Chemical Characterization of Atmospheric Particulate Matter using Nuclear Analytical Technique and Source Apportionment Studies

By

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DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/diploma at this or any other Institution/University.

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List of Publications arising from the thesis

Journal

1. Comparison of two receptor model techniques for the size fractionated particulate matter source apportionment, **P. Kothai**, S.K. Sahu and G. G. Pandit. Accepted in Aerosol Air Qual. Res., 2015.
2. Concentration levels and temporal variations of heavy elements in the urban particulate matter of Navi Mumbai, India, **P. Kothai**, I.V. Saradhi, P. Prathibha, G.G. Pandit and V.D. Puranik, J. RadioanalNuclChem, 2011, Vol. 294, Issue 3, pp: 453-459.
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1. Comparison of two receptor model techniques or the particulate matter source apportionment, **P. Kothai** and G. G. Pandit, In the proceedings of National Symposium on Environment -19, 2014, pp: 125.
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P. Kothai

Dedication

The end of education is character.

The end of knowledge is love.

Humbly dedicated to the lotus feet of

Swamy

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Contents

SYNOPSIS

Preamble

Particulate pollution has been an area of major scientific interest over the past decade considering its adverse effects on human health and welfare. Airborne Particulate Matter (PM) is a complex mixture of many different chemical species originating from a variety of sources with sizes ranging from a few nanometers to several hundred micrometers. This complexity has implications also for the multiplicity of their effects. Sources of Respirable Suspended Particulate Matter (RSPM) mainly include natural and anthropogenic (man made or man-accentuated) sources. The natural sources include soil, dust, volcanic action, forest fires, vegetation (biogenic) and salt particles from sea spray. The anthropogenic sources include combustion generated particles such as diesel soot or fly ash, photo chemically produced particles, resuspended dust, motor vehicles, high temperature industries, iron and steel manufacturing processes and refuse incineration.

The increased concern for particulate matter is primarily related to their recognized adverse effects on public health, sensitive ecosystems and climate. Recent research and epidemiological studies strongly support that the elevated levels of fine particulate matter ($PM_{2.5\mu m}$, PM of size $\leq 2.5\mu m$) concentrations were associated with more fatalities when compared to coarse particulate matter ($PM_{10-2.5\ \mu m}$, PM of size 10-2.5µm). Although there is no evidence to pinpoint any single feature or component of PM as the cause for the observed epidemiological effects, it is apparent that metals contribute to the toxic and carcinogenic effects associated with exposure to airborne PM and particularly for this reason monitoring as well as assessment of PM has emerged as the object of several epidemiological studies. In addition, trace metals are proven to be useful tracers and are extensively used to identify sources of emissions to be targeted by the emission reduction policies. Therefore, monitoring of elemental composition of PM has become a crucial part of air quality programs in many countries around the world. Also, from a mechanistic perspective, it is highly plausible that the chemical composition of particulate matter would better predict health effects than other characteristics, such as PM mass or size. This is consistent with the large number of laboratory studies that have demonstrated compositional variability in PM toxicity and epidemiologic studies that portray the regional heterogeneity in PM-related health effects.

Particulate matter is a critical pollutant for most of the cities worldwide and particularly for the asian cities. A study conducted in 230 asian cities revealed that only two cities complied with the WHO air quality guidelines that too for PM10 (PM of size ≤10 µm) while a majority of cities cannot even comply with WHO interim target of 70 µg/m^3 (CAI – Asia fact sheet No.3, 2010). Megacities of India are no exception to the global pattern of deteriorating urban air quality. Indian cities are among the most polluted in the world, with concentrations of a number of air pollutants being well above the recommended World Health Organization (WHO) levels and Indian national air quality limits. The Central Pollution Control Board (CPCB) of India, under the Ministry of Environment and Forests, has stipulated national ambient air quality standards for twelve key pollutants including particulate matter below 2.5 µm and 10 µm. The CPCB prescribed annual and 24 hours standards for PM_{10} is 60 µg/m^3 and 100 µg/m^3 respectively. Air pollution in India has been aggravated over the years by developments that typically occur as economies become industrialized. In India, air pollution is restricted mostly to urban areas, where automobiles are the major contributors, and to a few other areas industries and thermal power plants. Therefore in general, the major sources of air pollution in the country are identified as industries (toxic gases), thermal power plants (fly ash and sulphur dioxide), and motor vehicles (carbon monoxide, particulate matter, hydrocarbons and oxides of nitrogen). Major polluting industries and automobiles emit tonnes of pollutants every day, putting citizens, at great health risk. The air is highly polluted with PM in most Indian cities. This has led to a high incidence of associated health effects on the population manifested in the form of sub-clinical effects, impaired pulmonary function, use of medication, reduced physical performance, frequent medical consultations and hospital admissions with complicated morbidity and even death in the exposed population. Respiratory infections account for 10.9 per cent of the total burden of diseases in India, which may be due to both the presence of communicable diseases and high air pollution levels.

The need of knowledge on occurrence, source strengths, distribution and fate of atmospheric pollutants is increasing. This knowledge becomes crucial in the effective reduction of atmospheric levels of chemical substances like trace elements in microenvironments that are harmful for human health and the environment. The only mechanism that ultimately leads to the cost effective reduction in population exposure is identification of sources that release various toxic substances into atmospheric air. Knowing the sources also allows prioritization of substances/sources that are contributing significantly to the target population exposure. Also identifying major contributing sources elevating ambient concentrations of critical pollutants is the first step toward designing an effective policy package for air quality management. Therefore, the essentiality of source identification introduced various mathematical multivariate techniques and the different existing source apportionment techniques are mainly based on source markers, chemical mass balances, and statistical regression and factor analyses. Chemical Mass Balance (CMB), Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) are the most effectively and commonly used factor analysis tools for the identification and apportionment of potential sources of atmospheric particulate matter. While each of these methods varies in their approach to grouping PM components and as mentioned above all are based on the principle of mass balance, in which a chemically speciated sample (or series of samples) is assumed to be composed of a linear combination of contributions from a limited number of unique factors. CMB relies on pre-determined factor profiles while the other two methods generate factor profiles directly from the data.

As underlined in the previous paragraphs, atmospheric aerosols have a relevant impact on human health, earth's radiative budget, and on the environment. Especially, the rapidly increasing rates of urbanization in Indian cities show alarmingly raising air pollution levels and is becoming a critical threat to the environment and to the quality of life among the urban population of India. Due to the concerns over the health and environmental impacts, several studies were conducted at different parts of India mainly focusing the Total Suspended Particulate Matter (TSPM) and PM10. But in the recent years fine particulates (PM2.5) gained immense importance based on their health implications. Also from the year 2009, it has become mandatory to monitor PM 2.5 levels in India. CPCB has prescribed 60 $\mu g/m^3$ as 24 hours average and 40 $\mu g/m^3$ as annual average for the fine particulate matter. However, most of the research work in India is still focused on TSPM and PM10, whereas, only a few studies are observed to be aimed on the levels and sources of PM2.5.

The current study is conducted in a residential place near Thane Belapur Industrial Area (TBIA) in Mumbai and is the first attempt of its kind in delineating the potential sources of coarse ($PM_{2.5\text{-}10\ \mu m}$) and fine ($PM_{2.5\mu m}$)particulate matter contributed from the industries as well as from the heavy traffic around the study area. TBIA is an industrial estate established by Maharashtra Industrial Development Corporation and is a thriving industrial belt with over 2200 industrial units. It houses various, petro-chemical, chemical, dyes, dye-intermediates, bulk drugs, pharmaceutical, textile auxiliaries, pesticides, textile processors, engineering, plastic industries along with several other big industries and thousands of small-scale industries. Besides the industries, there are other sources which are the major contributors for pollution, especially air pollution in the study region. Since Navi Mumbai is a developing town so many construction activities are going on and another major source for air pollution is the transport. Also as Navi Mumbai is the major pass-way for Mumbai and Thane, lakhs of vehicles pass through the highway. The auto exhausts as well as resuspended dust emissions from these vehicles contribute highly to the air pollution load. There are also other sources of stationery emissions nearby the study area such as Rail/Bus transport, Market places etc. To comprehend the impact of increasing levels of particulate matter, the study area was chosen as a residential area which is very closer to the TBIA as well as to the national highway which passes 2km from the sampling site. In the present study particulate matter of two size fractions coarse and fine were collected using Gent sampler on regular basis and the chosen trace elements giving emphasis on source markers were determined using Nuclear Analytical Techniques. The size fractionated particulate matter speciation data set collected over 3 year time period at a residential place of Vashi, Navi Mumbai is then used for the identification of the major contributing sources of particulate matter in the study region.

The scope of the present study is based on an integrated approach which includes (i) Monitoring coarse and fine particulate matter (ii) Extraction of major chemical components contributing to PM i.e. chemical characterization of size fractionated particulate matter using the three major key nuclear analytical techniques viz. Instrumental Neutron Activation Analysis (INAA), Energy Dispersive X-Ray Fluorescence (EDXRF) and Particle Induced X-ray Emission (PIXE) (iii) Ensuring the accuracy and reliability of the three techniques (iv) Temporal and seasonal trends of measured chemical components (v) Source identification and apportionment using two receptor techniques such as PCA and PMF (vi) Affirmation of sources identified by receptor model techniques using deterministic mass reconstruction and experimental source profile studies. The study is focused keenly in the comparison of source apportionment results obtained after the application of two most widespread receptor models (PCA and PMF) and the commonly used method of mass reconstruction of pseudo elements. The particulate matter levels and their inorganic trace metal concentrations of the study brings insight into the conclusions regarding the temporal variations and the contributing sources of the study area. Strong seasonal variations were observed for mass concentrations of particulate matter and for trace metal concentrations. As the analysis of trace elements are concerned elemental sensitivity, accuracy and the reliability of the three nuclear analytical techniques were compared by selecting the common elements between the techniques and quality control was studied through the reference material analysis. An attempt was made for the screening and data treatment for elemental results to perform further source identification studies using receptor model technique. Major contributing sources of coarse and fine fraction of particulate matter in the study region were then identified using the screened data by applying Principal Component Analysis, the most widely used receptor model technique. Soil and marine sea salt were identified as the major and naturally contributing sources of coarse particulates whereas in the fine fraction anthropogenic sources such as industries and vehicular emission contributed to the maximum. Attempt is also made to determine the percentage contribution of various sources using Multiple Linear Regression technique. Derived sources were confirmed and validated using three distinguished steps. PCA results were first compared with the results of PMF model, consequently some of the source profiles obtained using PMF were rechecked with the experimentally measured trace elemental values of their respective sources and in the final step the speciation data was used for mass reconstruction to verify the modeled values of percentage contribution of each source.

The thesis has been organized into five chapters, elaborating the work done on the above mentioned theme

1. Introduction
2. Materials and Methods
3. Source Identification and apportionment
4. Results and Discussion
5. Conclusions and Future Prospects

The contents of each chapter are explained in brief in the following sections.

Chapter – 1: Introduction

Chapter 1 describes in detail regarding the formation, size distribution, composition, its environmental effects, health effects and other salient features of the atmospheric particulate matter. In the first section introduction about the particulate matter pollution is presented with an emphasis on the need of the study in the present day scenario.

Following section gives an insight into the formation of aerosols in the atmosphere, their size distribution and various modes of particles with respect to their size and origin, transport of particulate matter, atmospheric deposition such as dry and wet deposition. Third section gives an outline about the chemical composition and the potential emission sources of atmospheric particles. Subsequent two sections are dealing with the adverse impacts of particulates on human health and environment. Studies related to the series of significant health problems associated with different size fractions of particles have been discussed in detail. The section also summarizes the impact of particles over the ecosystem and the consequent effects such as climate change and visibility reduction problems.

Final section of the chapter outlines the details regarding the adversely affected ambient air quality from domestic, industrial, power and transport sectors of Mumbai and Navi Mumbai region. Literature and international studies explain there are only few studies conducted in the Mumbai region viewing the alarmingly raising particulate levels. As the Navi Mumbai region is concerned, present study is the first attempt focusing on particulate matter issue and on their potential contributing sources. The significance and the need of the present study in the Navi Mumbai region of Maharashtra is elaborated in this section. Various air quality issues and the expected major contributors to the elevated ambient particulate concentrations related to the growing industrial units in the Thane Belapur Industrial Area (TBIA), excessively increasing transport systems, hazardous waste landfills and waste incineration facilities around the study region are also addressed in detail. The section also throws light into the main objectives of the comprehensive study undertaken at the study region such as (i) Monitoring and trend anlaysis of PM and their constituent trace elements (ii) Measurement of inorganic trace metal levels in the air filter samples using Nuclear Analytical Techniques (iii) identification, apportionment and validation of potential source contributors of the study area.

Chapter – 2: Materials and Methods

Chapter 2 discusses sampling methodologies and various analytical techniques adopted in the present work. The first two sections of the chapter describes the working principle of sampling instruments utilized for the collection of size fractionated particulate matter of size ≤10μm. It also reviews the basic sampling criteria such as selection of sampling location, sampling height, sampling frequency, preservation and the gravimetric analysis of the samples.

Subsequent sections elaborate the necessity of performing chemical composition study, major components of particulate matter, state of - the – art analytical methods and instruments typical of those used to measure the concentrations in the filter media, and the advantages and disadvantages associated with the analytical options. The chapter highlights the instrumentation and methodology followed for the trace elemental analysis using three key Nuclear Analytical Techniques such as Instrumental Neutron Activation Analysis (INAA), Energy Dispersive X-ray Fluorescence (EDXRF) and Proton Induced X-ray Emission, which are widely used for the non-destructive multi-elemental analysis of ambient aerosols. Destructive techniques viz., Atomic Absorption Spectrometry for trace element analysis of particles collected on glass fibre filters and Ion chromatograph technique for the analysis of inorganic anions and their respective sample digestion procedures are mentioned briefly in this chapter. The working principle and methodology of the black carbon measurement in the nuclepore air filters using EEL Smoke Stain Reflectometer is also presented. The section also discusses accuracy, precision and quality control studies performed during the analysis of various inorganic pollutants.

Chapter – 3: Source Identification and Apportionment

Natural and anthropogenic sources both have the greatest impact on the urban particulate matter concentrations in India. The identification as well as distinction between the natural and anthropogenic sources becomes a difficult task. Therefore in this particular chapter, effective methodologies used for the screening, identification and apportionment of potential contributing sources of atmospheric aerosols are discussed. Initially a methodology for the screening of natural and anthropogenic sources, Enrichment Factor (EF) Analysis is described. EF analysis is considered as the first step to discriminate the natural crustal and sea salt sources from the anthropogenic emission. Following sections of EF analysis introduces receptor model techniques based on mass balance analysis.

Receptor modeling techniques are based on the evaluation of the data acquired at receptor sites, and most of them do not require previously identified emission sources. Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) are such techniques performed to identify the main chemical groupings and likely sources of airborne particulate matter. Forthcoming sections in the chapter discuss the theoretical basis of the above mentioned techniques.

Chapter – 4: Results and Discussion

The goal of the study is to investigate temporal behaviour and source signatures of particulate matter load at the selected receptor site in an urban area Navi Mumbai, India. The sampling site can be considered as one of the hot spots. The site is situated nearby India's one of the largest industrial belt and the township established on either side of the industrial region known as Navi Mumbai bears population above 1 million. To achieve the objective of the study regular sampling program has been initiated in the study site to collect particulate matter on nuclepore filter papers using a size fractionated Gent sampler and detailed analysis of constituent fractions were performed subsequently. Gent sampler has an automatic dichotomous size segregation unit which used to collect two ranges of air particulate samples. It has an inlet with a PM_{10} cut-off, which collects only particles smaller than 10 µm. The particles are then size-segregated into fine particles smaller than 2.5 µm and coarse particles between 2.5 and 10 µm ($PM_{2.5–10}$). Annual average concentrations during subsequent years of sampling showed an increasing trend and that could be attributed to multiple factors including meteorology, neighbourhood activity patterns etc. The daily average mass concentrations of coarse ($PM_{2.5\text{-}10\mu m}$) and fine ($PM_{2.5\mu m}$) particulate matter collected at the sampling site is observed to be 89.92 µg/m^3 and 42.25 µg/m^3 respectively. Coarse particulate is in the range of 24.57-296.45 (µg/m^3) with a median of 85.26 µg/m^{3}and in fine particulates concentration ranges from 8.62-93.33 (µg/m^3) with a median of 39.74 µg/m^3.

The temporal variations of monthly averages of PM dominantly showed a pattern of high concentrations during the months of winter (December, January and February) and this could be due to temperature inversion. The lower temperature during winter decreases the mixing height and in turn which causes high particulate concentrations with wide variation in the concentration range. The lowest mass concentrations were observed during the monsoon periods (June, July and September). The average coarse concentrations found to be 108.59, 87.14, 60.63 and 82.3 μg/m^{3}during winter, summer, monsoon and post monsoon periods while the average fine mass concentrations found to be 64.71, 41.17, 25.53 and 45.82 μg/m^3, respectively. High levels of particulate matter and their exceedance were examined against the air quality standards laid by Central Pollution Control Board. When the data of present study was compared with the air quality standards stipulated for residential area, around 70% of the total samples collected were exceeding the prescribed air quality standards. The severity of particle pollution in the study area was indicated by the temporal and seasonal variation analysis of PM concentrations during the course of measurement period. The scenario emphasized further detailed study on the characterization and identification of potential contributing sources of air particulates as the need of the hour.

In order to assess the impact of coarse and fine particulate pollution elemental composition of the samples were determined by INAA, EDXRF and PIXE. Quality control studies were performed to check the precision and accuracy of the techniques by analyzing certified reference materials. Analytical accuracy and sensitivity for different elements were also compared among the three techniques. Concentrations of elements which are well above the Minimum Detection Limit and elements that can be analyzed by both XRF and PIXE were selected for the comparison of the two techniques. XRF and PIXE measurement of elements found to be in good agreement with each other. The correlation coefficients obtained between the techniques for the selected elements found to be higher than 0.8 in both the size fractions. Differences between the concentrations obtained were found to be within 10%. But, comparatively higher difference was observed in the case of Si measurement. Si concentrations characterized by PIXE technique found to be higher than

EDXRF. Similar studies were also performed to compare INAA & EDXRF and INAA & PIXE.

To comprehend and compare the levels of trace metals in both the size fractions self-explanatory Box-Whisker diagrams were plotted to determine 25-75th percentiles, 5-95th percentiles, maximum, minimum, mean and median concentrations. Trends and seasonal variation analysis of the trace metals yielded results similar to that of particulate matter showing maxima during winter and minima during monsoon season. As exceptions some of the elements like Ni, Se, Cr etc. showed higher concentrations during summer and some other during post monsoon period.

The trace elemental data obtained in this work were subjected to Enrichment Factor (EF) computation besides the above mentioned descriptive statistics analysis. EF analysis was utilized as the first step before performing source identification process. The analysis discriminated whether a specific metal found in greater abundance in air expected to be natural origin. In the present study EF analysis was performed to assess the level of contamination and the possible anthropogenic impact in the study region. To identify anomalous metal concentration, geochemical and marine normalization of the trace metals data to a conservative element have been employed. In this study Fe is used as a reference element to determine the EF with respect to crustal abundance. Whereas Na is used as a reference element to determine the marine based EF values. EF values of Al, Ca, Mg, Si in both the size fractions are small indicating their origin from crustal source. Few elements such as Ni and V were found to possess EF values in the range of 20 to 43. As, Br, Pb and Zn in the fine fraction exhibit the maximum enrichment ranging from 563–1253, whereas in the coarse fraction except Zn, the EF of other three elements are within 100. Elements like Mn, Cr, and Cu are showing enrichment only in the fine fraction which indicates their anthropogenic origin from traffic or industrial emissions. Enrichment of Na, K and Cl can be attributed to sea salt.

As a second step, correlation matrix was developed to understand the interrelationship among the analyzed elements. Correlation coefficient matrix pertaining to trace elements presented strongly correlated crustal and marine based elements supporting the results of EF analysis. Further the study revealed many of the strongly correlated elemental pairs such as V-Ni, As-Se, S-BC etc. laying strong basis to their anthropogenic origin of fine particles showing their independent variations as well as multisource origin in the urban environment.

The ultimate objective of the study, source identification is then achieved by applying receptor model techniques. The Principal Component Analysis technique identified six contributing sources for coarse particles namely soil, sea salt, fugitive dust, vehicular emission, industrial emission and a source related to construction activities. Further apportionment of sources based on Multiple Linear Regression (MLR) technique explained the percentage contribution of soil, sea salt, fugitive dust, vehicular emission, industrial emission and emission from construction activities as 21, 28, 11, 10, 9 and 5 percentages respectively. Apportionment of $PM_{10-2.5\mu m}$ size particles indicated maximum contribution of coarse particulates from natural sources and fugitive road dust. On the other hand, seven likely contributing sources for fine fraction particles like soil, sea salt, oil combustion, coal combustion, vehicular emission, textile or dye intermediate industry emission and fugitive dust were identified with their respective contributions as 6, 10, 13, 9, 27, 11 and 5 percentages. Apportionment of fine particulates represented maximum contribution from anthropogenic emissions from vehicular and industrial sources. The sources thus obtained by PCA technique was then compared with the sources identified using another receptor model Positive Matrix Factorization. The comparability between the two applied receptors techniques were evaluated as a function of four parameters. The ability of the models to reproduce the measured PM concentrations was verified. The dispersion between gravimetrically measured and modeled data was observed to be lowest for both PCA and PMF (r^2= 0.87 and 0.83 for respectively). Further the number and nature of the sources identified, the similarities (or) dissimilarities observed between the different source profiles and the quantification of the percentage contribution of the sources were compared between the two models. Characteristic marker elements of the different sources and their magnitude of contribution to the PM mass were found to be in good agreement between both the models with the minor differences in few sources. Furthermore, some of the source profiles obtained by PMF model such as road dust, soil and vehicular emission were validated by comparing it with the experimental results. Road dust, soil, petrol and diesel soot samples were collected, processed and analysed for trace elements to validate the model results.

Prior to the performance of PMF, the speciation data was used for the Re-Construction of Mass (RCM) to confirm the source contribution. Reconstruction of mass profile is a quick and practical way of summarizing chemical speciation data, and is commonly used in the development of receptor models. In general, this deterministic method is considered as an important parameter to confirm the percentage contribution of sources to the total particulate mass and can also be compared with the receptor model apportioned source profiles. By applying the RCM technique, 80-90% of the gravimetric particulate mass was reconstructed for coarse and fine fraction particles. Where, the RCM results found to be comparable with the model values obtained from receptor model techniques. However, the reconstructed mass observed to be marginally higher than the modeled mass because of the addition of inorganic anion concentrations.

Chapter – 5: Conclusions and Future Prospects

The concluding chapter summarizes the outcomes which are successfully achieved by the study and it presents some of the ideas in line with the present work that can be carried out in the future. The thesis had three major objectives, first objective: monitoring and trend analysis of PM and the constituent trace elements, yielded significant results typical to the urban atmosphere of Navi Mumbai. The study revealed elevated annual average concentrations of particulate matter and enhanced levels of atmospheric trace metal concentrations in the study site. A clear seasonal variation was noticed during the entire sampling period. It was also observed that most of the toxic or harmful elements are mainly enriched in the fine particles emphasizing the importance of PM2.5 monitoring and characterization. Following the second objective, trace metals were measured in the air filters using three key Nuclear Analytical Techniques and the results were validated by performing regression studies among the three techniques.

The third objective, identification of potential source contributors and validation of identified sources was achieved by apportioning the size fractionated atmospheric particulate matter using two multivariate models based on factor analysis such as PCA and PMF. The major source categories of coarse particles were natural sources like crustal and sea salt. Whereas, emissions from vehicles and industries were found to be the dominant contributors for fine particulate matter followed by the less influential crustal and sea salt source categories. Despite the minor differences in the source profiles both the models were able to identify the main sources contributing to the PM and a reasonable agreement between PCA and PMF was found with the good correlation between the identified sources. Reconstruction of mass computed comparable percentage contribution of different sources.

In the future, the source apportionment study can be refined by including the molecular tracers and organic markers of atmospheric particulate matter and the approach may help in overcoming the underestimation of plausible sources, by providing additional source attribution information. An attempt can be made to use receptor modeling in conjunction with routine monitoring and emission inventories to establish the key sources where this method can be used as a complementary technique to the demonstrated receptor techniques. Also the trans-boundary sources and their preferred transport pathways can be predicted to confirm the long range transport of fine particulates by applying various trajectory ensemble models. In view of health perspectives, studies related to the estimation of integrated inhalation risk due to the exposure of atmospheric trace elements through inhalation pathway can be carried out in the future. The risk estimation study has been initiated already and as a preliminary step inhalation non cancer risk for children and adults are being computed based on the present ambient level of trace elements.

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PM	Particulate Matter
PM$_{10}$	Particulate Matter with diameter ≤ 10μm
PM$_{10-2.5}$	Particulate Matter with diameter 10-2.5 μm
PM$_{2.5}$	Particulate Matter with diameter ≤ 2.5 μm
RSPM	Respirable Suspended Particulate Matter
BC	Black Carbon
EC	Elemental Carbon
OC	Organic Carbon
OM	Organic Matter
CPCB	Central Pollution Control Board
MPCB	Maharashtra Pollution Control Board
NAAQS	National Ambient Air Quality Standard
TBIA	Thane-Belapur Industrial Area
HAP	Hazardous Ai r Pollutant
US EPA	United States Environmental Protection Agncy
WHO	World Health Organization
INAA	Instrumental Neutron Activation Analysis
EDXRF	Energy Dispersive X-Ray Fluoresence
PIXE	Proton Induced X-ray Emission
AAS	Atomic Absorption Spectrometry
IC	Ion Chromatograph
EF	Enrichment Factor
CMB	Chemical Mass Balance
PCA	Principal Component Analysis
FA	Factor Analysis
MLR	Multiple Linear Regression
PMF	Positive Matrix Factorization
AAE	Average Absolute Error
APCS	Absolute Prinicipal Component Scores

Chapter - 1

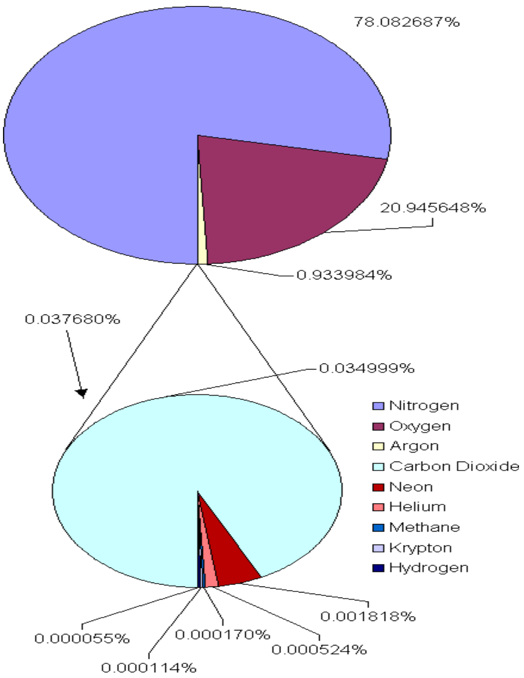
Introduction

Ambient air pollution is an emerging environmental issue in major cities of Asia and has attracted attention from variety of corners with a proven direct impact on health & ecosystem of earth. Air pollution extends from local (urban pollution) to regional (dispersion, deposition and chemical transformation of the pollutants, acid rain, photochemical reactions) and then to global level (greenhouse effect and depletion of the stratospheric ozone layer). Specially, urban air pollution is considered as a complex issue, fueled by multiple sources ranging from vehicle exhaust, on-road resuspended dust due to vehicles, industrial emissios, construction dust, garbage burning, domestic cooking and heating, and some seasonal sources such as agricultural field residue burning, dust storms, sea salt etc. and the air quality issues have emerged as a major concern impacting the quality of life. The high disease burden due to air pollution has even started to impact on the economy of the urban centers. The common knowledge of air pollution impacts on human health has not yet led to comprehensive plans to combat the rising levels of air pollution level exposure. Quantification of the impact of air pollution on public health has gradually become a critical component in policy discussions as governments weigh options for the control of pollution. At the same time, evaluation of the magnitude of the impact presents considerable challenges owing to the limited availability of information on both effects on health and on exposures to air pollution in many parts of the world. If at all, measurements of urban air pollution, when available, are available largely for a non representative sample of urban areas.

Air quality is generally described as combination of physical and chemical characteristics that make air an essential resource for man, animals, and plants. It enables man to continue his domestic, social, industrial and recreational activities. The physical characteristics include factors such as temperature, density, water content, pressure variations which dictates the wind profile. The chemical characteristics comprise the concentrations of various gaseous and aerosol matter from natural and anthropogenic i.e. man made sources and transformed products. Both the physical and chemical characteristics of air are constantly changing. Natural forces are responsible for physical changes while chemical changes are caused by human activities which are of concern. Man-made urban air pollution, which is derived largely from combustion processes, is a complex mixture containing many toxic components. Especially, combustion of fossil fuels for transportation, power generation, and other human activities produces a complex mixture of pollutants comprising literally thousands of chemical constituents.

Due to urbanization and heavy industrialization the present day atmosphere is quite different from the natural atmosphere that existed during the preindustrial times in terms of chemical composition. If the natural atmosphere is considered to be “clean”, then this means that clean air cannot be found anywhere in today’s atmosphere. To understand the air quality status in comparison with preindustrial days, atmospheric composition of air is given in Figure 1.1 and the chemical composition of the pre-industrial natural global atmosphere is compared to current compositions in Table 1.1:

Figure 1.1: Atmospheric composition of air



(Courtesy: Atmosphere of earth, Wikipedia)

Table 1.1: Atmospheric Air Chemical Composition

Gas	Symbol	Percent by volume (Current Atmosphere)	ppm (Natural Atmosphere)	ppm (Currrent Atmosphere)
Nitrogen	N_2	78.1		
Oxygen	O_2	20.9		
Argon	Ar	0.92		
Neon	Ne		18.2	
Helium	He		5.2	
Krypton	Kr		1.14	
Xenon	Xe		0.09	
Carbon di oxide	CO_2		280	370.0
Methane	CH_4		0.75	1.77
Nitrous Oxide	N_2O		0.27	0.318
Water Vapor	H_2O	Variable (0.004 to 4)		

Defining air pollution is not simple. All manmade emissions in to the air can be called air pollution because they alter the chemical composition of the natural atmosphere. Air may be regarded as polluted when it is changed in its quality & composition as a result of human activities. The release of low amounts of pollutant into the air does not lead to any serious effects because the atmosphere has a considerable absorptive capacity. For example, the increase in the global concentrations of greenhouse gases CO_2, CH_4, and N_2O (shown in Table 1.1), can be called air pollution using this approach, even though the concentrations have not found to be toxic for humans and the ecosystem. When the concentration of pollutants in air becomes so high that they cannot be tolerated by atmosphere's regulating cycles, dangerous consequences arises as polluted air is not suitable for breathing. In general view, air pollution can be defined as, ***"The excessive presence or concentration of foreign substances in the air which can endanger human health and welfare of plants and animals, causes damage to the materials and property, reduce visibility and can lead to multiple undesirable effects".***

The evaluation of ambient air quality is fundamental requirement towards characteristic ambient air in a area and also for the assessment of nature and extent of environmental quality variable in urban environments and towards planning for prevention and control of air pollution. The assessment of air quality, it's present and anticipated pollution status in parts of urban areas, which are in the process of continuous urbanization and industrialization is necessary. Air pollution in India has been aggravated over the years by developments that typically occur as economies become industrialized. In India, air pollution is restricted mostly to urban areas where automobiles are the major contributors and to a few other areas with a concentration of industries and thermal power plants. While air quality is slowly improving in the developed countries like India, it is rapidly deteriorating in developing countries due to rapid industrialization and increased vehicular traffic. Admittedly, the constituents of air pollution in different parts of the world are largely similar, but the magnitude of exposure, general health status of the people, nutritional and other disparities and level of health care facilities are different across the globe [1] which emphasize the importance of site specific studies.

The Science of air pollution centers on measuring, tracking, and predicting concentrations of key chemicals in the atmosphere. Normally, four types of processes affect air pollution levels,

- **Emissions**: chemicals are emitted to the atmosphere by a range of sources which include natural, biogenic and anthropogenic emissions
- **Chemistry**: many types of chemical reactions in the atmosphere create, modify and destroy chemical pollutants.
- **Transport**: Winds can carry pollutants far from their sources, so that emissions in one region cause environmental impacts far away. Long-range transport complicates efforts to control air pollution because it can be hard to distinguish effects caused by local versus distant sources.
- **Deposition**: Materials in the atmosphere return to Earth, either because they are directly absorbed or taken up in a chemical reaction (such as photosynthesis) or because they are scavenged from the atmosphere and carried to Earth by rain, snow, or fog.

As a first and foremost step in the control of air pollution, US-EPA has set National Air Quality Standards (NAAQS) for six principal or criteria air pollutants: nitrogen oxides (expressed as NO_2), ozone, sulfur dioxide, PM, carbon monoxide (CO), and lead (Pb). Four of these pollutants (CO, Pb, NO_2, and SO_2) are emitted directly from a variety of sources. Ozone is not directly emitted, but is formed when nitrogen oxides (NO_X) and VOCs react in the presence of sunlight. PM is mostly directly emitted, but $PM_{2.5}$ particles can also be added as secondary pollutants (sulfates, nitrates, and organic particles).

Among all the criteria air pollutants, particulate matter has emerged as the most critical pollutant in almost all urban areas, globally. Anthropogenic aerosol particles have substantially increased the global mean burden of aerosol particles from pre-industrial times to the present day. In recent pasts, considerable attention has been paid to air quality degradation caused by particulate matter. The term “aerosol” is used to describe suspended particles and all other gas-phase species that exist in an air mass. The term aerosol, however, is also often used to describe only the suspended particle fraction of an air mass. The main reason which brings significance to aerosols and attracts the attention of the researchers is that the ambient PM is not a single pollutant but is composed of a variety of chemical species including trace metals (including toxic, crustal, and transition metals), elemental carbon, nitrate, sulfate, and a variety of organic species. The ambient air concentration of particulate matter is universally high in developing areas. Particulate matter is important as vector of transport and deposition of various pollutants like sulphate, nitrate, heavy metals and persistent organic products and also efficiently contributes to visibility problems. Numerous studies and reviews focusing on individual components of PM have reported linkages with adverse health effects. For example, particulate pollution has been implicated in numerous health outcomes, including asthma, respiratory symptoms, impaired lung function, total mortality and cardio vascular mortality and it has also been linked to different toxicological effects. Some argue that particle surface contaminants, such as transition metals contribute towards ill health, while others argue that the physical characteristics (e.g. number, size, shape and aggregation properties) are the determinants of health effects [2]. The prime factors associated with the pollutants affecting the human health are:

- Nature of the pollutants
- Concentrations of the pollutants
- Duration of exposure

- State of health of the receptor
- Age group of the receptors

India’s air pollution is a known public health and environmental challenge. Particularly, while considering the high concentration levels of particulate matter and the percentage of exceedance of its prescribed standards in urban areas India is not an exception. In the recent period particulate matter pollution has been evolved as a primary issue compared with the other air pollutants. Also it has been established recently that amidst different size fractions of PM, coarser fraction (> PM_{10}) of Suspended Particulate Matter (SPM) concentrations are primarily and may not have much relevance to direct health consequences as compared to effects of its respirable fractions (PM_{10} and $PM_{2.5}$), which can penetrate the human respiratory systems deeper. A study conducted by world bank in Indian cities declares that fine particulate ($PM_{2.5} \leq 2.5$ μm in size) emissions is the largest killer in Indian region and the study also emphasize that eighty percent of Indian cities violate the National Ambient Air Quality Standards (NAAQS) for Particulate Matter [3]. Considering the severity of particle pollution, since the year 2000, focus has shifted from SPM to PM_{10} monitoring and in the latest 2010 standards limits were also prescribed for $PM_{2.5}$ by Central Pollution Control Board (CPCB) for the first time in India[4]. Figure 1.2 presents the overview of PM_{10} levels in the four megacities of India [5] and Figure 1.3 illustrates the exceedance of three important air quality parameters like PM_{10}, SO_2 and NO_x compared with the prescribed standards [6]. Both the figures indicate exceedance of PM levels to a high extent and certainly suggests for stringent monitoring and control strategies in India.

Figure 1.2: Annual Average of PM10 in Major cities of India

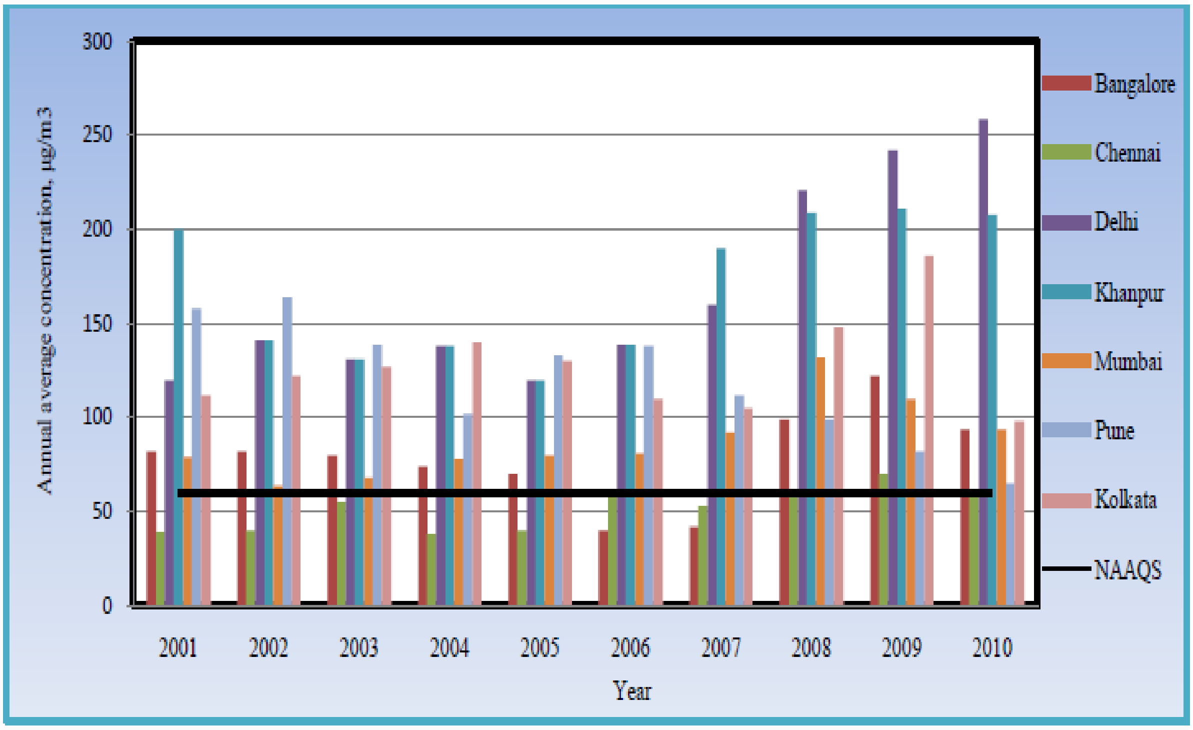
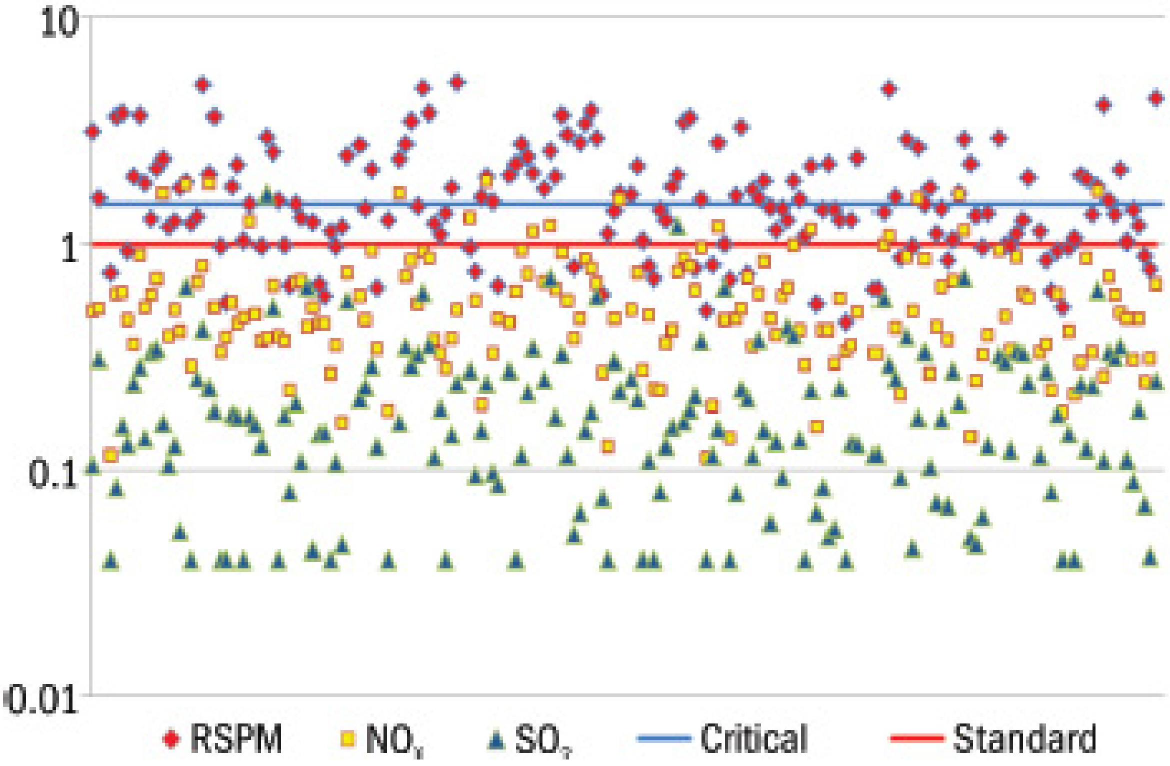


Figure 1.3: Ratio of annual average pollutant concentrations to prescribed standards in 172 cities of India in 2010



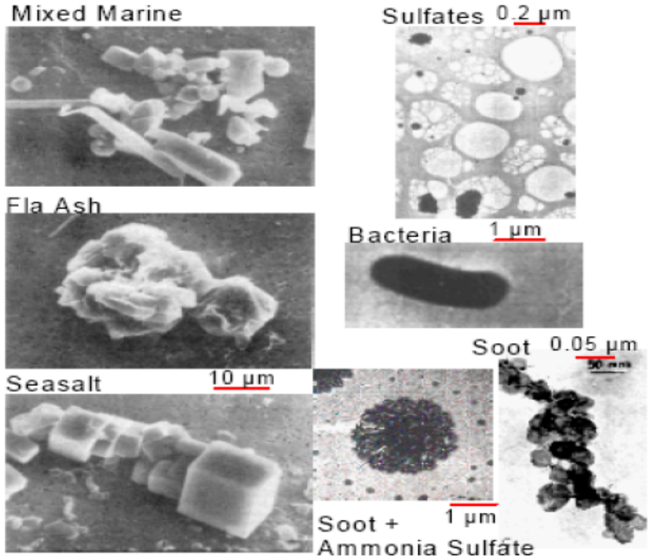
In general, a cost effective approach for improving air quality in polluted areas involves not only identification of emission sources as a primary step. Besides the source identification assessment of extent of contribution of these sources to ambient air, prioritization of sources, evaluation of various options for controlling the sources with regard to feasibility and economic viability also carries prime importance. In the case of particulate pollution control measurements, major problem arises because particulate matter is made up of a number of components, including acids (such as nitrates and sulfates), organic chemicals, metals, and soil or dust particles. Therefore, examining the relationship between a large number of ambient PM components and a large number of health outcomes also becomes a vital part of air pollution control strategy. But, it presents difficulties that pertain to both the complex nature of ambient PM and the varying methods of quantitative analysis used. Characterizing the emission sources, concentrations, transport patterns, and impacts is particularly difficult in developing countries, where data are scarce, emissions are high, and health impacts are often severe. First, the number of components that comprise PM is not only large, but the correlations between them can be high and complex. Reducing the correlation between components can be accomplished through mathematical models. Principally, various forms of multivariate methods which are in practice generally groups ambient PM components into less correlated groups or factors. Common factor analysis tools applied for source identification of PM used throughout the literature include chemical mass balance (CMB), principal components analysis (PCA), positive matrix factorization (PMF), multilinear engine (ME) and UNMIX. While each of these methods varies in their approach to grouping PM components, all are broadly based on the principle of mass balance, in which a chemically speciated sample (or series of samples) is assumed to be composed of a linear combination of contributions from a limited number of unique factors.

Following sections of the chapter throws light upon the definition of PM and its various physical and chemical parameters like shape, size distribution, atmospheric life time, removal mechanism, chemical composition, potential sources, human health effects and environmental effects. The chapter also discusses about various ambient air quality standards prescribed by international as well as national agencies and the importance of source apportionment is also described briefly.

1.1. Particulate Matter and shape

As described in the previous sections "Particulate matter," is a complex mixture of extremely small particles and liquid droplets made up of many subclasses of pollutants that contain number of different chemical species. The complex mixture of inorganic and organic compound, dealing with the particulate matter composition, is one of the main aspects either for their characterization or for the source apportionment. Other important parameters to be taken into account are the morphology and dimensions of the particles. The shape and the dimension of the particles have a direct interaction with their nature and with the risk assessment for human health. Atmospheric aerosols exhibit a variety of shapes such as fractal, aggregate, cubic, plate like and spherical when viewed using transmission electron microscopy. Most commonly, they are spherical, liquid droplets. Shapes of few common aerosol types are depicted in Figure1.4.

Figure 1.4: Shapes of few common atmospheric aerosols



Courtesy: Introduction to marine aerosol, 2009 SOLAS summer school

1.2 Particle Size Distribution

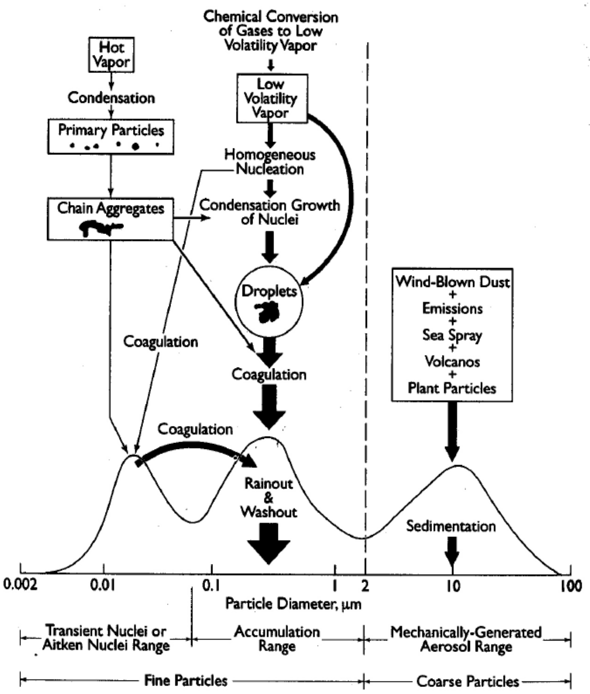
Atmospheric PM is often classified by the size of particles. Aerosol number, surface and mass size distributions of chemical elements and species are of interest in atmospheric chemistry and air pollution research for a wide variety of reasons. Size distributions of particles become important when related to health effects, visibility, and climate change. In particular, knowledge of the size distribution of trace metals in atmospheric particles is important because this not only influences the toxicity of a metal but also controls the extent to which metals might be dispersed via atmospheric transport. Such knowledge is thus a prerequisite for determining the deposition rates of metals to the Earth's surface [7]. Furthermore, they are of value when examining relationships between the physico-chemical and radiative aerosol properties, for assessing the inhalability of the particles and species and their associated possible impact on human health, and they are also needed for estimating dry deposition velocities [8].

The size distributions of trace metals in aerosols are mainly controlled by their sources, life time in the atmosphere, and the meteorological conditions [9, 10, 11]. After particulate matter being emitted into the atmosphere, the sizes of particles may increase by coagulation or decrease due to evaporation of the water content in particles [12], resulting the changes in the size distributions. Besides, meteorological parameters, such as wind speed, temperature and relative humidity, could also influence the size distributions of trace metals in aerosols [12,9]. Therefore, the size distributions of ambient particulate and their trace metal content are characterized by multiple chemical and physical processes occurring in the atmosphere.

Particle size, as indexed by one of the “equivalent” diameters namely “aerodynamic diameter” is an important parameter in determining the properties, effects and fate of atmospheric particles. The aerodynamic diameter depends on the density of the particle. Aerodynamic diameter is defined by [13] as the diameter of a standard- density sphere (1000 kg m^{-3} or 1 g cm^{-3}) with the same gravitational setting velocity as the particle being measured. Particles with the same physical size and shape but different densities will have different aerodynamic diameters. Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks [14, 15, 16, 17, 18].

Whitby and co-workers described extensively regarding the characterization of atmospheric particle sizes with the fundamentals of the sources, removal processes and chemical properties of different size particles addressed. They observed three distinct modes of atmospheric particulate matter each of which can be characterized by different formation and removal mechanisms as illustrated in Figure 1.5.

Figure 1.5: Schematic diagram of aerosol distribution with principal modes, sources, and particle formation and removal mechanisms



The most commonly used size fractions in the PM studies are.

- TSP (total suspended particulates) comprises all airborne particles
- The term PM_{10} is used for particles with an aerodynamic diameter ≤ 10 µm.
- The term $PM_{2.5}$ (Fine fraction) is used for particles with an aerodynamic diameter $\leq$ 2.5µm.
- The term coarse fraction is used for particles with an aerodynamic diameter 2.5-10 µm
- The term ultrafine particles is used for particles with an aerodynamic diameter <0.1 µm.

The details of particle size ≤ 10µm are discussed in the following subsections.

1.2.1 Coarse mode

The largest mode includes particles in the range of 2.5 µm - 10 µm and is called the coarse particle mode. Coarse particles are generated mostly by physical or mechanical processes and normally settle out of the atmosphere relatively quickly. These processes, including surface abrasion and crushing and grinding, generate coarse particles such as marine aerosol and wind-blown dust. Bursting bubbles release large and smaller droplets of water from the sea. The large droplets fall back into the water, while the smaller ones become airborne and are transported long distances by the wind. Bio aerosols (such as pollen, spores, leaf-litter decay and viruses) may also be found in the coarse particle mode, with some, such as viruses and bacteria, present in the fine particle fraction <2.5 µm). Coarse particles do not remain in the atmosphere for long periods as high sedimentation rates lead to quick removal.

1.2.2 Fine mode

Particles less than 2.5 µm in aerodynamic diameter ($PM_{2.5}$) are called fine particles. The fine particle mode consists of a large majority of the total particle number and also a large fraction of particle mass (~1/2 in urban and 1/3 in rural aerosols) in the atmosphere. These fine particles can remain suspended in the atmosphere for long time periods. The formation and growth of fine particles can occur via a variety of mechanisms. Coagulation of two particles can occur to form one particle. Gas-phase material can nucleate to form a particle as the gases in an emission source cool. The growth of particles can occur as gas-phase material condenses on existing particles. The fine particle mode is divided into two subsets consisting of particles between 0.15 and 2.5 µm called the accumulation mode and particles between 0.015 and 0.04 µm called the nuclei mode.

1.2.3 Nucleation and accumulation mode

Nucleation mode is the smallest group in size, with particles with the smallest diameters, mainly directly emitted from the source, with short atmospheric lifetimes and subject to Brownian motion or diffusion. Particles in the nucleation mode can be formed by nucleation of gases or by condensation. These particles can easily coagulate to larger ones. The second mode, accumulation mode, also includes condensation particles. Accumulation mode particles have bigger d_{50} and longer atmospheric lifetimes than the nucleation mode particles, because these particles are too large to be subject to Brownian motion and too small to settle from air rapidly. Accumulation mode particles are usually eliminated from the atmosphere by washout, dry or wet deposition. Dry deposition to plant and soil can occur by gravitational settling or inertial impaction of particles.

These fine particles are chemically different from their coarse particle counterparts, mainly consisting of chemical species resulting from combustion, including high concentrations of organic material and soluble inorganic species (i.e., sulfate and nitrate). Also, fine particles are more relevant than coarse particles with respect to effects on health, visibility, and climate change, more attention has been focused in recent years on $PM_{2.5}$ than PM_{10}. Table 1.2 compares different properties of fine and coarse mode particles from the formation mechanism to their lifetime.

Table 1.2: Comparison of Fine and Coarse particles

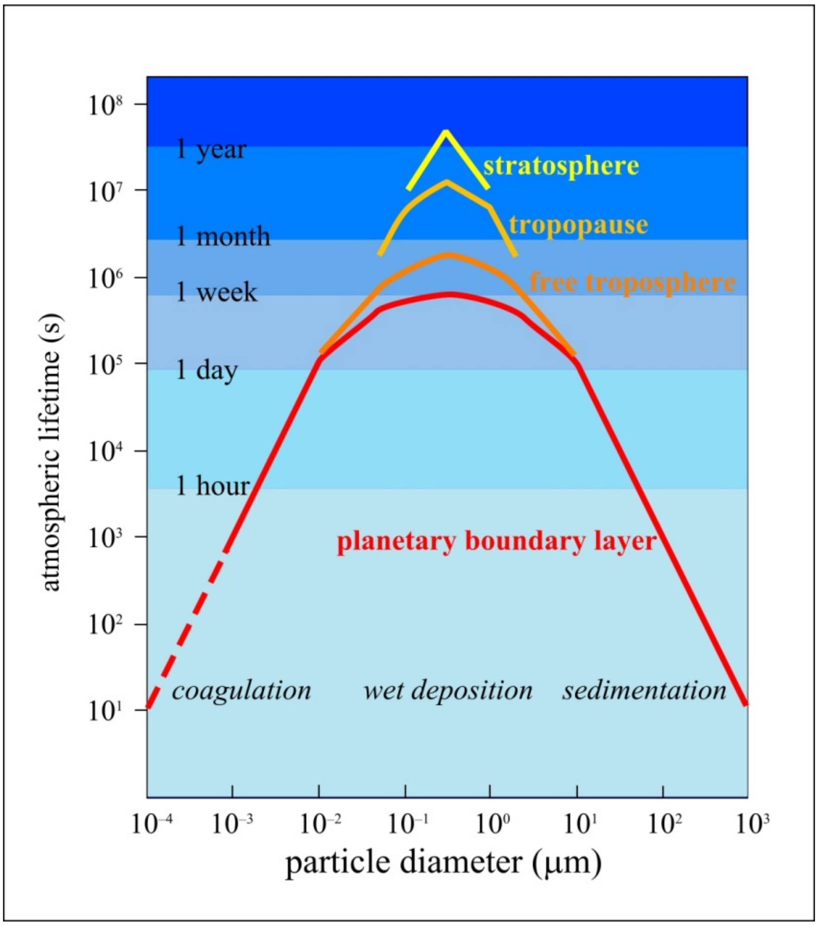
	Fine Particle	**Coarse Particle**
Formed from	Gases	Large solids/droplets
Formed by	Chemical reaction, nucleation, condensation, coagulation; evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (e.g. crushing, grinding, abrasion of surfaces); evaporation of sprays; suspension of dusts
Composed of	Sulfate (SO_4^{2-}); Nitrate (NO_3^-); ammonium (NH_4^+); hydrogen ion (H^+); elemental carbon; organic compounds (e.g. PAHs, PNAs); metals Pb, Cd, V, Ni, Cu, Zn, Mn, Fe); particle bound water	Resuspended dust (e.g. soil dust, street dust); coal and oil fly ash; metal oxides of crustal elements (Si, Al, Ti, Fe); $CaCO_3$, NaCl, sea salt; pollen, mould spores; plant/animal fragments; tyrewear debris
Solubility	Largely soluble, Hygroscopic and deliquescent	Largely insoluble and non-hygroscopic
Sources	Combustion of coal, oil, gasoline,	Resuspension of industrial dust and

	diesel, wood; atmospheric transformation products of NO_x, SO_2 and organic compounds including biogenic species (e.g. terpenes); high temperature processes, smelters, steel mills, etc.	soil tracked onto roads; suspension from disturbed soil (e.g. farming, mining, unpaved roads); biological sources; construction and demolition; coal and oil combustion; ocean spray
Lifetimes	Days to weeks	Minutes to Hours
Travel distance	100s to 1000s of kilometers <	<1 to 10s of kilometers

1.3 Atmospheric life time and removal mechanism of PM

The lifetime of atmospheric aerosol particles depends on their properties (size, chemical composition, etc.) and on altitude range, too (Figure 1.6) [19].

