Air Pollution

It is the phenomenon of release of one or more contaminants by anthropogenic activities, which disturbs the dynamic equilibrium in atmosphere and there by affect man and it's environment.

Air Pollutants :-

These are the contaminants in air, those may affect directly the human, plant and animal life or undergo some chemical changes to produce harmful products, which unreasonably interfere the comfortable enjoyment of life.

Equilibrium :-

Atmosphere is a dynamic system. It acts as a natural sink by absorbing steadily the various pollutants from natural and man made sources, due to which an equilibrium is established.

Classification of Air Pollutants

Natural Pollutants :-

The gases like CO, CO_2, H_2S, SO_2, NO_2 etc and the particulate matter like dust, sand, etc. are continuously released in to atmosphere through the natural activities such as volcanic eruptions, forest fires, vegetation decay, storms, wind etc.

Man Made Pollutants :-

These are CO_2, NOx, SO_2, CO, HCs, SPM, etc. Their quantity discharged is some thousand times to that of natural pollutants and it is increasing day by day due to:-

- Population Explosion,
- Industrialization,
- Urbanization,
- Automobiles & the proclivities of greater comfort

Classification of Air Pollutants

These pollutants travels through air, disperse and interact before they reach a sink like Ocean or human receptor. Their rate of discharge is higher than rate of absorption in a natural sink. Therefore, they get gradually accumulated in atmosphere and affect every life on the earth and It's environment.

Classification [Origin]

Primary Pollutants:- Directly emitted in atmosphere.

Ex. CO, CO_2, SO_2, NO_2, and HCs.

Secondary Pollutants:- Derived from Primary Pollutants due to chemical or photochemical reactions.

Ex:- Ozone, Smog, Peroxy Acyl Nitrate (PAN), etc

Classification of Air Pollutants

Classification [Chemical composition]:-

Inorganic Pollutants:-

Carbon compounds:- Carbonyls, Carbonates, etc

Nitrogen compounds:- NO_X, NH_3, etc.

Sulphur compounds:- H_2S, SO_2, SO_3,H_2SO_4, etc.

Halogen compounds:- HF, HCl, HBr, Metallic Flourides, etc.

Oxidizing agents:- Ozone

Particulate matter:- Fly ash, silica, asbestos and the dust from transport, mining, metallurgical and other industrial operations.

Classification of Air Pollutants

Organic Pollutants:-

HCs, Aldehydes, Ketones, Amines, Alcohols, etc.

Classification [State of matter]

Gaseous Pollutants:-

Thoroughly mixed with air and normally do not settle own.

Ex:- CO, NOX, SO_2, etc

Particulate Pollutants (SPM):-

Finely divided solids or liquids and often exist in colloidal state as aerosols.

Ex:- Smoke, fumes, dust, mist, fog, smog, sprays etc.

Causes and Effects of Air Pollutants

1. Carbon monoxide [CO]
2. Carbon dioxide [CO_2]
3. Oxides of Sulphur [SO_X]
4. Hydrogen Sulhide [H_2S]
5. Oxides of Nitrogen [NO_X]
6. Hydrocarbons [HCs]
7. Particulates [SPM]
8. Ozone [O_3]
9. Toxic Metals [Pb, Hg, As, Cd & Cr]

Carbon monoxide [CO]

Air contains 0.1 to 0.12 ppm carbon monoxide.

Causes:-

Natural sources	Man made sources
i) Volcanic eruption	i) Automobile exhaust
ii) Natural and Marsh gas emission	ii) Fossil fuel combustion
iii) Electrical discharges burning during storm's	iii) Forest Fires
iv) Seed germination	iv) Agricultural waste burning
iv) Seed germination	v) Tobacco smoking
v) Vegetation Decay vi) Oceanic activity	vi) Coal mining vii) Industrial operations: Iron, Steel, Paper, Petroleum, etc

Carbon monoxide

Annual global CO emission ≈ 350 m.t.s

Natural sources ≈ 75 m.t.s.

Human sources ≈ 275 m.t.s. (USA ≈ 100 m.t.s.)

