Organic Matter $\xrightarrow{\text{Anaerobic decomposition}}$ CH_4

$CH_4 \xrightarrow{\text{oxidised}}$ CO.

AIR POLLUTION

1.) **CO** [colourless, odourless, tasteless gas, poorly soluble in water, has lower density than air].

This gas is produced by incomplete combustion of coal[1], charcoal[2], petrol[3] & its products.

Internal combustion engines are the largest source of combustion produced CO.

[Automobiles, combustion process of stoves, furnaces, forest & bush fires, burning coal mines, factories, power plants are sources.] [Also oceanic & atmospheric reactions are the major sources of CO.]

From combustion sources, CO emission per year in the world is about 2.6×10^8 tonnes (2600 million tonnes)

→ There is a flux of CO from ocean surface to the atmosphere. In surface water, supersaturation of CO is increased in sunlight. 2 mechanisms operate for this,

→ Photochemical oxidation of organic matter

→ Biological oxidation by living marine organisms. Higher animals produce CO from breakdown of Haemoglobin.

* Source of atmospheric CO is oxidation of CH_4. Anaerobic decomposition of organic matter produces CH_4 which is oxidised to produce CO.

$$O_3 + h\nu \text{ (photochemical decomposition)} \longrightarrow O_2 + O$$

(Atomic oxygen)

$$O + H_2O \longrightarrow 2\,OH$$

(Atomic oxygen; water vapour; hydroxyl radicals)

The hydroxyl radical initiate methane oxidation. OH + Thus CO production in the atmosphere is associated with photochemical reaction.

- CO is also liberated from bile juice
- Breakdown of photosynthetic pigments in algae release CO
- Plants produce 10^8 tonnes of an CO/year on average

In upper stratosphere, CO maintains constant concentration.

In troposphere (upto 5 km) CO is oxidised to CO_2.

Imp. But when there is higher conc. of CO it forms photochemical SMOG.

→ Soil Fungi & higher plants also absorb CO in presence of sunlight & is reduced to 5-formyl-tetrahydrofolic acid.

which is fixed as Serine (amino acid) & enters protein & carbohydrate metabolism.

Imp. → In the dark, CO is oxidised to CO_2 in leaves & released in atmosphere.

Hence plants destroy CO with no dependence on light.

Toxic Effect of CO :

1.) CO causes difficulty in breathing, headace, irritation of mucous membranes.

2.) ★ It combines with haemoglobin of blood reducing its O_2 carrying capacity. (The gas is fatal over 1000 ppm causing unconsciousness in an hour & death in four hours).

→ If this gas is inhaled for few hours at even low concentration of 200 ppm, it causes symptoms of poisoning.

→ Inhaled CO combines with blood haemoglobin to form Carboxyhaemoglobin (Hb CO) about 210 times faster than O_2 can combine. Formation of Hb-CO

O_2 carrying capacity of haemoglobin is affected

CO competes with O_2 to combine with haemoglobin. It combines with Hb

decreases overall O_2 carrying capacity of blood to cells resulting into (Oxygen deficiency) ← Hypoxia.

Increase in Hb-CO level from 1–2% to 3-4% may cause Cerebral anoxia causing psykhomotor disorder activity & vision impairing.

An exposure of 120 mg/kg CO for 1hr increases Hb CO content in blood to 5%, a level usually found in blood of cigarette smokers.

Sulphur Dioxide as Primary Pollutant

Sulphur remains in atmosphere in three forms — SO_2, H_2S & sulphate particles (aerosol ~~sulphates~~)

→ Chief source of oxides of sulphur are the combustion of coal & petroleum & mobil oil (3% S). Thus most oxides come from thermal power plants & other coal based plants & smelting complexes (smelting of sulphide ores). Automobiles also release SO_2 in air.

H_2S — Source of H_2S is decomposition of organic waste. Its conc. in polluted areas reach 100 $\mu g/m^3$ while in unpolluted areas is 0.3 $\mu g/m^3$.

→ H_2S is oxidised to SO_2 at atmospheric pressure & temp. though slowly.

$H_2S \xrightarrow{\text{oxidised}} SO_2$ (Slow process)

Its reaction with Ozone is measurable

$$H_2S + O_3 \longrightarrow SO_2 + H_2O$$

→ A chain oxidation raction may occur with atomic oxygen derived from photochemical dissociation of O_3 or photochemical smog reaction.

$$O_3 + h\nu \xrightarrow{\text{Photochemical Decomposition}} O_2 + O \text{ (atomic Oxygen)}$$

* It has a sharp odour
* SO_2 is highly soluble in water.

SO_2 is oxidised to SO_4 & returned to earth through rain. Solution of SO_2 in water contains :-
SO_2, H_2SO_3 ($H_2O \cdot SO_2$), HSO_3^-, SO_3^{2-} & $S_2O_5^{2-}$ in proportions depending on pH & conc.

* Rain water has pH of 4–6 & (predominant ion is HSO_3^-)

From data collected it is estimated that mean residence time of SO_2 in atmosphere ranges from 12 hrs to six days.

