

DRAFT

CONCEPTUAL GUIDELINES
AND
COMMON METHODOLOGY
FOR
AIR QUALITY MONITORING,
EMISSION INVENTORY & SOURCE
APPORTIONMENT STUDIES FOR INDIAN
CITIES

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This guideline document is prepared for use in 'Air Quality Monitoring, Emission Inventory & Source Apportionment Studies' being carried out for six Indian cities viz. Bangalore, Chennai, Delhi, Kanpur, Mumbai & Pune. The objective of preparing this document is to provide a conceptual framework on common methodology to all the participating agencies. Document is based on information on similar studies conducted in the past and literature on various issues. However, methodology framework has been designed considering specific project objectives and available infrastructure, resources, technical know-how, time frame, etc. Users are advised to keep in mind the above facts & limitations, while referring the document.

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CHAPTER – I

Study Framework

1.0 Mission

Ambient air quality monitoring is being carried out in various cities & towns in India under the National Air Monitoring Programme (NAMP). Air quality data generated over the years reveal that particulate matter concentrations are exceeding the standard permissible limits at many places, particularly in urban areas. Based on these data, Central Pollution Control Board (CPCB) identified more than 50 non-attainment cities and towns including 16 major cities, which recorded significantly higher levels of SPM & RSPM (PM₁₀). These cities have problems due to multiplicity and complexity of air polluting sources (e.g. industries, automobiles, generator sets, fuel burning, construction activities, etc.) and even the background contribution of natural dust (crustal origin) cannot be ruled out, particularly, in the cities developed on alluvial plains having loose topsoil. Due to multiplicity and complexity of air polluting sources, apportionment of these sources indicating their contribution to ambient air pollution is vital for planning cost-effective control strategies.

The Auto Fuel Policy document of Government of India made recommendations on implementation of EURO III equivalent norms for entire country and EURO IV equivalent norms for 11 major cities with effect from April 01, 2010. It also recommended that the schedules for introduction of EURO III (entire country) and EURO IV (11 major cities) norms would be reviewed in the year 2006. While dealing with air pollution scenarios, the policy document, observed that there were no reliable emission inventories available and as such there was a need to undertake real life emission inventories and source apportionment studies based on realistic emission factors and vehicle utilization factors. It also suggested that for assessing source contribution in ambient air, an integrated approach with use of dispersion as well as receptor (Chemical Mass Balance – CMB 8) models could be followed.

Air quality scenario demands formulation of comprehensive action plans for improvement in the non-attainment cities and towns. These Action Plans need to be realistic, technically feasible & economically viable to deliver the intended benefits. The steps & activities required for formulating a sound action plan necessarily include the following: (i) appropriate air quality monitoring networks & data generation; (ii) identification of emission sources; (iii) estimation of pollution load; (iv) assessment of contribution of these sources on ambient air concentrations and prioritization of the prominent sources that need to be tackled; (v) techno-economic evaluation of the control options & intervention analysis; and (vi) selection/introduction of the

best practical mitigation measures for short and long term city-specific Action Plans.

With the above background, source apportionment studies have been initiated in six cities viz. Delhi, Bangalore, Pune, Kanpur, Mumbai and Chennai. The study would focus on apportionment of respirable particulate matter [PM_{10} and $PM_{2.5}$ (limited)], being most critical. In addition, three studies viz. (i) development of emission factors for vehicular sources; (ii) development of source profiles for vehicular sources; and (iii) development of source profiles for non-vehicular sources have also been initiated. Outcome these studies would be required as input to source apportionment studies in six cities.

2.0 Objectives of the Study

Since, air quality in urban centers are affected by a variety of complex sources, detailed scientific studies are required for identification of major sources, assessing their contributions to urban air pollution and suggest mitigation measures taking into consideration the techno-economic feasibility and other social factors. Accordingly, this study has been initiated to promote and demonstrate a more rational & proactive approach to air quality management in urban areas.

The study objectives are:

- To profile Ground Level Concentration (GLC) of air pollutants in different parts of the city including background, residential, commercial/mixed areas and source specific "hot spots" viz. kerbside/roadside, industrial zones, etc.
- To develop "Emission Factors" (EF) for different categories of vehicles with due consideration to variations in fuel quality, technology, size and vintage of sources, control systems, etc.
- To select appropriate emission factors for other non-vehicular sources viz. industries, industrial & domestic fuel combustions, roadside dust, construction activities, generator sets, etc.
- To prepare inventory for different air pollutants, their emission rates & pollution loads from various sources along with spatial and temporal distribution in the city covered under this project.
- To profile the source emission characteristics of different possible sources.
- To conduct source apportionment studies for PM_{10} and $PM_{2.5}$ (limited) and prioritize the source categories for evolving cost-effective air pollution mitigation strategies/plans.
- To assess the impact of sources on ambient air quality under different management/interventions/control options and draw a roadmap of short

term and long term measures as considered appropriate and cost effective to ensure "Cleaner air in urban areas".

3.0 Scope of the Project

The proposed study is being executed under Indian Clean Air Programme (ICAP). The scope of the project is as follows:

3.1 Focus on PM₁₀

Among all the criteria air pollutants, particulate matter (SPM and RSPM) have emerged as the most critical one in almost all urban areas of India. High SPM concentrations are primarily irritants but do not have much relevance for direct health consequences as compared to effects of its respirable fractions (PM₁₀ and PM_{2.5}). Due to this reason, the worldwide focus of monitoring is now increasingly being shifted to measurement of finer particles (PM_{2.5} and even PM₁), which can penetrate the human respiratory systems. Since 2000 the focus on suspended particulate monitoring has shifted to PM₁₀ in India as well. Being a critical pollutant, PM₁₀ has also been included in National Ambient Air Quality Standards. In view of this, the main focus of this study is on characterization and apportionment of PM₁₀. Limited exercise on characterization and apportionment of PM_{2.5} has also been included in order to have a better understanding and correlation between these two fractions at source and receptors.

It may be pertinent to first briefly highlight the relationship between different size ranges of ambient particulate matter (as shown in Fig-1) that is typically found in urban atmosphere. It is relevant to assume that such a tri-model size distribution should be true with Indian urban scenario though the relative percentages and chemical characteristics would vary due to typical urban set up, which is likely to have similar activity pattern.

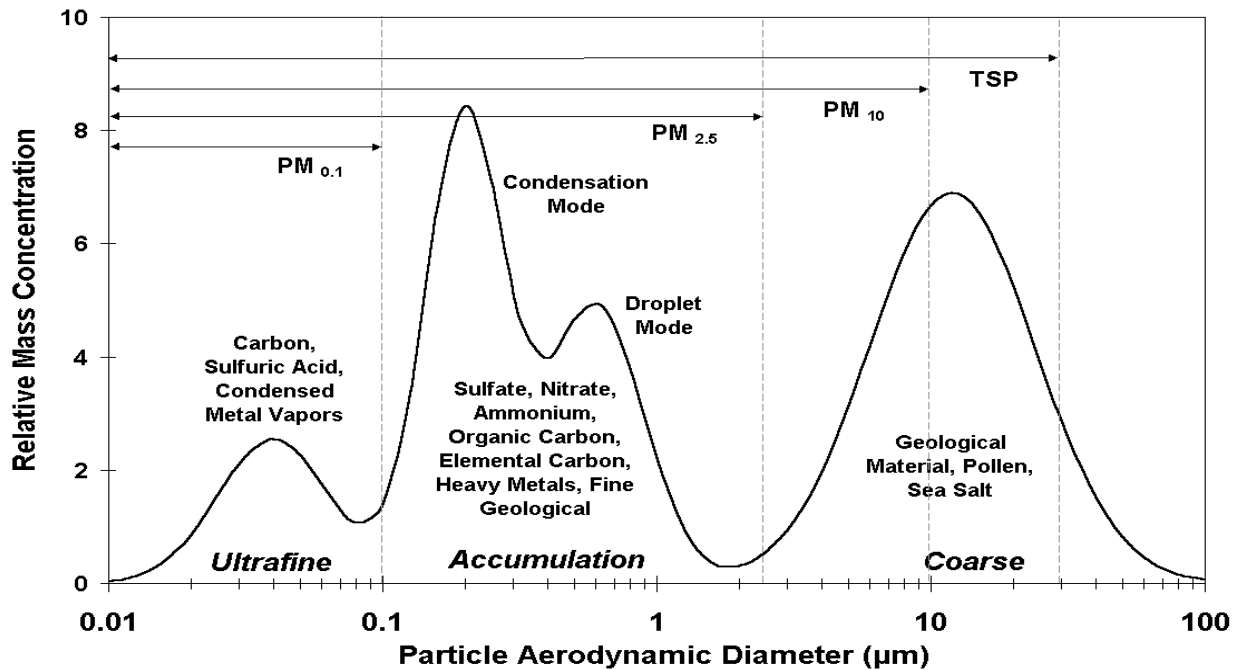


Fig. 1 (a): Relationship between different size ranges of ambient particulate matter

There are a large number of urban man made/background sources of such a high particulate pollution including large, medium and small-scale industries, household fuel use for cooking and heating, refuse burning, vehicular emissions, re-suspended road dust, construction activities, agricultural activity, naturally occurring dust and trans-boundary migration from other regions, etc. The configuration of possible contributing sources in different cities does vary widely as different responsible sources emit particles of varying composition and sizes. However, small particles (10 microns and fine) affect public health much more than large particles. Though studies on health effects are important, realizing that the problem is real in many Indian cities various mitigation strategies primarily focusing on traffic emissions had been initiated earlier. For any effective control strategy, it is important to have a good understanding of not only the level of exposure to various ecological resources, but also the relative contributions from different sources along with impacts and cost-benefit analysis of various control options.

Regular ambient air monitoring of PM₁₀ and PM_{2.5}, though an important step has a limited role to play in policy appraisal because it can merely signal the existence and extent of problem. Ambient air monitoring needs to be supplemented by studies to quantify the contribution made by different sources and to assess the impacts on damage cost (including public health consequences) in order to prioritize the cost-effective interventions. Hence, the scope of the study focusing action plan on control of PM₁₀ is detailed further.

3.2 Scope of Work

One important lesson learnt from different international & national monitoring experiences is that implementation of same interventions in two cities having different meteorology, topography and different typology of air polluting sources is unlikely to give same results. Therefore, the choice of interventions to control urban air pollution has to be city-specific, drawn on the basis of scientific study with adequate & representative set of quality data/information.

The scope of the study shall focus on following:

- The overall project scope includes city-specific air quality monitoring, complete characterization of ambient dust (PM_{10} and $PM_{2.5}$), emission inventory, source profiling, source apportionment using dispersion & chemical mass balance models. The first phase of the study covers six major cities of the country, the study is expected to be extended to other 11 non-compliant cities in the subsequent phases.
- To address all the expected anthropogenic emission sources in urban areas, it is planned to include many non-criteria pollutants in the study for understanding the extent of problem and comparison with earlier database. The major air pollutants covered in this project include SO_2 , NO_x , CO, Benzene, Aldehydes, Alkenes, NMHC, THC, PAH, PM_{10} , $PM_{2.5}$.
- The ambient air monitoring will be carried out over a period covering all three seasons in year to get representative data on seasonal variations in meteorology as well as activities that have bearing on air quality. The purpose of ambient air quality monitoring is not compliance verification. Therefore, it is proposed to carry out continuous monitoring for one month in each season for three seasons covering the whole year at all the monitoring locations.
- Air monitoring stations will be installed at locations such as kerbside, residential, industrial and background (away from all the sources and in upwind direction). Each city will have minimum seven air monitoring stations (with exception at Delhi having 10 stations). However, the number of monitoring stations can be extended to more depending upon the activity profile of a particular city.
- In order to catch the diurnal variations of sources as well as the typical meteorological changes, it is proposed to conduct 8-hourly monitoring (06.00 to 14.00s, 14.00-22.00, 22.00-06.00 hrs.) in a day. Thus, total 90 sampling days would cover the all days of week to give a fair representation of three seasons of a year.
- Monitoring of meteorological parameters would be carried out simultaneously at each station at same height of ambient air monitoring to

ensure proper representation of the activities of the surrounding area for a given monitoring location. Additional meteorological data for the study period will also be collected from India Meteorological Department (IMD).

- A detailed emission inventory would be carried out for line, point and area sources. Information/data on emission inventory available through secondary sources will be collected. Besides, primary surveys shall be carried out for identification & spatial distribution of sources and preparation of detailed emission inventory for zone of influence (2km x 2km area) around each ambient air quality monitoring location. City level emission inventory, available through secondary sources, shall be refined based on the data generated through primary surveys carried out within the zone of influence around each monitoring location.
- In order to get a wider cross section of vehicles in-use or on-road and the actual distance traveled by each sample vehicle, inspection & maintenance practices being adopted etc., a systematic survey of vehicle population will be undertaken in the city. Also, special emphasis will be laid on the emissions from vehicles of pre Euro/India 2000 for assessing cost-effective solutions as these represent major segment in total vehicle population.
- Emission factors developed by ARAI for each representative vehicles considering vehicle technology, age, fuel, traffic conditions and prevailing Inspection & Maintenance practices including influence of fuel quality with or without tail pipe treatment, will be used.
- Emission inventory of industrial and other sources will be prepared through secondary sources. Primary surveys will be also be conducted to crosscheck & validate the secondary data.
- With regard to emission factors for point sources, firstly the database available on emission characteristics with Pollution Control Boards & other sources (particularly for small-scale industries) would be scanned. For area sources, certain database generated in a few US-EPA studies (for India, Bangladesh and other countries of the region) would also be reviewed. For other source types, for which information is not available, the factor developed by US-EPA, EU, WHO would be scanned and then their normalization for Indian conditions have to be done.
- The Emission inventory (EI) data will be analyzed using appropriate technique like IPIECA tool, IVE model or other equivalent technique being used by reputed organizations like CARB, US EPA or EPEFE.

- Source apportionment analysis will be carried out for PM_{10} and $PM_{2.5}$ using receptor model like CMB model. For this purpose, detailed analysis of PM_{10} and $PM_{2.5}$ will be carried out.
- A study on source profiling of various polluting sources in Indian context has been initiated separately. The outcome of this study will be used as input to CMB model for source apportionment study.
- With regard to dispersion modeling and intervention analysis, refined city-level emission inventory will be used.
- On completion of data collection, validation and interpretation of the assimilated information, a detailed road map will be drawn considering all possible measures for air quality improvement. These measures will be classified into short and long term with due priority to low cost measures that give maximum benefits.

4.0 Study Framework

The framework proposed for the present study is as below as Fig. 1 (b)

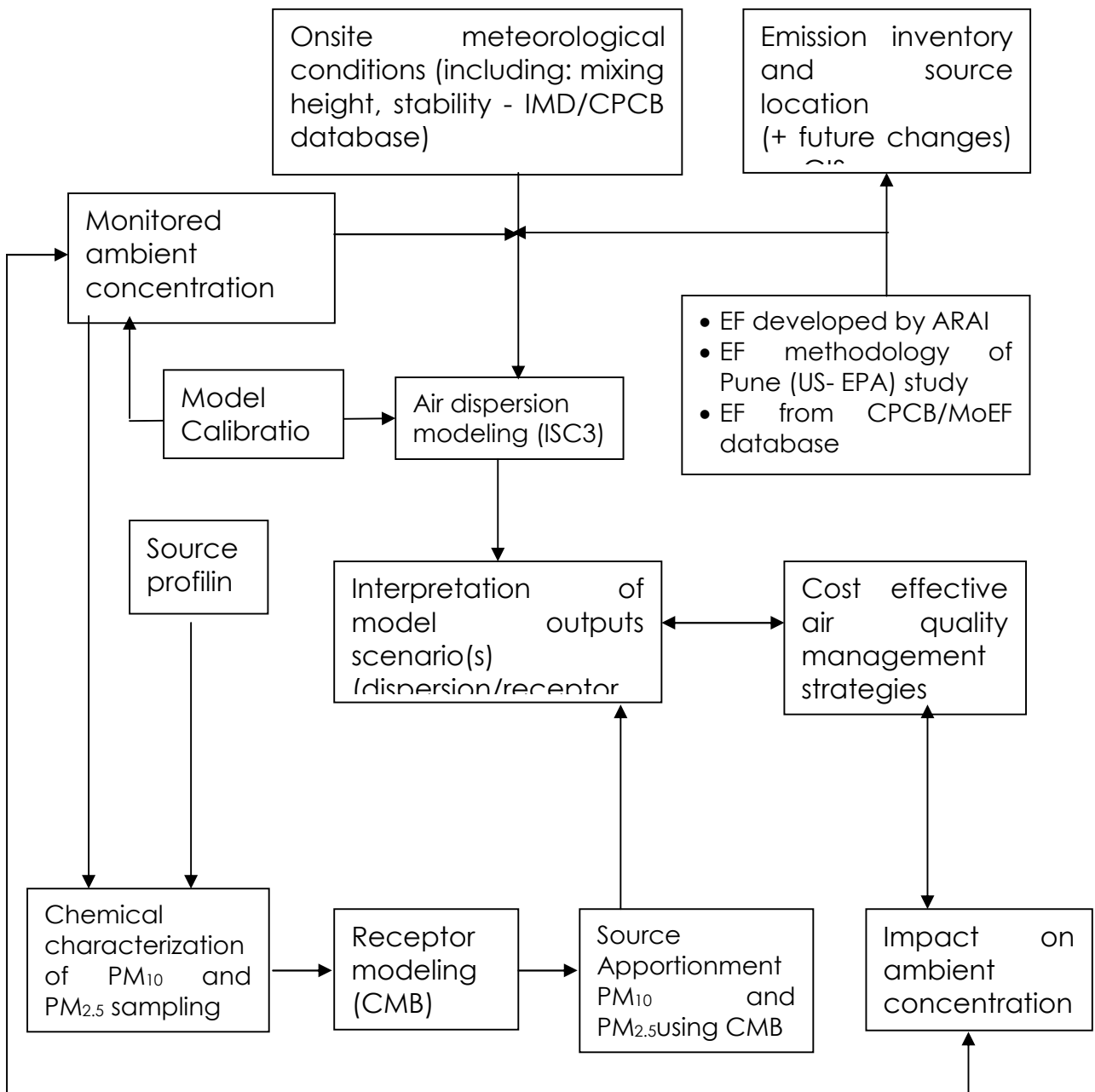


Fig. 1 (b): Proposed Study Framework

5.0 Evolving a Comprehensive Study Plan

This study was initially designed to address primarily the issue of contributions of auto exhaust air pollutants and then the scope was expanded to all major polluting sources because the extent of contribution and its significance vary with the land use pattern of the city.

5.1 Ambient Air Quality Monitoring

The first step in designing or implementing any monitoring programme is to define its overall objectives. Setting diffuse, overlay restrictive or ambitious monitoring objectives will result in cost ineffective programme with poor air quality data. In such circumstances, it will not be possible to make optimal use of the available resources. So, it is vital that the monitoring network should focus specifically on the given objectives.

- To collect representative ambient pollutant samples at defined receptors.
- To calibrate the dispersion modeling predictions with observed ambient air concentration.
- To establish the conclusion through ambient air quality, as “hot spots” & responsible sources e.g. concentrations on roadside, Kerbside locations to link it with nearest road traffic activity, particularly with respect to PM₁₀ and PM_{2.5} (limited exercise).
- To establish diurnal variation and subsequent impact on receptor based on changes in activity during a day.
- To establish impacts of meteorological variations during different seasons on the ambient concentrations of indicator pollutant in different micro-meteorological locations of the city.

5.1.1 Ambient Air Monitoring Components

- The parameters of ambient monitoring should be specific to the requirements of objectives and should also be useful for the model application as well as for establishing cause–effect relationship between emission rates of different sources of pollutants monitored and observed ambient concentration of respective pollutant serving as indicator(s) of the source.
- The ambient air quality network should normally include 1 background and 2 residential locations. Other sampling locations may be selected to represent Kerbside, Busy Industrial zone, Traffic activity zone. The criteria for selection of these stations are detailed in Chapter II.

- The total number of monitoring stations may vary from 7 to 10 depending upon the activity level of a specific city.
- The parameters of monitoring, proposed are the following: SPM, PM₁₀, RSPM, PM_{2.5} (limited), SO₂, NO_x, Benzene, CO, Aldehyde, NMHC and total HC. For PM₁₀ monitoring, speciation samplers are proposed (with PM₁₀ cut-off head). The details of sampler and other monitoring background are provided in Chapter II. There should be more focus on the proper analysis (methods as well as instruments) of the selected indicator/tracer/signature components to be analyzed in ambient dust samples as well as in source dust through source profiling. The matrix proposed for analysis as well as sampler configuration are also attached.
- The suitable methodologies proposed to be adopted for sampling and analysis of various pollutants in the study are described in Table 1(a).
- To cope up with the limitation in infrastructure, it is planned to perform simultaneous sampling at (3-4) locations at a time for one month (say Dec for winter months) and then the equipment can be shifted to next (3-4) sites for the next month monitoring (say January for same winter period). One background and one residential area should always be included in both monitoring phases. This bifurcation will not affect the basic requirements of the study. In case of one background station selected in a city for the study, sampling period (20/30 days) may be split to represent background for both the batches to have a more realistic comparison.
- To ensure proper representation of the activities of the surrounding area for a given monitoring location, a combined team of experts along with the agency carrying out the study would visit and finalize the locations.
- The project-executing agencies should ensure QA/QC aspects. There is requirement for analysis of different blanks; during calculation as well as data analysis and also provision for a third party audit may be explored.
- Continuous power supply (24 hours) is to be ensured at the chosen sites. Diesel Generator sets should not be used for generating power. This is to be ensured that the power being used is reliable and data collection goes unhindered. Any sample collected for less than 80% of time duration (8hrs) should be flagged separately.

5.1.2 Meteorological Monitoring

The meteorological factors affect a range of atmospheric characteristics and dispersal of pollutants. These factors and their frequent changes control the gravity and intensity of air pollution in an area and cause seasonal variations in horizontal as well as vertical distribution and fate of respective pollutants. The essential meteorological parameters are wind speed, wind direction,

ambient air temperature, relative humidity, rainfall, atmospheric pressure and mixing height.

Meteorological monitoring for wind speed & direction, temperature, relative humidity, etc. should be carried out simultaneously on each station at same height of ambient monitoring to ensure proper representation of the activities of the surrounding area for a given monitoring location. Additional meteorological data for the study period will also be collected from Indian Meteorological Department (IMD).

5.1.3 Collection of Secondary Data on Existing Air Quality

It involves collection of data/documents relating to study area, major traffic networks, topographical and climatological features etc. from agencies like Delhi Development Authority (DDA), Directorate of Industries, different monitoring agencies, Publications, Central/State Pollution Control Boards, Indian Meteorology Department (IMD), etc.

5.1.4 Quality Assurance and Quality Control (QA/QC)

Quality assurance and Quality control (QA/QC) is an essential part of any monitoring system, it is a programme of activities that ensures that measurements meet defined and appropriate standards of quality, with a stated level of confidence. The outline of QA/QC for different activities involved in this study is given in respective chapters. The executing agencies may adopt any acceptable scientific/statistical techniques to prepare QA/QC protocol and strictly follow it to generate acceptable and validated data.

Table 1 (a): Ambient Air Pollutants and their Standard Measurement Procedure

Particulars	Pollutants						
	SPM	RPM	So ₂	No _x	PM _{2.5}	CO	VOC
Equipment	High Volume Sampler	Multi-speciation sampler/ Respirable dust sampler (For Delhi only)	Impingers attached to HVS	Impingers attached to HVS	PM _{2.5} Analyzer	Automatic Analyzer	VOC Sampler
Measuring Principle	Aerodynamic Sampling followed by Gravimetric measurement	Gravimetric	Colorimetry	Colorimetry	Sampling by Impaction and measurement by Gravimetry	NDIR	GC-FID
Flow rate	0.8-1.2m ³ /min	0.8-1.2 m ³ /min	0.5 lpm	0.5 lpm	1 m ³ /hr	1 lpm	0.5 lpm
Sampling period	8/24 hrly	8/24 hrly	8/24 hrly	8/24 hrly	8/24 hrly	4/24 hrly	One in a month
Sampling frequency	One month Continuous (3 seasons)	One month Continuous (3 seasons)	One month Continuous (3 seasons)	One month Continuous (3 seasons)	One month Continuous (3 seasons)	One month Continuous (3 seasons)	One week Continuous
Analytical Method	Gravimetric	Gravimetric	Improved West & Gaeke	Jacobs & Hochheiser modified	Gravimetric	NDR	GC-FID
Min. Detection limit	1 µg/m ³	1 µg/m ³	0.04 µg/m ³	0.03 µg/m ³	0.5 µg/m ³	0.04 ppm	1 µg/m ³
Absorption wave length(λ max)	-	-	560nm	550nm	-		
Minimum reportable value	10 µg/m ³	10 µg/m ³	3 µg/m ³	9 µg/m ³	5 µg/m ³	4.67 µg/m ³	As specified in method

5.2 Emission Inventory

Emission inventory is a major tool for identifying the sources of pollution and quantitative expression of pollution load in a defined area. The study would involve preparation of detailed emission inventory with estimation of emissions from various activities such as vehicular, industrial, residential, commercial, etc. to be made using primary as well as secondary data collection through questionnaire survey, wherever necessary. Impact of pollution from these sources depends on many factors, viz. vicinity of emission sources, the concentration of pollutants, temporal and spatial variations in emission pattern and receptor types, etc. Extensive survey and primary data generation in zone of influence (2X2 Km²) around each monitoring location would be a major component in the study.

5.2.1 Scope of Work

- Identify sources of emissions under broad categories of point, area and line sources to inventorise various pollutants.
- Collection of secondary data on industrial, domestic, commercial, vehicular emissions, etc. through appropriate/authorized agencies.
- Collection of primary data on different types of vehicles (population count) in use/on road, average distance traveled by each type of vehicles, their inspection & maintenance schedule/practice adopted. This data bank would help to estimate pollution load by traffic through application of proper emission factor being generated by ARAI under this project.
- Primary data collection on various industrial, commercial and domestic sources through questionnaire, wherever necessary particularly in zone of influence (2X2 Km²). The plotting of potential pollution sources on map projecting 2X2 Km² area surrounding the monitoring site.
- Analysis of primary as well as secondary data using appropriate techniques as being used by internationally reputed agencies viz. USEPA.
- Estimation of emission loads of air pollutants from various identified sources with due consideration to:
 - Contribution of emission load from different categories of vehicles.
 - Contribution of domestic, commercial, industrial and other sources.
 - Projection of emission load under different scenarios.

There should be an in-built QA/QC plan before these data are incorporated in the study.

In this study, one needs to identify the type of pollution sources relevant to each sampling location (within the impact zone) and then these sources should be marked on map using GIS. One important factor requiring expert judgment is the extent of zone of influence around a given sampling site. The emissions from sources lying within the decided influence zone should primary control the ambient pollution variations at that site. The zone of influence decided for low height ambient air monitoring (3-4 Mts.) is 1km but not exceeding 2 kms radius around each sampling site. Monitoring of relevant meteorological attributes at the same height is essential.

For determining activity levels of different sources (namely: point, line and area source) the following approaches were thought of as minimum requirement.

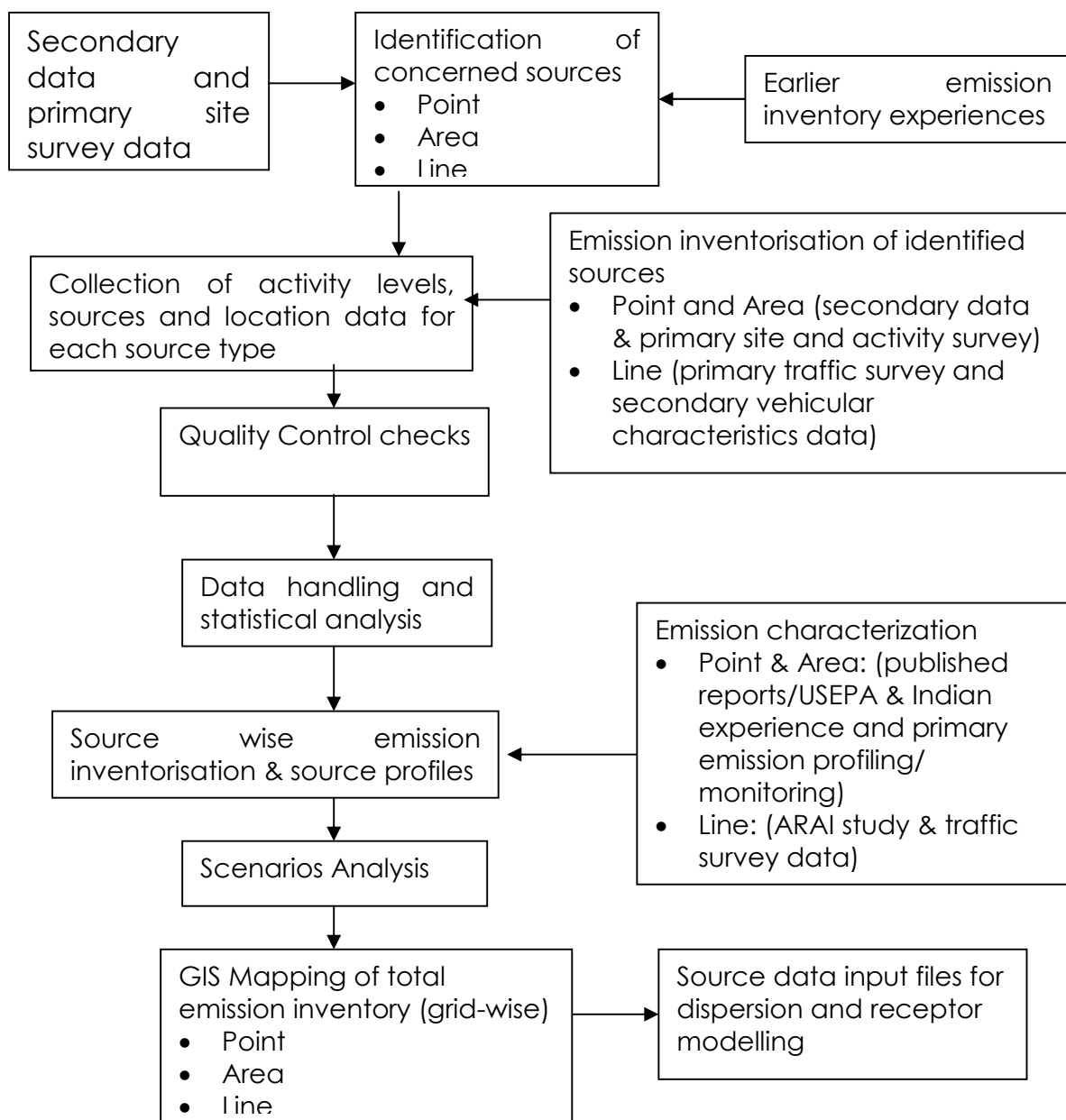


Fig. 1 (c): Proposed Framework on Emission Inventory

5.2.2 Inventory of Point Sources

For obtaining comprehensive list of different types of potential air polluting industries in the region, State Government, State pollution control boards/committees, concerned government institutions, Office of commissioner for Industries, District Industrial Center (DIC) and other organizations in the concerned city should be approached. Specific information on production capacities, raw materials used, manufacturing process, fuel consumption, etc. should be collected from the available secondary records followed by eventual collection of primary data through surveys and questionnaires for the cross checking & validation of the secondary data.

