CHAPTER II
MATERIALS AND METHODS EMPLOYED FOR DUST FALL-OUT ANALYSIS
The dust fall-out measurement at different sites of Raipur city i.e. Birgaon, Shankar Nagar, Gudhiyari, Kota, Tikrapara and Jaistambh is described. The samples at each site have been collected once in a month. In all sites a total of 48 dust samples have been collected and about 270 analyses have been performed. Samples were collected month wise in pre and post monsoon seasons during one hydrological year. About 15 physical and chemical parameters of these individual samples, including soluble, insoluble parts, pH, conductivity, major ions viz. Na⁺, K⁺, Ca²⁺, and Cl⁻, SO₄²⁻ and metals viz. Cr, Mn, Fe, Ni, Cu, Zn, Sb and Pb have been determined. The concentration, flux, deposition patterns and trends of ions, their sources, dust fall rate have also been determined. In this chapter, only the methodology of dust sampling, study area and instrumentation used for the study of physico-chemical parameters, dust fall rate, soluble part, insoluble part, total dust, pH, conductivity and major ions etc., have been discussed.

Keywords: Materials and methods; Standard solutions; Geographical profile; Dust fall sampling; Sampling stations.
1. Introduction

Environmental pollution is an unwanted side effect of the accelerated pace of industrialization during the past century. However, industrialization cannot be stopped at this stage of our development, since it has become indispensable for providing the basic necessities of life but every possible effort should be made for the control and abatement of environmental pollution (1-3).

The implementation of dust fall measurement programme can be an extremely complicated and expensive task. It is necessary that the measurement programme be well designed so that the resulting data will be useful and the programme cost effective (4, 5). There are now few number of dust fall study programmes going on throughout the world (6-10) because it is very necessary to learn the nature and physicochemical properties of dust present in the environment.

The nature of dust means whether acidic or alkaline can be learnt with the help of pH. Moreover, conductivity can be found out in that. Conductivity in dust is due to presence of positive and negative charged ions in it. Pertaining to this, we have very scanty reports (11-16).

Analysis of dust fall is conveniently divided into three categories -(a) Major ions, (b) trace metals and (c) organic compounds. Major ions generally included Na+, K+, Ca²⁺, H⁺, Cl⁻, SO₄²⁻, etc. The parameters generally related to geochemical mass balance studies. The cations (Na⁺, K⁺, Ca²⁺) are generally related to weathering reaction (dust reaction) involving common minerals; H⁺, Cl⁻, SO₄²⁻ ions are related to natural and anthropogenic sources (17-21).

Trace metals are often studied in order to compare natural geochemical cyclin with anthropogenic analysis. Those metals, which often show larger anthropogenic than natural emission, are Cu, Pb, Zn and Sb (22-27).
Trace organic studies generally consider the atmospheric transport and fate of synthetic volatile organic chemicals such as DDTs and PCBs. Typically, this analysis is related to mass budget estimates for watershed and assessment of chemical reactivity (28,29).

There are many methods for the analysis of major ions in dust fall analysis. Typically, flame photometry, flame/flame-less photometric, colorimetric, potentiometric technique are used (30-32).

Several techniques have been applied for the determination of metal pollutants in airborne dust particulates (33-39). Trace metals are generally estimated by flame (FAA) or furnace atomic absorption (GFAA). When facilities are available, instrumental neutron activation analysis (INAA) or proton included X-ray analysis (PIXE) offer sensitive non-destructive methods. Instrumental neutron activation analysis (INAA) offers an excellent analytical tool for many trace metals and major parameters. These techniques may not be employed universally due to the need for a reactor (40-42).

In present investigation, we calculate dust fall rate by Kikuo equation (43). The total composition of dust is often of two kinds i.e. one is soluble in water and other is insoluble in water. Insoluble portion generally consist of heavy toxic metals and soluble portion contains namely ions Na⁺, K⁺, Ca²⁺, Cl⁻, SO₄²⁻, etc. (44, 45).

