

Development of Air Pollution Source Profiles – Stationary Sources Volume 1

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Final Report

**Submitted (as Volumes 1 and 2) to
Central Pollution Control Board, Delhi**

By

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Volume 1 of 2

**Air Pollution Source Profiles for
Stationary Sources**



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1.1 Background

Despite substantial efforts to bring improvements in air quality during recent times at state and national level, air pollution still remains a significant concern for most of the Indian cities. Measurements of criteria pollutants indicate that Indian cities experience high concentrations of particulate pollutants (PM). Formulation of effective air pollution control policy would require evidence based analysis using scientific data obtained under conditions that are specific to India. Such data are not available and development of reliable source inventory database and assessment of contribution of different sources to air pollution are needed. In this view, a source apportionment study has been initiated in six cities by Central Pollution Control Board (CPCB).

Identification of the sources which contribute significantly to particulate pollution provides an access to manage air quality in a region. Chemical mass balance (CMB) is one of the receptor modeling methods proposed for use in the present 6-city source apportionment study. Use of CMB has been reported by several researchers (Chow et al., 1992; Chow and Watson 2002) and requires chemical source profiles for the sources that are known to affect the receptor. Source profile databases have been reported by USEPA as SPECIATE and are a repository of profiles developed by numerous researchers and reported in the literature. Differences in sources, operating conditions, geology and meteorology make the available profiles un-suitable for the conditions and sources in Indian cities. Thus, a key component of the effort in the 6-city project was to develop source profiles for stationary and vehicular sources in India. An overall framework of the project is given in Figure 1.1, which also specifies the roles of the partner institutes.

This report provides the details of source profiling carried out by IIT Bombay for stationary sources in the 6 cities of Bangalore, Chennai, Delhi, Kanpur, Mumbai and Pune.

1.2 Objectives

The objectives of this study were:

- Document source sampling and chemical analysis methods for stationary sources.
- Document and compile the database for stationary air pollution source profiles in 6 Indian cities.

1.3 Need for Source Profiles

Broadly speaking, there are two approaches for quantifying the contributions of pollution sources. The first approach, dispersion modeling, starts with emissions from different sources (emissions inventory) and calculates ambient concentrations in the vicinity of the “receptor” (where ambient concentrations are measured). Ambient concentrations are used to calibrate the models for running future scenarios. The second approach, receptor modeling, analyzes PM in the atmosphere at a given location and matches their characteristics with those of chemically distinct source types. Receptor modeling is a research and analytical tool to apportion the PM mass concentrations to the possible sources. The first method, dispersion model provides a link between emission changes from source control measures and resulting changes in air borne concentrations. A number of factors may often limit the application of these dispersion models including need for spatially resolved time-dependent emission inventories and meteorological fields. A receptor model, which approaches the source contribution identification problem in reverse order, proceeding from particulate concentrations at a receptor site backward to responsible emission sources, becomes useful in such situations. These models attempt to relate measured concentrations at a given site to sources without having to reconstruct the dispersion patterns.

The fundamental principle of receptor modeling is based on the assumption that mass is conserved, and that a mass balance analysis can be used to identify and apportion sources

in the atmosphere. Receptor models usually reduce the number of factors needed to describe the measured data. Typically, the relationship can be expressed as

$$x_{ij} = \sum_{p=1}^P g_{ip} f_{pj} + e_{ij}$$

Where:

x_{ij} is the measured concentration of the j^{th} species in the i^{th} sample,

f_{pj} is the concentration of the j^{th} species in material emitted by source P (Source Profile),

g_{ip} is the contribution of the p^{th} source to the i^{th} sample, and

e_{ij} is the portion of the measured elemental concentration that cannot be fit by the model.

The intent of all the source apportionment methods is to determine the source contribution (g_{ip}) to the sample. Conventional factorization and Chemical Mass Balance (CMB) strategies perhaps represent the two extremes. Conventional factorization strategies such as Principal Component Analysis (PCA) assume in principle little prior knowledge of either source profile or source strength. It extracts statistically valid solutions for both f_{pj} and g_{ip} matrices from a receptor site. By contrast, CMB method requires that the number of sources and their profiles be known to estimate source contributions.

1.4 Scope of the Work

The database of source profiles developed as part of this project forms the basis for source apportionment studies using CMB receptor model. The air pollution sources to be profiled in each city were identified by respective partner agencies in consultation with CPCB. These sources were categorized and suitable source sampling methods were finalized. Guidelines given by international agencies or other reported methods were followed for the development of the sampling protocols. The source samples were characterized for ions, elements, elemental carbon, organic carbon and molecular markers. The guidelines given by CPCB were followed for all chemical analyses and standard operating procedures have been documented. Various work elements involved in this project are illustrated in Figure 1.2.

1.5 Organisation of the Report

The final report has been organized in two volumes viz. Volume 1 and Volume 2. Volume 1 provides the background and the process details, while Volume 2 is exclusively the database for the 79 profiles developed in the present project.

Further, in Volume 1, Chapter 1 describes the background and scope of the work. Chapter 2 provides details and approaches for identification, selection and categorization of stationary sources in the cities for profiling. Chapter 3 documents the sampling protocol development and details of onsite and laboratory source sampling. Chapter 4 presents the chemical characterization methods, analyzed chemical species, quality assurance /quality control (QA/QC) involved and estimations of uncertainty. The report is summarized in Chapter 5 with a discussion on the developed profiles and scope for future work. The tables, figures and references for each Chapter are organized at the end of respective chapters.

References for Chapter 1

Chow, J. C., Watson, J. G., Lowenthal, D. H., Solomon, P. A., Magliano, K. L., Ziman, S. D. and Richards, L. W. (1992), PM10 Source Apportionment in California's San Joaquin Valley, *Atmos. Environ.* 26A(18), 3335-3354.

Chow, J. C. and Watson, J. G. (2002), Review of PM2.5 and PM10 apportionment for fossil fuel combustion and other sources by the chemical mass balance receptor model, *Energy & Fuels* 16(2), 222-260.

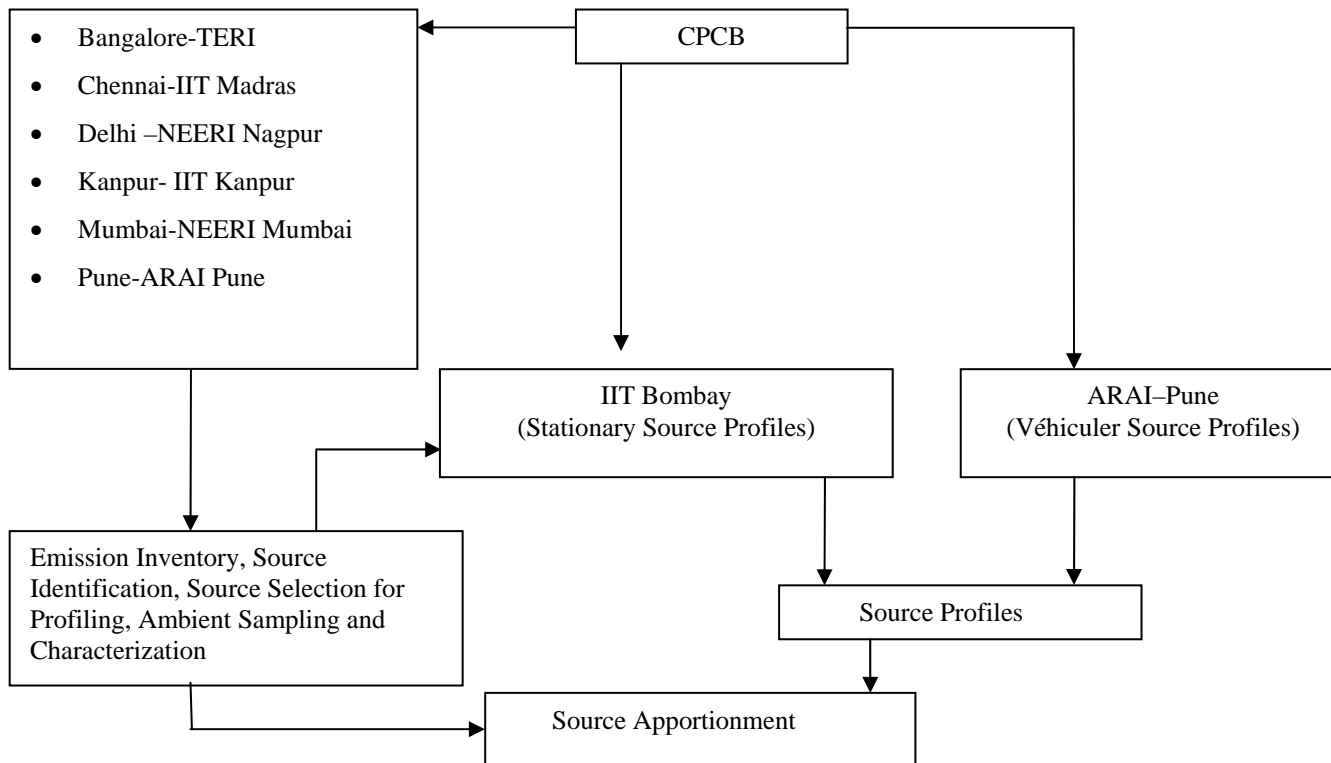


Figure 1.1 Overall frame work of six-city source apportionment study with the role of partner institutes

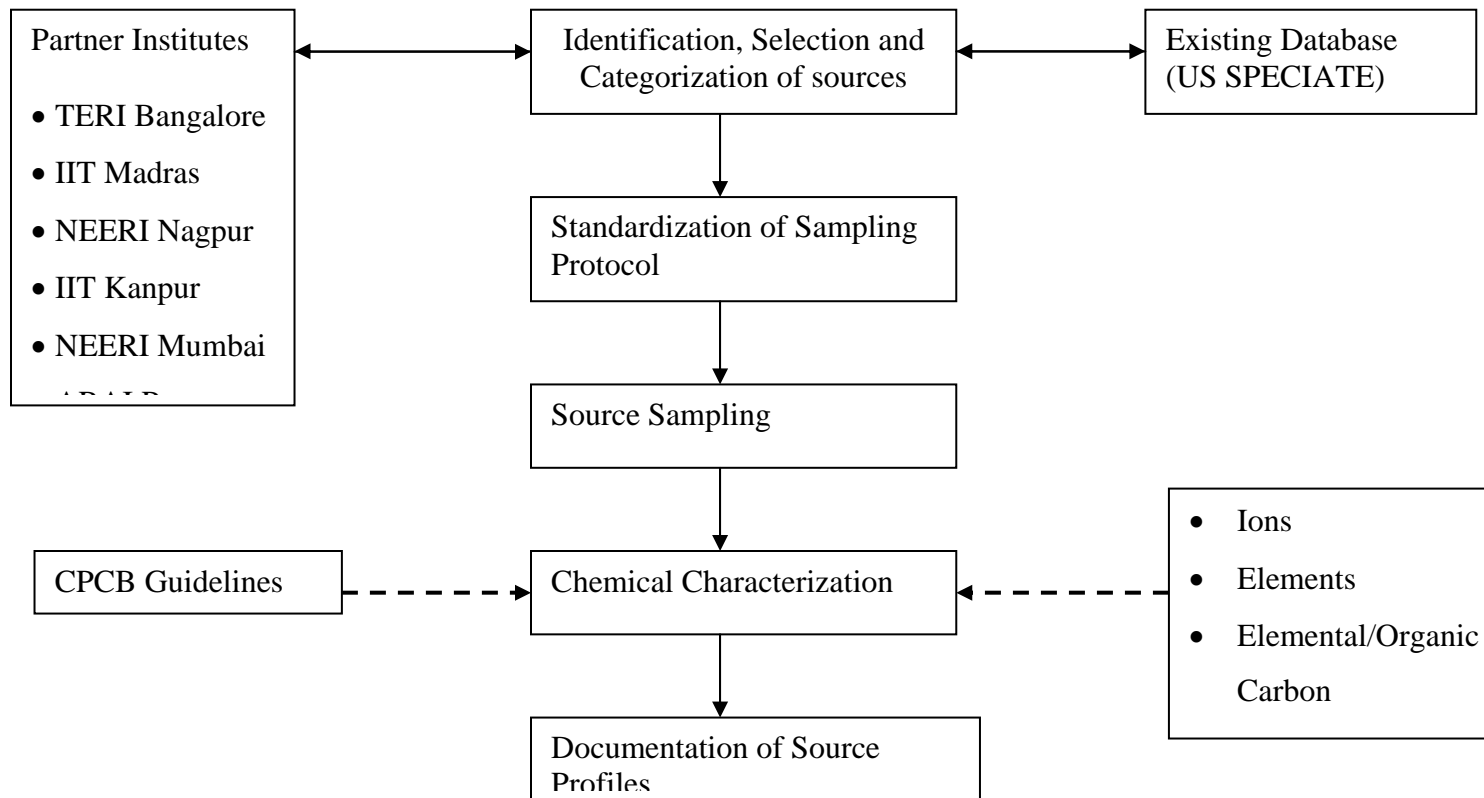


Figure 1.2 Work elements involved in the development of stationary source profiles

Chapter 2

Source Selection for Profiling

2.1 Background

CMB receptor modeling method for source apportionment requires source profiles as an input along with the speciated ambient data. The success of CMB method of source apportionment depends on precise identification of the sources that contribute to the receptor pollution concentrations, and using their chemical profiles for receptor modelling.

In the present work, the stationary air pollution sources for profiling were selected based on a list of possible sources developed by the six agencies accountable for the six cities respectively. The lists were developed from an emission inventory exercise in a 2 km x 2 km grid around each receptor site for identifying prominent sources which could contribute to the ambient particulate concentrations. The lists of all air pollution sources were then compiled from the six cities- Bangalore, Chennai, Delhi, Kanpur, Mumbai and Pune. These included all non-vehicular sources such as geological material (paved and unpaved road dust), domestic sources like kerosene, wood, LPG and small and large scale industrial sources. Some of these sources were specific to a particular city and some of them were common to all the cities. Sources were also categorized based on whether they were combustion based or not. Details are given in the following sections.

2.2 Categorization of Sources

The sources were categorized based on the combustion and non-combustion sources and they are further classified as sources that were city-specific or common to all cities. The combustion sources from all the six cities were classified into two categories – Combustion Common Sources (CC) and Combustion City Specific Sources (CS). The non-combustion sources were

also classified into the following two categories – Non-combustion Common Sources (NCC) and Non-combustion City Specific Sources (NCS).

2.3 List of Sources for Profiling

Based on the magnitude of the emission by the sources at a particular site in a city, the sources were ranked relatively, on the basis of scales assigned by the agency of the respective cities. Bangalore and Kanpur used a 1-5 point scale, Chennai and New Delhi used a 0-10 point scale, Pune used a 1-15 point scale and Mumbai used a 0 or 1 scale. The lists and the rankings are included in Tables 2A.1 to 2A.6. These lists were combined and a committee short-listed a total of 45 sources for profiling based on commonality, weightage and relevance (Table 2A.7).

Table 2.1 represents the list of 58 sources that were profiled as part of this project. A code number was assigned for each of the sources, which are also listed in Table 2.1. The database uses this source code for referring to a specific profile.