5.2.3 Inventory of Area Sources

In order to assess the fuel consumption in domestic sector, necessary information should be collected from some representative localities covering all socio-economic groups with a view to assess variation between urban and sub urban areas. The information proposed to be collected includes number of houses and family members in each house, type, source, quantity and cost of fuel used. Data on gross fuel consumption will also be collected from fuel supply agencies. Based on the above information, daily per capita consumption of different fuels will be estimated. The questionnaire should include seasonal implication of fuel use particularly wood and tyre burning in winter.

Information on refuse burning, commercial hotels and restaurants, bakeries, crematoria and other commercial activities, etc. should be obtained from the municipal or other concerned departments of the city. The emissions will then be estimated using relevant emission factor for each type of fuel. Emission factors from different Indian agencies will be used for various area sources.

5.2.4 Inventory of Line Sources

Various transport related project reports should be examined to determine the profile of vehicular traffic emissions within the city. The quantity of air pollutants emitted by the different categories of vehicles is directly proportional to the average distance traveled by each type of vehicles, number of vehicles plying on the road, quantity & type of fuel being used, age and technology of vehicle in use, etc. However, several other factors like geographical locations, unplanned developed business areas, inadequate and poorly maintained roads as well as adopted practices of inspection & maintenance of vehicles, unplanned traffic flow, meteorological conditions and non availability of effective emission control technology would also affect emissions. In order to arrive at the actual vehicular emission scenarios, vehicle counts on major traffic corridors within the city would be undertaken. The vehicles will be categorized under various groups viz. heavy-duty

vehicles, light-duty vehicles, passenger cars, taxis, two/three wheelers, etc. Hourly variation in the vehicles count will be recorded (manually/ videotapes) during periods of day/night. For line sources, the traffic volume and its characteristics (including vehicle speed) at the major traffic lanes are to be conducted. Whereas, the emissions from a road network of side lanes within the defined impact zone for a sampling site can be considered as an area source and the method proposed is based on the field surveys/personnel interviews with the local residents on attributes like number of vehicles, number of trips per day, trip length, local distance traveled, speed of the vehicles, etc. In order to know the configuration of different types of vehicles among each vehicle class, the interview/field surveys in parking lots or at petrol stations should be carried out for the statistically valid sample size.

Emission load should be estimated using emission factors, being developed by ARAI for different possible scenarios. The task of estimating emission load will be carried out with due consideration to various parameters viz. type/ technologies of vehicle, age groups, fuel quality, with/without tailpipe treatment, etc.

The emission inventory is proposed to be used for estimating projected emission load. The projection of emission inventory using data generated as the baseline would be carried out for the next 5 years based on vehicle technology, fuel quality change and other activities having impact on air quality.

5.2.5 Data Analysis and Emission Load Estimation

- The secondary data collected to be analyzed with due consideration to data limitations/constraints for preparation of EI using appropriate state of art methodologies/equivalent techniques as used by reputed organizations like USEPA.
- For area sources, there are options to use certain database generated in few US-EPA studies (for India, Bangladesh and other countries of the region) or the factors developed by US-EPA, EU, WHO after normalization for Indian conditions.
- For line sources Emission Factors for various types of vehicles in designed matrix shall be provided by ARAI, Pune, which will be utilized to estimate vehicular emission load.
- Projections of various air pollutant emissions for different vehicle categories for next five years will be extrapolated.
- Emission load for present as well as for future shall be estimated using the state of art models/ appropriate techniques like IPICEA, IVE model, basic statistical tools or any other equivalent techniques.

- For emission load/emission rate calculations, there should be specific cross checks built in for quantifying the activity levels. For example, the production level in an industry is proportional to total fuel use or power bills or water use/wastewater discharge, etc. that are often related to production process as well as quantity.

5.3 Source Dispersion & Receptor Modeling

Dispersion modeling is proposed to be used for all the major sources (Point, Line and Area). This exercise is important because it will provide information on impacts of different control options/strategies on exposure concentrations. Air quality management using receptor model predictions, which are based on roll back models, are qualitative in nature. To get comparable and useful results, the following factors should be incorporated:

- A detailed and relatively reliable emission inventory is required by adopting common methodology for all the major sources within 2x2 km. Impact of distant large point sources shall be difficult to address in this study. So, correct location mapping (preferably on GIS) is essential for sampling locations being focused for dispersion modeling predictions.
- The location of different sources can be marked on base map of the zone of influence using GPS so that all sources considered for "dispersion" modeling are marked on GIS scale.
- The next important factor is local meteorological data inputs. For example, this study also focuses on Kerbside concentrations for which micrometeorology becomes very important. So, certain portable wind speed/direction gadgets will be very useful. For mixing height and stability pattern, the secondary data sources and/or calculation procedure should be defined and used for all the cities.
- The separate correction factors may be determined for various sampling locations and then, accordingly, ambient concentration scenarios may be predicted based on different management options. Common correction factor for all the locations may not be proper because the sampling locations represent the ground exposure conditions. The locations are not at height (about 10 mts.) as per NAMP.
- For the Model calibration exercise, the correlation curves adopting PM₁₀, (which is the pollutant of concern) for the measured versus observed concentration for different seasons and pollution loads should be drawn for regression analysis.
- The correlation between the diurnal variations of source activity and ambient air concentration (preferably for the pollutants being monitored

on the real time basis or otherwise for 8 hrs-averaged concentrations) should be established.

- Iso-concentration plots are required to be generated for the entire city for projecting impacts of large industrial sources in different seasons. This will help in determining the contributions at sampling locations.
- In context with dispersion modeling a comparison was made between Air-Mode model and ISCST-3 model. It was decided to retain ISCST-3 because of less data requirement, better hands on experience and required adequacy.

5.4 Source Apportionment Analysis

The contribution of pollutants by various sources and their respective share with respect to ambient air quality in any given area can be assessed in two ways. One is through the calculation of emissions from various activities or source categories and the other is the estimation of percent fraction contributed by different source categories to any receptor.

Emission of pollutants from the sources and effects i.e. pollutant levels in ambient air can be related using modeling techniques. The two widely used modeling techniques are dispersion modeling and receptor modeling.

Dispersion models use detailed emission inventory of air pollution sources and local wind fields to estimate the impact of those sources on pollutant concentration to any desired location in the impact zone. Dispersion models are prospective in the sense that they are extremely useful for estimating projected impacts of new air pollution sources.

Receptor models use monitored pollutant concentration and some information (signature) about chemical composition of local air pollution sources to estimate the relative influence of these sources on pollutant concentrations at any single monitoring location. Receptor models are retrospective in the sense that they can only assess the impact of air pollution source categories on pollutant concentrations that have already been monitored.

5.5 Application of the Receptor Modeling for Apportionment of Sources in the Present Study

It is proposed to use CMB model in this study for source apportionment.

Source Apportionment study will be carried out in all seasons (except rainy season, which will not be representative of the actual situation on contribution of different sources) for PM₁₀ only.

The project envisages the source apportionment of not only vehicular emissions but also, contribution from different area and point sources including trans-boundary pollutants. However, CMB8 model proposed has certain in-built limitations as under:

Impact forecast for future, as anticipated in the proposed CMB based prediction, is based on roll back models. But, these are highly qualitative. CMB is intended to complement rather than replace other modeling methods. So, the use of dispersion modeling is warranted.

The CMB modeling procedure requires: (i) identification of the contributing sources types; (ii) selection of chemical species or other properties to be included in the calculation; (iii) estimation of the fraction of each chemical species, which is contained in each source type (Source Profile); (iv) estimation of the uncertainty in both ambient concentrations and source profile; and (v) solution of chemical mass balance equations.

The most widely use of CMB over the past decade has been to justify emissions reduction measures in PM₁₀ non-attainment areas.

The most important assumptions for CMB model relevant to this project are:

1. Chemical species do not react with each other (i.e. they add linearly).
2. All the sources with a potential to contribute to the receptor have been identified and their emission characterized.
3. Measurement uncertainties are random, uncorrelated and normally distributed.

5.6 Techno-Economic Analysis of Mitigation Plans & Project Deliverables

On having completed the intended data collection, validation, interpretation of assimilated information, a detailed road map will be drawn considering all possible measures for air quality improvement. These measures will be classified into short and long term with due priority to low cost measures that gives maximum benefits.

The cost- benefit analysis based on health impact would be beyond the scope of the present study. Therefore, it was agreed to consider ambient air quality standards (which are health based) as the upper thresholds.

For comprehensive Health Impact Assessment and Benefits, a separate study, if required, can be initiated.

For ranking of the various mitigation/intervention options on the different sources namely industrial, vehicular, fugitive, etc. the cost effective analysis shall be adequate.

6.0 Project Management

Project management involves participation of various stakeholders including Ministry of Environment & Forests, Central Pollution Control Board, Oil companies represented through Indian Oil Corporation (R&D), Society of Indian Automobiles' Manufactures (SIAM), India Meteorology Department, Research Institutes, IITs, etc. For smooth implementation of the project, a Steering Committee for overall supervision and a Technical Committee to look into and guide on technical aspects of the project have been set up.

6.1 Steering Committee

Ministry of Environment & Forests has constituted a national level Steering Committee for guidance and successful completion of this project. This would be the apex body that shall not only supervise the project but also interact with other ministries/organizations for evolving a national framework to ensure clean air in critically polluted Indian cities. Composition of Steering Committee is as follows:

- | | |
|---|--------------------|
| 1. Secretary, MoEF | - Chairman |
| 2. Additional Secretary (PA Division), MoEF | - Member |
| 3. Joint Secretary (PA), MoEF | - Member |
| 4. Chairman, CPCB | - Member |
| 5. Representative of Oil Companies (Director Level) | - Member |
| 6. Representative of SIAM | - Member |
| 7. Representative of MoP&NG (JS Level) | - Member |
| 8. Representative of MoRT&HW (JS Level) | - Member |
| 9. Representative of project executing Agencies | - Member |
| 10. Member Secretary, CPCB | - Member |
| 11. Director (PA), MoEF | - Member Secretary |

6.1.1 Terms of Reference

1. The Committee shall review and monitor the progress of the programme and set policy/guidelines on all relevant issues like copyrights, publication of the results of the studies, communication with general public/NGO etc.
2. The Committee will be the final authority for decisions concerning the award of different contracts and their financial implications.
3. The Committee shall guide through the study and periodically assess the achievements of predefined milestones.
4. The Committee shall set policy framework on city specific action plan and its implementation mechanism.

5. The Committee may include "Special invitees" depending on the work requirement as to capture the available " intellectual capital" from the pool of eminent environmentalists, healthcare bodies/ Institutions and NGO's in the country.
6. The Committee shall evolve the funding mechanism for the programme and shall monitor and ensure timely release of the funds to project executing agencies.
7. The committee shall take the necessary technical inputs for the project from the Technical Committee constituted by Central Pollution Control Board. The Committee may also seek technical inputs from other experts, if required.

6.2 Technical Committee

In order to provide technical guidance and support to the studies, with the approval of MoEF, a Technical Committee comprising following members is constituted:

- | | |
|---|--------------------|
| 1. Chairman, CPCB | - Chairman |
| 2. Member Secretary, CPCB | - Member |
| 3. Representative of Oil Companies | - Member |
| 4. Representative of SIAM | - Member |
| 5. Representatives of project executing agencies | - Member |
| 6. Dr. Nalini Bhat, Director (CP), MoEF | - Member |
| 7. Prof. H.B. Mathur, Retd. Professor, IIT, Delhi | - Member |
| 8. Prof. Mukesh Sharma, IIT, Kanpur | - Member |
| 9. Dr. B. Mukhopadhyay, Director, IMD | - Member |
| 10. Dr. Rakesh Kumar, Head, NEERI - ZO, Mumbai | - Member |
| 11. Dr. S. A. Dutta, Tata Motors Ltd., Pune | - Member |
| 12. Representative of concerned SPCBs | - Member |
| 13. Dr. Prashant Gargava, EE, CPCB | - Member Secretary |

6.2.1 Terms of Reference

1. Technical Committee shall identify the project-executing agency and recommend to the Steering Committee for approval.
2. Technical Committee shall approve the TORs including approach, methodology, and scope of work and work plan for the study that would be submitted by the project execution and funding agencies. It may also seek comments from national/ international experts/ organizations on the TORs as well as findings before forwarding the same to the Steering Committee for approval.

3. Technical Committee shall review the progress of work from time to time and provide necessary technical guidance to the project execution agency.
4. Technical Committee shall scrutinize and accord necessary approvals to all reports & technical matters as submitted by the project execution agency and put up to the Steering Committee for final approval.
5. Whenever required, Technical Committee may invite members from other expert organizations, individual experts, local bodies, etc.

6.3 Funding Mechanism

Funds for the project shall be administered by the funding agencies and release of funds to the project-executing agency(s) shall be regulated through "Memorandum of Collaboration" between project executing & funding agencies.

All management issues including financial disbursement of expenses towards organizing meetings of steering & Technical Committees including TA/DA expenses & honoraria to the ex-officio member's etc., shall also be managed by the funding agency.

Regarding project administration & release of payments, following sub-committee is constituted:

- | | | |
|----|---|-------------------|
| 1. | Shri V. K. Minocha, Director, CP Division, MoEF | - Chairman |
| 2. | Dr. B. Sengupta, Member Secretary, CPCB | - Member |
| 3. | Dr. R. K. Malhotra, GM, IOC (R & D), Faridabad | - Member |
| 4. | Shri M. Arumugam, FAO, CPCB | - Member |
| 5. | Dr. Prashant Gargava, EE, CPCB | - Member Convener |

Above sub-committee will examine the deliverables/reports submitted by different project executing agencies and recommend release of payments as per terms specified in the Memoranda of Collaborations.

CHAPTER – II

Guidelines for Ambient Air Monitoring Site Selection and Selection of Sampler

1.0 Introduction

The National Ambient Monitoring Programme (NAMP) intends to determine compliance to ambient air quality standards and does not provide answers on sources, their contributions, pollution loads and development of control strategies. Therefore, source apportionment studies based on “Receptor Modeling” is adopted in many countries to get information on causes of elevated PM concentration. For this purpose, chemical characterization of PM along with the application of source dispersion models is a prerequisite to attribute ambient concentrations to their sources for the development of emissions reduction strategies.

Particulate sampling on filters are the most practical method currently available to characterize the sizes and chemical constituents of PM₁₀ and their sub-fractions. Ambient sampling systems consist a combination of monitoring hardware, filter media, laboratory methods and operating procedures, which are specially tailored to suit different monitoring objectives. No single sampling system can meet all needs and it is often necessary to adopt existing sampling components to specific situations being studied.

Chemical analysis of filter deposits cannot be separated from the methods used to collect the sample. Sampling for chemical analysis requires stringent attention to choice of filter media, sample handling, and sample storage and to the sampler used to obtain the filter deposits. When chemical analysis is intended for source apportionment modeling, various monitoring systems are possible namely FRMs, FEMs, sequential sampling systems, particle and gas sampling system with denuders, dichotomous samplers, or even combination of several samplers. So, proper sampling as well as filter media selection is important.

2.0 Ambient Air Monitoring Design

Designing monitoring plan and its implementation involve the following six steps:

- (i) First step is the over all planning and network designing of complete ambient monitoring program through Field Planning.
- (ii) Second step is to determine the specific monitoring objectives. Compliance PM₁₀/RSPM monitoring does not provide samples amenable

to all chemical analysis because of the limitation of single-filter media. Source apportionment and control strategy evaluation require chemical speciation, so sampling strategy shall address these concerns.

- (iii) Third step is to determine matrix of pollutants that need to be measured and at what level they are expected. In source apportionment study, the objective is to prepare chemical mass balance between the pollution potential of surrounding sources and their suspected contribution to PM₁₀/PM_{2.5} at the receptor end. The potential contributors may first be determined from initial/broad field survey and emissions inventory in the study area. Particle size and their signature chemical constituents help in identifying/segregating one source from another. Particle size fractions, chemical analysis, sampling frequencies, and sample durations need to address it. The desired types of analysis and size fractions affect the number of sampling ports and different filter media needed.
- (iv) Fourth step is to calculate the amount of deposit on each filter for each of the chemical species and compare it to typical detection limits for the types of analysis expected.
- (v) Fifth step is to apply, create, adapt, or purchase the sampling system, which provides the most cost-effective and reliable means of meeting the monitoring needs. Appendix identifies several sampler designs, which have been applied to PM studies.
- (vi) The final step is to create a plan including adequate SOP on sampling locations, analysis methods, filter-media, sampling systems, sampling frequencies and durations, nominal flow rates, methods and schedules for internal cleaning, calibration and performance tests, filter transport and handling procedures, database management system, data analysis methods, and record keeping protocols.

2.1 Field Survey & Planing

Before site/equipment selection, there is a need to prepare "Field Plan" (FP) and SOP as a first step for field studies. The Field Planning is the design for the field measurement program, specifies the details of field planning and will be the basis for preparing requests for proposal to field staff. The field planning represents the design for the field measurement program and provides the basis for preparing statements of work for potential measurement group, both contractors and in-house personnel. The field planning specifies the details of how the field measurements will be carried out. Key elements include:

- The experimental approach and technical objectives of the network design plan.

- Information requirement of new sampling site.
- Evaluation of measurement methods with respect to needed averaging time, detection limits, accuracy, precision, and cost-effectiveness. Continuously versus integrated samples? Off-site laboratory analysis?
- Specifications for accuracy, precision, validity and completeness of field measurements.
- Time and locations for each category of measurements.
- Quality assurance needs, including standard operating procedures, observable to be audited, auditing schedules, primary standards, transfer standards, dynamic blanks, replicate analysis, performance tests, and collocated sampling.
- Variable-naming conventions, units, and file-naming conventions for data to be submitted by investigator.
- Data validation tests to be performed by measurements contractors and to be verified by the data management contractor.
- Elements needed for data management that will facilitate the receipt, tracking, organization, and dissemination of data acquired during the study.
- Episode forecasting method that will be implemented and who and how to go/no to go decisions will be made and disseminated to project participants.
- Schedule of milestones and a criteria path diagram showing which operational tasks must be completed prior to undertaking other operational tasks and identify the groups responsible for each task.

Filed planning specifies the details of how the field study will be carried out. It identifies measurement locations, observable, monitoring methods, averaging times, and calibration methods, specifies data management and reporting conventions, and outline the activities needed to ensure data quality.

2.2 General Guidelines for Site Selection

The budget, minimum monitoring requirements, and its objective adequacy criteria is to be first established as mentioned above during monitoring network-planning stage of a monitoring campaign. Items that should be considered in sampler selection include: flow control and measurement systems, maintenance requirements, reliability, ease of operation, and

ancillary capabilities such as sequential sampling and data downloading and finally Calibration.

Most of the existing guidance on the subject is for design of monitoring network proposed to assess compliance with national ambient air quality objectives or standards. Siting guidelines refer to the environs surrounding a measurement location, and these differ depending on the zone representation intended for a specific monitoring site. Large nearby buildings and trees extending above the height of the monitor may present barriers or deposition surfaces. Certain trees may also be sources of PM in form of detritus, pollen, or insect parts. For example, these can be avoided by locating samplers by placing them >20 m from nearby trees, and twice the difference in elevation difference from nearby major buildings or other obstacles.

Another example is for background monitoring sites, which should be located >10 km from large population centers, and >100 m from roads and wood burning (burning is common, though often intermittent, in camping, forested, and agricultural areas).

But, here the objective of study is not compliance monitoring but to select "Hot Spots" representing maximum impact zone of different source categories. Compliance PM_{2.5/10} monitoring networks do not provide samples amenable to all chemical analyses because of the limitations of single-filter media. Source apportionment and control strategy evaluation require chemical speciation, so different criteria must be considered when these are to be addressed. As such, recommended guidelines are as follow:

2.2.1 Distance from Nearby Emitters

The monitor should be located within the zone of influence of sources it represents. It should be located within the designated zone of representation for the monitoring site. Neighborhood and urban zones of representation are needed for community-oriented compliance monitoring. These can generally be at least 1 km from very large, visibly identifiable point source areas occupied by major industries such as cement and steel production or ore processing. Regarding vehicular exhaust and road dust emissions from paved roads, earlier studies provide guidance on the recommended monitoring distances from paved roads with different levels of average daily traffic for neighborhood and urban-scale sites. A minimum distance of ~50 m from busy paved highways is usually outside the road's immediate zone of influence for a roof top monitor. These siting criteria were established for PM₁₀ compliance monitoring siting by U.S.EPA, (1987), and they have their validity in PM₁₀ network design. For larger than middle-scale monitoring requirements, no unpaved roads with significant traffic or residential wood-burning appliances should be located within 100m of the monitoring location.

A PM monitor siting evaluation is to ensure simultaneous assessment of local meteorology and also survey of, geology, land use, and PM sources within the defined impact zone. Any local or regional parameters that may affect the ability of the PM monitor data to meet the objectives of the monitoring programme should be considered. Micro inventories aid in determining the location of contributing sources and identifying the species that may be present at a location. Micro inventories include detailed surveys and locations of various area sources, storage piles, major highways, construction sites and industrial operations etc. Written descriptions and notes regarding each potential PM source are normally included with the in-situ surveys sheets.

2.2.2 Spatial Scale

The spatial scale for the monitoring programme depends on its objectives and estimated size of the area of impact of sources of interest. Area of impact of sources, in this study, is taken as 1-1.5 kms around each sampling location.

2.2.3 Temporal Scale

For Canadian and U.S. national survey networks and regional monitoring networks, the temporal scales of greatest interest are annual geometric mean concentration or 24-hour average concentration. Since meteorological conditions change with time, in order to collect representative samples and for considering temporal scale impacts at any siting location, these meteorological changes are taken into account during location siting. The temporal scale selected in this program is 8 hrs to catch diurnal source variations as well as impact of diurnal changes in meteorological settings.

2.2.4 Obstructions and Interfering Sources

The airflow radius within 2 meters around the sampler should remain unobstructed. Distance from the sampler to obstacle such as buildings must be at least twice the height of the obstacle protruding above the sampler. Distance from trees must be greater than 20 meters. A distance of 5 meters upwind in the most common wind direction must be maintained from building exhausts and intakes. Spacing from roads varies with the height of monitor. Here, the objective of sampling is to cover different "Hot Spots" representing dominance of different sources.

2.2.5 Sampler Height

The sampler inlet is proposed to be kept at about 3mts above ground level so that emissions of low height local sources is captured but undue influence of larger size air borne local dust is avoided.

2.2.6 Collocated Samplers

If a collocated sampler is required, sufficient clearance for the additional sampler should be provided at the sample location. The spacing between sampler inlets must be ≥ 1 m for other $PM_{10}/PM_{2.5}$ samplers (sampler with a flow rate less than 16.67 L/min) and ≥ 2 m for a HVS sampler (sampler with a flow rate greater than 16.67 L/min).

2.2.7 Safety

An operator must be able to safely reach the sampler location regardless of weather conditions. The operator may often be carrying supplies to the sampling locations.

2.2.8 Electrical Requirements

A stable electrical supply must be provided for the primary sampler and any additional samplers to be located at the monitoring site. The sampler is required to operate at 240 volts alternating current (AC) and a frequency of 59-61 hertz (Hz)

2.2.9 Security

The security of the monitoring equipment and personnel should be considered in sampler placement. Samplers are often placed on roofs with restricted access. Fenced in sampler locations are also utilized but the fence should be a non-obstructing variety such a chain-link and the sampler inlet must extend above the top of the fence.

3.0 CPCB Guidelines for Ambient Monitoring

Another set of guidelines (general) for site selection, summarized as under, is prepared by CPCB for NAM. These are typical general requirements, which could be observed while selecting a site for compliance.

3.1 Physical Requirements of Site

- A large, flat space, elevated at least 2 to 3m is needed to place instruments.
- The space available for samplers should be at least 5 m distant and upwind (most common wind direction) from building exhausts and intakes and at least 2 m from walls, parapets that might influence airflow.
- Buildings having large emitters, such as coal-, waste-, or oil-burning boilers, furnaces or incinerators, should be avoided.

- Access to the sampling platform should be controlled by fencing or elevation above ground level.
- Sampler inlets should be sufficiently distant (>10 m) from public access to preclude purposeful contamination from reaching them.
- Access should be controlled by a locked door, gate, or ladder with documentation of site visitations and the purposes of those visits.
- Power should be sufficient for the samplers to be operated on a long-term basis. Wherever possible, a separate circuit breaker should be provided for each instrument to prevent an electrical malfunction in one monitor from shutting off power to the other monitors at the site.
- Environments surrounding monitoring instruments should be maintained within the manufacturer's specifications for proper instrument function.
- Most FRM filter-based samplers are designed to operate under a wide range of environmental conditions and can be located outdoors in most types of weather. Several continuous monitoring methods may require environmental shelters with temperature and humidity controls to protect their electronic sensing and data acquisition mechanisms.

3.2 General Requirements for Sitting Monitoring Station

- The monitor should be outside the zone of influence of sources located within the designated zone of representation for the monitoring site.
- Height of the inlet must be 3 – 10 m above the ground level.
- Large nearby buildings and trees extending above the height of the monitor may present barriers or deposition surfaces for PM. Distance of the sampler to any air flow obstacle i.e. buildings, must be more than two times the height of the obstacle above the sampler.
- There should be unrestricted airflow in three of four quadrants.
- The instrument must be located in such a place where free flow of air is available. The instrument should not be located in a confined place, corner or a balcony.
- There should be no nearby furnace or incinerator fumes.
- Certain trees may also be sources of PM in the form of detritus, pollen, or insect parts. These can be avoided by locating samplers by placing them >20 m from nearby trees.

- Sampling in the vicinity of unpaved roads and streets results in entrainment of dust into the samplers from the movement of vehicles. Samplers are therefore to be kept at a distance of 200m from unpaved roads.
- The site should be away from absorbing surfaces such as absorbing building material. The clearance to be allowed will depend on the absorbing properties of the material for the pollutant in question, but it will normally be at least 1m.

3.3 Specific Requirements for Various Area Classes

Residential Area: The area selected for residential area may meet following criteria:

- The site should be away from major pollution sources. The distance depends upon the source, its height and its emissions. The station should be at least 25m away from domestic emission sources; with larger sources the distance should be greater.
- The area must predominantly consist of people residing with population density of more than 4000 inhabitants/km².
- There must not be any industrial activities in the area within 2 Kms. There must not be any commercial activities like trading centers or offices with typical sources as DG sets etc. in the area.
- The site must be away from major roads, highways and traffic zones. Station should be more than 100 m away from any street having a traffic volume in excess of 500 vehicles/day.
- These should generally be at least 1 km from very large, visibly identifiable source areas occupied by major industries such as cement and steel production or ore processing.

Traffic/Commercial Area: *Traffic/Commercial Areas may meet following criteria:*

- Monitoring site, representing traffic/commercial zone should not be very near with undue influence of traffic emissions. It should be near center of heavy commercial activities.
- The monitoring station must be located near traffic roads with at least 10,000 vehicles/day.
- The distance from the road may be as per following Table 2 (a):

Table 2 (a): Minimum Distance of the Sampler from Road
(Source: ETC, Canada, 1995)

Average Traffic (vehicles per day)	$\leq 10,000$	15,000	20,000	40,000	70,000	$\geq 110,000$
Minimum distance of sampler from road (meters)	≥ 10	20	30	50	100	≥ 250

Kerbside: Kerbside, by definition, will be the sites with sample inlets within 1m of the edge of a busy road and sampling heights are at 3m elevation from ground level. If for reasons, 1m of the road edge is not possible, declare the site as roadside location, which has the definition of being a site with sample inlets between 1m of the kerbside of a busy road and the back of the pavement. Typical will be within 5m of the kerbside and the sampling height remains at 3m elevation.

- Locate station in the central urban area in a congested street surrounded by building where many pedestrian walk.
- Average daily travel on the street should exceed 10,000 vehicles with average speed of less than 6.7 m/s.
- Monitoring probe is to be located 0.5-1m from the curb at a height of 3m.

Background Station: Background station may be selected using following criteria:

- Background monitoring station at times for urban network may even 100km away from a large size city. It should be located upwind at distance, so that there are no sources within 3-4 kms around that site.
- The monitoring station must be located in rural area with no nearby sources such as vehicles, industries, DG sets, etc.
- The monitoring station must be located away from domestic emission sources such as coal burning and other household emissions.

Industrial Area: Industrial monitoring locations may be chosen as per following criteria:

- The station must be located in a designated industrial area within the cluster of air polluting industries.
- The monitoring station must be located in the area where maximum ground level concentration is expected. The maximum ground level

concentrations may be determined, if possible, based on modeling exercises.

4.0 Aerosol Sampler Selection

The next requirement is proper equipment selection for the parameters required for ambient air particulate characterization. Besides typical monitoring systems for criteria pollutants, there is specific requirement for "Source Apportionment" related monitoring. The discussions here confine to these specific requirements.

4.1 Sampling Options

Widely used samplers for chemical characterization of particulate matter are as below:

Table 2 (b): Widely used Samplers for Chemical Characterization of Particulate Matter

Sampler Design	Brief Description of operating conditions
IMPROVE	Accommodates up to four channels, Cyclone based, Flow rate 22.7 LPM
Met One SASS	Five separate sample channels having independent flow controller (critical orifice), Flow rate 7L/Min
Anderson RAAS	Four channels configuration controlled with interchangeable critical orifice, Particle size cut is done by AIHL-design cyclone
URG MASS 400 / MASS 450	Consist two separate but identical samplers having four channels, Inlet particle separator is identical to FRM WINS and volumetric flow meets FRM specifications
Partisol 2300 Speciation Sampler	Four to 12 individual channels of desired size selection inlet, Provision of denuder attachment, Selectable flow rate, Flow rate 16.7 LPM

4.2 Sampler Types and Rationale

Chemical speciation samplers have been developed and manufactured by three different manufacturers (as per 40 CFR, Part 58, Appendix C). The three samplers are the Reference Ambient Air Sampler (RAAS) developed by Andersen, Mass Aerosol Speciation Sampler (MASS) developed by University Research Glassware (URG), Spiral Ambient Speciation Sampler (SASS) developed by MetOne and Partisol 2300 Speciation Sampler developed by R & P.

4.3 Descriptions of Sampler (Chemical Speciation Samplers)

Design of the three chemical speciation samplers for the National PM Network can be found in the EPA chemical speciation guidance document (EPA, 1998). Specific designs of the samplers for the inter-comparison are

given below. In general, each sampler draws air at a specified flow rate through a size selective inlet with a 50% collection efficiency (cut point) of 2.5 micrometers.

4.3.1 Reference Ambient Air Sampler (RAAS) developed by Andersen Instruments

A schematic flow diagram of the Andersen RAAS is shown in Fig. 2 (a). It consists a size selective inlet followed by two cyclone fractionators. These cyclones are used to remove particles greater than 2.5 micrometers. The flow is then split into four channels. The first channel (labeled 1 in Fig. 2 (a)) is used to estimate atmospheric concentrations of particulate organic and elemental carbon (OC/EC). After passing through the cyclone and manifold the PM is collected on a baked (to lower background OC) quartz-fiber filter. The flow rate in this channel is 7.3 LPM. In the second channel (labeled 2 in Fig. 2 (a)), particulate matter is collected on a Teflon filter for analysis of mass, and elements using XRF. The flow rate for channel 2 is 16.7 LPM. The third channel (labeled 3 in Fig. 2 (a)) also uses a Teflon filter, but this filter is extracted in water and the extract is analyzed for sulfate, nitrate, and ammonium ions by ion chromatography (IC). The last channel (labeled 4 in Fig. 2 (a)) is used to obtain a nearly unbiased estimate of fine particle nitrate by removing acidic gases (e.g., HNO_3) from the air stream using a MgO denuder and collecting aerosol nitrate on the reactive Nylasorb (Nylon) backup filter. The filter is extracted in IC eluent and analyzed by IC for nitrate. In all channels, critical orifices control the flow and the flow rates are monitored using calibrated Rota meters.

