This material is for reference only. Points present in the slides are only for assistance and their elaboration are present in book. Examination questions will be in depth and can be solved by following text book only.

Tropospheric Chemistry

- Unit-2

Environmental Studies, 2e

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Concentration Units for Atmospheric Pollutants

There is no consensus regarding the appropriate units by which to express concentrations of substances in air. Generally ratios involving numbers of molecules — the "parts per" system — were emphasized as a measure.

Other measures are often also encountered, and will be used in this chapter: Important are

a) Molecules of a gas per cubic centimeter of air

b) Micrograms of a substance per cubic meter of air, µg/m3

c) Moles of a gas per liter of air, moles/L

- Partial pressure of a gas is synonymous to "parts per" scale e.g. 0.002 atm is equivalent to 2000 ppm.

Concentrations and Other Units of Measure

The concentration of a substance is the “amount” of it per “amount” of containing material (air, water, soil).
It can be expressed in various units.
If the containing medium is air for example:

It can be expressed in various units.
If the containing medium is air for example:

C_A = mass of A / volume of air	used with mass balances
$[A]$ = moles of A / volume of air	used with chemical reactions
X_A = mass of A / mass of air	used when air pressure varies
Y_A = moles of A / moles of air	occasionally handy
P_A = partial pressure of A (compared to atmospheric pressure)	used for air-water exchange

The Interconversion of Gas Concentrations

Unit conversion

It is often necessary to switch units, for example,
to pass from a chemical reaction
(in which amounts are most naturally expressed in moles)
to a mass budget
(in which amounts are most naturally expressed in grams).

Rule 1:

Mass in grams = Molecular weight x Number of moles

where

Molecular weight = Σ Atomic weights

Examples:

H_2O: MW = 2x1 + 1x16 = 2 + 16 = 18 grams per mole
CO_2: MW = 1x12 + 2x16 = 12 + 32 = 44 grams per mole
H_2SO_4: MW = 2x1 + 1x32 + 4x16 = 2 + 32 + 64 = 98 grams per mole

Rule 2:

Pressure of a gas is determined from the ideal-gas law

$$\boxed{P_A V = n_A RT}$$

where P_A = partial pressure of A, in atm (atmosphere)
V = volume occupied, in m^3 (entire volume, even if shared with other gases)
n_A = number of moles of A in that volume
R = universal constant
= 8.205×10^{-5} atm • m^3 / (mol • K) = 8.314 J / (mol • K)
T = absolute temperature, in degrees Kelvin (K)

Recall:
Absolute temperature (K) = temperature in degrees Celsius (°C) + 273.15

When several gases occupy a common volume in a mixture, their partial pressures simply add up to the total pressure, which is usually the atmospheric pressure:

$$P_{atm} = P_{\text{total}} = P_A + P_B + P_C + \ldots = (n_A + n_B + n_C + \ldots)\frac{RT}{V}$$

shared temperature

shared volume

Properties of air

Apply ideal-gas law to air.
At standard pressure (P = 1 atm) and temperature (T = 15ºC = 288.15 K), one mole (n = 1 mol) of air occupies a volume V equal to

$$V = \frac{nRT}{P} = \frac{(1\,\text{mol})(8.205\times10^{-5}\,\text{atm}\cdot\text{m}^3/\text{mol K})(288.15\,\text{K})}{(1\,\text{atm})}$$

$$= 0.02364\,\text{m}^3 = 23.64\,\text{L (liters)} = 6.25\,\text{gallons}$$

Also,

Air = mixture of 79% nitrogen + 21% oxygen

$$\begin{aligned} MW_{air} &= (0.79)\,MW_{nitrogen} + (0.21)\,MW_{oxygen} \\ &= (0.79)(2 \times 14) + (0.21)(2 \times 16) \\ &= 22.12 + 6.72 = 28.84 \text{ grams per mole} \end{aligned}$$

Actually, the value is **28.95 g/mol** because of CO_2 and rare gases (heavier).

Central to conversion between different gas concentrations is PV = nRT

2ppm of a gas means:

- there are 2 gas molecules for every 1 million molecules of air
- there are 2 moles of gas for every 1 million moles of gas
- 2×10^{-6} atm partial pressure of gas for 1 atm total air pressure

Example: Assuming a temperature of 25 °C, and a pressure of 1 atm; Convert 2 ppm to molecules/cm^3

Since molecules of air = 1000, 000, can convert this to a volume using PV = nRT

Using Avogadro's number can determine moles of air

$$1000,000 \times \frac{1mol}{6.023 \times 10^{23}} = 1.66 \times 10^{-18} mols$$

Rearrange the ideal gas equation to solve for the volume

$$V = \frac{nRT}{P} = \frac{1.66 \times 10^{18} mols \times 0.0821 L\ atm\ mol^{-1}\ K^{-1} \times 298K}{1.0\ atm} = 4.06 \times 10^{-17} L$$

Convert from L to cm^3: **4.06×10^{-14} cm^3**

Thus there are 2 molecules in **4.06×10^{-14} cm^3**

Properties of water

Water is a liquid, which may be considered as incompressible in all environmental applications.

Numbers for water are:

$H_2O \rightarrow$ MW = 2x1 + 1x16 = 18 $\rightarrow$ **18.0 g/mol**

Density = **997 g/L** (Think: 1 kg per liter)

Combine the above:

(997 g/L) / (18.0 g/mol) = **55.4 mol/L**

Summary of unit conversion

1 mole weighs **MW** grams and occupies **V** liters

$$
\begin{tikzcd}
\textbf{moles} \arrow[rr, "\mathbf{MW}"] \arrow[dr, "\mathbf{V}"'] & & \textbf{grams} \\
& \textbf{liters} \arrow[ur, "\mathbf{MW/V}"'] &
\end{tikzcd}
$$

moles to grams: multiply by **MW**

moles to liters: multiply by **V**

liters to grams: multiply by **MW/V** if gas; use density if liquid

SMOG

Formation of Photochemical Smog

- The term smog was derived from the words 'fog' and 'smoke'. The term was first used in 1905 by H.A. Des Voeux.
- VOCs and NOx react in presence of sunlight to produce ozone and PAN (peroxy acetyl nitrate)
- breathing ozone results in respiratory distress, headaches.
- In 1952 the London smog incident killed 6, 500 people .
- In 1963, New York City smog incident killed 400 people.

Photochemical smog ??

Noxious mixture of highly reactive and oxidizing air pollutants including:

- Oxides of Nitrogen (NO_x)
- Volatile organic compounds
- Troposphere Ozone
- Peroxyacetyl Nitrates (PAN)