Basic reactions –

1. Incomplete combustion of fuels:

$$C+1/2\ O_2 \rightarrow CO$$

2. At high temperature in industrial operations (such as Blast Furnace)

$$C+\ CO_2 \rightarrow 2CO$$

3. At high temperature in electrical operations in industries

$$CO_2 \rightarrow CO+[O]$$

Carbon Monoxide

Balance:

- Soil micro-organisms act as major sink for CO.
- Air oxidation:- $CO + ½\ O_2 \rightarrow CO_2$

Effects:- CO is a colourless, odourless, water soluble, toxic gas with very high affinity towards Haemoglobin. Displaces O_2 from Oxy- Haemoglobin , which reduces O_2 carrying capacity of blood (co-poisoning).

$$Hb + O_2 \rightarrow HbO_2$$

$$HbO_2 + CO \rightarrow HbCO + O_2$$

Immediate response to co-poisoning is loss of judgment, which causes many automobile accidents and the further exposure to CO causes death.

Co-poisoning can be cured by providing fresh O_2, which reverses the reaction

$$2\ HbCO + 3O_2 \rightarrow 2\ HbO_2 + 2CO_2$$

Carbon monoxide

Control Measures:-

Since transportation sector accounts for 74% of the entire global CO emission out of which major contribution of 60% comes from the gasoline fed IC Engines, lot of attention and efforts have been directed towards controlling CO-emission in following manner:

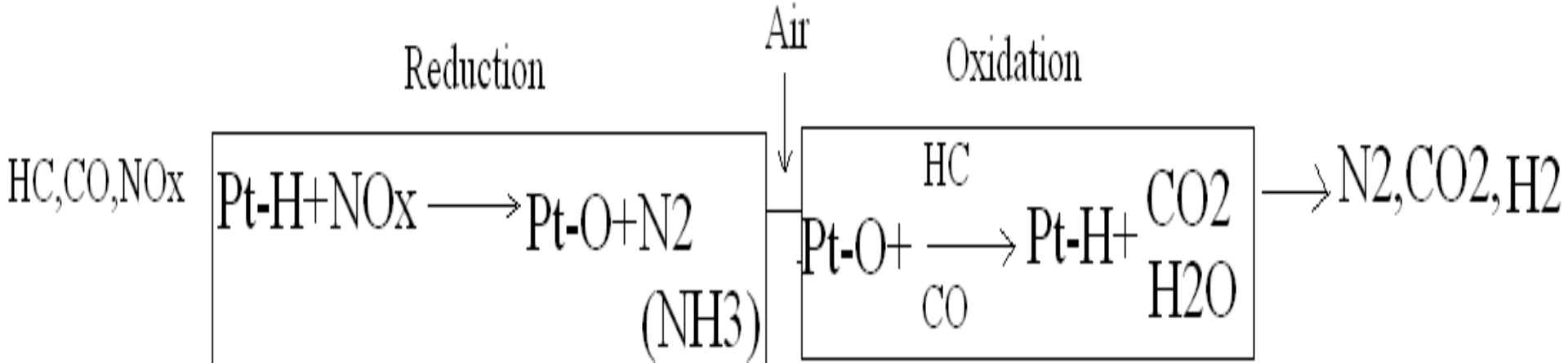
1. Use of exhaust system reactor
2. Modification of engine design
3. Fuel modification / development of substitute fuel.
4. Exhaust gas treatment and recirculation.

Carbon monoxide

Extensive investigations have been and are being made for the control of automotive emissions along the following lines:-

1. Development of exhaust system reactors:- To complete the combustion process and change the potential pollutants into more acceptable materials.

Ex:- Catalytic Converters



Carbon monoxide

2. Modification of Engine Design:-

To reduce the amounts of pollutants formed during fuel combustion.

Automobile emissions consist of CO, NO_X, HCs & spm. If some control measures are applied to reduce one of these pollutants, the amounts of other pollutants are also affected.

Combustion of rich mixture (little air) i.e. that with low air-fuel ratio reduces NO_X formation considerably but increases CO & HCs emissions whereas combustion of lean mixture (more air) i.e. that with stoichiometric air-fuel ratio ensures complete oxidation of C & H_2 to CO_2 & H_2O.

Carbon monoxide

Stratified IC Engine designed by Honda Japan, has utilized this principle for the first time in 1995.

Rich mixture (little air) is burnt first in prechamber (small) and then fed to main chamber (large) for complete combustion.

The stratified IC engine suffered from the drawback of more fuel consumption and less power output.

Carbon monoxide

3. Development of substitute fuels for gasoline:-

Which yield a low concentrations of pollutants upon combustion.

Ex:- Natural gas (CNG as well as LNG);

Though pollution free but has problems of steady supply and economic storage,

Ex:- Power Alcohol,

which produce eye irritant combustion products like aldehyde & acetic acid.

