

1479

**INFLUENCE OF ATMOSPHERIC POLLUTANTS ON WET
DEPOSITION IN DELHI**

*Dissertation submitted to the Jawaharlal Nehru University
in partial fulfilment of the requirements
for the award of the degree of*

MASTER OF PHILOSOPHY

Submitted by

S. BALACHANDRAN

81p + Fig + tables

**SCHOOL OF ENVIRONMENTAL SCIENCES
JAWAHARLAL NEHRU UNIVERSITY
NEW DELHI - 110067**

July, 1996



जवाहरलाल नेहरू विश्वविद्यालय
JAWAHARLAL NEHRU UNIVERSITY
SCHOOL OF ENVIRONMENTAL SCIENCES
New Delhi-110067

CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "**Influence of Atmospheric Pollutants on Wet Deposition in Delhi**" has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, for the partial fulfilment of the award of Master of Philosophy. This work is original and has not been submitted, so far, in part or full, for any other degree or diploma of any University.

[Professor V. Rajamani]
Dean

[S. BALACHANDRAN]
Candidate

[Dr. P.S. Khillare]
Supervisor

ACKNOWLEDGEMENTS

I express my heartfelt gratitude to Dr. P.S.Khillare for his excellent guidance, valuable suggestions and encouragement throughout the course of this work. I wish to thank the Dean, School of Environmental Sciences, for providing the necessary laboratory facilities. I am also grateful to Prof. D.K.Banerjee for his constant encouragement during this work.

I am also grateful to CPCB and IMD for providing the required data.

I am thankful to Mr. Brahma Dutt Sharma for his kind assistance in chemical analysis. I express my thanks to Dr. S. Annadurai, Venkat, Subramanian, Guna and his room mates, Perumal, Krishna, Meenakshi, Siva, Archana, Madhavan, Subhakar, Ramkey, Chelladurai, Shyamlal, Vineet, Manju for their timely help and encouragement. I also wish to express my gratitude to Seema, Ashima, Faizan Ali for having helped me during sample collection.

I am thankful to my parents and my family members for their continuous encouragement throughout my study period in JNU.

Last but not the least, I would also like to sincerely thank Basanta and Sivaprakash for their excellent typing.

Finally I would like to extend my gratitude to UGC for having provided me with the junior research fellowship during the tenure of my work.

(S. BALACHANDRAN)

CONTENT

		Page No.
	ACKNOWLEDGEMENT	
CHAPTER - 1	INTRODUCTION	1-19
CHAPTER - 2	LITERATURE REVIEW	20-39
CHAPTER - 3	BACKGROUND AND OBJECTIVES OF THE STUDY	40-48
CHAPTER - 4	MATERIAL AND METHODS	49-56
CHAPTER - 5	RESULTS AND DISCUSSION	57-69
CHAPTER - 6	CONCLUSION	70-71
	REFERENCES	72-81

CHAPTER I

INTRODUCTION

OVERVIEW:

Human activities are changing the chemical climate throughout the world, leading to regional and global phenomena like global warming, ozone depletion, acid rain, etc. The root cause for all these changes is the over exploitation of fossil fuel, which leads to the imbalance in the carbon, sulfur and nitrogen budget, existing in nature. This imbalance is due to the introduction of excess amount of CO₂, SO₂ and NO_x into the atmosphere, which have caused the above mentioned phenomena and poses a threat to the survival of the human kind.

Since the industrial revolution, various human activities have been influencing the chemical climate namely,

- generation of electricity,
- smelting and refinement of metals,
- production and use of concrete, glass, ceramic and plastic materials,
- decomposition and incineration of sanitary and solid wastes,
- refinement and use of petroleum and petrochemicals,
- use of transportation vehicles,
- production and application of fertilizer, pesticides and other agricultural and silvicultural chemicals,
- disposal of excreta from human and domestic animals,

- burning of biomass and farm and forest residues and
- use of explosive devices in peace and war

There are essentially two kinds of pollutants, gaseous and particulates, which can be defined on the mode of formation as primary and secondary pollutants. Primary pollutants are directly produced from industrial and domestic activities, where as secondary pollutants are formed from the primary pollutants in the atmosphere by various chemical processes. On this basis Last and Watling (1991) defined four groups of pollutants as shown in Table 1.1

Trace species concentration in the clean troposphere and in polluted urban air is given in Table 1.2: The direct and indirect effect of sulfur and nitrogen oxide pollution has been summarized in Fig.1.1

Rain water is the main scavenger for most of the pollutants mentioned above. The rain water scavenges by reacting with the pollutants. High concentrations SO_2 and NO_x in the atmosphere leads to the lowering of the pH of rain water considerably. This phenomenon is called acid rain. Broadly acid rain can be defined as " A condition in which natural precipitation becomes acidic, after reacting with various pollutants in the atmosphere". The acidity of rain is governed by the overall charge of balance equation of ions in solution. When it is in equilibrium with existing carbon dioxide, the pH value of rain water is about 5.6. This is the lowest pH value that can be brought about by carbonic acid if distilled water were in equilibrium with atmospheric carbon-dioxide. But increasing quantities of strong acids in the atmosphere mostly from anthropogenic sources, are responsible for pH reading

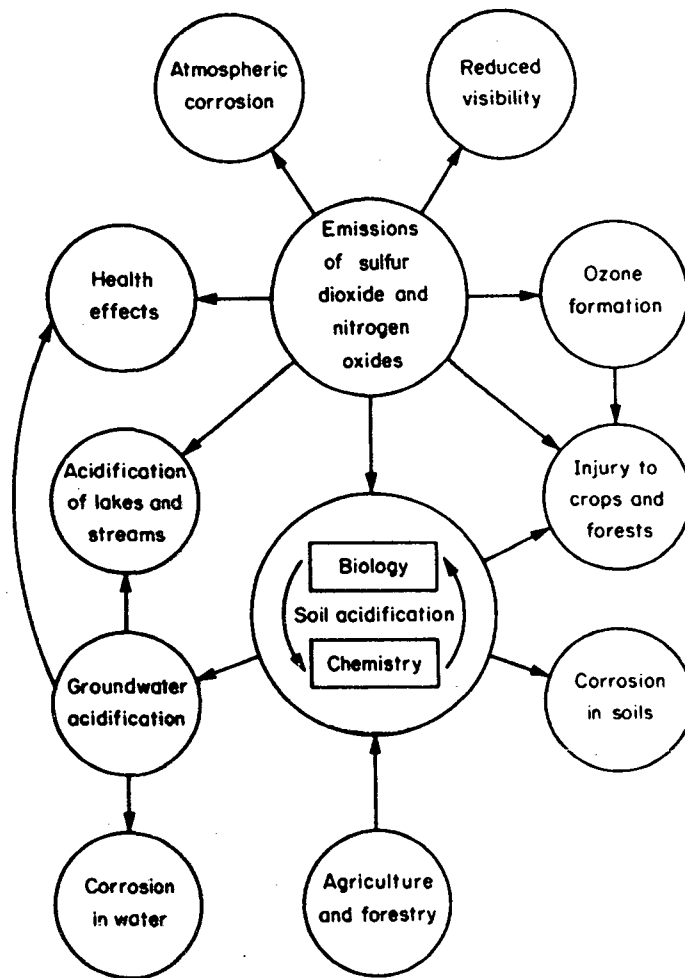


Figure 1.1 Direct and indirect effects of sulfur- and nitrogen-oxide emissions

Source :- Rodhe and Herrera (1988).

from 3.0 to 5.0. However, values as low as 2.1 have been recorded for individual storm at certain locations (Likens and Borman, 1974). Most of the acidity (70%) is due to SO_4^{2-} ions and the remainder to oxides of nitrogen (Marsh, 1978).

Table 1.1: Principal Chemical Pollutions

Gaseous; Primary	
Sulfur dioxide	SO_2
Nitric oxide	NO
Nitrogen dioxide	NO_2
Hydrocarbons	HC
Ammonia	NH_3
Carbon dioxide	CO_2
Gaseous; Secondary	
	NO ₂ from oxidation of NO
	Ozone (O ₃) and other photochemical oxidants formed in the lower atmosphere by the action of sunlight on mixtures of NO _x and hydrocarbons.
	Nitric acid from oxidation of NO _x
Particulate; Primary	
	Fuel ash
	Metallic particles
Particulate; Secondary	
	The reaction products of sulphuric acid and nitric acid with other atmospheric constituents, notably ammonia (NH_4) ₂ SO ₄ , NH ₄ NO ₃ etc).
	Sulfuric and nitric acid formed by oxidation of SO ₂ and NO _x respectively.

Source: Last and Watling, (1991)

Table 1.2: Trace species concentrations in the clean troposphere and polluted urban air, (Seinfeld, 1980).

Species	Concentration in ppb	
	Clean troposphere	Polluted Air
SO ₂	1-10	20-200
CO	120	1000-10000
NO	0.01-0.05	50-75
NO ₂	0.1-0.5	50-250
HNO ₃	0.02-0.3	3-15
O ₃	20-80	100-500
NH ₃	1	10-15
HCHO	0.4	20-50

The influence of airborne chemicals in acidification of air and precipitation is most pronounced in the region where gaseous sulfur and nitrogen oxide emissions are large and where the air contains only modest amount of acid-neutralizing substances such as ammonia, or alkaline dust (containing ammonium, calcium, sodium, magnesium and potassium). The role of airborne acidic and acidifying substances in the acidification of aquatic and terrestrial ecosystem is mostly pronounced in the regions where soils are naturally acidic and have very low cation exchange capacity and low sulfate absorption capacity. This usually occurs in the area where the bed rock contains only small amounts of limestone and other acid neutralizing minerals.

Acid precipitation is a problem of many dimensions and its ecological impact may be manifested in terrestrial and aquatic ecosystems. Some of the effects of acidic and alkaline substances present in the atmosphere on aquatic and terrestrial ecosystems are given (Table 1.3). Certain amount of acid rain can be buffered by the ecosystems without any serious consequences. However, the buffering capacity of ecosystems is finite and varies from one ecosystem, to another.

Table 1.3: Acidic and alkaline substances observed in the atmosphere and their effect on terrestrial and aquatic systems (+ acidifying, -neutralizing, 0 no significant effect).

Substance	Role in acidification	
	Terrestrial	Aquatic
H ₂ S, SO ₂ , H ₂ SO ₄	+	+
NO _x , HNO ₃	+,0	+,0
HCL, HF	+	+
Organic acids	+,0	+,0
NH ₃	+,0,-	0,-
Ammonium salts,	+	+
Alkaline dust	-	-

Source : Rhode and Herrea, 1988

1.2 HISTORICAL BACKGROUND OF ACID RAIN

Acid rain phenomenon was first identified in the city of Manchester, England in 1852, by an English chemist Robert Angus Smith. In 1872 Smith extended his studies to cover the United Kingdom, and published his classic book "Air and Rain".

Swedish researchers observed in 1920's that numerous small mountain lakes located at a high elevation in Scandinavia were 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. A new era in study of acid deposition began in 1955, when Acid rain was discovered to be a widespread phenomenon, as it was observed even in rural areas, far from urban anthropogenic sources. In 1955, Barrett and Brodin discovered acid rain in Scandinavia. In 1966, the highest acidic precipitation was measured in Netherlands (average annual pH 3.78).

The major foundation of our present understanding about acid rain and its effects were laid out by Eville Gorham. On the basis of his research in England and Canada, Gorham showed, in as early as 1955, that much of the acidity in precipitation near industrial regions can be attributed to combustion emissions. The progressive acidification of surface water can be traced to acid precipitation, and that the free acidity in soils receiving acid precipitation is primarily due to sulfuric acid.

Occurrence of acid rain in India had been a controversial issue until recently. The first-report on acid rain in India was presented by Mahadevan et al (1984) at Chembur, Bombay.

In 1972, acid rain problem was first raised by Sweden, as an international issue at United Nation's Conference on Human Environment at Stockholm. It is now one of the most significant international environmental issues. Acid rain has been correlated with environmental damage in many parts of the world including Japan, Norway, Sweden, Canada, Northern Europe and United States.

1.3 ATMOSPHERIC SCAVENGING PROCESSES

In principle, the available routes for scavenging foreign material from the atmosphere may be separated into:

- a) Deposition,
- b) Conversion to normal atmospheric constituents.

Any pollutant not eliminated by the above mentioned mechanisms, accumulates in the atmosphere. The former, which principally, occurs in the lower atmosphere by oxidation and combination of pollutants to give solid or liquid particulates, transported to the ground by a hydrometeor (rain, snow, hail, etc.), is termed as wet deposition: deposited directly, the process known as dry deposition (Irwin and Williams, 1988). The latter occurs in the upper atmosphere, through disruption of more complex gaseous or vapour molecules by high energy, short wavelength radiation from the sun (Stern 1976).

1.3.1 Wet deposition

Wet deposition is an important and highly variable intermittent process in the pathway from source to receptor. During precipitation, removal of pollutants may be brought about by capture and transformation within cloud droplets (in-cloud scavenging) or by interception of the pollutants beneath the cloud by the falling precipitation (below-cloud scavenging). The relative importance of in-cloud and below-cloud scavenging is not known, but probably depends on cloud.

1.4 MECHANISMS OF WET DEPOSITION

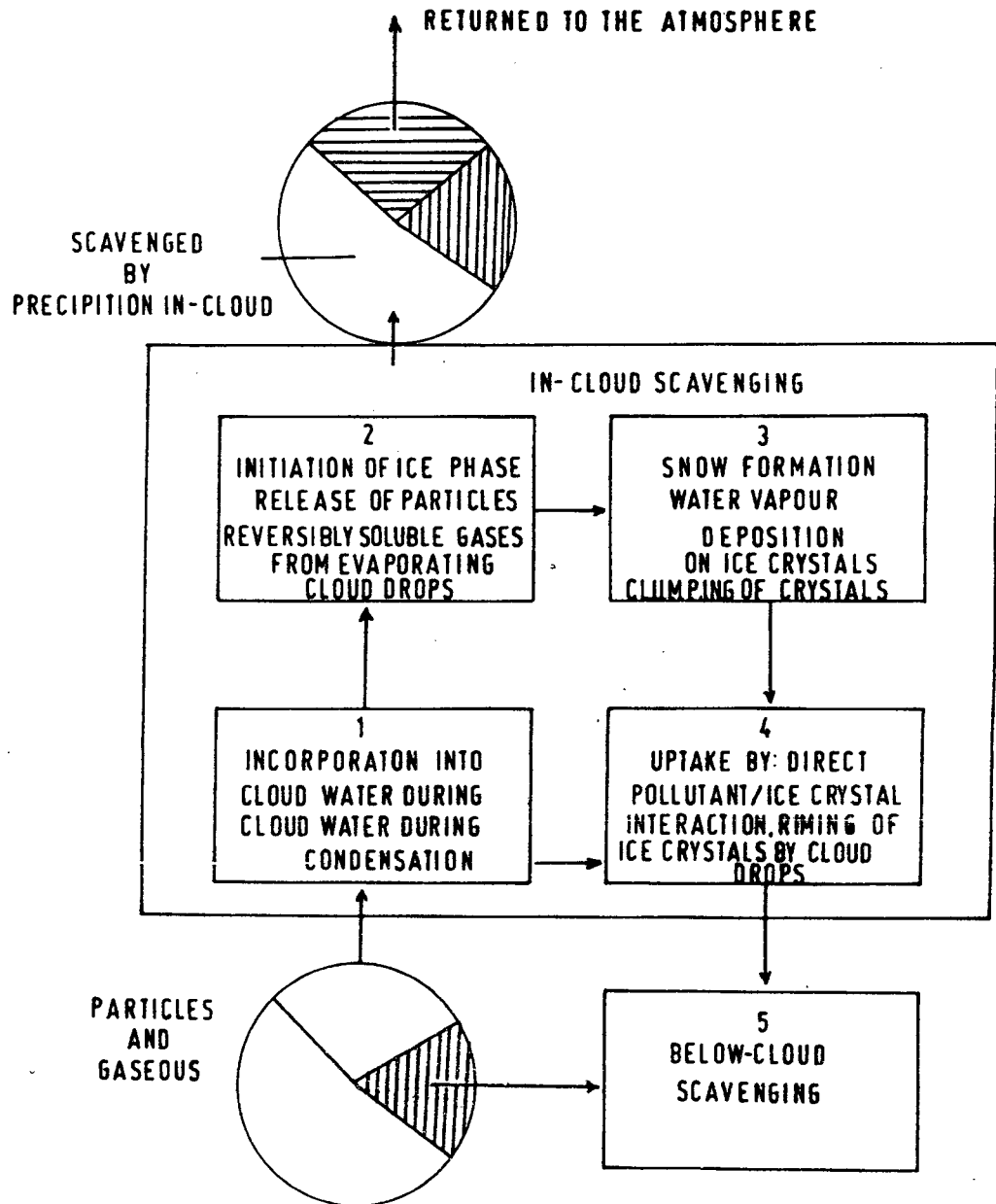
1.4.1 Precipitation scavenging

Pollutants are scavenged from the atmosphere by precipitation in the sequence of process depicted in Fig.1.2.

Condensation of water on hygroscopic aerosols entering a cloud as well as dissolution of soluble gases such as HNO_3 and SO_2 (step 1) leads to supercooled cloud droplet containing inorganic ions, insoluble matter and organic constituents. A fraction of SO_2 and NO_2 may also be converted to SO_4^{2-} and NO_3^- , shortly there after. Barrie (1985) deduced that 20 to 100 % of SO_2 entering rain storms is oxidized to SO_4^{2-} . Leitch et al (1985) says considerable amounts of cloud water NO_3^- are formed by NO_2 oxidation in both winter and summer.

Two things can happen to the cloud water: (i) if ice is present in-cloud, cloud water can evaporate. Water vapor, driven by the difference in saturation vapor pressure of water and ice, diffuses from the drops to ice crystals (steps 2 and 3). The gaseous and particulate matter in cloud water is then returned to the atmosphere in a form that is not necessarily the same as when it entered the water (ii) cloud water can be captured by large snow crystals (diameter $> 200 \mu\text{m}$). This process is called "rimming". It is the collection by snow of supercooled cloud drops 2 to 50 μm diameter by inertial impaction and interception as the heavier snow crystals fall past the smaller drops. The cloud drops freeze upon contact. Pollutants trapped in cloud water thereby, enter precipitation and fall from the cloud.

Fig.1.2 The Precipitation Scavenging process



Source :- Barrie and Schemenauer (1986).

Particles and gases that do not enter cloud water during condensation (step 1) or that are released back into the air during vapor growth of the ice phase (step 2) can be incorporated into ice crystals (steps 3 and 4). This occurs by Brownian diffusion, electrical attraction and inertial impaction. Particles and gases that are not scavenged from the cloud by the precipitation processes discussed above leave the cloud at the evaporating edges. As a result of chemical reactions in cloud water, the chemical composition of air at the outflowing edges can be different than that at the inflow. Furthermore, the size distribution of particulate matter can be changed as a result of in-cloud chemical and physical transformations (Barrie and Schemenauer, 1986). Rain and snow falling below the cloud base scavenge particles and reactive gases from the atmosphere by the same mechanisms as they do within cloud with the exception of the rimming process and with the addition of phoretic forces caused by evaporation in the sub-saturated air beneath the cloud (Martin et al., 1980).

1.5 PATHWAYS FOR FORMATION OF SULFATES AND NITRATES

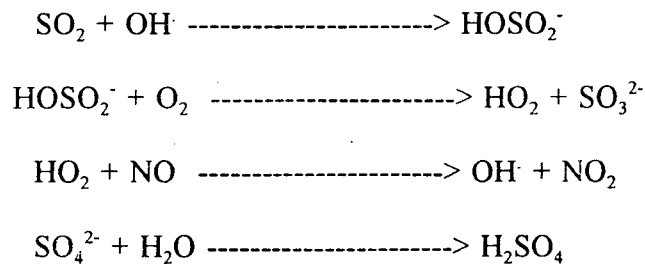
There are many different pathways for transforming SO_2 and NO_x into sulfates and nitrates. These processes are of two types, homogenous and heterogenous. In the homogenous process, some take place in gaseous phase and some take place in aqueous solution in liquid droplets. The heterogenous process takes place on the surface of solid particles as well as on liquid droplets.

SO_2 has been observed to be oxidized in the atmosphere by homogeneous gas phase reaction at the rate of few percent per hour and by liquid phase of cloud at a

much faster rate. Under various meteorological conditions different pathways may be dominant for the formation of sulfuric acid.

1.5.1. Homogeneous gaseous phase reaction

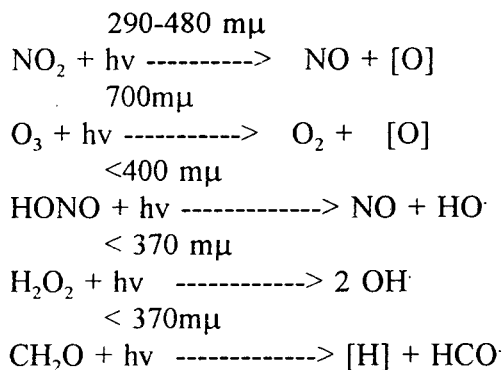
Oxidation of SO₂ to sulfate in gaseous phase may occur by reaction of SO₂ with various oxidants, like OH radicals. According to reviews of Burton et al (1983); Calvert and Stockwell (1983) in SO₂ gas phase chemistry, the reaction of SO₂ with OH radical appears to be major gaseous phase oxidation of SO₂ at high humidity.



White (1988) illustrated that there are certain central features in the atmospheric chemistry sequence that tend to wed the pollution chemistry of sulfur species, carbon species, nitrogen species, even halogen species. For this he used allegorical reference earlier used by Dan Albritton of NOAA, where he depicted ozone as pollutant "**godfather**" and hydroxy radical as "**hitman**".

There are a limited number of reactions that can absorb photons from the sun and the troposphere, which are referred to as "**trigger**" mechanism.

"The Triggerman"

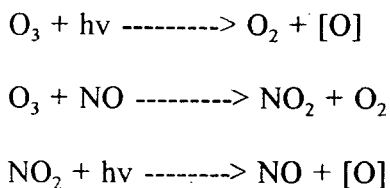


Source: (White, 1988)

The chemical reaction which leads to acid rain begins as a photon hits an ozone molecule to form oxygen and free oxygen atom which is very reactive (Pickering and Owen, 1992).

Ozone photolyses within the visible and near ultraviolet ranges of wavelength forming oxygen atom. Ozone reacts with nitric oxide to form NO_2 , and NO_2 is a very effective source for reactive oxygen atom. So ozone plays an essential role in setting the stage for all the other chemistry that goes on behind it, and also it plays an essential role in setting the stage for the "hit man".

Ozone: "**The god father**". (Albritton).

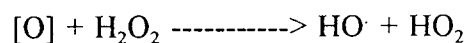
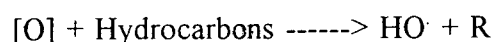
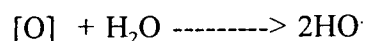


The oxygen atoms shed by the photo decomposition of ozone are reactive with water vapor molecules to forming hydroxyl radicals. This oxygen also can react with

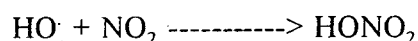
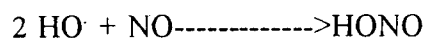
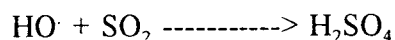
hydrocarbons again to form hydroxy radicals and organic free radicals. In addition, atomic oxygen can react with H₂O₂ to form hydroxyl radicals and also HO₂. These are not only the mechanism for formation of hydroxyl radicals but they are probably among the most important.

Hydroxyl Radical: "**The hit man**"

Formation:



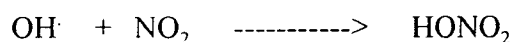
Attack:



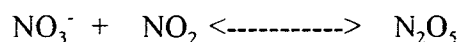
The hydroxyl radical is a tremendously effective oxidation agent for converting SO₂ to sulfate or sulfuric acid in the atmosphere. It is only the amount of pollutant in the atmosphere which determines the amount of acid ultimately generated. It is technically a very important reaction but it is a complex reaction. In the stratosphere the rate-limiting step for oxidation of SO₂ to H₂SO₄ is believed to be the reaction of SO₂ with the hydroxyl ion (OH⁻), leading through a sequence of reactions to the production of new sulphate particles, or condensation of pre-existing particles. SO₂ acts as a catalyst in the production of O₃ but SO₂ can inhibit production

by absorbing incoming radiation, since it absorbs radiation strongly in the range 235-180 nm, weakly in the range of 340-260 nm, and very weakly in the range of 390-430 nm (Pickering and Owen, 1992).

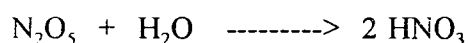
This hydroxyl radical also reacts with nitrogen oxide to form nitrous acid and with NO₂ to form nitric acid. Nitric acid is formed rapidly from OH reaction with NO₂ during daylight hours.



At night, however, the concentration of OH[·] is small and this reaction may be negligible. Nitric acid generation can take place at night by other pathways (Richard, 1983). One pathway which is believed to be important, involves N₂O₅, which is held in an equilibrium concentration by



The reaction N₂O₅ with H₂O is believed to generate nitric acid

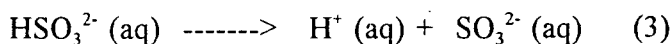
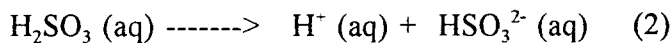
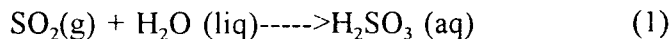


This reaction can occur homogeneously in the gas phase as well as heterogeneously at the surface of aerosol or droplet. So in the formation of sulfates and nitrates, ozone the "godfather" hydroxyl as the "hitman" and the "trigger" reactions of the sun play an important role.

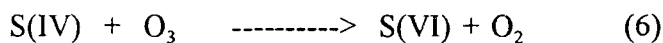
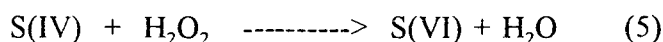
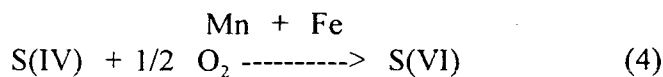
1.5.2 Aqueous phase reaction

Major aqueous sulfate formation mechanism includes the reaction of dissolved SO₂ with H₂O₂, O₃ and O₂, catalyzed with Fe and Mn. (Seigneur and Saxena, 1987).

Sulfur dioxide is soluble in water and forms sulfurous acid, H_2SO_3 or $\text{SO}_2 \cdot \text{H}_2\text{O}$, a weak acid that ionizes to bisulfite, HSO_3^{2-} , and sulfite, SO_3^{2-} ions.

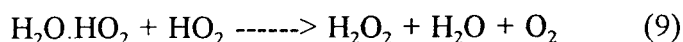
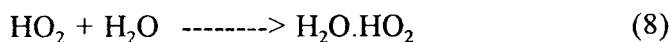
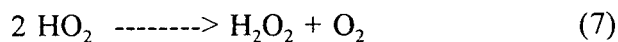


Both hydrogen peroxide (H_2O_2) and Ozone (O_3) are capable of oxidizing SO_2 in aqueous solution. The aqueous phase oxidation of SO_2 is described by the following reactions



Species S(IV) and S(VI) represents two different oxidation states of sulfur corresponding to SO_2 (H_2SO_3 , HSO_3^{2-} and SO_3^{2-}) and SO_4^{2-} (H_2SO_4 , HSO_4^-). The reaction rate of equation (6) decreases as the pH decreases this oxidation rate is therefore self limiting. The reaction rate of equation (5) increases as pH decreases, however this reaction may be oxidant limited. The oxidation of S(IV) catalyzed by trace metals equation (6) is of zero order with Mn, first order with Fe and synergism may occur when both metals are present.

H₂O₂ is formed in the atmosphere mainly by reaction of hydro-peroxy radicals (HO₂).



Calculations of Middleton et al (1980) suggest that under day time conditions, the gas phase formation of H₂SO₄ and the subsequent condensation of aerosol and aqueous phase oxidation of SO₂ by H₂O₂ are principal mechanism for atmospheric sulfate formation. Middleton et al (1980) found out that sulfate formation at night was dominated by aqueous phase mechanism and was generally lower than the day time sulfate formation. Saxena et al (1986) suggests reason for predominant aqueous phase pathway in night that the reaction of SO₂ with O₂ depends strongly on Fe and Mn concentration and on the liquid water content of aerosol which in turn is dependent on the relative humidity and background concentration of sulfate, nitrate and ammonia. The aqueous reaction of SO₂ with H₂O₂ becomes important only at low temperature when the solubility of these gases is very high. The aqueous phase oxidation of SO₂ by O₃ and other oxidants like PAN, HNO₂, CH₃COO₂H and CH₃O₂H are not important for aerosols because atmospheric aerosols are not generally too acidic for these reactions, which become significant at relatively high pH. Therefore, the study of SO₂ oxidation in polluted background atmosphere needs to include only the gas phase reaction of SO₂ with OH radicals and aerosol phase reaction of SO₂ with O₂ and H₂O₂, other chemical pathways seem to be insignificant.

Table 1.4 : Mechanism by which SO₂ is converted to sulfates

Mechanism	Overall reaction	Factors on which sulfate formation primarily depends
1. Direct photooxidation	$\text{SO}_2 \xrightarrow[\text{+ water}]{\text{light, O}_2} \text{H}_2\text{SO}_4$	Sulfur dioxide concentration, sunlight intensity
2. Indirect photooxidation	$\text{SO}_2 \xrightarrow[\text{HO}_2, \text{HO}_2, \text{RO}_2 \text{ radicals}]{\text{smog water, NO}_x, \text{organic oxidants}} \text{H}_2\text{SO}_4$	Sulfur dioxide concentration, organic oxidant concentration OH, NO _x , HO ₂ , RO ₂
3. Air oxidation in liquid droplets	$\text{SO}_2 \xrightarrow[\text{NH}_3 + \text{H}_2\text{SO}_3 \xrightarrow{\text{O}_2} \text{NH}_4^+ + \text{SO}_4]{\text{liquid water}} \text{H}_2\text{SO}_3$	Ammonia concentration
4. Catalyzed oxidation in liquid droplets	$\text{SO}_2 \xrightarrow[\text{heavy metal ions}]{\text{liquid water, oxygen}} \text{SO}_4^{2-}$	Concentration of heavy metal (Fe, V, Mn) ions.
5. Catalyzed oxidation on dry surfaces	$\text{SO}_2 \xrightarrow[\text{carbon particle}]{\text{oxygen, water}} \text{H}_2\text{SO}_4$	Carbon-particle concentration (surface area).

Source : Wilson E.W., (1978)

1.6 NEUTRALIZATION IN WET DEPOSITION

Rain water having pH greater than 5.6 implies its interaction with alkaline acid-neutralizing materials, while Munger (1982); Lewis et al (1984); Pratt et al (1984); Wagner and Steele (1987) and Zhao et al (1988) suggests that soil derived alkaline dust containing mainly Ca^{2+} , K^+ , Mg^{2+} and Na^+ may react with and neutralizing strong acids in the atmosphere.

"Buffering is a broad term that can include all forms of H^+ removal from solution but is often used specifically to refer to removal in a potentially reversible reaction, such as ion exchange. "Neutralization" is a narrow term, referring specifically to removal of H^+ in an irreversible reaction such as formation of water in a reaction of strong base with a strong acid. For convenience, acid and neutralizing capacity (ANC) is used as the general term for removal of H^+ from solution (Gatz et al., 1986).

The major H^+ removal reaction in cloud originated precipitation water includes:

- i) Ion exchange in which cation absorbed by clay minerals or other substrates are exchanged for H^+ ion in solution and
- ii) Mineral weathering (dissolution).

Cation exchange reactions are essentially instantaneous, reaction rates being usually diffusion limited. Mineral weathering, on other hand, may be relatively rapid as in the case of finely divided CaCO_3 particles or quite slow (days to weeks) as in the case of silicates.

The general situation is that the ANC attributed to a "base cation" in precipitation is less than or equal to the soluble portion of the element (since the element can also be introduced as unnatural salt). This value in turn is less than or equal to the total concentration of the element in precipitation, since elements can also occur in essentially insoluble form. Few measurements found in the literature of Gatz (1984), Gatz et al (1985) suggest that Na^+ and Ca^{2+} are about 95 to 100% soluble in precipitation, Mg^{2+} about 80%, and K^+ near 50%.

Saxena et al (1991) suggests that in Agra (India) the alkaline constituents of rain water are mainly the crustal elements Ca^{2+} and Mg^{2+} derived from soil. The neutralization is substantiated by the fact that there is an excellent positive correlation between HCO_3^- and Ca^{2+} and Mg^{2+} . It can therefore be interpreted that HCO_3^- is produced from MgCO_3 and CaCO_3 which are generated from soil and air and pH of soil varies from 6.5 to 10.5. So soil is also one of the major contributing factors in sustaining the alkaline nature of rain water. The pH has a high correlation with Ca^{2+} and Mg^{2+} and a poor correlation with SO_4^{2-} and NO_3^- at both sites in Agra. This further shows that the alkaline components, Ca^{2+} and Mg^{2+} contribute to pH, whereas the secondary pollutants SO_4^{2-} and NO_3^- do not affect pH significantly.

