

CHAPTER:11

ACID RAIN: IMPACT ON SURROUNDING ENVIRONMENT

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Abstract:

Rain is a natural phenomenon which is a result of water cycle happening in nature. The increasing pollution due to various human activities trying to make life of man luxurious, has disturbed many natural phenomena. Water cycle is one of them. The increased air pollution has disturbed the quality of rain water. Presence of acidic gases like sulphur dioxide, nitrogen oxides, excess of carbon dioxide in air makes the rain water acidic by dissolving in water and forming acids such as sulphuric acid, nitric acid, carbonic acid. These dissolved acids not only decrease the pH of rain water but also have disadvantaging effect on living forms, nonliving forms, aquatic systems, vegetation. This review discusses the formation of acid rain, causes of acid rain and its effects on mankind, aquatic systems, vegetation, buildings etc.

Keywords: Acid Rain, pH, nitrogen oxides, sulphur dioxide, dry and wet deposition.

Introduction

Rain comes when water vapors condensed to form clouds and when clouds become heavy, these precipitate in the form of rain on the earth. Rainwater is considered to be the purest form of water if there is no pollution in the environment. The clouds which precipitate in the form of rain are made from the water vapors evaporated from various water bodies (such as ocean, sea, lakes, rivers, etc.), from living organisms via various processes, and also by the different physical and chemical phenomenon. The composition of cloud in an ideal environment i.e. pollution-free environment is water (H_2O). But our environment is no longer pollution free. Many pollutants like dust particles, smoke, carbon vapors, metallic vapors, gases such as nitrogen oxides (NO_x), sulfur oxides (SO_2), etc. resulting from various mechanical, chemical and human activities are present in the environment which in turn dissolve in rainwater to make it impure. So, when water drops from heavy clouds in the form of rain, it gets mixed with various pollutants present in the air, and the composition of rainwater changes, it no longer remains only H_2O . it gets dissolved solutes, gases which change its pH values and make it acidic. Hence, when the rainwater has acidic pH then it is

considered Acid Rain. It is one of the recognized environmental problems. It has a higher concentration of active hydrogen ions as it is contaminated by sulphuric and nitric acids. It decreases the pH of water bodies like ponds, lakes, etc. present on the earth's surface affecting all types of life forms and it is one of the serious problem for living organisms on earth (Likens, 1974).

The word ACID RAIN was invented in 1872 by Scottish chemist Robert Angus Smith as he used the term 'acid rain' for the first time in his remarkable publication entitled "Air and Rain: The Beginnings of Chemical Climatology" (Smith, 1872). He proposed detailed procedures for the proper collection and chemical analysis of precipitation. He also noted acid rain damage to plants and materials and atmospheric deposition of arsenic, copper, and other metals in the industrial region. He is often regarded as the "Father of Acid Rain" according to 'The Royal Society of Chemistry '(Smith, 1872).

Historical review

The features of the acid rain phenomenon were first discovered by Robert Angus Smith, an English chemist in the middle of the 19th century. He published a detailed study of the chemistry of rain in and around the city of Manchester, England (Smith, 1872). He pointed out that the sulphuric acid in the city air caused the color of textiles to fade and metals to corrode. He also demonstrated that the chemistry of rain is affected by certain factors like the decomposition of organic matter, combustion of coal, wind trajectories, proximity to the sea, and frequency of rain. An American limnologist, Eville Gorham (1981) developed the first detailed analysis of Smith's early work as Smith's book had been overlooked. Based on his research in England and Canada, Gorham with his colleagues demonstrated some principles as follows:

- Atmospheric emissions produced by the combustion of fossil fuels affect the acidity in precipitation near industrial regions.
- Atmospheric deposition of acidic substances by precipitation results in progressive losses of alkalinity in surface waters.
- The free acidity in soils receiving acid precipitation is primarily due to sulphuric acid. Such precipitation results in the deterioration of vegetation, and soil.
- The incidence of bronchitis in humans can be correlated with the acidity of precipitation.