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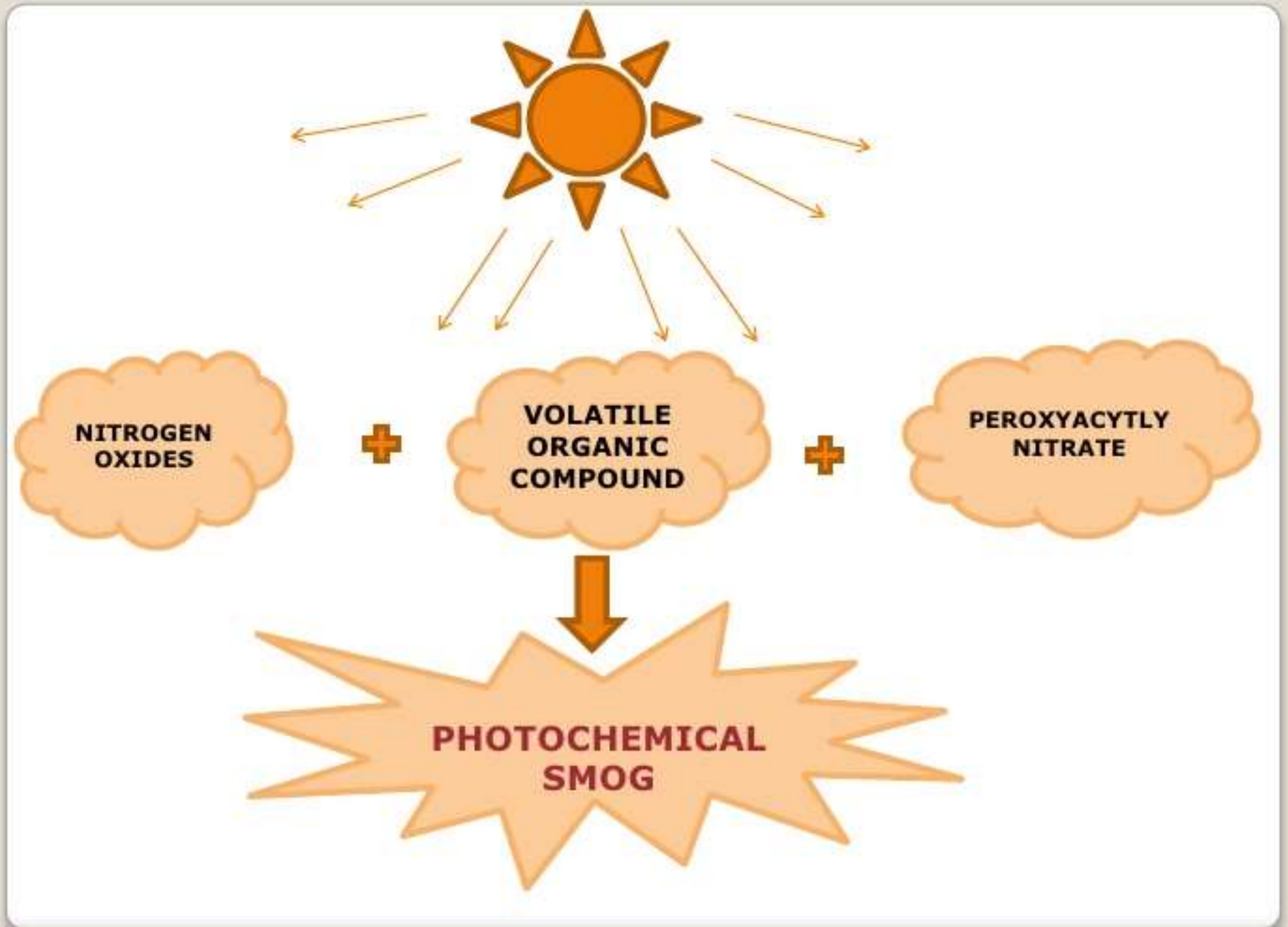

NITROGEN OXIDES
VOLATILE ORGANIC COMPOUND
PEROXYACYTLY NITRATE
PHOTOCHEMICAL SMOG

Urban Ozone: The Photochemical Smog Process

Smog: Resulting from smoke and fog, a type of air pollution.
The photochemical smog phenomenon was first observed in Los Angeles in the 1940s

The chemical fate of Trace gases in Clean Air

TABLE 3-1 Some Important Gases Emitted into the Atmosphere from Natural Sources

Formula	Name	Main Natural Source	Atmospheric Lifetime
NH_3	Ammonia	Anaerobic biological decay	Days
H_2S	Hydrogen sulfide	Anaerobic biological decay	Days
HCl	Hydrogen chloride	Anaerobic biological decay, volcanoes	
SO_2	Sulfur dioxide	Volcanoes	Days
NO	Nitric oxide	Lightning	Days
CO	Carbon monoxide	Fires; CH_4 oxidation	Months
CH_4	Methane	Anaerobic biological decay	Years
CH_3Cl	Methyl chloride	Oceans	Years
CH_3Br	Methyl bromide	Oceans	Years
CH_3I	Methyl iodide	Oceans	

$$\text{VOCs} + \text{NO} + O_2 + \text{sunlight} \longrightarrow \longrightarrow \text{mixture of } O_3,\ HNO_3,\ \text{organics}$$

Primary pollutants **Secondary pollutants**

VOC's : Volatile Organic compounds, coming from petroleum, chemical industries and laboratories. Some are naturally occurring.

Formation of nitric oxide (Unnatural): **Fuel NO** and **Thermal NO**

Nitrogen contained in fuels is converted to NO **Fuel NO**

$$N_2 + O_2 \xrightarrow{\text{hot flame}} 2\ NO$$ **Thermal NO**

NO produced in such a way undergoes oxidation reaction to give NO_2, Combination of nitrogen oxides is called NOX.

The brown color of the smog results from absorption of visible light by NO_2 molecule.

NOX are also generated naturally during lightening and from some biological sources.

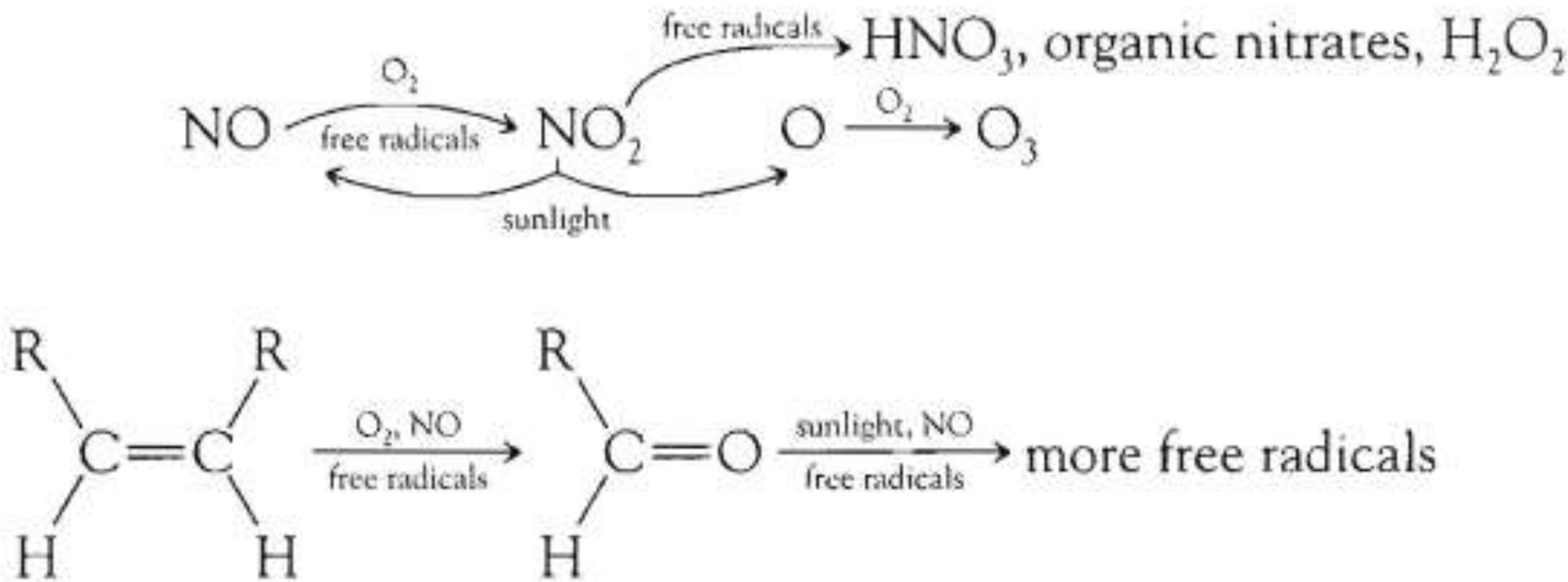
$$VOCs + NO + O_2 + \text{sunlight} \longrightarrow \longrightarrow \text{mixture of } O_3, HNO_3, \text{organics}$$

In order to generate photochemical smog:

- Presence of sufficient vehicular traffic to generate NO, reactive hydrocarbons and VOC's
- Availability of sunlight.
- Little movement of air mass.

