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The Atmosphere

- The density, or number of gas molecules per unit of air volume, varies throughout the atmosphere because gravity pulls gas molecules toward Earth's surface, density of decreases with increase in altitude.
  - **Atmospheric pressure** is the force, or mass, per unit of area of a column of air. Atmospheric pressure *decreases* with *increase* in altitude because there are fewer gas molecules at higher altitudes.

The troposphere and the stratosphere: the atmosphere's innermost layers

- **Troposphere**
  - The troposphere is the layer closest to the Earth's surface and contains about 75–80% of the Earth's air mass. ***All of the weather happens in the troposphere***.
  - Chemical composition of air: 99% of the volume of air consists of two gases, nitrogen (78%) and oxygen (21%). The remainder consists of water vapor (varying from 0.01% at the poles to 4% in the tropics; average of 1%), 0.93% argon, 0.039% carbon dioxide, and trace amounts of dust and soot particles as well as other gases including methane, ozone, and nitrous oxide.
- **Stratosphere**
  - The stratosphere has a similar composition to the troposphere, with two exceptions:
    - There is much less water vapor in the stratosphere, which explains why all of the weather happens in the troposphere ($1/1000^{th}$ that of the troposphere).
    - The stratosphere has the **ozone layer** (O_3), which filters 95% of harmful UV radiation.
    - The ozone layer exists just above the boundary between the troposphere and the stratosphere known as the tropopause.
    - The UV filtering effect of ozone allows us and other life to exist on land and protects us from sunburn, skin cancer, and eye damage such as cataracts. More on the ozone layer in Chapter 19…

Major Air Pollutants and Their Sources

- **Air pollution**: The introduction of chemicals, particulate matter, or microorganisms into the atmosphere at concentrations high enough to harm plants, animals, materials such as buildings, or alter ecosystems.
- **The U.S. Clean Air Act of 1970** identified six major air pollutants to monitor and control. These were called *criteria pollutants* because under the Clean Air Act, the EPA must specify allowable concentrations of each pollutant. The original act identified *six pollutants* that significantly threaten human well-being, ecosystems, and structures: sulfur dioxide, nitrogen oxides, carbon monoxide, particulate matter, tropospheric ozone, and lead.
- In addition, volatile organic compounds and mercury, though not officially listed in the Clean Air Act, are commonly measured air pollutants that have the potential to be harmful.
- **Sulfur dioxide**
  - Sulfur dioxide (SO_2) is a corrosive gas that comes from combustion of fossil fuels such as coal and oil; it is a colorless gas with an irritating odor.
  - About one-third of the SO_2 comes from natural sources as part of the sulfur cycle; to a large extent from volcanic eruptions and to a much lesser extent from forest fires.
  - The other two-thirds (and as much as 90% in urban areas) come from human sources.
  - It is a respiratory irritant and can adversely affect plant tissue as well.
  - Because all plants and animals contain sulfur in varying amounts, the fossil fuels derived from their remains contain sulfur. When these fuels are combusted, the sulfur combines with oxygen to form sulfur dioxide.
  - In atmosphere SO_2 can be converted to aerosols, which consist of microscopic suspended droplets of sulfuric acid (H_2SO_4) and suspended particles of sulfate (SO_4^{2-}) salts that return to the earth as acid deposition. Sulfur dioxide, sulfuric acid droplets and sulfates reduce visibility and aggravate breathing problems. They can also damage crops, trees, soils, and aquatic life in lakes, and they can corrode metals and damage paint, paper, leather, and stone on buildings and statues.

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- **Nitrogen oxides**
  - Nitrogen oxides are generically designated NO_x, with the X indicating that there may be one or two oxygen atoms per nitrogen atom: nitrogen oxide (NO), a.k.a. nitric oxide or nitrogen monoxide, a colorless odorless gas; and nitrogen dioxide (NO_2), a pungent, reddish-brown gas, respectively.
  - The term *nitrogen oxides* refers to either nitrogen oxide or nitrogen dioxide since they easily transform from one to the other in the atmosphere.
  - The atmosphere is 78% nitrogen gas (N_2), nitrogen oxide forms when nitrogen and oxygen gas react under high-combustion temperatures in automobile engines and coal-burning power plants.
  - In the air nitrogen oxide (NO) reacts with oxygen to form nitrogen dioxide (NO_2).
  - Some of the NO_2 reacts with water vapor in the air to form nitric acid (HNO_3) and nitrate salts (NO_3), components of harmful acid deposition.
  - Motor vehicles and stationary fossil fuel combustion are the primary anthropogenic (human-caused) sources. Natural sources include forest fires, lightning, and microbial action in soils.
  - Both NO and NO_2 play a role in the formation of *photochemical smog*—a mixture of chemicals formed under the influence of sunlight in cities with heavy traffic.
  - At high enough levels, nitrogen oxides can irritate the eyes, nose, and throat, aggravate lung ailments such as asthma and bronchitis, suppress plant growth, and reduce visibility when converted to nitric acid and nitrate salts.
- **Carbon oxides**
  - Carbon monoxide (CO) is a colorless, odorless, and highly toxic gas that is formed during incomplete combustion of carbon contain materials (most matter), and therefore is a common emission in vehicle exhaust and most other combustion processes. Major sources of carbon dioxide are motor vehicle exhaust, burning of forests and grasslands, smokestacks of fossil fuel power plants and industries, and inefficient stoves used for cooking.
  - Carbon monoxide can combine with hemoglobin in red blood cells, which prevents the normal binding of oxygen with hemoglobin molecules. This, in turn, reduce the body's ability to transport oxygen to body cells and tissues. At high levels, CO, can cause headache, nausea, drowsiness, confusion, collapse, coma, and death.
  - Carbon monoxide can be a significant pollutant in urban areas. It can also be a dangerous indoor air pollutant when exhaust systems on natural gas heaters malfunction.
  - Carbon monoxide is a problem in developing countries, where people may cook with manure, charcoal, or kerosene within poorly ventilated structures.
  - Carbon dioxide (CO_2) is a colorless, odorless gas that is formed during the complete combustion of most matter, including fossil fuels and biomass.
  - 93% of the carbon dioxide in the atmosphere is the result of the natural carbon cycle. The rest comes from human activities, mostly burning of fossil-fuels and the burning of CO_2-absorbing forest and grasslands.
  - The burning of fossil fuels has added additional carbon dioxide the atmosphere and led to it becoming a major pollutant. It recently exceeded a concentration of 440 parts per million in the atmosphere and appears to be steadily increasing each year.
  - Though it is a greenhouse gas that is contributing to global warming and climate change, carbon dioxide is not classified as a pollutant by the Clean Air Act. However, in 2007, the U.S. Supreme Court ruled that carbon dioxide should be considered an air pollutant under the Clean Air Act and in 2012, a federal appeals court agreed that the EPA is required to impose limits on harmful greenhouse gases, including carbon dioxide. CO_2 is not yet a monitored and regulated pollutant under the Clean Air Act.