Table 2.1 List of all 58 sources with category and its source code

No.	Name of Sources (in alphabetical order)	Source Code	Class	PM10	PM2.5
1	Aggregate Dust	6004	NCC	1	0
2	Agricultural Waste Burning	15	CC	1	0
3	Asphalt Paving Operations	24	NCC	1	0
4	Bagasse Combustion	5	CC	1	0
5	Bricks and Related Clay Products	40	CS	1	0
6	Cement	6002	NCC	1	0
7	Chulah (Wood)-Chennai	9	CC	1	0
8	Chulah (Wood)-Kanpur	9	CC	1	0
9	Chulah (Wood)-Mumbai	9	CC	1	1
10	Coal Combustion - Domestic-Kanpur	8	CC	1	0
11	Coal Combustion - Domestic -Mumbai	8	CC	1	1
12	Coal Combustion Power Plant-Delhi	12	CS	1	0
13	Coal Combustion Power Plant-Kanpur	12	CS	1	0
14	Construction and Aggregate Processing	43	NCC	1	0
15	Diesel Industrial Generators	21	CC	1	1
16	Electric Arc Furnace	45	CC	1	1
17	Fertilizer Plant Stack	6007	CC	1	0
18	Fuel Oil combustion	2	CC	1	1
19	Fugitive Rock Phosphate Emission from Fertilizer Plant	6005	NCC	1	0
20	Garden Waste Combustion	5001	CC	1	0

21	Kerosene Combustion-Domestic	7	CC	1	1
22	Kerosene Generators- 80 % Load	20	CC	1	1
23	Kerosene Generators- Full Load	20	CC	1	1
24	Kerosene Generators-No load	20	CC	1	1
25	Leather Waste Burning	13	CS	1	0
26	Liquified Petroleum Gas Combustion	4	CC	1	0
27	Low Sulphur Heavy Stock-Power Plant	6000	CS	1	1
28	Marine Aerosols	26	NCS	1	0
29	Medical Waste Incineration (Controlled)	17	CC	1	0
30	Medical Waste Incineration (Uncontrolled)	17	CC	1	0
31	Paint Spray Booth	31	NCS	1	0
32	Paved Road Dust-Bangalore	52	NCS	1	0
33	Paved Road Dust- Chennai	52	NCS	1	0
34	Paved Road Dust- Delhi	52	NCS	1	0
35	Paved Road Dust- Kanpur	52	NCS	1	0
36	Paved Road Dust- Mumbai	52	NCS	1	1
37	Paved Road Dust- Pune	52	NCS	1	1
38	Petroleum Refining-Combustion	27	CC	1	0
39	Petroleum Refining-Non-Combustion	28	NCC	1	0
40	Power Plant Natural Gas based	5002	CS	1	0
41	Sand	6003	NCC	1	0
42	Secondary Metal (Lead) Smelting and other operations-Bangalore	46	CC	1	1

43	Secondary Metal (Lead) Smelting and other operations-Kanpur	46	CC	1	0
44	Soil Dust-Bangalore	54	NCS	1	0
45	Soil Dust-Chennai	54	NCS	1	0
46	Soil Dust-Delhi	54	NCS	1	0
47	Soil Dust-Kanpur	54	NCS	1	0
48	Soil Dust-Mumbai	54	NCS	1	1
49	Soil Dust-Pune	54	NCS	1	1
50	Solid Waste Open Burning-Commercial Area	18	CC	1	1
51	Solid Waste Open Burning-Residential Area	18	18	1	1
52	Steel Rolling Mills	6001	CC	1	1
53	Tar Melting	6006	CC	1	1
54	Unpaved Road Dust-Bangalore	53	NCS	1	0
55	Unpaved Road Dust-Delhi	53	NCS	1	0
56	Unpaved Road Dust-Kanpur	53	NCS	1	0
57	Unpaved Road Dust-Pune	53	NCS	1	1
58	Wood Residue Combustion in Boilers	11	CS	1	1
			TOTAL	58	21

APPENDIX 2A

List of Sources in the Six Cities

Table 2A.1 List of Sources to be sampled in Bangalore (Scale 1-5)

No	Sub Category	Class	Speciate	AP-42	Remarks	S-1	S-2	S-3	S-4	S-5	S-6	S-7
1	Polyester Resin Plastic Products Fabrication	CS	0	1		-	-	-	-	-	2	-
2	Paved Roads	NCS	1	1	Sample from all 6 cities	1	2	2	3	2	2	1
3	Unpaved Roads	NCS	1	1	Sample from all 6 cities	2	1	2	1	2	3	3
4	Soil Dust (Background)	NCS	1	0	Sample from all 6 cities	1	1	1	1	1	1	1
5	Fugitive Dust (open area near sampling site)	NCS	0	0	Sample from all 6 cities							

Table 2A.2 List of Sources to be sampled in Chennai (Scale 0-10)

No	Sub Category	Class	Speciate	AP-42	Remarks	S-1	S-2	S-3	S-4	S-5	S-6	S-7
1	Bagasse Combustion in Sugar Mills	CC	0	1								
2	Carbon Black	NCS	0	1		0	0	0	0	0	2	0
3	Saw mills	NCS										
4	Paved Roads	NCS	1	1	Sample from all 6 cities							
5	Unpaved Roads	NCS	1	1	Sample from all 6 cities	1	1	1	2	2	6	1
6	Soil Dust (Background)	NCS	1	0	Sample from all 6 cities							
7	Fugitive Dust (open area near sampling site)	NCS	0	0	Sample from all 6 cities							

Table 2A.3 List of Sources to be sampled in New Delhi (Scale 0-10)

No	Sub Category	Class	Speciate	AP-42	Remarks	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
1	Cupolla cast iron	NCC	1	1					1		1				
2	Glass Manufacturing	NCC	1	1					1						
3	Construction (buildings)	NCC													
4	Construction Roads (a) Aggregate alying and (b) Asphalt	NCC													
5	Construction of Flyovers	NCC													
6	Paint Applications (Auto/Furniture)	NCS	1	1					2						
7	Paved Roads	NCS	1	1	Sample from all 6 cities										
8	Unpaved Roads	NCS	1	1	Sample from all 6 cities	1		1	1	1	1	1	1	1	
9	Soil Dust (Background)	NCS	1	0	Sample from all 6 cities										
10	Fugitive Dust (open area near sampling site)	NCS	0	0	Sample from all 6 cities										

Table 2A.4 List of Sources to be sampled in Pune (Scale 0-15)

No	Sub Category	Class	Speciate	AP-42	Remarks	S-1	S-2	S-3	S-4	S-5	S-6	S-7
1	Bagasse Combustion in Sugar Mills	CC	0	1								
2	Medical Waste Incineration	CC	0	1		0	0	2	0	0	1	2
3	Bricks and Related Clay Products (earthen pot kiln)	CS	0	1		3	2	0	0	3	0	0
4	Stone Pulverization Industry, Quarries	NCS	0	0		2	2	4	1	1	1	1
5	Fugitive Dust (open area near sampling site)	NCS	0	0	Sample from all 6 cities							
6	Paved Roads	NCS	1	1	Sample from all 6 cities							
7	Unpaved Roads	NCS	1	1	Sample from all 6 cities	10	7	13	12	8	7	4
8	Soil Dust (Background)	NCS	1	0	Sample from all 6 cities							

Table 2A.5 List of Sources to be sampled in Kanpur (Scale 1-5)

No	Sub Category	Class	Speciate	AP-42	Remarks	S-1	S-2	S-3	S-4	S-5	S-6	S-7
1	Secondary Metal Smelting and Other Operations (Foundries)	CC	1	0		-	-	-	-	-	2	-
2	CAST IRON Furnace	CC										
3	Foundries	NCC	1	1								
4	Plastic and Leather Waste Burning	CS	0	0		-	-	-	-	-	1	1
5	Bricks and Related Clay Products (earthen pot kiln)	CS	0	1		2	-	-	-	-	-	2
6	Paved Roads	NCS	0	0	Sample from all 6 cities	2	1	2	2	1	1	1
7	Unpaved Roads	NCS	1	1	Sample from all 6 cities	1	1	2	2	1	1	1
8	Soil Dust (Background)	NCS	1	0	Sample from all 6 cities	1	1	1	1	1	1	1
9	Fugitive Dust (open area near sampling site)	NCS	0	0	Sample from all 6 cities							

Table 2A.6 List of Sources to be sampled in Mumbai (Scale 0-1)

No.	Sub Category	Class	Speciate	AP-42	Remarks	S-1	S-2	S-3	S-4	S-5	S-6	S-7
1	Fuel Oil Combustion	CC	1	1	Small scale Uncontrolled, Medium w and w/O control							
2	Kerosene combustion DOMESTIC	CC	1	1								
3	Garden Waste Combustion	CC	0	1		1	1	1	1	1	1	
4	Medical Waste Incineration	CC	0	1								
5	SOLID WASTE BURNING	CC	1	1								
6	Kerosene GENERATORS domestic	CC	0									
7	Diesel Industrial GENERATORS Large Stationary Diesel and All Stationary Dual-fuel Engines	CC	0	1								
8	Petroleum Refining (COMBUSTION)	CC	1									
10	Municipal Solid Waste Landfills	NCC	0	1								
11	Manufacture of Rubber Products / PLASTICS Small Scale	NCC	0	1								
12	Petroleum Refining (NON-COMBUSTION) Catalyst powder BP/HP	NCC	0	1								
13	FERTILIZER PLANT PACKAGING, FUGITIVE	NCC	1									
14	Hot Mix Asphalt Plants	NCC	0	1								
15	Lead Oxide and Pigment Production	NCC	1	1								
16	Construction (buildings)	NCC										
17	Construction Roads (a) Aggregate alying and (b) Asphalt	NCC										
18	Construction of Flyovers	NCC										
19	Power Plant - Natural Gas	CS										
20	Wood Residue Combustion in Boilers / BAKERIES	CS	1	1								
21	Coal Combustion - Power Plant	CS	1	0			1	1				
22	Marine Aerosols	NCS	1			1	1			1		1
23	Paint Applications (Auto/Furniture)	NCS	1	1			1					
24	Paved Roads	NCS	1	1	Sample from all 6 cities			1				1
25	Unpaved Roads	NCS	1	1	Sample from all 6 cities			1			1	
26	Soil Dust (Background)	NCS	1	0	Sample from all 6 cities							
27	Fugitive Dust (open area near sampling site)	NCS	0	0	Sample from all 6 cities							

TABLE 2A.7 Committee Approved List of Sources for Profiling for the Present Study

Sr. No.	Source Code	Sub Category	Class
1	7	Kerosene combustion (Domestic)	CC
2	5001	Garden Waste Combustion	CC
3	3	<i>Natural Gas Combustion</i>	CC
4	4	<i>Liquified Petroleum Gas Combustion</i>	CC
5	6	<i>Residential Wood Stoves / RESTAURANTS</i>	CC
6	8	<i>Coal Combustion - Tandoor / DOMESTIC</i>	CC
7	9	<i>Chulha (Wood/Dung)</i>	CC
8	15	<i>Agricultural Waste (from Pune and Kanpur)</i>	CC
9	52	Paved Roads	NCS
10	53	Unpaved Roads	NCS
11	54	<i>Soil Dust</i>	NCS
12	56	<i>Fugitive Dust</i>	NCS
13	31	Paint & Varnish	NCS
14	57	Road Construction	NCS
15	43	Construction and Aggregate Processing	NCC
16	5003	Constrcution Flyovers	
17	18	Open Burning SOLID WASTE BURNING	CC
18	25	Manufacture of Rubber Products / PLASTICS	NCC
19	5002	[POWER PLANT - NATURAL GAS BASED]	
20	11	Wood Residue Combustion in Boilers / BAKERIES	CS
21	12	<i>Coal Combustion - Power Plant</i>	CS
22	19	Municipal Solid Waste Landfills	NCC
23	20	Kerosene Industrial Engines GENERATORS	CC
24	21	Diesel Industrial Engines GENERATORS Large Stationary Diesel and All Stationary Dual-fuel Engines	CC
25	26	<i>Marine Aerosols</i>	NCS
26	27	Petroleum Refining (COMBUSTION)	CC
27	28	Petroleum Refining (NON-COMBUSTION)	NCC
28	32	FERTILIZER PLANT PACKAGING, FUGITIVE	NCC
29	41	Hot Mix Asphalt Plants	NCC
30	49	Lead Oxide and Pigment Production ?	NCC
31	2	Fuel Oil Combustion	CC
32	23	Polyester Resin Plastic Products Fabrication	CS
33	5	Bagasse Combustion in Sugar Mills Also as (38)	CC

34	30	Carbon Black	NCS
35	5004	Saw mills	
36	24	Asphalt Paving Operations	NCC
37	42	Glass Manufacturing	NCC
38	47	Iron and Steel Production CUPOLLA CAST IRON	NCC
39	13	<i>Plastic and Leather Waste Burning</i>	CS
40	45	Electric Arc Welding @ CAST IRON FURNACE [FORGING]	CC
41	46	<i>Secondary Metal Smelting and Other Operations</i>	CC
42	48	Gray Iron Foundries	NCC
43	17	Medical Waste Incineration	CC
44	40	Bricks and Related Clay Products (same as 51)	CS
45	55	<i>Stone Pulverization Industry, Quarries</i>	NCS

Chapter 3

Sampling Method Development

3.1 Background

The sources in this study were categorized as (1) combustion and (2) non-combustion sources. Combustion sources are different from non-combustion sources in that the particulate-vapour and particle–particle processes are dynamic in nature. Attention is therefore required to mimic conditions that would typically be experienced by the source sample before it is received by the receptor.

The first part of this chapter provides the details of the literature review carried out to assess the existing source sampling methods. The later part of this chapter explains the development and design of sampling methods adopted in this study. Details of the sampling carried out for the 58 sources identified for this study are listed as Tables 3.1 (Laboratory) and 3.2 (Field).

3.2 Literature Review of Existing Sampling Methods

Sampling methods for particulate matter need to be designed to obtain statistically significant mass, averaged over a reasonable time. Other considerations of prime importance are the ability to obtain a representative sample with respect to particle size distribution (PSD). Particulate emissions are affected by simultaneous processes of particle-particle coagulation, vapour–particle condensation, vapour to particle conversion by nucleation, chemical reactions, and transport processes such as inertial impaction, diffusion, thermophoresis and gravitational settling. These processes are natural and expected to take place between the time of “release” of particulate from the source and that at which the particles are “received” by the receptor. The duration of these processes and the concentrations of the species together determine the extent of the change, and it is desirable for the design of sampling method to estimate a range of conditions that would allow the emission to reach semi-stable state.

3.2.1 Combustion Sampling

Combustion of liquid, solid or gaseous fuels generates various forms of gaseous and particulate pollutants. Some of these combustion byproducts are simultaneously present in both gaseous and particulate phase depending on the local concentration and temperature. Change of temperature and local concentration can shift the equilibrium between gaseous and particulate phases. Studies by Hildemann *et al.* (1989) and Lipsky and Robinson (2005) have investigated the effect of dilution and residence time of such particulate-vapour processes.

Dilution sampling is adopted to simulate atmospheric processes resulting in semi-stable particulate matter composition. To measure the particulate matter in near atmospheric conditions, the sampling system needs to operate such that the diluted gas stream mimics atmospheric dilution as closely as possible. Several researchers have used the principle of dilution for combustion source sampling (England *et al.*, 2005). Dilution system is also used for vehicular exhaust measurements (Kittelson *et al.*, 1999). The key steps are dilution followed by time allowed for “conditioning”. Dilution with clean particle-free air has the following effects : (a) the gas remains unsaturated even at the ambient temperature thereby preventing condensation/nucleation; (b) dilutes the aerosol concentration to slow down the coagulation and (3) brings the temperature to near ambient temperature, which is suitable for the measuring instruments. The control on the time for conditioning is provided by using a plenum of a designed volume to affect the residence time before samples are “collected” for measurements.

The dynamics of particle-vapour system under atmospheric dilution is not well understood. The dynamics of the atmospheric dilution may vary from system to system. For example, vehicular exhaust experiences very high dilution in a short time, whereas, pollutant plume from a stack gets diluted much more slowly by the ambient air. The conditioning time to complete mass transfer is small (~1 sec) when high concentration of particulates are present. At high dilution ratios (>300), however, the time required to achieve equilibrium can be considerably large. A dilution ratio in the range of 10 and a conditioning time in the range of 2.5 seconds were found to be suitable for the present study. The list of sources that would require dilution sampling is shown in Figure 3.1.

3.2.2 Non-Combustion Sampling

Non-combustion sources are also subject to changes due to aerosol transport processes. Wind or vehicle entrained dust, for example, include a large range of sizes of particles, each influenced by different transport mechanisms. Laboratory simulation for entrained dust has been used for sampling of soil component of the atmospheric aerosols (Chow *et al.*, 1994; Chow *et al.*, 2003). Compressed air puffs have been used to resuspend the dust into a chamber, and the samples were withdrawn from the chamber.

3.3 Development of Sampling Methods

3.3.1 Combustion Sources (Dilution Sampling)

The design of the sampling probe required the following :

- a) Isokinetic sampling capability for a large range of stack velocities
- b) Capability of measuring the sample flow rate
- c) Minimal particle losses by transport processes for particles $<10\ \mu\text{m}$.

Isokinetic sampling is used to obtain a representative sample from a process flowstream. The design requires that the face velocity at the point of sampling and that of the sampling intake should be matched. A typical range of stack velocities are 3 to 20 m/s (Liu and Pui, 1985). The stack velocities were measured using a pitot tube arrangement. These were matched using a choice of right angle bent nozzles of diameters 3.5, 4.5, 6 and 7.5 mm on the inlet, and 10 mm on the outlet (Figure 3.2). The 10 mm outlet was selected in order to minimise any particle losses by inertial impaction in the right angle bend for up to 8 lpm sample flow. The probe nozzle was followed by a laminar flowmeter (45 cm long, 5 mm diameter) with a magnehelic gauge for pressure measurements. The pressure drop varied in the 7-12 mmH₂O range for a 4-8 lpm flowrate in the laminar flow regime. This was used to accurately monitor the flow as a laminar flow meter. Temperature influences were taken into account in the measurement of the pressure drop for sample flowrate estimation.

A single stage dilution was included in the sampling system by using a 3.75 liter cylindrical chamber. Dilution air was introduced in the 36 to 72 lpm range to effect a dilution ratio of 10 for the 4-8 lpm sample intake. The corresponding residence times were 2.75 to 5.50 seconds. The design was well within the intended range of operation based on studies reported in literature. A schematic diagram of the sampling system is shown in Figure 3.3. Details of the equipment are listed in Table 3.3.

3.3.2 Non-Combustion Sources

There are two broad categories for these kinds of sources. First, samples that are re-entrained by wind or vehicle motion such as dust from paved, unpaved and soil surfaces. Two, sources such as marine aerosols and spray-paint booths where the source aerosol is already air-borne. The latter is usually sampled by placing the sampling device inlet directly into a source dominated volume. For the former, various re-suspension methods have been developed (Chow *et al.*, 1994; Carvacho *et al.*, 2004 and Gill *et al.*, 2006).

For the present study, the design used by Chow *et al.*, (1994) was adapted for the sampling of resuspended dust. Four PM₁₀/PM_{2.5} samplers (5 lpm each) were mounted at the bottom of a 1m high chamber with volume of 100 liters allowing a residence time of 5 minutes (which was the same as that by Chow *et al.*, 1994). The air intake into the chamber was through an 8 cmx8 cm glass fiber filter. A vacuum flask with a solenoid-valve operated jet puff was used to introduce the soil/dust samples into the chamber every four minutes (Figure 3.4). Typically 7 puffs were found to be sufficient to collect adequate mass on the filters for analysis. The following section describes the collection and pre-conditioning for the dust samples.

3.3.2.1 Dust Sample Collection System

The dust samples from the paved, unpaved roads and soil dust were collected by sweeping with a broom or a shovel (Chow *et al.*, 1994, Chow *et al.*, 2003, Ashbaugh *et al.*, 2003). Domestic broom was used for collecting the sample. The dust samples were collected from 2 km x 2 km of grid surrounding the ambient site. Samples near shoulders and kerb were collected in case of paved road as most of the soil mass accumulates along the edges of the roads. The mass

collected from each cell was about 0.5 to 1 kg. The soil samples were pre-conditioned by first drying the samples at 40 °C for 4 hours in an oven, followed by sieving through 75 µm sieve.

