., 2015 EST 49: 8057



Attributable premature mortality surfaces for PM2.5 at 10 km resolution for (A) the northern Americas, (B) Europe and northern Africa, and (C) Asia; units for logarithmic color scale: premature deaths km–2 y−1. Dark gray regions indicate areas without attributable mortality, owing to ambient PM2.5 below the theoretical minimum-risk concentration level or to unavailable input data. Spatial patterns reflect the multiplicative effect of (i) local variations in PM2.5 mortality risk and population density and (ii) regional variation in per-capita cause-specific disease rates. See SI for population-normalized maps.

Published in: Joshua S. Apte; Julian D. Marshall; Aaron J. Cohen; Michael Brauer; *Environ. Sci. Technol.* **2015,** 49, 8057-8066.
DOI: 10.1021/acs.est.5b01236



Global and regional distributions of population (A) and premature mortality attributable to year-2010 PM2.5 (B) as a function of ambient PM2.5 concentration. Plotted data reflect local smoothing of bin-width normalized distributions computed over 400 logarithmically spaced bins; equal-sized plotted areas would reflect equal populations (A) or equal mortality (B). Dashed vertical lines (in both plots) demarcate boundaries of mortality quintiles (Q1–Q5, Table 1) that apportion the PM2.5 concentration distribution into 5 bins with equal number of premature deaths.

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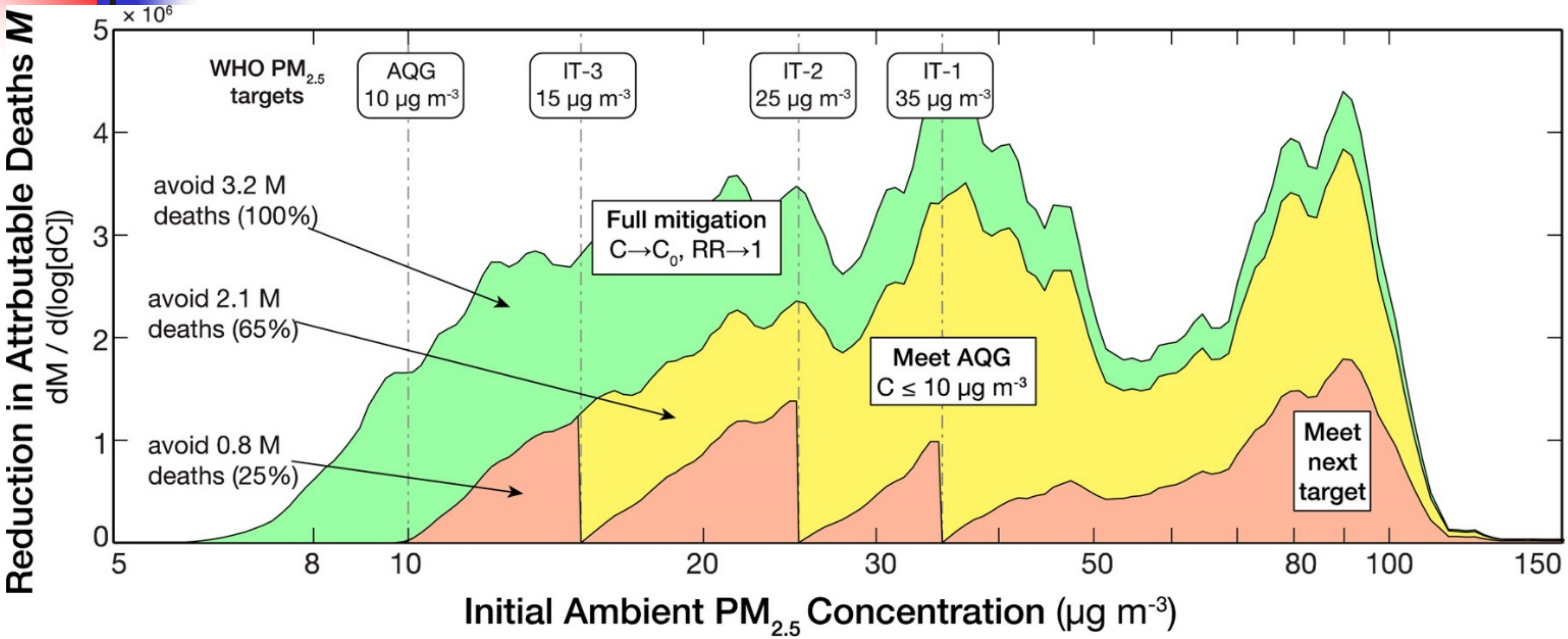

Potential to avoid premature mortality attributable to PM2.5 for the year-2010 global ambient concentration distribution. Plots indicate reduction in attributable mortality (vertical axis) for three alternative scenarios with lower PM2.5, displayed as a function of initial ambient PM2.5 concentration (horizontal axis). For "meet next target" scenario, initial concentrations are reduced globally to the next available WHO PM2.5 air quality target (see vertical dashed lines). For "meet AQG" scenario, all regions with concentrations above the WHO air quality guideline target attain 10 µg m–3. In "full mitigation" scenario, global PM2.5 levels are set to the counterfactual concentration *C*0 = 5.8 µg m–3. The integral of a single curve between two concentration end points reflects the mortality reduction potential for a particular scenario applied to all areas with PM2.5 in that concentration range.