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- **Particulate matter**
  - Particulate matter (PM), also called particulates or particles, is solid or liquid particles suspended in air. Particulate matter comes from the combustion of wood, animal manure and other biofuels, coal, oil, and gasoline.
  - It is most commonly known as a class of pollutants released from the combustion of fuels such as coal and oil. Diesel powered vehicles give off more particulate matter, in the form of black smoke, than do gasoline powered vehicles.
  - Particulate matter can also come from road dust and rock-crushing operations. Volcanoes, forest fires, and dust storms are important natural sources of particulate matter.
  - Particulate matter larger than 10 µm is usually filtered out by the nose and throat and is not regulated by the EPA.
  - Particles smaller than 10 µm are called Particulate Matter-10, written as PM_{10}, and are of concern to air pollution scientists because they are not filtered out by the nose and throat and can be deposited deep within the respiratory tract.
  - Particles of 2.5 µm and smaller, called $PM_{2.5}$, are an even greater health concern because they deposit deeply in the respiratory tract and they tend to be composed of more toxic substances than particles in the larger size ranges.
  - These particles can irritate the nose and throat, damage the lungs, aggravate asthma and bronchitis, and shorten life. Toxic particulates such as lead, cadmium, and PCB's can cause genetic mutations, reproductive problems, and cancer.
  - According to the EPA, in the U.S. particulate air pollution, mostly from coal burning power plants is responsible for 70,000 premature deaths a year.
  - Particulate matter is light enough to remain suspended in the air for long periods. PM can scatter and absorb sunlight (causing a cooling effect) and interfere with photosynthesis and cause reduced visibility, known as haze.
- **Photochemical oxidants**
  - Photochemical oxidants are a class of air pollutants formed as a result of sunlight acting on chemical compounds such as nitrogen oxides and sulfur dioxides emitted from burning fossil fuels.
  - They are generally harmful to plant tissue, human reparatory tissue, and building material.
  - **Ozone**, a photochemical oxidant, is made up of three oxygens bound together and is harmful to both plants and animals and impairs respiratory function.
  - **Smog** is a type of air pollution that is a mixture of photochemical oxidants and particulate matter; formed in the presence of sulfur and nitrogen oxides. Causes hazy view and reduced sunlight and visibility. The brownish tint that characterizes these clouds of pollution is typically caused by the presences of carbon particles and nitrogen dioxide.
  - Negative ecological impacts of ground-level/tropospheric ozone are**:**
    - Damages to plant tissue;
    - Reduces primary productivity/inhibits photosynthesis;
    - Stresses plants, making them more vulnerable to disease and pests.
  - Negative human health impacts of ground-level/tropospheric ozone are**:**
    - Irritates respiratory system (throat irritation, coughing, decreased lung function);
    - Exacerbates diseases of the respiratory systems (asthma, bronchitis, emphysema);
    - Irritates eyes.

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- **Lead and other metals**
  - **Lead** (Pb) is a trace metal that occurs naturally in rocks and soils. It is present in small concentrations in fuels including oil and coal.
  - Lead compounds were added to gasoline for many years to improve vehicle performance. During that time, lead compounds released into the air traveled with the prevailing winds and were deposited on the ground by rain or snow. They became pervasive around the globe, including Polar Regions far from sources; transporting of pollutants to Polar Regions is known as the *grasshopper effect.*
  - Lead was phased out as a gasoline additive in the United States between 1975 and 1996, and since then its concentration in the air has dropped considerably.
  - Lead is toxic to the central nervous system (neurotoxin) and can affect learning and intelligence, particularly for young children. It can cause mental retardation, blindness, deafness, dementia, and in cases of acute lead poisoning, even death.
  - **Mercury** (Hg), another trace element, is also found in coal and oil and, like lead, is toxic to the central nervous system of humans and other organisms.
  - Due to the combustion of fossil fuels, primarily coal, the concentrations of mercury into the air and water has increased dramatically in recent years. Because of this mercury concentration in many fish has also increased; therefore, people who eat these fish increase their mercury concentrations.
  - The EPA regulates mercury through its hazardous air pollutants program.
  - Both lead and mercury are considered persistent organic pollutants (POP's) because they do not break down in the environment.
- **Volatile organic compounds**
  - Organic compounds that evaporate at typical atmospheric temperatures are called **volatile organic compounds (VOC's)**.
  - Many VOC's are hydrocarbons such as gasoline, lighter fluid, dry cleaning fluid, oil-based paints, and perfumes. Compounds that give off a strong aroma are often VOC's since the chemicals are easily released into the air.
  - *Methane* is a VOC that is emitted naturally from plants and wetlands (about a third of global methane emissions), and from human activity from man-made reservoirs for hydroelectric power, rice paddies, landfills, oil and natural gas wells, and cows (belching); the other two-thirds of global methane emissions.
  - *Benzene* is a VOC that composes about 2% of every gallon of gasoline and easily vaporizes when gasoline comes into contact with air.
  - VOC's play and important role in the formation of photochemical oxidants such as ozone.