The pH of precipitation is determined by its content of both acids and bases, Gatz et al (1986) by a simplified model of acid buffers which indicate that NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ and Ca^{2+} buffer between 25 and 50% of patented acid in U.S. precipitation.

When NH_3 is released, the upward flues of NH_3 are depleted by conversion to NH_4^+ ion by reaction with acidic species. Reaction with OH radical also reduces NH_3 concentration but only at an insignificant rate. When high humidity is there NH_3 will increase SO_2 oxidation to $(\text{NH}_4)_2\text{SO}_4$ particulate.

CHAPTER II

LITERATURE REVIEW

There are very good reasons to consider acidification as one of the most serious environmental problems facing industrialized tropical countries where significant rate of pollution growth and current emphasis on agriculture and economic development virtually ensures that large increases in SO₂ and NO_x emissions will occur in the decades to come.

The phenomenon of acid rain has been known for about thirty years, but it is only very recently that research in precipitation chemistry has been developed so as to understand and prevent the acidification of precipitation. 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 rain water can change ecosystems considerably. It includes the following adverse effects:

- Acidification of natural water resources and fresh water system,
- Acidification of Terrestrial ecosystem,
- Leaching of the soil,
- Damage to construction materials and cultural resources (corrosion, old monuments deterioration),
- Atmospheric visibility,
- Human health and
- Ground water

Lakes and reservoirs 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. As the pH of lake decreases, the concentration of several potentially toxic metals such as Aluminium (Al), Iron (Fe), Manganese (Mn), Copper (Cu), Nickel (Ni), Zinc (Zn), Lead (Pb), Cadmium (Cd), and Mercury (Hg) increases (Dickson, 1980; Schofield, 1980). 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 now it appears that aluminium which dissolves from the soil by acid precipitation, is primarily responsible. As pH decreases, insoluble aluminum becomes soluble and maximum toxicity of aluminum to fish occurs around pH 5.0.

The adverse effects of increasing acidity on aquatic ecosystem can be understood well by focusing on a report by Environment Canada (1983). Scientists, gradually and artificially after the interval of one year period, increased the acidity of a lake by adding H_2SO_4 and made a detailed study on chemical and biological changes in it. The important observations of their research have been summarized in the Table 2.1.

The above experiment provides a valuable guidance in the process of acidification, which might be expected in the near future. It also shows that a small decrease in pH causes major changes in the aquatic life.

Researchers are beginning to evaluate the role of acid rain in increasing the vulnerability of trees to disease and insects. Direct, visible acid rain damage to



foliage is not being seen, but the dramatic and striking death and die back of trees in Central Europe, Czechoslovakia and Germany is a catalyst for such concerns. A paper by Hinrichsen (1987) and Nihlgard (1985) says, increased acidity causes leaching of calcium and magnesium and at the same time increases aluminum concentration, which is toxic to plants.

Another effect of acid rain on the forests includes leaching of easily acid soluble components from foliage, from trunks of trees, and from the upper layers of the soil. For two reasons, high aluminum concentration appears to be harmful to many higher plant species through effects on their root system, firstly, cell division in root is inhibited and the roots lose their flexibility and plasticity, becoming short and brittle and secondly, aluminum has a number of effects on other ions, amongst which the interference with phosphorus uptake and precipitation as aluminum phosphate, are chief. Many people like Binns (1985); Casado et al (1989) have worked on acid rain and forest decline

Groundwater accumulates very slowly by the percolation of surface water through soil and bedrock to the water table. Scientific evidence indicates that ground water acidification and its consequent contamination by acid soluble metals, is occurring in soil areas, where the major metals of concern being lead, copper and zinc, which may leach out from water pipes and containers and aluminum coming from the bed rock itself.

Table 2.1: Effect of Acidification on a aquatic ecosystem.
(Environment Canada, 1983).

pH	Impacts
6.1	<ul style="list-style-type: none"> * Increase in bacterial activity, * Increase in invertebrate aquatic animals, small animals which are food for larval fish, insects and large crustaceans, * Increase of green algae, * Decrease of brown algae, which is normally dominant, and * Increase of insects.
5.8	<ul style="list-style-type: none"> * 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.
5.6	<ul style="list-style-type: none"> * 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.
5.4	<ul style="list-style-type: none"> * 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,
5.1	<ul style="list-style-type: none"> * Reproduction failure of white sucker.

Stone buildings, statues, and monuments are eroded by a number of airborne pollutants, including acid rain. Building materials like steel, paint, plastics, cement, masonry, galvanized steel, limestone, marble and sandstone also risk damage (Cheng et al.,1987).

The effects of the various pollutants cannot yet be reliably separated from each other. However, it is generally accepted that the major single corroding agent of building material is sulfur dioxide and its by-products,(Zhao and Xiong, 1987).

Sandstones and limestones have often been employed as a material for monuments and sculptures. When sulfur pollutants are deposited on a sandstone or a limestone surface they react with the calcium carbonate in the material, converting it into the readily soluble calcium sulfate (Gypsum), which washes off with the rain. The disfiguration and dissolution of famous statues and monuments like the Acropolis in Athens, Taj Mahal in Agra, India (Gauri and Holdren, 1989); famous art treasures in Italy, etc., has accelerated greatly over the past 30 years, often after they have stood for centuries.

Much work is going on through out the world on acid precipitation, some of the recent major work done are;

Table 2.2: Recent works on acid rain in the world

Countries	Researchers
Spain	Casado et al., (1989) Camarero and Catalan, (1993)
France	Collins et al., (1989), Sansui et al., (1996)
Greece	Dikaiakos et al., (1990), Samara et al., (1992), Simirioudi and Siskos, (1992).
Canada	Chan et al., (1987), Ru.(1988) Treolar (1993).
USA	Sisterson and Shannon (1990); Byron et al., (1991); Kessler et al., (1992).
Turkey	Al-Momani et al., (1995).
Arabian- Gulfcoast	Ahmed et al., (1990) .
Australia	Low, (1988), Ayers & Gillet (1988).

The concentrations of sulfate, nitrate, ammonium, calcium, and hydrogen ions (pH in rain) have been measured occasionally at many tropical locations during the past decades by, Eriksson (1952); and Granat et al (1976). Some of these data are unacceptable today because the methods used in collecting, preserving and analyzing the samples in some cases do not conform to current standards for field collection and laboratory analysis procedures.

Recent observations show large variations in the acidity of rain water from region to region in the tropics. Over continental Australia and South America, rain water with pH values in the range 4.3 to 4.8 have been observed by Galloway et al

(1982); Ayers and Gillett (1988); Sanhueza et al (1988). Over India, the pH values are most often above 6.0 as observed by Khemani et al (1987). Similar high values are found at some stations in China by Zhao and Sun (1986); Zhao and Xiong (1987). Cloud water over Northern Australia has been observed to have pH values as low as 3.8 (Ayers and Gillett, 1988). Thus throughout the world Acid precipitation is the subject of several research projects.

SO₂ emission is primarily a result of fossil-fuel combustion, while natural emissions, arise in approximately equal proportions from terrestrial and marine sources. Global natural emission of sulfur have been estimated to lie in the range of 50-100 Tg S y⁻¹ (Moller, 1984) (1Tg = 10¹²g), while man-made emissions have been calculated to be ~ 80 Tg S y⁻¹ in 1979 and ~ 64 Tg Sy⁻¹ in 1970 (Varhelyi, 1985). Consideration of spatial distribution, however shows that sulfur emissions are greatest in tropical areas (Moller, 1984; Rodhe and Herrera, 1988).

Estimates of tropical emissions of sulfur and oxidized nitrogen are given in Tables 2.3 and 2.4. Some recent measurements of NO emissions from tropical soils by Johansson et al (1988); Kaplan et al (1988), are also taken into account.

The most significant contribution to the sulfur flux over tropical land areas comes from natural emissions from soils and plants (mainly as H₂S), emission of SO₂ from burning of biomass, and combustion of fossil fuels. Although industrial sulfur emissions in the tropics are smaller than those in northern temperate latitudes, it is clear that human activities, in the form of industrial processes as well as biomass burning, already represent a major proportion of all sulfur emissions in tropical land areas (Table 2.3).

Table 2.3: Estimated sulfur budget of the atmosphere of terrestrial tropics (between 30°N and 30°S). Unit: Tg S per year (1 Tg=10¹²g)

Emission	
Forest soils and wetlands (mainly H ₂ S)	5-25
Biomass burning (mainly SO ₂)	1-10
Volcanoes (mainly SO ₂)	1-10
Soil dust (sulfate)	?
Fossil fuels and industry (mainly SO ₂)	6-15
Total	13-60(+)
Deposition	
By precipitation (sulfate)	5-20
Dry deposition (SO ₂ , sulfate)	2-10
Total	7-30

Source: Rhode and Herrera, 1988.

Table 2.4: Estimated budget of oxidized nitrogen for the atmosphere of terrestrial tropics (between 30° N and 30° S). Unit: Tg N per year (1 Tg = 10¹²g).

Emissions		
Soils		
Rain forest	2-5	
Savanna	3-8	
Cultivated land	1-6	6-19
Biomass burning		
Plumes	3-6	
Excess soil emissions	0.5-3	3-9
Lightning		
Fossil fuel combustion		3-7
Total		13-40
Deposition		
By precipitation		
Dry deposition		
NO ₂	< 2	
HNO ₃	< 2?	
Other nitrogen compounds	?	1-5 (+)
Total		3-15(+)

Source: Rodhe and Herrera, 1988.

Chan et al (1987) deduced that apart from H_2SO_4 and HNO_3 , organic acids also contribute acidity to precipitation. Su et al (1979) found that formaldehyde which produced formic acid by oxidation is also found in rain water. Organic acids, primarily formic (HCOOH) and acetic acid (CH_3COOH), have been shown by Keene et al (1983), to contribute substantially to the acidity of tropical rain, but little is known about the mechanisms that introduce or produce them within the atmosphere.

HCl which has anthropogenic origin, such as paper industries and refuse, is found to be a source of precipitation acidity together with HNO_3 and H_2SO_4 in Ban sur Meurthe, Eastern France by Sansui et al (1996). Its high solubility in water does not permit transport over long distance.

Al-Momani et al (1995) found that the main bases which neutralize the acidity in precipitation are CaCO_3 and NH_3 , while Khemani et al (1985) found that Ca^{2+} , Mg^{2+} and Na^+ may also neutralize strong acids. The main source of CaCO_3 are the suspended soil particles. Wind-blown soil consists of coarse particles with diameter larger than $2.5 \mu\text{m}$ (Raemdonck et al., 1986). Source of NH_3 are more variable than CaCO_3 . While Vong (1990), says that on a global scale, the ocean is a dominant source for ammonia whereas on a regional scale, Buijsman et al (1987) deduced that the NH_3 present in precipitation was due to livestock farming. Bridgman (1992); Crawley and Sievering (1986) say it might be due to the application of NH_4^+ containing fertilizers. Barnard (1986), showed that unpaved roads have also been shown to have a role in the neutralization processes.

Many long range transport-transformation models done by Fay et al (1985); Irwin and William (1988), assume a proportional relationship between emission level and consequent transformation to acid species. However, there are many physical and chemical factors that, alter this proportional relationship. These factors include distance from source region (Clarke et.al., 1987), short term meteorology (Dillon et al., 1988) long term climatic factor (Irwin and William, 1988), the abundance of potential catalyst, hydrocarbons, and oxidising agent like O_3 , H_2O_2 , as well as other competing acid forming species (Rodhe et al., 1981; Clark et al., 1987), precipitation pH (Winkler, 1984; Cheng et al., 1971; Morgan, 1982). All these factors can affect the rate of transport, transformation and deposition.

The atmospheric pollutants, SO_2 and NO_x undergo various chemical transformation and are incorporated into sulfates and nitrates. These solutions are acidic. The acidic sulfates and nitrates are removed by wet or dry deposition to earth surface.

In the tropics, there have been no studies on the rate of oxidation of hydrocarbons or nitrogen oxides, while only one study on the rate of homogeneous oxidation of sulfur dioxide to sulfuric acid done by Roberts and Williams (1979) in the Mt. Isa copper smelter plume in Northern Australia is available. This study has shown a far slower oxidation rate than those expected from the modelling studies (based on the understanding from temperate latitude studies) but reasons for the difference remain unknown. Absolute neutral pH of rain water should be 7.0. In equilibrium with pH acidity of rain water will be 5.6, which is the demarcation

line for acid precipitation. However, in absence of common basic components like NH_3 , CaCO_3 , rain water pH could be expected to be about 5.0 due to natural sulfur compounds (Charlson and Rodhe, 1982).

Some measurements of the inorganic composition of aerosols exist for the tropical atmosphere, e.g. sulfate, nitrate, ammonium and calcium (Huebert and Lazrus, 1980; Savoie, 1984; Ayers and Gillett, 1988). These can be used to interpret rain water composition measurements and to estimate atmospheric rates of scavenging by precipitation, but only a few measurements of the gas-phase precursors of these inorganic species exist for the tropics.

Galloway et al (1982) found the background pH value of 5.0 or greater in remote areas with relative contribution of H_2SO_4 , HNO_3 and other organic acids to the acidity of precipitation. The pH value below 5.0 were observed in Silent Valley forest, India. (Rao et al., 1993) and also pH value below 3.0 are also found in rural parts of Europe (WHO, 1978). So it can not be said that the precipitation below pH 5.0 is mainly influenced by man-made sources and can be considered as acid rain (Seinfeld, 1985)

At normal concentration and pressure of carbon dioxide in the atmosphere the equilibrium value of pH of rain would be 5.65 at 20°C. But, Mukherjee and Krishnanand (1981) suggest that in tropical countries where atmospheric temperature is high, lower solubility and dissolution rate of carbon dioxide added with rapid process of cloud formation and precipitation results in higher pH, and concluded that pH of rain water over India should be close to 7.0 which is the neutral value of pure distilled water.

Chan et al (1987); Meenakshy et al (1992); Dasch and Cadle (1984), (1985) have observed that sulfates were main contributors to the acidity of precipitation in most places but Ahmed et al (1990) deduced in West Arabian coast that nitrates are found to be contributing more to acidity in India. Mukopadhyay et al (1992), found that pH was highly related to nitrates than sulfates in Indian Background Air Pollution Monitoring Network (BAPMoN) stations.

During the early rainfall when airborne dust is more, the precipitation pH is low, neutralization capacity is more rapid and extensive than during the latter stages of rainfall when the wet precipitation pH is higher and amount of airborne dust is low (Applin and Jersak 1986, Ravichandran and Padmanabhamurthy, 1994).

Byron et al (1991) found that the variation in pH was closely associated with change in nitrate concentration in central Sierra, Nevada. While Samara et al (1992) says that change in pH was due to chloride in Tessoloniki, Greece and Low (1988) found that it was due to fluoride in lower Tamar valley, Australia.

Farmer (1987) demonstrated that time trends in sulfate and nitrate deposition may differ in response to the influence of changes in precipitation amount.

Dillon et al (1988) have demonstrated a strong correlation between emissions of SO_2 and concentrations and rates of bulk deposition of SO_4^{2-} and H^+ in central Ontario from 1976 to 1985. Hedin et al (1987) found significant decreasing trends in SO_4^{2-} concentration at Hubbard Brook, NH and at five out of eight NADP monitoring scale in NE and Midwest U.S. since 1978, due to declining annual emission level of SO_2 and NO_x .

Gatz (1991) demonstrated, high concentration of H^+ in U.S were in convective showers and thunderstorms during summer. Ahmed et al (1990) deduced that, dissolved ions showed an inverse relationship with rainfall depth. While Lindberg, (1982); and Mukherjee et al (1985) showed that ionic concentration decreased with increased rainfall amount. Higher concentrations of H^+ in precipitation were reported during summer in North American countries by Wolff et al (1979); Chan et al (1987); Byron et al (1991); and Gatz (1991), while in Europe it was reported to be higher in winter by Gatz (1991) and also in Japan by Yamaguchi et al (1991). H^+ ion concentration was reported to be maximum in winter and minimum in summer by Yamaguchi et al (1991).

Subramaniam and Saxena (1980), have deduced that the earlier shower has higher total dissolved solids (TDS) concentration which decreases afterwards. Sisterson and Shannon (1990) & Marquardt and Ihle (1988) have shown that drizzle and snow has more concentration of all ions than normal rain and drizzle falling from lower clouds and very small droplets is very effective in capturing the air pollutant.

Ahmed et al (1990) deduced that the H^+ increases with increase in rain depth. Both sulfates and nitrates in precipitation are due to rain-out process incorporated in the clouds where as magnesium and calcium are due to wash-out which nutrients, acidity. Ravichandran and Padmanabhamurthy (1994) showed that after complete wash-out of cations, the acidity is due to the rain-out of sulfate and nitrate picked up .

Khemani et al (1987) studied the ionic composition of cloud and rain water samples along with pH value at Pune region in India. They have shown that pH is influenced by alkaline properties of soil-oriented components (Ca^{2+} , K^+ , Mg^{2+}) present in high concentrations in cloud and rain water. The effect of acidic components (SO_4^{2-} and NO_3^-) are negligible and are completely neutralized by the alkaline components.

Diakaiakos et al (1990); Samara et al (1992); Sanusi et al (1996) have shown acidity is largely due to anion deficit and probably also due to lack of bicarbonate ion and short chain organic acids. While, Galloway et al (1982); Dokiya et al (1987), and Sanusi et al (1996) when comparing the urban area, found that ionic concentration in rural areas are generally lower since human industrial activities are very less. In Eastern France, Sansui et al (1996), have demonstrated that, NH_4^+ is equal to NO_3^- and SO_4^{2-} which shows that NO_3^- and SO_4^{2-} in rain essentially originated from ammonium sulfate and ammonium nitrate aerosol.

There is no substantial evidence yet of soil or water acidification or forest damage due to acid rain in India. Because in India rain water is supposed to have substantially higher pH value than that of CO_2 - equilibrated water because our soils are by and large rich in alkaline components like Ca^{2+} , Mg^{2+} etc which is a major source of aerosols in the atmosphere which acts as a condensation nuclei for water vapor. The influence of alkaline particle, on the increase of pH in rain water in India has been demonstrated by Varma (1989a) and Khemani et al (1985b). Naik et al (1988) has ruled out long range transport of acid precursors coupled with

cations. In India, coal has low sulfur content, and with relatively few automobiles the rainy season acts as an effective air scrubber. Varma (1989a) has assessed that, the over all possibility of occurrence of acid rain in India is about 2%.

These are the advantages, but in recent years, rapid industrialization 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 measurement of total ionic composition in precipitation helps to investigate the source regions, the atmospheric transport time of precursor as well as the deposition patterns which was revealed by the precipitation chemistry studies by, Rhode and Grandell (1987); Bolin and Persson (1974). These facts have led to some studies on rain water composition in India at different place by different research group and organization.

In India, the study of chemical composition of precipitation was started long ago by Narayanaswami (1939); Mukherjee (1957); Khemani et al (1968); Handa (1969), and only during the last two decades extensive work has been done by Sequeria (1976); Sadasivam (1979); Subramanian and Saxena (1980); Krishnanand (1984); Mahadevan (1984); Mukherjee et al (1986); Varma (1989a, 1990, 1991); Mukhopadhyay et al (1992); Ravichandran and Padmanabhamurthy (1994), at various places in India. Mukherjee et al (1985), Varma (1989a); Khemani et al (1989a, 1989b) deduced that elsewhere in India, occurrence of acid rain is ruled out due to higher concentration of soil derived particles. Indian Meteorological Department, guided by WHO, collects and analyses rainfall samples on a monthly

basis at Allahabad, Jodhpur, Kodaikanal, Minicoy, Mohanbari, Nagpur, Port Blair, Pune, Srinagar and Vishakapatnam. All these places are called as BAPMoN stations.

The problem of acid rain has not yet been widely acknowledged in India. However, potential effects of recent industrialization and coal based power generation over the last decades, warrants a closer examination of the impacts of emissions of SO_2 from various large sources and the overall long range transport and deposition of $\text{SO}_2/\text{SO}_4^{2-}$ on some sensitive receptors in northern India (Sharma et al., 1995). For example, coal based power generation produces about 70% of the total power generation in India.

Divergent views are expressed on the neutralizing capability of fly ash particles released from the stack of coal-fired power plants. Shannon and Fine (1974) measured pH values of 9-11 from water extracts of fly ash. Likens and Bormann (1974) suggested that the removal of alkaline fly ash emissions by industrial and utility electrostatic precipitators contributes to acid rain. On the other hand, Ananth et al (1977) indicated that the removal of fly ash may not be a contributor because the particles removed by the precipitator are probably larger in size than those remaining to the plume and thus, if left uncontrolled, would settle more rapidly. They further indicated that there was insufficient data to determine whether the alkalinity of fly ash had significant effect on the neutralization of the acid rain. But Khemani et al (1989a) deduced, that in Delhi, the Indraprasta power plant after being fitted with electrostatic precipitators in 1982, during the south west monsoon season on upwind and downwind in 1985, the samples were acidic on 11

occasions and pH value varied between 4.2 and 5.3, and 16 times in the alkaline range, with the pH varying between 5.7 and 7.8, but rain water samples in the upwind and downwind region within 4 km from power plant were alkaline with pH varying between 5.7 and 8.2. This confirms that the fly ash particles are capable of neutralizing acidic precipitation and also confirming that the acid rain, wherever it occurs, in India is a purely local phenomenon.

In India, first occurrence of acid precipitation was reported by Mahadevan et al (1984) at Chembur an isolated pocket in Bombay and also in Delhi by Khemani (1989a), Ravichandran and Padmanabhamurthy (1994), and a decreasing trend in pH was observed by Varma (1989a) in BAPMoN stations like Kodaikanal, Portblair, Minicoy, Nagpur and Mohanbari, while Das (1988) reported that in Calcutta, most rain water samples have a tendency towards being slightly acidic in character.

The atmosphere in India has a high dust load and the dust from arid and semi-arid tracts of Rajasthan have their additional impact in northern India (Khemani et al 1985) and also surface erosion of soil appears to be the major contributor for many areas studied by Mahadevan et al (1985) and Sharma et al (1983). High pH value together with high concentration of Ca^{2+} and NH_4^+ has been observed by Munger (1982); Loye-Pilot et al (1986). While Mukherjee et al (1985); Chan et al (1987); Khemani et al (1989a,b); Ahmed et al (1990); Varma et al (1990); Ravichandran and Padmanabhamurthy (1994), Al-Momani et al (1995) Sanusi et al (1996), deduced that, the pH of the precipitation is determined not only

by anions but also by the concentration of cations in the atmosphere which neutralizes the acidity by forming salts. Calcium present in brown coal emitted as CaO can counteract the formation of acid rain as observed by Marquardt and Ihle (1988). While Munger (1982); Lewis et al (1984); Wagner and Steel (1987); Zhao et al (1988) and Pratt et al (1984) have also indicated the importance of calcareous, soil derived material in wet deposition.

It is well documented that the dust load in the atmosphere over North western parts of India is higher and a significant amount of dust incorporates into rainfall either as condensation nuclei or by collision with falling rain drops. However the extent to which air borne dust influences the precipitation chemistry of certain geographic regions, varies with its composition and abundance. Significant research work by Khemani et al (1985, 1987), Applin and Jarsak (1986) and Barnard et al (1986), has shown the reason for pH values greater than 5.6, which reflects the possible neutralization effects of airborne dust.

The dust particles play an important role in deciding the pH of rain water (Mukopadhyay et al., 1992). When the dust load increases, the pH increases, the main reason being the presence of more Ca^{2+} and K^+ in dust, which originate from the soil and vegetations, and alkalinity of rain decreases with increasing distance from the desert area. While Gatz et al (1986) showed that, NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ and Na^+ are known to buffer between 25-50% of potential acid in U.S. precipitation

A study of water soluble components of aerosols in different environment in India by Khemani et al (1985) has shown that atmospheric aerosols in India are

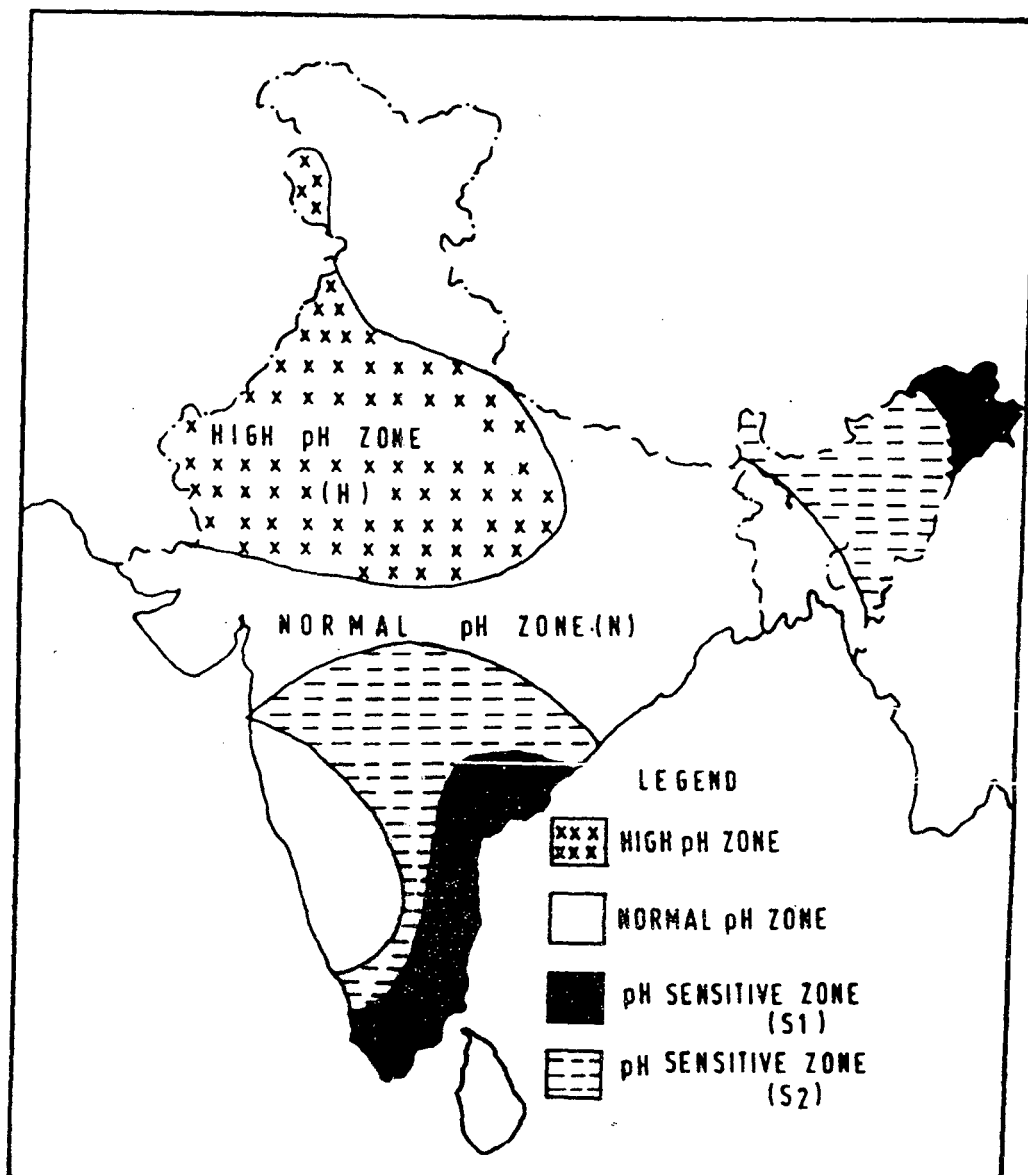
rich in soil-oriented basic ions. The ionic balance is in favor of basic components suggesting that it is this feature which is responsible for the alkaline pH of rain water over the Indian subcontinent.

The rainfall pH zoning in India has been made by the TSP study by Varma (1989) and divided into four Zones (Fig. 2.1).

- Zone 1. - Highly sensitive to acid rains (S1) where pH below 6.0
- Zone 2. - Moderately sensitive to acid rain (S2) where pH ranges between 6.0 and 6.5.
- Zone 3. - Normal pH zone (N) where pH range between 6.5 and 7.0
- Zone 4. - High pH zone (H) where pH is 7.0 and above.

North western India experiences, high pH values ranging 7.0 to 8.5, because of the dust from the desert region which contains mainly carbonates and bicarbonates of Ca^{2+} , Mg^{2+} , Na^+ , K^+ cations. Mukherjee et al (1985); Ahmed et al (1990), have found that sodium, chloride and magnesium are mostly of maritime origin and Mukhopadhyay et al (1992), found that the alkalinity of rain decreases with increasing distance from the desert area. Sanusi et al (1996), showed that, Ca^{2+} is more in urban areas while NH_4^+ is more abundant in rural areas. Sea salt will be higher in coastal regions with its concentration decreasing with increasing distance from the coast; as well as in south east coastal belt, because of the fact that its geological and geographical setting does not possess high density of soil particulate in atmosphere.

Fig.2.1 Rainfall pH-Zoning in India



Source :- Varma (1986).

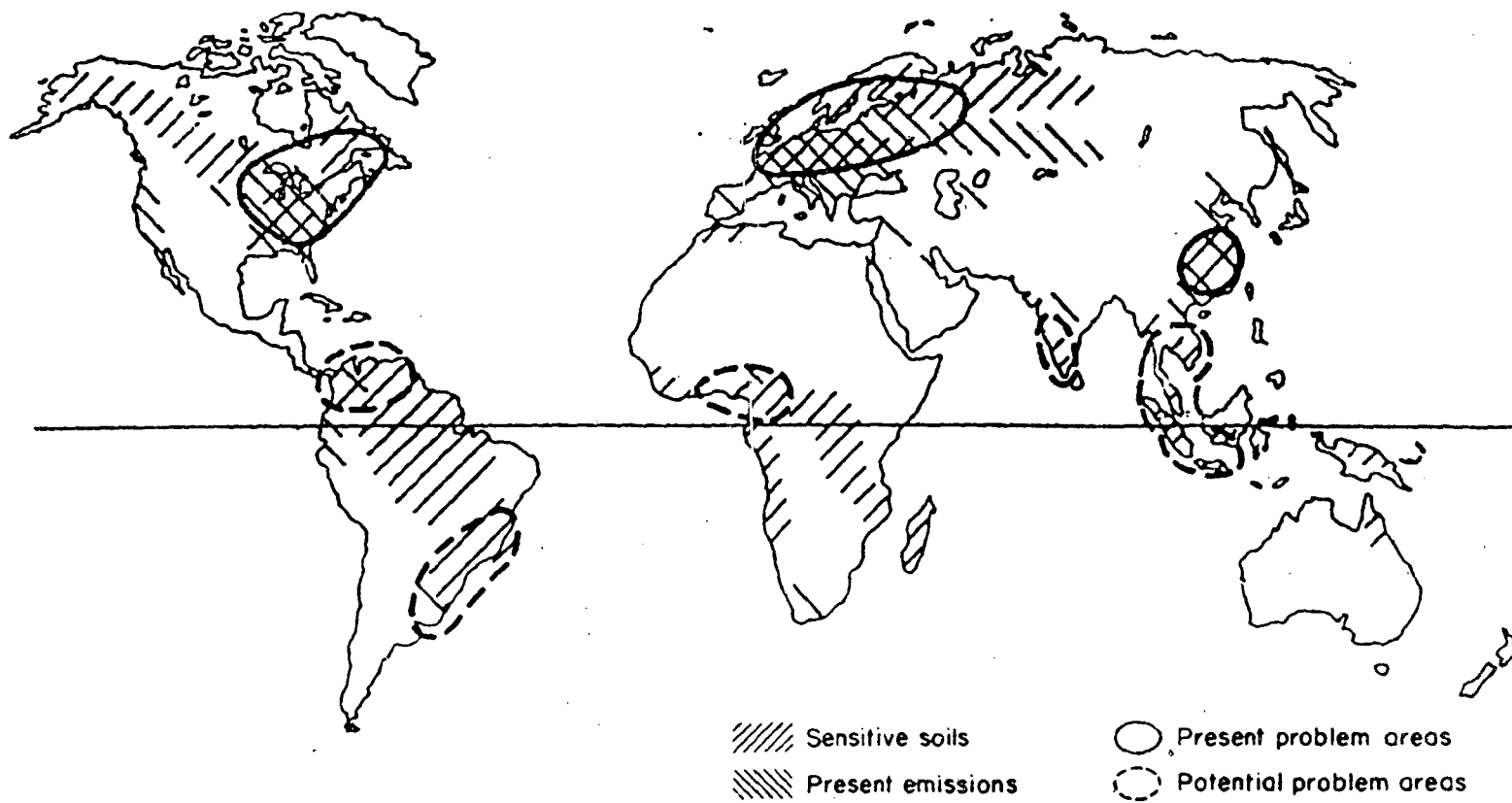


Figure 2.2 Present sensitive and future potential areas of acidification.

Source: Rhode and Herrera (1988)

Rhode and Herrea (1988), has classified the regions (Fig.2.2) of the world that have currently acidification problem. Also regions where soils are presently sensitive to acidification and future potential problematic area due to increased fossil fuel emission, population density etc.,

Khemani et al (1989b) has for the first time in India observed the long term effect of pollutants on the chemistry, and pH of rain water. However, these effects are comparatively slow when compared with those observed in Western countries. The growth of industry in India is very slow and therefore, the anthropogenic pollutants have still not overpowered the natural pollutants released from soil.

