Acid Rain: A Challenge to the Global Environment
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Abstract:
Environmental challenges by their nature are universal. Most of them are harmful for us and also for future generations. This article addresses a particular global challenge of today which is typical of the challenges we are likely to face in future. In recent decades, urbanization and industrialization have been two interlinked phenomena, occurring globally. Apart from the inevitability of these phenomena, one notices their negative effect on global environment and quality of life. An important ill effect of them is abundance of chemical and gaseous wastes. Naturally their safe management has become a major challenge for environmentalists and scientists. A second related problem is the pressure on land, materials and other resources crucial to developmental activities. Various industries as well as automobiles discharge large quantities of liquid and gaseous wastes. This study attempts to identify the pollution hazards due to such discharges and explores possible remedies. The specific instance analyzed in this paper is “Acid Rain”. Acid rain is likely to bring irreversible ecological changes. It may kill aquatic flora and fauna, and slow down the decomposition of organic matter. In addition, it could induce sterility in living beings, retardation in plant growth and reduction in soil fertility. This paper reviews the nature, causes, expected damage and remedies of this serious challenge. Global efforts are needed to tackle it so that future generations can be saved from environmental catastrophe.

Keywords: Global environmental challenges, acid rain, urbanization, industrialization, chemical and gaseous wastes, pollution hazards, ecological changes

1. Introduction:
Pollution is a challenging area for environmentalists and scientists. The pollution may be of various types; air, water, noise or soil. One cause of such pollution is rise in population; it increases the requirements of everything. Amongst all pollution creating agencies, vehicles produce maximum percentage of air pollution in the atmosphere and chemical industries are the second largest producer of atmospheric pollution. Air pollution, the most serious environmental concern, consists of excess concentration of foreign matter in the air which adversely affects the well being of the living beings and causes damage to property. In this paper, a particular problem related to air pollution, namely acid rain, has been discussed.

A US study estimates that as of 2010 there were 1.015 billion motor vehicles in use in the world. Further two US researchers have estimated that the world’s fleet will reach 2 billion motor vehicles by 2020 [1]. The vehicles are the main cause of Sulphur dioxide (SO$_2$) and Oxides of nitrogen (NO$_x$) emissions in the atmosphere. These are the main constituents of acid clouds, which ultimately cause “acid rain”.

Acid rain does not spare anything which is exposed to it. What has taken mankind decades to build and billions of years for nature to evolve, is being destroyed in a matter of a few years: a mere blink in the geological time scale. Acid rain has the potential to convert forests in to wasteland by damaging trees, plants crops and vegetables. Acidified surface water in lakes, ponds, rivers, reservoirs, springs wells and ground water sources induce respiratory illness in human beings. They are poisonous to wild life and inflict damage on buildings to deface most treasured monuments.

2. Acid Rain-The Phenomenon:
When fossil fuels such as coal, oil and natural gas are burned, chemicals like SO$_2$ and NO$_x$ are produced. These chemicals react with water and other chemicals present in air to form sulphuric acid, nitric acid and other harmful pollutants like sulphates and nitrates. These acid pollutants spread...
upwards into the atmosphere, and are carried by air currents, to finally return to the ground in the form of acid rain, fog or snow. The corrosive nature of acid rain causes environmental damage. Acid pollutants also occur as dry particles and gases, which when washed from the ground by rain, add to the acids in the rain to form an even more corrosive solution. This is called acid deposition. Damage from acid rain is widespread in North America, Europe, Japan, China and South-east Asia. In the US, coal-burning power plants contribute to about 70% of SO$_2$ \cite{2}. In Canada, oil refining, metal smelting and other industrial activities account for 61% of the SO$_2$ pollution \cite{2}. Motor vehicle exhaust fumes are the main source of nitrogen oxides. The acids in acid rain chemically react with any object they come in contact with. The term “acid rain” can be used to describe all precipitation—rain, snow and dew, which is more acidic than normal. Acidic taste is typically sour in nature and this acidity is measured on a logarithmic pH scale, ranging from 0 to 14. From pH 14 to 7, liquids are alkaline, at pH 7 liquids are neutral and from 7 to 0 they have acidic nature \cite{3}. Generally, ‘clean’ rain is slightly acidic as it dissolves varying amounts of carbon dioxide, which is a common constituent of the earth atmosphere. The lowest pH value of rain is 5.6 when it is ‘clean’. This is the pH level produced by carbonic acid if distilled water were in equilibrium with atmospheric carbon dioxide. Acid rain on precipitation is defined as one which pH less than 5.6 \cite{3}. The acidity of rain water is caused due to the formation of secondary pollutants like sulphuric acid, nitric acid and hydrochloric acid. The formation is due to the reaction of water vapour with SO$_2$, NO$_x$ and HCI gases.