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- **Primary pollutants**
  - Primary pollutants are polluting compounds that come directly out of a smokestack, exhaust pipe, or natural emission source. They include CO, CO_2, SO_2, NO_x, and most suspended particulate matter.
  - Many VOC's are also primary pollutants. Example, when gasoline is burned in a car, it volatilizes from liquid to vapor, some of which is emitted from the exhaust pipe in an uncombusted form.

Formation of primary pollutants

All fossil fuels contain large amounts of carbon (from the molecules of decomposed life forms).
The combustion of fossil fuels (reaction with oxygen) produces carbon dioxide and carbon monoxide:

$C + O_2 \rightarrow CO_2$ (the #1 man-made greenhouse gas)

$2C + O_2 \rightarrow 2CO$ (incomplete combustion)

Coal may also contain sulfur, which reacts during combustion:

$S + O_2 \rightarrow SO_2$

During combustion, the nitrogen that composes 78% of the air in the troposphere reacts:

$N_2 + O_2 \rightarrow 2NO$

Primary air pollutants undergo reactions in the atmosphere to form secondary air pollutants.

- **Secondary pollutants**
  - Secondary pollutants are primary pollutants that have undergone transformation in the presence of sunlight, water, oxygen, or other compounds.
  - Ozone is an example of a secondary pollutant, it is formed as a result of the emission of primary air pollutants NO_x and VOC's in the presence of sunlight.
  - Acid deposition and its main components sulfate (SO_4^{2-}) nitrate (NO_3^-) are also secondary pollutants.
  - When trying to control secondary pollutants, it is necessary to control or reduce the compounds that lead to their formation such as SO_2 and NO_x.
- **Air pollution comes from both natural and human sources**
  - <u>Natural emissions</u>
    - Volcanoes release sulfur dioxide, particulate matter, carbon monoxide, and nitrogen oxides.
    - Lightning strikes create nitrogen oxides from atmospheric nitrogen.
    - Forest fires release particulate matter, nitrogen oxides, and carbon monoxide.
    - Living plants release a variety of VOC's including ethylene and terpene. The fragrant smell from conifer trees such as pine and fir and the smell of citrus fruits are mostly terpenes; though we enjoy their fragrance, they can be precursors to photochemical smog.
      - ❖ The Great Smoky Mountains—along the Tennessee–North Carolina border in the southeastern United States—get their name from natural smog that is derived from plants that release natural VOC's and photochemical oxidant.
    - Globally, sulfur dioxide emissions are 30% natural, nitrogen oxides are 44% natural, and VOC emissions are 89% natural. However, in certain locations, such as North America, the anthropogenic contribution is much greater, as much as 95% for nitrogen oxides/sulfur dioxides.
  - <u>Anthropogenic emissions</u>
    - *Human sources*: mostly in industrialized and/or urban areas
      - *Stationary sources*: power plants and industrial facilities
      - *Mobile sources*: motor vehicles
    - On-road vehicles, also referred to as the general category of transportation, are the largest source of carbon monoxide and nitrogen oxides.
    - Electricity generation, 40 percent of which is fueled by coal, is the major source of anthropogenic sulfur dioxide.
    - Particulate matter comes from a variety of sources including natural and human made fires, road dust, and the generation of electricity.

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The Clean Air Act, which was last amended in 1990, requires EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment.

- The Clean Air Act identifies two types of national ambient air quality standards.
  - ***Primary standards*** provide public health protection, including protecting the health of "sensitive" populations such as asthmatics, children, and the elderly.
  - ***Secondary standards*** provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings.
- The EPA has set National Ambient Air Quality Standards for six principal pollutants, which are called "criteria" air pollutants. Periodically, the standards are reviewed and may be revised. The current standards are listed below. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micrograms per cubic meter of air (µg/m^3).

