UNIT 1 AIR POLLUTION

Structure

1.0 INTRODUCTION

Our present climatic conditions are relatively different from the pre-industrial period's atmosphere concerning pollution. We cannot find clean air nowadays due to atmospheric pollution. Although, developing nations like India especially with an upcoming economy, face infinite challenges with its increase in population and ubiquitous scarcity and deprivation, in meeting consequential loyalty connected with Sustainable Development Goals such as "poverty and hunger eradication". In the last 30 years, India has been growing steadily towards industrialization which leads to environmental pollution specifically air pollution. We can realize that air pollution started only after anthropogenic activities such as the burning of fossil fuels. Continuous addition of air pollutants to the atmosphere from diversified sources are accumulated in the atmosphere and changes its natural composition and show adverse effects on the environment. In the environment, the duration of stay of these pollutants will depend on the quantity of pollutants that accumulate from different sources and the ability of the cleaning mechanism of the atmosphere either to absorb or to disintegrate into harmless substances and disperse them. If it is so we need to understand some of the facts about pollution that damages the health of our beautiful natural environment including us. This unit makes you understand the basic concepts of air pollution-related facts.

1.2 OBJECTIVES

After studying this unit, you should be able to

- define air pollution and describe its constituents;
- explain various types of air pollutants and their sources;
- describe sources of volatile organic compounds and their impacts;
- explain tropospheric ozone and describe its effects and
- describe air pollution management techniques and policies.

1.3 DEFINITION OF AIR POLLUTION

According to the United States Environmental Protection Agency (2007), air pollution is defined as "the presence of contaminants or pollutant substances in the air that interfere with human health or welfare, or produce other harmful environmental effects".

"Air pollution can also be defined as the presence of impurities in the air like toxic gases, particulate matter of solid and liquid material at elevated concentrations, aerosols that interfere with human health or welfare, or produce other harmful environmental effects by changing the chemical composition of the natural environment. In other words, a substance which is potentially harmful to the natural environment and humans as well is known as air pollutant". Now we have to understand exactly what do you mean by harmful? Harmful means any negative effect that can damage and destroy all living things and the natural environment. Let us first discuss the air pollutants and their sources. Air pollutants are the substances such as any gaseous substance or aerosols or complex chemical mixtures in the atmosphere which have negative effects on living things and the environment. Air pollution is considered an alphabetical soup of gaseous and particulate pollutants mixed with the normal unpolluted constituents of air. The level of air pollution is depending on the following.

i. Quantity of pollutants released into the atmosphere

ii. Dispersion area of pollutants

iii. Removal mechanism of air pollutants.

1.4 TYPES OF AIR POLLUTANTS AND THEIR SOURCES

Pollutants are categorized into two groups. They are primary and secondary pollutants.

1.4.1 PRIMARY AIR POLLUTANTS

Primary air Pollutants: Primary pollutants are the pollutants that are the direct products of combustion and evaporation of fossil fuels. Most of the combustion processes are incomplete and involve complex compounds. The evaporation of volatile organic compounds combined with dust and smoke enters the atmosphere.

Particulate matter (PM) / Suspended Particulate Matter (SPM): They exist in liquid and gaseous form and their size is measured in terms of aerodynamic diameter (Table1.1).

Table 1.1 Size of air pollutants and their description

Particle size	Description
Less than 100 microns	'**Inhalable**' particles, enter the nose & mouth easily
Less than 10 microns (PM_{10})	'**Fine**' particles known as 'thoracic' enter the respiratory system easily
Less than 4 microns	'**Respirable**' particles enter the blood through the respiratory system
Less than 2.5 microns ($PM_{2.5}$)	**'Fine'** particles
Less than 0.1 microns ($PM_{0.1}$)	**'Ultrafine'**

The particulate matter is in the form of smoke, soot, metal powder, and dust released by wind and by atmospheric reactions. This suspended particulate matter is generated from the condensation of gases and the pattern of the wind. These particles scatter in space and absorb visible light and diminish visibility. Fine particles are composed of precursor gas such as sulphuric acid that is generated in the atmosphere by Sulphur dioxide oxidation. SO_2 is released by the combustion of fossil fuels, volcanic eruptions and various other sources. Because of the low vapour pressure of H_2SO_4, they condense into aqueous sulphate particles under any atmospheric conditions. It is produced by the various combustion process. These sulphate particles further react with gases that have low vapour pressure such as ammonia, nitric acid and organic compounds. The other key component in the SPM is organic carbon, which is a major fraction formed by the condensation of hydrocarbons released from anthropogenic and biogenic sources. Earth's surface releases soil dust, sea salt and detritus of vegetation by the mechanical action of wind. These SPM consists of particles with 1-10 micrometre diameter. Another type of SPM which is produced by gaseous condensation during the combustion process is soot mainly consists of elemental carbon and accumulated black carbon. In the atmosphere, these particles scatter the radiation beam in its path without absorption. The scattering of light radiation takes place by the process of reflection, refraction or diffraction of the beam of radiation. These particles affect the lungs, trigger cardiovascular disease, and impair the growth of lungs in children with increased mortality.

