6.10 WHAT IS ACID RAIN—HAVE HUMAN ACTIVITIES BEEN RESPONSIBLE?

Oxides of sulfur and nitrogen originating from industrial operations and fossil fuel combustion are the major sources of acid forming gases. Acid forming gases are oxidised over several days by which time they travel several thousand kilometers. In the atmosphere these gases are ultimately converted into sulfuric and nitric acids. Hydrogen chloride emission forms hydrochloric acid. These acids cause acidic rain. Acid rain is only one component of acidic deposition. Acidic deposition is the total of wet acidic deposition (acid rain) and dry deposition.

Rainwater is turned acidic when its pH falls below 5.6 (Fig. 6.7). In fact clean or natural rainwater has a pH of 5.6 at 20°C because of formation of carbonic acid due to dissolution of CO_2 in rain water.

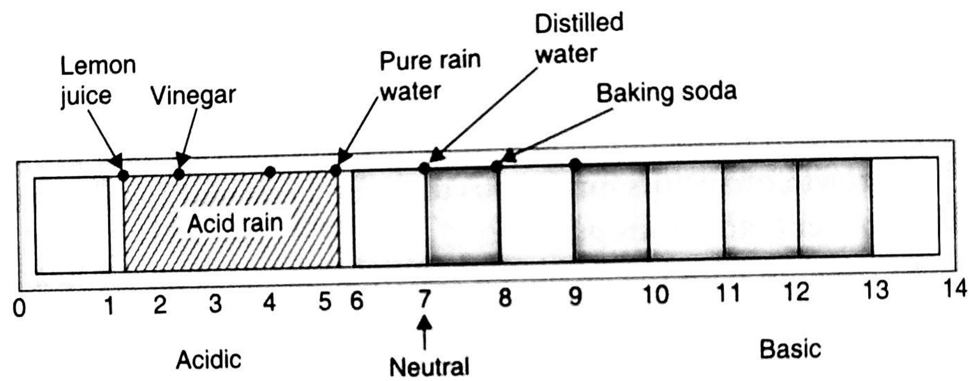

Fig. 6.7 The pH scale of common substances.

The Adirondack Lakes located in the state of New York are known to receive acid rains.

The strong acids like sulphuric acid (H_2SO_4) and nitric acid (HNO_3) dissolved or formed in rainwater dissociate or release hydrogen ions thereby increasing the acidity in rain drops.

Generally sulfuric acid forms a major fraction of acid rain, followed by nitric acid and a very small fraction of other acids. However, in urban areas Calcium (Ca^{2+}), Magnesium (Mg^{2+}) and ammonium (NH^{4+}) ions help to neutralize the rain drops shifting the overall H^+ towards basic scale. The overall pH of any raindrop is due to the net effect of carbonic acid, sulfuric acid, nitric acid and other acidic constituents or any neutralizers such as ammonia.

In the absence of rain, dry deposition of acid may occur. Acid forming gases like oxides of sulphur and nitrogen and acid aerosols get

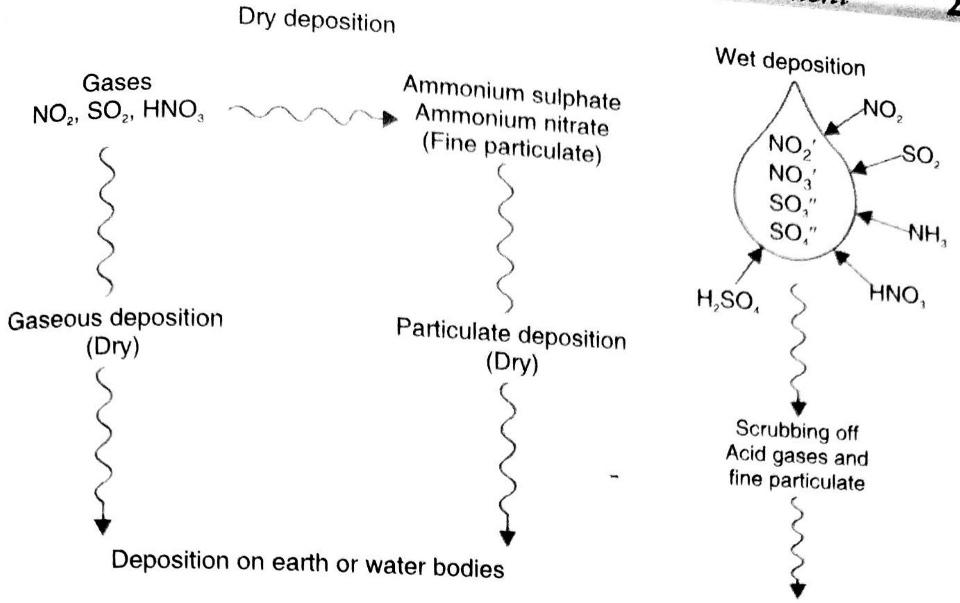

Fig. 6.8 Acid deposition (dry deposition and wet deposition).

