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Review Paper

Acid rain and its ecological consequences

Anita Singh and Madhoolika Agrawal*

Ecology Research Laboratory, Department of Botany, Banaras Hindu University, Varanasi - 221 005, India

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Abstract: *Acidification of rain-water is identified as one of the most serious environmental problems of transboundary nature. Acid rain is mainly a mixture of sulphuric and nitric acids depending upon the relative quantities of oxides of sulphur and nitrogen emissions. Due to the interaction of these acids with other constituents of the atmosphere, protons are released causing increase in the soil acidity. Lowering of soil pH mobilizes and leaches away nutrient cations and increases availability of toxic heavy metals. Such changes in the soil chemical characteristics reduce the soil fertility, which ultimately causes the negative impact on growth and productivity of forest trees and crop plants. Acidification of water bodies causes large scale negative impact on aquatic organisms including fishes. Acidification has some indirect effects on human health also. Acid rain affects each and every components of ecosystem. Acid rain also damages man-made materials and structures. By reducing the emission of the precursors of acid rain and to some extent by liming, the problem of acidification of terrestrial and aquatic ecosystem has been reduced during last two decades.*

Key words: *Acid rain, Causes, Effects, Control*
PDF of full length paper is available with author ***(*madhoo58@yahoo.com)***

Introduction

Since the beginning of civilization, human beings have used various natural resources for their benefit. To make their life easier, they have produced facilities that use many of the Earth's energy resources. Energy is mainly produced by burning fuels such as coal, oil and natural gases. On one side this kind of development makes our lives easier, but on the other hand it results into pollution by release of harmful substances into the environment. Burning of fossil fuels in industries and transport sector, industrialization and urbanization have led to increase in concentrations of gaseous and particulate pollutants in the atmosphere leading to air pollution (Tripathi and Gautam, 2007; Dwivedi and Tripathi, 2007). Acid rain is one of the most serious environmental problems emerged due to air pollution.

Acid rain is a broad term that describes several ways through which acid falls out from the atmosphere. Acid rain includes acidic rain, fog, hail and snow. Robert Angus Smith first used this term in 1872 to describe the acidic nature of rain around industrial town of Manchester, U.K. in a paper entitled "The air and rain beginning of chemical climatology". Scientists often refer to "acid deposition" as a more accurate term for acid rain. Along with the wet deposition there are also dry depositions of acids, which can be transformed into salts in the soil and cause the same environmental damage, as do the wet deposits. Dry deposition generally occurs close to the point of emission. Wet deposition, however, may occur thousands of kilometers away from the original source of emission.

The problem of acid rain is widely believed to result from the washout of oxides of sulphur, nitrogen and other constituents present in the atmosphere. Main sources of these oxides are coal fired power stations, smelters (producing SO_2) and motor vehicle exhausts (producing NOx). These oxides may react with other chemicals and produce corrosive substances that are washed out either in wet or dry form by rain as acid deposition. Initially events of acidic rainfall were frequent only around industrial areas. But with the increased use of tall stacks for power plants and industries, atmospheric emissions are being transported regionally and even globally (Galloway and Whelpdale, 1980; Wagh *et al.,* 2006).

Atmospheric acid deposition in form of rain, fog or snow was identified as major environmental problems for the countries in Europe, East Asia and North America (Bouwman *et al.,* 2002), including Canada, England, Scotland, Sweden, Norway, Denmark, West Germany, The Netherland, Austria, Switzerland, Russia, Poland and Czechoslovakia, Southwest China and Japan. Acid rain affects the quality of human life, threatens the environmental stability and the sustainability of food and timber reserves, thus posing an economic crisis. Acid rain has broad economic, social and medical implications and has been called an unseen plague of the industrial age (Anon, 1984).

Causes of acidification: Sulphur dioxide (SO_2) and oxides of nitrogen and ozone to some extent are the primary causes of acid rain. These pollutants originate from human activities such as combustion of burnable waste, fossil fuels in thermal power plants and automobiles. These constituents interact with reactants present in the atmosphere and result into acid deposition. The natural sources of sulphur pollutants are oceans and to much smaller extent from volcanic eruptions. The man-made sources of SO_2 emissions are the burning of coal and petroleum and various industrial processes (Cullis and Hischler, 1980). Other sources include the smelting of iron and other metallic (Zn and Cu) ores, manufacture of sulphuric acids, and the operation of acid concentrators in the petroleum industry. The levels of NOx are small in comparison to SO_2, but its contribution in the production of acid rain is increasing. Main natural sources of NOx include lightening, volcanic eruptions and biological processes (especially microbial activity). Man-made sources are power stations, vehicle exhausts and industrial emission.

The degree of acidity is measured by pH value, it is shorthand version of potential hydrogen. The pH of normal rainwater is also acidic; the reason is that water reacts to a slight extent with atmospheric carbon dioxide (CO_2) to produce carbonic acid.

$$CO_2 + H_2O \longrightarrow H_2CO_3 \text{ (carbonic acid)}$$

Small amount of nitric acid is also responsible for the acidity of normal rainwater, which is produced by the oxidation of nitrogen in presence of water during lightening storms.

$$2\,N_2 + 5O_2 + 2H_2O \longrightarrow 4\,HNO_3 \text{ (nitric acid)}$$

Rain that presents a concentration of H^+ ion greater than 2.5 μeq^{-1} and pH value is less than 5.6 is considered acid (Evans, 1984). Galloway *et al.* (1982) proposed a pH of 5.0 as a limit of natural contribution.

