Physico-chemical characterization of airborne Particulate matter and source apportionment using different receptor models

By

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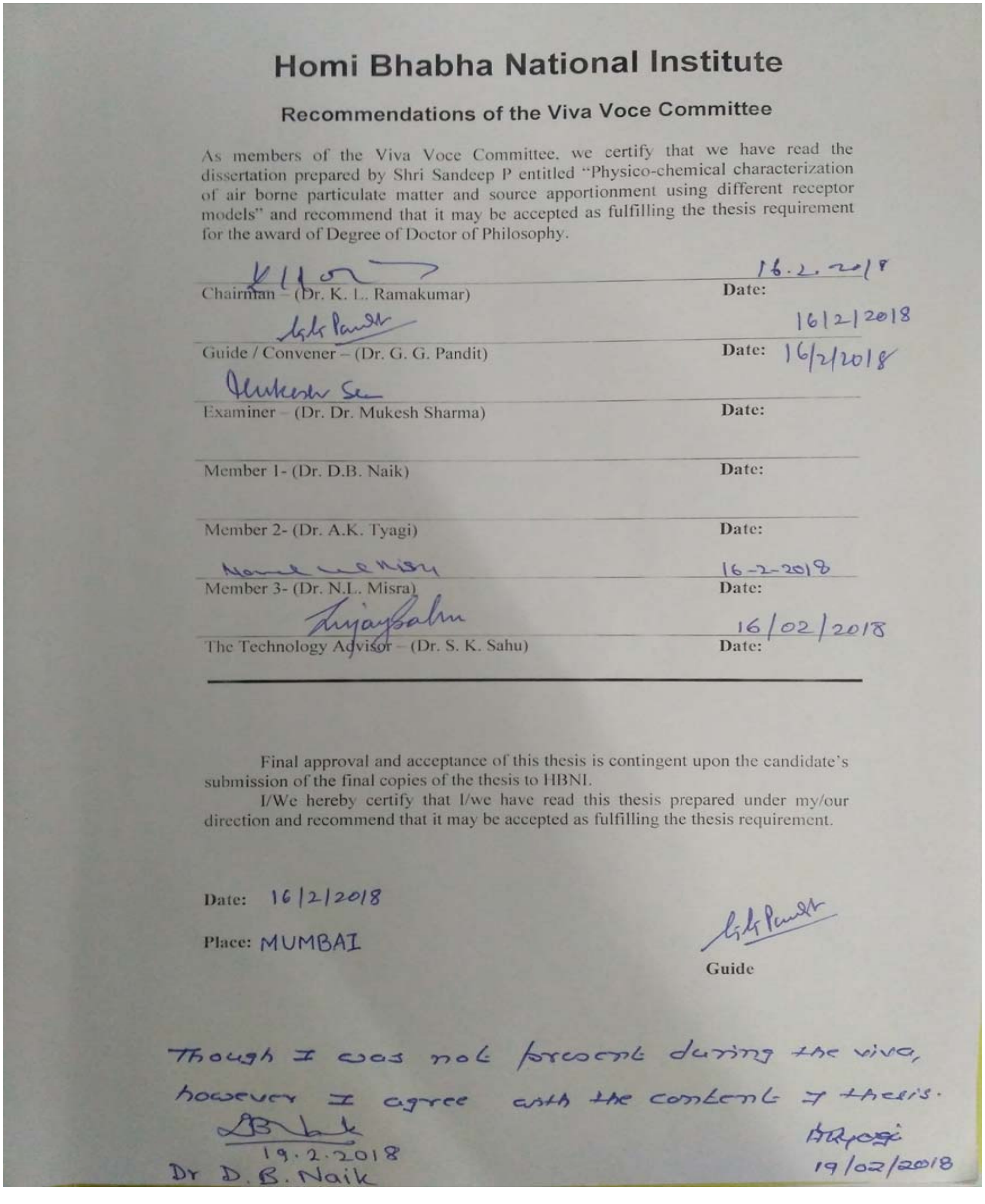

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DECLARATION

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List of Publications arising from the thesis

Journals

1. Seasonal Variation of Black Carbon in Fine Particulate Matter ($PM_{2.5}$) at the Tropical Coastal City of Mumbai, India
   P. Sandeep, I. V. Saradhi and G. G. Pandit
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2. Determination of multi-element profiles of soil at Visakhapatnam using EDXRF technique
   P. Sandeep, P. Kothai, C. B. Dusane, S. K. Sahu and G. G. Pandit
   Journal of Radioanalytical and Nuclear Chemistry, **2014**, 302, 1371–1376.
3. Chemical characterization of atmospheric particulate matter and their source apportionment at an emerging industrial coastal city, Visakhapatnam, India
   P. Sandeep, S. K. Sahu, G. G. Pandit
   Atmospheric Pollution Research, **2016**, 7(4), 725–733.
4. Chemical composition and source apportionment of $PM_{2.5}$ and $PM_{2.5–10}$ in Trombay (Mumbai, India), a coastal industrial area
   P Sandeep, S.K. Sahu, M. Tiwari and G.G. Pandit
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Conferences/Symposia

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2. Determination of multielement profiles of soil at Visakhapatnam using EDXRF technique
   P. Sandeep, P. Kothai, C.B. Dusane, S.K. Sahu and G.G. Pandit
   Proceedings of Nuclear Analytical Chemistry symposium January 20-24, **2014**, 190-191.
3. Estimation of Pb, Cr and Ni in size fractionated atmospheric aerosols using X-ray fluorescence spectrometry
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   In the proceedings of NUCAR-12 held at Nabhikiya Urja Bhavan, Mumbai during 9-13th February, **2015**, 601-602.
4. Chemical characterization of air borne particulate matter using EDXRF and source identification at an industrial area Trombay, Mumbai, India
   P. Sandeep, M. Tiwari, S.K. Sahu and G.G. Pandit,
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LIST OF ABBREVIATIONS

AAS- Atomic Absorption Spectrometry

AI (Alloy industry)

AO (Ore industry)

AP-Andhra Pradesh

BC- Black Carbon

CMB-Chemical Mass Balance

CPF- Conditional Probability Function

CPCB- Central Pollution Control Board

CR-(road dust)

DAE-Department of Atomic Energy

DPASV- Differential Pulse Anodic Stripping Voltammetry

EC-Elemental Carbon

EDXRF- Energy Dispersive X-ray Fluorescence

EF-Enrichment Factor

FA-Factor Analysis

EU- Europion union

GI-(Granite industry)

HYSPLIT- Hybrid Single Particle Lagrangian Integrated Trajectory

ICP-AES- Inductively Coupled Plasma Atomic Emission Spectrometry

IC- Ion Chromatography

NAAQS- National Ambient Air Quality Standard

OC-Organic carbon

OPC-Optical particle counters

PCFA- Principal Component Factor Analysis

PMF-Positive Matrix Factorization

PM-Particulate matter

PR-(petroleum refineries)

RSPM-respirable suspended particulate matter

RM-Receptor Model

SA- Source apportionment

SB (southern biotech industry)

SFU-Stacked Filter Unit

SSR- Smoke Stain Reflectometer

TEOM-Element Oscillating Microbalance

TPP (thermal power plant)

USEPA- United States Environmental Protection Agency

WHO- World health organization

Na- Sodium; **Mg**-Magnesium; **K**- Potassium; **Al**- Aluminum; **Ca**- Calcium; **Si**-Silicon; $\mathbf{Cl^-}$-Chloride; $\mathbf{SO_4^{2-}}$- sulfate; $\mathbf{NO_3^-}$ - Nitrate; $\mathbf{F^-}$ - Floride; **V**- Vanadium; **Cr**- Chromium; **Mn**-Manganese; **Fe**- Iron; **Cu**- Copper; **Ni**-Nickel; **Zn**- Zinc; **Pb**- Lead; **As**-Arsenic;

SYNOPSIS

Clean air is the foremost requirement to sustain healthy lives of mankind and those of the supporting ecosystems which in return affect the human well-being. Release of various gaseous pollutants and particulate matter (PM) into the ambient air is enhanced enormously in the recent times due to global industrialization. Among different air pollutants, atmospheric PM became a serious environmental issue all over the world. Ever since the advent of the industrial era, anthropogenic sources emissions have been increasing rapidly [1]. These sources can emit particles having wide size ranges; out of which PM having diameter less than 10 μm is the most important as these particles have the ability to penetrate the human respiratory system, hence called Respirable Suspended Particulate Matter (RSPM or PM_{10}). RSPM is generally grouped into three modes: ultra-fine (particles having aerodynamic diameter < 0.1 μm), fine (particles having aerodynamic diameter ≤ 2.5 μm) and coarse (particles having aerodynamic diameter between 2.5–10 μm) [2]. Previous research studies on PM proved that, PM_{10} can play pivotal role in the climate change, cloud dynamics, human health, fog formation and reducing visibility through a variety of atmospheric processes. Hence, the studies on PM having diameter less than or equal to 10 μm are growing day by day all over the world.