4.3.2 Spiral Ambient Speciation Sampler (SASS) developed by MetOne

The Met-One SASS has five channels as illustrated in Figure 2 (b). Each channel contains a spiral impactor designed to give a 50% cut-point at 2.5 micrometers with a slope similar to the FRM. The first channel (labeled 1 in Fig. 2 (b)) contains a Teflon filter that will be analyzed for mass and elements by XRF. The second channel (labeled 2 in Fig. 2 (b)) also uses a Teflon filter to collect PM. The filter is extracted in water and the extract is analyzed for sulfate, nitrate, and ammonium using IC. An MgO coated Al honeycomb denuder is placed in the third channel (labeled 3 in Fig. 2 (b)) behind the spiral impactor. This denuder is used to remove acidic gases (e.g., HNO_3) from the sampled air stream and is followed by a Nylon filter that will be analyzed for nitrate by IC. As in the RAAS sampler, the denuder/reactive filter pair is used to obtain a nearly unbiased estimate of aerosol nitrate. The fourth channel (labeled 4 in Fig. 2 (b)) contains two baked quartz-fiber filters located behind the spiral impactor. The first quartz-fiber filter will be analyzed for OC/EC by thermal-optical reflectance, while the second quartz-fiber filter will be archived. The fifth channel (labeled 5 in Fig. 2 (b)) will also include 2 baked quartz-fiber filters, however, a carbon black honeycomb denuder will precede them. This denuder is used to remove semi-volatile organic

compounds that may interfere with the OC measurement. The flow rate through each channel is nominally 6.7 LPM and is controlled by a critical orifice. The flow rate in this instrument is monitored using calibrated mass flow meters.

4.3.3 Mass Aerosol Speciation Sampler (MASS) developed by University Research Glassgow (URG)

The URG MASS sampler is shown in Figure 2 (c). This sampler consists two modules; each with a size selective inlet and a WINS impactor to obtain a $PM_{2.5}$ cut point. The first module is equipped with a Na_2CO_3 denuder before the WINS impactor but after the size selective inlet. This denuder is used to remove acidic gases much like the MgO denuders discussed above. The particles less than 2.5 micrometers are collected on a dual filter pack. The top filter is an inert Teflon filter that will be analyzed for $PM_{2.5}$ mass and elements by XRF. The backup filter is a nylon filter that efficiently collects any nitrate that may have vaporized during sampling. Nitrate ion will be quantified using IC after extraction from the Teflon and nylon filter. The sum of nitrate measured on the Teflon plus nylon filters provides a nearly bias free estimate of fine particle nitrate. The second module contains a single filter pack containing one baked quartz-fiber filter. OC/EC will be determined by thermal optical reflectance and IC will be utilized for the analysis of sulfate, nitrate, and ammonium ions. The flow rate through each module is nominally 16.7 LPM.

4.3.4 IMPROVE Sampler

A schematic diagram of the IMPROVE is given in Figure 2 (d). In general, the IMPROVE sampler consists several modules each of which is dedicated to collecting a series of related chemical components of the atmospheric aerosol. Each module consists a size selective inlet, a cyclone to provide $PM_{2.5}$ size cut point based on the specified flow rate, filter media for sample collection, a critical orifice that provides the proper flow rate for the desired size cutoff, and a vacuum pump to produce the flow. IMPROVE samplers consist up to four parallel modules, and a common controller. The first module (labeled 1 in Fig. 2 (d)) collects PM on a Teflon filter, which will be analyzed for $PM_{2.5}$ mass and elements by XRF. The second module (labeled 2 in Fig. 2 (d)) includes a Na_2CO_3 denuder before the $PM_{2.5}$ cyclone to remove acidic gases (e.g., HNO_3) followed by the cyclone and a nylon filter. This nylon filter is extracted in water and the extract is analyzed for sulfate, nitrate, and ammonium ion by IC. The third module (labeled 3 in Fig. 2 (d)) collects PM on a baked quartz-fiber filter that is analyzed for OC/EC using the thermal-optical method.

4.3.5 Federal Reference Method

The experimental design of the two FRM samplers schematically illustrated in Fig. 2 (e). Two FRM samplers will be used at each site to obtain chemical characterization of the collected aerosol in a manner similar to the other samplers. One FRM will use a Teflon filter to obtain $PM_{2.5}$ mass by gravimetric analysis. This same filter will be analyzed for elements by XRF. The second FRM will use a baked quartz-fiber filter that will be analyzed for OC/EC by thermal-optical reflectance and for sulfate, nitrate, and ammonium ions by IC.

4.3.6 Partisol Speciation Sampler of (R&P)

Above all, the best option is to collect the sample by Speciation sampler having at least 3 channels to accommodate three different (1 Teflon, 1 Quartz and 1 Nylon filter paper). It may be used with both PM_{10} and $PM_{2.5}$ heads. 4X3 independent channels may be operated simultaneously. This instrument also has an option to attach denuders for gaseous pollutant sampling. The variable flow selection is an additional advantage of this system. The schematic flow diagrams of speciation samplers are shown in following figures:

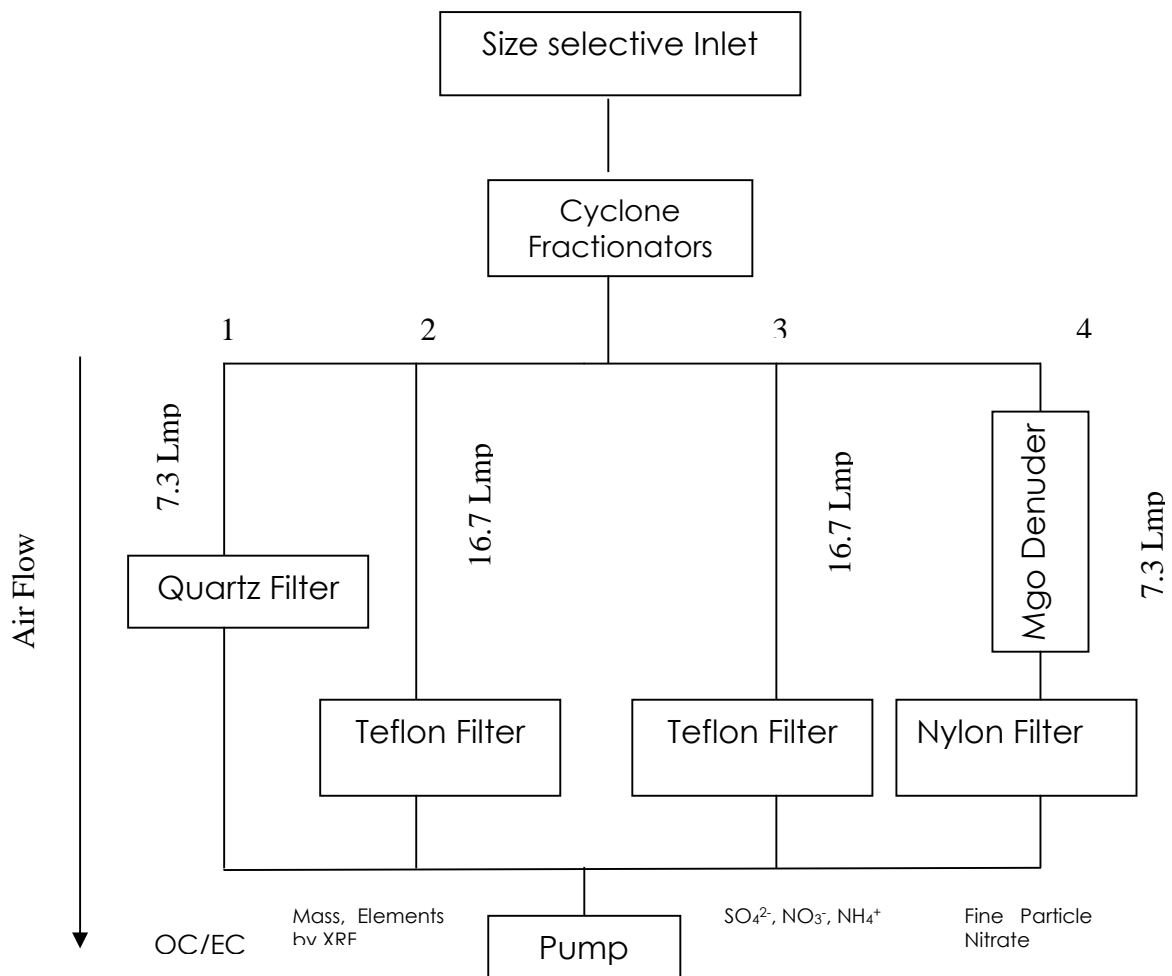


Fig. 2(a) Andersen RAAS Sampler

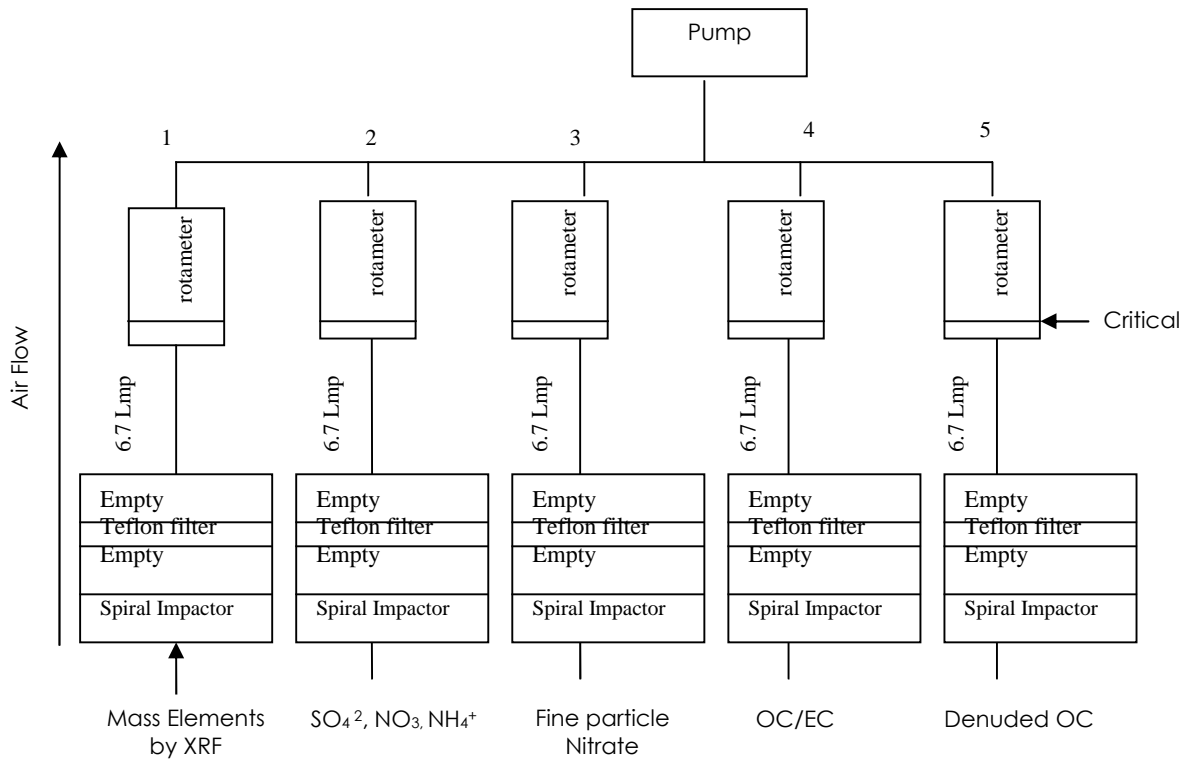


Fig. 2(b) Met One SASS Sampler

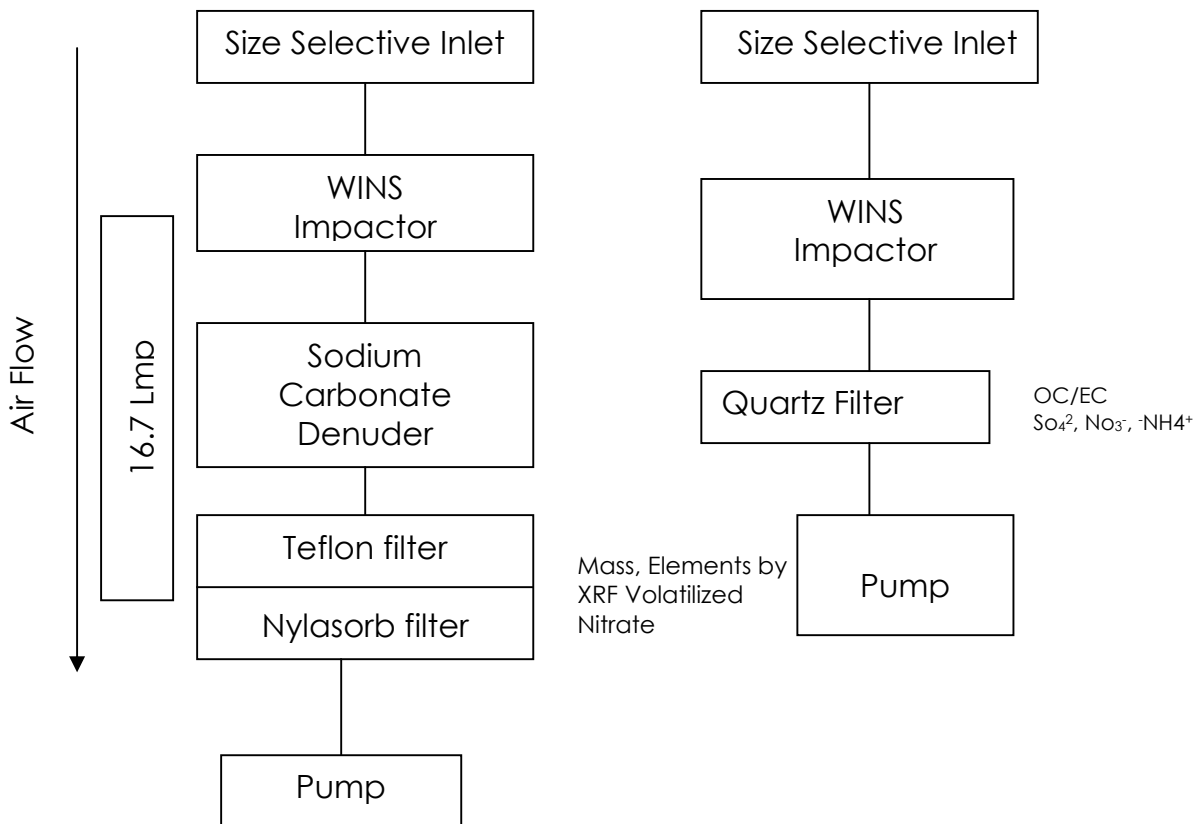


Fig.2 (C): The URG MASS Sampler

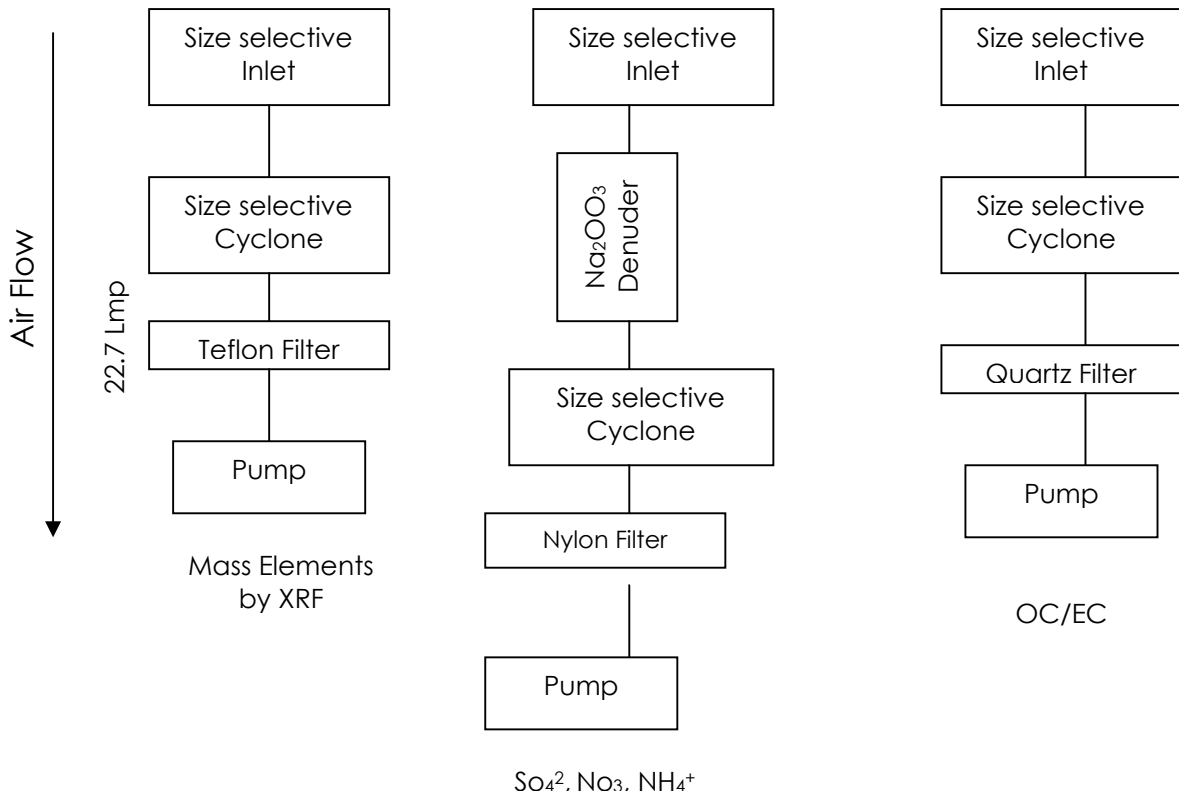


Fig. 2 (D1): The IMPROVE Sampler

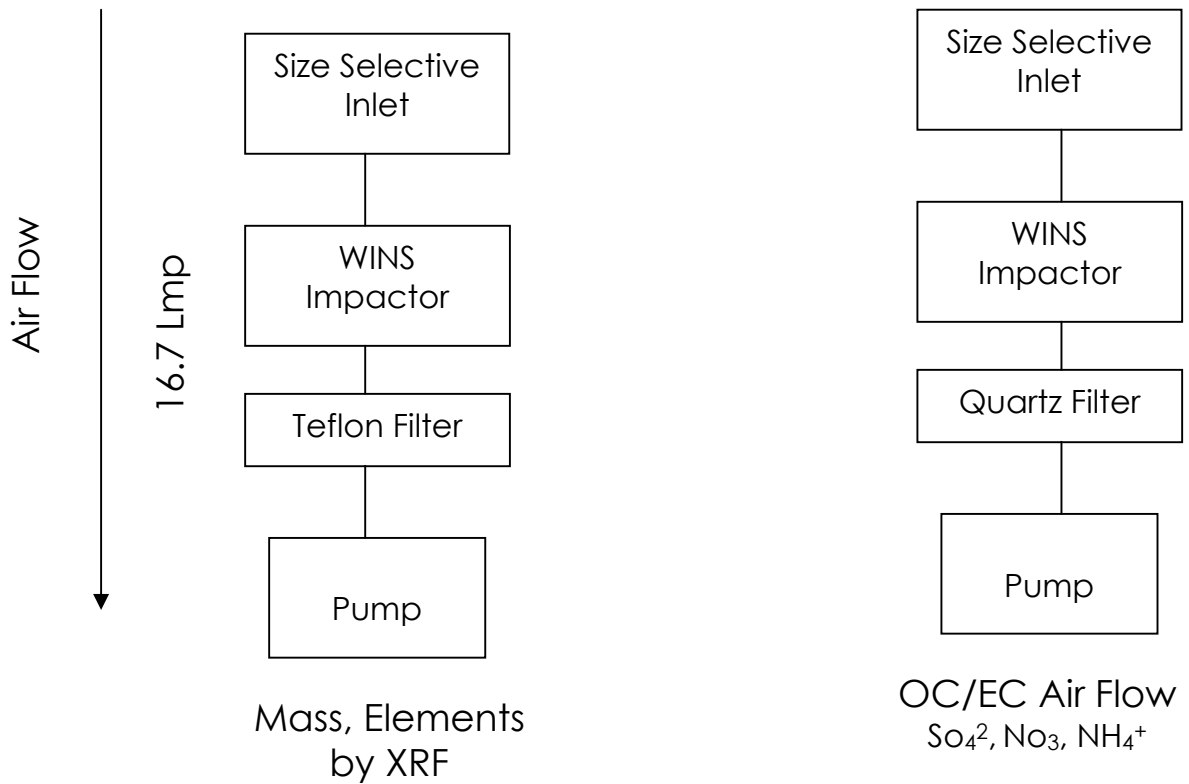


Fig. 2 (D2): The IMPROVE Sampler

The use of speciation sampler having at least 3 channels to accommodate three different (1 Teflon, 1 Quartz and 1 Nylon filter paper or 2 Teflon and 1 quartz filter paper) is essential for source apportionment studies.

5.0 Brochure for Sampling Equipment

In view of specific requirements of sampling system and monitoring methods, it may be pertinent to provide more information on availability of these systems. One example of such a equipment is given below. This particular sampler is best suitable for this type of monitoring to collect simultaneous samples in different filter matrix essentially required for characterization of particulate matter.

Partisol Model 2300 Sequential Speciation Sampler

Description: The Partisol Model 2300 Sequential Speciation Sampler is a flexible sampling platform for the collection of particulate matter and gases from ambient air for analysis in a laboratory.

Applications: The sampler and the associated collection hardware can be easily configured to meet specialized sampling requirements. The device is available in 4-12-channel configuration, both of which allow for the simultaneous sampling of airborne pollutants.

Technology: The Partisol Speciation Sampler is built upon the expertise gained by Rupprecht & Patashnick in supplying the majority of sequential PM samplers to the USEPA PM_{2.5} sampling network. The ChemComb Speciation Sampling Cartridge developed by the Harvard School of Public Health includes a denuder/filter pack configuration with a PM_{2.5} or PM₁₀ inlet. Other configurations include specialized cartridges for organics sampling.

Regulatory Status: The Partisol Speciation Sampler is designed to meet the sampling and quality assurance requirements of the USEPA PM speciation sampling network. The USEPA has executed a contract with Research Triangle Institute for the handling and analysis of the ChemComb Speciation Sampling Cartridges used in the sampler.

High Quality Speciation Sampling: The Partisol Model 2300 Sequential Speciation Sampler is a flexible sampling platform for characterizing the particles and/or gases contained in ambient air. PM_{2.5} and PM₁₀ inlets provide the user with the ability to sample two size fractions simultaneously. The device contains the same user interface and is built upon the same hardware platform as the popular Partisol Model 2025 Sequential Air Sampler.

The Partisol Model 2300 Sequential Speciation Sampler was conceived from the ground up as a sequential sampling platform. Both the 4- and 12-channel versions of the device provide sequential sampling capabilities. Four-channel

samplers can be upgraded at a later date to the 12-channel configuration should a user's needs change.

ChemComb Cartridges: Using ChemComb Speciation Sampling Cartridges developed and characterized by the Harvard School of Public Health, the sampler is designed to meet the USEPA PM_{2.5} chemical speciation sampling requirements. The sampling cartridges can contain up to 2 honeycomb denuders for collecting or stripping gases from the sample stream selectively, followed by a four-stage filter pack for 47 mm diameter filters.

USEPA has contracted with Research Triangle Institute of Research Triangle Park, North Carolina, for the handling and analysis of ChemComb Cartridges. The modularity of the ChemComb Cartridge helps to maintain the integrity of field samples. All sampling components can be assembled in the laboratory and enclosed in the module's container. This eliminates the risks inherent in the in-field assembly of sampling components. A small, rugged form factor permits easy transport of shipment of ChemComb Cartridges in their assembled form between the laboratory and the air-sampling site. The cartridges install easily and quickly into the Partisol Speciation Sampler.

Flow Control: Both the 4- and 12-channel configurations of the sampler contain four flow independent mass flow controllers. These provide Activol flow control by using information from ambient temperature and pressure sensors to maintain a constant volumetric flow rate. Flow rates are generally maintained at either 10 or 16.7 LPM, with a user-selectable range of 5 to 18 LPM. The device reports sampled volumes in either standard or volumetric terms.

Built-in software support provides straightforward flow audits using the innovative Streamline FTS Flow Transfer Standard, as well as leak checks using a leak check plug. Leak check plugs are available for insertion in the input ports of the Partisol Speciation Sampler, as well as for PM_{2.5} ChemComb Cartridges configured with a greased inlet.

Sample Programming: The user can group flow channels in sets of 1, 2, 3 or 4. The sampling program of these groups can be based upon a number of factors, such as time/date, wind speed, wind direction, and/or the values of three user-defined analog inputs. Up to four flow channels can be operated simultaneously. The sampler activates one group of channels at a time. Operating four channels concurrently allows for the sampling of mass, elements, EC/OC, nitrate, sulfate, ammonia and/or other species to occur concurrently. PM_{2.5} channels can also be operated at the same time as channels configured for PM₁₀.

Flexible Sampling Platform: The third major configuration of the Partisol Speciation Sampler is called the Flexible Sampling Platform. In this case, the sampler does *not* contain the upper support structure for housing

ChemComb Cartridges. Rather, it contains 12 flow channels that exit the enclosure as barbed hose fittings. This allows users to attach a selection of ambient air sampling equipment designed for flow rates between 5 and 18 LPM. The standard features of the sampler allow for the same flow control, conditional sampling and data handling as the two ChemComb-based versions of the sampler.

CHAPTER – III

General Guidelines on Ambient Air Quality Monitoring & QA/QC Field Sampling

1.0. Introduction

The scope of ambient air quality monitoring designing is to create a centralized database of measurements to address the specific objectives. These objectives drive the study design process, including the monitoring network design. The various components for this monitoring network design start with the conceptual designing, field planning and then proceed to placement of monitors, selection of monitoring methods, sampling equipment selection & procurement, sampling duration & frequency, and setting QA/QC procedures, etc.

Prior to the initiation of an air quality study, the monitoring network is designed to ensure that the resulting data will be adequate to address the specific objectives of the study. Likewise *allowable tolerance levels* measurement and also the uncertainties are established based on the expected use of the data. For example, the measurement uncertainties must be much smaller for data that will be used for modeling activities and there are extensive monitoring requirements in this project. The terms used in whole set of guidelines are given in Box 1.

Box 1

Definition OF QA/QC

Quality Control (QC) is a system of routine technical activities, to measure and control the quality of the inventory as it is being developed. The QC system is designed to:

- (i) Provide routine and consistent checks to ensure data integrity, correctness, and completeness;
- (ii) Identify and address errors and omissions; and
- (iii) Document and archive inventory material and record all QC activities.

QC activities include general methods such as accuracy checks on data acquisition and calculations and the use of approved standardized procedures for emission calculations, measurements, estimating uncertainties, archiving information and reporting. Higher tier QC includes technical reviews of source categories, activity and emission factor data, and methods.

Quality Assurance (QA) activities include a planned system of review procedures conducted by personnel not directly involved in the inventory compilation/development process. Reviews, preferably by independent third parties, should be performed upon a finalized inventory following the implementation of QC procedures. Reviews verify that data quality objectives were met, ensure that the inventory represents the best estimates of emissions and sinks given the current state of scientific knowledge and data available, and support the effectiveness of the QC programme.

Accuracy [A]: the degree of correctness with which a measurement system yields the true value of an observable. Specially the percent difference between the measure and true value (the "true" value is determined by standard Reference Material or the use of two or more independent procedures to measure the same observable).

$$A=100 (C_m - C_t) / C_t$$

Where, A = accuracy (%)
C_m = measured value
C_t = true value

Allowable Tolerance Levels: the maximum deviation from ideal conditions that is acceptable given the application. For example, the maximum detection limits, precision, and accuracy, also the maximum change in flow rate during sampling, value of an unusual substrate that would be considered to pass the acceptance test, and the lowest validity code that would yield data capable of meeting the study objectives. Allowable tolerance levels must be selected to provide database of sufficient quality to test the stated hypotheses.

Data Qualification Statement: A summary of data set quality that evaluates measurements with respect to allowable tolerance levels. It specifies data completeness, values above lower quantifiable limits, and relative precision as a function of concentration, accuracy as determined by performance audits, and numbers of data validation flags. The data qualification statement defines the level of signal in an environmental cause that is needed to exceed the noise of the measurements system; it should be used by data analysts to evaluate the extent to which sought relationships are real or are an artifact of the measurement process.

Precision[sm]: the standard deviation of repeated measurements of the same observable with the same measurement method. When *n* periodic measurements are made using a transfer standard of known value, precision defined as:

$$s_m = \{[\sum(C_i - \text{Avg}(C_i))^2 / (n - 1)]\}^{1/2}$$

Where, C_i is the *i*th measurement of observable C in response to the same concentration, and Avg (C_i) is the average concentration of the *n* measurements of C_i

Standard Operating Procedures (SOPs): Complete description of the measurement process. SOPs include: (1) Summary of measurement method, principles, expected accuracy and precision, and the assumption for validity; (2) Materials, equipment, reagents, and suppliers; (3) Individuals responsible for performing each part of the procedure; and (4) Traceability path, primary standards or reference.

Systems Audits: Independent examination of all phases of measurement and data processing to determine that SOPs define a valid measurement method and that these procedure are implemented in practice.

Transfer Standards: Easily produced or commonly available gases, liquids, or solids that are traceable to primary standards and used for calibration, performance testing, and auditing.

Uncertainty: The combination of the uncorrected and precision.

In this project the overall objective is to develop effective emissions control strategies, based on characterization of emission as well as ambient air sampling, source profiling and diffusion modeling studies. Source sampling results are used to quantify contribution from excessive emitters as inputs to models that relate contributions of various source types to ambient pollutant concentrations. The protocols required for this type of source sampling differ substantially from the typical source sampling protocols.

2.0. Monitoring Network Design

The general guidelines given under focuses on the network design or measurement attributes (i.e. monitor siting, measurement duration and frequency, analyses to be conducted and analytical methods) which should be tailored to best meet the specific objectives defined earlier.

2.1 Monitoring Locations

The siting of monitor is determined by the size of the spatial scale that the measurements are intended to represent. Here, the monitoring scale can at best be taken as neighborhood or urban scale as given below:

2.1.1 Neighborhood Scale (500m to 4km)

Such a monitoring do not show significant difference with spacing of few kilometers and the dimensions are often the size of emissions and modeling grids used in large urban areas. For source assessment, source affecting neighborhood-scale sites typically consist small individual emitters, such as clean, paved, curbed roads, un-congested traffic with a low number of heavy-duty vehicles, or neighborhood use of residential heating devices such as fireplaces and wood stoves.

2.1.2 Urban Scale (4 to 100 km)

Urban-scale monitoring represents mixtures of pollutants from many sources within an urban complex. Urban-scale sites are often located at higher elevations and away from highly traveled roads, industries, and residential heating. Monitors on the roofs of two to four storied buildings in the urban core area often represent the urban scale well. This is the scale, which is normally used for compliance monitoring also. In this project, the requirement is not compliance monitoring and hence urban scale is not representative scale of monitoring.

The scale of monitoring being on hot spot focusing neighborhood sources; the sampling height is also taken up to 3 mts just to avoid undue influence of road dust.