Figure 1.6: Atmospheric lifetime of different size particles at different levels of the atmosphere



In the atmospheric boundary layer (lower troposphere), the residence time of aerosol particles is usually less than a week, often on the order of a day, depending on aerosol properties and meteorological conditions. In the free troposphere, the typical particle lifetime is 3–10 days on average. During this time, particle can easily be transported to a long distance. Therefore, there is a large variability in particle concentration, reflecting the geographical distribution of sources and sinks. The stratosphere also contains aerosol particles, which have much longer lifetime (up to 1 year), than in the tropospheric particles, due to the lack of precipitation.

Smaller particles are efficiently removed by coagulation with other particles. Therefore, their lifetime is very short (in a range of ten minutes to day). Similarly, the large particles spend only a short time in the atmosphere due to the sedimentation. Particles in the accumulation mode have the longest lifetime (7–10 days on average), as in this range, both the Brownian diffusion and sedimentation are less important. These particles removed from the atmosphere predominantly by wet deposition. One of the critical parameter governing the atmospheric removal mechanism of PM is its settling velocity. The settling velocity of any particle derived from the stoke's law is given as,

$$V = \frac{(\rho_p - \rho_g)d^2 g}{18\eta} \qquad (1)$$

While, this equation is not valid for particles less than1.0 μm size as this equation explains the predominant gravitational settling. Therefore, settling velocity with a slip correction is applied for particles of size less than 1 μm and is stated as equation 2.

$$V = \frac{(\rho_p)d^2 gC_C}{18\eta} \tag{2}$$

Emissions to the atmosphere in the form of gases and particles from natural (e.g., sea spray and soil erosion) and anthropogenic sources such as fossil fuel combustion can be returned to the land and water bodies via atmospheric depositional processes [20]. Removal of aerosol as a whole occurs by dry and wet deposition to the earth surface.

The effectiveness of deposition depends strongly on particle size. For small particles especially those with diameters below 0.1 µm, Brownian diffusion becomes increasingly important with decreasing particle size. Particles in size range between 0.1-1µm represent a rather stable tropospheric aerosol. The only tropospheric sink of importance for this range seems to be their incorporation as condensation nuclei into cloud droplets. Inertial impaction is an important removal mechanism when the momentum of a particle is sufficient to maintain a nearly linear trajectory in a moving air mass. Particularly for particles of aerodynamic diameters between 0.5-15 µm inertial impaction becomes an important phenomenon. Coarse particles on other hand are removed by dry deposition due to sedimentation or gravitational settling. As far as particles are concerned, both dry and wet deposition may contribute significantly to their removal.

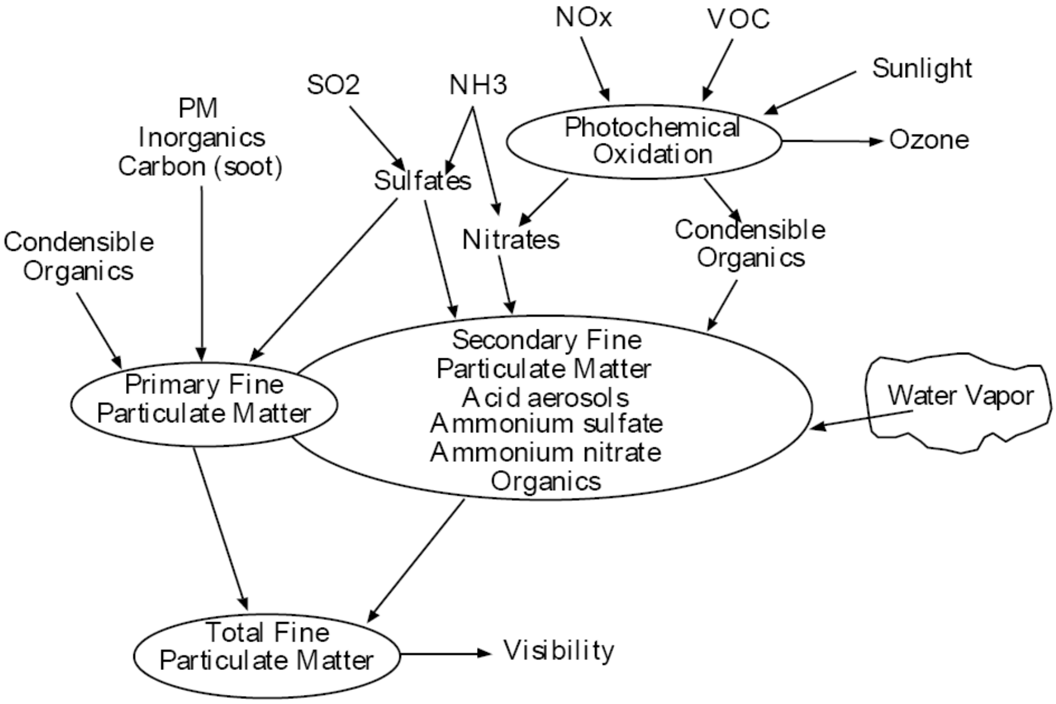
Wet depositions is the name given to deposition pathways involving water. They include rainout, washout, sweepout,, and occult deposition but the first two mechanisms are the most important [21]. The rain out process takes place in clouds producing rain. Where, aerosol nuclei condense as cloud droplets and the drops grow to such a large size that they fall to the surface as rain drops. In the sweepout process aerosol remaining below the cloud base of a raining cloud are removed along with the raining droplets. In occult deposition, aerosol can be incorporated into droplets in clouds making contact with the surface of the ground (e.g. Fog). However, rainout and washout are considered as the principal mechanisms leading to wet deposition of trace substances. The sufficiency of these scavenging processes depends on the intensity of precipitation, the drop size-spectrum, pH value and temperature of drops as well as on the vertical distribution of trace substances in the atmosphere. Chemical conversion processes within the atmosphere plays an important role in precipitation chemistry and in wet deposition. Incorporation of certain trace-substances into cloud and precipitation elements leads to the formation of "acid precipitation".

1.4 Chemical composition and potential sources

PM is a complex mixture of different pollutants from a variety of sources. In order to determine its origin, an analysis of the individual chemical components is necessary. This section provides a discussion of the sources and nature of ambient PM. A basic understanding of PM characteristics provides improved insight into critical factors that should be considered in the design of a PM monitoring program.

Particulate matter may be either directly emitted into the atmosphere (primary particulate) or formed there by chemical reactions (secondary particulate). The relative importance of primary and secondary particles depends mainly on the geographical location, with its particular mix of emissions, and on the atmospheric chemistry. For example, in areas where fire wood is consistently used as household fuel, most of the particles are primary in nature especially in the winter season, whereas during summertime, a substantial fraction of the particulate matter is attributed to secondary reactions in the atmosphere such as photochemical reactions. These secondary reactions typically involve secondary PM precursor gases such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), and a wide variety of organic compounds. The resulting secondary PM compounds include sulphates, nitrates, and condensed organic compounds. As shown in Figure 1.7, these particles are formed via several pathways.

Figure 1.7: Fine particulate formation pathways



1.4.1 Primary Particles

Atmospheric concentrations of primary particles are, on average, proportional to the quantities that are emitted. Primary particles are emitted in several size ranges, the most common being less than 1µm in aerodynamic diameter from combustion sources and larger than 1µm in aerodynamic diameter from dust sources. Particles larger than 10 µm in aerodynamic diameter usually deposit to the surface within a few hours after being emitted and do not have a large effect on light scattering, unless high winds and turbulence re-suspend the particles.

Emission source categories include: 1) major stationary (point) sources (e.g., boilers, process heaters, incinerators, and steam generators); 2) area sources (e.g., fires, windblown dust, petroleum extraction operations, and residential fuel combustion); 3) mobile sources (e.g., automobiles, buses, trucks, trains, and aircraft); 4) agricultural and ranching activities (e.g., fertilizers, herbicides, tilling operations, and ammonia emissions from livestock); and 5) biogenic sources (e.g., pollen fragments and particulate abrasion products from leaf surfaces).

1.4.2 Secondary Particles

Once released into the atmosphere, primary particle emissions are subjected to dispersion and transport and, at the same time, to various physical and chemical processes that determine their ultimate environmental fate. The role of the atmosphere may be compared in some ways to that of a giant chemical reactor in which materials of varying reactivities are mixed together, subjected to chemical and/or physical processes and finally removed. Primary emissions from various sources such as motor vehicles, residential wood combustion, etc., are very complex mixtures containing thousands of organic and inorganic constituents in the gas and particulate phases. These compounds have different chemical reactivities and are removed by dry and wet deposition processes at varying rates. Some of the gaseous species, by a series of chemical transformations, are converted into particles, forming secondary aerosols. Sulphates and nitrates are the most common secondary particles, though a fraction of organic carbon can also result from volatile organic compounds (VOC) via atmospheric reactions.

Atmospheric gases can also become suspended particles by absorption, dissolution, or condensation. Several of these mechanisms may operate in series in the process of secondary particle formation. In absorption, gas molecules are attracted to and adhere to existing particles. Sulphur dioxide and many organic gases have an affinity for graphitic carbon, and most graphitic carbon particles in the atmosphere are usually found in association with an organic component. Most gases are somewhat soluble in water, and liquid particles will rapidly become saturated in the presence of sulphur dioxide, nitrogen dioxide, and certain organic gases. Many hydrocarbons are emitted at elevated temperatures as a result of incomplete combustion and condense rapidly upon cooling to ambient temperatures. These are usually considered to be primary emissions if the condensation takes place rapidly, within approximately 1 minute of exiting the stack and the particles formed are sensitive to changes in temperature and the surrounding gas concentrations.

1.4.3 Major components of PM

Six major components account for the particulate mass in most urban areas: 1) geological material (oxides of aluminum, silicon, calcium, titanium, and iron); 2) organic carbon (consisting of hundreds of compounds); 3) elemental carbon; 4) sulphate; 5) nitrate; and 6) ammonium. Liquid water absorbed by soluble species is also a major component when the relative humidity exceeds approximately 70 percent, but much of this evaporates when filters are equilibrated prior to weighing. Water-soluble sodium and chloride are often found in coastal areas, and certain trace elements are found in areas greatly influenced by industrial sources.

(i) **Geological Materials :** Suspended dust consists mainly of oxides of Aluminum, silicon, calcium, titanium, iron and other metal oxides. The precise combination of these minerals depends on the geology of the area and industrial processes such as steel-making, smelting, mining and cement production. Geological material is mostly in the coarse particle fraction and typically constitutes 50% of PM_{10} and 5 to 15% of $PM_{2.5}$.

(ii) **Sulfate :** Ammonium sulfate, ammonium bisulfate and sulfuric acid are the most common forms of sulfate found in atmospheric particles, resulting from conversion of gases to particles as described below. These compounds are water-soluble and reside almost exclusively in the PM2.5 size fraction. Sodium sulfate may be found in coastal areas where sulfuric acid has been neutralized by sodium chloride in sea salt.

(iii) **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. Because this equilibrium is reversible ammonium nitrate particles can easily evaporate in the atmosphere or after they have been collected on a filter owing to changes in temperature and relative humidity. Sodium nitrate is formed in the PM2.5 and coarse size fractions where nitric acid vapour irreversibly reacts with sea salt.

(iv) **Ammonium :** Ammonium sulfate, ammonium bisulfate and ammonium nitrate are the most common compounds containing ammonium from irreversible reactions between sulfuric acid and ammonia gas.

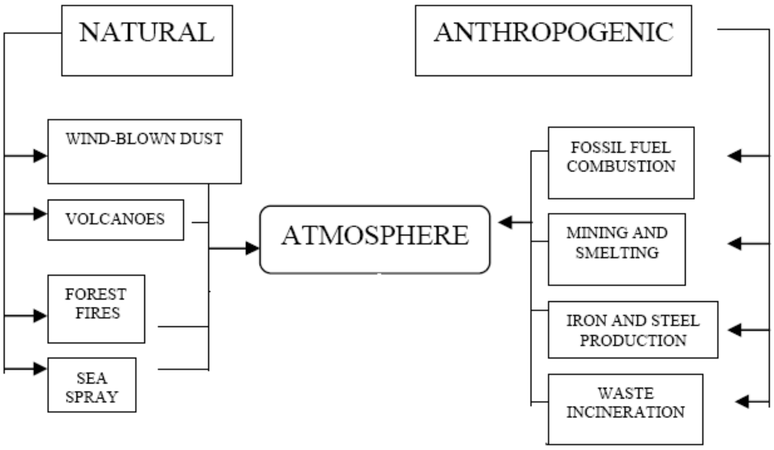
(v) **Organic Carbon :** Particulate organic carbon consists of hundreds, possibly thousands of separate compounds that contain more than 20 carbon atoms.

(vi) **Elemental Carbon :** It 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, biogenics and coke.

1.4.4 Atmospheric Trace Metals and sources

About 90 elements are found in the earth's crust, out of which a mere 9 elements (Al, Fe, Ca, Mg, O, Si, Na, K and Ti) only account for over 99% by weight. The remaining 81 elements together, which account for hardly 0.14% by weight, constitute the so called "trace elements". These elements, notwithstanding their low abundance in nature, play a vital role in plant and animal nutrition. Contamination of the atmosphere by pollutant trace metals contributed from the natural and anthropogenic sources affects the environment directly through its impact on air quality and indirectly by the impact on terrestrial and aquatic ecosystems following deposition on the land surface or in water bodies. The major sources of atmospheric trace elements are depicted in Figure 1.8.

Figure 1.8: Sources of trace elements in the atmosphere



1.4.4.1 Natural sources of trace metals

Windblown soil is one of the largest sources of natural metal emissions to the atmosphere. Through the process of weathering and erosion, metals that naturally occur in the Earth's crust will also be found in soil. Several authors have estimated the amount of soil that is entrained into the atmosphere via the wind, with the general range of 200-500 x 10^9 kg/yr globally.

An assessment of trace metal emissions from natural sources is indeed in order to discuss the extent of regional and global contamination of the environment by these pollutants. It is generally assumed that the principal natural sources of trace metals include wind-borne soil particles, volcanoes, sea-salt spray and wild forest fires.

1) Soil derived dust accounts for over 50% of the total Cr, Mn and V emissions, as well as for 20 – 30% of the Cu, Mo, Ni, Pb, Sb and Zn released annually to the atmosphere.

2) Volcanic emanations can account for 40-50% of the total natural Cd & Hg & 20-40% of the total As, Cr, Cu, Ni, P and Sb emitted annually.

3) Recent studies have shown that over 60% of the airborne trace metals in forested regions can be attributed to aerosols of biogenic origin. Indeed, Nriagu estimated that

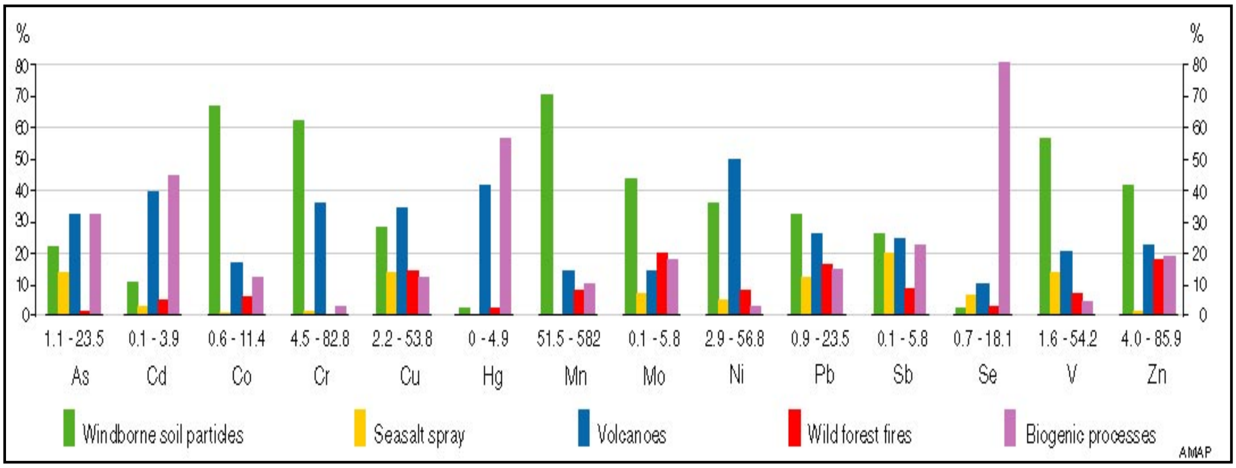
biogenic sources contribute, on average, over 50% of Se, Hg and Mo and from 30-50% of the As, Cd, Cu, Mn, Pb and Zn, to the total atmospheric emissions from all natural sources.

4) Sea-salt aerosols seem to account for <10% of atmospheric trace metals from natural sources. The production mechanisms for sea-spray aerosols are quite well known. Two of these mechanisms are important for release of trace metals with sea-salt: ‘bubble bursting’, important primarily for Cd, Ni, Cu, Pb & Zn and gas exchange, important for As.

5) In certain parts of the world, forest fires are the major emission sources of particles and particle – containing trace metals. In general, more than 10% of the atmospheric Cu, Pb and Zn from natural sources can originate from this source.

Worldwide emissions of trace metals from natural sources is presented in Figure 1.9.

Figure 1.9: Global emissions of trace metals from natural sources



Courtesy: Arctic Monitoring and Assessment Programme (AMAP)

1.4.4.2 Anthropogenic sources of trace metals

The predominant anthropogenic sources are pyrometallurgy, biomass burning (veld fires), fossil-fuel combustion and incineration. Atmospheric trace metal species usually associated with anthropogenic activities include arsenic (As), cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), vanadium (V), mercury (Hg) and lead (Pb). Metal smelting is regarded as one of the most important anthropogenic trace metal emission sources. During smelting processes, metals in the ores are evaporated from the matrix, which could be emitted into the atmosphere if proper pollution control technology is not applied. Industrial metallurgical processes produce the largest emissions of As, Cd, Cu, Ni and Zn [22].

1) The global emission inventories show that most anthropogenic Be, Co, Mo, Sb and Se are emitted from coal combustion.

2) Large amounts of As, Cd, & Cu are emitted by smelters and secondary non-ferrous metal plants.

3) Mn and Cr are released mainly from factories producing iron, steel and ferro-alloys. Mn is the most widely used element in ferro-alloys, followed by Si, Cr & P. Mn particles with Zn and Fe are derived from the ferrous manganese process.

4) Cr vapours from steel production can condense as oxides on the surface of different sorts of airborne particles. Cr was found to be significantly concentrated on the surface of combustion particles, a process that forms a wide variety of Cr – containing particles and complicates source identification. The cement industry is another potential source of atmospheric Cr as they use in their high temperature process more than 30 raw materials containing Cr concentrations in the ppm range.

5) The emission of Fe rich particles mainly results from metallurgical processes. Fe–S particles can be formed by reaction between FeO_2 and H_2SO_4, during their release in ferrous metallurgy related combustion processes.

6) Most Zn production originates from ZnS minerals, which are converted into metallic Zn in the series of processes. The main use of Zn is in resistance. ZnS is related to Zn ores, which are mostly stored uncovered and therefore easily taken up by the wind.

7) Pb- The average emission of all sources was estimated to be around 0.123×10^3 kg /yr in Europe. The most important source is the combustion of gasoline contributing for more than 50% of the total Pb emission. Other major emitters are coal combustion, steel industry

and cement factory. According to Fergusson, metallic Pb comes mainly from emission of coal fired stations, cement and fertilizer production, base metal smelting and even automotive exhaust. Particle type of Pb together with Cl and Br originate from car exhaust emissions have been studied extensively, while particles of Pb associated with Ca or P are linked with emissions of fertilizer productions or cement manufacturing.

8) Elements like Ni and V are released by oil combustion processes in power plants due to oil fired furnaces. The contribution of natural sources to the total emission of Ni and V are 14% & 16% respectively and therefore these elements are used as indicator elements of oil fired power plants and oil combustion sources in numerous industries. The main source for Ti release into the atmosphere is pigment spray, but also minor pollution processes and sources such as soil dispersion, asphalt production and coal fired boilers and power plants are known.

9) Cd is emitted from stabilizers, alloys and batteries, but the trace element emissions from these sources are relatively small and can be neglected.

World wide emissions of trace metals from anthropogenic sources is presented in Figure 1.10 (**Source:** Arctic Monitoring and Assessment Programme (AMAP)). Also various trace metals and major ions emitted from different sources in coarse and fine fractions are listed in Table 1.3.

Figure 1.10: Worldwide emissions of trace metals from anthropogenic sources

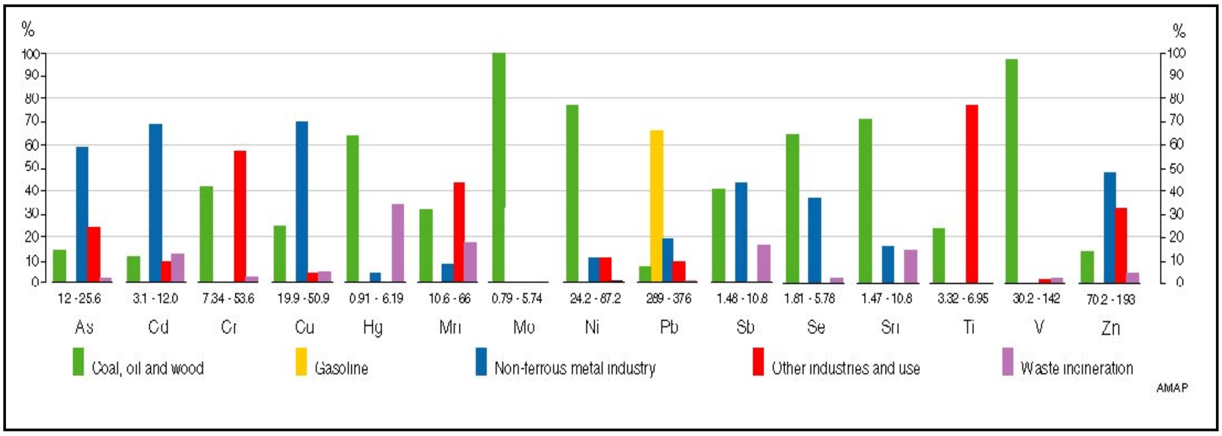


Table 1.3: Chemicals Emitted Directly from Different Emission Sources

Source Type	**Dominant Particle Size**	**Chemical abundances in Percent Mass**			
		<0.1%	**0.1 to 1%**	**1-10%**	**>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, Ca, P, 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, V, Mn, Cu, Ag, Sn	NH^+,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
Marine (Natural)	Fine 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

Source: CPCB, Conceptual guidelines and common methodology for air quality monitoring, emission inventory and source apportionment studies for Indian cities

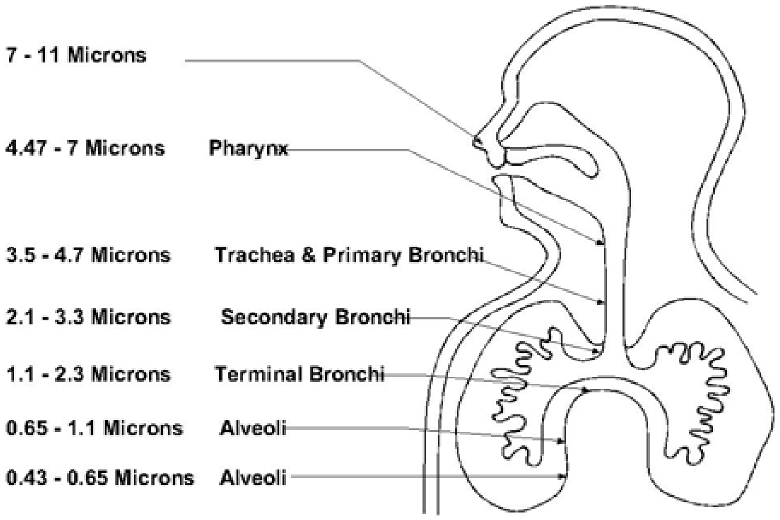
1.5 Human Health Effects

As toxicity of PM is influenced by its physical and chemical composition, many carcinogens and co-carcinogens such as PAHs, transition metals, and aldehydes that are present in PM and contribute to PM-related carcinogenesis [23]. Transition metals, although poor mutagens and carcinogens themselves, can enhance the mutagenicity and carcinogenicity of other potential carcinogens such as PAHs [24] and are considered to contribute to PM induced cytotoxicity and oxidative stress. By inhalation and respiration, airborne particles enriched with potentially toxic trace metals could deposit in hyman body and cause chronic and acute health problems [25, 26, 27].

The capacity of particulate matter to produce adverse health effects in humans depends on its deposition in the respiratory tract. Particle size, shape, and density affect deposition rates. The most important characteristics influencing the deposition of particles in the respiratory system are size and aerodynamic properties. Particles between 2.5 and 10µm in aerodynamic diameter correspond to the inhalable particles capable to be deposited, in the upper respiratory tract. Particles with aerodynamic diameter smaller than 2.5µm ($PM_{2.5}$), called fine particles, correspond to the respirable particle fraction capable of penetrating the alveolar region of the lung.

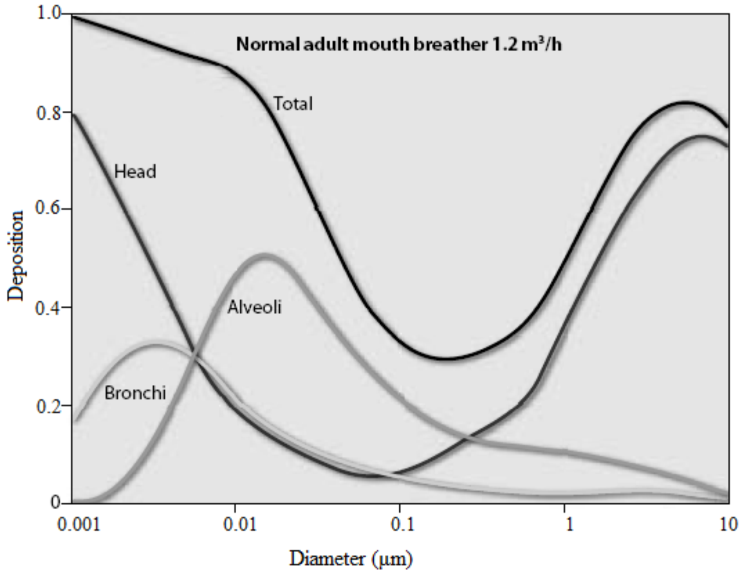
Inhaled particles come in contact with surface of the respiratory system and there are five mechanisms that influence particle deposition within the respiratory tract. The primary mechanisms are gravitational settling, impaction, and Brownian diffusion. Secondary mechanisms are electrostatic attraction and interception. These last two processes have minimal importance for inhalation and deposition of particulate matter. Deposition by gravitational settling occurs as a result of the influence of gravity on particles suspended in the air. The settling rate of particles is directly proportional to particle size. This process is most important in the distal region of the bronchial airway and in proximal portions of the gas exchange region. Another mechanism of particle deposition is impaction. Due to inertia airborne particles do not follow changes in direction or speed of airflow and they may impact on the wall of the airway. This mechanism occurs primarily in the throat and larynx with particles larger than 3µm and increases with increasing particle size. Brownian diffusion involves collision between gas molecules and micrometer-sized particles, which push the particle in an irregular manner. It depends on the diffusive or thermodynamic diameter of the airborne particle rather than on the aerodynamic diameter. Due to this, Brownian diffusion increases with decreasing particle size. This mechanism is predominant in the gas exchange alveolar region of the lung for particles smaller than 0.5µ m. Figure 1.11 depicts the deposition potential for particles of varying sizes in the respiratory system.

Figure 1.11: Deposition potential for particles of varying sizes



Also, Figure 1.12 shows schematically how the deposition of particles in the respiratory tract vary with respect to the size of the particle. Smaller particles (in particular $PM_{2.5}$) penetrate more deeply into the lung and may reach the alveolar region. Ultrafine particles contribute only slightly to PM_{10} mass but may be important from a health point of view because of the large numbers and high surface area. They are produced in large numbers by combustion (especially internal combustion) engines. As stated above, PM in ambient air has various sources. In targeting control measures, it would be important to know if PM from certain sources or of a certain composition gave rise to special concern from the point of view of health, for example owing to high toxicity.

Figure 1.12: Respiratory tract deposition probability of inhaled particles



There are other factors that also influence particle deposition, including mode of breathing like oral breathing permit the passage of particles greater than 10µ m to the lung, physical activity (exercise), age, lung diseases (chronic obstructive lung disease), and ambient conditions (increase in temperature or the presence of other pollutants). The ability of the lung trying to protect itself against inhaled particles, clearance, will determine the adverse health effects of particulate matter. There are two clearance mechanisms: the mucociliary system and the alveolar macrophages. Particles deposited in the ciliated region of the trachea-bronchial airway, rise on the mucociliary ladder to be expelled by coughing or swallowing. Particles deposited on the terminal bronchioles are cleared by lung macrophages. An early cellular response to an acute particulate exposure is damage to epithelial cells of respiratory tract, which also produce many different types of inflammatory mediators. The local pulmonary inflammation induced by PM_{10} could impact on the cardiovascular system via the local production of procoagulant factors in the lung or as a result of the effects of mediators released from the lungs which act on the liver, to increase the levels of procoagulant factors which could promote myocardial infarction.

The adverse cardiovascular effects associated with increases in PM are well documented [28, 29, 30, 31]. The mortality and morbidity time series studies have shown, much more clearly than before, that cardiovascular deaths and morbidity indicators are related to ambient PM. Increased air pollution particles are related to increases in deaths and hospital admissions in time series studies [32, 33] and population studies [34, 35].

It is estimated that approximately 3% of cardiopulmonary and 5% of lung cancer deaths are attributable to PM globally. There is good evidence of the effects of short-term exposure to PM_{10} on respiratory health, but for mortality, and especially as a consequence of long-term exposure, $PM_{2.5}$ is a stronger risk factor than the PM_{10} (particles in the 2.5–10 μm range). All-cause daily mortality is estimated to increase by 0.2–0.6% per 10 $\mu g/m^3$ of PM_{10}. Long-term exposure to $PM_{2.5}$ is associated with an increase in the long-term risk of cardiopulmonary mortality by 6–13% per 10 $\mu g/m^3$ of $PM_{2.5}$ [36]. Also a mechanism is suggested to explain part of the toxic effects of inhaled PM is the oxidative stress arising from interaction of the particles with inflammatory cells, as alveolar macrophages [37]. As underlined by [35], the ability of PM to cause oxidative stress probably underlies the association between increased exposure to PM and the exacerbation of lung diseases.

Both short-term (24 hours) and long-term (annual average) guidelines are recommended by WHO for particulate exposure. The effects of short-term exposure to PM have been documented in numerous studies many of them conducted in Europe. These indicated large numbers of outcomes, such as attributable deaths and hospital admissions for cardiovascular and respiratory conditions. The WHO defines the principal short and long-term health effects attributed to Particulate Matter according to Table 1.4:

Table 1.4: Health Effects of PM

Short - Term	Long - Term
Lung inflammatory reactions	Increase in lower respiratory symptoms
Respiratory symptoms	Reduction in lung function in children
Increase in medication usage	Increase in chronic obstructive
Increase in hospital admissions	Reduction in lung function in adults
Increase in mortality	Reduction in life expectancy

Both peak and cumulative exposures to PM in ambient air are significantly associated with adverse health effects and account for increases in mortality and morbidity more than any other regulated environmental pollutant [38, 39]. In particular, (1) the mass concentration of $PM_{2.5}$ has generally been significantly associated with excess cardiovascular mortality and morbidity in urban areas around the world [39]; (2) the mass concentration of $PM_{10-2.5}$ in ambient air has often been significantly associated with excess respiratory mortality and morbidity in urban areas; (3) the associations with adverse health effects are usually stronger for combustion products of solid and liquid fossil fuels (e.g., transition metals and BC) than for other components of PM, which suggests that mass concentrations are, at best, crude indicators of health risks [40]; and (4) interventions that have reduced exposures to metals and BC have led to prompt improvements in public health.

From a mechanistic perspective, it is highly plausible that the chemical composition of particulate matter (PM) would better predict health effects than other characteristics, such as PM mass or size. This is consistent with the large number of laboratory studies that have demonstrated compositional variability in PM toxicity and epidemiologic studies that portray the regional heterogeneity in PM-related health effects [41, 42]. Studies and reviews focusing on individual components of PM have reported linkages with adverse health effects and are presented in Table 1.5 as referred by [43].

Components for which direct and indirect evidence of associations have been found include metals (i.e., Ni, V, Pb, and Zn) at or near ambient concentrations [44], and organic (carbonaceous) aerosols [45]. The role of some components, such as inorganic sulfate (SO_4^{2-}), nitrate (NO_3^-) and crustal-derived components of $PM_{2.5}$ has been less conclusive due to limited data, as well as inconsistent results across disciplines [46].

Table 1.5: PM$_{2.5}$ source categories associated with respiratory health effects

Grouped Components	Named Source	Location	Health Effects	Type of Study	Reference
Al, Ca, Fe, Si	Soil	Santiago, Chile	↑ Mortality	E	Cakmak et al. (2009)
Si, Fe, Al, Ca, Ba, Ti	Road Dust	New Haven, CT	↑ Respiratory Symptoms	E	Gent et al. (2009)
Si, Al, Ca, Fe, Mn	Soil	Helsinki, Finland	↓ Lung Function	E	Penttinen et al. (2006)
Al	Road dust	Boston, MA	↓ Lung Function	T	Nikolov et al. (2008)
Na, Cl	Salt	Helsinki, Finland	↓ Asthma medication use	E	Penttinen et al. (2006)
Na, Cl	Not provided	Boston, MA	↑ Lung inflammation	T	Saldiva et al. (2002)
SO_4^{2-}, NH_4^+, OC	Secondary sulfate, Ammonium sulfate	Atlanta GA,	↑ ED Visits	E	Sarnat et al. (2008)
Not provided	Secondary inorganic compounds	Copenhagen, Denmark	↑ Hospital Admissions	E	Anderson et al. (2007)
S, K, Zn, PM Mass	Long range transport	Helsinki, Finland	↓ Lung Function	E	Penttinen et al. (2006)
SO_4^{2-} (+NO_2)	Not provided	Los Angeles, CA	↓ Lung Function	H	Gong et al. (2005)
CO, NO_2, EC, OC	Vehicle	Santiago, Chile	↑ Mortality	E	Cakmak et al. (2009)
EC, Zn, Pb, Cu, Se	Vehicle Exhaust	New Haven, CT	↑ Respiratory symptoms	E	Gent et al. (2009)
NOx, ultrafine PM, Cu, Zn, Mn, Fe	Local combustion	Helsinki, Finland	↓ Lung Function	E	Penttinen et al. (2006)
Not provided	Gasoline + Secondary Nitrate	Birmingham, AL; Atlanta, GA; Pensacola, FL; Centreville, AL;	↑ Cytotoxicity	T	Seagrave et al. (2006)
Not provided	Gasoline + Diesel	Birmingham, AL; Atlanta, GA; Pensacola, FL; Centreville, AL;	↑ Inflammation	T	Seagrave et al. (2006)
Ni	Oil Combustion	Boston, MA	↓ Respiratory rate	T	Nikolov et al. (2008)
V, Ni	Not Provided	Boston, MA	↑ Lung inflammation	T	Saldiva et al. (2002)
Cr, Cu, Fe, Mn, Zn	Combustion	Santiago, Chile	↑ Mortality	E	Cakmak et al. (2009)
Not provided	Biomass combustion	Copenhagen, Denmark	↑ Hospital Admissions	E	Anderson et al. (2007)
Total Carbon	Vegetative burning	Spokane, WA	↑ ED visits	E	Schreuder et al. (2006)
Fe-Se- SO_4^{2-}	Not provided	Chapel Hill, NC	↑ Lung inflammation	H	Huang et al. (2003)
Br, Cl, Pb	Not provided	Santiago, Chile	↑ Mortality	E	Cakmak et al. (2009)
Br, Pb	Not provided	Boston, MA	↑ Lung Inflammation	T	Clarke et al. (2000)
Br, Pb	Not provided	Boston, MA	↑ Lung Inflammation	T	Saldiva et al. (2002)

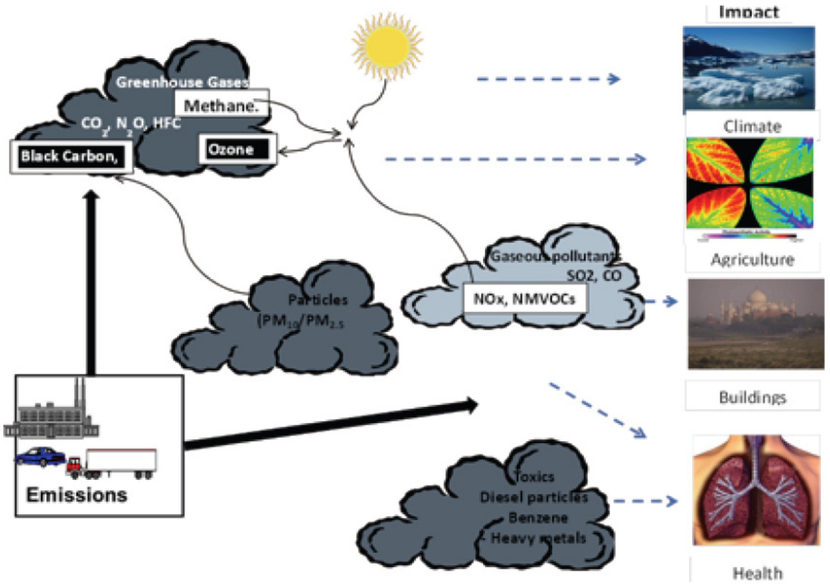
1.6 Environmental and Climate Effects

The major effects of air pollution are not just limited to the effects of primary particles, but also to secondary products of airborne compounds that form particulate matter. The very different chemical natures of the components of $PM_{2.5}$ mean that their effects in natural systems also differ greatly. The three major effects of PM are,

- Climate change
- Acid deposition
- Changes in visibility
- Ozone

The deposition of PM on surfaces may also cause damages by corrosion and deteriorate painted surfaces and other building materials [47]. Some of the major impacts of air particles are portrayed in Figure 1.13.

Figure 1.13: Air Pollutant classification and their major impacts

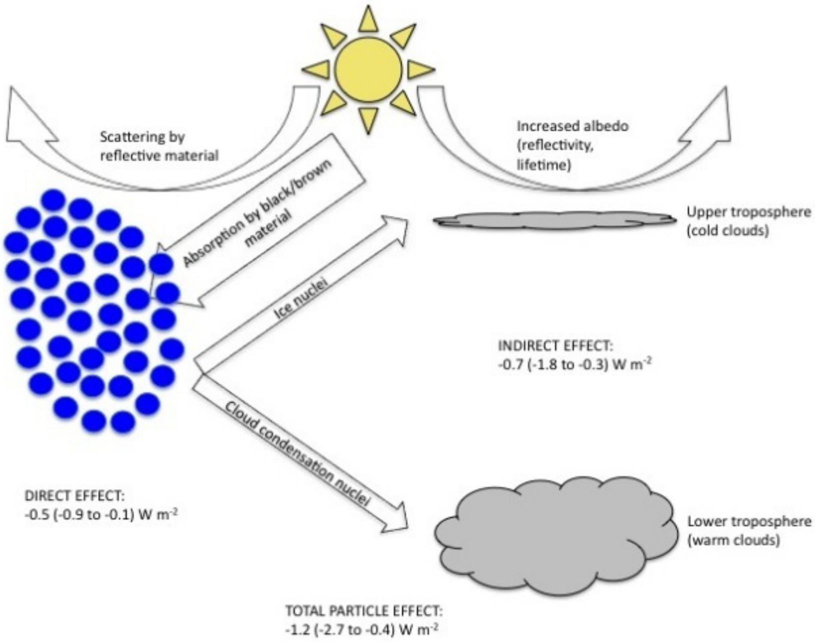


1.6.1 Radiative Forcing and Climate Change

Climate change and Air pollution are intimately linked through emissions from common sources, primarily those related to the use of fossil fuels. Recent research confirms that global climate changes will likely trigger increases in smog and health problems even if the level of man-made smog-causing pollutants remains the same. Climate change is strongly influenced by both by gaseous and aerosol anthropogenic emissions and, in past decades, it has become a problem of serious concern. Human activities result in emissions of four principal greenhouse gases: Carbon dioxide (CO_2), methane (CH_4), Nitrous Oxide (N_2O) and the halo carbons. While knowledge about green house gases is well advanced, the influence of aerosol particles to climate change is far less understood. Among the atmospheric pollutants particulate matter is one of the most important pollutant as the earth's climate change effects are considered. These particles can scatter or absorb both incoming solar radiation and thermal radiation emitted from the Earth's surface to directly change the radiation balance [48, 49] and thus leading to climate effects [50, 51].

Climate forcing is defined as the change imposed by certain forcing agents which include greenhouse gases and aerosol particles in the energy balance of the earth (in units of Wm^{-2}) that eventually alters global temperature [52]. Fine particulate matter influences the climate directly (through scattering and absorption of the solar radiation) and indirectly through the formation of Cloud Condensation Nuclei (CCN). The direct aerosol contribution to radiative forcing is due to sulphate aerosols, fossil fuel soot and biomass burning. Submicron particles scatter more light per unit mass and have a longer atmospheric lifetime than larger aerosols. They have a direct radiative forcing because they scatter and absorb solar and infrared radiation in the atmosphere. Particles also alter warm, ice and mixed-phase cloud formation processes by increasing droplet number concentrations and ice particle concentrations [53]. A thorough review of this matter can be found in the United State's Environmental Protection Agency's report about environmental effects of airborne PM [47]. The overall radiative forcing due to indirect and direct effects along with the magnitude is illustrated in Figure 1.14 [54].

Figure 1.14: An illustration of the magnitude of the direct and indirect effects of particles on climate



1.6.2 Acid deposition on Materials

An important part of particulate matter pollution is the soiling of man-made surfaces. Hence, the processes of cleaning, painting and repairing exposed surfaces become an economic burden. Acid particles can severely deteriorate artwork and historic monuments (cultural heritage) and result in the reduction of their aesthetic appearance and life span [55]. Chemical degradation of materials due to deposition of atmospheric acid particles is an important aspect of material damage [56, 57]. The deposition of airborne particles on the surface of building materials and culturally important articles can cause damage and soiling, thus reducing the life usefulness and aesthetic appeal of such structures Furthermore, the presence of particles on surfaces may also exacerbate the physical and chemical degradation of materials that normally occur when these materials are exposed to factors such as sun, wind, temperature fluctuations and moisture. Beyond these effects, particles, whether suspended in the atmosphere, or already deposited on a surface, also adsorb or absorb acidic gases from other pollutants like sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), thus serving as nucleation sites for these gases. The deposition of "acidified" particles on a susceptible material surface is capable of accelerating chemical degradation of the material.

1.6.3 Visibility

Interest in protecting visibility in urban areas has a long history and is strong in today's society. The most immediate and obvious impact of urban air pollution is its impairment of visibility.

"Visibility is the degree to which the atmosphere is transparent to visible light." Section 169A of the 1977 Clean Air Act (CAA) Amendments (42 U.S.C. 7491) and the 1979 Report to Congress [58] define visibility impairment as a reduction in visual range and atmospheric discoloration. Visibility may also be defined as the clarity (transparency) and color fidelity of the atmosphere. Transparency can be quantified by the contrast transmittance of the atmosphere. The perception of color depends on illumination and setting. Particulates with a diameter less than 10µm (PM_{10}) and particularly of diameter less than 2.5µm ($PM_{2.5}$) are characterized by optimum sizes that scatter light with wavelength in the visible range. This is one of the reasons PM_{10} and $PM_{2.5}$ are acceptable measures of visibility degradations even though they are commonly used for assessing health effects [59]. One way to measure the effect of particulate matter on visibility is to measure the light scattering efficiency of particles. The higher the light scattering efficiency, the less light from any given object reaches an observer's eyes, decreasing visibility. The light-scattering efficiency differs considerably for fine and coarse particles, ranging from 2.4 to 3.1 m^2/g for fine particles and 0.2 to 0.4 m^2/g for coarse particles [60]. Larger light-scattering efficiencies for fine particles have been observed when significant numbers of the particles are in the 0.5 to 1.0 µm size range. The great majority of light absorption by particles is caused by elemental carbon. Table 1.6 describes the contribution of $PM_{2.5}$ particles to various environmental effects including reduced visibility.

Table 1.6: Contributions of $PM_{2.5}$ particles to environmental effects

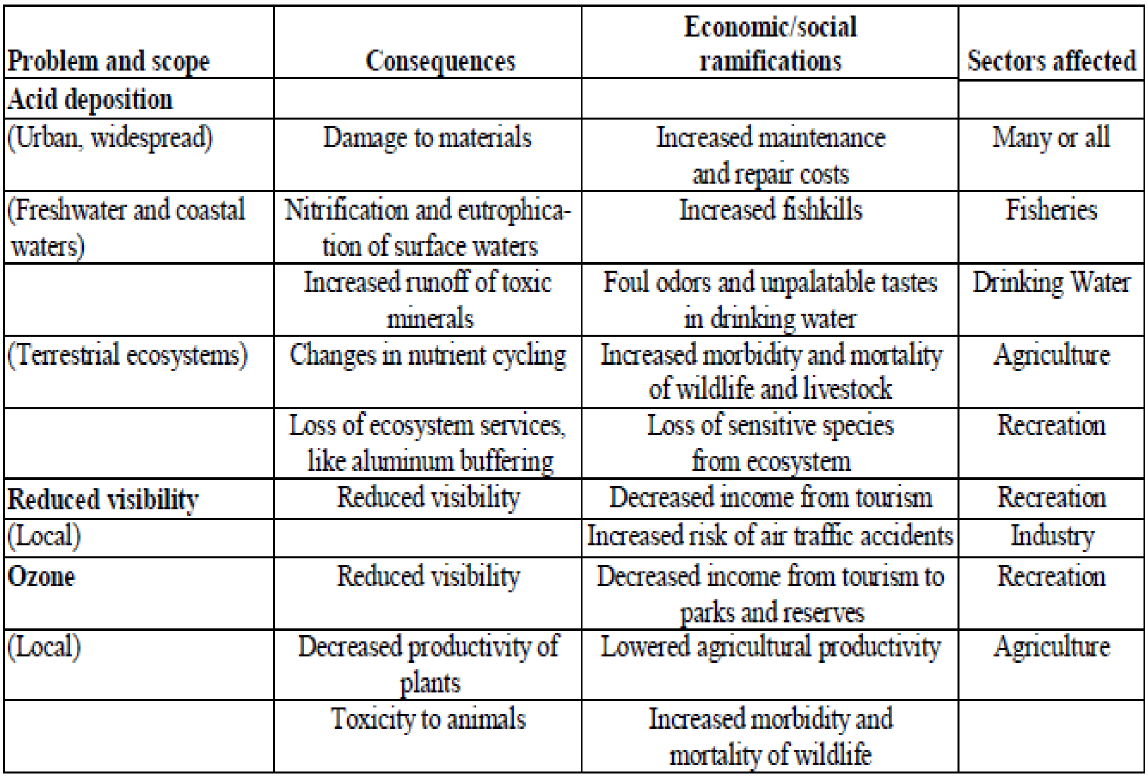
Particle type	**Contributes to**
Soil	Reduced visibility
Organic compounds	Ozone Reduced visibility
Sulfates	Acid deposition Reduced visibility
nitrates	Acid deposition Ozone

Source: www.princeton.edu/step/conferences-reports/ch5

1.6.4 Ozone

Ozone is the most important photochemical oxidant in the troposphere. It is formed by photochemical reactions in the presence of precursor pollutants such as NO_x and volatile organic compounds. O_3 is subject to long-range atmospheric transport and is therefore considered as a trans-boundary problem [61]. Strong sunlight and hot weather cause ground-level ozone to form in harmful concentrations in the air. Many urban areas tend to have high levels of ground-level ozone, but other areas are also subject to high ozone levels as winds carry NO_x emissions hundreds of miles away from their original sources. The environmental and ecological consequences of acid deposition, reduced visibility and ozone are listed in Table 1.7 (Source: www.princeton.edu/step/conferences-reports/ch5).

Table 1.7: Environmental and ecological consequences of acid deposition, reduced visibility and ozone



Problem and scope	**Consequences**	**Economic/social ramifications**	**Sectors affected**
Acid deposition			
(Urban, widespread)	Damage to materials	Increased maintenance and repair costs	Many or all
(Freshwater and coastal waters)	Nitrification and eutrophication of surface waters	Increased fishkills	Fisheries
	Increased runoff of toxic minerals	Foul odors and unpalatable tastes in drinking water	Drinking Water
(Terrestrial ecosystems)	Changes in nutrient cycling	Increased morbidity and mortality of wildlife and livestock	Agriculture
	Loss of ecosystem services, like aluminum buffering	Loss of sensitive species from ecosystem	Recreation
Reduced visibility	Reduced visibility	Decreased income from tourism	Recreation
(Local)		Increased risk of air traffic accidents	Industry
Ozone	Reduced visibility	Decreased income from tourism to parks and reserves	Recreation
(Local)	Decreased productivity of plants	Lowered agricultural productivity	Agriculture
	Toxicity to animals	Increased morbidity and mortality of wildlife	

1.6.5 Ecological Effects

Current regulatory and research initiatives involving suspended particulate matter (PM) are driven first by effects of PM on human health, second by effects on visibility, and only third by the more diverse and ill-defined effects of PM on the function of managed and natural ecosystems. Yet the most injurious long-term impact of PM, from a human perspective, may ultimately prove to be the environmental consequences of reduced biodiversity and the loss of ‘ecosystem goods and services’.

Atmospheric particulate matter (PM) is a heterogeneous material. Though regulated as un-speciated mass, it exerts most effects on vegetation and ecosystems by virtue of the mass loading of its chemical constituents [62]. Coarse and fine PM have a number of contrasting properties that affect their impact on vegetated systems. The presence of PM in the atmosphere directly affects vegetation following physical contact with foliar surfaces, but in many cases the more significant effects are indirect. These effects may be mediated by suspended PM (i.e., through effects on radiation and climate) and by particles that pass through vegetative canopies to reach the soil.

Little attention has been paid to the effects of PM on organisms other than humans or on the processes that underlie ecosystem functioning, it may ultimately prove to be the environmental consequences of reduced biodiversity and the loss of ecosystem goods and services. Direct physical effects of mineral dusts on vegetation became apparent only at relatively high surface loads [63]. Whereas, the chemical effects of reactive materials such as particulate sulphates and nitrates have indirect effects on ecosystems.

1.7 Ambient Air Quality Standards

The US Environmental Protection Agency (US EPA) has classified six principal pollutants as "criteria pollutants". These pollutants are monitored by the EPA, as well as national, state and local organizations. Under the Clean Air Act, EPA's Office of Air Quality Planning and Standards (OAQPS) is responsible for setting standards, also known as National Ambient Air Quality Standards (NAAQS), for pollutants which are considered harmful to people and the environment.

In 1971, the U.S. Environmental Protection Agency (EPA) promulgated the first National Ambient Air Quality Standards (NAAQS) for particulate matter. The original standard was for Total Suspended particulates or TSP. The primary standard for PM (measured as TSP using “high volume” sampler) was 260µg/m^3 over a 24-hour average and an annual standard of 75 µg/m^3**.** In 1987, NAAQS was revised and the previous indicator of particulate matter (TSP) was replaced by PM_{10} (diameter ≤10 µm) and the revised values of PM_{10} are 150 µg/m^3 over a period of 24-hour average period and 50µg/m^3 on annual basis. EPA’s 1997 revisions to the PM NAAQS revised the standards focused on particles smaller than 10 microns (PM_{10} or coarse particles) established in 1987, and introduced standards for "fine" particles smaller than 2.5 microns ($PM_{2.5}$) for the first time. The standard of PM_{10} was retained as prescribed earlier. But the 1997 primary and secondary standards of $PM_{2.5}$ for 24 hours were reduced from 65 to 35 μg/m^3 whereas, the annual average was maintained as 15 μg/m^3 during the revision of 2006. Till 2006 EPA's primary and secondary standards for PM_{10} and $PM_{2.5}$ were identical. After reviewing the science on particle pollution and haze EPA decided the secondary standards are not adequate for visibility protection. In the latest 2012 revision of NAAQS for particulate matter EPA added a separate secondary standard for the annual average of $PM_{2.5}$. i.e. the $PM_{2.5}$ primary standard was retained as 15 μg/m^3 and the secondary standard was made stringent by reducing it from 15 to 12 μg/m^3.

