CHAPTER - 15

ACIDIFICATION

Acid rain is the rainfall that has been acidified. It is formed when oxides of sulfur and nitrogen react with the moisture in the atmosphere. It is rain with a pH of less than 5.6. Acid rain is particularly damaging to lakes, streams, and forests and the plants and animals that live in these ecosystems.

15.1. TYPES OF ACID DEPOSITION

"Acid rain" is a broad term referring to a mixture of wet and dry deposition (form of deposition material) from the atmosphere

(a) Wet Deposition

- If the acid chemicals in the air are blown into areas where the weather is wet, the acids can fall to the ground in the form of rain, snow, fog, or mist.
- As this acidic water flows over and through the ground, it affects a variety of plants and animals.
- The strength of the effects depends on several factors, including how acidic the water is; the chemistry and buffering capacity of the soils involved; and the types of fish, trees, and other living things that rely on the water.
- Precipitation removes gases and particles from the atmosphere by two processes :
  - (i) rain-out which is the incorporation of particles into cloud drops which fall to the ground, and
  - (ii) washout which occurs when materials below the cloud is swept down by rain or snow it falls.

Do you know?

Gharial crocodile counts amongst the largest crocodile species in the world. It is also one of two surviving members of the Gavialidae family. Gharial Crocodiles of India have an elongated and narrow snout. It is mainly found in the river systems of Indus, Brahmaputra, Ganges, Mahanadi, Kaladan and Ayeyarwady

(b) Dry Deposition

- In areas where the weather is dry, the acid chemicals may become incorporated into dust or smoke and fall to the ground through dry deposition, sticking to the ground, buildings, vegetation, cars, etc.
- Dry deposited gases and particles can be washed from these surfaces by rainstorms, through runoff.
- This runoff water makes the resulting mixture more acidic.
- About half of the acidity in the atmosphere falls back to earth through dry deposition.

The pH scale

- The pH scale is a measure of how acidic or basic (alkaline) a solution is.
- It ranges from 0 to 14. A pH of 7 is neutral.
- A pH less than 7 is acidic, and a pH greater than 7 is basic.
- It was devised in 1909 and it is a logarithmic index for the hydrogen ion concentration in an aqueous solution.
- pH values decreases as hydrogen ion levels increases.
- A solution with pH 4 is ten times more acidic than solution with pH 5, and a hundred times more acidic than solution with pH 6.
- Whilst the pH range is usually given as 0 to 14, lower and higher values are theoretically possible.

15.1.1. Sources of compounds causing acid rain

(a) Sulphur

(i) Natural sources:

- seas and oceans,
- volcanic eruptions,
- Biological processes in the soil e.g., Decomposition of organic matter.

(ii) Man-made sources:

- burning of coal (60% of SO2) and
- petroleum products (30% of SO2), and
- The smelting of metal sulfide ores to obtain the pure metals.
- Industrial production of Sulfuric acid in metallurgical, chemical and fertilizer industries.

(b) Nitrogen

Natural sources:

- lightening,
- volcanic eruption, and
- Biological activity.

Anthropogenic sources:

- Forest fires
- Combustion of oil, coal, and gas

(c) Formic acid

- Biomass burning due to forest fires causes emission of formic acid (HCOOH) and formaldehyde (HCHO) into the atmosphere.
- Large fraction formaldehyde gets photo – oxidation and forms formic acid in the atmosphere.

These are three main compounds that cause acidification of rain in the atmosphere.

(d) Other Acids:

- Chlorine
- Phosphoric acid
- Hydrochloric acid (smokestacks).
- Carbon monoxide and carbon dioxide (automobiles). These become carbonic acid.

Does it occurs only in industrial areas alone?

SOX and NOX that create Acid Rain are often transported to distances far away from their points of origin by the wind so that the adverse effects of pollution are also experienced at place remote from the place of genesis. The problem is further compounded as the environmental damage caused by acid rain is not uniform, but is area-specific.

15.1.2. Common characteristics of acid rain areas:

Areas which are prone to acid-rain attacks have some common characteristics :

- They are concentrated in the industrialized belt of the northern hemisphere.
- They are often upland and / or mountainous areas, which are well-watered by rain and snow.
- Due to the abundance of water, they possess numerous lakes and streams and also have more land covered with vegetation.
- Being upland, they often have thin soils and glaciated bedrock.

Do you know?

The banana tree (plant) has only a thick false stem (pseudostem), which is not woody but made up of a central core of soft tissues concealed by the fibrous and sheathing bases of large leaves. Strictly speaking, the banana plant is a giant herb.