References for Chapter 3

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Table 3.1 Sampling details for the sources sampled in the laboratory

Sources	CPCB Code	Fuel	Dilution ratio	Sampling duration (minutes)
Liquified Petroleum Gas Combustion	4	LPG Gas	NIL	180
Bagasse Combustion in Sugar Mills	5	Bagasse-Mumbai	1:10	15
Kerosene combustion (Domestic)	7	Kerosene local vendor-Mumbai	1:5	145
Coal Combustion - Tandoor / DOMESTIC	8	Coal from local vendor- Mumbai	1:10	130
Coal Combustion - Tandoor / DOMESTIC	8	Sample collected from Kanpur	1:10	60
Chulha (Wood)	9	Sample collected from Mumbai	1:10	15
Chulha (Wood)	9	Sample collected from Kanpur	1:10	15
Chulha (Wood)	9	Sample collected from Chennai	1:10	20
Leather Waste Burning	13	Leather collected from Kanpur	1:10	15
Agricultural Waste (from Kanpur)	15	Sample collected from Kanpur	1:10	10
Paved Roads	52	Samples collected from all six cities	NIL	28
Unpaved Roads	53	Samples collected from four cities	NIL	28
Soil Dust	54	Samples collected from five cities	NIL	28
Garden Waste Combustion	5001	Samples from Mumbai	1:10	10
Kerosene Generators-with no load	20	Kerosene from local vendor	1:10	75
Kerosene Generators- with 80% load	20	Kerosene from local vendor	1:10	90
Kerosene Generators- with full load	20	Kerosene from local vendor	1:10	75
Paint and Varnish	31	Automotive paints mixed with thinner	NIL	20

Solid Waste Burning-Hiranandani site	18	Sample from Hiranandani-Mumbai	NIL	10
Solid Waste Burning-IIT-B site	18	Sample from IIT Campus-Mumbai	NIL	7
Cement	6002	Sample collected from construction site	NIL	8
Sand	6003	Sample collected from construction site	NIL	28
Industrial Raw material (Rock phosphate)	6005	Suphala power plant	NIL	16
Tar	6006	Sample collected from local vendor-Mumbai	NIL	5
Aggregate dust	6004	Sample collected from construction site	NIL	16

Table 3.2 Sampling details for the sources sampled in the field

Source	City	CPCB Code	Sampling location	Date of sampling	Control device	Process	Fuel	Dilution ratio	Sampling duration (minutes)
Fuel oil combustion	Bangalore	2	Bangalore milk dairy	25/10/07	NIL	Furnace oil combustion in the boiler to produce steam for pasteurization	Furnace oil (product code-3080-from Chennai petroleum corporation limited)	1:08	60
Secondary Metal Smelting and other operations (lead)	Bangalore	46	Mekkala metals limited-PEENYA	26/10/07	Baghouse filters	Lead smelting from old batteries	Coal	NIL	90
Industrial Diesel Generators	Bangalore	21	MICO	27/10/07	NIL	Manufacturing fuel injection pumps for vehicles	20 lt/hr of low sulphur diesel	1:15	15
Wood Residue Combustion in Boilers	Bangalore	11	Kamlam Handloom, Peenya industrial Area	29/10/07	Diffusion battery	Boilers use to produce steam to be used in dyeing operations	wood-Tamarind	1:10	50
Electric Arc Melting at Cast Iron Furnace	Bangalore	45	Rail wheel Factory, Ministry of Railways, Yelahanka	30/10/07	NIL	Casting wheel and axels for locomotives	Steel Scrap	1:10	10
LSHS Power Plant	Chennai	6000	GMR Power plant basin bridge	5/11/07	NIL	Production of electricity 200 MW using engine Hyundai	Low Sulphur heavy stock	1:8	45
Steel Rolling Mills	Chennai	6001	Associated Re-rolling mills, R.K.Nagar	6/11/07	NIL	High temperature treatment of scrap steel for re-rolling them to flats of standards size	Pulverized coal	NIL	10
Coal Power Plant CPCB	Delhi	12	NTPC-Badarpur	27/11/07	ESP	Power generation –705 MW	Pulverized coal	1:10	60
CNG- Power plant	Delhi	5002	Pragati Power Plant	28/11/07	NIL	Power generation –330 MW	Natural Gas supplied from HPCL	1:04	180
Secondary Metal Smelting (lead)	Kanpur	46	Manoj Metals, Panki Industrail Area	3/12/07	Cyclone	Recycling of lead from old batteries	Charcoal	1:10	10
Coal Power Plant	Kanpur	12	Panki power plant	4/12/07	ESP	generation of 220 MW power	Pulverized Coal	1:10	10
Bricks and Related Clay Products	Kanpur	40	Northern Ceramics, G. T Road, Bhawanipur, Mandhana	6/12/07	NIL	Kiln for seasoning ceramics bottom pouring sets	Coal	1:20	10
Medical Waste Incinerator	Kanpur	17	MPCC, Central biomedical waste treatment plant, Panki	8/12/07	Wet Scrubber	Incineration of bio-medical waste (100 kg per day)	Medical Waste	NIL	10
Petroleum Refinery (Non-Combustion)	Mumbai	28	HPCL, Chembur	14/12/07	NIL	Catalytic regeneration	NIL	1:05	45
Petroleum Refinery (Combustion)	Mumbai	27	HPCL, Chembur	18/12/07	NIL	Furnace oil combustion	NIL	1:10	45

Table 3.3 Details of the Sampling Equipment

Equipments	Specifications	Manufacturers
Vacuum Pumps	Oil free-Compressor cum vacuum diaphragm pump Model No. MS-WP-2 1HP, 150 lpm, 26 mm Hg	High Speed Appliances, Mumbai
Rotameter	Glass Tube with SS316 float, maximum flow rate of 100 lpm, Model No. SDG-40(M)	Scientific Devices Pvt. Ltd., Mumbai
Portable Air Samplers	PM10 and PM2.5 Impactor based sampler with a designed flow rate of 5 lpm	Airmetrics, Eugene, USA
Pitot Tube	S-Type Stainless Steel Model No.160S-36 inch	Dwyer Instruments Pvt.Ltd., Michigan, USA
Magnehelic Gauge	0 - 25 mmH2O	Dwyer Instruments Pvt.Ltd., Michigan, USA

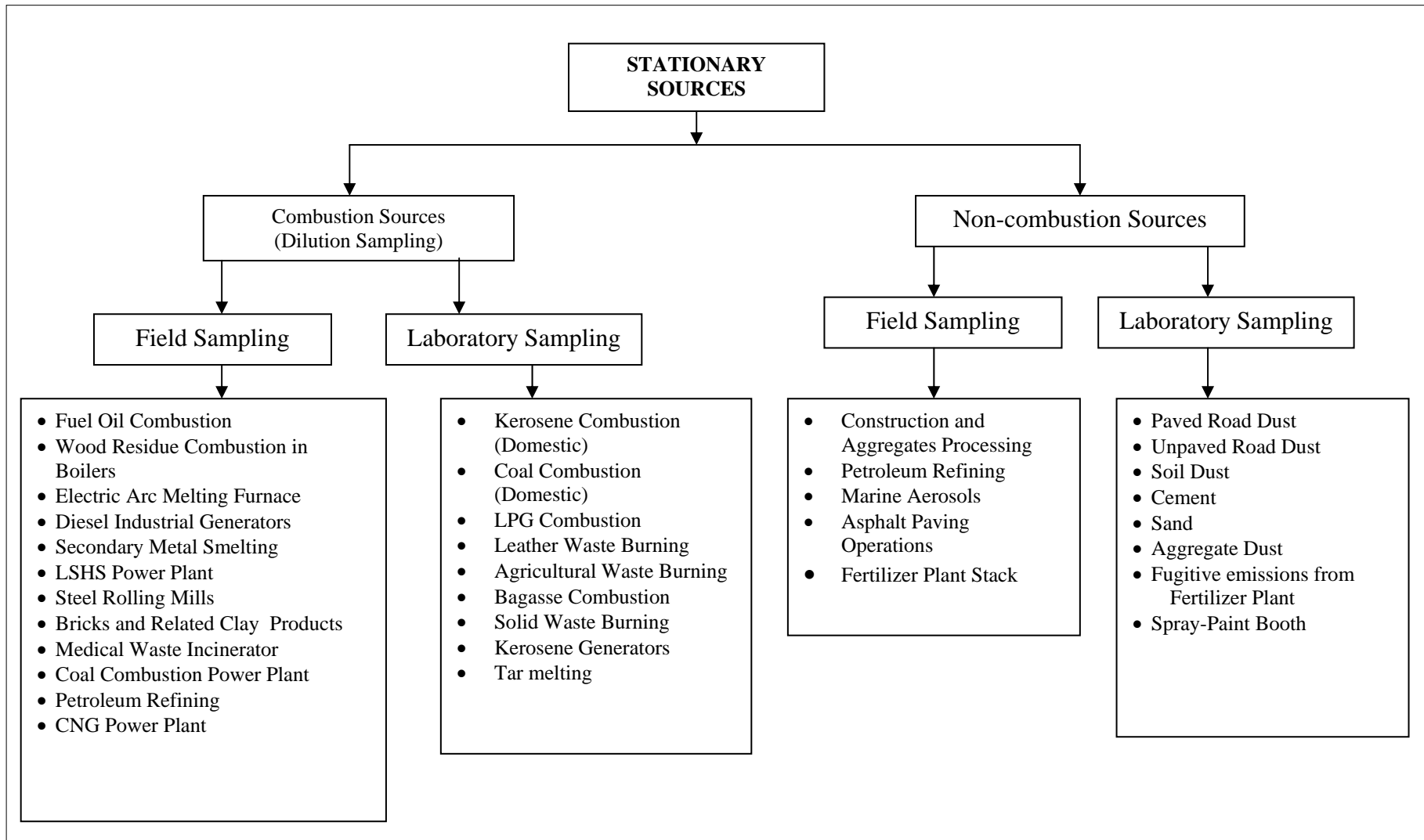


Figure 3.1 Categorisation of Sources for Sampling



Figure 3.2 Photograph of iso-kinetic sampling probe with interchangeable nozzles.

Figure 3.3 Schematic diagram for dilution sampling setup

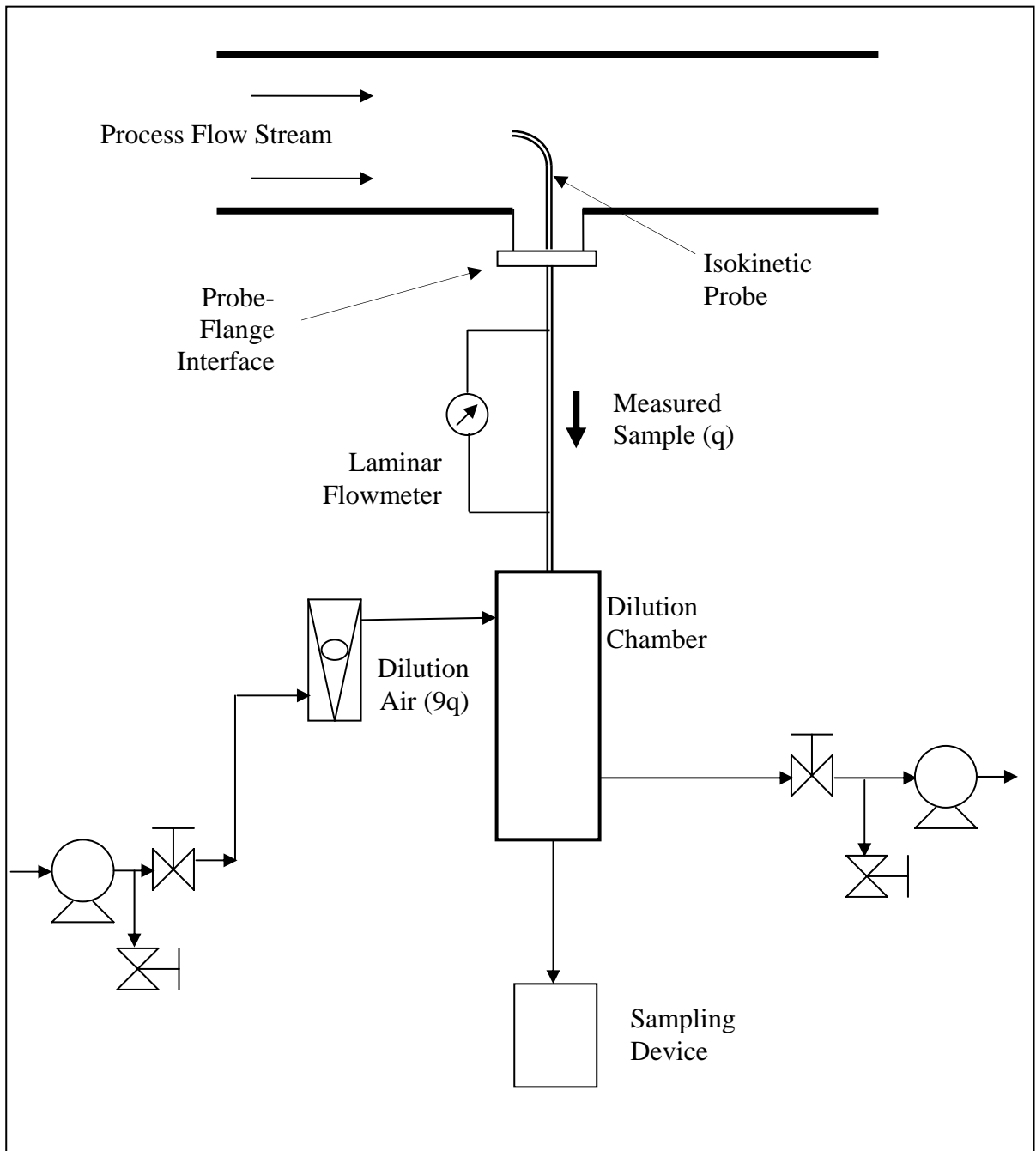




Figure 3.4 : Laboratory setup for the Resuspended Dust Chamber

Chapter 4

Gravimetric and Chemical Analysis

4.1 Background

Species required to be characterized for source profiles in the present study are listed in Table 4.1. Previous studies (Chow and Watson, 1989) have shown that there are six major components that account for all the particulate mass namely : a) geological materials (oxides of metals like Zn, Al, Si, Ti, Fe, etc), b) organic carbon (consisting many compounds), c) elemental carbon, d) sulfate, e) nitrate and f) ammonium. In addition, coastal areas also show higher concentration for sodium and chloride. Broadly from characterization and chemical analyses point of view, these species could be classified in 4 major classes, i) ions, ii) elements, iii) organic molecular markers and iv) elemental carbon/organic carbon (EC/OC).

4.2 Design Considerations for Chemical Analyses

Preliminary estimation of the expected mass concentrations and the compositions were made based on the SPECIATE profiles. A minimum amount of a particular species must be present in the collected mass to enable reliable detection by the instrument. The list of 58 sources has been identified for the six cities as described in Table 2.1. Some of the profiles in the USEPA SPECIATE database were used as guidelines for the expected range of concentrations of the species in the samples. The sampling duration and mass to be collected was decided based on the requirement of mass for chemical analyses step. For various source profiles that were “similar” to the sources of interest in the present study, the species with the minimum percentage was used as a basis to collect a certain minimum mass for reliable detection by the instruments available (Table 4.3).

4.3 Materials and Methods

4.3.1 Gravimetric Analysis

4.3.1.1 Background

Teflon (PTFE) and Quartz-fiber filters were used in collecting particulates from different stationary air pollution sources for further chemical characterization. Each filter was checked

properly for any pinhole, discoloration, creases, separation of ring, chaff or flashing, loose material or any other defects.

A Sartorius microbalance (Model Number- ME-5-F) with static charge neutralizer was used. The least count instrument was 0.001 mg.

4.3.1.2 Conditioning of the Filter

- a) The quartz filters were pre-baked in an oven for about 4 hours at 600 °C in order to remove the carbonaceous matter from the filter.
- b) For PM 2.5 reference methods, the filters were equilibrated for 24 hours at a constant relative humidity between 30% and 40% (within $\pm 5\%$) at a constant temperature range between 20°C and 30°C in order to minimize particle volatilization and aerosol liquid water bias. These conditions are more stringent as compare to PM10 filter equilibration.
- c) PM₁₀ filters were equilibrated at 20% to 45% relative humidity ($\pm 5\%$) at a temperature between 15° C to 30° C temperature ($\pm 3^\circ$ C).
- d) The equilibrium conditioning of the filters were intended to minimize the liquid water associated with soluble compounds and to minimize the loss of volatile species.

4.3.1.2.1 Preweighing

The desiccated filters were picked by Teflon coated forceps. Teflon filters were kept for 1 minute under ionic blower to remove static charge that gets developed during sampling. Weighing was performed in triplicate to ensure the mass of the filter.

Petri-slides were marked as per source code. The pre-weighs were recorded in the logbook and then entered in an excel sheet for further need. Approximately one out of ten filters was re-weighed by a different person at a later time. These re-weighed values were used to calculate precision of the measurement.

4.3.1.2.2 Post Weighing

The same procedure was followed as for pre-weighing above. After collecting sample on the filters, it was desiccated to bring it in equilibrium. The Teflon filters were neutralized and weighed. Triplicate weighing was done in this case also.

4.3.2 Ion Analysis

Metrohm Ion Chromatograph (model IC Basic 792) was used for ion analysis (Table 4.2) with a conductivity detector. A filtered solution of tartaric acid and dipicolinic acid in deionised water was used as mobile phase. The baseline conductivity of IC for anions analyses was generally stable at 600-700 $\mu\text{S}/\text{cm}$.