3. Causes of Acid Rain:
Acidification of our environment is a man-made phenomenon. The two primary sources of acid rain are sulphur dioxide and nitrogen oxide. Automobiles are the main source of nitrogen oxide emissions, and utility factories are the main source for sulphur dioxide emissions. These gases enter the atmosphere and then oxidize in clouds to form nitric or nitrous acid and sulphuric acid. Acid rain therefore, is a cocktail of sulphuric acid and nitric acids. Currently, about 60%-70% of the acidity is assumed to be due to sulphuric acid and 30%-40% to nitric acid \cite{4}. Burning of fossil fuels for electricity generation is a major contributor of sulphur dioxide to the atmosphere. Smelting of sulphide ores, particularly of lead, zinc and copper is also responsible for an increase in the sulphur dioxide content of the atmosphere. The major contributors of oxides of nitrogen are automobile exhaust, power houses and smelters.

3.1 Sulphur dioxide:
Although there are several reactions may make a minor contribution to the oxidation of SO$_2$, here is thought to be only one significant reaction. The reaction occurs as follows:

$$\text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HOSO}_2 + \text{M}$$ \hspace{1cm} (1)

This reaction occurs at an appreciable rate and is thought to be the sole contributor to the oxidation of SO$_2$ in the atmosphere. The hydroxyl radical is produced by the photodecomposition of ozone and is considered to be highly reactive with many species.

3.2 Nitrogen Oxide:
As with SO$_2$, the principal contributor to the formation of nitric acid is the reaction with hydroxyl radicals. These radicals are highly reactive and abundant in the atmosphere. The reaction proceeds as follows:

$$\text{HO} + \text{NO}_2 + \text{M} \rightarrow \text{HONO}_2 + \text{M}$$ \hspace{1cm} (2)

There are several other possibilities such as oxidation by atmospheric oxygen; however none occurs at a substantial rate in the atmosphere to be significant in the formation of nitric acid.

4. Effects of Acid Rain:
Acid rain has a number of harmful effects on people and the natural ecosystem of the world. Scientists today are convinced that acid rain is severe in many areas and that it is having an adverse effect on the environment. The problem of acid rain is rapidly spreading. Because it is mainly caused by industrial processes, automobiles and thermal power plants, developed countries have the most severe acid rain problems. However, as the undeveloped nations begin to industrialize, instances of
Acid rain will increase greatly. Determining just how the planet is being hurt by acid rain is very difficult because the ecosystem that it affects is so diverse and complex. Acid rain adversely affects quality of surface water, life of aquatic animals, forests, automotive coatings, materials, visibility and human health. If the acid rain destroys our environment, eventually it will destroy us as well. Acid rain can affect the earth in many different ways. Below one can see how soil, trees, lakes, buildings and people are affected when acid rain falls on the earth.

4.1 Effects on human beings:
Acid rain does not directly affect human health. The acid in the rainwater is too dilute to have direct adverse effects. However, the particulates responsible for acid rain (sulphur dioxide and nitrogen oxides) do have an adverse effect. Increased amount of fine particulate matter in the air contribute to heart and lung problems including asthma and bronchitis. Although surface water polluted by acid rain does not directly harm people, the toxic substances leached from the soil can pollute the water supply. Fish caught in these waters may be unsuitable for human consumption. Acid, along with other chemicals in the air, produces urban smog, which causes respiratory and visibility impairment problems.

4.2 Effects on Buildings and Materials:
Acid rain and dry acid deposition damages buildings, automobiles and other structures made of stone or metals. Acid corrodes the materials causing extensive damage to them and ruins historic buildings. For example, the Parthenon in Greece has been affected by acid rain and in India the marble of Taj Mahal has been reported to the affected due to the air pollutant sulphur dioxide from the nearby Mathura oil Refinery [5]. Some environmentalists call it is ‘stone cancer’. Acid rains have a corrosive effect on limestone or marble buildings or sculptures. It is well established that either wet or dry deposition of sulphur dioxide significantly increases the rate of corrosion on limestone, sandstone, and marble.