Carbon monoxide

4. Development of pollution free alternative power sources:-

To replace the IC Engines.

Ex: Electric Engines, Steam Engines, Gas turbine engines, etc.

However, none of these are economically viable as compared to gasoline.

Oxides of Sulphur [SO_X]

Air contains 0.002 ppm Sulphur dioxide (SO_2), accompanied by little Sulphur trioxide (SO_3) i.e. (≈ 1 to 3%)

Annual global SOx emission is about ≈ 147.5 mts, out of which SO_2 is ≈ 146 mts and SO_3 ≈ 1.5 mts.

Causes:-

Natural sources:

These contribute to about 67% global SOx emission, over which we have no control.

Ex: Volcanic activity, Hot water springs, etc

Man made Sources:-

These contribute to rest 33%. It is on account of the human activities concentrated in Urban and Industrial areas.

SOx

These could be illustrated as under:

i) **Combustion of fossile fuels:** Thermal power stations account for about 74% emission.

ii) **Industrial operations** ≈ 22 %: Metallurgical operations- smelting of sulphide ores. Chemical plants – manufacture of Sulphuric acid, paper etc.

iii) **Transportation** ≈2 %

iv) **Others** ≈2 %: Burning of municipal waste.

Basic reactions:-

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + 1/2\ O_2 \rightarrow SO_3$$

1. Photochemical smog- It is a photolytic and catalytic reaction involving O_3, NOx, HCs, metal oxides, soot, dust, etc.

SOx

2. Acid Rain- Under normal humid conditions;

$$SO_2 \underset{-O2}{\overset{+O3}{\rightleftharpoons}} SO_3 \xleftarrow{1/2O2} SO_2$$

$$\downarrow \mathbf{+H_2O}$$

$$H_2SO_4$$

$$\downarrow$$

$$[H_2SO_4]_n$$

SOx

Properties that cause damaging impact:

SOx comprises 97-99% SO_2 and 1-3% SO_3.

It is a colourless, heavy, water soluble gas with irritating pungent smell.

It is rapidly diffusing and acid forming oxidizing agent.

It reacts with water to form H_2SO_3 and H_2SO_4, both react with organic matter, metals and materials.

SOx

Effects:-

i) Aerosols (d≈2μ) present in Urban air can easily reach eyes and throat, get absorbed and cause irritation.

ii) React with cellular constituent chemicals (enzymes), lowers pH and empires enzymatic functions thereby affecting metabolism.

iii) Leads to bronchial spasm, breathlessness, empired pulmonary function via airway resistance, empired lung clearance and increase in susceptibility for infection.

This causes increased breathing rates, air starvation, suffocation, aggravation of asthma, chronic bronchitis, respiratory and sensory irritation.

SOx

Control:-

SOx emission from anthropogenic activities can be minimized by:

i) Utilising low sulphur fuels.

ii) Removing S from fossil fuels with high S-content.

iii) Removing SOx from flue gases before letting them out into atmosphere by making use of chemical scrubbers.

iv) Generating power from alternative energy sources & discouraging fossil fuels based thermal power plants.

SOx

Control Measures:

Following four possible approches are there for the removal & control of SOx emissions.

1. Removal of SOx from flue gases:-

The major anthropogenic source of SOx pollution are power plants. These are normally built with tall smoke stacks to disperse the plum over a wide area. This reduces local problems but at the same times creates problems in far areas.

SOx from the flue gases can be conveniently eliminated by making use of chemical scrubbers. The flue stack gases are passed through a slurry of lime stone, which absorbs SO_2 quite efficiently.

SOx

$$CaCO_3 + SO_2 + ½\ O_2 \rightarrow CaSO_4 + CO_2$$

The method is economical, but has a draw back of CaSO4 waste disposal. Therefore an alternative process can be used, in which the flue gas is cooled below 50^0C and led in to an absorption tower containing citrate ions solution.

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+$$

$$HSO_3^- + H2\ Cit^- \leftrightarrow HSO_3^- . H_2\ Cit^{--}$$

This solution is fed into a closed vessel and H_2S is bubbled.

$$HSO_3 . H_2\ Cit^{--} + H^+\ H_2S \leftrightarrow 2S + H_2\ Cit^{-} + 3H_2O$$

The precipitated S is melted and removed from the solution.

