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ENVIRONMENTAL CHEMISTRY

2

Navindu Gupta, R.S. Khoiyangbam, and Niveta Jain

2.1 INTRODUCTION

Environmental chemistry is the study of the chemical and biochemical phenomena that occur in nature. It involves the understanding of how the uncontaminated environment works, and which naturally occurring chemicals are present, in what concentrations and with what effects. Without this it would be impossible to study accurately the effects that humans exert on the environment through the release of chemical species. It is a multi-disciplinary science that, in addition to chemistry, involves physics, life science, agriculture, material science, public health, sanitary engineering, and so on. More or less, it is the study of the sources, reactions, transport, effects, and fate of chemical species in the air, water, and land, and the effect of human activities upon the various environmental segments, such as atmosphere, hydrosphere, lithosphere, and biosphere.

Importance of the environment across the developed countries was realized in the 1960s and reached its climax in 1970, with the celebration of “Earth Day” under the auspices of the United Nation. From 1972 onwards, with the conclusion of the UN Conference on Human Environment at Stockholm, the important environmental issues were percolated across India and other developing nations. The need for environmental education, both formal and non-formal, was keenly felt at the national level. The objective of environmental education is to enlighten the public about the importance of protection and conservation of our environment and about the needs to restrain human activities that lead to indiscriminate release of pollutants into the environment.

At present, many environmental issues exist that have grown in size and complexity day by day, threatening the survival of mankind on earth. The various incidences of such environmental issues include London smog of 1952—killing about 4000 people, the Mediterranean sea turning into Dead Sea in the 1950s—unable to support aquatic life, death of a number of Japanese people because of eating fish from the Minamata Bay in the 1960s, historical monuments and statues in Greece and Italy getting damaged by the effect of rainwater, white marble of Taj Mahal in India

becoming yellow by the action of sulphur dioxide fumes, leakage of methyl isocyanate (MIC) vapours at Bhopal in India in 1984, and the hazardous effects of nuclear weapons and radiations on the people of Hiroshima and Nagasaki. Pollution of river water in India, use of plutonium or other isotopic fuel-based breeder/nuclear reactors for energy production, use of dangerous artificial food additives, and ozone hole in the Antarctic and Arctic regions are some typical chemical issues that need to be resolved critically.

2.2 ENVIRONMENTAL SEGMENT

There are four environmental segments: atmosphere, hydrosphere, lithosphere consisting of abiotic or physical environment, and biosphere—the fourth segment of environment that consists of flora and fauna. Abiotic and biotic components together constitute the biome environment.

Atmosphere

Atmosphere is a protective blanket of gases surrounding the earth, which supports life and protects it from the hostile environment of outer space. Atmosphere absorbs most of the cosmic rays from outer space and a major portion of the electromagnetic radiation from the sun, and also maintains the heat balance of the earth. It transmits only near-ultraviolet, visible, near-infrared (IR) (300–2500 nm), and radio waves (0.14–40 m), and absorbs energy re-emitted from the earth in the form of IR radiation. It serves as an insulator against heat loss from the surface of the earth, and stabilizes weather and climate owing to the heat capacity of the air.

The major gases of the atmosphere are nitrogen and oxygen, while the minor gases are argon, carbon dioxide, and some trace gases. Atmosphere is the source of oxygen and carbon dioxide. Several cycles that relate to the movement of matter between an organism and its environment are also present in the atmosphere—hydrological cycle, carbon cycle, nitrogen cycle, phosphorus cycle, and many others. It also supplies nitrogen, which is used by nitrogen-fixing bacteria and ammonia manufacturing plants to yield chemically bound nitrogen that is essential for life. The details of these cycles are discussed in the later part of the chapter.

The atmosphere can be divided into the following five concentric layers, depending on the temperature variations:

- (i) **Troposphere:** In this layer, humans and other organisms live.
- (ii) **Stratosphere:** In this layer, the the temperature is very low, because of which there are no clouds, dust, or water vapours.
- (iii) **Mesosphere:** In this layer, the temperature drops to about -95°C . The principal chemical species in the mesosphere are N_2 , O_2 , O_2^+ , and NO^+ .

- (iv) **Thermosphere or ionosphere:** In this layer, most of the gaseous components are ionized under the influence of radiant energy and so ionosphere contains electrically charged particles such as O^+ , O_2^+ , and NO^+ . Radio messages can be transmitted through this layer round the curve of the earth.
- (v) **Exosphere:** In this layer, the temperature is very high due to solar radiation. This region lacks atoms except hydrogen and helium.

Human beings, on the one hand, are enjoying all the advantages of the development in science and technology and, on the other hand, have been dumping waste materials into the atmosphere and producing a large number of pollutants, which are threatening the survival of mankind itself on earth.

Hydrosphere

Hydrosphere, which covers more than 75% of the earth's surface, includes all types of water resources—oceans, sea, rivers, lakes, streams, reservoir, glaciers, polar ice caps, and groundwater (that is, water below the earth's surface). About 97% of the total water available on earth is in the form of oceans, which cannot be used for human consumption owing to its high salt content. About 2% of the water resources are locked in the polar ice caps and glaciers, while only 1% is available as freshwater (surface water—river, lakes, streams, and groundwater) for human consumption and other uses. Freshwater is also available in the form of rains, snow, dew, and so on.

Among all liquid substances, water possesses the highest heat of fusion and evaporation at ordinary temperature. These properties of water moderate the temperature of the biosphere. The history of ancient civilization—growth and decline—is intimately linked with the quantum of the water supply. The major uses of water are for irrigation (30%) and thermal power plants (50%), while other uses include domestic (7%) and industrial consumption (about 12%). Water is also a buoyant medium. Organisms can survive in it without specialized supportive structures.

Surface water gets contaminated by pesticides and fertilizers from agricultural run-off water, human and animal wastes in sewage, and industrial wastes. Salinity in water is one such example. Salinity of marine water is about 3–3.5%.

Lithosphere

This is the outer mantle of the solid earth, consisting of minerals occurring in the earth crust and the soil. The earth is a cold, spherical solid planet of the solar system, which spins on its axis and revolves around the sun, maintaining a certain constant distance. It comprises a complex mixture of minerals, organic matter, air, and water.

Lithosphere mainly consists of three layers: crust, mantle, and outer and inner core. The surface of the crust is covered with soil, which is the most important part of lithosphere. Soil is a mixture of organic as well as weathered rock and materials necessary for the growth of plants. It is a storehouse of minerals, a reservoir of water, a conserver of soil fertility, a producer of vegetative crops, and a home of wildlife and livestock.

Biosphere

Biosphere denotes the realm of living organisms and their interaction with the environment, that is, atmosphere, hydrosphere, and lithosphere. Both the biosphere and the environment are influenced by each other considerably. Thus, the levels of oxygen and carbon dioxide in the atmosphere depend entirely on the plant kingdom. As a matter of fact, green plants alone are responsible for the accumulation of oxygen in the atmosphere, through photosynthesis and decay; the original atmosphere was devoid of oxygen. The biological world, in general, is intimately related to the energy flow in the environment and water chemistry. The interactions among organisms are symbiotic (living together for mutual benefits) and antagonistic (living together, but at least one is harmed).

Biosphere as a whole supplies us with food, and there exists a cycling of materials through expiration, excretion, and extinction of the form.

2.3 TOXIC CHEMICALS IN THE ENVIRONMENT

The chemicals present in the environment are toxic as well as non-toxic in nature. The toxic chemicals that are discharged by industries into air, water, and soil get into the human food chain from the environment. Once these chemicals enter the biological system, they perturb the natural biochemical processes, causing adverse effects.

Toxic chemicals are huge in number; however, toxicity levels of many compounds are still unknown. Some useful chemicals are being controlled rigorously as their non-toxicity has not yet been proved. Many metals that are known to cause environmental hazards are essential dietary trace metals required for normal growth and development of animals and human beings. These elements are Al, Sb, As, Ba, Be, Cd, Co, Cu, Ce, In, Pb, Hg, Mo, Ag, Te, Tl, Sn, Ti, W, U, and Zn (Table 1). For instance, As, Pb, and Cd—which are well-known toxic metals—are required in trace quantities for the growth of animals.

Schwartz used the term “concentration window” to draw the arbitrary lines of demarcation:

- (i) “Essential” at the trace level for sustenance of life processes

- (ii) “Deficient” at lower level than (a), causing metabolic disorder
- (iii) “Toxic” at higher level than (a), causing adverse effects

According to the “International Register of Potentially Toxic Chemicals” of the United Nations Environment Programme, 4 million known chemicals exist in the world today and another 30,000 new compounds are added to the list every year. Among these, 60,000–70,000 chemicals are commonly used. Apart from their benefits to increasing production, living standards, and health, many of them are potentially toxic.

Classification of Toxic Matters

Toxic matters may be classified according to their function and effects, such as mutagens, carcinogens, and pesticides; food additives, preservatives, and so on; or heavy metals, metal carbonyls, organochlorine compounds, radioactive chemicals, and so on.