Published in: Joshua S. Apte; Julian D. Marshall; Aaron J. Cohen; Michael Brauer; *Environ. Sci. Technol.* **2015,** 49, 8057-8066.
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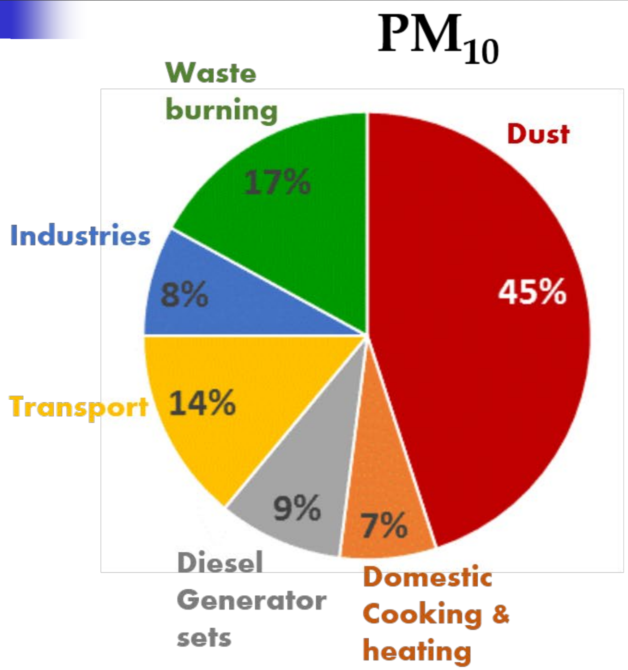
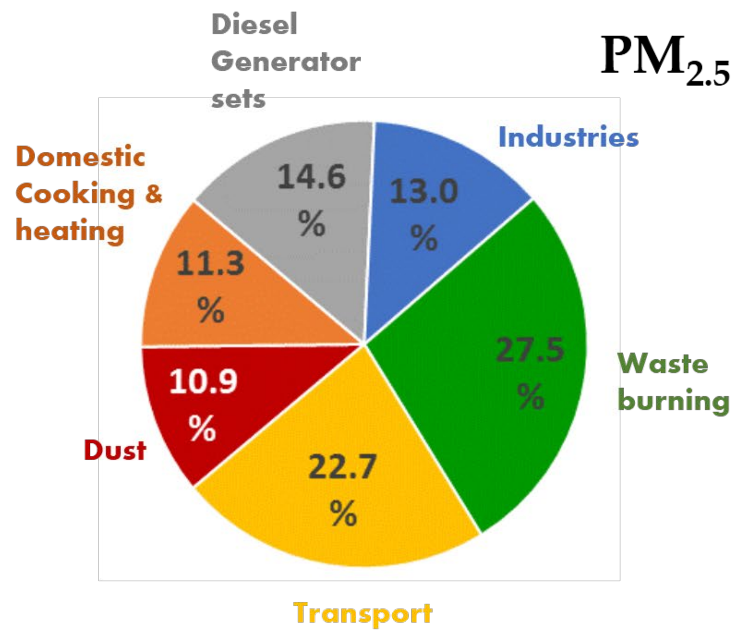
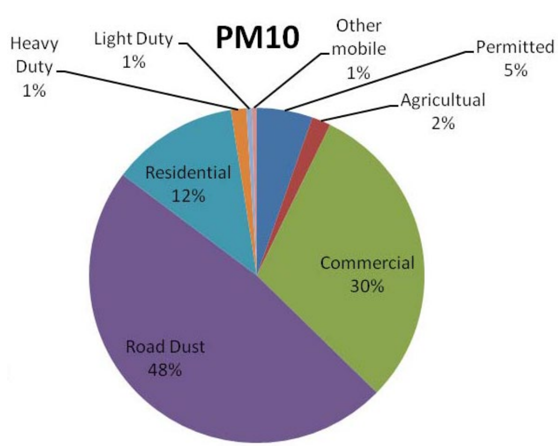
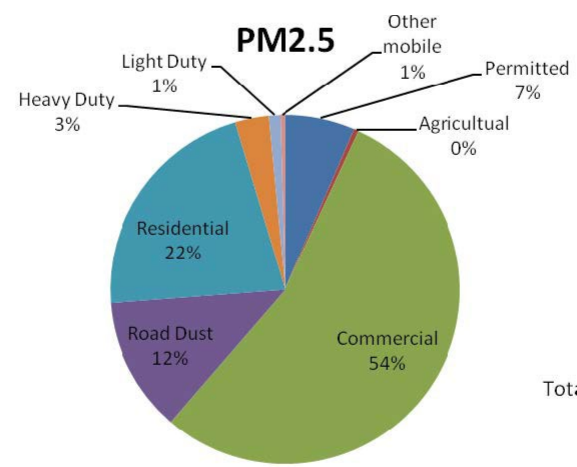
PM sources in Delhi





