Chapter 14

Environmental Chemistry (For Advance)

INTRODUCTION

Environmental studies encompass the interconnected examination of biological, social, economic, physical, and chemical aspects in relation to our surroundings. This field delves into the complex web of relationships between living organisms and their environment. One prominent and pervasive issue within this realm is environmental pollution, which stands as a paramount global health threat.

Environmental pollution is defined as the undesirable alteration in the physical, chemical, or biological attributes of air, water, and land. This deleterious transformation poses a significant risk to human life and various other living organisms. Moreover, pollution adversely impacts living conditions, cultural assets, and impedes industrial progress. The repercussions extend to the detriment of our valuable resources, making it imperative to address and mitigate the multifaceted challenges posed by environmental pollution.

Environmental Pollution

Environmental chemistry is the scientific discipline that focuses on the chemical processes and occurrences within the environment

The environment means surroundings. It has 4 following components.

(I) Atmosphere

(A) Function of the Atmosphere

- It encompasses all the gases vital for sustaining life on Earth.
- It serves as a transporter of crucial water vapor necessary for all living organisms.
- O3, found within it, functions as a shield against harmful U.V. radiations.
- By absorbing incoming solar infrared radiation and re-emitted heat from the Earth, it regulates the planet's thermal equilibrium.

(B) Pressure, Weight and Temp of the Atmosphere

- Pressure of atm = 10^5 N/m^2
- Mass of atm = 5×10^{15} tones.
- Temp. of atm = – 100° C to 1200° C
- Increases in altitude of 5 km, the pressure and the density of air decrease by one half.

(C) Composition of Air (or atmosphere)

- It is divided in 3 categories.
- Major component = N_2, O_2, water vapour.
- Minor component = Ar, CO_2
- Traces component = He, Ne, Ar, Kr, CH_4, H_2, CO, N_2O, SO_2, NO, NO_2, HCHO, NH_3, O_3.

(D) Regions (or structure) of the Atmosphere

It has 4 regions. These regions are defined by the temp.

Region	Altitude from earth's surface	Temp. range	Species present or gasses present
Troposphere vapour	0-11 km	decrease from 15 to – 56°C	N_2, O_2, CO2, H_2O
Stratosphere or crayons sphere	11-50 km	increase from – 56° to – 2°C	N_2, O_2, O_3,0-atm
Mesosphere	50–85 km ionosphere	decreases from – 2° to – 92°C	N_2, O_2, NO^+, O_2^+
Thermosphere	85 – 500 km ionosphere	increase from – 92° to 1200°C	O_2^+, O^+, NO^+, e^-

(II) Hydro Sphere (75% of earth)

The part in which contain water in the form of sea, oceans, rivers, lakes, ponds.

(III) Lithosphere

It is solid component of the earth consisting of soil, rocks, mountains.

(IV) Biosphere

It is the part of the lithosphere, hydrosphere and atm. Where living organism interact with these parts and lived together.

Ex. Green plants.

Environmental Pollution & Environmental Pollutant

Environmental pollution is defined as the introduction of unwanted substances into the air, water, or soil through natural processes or human actions, resulting in a deterioration of environmental quality. These undesirable substances introduced into the environment are referred to as pollutants.

Causes of pollution

- Fast population growth.
- Rapid urbanization.
- Excessive industrialization.
- Use of pesticides in agriculture.

Types of pollutants: 2 types

(I) Primary and Secondary Pollutants

(A) Primary Pollutants

Those which after their formation enter the environment and remain as such.

Ex.: NO, NO_2, SO_2

(B) Secondary Pollutants

The harmful material which are formed by chemical reaction between primary pollutants in the atm.

Ex.: Hydrocarbon + Oxide of nitrogen $\xrightarrow{hv}$ compound

(II) Bio Degradable and Non Bio Degradable Pollutants

(A) Bio Degradable Pollutants

Materials like cow dung are readily biodegradable by microorganisms and are typically non-harmful. However, when present in excessive quantities within the environment, they may not undergo complete degradation and can consequently become pollutants.