The PM air pollution is a serious issue in Asian countries especially in India because of enormous growth in industrialization, urbanization, population, construction sector and transportation sector [3]. According to WHO (WHO, 2015), Indian cities today are among the most polluted areas in the world and it is estimated that outdoor air pollution leads to approximately 6, 70,000 deaths annually [4]. Based on numerous epidemiological studies, the national authorities of India (Central Pollution Control Board, CPCB) are introducing steps to control ambient pollution in India. Although, the lack of coherent policy as well as unplanned growth across sectors is exacerbating pollution levels in most Indian cities.

In India, many studies on $PM_{2.5}$ and PM_{10} were conducted majorly in urban areas. The PM studies conducted previously [5-8] discussed the chemical species (inorganic and organic) concentration variations and the sources contribution to the collected PM at urban sites. These studies identified the sources solely based on the presence of marker/finger print elements without any experimental confirmation.

Thorough literature survey indicates that there are no much studies reported in India on PM pollution level, their chemical characterization and source apportionment at in and around DAE (Department of Atomic Energy) facilities. In view of ongoing developments in India, there is a need to extend the PM studies to the locations where DAE facilier are present.

With this adequate background current study was carried over two consecutive years i.e., from 2010 to 2011 at Jogannapalem, Parawada and Trombay locations of India. Jogannapalem (Visakhapatnam, AP) is a new DAE site, whereas, Trombay (Mumbai) is an established DAE site. Parawada (Visakhapatnam, AP) is a suburban location near Jogannapalem. These study sites are surrounded by many major and minor industries that may cause serious air pollution.

The Purview of the current study was to assess the PM and particle bound chemical species concentration levels; identification and quantification of PM sources using different receptor models; experimental confirmation of source profiles observed in receptor model and to carry out the chemical speciation of metals bound to PM at study locations. The data that generated in this study is important as it gives the baseline concentrations of PM_{10} pollution levels, trace and toxic metals concentrations at Jogannapalem. The source apportionment data of the present study can also be used to plan pollution mitigation strategies at study locations.

The thesis of the proposed Ph.D. work was divided into six chapters which briefly elaborate the work done during entire study period.

1. Introduction
2. Literature review
3. Mateirlas and Methods
4. Physico-chemical characterization of PM and chemical speciation of Arsenic at study sites
5. Source Identification and apportionment using different receptor models
6. Summery and Conclusions

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

Chapter-1: Introduction

This chapter starts with a discussion on the basic need of good air quality followed by a discussion on adverse effects of poor air quality on human health [1] as well as on environment. Further discussion was continued on various air pollutants that are important with respect to human and environmental health. After that, the definition of particulate matter (PM) and why PM studies are attracting many researchers from all over the world was also discussed.

In the next topic, most important and basic property of particulate matter i.e., size was discussed in brief [9]. This section also provided the information on the importance of studies on PM chemical composition and the various possible sources (natural and anthropogenic) that can contribute to PM [10]. These topics are followed by a discussion on various health effects [11] of PM. Additionally, different analytical techniques that are used for the chemical analyses of PM were also discussed [12, 13]. Different receptor model techniques that are used for the source apportionment study was also discussed [14, 15] in detail.

At the end of this chapter, the main reasons for selecting the present study locations are explained along with limitations of previous studies. The introduction chapter also briefly discusses the main objectives of the present study.

Chapter-2: Literature review

This chapter mainly discussed about the various studies that are carried out on PM in recent past [16-18]. Different kinds of instruments used in previous studies for sampling and chemical characterization of PM were also discussed in this chapter. Information on number of source apportionment studies been carried out till date in India were provided along with details on various mathematical tools used for source apportionment [19-21]. This chapter also highlights the limitations of previous studies which were carried out in India and how current study is important with respect to previous literature was also discussed.

Chapter-3: Mateirlas and Methods

This chapter mostly discussed about the various instruments and methodologies used in the present study for PM sampling [22, 23], particles bound elemental analyses [24], chemical speciation and source apportionment [25]. At the beginning of the chapter, different samplers used for PM_{10} sampling, their working principles were described. Chemical processing procedures (e.g. acid and water digestion) adopted for the extraction of various chemical constituents (metals and inorganic ions) bound to PM were also provided.

Further discussion was continued on the method optimization of destructive (Atomic Absorption Spectrometry (AAS), Inductively Coupled Plasma Atomic Emission Spectrometry

(ICP-AES) and Differential Pulse Adsorptive Stripping Voltammetry (DPASV) and Ion Chromatography (IC)) and non-destructive analytical techniques (Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) and smoke stain reflectometer) for the chemical analyses of collected PM. In the next step, the step wise approaches followed for identification and quantification of the sources contributing to collected PM were elaborated.

Chapter–4: Physico-chemical characteristics of PM and chemical speciation of Arsenic at sampling sites

4.1. Physico-chemical characteristics of PM at sampling sites

This chapter discussed and compared the PM_{10} concentration levels observed at all the three sampling sites. Experimental results of the comparison study carried out to evaluate the performance of PM_{10} samplers used (high volume sampler and Gent's dichotomous sampler) in the present work was also provided. Chemical characterization results of collected PM_{10} samples using different analytical techniques were discussed for all the study sites. Temporal and seasonal variations of PM_{10} and particulate bound chemical species were elaborated in detail.

In the present study, PM_{10} annual average concentrations were found to be 63.6 $\mu g/m^3$, 71.4 $\mu g/m^3$, 99.7 $\mu g/m^3$ in 2010, whereas for 2011 the observed annual average concentrations are 67.2 $\mu g/m^3$, 76.9 $\mu g/m^3$, 80.7 $\mu g/m^3$ at Jogannapalem, Parawada and Trombay sites, respectively. At all the study sites, the annual average PM_{10} concentrations were exceeding the Indian ambient air quality standard (60 $\mu g/m^3$) [26].

For quality control and quality assurance, NIST SRM 1649a reference material and some spiked filter samples were processed in the present study. Calibration of EDXRF for different elements was checked by analyzing known thin film standards and estimated bias (if any) was used as a correction factor to get final elemental concentrations. Inter comparison of elemental concentrations quantified using different analytical techniques viz. ICP-AES and DPASV was also done for few elements.

In the present study, no metal concentration was exceeded the Indian ambient air quality standards at Jogannapalem and Parawada sites. But, Ni concentration at Trombay site (33.3 ng/m^3) was exceeded the NAAQ standard. Concentration variation observed for Black carbon associated with PM was discussed along with its temporal and seasonal variations at study locations. In the present study, high BC concentrations observed at Trombay site are explained using HYSPLIT model.

4.2. Chemical speciation of toxic metal associated with PM

This section dedicatedly discussed the optimization of Hydride Generation Atomic Absorption Spectrometry (HG-AAS) technique for As chemical speciation and method validation using spiked samples. Using optimized method, chemical speciation analyses was carried out for As in PM collected at all the study locations. Results indicate that, As exists mostly in As^{+5} form.

In the current work, an attempt was made to do the chemical speciation of Cr using catalytic adsorptive stripping voltammetry (CAdSV). Diethylene triamino pentaacetic acid (DTPA) was used as a complexing agent for Cr speciation. Analysis was carried out as per the standard procedures given in the literature. Due to very low concentration of Cr in PM and high chemical interferences the Cr peak and peak shape was found to be distorted and suppressed. Hence, the Cr speciation in PM using other analytical techniques was taken up as a future work.

Chapter–5: Source Identification and apportionment using different receptor models

In this chapter, initial steps carried out to identify the PM sources are discussed. Later, PMF receptor model results were elaborated for each site; in the next topic, a discussion was made on the comparison of different receptor models viz. PCFA and PMF for the source identification and quantification. This chapter ends with a discussion on experiments carried out to verify the receptor model results. Source apportionment results using PMF model are briefly discussed below.

PMF results indicate that the three study locations share five common sources viz. crustal material, sea salt spray, coal combustion, fuel oil combustion and metal industry. The other sources include biomass burning at Jogannapalem; road traffic source contribution was observed at Trombay and Parawada site. Additionally, secondary aerosols source contribution was found at Parawada.

The comparison study on the receptor models (PMF and PCFA) clearly suggests that, PMF is more efficient in source identification and apportionment as compared to PCFA model. In the present study, the PMF factor profiles were experimentally verified by using source profiling technique.

Chapter 6: Summery and Conclusions

This chapter summarizes the results and overall conclusion of the present study. Few findings of the study are given below.

- Among all study sites, Trombay has the highest PM_{10} and particle bound chemical species concentration followed by Parawada and Jogannapalem.

