

ACID RAIN AND ITS IMPLICATIONS



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1992-93

## PREFACE

The problem of acid rain that was previously considered to be the problem of developed countries is considerably growing in the developing countries also. The air pollution is increasing due to growing industrialization, increase in number of vehicles on roads and manmade activities, which in turn is leading to increase in acid rain events. In India also, cases of acid rain have been observed. The reasons for concern about acid rain are that it can acidify the lakes and streams on soils low in lime and may have considerable impact on terrestrial ecosystems including vegetation, animals and soils, aquatic ecosystems, monuments etc.

In the present report an attempt has been made to review the studies carried out on sources of acid gases, chemistry and transport of acid deposition, consequences of acid rain and the spread of acid rain over India and the possible implications. The report has been prepared by Dr Divya, Sc. 'B', Atmospheric and Surface Modelling Division and has been typed by Sri Rajneesh Kumar Goyal.

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## ABSTRACT

Acid rain, generally described as a European and North American problem caused largely by anthropogenic emissions of the oxides of sulphur and nitrogen during burning of fossil fuels, is spreading to the developing countries of the world. Although developing countries consume only one fifth of the world's commercial energy, the share is growing. The primary reason for concern about acid deposition is that it acidifies streams and lakes on coarse sandy soils low in lime. The environmental concern of acid deposition includes the effects on terrestrial ecosystems, aquatic ecosystems, monuments and construction material etc.

In the present report, a review has been made on sources of acid gases, chemistry and transport of acid deposition, effects of acid rain on terrestrial and aquatic ecosystems . Procedures for regional acidification studies have also been presented . The spread of acid rain over India and the possible implications is focused upon. Studies carried out in India point out that the problem of acid rain in India is still localized and the alkaline soil dust prevents the spread of acid rain in india.

## 1.0 INTRODUCTION

The problem of acid rain and its consequences have gained considerable attention during recent years. Though, extensive work has been carried out on the so called European and North American problem, studies have also been made to analyze the growing problem of acid rain in tropical countries including India.

The phenomenon of acid deposition may have occurred in some cities as far back as the seventeenth century. Acid precipitation was first described ( in cities) by Smith in 1852 (Smith, 1852) in and around the city of Manchester in Northern England, which followed the extended studies by Smith to cover the United Kingdom (Smith, 1872). Crowther and Ruston (1911) and Cohen and Ruston (1912) carried out experiments on the effects of acid rain on plants. Acid rain in rural areas was probably first demonstrated by Bottini (1939) near the Volcano Vesuvius . Between 1939 and 1954 there were scattered pH measurements of rain in a variety of areas, (Gorham, 1981) but the data were not subjected to detailed analysis.

A new era in studies of acid deposition began in 1955, when it was discovered to be wide spread in rural areas far from urban, anthropogenic sources. In that year Barrett and Brodin (1955) discovered acid rain in Scandinavia, Houghton (1955) in New England and Gorham (1955) in English lake district. Recognition that the ecological damage done by acid deposition could be a major international problem came in 1968 with the work of Oden in



Sweden ( Oden, 1968). Similar problems were recognized in the United States by Likens et al ( Likens et al, 1972).

## 2.0 WHAT IS ACID RAIN

The word 'acidification' literally implies a change toward more acidic conditions e.g. in rain and cloud water, lakes, rivers, ground water or soils. If this change is in the rainwater, the rain is known as acid rain. It is generally measured in terms of pH value,  $\text{pH} < 5.6$  is taken to be acidic. The reference level commonly used to compare acidic precipitation to natural precipitation is  $\text{pH} 5.6$ , the  $\text{pH}$  that results from the equilibrium of atmospheric  $\text{CO}_2$  with precipitation. Such changes may occur as a result of processes taking place slowly by biological and geological processes, more rapidly in connection with short-term climatic fluctuations or volcanic eruptions or by human activity, such as emission of acid-forming gases into the atmosphere.

In a more general sense word 'acidification' includes all perturbations by human activities of the natural biochemical cycles of sulphur ( mainly sulphur dioxide  $\text{SO}_2$  and sulphate ions  $\text{SO}_4^{2-}$  ) and nitrogen ( mainly oxides of nitrogen  $\text{NO}_x$  , ammonia  $\text{NH}_3$  , ammonium and nitrate ions  $\text{NH}_4^+$  and  $\text{NO}_3^-$  ) and other acid and alkaline substances (Table 2.1) as well as the environmental effects of such perturbations.

Table 2.1: Acid and alkaline substances observed in the atmosphere and their effect on terrestrial and aquatic systems (+ acidifying, - neutralizing, 0 no significant effect)

| Substance             | Role of acidification |         |
|-----------------------|-----------------------|---------|
|                       | Terrestrial           | Aquatic |
| $H_2S, SO_2, H_2SO_4$ | +                     | +       |
| $NO_x$                | +,0                   | +,0     |
| HCl, HF               | +                     | +       |
| Organic acids         | +,0                   | +,0     |
| $NH_3$                | +,0,-                 | 0,-     |
| Ammonium salts        | +                     | +       |
| Alkaline dust         | -                     | -       |

Systems are considered to be sensitive to acidification if they have a low buffer capacity with respect to input of acid and acidifying substances. For aquatic systems, this means that waters with low alkalinity are sensitive to acidification. Sensitive soils are those with low to moderate base saturation and low cation exchange capacity (CEC). Soils with a high anion adsorption capacity, as well as surface waters associated with

such soils, can be sensitive to acidification but may not be immediately susceptible due to the retention of anions ( e.g. sulphate) in the soil ( Galloway, 1988; McDowell, 1988). This usually occurs in areas where the bedrock contains only small amounts of limestone and other acid - neutralizing minerals.

### 3.0 SOURCES OF ACID GASES AND THEIR PRECURSORS

Research in the industrial regions of the world has taught us a great deal about the role of air pollutants in acidification processes. The influence of air borne chemicals in the acidification of air and precipitation is most pronounced in regions where gaseous sulphur and nitrogen oxide emissions are large and where the air contain only modest amounts of acid neutralizing substances such as ammonia or alkaline dust containing ammonium , calcium, sodium, magnesium and potassium.

These airborne substances and their reaction products are carried by winds and clouds wherever the wind blows . They are then deposited in the form of gases, fine aerosols and coarse particles or as dissolved or suspended substances in precipitation. Such deposition particles deliver the airborne chemicals to the surfaces of vegetation , soils, surface waters, and engineering and cultural resources at short or long distances from the original emission sources.

Estimates of tropical emissions of sulphur and oxidized nitrogen are given in Tables 3.1 and 3.2.

Table 3.1: Estimated sulphur budget of the atmosphere of terrestrial tropics ( between  $30^{\circ}\text{N}$  and  $30^{\circ}\text{S}$  ), Unit: Tg S per year (1 Tg =  $10^{12}$ g)

---

| Emissions   |          |
|---|----------|
| Forest soils and wetlands ( mainly $\text{H}_2\text{S}$ ) | 5-25     |
| Biomass burning ( mainly $\text{SO}_2$ )                  | 1-10     |
| Volcanoes ( mainly $\text{SO}_2$ )                        | 1-10     |
| Soil dust ( sulphate )                                    | ?        |
| Fossil fuels and industry ( mainly $\text{SO}_2$ )        | 6-15     |
| Total   | 13-60(+) |

| Deposition                                  |      |
|---|------|
| By precipitation ( sulphate )               | 5-20 |
| Dry deposition ( $\text{SO}_2$ , sulphate ) | 2-10 |
| Total                                       | 7-30 |

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Table 3.2: Estimated budget of oxidized nitrogen for the atmosphere of terrestrial tropics ( between  $30^{\circ}\text{N}$  and  $30^{\circ}\text{S}$  ).Unit Tg N per year

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| Emissions             |       |            |
|-----------------------|-------|------------|
| Soils                 |       |            |
| Rainforest            | 2-5   |            |
| Savanna               | 3-8   |            |
| Cultivated land       | 1-6   | Total 6-19 |
| Biomass burning       |       |            |
| Plumes                | 3-6   |            |
| Excess soil emissions | 0.5-3 | Total 3-9  |

|                            |     |         |
|----------------------------|-----|---------|
| Lightning                  |     | 0.5-5   |
| Fossil fuel combustion     |     | 3-7     |
| Total                      |     | 13-40   |
| Deposition                 |     |         |
| By precipitation           |     | 2-10    |
| Dry deposition             |     |         |
| NO <sub>2</sub>            | <2  |         |
| HNO <sub>3</sub>           | <2? |         |
| Other nitrogen compounds ? |     |         |
| Total                      |     | 1-5(+)  |
|                            |     | -----   |
| Total                      |     | 3-15(+) |

On a global scale , anthropogenic and natural emissions of sulphur and nitrogen compounds are similar in magnitude. Since most sources of anthropogenic emissions are not distributed uniformly and the atmospheric residence times of most sulphur and nitrogen compounds are limited to a few days, the relative importance of anthropogenic and natural sources varies widely over the globe . In the industrialized parts of the temperate zones especially in Europe, North America and Japan anthropogenic emissions dominate over natural emissions.

The most significant contributions to the sulphur flux over tropical land areas come from natural emissions from soils and plants ( mainly as H<sub>2</sub>S), emission of SO<sub>2</sub> from burning of biomass and emission of SO<sub>2</sub> from combustion of fossil fuels (Delmas and Servant, 1988). In some regions volcanoes are a major

episodic source. Although industrial sulphur emissions in the tropics are smaller than those in northern temperate latitudes, the human activities in the form of industrial processes as well as biomass burning represent a major proportion of all sulphur emissions in tropical land areas.

In a few highly industrialized regions of the tropics such as parts of south-eastern Brazil (Moreira-Nordemann et al, 1988) sulphur emission density may be comparable to those of industrial regions of North America and Europe.

Figure 3.1 shows anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_2$  from fossil fuel combustion on the major continents of the world. The large emissions in Europe and North America stand out clearly, and very significant emissions also occur on the Asian continent.

The magnitudes of sulphur and nitrogen oxide emissions are only moderately well known, thus a need exists for basic information on the area and amounts of biomass burned per year in each tropical country and for quantitative estimates of natural emissions of sulphur and nitrogen gases in the tropics. These include emissions from soils plants, lightning, continental wetlands, coastal marshes, and volcanoes.