In the present work, Delhi has been taken as the study area because survey carried out by CPCB, NEERI and some individual research groups like Khemani, Ravichandran and Padmanabhamurthy, Singh, Dave and Sharma, revealed the excessive concentration of trace gases and TSPM in the ambient air of Delhi. These pollutants may cause acid rain. Description of the study area and emission sources are given in chapter III.

CHAPTER III

BACKGROUND AND OBJECTIVES OF THE STUDY

3.1 Description of the study area:

Delhi, the capital city of India is situated in North India 160 km to the South of Himalayas, bounded by the state of Haryana, in the south and by Uttar Pradesh, in the east. The river Yamuna, a tributary of Ganga, forms the eastern boundary of the city. It is also bounded by the Thar desert of Rajasthan in the west and the hot plains central India in the south.

Table 3.1. Physiographical Feature Of Delhi

Latitude	Between 28°25' and 28°53' N
Longitude	Between 76°50' and 77°22' E
Elevation	Between 213.3 to 305.4m above msl
Area	1,483 sq. km
Maximum Length	59.90 km
Width	48.48 km
Population (1991 census)	
Total	9,420,644
Suburban	88,91,635
Density	6,352 People/km ²
Total forest area	1% of total land (1:100 hec.)
Total No. Industries	93,000
Total No. Vehicles	21,98,908

Source: CPCB, (1995); Delhi statistical Handbook (1990).

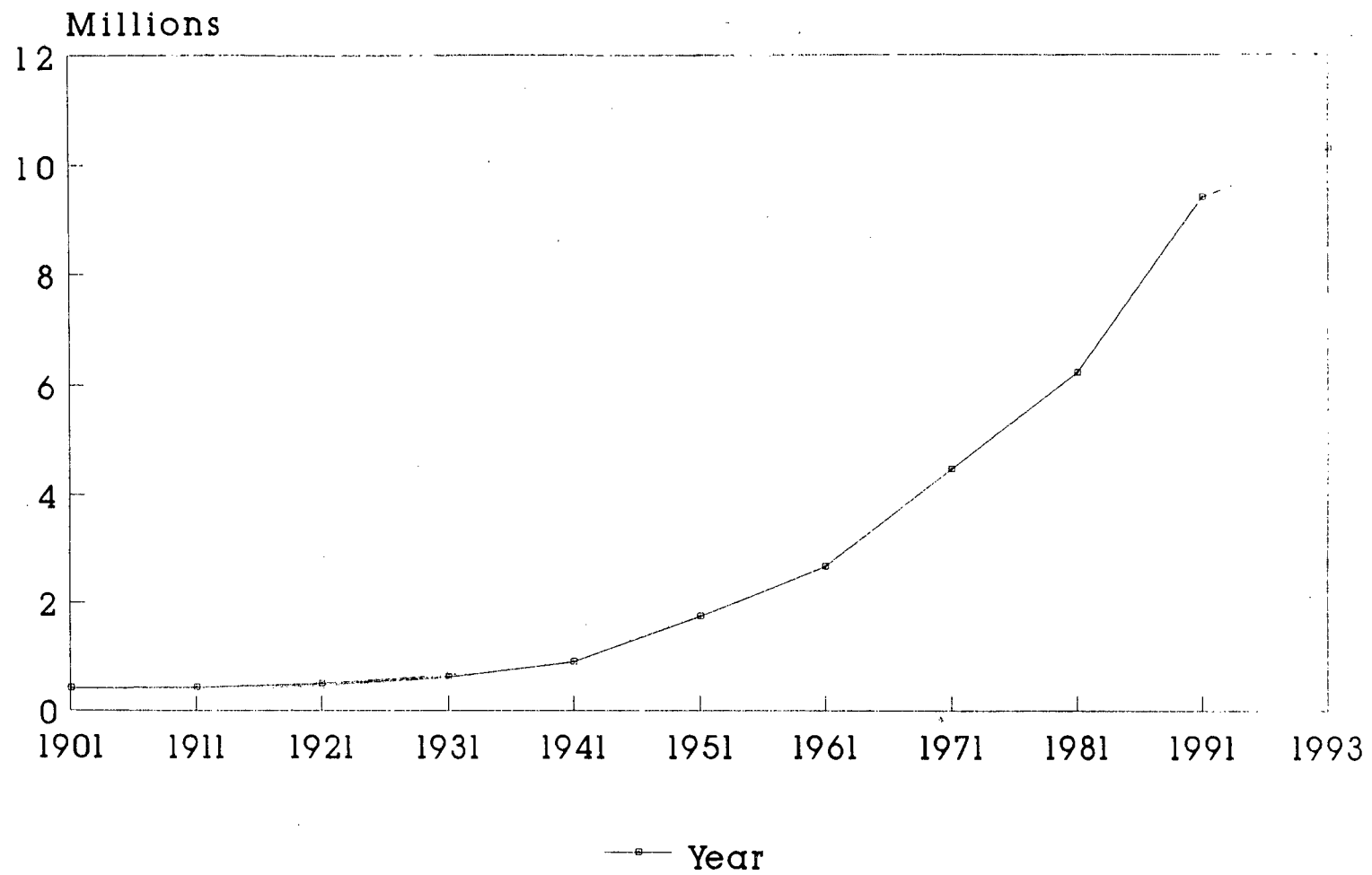


Figure 3.1 Increase in growth of population in Delhi

Source :- Delhi pollution statistics (1995).

The land comprises the ridges and flood plains, of Yamuna. The soil of Delhi is alluvial in nature and has been influenced by the flow of river Yamuna, its flood waters, the ridges and the wind from South West. It is rich in minerals like calcium, magnesium and potassium.

Delhi has a Sub-tropical climate with extremely hot summers and moderately cold winters. Its climate is influenced by the Himalayas in north and the Thar desert in the west. The monthly mean temperature ranges from 14.3°C in January (minimum up to 2°C), to 34.5°C in June (maximum 48°C). The monsoon season lasts for about three months from July to September showing an average annual rainfall of 666 mm (Gazeteer of Rural Delhi, 1984). The heavy rains of monsoon acts as a "Scrubber" while the winter rains are scanty and uncertain. The rainfall in this region is generally erratic in geographical distribution so that the total amount received at any particular place may vary considerably sometime to the extent of 100% from year to year. Moreover, the rainfall at a given locality is very uncertain. North-West wind usually prevails, except during monsoon when South-East winds are predominant (Padmanabhamurthy and Ravichandran, 1991).

The population of Delhi has more than doubled since 1970 (3.53 million to its present level of about 95×10^5). This is due to rapid influx of migrants from other parts of country. Population trend for the past 90 years is given in the Fig3.1. Total population of Delhi is projected to cross 12.77×10^6 by the year 2000 (UN, 1989). Among 30 states and Union Territories of the country, Delhi has the highest population density 6.352, out of the total population, 89.93% is urban.

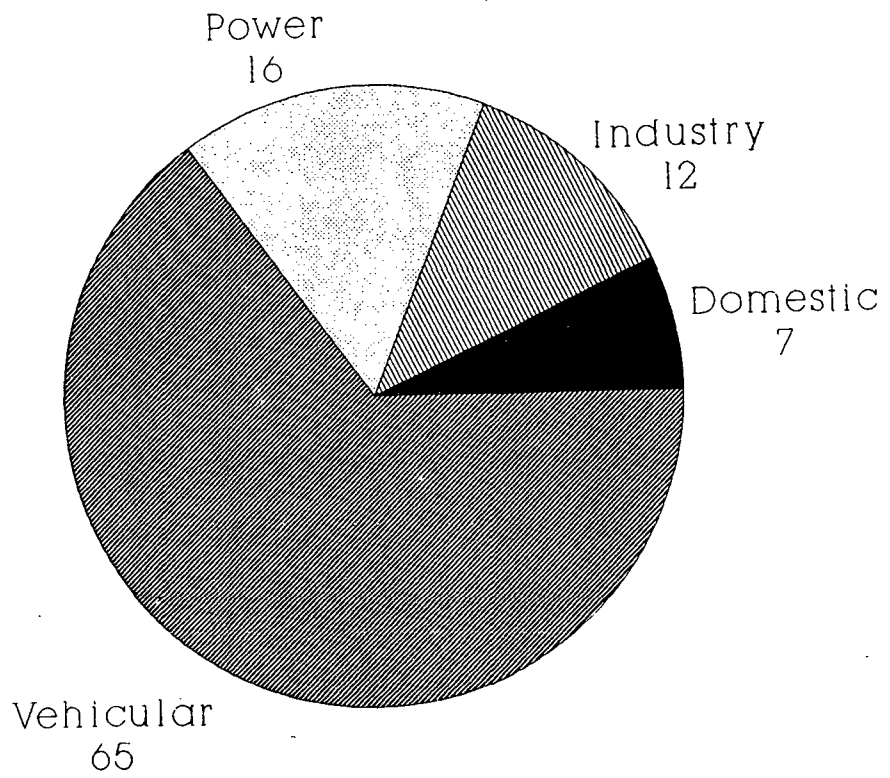


Figure 3.2 Sectorwise distribution of pollutants

Source :- Delhi pollution statistics (1995)

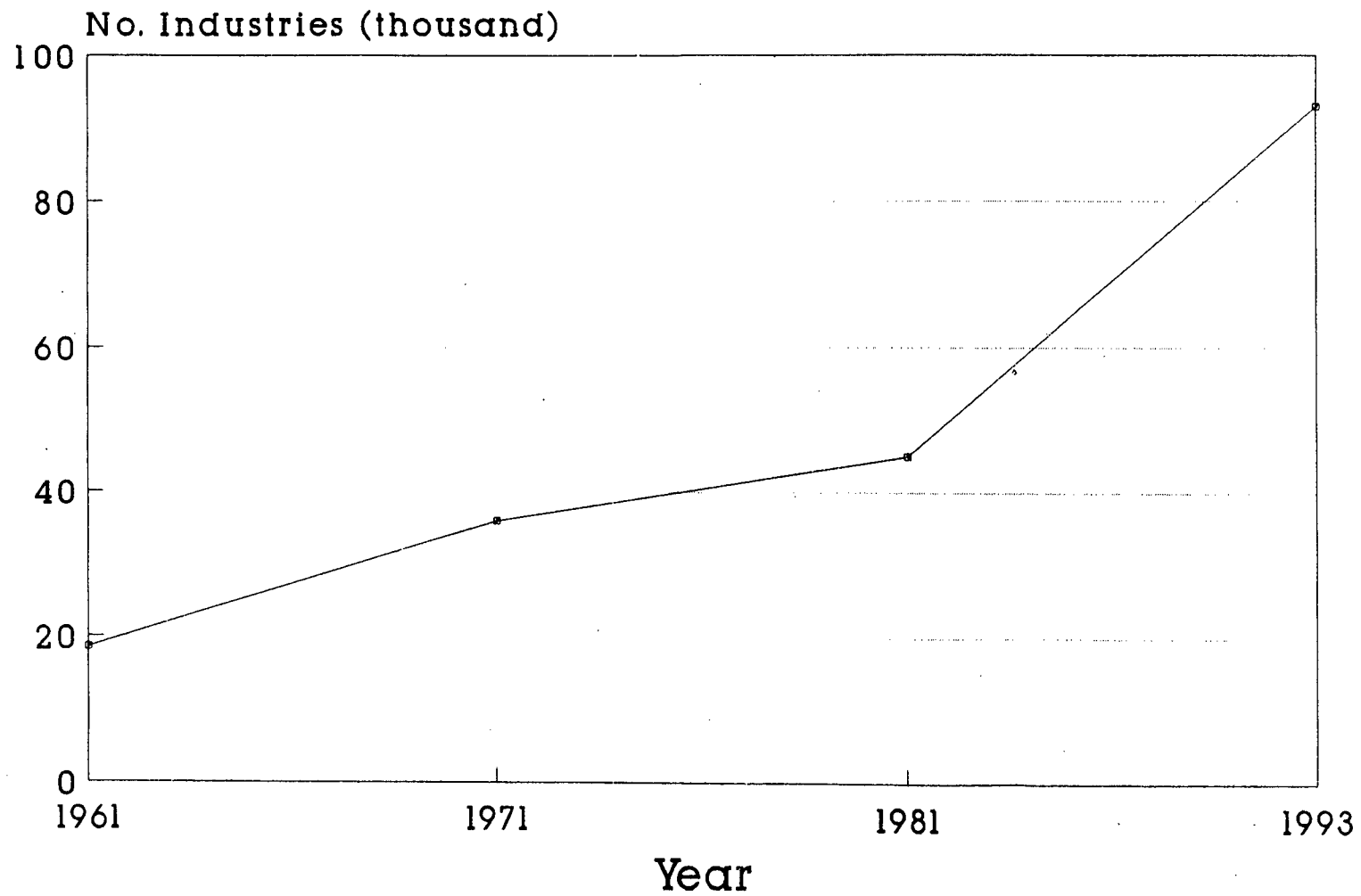


Figure 3.3 Increase in growth of industries in Delhi
Source :- Delhi pollution statistics (1995).

3.2 Ambient air quality:

The Central Pollution Control Board (CPCB) monitors the ambient air quality regularly at 6 locations in Delhi, measuring sulfur dioxide, nitrogen dioxide and suspended particulate matter. The concentration of SO₂ and NO_x has increased in 1992 over 1989 at most of the locations whereas, no significant change is observed in the case of TSPM.

3.3 Total emissions:

Major sources of air pollution in Delhi are vehicles, thermal power plants, and industrial and domestic coal burning. An estimated 2000 metric tonnes of pollutants are emitted into the atmosphere of Delhi everyday (Delhi Pollution Statistics, 1995). Carbon monoxide (CO) topped the list of pollutants with an estimated emission of 1063 metric tonnes per day followed by nitrogen dioxide at 323, hydrocarbons at 320 and sulfur dioxide at 179 metric tonnes. Vehicular sources contribute to about 64% of the total pollutants emitted followed by thermal power plants at 16%, industries at 12% and domestic sector at 7%. (Fig.3.2)

3.4 Industries:

Delhi is often categorized as a service town with government office complexes and medical, agricultural and educational institutions. However, Delhi has experienced a phenomenal growth in industries. There is a 500% increase in industrial units from 18,500 in 1961 to 93,000 in 1993 (Fig.3.3). At present, in

Delhi there are 45 large and medium industrial units. There is no count of the number of small units which are scattered all over the city. The large units, though they are located in the conforming areas, they have not come up in the industrial estate meant for them (Biswas, 1994). Major industries which pollute Delhi's atmosphere are cotton, textile, wool, silk, synthetic fibre, textile products, leather, fur products, rubber, plastics, petroleum products, electrical and electronic appliances, metal and metal products, alloy machine tools, transport equipment parts, food, chemical and chemical products and misc. products.

Major Industrial estates are, Motia Khan, Shahzada Bagh, Jhilmil, Tahirpur, Kirti Nagar, Anand Parbat, Keshopur, Badar Pur, Gulabi Bagh, Okhla, Naraina, Wazirpur, Lawrence Road, Moti Nagar, Chillia, Najafgarh Road, Mayapuri, Patparganj, Samapur Badli...etc. Most of the industries in Delhi are located in the west south east and south. (Fig 4.1)

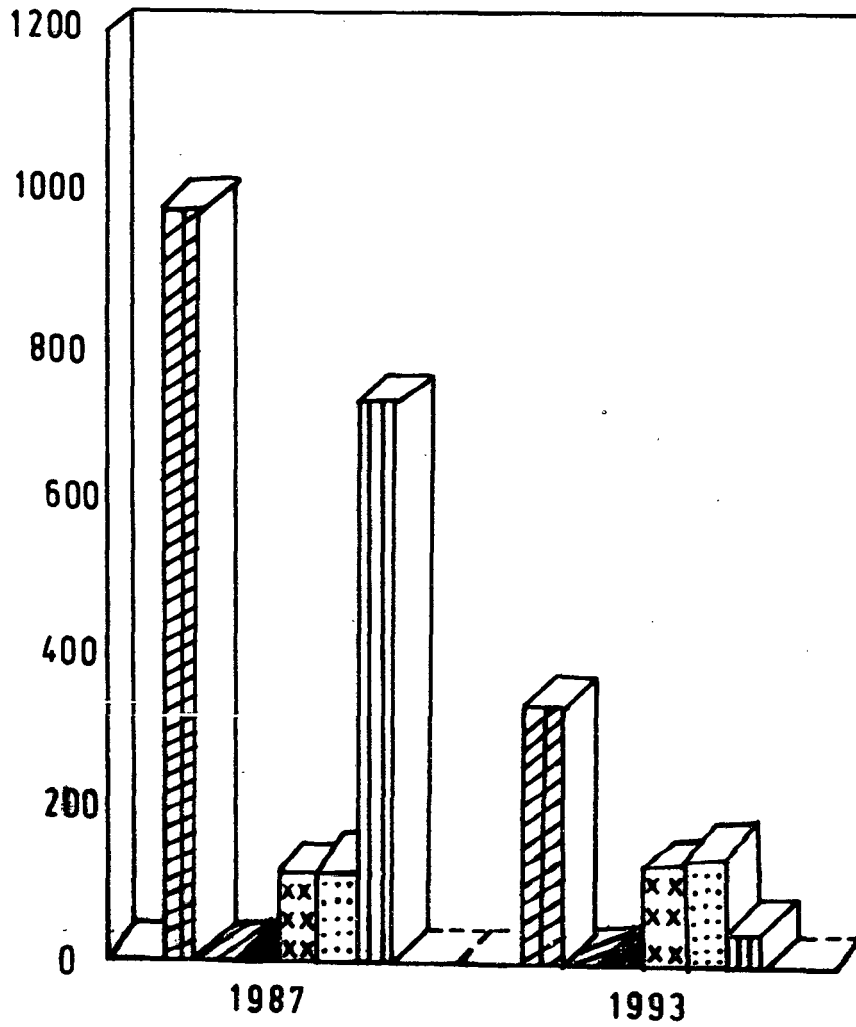
In Delhi, there is one chemical, pesticide, cement and 40 hot mix plants and about 10,000 other industries which pollute the atmosphere. An estimated 240 metric tonnes of pollutants are emitted from the industrial sector which is 12% of the total pollutants emitted in Delhi ((Delhi Pollution Statistics, 1995).







3.5 Thermal power plants:

Delhi has three major power plants viz. Indraprastha, Rajghat and Badarpur, which produce 210 MW, 60 MW and 540 MW respectively. These power plants are one of the major sources of SO₂ emissions in Delhi. These three power plants emit

Fig. 3.4

Emission From Power Plants in Delhi
MT/Day



- 1 Total 
- 2 CO 
- 3 HC 
- 4 SO₂ 
- 5 NO_x 
- 6 SPM 

Source :- Delhi pollution statistics (1995).

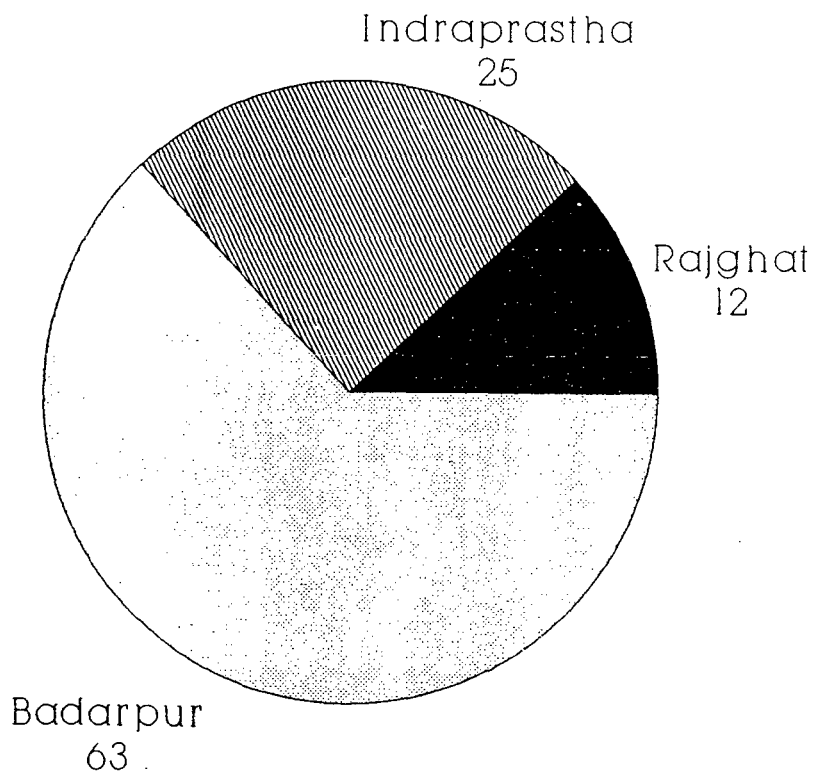


Figure 3.5 Contribution of pollutants from three power plants

Source :- Delhi pollution statistics (1995).

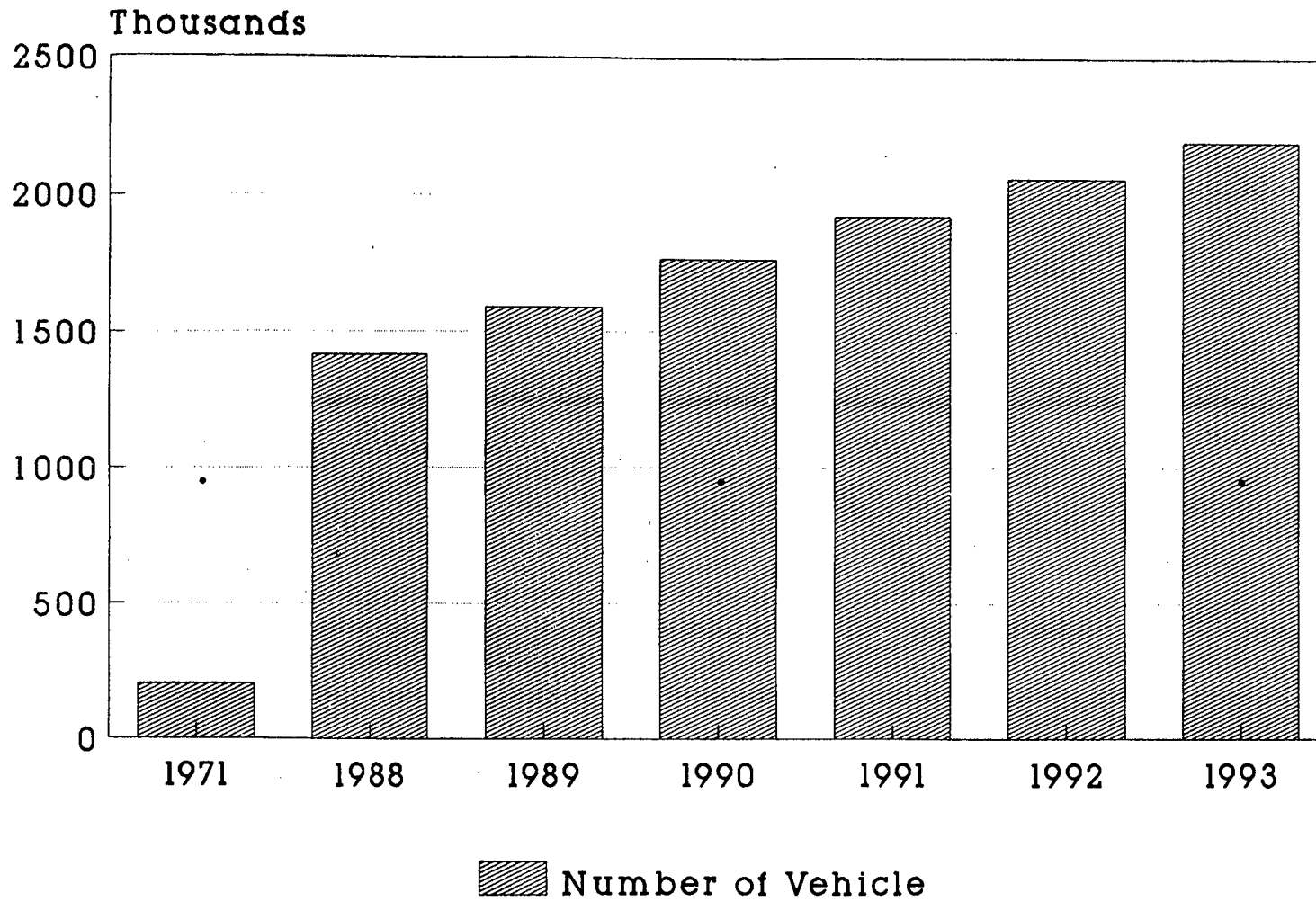
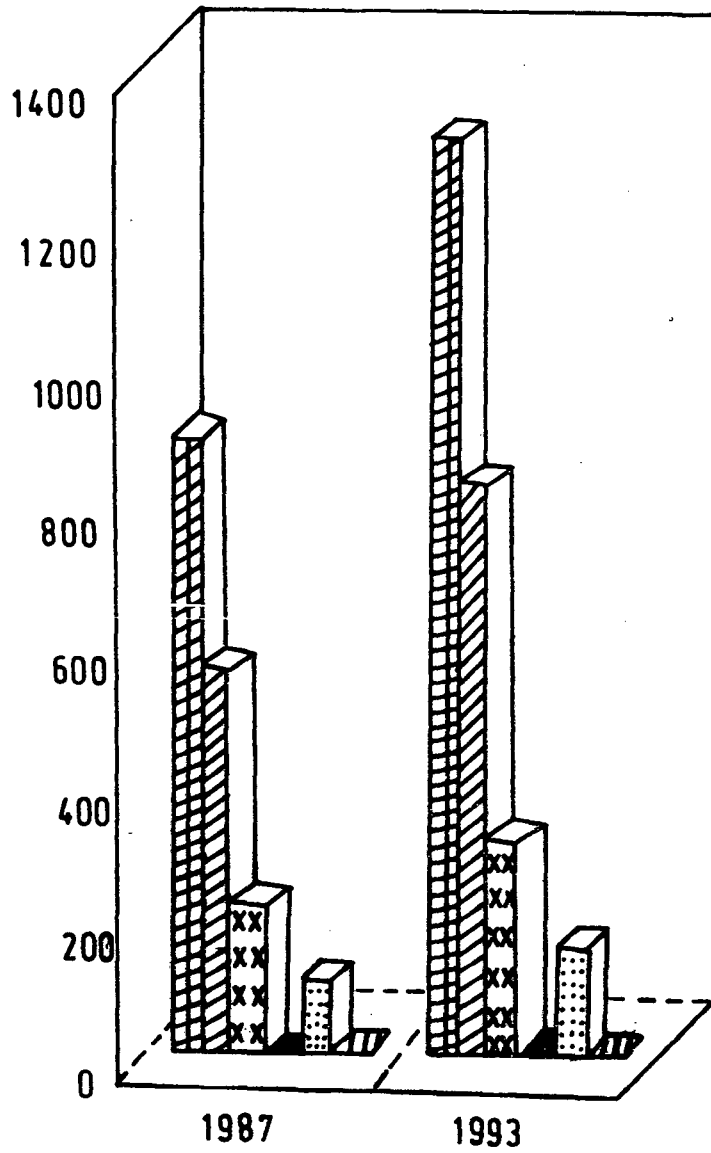








Figure 3.6 Increase in No. of vechiles in Delhi

Source :- Delhi pollution statistics (1995).

Fig.3.7
 Vehicular emissions in Delhi

MT/Day



- 1 Total 
- 2 CO 
- 3 HC 
- 4 SO₂ 
- 5 NO_x 
- 6 SPM 

Source :- Delhi pollution statistics (1995).

an estimated 302 metric tonnes of pollutants every day (inclusive of particulate matter, SO₂, NO_x and hydrocarbons) which is 31% of 935 metric tonnes emitted per day in 1987. Due to improvement in the efficiency of electrostatic precipitators (ESP) installed in these plants, the particulate matter emission has reduced from 720 metric tonnes per day in 1987 to less than 30 metric tonnes per day in 1993. Indraprastha and Badarpur alone produce about 25,500 tonnes of SPM and 25,5000 tons of SO₂ per annum respectively, while about 90% of industrial NO_x is produced by these two power plants (Delhi Pollution Statistics, 1995). Contribution of pollutants from three power plants and emission from power plant in Delhi are given in Fig.(3.4 & 3.5)).

3.6 Vehicular pollution:

Motor vehicle registration rose by 51 times between 1961 and 1991, whereas population is increased 4 times over the same period. It is estimated that in 1993, about 2.1 million vehicles were registered in Delhi (Delhi Pollution Statistics, 1995) (Fig.3.6). This is more than the total number of vehicles registered in Mumbai, Madras, and Calcutta together. In 1993, two wheelers represented 67% of total motor vehicles registered in Delhi.

Delhi has the highest rate of vehicular traffic, twice as that of Bombay and thrice as that of Calcutta and Madras. Its number is increasing at the rate of approximately 14,000 per month. The number of vehicles and their emissions are given in the Table 3.2 (CPCB, 1989).

Table 3.2. No. Vehicles and their emission in Delhi during 1986-1987

Category of Vehicles	No. of Vehicles	Pollution load (Tonnes per day)				
		SPM	SO _x	NO _x	CO	HC
A: Petrol driven						
1) Cars, Jeeps & Station Wagons	21,774	1.49	0.36	14.47	180.85	27.1
2) Taxis	8,809	0.09	0.02	0.86	10.7	1.61
3) Two Wheelers	7,70,110	3.02	0.302	1.05	256.7	151.57
4) Three Wheelers	45,151	0.331	0.331	0.11	33.1	15.15
B: Diesel Driven						
1) Bus	16,266	1.4	2.8	38.9	23.5	3.9
2) Goods Vehicles	64,555	2.27	3.96	0.59	39.9	8.8
TOTAL	1,111,664	8.58	7.45	150.35	535.9	207.9

Total Vehicular Pollution load = 865.315 tonnes per day.

Transport emissions have increased significantly over the past 20 years. The goods vehicle and buses which are only 7% of total contribute to 85.1% of vehicular NO_x emissions (NEERI, 1991). Presently more than 1300 metric tonnes of pollutants are emitted by the vehicles plying in Delhi. This is about 50% more than that emitted in 1987. Diesel driven vehicles contribute about 6% of total

vehicles and about 19% of total vehicular emissions. Contribution of SO₂ and NO_x emission (g s⁻¹) in Delhi are estimated by Singh et al (1990) is given in Table 3.3.

Table 3.3 The contribution of SO₂, SPM and NO_x emission in Delhi (g s⁻¹)

Source	SO ₂	SPM	NO _x
1. Domestic and Vehicular Traffic	73.47	77.38	18.8
2. Industrial	86.00	528.50	4.2
3. Railway shunting yards	150.00	600.00	50.2
4. Indraprasta Power Plant	128.9	330.00	75.24

Glass ceramic industries are also a major source of SPM after power plants (NEERI, 1991).

From the air pollution point of view, Delhi ranks 4th in the world and first in India for its SPM concentration level, 27th in the world and second in India for its SO₂ level (WHO - 1991). Its daily pollution load is about 872 tonnes (Surendran, 1993). SPM load has been estimated to be as 111,7000 Tonns (with an average of 400 µg/m³) per annum. Lead emission from petrol driven vehicle contributes 600 tonnes/annum of SPM; NO_x emissions of 73,000 tonnes/annum and CO emissions, as 2,65,000 tonnes/annum as per NEERI, 1991.

3.7 Climate and natural sources:

Climate and natural sources also play an important role in the pollution level of Delhi in addition to anthropogenic sources. The region has regular pre-monsoon feature of "Andhi," the dust storm. Westerly winds from the great Indian desert bring a large amount of SPM, as high as 500-800 tonnes/sq. miles.

Ground based temperature inversions are a regular feature in winters which restricts the mixing height to low levels, limiting the pollutant dispersal.

3.8. OBJECTIVES OF THE STUDY

Quality of precipitation basically depends on the type and amount of pollutants, it generally comes in contact. These pollutants may be anthropogenic or natural in origin and may be locally emitted or transported from a different region. In all the urban studies on precipitation the local factors have always played a dominant role. The phenomenal growth in industries and vehicular population of Delhi in addition to three coal based thermal power plants operating in the interiors of the city have been the initiating factors behind the present work.

Thus the main objectives of the study are:

- 1) To quantitatively assess the rainfall during monsoon different locations in Delhi.
- 2) To study the influence of some atmospheric pollutants on the rain water quality in Delhi.
- 3) To find out the relationship between rain water quality and the existing sources of pollution in Delhi

The present work comprises therefore:

I. Rain water sampling at five different location in Delhi, for the monsoon period of 1995.

II. Studies on rain water chemistry

A) This consists the determination of the following major cations and anions.

a) Cations

- i) Hydrogen ion
- ii) Sodium
- iii) Potassium
- vi) Calcium
- v) Magnesium
- vi) Ammonium

b) Anions

- i) Sulfate
- ii) Nitrate
- iii) Chloride

B) pH and conductivity measurements.

