An Introduction to Air Quality

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Outline

- What do we mean by “air quality”?
- What causes air pollution?
- What are the most common air pollutants?
- How do pollutants spread through the air?
- How do we measure air pollution?
- Is indoor air cleaner than outdoor air?

I. What Do We Mean by “Air Quality”?

Air Quality

- “Air quality”: The degree to which the atmosphere is polluted

Air Quality

- "Air quality": The degree to which the atmosphere is polluted

- An "air pollutant" is a material that
  - Is present in the atmosphere in excess of naturally-occurring amounts because of human activities
  - Has adverse effects on human health or welfare, or on the environment

Air Pollutant

- Can be a material that
  - Is toxic to humans
  - Adversely affects plants and wildlife
  - Degrades materials (e.g., sandstone, rubber)
  - Leads to an undesirable condition, such as visibility reduction

Human vs. Natural

- Many air pollutants are materials that also occur naturally, sometimes in amounts exceeding what is created by humans
- Then why worry about the lesser amounts created by human activities?

Human vs. Natural

- Many air pollutants are materials that also occur naturally, sometimes in amounts exceeding what is created by humans
- Then why worry about the lesser amounts created by human activities?
- Human activities lead to high amounts in localized areas

Quantifying Air Pollutants

- Amount emitted from a particular source
  - Mass per time period
  - Typically lbs/year, tons/year, kg/year

Quantifying Air Pollutants

- Concentration in air
  - milligrams of pollutant per cubic meter of air (mg/m^3)
  - milligrams of pollutant per kilogram of air (mg/kg)
  - parts per million: 1 ppm = 1 mg/kg
  - parts per million by volume:

    1 ppmv = 1 mL of pollutant vapor per 1000 L of air

II. What Causes Air Pollution?

Human Sources

- Any kind of combustion process
  - Coal-fired power plants
  - Internal combustion engines
  - Gas-fired boilers, furnaces, stoves
  - Flaring of gas
  - Incinerators
  - Wood-burning stoves and fireplaces
  - Burning of farm fields, ditches, leaves

Human Sources

- Other industrial processes (examples)
  - Manufacture of materials that are “volatile” (have a tendency to evaporate)
  - Use of volatile materials, such as organic solvents

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  - Manufacture of materials that are “volatile” (have a tendency to evaporate)
  - Use of volatile materials, such as organic solvents
- Other agricultural processes
  - Application of ammonia
  - Application of pesticides, herbicides

Human Sources

- Bare ground: plowed fields, unpaved roads, soil disturbed by any activity that removes vegetation and disrupts soil surface