Organic acids, primarily formic ( $\text{HCOOH}$ ) and acetic ( $\text{CH}_3\text{COOH}$ ) have been shown to contribute substantially to the acidity of tropical rain (Keene et al, 1983) but little is known about the mechanisms that introduce or produce them within the atmosphere. In a modelling study, Brewer et al (1984) identified

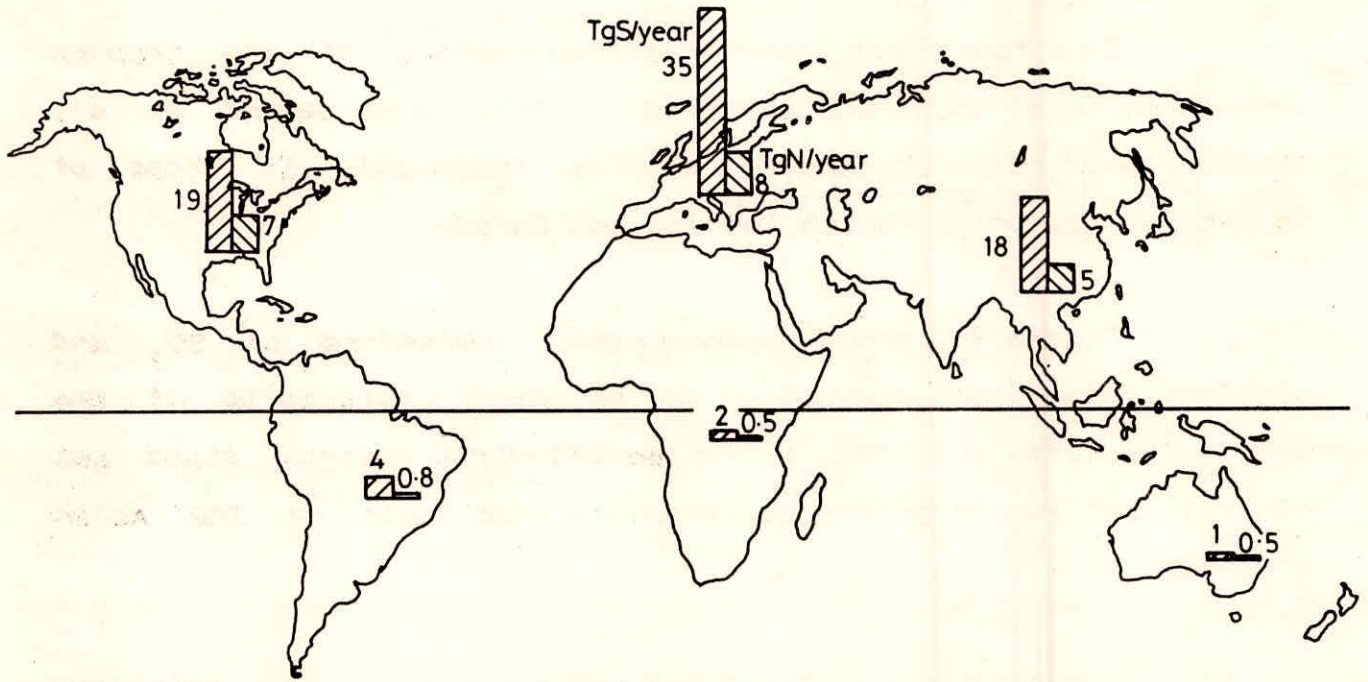


Fig. 3.1 : Anthropogenic emissions of  $\text{SO}_2$  and  $\text{NO}_2$  from fossil fuel combustion on major continents of world around 1979. Units: Tg S and Tg N per year (Rodhe et al, 1988)

some of these organic acids as products of oxidation of non methane hydrocarbons. It is possible, however that these acids also arise as partially oxidized products of biomass burning . Biomass burning and volatile emissions of organic compounds from vegetation are likely to be the main sources of non methane hydrocarbons ( Penkett, 1982; Duce et al, 1983; Greenberg and Zimmerman, 1984).

Sources of alkaline material in the tropical atmosphere include the emission of  $\text{NH}_3$  from volatilization of excreta and fertilizers and from biomass burning. Alkaline dusts arise from soil erosion and from agricultural and mining operations. The magnitude of these emissions is poorly known although some estimates of the  $\text{NH}_3$  source are available (Galbally and Gillett, 1988).

#### 4.0 ACID DEPOSITION

Pollutants emitted from the sources may travel a long distance ( as far as 2000 km) through the atmosphere. During their journey they are diluted and transformed chemically into secondary pollutants, which may have greater environmental impacts than the primary pollutants from which they are formed. Along the way they are also deposited to the receiving surfaces, such as water, soil, vegetation and manmade structures. The deposition is either on a surface directly ( dry deposition) or by being incorporated into precipitation and brought down to earths surface by rain or snow (wet deposition) . Fig.4.1 shows the flow of a pollutant from source to receptor via atmosphere.



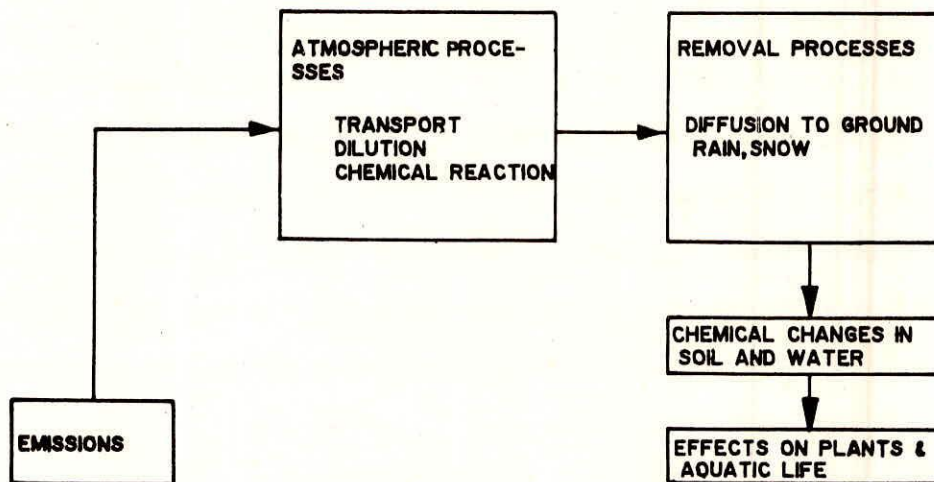


Fig. 4.1 : Flow of acidifying pollutants from source to receptor

#### 4.1 Atmospheric Transformation and Transport Process

Two questions are of special importance regarding the transportation of sulphur and nitrogen compounds in the atmosphere: what are the chemical processes that lead to the oxidation of sulphur, nitrogen gases and hydrocarbon compounds and how do these processes interact, i.e. do they tend to stimulate or negate each other? In a study of emission of  $\text{SO}_2$  in tropical Australia, Galbally et al (1982) suggested that the cycling of  $\text{NH}_3$  through the atmosphere was enhanced due to the formation of ammonium sulphate aerosol after the oxidation of  $\text{SO}_2$  to sulphate in the atmosphere.

Two pathways have been fairly well established for oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  :

1. Gas phase oxidation by photochemically produced radicals, especially OH: the  $\text{SO}_2$  oxidation rate via this pathway varies from about 0.1 to about 1% , depending on latitude and time of year; and
2. Oxidation of  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  with cloud and rain drops, other dominant liquid phase oxidant for  $\text{SO}_2$  expected to be  $\text{H}_2\text{O}_2$  although the role of catalysts for other dissolved oxidants such as  $\text{O}_3$  needs to be investigated further.

Because both OH and  $\text{H}_2\text{O}_2$  are photochemically produced oxidants, the oxidation also depends on latitude and season of the year because they effect the intensity of solar radiation. This is illustrated for OH in Fig.4.2 which shows that the rate of

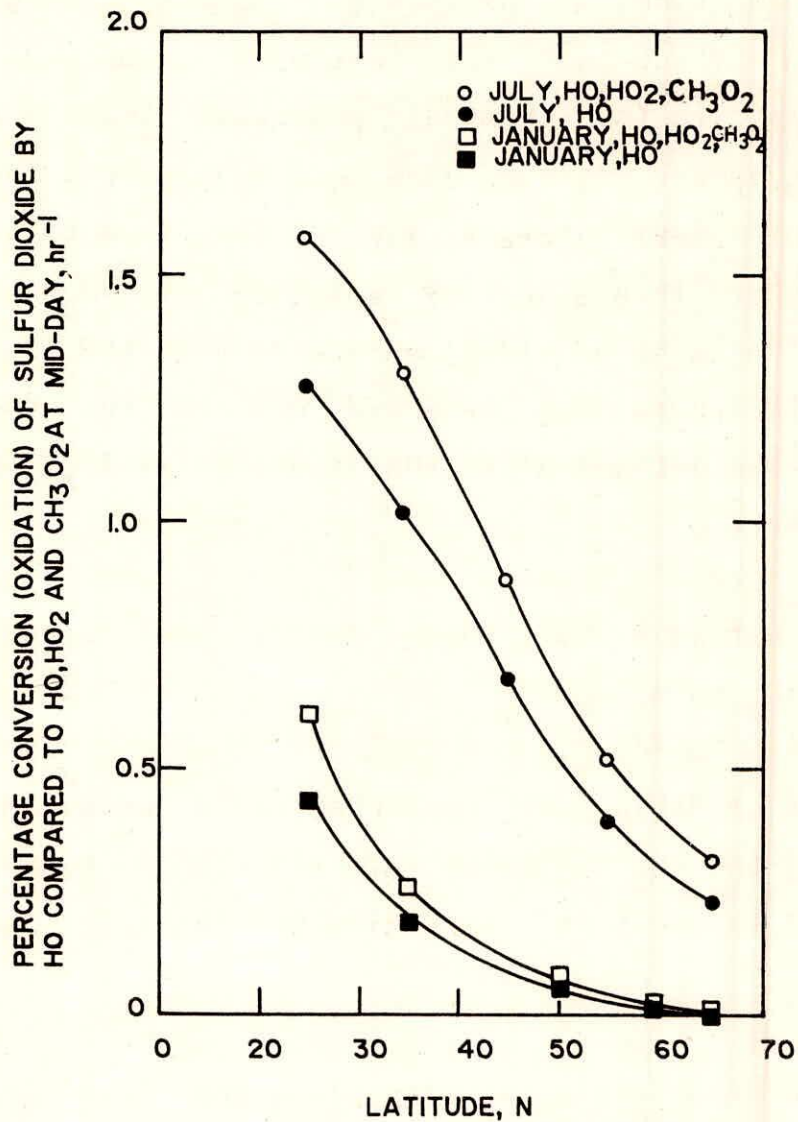


Fig. 4.2 : Percentage conversion per hour of SO<sub>2</sub> to sulphate by HO alone and by HO<sub>2</sub>, and OH<sub>3</sub>O<sub>2</sub> radicals together as a function of latitude in summer and winter at mid-day (Altshuller, 1979)

conversion by OH at 50°N in January is one fifth that at 25°N in January and one twelfth that at 25°N in July. In temperate latitudes the transformations of NO<sub>2</sub>, SO<sub>2</sub> and non methane hydrocarbons have been studied in laboratories and by numerical modeling and field observations. The role of hydroxyl radicals in homogeneous gasphase oxidation is well established, liquid phase reactions in cloud droplets and heterogeneous aerosol reactions involving ozone, hydrogen peroxide, oxygen and metallic catalyst reactions have begun to be investigated ( Davis et. al, 1984).