- At Trombay site, Ni annual average concentration was observed to exceed the CPCB limit value (20 ng/m^3), whereas the metals viz. As, Pb and Cd concentrations were found to be well within the CPCB limits at all study sites.
- Chemical speciation analysis of As indicates that, As predominantly exists in As^{+5} at all the sampling sites.
- Source identification using PMF model shows that, Jogannapalem has predominant contribution from biomass burning activity and the least PM contribution was observed from fuel oil combustion. Parawada and Trombay sites have major PM contribution from coal combustion sources. From results, it can also be observed that, fuel oil combustion and road traffic sources are having the highest contribution at Trombay site as compared to other study sites.
- Source profiling technique opted in the current work supported the PMF receptor model results.

References

1. R. Mohanraj, and P.A. Azeez, Current sci., 2004, **87(6)**, 741-748.
2. Y. Cheng, S. Lee, Z. Gu, K. Ho, Y. Zhang, Y. Huangc, J.C. Chow, J.G. Watson, J. Cao, and R. Zhang, Particuology, 2015, **18**, 96–104.
3. R. Das, K. Bahareh, S. Bijayen, D. Subhajit, K.S. Pradip, D. Richard, and X.W. Webster, Atmos. Pollut. Res., 2015, **6**, 742-750.
4. WHO. (2015, May 21). Global Health Observatory Data Repository. Geneva, Switzerland.
5. S. Tiwari, D.M. Chate, P. Pragya, K. Ali, and D.S. Bisht, Aerosol Air Qual. Res., 2012, **12**, 20–29.

6. S. Gummeneni, Y.B. Yusup, M. Chavali, and S.Z. Samadi, Atmos. Res., 2011, **101(3)**, 752-764.
7. D. Massey, A. Kulshrestha, J. Masih, and A. Taneja, Build. Environ., 2012, **47**, 223–231.
8. S.-P. Wu, J. Schwab, B-L. Liu, T.-C. Li, and C.-S. Yuan, Atmos. Res., 2015, **155(15)**, 37–51.
9. W.C. Hinds, Aerosol technology: properties, behavior, and measurement of airborne particles. Wiley-Blackwell, 2nd Edition, 1999.
10. Zs. Kertész, Z. Szoboszlai, A. Angyal, E. Dobosand I. Borbély-Kiss, Nucl. Instrum. Methods. Phy. Res. B, 2010, 268, 1924–1928.
11. P.E. Schwarze, J. Øvrevik, M. Låg, M. Refsnes, P. Nafstad, R.B. Hetland and E. Dybing, Hum. Exp. Toxicol., 2006, 25(10), 559–579.
12. S. Abdul Rahman, M. Suhaimi Hamzah, A. Khalik Wood, M. Suhaimi Elias, N. A. Adullah Salim and E. Sanuri, Atmos. Pollut. Res., 2011, 2, 197-206.
13. B.A. Begum, S.K. Biswas, A. Markwitz and P.K. Hopke, Aerosol Air Qual. Res., 2010 10, 345–353.
14. A.E. Gildemeister, P. K. Hopke and E. Kim, 2007, Chemosphere, 69, 1064–1074.
15. C.A. Belis, F. Karagulian, B.R. Larsen and P.K. Hopke, Atmos. Environ. 2013, 69, 94–108.
16. K. K. Shandilya, M. Khare, and A. B. Gupta, Environ. Monit. Assess., 2007, **128**, 431–445.
17. A. Kulshrestha, P.G. Satsangi, J. Masih, and A. Taneja, Sci. Total Environ., 2009, **407,** 6196–6204.
18. A.S. Pipal, A. Kulshrestha, and A. Taneja, Atmos. Environ., 2011, **45**, 3621-3630.

19. S.K. Sharma, T.K. Mandal, M. Saxena, Rashmi, A. Sharma, A. Datta, and T. Saud, 2014, J. Atmos. Solar-Terres. Phys., **13**, 10–22.
20. T. Banerjee, V. Murari, M. Kumar, and M.P. Raju, Atmos. Res., 2015, **164–165**, 167–187.
21. M. Habil, D.D. Massey, and A. Taneja, Air Qual. Atmos. Health, 2013, **6**, 575–587.
22. B.A. Begum, S.K. Biswas, A. Markwitz and P.K. Hopke, Aerosol Air Qual. Res., 2010 10, 345–353.
23. J.G. Watson, L.-W. Antony Chen, J.C. Chow, P. Doraiswamy and D.H. Lowenthal, J. Air Waste Manage. Assoc., 2008, 58, 265–288.
24. P. Deka and R. R. Hoque, Atmos. Res. 2014, 143, 380–391
25. P. Gursumeeran Satsangi, S. Yadav, A. S. Pipal and N. Kumbhar, Atmos. Environ., 2014, 92, 384-393.
26. MoEF Ministry of Environment and Forests, Environment (Protection) Seventh Amendment Rules. Government of India Press, New Delhi. 2009.

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Chapter-1

INTRODUCTION

1.1. General introduction on air pollution

Clean atmospheric environment is considered to be a basic requirement for human health and well-being. Among variety of factors influencing the human health, natural elements like the air we breathe, food we eat, the water we drink, the radiation we are exposed to, etc. play a crucial role [1]. Among these, air we breathe is the primary component for human life; quality of air is a critical public health as well as environmental concern in many parts of the globe. The air quality is deteriorated due to enormous increase in urbanization and industrialization during the last few decades [2]. Air pollution can be defined as "*the contamination of indoor or outdoor environment by chemical, physical or biological agent that modifies the natural characteristics of the atmosphere*". These chemicals and toxic agents can enter into the body via respiration system and cause disorders, including mortality [3]. Household combustion devices, motor vehicles, varioud kind of waste incinerations and industrial emissions are the common sources of air pollution. According to WHO (last global update, 2005), outdoor and indoor air pollution caused more than 2 million premature deaths [4]. Perhaps, the first air pollution incident took place in 1930s in the Meuse valley of Belgium. A heavy smog (the combination of smoke and fog) blanket settled over the valley, sickening more than 6000 and killing 63 people [5]. Although, the most famous air pollution event happened when dense smog formed over London on December 4, 1952.

US-EPA has identified six criteria air pollutants viz. nitrogen oxides (NO_x), ozone (O_3), sulfur dioxide (SO_2), Particulate matter (PM), carbon monoxide (CO), and lead (Pb). Among these, PM was considered to be one of the most dangerous air pollutants all over the world due to its adverse effects on humans as well as on surrounding environment [6]. PM can be defined as "*a mixture of fine solid and liquid particles suspended in the air medium*" and is also known as aerosols. In a broader sense, the term applies to particles suspended in air having a lower size (aerodynamic diameter) limit of the order of 10^{-3} μm and an upper limit of 100 μm. Out of this whole size range, PM having aerodynamic diameter ≤ 10 μm are important. Air s*uspended particles which are having aerodynamic diameter less than or equal to 10 μm are defined as* PM_{10} *or respirable suspended particulate matter (RSPM). Similarly, suspended particles which are having aerodynamic diameter less than or equal to 2.5 μm are defined/denoted as* $PM_{2.5}$ [7].

In the case of PM, it is believed that aerodynamic size, concentration of PM and associated toxic chemical specie's concentration play vital role in human health. The chemical composition of PM includes semi-volatile (most organic compounds and the major inorganic ions – ammonium, sulfate and nitrate) and non-volatile (metals, elemental carbon and few organic compounds) species arising from both natural and anthropogenic sources [8].

It has been shown through worldwide studies that the population is at risk due to elevated levels of PM in the atmosphere [9-14]. Fig.1.1 shows the leading causes of deaths in the world (as of 2010). Lim et al. (2012) [15] mentioned that the household air pollution from solid fuel burning and tobacco smoke are the major cause of these health effects. The carcinogenic organic pollutants [16] and other toxic chemical species [17-18] are main pollutants emitted during combustion of solid fuels. According to WHO (2015) in 2012 alone, 7 million deaths in the world were attributable to the combined effects of ambient and household air pollution [19].

