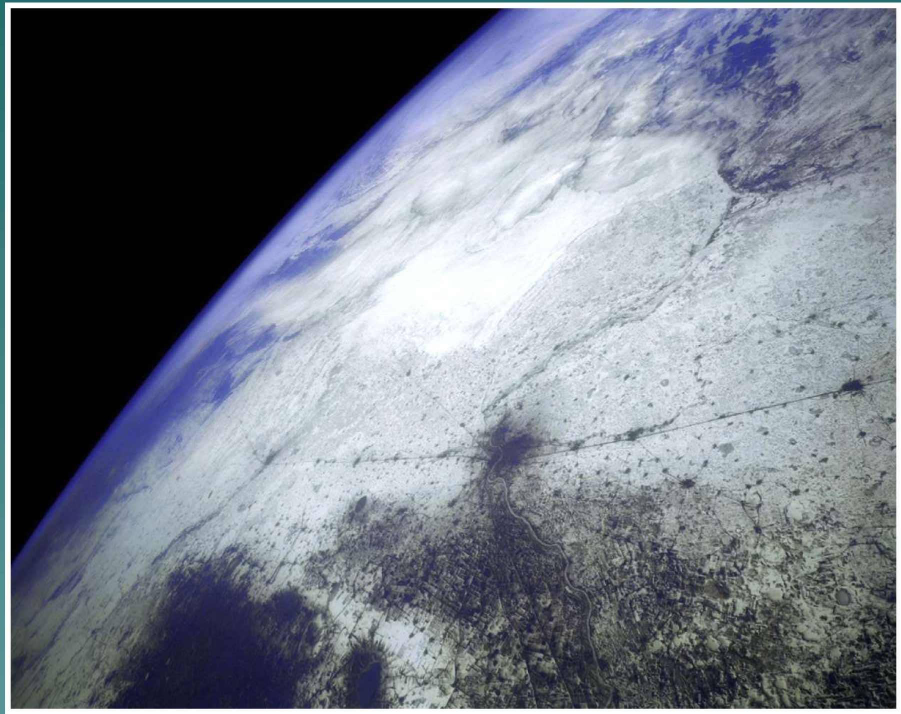
Gas Air Pollution (Sources and classification)

Atmosphere as a Resource

- Atmospheric Composition
  - Nitrogen 78.08%
  - Oxygen 20.95%
  - Argon 0.93%
  - Carbon dioxide 0.04%
- Ecosystem services
  - Blocks UV radiation
  - Moderates the climate
  - Redistributes water in the hydrologic cycle



Types and Sources of Air Pollution

- Air Pollution
  - Chemicals added to the atmosphere by natural events or human activities in high enough concentrations to be harmful
- Two categories
  - Primary Air Pollutant
    - Harmful substance that is emitted directly into the atmosphere
  - Secondary Air Pollutant
    - Harmful substance formed in the atmosphere when a primary air pollutant reacts with substances normally found in the atmosphere or with other air pollutants

Basic Pollutants - Sources (1 of 4)

- Combustion
- Evaporation
- Natural Production

Basic Pollutants - Sources (2 of 4)

Combustion

- Complete combustion

  Fuel → water and carbon dioxide (CO_2)

- Incomplete combustion

  Fuel → water, CO_2, and other pollutants

  Pollutants are both gases and particles

Basic Pollutants - Sources (3 of 4)

Evaporation

- Thousands of chemical compounds
- Liquids evaporating or gases being released
- Some harmful by themselves, some react to produce other pollutants
- Many items you can smell are evaporative pollutants
    - Gasoline – benzene (sweet odor, toxic, carcinogenic)
    - Bleach – chlorine (toxic, greenhouse gas)
    - Trees – pinenes, limonene (ozone- and particulate matter forming)
    - Paint – volatile organic compounds (ozone- and particulate matter forming)
    - Baking bread, fermenting wine and beer – VOCs and ethanol (ozone-forming)

Basic Pollutants - Sources (4 of 4)

Natural Production

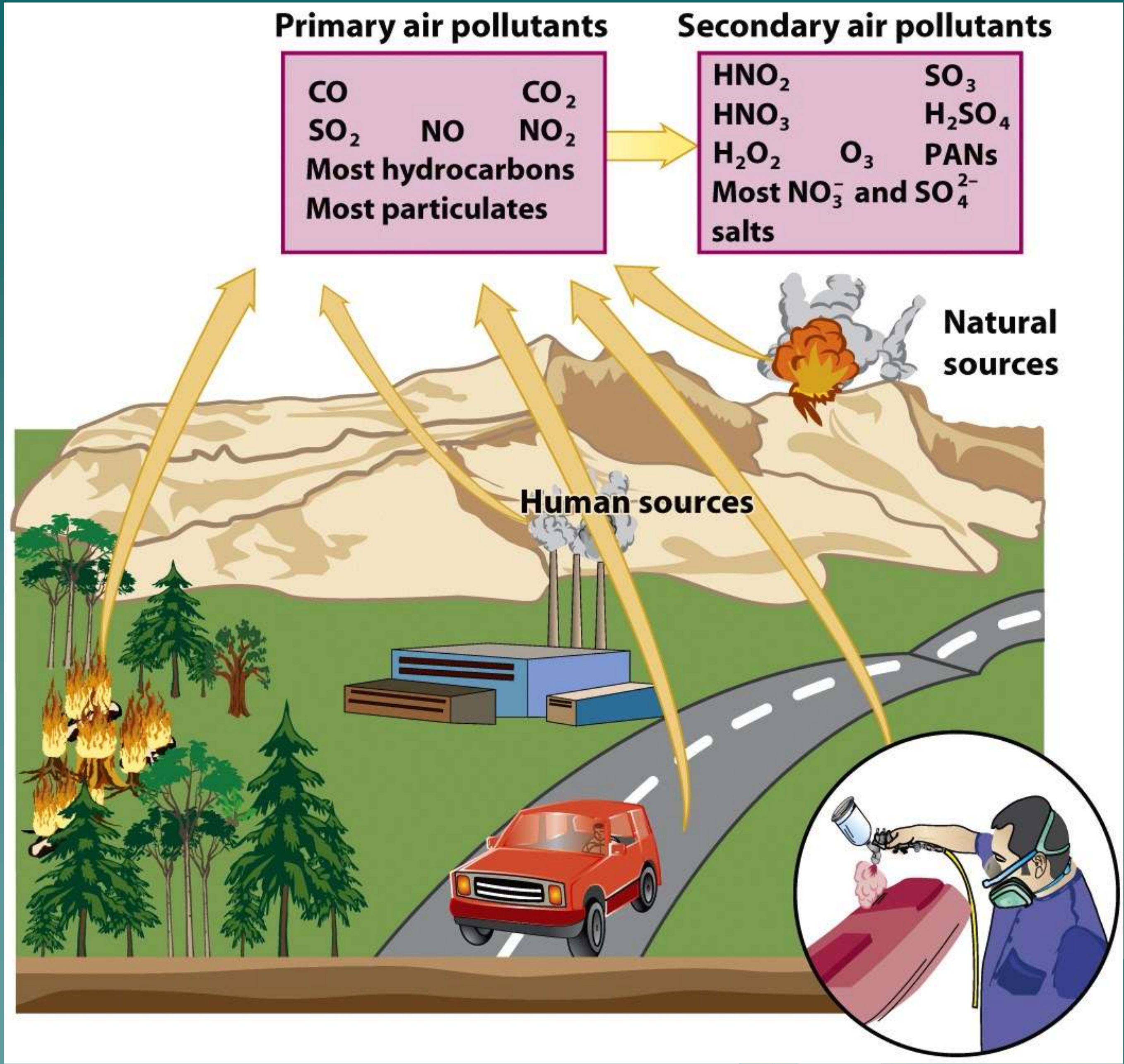
- Fires (combustion) produce gases and particles
- Winds "pick up" dust, dirt, sand and create particles of various sizes
- Biosphere emits gases from trees, plants, soil, ocean, animals, microbes
- Volcanoes and oil seeps