Mutagens

In reference to the field of genetics, a mutagen is a physical or chemical agent that changes the genetic material, usually DNA. A large number of chemicals may interact directly with DNA. However, many chemicals such as PAHs (polycyclic aromatic hydrocarbons), aromatic amines, and benzenes are not necessarily mutagenic by themselves, but produce mutagenic compounds through metabolic processes in cells.

Other chemical species are reactive oxygen species, which include superoxide, hydroxyl radicals, and hydrogen peroxide. A large number of these highly reactive species are generated by normal cellular processes, for example, as by-products of mitochondrial electron transport or lipid peroxidation. Deaminating agents such as nitrous acid, aromatic amines (2-acetylaminofluorene), alkaloids, sodium azide, bromine and its compounds, and alkylating agents such as ethyl nitrosourea, which transfer methyl or ethyl group to bases or the backbone phosphate groups, also react with DNA. Guanine when alkylated may be mispaired with thiamine. Some may cause DNA crosslinking and breakages. Nitrosoamines are an important group of mutagens found in tobacco; other alkylating agents include mustard gas and vinyl chloride.

Carcinogens

A carcinogen is a substance that is capable of causing cancer in humans and animals. If a substance is known to promote or aggravate cancer, but not necessarily cause cancer, it may also be called a carcinogen. A number of substances have been identified as being carcinogenic. Some commonly known carcinogens include asbestos, radon and other radioactive isotopes, certain pesticides, arsenic and other heavy metals,

and tobacco smoke. In addition to chemical substances, ultraviolet ray is also known to cause a variety of cancers that affect the skin.

Pesticides

Pesticides are the chemicals used to protect the crops and fodders from insects and pests, including rodents and weeds. Biochemical processes constitute the major mechanism by which pesticides in the environment are degraded and detoxified. One good example of such pesticides is DDT, whose biological action on the environment has been studied most extensively. Like many other insecticides, DDT targets the central nervous system. DDT dissolves in lipid (fat) tissue and accumulates in the fatty membrane surrounding nerve cells. This is likely to interfere with the transmission of nerve cells. The net result is disruption of the central nervous system, killing the target insect. While DDT is fairly stable and persists in the environment, the other groups—organophosphates and carbamates—degrade quite rapidly. The latter react with O_2 and H_2O , undergoing decomposition within a few days in the environment.

Food additives

Food additives are chemical substances that are added voluntarily to food to preserve its flavour or enhance its taste and appearance. Some additives have been used for centuries, for example, for preserving food by pickling with vinegar, salting, preserving sweets, or using SO_2 gas as in some wines. Food additives are of both natural and artificial origins.

Types of food additives

The different types of food additives, their uses, and examples include the following:

- **Anti-caking agents**—prevent ingredients from becoming lumpy, for example, calcium polyphosphate and potassium aluminium silicate
- **Antioxidants**—prevent foods from being oxidized or going rancid, for example, disodium EDTA, oxystearin, and vitamin C
- **Artificial sweeteners**—increase the sweetness, for example, saccharin, aspartame, and cyclamates
- **Emulsifiers**—prevent fats from clotting together, for example, dimethyl polysiloxane
- **Food acids**—maintain the right acid level in the food, for example, sodium or potassium fumarate and 1,4-heptonolactone
- **Colours**—enhance or add colour to food, for example, niacin, nicotinamide, tartrazine, riboflavin, and turmeric
- **Humectants**—keep foods moist, for example, maltitol, lactitol, xylitol, and triacetin

- **Flavours**—add flavour to food
- **Flavour enhancers**—increase the power of a flavour added to food, for example, monopotassium glutamate, MSG, and zinc acetate
- **Foaming agents**—maintain uniform aeration of gases in foods
- **Mineral salts**—enhance texture and flavour of food, for example, aluminium sodium sulphate, calcium hydroxide, and magnesium hydroxide
- **Preservatives**—prevent microbes from multiplying and spoiling the food, for example, lysozyme, isopropyl citrate, and sodium benzoate
- **Thickeners and vegetable gums**—enhance texture and consistency of food
- **Stabilizers and firming agents**—maintain even food dispersion, for example, sodium or potassium gluconate
- **Flour treatment**—improves baking quality
- **Glazing agents**—improve appearance of food and can protect it
- **Gelling agents**—alter the texture of foods through gel formation, for example, agar, alginic acid, and carrageenan
- **Propellants**—help propel food from a container
- **Raising agents**—increase the volume of food through the use of gases
- **Bulking agents**—increase the volume of food without major changes to its available energy, for example, starch, mannitol, pectin, and polydextrose

Reactions due to food additives

A number of food additives are more likely than others to cause various hypersensitive reactions in people, which include:

- **Digestive disorders**—diarrhoea and colicky pains
- **Nervous disorders**—hyperactivity, insomnia, and irritability
- **Respiratory problems**—asthma, rhinitis, and sinusitis
- **Skin problems**—hives, itching, rashes, and swelling

2.4 WATER POLLUTION

Out of all natural resources, water is the most essential for the existence of living beings. Water sustains life on the earth. Unfortunately, civilization has perished it and is responsible for its pollution.

Water pollution may be defined as the deterioration in the physical, chemical, and biological properties of water, brought about mainly by anthropogenic activities. It can also be caused by natural weathering of the product of rocks, minerals, soil sediments, nutrients, as well

as organic matters of soil (decomposed animals, microorganisms, and vegetable materials) that are transported by erosion. This deterioration in quality of water body (both surface and ground) has increased during the past few decades mainly by enhanced human activities in industrial and agricultural sectors.

In recent years, there has been an increasing concern around the world regarding the widespread distribution of the pollutants stemming from human activities and the potential harmful effects of these pollutants on human or the ecological systems. Some environmental problems such as contaminated water have arisen from poorly controlled discharges of industrial effluents into the water bodies, while others such as air pollution have arisen from poor emission control on the energy generation industry and motor vehicles.

Parameters of Pollution

The following parameters determine the nature and extent of pollution in water:

- (i) **Physical parameters**—colour, odour, turbidity, density, temperature, and so on
- (ii) **Chemical parameters**—pH, total dissolved solids (TDS) and their ionic composition, suspended solids, dissolved oxygen (DO), residual chlorine, COD, biochemical oxygen demand (BOD), redox potential, radioactive substances, organic materials, metallic ions (including heavy metals), oxides, by-products of industries, and so on
- (iii) **Biological parameters**—different types of microorganisms, bacteria, algae, small animals such as protozoa and crustaceans, and so on

Water Pollutants

Nature and concentration of the pollutants depend upon their sources, physical and chemical conditions, and reactivity with the surrounding environment. The large number of water pollutants may broadly be classified under the following categories:

- (i) **Organic pollutants**—These include degradable and non-degradable products, as well as disease-causing agents, plant nutrients, sewage, synthetic organic compounds, and oil. DO is an essential requirement for aquatic life. Its level in the water body should be 4–6 ppm. Decrease in this value is an indication of pollution mainly caused by organic matter, for example, sewage, industrial wastes, and run-off from agricultural lands
- (ii) **Inorganic pollutants**—These pollutants consist of inorganic salts, finely divided metal or metal compounds, trace elements, complexes of metal with organic moiety mineral acid, and so on

- (iii) **Sediments**—Sediments are insoluble soil particles of unknown composition that enter water bodies by soil erosion. In fact, sediments are the most extensive pollutants of surface water. It has roughly been estimated that suspended solids loading reaching natural waters are about 700 times as large as the solids loading from sewage discharge. Several factors such as agricultural practices, construction activities, and strip mining activities have great influences on solid erosion rates in the given area.
- (iv) **Radioactive substances**—Radioactive pollution is the worst pollution among all and it is detrimental to health. Sources of environmental radioisotopes may broadly be grouped as natural and artificial. Natural radioisotopes produced by cosmic rays find their way into soil and water courses through precipitation (rainfall and snow) and run-off, whereas those occurring on the surface of the earth and below enter the water-bearing formulations through weathering. On the other hand, man-made radioisotopes enter the environment mainly through nuclear installations and research organizations. Some of the radioisotopes such as K-40; Ra-222, Ra-226, and Ra-228; Pb-210; and C-14 are incorporated into the human body through different pathways.
- (v) **Thermal pollutants**—Coal-fired or nuclear fuels used by steam power plants are among the most important sources of thermal pollutants, as only a fraction of the heat generated using these fuels is successfully converted to work and the remaining is wasted. Even in the modern coal-fired plants, the efficiency does not exceed 40%. The condensers used in these plants utilize water from nearby river or lake or municipal sources and discharge the wastewater back to the water body, with its temperature being raised by about 10°C in the process. This decreases the DO level of water and adversely affects the aquatic life.