Chemical reactions during acid rain formation:

The chemical reaction that results in the formation of acid rain involves the interaction of SO_2, NOx and O_3. When the pollutants are vented into the atmosphere by tall smoke stakes, molecules of SO_2 and NOx are caught up in the prevailing winds, where they interact in the presence of sunlight with vapours to form sulphuric acid and nitric acid mists. These acids remain in vapour state under the prevalent high temperature conditions. When the temperature falls, condensation takes the form of aerosol droplets, which owing to the presence of unburnt carbon particles will be black, acidic and carbonaceous in nature. This matter is called “acid smut”. The presence of oxidizing agents and the characteristics of the reaction affects the rate of acid generation (Calvert *et al*., 1985).

Acid reactions involving O_3:

$$O_3 \longrightarrow O_2 + O$$

$$O{+}H_2O \longrightarrow OH^{\bullet} \text{ (hydroxy radical)}$$

$$OH^{\bullet}{+}SO_2 \longrightarrow HSO_3$$

$$HSO_3^- + OH^{\bullet} \longrightarrow H_2SO_4$$

$$OH{+}NO_2 \longrightarrow HNO_3$$

$$HSO_3 + O_2 \longrightarrow SO_3^{2-} + HO^{\bullet}_2 \text{ (peroxy radical)}$$

Peroxy radicals react with formaldehyde, acetaldehyde and form formic and acetic acids and some other organic acids, contributing to 5-20% acidity in total acid rain load.

Acid reactions involving sulphur:

Coal is especially rich in sulphur. As coal is burned, its component get oxidized

$$S + O_2 \longrightarrow SO_2$$

The oxidation of sulphur to SO_2 occurs directly in the flame; therefore SO_2 is discharged to the atmosphere from the smoke stacks. As SO_2 is swept along by the prevailing wind, it is slowly oxidized at ordinary temperature to SO_3^{2-}

$$2\,SO_2 + O_2 \longrightarrow 2\,SO_3^{2-}$$

$$SO_3^{2-} + H_2O \longrightarrow H_2SO_4$$

$$SO_2 + H_2O \longrightarrow H_2\,SO_3$$

$$H_2SO_3 \longrightarrow H^+ + HSO_3^-$$

$$HSO_3^- + O_3 \longrightarrow SO_4^{2+} + H^+ + O_2$$

Oxidant property of atmosphere plays an important role in conversion of SO_3^{2-} to SO_4. Sulphur dioxide oxidation is most common in clouds and especially in heavily polluted air where compounds such as ammonia and O_3 are in abundance. These catalysts help to convert more SO_2 into sulphuric acid.

$$H_2\,O_2 + HSO_3 \longrightarrow HSO_4^- + H_2O$$

Acid reactions involving nitrogen:

$$N_2 + O_2 \longrightarrow 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3$$

$$O_3 + NO_2 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow 2\,HNO_3$$

Reports on acidic Episodes:

The first incidence of acid rain seems to have coincided with onset of the industrial revolution in the mid 19th century. Gorham (1958) observed acid rain problem in England then as a regional phenomenon in Scandinavia in the late 1960’s. By 1965, the pH of rainwater in Sweden was about 4 or less and it was reported in 13th UN conference on the Human Environment held at Stockholm in 1972. This was the beginning of acid rain research. It was suggested that rain and snow in many industrial regions of the world are between five and thirty times as acidic as would be expected in an unpolluted atmosphere (Jickells *et al*., 1982). In 1974, over the northeast United States, the pH of rain and snow was found to be around 4.0 (Likens and Butler, 1981).

Until the mid 1970s, the problem of acid rain was mainly confined to north America and Scandinavia, but thereafter pH of precipitation well below 4.5 in much of central and northern Europe and it was recorded (Table1). American records include a rain of pH 2.7 at Kane in Pennsylvania and a rain of pH 1.5 falling over wheeling in west Virginia in 1979 (La Bastille, 1981). At Banchory in northeast Scotland, the pH of rain was sometimes as low as 3.5 (Last and Nicholson, 1982).

Regions that have been most affected by acidic deposition include Europe, eastern north America, and southeast Asia,

Table - 1: Rainwater pH values in different regions of the world (modified from Khemani *et al.,* 1994)

Countries	Range of pH
Japan	4.7
Europe	4.1 - 5.4
China acid rain area	4.1 - 4.9
China non - acid rain affected area	6.3 - 6.7
US north west	5.1 - 5.2
US west- middlewest	5.0 - 5.5
US north west	4.1 - 4.2

Table - 2: Range of rainwater pH in different parts of India (modified from Khemani, 1993)

Regions	Cities	pH
Coastal area	Trivendrum	5.3
Industrial area	Chembur	4.8
Power plant	Inderprasth	5.0
	Koradi	5.7
	Singrauli*	5.8*
Urban area	Pune	6.3
	Delhi	6.1
Non urban area	Sirur	6.7
	Muktsar	7.3
	Goraur	5.3

* Singh and Agrawal (2005)

Table - 3: Range of rainwater pH in different parts of India measured at Bapmon station (modified from Datar *et al.,* 1996)

Stations	pH
Allahabad	6.93
Jodhpur	7.42
Kodaikanal	6.28
Mohanbari	5.98
Visakhapatnam	6.01
Nagpur	5.97
Port Blair	6.15
Pune	6.43
Srinagar	7.22
Minicoy	6.58

Table - 4: Chemical characteristics of three studies stream in the western Adirondack region of New York (1991- 2001) (modified from Lowrence *et al.,* 2001)

Parameters	Mean of six monthly samples January - June 2001		
	Buck creeck	Bald mountain brook	Pond outlet
pH	5.55	6.22	7.11
SO_4^- (µmol^{-1})	60	54	52
NO_3^- (µmol^{-1})	35	32	25
K^+ (µmol^{-1})	7.1	7.5	15
Mg^{2+} (µmol^{-1})	18	22	43

Table - 5 : Percentage decrease (-) or increase (+) in selected physiological characteristics of SAR treated cultivars as compared to their respective control