Major Air Pollutants

Table 20.1 Major Air Pollutants

Pollutant	*Composition*	*Primary or Secondary*	*Characteristics*
Particulate matter			
Dust	Variable	Primary	Solid particles
Lead	Pb	Primary	Solid particles
Sulfuric acid	H_2SO_4	Secondary	Liquid droplets
Nitrogen oxides			
Nitrogen dioxide	NO_2	Primary	Reddish-brown gas
Sulfur oxides			
Sulfur dioxide	SO_2	Primary	Colorless gas with strong odor
Carbon oxides			
Carbon monoxide	CO	Primary	Colorless, odorless gas
Carbon dioxide*	CO_2	Primary	Colorless, odorless gas
Hydrocarbons			
Methane	CH_4	Primary	Colorless, odorless gas
Benzene	C_6H_6	Primary	Liquid with sweet smell
Ozone	O_3	Secondary	Pale blue gas with acrid odor
Air toxics			
Chlorine	Cl_2	Primary	Yellow-green gas

* Discussed in Chapter 21.
Source: Environmental Protection Agency.



Primary air pollutants
CO
CO_2
SO_2
NO
NO_2
Most hydrocarbons
Most particulates
Secondary air pollutants
HNO_2
SO_3
HNO_3
H_2SO_4
H_2O_2
O_3
PANs
Most NO_3^- and SO_4^{2-} salts
Natural sources
Human sources

Major Classes of Gas Air Pollutants

- Nitrogen Oxides
- Sulfur Oxides
- Carbon Oxides
- Hydrocarbons
- Ozone

Nitrogen and Sulfur Oxides

- Nitrogen Oxides
  - Gases produced by the chemical interactions between atmospheric nitrogen and oxygen at high temperature
- present in car exhaust and power plants
- Sulfur Oxides
  - Gases produced by the chemical interactions between sulfur and oxygen
- produced when coal and fuel oil are burned
- present in power plant exhaust

Carbon Oxides and Hydrocarbons

- Carbon Oxides
  - Gases carbon monoxide (CO) and carbon dioxide (CO_2)
- colorless, odorless
- produced when carbon does not burn in fossil fuels
- present in car exhaust

- Hydrocarbons
  - Diverse group of organic compounds that contain only hydrogen and carbon (ex: CH_4- methane)

Ozone

- Tropospheric Ozone
  - Man- made pollutant in the lower atmosphere
  - Secondary air pollutant
  - Component of photochemical smog
- Stratospheric Ozone
  - Essential component that screens out UV radiation in the upper atmosphere
  - Man- made pollutants (ex: CFCs) can destroy it

Ozone

- Colorless gas
- Composed of three oxygen atoms
  - Oxygen molecule (O_2)—needed to sustain life
  - Ozone (O_3) —the extra oxygen atom makes ozone very reactive
- Secondary pollutant that forms from precursor gases
  - Nitric oxide – combustion product
  - Volatile organic compounds (VOCs) – evaporative and combustion products

Solar radiation and chemistry

- The reaction that produces ozone in the atmosphere:

$$O + O_2 + M \rightarrow O_3 + M$$

- Difference between stratospheric and tropospheric ozone generation is in the source of atomic O
- For solar radiation with a wavelength of less than 242 nm:

$$O_2 + hv \rightarrow O + O$$

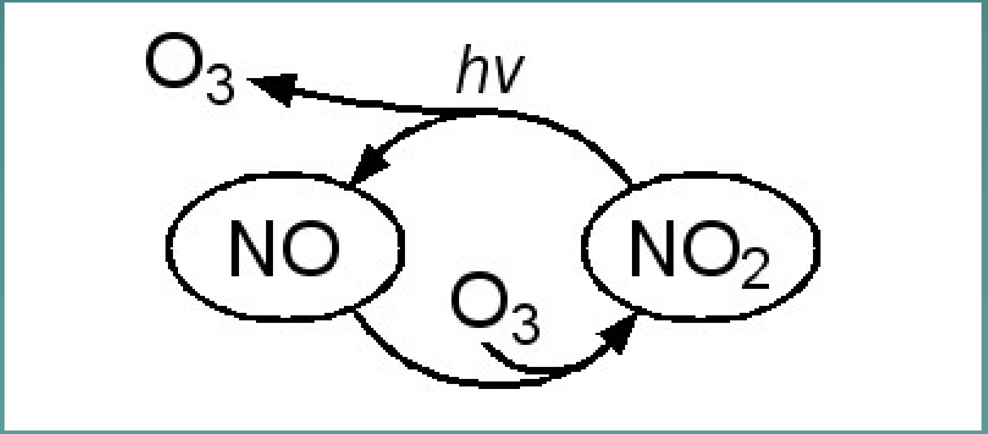
Solar radiation and chemistry

- Photochemical production of O_3 in troposphere tied to NO_x ($NO + NO_2$)
- For wavelengths less than 424 nm:

$$NO_2 + hv \rightarrow NO + O$$

- But NO will react with O_3

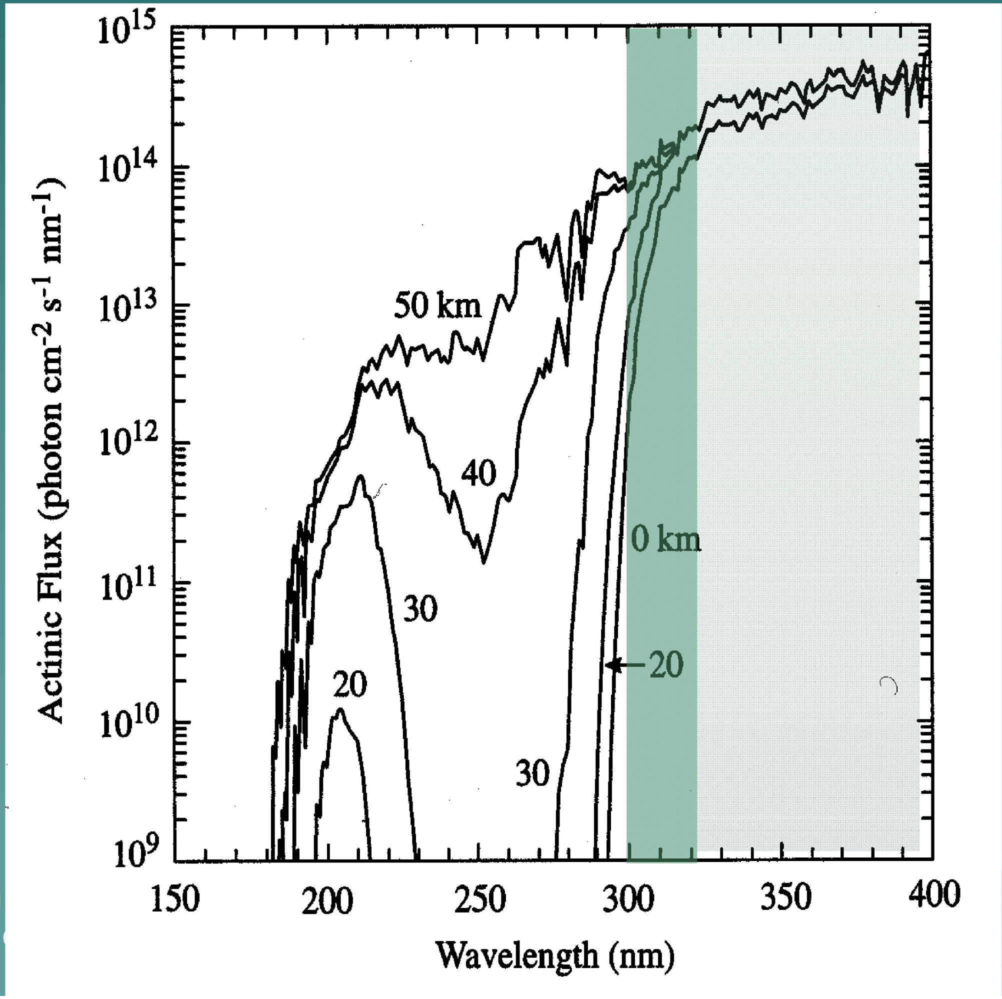
$$NO + O_3 \rightarrow NO_2$$



- *Cycling has no net effect on ozone*

Tropospheric Ozone Photolysis

Troposphere ozone photolysis takes place in a narrow UV window (300-320 nm), NO2 broadly below 428



30° equinox midday Solar spectrum

Nitrogen Oxides

- Nitrogen oxides, or NO_x, is the generic term for a group of highly reactive gases, all of which contain nitrogen and oxygen in varying amounts.
- Nitrogen dioxide is most visually prominent (it is the yellow-brown color in smog)
- The primary man-made sources of NO_x are motor vehicles; electric utilities; and other industrial, commercial, and residential sources that burn fuels
- Affects the respiratory system
- Involved in other pollutant chemistry
    - One of the main ingredients in the formation of ground-level ozone
    - Reacts to form nitrate particles, acid aerosols, and NO_2, which also cause respiratory problems
    - Contributes to the formation of acid rain (deposition)

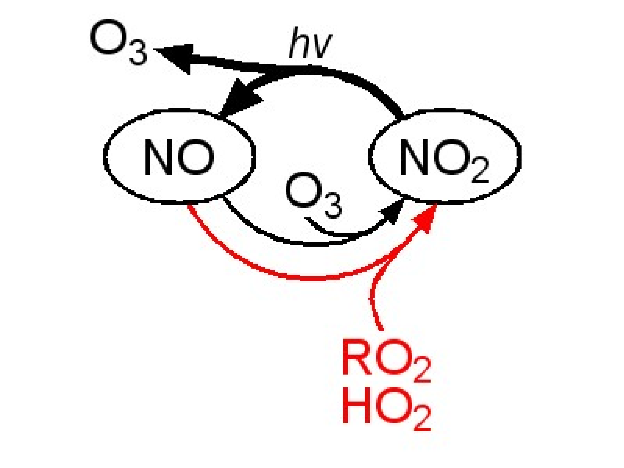
Must make NO_2

- To make significant amounts of ozone must have a way to make NO_2 without consuming ozone
- Presence of peroxy radicals, from the oxidation of hydrocarbons, disturbs O_3-NO-NO_2 cycle

$$NO + HO_2\cdot \equiv NO_2 + OH\cdot$$

$$NO + RO_2\cdot \equiv NO_2 + RO\cdot$$

  - leads to net production of ozone



The Hydroxyl Radical

- produced from ozone photolysis
  - for radiation with wavelengths less than 320 nm:

$$O_3 + hv \equiv O(^1D) + O_2$$

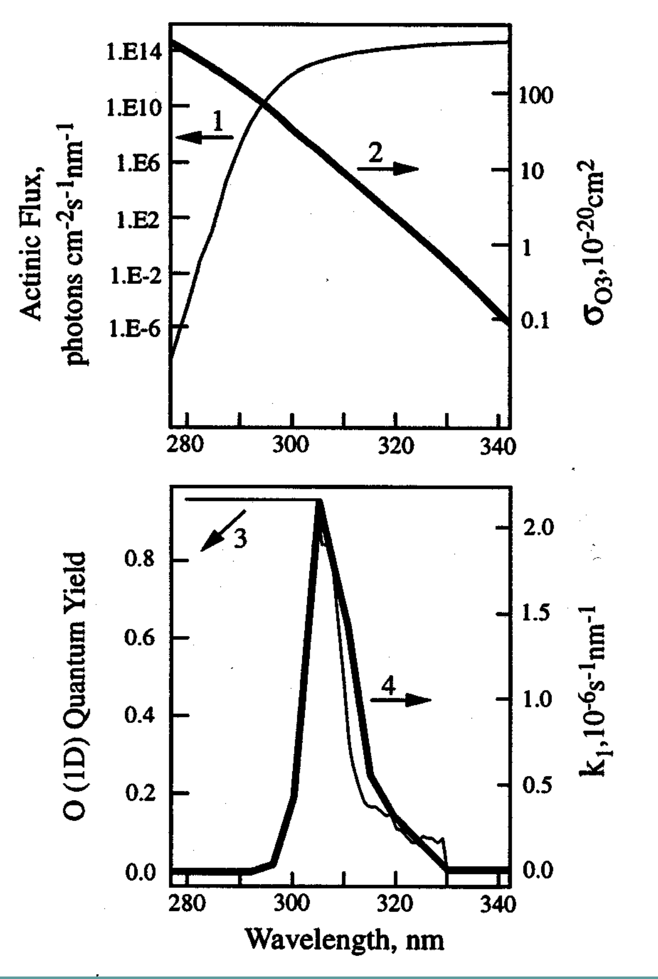
followed by

$$O(^1D) + M \equiv O(^3P) + M \ (+O_2 \equiv O_3) \qquad (\sim 90\%)$$

$$O(^1D) + H_2O \equiv 2\ OH\cdot \qquad (\sim 10\%)$$

- OH initiates the atmospheric oxidation of a wide range of compounds in the atmosphere
  - referred to as 'detergent of the atmosphere'
  - typical concentrations near the surface ~10^6 - $10^7 cm^{-3}$
  - very reactive, effectively recycled