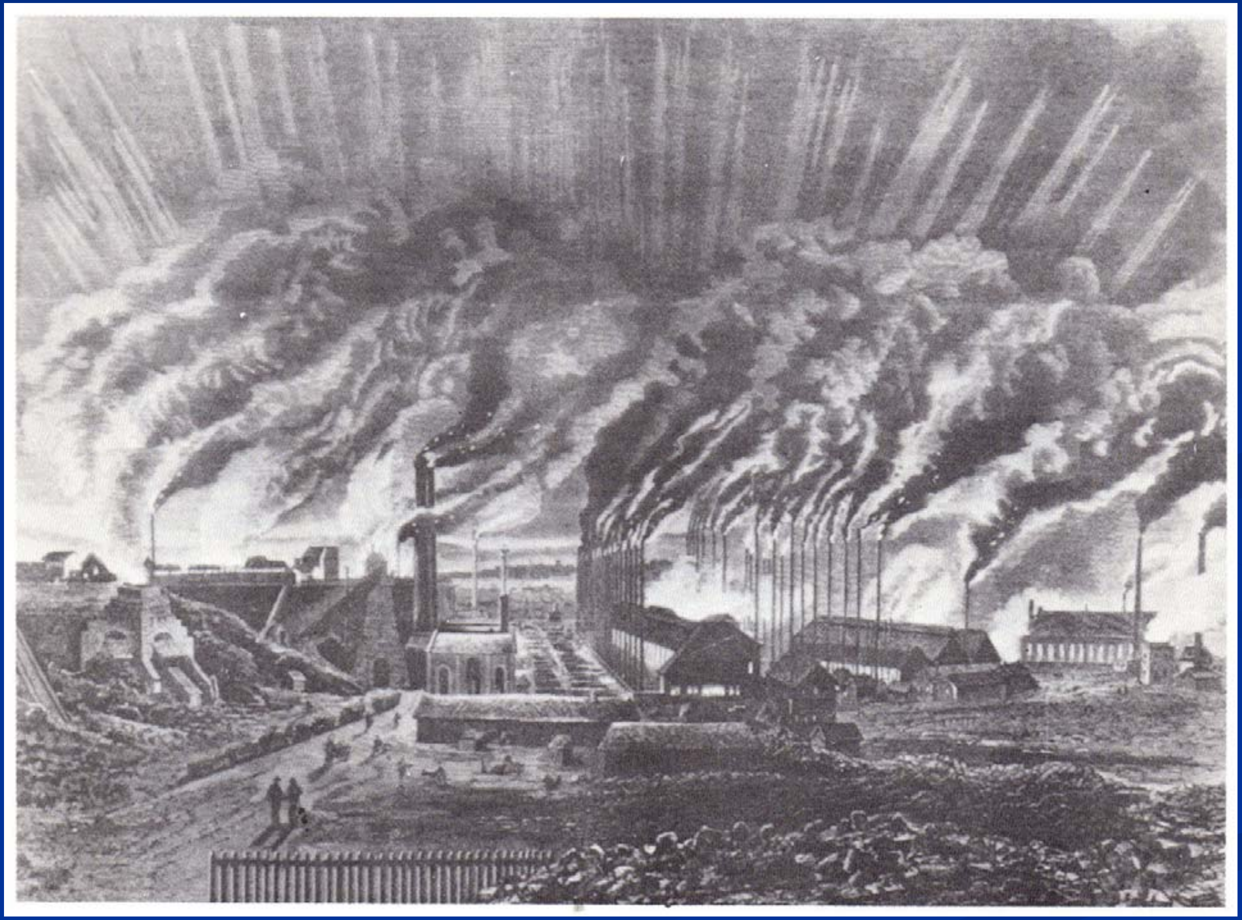
Human Sources

- Bare ground: plowed fields, unpaved roads, soil disturbed by any activity that removes vegetation and disrupts soil surface
- Landfills: gases from decomposition of food, yard waste, paper etc

Natural Sources

- Forest fires, grass fires
- Soil erosion by wind
- Biological processes
- Chemical reactions in the atmosphere
- Volcanoes

III. What Are the Common Air Pollutants?



Carbon Monoxide

- Gas
- Colorless
- Odorless
- Tasteless

Carbon Monoxide

- Human sources – primarily incomplete combustion
  - Fossil fuel power plants
  - Boilers, furnaces, space heaters, stoves
  - Vehicles
  - Non-vehicle small engines
  - Incinerators
  - Agricultural burning
- ~60% of human emissions in U.S. are from vehicle exhaust

Carbon Monoxide

- Natural sources
  - Fires
  - Oxidation of hydrocarbon gases
  - Decomposition of plant matter
  - Microorganisms in oceans
  - Volcanic eruptions

Carbon Monoxide

- Sinks (processes that remove carbon monoxide from air)
  - Conversion to carbon dioxide by soil microorganisms
  - Conversion to carbon dioxide by chemical reactions in the atmosphere

Carbon Monoxide

- Estimates of U.S. annual emissions (excluding wildland fires)
  - 1970: 197 million tons
  - 2003: 93.7 million tons
- http://www.epa.gov/air/airtrends/carbon.html

Carbon Monoxide

- Global average concentration is 0.19 ppm
- Average hourly concentration in urban areas ranges from a few ppm to 60 ppm
  - Average hourly concentrations in urban areas vary over the course of a typical day
  - Concentrations are higher in colder weather
- Ambient air quality standards
  - 35 ppm average over a 1 hour period
  - 9 ppm average over an 8 hour period

Particulate Matter

- Human sources (examples)
  - Combustion sources mentioned for CO
  - Roads (sanding, traffic on unpaved)
  - Mining
  - Cement production
  - Metal smelting
  - Grain milling

Particulate Matter

- Natural sources
  - Soil erosion by wind
  - Fires
  - Pollen
  - Sea spray

Particulate Matter

- Sinks
  - Dry deposition: Particulates settle to ground because of gravity
  - Wet deposition: Particulates are “washed out” of the air by rain

Particulate Matter

- Also referred to as aerosols
- Primary particles: Emitted directly into atmosphere from source
- Secondary particles: Formed in the atmosphere from condensation of gases (such as sulfur dioxides and nitrogen dioxides)

Particulate Matter

- Composition
  - Particulates from soil: Mineral matter
  - Particulates from combustion
    - Primarily elemental carbon
    - Also hydrocarbons, sulfate, nitrate

Particulate Matter

- Size classification
  - Fine (PM2.5)
    - Particles < 2.5 micrometers in diameter
    - Primarily from combustion
  - Inhalable coarse (PM2.5-10)
    - Particles between 2.5 and 10 micrometers in diameter
    - Primarily from road dust and crushing/grinding of solids
  - Particles < 10 micrometers in diameter (PM10)

PM10

- Estimates of U.S. annual emissions (excluding fires)
  - 1970: 12.2 million tons per year
  - 2003: 2.3 million tons per year
- http://www.epa.gov/air/airtrends/pm.html

PM2.5

- Estimates of U.S. annual emissions (excluding fires)
  - 1970: not measured
  - 2003: 1.8 million tons
- http://www.epa.gov/air/airtrends/pm.html

PM10

- Concentrations in urban areas range up to 300 micrograms per cubic meter of air
- Current ambient air quality standards
  - 150 μg/m^3 average over a 24-hour period
  - 50 μg/m^3 average over a year

PM2.5

- Average concentration in urban areas is roughly 12 micrograms per cubic meter
- Current ambient air quality standards
  - 65 $\mu g/m^3$ average over a 24-hour period
  - 15 $\mu g/m^3$ average over a year
- Proposed revised standard
  - 35 $\mu g/m^3$ average over a 24-hour period

Nitrogen Oxides (NO_x)

- Includes N_2O, NO, and NO_2
- In context of pollution, our focus is mostly NO_2 and to a lesser extent NO

Nitric Oxide (NO)

- Gas
- Colorless
- Odorless
- Tasteless

Nitrogen Dioxide (NO_2)

- Gas
- Light yellowish at low concentrations
- Reddish-brown at high concentrations
- Pungent, irritating odor

Nitric Oxide

- Produced by oxidation of N_2 during high-temperature combustion

  $N_2 + O_2 \rightarrow 2\,NO$

- Human sources are essentially same as those combustion-related sources listed for CO