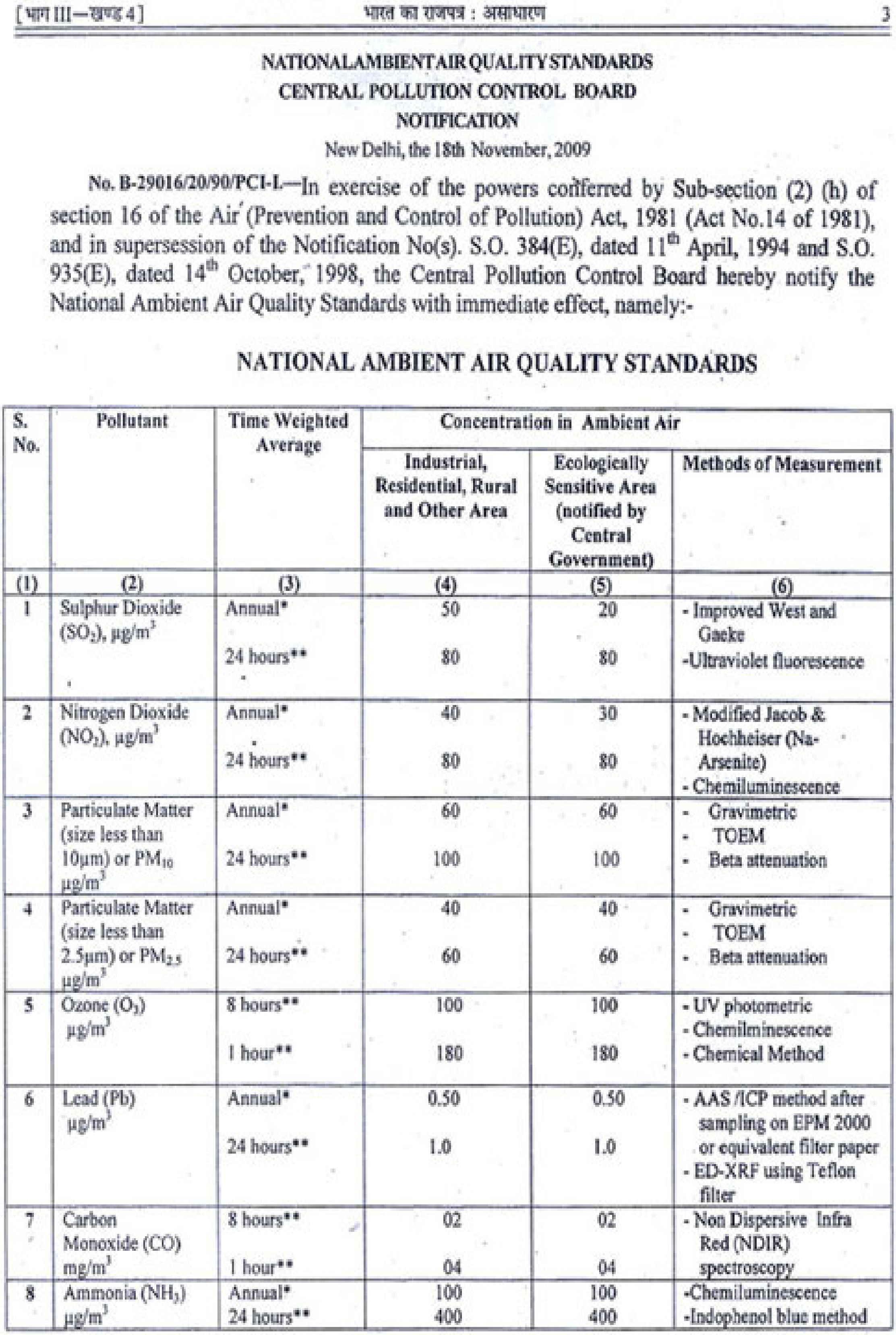
WHO first came up with air quality guidelines in 1987 which were updated in 1996 and subsequently revised in 2000. These were known as Air Quality Guidelines for Europe. There after WHO issued guidelines in 2005 on air quality.

In India Central Pollution Control Board (CPCB) initiated National Ambient Air Quality Monitoring (NAAQM) programme in the year 1984. National Ambient Air Quality Standards (NAAQS) were earlier notified in the year 1994 under the Air Act and has provided separate limits of each air pollutant for the three sectors such as industrial area; residential, rural & other area; and finally for sensitive areas. As per the norms of the revised NAAQS 2009 released by the ministry of environment and forests, residential and industrial areas have same standards. The new NAAQS include limits for benzene, ozone, benzopyrene, arsenic, nickel and ammonia which are not covered in 1994 standards. As the particulate matter standards are concern, standard for $PM_{2.5}$ has been introduced for the first time in the revised limits. But in the earlier 1994 CPCB standards, limits were prescribed for suspended particulate matter and respirable particulate matter. Table 1.8 presents the comparison of ambient air quality standards for particulate matter prescribed by CPCB, US EPA and WHO and Table 1.9 presents NAAQS 2009 of India.

Table 1.8: Ambient air quality standards for PM (CPCB, US EPA and WHO)

Pollutant	**Time weighted average**	**Indian CPCB limits Concentration in ambient air**		**US EPA standard**	**WHO standards**
		Industrial, Residential, Rural and other area	**Ecologically sensitive area (notified by central government)**		
Particulate matter (Size less than 10 µm) or PM10 µg/m^3	Annual	60	60	N.S.	20
	24 hours	100	100	150	50
Particulate matter (Size less than 2.5 µm) or PM2.5 µg/m^3	Annual	40	40	15 (Primary standard) 12(Secondary standard)	10
	24 hours	60	60	35	25

Table 1.9: National Ambient Air Quality Standards, India



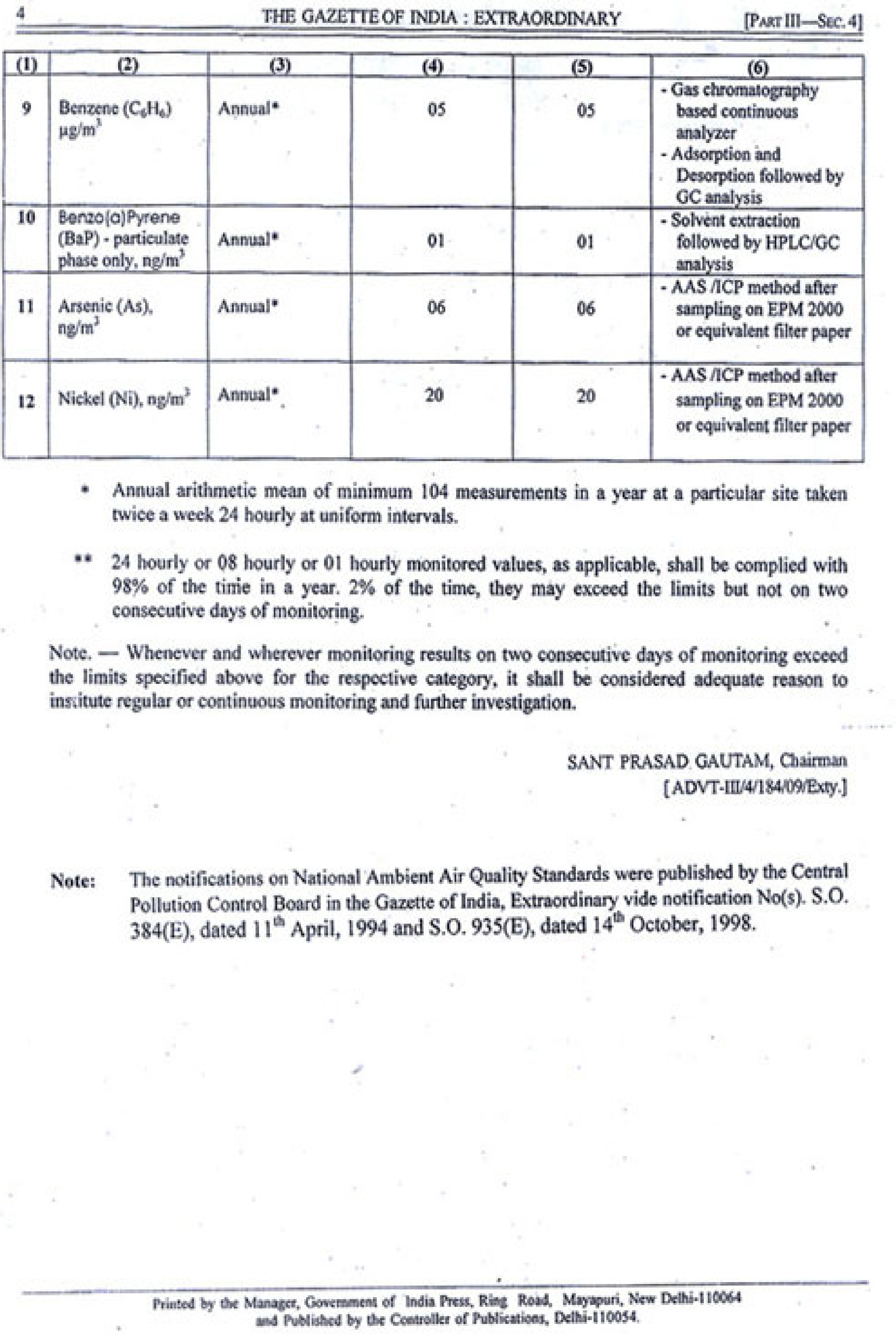
[भाग III—खण्ड 4] भारत का राजपत्र : असाधारण 3

NATIONALAMBIENTAIR QUALITYSTANDARDS
CENTRAL POLLUTION CONTROL BOARD
NOTIFICATION
New Delhi, the 18th November, 2009

No. B-29016/20/90/PCI-L.—In exercise of the powers conferred by Sub-section (2) (h) of section 16 of the Air (Prevention and Control of Pollution) Act, 1981 (Act No.14 of 1981), and in supersession of the Notification No(s). S.O. 384(E), dated 11th April, 1994 and S.O. 935(E), dated 14th October, 1998, the Central Pollution Control Board hereby notify the National Ambient Air Quality Standards with immediate effect, namely:-

NATIONAL AMBIENT AIR QUALITY STANDARDS

S. No.	Pollutant	Time Weighted Average	Concentration in Ambient Air		
			Industrial, Residential, Rural and Other Area	Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
(1)	(2)	(3)	(4)	(5)	(6)
1	Sulphur Dioxide (SO_2), µg/m^3	Annual*	50	20	- Improved West and Gaeke -Ultraviolet fluorescence
		24 hours**	80	80	
2	Nitrogen Dioxide (NO_2), µg/m^3	Annual*	40	30	- Modified Jacob & Hochheiser (Na-Arsenite) - Chemiluminescence
		24 hours**	80	80	
3	Particulate Matter (size less than 10µm) or PM_{10} µg/m^3	Annual*	60	60	- Gravimetric - TOEM - Beta attenuation
		24 hours**	100	100	
4	Particulate Matter (size less than 2.5µm) or $PM_{2.5}$ µg/m^3	Annual*	40	40	- Gravimetric - TOEM - Beta attenuation
		24 hours**	60	60	
5	Ozone (O_3) µg/m^3	8 hours**	100	100	- UV photometric - Chemilminescence - Chemical Method
		1 hour**	180	180	
6	Lead (Pb) µg/m^3	Annual*	0.50	0.50	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper - ED-XRF using Teflon filter
		24 hours**	1.0	1.0	
7	Carbon Monoxide (CO) mg/m^3	8 hours**	02	02	- Non Dispersive Infra Red (NDIR) spectroscopy
		1 hour**	04	04	
8	Ammonia (NH_3) µg/m^3	Annual*	100	100	-Chemiluminescence -Indophenol blue method
		24 hours**	400	400	



(1)	(2)	(3)	(4)	(5)	(6)
9	Benzene (C_6H_6) µg/m^3	Annual*	05	05	- Gas chromatography based continuous analyzer - Adsorption and Desorption followed by GC analysis
10	Benzo(a)Pyrene (BaP) - particulate phase only, ng/m^3	Annual*	01	01	- Solvent extraction followed by HPLC/GC analysis
11	Arsenic (As), ng/m^3	Annual*	06	06	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper
12	Nickel (Ni), ng/m^3	Annual*	20	20	- AAS /ICP method after sampling on EPM 2000 or equivalent filter paper

* Annual arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.

** 24 hourly or 08 hourly or 01 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, they may exceed the limits but not on two consecutive days of monitoring.

Note. — Whenever and wherever monitoring results on two consecutive days of monitoring exceed the limits specified above for the respective category, it shall be considered adequate reason to institute regular or continuous monitoring and further investigation.

SANT PRASAD GAUTAM, Chairman
[ADVT-III/4/184/09/Exty.]

Note: The notifications on National Ambient Air Quality Standards were published by the Central Pollution Control Board in the Gazette of India, Extraordinary vide notification No(s). S.O. 384(E), dated 11th April, 1994 and S.O. 935(E), dated 14th October, 1998.

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1.8 Source Apportionment

Source apportionment of particulate matter refers to the quantitative estimation of the contributions from different source categories to the concentrations of the measured PM in the atmosphere, based on chemical and physical characteristics of the particulate matter and temporal covariation of PM components. This procedure can be divided to identification of the sources and to apportionment of the measured PM to these sources. Source apportionment of urban ambient PM is complicated due to several reasons such as, (1) there are numerous anthropogenic and natural source categories that contribute to urban primary and secondary PM; (2) not all PM emissions are adequately characterized; and (3) the geographic impact area(s) of different emissions are highly variable due to the different particle sizes, lifetimes of pollutants, varying weather conditions, and atmospheric chemistries.

Also, for urban areas to be in compliance with the NAAQS, efficient emissions control strategies need to be developed and implemented. Thus, a comprehensive assessment of prevailing pollution levels and a detailed knowledge of major source categories and their contribution are required for effective air quality management in urban areas [64].

The term source apportionment refers to a variety of techniques that attempt to apportion the contributions of individual sources to ambient PM concentrations. The apportionment of sources is a key tool used in the assessment and management of air quality. There are three main categories of source apportionment methods available:

- Emission inventories
- Dispersion modeling
- Receptor modeling

1.8.1 Emission inventories

Air quality is determined by the concentrations of pollutants in the atmosphere, which are, in turn affected by the dispersion of pollutants from emission sources. An emission inventory is an accounting of the amount of pollutants discharged into the atmosphere and the inventory usually contains the total emissions for one or more specific air pollutants, originating from all source categories in a certain geographical area and within a specified time span, usually a specific year. Emission inventories are regarded as essential tools for evaluating, managing and regulating air pollution and they provide measured data or calculated estimates of pollutants emanating from transportation, industrial, biogenic or other anthropogenic sources [65].

In general, Emission inventories suffer from many uncertainties as a result of the need to obtain information from a wide range of sources and the use of approximations and empirical models in their compilation. There are few more drawbacks of emission inventories which include its inability to include long range transport of pollutants and a definite evidence of the pollutants responsible for an air pollution episode.

1.8.2 Dispersion Modeling

Atmospheric dispersion modeling refers to the mathematical description of contaminant transport in the atmosphere. The term dispersion in this context is used to describe the combination of diffusion (due to turbulent eddy motion) and advection (due to the wind) that occurs within the air near the Earth's surface. Air dispersion models generally incorporate emission data and basic meteorological data with numerical processing to yield concentrations of pollutants over space and time. Consequently emission data is needed as a first step.

From the operational point of view, in air quality assessments there are used models with semi-empirical or analytical approach (ex. Gaussian plume or puff) that require as input meteorological data coming from local surface measurements. As an alternative to the operational applications using measured input data there are the 3D prognostic models that solve the fluid dynamics and scalar transport fundamental equations in order to predict the meteorology and pollutant concentrations. The quality of the predicted weather data is very important for the dispersion models used to assess air quality [66]. In general, dispersion models are often the only cost-effective method to understand the interaction of existing or future emission sources, with meteorology, topography, and existing air quality. They generate quantitative answers to "what if" questions and inform decisions that govern many day-to-day activities. These answers are needed to support environmentally sound, and scientifically based air management decisions.

1.8.3 Receptor Modeling

Receptor models form a subset of source apportionment techniques and apportion the pollutant concentrations based on the measured ambient air data and the knowledge about composition of the contributing sources. The key outputs are the percentage contributions of different sources to pollutant concentration. Such models are particularly helpful in cases where complete emission inventories are not available. Receptor models have been used for identification of sources and their respective contributions to airborne particulate matter across the world. Receptor models can be microscopic and chemical. Microscopic methods, including optical, scanning electron microscope (SEM) and automated SEM analyses are primarily based on the analysis of morphological features of many individual particles in the ambient air. However, they are not very feasible for large-scale use since they do not produce quantitative results in most cases. Chemical methods, on the other hand, utilize the chemical composition of airborne particles for identification and apportionment of sources of PM in the atmosphere. A number of different models are included in this category [67].

In particular, receptor models provide the theoretical and mathematical framework for quantifying source contributions at that receptor. There are two basic types of receptor models :

- Sources are known (e.g. Chemical Mass Balance); or
- Sources are unknown (e.g. Factor Analysis and Positive Matrix Factorization).

In the first type, a regression technique is used to match chemical profiles or "fingerprints" in the measured ambient particulate matter to those in the emissions from potential sources. Chemical Mass Balance (CMB) requires a prior knowledge of major sources and their emission characteristics in the study area. CMB modeling provides a means by which to estimate the percentage contribution of each source to the measured pollutant concentration. These statistical techniques are used for identifying and quantifying the contribution of important emission sources.

The second type requires only ambient measurement data to perform source apportionment. These models rely on the internal variability of the data to determine factor profiles and their contributions to each sample. These factor profiles are related back to specific sources. At a minimum, a hundred or more samples from many locations and/or one location over a long time period are needed for this type of receptor modeling. Principles and methods of various receptor model techniques of particulate matter have been reviewed in chapter -3 of this thesis.

1.9 Literature Review

Over the last five decades, many studies have assessed levels of particulate matter, especially TSPM and PM10 fractions worldwide. Two distinct types of studies seem to be exist among the numerous number of urban aerosol studies. One type of study is based on data from long term monitoring to gain relatively basic information of aerosols [68].

Another type of study is based on data from a relatively short period of time and from a limited number of sites. The monitoring, sampling and chemical analysis in these studies cover a whole range of characteristics of the aerosols and the related gaseous pollutants [69]. Source apportionment studies are started from the 1970's and most of them used the receptor modeling approach. In the last twenty years, apart from source apportionment, urban aerosol studies have diversified their objectives into studying the formation/removal mechanisms aerosols, indoor/outdoor relationships in aerosol compositions, and optical properties of aerosols. This trend is mostly due to advancements in analytical instruments which have enabled a more detailed characterization of aerosols.

Boston aerosol study [70] is one of the earliest source apportionment studies of urban aerosol. About 90 TSP samples were taken from 8 sites during a five months period. The samples were analysed with INAA. Six contributing sources were identified using factor analysis and cluster analysis techniques. One of the early studies based on long term data base (1977-1985) was the Japanese national study reported by [68]. Where, INAA and XRF were used for elemental anlaysis. CMB with Japanese source profiles were used for source apportionment. In this study soil was found to be the most significant contributor to PM_{10} mass at all the sites. As far as India is concerned particulate matter is considered as one of the key indicator air pollution and Respirable Suspended Particulate Matter is being monitored in 7 important cities of the country by CPCB on regular basis over a period more than two decades. The studies conducted by CPCB during the past one decade indicated the significance of continuous monitoring of PM levels, because the concentration is in increasing order in most of the cities. After the compilation of details of PM concentrations of seven cities [71] attributed vehicular traffic, Diesel/kerosene generator sets, small scale industries, biomass incineration, suspension of traffic dust, commercial and domestic use of fuels as some of the major reasons for high particulate matter levels.

The first and foremost important step in the aerosol study is the characterization of ambient particulate matter because which could ultimately lead to the identification of source signatures of atmospheric PM. In different parts of the world many scientific research on the characterization of aerosols in various environments have been conducted from the early 80's to till date [72, 73, 74, 75, 76]. In India ample number of studies can be identified in association with the characterization of PM_{10}. On the other hand, only few studies can be found on the characterization and source apportionment of size fractionated PM. Occurrence of higher uncertainties in the chemical characterization of PM, especially PM_{10} measured at different environmentally defined microenvironments of various urban areas in India has shown higher degree of multi-complexity in the particulate source signatures [77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89]. Most of Indian source apportionment studies conducted earlier was based on simple factor evaluation from the chemical data of PM [90, 91, 92, 93] some of the studies conducted worldwide and India using this method have shown various types of sources for the pollutants, for instance, fossil fuel combustion contributes Al, Fe, Ca, Mg, K, Na, As, Pb, Cd, Sc and Hg elements [94, 95, 96] vehicular traffic contributes Cd, Cr, Cu, Ni, Pb, Zn [80], electroplating contributes Cr [97] and metal alloy industries emits Cd, Cr, Al, Fe, Ni, Zn, Pb, Cu [98].

The determination of the origins of the elements observed in urban aerosols has been the subject of a number of recent studies. Because, metals are excellent receptor species and they have been used from the very beginning of receptor modeling. The majority of these investigations employ the chemical balance approach first introduced by S. K. Friedlander and his coworkers [99, 100]. Later on, the development and application of multivariate statistical techniques such as Factor Analysis permitted the determination of number and nature of the sources contributing to a given aerosol, as well as the ability to estimate the particulate loading contribution of each source. Comprehensive chemical speciation in combination with information on size distribution and morphology of PM, temporal variation of PM and the respective components and meteorology allows for identification of PM sources. Worldwide, numerous studies have been targeted to the source determination of urban particulate matter chiefly via a physico-chemical characterization of PM.

Promoted by freely available stand alone software from the US-EPA, the chemical mass balance model has become highly popular. In spite of the development of many other receptor techniques CMB was widely used for and most of the studies on PM sources are based on this technique even in the recent periods [101, 102]. As India is concerned, a detailed review on source apportionment is performed by [67] in the recent period. The review states that there is a growing body of literature on source apportionment of PM in India using receptor modeling. A majority of the SA studies have been conducted using multivariate methods; PCA being the most commonly used technique although there are some cases of application of the CMB model even today.

High concentration of PM across all the regions has always been a concern in the Maharashtra state. The emission from various industries involved in activities like cement manufacturing, quarrying activities, power plants and so on, coupled with increasing construction activities, traffic movement and so on increases the dispersion of RSPM (Respirable Suspended Particulate Matter) in the air. Ambient Air Quality Monitoring Stations (AAQMS) are established in 72 places throughout the state by CPCB and of the 72 stations 7 are located in Navi Mumbai region. All the AAQMS monitor three parameters namely, RSPM, NO_x and SO_2 regularly. A recent report of 2013-14 air quality status of Maharashtra states that RSPM exceeds annual standard at almost all the 72 monitoring stations and it was also found that the high RSPM levels are the major cause of severe air pollution status in Navi Mumbai. The RSPM concentration levels reported are in the range of 182-203 µg/m^3 in various parts of Navi Mumbai region whereas, the annual standard is only 60 µg/m^3 [103].

As a matter of fact, Maharashtra has very prominent industrial zones and is one of the highly populated states in the country where air quality monitoring becomes crucial. However, owing to the population growth and expansion of the cities the residential areas have now grown so large that they are now located in very close vicinity of the industrial belts. One such example is Navi Mumbai where residential zones are very close to the industrial areas. As mentioned above, air quality monitoring is being carried out by Maharashtra Pollution Control Board (MPCB) in different parts of the Navi Mumbai and Thane-Belapur Industrial Area (TBIA) for regulatory purposes. Prior to the recent 2014 report, MPCB has published a report on comprehensive environmental assessment of industrial cluster in December 2009 and subsequently published about the action plans to be executed in the future [104]. The 2010 report mentions that in respect of industrial estates in the Maharashtra state, Navi Mumbai region has been declared as one of the critical/severely affected place from the angle of environmental pollution.

Unfortunately, very few studies have been conducted in this region regarding the air pollutants and their effects. Other than the studies conducted by MPCB, [105] monitored the ambient levels of Hazardous Air Pollutants (HAP's) during different seasons in TBIA. The study explains about the distribution of HAP's at different component of environment, their persistence and long range transport potential. They have also estimated the hazard and risk of HAP's. But this particular work is mainly focused on the monitoring of organic pollutants which are designated as HAP's. Literature survey indicates that there were no adequate studies performed in detail in the industrial region targeting the chemical composition of ambient particulate matter, their potential contributing sources and health effects. On the grounds of present scenario of severe air pollution in TBIA, a comprehensive air particulate monitoring and characterization program has been initiated. This study was conducted in a residential area nearby the industrial belt and a high way passes 2 km away from the site. Primarily, the present study is aimed to assess the various sources of air particulate matter and their impact on a residential area of Navi Mumbai. Details of the sampling site and the nearby industrial area are briefed in the following chapter.

1.10 Objectives of thesis

As mentioned above, air pollution is perceived as an important issue in the Navi Mumbai region. The latest report of MPCB and TERI of the year 2013-14 on the air quality status of Mumbai and Navi Mumbai explains the present day scenario and exceedance of air pollutant levels against the prescribed standards. The consistently increasing levels of nitrogen oxides, sulphur dioxide and RSPM are alarming in the Navi Mumbai region. Especially RSPM in the Navi Mumbai area is considered as a distressing factor regarding the health and ecological point of view. Not only the MPCB report but a recent report on Global Burden of Disease (GBD) by WHO declares that one third of the Indians live in polluted areas which have critical levels of PM_{10}. The report further explains that Indian cities like Delhi, Mumbai, Ghaziabad, Patna, Varanasi, Allahabad, Jaipur, Navi Mumbai and Chandigarh are falling under the critically polluted areas, among other places and the report says that in 2010, about 620,000 premature deaths occurred in India from air pollution related diseases. In spite of rapidly increasing industrial and commercial activities at Navi Mumbai, meticulous air quality monitoring becomes imperative. Keeping in mind about the indispensable parts of particulate pollution monitoring and source identification, objectives of the present study were framed.

The main objectives are,

- Monitoring and trend anlaysis of size fractionated PM and their constituent trace elements
- Characterization of inorganic trace metal levels in the ambient air particulate matter using Nuclear Analytical Techniques
- Identification, apportionment and validation of potential PM source contributors of the study area.

Chapter – 2

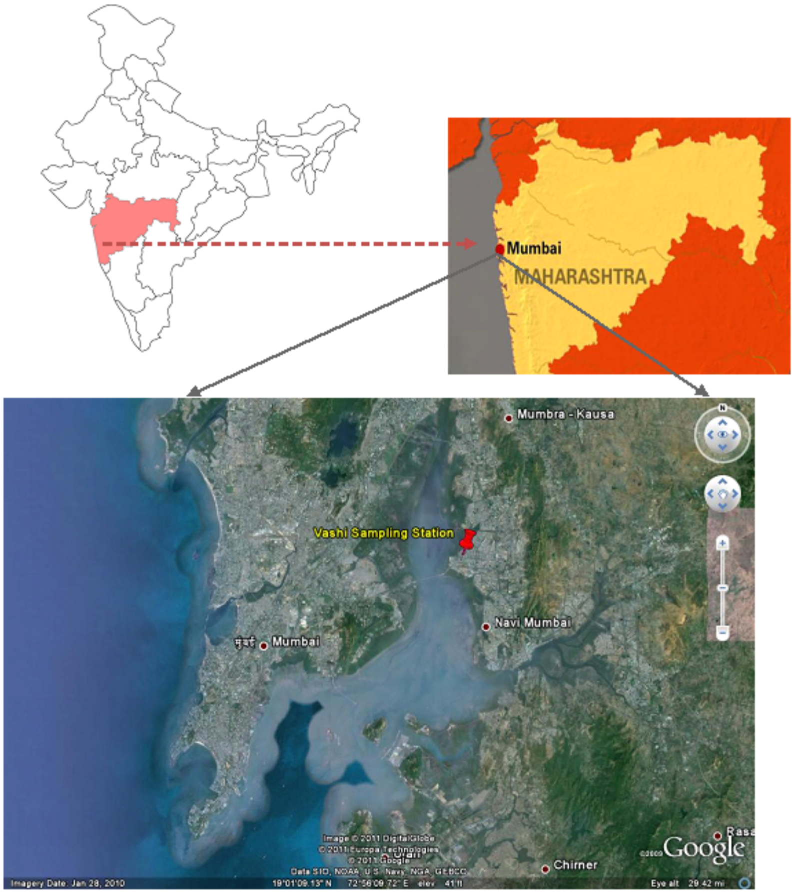
Materials and Methods

This chapter has been divided into four sections. The first section is elucidating the details of sampling site and further sections expound the virtues of the various particulate matter collection devices as well as analytical techniques adopted for the present study.

2.1 Sampling site

Present study was conducted in a residential place at Vashi, Navi Mumbai situated in Maharashtra state of India. Vashi in Navi Mumbai is situated within 5 km distance from the Thane-Belapur industrial belt. Navi Mumbai is the largest planned new city near Mumbai and is situated at 73˚ east longitude and 20˚ north latitude. Geographically speaking, Navi Mumbai Municipal Corporation is a coastal land of the Kokan in Maharashtra separated from the mainland by the Parsik Hills. The Navi Mumbai region is covered by hills in the East and the West is covered by Thane Creek as well as by Mumbai city. North to Navi Mumbai is the Thane – Belapur industrial belt and towards South is the newly developed Panvel city. It is considered as the Infotech and industrial capital city of Maharashtra State. It has the well established & biggest industrial sector of Asia. It has global importance since many of the multinational companies have set up their commercial base in Navi Mumbai. It is also well connected with other parts of India by Express Highway and Eastern Express Highway through Airoli and Vashi. Particulate matter monitoring has been conducted at Vashi and the sampling was performed at a height about 15m. Although the sampling site is located at a residential area, it is very near to the industrial area (TBIA) as mentioned above. Location map of the study area is presented below (Figure 2.1).

Figure 2.1: Location Map of the study area



Sampling of PM at the study site was performed following the criteria for ambient particulate matter sampling guidelines stipulated by CPCB. Following the regular air monitoring guidelines sample were collected on a twice a week basis in the sampling site using Gent sampler. The number of samples collected was comparatively less during monsoon season due to heavy pouring rain. However, on an average 90 samples were collected every year and the sampling was conducted from the year 2008-2010. A Ghent dichotomous sampler was used throughout the sampling period for the size fractionated PM collection and a high volume sampler was used for RSPM collection for a short time period. The details of particulate matter collection devices and the analytical techniques employed in the present study are summarized in the following sections.

2.1.1 Details of air pollution sources in the site

Maharashtra Industrial Development Corporation established an industrial estate at Thane Belapur Road, Navi Mumbai in 1963 which is oftenly known as TTC MIDC Estate. Thane is the third Most industrialized district in the State. The Thane Belapur-Kalyan industrial belt is the centre of highly sophisticated modern industries. The industrial growth in the district, however, is concentrated in this industrial belt [106]. The Estate is located along Thane Belapur Road towards Northern side of road and total area of the industrial estate is 27 sq.kms. There are about 2200 industrial units of various category engaged in the manufacture of chemicals, dyes, dye-intermediates, Bulk drugs, pharmaceuticals, Textile auxiliaries, Pesticides, Petrochemicals, Textile processors, Engineering units etc. [104]. The population pressure on the city is ever growing. As per the 2001 census, the Population of the residential area around the industrial area of Navi Mumbai is about 7.5 lacs numbers and as per growth rate considered as 10% per annum, the present population is about 12.5 lacs. In TBIA temperature varies from 22˚C and 36˚C. In winter the temperature ranges from 17˚C to 20˚C and during summer temperature ranges from 36˚C to 41˚C. Out of total rainfall, 80% rainfall is experienced during June–October. Average annual rainfall is 2000–2500 mm and humidity is 61–86.

The TTC-MIDC is one of the biggest industrial zones in India. This industrial cluster consists of mainly Chemical, Textile, Bulk-drug manufacturing Units and also has IT Parks. Predominant sources contributing to various air pollutants are industries, vehicles, construction activities, quarries and stone crushers, public places and unauthorized burning of domestic and other waste in residential areas. Most of the industries perform fuel burning consequently process emissions and the fugitive emissions increase the pollutant levels of atmosphere. Coal and biomass are identified as the main fuel used for domestic purposes. Other than domestic burning, more than 20 industries using coal as fuel and the total quantity of coal consumed by these industries is around 300 Ton/day. Also transport in around Navi Mumbai contributes maximum to the fine particle pollution through fuel burning.

The total number of the industries up to 1980 was 6%. The growth of the industries in next decade 1981-91 was 17%, in 1991-95, 19% of the industries were established and next five years, i.e. 1996-2000, 25% of the industries were added. From 2001 to 2006, the growth of industries escalated by 35%. The total Industrial units are classified into 14 groups. Engineering units comprise of 47% followed by Chemical units 20%, Fabrication units 8%, Pharmaceuticals & Food processing units 4% each, Electronics and Garment units 3% each, Packaging and Printing about 2% each, Ice factories 1.2% and Stationary units 0.4% and other units such as Electrical, Computers, Oil, Automobile etc are 6%. Also due to heavy urbanization and industrialization this area is facing unique environmental issues related to the municipal solid waste, bio medical waste and hazardous waste disposal. The incineration facilities of Navi Mumbai can also contribute to the particle pollution load of the region.

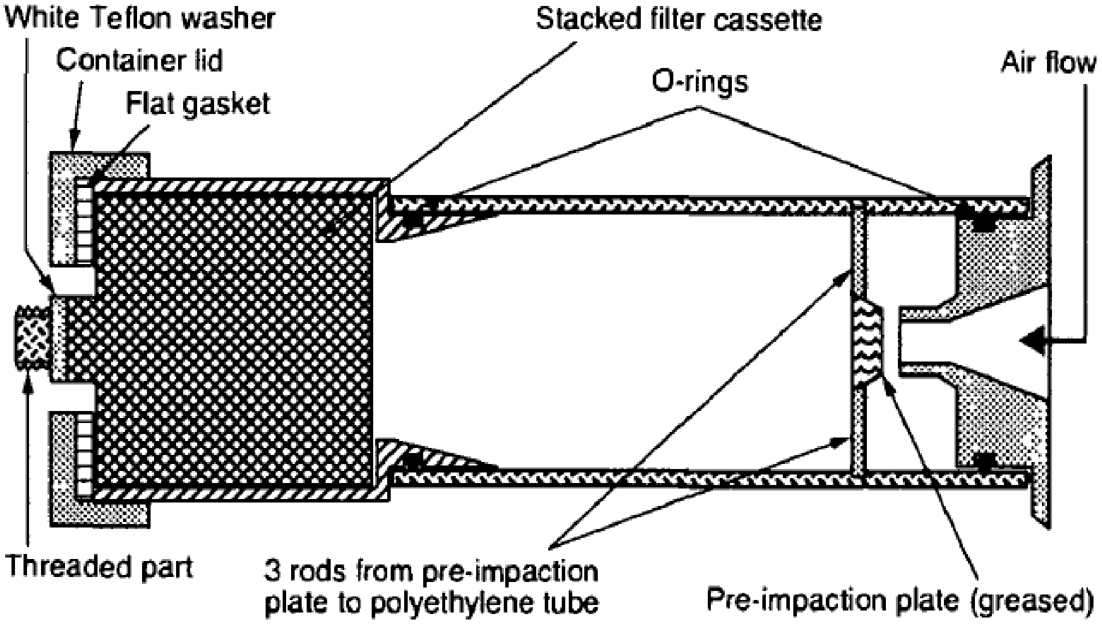
2.2 Particulate Matter collection devices

Ambient aerosol sampling is substantially different from that of atmospheric trace gases. There are a variety of monitoring techniques available for the measurement of mass concentrations of atmospheric PM. In general, monitoring systems can be broadly classified in to two types, continuous systems which provide direct values of the mass concentration and filter based gravimetric samplers that collect the particles onto a filter material which can be weighed and analyzed by established physical, chemical and biological methods for the concentration levels which are the effective average over the period of sampling. Filtration and impaction are the two principal methods used for the collection of particulate matter on a substrate. Following subsections of the chapter illuminates the principle and working mechanism of the PM samplers employed in the study.

2.2.1 Gent Dichotomous Sampler

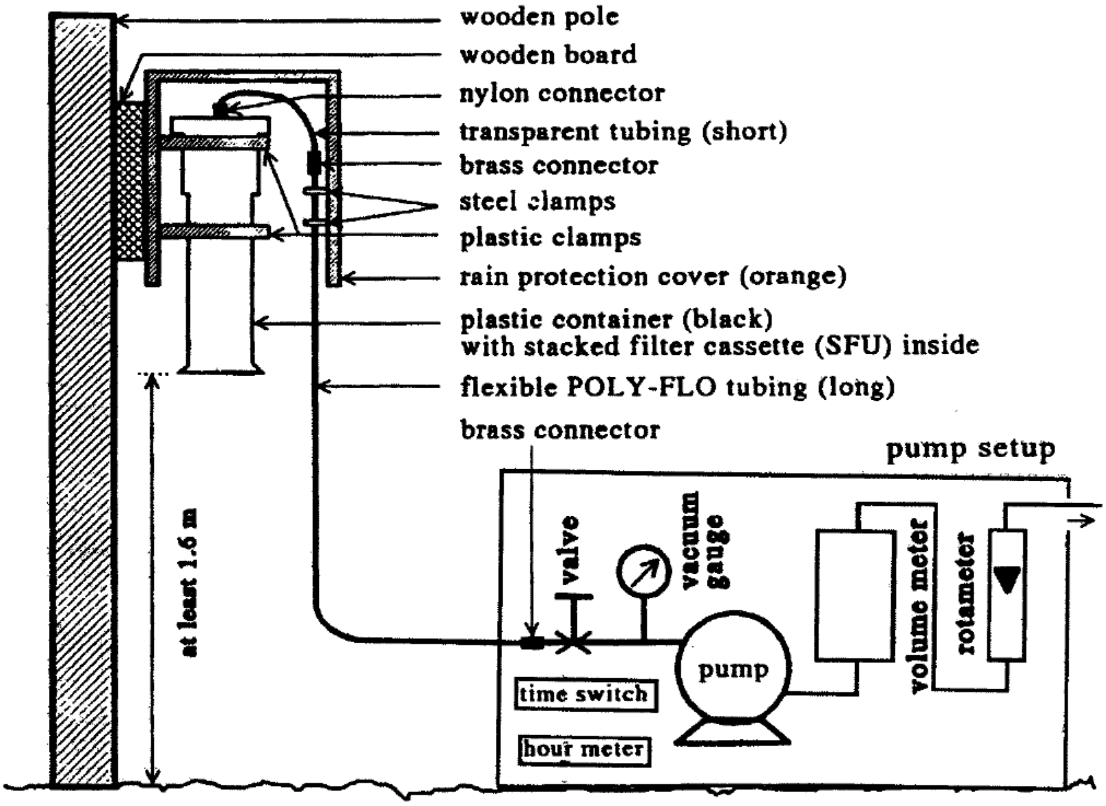
A size segregation automatic dichotomous Gent sampler was used to collect two ranges of air particulate samples. In the Gent sampler air enters the unit through an impactor stage, where particles of size greater than 10 μm were removed through impaction. The air is then drawn through a Stacked Filter Unit (SFU). The Gent SFU sampler is a low volume sampler. The SFU consists of a holder for two sequential filters constructed by the Norwegian Institute for Air research [107, 108]. The stacked filter unit system uses the principle of sequential filtration, where particle fractionation is achieved by partially efficient polycarbonate filters. The schematic diagram of sampling head with the pre impaction stage and the sequential filtration is depicted in Figure 2.2. These filters are utilized due to their specific particle capture behaviour for the desired size fractions.

Figure 2.2: Schematic diagram of the sampling head of the Gent sampler



Normally, an SFU consists of two filters in series, which are located upstream of a pump. The initial filter is an 8 µm Nuclepore filter and the second filter is an 0.4 µm pore Nuclepore filter. It is designed to operate at an flow rate of about 16-17 lpm. At this flow rate of 16 lpm the unit acts as a dichotomous sampler, where, the pre impaction stage inside of the container has a 50% collection efficiency of (cut point) 10 µm Aerodynamic Diameter (AD, Acts as a PM_{10} inlet) and the coarse polycarbonate filter (Pore size 8 µm) has a 50% cut off point (d_{50} value) of about 2.5 µm AD. This means that the fine filter with pore size 0.4 µm collects the < 2.5 µm AD size fraction, whereas the coarse filter collects 2.5-10 µm size range. The complete unit design is presented in Figure 2.3.

Figure 2.3: Schematic of the Gent Dichotomous sampling unit



The sampler is an integrated system with the simple flow control unit provided with a suction pump and a flow meter. Also a dry gas meter is provided to measure the total volume of air sampled. The plates of sampling head and pump unit is exibited as Plate 2.1.

[109] calibrated the Gent sampler by performing inter comparisons with commercially available PM_{10} dichotomous sampler and obtained quite reasonable agreement. [108] compared the Gent collector with a commercial beta gauge and also with an IMPROVE design 2.5 µm cut point cyclone.

Plate 2.1: Sampling head and the integrated vaccum pump unit of Gent sampler with flow meter & dry gas meter

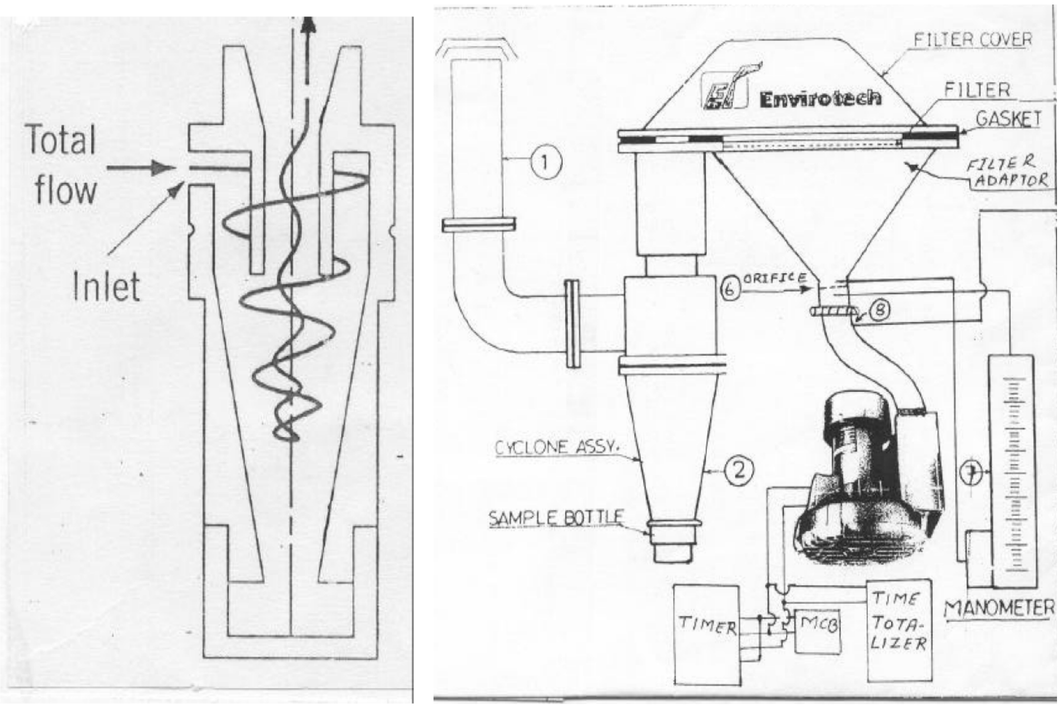
As mentioned in the sampling frequency section 24 h representative samples were collected using Gent sampler in a twice a week basis for three years. 47mm nuclepore polycarbonate filters of 8 and 0.4 µm pore size were used for the collection of coarse and fine PM respectively. Initial flow rate of the sampler was set as 18 lpm and the flow rate was maintained as 16 lpm on an average during the entire sampling period. Depending upon the season the effective sampling time was varied between 15 and 22 h distributed uniformly over 24 hours of the day to avoid filter clogging and so that the flow rate remains within the prescribed limits of the sampler. This also ensured the proper size fractionation and collection efficiency. Mass of the loaded poly carbonate filters were then measured by gravimetry and subsequently analysed for the chemical components using nuclear analytical techniques.

2.2.2 High Volume Sampler

Several methods are available for measuring PM10 in ambient air. But the most commonly used device is the high-volume sampler, which consists essentially of a blower and a filter, and which is usually operated in a standard shelter to collect a 24-h sample. Especially the high volume sampler is considered as a reliable instrument for measuring the mass concentration of PM10 in ambient air [111].

The PM10 sampling was carried out using a High Volume Sampler of model HVS–460 NL, Envirotech. The APM 460 NL Hi-vol sampler uses a cyclone type particle size classifier, illustrated in Figure 2.4, to separate out particles of diameter greater than 10 µm aerodynamic diameter. Ambient air with PM10 enters the cyclone near its top where the air stream is given a swirling motion. The resulting centrifugal acceleration moves the coarse and heavier air borne particles to the outer wall. These separated particles fall through the cyclone conical hopper and are collected in the sampling bottle placed at the bottom. The air containing the respirable dust exits through a cylindrical outlet, mounted concentrically at the top of the cyclone, and enters the filter assembly.

Figure 2.4: Cyclone type particle classifier and the schematic diagram of Hi-Volume sampler



The filter assembly of hi-volume sampler consists of two parts, a top cover connected to the outlet port of the cyclone and a filter adapter with a backing screen for the filter paper. A rectangular 20.3 cm x 25.4 cm (8 in x 10 in) glass fibre filter paper is placed on the backing screen and the top cover is bolted. Suitable gasket is used to obtain an airtight connection. The collected matter on the filter is classified as PM_{10}. A standard regenerative blower is used for sucking the ambient air through the High-Volume sampler. The blower is capable of maintaining a flow rate in the range of 0.9 to 1.4 m^3/min through the assembly. Airflow is measured from the pressure drop across a calibrated orifice which is built in the lower part of the filter adapter. The manometer recording the pressure drop is graduated in terms of flow rate in m^3/min. A time totaliser is provided to record the period of sampling. It has been wired in such a way that it operates only when the blower receives power. Thus it records the true time in hours for which the sampler samples the air. Readings must be noted before and after each sampling occasion to determine the duration of the sampling. The total reading on the totaliser also facilitates timely preventive maintenance. The HVS-460 NL model sampler is illustrated in Plate 2.2.

Plate 2.2: Hi-Volume Sampler, HVS-460 NL, Envirotech

PM10 was collected on pre– desiccated glass micro fibre filter paper using the high volume sampler. No chemical treatment of the filter papers were carried out before sampling. Flow rate of HVS was kept about 1.1 m^3/min and the average sampling time was 24 hours. Glass micro fibre filters having low resistance to air flow, low affinity for moisture and 99% collection efficiency for particles of 0.3 microns or larger size were used for this purpose. Pre-sampling and post-sampling weighing of filters was performed using a Mettler balance with 10 μg sensitivity.

2.3 Gravimetric Analysis

Individual filter paper has to be weighed in an electronic microbalance before and after field sampling. Gravimetric measurement encounters a challenge as interest moves to masses on a microgram scale. When the measured masses are very small, the relative humidity, temperature and pressure of the ambient air, as well as the firmness of the weighing table and the static charge of the sample, start to play significant roles. After collection of particulates, the nuclepore polycarbonate filters were equilibrated for 24h, weighed in an air conditioned room with approximate temperature of 22° C and relative humidity of 50%. The filters were then stored in air tight petri slides. Immediately after the sampling the dichotomous stack filter unit was carried to the laboratory for the recovery of the filters and the samples were then equilibrated under same conditions as mentioned above. The post-sampling weighing of the samples was usually completed within one month of the sampling date. Since the polycarbonate filters accumulate surface electrical charge which can affect the filter weight, each time prior to weighing the filters, they were treated with static charge neutralizer. A ^{210}Po (Alpha emitter) electrostatic charge eliminator (STATIC MASTER) was used for the neutralization.

The aerosol masses of both the coarse and fine fractions were determined by weighing the filters before and after the exposure. A Mettler micro balance of readability 10 μg was used for gravimetric analysis and the quality assurance exercise. A standard operating procedure was followed throughout the study [112]. A criterion for valid weighing was that duplicate mass readings should lie within 1% mass of each other.

Similar protocol of gravimetric weighing was followed for the glass fibre filters used in high volume sampler except the equilibration part. To avoid moisture absorption and the consequent erroneous weighing, glass fibre filters were conditioned in a desiccator for 48 h before and after sampling.

2.4 Chemical Characterization

As explained in the earlier chapter characteristics and composition of aerosol particles plays an important role in determining the health and ecological effects. Chemical characterization of coarse and fine particles are important, as they are necessary for investigations aimed at establishing toxicity levels of breathable particles and for models of the generation of secondary particles. Mass concentrations of the particulate matter in the ambient air are usually very low (μg/m^3), as are the concentrations of some elements in the particles (μg/g). This makes chemical analysis by conventional techniques difficult and calls for innovative methods. Also, most of the conventional methods involve dissolution of the sample and possibly subsequent chemical separation or preconcentration steps with a inherent danger of analyte loss or contamination. The microchemical methods on the other hand are faced with the inherent inhomogenity of most environmental samples and with the difficulty of calibration. Standards almost identical to the samples are often needed for an accurate calibration. This is not the case with Nuclear Analytical Techniques (NAT's). Nuclear techniques are very suitable for non-destructive multielement analysis of PM in filter samples particularly for the samples collected on membrane filters. Especially, in air filter analysis a good time and spatial resolution, as well as particle size separation, calls for vast numbers of analyses and thus fast quantitative methods are required. Since in the size separated PM samples, total quantity of aerosol mass available for compositional analysis is usually small therefore high sensitivity of the analytical technique becomes compulsory. As most of the elements are potentially important in aerosol studying, multi elemental analysis is a great advantage and non-destructiveness is important in order to extend the range of detectable elements by complementary techniques applied to the same sample. All the above mentioned reasons create severe restrictions in the path of standard chemical methods and suggests the application of NAT's.

In principle nuclear techniques are based on properties of the nucleus itself, compared to non-nuclear techniques which use properties of the atom as a whole. Customarily, not all the NAT's are applied in environmental research. INAA, EDXRF and PIXE are the three key techniques commonly applied for environmental matrices. The characteristics of the methods and in particular their non-destructiveness make these techniques extremely useful for the analysis of soil, sediment, plant materials, biological samples and air particulate matter.

The choice of analytical method is depending on the inorganic compounds of interest and the detection limits desired. Also, other factors such as element specificity and sensitivity are critically essential, while consideration cost and throughput are also important. However, no one analytical method can address all the data quality objectives for a particulate ambient air quality monitoring program. Every method has its own attributes, specificities, advantages and disadvantages. The technical advantages and disadvantages of different analytical techniques are displayed in Table 2.1.

Actually, NAT's may act also as "pioneers" for non-nuclear techniques, where NAT's may disclose analytically new fields of interest. Also NAA and XRF are considered as the multi-element analysis techniques and demonstrated the opportunities of multivariate analysis techniques such as factor analysis for e.g. source apportionment in environmental pollution studies.

Table 2.1: Technical advantages and disadvantages of the analytical techniques used for PM analysis

Method	Advantage	Disadvantage
INAA	• multielemental (Na – U) • non-destructive • minimal sample preparation • percent to ppb range • high sample throughput • well documented applications • quick, irradiation time less than 15 minutes • high sensitivity • can handle small sample sizes (< 1 mg)	• some elemental interferences • standard sample matrix corrections • slow, requires multiple counting regimes to detect many elements • not cost effective for few samples • does not include all elements from Na – U • requires access to research nuclear reactor
PIXE	• multielemental (Na – U) • non-destructive • minimal sample preparation	• cheap • standard/sample must match closely (matrix) • matrix offsets and background

	• quantitative • quick, typically 15 min per analysis • high sensitivity • can handle small sample sizes (< 1 mg) • cost effective for large sample numbers, more than 10.	• impurities may be a problem • requires access to particle accelerator
XRF	• multielemental (Na to U) • non-destructive • minimal sample preparation • shorter analysis time than NAA • high sensitivity for many elements • good accuracy and precision • automation possible	• standard/sample must match closely (matrix) • matrix offsets and background • impurities may cause problems • analysis time longer than PIXE/IBA • particle size effects for low Z elements • inter-element interferences • blind spots due to limitations of excitation • mode or overlapping X-ray lines
F AAS	• easy to use • extensive applications • low detection limits	• higher concentration • sample dissolution is required • one (1) element at a time
GF AAS	• well documented applications • lower detection limits than Flame AA	• limited working range sample • low sample throughput • one element at a time • sample dissolution is required
ICP-AES	• multi-element • high sample throughput • well documented applications • linear range over 5 orders of • magnitude	• more expensive (~120K) • sample dissolution is required • other elements can interfere
ICP-MS	• multi-element • low concentrations • isotopic analysis	• most expensive (~250K) • limited documented applications • sample dissolution is required

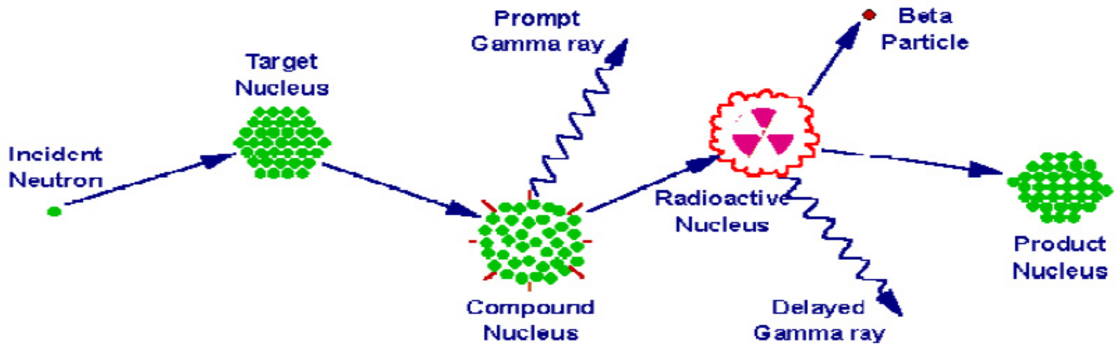
In the present study three key nuclear analytical techniques such as EDXRF, PIXE, INAA for size fractionated PM sampled on polycarbonate filters and a destructive technique AAS for PM_{10} samples collected on glass fibre filters were employed for the trace metal analysis. Ion chromatography was used for the detection of major anions contributing to the particulate mass concentration and black carbon was determined using smoke stain reflectometer. Brief descriptions of these six techniques are presented in the subsequent sections.

2.4.1 Instrumental Neutron Activation Analysis

In INAA [113, 114], a sample is irradiated in the core of a nuclear reactor for periods ranging from a few minutes to several hours. The neutron bombardment chemically transforms the trace elements into radioactive isotopes. The energies of the gamma rays emitted by these isotopes identify the parent elements. The intensity of the gamma rays of specific energy is proportional to the concentration of the respective element present in the sample. Figure 2.5 depicts the successive events of neutron activation analysis after irradiation. In this technique minimum amount for detecting an element strongly depends on several factors such as the cross-section, the half-life of the isotope produced and the abundance of the gamma rays emitted. As a result the detection limits for the different elements vary over many orders of magnitude.

Unlike most analytical techniques INAA requires no chemical processing of the samples; therefore it is described as Instrumental NAA rather than radiochemical NAA. This characteristic has several advantages like rapidity and which precludes the possibility of contaminating the samples.

Figure 2.5: Sequence of events occur during the most common type of nuclear reaction used for neutron activation analysis



Different irradiation times and cooling periods are used before counting with a germanium detector. INAA does not quantify some of the abundant species in ambient particulate matter such as silicon, nickel, tin, and lead [115]. While INAA provide better sensitivity for other elements: Sb, As, Cr, Co and Se. Although INAA is technically nondestructive and requires minimum sample preparation i.e. it involves folding the sample tightly and sealing it in a plastic. But the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses. However, the main advantages of the method are high precision, high selectivity and sensitivity, and with a small quantity of sample it can be used to quantify a wide range of elements with low detection limits [116].