(B) Non Bio Degradable Pollutants

Materials like Hg, Al, and DDT do not readily degrade, or their decomposition occurs at a very slow pace. Even in minute quantities, their presence in the environment can be highly detrimental. These substances may interact with other compounds in the environment, leading to the formation of even more toxic compounds.

ATMOSPHERIC POLLUTION

The introduction of particulate matter, gases, and various elements into the air can lead to detrimental effects on vegetation, animals, human beings, as well as human assets and resources. The Earth's atmosphere consists of distinct layers, with the lowest layer being the troposphere. This layer comprises dust, water vapor, and clouds. In contrast, the stratosphere contains the ozone layer.

Atmospheric pollution encompasses both tropospheric and stratospheric pollution. Tropospheric pollution is concerning as it directly affects the layer closest to the Earth's surface, impacting the elements within it and posing risks to living organisms and resources. Simultaneously, stratospheric pollution can have significant consequences, particularly concerning the depletion or alteration of the ozone layer. Understanding and addressing atmospheric pollution is crucial for safeguarding the health of our environment and its diverse components.

Tropospheric Pollution

Extending up to an elevation of 10 km from sea level, the Earth's atmosphere plays host to pollutants categorized into two main types: Primary pollutants and Secondary pollutants. Primary pollutants persist in the environment in the same form as they are initially produced. An example of this is carbon monoxide, which retains its original chemical structure throughout its presence in the atmosphere.

In contrast, secondary pollutants are generated through reactions or changes that occur in the environment, often stemming from primary pollutants. This category of pollutants is induced by both gaseous and solid substances. Examples include natural occurrences such as fog, pollen grains, bacteria, volcanic eruptions, as well as human-made sources like dust, smoke, mist, fumes, gases, and vapors. Understanding the distinctions between primary and secondary pollutants is crucial in comprehending the diverse origins and impacts of atmospheric pollution.

Gaseous Air Pollutants

(1) Carbon Oxides

(i) Carbon Monoxide

Carbon monoxide is a gas that lacks color and odor. Its production stems from the incomplete combustion of fuels, and in natural settings, it arises from oceanic processes or the decay of organic matter facilitated by bacteria. The substance poses a significant health risk as it is poisonous. Upon inhalation, carbon monoxide combines with hemoglobin, forming carboxyhemoglobin, a stable compound that is 300 times more enduring than its oxygen-carrying counterpart. This interaction diminishes the blood's capacity to transport oxygen, leading to symptoms such as dizziness, headaches, reduced vision, cardiovascular irregularities, and asphyxia.

It's noteworthy that cigarette smoke contains a substantial amount of carbon monoxide. The exposure to this gas in pregnant women through smoking is associated with adverse outcomes such as premature births, the birth of deformed babies, and spontaneous abortions. Understanding the sources and health implications of carbon monoxide is vital for developing effective strategies to mitigate its impact on both environmental and human well-being.

Controlling of CO pollution

Human-induced carbon monoxide (CO) pollution primarily stems from the utilization of internal combustion engines in vehicles. To mitigate CO emissions, various alterations are employed in both the engine and the fuel quality. These measures include:

- Calibration of the carburetor to achieve an appropriate air-fuel ratio.
- Adjustment of the exhaust system to promote complete combustion.
- Installation of a catalytic converter within the exhaust pipe to convert toxic gases into harmless ones.

- Implementing engine modifications by specific manufacturers.
- Substituting traditional gasoline with Compressed Natural Gas (CNG) and Liquefied Natural Gas (LNG).
  CNG = Condensed Natural Gas.
  LNG = Liquified Natural Gas.

(ii) Carbon Dioxide

Carbon dioxide is naturally generated through processes such as volcanic eruptions and respiration. Additionally, the combustion of fossil fuels is a significant anthropogenic source of this gas. Green plants play a crucial role in regulating elevated levels of CO_2 through the process of photosynthesis. Notably, carbon dioxide is classified as a greenhouse gas, contributing to the phenomenon of global warming.