III. Monitoring of ambient air for the following:

- a) SO₂
- b) NO_x
- c) SPM

CHAPTER IV

MATERIALS AND METHODS

4.1. SAMPLING OF RAIN WATER

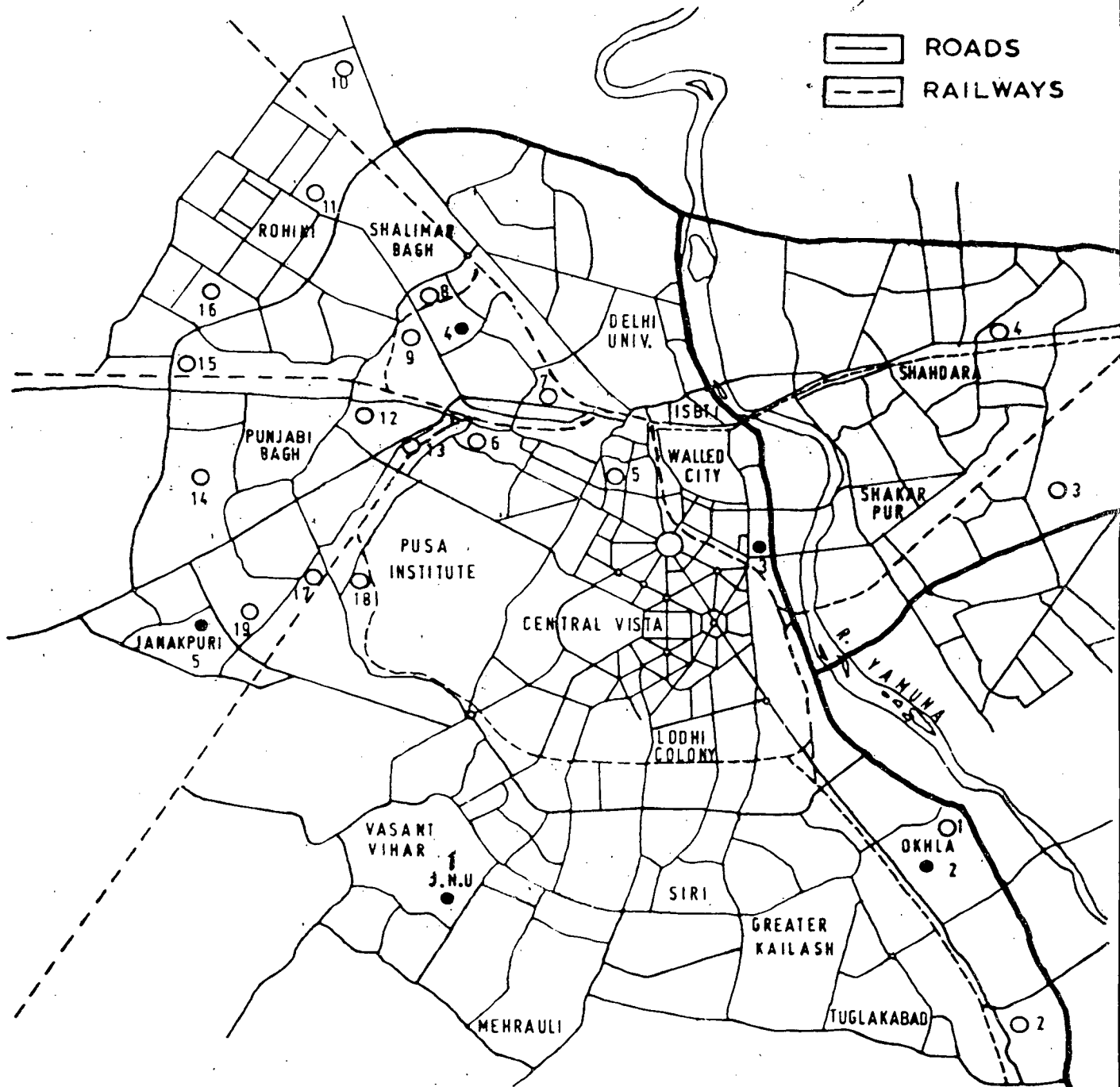
Rain water samples were collected on event basis for almost every shower during monsoon season in Delhi at five locations of different anthropogenic activities in order to obtain spatial variation in chemical composition of rain water. These sites are located at ITO, Okhla, JNU, Janakpuri and Ashok Vihar. JNU is a considered as rural area without industrial activity which is a residential university covered by shrub forests. ITO is highly polluted by vehicular traffic and possess two power stations near by and also a highly commercial area. Okhla is a high industrial area, Janakpuri is a residential area surrounded by industrial area like Mayapuri. Ashok Vihar is a residential cum Industrial area. Contribution from dry deposition during the rain has been considered insignificant.

4.2 SAMPLING STRATEGY

For collecting the precipitation samples, wet-only samplers are recommended in order to prevent any contamination from atmospheric dust. Since, it is a costly one, most of the Indian studies used only manual collectors. In this study also, the manual collector was used.

Care was taken so that the collection procedure resulted in samples of wet deposition only and not bulk samples. In order to achieve this, the collector was opened only during the period of precipitation and closed tightly at other times.

Fig.4.1 Map showing the area of study and Industrial area in Delhi



○ Major Industrial estate

- | | |
|---------------------|--------------------|
| 1. OKHLA | 9. LAWARANCE ROAD |
| 2. BADARPUR | 10. SAMAPUR BADLI |
| 3. PATPARGANJ | 11. JAHANGIRPUR |
| 4. JHILMIL TAHIRPUR | 12. MOTINAGAR |
| 5. MOTIA KHAN | 13. NAJAFGARH ROAD |
| 6. ANAND PARBAT | 14. KESHOPUR |
| 7. GULABI BAGH | 15. ROTAK ROAD |
| 8. WAZIRPUR | 16. MONGOL PURI |
| | 17. KIRTI NAGAR |
| | 18. MARINA |
| | 19. MAYAPURI |

● Area of study

1. J.N.U
2. OKHLA
3. I.T.O
4. ASHOK VIHAR
5. JANAKPURI

The precipitation samples were collected on volume basis. The collector consisted of conical flask (1000 mL) funnel, (18 cm diameter) and a mesh to prevent the insects from falling inside. These components were assembled in a single unit by means of a steel wire. The collector was placed into a wooden holder keeping the funnel's mouth out. The whole assembly was clamped to one meter wooden stacks for preventing splashed rain from the ground entering into the funnel.

The collector was always cleaned and dried before use. During dry spell, the funnel was covered to avoid dry deposition. When the shower was over or when sufficient amount of rain water ($> 70 \text{ cm}^3$) was collected for analysis, rain water was transferred to a plastic bottle and was brought to laboratory immediately for pH and conductivity measurement. The conical flask and funnel was quickly rinsed with double distilled water to remove any surface debris and covered with aluminum foil until the next shower.

4.3. CHEMICAL ANALYSIS OF RAIN IN WATER

pH of the rain water was determined with a digital pH meter using an Ingold electrode standardized with pH buffers of 4.0 and 7.0. A clean teflon stirring bar was placed into the bottle and while stirring at a moderate speed, the electrode was lowered into the rain water sample. The sample was allowed to equilibrate at one minute interval until a constant value was obtained. The pH was recorded to 0.01 pH units.

Conductivity of the samples was also measured immediately. The sample was filtered by using Whatman no. 41 filter paper and stored in cold room at 4°C. Major anion like SO_4^{2-} , NO_3^- , Cl^- and cations like NH_4^+ were analyzed at the earliest. HCl was then added to reduce the pH below 2.0 and the sample was stored in cold room at 4°C for further analysis of metals (Ca^{2+} , Mg^{2+} , Na^+ and K^+).

4.4. ANALYSIS OF ANIONS

Analysis of anions has been done based on the following principles. (Procedure has been followed from APHA 1992).

4.4.1. a) Sulphate

The concentration of sulphate was determined by turbidity method (APHA, 1992). Sulphate ions precipitated in acetic acid medium with BaCl_2 to form BaSO_4 crystals of uniform size. Light absorbance of BaSO_4 suspension was measured at 410 nm on a spectrophotometer and SO_4^{2-} concentration was determined by comparison with standard

Procedure

To 100 mL of sample (10 mL of sample made up to 100 mL), 20 mL of buffer solution (30 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 5.0 g of $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$, 1.0g of KNO_3 and 20 mL of acetic acid in 500 mL distilled water and made up to 1000 mL) was added and mixed thoroughly. While stirring a spoon full of BaCl_2 crystals were

added. Standards was made with anhydrous NaHSO_4 the concentration ranging from 0.1 to 2.0 ppm and treated as above (for samples) turbidity was measured at 410 nm for both samples and standards.

4.4.2. b) Nitrate

UV absorption techniques for the sample with low organic matter was used. The nitrate calibration curve follows the Beer's law up to 11 mg N/L. Measurement of UV absorption at 220 nm enables rapid determination of NO_3^- . Because dissolved organic matter may also absorb at 220 nm, a second measurement made at 275 nm may used to correct NO_3^- values. Acidification with 1 N HCl prevents interference from hydroxide or carbonate upto 1000 ppm CaCO_3 .

Procedure:

To a 50 mL sample, 12 mL HCl was added and mixed thoroughly. NO_3^- calibration standards was prepared in the range of 0 to 7 mg NO_3^- N/L. NO_3^- samples were treated like samples. Absorbance of distilled water was set at zero absorbance or 100% transmittance. NO_3^- was read at 220 nm and interference by dissolved organic matter was read at 275 nm.

For standards and samples two times the absorbance reading at 275 nm was subtracted from the reading at 220 nm to obtain the absorbance due to NO_3^- . Construct a standard curve by plotting absorbance due to NO_3^- against NO_3^-/N concentration of standard.

4.4.3 c) Chloride

In a neutral or a slightly alkaline solution, potassium chromate can indicate the end point of silver titration of chloride. Silver chloride is precipitated before red silver chromate is formed.

Reagents:

- a) Potassium chromate indicator solution: 50 g K_2CrO_4 was dissolved in a little distilled water. $AgNO_3$ solution was added until a red precipitate is formed which is allowed to settle for 12 hours then filtered and made up to 1 L.
- b) Standard silver nitrate titrant 0.0141 M (0.0141 N): 2.395 g of $AgNO_3$ was dissolved in distilled water and diluted to 1000 mL.
- c) Standard sodium chloride, 0.0141 M (0.0141 N): Dissolved 824 mg $NaCl$ in distilled water and diluted to 1000 mL.
- d) 30% Hydrogen peroxide
- e) H_2SO_4 , 1 N
- f) $NaOH$ 1 N.

Procedure:

A portion of the sample was diluted to 100 mL if sulfite or thiosulfate present added 1 mL H_2O_2 and stir for 1 min.

$NaCl$ standards and samples were titrated in the pH range of 7 to 10. pH was adjusted to 7 to 10 with H_2SO_4 or $NaOH$. 1 mL of Potassium chromate indicator solution was added and titrated with standard $AgNO_3$ titrant to a pinkish yellow end point.

Blank was standardized with AgNO_3 titrant. A standard curve was constructed and plotted.

4.4.4. d) Ammonia

Indophenol blue method was used for the estimation of ammonia. In an acidic medium an intensely blue compound indophenol is formed by the reaction of ammonium ion with phenol and hydrochloride in presence of manganous salt as catalyst. The absorbance was measured at 630 nm.

Procedure

To a 10 mL sample, a drop of MnSO_4 solution was added and placed on a magnetic stirrer and 0.5 mL Hypochlorous acid reagent 40 mL water and 10 mL of 5% NaOCl solution was added and pH was adjusted to 6.5 to 7.0 with HCl . Then 0.6 mL phenate reagent (2.5 g of NaOH , 10 g phenol and $\text{C}_2\text{H}_5\text{OH}$ in 100 mL water) was added drop wise and stirred vigorously during the addition of reagents. Blank and standards solutions were also analyzed by the above procedure. Color formation after 10 minutes was read at 630 nm.

4.5. ESTIMATION OF METALS

Metals were analyzed by Atomic absorption spectrophotometer method. Phillips PU-9200 X Atomic Absorption Spectrophotometer (AAS), with air - acetylene flame was used .

4.5.1. Calcium

Standards were prepared by using CaCO_3 and 0.2% m/v potassium was added to the standards and samples as an ionization buffer and analyzed by AAS in the absorption mode, aspirated in air/acetylene, flame at 422.7 nm

4.5.2. Magnesium

Standards were prepared by using MgO and 0.2% m/v potassium was added to the standards and samples as an ionization buffer and analyzed by AAS in the emission mode, aspirated in air/acetylene, flame at 217 nm

4.5.3. Sodium

Standards were prepared by using NaCl and 0.2% m/v caesium was added to the standards and samples as an ionization buffer and analyzed by AAS in the emission mode, aspirated in air/acetylene, flame at 589 nm.

4.5.4. Potassium

Standards were prepared by using KCl and 0.2% m/v caesium was added to the standards and samples as an ionization buffer and analyzed by AAS in the emission mode, aspirated in air/acetylene, flame at 766.5 nm.

Table 4.1: Analytical proccessure followed.

Parameters	Instrumentation	Technique
Na ⁺	Atomic Absorption Spectrometer (Phillips PU - 9200 X	Emission mode. Aspirated in air/acetylene flame. 0.2% m/v caesium was added as an ionization buffer. Read at 589 nm.
K ⁺	Atomic Absorption Spectrometer (Phillips PU - 9200 X	Emission mode. Aspirated in air/acetylene flame. 0.2% m/v caesium was added as an ionization buffer. Read at 766.5 nm.
Ca ²⁺	Atomic Absorption Spectrometer (Phillips PU - 9200 X	Emission mode. Aspirated in air/acetylene flame. 0.2% m/v potassium was added as an ionization buffer. Read at 422.7 nm.
Mg ²⁺	Atomic Absorption Spectrometer (Phillips PU - 9200 X	Absorption mode. Aspirated in air/acetylene flame. 0.2% m/v potassium was added as an ionization buffer. Read at 217 nm.
Cl ⁻	Hitachi U-2000 UV-VIS, Spectrophotometer.	Colorimetric as Mercury Thiocyanate methods. Read at 461 nm.
SO ₄ ²⁻	Hitachi U-2000 UV-VIS, Spectrophotometer.	Colorimetric as Turbidity method. Read at 410 nm.
NH ₄ ⁺	Hitachi U-2000 UV-VIS, Spectrophotometer.	Colorimetric as Indophenol blue. Read at 630 nm.
NO ₃ ⁻	Hitachi U-2000 UV-VIS, Spectrophotometer.	UV absorption method. Read at 220 nm.

CHAPTER V

RESULTS AND DISCUSSION

5.1 METEOROLOGY AND AIR QUALITY AT THE SAMPLING SITE

Incorporation of gases like SO_2 and NO_x emitted from industries in the South East monsoon wind during precipitation occurs by two mechanisms. The first mechanism involves dissolution of plume gas in cloud droplets and their subsequent rainout. This mechanism is favored under unstable conditions when the plume rises quickly to the cloud level. But under stable conditions of the atmosphere, generally the distance between the industries and sampling site is so short (5 - 20 km) that the plume is confined under the cloud level. So, SO_2 and NO_x are incorporated into the rain by dissolution in falling hydrometeors. The relative contribution of each of these mechanism depends on the frequency of the occurrence of stable and unstable conditions in Delhi. The most frequently observed stability class during monsoon (July to September) is the neutral condition during day time and extreme to moderately stable conditions in the night which dominates (Kumar, 1995) due to high frequencies of neutral and stable conditions favouring the confinement of industrial plumes below the cloud base. Hence, the below cloud scavenging is an important mechanism for incorporation of SO_x and NO_x released from industries to rain, and it is important to know the concentration of SO_2 and NO_x in the atmosphere.

Table - 5.1: Ambient Air Quality of five stations in Delhi ($\mu\text{g}/\text{m}^3$)

5.1(a) AMBIENT AIR QUALITY OF JANAKPURI,

MONTH	SO ₂				NO ₂				SPM			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
JULY	9.0	19.0	15.0	4.0	22.0	43.0	33.0	8.0	337.0	545.0	403.0	71.0
AUGUST	13.0	24.0	28.0	4.0	32.0	44.0	38.0	5.0	318.0	456.0	401.0	52.0
SEPTEMBER	9.0	18.0	15.0	3.0	35.0	43.0	39.0	3.0	386.0	848.0	534.0	168.0

5.1(b) AMBIENT AIR QUALITY OF JNU,

MONTH	SO ₂				NO ₂				SPM			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
JULY	4.0	13.6	8.3	3.4	6.3	16.3	11.3	3.7	48.0	152.0	98.0	43.1
AUGUST	4.9	8.6	6.4	1.8	4.6	21.6	12.0	7.1	140.0	301.0	201.0	68.5
SEPTEMBER	3.7	9.6	6.2	2.0	4.0	28.0	12.2	9.4	24.0	240.0	108.0	76.7

5.1(c) AMBIENT AIR QUALITY OF OKHLA,

MONTH	SO ₂				NO ₂				SPM			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
JULY	14.0	28.0	22.2	6.0	21.2	39.8	32.3	7.9	508.0	145.0	332.0	143.9
AUGUST	19.5	37.2	25.3	6.9	20.8	42.2	28.2	8.7	131.0	400.0	285.0	114.3
SEPTEMBER	20.0	32.1	25.8	5.2	20.0	48.0	32.0	10.7	381.0	103.0	210.0	134.5

5.1(d) AMBIENT AIR QUALITY OF ASHOK VIHAR,

MONTH	SO ₂				NO ₂				SPM			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
JULY	16.0	18.0	17.0	1.0	27.0	31.0	39.0	2.0	284.0	375.0	330.0	37.0
AUGUST	19.0	21.0	19.0	2.0	48.0	62.0	54.0	5.0	241.0	513.0	419.0	109.0
SEPTEMBER	15.0	19.0	18.0	1.0	30.0	32.0	31.0	1.0	211.0	475.0	341.0	107.0

5.1(e) AMBIENT AIR QUALITY OF ITO,

MONTH	SO ₂				NO ₂				SPM			
	Min	Max	Avg	SD	Min	Max	Avg	SD	Min	Max	Avg	SD
JULY	17.33	128.66	35.45	22.9	22.5	70.5	45.21	12.2	177.0	622.4	324.6	172.0
AUGUST	9.0	62.66	27.12	18.13	3.0	64.66	44.19	16.63	109.0	325.33	228.8	74.43
SEPTEMBER	16.0	67.66	31.11	13.59	43.0	83.66	52.19	16.30	257.3	831.0	507.0	138.4

Source with prior permission from :- a,d,e from Central Pollution Control Board, New Delhi, b&c from Kumar (1995).

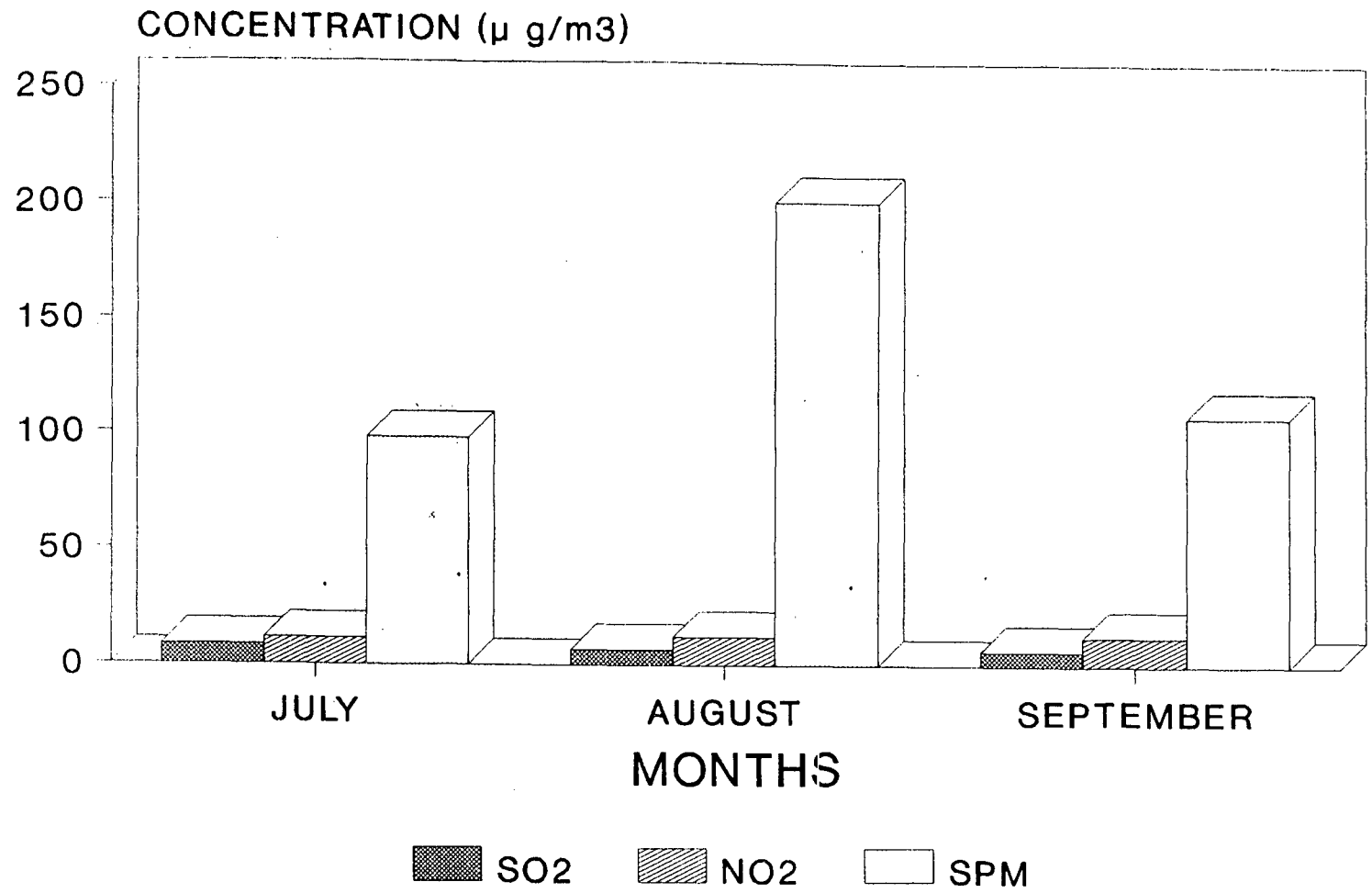


Fig. 5.1: Average Ambient concentration of SO₂, NO₂ and SPM at J.N.U.

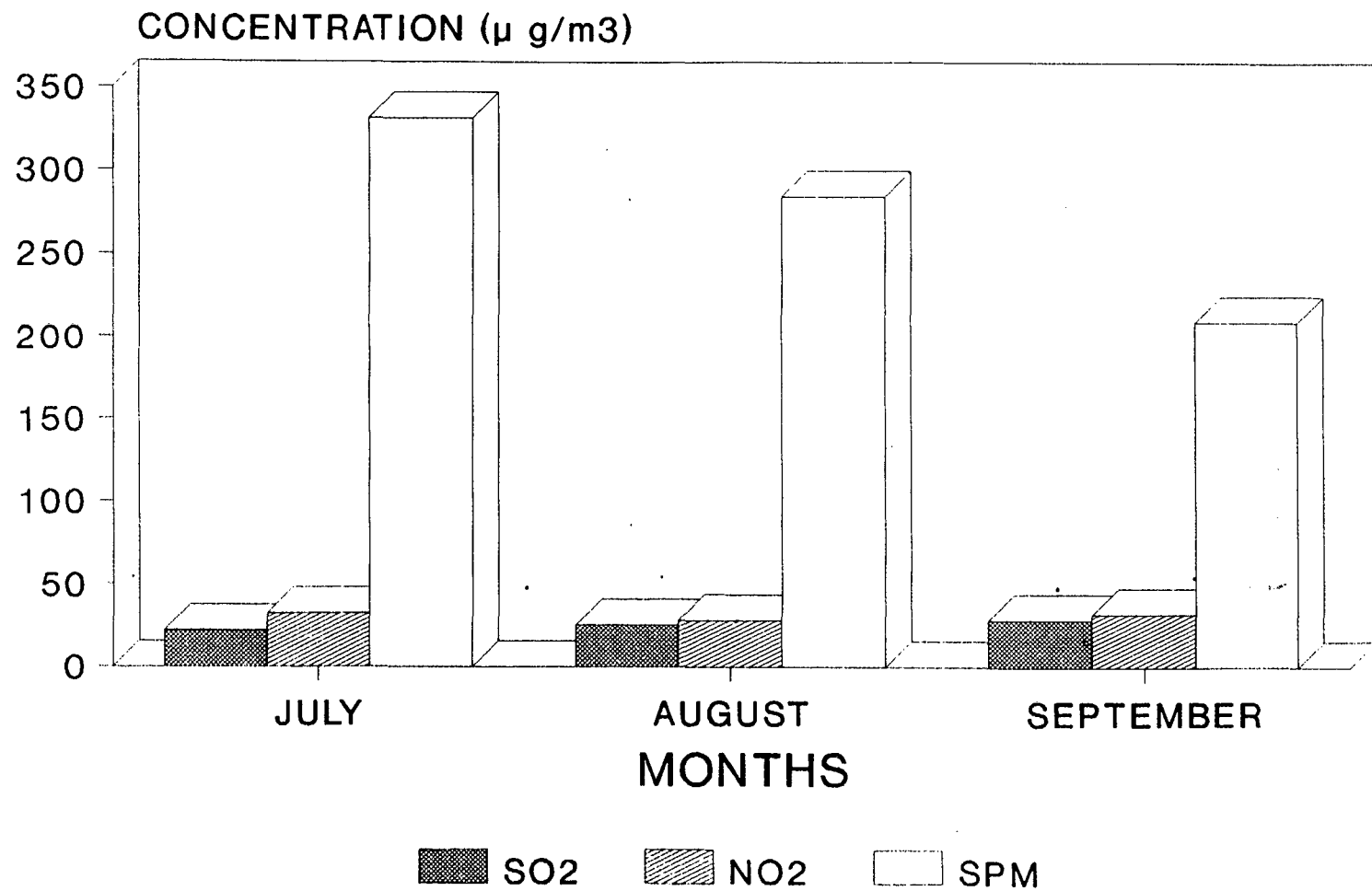


Fig. 5.2: Average Ambient concentration of SO₂, NO₂ and SPM at Okhala

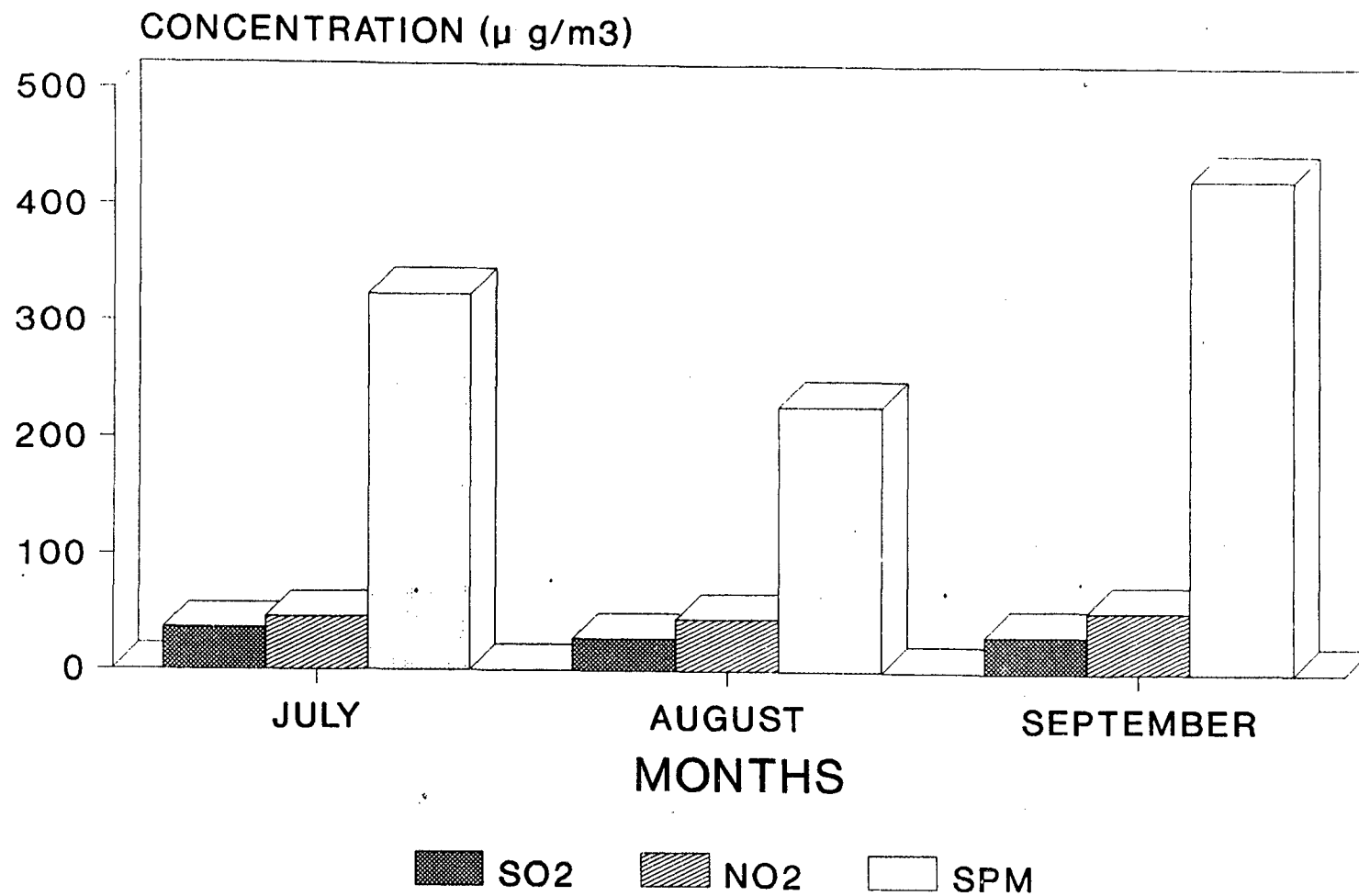


Fig. 5.3 : Average Ambient concentration of SO₂, NO₂ and SPM at I.T.O.