Thus, Gorham was the second scientist to establish the sources and consequences of acid rain around mid-20th century. In the 1950s, Eriksson, a Swedish scientist enunciated a general theory of the biogeochemical circulation of matter through the atmosphere. In 1967, Svante Oden a Swedish soil scientist analyzed air mass trajectories and temporal and geographical changes in precipitation and concluded that acid precipitation is a large-scale regional phenomenon making surface water more acidic and there can be long distances (100-2000km) transport of sulfur and nitrogen-containing air pollutants (Cowling, 1988).

pH

pH value is the measure of hydrogen ion activity. For a given solution having active hydrogen ions, pH can be defined as the negative logarithm of hydrogen ion concentration present in the given solution.

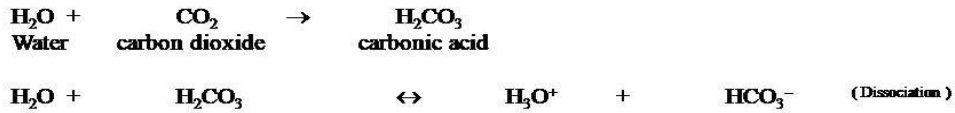
$$\text{pH} = - \log_{10} [\text{H}^+]$$

Water slightly ionizes (or is converted into ions, which are electrically charged particles), yielding hydrogen (H^+) and hydroxyl (^-OH) ions. When the activity of these ions is equal, water is neither acidic nor alkaline and is said to be neutral. This neutrality point is represented by the pH value of 7 on a pH scale of 1-14 developed by Sorensen in 1909 to describe the acidity of aqueous solutions, which varies slightly according to temperature. At pH value below 7 water becomes acidic and at pH value above 7, it becomes alkaline or basic. The pH scale is logarithmic i.e. Each pH unit changes the concentration of hydrogen ions in a given solution tenfold. Thus, a water solution having a pH value of 6 is ten times more acidic than a water solution having a pH value of 7. Similarly, a water solution with having pH of 5 is 100 times more acidic than a water solution having a pH value of 7, and so on.

pH of rainwater

Heavy clouds that precipitate to form rain contain distilled water that is neither acidic nor alkaline which means it is neutral. While precipitation, rainwater comes in contact with carbon dioxide (CO_2) in the air and becomes slightly acidic since carbon dioxide combines with water to form carbonic acid. Some of the carbonic acid in rainwater dissociates to form bicarbonate ions and hydrogen ions, both of which are dissolved in rainwater (Charlson, and Rodhe, 1982).

The chemical reactions involved are as follows:



In the above reaction, H_3O^+ is known as hydronium ion, it represents active hydrogen ion (H^+) in rainwater and it is responsible for lowering of pH of rainwater. Carbonic acid is a weak acid. It has a very low concentration of active hydrogen ions and it is not harmful to the environment.

Normally, the pH of rainwater is regulated by the presence of carbon dioxide gas in the air. In other words, the more the concentration of carbon dioxide in the air, the more carbonic acid is produced, and the more acidic will be the rainwater. On average, air contains 0.3% of CO_2 . Using this value, the hydrogen ion concentration in rainwater is $10^{-5.7}$ mol/l at equilibrium and this is equivalent to a pH value around 5.7 or the rainwater is slightly acidic. However various studies on rainwater, have reported increasing amounts of much stronger acids such as sulphuric acid, and nitric acid in rain and snow, producing pH values between 3 and 5. The presence of such strong acids in rainwater is presumably related to air pollution (Kulshrestha et. al., 2003).