2.2 Sample Duration

Sequential, one-hour average concentrations for compliance are most commonly measured with *in situ* monitors for compliance. Workplace alert monitoring usually requires short duration monitoring, of the order of 5 minutes to 8 hours, while long term health studies frequently use data averaged over days to weeks. Twenty-four hour integrated measurements are commonly used for PM₁₀ and PM_{2.5} monitoring to overcome detection limits associated with gravimetric analysis of filter-collected samples. *In situ* particle measurement technologies report hourly particle concentrations in some networks and provide some insight into the effects of averaging time on different statistical indicators. However, in this project, because the ambient air concentrations are in general high, 8-hours sampling duration is recommended in order to capture the differences during traffic peaks/non-peaks hours as well as diurnal climatic variations. However, for certain parameters like CO continuous real time monitoring has been recommended.

2.3 Sampling Frequency

Table 3 (a) below compares the annual average and standard deviation, highest, and several upper percentiles of 24-hours PM₁₀ concentrations for samples collected daily and at second, third, sixth, twelfth, and thirtieth day intervals. As can be seen, the sampling has little effect on the annual average (up to one in 12 days) but the sampling frequency has a substantial effect on measures of high concentration events (i.e., maximum, second maximum, 99th%, 98th%). So, in order to capture highest concentrations during winter season, continuous sampling is recommended in this project.

Table 3 (a): Effects of sampling frequency on statistical indicators for 24-hour PM₁₀ concentrations (Data from Las Vegas, NV, 1995)

Sampling Frequency	Annual Average	Standard Deviation	Min.	Max.	Second Maxi.	99 th %	98 th %	95 th %	90 th %
Every Day	49	31	8	318	219	176	128	92	76
Second Day	48	25	8	186	128	128	115	86	76
Third Day	48	29	11	219	136	128	104	92	77
Sixth Day	48	34	11	219	136	135	104	92	81
Twelfth Day	50	29	14	136	104	104	104	92	91
Thirtieth Day	58	56	11	219	91	91	91	91	91

3.0 Measurements Methods

Measurement technology and cost limit the specificity with which different observable can be quantified. In the case of PM₁₀ mass concentrations are acquired because mass is an observable that can be practically measured. But PM₁₀ consists thousands of different compounds in an even greater variety of mixtures and sizes. Analysis methods are costly and require large sample volumes, necessitating long averaging times and limited sampling frequency. These are some of the considerations that were considered before recommending sampling and analytical instrumentation selection. The guidelines for instrument selection is given in Chapter I.

Several choices of measurement methods often exist for the same observable. The accuracy, precision, detection, averaging time, manpower involved, physical size, and cost all play a part in the method selection process. Recommendations made were based on similar project experience elsewhere. Overall measurement methods proposed in this study are given in Tables 3 (b) and 3 (C).

Table 3(b): Guidelines on Analytical Support/ Procedure for Gaseous Pollutants

Pollutants	Methods
SO ₂	Spectrophotometric measurement, Improved West & Gaeke Method
NO ₂	Spectrophotometric measurement, Jacobs & Hochheiser Method
CO	Automatic Analyser, NDIR Method
O ₃	Automatic Analyser, UV Photometric Method
Aldehydes	Spectrophotometric measurement
Benzene	By Online BTEX Analyser or Active sampling in adsorption Tube, USEPA Method TO-1 or TO-2 GC-ATD Method
1,3 Butadiene	GC - ATD – FID Method with suitable sorbent
Alkanes	Selected alkanes, Alkenes, Aromatic / Cyclic Hydrocarbons more volatile than Ethane but less Volatile than C ₂₀ following USEPA Method TO –17, GC - ATD – FID Methods are recommended
HC	Sampling in Tedler Bag followed by GC - FID
NMHC	Preconcentration followed by GC-FID analysis, USEPA Method TO - 12 or by Automatic NHMC analyser

4.0 Quality Control/Quality Assurance

Quality control is in fact the responsibility of the laboratory conducting the work. Quality control tasks generally include: (1) efforts made to ensure that the quality of measurements are within established tolerance levels; (2) measurements and analytical performance checks need to characterize data quality (i.e. detection limits, precision and accuracy); and (3) verification of comparability with related measurements and between operators/analysts. Whereas *Quality assurance* is the responsibility of an

independent auditor. The tasks of the auditor are the following questions: Are the Documented procedures complete and accurate? Are the performance checks adequate so that a problem with the instrument will not go undetected? Are there laboratory/field practices that might adversely affect the quality of the data? Do the reported measures of data quality hold up to scrutiny?

To address these questions, the auditor (if nominated) identifies deviations from standard operation procedures, evaluates laboratory quality control procedures, looks for gaps in sampling and analytical performance checks, observes sample handling, and looks for the sources of contamination. In addition, the auditor often conducts a performance audit. Standards blanks, spiked samples, and sometimes previously analyzed samples are presented to the laboratory for blind analysis. The auditor uses these results to independently assess measurement accuracy, precision, and detection limits. These values are compared to the laboratory-reported values.

Quality control activities begin with the design of the measurement strategy and continue through the final validation of the database. These activities include: (1) development of standard operating procedures with comprehensive measurement performance checks; (2) inclusion of measurements for the estimation of accuracy, precision, and detection limits (i.e., to characterize data quality); (3) documentation of field and analytical activities; and (4) data validation.

It is recommended that in order to ensure proper QA/QC process *Standard operating procedures (SOP)* should be developed, which delineate step-by-step procedures to be followed for sample collection, analysis, substrate preparation, or other activity critical to the study. It is normally expected that the SOP will accurately reflect laboratory practice and will be located where the measurement is being performed. For example, a SOP for thermal-optical carbon analysis could also be developed at laboratory and then it should be found with the thermal-optical carbon analyzer. QA/QC requirements are highlighted in Table 3 (c).

4.1. QC Procedures for PM₁₀

No matter how much air is drawn through a filter and despite high particle loadings in Indian urban areas, the amount of sample available for the required chemical analysis shall be still small. The typical mass loadings on filters from low-to medium-volume samplers are less than 5 mg to 20 mg for 60 to 200 $\mu\text{g}/\text{m}^3$, and many of the chemical species of interest must be measured when less than 1 μg is in the deposit.

Therefore, listing of minimum detectable limits for elemental, ionic, and carbon analysis methods that are commonly applied to filter samples are needed so that sample durations and flow rates can be adjusted to acquire desired flow rate, and filter size. Depending on the study objectives and

source mixture in the study area, different chemical species may need to be added to or omitted. So, the selection of appropriate analysis methods, and sampling hardware must be complemented with detailed sample handling and analysis procedures.

4.1.1 Filter Handling & Weighing

No chemical analysis method, no matter how accurate or precise, can adequately represent atmospheric concentrations if the filters to which these methods are applied are improperly selected or handled. PM₁₀ filter mass deposits are usually measured in micrograms (one-millionth of one gram). These are very small quantities, and even the slightest contamination can bias these mass measurements. Small bias in chemical concentrations can greatly affect the decisions that are made with respect to source apportionment or health effects, so extra precautions are warranted when selecting and using filters.

Teflon-membrane and quartz-fiber filters are most commonly used for chemical analysis. Cellulose-fiber filters are easily impregnated with chemicals that absorb gaseous precursors, and etched polycarbonate-membrane filters are best suited for microscopic or individual particle analyses. The recommended filters have to be used primarily in the low-volume or medium-volume samplers. The manufacturer's identification numbers are important specifications since only these particular filters have been found to acceptably meet the requirements for the characterization in previous studies. Besides for QC at least two filters from each lot (typically 100 filters) or a minimum of 2% of the filters purchased from the specified manufacturers are recommended to be analyzed for all species to verify that pre-established specifications have been met. Average blank levels are typically less than 0.5 µg/filter for ions and less than 0.5 µg/cm² for carbon. Lots may be rejected for chemical analysis when blank levels for individual species exceed 1µg/filter. Each filter should also be individually examined prior to labeling for discoloration, pinholes, creases, separation of ring, chaff or flashing, loose material, or other defects. Testing of sample media is continued throughout the course of a monitoring project. In addition to 2% to 5% of laboratory blanks, approximately 10% of all samples are designated as field blanks, and these follow all handling procedures except for actual sampling.

Gravimetry measures the net mass on a filter by weighing the filter before and after sampling with balance in temperature- and relative humidity-controlled environment. To minimize particle volatilization and aerosol liquid water bias, PM_{2.5} reference methods require that filters be equilibrated for 24 hours at a constant (within ±5%) relative humidity between 30% and 40% at a constant (within ±2° C) temperature between 20° C and 23° C, which is a more stringent requirement than for PM₁₀ filter equilibration. PM₁₀ filters are required to be equilibrated at 20% to 45% relative humidity (±5%) and 15° C to

30° C temperature ($\pm 3^\circ$ C). These filter equilibrium conditions are intended to minimize the liquid water associated with soluble compounds and minimize the loss of volatile species. Nominal values of 30% RH and 20° C best conserve the particle deposits during sample weighing. Accurate gravimetric analysis require the use of filters with low dielectric constants, high filter integrity, and inertness with respect to absorbing water vapor and other gases. Further gravimetric analysis of the filters is performed with a microbalance (Feeney et al., 1984). The sensitivity and reliability of the electro balance is about ± 0.001 mg or $\pm 1\mu\text{g}$, though tolerances on re-weights of Teflon-membrane filters are typically ± 0.010 mg. These sensitive balances require isolation from vibration and air currents.

Balance calibration should be established before and after each weighing session using Class M and S standards traceable to National Standards. Approximately one out of ten filters should be re-weighed by a different person at a later time. These re-weighed should be used to calculate precision of the measurement.

Table 3 (c): Guidelines for Ambient Air Quality Sampling/Analysis Methodology for Target Pollutants

Particulars	Pollutants													
	SPM	PM ₁₀	PM _{2.5}	NO _x	SO ₂	CO	OC/EC	Ions	VOC	O ₃	Aldehyde	NMHC	HC	PAHs
Sampling Instrument	High Volume Sampler	Multichannel Speciation Sampler Or Two PM ₁₀ FRM Partisol sampler stationed at same location Or RDS	FRM Partisol (PM _{2.5}) sampler Or Dicotomous sampler Or Beta Attenuation Monitor (BAM) Or Equivalent	Impingers attached to HVS or RDS	Impingers attached to HVS or RDS	Automatic analyser Or Low volume sampling pump connected to Tedlar bags	PM10 Sampler Particulate collected on Quartz filter	PM10 Sampler Particulate collected on Quartz filter	Low volume sampling pump connected to Adsorption Tube / Tedlar bags Or Pressurised canister sampling	Automatic analyser Or Impingers attached to HVS or RDS	Impingers attached to HVS / RDS Or Low volume sampling pump connected to DNPH adsorption tube	Automatic analyser Or	Automatic analyser Or Low volume sampling pump connected to Tedlar bags	HVS/RDS/PM _{2.5} Sampler depending on sizes of interest
Sampling Principle	Filtration of aerodynamic sizes	Filtration of aerodynamic sizes with a size cut by impaction	Filtration of aerodynamic sizes with a size cut by impaction followed by cyclone separation	Chemical absorption in suitable media	Chemical absorption in suitable media	Suction by Pump As per instrument specification	Filtration of aerodynamic sizes with a size cut by impaction	Filtration of aerodynamic sizes with a size cut by impaction	Active pressurised sampling / Adsorption	Suction by Pump Or Chemical Absorption	Chemical Absorption Or Active pressurised sampling	Suction by Pump	Auto suction by pump Or Active adsorption	Filtration of aerodynamic sizes
Flow rate	0.8-1.2 m ³ /min	16.7 LPM Or 0.8-1.2 m ³ /min (for RDS only)	16.7 LPM	As per method it is 0.2 LPM but due to limitation in sampling equipment maximum achievable flow rate may be 0.5 LPM	1.0 LPM	0.1 ppm	16.7 LPM Or 0.8-1.2 m ³ /min (for RDS only)	16.7 LPM	0.2 - 0.5 LPM	As per instrument specification	0.5 LPM	As per instrument specification	As per instrument specification	16.7 LPM Or 0.8-1.2 m ³ /min (for RDS only)
Sampling Period	8 / 24 Hourly	8 / 24 Hourly	24 hourly	8 / 24 Hourly	8 / 24 Hourly	8 / 24 hourly	8 / 24 Hourly	24 hourly Or 8 / 24 Hourly	Grab	8 / 24 hourly	4 / 24 hourly	Grab	Grab	24 hourly
Sampling frequency	Twice in Week	20 Days in Month for three season	Once in week	20 Days in Month for three season	20 Days in Month for three season	Twice a week	20 Days in Month for three season	20 Days in Month for three season	Once in Month	Twice a week	Once in Month	Once in 15 days	Once in 15 days	Once in Month
Analytical instrument	Electronic Balance	Electronic Micro Balance	Electronic Micro Balance	Spectrophotometer	Spectrophotometer	Automatic CO analyser	OC/EC Analyser	Ion Chromatography	GC-ATD-FID/MS Or GC-FID/MS	Automatic analyser	Spectrophotometer	Automatic analyser	Automatic analyser	GC-FID Or GC-MS
Analytical method	Gravimetric	Gravimetric	Gravimetric	Colorimetric Improved West & Gaeke Method	Colorimetric Jacobs & Hochheiser Modified method	NDIR	TOR/TOT Method NIOSH 5040	Ion Chromatography	USEPA method TO-1/ TO-2 / TO-4 / TO-10 / TO-14	UV-Photometry Or Colorimetric	Colorimetric (MBTH method) Or HPLC analysis	FID Analysis	FID Analysis	GC-FID Or HPLC
Minimum Reportable value	5 µg/m ³	5 µg/m ³	5 µg/m ³	9 µg/m ³	4 µg/m ³		0.2 µg / 0.5 cm ² punch		0.1 ppb	2 ppb Or 10 µg/m ³	µg/m ³ Or 0.1 ppb	0.05 ppm	0.05 ppm	1 ng/m ³

- Notes: 1. Benzene and 1,3 Butadiene and alkanes in Volatile phase are included in VOCs
 2. Methodology for molecular marker has been provided separately

5.0 Performance Checks for Standard Operating Procedure

During the development of SOP, one must attempt to identify all possible sources of bias and incorporate adequate *performance checks* to ensure that, measurement errors, if occur, would be identified. One critical performance check in air sampling is leak check. For example, if PM₁₀ filter sampler (inter, filter holder, volume-flow meter, vacuum gage, and vacuum pump) has leak between the filter holder and flow meter downstream, then, the volume of air measured by flow meter will be greater than the volume pulled through the filter, and the PM₁₀ mass concentration (mass/volume) will be biased low. Flow calibrations and flow audits are also critical to the accurate collection of air samples. Ideally, air sampling equipment should be calibrated (multi-point) in the configuration in which it will be in the field, and the sampler flow rate is validated with an independent meter in the field. For example, filter samples collected for analysis of organic particulate matter are typically collected on quartz-fiber filters. The filters must be baked prior to use to lower blank levels, and samples must be stored and archived cold to prevent volatile losses. Subjecting baked filters (some from each batch) to *acceptance test* (i.e. requiring blank substrate values to be smaller than a certain value) is useful in ensuring that allowable tolerance levels for measurement uncertainties are met.

The issue of contamination of samples, if any, in transit or storage can be identified through use of dynamic blanks. *Dynamic blanks* (or field blanks) are substrate that are prepared with sample substrates and kept with them through analysis. To the greatest extent possible, these substance are handled identically to sample substrate with the exception of actual sample collection.

Additional performance checks are also desirable for each specific analytical system to ensure that every component of the system is working correctly. One common performance check is the analysis of *independent standards*, standard that are independent of those used for calibration. Table 3 (d) summarizes commonly measured atmospheric observable with appropriate primary and transfer standards for calibration, performance test, and quality auditing. Methods for presenting these standards to instruments depend on the instrument audited.

6.0 Data Quality Requirements

Tasks required to ensure data quality measures are built into the measurement in the form of dynamic blanks, independent standards, and collocated samplers (replicate analyses). Measurement detection limits are proportional to the variability of the blank signal, and because a number of different definitions are in use, it is important to indicate while reporting data as to how detections were estimated. Measurements below detection limits must be labeled appropriately (e.g., "ND" for non-detect).

The measurement accuracy expressed as the percent difference between the “true” (C_t) and measured (C_m) values, and true value falls outside the range defined by precision of the measurement, the measurement is considered *biased*. For sampling, artifacts (i.e., adsorption of gases on the sampling filter, volatilization of material from the filter, or chemical reactions alerting collected materials) can result in substantial bias in the measurement of particulate organic carbon, nitrate, and other multiphase species. Care must be taken to minimize sampling artifacts, and their contribution to measurement bias should be acknowledged in the reporting of data at least qualitatively.

Precision describes the variation of repeated measurements of the same observable with the same measurement method, and is usually expressed as plus or minus one standard deviation ($\pm 1s$), or as a percentage using coefficient of variation, or as a 95% confidence interval. And t-table used for the purpose takes into consideration the number of measurements taken.

Analytical precision is typically determined from replicate analysis of more than 10% of the samples. Using these data, the pooled coefficient of variation can be calculated.

Propagation of error techniques are applied for precision estimates for filter-based PM_{10} measurements, for example, the concentration, C , is given by:

$$C = m/v$$

Where, m is the mass of particulate matter, v is the sample volume, and s_m and s are the precision of m and v , respectively. The overall precision of C is:

$$S_C = \{(s_m/v)^2 + (ms\sqrt{v^2})^2\}^{1/2}$$

7.0 Documentation/Record keeping

In addition to developing standard operating procedures with comprehensive performance checks, and inclusion of measurements to characterize data quality, the documentation of the field and laboratory activities is important to the development of a high quality database. Documentation of field activities frequently takes place through the development and use of a standard field log. The field log prompts the field technician to record all critical sampling parameters and includes a column for comments. First of all, a chain of custody form can be used to track samples, avoid sample mix-ups, and identify affected samples, should contamination occur.

Documentation also includes sample analysis logbook. Such records, in ink, should provide, everything that is done with the analyzer, in sequential order. Operator name, date, samples analyzed (by sample identification number),

calibrations, leak tests, gas cylinder changes, instrument maintenance & repair, and other interaction with the instrument are recorded. It is recommended that all the analyses, whether valid or invalid, are required to be accounted for in this record. It is necessary to note analyzer maintenance and repairs in the analyses logbook. The following types of information are typically recorded in data reporting.

Measurement Locations: One can assign each measurement location a proper identification with a unique alphanumeric site.

Variable Definition: Each variable can be assigned a unique code that is accompanied by its definition, units, averaging time, and measurement method.

Data Validation Flags: One can flag certain observations. Such flags are defined to specify the validation level as well as specific deviations from SOPs.

Data: Value, precision, accuracy, and validation level are provided for each sample. Separate tables are produced for different averaging times and for non-uniform data sets.

Validation Tables: These include detailed information on specific samples indicating the nature of the data qualification.

8.0 Data Validation Requirements

The final step of the quality control process is data validation. The first step under data validation is to examine field log, analysis log, and chain-of-custody forms as described earlier to identify data that are invalid or suspect. The transcription of data from and written log sheets to an electronic database can also be one possibility for database errors.

Data validity levels are designated in the validation tables for different stages of data acquisition and interpretation.

Level 0: Data sets downloaded from a field instrument prior to examination. It may be noted that level 0 data are not used for interpretive purposes.

Level 1: At this level, data are evaluated by measurement investigator prior to submission to database. Values are removed for instrument and performance test, adjustments for calibration deviation are applied, extreme values are investigated, internal comparisons are made, blanks are subtracted, precision are estimated and propagated, and then appropriate data qualification flags are assigned.

Level 2: At this level, Inter-comparison tests between data sets are completed. These tests often result in the investigation of several samples that do not follow the same pattern as other measurement (i.e., outliers).

Level 3: Values that are found to be contradictory to other values are now investigated. These measurements are used to test hypotheses. The quality of these measurements is especially important, as they often indicate large deviations that do justify others and such values should not be confused with measurement error.

9.0 CPCB QA/QC Guidelines under National Ambient Air Quality Monitoring program

CPCB report 'Guidelines for Ambient Air Quality Monitoring' provided for NAMP is reproduced below for reference (this is pertinent for typical primary parameters e.g. SO_x, NO_x, SPM, etc.):

9.1 Methods

Following methods will be used for measuring air pollutants:

- Sulphur dioxide (SO₂) – Modified West and Gaeke method
- Nitrogen dioxide (NO₂) – Sodium Arsenite method
- Suspended Particulate Matter (SPM) – High volume method (Gravimetric method)
- Respirable Suspended Particulate Matter (RSPM) – Gravimetrically with GFA/EPM 2000 filter paper using respirable dust sampler (Cyclonic Flow Technique)

9.2 Information to be collected during Monitoring

- Major sources of air pollutants near the monitoring location including any major highway, any major industries with details of air pollutant(s) emitted from industries, location of industries with respect to site & predominant wind direction at site.
- Any traffic jams on roads near monitoring site during monitoring or any other situation that may result in very high or low values.
- Incidence of rainfall during monitoring and weather conditions.
- Duration of power failure & machine failure during monitoring, if any.

9.3 Precautions for Sampling, Analysis and Data Reporting

Sampling: The following precautions must be followed in sampling of air pollutants:

- The high volume sampler (HVS)/respirable dust sampler (RDS) must be properly calibrated to get the correct flow rate.
- Corrective and preventive maintenance of the HVS/RDS must be done.
- The filter used for sampling should be of good quality (having better mechanical stability, chemical stability, particle sampling efficiency, flow resistance, cost and availability etc.).
- Filter should be mounted properly on the support screen with the rough side of the filter facing upwards.
- The wing nuts should be tightened properly to avoid any leakage.
- Weighing of filter paper must be done after conditioning in desiccators having active moisture absorbent.
- Weighing of filter paper must be done in balance having accuracy of 0.01 mg and silica gel bottle must be kept in weighing chamber to avoid error while weighing.
- Distilled water must be used in manometer tube and water must be changed every fortnightly and zero level must be checked every time.
- Shelter should be provided at the sampling site for protection of instruments during rainy season.
- Ice should be kept in the sampling tray during sampling to avoid evaporation loss and better absorption.
- Evaporation loss if any must be made up with distilled water.
- Proper preservation of samples must be done after sampling. Gaseous samples must be preserved properly in an icebox or refrigerator (below 5° C) prior to analysis.

Analysis: The following precautions must be followed in analysis of air pollutants:

- Properly clean glassware must be used.
- One set of glassware must be calibrated as per requirement.

- All critical chemicals used must be of analytical grade.
- Double distilled or nano-pure water must be used for preparation of reagents and analysis.
- Glassware and storage bottles must be rinsed with distilled water and chemicals, respectively.
- Reagent bottles must be properly marked by name, strength and date of preparation, expiry date and initial of chemist who has prepared the reagent.
- Desiccant in the desiccators must be changed as per requirements.
- The chemicals whose strength changes with time must be standardized before use.
- Calibration graphs must be made every time a new stock solution is prepared.
- Reagent bottles must be made air tight before storage.
- Key reagents must be prepared fresh on the date of analysis.
- Storage of chemicals must be done as per recommendations like away from sunlight, etc.
- Active silica gel bottles with holes must be placed inside the weighing chamber.
- The analytical balance must have a sensitivity of 0.1 mg or better.

Data Reporting: Data must be reported in the prescribed format. The following must be followed for reporting data:

- SPM/RSPM values, which are very high, should be reported in round figures (without decimal place).
- Any outlier values found should be checked for contamination of sample, sudden change of environmental conditions in the vicinity of the monitoring site, etc. and discarded, if necessary.
- SPM values must always be greater than corresponding RSPM values. In case Respirable Dust Sampler is used for measuring SPM and RSPM, then,
 - Particulate matter collected on filter paper represents RSPM (size < 10 μm).

- Particulate matter collected in cup below cyclone represents Non-respirable suspended particulate matter (NRSPM, size > 10 μm).
 - Sum of particulate matter collected in cup below cyclone and filter paper gives an indication of SPM.
 - In case SPM is less than corresponding RSPM, then data may be rechecked.
- The values should not be reported below the detection limit as per the method:

Parameter	Lower Detection Limit	Method
SO ₂	4 $\mu\text{g}/\text{m}^3$	Modified West and Gaeke method
NO ₂	9 $\mu\text{g}/\text{m}^3$	Sodium Arsenite method
RSPM and SPM	5 $\mu\text{g}/\text{m}^3$	High volume sampling/ Respirable Dust Sampling

- For calculating 24 hourly average of various parameters, BDL is considered as half the lower detection limit, i.e.
 - For calculating 24 hourly average of SO₂, if any 4-hourly average is BDL then for calculation purpose its value is taken as 2 $\mu\text{g}/\text{m}^3$
 - For calculating 24 hourly average of NO₂, if any 4-hourly average is BDL then for calculation purpose its value is taken as 4.5 $\mu\text{g}/\text{m}^3$
 - For calculating 24 hourly average of SPM and RSPM, if any 8-hourly average is BDL then for calculation purpose its value is taken as 3 $\mu\text{g}/\text{m}^3$

Abbreviations in the Data: Abbreviations such as N.D., V.D., I.F., P.F., M/F, P/F, Nil, 0, etc. should not be mentioned in the data sheets.

Data Values	Abbreviations
Values less than Lower Detection Limit	B.D.L.
No Monitoring carried out	' - '

For no monitoring carried out for specific reason, an asterisk '*' may be mentioned in the respective place in datasheet and reason may be mentioned at the bottom of data sheet.

Calculation of 24-hourly Average and Monthly Average: Values monitored for 16 hours and more in a day are considered for calculation of 24-hour average. Average of 24-hourly averages (calculated as mentioned above) is taken as monthly average.

CHAPTER – IV

Guidelines on Analytical support/procedure for PM₁₀

1.0 Analytical Requirement for PM₁₀ Characterization

Ambient particulate matter is a combination of primary as well as secondary aerosol mass. It is important to have particulate characterization data to use receptor model for source apportionment study. The target physical and chemical parameters required for characterization of PM₁₀ are presented in Table 4 (a). It is desirable to carry out analysis of all the components listed in Table 4 (b) (Signature elements, OC/EC) and Table 4 (c) (Molecular Organic Markers) to have a better understanding in proportional contribution of different sources synergistically affecting the PM₁₀ concentration at receptor end. Individual selection of Signature elements/markers to be used for modeling may be done applying logistic to both the set of analytical data for particulate matter and source profile. The respective parameters listed in Table 4 (b) and Table 4 (c) indicating a possible source should be analyzed for source profiling.

Analytical data for following components (groups) are required for characterization of particulate matter. Apart from the direct measurement of proportionate contribution of each group of analytes, identification and estimation of individual target elements/compounds to apportion respective sources, the same analytical exercise has to be performed to generate source profile data. The target analytical components are listed in Table 4 (c) and Table 4 (e).

Table 4 (a): Target Physical and Chemical components (groups) for Characterization of Particulate Matter

Components	Required filter matrix	Analytical methods
PM ₁₀ / PM _{2.5}	Teflon or Nylon filter paper. Pre and post exposure conditioning of filter paper is mandatory	Gravimetric
Elements (Na, Mg, Al, Si, P, S, Cl, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cr, Cd, In, Sn, Sb, Ba, La, Hg, Ti, and Pb)	Teflon filter paper	ED-XRF, GT-AAS or ICP-AES or ICP-MS
Ions (F ⁻ , Cl ⁻ , Br ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ⁻² , K ⁺ , NH ₄ ⁺ , Na ⁺)	Nylon or Teflon filter paper (Same teflon filter paper can be utilised if ED-XRF is used for elements analysis)	Ion chromatography with conductivity detector

Components	Required filter matrix	Analytical methods	
Carbon Analysis (OC, EC and Carbonate Carbon)	Quartz filter. Pre-baking of quartz filter paper at 600 °C is essential	TOR/TOT method	
Molecular markers	The left over quartz filter paper after OC/EC analysis should be taken as composite sample to represent a location and specified duration of exposure	Extraction, followed by GC-MS analysis with and without derivatization	
Alkanes			n- Hentriacontane n-Tritriacontane n- Pentatriacontane
Hopanes			22, 29, 30 – Trisnorhopane 17a(H), 21β(H)-29 Norhopane 17a(H),21β(H) norhopane
Alkanoic acid			Hexadecanamide Octadecanamide
PAHs			Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[e]pyrene Indeno[1,2,3-cd]fluoranthene Indeno[1,2,3-cd]pyrene Phenylene pyrene Picene Coronene
Others			Stigmasterol Levoglucozan

The prescribed instrumentation and different options of analytical methodologies for estimation of different group of target analytes are listed in Table 4 (d). The advantages and disadvantages of different methodologies are also discussed in the Table 4 (d).