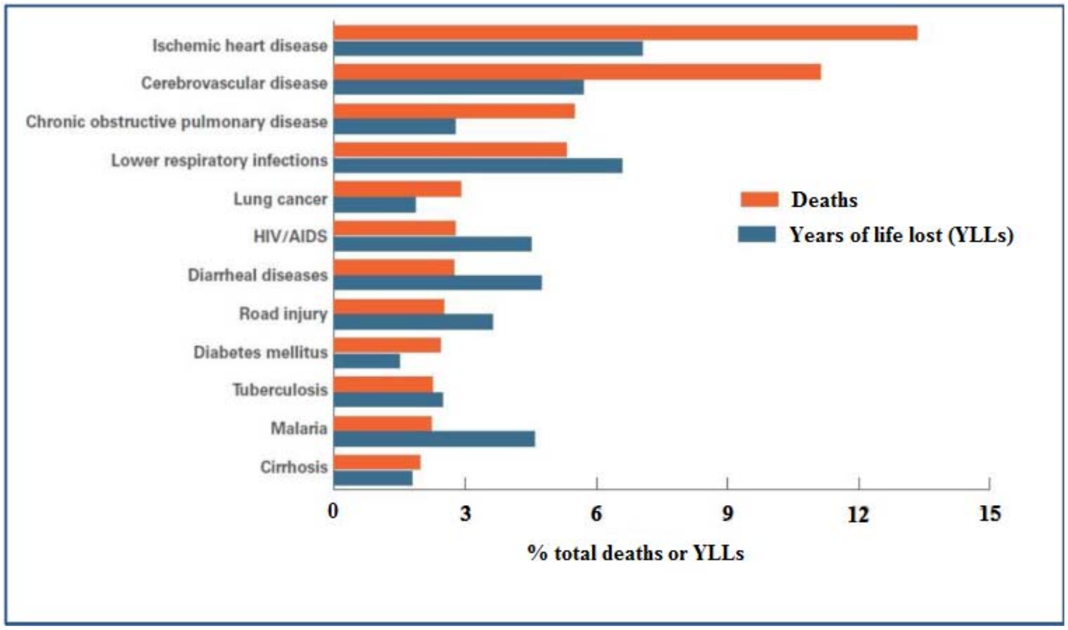
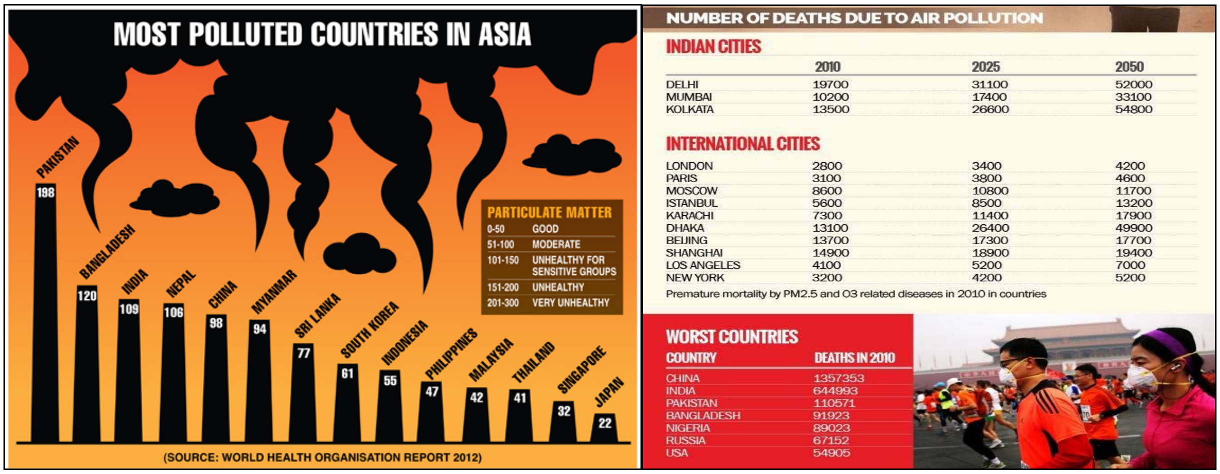


Fig.1.1. Figure showing leading causes of global deaths and premature deaths (Source: Global Burden of Disease (2010)) [15]

According to recent studies, there is mounting evidence that concentration of PM is increasing in Asian countries [20]. Enormous growth in industrialization, personal vehicle transport, waste burning, real estate, etc., and the lack of coherent policy could be the main cause of higher pollution levels in Asian countries. Fig. 1.2 shows the PM concentration levels all over the world. The interactive map shows that, South Asia is badly hit by pollution caused by PM. Countries like Bangladesh, Nepal and India are placed by the WHO in a category called "unhealthy for the sensitive people". That means public in these countries suffering from respiratory and heart disease, as well as elderly and children should limit outdoor exertion [21]. Air pollution in China is as bad, if not worse, than in India but according to the WHO, the PM concentration in China and in countries such as Myanmar, Sri Lanka, South Korea and Indonesia remains moderate. There is the least presence of particulate matter in Philippines, Malaysia, Thailand, Singapore and Japan [22].

Indian scenario

Ambient air pollution has been identified as the fifth biggest cause of mortality in India [23]. According to WHO study, 13 of the 20 most polluted cities in the world are in India, and it is estimated that outdoor air pollution leads to 6, 70,000 deaths annually [15]. Fig.1.3 shows the PM air pollution in different Indian cities over last few years. It can be observed that the concentrations are increasing at a fast pace in most of the Indian cities. The slight decline in PM concentrations during 2003-2006 could be due to the decrease in the local emission sources activities and also could be due to variation in meteorological conditions.



(SOURCE: WORLD HEALTH ORGANISATION REPORT 2012)

NUMBER OF DEATHS DUE TO AIR POLLUTION

INDIAN CITIES

	2010	2025	2050
DELHI	19700	31100	52000
MUMBAI	10200	17400	33100
KOLKATA	13500	26600	54800

INTERNATIONAL CITIES

	2010	2025	2050
LONDON	2800	3400	4200
PARIS	3100	3800	4600
MOSCOW	8600	10800	11700
ISTANBUL	5600	8500	13200
KARACHI	7300	11400	17900
DHAKA	13100	26400	49900
BEIJING	13700	17300	17700
SHANGHAI	14900	18900	19400
LOS ANGELES	4100	5200	7000
NEW YORK	3200	4200	5200

Premature mortality by PM2.5 and O3 related diseases in 2010 in countries

WORST COUNTRIES

COUNTRY	DEATHS IN 2010
CHINA	1357353
INDIA	644993
PAKISTAN	110571
BANGLADESH	91923
NIGERIA	89023
RUSSIA	67152
USA	54905

Fig.1.2. PM Pollution levels in Asian countries and the statistics on number of deaths due to air pollution (2010)

Re-suspended soil dust, fuel wood and biomass burning, fuel adulteration, vehicle emission, construction activities, large variety of industrial emissions, huge waste incinerations and crop residue burning in agriculture fields are the major sources of smoke, smog and particulate matter pollution in India [24]. Majority of Indians still use traditional fuels such as dried cow dung, agricultural waste, and firewood as cooking fuel at rural and suburban location. From the most recent available nationwide study, India used 148.7 million tons coal replacement worth of fuel wood and biomass annually for domestic energy use [25]. This form of fuel is inefficient source of energy, it's burning releases high levels of smoke, PM, NOx, SOx, PAHs, poly-aromatics, formaldehyde, carbon monoxide and other air pollutants [26-28].

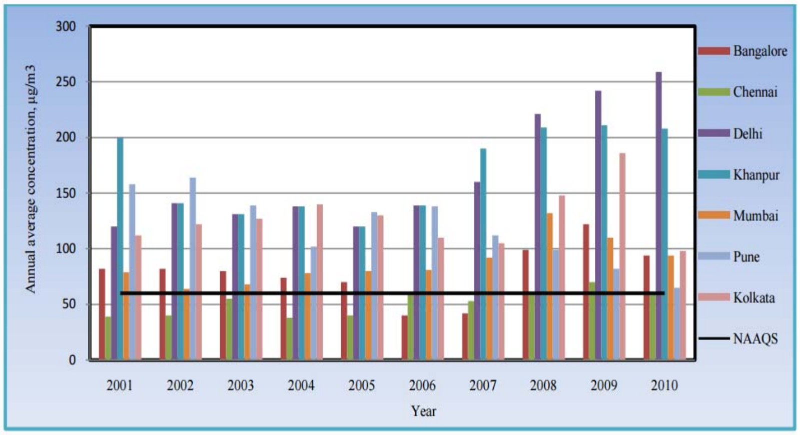


Fig.1.3. Year wise concentration variation of RSPM (PM_{10}) at residential and Industrial areas in major cities of India (https://wattsupwiththat.com/2017/11/28/does-air-pollution-really-shorten-life-spans/comment-page-1/)

1.2 Physico-chemical characteristics of PM

Size is the most important property of particle and it has implications on physical properties, deposition rates, and deposition patterns within the lung, their residence time in the atmosphere, transformation, transport and removal of particles from the atmosphere. Hence, it is important to know the size of the atmospheric PM present in the surrounding environment.