- Compare to BC in Canada



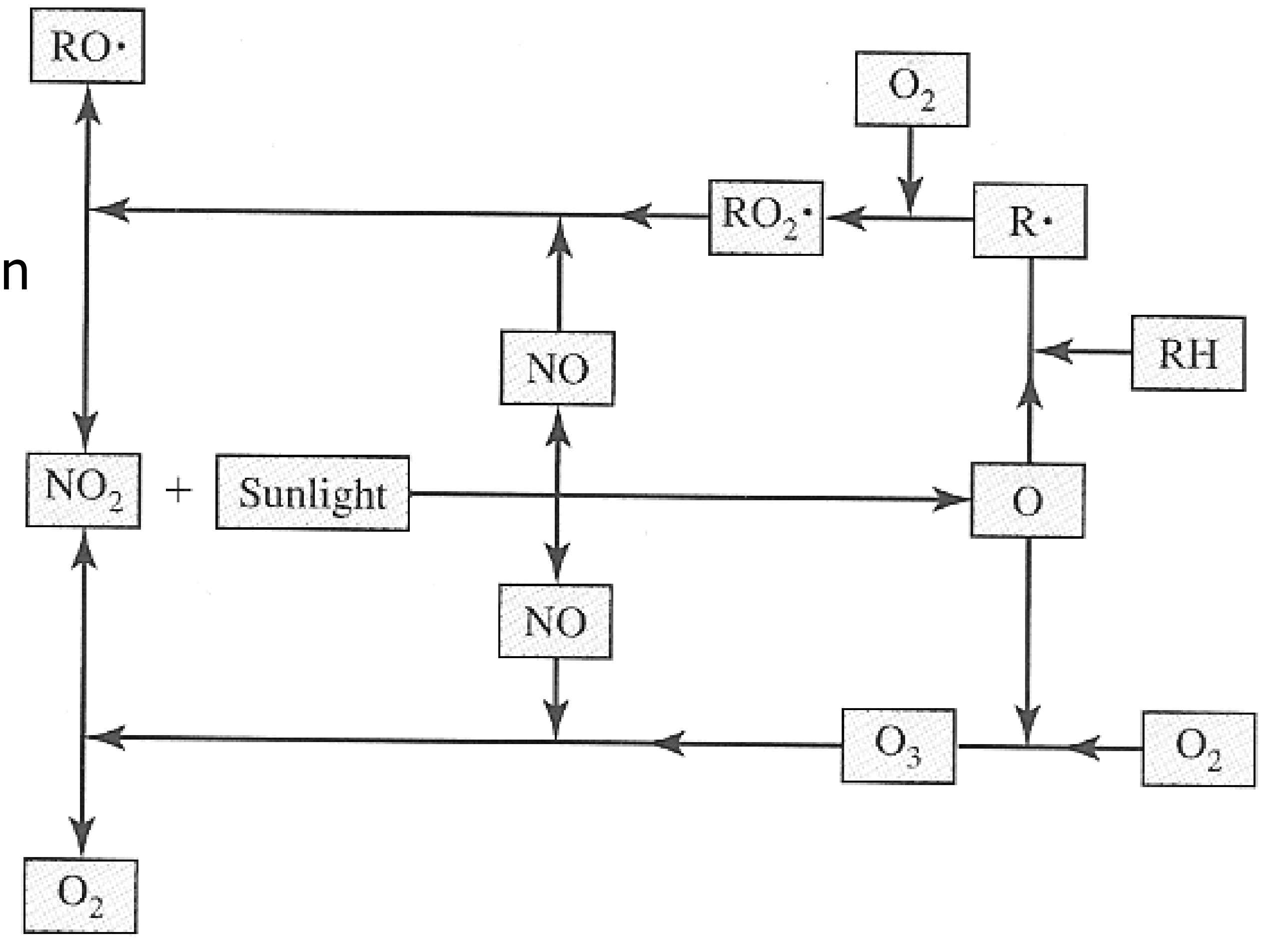


Tropospheric Photochemical Pollutants

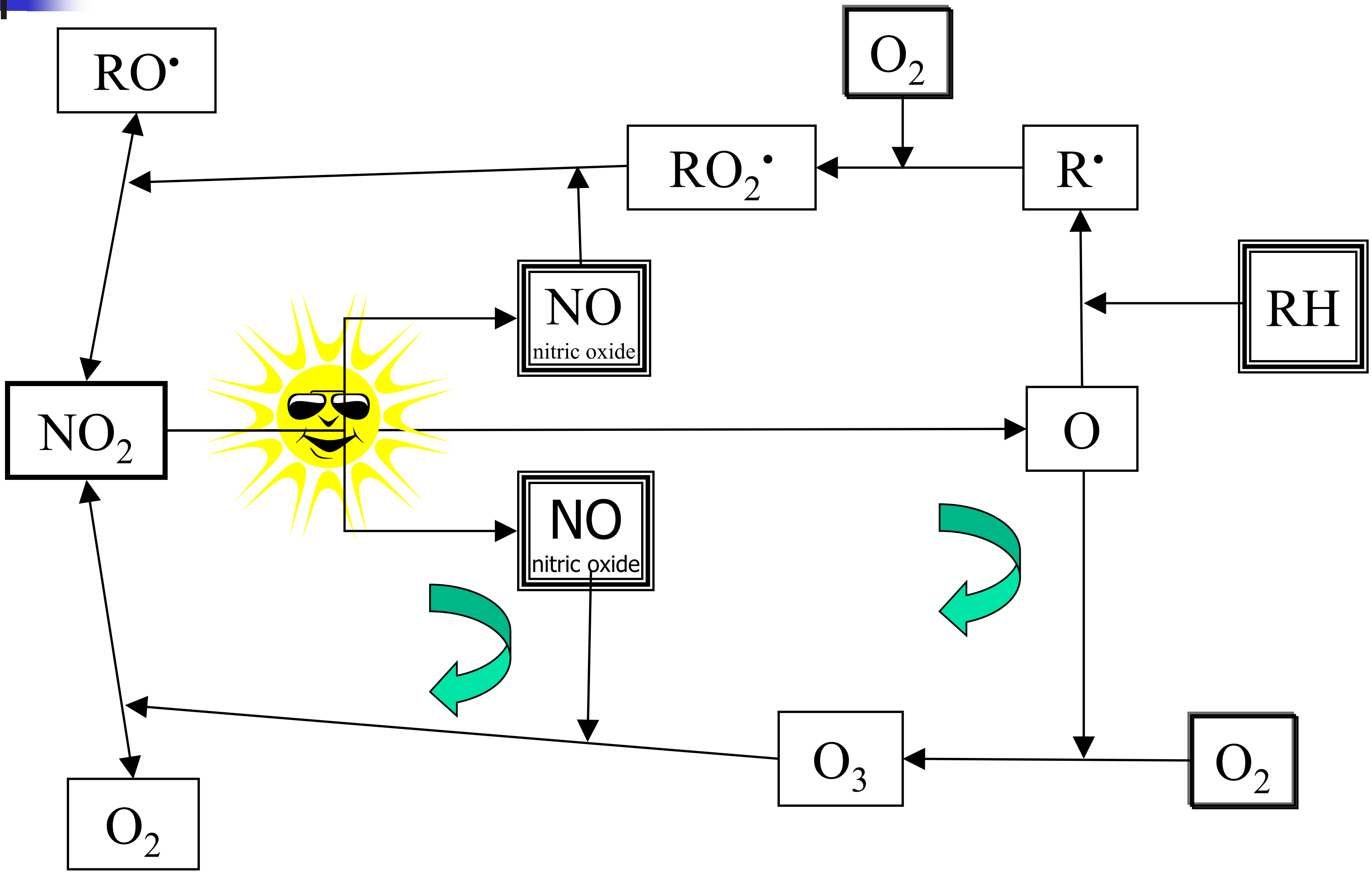
- Photochemical reactions which lead to ozone formation
- from release of nitric oxide (NO) and aggravated by volatile organic compounds (RH)
- Ozone is toxic and causes respiratory inflammation

Photochemical Reactions

- AKA, Smog
  - RH=reactive hydrocarbon
  - R· = hydrocarbon radical
  - See 11.4.7



Smog Reactions



Stratospheric Ozone Chemistry

- Stratosphere is layer above troposphere (12-70 km high)
- ozone is formed from 15-30 km, from atomic oxygen and molecular O_2
  - Dobson Units (0.001 mm thickness of pure ozone)
  - 90 DU: ozone hole
  - 450 DU normally at poles
- Balance of ozone forming reactions and ozone destroying reactions

241 nm

$$O_2 \xrightarrow{h\nu} 2O$$

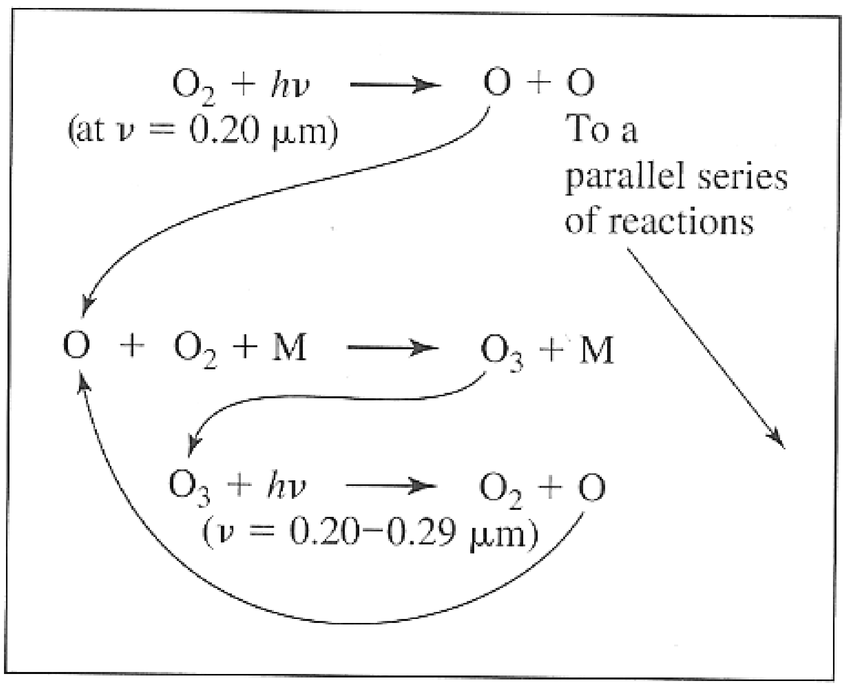
$$O + O_2 \rightarrow O_3$$

$$O_3 \xrightarrow{h\nu} O_2 + O$$

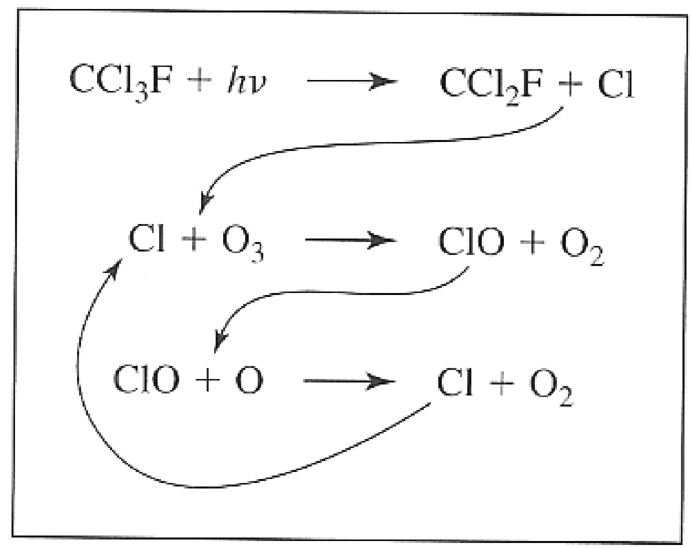
Stratospheric Reactions

- Role of chlorofluorocarbons

Photoreactions of ozone.



Ozone destruction by chlorofluoromethane.