Acid rain can be defined as a form of precipitation in our surrounding environment that has unusually acidic pH i.e. rainwater has elevated levels of hydrogen ions (H^+). The pH value of acid rain water is lower than normal rainwater, it is lower than normal drinking water whose pH exists between 6.5 and 8.5. The pH value of acid rain ranges from 3 to 5 on average. The lower the pH of acid rainwater, the more acidic the acid rain. Most simply, acid rain can be said as the precipitation of acid along with the rain. In other words, acid rain is made up of highly acidic water droplets due to air emissions. The comparison of pH of acid rain with normal water and acid & base is tabulated in table 1.1.

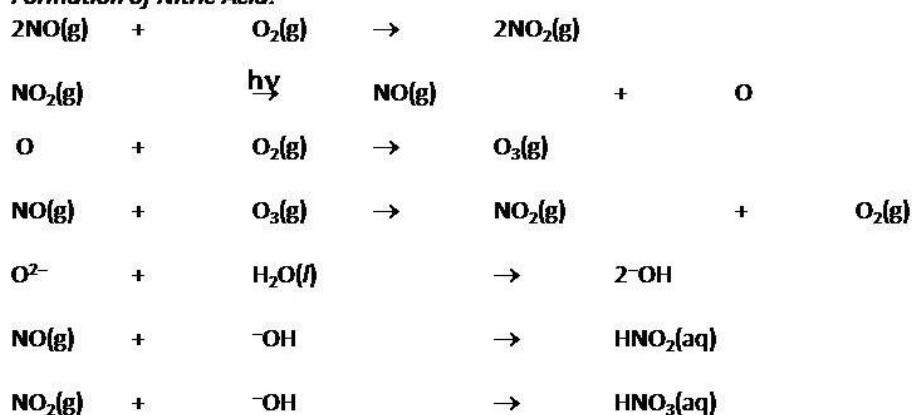
Table 1.1

Type of liquid	pH range
Normal water	6.5 – 8.5
Acid rain water	4 – 5
Acid	Below 7
Base	Above 7

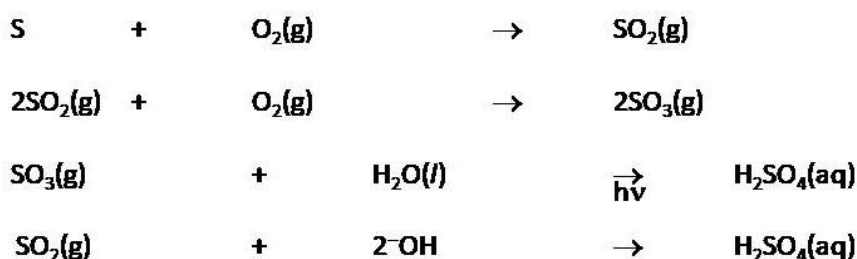
Chemistry of acid rain

All types of acid depositions either wet or dry from the atmosphere are commonly described by the term "acid rain". These depositions may cause damage to trees, fisheries, buildings, human health, etc. The dry deposition (gas, vapor, aerosols, and dry particles) means the removal of acidifying pollutants from the atmosphere by deposition on the earth's surface directly in gaseous or particulate form whereas the wet deposition (hail, dew, snow, fog, mist, rain, etc.) means removal of acidifying pollutants from the atmosphere by deposition on the earth's surface after incorporation in clouds and rain drops. These acidifying pollutants mainly sulfur oxides (SO_x) and nitrogen oxides (NO_x) undergo a chemical transformation in the atmosphere through complex chemical reactions (Dondapati, 2013). After emission, the gaseous pollutants are dispersed in the atmosphere. These pollutants may get deposited in dry form near the source of emission within 1-2 km and may also travel for hundreds of kilometers. The polluting gases get oxidized during their movement in the atmosphere and converted into acids like sulphuric acid and nitric acid either in the liquid phase or gas phase. The conversion of oxides of nitrogen and sulfur into acids is more effective when these oxides are captured by clouds and raindrops as these reactions are faster in the liquid phase (Gorham, 1984). These acids are then brought down to the earth's surface along with rain and cause acid rain. Some of the important reactions involved in the formation of acids in acid rain are as follows: -

Formation of Nitric Acid:



Formation of Sulphuric Acid:



When acid is mixed with rain water, the pH falls below 5.6. The burning of fossil fuels is the main source of these polluting gases mainly responsible for acid rain. Most of the SO₂ pollutants are released by industrial sources and power plants whereas nitrogen oxides are emitted from airplanes, motor vehicles, steamers, ships, and other forms of transportation.