THE OH RADICAL: MAIN TROPOSPHERIC OXIDANT



- Primary source:
  - O_3 + hn → O_2 + O(1D) (1)
  - $O(^1D)$ + M → O + M (2)
  - $O(^1D)$ + H_2O → 2OH (3)
- Sink: oxidation of reduced species –leads to HO2(RO2) production
  - *CO + OH → CO_2 + H*
  - *CH_4 + OH → CH_3 + H_2O*
  - *HCFC + OH*

  } **Major OH sinks**
- Global Mean [OH] = 1.0×10^6 molecules cm^{-3}

Oxidation of CO - production of ozone

$$CO + OH\cdot \equiv CO_2 + H\cdot$$

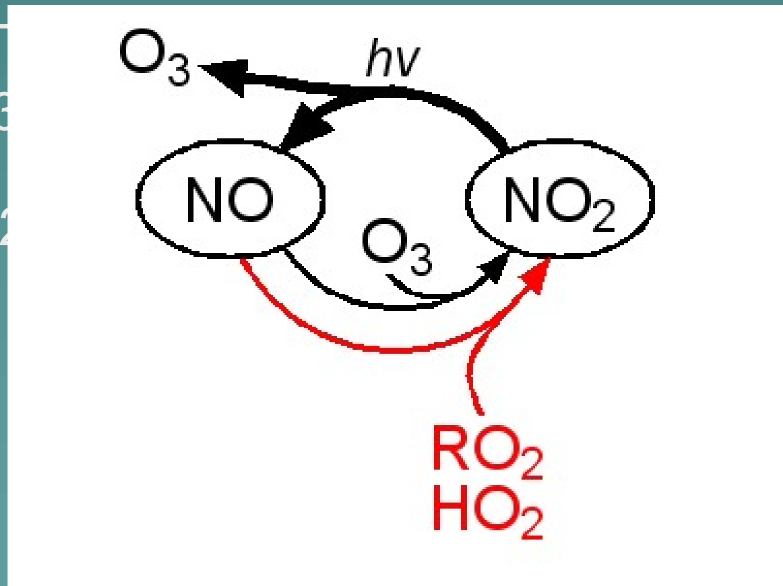
$$H\cdot + O_2 + M \equiv HO_2\cdot + M$$

$$NO + HO_2\cdot \equiv NO_2 + OH\cdot$$

$$NO_2 + h\nu \equiv NO + O$$

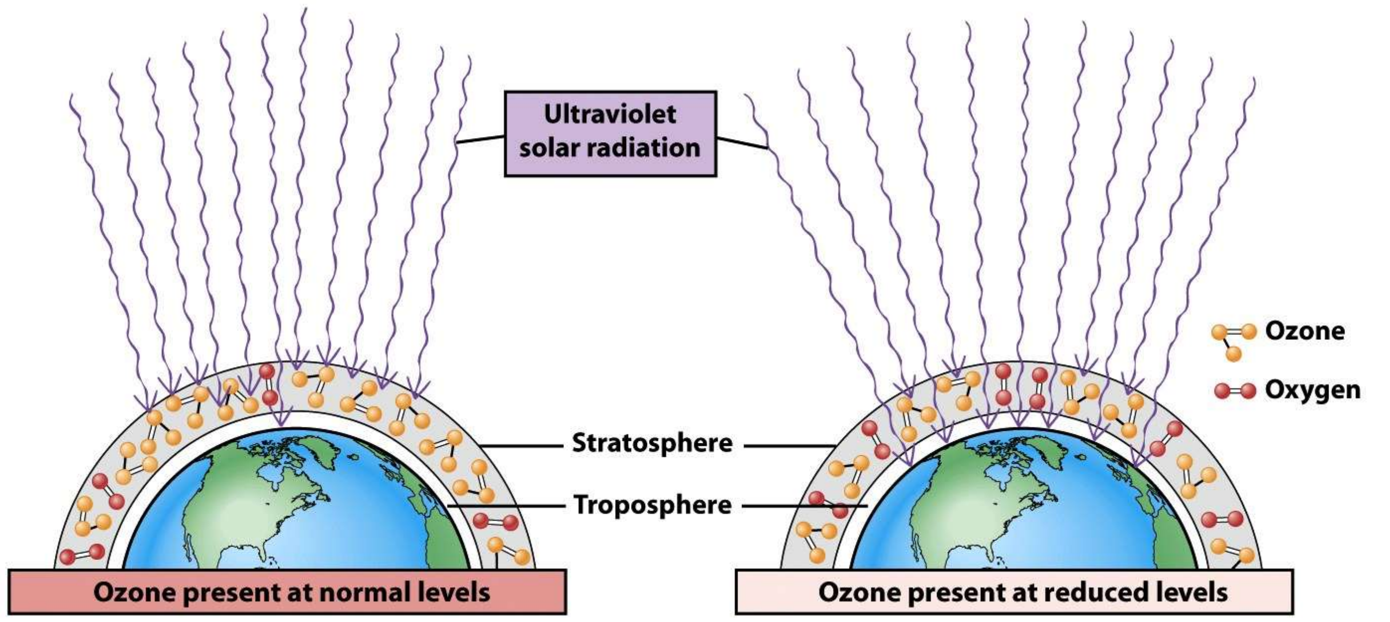
$$O + O_2 + M \equiv O_3$$

$$CO + 2\,O_2 + h\nu \equiv CO_2$$



Ozone Depletion in Stratosphere

- Ozone Protects earth from UV radiation
  - Part of the electromagnetic spectrum with wavelengths just shorter than visible light