deposited on the surface of water bodies, vegetation, soil and other materials (Fig. 6.8). On moist surfaces or in liquids these acid forming gases can dissolve and form acids similar to that formed in acid rain. If the oxidizers are present on the liquid surfaces then these gases undergo oxidation to form acids. Fine particles or acid droplets can act as nuclei for water to condense to form rain droplets. By such process sulfuric acid is incorporated into the droplets. In the clouds additional SO_2 and NO_2 contact the droplets and get absorbed which can be oxidized by the dissolved hydrogen peroxide (H_2O_2) or other oxidizers. In the droplets falling from the clouds additional acidic gases and aerosol particles get incorporated, further decreasing their pH. A unit decrease in pH value causes 10 times increase in acidity. Average pH in rainfall over eastern United States from April 1979 to March 1980 was less than 5.0. In India acid rain is recorded from certain places:

Name of place	pH of rainwater
Kodaikanal	5.18
Minicoy	5.52
Mohanbari	5.50

Effects of Acid Rain

Acid rain causes a number of harmful effects below pH 5.1. The effects are visible in the aquatic system even at pH less than 5.5.

- It causes deterioration of buildings especially made of marble *e.g.* monuments like Taj Mahal. Crystals of calcium and magnesium sulphate are formed as a result of corrosion caused by acid rain.

- It damages stone statues. Priceless stone statues in Greece and Italy have been partially dissolved by acid rain.
- It damages metals and car finishes.
- Aquatic life especially fish are badly affected by lake acidification.
- Aquatic animals suffer from toxicity of metals such as aluminium, mercury, manganese, zinc and lead which leak from the surrounding rocks due to acid rain.
- It results in reproductive failure, and killing of fish.
- Many lakes of Sweden, Norway, Canada have become fishless due to acid rain.
- It damages foliage and weakens trees.
- It makes trees more susceptible to stresses like cold temperature, drought, etc. Many insects and fungi are more tolerant to acidic conditions and hence they can attack the susceptible trees and cause diseases.

Control of Acid Rain

- Emission of SO_2 and NO_2 from industries and power plants should be reduced by using pollution control equipments.
- Liming of lakes and soils should be done to correct the adverse effects of acid rain.
- A coating of protective layer of inert polymer should be given in the interior of water pipes for drinking water.

6.11 IS OZONE LAYER DEPLETION A THREAT TO LIVING BEINGS?

For the last 450 million years the earth has had a natural sunscreen in the stratosphere called the ozone layer. This layer filters out harmful ultraviolet radiations from the sunlight and thus protects various life forms on the earth.

Ozone is a form of oxygen. The molecule of oxygen contains two atoms whereas that of ozone contains three (O_3). In the stratosphere ozone is continuously being created by the absorption of short wavelength ultraviolet (UV) radiations. Ultraviolet radiations less than 242 nanometers decompose molecular oxygen into atomic oxygen (O) by photolytic decomposition.

$$O_2 + h\nu \longrightarrow O + O$$

The atomic oxygen rapidly reacts with molecular oxygen to form ozone.

$$O + O_2 + M \longrightarrow O_3 + M$$

(M is a third body necessary to carry away the energy released in the reaction).

Ozone thus formed distributes itself in the stratosphere and absorbs harmful ultraviolet radiations (200 to 320 nm) and is continuously being converted back to molecular oxygen.

$$O_3 + h\nu \longrightarrow O_2 + O$$

Absorption of UV radiations results in heating of the stratosphere.

The net result of the above reactions is an equilibrium concentration of ozone. Ozone concentration in about 24 km of the stratosphere i.e. from 16 km to 40 km away from earth is about 10 ppm (as compared to 0.05 ppm concentration of harmful tropospheric ozone). This equilibrium is disturbed by reactive atoms of chlorine, bromine etc. which destroy ozone molecules and result is thinning of ozone layer generally called ozone hole.

The amount of atmospheric ozone is measured by 'Dobson Spectrometer' and is expressed in **Dobson Units (DU)**. One DU is equivalent to a 0.01 mm thickness of pure ozone at the density it would possess if it were brought to ground level (1atm) pressure. Normally over temperate latitude its concentration is about 350 DU, over tropics it is 250 DU whereas at subpolar regions (except when ozone thinning occurs) it is on an average 450 DU. It is because of the stratospheric winds which transport ozone from tropical towards polar regions.

Thinning of Ozone Layer

The Antarctic ozone hole was discovered by Dr Joe C. Farman and his colleagues in the British Antarctic Survey who had been recording ozone levels over this region since 1957. During spring season of south pole *i.e.* September to November each year ozone depletion is observed. Steep decline has been observed since mid 1970s with a record low concentration of 90 DU in early October of 1993.

