Chapter 2

The Experimental Methodology

2.1 The Study Area

Delhi, the capital city of India, with a population of over 14 million, is situated on the western bank of Yamuna River. To the west of Delhi is the northern extension of the Aravali ranges called Delhi ridge. The city and ridge stand about 160 km to the south of Himalayas. It lies in the subtropical belt between $76^0 50' E - 77^0 23' E$ and $28^0 12' N - 28^0 53' N$. Its climate is semi-arid and consists of pre-monsoon (summer), monsoon, post-monsoon and winter seasons. It experiences a maximum temperature of $\sim 45 - 48^0 C$ in June during summer and minimum of $\sim 1 - 2^0 C$ in January during winter. Delhi has a normal annual rainfall of 611mm. A major percentage ($\sim 81\%$) of this is received during the monsoon months (July, August and September) and the rest is received as the winter rains and thunderstorm rains in the pre and post monsoon months. The rainfall increases from the southwest to the northeast. The air over Delhi is dry during the greater part of year. Humidity is high in the monsoon season while April and May are the driest months. Winds are predominantly westerly or northwesterly and tend to be more northerly in the afternoons except in the monsoon season, when it is easterly and northeasterly. Yearly mean wind speed varies in the range of 0.9-2.0 m/s. April to June is the period witnesses the highest frequency of thunderstorms and duststorms.
Some of these are associated with violent squalls. While these storms are generally dry but some are accompanied with heavy rains. Thunderstorms also occur in winter months in association with western disturbances. The natural vegetation of Delhi is dry deciduous forest, which has suffered severely from urbanization.

2.1.1 The Sampling Sites

With a view to examine the indoor / outdoor relationship between pollutants, the sampling of SPM was carried out from January 2000 to August 2001 in several phases with the help of different local air quality samplers (APM-417, Vayubodhan Pvt. Ltd., New Delhi) at 24 different sites. Among the selected sites, 6 sites namely Jawaharlal Nehru University, Vasant Vihar, Dhaula Kuan, Hauz Khas, Cannaught Place and Okhla were chosen for the study of particle size distribution. Consequently, samples of SPM were also collected in various size intervals using a 5-stage high volume cascade particulate sampler (CPS) (Kimoto Electric Co. Ltd., Japan). The locations of sampling sites are indicated in fig 2.1. The description of site characteristics and measurement details are given below.

1. Jawaharlal Nehru University (JNU): Sampling site at JNU campus is far-off from any industrial activity, with no industrial unit nearby within several km of it. It is characterized by very low vehicular traffic. This site is full of vegetation. This site was also used for simultaneous indoor / outdoor sampling. The 5-stage high volume CPS-sampler was kept at the rooftop about 16Mts. above the ground.
*Sampling Sites


Figure 2.1: Map of Delhi showing various sampling sites
2. **Vasant Vihar:** This site is very close to a heavy vehicular traffic. In addition a number of automobile and furniture workshop and a busy commercial area is in its vicinity. The samplers were kept at 10 Mts. above the ground for both I/O and particle size measurements.

3. **Dhaula Kuan:** This site is in proximity to one of the busiest traffic roundabouts in Delhi. This was the site for I/O sampling as well as particle size measurements.

4. **Hauz Khas:** This is a residential complex with moderate traffic density. The vegetation cover is sparse to moderate. The samplers were placed at about 12 Mts. above the ground for I/O sampling. The 5-stage impactor was kept at roof top at a height of ~16 mts.

5. **Cannaught Place:** This site is full of commercial activity and has a high traffic density. The sampler was placed at about 30 Mts. above the ground. This was the site for both I/O sampling and particulate measurement.

6. **Okhala:** It is highly industrialized area where a variety of industrial activities go on. This site is close to moderate to heavy traffic and has low vegetation cover. Both I/O sampling and particle size measurements were carried out at this site.

7. **Ansari Nagar:** It is a residential cum commercial complex and is close to All India Institute of Medical Sciences (AIIMS). It is in heavy traffic zone and is densely populated. The vegetation cover is insignificant.