There are some more acid-forming pollutants other than sulfur oxides and nitrogen oxides such as chlorine and hydrochloric acid, organic acids like formic acid, acetic acid, etc., and some ions like nitrate ion, and sulfate ion. These also increase the acidity of rainwater. The carboxylic acids mentioned contribute significantly to rainwater acidity (Bastidas, and La Iglesia, 2007.). Formic acid formed as a result of forest fire before the rainy season may cause occasional acid rain in tropical forest regions.

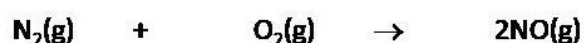
The atmosphere contains some other substances such as ammonia, calcium, and magnesium carbonate that neutralize acids and help in decreasing the acidity of rainwater. These substances are known as neutralizing substances. The net acidity of rain depends on the relative concentration of these substances in an atmosphere with respect to acid-forming substances. Some other ions like sodium, potassium, carbonate, and bicarbonate also influence the pH of rainwater.

Causes of Acid Rain

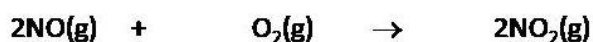
When precipitation occurs, rainwater comes across acid-forming substances present in the air. The polluting gases mainly responsible for acid rain are sulfur oxides (SO₂ and SO₃ commonly referred to as SO_x) and nitrogen oxides (NO₂, N₂O, and NO, commonly referred to as NO_x). Mists of acids such as phosphoric acid and vapors of hydrochloric acid may also be present in the air (Grennfelt, 2020). These polluting substances get dissolved in rainwater making it acidic. There are many factors man-made as well as natural, responsible for the

addition of pollutants in the atmosphere causing acid rain. Some of the factors are fossil fuel combustion, coal burning, transportation, industrial combustion, smelting of metal sulfide ores to obtain pure metal, volcanic eruptions, sea spray, forest fires, organic decay, rotting vegetation, lightning, etc.

- **Industrial Revolution:-** The development of industries increases the manufacturing of various products useful for human needs. It was the transition from old hand production methods to new manufacturing processes which used the machines for various manufacturing processes. And these machines operated on power generated mainly through coal combustion producing harmful emissions in the environment resulting in acid depositions along with rain. The various industries responsible for the addition of major acid rain-causing pollutants in the atmosphere include chemical industries, iron and steel industries, refineries, petrochemical industries, etc. Also, the large productions to meet the demands of the increasing population required transportation. Vehicles also emit harmful gases like sulfur dioxide and nitrogen oxides into the environment responsible for acid rain. Before the industrial revolution, the pH of rainwater was used around 5 to 6. After the industrial revolution, the emissions of SO₂ and NO_x into the atmosphere have increased and become a threat to nature (Mason, 1988). The emission of sulfur dioxide and nitrogen oxides is highly influenced by the development of transportation facilities, the discovery of new uses for the resources and products, development and availability of new technologies. Rapid and unplanned industrialization is the main cause of acid rain.
- **Sea Spray:-** it is also responsible for dissolved constituents in rainwater. It is carried by winds and dissolved minerals get spread throughout the atmosphere. It is the primary source of chloride ions in rainwater.
- **Automobiles:-** In the modern world, the increase in the use of vehicles for transportation facilities is one of the factors responsible for the increase in pollutants in the atmosphere causing acid rain. The vehicle engine needed the power to move the vehicle, it gets it from burning petrol or diesel. When this fuel is burned inside the engine, the air is drawn in and nitrogen oxides are produced at a high temperature inside the engine.