Main Sources of Pollutants

Water pollution is caused by one or more of the following sources:

1. **Point sources:** Sources that are readily identifiable at a single location, such as the following:
 - (a) Industrial waste disposal
 - (b) Water treatment plant
 - (c) Municipal sewage leakage
 - (d) Combined sewer overflows
 - (e) Raw sewage disposal
 - (f) Leaching residue tips
 - (g) Sanitary landfills

- (h) Aerial fallout
- (i) Industrial effluent seepage

2. Non-point sources: Sources whose location cannot be identified, such as the following:

- (a) **Pollution due to industrial chemicals:** With the increase in global population, industrial activities have also increased. The effects of population growth have been recorded not only on industrial areas, but also on global commons such as Antarctic, the Arctic, and remote natural reserves. In addition, increasing concentrations of chemical substances originating from industrial sources and other human activities have been detected in water, air, and soil. Such elevated concentrations and consequent bioaccumulation of some substances have given rise to environmental and ecotoxicological effects. Over 11 million chemical substances are known, of which 60,000–70,000 are in regular use. Data on environmental and ecotoxicological effects of these chemicals are sparse; however, many cases have been reported about the heavy metals and metalloids, pesticides, fertilizer, aromatic polychlorinated compounds, flame-retardant chemicals, wood preservatives, washing powders and detergents, polymeric resins, and so on poisoning the water bodies.
- (b) **Pollution due to agricultural activities:** The key role of fertilizers in increasing the crop production is now well established. Fertilizer consumption in India has registered a spectacular growth during the last four decades. In addition to chemical fertilizers, large quantities of organic manures and pesticides are also being used for increasing crop production. Unfortunately, increasing use of the above-mentioned inputs for achieving the planned agricultural growth is creating environmental problems. Reports say that, in India, the efficiency of nitrogen fertilizers is about 30–40% for paddy and about 50–60% for wheat. For potassium and phosphate fertilizers, the efficiency values are around 50% and 15–20%, respectively. This shows that a huge amount of applied fertilizers not used by plants is available for leaching into groundwater, which can cause water pollution. Micronutrients added as fertilizers may be toxic if they get into groundwater. Nutrients can flow into groundwater at many points. It should be recognized that only a small portion of the nitrogen load comes from the agricultural land surface, while the major portion comes from the air and the domestic and industrial wastes of the cities.
- (c) **Oil pollution:** Besides the problems of dwindling petroleum reserves and global oil pollution, the use of fossil fuels contributes to the increase in greenhouse gas (GHG) and change in global

climate. Petroleum hydrocarbons enter freshwater environment in a variety of ways, including land run-off, airborne contaminants, shoreline facilities, and leaks and spills from vessels, pipelines and underground storage tanks.

- (d) **Eutrophication:** The word eutrophication literally means “the process of becoming well fed”; it can also be referred to as excessive fertilization of lakes, reservoirs, slow-flowing rivers, and certain marine coastal waters by nutrients, which result in the nuisance growth of aquatic plant materials such as algae and macrophytes. This in turn leads to deterioration of water quality and taste, odour problems, oxygen depletion, reduced transparency, declines of fisheries, possible fish kill, and toxic effects on animals and human beings.
- (e) **Consequences of eutrophication:** Eutrophication of lakes, reservoirs, impoundments, rivers, and coastal waters is related to the impairment of recreation for bathers, health concern from contact dermatitis, and ingestion of toxin-producing algae. In addition to these factors, eutrophication also causes impairment of fisheries and consumption of contaminated shell fish, adverse effects on livestock, drinking of toxicologically contaminated water, macrophyte-impaired navigation, and increased habitat for some disease vectors such as schistosomiasis or bilharzias.
- (f) **Control of eutrophication:** Eutrophication can be controlled effectively by drastic reduction in the total nutrient load in an overloaded water system. An integrated approach based on water body nutrient mass balance, taking into consideration specific geographical, climatological, and ecological conditions, can be effective.
- (g) **Heavy metals:** When heavy metals on a site, which either may have been produced by mining operation or occur naturally, are mobilized, these cause potential health and environmental problems in the overburden in soil and water. When acid mine drainage is detected, there is a high probability that heavy metals are present in abundance. Sulphuric acid derived from the oxidation of sulphides normally carries many heavy metals usually in fairly high quantities. The management of acid mine drainage, which contains these metals, includes neutralization and pH increase of the solution to precipitate most of these metals, most commonly as metallic salts. These salts would then become soluble and may enter the local water regime.

It is, therefore, necessary to review the heavy metals that are detrimental to humans, animals, plants, and fish life.

- **Arsenic, cadmium, lead, nickel, manganese, and molybdenum:** These metals are potentially harmful to human life as they are bioaccumulative and can seriously affect health even in relatively small dosages. Also, with the addition of copper and chromium, all these metals become very detrimental to aquatic life.
- **Zinc, lead, aluminium, boron, and iron:** These metals may rapidly become available either in acid soils or as salts precipitated by neutralizing acid solutions. They are all, to a greater or lesser extent, toxic to plant growth.
- **Mercury:** Mercury is highly toxic as a liquid, a vapour, and organic complexes. It is bioaccumulative and is, therefore, a major health risk to workers who are handling it. Its detrimental effects on animals and humans are irreversible. Mercury can be absorbed through the skin, inhaled as a vapour, or taken in by eating contaminated fish and drinking contaminated water. Mercury is used extensively by small mines in some developing countries; these mine workers should be educated about the health hazards associated with mercury and how to handle it safely.

Mercury can also cause major environmental damage to all types of animals and plants. Residual mercury should be carefully collected and returned to the supplier. In addition, all purchases and uses of the mercury should be recorded.

- **Copper:** Copper is commonly toxic to most aquatic vegetation. Therefore, care must always be taken not to allow copper to enter drainage systems where there may be aquatic life.
- (h) **Pesticides:** Pesticides are the chemicals used to protect the crops and fodders from insects and pest including rodents and weeds. Biochemical processes constitute the major mechanism by which pesticides in the environment are degraded and detoxified. One good example of such a pesticide is DDT, whose biological action on the environment has been studied most extensively. Like many other insecticides, DDT targets the central nervous system. DDT dissolves in lipid (fat) tissue and accumulates in the fatty membrane surrounding nerve cells. This is likely to interfere with the transmission of nerve cells. The net result is disruption of the central nervous system, killing the target insect. While DDT is fairly stable and persists in the environment, the other groups—organophosphates and carbamates—degrade quite rapidly. The latter react with O_2 and H_2O , undergoing decomposition within a few days in the environment.
- (i) **Radioactive waste:** Radioactive wastes are derived from the mining and processing of uranium ores. Other sources of radioactive waste

Table 1 Toxic trace elements in natural water and wastewater

<i>Metal</i>	<i>Source</i>	<i>Effects</i>
Arsenic	Mining by-products, pesticides, chemical waste	Toxic, possibly carcinogenic
Cadmium	Industrial discharge, mining waste, metal plating, water pipes	Replaces zinc biochemically; causes high blood pressure, kidney damage, destruction of testicular tissue and red blood cells, toxicity to aquatic biota
Beryllium	Coal, nuclear power, space industries	Acute and chronic toxicity, possibly carcinogenic
Boron	Coal, detergent formulations, industrial waste	Toxic to some plants
Chromium	Metal plating, cooling tower water additive; normally found as Cr(VI) in polluted water	Essential trace elements; possibly carcinogenic as Cr(VI)
Copper	Metal plating, industrial and domestic waste, mining and mineral leaching	Essential trace elements, not very toxic to animals, toxic to plants and algae at moderate levels
Fluorine (fluoride ions)	Natural geological sources, industrial waste, water additive	Prevents tooth decay at about 1 mg/L, causes mottled teeth and bone damage at about 5 mg/L
Lead	Industry, mining, plumbing, coal, gasoline	Toxic (anaemia, kidney diseases, nervous disorder), destroys wild life
Manganese	Mining industrial waste, acid mine damage, microbial action on manganese minerals at low pE	Relatively non-toxic to animals, toxic to plants at a higher level
Mercury	Mining, industrial waste, pesticides, coal	Highly toxic
Molybdenum	Industrial waste, natural sources	Possibly toxic to animals, essential for plants
Selenium	Natural geological sources, sulphur, coal	Essential at low levels but toxic at higher levels
Zinc	Industrial waste, metal plating, plumbing	Essential in many metalloenzymes, toxic to plants at higher levels

include contamination from radioactive sources used for monitoring purposes and where radionuclides occur naturally with the ore being mined, such as some gold and mineral sand deposits. Radioactive wastes occur as gases, liquids, and solids. Certain characteristics,

such as toxicity, mobility, radioactive half-life, and type of radioactive emission, govern the choice of management procedures.

The following three basic principles are employed in the disposal of radioactive waste:

- (a) Dilution and dispersion of short-lived or very diluted radioactive wastes
- (b) Delay to allow decay of very short-lived radioactive wastes into non-radioactive species
- (c) Containment of long-lived radioactive wastes by methods such as water submersion and impervious covers

Biological Effects of Radiation from Radioactive Waste

The biological effects of radiation are thought of in terms of their impacts on living cells. For low levels of radiation, biological effects are so small that they may not be detected in epidemiological studies. Body itself repairs many types of radiation and chemical damages. Biological effects of radiation on living cells may result in a variety of outcomes, including the following:

- (i) Cells experience DNA damage and are able to detect and repair the damage.
- (ii) Cells experience DNA damage but are unable to repair the damage. These cells may go through the process of programmed cell death, or apoptosis, thus eliminating the potential genetic damage from the larger tissue.
- (iii) Cells experience a non-lethal DNA mutation that is passed on to subsequent cell divisions. This mutation may contribute to the formation of a cancer.
- (iv) Cells experience “irreparable DNA damage”. Low-level ionizing radiation may induce irreparable DNA damage, leading to replicational and transcriptional errors needed for neoplasia, or may trigger viral interactions, leading to premature ageing and cancer.