8. **Chandani Chowk:** It is an important commercial cum residential area. It has very high traffic density and has poor vegetation.

9. **Dariya Ganj:** It is a vibrant commercial cum residential area with very high
traffic density and frequent traffic jams. It has poor vegetation cover and is densely
populated.

10. Delhi Cantt.: It is a residential complex close to a railway station. It has high
traffic density with moderate amount of vegetation.

11. Delhi University: It is in sensitive zone with moderate population and moderate
traffic density. It has high vegetation cover.

12. Ganesh Pura: It is a residential area with moderate traffic density and moderate
amount of vegetation.

13. Indian Institute of Technology (IIT): It is an educational institute. It has low
population, good vegetation cover and low traffic density.

14. I.T.O.: It is a commercial complex with very heavy traffic density and is
moderately vegetated.

15. Karol Bagh: It is a vibrant commercial cum residential area with very heavy traffic
density and low vegetation. It is also dotted with small scale industrial units.

16. Khel Gaon: It is a residential complex with moderate traffic density and moderate
amount of vegetation.

17. Pusa: It is a commercial cum institutional area with very heavy traffic density and
moderate vegetation.

18. Punjabi Bagh: It is a residential complex with moderate traffic density with
significant amount of vegetation.

19. R. K. Puram: It is primarily a residential complex with moderate traffic density
and some amount of vegetation.
20. Shahdara: It is a residential cum commercial area with heavy traffic density. It has moderate amount of vegetation.

21. South Extension: It is a residential cum commercial complex. It has high traffic density and full of commercial activities with moderate amount of vegetation.

22. Timar Pur: It is a residential area with moderate traffic density and poor vegetation.

23. Uttam Nagar: It is a residential complex with moderate traffic density. The vegetation is sparse.

24. Wazir Pur: It is densely populated, commercial cum small-scale industrial area. It is also characterized by heavy traffic density and poor vegetation.

2.2 Air Sampling

All indoor and outdoor measurements were done simultaneously using two APM-417, local air handy sampler. The ambient air is drawn in a laminar flow at a rate of 25 l min⁻¹ through a pump which collects the particles at a filter paper of 47 mm diameter. The data set was collected in three different phases

Phase 1: In this phase the data set was collected at JNU, New Delhi for continuously 20 days with a 24 hour sampling period from 25 February to 15 March 2000. This period was representative of transition period between winter and summer. The indoor samples were collected in a room (volume is around 425 m³) situated above 12 meters
from ground, the sampler was placed in the center of the room. While the outdoor sampler was placed at the roof top of the building at a height of 16 meters from the ground. This room is naturally ventilated with heavy vegetation around. This site is considered to be the cleanest area of Delhi and is far away from any industrial activity and heavy vehicular traffic. Thus this area was chosen as a reference.

**Phase 2:** In this phase the data set was collected at 24 different places of Delhi, from 20 February 2001 to 28 July 2001. The duration of sampling was three hours at each site.

**Phase 3:** Sampling with the help of Kimoto 5-stage CPS sampler was done on seasonal basis (winter, summer and monsoon) at six different sites. It was done for 24-hrs in each season at JNU, Vasant Viahr, Dhaula Kuan, Hauz Khas, Cannaught Place and Okhla from Feb. 2001 to Aug. 2001.

### 2.2.1 Description of Filter Papers

The filter papers used were:

(i) Whatman Glass Fiber filter papers (47 mm) were used in the APM-417 local air quality sampler, (ii) Whatman GF filter paper was cut in doughnut shape for use in Kimoto 5-stage high volume CPS-sampler. The description of various size and shapes used in 5-stage CPS-sampler is given in Table 2.1.
Table 2.1: Description of the size of filter papers used in 5-stage CPS-sampler