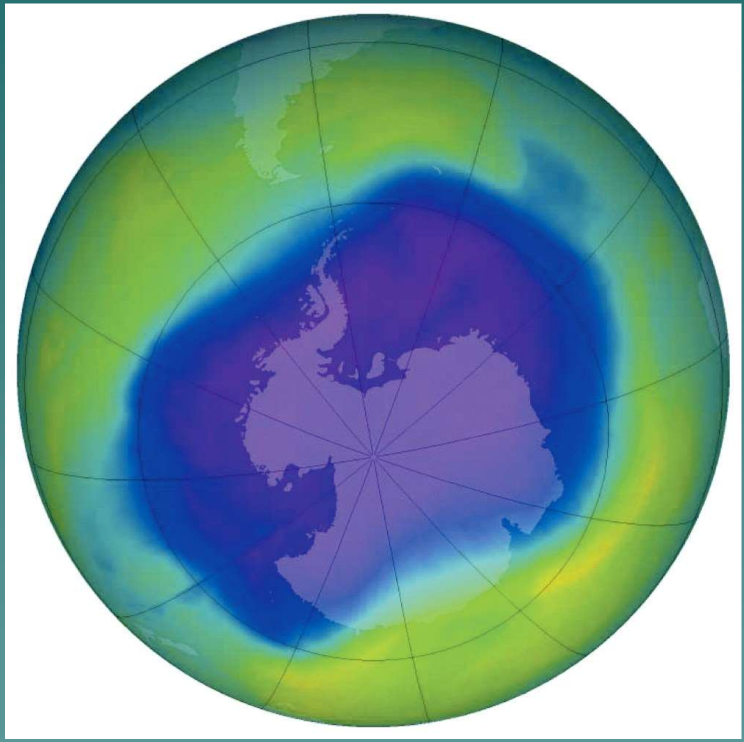


(a) Stratospheric ozone absorbs about 99% of incoming solar ultraviolet (UV) radiation, effectively shielding the surface.

(b) When stratospheric ozone is present at reduced levels, more high-energy UV radiation penetrates the atmosphere to the surface, where its presence harms organisms.

Ozone Depletion in Stratosphere

- Ozone thinning/hole
  - First identified in 1985 over Antarctica
- Caused by
  - human-produced bromine and chlorine containing chemicals
  - Ex: CFCs



Ozone Depletion in Stratosphere

- Hole over Antarctica requires two conditions:
  - Sunlight just returning to polar region
  - Circumpolar vortex- a mass of cold air that circulates around the southern polar region
    - Isolates it from the warmer air in the rest of the planet
- Polar stratospheric clouds form
  - Enables Cl and Br to destroy ozone

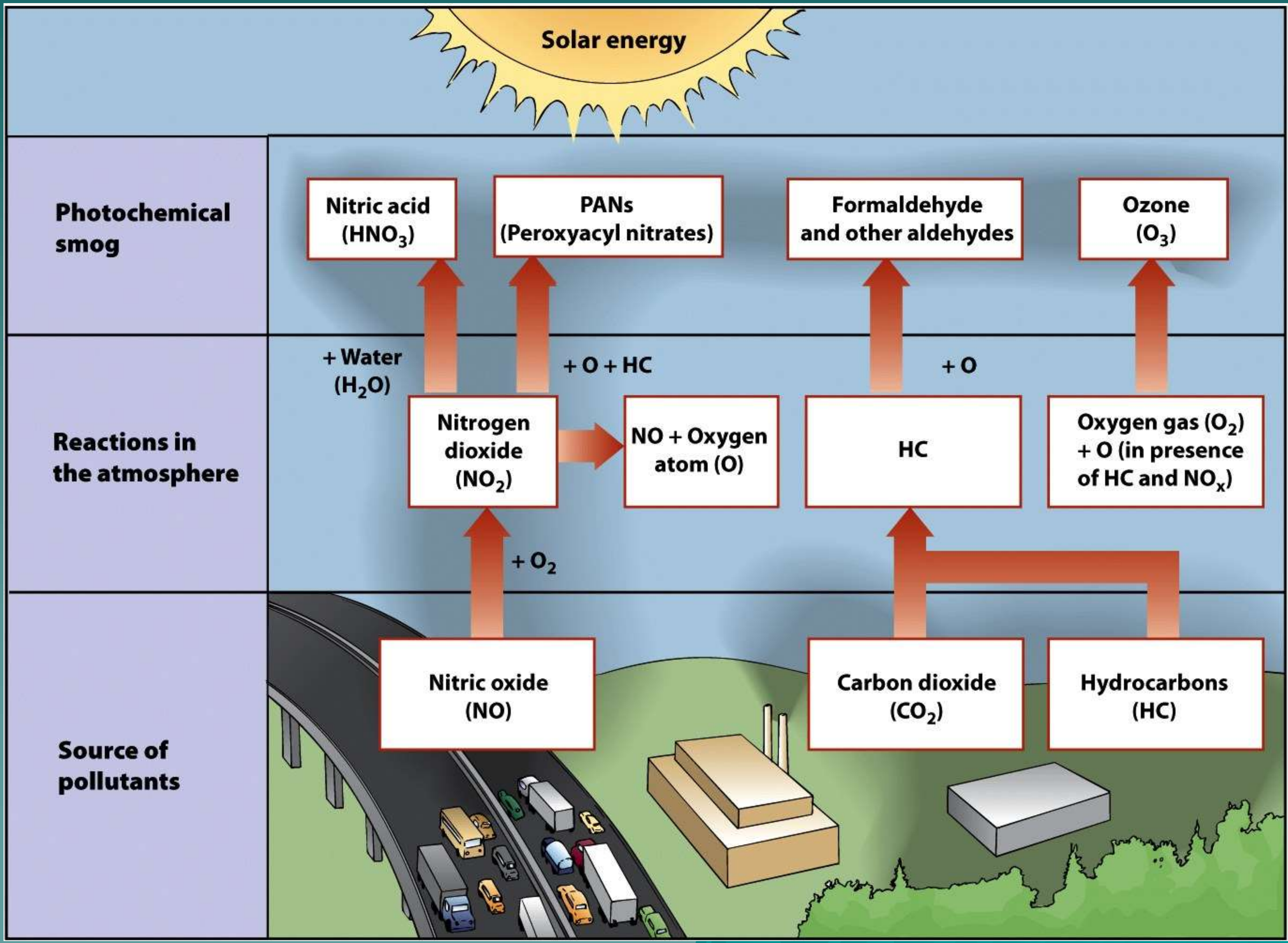
Recovery of Ozone Layer

- Montreal Protocol (1987)
  - Reduction of CFCs
  - Started using HCFCs (greenhouse gas)
- Phase out of all ozone destroying chemicals is underway globally
- Satellite pictures in 2000 indicated that ozone layer was recovering
- Full recovery will not occur until 2050

Urban Air Pollution

- Photochemical Smog (ex: Los Angeles below)
  - Brownish-orange haze formed by chemical reactions involving sunlight, nitrogen oxide, and hydrocarbons