Nitric Oxide

- Natural sources
  - Biological processes in soil and water
  - Photochemical reactions in atmosphere
  - Fires

Nitrogen Dioxide

- Sources
  - Direct oxidation of NO:

    $$2\,NO + O_2 \rightarrow 2\,NO_2$$

  - Photochemical reactions of NO with certain other gases

    $$NO + O_3 \rightarrow NO_2 + O_2$$

    $$NO + RO_2 \rightarrow NO_2 + RO$$

    $$NO + HO_2 \rightarrow NO_2 + OH$$

Nitrogen Oxides

- Sinks:
  - NO: Conversion to NO_2
  - NO_2: Conversion to HNO_3

Nitrogen Oxides

- Estimates of U.S. annual emissions
  - 1970: 26.9 million tons per year
  - 2003: 20.5 million tons per year
- http://www.epa.gov/air/airtrends/nitrogen.html

Nitrogen Oxides

- Background concentrations
  - NO: ~0.5 parts per billion
  - NO_2: ~1 parts per billion
- Concentrations in urban areas
  - NO: Up to 1 to 2 parts per million
  - NO_2: Up to 0.5 parts per million, but most typically between 0.01 and 0.03
- Ambient air quality standard for NO_2:

  0.053 ppm averaged over a year

Sulfur Oxides (SO_x)

- Includes SO_2 and SO_3
- Our focus is SO_2

Sulfur Dioxide (SO_2)

- Occurs as a gas
- Occurs as an aerosol (SO_2 gas is a major precursor to formation of PM2.5)
- Colorless
- Can be tasted and smelled at concentrations > 0.38 parts per million
- Has pungent, irritating odor > 3 parts per million

Sulfur Oxides

- Human sources
  - Smelting of metal sulfide ores
  - Combustion of fuels containing sulfur
- Natural sources
  - Oxidation of hydrogen sulfide
  - Fires
  - Volcanoes

Sulfur Oxides

- Sinks
  - Dry deposition
  - Wet deposition
  - Oxidation to sulfuric acid, H_2SO_4

Sulfur Dioxide

- Estimates of U.S. annual emissions
  - 1970: 31.2 million tons per year
  - 2003: 15.8 million tons per year
- http://www.epa.gov/air/airtrends/sulfur.html

Sulfur Dioxide

- Background concentration ~0.001 ppm
- Concentrations of up to 0.5 ppm in urban areas, but more typically 0.02 ppm to 0.12 ppm
- Concentrations up to 2.3 ppm near smelters
- Ambient air quality standard
  - 0.14 ppm averaged over a 24-hour period
  - 0.03 ppm averaged over a year

Volatile Organic Compounds

- Hydrocarbons
  - Paraffins (e.g. methane, ethane, propane)
  - Olefins (e.g. ethylene, propylene)
  - Aromatics (e.g. benzene, toluene, xylene, PAHs)
- Oxygenated hydrocarbons
  - Aldehydes (e.g., formaldehyde)
  - Others

Volatile Organic Compounds

- Human sources
  - Incomplete combustion of hydrocarbon fuels
  - Evaporation of fuels and organic solvents
  - Oil and gas production
  - Petroleum refining

Volatile Organic Compounds

- Natural sources
  - Plant and animal metabolism
  - Evaporation of plant oils
  - Biological decomposition
  - Emissions from fossil fuel deposits

Volatile Organic Compounds

- Sinks
  - Photochemical reactions converting the organics to CO_2 and H_2O
  - Photochemical reactions converting the organics to soluble or condensable compounds, which leave atmosphere by deposition
  - Photochemical reactions to produce ozone

Volatile Organic Compounds

- Estimated U.S. annual natural emissions: 70 million tons per year
- Estimates of U.S. annual anthropogenic emissions
  - 1970: 33.7 million tons per year
  - 2003: 15.4 million tons per year

Photochemical Smog

- Composed of
  - Particulate matter
  - Photochemical oxidants
    - Created <u>in the atmosphere</u> by reactions involving sunlight, non-methane hydrocarbons, oxygen, and nitrogen oxides
    - Includes ozone (O_3), which is our primary focus, and peroxyacetyl nitrate (PAN)

Photochemical Smog

- Sources
  - Requires sources of NO_x
  - Requires sources of hydrocarbons

Ozone

- Background concentration at remote sites is ~0.02 ppm during summer
- In worst urban areas, concentrations have reached 0.4 ppm. Values more commonly reach up to 0.10 ppm
- Ambient air quality standard is 0.08 ppm averaged over an 8-hour period
- http://www.epa.gov/air/airtrends/ozone.html

Visibility Reduction

- Photochemical smog (described above)
- London smog: Combination of particulate matter, SO_2, and fog
- Both smogs typically occur over urban areas and can be very intense
- Haze: A less-intense reduction over a more widespread area

Visibility Reduction

- Cause: Primarily scattering of light by particulate matter
- Other factors affecting visibility
  - Humidity
  - Wind speed and atmospheric stability
  - Sunlight

Visibility Reduction

- Effect of air pollution in national parks
  - Eastern parks: Reduced from 90 miles down to 15-25 miles
  - Western parks: Reduced from 140 miles down to 35-90 miles
- Reduction in Grand Canyon has drawn particular attention
  - Formation of Grand Canyon Visibility Transport Commission
  - Increased regulation of nearby power plants