Crop/Variety	Parameters	45 Days				65 Days			
	Acid rain pH	5.0	4.5	4.0	3.0	5.0	4.5	4.0	3.0
T. aestivum cv. Sonalika	Photosynthetic rate (µmol $CO_2 m^{-2}$ Sec^{-1})	(+) 13.9	(-) 25.2	(-) 19.5	(-) 33.7	(-) 10.9	(-) 21.9	(-) 34.7	(-) 48.3
	Stomatal conductance (cm S^{-1})	(+) 84.9	(+) 54.2	(+) 35.9	(+) 20.9	(-) 63.5	(+) 7.79	(-) 15.9	(-) 33.7
T. aestivum cv. M213	Photosynthetic rate (µmol $CO_2 m^{-2}$ Sec^{-1})	(+) 62.2	(-) 1.55	(+) 7.05	(-) 19.3	(-) 8.73	(-) 9.62	(-) 21.7	(-) 37.5
	Stomatal conductance (cm S^{-1})	(+) 103.2	(+) 26.4	(+) 93.5	(+) 7.18	(+) 9.86	(+) 22.4	(+) 7.67	(+) 29.1
G. max cv. JS335	Photosynthetic rate (µmol $CO_2 m^{-2}$ Sec^{-1})	(-) 11.6	(-) 11.9	(-) 33.2	(-) 38.3	(-) 2.30	(-) 34.1	(-) 41.5	(-) 68.6
	Stomatal conductance (cm S^{-1})	(-) 43.8	(-) 5.78	(-) 78.3	(-) 72.4	(-) 13.2	(-) 58.5	(-) 72.2	(-) 90.4
G. max cv. PK472	Photosynthetic rate (µmol CO_2 m^{-2} Sec^{-1})	(-) 2.3	(-) 17.0	(-) 49.2	(-) 54.7	(-) 9.42	(-) 14.1	(-) 19.0	(-) 43.9
	Stomatal conductance (cm S^{-1})	(+) 32.2	(+) 1.34	(-) 27.3	(-) 57.9	(+) 25.2	(+) 10.5	(+) 0.46	(+) 35.32

especially central and southern China (Kuylenstierna *et al*., 2001). Sulphur emissions have played the dominant role in these regions. However, there have been large reductions in SO_2 emissions in Europe and north America during the last two decades; the reduction being about 65% in Europe and 40% in the United States from 1982 to 1999. Emission of NOx in United States remained relatively stable from 1980 to 1999 (USEPA, 2001). Sulphur emissions in China decreased in the late 1990, but increased from 1999 to 2002 (Li and Gao, 2002). NOx emissions are more difficult to curb than sulphur emissions, and reduction of ammonia emissions is particularly challenging (Kaiser, 2001). Ammonia emission neutralizes the precipitation or even makes it alkaline, but may cause soil acidification through nitrification and the emissions have increased greatly over the last couple of decades particularly in some Asian countries due to increased use of fertilizers and greater amounts of animal waste (Galloway and Cowling, 2002).

Acid rain has also been reported in India (Table 2, 3). A rainfall of pH 3.5 was reported in Mumbai (Burman, 1985). The air pollution levels are steadily rising in the metropolitan cities like Kolkata, Delhi, Mumbai. The mean pH value of rain water was 9.1 during 1963 and 6.2 during 1984 at Delhi (Khemani *et al.,* 1989). The world Meteorological organization has predicted substantial increase in acidity in cities like Hyderabad, Chennai, Pune and Kanpur (Banerjee, 1997). Acid rain problem in Bihar, West Bengal, Orissa and southern coastal India has been predicted to lead to infertile soil.

Korba is one of the industrial areas, where industrial activities are totally based upon the coal mining, thermal power plants, aluminium plant and several small-scale industries using coal as the energy source. Acid rain has been detected in Korba city, and H_2SO_4 is mainly responsible for causing this problem. (Chandrawanshi *et al.,* 1997). In Singrauli region of Sonbhadra district in India, the acid depositions were found to be higher near the thermal power plant stations as compared to distantly situated site (Agrawal and Singh, 2001; Singh and Agrawal, 2005). The rainfall having pH 5.0 and 4.8 was reported towards the end of monsoon season at two sites close to thermal power stations (Agrawal and Singh, 2001). The seasonal average pH of clear fall deposition varied from a minimum of 5.98 at site situated at 18 km northeast from a thermal power station in winter to a maximum of 6.91 at 29 km northeast away from thermal power station in the rainy season (Singh and Agrawal, 2005).

Effects of acid rain on soil:

Soil is one of the most important ecological factors. Every plant depends on it for their nutrient and water supply. Soil system is very complex and dynamic. Acid rain results into acidification of soil, which increases the exchange between hydrogen ion and nutrient cations like potassium (K), magnesium (Mg) and calcium (Ca) in the soil. These cations are liberated into soil and can be rapidly leached out in soil solution along with sulphate from acid input (Van Breeman *et al.,* 1984). Acid induced leaching leads to nutrient deficiency in the affected soils, and this loss of soil fertility results into decrease in the growth of plants including trees on acidified soil. Nutrient cycling and decomposition rate is also negatively affected by acidification of soil. It was shown that strong acidification retards the decomposition of litter of spruce, pine, birch and other cellulose-rich materials (Francis, 1982; Kilham *et al.,* 1983).

Soil quality plays very important role in maintenance of structural diversity of Boreal forest ecosystems. Variations in soil acidity and its relation with biodiversity were analyzed in the National Natural Park "Russian North" of Russia (Kopstik *et al*., 2001). Soil acidification led to changes in soil quality from podzol, podzolic soil, dernopodzolic soil and brown earth to Pararendzina that changes the floristical composition, followed by changing of pine and spruce forest to mixed and birch forest (Kopstik *et al.,* 2001).