Na⁺, K⁺ and Ca²⁺ are almost universally analysed by flame photometric method. Chloride is readily determined using specific ion electrode (The chloride ion electrode consist of silver chloride-silver sulphide solid membrane which has detection limit of about 50 μ eq l⁻¹). Sulphate is determined by turbidimetric method (46).
2. Methods and Materials

The analytical steps involved in the determination of various constituents in the dust fall-out samples have been shown via flow-chart diagram in Fig. 1.

2.1. Instruments and reagents

All chemicals/reagents used were of A.R. grade (E. Merck/BDH/Glaxo or SD fine chemicals).

The following equipments and reagents were employed for the determination of anions, cations, metal ions and other parameters in the dust fall-out samples.

2.1.1. pH meter

pH values of all aqueous solutions were measured by using a Systronic pH meter, type 335.

*Standardization of pH meter:* Standardization of pH meter was done by using buffer solution of pH 4.0 and 9.0.

*Preparation of Buffer:* Buffer solutions of following pH were used for adjustment of the pH values of the aqueous solutions.

pH 4.0: NaOH-KHC₈H₄O₄ buffer of pH 4.0, prepared by mixing 0.04 ml of 0.1 N NaOH with 50 ml of 0.1 M KHC₈H₄O₄ and diluting to 100 ml.

pH 9.0: NaOH - H₃BO₃ buffer of pH 9.0 was prepared by mixing 21.30 ml of 0.1 N NaOH with 50 ml of 0.1 M H₃BO₃ and diluting to 100 ml (47).
Figure 1. Flow-chart diagram for depicting the various steps in the analyses of dust fall-out samples.

Sample Collection in Glass jar type collector 30-cm height & 10-cm diameter

Dissolution of sample in about 300 ml distilled water

Measurement of pH by Systronic pH meter, type 335

Conductivity measurement by Cole Parmer Instrument Co., Singapore, model no. 19820-00

Filtration by Whatman Filter paper #41

Filtrate evaporation Soluble part of dust

Residue dried Insoluble part of dust

Total dust

Major ions measurement
Na⁺, K⁺, Ca²⁺-by Flame Photometer (Systronic Flame Photometer, type 336)
SO₄²⁻-by Turbidimetry (Carl Zeiss Jena Spekol)
Cl⁻-by Orion Specific Ion Analyser

Metal ions analyses
Viz. Cr, Mn, Fe, Ni, Cu, Zn, Sb, Pb by Atomic Absorption Spectrophotometer GBC 932
2.1.2. Conductivity meter

The ionic conductance in aqueous solutions, in micro-Simance unit, was measured by employing a conductivity meter, Cole-Parmer Instrument Co., Singapore, model no. 19820-20.

*Standardization of conductivity meter:* The standardisation of the conductivity meter was done using carbon dioxide-free conductivity water, according to the procedures given in the instruction manual.

2.1.3. Flame photometer

A Systronic flame photometer, type 336, with respective filters, was used for analysis of Na⁺, K⁺ and Ca²⁺ ions in the solutions.

*Preparation of standard solution for calibration curve:* The following suitable concentrations of Na⁺, K⁺ and Ca²⁺ were prepared (48):

i. **Sodium:** 2.542 g of dried sodium chloride (A.R.) was dissolved in water, and the solution diluted to 1 litre (1 ml = 1000 mg Na⁺).

ii. **Potassium:** 1.909 g of dried potassium chloride was dissolved in water, and the solution diluted to 1 litre (1 ml = 1000 mg K⁺).

iii. **Calcium:** 2.497 g of dried (A.R.) calcium carbonate was dissolved in a minimum volume of nitric acid (1:4), and the solution diluted to 1 litre (1 ml = 1000 mg Ca²⁺).