INAA is feasible only when the activity induced in the matrix is not prohibitively high and no single major activity produced that overshadows gamma energy of other radioisotopes. As discussed earlier major components of aerosol samples are organic compounds, carbon, water, anions like sulphate, nitrate etc. As the trace elements are concern crustal based elements found in high concentrations. But the most abundant elements such as Si, Ca, Mg and Cl have relatively low cross sections or low probability for gamma transitions. Mainly in a sample collected near coastal area the high sodium content of marine aerosol can give rise to a troublesome activity. Also in urban aerosols another predominating element is Bromine. High levels of sodium and bromine demands comparatively longer cooling time period after a long (~ 8h) irradiation to measure most of the medium half life isotopes. For this purpose different parameters of analysis, which include irradiation, waiting and counting times, amount of sample, and counting geometry has to be optimized.

In spite of all these optimization procedures a major breakthrough in INAA came with the introduction of high purity Germanium detectors (HPGe); the high resolution of these detectors played a crucial role in the accurate determination of many elements at a time and made the technique a real successful multi-elemental technique. Although the present germanium detectors have a high resolution, the detection of gamma ray line specific to radionuclide still depends on other nuclides present in abundance in the sample. Therefore, an irradiation-counting scheme has to be adapted based on intensity and half-lives of the isotopes.

In the present work, the dust loaded poly carbonate filter papers were irradiated in a nuclear research reactor Apsara, BARC, Mumbai. Thermal neutron flux of the reactor is 1×10^{12} neutrons/cm^2/Sec and the samples were co irradiated with the standard for 7 hours. Formerly the air filter samples were folded and triple sealed in small polythene packets. Each time around 15 samples were packed along with a blank and a comparator. The entire set together was then kept inside a small plastic container for irradiation. The irradiated samples were then allowed for one day cooling time to reduce the activity level and for the decay of short lived isotopes. Subsequently, 15 elements were measured using P-type HPGe detector following two sequential steps. In the first step, samples were counted for 720 seconds to measure short lived isotopes like Na, K, As, Br, Sm, Sb and La. Prior to the determination of the other isotopes, samples were again allowed for a cooling period of 20 days to avoid the interference of high intensity gamma rays from the abundant Na and Br present in air filter samples. Consequently, the second stage counting was performed for 1500 seconds and the remaining major and trace elements were measured. Details of elements determined, their corresponding nuclear data and the irradiation-counting scheme followed during the experiment is presented in Table 2.2.

Table 2.2: Nuclear Data of few isotopes determined in air filters, their irradiation and counting scheme (After 7 hours irradiation)

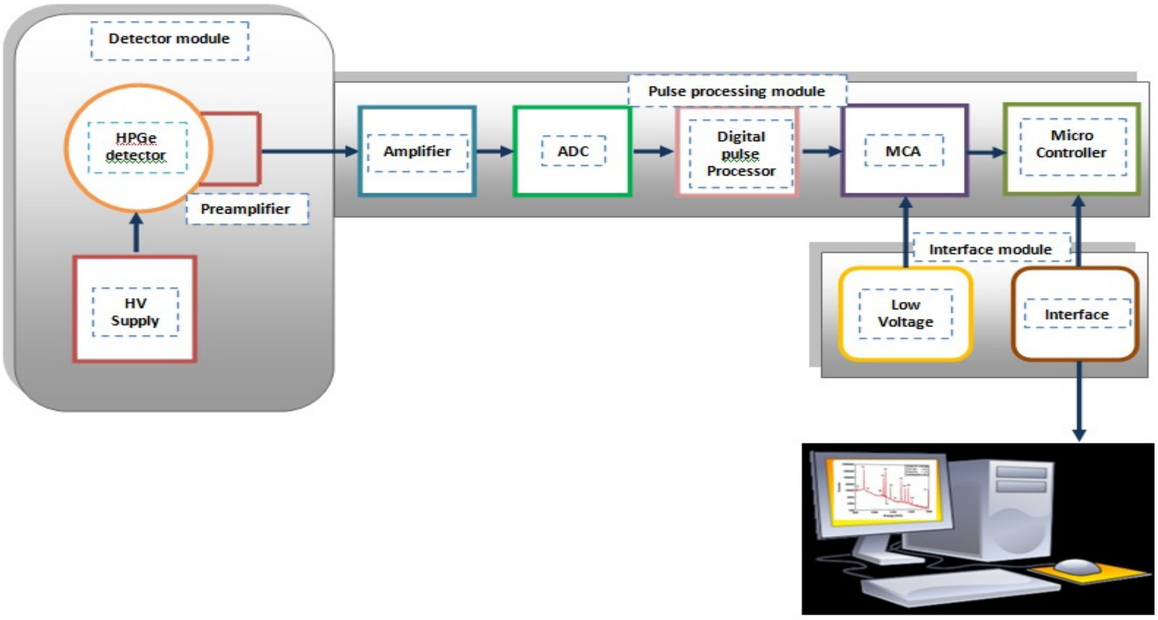
Element	Isotope	Half life	Gamma ray Energy (keV)
Elements determined in 1st stage counting, Counting time: 720 sec			
Na	^{24}Na	15 h	1368.6
K	^{42}K	12.4 h	1524.7
As	^{76}As	26.3 h	657;1215.8
Br	^{82}Br	35.3 h	619.1;776.5
Sm	^{103}Sm	46.5 h	103.2
Sb	^{122}Sb	2.7 d	564.1
La	^{140}La	40.2 h	1596.2
Elements determined in 2nd stage counting, Counting time: 1500 sec			
Sc	^{46}Sc	83.8 d	889.3;1120.5
Cr	^{51}Cr	27.7 d	320.1
Fe	^{59}Fe	45.1 d	1099.2; 1291.6
Co	^{60}Co	5.2 y	1173.3;1132.5
Zn	^{65}Zn	144 d	1115.5
Se	^{75}Se	120 d	264.6
Sb	^{124}Sb	60.2 d	1691.0
Eu	^{152}Eu	12 y	963.5

Concentrations of elements in a sample are determined by NAA either by relative or single comparator method. In relative method a suitable elemental standard is irradiated with the sample and activities produced in the sample and standard are compared to arrive at the analyte concentrations. In the single comparator NAA (K_0-NAA), a sample and a neutron flux monitor, such as ^{197}Au, are co-irradiated and the activity of each isotope in the sample is compared with the activity of the comparator.

As mentioned above, based on the comparator method unknown samples and known amount of comparator standards were co irradiated and subsequently both the standard & samples were analysed for elements in the same detector. Error due to the time delay between the counting of sample and the standard was corrected using decay correction methods. Also decay corrections were applied to the measured activity for both samples and standard back to the end irradiation using the half life of the measured isotope. Using the mass of the standard ($M_{x,std}$) and activities of standard ($cps_{x,std}$) and sample ($cps_{x,sample}$), the mass of the element in the sample ($M_{x,sample}$) is determined for the same counting time. Though the relative method is simple and precise, prior knowledge of the elements present in the sample is necessary to prepare multielemental standards or to use certified reference materials of similar matrices.

The gamma spectrometric system consisting P-type coaxial HPGe detector with 50% relative efficiency, energy resolution 2 keV at 1,332 keV energy and a multichannel analyser with a PHAST software, developed by Electronics Division, BARC and NIM bin associated with a HV supply, low voltage supply and amplifier was used for the evaluation of gamma spectrum. A schematic representation of a typical gamma spectrometry system is depicted in Figure 2.6. In this study, INAA was used for the determination of 15 elements, whereas rest of the marker elements contributed by different natural and anthropogenic emissions was measured by EDXRF designated as one of the complementary technique for INAA.

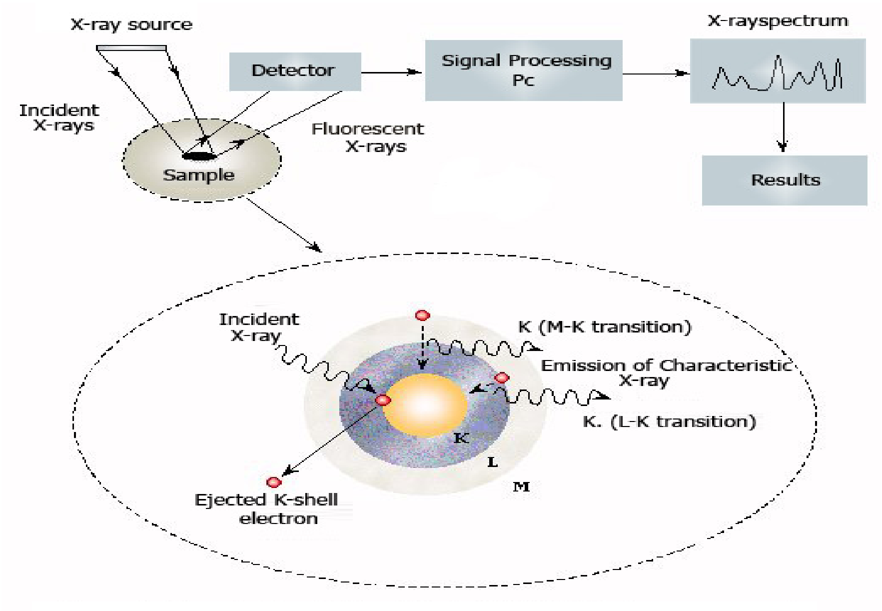
Figure 2.6: Schematic representation of Gamma spectrometric system



2.4.2 Energy Dispersive X-Ray Fluorescence

One of the ideal and challenging technique in the analysis filter samples to analyse a wide spectrum of elements from Na to U is X-ray Fluorescence analysis. It principally works on the basis of detection of characteristic x-rays emitted subsequently after the electroninc excitation of a particular atom. When a primary X-ray from an X-ray tube or a radioactive source interacts with a sample, the X-ray can either be absorbed by an atom or scattered through the material. The process in which an X-ray is absorbed by an atom by transferring all of its energy to an innermost electron is called the "photoelectric effect." If the primary X-ray had sufficient energy, electrons are ejected from the inner shells, creating an excited atom with vacancies on inner shells. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process emit a characteristic X-ray whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X-rays at a unique spectrum of energies, allowing one to identify the element and to measure the elemental composition of a sample. The measurement of trace elements in samples by XRF is illustrated in Figure 2.7.

Figure 2.7: Principle of XRF and block diagram of XRF arrangement

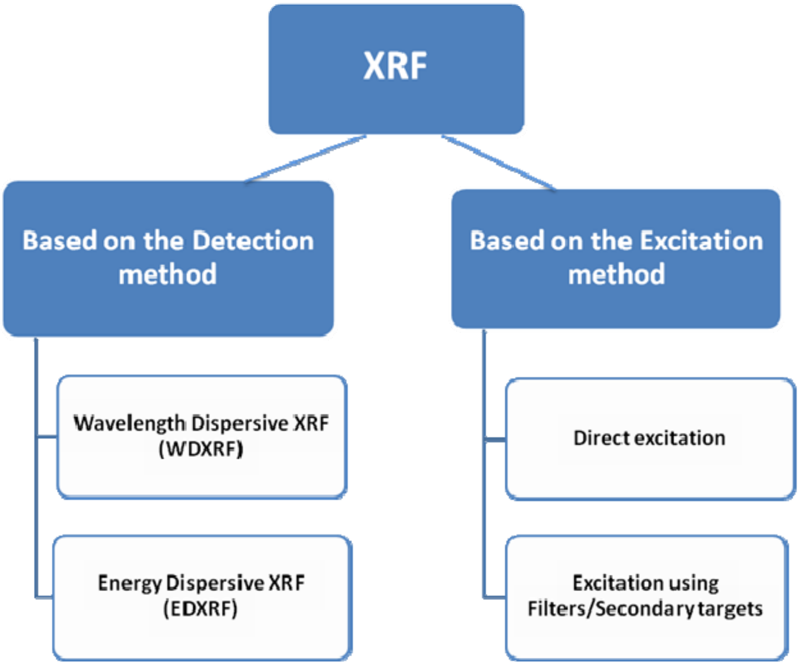


In XRF measurements, concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration. Emitted x-rays with energies less than ~4 kev (viz., sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium) can be absorbed in the filter, in a thick particle deposit, or even by large particles in which these elements are contained. Very thick filters also scatter much of the excitation radiation or protons, thereby lowering the signal-to-noise ratio for XRF. For this reason, thin membrane filters with deposits in the range of 10 to 50 µg/cm^2 provide the best accuracy and precision for XRF analysis. In the case of dust load collected on polycarbonate filters i.e. the samples as a thin layer of particles, matrix effects substantially disappear. So, the method is applicable to measure a broad range of elemental anlaysis.

XRF methods can be broadly divided into two categories based on their detection methods: wavelength dispersive (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution, which minimizes peak overlaps. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

XRF methods can be further categorized as direct/filtered excitation, where the x-ray beam from the tube can be used for the excitation directly. In the indirect excitation method the beam is optionally filtered and then focused directly on the sample, or the beam can be passed through the secondary target, where the beam is focused on a target of material selected to produce x-rays of the desired energy. The secondary fluorescent radiation is then used to excite the samples. The direct and filtered approach has the advantage of delivering higher incident radiation flux to the sample for a given x-ray tube power. But, the secondary fluorescer approach, however, produces a more nearly monochromatic excitation that reduces unwanted scatter from the filter, yielding better detection limits. Classification of XRF methods are depicted in Figure 2.8.

Figure 2.8: Classification of XRF technique



XRF displays high analytical specificity combined with moderate to high sensitivity and high dynamic range covering several concentration decades, but also good accuracy and high versatility. A specific and challenging problem of dust analysis is the small available mass for analysis, its a-priori unknown elemental composition and its chemical complexity with elements varying from main component level to trace elements.

In this work, coarse and fine particulate matter sampled on nuclepore filters were analysed for more than 20 trace and toxic elements using an EDXRF spectrometer of make Xenemetrix (Model: Ex 6600)(Plate 2.3) provided with the liquid nitrogen cooled Si(Li) detector of area 20 mm^2. The resolution of the detector was 131 eV at 5.9 keV Mn K_α x-rays. The system is equipped with a oil cooled Rh anode X-ray tube as the primary excitation source with the maximum operating voltage and current as 60kV and 6.6 mA respectively. 8-sample turret enables mounting and analysing 8 samples at a time. Quantitative analysis was performed using the built-in nEXT software. Measurements were carried out in vaccum for low Z elements. Whereas, medium and high z elements were analysed in the air atmosphere. For the excitation of the sample targets, secondary excitation method was used. Sensitivity of a set of elements were improved by the application of secondary targets. Suitable thin film standards from micro matter were used for the calibration of the EDXRF system and (National Institute of Standards and Technology) NIST – SRM 2783, PM deposited on polycarbonate filter paper was used for the quality control. The entire elemental profile was measured following a three step procedure where suitable secondary targets were used in each step and the operating parameters such as current, voltage and time of counting were optimized for minimum counting error and the dead time during the analysis was maintained within 20% throughout the analysis. The parameters used for the study are presented in Table 2.3. K x-rays of low and medium z elements and L x-rays of Pb are used for the quantification of elements.

Plate 2.3: EDXRF spectrometer, Xenemetrix, Model: Ex-6600

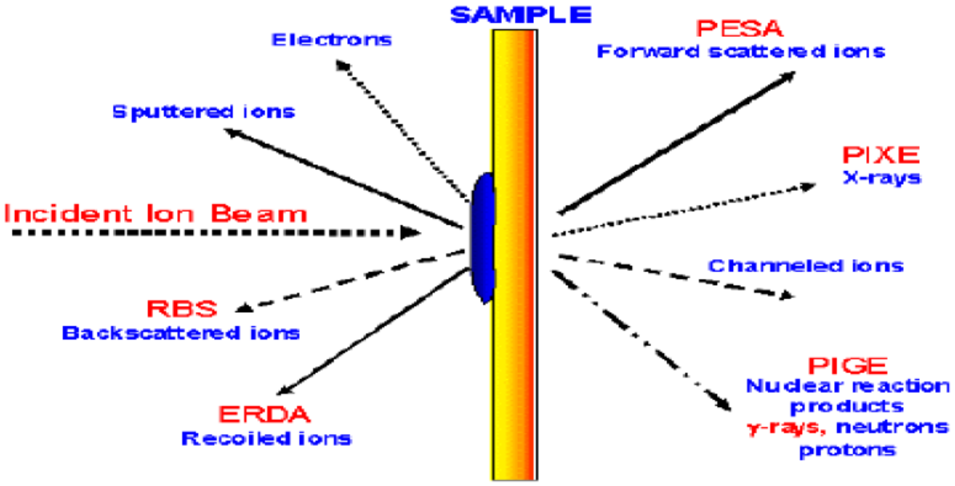
Table 2.3: Parameters and conditions of Air filter analysis using EDXRF technique

Secondary Target	Voltage (kV)	Current (μA)	Atmosphere	Elements
Ti	25	4800	Vaccum	Na, Mg, Al, Si, P, S,Cl, K, Ca
Ge	40	800	Air	Ti, V, Cr, Mn, Fe, Ni, Cu, Zn
Mo	40	1000	Air	As, Pb, Br

2.4.3 Proton Induced X-Ray Emission

Proton Induced X-ray Emission (PIXE) is one of the powerful tools employed for elemental analysis among the Ion Beam Analysis (IBA) techniques. The term IBA is used to describe a range of elemental analysis techniques based on the use of ion beams generated by particle accelerators, including particle induced X-ray emission (PIXE), particle induced gamma-ray emission (PIGE), Rutherford backscattering analysis (RBA) and particle elastic scattering analysis (PESA). A Figure (2.9) depicting the Ion Beam techniques is presented below. All the IBA methods are based on the interaction at both the atomic and nuclear level, between the accelerated charged particles and the bombarded material. When a charged particle moving at high speed strikes a material, it interacts with the electrons and nuclei of the material atoms, slows down and possibly deviates from its initial trajectory. X-rays are then emitted following the ionization of an atom, due to the rearrangement of the electrons after the ejection of the deeply bound electron [117]. In the PIXE technique the ionization can be induced either by light particles like protons, electrons and alpha or by heavy ions. These charged particles are produced with accelerators and have the advantage that their beam can be focused.

Figure 2.9: Ion Beam Analysis methods.



Using PIXE is extremely sensitive on an extended range of elements because it gives a detectable x-ray energy range (1-30 keV), elements with medium atomic number ($10 < Z < 40$) and high atomic number ($Z > 40$) can be detected by K and L lines respectively. As a rule of thumb one might state that in a single measurement – typically lasting for few minutes – all elements with $Z > 10$ can be detected with minimum detection limits down to trace levels. As mentioned above PIXE has got several advantages from the fast quantitative results up to providing high absolute sensitivity, but the impossibility of PIXE of detecting light elements becomes an important limitation to the technique. When compared with XRF, PIXE suffers from the same disadvantage in quantifying lighter elements but PIXE can detect potentially harmful elements like As, Se, Ni, Cr, Zn, Cu etc. with greater efficiency and sensitivity.

As a special case, in the characterization of thin aerosol samples, PIXE holds an outstanding position, because of its multi-elemental ability, and high sensitivity, which allow the analysis of several particulate samples in short times. [118] explains that 5-10 minutes of bombardment are sufficient to detect up to 20 elements from Na-Pb, including important anthropogenic elements (S, V, Ni, Cu, Zn As and Pb) and all the crustal elements (Al, Si, K, Ca, Ti, Mn and Fe) and its high efficiency is very useful when hundreds of samples have to be analyzed which is a quite common need in aerosol studies. Also a review on applications of PIXE technique by [119] describes PIXE as an ideal technique for the fast and routine analysis of aerosol particles and it is also mentioned that the low detection limits allow characterization of dilute fraction of particulates and the sample is not destroyed allowing further analysis or long term archiving.

In this work, PIXE was used to determine elemental concentrations of aerosol deposited on polycarbonate filters. To acquire the elemental profile air filters were exposed to a proton beam accelerated with 2.5 million volts from the Van-de- Graaff accelerator at GNS Science, New Zealand [120]. The typical PIXE set up at GNS, New Zealand is given in Figure 2.10. While all elements heavier than boron emit K X-rays, the production of them become too few to satisfactorily measure for elements heavier than strontium. Elements heavier than strontium are detected via their lower energy L X-rays. The X-rays were detected by means of a Si(Li) detector. The sensitivities were further improved by using two X-ray detectors, one for light element X-rays and the other for heavier element X-rays, each with different filtering and collimation. The proton beam size used for this analysis is 5 mm high and 3mm wide and the intensity of the beam is constant over the area of 3×5 mm^2. The typical beam current used in this study is 5–7 nA and charge collected is 10 µC. The exact limits of detection of each element depend on the method of detection, filter composition, sample composition, the detector resolution, and spectral interference from other elements. GUPIX software [121] was used to determine the concentration of each element by background subtraction and peak area fitting. Mainly the peaks of light elements in the spectra that have interferences or backgrounds from other elements present in the air particulate matter, or filter matrix itself, have higher limits of detection. Measurements of blank filters were performed to correct for filter derived analytical artifacts as a part of the

QA/QC procedures. Typical LODs achieved by PIXE for each element are shown in Figure. 2.11.

Figure 2.10: Typical PIXE set-up at GNS

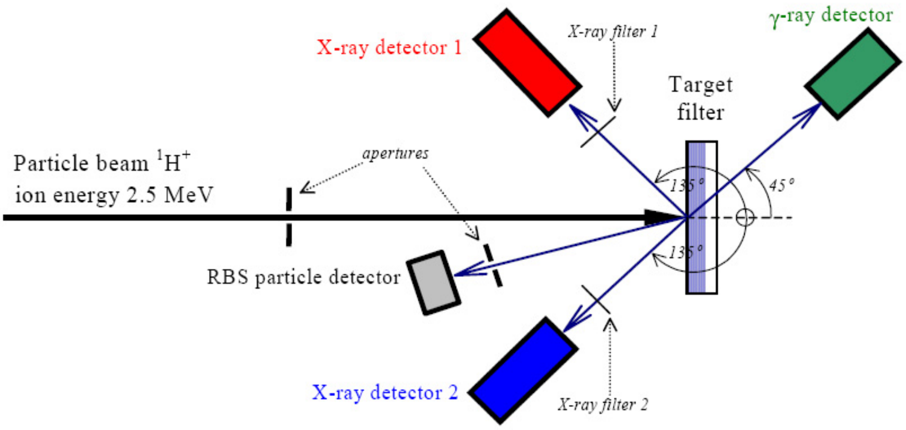
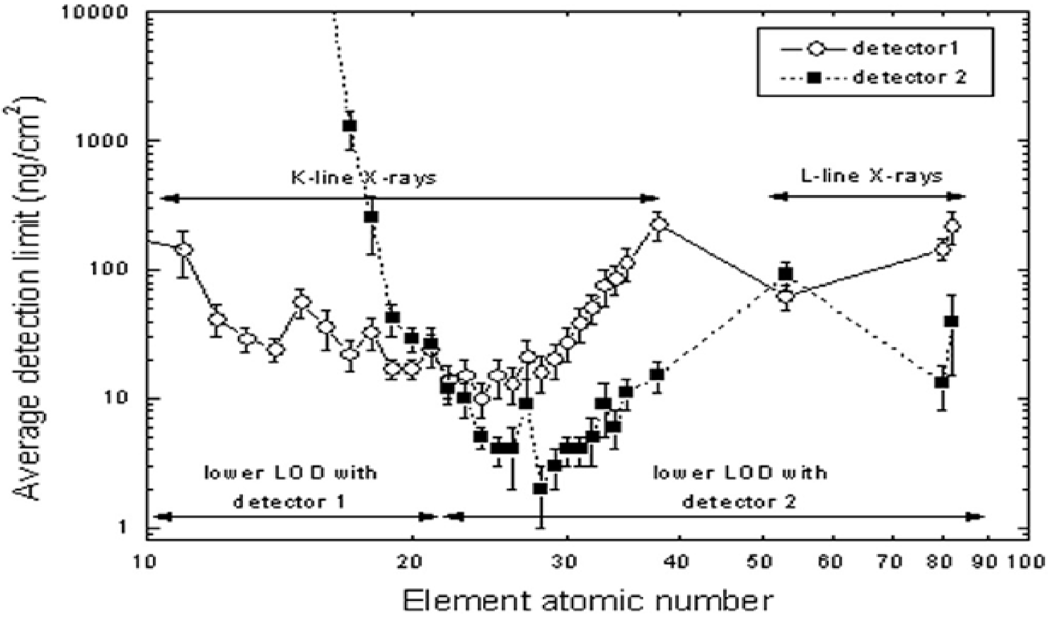


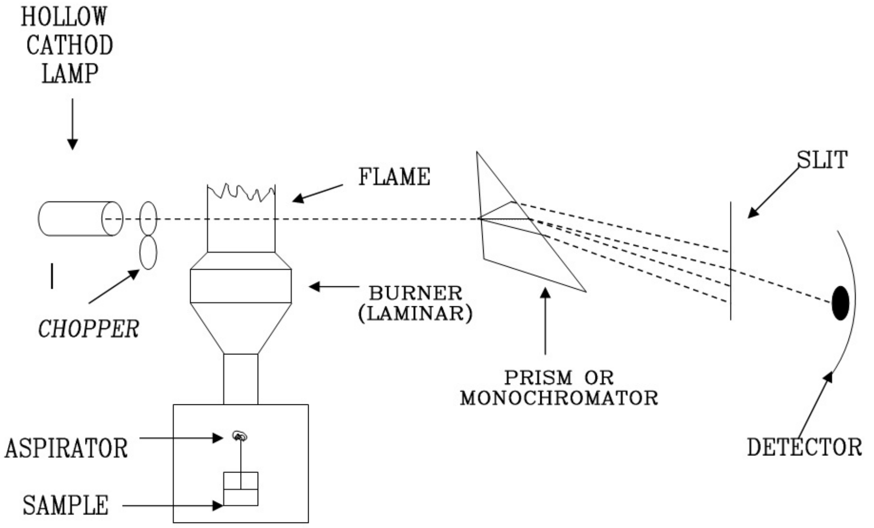
Figure 2.11: Elemental limits of detection of the PIXE method achieved at the GNS, IBA facility



2.4.4 Atomic Absorption Spectrometry

Atomic Absorption Spectrometry (AAS) is wide spread and a comparatively simple technique used for the analysis of metals and few metalloids in environmental matrices. In AAS [122], the sample is first extracted/digested in a strong hot acid mixture to digest/dissolve the solid material. A few millilitres of the extracted/digested solution are introduced to a flame (FAAS), where the sample is vaporized and atomized. Most elements absorb light at specific wavelength in the visible spectrum. A light beam with wavelength specific to be absorbed by the element being measured is passed through the flame, and then detected by a monochromator at a selected wavelength. The analyte concentration is determined from the amount of light absorption. The atomic density determines the absorption rate and the Lambert's Beer's law give the value of absorbance from each element of the sample which is proportional with the concentration of that element [123]. By comparing with the absorption from known standards, the concentration of the element in the sample is quantified. Schematic representation of AAS is illustrated in Figure 2.12. AAS can be classified in to two main types, they are Flame AAS (FAAS) and Graphite Furnace AAS (GFAAS). In the field of ambient air particulate matter analysis high volume samplers are normally used for sampling when FAAS or GFAAS analysis is planned.

Figure 2.12: Schematic representation of AAS



In general, AAS measurements are subject to interference from a number of confounding influences: background, spectral, ionization, chemical and physical interferences have all been identified. Appropriate choice of filter media and matrix matching of the samples to standards tend to minimize interferences [124]. But in over all, AAS has less interference than other destructive techniques used for measuring metals in air. AAS generally requires an individual analysis for each element and a large air filter or several filters are needed to obtain concentrations for all of the elements interested.

In the current study, PM_{10} samples were collected using high volume sampler for few months to compare the mass concentrations of PM_{10} obtained by the US EPA certified cyclonic sampling method for particle sampling and virtual impaction (Gent sampler) based sample collection. One forth portion of the deposited glass fibre filter papers were used for further analysis using AAS. Necessary precautions were taken during the cutting and digestion procedure of filters to avoid any contamination. Acid digestion, required for the metals determination by AAS (AAS, –GBC, Avanta, Australia, Plate 2.4. was carried out according to a standard procedure and the digestion was performed following these steps: (1) samples of dry filters were dissolved in nitric acid and perchloric acid (15:3), (2) digestates were evaporated till white fumes arose and reduced to 2–3 ml, (3) the content was filtered through a Whatman filter 42 and the final volume was adjusted to 25 ml by 0.25% HNO_3. A series of blanks were prepared using the same digestion method. The filtrates were analyzed for trace metals using AAS. All chemicals used were Merck, Suprapure, Analar or electronic grade. The trace metal amounts in the samples were calculated by subtracting the blank value for the respective metal.

As and Se were analyzed using Hydride Generation (HG)-AAS. Sodium borohydride solution was prepared by dissolving 3.0 g of $NaBH_4$, and 3.0 g of NaOH in 500 ml of ultra pure water. After filtration the solution was transferred to the HG container. The experiments were performed with a double beam atomic absorption spectrometer, coupled with a hydride generation system. A deuterium lamp background corrector was used in all instances. A GBC hollow cathode lamp was used as a light source. Pure nitrogen gas was used as the carrier gas. In order to evaluate the accuracy of the dissolution scheme as well as the capability of the analytical method, the NIST urban particulate matter standard (SRM 1648) was used as a reference. Few mg of SRM 1648 nearly equivalent to the average mass of particulate matter collected in the air filter was utilized for quality control purpose. For the measurement of metals only quarter portion of the glass fibre filter was digested following the above mentioned procedure for general trace metals and for volatile elements hydrochloric acid was used for digestion. Since As and Se are volatile in nature HG-AAS was adapted for the analysis but it is believed that the volatile elements may also be lost during the evaporation process. Tests have been done to verify the influence of acid evaporation after the digestion procedure. Spike tests were also carried out using standard solutions.

Plate 2.4: Atomic Absorption Spectrometry system, GBC Avanta

2.4.5 Ion Chromatography

The determination of the anionic concentration of PM is of increasing interest in the context of working towards the mass closure in PM studies. Ionic species can represent a large fraction of particulate matter, especially for the fine fraction of PM, thus their determination is critical in order to meet the data analysis objectives of the present study. Usually, ions present in aerosols are soluble in water. Studying these ions carry importance, because the water soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Also, different emission sources may be distinguished by their soluble and non-soluble fractions. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material. As a matter of fact anthropogenic acid precursor emissions in Asia are increasing at a rate and this is expected to continue for the next several years [125]. Moreover these anions in PM become precursors for acid rain formation [126]. In view of the above mentioned multiple environmental problems that can be caused by the atmospheric ionic content, it becomes mandatory to characterize the aerosols for their ionic counterpart.

Ion chromatography (IC) is a well established methodology for the analysis of anionic and cationic components of environmental samples like water, soil, sediment and particulate matter samples. Particularly, for the ion characterization of aerosols samples IC is considered as a simple, sensitive, convenient and powerful tool [126, 127]. IC is used as one branch of liquid chromatography, where IC refers to the separation of ions in solution with ion exchange resins, followed by their determination. In this technique, the sample extract passes through an ion-exchange column which separates the ions for individual quantification, usually by a electro-conductivity detector. The anions are separated when passed through a resin consisting of polymer beads coated with quaternary ammonium active sites. The separation is a result of the different affinities of the anions for these sites. After separation and prior to detection, the column effluent and anions enter a suppressor column here the cations are exchanged for H^+ ions. Species are then detected as their acids by conductivity meter. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. The IC is especially desirable for particulate samples because it provides results for several ions with a single analysis, low detection limits, and uses a small portion of the filter extract with low detection limits. The cations are analyzed in the same manner except the sample extract passes through a surface-sulfonated ion exchange resin where separation occurs. The conductivity change of electro-conductivity detector is directly proportional to the concentration of measured ions. Based on the incorporation of suppression step IC is classified in to two categories as suppressor and non-suppressor type IC's.

For the analysis of ions in the particulates, sampled on glass fibre filter using high volume sampler, quarter part of each filter paper was taken and cut into small bits and the samples were then water digested after adding 80ml of Millipore water using a hot plate. Samples were allowed to boil and the water was simultaneously evaporated to reduce the volume to one third of the original volume at least for 8 hours. The samples were filtered through Millipore filter (cellulose nitrate filter – 0.45 µm) and the final volume was made up to 25ml using Millipore water for the analysis of ions. Few samples of size fractionated particles were also extracted in 25 ml of Millipore water for the purpose of mass closure studies.

Measurements of anions and cations were carried out using ion chromatography (Metrohm make, 733 IC Separation Centre, Plate 2.5) with conductivity detector. For the present study, only major ions (Na^+, K^+, Ca^{+2}, Mg^{+2}, NH^{+4} , Cl^-, SO_4^{2-}, and NO_3^-) are analyzed. Anion analysis is carried out by analytical column of 25 cm length and 0.46 cm diameter packed with polystyrene divinyl benzene with a guard column preceding the analytical column [128]. The eluent used is 3 m molar sodium carbonate at a flow rate of 1 ml/min. The background conductivity is 14 µS after suppression. Cl^-, NO_3^- , and SO_4^{2-} are the anions determined in the filtered water digested air particulate samples. The analytical column for cation analysis is 12.5 cm in length and 0.4 cm in diameter packed with poly butadiene maleic acid groups with a guard column preceding the analytical column. A mixture of 4 mM tartaric acid and 1 mM pyridine-2,6-dicarboxylic acid is used as the mobile phase. Direct chromatographic detection with electronic background suppression is used in the case of cation analysis. The cations analyzed are sodium, ammonium, potassium, calcium, and magnesium.

Plate 2.5: Ion Chromatography system, Metrohm, 733 IC separation centre

2.4.6 Smoke Stain Reflectometer

Black carbon aerosol plays a unique and important role in Earth's climate system. It's a type of carbonaceous material with the unique combination of physical properties. Small concentrations of black carbon itself is enough to be easily inhaled into the lungs and has been associated with adverse health effects. Whether black carbon itself is toxic or functions as an indicator of other co-pollutants is currently under debate. The black carbon content in PM is regularly measured using methods based on the chemical, physical and light absorption properties of the particles. Each carbon measurement technique provides unique information about these properties. All current analysis methods are operationally defined, meaning that there is no universally accepted standard measurement [129].

After the gravimetrical analysis, the filters were examined for black carbon by measuring the reflectance using an EEL 43D Smoke Stain Reflectometer (Diffusion Systems Ltd., London, UK). Each filter was examined five times to check homogeneity of the deposited air filters and the average value was used in the calculations. A light source shines its light on the filters, and the reflected light is measured by photocells located in a black housing. The reflector reading is obtained directly from the DS 29 universal digital readout. The amount of light absorbed is directly attributed to BC. This is based on the premise that BC is the most highly absorbing chemical compound present in particulate matter [130]. Reflectance readings (output voltages readings) were also obtained for the blank filters after every series of five sampled filter reading to rectify the errors in the calibration due to any fluctuation during the analysis. The output voltages obtained from the smoke stain reflectometer measurement are converted to a measure of blackness. The blackness is essentially determined by the use of Lambert-Beer's law [131]. Provided that thin layers of aerosol particles are collected on the filter.

Prior to the anlaysis of BC, the instrument was calibrated using the white or gray standard marked with their reflectance value which was supplied along with the instrument. A Linearity check of the instrument is readily obtainable. The mask and measuring head are placed on the white standard and the sensitivity control adjusted to produce a reading of 100. They are then transferred to grey standard and the new reading is taken. This should equal the value given on the standard within ±1½divisions. The mass attenuation coefficient Vs black Carbon content was determined. The mass attenuation co efficient which is specific for BC has been evaluated by controlled combustion of candle, kerosene, diesel, camphor and benzene in a combustion unit under laboratory conditions and the values obtained as mean mass attenuation co efficient for aerosol size < 2 µm is ε = 5.93 and for 2-10 µm aerosol size it is 1.99. The equation using which the black carbon level calculated is,

$$BC(\mu g/cm^2) = \frac{100}{2F\varepsilon}\ln\left(\frac{R_0}{R}\right)$$

Where, F = correction factor of order 1

ε = Mass attenuation co efficient (m^2/g)

R_o= Unloaded filter reflectance

R = Loaded filter reflectance

The model of smoke stain reflectometer used is presented in Plate 2.6.

Plate 2.6: EEL Smoke stain reflectometer (Model 43D)

Chapter – 3

Source Identification and Apportionment

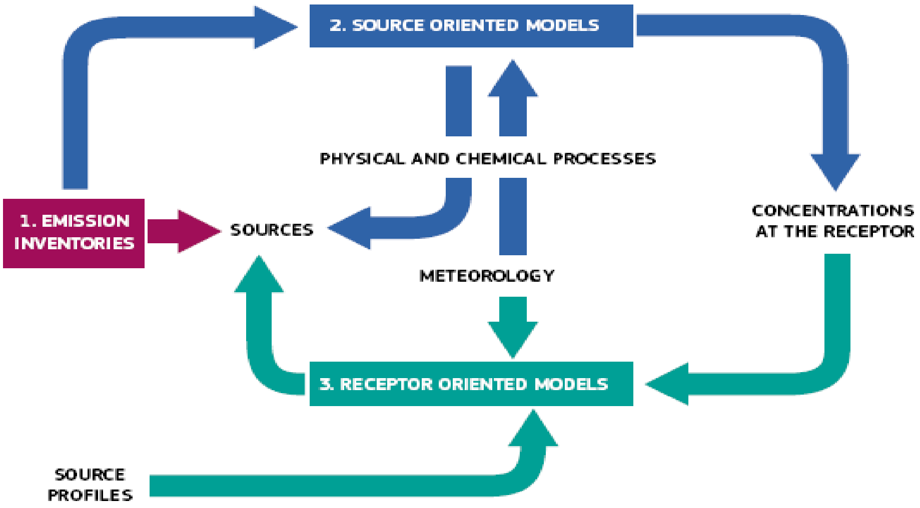
The main goal of the chapter is to discuss scrupulously about the primarily employed source apportionment techniques of PM as well as to analyze the advantages and disadvantages of the tools used globally. In the field of atmospheric sciences, source apportionment (SA) models aim to re-construct the impacts of emissions from different sources of atmospheric pollutants, e.g., particulate matter (PM), based on ambient data registered at monitoring sites. The main objective of the source apportionment studies are to identify the possible sources of PM and to obtain data on their contributions to the bulk PM mass. Even human exposure to these pollution components has been evaluated to assess their health effects and risks. Furthermore, policy-makers require sound scientific knowledge of the PM sources and their contributions to atmospheric PM levels and associated health risks for the development and implementation of policies to protect human health and the environment. Thus the information provided by receptor models is key to the design of effective mitigation strategies on the local- and meso-scale [132, 133].

There are an enormous number of possible chemical species associated with particles and a potentially more effective approach and methodology is required to consider the airborne PM as mixture of mass contributions by various source classes. Normally different types of sources like vehicular emission, coal/oil combustion, various industrial activities have their own characteristic chemical and/or physical patterns. It will be a great advantage to examine the relationship of specific source emissions and their health effects. If a limited number of sources contributed significantly to the effects, more targeted control strategies could then be devised to focus on those sources producing maximum health problems. Chiefly, source composition or physical property profiles permit the contribution of the identified sources to the airborne particulate mass to be apportioned.

Source apportionment requires ambient data as well as source emission profiles. In most of the studies source profiles were taken from the literature with the assumption that these profiles do not necessarily represent the location. For example, “Speciate” of US EPA is a repository of volatile organic gas and particulate matter speciation profiles of air pollution sources. But in realism, these profiles differ with sources, process operating conditions, geology and geographic seasonality [134]. For this reason, development of site specific source profile becomes necessary. A large number of methods has been developed in order to apportion atmospheric aerosols to their emission sources. These methods range from a simple screening test of anthropogenic sources using enrichment analysis to approaches developed to construct and quantify the pseudo elements (soil, sea salt, smoke etc.), up to more sophisticated statistical modeling of chemical composition speciation data of PM at a receptor site (termed as receptor modeling).

Different approaches have been proposed to understand the source diversity of aerosols. In a broader sense there are three approaches for quantifying the contributions of pollution sources. The first approach is based on quantification and establishing the emission inventories, the second one is dispersion modeling, starts with emissions from different sources (emissions inventory) and the third one calculates ambient concentrations in the vicinity of the “receptor” (where ambient concentrations are measured). Ambient concentrations are used to calibrate the models for running future scenarios. The last and the third approach, receptor modeling analyzes PM in the atmosphere at a given location and matches their characteristics with those of chemically distinct source types. Receptor modeling is a research and analytical tool to apportion the PM mass concentrations to the possible sources [135]. A schematic representation of different source identification method is presented in Figure 3.1.

Figure 3.1: Schematic representation of the different methods for source identification



In the following sections of this chapter, methods used for the screening of the anthropogenic sources of PM from the natural sources, mass reconstruction details and the receptor model techniques commonly adopted in the PM source apportionment are briefed.

3.1 Enrichment Factor Analysis

As mentioned above, trace metals in aerosols were derived from various sources. The degree to which trace elements in the aerosols are enriched, or depleted, relative to a specific source can be assessed using enrichment factor analysis. The concept of Enrichment Factor was introduced by [136] and is widely used to identify the anthropogenic sources of metallic elements and it is generally applied to show the degree of enrichment of a given element compared to the relative abundance of that element in crustal material or Sea salt [137]. Specifically, enrichment of elements in atmospheric particles relative to the upper continental crust composition is considered as an indication of emission from anthropogenic sources [138]. The atmospheric and the crustal concentration levels of elements are standardized with the use of information on concentration of certain reference metals, such on Al, Si, Ti, Fe or Sc [139].

EF is calculated using the following equation,

$$EF_i = \frac{\left(i/j \right)_{Air}}{\left(i/j \right)_{Crust}}$$

Where EF_i is the enrichment factor of a species i, j is a reference material for crustal or marine source. $(i/j)_{air}$ is the ratio of species i to j in the aerosol sample and $(i/j)_{crust}$ is the ratio of species i to j in the crust [140]. Reference elements selected for the purpose of EF analysis normally are those ones in the soil that are stable, spatially homogeneous, and least impacted by anthropogenic pollution. Conventionally, a "cut off" EF_i value of 10 is used to distinguish between two types of atmospheric aerosols. If $EF_i < 10$, element i is considered to have a significant dust/soil source and is termed non enriched. If $EF_i > 10$, element i is enriched and has a significant fraction which is contributed by non-mineral sources. If EF's are in the 10–500 range, they are considered moderately enriched and those with EF over 500 are assumed to be highly enriched.

3.2 Reconstruction Mass Analysis

Over the years efforts have been made to get knowledge about the composition of atmospheric aerosols as a function of size and to achieve mass closure on the chemical species for the whole mass of aerosol collected. The reconstructed mass is considered as an important parameter and which should be above 70% of the gravimetric mass for successful source apportionment.

By comparing the sum of the masses of the individually identified chemical species to the gravimetric particulate matter, aerosol chemical mass closure can be constructed. Usually chemical components and gravimetric mass are analyzed from filter samples. A majority of particle mass can be determined by using different combinations of analytical methods. Though multi-elemental techniques like PIXE and EDXRF can provide a wide spectrum of elemental analysis, presence of hetero atoms (e.g. Oxygen) remains unaccounted and they require some assumptions to complete the reconstruction [141]. But it is useful to combine some of these elements and estimate the concentrations of few compounds which are likely to represent most of the measured element; such as estimating the amount of ammonium sulfate from the measured sulphur concentration and it is also assumed that sulphur occurs in the atmosphere as fully neutralized ammonium sulfate. Other combinations of elements that represent interesting aerosol components can be estimated using pseudo-element construction, such as “soil” as described by [142]. In the soil reconstruction it was assumed that both fine and coarse soil are composed mainly of the oxides of Mg, Al, Si, Ca, Ti and Fe with other many trace elements.

The equation of ammonium sulfate and soil is,

$$\text{Ammonium sulfate} = 4.125\,[S] \qquad (1)$$

$$\text{Soil} = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 1.94[Ti] + 2.42\,[Fe] \qquad (2)$$

Equation 2, also assumes that the two common oxides of iron Fe_2O_3 and FeO occur in equal proportions. The factor of 2.42 for iron also includes the mass of K_2O in soil, based on the (K / Fe) = 0.6 ratio for sedimentary soils.

Six major ions make more than 99% of the mass of salts dissolved in seawater: four cations, sodium (ss-Na^+), magnesium (ss-Mg^{2+}), calcium (ss-Ca^{2+}), and potassium (ss-K^+); and two anions, chloride (ss-Cl−) and sulfate (ss-$SO_4^{-\ 2}$). In general based on the ratio of Na^+ and Cl^- in sea water, sea salt content in the particulate matter can be reconstructed using the formula given by [143].

$$\text{Sea salt} = 3.27[Na^+] \quad \text{(or)} \quad 2.54[Na] \qquad (3)$$

But, the reduction in ratio may occur due to the reaction of NaCl particles with nitric and sulfuric acid and the subsequent volatilization of HCl. For this reason, sea salt concentrations can be calculated from the following equation:

$[\text{Seasalt}] = [Na^{+}] + [Cl^{-}] + [Mg2^{+}] + [ss{-}K^{+}] + [ss{-}Ca^{2+}] + [ss{-}SO_4^{2-}]$

(4)

Based on the sea water composition, sea-salt sulfate [ss-SO^{2-} $_4$] is calculated as total [Na+] times 0.252, sea-salt calcium [ss-Ca2+] as total [Na+] times 0.038, and sea-salt potassium [ss-K+] as total [Na+] times 0.036 [144].

In most closure experiments between gravimetric mass and chemical species measurements, particulate organic matter (POM) is estimated by multiplying OC by a conversion factor (*CF*), which is the ratio of the average molecular mass to the carbon mass for the organic aerosol:

$$[\text{POM}] = CF\,[\text{OC}] \qquad (5)$$

CF is usually taken to range from 1.4 for urban aerosols to 1.8 for remote aerosols. [145] revised these conversion factors and proposed values of 1.6±0.2 and 2.1±0.2 for urban and non-urban aerosols, respectively.

Usually fine potassium is an accepted indicator for smoke from biomass burning /brick kiln. In order to obtain a reliable smoke indicator from fine potassium, it is necessary to subtract fine potassium associated with soil and sea salt from the total K concentrations [146]. Hence , smoke K is obtained by,

$$\text{Smoke} = (K_{tot}) - (0.036\times Na + 0.6\times Fe) \qquad (6)$$

Summation of all the pseudo elements thus built results in reconstruction of PM mass and the equation is given as,

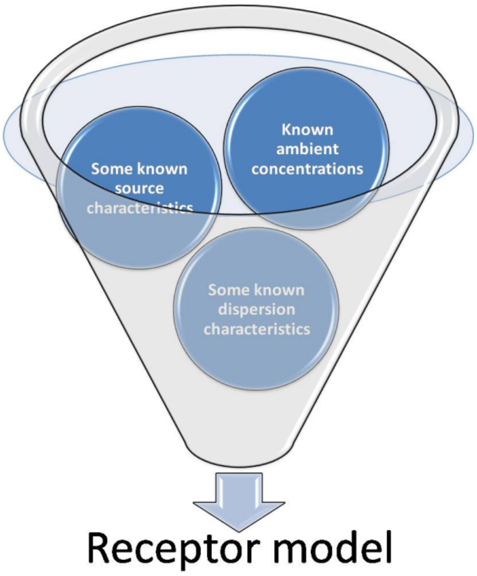
RCM = Sea salt + Soil + Smoke + Ammonium sulfate + Organics + BC + Trace elements (7)

Above mentioned equations are the widely used IMPROVE equations developed to characterize particle light extinction in U.S. National Parks and the details of the different equations are provided in detail by Chow et. al. [147] as a review of mass reconstruction studies. Analytical chemistry has been used to measure a large proportion of the periodic table elements, in the aerosol, attempting to gain knowledge as complete as possible about the chemical composition and emission sources. However, despite very extensive chemical analyses, mass closure is rarely achieved. Even if the important aerosols components (inorganic and carbonaceous compounds, minerals and metals) are analysed, a fraction of PM mass remains unidentified [148] and was considered a main drawback of source reconstruction studies.

3.3 Receptor Models

Receptor modeling is one of the principal technique administered for the identification and apportionment of PM sources and has been an area of active research for over 30 years. Depending upon the information that is available a priori, there are a number of receptor model techniques available today. The fundamental principle of receptor modeling is that mass conservation can be assumed and a mass balance analysis can be used to identify and apportion sources of airborne PM in the atmosphere. Customarily, source models like dispersion models uses source emissions as inputs and calculates ambient concentrations. The receptor model uses ambient concentrations as inputs and calculates source contributions and the basic requirements in the application of receptor model is depicted in Figure 3.2. Compared with other methods, such as diagnostic ratios and dispersion models, receptor models can be employed to not only identify PM sources, but also make quantitative assessment of the relative contribution of each source to the pollution loading.

Figure 3.2: Pre requirements to perform receptor modeling



The approach to obtaining a data set for receptor modeling is to determine a large number of chemical constituents such as elemental concentrations in a number of samples. A mass balance equation can be written to account for all j chemical species in the i samples as contributions from p independent sources,

$$X_{ij} = \sum_{p=1}^{p} g_{ip} f_{jp} + e_{ij} \qquad (1)$$

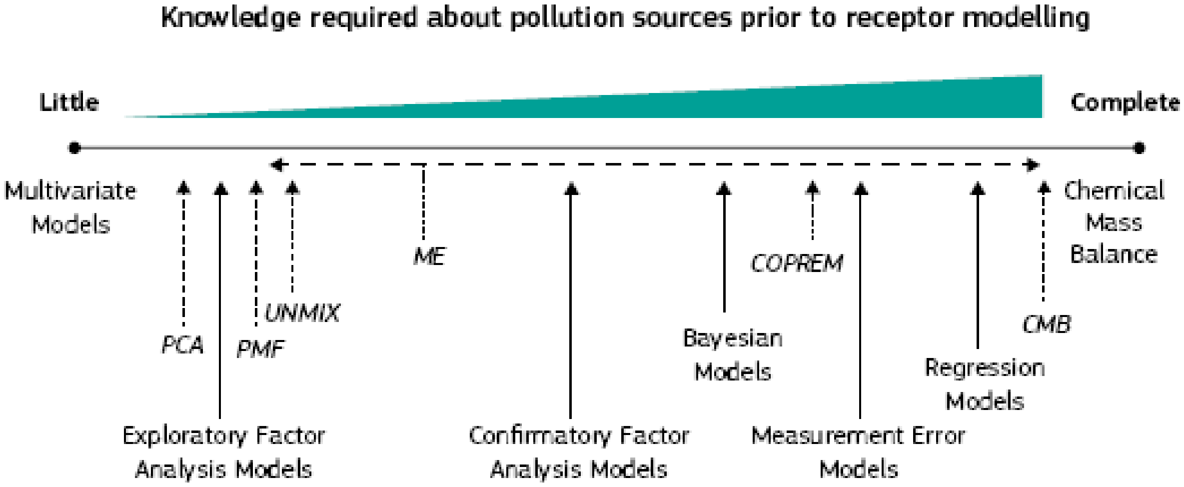
Where, x_{ij} is the measured concentration of the j^{th} species in the i^{th} sample, f_{jp} is the concentration of the j^{th} species in material emitted by source p, g_{ip} is the contribution of the p^{th} source to the i^{th} sample, and e_{ij} is the portion of the measurement that cannot be fit by the model. Therefore Equation 1 assumes that the measured parameters or concentrations x_{ij}, (apart from noise) are a weighed (scores, g_{ip}) sum of a reduced number (N<< I or J number of samples or number of variables) of contributions from distinct environmental sources. Written in matrix form the same bilinear equation is represented as equation 2,

$$X = GF^{T} + E \qquad (2)$$

Where, now **X** is the matrix of all measurements (j=1,...,J variables in i=1,...,I samples) **G** is the matrix of score profiles (distribution of the P contamination sources among samples), $\mathbf{F}^{\mathbf{T}}$ is the matrix of loading profiles (composition of the P composition sources) and **E** is the noise or error matrix containing the variance not explained by the model defined by the P environmental sources described in **G** and **F.** Since only **X** is known initially, the matrix decomposition described by Equations 1 and 2 is ambiguous (not unique) unless constraints are applied.

The number of existing source apportionment techniques is relatively large, and it includes methods such as principal component analysis (PCA, [149]), CMB (chemical mass balance, [150]), positive matrix factorization (PMF, [151]), UNMIX, multi-linear engine (ME, [152]), Lenschow approach [153], backtrajectory analysis, constrained physical receptor model (COPREM, [154]) and isotopic mass balance using C-14 [155]. These techniques require different degrees of knowledge about the number of sources at a given site, as well as of the source profiles [156]. Figure 3.3 shows specific receptor models and more general modeling concepts in relation to the a priori knowledge about the emissions sources that is required for application of the corresponding approach. The approaches range from Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) where only qualitative a priori information about the number and the chemical profiles of the sources are needed, up to the Chemical Mass Balance (CMB) model where detailed knowledge of the chemical profiles of all of the important sources is required.

Figure 3.3: Receptor model approaches for the estimation of source contributions



Principally, most of the receptor models are built on the basis of some assumptions. Especially, they assume that the particle characteristics must be in such a way that,

- They are present in different proportions in different source emissions
- These proportions remain relatively constant for each source type
- Changes in these proportions between source and receptor are negligible or can be approximated.

Remarkably, all the receptor techniques derived from the mass conservation concept are not considered statistical in nature. Because they don't test hypotheses or determine statistical significance; they are physically based on the statements of simplifying assumptions and evaluation of deviations from assumptions; they infer mechanisms and interactions rather than explicitly calculate them; receptor models recognize and elucidate patterns in measured components, space and time that bound the types, quantities, and locations of source contributions; some of them explicitly use input data uncertainties to weight influence of inputs and estimate uncertainties of outputs. In summary, the receptor modeling is done in five steps [157],

- Identification of uncorrelated sources
- Selection of "Targets" molecules to be included into the calculation

- Knowledge of the composition of the sources
- Estimation of the uncertainty associated to both sources and receptors
- Evaluation of the performance criteria, which indicates the robustness of the model

3.3.1 Chemical Mass Balance method

One of the old and most popular tool which is being used currently to quantify the source contributions to particulate matter is the chemical mass balance model. The CMB model identifies source contributions to primary particulate matter at specific receptor sites where PM composition measurements are available. The model is relatively easy to apply since it has a low computation burden and it does not require information about meteorological conditions. CMB calculations have been carried out in numerous studies around the world [158, 159, 160] The chemical mass balance method, as applied in the US-EPA CMB (Chemical Mass Balance) model, uses an effective variance-weighted least-square solution to a set of linear equations that express the receptor concentration of a chemical species as the sum of the products of source contributions and source compositions. A large number of species must therefore be measured in the ambient samples. Successful application of the CMB model depends on that, all of the important sources has to be identified, accurate source profiles has to be gathered and reasonable uncertainties must be estimated for both ambient concentrations and source fingerprints. The best results are therefore obtained when profiles representative of the actual sources in the area are used.