When this nitrogen oxide leaves the exhaust of the vehicle it cools very quickly and is rapidly oxidized to nitrogen dioxide (NO₂), a major pollutant responsible for acid rain.



Both nitrogen oxide and nitrogen dioxide dissolve in rainwater to form nitrous and nitric acid, components of acid rain.

- **Agricultural fertilizers:-** Nitrogenous fertilizers, added to the soil for the better growth of crops are added as ammonium and nitrate salts. These may be converted to nitrogen oxides and emitted into the air. These oxides on mixing with rain water form acid rain(Curtis, and Childs, 2010).
- **Natural causes:-** volcanoes and geysers contribute sulfur oxides and nitrogen oxides to the atmosphere. In forest fires, a large amount of biomass burning causes the emission of formic acid and formaldehyde into the atmosphere. The photooxidation of formaldehyde produces formic acid further adding to the acidity of rainwater.
- **Lightening:-** Lightening in the atmosphere provides a large amount of energy required by various reactions occurring in the atmosphere generating free radicals, ions, or reactive species which by mixing with rainwater increases the acidity of rainwater. Formaldehyde emitted from the burning of biomass gets photo oxidized to form acid which on mixing with rain water increases its acidity. Sulfur dioxide may get photo oxidized to sulfur trioxide which on mixing with water produces sulphuric acid further increasing the acid character of rainwater. The presence of sulphuric acid in rain can drop the pH of rainwater to as low as 2.
- **Burning of fossil fuel:-** Burning of fossil fuels adds a large amount of sulfur and nitrogen oxide into the atmosphere in addition to being naturally present in the air. K.K. Bertin and E.D. Goldberg estimate that about 3,740,000 tons of sulfur are released into the atmosphere each year by the combustion of fossil fuels. These are oxidized and hydrolyzed to sulphuric acid in the atmosphere making rain acidic. Likewise, various nitrogen oxides are converted into nitric acid also adding to the acidity of rainwater. If these are not neutralized by basic substances present in the air, these ultimately get precipitated to the earth's surface and cause harmful effects.

Effects of acid rain

Acid rain is the result of air pollution caused by various human activities in this fast-moving world. It is affecting every living organism in one or the other way. The buildings and monuments also are not safe from acid rain. Some of the impacts of acid rain are as follows:

- **Chemical weathering of landscape:-** In chemical weathering (decomposition of rocks), the weak acidic character of carbonic acid present in precipitation plays an important role. The process of chemical weathering is responsible for the slow but steady leaching of nutrients from primary and secondary minerals in rocks and soil. But due to various factors, this change in the acidity of precipitation affects the process of chemical weathering and so the natural ecosystem (Baedecker et al. 1992).
- **Metal toxicity in the aquatic system:-** Acid rain causes a decrease in the pH of water in the aquatic ecosystem making it more acidic thus affecting the life of aquatic living organisms. In natural water bodies, the metal toxicity is decreased by forming complexes with naturally occurring ligands such as fulvic acid but at lower pH value, these complexes are destabilized releasing metal ions into the water. Lower pH value in water bodies also increases the mobility of metal ions from sediments to the overlaying water (Driscoll et al. 1989). Both factors are responsible for the increase in the concentration of metals such as zinc, copper, cadmium, nickel, etc. in water causing chronic toxicity to aquatic organisms.
- **Aquatic biota:-** All trophic levels of aquatic biota are affected by increased acidification of water. Studies have shown that microbial activity is reduced in more acidic water. Also, the species' dominance shifts from bacteria to fungi. The phytoplankton species diversity decreases at low pH. Also, the number of zooplankton decreases as the pH value decreases. The toxic trace elements can get accumulated in invertebrates and may get passed to vertebrates through the food chain. Increased acidity of water bodies also affects amphibians. Pough (1976) found that the salamander, *Ambystoma macalatum*, was sensitive to acid. The mortality of its embryos was high at $\text{pH} < 6.0$. The molluscs, plecoptera, crustaceans, and ephemeroptera are also sensitive to the acidification of their water bodies.
- **Human health:-** There are many effects on human health such as irritation of the skin and eyes, reduced visibility, bad smells, irritation of the respiratory tract, etc.