Sulphur dioxide reacts with water to form sulphurous acid

$$SO_2 + H_2O \rightarrow H_2SO_3$$  

(3)

Sulphur trioxide plus water makes sulphuric acid

$$SO_3 + H_2O \rightarrow H_2SO_4$$  

(4)

The sulphuric acid then further reacts with the limestone in a neutralization reaction.

Limestone: $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3$  

(5)

$$H_2CO_3 \rightarrow CO_2 \text{ gas} + H_2O$$  

(6)

The calcium sulphate formed is soluble in water and hence the limestone dissolves and crumbles.

Acid deposition has also caused deterioration of buildings and monuments. Many of these are built of stone that contains calcium carbonate. Marble is one such material. Acid rain can turn the calcium carbonate to calcium sulphate. The calcium sulphate present can crumble and be washed away.

4.3 Effects on Soil:
Acid rain dissolves and washes away nutrients in the soil, which are needed by plants. It can also dissolve naturally occurring toxic substances like aluminium and mercury, freeing them to pollute water or poison plants. Acid rain can damage soil by destroying vital substances and washing away the nutrients. Soils naturally contain small amounts of poisonous minerals such as mercury and aluminium. Normally present of these minerals does not cause serious problems, but when acid rain falls on the ground and the acidity of the soil increases, chemical reactions occur allowing the poisonous minerals to be absorbed by the plant roots. Trees and plants are then damaged and any animals eating them will absorb the poisons, which will stay in their bodies.

4.4 Effects on trees:
Acid rain indirectly affects plants by removing nutrients from the soil in which they grow. It affects trees more directly by creating holes in the waxy coating on leaves, causing brown dead spots which affect the plant’s photosynthesis. Such trees are more vulnerable to insect infestations, drought and cold. Spruce and fir forests at higher elevations seem to be most at risk. Farm crops are less affected.
by acid rain than forest. The acid takes important minerals away from the leaves and the soil. Without such minerals, trees and plants cannot grow properly. Damaged trees tend to lose their leaves, have stunted growth and damaged bark. This makes it easier for fungi and insects to attack the tree, and as a result the tree may die. Pollutants can block or damage the little pores on the leaves through which the plant takes in the air, it needs to survive.

4.5 Effects on surface water (Lakes & ponds and aquatic animals):
Water from acid rain ultimately enters ground water reservoir. It then reaches rivers, lakes and wetland, causing the water in them to become acidic. This affects plant and animal life in aquatic ecosystems. Acid rain also has far reaching effects on wildlife. By adversely affecting one species, the entire food chain may be disrupted, ultimately endangering the entire ecosystem. Different aquatic species can tolerate different levels of acidity. For instance, clams and mayflies have a high mortality when water has a pH of 6.0. Frogs can tolerate more acidic water, although with the decline in supply of mayflies, frog populations may also decline [6]. Land animals dependent on aquatic organisms may also be affected. As the lake becomes more acidic the fish find it increasingly difficult to reproduce successfully. It is not only the acid in the water that kills them, but also poisonous minerals like aluminium that are washed out of the surrounding ground into the water. Birds that eat the fish also begin to suffer as the harmful minerals build up inside.

4.6 Effects on the Environment:
- Acid rain increases the acidity of lakes and dams and may kill off much aquatic life.
- Acid rain increases the acidity of soil and ground water meaning that plants and crops will not grow.
- Acid rain has been blamed as possible cause for the death of trees in forests in Europe and North America. In spite of research nobody yet knows the exact way in which forests are harmed by Acid Rain.

4.7 Effects on Automotive Coatings:
- Over the past two decades, there have been numerous reports of damage to automotive paints and other coatings. The reported damage typically occurs on horizontal surfaces and appears as irregularly shaped, permanently etched areas. The damage can best be detected under fluorescent lamps, can be most easily observed on dark coloured vehicles, and appears to occur after evaporation of a moisture droplet. In addition, some evidence suggests damage occurs most frequently on freshly painted vehicles. Usually the damage is permanent; once it has occurred, the only solution is to repaint.