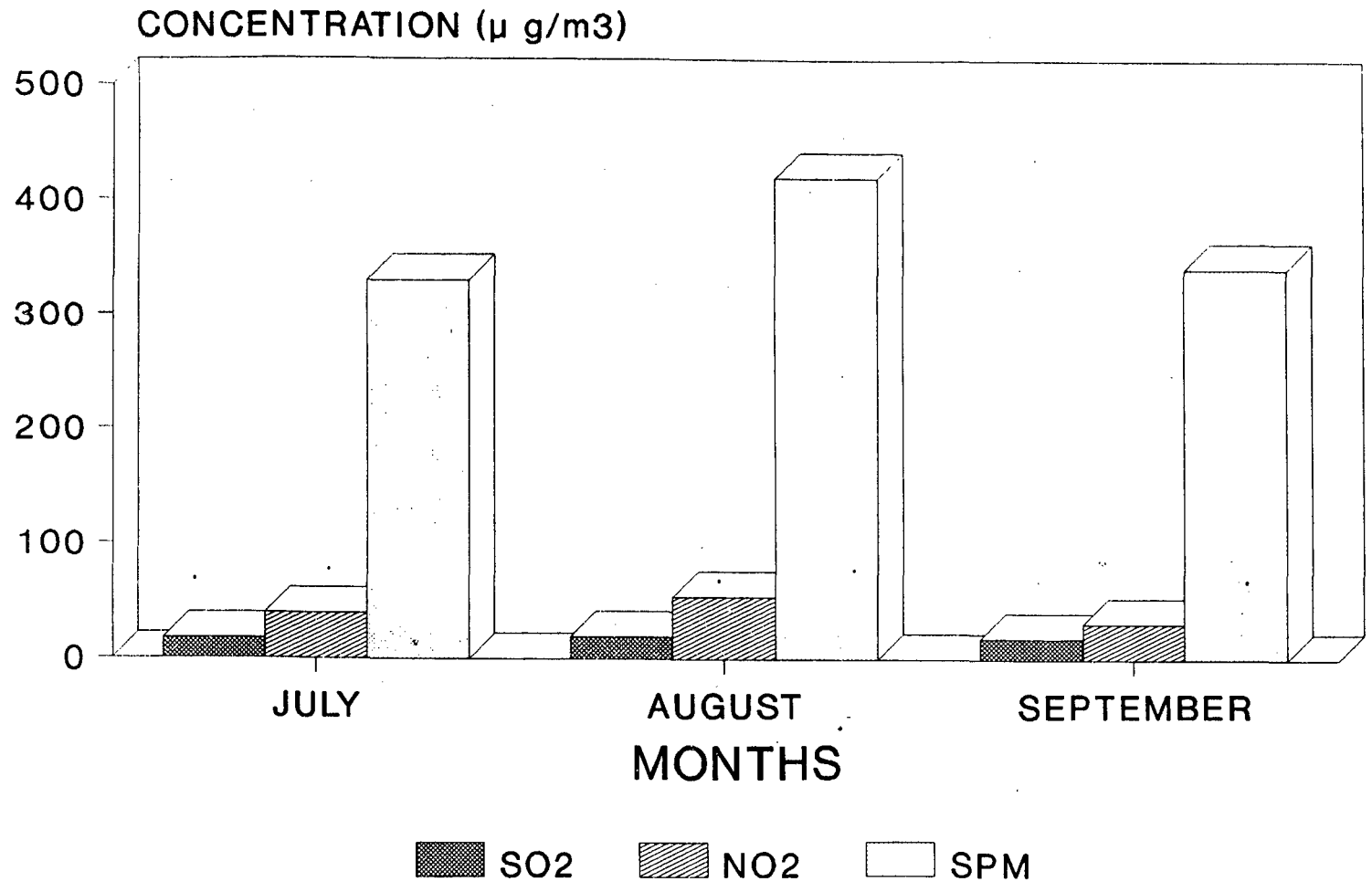


Fig. 5.4 : Average Ambient concentration of SO₂, NO₂ and SPM at Ashok Vihar

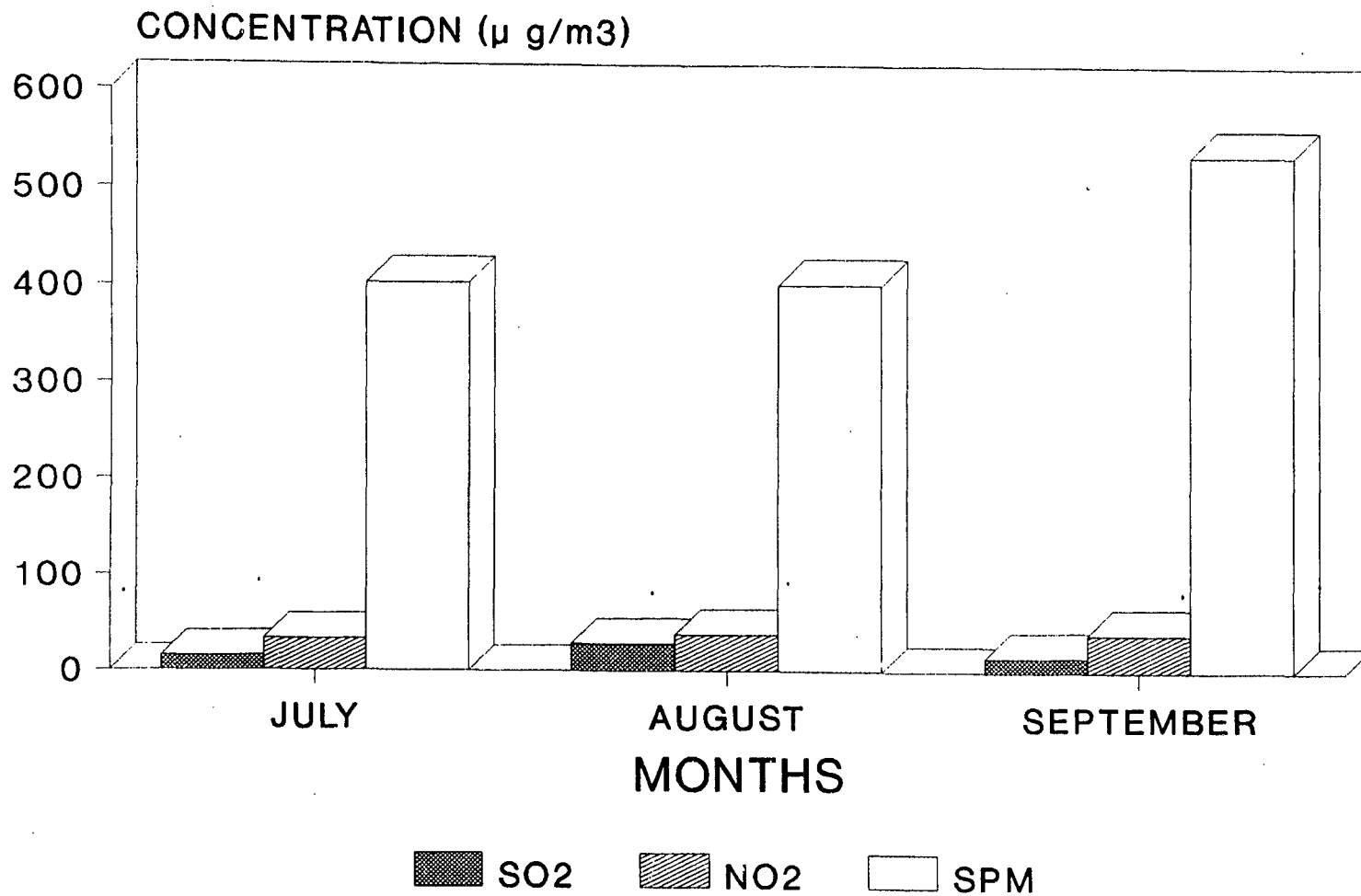


Fig. 5.5 : Average Ambient concentration of SO₂, NO₂ and SPM at Jankpuri

SO₂ and NO₂ are precursor acidic gases which form sulfuric and nitric acids in the atmosphere formed by the various oxidation processes. The concentration of these gases along with total suspended particulates (TSP) for the five sites during the monsoon period of 1995 (July to September) are given in the Table 5.1 (a,b,c,d,e) and their variation at different site is given in the Fig 5.1 to 5.5.

The monthly average concentration of SO₂ in Delhi varied between 6 and 52.4 µg/m³ (Table 5.1). At JNU the concentration was varying between 6.2 and 8.3 µg/m³, from 28 to 32.3 µg/m³ at Okhla, between 27.12 and 35.45 µg/m³ at ITO, from 26.0 to 31.0 µg/m³ at Ashok Vihar and between 33 and 39 µg/m³ and at Janakpuri. The maximum concentration of SO₂ in Delhi 128.7 µg/m³ was observed in July and it was at ITO. The high concentration of SO₂ at ITO may be due to emissions from the power plant and at Okhla, Ashok Vihar and Janakpuri may be attributed to the increase in Industrial pollution.

The average monthly concentration of NO₂ is given in the Table (5.1). It varied between 11.3 and 12.2 µg/m³ at JNU, between 28 and 32.3 µg/m³ at Okhla, at ITO concentration was between 44.19 to 52.19 µg/m³, varied between 26 and 36 µg/m³, and between 33 and 39 µg/m³ at Janakpuri. The minimum concentration of 11.3 µg/m³ was observed at JNU in July and a maximum concentration of 836.66 µg/m³ was observed during september at ITO. The average monthly concentration of NO₂ was higher than the concentration of SO₂ in Delhi. The high value of NO₂ is attributed to the increase in vehicular pollution at I.T.O. which might due to increased vehicular population.

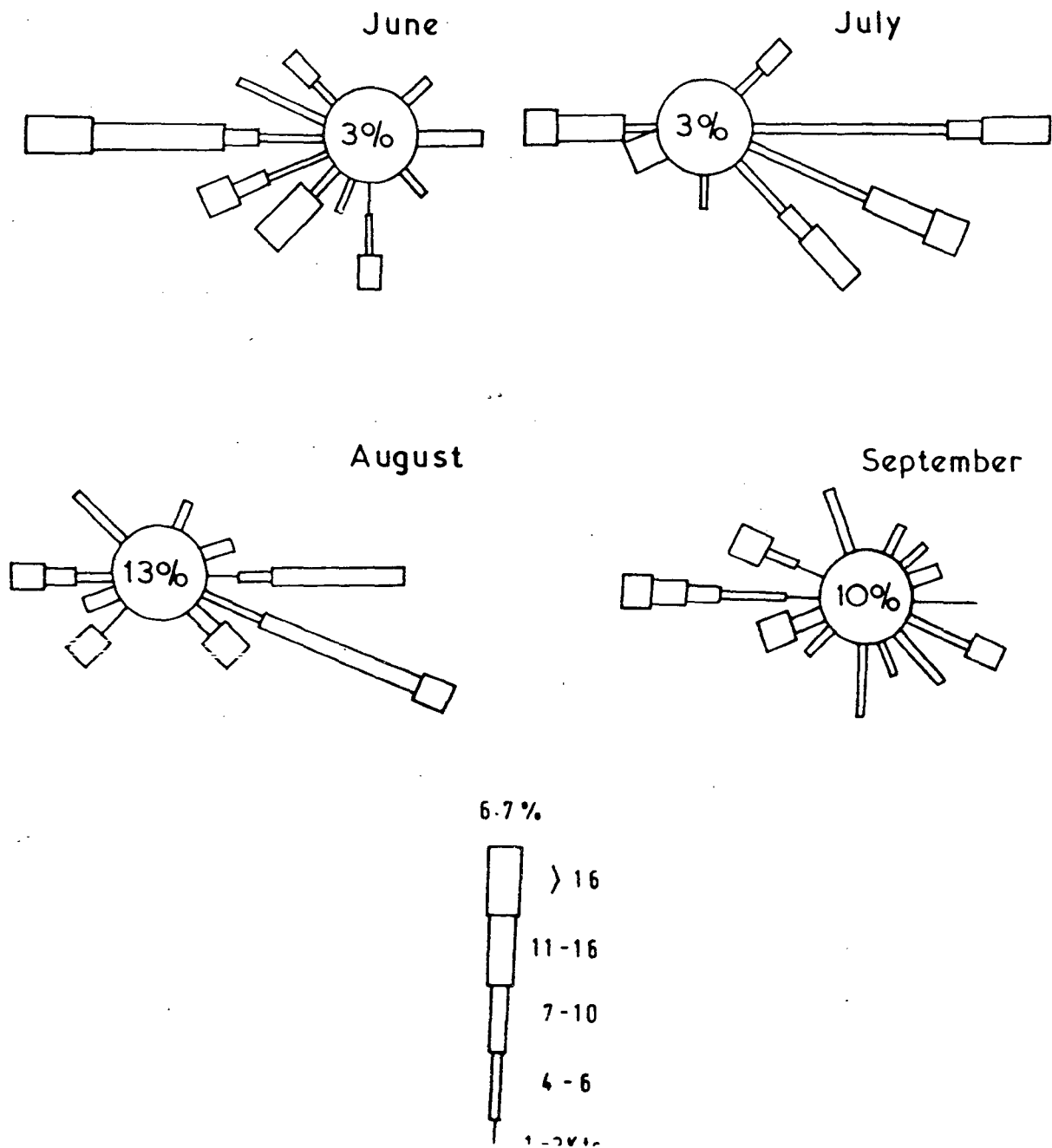
The monthly average concentration of total suspended particulate for all the five stations are given in the Table 5.1. The monthly average TSP concentration varied between 98 to 201 $\mu\text{g}/\text{m}^3$ at JNU. At Okhla, the concentration of SPM was between 228 to 332 $\mu\text{g}/\text{m}^3$. At ITO, the concentration varied between 228.8 to 507.4 $\mu\text{g}/\text{m}^3$ and at Ashok Vihar the concentration varied between 330 to 419 $\mu\text{g}/\text{m}^3$. At Janakpuri, the concentration varied between 401 to 534 $\mu\text{g}/\text{m}^3$. The concentration for whole Delhi was varying between 98.0 to 534.0 $\mu\text{g}/\text{m}^3$. At Okhla the increase might be due to the Badarpur power plant and increased industrial pollution. At ITO the increase might be due to power plants like Indraprastha, Rajghat and Badarpur and also due to increased vehicular pollution.

The wind pattern for Delhi at Safdarjung and Palam is given in the Fig 5.6 and 5.7 which shows the direction of the wind through out the month of June, July, August & September. During June, the wind was from North-West but during July and August the wind direction was from South-East.

5.2 RAIN WATER CHEMISTRY

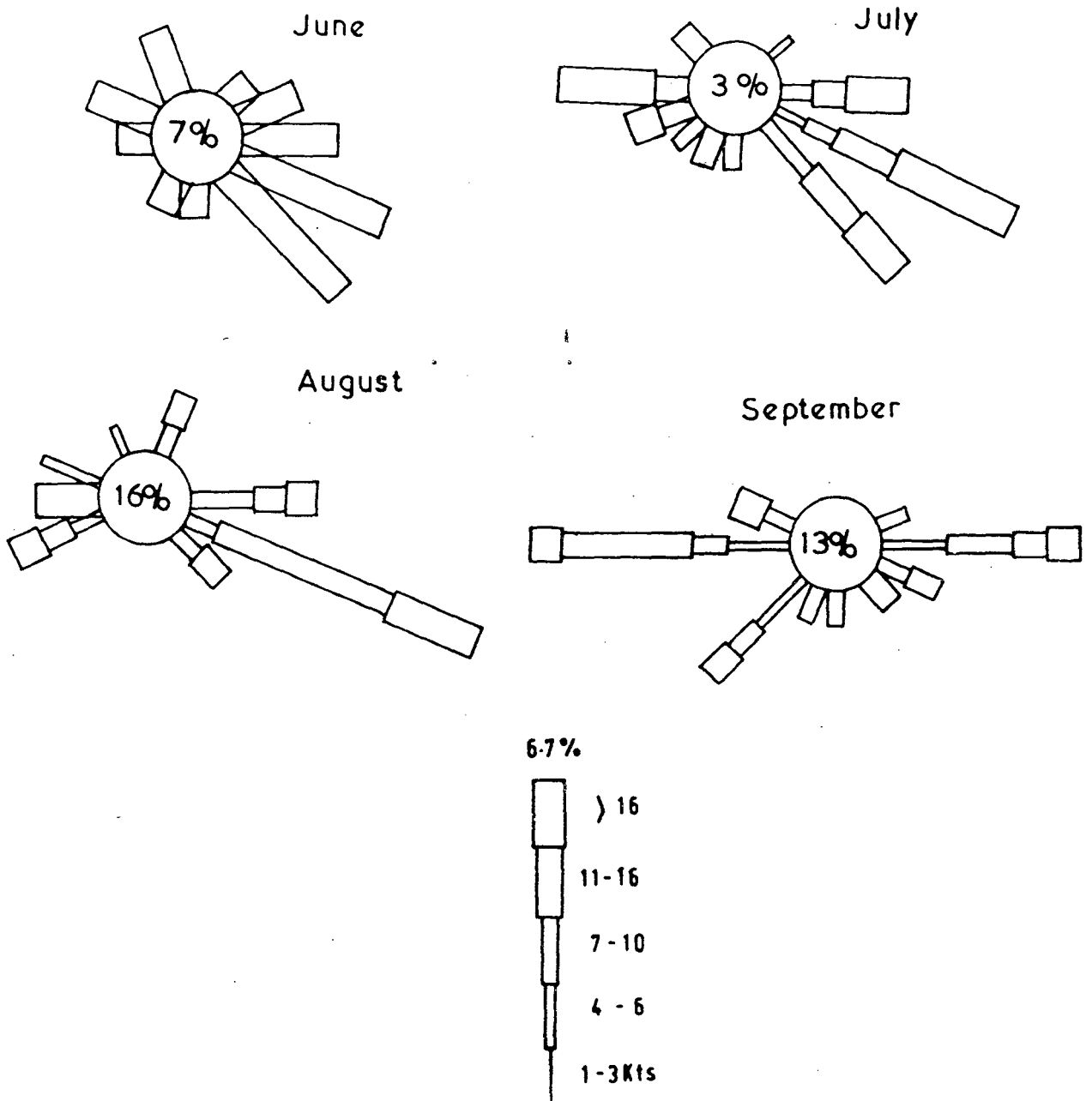
Concentration of major ionic components for individual showers with pH, EC, anion and cation with their average, maximum, a minimum and standard deviation for all the five stations are given in Tables 5.2 to 5.6. All the concentrations are expressed in $\mu\text{eq}/\text{L}$, so that a simple arithmetic procedure can be used to obtain a comparison between the various parameters.

Fig. 5.6 Windrose for Safdarjung



Source :- Indian Meteorological Department.

Fig.5.7 Windrose for PALAM



Source :- Indian Meteorological Department .

Table 5.2: Chemistry wet deposition at JNU, during monsoon '95

S.No	Date	pH	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	Sum	NO3+SO4
		Unit	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)	(µeq/L)
4	22.09.95	7.33	65.10	168.05	47.66	67.61	283.31	0.129	58.06	239.75	45.00	81.73	18.42	443.09	0.639	0.284	1.381	
5	11.7.95	6.63	124.60	166.35	43.06	96.06	305.46	0.234	93.34	438.35	42.50	22.60	36.05	633.07	0.483	0.259	2.539	
6	18.7.95	7.05	47.80	204.19	11.25	90.97	306.41	0.089	86.96	239.75	67.50	193.04	19.21	606.55	0.505	0.055	1.517	
7	22.7.95	7.25	70.10	160.83	39.80	117.70	318.33	0.056	69.78	252.15	59.17	238.26	27.63	647.05	0.492	0.247	1.605	
8	24.7.95	6.87	21.80	110.61	24.44	60.44	195.48	0.135	39.47	252.85	81.67	10.43	7.89	392.44	0.498	0.221	2.165	
9	27.7.95	6.18	28.50	102.19	5.93	80.44	188.55	0.661	25.48	177.70	102.50	73.04	8.68	388.06	0.486	0.058	1.879	
10	28.7.95	6.37	26.20	79.46	12.82	75.31	167.58	0.427	22.40	190.10	181.67	24.37	8.15	427.12	0.392	0.161	2.303	
11	2.8.95	6.27	29.20	108.25	40.76	60.76	209.77	0.537	65.86	252.85	17.67	7.02	7.36	351.30	0.597	0.377	2.139	
12	3.8.95	5.37	25.20	70.43	114.04	91.21	275.68	4.266	44.92	128.08	51.67	18.26	4.21	251.41	1.097	1.619	0.938	
13	3.8.95	6.24	13.70	80.28	45.48	80.15	205.91	0.575	79.50	140.45	67.50	42.60	11.31	341.94	0.602	0.567	1.749	
14	5.8.95	5.73	22.20	102.36	39.07	92.03	233.45	1.862	19.46	52.85	130.00	59.65	2.68	266.50	0.876	0.382	0.511	
15	6.8.95	6.47	20.10	140.99	103.76	71.15	315.90	0.339	8.13	180.45	133.33	10.43	13.07	345.75	0.914	0.736	0.770	
16	7.8.95	6.47	16.40	120.84	49.84	48.75	219.42	0.339	13.23	28.05	125.83	54.78	17.90	240.13	0.914	0.412	0.242	
17	15.8.95	6.85	55.20	52.04	42.86	63.62	158.52	0.141	106.16	128.05	40.00	5.21	6.05	285.61	0.555	0.824	2.468	
18	16.8.95	6.51	60.10	45.43	57.28	80.65	183.35	0.309	105.48	63.50	11.67	48.69	7.36	237.01	0.774	1.261	1.645	
19	17.8.95	6.63	74.60	145.68	25.99	71.27	242.93	0.234	145.67	127.35	23.33	51.30	3.94	351.82	0.690	0.178	1.590	
20	20.8.95	6.16	25.40	157.08	137.37	71.27	365.72	0.692	150.23	102.50	26.67	70.43	4.70	355.22	1.030	0.875	0.858	
21	21.8.95	6.49	33.40	162.03	97.67	48.31	308.00	0.324	78.21	190.10	23.33	30.43	3.94	326.33	0.944	0.603	1.033	
22	22.8.95	5.41	58.10	180.13	120.60	93.93	394.65	3.890	72.97	65.30	98.33	91.30	16.57	348.36	1.133	0.670	0.460	
23	25.8.95	6.38	25.80	80.75	50.13	48.62	179.50	0.417	40.04	152.85	24.00	73.91	10.52	301.74	0.595	0.621	1.474	
24	26.8.95	6.42	25.40	85.42	67.15	53.24	205.80	0.380	42.16	128.05	46.67	18.26	3.94	239.46	0.859	0.786	1.116	
25	27.8.95	5.67	27.50	70.88	24.42	60.03	155.32	2.138	38.67	52.85	19.17	52.17	6.57	171.57	0.905	0.344	0.960	
26	28.8.95	6.61	25.20	88.36	80.63	38.10	207.09	0.245	41.33	80.05	50.00	87.39	7.89	266.91	0.776	0.913	0.718	
27	28.8.95	4.23	19.00	191.16	169.91	40.32	401.39	58.884	48.59	150.65	23.33	44.34	5.26	331.05	1.212	0.889	0.552	
28	29.8.95	4.28	22.70	255.11	204.49	25.49	485.09	52.481	40.30	228.05	80.33	32.17	5.26	438.59	1.106	0.802	0.584	
29	30.8.95	4.98	19.50	240.50	163.55	28.18	432.23	10.471	44.52	125.08	75.00	28.69	26.30	310.06	1.394	0.680	0.420	
30	2.9.95	5.27	24.60	193.09	150.56	13.24	356.88	5.370	44.94	95.30	43.33	94.78	27.10	310.82	1.148	0.780	0.408	
31	3.9.95	4.95	9.00	238.66	163.06	12.25	413.96	11.220	83.70	215.65	13.33	78.26	5.26	407.42	1.016	0.683	0.745	
32	4.9.95	4.94	3.01	154.48	111.64	9.15	275.27	11.482	38.89	128.05	11.67	23.47	15.78	229.34	1.200	0.723	0.627	
Avg		6.16	37.65	136.39	74.59	63.44	274.43	5.269	66.81	164.50	59.91	57.61	13.74	367.84	0.79	0.56	1.28	
SD		0.84	26.30	56.00	54.43	31.10	88.77	13.647	48.76	83.92	41.43	49.93	13.11	124.22	0.28	0.35	0.68	
Max		7.44	124.60	255.11	204.49	150.33	485.09	58.884	258.18	438.35	181.67	238.26	69.21	655.08	1.39	1.62	2.54	
Min		4.23	3.01	45.43	5.93	9.15	155.32	0.036	8.13	28.05	11.67	5.21	2.68	171.57	0.39	0.06	0.24	

Table 5.4 Chemistry of wet deposition at ITO, during monsoon '95

S No	Date	pH Units	EC ($\mu\text{mhos/cm}$)	SO ₄	NO ₃ ($\mu\text{eq/L}$)	Cl	Anion Sum	H+	NH ₄	Ca	Mg ($\mu\text{eq/L}$)	Na	K	Cation Sum	An/Cat	NO ₃ /SO ₄	NH ₄ +Ca/ NO ₃ +SO ₄
1	22.6.95	6.95	57.10	275.52	152.98	110.00	538.50	0.112	163.76	190.10	160.00	59.13	18.42	591.52	0.910	0.555	0.826
2	11.7.95	6.71	111.30	161.72	256.05	108.21	525.98	0.195	201.94	363.30	19.17	75.65	26.84	687.09	0.766	1.583	1.353
3	17.7.95	7.00	28.30	249.40	216.21	118.03	583.63	0.100	245.44	553.00	67.50	177.82	65.78	1109.64	0.526	0.867	1.715
4	18.7.95	6.60	42.70	134.57	161.97	86.06	382.60	0.251	147.22	114.95	151.67	68.69	8.68	491.46	0.778	1.204	0.884
5	23.7.95	6.48	43.00	154.27	169.27	14.49	338.03	0.331	128.78	147.35	25.83	85.20	33.42	420.91	0.803	1.097	0.853
6	24.7.95	7.60	81.10	188.02	132.61	70.63	391.26	0.025	135.09	251.50	25.83	40.00	26.84	479.29	0.816	0.705	1.206
7	1.8.95	6.61	82.40	215.96	87.38	29.30	332.64	0.245	166.96	139.75	35.00	57.39	26.31	425.66	0.781	0.405	1.011
8	1.8.95	6.48	19.20	89.30	115.12	32.96	237.38	0.331	168.85	251.50	77.50	15.65	52.10	565.93	0.419	1.289	2.056
9	2.8.95	6.08	74.00	127.35	82.54	56.52	266.40	0.832	63.30	934.50	17.50	12.17	6.05	1034.35	0.258	0.648	4.754
10	3.8.95	6.19	17.40	113.85	76.89	30.14	220.88	0.646	13.04	934.20	27.50	23.47	12.36	1011.22	0.218	0.675	4.966
11	6.8.95	5.71	21.80	176.88	202.50	82.96	462.33	1.950	108.75	401.45	43.33	26.08	5.26	586.82	0.788	1.145	1.345
12	7.8.95	6.88	19.20	68.48	42.80	28.88	139.88	0.209	42.96	90.12	35.00	30.43	8.65	207.37	0.673	0.621	1.199
13	8/8/95	5.92	20.10	135.52	139.05	18.59	293.16	1.202	72.20	177.00	17.50	19.13	32.63	319.66	0.917	1.026	0.908
14	11.8.95	6.23	274.30	140.44	142.21	32.41	315.05	0.589	94.22	190.10	25.83	44.34	76.84	431.92	0.729	1.013	1.006
15	13.8.95	6.48	91.90	137.98	58.23	45.21	241.42	0.331	53.15	226.65	23.33	45.21	80.26	428.93	0.563	0.422	1.426
16	17.8.95	5.78	13.10	113.17	144.50	20.24	277.91	1.660	63.61	102.50	79.16	86.08	6.57	339.58	0.818	1.277	0.645
17	20.8.95	6.71	23.90	130.94	141.94	30.59	303.47	0.195	65.05	251.50	40.00	38.26	90.52	485.52	0.625	1.084	1.160
18	21.8.95	5.15	8.10	111.15	113.38	21.80	246.33	7.079	58.25	77.50	11.66	38.69	11.84	205.02	1.201	1.020	0.605
19	25.8.95	6.59	89.30	115.42	76.73	30.01	222.16	0.257	14.10	165.30	23.33	97.23	8.68	308.90	0.719	0.665	0.934
20	26.8.95	5.53	21.70	101.73	58.10	14.99	174.82	2.951	30.87	77.50	26.67	20.86	9.21	168.06	1.040	0.571	0.678
21	27.8.95	7.41	30.10	96.13	64.15	34.93	195.20	0.039	71.17	152.85	22.50	41.30	11.05	298.91	0.653	0.667	1.398
22	28.8.95	6.32	24.10	96.80	80.17	34.31	211.27	0.479	96.27	114.95	17.50	58.26	9.21	296.67	0.712	0.828	1.194
23	28.8.95	5.94	11.90	109.17	135.00	12.82	256.98	1.146	76.73	40.45	59.16	52.17	16.05	245.71	1.046	1.237	0.480
24	28.8.95	5.31	17.50	119.01	154.20	29.30	302.50	4.898	81.03	65.30	35.50	27.82	7.36	221.91	1.363	1.296	0.536
25	29.8.95	5.25	9.50	93.55	66.21	43.94	203.70	5.623	38.21	94.21	67.50	14.78	6.84	227.16	0.897	0.708	0.829
26	29.8.95	5.41	19.10	54.27	130.91	26.62	211.79	3.890	42.12	65.30	5.00	70.86	4.73	191.90	1.104	2.412	0.580
27	30.8.95	4.97	12.10	82.97	100.96	2.39	186.32	10.715	33.11	40.45	19.16	56.24	13.90	173.58	1.073	1.217	0.400
28	30.8.95	4.81	12.30	86.13	104.20	23.50	213.83	15.488	41.40	140.50	16.67	18.26	11.31	243.63	0.878	1.210	0.956
29	3.9.95	5.35	15.10	68.79	160.19	35.35	264.33	4.467	42.62	65.30	67.50	72.54	8.15	260.58	1.014	2.329	0.471
30	3.9.95	5.92	15.60	88.24	190.36	35.35	313.95	1.202	54.25	92.36	47.25	19.56	7.89	222.51	1.411	2.157	0.526
31	3.9.95	6.10	9.50	50.40	88.60	36.69	175.69	0.794	36.81	65.30	3.33	39.13	19.00	164.36	1.069	1.758	0.735
32	4.9.95	6.08	6.60	67.21	104.32	39.44	210.96	0.832	64.75	65.30	6.67	77.39	21.05	235.99	0.894	1.552	0.758
33	4.9.95	5.52	10.00	77.05	131.57	21.97	230.58	3.020	38.47	64.95	2.50	84.34	32.63	225.91	1.021	1.708	0.496
34	5.9.95	5.52	6.10	60.30	145.12	23.10	228.52	3.020	34.26	94.25	4.25	30.86	20.12	186.76	1.224	2.407	0.626
Avg		6.10	39.39	120.34	124.30	40.63	285.27	2.21	82.02	200.04	38.46	50.74	23.43	396.89	0.84	1.033	1.153
SD		0.68	50.60	52.75	49.09	28.81	107.84	3.35	56.51	216.94	36.68	33.00	23.09	250.30	0.27	0.931	2.685
Max		7.60	274.30	275.52	256.05	118.03	583.63	15.49	245.44	934.50	160.00	177.82	90.52	1109.64	1.41	0.929	2.220
Min		4.81	6.10	50.40	42.50	2.39	139.58	0.03	13.04	40.45	2.50	12.17	4.73	164.36	0.22	0.843	0.576

Table 5.5: Chemistry of wet deposition at Ashok Vihar, during monsoon '95

S.No	Date	pH Units	EC (μ mhos/cm)	SO ₄	NO ₃ (μ eq/L)	Cl	Anion Sum	H+	NH ₄	Ca	Mg (μ eq/L)	Na	K	Cation Sum.	An/Cat	NO ₃ /SO ₄	NH ₄ +Ca/ NO ₃ +SO ₄
1	19.6.95	7.08	132.00	72.40	115.97	50.42	238.79	0.083	168.86	412.85	48.33	52.17	22.89	705.18	0.339	1.602	3.088
2	11.7.95	6.23	85.30	198.07	125.73	56.86	380.66	0.589	173.30	226.65	84.17	48.69	15.78	549.18	0.693	0.635	1.235
3	17.7.95	6.53	38.60	105.26	257.22	42.39	404.87	0.295	142.62	202.50	65.00	84.34	3.94	498.70	0.812	2.444	0.952
4	22.7.95	5.13	63.30	168.13	167.86	61.93	397.91	7.413	95.28	177.00	68.33	92.17	7.89	448.08	0.888	0.998	0.810
5	30.7.95	6.73	57.10	163.86	144.27	60.85	368.97	0.186	105.77	252.15	35.00	32.17	11.57	436.85	0.845	0.880	1.162
6	3.8.95	6.52	42.10	160.21	40.74	25.63	226.57	0.302	44.94	114.95	25.83	102.60	5.52	294.14	0.770	0.254	0.796
7	4.8.95	7.21	41.50	127.80	170.28	39.86	337.93	0.062	149.77	190.10	30.83	62.60	17.63	450.99	0.749	1.332	1.140
8	5.8.95	6.51	69.20	155.34	154.27	59.30	368.90	0.309	192.05	201.85	30.83	13.91	14.73	453.68	0.813	0.993	1.272
9	6.8.95	6.53	68.70	157.44	126.19	25.63	309.25	0.295	184.79	226.65	25.83	13.04	15.00	465.61	0.664	0.802	1.451
10	7.8.95	6.54	68.70	146.02	58.00	25.63	229.65	0.288	144.18	65.30	23.33	70.43	15.00	318.53	0.721	0.397	1.027
11	10.8.95	6.75	70.10	60.67	92.34	34.08	187.08	0.178	203.46	164.60	6.67	46.08	4.21	425.20	0.440	1.522	2.406
12	16.8.95	6.78	42.80	100.58	85.05	12.54	198.16	0.166	122.31	139.75	6.67	56.52	63.15	388.57	0.510	0.846	1.412
13	20.8.95	5.71	30.10	102.87	111.94	18.72	233.52	1.950	50.15	90.10	30.83	16.52	39.73	229.28	1.018	1.088	0.653
14	26.8.95	5.53	47.60	117.55	147.70	46.72	311.96	2.951	88.97	127.35	12.50	20.86	17.67	270.30	1.154	1.256	0.816
15	30.8.95	5.10	14.80	106.88	181.29	22.55	310.71	7.943	47.15	194.40	3.33	27.82	21.05	301.69	1.030	1.696	0.838
16	2.9.95	6.20	50.20	83.49	111.57	30.32	225.37	0.631	25.59	189.40	3.33	39.13	2.63	260.71	0.864	1.336	1.102
17	3.9.95	5.02	7.20	99.17	117.72	19.05	235.93	9.550	22.89	152.85	1.67	16.52	5.52	209.00	1.129	1.187	0.810
18	4.9.95	5.10	12.01	26.98	167.74	2.96	197.68	7.943	19.73	107.70	0.00	14.78	3.42	153.57	1.287	6.217	0.654
Avg		6.18	52.30	119.59	131.99	35.30	286.88	2.285	110.10	179.79	27.92	45.02	15.96	381.07	0.818	1.416	1.201
SD		0.72	29.51	43.80	49.68	17.83	75.56	3.362	63.15	77.17	24.87	28.54	14.94	137.84	0.248	1.301	0.622
Max		7.21	132.00	198.07	257.22	61.93	404.87	9.550	203.46	412.85	84.17	102.60	63.15	705.18	1.287	6.217	3.088
Min		5.02	7.20	26.98	40.74	2.96	187.08	0.062	19.73	65.30	0.00	13.04	2.63	153.57	0.339	0.254	0.653

Table: 5.6: Chemistry of wet deposition at Janakpuri during monsoon '95

S.No.	Date	pH Units	EC ($\mu\text{mhos/cm}$)	SO ₄	NO ₃ ($\mu\text{eq/L}$)	Cl	Anion Sum	H ⁺	NH ₄	Ca	Mg ($\mu\text{eq/L}$)	Na	K	Cation Sum.	An/Cat	NO ₃ /SO ₄	NH ₄ +Ca/ NO ₃ +SO ₄
1	20.6.95	6.40	82.90	162.98	120.00	39.72	322.70	0.398	179.13	214.25	81.67	98.26	46.31	620.02	0.520	0.736	1.390
2	22.6.95	6.81	90.30	158.07	93.2	86.06	337.33	0.155	61.63	190.10	50.83	94.78	79.47	476.96	0.707	0.590	1.002
3	7.7.95	7.81	63.80	173.44	98.28	81.97	337.33	0.015	119.73	586.65	60.00	89.56	56.05	912.01	0.388	0.567	2.600
4	18.7.95	7.12	114.80	106.53	148.65	29.72	353.69	0.076	120.19	114.95	75.83	15.65	37.89	364.59	0.781	1.395	0.921
5	26.7.95	7.01	60.30	149.71	148.89	73.66	284.90	0.098	102.20	227.35	18.33	66.95	18.42	433.35	0.859	0.995	1.104
6	3.8.95	6.17	11.30	123.42	182.50	29.01	334.93	0.676	97.37	139.75	42.50	69.56	28.15	378.01	1.501	1.479	0.775
7	4.8.95	6.01	2.81	258.67	263.75	44.79	567.21	0.977	50.07	114.95	25.83	99.13	178.42	469.38	1.208	1.020	0.316
8	5.8.95	5.31	28.14	110.34	115.24	56.48	372.26	4.898	38.70	127.35	43.33	65.22	37.10	316.60	0.806	1.044	0.736
9	8.8.95	5.81	67.13	174.44	35.50	45.21	255.15	1.549	71.17	152.15	10.00	70.43	13.94	319.24	0.658	0.204	1.064
10	10.8.95	6.73	48.19	73.02	111.37	25.63	210.02	0.186	107.45	87.70	26.67	53.91	31.31	307.23	0.762	1.525	1.058
11	27.8.95	5.11	35.30	65.84	152.59	15.63	234.06	7.762	80.49	90.10	15.00	14.78	12.36	220.49	1.370	2.318	0.781
12	29.8.95	4.91	12.81	105.27	195.18	1.55	301.99	12.303	41.33	102.50	15.00	67.82	10.52	249.47	1.403	1.854	0.479
13	30.8.95	4.89	7.81	206.04	134.31	9.58	349.92	12.882	98.26	144.60	16.67	20.86	5.52	298.79	0.721	0.652	0.714
14	3.9.95	5.31	14.80	117.17	69.63	28.73	215.53	4.898	77.03	52.85	4.67	58.26	4.21	201.92	0.931	0.594	0.695
15	4.9.95	5.10	38.10	127.13	49.36	11.41	187.89	7.943	44.94	78.21	7.67	24.78	3.94	167.48	1.857	0.388	0.698
Avg		6.03	45.23	140.80	127.90	38.61	310.99	3.654	85.98	161.56	32.93	60.66	37.57	382.37	0.965	1.024	0.955
SD		0.92	33.93	50.60	58.65	26.30	89.11	4.570	37.91	127.56	24.84	29.56	44.48	188.98	0.411	0.588	0.526
Max		7.81	114.80	258.67	263.75	86.06	567.21	12.882	179.13	586.65	81.67	99.13	178.42	912.01	1.857	2.318	2.600
Min		4.89	2.81	65.84	35.50	1.55	187.89	0.015	38.70	52.85	4.67	14.78	3.94	167.48	0.388	0.204	0.316

The imbalances in ionic balance may be due to missing anion HCO_3^- which is mostly associated with Ca^{2+} and Mg^{2+} released from the soil (Khemani et al., 1987). HCO_3^- has not been measured in the present study. However, it has varied between 270 and 1032 $\mu\text{eq/L}$ at Delhi (Subramanian and Saxena, 1980).