D&M figs 12.8 & 12.9

Ozone destruction

- Chlorine Catalysis
  - Initiation from CFCs

200-280 nm

$$CF_2Cl_2 \xrightarrow{h\nu} CF_2Cl\bullet + Cl\bullet$$

  - Then catalytic destruction

$$\begin{array}{l} Cl\bullet + O_3 \rightarrow ClO\bullet + O_2 \\ ClO\bullet + O \rightarrow Cl\bullet + O_2 \\ \hline O_3 + O \rightarrow 2O_2 \end{array}$$

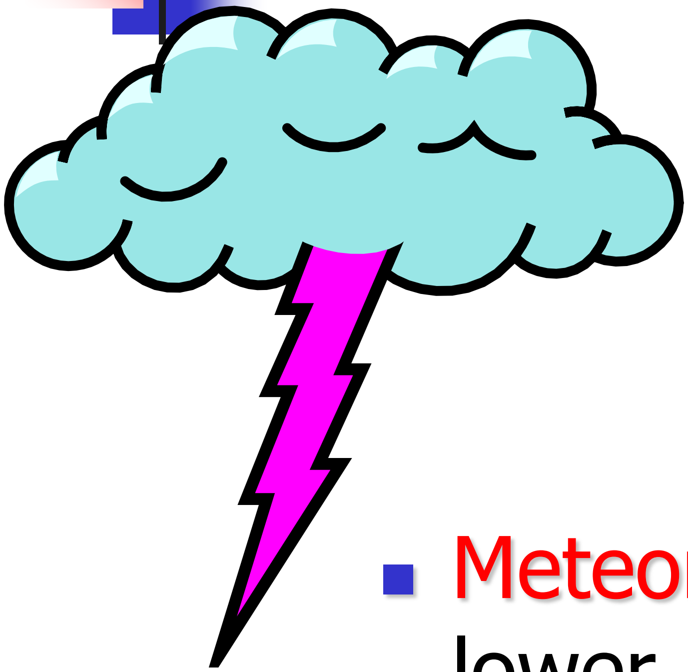
Greenhouse Pollutants

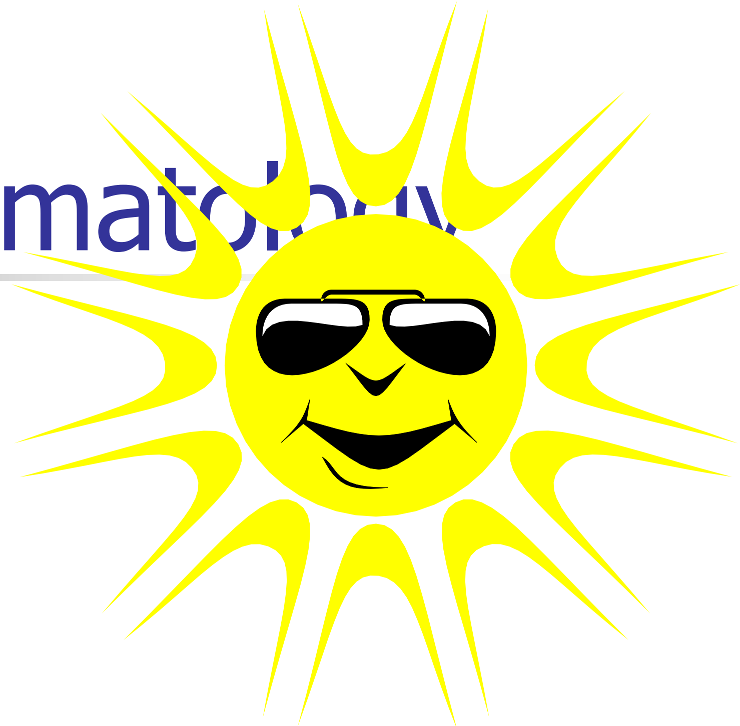
- Gases which impede the exit of reflected solar radiation from the earth's atmosphere
  - carbon dioxide and others
- Cause global warming, leading to many secondary effects (changing sea levels)
- Exact impact is uncertain
  - limited historical data on global temperature

Major Greenhouse Gases

Gas	Sources	Fraction of trapped energy attributable to gas	Annual increase in gas conc., percent
Carbon dioxide	Fossil fuel combustion	0.66	0.5
Chlorofluorocarbons	Vehicle and residential cooling systems, foams, aerosol propellants	0.10	4
Methane	Cattle, rice paddies	0.20	0.9
Nitrous oxide	Combustion processes	0.04	0.25