World scenario

Many parts of Scandinavia, Canada, the North and Northeast United States and Northern Europe (particularly West Germany and upland Britain) share these features. Across the Atlantic there are number of acid rain hot spots including Nova Scotia, Southern Ontario and Quebec in Canada, the Adirondack Mountains in New York, Great Smoky mountains, parts of Wisconsin, Minnesota, and the Colorado Rockies of the US.

In India

In India, the first report of acid rain came from Bombay in 1974. Instances of acid rain are being reported from metropolitan cities.

In India, the annual SO2 emission has almost doubled in the last decade due to increased fossil fuel consumption. Lowering of soil pH is reported from north-eastern India, coastal Karnataka and Kerala, parts of Orissa, West Bengal and Bihar.

Indicators

Lichens serve as good bio-indicators for air pollution. In the variety of pH around 6.0, several animals, those are important food items for fish decline. These include the freshwater shrimp, crayfish, snails and some small mussels.

15.1.3. Chemistry of Acid Rain

Six basic steps are involved in the formation of acid rain:

1. The atmosphere receives oxides of sulfur and nitrogen from natural and man-made sources.
2. Some of these oxides fall back directly to the ground as dry deposition, either close to the place of origin or some distance away.

3. Sunlight stimulates the formation of photo-oxidants (such as ozone) in the atmosphere.
4. These photo-oxidants interact with the oxides of sulfur and nitrogen to produce H2SO4 and HNO3 by oxidation.
5. The oxides are of sulfur and nitrogen, photo-oxidants, and other gases (like NH3)
6. Acid rain containing ions of sulfate, nitrate, ammonium and hydrogen falls as wet deposition.

Difference between normally and anthropogenically acidified lakes

Naturally acidic lakes	Anthropogenically acidified lakes
Brown to yellow colour caused by humic substances	Very clear water caused by reduced primary productivity
Concentrations of dissolved organic carbon are high while transparency is low	Dissolved organic carbon concentrations are low. Whereas the transparency is high.
Low pH but well buffered.	Poorly buffered
Abound with aquatic life.	Some of the more sensitive taxa, such as blue-green algae, some bacteria, snails, mussels crustaceans, mayflies and fish either decrease or / are eliminated.

Do you know?

The Indian giant squirrel is a large-bodied diurnal, arboreal, and herbivorous squirrel. The species is endemic to deciduous, mixed deciduous, and moist evergreen forests of peninsular India, reaching as far north as the Satpura hill range of Madhya Pradesh. IUCN Status – least concern.

15.1.4. Impact Of Acid Rain

(a) Soil

- The exchange between hydrogen ions and the nutrient cations like potassium and magnesium in the soil cause leaching of the nutrients, making the soil infertile.
- This is accompanied by a decrease in the respiration of soil organisms.
- An increase in ammonia in the soil due to a decrease in other nutrients decreases the rate of decomposition.
- The nitrate level of the soil is also found to decrease.
- The impact of acid rain on soil is less in India; because Indian soils are mostly alkaline, with good buffering ability.

(b) Vegetation

Acid rains affect trees and undergrowth in forest in several ways, causing reduced growth or abnormal growth:

➢ The typical growth-decreasing symptoms are:

- Discoloration and loss of foliar biomass
- Loss of feeder-root biomass, especially in conifers
- Premature senescence (aging) of older needles in conifers
- Increase in susceptibility of damage to secondary root and foliar pathogens
- Death of herbaceous vegetation beneath affected trees
- Prodigious production of lichens on affected trees.
- Death of affected trees.

(c) Micro organisms

- pH determines the proliferation of any microbial species in a particular environment and the rate at which it can produce.
- The optimum pH of most bacteria and protozoa is near neutrality; most fungi prefer an acidic environment, most blue-green bacteria prefer an alkaline environment.
- So after a long run of acid rain, microbial species in the soil and water shift from bacteria-bound to fungi-bound and cause an imbalance in the microflora.
- This causes a delay in the decomposition of soil organic material, and an increase in fungal disease in aquatic life and forests.

(d) Wild life

The effects of acid rain on wild life are not very obvious and are therefore, difficult to document. Nevertheless, several direct and indirect effects of acid rain on the productivity and survival of wildlife populations have been reported.

- Acid rain can directly affect the eggs and tadpoles of frogs and salamanders that breed in small forest ponds.

- It has been postulated that acid rain can indirectly affect wildlife by allowing metals bound on soils and sediments to be released into the aquatic environment, where toxic substances may be ingested by animals, like birds, that feed in such an environment.
- Other indirect effects of acid rain on wildlife are loss or alteration of food and habitat resources.