Volatile Organic Compounds (VOC), Carbon monoxide (CO), Carbon dioxide (CO_2), Oxides of Nitrogen (NO_X), Oxides of Sulphur (SO_X) and Radon (Rn) are examples of primary pollutants.

Source: Combustion of fossil fuels, and waste liberates soot or smoke which contains carbon particles. Incomplete combustion of fossil fuels releases Volatile Organic Compounds (VOC). In the presence of air and at high temperatures combustion of fuels generates nitric oxide (NO), nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4). Sulphur present in the coal oxidized during combustion releases SO_2. These oxides of sulfur are the reason to cause Sulphur Smog' due to the light absorption witnessed in the year 1952, as the London Smog episode. Chemical toxins like benzene are produced from the combustion of fuels used in transportation. Lead was added to gasoline as an anti-knocking agent and other heavy metals were also primary pollutants released from automobile exhaust. Some primary pollutants, their sources and their effects are discussed here.

Carbon monoxide: It is formed by the incomplete combustion of fossil fuels. It binds to haemoglobin in the blood and blocks the oxygen delivery to the tissues which leads to dizziness, headache, unconsciousness and finally, death occurs.

Volatile organic compounds (VOC): They are produced from incomplete combustion of fossil fuels, emissions from various industries, and evaporation of gasoline and solvents. VOCs are carcinogenic. VOCs are described in detail in the latter part of this unit.

Oxides of Sulfur (SOx): Burning of sulfur-containing fossil fuels such as coal, volcanic emissions, sea spray and microbial processes release oxides of sulphur. It reacts with nitric acid droplets to form acid rain and impairs breathing. Exposure for a longer duration to SO_2 can cause bronchitis.

Oxides of Nitrogen (NOx): Oxides of nitrogen are generated and released into the atmosphere by burning nitrogen-containing fuels, biomass at high temperatures, lightening and microbial processes. It reacts with sulphuric acid droplets in the atmosphere to contribute to acid rain. Chronic exposure may impair lung function and affect the immune system.

Radon (Rn): Radon breakdown of radium and uranium-containing rocks. Exposure to radon for a longer duration causes lung cancer.

Lead (Pb): Previously lead was used to prevent engine knockout by adding it to gasoline. It is also emitted by the burning of lead-containing fuels and solid waste and remained airborne. Lead shows toxic effects at low concentrations also. Once it is accumulated in the body that can lead to death by damaging the brain.

Chlorofluorocarbons (CFC): CFCs are released into the atmosphere from l**eakages from refrigerants and aerosols. CFCs are one main cause of depleting the** ozone layer and cause skin cancer.

According to Clean Air Act (1970) established National Ambient Air Quality Standards, Particulate matter, ozone, carbon monoxide, Sulphur dioxide, nitrogen dioxide and lead are considered 'criteria air pollutants' because US-EPA controlled them by primary and secondary pollution criteria standards. Primary standards protect public health and secondary standards prevent environmental damage.

CHECK YOUR PROGRESS 1

Note: i) Use the space given below for your answers.

ii) Check your answers with those given at the end of the unit.

1. Define air pollution.

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1.4.2 SECONDARY AIR POLLUTANTS

Secondary air Pollutants: Primary pollutants undergo some chemical reactions and produce additional unwanted compounds known as secondary pollutants. Ex: Ozone, peroxyacetyl nitrates (PAN), H_2SO_4 and HNO_3.

Sources: In the presence of sunlight VOC and NO_X both undergo reactions in the atmosphere to form ozone and these are collectively known as photochemical oxidants. NO_2 splits into atomic oxygen and NO in the presence of UV radiation and forms ozone by further oxidation. In the presence of VOCs, nitric oxide form highly reactive peroxyacetyl nitrates (PAN), Aldehydes and ketones by the process of oxidation. These repeated reactions increase the ozone concentrations in rural and urban areas. Sulfuric acid and Nitric acid produced from SO_X and NO_X are the main components of acid rain.

Ozone O_3: Tropospheric ozone is a secondary pollutant and is emitted into the atmosphere by photochemical reactions of VOCs & NOx. The ozone concentrations are likely to increase by afternoon and damage the rubber material by oxidation, damage the lungs and show adverse effects on animals and plants.

1.5 TROPOSPHERIC OZONE

Tropospheric ozone is considered a Secondary Pollutant because it is generated by a series of reactions in the Troposphere mainly by the reaction between primary pollutants such as NO_2 and oxygen-containing organic compounds. It can be easily identified even at the 0.02 ppm concentrations. Tropospheric ozone is also known as ground-level ozone, which cannot be emitted directly into the environment but is generated in the atmosphere by the chemical reactions between NOx and VOC. Since it is formed in the lower atmosphere and present in the ambient air and exposed daily to humans and the ecosystem.