Acid Deposition

- Culprits
  - Primarily sulfur dioxide
  - Nitrogen dioxide is also significant
  - Undergo reactions in air that lead to formation of sulfuric acid and nitric acid in water droplets

Acid Deposition

- Wet deposition: Acidified rain, snow, fog, dew, frost
- Dry deposition: Acid gases and particles
- Roughly half of acid deposition is wet, half dry

Acid Deposition

- Recall pH as a measure of how acidic something is
- Water in contact with air free of any acidic gases or particles: pH = 5.7
- Currently, most acidic precipitation in U.S. has pH ~ 4.3

Lead

- Big success story!
- Estimates of U.S. annual emissions
  - 1970: 221,000 tons per year
  - 2003: 3,000 tons per year
  - http://www.epa.gov/airtrends/lead.html#pbnat
- Why?

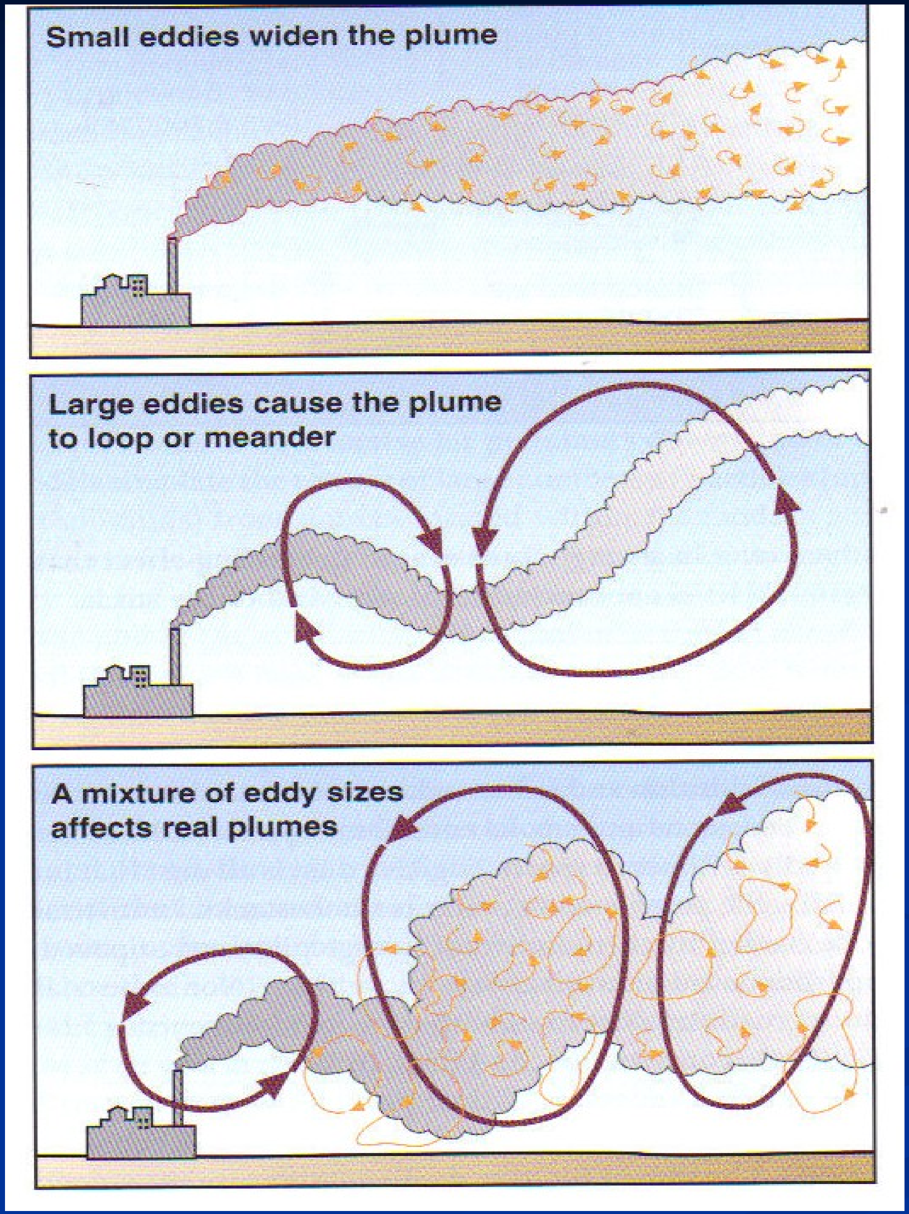
IV. How Do Pollutants Spread Through the Air?