(e) Humans

Acid rain affects human health is a number of ways.

- The obvious ones are bad smells, reduced visibility; irritation of the skin, eyes and the respiratory tract.
- Some direct effects include chronic bronchitis, pulmonary emphysema and cancer.
- Some indirect effects include food poisoning vis a vis drinking water and food.
- An increase in the levels of toxic heavy-metals like manganese, copper, cadmium and aluminium also contribute to the detrimental effects on human health.

Do you know?

- Bonsai—i.e., tailored or human-made miniature or dwarfed living trees that have been prevented from reaching their normal size—are grown in pots and kept in greenhouses, drawing rooms, etc. This technique was first perfected by the Japanese.
- Bamboos are trees without a main trunk but with a cluster of culms arising from the underground rhizome. These culms are unbranched, with distinct nodes and internodes that give them a jointed appearance.
- Trees reduce oxides of carbon in the air, can also fix atmospheric nitrogen, disintegrate waste and act as sinks of pollution.
- Sometimes seeds of a plant are formed without fertilization. This phenomenon is called "agamospermy," a kind of parthenogenesis. A fruit that matures without seed formation is called "parthenocarpic fruit."
- Beverage plants are those plants which yield beverages or drinks—nonalcoholic or alcoholic—that are palatable and refreshing. Nonalcoholic beverages usually contain caffeine, an alkaloid, which has stimulating and refreshing qualities. Alcoholic beverages are those that contain one or more hydroxyl (–OH) groups, e.g., ethanol.

(f) Acid rain damage on Materials

Material	Type of Impact	Principal Air Pollutants
Metals	Corrosion, tarnishing	Sulphur Oxides and other acid gases
Building stone	Surface erosion soiling, black crust formation	Sulphur Oxides and other acid gases
Ceramics and glass	Surface erosion, surface crust formation	Acid gases, especially fluoride-containing
Paints and organic coatings	Surface erosion, discolouration, soiling	Sulphur dioxides, hydrogen sulphide
Paper	Embrittlement, discolouration	Sulphur Oxides
Photographic Materials	Micro-blemishes	Sulphur Oxides
Textiles	Fading, colour change	Nitrogen oxides, ozone
Leather	Weakening, powdered surface	Sulphur oxides
Rubber	Cracking	Ozone

(g) Socio-economic impacts of acid rain :

The adverse impact of acid rain on farming and fishing leads to the deterioration of life quality indices like GNP and per capita income, especially in the predominantly agricultural and developing countries like India

15.1.5. Trigger Effect of Acid Rain on Pollutants:

A low pH of the rainwater and subsequent increased acidity in the environment can trigger off or aggravate the effects of certain harmful pollutants.

(i) Mercury:

- Methyl mercury and related short chain alkyl mercurial compounds are most dangerous to humans, as they accumulate in edible fish tissue.
- Although acid deposition may not increase the production of methyl mercury, it may increase the partitioning of methyl mercury into the water column.
- The use of lime has helped in reducing the mercury levels in fish.

(ii) Aluminium:

- Acidified waters are known to leach substantial amounts of aluminium from watersheds.
- Even at relatively low levels, aluminium has been implicated in dialysis dementia, a disorder of the central nervous system, which may be toxic to individuals with impaired kidney function.

(iii) Cadmium:

- Cadmium can enter the drinking water supply through corrosion of galvanized pipe or from the copper-zinc through corrosion of galvanized piper or from the copper-zinc solder used in the distribution systems.
- A decrease in water pH from 6.5 to 4.5 can result in a fivefold increase in cadmium and could cause renal tubular damage.

(iv) Lead:

- Foetuses and infants are highly susceptible to drinking water lead contamination.
- High blood lead levels in children (>30 mug/Ml) are believed to induce biochemical and neurophysiological dysfunction.
- However, lower than normal blood levels of lead can cause mental deficiencies and behavioural problems.

(v) Asbestos:

Asbestos in natural rock can be released by acidic waters.

Do you know?

Tree ferns like Cyathaea and Alsophila have erect rhizomes with generally unbranched trunks, topped by a crown of graceful, feathery fronds that form a rosette at the apex.

15.1.5. Control Measures :

Reducing or eliminating the sources of pollution by

- Buffering- the practice of adding a neutralizing agent to the acidified water to increase the pH is one of the important control measures. Usually lime in the form of calcium oxide and calcium carbonate is used.
- Reducing the emission of SO2 from power stations by burning less fossil fuel, using alternate energy sources like tidal, wind, hydropower etc.,
- using low sulphur fuel;
- desulphurization
- decreasing emission of NOx from power stations and
- Modification of engines.
- Emissions of SOx can be controlled by
  - Converting to sulphuric acid.
  - Converting it to elemental sulphur.
  - Neutralizing it and using it in the manufacture of other products.