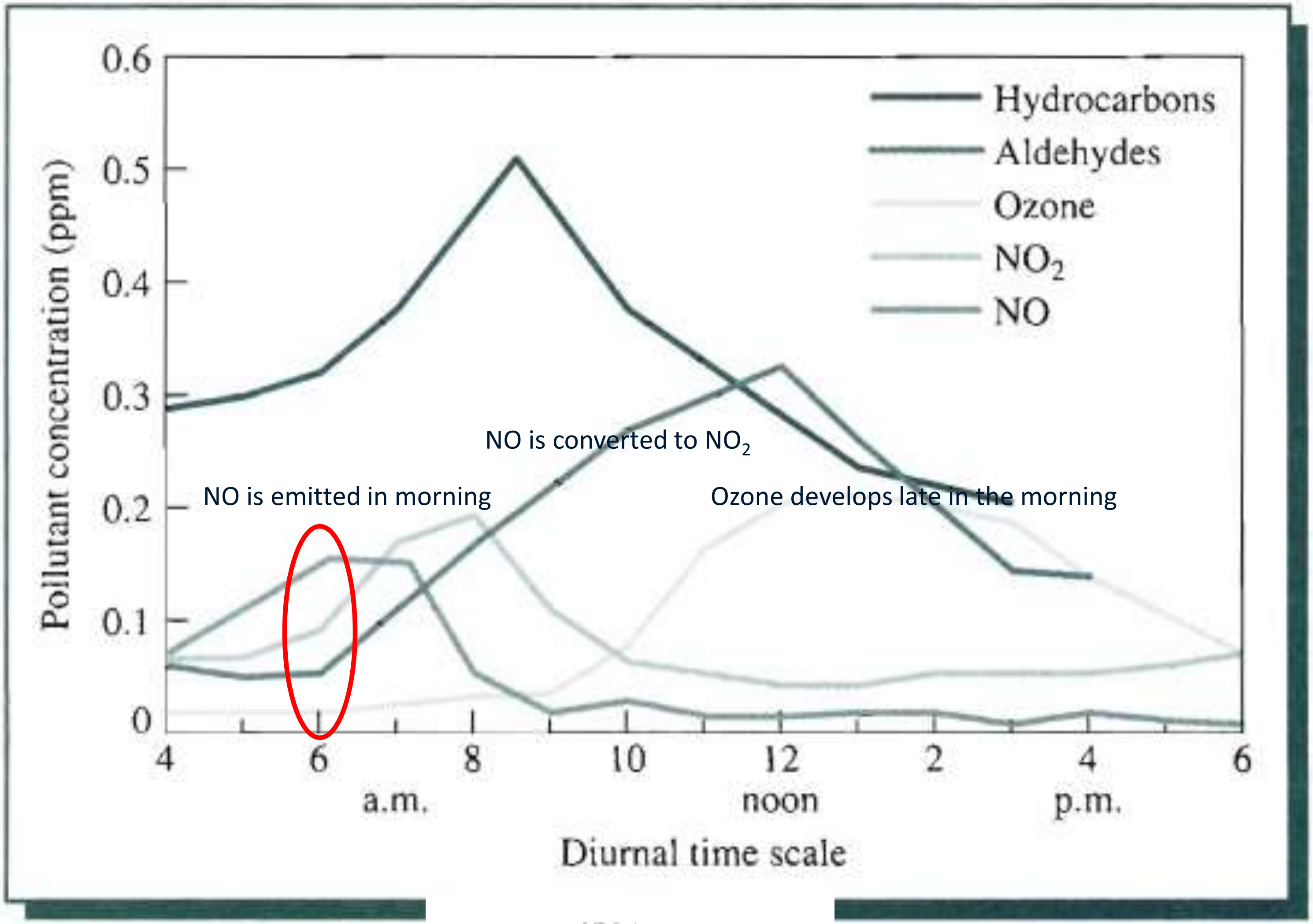
$$NO_2 \xrightarrow{\text{UV-A}} NO + O$$

$$O + O_2 \longrightarrow O_3$$



an ethene derivative

an aldehyde



$$NO_2 \xrightarrow{\text{UV-A}} NO + O$$

$$O + O_2 \longrightarrow O_3$$

Morning time:

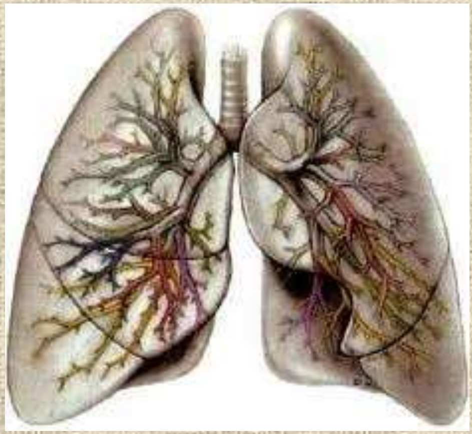
$$NO + O_3 \longrightarrow NO_2 + O_2$$

Effects of smog on health

Responsible for the respiration diseases like: emphysema, bronchitis, and asthma

It can inflame breathing passages, decrease the lungs' working capacity, cause shortness of breath, pain when inhaling deeply, wheezing, and coughing.

It can cause eye and nose irritation and it dries out the protective membranes of the nose and throat and interferes with the body's ability to fight infection, increasing susceptibility to illness.



Limiting VOC

- Natural sources and Anthropogenic
- Reducing the evaporation of gasoline
- Limiting use of household aerosols, oil based paints etc.