Table 4 (b): Signature Elements and Their Combinations for Respective Sources

Source Type	Dominant Particle Size	Chemical Abundances in Percent Mass			
		< 0.1%	0.1 to 1%	1 to 10%	> 10%
Paved Road Dust	Coarse	Cr, Sr, Pb, Zr	SO ₄ ⁻ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	EC, Al, K, Ca, Fe	OC, Si
Unpaved Road Dust	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , P, Zn, Sr, Ba	SO ₄ ⁻ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO ₄ ⁻ , K ⁺ , S, Ti	OC, Al, K, Ca, Fe	Si
Agricultural Soil	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , Cr, Zn, Sr	SO ₄ ⁻ , Na ⁺ , K ⁺ , S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl, Na ⁺ , EC, P, S, Cl, Ti	OC, Al, Mg, K, Ca, Fe	Si
Lake Bed	Coarse	Mn, Sr, Ba	K ⁺ , Ti	SO ₄ ⁺ , Na ⁺ , OC, Al, S, Cl, K, Ca, Fe	Si
Motor Vehicle	Fine	Cr, Ni, Y	NH ₄ ⁺ , Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁻ , NH ₄ ⁺ , S	OC, EC
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO ₃ ⁻ , SO ₄ ⁻ , NH ₄ ⁺ , Na ⁺ , S	Cl ⁻ , K ⁺ , Cl, K	OC, EC
Residual/Crude Oil Combustion (including fires)	Fine	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se	NH ₄ ⁺ , Na ⁺ , Zn, Fe, Si	V, OC, EC, Ni	S, SO ₄ ⁻
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K ⁺ , Al, Ti, Zn, Hg	NO ₃ ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	SO ₄ ⁻ , NH ₄ ⁺ , OC, Cl
Coal-Fired Power Plant	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO ₄ ⁻ , OC, EC, Al, S, Ca, Fe	Si
Oil-Fired Power Plant	Fine	V, Ni, Se, As, Br, Ba	Al, Si, P, K, Zn	NH ₄ ⁺ , OC, EC, Na, Ca, Pb	S, SO ₄ ⁻
Smelter Fine	Fine	V, Mn, Sb, Cr, Ti	Cd, Zn, Mg, Na, Ca, K, Se	Fe, Cu, As, Pb	S
Antimony Roaster	Fine	V, Cl, Ni, Mn	SO ₄ ⁻ , Sb, Pb	S	None Reported
Marine (Natural)	Fine and Coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca, Fe, Cu, Zn, Ba, La	NO ₃ ⁻ , SO ₄ ⁻ , OC, EC	Cl ⁻ , Na ⁺ , Na, Cl

EC – Elemental Carbon
 OC – Organic Carbon

Table 4 (c): Desirable Molecular Markers and Their Likely Sources

Molecular type	Molecular marker	Major urban sources
Alkanes	n-Pentacosane	Gasoline, diesel, fuel oil
Alkanes	n-Hexacosane	Gasoline, diesel, fuel oil
Alkanes	n-Heptacosane	Gasoline, diesel, fuel oil
Alkanes	n-Octacosane	Gasoline, diesel, fuel oil
Alkanes	n-Nonacosane	Detritus burning
Alkanes	n-Triacontane	Gasoline, diesel
Alkanes	n-Hentriacontane	Vegetative detritus,
Alkanes	n-Dotriacontane	cigarette smoke
Alkanes	n-Tritriacontane	Variety
Alkanes	n-Tetratriacontane	Vegetative detritus,
Alkanes	n-Pentatriacontane	cigarette smoke
		Tire wear debris
Steranes	20S&R-5a(H), 14b(H), 17b(H)-	Tire wear debris
Steranes	Cholestanes	
Steranes	20R-5a(H), 14a(H), 17b(H)-Cholestane	Gasoline, diesel, fuel oil
Steranes	20S&R-5a(H), 14b(H), 17b(H)- Sitostanes	Gasoline, diesel, fuel oil
	20S&R-5a(H), 14b(H), 17b(H)- Ergostanes	Gasoline, diesel, fuel oil
Hopanes		Gasoline, diesel, fuel oil
Hopanes	22, 29, 30-Trisnorneohopane (T m)	
Hopanes	17a(H), 21b(H)-29-Norhopane	Gasoline, diesel, fuel oil
Hopanes	17a(H), 21b(H)-Hopane	Gasoline, diesel, fuel oil
Hopanes	22S-17a(H), 21b(H)-30-Homohopane	Gasoline, diesel, fuel oil
Hopanes	22R-17a(H), 21b(H)-30-Homohopane	Gasoline, diesel, fuel oil
Hopanes	22S-17a(H), 21b(H)-30-Bishomohopane	Gasoline, diesel, fuel oil
Hopanes	22R-17a(H), 21b(H)-30-Bishomohopane	Gasoline, diesel, fuel oil
Alkanoic acids	n-9-Hexadecanoic acid	
Alkanoic acids	Hexadecanamide	Meat cooking
Alkanoic acids	Octadecanamide	Biomass (cow dung)
Alkanoic acids	Pimaric acid	Biomass (cow dung)
Resin acids	sopimaric acid	Softwood Burning
Resin acids		Softwood Burning
PAH	Benzo[b]fluoranthene	
PAH	Benzo[k]fluoranthene	Gasoline, natural gas,
PAH	Benzo[e]pyrene	coal, fuel oil
PAH	Indeno[1,2,3-cd]fluoranthene	Gasoline, natural gas,
PAH	Picene	coal, fuel oil
PAH	Coronene	Gasoline, natural gas,
PAH		coal, fuel oil
PAH	beta-Tocopherol	Gasoline, natural gas,
	Coprostanol	coal, fuel oil
Others	Stigmastan-3,5-dien	Coal
Others	Vitamin E	Gasoline vehicles
Others	Cholestanol	without catalyst
Others	Campesterol	
Others	Stigmasterol	Biomass
Others	(3 beta, 5 beta) Stigmastan-3-ol	Biomass (cow dung)

Molecular type	Molecular marker	Major urban sources
Others	beta-Sitosterol	Biomass (cow dung)
Others	(3beta, 5alpha) Stigmastan-3-ol	Biomass
Others	Stigmasta-3,5-dien-7-one	Biomass (cow dung)
Others	Cholesterol	Biomass
Others	Levoglucosan	Biomass
Others	Galactosan	Biomass
Others	Mannosan	Biomass
Others		Biomass
Others		Biomass
Others		Meat cooking
Others		Hardwood, softwood
		Biomass
		Biomass

Table 4 (d): Analytical Measurement Alternatives for Chemical Speciation

Target Species	Measurement Method	Remarks
Elements (Na, Mg, Al, Si, P, S, Cl, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Pd, Ag, Cr, Cd, In, Sn, Sb, Ba, La, Hg, Ti, and Pb)	ED-XRF	Non destructive, simultaneous multielement analysis with high sensitivity could be performed. Analysis of deposit only on teflon filter paper is possible firstly because the standards in urban air matrix is available only on Teflon and secondly only teflon has very low blank values for all the target analytes.
	ICP- AES or ICP-MS	Destructive method, have capability for simultaneous analysis. Type of Filter papers used will dictate the possibility to include Si analysis. Teflon is recommended
	GT-AAS	Destructive method, less sensitive for Hg, As, S, P and Cl. Individual run is required for each element. Type of Filter papers used will dictate the possibility to include Si analysis. Teflon is recommended.
Ions (F ⁻ , Cl ⁻ , Br ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SO ₄ ⁻² , K ⁺ , NH ₄ ⁺ , Na ⁺)	Ion Chromatography with Conductivity Detector	Destructive methodology, Nylon / Teflon filter paper is recommended.

Target Species	Measurement Method	Remarks
Carbon Analysis (OC, EC and Carbonate Carbon)	Thermal Optical Reflectance (TOR) or Thermal Optical Reflectance (TOT) method (NIOSH 5040)	Best suitable method for OC/EC in chemical speciation. Pyrolytic Carbon correction is done by lesser reflectance or transmittance. IMPROVE Protocol for OC/EC analysis give four fractions of OC and 3 fractions of EC which can be directly correlated with combustion fuel type.
Molecular Markers	GC-MS analysis	Selected Organic Markers indicate likely sources.

Essential compounds (minimum number of molecular markers) covering almost all the anticipated sources in urban areas in India required to be analyzed in source apportionment study are listed in Table 4 (e).

Table 4 (e): Essential Molecular Markers Required to be Monitored and Their Likely Sources

Molecule Type	Molecular Marker	Major Urban Sources
Alkanes	n- Hentriacontane n-Tritriacontane n- Pentatriacontane	Vegetative detritus, Cigarette smoke Tyre wear debris Tyre wear debris
Hopanes	22, 29, 30 – Trisnorneohopane 17 α (H), 21 β (H)-29 Norhopane 17 α (H), 21 β (H) Norhopane	Gasoline, diesel, fuel oil Gasoline, diesel, fuel oil Gasoline, diesel, fuel oil
Alkanoic acid	Hexadecanamide Octadecanamide	Biomass (Cow dung) Biomass (Cow dung)
PAHs	Benzo[b]fluoranthene Benzo[k]fluoranthene Benzo[e]pyrene Indeno[1,2,3-cd]fluoranthene Indeno[1,2,3-cd]pyrene Phenylenepyrene Picene Coronene	Gasoline, Natural gas, Fuel oil Gasoline, Natural gas, Fuel oil Gasoline, Natural gas, Fuel oil Gasoline, Natural gas, Fuel oil Gasoline, Natural gas, Fuel oil Coal Gasoline vehicles without Catalyst
Others	Stigmasterol Levoglucosan	Biomass burning Hardwood, Softwood

Methods for extraction, fractionation, pretreatment and estimation by Gas Chromatography for organic molecular markers are given below:

2.0 Sample Collection Transportation and Preservation

Ambient PM₁₀ samples should be collected using a suitable sampler at a desired flow rate recommended by manufacturer. Even RDS capable to hold 8"X10" quartz filter paper may be useful. Prior to sampling, filters have to be baked out at 600°C for three hours to minimize the organic background contaminants. Filters should be wrapped carefully with aluminum foil (baked out at 200°C for 10 minutes) and store in re-sealable plastic bags until the sampling days.

A re-sealable plastic bag with a new filter inside is transported in a cooler container to the sampling site in the morning of a sampling day. At the sampling site, the filter that collected the particle sample on the previous day is taken out of the filter holder and immediately wrapped with baked aluminum foil and sealed in the plastic bag. The bag with the sample filter inside is transported back to the laboratory in an isolated cooler container with blue ice, and then frozen at -10°C until analysis.

3.0 Methods for Sample Preparation & Analysis of Organic Molecular Markers

Three different sample pretreatment and analytical methodologies for Organic Molecular markers are described in following sections. The methodologies are being used for broad application in source characterization. The executing agencies may adopt suitable part of it to fulfill the requirement of present study. The outlines for other analytical activities are not detailed here as it is being done in routine exercises or is very specific (as Carbon) to instrumentation involved.

3.1 Method I

3.1.1 Sample Extraction and Pretreatment

The PM₁₀ sample filters are prepared and analyzed following the procedure shown in Figure 4.1. Soxhlet extraction is well-established particulate matter extraction method to remove the solvent-soluble organic components of the particles. An alternative extraction technique is to ultrasonicate the sample filters with one or more organic solvents such as hexane, benzene and/or isopropanol (Cautreels et al., 1976; Sheu et al., 1997; Yang et al., 1999; Mazurek et al., 1989; Rogge et al., 1993a).

The analysis of Organic Molecular Markers on filter deposit requires at least 200µg Organic Carbon in sample, therefore normal practice is to club the required number of exposed filter papers to have sufficient mass (about 600 - 1000 µg OC) to represent the whole monitoring period. Prior to analysis, sample filters are extracted by Soxhlet extraction in 500 ml of a 1:1 methylene chloride: acetone mixture for a period of 04 hours. The combination of non-

polar (methylene chloride) and polar (acetone) solvents is an efficient technique proved by preliminary analysis and has been used widely. The extracts are evaporated to 5 ml by using a Kuderna-Danish/other suitable apparatus and concentrated to 1 ml by a stream of pure nitrogen gas purging. The advantage of the Kuderna-Danish apparatus evaporation is that it gives higher recovery than any other techniques (Shinohara et al., 1977). The glass Soxhlet extraction apparatus should be cleaned and rinsed with acetone. Only Teflon-coated and solvent-cleaned forceps should be used to handle filters during the extraction process.

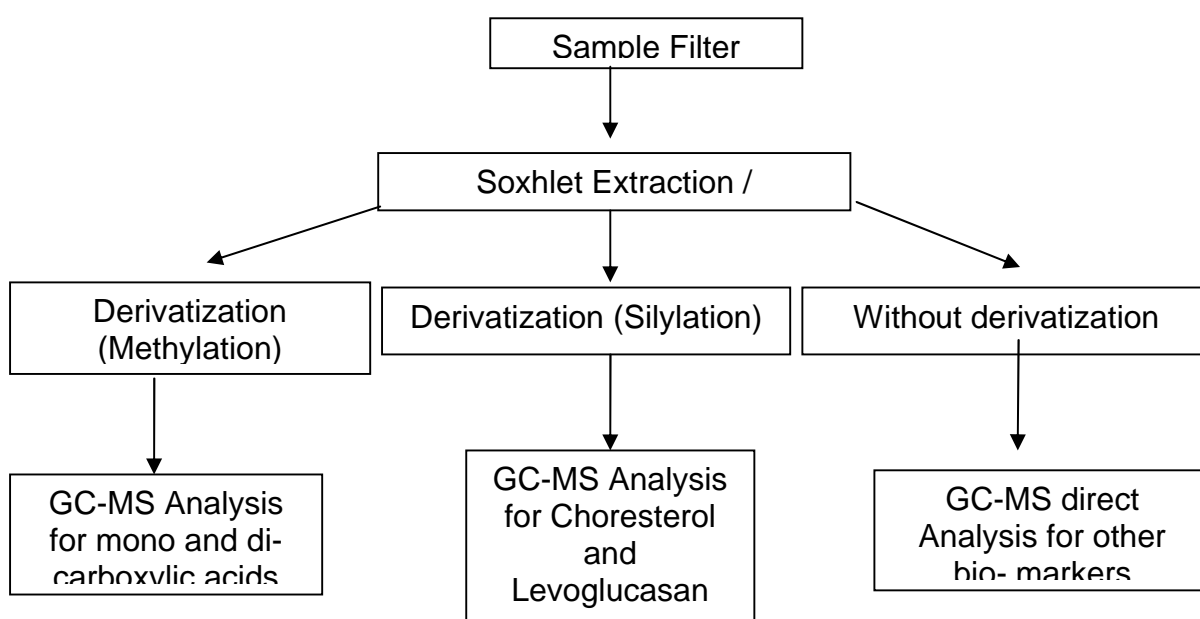


Fig. 4 (a): Schematic Diagram of Sample Preparation for Organic Markers

Each individual sample extract is divided into two portions after concentration to about 1 ml. One portion is derivatized by adding freshly prepared diazomethane in at least 100-fold excess to convert organic acids to their methyl derivatives. The conversion reaction is complete in seconds, and provides the equivalent methyl ester. After the first run the same sample aliquot is then silylated by adding *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) (Pierce Biotechnology, Inc.) and analyzed by GC/MS for the second round for the quantification of levoglucosan and cholesterol.

Gas chromatograph-mass spectrometry (GC/MS) using a 30 m 0.25 mm i. d. fused silica capillary column coated with DB-1701 or equivalent column is suitable. DB-1701 consists 7% cyanopropyl, 7% phenyl, 86% dimethylpolysiloxane and is used for compounds of low/mid polarity. Another widely used column is DB-5 (SPB-5; OV-5; HP-5) column, which is coated with 5% phenyl, 95% dimethylpolysiloxane, is a general-purpose column and most

suitable for non-polar analysis with a high temperature limit. DB-1701 column is better choice for analysis of the organic complex mixtures. It gives more separation between benzo[b]fluoranthene and benzo[k]fluoranthene than a DB-5 column. Another aliquot of extract is used for other molecular markers.

3.1.2 Instrumental Analysis

GC/MS has proved to be the most successful technique in quantifying various organic compounds associated with atmospheric particulate matter (Mazurek et al., 1987; Rogge et al., 1993a). Other instruments like high-pressure liquid chromatography (HPLC) or liquid chromatography/mass spectrometry (LC/MS) are good choices for characterization of high molecular weight and polar organic compounds. However, the molecular markers to be identified in source apportionment study have low molecular weight (less than 300) and low polarity too. Thus, GC/MS is more suitable for this particular purpose. It is reported that the GC/MS method measures and identifies only 10-15% of the organic mass (Rogge et al., 1993a). The reason is that high molecular weight and polar compounds either do not elute through the gas chromatography column or are not resolved in the GC column (Turpin et al., 2000). Thus, prior to GC injection, polar organics in samples have to be derivatized to non-polar compounds, which will elute through the GC column. For example, derivatization is used to convert mono- and di-carboxylic acids to their esters. By measuring the concentration of the ester derivatives, one can quantify the parent acids that would otherwise not have eluted through the column. Diazomethane (CH_2N_2) is the most common methylating reagent for carboxylic acids, and is widely used in soil analysis (Chaudot et al., 2000), natural and waste water analysis (Oller et al., 2001), and organic PM analysis (Mazurek et al., 1987; 1989; Rogge et al., 1993; Standley et al., 1987; Fine et al., 2001; Schauer et al., 1996).

The GC analytical method is recommended for 60.5 minutes. The initial column temperature should be 50°C when the injection started, hold at isothermal for 3 minutes at 50°C, followed by a temperature ramp of 20°C/min up to 150°C, with another isothermal hold for 3 minutes, then next ramp @ 4°C/min until 280°C with a final isothermal hold of 17 minutes.

3.1.3 Target Compounds

The target compounds that could be analyzed in this method are listed in Table 4 (f). The 53 target compounds were selected for analysis based on potential toxicity and capacity to be major air pollution molecular source markers. For example, n-alkanes are associated with plant wax emissions and automobile exhausts, hopane isomers have been considered as biomarkers of fossil fuel emissions (Schauer et al., 1996), while PAHs could indicate any combustion sources. n-Alkanoic acids were the most abundant organic group identified in atmospheric particulate organic matter in most sites in the Los Angeles area (Rogge et al., 1993a). Dicarboxylic acids have been

considered as important organic components in secondary organic aerosols (Shuetzle et al., 1975; Cronn et al., 1977; Appel et al., 1979).

Table 4 (f): Applicability of method for at least 53 Organic Molecular Markers

Alkanes	PAHs	Acids	Other
n-pentacosane n-hexacosane n-heptacosane n-octacosane n-nonacosane n-triacontane n-hentriacontane n-dotriacontane	benzo[b]fluoranthene benzo[k]fluoranthene benzo[e]pyrene indeno[1,2,3-cd]pyrene indeno[1,2,3-d]fluoranthene	21 n-alkanoic acids (with C ₁₀ to C ₃₀) 10 aliphatic dicarboxylic acids 1 aromatic polycarboxylic acids	9 hopanes Levoglucosan Stigmasterol

3.1.4 Internal Standard

To correct the potential loss associated with extraction, concentration, injection and chromatographic elution, internal standards are added to the filter right before the extraction started. The internal standards are used to account for the component losses associated with extraction, volatilization and instrument bias from the sample filters.

Perdeuterated n-tetracosane (C₂₄D₅₀) may be successfully used as an internal standard for quantifying organic fraction of aerosol samples (Mazurek et al., 1987, Rogge et al., 1993a). C₂₄D₅₀ may be added in both the sample extracts and the standards. Additional perdeuterated standards besides C₂₄D₅₀ may also be spiked on the sample filters before extraction, including C₃₀D₆₂, pyrene-d₁₀, lauric acid (C₁₂D₂₃) in order to improve recovery estimates for individual target groups.

3.1.5 Authentic Standards

An organic acid standard mixture should be prepared with mono-carboxylic acids, starting from C₁₀ to C₃₀ and di-carboxylic acids from C₃ to C₉. The acidic standard mixture has to be derivatized by diazomethane prior to analysis. n-alkane standard mixture should be prepared including C₂₅ to C₃₂. This carbon number range was established since n-alkanes with carbon number less than 25 have a significant gas phase component making it difficult to measure accurately the particulate concentration, and those with carbon number greater than 32 have difficulty eluting through the column. The PAH standard containing desired species with molecular weight of 252 and above, which exists at particle phase by over 80% throughout a year (Baek et al., 1991a; Gardner et al., 1995). Only one hopane constitutes the hopane standard due to unavailability of the other homologues.

3.1.6 Five-point Mass Calibration

Developing an accurate mass calibration method is a critical task in the analytical procedure. A successful mass calibration underlies precise and accurate analytical measurements. A five-point calibration curve is essential to obtain the concentrations of the molecular markers in the particulate samples, although single point calibration has been widely used in organic aerosol analysis (Mazurek et al., 1987, 1989; Rogge et al., 1993a). Concentration levels of the molecular markers in the samples vary by one or two orders of magnitude based on the preliminary analysis. Thus, the advantage of five-point over single-point calibration is that five-point calibration covers a wide range of concentrations in actual ambient samples, which potentially results in less bias than a single-point calibration. The five-point calibration curve can be generated by calibration standards with various concentrations but the same internal standard concentration.

The initial calibration is done at the following five levels (four levels for hopanes): 0.5, 5.0, 10.0, 20.0 and 50.0 µg/ml for alkanes; 1.0, 5.0, 10.0, 15.0 and 20.0 µg/ml for PAH; 0.5, 1.0, 3.0 and 6.0 µg/ml for hopanes; 5.0, 10.0, 25.0, 50.0 and 75.0 µg/ml for di-carboxylic acids; 3.0, 9.0, 27.0, 51.0 and 75.0 µg/ml for n-akanoic acids. Levels of calibration standards were selected based on the concentration ranges of the particle samples from the preliminary analysis and detection limits. Response factors were calculated for each analyte at each level.

Table 4 (g): Calibration Standards for Non-polar Molecular Markers

Concentration Ratios to IS (Internal Standards) 10µg/ml					IS(C ₂₄ D ₅₀) =	
Target Markers	L I	L II	L III	L IV	L V	
Calibration Standards for n - Alkanes						
C ₂₅	0.05	0.5	1.0	2.0	5.0	
C ₂₆	0.05	0.5	1.0	2.0	5.0	
C ₂₇	0.05	0.5	1.0	2.0	5.0	
C ₂₈	0.05	0.5	1.0	2.0	5.0	
C ₂₉	0.05	0.5	1.0	2.0	5.0	
C ₃₀	0.05	0.5	1.0	2.0	5.0	
C ₃₁	0.05	0.5	1.0	2.0	5.0	
C ₃₂	0.05	0.5	1.0	2.0	5.0	
Calibration Standards for PAHs						
BbF	0.1	0.5	1.0	1.5	2.0	
BkF	0.1	0.5	1.0	1.5	2.0	
BeP	0.1	0.5	1.0	1.5	2.0	
InF	0.1	0.5	1.0	1.5	2.0	
InP	0.1	0.5	1.0	1.5	2.0	
Calibration Standards for Hopanes						
17 α ,21 β , Hopanes	0.05	0.1	0.3	0.6		

Table 4 (h): Calibration Standards for Polar Molecular Markers

Concentration Ratios to IS (Internal Standards)					IS(C ₂₄ D ₅₀) = 10µg/ml
Target Markers	L I	L II	L III	L IV	L V
Calibration Standards for n-Alkanoic Acids					
C ₁₀	0.3	0.9	2.7	5.1	7.5
C ₁₁	0.3	0.9	2.7	5.1	7.5
C ₁₂	0.3	0.9	2.7	5.1	7.5
C ₁₃	0.3	0.9	2.7	5.1	7.5
C ₁₄	0.3	0.9	2.7	5.1	7.5
C ₁₅	0.3	0.9	2.7	5.1	7.5
C ₁₆	0.3	0.9	2.7	5.1	7.5
C ₁₇	0.3	0.9	2.7	5.1	7.5
C ₁₈	0.3	0.9	2.7	5.1	7.5
C ₁₉	0.3	0.9	2.7	5.1	7.5
C ₂₀	0.3	0.9	2.7	5.1	7.5
C ₂₁	0.3	0.9	2.7	5.1	7.5
C ₂₂	0.3	0.9	2.7	5.1	7.5
C ₂₃	0.3	0.9	2.7	5.1	7.5
C ₂₄	0.3	0.9	2.7	5.1	7.5
C ₂₅	0.3	0.9	2.7	5.1	7.5
C ₂₆	0.3	0.9	2.7	5.1	7.5
C ₂₇	0.3	0.9	2.7	5.1	7.5
C ₂₈	0.3	0.9	2.7	5.1	7.5
C ₂₉	0.3	0.9	2.7	5.1	7.5
C ₃₀	0.3	0.9	2.7	5.1	7.5
Calibration Standards for Di Carboxylic acids					
Malanoic	0.5	1.0	2.5	5.0	7.5
Succinic	0.5	1.0	2.5	5.0	7.5
Methyl succinic	0.5	1.0	2.5	5.0	7.5
Glutaric	0.5	1.0	2.5	5.0	7.5
Malic	0.5	1.0	2.5	5.0	7.5
Adipic	0.5	1.0	2.5	5.0	7.5
Suberic	0.5	1.0	2.5	5.0	7.5
Phthalic	0.5	1.0	2.5	5.0	7.5
Isophthalic	0.5	1.0	2.5	5.0	7.5
Azelaic	0.5	1.0	2.5	5.0	7.5

3.1.7 Compound Identification and Quantification

All the molecular markers are identified by comparing the detected compound retention times and mass spectra with the authentic standards and National Institute of Standards and Technology (NIST) spectral reference library. Most markers are identified positively with the complete sets of standards, with an exception for hopanes. Only one hopane, 17 α ,21 β -hopane was positively identified with a corresponding authentic standard. The other eight hopane homologues may be identified by referring the

retention time of 17 α ,21 β -hopane standard and the unique distribution pattern to published chromatographs and spectra (Fraser et al., 1999; Philp, 1985) due to lack of commercially available authentic standards. Identification of the organic molecular source markers associated with atmospheric particulate matter is extremely elaborate since the markers are generally present at trace levels in a complex mixture. Application of GC/MS with low detection limits has allowed significant progresses for improving the characterization techniques of organic particulate matter. However, there are still some difficulties associated with the identification process using GC/MS. The greatest concern is the co-elutions of unresolved isomers for some molecular markers, which result in combined mass spectra. Appropriately selected quantification ions can be beneficial to distinguish a particular mass spectrum of an individual compound from the co-eluted complex. In general, the most abundant ion serves as the quantification ion, which is the case for the PAH, the diacids and the hopanes. For the n-alkanes and the n-alkanoic acids, however, the selection of quantification ions is not that simple since more than one ion are involved. For example, ion mass-to-charge (m/z) 57, 71 and 85 are of almost the equivalent abundance for n-alkane series, but only m/z 85 if selected as quantification ion the analyst will face less interference. Quantification ions proposed and selected for qualitative analysis of the molecular markers in the particulate samples are listed in Table 4 (i).

Table 4 (i): Mass-to-charge (m/z) Ions for Compound Identification and Quantitation

Compound or Class	Selected Ion	Potential Ions
n-Alkanes	85	85, 71 or 57
BbF, BkF, BeP	252	252 or 126
InF, InP	276	276
Hopanes	191	191
n-Alkanoic Acids	74	74
Dicarboxylic acids	Molecular weight	Molecular weight

The molecular markers may be identified by comparing first the retention time with authentic standards within a range of ± 0.1 min, secondly the quantification ions, and finally the particular ratios of several relatively abundant ions. The latter is called verification of the identification. The purpose of verification is to further examine the identity of the mass spectra of the molecular markers from the samples and the authentic standards.

3.1.8 Optimization of GC/MS

The carrier gas flow rate and column temperature program have been optimized along with a proper selection of column coating thickness and length to maximize the compound resolution by gas chromatography. The resolution of the gas chromatography is an important factor influencing the analytical results. It depends largely on the carrier gas flow rate, the coating

thickness and length of the selected column, and the column temperature program. Ideally, slow carrier gas flow rate, thick stationary phase film coated on the column, a long column, and a slow column heat rate would be required for maximum resolution. However, in reality, the individual compounds would suffer substantial losses and the analysis period would be too long.

As for the mass spectrometry, the sensitivity has been optimized in several ways, for example, adjusting the filament emission current. High filament emission current may increase the sensitivity, but cause over-population of ions in trap. The GC/MS has also been maintained properly to provide consistent analytical conditions, particularly (e.g. compound detection limits). The setting values of the parameters with regard to optimized analytical conditions are given below:

Gas Chromatograph and Mass Spectrometry (GC/MS) Conditions:

Gas chromatograph

Mode Split

Inlet temperature 290 °C

Pressure 15.0 psi

Split ratio 10:1

Split flow 29.3 mL/min

Oven

Initial temperature 50 °C

Initial hold time 3 min

Rate 20 °C/min

Intermediate temperature 150 °C

Intermediate hold time 3 min

Rate 4 °C/min

Final temperature 280 °C

Final hold time 17 min

Oven max temperature 280 °C

Column DB-1701 fused silica capillary or equivalent

Length 30 m

Diameter 250 µm

Film thickness 0.25 µm

Column flow 0.7 mL/min

Average velocity 37.0 cm/sec

Mode Constant pressure

Inlet Front

Outlet MS

Outlet pressure Vacuum

Mass spectrometer

Parameters as recommended by manufacturer

3.2 Method II

3.2.1 Sample Preparation & Pretreatment

Another popular method of particulate extraction for bio-markers is repeated extraction with hexane followed by 2:1 mixture of Benzene and 2-propanol by ultrasonication. Each composite sample is placed in a pre-baked jar first, and then 40 ml of hexane is added. After spiking with deuterated standard mixtures, sample is extracted twice with hexane and then three successively extractions by 2:1 mixture of benzene and 2-propanol. Benzene is distilled before use. About 40 ml solvent is used for each extraction. The extraction is conducted under mild sonication with ice bath under room temperature. The extracts of each sample, about 200 ml in total volume, are filtered through pre-baked glass wool and concentrated into 5-10 ml by a rotary evaporator. The volume of the extract is then 5 blown down to the volume of IS spiked (250 μ l) by nitrogen gas purging. It is then equally divided into three aliquots with one aliquot stored in the freezer and one injected directly to GC system for bulk analysis. The third aliquot is derivatized by freshly prepared diazomethane to convert organic acids to their methyl esters. The methylated samples are analyzed by gas chromatography/mass spectrum (GC/MS) for the first round to quantify all compounds except for levoglucosan and cholesterol, and then silylated by adding *N,O*-bis(trimethylsilyl) trifluoroacetamide (BSTFA) plus 1% trimethylchlorosilane (TMCS) (Pierce Biotechnology, Inc.) and analyzed by GC/MS for the second round for the quantification of levoglucosan and cholesterol.

3.2.2 Internal Standards

Two deuterated internal standard mixtures are carefully spiked into the jar, which include 16 isotopically labeled compounds, benzaldehyde-*d*6, dodecane-*d*26, decanoic acid-*d*19, phthalic acid-3,4,5,6-*d*4, acenaphthene-*d*10, levoglucosan-¹³C6 (carbon-13 uniform-labeled compound), hexadecane-*d*34, eicosane-*d*42, heptadecanoic acid-*d*33, 4,4'-dimethoxybenzophenone-*d*8, chrysene-*d*12, octacosane-*d*58, 20R-5 \acute{a} (*H*),14 \acute{a} (*H*),17 \acute{a} (*H*)-cholestane-*d*4, cholesterol-2,2,3,4,4,6-*d*6, dibenz(*ah*)anthracene-*d*14, and hexatriacontane-*d*74. Their concentrations are shown in Table 4 (j).

Table 4 (j): Concentration of the Deuterated Internal Standards

Compounds	IS Concentration (ng / μ L)
benzaldehyde- <i>d</i> 6	10.2
dodecane- <i>d</i> 26	10.9
decanoic acid- <i>d</i> 19 methyl ester	4.5
phthalic acid 3,4,5,6- <i>d</i> 4 methyl ester	4.6

acenaphthene-d10	2.4
levoglucosan-U-13C6	31.3
hexadecane-d34	2.4
eicosane-d42	1.9
heptadecanoic acid-d33 methyl ester	4.4
4,4'-dimethoxybenzophenone-d8	9.6
chrysene-d12	1.8
octacosane-d58	4.9
20R-5 α (H),14 α (H),17 α (H)-cholestane -d4	0.4
cholesterol-2,2,3,4,4,6-d6	9.9
dibenz(ah)anthracene-d14	4.8
hexatriacontane-d74	10.2

3.2.3 Sample Methylation

Diethyl ether from Sigma-Aldrich, Inc. (3 ml) is added into the outer tube of the standard diazomethane generation apparatus, and then 1 ml of diethyl ether and 1 ml of carbitol (diethylene glycol monoethyl ether, 99%) is placed into the inner tube. The lower part of the outer tube, 1-2 inches below the joint of inner and outer tube, was immersed into the ice bath. About 0.4 grams of diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, 99%) is weighed and transferred carefully into the inner tube, and then about 1.5 ml of 5N KOH is injected into the inner tube by using 5 ml syringe through the cap of inner tube. The gas-phase diazomethane is then generated gradually and dissolved in the diethyl ether in the outer tube. The whole reaction is complete after 40 minutes from KOH injection (Nugan and Toofan, 1991). Freshly prepared diazomethane in diethyl ethyl (200 μ L) is transferred into each extract, which contains 10 μ l pre-added methanol. In about an hour, the methylated samples are ready for the first round of GC/MS analysis.

3.3.4 Sample Silylation

300 μ L of BSTFA plus 1% TMCS is added into each extract, which is then immediately placed in an oven at 70°C for one hour (Simoneit and Elias, 2000). The extract is then blown down to about 200 μ L for the second round of GC/MS analysis.

3.3.5 Authentic Standards

Combination of authentic standards solely depends on target analytes fixed by the analysts. For a complete range of analysis in source apportionment study huge number of standards is used even though each and every target analytes could not be analyzed directly by GC-MS analysis due to non-availability of standards in market. Six combinations covering whole range of standards along with their required concentrations are listed in the Table 4 (k).