SOx

A part of S converted to H_2S is circulated to above system. About 99% SO_2 is removed.

2. Removal of S from fuel before burning:-

Depending upon the type of fuel and the form of S a variety of techniques such as carbonization, Liquefaction, Gasification, Desulphurization etc. are used for removal of bounded S while the physical techniques such as grinding followed by washing are used for removal of pyretic S.

SOx

3. Use of low sulphur fuels:-

It is a more costly proposition in case of coal.

4. Substitution of low sulphur fuel combustion by other energy sources:-

Alternative energy sources such as Hydroelectric plants and nuclear power plants are still not economically viable.

Oxides of Nitrogen [NOx]

Out of 8 possible NOx, only N_2O, NO & NO_2 are found in atmosphere to an extent of 0.6 to 6 ppm.

Basic Chemical Reactions:-

i) Combustion of fossil fuels at high temperature

$$N_2 + O_2 \rightarrow 2NO$$

ii) High temperature oxidation in combustion chamber

$$NO + ½\ O_2 \rightarrow NO_2$$

iii) Photolytic oxidation in atmosphere

$$O_2 + h\mu(242nm) \rightarrow O + O$$

$$O2 + O + M(\text{third body}) \rightarrow O_3 + M$$

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

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$2NO + O_3 \rightarrow N_2O_5 + O_2$$

$$NO_2 + NO_3 \rightarrow N_2O_5$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

$[HNO_3]n$ photochemical smog

NOx

Natural Sources:-

Every year, more than $5x10^8$ tones of NOx (mainly NO)

i) Bacterial Activity-

Denitrifying bacteria in soil bring out NOx emission either by nitrogen fixation from air or by decomposing nitrogen compounds in organic matter in soil.

ii) Photochemical decomposition –

N_2O & NO_2 are converted into NO by Photochemical decomposition in air.

NOx

Man made Sources:-

The annual global emission= $5x10^7$tonns (USA alone= 10 mts)

i. **Combustion of fossil fuels**- coal, oil, natural gas & organic matter. NOx emission is mainly from automobile exhaust, incinerators, based power plants etc. Residence times of NO is 4 days & that of NO_2 is 3 days.

ii. **Industries**- Manufacture of HNO_3, Fertilizers, explosives, etc.

iii. **Explosion** – Explosives, chemical fuels, etc.

iv. **Aircrafts**- Exhaust fumes of SST(Super sonic Transport)

NOx

Properties that cause damaging impact:

NO (Nitrous Oxide) is a colourless gas and slightly water soluble.

NO_2 (Nitrogen di oxide) is a reddish brown gas, some what water soluble and a good oxidizing agent. In atmosphere, NO_2 is involved in O_3 formation.

HNO_3 is more powerful oxidizing agent and capable of reacting with almost all metals and organic compounds.

SOx

Biochemical Effects:-

i. Corrosion of teeth.

ii. Headache, loss of appetite, lachrymatory effect

iii. Respiratory irritation, impairment of lung defenses, pulmonary emphysema, lung edema, etc. At higher NOx level and prolonged exposure may cause pulmonary fibrosis and inflammation of lung tissues, which finally causes death.

iv. Disrupts some cellular enzyme systems

v. Oxidizes cellular lipids and forms bond with hemoglobin that causes reduction in O_2 carrying capacity of blood. NO forms addition compounds with hemoglobin, after entering blood stream.

NOx

Control:-

i) NOx emission from power plants can be reduced by 90%, using a two stage combustion process. Fuel first fired in 90% of stoicheometric air at temperature, which allows minimum NO formation. Then combustion is completed in excess air at low temperature, which does not allow any NO formation].

ii) NO_x emission from automobile exhausts can be minimized by using a two stage catalytic converter.

NOx

iii) NO_x from the stack gas can be removed by chemical sorption- process, using acidic (H_2SO_4) or alkaline [$Ca(OH)_2$, $Mg(OH)_2$] solution. SO_2 is also removed in this scrubbing simultaneously.

Chemical Scrubbing:-

This process involves following four steps.

i. Flue gas (NO_2) are introduced in to an oxidizer.

$$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$$

ii.The NO produced reacts with the NO_2 of flue gas to form N_2O_3 thus formed is observed by H_2SO_4 and the cleaned flue gas is released into the atmosphere.