These chemical reactions occur when these pollutants emitted from point sources and non-point sources react with each other in the presence of UV radiation. This reaction is also known as the photodissociation reaction of NOx. The concentration of ozone increases in the summer season in urban areas but in some countries, it can reach even higher levels in the winter season. Ozone will travel for longer distances by wind, hence rural areas can also experience the effects of ozone. In contrast to stratospheric ozone, tropospheric ozone present in the air we breathe is a harmful secondary air pollutant that has adverse health effects on the environment hence it is known as bad ozone.

The tropospheric ozone is a secondary air pollutant and not easily controlled because it is continuously created with the continuous emissions from automobile exhaust and the presence of sunlight. Ozone is continuously formed by the reaction of VOCs, NOx and atmospheric oxygen at low levels. In the winter season due to low temperatures, low intensity of light and high wind speeds the ozone concentrations are low. Whereas in the summer season at high temperatures, high intensity of light and stagnation of wind the concentrations of ozone are high relatively.

1.5.1 Tropospheric Ozone Formation

The tropospheric ozone formation is dependent on many precursors. Dear learner here we would like to give a simple way to understand the formation of tropospheric ozone.

1. Some portion of the ozone is transported from stratosphere to troposphere through tropopause which is a precursor for tropospheric hydroxyl ion (OH). The transportation rate of ozone is in the range of 1-2 X 10^{13} moles/year. Each ozone molecule that enters the troposphere can produce two hydroxy molecules. A portion of the transferred ozone is consumed by some

reactions in the troposphere and the remaining portion is deposited on the surface of the earth. Apart from this, in the troposphere, the ozone is formed by the following reactions.

2. The tropospheric ozone is formed by the reaction between oxides of nitrogen, carbon monoxide and VOC in the presence of sunlight, hence these are also called ozone precursors. The major source of these ozone precursors are emissions from vehicles, industries and solvents. The reactions involved in the formation of ozone are as follows.

Oxidation of CO by hydroxyl ion generates peroxyl radical (R1), which undergoes self-reaction that gives rise to hydrogen peroxide (H_2O_2) (R2). Some of the hydrogen peroxides undergo photolysis to produce hydroxyl radicals and because of their high soluble nature in water, they can be removed from the atmosphere by rain (R3). Hydrogen peroxide reacts with additional hydroxyl radical to produce peroxyl radical again (R4). The peroxyl radical in the presence of nitric oxide regenerates hydroxyl radical and nitrogen dioxide (R5) that immediately photolyze to produce ozone (R6). Hence, the net reaction is the generation of ozone (R7) in a chain reaction initiated by peroxyl radical and terminated by the loss of peroxyl radical in reaction (R2) through propagation reactions in the presence of abundant NOx. The coupling reaction between ozone, oxides of nitrogen and peroxyl radical is shown in Figure 1.1.

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \quad \text{(R1)}$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad \text{(R2)}$$