Diffusion

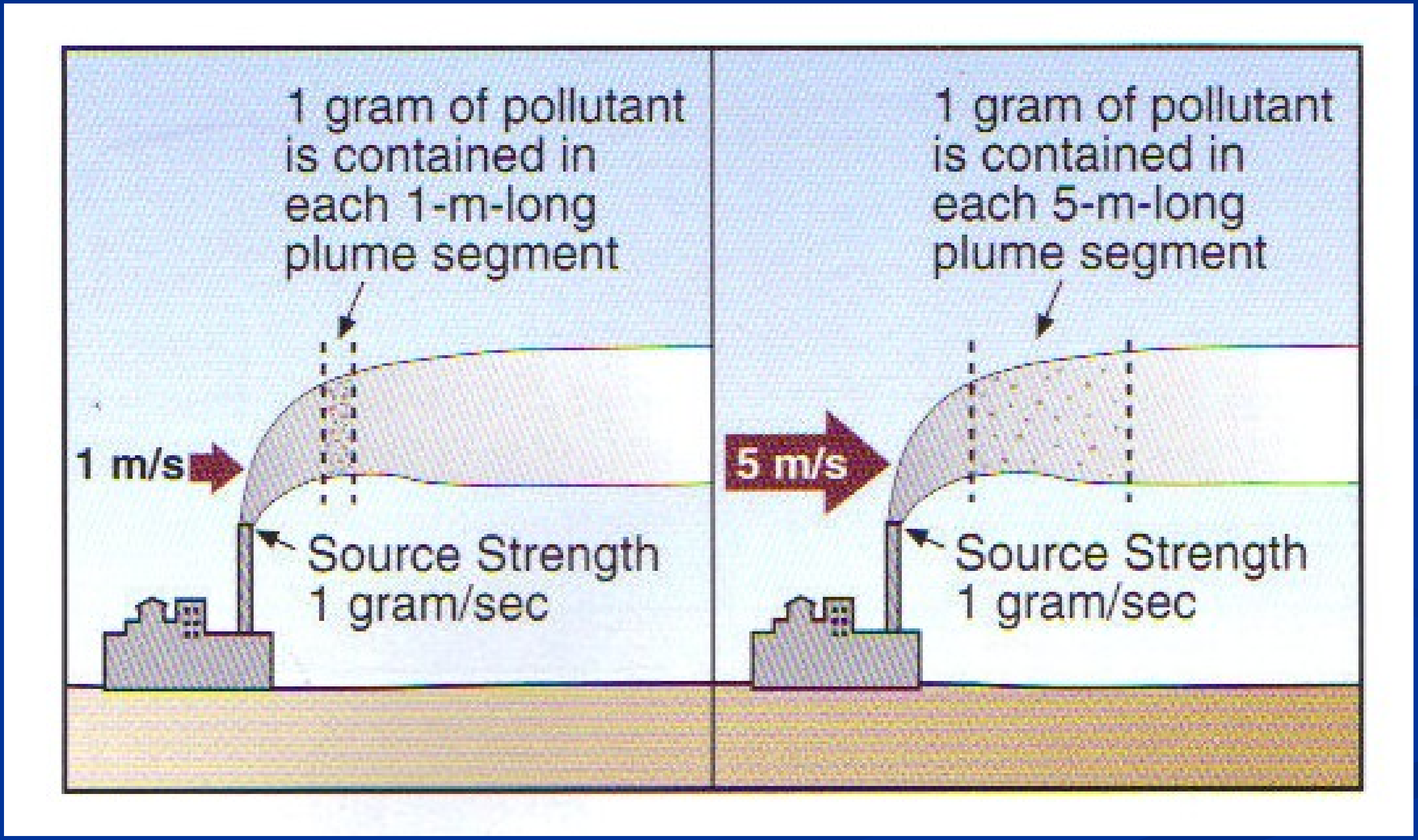
- Air pollutant moves from locations where concentration is high to locations where concentration is low
- Results in dispersal of pollutant
- Significant only in absence of wind

Advection

- Occurs when there is wind
- Pollutant is carried along by the moving air
- Air movement isn't very uniform – air turbulence (eddies) disperses the pollutant over a larger volume of air
- Emission from stack: Picture pollutant spreading downwind in a cone shape


Small eddies widen the plume
Large eddies cause the plume to loop or meander
A mixture of eddy sizes affects real plumes