Wind direction and speed are also important factors for governing the concentration of air pollutants. The importance of direction of atmospheric flow may be seen clearly in Fig. 4.3. The back trajectories are drawn from a monitoring site in Nova Scotia. Air and precipitation samples arriving via trajectories that have passed over sparsely populated land areas or the ocean have lower concentrations of sulphate than those coming from more densely populated areas. All factors being equal, the concentration is inversely proportional to the wind speed at the point of emission.

A body of observational and experimental data about these compounds has accumulated from field studies in temperate regions and is used for testing the processes incorporated into modelling studies.

In the tropics, however, there have been no studies of the rate of oxidation of hydrocarbons or nitrogen oxides, and only one study of the rate of homogeneous oxidation of sulphur dioxide to sulphuric acid in the Mt Isa copper smelter plume in Northern

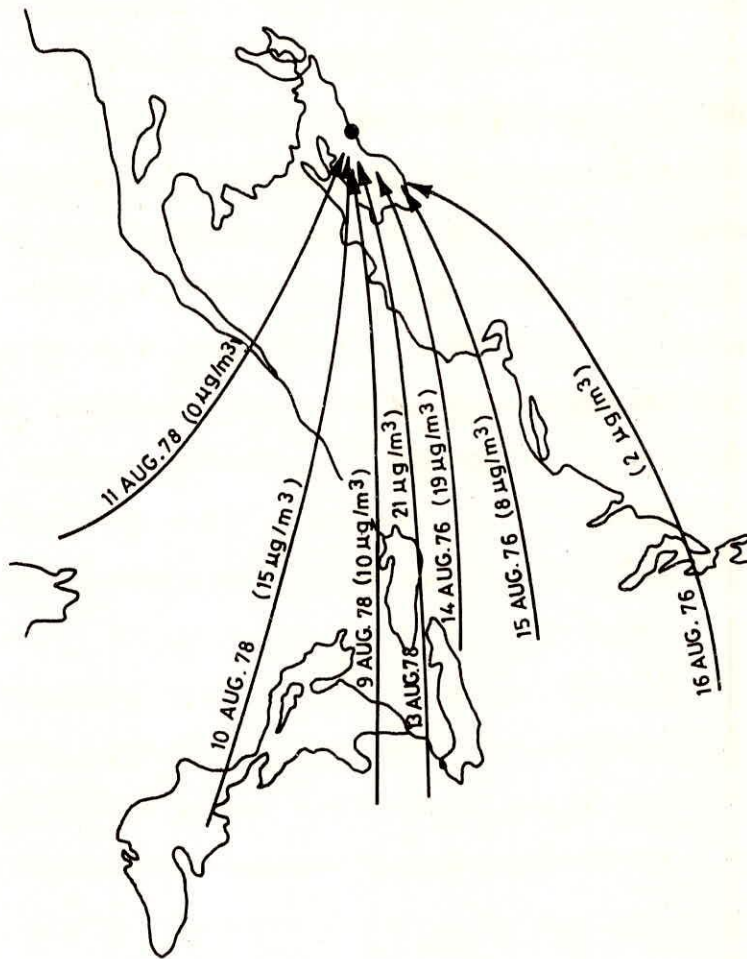


Fig. 4.3 : Importance of direction of atmospheric flow in governing the concentration of air pollutants (Shaw, 1983)

Australia ( Roberts and Williams, 1979). This study showed far slower oxidation rates than expected from modeling studies ( based on understanding from temperate latitude studies) but the reasons for the difference remain unknown.

## 4.2 Wet Deposition

Wet deposition of pollutants is a function of meteorological variables and of the kinetics and equilibria of atmospheric chemical reactions. Precipitation scavenging has been defined as the composite process by which airborne pollutant gases and particles attach to precipitation elements and thus deposit to the Earth's surface ( NRC, 1983) . The scavenging process can be viewed as consisting of four steps ( NRC, 1983):

- (i) mixing of pollutant and condensed atmospheric water ( cloud, rain , snow ) within the same airspace,
- (ii) attachment of pollutant to atmospheric water ,
- (iii) physical and/or chemical reaction within the aqueous phase,
- (iv) delivery to the earth's surface of pollutant laden atmospheric water.

Fog and cloud water appear to be especially effective in scavenging pollutants from the atmosphere, and hence may serve as early indicators of increasing anthropogenic inputs of acidic components. Concentrations of  $H^+$  can be an order of magnitude higher in cloud water than is ordinarily found in rain water

(Jacob et al, 1985) and could be an important source of elemental input in some coastal, montane, and desert environments.

Acidity of wet deposition in much of the tropics appears to be low relative to most of the industrialized temperate zone (Table 4.1). Total  $H^+$  deposition in many tropical areas will be greater than expected on the basis of pH alone because of higher rainfall.

The relative contribution of organic acids to total and free acidity in remote tropical sites may be considerably greater than corresponding values for temperate sites. Keene et al (1983) found that weak organic acids (predominantly formic and acetic acids) contribute 64% and 63% of free and total acidity, respectively, in wet-only precipitation samples collected in Katherine, Australia. Average concentration of organic acids was  $19.8 \mu\text{eq/liter}$ . In Virginia, USA, Keene and Galloway (1984) measured organic acid concentrations (formic and acetic acids) equivalent to 16% of free acidity ( $10.9 \mu\text{eq/liter}$ ). More detailed characterization of both temperate and tropical precipitation is needed to assess whether increased concentrations of organic acids in precipitation are characteristic of tropical areas in general.

Several variables warrant a tropical temperate comparison. The conversion of  $\text{SO}_2$  and  $\text{NO}_2$  to sulphuric and nitric acids, respectively, may be affected by increased air temperatures and solar irradiance in the tropics. Given equal amounts of acidic precursors in the temperate and tropical environment, one would predict more rapid production of acidic compounds in the tropics.

With higher precipitation in the humid tropics than in the temperate zone, total deposition may be higher for a given quantity of pollutant emitted to the atmosphere. Recycling of atmospheric moisture within a given air mass may be considerably greater in much of the forested tropics than in temperate areas, allowing for greater opportunity for precipitation scavenging of a given pollutant molecule. In the Amazon basin for example, it is thought that rain water falls, evaporates and falls again several times before leaving the basin ( Salati and Vose, 1984).

Seasonal changes in the deposition or delivery of acids to temperate ecosystems are important in determining the overall effects of acid deposition . Because acids tend to accumulate in the snowpack of northern latitudes, spring snowmelt can result in pulsed, episodic delivery of acids to terrestrial and aquatic ecosystem even though actual rates of deposition to the earth's surface are relatively uniform. The pulsed input of acid associated with snowpack melting is important in determining the effects of acidic deposition on aquatic ecosystems in the temperate zone . Seasonal changes in precipitation chemistry and deposition rate do occur in the tropics ( Lewis, 1981; Kellman et al, 1982).

#### 4.3 Dry Deposition

Dry deposition refers to a wide range of processes by which pollutant gases and aerosol particles reach the earth's surface. Both small scale meteorological conditions at the time of deposition and the nature of the collecting surface affect dry deposition rates. Accurate estimation of dry deposition rates is



difficult due to problems in modeling small scale turbulent diffusion and the biological factors ( e.g. stomatal openings) that influence deposition rates . No uniformly accepted method for assessing dry deposition has been developed , although progress has been significant in recent years (Hicks, 1986; Knapp et al, 1986; Lindberg et al, 1986). Despite difficulties in quantifying dry deposition, measurements to date indicate that it can be a significant fraction of total deposition of N and S, and is generally assumed to be roughly equivalent to wet deposition in the northeastern US (NRC, 1983). Data for remote continental areas with little anthropogenic influence, however, indicate that dry deposition of N and S species is as little as 10%-25% of wet deposition ( Galloway et al, 1985). Dry deposition fluxes for aerosol particles,  $SO_2$  and  $HNO_3$  can be roughly estimated (Galloway et al, 1985) and are presented in Fig. 4.4 and 4.5.

Differences in rates of dry deposition in tropical relative to temperate systems might be expected due to differences in ambient humidity and forest canopy structure. Ambient relative humidity, total leaf surface area, surface roughness and density of strata openings would all need to be evaluated for tropical and temperate sites. Most tropical plants have stomata on the underside only, as opposed to temperate plants, which have stomata on upper and lower leaf surfaces. This could have important implications for rates of dry deposition.