Anions were separated when passed through quaternary ammonium active sites due to the different affinities of the anions for the resin sites. After separation, the anions are passed through a suppressor column which exchanges all cations for H^+ ions which lowers the baseline conductivity. The baseline conductivity of IC for cations analyses was generally stable at 18–21 $\mu\text{S}/\text{cm}$. A solution of sodium carbonate and sodium bicarbonate in filtered deionized water was used as eluent. Dilute sulfuric acid was used as suppressor.

4.3.2.1 Instrument Details

Anion Column: METROSEP A Supp 5, 250/4.0 mm.

Cation Column: METROSEP C 2 250, 250/4.0mm.

Anion Guard Column: METROSEP A Supp 4/5 Guard.

Cation Guard Column: METROSEP C 2 Guard.

High-pressure pump: Extremely low-pulsation double piston pump with a flow range from 0.2-2.5 mL/min and a maximum pressure of 25 MPa.

Peristaltic Pump: Integrated two channel pump with a flow rate of 0.5-0.6 mL/min.

Detector: Thermostatted conductivity detector with 2 ring-shaped steel electrodes which make alternating current measurement with 1 kHz frequency and ca.1.7 V amplitude, 0.8 μL effective cell volume and approx.17/cm cell constant with a temperature stability of $\leq 0.01^\circ\text{C}$ at constant ambient temperature.

Auto Sampler: Metrohm 838 advanced sample processor and manual injection through 20 μL loop.

4.3.2.2 Preparation of Standards and Eluents

Reagent Details

Anion Eluent:

3.2mM Sodium Carbonate Solution.

1mM Sodium Bicarbonate Solution.

Cation Eluent:

4mM Tartaric Acid Solution.

0.75mM Dipicolinic Acid Solution.

Anion Suppressor:

50mM Sulfuric Acid.

Anion Analysis

1. Standards from Accu standard, Inc. USA was used for standardization.
2. Standards in the concentration range of 0.4ppm to 4ppm were prepared by serial dilution of Accu standard. The ion concentration in the mix standard was Fluoride (20 ppm), Chloride (30ppm), Bromide (100ppm), Nitrate (100ppm), Phosphate (150ppm) and Sulphate (150ppm).
3. For the preparation of 0.4 ppm working standard, 0.5 ml of Accu standard was taken and diluted to 25 ml using deionised water.
4. Preparation of Anion Eluent: 3.2mM solution of Sodium Carbonate was prepared by dissolving 678mg of salt in 2 liter of deionised water and 1 mM solution of Sodium Bicarbonate was prepared by dissolving 168mg of salt in 2 liters of deionised water.
5. Preparation of suppressor: 50 mM of H₂SO₄ was prepared by taking 2.66 ml of H₂SO₄ solution in 1 liter of deionised water.

Cation Analysis

1. Standards from Accu standard Inc., USA were used for standardization.
2. The concentration range of standards were (2ppm to 10ppm) prepared by serial dilution of Accu standard, USA. Accu standard mixture contained Sodium (200 ppm), Ammonium (400 ppm), Potassium (201ppm), Calcium 1005 (ppm), Magnesium (201 ppm) and Lithium (50 ppm) ions.
3. For preparation of 2 ppm working standard, 0.25 ml of Accu standard was taken and diluted to 25 ml using Deionised water.
4. Preparation of Cation Eluent: For 4 mM Tartaric Acid solution, 1200 mg and for 0.75 mM Dipicolinic Acid solution, 250.50 mg of salt were dissolved in 2 liters of deionised water.

4.3.2.3 Extraction Protocol

1. Petri dish (containing sample filter paper quartz) was taken from the cold room and allowed to equilibrate to room temperature (nearly 2h).
2. Filter paper from Petri dish was placed on filter paper cutter base and cut it into equal half with pizza cutter.
3. Half filter paper was kept back into Petri dish and preserved it for EC/OC analysis.
4. Remaining half filter paper was used for Cation and Anion analysis.
5. These half filters were transferred into pre-labelled (as per sample ID) centrifuge tube carefully using forceps.
6. 25 ml of deionised water was added into centrifuge tube. The cap of tube was tightened and sonicated for 60 min. Temperature was not allowed to exceed more than 27°C during sonication. Ice was used to maintain the temperature.
7. After sonication, all centrifuge tubes were placed into a mechanical shaker maintained at 4°C and 60 rpm and were incubated overnight (12 h).
8. Extractant was transferred into pre-labeled beaker and filtered each sample using 0.45µm Millipore filter paper in to pre labeled storage bottle.
9. Anions were quantified using the instrument conditions as given in Table 1.
10. Once anions are analyzed, sample was acidified to pH 4-4.5 using conc. HNO₃ for cation analyses.

4.3.2.4 Standard Operating Procedure

1. Ensure the eluent reservoir is filled with eluent and tubings are well connected without any air bubbles in it.
2. Switch on the computer and IC instrument.
3. In computer, click IC Basic icon. Instrument control window will appear on screen.
4. Click on “file” icon and go to “open” and click to “system”. Select desired method (asupp5.smt for anion and “cation.smt” for cation analyses).
5. When method window appears, click on “system” icon.
6. Switch on the both pumps in case of anion analyses and only IC Pump in case of cation analyses.
7. Increase flow rate gradually to 0.7 ml/min and 1.0 ml/min for anion and cation analyses respectively.

8. Allow baseline to stabilize at 78-21 $\mu\text{S}/\text{cm}$ and 600-700 $\mu\text{S}/\text{cm}$ for anion and cation analyses respectively.
9. Once conductivity is stabilized, go to method window, click on “control” then click on “start determination” and fill the sample information.
10. Fill the injection loop.
11. When window show the message, “waiting for injection”, start the run by clicking “inject”
12. Set the run time by clicking on passport. Normal settings are 20 min for cation analyses and 30 min for anion analyses.
13. When run is over, follow point 9-11.
14. Click on “file” and select “chromatogram” and note the results.

4.3.2.5 Calibration

Four point calibrations was done for both cations and anions in concentration range of 1-10 ppm using standard operating procedure (section!). The retention time of each ion was determined by injecting the sample spiked with only one specific ion.

The results for anions and cations are shown in Figures 4.6 and 4.7. The responses were linear for all the tested concentrations. In case of anions, Fluoride shows the highest response and in case of cations, ammonium shows the highest response. The area for each peak was auto calculated by instrument from base to base which is indicative of good resolution among peaks.

4.3.2.6 Quality Control and Quality Assurance (QA/QC)

QA/QC was maintained by

1. Making sure that standard operating procedure (SOP) is being followed strictly.
2. Using certified IC standards (AccuStandard) as analytical quality control samples at the beginning of every analytical run. These results are compared with those observed in past. Difference of less than 10% is considered as reliable.
3. Analysing a field sample in duplicate, 2 QA/QC sample (AccuStandard) after every 10 sample.
4. Analysing QA/QC samples whenever the eluent is changed.

Figures 4.3 and 4.4 depicts the repeatability and reproducibility of the instrument for same sample for anions and cations respectively. The results clearly show that variation in response of the instrument is less than 5% which indicate the reliability of instrument.

4.3.3 Elemental Analysis

4.3.3.2 Background

Inductively Coupled Plasma with Atomic Emission Spectroscopy was used for the elemental analysis. In ICP-AES the samples of PM_{2.5} or PM₁₀ were extracted by acid digestion protocols (USEPA, 2005). The sample was then introduced into an atmosphere of argon gas having free electrons induced by high voltage. The high temperature in the plasma raises valence electrons of the elements above their normal stable states and when they return to their original state, they emit photons, which are unique and used to identify and quantify the elements. Horiba Jobin-Yvon ICP-AES (Ultima 2000) was used for elemental analysis.

4.3.3.2 Reagent Details

Mix Standards (AccuStandard, Inc):

Standard 1 : Ce, Dy,Er,Eu,Gd,Ho,La,Lu,Nd,Pr,Sm,Sc,Tb,Th,Tm,Yb,Y

Standard 2: Al,As,Ba,Be,Bi,Cd,Ca,Cs,Cr,Co,Cu,Ga,In,Fe,Pb,Li,Mg,Mn,Ni,K,Rb,Se,
Ag,Na,Sr,Ti,U,V,Zn

Standard 3 : Sb,Au,Hf,Ir,Pd,Pt,Rh,Ru,Te,Sn

Standard 4 : B,Ge,Mo,Nb,P,Re,S,Si,Ta,Ti,W,Zr

Standard 5 : Hg

Reagents for extraction:

Aqua regia-1:3 mixture of Conc. Nitric Acid (70%) and Conc. Hydrochloric Acid (35 %)

4.3.3.3 Extraction Protocol

- 1) The Petri dishes were removed (having sample on Teflon filter paper) from the cold room and allowed to equilibrate to room temperature (for about 2 hours).
- 2) The Teflon filter was removed from Petri dish and placed it in a clean and labeled 100 ml beaker. (Place the Teflon filter paper down in to the lower portion of beaker to ensure acid volume will cover entire Teflon filter paper).

- 3) 5 ml of extracting acid (aqua regia) was added. 15ml of concentrated HCl (GR grade) and 5ml of HNO₃ (GR grade) with high purity. Acid volume should cover the Teflon filter completely.
- 4) The beaker was placed on hot plate and refluxed gently while covered with a watch glass for 4 -5 hours at 90 °C. Sample was prevented from drying. If so then add 1-2 ml of extracting acid. Filter was allowed to get digested properly (till the time so that the minimum volume remains in beaker).
- 5) Beaker was taken off from hot plate and allowed to cool (nearly 20 min).
- 6) Walls of beaker were rinsed with 10 ml DI water and allowed to stand for 30 minutes, so that acid gets diffused from Teflon filter into the rinse.
- 7) Extraction acid was transferred from the beaker to 25 ml volumetric flask using a syringe filter. Beaker was rinsed with DI water and added to 25 ml volumetric flask. Make-up the volume with DI water i.e. 25 ml.
- 8) Sample was ready for analysis of elements using an ICP-AES.

4.3.3.4 Preparation of Standards

All standards of the elemental analysis were prepared in de-ionized water. Different concentrations of standards were prepared (100ppb, 200ppb, 500ppb, 1000ppb, 2000ppb and 5000 ppb) for the calibration of elemental analysis on ICP-AES using Accu Standard, USA of 10000 ppb.

4.3.3.5 Calibration

The calibration was done for all the 39 elements in the concentration range of 100 ppb to 1000 ppb using standard operating procedure. The intensity of each element was determined by injecting the standards which have respective elements.

The results for elements calibration are shown in figure. It is clear that the fig that responses of elements were linear for all tested concentrations. In case of elements, Sodium, Potassium, Calcium, Phosphorus, Iron, Tin shows high response in sample so these elements are calibrated at high concentration (2000 ppb to 5000 ppb). The intensity of wavelength was auto calculated by the instrument which corresponds to concentration of each element. Calibration graphs are given in Appendix 4A as Figure 4A.1.

4.3.3.6 Standard Operating Procedure

- 1) Switch-on the exhaust fan of ICP-AES, the chiller assembly and the air-conditioner (regulated at 20 °C, Air is used for Plasma & optic purge).
- 2) Open the Argon gas cylinders (one for the “carrier gas” and other for purge gas) and check the pressure (minimum 10 kg/cm²). The carrier gas pressure is regulated at 6 kg/cm² for plasma and purge gas at 1.5 kg/cm².
- 3) Switch-on the ICP-AES instrument followed by the computer connected to the machine.
- 4) Align the tubings of peristaltic pump and ensure the sample inlet tube is dipped in DI water (~100 mL) & drain tubing into drain container.
- 5) Open the ICP-AES software program in the computer and click the check button named “Control” and set the carrier gas flow rate as “PL1” and gainage as “G2” (default values, PL1 = 12-14 LPM and G2 = 0.4 LPM) & power is 1200.
- 6) Click on the “Start” button to ignite the plasma. A stabilization time of ~20 minutes is given before starting the analysis work.
- 7) After communication choose appropriate method in the “Tasks and Sequence” tab and make the desired sequence of analysis or calibration as required. Click the “Run” button to begin the analysis and follow the on-screen instructions until the analysis is complete.
- 8) After the completion of analysis, close the “Tasks and Sequence” tab, Click on the “Stop” button to extinguish the plasma and print the results.
- 9) Close the gas cylinders and release the pressure from the gas lines. Turn-off the machine and wait for ten minutes before turning off the chiller, exhaust, air-conditioner and computer.

4.3.3.7 Quality Control and Quality Assurance (QA/QC)

QA/QC was maintained by

1. Making sure that standard operating procedure (SOP) is being followed strictly.
2. Using certified ICP standards (AccuStandard Inc., USA) as analytical quality control samples at the beginning of every analytical run.
3. Spiking the filter paper with known amount of element standards and then analysing to check the extraction efficiency
4. Running QA/QC sample after every 15 samples to assess the performance of the instrument.

5. Running QA/QC samples each time when the analysis was started.

Figure 4.5 , depicts the reproducibility of the instruments for a particular sample. The results show that variation in response of the instrument is less than 5% which indicate the reliability of instrument.

4.3.4 EC/OC Analysis (Excerpt from Report of Analysis carried out at IIT Kanpur)

4.3.4.1 Background

This is the brief report of EC-OC analysis for PM₁₀ and PM_{2.5}, collected on quartz filter paper from various emitting sources. The Indian Institute of Technology Bombay, Mumbai had collected the samples. There were total 149 samples, comprising 110 samples for PM₁₀ and 39 samples for PM_{2.5}. Total eight fractions of OC and EC were analyzed. These include: OC1, OC2, OC3, OC4, EC1, EC2, EC3 and OP (pyrolysis organic carbon).

4.3.4.2 Instrumentation and Calibration

The instrument used for analysis was Thermal/Optical Carbon Analyzer (Model 2001, DRI, USA). Analyzer is based on the preferential oxidation of organic carbon and elemental carbon compounds at different temperatures. Organic compounds are volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The carbon compounds are liberated under temperature and oxidation environments from a small sample using a 5/16 inch diameter punch (0.512 cm²) taken from a quartz fiber filter. These compounds are converted to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂). The CO₂ is reduced to methane (CH₄) by passing the flow through a methanator (hydrogen – enriched nickel catalyst). A flame ionization detector (FID) is used to quantify the methane. The optical component of the analyzer is used to correct for pyrolysis of organic carbon compounds to elemental carbon in order to avoid underestimation of OC and overestimation of EC.

The instrument was freshly calibrated before analysis. The following gases were used for calibration of the instrument: 5% CO₂ in helium, and 5% CH₄ in helium. Calibration injections of 5% CO₂ in helium and 5% CH₄ in helium were performed at the beginning and ending of everyday to verify proper performance of the analyzer. The CH₄ in helium was also used as the end-of-run calibration, which is automatically injected by the instrument. 5% samples were repeated to ensure precision of the analysis.

Explanation of various parameters of EC and OC are given below.

- OC1: Carbon evolved from the filter punch in a He-only (>99.999%) atmosphere from ambient (~25 °C) to 140 °C.
- OC2: Carbon evolved from the filter punch in a He-only (>99.999%) atmosphere from 140 to 280 °C.
- OC3: Carbon evolved from the filter punch in a He-only (>99.999%) atmosphere from 280 to 480 °C.
- OC4: Carbon evolved from the filter punch in a He-only (>99.999%) atmosphere from 480 to 580 °C.
- EC1: Carbon evolved from the filter punch in a 98% He/2% O₂ atmosphere at 580 °C.
- EC2: Carbon evolved from the filter punch in a 98% He/2% O₂ atmosphere from 580 to 740 °C.
- EC3: Carbon evolved from the filter punch in a 98% He/2% O₂ atmosphere from 740 to 840 °C.
- OP: The carbon evolved from the time that the carrier gas flow is changed from He to 98% He/2% O₂ at 580 °C to the time that the laser-measured filter reflectance (OPR) reaches its initial value. A negative sign is assigned if the laser split occurs before the introduction of O₂.
- OC: OC1 + OC2 + OC3 + OC4 + OP
- EC: EC1 (corrected) + EC2 + EC3
- Total Carbon: OC + EC

4.3.5 Molecular Marker Analysis

4.3.5.1 Background

Organic molecular markers attached or adhered to the particles are extracted in suitable organic solvents. The particles were cleaned and pre-treated according to requirement and finally analysed using Gas Chromatography with Flame Ionization Detector (GC-FID).

Perkin Elmer (Clarus 500) GC was used for the analysis of Molecular Markers. Molecular markers are separated on the surface of Phenyl Silicone resin, due to their different affinities

to the active sites of resin. After separation, the molecular markers were detected and analyzed using GC-FID and quantified with respect to their ionization potential. Constant flow of 2.5 ml/min of carrier gas (He) was maintained through the column. Injector and Detector temperature were maintained at 300 °C. Oven ramping programme is given below:

Oven Ramp	Rate (°C /minute)	Temperature °C	Hold Time (min)
Initial	0.0	60	2.00
1	15.0	290	15.00

GC-FID column which been used to separate Molecular Markers has its

Following specifications:

1. Phase: Bonded Methyl 5% Phenyl Silicone
2. Length: 25 m
3. Inside Diameter: 0.25 mm
4. Film Thickness: 0.25 µm
5. Sr.No: 50827M
6. Part No: 0092326

Injector specification is as follows:

1. Temperature: 300°C
2. Split Ratio: 5:1
3. Carrier gas flow: 2.50 ml/min (He)
4. Total run time for Molecular Marker analysis is 32.33 minutes.
5. Mode: Constant flow

4.3.5.2 Sample Extraction and Filtration Protocol

HPCL grade solvents were used to extract molecular markers (MM) deposited/collected on quartz fiber filters. Following procedure was used to extract these compounds.