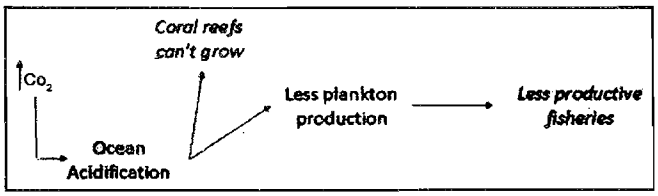
15.2. OCEAN ACIDIFICATION

Oceans are an important reservoir for CO_2, absorbing a significant quantity of it (one-third) produced by anthropogenic activities and effectively buffering climate change.

Ocean acidification is the change in ocean chemistry - lowering of ocean pH (i.e. increase in concentration of hydrogen ions) driven by the uptake of carbon compounds by the ocean from the atmosphere.

As the uptake of atmospheric carbon dioxide by the ocean increases, the concentration of hydrogen ions in the ocean increases, the concentration of carbonate ions decreases, the pH of the oceans decreases and the oceans become less alkaline – this process is know as ocean acidification.

15.2.1. CO_2 effect on ocean acidification



The uptake of atmospheric carbon dioxide is occurring at a rate exceeding the natural buffering capacity of the ocean.

The pH of the ocean surface waters has decreased by about 0.1 pH unit (i.e. 26% increase in ocean hydrogen ion concentration) since the beginning of the industrial revolution.

The ocean currently has a pH around 8.0 and is therefore 'basic' and it is nearly impossible, chemically, for all of it to actually become a pH less than 7.0. Why do we therefore refer to 'ocean acidification'?

That is because acidification is the direction of travel, the trend, regardless of the starting point. Acidification refers to lowering pH from any starting point to any end point on the pH scale.

Forms of calcium carbonate

Calcite and aragonite are two different forms of calcium carbonate.

1. Calcite is the mineral form found in the shells of planktonic algae, amoeboid protists, some corals, echinoderms, and some molluscs (e.g. oysters); it is relatively less soluble.
2. Aragonite is a more soluble form of calcium carbonate; it is found in most corals, most mollusks (small planktonic snails), as well as some species of algae.

15.2.2. Influence of other factors

Various factors can locally influence the chemical reactions of CO2 with sea water and add to the effects to ocean acidification. For example,

i. Acid rain

Acid rain can have a pH between 1 and 6 and has impact on surface ocean chemistry. It has major effect on ocean acidification locally and regionally but very small globally.

ii. Eutrophication

Coastal waters are also affected by excess nutrient inputs, mostly nitrogen, from agriculture, fertilizers and sewage. The resulting eutrophication leads to large plankton blooms, and when these blooms collapse and sink to the sea bed the subsequent respiration of bacteria decomposing the algae leads to a decrease in sea water oxygen and an increase in CO_2 (a decline in pH).

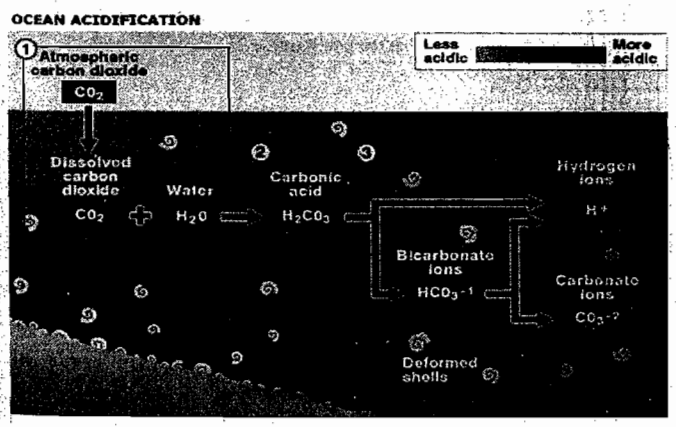
How it reacts?

The term 'ocean acidification' summarizes several processes that occur when CO_2 reacts with sea water.

Two reactions are particularly important. Firstly, the formation of carbonic acid with subsequent release of hydrogen ions:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

(Carbon dioxide) + (Water) (Carbonic acid) (Hydrogen ions) + (Bicarbonate ions)



The above reaction and release of hydrogen ions increases acidity and thus pH level is reduced.

A second reaction, between carbonate ions, CO2 and water produces bicarbonate ions.

The combined effect of both these reactions not only increases acidity but also lowers the availability of carbonate ions.