Humidity appears to play an important role in regulating rates of dry deposition. Horntvedt et al (1980) found that dry deposition rates of  $SO_2$  increased by as much as ten fold when leaf surfaces were wet. They also observed that dry deposition rates

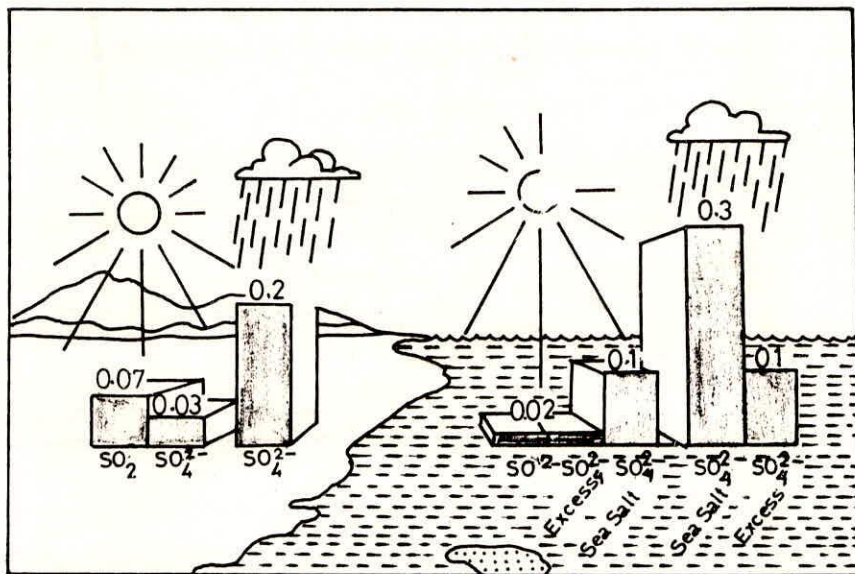


Fig. 4.4 Wet and dry deposition rates of sulphur species in remote regions (Rodhe et al, 1988)

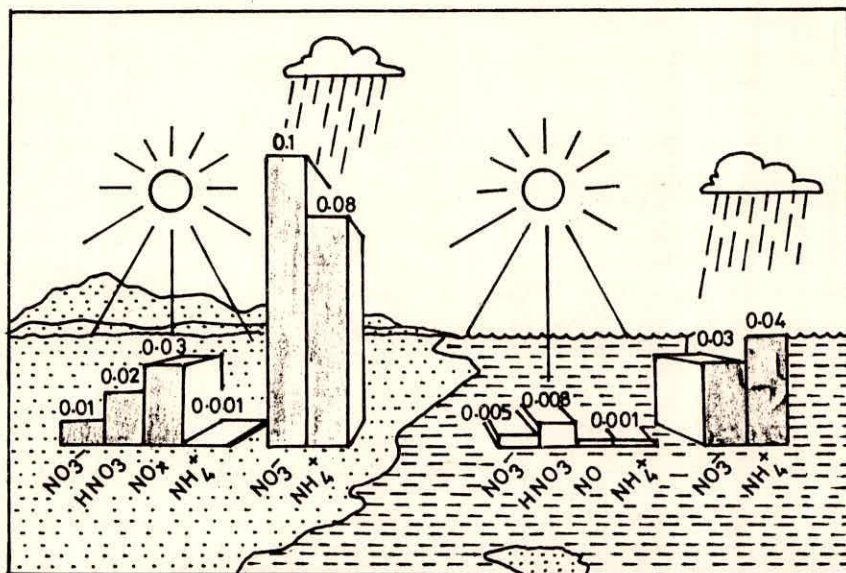


Fig. 4.5 : Wet and dry deposition rates of nitrogen species in remote regions (Rodhe et al, 1988)

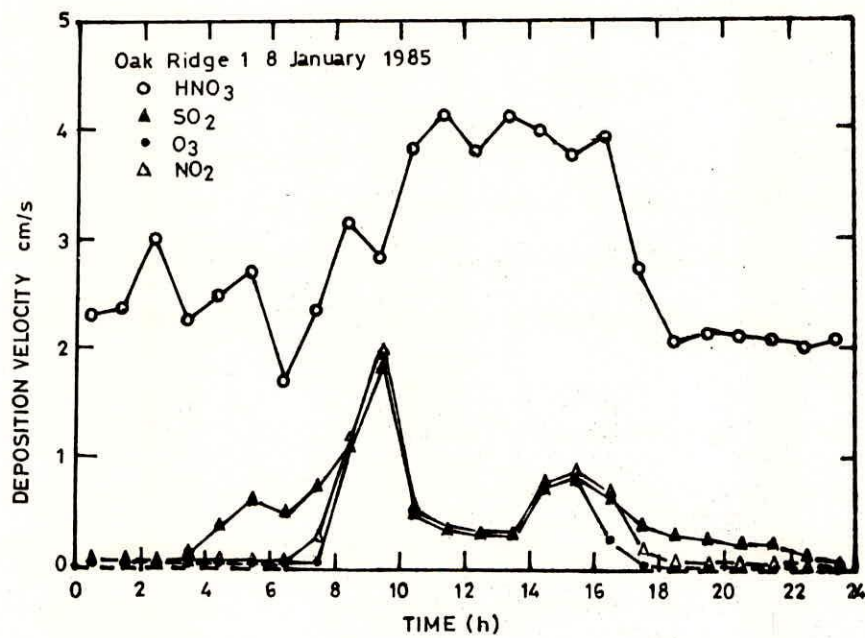


Fig. 4.6 : Average estimated diurnal cycles of deposition velocities for HNO<sub>3</sub>, SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub>, deduced from seven days data obtained for a deciduous forest at Oak ridge, Tennessee, USA (Hicks, 1986).

decreased in the absence of light, presumably due to closure of stomata. Hicks (1986) obtained similar results, finding an increase in dry deposition of N and S during daylight with highest deposition values generally found in early morning when leaf surfaces were wettest (Figure 4.6). These results from temperate sites suggest that light and humidity regimes might be critical in determining rates of dry deposition in tropical environments. Dry deposition of N and S for a given ambient concentration would appear to be larger in the humid tropics than in the temperate zone due to higher humidity.

## 5.0 ENVIRONMENTAL CONCERNS

Assessing the environmental concerns requires the study of its effects on terrestrial ecosystems, lake acidification, aquatic ecosystems, monuments and construction materials.

### 5.1 Terrestrial Ecosystems

Following the movement of water through a terrestrial ecosystem provides an effective means of assessing the direct effects of acidic deposition. Much incoming acidity will enter in the aqueous phase, or be transported by the movement of water within the ecosystem.

An important consideration in assessing the impact of acidic deposition is to distinguish between the intensity of precipitation acidity (pH) and the total quantity of  $H^+$  entering an ecosystem (deposition). Vegetation is more likely to respond to the frequency of highly acidic events, while soils are most

likely to be affected by long term rates of acidic deposition.

The mobility of the anion accompanying  $H^+$  deposition is a determinant of acidic deposition effects ( Johnson et al, 1982). If incoming  $H^+$  is associated with an anion that is immobilized within the ecosystem, then the associated  $H^+$  must also be retained to maintain electroneutrality. Mobility within an ecosystem is determined by biological processes , such as assimilation or oxidative respiration, and by chemical processes, such as adsorption and anion exchange, which can occur as water moves the acid through the ecosystem.

Simple organic acids of low molecular weight, especially formic and acetic acids, are important components of total acidic deposition, especially in the tropics ( Keene et al, 1983) but they are not likely to be mobile within terrestrial ecosystems due to rapid decomposition. Organic acids found in wet deposition are rapidly oxidized in samples of rainwater alone ( Keene et al, 1983; Keene and Galloway, 1984), and would likely be rapidly oxidized within a terrestrial ecosystem. Nitrate is somewhat more mobile than organic acids, although in many ecosystems nitrate assimilation by vegetation can exert a measurable impact on nitrogen flux through the system (e.g. Likens et al , 1977). Nitrate generally does not participate in soil adsorption reactions, and hence its mobility is controlled predominantly by biological processes. The mobility of sulphate in terrestrial ecosystems is determined in large part by soil adsorption processes. Because sulphate is generally the most mobile of the three acidic anions common in precipitation, it most often controls the effects of acidic deposition on soils as well as

aquatic ecosystems (Galloway, 1988).

### 5.1.1 Vegetation

Effects of acidic deposition on vegetation can be direct (effects of acid impinging directly on vegetative surfaces) or indirect (through effects of acid deposition on soils or biota). Cuticular (rather than stomatal) absorption appears to be the main avenue by which aqueous solutes enter leaf tissue (Evans, 1984). Foliar wettability, presence or absence of cuticular micro pores, and cuticular composition are all likely to determine the susceptibility of vegetation to damage by acidic deposition (Evans, 1984).

Throughfall pH generally increases under deciduous canopies relative to incident precipitation (Parker, 1983) (Figure 5.1) apparently due to exchange of base cations for  $H^+$  and removal of nitrate by foliar absorption. Deposition and washing of aerosol particles from leaf surfaces also occurs in the field, however, and this complicates analysis of the actual impact of wet deposition on nutrient leaching from vegetation.

The direct effects of wet and dry deposition of acidic substances on terrestrial vegetation in the temperate zone appear to be significant. Decline of forest productivity, direct mortality, and increased susceptibility to ancillary causes of mortality (e.g. fungus, insect infestation) have all been postulated as effects of acidic deposition. In the Black Forest of West Germany and the Green Mountains of Vermont, USA, striking diebacks of coniferous trees have occurred, and direct or indirect

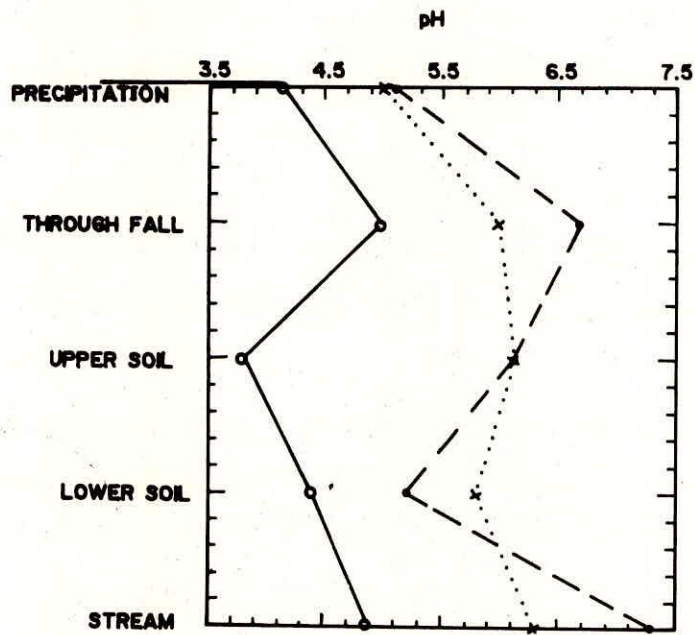


Fig. 5.1 : pH of precipitation, throughfall, soil solution and stream water at one temperate (Hubbard Brook; ) and at two tropical sites (La Selva, and El Verde, ) [Parker, 1983]



effects of acidic deposition are though to be possible causes (FRG, 1984; Johnson and Siccama, 1983).

Precipitation in the northeastern USA does not appear to be sufficiently acidic to cause much direct foliar injury to crops and trees. In a review of greenhouse and chamber studies of the effects of acid precipitation on crops and trees, Jacobson (1984) found that significant damage occurred only at a pH of 3.5 or less for most species studied. When this is compared with the frequency of rainfall events with a given pH (Fig.5.2), one can see that foliar damage as a result of exposure to ambient precipitation would be predicted only infrequently.

Moskowitz et al.(1985) carried out studies for US crops and found that precipitation acidity does not appear to be affecting growth and yield of US crops on a national level. Increases as well as decreases in growth and yield of various crops have been observed (Irving, 1983), but the majority show no effect. No particular crops appear to be especially sensitive to acid depositon, or to synergistic effects with other variables.