Atmospheric particles emitted from air pollution sources have a multitude of different shapes and densities that causes problems in measuring exact size of the particle. To overcome this problem, Hinds (1990) [29] proposed the concept of equivalent diameter. In air pollution studies, *particle size (diameter) is normally given as the aerodynamic diameter, which refers to the diameter of a unit density sphere of the same settling velocity as the particle in question*. The

Total Suspended Particulate (TSP) consists of all particles that remain suspended in the atmosphere and have a diameter ranging from less than 10 nm up to 100 μm. Particles size was classified based on different conventions viz. 1) *modes*, based on the observed size distributions and formation mechanisms [30, 31]; 2) *occupational health sizes*, based on the entrance into various compartments of the respiratory system [32]; 3) *cut point*, based on the 50% cut point of the specific sampling device [33].

1.2.1. Chemical composition and sources of particulate matter

Knowing the chemical composition of PM is an important task in PM research area. The generated data will be useful in comparing the toxic chemical's concentration levels with National ambient air quality standards, to estimate the risk associated with PM inhalation, in determining radiative forcing effect and also in identifying the PM sources [34-36]. The following section discusses about the various chemical species associated with PM and the most likely sources that can contribute to PM.

A list of possible contributing sources of PM and various chemical components associated with source emissions are shown in Fig.1.4. The major PM sources include mineral dust, biomass burning, marine emissions, industrial emissions, vehicular emissions, etc [37]. Most likely chemical components emitted by pollution sources include crustal elements (such as SiO_2, Al_2O_3, FeO, Fe_2O_3, and CaO), inorganic ions (sulphate, nitrate, sodium, chloride, etc.), organic and elemental carbon, trace metals and water [38].

Trace metals like V, Cr, Mn, K, S, Cu, Ni, Zn, Pb, As and Cd are an important fraction of PM samples. The concentration of these metals depends on the season, the nature of area (residential, industrial, rural and urban) and also on the strength of sources emitting these metals. Many authors from all over the world have reported the association of these metals to PM [39-

45]. These metals can be contributed from anthropogenic sources like biomass burning, smelters, and coal power plants, metal industries, petrochemical industries mining, cement industries, road traffic and vehicular emissions [46-53]. These metals can also be contributed from natural sources like crustal material.

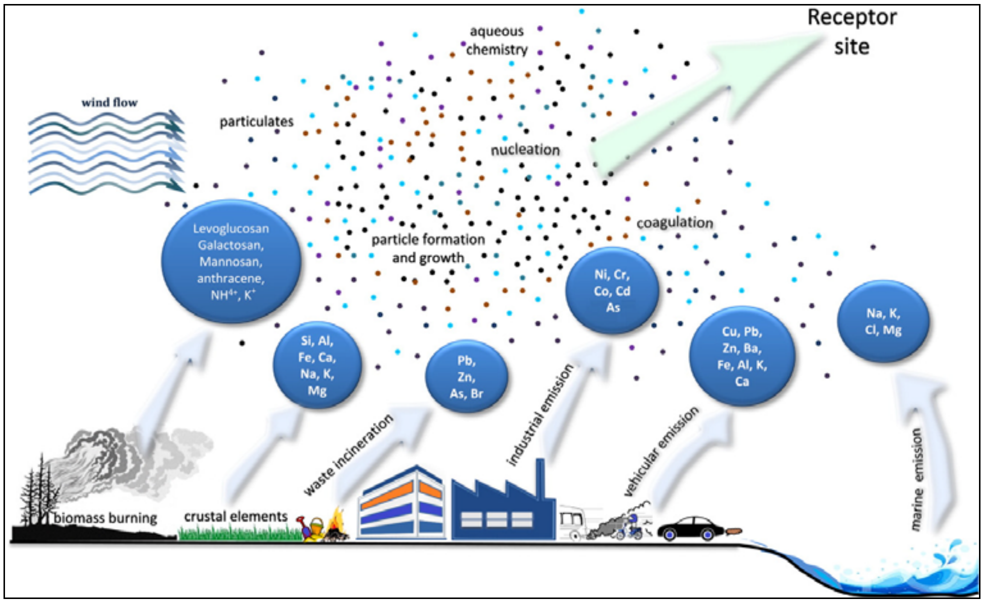


Fig.1.4. Figure representing the possible sources contributing to particulate matter and their signature molecules

Carbonaceous particles are principally consists of both elemental carbon (EC, also known as black carbon, BC) and OC (organic carbon) and are known as soot. Soot particles absorb organic compounds when the combustion products cool down [54]. A group of most harmful organic substances present in aerosol is the family of polycyclic aromatic hydrocarbons (PAHs). Sources of primary carbonaceous particles in urbanized areas are fossil fuel burning (transportation and energy production), domestic burning (cooking and heating), biomass burning, including deforestation and agricultural waste fires [55-56].

1.3. Health effects associated with PM

Several worldwide epidemiological and toxicological studies have proven that the exposure to PM causes numerous health effects including increased hospital admissions, emergency room visits, respiratory symptoms, exacerbation of chronic respiratory and cardiovascular diseases, decreased lung function, and premature mortality [57-59]. Exposure to PM was reported to affect lung development in children, including reversible deficits in lung function, chronically reduced lung growth rate, and a deficit in long-term lung function [60]. Parameters and components potentially relevant for these adverse effects are the specific surface area, the particle size and the concentrations of toxic metals, strong acids and carcinogenic organic compounds [61]. The importance of particles size on adverse health outcomes has been evaluated and positive relations both with PM_{10} and $PM_{2.5}$ were found [62]; the coarse fraction ($PM_{10-2.5}$) resulted to be as strong as fine PM in increasing hospital admissions for respiratory diseases [63], while the correlation with cardiovascular diseases is weaker [64].

1.4. Particulate matter concentration measuring techniques

As discussed above, the PM has its adverse effects on humans as well as on surrounding environment. Hence, it is important to measure the ambient PM concentration to check the air quality status at a given location. PM concentration can be measured using both the online and off-line samping techniques. Online PM measuring techniques include beta-gauge [65], Tapered Element Oscillating Microbalance (TEOM) [65] and Optical particle counter (OPC) [66].

These in-situ techniques are proven to be efficient in measuring the PM concentrations in different size range, but the PM samples collected using these techniques are not suitable for the analysis of various chemical species like major, trace metals, Ions, OC and EC. The off-line sampling techniques are useful in measuring the PM concentrations as well as in determining the chemical constituents concentrations associated with PM. Different off-line instruments viz. high volume sample [67, 68], Anderson cascade impactor sampler [69, 70] and Gent's dichotomous sampler [71-73] are available in the market for PM sampling.

1.5. Chemical analyses of PM using different analytical techniques

As discussed in previous section, the PM is associated with different chemical species such as inorganic ions, organic compounds, elemental carbon (or black carbon-BC), major and trace metals. These chemical species concentrations can have a wide variation at a given location due to changes in source emissions and atmospheric conditions. Hence, there is a need to choose a suitable instrument to analyze wide variety of chemical species and that has wide analytical range.

The available analytical techniques can be divided into two types viz. destructive and non-destructive. Non-destructive techniques that are used for metal analyses include EDXRF (Energy Dispersive X-ray Fluorescence), Instrumental Neutron Activation Analysis (INAA), Proton Induced X-ray Emission (PIXE), Proton Induced Gamma-ray Emission (PIGE), Proton Elastic Scattering Analysis (PESA) and Rutherford Back-Scatter (RBS) measurements. Non-destructive techniques for black carbon (BC) analysis include Smoke Stain Reflectometer [35, 74-75] and Aethalometer [76-77]. Aethalometer measures the real time BC concentrations which would increase the amount and frequency of data being collected, whereas Smoke Stain Reflectometer is an off-line method. These non-destructive techniques although have some advantages, but setting these facilities are of high cost and required skilled persons to do the chemical analyses. Authors from different parts of the world [39, 44, 78-83] have analyzed the major and trace metals associated with PM using these non-destructive analytical techniques.