Meteorology & Climatology



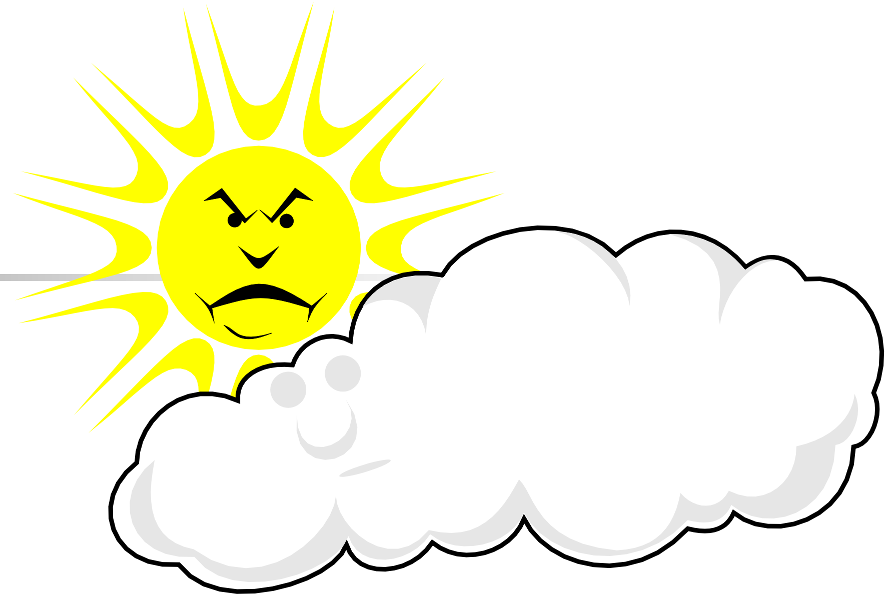


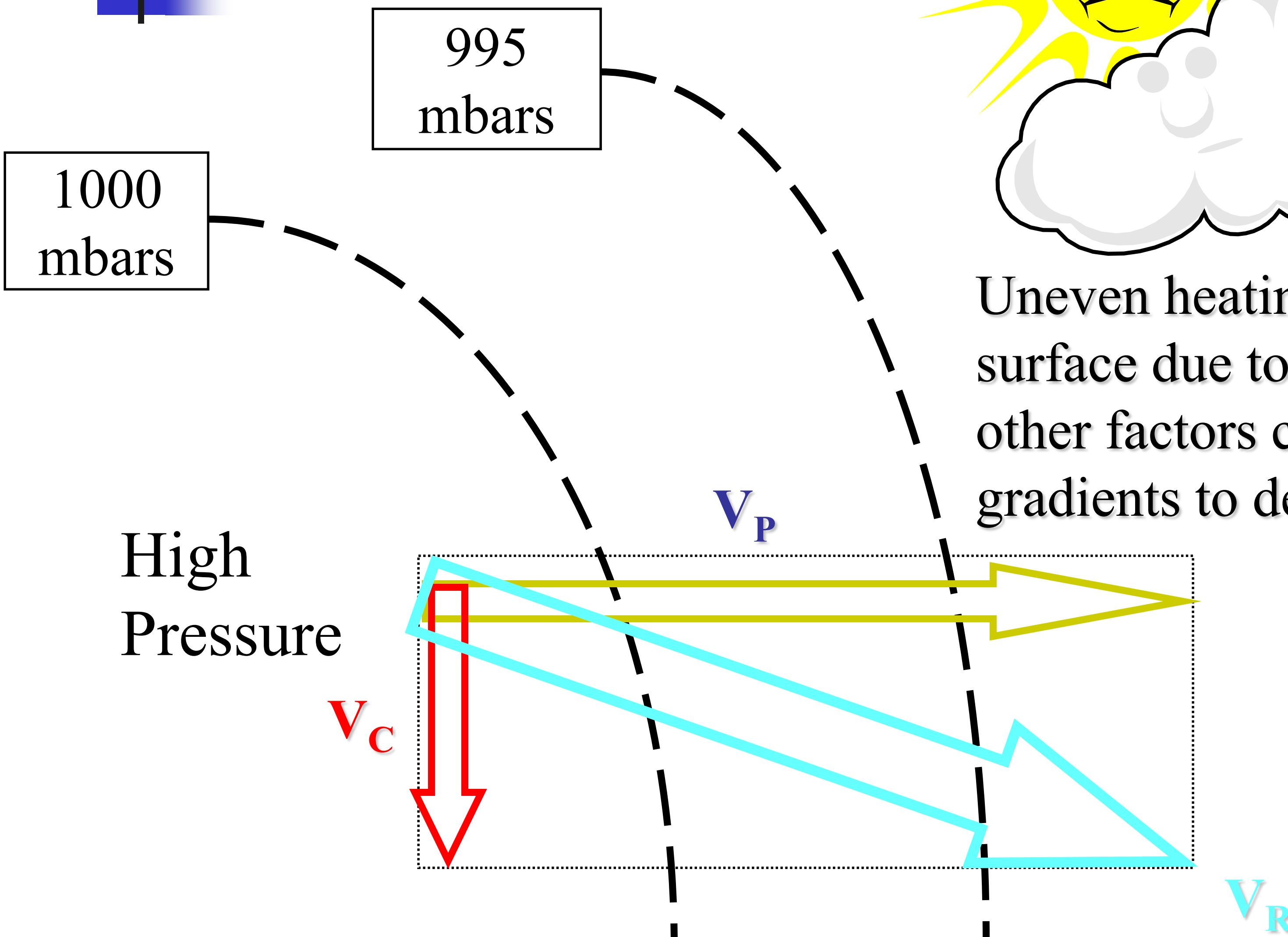
- Meteorology: the study of the lower atmosphere, particularly of weather
- Climatology: the study of weather over long periods of time

Composition of the Earth's Atmosphere

Gas	Chemical Formula	Concentration, % by volume
Nitrogen	N_2	78.1
Oxygen	O_2	21.0
Argon	Ar	0.9
Carbon dioxide*	CO_2	3.3×10^{-2}
Hydrogen	H_2	5×10^{-5}
Ozone*	O_3	1×10^{-6}
Methane*	CH_4	2×10^{-4}

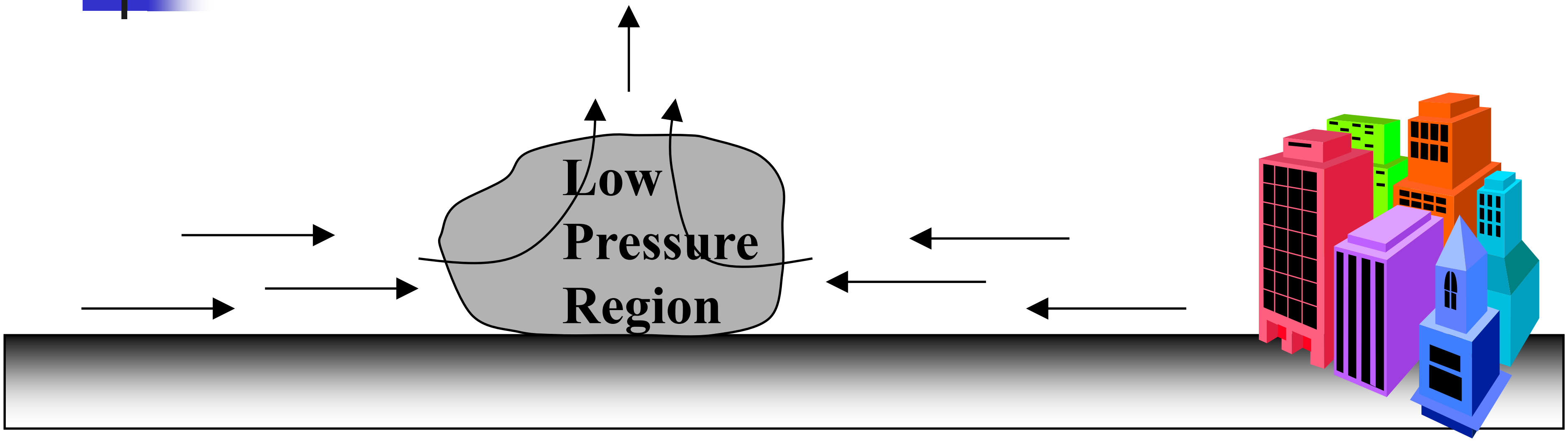
Air movement in the lower atm.

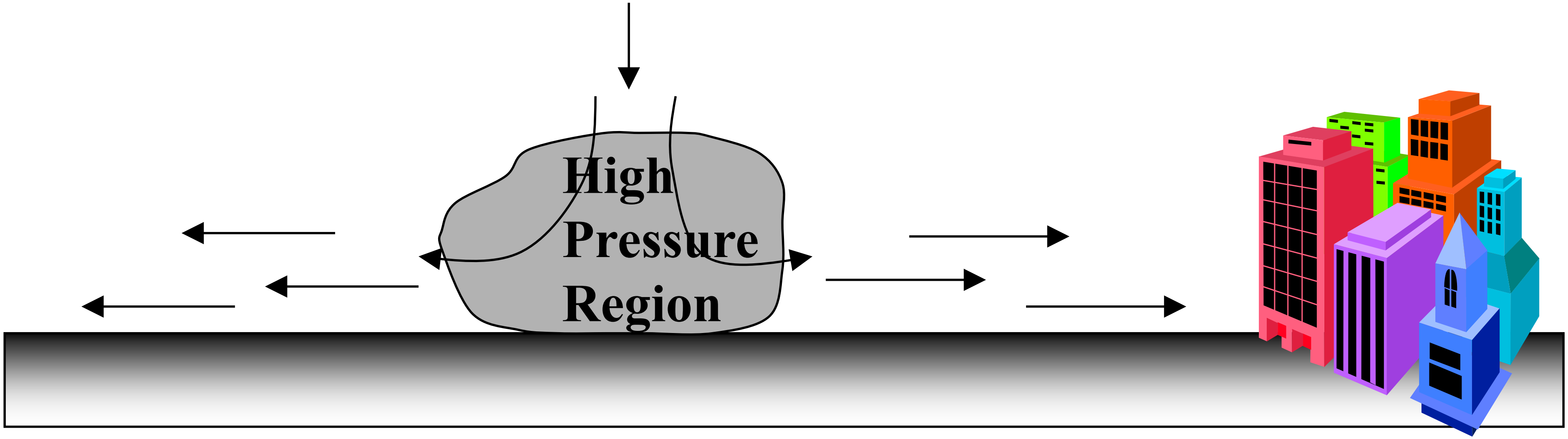




Uneven heating of the earth's surface due to cloud cover and other factors causes pressure gradients to develop