Soils are found to be more resistant against acidification than surface waters because of higher buffer capacity. Most of the soils can tolerate higher levels of acidity than lakes and rivers without visible damage. A large increase in acidity was found in forest of Europe throughout the soil profile during 1982-1983 as compared to those observed in 1927 (Tamm and Hallbacken, 1988). The pH level of 1927 and 1982-83 observations were respectively 4.5 and 3.8 for humus layer, 4.5 and 4.2 for A2 layer, 4.9 and 4.6 for B layer and 5.3 and 4.7 for C horizon under *Fagus sylvatica* forest stands. Maximum change in acidity was observed in humus layer. It was suggested that the main cause of acidification of deeper horizon was the acidifying substances that are deposited from the atmosphere. Soil acidification has occurred in Europe (Tamn and Hallbacken, 1988), eastern north America (Watmough and Dillon, 2003) and in China (Dai *et al*., 1998). Since a number of factors may cause soil acidification including vegetation changes, it is difficult to determine the contribution from acidic deposition. There is also uncertainty about the time scale over which effects on soils might occur.

Effects of acid rain on aquatic ecosystem:

Acid rain makes the water bodies acidic. Streams and lakes normally show clear signs of acidification as these have less prospect of buffering acid inputs than do soils and plants. The acidic deposition changed the lake chemistry in the Adirondack region of New York (Table 4). A survey report of Adirondack lake during 1991-1994 showed that 41% of lake either chronically acidic or susceptible to episodic acidification (Driscoll *et al*., 2001).

Acid lakes have also been found in Belgium, Denmark, West Germany and The Netherland (Whelpdale, 1983). All components of aquatic ecosystem are affected by acid rain, whether it is phytoplankton, amphibian, invertebrate or icthyofauna. During 1970's in southern Norway over 20% of lakes have lost their fishes (Wright and Henriksen, 1983). Losses of sport fish populations have occurred in acidified lakes and river in Canada. Due to acidic precipitation, fishes showed increases in mortality rate, reproductive failure, reduced growth rate skeletal deformities and increased uptake of heavy metals (Watt *et al.,* 1983).

The amphibians are also affected by acidification of water bodies (Freda, 1986). At low pH, many species of amphibians including frogs, toads and salamander are particularly sensitive (Whelpdale, 1983; Berlekom, 1985). The number of snails and phytoplankton also fell below pH 5.5. When pH was less than 5.2, snail disappeared; at pH 5.0, zooplankton disappeared; and below pH 4.0, stocks of all fish species declined rapidly because embryos failed to mature at this level of acidity (Carrick, 1979). Some species can, however, grow in the adverse condition of acid rain. Swedish lakes were first dominated by *Lobella* species and later by *Sphagnum* sp (Grahn, 1977) or *Juncua bulbosus* (Nilssen, 1980) tolerant to acidity.

At various pH, different species have different tolerance range. Larger aquatic plants (macrophytes) often decline, but acid tolerant white moss (*Sphagnum*) colonized acid lakebeds. *Sphagnum* moss and filamentous algae grow very fast and become very large in acid waters (pH < 5.5). They can form impenetrable mats that seal off oxygen and slow down the decay of litter on the lake floors (La Bastille, 1981; Pearce, 1982). Decomposition rate of acidified lakes is slowed down because the fungi and bacteria are not tolerant of acidic conditions. Acidification alters species structure in the polluted lakes and rivers. The impact of acidity is transmitted along food webs, like decrease in number of benthos, leads to a decline in the number of species of flies, mosquitoes and mayflies (Likens, 1985).

In Scandinavia and north America the concentration of Al was found to be abnormally high (Cronan and Schofield, 1979). High concentrations of Al and other heavy metals, such as Cd, Hg, Fe and sometimes Zn were found in acidified lakes and the sources of these metals are leaching of ions from soils and rocks in the catchments (Dickson, 1978). In the Hubbard's Brook Experimental forest in New Hampshire, USA, detailed measurements of water chemistry have shown that acidification causes increase in concentrations of Al, Cd, Mg and K, mobilized from sediments on the stream bed (Likens, 1985). Acid rain caused leaching of Ca ion so it disturbed the shell formation process in mollusks. Mollusks are more susceptible towards acidification and are not found in Ontario lakes with pH at or below 5 (Roff and Kwiatkowski, 1977).

Effects of acid rain on forest trees:

The effect of acid depositions on higher plants arises in two ways-either through foliage or through roots. The symptoms include direct damage to plant tissue (especially roots and foliage), reduced canopy cover, crown dieback and whole tree death (Tomlinson, 1983). The germination rate of Norway spruce, Scots Pine and silver birch seeds were found to be moderately inhibited at pH 3.8 and 5.4 (Abrahamsen *et al*., 1983). Possible effects of acidic deposition and its precursors on forests have been the topic of intensive research efforts in both Europe (UN/EC, 2002) and the United States (NAPAP, 1998). West German forests faced great loss due to acid rain. In 1982, 7.7% of 7.4 million hectares of West Germany's forest were visibly damaged; within a year 34% of trees had suffered discolouration and some loss of needles and leaves; by late 1984 around half the country's woodlands showed symptoms of the disease (Tift, 1985).

A field experiment was conducted to determine the effect of acidic mist containing S and N on stem wood growth of sitka spruce (Crossley *et al*., 2001). A monoclonal stand of sitka spruce was grown on a base rich soil and acid mist at pH 2.5 ($H_2SO_4 + NH_4NO_3$ equimolar 1.6 mole m^{-3}) was sprayed on canopy. The acid mist provided 48 kg N and 50 kg S haY^{-1} for 3 years. The stem wood growth was rapidly and consistently reduced by acid mist. Acid mist was found to be responsible for leaching of Ca^{2+} ion and the excessive proton uptake causing displacement of membrane associated Ca^{2+}, leading to membrane destabilization and foliar injury in red spruce (Jiang and Jagels, 1999).

