CHAPTER I

Introduction

Industrialisation has provided humanity with many material and social benefits. At the same time it has brought in its wake many material and social problems. One of these problems are Environmental Pollution which is defined as "the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity or interference with the legitimate use of the environment". Thus most of the ecologists recognise environmental pollution as a serious threat to the quality of our life and possibly to its very existence. Air, Water, Soil, Waste, Chemical, Noise and Thermal Pollution are the major types of the environmental pollution.

Air Pollution is defined as "the presence in the atmosphere of solid particles, liquid droplets, or gaseous compounds which are not normally present or which are present in a concentration substantially greater than normal" (Crawford, 1980). The sources of air pollutants are both anthropogenic and natural. Chemical compositions of these pollutants range from inorganic to organic. On the basis of their chemical composition they are grouped broadly as follows:

a. Sulfur containing compounds
b. Nitrogen containing compounds
c. Halogen containing compounds
d. Carbon containing compounds
e. Toxic compounds and
f. Radioactive compounds

(Seinfeld, 1986)
These contaminants may either be harmful or harmless depending on their residence time, concentration and duration of exposure and the susceptibility of the receptors. The residence time and concentration of these air contaminants at any time depends on their physical and chemical transformations and on the meteorological parameters. Of all the meteorological parameters wind profoundly influences the source-receptor relationship. Air pollutants are transported by wind, diffused by turbulence and scavenged either by wet deposition (rain-out and wash-out) or by dry (gravitational) deposition.


Apart from direct effects on human health, material damage, ecological damage and meteorological changes, a group of new problems have also emerged due to air pollution over the past two decades. They are acidic deposition (Acid Rain), Global warming due to increased carbon dioxide, Indoor pollution, Lead deposition, Long range transport of pollutants, Radioactivity, Non-ionizing radiation, Stratospheric ozone hole, Environmental toxicity and Visibility reduction (Stern, 1986).

Amongst these problems acid deposition is a major concern for the scientific community as it has been continuing to defile major areas of our planet. The present thesis is aimed at this important problem.
1.1 Deposition:

Deposition is the last stage in the pathway of the acidifying pollutants from their source to receptor. It contributes the atmospheric pollutants through both dry and wet mechanisms to both natural and managed eco-systems. Dry deposition is aerodynamic transfer of atmospheric gases and particles to the earth's surface by mechanisms not associated with the fall of hydrometeors. This is caused by diffusion to and adsorption on the surface. This process is important for large particles (particles above 2 μm) which are removed by gravitational settling and for very small particles (Aitken's nuclei) and gases which are removed by diffusion processes (particles below 0.2 μm). The effectiveness of this type of process depends on both the meteorological parameters and the surface factors.

Wet deposition is an important, and highly variable and intermittent process in the pathway from surface to receptor. It involves rain-out (in-cloud scavenging) and wash-out (scavenging below the cloud) mechanisms. Particles are scavenged by precipitation due to impaction, electrical effects, Brownian motion, and by serving as cloud condensation nuclei. The amount of deposition by wet process depends on:

i. microphysical characteristics (size and numbers of cloud droplets as well as other characteristics, e.g. evaporation),

ii. rain drop size distribution and

iii. rate of precipitation (dilution effect).

Further, taking into account the large flux of water in the atmosphere (about $577 \times 10^{12} \text{m}^3$ per year) and a mean
residence time of 11 days, the atmospheric water plays an important role in the atmosphere cleaning. In fact it has been estimated that precipitation scavenging accounts for 75 to 80 percent of the total atmospheric pollutants from the atmosphere to the earth (Radke et al., 1980; Beattie and Whelpdale, 1989).

Wet deposition is greatly influenced by pattern of atmospheric circulation and may occur up to hundreds of kilometers from the emission sources whereas dry deposition is more of a short range phenomenon. The long distance transport of acidic gases along air sheds makes the problem of acid precipitation both a regional and international problem.

Increase in acidity of the precipitation over Norway is primarily caused by the emission and large-range transport of SO\textsubscript{2} and NO\textsubscript{x} released in the highly industrialized and densely populated regions of Europe. Similarly, acid precipitation recorded in remote areas in Canada, U.S.A. and Europe, amply demonstrate the long distance transport of acidic gaseous pollutants (Dochinger et al., 1976).

Because of the difficulty of knowing exactly how much dry deposition a region is receiving, measurements of effects of acid deposition have been correlated with wet components only. The removal of acidic components through wet deposition is called ACID RAIN. Recently this term (Acid Rain) has become very common to the language of Environmental Scientists, but the phenomenon of acidic precipitation and deposition in fact, dates back to the industrial revolution of the late 18th century.
1.2 Historical Background of Acid Rain:

The phenomenon of rain acidification by pollutant emission was first recognised by Hales as early as 1857 in England but the term "Acid Rain" was first used by a chemist, Robert Angus Smith in his remarkable work, entitled "Air and Rain: The Beginning of A Chemical Climatology" (1872). He formally identified it as a problem in Manchester, England in 1852 and enunciated many of the ideas that we now consider as a part of acid precipitation problem (Swedish Ministry of Agriculture, 1982). After that, from time to time several authors (MacIntyre and Young, 1923; Erichsen and Jones, 1939; Katz et al., 1939; Junge and Werby, 1958; Jordan et al., 1959) contributed to the understanding of this phenomenon and its biological consequences. Swedish researchers observed in 1920 that numerous small mountain lakes located at high elevations in Scandinavia are becoming more acidic and in some cases devoid of fishes. However not enough evidence was compiled to correlate acid rain to the acidification of surface water until the 1960's and early 1970's. But for last 40 years scientists have been aware of the fact that the rain and snow falling on many areas of the world are acidic. In Europe, the acidification of precipitation was found to increase gradually in various countries. In 1952, at the initiative of Sweden, an extensive European network was installed for measuring the rain acidity. In 1966, the highest acidic precipitation was measured in Netherlands (average annual pH = 3.78). A study by Oden (1968), which showed the increasing trend of acidity in parts of Europe directed a large number of researchers towards the study of "Acid Rain" - its nature and extent
over large areas of Europe and East-North America. In 1972, it was first raised as an international issue by Sweden at the United Nations conference on Human Environment at Stockholm. Presently the acid precipitation problem has grown to such an extent that it is now considered to be one of the most significant International Environmental issues. The current rate of scientific publications keyword by acid rain or acidic deposition has exceeded 600 per year (Stern, 1986). Acid rain has been correlated with environmental damage in many parts of the world including Japan, Norway, Sweden, Canada, Northern Europe and United States. A study prepared at the university of Wyoming for U.S. Environmental Protection Agency in 1980 estimated the cost of damage to natural and manmade resources from acid rain, in the Eastern one third of the United States, at $5 billion per year.