- The higher the wind speed, the better the pollutant is dispersed

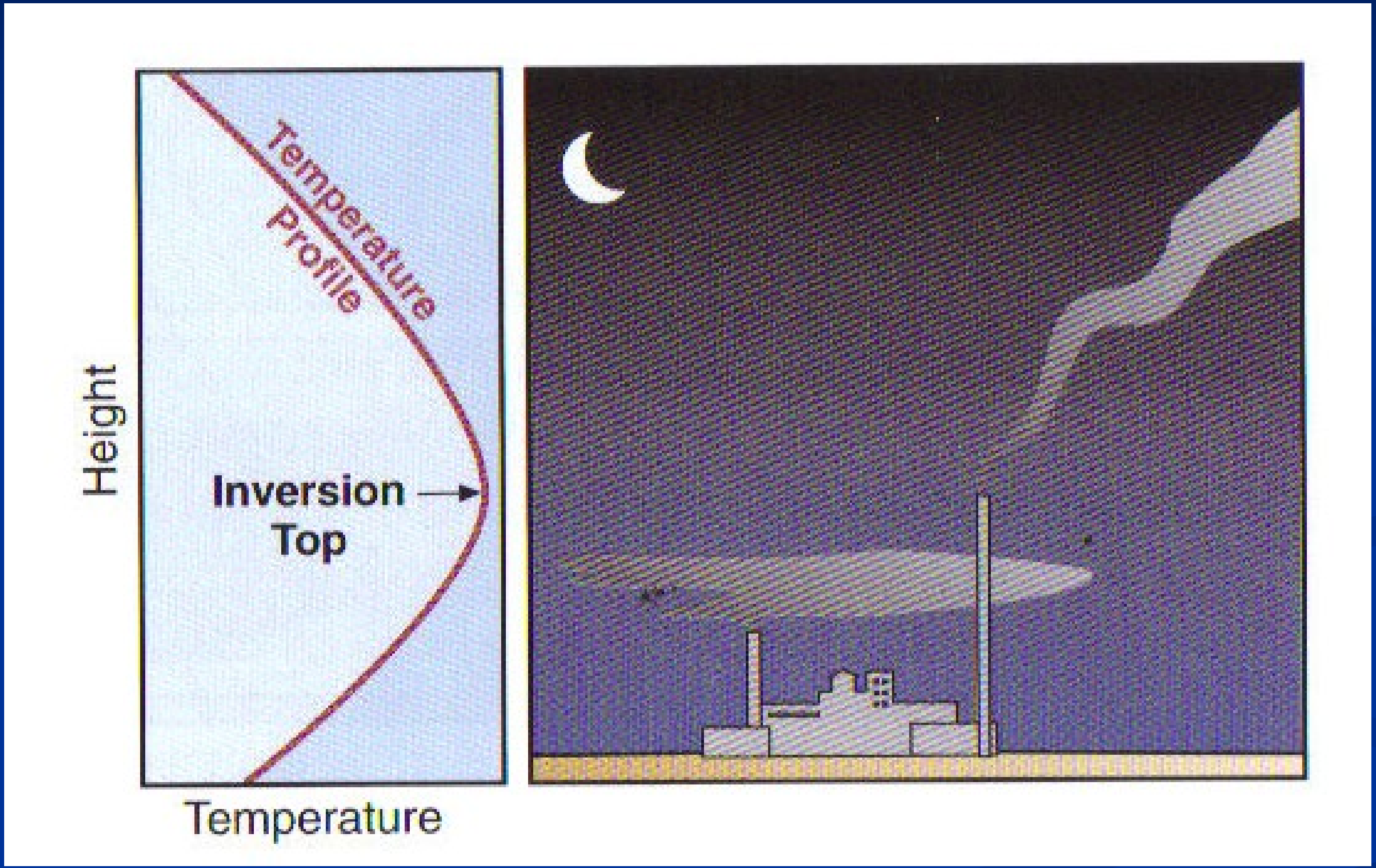


Effects of Air Stability

- Normal
  - Air temperature decreases with increasing elevation
  - Is unstable - - there is little resistance to vertical motion

Effects of Air Stability

- Normal
  - Air temperature decreases with increasing elevation
  - Is unstable - - there is little resistance to vertical motion
- Inversion
  - Layer of cold, more dense air below
  - Layer of warm, less dense air above
  - Is stable - - lots of resistance to vertical motion