$$H_2O_2 \xrightarrow{h\upsilon} 2OH \quad \text{(R3)}$$

$$H_2O_2 + OH \longrightarrow HO_2 + H_20 \quad \text{(R4)}$$

$$HO_2 + NO \longrightarrow NO_2 + OH \quad \text{(R5)}$$

$$NO_2 + O_2 \xrightarrow{h\upsilon} NO + O_3 \quad \text{(R6)}$$

$$CO + 2O_2 \qquad CO_2 + O_3 \quad \text{(R7)}$$

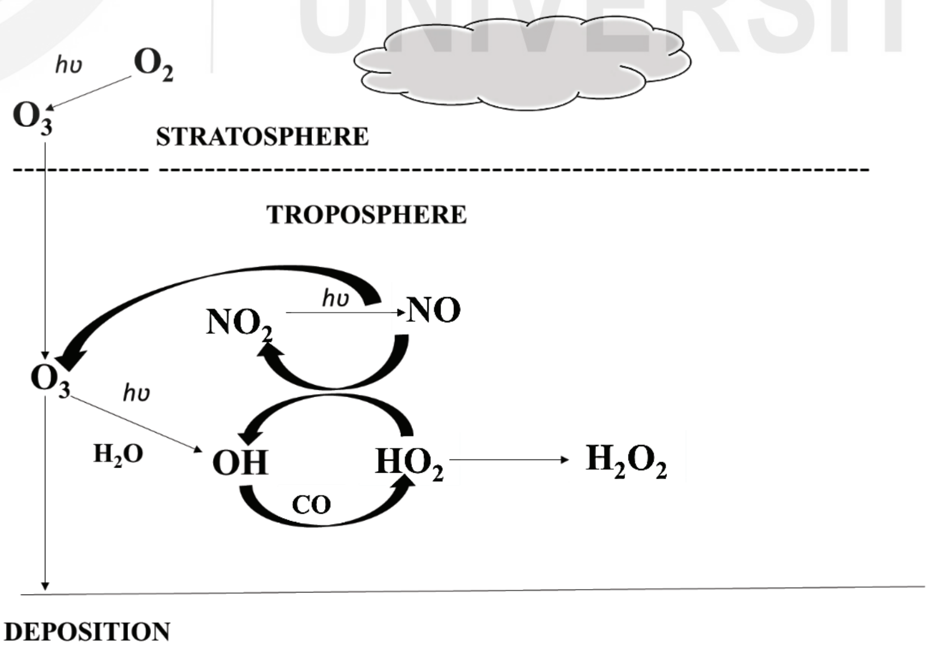

Fig. 1.1 Mechanism of O_3 generation in a chain reaction cycle

1.5.2 Tropospheric Ozone Concentration

The concentrations of tropospheric ozone depend on the influence of various concomitant processes such as precursors gas-phase surface emission, transportation, meteorological parameters like temperature and wind, hydrologic cycle, solar radiation and exchanges between stratosphere-troposphere (STEs). Monitoring of ozone can be done both horizontally and vertically in space. If we will consider the vertical dimension, the space is divided into lower, middle troposphere and stratosphere. The lower troposphere is termed the boundary layer where ambient air is present. In the horizontal dimension, often the space is divided into socio-economic zones like urban, rural and remote regions. The tropospheric ozone concentrations at the ground level are due to the following reasons.

- Local photochemical reactions between NOx and VOCs are emitted from both natural and anthropogenic sources. Once ozone is formed it travels for long distances. This dispersion is also known as **the Urban O_3 plume.**
- Mixing of O_3 rich air at the lower tropospheric boundary layer with ambient air results in an increase in the O_3 concentrations during the morning and this increase in ozone levels is independent of local region production of photochemical reactions.
- Due to the mesoscale transport of ozone from long distances and present in an area where the production of ozone is nil.
- Invasion of stratospheric ozone into the troposphere due to the tropopause folding events that occurred on the backside of a frontal system that results in a hole in the tropopause, through which the stratospheric ozone enters into the troposphere. And this exchange is minimum from July-October in a year.
- Mid tropospheric ozone formed from photochemical reactions transported to the lower troposphere.
- Removal of tropospheric ozone by chemical scavenging by most potential chemical scavengers such as nitric oxide.
- Removal of tropospheric ozone is also done by physical scavengings such as rain washout and chemical decomposition mechanisms which are temperature-dependent.

Tropospheric ozone is a secondary pollutant and a greenhouse gas. The source of earth's heat is solar energy, which is transferred from the Sun to the Earth by radiation energy and is transformed to heat energy on the surface of Earth. The earth has to balance this input of absorbed solar radiation with an output of terrestrial radiation. Some of the reflected solar radiation from the earth is captured by greenhouse gases in the atmosphere and radiated back to the Earth, resulting in the surface warming known as the greenhouse effect. Dear learner as you have learnt, in the previous courses trapping terrestrial radiation by natural greenhouse gases is one of the key factors for maintaining the Earth's surface temperature above the freezing point. The ozone concentrations in the troposphere are influenced by other greenhouse gases in different regions.

For example, the NOx and CO concentrations are high at midlatitudes of the northern region in the lower troposphere showing that there is more fossil fuel combustion. In the upper troposphere, the concentration of NOx is more due to lightning. The NOx concentrations will be balanced in the range of 10-50 parts per trillion by volume in the entire troposphere. The concentrations of tropospheric ozone increase with altitude due to the absence of upper troposphere chemical loss. In the northern hemisphere, the concentrations of ozone are higher than southern hemisphere because of abundant NOx.

In the tropics, the concentrations of OH are highest, where the concentrations of water vapour and UV radiation are high, and maximum in the mid-troposphere due to the opposite vertical trends of water vapour that will decrease with altitude and UV radiation that will increase with altitude. Concentrations of hydroxyl radical tend to be higher in the northern than in the southern hemisphere due to the higher O_3 and NOx concentrations and will be compensated for the swift loss of OH in the northern hemisphere due to elevated concentrations of carbon monoxide. Increasing the concentrations of NOx and O_3 will increase OH, whereas the increase in CO and hydrocarbons deplete the concentration of OH since CO and CH_4 have longer lifetimes than NOx and O_3, their anthropogenic accumulations are evenly spread in the troposphere.

1.5.3 Health Impacts

Ozone is a powerful oxidizing agent and can irritate the muscle in the passage of air and trap the air in the alveoli in humans leading to the breathing problems such as wheezing, breath shortness, cough, sore throat, inflammation of the airways. In higher concentrations, it worsens the lung ailments like asthma, bronchitis and emphysema. It weakens lung functioning there by humans experience recurrent asthma attacks, susceptible to infection and finally cause Chronic Obstructive Pulmonary Disease (COPD). Long term exposure aggravates asthma, permanent lung damage and finally leads to death and irregular lung development in children.