1.3 Effects of Acid Rain:

Acid precipitation is a problem of many dimensions. Certain amounts of acidity in rain may be buffered by the ecosystems without any serious dislocation. But excess of acidity in rainwater can change ecosystems considerably. It includes the following adverse effects:

- acidification of natural water resources and fresh water system,
- leaching of the soil,
- damage to construction materials and cultural resources (corrosion, old monuments deterioration),
- atmospheric visibility, and
- human health.
Lakes and rivers were the first and fast victims of acid rain to become evident. The type of acidity in a lake has profound effects both on lake water chemistry and on the biota (Havas et al., 1984). As the pH of lake decreases, the concentration of several potentially toxic metals such as Aluminum (Al), Iron (Fe), Manganese (Mn), Copper (Cu), Nickel (Ni), Zinc (Zn), Lead (Pb), Cadmium (Cd), and Mercury (Hg) increases (Dickson, 1980; Schofield, 1982; Haras and Hutchison, 1983). Abundant data exists to show significant correlation between increasing acidity and decreasing fish population (Schofield, 1982). Previously it was thought that acid alone was killing the fish, but it appears that Aluminum dissolved from the soil by acid precipitation is primarily responsible.

The adverse effects of increasing acidity on aquatic ecosystem can be understood well by focusing on a report by Environment Canada (1983). Scientists artificially and gradually after the interval of one year period increased the acidity of a lake by adding H₂SO₄ and made a detailed study on chemical and biological changes in it. The important observations of their research have been summerised below:

\[ \text{pH} = 6.1 \]

- increase in bacterial activity,
- increase in invertebrate aquatic animals, small animals which are food for larval fish, insects and large crustances,
- increase of green algae,
- decrease of brown algae, which is normally dominant, and
- increase of insects.
pH = 5.8
- disappearance of one type of copepod, a crustacean species,
- reproductive failure of the fathead minnow,
- increase in deaths of lake trout embryos, and
- decrease in slimy sculpin.

pH = 5.6
- increase in the plant production in the depths of the lake,
- developments of mats of algae along shorelines,
- disappearance of opossum shrimp, a major food source for lake trout,
- decrease in hardness of crayfish exoskeleton,
- severe decline in fathead minnow,
- decrease in white sucker abundance, and
- decrease in lake trout abundance.

pH = 5.4
- disappearance of another copepod,
- infestation of parasites in crayfish,
- decreased reproduction and abundance of crayfish,
- increase of pearl dace, a small minnow and,
- reproduction failure of lake trout,

pH = 5.1
- reproduction failure of white sucker.

The above experiment provides a valuable guidance in the process which might be expected in the future. It also shows that a small decrease in pH causes major changes in the aquatic life.
1.4 Definition and causes of Acid Rain:

Acid precipitation is a mixture of strong mineral acids i.e. $H_2SO_4$, $HNO_3$, $HCl$ and numerous "weak" organic acids in the rain and snow. It is measured in terms of pH unit. pH is the negative logarithm of the concentration of Hydrogen ions. The term acid rain is defined as rain and snow containing a higher concentration of free $H^+$ (Hydrogen ion) than produced from equilibrium of pure water with 330 ppm of $CO_2$ (concentration of $CO_2$ in the atmosphere) at NTP ($pH = 5.6$) (Oden, 1968).

$pH$ of atmospheric precipitation at any given location is influenced by the physio-chemical nature of the atmosphere. In the absence of $NH_3$ and $CaCO_3$, rainwater $pH$ could be expected to be about 5.0 due to natural sulfur compounds (Charlson and Rodhe, 1982). In tropics due to lower solubility and dissolution rate of $CO_2$ (about 1.5 times) than that in temperate regions, the $pH$ of neutral rain is expected to be 6.0 (Mukherjee and Krishnand, 1981). But the influence of anthropogenic acid on rain in the areas where, alkaline soils prevail (like India) may be probably better signified by temporal decrease in alkalinity rather than a decrease in $pH$ (Sequeria, 1982). The $pH$ of precipitation in remote areas of the world are given in the Table 1.1.

$pH$ of precipitation decreases when there is an excess of acidic gases and particles in the atmosphere and insufficient neutralising alkaline substances in the air on which the deposition occurs. Acid and alkaline substances observed in the atmosphere and their role in acidification has been given in the Table 1.2. The table indicates that sulfur and nitrogen are the main
contributors to acid rain formation. They are found in different oxidation states, molecular forms, and physical states in the atmosphere (Table 1.3 and 1.4).

1.4.1 Sources of Acidic Pollutants:

In addition to the natural sources that result from geological weathering, volcanic activity, anaerobic decomposition of organic matter, air borne sea salt sprays and lightening most of the increased acid precipitation burden is attributed to the anthropogenic activities which include:

- generation of electricity,
- smelting and refinement of metals,
- production and use of concrete, asbestos, glass, ceramic and plastic materials,
- use of transportation vehicles,
- space and water heating,
- decomposition and incineration of sanitary and solid waste,
- production and application of fertilizers, pesticides and other agricultural and silvicultural chemicals,
- burning of biomass, and farm and forest residue and
- use of explosive devices in peace and war.

On the global basis, the natural emission of acid precursors in the atmosphere exceeds anthropogenic emissions by about 40% (Cullis and Herschler, 1980). But with increasing global emissions, the anthropogenic contribution is continually narrowing this gap. The anthropogenic contribution is more harmful than natural
one because the later is evenly distributed throughout the world while the anthropogenic are generally concentrated in the urban and industrialized areas (Sevensson and Soderland, 1976).

1.5 Chemistry of Acid Rain Formation:

Atmosphere is an oxidising environment. The primary pollutants are oxidised through photochemical and chemical reactions as they are dispersed into it. Oxides of Nitrogen and Sulphur are converted to low volatile oxidation products, HNO₃ and H₂SO₄. These strong acids are incorporated into various forms of precipitation and lead to an increase in local and regional fluxes of acidity to the earth’s surface. The acidity of cloud droplets, rain, snow, dew and fog is largely determined by these acids. The rates of oxidation of SO₂ and NOₓ (NO + NO₂) in the atmosphere control the rate of acid deposition. The rate of this conversion depends on the amount of pollutants (NOₓ, organic substance), intensity of sunlight, the presence of oxidants and/or oxidant precursors, relative humidity, temperature and the presence of fog and clouds.

There are many different pathways for transforming SO₂ and NOₓ into sulphate and nitrate compounds. It includes both homogeneous and heterogeneous phase reactions. Homogeneous reactions take place in the gas phase or in the aqueous solution. Heterogeneous reactions take place on the surfaces of solid particles or liquid droplets.

The details of the reaction pathways for the formation of H₂SO₄ and HNO₃ are still unclear. Calvert et al. (1984), U.S. National Academy of Sciences (1985) has reviewed the current scientific research understanding of acid rain formation.
Total emission into the atmosphere of \( \text{H}_2\text{SO}_4 \) precursors outweighs those of \( \text{HNO}_3 \) by a factor of 2-3 on an equivalent basis. The residence time of \( \text{SO}_2 \) is longer than \( \text{NO}_x \). These two factors and the involvement of \( \text{NO}_x \) oxidation also in \( \text{SO}_2 \) oxidation make the study of \( \text{SO}_2 \) oxidation very important.