1. Sample collected on quartz filter was placed in 250 ml pre-baked beaker.
2. 40 ml HPLC grade Hexane was added to the beaker.
3. Sample was sonicated for 15 minutes using ultrasonicator.
4. Step 2 and 3 were repeated one more time to ensure complete extraction in hexane.
5. 40 ml mixture of HPLC grade Benzene: Isopropanol in ration of 2:1 were added to above extract.

6. Sample was sonicated for 15 minutes.
7. The steps 5 and 6 are repeated twice to ensure the complete extraction of molecular markers.
8. The extracted sample was transferred into a flat bottom flask (250 ml) and excess solvent was evaporated using rotary evaporating apparatus.
9. Necessary care was taken to avoid the contamination or loss of samples.

4.3.5.3 Preparation of Standards

Standards of all molecular markers, individual as well as in mixed form were prepared using HPLC grade n-Hexane. Calibrated micro-balance was used to weigh the standards. Different concentrations of standards were prepared (25 ppm, 50 ppm, 75 ppm and 100 ppm) for the calibration of molecular markers using GC-FID.

4.3.5.4 Calibration:

1. The retention time of each Molecular Markers was determined by injecting individual standards using GC-FID.
2. The calibration curve in the concentration range of 25-100ppm for mixed standards was prepared.
3. The results for Molecular Markers calibration are shown in Figure 4.8 and reproducibility in Figure 4.9.

4.3.5.5 Quality Control and Quality Assurance (QA/QC)

QA/QC were maintained using the following approach :

1. By making sure that the Standard Operating Procedure (SOP) is being followed strictly.
2. The extraction protocol was carried out inside an exhaust hood and hand gloves were used to avoid any toxic effects (according to MSDS) that the solvents may cause.
3. Certified Molecular Marker Standards purchased from Sigma Aldrich were used for all analytical runs.
4. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance.

5. Solvent blanks were run on GC-FID before and after analyzing samples, to avoid the sample carry over & column cleaning.

References for Chapter 4

Chow, J. C., and Watson, J. G., 1989. Summary of Particulate Data Bases for Receptor Modeling in the United States. In *Transaction: Receptor Modelling in Air Resource Management*. J. G. Watson (Ed.). Air and Waste Manage. Assoc. Pittsburg. 108-133.

Chow, J. C., 1995. Measurement Methods to Determine Compliance with Ambient Air Quality Standard for Suspended Particles. *Air and Waste Manage. Assoc.* **45**: 320-382.

Table 4.1 List of the elements, ions and molecular markers identified for the source profile and apportionment study

Component		Analytical methods/Instruments	Required filter matrix
Elements (Na, Mg, Al, Si, P,S, Cl, Ca, Br, V, Mn, Fe, Co, Ni, Cu, Zn, As, Ti, Ga, Rb, Y, Zr, Pd, Ag, In, Sn, La, Se, Sr, Mo, Cr, Cd, Sb, Ba, Hg and Pb)		ICP-AES (Monochromator)	Teflon filter paper.
Ions (F ⁻ , Cl ⁻ , Br ⁻ ,NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ⁻² , K ⁺ , NH ₄ ⁺ Na ⁺)		Ion Chromatography with conductivity detector	Teflon filter paper
EC/OC		DRI EC-OC analyzer	Quartz filter
Molecular Markers		Extraction, followed by GC-FID analysis with and without derivatization	The left over quartz filter paper after OC/EC analysis should be taken as composite sample (for one week) to represent a location and specified duration of exposure. This implies that 30 composite samples will be analyzed in each season.
Alkanes	n-Hentriacontane n-tritriacontane n-pentatriacontane		
Alkonoic Acids	Hexadecanamide Octadecanamide		
PAHs	Benzo[b]fluranthene Benzo[k]fluranthene Benzo[b]pyrene Indeno[1,2,3- cd]fluranthene Indeno[1,2,3-cd]pyrene Phenylene pyrene picene Coronene		

Table 4.2 Details of the instruments used at CESE, IIT for chemical characterization study

S. No.	Species to be analyzed	Instrument	Make and Model	Remarks
1	Elements	Inductive Coupled Plasma (ICP)	Horiba Jobin-Yvon, Ultima 2000	Monochromatic i.e. analyze one element at a time. Minimum detection limit: 1mg/l Expected Time for a sample run:~12 min
2	Ions	Ion Chromatography (IC)	Metrohm, IC Basic-792	With conductivity detector. Cation column: Metrosep C2 250, Anion column: Metrosep A Supp5, Minimum Detection Limit: 100 mg/l. Expected time for one sample run: 1hrs.
3	Molecular Markers	Gas Chromatograph-Mass Spectroscopy (GC-MS)	RSIC	Require polar or non polar column.

Table 4.3 Minimum mass required to be collected on filter paper for elemental analysis from various sources based on USEPA SPECIATE profiles that are similar to sources of interest in the present work

Sl. No.	Source	Element present (with minimum percentage of total mass)	Symbol	(%)	Minimum mass required on filter paper (μg)
1	Residential Wood Combustion-Composite	Aluminium	Al	0.0210	119.0
2	Agricultural Field Burning	Manganese	Mn	0.0040	625.0
3	Cast Iron Cupola	Selenium	Se	0.0020	1250.0
4	Cast Iron Induction Furnace	Cobalt	Co	0.0020	1250.0
5	Coal -Fired Power Plant	Rubidium	Rb	0.0090	277.8
6	External Combustion-Coal Fired Composite	Cesium	Cs	0.0010	2500.0
7	Boiler - #2 Fuel oil Fired	Copper	Cu	0.0010	2500.0
8	Glass Furnace	Copper	Cu	0.0010	2500.0
9	Gray Iron Foundries-Average	Selenium	Se	0.0010	2500.0
10	External Combustion-Kerosene - Fired Boiler Composite	Antimony	Sb	0.0020	1250.0
11	Marine Aerosol	Bromine	Br	0.2000	12.5
12	Natural Gas Home Appliances	Vanadium	V	0.0180	138.9
13	NPK Fertilizer	Potassium	K	18.0000	0.139
14	Paint spray booth	Bromine	Br	0.0500	50.0
15	Paved Road Dust - Composite	Gallium	Ga	0.0010	2500.0
16	Residual Oil - Fired boiler /Petroleum refinery	Bromine	Br	0.0010	2500.0
17	Primary Lead Smelting -	Chromium	Cr	0.0240	104.2

	Composite				
18	Secondary Metal production - Average	Strontium	Sr	0.0010	2500.0
19	Soil Dust - Composite	Palladium	Pd	0.0020	1250.0
20	External Combustion-Solid Waste - Fired Boiler	Cobalt	Co	0.0010	2500.0
21	Steel Foundry - General	Bromine	Br	0.0250	100.0
22	Tar Pot	Iron	Fe	0.0010	2500.0
23	Unpaved Road Dust - Composite	Nickel	Ni	0.0040	625.0
24	Urea Fertilizer Production	Bromine	Br	0.0500	50.0
25	Wood - Fired Boiler	Nickel	Ni	0.0060	416.7
26	Wood - Fired Boiler	Selenium	Se	0.0020	1250.0
27	External Combustion-Wood Fired Boiler Composite	Silver	Ag	0.0010	2500.0

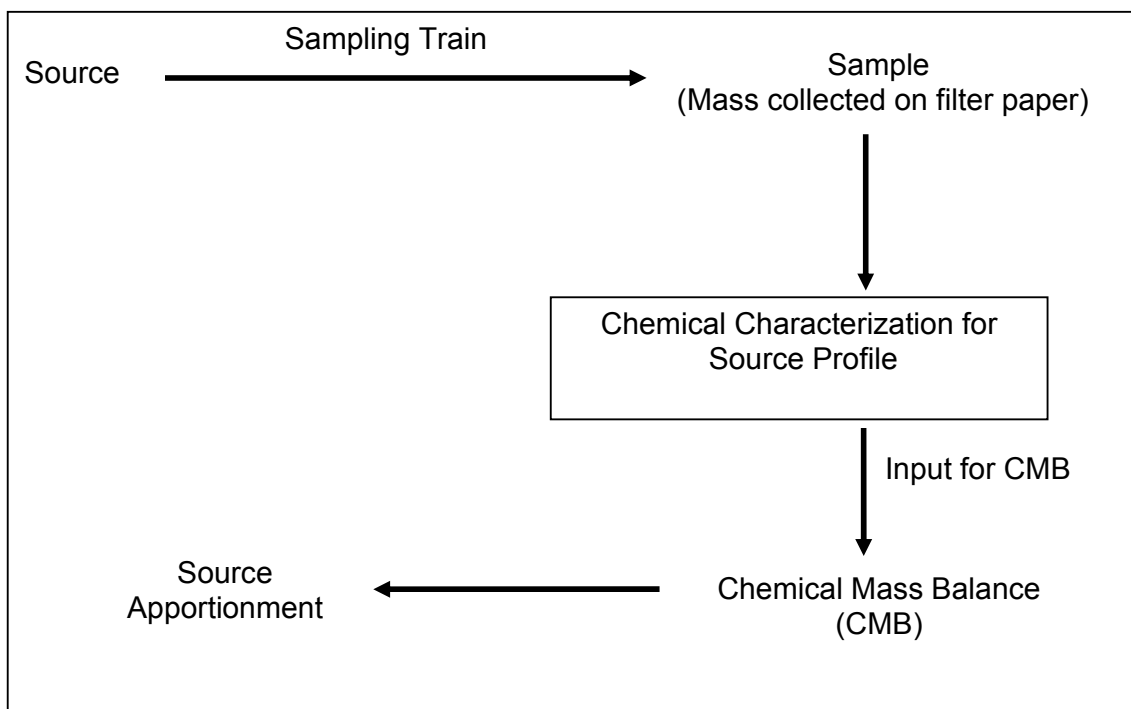


Figure 4.1 Need and role of chemical characterization for source apportionment study.

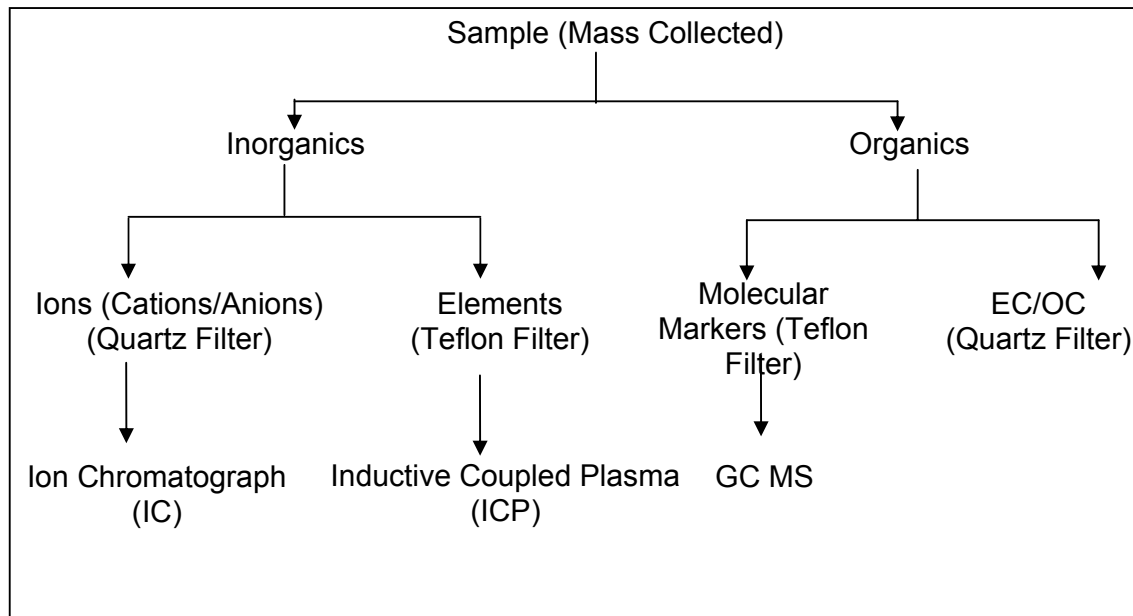


Figure 4.2 Overview of Chemical Analyses of collected mass and the filter substrate