5. Reduction Techniques and Control Measures for Acid Rain:
There are several ways to reduce acid rain—more properly called acid deposition—ranging from societal changes to individual action. It is critical that acid deposition be reduced, not only in the United States and Canada, but also throughout the world to preserve the integrity of natural habitats, as well as to reduce damage to man-made structures. US Environmental Protection agency (EPA) has taken steps to limit the amount of $SO_2$ and $NO_x$ emitted into the atmosphere because they are the main contributors to acid deposition.

5.1 Reduction of $SO_2$:
Prevention of Acid rain is very important for the future of environment. Since acid rain is caused mainly by the emission of sulphur dioxide from coal-fired power plants. There are a number of preventive measures, including:
- Switching from fuel sources to natural gas, oil, or renewable energy sources;
- Switching to low-sulphur coal; removing the sulphur from the coal before burning;
- Using fluidised-bed combustion processes to burn the coal; and
- Removing sulphur from the smoke stack after combustion, through the installation of pollution control equipment.

Other preventive methods are: Catalytic converters, road traffic restrictions, and equalising acidity in affected water systems by using powdered limestone and reduction in the sulphur content of fuels.
5.2 Reduction of NO\textsubscript{x}:

NO\textsubscript{x} reduction technologies can be grouped into two broad categories: combustion modifications and post-combustion processes. Some of the more important NO\textsubscript{x} control technologies are briefly discussed below.

5.2.1 Combustion Modifications:

Reducing the flame temperature at peak combustion area will mean reduction of NO\textsubscript{x} formation. This is the most effective method to control NO\textsubscript{x} and Fluidized Bed Combustion which maintains low temperature (850\textdegree{}-950\textdegree{}C) combustion area is proven to be the best method to combat NO\textsubscript{x} problem [7].

\textit{a) Flue gas treatment:}

Flue gas treatment to remove NO\textsubscript{x} is useful if higher removal efficiencies are required than may be achieved through combustion control. Selective Catalytic Reduction (SCR) is the most advanced and effective method for reducing NO\textsubscript{x} emissions. In selective catalytic reduction, the NO\textsubscript{x} species are reduced by NH\textsubscript{3}, ultimately to N\textsubscript{2} gas. The predominant reactions are:

\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 &\rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 &\rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}

Ammonia is vaporized and injected downstream from boiler feed water.

\textit{b) Low-NO\textsubscript{x} Burners:}

Low-NO\textsubscript{x} Burners (LNBs) are designed to control the mixing of fuel and air to achieve what amounts to staged combustion. This staged combustion reduces both flame temperature and oxygen concentration during some phases of combustion, in turn, reduces both lower thermal NO\textsubscript{x} and fuel NO\textsubscript{x} production.

\textit{c) Over fire Air:}

Over fire Air (OFA) is air that is injected into the furnace above the normal combustion zone. Generally when OFA is employed, the burners are operated at a lower than normal air-to-fuel ratio, which reduces NO\textsubscript{x} formation. OFA, which is frequently used in conjunction with LNBs, completes the combustion process at a lower temperature.

\textit{d) Reburning:}

OFA is air that is injected into the furnace above the normal combustion zone. Generally when OFA is employed, the burners are operated at a lower than normal air-to-fuel ratio, which reduces NO\textsubscript{x} formation. OFA, which is frequently used in conjunction with LNBs, completes the combustion process at a lower temperature.

\textit{e) Operational Modification:}

Changing certain boiler operational parameters can create conditions in the furnace that will lower NO\textsubscript{x} production. Examples include burners-out-of-service (BOOS), low excess air (LEA), and biased firing (BF). In BOOS, selected burners are removed from service by stopping fuel flow, but airflow is maintained to create staged combustion in the furnace. LEA involves operating at the lowest possible excess air level without interfering with good combustion, and BF involves injecting more fuel to some burners (typically the lower burners) while reducing fuel to other burners (typically the upper burners) to create staged combustion conditions in the furnace.