1.5.1 Pathways For Forming Atmospheric Sulphate:

Once emitted, the gaseous \( \text{SO}_2 \) is oxidised in plume/or ambient atmosphere to \( \text{H}_2\text{SO}_4 \) aerosol, or sulphate by reactions occurring in the gas phase. In the liquid phase, on the surface of solids or combinations of the three. In power plant plumes, oxidation rates of \(< 10\% \text{ h}^{-1}\) have been reported in many studies (Gillani et al., 1981; Newman, 1981). Much higher rates are often obtained when the plume passes through a cloud or fog bank (Eatough et al., 1984). Rate of conversions is also influenced by atmospheric parameters. It appears generally high in the summer than in the winter and higher at noon compared to night time. For example, Richards et al. (1981) reported maximum rate of \( \text{SO}_2 \) conversion of \( 0 - 0.8\% \text{ h}^{-1} \) in the summer and \( 0-2\% \text{ h}^{-1} \) in the winter for the plume from a coal fired power plant. Similarly Lusis and coworkers (1978) reported \( \text{SO}_2 \) oxidation rates generally less than \( 1-3\% \text{ h}^{-1} \) at mid day in June from a coal fired power plant in Alberta, Canada. Noon time conversion rates in a power plant plume were found to be \( 1-4\% \text{ h}^{-1} \) compared to night time rates of \( 0.5\% \text{ h}^{-1} \) (Gillani, 1978; Husar et al, 1978b; Forrest et al., 1981). Details have been given at the end of this section.
1.5.1. a **Homogeneous Gas-phase Oxidation:**

The homogeneous gas phase oxidation reaction pathways of SO$_2$ are grouped as follow:

a. Direct photo-oxidation involving the reactions of excited SO$_2$ molecules produced by absorption of solar uv radiation in the first and second bands of SO$_2$.

b. Reactions with unstable intermediate species i.e. excited molecules, atoms and free radicals which result from absorption of sunlight by trace gases.

SO$_2$ molecules absorb uv radiation (290-340 nm) quite strongly. But the energy involved is insufficient to break the O-S-O bond. Though a number of reactions of electronically excited molecules have been reported in the ambient air, the net oxidation of SO$_2$ doesn't occur at an appreciable rate as the excited state is quenched to ground state by N$_2$, O$_2$ and H$_2$O. This process is summarised as:

\[
\begin{align*}
\text{SO}_2 + h\nu & \rightarrow \text{SO}_2^* & 0.29 < \lambda < 0.40 \text{ } \mu\text{m} \\
\text{SO}_2^* + 2\text{O}_2 & \rightarrow \text{SO}_3 + \text{O}_3 \\
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4
\end{align*}
\]

The observed rate of oxidation indicates that the gaseous oxidation of emitted sulfur compounds proceed by its reaction with unstable intermediate oxidisers. The important intermediate atmospheric oxidisers are of the following nature:
i. $N_xO_y$ species,
nii. Oxygen species,
niii. Peroxy radicals,
iv. Alkoxy radicals, and
v. Peroxynitrate radicals.

The sources and generation of these airborne atmospheric oxidizers have been summarized as follows:

In the urban and regional scale troposphere, combustion of fossil fuels is an important source of the atmospheric oxidizers. As the fuels burn, $N_2$ and $O_2$ combine to form NO. A few percent of NO is oxidised in the flame to gaseous $NO_2$. The latter compound plays a significant role, since it absorbs ground level solar radiation ($\lambda = 4300$ Å) to produce oxygen atom in ground state $O (^3P)$ and NO. The generated oxygen atom reacts rapidly with oxygen molecule to form ozone ($O_3$), a very important oxidising agent in the atmospheric chemistry.

\[
NO + h'v \quad \text{--------} \quad NO + O(^3P) \quad \cdots \quad \text{I}
\]
\[
O(^3P) + O_2 \quad \text{--------} \quad O_3 + M \quad \cdots \quad \text{II}
\]

Where $M$ is another gaseous molecule, usually $N_2$, $O_2$, or $H_2O$ in the air. It prevents redissociation of $O_3$ molecule by its collision with the newly formed ozone. The collision removes some of the excess vibrational energy of ozone which was formed as the new bond was formed.

The ozone formed by reaction (II) either reoxidises NO and $NO_2$ to $N_xO_y$ species or reacts with alkenes to give highly reactive ozonides which then break up into aldehyde or ketone and a peroxy biradical.
$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \ldots \text{III}$

$\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_4 + \text{O}_2 \ldots \text{IV} \quad \text{N}_2\text{O}_y \text{Species}$

$\text{NO}_3 + \text{NO}_2(+\text{M}) \rightarrow \text{N}_2\text{O}_5(+\text{M}) \ldots \text{V}$

Further, photodecomposition of $\text{O}_3$ with sunlight absorption at the short wavelength region of the spectrum generates electronically excited oxygen atom $\text{O}(^1\text{D})$ and excited molecular oxygen, whereas absorption of long wavelength region generates $\text{O}(^3\text{P})$ and oxygen molecule.

$\lambda = 2900-3060 \ \text{Å}$

$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2(\text{^1\Delta}_g) \ldots \text{VIII}$

$\lambda = 2900-3500 \ \text{Å}$

$\text{O}_3 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}_2(\text{^3\E}_g) \text{ or } \text{O}_2(\text{^1\Delta}_g) \ldots \text{IX}$

$\lambda = 4500-4700 \ \text{Å}$

$\text{O}_3 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}_2(\text{^3\E}_g) \ldots \text{X}$

Where ($^1\Delta_g$) is the first excited state of oxygen molecule and ($^3\E_g$) is the ground state of the molecule.

$\text{O}(^1\text{D})$ state of the oxygen is much more reactive than the ground state oxygen atom $\text{O}(^3\text{P})$. The ground state oxygen combines rapidly with the $\text{O}_2$ molecule to form $\text{O}_3$. But for $\text{O}(^1\text{D})$ transition to $\text{O}(^3\text{P})$ is forbidden. It collides with the water molecule to form a highly important transient species in the atmosphere, the HYDROXYL RADICAL, $\text{HO}^-$ (Lexy, 1971, 1972). This $\text{HO}^-$ is the main agent for oxidising $\text{NO}_2$ into $\text{HNO}_3$. 

15
This radical is unreactive towards oxygen, but it reacts virtually with all trace atmospheric species such as Carbon Monoxide (CO), Hydrocarbons (HC), Aldehydes (-CHO), NO, NO2, and SO2 present in the atmosphere. It is treated as a primary link between emittents and products in all tropospheric chemical reactions and most favoured radical for the transformation of SO2 to H2SO4 (Atkinson and Lloyd, 1984).

\[
\text{SO}_2 + \text{HO}^\cdot + \text{M} \rightarrow \text{HOSO}_2 + \text{M} \quad \text{... XII}
\]

\[
\text{HOSO}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{SO}_3 \quad \text{... XIII}
\]

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad \text{... XIV}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{HO}^\cdot \quad \text{... XV}
\]

Again the reaction of HO\cdot with CO and RH leads to the formation of another class of reactive transient species, the peroxy (XVII) and alkoxy (XIX) radical.

\[
\text{HO}^\cdot + \text{CO} \rightarrow \text{H} + \text{CO}_2 \quad \text{... XVI}
\]

\[
\text{H} + \text{O}_2(+\text{M}) \rightarrow \text{HO}_2(+\text{M}) \quad \text{... XVII}
\]

\[
\text{HO}^\cdot + \text{RH}^\cdot \rightarrow \text{R}^\cdot + \text{H}_2\text{O} \quad \text{... XVIII}
\]

\[
\text{R}^\cdot + \text{O}_2 (+\text{M}) \rightarrow \text{RO}_2(+\text{M}) \quad \text{... XIX}
\]

\[
\text{HO}^\cdot + \text{RCHO} \rightarrow \text{RCO} + \text{H}_2\text{O} \quad \text{... XX}
\]

\[
\text{RCO} + \text{O}_2 \rightarrow \text{RCO}_2(+\text{M}) \quad \text{... XXI}
\]

Where R = alkyl group

Peroxy radicals formed in this way react rapidly with NO to form NO2 and another class of reactive species. In case of HO2-NO reaction (XXII), HO\cdot is generated while with RO2 and RCO2 radicals alkoxy (RO) and aceloxo (RCO2) radicals respectively are formed.
Thus, the combination from reactions XI to XXV gives a chain reaction, where the oxidising agents HO·, NO, and NO2 are consumed and regenerated in polluted environment. By homogeneous reactions, vapour phase sulphuric acid is formed. This vapor condenses in the air by bimolecular condensation. The rate of this process depends, amongst other things, on the concentration of H2O and H2SO4 molecules as well as on the temperature (Kiang et al., 1973).