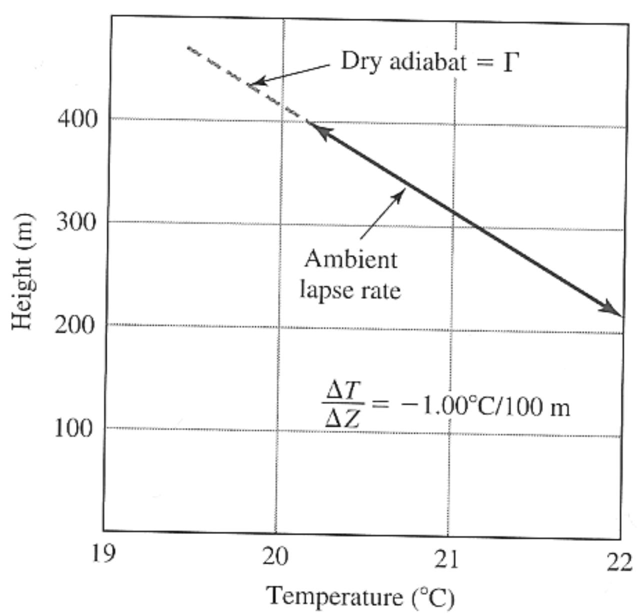
Large-scale air movement

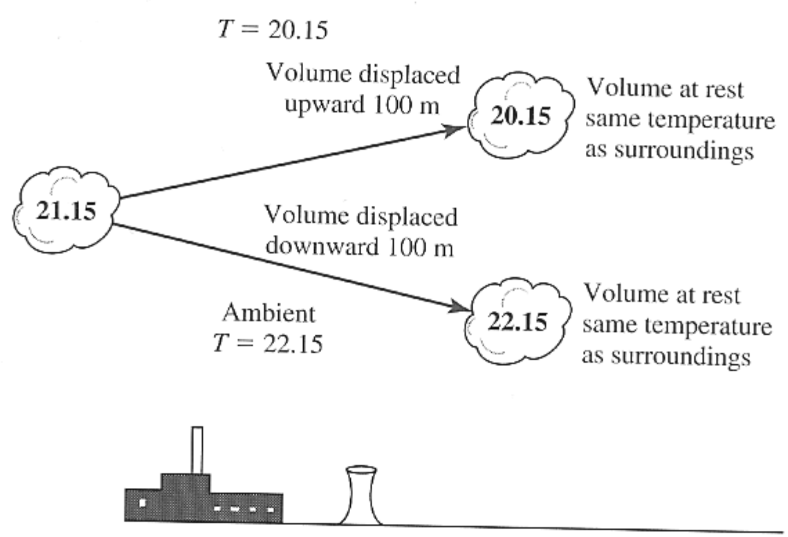




Stability I

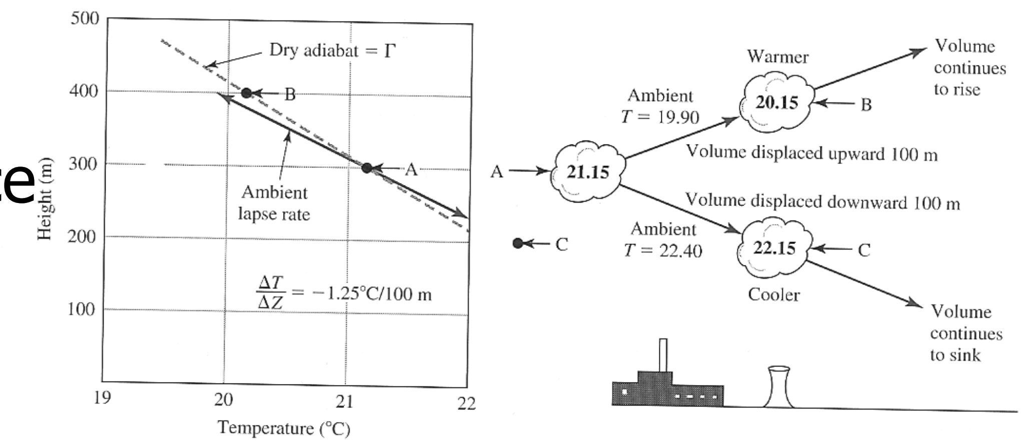
- Tendency of atmosphere to resist motion
- Related to lapse rate
  - Change of air temperature with height
- Stable air
  - Thermal structure matches adiabatic lapse rate



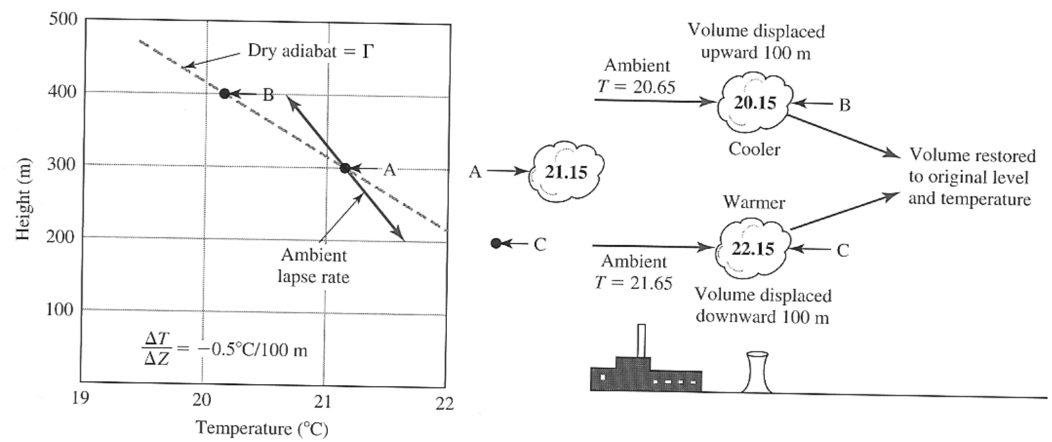


Stability II

- Unstable air
  - Thermal structure enhances turbulence
  - Lapse rate is superadiabatic
- Stable air
  - Thermal structure inhibits turbulence
  - Lapse rate is subadiabatic



(b)



See: section 11.7.3 in M&Z

Land-Sea

- See figure 11.30 in M&Z

FIGURE 11–14

Land breeze during the night.

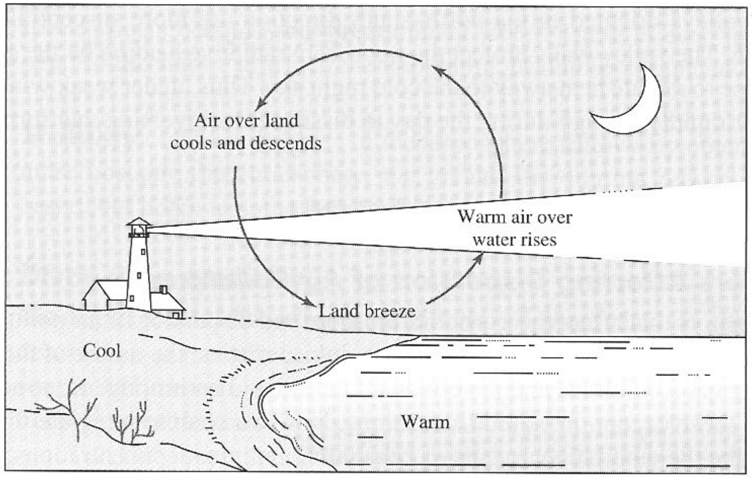


FIGURE 11–15

Lake breeze during the day.