Chlorofluorocarbons (CFCs) are mainly responsible for ozone depletion in the stratosphere. CFCs are a group of synthetic chemicals first discovered by Thomas Midgley Jr. in 1930. CFC-11 and CFC-12 are the CFCs most commonly used. CFCs are used as coolants in refrigerators and air conditioners, as propellants, cleaning solvents, sterilant and in styrofoam etc. CFCs released in the troposphere reach the stratosphere and remain there for 65–110 years destroying O_3 molecules. In 1974, Rowland and Molina warned that CFCs are lowering the concentration of ozone in the stratosphere and predicted severe consequences. It was however, in 1985 that scientists for the first time discovered that 50% (98% in some areas) of upper stratospheric ozone over Antarctica was destroyed during the Antarctic spring and early summer (September-December). At Antarctic region the temperature during winter drops to – 90°C. The winds blowing in a circular pattern over earth's poles create polar vortices. Water droplets in clouds when they enter these vortices form ice crystals. CFCs get collected on the surfaces of these ice crystals and destroy ozone much faster. Similar destruction of ozone over North Pole occurs during Arctic spring and early summer (February-June). The depletion is 10–25% and it is less than that observed at south pole.

Nitrous oxide emitted by supersonic aircrafts during combustion of fossil fuel, and use of nitrogen fertilizers breaks ozone molecules. Chlorine liberated from chlorofluorocarbons also break ozone molecules. The chain reaction started in Antarctic spring *i.e.* August/September continues till nitrogen dioxide is liberated from nitric acid (formed in the stratosphere) by photolysis (breakdown by sunlight). Nitrogen dioxide combines with chlorine and stops further destruction of ozone.

ARCTIC OZONE HOLE

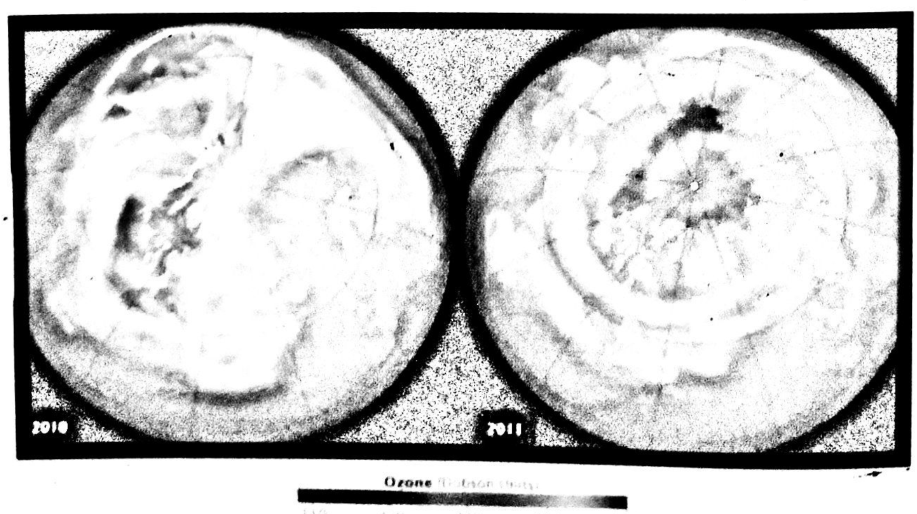

Fig. 6.9 Levels of ozone above the Arctic on 19 March 2010 (left) and 26 March, 2011 (right), (Source of photograph: OMI/Aura/NASA)

(Contd.)

For the first time above the Arctic, a very large hole (thinning of ozone beyond certain level), almost five times the size of California, has been reported during early 2011 (Fig. 6.9). This time it is comparable to the Antarctic ozone hole. Chemically induced destruction of ozone occurs over both the poles and the hole above the Arctic was always much smaller than that reported over Antarctic. In March 2011 unusually long-lasting intense cold temperatures and powerful wind patterns in the Arctic's lower stratosphere created the right conditions for already-present, ozone-destroying forms of chlorine to cause more than 80 percent ozone loss over an altitude of 18–20 kilometres. The findings, published on 3th October in the journal Nature reveal that the hole is formed over northern Russia, parts of Greenland, and Norway. This means that people in these areas are likely to be exposed to high levels of UV radiations. The risk of UV exposure in these areas would increase if occurrence of similar Arctic hole becomes an annual feature.

Effects of Ozone Depletion

- Ozone depletion in the stratosphere will result in more UV radiation reaching the earth especially UV-B (290–320 nm). The UV-B radiations affect DNA and the photosynthetic chemicals. Any change in DNA can result in mutation and cancer. Cases of skin cancer (basal and squamous cell carcinoma) which do not cause death but cause disfigurement will increase.
- Easy absorption of UV rays by the lens and cornea of eye will result in increase in incidents of cataract.
- Melanin producing cells of the epidermis (important for human immune system) will be destroyed by UV rays resulting in immuno-suppression. Fair people (who can not produce enough melanin) will be at a greater risk of UV exposure.
- Phytoplanktons are sensitive to UV exposure. Ozone depletion will result in decrease in their population thereby affecting the population of zooplankton, fish, marine animals, in fact the whole aquatic food chain.
- Yield of vital crops like corn, rice, soybean, cotton, bean, pea, sorghum and wheat will decrease.
- Degradation of paints, plastics and other polymer material will result in economic loss due to effects of UV radiation resulting from ozone depletion.