ABSTRACT

Acid rain has been a rallying cry of the environmentalists over the past three decades in most parts of the industrialised world. This phenomenon is attributed to ever increasing $\text{SO}_2$ and $\text{NO}_x$ ($\text{NO} + \text{NO}_2$) pollution in the air. The net acidity of the rain is controlled by the interaction of sulphuric and nitric acid with basic ammonia and soil dust and the existing meteorological parameters.

In the present work, Delhi has been taken as the area of study. Since the concentration of primary acidic pollutants have increased here many times due to rapid expansion in population, automobiles and industries, possibility of occurrence of acid rain exists over this region. A detailed description of the study area has been given in chapter II of this thesis.

The present work includes following objectives:

a. Determination of the concentration of Total Suspended Particulate Matters (TSPM) and its major elemental components and a statistical analysis of the relationship between these components as a means of investigating their possible source/sources.

b. Ratio of anions and cations of TSPM in order to predict the nature of the rain.

c. Measurement of the concentration of gaseous pollutants ($\text{SO}_2$ and $\text{NO}_x$) in the ambient air.
d. Since the final fate of these gaseous pollutants in the atmosphere is the formation of $\text{SO}_4^{2-}$ and $\text{NO}_3^-$, a ratio between the particulate sulphate and gaseous $\text{SO}_2$, and particulate nitrate and its gaseous precursor $\text{NO}_x$ was also calculated.

e. Spatial and seasonal variability in the precipitation chemistry parameters.

f. Calculation of scavenging-ratio of the major ions which control the acidity of the rain.

g. A study on wind pattern, atmospheric stability, mixing height and ventilation coefficient in order to correlate the above factors with the meteorological parameters.

It is a difficult task to get a complete picture of Delhi atmosphere with its pollutants due to various anthropogenic activities in its different areas. So, in order to get spatial variation, four different sites of different anthropogenic activities were selected. The description of sampling sites along with the various sampling and analytical methods for different constituents that participate in acid rain formation have been detailed in chapter III.

The TSPM, $\text{SO}_2$ and $\text{NO}_x$ were measured on a week interval between Jan.'93 to Dec.'93 at four different sites in Delhi viz. JNU, Dariaganj, Karolbagh and Okhla. The mass concentration of TSPM as well as of its various chemical constituents [water soluble (Na, K, Mg, Ca, $\text{NH}_4^+$, $\text{SO}_4^{2-}$, $\text{NO}_3^-$, and Cl) and acid soluble (Fe, Mn, Zn, Cd, Cu, Ni and Pb) fractions] were obtained and the results of the above measurements have been presented in chapter IV. The observations were stratified according to the season and
the sampling site. The values of cross-correlation of the TSP and its components were evaluated. In comparison to seasonal variation, the spatial variation in the concentration of these pollutants were low.

High TSPM concentration levels were observed during summer period associated with hot and dry weather of the region. Frequent dust storm in this season also contribute high TSPM. Low TSPM concentration was observed during the monsoon period at all the four sampling sites. The concentration of SO$_2$ and NO$_x$ peaked in winter months due to the poor dispersion ability of the atmosphere during these months.

Analysis of TSPM and gases has revealed the following facts:

a. Spatial and seasonal variations were observed in the concentration of TSPM, SO$_2$ and NO$_x$.

b. Dariaganj was the most polluted area followed by Okhla and Karolbagh. JNU was the least polluted area. Although on rare occasions the concentration of these gaseous pollutants exceeded their standard limit, their concentration was high. At Dariaganj the 24 hour averaged concentration of NO$_x$ ranged between 22.0 $\mu$g/m$^3$ to 98.8 $\mu$g/m$^3$.

c. The concentration level of NO$_x$ was higher than that of SO$_2$ at all the sampling sites.

d. On the basis of annual arithmetic mean value it was concluded that the concentration of gaseous pollutants at Dariaganj, Karolbagh and Okhla was 3.5, 2.7 and 2.94 times higher than at JNU.