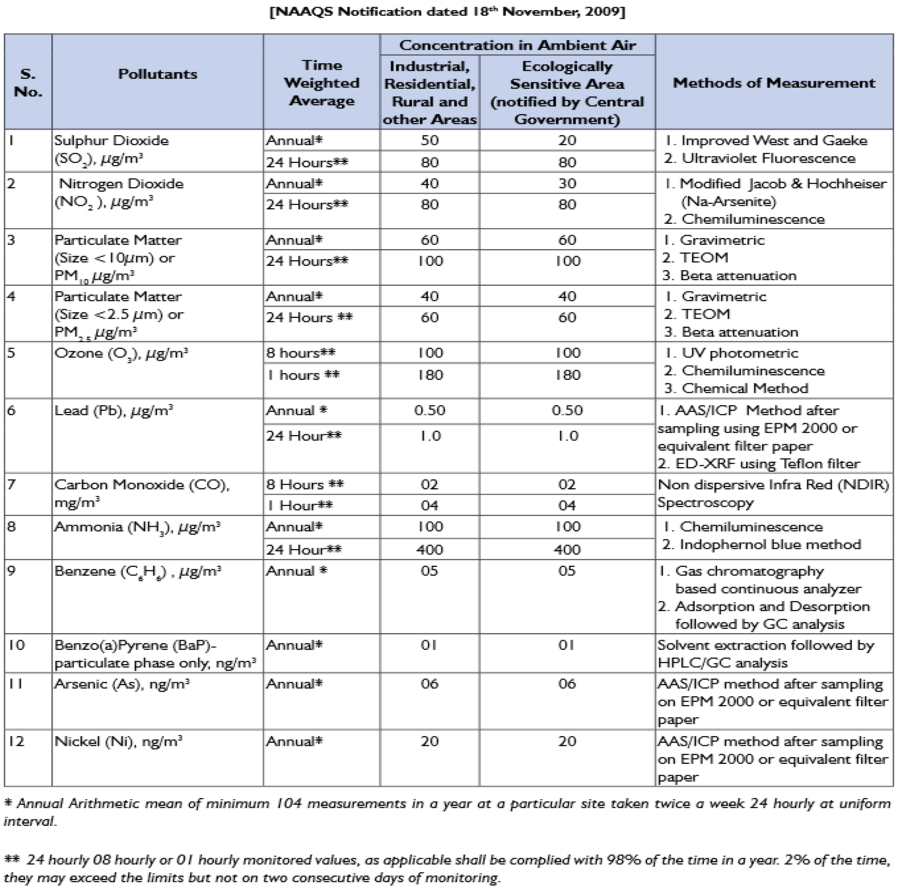
The destructive analytical techniques include mass spectrometry, atomic emission spectrometry, atomic absorption spectrometry, voltammetry, chromatography techniques (IC and HPLC), and carbon analyzers. These are the most common destructive analytical techniques used for the analyses of metals, inorganic ions and organic compounds in PM [84-89].

1.6. Ambient air quality standards

Short term health impacts of air pollution have been extensively studied for developed countries using time series and case-crossover studies [90-92]. These findings have played an important role in determining air quality standards in the respective countries. For instance, the U.S. Environmental Protection Agency (USEPA) reviews health research every five years to recommend revisions to National Ambient Air Quality Standards, as mandated by the Clean Air Act [93-94]. However, epidemiological studies, to inform air pollution policy are largely limited in the context of developing countries such as India [95].

The daily and annual average standard values for PM_{10} set by USEPA are 150 $\mu g/m^3$ and 50 $\mu g/m^3$, respectively. The World Health Organization (WHO) also recommended air quality guidelines to avoid significant harmful health effects on the human; the daily (24hrs.) and annual standards of PM_{10} are 40 $\mu g/m^3$ and 20 $\mu g/m^3$, respectively [96].

In India, the Central Pollution Control Board (CPCB) was set up under the Air Act of 1981, with a mandate of setting and reviewing the National Ambient Air Quality Standards (NAAQS). The annual and daily limits for different pollutants given by CPCB are summarized in Fig.1.5.



[NAAQS Notification dated 18th November, 2009]

S. No.	Pollutants	Time Weighted Average	Concentration in Ambient Air: Industrial, Residential, Rural and other Areas	Concentration in Ambient Air: Ecologically Sensitive Area (notified by Central Government)	Methods of Measurement
1	Sulphur Dioxide (SO_2), µg/m³	Annual*	50	20	1. Improved West and Gaeke 2. Ultraviolet Fluorescence
		24 Hours**	80	80	
2	Nitrogen Dioxide (NO_2), µg/m³	Annual*	40	30	1. Modified Jacob & Hochheiser (Na-Arsenite) 2. Chemiluminescence
		24 Hours**	80	80	
3	Particulate Matter (Size <10µm) or PM_{10} µg/m³	Annual*	60	60	1. Gravimetric 2. TEOM 3. Beta attenuation
		24 Hours**	100	100	
4	Particulate Matter (Size <2.5 µm) or $PM_{2.5}$ µg/m³	Annual*	40	40	1. Gravimetric 2. TEOM 3. Beta attenuation
		24 Hours **	60	60	
5	Ozone (O_3), µg/m³	8 hours**	100	100	1. UV photometric 2. Chemiluminescence 3. Chemical Method
		1 hours **	180	180	
6	Lead (Pb), µg/m³	Annual *	0.50	0.50	1. AAS/ICP Method after sampling using EPM 2000 or equivalent filter paper 2. ED-XRF using Teflon filter
		24 Hour**	1.0	1.0	
7	Carbon Monoxide (CO), mg/m³	8 Hours **	02	02	Non dispersive Infra Red (NDIR) Spectroscopy
		1 Hour**	04	04	
8	Ammonia (NH_3), µg/m³	Annual*	100	100	1. Chemiluminescence 2. Indophernol blue method
		24 Hour**	400	400	
9	Benzene (C_6H_6) , µg/m³	Annual *	05	05	1. Gas chromatography based continuous analyzer 2. Adsorption and Desorption followed by GC analysis
10	Benzo(a)Pyrene (BaP)-particulate phase only, ng/m³	Annual*	01	01	Solvent extraction followed by HPLC/GC analysis
11	Arsenic (As), ng/m³	Annual*	06	06	AAS/ICP method after sampling on EPM 2000 or equivalent filter paper
12	Nickel (Ni), ng/m³	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 interval.*

*** 24 hourly 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.*

Fig.1.5. National ambient air quality standards prescribed by CPCB, India

1.7. Source apportionment of PM

Increasing levels of PM concentrations around the globe has created the need to identify the potential PM sources at study area which will be helpful in pollution mitigation studies as well. Source Apportionment (SA) is the practice of deriving information about pollution sources and the amount they contribute to ambient air pollution levels. Different approaches are used to determine and quantify the air pollution sources. But, the receptor model techniques are proven to be simple and effective in source identification and apportionement. Some of the most popularly used receptor model techniques are Factor analysis (FA), PCA, edge analysis (Unmix), chemical mass balance (CMB) and Positive Matrix Factorization (PMF) [97-112]. HYSPLIT (Hybrid Single Particle Lagrangian Integrated trajectory) model [113] and CPF (Conditional Probability Function) [114] models were used in addition to RMs to confirm the PM sources.

1.8. Previous Work and Identification of Research Problem

PM air pollution is one of the serious issues in India due to the countries enormous growth in various sectors as mentioned above. Due to which Indian public are exposed to one of the highest PM pollution levels in the world causing increase in number of premature deaths, hospital admissions and respiratory diseases. Most of the PM studies conducted in India are focused their research work on Indian mega cities such as Delhi, Hyderabad, Mumbai, Bangalore, Kolkata, Chennai, etc. These studies gave information on PM concentrations; particle bound chemical species concentration, temporal, seasonal variations and also gave information on sources contributing to PM. These studies identified the PM sources solely based on the presence of marker/finger print elements in the factor profiles provided by receptor models, without any experimental confirmation of identified source via. receptor models. Thorough literature survey indicates that, very less PM studies are reported in and around the Department of Atomic Energy (DAE) sites. In view of country's enormous growth in industrialization and urbanization there is a need to extend the PM studies to DAE sites also. This is one the main motivation to carryout the present work.

With this adequate background the present study was carried out at Jogannapalem, Parawada and Trombay sites. Jogannapalem was chosen for the present study, as it is a new site selected to establish DAE facilities, whereas, Trombay, is an established DAE site. All the selected study locations are near to many major and minor industries which can cause particulate matter air pollution. It is important to assess the PM pollution levels and the sources contributing to the PM at these sites. The present study results will be useful as a baseline survey for new DAE sites (Jogannapalem) as there were no PM studies at this site till date. Whereas, the present study at Trombay is helpful in knowing the impact of nearby industries on Tormbay air quality. The source apportionment data of the present study can be helpful in planing PM pollution mitigation strategies.

1.9. Objective and scope of the present study

The aim of the present study was to assess the PM_{10} levels, particle bound chemical components concentration levels and to identify the sources contributing to PM using different receptor model techniques. With this aim, the present study was carried out for two consecutive years (2010 to 2011) at Jogannapalem, Parawada and Trombay sites of India with following objectives;

1) Collection of PM_{10} and assessing the PM_{10} concentration levels at selected study locations.
2) Chemical characterization of collected PM using different analytical techniques including destructive and non-destructive techniques.
3) Studying the temporal and seasonal variations of PM_{10} and particle bound chemical constituents at study sites.
4) Identification and quantification of the sources contributing to collected PM using different receptor model techniques.

The frame work of the current study is represented in the form of flow chart as shown below.