Impact on Ecosystem

The adverse effects of ozone extend to plant ecosystems in sensitive species of vegetation in forests, and parks and destroy them, particularly during the growing season. If the ozone concentrations are high in the atmosphere, it reduces the process of photosynthesis thereby reducing the plant's growth. In sensitive plants like tulip poplar, white pine etc., it increases the risk of disease, copes up with harsh weather, and insects and shows certainly visible evidence on the plants. In some species, it has adverse effects individually and negative effects on the whole species diversity, behaviour towards other plant species in the forest and alters the water and nutrient cycle.

CHECK YOUR PROGRESS 2

Note: i) Use the space given below for your answers.

ii) Check your answers with those given at the end of the unit.

1. Describe the formation of tropospheric ozone.

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2. Which factors influence the concentrations of tropospheric ozone?

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1.6 VOLATILE ORGANIC COMPOUNDS

- Volatile organic compounds are one of the significant categories of air pollutants present at the ground level in urban regions and industrial areas. There are many organic compounds listed under VOC with different definitions. If we see by term volatile organic compounds suggests that these compounds exist as liquids and solids at normal temperature and pressure but in the atmosphere, they exist as gases. As per definition any organic compound whose vapour pressure is less than 760torr and more than 1, at 20^0C, and the boiling points range from 50^0-100^0C to 240^0-260^0C.
- According to 40 CFR Part 51.100. "Volatile Organic Compounds (VOC) are any compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions". VOCs have various levels of reactivity and have varying levels of formation of ozone. Some VOCs undergo reactions slowly and some produce less ozone. Hence, local regions experience different levels of adverse effects on exposure to ozone.
- **1.6.1 Sources**: VOCs are released into the atmosphere as a consequence of anthropogenic activities, such as evaporation of petrol from vehicles, storage & distribution of petrol, numerous industrial processes (oil refining, chemical manufacture, oil and gas production etc.), photocopying, cosmetics, tobacco smoke, solvents, landfills, food processing units and agricultural activities. Natural biogenic processes like discharges from plants, animals, forest fires and anaerobic processes in wetlands are also responsible for VOC emissions.
- **Biogenic Sources:** Volatile Organic Compounds are ozone precursors and most of them are released from the terrestrial ecosystem. Biogenic Volatile Organic Compounds (BVOCs) are released from a functional group of plants and are strictly regulated by meteorological actions. Isoprene (C_5H_8) and monoterpene ($C_{10}H_{16}$) are the some of the most abundant biogenic species in terrestrial vegetation. These emissions are temperature-dependent because of the rate of photosynthesis. BVOCs are one of the important constituents of the atmosphere and influence tropospheric chemical reactions.
- According to EPA standard method TO 15/17, the list of 62 VOCs is presented in Table 1.1

Table1.1 List of 62 VOCs as per EPA Standard TO 15/17

Acetone	Ethyl dibromide (1,1-Dibromoethane)	Ethanol
Benzene	4-Ethyltoluene	Ethyl acetate

Benzyl chloride	Trichlorofluoromethane (Freon 11)	Ethyl benzene
Bromoform	Dichlorodifluoromethane (Freon 12)	1,4-Dioxane
Bromomethane	1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113)	Propylene
Bromodichloromethane	1,2-Dichlorotetrafluoroethane (Freon 114)	Styrene
1,3-Butadiene	Hexachloro-1,3-butadiene	Carbon disulfide
2-Butanone (MEK)	2-Hexanone (MBK)	Carbon tetrachloride
Dibromochloromethane	4-Methyl-2-pentanone (MIBK)	Chlorobenzene
1,2-Dichlorobenzene	Methylene chloride	Chlorethane
1,3-Dichlorobenzene	Methyl-tert-butylether (MTBE)	Chloroform
1,4-Dichlorobenzene	2-Propanol	Cyclohexane
1,1-Dichloroethane	1,1,2,2-Tetrachloroethane	Chloromethane
1,2-Dichloroethane	Tetrachloroethene	Heptane
1,1-Dichloroethene	Tetrahydrofuran	Toluene
cis-1,2-Dichloroethene	1,1,1-Trichloroethane	o-Xylene
trans-1,2-Dichloroethene	1,1,2-Trichloroethane	m-Xylene
1,2-Dichloropropane	Trichloroethene	p-Xylene
cis-1,3-Dichloropropene	1,2,4-Trichlorobenzene	Vinyl acetate
trans-1,3-Dichloropropene	1,2,4-Trimethylbenzene	Vinyl chloride
Hexane	1,3,5-Trimethylbenzene	

1.6.2 Impacts

- Ozone depletion in the stratosphere
- Ozone formation at ground level
- Chronic health effects

Most of these impacts are already discussed in the previous sections. The known chemicals in general use under VOCs are Benzene, Toluene and Xylene (BTX). The BTX compounds are toxic in nature and harmful pollutants.

Health Effects

Acute Effects: On exposure to these chemicals' humans experience dizziness, Headache, Nausea/Vomiting, Eye irritation/watering, Nose irritation, Throat irritation, Asthma exacerbation.

Chronic Effects – Cancer, damage of Central Nervous System, Liver & Kidney damage.