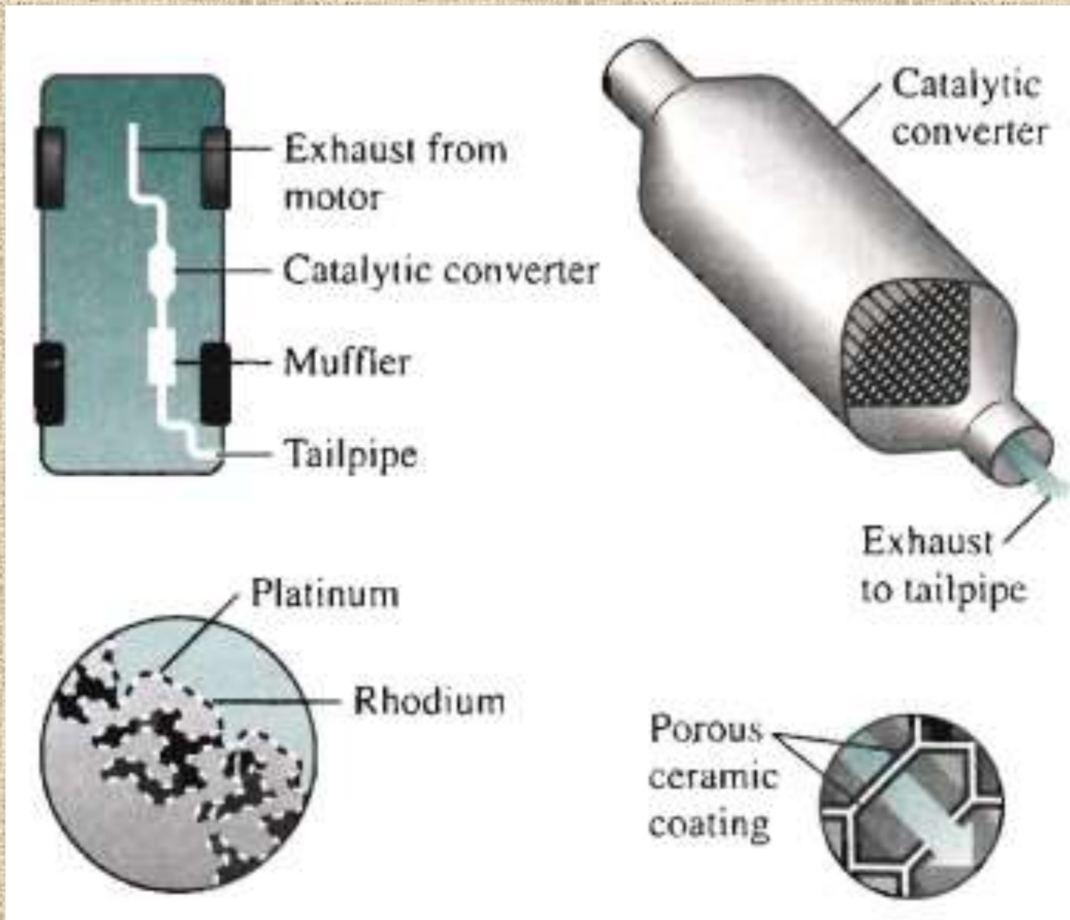
Limiting NOx in engine

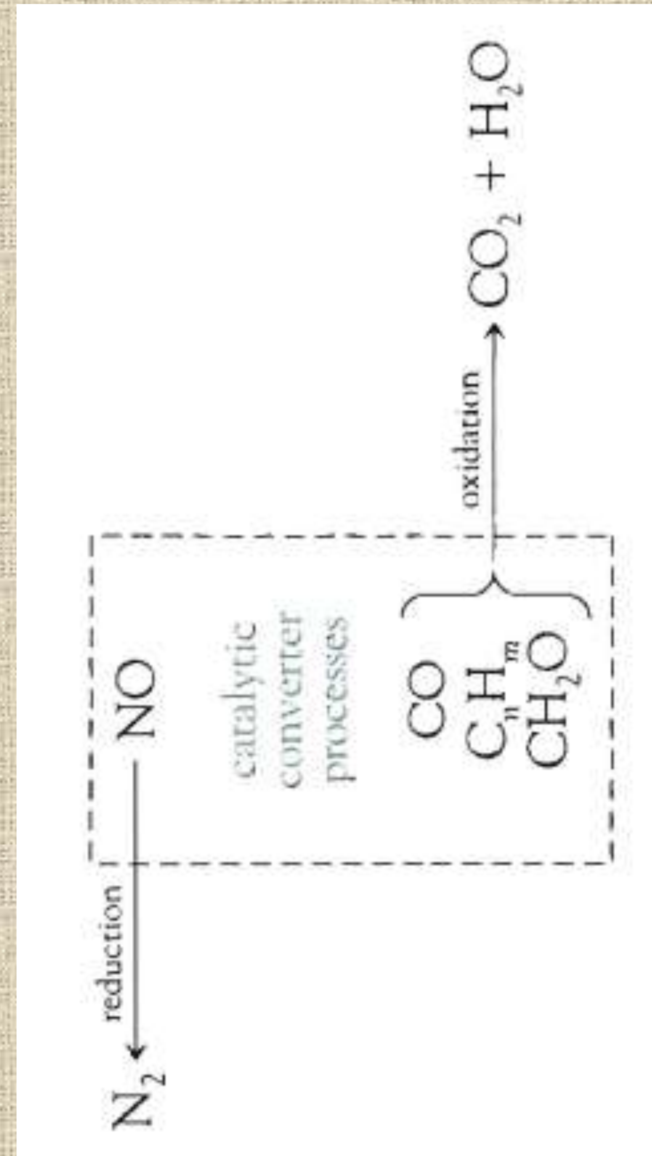
- Lowering combustion temp. by recirculation of exhaust
- Catalytic Conveter:
- Two way: only carbon containing gases
- Three way: Changing NOx to N_2 by reduction and oxidation of carbon containing gases

$$2\,NO \longrightarrow N_2 + O_2 \quad \text{overall}$$

$$2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$$

Control of VOC's and NOX from the Emissions





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Drawbacks of using catalytic converter:

• Made of heavy metals, which are released in minute amounts during the process.

• Reduces the SO_2 present in petroleum (>1000 ppm) to H_2S gas which has horrible smell.

•Takes time to come in working status (heating >300 ˚C).

Possible modifications

• Devising a converter that will operate at lower temperatures or that can be preheated so it begins to operate immediately.

• Storing pollutants until the engine and converter are heated.

•Recirculating engine exhaust through the engine until the reactions are more complete.

Petrol Vs Diesel engines

The emission of NOX is less in Diesel engines as compared to petrol engines but they emit a lot of carbon soot particles.

$$C(s) + NO_2 \longrightarrow CO + NO$$

- Particle Trap and ignition using Fe and Cu as catalyst to regenerate filter
- HCCI: homogeneous charge compression ignition

FUEL Cells: future alternative

Control of Nitric Oxide Emissions from Power Plants

- Some power plants use special burners designed to lower the temperature of the flame. Alternatively, the recirculation of a small fraction of the exhaust gases through the combustion zone has the same effect.

- combustion of the fuel occur in stages : In the first, high-temperature stage, no excess oxygen is allowed to be present, thus limiting its ability to react with N_2; In the second stage, additional oxygen is supplied to complete the fuel's combustion but under lower temperature conditions, so that again little NO is produced.

- Use of big scale catalytic converters that change Nox back to N_2.

$$4\,NH_3 + 4\,NO + O_2 \longrightarrow 4\,N_2 + 6\,H_2O$$

- Wet scrubbing of exhaust gases: Solutions of sodium hydroxide, NaOH, react with equimolar amounts of NO and NO_2 to produce an aqueous solution of sodium nitrite, $NaNO_2$

$$NO + NO_2 + 2\,NaOH \longrightarrow 2\,NaNO_2 + H_2O$$

Atmospheric aerosols

Particulate Matter Air Pollution
and
Health Risks

Particulates

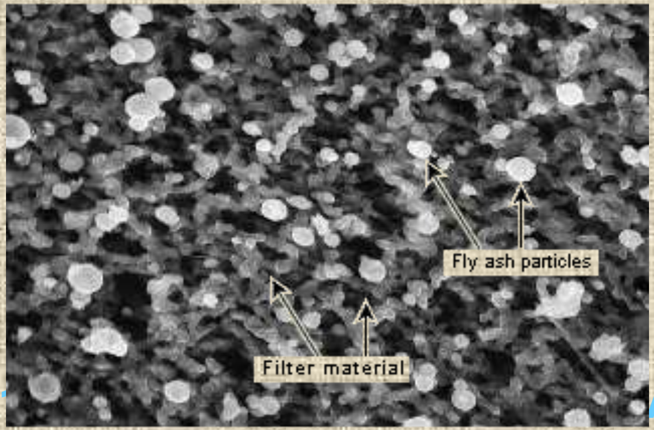
Tiny solid or liquid particles- other than those of pure water- that are temporarily suspended in air and that are usually individually invisible to the naked eye.

Particulate Matter

Particulate matter (PM) describes a wide variety of airborne material. PM pollution consists of materials (including dust, smoke, and soot), that are directly emitted into the air or result from the transformation of gaseous pollutants.

Particles come from **natural sources** (e.g., volcanic eruptions) and **human activities** such as burning fossil fuels, incinerating wastes, and smelting metals.

Figure 1. Photomicrograph of Fly Ash Particles on an MCE Filter



Source: Courtesy of Air Control Techniques, P.C.

Where Does PM Originate?

Sources may emit PM directly into the environment or emit **precursors** such as **sulfur dioxide (SO_2), nitrogen dioxide (NO_2), and volatile organic compounds (VOCs),** which are transformed through atmospheric chemistry to form PM.

VOCs $\longrightarrow$

NO_2 $\xrightarrow{\text{Ammonia } (NH_3)}$ **PM**

SO_2 $\xrightarrow{\text{Ammonia } (NH_3)}$

Sources of PM and PM Precursors

Mobile Sources
(vehicles)
VOCs, NO_2, PM

Stationary Sources
(power plants, factories)
NO_2, SO_2, PM

Area Sources
(drycleaners, gas stations)
VOCs

Natural Sources
(forest fires, volcanoes)
PM

Determinants of PM Concentration

- Weather patterns
- Wind
- Stability (vertical movement of air)
- Precipitation
- Topography
- Smokestack height and temperature of gases

Nearby natural and built structures may lead to downward moving currents causing **aerodynamic or building downwash** of smokestack emissions.

Size and shape of PM

- Based on size PM are mainly two types

(a) **Coarse particles:- Coarse particles** are the relatively large airborne **particles** mainly produced by the mechanical break-up of even larger solid **particles**. Examples of **coarse particles** include dust, pollen,fly ash, and plant and insect parts not of same size, shape and chemical composition(Size greater than 2.5 μm).

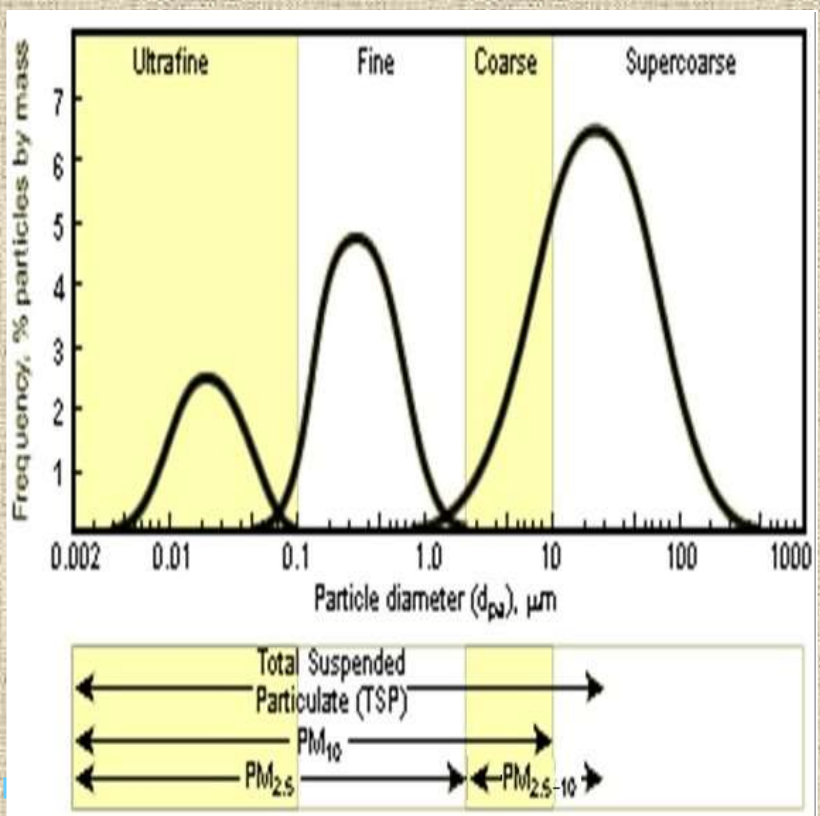
(b) **Fine Particles:- Fine particles are smaller than Coarse particles. Examples-oil smoke, virus etc.**