5.3 Post-Combustion Treatment:

5.3.1 Selective Catalytic Reduction:

In SCR, a catalyst vessel is installed downstream of the furnace. Ammonia (NH\textsubscript{3}) is injected into the flue gas before it passes over the fixed-bed catalyst. The catalyst promotes a reaction between NO\textsubscript{x} and NH\textsubscript{3} to form nitrogen and water vapour. NO\textsubscript{x} reductions as high as 90\% are achievable, but careful design and operation, such as control of the reagent dosage and assuring good mixing, are necessary to keep NH\textsubscript{3} emissions (referred to as NH\textsubscript{3} slip) to a concentration of a few ppm.

5.3.2 Selective Non catalytic Reduction:
In SNCR, a reducing agent (typically NH₃ or urea) is injected into the furnace above the combustion zone, where it reacts with NOₓ as in the case of SCR. Critical factors in applying SNCR are sufficient residence time in the appropriate temperature range and uniform distribution and mixing of the reducing agent across the full furnace cross section.

5.3.3 Hybrid Processes:
SNCR and SCR can be used together with some synergistic benefits. Also, either process can be used in conjunction with Low-NOₓ Burners.

6. Suggestions and Recommendations:
   i. Improvement in technologies and switching to clean combustion technologies is highly essential. Coal with lower sulphur content should be preferred thermal plants.
   ii. Replacement of coal by natural gas would also reduce the problem substantially. Installation scrubbers to reduce smoke-stack emissions, though expensive, would be economical compared to the losses due to damage done to lakes, forests, monuments, food production and so on.
   iii. Acid rain can only be managed by checking the sources of pollution. Some measures can be taken locally to neutralize the acid or by countering acidification. Addition of calcium carbonate or calcium oxide to acidified water raises the pH of water. Regular monitoring of water bodies is essential. Emission of sulphur oxide and nitrogen oxide should be minimized and kept in check.
   iv. Chlorine leak or discharge should be stopped. Vehicular exhaust should be minimized by using control valves or systems in the outlet of the exhaust pipeline of the automobiles. Effective burning of the fuel should be ensured by increasing the efficiency of the engines.

One simple solution is to neutralise the acid with lime. It is a short-term measure, and it is required to be repeated periodically. However, it is quite expensive, especially when large areas of water bodies have to be limed. Further, there is a possibility that large-scale liming may create its own ecological problems and affect the ecological system.

Because of these problems and the adverse effects air pollution has on human health, a number of steps are being taken to reduce sulphur and nitrogen emissions. Most notably, many governments are now requiring energy producers to clean smoke stacks by using scrubbers which trap pollutants before they are released into the atmosphere and catalytic converters in cars to reduce their emissions. Additionally, alternative energy sources are gaining more prominence today and funding is being given for the restoration of ecosystems damaged by acid rain worldwide.

7. Individual action:
   It may seem like there is not much that one individual can do to stop acid deposition. However, like many environmental problems, acid deposition is caused by the cumulative actions of millions of individual people. Therefore, each individual can also reduce their contribution to the problem and become part of the solution. Individuals can contribute directly by conserving energy, since energy production causes the largest portion of the acid deposition problem. For example, one can:
   • Turn off lights, computers, and other appliances when you're not using them.
   • Use energy-efficient appliances: lighting, air conditioners, heaters, refrigerators, washing machines, etc.
   • Only use electric appliances when you need them.
   • Keep the thermostat at 68°F in the winter and 72°F in the summer. One can turn it even lower in the winter and higher in the summer when away from home.
   • Insulate the home as best you can.
   • Carpool, use public transportation, or better yet, walk or bicycle whenever possible
   • Buy vehicles with low NOₓ emissions, and properly maintain your vehicle.
   • Be well informed.
Conclusion:
Acid rain is a pressing issue; it causes death of aquatic and wild life and it adversely affects the human health, plants and vegetation. It is the cause of other serious problems as well such as the release of SO$_2$ and NO$_x$ into the environment. Obviously, one must cut down the release of chemicals that form the root cause. This reduction may take time. Even if stopped today, the problem would persist for years to come because of the damage already done to the soil. Process of prevention requires effective air pollution control and moderation of stationary sources (like industries) as well as mobile sources (like automobiles) of pollution. In India, acid rain is not a problem as yet but recent information indicates occurrence of acid rain in localized areas. In future, acid rain may become a major threat to developed countries like U.S.A., U.K., Canada and Sweden and may start seriously affecting the rest of the world. If the acid rain destroys our environment, eventually it will destroy us as well. So urgent measures are necessary; some of them have been described above.

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