Formation of Photochemical Smog

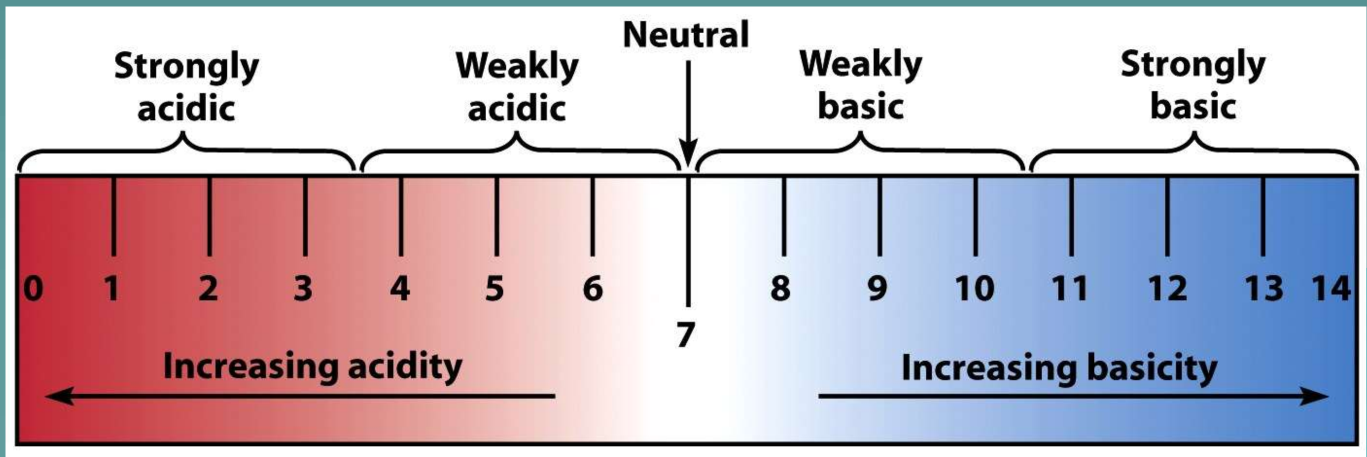


Lead

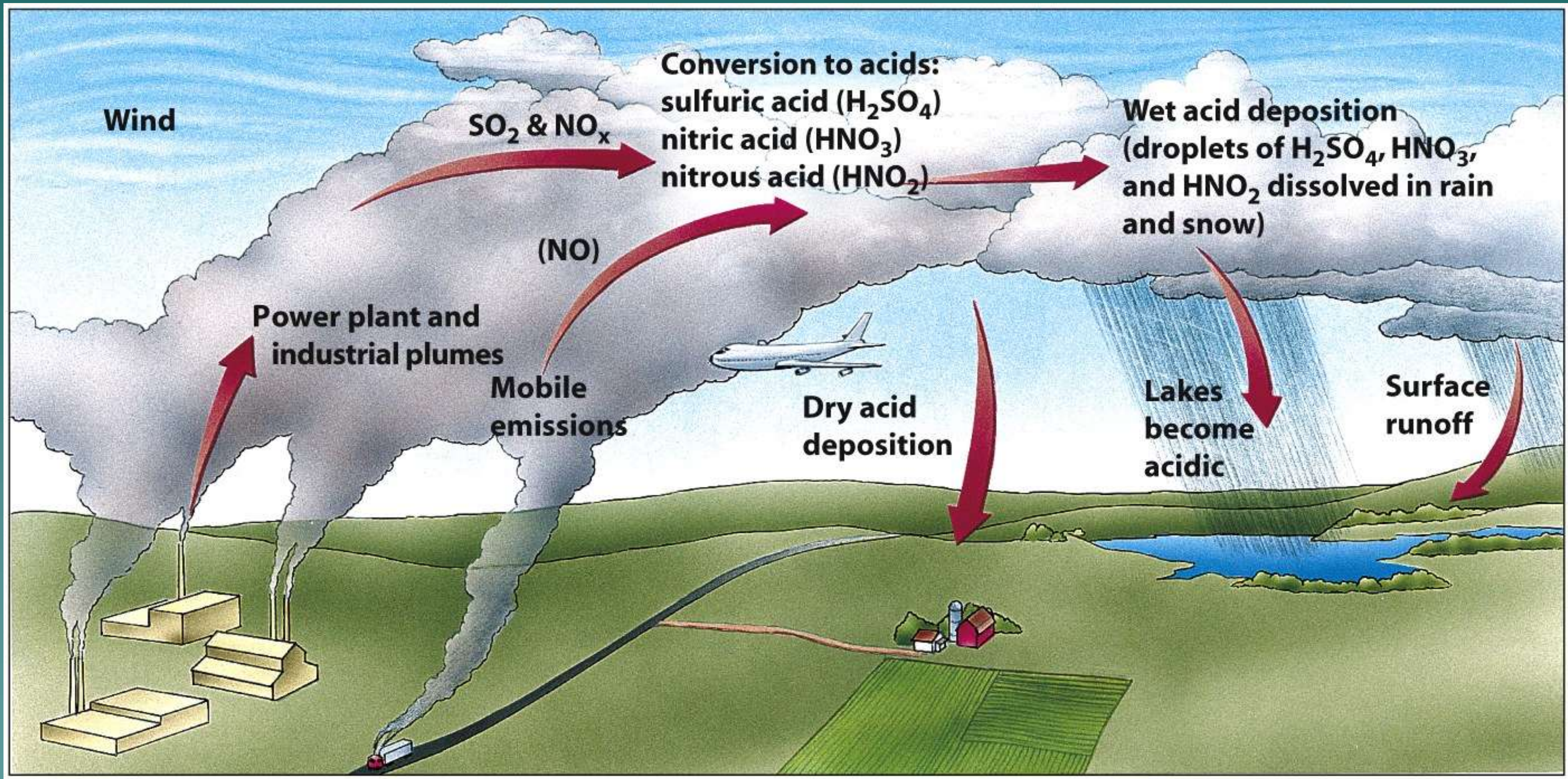
- Sources of lead emissions vary from one area to another.
  - At the national level, major sources of lead in the air are ore and metals processing and piston-engine aircraft operating on leaded aviation fuel.
  - Other sources are waste incinerators, utilities, and lead-acid battery manufacturers. The highest air concentrations of lead are usually found near lead smelters.
  - Volcanic activity and airborne soil are the primary natural sources of atmospheric lead.