<table>
<thead>
<tr>
<th>Stage</th>
<th>Shape</th>
<th>Measurement (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Doughnut</td>
<td>197.5 (outer diameter), 171.6 (inner diameter)</td>
</tr>
<tr>
<td>2</td>
<td>Doughnut</td>
<td>177.5 (outer diameter), 147.5 (inner diameter)</td>
</tr>
<tr>
<td>3</td>
<td>Doughnut</td>
<td>149.5 (outer diameter), 120.6 (inner diameter)</td>
</tr>
<tr>
<td>4</td>
<td>Doughnut</td>
<td>132.0 (outer diameter), 97.6 (inner diameter)</td>
</tr>
<tr>
<td>5</td>
<td>Rectangular</td>
<td>203 x 254</td>
</tr>
</tbody>
</table>

2.2.1 Sampling Procedure

The filter papers were kept in a vacuum desiccator for 24 hrs to remove any moisture content before mounting them on the respective air samplers. The rotameter was fixed for desired airflow. After the sampling the filter papers were again kept in desiccator for 24 hrs to demoisturise them again.

2.2.2 SPM Estimation

Weight of suspended particulate matter (W) in grams was obtained by taking the difference in weights of filter papers before and after sampling.

Thus, \[ W = W_2 - W_1 \]

Where, \( W_2 \) = weight of filter paper after sampling (grams)

\[ W_1 = \text{weight of filter paper before sampling (grams)} \]

The volume of air sampled (V) is calculated by multiplying the average air flow rate with sampling time i.e.,
\[ V = Q \times T \text{ (cubic meters)}; \]

Where, \( Q = \text{Average flow rate (cubic meters per minute)} \)

\[ T = \text{Sampling Time (minutes)} \]

\[ Q = \frac{Q_1 + Q_2}{2} \]

\( Q_1 = \text{Initial sampling rate} \)

\( Q_2 = \text{Final sampling rate} \)

The concentration of suspended particulate matters is, then \( W / V \) (grams per cubic meter)

### 2.2.3 Metal Estimation

For metal estimation following procedure were adopted

#### 2.2.3.1 Sample Digestion

The digestion was carried out as per the method described by Belgium Institute of Standardization (1976) and methods of air sampling and analysis (Katz, 1977). The filter papers of the APM-417 were digested in its original size. In the case of doughnut shaped filter papers, which were used in first four stages of the CPS sampler, only 1/3rd portion was taken for digestion. The stage-5 filter paper was cut into 47 mm diameter piece before digestion. The reagents used were \( \text{HNO}_3 \) 70\% (S.G. 1.41), \( \text{HCl} \) 36\% (S.G. 1.18) and \( \text{HF} \) 40\% (S.G. 1.13). Acid digestion was needed for the metal estimation by AAS. Acid digestion was performed in teflon bombs following the steps given below:
Step1: Samples (dry filter papers) were dissolved in 3ml HF, 6ml HNO₃ and 1.55 ml HCl in teflon bombs and kept at 120⁰ C for 1hr.

Step2: Samples were evaporated to dryness at 70⁰ C for 1/2 hr.

Step3: Residue was dissolved in 10 ml of 10 M HNO₃ and evaporated to dryness.

Step4: Step3 was repeated until it was fully dissolved

Step5: Solution was diluted to 25 ml

A series of blanks were prepared using the same digestion method. Standard solutions of metals were prepared as described in EPA manual (1983). Some metals and some AR grade reagents were used for standard solution. The samples were analyzed by Atomic Absorption Spectrometer (AAS) using models Phillips PU-9200X.

2.2.3.2 Standard Metal Solutions: Standard metal solutions were prepared in the optimum concentration range present in total suspended particulate matter of Delhi by appropriate dilution of the stock metal solutions of 1000 ppm. The stock solutions (1000 ppm) of different metals were prepared as per the details given below.

Copper (Cu): 1.0000 grams copper metal was dissolved in 50 ml of 5M hydrochloric acid.

Magnesium (Mg): 1.0000 grams of magnesium metal was dissolved in 50 ml of 5M hydrochloric acid.

Calcium (Ca): 2.7693 grams of calcium chloride (CaCl₂) was dissolved in 100 ml of
deionised water.