On a Japanese cedar (*Cryptomeria japonica*) forest, a one-year field experiment was conducted to estimate the dry deposition of acidifying components. The dry deposition of SO_2, HNO_3, NO_2 and HCl was estimated by using the inferential method, and it was suggested that the dry deposition is an important pathway for the atmospheric input of H^+ to the forest at sandy site. The contribution of these gases on dry deposition was 32% by HNO_3, 33% by HCl, 20% by SO_2 and 10% by NO_2. (Takanashi *et al*., 2001). Acid rain caused reduction in protein concentration of *Betula alleghaniensis* and white spruce (Scherbatskoy and Klein, 1983).

Leaf is the most sensitive organ to pollutant damage, and has been the target of many studies. It was found that acid rain caused anatomical alterations in the leaves of tropical species, seedlings and sapling of *Spondias dulcis* Forst. F., *Mimosa artemisiana* Heringer and Paula and *Gallesia integrifolia* (Sant Anna-Santos *et al.* 2006). When exposed to simulated low pH acid rain (pH 3.0), necrotic spots on the leaf blade occurred which were mostly restricted to epidermis in all the species. *S. dulcis* displayed epicuticular wax erosion and rupture of epidermis. The abaxial surface of *M. artemisiana* was colonized by a mass of fungal hyphae and stomatal outer membrane ruptured. Some epidermal cells of *G. integrifolia* showed appearance similar to plasmolysis. The plants accumulated phenolic compounds in necrotic areas. Afterwards, leaves presented injuries in the mesophyll and collapsed completely. Cells surrounding the injured areas accumulated starch grains in *S. dulcis* and *M. artemisiana* showed more drastic symptom intensity (necrosis and chlorosis found on 5-30% of leaves) in response to acidic rain than *S. dulsis* and *G. integrifolia* (necrosis and chlorosis found on less than 5% of leaves). (Sant Anna-Santos *et al*., 2006).

Effects of acid rain on crop plants:

Crop plants showed a wide range of sensitivity to the acidity of rain. Norby and Luxmoore (1983) found reduction in CO_2 fixation in soybeans when treated with rain of pH 2.6. This decrease was ascribed to reduction in leaf area. Porter and Sheridan (1981), also found reduction of CO_2 fixation in alfalfa at pH 3.0. In laboratory and green house studies photosynthesis was decreased at pH 2.0 in *Platanus occidentalis* (Neufield *et al.,* 1985). The primary productivity in pintobean and soybean reduced by high levels of acidity (pH < 3.0) (Evans and Lewin, 1981). Ashenden and Bell (1987) found that there was 9-17% reduction in yield of winter barley at a range of ambient pH of 3.5 to 4.5.

Various physiological (photosynthetic rate, stomatal conductance, etc) and morphological characteristics of plants were found to be negatively affected by Acid rain. A field experiment was conducted in which two cultivars of wheat (Sonalika and M 213) and soybean (JS 335 and PK 472) were exposed to simulated rain acidified to pH 5.6(control), 5.0, 4.5 and 3.0 to evaluate the responses of these cultivars to acid rain at different ages. It was reported that *T. aestivum* showed significant reductions in photosynthesis rate at pH 4.0 after 45 days and at pH 5.0 and 4.5 after 65 days age in cv. M 213 (Table 5). In cv. Sonalika, reductions were found significant at pH 4.5 after 65 days. Maximum reduction was observed at pH 3 in both the cultivars at both the ages of observation (Table 5). As compared to the control, at pH 3.0, respective reductions in photosynthesis rate were 19.3 and 37.5% in M 213 and 33.7 and 48.3% in Sonalika at 45 and 65 days ages. In case of *G. max,* reductions in photosynthetic rate were significant at and below pH 5.0 in PK 472 and at pH 4.5 and below in JS 335 at 65 days age in comparison to their respective control (Table 5).

Maximum reduction of 54 and 44% in PK 472 and 38 and 68% in JS 335 at 45 and 65 days ages, respectively were observed at pH 3 as compared to the control (Table 5).

Variations in stomatal conductance (Cs) were also found significant. In *T. aestivum* significant increase was observed in Cs at pH 5 and 4 at 45 days and at pH 4.5 and 3 at 65 days in M 213, whereas in Sonalika at 45 days significant increase was observed at and below pH 5, but at 65 days it declined significantly at pH 5 and pH 3.0 (Table 5). In *G. max* cv. PK 472, Cs declined significantly at pH 4 and 3 at 45 days. In JS 335, significant reduction in Cs was observed at and below pH 5.0 at both the ages (Table 5).

Morphological characteristic of two varieties of wheat (Sonalika and M 213) were found to be negatively affected by acid rain treatments (Singh and Agrawal, 2004). There were significant reductions in shoot length at pH 3.0 in M 213 at both 45 and 75 days and at pH 3.0 in Sonalika at 75 days only. The root length was reduced significantly at pH 3.0 in both cultivars only at 75 days; the reductions being 13.1% in M 213 and 15.5% in Sonalika. Leaf number was also reduced significantly at pH 4.0 and 3.0 in Sonalika at 75 days. As compared to the control (pH 5.6), there were significant reductions in weight of 1000 seeds in both cultivars at pH 3.0. Yield reductions were also found significant at pH 4.0 and 3.0 in M 213 and at pH 3.0 in Sonalika.