Assumptions of CMB model are,

- Compositions of source emissions are constant over the period of ambient and source sampling
- Chemical species do not react with each other, i.e. they add linearly.

- All sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized.
- The source compositions or source categories is less than or equal to the number of chemical species.
- Measurement uncertainties are random, uncorrelated, and normally distributed.

Also, this method assumes a priori that certain classes of sources are responsible for ambient concentrations of elements measured at the receptor. Furthermore it is assumed that each source under consideration emits a characteristic and conservative set of elements. However, these requirements are almost never completely fulfilled, and thus, pure CMB approaches are often becomes problematic. For sources that have known tracers but do not have complete emission profiles, factor analysis tools such as Principal Component Analysis (PCA), UNMIX, Positive Matrix Factorization (PMF) can be used to identify source tracers.

3.3.2 Principal Component Analysis and Factor Analysis derived methods

One first approach to solve the bilinear model of Equation 2 is Principal Component Analysis (PCA).Principal component and factor analyses attempt to simplify the description of a system by determining minimum set of basis vectors that span the data space to be interpreted. PCA derives a limited set of components that explain as much of the total variance of all the observable variables as possible, in the sense, these models assume that species of similar variability are grouped together in a minimum number of factors that explain the variability of the whole dataset, or rather that each factor is associated with a source or source type [161, 162]. To produce quantitative apportionments an alternate approach called Absolute Principal Components Analysis (APCA, [149]) has also been introduced. The methods employed in the APCA i.e. PCA followed by a Multi Linear Regression (MLR) step known as PCA - MLR model have been described thoroughly in the literature by [163] and [164].

In PCA, matrix factorization or decomposition of Equation 2 is performed under orthogonal constraints for both **G** and $\mathbf{F}^T$. Moreover, loadings (rows of $\mathbf{F}^T$ matrix) are also normalized (i.e. this matrix becomes orthonormal) and forced to be in the direction of explaining maximum variance. Under such constraints, PCA provides unique solutions and interpretation of variance is straightforward since scores and loadings are orthogonal (not overlapped). It makes interpretation and visualization of main features and trends of the data, i.e. the ultimate goal of identification of contamination source becomes readily available from the scores and loadings. PCA decomposition does not estimate the ‘true’ (latent) underlying sources of data variance but a linear combination of them fulfilling orthogonal constraints. Therefore, in PCA method loadings and scores do not have a physical meaning. For instance, both **G** and $\mathbf{F}^T$ will have negative values and uncorrelated profiles, whereas expected profiles for 'true' environmental sources defined by **G** and $\mathbf{F}^T$ should not have these profiles negative and they may be also strongly correlated. Moreover source apportionment (quantitative assessments of source contributions at each sample) cannot be performed due to the applied constraints also.

The problem related with the extraction of nonnegative profiles, improving interpretation and allowing source apportionment has been addressed in different ways. For instance rotation of PCA factor matrices to simplify interpretation like in varimax orthogonal rotation, scores uncentering (to make them positive) and regression to total sample mass has been proposed in the alternative APCA approach. The stepwise mathematical procedures of PCA/APCS or PCA-MLR are explained briefly in the following paragraphs. In the first step chemical composition data are transformed into a dimensionless standardized form:

$$Z_{ij} = \frac{C_{ij} - \overline{C_j}}{\sigma_j}$$

Where, i= 1, …, n samples; j= 1, …, m elements; C_{ij} is the concentration of element j in sample i; and $\overline{C_j}$ and σ_j are the arithmetic mean concentration and the standard deviation for element j, respectively. The PCA model is expressed as

$$Z_{ij} = \sum_{k=1}^{p} g_{ik} h_{kj}$$

Where, k= 1, …, p sources, and g_{ik} and h_{kj} are the factor loadings and the factor scores, respectively. This equation is solved by eigenvector decomposition. Varimax rotation is often used to redistribute the variance and provide a more interpretable structure to the factors. APCS is then used, based on the PCA factor scores, to derive quantitative estimates of source contributions and source profiles [149]. Because the PCA results are based on normalized data, the true zero for each factor score should be calculated as,

$$(Z_0)_j = \frac{0 - \overline{C_j}}{\sigma_j} = -\frac{\overline{C_j}}{\sigma_j}$$

The rescaled scores are known as APCS. Finally, regression can be used to derive the source contributions, expressed as

$$M_i = \varsigma_0 + \sum_{k=1}^{p} \varsigma_k APCS_{ki}$$

Where, M_i is the measured mass concentrations in sample i. In general, M_i could be the sum of the mass concentrations of the chemical species or the total mass concentrations measured directly, such as by gravimetric filter weighing. $APCS_{ki}$ is the rotated absolute component score for source k in sample i. $\zeta_k APCS_{ki}$ is the mass contribution in sample i made by source k. ζ_0 is the mass contribution made by sources unaccounted for in the PCA. Subsequently, the source profiles can also be obtained from the regression between C_{ij} and $\zeta_k APCS_{ki}$. The source contributions to individual species can be calculated from the source profiles and the mass contribution.

As mentioned above, the multivariate method, followed by multi-linear regression analysis, is performed by orthogonal transformation method with varimax rotation and retention of principal components whose eigenvalues are greater than one. The main limitations of the multivariate techniques are that they can only identify 5-8 sources and that the dataset must contain a large number of samples, usually no less than 50.

3.3.3 Positive Matrix Factorization

New approaches have been proposed in the recent years to solve the factor analysis problem and one of the solution is Positive Matrix Factorization (PMF). In recent years, PMF has been accepted as a powerful receptor modeling tool being applied for particulate matter data characterized for trace elements, Polycyclic Aromatic Hydrocarbons, Volatile Organic Carbons etc. and it has also been used for the source identification based on number concentration of size fractionated particulate matter recently [165, 166, 167, 168]. Many researchers compared PCA-APCS, UNMIX, CMB and PMF. Where UNMIX uses geometrical objects called the edges to identify factors. UNMIX does not allow individual weighing of data points as does PMF and was considered as one of the advantage of the technique. A study of [169] comparing three multivariate receptor models concluded that greater requirements of measure of uncertainty in PMF permitted to obtain better results than with the other two models: PCA-APCS and UNMIX.

PMF technique solves the general receptor modeling equation using a constrained, weighted, least squares approach. These methods place restrictions on the possible source profiles defined in **G** and $\mathbf{F}^{\mathbf{T}}$**,** to require them to met certain physical constraints (e-g. non-negative source impacts and composition) instead of purely based mathematical constraints like orthogonality or variance independency. Generally, PCA based methods are essentially based on eigenvector analysis, which in fact can be also considered as a least-squares analysis using a particular set of constraints and minimizing the sum of squared residuals for the model described by Equations 1 and 2, Positive Matrix Factorization (PMF, [170]) takes a very different approach to the same factor analysis problem.

PCA and related methods usually scale or normalize data and this scaling will lead to distortions in the analysis. In fact the optimal scaling of the data would be to scale each data point individually so as to have the more precise data having more influence on the solution than points that have higher uncertainties. PMF takes the approach of an explicit least squares approach in which the method minimizes the objective function Q:

$$Q = \sum_{i=1}^{I} \sum_{j=1}^{J} \left| \frac{X_{ij} - \sum_{n=1}^{N} g_{in} f_{nj}}{S_{ij}} \right|^{2}$$

(3)

Where, s_{ij} are estimates of the uncertainties in the jth variable measured in the ith sample. The factor analysis problem is to minimize Q(E) with respect to **G** and $\mathbf{F}^{\mathbf{T}}$ with the constraint that each of the elements of these two matrices are to be nonnegative.

In this study the robust mode has been used for analyzing element concentrations in bulk atmospheric deposition data set. The robust mode was selected to handle outlier values (that is any data that significantly deviates from the distribution of the other data in the data matrix) meaning that outliers are not allowed to overly influence the fitting of the contributions and profiles. This can be achieved by a technique of iterative reweighing of the individual data values, thus, the least-squares formulation becomes to

$$Q = \sum_{i=1}^{I} \sum_{j=1}^{J} \left(\frac{e_{ij}}{h_{ij} s_{ij}} \right)^{2}$$

Where,

$$h_{ij}^{2} = \begin{cases} 1 & if \left| {e_{ij}}/{s_{ij}} \right| \le \alpha, \\ \left| {e_{ij}}/{s_{ij}} \right| / \alpha & otherwise \end{cases}$$

The parameter α is called the outlier threshold distance. One of the main and important advantages of PMF is the ability to handle missing and below detection limit data by adjusting the corresponding error estimates.

Chapter - 4

Results and Discussion

The three year sampling program carried out at Vashi, Navi Mumbai for the purpose of identification and apportionment of potential contributing sources of particulate matter yielded a comprehensive data set explaining the concentration levels, the daily and seasonal variability of PM and their respective chemical components. The mass concentrations, chemical composition of $PM_{2.5-10}$ and $PM_{2.5}$, as well as the details with respect to the assessment of sources are presented in the following sections.

4.1 Concentration levels of Particulate Matter

Mass concentrations and the trend of size fractionated particulate matter collected using the dichotomous Gent sampler during the present study is elaborated in the following sections. Descriptive statistics of the coarse ($PM_{10-2.5\mu m}$) and fine ($PM_{2.5\ \mu m}$)particulate matter collected at Navi Mumbai during the three year sampling period (2008-2010) is summarized in the following Tables. 4.1, 4.2 and 4.3.

Table 4.1: Statistical summary of coarse and fine PM during 2008

Parameter	$PM_{2.5-10}$ (μg/m^3)	$PM_{2.5}$ (μg/m^3)
Mean	113.11	47.14
Median	109.56	42.12
Standard deviation	35.57	18.98
Maximum	235.45	115.43
Minimum	34.32	8.69
No. of samples	80	80

Table 4.2: Statistical summary of coarse and fine PM during 2009

Parameter	$PM_{2.5-10}$ (μg/m^3)	$PM_{2.5}$ (μg/m^3)
Mean	84.86	44.49
Median	86.12	41.32
Standard deviation	18.18	13.12
Maximum	147.69	79.85
Minimum	47.47	28.14
No. of samples	91	91

Table 4.3: Statistical summary of coarse and fine PM during 2010

Parameter	$PM_{2.5-10}$ (μg/m^3)	$PM_{2.5}$ (μg/m^3)
Mean	82.49	39.16
Median	81.52	35.21
Standard deviation	22.61	18.68
Maximum	150.25	78.23
Minimum	22.22	7.14
No. of samples	101	101

The annual average of coarse and fine fraction particulate matter show that the trend of PM annual average of the three sampling years persistently high in both size fractions. At the same time, a slightly decreasing trend is observed in both the fractions. Particularly, in the coarse fraction remarkable decrease is observed from 2008 to 2009. But there could not be any specific reason to be pin point this decrease in coarse fraction. Because the mean particulate matter concentration has been fluctuating throughout India over the years and no definite trend has been observed as the major contributing sources of PM in this fraction are natural dust, resuspension of dust etc. However, only marginal change is observed in the fine fraction average during the study period even though measures were taken by CPCB to mitigate high ambient PM levels through the implementation of stricter vehicle emission norms and commensurate fuel quality, use of cleaner fuels etc [171].

The overall three year average concentration of $PM_{2.5–10}$ and $PM_{2.5}$ were 89.92 (µg/m^3) and 42.25 (µg/m^3) and the highest concentration was observed to be 296.45 (µg/m^3) and 93.33 (µg/m^3) respectively. These values are within the average ranges of PM_{10} concentrations obtained from the PM pollution data collected by CPCB from a wide range of sites across India, covering all climatic conditions and anthropogenic activities [172]. As much as India is considered RSPM was measured regularly and was considered as the indicator for particulate pollution in the past. The RSPM trends in seven cities of India were measured by CPCB consistently for years together. The study conducted in the past decade revealed fluctuating trends in RSPM levels of the major cities [71]. Overall results of studies conducted by CPCB emphasize the necessary of particulate monitoring in the cities and urban regions of the country. In the present study, the annual average of PM_{10} is observed to be 132.17 µg/m^3 and is more than two times above the standard set by NAAQ (60 µg/m^3) for PM_{10}.

The RSPM concentrations measured in this study at Navi Mumbai is comparable with the levels of Delhi and Agra but found to be higher than the levels in metro cities like Chennai and Kolkata [174, 175, 176, 87, 82, 89]. Also, studies conducted in a few urban places of andrapradesh and odisha showed approximately 5 times lower levels of PM_{10} than the concentrations obtained in the present study [177, 87]. But in the recent period except PM_{10} measurement, studies are keenly focused on the monitoring and composition of fine particulate matter in various parts of the country.

As regards, fine particulate matter, ample studies can be marked which has measured $PM_{2.5}$ in different regions of India. Although several air quality studies included measurement of $PM_{2.5}$, routine long term measurements were not noticed. Nevertheless, it is worth mentioning that this research work does provide sufficient $PM_{2.5}$ data along with the speciation information of one of the industrial hotspot area of India. When the $PM_{2.5}$ levels of Navi Mumbai were compared with the other cities of India like Delhi, Agra, Kanpur, Noida and Gurgaon, surprisingly the present values found to be approximately one half times lower [178, 179, 180]. This indicates that the pollution load in the northern region of India is definitely higher than the other parts of the country in terms of $PM_{2.5}$. In overall, fine particulate concentrations are appreciably lower in the study area; however the annual average $PM_{2.5}$ concentration was marginally higher than the NAAQ standard prescribed by CPCB which demands extra attention in the monitoring of fine particulates in the study region.

Levels of PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ measured worldwide and other locations of India are compared in Table 4.4 with the levels of particulate matter obtained in this study.

Table 4.4: Concentrations of PM_{10}, $PM_{10-2.5}$ and $PM_{2.5}$ worldwide and in India

Place	Type of site	PM_{10} (µg/m^3)	$PM_{10-2.5}$ (µg/m^3)	$PM_{2.5}$ (µg/m^3)	Reference
Bangladesh	Hot spot area		140	40.8	[181]
	Residential area		112	37.7	
China	Beijing, city		66	32.5	[182]
Indonesia	Bandhung, city		17.5	43.5	[183]
Indonesia	Industrial area-1		49.3	23	[184]
	Industrial area-2		36.5	26.1	
	Residential area-1		26.7	21	
	Residential area-1		22.4	18.5	
Italy	Florence		120	45-76	[185]
Italy	Milan		6.79	34.5	[186]
Kenya	Nairobi, Industrial		48	30	[187]
Sri Lanka	Colombo, city	53-65	45	22.9	[188]
Taiwan	Seven monitoring stations	31-70		16-45	[189]

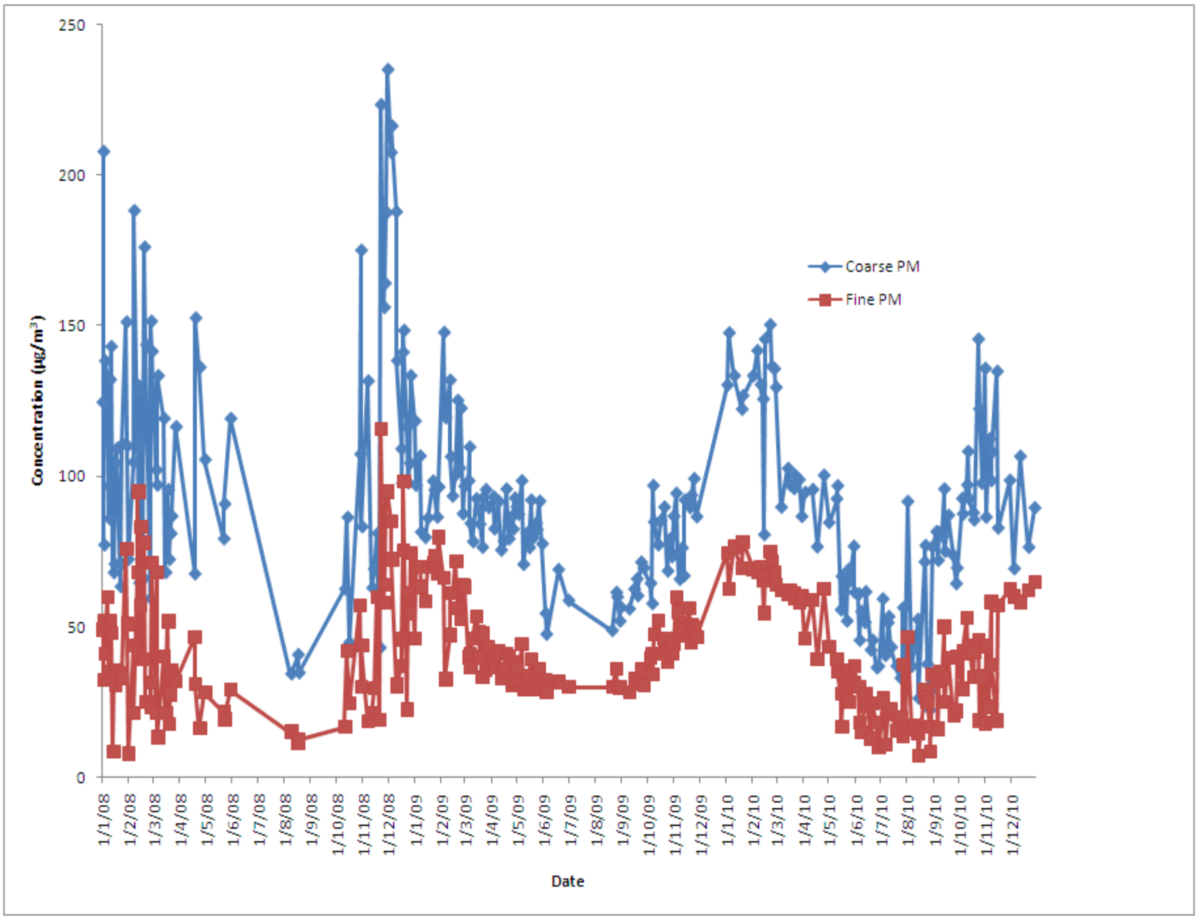
Tanzania	Dar es Salaam	21-130	18-111	8-22	[190]
Pakistan	Lahore, City		141.76	196.22	[191]
Mexico	Tijuana, City	32	13	19	[192]
Turkey	Zonguldak city		24.9	29.6	[193]
Malaysia	Kuala Terengganu city		1.17-28.45	3.82-35.58	[194]
Colorado	Denver, industrial suburb		64.8	79	[195]
Morocco	Kenitra city		110.42	50.73	[196]
Indian studies					
Western India	Mount Abu		10-102	5-43	[197]
North East India	Near Jorhat city, Sub Uraban area			125.75	[198]
Agra	Urban site	154.2		104.9	[179]
	Rural site	148.4		91.1	
North India	Delhi	219		97	[199]
	Lucknow	204.06		99.26	[86]
North India	Delhi			100.25	[200]
Andrapradesh	Anantapur	18.7		17.02	[87]
Chattissgarh	Raipur	270.5	119.6	150.9	[88]
Tamil Nadu	Chennai, Urban area	75-188		42-84	[89]
Present study	Navi Mumbai, Urban area	132.1	89.92	42.25	

The compilation of studies indicates that the coarse and fine particulate matter levels of other Asian-Pacific countries like Bangladesh, China and Indonesia found to be comparable with the Indian mass concentrations. Whereas, remarkably low values were reported for Srilanka and Malaysia in comparison with the present work. Especially, the coarse particulate concentrations were noticed to be very low at Malaysia emphasizing domination of fine particulate matter in the country. On the other hand high annual averages of coarse and fine particulate matter were observed at Pakistan than at Navi Mumbai.

4.1.1 Temporal and seasonal variation of particulate matter

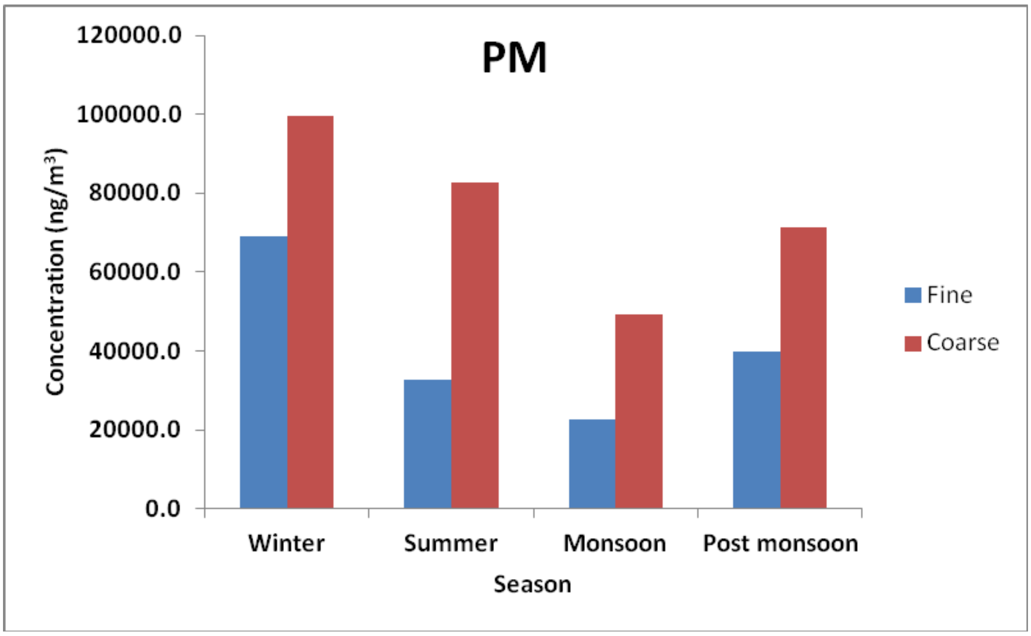
The time series plot of the particulates in both the size fractions is depicted in Figure 4.1.

Figure 4.1: Time series plot of $PM_{2.5-10}$ and $PM_{2.5}$ mass concentrations during the study period



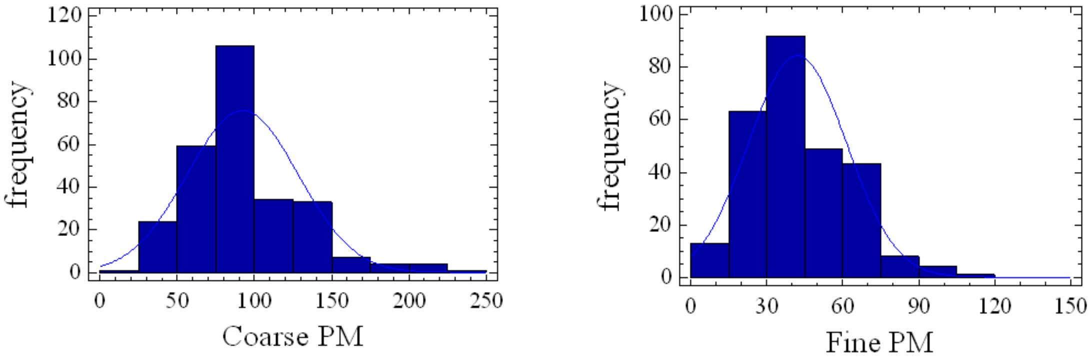
At Mumbai the period between October to February is the season of winter. From March the temperature gradually increases and it becomes very hot just before the monsoon break at the middle of the June and the rainy season lasts up to September. The time series plot clearly indicates that the concentrations of $PM_{2.5-10}$ and $PM_{2.5}$ in the season of winter were about two times higher than the concentrations during summer and monsoon seasons because it is well known that during winter due to lower temperatures the mixing height becomes lower, further the frequent thermal inversions, foggy conditions and stable atmospheric boundary layer during winter causes stagnation of particulates in the lower region and it has been identified and discussed in few of the previous studies conducted by [201, 202]. Sudden drops in the figure can be attributed to the less number of samples collected during the monsoon season. The seasonal variation is depicted clearly in Figure 4.2.

Figure 4.2: Seasonal variation of Particulate matter



As discussed earlier in this chapter, coarse and fine particulate matter displayed highest concentration during winter and lowest during the monsoon season. In the present work, time series of coarse and fine concentrations were statistically examined for the determination of their parent frequency distribution. For examining the frequency of high concentration and to analyse the distribution of pollutant data probability density functions have been used. The obtained $PM_{10-2.5}$ and $PM_{2.5}$ concentrations were fitted to selected probability distributions. The distributions chosen to fit the data were those that are being used in the context of air pollution, namely beta, extreme value, gamma, lognormal and weibull distributions. Following the probability distribution fitting of the entire data set, fitting was analysed by quantile-quantile plots. The performance indicators like Mean Absolute Error (MAE) and Root Mean Square Error (RMSE) were smallest for log normal distribution and the highest value R^2 (0.89) was also obtained, proving log normal probability density function as a better fit for the particulate matter data set. Log normal distribution over plotted on the density histogram of coarse and fine particulates is presented in Figure 4.3 and 4.3b.

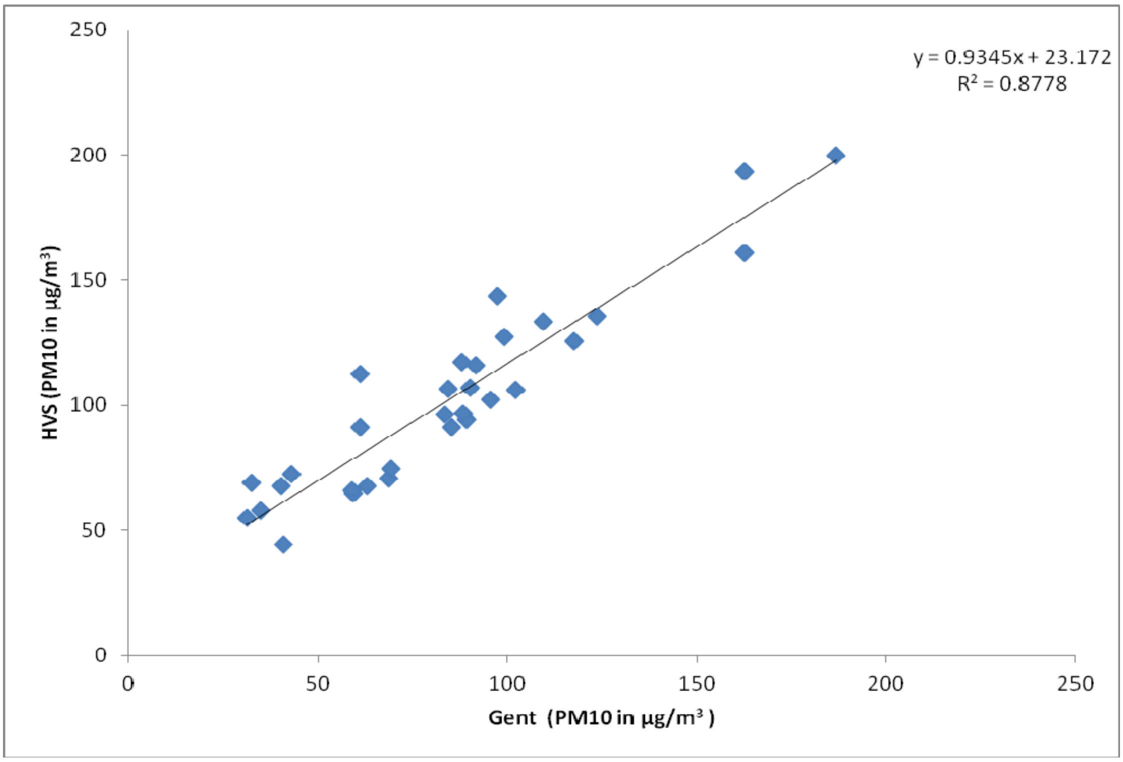
Figure 4.3: Log normal imposed on density histograms of coarse and fine PM concentrations



4.1.2 Quality assurance in PM sampling

As mentioned above, data of respirable suspended particulate matter of size up to 10 µm measured in two size fractions using Gent sampler is used as the PM data for the present study. Hopke et al., (1997) specify in their work that the Gent sampler is not a Federal Reference Method (FRM) sampler and but further the study proves that Gent sampler provides aerodynamically well-defined samples through the inter comparison of Gent sampler with the Philips beta gauge PM_{10} sampler and ASP/IMPROVE $PM_{2.5}$ cut point sampler. Similarly a short term comparison study was conducted in the present study to examine the sample mass collection efficiency of the Gent sampler. Where, PM_{10} samples were collected using a hi volume sampler of cyclone type particle classifier for a period of three months and the gravimetric mass measured was compared with the PM_{10} mass concentrations resulted from the summation of coarse and fine PM collected by Gent sampler. The two samplers were operated side by side from 19th February, 2009 to 29th April, 2009. Figure 4.4 illustrates the comparison of PM_{10} mass measured by both the samplers.

Figure 4.4: Comparison of PM_{10} mass for Gent dichotomous and Hi-volume sampler

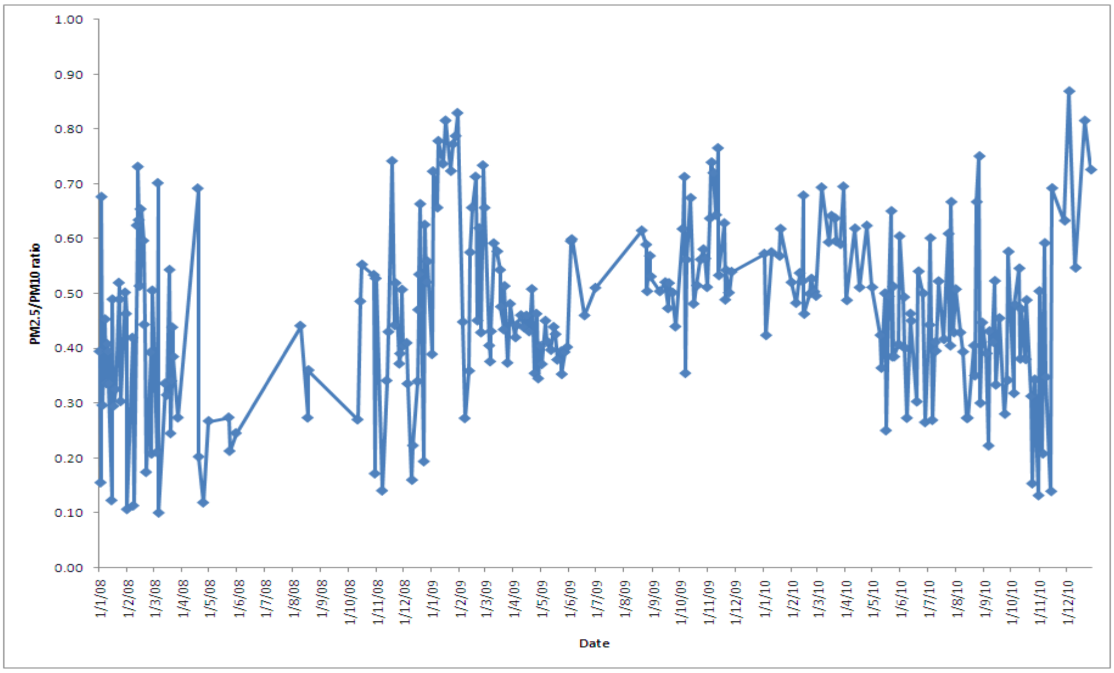


On an average, the two samplers operated at different flow rates (Hi-Volume sampler-1.1m^3/min and Gent sampler-16lpm) returned similar results with slope close to unity. Minimum scattering was observed for both the samplers as reflected by the high correlation coefficient (0.87). But in the case of Hi-volume sampler, the mass concentrations found to be marginally higher for all the samples. This can be attributed to the comparatively high collection efficiency of glass fibre filters used in the hi-volume sampler operated at a flow rate of 1.11m^3/min, especially in the fine particle size range. But the Gent sampler was typically operated at an average flow rate of 16 lpm resulting in an 50% cut point at 2.2µm size particles. Therefore, the comparatively lower concentrations measured by the Gent sampler may be due to the low collection efficiency in the fine particulate size fraction. Hopke et al., [108] have also addressed similar problem with Gent sampler, that it collects less of fine particles mass than the FRM samplers. In the meanwhile, it was proved by them when the average flow rate is maintained and when the overloading of the filters are carefully addressed the Gent sampler provides aerodynamically well-defined samples with comparable mass concentrations. The overall PM_{10} mass concentrations measured in this study using high and low volume samplers exhibited comparable results with the high correlation coefficient.

4.1.3 Site specific $PM_{2.5}$ to PM_{10} ratio

It brings up a significant point that although PM_{10} is a better indicator of atmospheric particulate matter, it may not necessarily represent true picture of more hazardous fine particulates ($PM_{2.5}$). This situation is particularly important in Indian context, where significant portion of PM_{10} may be locally generated wind-blown dust in the coarse fraction ($PM_{10-2.5}$) which may not be as harmful as $PM_{2.5}$. This point that $PM_{2.5}$ may not be represented by PM_{10} levels also becomes clear when one looks at the $PM_{2.5}/PM_{10}$ ratios. Also the mass ratio gives an indication of the relative importance of natural and anthropogenic sources to PM. Generally a low $PM_{2.5}/PM_{10}$ mass ratio indicates a relatively large contribution from natural sources because they tend to dominate in the particle size range 2.5-10 µm. The time series plot of ratio between $PM_{2.5}$ and PM_{10} is presented in Figure 4.5.

Figure 4.5: Time series plot of $PM_{2.5}$/ PM_{10} ratio during the study period



It was observed that there was an insignificant variation in the fine to coarse ratio with respect to the seasons of the year and the average $PM_{2.5}$ to PM_{10} ratio is 0.47 ± 0.15 with the range of 0.21–0.81. The average ratio evaluated is in the lower end of the results reported by [203, 204, 205] and in their studies the range of the ratio obtained were 0.41–0.81 and 0.57–0.71 respectively. Even in Indian cities the ratio is observed to be in the range of 0.4-0.7 [176, 89]. But it is remarkable in the present study that the minimum value (0.21) of the fine to PM_{10} ratio is comparatively lower suggesting the thorough analysis of the time series plot. When the sudden hikes of coarse fraction data was verified with the respective fine PM concentration, it was noticed that not all the corresponding fine fraction mass was high. But in few samples, drastic increase in mass concentrations was observed only in the coarse fraction of the PM indicating the contribution of some fugitive source in that particular particle size. The average ratio decreased from 0.49 on normal days to 0.22 in those specific days. However, the entire data set revealed comparatively low $PM_{2.5}$ to PM_{10} ratio illustrating the domination of fine particles over the coarse particles is marginal or insignificant. The $PM_{2.5}/PM_{10}$ ratio was compared with those in different urban locations across Europe, Asia and India in Table 4.5.

Table 4.5: Comparative levels of $PM_{2.5}/PM_{10}$ ratio

Site	Type of site	$PM_{2.5}/PM_{10}$	Reference
Barcelona, Spain	Urban	0.64	[206]
Finokalia, Greece	Coastal	0.63	[207]
Izmir, Turkey	Urban	0.80	[208]
Cairo, Egypt	Urban	0.43	[209]
Beirut, Lebanan	Urban	0.37	[210]
Hong Kong, China	Urban	0.78	[211]
Indian sites			
Hyderabad	Urban	0.37	[159]
Agra	Residential area	0.41-0.71	[176]
Kanpur	Residential area	0.45-0.74	[178]
Chennai	Residential and commercial area	0.44-0.73	[89]
Navi Mumbai	Urban, Residential area	0.47	Present study

The average ratio of Vashi is 0.47 and is significantly lower than most of the urban locations of other countries as mentioned above. Yet the value obtained in this study is in the same range as of the ratios of different urban residential sites of India. Therefore the results clearly indicate significant contribution of coarse particles in the total PM_{10} concentration. Most likely this higher levels of coarse particles could be due to windblown dust and unpaved roads.

The severity of particulate pollution and seasonal variations motivated detailed characterization of PM at Vashi, Navi Mumbai. Of particular interest, in the present study black carbon and elemental characterization were carried out in detail for the entire three year sampling period. There are great needs for better characterization of seasonal and long term variations in elemental concentrations at the study site as well as a better understanding of the governing effects due to the changes in urban development. Therefore in the following sections the seasonal variations in the concentrations levels of elements are presented and discussed in relation to natural and anthropogenic emissions taking place in the proximity of the sampling site.

4.2 Concentration level of BC in $PM_{2.5}$

Black carbon concentration was meausred in the fine fraction air filters using EEL 43D smoke stain reflectometer to account the carbanaceous aerosols produced by the incomplete combustion of fossil fuel. The statistical summary of BC concentration levels over the three year study period is exhibited in Table 4.6.

Table 4.6: Statistical summary of BC during the study period

Parameter	BC (µg/m^3) **2008**	BC (µg/m^3) **2009**	BC (µg/m^3) **2010**
Mean	8.93	8.69	4.76
Median	7.74	8.11	4.62
Standard deviation	5.19	3.91	2.15
Maximum	25.74	18.31	9.65
Minimum	0.36	1.4	0.64
No. of samples	80	91	101

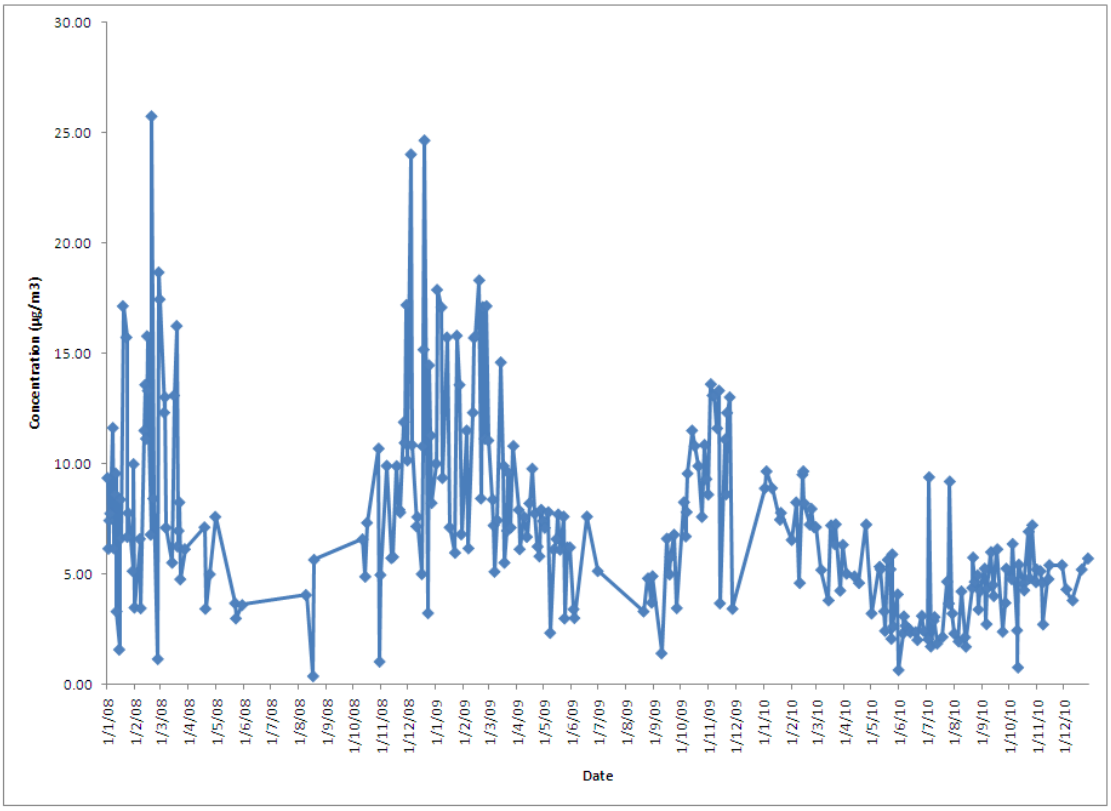
Slight variation in the annual average of BC was observed from 2008 to 2010. However, evidently a marginally decreasing trend can be recognized from the results which may be attributed to the slow progress in the establishment of natural gas usage in alternate to the utility coal combustion industries situated in the MIDC industrial belt. The average BC concentration in $PM_{2.5}$ in comparison with other cities of India and globe is listed in Table 4.7.

Table 4.7: BC concentration in $PM_{2.5}$ in comparison with the cities of India and world

Site	BC ($\mu g/m^3$)	Reference
Shangai, China	3.9	[212]
Beijing, China	6.3	[213]
Toulon, France	0.64	[214]
Kathmandu, Nepal	8.6	[215]
Pune, India	3.9-6.79	[216]
Nagpur, India	1.5-4.5	[217]
Hyderabad, India	1-12.5	[218]
Ahamedabad, India	0.2-10	[219]
Sinhagad, India	1.5	[220]
Mumbai, India	7.5-17.5	[221]
Navi Mumbai, India	7.31	Present study

Results of present study demonstrated that three year average concentration of BC in Navi Mumbai was 7.31$\mu g/m^3$ and the measured BC concentration was observed to be higher than few cities such as Pune, Nagpur, Hyderabad and Sinhagad [216, 217, 218, 220] of India. But surprisingly, the present level of BC in Navi Mumbai is matching with the range of BC concentrations mentioned in the earlier study of Mumbai [221]. The annual average of BC concentrations in the present work is slightly higher than but comparable with the value reported for Beijing by [213], and is marginally lower than the levels mentioned by [215] for Nepal. But obviously the BC concentrations are many fold higher than Toulon in France [214]. To understand the pattern of daily variations of BC concentrations time series plot was constructed and was presented as Figure 4.6.

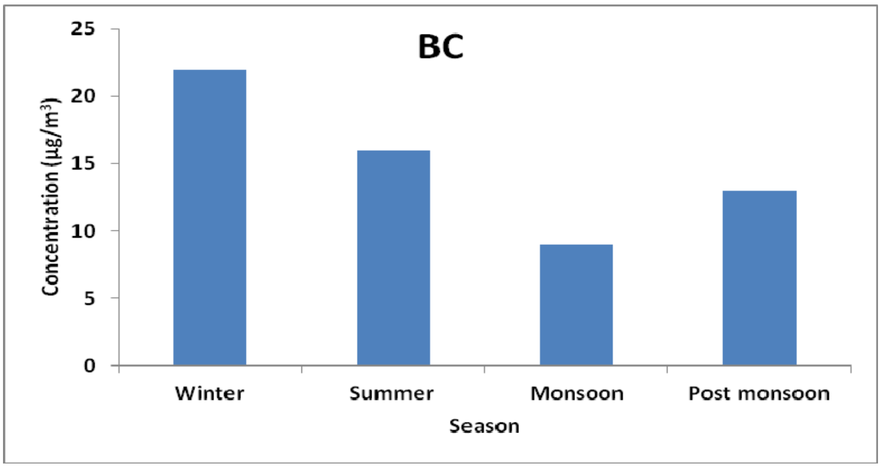
Figure 4.6: Time series plot of BC during the study period



From the results, it can be seen that the highest concentration during the study period was in February, 2008 (25.7µg/m^3). Lowest concentrations were observed during monsoon and summer seasons. The overall BC concentrations during the entire study period showed strong seasonal variability with a decreasing trend in the levels from 2008 to 2010. But the local anthropogenic activities are not believed to contribute so much in the seasonal cycle of BC mass concentration, since the urban emissions are continuous throughout the year. Particularly in India, diesel and petrol are the major fossil fuels used for road transportation. Especially, diesel vehicles are known to produce much more black carbon particles than the vehicles which run on gasoline. Since the study site is located nearby Pune-Mumbai high way, mixture of large number of heavy duty and light duty vehicles ply on the roads and contribute to the BC concentration. Similar variation of daily BC mass concentration as shown in Figure 4.6 has been found over other urban locations in India

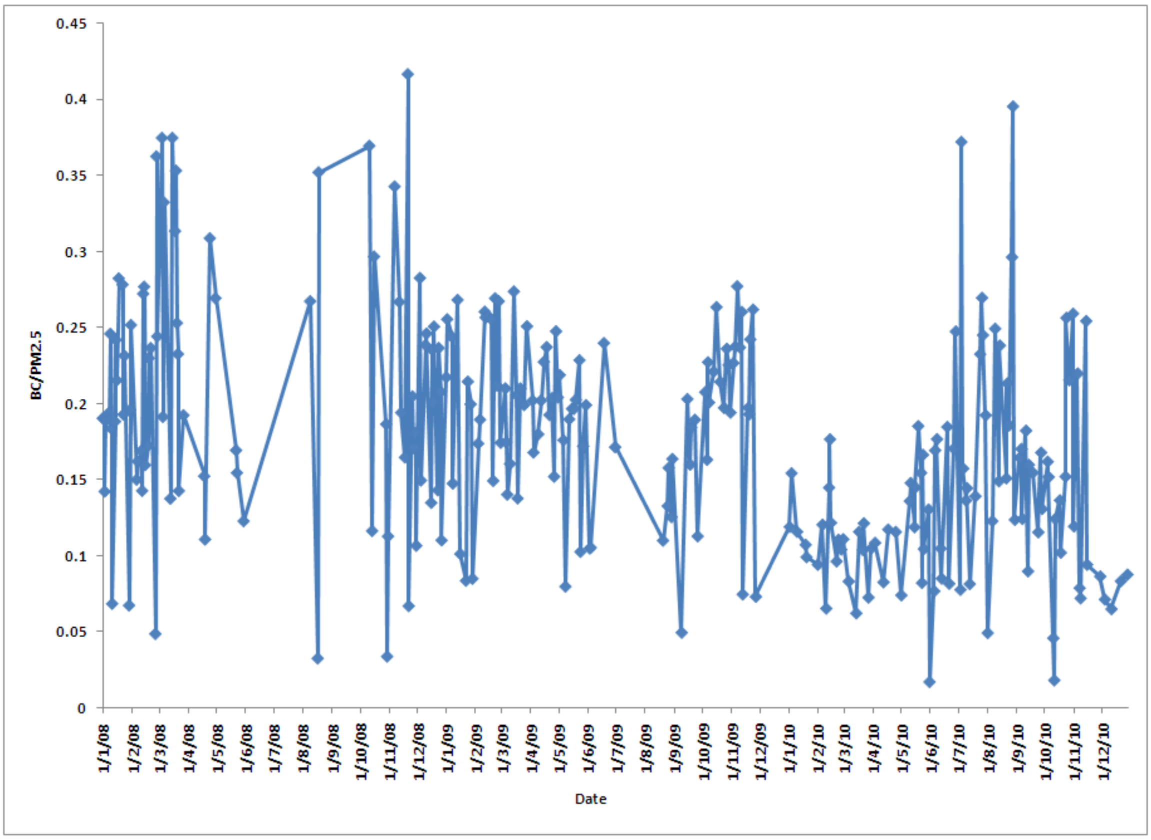
[218, 51]. The average BC concentrations during different seasons were depicted in Figure 4.7.

Figure 4.7: Seasonal variation of BC in fine fraction



The results apparently indicate maximum BC concentration during winter followed by summer and post monsoon seasons. The mean values of BC during winter, summer, monsoon and post monsoon seasons were 22, 16, 9 and 13 µg/m^3 respectively. As the life time of BC particles is 7–10 days and they are present in the fine fraction of the air PM, BC particles have the possibility of migrating long distances in the atmosphere. Therefore, there is a strong probability for a part of BC mass to be contributed from distant sources along with the local sources during winter. Notably, higher BC levels are reported at central and northern region of India specifically during winter due to biomass burning, low mixing heights and a stable atmospheric boundary layer. Also a study conducted by [222] confirms the long range transport of BC from central India to Mumbai during winter, based on the backward trajectory studies. The high seasonal variations highlights the importance of wet scavenging of PM particularly in monsoon season in Mumbai where high precipitation occurs. Another important parameter which explains the level of BC present in fine particulate mass is BC to $PM_{2.5}$ ratio. The ratio illustrates the significance of mass contributed by BC to fine fraction and its variability depicts the trend of BC emissions. Figure 4.8 shows the time series plot of the daily BC/$PM_{2.5}$ mass ratios.

Figure 4.8: Time series plot of BC/$PM_{2.5}$ ratio



The maxima is found to be around 0.41 and the minima was 0.017 with the average ratio of 0.17. BC/$PM_{2.5}$ ratio throughout the study is following similar trend as that of fine particles and BC with a relatively higher contribution to $PM_{2.5}$ during the winter season . Since black carbon is a tracer of primary anthropogenic emissions and variability of BC/$PM_{2.5}$ reflects changes in local emission source strengths atmospheric mixing characteristics. The BC concentration in fine particulate mass in this study is comparable with the ratio obtained by [223]for Bangladesh.

4.3 Elemental characterization using Nuclear Analytical Techniques

Three main nuclear analytical techniques (INAA, EDXRF and PIXE) were chosen and employed for the elemental analysis of air filter samples collected during the entire study period. The combination of EDXRF-INAA or PIXE-INAA used as complementary to each other and a total of 24 elements were determined in all the coarse and fine filter samples. Some elements that cannot easily be analyzed by INAA such as Si and Pb are well analyzed by other two techniques. On the contrary, other element such as Na and K were better analyzed by INAA than PIXE and EDXRF. Elements like Co, Sb, Sc and Se were also well analyzed by INAA.

In INAA and PIXE, the detection limits highly depend on the presence of other elements in the samples because of their impact on the Compton γ-ray background in INAA or on spectral interferences mainly in PIXE. As a consequence, the detection limits vary from one sample to other sample [224]. In the case of MDL of an XRF system is typically in the range of nanograms to micro grams. The actual MDL attained depends on characteristics of the XRF source which determines the energy contribution of the incident x-rays, the detector, which determines the energy resolution of the fluorescence X rays peak along with the detection efficiency; the target, since the thickness and matrix determine the transmission and the scattered radiation; and the measurement time. In the case of air filter analysis monochromatic x-ray beams were produced using secondary targets, high resolution Si(Li) detector was employed for the detection and including the measurement time, voltage, tube current and other parameters were optimized to improve the MDL and sensitivity. The details of analysis by all the three techniques were furnished in chapter-2. The detection limits of the measured elements using the three techniques are presented in Table 4.8.

Table 4.8: Detection limits in ng/m^3 for the elements measured by INAA, EDXRF and PIXE

Element	**INAA** (ng/m^3)	**EDXRF** (ng/m^3)	**PIXE** (ng/m^3)
Na	0.25	28.21	30.56
Mg		27.34	25.62
Al		21.17	20.41
Si		20.20	13.58
P		27.84	14.73
S		48.43	12.37
Cl		39.41	9.04
K	4.00	9.49	8.39
Ca		27.40	8.31
Sc	0.10		
Ti		9.69	7.38
V		10.83	4.87
Cr	3.10	10.30	6.62
Mn		11.71	6.08
Fe	2.20	7.56	4.52
Co	0.50		
Ni		4.83	3.86
Cu		9.35	5.82
Zn	0.70	7.49	6.34
As	0.30	8.11	8.32
Se	7.60	10.31	9.12
Br	0.20	18.63	14.74
Sb	0.80		21.45
Pb		6.15	5.49

From the results it was observed that MDL of PIXE and EDXRF techniques observed to be higher than INAA. But, PIXE MDL's were found to be better or comparable with those of XRF. MDL of Low-Z elements like Na, Mg, Al and Si found to be high in both XRF and PIXE techniques. However, these elements present in large concentrations in the atmospheric aerosol and therefore higher MDLs do not create problems in their detection. Also from Na to Ni a decreasing trend of MDL was observed in the case of PIXE, while beyond Ni (Z=28) PIXE MDL's increased and became almost equivalent to XRF values. Basically to evaluate the MDLs background values become essential. In PIXE spectra the background is originated by compton interactions in the detector and by secondary Bremsstrahlung. Whereas, in XRF spectra the background is a continuum due to the Bremsstrahlung radiation of the exciting beam, therefore the background evaluation and the difference in the photon/proton ionization cross section of different elements can be attributed as the major reasons for the highly varying MDL's of XRF and PIXE [225].

As an overall view, INAA provided higher sensitivity and many fold lower MDL for the measured elements in comparison with the other two techniques. At the same time, INAA exhibited comparably longer measurement time and lower sample through put. While, EDXRF and PIXE have proved to be versatile nondestructive methods for the rapid, simultaneous determination of several trace elements. However, limitations of sensitivity and spectral interferences exist for some trace elements in these two techniques.

4.3.1 Quality Control

The NIST standard reference material SRM 1648 airborne particulate matter was analyzed using INAA, while NIST SRM 2783 particulate matter deposited on polycarbonate filter was analyzed using PIXE and EDXRF for the purpose of method validation to evaluate the precision and accuracy of the analytical techniques. The result of SRM 1648 and SRM 2783analyses were summarized in Table 4.9. These analysis results had a good agreement with the value quoted in the NIST certificate. The percentage of error between the measured and the certified value found to be less than or equal to 2% for Na, K, Cr, Fe, Co, Zn and Br when analysed using INAA. While, other elements presented an error between 4-8 %. On the other hand 2-9 % error was observed for different elements when the NIST SRM 2783 is measured using PIXE. Similarly EDXRF also exhibited error in the range of 4-12 %. Where Na, Ni and As demonstrated more than 10% error. Though significant error variation was observed among the three techniques, exceptionally good precision was noticed for all the techniques. The precision was within 5% for all the three analytical techniques. The details of the elemental concentrations of the samples collected for this study are presented and discussed in the subsequent section of the chapter.

Table 4.9: Analytical results for major and trace elements in urban particulate matter standard reference materials

Element	Certified value[a] (NIST1648) (ug/gm)	Measured Value[b] INAA (µg/gm)	Certified value[a] (NIST2783) (ng)	Measured Value[b] EDXRF (ng)	Measured Value[b] PIXE (ng)
Na	4240 (60)	4198 (72)	1860 (100)	1614.4 (132)	1677.7 (82)
Mg	8130 (120)		8620 (520)	7673 (421)	8092 (499)
Al	34300 (1300)		23210 (530)	21320 (572)	21848 (531)
Si	128000 (4000)		58600 (1600)	53721 (1750)	55825 (1825)
P	8000 (2800)		NR		
S	55100 (3600)		1050 (260)	995 (197)	1011 (219)
Cl	4543 (47)				
K	10560 (490)	10433 (485)	5280 (520)	4898 (468)	5642 (484)
Ca	58400 (1900)		13200 (1700)	12554 (1589)	13673 (1409)
Ti	4021 (86)		1490 (240)	1569 (257)	1410 (235)
V	127 (11)		48.5 (6)	45.1 (4)	51 (11)
Cr	402 (13)	392 (18)	135 (25)	126 (21)	129 (28)
Mn	790 (44)		320 (12)	297 (22)	299 (16)
Fe	39200 (2100)	38572 (1853)	26500 (1600)	24849 (1763)	27931 (999)
Co	17.93 (0.68)	18.32 (1.3)			
Ni	81.1 (6.8)		68 (12)	58.7 (17)	74 (12)
Cu	610 (70)		404 (42)	371.2 (49)	413 (31)
Zn	4800 (270)	4689 (320)	1790 (130)	1652.91 (115)	1698 (23)
Br	502 (10)	481 (14)			
Pb	6550 (330)		317 (54)	287 (43)	326 (34)
Sc					
As	115.5 (3.9)	108.2 (5.3)	11.8 (1.2)	10.32 (2.3)	11.2 (1.5)
Se	28.4 (1.1)	26.1 (3.2)			
Sb	45.4 (1.4)	42.8 (2.7)			

[a]- Certified reference value with the uncertainty in the parenthesis, [b] -Measured value with the respective standard deviation in the parenthesis

4.3.2 Comparison of Nuclear Analytical Techniques

An attempt is also made to compare the concentration of metals derived from each technique and the results are presented in Table 4.10 and Table 4.11 for coarse and fine fraction respectively. Concentrations of elements which are well above the Minimum Detection Limit and elements that can be analyzed commonly by any two techniques were selected for the comparison between the techniques. When XRF and PIXE measurement of elements were compared, the results found to be in good agreement with each other. The correlation coefficients obtained between the techniques for the selected elements found to be higher than 0.8 in both the size fractions. Differences between the concentrations obtained were found to be within 10%. But, comparatively higher difference was observed in the case of Si measurement. Si concentrations characterized by PIXE technique found to noticeably higher than EDXRF. Similar comparisons were also performed between INAA & EDXRF and INAA & PIXE. Results revealed good agreement among the techniques. Also it was found that INAA is more sensitive and reliable than PIXE & EDXRF for certain elements like Na, Fe, Br etc. The study also explained that INAA is a prospective and sensitive method for trace elemental analysis. Whereas, PIXE & EDXRF proved to be two promising tools to complement INAA in the determination of Pb, S and Si.