Ground-level ozone formation

Ozone is an important photochemical oxidant. Ozone in the troposphere is formed by the reaction of VOC and oxides of nitrogen in the presence of UV radiation. Ozone is formed in the stratosphere in the same way as in the troposphere but the source of oxygen atoms is different. In the stratosphere, the oxygen atom is available from the photodissociation reaction of the oxygen molecule in the presence of UV radiation at < 240nm whereas in the troposphere oxygen atom is from the photodissociation reaction of nitrogen oxides under UV radiation at > 290nm.

The overall reaction is as follows

$$NO + VOC \longrightarrow NO_2$$

$$NO_2 \xrightarrow[>290nm]{>h\nu} NO_{(g)} + O_{(g)}$$

$$O_{(g)} + O_{2\,(g)} \longrightarrow O_{3(g)}$$

1.6.3 Management and Policy

a. **The Air (Prevention and Control of Pollution) Act**, 1981 in India is an Act of the Parliament of India to control and prevent air pollution and was amended in 1987. This is the first act of India established to prevent, control and abate air pollution.

b. **The Ozone-Depleting Substance (Regulation and Control) Rules, 2000,** states that under Article 5, 1st paragraph of the **Montreal Protocol Regulation** production and consumption of ozone-depleting substances. This act also deals with monitoring and reporting requirements. In India, MoEFCC has established an Ozone Cell that carries out the tasks of the phaseout of the ozone-depleting substance.

c. National level strategy for pan India implementation to handle the problem of increasing air pollution across the country in a comprehensive manner in the form of the National Clean Air Programme (NCAP) was launched under the Minister of Environment, Forest and Climate Change. "The main objective of the NCAP is comprehensive mitigation actions for prevention, control and abatement of air pollution besides augmenting the air quality monitoring network across the country and strengthening the awareness and capacity building activities." The NCAP function with an aim of collaborative, multi-scale and cross-sectoral coordination between the relevant central ministries, state governments and local bodies.

   There is no specific legislation of VOC specifically in India besides National Ambient Air Quality Standard for Benzene by the Central Pollution Control Board of India. Worldwide, the United States Occupational Safety and Health Administration (OSHA) and World Health Organization (WHO) have suggested a few regulations and guidance for VOCs and made them not compulsory for individual governments to follow.

International Conventions

The 1991 Geneva Protocol

The 'Geneva Protocol on the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes' was signed in Geneva (Switzerland) on 18 November 1991. The main objective of this protocol is the reduction of Volatile Organic Compounds (VOCs), which is a key air pollutant that is responsible for the formation of ground-level ozone. The options are given by this Protocol for the reduction in emission targets that have to be chosen upon signature or upon ratification. The first option is by the year 1999 a thirty per cent reduction in emissions of volatile organic compounds. The second option is a 30% reduction within a Tropospheric Ozone Management Area (TOMA) mentioned in annexe I to the Protocol and by ensuring the total 1999 national emissions should not exceed the levels of 1988. Thirdly, if the 1988 emissions did not exceed specified levels then Parties may choose for stabilization at that emission level of 1999.

The 1999 Gothenburg Protocol

Gothenburg protocol is to Abate Acidification, Eutrophication and Ground-level Ozone and signed on 30th November 1999 in Gothenburg, Sweden. The main objectives of this protocol are to control and reduce emissions, establish national emission ceilings for 2010-2020 for four pollutants (SO_2, NOx, NH_3) including VOC and provide negotiation facilities based on "Scientific Assessments of Pollution Effects and Abatement Options". The protocol also emphasizes stringent limit values for emission sources such as combustion, electricity production, dry cleaning, paints and aerosols have to be controlled. The protocol was amended in 2012, to include national emission reduction commitments to be achieved by 2020 and beyond.

1.7 ATMOSPHERIC DEPOSITION OF AIR POLLUTANTS

The adverse effects of these pollutants may be additive, synergistic or antagonistic but more often synergistic. One of the important effects of air pollution is the smog that reduces visibility and is comprised of tropospheric ozone (O_3). In this unit, we will discuss different types of smog.

1.7.1 Photochemical Smog

The primary pollutants trapped in the lower atmosphere on exposure to UV radiation from the sun form a thick blanket of smog known as photochemical smog. The pollutants like ozone (O_3), hydrogen peroxide (H_2O_2), organic peroxides (ROOR'), organic hydroperoxides (ROOH), and peroxyacetyl nitrates (RCO_3NO_2) PAN are the main pollutants of photochemical smog. The latter is formed by the irradiation of mixtures of alkanals, ozone and nitrogen dioxide. The oxides of nitrogen emitted from the combustion process are released into the atmosphere and initiate the process of ozone formation and photochemical smog. The reactions involved in the formation of photochemical smog are explained here. Small amounts of atmospheric oxides of nitrogen are sufficient to initiate atmospheric chemical reactions for ozone formation and photochemical smog formation.