5.2.1 pH of the rain water

The average pH value in all the stations are given in Tables 5.2 to 5.6. During the monsoon period, the average pH for JNU was 6.78 ± 0.49 , for Okhla it was 6.16 ± 0.84 , for I.T.O., it was 6.10 ± 0.68 for Ashok Vihar 6.18 ± 0.72 and for Janakpuri 6.03 ± 0.92 .

The number of acidic events at Okhla was eight, while at ITO, Ashok Vihar, Janakpuri and JNU it was nine, five, six and none respectively.

When compared with the reports of Subramanian and Saxena (1980), the pH values are less alkaline. The results in the present study also agree with the observations of Varma (1989a); Khemani et al (1982); Khemani et al (1989b) and Ravichandran and Padmanabamurty (1993), where they all have indicated that the trend in pH of Delhi is decreasing.

Variation of pH with anions (SO_4^{2-} , NO_3^- , and Cl^-) are given in Fig. 5.8 to 5.12. At JNU the pH values were always above 5.6 which indicates that the alkaline compounds were neutralizing the anions substantially. Only ITO experiences lower pH during the late August and September which could be due to the higher NO_3^- concentration and lower concentrations of cations. While in Janakpuri Okhla and

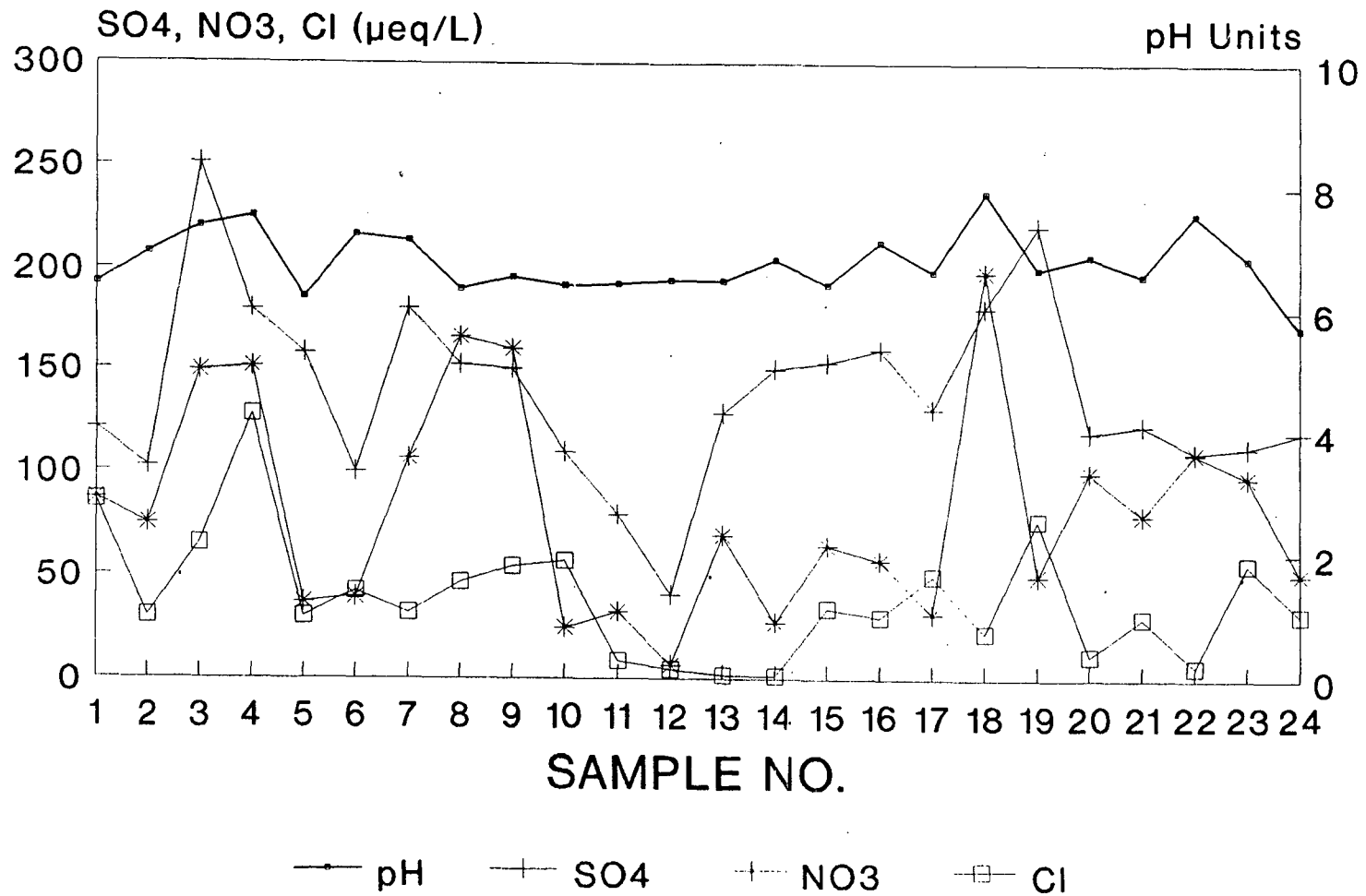


Fig. 5.8 : Variation of SO₄, NO₃ and Cl with pH at J.N.U.

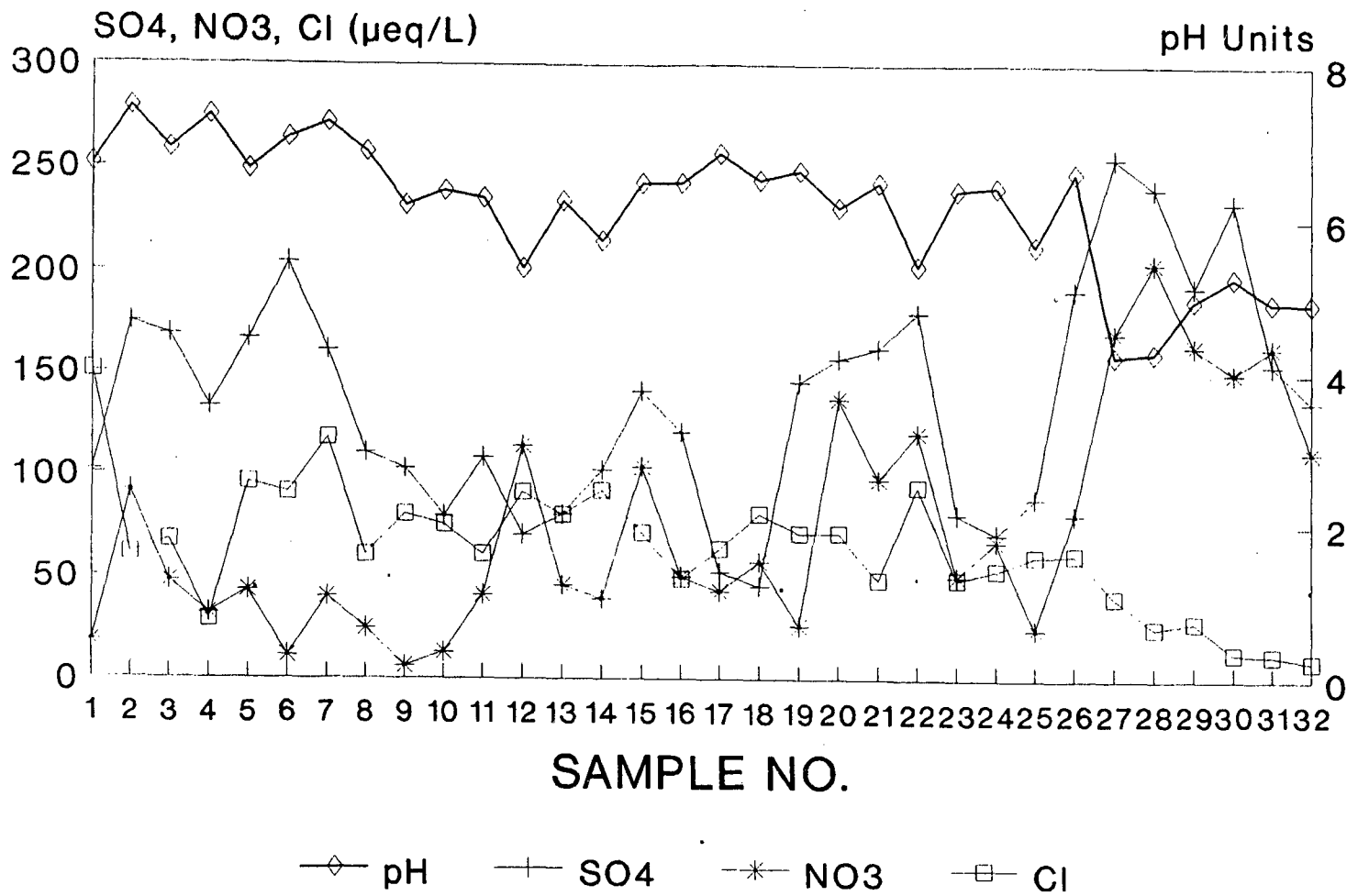
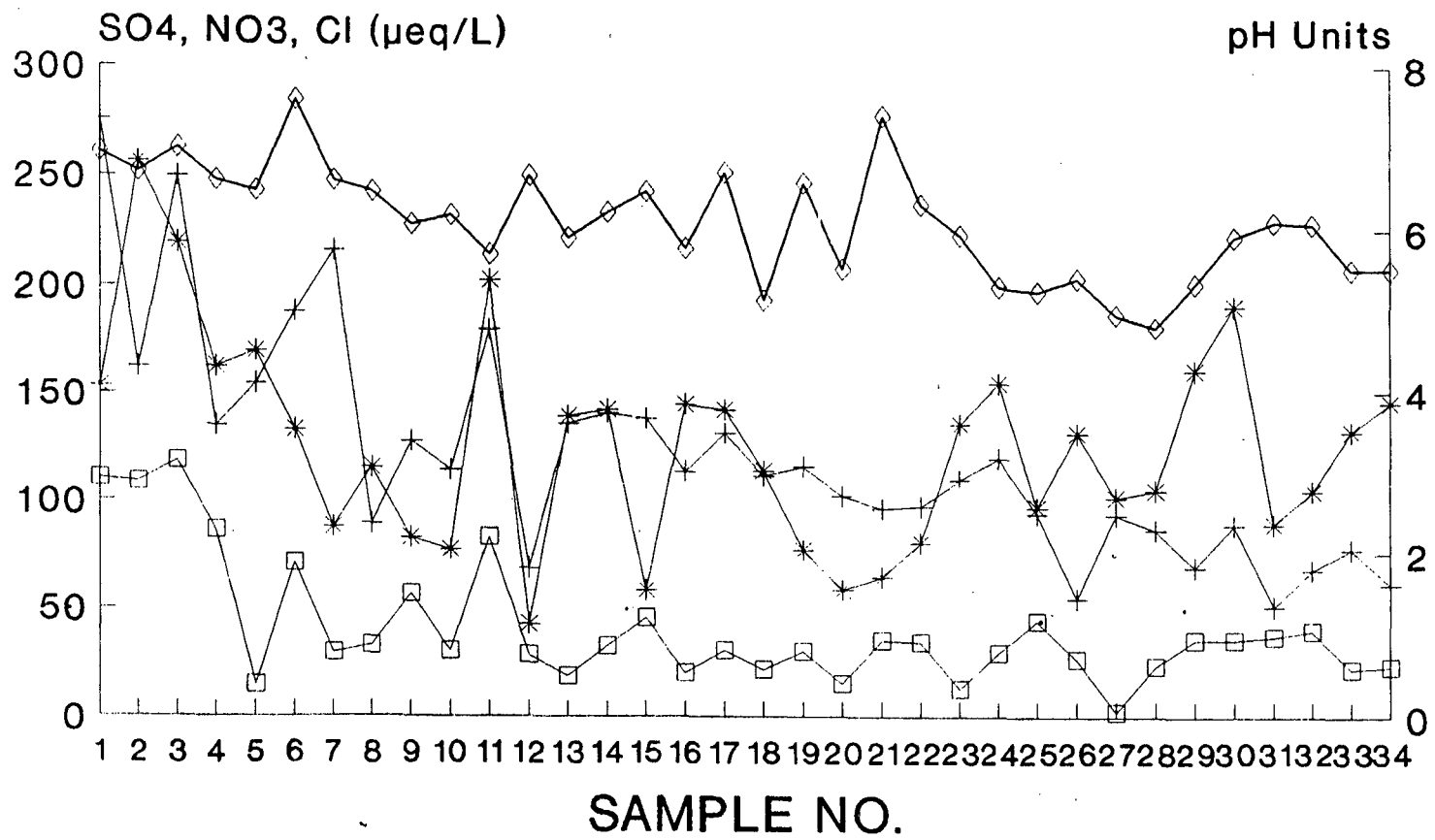


Fig. 5.9 : Variation of SO4, NO3 and Cl with pH at Okhla



—◇— pH —+— SO4 —*— NO3 —□— Cl
 Fig. 5.10 : Variation of SO4, NO3 and Cl with pH at I.T.O.

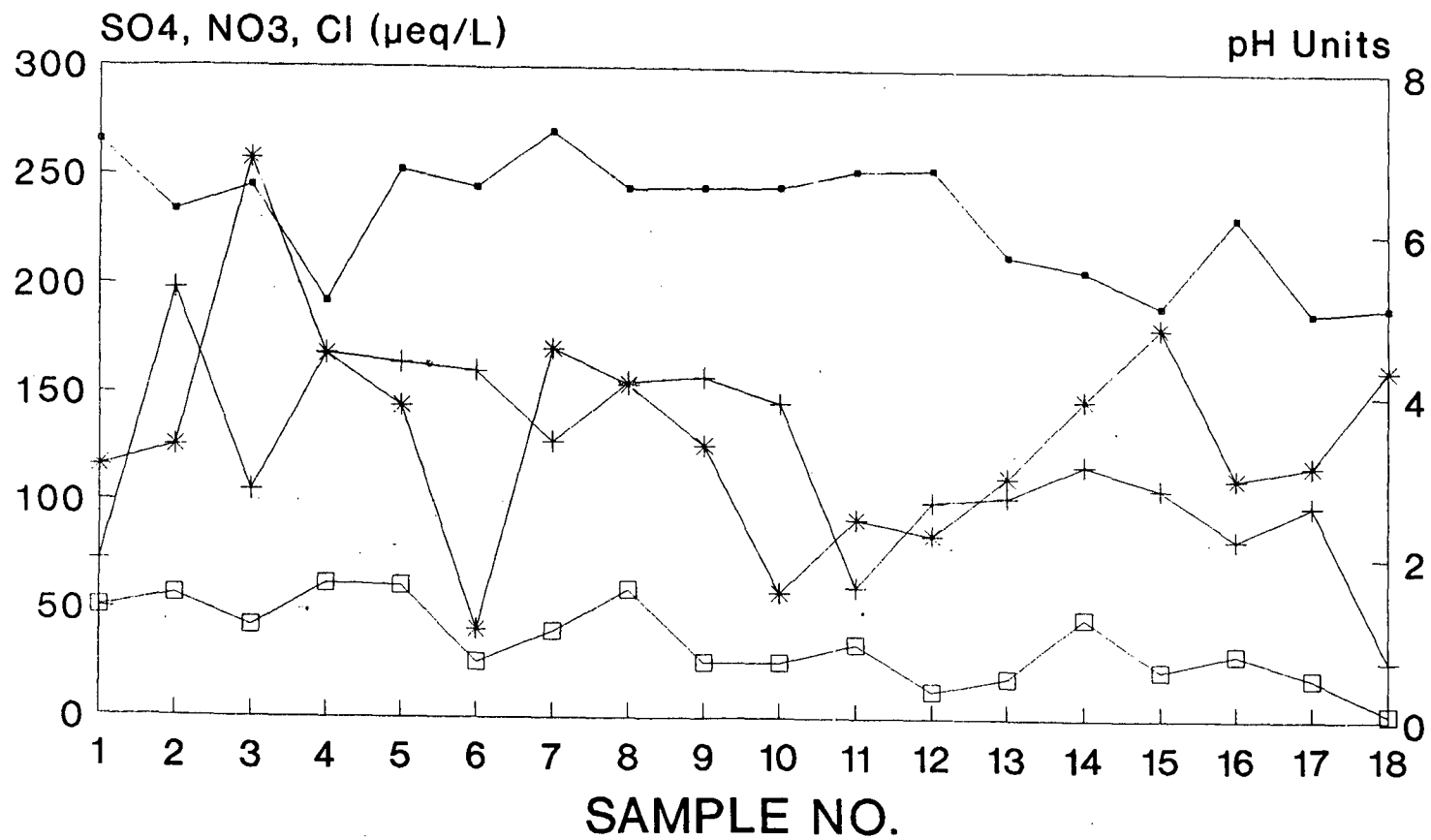


Fig 5.11 : Variation of SO₄, NO₃ and Cl with pH at Ashok Vihar

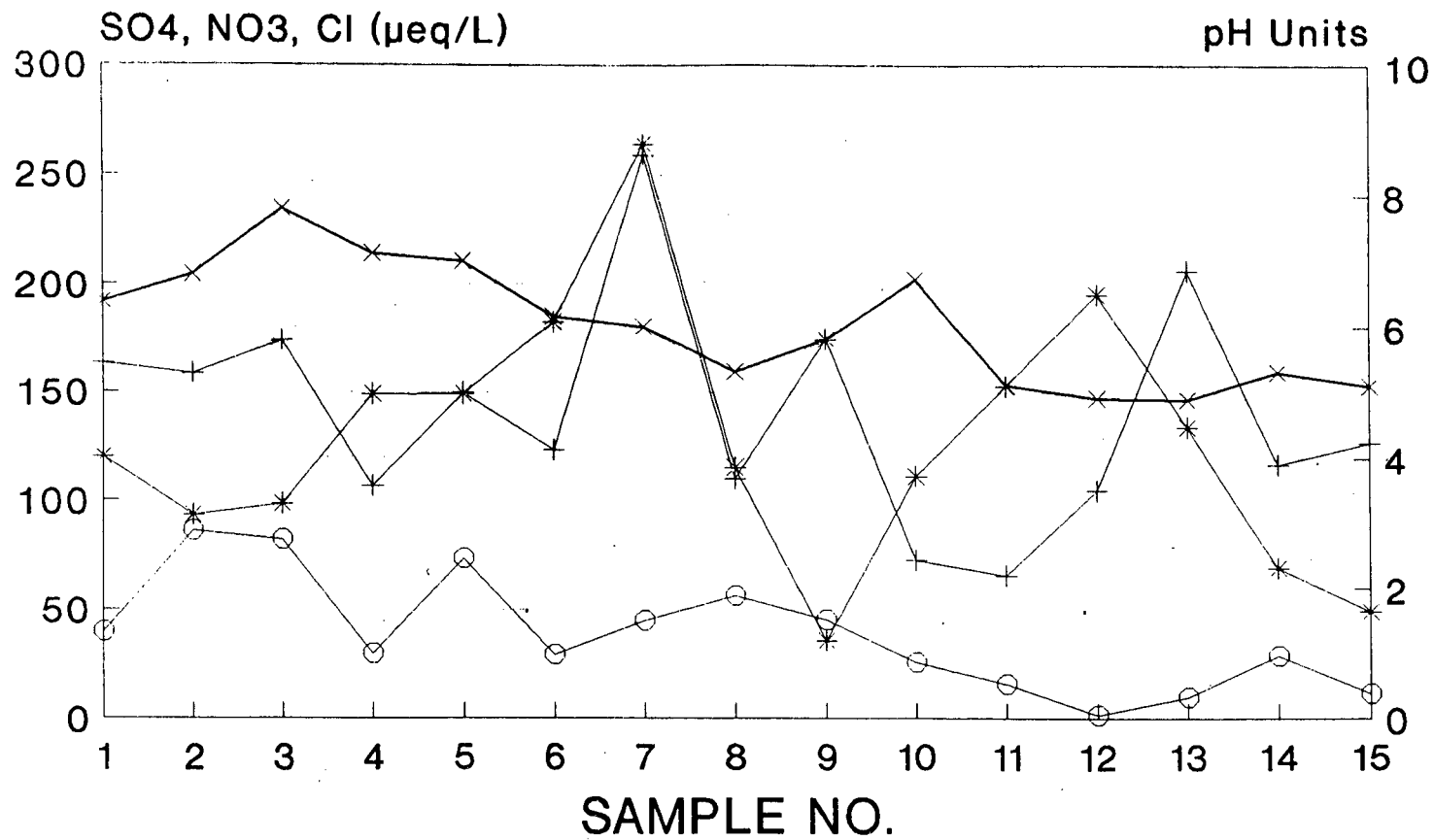


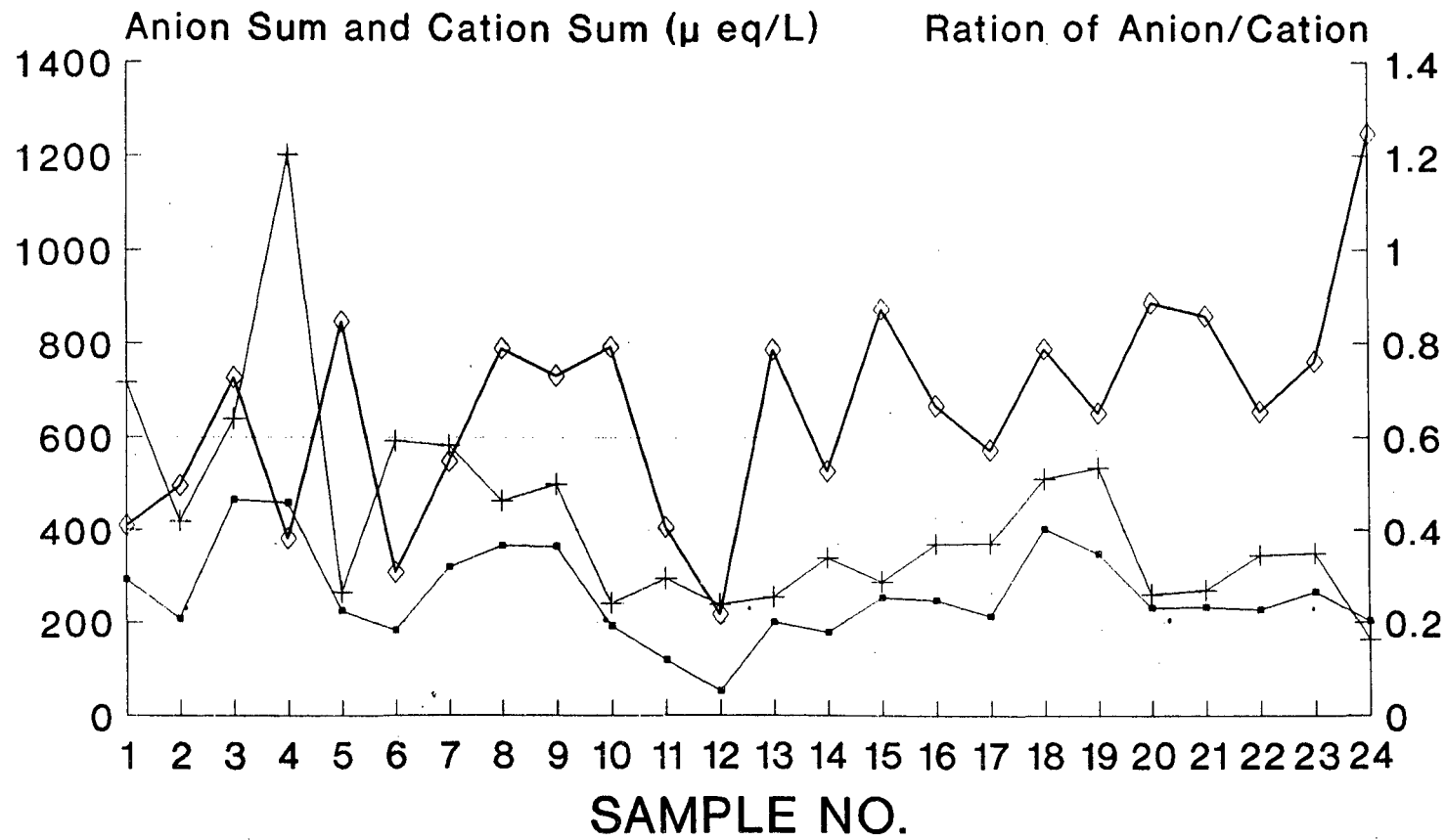
Fig. 5.12 : Variation of SO4, NO3 and Cl with pH at Jankpuri

Ashok Vihar, nitrate as well as sulphate increased acidity during the end of August and September. This can be attributed to the high industrial and vehicular pollution and also due to the lack of neutralizing ions.

5.2.2 Ratio of major ionic components

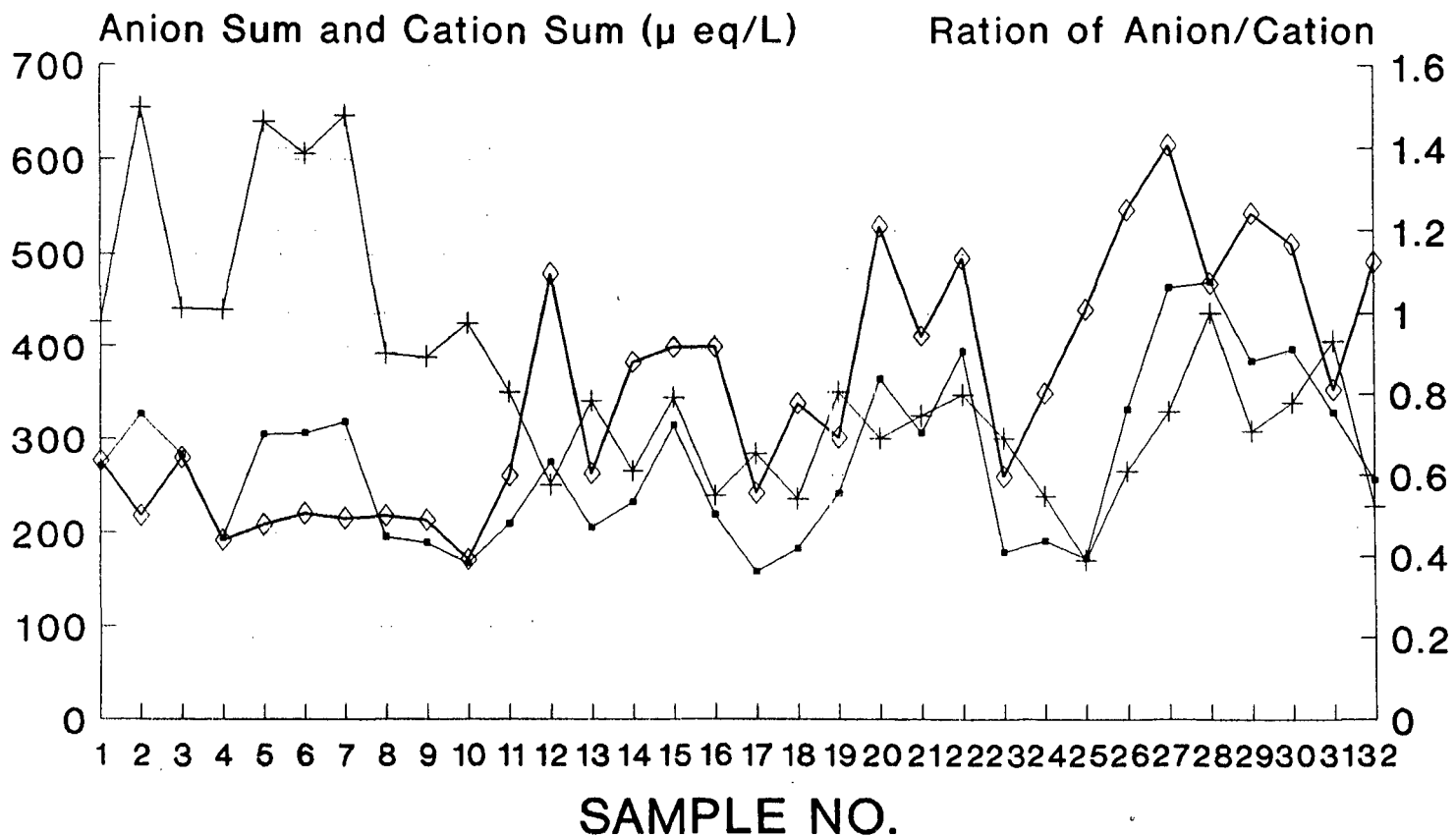
SO_4^{2-} and NO_3^- are the acidic ions. In precipitation the relative contribution by these ions are variable. The ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ shows their relative importance in acidification. When the ratio was above 1.0, HNO_3 influences acidity and while below 1.0 indicates H_2SO_4 is dominating (Khemani et al 1994). The ratio of $\text{NO}_3^-/\text{SO}_4^{2-}$ were calculated for all the five sampling stations and given in Table 5.2 to 5.6. The average which indicates that at these sites pH is more influenced by nitrate than sulphate while at the rest of the sites like JNU and Okhla the ratio was below 1 which indicates that here the sulphate influence is more. $\text{NO}_3^-/\text{SO}_4^{2-}$ ratio was more than 1.0 at ITO, Ashok Vihar and Janakpuri. In Bombay two locations had the $\text{NO}_3^-/\text{SO}_4^{2-}$ ratios above 1.0 which showed that the acid rain was influenced by HNO_3 (Khemani et al., 1994).