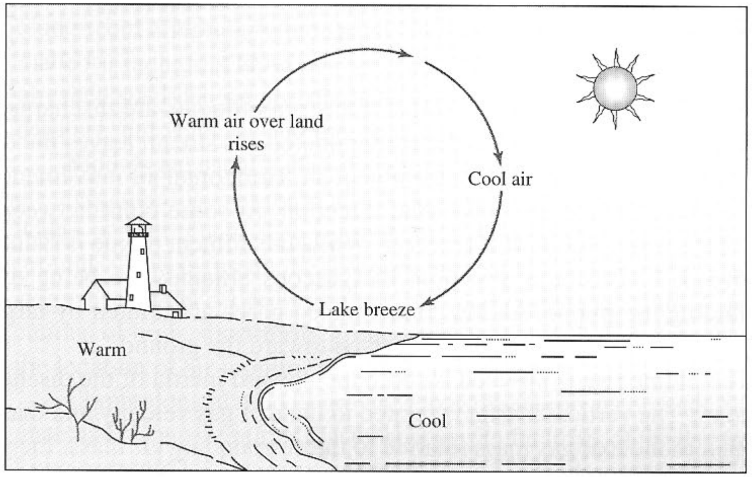
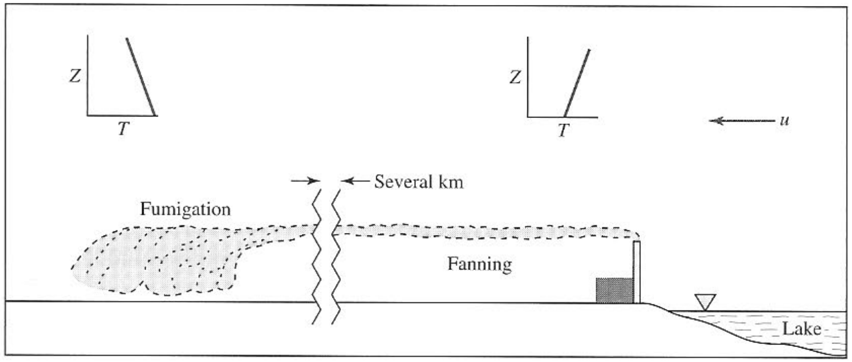


FIGURE 11–16

Effect of lake breeze on plume dispersion.



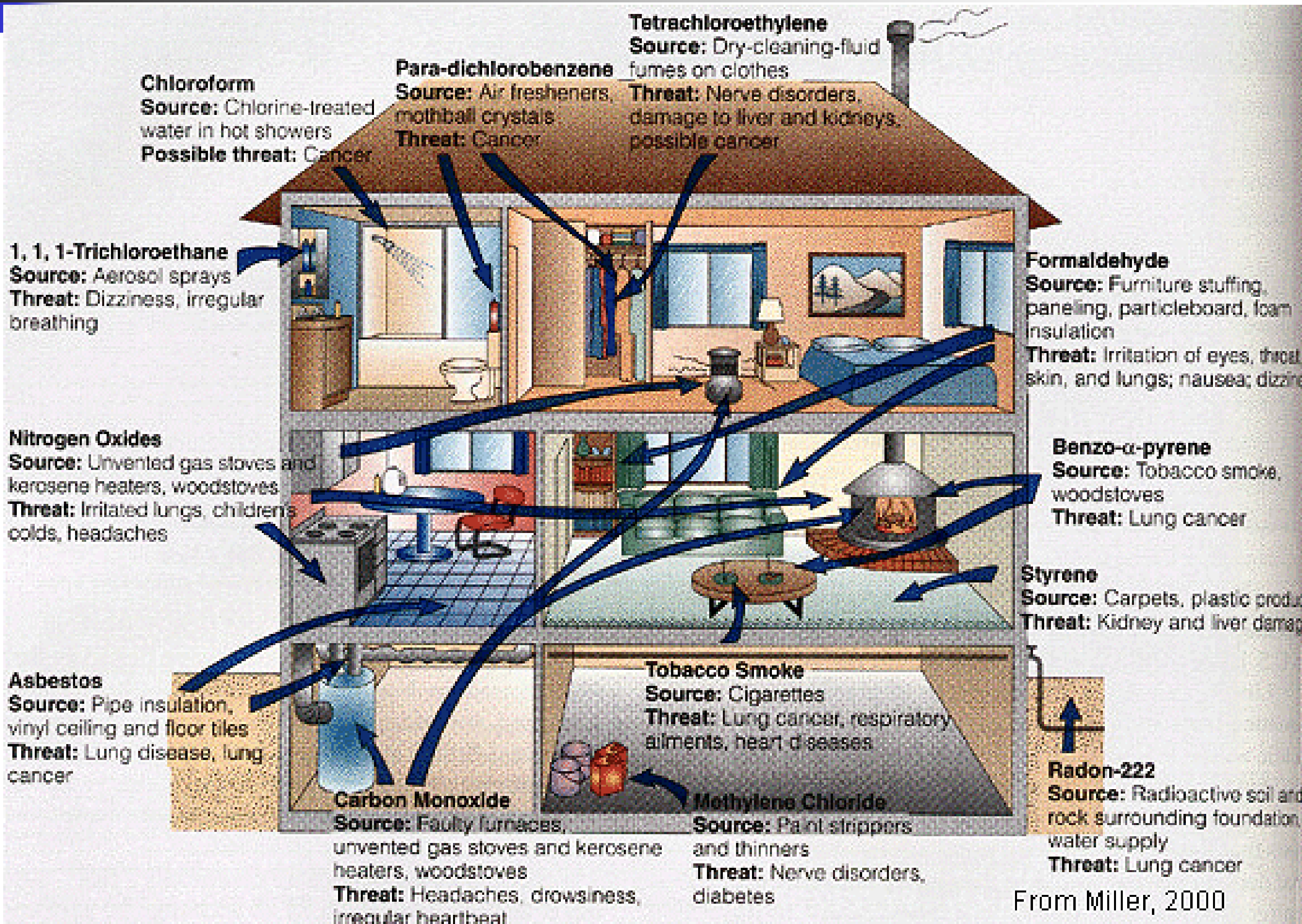
Indoor Air Pollution

- Problem was aggravated by improvements in home energy efficiency
- Detection and identification can be difficult
- secondary pollutants may form (e.g., carpet off gases with chlorine dioxide in drinking water)
- In-home combustion: stoves, heaters, cigarettes
  - See Table 11.14 in M&Z
    - Also Table 12-4 & Figure 12-6 in Davis & Masten

Common Sources

Source	Contaminant	Effects
Urethane foam building insulation	Formaldehyde	Carcinogenic
Poor foundation or basement seal	Radon gas	Carcinogenic, particularly lung cancer
Ventilation systems	Mold	Allergies
Old asbestos building insulation	Asbestos fibers	Carcinogenic
Permeate from soil through basement floors and walls	Radon gas	Carcinogenic
Heater and stove fumes	Products of incomplete combustion	Various
Household pesticides (for termites or interior insects)	Chlorinated or phosphorylated pesticides	Some chlorinated pesticides are known carcinogens
Secondhand tobacco smoke	Various, including nicotine, and nicotine decay products	Carcinogenic, increased bronchitis and pneumonia.