1.5.1.b Oxidation of SO2 in Aqueous Solution:

SO2 dissolves in water according to following equilibrium reaction:

\[
H
\]

\[
SO_2 + H_2O \rightleftharpoons SO_2\cdot H_2O \quad \quad \cdots \text{I}
\]

\[
k_1
\]

\[
SO_2\cdot H_2O \rightleftharpoons HSO_3^- + H^+ \quad \quad \cdots \text{II}
\]

\[
k_2
\]

\[
HSO_3^- \rightleftharpoons SO_3^{2-} + H^+ \quad \quad \cdots \text{III}
\]

Where H is Henry’s law constant for SO2 and \( k_1 \) and \( k_2 \) are the dissociation constants. The total of physically dissolved SO2 (SO2·H2O), the bisulfite (HSO3^-), and sulphite (SO3^{2-}) ion is designated by \( S(IV) \). The aqueous phase oxidation of this S (IV) to H2SO4, i.e. S (VI) is described by the following reactions:
Autoxidation

\[ S^{(IV)} + \frac{1}{2} O_2 \rightarrow S^{(VI)} \quad [\text{Martin, 1984}] \]

Catalyst (Mn\(^{2+}\), Fe\(^{3+}\))

\[ S^{(IV)} + H_2O_2 \rightarrow S^{(VI)} + H_2O \quad [\text{Mcardle and Haffmann, 1983}] \]

\[ S^{(IV)} + O_3 \rightarrow S^{(VI)} + O_2 \quad [\text{Maahs, 1983}] \]

Although other chemical pathways also exist for the aqueous-phase oxidation of \( S_\text{O}_2 \), these three pathways have been shown to be most important for the polluted environments (Jacob and Hoffmann, 1983; Seigneur and Saxena, 1984, 1987).

The autoxidation of sulfite ions are given as follow:

\[ k \]

\[ SO_3^{2-} + \frac{1}{2} O_2 \rightarrow SO_4^{2-} \]

Where \( k \) is a constant which depends on the pH of the solution. Beilke et al. (1975) found that

\[ k = 1.2 \times 10^4 [H^+]^{-0.16} \text{ in a pH range of 3 to 6 and at a temperature of } 25^\circ C. \]

Catalytic autoxidation of \( S_\text{O}_2 \) in aqueous microdroplets has been suggested as a nonphototype pathway for rapid production of sulfuric acid in humid atmosphere.

Metal catalysed autoxidation tends to exhibit decreasing reaction rates with decrease in pH (fig. 1.1).

The kinetics of metal catalysed oxidation may be given as:

\[ k_1 \]

\[ \text{Fe (III) + } S_\text{O}_2\cdot H_2O \rightarrow \text{Fe (II) + } HSO_3^- + H^+ \quad \]

\[ k_2 \]

\[ 2 HSO_3^- \rightarrow H_2S_2O_6 \]
\[ k_3 \]
\[ \text{HSO}_3^- + \text{Fe(III)} \rightarrow \text{Fe(II)} + \text{SO}_3^- + \text{H}^+ \]
\[ \text{SO}_3^- + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 \]

In addition to direct oxidation, \( \text{H}_2\text{O}_2 \) and \( \text{O}_3 \) are the major oxidants of dissolved \( \text{SO}_2 \). Oxidation by \( \text{H}_2\text{O}_2 \) is the most favorable because of its extremely high rate of reaction. The mechanism of the oxidation of \( \text{S(IV)} \) by \( \text{H}_2\text{O}_2 \) is fairly well understood. This reaction proceeds via nucleophilic displacement of \( \text{H}_2\text{O}_2 \) on bisulfite (\( \text{HSO}_3^- \)) ion. The reaction rate increases with decrease in pH.

\[ k_f \]
\[ \text{HSO}_3^- \rightarrow \text{A}^- + \text{H}_2\text{O} \]
\[ k_b \]
\[ k_2 \]

\[ \text{A}^- + \text{H}^+ \rightarrow \text{H}_2\text{SO}_4 \]

where \( k_f, k_b, k_2 \) are the rate constants for the reactions. Species A is peroxymonosulfurous acid ion.

On the other hand, the mechanism of the oxidation of sulfite by ozone and its various catalytic influences are less understood. Most likely, the reaction with ozone proceeds via a free radical mechanism involving the sulfite radical and peroxymonosulfite radical species (Penkett, 1979).

According to a study by Martin (1984), no sensitivity of the ozone reaction was found to metal ion catalysis by \( \text{Fe}^{3+}, \text{Mn}^{2+}, \text{Cu}^{2+} \), but on the other hand a modest rate increase due to catalysis by \( \text{Mn}^{2+} \) and \( \text{Fe}^{3+} \) have been reported by Harrison et al. (1982). Again the reaction rates of \( \text{O}_3 \) with \( \text{S(IV)} \) decreases with decrease in pH.
The above discussion of oxidation and rate of sulfate formation have been shown diagrammatically in fig.1.1.

![Diagram](image)

This diagram has been taken from Beilke and Gravenhort (1978). In the diagram there are three curves. The dashed line shows the uncatalysed sulfate formation rate as a function of pH as by Beike et al. (1975) for 10°C and for a SO$_2$ concentration of 1 ppb. The solid line indicates the results of Betz obtained with natural rain water containing manganese and iron in concentration between $10^{-7}$ - $10^{-6}$ and $10^{-6}$ - $10^{-5}$ molar, respectively. The pH of the rainwater samples ranged from 3.2 to 5.2. The upper line is based on the experimental results of Penkett (1972) obtained with ozone concentration of 40 ppb. This figure clearly suggests that oxidation by O$_3$ is a dominant pathway for the oxidation of SO$_2$ in clouds.

Apart from the above discussed reactant species and medium of the reaction, atmospheric parameters also effect the sensitivity of SO$_2$ oxidation. Important among them are

a. Relative Humidity,

b. Temperature, and
c. Trace metal concentration

During day time, the gas phase formation of $\text{H}_2\text{SO}_4$ and the aqueous-phase oxidation of $\text{SO}_2$ by $\text{H}_2\text{O}_2$ are the principal mechanisms for atmospheric sulfate formation (McMurry and Willson, 1983; Middleton et al., 1980). Middleton et al (1980) also found that sulfate formation at night was dominated by aqueous phase mechanism and was generally lower than day time sulfate formation. At night, the HO$^-$ concentration is low and the aqueous-phase oxidation of $\text{SO}_2$ by $\text{O}_2$ (catalysed by Mn$^{2+}$, Fe$^{3+}$) and by $\text{H}_2\text{O}_2$ accounts for 82% and 15% respectively of the total sulfite formed (Saxena and Seigueur, 1987). The difference between the sulfate formation rates during day and night time depend upon atmospheric conditions such as pollutant concentrations and solar radiation. For example, during the winter, daytime $\text{SO}_2$ oxidation by HO$^-$ radical will be significantly slower than during the summer. Therefore, the aqueous-phase mechanisms to sulphate formation will be more significant during winter than during the summer.