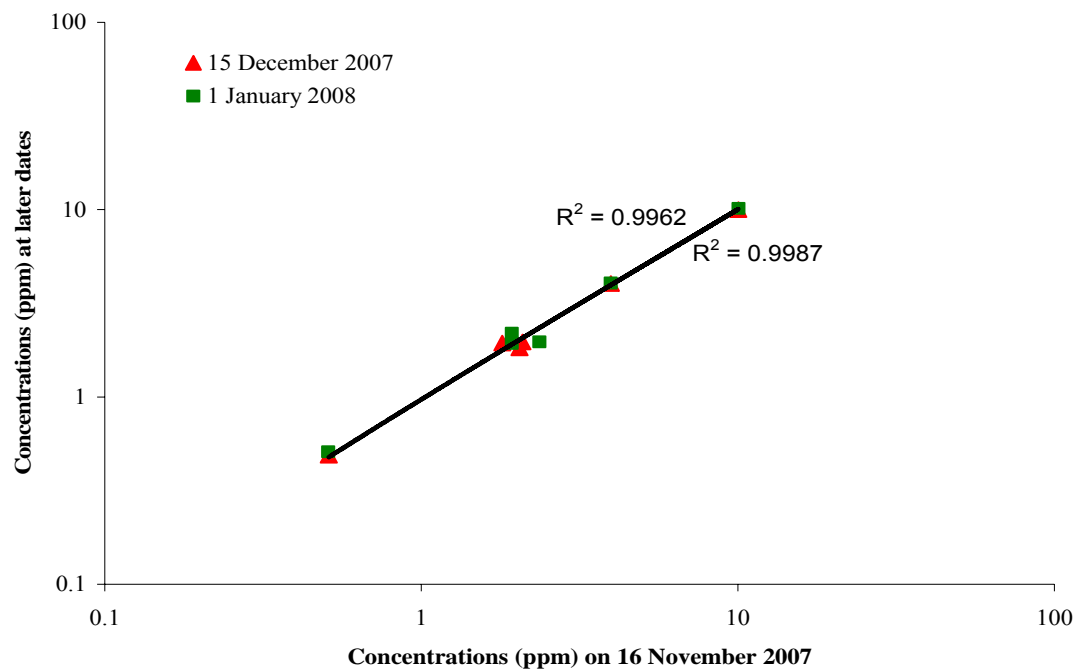


Figure 4.3 Reproducibility of IC for cation analysis

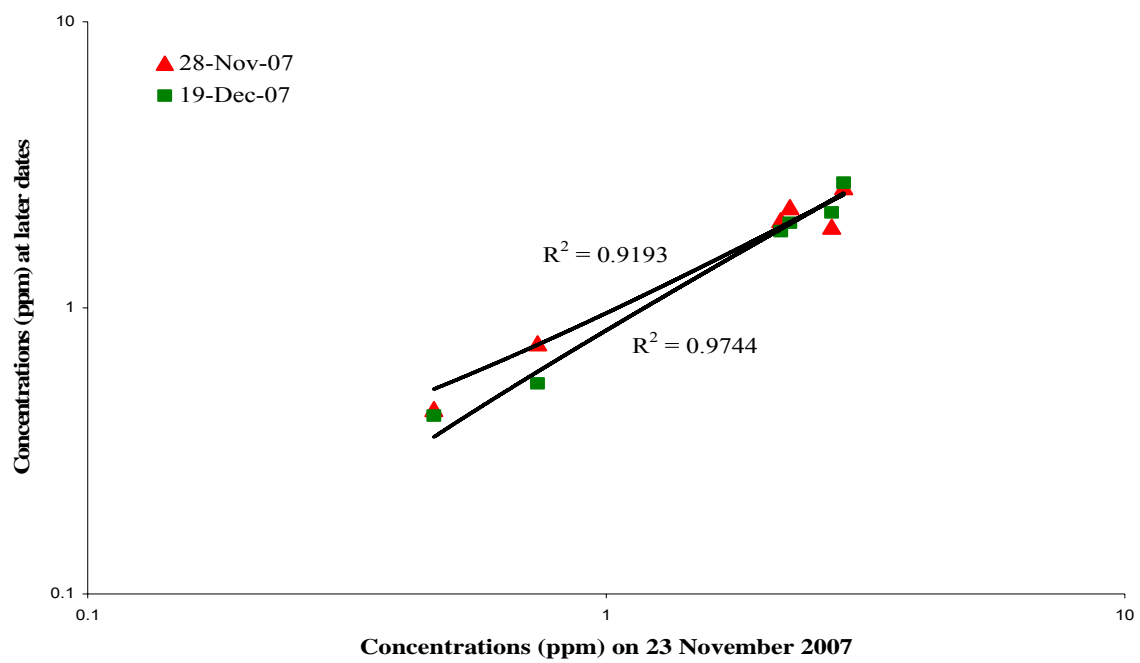


Figure 4.4 Reproducibility of IC for anion analysis

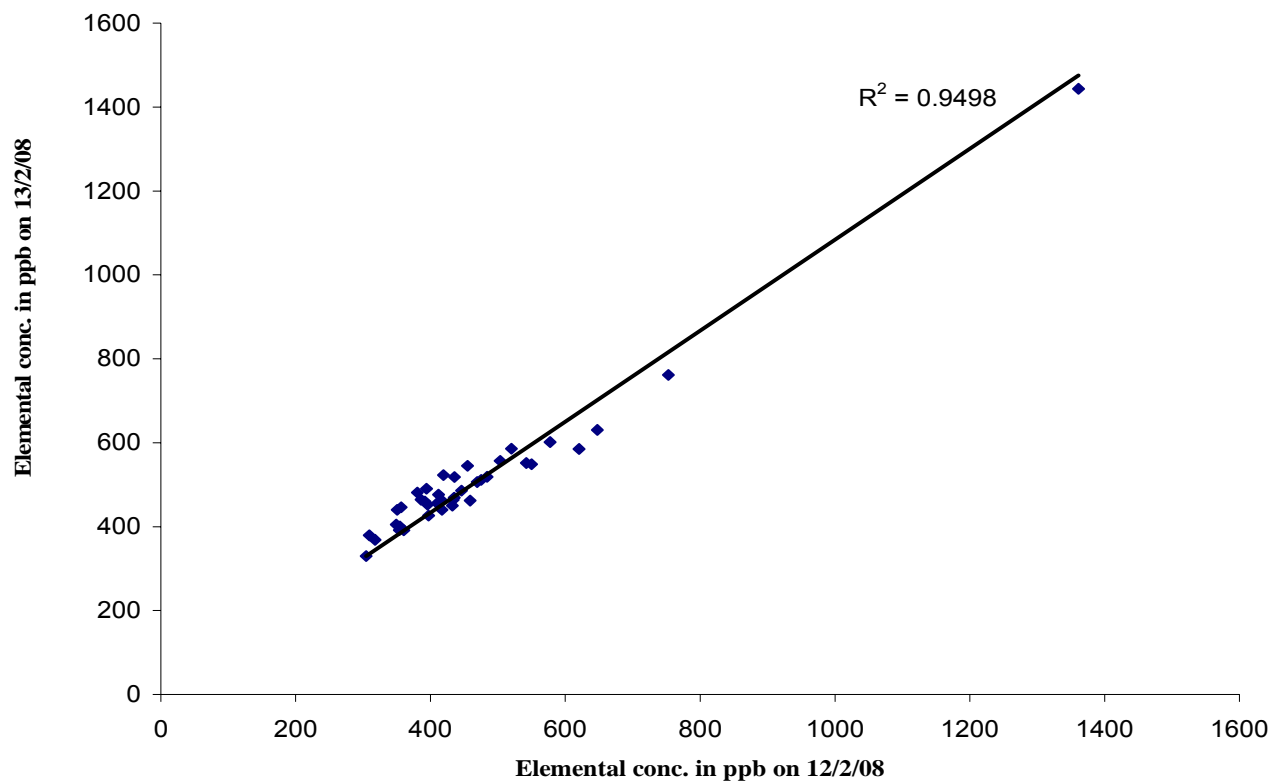


Figure 4.5 ICP reproducibility for laboratory standards

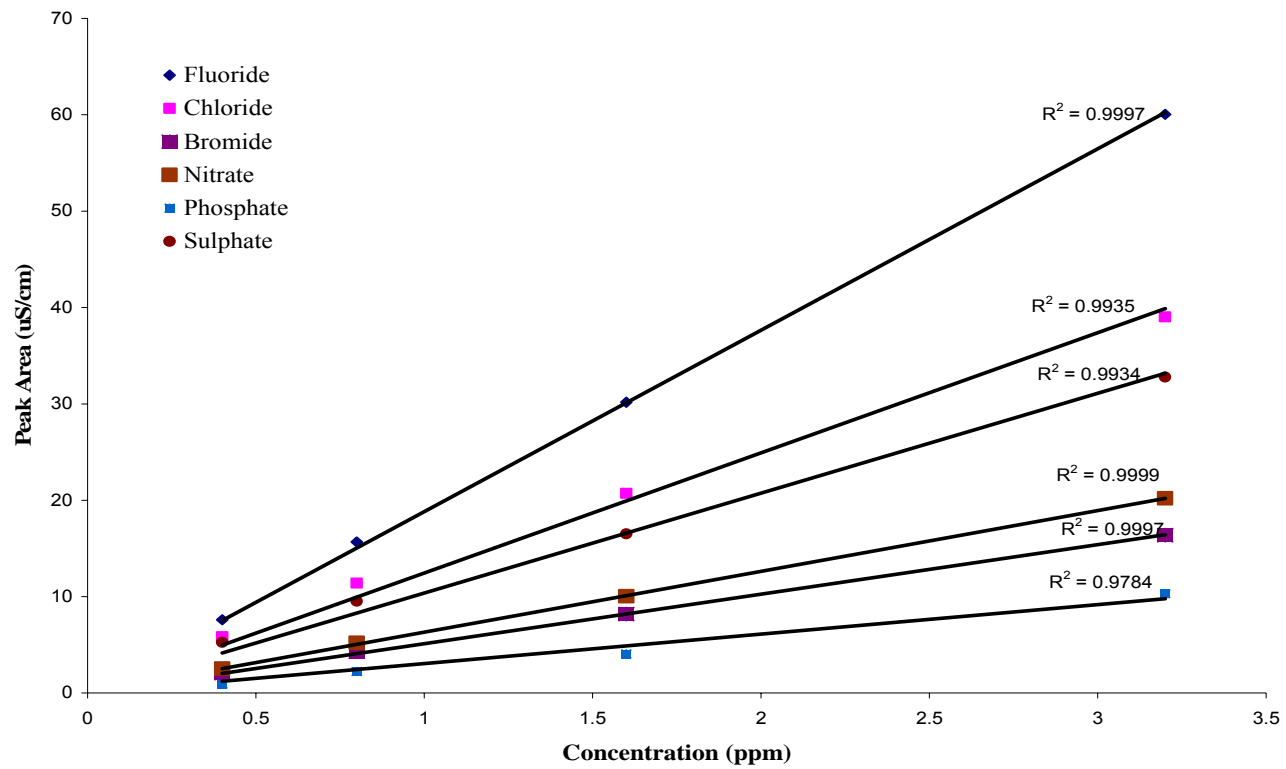


Figure 4.6 IC calibration curve for anions

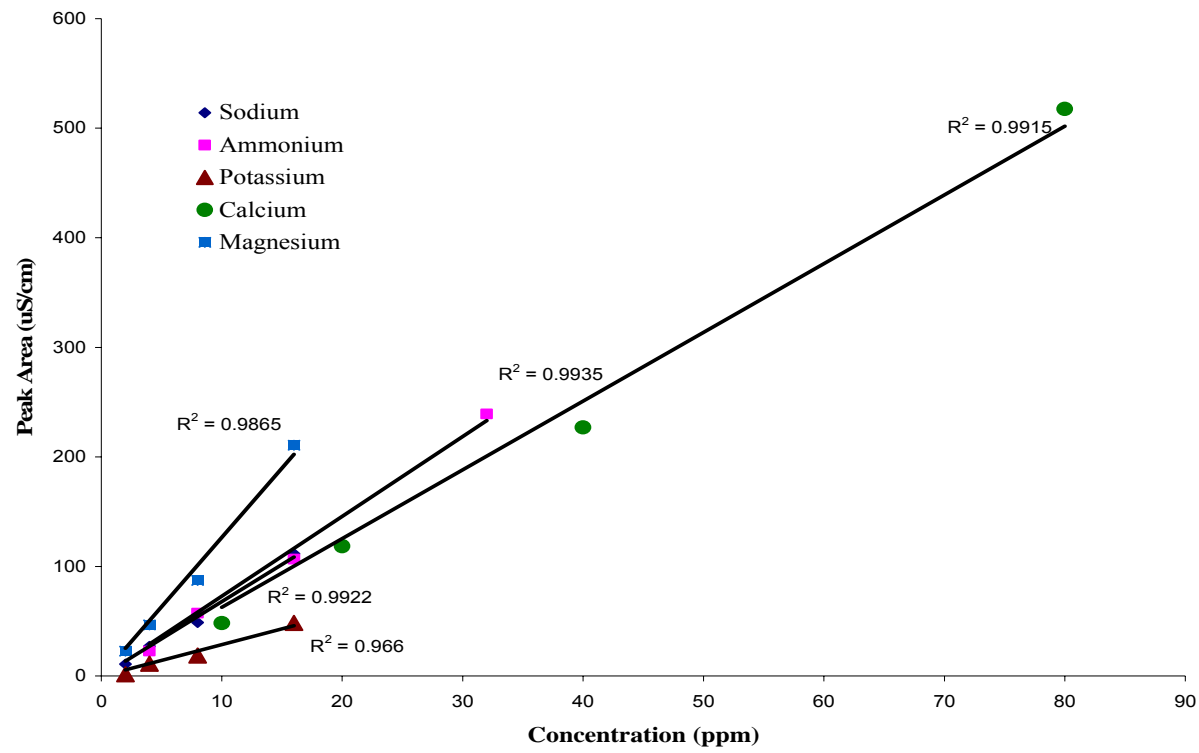


Figure 4.7 IC calibration curves for cations

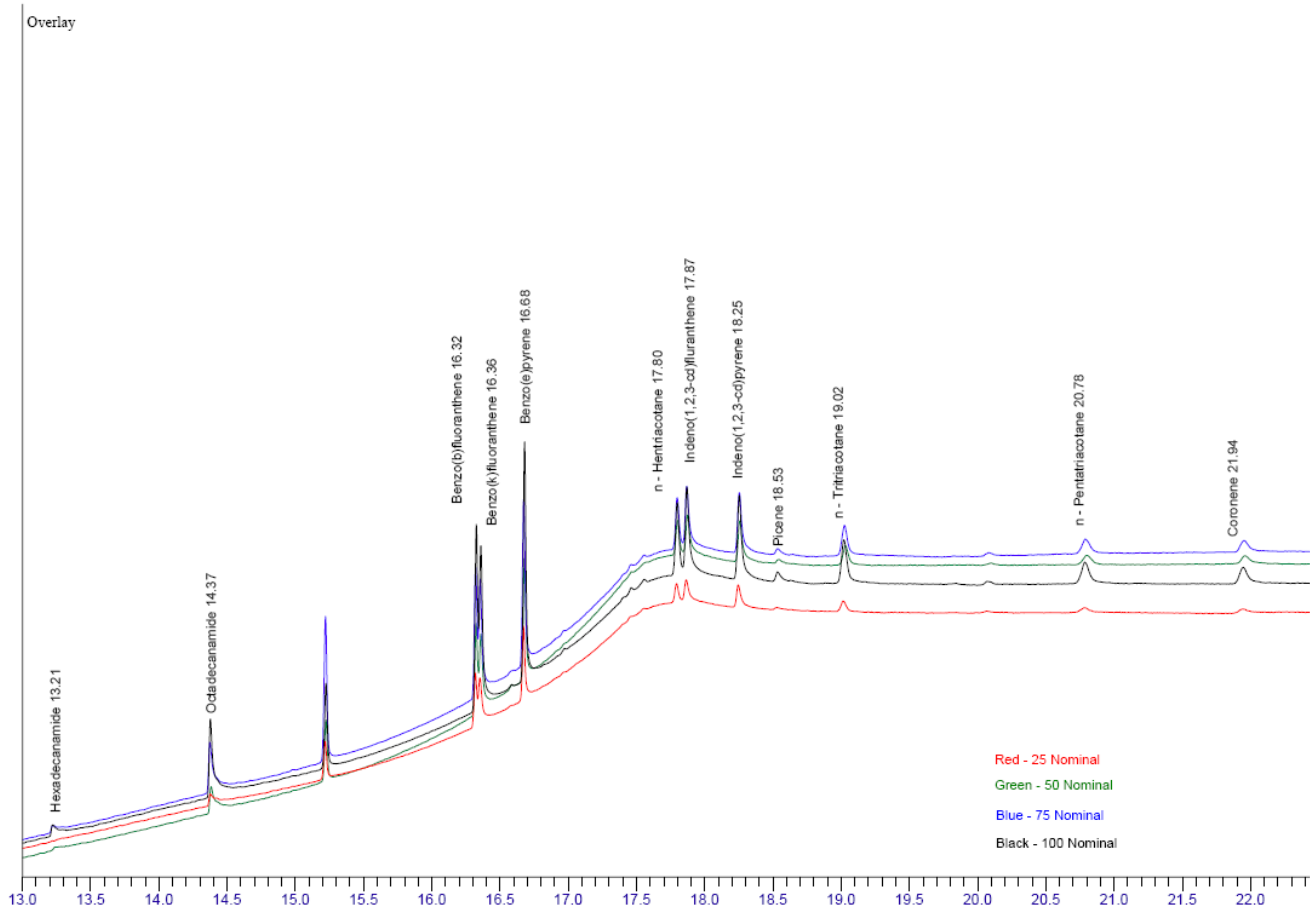


Figure 4.8 Response of the GC –FID for the Molecular Markers

Reproducibility of GC-FID

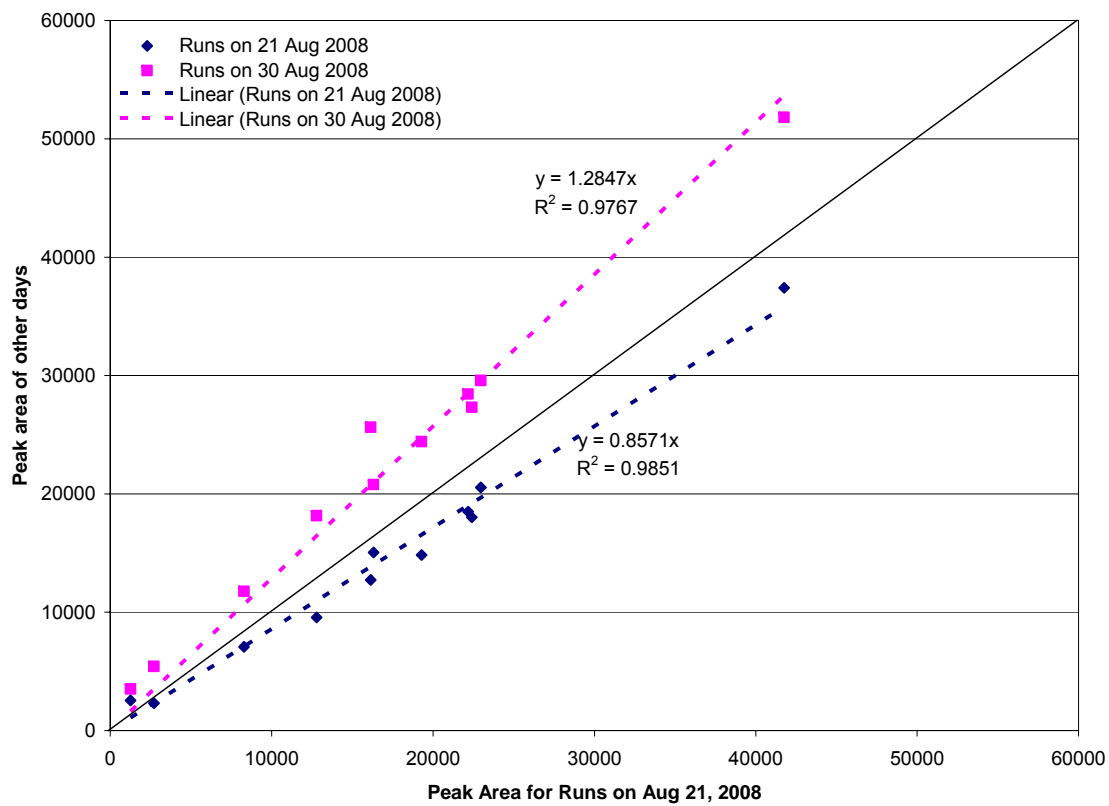


Figure 4.9 Reproducibility of the GC –FID for the Molecular Marker

5.1 Source Profiles

The source profiles for 58 sources listed in Table 2.1 are reported in Volume 2 of this report. The profiles are organised as tables, one for each of the 58 sources. The profile includes relative abundance of elements, ions, EC/OC and molecular markers. All 58 sources were analysed for these for PM₁₀ samples, and additionally 21 source profiles were also developed for PM_{2.5} samples. The data are also prepared as a database in a format for input into the CMB model.

Details of the sampling for each of the 58 sources are included in Tables 3.1 and 3.2

5.2 Evaluation of Source Profiles

Source profiles have been developed in several studies (SPECIATE : Beck, 2006) with different objectives, thereby leading to databases that are varied in terms of the content, level of the state of the art, technology, source and sampling conditions. These variations have motivated the development of the source profiles specific to the cities in India where the air pollution source apportionment effort is underway.

Comparison of the profiles developed in the present study with those reported in literature is useful in substantiating the quality of the source profile.

58 sources were studied in this project, and among these, 14 similar sources were found to be reported in the SPECIATE database (Table 5.1). A representative set of these were selected for comparison and are discussed in the following sections.

Further, there are other studies that have reported source profiles. A comparison was also made with the results reported for a study in Turkey (Yatkin and Bayram, 2008) that is similar in nature to the present work.

5.2.1 Comparison with SPECIATE

The comparison for the following four profiles with SPECIATE is shown in Figures 5.1. to 5.4 respectively : electric arc furnace, petroleum refining (combustion), coal combustion power plant and paved road dust. The graph is presented as a correlation between the relative abundances for the species that are common to both the present study as well as those in SPECIATE. A slope of 1 would indicate that the profiles were very similar in terms of the abundance of species in both the profiles. Further, even if the slope varied from 1.0, the R^2 value would indicate a high correlation for the relative abundance in each of the profiles.

For the electric arc furnace (Figure 5.1), the correlation is high as the variation in the process is limited, or in stated in another way, the process is as “pure” as one could expect with minimal variations as a process globally.

For the petroleum refining profiles (Figure 5.2), the abundances are consistently higher than those in SPECIATE. The comparison is often limited because the number of species reported in SPECIATE is fewer than those reported in the present work, and the mass closure is therefore not 100%. Further, the processes and/or the control devices in operation may not be the same for the profiles being compared, and this is usually the limitation of such a comparison.

