The Atmosphere

- Nitrogen
- Oxygen
- Ar, Ne, He, Kr, H₂
- Water vapor
- CO₂, CH₄, CO, NO, O₃
- NH₃, SO₂
Temperature of the atmosphere
• normally, air cools with increased altitude
• with an inversion, air warms with increased altitude and normal buoyancy flow ceases, air stagnates
• inversions are caused by:
  1. radiation inversion (usually nocturnal)
  2. subsidence inversion
  3. natural terrain obstructions
Inversion refers to an abnormal temperature profile in the atmosphere that inhibits the flow of air over a land mass.

- Normal lapse rate: $-6.5 \text{ deg C/km}$
- Dry adiabatic lapse rate: $-10 \text{ deg C/km}$
- Environmental lapse rate: $-6.5 \text{ deg C/km}$

Subsidence inversion layer
Major Pollutants

- **Carbon monoxide** - produced by the incomplete burning of carbon-containing fuels.

- **Nitrogen oxides** - produced by petrol- or diesel-burning engines and coal/oil furnaces. Diesel engines produce much less carbon monoxide but a lot more nitrogen oxides than engines.

- **Hydrocarbons** - formed from the evaporation of materials such as petrol, diesel and solvents when exposed to air. They can also be found in car exhaust as unburned hydrocarbons.

- **Particulates** - produced by refuse incineration, factories, diesel vehicles, construction sites, and coal/charcoal burners. Particulates are solid or liquid particles which are so small that they remain suspended in the air for a long period of time. Particles in mass appear as smoke or haze.

- **Sulfur dioxide** - produced by burning fossil fuels. A large proportion is produced by power stations and metal smelters which burn sulfur containing coal, and also by the manufacturing industries which burn fuel oil.
Photochemical Smog

\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \]

\[ \text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{other products} \]

\[ \text{NO}_2 + \text{sunlight} \rightarrow \text{NO} + \text{O} \]
\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]

\[ \text{NO}_2 + \text{R} \rightarrow \text{products such as peroxycetyl nitrate (PAN)} \]

container of nitrogen oxide induced smog in the laboratory.
• 1952 - London, England, 4000 deaths
• 1950’s and 1960’s - Los Angeles and New York resulted in the Clean Air Act of 1963 and the creation of EPA
• capillary dilation, hemorrhaging, purulent bronchitis, edema
• corrosion of metal, soiling of buildings, degradation of paints, leather, paper, etc.
- 1963 Clean Air Act establishes government intervention
- 1965 Amendment setting emission standards for vehicles in 1968
  - established 6 pollutant levels
  - gave rights to Americans to sue private and public government entities
- 1989 Clean Air Act Amendment regulates ozone depleting chemicals
- Kyoto Protocol
History of U.S. Standards

automobile

heavy duty
Sources of Air Pollution

- Engines
  - Gasoline, or Spark Ignited, SI (Otto Cycle)
  - Diesel, or Compression Ignited, CI (Diesel Cycle)
- Stationary Sources
  - Incineration (burning, combustion)
  - Electrical Power Generation
- Other Discharges
Internal Combustion Engines
1. performance
2. emissions

- mixture preparation
- intake tuning
- combustion, autoignition
- exhaust tuning
- wear
- inertia
- lubrication
- C_{x}H_{x}
- CO
- NO_{x}
- emissions
Exhaust Emissions

Gasoline Engines
- CO
- NO\textsubscript{x}
- CH\textsubscript{x}

Diesel Engines
- NO\textsubscript{x}
- CH\textsubscript{x}
- soot

Exhaust Emissions
Catalytic converters on motor vehicle exhausts are either platinum or a combination of platinum and rhodium.

In the presence of a platinum surface...

Unburned fuel + O2 -> CO2 + H2O

In the presence of a rhodium surface...

2CO + 2NO -> 2CO₂ + N₂

The reduction of nitric oxide (NO) to nitrogen gas (N₂) must proceed more quickly than the oxidation of carbon monoxide (CO) to carbon dioxide (CO₂) or else all the carbon monoxide will be oxidized to carbon dioxide before it can be used to reduce the nitric oxide.
• Closed crankcase and gasoline tank ventilation
• Precise fuel flow with electronic (digital) injection
• Controlled production of $\text{CH}_x$, $\text{CO}$, and $\text{NO}_x$ throughout the useable speed-load range of the engine
• Use of a 3 way catalyst

Control of Gasoline Engine Emissions
Precise control air/fuel ratio at engine leads to appropriate ratio of $\text{CH}_x$ and NO in the exhaust for operation of the three way catalyst.

A three way catalyst will reduce concentrations of NO, CO and $\text{CH}_x$ in the exhaust to negligible amounts.
Particulate Emissions

- Composed of agglomerated carbon spherules
- Formed primarily in diesel engines most probably from PAH (poly aromatic hydrocarbons) present in the bulk gases
- Provide nucleation sites for hydrocarbon condensation in the ‘exhaust stream’
- Smaller diameter particles may be harmful
- Treated with engine design (turbochargers) and trap filtration
Control of Diesel Engine Emissions

- 3 way catalysis does not work in the presence of particulate matter; the unit will plug easily
- Carbon filtration must be used; filters must be either changed at regular intervals (cumbersome) or regenerative (the carbon particles are burned off during regeneration)
- $\text{NO}_x$ must be treated with a urea system
- CO is not a problem with Diesel engines
• The system, urea SCR or "urea-based selective catalytic reduction," is the only technology available that can remove enough NOx from diesel exhaust to comply with strict new limits imposed by the U.S. Environmental Protection Agency (EPA).