Toxicity of SO_2 :-

1. Causes intense irritation to eyes & respiratory tract. Continous inhalation of this gas cause severe headache. If it reaches lungs, it causes respiratory problem.

2. Effects On Plants :-

a) Plants are affected at lower concentrations of SO_2 than human beings.

b) Continous exposure to SO_2 for considerable time 300 $\mu g/m^3$ causes

→ Lichens are sensitive to SO_2. In areas where sulphur dioxide conc. is high, lichens are absent.

→ Causes Chlorosis of leaves without cellular collapse. Pine trees are more susceptible than broad leaf trees.

→ severe leaf damage & defoliation in sensitive species.

c.) Leaf blotching, necrosis & loss of yield are the main damages caused by SO_2. (Alfalfa[1], barley[2], cotton[3] & wheat[4] are sensitive to SO_2). [Potato, onion & corn are resistant]

d.) Exposure to SO_2 causes bleaching of leaf pigments due to conversion of Chl-a to phaeophytin-a.

e.) Some plants like Nerium indicum in Delhi serves as indicators of SO_2 pollution.

SO_2 affects stomatal pores, ~~stomatal frequency~~ & trichomes as well as chloroplast sts. (f.) SO_2 enters plants through stomatal opening. (While passing through stomata SO_2 gets oxidised to H_2SO_4 or sulphate ions. Sulphuric acid aerosols are toxic to plants).

3. → Limestone & marble are severely affected by SO_2. It gets absorbed by limestone which is maximum at high relative humidity. → Absorbed SO_2 is oxidised to sulphate in the $CaCO_3$ matrix. Mechanical stress arises as molecular volume of $CaSO_4$ is greater than that of $CaCO_3$ (chemical reaction leads to formation of $CaSO_4$) which causes pores. $CaSO_4$ leaches out in rain water as its solubility in it is higher than $CaCO_3$.

Marble has low porosity so is less damaged.

4. Leather is damaged by SO_2 due to formation of H_2SO_4 on leather causing acid hydrolysis of leather protein.

5. Iron & Steel in Delhi gets corroded by SO_2 laden air, when Relative humidity is high

Photochemical Products causing Photochemical Smog

Photochemical Smog is a case of Synergism where 2 primary pollutants react with one another in presence of sunlight to produce sec. pollutant, which is highly dangerous.

eg. Primary pollutants [Hydrocarbon + nitrogen oxide (NO)] $\xrightarrow{O_2 / \text{Sunlight}}$ produce PAN (peroxyacetyl nitrate) + O_3 is also formed + PBzN (organic perox.)

This appears as yellowish brown haze called Photochemical Smog which reduces visibility.

⇒ The principle photochemical products are Olefins (1), aldehydes (2), Ozone (3), Peroxyacetyl nitrate (PAN) (4), PBzN (5) (Peroxybenzoil nitrate) & H_2O_2 (6) ; organic peroxides (7)

⇒ photochemical Smog comprises of O_3, PAN, PBzN, ...

Formed only during night or cloudy days.

Toxicity : Olefins affect plants seriously at very low conc.

a.) They wither the sepals of orchid flowers,
b.) retard opening of carnation flowers & may cause dropping of their petals.
c.) At high levels they retard the growth of tomatoes.

⇒ Olefins are produced in atmosphere from ethylene (Hydrocarbon) & are produced directly from exhaust.

Toxicity of

PAN — is an eye irritant at about 1 ppm or less. It persists for more than 24 hrs. in photochemical smog. PAN & O_3 both cause respiratory distress & are toxic to plants.

⇒ NO_x & PAN cause death of forest trees.
⇒ PAN blocks Hill reaction in plants.
⇒ PAN causes injury in Spinach, beets, celery, tobacco, pepper, lettuce, alfalfa, primose, aster etc.
⇒ It causes silvering of underside of leaves

⇒ Aldehyde of photochemical smog cause eye irritation, sore throat, respiratory irritation etc.

In 1987, Bombay experienced heavy smog for about 10 days. Formation of oxidants, particularly of O_3 when exceeds

2011. The reason was stagnant winds trapping various sources of smoke. Primary source of smoke was stubble burning, lit garbage, road dust, power plants, factories & vehicles.

Air quality.

O_3: the destroyer

Ozone is also formed in the atmosphere through chemical reactions involving pollutants like SO_2, NO_2, aldehydes on absorption of UV radiations.

TOXICITY OF OZONE

In plants O_3 enters through stomata. It damages leaves, reduce crop yields. → O_3 cause tip burn in plants.

→ At 0.02 ppm, it damages tobacco, tomato, bean, pine & other plants.

→ O_3 alone & in combination with pollutants SO_2 & NO_x is causing crop losses of over 50% in several European countries.

→ In Netherlands & Denmark O_3 presence in troposphere (atmosphere) reduced yields of potato & beans.

→ O_3 reacts with fibres, rubber, cotton, nylon & polyester & dyes. Presence of light & humidity aggravates the extent of damage.

→ O_3 hardens rubber.

→ Weakens plants & increase the infestation by pests.