**Cadmium (Cd):** 1.0000 grams of cadmium metal was dissolved in 20 ml of 5M hydrochloric acid and 2 drops of nitric acid (S.G. 1.42).

**Lead (Pb):** 1.0000 grams of lead metal was dissolved in 50 ml 2M nitric acid.

**Chromium (Cr):** 1.0000 grams of chromium metal was dissolved in 50 ml of hydrochloric acid (S.G. 1.18) and 2 ml of nitric acid (S.G. 1.42).

**Iron (Fe):** 1.0000 grams of iron powder was dissolved in 20 ml of 5M hydrochloric acid and 5 ml of nitric acid (S.G. 1.41).

**Nickel (Ni):** 1.0000 grams of nickel was dissolved in 550 ml of 5M nitric acid (HNO₃).

**Manganese (Mn):** 3.6077 grams of manganese chloride (MnCl₂.4H₂O) was dissolved in 50 ml HCl (S.G. 1.18).

All the standard solutions prepared were diluted to 1 liter with deionised water.

### 2.2.4.3 Instrument Operation:

A hollow cathode lamp of the desired metal was installed in the instrument. The wavelength and slit-width was set accordingly. After alignment of the lamp and position of burner, acetylene mixed with air was used to ignite the flame. Both acetylene and air cylinders were commercial grade. Before mixing with acetylene, air is cleaned and dried through suitable filter to remove oil, water and other foreign substances. Acetone which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing the cylinder of acetylene
when its pressure falls below 689 K Pa (100 psi). Instrument was set at zero. A blank (deionised water) was aspirated. Then standards (freshly diluted) were aspirated and the absorbance was recorded. Then each sample was aspirated one by one after rinsing the nebuliser with deionised water after each reading.

The final estimation of concentration of metals was done using the formula:

Concentration of metals (µg/m³) =

(concentration of metals (ppm) × dilution factor × B)/ volume of total air sampled

Where, B (Area of aliquot) = Total area of filter paper / Area of filter paper cut

2.3 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscope (SEM) is a powerful instrument, which permits the characterization of heterogeneous materials and surfaces on a local scale. In the present study, a computer controlled Philips XL-20 scanning electron microscope has been used. In SEM, the area to be examined is irradiated with a focused (10 nm spot size) electron beam, which may be static, or swept in raster across the surface of specimen. The types of signals which are produced when the focused electron beam impinges on a specimen surface, include secondary electrons, back scattered electrons, characteristic X-rays, Auger electrons, and photons of various energies. They are obtained from specific emission volumes within the sample and are used to measure many characteristics of the sample (composition, surface topography, crystallography, magnetic and electric fields, light emitting properties, etc.).
In scanning electron microscope, the primary signal of interest is the variation in secondary electron emission that takes place as the electron beam is swept in raster across the surface of a specimen due to differences in surface topography. The secondary electron yield is confined near the beam impact area, which permits images to be obtained at relatively high resolution (~10 nm). The three dimensional appearance of the images is due to large depth of focus of the scanning electron microscope.

There are several different modes of operation of the SEM, each corresponding to the collection of a different type of signal arising from the incident primary electron beam. The main modes are Emissive, Reflective, Absorptive, Transmission, Beam-induced conductivity, Cathodoluminescent and X-ray. In the present investigation the SEM was used in its most common mode the emissive mode.

The samples (dry filter papers) were cut in the size of 1 mm\(^2\). A very thin silver film was deposited on the surface of the sample to make it electrically conductive using vacuum coating unit. This extremely fine silver coating was done through arc evaporation of silver coil under inert atmosphere (e.g. Helium environment). This deposition of film is achieved by maintaining the plasma under controlled conditions. The helium is introduced through a needle valve at a regulated pressure into the vacuum chamber after creating a high vacuum of \(10^{-5}-10^{-4}\) torr (1 torr =1.06 m-bar). These samples were mounted on a stage with the help of silver glue. This stage was
kept inside the SEM chamber for the electron micrographs.

Electron micrographs were taken on SONY (110mm × 20mm) high speed printing films.