Table 4.10: Comparison of elemental concentrations measured by three nuclear analytical techniques in coarse PM

Element	INAA	EDXRF	PIXE
Na	921±345	837±543	905±412
Mg		993±681	1088±436
Al		3341±1436	3542±879
Si		5807±2147	6685±1857
P		126±92	138±84
S		944±453	1003±421
Cl		2169±1134	2286±982
K	869±425	771±443	831±324
Ca		3442±1097	3733±1131
Sc	15.21±5.83		
Ti		349±129	361±97
V		7.26±5.23	8.11±4.73
Cr	43±12.32	38±15.34	41±12.45
Mn		75±31	79±19
Fe	2869±1264	2596±975	2758±786
Co	17.86±9.11		
Ni		8.57±6.11	9.28±4.32
Cu		46±18	48±13
Zn	291±143	262±99	276±62
As	12.62±7.85	11.21±6.34	12.36±7.31
Se	5.42±3.21		
Br	27±12.73		
Sb	32±17.12		
Pb		61.26±24.31	67.52±18

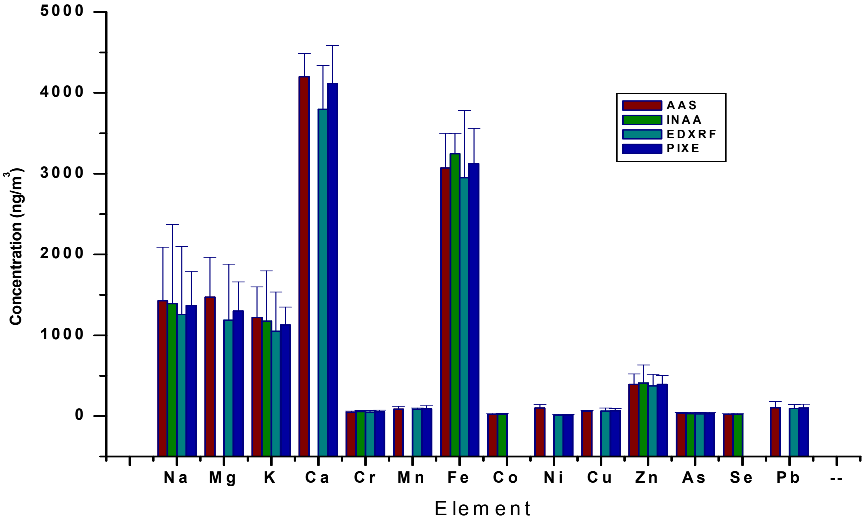
Table 4.11: Comparison of elemental concentrations measured by three nuclear analytical techniques in fine PM

Element	INAA	EDXRF	PIXE
Na	469±287	420±311	460±196
Mg		194±87	209±79
Al		442±196	467±139
Si		754±349	938±297
P		36±24	38±16
S		1475±651	1600±526
Cl		293±114	312±87
K	305±147	278±127	295±93
Ca		355±97	381±71
Sc	5.31±1.94		
Ti		45±17	47±15
V		17.29±14	18.57±9
Cr	10.81±4.63	9.71±5.11	10.28±4.7
Mn		10.51±4.36	10.85±3.94
Fe	375±214	350±129	367±103
Co	6.72±4.11		
Ni		3.92±1.7	4.23±1.6
Cu		14.84±5.12	15.71±3.89
Zn	119±89	111±47	115±39
As	16.56±9.45	14.94±8.31	16.11±6.23
Se	17.25±8.52		
Br	19.46±11.34		
Sb	27±14.65		
Pb		29.32±17.43	37.51±14.67

4.3.3 Comparison of Nuclear analytical techniques with AAS

To verify the analytical performance of the nuclear analytical techniques (INAA, EDXRF and PIXE) employed in this study, other than the analysis of standard reference material, the concentration of elements measured were also compared with one of the most widely utilized destructive analytical technique Atomic Absorption Spectrometry (AAS). For this part of the study, glass fibre filter samples used for the collection of PM_{10} using hi volume sampler were acid digested and analysed for elements like Na, Mg, K, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se and Pb using AAS. Among the 14 elements, As and Se were determined following the highly sensitive hydride generation technique of AAS. Later, the results were compared with the metal concentrations present in PM_{10} collected by Gent sampler. As mentioned earlier, the hi volume and gent samplers were operated in parallel for three months and the samples were then used for comparison. In the case of Gent sampler, average concentrations obtained for coarse and fine PM were summed up, to get the PM_{10} concentrations. Figure 4.9 presents the comparison of concentration of elements present in PM_{10} determined by three NAT's and AAS .

Figure 4.9: Comparison of elements in PM_{10} determined by nuclear analytical techniques and AAS



Comparison of all the four techniques showed fairly high concentrations of most of the elements determined by AAS. It has already been noticed that PM mass collected by hi volume sampler was itself higher than the mass collected by Gent sampler. Which could be one of the reasons attributing to the higher concentrations attained by AAS.

From the results, it can be observed that there is a good agreement between the measurements of all the three nuclear analytical techniques with the results of AAS. Concentrations of Na, Mg, K and Ca was found to be reasonably high with a higher error values. Still the errors of Na and K found to be marginally lesser than the one observed in INAA technique. The hydride generation technique used in AAS in the case of As and Se demonstrated challenging sensitivity when compared with other techniques. But Se results of AAS showed a difference of almost 15% in comparison with INAA values. Among the 14 elements measured by AAS, Ni was observed to be highest in AAS (99 $\mu g/m^3$), while PIXE and XRF determined concentrations within 15$\mu g/m^3$. Since the Nickel concentration is very less in the PM samples, analytical error found to be high in all methods, especially in AAS (error ± 41 $\mu g/m^3$). When AAS measurements were compared with INAA, error percentage range from 2-20 % with the maximum error for Co. In comparison with EDXRF the range of measurement error was 2-23 %, with a lowest for Cu and highest for Mg. When compared with PIXE data, a minimum error of 1.7 % was observed for Fe & Mn and a maximum error was determined for Mg as 13%. In overall, higher concentrations and error percentages noticed in AAS measurements would have raised due to the different sampling techniques applied for the PM collection as well as from the analytical uncertainties. But the results of most of the elements are very much comparable among all the four techniques proving the capability of each technique in the trace element analysis.

4.4 Trace metal concentrations in PM

The average concentrations of the measured elements in the coarse and fine fractions for the samples of 2008, 2009 and 2010 are presented in Tables 4.12, 4.13 and 4.14 respectively. Specifically, average and standard deviations of the elements were included in the table to facilitate a comparison with the values reported in literature for similar sites.

Table 4.12: Concentration of elements in coarse and fine particulate matter during 2008

Element	**Coarse (ng/m^3) (n=80)**		**Fine (ng/m^3) (n=80)**	
	Average	**S.D.**	**Average**	**S.D.**
Na	1393	965	487	320
Mg	992	749	223	211
Al	2504	2078	433	405
Si	6229	4801	871	683
P	336	240	92	82
S	1504	1091	1615	1212
Cl	2343	1791	269	203
K	672	506	231	151
Ca	3601	2549	315	248
Sc	8.54	7.59	2.46	2.13
Ti	268	224	23	19
V	7.84	5.17	13	10.98
Cr	43	22	7.68	5.70
Mn	64	55	10.46	9.60
Fe	2917	2357	316	220
Co	11.8	9.84	3.18	2.07
Ni	6.54	5.81	6.69	5.25
Cu	30	23	6.67	4.88
Zn	137	215	61	45
As	8.54	6.59	13	9.44
Se	4.74	2.33	10.39	8.38
Br	21	16	13	9.49
Sb	29	21	25	22
Pb	85	78	36	33

Table 4.13: Concentration of elements in coarse and fine particulate matter during 2009

Element	**Coarse (ng/m^3) (n=91)**		**Fine (ng/m^3) (n=91)**	
	Average	**S.D.**	**Average**	**S.D.**
Na	1199	1011	305	
Mg	778	469	162	141
Al	1944	1155	345	224
Si	4788	3901	736	522
P	248	184	67	43
S	1187	891	1208	854
Cl	1982	1250	191	122
K	525	384	199	165
Ca	2954	2088	240	183
Sc	17	11	2.71	1.85
Ti	197	175	18	14
V	5.46	3.84	9.12	4.86
Cr	32	24	5.94	4.13
Mn	53	47	6.21	5.11
Fe	2605	1830	250	112
Co	8.62	5.24	2.09	0.96
Ni	4.92	2.31	3.12	2.13
Cu	23	18	4.31	1.86
Zn	123	114	48	23
As	3.73	2.12	9.64	4.87
Se	2.93	2.12	7.71	5.41
Br	16	13	8.96	3.93
Sb	24	20	19.23	8.52
Pb	66	59	25.61	10.43

Table 4.14: Concentration of elements in coarse and fine particulate matter during 2010

Element	**Coarse (ng/m^3) (n=101)**		**Fine (ng/m^3) (n=101)**	
	Average	**S.D.**	**Average**	**S.D.**
Na	1454	1098	550	226
Mg	745	359	167	91
Al	1619	996	293	198
Si	4265	2768	665	476
P	238	134	66	44
S	1097	584	1196	513
Cl	2663	1747	255	170
K	470	291	169	94
Ca	2661	1603	236	159
Sc	19	14	2.34	1.91
Ti	167	115	17	12
V	4.92	3.11	6.99	4.62
Cr	11.15	9.27	4.54	3.22
Mn	41	28	6.07	4.56
Fe	1898	1257	241	148
Co	9.93	7.12	2.18	1.74
Ni	6.72	5.91	4.71	3.28
Cu	18	14	4.67	1.92
Zn	112	68	41	26
As	6.26	5.92	7.17	2.83
Se	4.09	2.81	9.51	5.46
Br	17	11	9.46	6.37
Sb	28	22	30	25
Pb	54	38	20	19

Results showed marginal difference in each year's concentration and any remarkable trend was not observed in the three year data. Meanwhile, slightly decreased concentration levels were observed from 2008-2010 similar to the PM level in the site. But with this minimal changes in the levels of PM and elemental concentrations it becomes difficult to conclude that there is a decreasing trend in the air particulate levels in the study site. Definitely consistent monitoring and characterisation of PM in the site for a longer period will provide the complete scenario of the trend of pollution in that area. Results of elemental characterization revealed that in the coarse fraction metals ranged from 2.93-6229.58 ng/m^3. The lowest concentration was measured for Selenium and the highest concentration was for Silicon. In the case of fine fraction lowest concentration measured corresponded to Scandium, whereas the highest concentration was measured for Silicon. The average concentrations of elements in fine PM varied from 2.09-1615 ng/m^3. The frequency distribution of the elements were plotted and tested using the performance indicators like MAE and RMSE to verify the goodness of fit. Most of the elements were log-normally distributed within a 95% confidence interval, which indicated that the median or the geometrical mean is a better indicator of the data population than the average of all measured elements. Therefore, to comprehend and compare the levels of trace metals in both the size fractions self-explanatory Box-Whisker diagrams were plotted to determine 25-75th percentiles, 5-95th percentiles, maximum, minimum, mean and median concentrations. In the Box-Whisker plot, the box represents the distribution of 25-75 percentile values and the symbol □ represents the mean value. The values beyond 75 percentile and 25 percentile are given as whiskers. Maximum and minimum values are represented by × symbol. Figure 4.10 and 4.11 shows the variation of each component in the coarse and fine fraction particles respectively. In the coarse fraction higher values of elements with uniform distribution was observed in Na, Mg, Al, Si, Cl, S, K, Ca and Cr. Whereas, maximum fluctuation was noticed in As, Se, Pb and Ni components. On the other hand, fine fraction showed higher fluctuations for Co, Ni, Cu, Zn, Br, Pb, As and Se. Also apparent fluctuations were observed in Na, Mg, Al, Si and Cl.

Figure 4.10: Box whisker plot explaining coarse PM elemental concentration

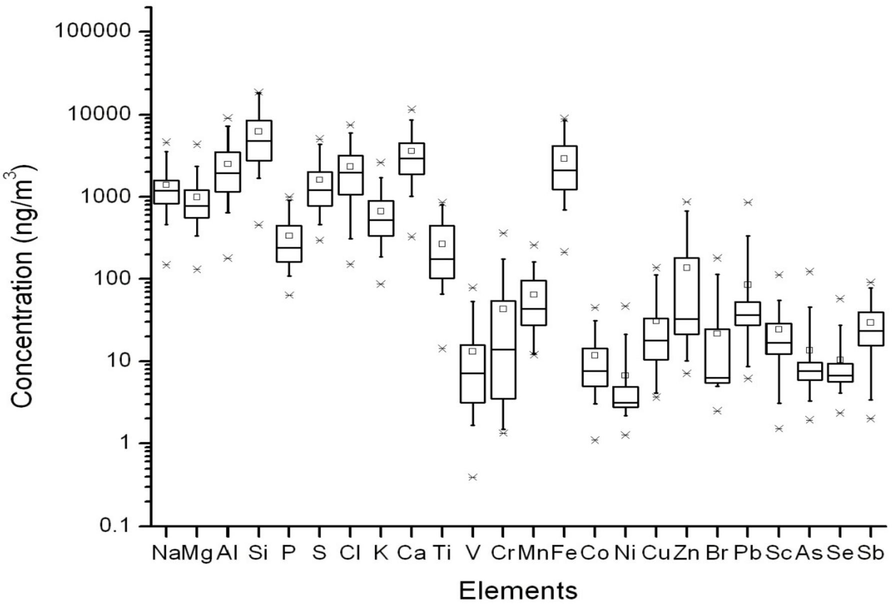
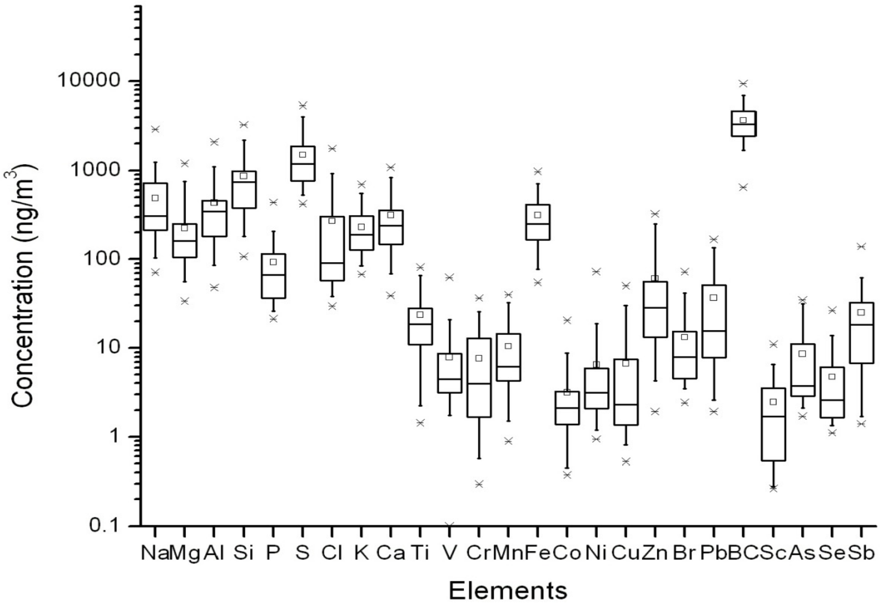


Figure 4.11: Box whisker plot explaining Fine PM elemental concentration



The level of pollution in the study site can be assessed by either comparing the measured concentrations of elements in this area with the regulatory standards or as an alternative approach would be compared with those of well documented polluted or clean sites around the world. As there were no stipulated standards for most of the metals, second approach was adopted in the present study, and the concentrations were compared with the information compiled from literature. The heavy metals and crustal derived metal concentrations found in the present study were compared with the coarse and fine elemental concentrations of studies conducted in few cities of Unites States [195]. It was found that the average elemental concentrations in both the size fractions are 10-15 times higher in the present study irrespective of its nature of origin. Whereas, concentrations of Cr and Cu in both the size fractions observed to be 5-10 times lower in comparison with the levels found in Morocco as studied by [196]. Appreciably, other toxic elements like Ni, Pb and Zn were about 10-100 times lesser in Navi Mumbai region than at Morocco. Similarly, levels of all the elements in the present work including naturally and anthropogenically derived are observed to be approximately 2 times higher than the elemental concentrations measured in coarse and fine fractions of Bangkok, Thailand [226]. But when compared with the levels of neighbouring country Bangladesh, in Navi Mumbai soil derived and marine derived elements like Na, Mg, Al, Cl and Fe were found to be two times higher in the coarser fraction [227]. But, concentrations of Zn, Br and Pb in the coarser particles found to be one half of the values observed by Bilkis et al., at Bangladesh. As far as the fine fraction elemental levels are concerned 10 times lower values of Cu, Zn and Pb were observed in the present study. Whereas, sulphur was found to be comparable in both the fractions at Bangladesh and Navi Mumbai. It was found that the levels of all the metals were 5–10 times higher than the levels in European countries like Spain and Norway.

4.5 Concentration of Inorganic ions

While identifying the various PM sources, among the various aerosol types secondary inorganic aerosols, carbonaceous matter, sea salt and mineral dust contributes in large scales to the PM mass. Especially, sulphate, nitrate and ammonium are considered as the major components in coarse and fine particulate matter. Besides the above mentioned ions other water soluble inorganic ions are also present in atmospheric aerosols. They include Cl^-, Na^+, Ca^{2+}, K^+ and Mg^{2+} and a lesser extent Br^-, NO_2^-, and phosphate. Although these ions are often only responsible for minor fraction of the PM mass, these inorganic species are of importance for aerosol mass closure calculation. Therefore, in the present study two collocated Gent samplers were operated for a short time period especially to facilitate the reconstruction study and the filter samples collected from one of them was utilized for the ionic measurements. For this purpose, nine major water soluble inorganic components (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were measured using Ion Chromatograph system (Metrohm make) and were presented in Table 4.15.

Table 4.15: Inorganic ion concentration in coarse and fine particulate matter

Ions	**Coarse (µg/m³) (n = 50)**		**Fine (µg/m³) (n = 50)**	
	Average	**S.D.**	**Average**	**S.D.**
Anions				
F^-	N.D.	N.D.	N.D.	N.D.
Cl^-	1.81	0.62	0.98	0.28
NO_2^-	1.14	0.53	0.89	0.16
NO_3^-	6.69	0.88	5.73	0.75
PO_4^{3-}	N.D.	N.D.	N.D.	N.D.
SO_4^{2-}	11.06	0.93	7.89	0.85
Cations				
Na^+	0.89	0.28	0.52	0.09
NH_4^+	5.13	1.24	4.76	1.58
K^+	0.34	0.16	0.19	0.09
Mg^{2+}	0.76	0.21	0.17	0.08
Ca^{2+}	2.72	0.79	0.31	0.13

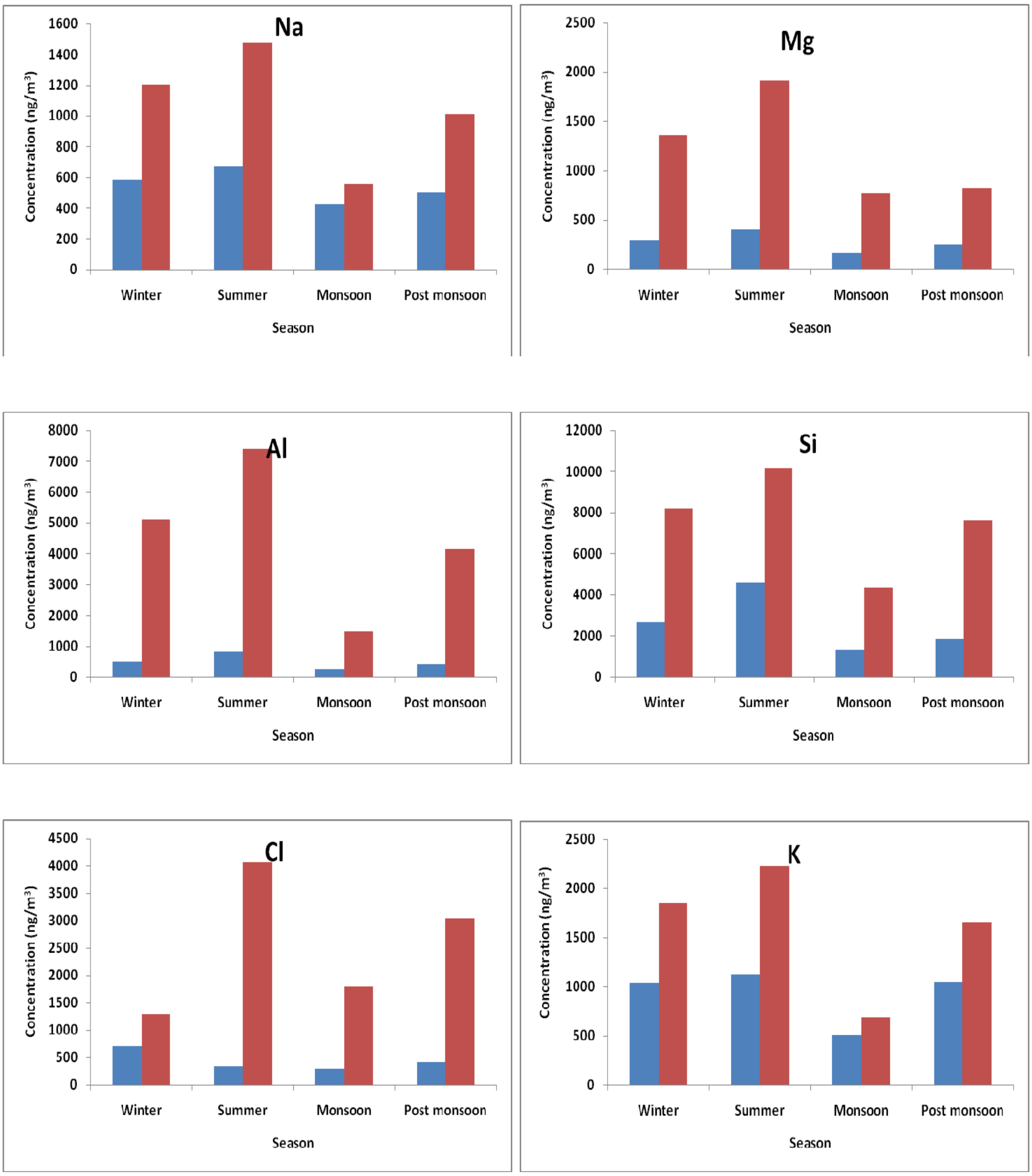
Among the inorganic species sulphate and nitrate exhibited very high concentration, next to them ammonium had the highest concentration, demonstrating the strong contribution of secondary aerosols from their gaseous precursors emitted from the coal/oil based industries and from the vehicular emissions. All the other ions which are suspected to be originated from natural sources were also contributed considerably to the PM load indicating their strong influence from sea salt and resuspended soil in total mass. Compared with other metropolitan areas located in different parts of the world, the $PM_{2.5-10}$ ionic concentration observed at Navi Mumbai was higher than other cities like Beirut, Taiwan, Yamaguchi, Chirstchurch and Auckland but was found to be comparable with the values of Nanjing city of china. But, on the other hand, concentration levels of anions and cations of fine PM were found to be lower than levels the of other cities [228].

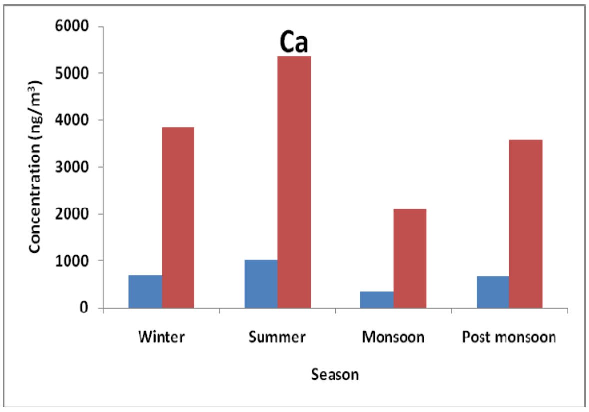
4.6 Temporal and seasonal variation of Trace metals

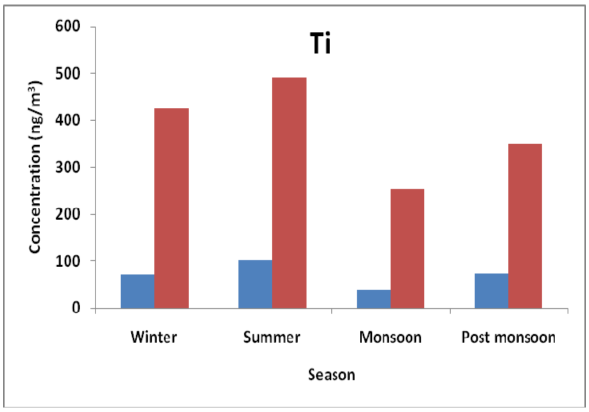
The temporal pattern of coarse and fine PM at the study site was investigated and the seasonal variations were depicted in Figure 4.12 to Figure 4.14. To examine the seasonal variation, entire year was divided into four seasons: winter (December, January and February), summer (March, April and May), monsoon (June, July, August and September) and post monsoon (October and November) based on the regional meteorological conditions.

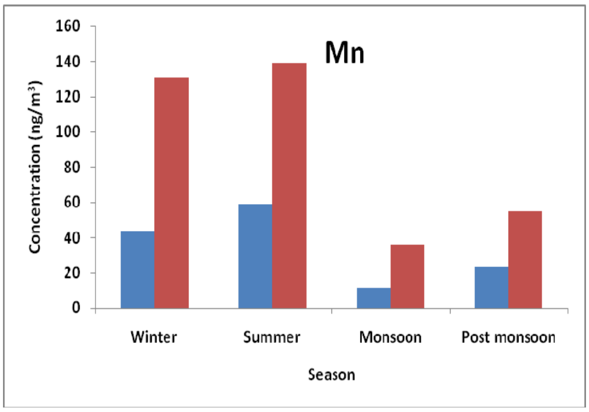
Prior to the investigation of seasonal variations in the concentration levels of measured trace metals, they were grouped into three categories based on their similar variations and 167ulphate167. First group consist elements like Fe, Sc, Ti, Al, Ca, Mg, Na, K Br and Cl, which are expected to be of natural origin. Among these elements crustal and marine based elements are included and their seasonal variations are explained in Figure 4.12.

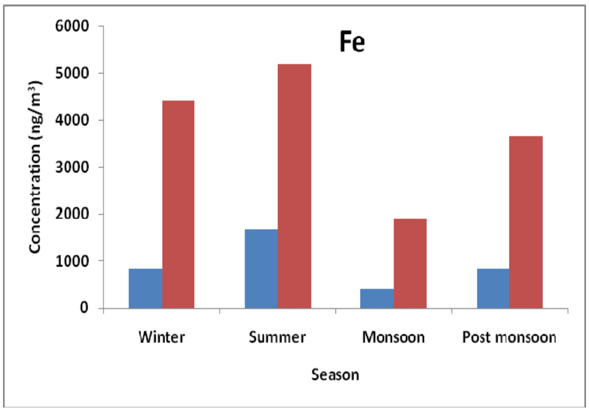
Figure 4.12: Seasonal variation of major elements categorized as first group

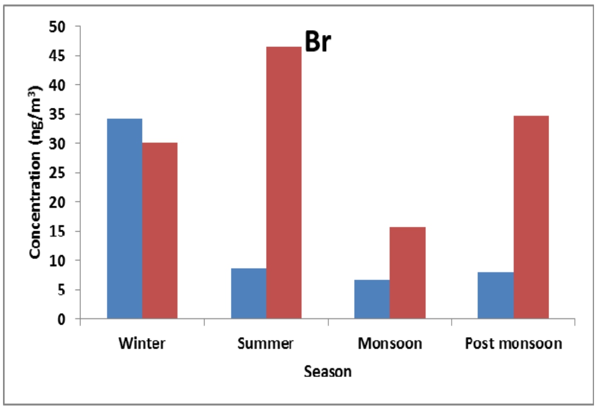


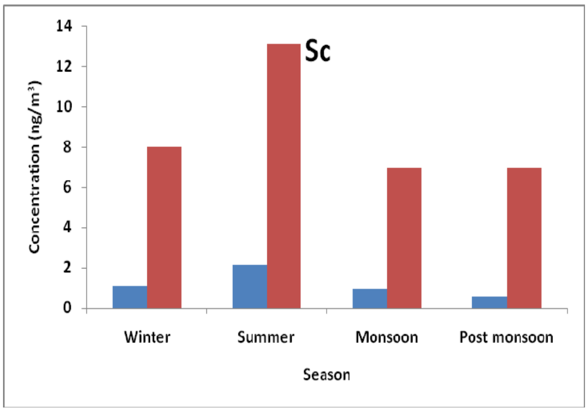






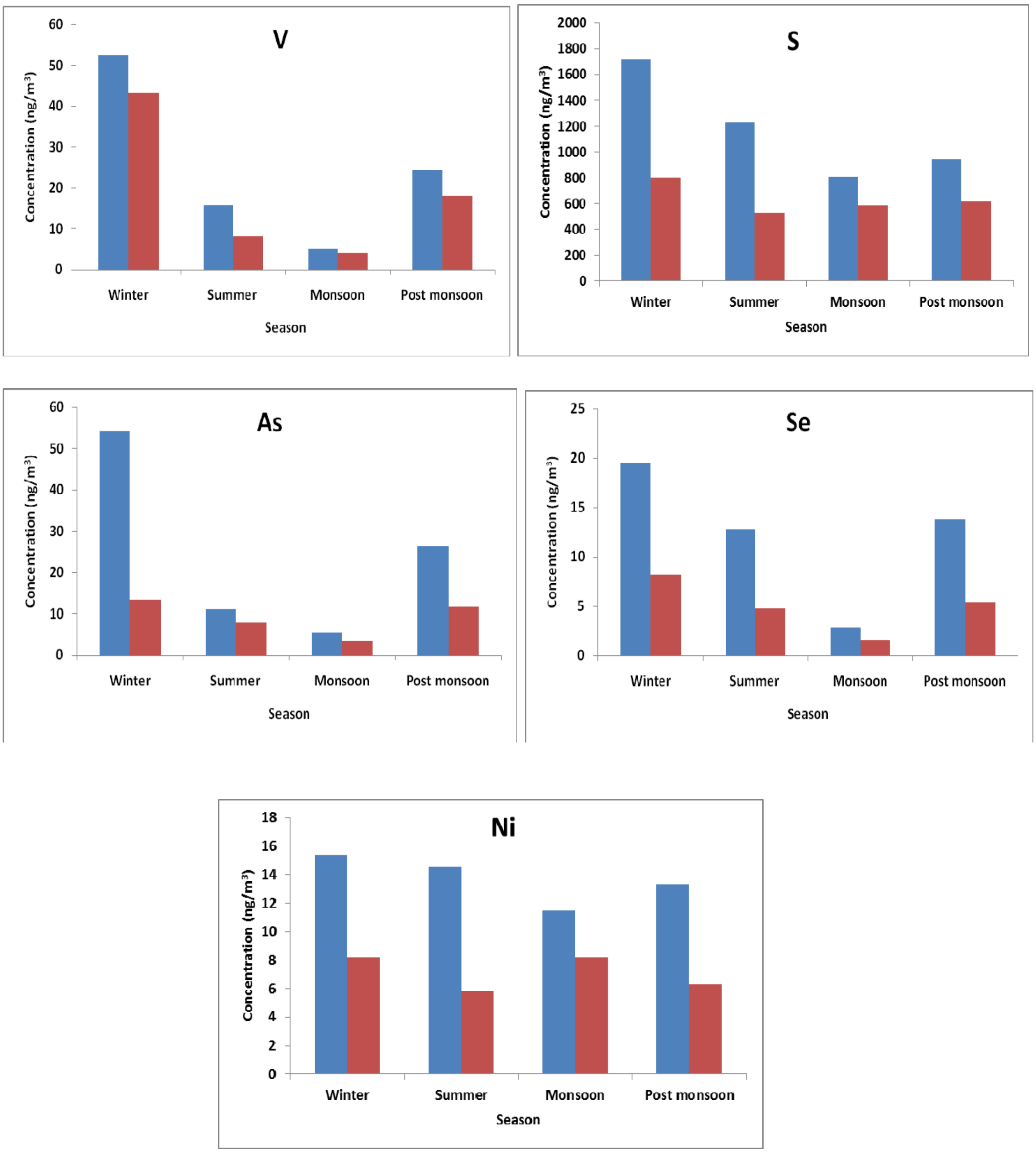






These elements show a pattern with a maximum during the summer season and a minimum during monsoon. This implies that crustal derived elements increase during summer mainly due to soil drought which ultimately enhance the re entrainment of soil dust in the atmosphere. Especially in the coarse fraction of PM, the concentration increases drastically and is evidencing that particles in this size are associated with windblown dust of crustal species and the suppression of the same during the wetter months which significantly influence coarse fraction PM in the atmosphere. Similarly highest mass concentrations of sea-salt elements (Na, Cl, Br etc.) were observed during summer indicating maximum evaporation of these elements because of high atmospheric temperature in this season. Variation of second group of elements with a group of trace elements consisting V, Ni, S, As and Se are illustrated in Figure 4.13.

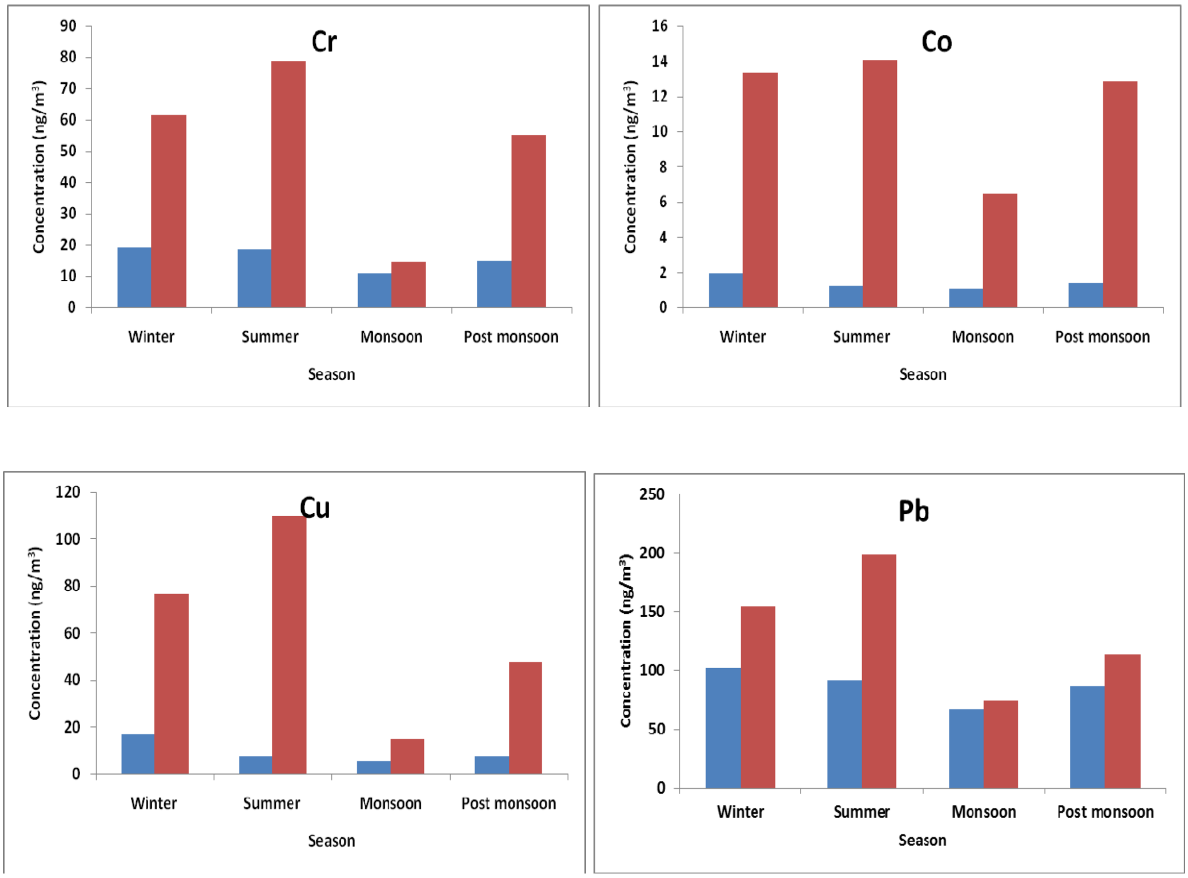
Figure 4.13: Seasonal variation of trace elements categorized as second group

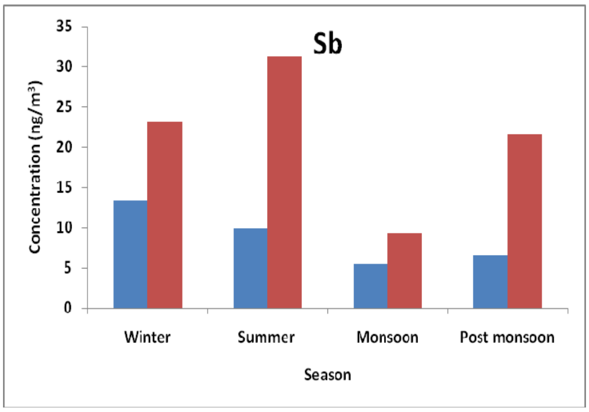


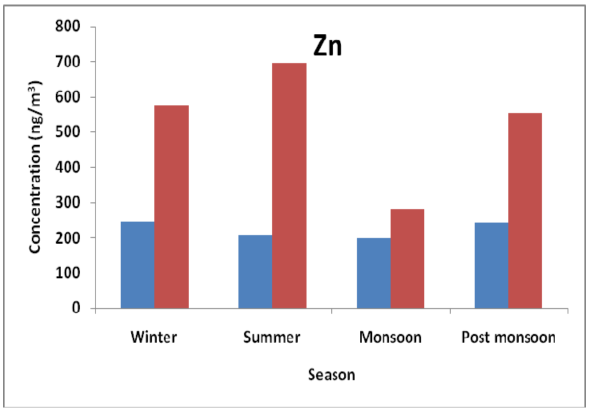
Distinctly higher concentrations were observed for the second group of elements during winter season [229]. All the five elements are apparently originated from anthropogenic emissions. It is very interesting to note that the strength of these elements are stronger mainly in the fine fraction and which can be attributed to both atmospheric stability and additional emission sources during winter season [230].

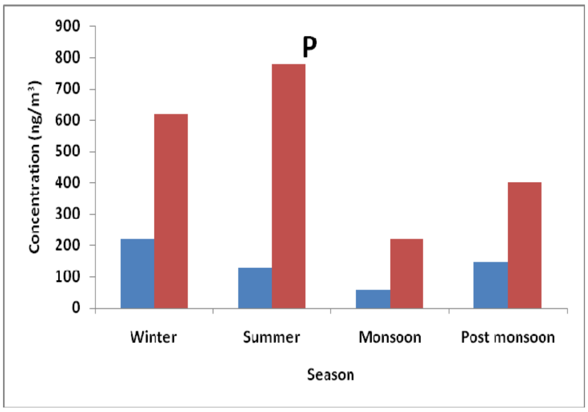
Seasonal variation of third group of elements(Cr, Co,Cu, Pb, Sb, Zn and P) are portrayed in Figure 4.14.

Figure 4.14: Seasonal variation of trace elements categorized as third group









These elements show contributions from both natural and anthropogenic sources. Especially, the concentration levels indicate input from natural sources mainly in the coarse fraction and anthropogenic source contribution in the fine fraction. Also in these cases the seasonal 172ulphate172 becomes more complex as the fine fraction increases during winter while the coarse fraction increases during summer [231].

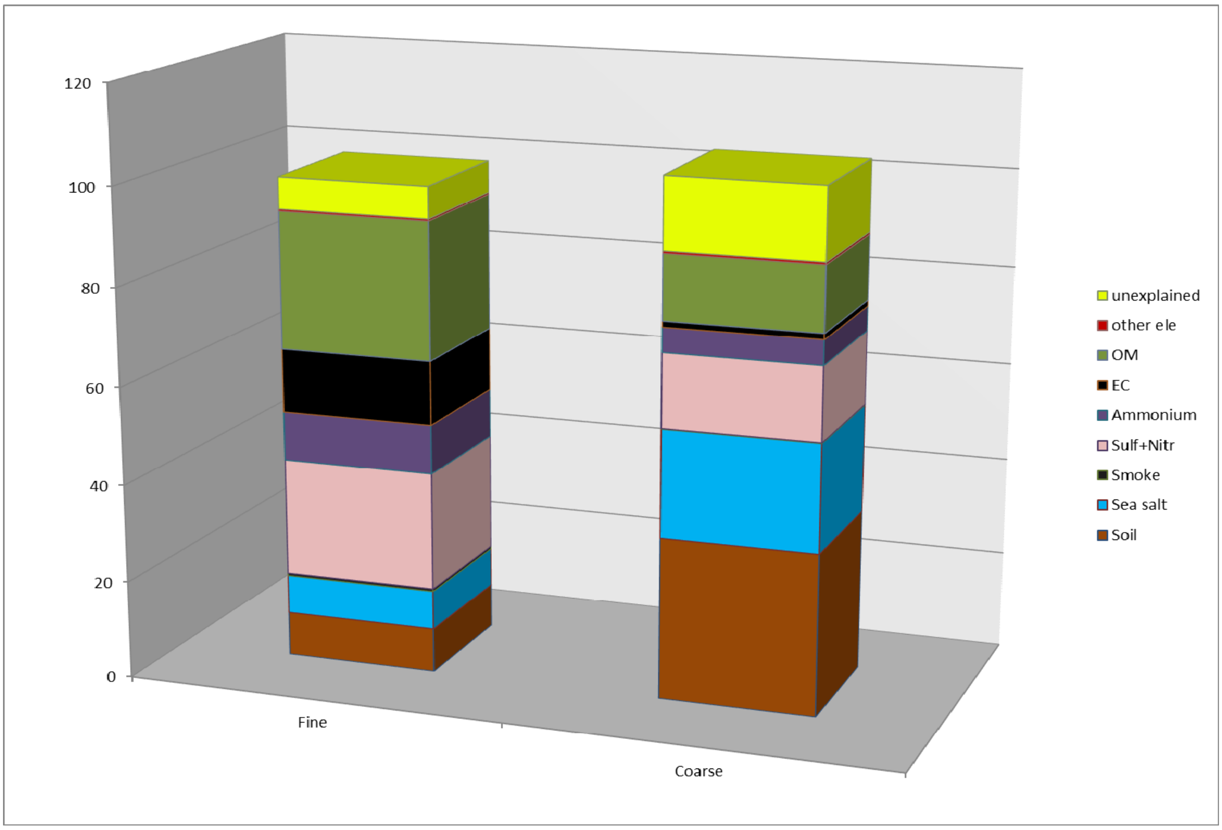
4.7 Re-construction of Mass

$PM_{2.5}$ and $PM_{2.5-10}$ results were subjected to a mass closure test to determine whether the measurement of gravimetric fine and coarse PM concentration of a sample is equal to the sum of the concentrations of the individually identified species. Further, material balance is considered as a preliminary source apportionment that allocates particulate matter to its various components like geological material, OM, EC, sulphate, nitrate, ammonium and marine salt [232].

For this particular part of the study, coarse and fine PM samples were collected from the two collocated Gent samplers and using a hi volume sampler PM_{10} samples were also collected simultaneously. In one of the Gent sampler the fine fraction polycarbonate filter was replaced by quartz glass fibre filter to facilitate the carbon speciation based on thermal method. Carbon speciation was then performed for PM_{10} obtained from hi volume and fine fraction filters from Gent samplers respectively. To facilitate the mass closure in both the size fractions, eight aerosol classes were considered: (i) Soil, (ii) Sea salt, (iii) smoke (iv) Sulfate+Nitrate, (v) Ammonium, (vi) EC, (vii) Organic aerosol, which was estimated by multiplying the corrected OC by a factor of 1.6 and (viii) other elements. The OC and EC data were obtained for PM_{10} and fine fraction particulate matter. Later, the concentration of carbon present in the coarse fraction was calculated by subtracting the fine fraction concentration from the PM_{10} carbon concentrations. The air filters were analyzed following the inter agency monitoring of protected visual environments protocol with a DRI 2100A system following the method presented by [233]. In the case of other components of PM empirical formulae were used for constructions of mass. The methodology adopted and the empirical formulae applied for the reconstruction of particulate matter gravimetric mass has been explained in detail in chapter – 3 of this thesis.

The percentage attribution of the gravimetric coarse and fine PM to different aerosol components is depicted in Figure 4.15, separately for $PM_{2.5}$ and $PM_{10-2.5}$. The sum of the various components in coarse and fine PM was 90% and 93% respectively indicating that good reconstruction was obtained.

Figure 4.15: Mass closure for coarse and fine particulate matter



Results present crustal matter and sea salt are the major aerosol types in the coarse fraction. But the crustal mass observed in the reconstruction found to be in higher side when compared with the source apportionment results and it can be attributed to the combined contribution of emissions from soil, road dust and construction which are resolved as separate sources by receptor techniques. Organic matter derived from the organic carbon contributed maximum to the fine fraction (28%). The total percentage of mass closure indicates that the OC to OM conversion factor 1.6 used in this study can be considered as appropriate. Also according to [234], a metropolitan region like Mumbai is considered as a major source for urban aerosols. Therefore, apart from local emission sources at the sampling site, the air quality is also likely influenced by the regional emissions. Hence a factor of 1.6 to convert OC to OM adopted in this study following [235] can be considered as reasonable. Next to organic matter, the component representing sulphate and nitrate together presented more to this fraction. Furthermore, substantial mass contribution was seen due to BC (13%) and ammonium (10 %) in $PM_{2.5}$. In the case of coarse PM, (sulphate+nitrate) component and ammonium contributed 18 and 5% to the total mass. It should be mentioned here that water is not included in the mass closure of both the fractions and therefore the unexplained portion of the total mass in the coarse and fine fraction could be attributed to the unidentified contribution of water to aerosol mass. According to [236], a significant amount of water can be associated with aerosol particles, even at RH below the low-humidity environment of the weighing room. [237] reported that strongly bound water mainly associated with inorganic species (175ulphate, nitrate) is not removed at these low RH. This water could be responsible for our remaining undetermined mass. To take the bound water into account and close the chemical mass balance, [238] applied a hydration multiplication factor of 1.29 to convert their inorganic species (Ammonium, Sulfate, Nitrate, Sea Salt) into hydrated species. This hydration factor was successfully used by [239] and the authors could achieve complete chemical mass closure for the fine and coarse size fractions. Similarly, when this multiplication factor (1.29) was applied to the respective species in our samples almost complete mass construction was achieved for fine and coarse fractions indicating that the same hydration factor can be used for Navi Mumbai region. The average mass contribution of each component in terms of mass ($\mu g/m^3$) is presented in Table 4.16 and Table 4.17.

Table 4.16: Average source contribution derived for coarse particulate mass

Parameter	Mass (µg/m^3) (n=50)
Soil	28.96±18.52
Sea salt	19.24±9.86
Smoke	0.09±0.04
Sulfate & Nitrate	8.21±5.36
Ammonium	4.04±1.96
EC	1.47±0.37
Organic Matter	15.01±6.82
Other elements	0.47±0.17
Reconstructed Mass	78.64±28.25
Measured Mass	87.92±24.74

Table 4.17: Average source contribution derived for fine particulate mass

Parameter	Mass (µg/m^3) (n=50)
Soil	3.87±1.91
Sea salt	3.4±1.03
Smoke	0.33±0.19
Sulfate & Nitrate	10.39±6.22
Ammonium	4.35±1.54
EC	7.09±4.36
Organic Matter	13.7±3.93
Other elements	0.25±0.11
Reconstructed Mass	44.35±9.72
Measured Mass	47.26±17.36

Mass reconstruction of different components of fine PM at various parts of Mumbai is presented in Table 4.18. There were no studies found in the literature identifying and reconstructing the coarse fraction mass seperately. Therefore, only the percentage contribution of fine fraction mass is illustrated to compare the present results.

Table 4.18: Mass closure for fine PM at different locations of Mumbai

Site	PM fraction	Component	Percentage contribution
Colaba	$PM_{2.5}$	Organic Matter	36
		Secondary inorganic aerosols	27
		Crustal	12
		Non crustal	7
		Seasalt	10
Dadar	$PM_{2.5}$	Organic Matter	42
		Secondary inorganic aerosols	23
		Crustal	11
		Non crustal	5
		Seasalt	11
Khar	$PM_{2.5}$	Organic Matter	52
		Secondary inorganic aerosols	21
		Crustal	6
		Non crustal	4
		Seasalt	6
Mahul	$PM_{2.5}$	Organic Matter	43
		Secondary inorganic aerosols	23
		Crustal	10
		Non crustal	8
		Seasalt	8
Present study	$PM_{2.5}$	Soil	9
		Sea salt	8
		Smoke	0.51
		Sulfate+Nitrate	24
		Ammonium	10
		Elemental Carbon	13
		Organic Matter	28
		Other elements	0.41

The reconstruction of $PM_{2.5}$ mass in Mumbai city as mentioned by [240] includes organic matter (36–52%) and secondary inorganic aerosols (21–27%). The contributions by crustal (6–12%), noncrustal (4–8%) and sea salt (6–11%) were low as compared to organic matter and secondary inorganic anions. Specifically when compared with the values of Khar , which was marked as residential area, the crustal , sea salt and secondary aerosol contribution of the present study observed to be falling in the same range. Whereas, organic matter in the $PM_{2.5}$ fraction of Vashi was appreciably lower than the level reported for Khar. However, the mass closure study proved that a significant component of fine particles at the study site is organic in nature.

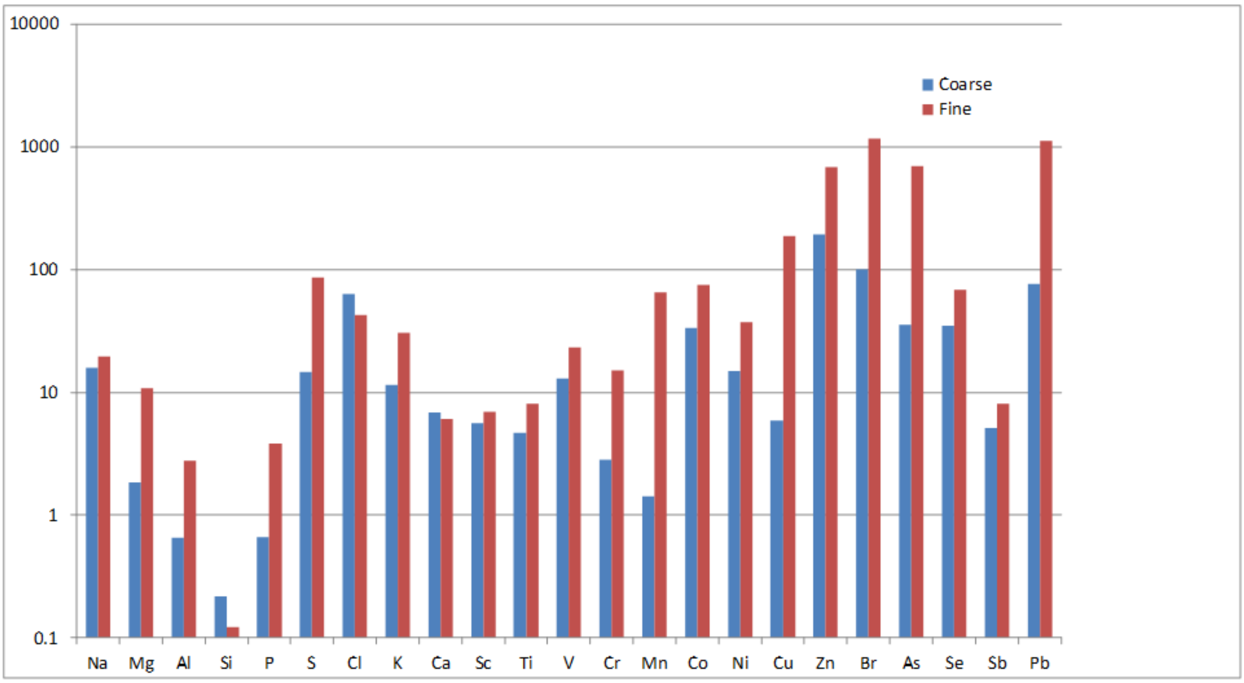
4.8 Enrichment Factor analysis

In order to discuss the abundance, variations and sources of these trace metals in aerosols we use the enrichment ratio. Generally, studies have observed that low enrichment ratio indicate a greater contribution from the crustal sources to the aerosol metal budget while higher ratios indicate a significant contribution from anthropogenic sources. By convention, an EF value of <10 is taken as an indication that a trace metal in an aerosol has a significant crustal source, and these are termed the non-enriched elements (NEE). In contrast, an EF value of >10 is considered to indicate that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEE) ([241]; [242]). For example, a simple application of EF analysis for PM source indication may be the study of heavy metals (e.g. brake-metals) at a road site. For those metals not emitted by traffic, the ratio between EF of ambient PM and the EF for mineral dust (crust) remains close to unity, while this ratio will be significantly higher than one for species like Cu. If source profiles are available for other sources, indications of their potential impact on ambient PM at the receptor site can likewise be inferred (e.g. tracers for metallurgic industries such as Zn, Fe, and Mn) [243].