- **Coarse and fine** depending upon their diameter less than or greater than 2.5 μm.
- **Aerosol** is a collection of particulates, whether solid or liquid droplets, dispersed in air and having very small size less than 100 μm (Example-Mist is an example of liquid aerosol)

Particulate Matter: Aerodynamic Diameter

Establishing a particle size definition for irregularly shaped particles necessitates the use of a standardized measure referred to as the **aerodynamic diameter**, measured in microns or micrometers (μm)

The graph at the right shows the distribution of the 4 main particle size categories, By comparison, a human hair is approximately 70 microns in diameter.



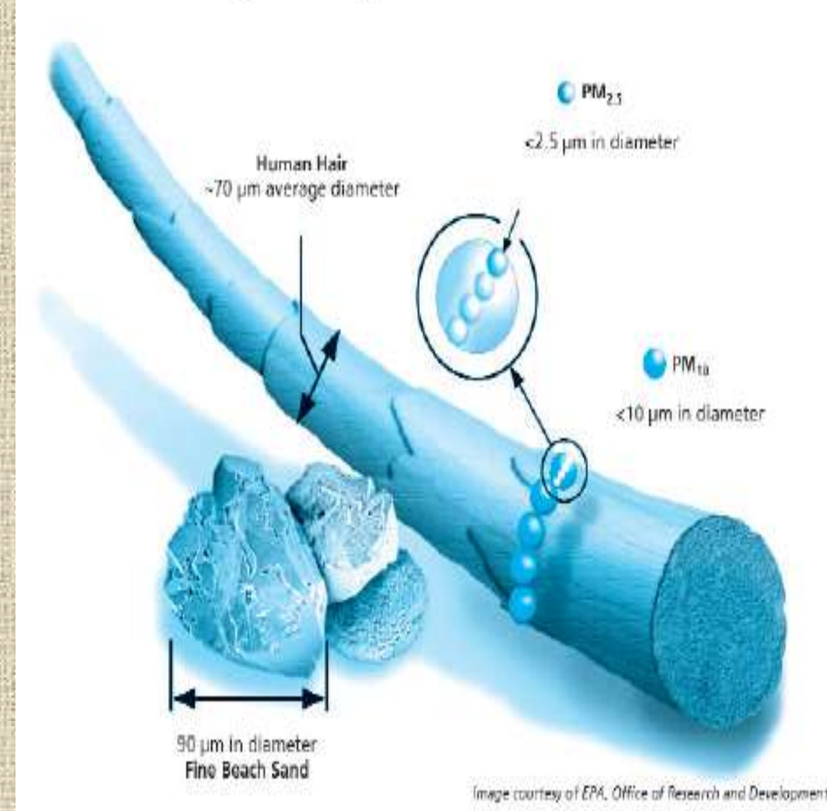
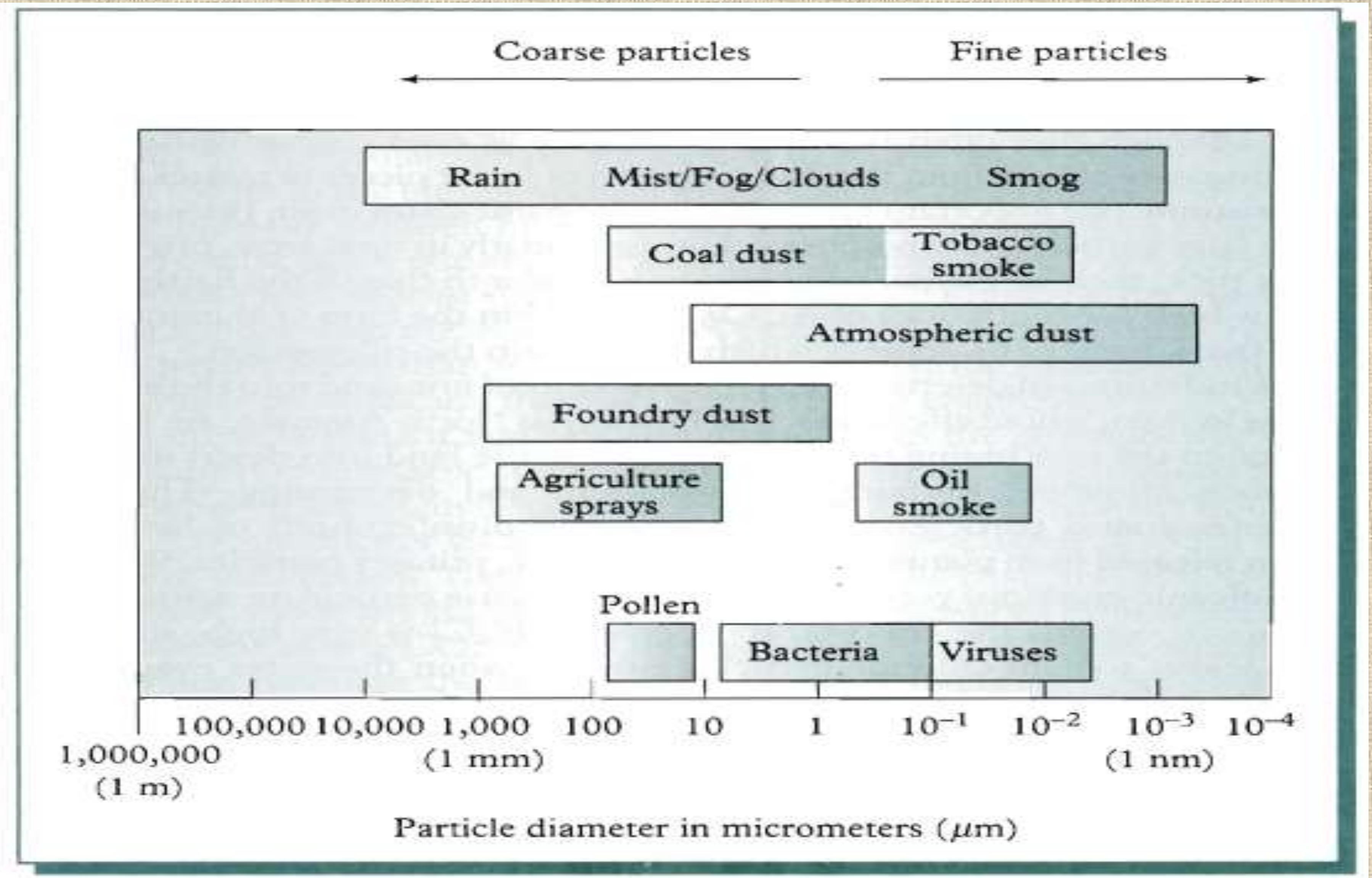


Figure 1. Comparison of PM sizes.



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Sources of Coarse particles (Mostly Primary PM)

Natural:

- Mineral from earth: Dust from soil or rock with elemental composition of Al, Ca, Si and O in the form of aluminium silicates.
- Wind storm in deserts
- Wind also generate coarse particles by the mechanical disintegration of leaf litter.
- Pollens
- Wildfires and volcanic eruptions
- NaCl near and above the sea.

Anthropogenic sources: Stone crushing, overgrazing, deforestation, land cultivation(soil erosion)

Sources of fine particles (Mostly Secondary PM)

- Primary fine particles from anthropogenic origin include ones generated by the wearing of tires and vehicle brakes as well as the dust from metal smelting.