Other observations at the tissue level are more complicated, which are discussed next.

In some cases, a small radiation dose reduces the impact of a subsequent larger radiation dose. This has been termed as an “adaptive response” and is related to hypothetical mechanisms of hormesis.

Acute

Acute radiation exposure is an exposure to ionizing radiation that occurs during a short period of time. There are routine brief exposures, and the boundary at which it becomes significant is difficult to identify. Extreme examples include the following:

- Instantaneous flashes from nuclear explosions
- Exposure durations ranging from minutes to hours during handling of highly radioactive sources
- Laboratory and manufacturing accidents
- Intentional and accidental high medical doses

The effects of acute events are more easily studied than those of chronic exposure.

Chronic

Exposure to ionizing radiation over an extended period of time is called chronic exposure. The term chronic (Greek “khronos” means time) refers to the duration, not the magnitude or seriousness. The natural background radiation is chronic exposure, but a normal level is difficult to determine due to variations. Geographic location and occupation often affect chronic exposure.

Methods of Analysis of Parameters of Wastewater

Several chemical and instrumental analytical methods have been developed for determining the concentrations of various ions or matters present in wastewater, since the quantity of these matters can determine its quality for use as irrigation water (Table 2). The principal factors taken into consideration when determining water quality are the following (Table 3):

- DO content
- Turbidity
- Acidity and alkalinity
- Trace elements and nutrients such as nitrogen, phosphorus, halogens (chloride and fluoride ions), alkali metals (sodium and potassium ions), calcium and magnesium ions
- Microorganisms status

Table 2 Methods of analysis

<i>Parameter</i>	<i>Method</i>	<i>Reason for testing</i>
Temperature	Use an alcohol thermometer in a hard plastic cover or digital temperature probe	Temperature influences the amount of DO in water, which in turn influences the survival of aquatic organisms (raising the temperature of a freshwater stream from 20°C to 30°C will decrease the DO saturation level from about 9.2 to 7.6 ppm), which again influences

Contd...

Table 2 Contd...

Parameter	Method	Reason for testing
pH	A pH meter with sensitive electrodes, pH paper, or Universal Indicator solution	<p>the biological status of the water bodies. Increasing temperature also increases the rates of chemical reactions taking place in the water. Increase in temperature is often associated with hot water discharge from power stations and industries</p> <p>The value of pH determines its suitability for irrigation, as it measures the acidity or alkalinity of water. pH of rainwater is about 5.5–6.6. Typically, natural water has a pH of 6.5–8.5. A pH <5 (acidic water) is most damaging to eggs and larvae of aquatic organisms. Natural alkalinity is due to CO_2 (g), HCO_3^-, CO_3^{2-}, and OH^-; carbonate rocks such as limestone and dolomite increase alkalinity.</p>
Turbidity	Use a Secchi disc or 500 mL of water in a measuring cylinder made to stand on a paper marked with a black cross	Turbidity is a measure of water clarity. Suspended solids in water can stop light reaching submerged plants and can raise water temperature. Suspended solids that are often present in water include mud, clay, algae, bacteria, and minerals such as silica, calcium carbonate, and ochre (iron oxide). The amount of these solids can be increased by the discharge of wastes (domestic sewage, industrial and agricultural effluents), leaching of wastes (from mines), and agitation (dredging or shipping)
TDS	Use an appropriate TDS meter. Freshwater meters: 0–1990 ppm. Dual-range brackish water meters: 0–19,900 ppm. Salt-water meters: to above 35,000 ppm	This is a conductivity test of available ions in the water, including Ca^{2+} , Na^+ , K^+ , Fe^{2+} , Fe^{3+} , HCO_3^- , and ions containing P, S, and N. High levels of Na^+ is associated with excessive salinity and is found in many minerals. Potassium is incorporated into plant materials and is released into water systems when plant matter is decayed or burnt
DO	Winkler titration method: Divide the water sample into two parts.	The DO test measures the current oxygen levels in the water. The DO level

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Table 2 Contd...

Parameter	Method	Reason for testing
	Place one part in the dark (for BOD). To the other part of the sample, add 2 mL MnCl_2 (aq.) + 2 mL alkaline iodide solution (3.3 g NaOH + 2.0 g KI dissolved in 10 mL distilled water). Shake the sample. Add 2 mL concentrated HCl and shake again. The iodine formed is directly proportional to the DO. Titrate 50.0 mL of this solution with 0.0125 M sodium thiosulphate solution using starch as an indicator. The endpoint is the disappearance of blue-black colour. Colorimetric method can also be used	varies with temperature; it is highest in the afternoon due to photosynthesis and lowest just before dawn. DO is lowered by an increase in temperature (such as by a discharge of hot water from a power station) and increased in aerobic oxidation (due to increases in organic matter from sewage or due to inorganic fertilizers such as phosphates and nitrate with over-stimulated algal growth)
BOD	The first water sample as above is kept in the dark for 5 days at the temperature at which the sample was collected. Then the DO is determined using the Winkler titration method as above. Subtract the mass of oxygen obtained on Day 5 from the mass of oxygen obtained on Day 1 to determine the BOD (mg/L). Unpolluted natural waters have BOD <5 mg/L. Treated sewage can have BOD 20–30 mg/L	BOD measures the rate of consumption of oxygen by organisms in the water over a period of 5 days. Increases in BOD can be due to animal and crop wastes and domestic sewage
Salinity	Titrate a known volume of the water sample with silver nitrate solution (2.73 g AgNO_3 per 100 mL distilled water), using K_2CrO_4 as indicator. The endpoint of the titration is given by the reddening of the silver chloride precipitate ($\text{AgCl}_{(s)}$). Volume of AgNO_3 used = chloride content in g/L	Many aquatic organisms can survive only in a narrow range of salt concentrations, since salt controls their osmotic pressure
Total phosphate test	Perform acid digestion using concentrated H_2SO_4 and ammonium persulphate. Titrate with NaOH, using phenolphthalein as an indicator. Use few drops	Total phosphate is used as an indicator of pollution from run-off in agricultural areas or domestic sewage. Concentrations of 0.2 mg/L are common. Concentrations of 0.05 eutrophication (increas-

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Table 2 Contd...

Parameter	Method	Reason for testing
Total nitrogen test	<p>of H_2SO_4 to turn the solution clear again. Add ammonium molybdate solution and then solid ascorbic acid. An intense blue complex (molybdenum blue) is formed, which can be measured colorimetrically at 882 nm</p> <p>Kjeldahl digestion: Digestion with concentrated sulphuric acid converts the nitrogen into ammonium sulphate. The solution is then made alkaline. Liberated ammonia is distilled and determined by titration with standard acid</p> <p>Or</p> <p>Add Nessler's reagent (100 g mercuric iodide + 70 g KI in 100 mL distilled water, and then add 160 g NaOH in 700 mL distilled water; dilute the solution to 1 L) to samples containing <1 mg/L and measure absorbance colorimetrically at 425 nm</p>	<p>ed nutrient mg/L indicate the possibility (possibility of concentrations) and algal blooms are likely. Natural phosphate occurs due to decayed organic matter and phosphate minerals.</p> <p>Total nitrogen is an important indicator of eutrophic waters, especially for those contaminated by animal wastes, fertilizer run-off, and domestic sewage. Aquatic nitrogen is essential for the growth of organisms and is produced by natural processes, decay of proteins, action of lightning, and action of nitrogen-fixing bacteria on ammonia</p>
Hardness	<p>Calcium ions, Ca^{2+}—complexometric titration using EDTA at a pH of 12–13 (at this pH, Mg^{2+} is precipitated and not complexed with EDTA)</p> <p>Or</p> <p>Potentiometric techniques using selective electrodes</p> <p>or</p> <p>Atomic absorption spectroscopy (AAS)</p> <p>Or</p> <p>Gravimetric method—measure the amount of CaCO_3 (s) precipitated by a known volume of 0.02 M Na_2CO_3</p> <p>Or</p> <p>Flame test—Ca^{2+} flame test, a brick-red colour in a non-luminous Bunsen flame</p>	<p>Calcium ions are a major contributor to water hardness and enter water bodies when water is running through rocks containing minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcite ($\text{CaCO}_3$), and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. Hard water has a noticeable taste and produces precipitates with soaps that inhibit lathering and form precipitates (scale) in boilers, hot water systems, and kettles. Temporary hardness (or bicarbonate hardness) is due to $\text{Ca}(\text{HCO}_3)_2$, which deposits CaCO_3 (s) as a scale on boiling the water. Magnesium ion levels are often high in irrigation water and can cause scouring in stock. Ca^{2+} and Mg^{2+} can combine with Cl^- and SO_4^{2-}, causing permanent hardness, which cannot be removed</p>

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Table 2 Contd...