Exposure to heightened concentrations of carbon dioxide can have adverse effects on human health, manifesting as symptoms like headaches, nausea, and asphyxiation. Understanding the natural and human-induced sources of carbon dioxide, as well as its impact on the environment and health, is pivotal for addressing concerns related to climate change and promoting sustainable practices.

(2) Hydrocarbons

Hydrocarbons, such as marsh gas, occur naturally and can also be generated through incomplete combustion processes. These compounds, composed of hydrogen and carbon, possess carcinogenic properties and can lead to irritation of mucous membranes and eyes. Their presence is associated with aging effects, tissue breakdown, and the shedding of flowers, leaves, and twigs in plants. Understanding the dual origins and diverse impacts of hydrocarbons is crucial for addressing environmental and health implications linked to these substances.

(3) Oxides of Sulphur (SO_3 and SO_2)

Approximately 67% of these oxides are generated through volcanic eruptions, while the remaining 33% results from the metallurgy of sulphide ores and the combustion of sulfur-containing fuels. In low concentrations, these oxides can contribute to respiratory diseases such as asthma, bronchitis, emphysema, and eye irritation. Elevated concentrations, on the other hand, can induce stiffness in flowers. When present as pollutants, SO_2 can convert into SO_3 through the chemical reaction:

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

Additionally, ozone (O_3) and hydrogen peroxide (H_2O_2) participate in the oxidation of SO_2, further influencing the atmospheric chemistry.

$$SO_2 + O_3 \longrightarrow SO_3 + O2$$
$$SO_2 + H_2O_2 \longrightarrow H_2SO_4$$

SO_3 is particularly concerning as it is more harmful than SO_2. This is due to its ability to combine with water to form sulfuric acid (H_2SO_4), a major contributor to acid rain. Acid rain, in turn, has detrimental effects such as the yellowing of iconic structures like the Taj Mahal and other monuments.

(4) Oxides of Nitrogen

Primarily originating from the combustion of fossil fuels, particularly in high-temperature conditions such as those found in automobile engines, oxides of nitrogen, primarily NO and NO_2, play a significant role in atmospheric chemistry. The production of these oxides involves the reaction sequence:

$$N_2 + O_2 \xrightarrow{1483\text{ K}} 2NO$$
$$2NO + O_2 \rightarrow 2NO_2$$

Additionally, NO reacts with ozone in the atmosphere, resulting in the production of NO_2:

$$2NO + O_3 \rightarrow NO_2 + O_2$$

Furthermore, oxides of nitrogen are generated during lightning strikes, where nitrogen (N_2) and oxygen (O_2) combine to form NO_2, which subsequently decomposes to release NO, acting as a fertilizer. The effects of these nitrogen oxides are notable, manifesting as a reddish-brown haze or brown air. NO_2 is considered more hazardous than NO, and exposure to these oxides can lead to various health issues, including pulmonary edema, arterial dilation, eye irritation, heart problems, liver and kidney damage, and contribute to the occurrence of acid rain. Higher concentrations of NO_2 can also adversely impact plants, causing damage to leaves and impeding the rate of photosynthesis.

Greenhouse Effect and Global Warming

The elevation in Earth's temperature caused by the re-radiation of solar energy absorbed by the Earth is known as the greenhouse effect. In this process, the re-radiation of heat by the Earth is absorbed by molecules like CO_2 and water vapor near the Earth's surface and then emitted back towards the Earth. This phenomenon is commonly referred to as global warming, resulting in an increase in the Earth's temperature.

Greenhouse Gases

(i) Carbon Dioxide (CO_2)

Emitted through the combustion of fossil fuels, burning wood, and respiratory processes, among other sources, carbon dioxide is experiencing a current growth rate of 0.5% per year.

(ii) Methane

Generated through the incomplete combustion of fossil fuels, methane is notably 25 times more potent than carbon dioxide in terms of its impact on the greenhouse effect.

(iii) Chlorofluorocarbons (CFCs)

Remarkably more effective than CO_2, CFCs are widely used in aerosol cans, jet fuels, air conditioners, refrigerators, and fire extinguishers. Unfortunately, their usage is contributing to the depletion of the ozone layer.