In some regions acidic deposition provides potentially significant amounts of nutrients of vegetation. In the southeastern USA, Lindberg et.al. (1986) estimate that deposition to the forest canopy supplied 40% and 100% of the N and S, respectively, needed for woody growth. Dry deposition was a major source of both N and S with direct foliar absorption an important uptake vector.

Differences in phenology, growth form, and nutrient

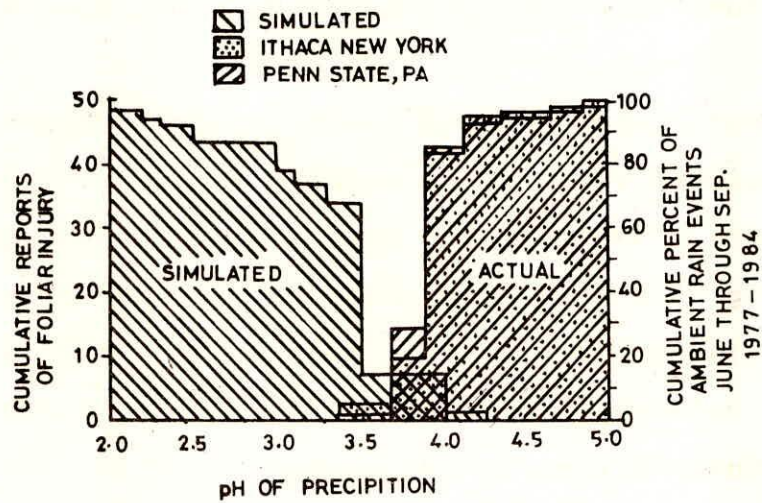


Fig. 5.2 : Comparison of acidity of ambient rain at two sites in the north-eastern USA with acidity causing foliar injury to experimental vegetation grown in greenhouses or chambers (McDowell, 1988)

status are likely to determine differences in the direct response of tropical and temperate vegetation to acid deposition. A factor that might make tropical forests inherently more susceptible to acidic deposition than their temperate counterparts is the greater average leaf life of tropical vegetation. Leaves of many tropical trees may last up to two years or more, in contrast to a year or less for many temperate trees. Thus, the effects of any environmental insult might be expected to be greater in the tropics where cumulative effects would be more pronounced.

Neutralization of acidity in incident precipitation by contact with vegetative surfaces appears to occur in tropical as well as temperate climates (Fig. 5.1). Results similar to those presented in Fig. 5.1 have been obtained in other tropical forests (Meguro et al, 1979). A striking example of neutralization of precipitation acidity by tropical vegetation occurs in the vicinity of Masaya volcano in Nicaragua. With the advent of active emission of acidic gases in the early 1950s, cloud forest was replaced by pioneer species such as *Malanthora* and *Lanana* (Johnson and Parnell, 1986).

Deposition could be a significant nutrient source for many forests in tropical areas. Low nutrient status in many tropical soils (Sanchez, 1976), combined with the potentially high rates of dry deposition in the tropics for a given atmospheric concentration, suggest that dry deposition may be an important vector for nitrogen and sulphur inputs in currently unacidified regions. Anthropogenic increases in ambient levels of acidity and deposition might further enhance the impact of dry deposition on nutrient cycles.

Recognizing deleterious effects of acidic deposition on tropical vegetation may be hampered by the high biological diversity characteristic of much of the tropics. High biological diversity, especially in the humid tropics, makes reliance on shifts in species abundance as an indication of significant biological change due to acidification very risky. Because of inherent uncertainties in measuring species distributions, the diversity of tropical biomes makes biological changes more difficult to detect than in counterpart temperate ecosystems.

### 5.1.2 Animals

Direct effects of acidic deposition are generally seen only in those animals which have an aquatic life phase. The effects of acid deposition on aquatic animals are described in section 5.2. In neotropical rain forests, amphibians such as frogs and salamanders are an integral part of the biota, with many species and high abundances. They must keep their skin surface moist at all times and would seem vulnerable to acidification of precipitation and cloud water. Many live in bromeliads, which collect rainwater directly. These animals would be exposed immediately to any changes in the pH of incident precipitation.

A second group of animals possibly at increased risk due to acidification would be the mosquitoes and flies with life stages in bromeliads or other water derived directly from precipitation in humid tropical forests. They play an important role in the food web and in the pollination of vegetation. Because tropical forest vegetation relies more heavily on animals

as agents of collimation than does temperate forest vegetation , a decline in animal populations could thus have an indirect effect on vegetation as well. Postulation of indirect effects of deposition on animals must await demonstration of direct effects on vegetation.

### 5.1.3 Soils

Changes in solution acidity occur as water passes through the forest canopy and into the soil profile of temperate forests. In many soils, organic acidity generated by soil processes (e.g. Figure 5.1) results in a net acidification as throughfall passes through the forest floor, followed by neutralization in underlying mineral horizons. This is particularly true in Spodosols, which are common in the areas of the USA and Europe most affected by acidic deposition.

It is generally agreed that moderately acid soils without large acid neutralizing capacity, such as some Alfisols, are most sensitive to acidification induced by atmospheric inputs (NAS, 1981). The factors that appear most important in regulating the degree of acidification are sulphate retention ability and the ability to supply base cations to soil solution (NRC, 1984). Soils with low sulphate retention capacity and low base saturation are most likely to acidify. Soils with high base saturation such as calcareous soils are able to replenish the pool of cations available for exchange fast enough to prevent acidification of soil solution. The intensity and the duration of acidic inputs will work together to determine the extent to which a soil will acidify and the time course of such acidification. Soils such as

Spondosols that generate protons are unlikely to show major changes in pH in the short term, as they are often more acidic than incoming precipitation due to organic activity (Johnson et al, 1982; McDowell and Wood, 1984). In the long term, however, their rate of acidification would also be controlled by sulphate adsorption and base saturation.

The flow path and velocity with which incoming precipitation moves through a watershed are also important in determining the susceptibility of a soil to acidification and the pH soil solution (NRC, 1984).

The mobility of sulphate or other anions within a soil can influence the impact of acid deposition on soil chemistry (Johnson et al, 1982) and stream water chemistry (Galloway, 1988). Sensitive soils in which sulphate is mobile will tend to be more susceptible to acidification, with consequent effect on soil chemistry and vegetation.

Major influences on the susceptibility of tropical soils to acidification are similar to those for temperate soils. Tropical soils most likely to become acidified with increased acidic deposition would be mildly weathered soils with low sulphate adsorption capacity and low base saturation. Many tropical soils are acidic, highly weathered, and have high concentrations of Fe and Al (Sanchez, 1976), and hence would not be expected to show large changes in acidity with increased acidic deposition (Johnson et al, 1982). Figure 5.3 illustrates the location of soils sensitive to acidification (Rodhe et al, 1988). However, due to high sulphate adsorption capacities, sensitive

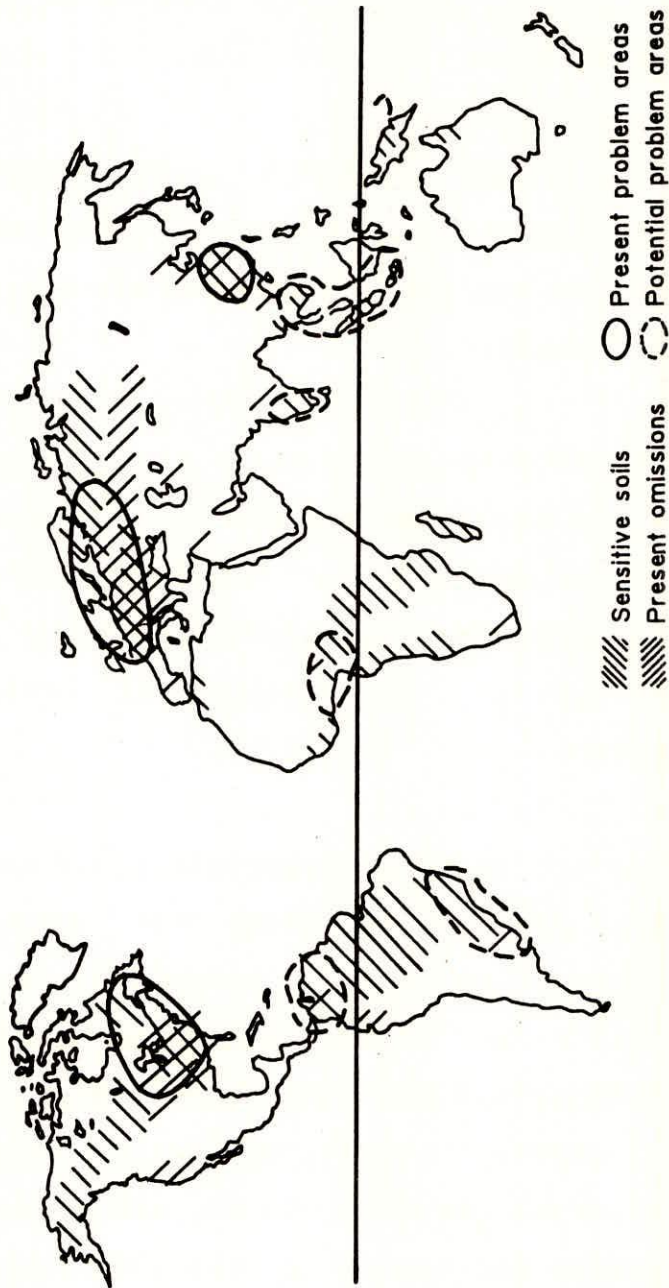


Fig. 5.3 : Regions currently having acidification problems and where based on soil sensitivity expected future emissions and population density, acidification might become severe in future (Rodhe et al, 1988)

soils may not be immediately susceptible to acidification (Galloway, 1988). Figure 5.4 shows such areas with potentially high sulphate adsorption capacities.

A significant difference between temperate and tropical soils relative to acidification potential is the amount of organic matter in each. Sulphate adsorption is inversely related to organic matter content, apparently due to preferential adsorption of organic matter at the expense of sulphate. At a given concentration of sesquioxides (predominantly Fe and Al), one would predict higher sulphate adsorption and thus less susceptibility to acidification, in the soil with lower organic matter content. Since accumulations of organic matter on the forest floor and in upper soil horizons are often lower in tropical forests than in the temperate zone, tropical soils might be less susceptible to acidification than their temperate counterparts.