Parameter	Method	Reason for testing
	<p>Mg^{2+}—complexometric titration using EDTA at pH = 10 (both Ca^{2+} and Mg^{2+} will complex with EDTA at this pH. [Mg^{2+}] can be found by subtracting the results of this titration from the results of the first titration)</p> <p>Or</p> <p>Potentiometric techniques using selective electrodes</p> <p>Or</p> <p>AAS</p>	<p>by boiling. Water can be softened by an ion exchange process using a solid material such as a resin or clay that is capable of exchanging Na^+ or H^+ for Ca^{2+} and Mg^{2+}</p>
Microorganisms	<p>Microorganisms in a water sample are counted under a microscope. Method for finding the number of coliform organisms in a water sample: Pass a known volume of water sample through a filter that retains microorganisms. Transfer the filter to a sterile petri dish containing appropriate agar and incubate at 35°C for 20–40 h. Also, incubate a control plate with agar only. Colonies will develop on the filter wherever bacteria are retained. Count the number of of coliform colonies either visually or by using a microscope. Express these values as CFU/100 mL</p>	<p>Many protozoa, bacteria, viruses, algae, and fungi are found in natural water systems. Some are pathogenic (typhoid, cholera and amoebic dysentery can result from waterborne pathogens). The excessive growth of algae (called algal bloom) can degrade water quality because it lowers DO levels, thereby killing other living things. The level of bacterial contamination of water due to animal waste is measured by determining the number of coliform organisms such as <i>E. coli</i></p>
Heavy metals	<p>The precipitation methods of various ions are as follows:</p> <p>Ni^{2+} + dimethylglyoxime in ethanol turns pink-red</p> <p>Fe^{3+} + ammonium thiocyanate turns blood-red</p> <p>Cu^{2+} + dithizone in 1,1,1-trichloroethane turns yellow-brown</p> <p>Cd^{2+} + dithizone in 1,1,1-trichloroethane turns blue-violet</p> <p>Pb^{2+} + dithizone in 1,1,1-trichloroethane turns brick-red</p> <p>Pb^{2+} + 2KI (aq.) → yellow precipitate of PbI_2 (s)</p>	<p>Heavy metals in concentrations above trace amounts are generally toxic to living things. Trace amounts (<0.05 mg/L) of Zn, Cu, and Mn are present in most natural waters. Zn and Cu may be present in higher levels in irrigation areas due to the use of galvanized iron, copper, and brass in plumbing fixtures and for water storage. In irrigation areas, acceptable levels are 0.2 mg/L for Cu^{2+} and 2.0 mg/L for Zn^{2+} and Mn^{2+}. Atomic ethane turns brick-red</p> <p>absorption spectrophotometer can analyse lower levels more accurately</p>

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Table 2 Contd...

Parameter	Method	Reason for testing
Other ions	Zn ²⁺ + dithizone in 1,1,1-trichloroethane turns pink The popular methods of acid digestion or DTPA extraction, followed by AAS, can be employed	A flame photometer can analyse lower levels more accurately
	Al ³⁺ + aluminon → pink-red	
	Mg ²⁺ + magneson I → light blue	
	Na ⁺ flame test → yellow flame	
	K ⁺ flame test → lilac flame	
	NH ₄ ⁺ and NH ₃ + Nessler's reagent (100 g mercuric iodide + 70 g KI in 100 mL distilled water, then add 160 g NaOH in 700 mL distilled water, and finally dilute to 1 L) → yellow-brown	
	NO ₃ ⁻ + conc. H ₂ SO ₄ + FeSO ₄ → brown ring forms at junction	
S ²⁻ + lead acetate solution → black deposit of PbS		
	SO ₄ ²⁻ + BaCl ₂ (aq.) → white precipitate of BaSO ₄ (s)	

Source Page A L, R H Miller, and D R Keeney. 1982. *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, 2nd ed., Agronomy No. 9. Madison, WI: ASA-SSSA.

5/3 Day BOD test for the examination of water and wastewater

The BOD test is a laboratory procedure used to determine the relative oxygen requirements of clean waters, wastewaters, effluent, and polluted waters. It measures the oxygen used in the breakdown of organic matter and in the oxidation of inorganic substances. In other words, this test measures the potency of a particular pollutant in that it shows the amount of oxygen which will be removed from water to dissipate each litre of the pollutant.

Principle: In this method, a bottle is filled with sample and incubated for 5 days at 20°C or for 3 days at 27°C. DO is measured before and after incubation. BOD is calculated from the difference between initial and final DO. Because the initial DO is determined immediately after the dilution is made, all oxygen uptake is included in the BOD measurement (Table 4).

Sampling and storage: Samples for BOD analysis may degrade significantly during storage, resulting in low BOD values. Minimize reduction of BOD by analysing sample promptly and keep holding time to a minimum.

Samples should be kept cool/cold until analysed. Ideally, analysis should be initiated within 24 h and in no case should it be delayed longer than 48 h.

2.5 AIR POLLUTANTS

Air is composed of around 78% nitrogen, 21% oxygen, 1% argon, and 0.03% CO₂. Air pollution refers to the presence of any substance in air at a concentration that is enough to produce an undesirable effect on humans, animals, vegetation, or materials, or to alter the natural balance of any ecosystem significantly. Air pollutants can be solids, liquids, or gases, and can have local, regional, and global impacts.

The main air pollutants are carbon monoxide, particulates, sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOCs), and so on.

Table 3 Water quality of a typical natural aquatic system—an example

Substance or quality	Yamuna River water	Sea water
pH	6.8	8.0
DO (ppm)	6–8	6–8
Na ⁺ (ppm)	6.7	1.1 × 10 ⁴
K ⁺ (ppm)	1.5	380
Ca ²⁺ (ppm)	17.5	400
Mg ²⁺ (ppm)	4.8	1.3 × 10 ³
Cl ⁻ (ppm)	4.2	1.9 × 10 ⁴
SO ₄ ²⁻ /HSO ₄ ⁻ (ppm)	17.5	2.6 × 10 ³
CO ₃ ²⁻ /HCO ₃ ⁻ (ppm)	33.0	142
Hg ²⁺ (ppb)	<1	0.03
Cd ²⁺ (ppb)	<1	0.1
Pb ²⁺ (ppb)	<1	4–5

Table 4 Saturated DO levels

Temperature (°C)	Saturated level of DO (ppm)	
	Freshwater	Sea water
10	10.9	9.0
20	8.8	7.4
30	7.5	6.1
40	6.6	5.0

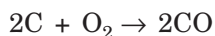
Source Kemker, Christine. 2013. Dissolved oxygen. Fundamentals of Environmental Measurements. Fondriest Environmental, Inc.

Carbon Monoxide

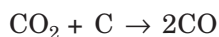
It is one of the most serious air pollutants, poisonous in nature, and 96.5% as heavy as air. Since CO is an odourless gas, its presence in the air is not detectable during breathing. The main source of carbon monoxide in the air is automobile exhaust. CO constitutes 80% of all automobile exhausts. Other sources of CO include combustion processes, such as stove, open fire, furnace, power plants, factories, coal mines, and smoke. Its natural sources are various plants and animals. Plants produce about 15–20 tonnes of CO per year. Breakdown of photosynthetic pigment in algae also releases some C into the atmosphere. Higher animals produce some CO during breakdown of haemoglobin and also from bile juice.

Chemical reactions that release CO in the atmosphere are the following:

- (i) Incomplete combustion of fuel or carbon-containing compounds



- (ii) A high-temperature reaction between CO₂ and carbon-containing material resulting in the formation of CO (for example, blast furnace)

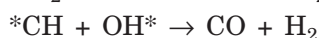
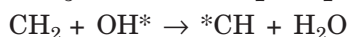
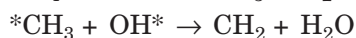
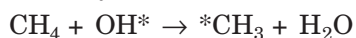


- (iii) Dissociation of CO₂ at high temperature



1% dissociation of CO₂ occurs at 1745°C.

- (iv) Methane produced by the decomposition of organic matter reacting with hydroxyl radicals (OH*) to yield CO



Decomposition of chlorophyll also gives CO:



- (v) Production of CO from haemoglobin breakdown in some animals: CO is the most widespread human poison on record, which can cause asphyxiation, resulting in instantaneous death. It has 200–300 times as great affinity for the haemoglobin of the blood as oxygen. In case of inhalation of CO, carry the patient to fresh air immediately and do not allow him to walk. Loosen all tight clothing. Apply artificial respiration if breathing has stopped or is irregular. Wrap the patient in a blanket to prevent chilling. If the patient is convulsing, keep him/her in the bed in a semi-dark room; avoid

jarring or noise. Life can also be saved by blood transfusion, by injecting **methylene** blue, or by making the person inhale carbogen (a mixture of 95% O₂ and 5% CO₂).