(iv) Nitrous Oxide (N_2O)

Possessing a potency 320 times that of CO_2, nitrous oxide is produced through the combustion of livestock waste, as well as the breakdown of nitrogenous fertilizers in the soil.

In addition to the mentioned greenhouse gases, water vapor and ozone (O_3) also contribute to the greenhouse effect.

Acid Rain

Rainfall that includes H_2SO_4, HNO_3 (along with trace amounts of HCl), resulting from the oxidation of sulfur and N_2 in the atmosphere, is referred to as acid rain. Acid rain typically exhibits a pH level between 4 and 5.

Formation of acid rain

The oxide of nitrogen undergoes oxidation reaction. The reaction with the water vapour present in the atm to form HNO_3.

step (I):

$$NO + O_3 \xrightarrow{hv} NO_2 + O_2$$

$$NO_2 + O_3 \xrightarrow{hv} NO_3 + O_2$$

$$NO_2 + NO_3 \xrightarrow{hv} N_2O_5$$

$$N_2O_5 + H_2O \xrightarrow{hv} 2HNO_3$$

HNO_3 come down with rain to earths.

The SO_3 react with water vapour and formed H_2SO_4.

step (II): $$2SO_2 + O_2 \longrightarrow 2SO_3$$

The HNO_3 and H_2SO_4 combine with HCl present in the air to produce acidic precipitation which is called as acid rain.

In acid rain	H_2SO_4	=	60–70%
	HNO_3	=	30–40%
	HCl	=	Very small amount.

Harmful Effect of Acid-Rain

- It damages to building and status which contain marble, lime stone, state, mortar etc.

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

- It damages iron and steel structure.
- It corrodes water pipe. So heavy metal (like Fe, Pb, Cu) are mixed with water which have toxic effect.
- The acid rain increases the acidity of the lake. Which is harmful to fishes.
- It damages the trees, plants and retards the growth of the plant.

Particulate Pollutants

The visible black smoke emitted into the air by diesel trucks is often the most apparent form of pollution we regularly encounter. This smoke primarily consists of particulate matter, which refers to minuscule solid or liquid particles suspended in the air. These individual particles are typically too small to be seen with the naked eye. However, when these small particles gather together, they often create a haze that hinders visibility.

Particulate matter in the atmosphere can be categorized as:

(i) viable

(ii) non-viable

Viable particulates comprise minute living organisms dispersed in the atmosphere, such as bacteria, fungi, molds, and algae. It's worth noting that certain fungi found in the air can trigger allergies in humans and also cause diseases in plants. Non-viable particulates of significance are created through either the disintegration of larger materials or the condensation of minute particles and droplets.

There are four main types of non-viable particulates in the atmosphere:

(a) Mists are generated by the particles of sprayed liquids and the condensation of vapors in the air. Examples include portions of herbicides and insecticides missing their targets and traveling through the air to create mists.

(b) Smoke consists of very fine soot particles produced during the burning and combustion of organic matter. Common examples include oil smoke, tobacco smoke, and carbon smoke.

(c) Fumes result from the condensation of vapors, particularly metallic vapors. Well-known examples include metallurgical fumes and alkali fumes.

(d) Dust comprises particles formed during activities like crushing, grinding, and the fragmentation of solid materials. Non-viable dust particulates in the atmosphere include ground limestone, sand tailings from flotation processes, pulverized coal, cement particles, fly ash, and silica dust.

The effects of particulate pollutants largely depend on the size of the particles. Coarser particles with a size greater than 5 microns are more likely to become lodged in the nasal passages, while smaller particles are more likely to penetrate the lungs. The rate of penetration is inversely related to the particle size. Several of these fine particulates are known carcinogens. Inhaling small particles can irritate the lungs, and long-term exposure to such particles can lead to lung lining scarring or fibrosis. This condition is commonly recognized in industrial settings and referred to as "**pneumoconiosis.**"
The suspended particulate matter in the atmosphere effectively reduces the number of light rays reaching the Earth's surface, resulting in a decrease in temperature. By obstructing sunlight, these particles contribute to a reduction in Earth's temperature and, by acting as condensation nuclei, they can enhance fog and precipitation in urban areas. Suspended particles in city atmospheres also reduce visibility, with visibility diminishing as atmospheric particulate concentrations increase.