## 5.2 Lake Acidification and Aquatic Ecosystems

Acid deposition acidifies streams and lakes on coarse, sandy soils low in lime. The effect is seen particularly in headwater areas and in wet montane environments, wherever sulphate loading from anthropogenic sources is strong. Nitric acid, the other major component of acid deposition, is likely to be less effective because it is consumed biologically and sequestered in biomass to a greater degree. In northern England, several lakes on soils poor in lime were very acidic by the 1950s (Gorham, 1957; Mackereth, 1957). In southern Scandinavia thousands of lakes and streams have been acidified over the past decades (Likens et al, 1979). Hundreds of lakes and streams in the Adirondacks, Maine,



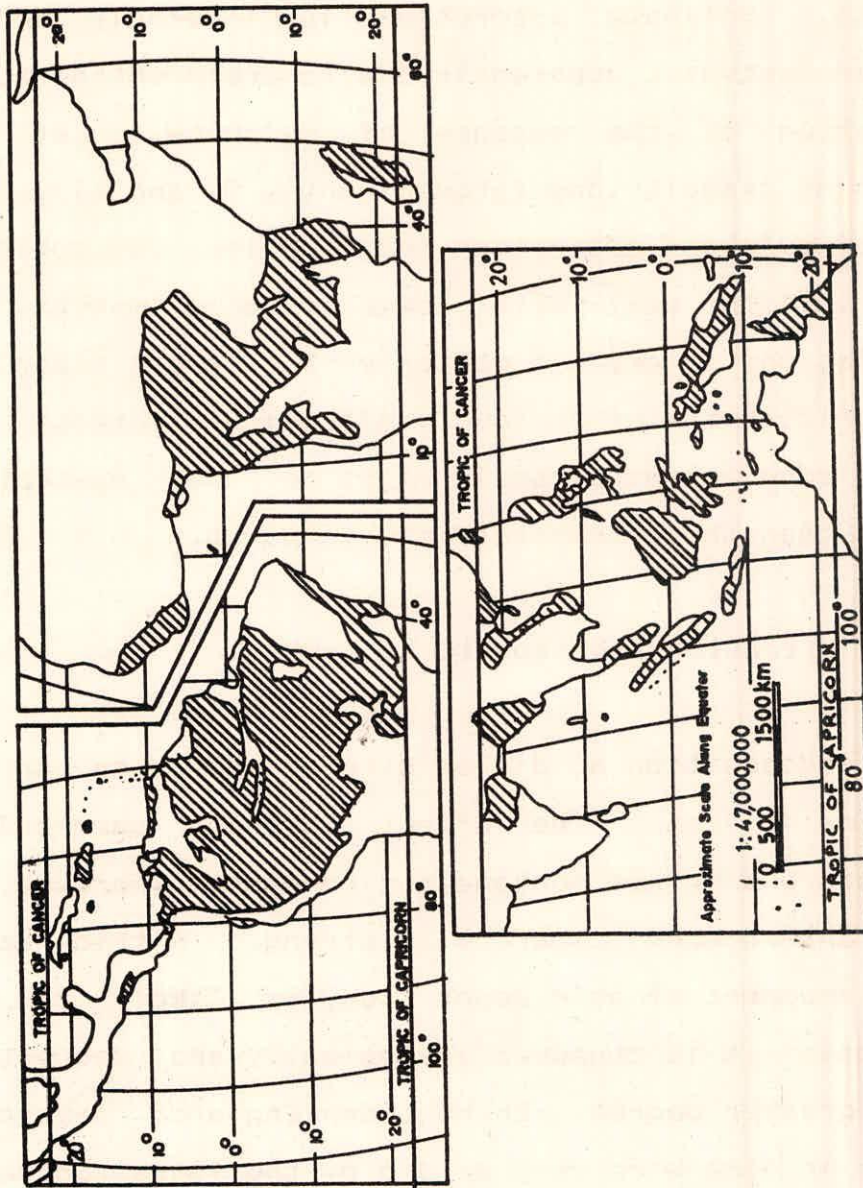


Fig. 5.4 : Generalized map of tropical soils with potential sulphate adsorption capacity (McDowell, 1988)

Ontario and Nova Scotia have likewise shown acid stress in recent years, and thousands more are threatened, particularly in Canada. Acidification may be exceptionally severe as the accumulated snowpack melts in spring (Galloway et al, 1980), and this may be the first sign of the phenomenon in lakes and streams that otherwise appear normal. (In such a case, nitric acid flowing over frozen ground can be an important contributor (McLean, 1981; Galloway et al, 1980)).

All of these acidified clearwater lakes are either near or downwind from major anthropogenic sources of sulphur and nitrogen oxides. Clearwater lakes on similar substrata upwind of or far from such sources have not become acidified in the same way, for example, in northern Norway and Sweden, Finland, eastern Newfoundland, northeastern Minnesota and the Experimental Lakes Areas of north-western Ontario. These areas are, however, at risk if acid rain continues, especially if it worsens and spreads.

It should be emphasized that neighboring lakes in the sensitive regions exposed to acid deposition may become acidified at quite different rates. For example, three lakes close together in the Adirondacks have exhibited very different responses that depend on different characteristics of their watersheds (Galloway et.al., 1980). Biological processes within the lakes themselves, such as photosynthesis, ion uptake and reduction reactions, can also influence the degree of lake acidification.

The chemical and physical consequences of lake acidification include increased leaching of calcium from terrestrial soils (Gordon and Gorham, 1963), mobilization of heavy

metals such as aluminum, zinc and manganese (Dickson, 1980), and an increase in the transparency of lakewaters (Schindler, 1980).

The biological consequences include marked changes in communities of aquatic plants and animals, with a progressive lessening of their diversity (Drablos and Tollan, 1980). Pough (1976) found that spotted salamanders in the northeastern USA were vulnerable to low pH during their development in vernal ponds. At pH less than 6.0 cumulative embryonic mortality shifted from less than 1% to greater than 50%. In addition to increased mortality, increases in developmental abnormalities were also observed as a function of pH (Pough and Wilson, 1976). In a few extreme cases, a lessening of primary productivity is observed, but in many cases there is merely a change toward lesser pelagic and greater benthic production. Whether or not primary plant production decreases, there is a progressive elimination of sensitive species of plants and animals, including fish which are completely exterminated under severe acidification. The European roach and the American small mouth bass and walleye are extremely sensitive. Perch are relatively resistant. Aluminum leached by acid rain from sensitive soils is strongly implicated in the effects on fish, chiefly through damage to gill epithelium (Muniz and Leivestad, 1980). Other effects include inhibition of spawning and hatching, embryonic malformation, upset of salt balance in the blood, and growth retardation (Drablos and Tollan, 1980). Where there is a sudden stress after snowmelt, fish kills can result. It should be pointed out again here that natural acid lakes are also known. Some are volcanic (Yochimura, 1933, 1935), others owe their acidity to oxidation of pyrites (Ohle, 1935), but most are the result of drainage from adjacent, strongly acid peat bogs. Such

bog lakes are tea colored owing to organic matter dissolved from the peaty drainage basin, and can be further acidified by acid rain, as shown by experience at Wawa (Gordon and Gorham, 1963). Their ecology and biogeochemistry deserve further study.

Acidification of aquatic ecosystems is both a natural and an anthropogenic phenomenon. In tropical areas with high rainfall, natural acidification of soils and surface waters is common, but aquatic ecosystems are especially sensitive to further acidification by increased atmospheric deposition of sulphate and nitrate ions.

According to Galloway (1988), generally three conditions must be met before aquatic ecosystems will be acidified by atmospheric deposition:

1. Atmospheric deposition of sulphate or nitrate or some other anion must increase.
2. The soils adjacent to the aquatic ecosystem must not retain the anion that is increased in deposition.
3. The aquatic ecosystem must have low alkalinity for acidification to result in biological damage. Aquatic ecosystems of this type are typically associated with acid soils.

Aquatic ecosystems will acidify only if the additional sulphate or nitrate ions are not retained by soils. Therefore, information must be available on the anion retention capacity of the soils in question (Reuss and Johnson, 1986).

Certain highly weathered tropical soils have large anion adsorption capacities (Galloway, 1988). Very little information is available on the spatial variability of the anion adsorption capacity of tropical soils. Most generally soil maps lack the necessary detail of the magnitude of anion adsorption capacity.

The third condition is that the aquatic ecosystem must have a alkalinity low enough so that increased acidity will result in pH reductions sufficient to cause biological damage. Information on the average alkalinities over large regions indicates that vast areas of some tropical regions (e.g. South America) have aquatic ecosystem with low alkalinities. The information on biological populations of potentially sensitive areas is sparse. In many areas the taxonomy of the populations is not known, nor is their sensitivity to pH reductions.

Husar and Husar (1985) published a global survey of sulphur runoff to river water. Whereas large parts of North America and Europe exhibit a specific runoff of more than 2 g S/m/year, clearly influenced by human activities, most tropical regions have values below 1 g S/m/year. The runoff of sulphur in tropical regions is likely to increase in the future as a result of increased circulation of pollution derived from sulphur and from mining activities.

### 5.3 Monuments and Construction Materials

Deterioration of engineering material and monuments is a serious problem in several countries, both economically and from a cultural point of view. Such deterioration is particularly rapid in coastal areas, exposed to seasalt aerosols, and in polluted cities and industrial areas where dry deposition of sulphur dioxide is a major factor. The corrosive effect of  $\text{NO}_x$  alone seems to be low. Combinations of sulphur and nitrogen oxides greatly intensify corrosion rates of copper and calcareous stone materials.

The influence of acid rain on corrosion is complex. On one hand it brings dissolved acids in contact with surfaces, and on the other hand it may wash away corrosive agents that were dry deposited in rain free periods.

Whereas most corrosion damage caused by air pollutants occurs in cities and close to pollution sources, corrosion of metals used in contact with soil and surface water can occur several hundred kilometers away from major emission sources (Kucera, 1988).

Only limited data exists on corrosion rates of different materials in tropical environments. Severe corrosion problems affecting, for example, sandstone and carbon steel, have been reported from southern China (Zhao and Xiong, 1988) and Brazil (Moreira Nordemann et.al., 1988). In general, corrosion rates of metals exposed above ground or water sites are comparable with those in temperate climatic zones.

## 6.0 PROCEDURE FOR REGIONAL ACIDIFICATION STUDIES FOR TROPICS

The previous discussion clearly shows a fundamental lack of knowledge about the occurrence of acidic and acidifying compounds and many basic processes relevant to assessing present and potential acidification and air pollution problems in tropical regions. Some emerging problems specially, e.g. regionally acidified precipitation in southwest China, increased ozone concentration over the Brazilian savanna, and a rapidly deteriorating situation with regard to air pollutants in and around many large cities, make it important to fill these knowledge gaps.