Particulates

Particulates are naturally found in the atmosphere in the form of dust, soot, sand, smoke, pollen, and ash. Combustion of fossil fuel also emits particulates. Solid- and liquid-**phase** materials in the atmosphere are variously referred to as particulate matter, particulates, particles, and aerosols. Although these terms are often used interchangeably, all refer to particles with diameters between approximately 1 nm and 10 μm that remain suspended in the atmosphere for long periods. The greatest threats to health are associated with the smallest particles because they have the greatest possibility of getting deposited deep within the respiratory system. Somewhat counter-intuitively, particles about 1 μm in size can remain suspended in the atmosphere much longer than gases, although those much larger than 1 μm in size will quickly settle out of the atmosphere because of gravity. The smallest particles will coagulate and coalesce quickly, forming larger particles. But particles of approximately 1 μm diameter do not grow as quickly as smaller particles and can remain suspended in the atmosphere for a week or more. It is not unusual, for example, for Saharan dust or particle plumes from Asia to be detected in the United States. Consequently, particulate matter is a continental- to global-scale air pollution problem. Unlike ozone and other gas-phase pollutants that are specific chemical species, particulate matter is a collection of chemical species defined mainly on the basis of particle size. The chemical constituents that make up particulate matter vary with particle size. Windblown dust is a main contributor to particles larger than 10 μm in diameter, whereas sulphates, nitrates, and organic compounds are the main constituents of smaller particles that can penetrate deep into the respiratory system and engender health effects. Organic particles can be emitted directly as soot from combustion processes or can be formed when large hydrocarbon molecules react with oxidants in the atmosphere and form chemicals that condense onto particles. Sulphate particles are formed via a series of reactions that convert sulphur dioxide (SO₂), which is released into the atmosphere by the combustion of sulphur-containing fuels, into sulphuric acid. Nitrate particles are formed via reactions that convert oxides of nitrogen, which are released into the atmosphere by combustion processes, into nitric acid. If particles containing sulphuric acid, nitric acid, and organic compounds retain their acidity and are washed out of the atmosphere by rainfall, the rainfall becomes acid rain. The continental and global scale of air pollution problems is not limited to particulate matter.

Emission of GHGs causes global climate change. The presence of ozone-depleting compounds in the stratosphere has created polar ozone holes. Atmospheric releases caused by volcanic eruptions and fires have global effects. Atmospheric particles also influence climate and rainfall. The challenges of reducing air pollution call for a sophisticated understanding of atmospheric chemistry, applied at local, regional, continental, and global scales.

Composition of particulates

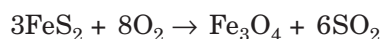
Particulates include organic and inorganic matters, nitrogen compounds, sulphur compounds, PAH, several metals, and radionuclides. An estimate indicates that particulate contaminants contain nearly 22 metallic elements. The most abundant elements are Ca, Na, Si, Al, and Fe. Considerable quantities of Zn, Pb, Cu, Mg, and Mn are also present in air. The concentration of these particulate matters depends upon the nature of industrial emission. For instance, the level of Pb increases with the traffic density because lead tetraethyl is added as an antiknock to the petroleum fuel. Spectrographic studies on the organic fraction conclude that a variety of aliphatic and aromatic hydrocarbons, organic bases, phenols, cresols, organic acids, carcinogenic compounds, and various types of complex compounds occur in the atmosphere as particulate matters.

Physical methods involved in particulate formation include the following:

- (i) Dispersion process mainly yields dispersion aerosol, for example, dusts that are solid dispersion aerosols. Particulates nearly 1 μm in size are formed by disintegration of larger particles.
- (ii) Adhesion of smaller particles by chemical process yields particulates of size ranging from 10 to 20 μm .
- (iii) Natural sources also produce dispersed aerosols from sea spray, windblown dust, dust during cultivation, volcanic dust, and so on.
- (iv) By coagulation, extremely small particles from larger aggregates, sorption, absorption, adsorption, and chemisorptions also result in the formation of particulate matter.

Formation of inorganic particulate matter: Inorganic particulates generally originate from metallic oxides, sulphides, carbonates, and so on when fuel-containing metals are burned. For instance,

- (i) The particulate Fe_3O_4 is formed during the combustion of pyrites containing coal.

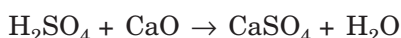
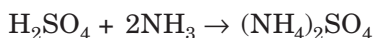


- (ii) A part of calcium carbonate in the ash fraction of coal gets converted to calcium oxide, which is released into the atmosphere through stack.



- (iii) Organic vanadium in residual fuel oil is converted to particulate vanadium oxide.
- (iv) Lead halides are generated by the combustion of leaded gasoline. Tetraethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$, in leaded gasoline combines with oxygen and halogenated scavengers, dibromoethane, and dichloroethane. These lead halides emerge through the exhaust system and condense to form particulates after entering the atmosphere.
- (v) Aerosol mists are formed by the oxidation of atmospheric sulphur dioxide to sulphuric acid, that is, $2\text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$.

It forms salts with basic air pollutants such as ammonia or calcium oxide:



Formation of organic particulate matter: Organic particulate matter originates mainly from combustion of fuels, automobiles, and vegetation. Chrysene, benzofluoroethane, benzo-alpha-pyrene, and so on are some organic particulate matter of carcinogenic nature. PAH compounds generally occur in urban atmosphere at the level of $20 \mu\text{g}/\text{m}^3$. Such particulates pose a serious health hazards and lie in the range of $1 \mu\text{m}$ size. Aldehyde, ketone, peroxide, epoxide, ester, quinine, and lactones are found among the oxygenated neutral organic compounds. Organic acids present in OPM include lauric, palmitic, stearic, myristic, oleic, linoleic, and behenic. Particulate paraffin is pyrolysed to yield $\text{C}_{10}\text{H}_{22}$, which again disintegrates into fine particles. Oxidized, polymerized hydrocarbons and nitrogenous azo heterocyclic compounds are released into the atmosphere from automobile exhaust. PAH compounds remain absorbed in soot particles. Soot itself is a highly condensed product of these compounds. A soot particle is composed of several thousands of interconnected crystallites, that is, graphitic platelets, each having 100 condensed aromatic rings. It consists of 1–3% hydrogen and 5–10% oxygen due to partial oxidation. Soot particles contain toxic trace metals such as Be, Cr, Mn, Ni, V, Cd, and Fe and poisonous organic compounds such as benzo-alpha-pyrene.

At urban scales, air pollution is frequently referred to as photochemical smog. “Smog” is a contraction of the words “smoke” and “fog” and was originally used to describe air pollution caused by coal burning in London. Urban smog is photochemical in nature because many of the chemicals

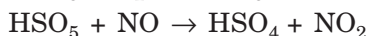
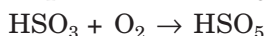
found in urban air are formed by chemical reactions driven by sunlight. Ozone (O_3) is one of the most abundant air pollutants in urban smog that are produced by photochemical reactions. In contrast to the ozone found in the upper atmosphere (stratospheric ozone), which protects the planet from **ultraviolet radiation**, ground-level or tropospheric ozone is a lung irritant and a danger to human health. It is also responsible for crop damage and is suspected to contribute to forest decline in Europe and in parts of the United States. Ground-level ozone and other photochemical pollutants are formed in urban atmospheres by the reactions of oxides of nitrogen (mainly NO and NO_2 , which are by-products of **combustion** processes) in the presence of hydrocarbons. At the high temperatures generated during combustion, some of the N_2 and O_2 in air are converted to oxides of nitrogen and, in general, the higher the combustion temperature, the greater the amounts of oxides of nitrogen produced. Hydrocarbons are emitted from natural sources and as a result of activities that involve using organic solvents, coatings, or fuel. These hydrocarbons and oxides of nitrogen participate in reactions that yield not only ozone, but also aldehydes, hydrogen peroxide, peroxyacetyl nitrate ($C_2H_3NO_5$), nitric acid, and molecular species of low volatility that accumulate in fine particles suspended in the atmosphere. Although many of these constituents of photochemical smog have environmental impacts, fine particulate matter presents the greatest health endangerment in most urban areas.

Sulphur Oxides

The combustion of coal is a man-made source of SO_2 and SO_3 . Volcanoes also emit SO_2 .

Reaction of SO_2 in the atmosphere

In the atmosphere, SO_2 does not remain in gaseous state for a long time. It reacts with the atmospheric moisture in the presence of sunlight to form sulphuric acid and comes down on land along with rainwater (acid rain).



In the presence of sunlight, the photochemically generated free radicals react as a catalyst in these reactions. Thus, sunny weather enhances the rate of conversion to acid, which decreases rapidly after sunset. HSO_4 as well as NO_2 undergoes hydrolysis to form their respective acids H_2SO_4 and HNO_3 . Although the actual mechanism of these reactions is not clear, these seem to occur in the presence of trace metal catalysts or oxidizing agents such as ozone or hydrogen peroxide. Recent studies have

shown that manganese, and not iron, is the only metal that can act as a catalyst in cloud droplets.