The contribution of the aerosol-phase reactions to sulphate formation decreases as the relative humidity decreases because the amount of water available for aqueous-phase reaction diminishes.

The effect of temperature on oxidation rate can be very well understood by the study of Saxena and Seiguere (1987). They did a comparative study between two reactions occurring at 5°C and 25°C between the same reactants. The gas phase reaction decreased with decreasing temp. This phenomenon results from two different effects:
i. The rate constant for the \((\text{SO}_2 + \text{HO}^+)\) reaction increases as the temperature decreases and

ii. The \text{HO}^+ concentration level decreases as the temperature decreases.

The effect of changes in the trace metal concentration on reaction rates have been shown by many researchers. As the Manganese (Mn) and Iron (Fe) concentrations are increased by a factor 5 and 17 respectively, the amount of sulfate formed via the \((\text{SO}_2 + \text{O}_2)\) aqueous-phase reaction increases from 0.14 to 0.45 \(\mu\text{g}/\text{m}^3\) (Saxena et al., 1986b). It is, therefore, of primary importance to obtain accurate data on ambient concentrations of trace metals for assessing the role of aqueous oxidation of \(\text{SO}_2\) to \(\text{SO}_4^{2-}\) in aerosols.

1.6 Acidification Problems in Tropics

It is clear from the previous discussions that the acidic species in the air available to be scavenged by clouds or rain depend on source magnitude of acidic precursors (mainly sulfur and nitrogen species) air trajectories, regional photochemical setting and humidity. Hence, the chemistry of acidification at one region may not be applicable as such to the other region. Previously air pollution problem was confined and has been studied extensively in the temperate or cool regions of the world. But, now in the tropical countries also, rapid industrialization and high energy demands have led to a drastic deterioration in the air/cloud and it is also assumed that if the current trends in urbanization, industrialization and increased use of fossil or biomass energy sources continues beyond 20th century, certain
areas are certainly going to experience severe air pollution and related acidification problems. The estimated budget of tropical emission of sulfur and oxidised nitrogen are given in the Tables 1.5 and 1.6. These tables indicate that anthropogenic activities (either in the form of industrial process or as biomass burning) are responsible for major proportions of all sulfur and nitrogen emissions in the tropical land area. In tropics, due to different climatic factors and different pattern of emission, the relative importance of many processes taking part in precipitation chemistry may be different compared to temperate region.

A tropical climate is characterised by:

- high temperature and very little temperature variation during the year,
- winds are relatively low and steady with a little change in direction over extended period of time,
- more and high rates of rainfall, and
- high humidity.

In tropics, the combination of intense solar radiation and high humidity results in the formation of high concentration of hydroxyl radicals (HO·). At higher air temperature (>15°C), the NOx and unburnt hydrocarbons in the vehicle exhaust can react in prolonged sunlight to form ozone, another powerful oxidant. This explains if equal amount of precursors are given in temperate and tropical environment, higher concentration of atmospheric oxidants will be produced in tropics which will lead to
more and rapid formation of acidic compound.

Again due to higher temperature there will be strong vertical mixing of air in the lowest layers of the atmosphere. This implies that the air close to the surface is regularly transported to a height of 1-4 km in contrast to 1-2 km in temperate latitudes and replaced by air originating from such altitude. Here many sulfur and nitrogen compounds may have substantially longer residence time and be transported over longer distance than those closer to the surface (Chatfield, 1984).

Wind pattern in tropics would lead to deterioration in air quality due to their poor transport ability, and hence, will favour acid rain formation.

In tropics, where, there is no strong wind, rain causes the seasonality in the ambient air quality. In the humid tropics due to more precipitation total deposition of the pollutants will be higher for a given quantity of pollutant emitted to the atmosphere. "Recycling" of atmospheric moisture within a given air mass is greater in tropics than in temperate areas. This process allows a greater opportunity for precipitation scavenging of a given pollutant molecule. In Amazon basin, for example, rain falls, evaporates and falls again several times before leaving the basin (Salati and Vose, 1984).

Due to higher rainfall the total concentration of $H^+$ in tropical area will be higher than expected on the basis of pH alone.

Thus the climatic factors of the tropics are more favourable for the formation of acid rain rather than temperate zone.

Apart from the climatic factors, the patterns of emissions in tropics are also more favorable for acid rain
formation. High rates of biomass burning which led to simultaneous $\text{NO}_x$, CH, $\text{SO}_2$ and CO emissions on a large scale in the tropics have a significant effect on the acidity of atmospheric deposition. Destruction of tropical forests (including burning) is apparently a significant factor in the global carbon cycle (Wood et al., 1983) and could be important for total acidity and trace gas concentrations as well (Crutzen et al., 1985). Significant amounts of $\text{NO}_x$ are released which on oxidation would contribute nitric acid to atmospheric deposition.

The relative contribution of organic acids to total and free acidity in remote tropical sites may be considerably greater than corresponding values of temperate sites (McDowell, 1988). Kneee et al. (1983) found that week organic acids (predominantly HCOOH, CH$_3$COOH) contribute 64% and 63% of free and total acidity respectively in wet-precipitation samples collected in Katherine, Australia. Average concentration of organic acids was 19.8 $\mu$eq/litre. In Varginia, USA, Kneee and Gallow (1984) measured organic acid concentration (HCOOH, CH$_3$COOH) equivalent to 16% of free acidity (10.9 $\mu$eq/l). But, organic acids are not mobile within the terrestrial ecosystems due to their rapid microbial decomposition. Nitrates generally do not participate in soil adsorption reactions. Hence, its mobility is controlled predominantly by biological processes. The mobility of sulfate in terrestrial ecosystem is determined in large part by soil adsorption processes, although Swank et al. (1984) have shown that rapid microbial uptake of $\text{SO}_4^{2-}$ can occur as well. Thus, sulfate may be considered as the most mobile of the three acidic anions common in precipitation and it most often controls the effects of acidic decomposition.
on soils as well as aquatic ecosystems in tropics (Johnson et al., 1982 and Galloway et al., 1987).

Due to unplanned industrialization, most of the tropical countries do not have any effective planning and regulation system for the industries. Again, to add to this problem, the tightening of pollution laws in developed countries have tempted the multinational corporations to transfer their so called "dirty industries" including smelters - to tropical and developing countries with less stringent regulations.

Thus, the conditions which could cause acid pollution exist in tropical regions. Evidences of acid pollution or conditions that could cause it have already been found in South and South East Asia, in the middle East, in Southern Africa and Latin America.

A comparative study of the acidity of the rainwater (pH = 4.1) in North East USA (Liken et al., 1977) with that of at four different locations i.e. by Stallard and Edmand (1981) for Améjan (pH = 5.1), by Galloway et al. (1982) for Australia (pH = 4.8), by Hendry et al. (1984) for Turrialba, Costa Rica (pH = 5.3) in tropics shows that the acidity of wet deposition in tropics is relatively low in most of the industrialised temperate zones. In parts of the tropics precipitation acidity appears to be buffered by dust and soil particles (Visser, 1961; Dalal, 1979).