Comparison for coal combustion power plant is shown in Figure 5.3. The difference in the quality and source of coal leads to a large variation in the chemical composition of the emissions.

Figure 5.4 represents the comparison for paved road dust profiles. These are likely to vary due to geological variations of the locations. The uncertainties associated with each species are also indicated in the Figure.

Comparison of coal based power plant and wood combustion reported for the study in Turkey are shown in Figures 5.5 and 5.6. The graphs are shown as histograms on a log scale. For coal combustion, the relative abundance of the reported elements varies from nearly same for Cr to a factor of two orders of magnitude for Al. Similar variations for all elements are seen for the wood combustion.

In summary, the source profiles are very specific to a particular source, conditions and geology, and care needs to be exercised for use in CMB or other receptor models. Specific choice of species is a matter of judgment based on experience of the modeler, supplemented with local information regarding the sources and other meteorological factors.

5.2.2 Comparison of PM₁₀ and PM_{2.5} Concentrations

Figure 5.7 shows the comparative correlations for the gravimetric analysis of 24 sources for PM₁₀ and PM_{2.5} samples. The highlight of the plot is that for combustion sources the PM₁₀ and PM_{2.5} are similar, or that most of the particulate matter is in the PM_{2.5} fraction.

5.2.3 Inter Laboratory Study (XRF – ICP) for Elemental Analysis

The extraction protocol for elemental analysis limits the extraction of elements such as silicon. The ICP used in the present study is intended for use for reagents that are compatible for use of glass, thereby inherently disallowing any reagents that would dissolve Si readily. This limitation was discussed during Technical Committee meetings and it was proposed to carry out an inter-instrumental comparative study for ICP and XRF.

A total of 29 PM₁₀ and 6 PM_{2.5} samples of soil/dust were generated, and the mass collected was ensured to be in the range suitable for XRF Instrument in the CPCB Laboratories in Delhi. The same samples were also extracted as per the elemental analysis protocol and analysed on the ICP-AES at IIT Bombay. Figure 5.8 shows the results of the analyses, represented as a ratio of respective concentrations measured for all the elements by the two instruments.

5.3 Scope for Future Work

The present study is a first effort towards development of a comprehensive database for source profiles for sources in India. The usefulness and the quality of the profiles will be reflected as further source apportionment studies are undertaken and with refinements and addition of new sources. The following areas of work are proposed for future work :

- Based on the rigorous emission inventories developed for the 6 cities, further refinement of the choice of sources for each city may be required.
- The delineation of sources in the model inherently requires that the profiles be unique. Issues of collinearity for sources such as kerosene, diesel and wood smoke for instance, require further investigation.
- Molecular markers are being incorporated in several recent studies and building confidence for organic analysis is crucial for further development in this work.

References for Chapter 5

Beck, L., (2006), Speciation Database Development Documentation, Final Report, EPA/600/R-06/161, USEPA, RTP, NC 27711

Yatkin S., and Bayram A., 2008. Determination of major natural and anthropogenic source profiles for particulate matter and trace elements in Izmir, Turkey, *Chemosphere* 71, 685–696.

Table 5.1 List of source profiles available in US SPECIATE database

Sr. No.	List of Sources Identified for the Present Study	Source Code	Profiles reported in SPECIATE	SPECIATE Code
1	Agricultural Waste Burning	15	Agricultural Field Burning	42304
2	Coal Combustion-Power Plant	12	Coal Fired Powerplant	11201
3	Fuel oil Combustion	2	Fuel Oil fired Boiler	12710
4	Power Plant-Natural Gas based	5002	Natural Gas Homeappliances	42107
5	Paved Road Dust-Composite	52	Paved Road Dust Composite	41130
6	Secondary metal (lead) smelting	46	Secondary Metal smelting and Other Operations	90008
7	Soil Dust Composite	54	Soil Dust Composite	41350
8	Unpaved Road Dust (Composite)	53	UnPaved Road Dust Composite	41220
9	Wood Combustion Boilers	11	Wood fired boiler	12705
10	Petroleum Refining Combustion	27	Residual Oil-Fired Boiler Petroleum Refinery	13505
11	Chulah (Wood)	9	Residential wood Combustion	42303
12	Paint and varnish	31	Paint Spraybooth	25403
13	Electric Arc Melting	45	Cast Iron Cupola	28202
14	Marine Aerosol	26	Marine Aerosol	43101

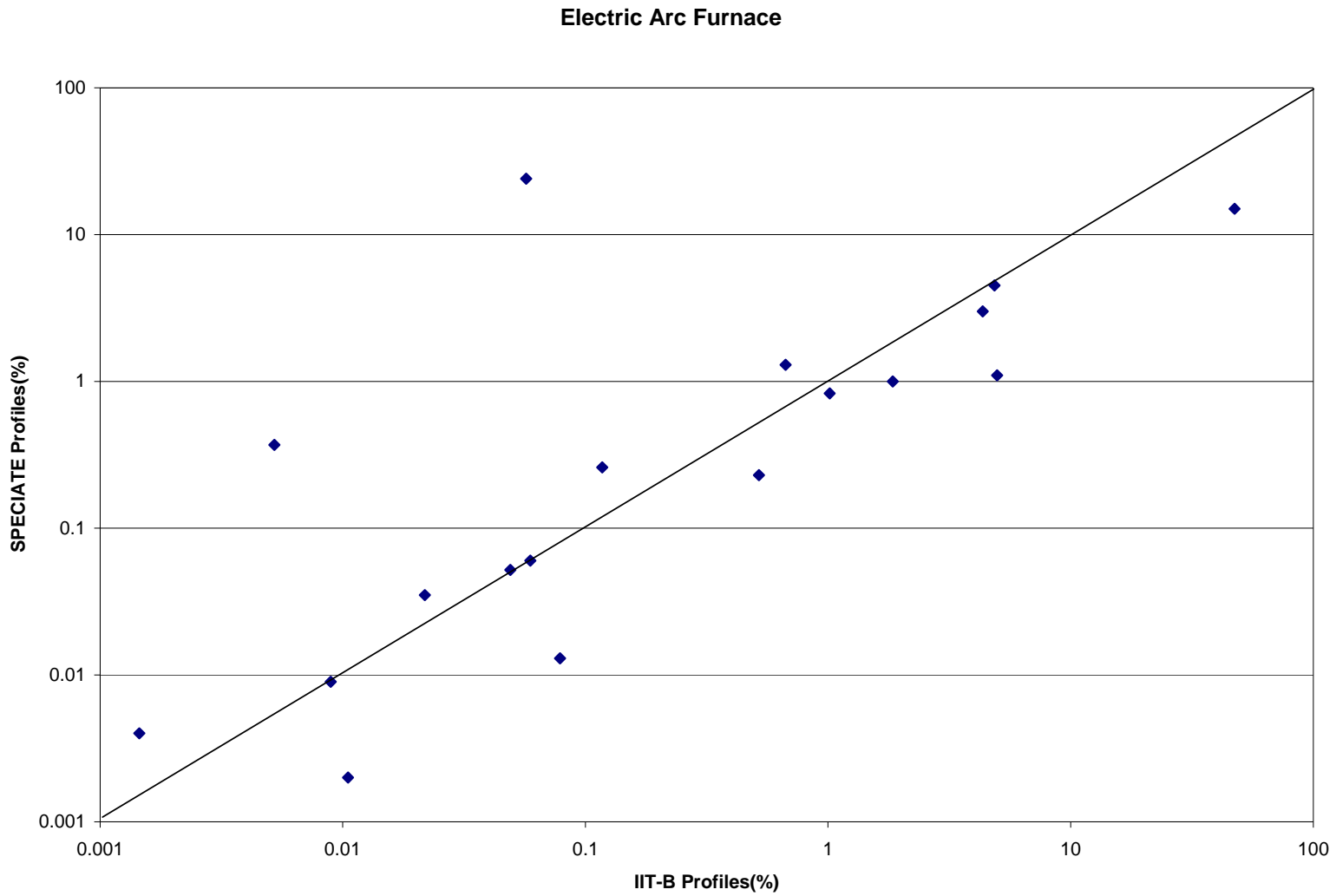


Figure 5.1 Comparison of Electric Arc Furnace Source Profile with SPECIATE Profile

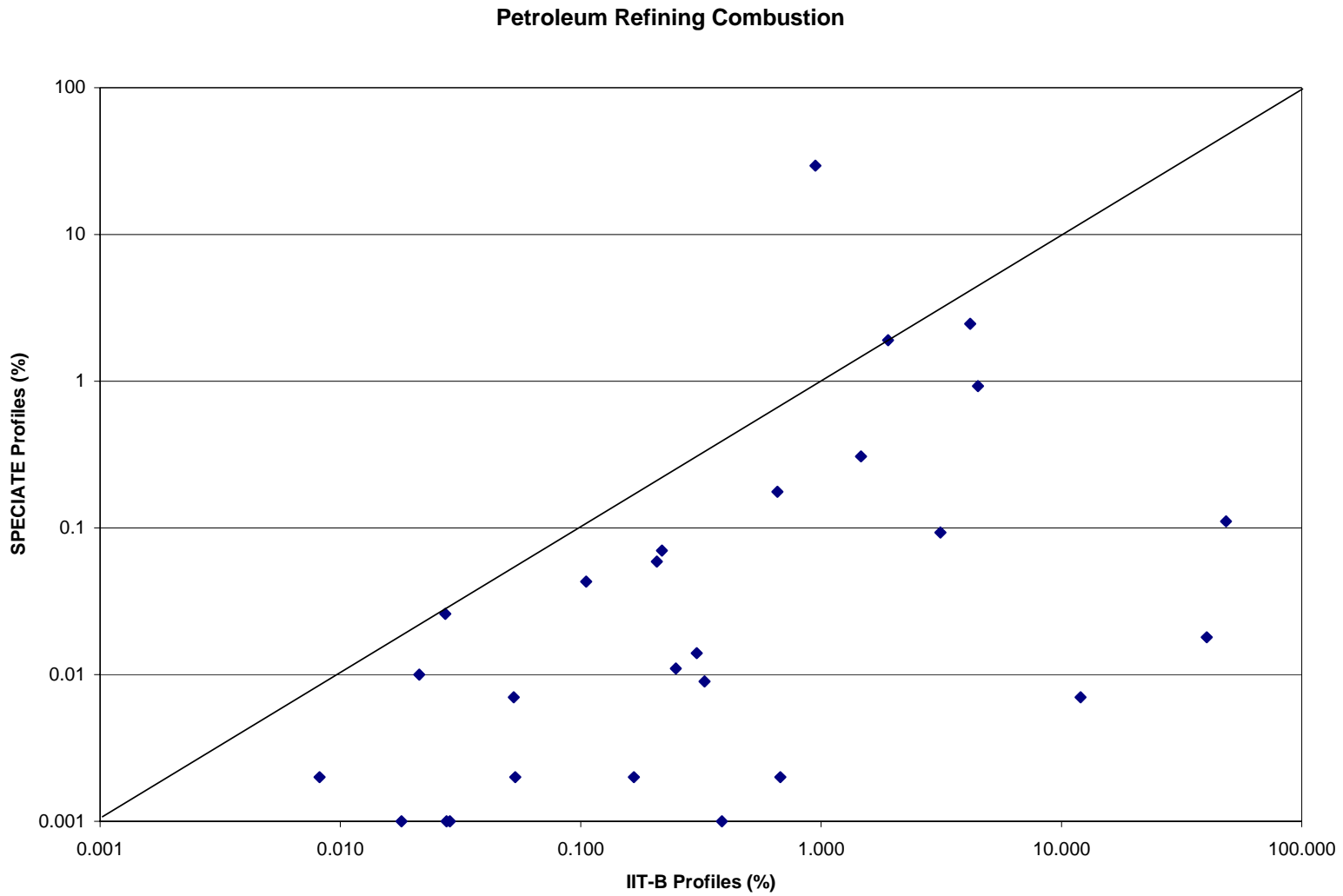


Figure 5.2 Comparison of Petroleum Refining (Combustion) Source Profile with SPECIATE Profile

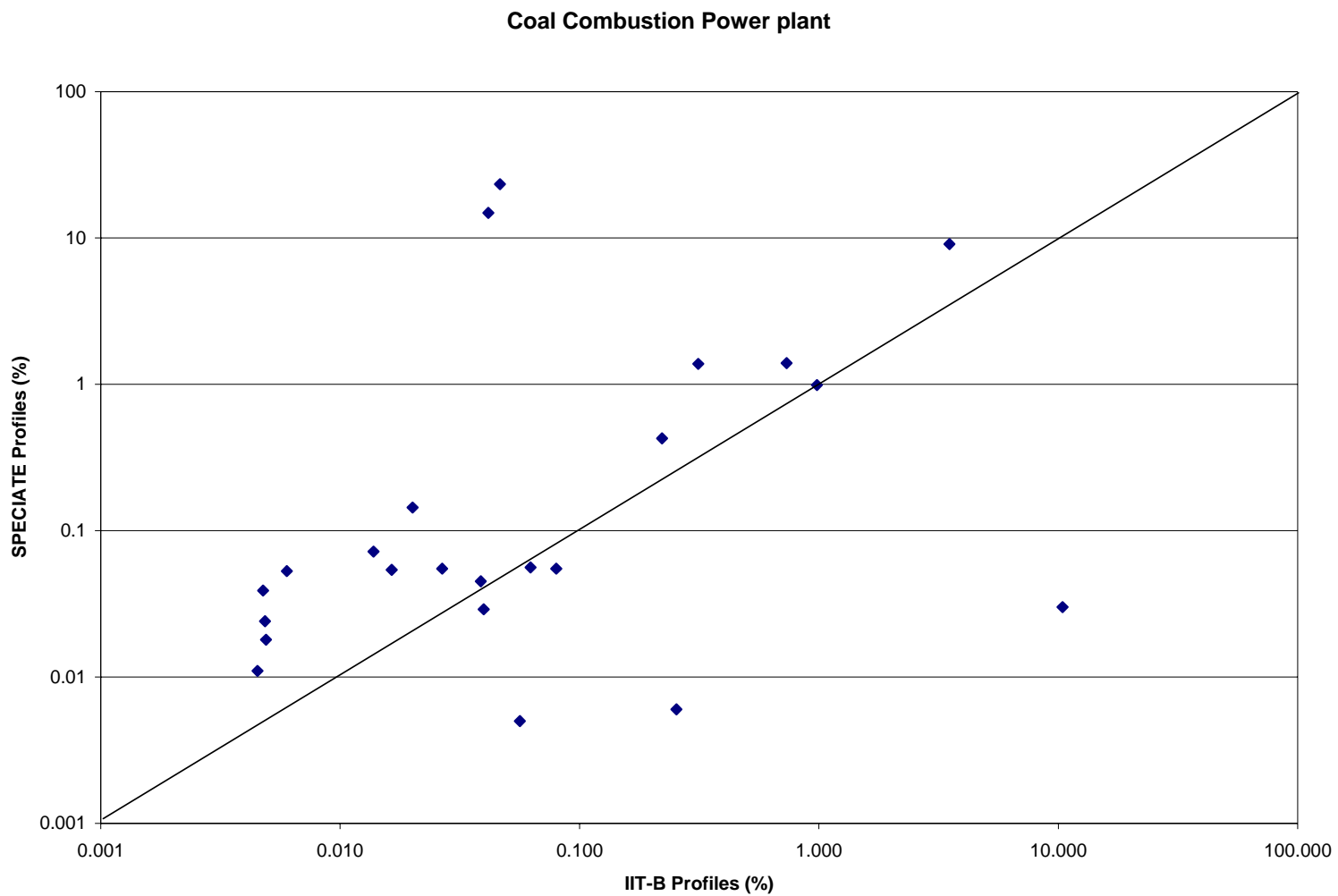


Figure 5.3 Comparison of Coal Combustion Power Plant Source Profile with SPECIATE Profile