Ratio of $(\text{NH}_4^+ + \text{Ca}^{2+})/(\text{NO}_3^- + \text{SO}_4^{2-})$ was also calculated in order to know if acidic components like NO_3^- , SO_4^{2-} are neutralized by NH_4^+ and Ca^{2+} . If the ratio is greater than one it indicates NH_4^+ and Ca^{2+} have neutralized SO_4^{2-} and NO_3^- . The ratio varies between 0.4 to 4.9 for all the sites and the average ratio for Delhi is greater than one which shows that NO_3^- and SO_4^{2-} ions are neutralized substantially by NH_4^+



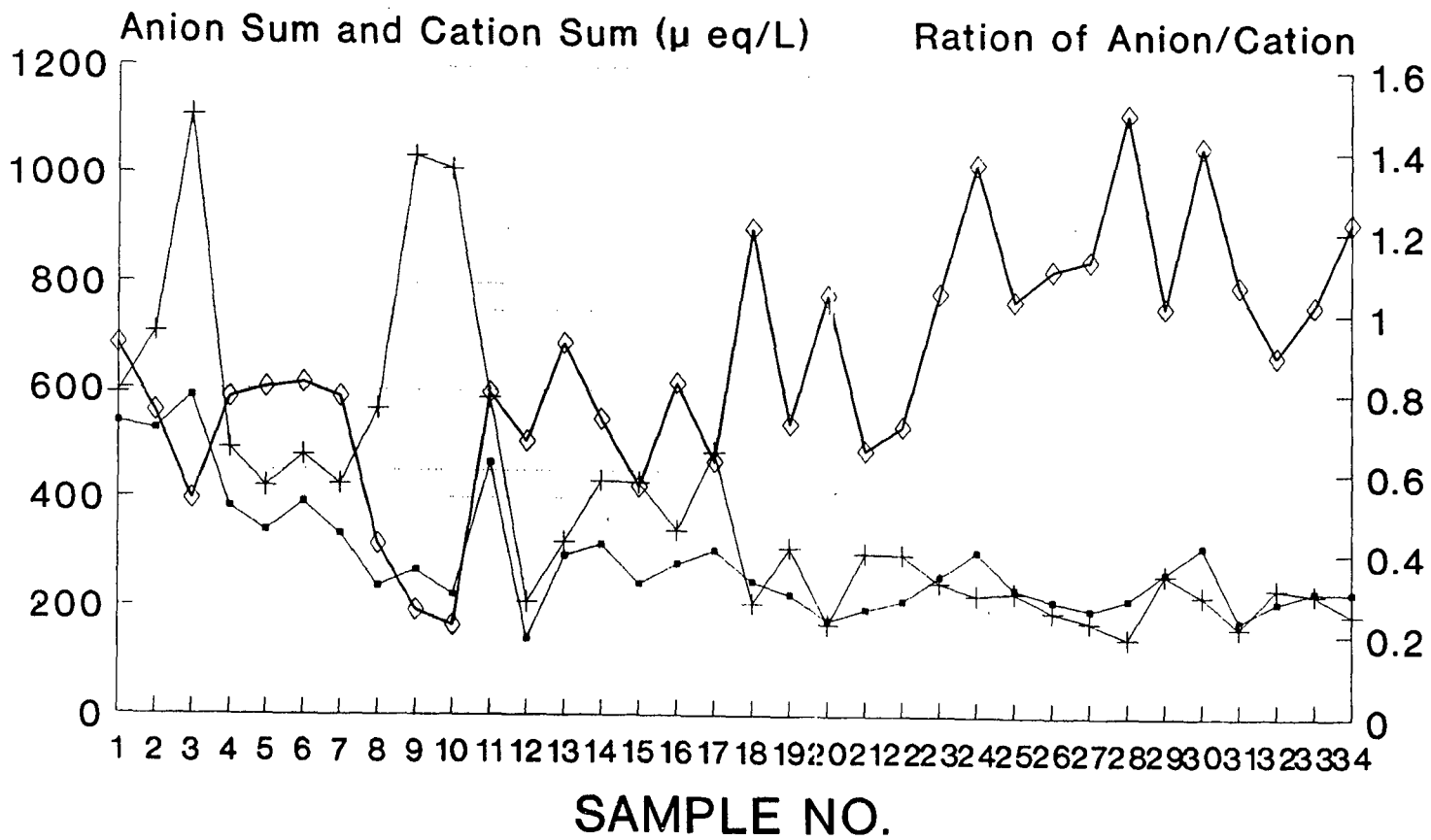
—●— Anion (Sum) —+— Cation (Sum) —◇— Anion/Cation

Fig. 5.13 : Variation of Anion Sum, Cation Sum and Ratio of Anion/Cation at J.N.U.



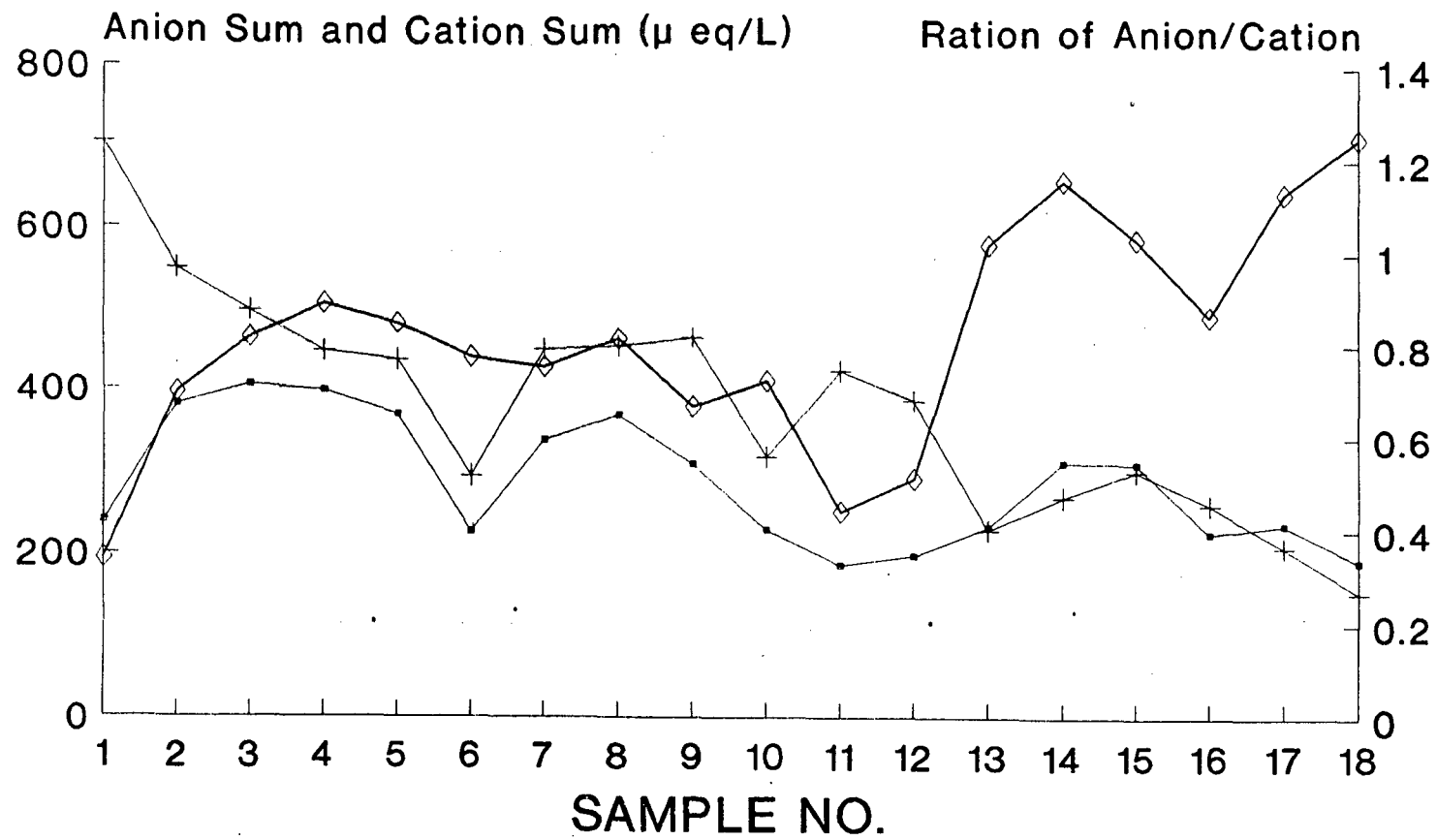
—●— Anion (Sum) —+— Cation (Sum) —◇— Anion/Cation

Fig. 5.14 : Variation of Anion Sum, Cation Sum and Ratio of Anion/Cation at Okhala



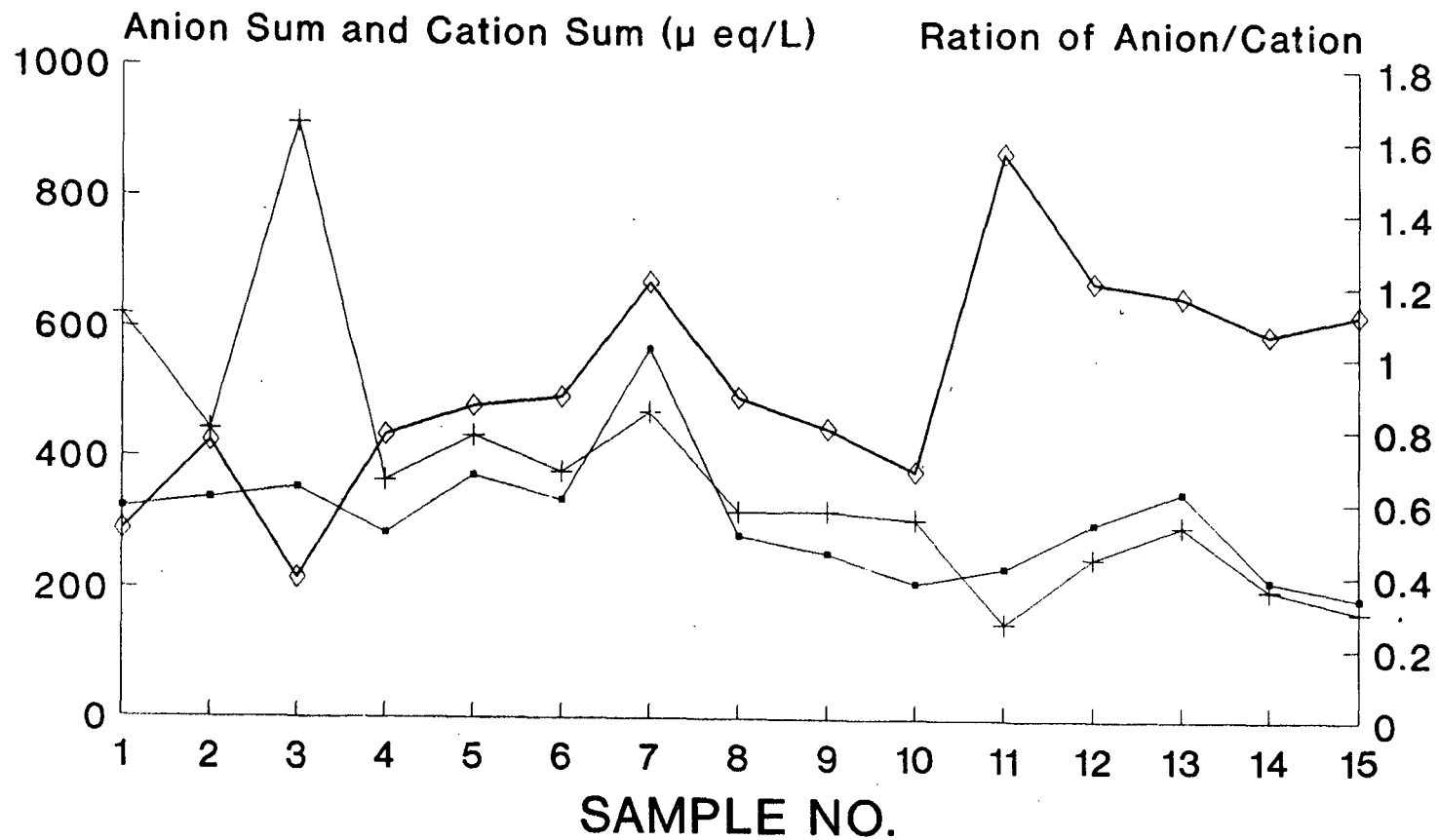
—●— Anion (Sum) —+— Cation (Sum) —◇— Anion/Cation

Fig. 5.15: Variation of Anion Sum, Cation Sum and Ratio of Anion/Cation at I.T.O.



—●— Anion (Sum) —+— Cation (Sum) —◇— Anion/Cation

Fig. 5.16: Variation of Anion Sum, Cation Sum and Ratio of Anion/Cation at Ashok Vihar



—●— Anion (Sum) —+— Cation (Sum) —◇— Anion/Cation

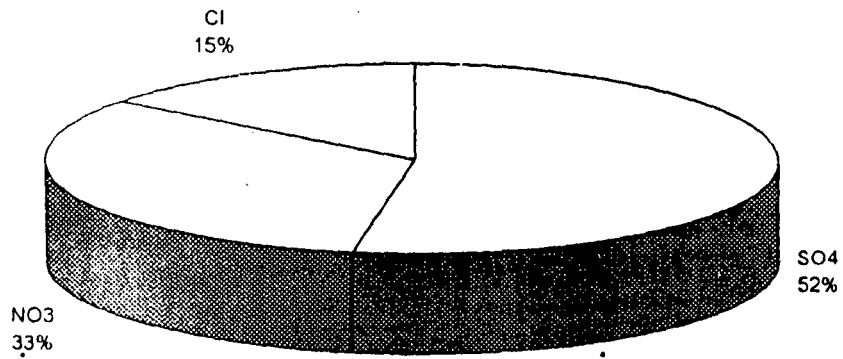
Fig. 5.17 : Variation of Anion Sum, Cation Sum and Ratio of Anion/Cation at Jankpuri

and Ca^{2+} . In the late August and early September, individual showers at various sites had this ratio below one except at JNU, which indicates that NO_3^- and SO_4^{2-} were not neutralised by ammonium and calcium ions but if neutralised, it might be due to other cations.

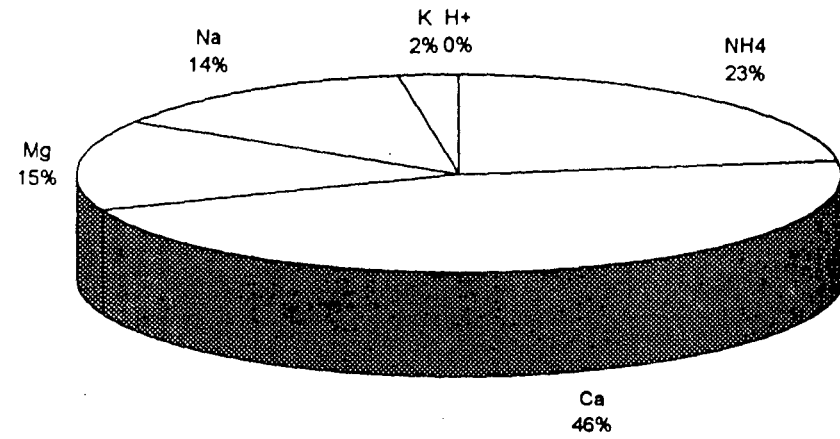
Ionic balance was done for all the samples collected at various sites, it is the "Sum of Anions / Sum of Cations" and the ratio should be one. If cations are more the ratio will be below 1.0 and if anions are dominating the ratio will be above 1.0. When the anions dominate, the chemistry of the water will be acidic (low pH). So, for ionic balance, the anion/cation ratio should always be 1.0. At all the sampling stations the ratio were always below 1.0 with an exception of a few samples. This shows that there is a deficit of anions and it might be due to the HCO_3^- which was not measured in the present study. The Fig 5.13 to 5.17 indicates that the ionic balance was above 1.0 during the end of the monsoon because of the wash-out of cations.

The contribution of each ion to sum of cations / sum of anions and total ion mass in precipitation is given in Fig 5.18 to 5.22. In JNU the anions followed the trend as $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$, while for cation it was $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. The contribution of each ion to total ion mass were $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{Na}^+ > \text{Cl}^- > \text{K}^+$. At Okhla, the anions followed the similar trend like JNU but for cations, it was $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+} = \text{Na}^+ > \text{K}^+ > \text{H}^+$. The contribution of each ion to total ion mass were $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{NO}_3^- > \text{NH}_4^+ = \text{Cl}^- > \text{Mg}^{2+} = \text{Na}^+ > \text{K}^+ > \text{H}^+$. At ITO, the trend in anion were $\text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$, and contribution of cation

Contribution of the Anions to the total Anion mass



Contribution of the Cations to the total Cation mass



Contribution of each ion to total ion mass

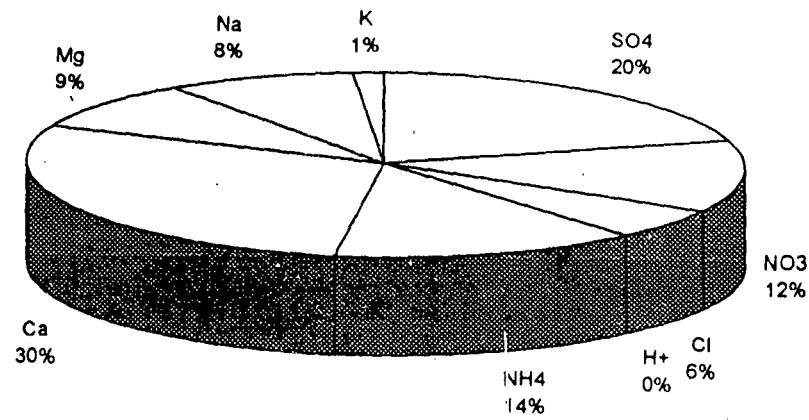
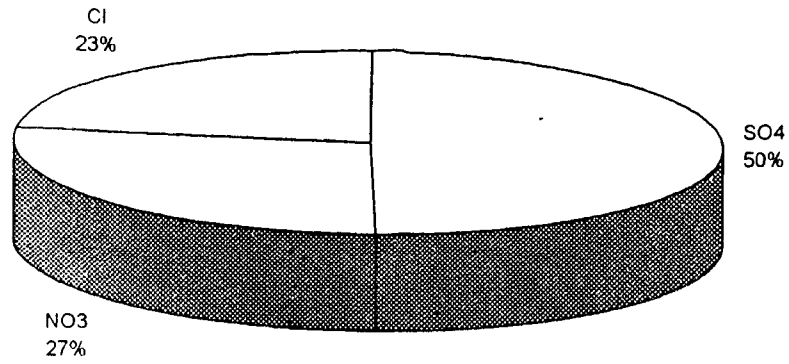
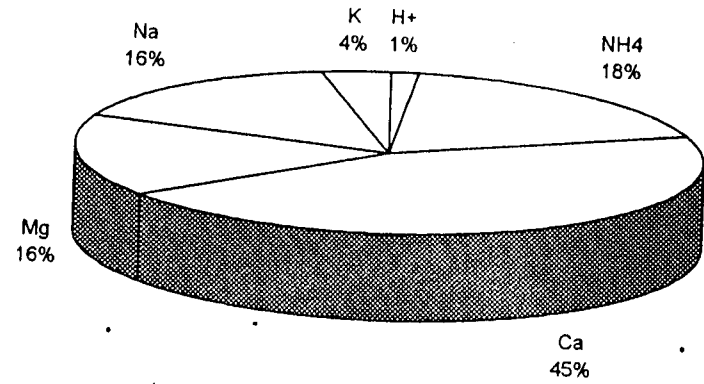


Figure 5.18 Contribution of each ion to anion, cation and total ion mass at JNU.

Contribution of the Anions to the Total Anion mass



Contribution of the Cations to the Total Cation mass



Contribution of each ion to the Total Ion mass

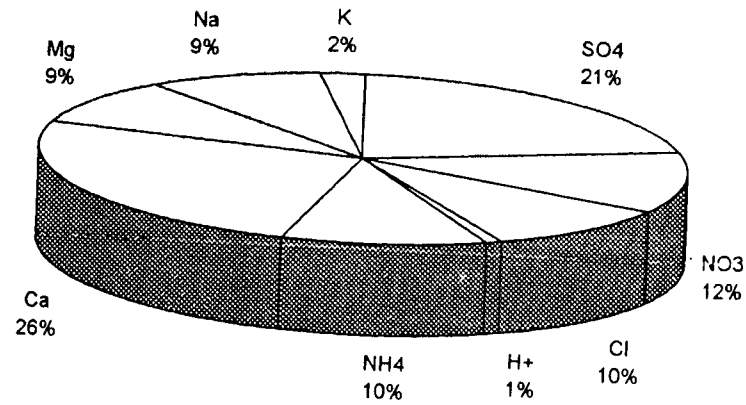
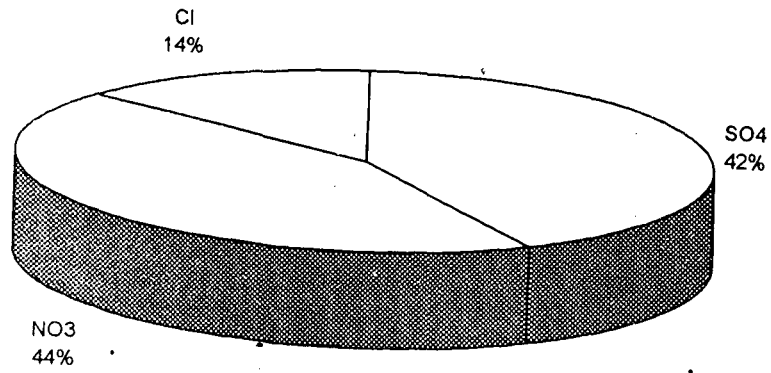
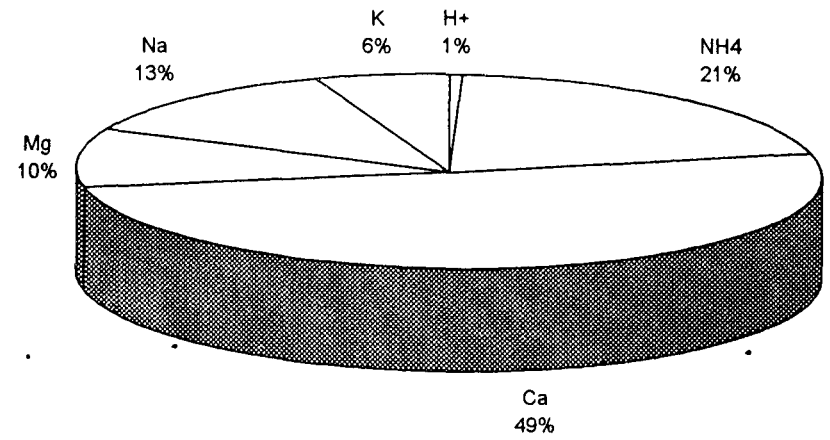


Figure 5.19 Contribution of each ion to anion, cation and total ion mass at Okhla.

Contribution of the Anions to the Total Anion mass



Contribution of the Cations to the Total Cation mass



Contribution of each ions to the Total Ion mass

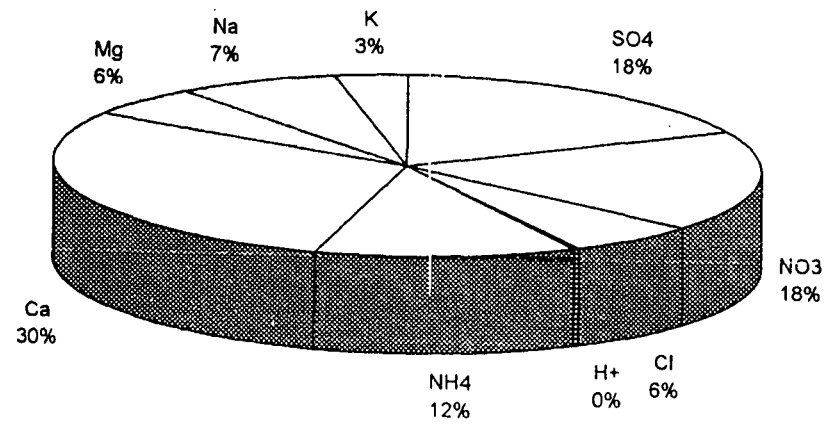
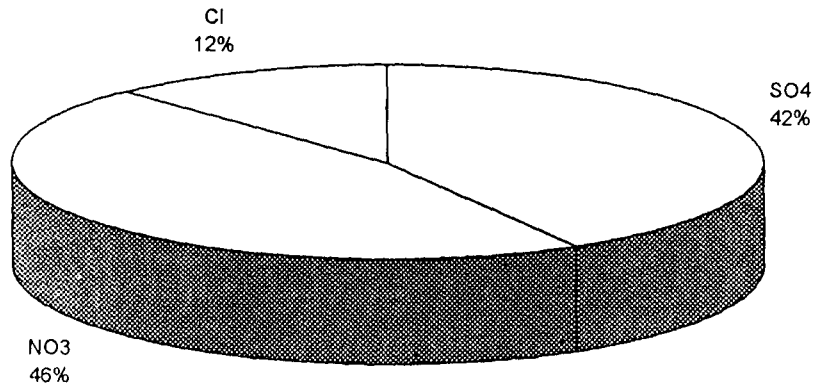
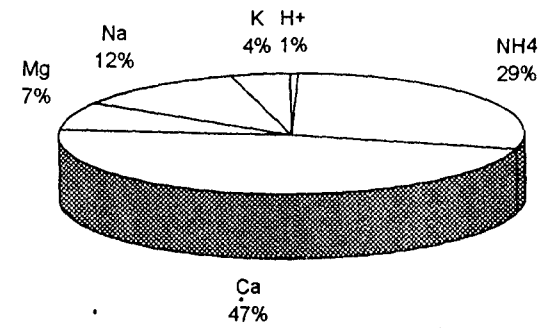


Figure 5.20 Contribution of each ion to anion, cation and total ion mass at ITO.

Contribution of Anion to Total Anion Mass



Contribution of Cations to Total Cation Mass



Contribution of each ion to Total Ion mass

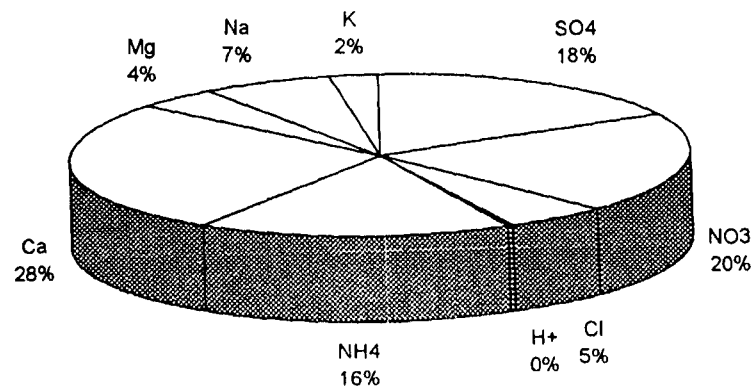


Figure 5.21 Contribution of each ion to anion, cation and total ion mass at Ashok Vihar.

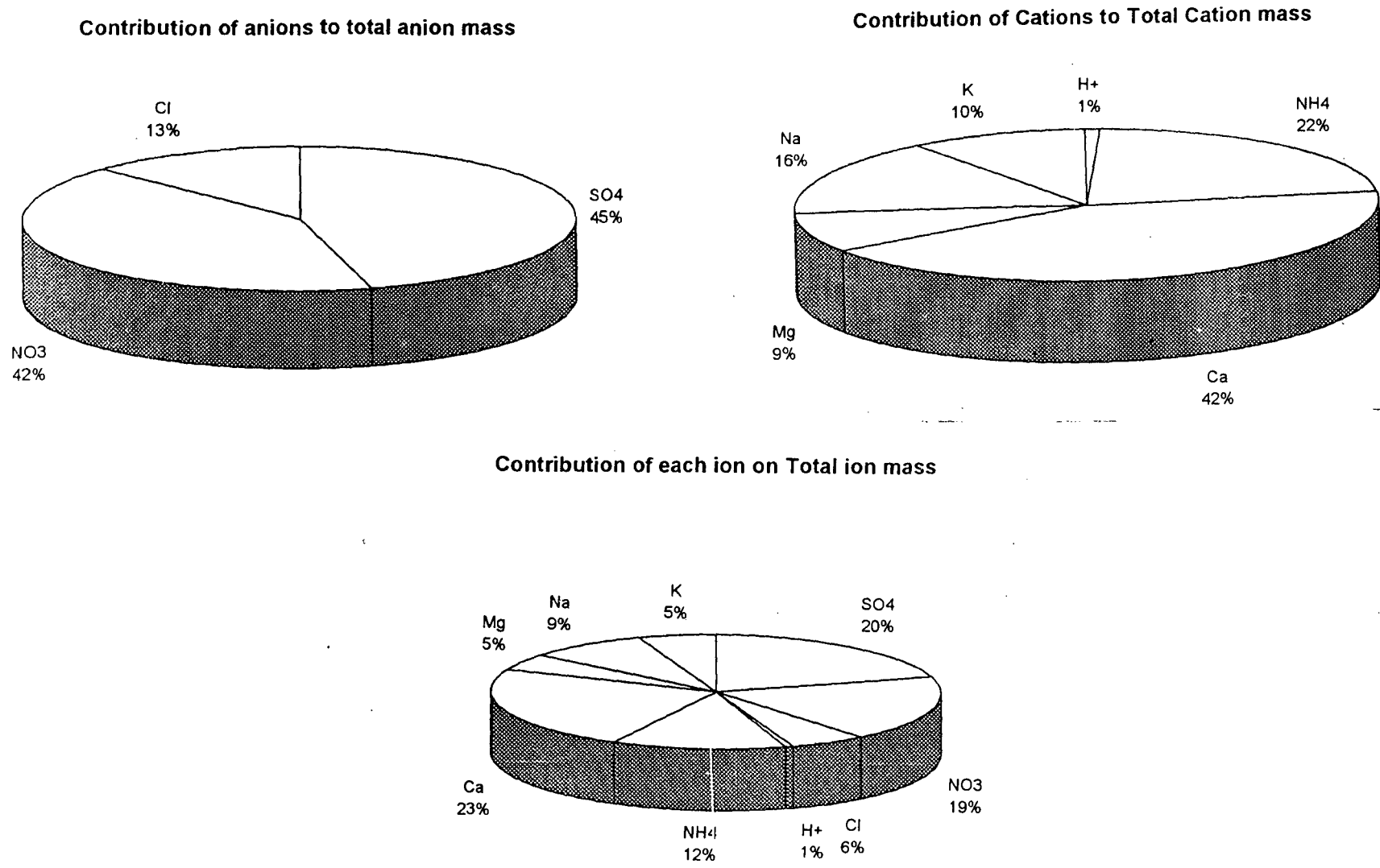


Figure 5.22 Contribution of each ion to anion, cation and total ion mass at Janakpuri.

were $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{H}^+$. The contribution of each ion to total ion mass was $\text{Ca}^{2+} > \text{SO}_4^{2-} = \text{NO}_3^- > \text{NH}_4^+ > \text{Na}^+ > \text{Mg}^{2+} = \text{Cl}^- > \text{K}^+$. At Ashok Vihar, the anion was following a similar trend as ITO, for cation the trend was $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ > \text{H}^+$. The contribution of each ion for total ion mass was $\text{Ca}^{2+} > \text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{Na}^+ > \text{Cl}^- > \text{Mg}^{2+} > \text{K}^+$. The anion trend at Janakpuri was following a trend like JNU and the cation trend was $\text{Ca}^{2+} > \text{NH}_4^+ > \text{K}^+ > \text{Mg}^{2+} > \text{H}^+$, and contribution of each ion to total ion mass were $\text{Ca}^{2+} > \text{NO}_3^- > \text{SO}_4^{2-} > \text{NH}_4^+ > \text{Na}^+ > \text{Cl}^- = \text{Mg}^{2+} > \text{K}^+$. Thus it is observed that at all the sites, in cation composition, calcium ion was predominant, varying between 42 to 49%. At JNU and Okhla around 50% of anionic composition was sulphate. Whereas for ITO, Ashok Vihar, Janakpuri, it was less than 50%. At JNU and Okhla, Nitrate concentration was roughly, half of the sulphate concentration, whereas, at ITO Ashok Vihar, and at Janak Puri, it was almost equal to sulphate concentration which can be attributed to the emission due to heavy vehicular traffic at ITO, Janak Puri and Ashok Vihar. In the total ionic mass composition, calcium has always been predominant at all the sites ranging from 26 to 30%. This shows that the calcium in Delhi, is contributed by some common source, probably aerosols from the Thar desert of Rajasthan.

5.3 GEOGRAPHICAL COMPARISON

In Delhi the first occurrence of acid rain was reported by Khemani et al (1989) near Indraprastha power station and later by Ravichandran and Padmanabamurthy in 1994. The chemical composition of Delhi was also compared

with China by Zhao et al. (1988). The pH value of in the present study corresponds to those reported in Northern China.

Table 5.1: Geographical comparison.

Location	pH	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	NH ₄ ⁺	Ca ²⁺	Na ⁺	K ⁺	Reference
Delhi	6.25	131.31	109.02	43.2	82.22	180.64	44.04	20.17	Present study
Turkey	5.64	66	23	117	43	81	117	17	Al-Momani (1995)
North DDR	4.57	173.3	42.5	94.0	95.5	67.6	56.7	9.2	Marquardt & Ihle (1988)
Saudi Arabia	5.48	233	181.6	144	45.6	462.9	130	11.5	Ahmed et al. (1990)
North China (Beijing)	6.7	337.5	81	59	1224.4	760	77.4	38.2	Zhao et al. (1988)
South China (ChongG -Jing)	4.07	411	21	8.2	78	231.2	10.1	126.4	Zhao et al. (1988)

The pH values of rain water in the present study correspond to those in northern China (non-acidic rain area) where alkaline dust particles are in high concentration like India, and neutral ion concentrations are formed by sulfuric and nitric acids.