But unfortunately, the tropical countries lack the knowledge about the interaction of chemistry and meteorology which is likely to affect the composition of tropical atmosphere.

In order to fulfill this study gap a joint project between the UNEP and SCOPE (a committee of the
international council of scientific unions) was also launched in 1984 to investigate in tropical countries the followings:

- the degree to which acidification has already become a problem;
- to assess the potential for the occurrence of harmful future effects if NOx and SO2 emissions were to increase;
- to identify susceptible areas in relation to soil and ecosystem; and
- to investigate the need for monitoring the status of the environment (including air, water, soil and vegetation);

so that a base line value can be established and possible changes be directed at an early stage. The countries proposed for the study include Brazil, China, India, Kenya, Malasiya, Mexico and Venezuela. The current knowledge about the tropical environment, and the impact of air pollution has been well documented in depth in a book entitled "Acidification in tropical countries" SCOPE 36 (edited by Rodhe H., 1988).

1.7 Air Pollution Meteorology:

The study of weather and climate occupies a central and important position within the broad field of acid rain studies. The atmosphere acts as a conduit between emission and deposition of acidic pollutants. The concentration and stay-time of these pollutants in the atmosphere depends on dispersion ability of the atmosphere. The dispersion ability of the atmosphere depends on its pollution potential which is a derivative of meteorological parameters. The longer the pollutants stay in the
atmosphere, the greater proportion converted to acid and they may be carried out to a longer distance before their deposition. Thus, meteorological parameters making acid rain is an international problem. So, for the establishment of a relationship between source and receptor at a place, considerable knowledge of air pollution meteorology is needed. Air pollution meteorology is mainly concerned with aggregate of weather parameters that influence the fate of air borne effluents of both anthropogenic and natural origin. The relevant elements are:

1.7.1 Wind:

Wind direction shows the way in which pollutants are to be transported and the speed specifies how rapidly the contaminants will advance forward. Wind plays a role in the dilution of contaminants also. However, the overall dilution of contaminants is dependent upon turbulence which is determined by atmospheric state which in turn is affected by wind speed.

1.7.2 Stability:

Stability is a state of the atmosphere which shows its tendency to resist the vertical motion of air parcel. It is characterised by Environmental Lapse Rate (ELR), which is a function of vertical thermal structure of the atmosphere. The thermal structure of the atmosphere is an integrated result of solar radiation at the top of the atmosphere, motion and composition of the air and the radiative properties of the earth's surface. Stability is classified as unstable, neutral and stable based on environmental lapse rate vis-a-vis Dry Adiabatic Lapse
Rate (DALR). DALR is a ratio of the gravitational attraction to the specific heat at constant pressure. Its approximate value is $-10 \, ^\circ\text{C/km}$. Stable atmospheric conditions occur at night when ground radiates faster into the atmosphere and the overlaying atmosphere gets heated up. This state of atmosphere is unfavorable for atmospheric diffusion because it inhibits turbulence within the layer. But unstable state which is characterised by light winds with strong solar heating, promotes turbulence and hence, can be considered favourable for atmospheric dilution of the pollutants.

1.7.3 Temperature:

Temperature plays a significant role in affecting the concentration of pollutants through chemical/thermochemical reactions and it also influences the turbulence and stability which are primary agents of diffusion. Further, the fall velocities for different depositing elements are also influenced by temperature, because this velocity depends on the shape of falling element and the shape of the falling element depends on ambient temperature (Zikmunda and Heymesfield, 1978).

1.7.4 Humidity:

Humidity is related to the water vapor content of the atmosphere. The different phases of water in the atmosphere interact with air pollutants in very significant ways. Both solid and liquid precipitation are effective scavengers of gaseous and particulate pollutants. Higher humidity may modify precipitation processes by encouraging aerosol formation where particulate pollutants act as condensation nuclei. Further, local and regional radiation budgets
1.7.5 Air Pollution Potential:

Air pollution potential may be thought as a measure of the inability of the atmosphere to adequately dilute and disperse pollutants emitted into it, vertically and horizontally, based on the values of specific meteorological parameters of the macroscale features (Gross, 1970). Thus meteorological conditions which allow for accumulation of pollutants denote high pollution potential whereas, conditions in which dispersal of pollutants can occur effectively denote low pollution potential.

Broadly speaking there are two important parameters to adjudge air pollution potential for a place viz.

1. Mixing height
2. Transport wind through the mixed layer.

1.7.5.1 Mixing Height:

It separates polluted surface air from clean air aloft and is defined as the height (meters) up to which air pollutants are transported, diffused and mixed primarily due to turbulence. The concept of mixing layer is based on the principle that when atmosphere is heated due to solar heating of the ground, it becomes unstable resulting in vertical motions and mixing of the pollutants which is accomplished by the vertical components of atmospheric turbulence. Hence this height varies diurnally, from season to season, and also affected by topographic features of a particular place. The occurrence of transport wind through mixing layer is essential for
mixing. The product of mixing height and wind speed averaged through the surface mixing layer is called ventilation Coefficient. Smaller the height, adverse is the condition for dispersal of air pollutants. High pollution potential results when the morning mixing height is \(<500\, \text{m}\) and transport wind, \(4\, \text{m/s}\) and afternoon ventilation coefficient \(<6000\, \text{m}^2/\text{s}\) (Gross, 1970).

1.8 Review of status of researches on the subject:

In the past, several studies have been made in India and abroad taking different aspects in the subject. Areas under the threat of acid rain have been shown in fig. 1.2. The rain quality depends on the air quality, which in turn, depends on the emissions. The final stage of several primary pollutants emitted into the atmosphere after a multi-phase and multi-stage chemical transfer is the formation of their acids and salts. These acids formed in the atmosphere are organic and inorganic in nature. They both contribute to the acidity of the precipitation (Chan et al., 1987 and Ayer, 1990).

The spread and intensification of precipitation acidity through Northern Europe and the U.S. is a well documented phenomenon. The increase in acidity is attributed to increased anthropogenic emission of \(\text{NO}_x\) and \(\text{SO}_2\) (Munger, 1982). The present magnitude of sulfur (\(\text{SO}_2, \text{SO}_4^{2-}\)) and nitrogen (\(\text{NO}_x, \text{NO}_3^-, \text{NH}_3, \text{NH}_4^+\)) is ten or more times larger than the estimated natural fluxes (Rodhe, 1976, 1980; Bonis et al., 1980, Galloway et al., 1983, 1984). While sulfuric acid is considered to be a major acid, the net acidity is controlled by the interaction of \(\text{H}_2\text{SO}_4\) and \(\text{HNO}_3\) with basic ammonia and soil dust. The influence of increasing sulfate and nitrate on decrease
MAP SHOWING THE GLOBAL ACID POLLUTION

Global acid pollution

Fig. 1-2
of the pH value in cloud and rainwater has been shown by many researchers (Okita, 1968; Scott, 1978; Falconer & Falconer, 1980; Hegg and Hobbs, 1981, 1982; Castillo et al., 1983; Daum et al., 1983, 1989; Leaith et al., 1983; Richards et al., 1983; Dasch and Cadle, 1984; Varma, 1986; Chan et al., 1987; Low, 1988, Khemani et al., 1989; Butter and Likens, 1991; Yamaguchi et al., 1992; Samara et al., 1990; Ahmed et al., 1990; Mukhopadhyay et al, 1993; Ravichandran and Padmanabhamurty, 1994).