Appropriate dilutions were made of these solutions to get a series of solutions with determinable concentration range of Na⁺, K⁺ and Ca²⁺.
2.1.4. **Orion specific ion electrode**

Orion Specific Ion Electrode was used for determination of chloride ion concentration in the aqueous solutions. The chloride ion electrode used was consisting of a silver chloride-silver sulphide solid membrane, which had a detection limit of about 50 µg per ml Cl⁻.

Calibration of the electrode systems was done according to Orion Research Manual(46).

i. **Chloride:** A 1.647 g of dried sodium chloride (A.R.) was dissolved in water, and the solution diluted to 1 litre (1 ml = 1000 mg Cl⁻).

2.1.5. **Spectrophotometer**

A Carl Zeiss Jena 'spekol' spectrophotometer, fitted with EK-5 unit and matched glass cells of 1-cm optical path length was used in all absorbance measurement.

*Preparation of Solutions:* The following solutions were prepared for the determination of sulphate.

i. **Sulphate:** A 0.1479 gm anhydrous Na₂SO₄ was dissolved in distilled water, and the solution diluted to 1 litre (1 ml = 0.01 mg SO₄²⁻).

ii. **Conditioning medium:** A 75 gm NaCl was dissolved in 300 ml of distilled water. To this added was 30 ml concentrated HCl and 100 ml of 95% ethyl alcohol. A 50 ml glycerol was added to this mixture.
2.1.6. Atomic absorption spectrophotometer

A flame atomic absorption spectrophotometer model GBC 932 was used for absorbance measurement.

Standard Metal Solutions:

Standard solutions of the following metals were prepared as per recommended procedure (49) described below –

\( \text{i. Chromium:} \quad 1 \text{ g of metal (wire form) was dissolved in HCl (1:1) with gentle heating; the solution was cooled and diluted to 1 litre (1 ml = 1000 mg Cr).} \)

\( \text{ii. Manganese:} \quad 1 \text{ g of the metal (wire form) was dissolved in a minimum volume of nitric acid (1:1), and the solution diluted to 1 litre (1 ml = 1000 mg Mn).} \)

\( \text{iii. Iron:} \quad 1 \text{ g of the metal (wire form) was dissolved in minimum volume of nitric acid (1:1), and the solution diluted to 1 litre (1 ml = 1000 mg Fe).} \)

\( \text{iv. Nickel:} \quad 1 \text{ g of the metal (wire form) was dissolved in minimum volume of nitric acid (1:1), and diluted to 1 litre (1 ml = 1000 mg Ni).} \)

\( \text{v. Copper:} \quad 1 \text{ g of the metal (wire form) was dissolved in minimum volume of nitric acid (1:1), and diluted to 1 litre (1 ml = 1000 mg Cu).} \)

\( \text{vi. Zinc:} \quad 1 \text{ g of the metal (granules) was dissolved in 40 ml hydrochloric acid (1:1), and diluted to 1 litre (1 ml = 1000 mg Zn).} \)
vii. Lead: 1 g of the metal (wire form) was dissolved in minimum volume of nitric acid (1:1), and diluted to 1 litre (1 ml = 1000 mg Pb).

viii. Antimony: 1 g of the metal (granules) was dissolved in 100 ml of hydrochloric acid containing 2 ml nitric acid diluted to 1 litre by 10 percent hydrochloric acid to prevent precipitation of antimony oxychloride (1 ml = 100 mg Sb).

For the calibrations, the standard solutions of the metal were suitably diluted to match the concentration of the sample solutions within the measurement sensitivity.