e. The concentration level of TSPM in Delhi was very high. In comparison to gaseous pollutants, the
urban/rural ratio for TSPM concentration was lower. The annual mean concentration of TSPM (495 μg/m³) was highest at Dariaganj. This annual average value is above the Indian Standard of 360 μg/m³ for an industrial area and much above 140 μg/m³ for a residential area as per Central Pollution Control Board recommendations.

f. Contribution to TSPM from anthropogenic sources has increased manifold resulting in increased aerosol acidity.

g. Seasonal variation in TSPM concentration was more pronounced than its spatial variation. During the summer periods, when the occurrence of dust storms is more frequent, the average TSPM value at all the sampling sites was very high, with an extreme reaching 1563 μg/m³ at Dariaganj. In general, the concentration of TSPM, NOₓ and SO₂ was also higher in winter and post monsoon period. Higher concentration of sulphate and nitrate was also observed during winter months which is due to maximum calm periods, lower mixing heights and ventilation coefficients in these periods. Minimum concentration of these pollutants was obtained in monsoon period.

h. There were significant differences in the constituents of TSPM (both water and acid soluble fraction) collected from different sites and in different season.

i. SO₄²⁻ concentration was always higher than NO₃⁻ at all the sampling sites, though the concentration of NOₓ was higher than SO₂. The annual mean concentration of SO₄²⁻ and NO₃⁻ at Dariaganj, Karolbagh and Okhla was nearly 1.4 and 1.3 times higher than at JNU. The
seasonal variation in the concentration of anions and cations were higher than spatial.

j. High concentration of Cl$^-$ in winter and summer was observed which suggests its non sea-salt origin. In comparison to other places, its concentration was higher in an industrial area (Okhla). It confirms its anthropogenic origin.

k. Except potassium and nickel all the ions displayed some tendency for higher concentrations in urban areas. K and Ni concentration tended to be higher in rural areas, which is consistent with its expected soil and vegetation sources.

l. Sources of NO$_3^-$ is mainly local whereas SO$_4^{2-}$ has its marine source of origin also.

m. A strong correlation of ammonium with sulphate, nitrate and chloride indicates that most of acid are effectively neutralised by ammonia.

n. A strong correlation of sulphate, nitrate and chloride with calcium, magnesium and potassium indicates that soil is also a source of origin for these acidic pollutants.

o. At all the sampling stations, the balance between the sum of basic and acidic constituents of TSPM is positive ($\Sigma$base -$\Sigma$acid), it suggests the alkaline nature of aerosols. So, it may be predicted that the pH of the rain water in Delhi would be in basic range. But in comparison to earlier studies, this balance was found to be very low. It is attributed to the heavy increase in the emission of acidic pollutants into the atmosphere of Delhi. This is also substantiated from the decreasing pH data of rain water collected during the study periods.
Correlation between heavy metals was different at different places. Therefore, it was difficult to draw any definite conclusion.

Wet precipitation samples were also collected in Delhi at JNU, Dariaganj, Karolbagh, Okhla, Nazafgarh and NOIDA for each rain event. At JNU, rainwater sampling was done for two years (in 1992 and 1993). At rest of the places, it was done only for the year 1993. These samples were analysed for major cations (\(\text{NH}_4^+, \text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}\)) and anions (\(\text{NO}_3^-, \text{Cl}^-\) and \(\text{SO}_4^{2-}\)) in addition to the pH and conductivity measurements. The concentration of these components has been expressed in \(\mu\text{eq}l\). The majority of samples showed an alkaline character as a result of neutralization, caused primarily by alkaline soil dust and secondly by atmospheric ammonia. In all rain samples, \(\text{SO}_4^{2-}\) concentration exceeded \(\text{NO}_3^-\) concentration. The contribution of maritime sources to the total \(\text{SO}_4^{2-}\) concentration was also observed. Following conclusions have been drawn from the precipitation sample analysis:

a. The overall pH during the sampling period varied from 4.8 (mild acidic) at JNU in 1992 to 7.6 (alkaline) at JNU itself in 1993. But most of the collected samples showed an alkaline pH.