- **Exhaust from vehicles:** The incomplete combustion of fuels such as coal, oil, gasoline and diesel produces many fine particles, which are mainly crystallites of carbon.
- **Organics:** reaction between VOC's and Nitrogen oxides in PC smog, partially oxidized to carboxylic acids, aromatic hydrocarbons with at least 7 carbons (e.g. toulene) from the evaporation of gasoline and other HCs having less than 7 carbons with substantial vapor pressure.

Inorganic Compounds: compounds of sulfur and Nitrogen.

Sulfur:

- as *dimethyl sulfide* $(CH_3)_2S$ emitted from oceans.
- A biproduct of its oxidation in air is *Carbonyl sulfide*, COS.
- Both the $(CH_3)_2S$ and H_2S are oxidized to SO_2.
- SO_2 is also released by volcanoes. In a period of hours to days it gets converted into sulfuric acid and sulfates in air.

Acid Base nature of Fine particles

Fine particle in many area are acidic , due to their content of sulfuric and nitric acids.

Nitric Acid: End product of Oxidation of Nitrogen containing gas such as NH_3, NO and NO_2.

Both the acids undergo acid-base reaction with ammonia which form soluble salts of ammonium sulfate, $((NH4)_2SO_4)$, ammonium nitrate, (NH_4NO_3).

$$H_2SO_4(aq) + NH_3(g) \longrightarrow NH_4HSO_4(aq)$$

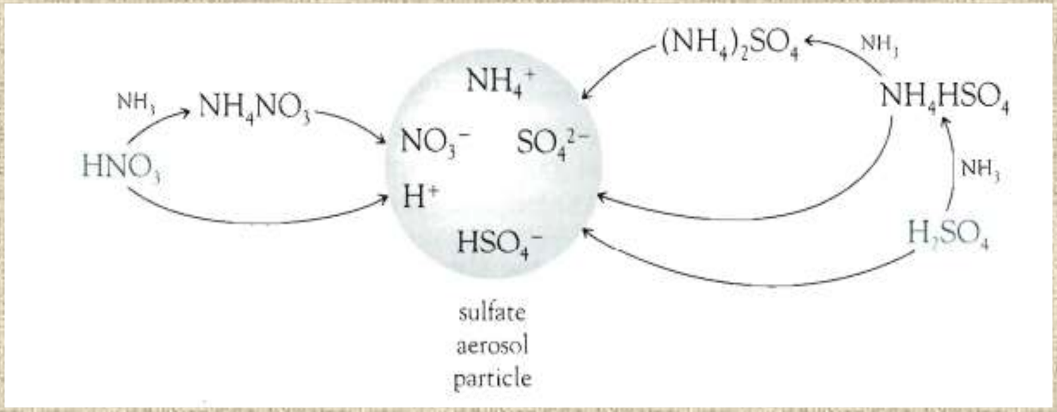
$$NH_4HSO_4(aq) + NH_3(g) \longrightarrow (NH_4)_2SO_4(aq)$$

Sources of Ammonia

- From biological decay
- Animal urine
- Use of fertilizers etc.

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

On evaporation of water, these salts become solid particles with predominant anions of sulfate, (SO_4^{2-}), bisulfate (HSO_4^-),and Nitrate (NO_3^-):
And Cations of ammonium (NH_4^+) and Hydrogen (H^+)



Summary

In summary, coarse particles are usually either soot or inorganic (soil-like) in nature, whereas fine ones are mainly either soot, or sulfate or nitrate aerosols. Fine particles are usually acidic due to the presence of unneutralized acids, whereas coarse ones are usually basic because of their soil content.

Particulate Matter: Size Matters

- Size is important to the behavior of PM in the atmosphere and human body and determines the entry and absorption potential for particles in the lungs.
- Particles larger than 10 mm are trapped in the nose and throat and never reach the lungs.
- Therefore, particles 10 mm in diameter or less are of most concern for their effects on human health.
- Particles between 5 and 10 mm are removed by physical processes in the throat.
- Particles smaller than 5 mm reach the bronchial tubes, while particles 2.5 mm in diameter or smaller are breathed into the deepest portions of the lungs.

Adverse Health Effects of PM

- Premature death
- Lung cancer
- Development of chronic lung disease
- Heart attacks
- Respiratory symptoms and medication use in people with chronic lung disease and asthma
- Decreased lung function
- Pre-term birth
- Low birth weight


ACID RAIN

Contents

- Definition
- Causes
- Formation
- Affected Areas
- Effects
- Preventive Measures

Definition of Acid Rain

- Precipitation that has a pH of less than that of natural rainwater (which is about 5.6 due to dissolved carbon dioxide).

$$CO_2(g) + H_2O(aq) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightleftharpoons H^+ + HCO_3^-$$

- It is formed when sulphur dioxides and nitrogen oxides, as gases or fine particles in the atmosphere, combine with water vapour and precipitate as sulphuric acid or nitric acid in rain, snow, or fog.

$$SO_2 \xrightarrow[H_2O]{O_2} H_2SO_4$$

$$NOx \xrightarrow[H_2O]{O_2} HNO_3$$

Causes of Acid Rain

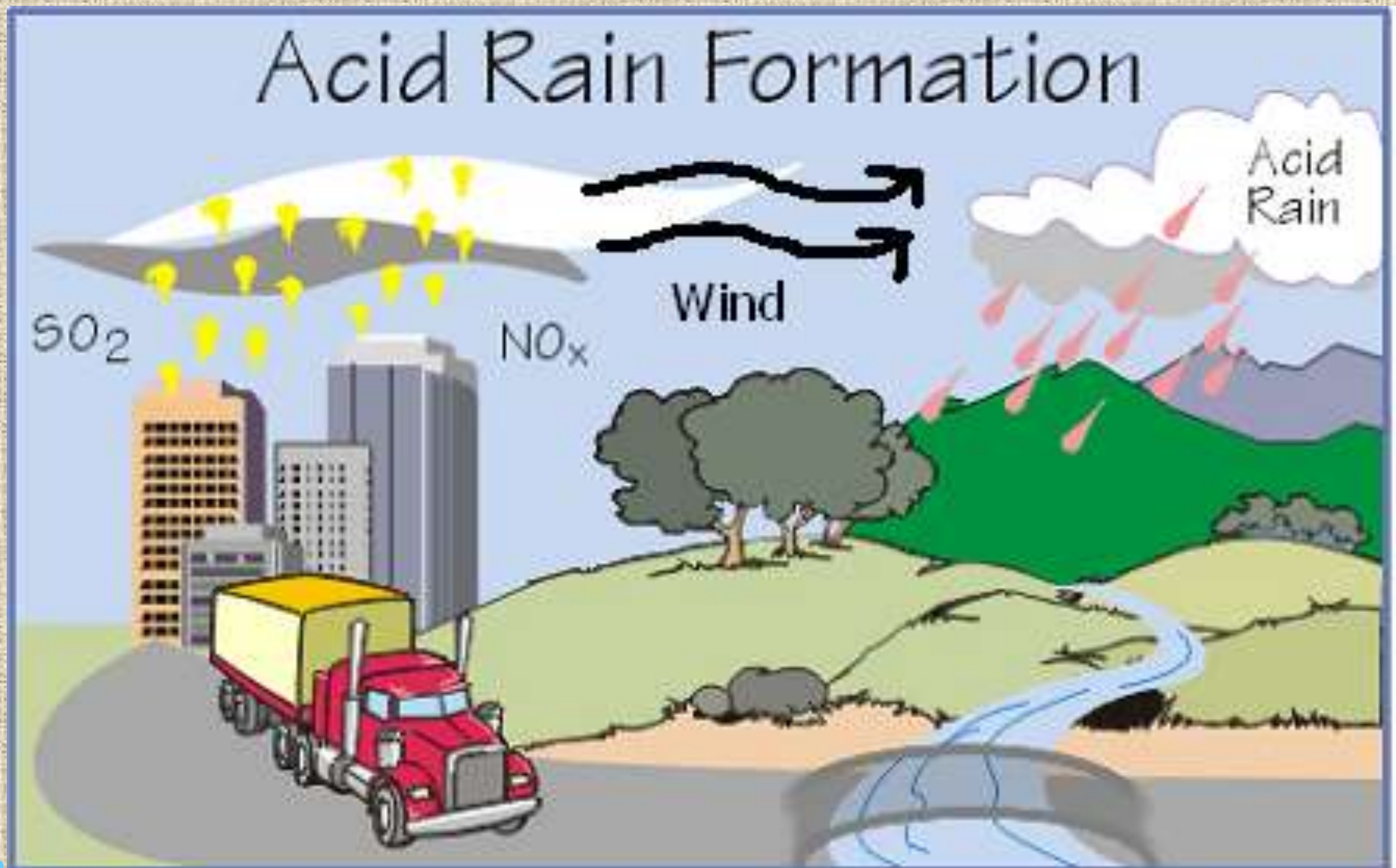
Natural Sources

- Emissions from volcanoes and from biological processes that occur on the land, in wetlands, and in the oceans contribute acid-producing gases to the atmosphere