5.4. CORRELATION BETWEEN RAIN WATER CHEMISTRY PARAMETERS:

Correlation analysis was done for major ionic components at the five stations in Delhi, which are as given in Table 5.8. Correlation analysis was done in order to know the relation between various components, so that the source could be known. At JNU calcium and sodium was correlated with chloride, but sodium and chloride ratio was always below 1.8. It shows that sodium and chloride are not of marine

Table 5.8: Correlation matrix for major ion in rainwater

a) JNU

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	H ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
SO ₄ ²⁻	1.00								
NO ₃ ⁻	0.24	1.00							
Cl ⁻	0.33	-0.15	1.00						
H ⁺	-0.12	0.04	-0.69	1.00					
NH ₄ ⁺	0.01	-0.06	0.13	-0.43	1.00				
Ca ²⁺	0.31	-0.11	0.65	-0.36	0.40	1.00			
Mg ²⁺	0.05	0.11	0.40	-0.55	0.63	0.45	1.00		
Na ⁺	0.48	0.16	0.63	-0.52	0.09	0.43	0.31	1.00	
K ⁺	0.63	0.56	0.41	-0.45	-0.09	0.16	0.30	0.59	1.00

b) Okhla

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	H ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
SO ₄ ²⁻	1.00								
NO ₃ ⁻	0.65	1.00							
Cl ⁻	-0.36	-0.55	1.00						
H ⁺	0.50	0.66	-0.37	1.00					
NH ₄ ⁺	0.15	0.03	0.11	-0.15	1.00				
Ca ²⁺	0.33	-0.14	0.14	0.03	0.23	1.00			
Mg ²⁺	-0.08	-0.23	0.27	-0.11	-0.43	-0.06	1.00		
Na ⁺	0.25	-0.16	0.34	-0.12	0.04	0.04	-0.01	1.00	
K ⁺	0.33	0.02	0.08	-0.16	0.53	0.39	0.00	0.18	1.00

c) ITO

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	H ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
SO ₄ ²⁻	1.00								
NO ₃ ⁻	0.40	1.00							
Cl ⁻	0.68	0.53	1.00						
H ⁺	-0.34	-0.10	-0.35	1.00					
NH ₄ ⁺	0.75	0.58	0.72	-0.38	1.00				
Ca ²⁺	0.34	0.06	0.39	-0.26	0.19	1.00			
Mg ²⁺	0.47	0.28	0.50	-0.20	0.45	-0.01	1.00		
Na ⁺	0.34	0.39	0.36	-0.22	0.44	-0.03	0.16	1.00	
K ⁺	0.31	0.15	0.13	-0.29	0.33	0.12	-0.03	0.20	1.00

d) Ashok Vihar

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	H ⁺	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
SO ₄ ²⁻	1.00								
NO ₃ ⁻	0.45	1.00							
Cl ⁻	0.45	0.29	1.00						
H ⁺	-0.19	0.09	-0.08	1.00					
NH ₄ ⁺	0.43	0.42	0.36	-0.43	1.00				
Ca ²⁺	0.35	0.37	0.79	-0.28	0.46	1.00			
Mg ²⁺	0.32	0.22	0.30	-0.40	0.40	0.34	1.00		
Na ⁺	0.36	0.11	0.67	-0.21	0.22	0.61	0.06	1.00	
K ⁺	0.12	-0.07	-0.03	-0.14	0.21	-0.10	-0.02	-0.17	1.00

e) Janakpuri

	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	H ⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
SO ₄ ²⁻	1.00								
NO ₃ ⁻	-0.09	1.00							
Cl ⁻	0.57	0.29	1.00						
H ⁻	-0.26	0.27	-0.30	1.00					
NH ₄ ⁺	0.31	0.03	0.50	-0.63	1.00				
Ca ²⁺	0.04	0.25	0.54	-0.23	0.42	1.00			
Mg ²⁺	0.59	0.31	0.70	-0.27	0.44	0.40	1.00		
Na ⁺	0.28	-0.10	0.21	-0.25	0.11	-0.03	0.46	1.00	
K ⁺	-0.01	-0.22	-0.24	-0.21	0.10	-0.05	-0.08	-0.11	1.00

origin and chloride which might be of industrial origin may form aerosol complexes with calcium and sodium (which are present more in the particulate matter) have a good correlation.

At Okhla sulfate and nitrate have good correlation which shows that nitrate might also be formed by industrial source in addition to vehicular source. At ITO, sulfate and chloride have very good correlation which shows that their source might be same i.e. industrial. Ammonium has a very good correlation with sulfate and nitrate showing that aerosols like NH_4^+ which forms $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 incorporates into the rain water. At Ashok vihar chloride is related to sulfate which shows that the source of chloride might be industrial in nature. Chloride and sulfate have a good correlation with magnesium which indicates that it might be incorporated into the magnesium aerosols. At Janakpuri, sodium and calcium have shown a good correlation with chloride while nitrate and sulphate are correlated with potassium.

5.5: MULTIPLE LINEAR REGRESSION ANALYSIS FOR DETERMINATION OF RAIN WATER QUALITY:

Rain water quality is determined mainly by the pH of the precipitation. In order to know how pH is influenced by the major cations and anions (i.e. sulphate, nitrate, chloride, sodium, magnesium, calcium, potassium and ammonium), a multiple regression analysis was done for all the five stations separately and in combination (for average values in Delhi). When this regression analysis was run, keeping pH as the dependent variable and the major cations and anions were taken as the independent variables the following results were obtained.

$$\text{pH} = 5.75 + 0.003 \text{ NO}_3 - 0.013 \text{ Cl} + 0.002 \text{ Na} + 0.002 \text{ Ca} + 0.004 \text{ Mg} \\
\begin{matrix} (2.4) & (3.62) & (1.33) & (3.28) & (2.07) \\ + 0.03 \text{ K} \\ (3.16) \end{matrix}$$

$$R^2 = 0.72 ; R^{-2} = 0.62$$

(The values in the parenthesis represent "t" values)

For JNU the overall fit is shown in the above equation. It is given by R^2 which shows that 72 % of the variation in pH is determined by nitrate, chloride, sodium, calcium, magnesium and potassium. Looking at the variables individually we observe that calcium is the most significant variable among cations which affects the changes in pH while potassium and magnesium influence only to some extent. Sodium is insignificant while chloride has inverse relationship with pH. Surprisingly, nitrate is seen to have a positive correlation with pH, which might be due to the association between nitrate and alkaline dust. Since all the cations like calcium, magnesium and potassium are crustal in origin and are known to influence the pH, whenever they show an increase, the pH also increased (became alkaline).

$$\text{pH} = 6.41 + 0.011 \text{ NO}_3 + 0.006 \text{ NH}_4 + 0.001 \text{ Ca} \\
\begin{matrix} (7.37) & (3.43) & (1.15) \end{matrix}$$

$$R^2 = 0.72 ; R^{-2} = 0.69$$

In the above analysis, for Okhla samples the overall fit given by R^2 which shows that 72 % of the variation in pH is explained by nitrate, ammonium and calcium where nitrate seems to be the most significant variable affecting the pH and

hence the increase in nitrate will decrease pH (towards acidity). Ammonium which increases pH (towards alkalinity) has the maximum significant coefficient while calcium and other variables are insignificant.

$$\text{pH} = 5.96 - 0.007 \text{NO}_3 + 0.005 \text{NH}_4 + 0.006 \text{K} + 0.009 \text{Cl}$$

$$\begin{matrix} & (3.16) & (2.06) & (1.70) & (2.06) \\ & & & & \end{matrix}$$

$$R^2 = 0.54 ; R^{-2} = 0.47$$

At ITO (the above analysis) the overall fit is given by R^2 which shows that 54 % of the variation in the pH is explained by nitrate, chloride, ammonium and potassium, where nitrate is the most significant anion affecting the pH. Hence when nitrate increases the pH decreases. Here again, surprisingly, chloride (anion) which is having a positively significant coefficient also having a good correlation with ammonium and calcium, showing thereby that these ions are having close association with each other. While in cations, ammonium and potassium have a good significance and influence pH.

$$\text{pH} = 4.9 - 0.006 \text{SO}_4 + 0.01 \text{NH}_4 + 0.007 \text{K} + 0.01 \text{Cl} +$$

$$\begin{matrix} & (1.9) & (2.66) & (1.88) & (2.05) \\ & & & & \\ & 0.002 \text{Ca} & & & \\ & (1.34) & & & \end{matrix}$$

$$R^2 = 0.82 ; R^{-2} = 0.72$$

In Janakpuri the fit shows that 82 % of the variable which influence pH are ammonium, calcium, potassium, sulphate and chloride. When these variables are observed closely ammonium (cation) shows the highest significance influencing the most, while surprisingly chloride (anion) has a positive coefficient.

$$\text{pH} = 4.67 + 0.01 \text{ Na} + 0.008 \text{ NH}_4 + 0.002 \text{ Ca} + 0.011 \text{ Mg} +$$

$$(2.17) \quad (3.57) \quad (1.34) \quad (1.76)$$

$$R^2 = 0.63 \quad ; \quad R^{-2} = 0.52$$

At Ashok Vihar the fit showed that 63 % of the variables have influenced pH which are sodium, ammonium, magnesium where sodium and ammonium had a high significance and magnesium had a significant negative coefficient which shows that when magnesium increases the pH decreases.

For Delhi, the overall result is given below.

$$\text{pH} = 5.8 - 0.002 \text{ SO}_4 - 0.005 \text{ NO}_3 + 0.002 \text{ Na} + 0.007 \text{ NH}_4 +$$

$$(1.94) \quad (5.73) \quad (1.82) \quad (7.10)$$

$$0.001 \text{ Ca} + 0.004 \text{ Mg} + 0.006 \text{ K}$$

$$(3.04) \quad (3.25) \quad (2.94)$$

$$R^2 = 0.52 \quad ; \quad R^{-2} = 0.49$$

The above equation gives the overall fit for all the sites is given by R_2 which shows that 62 % of the variation in the pH is explained by sulphate, nitrate, calcium, magnesium, potassium and ammonium. Looking at the variables individually we observe that nitrate is the most significant variable which influences the pH among anions while in cations ammonium influences most though magnesium, calcium, potassium and sodium also influence the pH to some extent. Since only 52 % of the variation is explained, there might be other variables like HCO_3 and organic acids which influence the pH of the rain water or it might also be due to the other unexplained factors like various meteorological parameters.

To have a more clear understanding of the problem, the study needs further extension in terms of long-term monitoring of ambient air, study of various meteorological factors influencing the rain water quality and some apportionment studies, and quantitative assessment of neutralization of sulphate and nitrate.

CHAPTER VI

CONCLUSION

From the present study the following important conclusions can be drawn.

- 1) In Delhi the pH of rain water ranged from 4.26 to 7.91, the average value being 6.25.
- 2) Only 18% of the collected samples showed the pH value below 5.6 which means in general the pH of rain water is alkaline.
- 3) At ITO, Ashok Vihar and Janakpuri the pH of precipitation is influenced more by nitric acid, (which may be due to NO_x from vehicular emissions) whereas at JNU and Okhla it is by sulfuric acid (which may be due to SO_2 emissions from thermal power plants and other neighbouring industries).
- 4) In Delhi nitrate and sulphate are substantially neutralised by ammonium and calcium.
- 5) The ratio of anion to cation in precipitation for overall Delhi is below 1.0, showing that the concentration of cations are more than that of anions.
- 6) At all the sites in Delhi Ca^{2+} was the predominant ion followed by SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , Mg^{2+} , Cl^- and K^+ in decreasing order.
- 7) In total ionic mass Ca^{2+} has always been predominant at all sites, ranging from 26-30%. This shows that Ca^{2+} in Delhi has got some

common source and aerosols from Thar desert may be one of the major contributor.

- 8) In Delhi the pH of rainwater was influenced most by NH_4^+ among cations and by NO_3^- among anions.

REFERENCES

- Ahmed A.F.M., Singh R.P. and Elmubarak A.H. (1990). *Atmospheric Environment*, 24-A, (12), 2927-2934.
- Al-Momani I.F., Ataman O.Y., Anwari M.A., Tuncel S., Kose C., and Tuncel G. (1995). *Atmospheric Environment*, 29, 1131-1143.
- Ananth K.P., Galoski J.B., Shanon L.J., Hona F.I. and Drehmal D.C. (1977). In: **Fourth Clean Air Congress, Japan Union of Air Pollution Prevention Association.**
- Andreae M.O. (1985). In: **The Biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere:** Galloway, J.N., Charlson, R.J., Andreae, M.O. and Rodhe, H. (Eds.) 5-25. D. Reidel, Dordrecht, Holland.
- APHA (1989) Standard methods for the examination of water and waste water.
- Applin K.R. and Jersak J.M. (1986). *Atmospheric Environment*, 20, 965-969.
- Ayers G.P. (1990). In: **Proceedings of Regional Symposium "Chemistry and Environment"**, Brisbane, 1989, Commonwealth Science Council, London, pp.121-132.
- Ayers G.P. and Gillett R.W. (1988). In: **Acidification in Tropical Countries:** Rodhe H. and Charlson R. (Eds.) SCOPE 36: 347-400. John Wiley and Sons, Chichester, England.
- Barnard W.R., Stensland G.J. and Gatz D.F. (1986). *Water, Air and Soil Pollution*, 30, 285-293.
- Barrie L.A. and Schemenauer R.S. (1986). *Water, Air and Soil Pollution*, 30, 91-104.
- Barrie L. A. (1985). *J. Geophys. Res.*, 90, 5789.
- Binns W.O. (1985). *The Environmentalist* 5, 279-288.
- Biswas D.K. (1994). *Times of India*, English Daily, Nov. 26th.
- Bridgmen H.A. (1992). *Atmospheric Environment*, 216, 1009-1022.

- Buijjsman E., Maas J.F.M, and Asman W.A.H. (1987). **Atmospheric Environment**, 21, 1009-1022.
- Burton C.S., Liu M.K., Roth P.M., Seignur C. and Whitten G.Z. (1983). In: **Air Pollution Modelling and its Application -II** ed. Wispelacre. C. pp. 3-58. Plenum Press, New York.
- Butler T.J., and Likens G.E. (1991). **Atmospheric Environment**, 25A, 305-315.
- Byron E.R., Axler R.P. and Goldman C.R. (1991). **Atmospheric Environment**, 25A 271-278.
- Calvert J.G. and Stockwell W.R. (1983). **Environ. Sci & Technol.**, 17, 428 A-443A.
- Camarerro L. and Catalan J. (1993). **Atmospheric Environment**, 27A, 83-94.
- Camuffo D. (1992). **Atmospheric Environment**, 26B, 241-247.
- Casado H., Ezcurra A., Durana N., Albala J. L., Garcia C., Ureta I., Lacaux J.P. and Van Dinh P. (1989). **Atmos. Res.** 22, 297-307.
- Chan W.H., Tang AL. J.S., Ching D.H.S. and Reid N.W. (1987). **Envir. Sci. Technol.** 21, 1219-1224.
- Charlson R.J. and Rodhe H. (1982). **Nature**, 295, . 683-685.
- Chatfield R.B. and Crutzen P.J. (1984). **J. Geophys. Res.**, 89, . 7111-7132.
- Cheng R. J., Hwu J.R., Kin J.T. and Leu S.M. (1987). **Anal. Chem.** 59, 104A-106A.
- Cheng R.T., Corn M. and Frohlinger J.O. (1971). **Atmospheric Environment**, 5, 987-1008.
- Clark P.A., Fisher B.E.A. and Scriven R.A. (1987). **Atmospheric Environment**, 21, 1125-1131.
- Collin J.L., Renard D., Lescoat V., Jaffrezo J.L., Gros J.M. and Srauss B. (1989). **Atmospheric Environment**, 23, 1487-1498.
- CPCB (1989). **Assessment of Vehicular Pollution in Metropolitan cities - Part II - Delhi:** Cups/18/1988-89, Central Pollution Control Board, Delhi.

- Crawley J. and Sievering H. (1986). **Atmospheric Environment**, 20, 1001-1013.
- Das D.K. (1988). **Mausam**, 39 (1), 75-82.
- Dasch J.M. and Cadle S.H. (1984). **Atmospheric Environment**, 18, 1009-1016.
- Dasch J.M. and Cadle S.H. (1985). **Atmospheric Environment**, 19, . 789-796.
- Daum P.H., Schwartz, S.E. and Newman L. (1983). In: **Precipitation Scavenging, Dry Deposition and Resuspension** (edited by Pruppacher H.R., Semonin R.G., and Slinn W.G.N.), New York: Elsevier.
- Dickson W. (1980). In: **Proceedings of International Conference on Ecological Impact of Acid Precipitation**. D. Drablos and A. Tollau (Eds.) Sanderfjord, Norway.
- Dikaiakos J. G., Tsitouris G.G. Sisjos P.A., Melissos D.A. and Nastos P. (1990). **Atmospheric Environment**, 24B, 171-176.
- Dillon P.J., Lulis M., Reid R. and Yap D. (1988). **Atmospheric Environment**, 22, 901-905.
- Dokiya Y., Aoyama M., Katsuragi Y., Yoshimura E. and Toda S. (1987). In: **The chemistry of Acid Rain** (edited by Gordon G.E.), vol. 349, pp. 258-272. American Chemical Society, University of Maryland.
- Environment Canada (1984). In: **The Acid Rain Story**. Published by Ministry of Supply and Service Canada Catalogue No. En-21-40/1984C.
- Eriksson E. (1952). **Tellus**, 4, 214-263.
- Farmer G., Barthlmie R.J., Davies T.P., Brimplacompe P. and Kelly P.M. (1987). **Nature**, 328, 757-789.
- Fay J.A., Golomb D. and Kumar S. (1985). **Atmospheric Environment**, 21, 1773-1782.
- Galbally I.E. (1985). In: **The biogeochemical Cycling of Sulfur and Nitrogen in the Remote Atmosphere**. Gallway J.N., Charlson R.J., Andreae M.O. and Rodhe, H. (Eds.) pp. 27-53. D. Reidel, Dordrecht, Holland.

- Galbally I.E. and Gillett R.W. (1988). In: **Acidification in Tropical Countries**. Rodhe H. and Herrera R. (Eds.). SCOPE Report 36: pp. 73-116. John Wiley and Sons, Chichester, England.
- Galloway J.N., Likens G.E. and Hawley M.E. (1984). **Science**, 226, 829-831.
- Galloway J.N., Likens G.E., Keene, W.C. and Miller J.M. (1982). **J. Geophys. Res.**, 87, . 8771-8786.
- Galloway J.N., Zhao D., Xiong J. and Likens G.E. (1987). **Science**, 236, 1559-1562.
- Galloway J.N. (1988). In: **Acidification in Tropical Countries**. Rodhe H. and Herrera R. (Eds.) SCOPE 36: pp. 141-166. John Wiley and Sons, Chichester, England.
- Gatz D.F. (1984). **Atmospheric Environment**, 18, 1895.
- Gatz D.F. (1991). **Atmospheric Environment**, 25-B, 1, 1-15.
- Gatz D.F., Barnard W.R. and Stensland G.J. (1985). **Air Pollution Control Association**, Pittsburing, PA.
- Gatz D.F., Barnard W.R. Stensland G.J., (1986). **Water, Air and Soil Pollution**, 30. 245-251.
- Grant L., Rodhe H. and Hallberg R.O. (1976). In: **Nitrogen, Phosphorus and Sulphur-Global Cycles**. Stevenson B.H. and Soderlund R. (Eds.) SCOPE 7, Ecol Bull. (Stockholm) 22, pp. 89-134.
- Gross E. (1970). **The National Air Pollution Potential Forecasting Program**. ESSA Tech. Mem. WBTM NMC 47, U.S. Department of Commerce.
- Hales J.M. (1988). In: **Acid Rain, The Relationship between Sources and Receptor**. ed., White, J.C. Elsevier Press.
- Handa B.K. (1969). **Tellus** 21, 95-100.
- Hedin L.O., Likens G.E. and Borrmann F.H. (1987). **Nature** 325, 244-246.
- Hinrichsen D. (1987). **Ambio**. 258-265.
- Huebert B.J. and Lazrus A.L. (1980). **J. Geophys. Res.** 85, 7322-7328.

- Irwin G. and Williams M.L. (1988). **Envir. Poll.**, 50, 29-59.
- Johansson C., Rodhe H. and Sanhueza E. (1988). **J. Geophys. Res.**
- Kaplan W.A., Wofsy S.C., Keller M. and da Costa J.M. (1988). **J. Geophys. Res.**
- Keene W.C., Galloway J.N. and Holden D., Jr., (1983). **J. Geophys. Res.**, 88, 5122-5130.
- Kessler C.J. Porter T.H., Firth D., Sager T.W. and Hen shill M. W. (1992). **Atmospheric Environment**, 26A, 1137-1146.
- Khemani L.T. (1989). In: **Air Pollution Control Technology**. pp. 401-452. Gulf Publications, U.S.A.
- Khemani L.T. and Ramana Murthy Bh. V. (1968). **Tellus**, 20, 284-292.
- Khemani L.T., Monin G.A., Naik M.S., Rao P.S.P., Kumar R., and Ramana Murthy Bh. V. (1985a). **Atmospheric Environment**, 19, 277-284.
- Khemani L.T., Monin G.A., Naik M.S., Rao P.S.P., Kumar R. and Ramana Murthy Bh. V. (1985b). **Water Air Soil Pollution**, 24, . 365-376.
- Khemani L.T., Monin G.A., Naik M.S., Rao P.S.P., Kumar R. and Ramana Murthy Bh. V. (1985c). **J. Atmos. Chemistry**, 2, 273-285.
- Khemani L.T., Momin G.A., Naik M.S., Rao P.S.P., Safai P.D. and Murthy A.S.R. (1987). **Atmospheric Environment**, 21, 1137-1145.
- Khemani L.T., Monin G.A., Naik M.S., Vijayakumari R. and Ramana Murthy Bh. V. (1982). **Tellus**, 34, . 151-158.
- Khemani L.T., Momin G.A., Rao P.S.P., Pillai A.G., Safai P.D., Mohan K. and Rao M.G. (1994). **Atmospheric Environment**, 28, 3145-3154.
- Khemani L.T., Momin G.A., Rao P.S.P., Safai P.D., Singh G., Chaterjee R.N. and Prakash P. (1989a). **Atmospheric Environment**, 19, 277-284.
- Khemani L.T., Momin G.A., Rao P.S.P., Safai P.D., Singh G and Kapoor R.K. (1989b). **Atmospheric Environment**, 23, 757 - 762.
- Krishnanand (1984). **Mausam**, 35, 225-231.

- Last F.T. and Watling R. (eds) 1991. In: **Acid deposition: Its nature and impacts**.
Edinburgh: The Royal Society.
- Leaitch W.R., Strapp J.W., Wiche H.A. and Issac G.A. (1983). In: **Precipitation Scavenging, Dry Deposition and Resuspension** (edited by Pruppacher H.R., Semoni R.G. and Slinn W.G.N.), Vol. 1, pp. 53-59, Elsevier, New York.
- Lewis W.M., Grant M.C.Jr. and Saunders J.F. (1984). **Water Resource Research**, 20, 1691-1704.
- Likens G.E. and Bormann F.H.C. (1974). **Science**, 184, 1176 - 1141.
- Lindberg S.E. (1982). **Atmospheric Environment** 16, 1701 - 1709.
- Low P.S. (1988). **The Science of the Total Environment**, 77, 253 - 268.
- Loye-Pilot M.D., Marten J.M. and Morelli J. (1986). **Nature**, 321, 429-428.
- Mahadevan T.N., Meenakshy V and Mishra U.C. (1985). **Indian. J. Envir. & Health**, 27, 9 - 14.
- Mahadevan T.N., Meenakshy V., and Sathe A.P. (1984). **Mausam**, 35, 87-90.
- Marquardt W. and Ilhe P. (1988). **Atmospheric Environment**, 22, 2707-2713.
- Marsh A.R.W. (1978). **Atmospheric Environment**, 12, 401.
- Martin J.J., Wang P.K. and Pruppacher H.R. (1980) **J. Colloid and Interf. Sci.**, 78, 44.
- McQuaker N.R., Kluckner P.D. and Sandberg D.K. (1983). **Envir. Sci. Technol.**, 17, 431-435.
- Meenakshy V., Mahadevan T.N. and Mishra U.C. (1992). Precipitation chemistry at BARC site in Bombay. In: **Proc. of Nat. Sym. on Environment**, Feb. 3-5, 1992.
- Middleton P., Kiang C.S. and Mohnene V.A. (1980). **Atmospheric Environment**, 14, 463-472.
- Mollar D.M. (1984). **Atmospheric Environment**, 18, 19 - 27.

- Morgan J.J. (1982). In: **Atmospheric Chemistry** (edited by Goldhergend E.D). Springer, Berlin.
- Mukherjee A.K. (1957). **Indian J. Meterol. Geophys.**, 8, . 321-324.
- Mukherjee A.K. (1978). **Indian J. Meterol. Geophys.**, 29, p.749.
- Mukherjee A.K. and Krishnanand (1981). **Mausam**, 32, 3, . 231-236.
- Mukherjee A.K., Krishnanand and Ghanekar S.G. (1986). **Mausam**, 37, 313-316.
- Mukherjee A.K. and Krishnanand., Mukhopadhyay B., Ramnath U.P. (1985). **Mausam**, 36, 267-274.
- Mukhopadhyay B., Datar S.V. and Srivastava, H.N. (1992). **Mausam**, 43, . 249-258.
- Mukhopadhyay B., Singh S.S., Datar S.V. and Srivastava H.N. (1993). **Mausam**, 44, 179-184.
- Munger J.W. (1982). **Atmospheric Environment**, 16, . 1633-1645.
- Naik M.S , Khemani L.T., Monin G.A. and Rao P.S.P. (1988). **Acta Meteorologica Sinica**, 2, 1, . 91-100.
- Narayana Swami R. (1939). **Proc. Ind. Acad. Sci., Section A**, 9, . 518-524.
- NEERI (1991). Air pollution aspects of three Indian megacities, Vol. 1: Delhi. National Environment Engineering Research Institute, Nagpur.
- Nihlgard B. (1985). **Ambio**, 14,4.
- Padmanabhamurty B. and Tangirala R.S. (1990). **Atmospheric Environment**, 24-A, 845-848.
- Pickering K.T. and Owen L.A. (1992). **An Introduction to global environmental issues**, Routledge Press.
- Pollution Statistics Delhi. (1995) **Central Pollution Control Board**.
- Kumar Pramod (1995) Ph.D. Thesis, School of Environmental Sciences, JNU, New Delhi.

- Pratt G.C., Casio M.R and Krupa S.O. (1984). **Atmospheric Environment**, 16, 1633-1645.
- Raemodonck H., Maenhaut W. and Andreae M.O. (1986). **J. Geophys. Res.** 91, 8623-8636.
- Ravichandran C and Padmanabhamurthy B.(1994). **Atmospheric Environment**, 28, 229 - 229.
- Ro C.U. (1988). **Atmospheric Environment**, 22, 2763-2772.
- Rao P.S.P., Momin G.A., Safai P.D., Pillai A.G. and Khemani L.T. (1993). In : **Int. Conf. on Sust. Dev. Strat. & Global/ Regional/Local Impacts on Atmos. Composition & Climate**, Jan. 25 - 30, 1993 New Delhi.
- Roberts D.B. and Williams D.J. (1979). **Atmospheric Environment**, 13, 1485-1499.
- Rodhe H. (1976). In: **Nitrogen, Phosphorus and Sulphur - Global cycles**. SCOPE: 7, Ecol. Bull. (eds) Stevenson, B.H. and Soderland, R. Stockholm, 22, 123-134.
- Rodhe H., Crutzen P. and Vanderpol A. (1981). **Tellus** 33, 132-141.
- Rodhe H., and Herrera R. (1988). In: **Acidification in tropical countries**. SCOPE 36, J.Wiley & Sons Ltd.
- Ryaboshapko A.G. (1983). In: **The global bioeochemical sulfur cycle**. SCOPE: 19, Invanov M.V. and Freney J.R. (eds) . 203-296. John Willey and Sons. Chichester, England.
- Sadasivam S. (1979). **Mausam**, 30, 449-456.
- Samara C., Tsitouridou R. and Balafoutis Ch. (1992). **Atmospheric Environment**, 26B, 359-367.
- Sanhueza E., Cuenca G., Gomez M.J., Herrera R., Ishizaki C., Martin J. and Paolini J. (1988). In: **Acidification in Tropical Countries**. SCOPE 36: (eds) Rodhe H. and Herrera R. 197-255. John Wiley and Sons, chichester, England.
- Sanusi A., Wortham H., Millet M., Mirabel P., (1996). **Atmospheric Environment**,30, 59-71.
- Saxena P., and Seigneur C. (1987). **Atmospheric Environment**, 21, . 807-812.

- Saxena P., Hudischevskyj A.B., Seigneur C. and Seionfeld J.H. (1986) **Atomospheric Environment**, 20, 1471 - 1484.
- Saxena A., Sharma S., Kulshrestha V.C. and Srivastva S.S. (1991). **Environmental Pollution**, 74, 129-138.
- Schofield C.L. (1982). In: **Acid Rain/Fisheries, Proceedings International Symposium on Acidic Precipitation and Fishery Impacts**.
- Seigneur C. and Saxena P. (1984). **Atmospheric Environment**, 18, . 2109-2124.
- Seigneur C., Saxena P., Roth P.M. (1984). **Science** Vol. 225, 1028-1029.
- Seinfeld J.H. (1980). In: **Atmospheric chemistry and physics of air pollution**. A Wiley Interscience Publ. John Wiley & Sons, New York.
- Sequeria R. (1976). **Tellus**, 28, 275-282.
- Shannon D.G. and fine L.O. (1974). **Envir. Sci. & Technol.**, 8, 1026.
- Sharma V.P., Arora H.C. and Gup0ta R.K. (1983). **Atmospheric Environment** 17, 1307 - 1314.
- Sharma M. and McBean E.A. (1995). **Atmospheric Environment**, 29, 2157-2162.
- Shrivastava H.N., Data S.V. and Mukhopadhyay B. (1992). **Mausam**, 43, (2) 183 - 190.
- Singh M.P., Goyal P., Panwar T.S., Agarwal P. and Nigam S. (1990). **Atmospheric Environment**, 23, 757-762.
- Singh M.P., Goyal P., Panwar T.S., Agarwal P., Nigam S. and Bagchi N. (1990). **Atmospheric Environment**, 24-A, 783-788.
- Sisterson D.L. and Shannon J.D. (1990). **Atmospheric Environment**, 24-B, 389-394.
- Smirmioudi V.N. and Siskos P.A. (1992). **Atmospheric Environment**, 26 B, ~~483~~ 490.
- Stern (1976). In: **Air Pollution**. Vol.I. Air Pollutants, Their Transformation and Transport. Ed. Stern. A.C.

- Subramanian V. and Saxena K.K. (1980). **Tellus**, 32, 558-561.
- Surendran P.K. (1993). Delhi: The most polluted city in India. **Times of India**, English Daily, Feb. 6th 1993.
- Swedish Ministry of Agriculture (1982). **Acidification today and tomorrow**. Swedish Ministry of Agriculture, Stockholm, Sweden.
- Treolar N.C., (1993). **Atmospheric Environment**, 27 A, 965-974.
- Varhelyi G. (1985). **Atmospheric Environment**, 19, 1029-1040.
- Varma G.S. (1986). **Atmospheric Environment**, 25, 747-751
- Varma G.S. (1989a). **Atmospheric Environment**, 23, 4, 747-751.
- Varma G.S. (1989b). **Atmospheric Environment**, 23, 2723-2728.
- Vong R.J. (1990) **Atmospheric Environment**, 24 A, 1007 - 1018.
- Wagner G.S. and Steele K.F. (1987). **Atmospheric Environment**, 21, 1353-1362.
- White J.C. (1988) In: **Acid Rain - The Relationship Between Sources and Receptors** ed. White S.C. Elsevier Press.
- Wirikler P. (1984). In: **Chemistry of Particles-Fogs and Rain** (Eds Durham J.L.), pp. 161-195. Butterworth, Stoneham, M.A.
- Wolff G.T., Liyo P.J., Golub H., and Hawkins J.S. (1979). **Environ. Sci. Tech.**, 13, 209-212.
- Yamaguchi K., Tatano T., Tanaka F., Nakao M., Gomyoda M and Hara.H. (1991). **Atmospheric Environment**, 25A, 285-291.
- Zhao D. and Sun B. (1986). **J.Air.Poll.Cont.Assoc.**, 36, 371-374.
- Zhao D. and Xiong J. (1987). In: **Acidification in Tropical Countries**. SCOPE 36. Rodhe H. and Herrera R. (Eds.) 317-346, John Wiley and Sons, Chichester, England.
- Zhao D., Xiong J., Xu.Y. and Chan W.H. (1988). **Atmospheric Environment**, 22, 349-358.