b. The dissolved mineral concentration differed from shower to shower depending upon the weather conditions and the amount of rain. It was found that the precipitation amount was negatively correlated to the concentration of all the rain water chemistry parameters except \(H^+\). \(H^+\) was positively correlated to the amount of rainfall.
c. The concentration of Nitrate and sulphate was higher at Dariaganj in comparison to other places which reflects the influences of local emission on precipitation chemistry. But in comparison to seasonal variation, this spatial variation was small. The concentration of major ions peaked in summer and was lowest in the monsoon months. These patterns are due to differences in summer and monsoon atmospheric chemistry and sources of air mass.

d. A non-significant correlation of sulphate, nitrate and chloride with $H^+$ but a significant correlation with Na, K, Mg, and Ca (upto 99 % of confidence level) was observed. It indicates that these ions originate from the ionization of their salts and not from their acids.

e. The contribution of Sulphate in rainwater acidity was the highest in comparison to other anions.

f. Scavenging ratio suggests high wet removal of water soluble constituents (Ca, Mg, $SO_4^{2-}$ and $NO_3^-$).

Air Pollution Meteorology:

Following facts were revealed from the observations of meteorological parameters:

a. Spatial variation in temperature on annual basis was about $\pm 0.5^\circ C$. In the winter months, Dariaganj and Okhla were warmer (upto 2$^\circ C$) than Karolbagh and JNU. This indicates that these areas are more polluted compared to other areas. The pollutants in these areas being more active in the radiation processes are keeping the temperature comparatively higher.
than the rest of the regions.

b. Wind pattern at Karolbagh and Dariaganj shows that these areas may receive pollutants released from the industrial areas like Zakhira, Shahzadabagh, Motinagar and Naraina causing higher concentration of pollutants in these regions.

c. Frequency of calm condition was minimum at JNU and maximum at Dariaganj.

d. On the basis of wind study, it can be said that Dariaganj will face maximum and JNU will face the minimum air pollution problem.

e. Out of the twelve months, maximum calm period was observed in October (58%). Calm conditions recorded in March, May, June, July and August were between 25-38%. The predominant winds were from N-W sector except monsoon period. In May, June and July winds were highly divergent whereas in September, winds were from the SE-NE sector.

f. Unstable condition in night time and stable condition in daytime was absent. During April-June, in the daytime high frequency of extremely unstable conditions and in nighttime high frequency of moderately stable conditions were noticed. In July-September, in daytime, neutral conditions and in nighttime extremely and moderately stable conditions dominated. From October-December in nighttime extremely stable conditions were observed.

g. Mixing heights and Ventilation coefficients were highest in April followed by May and March and minimum in December followed by January and February. The highest minimum mixing heights were obtained in September followed by August and July.
So, it may be concluded from the present study that the meteorological parameters for premonsoon season are the most and for the winter are the least favourable for the dispersion of pollutants with respect to other months.

From the available data base, it is very difficult to arrive at any definite conclusion because the source emissions differs from season to season according to the need of the society. However, the present study points out that the possibility of acid rain formation over Delhi exists despite of alkaline dusts in the atmosphere from the natural sources.

The present study suggests following works in the future:

1. Work on wet and dry deposition of trace elements is required for better assessment of their impact on the receiving systems.

2. The study on variability and relationship between concentrations and
   a. meteorological conditions, and
   b. local and regional sources should be made.

3. If rural-urban differences are under investigation the number of rural sites should be adequate to allow valid statistical testing of differences.

4. Measurements of organic acids should also be done in TSPM and rainwater in order to assess their contribution to the acidity.