Anthropogenic Source

- Industrial factories, power-generating plants and vehicles
- Sulphur dioxide and oxides of nitrogen are released during the fuel burning process (i.e. combustion)

Formation of Acid Rain



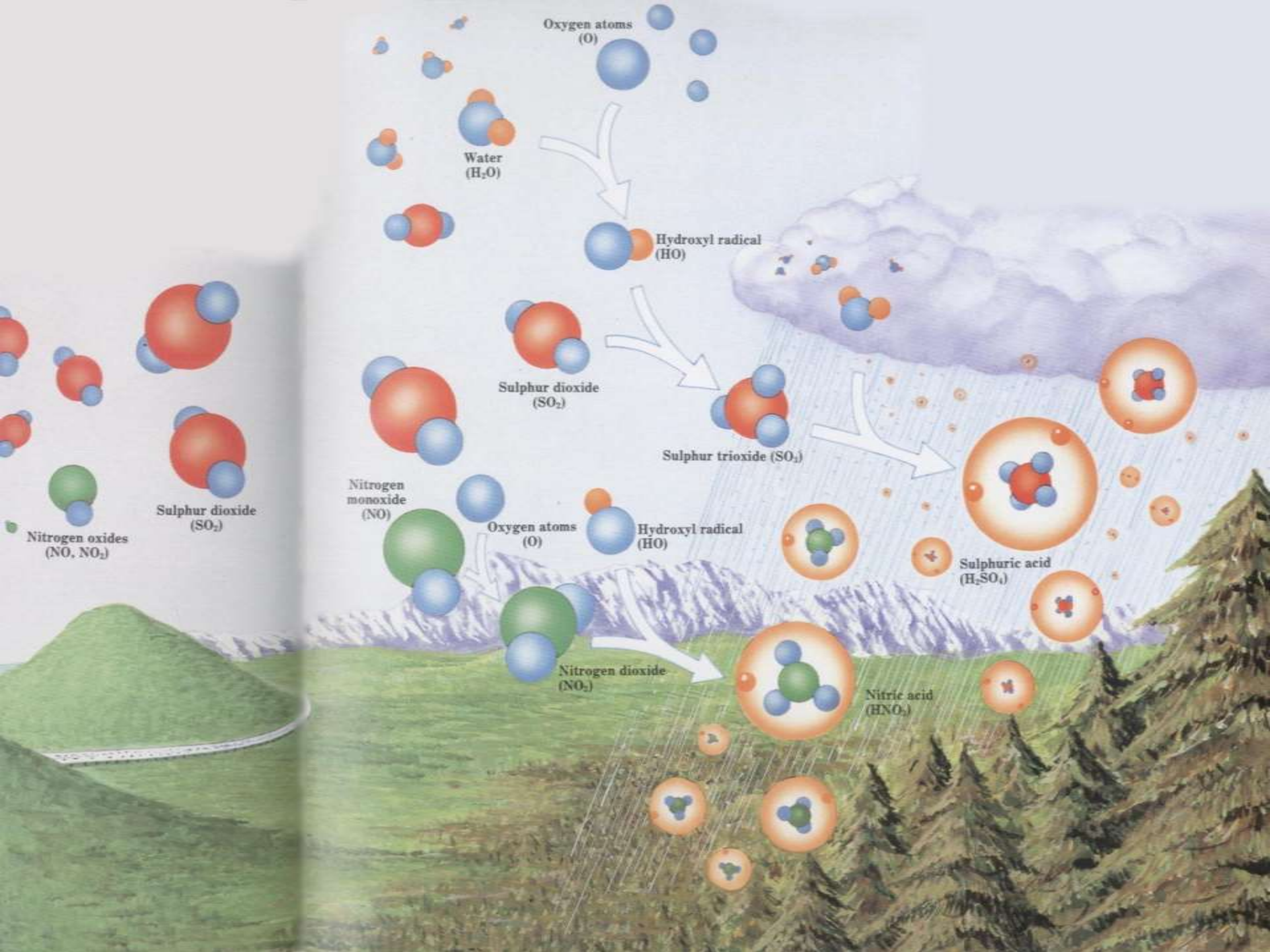
Formation of Acid Rain

- When water vapor condenses, or as the rain falls, they dissolve in the water to form sulphuric acid (H_2SO_4) and nitric acid (HNO_3).
- While the air in cleaned of the pollutants in this way, it also causes precipitation to become acidic, forming acid rain

$$SO_2 \xrightarrow[H_2O]{O_2} H_2SO_4$$

$$NO_X \xrightarrow[H_2O]{O_2} HNO_3$$

- Acidic particles and vapors are deposited via two processes - wet and dry deposition.
- Wet deposition is acid rain, the process by which acids with a pH normally below 5.6 are removed from the atmosphere in rain, snow, sleet or hail.
- Dry deposition takes place when particles such as fly ash, sulphates, nitrates, and gases (such as SO_2 and NO), are deposited on, or absorbed onto, surfaces. The gases can then be converted into acids when they contact water.


Oxygen atoms
(O)
Water
(H_2O)
Hydroxyl radical
(HO)
Sulphur dioxide
(SO_2)
Sulphur trioxide (SO_3)
Nitrogen oxides
(NO, NO_2)
Sulphur dioxide
(SO_2)
Nitrogen
monoxide
(NO)
Oxygen atoms
(O)
Hydroxyl radical
(HO)
Sulphuric acid
(H_2SO_4)
Nitrogen dioxide
(NO_2)
Nitric acid
(HNO_3)

Neutralization of Acid Rain by Soil

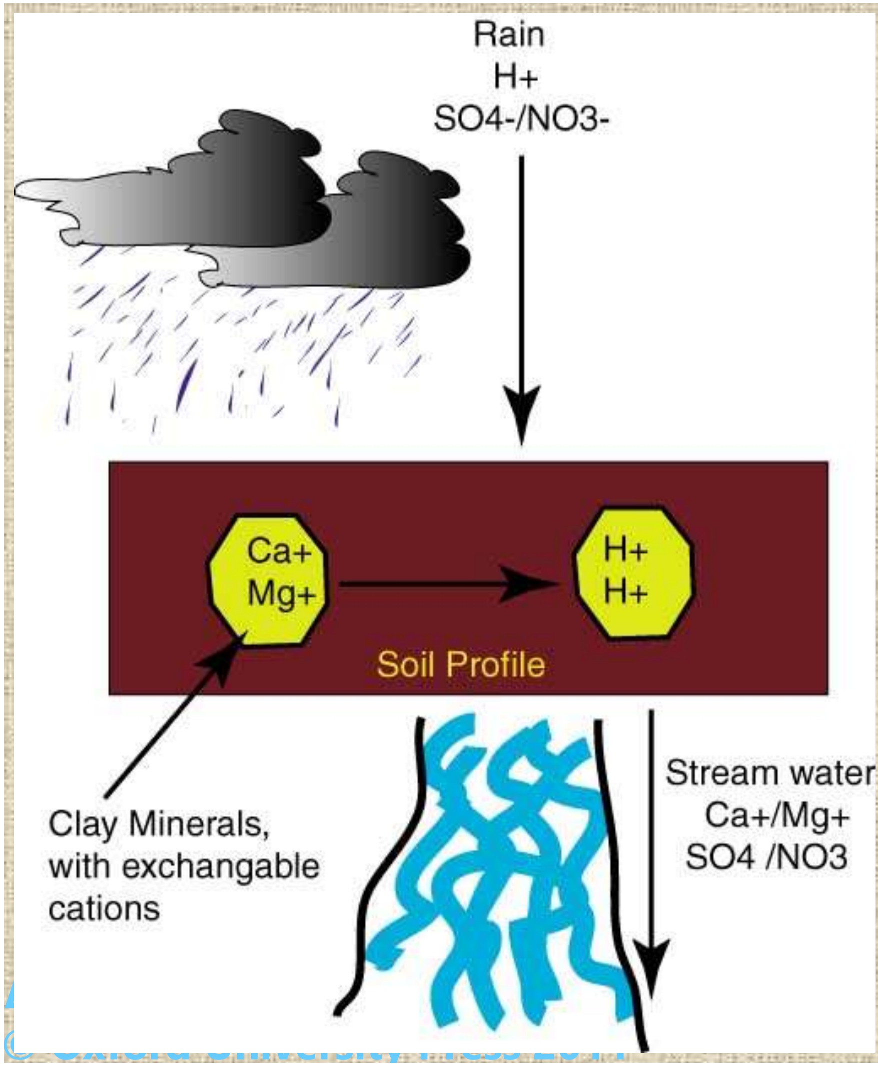
- Effects on biological life strongly depend on the composition of the soil and bedrock in that area i.e limestone/Chalk or graphite.