Higher concentration of \([H']\) in USA were found in convective showers and thunder storms in summer (Wolff et al., 1979; Dasch and Candle, 1985; Chan et al., 1987; Gatz et al., 1991) where as during winter in Europe (Gatz, 1991). The cation deficiency in North America is found to be the probable cause of acid rain over the region (Varma, 1990).

Ionic concentration decreases with increased rainfall (Subramanian and Saxena, 1980; Mukherjee et al., 1985) and after 12 hrs of rainfall 50% reduction in the initial values were noticed (Marquardt and Ihle, 1988). Marquardt and Ihle (1988) in their study found in the North Germany that the length of dry period before precipitation exceeding three days causes an increase by a factor of two in anthropogenic content and decrease in the pH.

Chlorides in Thessaloniki, Greece (Samara et al., 1992), Fluoride in the lower valley, Australia (Low, 1988) and Organic acids in the tropical regions (Keene et al., 1983) have been shown to contribute to the acidity of the rain. The aqueous phase reactions of aldehydes with hydroxyl radicals are thought to be a potentially important source of organic acids in cloud water (Chameides and Daxis, 1983; Graedal and Goldberg, 1983;
There is no substantive evidence yet of soil or water acidification or forest damage due to acid rain in India. Because in India rainwater is supposed to have substantially higher pH value than that of CO₂-equilibrated water because its soil is by and large rich in alkaline components i.e. Ca²⁺ and Mg²⁺. It is the major source of the aerosols in the atmosphere which acts as a condensation nuclei for water vapour. The influence of alkaline particles on the increase of pH in rainwater in India has been demonstrated by Varma (1983) and Khemani et al. (1985b). In rural areas, no incidence of acid rain has been reported. Naik et al. (1988) ruled out long range transport of acid precursors coupled with cations concentration. In addition to the above mentioned benefits the country has also some additional advantages like, low sulfur containing coal, relatively few automobiles and a rainy season that is an effective air scrubber.

The overall possibility of occurrence of acid rain in India has been assessed as about 2% (Rumshished, 1965 and Varma, 1989).

Despite all the above mentioned advantages, the rapid industrialisation and urbanisation has raised the air pollution level even above the permissible limits set by WHO in major cities like Calcutta, Bombay and Delhi. Since rain is a major atmospheric scavenger, the total ionic composition of precipitation helps in investigating the source regions, the atmospheric transport and hence the circulation processes. The residence time of their precursors as well as the deposition patterns are also revealed by precipitation chemistry studies (Rodhe and
Grandell, 1972; Bolin and Persson, 1974). These facts have led to some studies on rain water composition in India at different places by different research groups and organisations.

Although measurements of chemical composition of precipitation from the Indian sub-continent were started long ago (Narayanaswami, 1939; Mukherjee, 1955, 1957; Khemani et al., 1968; Handa, 1969), it is only during the last two decades that extensive work on it has been carried out (Sequeria, 1976; Sequeria and Kelkar, 1978; Sadasivan, 1979; Krishnanand, 1984; Zusti et al., 1978; Subramanian and Saxena, 1979; Mahadevan, 1984; Mukherjee, 1986; Gupta and Kothari, 1987; Varma 1989, 1990, 1991, Mukhopadhyay et al., 1992, 1993; Ravichandran and Padmanabhamurty, 1994) at various places in India. With a view to assess the prospects of acid precipitation over India all the ten Background Air Pollution Monitoring Network (BAPMoN) stations viz. Allahabad, Jodhpur, Kodaikanal, Minicoy, Mohanbari, Nagpur, Port Blair, Pune, Srinagar, and Visakhapatnam established at different topographical locations by India Meteorological Department under the auspices of W.M.O. are collecting and analysing the rainfall samples on a monthly basis.

In India the first controversy on impact of acidity started in 1982, when a major oil refinery was set up at Mathura just 40 km upwind of The Taj Mahal. But the first occurrence of acid rain was reported by Mahadevan et al. (1984) at Chembur, Bombay. After that it has been reported in different pockets of cities like Bombay (Meenakshi et al., 1992), Delhi (Khemani, 1989) and at some of the BAPMoN stations like Minicoy, Mohanbari, Nagpur, Port...
Blair and Kodaikanal (Varma, 1989).

$\text{Ca}^{2+}$ and $K^+$ mainly originate from rural areas from soil and vegetation and cause high pH (Mukhopadhyay et al., 1992). Sodium, Chlorides and to some extent magnesium are of maritime origin (Mukherjee et al., 1985; Ezcurra et al., 1988; Ahmed et al., 1990; Yamaguchi et al., 1991). Hence sea-salt will be higher in the coastal regions and its concentration decreases with increasing distance from the coast whereas, inland stations have high concentration of $\text{Ca}^{2+}$ (Khemani, 1989; Mukhopadhyay, 1992). However, the alkalinity of rain decreases with increasing distance from the desert areas (Mukhopadhyay et al., 1992).

The atmosphere through which rain drops travel from the cloud base plays an important role in deciding the rain acidification (Khemani, 1987). Indian atmosphere has a high dust load almost through-out the year except in the coastal belt. Therefore, the dust is considered to be an important factor in influencing the pH of rainfall. Higher the dust load higher is the pH value. Based on the available data on SPM studies and on the pH values of rain from the various parts of the country Varma (1989) has divided the country into four different parts representing the high and low sensitive zones for acid rain formation as follow:

i. Highly sensitive pH zones where pH $< 6.0$.

ii. Moderately sensitive pH zone where pH ranges between 6.0 and 6.5.

iii. Normal sensitive pH zone where pH ranges between 6.5 and 7.0.

iv. High pH zone where pH ranges between 7.0 to 8.5.
N-W India experiences high pH values ranging from 7.0 to 8.5 while S-E Indian coastal belt represents a region of acid rain occurrence. The main reason behind this being that N-W India contains a heavy load of soil originated particulate in the atmosphere which are predominantly alkaline in nature consisting mainly of carbonates and bicarbonates of Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$ cations while the S-E coastal belt, because of its geographical and geological setting, doesn’t possess a high density of soil particulates in the atmosphere.

Thus, the above discussion leads to the conclusion that the study of acid rain formation at a place includes studies of following aspects:

1. Magnitude of acid precursors emitted into the atmosphere,
2. Qualitative and quantitative analysis of existing aerosols,
3. Air pollution climatology and
4. Rain water chemistry.

In most of the earlier studies in India data on rainwater chemistry has been used of BAPMoN stations which are located away from the urban and industrial areas. Thus, it doesn’t represent the true picture of rainwater quality in the industrial and urban pockets of the country. Secondly, in no any other study the measurement of acid precursors ($SO_2$ and $NO_x$) and particulate matters have been done simultaneously with rain water quality. The above mentioned Indian work also lacks a correlation between rain acidity and meteorological parameters. An attempt has, therefore, been made in the present study to fill up
these gaps of our knowledge with the following objectives:

1. Analysis of particulate pollutants for cation (including heavy metals which acts as a catalyst in acid rain formation) and anions.
2. To obtain a seasonal and spatial variability in the ratio of cations and anions of SPM in order to measure its acidity.
3. Measurements of the concentration of gaseous acid precursors (NOx and SO2) on a regular basis.
4. To determine the ratio between SO4^{2-} and SO2, and NO3^{-} and NOx in relation to the meteorological parameters.
5. To measure the spatial and diurnal variation of cations and anions of the precipitation.
6. To study wind pattern, atmospheric stability, mixing height and ventilation coefficient in order to correlate the above factors with the meteorological parameters.
7. To calculate scavenging-ratio for the pollutants participating in acid rain formation.