Table 4 (k): Mix Standard Combinations and Their Concentrations

Compounds	ng/μl	Compounds	ng/μl
STD#1		STD#2	
naphthalene	20.0	decane	20.5
acenaphthylene	40.0	undecane	20.5
acenaphthene	20.0	dodecane	20.5
fluorene	4.0	tridecane	20.5
phenanthrene	2.0	tetradecane	20.5
anthracene	2.0	pentadecane	20.5
fluoranthene	4.0	hexadecane	20.5
pyrene	2.0	heptadecane	20.5
benzo(a)anthracene	2.0	octadecane	20.5
chrysene	2.0	eicosane	20.5
benzo(b)fluoranthene	4.0	tetracosane	20.5
benzo(k)fluoranthene	2.0	octacosane	20.5
benzo(a)pyrene	2.0	dotriacontane	20.5
benzo(ghi)perylene	4.0	hexatriacontane	20.5
indeno(cd)pyrene	2.0	tetracontane	20.5
dibenzo(a,h)anthracene	4.0	tetratetracontane	20.5
bis(2-ethylhexyl)phthalate	20.0	3-methylnonadecane	4.9
butyl benzyl phthalate	20.0	methylnonadecane	4.9
diethyl phthalate	20.0	cyclopenta(cd)pyrene	4.9
dimethyl phthalate	20.0	dibenzo(a,e)pyrene	1.0
di-n-butyl phthalate	20.0	pyrene	1.0
di-n-octyl phthalate	20.0	benzo(a)pyrene	9.8
20R-5 α(H), 14 β(H), 17 β(H)- cholestane	1.0	methylfluoranthene	1.0
20R-5 β(H), 14 α(H), 17 α(H)-cholestane	1.0	methylchrysene	1.0
20S-5 α(H), 14 α(H), 17 α(H)-cholestane	1.0	retene	4.9
20R-5 α(H), 14 α(H), 17 α(H)-cholestane	1.0	anthroquinone	11.8
20R-5 α(H), 14 β(H), 17 β(H)-ergostane	1.0	9-fluorenone	21.7
20R-5 α(H), 14 β(H), 17 β(H)-sitostane	1.0	benz(a)anthracene-7,12-	20.7
17 α(H)-22,29,30-trisnorhopane	1.0	dione	20.4
17 β(H)-21 α(H)-30-norhopane	1.0	1,8-naphthalic anhydride	41.4
17 β(H)-21 β(H)-hopane	1.0	squalene	43.0
17 β(H)-21 α(H)-hopane	1.0	triacontane	38.3
methylfluorene	1.0	1-octadecene	
octylcyclohexane	10.0		
decylcyclohexane	10.0		
tridecylcyclohexane	10.0		
nonadecylcyclohexane	10.0		
norpristane	10.0		
pristane	10.0		
phytane	10.0		
coronene	10.0		
1-methylnaphthalene	2.5		
2-methylnaphthalene	22.4		
2,6-dimethylnaphthalene	24.2		
9-methylantracene	19.2		
squalane	20.9		
STD#3		STD#4	
oxalic acid (C2)	11.8	levoglucosan	1540
malonic acid (C3)	12.7	cholesterol	2000
maleic acid (C4=)	11.6	stigmaterol	1664
fumaric acid (C4=)	12.2	monopalmitin (C16:1)	310

Compounds	ng/μl	Compounds	ng/μl
succinic acid (C4)	12.5	monoolein (C18:1)	310
glutaric acid (C5)	14.8	monostearin (C18:0)	310
adipic acid (C6)	12.8	glycerine	1500
pimeric acid (C7)	12.9		
subiric acid (C8)	12.9	STD#5	
azelaic acid (C9)	11.5	guaiaicol	32.8
19.2 sebacic acid (C10)	11.7	2-methoxymethylphenol	46.0
phthalic acid (1,2)	12.6	ethylguaiaicol	42.1
iso-phthalic acid (1,3)	13.1	propylguaiaicol	39.9
terephthalic acid (1,4)	12.4	eugenol	42.2
1,2,4-benzenetricarboxylic acid	12.3	acetovanillone	53.9
1,2,4,5-benzenetetracarboxylic acid	12.1	3,5-dimethoxy-4-	
methylphthalic acid	12.8	hydroxycinnamaldehyde	19.2
hexanoic acid	38.1	iso-eugenol	22.7
octanoic acid	37.8	vanillin	37.6
decanoic acid	29.9	syringaldehyde	35.3
dodecanoic acid	35.0	4-hydroxy-3-	
tetradecanoic acid	30.7	methoxycinnamaldehyde	24.1
hexadecanoic acid	30.0	3,5-dimethoxyphenol	39.3
octadecanoic acid	23.8	3,5-dimethoxy-4-	
eicosanoic acid	24.6	hydroxyacetophenone	34.3
docasanoic acid	24.9	dimethoxycoumarin	9.2
tetracosanoic acid	28.0	4-methylphenylacetone	10.6
abietic acid	36.0	octadecamide	8.4
octacosanoic acid	30.3	1-phenyl-naphthalene	8.9
triacontanoic acid	29.8		
pinonic acid	45.1	STD#6	
palmitoleic acid (C16:1)	32.1	dehydroabietic acid	54.6
oleic acid (C18:1)	33.7	isopimaric acid	57.3
linoleic acid (C18:2)	28.7	pimaric acid	(unknown)
linolenic acid	35.9	cholesta-3,5-diene	45.4

3.3.6 GC/MS Analysis

The methylated and silylated extracts are analyzed, respectively, by GC-MS equipped with a 30 m length, 0.25 mm i.d., 0.25 μm film thickness HP-5 MS capillary column coated with 5% phenyl methyl siloxane. The GC/MS conditions are as follow: oven temperature isothermal hold at 65°C for 10 minutes, rise to 300°C at rate of 10°C min⁻¹, then isothermal hold at 300°C for 22 minutes. Other settings should include GC/MS interface temperature as 300°C, ultra-pure 'He' as carrier gas with a flow rate of 1.0 ml min⁻¹, split less injection mode, scan range of 50-550 amu, and electron ionization mode with 70 eV. A series of authentic standards pre-mixed with internal standards should be analyzed by GC/MS along with the samples for assisting the identification and quantification of organic compounds in the ambient samples. For those compounds that are not present in the STD series, secondary standards including wax extraction (*n*-alkanes and branched alkanes), wood smoke standard (polycyclic aromatic hydrocarbons (PAHs) and resin acids), and picene standard may be used. Relative response factor (RRF) of each target compound to the respective deuterated internal

standard, which has similar retention time and chemical structure, may be used in the quantification. For those compounds, which RRFs are not available, RRFs from other compounds with similar polarity, retention time, and chemical structure may be used instead. A Possible mode of identification and quantization of molecular markers by GC-MS analysis is presented in Table 4 (I).

3.3 Method III

3.3.1 Sample Preparation

Third method of sample preparation is little cumbersome but produce very good results. Filters are extracted with dichloromethane (CH_2Cl_2) for 24 h in a Soxhlet apparatus. The extract is concentrated on a rotary evaporator and then under a blow-down apparatus with nitrogen to about 2 ml. An aliquot of the total extract is analyzed directly after derivatization with silylating reagent. One quarter of the total extract is used for further fractionation. It is diluted with 30 ml of CH_2Cl_2 and the carboxylic acids are extracted with 20 ml 1M sodium hydroxide solution. The organic layer with the neutral components is retained for further fractionation below, and the aqueous phase is acidified with HCl (pre-extracted with CH_2Cl_2) to $\text{pH} < 2$. The carboxylic acids are extracted with CH_2Cl_2 (20 ml), concentrated as above to 200 μl and derivatized with freshly prepared diazomethane. An internal standard (100 μg squalane) is added and the methyl ester fraction is concentrated to 200 μl for analysis. The neutral extract fraction from the separation above is concentrated to 1 ml and applied to a liquid chromatography column filled with silica gel (7 g, 100-200 mesh). The following eight fractions are eluted sequentially with the solvent mixtures indicated: F1 - 20 ml n-hexane, F2 - 15 ml hexane plus 5 ml toluene, F3 - 10 ml hexane plus 10 ml toluene, F4 - 19 ml hexane plus 1 ml ethyl acetate, F5 - 18 ml hexane plus 2 ml ethyl acetate, F6 - 17 ml hexane plus 3 ml ethyl acetate, F7 - 16 ml hexane plus 4 ml ethyl acetate, and F8 - 30 ml methanol. Fractions 3 and 4 are combined and 5 μg of internal standard added. All fractions are reduced to 100 μl prior to analysis. The internal standard (5 μg squalane) is also added to fractions 1 and 5. The total extract and fractions 6-8 are silylated after addition of the internal standard (F6, F7 - 5 μg , F8 - 10 μg squalane) by addition of 1 ml each of CH_2Cl_2 and BSTFA [bis(trimethylsilyl)trifluoroacetamide]. Each vial is heated at 40°C for 3 h, kept overnight and passed through a mini silica gel column prior to concentration for analysis.

Table 4 (I): A Possible Mode of Identification and Quantitation of Molecular Markers by GC-MS Analysis

Targets	Sources
pentacosane ^b	gasoline vehicles, diesel vehicles
hexacosane ^b	gasoline vehicles, diesel vehicles
heptacosane ^b	gasoline vehicles, diesel vehicles

octacosane ^a	gasoline vehicles, diesel vehicles
nonacosane ^b	vegetative detritus
triacontane ^b	variety
hentriacontane ^b	vegetative detritus
dotriacontane ^a	variety
triacontane ^c	vegetative detritus
20 <i>S,R</i> -5 α (<i>H</i>), 14 β (<i>H</i>), 17 β (<i>H</i>)-cholestanes ^a	gasoline vehicles, diesel vehicles
20 R -5 α (<i>H</i>), 14 α (<i>H</i>), 17 α (<i>H</i>)-cholestane ^a	gasoline vehicles, diesel vehicles
20 <i>S,R</i> -5 α (<i>H</i>), 14 β (<i>H</i>), 17 β (<i>H</i>)-ergostanes ^a	gasoline vehicles, diesel vehicles
20 <i>S,R</i> -5 α (<i>H</i>), 14 β (<i>H</i>), 17 β (<i>H</i>)-sitostanes ^a	gasoline vehicles, diesel vehicles
22,29,30-trisnorneohopane ^b	gasoline vehicles, diesel vehicles
17 α (<i>H</i>), 21 β (<i>H</i>)-29-norhopane ^b	gasoline vehicles, diesel vehicles
17 α (<i>H</i>), 21 β (<i>H</i>)-hopane ^a	gasoline vehicles, diesel vehicles
nonanal ^b	meat cooking
cholesterol ^a	meat cooking
levoglucosan ^a	wood combustion
benzo(<i>b</i>)fluoranthene ^a	wood combustion, gasoline vehicles
benzo(<i>k</i>)fluoranthene ^a	wood combustion, gasoline vehicles
benzo(<i>e</i>)pyrene ^c	wood combustion, gasoline vehicles
indeno(<i>cd</i>)fluoranthene ^c	wood combustion, gasoline vehicles
indeno(<i>cd</i>)pyrene ^c	wood combustion, gasoline vehicles
benzo(<i>ghi</i>)perylene ^c	wood combustion, gasoline vehicles

Note:

^a - May be Identified and quantified by using authentic standard (STD #1-6, IS#1, and IS#2);

^b - May be identified by using mass spectra and quantified using authentic standard with similar structure and retention time;

^c - May be identified by using secondary standards (picene standard, wood smoke standard, and wax extraction) and quantified using authentic standard with similar structure and retention time.

3.3.2 Instrumental Analyses

Bulk analysis by Gas chromatography (GC) may be carried out with a 30 mm 0.25 mm-capillary column coated with DB-5 and a Flame ionization detector. The GC-mass spectrometry (MS) analyses are conducted with a full mass spectra capable to acquire in the electron impact mode (70 eV) using a chemstation/suitable data system. The GC and GC-MS operating conditions for the column oven are the same: initial temperature 40°C for 1 min, program at 10°C/min to 150°C, then at 4°C/min to 280°C, and isothermal hold for 30 min. Compounds are identified from comparison with authentic standards, MS files, literature citations, and by interpretation of MS fragmentation patterns.

CHAPTER – V

Guidelines for Quality Assurance/Quality Control Process Applicable for Analytical Techniques/Tools Specific to Source Apportionment

QA/QC Guidelines for Analytical Processes

1.0 Introduction

Chemical analysis is a critical as well as most complex process in this project. The sample analysis to be performed in a monitoring program must be considered during the planning of the sampling methodology. Sampling and analysis of fine particulate is more challenging than coarse PM due to higher reactivity and volatility of these particles. The particles may often exist in equilibrium between reactants and reaction product. The equilibrium composition of the particle will change in response to change in reactant concentration, temperature, and to a lesser extent, atmospheric pressure. Fine particulates also include a wide variety of unstable and reactive semi-volatile organic compounds.

The standard PM analysis, which has been performed for years, is gravimetric analysis for mass. The primary chemical species of interest are selected elements, sulphates, nitrates and elemental & organic carbon. Chemical speciation analysis can be broken into the three most common categories: elements, ions and carbons. Typical analytical technique/methodology applicable for chemical speciation of particulate matter is described below:

1.1 Elements

In USA for characterization analysis of PM₁₀/PM_{2.5} Energy Dispersive X-ray fluorescence is utilized for the U.S. chemical speciation network. Other analytical tool for element analysis often utilized are proton induced x-ray emission (PIXE) spectroscopy, X-Ray fluorescence (XRF) and proton induced x-ray emission (PIXE) spectroscopy quantify the concentrations of elements with atomic numbers ranging from 11 (sodium) to 92 (uranium). Because these systems in addition to providing a large number of chemical concentrations, neither XRF nor PIXE requires sample preparation or long operator time after it is loaded into the analyzer. Even filters remain intact after analysis and can be used for many additional analyses by other methods. Inductively coupled plasma (ICP), instrumental neutron activation analysis (INAA), AAS are other common options. But AAS has many limitations and ICP could be a compromising solution in this study as an effective technique when many different elements are to be measured at a time.

1.2 Ions

Ionic species are those that are soluble in water. In various dust samples simple ions, such as sodium, magnesium, potassium, and calcium, are best quantified by AAS. But Poly-atomic ions, such as sulphate, nitrate, ammonium, and phosphate are typically quantified by ion chromatography (IC) and automated colorimetry (AC). Some of these methods can also be adapted to separately quantify metal ions with different valence states, such as iron and chromium; whereas hydrogen ion content is determined by pH electrode or by micro-titration.

1.3 Carbon Measurement

For this type of studies, three classes of carbon are commonly measured in aerosol samples collected on quartz fiber filters: (1) organic, volatilized or non-light absorbing carbon; (2) elemental or light absorbing carbon; and (3) carbonate carbon.

Many methods have been applied to the separation of organic and elemental carbon in ambient and source particulate samples. "Organic Carbon" and "Elemental carbon" generally refers to particles that appear black and are also called: Soot", "graphitic carbon" or "black carbon". The various methods include thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods for organic and elemental carbon. The TOR and TMO methods are the most commonly applied.

1.4 Speciated Organic Compounds

The most common method used is the extraction of filter with a suitable organic solvent (or combination of solvents), followed by analysis of the extract by gas chromatography (GC) combined with mass spectrometry (MS) or with other specific detectors. Combined GC/Fourier transform infrared (FTIR)/MS techniques or high performance liquid chromatography (HPLC)/MS techniques are also used.

2.0 QA/QC Requirements

Every measurement consists a value, precision, accuracy, and validity. Quality control (QC) and quality auditing establish the precision, accuracy, and validity of measured values. Quality assurance integrates quality control and quality auditing to determine these four attributes of each environmental measurement.

Quality assurance (QA) integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. The results of quality assurance are data values with

specified precisions, accuracies, and validities. Quality auditing is performed by personnel who are independent of those performing the procedures. A separate quality assurance officer performs these audits.

Though, Quality control (QC) is the responsibility of each executing institutes but still QC given here is intended to prevent, identify, correct, and define the consequences of difficulties that might affect the precision and accuracy, and or validity of the measurements. The QC activities include: (1) documenting standard operating procedures (SOPs) to be followed during sampling, chemical analysis, and data processing; (2) proper equipment selection with their overhaul, repair, acceptance testing, and spare parts requirements; (3) operator training, supervision, and support; (4) periodic calibrations and performance tests which include blank and replicate analyses; and (5) quality auditing.

The following section describes the requirements for SOPs and gives examples on quality auditing. Detailed quality assurance activities and requirements as documented in U.S. EPA's Quality Assurance Handbook.

2.1 Standard Operating Procedures (SOPs)

The first requirement under QA/QC process is to evolve proper SOPs starting from sampling to all analysis and reporting. Standard Operating Procedures (SOPs) codify the actions, which are taken to implement a measurement process over a specified time period. State-of-the-art scientific information is incorporated into the SOPs with each revision. Ideally SOPs may include the following basic elements:

- A brief summary of the measurement method, its principles of operation, its expected accuracy and precision, and the assumptions, which must be met for it to be valid.
- A list of materials, equipment, reagents, and suppliers with specifications.
- Defining the responsibilities of individuals to be responsible for each part of the procedure.
- A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
- Start-up, routine and shut-down operating procedures and an abbreviated checklist.
- Copies of data forms with examples of filled out forms.

- Routine maintenance schedules, maintenance procedures and troubleshooting tips.
- Internal calibration and performance testing procedures and schedules.
- External performance auditing schedules.
- References to relevant literature and related standard operating procedures.

A Quality Assurance Handbook by U.S. EPA, which though addresses PM_{2.5} monitoring with designated FRM or Class I FEMs, but are also applicable to PM₁₀. In addition to the field operations handbook, additional handbooks containing relevant procedures for laboratory operations and data processing/data validation operations are also available for the PM_{2.5} monitoring network. Table 5 (a) gives an example of the outlines of typical SOPs requirements for fine PM chemical speciation. These SOPs are required to be detailed further and reviewed periodically to ensure that procedures specified in the SOPs are actually being followed in field and laboratory operations.

2.2 Quality Audit Mechanism

Next important component under QA/QC is the process management. The quality auditing function consists systems and performance audits.

2.2.1 System Audits

System audits start with a review of the operational and QC procedures to assess whether they are adequate to assure valid data that meet the specified levels of accuracy and precision. After reviewing the procedures, the auditor examines all phases of the measurement or data processing activity to determine that the procedures are being followed and the operational staff are properly trained. The systems audit is intended to be a cooperative assessment resulting in improved data, rather than a judgmental activity.

2.2.2 Performance Audits

Performance audits establish whether the predetermined specifications are being achieved in practice. The performance audit challenges the measurement/analysis system with known standards traceable to a primary standard. For data processing, the performance audit consists independently processing sections of the data and comparing the results. Performance objectives should be specified for the field or laboratory instruments on which performance audits are conducted. Audit findings are compared against these values to decide whether or not remedial action is needed. Example of

a typical outlines of field & laboratory performance audits normally observed in such studies are summarized in Table 5 (b).

Table 5 (a): Examples of Standards Procedures to be Applied in the PM₁₀ Chemical Speciation Monitoring Network

Subject	Observable/Method	DRI Standard Operating Procedure
Chain-of-Custody	Filter Pack Handling Shipping and Receiving	Filter Pack Assembling, Disassembling, and Cleaning Procedure Sample Shipping, Receiving, and Chain-of-Custody
Sample Pretreatment	Potassium Carbonate Impregnation Citric Acid Impregnation Nylon Filter Cleaning Quartz Filter Pre-Firing	Impregnating, Drying, and Acceptance Testing Of Filters For Sampling Gases in Air Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling Pre-Firing of Quartz Fiber Filters for Carbonaceous material Sampling
Chemical analysis	Sample Sectioning Filter Extraction Mass 40 Elements (Na to U) Fluoride (F) Chloride (Cl) Nitrate (NO ₃ ⁻) Sulfate (SO ₄ ⁼) Sulfur Dioxide (SO ₂) as SO ₄ ⁼ Ammonium (NH ₄ ⁺) Ammonia (NH ₃) as NH ₄ ⁺ Soluble Sodium (Na ⁺) Soluble Potassium (K ⁺) High Temperature Organic Carbon (OH) Total Organic Carbon (OC) High Temperature Elemental Carbon (EH) Total Elemental Carbon (EC) Total Carbon (TC)	Sectioning of Teflon and Quartz Filter Samples Extraction of Ionic Species From Filter Samples Gravimetric Analysis Procedures X-ray Fluorescence (XRF) Analysis of Aerosol Filter Samples Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography Analysis of Filter Extracts and precipitation Samples for Ammonium by Automated Colorimetric Analysis Analysis Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy Thermal/Optical reflectance Carbon Analysis of Filter Samples

Aerosol Gas Data and Chemical Data Validation	Data Validation	Dry Deposition Field, Mass, and Chemical Data Processing and Data Validation
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Table 5 (b): Example of Laboratory Performance Audit Observables

Observable	Measurement Device	Performance Test Frequency	Performance Standards	Calibration Frequency	Calibration Standards	Audit Frequency	Audit Standard	Primary Standard
Aerosol Sample Flow	ERT/DRI Modified Sequential Filter Sampler with Bendix 240 Cyclone having SA254 PM ₁₀ inlet and HNO ₃ denuder	Once in day	Calibrated Rotameter	At the Beginning and End of One-Month Sampling Period or When performance Tests Out of Specified range	Calibrated Rotameter	Once/2-months	Mass Flow Meter	Certified root meter
PM _{2.5} and PM ₁₀ Mass	Electromicro-balance	1/10 Samples	NBS Class M Standard Weights	At Beginning of Weighing Session	NBS Class M Standard Weights	Once/2-months	NBS Class M Standard Weights	NBS Class M Standard Weights
PM _{2.5} and PM ₁₀ Elements	XRF Analyzer	3/10 Samples and 1/15 Samples respectively	Replicate NBS Thin Film Standard	Quarterly	Micromatter Thin Film Standard	Once/2-months	Prepared Standard	Thin film Standard
PM _{2.5} and PM ₁₀ Ions(So ₄ & NO ₃) and HNO ₃	Chromatographic analyser	1/10 Samples	Solution Standards	At Beginning of Each Run	ACS Certified Standard Solution	Once/2-months	N/A	ACS Certified Chemicals
Soluble PM _{2.5} and PM ₁₀ Sodium (Na ⁺) Ion	Atomic Absorption	1/10 Samples	Replicate Solution Standards	At Beginning of Each Run	ACS Certified Standard Solution	Once/2-months	N/A	ACS Certified Chemicals
Soluble PM _{2.5} and PM ₁₀ Sodium (K ⁺) Ion	Atomic Absorption	1/10 Samples	Replicate Solution Standards	At Beginning of Each Run	ACS Certified Standard Solution	Once/2-months	N/A	ACS Certified Chemicals
PM _{2.5}	Colormetric	1/10 Samples	Replicate	At Beginning of	ACS	Once/2-	N/A	ACS Certified

Observable	Measurement Device	Performance Test Frequency	Performance Standards	Calibration Frequency	Calibration Standards	Audit Frequency	Audit Standard	Primary Standard
Ammonium And Absorbent NH ₃	Analyzer		Solution Standards	Each Run	Certified Standard Solution	months		Chemicals
PM _{2.5} Carbon	Carbon Analyzer	1/10 Samples	Methane Gas	Once in 2-months or When Performance Test Tolerance Not Met	Methane, CO ₂ Gas and ACS Certified KHP	Once/2-months	Standard KHP Solution	ACS Certified Chemicals

Table 5 (c): Guidelines Primary standards and transfer standards with recommended calibration, performance test and performance audit frequencies for air quality parameters in ambient air

Observable(method)	Allowable Tolerance	Primary Standards	Calibration Standards	Calibration Frequency	Performance Test Standards	Performance Test Frequency	Performance Audit Standards	performance Audit Frequency
NO/NO _x (chemiluminescence)	±10%	NIST-Traceable No mixture	Certified NO mixture and dynamic dilution	Quarterly or when out of specified range	Span with certified NO and Zero With scrubbed air	Daily	Certified NO mixture and dynamic dilution	Yearly
O ₃ (Ultraviolet absorption)	±10%	Primary UV Photometer	Dasibi 1003H UV Photometer	Quarterly Or when Out of specified range	Span with internal ozone generator and zero with scrubbed air	Daily	Dasibi 1008 with teperature and presure adjustments	Yearly
CO (Infrared absorption)	±10%	NIST-Traceable CO mixture	Certified CO mixture and dynamic dilution	Quarterly Or when Out of specified range	Span with internal CO and zero with with scrubbed air	Daily	Certified CO mixture and dynamic dilution	Seasonal
SO ₂ (pulsed Fluorescence)	±10%	NIST-Traceable HC mixture	Certified HC gas dilution	Quarterly Or when Out of specified range	Span with internal HC and zero with with scrubbed air	Daily	Certified HC gas dilution	Yearly
PM ₁₀ and PM _{2.5} flow rate (high volume filter sampler)	±5%	Spirometer (>1,000 L/min)	Calibrated orifice/rootmeter	Quarterly	Calibrated orifice	Monthly	Calibrated orifice/rootmeter	Monthly

Observable(method)	Allowable Tolerance	Primary Standards	Calibration Standards	Calibration Frequency	Performance Test Standards	Performance Test Frequency	Performance Audit Standards	performance Audit Frequency
PM _{2.5} and PM ₁₀ mass and chemistry (low volume filter sampler)	±5%	Certified bubblemeter	Mass flowmeter/ bubblemeter	Quarterly	Calibrated bubblemeter	Monthly	Mass flowmeter	Monthly
Light scattering (nephelometer)	±10%	air/SUVA 134a refrigerant	Clean air/SUVA 134a refrigerant	Monthly	Clean air/SUVA 134a refrigerant	Weekly	Clean air/SUVA 134a refrigerant	Yearly
Light absorption (aethalometer)	±5%	Neutral Density Filter	Neutral Density Filter	Quarterly	Neutral Density Filter	Weekly	Mass flowmeter	Yearly
Mass (electrobalance)	±10%	NIST Class 1.1 weights	NIST Class 1.1 weights	3Months	NIST weight	10 Samples	NIST Class 1.1 weights	Monthly
Total elements (X-ray Fluorescence)	±5%	Std.Polymer films, NIST impregnated glass	Micromatter film deposits	6 months or when out of specified range	Multi-element impregnated glass	15 Samples	Micromatter film deposits	Yearly
Anions and cations (ion Chromatography)	±5% µg/mL	Mineral salt solution	Salt solution	100 samples	Mixed salt solution and distilled water	10 Samples	Mixed salt solution	Yearly
Carbon (Thermal/Optical)	±0.20% µg/cm ²	NIST CO ₂ and CH ₄	Pthalate and sucrose solutios	3 months or when out of specified range	Methane	Every Sample	Pthalate and sucrose solutios on filters CO ₂ and CH ₄	Yearly

3.0 QA/QC Requirements for Analytical Procedure

A comprehensive Quality Assurance/Quality Control plan (QA/QC) is backbone to generate healthy data. The QA/QC plan includes sample preparation bias, duplicate analysis precision, analysis bias, precision of the response factors from calibration curves, and contaminant in trip blanks. Most of the contents in the QA/QC plan should be addressed.

3.1 Parlor Blank Analysis

Regarding parlor blank samples, one or two trip blanks could be collected for each season, which make a total of 7% blanks over the entire samples. The trip blanks are identical quartz fiber filters going through the same pretreatment, storage and transportation procedures as the filters for sampling, but no air drawn through the filter.

The objective of collecting trip blanks is to demonstrate that the sample handling protocol for the molecular markers is within acceptable low limits for organic contaminants. The trip blanks are the same type of quartz fiber filters going through the same pretreatment, storage and transportation procedures as the filters for sampling, but no air should be drawn through the filter. The blank filter is never exposed to ambient air.

In one such study prior to sampling, filters were baked out at 600°C for three hours to minimize the organic background contaminants. Then trip blanks could be extracted with the same method and analyzed by the same protocol as the samples to determine the background level of possible contaminants. The recovery standards and internal standard added onto the blank samples filters prior to extraction. The framework for "Performance Audit" applicable to such studies is given as Table 5 (c).

3.2 Precision and Bias of Analytical Measurements

This work provides an in-depth study of the analytical precision and bias for the measurements of the organic molecular source markers in the atmospheric particles. The knowledge of the measurements precision and bias can be used to evaluate an analytical method. It indicates the quality of the measurements and to what extent the measurements can be trusted.

Analysis Precision of the Samples according to the Quality Assurance plan should be determined by duplicating the analysis for every tenth sample. Precision was expressed by as the average relative range (relative percent difference) of duplicate analyses.

Data Validation & Data Processing Requirements

4.1 Database Requirements

Dust characterization/ speciation data processing consists following six general tasks:

Recording: The relevant information obtained at the time an operation is performed is registered on a data sheet, data logger, or other transfer medium.

Input: The data are transferred from the recording medium into computer-accessible files.

Merging: Data from various files pertaining to an individual sample or sampling day are retrieved and related to each other. So, various files are merged.

Calculations: Data items are combined in mathematical expressions to yield a desired result. These include pollutant concentrations, accuracies, and precisions.

Data Validation: Data are verified against earlier or redundant recordings, with calibration and operating records, and with each other.

Output: Data are arranged into desired formats for input to data interpretation and modeling software. The database management system is required to fulfill the following:

- Quantitative and descriptive information could be recorded.
- Data from a number of sources must be merged in an efficient and cost-effective manner.
- Input data required by models should be easily accessible directly from the database.

4.2 Data Validation

A measurement has four attributes: (1) value – the center of the measurement interval; (2) precision – the width of the measurement interval; (3) accuracy – the difference between measured and reference values; and (4) validity – the compliance with assumptions made in the measurement method.

The typical components for ensuring precision, accuracy, and validity of ambient measurements of PM_{10} are as follow:

- Measurement method is the combination of equipment, reagents, and procedures, which provide the value of a measurement.
- Measurement method validity is the identification of measurement method assumptions, the quantification of effects of deviations from those assumptions, the determination that deviations are within reasonable

tolerances for the specific application, and the creation of procedures to quantify and minimize those deviations during that application.

- Sample validation is accomplished by procedures which identify deviations from measurement assumptions and assign flags to individual measurement for potential deviations from assumptions.
- Completeness measures how many environmental measurements with specified values, precisions, accuracies, and validities were obtained out of the total number attainable.

Data validation is also an important function of data processing. Sample validation consists procedures, which identify deviations from measurement assumptions and procedures. For the data validation process three levels of validation are desirable, which will result in the assignment of a rating to each measurement: (1) valid; (2) valid but suspect; or (3) invalid.

Level I sample validation takes place in the field or in the laboratory and consists the following:

- Flagging samples when significant deviations from measurement assumptions have occurred;
- Verifying computer file entries against data sheet;
- Eliminating values for measurements, which are known to be invalid because of instrument malfunctions;
- Replacement of data from a backup data acquisition system in the event of failure of the primary system; and
- Adjustment of measurement values of quantifiable calibration or interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master database. Level II applies consistency tests based on known physical relationships between variables to the assembled data. Chow et al. (1994) illustrate several internal consistency checks that can be applied to evaluate validity when different particle size fractions are measured and submitted to chemical analyses. These include:

- Comparisons between mass and chemical concentrations in different size fractions (e.g., $PM_{2.5-10}$ concentrations must always be less than or equal to PM_{10} concentrations) in dichotomous sampler sampling;
- Comparisons between mass concentrations and the weighted sum of chemical species;
- Charge balances between anions and cations; and
- Comparisons between concentrations of the same species measured by different analysis methods (e.g., sulfate and chloride by IC and total sulfur and chlorine by XRF or PIXE, soluble sodium and potassium by AAS and total sodium and potassium by XRF or PIXE).