Temperature Profile
Height
Inversion Top
Temperature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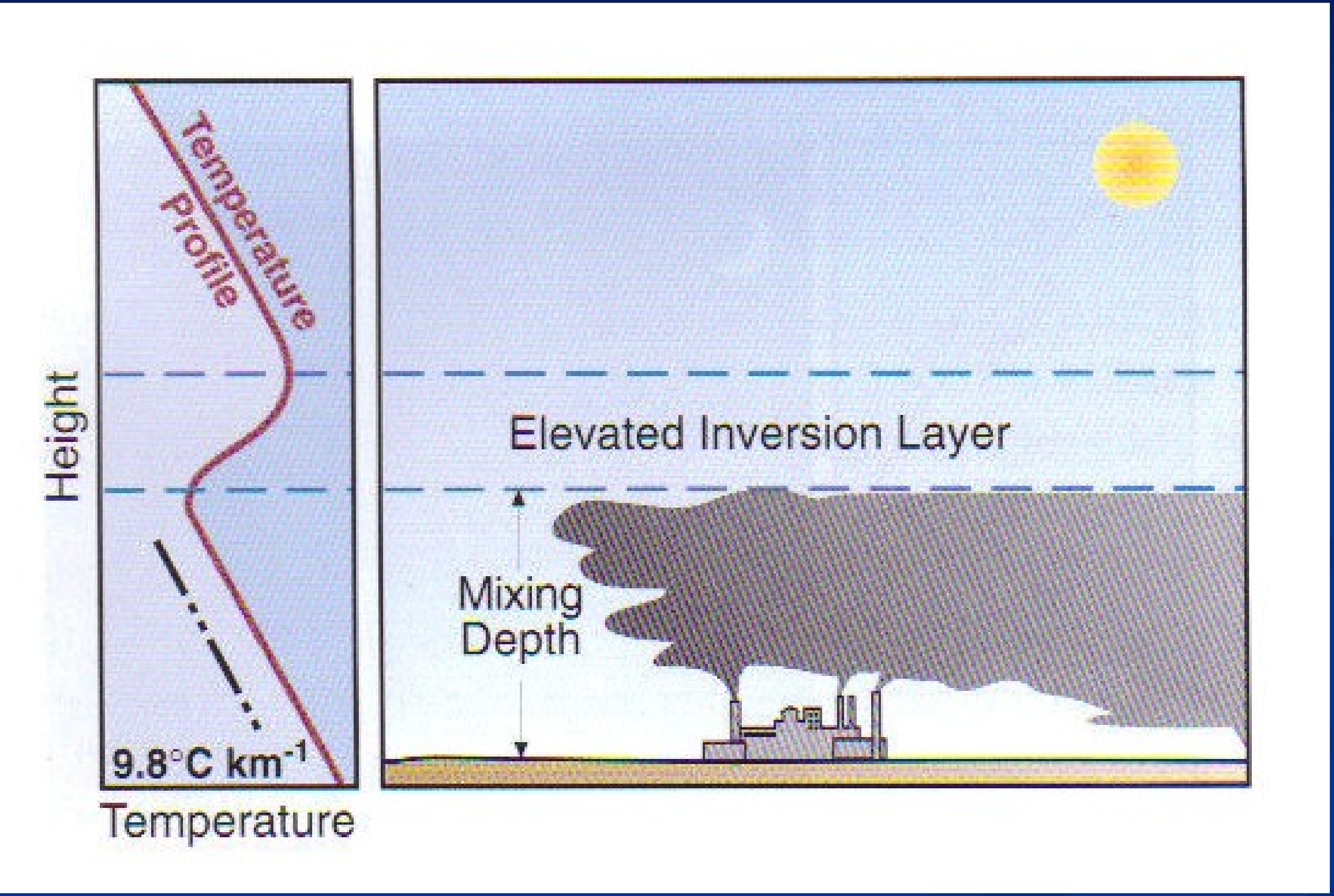
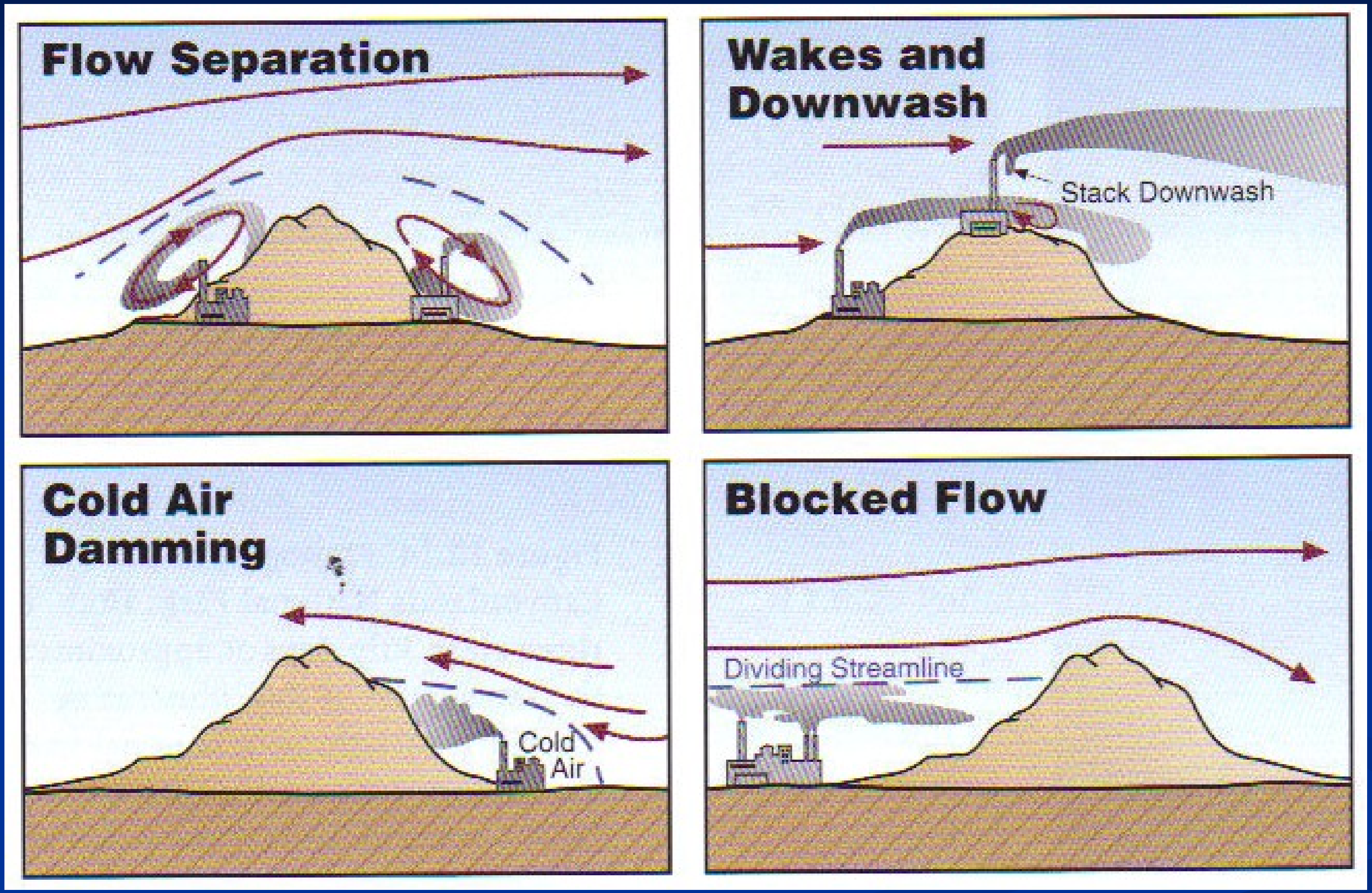


Temperature Profile
Height
9.8°C km-1
Temperature
Elevated Inversion Layer
Mixing Depth

Effects of Terrain

- Nearby hill or mountain can lead to poor dispersion conditions
  - Flow separation and eddy formation
  - Cold air damming
  - Blocked flow



Flow Separation
Wakes and
Downwash
Stack Downwash
Cold Air
Damming
Cold
Air
Blocked Flow
Dividing Streamline

Effects of Terrain – Valley Winds

- In evening, air just above land surface cools
  - Cool air moves down side slopes toward valley floor
  - Layer of stable, cool air deepens over valley floor
  - Cool air within valley moves along the valley axis toward the low end of the valley