In an another experiment, two cultivars of wheat (*Triticum aestivim* L. Malviya 206 and 234), varying in cuticular thickness and leaf area were exposed to simulated rain acidified to pH 5.6 (control), 5.0, 4.5, 4.0 and 3.0 from 30 days of age, twice a week for five weeks. Various characteristics like shoot and root lengths, leaf area, above and below ground biomass, no. of grains per plant and yield m^{-2} were decreased significantly in treated plants at different growth stages (Singh and Agrawal, 1996). It was found that both wheat cultivars showed significant growth reductions in response to simulated acid rain (SAR) treatments at pH 4.5 and below from 60 days onwards. At pH 5.0 shoot height of variety 206 was not affected by SAR treatment, but at pH 3.0, plants were significantly smaller compared to control plants from 45 days, and at pH 4.5 and 4.0 from 60 days to maturity. Shoot height at 75 days was reduced by 19, 15 and 25%, respectively at pH 5.0, 4.5 and 4.0. Root length showed significant reduction in all SAR treated plants of M 206 at pH 5.0 from 45 days and at different pH from 60 days onward. In case of M 234, shoot height was reduced significantly in SAR treated plants compared to the control from 45 days onwards. The present decrease in shoot height at 75 days was 11, 6, 14 and 37% respectively at pH 5.0, 4.5, 4.0 and 3.0. The values for root length in SAR treated M 234 plants were significantly lower than control at 75 days.

The dry weight of above and below ground parts also showed significant reductions. In M 234, total biomass was reduced by 53, 71, 83 and 90%, respectively at pH 5.0, 4.5, 4.0 and 3.0, whereas at the same age in 206, reductions were 58, 53, 72 and 75%, respectively compared to controls. Number of grains $plant^{-1}$, grains weight $plant^{-1}$ and yield m^{-2} declined significantly due to SAR treatment of wheat varieties M 206 and M 234 as compared to the control. In M 206, grain yield and numbers were reduced by 36 and 42% at pH 5.0, 40% and 30% at pH 4.5, 77 and 72% at pH 4.0 and 82 and 78% at pH 3.0, whereas in M 234 there were reductions of 39, 55, 80 and 76% in no. of grains at pH 5.0, 4.5, 4.0 and 3.0, respectively and grain yield were reduced by 39, 53, 82 and 78% at pH 5.0, 4.5, 4.0 and 3.0, respectively. This study indicated significant cultivars x pH interaction only for shoot height number of grains and weight of straw, whereas it was not significant for biomass accumulation and grain yield. M 206 has thinner cuticle and greater leaf area than M 234 that facilitate the entry of acid solution in leaf interior and because of this there were much reductions in biomass and yield. It was suggested that Indian cultivars might be more sensitive than those grown in the industrialized regions of the west.

The impact of simulated acid rain (SAR) on the photochemistry, net photosynthesis, morphological damage and crop yield were also studied on *Vaccinium angustifolium* Ait (wild blueberry) (Murray *et al*., 2004). It was found that, there was 8% decrease in fluorescence origin with the pH 1.5 SAR treatments as compared to the control (pH 5.6). There was no effect on quantum efficiency of photosystem II, photochemistry, photosynthesis, leaf and berry wax deposition and crop yield, but there was 6% reduction in total node number as compared to the control (pH 5.6).

The effect of repeated treatment with SAR on antioxidative enzyme activities, lipid peroxidation and chlorophyll concentration was studied in cucumber plants (*Cucumis sativus* L.) (Wyrwicka and Sklodowska, 2006). Measurements were carried out at one, five and seven days after triple spraying of acid rain having pH 3.0 and 1.8. At pH 1.8, the activity of ascorbate peroxidase was induced at one, five and seven days up to 209%, 193% and 204% of the control and at pH 3.0 it was increased significantly up to 215% of the control only one day after spraying. Glutathione transferase activity was found to increase during the whole experiment at all pH values. The leaves sprayed with acid rain having pH 1.8 exhibited induction of glutathione transferase at all times after treatment. The highest increase in its activity was appeared five days after the final spraying and reached 252% of the control, whereas activity of glutathione peroxidase was not changed considerably in acid treated leaves except for increase up to 153% and 159% of the control at one day after acid rain treatment at pH 3.0 and 1.8, respectively. The chlorophyll concentration was found to be decreased in leaf tissues one day after AR treatment at pH 3.0 (75% of control) and pH 1.8 (54% of control). It was suggested that prolonged acid rain stress is accompanied by oxidative stress. Results indicated that antioxidant enzymatic response to acid rain stress was quite sufficient in leaf tissues exposed to mild stress (pH less than 4.4).

Effects of acid rain on lower plants:

The lower plants including algae, fungi and lichen are also negatively affected by acid rain. Various microorganisms and microbial processes get affected because of changes in soil properties due to acid rain (Strayer *et al*., 1981; Johnson and Reuss, 1984). There were several reports on the impact of acid rain on mycorrhiza. These include negative influence on mycorrhizal association in *Betula papyrifera* (Kaene and Manning, 1988) and *Picea rubens* (Machara *et al*., 1993). Lichens are more sensitive to acidification of soil. They provide a sensitive biological litmus indicator (Ferry *et al*., 1973). Nitrogen fixation performed by lichen, *Peltigera* sp was found to be sensitive at pH 2.4 (Gunther, 1988). Photosynthetic activity was also found to be decreased at pH 3.0 in *Cladina stellaris* (Lechowiez, 1982).

It has been found that species of diatoms and golden brown algae are also sensitive to change in water chemistry and hence can be used as indicator of acidity of water (Smol and Glew, 1992). With acidification of lakes, golden brown algal species are replaced by other chlorophycean like *Chlorella mucosae* (Findlay and Kasian, 1986).