A major research program on the biogeochemical cycling of sulphur nitrogen, other nutrient elements, ozone, and other photochemical oxidants in tropical environments would yield a better understanding of the present situation with regard both to undisturbed ecosystems and to human induced perturbation of them. It would also help to identify potential problem areas and thus provide a scientific basis for actions to remedy or avoid such problems in the future.

In addition, monitoring programs provide an early warning system for detecting changes in the environment before they become serious. Specific steps in such a research and monitoring program may include the following.

1. The current and projected anthropogenic emissions of acidifying and alkaline substances (e.g.  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ ) must be

evaluated for the region under consideration. If information for a particular region is incomplete, comparable data derived elsewhere can give a preliminary estimate.

2. Local effects such as plant damage, health effects, and corrosion can be evaluated from atmospheric concentration distributions calculated with simple dispersion formulae, emission estimates, and some local meteorology. Plant damage effects should be studied as described later. This procedure should be sufficient to determine whether or not local undesirable effects are likely to occur.

3. It is more difficult to estimate the concentrations and rates of deposition of acidifying substances further afield. As a rough estimate one could assume that on a yearly basis all material emitted is deposited by wet and dry processes within 2,000 km. Then the deposition can be calculated for sectors from any given source. Meteorological observations of wind direction must be used to obtain the fraction of time during the year when large scale winds blow from the source to within a given sector. This calculated deposition can then be compared with expected natural deposition rates and its acidifying effect on terrestrial and aquatic ecosystems evaluated. The results obtained should be weighted according to the annual precipitation over the sector. If one part of the region, e.g. a mountain range, receives larger than average rainfall, then the deposition should be scaled up according to the ratio of the rainfall rate over the special area to the rainfall rate over the whole sector.

4. If an area is identified as a region of potential



concern then the next activity should be to set up a program at a few locations for measuring the acidity of rainfall events. The equipment, though simple and inexpensive, should conform to currently accepted standards; proper siting, use of plastic collectors that are rinsed in distilled water before each rainfall collection, and rainwater pH measurements taken with a calibrated pH meter within several hours of the rainwater collection. One site should be located upwind or away from the polluted area as a benchmark station for comparison with the polluted stations.

5. If significant acidity is encountered, or expected to occur in the future, terrestrial and aquatic ecosystems could be affected. More comprehensive studies are then required to properly assess the environmental impact of the acidification (steps 6-9).

6. Use of topographic, soil and geologic bedrock maps to identify areas within countries with well drained acid soils.

7. Determine alkalinity of perennial streams in these areas to assess the degree of sensitivity of the aquatic ecosystem.

8. Analyze representative soil samples associated with sensitive streams and vegetation to determine their pH, cation exchange capacity (CEC), percentage base saturation, aluminium concentration, and anion adsorption capacity.

9. In areas with sensitive streams and vegetation begin a baseline measurement program of the chemical composition of precipitation and streams.

## 7.0 ACID RAIN OVER INDIA

Though acid rain has usually been described as a European and North American problem, it is spreading to the developing countries of the world. The share of developing countries in the world's commercial energy which is about one fifth, is growing. The steadily rising trends in air pollution levels have been observed in Metropolitan cities like Calcutta, Delhi and Bombay ( Khemani et al, 1987). Acid rain has also been reported since 1974 at Chembur, a major industrial area in Bombay city ( Mahadevan et al, 1984).

Many studies on the chemical composition of rain water in India have been reported from urban areas which are greatly influenced by the local industrial sources ( Mukherjee, 1957,1964; Khemani et al, 1968, 1982; Khemani, 1985; Handa, 1969, 1973; Sequeria, 1976; Subramaniam and Saxena, 1980; Das et al, 1981 ). Naik et al (1988) have measured the pH of rain water in rural areas of India. Available data suggest that rain water in urban and rural areas is mostly alkaline. Since 80% of annual rainfall occurs in the summer monsoon season, the rain water samples for studying the chemical composition are collected in this season.

Subramaniam and Saxena (1980) analyzed the rainwater samples collected from various localities in Delhi throughout the monsoon of 1978. They found the pH values for Delhi rain water to be alkaline.

Varma (1989) examined the background trends of rainwater

pH at ten Indian Background Air Pollution Monitoring ( BAPMoN) stations during the period 1974-84 ( Table 7.1). The rain water samples were collected in specially designed polyethylene bottles and the pH value of individual showers was determined immediately at the cessation of precipitation at each station. The rain water for entire month was then collected in a big bottle and finally the mean pH value was determined after proper mixing following the instructions given by WMO.

Table 7.1 :Trends of rainwater pH at ten Indian BAPMoN stations  
(Varma,1989)

| Stations       | No of observations | pH        |            |                        |
|----------------|--------------------|-----------|------------|------------------------|
|                |                    | Variation | Trend      | Acid rain observations |
| Allahabad      | 56                 | 6.35-9.00 | Decreasing | 00                     |
| Jodhpur        | 58                 | 6.35-8.70 | Decreasing | 00                     |
| Kodaikanal     | 62                 | 5.18-8.70 | Decreasing | 03                     |
| Minicoy        | 66                 | 5.52-8.90 | Deceasing  | 01                     |
| Mohanbari      | 42                 | 5.50-8.30 | No trend   | 02                     |
| Nagpur         | 48                 | 5.55-7.35 | Increasing | 01                     |
| Port Blair     | 48                 | 5.30-8.50 | Decreasing | 05                     |
| Pune           | 76                 | 5.65-8.90 | Decreasing | 00                     |
| Srinagar       | 88                 | 6.15-8.40 | Decreasing | 00                     |
| Vishakhapatnam | 77                 | 5.92-8.20 | Decreasing | 00                     |

Fig. 7.1 shows the histogram of all the 621 monthly mean pH observations, the highest frequency of pH observed in the range 6.5 -7.0 and 86% of the observations found in pH range between 6.0 and 8.0. Varma (1989) found some pH values recorded at the stations in the acidic range ( $\text{pH} \leq 5.6$ ). The overall probability of occurrence of acid rain in India was assessed as about 2% . Fig. 7.2 shows the range of pH values at the different stations; the lowest value recorded at Kodaikanal (5.18) and the highest at Allahabad (9.0). The pH values in precipitation at most of the Indian background stations are decreasing.

The geographical distribution of mean rainfall weighted pH values for the period 1974-84 is shown in Fig. 7.3. Some values have been determined by other workers ( Das et al, 1981; Handa 1969, 1973; Subramaniam and Saxena, 1980; Kelkar, 1983). Figure shows that northwest India is exhibiting higher pH values than rest of the country. The main reason behind these high pH values is the incursion of sand/dust particulates into these areas from the adjacent Thar desert of Rajasthan. Varma (1989) further found that in a clean dust free environment the pH values of precipitation did not differ much and were observed to be of the order of 6.7-6.8.

Since precipitation is a function of its contents of both acids and bases and any attempt to understand the processes causing acid precipitation must deal with the potential acid neutralizing capacity of alkaline materials such as  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  which are released mostly from soil. It has been suggested that alkaline dust may react with and neutralize strong

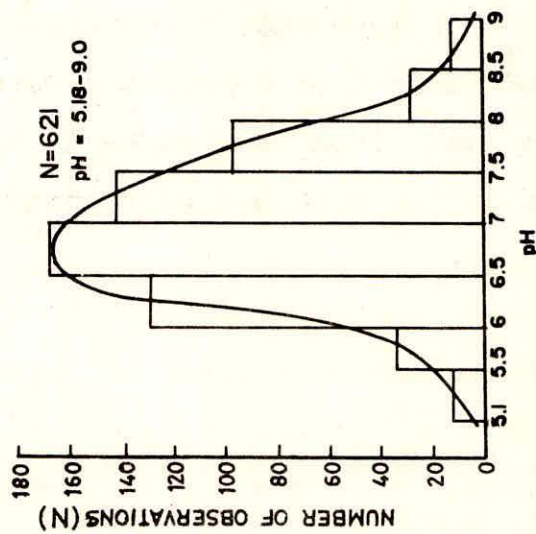


Fig. 7.1 : Frequency distribution of pH at Indian BAPMon stations (Varma, 1989)

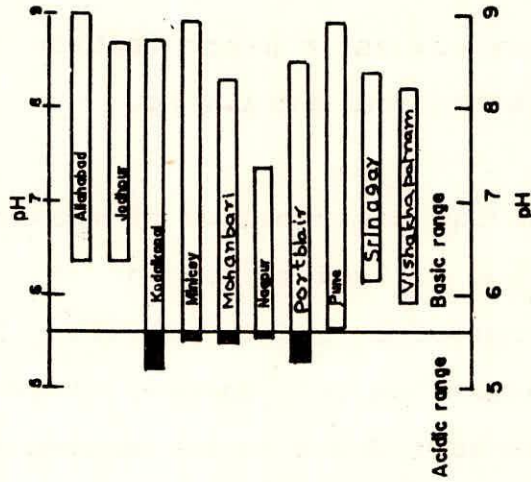


Fig. 7.2 : Range of pH values at Indian BAPMon stations (Varma, 1989)

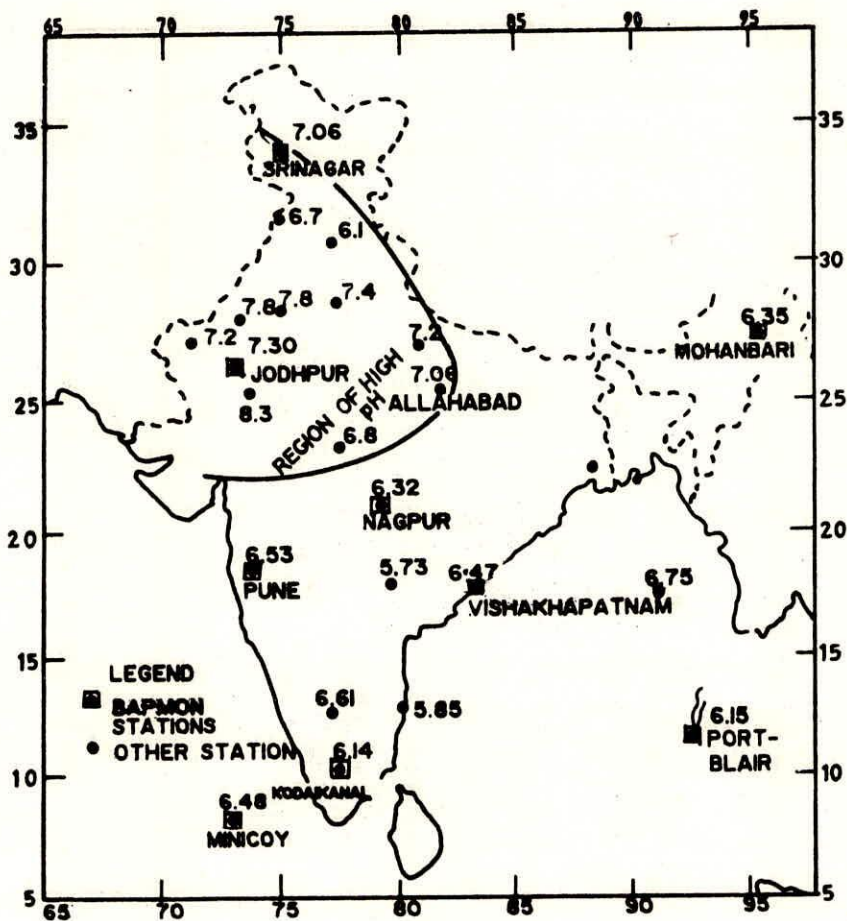


Fig. 7.3 : Geographical distribution of mean rainfall weighted pH values for 1974-84 (Varma, 1989)