Pollutant		Primary/ Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		Primary and secondary	Rolling 3-month average	0.15 µg/m^3	Not to be exceeded
Nitrogen Dioxide (NO_2)		Primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		Primary and secondary	1 year	53 ppb	Annual mean
Ozone (O_3)		Primary and secondary	8 hours	0.070 ppm	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	Primary	1 year	12 µg/m^3	annual mean, averaged over 3 years
		Secondary	1 year	15 µg/m^3	annual mean, averaged over 3 years
		Primary and secondary	24 hours	35 µg/m^3	98th percentile, averaged over 3 years
	PM_{10}	Primary and secondary	24 hours	150 µg/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		Primary	1 hour	75 ppb	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		Secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

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Industrial smog, photochemical smog, temperature inversions and acid deposition

- **Industrial smog (Sulfurous smog)** is dominated by sulfur dioxide, sulfate compounds, and particulate matter (soot); also known as London-type smog; gray smog; industrial smog.
  - The chemistry of industrial smog is simple. When burned, most of the carbon in coal and oil is converted to carbon monoxide (CO) and carbon dioxide (CO_2). Unburned carbon in coal also ends up as suspended particulate matter (soot). When coal and oil are burned they react with oxygen to produce sulfur dioxide (SO_2) gas, some of which is converted to tiny suspended droplets of sulfuric acid (H_2SO_4). Some of these droplets can react with ammonium sulfate (NH_3) in the atmosphere to form ammonium sulfate $(NH_4)_2SO_4$.
  - The suspended particles of salts and soot give the resulting gray smog color that is typical of industrial smog.
  - Today, urban industrial smog is rarely a problem in developed countries where coal and heavy oil are burned in industrial and power plants with good pollution control methods.
  - However, due to their heavy reliance on coal and little to no pollution control methods, industrial smog remains a problem in industrialized areas of China, India, and areas of eastern Europe such as the Ukraine and Poland.
- **Photochemical smog** is dominated by oxidants such as ozone; also known as Los Angeles-type smog; brown smog; common in Denver and referred to as the Denver brown cloud.
  - The formation of Photochemical smog is complex and not well understood.
  - A photochemical reaction is any reaction activated by light (most often UV radiation).
  - Basically, sunlight plus cars equals photochemical smog. The formation of photochemical smog begins when exhaust from morning commuter traffic releases large amounts of NO_x and VOC's into the air over a city. As traffic increases on a warm sunny day, photochemical smog begins to build up and reaches peak levels in the late morning/early afternoon.
  - The first part of the process takes place during the day in the presence of sunlight. When abundant nitrogen oxides are present in the atmosphere, with very few VOC's present, nitrogen dioxide (NO_2) splits to form nitrogen oxide (NO) and a free oxygen atom (O). In the presence of energy inputs from sunlight, this free oxygen atom combines with diatomic oxygen (O_2) to form ozone (O_3). With abundant nitrogen dioxide and abundant sunlight, ozone can accumulate in the atmosphere.
  - When sunlight intensity decreases and with nitrogen oxide still present in the atmosphere, the ozone combines with nitrogen oxide (NO), and re-forms into $O_2 + NO_2$. This is referred to as ozone destruction and it is a natural process that happens in the later part of the day and evening.
  - Volatile organic compounds come from human activity such as spilling of gas on pavement and from natural sources such as forests. When volatile organic compounds are absent or in small supply, the cycle of ozone formation and destruction generally takes places daily and relatively small amounts of photochemical smog form.
  - A different scenario occurs when VOC's are present. The first part is the same: sunlight causes nitrogen dioxide to break apart into nitrogen oxide and a free oxygen atom. The free oxygen atom combines with diatomic to form ozone. However, because VOC's have combined with nitrogen oxide in a strong bond nitrogen oxide is no longer available to combine with ozone. Since the nitrogen oxide is not available to break down ozone by recombining with it, a larger amount of ozone accumulates. This explains, in part, the daytime accumulation of ozone in urban areas with an abundance of both VOC's and nitrogen dioxide.
  - The chemical reactions that form ozone and other photochemical oxidants happen more rapidly at higher temperatures. Additionally, the evaporation of volatile liquids increases on hot days. NO_x emissions from electric utilities, due to increased air conditioner use, also increases on hot days.

- Forest fires during hot periods of summer also add NO_x emissions, VOC's and particulate matter to the atmosphere.
- Photochemical smog irritates people's eyes and respiratory tracts.
- Photochemical smog is most common in cities with sunny warm climates, such as Los Angeles, California; Denver, Colorado; Salt Lake City, Utah; in the United States; and internationally: Sydney, Australia; Sao Paulo, Brazil; Bangkok, Thailand; Mexico City, Mexico; Santiago, Chile.

❖ Photochemical smog chemistry:

VOCs + NOx + Sunlight → photochemical smog.

$2NO + O_2 \rightarrow 2NO_2$ (causes brownish haze)

NO_2 + UV light → NO + O followed by:

$O + O_2 \rightarrow O_3$

(O_3 is ozone and is very hazardous to plants, animals, and materials in the troposphere)

NO_2 reacts in complex ways with VOC's to form photochemical smog which is a mix of ozone, nitric acid, aldehydes, peroxyacyl nitrates (PAN's), and other secondary pollutants.

Hydrocarbons and/or VOC's + O_2 + NO_2 → PANs

(Peroxyacyl nitrates cause burning eyes and damage vegetation)

Thermal inversions (temperature inversions)

- Normally temperature decreases as altitude increases. This warm air, which is less dense than the colder air above it can easily rise, dispersing pollutants into the upper atmosphere; allowing pollutants from the surface to be reduced or diluted.
- However, a during a thermal inversion a relatively warm layer of air at mid-altitude covers a layer of cold, dense air below it. The warm layer of air trapped between the two cooler layers is known as an inversion layer.
- Because the air closest to the surface of the Earth is denser than the air above it, the cool air and the pollutants within it do not rise. Thus, the inversion layer traps emissions that then accumulate beneath it, and these trapped emissions can cause a severe pollution event.
- Two types of areas are especially prone susceptible to prolonged temperature inversions: The first is a town or city located in a valley or depression surrounded by mountains that experiences long cold nights during the winter, in which cold air flows down through the valley's and into town creating a ground-level layer of cold air beneath a layer of warm air. Second, is a city in an area with a sunny climate, mountains on three sides and an ocean on the fourth side. In this case, ocean breezes draw cool marine air onshore beneath a mass of warmer air above. Held in place by the mountains that shelter the town, the cool air then stabilizes, unable to rise through the warm air above.
- In towns or cities with either geographic scenario plus, many motor vehicles, heavy industry, and coal-burning power plants, severe pollution events can occur.