Acid Deposition

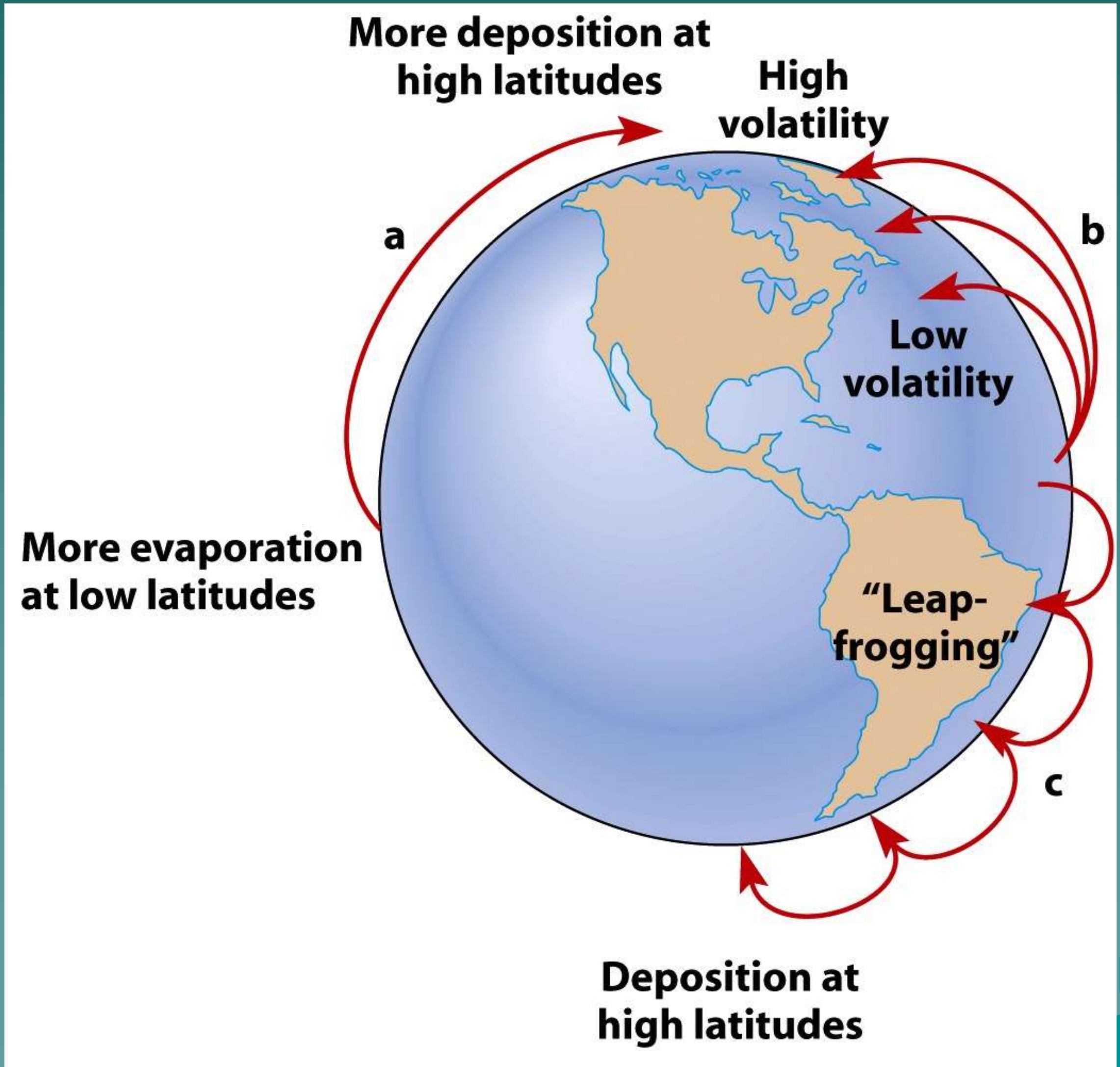
- Sulfur dioxide and nitrogen dioxide emissions react with water vapor in the atmosphere and form acids that return to the surface as either dry or wet deposition
- pH scale