NOx

$$NO_2 + NO \rightarrow N_2O_3$$

$$N_2O_3 + 2\,H_2SO_4 \rightarrow 2NOHSO_4 + H_2O$$

iii. The scrubbing solution is subjected to decomposition in a decomposer and the H_2SO_4 resulted is recycled to the scrubber, while the NO_2 produced is sent to a reactor.

$$2NOHSO_4 + 1/2O_2 + H_2O \rightarrow 2\,H_2SO_4 + 2NO_2$$

iv. In the reactor, most of the NO is converted into the formed HNO_3.

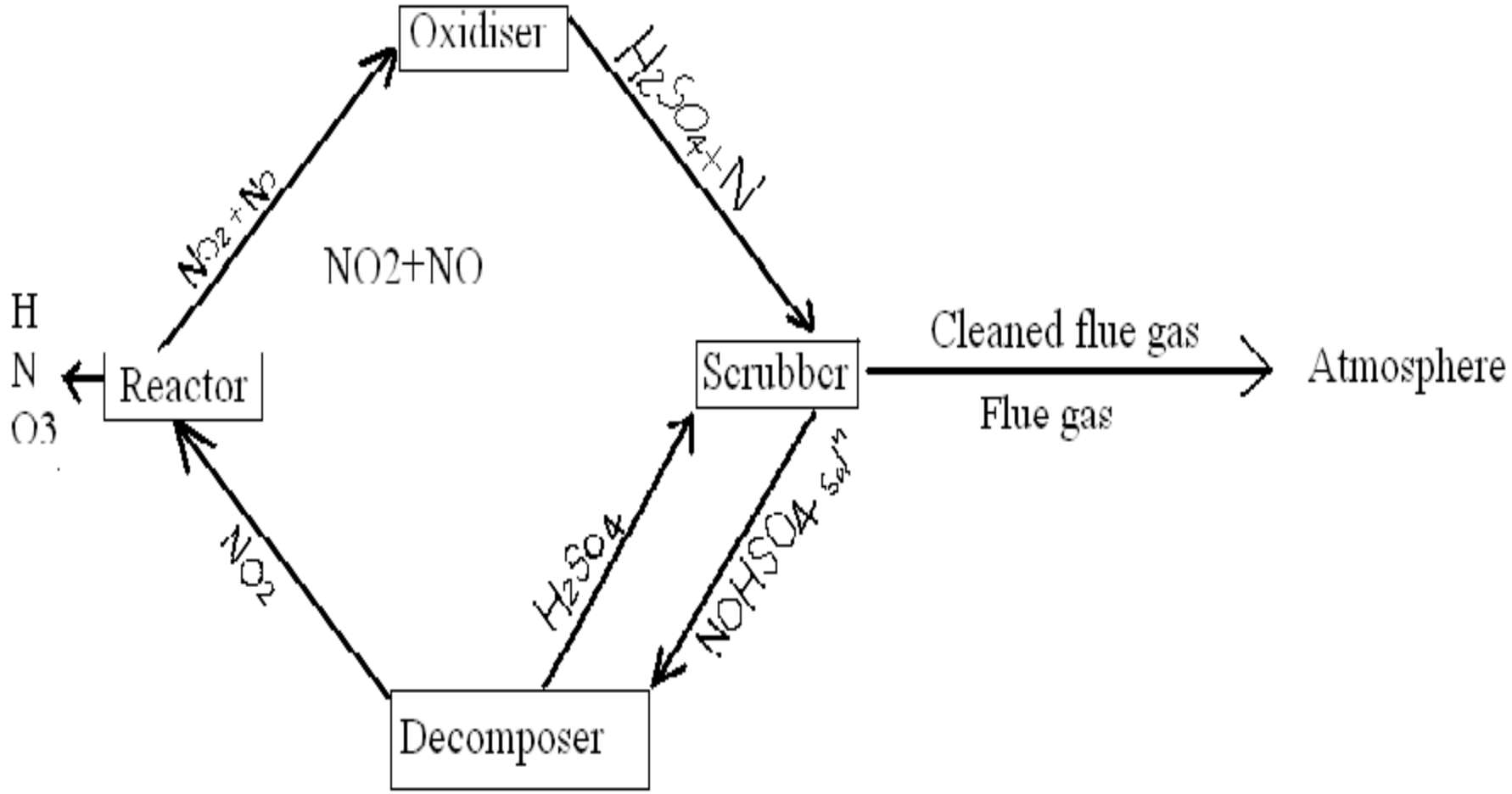
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The excess unreacted NO_2 and the formed NO are recirculated through the oxidizer (1st step).