Sulphur dioxide undergoes several chemical reactions in air, forming particulate matter and aerosols, which are scavenged from the atmosphere. The SO_2 and SO_3 gases are washed down from the atmosphere in the form of sulphuric acid. The presence of H_2SO_4 in increasing concentration in the troposphere is indicated by the increasing and more widespread occurrence of acid rain. A number of factors such as temperature, light, intensity, humidity, air traffic, and SPM may influence these reactions.

Sulphur dioxide reacts through several ways in the atmosphere, which are as follows:

- (i) Photochemical reactions
- (ii) Chemical reactions in presence of NO_x and hydrocarbons
- (iii) Chemical reactions in water droplets and solid particles

In the photolysis of air containing SO_2 , olefin hydrocarbons, and NO_x , the rate of oxidation of SO_2 has been found to increase, which results in the formation of aerosols.

Control of SO_x pollution

SO_x can be reduced and controlled by the following important methods:

- (i) Removal of the sulphur from fuel before burning
- (ii) Use of low-sulphur content fuel
- (iii) Using other energy sources for fuel combustion
- (iv) Removal of SO_x from fuel gases
- (v) Use of natural gases
- (vi) Use of nuclear power to generate electricity from power plants

About 15% of SO_2 emission is caused by oil combustion. General fuel oil is distilled over or left as residue in boiler during vaporization. While refining, the distillate gets separated from the residual mixture, leaving behind low content of S, which merely accounts for 0.05–0.035% by weight. Substitution of energy sources is a better technique to solve SO_x pollution problem.

For example, hydroelectric plants do not need any fuel, and so they are free from SO_x pollution. Removal of three forms of S (pyrites, sulphates, and organic sulphides) from fuel before burning can be achieved by adopting the physical technique. However, coal can be converted to gases by gasification process, in which powdered coal reacts with steam and oxygen in a fluidized bed at a high pressure ranging from 600 to 1000 psi. The product formed constitutes H_2 , CO, CO_2 , CH_4 , and H_2S . CO and H_2 react to form CH_4 , thereby reducing the S content. Some refining processes are also operated in petroleum industry, which lowers the

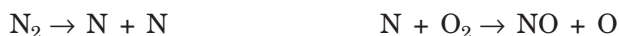
S content by 2.5–3%. Huge investment and heavy recurring costs are involved in the current technology for removal of SO_x from flue gases. However, double alkali process has been used commercially to some extent. SO_2 is scrubbed off by two alkalis, that is, $\text{Ca}(\text{OH})_2$ and NaOH , in two steps.

Nitrogen Oxides (NO_x)

Nitrogen naturally comes from thunderstorms and biological processes. Combustion engines in jets or cars also produce NO . In the atmosphere, the average residence life of NO is 4 days and that of NO_2 is 3 days. The residence life of NO_x may decrease in a highly polluted atmosphere because of formation of nitric acid, which is predicated as nitric salts with ammonia. HNO_3 reacts rapidly to form a particulate substance in the atmosphere and causes air pollution. Nitric acid as such is not considered to be a health hazard at the level it is found in the urban air; however, when it comes in contact with the atmospheric air, it undergoes a series of chemical reactions to form various secondary pollutants such as PAN, O_3 , and carbonyl compounds. On coming in contact with air, it readily forms NO_2 , which is the chief constituent of photochemical smog in metropolitan cities.

Reactions of NO_x in the atmosphere are given below:

NO is formed by the reaction of O_2 with atomic nitrogen:



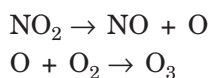
High temperature favours the formation of NO ; hence, automobiles such as motor and heavy engine vehicles that operate at higher temperatures are major sources for the production of NO . Oxidation of atmospheric NO is a very slow process, which may generally take place over a period of 6 days.



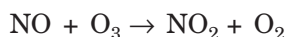
When NO and O_3 are formed in equal amounts, they combine together to produce NO_2 and O_2 .



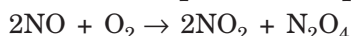
NO_2 is a highly reactive species occurring in atmosphere. It penetrates into the troposphere and absorbs UV light as well as visible light. NO_2 undergoes photodissociation using photo energy below 380 nm and is reduced to NO and atomic oxygen by UV light. The atomic oxygen reacts with oxygen to form ozone.



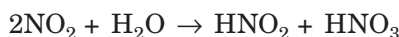
Ozone reacts with NO to form NO_2 and O_2 .



Microorganism reduces N_2O under anaerobic condition, producing the pollutant NO . NO_2 mainly exists as N_2O_4 (10%) in solid state. In gaseous state, there is 90% NO_2 and 10% N_2O_4 .



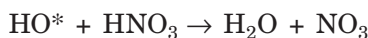
NO_2 reacts with water to form nitric acid and photochemical smog.



NO_2 also reacts with hydroxyl ions in the stratosphere.



Nitric acid thus formed is reduced to NO_2 by the attack of hydroxyl radicals.



Sometimes atomic oxygen formed as a result of photochemical reduction of NO_2 also reacts with reactive hydrocarbons such as CH_4 , C_2H_6 , and $\text{C}_6\text{H}_5\text{CH}_3$, which are generated by the burning of fossil fuels to form radicals in the presence of UV light and oxygen.



These photochemically generated radicals are extremely reactive and undergo a series of reactions in the presence of UV light to form more reactive radicals, which combine with a number of pollutants in the air to form NO_2 , O_3 , H_2O_2 , and a number of other toxic substances such as aldehydes, formaldehydes, and PAN. All these collectively form photochemical smog.

Oxides of nitrogen produce toxic and corrosive gases through the photochemical chain reaction. These gases produce nitric acid, which is washed down and contributes to acid rain. Acidity of rainwater increases when the amount of oxides of nitrogen and sulphur increases in the atmosphere to produce more nitric and sulphuric acids. Acid rain reduces fertility of the soil.

Photochemical Smog

NO_x , in combination with unsaturated hydrocarbons, CO , O_3 , hydrogen peroxide, and organic peroxide, forms photochemical smog in the presence of sunlight. Photochemical reactions are initiated by UV light in the air. Peroxybenzoyl nitrate is also produced in photochemical smog in the presence of NO_2 and olefins. The smog may have a 50 ppb of PAN also. Peroxybenzoyl nitrate is 100 times more toxic than PAN and 200 times as powerful as formaldehyde.

Effects of photochemical smog on human

- (i) Photochemical smog is characterized by a yellowish grey haze in the atmosphere. This smog along with ozone may irritate the eyes and nose, affect lung function, degrade physical performance of humans, and exacerbate asthma.
- (ii) Symptoms such as nasal block and discharge, sneezing, hacking cough, and airway obstruction may persist in highly vehicular areas.
- (iii) Studies have also revealed prevalence of chest problem and upper airway morbidity in the area with higher levels of oxidants, such as Mumbai and Delhi.
- (iv) Occurrence of cold, cough, and sputum and breathlessness are closely related to peaking of vehicular pollution.
- (v) Photochemical smog leads to respiratory problem, reduces visibility, alters various blood parameters, and aggravates diseases such as headache and bronchitis.

Effect of photochemical smog on plants

- (i) Photochemical smog is reported to cause injuries to petunia, lettuce, pinto bean, citrus, salad crops, and coniferous trees even at a very low concentration of 0.001 ppm.
- (ii) PAN causes injury in beets, celery, pepper, and aster. It causes silvering of leaves and death of forest tree.
- (iii) PAN inhibits important Hill reactions of photosynthesis.
- (iv) Photochemical smog is believed to cause early maturity in plants.
- (v) Exposure of 4 ppb of PAN for 4 h is known to create visible damage in plants. Vegetation damage may take several forms, such as chlorosis, leaf abscission, and curling.
- (vi) Photochemical smog alone or in conjunction with O_3 , PAN, and NO_x causes damage to forest, agriculture, and other materials such as rubber, paints, fibres, and polymers.

2.6 CONTROL TECHNIQUES FOR AIR POLLUTANTS

Some controls techniques can be used to remove gaseous contaminants from industrial gas streams. The appropriateness of these techniques depends on the chemical and physical characteristics of the specific gas- and vapour-phase compounds present in the gas stream. Commercially, four major techniques are used for the control of gaseous contaminants.

- (i) **Adsorption onto solid surfaces:** Adsorption involves the interaction between gaseous contaminants and the surface of a

solid adsorbent. The adsorbent can be available in a wide variety of physical forms, such as pellets in a thick bed, small beads in a fluidized bed, or fibres pressed onto a flat surface. There are two types of adsorption mechanisms: (1) physical and (2) chemical. The basic difference between physical and chemical adsorptions is the manner in which the gas or vapour molecule is held to the adsorbent surface.