Sources of Indoor Air Pollution



From Miller, 2000

Volatile Organic Compounds

- Small molecules with carbon base
- Easily vaporized
- Easily cross biologic membranes
- Can be stored in fat

Volatile and Semi-volatile Organic Compounds: Sources

- Paints, varnishes, shellacs
- Cleaners, sprays, "de-odorizers"
- Building materials: carpets, furniture, glues, particle board, oriented strandboard, plywood
- Plastics, computers, other electronic equipment
- Secondarily, from ozone reactions

Volatile, Semivolatile Organic Compounds

- Eye, respiratory tract irritants

direct irritation results in Inflammation

membranes become leaky

to outside (phlegm, mucous), and to inside: toxicants enter

Chronic inflammation can lead to scarring

VOCs: Special Concerns

- **VOCs as sensitizers**
  - Can lead to allergic skin and liver responses
  - Sensitization can mean that responder reacts to lower and lower concentrations
- **Toxic-Induced Loss of Tolerance:**
  - total exposure to VOCs can diminish ability to tolerate even compounds unrelated to the exposure causing it.
- Multiple chemical sensitivity

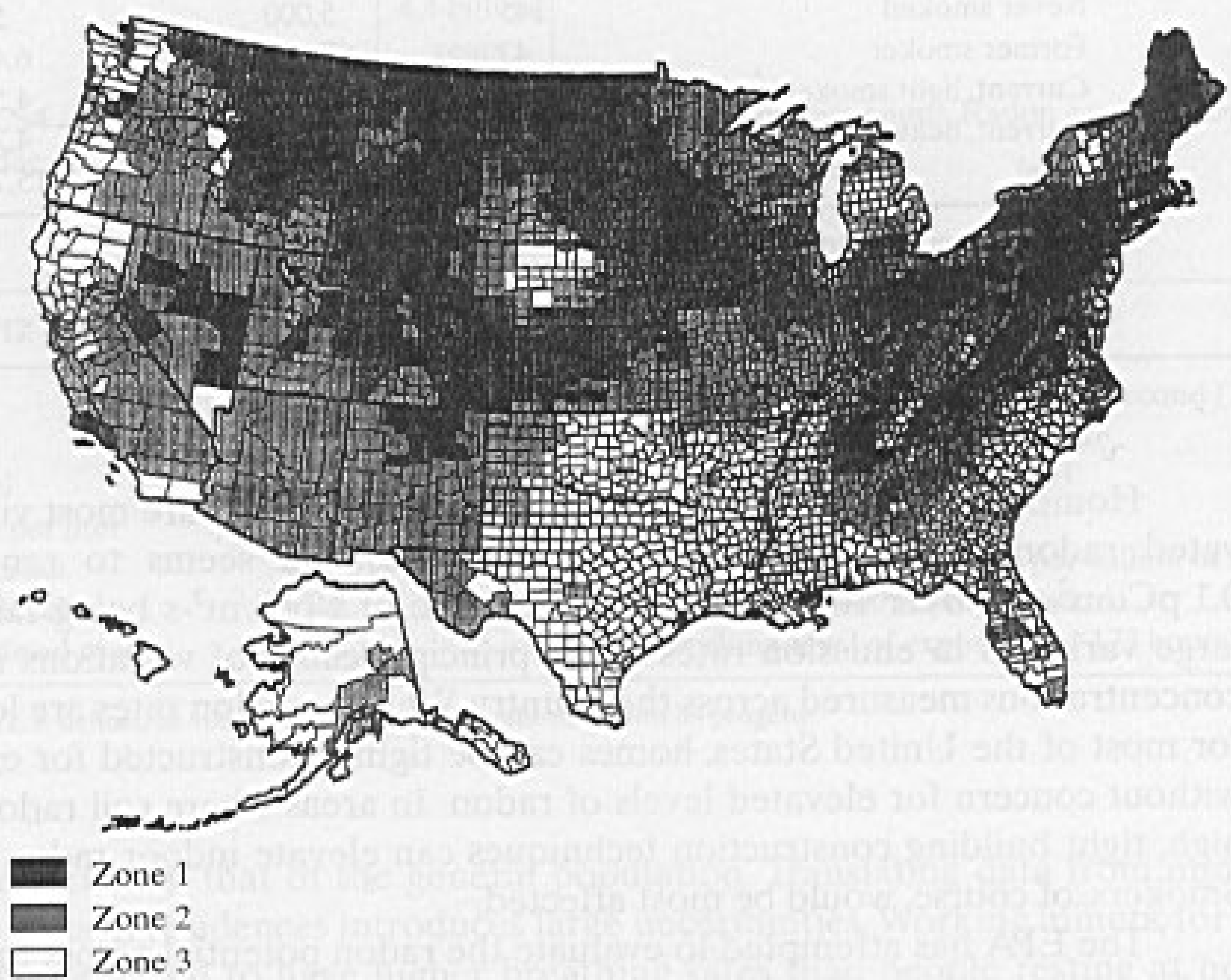
Engineered Wood products

4-day chamber emission tests (Bauman, 1999)

Compound (total) ug/m^3	Southern PB	Pine MDF	Other PB	Pines MDF	Hardwood PB	MDF	Doug Fir PB
Terpenes	97	8	56	10	7	4	11
Aldehydes	222	51	78	32	26	21	17
Ketones	44	10	16	5	4	2	3
Alcohols	21	6	8	1	0	0	0
2-pentylfuran	22	6	8	3	3	1	1

Particle Board & Medium density fiber board & particle board

Radon Potential



Radon Mitigation

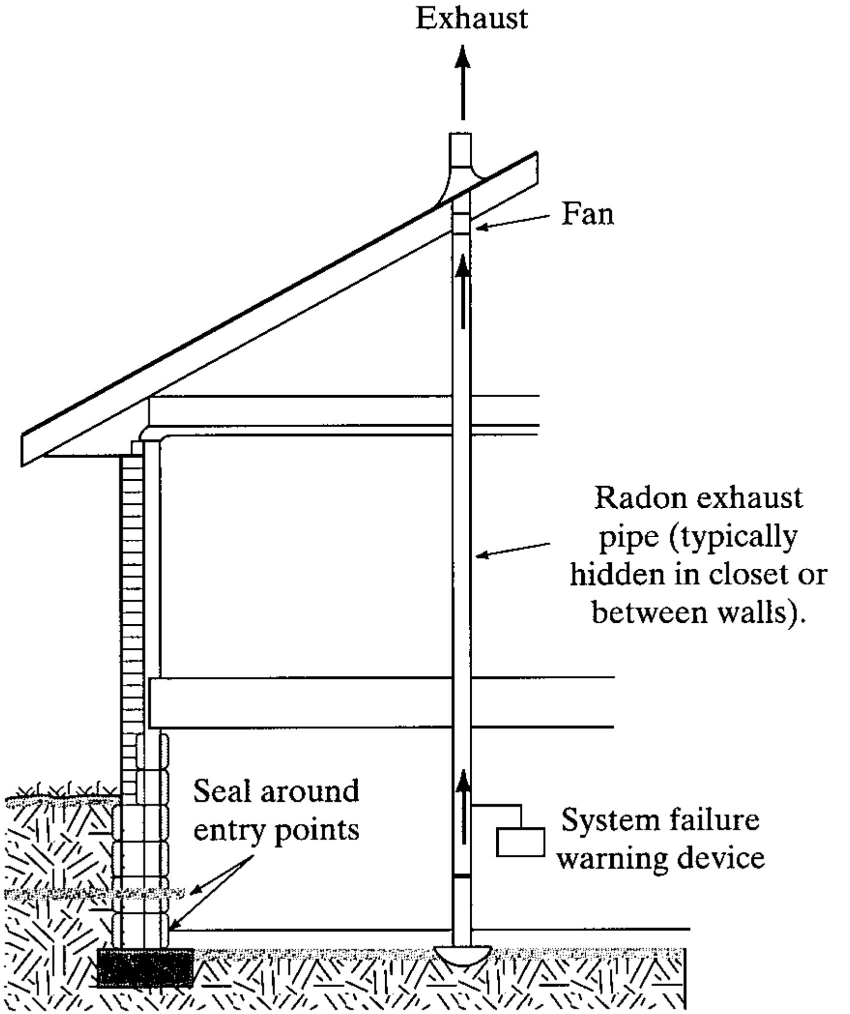


FIGURE 7.56 A subslab suction radon mitigation system. (U. S. EPA, 1993)

- To next lecture