Lamp current is automatically optimised in the AAS equipment used. The AAS used is of only flame type system without hydride generation. The operating conditions during the determination of the respective metals by AAS have been shown in Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wavelength (nm)</th>
<th>Slit width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>357.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Mn</td>
<td>403.1</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe</td>
<td>386.0</td>
<td>0.20</td>
</tr>
<tr>
<td>Ni</td>
<td>341.5</td>
<td>0.20</td>
</tr>
<tr>
<td>Cu</td>
<td>324.7</td>
<td>0.50</td>
</tr>
<tr>
<td>Zn</td>
<td>213.9</td>
<td>0.50</td>
</tr>
<tr>
<td>Pb</td>
<td>217.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Sb</td>
<td>206.0</td>
<td>0.20</td>
</tr>
</tbody>
</table>
3. Geographical Profile of Raipur City

The geographical and geological profile of Raipur city has been shown in Table 2, Fig. 2, the premier city of Chhattisgarh region, Raipur, has now emerged as an important commercial-cum-industrial centre of eastern Madhya Pradesh. Its cardinal points are latitude $21^\circ - 14' \ N$ and longitude $81^\circ - 38' \ E$. The city has an altitude of 298 meters above mean sea level. The city is linked with all modes of transportation viz. rail, road and air. It encircles the municipal corporation area of nearly 160 sq. km. The city has growth rapidly in recent decades by population shifts and increased industrial activities. Raipur has recorded more than 500 factories/industries in and around the city that are agro-forest, metal based and others.

Thus the increasing industrial growth is vigorously taxing the prevailing environment of this city and consequently affecting significant alteration in its natural composition. Around the clock working of steel plants, cement factories and other industries are, as a result, simultaneously contributing dust, smoke, gases and fumes through their continuously burning stacks in the atmosphere; iron-slag, fuel ash and scrape waste being dumped on open land for sedimentation and erosion, minerals and chemical effluents being drained out into the rivers and canals, whole of this environment is receiving significant amount of pollutants and it is bound to affect the sustained ecosystem and human population (50).

Table 2. Geographical and geological profile of Raipur city according to 1991 census

<table>
<thead>
<tr>
<th></th>
<th>Geography</th>
<th>21°-14'N, 81°-38'E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Area</td>
<td>4402 h.</td>
</tr>
<tr>
<td></td>
<td>Transportation area</td>
<td>- 820 14.26%</td>
</tr>
<tr>
<td></td>
<td>Commercial area</td>
<td>- 179 3.11%</td>
</tr>
</tbody>
</table>
Studies on Dust Fall-Out in Raipur City

<table>
<thead>
<tr>
<th>Study area</th>
<th>Population</th>
<th>area, sq. km.</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) Birgaon</td>
<td>17407</td>
<td>436.6</td>
<td>85.78</td>
</tr>
<tr>
<td>ii) Shankar Nagar</td>
<td>20799</td>
<td>21.1</td>
<td>985.73</td>
</tr>
<tr>
<td>iii) Gudhiyari</td>
<td>7407</td>
<td>36.3</td>
<td>204.02</td>
</tr>
<tr>
<td>iv) Kota</td>
<td>15119</td>
<td>168.5</td>
<td>89.72</td>
</tr>
<tr>
<td>v) Tikrapara</td>
<td>21489</td>
<td>88.0</td>
<td>244.16</td>
</tr>
<tr>
<td>vi) Jaistambh</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

8. Vehicles (No.) 19563 (fuel operated two, three and four wheelers)


3. Study Area

Raipur (21°-14'N, 81°-38'E), Fig. 2, the premier city of Chhattisgarh region of central India with urban population of approximately 0.45 million (1991 census), which is expected to be increased to above 1.0 million in the year 2001 according to the Raipur Development and Plan 2005 (Draft): Directorate of Town and Country Planning, Madhya Pradesh, December, 1995, is literally sandwiched between two industrial complexes on
its eastern and western outskirts. The western complex comprising of the colossal Bhilai Steel Plant at ~ 30 km's distance as its nucleus which has an accessory in the Jamul Cement Factory besides cores of allied industries producing chemical fertilizers and merchandise out of iron steel, and the eastern complex has a mixed nature were there are the industries of numerous kinds including oil extraction from forest and farm produce, manufacture of electrical good iron, steel aluminium and copper based industries and few cement factories at Siltara at ~ 5 km's distance, at Mandhar at ~ 30 km's distance, etc. The study area is the municipal corporation area encircling an area of about 160 sq. km. (51, 52).