Acid rain may cause chronic bronchitis, pulmonary emphysema, and cancer. Increased acidity of precipitation mobilizes the toxic elements and contaminants in water including groundwater. This affects human health adversely as this water is used for drinking purposes and even for cooking food.

- **Buildings:-** Many historical architectural buildings have been affected by acid rain. (Kaneko et al. 2006) reported that architectural titanium sheets are discolored by acid rain or acidic fog. The corrosion of materials such as copper, bronze, and marble is directly correlated with the ratio of SO_2/NO_x and climate. (Tsujino et al. 1995) . Copper specimens were found to be corroded by the presence of organic acids in rainwater (Bastidas and La Iglesia,2007). Organic acids can also corrode several other metals. Buildings made of sandstone, limestone, and marble are adversely affected by acid rain. Calcium carbonate is the main constituent of these materials and it forms calcium sulfate on reaction with sulphuric acid present in rainwater. Calcium sulfate being granular gets washed off with rain water further exposing the inner calcium carbonate of the building to acid attack. The Taj Mahal, a historical monument in India has been affected by "stone-cancer"(another effect of acid rain caused by the corrosive action of acid rain on building material). The other cultural attractions of the world such as St. Paul's Cathedral in Lonon, the Sphinx in Greece and Egypt, and the Statue of Liberty in New York are also affected by acid rain(Okochi et al. 1982). Metals, paints, ceramics, etc can easily be corroded by acid rain. It can also destroy rubber, leather, steel bridges, railway tracks, and textiles.
- **Microorganisms:-** Different microorganisms prefer different pH environments for their growth and development. Most bacteria and protozoa prefer pH optima near neutrality, most fungi prefer an acid environment and most blue-green bacteria prefer an alkaline environment. So, if there is a change in the pH of the soil or water body due to acid rain, it will disturb the balance of microflora. In an acidic or low pH environment, microbial species in water and soil shift from bacteria bound to fungi bound. This shifting of microflora has negative results such as decreased rate of decomposition of organic matter, and an increase in fungal diseases to aquatic life and forests.
- **Soil:-** The extent to which the soil is affected by acid rain depends on its acid-neutralizing ability. The impact of acid rain on soil is more in the UK and

European countries than in India because Indian soils are mostly alkaline, with good buffering ability. The concentration of hydrogen ions can get increased in soil due to acid rain(Savci, 2012) These hydrogen ions can undergo exchange with nutrient cations present in the soil like potassium ions and magnesium ions. This causes a loss of nutrients from the soil making it infertile. The reduction of nutrients in the soil causes ammonia to increase which reduces the rate of decomposition. This also affects the soil organisms by decreasing the rate of respiration.

- **Vegetation:-** The ideal pH range for plant growth is between 5 and 8. Acid rain causes reduced or abnormal growth of trees in forests by decreasing the pH of soil below 5. It causes discoloration and loss of foliar biomass, decrease in annual increment i.e. width of growth rings, premature aging of trees, increased susceptibility to foliar pathogens, prodigious production of lichens on affected trees, shedding of green shoots, etc. Acid rain causes a decrease in germination, pollination, and fertilization, and also it changes the chemistry of the leaf surface of the plants(Singh, and Agarwal, 2008). In addition to it, acid rain may cause water-stress symptoms in trees like altered water balance and increased incidence of wet wood disease. Acid rain may also cause a reduction in the population of beneficial earthworms. Acid rain sometimes may cause the loss of sensitive plants. Foliar browning in natural stands of two species of birch (*Betula papyrifera* and *Betula cordifolia*) growing adjacent to the Bay of Fundy, Canada, has been correlated with fog acidity and frequency of fog episodes (Koutrick et al., 1998).
- **Agriculture and fisheries:-** Acid rain has been found to enhance the accumulation of heavy metals in crops(Chen et al. 1998). This accumulation of heavy metals in grains and vegetables is harmful to humans and other animals who consume such crops. Acid rain has been shown to adversely affect the food crops such as wheat morphologically (Singh and Agarwal, 2004). The soil has a pH below 3 is harmful to the germination and growth of various plant species. (Balasubramaniam et al., 2007). Acid rain affects the development of fish. It retards egg development in fishes and also alters the blood chemistry. Freshwater shrimp die at a pH value lower than 6 and at a pH lower than 5 fish eggs do not hatch causing a decrease in the population of fish in the aquatic system.