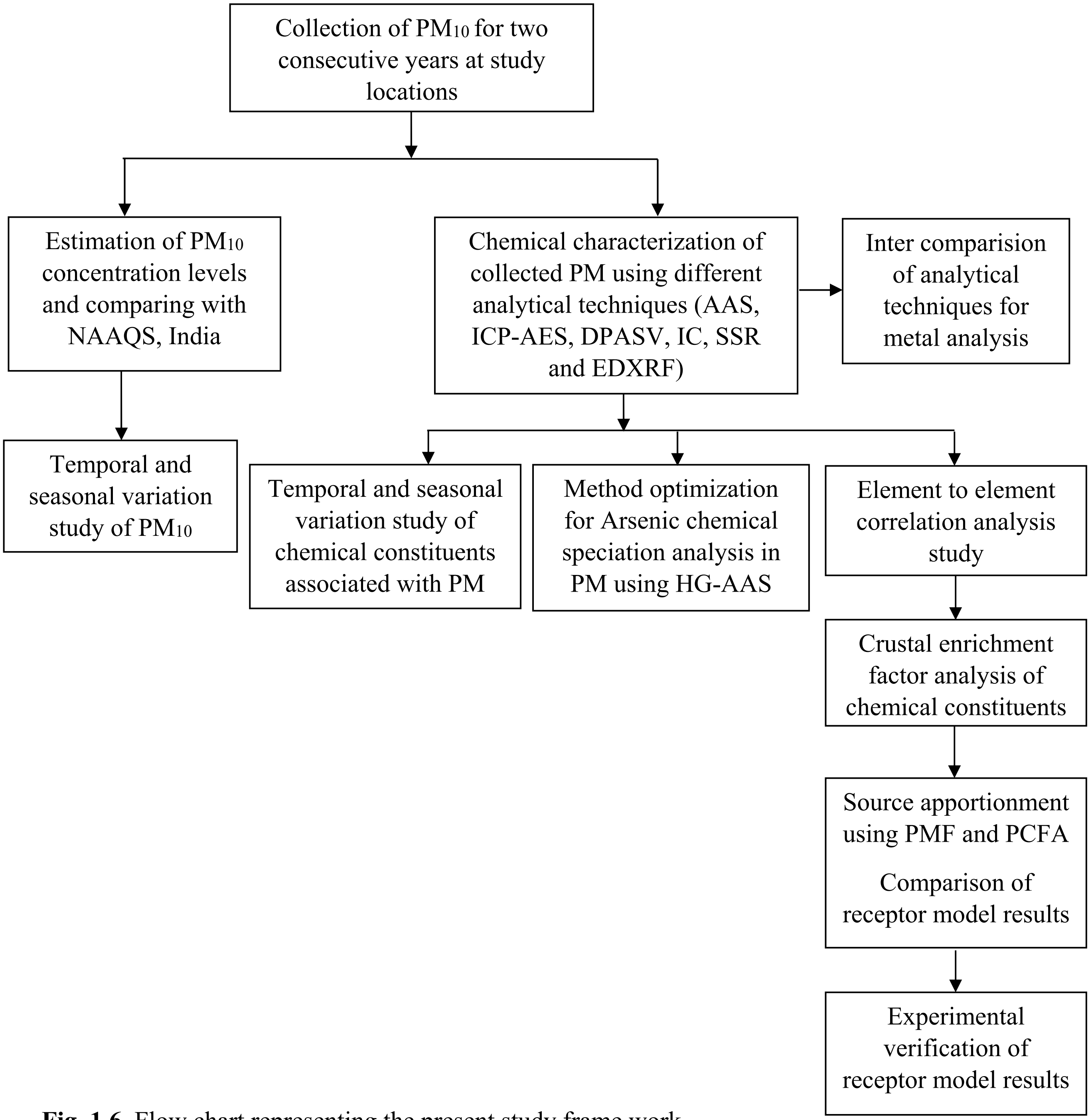


Fig. 1.6. Flow chart representing the present study frame work

Chapter 2

Literature review

2.1. Previous studies on PM

Thorough literature survey is mandatory to select the right problem that has not been covered earlier and will enlighten some new outcomes. This chapter discusses the PM studies that are carried out previously. Various analytical techniques that are used for the chemical characterization of PM and receptor models that are used for the source identification studies are discussed in detail.

In India, PM studies were carried out in different mega cities viz, Hyderabad, Delhi, Kolkata, Mumbai, Chennai, Kanpur, etc. [42, 50, 115-120] covering both the residential as well as industrial areas. Within India, the largest cities and the Indo-Gangetic basin have been identified as areas with the most severe air pollution [121]. The annual average of PM_{10} concentrations in Indian cities are observed to be 94.7±45.4 μg/m^3 in Pune, 73.1±33.7 μg/m^3 in Chennai, 118.8±44.3 μg/m^3 in Indore, 94.0±20.4 μg/m^3 in Ahmedabad, 89.4±12.1 μg/m^3 in Surat, 105.0±25.6 μg/m^3 in Rajkot [122], 98.72–276.64 μg/m^3 in Varanasi [123], 285.60 ± 145–491.92 ± 234 μg/m^3 in Delhi [124], 95–320 μg/m^3 in Coimbatore, [125], 220.5–352.7 μg/m^3 in Mithapur [126] and 107.84–176.07 μg/m^3 in Hyderabad [42] and are found to be exceeding the Indian NAAQS (60 μg/m^3). A number of previous studies have reported an enhancement in anthropogenic emissions during last few years in several India cities leading to high accumulation of toxic chemical constituents (e.g. metals, ions, organic pollutants, etc.) in PM_{10} [127-131] indicating the serious contamination of atmospheric air in India.

There are large numbers of studies reported especially in Delhi and Kanpur region. The outcomes of previous studies and their drawbacks are brief discussion in the following section.

Pandey et al., (2017) [123] carried out the speciation of carcinogenic and non-carcinogenic metal (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) in respirable suspended particulate matter (RSPM) using sequential extraction procedure (SEP) in ambient air of Varanasi, India. Scanning Electron Microscope-Energy Dispersive X-ray Spectroscopy (SEM-EDX) was used to assess weight percentage of elements. His study reported that PM contains significant wt% of Cu, Zn, Cd and Pb at study locations. His study doent reported the source apportionment results for studied area.

Tiwari et al., (2013) [132] reported the PM_{10} levels and analyzed the inorganic ions and metals bound to PM at Delhi. Source apportionment was carried using, UNMIX 6.0 and Positive Matrix Factorization (PMF 3.0). Four factors were derived to explain sources of PM_{10} (crustal origin, road-traffic and secondary aerosols). But, experimental confirmation of sources was not done.

Kulshrestha et al., [118] monitored PM concentration levels at rural and urban locations of Agra. He observed very low difference in PM concentration levels at rural and urban locations. In his study, chemical characterization of PM was carried out and the data was used for source identification using factor analysis technique. No experimental data was reported to confirmation of sources identified using receptor model technique.

A very short term (3 months) study on PM was reported at rural and suburban location of Roorkee, northern India [119]. His study showed that PM_{10} concentrations are much higher than the proposed CPCB standards for ambient PM levels in rural site. The study does not give any information on PM sources rural site. Another short term PM study was reported by Shandilya et al., (2007) [120] at rural industrial location of Delhi area. The study compared the PM_{10} and $PM_{2.5}$ levels at rural and urban industrial locations of Delhi without discussing the source responsible for observed PM at study location. Smilarly, the PM concentration levels at rural locations of Allahabad were reported by Kushwaha et al., (2013) [135].

Sharma et al., (2005) [133], carried out PM_{10} study at Kanpur and samples are analyzed for heavy metals and benzene-soluble organic fraction (BSOF) in PM. The study concluded that the overall air quality in the city of Kanpur was much inferior to other cities in India and abroad. This study reported that the heavy metals were almost 5–10 times higher than levels in European cities.

Dubey et al., (2012) [134] measured PM_{10} in Jharkhand and analyzed only few trace metals using AAS. His study showed that, Fe was the major metal in PM_{10} at study location followed by Cu and Zn. This study carriedout the source apportionment using Factor Analysis–Principal Component Analysis considering only few selected trace metals associated with PM. The major sources of airborne trace metals identified were mainly coal mining and associated activities, emissions from automobile exhaust and industries, resuspended soil dust and earth crust, biomass burning, oil combustion, and fugitive emissions.

Some PM studies which are carried out at rural, suburban and urban locations of other countries includes China, USA, Malaysia, Tokyo, Hong Kong, Australia, Switzerland, etc. [136-151]. These studies discussed the PM and associated chemical species concentration levels at study sites. Source apportionment study was carried out using different receptor model techniques. The out comes of few studies are discussed below.

Masiol et al., [141] conducted a PM study at coastal site of Italy. An improved application of the factor cluster analysis (FCA) is presented in his study. The identified sources of PM_{10} were sea spray (23%), secondary aerosol (21%), anthropogenic local pollution (13%) and combustions (8%). The main drawback of this study was that it was conducted for only 4 months. The nature of sources and their contribution could be different if the study was conducted for long period covering all seasons.