3.1. Sampling sites

Depending upon the meteorological conditions and anthropogenic activities, the entire area under study has been divided into 6 representative zones as described below –

Site#1: Birgaon. Birgaon is altogether an industrial area, situated approximately at an aerial distance 15-17 km apart from the heart or centre of city i.e. Jaistambh in the north-east direction of the city. This area comprises of enormous number of big and small-scale agro-forest, iron, oil, etc. based factories and industries.

Site#2: Shankar Nagar: Shankar Nagar is well-planned residential area with population around 21,000 along with few Government official buildings, hospitals and residence. This area is located at around 6-7 km away from Jaistambh in the east. The area is about 21.1 hectare and its population density is 985.23.

Site#3: Gudhiyari. Gudhiyari is an old and thickly populated area of the city. Its area is about 36.3 hectare and the population density is 204.04. Gudhiyari, situated at an aerial distance of around 7-8 km from Jaistambh in the north-west direction, comprises of a huge wholesale market of essential household commodities. Residential buildings
and houses in this part of the city are haphazardly constructed. Because of being most
near to the railway station, slums have also developed fast with time around this area.

Site#4: Ravishankar University. Situated in south-west direction of the city at a distance of 6-
7 km on the Great-Eastern national highway, encircles an area of approximately 200
acre land. It is the largest centre for higher education of this region in central India.

Site#5: Tikrapara. Around 8-9 km away from Jaistambh in south direction, it encircles
an area of approximately 88.0 hectare, density is about 244.19. Tikrapara is a slum area
with unplanned housing patterns. This area is adjacent to Vivekanand Sarovar, the
largest tank of the city.

Site#6: Jaistambh. Jaistambh is the heart of city and can be regarded as the centre of the
city. This particular area of the city experiences heavy load of traffic. Several thousands
of motor vehicles pass through this square daily. There are few multi-storied buildings
here and thus this site is also thickly populated.

4. Methodology Used for Analysis of Dust fall

4.1. Sampling

The dust fall measurements were carried out in accordance with the practice laid
down in the literature (52, 53). Dust collection jars used were cylindrical in shape
having 10-cm diameter and 30-cm height. In all, six sampling sites were selected in
the study area. In each sampling site, four separate samplers in different directions at
a radical distance ~ 50 meters were places for the sake of most precise sampling. All
values obtained at a particular sampling site were, thus the average of 4 sampling.
Distilled water was placed in each of the collectors to prevent sample loss by blowing
air. The collectors were then placed in position in guard-frames at elevation of 5-15
meters above the ground levels depending the obstructions in individual site (54),
Fig. 3. The jars were inspected every week and were replaced by fresh collection jars after duration of 30 days. The pre and post monsoon month wise measurements were made of dust fall rate and concentration and flux of metals for a whole hydrological period in each sampling site. Table 3, indicates the summary of sampling and analysis.

Gravity techniques are used to collect settleable particulates (e.g. fly-ash, shoot, smoke etc.) in air. Devices used include dust fall sampling instrument, such as dust fall bucket, dust fall, etc. Dust fall on jar is open-mouthed jar glass or polythene container with a little water at the bottom. It is exposed to the atmosphere for a month, in a bird-shield on a stand kept 1 m above the sampling floor. The mass of the dust deposits per unit area of jar water surface area is determined after evaporating the water to dryness and weighing. The result is reported in mg/cm²/month or tonnes/km²/month. Sedimentation techniques is used for connecting particulates of diameters > 5 m.

Dust fall is generally defined as those particles among atmosphere particulates pollutants including soot and dust that are not smaller than 20 μm and are large enough to settle by gravity. Dust fall is generally measured on a monthly basis with a dust fall jar. The measurement expressed in mt/km²/30 days, indicate the amount of pollutant deposit over a certain area but not the amount of pollutant deposit from any particular discharging source (55, 56).