NOx

Flue gas

NO_2, SO_2, H_2O



Air Pollution

Hydrocarbons [HCs]

More than 20 HCs have been identified in atmosphere in the areas of heavy vehicular traffic. They are methane, ethane, n and iso butane, n and iso pentane, propane, ethylene, acetylene, toluene, m-xylene, etc.

Causes:-

1) Natural sources:-

85% HCs emission is due to natural biological activity. Methane is major HC (1.8ppm) emitted by anaerobic decomposition of organic matter in water, soil and sediments by micro-organisms.

$$2[CH_2O] \longrightarrow CO_2 + CH_4$$

Mean residence time of CH_4 in atmosphere = 3 to7 years.

Air Pollution

2) Man made sources:-

15% HCs emission (i.e. $57x10^7$ tones/year) is due to the anthropogenic activities.

i) Automobile exhaust(50%)

ii) Combustion of coal, oil, gas, etc. (25%)

iii) Burning of wood refuse

iv) Rubber manufacture

v) Solvent evaporation from refineries storage tank, paint, thinner, etc.

Contribution to global HC emission : 55% petroleum,3.3% coal, 2.2% wood, 11.2% solvent evaporation & 28.3% incinerators and refuse burning.

Air pollution

Effects:-

i) HCs are thermodynamically unstable and tend to get oxidized in atmosphere by series of chemical and photochemical reactions. The end products formed are CO_2, Org.solid particles (which settle down) and water soluble Acids and aldehydes (which are washed down by rain). Some of these product are very reactive and have harmful effects on human beings (react with cell constituents) rather than HCs themselves.

The effects are:- Carcinogenic and Lachrymatory. Benzophrene reacts with DNA causing mutation and cancer.

ii) Volatile HCs and some products participate in atmospheric reactions and generates $O_{3.}$

iii) Photochemical Smog– HCs, $NO_{x,}$, some end products and free radicals undergo a series of photochemical reactions in intense sunlight and finally form ‘Aerosols’, which is characterized by specific odour and reduced visibility. This causes eye and lung irritation, vegetation damage and cracking of rubber.

Control:-

Formation of noxious photochemical smog (Aerosol-PAN) can be controlled by minimizing the emission of I^{ry} pollutants like HCs, NO_x etc.

Air Pollution

Particulates:-

Characteristics:- 1) These are generally Fe_2O_3, V_2O_5, CaO, $PbCl_2$, $PbBr_2$, fly ash. Aerosols, soot, etc. particles.

2) They are either solids or liquids, $d \approx 2x10^{-4}$ to $5x10^{+2}$ μ

3) They posses varying life times few secs to several months depending upon their size, density and turbulence of air, which controls their settling rates.

4) Their number per m^3 varies from few hundreds to several thousand. In industrial and urban areas, the number is more than a lakh per m^3. However their size and chemical nature are more vital than their number.

5) They posses excellent adsorption capacity due to their large surface areas. They absorb various organic and inorganic sps. Which encourage the heterogeneous phase reactions in atmosphere.

Air pollution

Causes:-

1) Natural sources:-

   About 2000 mts of the particulate matter is discharged to atmosphere, every year, from the natural agencies such as: 1) volcanic erruptions 2) wind and dust storms 3) salt sprays.

2) Man made sources:-

   About 450 mys/year is realesed due to man made activities like; 1) forest fires 2) burning of coal refuse and agriculral refuse, 3) mining operations 4) metallurgical processes-smelting 5) combustion of fuels 6) Industrial processes 7) power plants.

Air pollution

Effects:- i) Find particulates having size 3μ (air born asbestos, toxic metals, etc.) penetrate in nose, throot, reach lungs and creat breathing problems and irritation of lung capillaries. Prolongde exposure causes pulmonary fibrosis (Asbestos mine workers) black lung diseases (coal mine workers) and Emphysema (urban people)

ii) Air borne particulates like dust,mist,fumes soot etc cause damage to metals,paint ,sculptures,etc

iii) Particulates may influence pattern of cloud formation and snow formation.

iv) Absorb solar radiations and reduce visibility.

V) Polycyclic aromatic HCs (PAH) are imp constituents of many organic particulates. They produce a highly condensed product called soot, which can absorb many toxic trace metals such as Be,Cd, V,Cr,Ni, Mn etc and many organic like benzopyrenes those are carconogenic

Air Pollution