Effects of Terrain – Valley Winds

- In morning, air just above land surface warms
  - Warming air moves up side slopes away from valley floor
  - Warming air above valley floor moves along the valley axis toward the high end of the valley
  - Remaining "core" of stable, cool air gradually warms and breaks up

V. How Do We Measure Air Pollution?

Approaches

- Sampling: A representative amount of air and/or pollutant is collected over a specific period of time, then analyzed in a separate procedure
- Continuous monitoring: Air is continuously drawn through an instrument which analyzes for specific pollutants

Considerations in Sampling

- Must collect an amount of pollutant sufficient for the analytical method to be able to reliably detect and quantify it
- If the method isn't very sensitive, may need to collect sample over a long time period

Averaging Times

- Determined by time required to collect sufficient pollutant
- Also determined by intended use of data
  - 24-hour period if data used to evaluate long-term exposures or trends
  - 1-hour period if the pollutant concentrations tend to spike for short periods of time

Grab Samples

- Used to characterize transient problems rather than for routine monitoring
- Small volume of air collected over the course of seconds or minutes
- Devices for collecting grab samples
  - Evacuated flask (e.g., summa canister)
  - Tedlar bag
  - Gas syringe

Continuous Sampling

- "High volume sampler" is widely used
- Pump pulls ambient air into the sampler

Continuous Sampling

- "Gas sampling train" is widely used to collect pollutant gases
- Pump pulls air through a tube, which is submerged in an absorbing solution
- As the air bubbles through the solution, pollutant is retained in the solution
- The solution is analyzed for the pollutant

Collection of Particulate Samples

- Samples of particulate matter are collected by drawing air through a filter
- Weigh filter before and after to determine how much particulate was in the volume of air that flowed through the filter
- Special collectors are added to divide the particles into the desired size ranges


MAR

Accuracy vs. Precision

- Accuracy: How closely our measurement matches the true value of the quantity we're trying to measure
- Precision: How repeatable the result of our measurement is
- Our goal: Both high accuracy and high precision

Variability in Environmental Data

- Key concept: We don’t obtain the same result for repeated measurements on the same sample
- Measurement variability
  - Random errors are inherent in every measurement process
  - Systematic errors may also occur
- True environmental variability from place to place and time to time

VI. Is Indoor Air Cleaner than Outdoor Air?

Indoor Sources – Combustion

- Wood-burning appliances
  - Carbon monoxide
  - Nitrogen dioxide
  - Sulfur dioxide
  - Particulate matter
  - PAHs
  - Aldehydes and other hydrocarbons

Indoor Sources - Combustion

- Unvented gas and kerosene heaters, gas stoves
  - Carbon monoxide and carbon dioxide
  - Nitrogen dioxide
  - Sulfur dioxide (especially kerosene heaters)
  - Particulate matter
  - Aldehydes and other hydrocarbons

Indoor Sources - Combustion

- Tobacco smoke
  - Carbon monoxide
  - Nitrogen dioxide
  - Particulate matter
  - Formaldehyde
  - Acrolein
  - Nitrosamines
  - Hydrogen cyanide

Indoor Sources – Building Materials

- Urea-formaldehyde foam used as insulation
- Plywood, particle board, fiber board using adhesives and coatings containing urea-formaldehyde resins
- Indoor concentrations are often 10 times or more higher than outdoor background levels

Indoor Sources – Building Materials

- Paints and finishes
- Volatile organic compounds
- Have an initially high emission rate that then tapers off

Indoor Sources – Home and Personal Care Products

- Variety of organic compounds

Asbestos

- Is a silicate mineral that occurs as very small, fine fibers
- "Friable" asbestos is the primary concern – when crushed, releases small fibers that can be easily inhaled
- Sources: thermal insulation, acoustic insulation
- Degree of threat depends on age of the asbestos-containing material and the likelihood of disturbance

Radon

- Radon-222 is formed in the radioactive decay chain of uranium
- Is a gas, and thus is mobile and inhalable
- Undergoes radioactive decay with a half-life of 3.8 days
- Products of this decay also undergo radioactive decay, with half-lives from a small fraction of a second up to minutes
- Some of these readily attach to aerosols which can be inhaled and deposited in lungs

Radon

- Sources in indoor air: Seepage into structures from underlying soil and rock that contains uranium

Indoor vs. Outdoor Concentrations

- If there are no indoor sources of “reactive” gases such as SO_2, NO_2, O_3 :
  - When outdoor concentrations are high, indoor concentrations are about 1/10 to 1/2 as high
  - When outdoor concentrations are low, indoor concentrations appear to be about the same
- If there are no indoor sources of CO, a “non-reactive” gas, the indoor levels tend to be about the same as outdoors

Indoor vs. Outdoor Concentrations

- Indoor concentrations can readily be higher than outdoor concentrations for
  - Carbon monoxide
  - A variety of organic chemicals
  - Particulate matter
  - Radon
  - Formaldehyde
  - Asbestos
  - Mold spores

Sick Building Syndrome

A situation in which occupants of a building report a variety of symptoms of illness, but specific causal agents can't be identified

Sick Building Syndrome

- Typical symptoms
  - Irritation of eyes, nose, and throat
  - Skin irritation
  - General health problems (headache, mental fatigue, reduced memory and concentration, nausea)
  - Runny nose or eyes
  - Odor and taste

Acknowledgements

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