- (ii) **Absorption into liquids:** Gaseous contaminants that are soluble in aqueous liquids can be removed by the absorbers. This is one of the main mechanisms used for the removal of acid gas compounds (for example, sulphur dioxide, hydrogen chloride, and hydrogen fluoride) and water-soluble organic compounds (for example, alcohols, aldehydes, and organic acids). The contaminant gas or vapour is absorbed from the gas stream as it comes into contact with the liquid.
- **Oxidation to form non-toxic compounds:** Oxidizers can be used for the destruction of a wide variety of organic compounds. There are three main categories—thermal oxidizers, catalytic oxidizers, and flares. Thermal oxidizers and catalytic oxidizers are used for sources such as surface coaters, gasoline storage and distribution terminals, and synthetic organic chemical plants. Flares are used primarily to treat emergency vent gases in synthetic organic chemical plants and petroleum refiners.
- (iii) **Chemical reduction to form non-toxic compounds:** Reduction systems are used primarily for the destruction of NO_x compounds emitted from combustion processes. These systems include selective non-catalytic reduction systems (SNCRs) and selective catalytic reduction (SCR) systems. In both types of systems, a chemically reduced form of nitrogen is injected into the gas stream to react with the oxidized nitrogen compounds, such as NO and NO_2 . The reactions between the reduced and oxidized forms of nitrogen result in molecular N_2 , the major constituent of clean air.
- (iv) **Condensations of vapours to form liquids:** Condensation systems are used exclusively for the recovery of organic compounds present at moderate-to-high concentrations in industrial process for effluent gas streams. Based on the general operating temperature range, condensation systems may be grouped into three main categories:
- Water-based direct and indirect condensers (40°F to 80°F)
 - Refrigeration condensers (−50°F to −150°F)
 - Cryogenic condensers (−100°F to −320°F)

The most common types of condensers are those using cooling water in direct contact or indirect contact vessels. Refrigeration and cryogenic systems are used primarily for the high-efficiency recovery of high-value contaminants. Condensation systems are used primarily for the control of high concentrations of organic contaminants.

NO_x Control Technique

Flue gas treatment

Selective non-catalytic reduction—These systems are used to control NO_x emissions from boilers and waste incinerators. An SNCR system uses ammonia or urea to react with NO_x in a complex set of high-temperature, homogeneous gas-phase reactions. Ammonia can be used in an anhydrous or an aqueous form. The aqueous ammonia storage and feeding systems are similar to those used for urea. Ammonia is diluted prior to use, and the flow rate to each set of nozzles is controlled individually. In anhydrous ammonia injection systems, ammonia is stored in pressurized storage tanks and fed as a gas. The products of the reactions between ammonia and urea with NO_x are molecular nitrogen and water. In both ammonia and urea systems, small quantities of ammonia can remain in the gas stream after the reactions are completed. These emissions are termed as “ammonia slip”. The ammonia or urea should be injected into a portion of the boiler when the combustion gas temperature is in the range of 870–1100°C. Effectiveness of NO_x reduction depends on the adequacy of the gas temperature range at the area of injection. If the gas stream is in the 1600–2000°F temperature range, NO_x reductions of up to 60% are possible. If some of the ammonia or urea reagent is injected in portions of the combustion gas stream that are too cold, high ammonia slip emissions can occur. Injection of reagents in portions of the gas stream that are above 2000°F can result in the oxidation of the nitrogen in the reagents to form additional NO_x.

SCR systems—The SCR system uses a catalyst-impregnated bed to reduce NO_x emissions. Because of the effect of the catalyst, the chemical reduction reaction between ammonia and NO_x occurs at temperatures much lower than those required for SNCR systems. Most SCR systems operate in the range of 550–750°F (290–400°C), which is a very convenient temperature range that exists at the exit of the feedwater economizers in the boiler. The gas stream can be withdrawn from the boiler at this point, passed through a series of catalyst beds, and returned to the boiler upstream of the air preheater. When properly designed and operated, SCR systems are capable of sustained NO_x reductions in the range of 60–90%. However, to minimize reagent costs, SCR systems are applied

after all reasonable combustion modifications required to minimize the NO_x formation rates have been installed in the boiler.

Control Methodologies for Sulphur Oxides

Sulphur dioxide emissions from fossil fuel-fired combustion sources can be reduced by five techniques. Fuel treatment and FGD are the most common techniques being used to comply with the Clean Air Act requirements.

- (i) **Low sulphur fuel firing:** One of the most straightforward ways to reduce SO_2 emissions from combustion sources is by burning a low-sulphur-containing fuel. The coal-fired boilers use low-sulphur coal, low-sulphur fuel oil, or natural gas, instead of a high-sulphur coal. The use of low-sulphur coal can reduce SO_2 by more than 80%. Low-sulphur coal usually contains between 0.4% and 1% of sulphur, whereas high-sulphur coal contains sulphur between 1% and 5%.
- (ii) **Flue gas desulphurization (FGD):** FGD is the most common technology used for controlling emissions of sulphur oxides from combustion sources. FGD technology is also used to reduce SO_2 emissions from copper smelters. In this method, SO_2 gaseous emissions are usually removed by a post-combustion absorption process. FGD scrubbing processes can be “wet” or “dry”. Wet scrubbing processes use a liquid absorbent to absorb the SO_2 gases.
- (iii) **Dry scrubbing:** Dry scrubbing is basically a two-step chemical process. In the first step, the flue gas leaving the boiler or incinerator is scrubbed with a stream of alkali, usually calcium hydroxide. In the second step, the reaction products are collected in a high-efficiency particulate matter control device, such as a pulse jet bag house, a reverse air bag house, or an electrostatic precipitator. There are two types of dry scrubbers: spray dryer absorption and dry injection absorption.
- (iv) **Fluidized-bed combustion:** A fluidized-bed boiler using an alkali such as limestone can reduce emissions of sulphur oxides. In this type of boiler, a grid supports the bed of coal and limestone (or dolomite) in the firebox of the boiler. Combustion air is forced upwards through the grid, suspending the coal and limestone bed in a fluid-like motion. Natural gas is used to ignite the pulverized coal. Once the coal is ignited, the gas is turned off. The sulphur in the coal is oxidized to SO_2 and consequently combined with limestone to form calcium sulphate (CaSO_4). The CaSO_4 and fly ash particulate matter are usually collected in a bag house or in

an electrostatic precipitator. Fluidized-bed boilers usually require a calcium-to-sulphur stoichiometric ratio of 2.0:1.0 to 4.0:1.0 because of the limited amount of calcium oxide surface area available.

(v) **Fuel treatment**

- **Coal gasification:** Over 70 different processes have been developed for producing a combustible gas from coal. Three basic steps are common to all coal gasification processes: pretreatment, gasification, and gas cleaning. Coal pretreatment involves coal pulverizing and washing. The pulverized coal is gasified in a reactor with limited oxygen, producing a gas with a low, medium, or high heating value by applying heat and pressure or by using a catalyst to break down the components of the coal. The gas produced contains carbon monoxide, hydrogen, carbon dioxide, water, methane, and contaminants, such as hydrogen sulphide and char. During gasification, the sulphur content in the coal is converted to H_2S , which is then converted to elemental sulphur by partial oxidation and catalytic conversion. The synthetic gas produced is free of sulphur and can be burnt without releasing harmful pollutants.
- **Coal liquefaction:** A process for changing coal into synthetic oil is called coal liquefaction. It is similar to coal gasification. Two basic approaches are used for liquefaction. One approach uses gasifiers to convert coal to carbon monoxide, hydrogen, and methane, followed by condensation to convert the gases to oils. The other approach uses a solvent or a slurry to liquefy pulverized coal and then converts this liquid into a heavy fuel oil. Some processes produce both a synthetic gas and a synthetic oil. Hydrogen is used to convert sulphur present in the coal to hydrogen sulphide gas, which is partially oxidized to form elemental sulphur and water. More than 85% of the sulphur can be removed from coal by liquefaction.
- **Coal cleaning:** There are two types of coal cleaning processes: physical and chemical. Physical coal cleaning is used to remove the inorganic (mainly pyritic) sulphur compounds present in the coal, whereas chemical coal cleaning is used to reduce organic sulphur compounds. Physical coal cleaning is a well-established technology that has been used for more than 50 years to reduce the sulphur and ash content of high-sulphur coal supplies. Physical coal cleaning uses the differences in density of both the coal and the sulphur-bearing impurities in the coal. The coal is crushed, washed, and then separated by settling processes, using cyclones, air classifiers, or magnetic separators. Approximately 40–90% of the pyrite sulphur content

can be removed by physical coal cleaning. Its effectiveness depends on the size of pyritic sulphur particles and the amount of pyritic sulphur contained in the coal.

Chemical coal cleaning methods that reduce the organically bound sulphur are currently under development. In microwave desulphurization, the coal is crushed and then heated for 30–60 s by exposure to microwaves. Mineral sulphur selectively absorbs this radiation, forming H_2S gas, which is reduced to elemental sulphur by the Claus process. In another microwave process, calcium hydroxide $[\text{Ca}(\text{OH})_2]$ is added to crushed coal. The organic sulphur present in coal converts to CaSO_3 when exposed to this radiation. The coal is washed with water to remove the CaSO_3 and other impurities. As much as 70% of the sulphur can be removed by the microwave process.