- Acid mine drainage:- Increase in acidity of rainwater cause corrosion of minerals like pyrite. Stronger acid rain accelerates pyrite corrosion. Oxidation of pyrite causes leaching of sulfide and ferric ions, and polysulphides, ultimately causing acid mine drainage. (Zheng K. et al. 2017) Acid rain mobilizes metal elements from metal sulfides in sulfide mines increasing the concentration of metal ions in water and making it toxic. (Kucha et al. 1956).

Preventive measures for acid rain

The effects of acid rain are observed in long run. Most of the effects cannot be encountered directly like the effect on vegetation, animals, fishes, and human health. It is always said, "prevention is better than cure". Some of the control measures are as follows:

1. The emission of polluting gases causing acid rain like sulfur oxides and nitrogen oxides should be prevented.
2. Law should be formulated by the governments to regulate emissions.
3. Alternate energy sources like tidal, wind, hydropower, hydrogen, etc should be used to decrease the emission of SO₂ and NO_x.
4. The engines should be modified to increase their energy efficiency.
5. Fuel containing less amount of sulfur can be used to decrease the emission of sulfur oxides.
6. Power plants and industries should try to switch to a renewable source of energy instead of coal burning to prevent polluting emissions.
7. Low-sulfur coal must be used in coal-dependent electric power plants to reduce sulfur pollution in the air.
8. Humans should use minimum energy to reduce the burden on energy-producing power plants, in turn, to minimize the acid rain-causing pollutants in the atmosphere.
9. Private vehicles should be avoided to reduce the emission of nitrogen oxides.
10. Unnecessarily use of electrical appliances should be avoided.
11. Pollution control equipment such as efficient boilers, cleaning technologies, and fluidized combustion beds should be used in industries and power plants to reduce emissions of SO₂ and NO_x.
12. Liming (use of lime and limestone to reduce acidity) of soils and lakes can be done to reduce the harmful effects of acid rain. Highly acidic ponds and small

lakes can be neutralized by adding large quantities of an alkaline substance such as quicklime (Stoddard, et al. 1999).

There can be more ways in which the generation of pollutants can be controlled and the environment as well as living organisms can be saved. During the 1980s, acid rain was one of the environment's largest threats but as a result of The Convention on Long-Range Transboundary Air Pollution treaty under the United Nations Economic Commission for Europe (UNECE), the emissions of all key air pollutants have been reduced significantly and the most important acid rain pollutant, sulfur dioxide, emission in Europe have decreased by 80% since 1980-1990.

Conclusion

Acid rain is not a new environmental problem in 21st century but it is not the problem to be neglected. Many measures are being taken to reduce air pollution but still air quality index in some cities is not up to the mark. The human activities are affecting the quality of water coming on earth from clouds which in turn affects aquatic systems, human health, plants, animals, soil, aquatic animals etc. There is a great need to rectify the problem of acid rain which means more scientific and resourceful methods needed to be developed which can reduce the emitting pollutants from industries, construction sites, vehicles etc. More focus is needed on the development of clean and affordable fuel. Use of renewable energy resources can be brought in practice to reduce burden on coal industry.

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