Effects of acid rain on materials and buildings: The impact of acid deposition on stone monuments made of marble and limestone and on building materials containing large amounts of carbonate have been recognized for over a century and many studies have addressed the effect of acid wet deposition on stone materials of historic buildings and monuments. High buildings made of concrete in urban areas have damaged due to exposure to cloud water with high acidity for a long time (Okochi *et al.,* 2000). Acid precipitations with pH level ranging between 3.0 and 5.0 have affected the cement and concrete (Sersale *et al*., 1998). Acid rain causes chemical deterioration on carbonate stones and formation of soluble Ca^{2+}, HCO_3^-, SO_4^{2-}. Dry deposition of SOx and NOx on the surfaces of stones contributes to salt enrichment on carbonate stones and plays a major role in the deposition of acid substances on buildings (Keuken *et al*., 1990). The impact of local wet and dry deposition of acid compounds was investigated by Tsujino *et al.* (1995) by exposing different materials such as copper, bronze, marble, *etc.* under indoor and outdoor conditions and the results showed the corrosion was directly correlated with local pollution, especially the ratio of SO_2/NOx and climate. The incremental effects of wet and dry deposition on carbonate stone erosion due to hydrogen ion, SO_2 and NOx were quantified by Baedecker *et al.* (1992). The results suggested that approximately 30% of erosion by dissolution could be attributed to the wet deposition of hydrogen ion and the dry deposition of SO_2 and HNO_3.

Acid rain speeded up the natural chemical weathering and corrosion of exposed materials in a variety of ways like ferrous metals are attacked by SO_2 and rusted more quickly. Steel building, railway tracts and other structures built of iron are very seriously affected by air pollution with extensive economic losses (Anon, 1984). The corrosion rate is faster (two to ten times) in polluted urban and industrial air particularly in the presence of high concentrations of SO_2 than in the countryside (Tolba, 1983). Acid rain mainly affected those buildings, which are made of sand stone, limestone and marble. Calcium carbonate is the common constituent of these materials, which reacts with sulphur present in dry deposition and form calcium sulphate. This is soluble and the acids so formed are washed off from the surface of the stone when it next rains and damages the world's cultural heritage, ancient monuments, historic buildings, sculptures, ornaments, and other important cultural objects. Acid rain causes carvings and monuments in stones to lose their features.

$$CaSO_4 + H_2O \longrightarrow CaO + H_2SO_4$$

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2CO_3$$

For iron, the acidic water produces an additional proton giving iron a positive charge.

$$4Fe(s) + 2O_2\ (g) + 8(aq) \longrightarrow 4Fe^{2+}\ (aq) + 4H_2O\ (l)$$

When iron reacts with more oxygen it forms iron oxide (rust).

$$4Fe^{2+} + (aq) + O_2\ (g) + 4H_2O\ (l) \longrightarrow 2Fe_2O_3 + 8H^+ + (aq)$$

It was founded that H^+ ion in acid rain dissolves $Ca(OH)_2$ in the hardened cement paste and SO_4^{2-} further corrodes it. The dissolution effect of H^+ leads to the reduction of $Ca(OH)_2$ concentration in the concrete specimens. The corrosion of SO_4^{2-} produces the substances which are larger than $Ca(OH)_2$ in volume such as $Ca_3Al_6O_{12}.CaSO_4$ and $CaSO_4.2H_2O$ leading to a large reduction in strength. Power stations around Agra and oil refinery at Mathura have brought many problems to the Taj mahal. Delhi Red fort and Jama Masjid are also showing signs of damage from sulphur pollution (Dutt, 1984).

Damages by acidic deposition are not only confined to the major structure but it also erodes the treasures like paintings, drawings, fabrics, antique costumes housed within art galleries, museums, libraries and religious places. Maintenance of these damaged buildings and materials increases the cost. In 1981 economic commission for European study (Tolba, 1983) found that corrosion of painted and galvanized steel structures costed $2-10 per year for each person living in Europe.

Effects of acid rain on physiological activities of animals: Various reports are available to show the effect of acid rain on the metabolic activities of animals. The effect of acidification on female sexual behavior in brown trout (*Salmo trutta*) was studied and result was compared with those in hime (land locked sockeye) and salmon (*Oncorhynchus nerka*) (Kitamura and Ikuta, 2000). The spawning brown trout was found to be extremely sensitive towards the acidity of water and at pH less than 5, the nest digging behavior was inhibited. The female trout and salmon showed no digging below pH 5.0 and 6.0, respectively (Kitamura and Ikuta, 2000). When the pH of ambient water was returned to nearly neutral condition than these two species behaved differently. The digging in hime salmon reappeared in 4 of 6 fishes tested (Kitamura and Ikuta, 2000), whereas in brown trout, the digging behavior reappeared in all tested fishes. The spawning behavior is greatly reduced in acidic environment and that is the reason for the reduction of salmonid population in the early stage of acidification.

The normal functioning of animals is also get affected by acid rain. When the effect of low pH (4.5) condition was examined on endocrine and immune function in carp (*Cyprinus carpio*), the hormone plasma cortisol levels showed a drastic significant increase (about 100 ng/ml) as early as 3 hr after the initiation of low pH exposure and remained high for 2 days. Cortisol levels decreased to 8.14 ng/ml after 1 week, but were still significantly higher than those of control (pH 7.0). The immune response also showed some disturbance due to acid rain. The plasma levels of antibodies decreased significantly at 1 week after the initiation of low pH exposure (Kawahara *et al*., 2001). The metals, which are otherwise bound in soil and sediments are released into aquatic system and cause the indirect effect of acid rain on wildlife. These toxic metals may be ingested by wildlife and hence affected adversely.

Effects of acid rain on human health:

Acid rain is the invisible form of pollution, but has some indirect effects on human health. Indirect effects involve damage to humans by contact with materials that have themselves been affected by acidification like food and water supplies.