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Several factors can decrease or increase outdoor air pollution

- **Outdoor air pollution may be decreased by:**
  1. Settling of particles due to gravity pulls pollutants out of the air.
  2. Rain and snow partially cleanse the air of pollutants.
  3. Salty sea spray from the ocean washes out many pollutants.
  4. Winds sweep pollutants away and mix them with cleaner air (dilution).
  5. Chemical reactions can cause pollutants to precipitate and fall out of the air.
- **Outdoor air pollution may be increased by:**
  1. Urban buildings slow wind speed and reduce dilution and removal of pollutants.
  2. Hills and mountains reduce flow of air in valleys below them and allow pollutant levels to build up at ground level.
  3. High temperatures promote chemical reactions leading to the formation of photochemical smog.
  4. Emissions of VOCs from certain trees and plants in heavily wooded areas can play a large role in formation of photochemical smog.
  5. Grasshopper effect occurs when pollutants are transported at high altitudes from tropical and temperate areas to Polar Regions. Creates a reddish-brown haze over the arctic.
  6. Temperature inversions: warm air above cool air prevents mixing and dilution of pollutants.

Acid Deposition

- Prevailing winds can transport primary pollutants nitrogen oxides (NO and NO_2) and sulfur dioxide (SO_2) 1,000 km or more. While suspended in the atmosphere primary pollutants such as nitrogen oxides (NO and NO_2) and sulfur dioxide (SO_2) react with atmospheric oxygen and water to form secondary pollutants nitric acid (HNO_3) and sulfuric acid (H_2SO_4). These compounds later break down to form nitrate (NO_3^-) and sulfate (SO_4^{2-}) salts or aerosols, as well as, hydrogen ions (H^+) that generate acid deposition.
- All rain is somewhat acidic; the reaction between water and atmospheric carbon dioxide lowers the pH of precipitation from a neutral 7.0 to 5.6. Acid precipitation, formed through the reactions above, is pH 5.6 or lower.
- Acid deposition has regional impact on areas that are downwind of coal-burning power plants. Historically, due to east-to-west prevailing winds in the United States, Midwestern coal-burning power plants emitted large amounts of SO_2, which resulted in acid deposition in the Eastern and Northeastern United States; also mountain forests of the Sierra Nevada, east of Los Angeles, California, have experienced severe acid deposition.
- The worst deposition happens in China, which gets the majority of its energy from coal. The resulting acid precipitation harms crops and is threatening food security in China, Japan, and North and South Korea.
- Human health impact: Acid deposition contributes to human respiratory diseases.
- **Effects of acid deposition**
  - ❖ Aquatic ecosystems: Species can survive and reproduce only within a narrow range of environmental conditions. As pH of an aquatic system lowers due to acid deposition, the environmental conditions may go beyond a species range of tolerance, with respect to pH, and organisms may begin to have developmental or reproductive problems. *Most fish cannot survive with a pH less than 4.5*. Lower pH of lakes and streams of northeastern North America, Scandinavia, and the United Kingdom has caused decreased species diversity of organisms. Solution? Large amounts of limestone or ground lime are used to neutralize some acidified lakes and surrounding soils.

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- Mobilization of metals: Lower pH can lead to the mobilization of metals (such as lead and mercury), in soil and rocks, into surface water, sometimes in lakes used as sources of drinking water. These toxic metals can accumulate in the tissues of fish eaten by people and other animals. Also, acid deposition can release aluminum ions, in soil and rocks, into water, which causes physiological problems such as in fish and other organisms; for example, aluminum ions stimulate excessive mucus formation, clogging fish gills and leading to asphyxiation.
- Harmful effects on plants: Acidic water percolates through soil and leaches essential plant nutrients such as calcium and magnesium making them unavailable to plant roots. Also, as acidic water flows through soil it releases ions (that are usually bound chemically to other compounds in rock and soil) of aluminum, lead, cadmium, and mercury to the soil where they can damage tree roots. These tend to have a weakening effect on plants and trees and hinder growth. In mountain forest, where fog is very common, acidic fog can breakdown the waxy cuticle of a trees leaves or needles. This waxy coating serves as a protective barrier against bacteria, fungus, insect attack, and water loss. It also insulates the tree protecting it from extremes of warm and cold weather. Without this waxy covering trees are much more vulnerable to environmental stress. Finally, photosynthesis may be inhibited.
- Damage to human-built structures: Structures such as statues, monuments, and buildings, are harmed by acid deposition. For example, buildings from ancient Greece such as those on or near the Acropolis have been seriously eroded over the last half-century from acid deposition. The damage happens because acid deposition reacts with building materials. When the hydrogen ion in acid deposition interacts with limestone or marble, the calcium carbonate reacts with H^+ and gives off Ca_2^+. In the process, the calcium carbonate material is partially dissolved. Acid deposition also erodes many exposed painted surfaces, including automobile finishes.
- Buffering capacity: Many forests, streams, and lakes that experience acid rain don't suffer negative effects because the soil in those areas can ***buffer*** the acid rain by neutralizing the acidity in the rainwater flowing through it. This buffering capacity depends on the thickness and composition of the soil and the type of bedrock underneath it. Some soils have a large buffering capacity, such as soils derived from limestone bedrock. Other soils have low buffering capacity, such as soils derived from inert bedrock (granite) and thin soils (common at high elevations). In areas such as mountainous parts of the Northeast United States, the soil is thin and lacks the ability to adequately neutralize the acid in the rainwater. As a result, these areas are particularly vulnerable and the acid and aluminum can accumulate in the soil, streams, or lakes.
- Acid deposition chemistry:

Nitrogen dioxide reacts with water to form nitric acid:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Sulfur dioxide reacts with oxygen to form sulfur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

This then is followed by sulfur trioxide reacting with water to form sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Nitric acid and sulfuric acid dissociate to form nitrate (NO_3^-) and sulfate (SO_4^{2-}) and hydrogen ions (H^+)

$$HNO_3 \rightarrow \text{nitrate } NO_3^- + \text{hydrogen ions } H^+$$

$$H_2SO_4 \rightarrow \text{sulfate } SO_4^{2-} + \text{hydrogen ions } H^+$$

Acid deposition can be neutralized by the addition of calcium carbonate ($CaCO_3$)

$$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$$

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Pollution Control Measures

- As with other types of pollution, the best way to decrease air pollution emissions is to avoid them in the first place; this can be achieved through use of low-sulfur fuels (coal and oil) or to use less fuel through efficiency and conservation. These measures reduce emissions, but pollution is still emitted.
- Air pollution control focuses on control of air pollutants after combustion.
- **Control of sulfur and nitrogen oxides**:
  - Fluidized bed combustion: Burning granulated coal in close proximity to calcium carbonate can reduce Sulfur dioxide emissions from coal exhaust. The heated calcium carbonate absorbs sulfur dioxide and produces calcium sulfate, which can be used in the production of gypsum wallboard, sheetrock.
  - Reducing and controlling combustion temperatures: The atmosphere is 78 percent nitrogen gas and, as a result, nitrogen oxides are produced in virtually all combustion reactions. Hotter burning conditions in the presence of oxygen allow proportionally more nitrogen oxide to be generated per unit of fuel burned. Lowering and controlling burn temperatures is a procedure use in some power plants and industrial facilities. However, lowering temperatures can result in less-complete combustion, which reduces efficiency and increases particulates and carbon monoxide, plus more fuel must be burned to generate the desired level of power. Improving and refining combustion technology by finding the exact mix of air, temperature, oxygen, & other factors can xincrease efficiency and reduce nitrogen oxide emissions.
  - Catalytic converters:
    - A device attached to the exhaust system of an automobile engine to eliminate or substantially reduce polluting emissions. It consists of a stainless steel box attached to the muffler and containing ceramic materials coated with catalysts materials and various sensors that regulate the fuel and air passing through the engine.
    - It converts three harmful substances into harmless ones:
      1) *Carbon monoxide* (a poisonous gas) into carbon dioxide,
      2) *Nitrogen oxides* (cause acid rain and smog) into nitrogen and oxygen,
      3) *Unburned hydrocarbons* (cause smog & respiratory problems) into carbon dioxide and water.
    - Beginning in 1975 all automobiles sold in the United States were required to include a catalytic converter. To operate, catalytic converters use precious metals, platinum and palladium, which cannot be exposed to lead. Therefore gasoline could no longer contain lead, helping to significantly reduce atmospheric lead concentrations.

Control of particulate matter

- Sometimes the process of removing particulate matter also removes sulfur.
- Gravitational settling: As exhaust travels through a smokestack, particles settle out to the bottom. Depending on the materials burned, the ash residue that accumulates on the bottom may be disposed of in a landfill, or if they contain sufficiently high concentrations of metals, may require special disposal as hazardous waste.
- Fabric filters: Often called baghouse filters, allow gases to pass through them but remove particulate matter. Some baghouse filters can remove 100 percent of particulate emissions.
- Electrostatic precipitators: Electrostatic precipitators use an electric charge to make particles coalesce so they can be removed. Polluted air enters the precipitator and the electrically charged particles within are attracted to negative or positive charges on the sides of the precipitator. The particles collect and relatively clean gas exits the precipitator.
- Scrubbers: Scrubbers use a combination of water and air that actually separates and removes particles. Particles are removed in a liquid or sludge form and clean gas exits.
  - Borrowing from the concept utilized in the electrostatic precipitator, particles are sometimes ionized before entering the scrubber to increase its efficiency.

The electrostatic precipitator and the scrubber have significantly reduced air pollution.

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Smog reduction

- Control efforts are largely directed towards reducing the precursors of smog a.k.a. primary pollutants.
- Reducing nitrogen oxide emissions: The main component of photochemical smog, ozone, is a secondary pollutant formed when UV radiation decomposes nitrogen dioxide, releasing a single oxygen atom to bond with diatomic oxygen to form ozone. Reducing nitrogen oxide emissions is an effective way to control smog; encouraging alternative modes of transportation such as public transit, carpooling, or bicycling can achieve this.
- Reducing VOC's: With fewer VOC's in the air there are fewer compounds to react with nitrogen oxides, and thus more nitrogen oxide, will be available to recombine with ozone.