4.2. Dust fall-out analysis

Dusts were tested for the following items. The collected dust samples were dissolved in 300 ml distilled water (as per guidelines of NEERI MANUAL 1984).

pH and Conductivity - These were measured with pH meter (Systronic, type 335) and conductivity meter (Cole-Parmer Co., Singapore, model no. 19820-20) as soon as possible after sampling.
Figure 3. A simple glass jar type dust fall-out collector.

Grill Frame Guard
Dust Fall Jar
Stand

Table 3. Sampling and analysis programme during one hydrological year.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sampling sites</th>
<th>No. of Sampling</th>
<th>Month wise no. of sampling</th>
<th>Parameters investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Birgaon</td>
<td>5</td>
<td></td>
<td>Soluble, insoluble, pH, conductivity, Dust fall rate, Na⁺, K⁺, Ca²⁺, H⁺, Cl⁻, SO₄²⁻, Cr, Mn, Fe, Ni, Cu, Zn, Sb, Pb</td>
</tr>
<tr>
<td>1</td>
<td>Shankar Nagar</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Gudhiyati</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>University</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Tikrapata</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Jaistambh</td>
<td>5</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Dissolved and undissolved matter - The collected liquid was filtered with Whatman No. 42 filter paper. The residue on the filter was dried at 105° C for 3 h, allowed to cool in a desiccator to constant weight, and then weighed. The weight represented the total amount of undissolved matter. The filtrate was transferred to a beaker and concentrated to not more than 100 ml by evaporation. The concentrate was transferred to a platinum crucible to further concentrate. When the concentration had almost solidified, the evaporating dish was dried at 105° C for 2 h, allowed to cool in a desiccator, and weighed. The quantity of dissolved matter in the collected liquid was calculated from the weight difference against the evaporating dish.

Total dust fall matter - The calculation for the total dust fall matter was made by making summation of the weight of water-soluble matter and water-insoluble matters of individual samples.

\[
\text{Total dust fall matter} = \text{Weight of dissolved matter} + \text{weight of undissolved matter}
\]

Dust fall rate - The total dust fall quantity (W) is the sum of the amount of dissolved and undissolved matter, and the dust fall quantity is calculated from W using the following equation:

\[
\text{Dust fall rate} = \frac{1.273 \times W \times 30 \times 10^4}{D^2 \times n} \text{ (mt/sq km/30 days)}
\]

Where, W is the total dust in the collecting jar, D the diameter of jar (cm.), and n the number of days of collection.

Determination of Metal Content by AAS - Dust sample is transferred to a 100-ml flask and 20% (6M) hydrochloric acid is added. The sample is filtered through Whatman filter paper No. 41. The residue on the filter paper is then diluted with 20% (6M) hydrochloric acid. The filtrate is combined with the previously prepared filtrate to serve for determination of metal content by atomic absorption spectrophotometry emission spectrometry or colorimetry (43, 53).
Sample Preparation: The dried particulate fall-out sample (0.1 - 0.5 g) was taken in a 50-ml beaker and leached with cold and concentrated HNO₃ acid (2-4 ml). The residue after filtration was washed with dilute (1:10) HNO₃ acid (3 ml) and then digested at 60°C with concentrated HCl:HNO₃ (3:1) mixture (5 ml). The volume was made up to 25 ml in a 25-ml volumetric flask (GBC Manual 1984).

Aliquot of these diluted samples were then taken for analysis of atomic absorption spectrophotometer (model GBC-AAS 932). The wavelength, slit width and lamp current selected for some selected metal pollutants have been shown in Table 1.

Appropriate dilutions were made in case of samples with higher metal pollutants level. A calibration curve was prepared using different known concentration of each metal pollutant. Three repetitive measurements of each sample of each metal were taken and thus the values were obtained for each metal pollutant. Concentrations reported were the average of these three measurements.

References