The analyzed elements can be divided into three major groups: earth crust elements or soil tracers, marine tracers and anthropogenic tracers. Therefore, the separation of natural and anthropogenic components is one of the basic tasks of aerosol measurements. Enrichment Factor (EF) analysis is conventionally used for separating soil derived or marine derived elements from the anthropogenic components [244]. Therefore to verify the contributing elements of crustal and marine sources associated with $PM_{2.5-10}$ and $PM_{2.5}$, EF was calculated for each element. In this study Fe is used as a reference element to determine the EF with respect to crustal abundance. The elemental concentrations of background soil was taken from Mason (1966) [245]. Whereas, sea water composition is referred from Pytkowicz and Kester (1971) [246]. Whereas Na is used as a reference element to determine the marine based EF values. The greater value of enrichment factor shows the greater possibility of air pollution from anthropogenic sources [247].

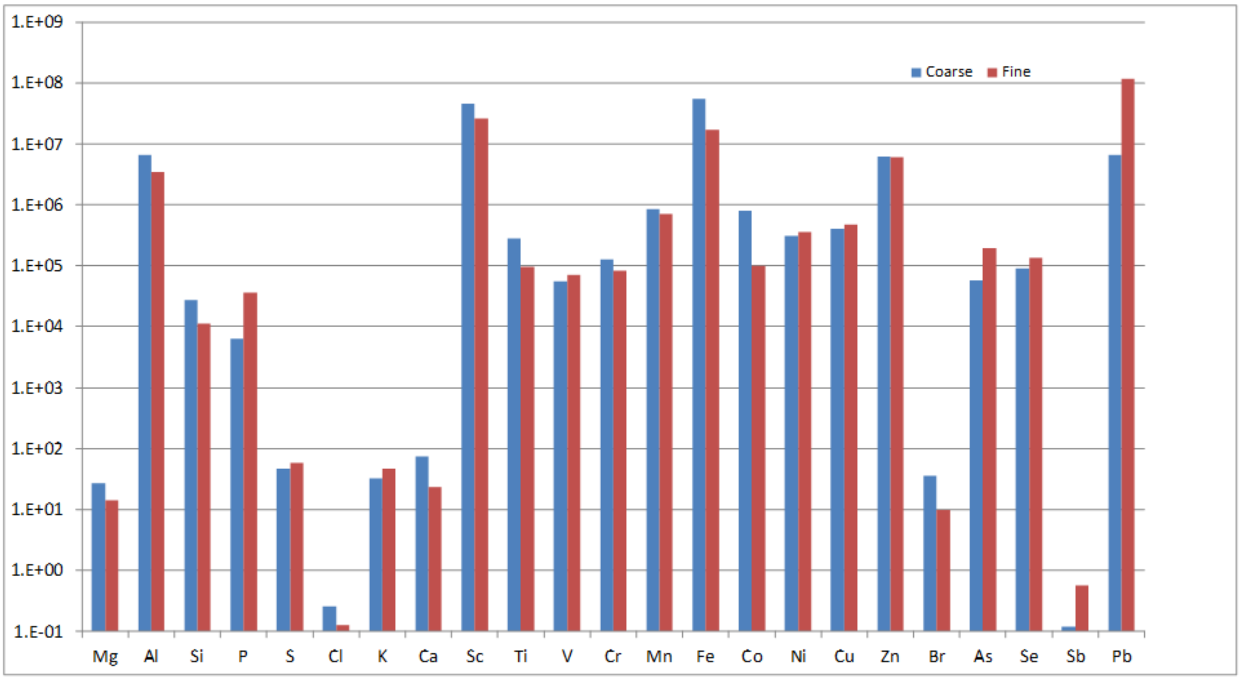
Figure 4.16 shows EF values obtained for the trace elements of coarse and fine particulate matter related to crustal concentrations.

Figure 4.16: Crustal enrichment factors of elements in $PM_{2.5-10}$ and $PM_{2.5}$



The plot shows EF values of Al, Ca, Mg, Si in both the size fractions are small indicating their origin from crustal source [248]. Few elements such as V and Ni were found to posses EF values in the range of 23 to 37 in the fine fraction but marginally crossed the cut off values in the coarse size particles. It is worthwhile to pay attention to the results of As, Br, Pb and Zn in the fine fraction which exhibit the maximum enrichment ranging from 685–1164 confirming that for these elements anthropogenic sources prevail over natural input. The high enrichment of these elements suggests that the dominant sources for these elements are non-crustal and a variety of pollution emissions may contribute to their loading in the ambient air. Among these elements Zn and Pb are often linked with traffic and smelter, As and Br are tracers for coal or oil burning [244]. Among the above mentioned four elements, except Zn, EF values of other three elements (As, Br and Pb) are within 100 in the coarse fraction. Elements like Mn, Cr, and Cu are showing enrichment only in the fine fraction which indicates their antropogenic origin from traffic or industrial emissions. Marine enrichment of elements is presented in Figure 4.17.

Figure 4.17: Marine enrichment factors of elements in $PM_{2.5-10}$ and $PM_{2.5}$



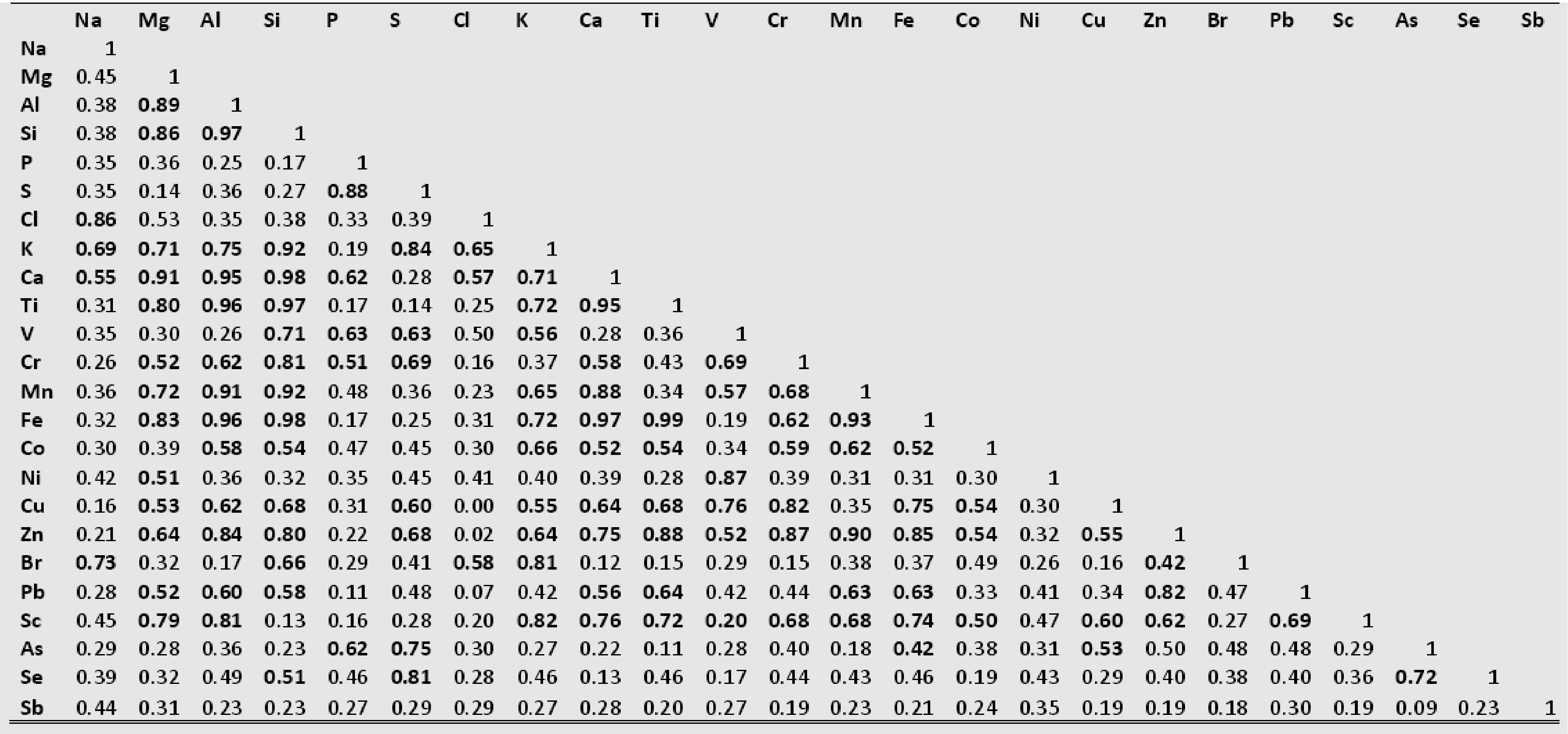
EF values found to be slightly greater than 10 for K, Ca and Mg. Other elements such as Al, As, Cr, Cu, Mn, Pb, Ni, Se, V, Fe and Ti found to possess EF around or greater than 10^5. The above set of elements showing very high EF values comprises both crustal derived as well as anthropogenically originated elements. Therefore, EF analysis suggested that there is a significant contribution from the natural pollutant sources such as soil and marine salt. Meanwhile, very high enrichment of many elements definitely emphasize that anthropogenic sources cannot be ignored in this study. Factors responsible for these high crustal and marine EF and the probable emission sources of these elements are discussed in the following sections.

4.9 Correlation studies

Table 4.19 and 4.20 demonstrates the correlation co efficients attained for various elements present in coarse and fine PM.

Statistically significant correlations were exhibited between crustal species like Si, Al, Fe, Ca, Mg and Ti in both the size fractions of particulate matter. Similarly sea salt related elements (Na, Cl, K and Br) were correlated strongly among themselves. Interestingly, K showed strong correlation with crustal species and moderate correlation with sea salt species in coarse and fine fraction PM. Therefore, it becomes clear that K has mixed origins indicating crustal being the predominant source. In the coarse fraction elements like V, Ni, Cu and Cr displayed moderate correlation with crustal based elements. Suggesting that, at least some of the measured concentrations of these elements are associated with crustal material. At the same time, V-Ni, Cr-Cu, Cr-Zn covary significantly demonstrating many anthropogenic source contribution including residual oil combustion. However, the anthropogenic contribution has been proved in the case of fine fraction correlation analysis. Where, very strong correlations were established between few pair of elements such as V-Ni, As-Se, BC-S and Cu-Cr etc. insisting and emphasizing considerable emissions from oil combustion, coal combustion, vehicular and other industrial emissions. But it becomes difficult to draw real conclusions regarding the sources from these correlations. Therefore, further analysis of sources was conducted based on receptor techniques and the results are presented in the following sections.

Table 4.19: Correlation of trace elements present in coarse PM



	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Pb	Sc	As	Se	Sb
Na	1																							
Mg	0.45	1																						
Al	0.38	**0.89**	1																					
Si	0.38	**0.86**	**0.97**	1																				
P	0.35	0.36	0.25	0.17	1																			
S	0.35	0.14	0.36	0.27	**0.88**	1																		
Cl	**0.86**	0.53	0.35	0.38	0.33	0.39	1																	
K	**0.69**	**0.71**	**0.75**	**0.92**	0.19	**0.84**	**0.65**	1																
Ca	**0.55**	**0.91**	**0.95**	**0.98**	**0.62**	0.28	**0.57**	**0.71**	1															
Ti	0.31	**0.80**	**0.96**	**0.97**	0.17	0.14	0.25	**0.72**	**0.95**	1														
V	0.35	0.30	0.26	**0.71**	**0.63**	**0.63**	0.50	**0.56**	0.28	0.36	1													
Cr	0.26	**0.52**	**0.62**	**0.81**	**0.51**	**0.69**	0.16	0.37	**0.58**	0.43	**0.69**	1												
Mn	0.36	**0.72**	**0.91**	**0.92**	0.48	0.36	0.23	**0.65**	**0.88**	0.34	**0.57**	**0.68**	1											
Fe	0.32	**0.83**	**0.96**	**0.98**	0.17	0.25	0.31	**0.72**	**0.97**	**0.99**	0.19	**0.62**	**0.93**	1										
Co	0.30	0.39	**0.58**	**0.54**	0.47	0.45	0.30	**0.66**	**0.52**	**0.54**	0.34	**0.59**	**0.62**	**0.52**	1									
Ni	0.42	**0.51**	0.36	0.32	0.35	0.45	0.41	0.40	0.39	0.28	**0.87**	0.39	0.31	0.31	0.30	1								
Cu	0.16	**0.53**	**0.62**	**0.68**	0.31	**0.60**	0.00	**0.55**	**0.64**	**0.68**	**0.76**	**0.82**	0.35	**0.75**	**0.54**	0.30	1							
Zn	0.21	**0.64**	**0.84**	**0.80**	0.22	**0.68**	0.02	**0.64**	**0.75**	**0.88**	**0.52**	**0.87**	**0.90**	**0.85**	**0.54**	0.32	**0.55**	1						
Br	**0.73**	0.32	0.17	**0.66**	0.29	0.41	**0.58**	**0.81**	0.12	0.15	0.29	0.15	0.38	0.37	0.49	0.26	0.16	**0.42**	1					
Pb	0.28	**0.52**	**0.60**	**0.58**	0.11	0.48	0.07	0.42	**0.56**	**0.64**	0.42	0.44	**0.63**	**0.63**	0.33	0.41	0.34	**0.82**	0.47	1				
Sc	0.45	**0.79**	**0.81**	0.13	0.16	0.28	0.20	**0.82**	**0.76**	**0.72**	**0.20**	**0.68**	**0.68**	**0.74**	**0.50**	0.47	**0.60**	**0.62**	0.27	**0.69**	1			
As	0.29	0.28	0.36	0.23	**0.62**	**0.75**	0.30	0.27	0.22	0.11	0.28	0.40	0.18	**0.42**	0.38	0.31	**0.53**	0.50	0.48	0.48	0.29	1		
Se	0.39	0.32	0.49	**0.51**	0.46	**0.81**	0.28	0.46	0.13	0.46	0.17	0.44	0.43	0.46	0.19	0.43	0.29	0.40	0.38	0.40	0.36	**0.72**	1	
Sb	0.44	0.31	0.23	0.23	0.27	0.29	0.29	0.27	0.28	0.20	0.27	0.19	0.23	0.21	0.24	0.35	0.19	0.19	0.18	0.30	0.19	0.09	0.23	1

Table 4.20: Correlation of trace elements present in fine PM

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Br	Pb	BC	Sc	As	Se	Sb
Na	1																								
Mg	0.46	1																							
Al	0.19	**0.71**	1																						
Si	0.37	**0.84**	**0.76**	1																					
P	0.26	0.20	0.26	0.17	1																				
S	-0.02	0.31	0.44	0.34	**0.56**	1																			
Cl	**0.81**	**0.64**	0.25	0.44	0.45	0.28	1																		
K	**0.63**	**0.56**	**0.62**	**0.74**	0.42	0.36	0.27	1																	
Ca	**0.52**	**0.84**	**0.67**	**0.93**	0.36	0.39	**0.59**	**0.84**	1																
Ti	0.10	**0.72**	**0.64**	**0.83**	**0.51**	0.38	0.03	**0.66**	**0.74**	1															
V	0.02	0.27	0.42	0.25	**0.76**	**0.66**	0.35	0.44	0.23	0.39	1														
Cr	0.18	0.37	0.21	0.43	**0.53**	**0.56**	0.38	0.36	0.46	0.50	**0.62**	1													
Mn	0.04	**0.70**	**0.72**	**0.79**	0.48	**0.56**	0.18	**0.87**	**0.52**	**0.77**	**0.64**	**0.62**	1												
Fe	0.26	**0.71**	**0.75**	**0.93**	0.50	0.45	0.28	**0.87**	**0.84**	**0.88**	0.26	0.46	**0.74**	1											
Co	0.25	**0.81**	**0.51**	**0.57**	0.33	0.28	0.26	0.47	**0.68**	0.31	0.22	0.42	**0.73**	0.48	1										
Ni	0.31	0.35	0.41	0.44	**0.79**	**0.75**	0.22	0.42	0.36	0.22	**0.82**	0.35	0.44	0.32	**0.79**	1									
Cu	0.45	0.37	**0.52**	0.44	0.28	0.27	0.33	0.20	0.45	0.38	0.35	**0.77**	0.44	0.42	0.49	0.36	1								
Zn	-0.04	**0.61**	**0.69**	**0.56**	**0.57**	**0.52**	0.21	0.21	0.49	0.43	**0.56**	0.49	**0.79**	**0.65**	**0.57**	0.40	0.28	1							
Br	**0.68**	0.03	**0.52**	**0.58**	0.29	0.44	**0.55**	**0.68**	**0.56**	0.29	0.49	0.35	0.34	0.25	0.43	0.39	0.05	0.44	1						
Pb	0.00	0.48	0.40	0.49	0.50	0.46	0.16	0.26	0.40	0.34	**0.51**	**0.51**	**0.59**	0.43	0.38	0.33	0.30	**0.77**	**0.62**	1					
BC	0.09	-0.11	-0.01	0.06	-0.07	**0.82**	-0.14	0.16	0.05	0.23	**0.55**	0.03	0.08	0.17	-0.08	**0.67**	-0.03	-0.06	-0.06	-0.05	1				
Sc	0.39	**0.62**	**0.72**	**0.59**	-0.05	0.05	0.20	0.39	**0.71**	**0.69**	-0.25	0.10	-0.26	0.03	-0.15	-0.15	0.19	-0.13	-0.03	0.04	0.04	1			
As	-0.16	0.00	0.18	0.10	0.13	**0.61**	-0.10	0.43	0.13	0.26	0.25	0.33	0.28	0.25	0.02	0.18	0.14	0.29	0.16	0.42	**0.63**	0.25	1		
Se	0.07	0.25	0.33	0.45	0.35	0.48	0.01	0.41	0.34	0.42	0.26	0.40	0.44	0.46	0.04	0.16	0.08	0.34	0.26	0.29	**0.52**	-0.13	**0.85**	1	
Sb	-0.08	0.03	-0.01	0.06	0.02	-0.33	-0.03	-0.16	-0.01	-0.01	-0.16	-0.03	-0.17	-0.05	0.05	-0.15	-0.11	-0.20	-0.15	-0.19	-0.26	0.09	-0.17	-0.05	1

4.10 Source identification using PCA

A Varimax rotated factor analysis was performed to identify the main chemical groupings and likely sources of airborne particulate matter collected at the sampling site using statistical software Statgraphics Plus (Version No: 4). Receptor modeling techniques are mainly based on the evaluation of data acquired at receptor sites, and most of them do not require previously identified emission sources. “factor loadings”, the correlation between the factor scores and original input variables, that aid in the interpretation of factors. The physical identification of the factors were achieved by comparing elements having the highest loading with each component with elements emitted in large amounts and/or in high enrichment by known source types. Any factor loadings with low significance (< .5) were not considered as a valuable loading in the present study. A six factor solution for coarse fraction and a seven factor solution for the fine fraction particulate matter was chosen as the “optimum” solution, based on an examination of both the factor eigen values (i.e. the data variance explained by the component) and the source related interpretability of the factors.

4.10.1 Source identification of coarse PM using PCA

Table 4.21 provides the factor loadings extracted for coarse particulate matter.

Table 4.21: Principal Component Analysis (PCA) with varimax rotation for all $PM_{2.5-10}$ data from vashi site.

Elements	**Soil**	**Fugitive dust**	**Coal combustion**	**Industry**	**Sea salt**	**Construction**	**Communality**
Na	0.226	0.216	0.013	0.021	**0.911**	0.151	0.951
Mg	**0.811**	0.047	0.017	0.042	0.11	**0.562**	0.990
Al	**0.851**	0.064	0.001	-0.001	0.002	**0.504**	0.982
Si	**0.825**	0.069	-0.001	-0.003	0.061	**0.511**	0.950
P	-0.023	0.107	**0.912**	0.181	0.008	-0.062	0.880
S	0.005	0.011	**0.861**	0.014	0.009	**0.506**	0.998
Cl	-0.072	0.124	0.051	-0.024	**0.941**	0.127	0.925
K	**0.537**	0.024	0.012	0.002	**0.836**	0.006	0.988
Ca	**0.711**	0.004	0.002	-0.001	0.016	**0.702**	0.999
Ti	**0.942**	0.079	0.024	0.009	0.008	0.221	0.943
V	0.057	0.114	0.236	**0.932**	0.007	-0.016	0.941
Cr	0.263	0.286	0.218	**0.884**	0.013	0.021	0.981
Mn	**0.801**	**0.586**	0.007	0.006	0.004	0.014	0.985
Fe	**0.938**	0.214	0.059	0.086	0.021	0.224	0.987
Co	0.223	**0.903**	0.093	0.068	0.006	0.092	0.887
Ni	0.021	0.026	0.186	**0.941**	0.005	0.008	0.921
Cu	0.215	0.178	0.147	**0.896**	0.084	0.075	0.915
Zn	0.083	**0.912**	0.168	0.126	0.091	0.035	0.892
Br	0.095	0.047	0.071	0.112	**0.914**	0.091	0.872
Pb	0.097	**0.887**	0.281	0.152	0.002	-0.021	0.899
Sc	**0.916**	0.312	0.046	-0.053	0.006	0.092	0.950
As	0.095	0.175	**0.922**	0.091	0.009	0.011	0.898
Se	0.068	0.172	**0.914**	0.096	0.018	0.085	0.886
Sb	0.143	**0.914**	0.205	0.076	0.019	0.025	0.905
Eigen value	6.389	4.037	3.590	3.464	3.282	1.763	
% Variance	26.622	16.821	14.960	14.433	13.678	7.346	93.86

Among the sources extracted for the coarse fraction crustal source with Mg, Al, Si, Ca, Ti, Fe and Sc as main tracers was identified as the major contributing source. Around 26 % of the total variance was explained by the soil derived source in the coarse fraction. Factor 2 was identified as fugitive dust comprising Mn, Co, Zn, Pb and Sb. This factor appeared to represent diffuse pollution sources from automobile emissions, road dustand mechanical abrasion blown by traffic and wind. Third factor with P, S, As and Se explaining 14.9% of the variance can be labelled as coal combustion source considering arsenic as the principal tracer, since As and Se are the prominent markers of coal combustion.

Factor 4 was clearly industrial because it is correlated with elements such as V, Cr, Ni and Cu, as these elements are generally of industrial origin. However, the elements grouped in the fifth factor suggests that the tracer elements of oil combustion (V and Ni) found to be merged along with the industrial source emitting Cu and Cr which could not be resolved as a separate factor. An MPCB report documents that there are 581 major air polluting industries in the MIDC cluster [104]. Factor 5 in coarse fraction was associated primarily with sea salt emission, because characteristic elements for this source Na, Cl, K and Br as discussed by [249] were observed to have very high loadings and this factor explained 13.6% variance.

The elements like Mg, Al, Si, S and Ca had a higher loading on the final source or factor 6. The marker elements associated with this factor represent the emissions from activities related to cement or construction work. Specifically, high loading of Ca [250]. The loading of the elements were comparatively lower than the other factors but surprisingly this source could be resolved from the crustal source pinpointing the substantial contribution from construction activities. Also, The MPCB report on industrial activities in Navi Mumbai insists that besides the industrial activities in TTC MIDC area, falling sources like quarries, stone crushers and contruction activities taking place in huge quantum and also impacts on air quality in Navi Mumbai region [104]. It should be pointed out that the six factors resolved in the coarse particulate matter satisfactorily explained 93.8% of the total variance and consequently, the addition of more factors was not indicated.

4.10.2 Source identification of fine PM using PCA

Principal component analysis of fine particulate matter resolved seven independent sources explaining a total variance of 90%. The factor loadings obtained were given in Table 4.22.

Results show factor 1was highly loaded in Mg, Al, Si, Ca, Ti, Fe and Sc and accounted for a variance of 24.4%. This factor with the strong loadings of crustal elements confirms the soil contribution to the particulate matter. Factor 2 had high loadings on Si, Mn, Co, Zn and Pb and accounted for another 6.2% of the total variance. As mentioned in the coarse fraction factor 3, this factor could be identified as fugitive dust. But the high loading of Si in this factor confirms the contributions from road dust. Also Zn is considered as one of the indicator of tyre wear and hence this factor could be attributed as road dust. Factor three has high loadings with P, S, V, Ni and Zn, and explained 14.4% of the total variance. Since the loadings of V and Ni were higher this factor might present industrial emissions related to oil combustion [251].

Factor 4 had loading on sea salt elements, such as Na, Cl, K and Br and explained 13.8% of the variance. Factor 5 showed high loadings on As, Se and Sb and accounted for 12.3% of the total variance. This factor might represent the coal combustion processes providing possible indicator elements. Studies conducted at various coal-fired power plants and utility coal combustion proved them as one of the largest source of Se for the atmospheric particles and hence Se has been widely used as a tracer for coal burning [252, 253].

Table 4.22: Principal Component Analysis (PCA) with varimax rotation for all $PM_{2.5}$ data from vashi site.

Elements	**Soil**	**Fugitive dust**	**Oil Combustion**	**Sea salt**	**Coal combustion**	**Industries**	**Vehicles**	**Communality**
Na	0.125	0.116	0.089	**0.941**	-0.095	0.079	-0.016	0.938
Mg	**0.928**	0.143	0.021	0.286	-0.031	0.028	0.009	0.966
Al	**0.902**	0.172	0.053	-0.003	0.164	-0.032	0.076	0.880
Si	**0.862**	**0.501**	0.015	0.002	0.016	0.004	0.011	0.995
P	0.023	0.0417	**0.915**	0.001	0.132	0.185	0.175	0.922
S	0.006	0.084	**0.503**	0.063	0.241	0.095	**0.811**	0.989
Cl	0.068	0.078	0.146	**0.921**	0.093	0.063	0.027	0.894
K	0.315	0.217	0.085	**0.864**	0.251	0.054	0.083	0.973
Ca	**0.878**	0.238	0.021	0.283	0.103	0.018	0.098	0.929
Ti	**0.917**	0.243	0.013	0.008	0.108	0.082	0.112	0.931
V	0.073	0.079	**0.914**	0.008	0.103	0.093	0.174	0.897
Cr	0.127	0.138	0.218	0.013	0.051	**0.884**	0.127	0.883
Mn	0.356	**0.896**	0.214	0.016	0.089	0.042	0.019	0.986
Fe	**0.923**	0.252	0.093	0.062	0.136	0.039	0.039	0.949
Co	0.241	**0.867**	0.028	0.004	0.212	0.062	0.198	0.899
Ni	0.026	0.083	**0.893**	0.016	0.314	0.036	0.069	0.910
Cu	0.189	0.162	0.273	0.072	0.276	**0.851**	0.131	0.959
Zn	0.092	**0.815**	**0.542**	0.042	0.064	0.048	0.083	0.982
Br	0.135	0.126	0.005	**0.893**	0.169	0.182	0.093	0.902
Pb	0.014	**0.872**	0.281	0.021	0.217	0.191	0.017	0.924
Sc	**0.892**	0.361	0.035	0.011	0.014	0.012	0.009	0.928
As	0.141	0.121	0.165	0.084	**0.931**	0.012	0.113	0.948
Se	0.021	0.124	0.134	0.019	**0.892**	0.253	0.017	0.894
Sb	0.093	0.092	0.389	0.062	**0.873**	0.184	0.083	0.975
BC	0.057	0.072	0.305	0.004	0.324	0.135	**0.873**	0.987
Eigen value	6.099	3.783	3.604	3.467	3.075	1.776	1.632	
% Variance	24.396	15.132	14.417	13.868	12.301	7.105	6.527	93.74

Factor 6 had strong factor loadings on Cr and Cu, and explained another 7.1% of the total variance. This factor could be attributed to the textile related industries. Since Cu and Cr complexes are mostly used in abundance in the industries of textile, dyes and intermediates, it is suspected that this could be the source of emission for these elements having high loadings in the fifth factor of fine particulates [254]. Also about 6% of the industries in the nearby industrial belt comprise dye and textile industries [105]. Elements such as Cu and Cr showed comparatively high enrichment in the fine fraction and have been resolved as a separate source in the PCA studies confirming their anthropogenic origin. Final factor was dominated by S and BC and explained further 12.5% of the total variance. This factor appeared to represent vehicular emission [255]. As mentioned by Brito *et. al.*, [256] a significant fraction of sulphur is either emitted directly from the tailpipes or quickly oxidized to the particle phase and the study further states, sulphur as one of the most abundant trace element emitted by vehicular sources. Specially, PM emitted by diesel fueled vehicles emit soot formed during combustion, heavy hydro carbons condensed or adsorbed on the soot and sulphates [257]. Therefore, sulphur and BC together could be considered as marker elements for vehicular sources.

Both in the coarse and fine fraction soil, sea salt and fugitive dust sources found to be the common sources and in the fine fraction industrial emissions could be resolved sharply. Similar studies conducted on source identification at various places of Mumbai region also indicated crustal matter and sea salt as the main sources contributing to particulate pollution along with other sources such as oil combustion, road dust, metal industries and coal combustion [258, 259, 84, 260]. Similarly, soil, road dust, vehicular emissions and coal combustion were proved to be the potential contributing sources of atmospheric particulate matter load in other parts India [261, 198, 179, 199, 262, 139].

Among the sources derived for coarse and fine fractions crustal source is found to be common and one of the significantly contributing source to both the size fractions. Apparently, elements like K, V and Mn present in the crustal source of coarse fraction were not resolved as separate source as in fine fraction. This clearly indicates the origin of these three elements from natural soil source especially in this size fraction. This statement is also supported by the crustal enrichment analysis of K, V and Mn. Which displays EF values near to unity for these elements in coarse size fraction, on the other hand significant enrichment was detected in the fine fraction. But in both the size fractions of PM, crustal source was identified as the primary potential source of the study region explaining maximum variance. Around 35 % of the total variance was explained by the soil derived source in the coarse fraction and about 26% variance was explained in the fine fraction. This revealed the association of Fe a key signature element for soil with the other crustal elements contributed from reentrained windblown crustal source [263, 252, 264].

4.11 Source apportionment using PCA-MLR

In this study, PCA followed by a stepwise regression analysis was performed using the estimated Absolute Principal Component Scores (APCS) to apportion the particulate matter mass concentration to the contributing sources. The APCS was calculated for each factor by separately scoring for a dummy sample, wherein all the elemental concentrations are zero. To enhance their degree of interpretability, the factors were transformed by VARIMAX rotation prior to their assignment to the sources. The Absolute Factor Scores were then obtained following the procedure of [265] and were regressed against the mass concentrations of coarse and fine particulate matter to apportion the percentage mass contribution of each identified source. Percentage mass contributions are presented in Figure 4.18 and 4.19.

Figure 4.18: Source apportionment of coarse PM in the study area

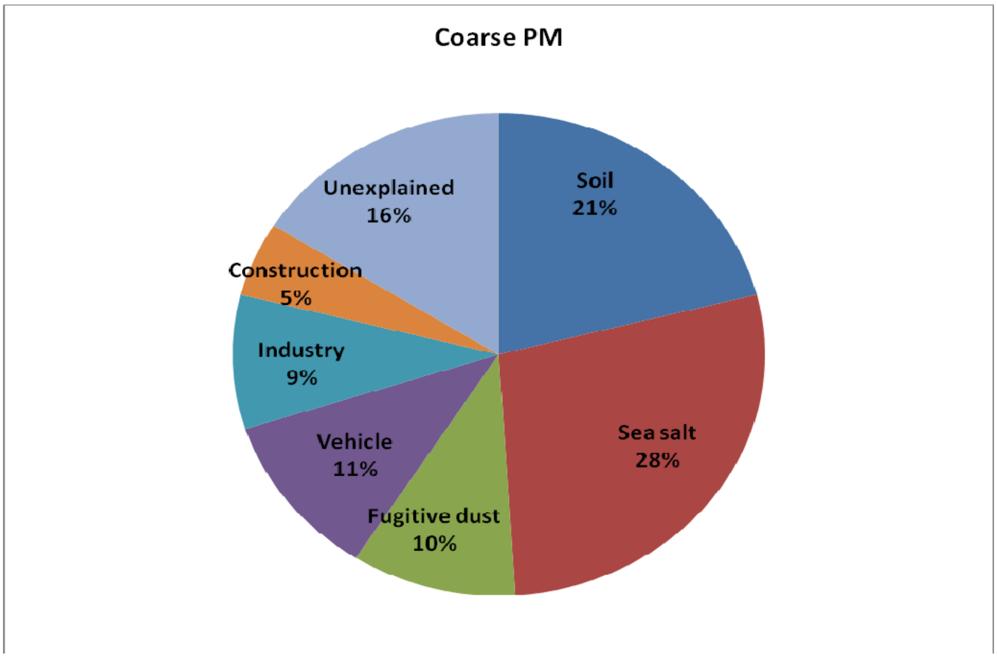


Figure 4.19: Source apportionment of Fine PM in the study area

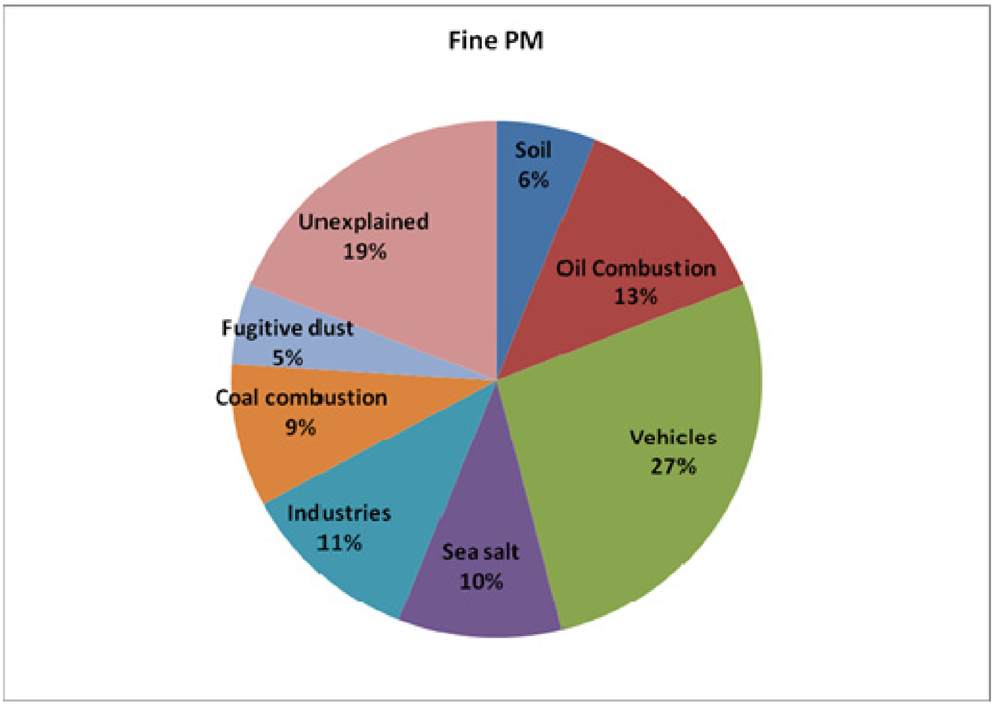


Figure 4.18 illustrates the average percentage contribution of each identified source of coarse and fine PM respectively. Coarse particulate matter collected over the sampling period in Vashi showed a maximum contribution of 28% from sea salt as the site is nearby coastal area. The crustal source contributed 25%, while the contribution from the fugitive emission was found to be 10%. Vehicular and industrial emissions contributed 11% and 9%, respectively. Source related to construction work contributed less compared to other sources and it was 5%. Apportionment of fine particulate mass is demonstrated in Figure 4.19.

In the case of fine particulate matter, the maximum mass has been contributed by vehicular sources and was around 27%. For fine mass, 11% of the mass has been contributed from industrial sources. Apart from this, specifically, oil combustion and coal combustion based industries accounted for 13% and 9% respectively of the total PM concentrations. These findings seem reasonable as most of the small scale and large scale industries situated in TTC industrial area are using oil or coal as fuel which create huge emission. Also some units are having coal fired boilers [104]. Natural sources like sea salt and crustal sources contributed to 10% and 6% respectively in the fine fraction. Therefore maximum percentage contribution in the fine fraction observed to be contributed from the anthropogenic sources especially from vehicular and industrial activities. Whereas, around 50% of the particulate matter load in the coarse fraction is due to natural sources and also another 10% contribution was contributed as a result of resuspension of road dust due to heavy traffic activities near the study area. Also only 25% mass found to be devoted by anthropogenic emission and the remaining 16% mass in the coarse PM is regarded as unexplained portion of the total mass. Whereas, 19% of the mass was not explained in the fine PM source apportionment.

4.12 Source Apportionment using PMF

Following PCA-MLR, the PMF multivariate receptor model was selected for the further confirmation of sources. The PMF model which conducts a least square analysis, was applied to the data set to characterise the key sources of PM. This particular model was chosen as the data are normalized and measurement uncertainties are taken into account during modelling process. Unlike the methods like PCA, the results can be used directly to assemble the source profiles and quantify relative source contributions. In this study, PMF 3.0 [266] was used to apportion the sources. The PMF 3.0 model requires two input files: one for the measured concentration of the species and one for the estimated uncertainty of the concentration. In the concentration file, missing values (denoted by the value of -999) were replaced by the median value of the species and assigned an uncertainty value of 4 × standard deviation (sd) by this model. The uncertainty of the concentration was estimated as:

For concentrations $<$ DL: Uncertainty $= 5 \times DL/6$

For concentrations $\geq$ DL: Uncertainty $= (DL^2+\text{Precision}^2)^{0.5}$

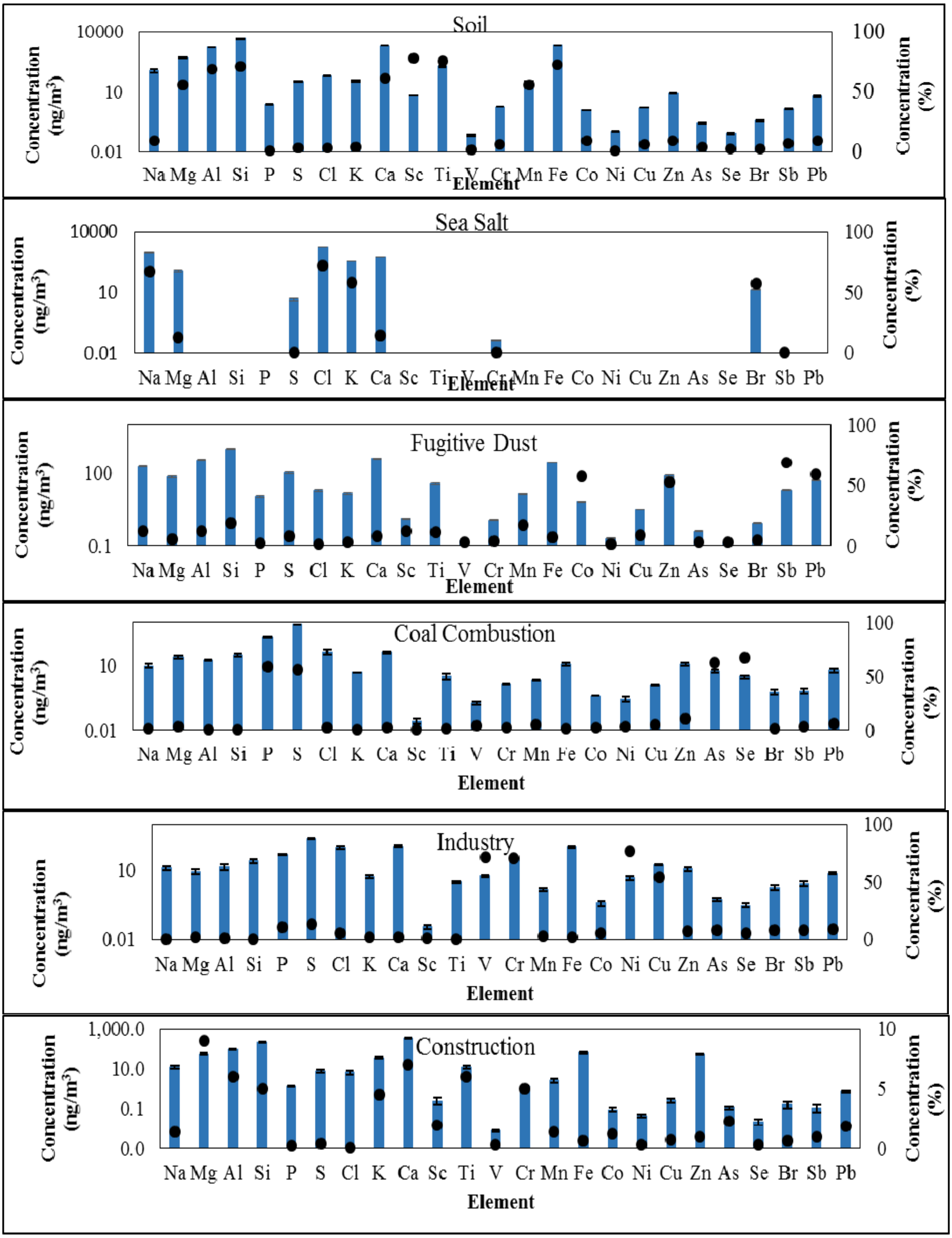
Concentrations beyond 4 × sd from the average concentration of the species were assigned a large uncertainty value of 10 × sd to minimise the distortion of data set by these outliers. Categorisation of quality of data was based on the signal to noise ratio (S/N) and the percentage of samples above DL [267]. Further based on the S/N ratio all the species were categorised as strong or weak and it is likely that the species categorised as weak will not provide enough variability in concentration and therefore further will not contribute to the noise in the results. The PMF receptor model was then applied to the final data set. Various parameters were adjusted, including the number of factors, until an acceptable Q-value (goodness of model fit) was achieved. Multiple PMF runs were required (trial-and-error) to optimize these parameters. Six and seven factors were eventually selected for coarse and fine PM respectively. Using PMF, for the coarse fraction data, a six-factor model was chosen as it gave the most satisfactory results in terms of explaining the underlying structure in the data.

4.12.1 Source identification of coarse PM using PMF

Figure 4.20 depicts the source profiles of the six possible sources and their associated source contributions.

The first source of coarse fraction is a typical soil source with dominant high concentrations of Mg, Al, Si, Ca, Ti and Fe. The second factor found to be the sea salt source due to higher concentrations of Na, Cl and other sea salt elements such as Mg, K, Ca and Br. The third factor is clearly identified as fugitive road dust due to the presence of most of the soil derived elements along with the high concentrations S and tyre wear marker element Zn. In comparison with the results of FA loadings of coarse fraction fugitive dust, PMF source profile clearly indicated the major elements present in this source and confirmed that the source is road dust. The forth factor with the presence of high sulphur implies the contribution from vehicular emission but the considerable contribution of As and Se in this factor emphasize that there may be overlapping of vehicular and coal combustion sources which could not be resolved by the model. The fifth factor is characterized by many of the anthropogenically derived toxic elements like P, S, V, Cr, Ni and Cu revealing the contributions from different industrial activities. The sixth factor is Ca rich source produced by some construction activities around the sampling site. Again in this case, the detailed elemental source profile obtained from PMF model sharply presents very high concentration of Ca in this factor which helps in the distinction of construction related sources from other fugitive sources. Whereas, the factor loadings of FA indicated strong loadings of Ca with other soil derived elements but the intensity of calcium concentration becomes unclear and leading to a troublesome footing in distinguishing the source.

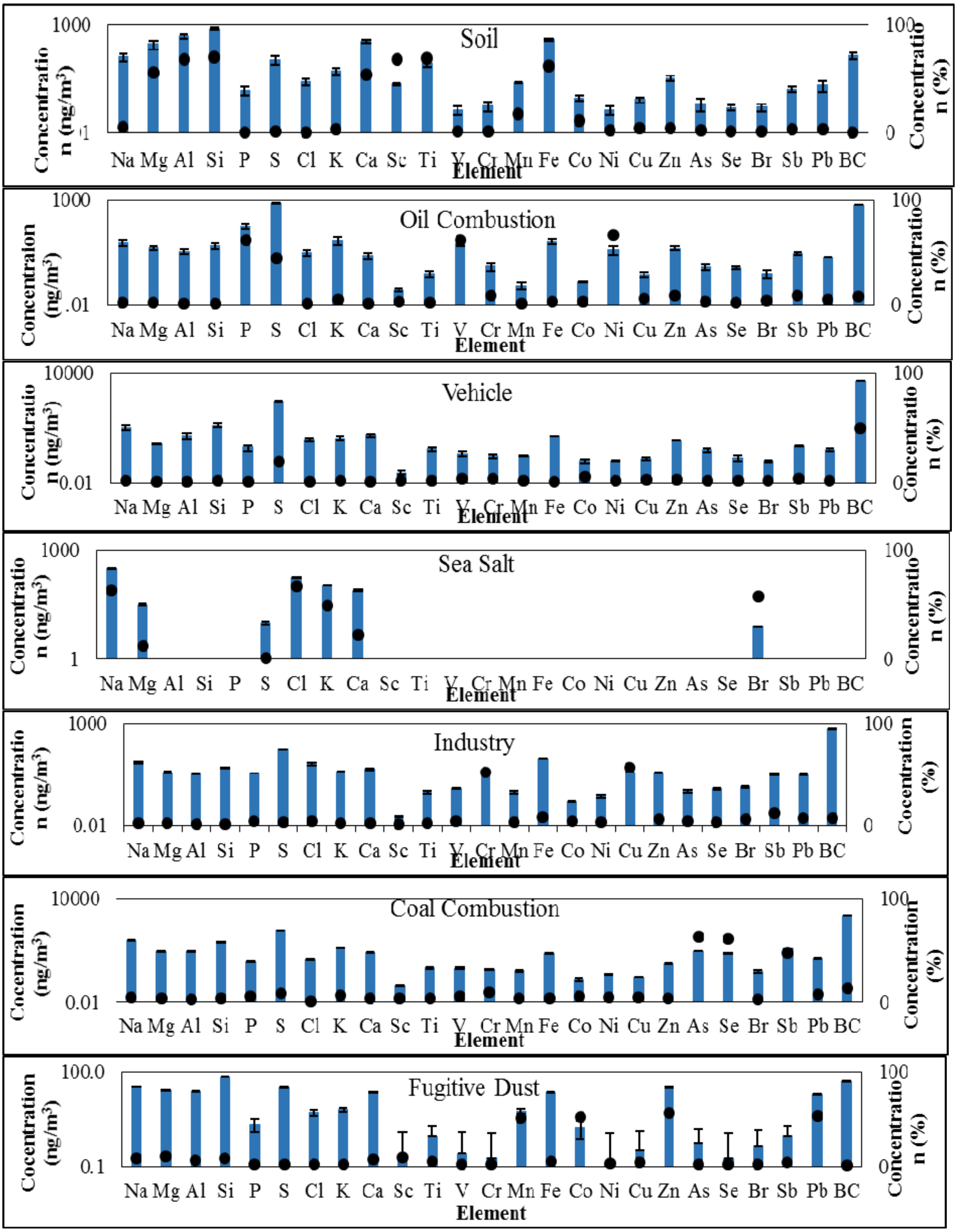
Figure 4.20: PMF results for coarse PM



4.12.2 Source identification of fine PM using PMF

In fine PM seven factor model was chosen and the source profiles are provided in Figure 4.21.

Figure 4.21: PMF results for Fine PM



The first source with the tracers of crustal elements was identified as soil. In the case of forth factor of coarse fraction vehicular and coal combustion markers found to be merged. However in the fine fraction these sources have been resolved in to two different factor (Factor 3&4) with their respective key identifying elements. Black carbon additionally added in the fine fraction apportionment used as the second key tracer element with sulphur to identify the vehicular emissions. Forth factor represents sea salt. Fifth factor is characterized by high concentrations of Cr and Cu. Also nominal concentrations of other metals used as pigments in the textile industries are also seen in this factor and hence this can attributed to the textile industry emission. Abundant S, As and Se presence in the sixth factor confirms the contribution from coal combustion in the fine fraction PM. The final seventh source possesses similar elements as in fugitive road dust of coarse fraction and was marked as fugitive dust.

4.13 Evaluation and comparison of PCA and PMF

One of the main aspects of the present study is that two different receptor models were applied to apportion the size fractionated PM data in order to compare results and the adequacy of models. The comparability between receptor models was evaluated as a function of four parameters:

(a) Model performance: The ability of the models to reproduce the measured coarse and fine concentrations.

(b) Source identification: The number and nature of the sources identified.

(c) Source profiles: The similarities or dissimilarities observed between the different source profiles obtained with FA and PMF

(d) Source contribution: The quantification of the mass contribution of the sources to the total coarse and fine PM.

The results of model performance and source identification by both the receptor model techniques were illustrated in Table 4.23 and the detailed discussion on the verification of the model performance is presented in the subsequent sections.

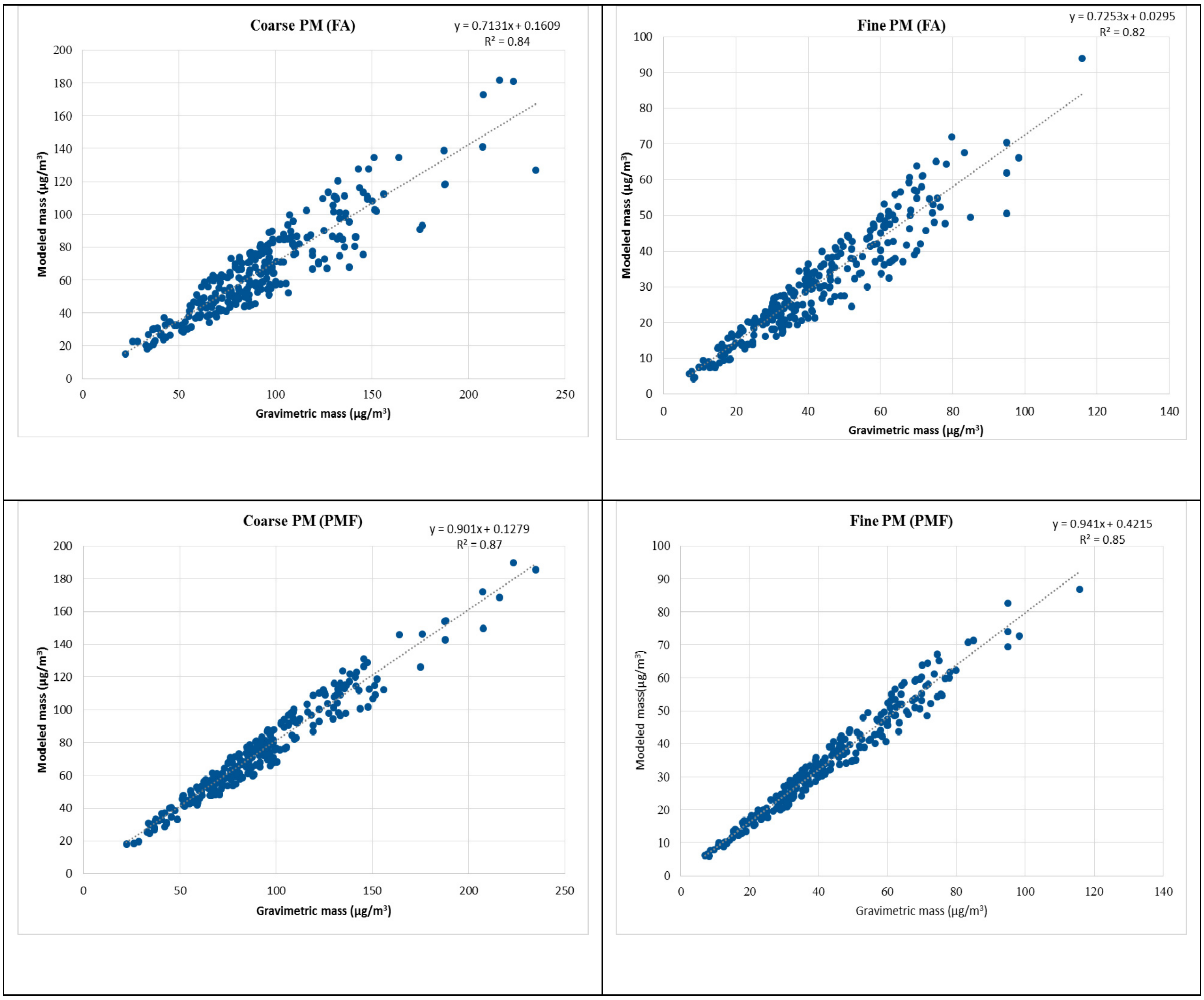
Table 4.23: Comparison of the results derived by the two receptor models (PCA-MLR and PMF)

Parameter		**PCA-MLR**		**PMF**	
		Coarse	**Fine**	**Coarse**	**Fine**
Model performance	r^2 of measured and modeled PM concentration	0.84	0.82	0.87	0.85
	Co efficient of Determination	0.82	0.81	0.84	0.82
Source identification	Number of sources	6	7	6	7
	Identified sources	Soil Seasalt Fugitive dust Vehicular emission Industry Construction	Soil Oil combustion Vehicular emission Sea salt Industry Coal combustion Fugitive dust	Soil Seasalt Fugitive dust Vehicular emission Industry Construction	Soil Oil combustion Vehicular emission Sea salt Industry Coal combustion Fugitive dust

4.13.1 Model performance

As a first step of evaluation of the models utilized in this study the ability of each model to reproduce the daily measured concentrations of coarse and fine PM was estimated. The daily measured and the modeled concentrations were regressed (Figure 4.22). It was found that both the models provided good results regarding their ability to reproduce the measured values. The dispersion between measured and modeled data was found to be lowest for PMF ($R^2 = 0.87$ and 0.85 for coarse and fine PM respectively) and also the slope of the correlation curve was near to unity with the low intercept. Whereas, intercept and slope were observed to be slightly higher in the case of PCA. Also, the correlation coefficient was comparably lower for PCA with the $R^2 = 0.83$ and 0.81 for coarse and fine fraction PM. Therefore, both the models provided highly satisfactory results, but at the same time PMF showed lowest dispersion and also the average difference between modeled and measured results was found to be minimal with PMF.

Figure 4.22: Regression plots of modelled and measured values of PM$_{10-2.5}$ and PM$_{2.5}$



4.13.2 Source Identification

FA and PMF models were able to distinguish 6 potentially contributing sources of coarse fraction and 7 sources for fine PM. The number of sources identified by FA and PMF were found to be similar. However, two different techniques were applied to confirm the appropriate number of sources while applying PCA and PMF. In the case of PCA number of factors was decided based on few aspects like, total variance explained by the resolved factors, variance explained by each factor and the eigen value of each factor. When each factor explains the maximum total variance of the data set, this set becomes completely uncorrelated with the rest of the data. The total variance explained in coarse and fine PM based on the decided number of factors were around 88 and 90 % respectively. Eigen value of each identified factor in both the size fraction ranged from 7.5-1. Next to the variance, rotation parameters play an important role in the identification of the factors. In this study one of the orthogonal method namely varimax rotation was incorporated. The factor loadings obtained after the varimax rotation gives the correlation between the variables and also this type of rotation uncorrelates one factor from other either by lowering the loading values near to zero or by maximizing it to one. Therefore, the complication due to overlapping of different sources has been avoided to some extent after the rotation. Thus, the chemical elements with higher loading in each factor were used for the interpretation of fingerprints of each emission source that it represents.