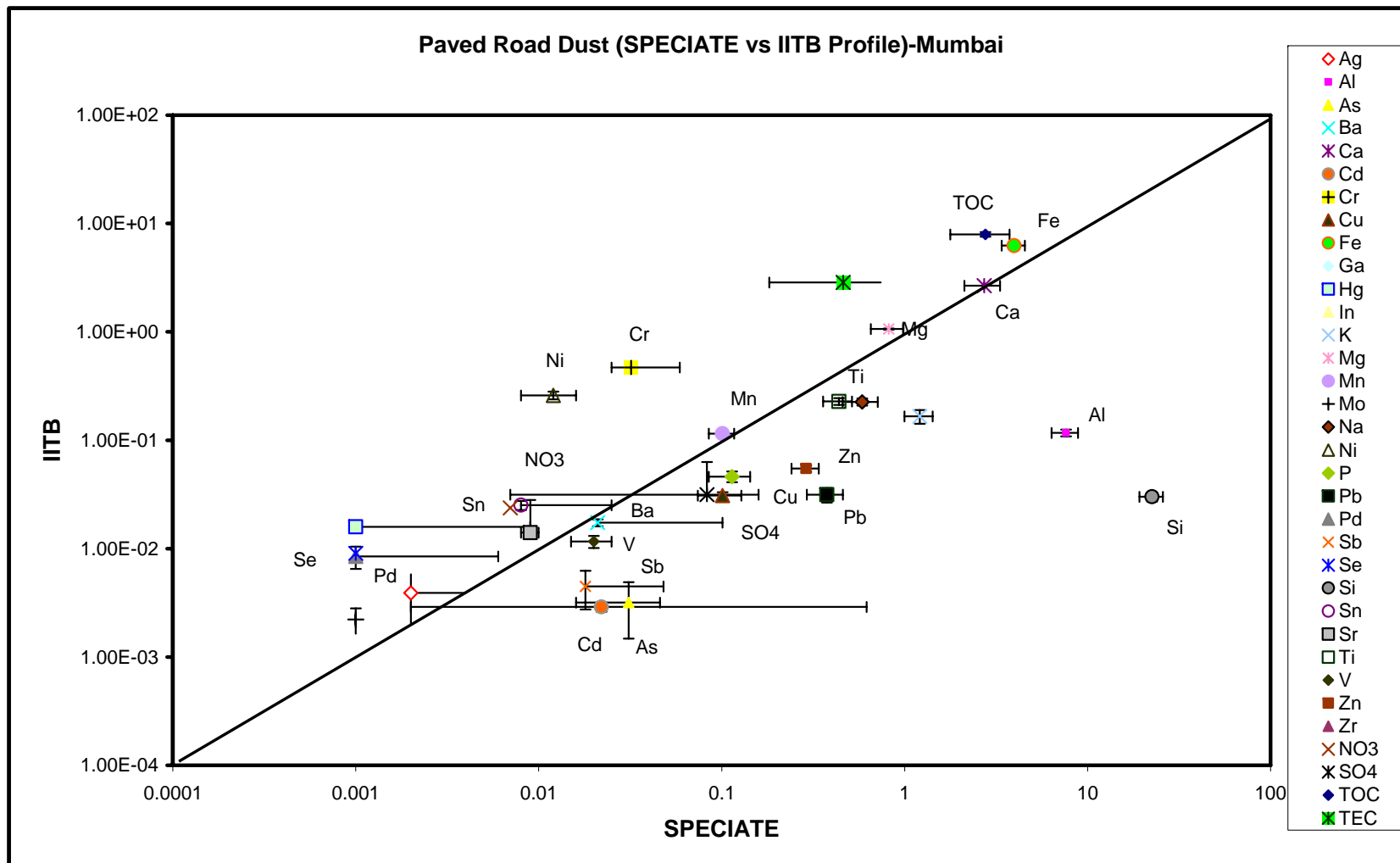


Figure 5.4 Comparison of Paved Road Dust (SPECIATE vs IITB Profile)- Mumbai Source Profile with SPECIATE Profile

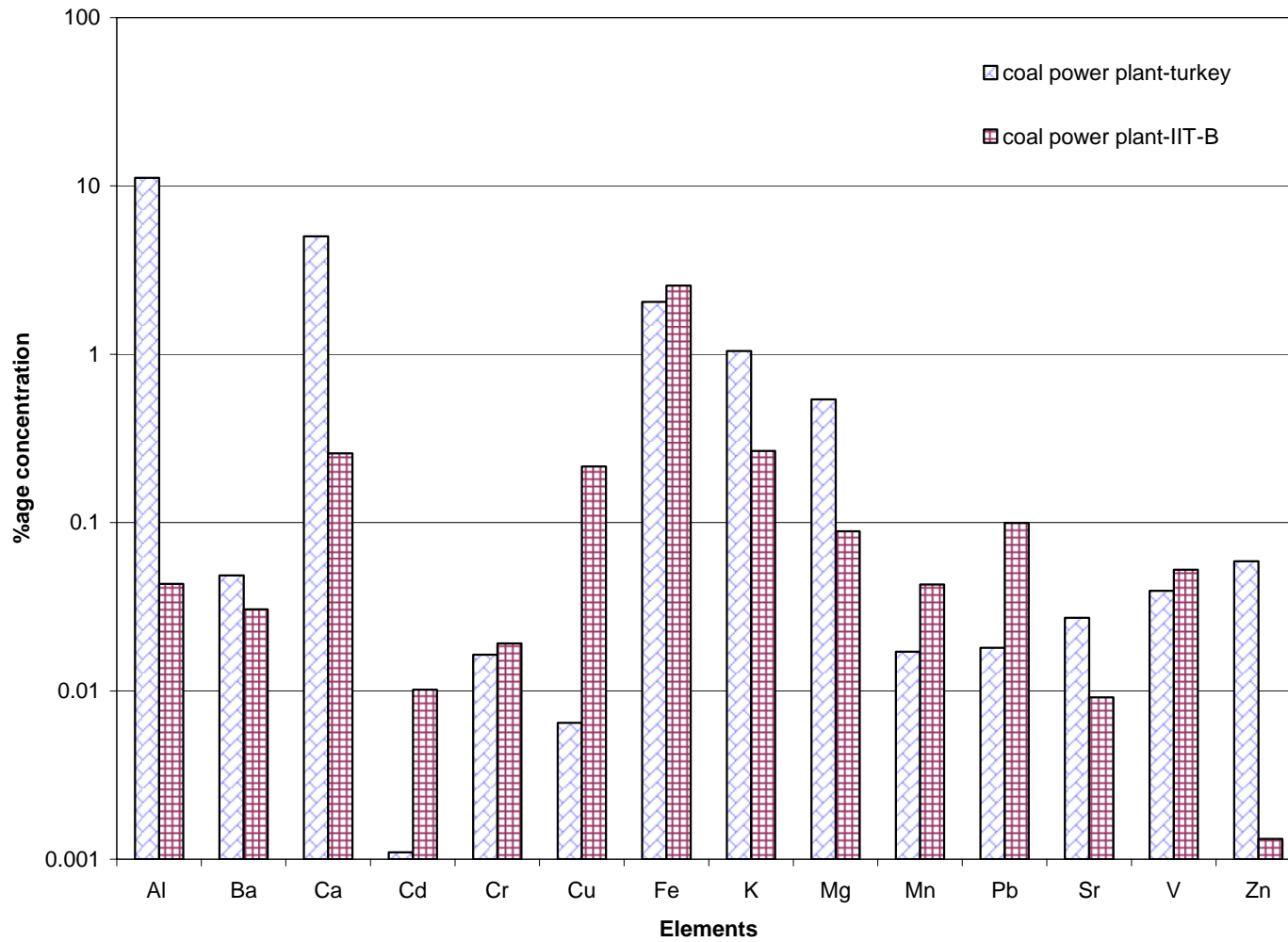


Figure 5.5 Comparison of Coal based Power Plant Profile with the study in Turkey

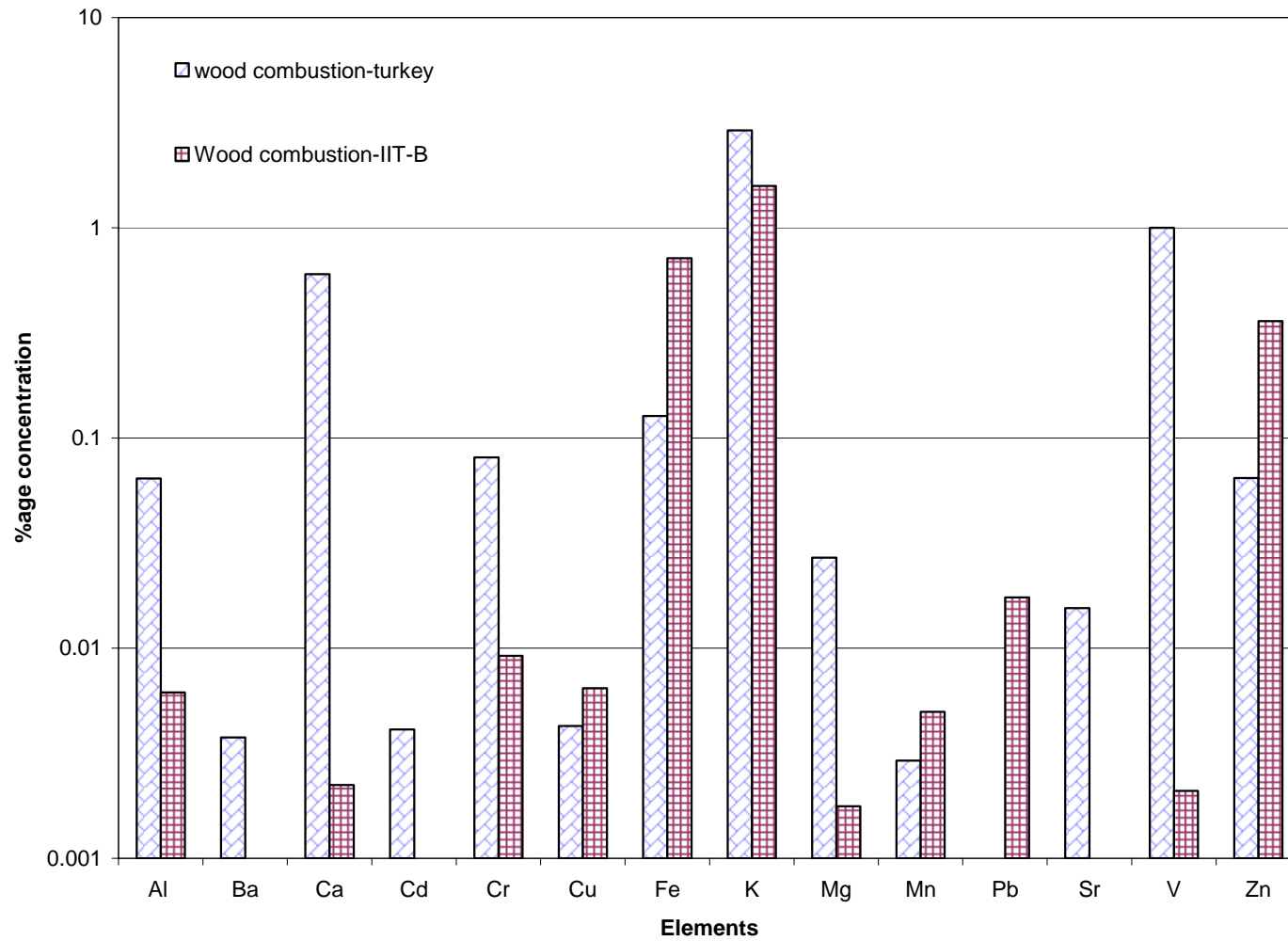


Figure 5.6 Comparison of Wood Combustion Profile with the study in Turkey

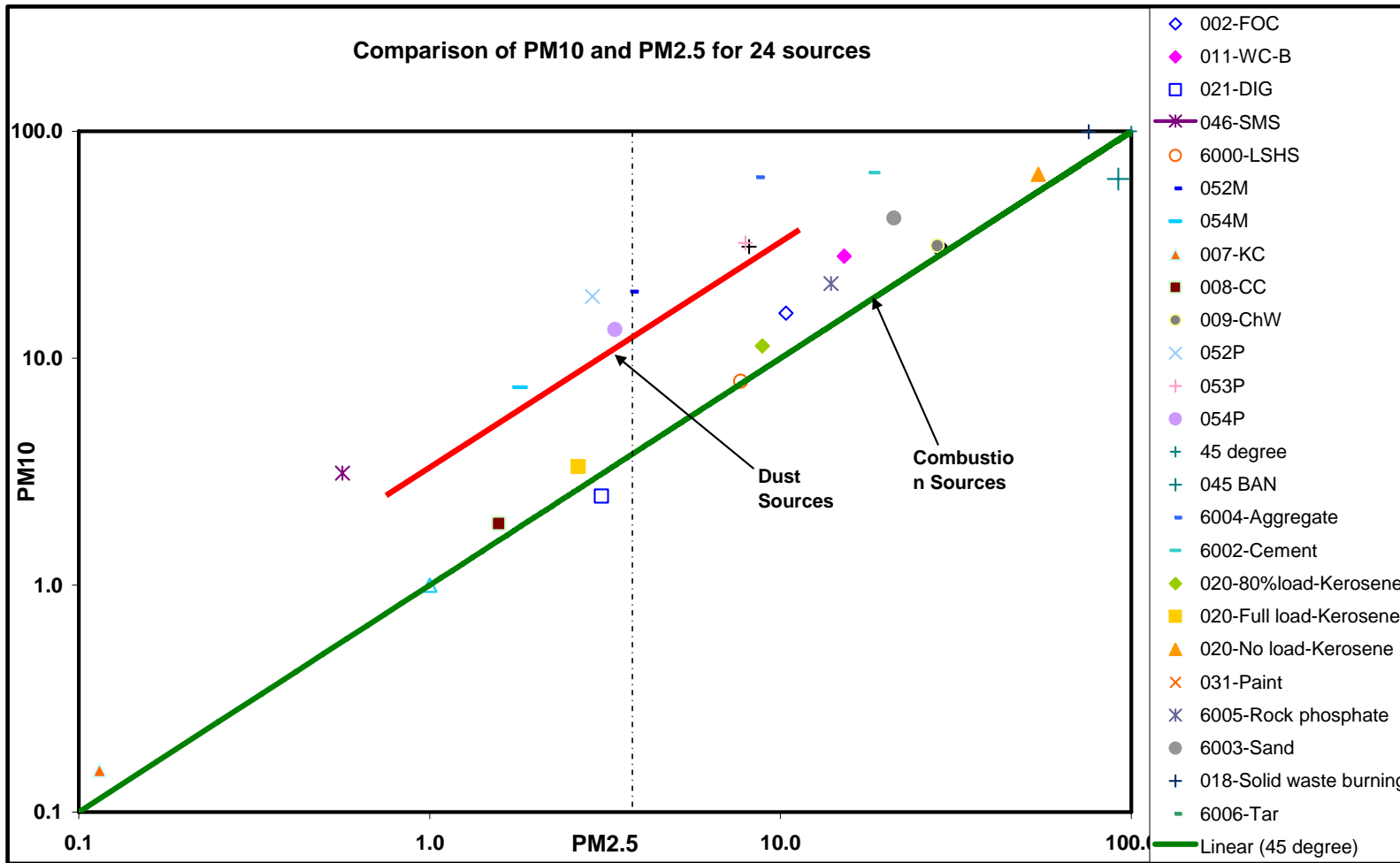


Figure 5.7 Comparison of PM10 and PM2.5 for 24 sources

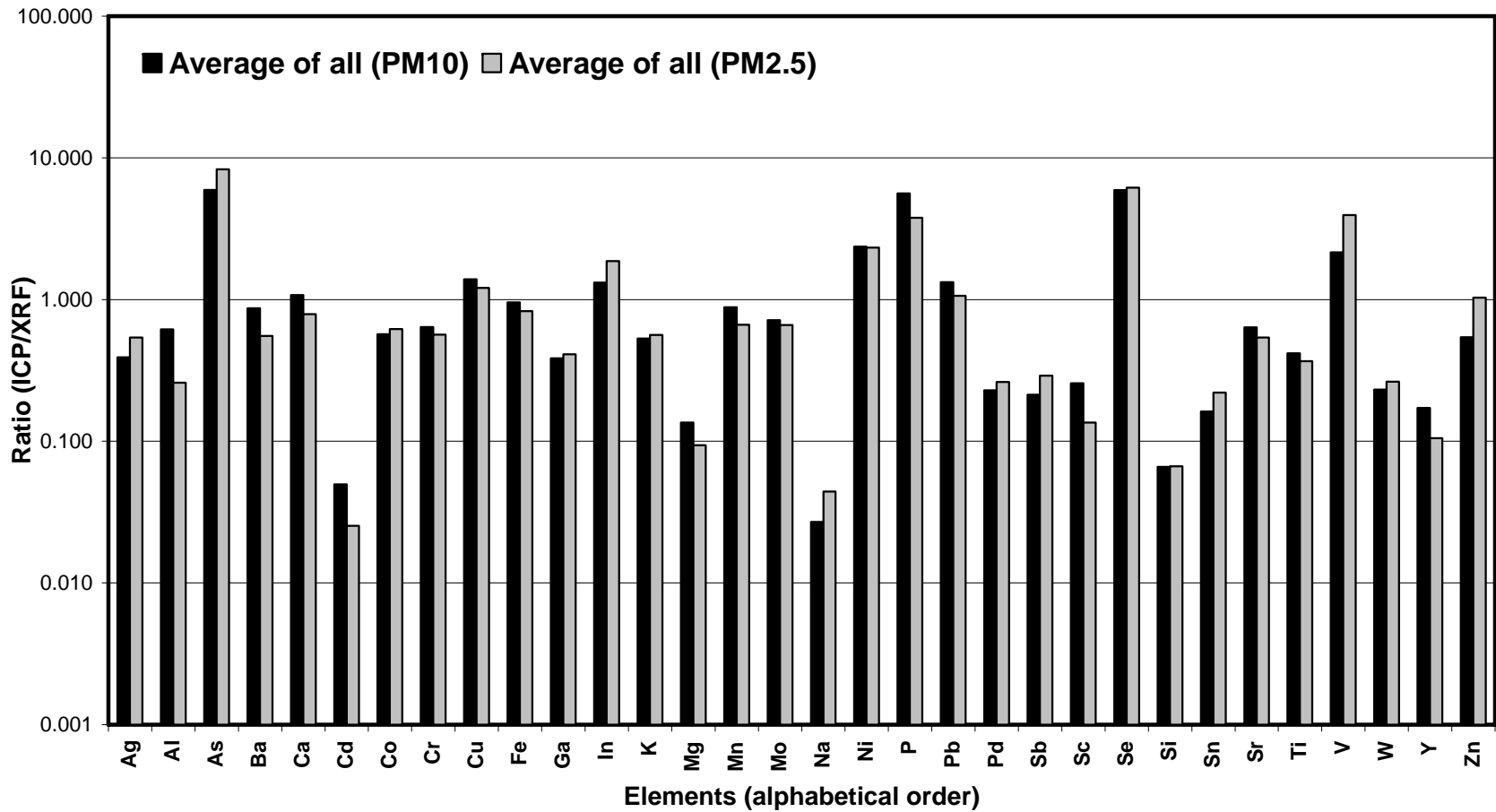


Figure 5.8 Average of Ratios of ICP/XRF for 29 PM10 samples (Paved Road, Unpaved Road and Soil Dust) and 6 PM2.5 (Paved Road) samples