$$NO_2 \xrightarrow[M]{h\nu} NO + O \qquad (R8)$$

$$O + O \longrightarrow O_3 \qquad (R9)$$

$$O_3 + NO \longrightarrow NO_2 \qquad (R10)$$

$$O_3 \longrightarrow O + O_2 \qquad (R11)$$

$$O + H_2O \xrightarrow{h\nu} 2OH \qquad (R12)$$

$$HCHO \longrightarrow H. + HCO. \qquad (R13)$$

$$HCHO + OH. \longrightarrow HCO. + H_2O \qquad (R14)$$

$$H. + O_2 \xrightarrow{M} HO_{2.} \qquad (R15)$$

$$HCO. + O_2 \longrightarrow HO_{2.} + CO \qquad (R16)$$

$$HO_2. + NO \longrightarrow NO_{2.} + OH. \qquad (R17)$$

$$OH. + NO_2 \longrightarrow HNO_3 \qquad (R18)$$

Note: The M in R9 is any 3rd molecule that is inert that is required to stabilize the intermediate by absorbing vibrational energy in its excited state.

The reaction initiates with the photolysis of nitrogen dioxide (R8), to produce nitric oxide and an oxygen atom. This dissociated oxygen atom quickly reacts with an oxygen molecule in (R9) to produce ozone. Once ozone is formed it reacts with nitric oxide (R10) to reproduce nitrogen dioxide. The steady-state ozone concentration is predicted and measured based on initial concentrations of nitrogen dioxide. At λ, 315 nm, ozone dissociates into an oxygen atom in the excited state and oxygen molecule (R11). Sometimes excited oxygen atom strikes water molecules and generates hydroxyl radicals (R12). The hydroxyl radical unlike other radicals formed from organic molecules does not react with abundant oxygen, but it reacts with other compounds such as CO, R-CHO, hydrocarbons etc. The next reaction in the series starts from formaldehyde, which undergoes photolysis and reacts with hydroxyl radicals resulting in hydrogen radical and formyl radical (R13 & R14). The hydrogen radical reacts with oxygen molecule swiftly to form hydroperoxyl radical (R15) and the formyl radical reacts with oxygen molecule resulting in both hydroperoxyl radicals and carbon monoxide (R16). These hydroperoxyl radicals react further with nitric oxide to reproduce nitrogen dioxide and hydroxyl radicals (R17). In the end, hydroxyl radical reacts with nitrogen dioxide to form nitric acid (R18).

Next in the reaction series that contributes to the photochemical smog, we will see the next higher aldehyde that is acetaldehyde, which undergoes a series of reactions in two pathways like formaldehyde, photolysis and reaction with hydroxyl radical to produce peroxyacetyl nitrate (PAN), which is a key component in the photochemical smog. The reactions involved in the formation of PAN are as follows.

$$CH_3CHO \longrightarrow CH_3 + HCO \qquad (R19)$$

$$CH_3CHO + OH \longrightarrow CH_3CO + H_20 \qquad (R20)$$

$$CH_3 + O_2 \longrightarrow CH_3O_2 \ (R21)$$

$$CH_3CO + O_2 \longrightarrow CH_3COO_2 \qquad (R22)$$

$$CH_3O_2 + NO \longrightarrow NO_2 + CH_3O \qquad (R23)$$

$$CH_3O + O_2 \longrightarrow HCHO + HO_2 \qquad (R\ 24)$$

CH_3COO_2+NO ⟶ NO_2+CH_3COO ________ (R25)

CH_3COO+O2⟶ CH_3O_2+$C0_2$ ________ (R26)

CH_3COO_2+NO_2 ⟶ $CH_3COO_2NO_2$ (PAN)________ (R27)

The photolysis reaction (R19) of acetaldehyde results in methyl radical and formyl radical. In the reaction with hydroxyl radical, it produces acetyl radical with the liberation of H_2O (R20). The methyl radical generates methyl peroxy radical in reaction with O_2(R21), while acetyl radical reacts with oxygen and produces acetyl peroxy radical (R22). The methyl peroxy radical rapidly reacts with nitric oxide to yield nitrogen dioxide and methoxy radical (R23). Likewise, in reactions (R24 - R27) resulting in peroxyacetyl nitrate. The general reactions representing the photochemical smog are as follows.

The general reactions of Photochemical Smog are given below:

1) NO + VOC → NO (nitrogen dioxide)
2) NO_2 + UV → NO + O (nitric oxide and molecular O)
3) O + O_2→ O_3 (ozone)
4) NO_2+ VOC → PAN (peroxyacetyl nitrate)

Overall reaction:

NO + VOC + O_2+ UV → O_3 + PAN + other particulates

1.7.2 Industrial Smog

Industrial smog is well known as **grey** or **black** smog that is formed in cold and humid temperatures, particularly in urban areas where industrial pollution is more with the emission of sulfur. The sulphur reacts with water vapour in the atmosphere to produce sulphur dioxide. SO_2 is oxidized to form sulphuric acid and sulphate particles as soon as it was produced. On catalytic oxidation of industrial dust particles in the presence of water vapour in the atmosphere makes the droplets more acidic. All these particulates form a thick layer of haze known as **acid smog** or **industrial smog**. The general reactions to industrial smog are given below.