15.2.3. Effect of ocean acidification

Seawater absorbs CO_2 to produce carbonic acid (H_2CO_3), bicarbonate (HCO_3--) and carbonate ions (CO_{32}-).

These carbonate ions are essential to the calcification process that allows certain marine organisms to build their calcium carbonate shells and skeletons (e.g. hard tropical corals, cold water corals, molluscs, crustaceans, sea urchins, certain types of plankton, lobsters, etc).

However, increases in atmospheric CO_2 levels lead to decrease in pH level, increase in the concentration of carbonic acid and bicarbonate ions, causing a decrease in the concentration of carbonate ions.

Thus carbonate ions are less available and calcification is therefore harder to achieve, and may be prevented altogether. Imagine trying to build a house while someone keeps stealing your bricks.

This impact of ocean acidification may therefore have potentially catastrophic consequences for ocean life and many marine species of economic importance.

15.2.4. Mitigation

- Reducing CO_2
- promoting government policies to cap CO_2 emissions,
- eliminate offshore drilling,
- by advocating for energy efficiency and
- Alternative energy sources such as wind power, solar, etc.

15.2.5. Saturation horizons

- Deep, cold ocean waters are naturally undersaturated with carbonate ions causing the shells of most calcifying organisms to dissolve.
- Surface waters are oversaturated with carbonate ions and do not readily dissolve shells of calcifying organisms.
- The saturation horizon is the level below which calcium carbonate minerals undergo dissolution.

- Those organisms that can survive below the saturation horizon do so due to special mechanisms to protect their calcium carbonate from dissolving.
- As ocean acidification causes this horizon to rise vertically in the water column so more and more calcifying organisms will be exposed to undersaturated water and thus vulnerable to dissolution of their shells and skeletons.
- The saturation horizon of calcite occurs at a greater ocean depth than that for aragonite, but both horizons have moved closer to the surface presently when compared to the 1800s.

Do you know?

Chameleons are seen inhabiting almost all the parts of south India and west of the Ganges. However, they are rarely seen in areas that receive heavy rainfall. Chameleons are mostly arboreal and are found in trees or on smaller bushes.

15.2.6. Ocean acidification and the short and long-term fate of carbon in the system

On long timescales (>100,000 years) there is a natural balance maintained between the up-take and release of CO2 on Earth; the CO2 produced by volcanoes, the main natural source of CO2, is taken up by the production of organic matter by plants and by rock weathering on land.

However, rock weathering takes tens of thousands of years so will not remove the current anthropogenic input of CO2 to the atmosphere and ocean fast enough.

On shorter time scales (>1,000 years), the ocean has an internal stabilizing feedback linking the ocean carbon cycle to the underlying carbonate rich sediment known as carbonate compensation.

The upper layers of the ocean tend to be supersaturated with CaCO3 so little dissolution takes place, whilst the deep ocean is undersaturated and carbonate readily dissolves.

The first boundary between these two states is known as the lysocline, the depth at which dissolution strongly increases in the deep ocean.

The CaCO3 in the form of dead shells sink to the sea bed. If it is of shallow water depth, the majority is buried in the sediment and trapped for a long time, but where the shells sink in deep water nearly all the $CaCO_3$ is dissolved, thereby not locking the carbon away for millions of years.

The current increased rate of dissolution of atmospheric CO_2 into the ocean results in an imbalance in the carbonate compensation depth (CCD), the depth at which all carbonate is dissolved.

As the pH of the ocean falls, it results in a shallowing of the lysocline and the CCD, thus exposing more of the shells trapped in the sediments to understaturated conditions causing them to dissolve, which will help buffer ocean acidification but over a long time scale of a thousand years.

UPWELLING

- Surface Coastal regions periodically experience upwelling events where deeper ocean water circulates onto continental shelves and near-shore areas.
- This exposes the productive upper ocean ecosystems to colder water containing more nutrients & more CO_2.
- As ocean acidification makes the upper oversaturated layer of sea water shallower each year, these natural upwelling events will more often cause undersaturated water to well up and flow to the shore.
- Coastal marine organisms that form shells are unaccustomed to such events, and periodic exposures to these significantly different conditions may affect these communities.

15.2.7. Winners and losers

- The growth and level of photosynthesis of certain marine phytoplankton and plant species may increase with higher CO_2 levels, but this is by no means a general rule.
- For others, higher CO_2 and rising acidity may have either negative or neutral effects on their physiology.
- Therefore, particular marine plants will be 'winners', while others will be 'losers' and some may show no signs of change but change is inevitable.

A reduction in atmospheric CO_2 levels is essential to halt ocean acidification before it is too late.