SO_2 causes more adverse impact to human health in gas and aerosol forms. Concentrations above 1.6 ppm breathing becomes detectable more difficult and eye irritation increases SO_2 is much more toxic and damaging when combined with aerosols, and mists, and suspended smoke (Lynn, 1976), because these mixture of chemicals form finer suspensions that penetrate the lungs further than the gas alone. In Tokyo the polluted drizzle droplets were resulted into eye and skin irritations (Okita, 1983).

Indirect effect of acid rain on human health involves toxic heavy metals because these are liberated from soil when soil gets acidified. The most common heavy metals are Al, Cd, Zn, Pb, Hg, Mn and Fe (Tolba, 1983). These mobilized contaminants are dissolved in soil and water make their way to groundwater that is drunk by humans and contaminate the food (Fish, meat, and vegetables) eaten by humans (Thornton and Plant, 1980). These heavy metals get accumulated in the body and resulted into various health problems like dry coughs, asthma, headache, eye, nose and throat irritations.

Control of acid rain:

This can be achieved by following ways:

Liming: The damage to lakes and other water bodies can be eliminated by adding lime. Many chemicals such as caustic soda, sodium carbonate, slacked lime and limestone are most popular for raising pH of acidified water (Khemani *et al*., 1985). Liming eliminates some of the symptoms of acidification; it is expensive and not real cure. Although liming can restore many species and improve water quality in lakes and streams, it must be repeated periodically (every 3-6 years) to remain effective.

Emission control: The most important solution for acid rain problem is reduction of SO_2 and NOx emissions. The use of fuel that is low in S is not really practical because the world supply of low S fuels is limited. Various techniques are available to reduce S emission from non-ferrous smelters. Oxides of nitrogen can also be reduced through reduction or better control of combustion temperature.

Policy Intervention: In 1970s and 1980s the effects of acid rain on natural resources and ecosystems became an issue of considerable public concern in both northwestern Europe and northeastern United States. Several northeastern States and the Province of Ontario, Canada, sued the US Environment Protection Agency in 1980 to take action to control acid precursor emissions emanating from states in the mid west. In response to pressure from governments in the affected areas, the scientific community, environmental organizations, the media, and the general public, U.S congress formed the national acid precipitation assessment programme (NAPAP) and mandated NAPAP to conduct a 10-year scientific, technological and economic study of the acid rain issue under the acid precipitation act of 1980. The purpose of the study was to inform public policy by providing information on:

1 Specific regions and resources affected by acidic deposition.
2 How and where acid precursor emissions are transformed and distributed?
3 Whether the effects are extensive and require mitigation?
4 What emission control technologies and mitigation options are available to reduce acidic depositions?

After contentious debate in the United States during the 1980s, legislation to control adverse effects of acidic deposition through reductions in annual emissions of SO_2 and NOx was included in the 1990 clean air amendments, known as the Acid deposition control programme. The acid rain programme was based on two phases, market based system to reduce SO_2 emissions from electricity generating facilities by 10 million tons below of their 1980 levels. The over all goal of acid rain programme was to achieve significant environmental and public health benefits through reductions in emissions of SO_2 and NOx the primary causes of acid rain. To achieve this goal at the lowest cost to society, the programme employed both traditional and innovative market based approaches for controlling air pollution. In addition the programme encouraged energy efficiency and pollution prevention.

By reducing SO_2 and NOx, many acidified lakes and streams significantly improved to once again support the fish life. There have been considerable improvements in acidified water bodies in Europe as a result of reduced acid precursor emissions in recent years (Stoddard *et al*., 1999; Evans *et al*., 2001). Stoddard *et al*. (1999) reported reduced acidification in water bodies in only one of five areas in north America (New England), despite a considerable reduction in S emission during the 1990s. However, a more recent study showed improvements in water bodies in several areas in the United State, including Adirondack lake (Stoddard *et al*., 2003)

The regional acidification information and simulation (RAINS) model was developed to understand acid rain in Asia and to help develop strategies to mitigate or avert the problem. It is a computerized scientific tool to help policymakers to assess and project future trends in emission, transport and their potential environmental impacts. The RAINS-ASIA model can be used for a variety of purposes: energy and environmental planning; identifying critical ecosystem and their sulphur carrying capacities; following emission from an area or point sources to estimate deposition; identifying the sources contributing to deposition in an ecosystem; exploring different mitigation strategies and estimating associated cost; selecting predefined energy pathway; modifying pathway to explore effects of alternative energy development strategies. It can be used to reduce emissions taking into account generation, atmospheric processes, environmental crip acts, and control costs for SO_2, NOx and ammonia (Alcamo *et al*., 1990).

With the rapid economic development and energy consumption throughout the world, fossil fuel consumption has increased significantly during the last few decades. Use of fossil fuel is the major cause of large-scale generation of acid precursors in the atmosphere. Earlier it has been identified as the problem of developed countries, but with increased industrialization and urbanization developing countries are also facing this problem. Acid rain is the result of many steps of chemical reactions between air borne pollutants (sulphur and nitrogen compounds) and atmospheric water and oxygen.

Acid rain has deleterious effect on ecosystem, which includes decline in growth of trees as well as other plants including crops, reduction in aquatic flora and fauna. Marble, limestone and sand stone can be easily destroyed by acid rain. Metals, paints, textiles and ceramics can be corroded due to acid rain. Acid rain can also affect indirectly the human health. Soil fertility is negatively affected due to acid rain as a result of leaching of essential nutrient cations and increase of availability of toxic heavy metals. Acid rain problem has been tackled to some extent in the developed world by reducing the emission of the gases causing acid rain. Such efforts need to be done in developing world so as to avoid the magnitude of potential of problem as faced by industrialized world.

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