1) C + O_2→ CO (Carbon dioxide)
2) S + O_2 → SO (Sulfur dioxide)
3) SO + O_2→ SO + O (Sulfur trioxide)
4) SO^2 + H_2 O → H_2 SO (Sulfuric acid)
5) H_2 SO_4 + NH → (NH^4) SO_4 (Solid ammonium sulfate)

1.7.3 Acid Precipitation

Acid precipitation is the type of deposition such as rain, fog, mist or snow that is relatively acidic than normal. The pH of rainwater without pollutants is approximately 5.6. Acid deposition is the deposition of rain and dry acidic particle with a pH of less than 5.5. It consists of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) mixture. Sulfur and nitrogen oxides are released into the troposphere either by the burning of fossil fuels or by natural sources. They are oxidized by hydroxyl radicals to sulfuric acid and nitric acids which dissolve in rainwater and reach the ground as acid deposition. Wet acid deposition is known as **acid rain.** Dry deposition is called **acid fog.**

CHECK YOUR PROGRESS 3

Note: i) Use the space given below for your answers.

ii) Check your answers with those given at the end of the unit.

1. What impact does VOCs pollution have on human health?

…………………………………………………………………………………
…………………………………………………………………………………
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1.8 LET US SUM UP

Several forms of air pollutants exist in the form of gases, fumes, clouds, smoke, mist, fog, smog, haze, dust, aerosols, etc. They are classified as natural/anthropogenic, primary/secondary, particulates/gases, ambient air/indoor air/global, stationary/mobile etc. Air pollutant concentrations are measured in the form of their threshold values which are different for different pollutants. In this unit, the emphasis has been made on the chemistry of tropospheric ozone formation and volatile organic compounds. Atmospheric depositions of air pollution such as industrial, photochemical and acid rain have been discussed. Above these values, the pollutants show adverse effects on human beings. The common problem is respiratory tract infection, bronchitis and other diseases that can occur due to inhalation of toxic pollutants. Pollutants such as arsenic, lead, fluoride, insecticides and pesticides affect human beings adversely. The unit is concluded with some international protocols on VOC.

1.9 KEY WORDS

Acid Deposition: Any form of acid precipitation and also the fallout of dry acid particles.

Acid Precipitation: Includes acid rain, acid fog, acid snow, and any other form of precipitation that is more acidic than normal (i.e., less than pH 5.6). Excess acidity is derived from certain air pollutants; namely, sulphur dioxide and oxides of nitrogen.

Aerosols: Microscopic liquid and solid particles originating from land and water surfaces carried up into the atmosphere.

Convection: The vertical movement of air due to atmospheric heating and cooling.

Ecosystem: A group of plants, animals and other organisms interacting with each other and with their environment in such a way as to perpetuate the grouping more or less indefinitely.

Greenhouse Effect: An increase in the atmospheric temperature caused by increasing amounts of carbon dioxide and certain other gases that absorb and trap heat, which normally radiates away from Earth.

Photochemical Smog: The brownish haze that frequently forms on otherwise clear, sunny days over large cities with significant amounts of automobile traffic. Photochemical smog results largely from sunlight-driven chemical reactions among nitrogen oxides and hydrocarbons, both of which come primarily from auto exhausts.

Primary Pollutants: Pollutants are released directly into the atmosphere mainly as a result of burning fuels and wastes, as opposed to secondary pollutants.

Secondary Air Pollutants: Air pollutants resulting from reactions of primary air pollutants resident in the atmosphere. Secondary air pollutants include ozone, other reactive organic compounds, and sulphuric and nitric acids.

Volatile Organic Compounds: A category of major air pollutants presents in the air in the vapour state. The category includes fragments of hydrocarbon fuels from incomplete combustion and evaporated organic compounds such as paints, gasoline, and cleaning solutions. VOCs are major factors in the formation of photochemical smog.

1.10 SUGGESTED FURTHER READING/ REFERENCES

1. http://cpcbenvis.nic.in/air_pollution_main.html#
2. Manahan, Stanley E. "Frontmatter" Fundamentals of Environmental Chemistry Boca Raton: CRC Press LLC,2001
3. Sources and Control of Volatile Organic Air Pollutants-United States Air Pollution Training Institute (APTI) November 2002 Environmental Protection Environmental Research Center, MD 17 (Revision 2) Agency Research Triangle Park, NC 27711
4. Fundamentals of Environmental Chemistry by A.K. De
5. Environmental Chemistry by Stanley Manahan
6. Textbook of Environmental Science by Pearson.
7. https://www.atmos-chem-phys.net › acp-15-8889-2015

1.11 ANSWERS TO CHECK YOUR PROGRESS

Check Your Progress 1

1. Please refer to section 1.3

Check Your Progress 2

1. Please refer to section 1.5.1
2. Please refer to section 1.5.2

Check Your Progress 3

1. Please refer to section 1.6.2