Smog

The term "smog" is commonly used to describe a hazy, "smoke-fog" condition that is a well-known form of air pollution in many cities around the world. There are two main types of smog:

(i) Classical smog, which typically forms in cool and humid climates and results from the accumulation of sulfur oxides and particulate matter generated by the combustion of fuels.

(ii) Photochemical smog, which tends to occur in warm, dry, and sunny climates and is the outcome of sunlight acting on nitrogen oxides and hydrocarbons produced by vehicles and industrial facilities. Photochemical smog is categorized as an oxidizing smog, characterized by high concentrations of oxidizing agents. In contrast, classical smog is considered a chemically reducing smog with elevated levels of SO_2.

Photochemical smog is more prevalent in cities with large populations and high vehicular traffic density.

Formation of Photochemical Smog

The chemistry behind the creation of photochemical smog revolves around nitric oxide (NO). When gasoline and diesel engines in cars and trucks operate at high temperatures, the nitrogen (N_2) and oxygen (O_2) present react to produce a small amount of NO, which is released into the atmosphere through exhaust emissions. This NO undergoes oxidation in the air to become NO_2, which, when exposed to sunlight, absorbs energy and undergoes a process of splitting into nitric oxide and free oxygen atoms. This phenomenon is referred to as photochemical decomposition.

$$NO_2(g) \xrightarrow{hv} NO(g) + O(g)$$

Oxygen atoms are very reactive and can combine with O_2 to form ozone;

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

The O_3 formed in the above reaction reacts rapidly with the NO(g) formed in reaction to regenerate NO_2.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

NO and O_3 are potent oxidizing agents and have the ability to interact with unburnt hydrocarbons present in the polluted air. This interaction leads to the formation of substances like formaldehyde, acrolein, and peroxyacetyl nitrate (PAN), which are known to cause eye irritation, burning sensations, and have detrimental effects on the respiratory system. The brownish appearance of photochemical smog is primarily due to the brown coloration of NO_2.

$$3CH_4 + 2O_3 \longrightarrow 3CH_2 = O + 3H_2O$$

Formaldehyde

Acrolein and peroxyacetyl nitrate (PAN) are particularly noxious.

Acrolein	Peroxyacetyl nitrate (PAN)
$CH_2 = CHCH = O$	$\underset{\underset{O}{\parallel}}{CH_3CO}ONO_2$

Effects of Photochemical Smog

Photochemical smog comprises three primary components: nitrogen oxides, ozone, and organic derivatives like acrolein, formaldehyde, and PAN (peroxyacetyl nitrate), among others. Each of these components contributes to the adverse effects of smog.

The pungent-smelling ozone produced by smog is recognized for its toxicity, capable of inducing symptoms like coughing, wheezing, and bronchial constriction. Additionally, smog components such as Peroxyacetyl nitrates and aldehydes are known to irritate the eyes. Certain materials are also negatively impacted by specific smog constituents. For instance, rubber is highly susceptible to ozone, leading to cracking and aging. Smog can further inflict harm on vegetation, resulting in reduced plant growth and crop productivity. Among all the smog components, PAN stands out for its high toxicity to plants, particularly affecting younger leaves and causing issues like "bronzing" and "glazing" on their surfaces.

Control of Photochemical Smog

Various initiatives have been undertaken to mitigate or regulate the creation of photochemical smog. One of the most direct methods for reducing smog formation is the installation of effective catalytic converters in vehicles, which effectively hinders the emission of nitrogen oxides and hydrocarbons into the atmosphere. Additionally, photochemical smog can be curbed through the use of specific compounds that function as free radical traps. When these substances are dispersed into the atmosphere, they generate free radicals that readily bond with the precursors of free radicals responsible for the formation of photochemical smog.