• The automotive urea, called "diesel exhaust fluid" (DEF) in the United States and AdBlue, a trademarked name in Europe, reduces NOx by as much as 90% alone, and can take NOx to near-zero levels when used in combination with diesel particulate filter technology.

• DEF and AdBlue are an aqueous urea solution of high-purity urea in demineralized water. The urea solutions are safe to handle, manufacturers claim. AdBlue can be bought in bulk in Europe or by the liter at some service stations.
Urea tanks are standard equipment for most new diesel trucks, buses, cars, and sport utility vehicles (SUVs) manufactured in the United States after Jan. 1, 2010. An automotive grade of urea is injected into the vehicles' exhaust stream to "scrub" nitrogen oxide (NOx) from the diesel exhaust.

Consumption of the urea solution is about 3% of the diesel consumption. Diesel trucks average 6.5 miles per gallon (2.8 km/liter). An average diesel truck will need to refill its 20-gallon tank of DEF every 4,000 to 6,000 miles (76 liters every 6,400 to 9,600 km).

Diesel Engine Aftertreatment: How Ford Knocks Out the NOx

Ford's new 6.7-liter Power Stroke® V8 turbocharged diesel engine employs a multifaceted aftertreatment process to meet federal emissions standards that call for a reduction of nitrogen oxide (NOx) levels by more than 80 percent compared with previous regulations. Ford’s solution incorporates industry-proven technology, world-class supply partners and Ford-developed strategies to create an efficient, seamless system.
DEF Replenishment Facts

The Ford system is designed so that DEF is replenished approximately every 7,500 miles, depending on customer use. The message center will alert the customer if the DEF needs to be replenished. The first message comes when the customer has about 800 miles worth of DEF remaining. The fill nozzle for the DEF is located next to the fuel cap. It has a blue cap. Ford-approved DEF will be available in 1- and 2-1/2-gallon bottles with nozzles and can be purchased from Ford dealers and other retailers.
Step One: Cleaning and Heating
The first step in cleaning the diesel exhaust occurs when the exhaust stream enters the Diesel Oxidation Catalyst (DOC). The role of the DOC is twofold. First, it converts and oxidizes hydrocarbons — at about 250 degrees Celsius — into water and carbon dioxide. Second, the DOC is used to provide and promote heat, using specific engine management strategies, into the exhaust system. Through appropriate thermal management, this heat increases the conversion efficiency of the downstream subsystem in reducing emissions.

Step Two: Knocking Out the NO\textsubscript{x}
The second step in the process is known as Selective Catalytic Reduction (SCR). In this process, the NO\textsubscript{x} in the exhaust stream is converted into water and inert nitrogen, which is present in the atmosphere and harmless. Before the exhaust gas enters the SCR chamber, it is dosed with Diesel Exhaust Fluid (DEF), also known as urea, an aqueous solution that is approximately 67.5 percent water and 32.5 percent pure urea.

When heated, the DEF splits into ammonia and carbon dioxide. These molecules are atomized, broken up and vaporized, then enter a mixer that resembles a corkscrew. This twist mixer evenly distributes the ammonia within the exhaust flow. The ammonia enters the SCR module, which contains a catalyzed substrate, and through chemical reactions combines and converts the NO\textsubscript{x} and ammonia into the harmless inert nitrogen and water. Dosing typically occurs between 200 and 500 degrees Celsius.

Step Three: Scrubbing Away the Soot
The final step of the cleansing system for the diesel exhaust gas involves the Diesel Particulate Filter (DPF). The DPF traps any remaining soot, which is then periodically burned away, known as regenerating, when sensors detect the trap is full. The regeneration process sees temperatures in excess of 600 degrees Celsius to burn away soot.
Combustion of fuels and materials from stationary sources represent a significant source of noxious exhaust emissions (hence, air pollution).

The major pollutants are particulates, nitrous oxides, and sulfur dioxide.

Particulates are mostly ‘fly ash’ or airborne ash particles of incombustible material. Fly ash is removed by electrostatic precipitators.

Nitrous oxides are removed by a large SCR system similar to that used in the transportation industry.

Sulfur dioxide is removed with the addition of lime.
Typical Powerplant Aftertreatment
Unpolluted rain water is slightly acidic owing to the presence of carbon dioxide in the air. Its pH is at 5.7. Therefore, rain water with pH values lower than 5.7 is called acid rain. In some parts of the world pH as low as 2.5 in rainwater has been recorded.

**Animals:** When pH is less than 4.5, calcium metabolism in fresh water fish will be affected, leading to poor health and stunted growth. As a result, diversity and population of some fish species will be reduced.

**Plants:** Acid rain washes away essential nutrients that the plants are in need. In addition, it makes the soil acidic and aids the release of aluminum and copper ions which are harmful to plants.

**Structures:** Acid rain will cause damage to common building materials (such as limestone and marble), statues and monuments. Many metals will become oxidized. Iron corrodes with the presence of acid rain to form rust.
• CO₂ is a naturally occurring gas in the atmosphere
• CO₂ is also a product of aerobic decay
• CO₂ is also a product of combustion (oil, natural gas, coal, wood, anything that burns)
• It is debatable whether man-made CO₂ is a significant component of increasing CO₂ presence in the atmosphere
Summary

- The Atmosphere and Weather
- Major Pollutants and Photochemical Smog
- History and Regulation in the U.S.
- Sources of Pollutants
- Internal Combustion Engines and Catalysis
- Stationary Sources and Acid Rain
- Ozone, and CO²