Level III sample validation is part of the data interpretation process. The first assumption upon finding a measurement inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause. Unusual values are identified and recorded during the data interpretation process as the following: (1) extreme values; (2) values which would normally track the values of other variables in a time series; and (3) values for observables, which would normally follow a qualitatively predictable spatial or temporal pattern. Data validation actions at each level are recorded in a data validation summary, which accompanies the database. Database records contain flags to identify the level of validation, which they have received at any point in their existence.

4.3 Data Processing

Data processing and validation requires the following:

- Assigning of the identification (ID) codes to substrates;
- Field data recording of the IDs and their corresponding sampling sites, sampling dates, sampling times, sampling durations, sample flow rates, and deviations from normal sampling procedures;
- Laboratory instrument recording of analytical outputs;
- Level I data validation, flagging, and editing of these individual data files;
- Merging field and laboratory data for sample sets;
- Level II data validation, editing, flagging, and re-analysis;
- Calculation of ambient concentrations and precisions; and
- Formatting and reporting of concentrations, precisions, and data validation activities. Field data are entered into computerized data forms. Substrate IDs can be bar-coded and then entered with a scanner rather than being typed.

A database structure, which contains fields for chemical concentrations and their uncertainties are to be formed. Each record contains sample IDs, sample volumes, sample times, sampling sites, and sampling dates are integrated into this structure from the field file. All other fields contain the missing data default value. These defaults are replaced by laboratory analysis data as they become available. In this way, it is always possible to determine which analyses have been completed and which have not. Besides the laboratory chain-of-custody database records the disposition of each sample and this database can be consulted to determine the fate of missing values in the master database. This independent tracking is needed to prevent sample IDs from being mixed up.

Every laboratory analysis instrument can be linked to IBM-PC compatible computers, and data should be recorded in Xbase (*.DBF) or ASCII text files. Even barcode readers can be used to enter each analysis ID for an analysis

run. Samples are keyed to sample ID codes, and database programs associate records in the laboratory files with data in the master file. In short, proper coding and recording is essential to ensure proper data processing. These programs also replace the defaults in the master data file with the laboratory values. Separate flags are entered at the time of analysis to indicate if a sample is an ambient sample, a source sample, a field blank, a laboratory blank, a replicate, a re-run, a performance test standard, or an audit standard. These flags are used to separate these quality control values from the individual database to generate quality control charts and precision estimates.

When data for a record have been assembled, Level II data validation comparisons should be conducted. These additional validity checks should be applied to chemically-specified particle samples whenever possible. Statistical summaries scatter plots, and time series plots of selected species concentrations are produced to identify outliers for investigation and potential re-run. A data validation summary is maintained in the character field associated with each record to provide a traceability trail for data adjustments, replacements, or deletions. When sample concentration data have been assembled, the database program creates another database of ambient concentrations. Propagated precision and blank subtraction calculations are made at this stage. The field and laboratory data validation flags are assigned as part of the data validation process. Data validation summaries desirably accompany such a final database report.

CHAPTER – VI

Guidelines on Quality Assurance and Quality Control of Emission Inventory

1.0 Introduction

The systematic collection and collation of detailed information concerning air pollution emissions in a defined impact zones referred to as an “emission inventory” (EI). An inventory should contain as much information as possible on the types of sources as well as their contribution to air pollution in terms of composition and rates of discharge for individual pollutants. This should be supplemented by information on the number, geographical distribution of sources and a description of processes, raw materials & control measures.

The inventory in principal should be kept up to date, not only to allow the effectiveness of the local control programme to be evaluated periodically and modified, if necessary, but also to take into account the changing character of pollution source in a rapidly expanding technology and development. While the inventory primarily focuses on the impact zone, attention must also be paid to emission sources lying out side the area but may contribute significantly to the air quality in study area. Although man-made sources of pollution will receive most attention, the contribution made by natural sources in certain cases, must be addressed too.

Various EI are able to provide:

- A reliable estimate of emissions of different pollutants.
- The spatial and temporal distribution of pollutants governed by source, activities and socio-economic structure.
- The evaluation of time weighted emissions and their distribution.
- Identification and characterization of main sources in study area.
- QA/QC on model predictions or source apportionment estimates.
- Tacking progress towards National Ambient Air Quality Standard attainment and emission reduction.
- Determine compliance with emission regulations.
- Serve as the basis for modeling of predicted pollutant concentrations in ambient air.
- Provide input for human health risk assessment studies.
- Helps to conduct/judge Environmental Impact Assessment (EIA) for proposed new sources.
- Siting ambient air monitoring stations.

2.0 Approaches to Emission Inventory

There are two main approaches that can be followed in estimating emissions: The Top-down approach and the Bottom-up approach.

Top-down: This approach means that an agency develops emission estimates based on national or regional estimates. One scales the national estimates to one's inventory area using some measure of activity data to be directly or indirectly related to the emissions in one's area of study. Typically sales data or per employee, or per capita emission factors are used. For example, the amount of fuel burned in combustion processes can be used to estimate fuel combustion emissions if one has other known information such as an emission factor based on kilogram or pollutant emitted per kiloliter of fuel burned. The amount of gasoline sold at a gas station is another example of activity data used to estimate VOC emissions from dry cleaning facilities if one has an emission factor available based on amount of VOC emitted per person.

Characteristics of a top – down approach for emission inventory are:

- Typically used for inventory of area sources.
- Requires minimum resources by grouping like emission sources together and making use of readily available activity and emission data.
- Used when (1) local data are not available, (2) the end use of the data does not justify the cost of collecting detailed site-specific data.
- Emission factors or national or regional-level emission estimates are used in a state or country based on a surrogate parameter such as pollution or employment in a specific sector.
- One potential problem with this approach is that an emission estimates will lose some accuracy due to the uncertainty associated and the representativeness of the estimates once extrapolated to the local level.

Bottom-up approach: This means one estimates emissions for individual sources and sum all sources to obtain state or country level estimates.

Characteristics of a bottom-up approach for emission inventory are:

- Typically used for inventory of point sources, however, it can be used for inventorization of area sources, when resources are available to collect local activity data through a rigorous survey.
- Requires more resources to collect site- specific information on emission sources, activity levels and emission factors.
- Results are more accurate estimates than a top-down approach because data are collected directly fro individual sources and not derived from a national or regional estimate.

2.1 Modeling Inventories

Modeling Inventories here are to be used as a tool for a number of purposes including diffusion model application, model performance evaluations, projection to future scenarios, evaluation of the impact of rulemaking, evaluation of control measures and technology, receptor modeling reconciliation and determination of design concentrations. One of the major roles for modeling inventories will be for development of control strategy and preparation of city specific Action Plan. Modeling inventories can be based on either allowable or actual emissions, depending on the purpose of the modeling. For instance, modeling inventories should be based on actual daily emissions for model performance evaluation. For control measure evaluation and the attainment demonstration, the modeling emission inventory consists the allowable emissions for the base year and projected allowable for the attainment year. Modeling inventories also have various additional data requirements (e.g. stack parameters). The guideline on ISC3 based Air Quality Models could also be consulted to determine the additional information needed for model inventories. General EI requirements are given in Table 6 (a).

Table 6 (a): Proposed Outline of Inventory Preparation Plan

Introduction

- Define the boundary of the impact zone.
- Describe the basics for the inventory (i.e., previous efforts/information that are viable and related).
- Define how the inventory plan is structured and what it contains.
- Specify who is responsible for the inventory and conduction plan.

Point Source Approach

- How will sources be identified and located?
- What categories will be addressed and why?
- What categories will be excluded and why?
- Define the sources and approaches to use existing data sources.
- Identify data collection methods to be used.
- Provide the basis for the activity level data and emission estimates.
- Provide the basis for control efficiencies.
- Discuss the application and customization plan of default EF (if used) in local conditions
- Indicate the mathematical basis for averaging EI

Area and Mobile Sources Approach

- What categories will be addressed and why?
- What categories will be excluded and why?
- What estimation methods will be used (e.g. various information sources

such as ARAI, Emission Inventory procedures Document, Site Specific traffic Surveys, etc)?

- What methods will be used for collecting activity/commodity level data?
- Provide specification of the mobile source emissions model if used.
- Discuss application of Emission rate (ER).
- Provide mathematical basis for ER and QC.

Documentation Approach

- Describe written presentation and documentation.
- Describe computerized compilations and documentation.
- Describe the data required to be analyzed (as defined by document) and the computerized format (data management) that will be used to submit the data.

QA Plan

- Describe the QA program.
- How will the QA program effect and benefit the inventory.
- Verify adhere to international QA guidance (U.S. EPA, EU)

Uncertainties Assessment/Documentation

QA/QC Guidance

The QA/QC Guidance outlined here reflects practicality, acceptability, cost-effectiveness, existing experience, and the potential for application in a harmonizing manner to all cities. A QA/QC programme contributes to the objectives of *the project*, namely to improve transparency, consistency, comparability, completeness, and confidence in national inventories of emissions estimates.

The outcome of QA/QC process may demand the re-assessment of inventory or source category uncertainty estimates. For example, if data quality is found to be lower than previously thought and this situation cannot be rectified in the timeframe of the current study, then uncertainty estimates ought to be documented and assessed to the extent possible.

Before implementing QA/QC activities, it is necessary to determine which techniques shall be used, and where and when they will be applied. There are number of technical and practical considerations involved in making these decisions. The technical considerations related to the various QA/QC techniques are discussed in general here. The practical considerations involve assessing the practical limitations such as available resources and expertise and the particular characteristics of the inventory etc. The level of QA/QC activities should be compatible with the level of estimate of emissions for different source categories.

3.1 Issues of Representativeness of Emission Inventory

Issues related to representativeness of emission arise because the inventory must capture the emission load data within the impact zone and over the period of inventory. However, measurements are limited by time and space. The data for both of these variables have to be representative of the reality of the spatial and temporal domain considered. An emission factor is considered representative if it is calculated as the weighted average of all the emission factors related to all the different typologies of a given emission source, where the weights are the percentages that different productions/products are the total. Activity data and emission factors may not be available for an impact zone or for a specific category of process. So, there is a need to estimate emissions using default emission factor that may be determined in a different region. This is the process of extrapolation. Otherwise, it may be possible to calculate the value using known as.

There are statistical methods to estimate the uncertainty associated with extrapolation provided the available data are generated by random sampling. If there are sufficient resources, it may be possible to undertake a monitoring campaign and design a stratified sample measurement choosing the most appropriate variables (product, process, plant, territory, population). The whole set can be used to estimate the probability density function and summary statistics. There is a need to establish the representativeness. General requirements of a typical EI are depicted in Table 6 (b).

3.2 QA/QC Planning for Emission Inventory

The first and foremost requirement is the QA/QC planning because implementing QA/QC procedures requires resources, expertise and time. In practice, the QA/QC system is only part of the inventory development process and it is realized that participating organizations do not have unlimited resources. Hence, it is unlikely that inventory agencies will have sufficient resources to conduct all the QA/QC procedures outlined in this chapter on all source categories. Quality control requirements, improved accuracy and reduced uncertainty need to be balanced against requirements for time and cost effectiveness.

So, focusing detailed QA/QC activities on key source categories will lead to the most significant improvements in the overall inventory estimates, However it is desirable to conduct at least the general QA/QC procedures outlined subsequently.

However, it is possible that resource requirements will be higher in the initial stages of implementing any QA/QC system than in subsequent studies. As capacity to conduct QA/QC procedures develops in the participating agency or in other associated stake holder organizations, improvements in

efficiency are expected. So, the capacity building is an important objective of QA/QC application.

General Inventory Level QC procedures, and a peer review of the inventory estimates are minimal QA/QC activities necessary for all inventory compilations. A review of the final inventory report by a person not involved in the compilation is also desirable, even if the inventory was compiled using only general methods. More extensive QC and more rigorous review processes should be encouraged if still better methods are deployed. Availability of appropriate expertise may limit the degree of independence of expert reviews in some cases. But, the review process is intended to ensure transparency and quality.

The participating agency in this project being national level expert agency are responsible for ensuring adequate QA/QC applications and development & documentation of QA/QC plans as well. It is desirable that the participating agency should designate a QA/QC coordinator, who would be responsible for ensuring that the objectives of the QA/QC programmes are implemented.

3.3 First Tier QA/ QC Procedures

The focus of general QC techniques is on the processing, handling, documenting, archiving and reporting procedures that are common to all the inventory source categories. General QC procedures list the general QC checks that the inventory agency should use routinely throughout the conduction of the inventory. Most of the general QC checks shown in Table 6 (b) could be performed by cross-checks, recalculation, or through visual inspections.

Table 6 (b): General EI QC Checks

QC Activity	Procedures
Check that assumptions and criteria for the selection of activity data and emission factors (used if any) are documented.	<ul style="list-style-type: none"> • Cross-check descriptions of activity data and emission factors with information on source categories and ensure that these are properly recorded and archived.
Check for transcription errors in data input and reference.	<ul style="list-style-type: none"> • Confirm that bibliographical data references are properly recorded. • Cross-check a sample of input data from each source category (either measurements or parameters used in calculations) for transcription errors.
Check that emissions are calculated correctly.	<ul style="list-style-type: none"> • Reproduce a representative sample of emissions calculations.
Check that parameter and emission units are correctly recorded and that appropriate conversion factors are used.	<ul style="list-style-type: none"> • Check that units are properly labeled in calculation sheets. • Check that units are correctly carried though from beginning to end of

	<p>calculations.</p> <ul style="list-style-type: none"> • Check that conversion factors are correct. • Check that temporal and spatial adjustment factors are used correctly.
Check the integrity of database files.	<ul style="list-style-type: none"> • Confirm that the appropriate data processing steps are correctly represented in the database. • Confirm that data relationships are correctly represented in the database. • Ensure that data fields are properly labeled and have the correct design specifications. • Ensure that adequate documentation of database and model structure and operation are archived.
Check for consistency in data between source categories.	<ul style="list-style-type: none"> • Identify parameters (e.g. activity data, constants) that are common to the multiple-source categories and confirm that there is consistency in the values used for these parameters in the emissions calculations.
Check that the movement of inventory data among processing steps is correct.	<ul style="list-style-type: none"> • Check that emissions data are correctly aggregated from lower reporting levels to higher reporting levels when preparing summaries. • Check that emissions data are correctly transcribed between different intermediate products.
QC Activity	Procedures
Check that uncertainties in emissions and removals are estimated or calculated correctly.	<ul style="list-style-type: none"> • Check that qualifications of individuals providing expert judgments for uncertainty estimates are appropriate. • Check that qualifications, assumptions and expert judgments are recorded. • Check that calculated uncertainties are complete as far as possible. • If necessary, duplicate error calculation.
Undertake review of internal documentation.	<ul style="list-style-type: none"> • Check that there is detailed internal documentation to support the estimates and enable checks of the emission and uncertainty estimates. • Check that the inventory data, supporting data, and inventory records are archived and stored. • Check integrity of any data archiving arrangements.
Check methodological and diurnal changes	<ul style="list-style-type: none"> • Change the temporal consistency in time series input data for each source category. • Check for consistency in the algorithm/method used for calculations throughout the time series.
Undertake completeness checks.	<ul style="list-style-type: none"> • Confirm that estimates are reported for all

	<p>source categories.</p> <ul style="list-style-type: none"> • Check that known data gaps that result in incomplete source category emissions estimates are documented.
Compare estimates to earlier estimates if any	<ul style="list-style-type: none"> • For each source category, current inventory estimates should be compared with earlier estimates. If there are significant changes or departures from expected trends, re-record and explain any difference.

These necessarily minimum requirements should be applied irrespective of the type of data used to develop the inventory estimates and are equally applicable to source categories where default values or secondary data are used as the basis for the estimates.

Due to the large quantity of data that needs to be checked for many air pollution source categories, automated checks are recommended wherever possible. For example, one of the most common QC activities involves checking that data keyed into a computer database are correct. A QC procedure could be set up to use an automated range check (based on the range of expected values of the input data from the original reference) for the input values as recorded in the database. A combination of manual and automated checks may constitute the most effective procedures in checking large quantities of input data. However, the procedures for such checks are required to be documented.

3.4 QC for Source Emission Inventory

Besides general inventory QC techniques, source category-specific QC procedures are required at specific types of data used in the methods for individual source categories and require knowledge of the emission source category, the types of data available and the parameters associated with emissions. The QC measures, which are specific to source category are applied on a case-by-case basis at least incorporating all key sources.

Source category-specific QC activities include the following:

- Emission data QC
- Activity data QC
- QC of uncertainty estimates

The first two types of QC analysis relate to the types of emissions or source activity data used to prepare the emissions estimates for a given source category. Whereas, the QC of uncertainty estimates covers various activities associated with determining uncertainties in the whole emissions estimates process.

4.0 Emission Data QC

The following sections describe QC checks on the use of default factors, secondary data on emission factors, and direct emission measurements from individual sources (used either as the basis for a city-specific emission factor or directly for emissions estimate).

4.1 Use of Default Emission Factors

Where default emission factors are used, it is recommended that organization responsible should assess the applicability and representability of these factors to national circumstances. This assessment may include an evaluation of national conditions compared to the context of the studies upon which the available default factors were based. If there is insufficient information on the context of the default factors, the inventory agency should take account of it in assessing the uncertainty in emissions estimates. For certain source categories like small scale industries, inventory agencies should consider options for obtaining emission factors that are known to be representative of national circumstances. The results of this assessment should be documented.

If possible, default emission factor checks could be supplemented by comparisons with stoichiometric calculations or earlier plant-level actual measurements to determine their representativeness relative to actual sources in the country. Such supplementary checks are desirable even if data are available to satisfy the local conditions.

4.2 Source-Specific Emission Factors

City-specific emission factors for certain specific sources may be developed by the respective organizations for the selected city based on local prevailing technology in use, science, local characteristics and other local factors. These factors are not necessarily city-specific, but are valid to represent a source category or sub-source category prevailing in that city. The following are the proposed guidelines:

- Perform QC checks on the data used to develop such specific emission factors. If emission factors were developed based on source-level testing, then the inventory agency should check if the measurement programme included appropriate QC procedures or not.
- In case the emission factors are based on secondary data sources, such as published studies or other literature, the inventory agency could attempt to determine whether the QC activities conducted during the original preparation of the data are consistent and applicable. General QC procedures outlined earlier in Table 6 (b) should be applied and any limitations of the secondary data have been identified and documented. The inventory agency could also attempt to establish whether the

secondary data have undergone peer review and record the scope of such a review, if any. If it is determined that the QA/QC associated with the secondary data is adequate, then the inventory agency can simply refer the data source for QC documentation.

- If it is determined that the QA/QC associated with the secondary data is inadequate, then the inventory agency can attempt to have QA/QC checks on the secondary data established. It should also reassess the uncertainty of any emissions estimates derived from the secondary data is to be recorded.
- In case default factors are used then circumstances should be compared with relevant default factors and the characteristics of the studies on which the default factors were based. The intent of this comparison is to determine whether the selected emission factors are reasonable, given similarities or differences between the source category and the 'average' source category represented by the source of default numbers.
- A supplementary step is to compare even common source EF with city-specific factors, if these are to be used in the study. This type of comparison provides an indication of both the reasonableness of the country-specific factor and its representativeness.

4.3 Direct Source Emission Measurements

In certain cases emissions from a specific source category can be estimated using direct measurements in the following ways:

- Sample emissions measurements from a facility may be used to develop a representative emission factor for that individual site or for the entire sector (i.e. for development of a common emission factor representing that category);
- Earlier representative monitoring data may be used to estimate emission rate for a particular process. In theory, the continuous monitoring data can provide a complete set of quantified emission inventory information for an individual facility/process, and does not have to be correlated back to a process parameter.
- Regardless of how direct measurement data are being used, the organization in-charge should review the processes and check the measurements as part of the QC activities.
- In fact direct measurements using standard measurement methods improve the consistency of resulting data and knowledge of the statistical properties of the data. If standard reference methods for measuring specific emissions attributes are available, this process should be

preferred. If specific standard methods are not available, the inventory agency responsible should confirm whether nationally or internationally recognized standard methods are used for measurements and whether the measurement equipment is calibrated and maintained properly.

- For example, ISO has published standards that specify procedures to quantify some of the performance characteristics of all air quality measurement methods wherein the QC aspects such as bias, calibration, instability, lower detection limits, sensitivity, and upper limits of measurement are well defined (ISO, 1994). While these standards are not associated with a reference method for specific emission parameters, they have direct application to QC activities associated with estimations based on measured emission values.
- Where direct measurement data from individual source/city are in question, discussions with experts can be useful to improve the QA/QC practices. There may be significant differences between international or national level default values, these should be further reviewed and checked on calculations. If large differences are observed, it should be explained and documented.

4.4 Emission Factor Comparisons

Another standard QC practice is to compare emission factors for selected source categories with factors previously estimated for the similar sources or against historical trends and or stoichiometric calculations. These comparisons (often referred to as 'reality checks') are required to ensure that the emission factors are not improbable or that they fall within a reasonable and acceptable range. If so, the emission factors developed may be reconfirmed with the activity data before emission inventory is proposed.

After calculating differences, the larger percentage deviations (in any direction) should be flagged. Inspection of the list and graphical presentation of differences (e.g. in a spreadsheet) may be done manually or a dedicated software may be used for flagging and rankings in the list of differences.

It is also desirable to check the annual increase or decrease of changes in emission levels in significant sub-source categories under some source categories. Sub-source categories may show greater percentage changes than the aggregated source categories. For example, total emissions from petrol cars are not likely to change substantially on an annual basis, but emissions from sub-source categories, such as catalyst-equipped petrol cars, may show substantial changes for the future regulatory requirements.

Supplementary emission comparisons can also be performed, if appropriate, including order-of-magnitude checks and reference calculations.

4.5 Order Of Magnitude Checks

Order of magnitude checks look for major calculation errors and unknowingly exclusion of major source categories. Comparisons are made depending on whether the emissions for the source category were determined using a top-down or bottom-up approach. If significant differences are found, further investigation using the source category-specific QC techniques described would be followed.

4.6 Random Calculations Checks

Another emission inventory check can be used particularly for source categories that rely on empirical formulas or default values as the case may be for the calculation of emissions. Where such approaches are used, final calculated emission levels should normally follow stoichiometric ratios and conserve energy and mass in cases where emissions are calculated based on the consumption of a specific commodity (e.g. fuels or other raw material). So, the emissions could be estimated using apparent consumption. However, it is pertinent to mention that discrepancies between inventory data and reference calculations do not necessarily imply that the inventory data are in error but there may be large uncertainties associated with the reference calculations themselves when analyzing discrepancies.

5.0 QC Consideration for Source-wise Activity

The QC is most important for estimation methods as many source emission categories rely on the use of activity data and associated input variables by the inventory agency. Activity data collated either using a secondary data or from site-specific data prepared by own measurements. EI exercise should take into account the practical considerations prevailing in the impact zone when determining the level of QC activities to be undertaken.

5.1 Use of Secondary Activity Data

Primary surveys are recommended for emission inventory. However, where activity data from secondary data sources are must in the inventory, it is desirable for the inventory agency to evaluate and document the associated QA/QC activities at the source of data. This is particularly important for activity data, as the originally prepared document may be applicable for other purposes in most of the cases. Though not always readily available, often sources of data may have their own procedures for assessing the quality independent of the desired end use. The typical general checks have been earlier listed in Table 6 (b).

It is necessary to quote the reference of data source and document the applicability with limitations for use in respective emissions estimates. The inventory agency should also reconsider if any alternative data exist, which can provide better emission estimates. If no alternative data sources are available, the inventory agency should desirably document the

inadequacies associated with the secondary data in QC and comments on Quality Assurance.

5.2 Site Specific Activity Data

It is always preferable to use the site-specific activity data. QC checks should focus on inconsistencies between sites, to establish the cause of errors reflected due to different factors like different estimation techniques, differences in emissions, changed operating conditions, differences in raw material and different control technologies.

The inventory team should desirably establish a proper methodology for measuring activities. If measurements are made by adopting proper survey following a QA/QC, the observations as per general checks (Table 6 (b)) should be recorded. If the Emission Inventory data generated do not fall within acceptable standard, these data should be carefully evaluated and uncertainty estimates documented.

Site-specific activity data checks may also be applied to methods based on raw material usage to evaluate the reasonableness of the production data.

6.0 Reporting of Uncertainties

Uncertainty in inventories primarily arises through three different processes. The sources are:

- Uncertainties due to incomplete, unclear, or faulty definition of an emission or uptake. These are related to completeness and attribution to source categories, which are required to be eliminated as far as possible before undertaking uncertainty analysis.
- Uncertainties caused by variability of the process and products. These are inherent to the emission process and can be assessed by statistical analysis of representative data.
- Uncertainties resulting from the assessment of various processes, or quantity depending on the method used. For example: (i) uncertainties from measuring; (ii) uncertainties from sampling; (iii) uncertainties from incomplete reference data; and (iv) uncertainties from expert judgment made, if any.

Such uncertainties include:

- Personal in measuring, recording and transmitting information;
- Finite instrument resolution or discrimination threshold;
- Inexact values of measurement standards are reference materials;

- Inexact values of constants and other parameters obtained from external sources and used in the data reduction algorithm (e.g. default values from AP-42);
- Approximations and assumptions incorporated in the measurement method and estimation procedure;
- Variations in repeated observations of the emission or associated quantity under apparently identical conditions.
- Rounding off calculated values

While continuous emission measurements can reduce overall uncertainty, it usually has limited application on the evaluation of GHG emissions. In built error sources in sampling may be explained as:

6.1 Random Sampling Error

This uncertainty source is associated with data where random sampling is performed to represent a finite sample size and typically depends on the variations of the population around selected sampling location. The number of data points may also contribute to uncertainty calculation as it is extrapolated to represent the whole study area.

6.2 Lack of Representativeness

This source of uncertainty is associated with lack of complete adherence to the conditions associated with real world emissions of activity. For example, emission data may be available for situations in which a plant is operating at full load but not for situations involving start-up or load changes. In this case, the data are only partly relevant to the desired emission estimate.

Whereas the uncertainties due to expert judgment cannot, by definition, be assessed by statistical means since experts' judgment are only used where empirical data are unavailable.

All of these sources of uncertainty are desirable in the assessment of the uncertainties in inventories.

7.0 Documenting Uncertainties

It is desirable to estimate uncertainties associated with EI (including both for source emission levels and source activity levels). Quantifying uncertainties associated with both are then combined to project the summary levels for the entire inventory. Some of the methods rely on the use of measured data associated with the emission factors or activity data to develop probability density functions from which uncertainty estimates can be made. In the absence of measured data, many uncertainty estimates rely on expert judgment.

However, it is desirable that the uncertainty checks may have to confirm that calculations involved are correct and that there is sufficient documentation. The basis of assumptions for uncertainty estimations should be documented for each source category. If source of error is identified then calculations on source category specific EF are checked and errors are addressed. For uncertainty estimates, if expert judgments are involved then, the qualifications/experience of experts should also be ensured and documented. It is recommended to use QA reviewers who were not involved in preparing same inventory. Preferably, these reviewers would be independent experts from other agencies. In case third party reviewers outside the inventory agency are not available, staff from another part of the inventory agency not involved in this particular study being reviewed can also fulfill QA roles.

It is also desirable for inventory team to conduct a basic expert peer review (Tier 1 QA) prior to submission of EI document in order to identify potential problems and make corrections wherever required. It is also desirable to apply this review to all source categories in the inventory. However, this may not always be practical due to time and resource constraints. Still it is strongly recommended for key source categories.

8.0 Documentation, Archiving and Reporting of EI

As part of general QC procedures, it is also desirable to document and archive all information required to produce a good EI. This includes:

- Assumptions and criteria for selection of activity data and emission factors;
- In case default value of emission factors are used, it can include references for default factors or to published references or other documentation for emission factors used;
- Activity data or sufficient information to enable activity data to be traced to the identified source;
- Information on the uncertainty associated with activity data and emission factors;
- Rationale for choice of methods for primary survey designs;
- Details of electronic database or software used in production of the inventory, including versions, operating manuals, hardware requirements and any other information required to enable their later use;
- Worksheets and interim calculations for source category estimates and aggregated estimates and any re-calculations of previous estimates;
- QA/QC plans and outcome of QA/QC procedures; and
- Any other relevant information/data.

9.0 Assessment, Recording and Propagation of the Uncertainties in Inventories

9.1 Determination and Recording of Uncertainties in Input Data

The measure of every physical quantity (input data) in inventory has some associated sources of uncertainty. In some selected cases, such as the ratio molecular weights, the uncertainty is negligible for the purposes of the inventory but in almost all other cases, the uncertainty requires evaluation.

There are several underlining principles to govern the estimation of uncertainties in input data. In ideal scenario hundreds of measurements validation of it by classical statistical evaluation of confidence intervals is required to minimize uncertainty. However, in of most these cases, the interlinking of data and their varying degrees are difficult to deal with. The ways to tackle these cases should be documented. Few specific cases are as follow:

- Number of measurements;
- Knowledge of extreme values;
- Knowledge of underlying processes affects the quantity and its variance; and
- Expert judgments.

The recording and documentation of information for input data are important in QA/QC to keep transparency in uncertainty analysis.

9.2 Expert Judgment

In situations where it is impractical to obtain reliable data or existing inventory data lack sufficient statistical information, it may be necessary to elicit expert judgments about the nature and properties of the input data.

The key in making estimates of uncertainty by expert judgment or otherwise, is that all possible source of uncertainty are addressed.

CHAPTER – VII

Guidelines on Quality Assurance and Quality Control for Source Profiling

Profiling of the Emission Characteristics of Various Air Polluting Sources – Study Guidance Framework

1.0 Introduction

As it is planned to use Chemical Mass Balance (CMB-8) model in Source Apportionment study, the chemical characteristics of particulate matter emitted from a particular source should be known. It is a prerequisite for input data in CMB – 8 model. Hence, Source profiling is another important task being taken up separately through other agencies. Once developed, these data would be useful for source apportionment studies in future as it would or with normalization satisfy city specific requirements.

2.0 CMB Model Overview

CMB software has evolved over more than two decades to facilitate model application and validation. The Chemical Mass Balance (CMB) receptor model was first applied by Winchester and Nifong (1971), Hidy and Friedlander (1972) and Kneip et al. (1972). The original applications used unique chemical species associated with each source-type, the so-called "tracer" solution. Friedlander (1973) introduced the ordinary weighted least-squares solution to the CMB equations, and this had the advantages of relaxing the constraint of a unique species in each source type and of providing estimates of uncertainties associated with the source contributions. Gordon (1980, 1988) and Kowalkzyk et al. (1978) subsequently applied this method to elemental concentrations measured in source and receptor samples. The ordinary weighted least squares solution was limited and only the uncertainties of the receptor concentrations were considered. The uncertainties of the source profiles, which are typically much higher than the uncertainties of the receptor concentrations, were neglected. The first interactive user-oriented software for the CMB model was programmed in 1978 in FORTRAN IV on a PRIME 300 minicomputer (Watson, 1979). The PRIME 300 was limited to 3 megabytes of storage and 64 kilobytes of random access memory. CMB Versions 1 through 6 updated this original version and were subject to many of the limitations dictated by the original computing system. CMB7 was written in a combination of the C and FORTRAN languages for the DOS operating system. With Windows 3.1, 95, and NT becoming the most widely used operating systems, CMB8 created a user interface for CMB7 calculations using the Borland Delphi object oriented language.