How Acid Deposition Develops

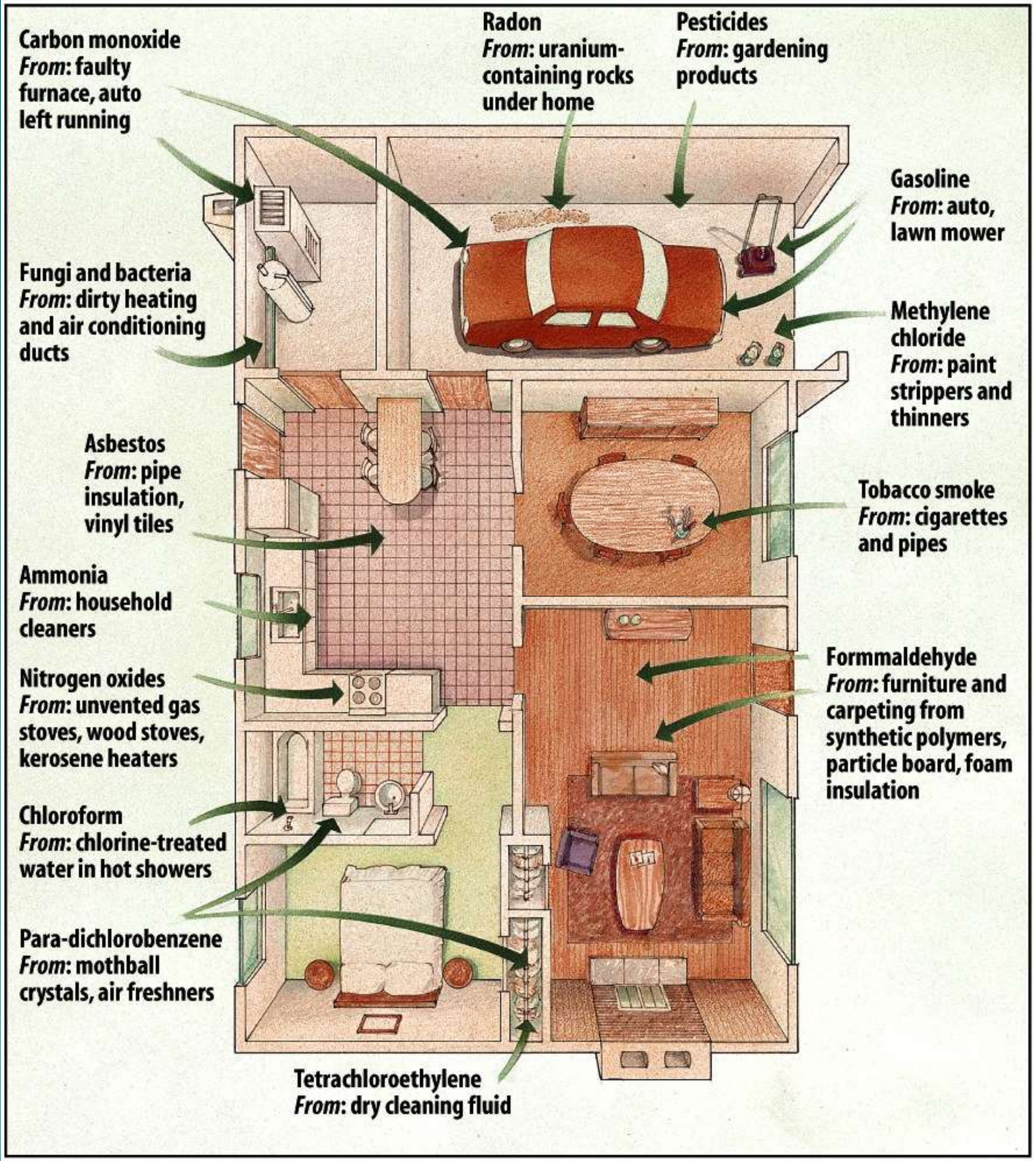


Long Distance Transport of Air Pollutants

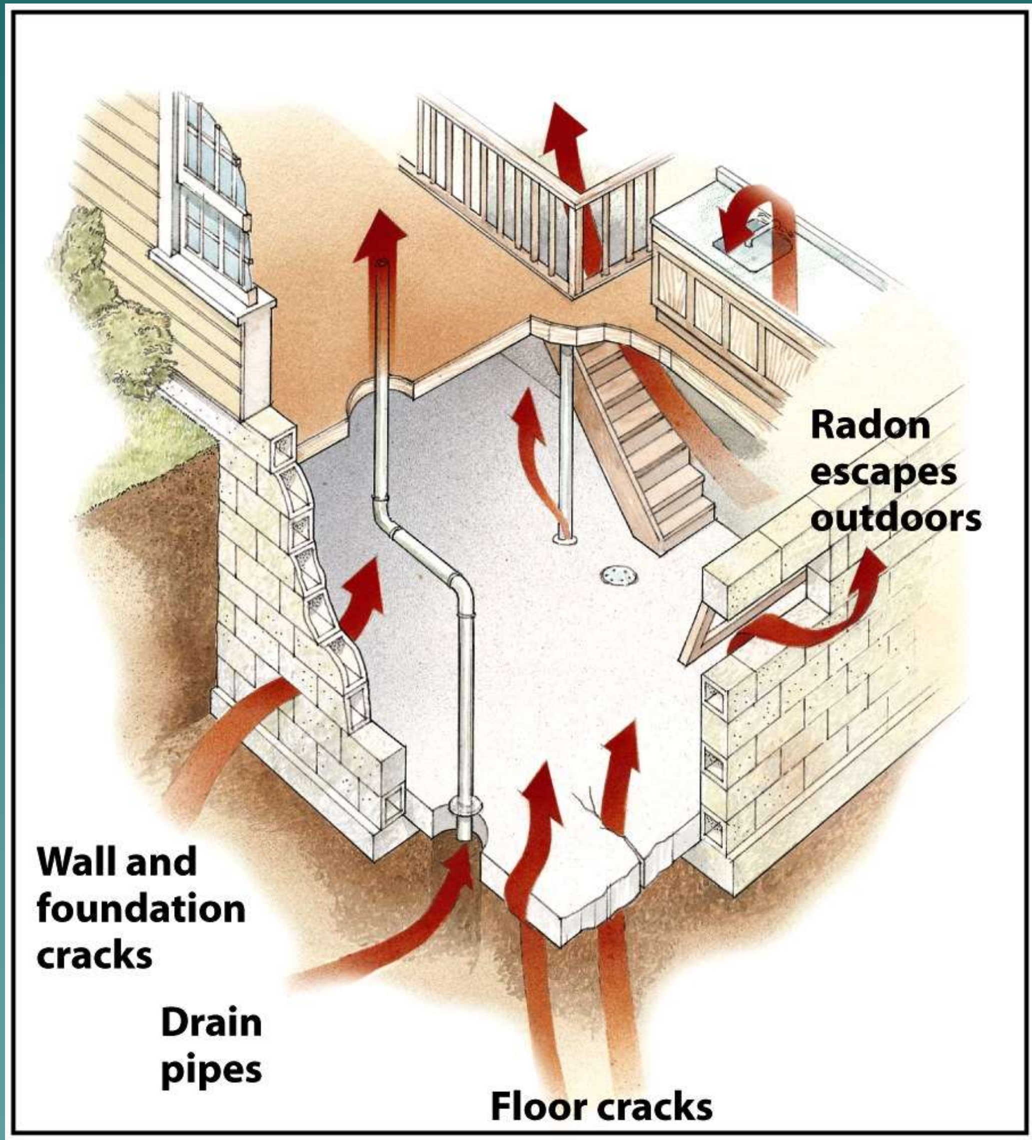


Indoor Air Pollution

- Pollutants can be 5-100X greater than outdoors
- Most common:
  - Radon, cigarette smoke, carbon monoxide, nitrogen dioxide, formaldehyde pesticides, lead, cleaning solvents, ozone, and asbestos

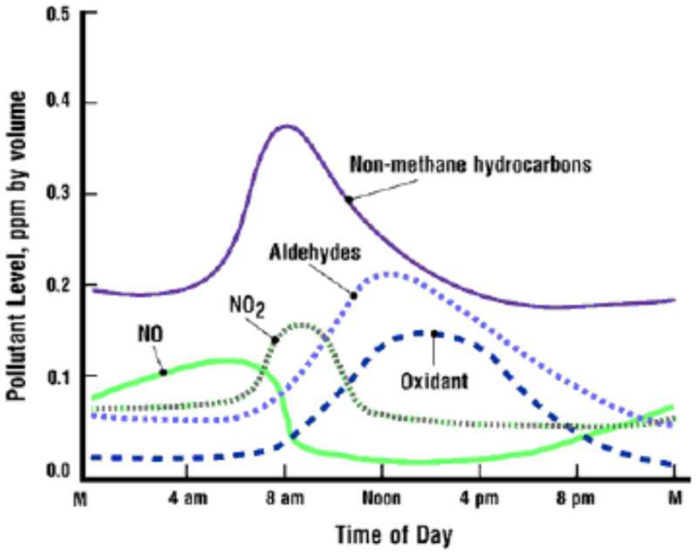


Indoor Air Pollution - Radon



Daily Variation

Variation of concentration of gases during the day



- Early morning traffic increases the emissions of both nitrogen oxides and VOCs as people drive to work.
- Later in the morning, traffic dies down and the nitrogen oxides and volatile organic compounds begin to react forming nitrogen dioxide, increasing its concentration.
- As the sunlight becomes more intense later in the day, nitrogen dioxide is broken down and its by-products form increasing concentrations of ozone.
- As the sun goes down, the production of ozone is halted. The ozone that remains in the atmosphere is then consumed by several different reactions.

http://jan.ucc.nau.edu/~doetqp-p/