In the present work Delhi has been taken as the study area because surveys carried out by CPCB, NEERI, and some individual research groups like Khemani et al. (1985), Singh (1987), Dave (1987) reveal excessive concentration of trace gases and total suspended particulate matter (TSPM) in the ambient air of Delhi. These pollutants may cause acid rain. Description of the study area and emission sources are detailed in Chapter II.
Table 1.1
The pH of precipitation in remote areas of the world

<table>
<thead>
<tr>
<th>Area</th>
<th>Median</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCEANIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Samoa</td>
<td>5.3</td>
<td>4.0</td>
<td>6.2</td>
</tr>
<tr>
<td>Mauna Loa</td>
<td>4.3</td>
<td>3.3</td>
<td>5.6</td>
</tr>
<tr>
<td>Hilo, Hawaii</td>
<td>4.7</td>
<td>3.7</td>
<td>6.0</td>
</tr>
<tr>
<td>Amsterdam Island</td>
<td>4.9</td>
<td>3.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Bermuda</td>
<td>4.8</td>
<td>4.0</td>
<td>5.6</td>
</tr>
<tr>
<td>WEST COAST</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>6.5</td>
<td>5.8</td>
<td>7.2</td>
</tr>
<tr>
<td>India (4 stations)</td>
<td>6.3</td>
<td>5.8</td>
<td>6.6</td>
</tr>
<tr>
<td>Ireland</td>
<td>4.8-5.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Norway</td>
<td>4.8-5.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>North America</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CONTINENTAL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>India (9 stations)</td>
<td>7.5</td>
<td>5.8</td>
<td>8.9</td>
</tr>
<tr>
<td>Grand Jet (Colo, U.S.A.)</td>
<td>6.5</td>
<td>5.4</td>
<td>8.0</td>
</tr>
<tr>
<td>Alamosa (Colo, U.S.A.)</td>
<td>6.8</td>
<td>5.0</td>
<td>8.2</td>
</tr>
<tr>
<td>San Angelo (Texas, U.S.A.)</td>
<td>6.6</td>
<td>5.2</td>
<td>7.3</td>
</tr>
<tr>
<td>POLAR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Canadian Arctic</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Island Antarctic</td>
<td>4.6-5.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Source: MOI 1982b)
Table: 1.2

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

<table>
<thead>
<tr>
<th>Substance</th>
<th>Role in acidification</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Terrestrial</td>
</tr>
<tr>
<td>( \text{H}_2 \text{S, SO}_2, \text{H}_2 \text{SO}_4 )</td>
<td>+</td>
</tr>
<tr>
<td>( \text{NO}_x, \text{HNO}_3 )</td>
<td>+,0</td>
</tr>
<tr>
<td>( \text{HCl, HF} )</td>
<td>+</td>
</tr>
<tr>
<td>Organic acids</td>
<td>+,0</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>+,0, -</td>
</tr>
<tr>
<td>Ammonium salts</td>
<td>+</td>
</tr>
<tr>
<td>Alkaline dust</td>
<td>-</td>
</tr>
</tbody>
</table>

(Source: Rodhe et al, 1988)
### Table: 1.3

**Atmospheric Sulfur Compounds**

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Molecular / Ionic Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
</tr>
<tr>
<td>+6</td>
<td>(SO₃)₂, (H₂SO₄)</td>
</tr>
<tr>
<td>+4</td>
<td>SO₂</td>
</tr>
<tr>
<td>+2</td>
<td>(SO)</td>
</tr>
<tr>
<td>0</td>
<td>H₂S, RSH, RSR, RSSR, CS₂, COS</td>
</tr>
<tr>
<td>-2</td>
<td></td>
</tr>
</tbody>
</table>

( ) denotes either a very low concentration or an improbable form. R = CH₃ appears to be dominant in almost all remote areas.

### Table: 1.4

**Atmospheric Nitrogen Compounds**

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Molecular / Ionic Forms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
</tr>
<tr>
<td>+5</td>
<td>NO₃, N₂O₅, HNO₃</td>
</tr>
<tr>
<td></td>
<td>R(0)O₂NO₂</td>
</tr>
<tr>
<td>+4</td>
<td>NO₂⁻, (N₂O₄)</td>
</tr>
<tr>
<td>+3</td>
<td>HNO₂</td>
</tr>
<tr>
<td>+2</td>
<td>NO</td>
</tr>
<tr>
<td>+1</td>
<td>N₂O</td>
</tr>
<tr>
<td>0</td>
<td>N₂</td>
</tr>
<tr>
<td>-3</td>
<td>NH₃, RNH₂</td>
</tr>
</tbody>
</table>

( ) denotes either a very low concentration or an improbable form. R = CH₃ appears to be dominant in almost all remote areas.
Table: 1.5

**Estimated Sulfur Budget of the Atmosphere of Terrestrial Tropics: (Unit: Tg s⁻¹)**

<table>
<thead>
<tr>
<th>Emission</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest Soils and Wet Lands</td>
<td>5 - 25</td>
</tr>
<tr>
<td>(mainly H₂S)</td>
<td></td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>1 - 10</td>
</tr>
<tr>
<td>(mainly SO₂)</td>
<td></td>
</tr>
<tr>
<td>Volcanoes (mainly SO₂)</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Soil Dust (Sulphate)</td>
<td>N.A.</td>
</tr>
<tr>
<td>Fossil Fuels and Industries</td>
<td>6 - 15</td>
</tr>
<tr>
<td>(mainly SO₂)</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>13 - 60 (+)</td>
</tr>
</tbody>
</table>

Table: 1.6

**Estimated Budget of Oxidised Nitrogen in the atmosphere of Tropics (Unit: Tg Y⁻¹)**

<table>
<thead>
<tr>
<th>Emission</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOIL</td>
<td></td>
</tr>
<tr>
<td>Rain Forest</td>
<td>2 - 5</td>
</tr>
<tr>
<td>Savana</td>
<td>3 - 8</td>
</tr>
<tr>
<td>Cultivated Land</td>
<td>1 - 6</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>6 - 19</td>
</tr>
<tr>
<td>BIOMASS BURNING</td>
<td></td>
</tr>
<tr>
<td>Plumes</td>
<td>3 - 6</td>
</tr>
<tr>
<td>Excess soil emission</td>
<td>0.5 - 3</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>3.5 - 9</td>
</tr>
<tr>
<td>Lightening</td>
<td>0.5 - 5</td>
</tr>
<tr>
<td>Fossil Fuel Combustion</td>
<td>3 - 7</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>13 - 40</td>
</tr>
</tbody>
</table>

1 Tg = 10¹² gram

Sources: The numbers are derived mainly from Galloway et al. (1985), Ryaboshapkp (1983) and from the book edited by H. Rodhe and R. Herrera (1988).