$$CaCO_3(s) + H^+(aq) \longrightarrow Ca^{2+}(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H^+(aq) \longrightarrow H_2CO_3(aq) \longrightarrow CO_2(g) + H_2O(aq)$$

- The same reaction is responsible for deterioration of marble structure.
- Geographical area determines the **Critical load**

Acid Neutralization



- How does this work?
- Cation Exchange on clay minerals
- Role of chemical weathering...

Release of Aluminum into Soil and water bodies

- High concentration of Al is found in acidified soil and water lakes.
- Aluminum is leached from rocks in contact with acidified water reaction with the hydrogen ions:

$$\text{Al compounds(s)} \xrightarrow{H^+} Al^{3+}$$

- Scientists believe that both acidity itself and the high concentration of aluminum together are responsible for the devastating decrease in fish population

Effects of Acid Rain

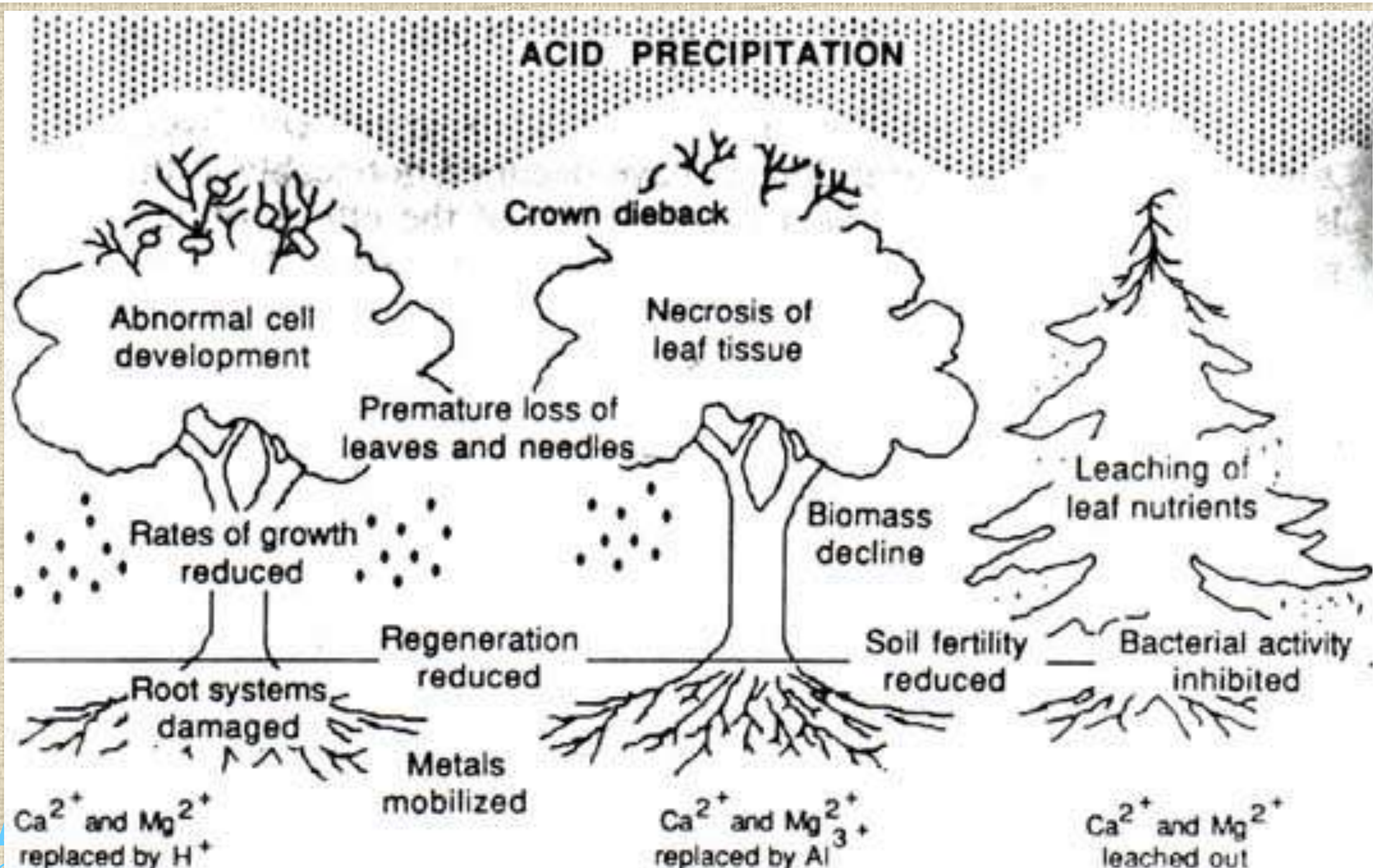
- Harmful to aquatic life
  - Increased acidity in water bodies
  - Stops eggs of certain organisms (e.g. fish) to stop hatching
    - Changes population ratios
    - Affects the ecosystem

- Harmful to vegetation
  - Increased acidity in soil
  - Leeches nutrients from soil, slowing plant growth
  - Leeches toxins from soil, poisoning plants
  - Creates brown spots in leaves of trees, impeding photosynthesis
  - Allows organisms to infect through broken leaves

Effects of Acid Rain

http://abacus.bates.edu/~ganderso/biology/bio270/clover_leaf_burns_pH2_30d.gif

Acid Rain and Trees



Forests affected by Acid Rain

Northeast US
Canada
Northern Europe
Asia

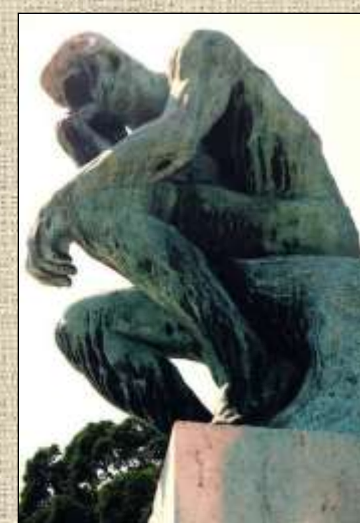
Acid Rain and Buildings

Many buildings are made of concrete and or stone

These compounds act as bases and react with acid

The building technically “weathers” very fast, or
Non technically “crumbles”
Example-Taj Mahal.


How acid rain affects stonework.
The picture on the left was taken in 1908.
The picture on the right was taken in 1968



Effects of Acid Rain

- Affects human health
  - Respiratory problems, asthma, dry coughs, headaches and throat irritations
  - Leaching of toxins from the soil by acid rain can be absorbed by plants and animals. When consumed, these toxins affect humans severely.
  - Brain damage, kidney problems, and Alzheimer's disease has been linked to people eating "toxic" animals/plants.

Preventive Measures

- Reduce amount of sulphur dioxide and oxides of nitrogen released into the atmosphere
  - Use less energy (hence less fuel burnt)
  - Use other sources of electricity (i.e. nuclear power, hydro-electricity, wind energy, geothermal energy, and solar energy)
  - Use cleaner fuels
  - Remove oxides of sulphur and oxides of nitrogen before releasing
    - Flue gas desulphurization
    - Catalytic Converters
- Liming
  - Powdered limestone/limewater added to water and soil to neutralize acid