Innovative and controversial pollution control methods

- To reduce VOC's municipalities have:
  - Passed measures to reduce the amount of gasoline spilled at gas stations;
  - Restricted the use of dry-cleaning fluids to prevent evaporation;
  - Restricted the use of lighter fluid to light charcoal barbecues;
  - Discussed reducing the number of bakeries in one area;
  - Implemented tighter restrictions on leaky natural gas drilling operations and wells.
- Wood burning restrictions: To reduce a variety of are pollutants municipalities have called for action to reduce the use of wood burning stove, fireplaces, and open fires t reduce emissions of nitrogen oxide, particulates, carbon monoxide, and VOC's.
- Restrictions automobile use to reduce nitrogen oxides and VOC's:
  - Driving every other day: for example, license plates ending with odd numbers may be used on one day and those with even-numbered on alternated days.
  - Temporarily shutting down industries when pollution is at hazardous levels.
  - Carpool lanes available in many areas, reduce the number of cars on the road by encouraging two or more people to share one vehicle.
  - Improving the quality and accessibility of public transportation.
  - Charging tolls on congested roads to reduce traffic.
  - Raise fuel-efficiency for cars, SUVs, and light trucks.

Clean Air Act Amendments 1990 & 1995

- *The Acid Rain Program* was created under Title IV of the 1990 Clean Air Act Amendments to reduce the adverse effects of acid deposition through reductions in annual emissions of $S0_2$/NOx.
- Market-based cap and trade program: The buying and selling of allowances that authorized the owner to release a certain quantity of sulfur. Each allowance authorizes a power plant to or industrial source to emit one tone of SO_2 per year.
  - Sulfur allowances are awarded annually to existing sulfur emitters proportional to the amount they emitted before 1990, and the emitters are not allowed to emit more sulfur than the amount for which they have permits.
  - End of the year, the emitter must possess the amount of allowances equal to its emissions. Example, a facility that emits 1,000 tons of SO_2 must possess at least 1,000 allowances that are usable that year. Facilities that emit quantities of SO_2 above their allowances must pay a financial penalty.
  - Sulfur allowances can be bought and sold on the open market by anyone. If emitters wanted to exceed their allowance level they would be required to purchase more allowances from another source. If a company decreased its sulfur emissions, it could sell unused sulfur emission allowances.
  - The total SO_2 emissions from all sources declined from 23.5 million metric tons in 1982 to 10.3 million metric tons in 2008.
  - NOx reductions under the Acid Rain Program are achieved through a program closer to a more traditional, rate-based regulatory system.

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- National Emission Standards for Hazardous Air Pollutants (NESHAP's):
  - Stationary source standards for hazardous air pollutants (HAPs). HAP's are those pollutants that may cause serious health problems—are known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects—or adverse ecological effects.
  - Most of these chemicals are chlorinated hydrocarbons, volatile organic compounds, or compounds of toxic metals.
  - Toxic Release Inventory (TRI): An important public source of information about HAP's is the Toxic Release Inventory (TRI). The TRI passed requires about 21,000 refineries, power plants, mines, chemical manufacturers, and factories to report their releases and waste management methods for 667 different chemicals (passed in 1990 as part of the Pollution Prevention Act).

Indoor Air Pollution

- Although it receives less attention than outdoor air pollution, indoor air pollution is a hazard all over the world. The reasons for indoor air pollution and its characteristics differ between the developing and the developed world.
- **Developing countries**
  - Throughout the developing world people use biomass fuel, such as wood, animal manure, and charcoal, to heat their homes and cook food.
  - Often, there is no exhaust or little to no ventilation available in the home, which makes carbon monoxide and particulate matter a serious health hazard.
  - This increases the risk of acute respiratory infections, pneumonia, bronchitis, and even cancer.
  - The World Health Organization estimates that indoor air pollution is responsible for 4 million deaths annually worldwide, 50 percent of those are of children less than five years old; ninety percent of the 4 million deaths are in developing countries.
- **Developed countries**
  - In recent decades much of the developed world has begun to spend much more time indoors. Additionally, while improved insulation and tightly sealed buildings improve energy efficiency, these tightly sealed buildings also keep existing air in contact with the inhabitants of the home, office, or building.
  - An increasing number of materials are made from plastics and other petroleum-based materials that can give off vapors. Since most homes and other structures are tightly sealed, they become closed systems in which indoor air pollutants can accumulate and inhabitants come into regular contact with harmful substances.
  - VOC's in home products:
    - Volatile organic compounds (VOC's) are emitted as gases from certain solids or liquids. VOC's include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOC's are consistently higher indoors (up to ten times higher) than outdoors. VOC's are emitted by a wide array of products numbering in the thousands.
    - Many volatile organic compounds are used in building materials, furniture, and other home products such as glues and paints.

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- **Formaldehyde**: One of the most toxic compounds used in building materials, furniture, and other home products such as particleboard and carpeting glue, is formaldehyde.
  - Formaldehyde is common in new homes and new products made from pressed wood, such as cabinets. The pungent smell that you may have noticed in a new home or one with new carpeting comes from formaldehyde, which is volatile and emits gases over time.
  - A high enough concentration in a confined space can cause burning of the eyes and throat and breathing difficulties and asthma in some people.
  - Formaldehyde has been shown to cause cancer in laboratory animals and has recently been suspected of being a human carcinogen.
- Many other consumer products such as detergents, dry-cleaning fluids, deodorizers, and solvents may contain VOC's and can be harmful if inhaled. Plastics, fabrics, construction materials, and carpets may also release VOC's over time.
- **Sources of VOCs**
  - Household products, including:
    - paints, paint strippers and other solvents
    - wood preservatives
    - aerosol sprays
    - cleansers and disinfectants
    - moth repellents and air fresheners
    - stored fuels and automotive products
    - hobby supplies
    - dry-cleaned clothing
    - pesticide
  - Other products, including:
    - building materials and furnishings
    - office equipment such as copiers and printers, correction fluids and carbonless copy paper
    - graphics and craft materials including glues and adhesives, permanent markers and photographic solutions.