Table 7.2: Average concentrations in  $\text{mg l}^{-1}$  of major ionic components and pH values in rainwater samples at different stations in India (Khemani et al, 1989)

| Station            | $\text{Cl}^-$ | $\text{SO}_4^{2-}$ | $\text{NO}_3^-$ | $\text{NH}_4^+$ | $\text{Na}^+$ | $\text{K}^+$ | $\text{Ca}^{2+}$ | $\text{Mg}^{2+}$ | pH  | $\text{H}^+$<br>( $\mu\text{eq l}^{-1}$ ) |
|--------------------|---------------|--------------------|-----------------|-----------------|---------------|--------------|------------------|------------------|-----|---|
| <i>Coastal</i>     |               |                    |                 |                 |               |              |                  |                  |     |   |
| Alibag             | 5.97          | 1.11               | 0.57            | 0.27            | 3.84          | 0.88         | 2.38             | 0.60             | 7.2 | 0.063                                     |
| Colaba             | 4.14          | 2.58               | 0.40            | 0.51            | 3.12          | 1.13         | 2.56             | 0.64             | 7.1 | 0.079                                     |
| <i>Industrial</i>  |               |                    |                 |                 |               |              |                  |                  |     |   |
| Kalyan             | 3.95          | 5.20               | 1.92            | 0.38            | 2.36          | 1.02         | 1.86             | 0.47             | 5.7 | 2.00                                      |
| Chembur            | 5.0           | 20.20              |                 | 2.10            | 2.20          | 1.10         | 3.10             | 0.68             | 4.8 | 15.85                                     |
| <i>Power plant</i> |               |                    |                 |                 |               |              |                  |                  |     |   |
| Indraprastha       | 2.06          | 2.10               | 3.3             | 0.93            | 0.98          | 0.25         | 2.03             | 0.31             | 5.0 | 10.00                                     |
| <i>Urban</i>       |               |                    |                 |                 |               |              |                  |                  |     |   |
| Pune               | 2.57          | 1.78               | 0.48            | 0.10            | 1.84          | 0.20         | 2.07             | 0.45             | 6.3 | 0.50                                      |
| Delhi              | 2.54          | 2.73               | 2.54            | 0.53            | 1.75          | 1.28         | 2.95             | 0.62             | 6.1 | 0.79                                      |
| <i>Non - urban</i> |               |                    |                 |                 |               |              |                  |                  |     |   |
| Sirur              | 2.64          | 1.53               | 2.64            | 0.07            | 1.84          | 0.95         | 3.53             | 0.80             | 6.7 | 0.20                                      |
| Ranjangaon         | 2.02          | 1.53               | 1.37            | 0.08            | 1.81          | 1.41         | 3.30             | 0.96             | 6.8 | 0.16                                      |

acids in the atmosphere ( Khemani, 1985).

Khemani et al (1989) studied the role of alkaline materials in preventing the extension of acid rain over India. They analysed the rain water collected during the summer monsoon season for  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$  and determined the pH values. Table 7.2 shows the average concentrations in  $\text{mg l}^{-1}$  of major ionic components and pH values in rain water sample at different stations in India. As seen from the table, except in the vicinity of industrial and power plant areas, the rain water samples at all stations are in the alkaline range.

Khemani et al (1989), using information derived by other investigations, found that the pH values were high (  $\text{pH} > 7.0$ ) at Srinagar, Allahabad, Jodhpur, Amritsar, Bikaner, Jaisalmer, Lucknow and Ahmedabad; the values were comparatively low but still in the alkaline range (  $\text{pH} = 6.0-7.0$ ) in industrial towns and cities like Nagpur, Vishakhapatnam, Delhi, Agra, Bhopal, Calcutta and Chandigarh; still lower values of pH seen at Trivandrum ( $\text{pH}=5.7$ ). The pH was acidic (  $\text{pH}=4.5$ ) at Chembur, a highly industrialized location in Bombay city ( Table 7.3).



Table 7.3: pH values in rainwater reported at different stations in India

| pH      | Stations  |
|---------|---|
| >7.0    | Srinagar, Allahabad, Jodhpur, Amritsar, Bikaner, Jaisalmer, Lucknow and Ahmedabad |
| 6.0-7.0 | Nagpur, Vishakhapatnam, Delhi, Agra, Bhopal, Calcutta and Chandigarh              |
| 5.7     | Trivandrum  |
| 4.5     | Chembur, Bombay   |

Khemani et al (1989) compared the pH values of rain water with the data on pH of soil in India published by ICAR (1982). The pH values of soil between 15°N and 35°N are reported to be quite high and the values are substantially lower in the longitude belt of 85° E to 95° E. High soil pH values (pH = 6.5-10.5) are reported in Jammu and Kashmir, Punjab, Haryana, UP, Rajasthan, MP, Gujarat, Maharashtra, Karnataka, Andhra Pradesh and some parts of Tamilnadu. The pH values of soil are reported to be quite low (pH =4.8-5.3) in coastal Kerala and also at Kodaikanal in Tamilnadu. The values in Bihar and West Bengal lie between 4.8 and 6.0 and east of these states it is still lower (pH =4.0-5.4). The dust load in the atmosphere over NW parts of India is higher and a significant amount of dust is incorporated into rainfall either as condensation nuclei or by collision with falling rain drops. However, the extent to which airborne dust influences the precipitation chemistry of certain geographic regions varies with its composition and abundance. They inferred that the acid rain, wherever it occurred in India, is a purely local phenomenon.

Khemani et al (1987) collected the cloud and rain water samples on board aircraft by specially designed equipment during three monsoon seasons 1983, 1984 and 1985 in Pune region in India. Based on the study of ionic composition of cloud and rain water samples along with the pH values they found that pH is influenced by alkaline properties of soil oriented components (Ca, K, and Mg) present in high concentrations in cloud and rain water. They found that the effects of acidic components ( $\text{SO}_4$  and  $\text{NO}_3$ ) were negligible and were completely neutralized by the alkaline components. They suggested that the long range transport of pollutants ( $\text{SO}_4$  and  $\text{NO}_3$ ) does not seem to be effective in a tropical country like India during SW monsoon season when the meteorological factors are favorable for quick dispersal of pollutants with weak sources. Khemani et al (1987) pointed out that presence of alkaline particulates in cloud and rain water have been responsible for controlling acid rain in India, whereas deficiency of soil oriented components (Ca and Mg and high concentrations of acidic components ( $\text{SO}_4$  and  $\text{NO}_3$ ) are the main causes of acid rain in NE United States, Europe and Scandinavian countries.

Khemani et al (1989) studied the long term effects of pollutants on pH of rain water in north India for the first time taking the data of Agra and Delhi (Table 7.4) They found that the pH values had decreased by 2.8 (9.1-6.3) and 0.9 (7.0-6.1) units, respectively after the period of two decades during which the cities developed industrially to a great extent. They concluded that these effects were comparatively slow compared with those observed in western countries, as the anthropogenic pollutants have still not overpowered the natural pollutants released from

soil and sea.

Table 7.4: Average concentrations ( $\mu\text{eq l}^{-1}$ ) at Agra and Delhi in monsoon season in different years

|         |                               | Agra |        | Delhi |      |
|---------|-------------------------------|------|--------|-------|------|
|         |                               | 1984 | 1963   | 1984  | 1965 |
| Cations | Na <sup>+</sup>               | 101  | 94     | 76    | 80   |
|         | K <sup>+</sup>                | 41   | 51     | 33    | 11   |
|         | Ca <sup>2+</sup>              | 237  | 468    | 148   | 242  |
|         | NH <sub>4</sub> <sup>+</sup>  | 18   | 11     | 29    | 13   |
|         | Sum                           | 397  | 624    | 286   | 346  |
| Anions  | Cl <sup>-</sup>               | 76   | 63     | 71    | 71   |
|         | SO <sub>4</sub> <sup>2-</sup> | 52   | 38     | 57    | 26   |
|         | NO <sub>3</sub> <sup>-</sup>  | 40   | 11     | -     | -    |
|         | Sum                           | 168  | 112    | 128   | 97   |
|         | pH                            | 6.3  | 9.1    | 6.1   | 7.0  |
|         | H <sup>+</sup>                | 0.50 | 0.0008 | 0.79  | 0.10 |
|         | OH <sup>-</sup>               | 0.02 | 12.6   | 0.12  | 0.10 |

## 8.0 REMARKS

Although there are gaps in our understanding of acid deposition and its effects, the evidences of the acid rain clearly indicate that it is a very serious and widespread environmental problem caused largely by anthropogenic emissions of the oxides of sulphur and nitrogen during burning of fossil fuels. The major

concern for acid rain is that it acidifies streams and lakes on coarse, sandy soils low in lime. This results in increased leaching of calcium from terrestrial soils, mobilization of heavy metals such as aluminum, zinc and manganese, increase in the transparency of lake waters and marked changes in communities of aquatic plants and animals with a progressive lessening of their diversity. Some other impacts of acid rain include deterioration of engineering material and monuments due to corrosion by acid rain, effects on vegetation either direct (impinging directly on vegetative surfaces) or indirect (through effects of acid deposition on soils or biota).

The problem of acid rain, which was mainly observed in Europe and Northern America, is spreading in the tropical countries including India. In India, the studies carried out on chemical analysis of rainwater at different stations in India has shown that pH of rainwater at the most of these station is basic. However, the long term trend in pH has been found to be decreasing. Studies suggest that the alkaline soil dust in most part of India, specially in northwest region is responsible at present for preventing the spread of acid rain in India.

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