CMB model assumptions are: 1) compositions of source emissions are constant over the period of ambient and source sampling; 2) chemical species do not react with each other (i.e., they add linearly); 3) all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized; 4) the number of sources or source categories is less than or equal to the number of species; 5) the source profiles are linearly independent of each other; and 6) measurement uncertainties are random, uncorrelated, and normally distributed.

The degree to which these assumptions are met in applications depends to a large extent on the particle and gas properties measured at source and receptor. CMB model performance is examined generically, by applying analytical and randomized testing methods, and specifically for each application by following an application and validation protocol. The six assumptions are fairly restrictive and they will never be totally complied with in actual practice. Fortunately, the CMB model can tolerate reasonable deviations from these assumptions, though these deviations increase the stated uncertainties of the source contribution estimates. Section 4 explains these assumptions and summarizes the results of tests that evaluate deviations from them.

The seven-step applications and validation protocol includes : 1) determines model applicability; 2) selects a variety of profiles to represent identified contributors; 3) evaluates model outputs and performance measures; 4) identifies and evaluates deviations from model assumptions; 5) identifies and corrects model input deficiencies; 6) verifies consistency and stability of source contribution estimates; and 7) evaluates CMB results with respect to other data analysis and source assessment methods.

3.0 Scope of Work for Proposed Study

This section describes the types of measurements that are required for both source and receptor input data to the CMB. Receptor data are generated through monitoring and chemical characterization but source data would be a combination of Emission Inventory, Emission Factor and Source profiling. Source profile data shall help to identify possible sources putting an impact on pollution level at receptor site.

3.1 Source Profiles

Source profiles are the mass abundances (fraction of total mass) of chemical species in source emissions. Source profiles are intended to represent a category of source rather than individual emitters. The number and meaning of these categories are limited by the degree of similarity between the profiles. Mathematically, this similarity is termed "co-linearity," which means that two or more of the CMB equations are redundant and the set of equations cannot be solved owing to measurement error. However, CMB

equations shall never be completely collinear in a mathematical sense. If two or more source profiles are “collinear” in a CMB solution, standard errors on source contributions are often very high. Some source contributions may be outlandishly high, while others may be negative. Therefore, determination of degree of co-linearity becomes very important in CMB model validation.

3.2 Typical Emission Sources

Field surveys are essential to identify the source type (from activity and inventory data) and their respective expected chemical species coming out through emission in prevailing conditions at site. There may be numerous sources of individual emitters but once categorized under different types, the overall source categories shall be limited. To make input data useful for receptor modeling, such categories must be grouped into more generalized categories with similar source profiles. For example, a source may often contain separate entries for power generation, industrial and institutional coal combustion. Since these combustion processes, and often the coal, are similar in a given air-shed, it is unlikely that their contributions can be distinguished by the CMB and they must be combined into a “coal-burning category” unless the aim is to assess emissions from such different sources and appropriate tracers/signatures are possible. The actual combinations depend on the profiles available or that are likely to be acquired for a CMB study. The ranges of various typical categories that often contribute towards ambient particulate concentration are:

Vegetative refuge burning and cooking: Fireplaces, wood stoves, prescribed burns, wildfires, char-broiling, meat cooking, garbage or refuge burning, tyre burning. Some of these sub-categories may be important and in some specific studies.

Vehicular exhaust: emissions from different vehicles-fuel technology combinations.

D.G. Sets: Small & medium size commercial D.G. sets are though based on diesel combustion but source emission characteristics may be different. A case to case field monitoring is proposed to be carried out.

Diesel exhaust: Source profile data for heavy and light duty cars and trucks, off-road equipment, stationary engines for pumps and generators, and locomotives are proposed to be generated.

Gasoline exhaust: Heavy and light duty cars and trucks, and small engines. Emissions inventories do not usually contain breakdowns by cold-starts and visibly smoking vehicles, although these might be discriminated by certain organic compounds in a profile. Since leaded fuels are no longer used, there is no need to seek this separation.

Gasoline evaporative emissions: Fueling stations, hot-soak vehicles for VOCs in particular.

Fugitive dust: Paved roads, unpaved roads, agricultural tilling, construction, wind erosion, and industrial aggregate. These can sometimes be divided into sub-categories based on single particle profiles or the measurement of specific mineral composition. City-specific modifications are needed to be done in this case.

Solvents and coatings: Paints, degreasers, and solvents. These can also be broken down into sub-categories, not usually identified in emissions inventories, when the specific types of solvents have been determined (This source is of low priority in this study).

Metals (Copper works, Lead batteries, Iron & steel units, and Aluminum works, if any): These often have similar metal emissions but difference in abundances depending on the process that use these materials can be classified into separate categories. The study area under focus being urban, the large sources of this category are unlikely but small/medium scale industrial units like foundries, cupolas, different metal work plants would also be important source under point source categories.

Aggregate handling: Cement, quarrying, and construction activities. Ores, in particular, are often enriched in the materials being extracted and sub-categories may be defined for these cases.

Others: There may be few city-specific emission sources such as Architectural (i.e., paints), industrial solvents (i.e., cleaning and process solvents, as in printing), dyes, battery handling units in most urban areas. Oil refining or waste oil processing may be important in certain cases. Biogenic emissions may also be significant where forests are lush. Urban distribution stations are important VOC sources.

In addition to these common emission sources to be found in all urban locations, there are many other specific area sources like landfills, where variety of reactive organic gases may accompany the methane, depending on the nature of the landfill wastes and disposal practices.

Note: Based on field survey within zone of influence around each sampling location, a common and city specific list on source categories shall be prepared for all the project cities.

These examples show that there may be similarities in chemical compositions for different sources, using source profiles from one air-shed or time period may not provide a valid CMB apportionment for ambient samples in another air-shed or in another time period. Source emissions of precursor gaseous and primary particles are highly variable due to differences in fuel use, raw

material, operating conditions, and processes. Source and ambient measurements must be paired as far as possible to establish reasonable estimates of source/receptor relationships possibly for a season in one city so as to match the receptor and source dust characteristics.

3.3 Source Profile Normalization Requirements

A source profile shall be created by sampling emissions from a variety of single emitters or small groups of emitters. These samples are then submitted to a variety of chemical and physical analyses to determine those properties that will allow apportion the contributions from the sources they represent and can be distinguished at receptors. Each of these properties is to be normalized to some common property in the emissions from all sources. The two most widely used normalization properties are particle mass and/or total volatile organic compound emissions that accompany the chemical components. Gas or particle species may be normalized to either one of these aggregates, and the selection is made based on the source mixture and objectives of the study.

The focus of study being PM_{10} and $PM_{2.5}$ (limited monitoring), it is logical for normalization to total PM_{10} & $PM_{2.5}$ mass emissions. Besides, the particle mass being well-defined and easy to measure, most particle profiles for a stated size fraction are reasonably comparable, regardless of how they were measured.

Individual profiles shall be formed from individual samples, and the precisions of the numerator and denominator are propagated to assess the individual profile uncertainties. These individual profiles are further composite to obtain the source profiles formats to be used for CMB source apportionment. The simplest composite shall consist the average and standard deviation of abundances for all individual profiles within a group. For example, if ten tests of diesel vehicle exhaust are taken, each abundance is an average of the ten individual abundances and the uncertainty is the standard deviation of that average. Outlier tests are often applied to reject individual profiles that unduly bias to average standard deviation of the profile. In general, abundances that exceed two standard deviations calculated without the inclusion of that abundance shall be omitted from a profile (with 95% confidence level). There are always some outliers in any series of source tests, usually for reasons that can never be determined. For this reason, it is important to obtain ten or more samples that run the range of operating conditions and fuels in an area to estimate source profiles. But, better statistical analysis is welcome.

3.4 Compatibility of Terms in Source Profiling/Ambient Concentration/Emission Rate Measurements

Several terms have been earlier used inconsistently but interchangeably to describe different fractions of atmospheric dust particularly concerning organic material. Common definitions and units are essential for ambient concentrations, source profiles and emissions rates, which should be understood. The following terms are adopted for use in "Source Profiling" studies:

C_x: Molecules containing x carbon atoms (e.g., C₇ means the molecule contains seven carbon atoms). This notation is useful since many sampling and analysis techniques respond to different numbers of carbon atoms rather than to specific compounds.

Organic carbon: Gases and particles containing carbon and hydrogen atoms in various ratios. Organic compounds found in ambient air may also be associated with other elements and compounds, particularly oxygen, nitrogen, sulfur, halogens, and metals. Various operational definitions based on measurement method are applied to different subsets of organic compounds like IMPROVE protocol of OC/EC analysis can provide data for 4 OC fractions (OC1, OC2, OC3 & OC4).

Inorganic carbon: Carbon dioxide and carbon monoxide are the most abundant inorganic gases found in the atmosphere, while amorphous graphite is the most common particulate component. Particulate elemental carbon is operationally defined by optical and combustion methods (Chow et al., 1993) and it contains heavy organic material as well as inorganic carbon. Only TOR/TOT method of Carbon estimation can overcome bias for pyrolytic carbon. IMPROVE protocol of OC/EC analysis can provide data for 3 EC fractions (EC1, EC2 & EC3).

Hydrocarbons: Organic compounds that consist only of carbon and hydrogen atoms.

Reactive organic gases (ROG): Organic gases with potential to react (<30 day half-life) with the hydroxyl radical and other chemicals, resulting in ozone and secondary organic aerosol. The most reactive chemicals are not necessarily the largest contributors to undesirable end-products; however, this depends on the magnitude of their emissions as well as on their reactivity.

Total organic gases (TOG): Organic gases with and without high hydroxyl reactivity. TOG typically includes ROG plus methane and halocarbons.

Non-methane hydrocarbons (NMHC, also termed "light" hydrocarbons): C₂ through C₁₂ (light) hydrocarbons collected in stainless steel canisters or other activated adsorption media and measured by gas chromatography with flame ionization detection (GC-FID) by standard method such as EPA method TO-14, TO-1 or TO-2. NMHC excludes carbonyls, halocarbons, carbon dioxide, and carbon monoxide even though some of these may be

quantified by the same method. NMHC is most often used to quantify ozone precursors.

Halocarbons: HC with chlorine, fluorine, or bromine compounds attached, quantified from canisters by gas chromatography with electron capture detection (GC-ECD). Methylchloride, methylchloroform, methylbromide, and various refrigerants (Freon-12, Freon-22, SUVA) are most commonly measured (Rasmussen et al., 1980; Khalil et al., 1985; Wang et al., 1997). These compounds have long lifetimes and are not reactive enough to cause major changes in troposphere ozone and secondary organic aerosol. Halocarbons have been implicated in the long-term depletion of stratospheric ozone (Lovelock et al., 1973).

Heavy hydrocarbons: C10 through C20 hydrocarbons collected on suitable adsorbing substrate such as Tenax and analyzed by thermal desorption and gas chromatography. These are sometimes termed "semi-volatile" compounds because the >C15 compounds are often found as both gases and particles. Most of the total hydrocarbon mass is measured in the gas phase.

Carbonyls: Aldehydes and ketones, the most common being formaldehyde, acetone, and acetylaldehyde. Carbonyls are operationally defined as C1 through C7 oxygenated compounds measured by collection on acidified 2,4-dinitrophenylhydrazine (DNPH)-impregnated C18 cartridges and analyzed by high performance liquid chromatography HPLC with UV detection.

Non-methane organic gases (NMOG): NMHC plus carbonyls.

Semi-volatile organic compounds (SVOCs): Particles and gases collected on filters backed with solid absorbent such as polyurethane foam (PUF) and XAD, extracted in a variety of solvents, and analyzed by gas chromatography/mass spectrometry or HPLC/UV. This class includes compounds such as polycyclic aromatic hydrocarbons (PAHs), methoxyphenols and lactones, pesticides, and other polar and non-polar organic compounds. The heavy hydrocarbons are often classified as SVOCs, but they are given a separate identity here for precision and clarity.

Volatile organic compounds (VOCs): NMHC plus heavy hydrocarbons plus carbonyls plus halocarbons, typically <C20. VOC has been imprecisely used to describe most of the other categories defined above.

Table 4 (b) depicted in Chapter IV also provides an example of typical abundance of elements identified in earlier studies found useful for CMB modeling, which include list of chemicals/elements (Table 4 (b) through Table 4 (e) in Chapter IV) expected in particles/aerosols in different emission sources.

Besides organic fraction mentioned above, there will be other parameters (physical & chemical) requiring analysis. The typical matrix of chemicals is given under:

Geological Material/Elements: Suspended dust consists mainly of oxides of aluminum, silicon, calcium, titanium, iron and other metal oxides. The precise combination of these materials depends on the geology of the area and industrial process such as steel-making, smelting, mining and cement production.

Organic carbon: Particulate organic carbon consists hundreds, possibly thousands, of separate compounds. The mass concentration of organic carbon can be accurately measured by TOR TOT method.

Elemental carbon: Elemental carbon is black, often called "soot". Elemental carbon contains pure graphite carbon, but it also contains high molecular weight, dark colored, non-volatile organic materials such as tar, biogenic and coke. Carbonate Carbon is another species of inorganic fraction that plays important role in altering pH characteristics and synergistically affects secondary aerosol formation.

Nitrate: Ammonium nitrate is the most abundant nitrate compound resulting from reversible gas/particle equilibrium between ammonia gas, nitric acid gas and particulate ammonium nitrate.

Sulphate: Ammonium sulphate, ammonium bisulphate and sulphuric acid are the most common forms of sulphates found in atmospheric particulates, resulting from conversion of gases to particles.

Ammonia: Ammonium sulphate, ammonium bisulphate and ammonium nitrate are the most common compounds.

Sodium Chloride: Salt is found in suspended particles near sea coasts, open playas, and after de-icing material is applied.

Liquid Water: Soluble nitrates, ammonium, sodium, other inorganic ions and some organic material absorb water from the atmosphere.

3.5 Typical Sampling Methods for Source Profiling

There are several methods used earlier to extract samples from sources, having similar chemical and physical properties to those found at a receptor. In each of these methods, emitted particulate matter or gases are collected on substrates or in containers that are subsequently analyzed for chemical content in a laboratory.

A recommended source sampling method would allow for chemical and physical transformations of source emissions to occur prior to sample collection. The sampling would at least be able to quantify the precursors of the receptor profile so that a theoretically or empirically derived transformation could be applied. The typical methods used to sample source emissions in receptor model studies include: 1) hot exhaust sampling; 2) diluted exhaust sampling; 3) ground-based sampling of single-source dominated air; and 4) grab sampling for re-suspension.

Hot exhaust sampling: Hot exhaust sampling is well established for determining the emission rates of criteria pollutants, including primary particulate matter. Hot exhaust does not permit the condensation of vapors into particles prior to sampling, and it sometimes interferes with the sampling substrate or container. Although most commonly applied in emission monitoring, hot exhaust sampling rarely yields profiles that represent profiles as detected at receptors, because it does not account for transformations, which might take place when the emissions are cooled down. Hot exhaust sampling is not appropriate for receptor modeling studies but in certain high stack emissions this may be an option.

Dilution sampling: Dilution sampling has been developed to bring hot exhaust effluents to ambient temperature by mixing with clean, cool air dilution. Here, the hot exhaust gases are dragged into a chamber and get mixed with filtered ambient air. After an aging period, the particles are drawn through a size-selective inlet and onto substrates or into sample containers to represent ambient condition and allow transformation. Multiple samples for different chemical analyses are obtained simultaneously or via sequential sampling of the same gas stream. Stainless steel or Teflon-coated chambers are used where species might be reactive. Recent sampling systems (like VOST) acquire gaseous as well as particulate samples that can be used to apportion both particles & VOCs. Diluted exhaust samplers lend themselves to laboratory simulations of emissions from individual sources. For example, wood stoves or fire places can be operated under different burning cycles with emissions sampled from a dilution tunnel. Dilution tunnels attached to a dynamometer for vehicle exhaust testing serves the similar purpose.

Ground-based source sampling: This is identical to receptor sampling, but it is applied in situations for which the air being sampled is known to be dominated by emissions from a given source. The requirements of this method are: 1) meteorological conditions and sampling times to represent domination by a particular source; 2) samples short enough to take advantage of those conditions; and 3) a minimum of other interfering source contributions. Kerbside monitoring on a heavy traffic road is a good example to represent road lifted dust.

Grab sampling and re-suspension in the laboratory (Chow et al., 1994) is most often applied to fugitive dust sources that are usually not ducted and require

numerous samples to represent a large population. Grab sampling and re-suspension involves: 1) removal of a precipitated residue of the emissions; 2) re-suspension and sampling onto substrates through size-selective inlets; and 3) analysis for the selected species. A simple sample swept, shoveled, or vacuumed from a storage pile, transfer system, or road bed can be taken to represent these source types. Five to ten different samples from the same source are averaged to obtain a representative source profile. This method is semi-established, or at least as established as the chemical and physical analyses applied to it, because procedures are widely accepted and results are reproducible within the method, though not necessarily among methods. The main advantages of grab sampling and re-suspension are simplicity, reliability, and low cost.

Note: One or more of the above monitoring systems shall be suitably adopted for different source sampling.

4.0 Sources Profile Database

Selection Criteria are not aimed at to catalog all measurements of particulate matter earlier done in such studies. Often, various international studies specify the following criteria for a typical particulate matter database:

- A large number of chemically and size classified concentration
Mass, elements, ions and carbons have been found to be most easily measured and useful species while PM_{10} and $PM_{2.5}$ are most useful size fractions.
- Comprehensive coverage with respect to time, space and in the case of source samples the operating conditions
Source samples need to represent the full range of profile from a given source category so that uncertainties can be estimated for input in receptor models.
- Documentation of measurement methods, locations and sampling times
Written records of the entire experimental program, which acquired the database, are essential to its extended use. In the case of source characterization, this information should include the fuels, operating cycle, type of facility, location and time of test.
- Quality control and quality audits
Replicates, field blanks and independent verifications of field monitoring and laboratory operation are needed to assure compliance with the stated procedure.

- Precisions and accuracy estimates
State of art receptor modeling treats measurement uncertainties as a part of the input data and returns uncertainties on source contribution estimates derived from those inputs. Quality control and quality audit data should be processed to quantify these uncertainties.
- Validation of summaries or flags.
Validation criteria should have been applied to every sample, and the results of that validation should be reported with the data.
- Availability in computerized formats
For research purposes, data cannot be proprietary or secret. If it is not in computerized and documented form (preferably accessible by desktop computers) the expense of putting it in such form usually outweigh the potential benefits derived from examining the data.
- Availability of reference describing data and its use
No data sets are included without the identification of a reference to written documents which specify their origin and methods used to acquire them. In most cases, the references are in the public record as journal articles, proceeding papers, formal reports or publicly-accessible memoranda.

4.1 Requirements for Description of Database

The data profiles are required for application of Receptor Model that is CMB8. So, database are to be collected in or X-base (*.DBF) format, using FoxPro2.0 (Fox Software, Inc., 1991) a commercially available relational database management system. This system can be implemented on most IBM PC- compatible desk computers and can handle 256 fields upto 4,000 character per record and up to one billion records per file. The database files can also be read directly into a variety of popular statistical, plotting, database and spreadsheet programs without any specific conversion software.

The structure of each database file can be established by defining the fields for data to be stored. One of the five field types- character, data, numerical, logical or memo can be assigned to each observable. Sampling sites and particle size fractions to be defined as "Character" fields, sampling dates are defined as "Date" fields, and measured data are defined as "Numeric" fields. "Logical" fields are used to represent a "yes" or "No" value applied to a variable and "Memo" fields are to be designed to accommodate large blocks of textual information. The same would be used to document the data validation process. Each measurement method associated with a separate validation field to document the sample validity for that method. These flags, as well as the comments should to be recorded in validation flags summary file which accompanies each record.

CHAPTER – VIII

Quality Assurance and Quality Control (QA/QC) Guidelines on Model Application

1.0 Introduction

The use of computer models is an activity that requires an extremely high degree of quality QA/QC and this guidance document would specify the types of QA/QC procedures that should normally be followed. Modeling input data for QA/QC and output data for comparison against ambient air quality objectives, standards or guidelines are to be streamlined to reduce review time while ensuring that the simulation is valid. This could involve creating a post-processing program that would also do quality assurance checks on the model output file including such simple things as:

- Plotting model topography vs. real topography;
- Analysis of meteorological inputs vs. standardized regional datasets;
- Order of magnitude analyses of concentrations vs. emissions; and
- Other methods locally devised

Two models are proposed in this project. One is “Receptor Model” (CMB8) and other is “Source diffusion model” (ISC3).

The data requirement along with QA/QC requirements have been addressed in various other Chapters. So, the discussions here are confined to “Dispersion Model” applications highlighting the model input requirements and checklist designed on data inputs for the soft-ware run for the model application.

2.0 Data Input Requirements

Each of data input issues are summarized and are discussed below.

2.1 Duration of Data

Consistent with the general practice data for modeling purposes is one year, to a maximum of 5 years. However, the guideline does not explicitly state that a minimum of one year of data is a requirement, or what proponents are to do if even one year of data is not available. However, the guideline suggests that proponents may look to available data from nearby meteorological stations (e.g., airport stations) if it can be demonstrated that such data are representative of conditions for the area to be modeled. It is also proposed a minimum one year of representative on-site data, or 5 years of local airport data, will be required for permitting purposes. If the decision criterion for the acceptability of air quality impacts is based on percentile value such as the

95th, 98th, or 99th percentile, then a modeling analysis based on one year meteorological data may be equivalent to that would be expected to occur for 5-year data.

2.2 Representativeness of Data

The decision on suitability of alternate site data for the modeling application is left to the subjective and professional judgment of qualified individuals as an integral part of the decision making process in evaluating whether available meteorological data are representative of the area of interest or not. However, in this project, it is clearly indicated that simultaneous (3 seasons) one-year of on-site data is the default, first choice option for modeling purposes.

2.3 On Site Data Collection

The guidance states that the use of on-site meteorological data is 'ideal', but not an essential 'requirement'. As discussed above in previous section, this leaves the door open for proponents to look into alternate data sources but on-site data collection is mandatory, if suitable alternate station data cannot be obtained.

In its most recent meteorological monitoring guidance document and in the Guideline on Air Quality Models, the USEPA recommended the use of "site-specific" as the qualifier for representativeness of data instead of "on-site" in recognition of the fact that location of a meteorological tower within the property boundaries of a facility is neither a requirement for, nor a guarantee of the representativeness of the data for site specific applications. It is observed that the MWLAP also adopt this new language convention.

2.4 Atmospheric Stability Classification

The guidance identifies the Turner method as the most frequently used approach, but cities lacking the hourly cloud cover data have significant limitation to many applications. The guidelines also discuss alternative methods using solar radiation and temperature gradient (SRDT), and turbulence fluctuations (ó A and ó E). However, in this project it is recommended to follow CPCB guidance document on modeling. The guidance document states that the need to define atmospheric stability class using the various methods on solar radiations.

2.4.1 Mixing Heights

Approach options to determining mixing heights for use in dispersion modelling include: 1) conducting profiling studies using mini-sonde or tether-sonde balloons, 2) installing a SODAR monitor following EPA (1995) guidance, 3) calculating the screening-level mixing heights using MWLAP's program

MIXH. But, in this project it is recommended to use CPCB monograph on mixing height, which is in harmony of the practices in India and further, this information is not highly critical for low height sources and longer average period.

2.4.2 Treatment of Light Wind Conditions

This is very important for high calm percentages generally encountered in India. The proposed method is that the total calm period should be randomly distributed for the respective calm periods recorded.

2.5 Geo-physiological Data

While digital terrain data is being used in the ISC3 model in the past, the correct specification of terrain elevations, land/water boundaries and land use is of critical importance to more technically advanced models such as AERMOD and CALPUFF. However, It is desirable do some basic QA/QC on the project geophysical data before running any dispersion model. The simplest form of QA/QC is to take the model output terrain and compare it to a map. It should be a basic requirement of the guidelines that the documentation supplied in support of the modeling analysis include such a comparison.

2.5.1 Emission Rates

The model guideline states that source data should reflect emissions at maximum capacity or production (e.g., maximum permitted in-stack concentration multiplied by the total gas volume at normal operating conditions). Since maximum air quality impacts may not occur at maximum operating conditions, the guideline states that the modeling could also be done for 75% and 50% capacity in screening mode for intermediate and complex terrain situations just to have more confidence on predictions. In addition, citing the precautionary principle, the guideline desires that worst-case scenarios for abnormal or upset operating conditions shall also be evaluated.

3.0 Checklist of Input Data (ISC3/AIRMOD models)

This checklist should not be considered exhaustive for all modeling studies – it provides the essential requirements for a general assessment. All sites can have site-specific scenarios that may call for additional information and result in a need for different materials and data to be submitted.

3.1 General Information

Submittal Date:

Facility Name:

Facility Location:

Modeller Name:

3.2 Air Dispersion Model Options

a) Model selection:

- ISC 3
- AERMOD – most recent version
- SEC3 – Specify reasons for Use

b) Regulatory options used:

- Provide justification for use for strategic planning options. Note that use of non-regulatory options requires prior approval from the regulatory agency.

c) Dispersion Coefficients:

- Urban
- Rural
- Urban or Rural conditions can be determined through the use of an Area Land Use or Population Density analysis.

d) Coordinate System

- UTM Coordinates
- Local Coordinates
- Other

Notes: AERMOD requires UTM coordinates be used to define all model objects. Use of an alternative coordinate system requires pre-consultation with the regulatory agency.

3.3 Source Information

a) Source Summary

Summarize the locations, emission rates and release parameters for all point, area, and volume sources included in the modeling analysis. Information required is summarized in the tables below, each of which can be repeated as often as needed.

b) Point Sources Summary

Name (ID) of the Source:

Location:

X(m):

Y(m):

Name of Pollutant Modeled Emission Rate [g/s]

1)

2)

3)

4)

5)

Note: If additional pollutants are modeled, provide a tabular emission summary similar to the above for all pollutants.

Following detail information of stack has to be collected:

Stack Height [m]:

Stack Diameter [m]:

Stack Exit Temperature [K]:

Stack Exit Velocity [m/s]:

Horizontal Stack

Rain Cap Present

Notes: If the stack is either horizontal in orientation or has a rain cap, stack parameters must be adjusted as per guidance.

b) Area Sources Summary

Source Name:

Location (Southwest Vertex):

X(m):

Y(m):

Name of Pollutant Modeled Emission Rate [g/(s-m²)]

1)

2)

3)

4)

5)

Note: If additional pollutants are modeled, provide a tabular emission summary similar to the above for all pollutants.

Source Height [m]:

Easterly Dimension [m]:

Northerly Dimension [m]:
Initial Vertical Dimension [m]:
Angle From North [degrees]:

c) Volume Sources Summary

Source Name:
Location (Center of Source):
X(m):
Y(m):
Name of Pollutant Modeled Emission Rate [g/s]
1)
2)
3)
4)
5)

Note: If additional pollutants are modeled, provide a tabular emission summary similar to the above for all pollutants.

Source Height (m):
Initial Horizontal Dimension (m):
Initial Vertical Dimension (m):

3.4 Source Parameter Selection

Summarize the reasoning for all emission rate and source parameter values, assumptions, locations, emission rates and release parameters for all point, area, and volume sources included in the modeling analysis.

3.5 Variable Emissions – Potential Emissions during Abnormal Operations, Start-Up or Shutdown

If variable emission rates are used, such as potential emissions during abnormal operations, start-up or shutdown, summarize time variations for each relevant source, the period of emissions, and a description of the condition.

3.6 Building Downwash

Is the stack(s) located within 5L of a structure that is at least 40% of the stack height (L is the length of the height or the maximum projected building width for a structure).

- No.

- Yes. Perform a building downwash analysis using the current version of the Building Profile Input Program – PRIME (BPIP-PRIME) and include results in air dispersion modeling assessment.

3.7 Scaled Plot Plan

Provide a scaled plot, preferably in electronic format, displaying source, structure and related locations including:

- Emission Release Locations
- Buildings (On site and neighboring)
- Tanks (On site and neighboring)
- Property Boundary
- Model Receptor Locations
- Sensitive Receptors

3.8 Receptor Information

a) The following minimal receptor configuration must be met:

- Receptor definition must ensure coverage to capture the maximum pollutant concentration. Please refer to Section 7.2 of this Guideline for Air Dispersion Modelling document for a complete discussion of receptor approaches. Model runs with the following receptor densities would ensure that maximum ground level off property concentrations is captured.
- 20 m spacing within

b) Fence line Receptors

- Receptors must have not more than 50 meter spacing along property lines.

c) Sensitive Receptors

- If applicable, provide a summary describing the location and nature of any nearby sensitive receptors (e.g. apartments, schools, etc.).

d) Capture of Maximum

- Demonstrate that maximum has been reached and ensure the levels have dropped well below the standard and/or the guideline of the contaminants being studied. Describe the receptor coverage used to achieve this requirement.

3.9 Terrain Conditions

a) Does the modeled area contain elevated or complex terrain?

- No.
- Yes.

In both cases, provide a discussion on the approach used to determine terrain characteristics of the assessment area.

b) Digital Terrain Data

- CDED 1-degree
- CDED 15-minute
- USGS 7.5-minute Ontario dataset
- Other

c) Elevation data import

- Describe the technique used to determine elevations of receptors and related model entities such as sources.

3.10 Meteorological Data

i) Whether the Pre-processed Regional Meteorological data used?

- No.
- If yes - Specify what data set was used from the typical table below and note the various requirements.

Check Box	Meteorological Data Set	Climatic Region	Observation district/area

ii) Whether a Regional Meteorological Merge data files were used for large source category?

- No.
- If yes, specify the Meteorological Data Set Merge file used and summarize land characteristics specified in its processing.

iii) Were hourly surface data and upper air Regional Meteorological data files used?

- No.
- If yes, specify the Meteorological Data files used and summarize all steps and values used in processing these standard meteorological data files.

iv) Whether, local meteorological data were used?

- No.
- If yes, specify the source, reliability, and representativeness of the local meteorological data as well as a discussion of data QA/QC and processing of data. State the time period of the measurements, wind direction dependent land use (if used), and any topographic or shoreline influences.

v) Wind Information – the following items should be provided and discussed in details wherever applicable

- Speed and direction distributions (wind roses)
- Topographic and/or obstruction impacts
- Data completeness
- Percentage of calms

vi) Temperature, clouds, and upper air data – the following items should be provided and discussed where applicable:

- Data completeness
- Mixing layer heights, diurnal and seasonal variations

vii) Turbulence – the following should be provided and discussed if site data is being used:

- Direct measurements – frequency distributions, diurnal and seasonal variations

4.0 Results – Dispersion Model Predictions

i) Model files – the following electronic model input and output files are to be provided:

- ISC-PRIME or AERMOD Input and Output files
- ISC-PRIME or AERMOD Plot files

ii) Meteorological Data – the following electronic meteorological data files must be provided:

- Pre-processed data files
- If files other than the Regional Pre-processed meteorological data files were used, you must include all meteorological data files as well as the AERMET input and output files.

iii) Terrain Data

- If elevated or complex terrain was considered, include the digital elevation terrain data files.

iv) Plots and Maps – include the following:

- Drawing/site plan with modeling coordinate system noted (digital format preferred).
- Plots displaying concentration/deposition results across study area.

v) Emission Summary

- An emission summary table should be provided.

5.0 Discussion

The results overview should include a discussion of the following items, where applicable:

- The use of alternative models
- Use of any non-default model options
- Topographic effects on prediction
- Predicted 30-minute average
- 1-hour, 24-hour or other averaging period maximum, if used
- Comparison with existing standards