In the case of PMF analysis, the optimal number of factors was identified after analyzing the goodness of fit Q-values for the entire run, the scaled residual matrices, G-space plots, and physical meaningfulness of the factor profiles and contributions [268]. The model was run for 20 times each for coarse and fine PM data set with a 6-factor and 7-factor solutions respectively. All runs converged and a global minimum was found. The Q-robust of the present study was found to be equal to the Q-true, indicating no outliers impacting the

Q value. Since Q values are considered as goodness of fit values, table explaining Q-robust and Q-true are provided in appendix (Appendix A1). Also G-space plots of the base solutions derived for coarse and fine PM are provided in the appendix to analyse the distinct edges as well as any interdependence among the sources. The G-space plots showed least edges for 6 and 7 factor solutions of coarse and fine PM. G-space plots are presented in appendix A2. After a reasonable solution was found, the uncertainties in the modelled solution were estimated using a bootstrapping technique. A total of 100 bootstrap runs were performed to assess the uncertainty of the factor loadings and scores. Of the 100 runs, all the 6-factors of coarse and 7-factors of fine were mapped to a base factor in every run indicating a stable result. Residuals were also found to be between 3 and –3 for all the species. Other than the model performance parameters sources were also identified and confirmed on the basis of major marker elements of the sources and the percentage of the species in each source.

A sensitivity analysis was also carried out to evaluate the performance of the receptor models regarding the identification of sources [269]. Generally, model precision can be expressed in terms of Average Absolute Error (AAE %), which is the average of the absolute percent differences between the estimated and experimental PM data, when different number of sources or factors were considered. To evaluate the modelled values χ^2 values were also calculated following Watson et. al., [270]. The chi square is the weighted sum of squares of the differences between the calculated and measured fitted species concentrations. The weighing is inversely proportional to the squares of the precisions in the source profiles and the ambient data for each species. It is considered that a value less than 1 indicates a very good fit of the data. Number of factors varied from 3 to 8 with PCA and PMF and the corresponding AAE % is presented in Table 4. 24.

Table 4.24: Sensitivity analysis results of PCA and PMF

No. of Sources	**PCA, AAE%**		**PMF, AAE%**		**PCA, χ^2**		**PMF, χ^2**	
	Coarse	**Fine**	**Coarse**	**Fine**	**Coarse**	**Fine**	**Coarse**	**Fine**
3	23	26	20	25	8.42	9.56	6.85	7.41
4	20	22	17	18	4.84	8.93	5.99	7.14
5	18	19	16	15	2.35	8.23	3.23	6.61
6	**14**	15	**11**	14	**0.83**	2.97	**0.34**	2.98
7	NVS	**12**	13	**10**	6.92	**0.56**	4.75	**0.29**
8	NVS	16	14	13	9.11	3.79	5.23	3.17

For coarse particles when PCA was applied, AAE improved significantly from the 3-factor to the 6-factor model. But PCA produced invalid solutions for 7 and 8 factor models. Whereas, when PMF was used AAE improved progressively from 3-7 factors providing minimum AAE for 6 and 7 factor solutions. But when the F-matrix of 7-factor solution was analyzed the results had no physical meaning. When the solution was derived for 8-factor error started increasing confirming the 6-factor model selected was suitable for the coarse particulate data set. When fine PM data set was used for the source identification using PCA and PMF gradual decrease in the AAE was observed from 3-8 factor solutions but abruptly higher error was attained as well as the solution was not found meaningful for 8-factor solution in both the models emphasizing that the 7-factor model is appropriate for the fine PM. Similarly when χ^2 value was evaluated, 6 factor model of coarse and 7 factor model of fine PM values less than one was obtained which confirmed the number of sources identified were explaining the observed values closely.

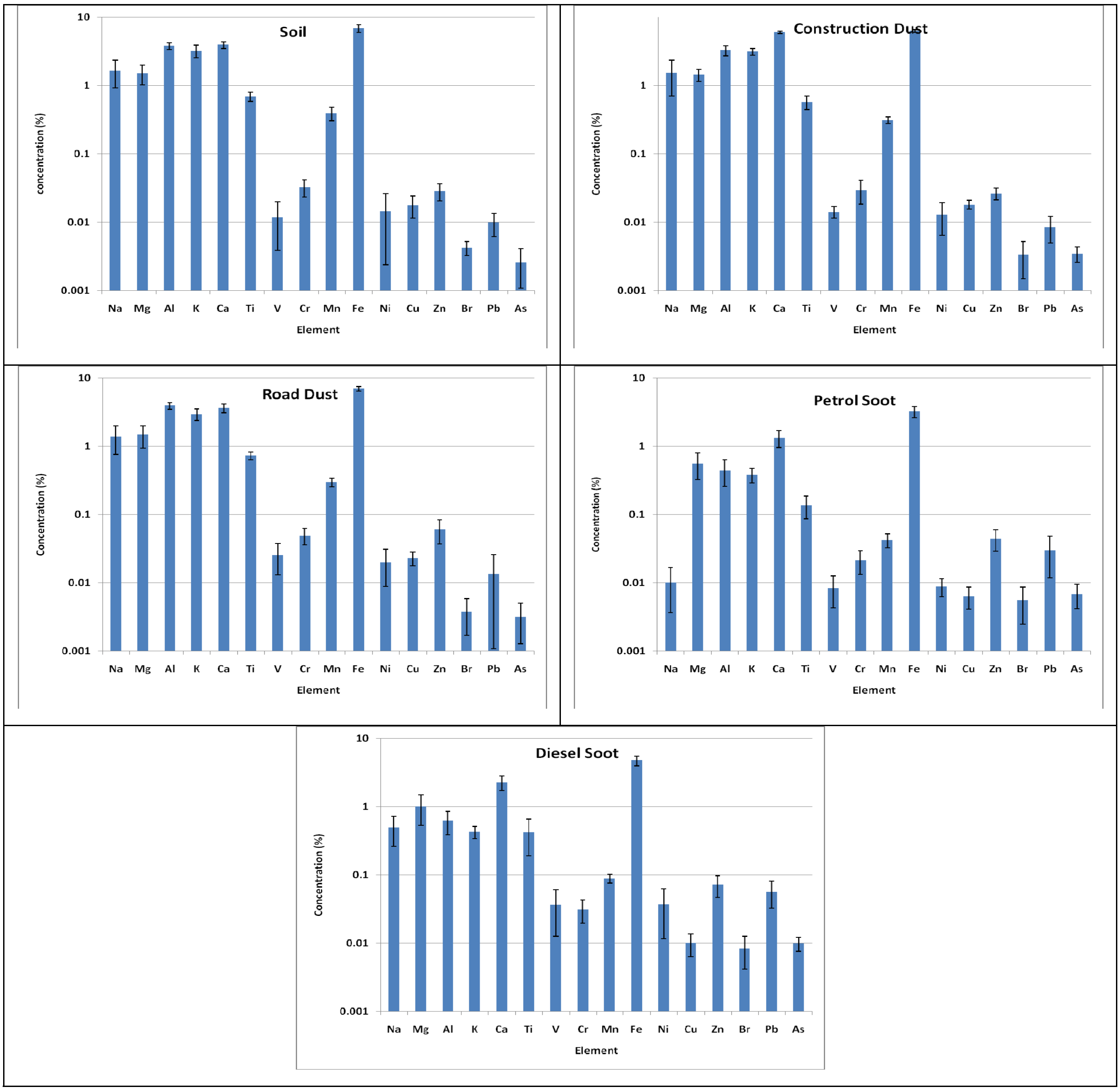
4.13.3 Source Profiles

Same numbers of sources have been obtained in this study for coarse and fine PM after the application of different source apportionment techniques. But the source profiles obtained in both the cases cannot be compared directly. As for the PCA results are concerned, the magnitude of the species contributions are in different unit because the concentration of different species were normalized prior to the analysis. But the key marker elements were clearly identified for all the sources. However, the strong loadings of a group of tracer species indicated the emission of possible source which were again confirmed by the high concentrations of those species in a particular factor profile resolved by PMF. Further, some of the source profiles derived by PMF analysis were validated by comparing it with experimental results. Road dust collected from paved roads, construction dust collected from building sites, soil samples, soot samples of petrol and diesel vehicles sampled from the tailpipes were analyzed for various trace elements and the elemental profile acquired are highlighted in Figure 4.23.

Chemical profiles of soil, road dust and construction dust were seem to be dominated by crustal elements such as Al, Ca, Fe and Ti. But the road dust samples were characterized with higher levels of Zn, Cu and Pb indicating contributions from tyre wear and lead prevalence in the soil even after the usage of unleaded gasoline in Mumbai [134]. Speciation of construction dust revealed almost two percent higher calcium concentration in the construction dust suggesting the input from cement usage. However, the percentage contribution of calcium was marginally lower than calcium levels of construction dust reported by [271]. Whereas, diesel and petrol soot samples showed appreciable contribution of elements like V, Ni, Cr, Zn, Pb and Cu other than the crustal based elements. The combustion of the fuels is the principal source for Co, Ni, and V, while tire rubber abrasion and brakes are found to be the major contributors to Cd, Pb, Cu, Sb and Zn in the ambient air near high–traffic zones. These elements are considered as the most abundant elements in gasoline and diesel exhaust emissions as mentioned by Li et al., 2013 [272]. Also the metal concentrations were found to be higher in the case diesel exhaust emission as found in the study of Li et al., [272]. The experimental results of bulk fugitive dust samples of different sources provided similar markers as that of the elemental tracers identified by PMF model.

However, further study on size fractionated fugitive dust samples based on re suspension technique will definitely provide a deep insight into the finger prints of different emission sources in the study region.

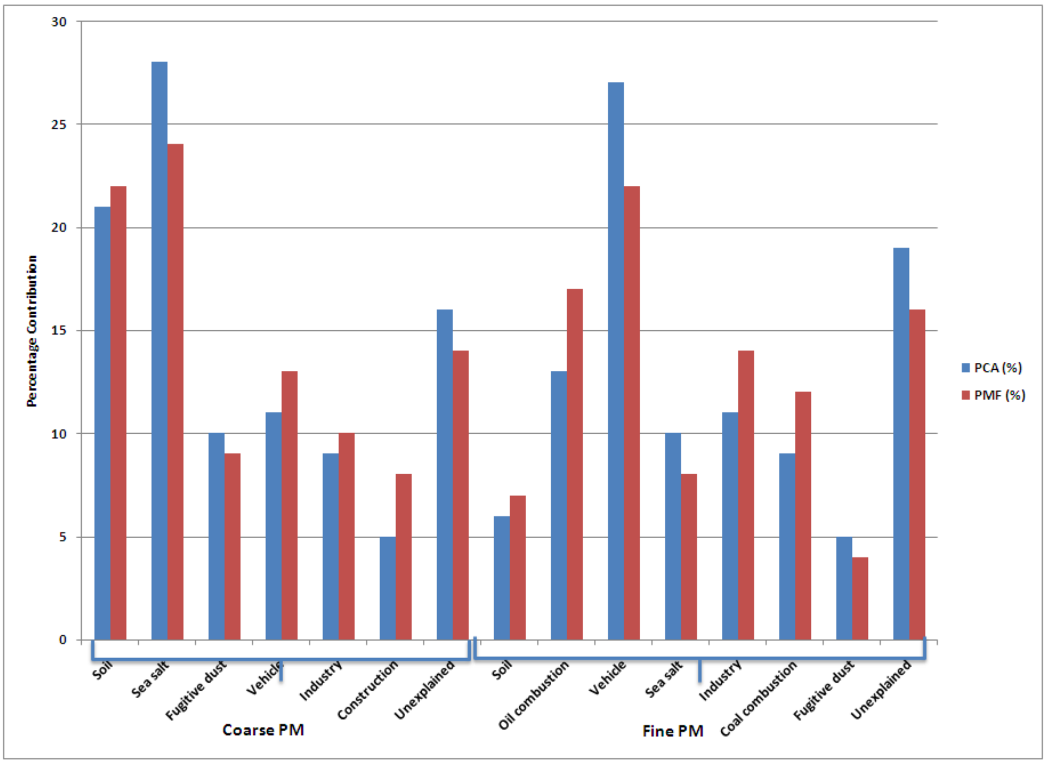
Figure 4.23: Chemical profiles of selected Fugitive sources of PM in the study area



4.13.4 Source contribution

Figure 4.24. presents the comparison of estimated average source contribution obtained from PCA and PMF model calculations.

Figure 4.24: Comparison of source contributions by PCA and PMF



Both the modeling technique could produce comparable results, both for coarse and fine PM. In case of coarse fraction sea salt and construction soure contribution found to be higher than PCA. But the comparison of the two models strongly suggested that the highest contribution to the coarse fraction is from natural sources like sea salt and soil. Percentage mass contribution from other man made sources found to vary minutely between the two models. While comparing the source contributions for fine fraction PM vehicular emission contributed to the highest. But there was approximately 5% enhancement of vehicular contribution was observed in PCA results compared with PMF analysis. On the other hand, around 3-4% reduction was seen for coal and oil combustion based sources in PCA. Contribution obtained by both the models for all the sources were comparable, especially for coarse fraction PM. However, marginal variations of mass contributions computed by PCA and PMF were observed in the case of fine fraction of the particulate matter.

Chapter – 5

Conclusions

The focus of this work has been to investigate the issues and severity regarding the current PM pollution in Navi Mumbai region. Therefore a comprehensive size fractionated aerosol study was conducted at an urban site Vashi, Navi Mumbai which is enveloped by various industries and a highway. The chemical composition and sources of atmospheric aerosols with differing environmental conditions has been examined. In particular, the focus was put on the analysis of present day PM composition in two size fractions, on the identification and quantification of present day PM sources. The study derived many interesting conclusions and from the study it is evident that local emissions and climatic conditions of the region play important roles in measured PM concentrations.

Concentration levels and temporal variations of PM:

- The ambient concentrations of coarse and fine particulate matter were measured for a period of 2008-2010. Comparatively high $PM_{2.5}$ and $PM_{10-2.5}$ were observed in this study with the annual means of 89.92 $\mu g/m^3$ and 42.25 $\mu g/m^3$. These results are in agreement with the results from previous studies in India/Mumbai.
- High levels of particulate matter and their exceedance were examined against the air quality standards laid by Central Pollution Control Board. Levels of PM in the present study was compared with the air quality standards stipulated for residential area which revealed around 70% of the total samples collected were exceeding the prescribed air quality standards. High concentrations were not just limited to the winter period as there were considerable exceedences observed throughout the study period irrespective of the seasonal cycles.

- Analysis of temporal variations of PM displayed that coarse and fine particles were seasonally distributed, with higher concentrations evident during the winter months. A maximum 24-hour average concentration of 93.3 μgm^{-3} was measured for $PM_{2.5}$. As far as the coarse fraction is considered the maximum 24-hour average measurement was 296.4 μgm^{-3}• Meanwhile, it was observed that there was an insignificant variation in the $PM_{2.5}/PM_{10}$ ratio with respect to the seasons and the average value (0.47) evaluated was found to be in the lower end of other similar studies which illustrated that domination of fine particles over the PM_{10} is insignificant in the study area.

- The consistent variation of coarse and fine PM suggested that perhaps there could be a steady input of local emissions to the particulate load in the site. Further detailed analysis of temporal variations of their corresponding chemical component confirmed the consistent nature of the contributions to the PM from various local sources such as traffic, re-suspended soil and industrial emissions rather than the influence of long range transport of aerosols.

<u>Characterization and mass closure of PM:</u>

- The combination of INAA –PIXE or INAA-EDXRF is advantageously used in aerosol studies, to enlarge the number of environmental important elements to be measured and also to evaluate and check the accuracy of the analytical procedures. Further, quality control studies were performed to check the precision and accuracy of the techniques by analyzing certified reference materials.
- All the three techniques were compared with each other by plotting linear regression plots and the comparison study explained the sensitivity of different techniques for the selected element. Results also showed that INAA is more sensitive and reliable than PIXE & EDXRF for certain elements like Na, Fe, Br etc. Whereas, PIXE & EDXRF

proved to be two promising tools by which most of the desired elements can be measured and are the best complement to INAA in the determination of Pb, S and Si in aerosol samples.

- Chemical characterization of coarse fraction depicted lowest concentration for Selenium and the highest for Silicon with the average of metal concentrations ranging from 2.93-6229 ng/m^3. In the case of fine fraction lowest concentration measured corresponded to Scandium, whereas the highest concentration was measured for Silicon and the average concentrations of elements in fine PM varied from 2.09-1615 ng/m^3.
- Among the inorganic ions measured sulphate and nitrate exhibited very high concentrations in both the size fractions demonstrating strong contribution of secondary aerosols. The average concentration of sulphate in coarse and fine fraction was 11.06 and 7.89 µg/m^3 respectively. Whereas the average concentration of nitrate was 6.69 and 5.73 µg/m^3 in coarse and fine PM respectively.
- Seasonal variation of trace metals during the entire sampling period was examined. Measured trace elements were grouped into three categories. First group of elements consisting Fe, Sc, Ti, Al, Ca, Mg, Na, K, Br and Cl which are expected to be natural origin showed a maximum during summer and a minimum during monsoon indicating soil drought and maximum evaporation of sea salt in the summer season. On the other hand second group of elements V, Ni, S, As and Se are distinctly higher during winter showing their anthropogenic origin. The third group of elements (Cr, Co, Cu, Pb and Sb) demonstrated high concentration coarse particles during summer and fine particles during winter suggesting contributions from both natural and anthropogenic sources.
- Results of seasonal variations of trace elements in this location illustrates that the atmospheric elemental concentration were likely affected by industrial emissions,

traffic volume and other meteorological parameters. As an evident enhanced concentration of BC and several traffic as well as industrial realated trace elements were measured.

- Aerosol mass closure was examined and this step was used as a key for the affirmation of percentage mass contribution of few sources to the atmospheric particulate load in the coarse and fine fractions. The mass concentrations of both the size fractions were reconstructed to a extent with a help of detailed analysis of chemical constituents. The major component in the fine particle size range were carbonaceous compounds (OC & EC), secondary ions (Sulfate+Nitrate) and ammonium. But results illustrated a reasonable contribution from soil and sea salt in the fine fraction. Whereas, maximum contributors in the coarse particle size range were soil and sea salt. All the measured and estimated components together accounted for 93% of fine particle mass and 90% of coarse particle mass. The remaining unidentified matter probably resulted from aerosol-bound water and possible systematic errors in the estimation of organic and crustal materials.

Source apportionment based on receptor model techniques:

- Enrichment Factor analysis was performed as a screening technique to mark the elements anthropogenically contributed in the site. The crustal enrichment factor of Silicon approached to unity in both the coarse and fine PM which indicated the strong contribution of resuspended soil in the atmospheric air of Navi Mumbai. Also EF's of other elements like Al, Ca, Sc, Ti, Mn and Mg in both the fractions were within 10 indicating their origin from crustal source.
- The moderately higher EF's of K, Cr, Mn, Co and Cu in $PM_{2.5}$ denoted that parts of these elements are derived from anthropogenic sources. Besides the aforementioned elements the atmospheric aerosols in Navi Mumbai were found to be extremely

enriched by As, Zn and Pb during the entire sampling period. The high EFs calculated for these elements indicated that they are present in atmospheric particulates in concentrations too high to be explained in terms of normal crustal weathering processes; consequently, it was assured that these elements are immensely originated from the anthropogenic sources.

- In the case of Marine enrichment analysis, K, Ca and Mg presented EF's slightly greater than 10. But Al, As, Cr, Cu, Mn, Pb, Ni, Se, V, Fe and Ti found to possess EF around 10^5. Broadly, the crustal and marine enrichment analysis suggested significant contribution of natural sources and in the meantime high enrichment of many elements emphasized that anthropogenic contributions cannot be ignored in the present study.
- Following EF analysis Spearman correlation study was performed to encounter the relation between the measured elements. The results revealed several strong and significant correlations among different pairs. Where, statistically significant correlations were exhibited between crustal species like Si, Al, Fe, Ca, Mg and Ti in both the size fractions of particulate matter. Similarly sea salt related elements (Na, Cl, K and Br) were correlated strongly among themselves. However, very strong correlations were established between few pair of elements such as V-Ni, As-Se, BC-S and Cu-Cr etc. in the fine fraction insisting and emphasizing considerable emissions from oil combustion, coal combustion, vehicular and other industrial emissions.
- As a first attempt in the identification of potential contributing sources of the study region a multivariate receptor model PCA was applied. Six potential sources with significant eigen values (>1.0) were obtained for coarse PM explaining 88% of the total variance and for fine PM PCA yielded seven sources explaining 90% cumulative variance of the data.

- The most probable sources identified by PCA were then apportioned by following multiple linear regression technique. The study revealed Crustal source, sea salt, fugitive dust, vehicular emission, industrial emission and construction activities as the major contributors for coarse fraction PM and the apportioned percentage of mass was 21, 28,10,11, 9 and 5 percentages respectively. Whereas, vehicular emission (27%), oil combustion (13%), industrial emission (11%) and coal combustion (9%) contributed maximum to the fine fraction along with considerable mass fraction of soil (6%), sea salt (10%) and fugitive dust (5%). These results are in line with those source identification studies conducted at different parts of India, specifically at Mumbai.
- Validation of source apportionment results by cross-checking with independent methods is advisable for every source apportionment study. Consequently, considering inter-comparison of the different source apportionment methods as a crucial step for the validation of model results and for the identification of advantages in the different methods, another receptor model PMF was employed for the same data set.
- PMF was able to extract all the sources as that identified by PCA and the factors extracted represent specific chemical species or important classes of substances and were similar to those extracted by PCA. The outputs of PCA and PMF certainly confirmed the large impact on atmospheric particles of the multiple anthropogenic activities in the study area that too to a high extent especially in the fine fraction.
- Inter-comparison of source apportionment of coarse and fine PM obtained by PCA and PMF approaches has been performed. This allowed on the one hand a reciprocal validation of the results obtained by the single individual apportionment methods, and on the other hand permitted the identification and discussion of the strengths and weaknesses of the different methods. The agreement between source contributions estimated with the different source apportionment approaches was better for both the

size fractions. But definitely, PMF analysis applied for the speciation data set presented very clear, well defined and characterized chemical profiles in the comparison of PCA analysis.

- The overall performance of the two receptor models analyzed (PCA and PMF) could be defined as good, with R^2= 0.83 and 0.81 for coarse and fine PM respectively when regression analysis was performed between modeled and measured results of PCA and R^2 value was 0.87 and 0.85 for the PMF model. AAE were calculated for different numbers of factors/sources for both the models, and they improved significantly in all cases towards the optimal solution (23–14% & 26-12% for coarse and fine PM using PCA, 20–13% for coarse & 25-10% for fine fraction using PMF).
- To strengthen the conclusions regarding source profiles derived by PMF, bulk samples of soil, road dust, construction dust, diesel and petrol soot were analyzed for their chemical composition. Results showed crustal elements as the most abundant species contributing to the maximum in soil, road dust, construction dust and even in soot samples. But, along with this the elemental markers of different sources resolved by both the receptor techniques were also confirmed through the high percentage contributions in the bulk samples.

Overall, the study showed elevated levels of mean fine and coarse particle concentrations Thus, the presented chemical and source analyses of size-segregated particulate samples can be considered as useful background information for any further studies to be conducted in the study region. Variations were observed in the atmospheric aerosol loading and trace elements as a function of particle size and season. The observed variations can be attributed to source diversity, different season and meteorological conditions. Principal component analysis in combination with multivariate linear regression proved to be a useful tool for extracting sources of PM from complex urban PM mixtures.

PMF has also been proved as a effective tool in the extraction of elemental profiles of major contributing sources. Although PCA and PMF techniques were able to identify six and seven sources for coarse and fine PM in Navi Mumbai during the study period, it is not reasonable to assume that all sources were identified. In a sense, that the factors determined by receptor techniques may not contain all emission sources in the region. However, the dominant or major sources of $PM_{10-2.5}$ and $PM_{2.5}$ in the site during the sampling period were identified by receptor model techniques. Therefore, the impact of regional pollution is evident in this study.

The major source categories identified for coarse fraction are of natural origin (Soil and sea salt) with a substantial contribution from road dust. Whereas, fine particles illustrated highest contributions from anthropogenic sources with a less influential crustal and sea salt sources. The maximum contribution of vehicular, industrial emissions and the local combustion of coal and oil to the average $PM_{2.5}$ concentration highlights the great importance of this PM fraction as a determinant of ambient particulate pollution at Navi Mumbai rather than measuring PM_{10} as a whole.

Suggestions for future research

As demonstrated in this study long-term chemical characterization measurements are useful to determine trends in PM composition and source contributions. Several issues related to sources and characteristics of particulate matter that will require further research were recognized during the course of this work. There is a need to compile an accessible database on tracers and elemental profiles for various emission sources in TTC industrial estate and enhance the use of source apportionment techniques.

The source apportionment study can be refined by including the molecular tracers and organic markers of atmospheric particulate matter and the approach may help in overcoming the underestimation of plausible sources, by providing additional source attribution information. An attempt can be made to use receptor modeling in conjunction with routine monitoring and emission inventories to establish the key sources where this method can be used as a complementary technique to the demonstrated receptor techniques. Also the trans-boundary sources and their preferred transport pathways can be predicted to confirm the long range transport of fine particulates by applying various trajectory ensemble models. In view of health perspectives, studies related to the estimation of integrated inhalation risk due to the exposure of atmospheric trace elements through inhalation pathway can be carried out in the future. The risk estimation study has been initiated already and as a preliminary step inhalation non cancer risk for children and adults are being computed based on the present ambient level of trace elements.

Appendix

Appendix: A1

Goodness of fit Q-values of PMF base runs

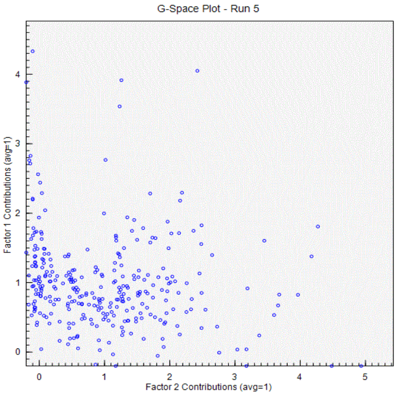
Run	**Coarse PM**			**Fine PM**		
	Q (robust)	**Q (True)**	**Q_t/Q_r**	**Q (robust)**	**Q (True)**	**Q_t/Q_r**
1	4815	5761	1.19	4315	5272	1.22
2	4894	5776	1.18	4317	5312	1.23
3	4834	5753	1.19	4340	5284	1.21
4	4766	5766	1.21	4427	5351	1.20
5	4821	5705	1.18	4255	5268	1.23
6	4835	5768	1.19	4371	5313	1.21
7	4789	5693	1.18	4318	5312	1.23
8	4817	5802	1.20	4358	5289	1.21
9	4756	5722	1.20	4367	5326	1.21
10	4802	5784	1.20	4431	5352	1.20
11	4822	5704	1.18	4263	5310	1.24
12	4836	5765	1.19	4256	5309	1.24
13	4782	5740	1.20	**4185**	**5220**	**1.25**
14	**4742**	**5731**	**1.20**	4222	5254	1.23
15	4756	5723	1.20	4340	5284	1.21
16	4800	5730	1.19	4373	5324	1.21
17	4756	5721	1.20	4391	5355	1.21
18	4817	5766	1.19	4273	5247	1.22
19	4784	5709	1.19	4273	5265	1.23
20	4838	5757	1.18	4351	5329	1.22

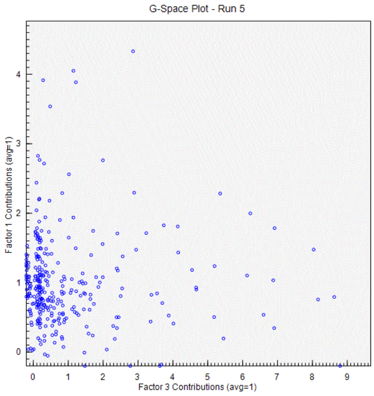
Appendix A2:

G-space plots for 3-8 factor models of PMF analysis

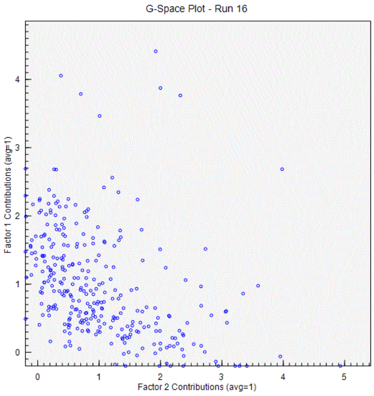
Coarse PM:

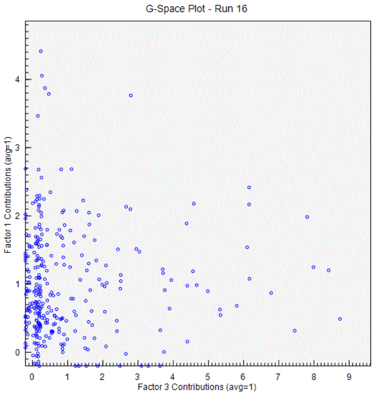
3 factor model

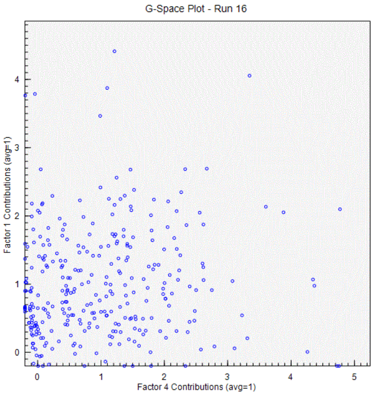




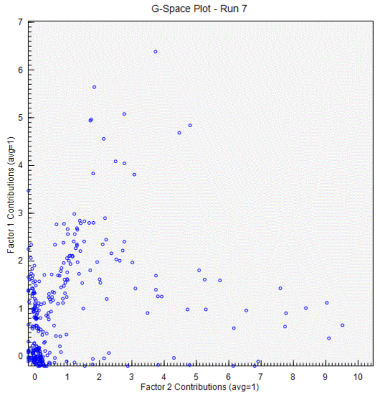
4 Factor model

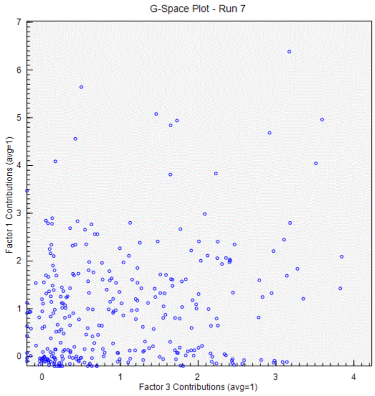






5 Factor model





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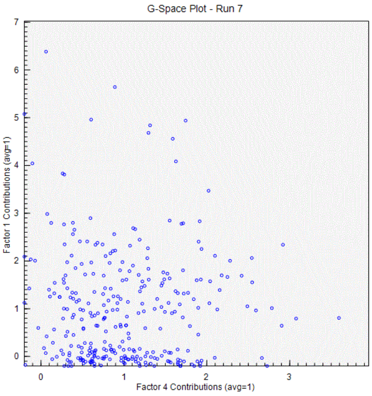
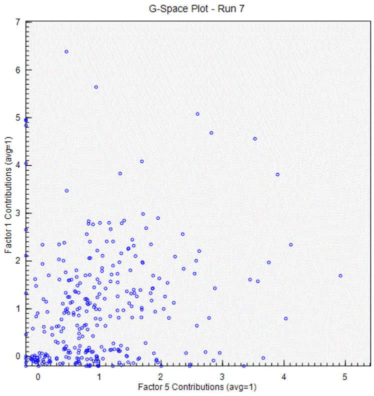
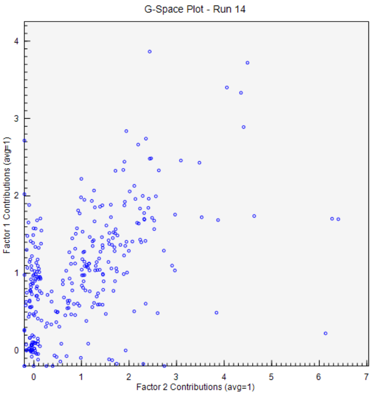
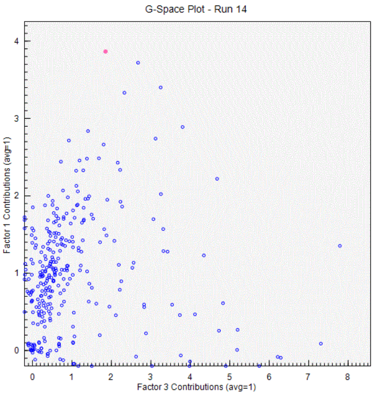

G-Space Plot - Run 7


G-Space Plot - Run 7

6 Factor model


G-Space Plot - Run 14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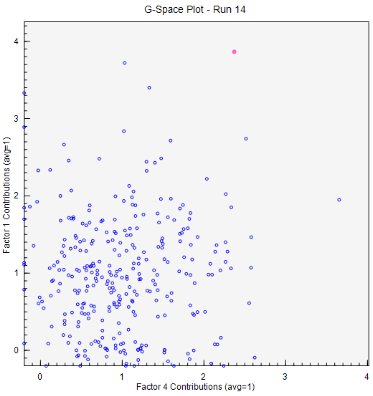
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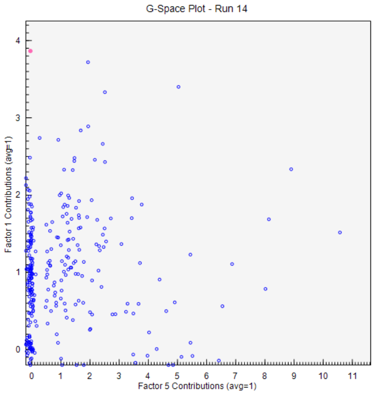
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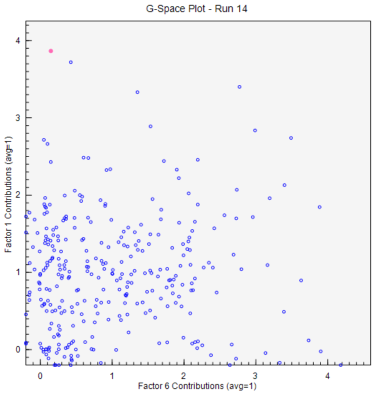
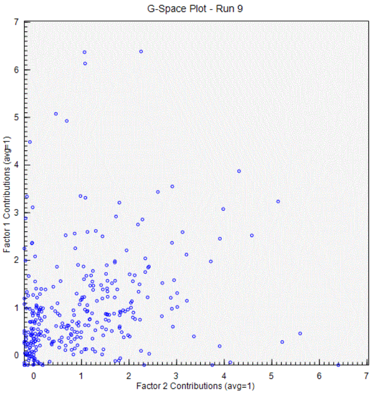
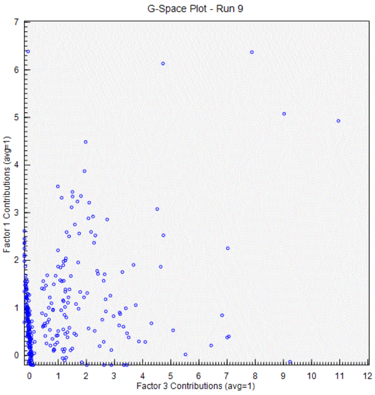
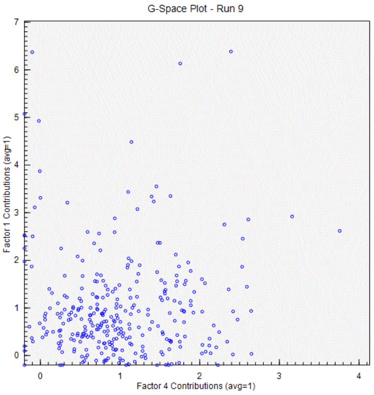
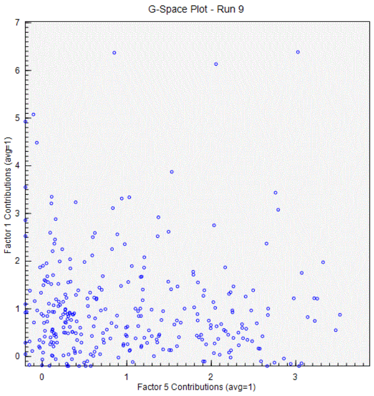

G-Space Plot - Run 14

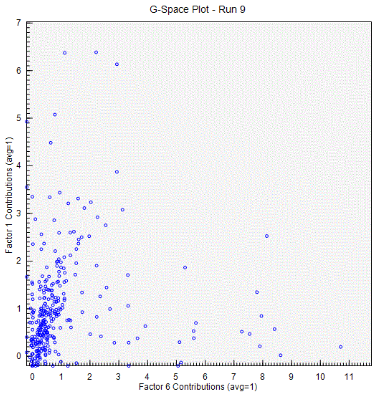
7 Factor model

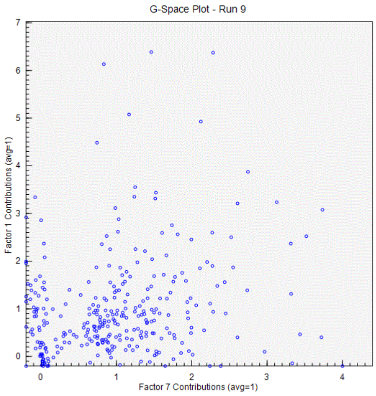

G-Space Plot - Run 9


G-Space Plot - Run 9

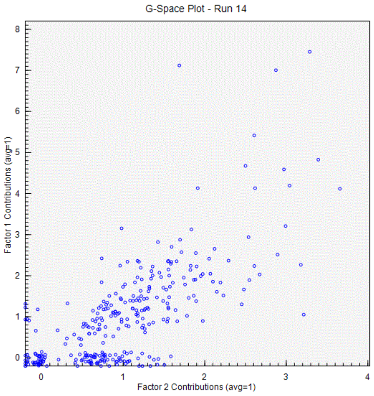

G-Space Plot - Run 9

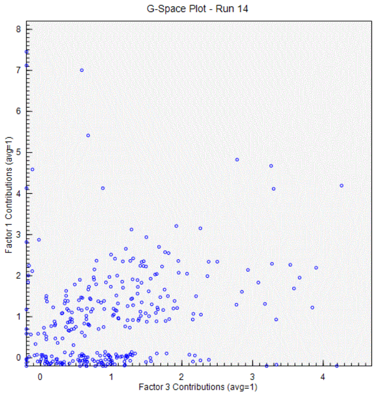


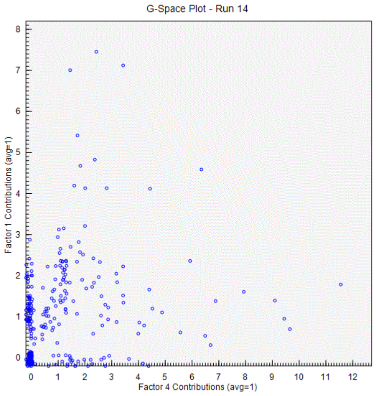


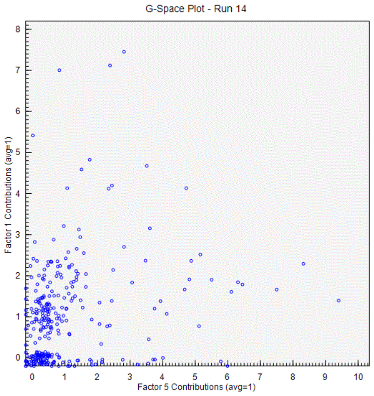


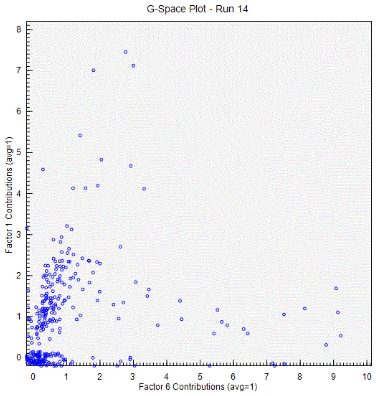
8 Factor model

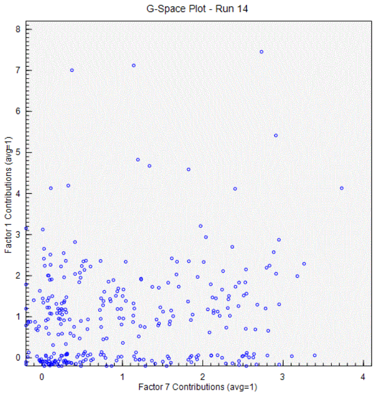


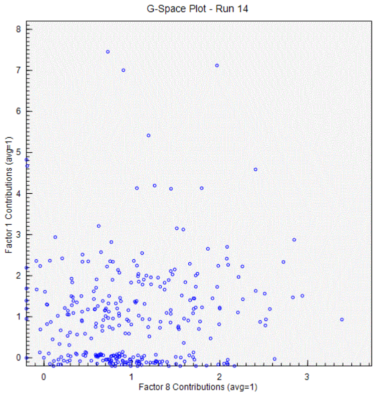






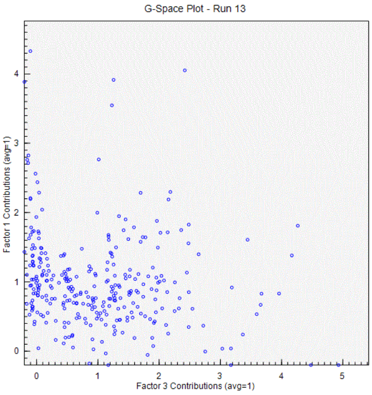


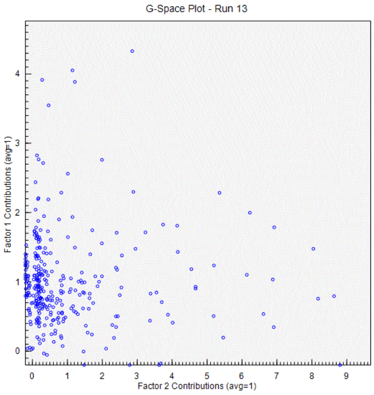




Fine PM:

3 Factor model





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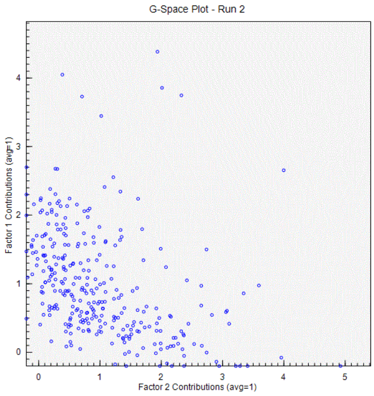

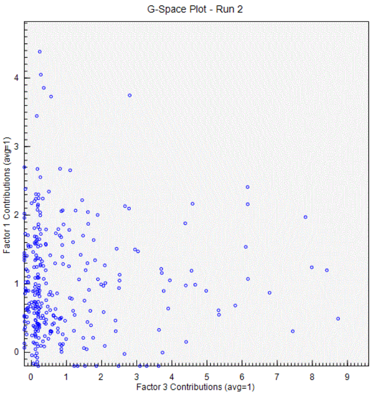

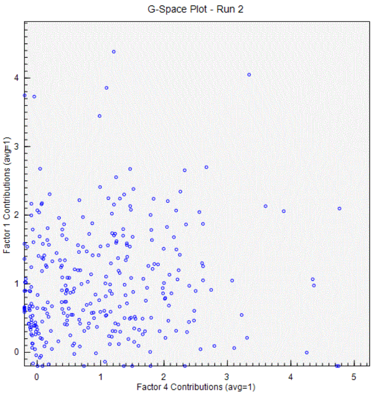

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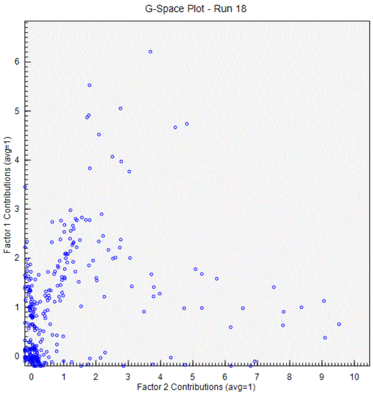

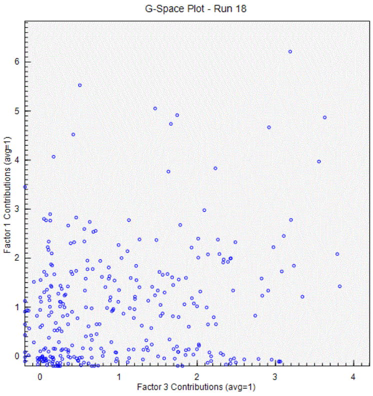

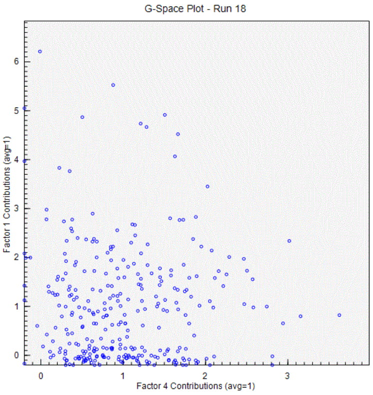

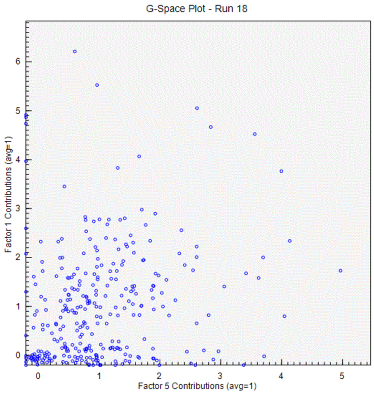

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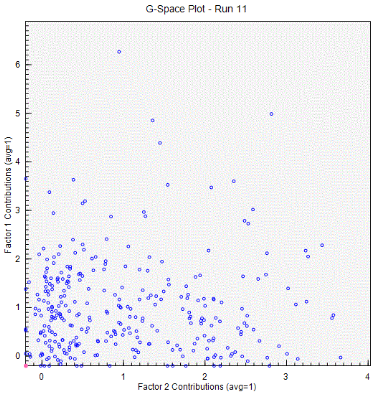
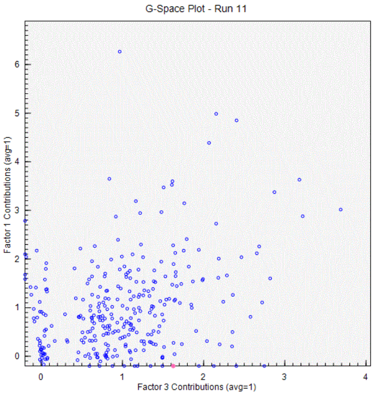
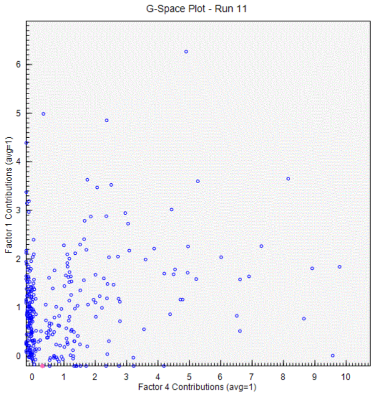
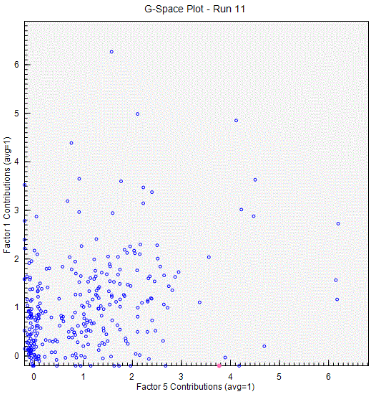
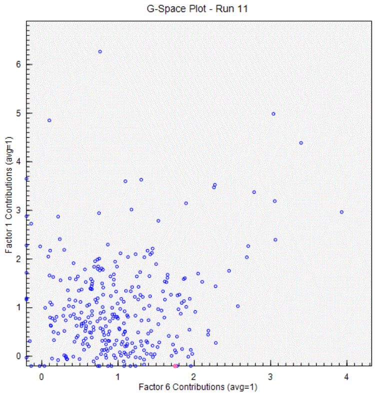


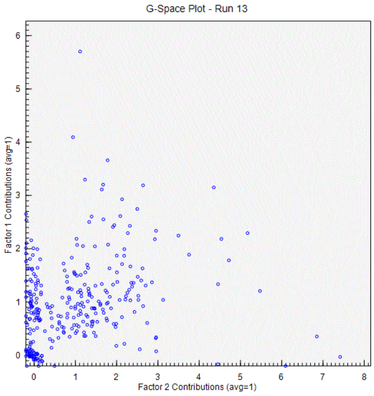


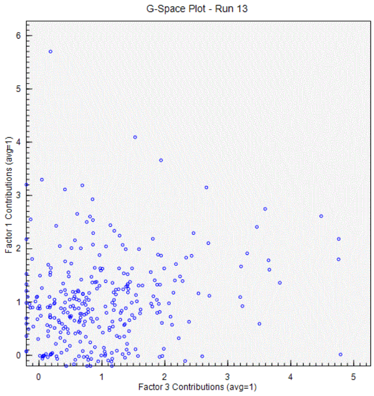


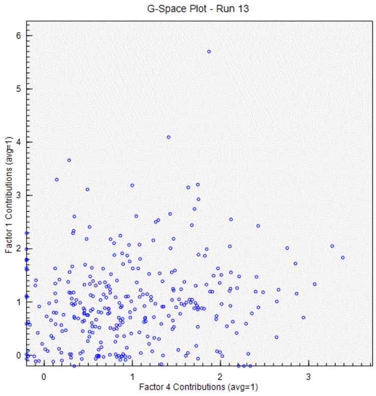


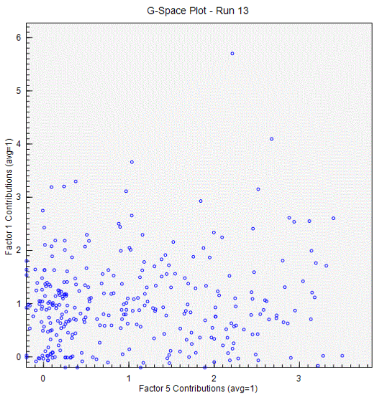


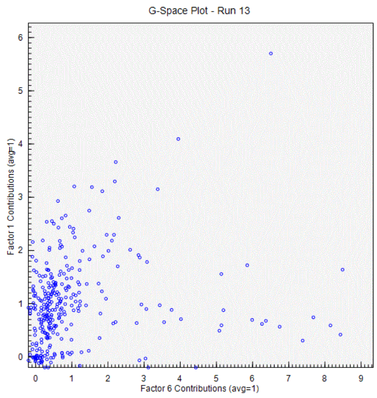
7 Factor model

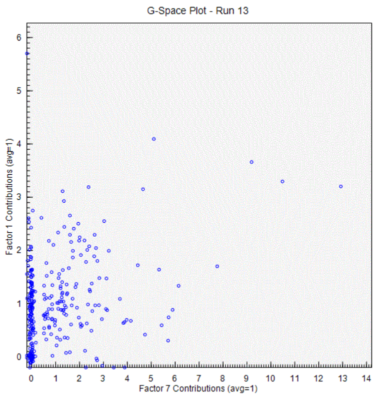




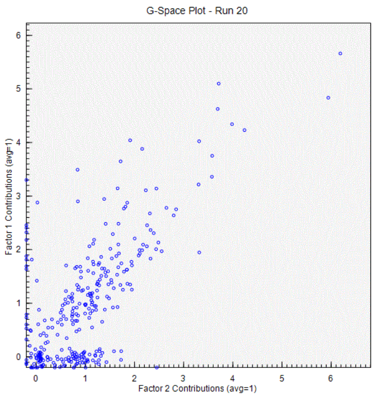


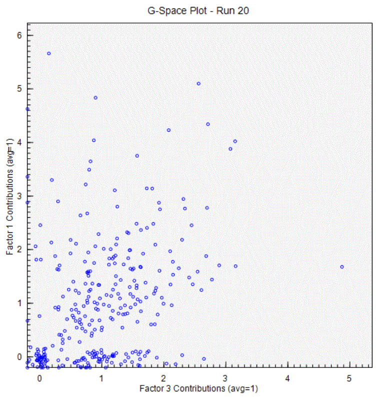


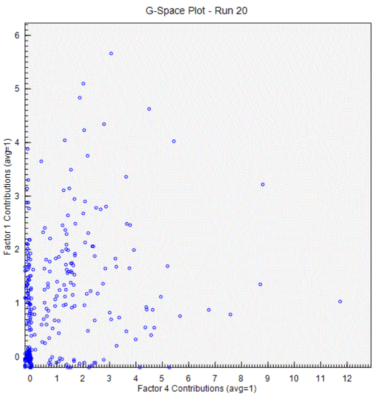


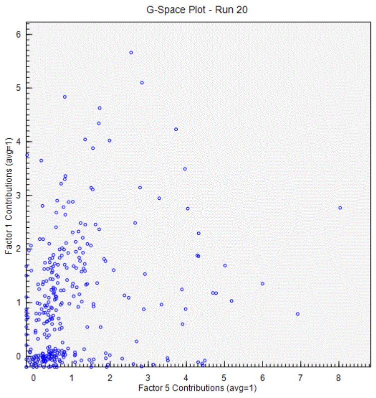


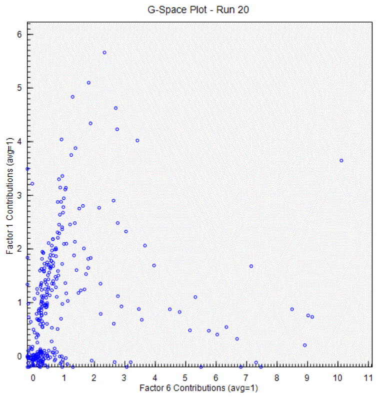
8 Factor model

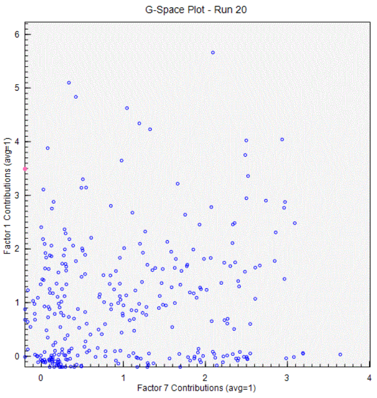


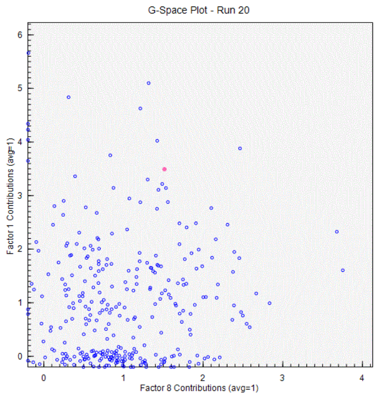












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