Stratospheric Pollution

Ozone Formation and its Breakdown

Formation of Ozone Layer

Within the stratosphere, ranging from 11 to 50 kilometers in altitude, a portion of O_2 undergoes a conversion into O_3. This process results in the formation of an ozone layer situated at an elevation of 25-30 kilometers, characterized by an O_3 concentration of 10 parts per million (ppm). This layer is commonly referred to as the ozone layer, and its creation occurs through a two-step transformation.

Step (I): $O_2 \xrightarrow{hv} O^{\bullet} + O^{\bullet}$

Step (II): $O_2 + O^{\bullet} \xrightarrow{hv} O_3$

In I step: The ultraviolet radiation coming from the sun have sufficient energy to split the O_2 into 2 oxygen atoms.

In II step: The oxygen atom reacts with more O_2 to form O_3 the O_3 absorbed the U.V. radiations and again broken into O_2 and O atom. The heat is also given out from this reaction which warm up stratosphere. For this reason, stratosphere is a ozone of increasing temp.

$$O_3 \xrightarrow{hv} O_2 + O^{\bullet} + \text{xk cal.}$$

In this way the O_3 cycle is completed in this region.

Depletion of Ozone Layer

Due to human activity 2 compounds NO and CFC are responsible for depletion of O_3 layer.

(a) **NO (Nitric oxide)**

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

$$NO_2 + O \longrightarrow NO + O_2$$

The NO reacts with O_3 so decrease the amount of O_3 and forms NO_2 which react with oxygen atoms available in the stratosphere and producing back NO.

Thus, NO is consumed but O_3 gets depleted.

(b) **Chloroform Carbons (CFC) or Freon**

The freons decomposes in the presence of U.V. radiation coming from the sun.

$$CF_2\,Cl_2 \xrightarrow{hv} \dot{C}\,F_2Cl + \dot{C}\,1$$

$$CFCl_3 \xrightarrow{hv} \dot{C}\,1 + \dot{C}\,FCl_2$$

The reactive chlorine atoms then destroy the ozone layer through the following sequence of reaction. Which are repeated because chlorine atom is regenerated in the second reaction:

Reaction.

$$+ O_3 \longrightarrow + O_2$$

$$+ O \longrightarrow + O_2$$

The one molecule CFC can destroy more than one thousand O_3 molecules in the stratosphere.

Ozone Hole

Ozone depletion occurring in a localized region, such as over Antarctica, is referred to as an ozone hole. In the stratosphere above Antarctica, unique atmospheric conditions lead to the formation of stratospheric clouds. On the surface of these clouds, chlorine nitrate undergoes hydrolysis, producing hypochlorous acid, and reacts with hydrogen chloride to form molecular chlorine. The chemical reactions involved are represented as follows:

$$CIONO_2(g) + H_2O(g) \rightarrow HOCl(g) + HNO_3(g)$$

$$CIONO_2(g) + HCl(g) \rightarrow Cl_2(g) + HNO_3(g)$$

These $CIONO_2$ and HCl are generated during the summer season through the reactions involving nitrogen dioxide and chlorine monoxide radical, as well as the reaction between methane and chlorine radical:

$$ClO(g) + NO_2(g) \rightarrow CIONO_2(g)$$

$$Cl(g) + CH4(g) \rightarrow CH_3(g) + HCl(g)$$

As spring arrives, sunlight initiates the breakdown of HOCl and Cl_2, releasing chlorine radicals:

$$HOCI(g) \xrightarrow{hv} OH(g) + CI(g)$$

$$Cl_2(g) \xrightarrow{hv} 2CI(g)$$

These chlorine radicals, being free radicals, contribute to the depletion of the ozone layer. The intricate series of reactions and interactions outlined here underscore the complex mechanisms involved in the formation and depletion of ozone, particularly in regions like Antarctica.

Effects of Depletion of The Ozone Layer

Effect of depletion of O_3 layer

Due to depletion of O_3 layer, U.V. radiation fall on the earth.

- The U.V. radiation, damage the cornea and lens of the eyes.
- The U.V. radiation affect the plant proteins so reduce the chlorophyll.
- The U.V. radiation, upset the heat balance of the earth.