- **Sick building syndrome:** A buildup of toxic pollutants in an airtight space, seen in newer buildings.
  - In newer well-insulated, airtight buildings where many new products contain synthetic materials, a significant amount of off-gassing occurs. This can result in high indoor levels of VOC's, hydrocarbons, and other potentially quite toxic materials. This often occurs in new office buildings and workers report headaches, nausea, throat or eye irritations, and fatigue.
- **Carbon monoxide**
  - When the exhaust system of a household heating system malfunctions, typically a natural gas furnace, exhaust air escapes into the living space, rather than out the flue pipe in the roof.
  - Odorless carbon monoxide can buildup in a house without the occupants knowing, particularly while they are asleep.
  - In the body, carbon monoxide binds with hemoglobin more efficiently than oxygen, thereby interfering with oxygen transport in the blood; Extended exposure to high concentration carbon monoxide in air can lead to oxygen deprivation in the brain and, ultimately, death.

- **Asbestos:** Asbestos is a long, thin, fibrous silicate mineral with insulating properties.
  - Asbestos causes respiratory diseases such as mesothelioma, asbestosis, and lung cancer.
  - Asbestos was used as an insulating material until the 1970's and 1980's when it was phased out due to health concerns.
  - When intact asbestos materials do not pose an immediate health risk. However, when disturbed, fibers can enter the air and pose a significant health threat.
  - Buildings with remaining asbestos materials must have asbestos removed by qualified professionals.
- **Radon:** Radon-222, is a radioactive gas that occurs naturally from the decay of uranium, that exists in granitic and some other rocks and soils.
  - Humans can receive significant exposure to radon if it seeps into a home through cracks in the foundation, from underlying rock, soil, or groundwater.
  - Radon decays in four days into a radioactive daughter product, Polonium-210. Either Radon or Polonium can attach to dust and other particles in the air and then be inhaled by the inhabitants of the home.
  - 21,000 people die annually from radon-induced lung cancer; 15% of annual lung cancer deaths.
  - High Radon levels can be reduced to safe levels through active ventilation systems. In homes with high radon levels pumps can be installed in basements that pump air from the foundation out through the roof where it disperses into the atmosphere and poses no health risk. It is also important to seal cracks in basement floors to stop the seepage of radon into the home.

Air pollution is a global problem

- Since the atmosphere envelops the entire globe we must think of the air pollution as a global system.
- Annual satellite images have found massive, dark brown clouds of pollution—called the South Asian Brown Cloud—stretching across much of India, Bangladesh, and the industrial heart of China as well as parts of the Western Pacific Ocean.
- The clouds reflect light back to space, changing weather patterns (decreased rainfall in the north and flooding in the south) and inhibiting photosynthesis affecting food production in parts of Asia.
- The soot is even darkening glaciers of the Himalaya Mountains, a crucial water reservoir for Asia, the darker surface in turn decreases albedo and increases absorption of sunlight, causing the glaciers to melt faster.
- The clouds contain small particles of dust, smoke, and ash resulting from clearing and burning forest to plant crops. They also contain particles of soot (mostly from burning biomass such as wood and animal manure); acidic compounds from vehicle exhaust (much of it from diesel exhaust) and from emissions from coal-burning power plants; particles of toxic metals such as mercury and lead, produced mostly by coal burning facilities, smelters, and waste incinerators.
- Scientists have tracked the movement of these massive clouds of pollution from northern China across the Pacific Ocean to the west coast of the United States.
- The United States Environmental Protection Agency estimates that, on certain days, nearly 25% of the particulate matter, 77% of the black carbon (soot), and 33% of the toxic mercury in the skies above Los Angeles, California can be traced to China's coal-fired power plants, smelters, wood and dung fires, diesel trucks, and dust storms blowing out of drought stricken deforested areas.
- In recent years air pollution in Asia has been responsible for acidic deposition and forest damage on the West Coast of the United States.
- In fact, mercury levels in rainfall are rising in Rocky Mountain, and West Coast regions. This is due to increased emissions of mercury from coal-burning power plants in Asia that are transported over long distances in the upper atmosphere. The influence of the Sierra Nevada and Rocky Mountains on weather systems results in mercury from the upper atmosphere being deposited in precipitation in western states.

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Air Pollution is worse in developing countries

- There are fewer restrictions on air pollution in developing countries. This is due, in large part, to their industrial growth and economic growth.
- As a result air pollution remains a significant environmental problem in the developing world.
- Shanghai and Beijing, China as well as Delhi, India are among the most polluted cities in the world.

Air Pollution Is a Big Killer

- According to the World Health Organization 2.4 million deaths per year worldwide are attributed to the effects of air pollution.
- These are mostly in Asia, with about 750,000 in China. Although, 150,000 to 350,000 are in the United States, mostly in urban areas. These are mostly due to pollution from coal-burning power plants; diesel trucks play a role as well.