Li et al., 2014 [148] observed similarities in PM_{10} concentrations between urban and rural areas of China. His study reported that, over 40% of the measurements were exceeded the national ambient air quality standard at study areas. He attributed the strong localized emissions and solid fuels combustion in house holds for observed severe contamination at study areas.

Aldabe et al., [152] carried out chemical characterisation and source apportionment of PM at rural, urban and traffic sites of North of Spain. He reported that the mean PM concentrations were below the annual limit value for PM_{10} established by the European Directive 2008/50/EC. PMF model identified four sources for PM_{10} at study sites viz. crustal, secondary sulphate, secondary nitrate and sea-salt. But the study did not report any experimental verification of observed sources.

2.2. Chemical characterization of PM

A chemical analysis of PM is an important aspect in PM related research studies. Chemical analysis data of PM can be useful in many ways i.e., in source apportionment studies, in assessing inhalation health risk, in calculating radiative forcing effect, etc. The PM in general is associated with wide varieties of chemical species such as inorganic ions, metals, organic compounds and elemental carbon as discussed above. Different analytical techniques are required to quantify wide variety of chemical costituents in PM.

Quantification of metals in PM is important as CPCB and USEPA have given annual safety limits to some toxic metals (As, Ni, Pb and Cd). There are varieties of instruments that are available in the market for the metal analysis. Many authors from all over the world [153-160] have used destructive techniques (ICP-MS, AAS, ICP-AES), for the quantification of trace and major metals. Similarly, some authors [161-164] have used the non-destructive techniques (PIXE, INAA and XRF) for the quantification of metals in PM. Ion chromatography (IC) is the most famous and reliable technique to quantify the inorganic ions. Many authors [141, 152, 165-166] have used IC to quantify the inorganic ions in PM.

Analysis of organic carbon (OC) and black carbon (BC) content associated with PM have gained importance because of their influence on climate and human health [167]. BC is possesses a strong capability of absorbing solar radiation and is considered to play an important role in global climate change as it causes positive radiative forcing. It is listed as the second most important component of global warming after CO_2 [168]. Various analytical techniques such as HPCL, GC-MS, Aethalometer, smoke stain reflectometer and Thermo-Optical Transmittance techniques are available for the quantification of OC and BC in PM. Various researchers from around the world [169-176] have used above mentioned instruments for the quantification of OC and BC in PM. The PM studies carried out in India, have reported water soluble inorganic ions [177-178], metals [42,128-130], BC and OC [179-183] in many Indian cities.

2.3 Source Apportionment of PM

Many previous studies have accomplished this task using emission inventories, source-oriented models and receptor-oriented models [98-102]. The schematic diagram of different model’s approach for source identification is shown in Fig.2.1.

Emission inventories are detailed compilation of the emissions from all source categories in a certain geographical area and within a specific year. Emissions are estimated by multiplying the intensity of each relevant activity (activityrate) by a pollutant dependent proportionality constant (emission factor).

Source oriented or dispersion model is the mathematical simulation of how air pollutants disperse in the ambient atmosphere. The dispersion models are used to estimate the downwind ambient concentration of air pollutants or toxins emitted from sources such as industrial plants, vehicular traffic or accidental chemical releases. They can also be used to predict future concentrations under specific scenarios [97-98].

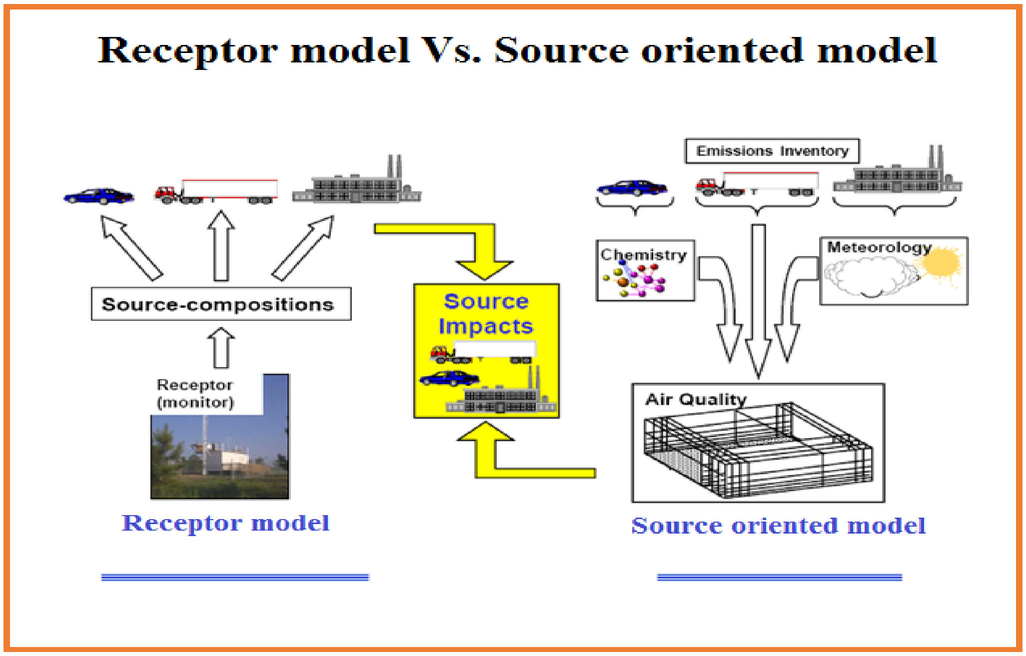


Fig.2.1. Schematic diagram representing the source and receptor oriented model's approach for the source apportionment of PM

Receptor oriented model

Receptor-oriented or receptor model (RM) is the application of multivariate statistical methods for the identification of PM sources and quantitative apportionment of air pollutants to their sources [99]. The foundation of all receptor based models is mass conservation which may simply be explained by Eq. 1:

$$X=G \times H+ e \tag{1}$$

Where, ‘X’ is the elemental concentration profile at the receptor site, ‘G’ denotes the source contribution which needs to be measured, ‘H’ is the source profile and ‘e’ denotes error between the measured and predicted concentrations. However, mass balance equation itself based on certain assumptions is critical for specific RM techniques than for others [100].

It is usually impractical to conduct an emission inventory study on all the major air pollution sources in a large region. Hence, the best alternative technique that is being followed by many researchers all over the world for source apportionment is the receptor-oriented models [101]. RMs identifies the sources based on presence of specific signatory molecules which virtually establish missing links between sources and receptors [100]. During the last few years, these models have been accepted for developing effective and efficient air quality management plans. Different RMs including principal component analysis/absolute principal component scores (PCA–APCS) [102-104], Factor analysis (FA) [105], edge analysis (Unmix) [106-107], chemical mass balance (CMB) [108] and positive matrix factorization (PMF) [109-111] have been applied to identify and establish the sources contribution to observed ambient PM concentrations.

Other models such as HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) and CPF (Conditional Probability Function) are in use to identify the source direction. These models are used to support the receptor model results. The CPF is a simple but effective technique for providing directional information concerning major sources (Vedantham et al., 2013) [112]. Bae et al. (2011) [113] used a CPF technique to identify the directionality of sources contributing to observed pollutant concentrations. Coupling of CPF technique with back trajectory calculations enhances the information on mid to long distance sources [113]. HYSPLIT is the most widely applied air trajectory model which is capable of establishing source-receptor relationships over long distances [114]. HYSPLIT moves backward in time to calculate the possible origin of an air parcel arriving at a receptor at a particular time.

2.3.1. Source Apportionment studies in India

Understanding the potential sources of the particulate matter in the ambient air is important for air quality management. Source apportionment technique quantifies the contribution of individual sources to particulate mass loading based on source and receptor characteristics [152].

During the recent past, the receptor model techniques are proven to be simple and effective in identifying the sources. The concept of RMs is based on proper identification and quantification of specific signatory molecules which virtually establish missing links between sources and receptors [184]. Chemical signatures of specific sources are extremely sensitive and may undergo chemical phase transformations and eventually be masked, which critically limits its applications as a tracer. Therefore, selection of the specific RMs for SA studies is extremely important as only few RMs can tolerate deviations of pre-identified assumptions [100-101].

A number of SA studies for different atmospheric pollutants with some degree of certainty are carried out in India with majority of studies being conducted using receptor models (RMs) based on monitored particulate concentrations and their chemical profile [185-186]. Initially, during 1960s to 1990s, SA was only conducted through multivariate statistical models based on factor analysis and PCA as speciated emission inventories and source profile information were extremely limited. Until 1990s, there were only 9 publications (10% of total) available typically originated using EF (42%) and FA (33%), while only 3 instances were there when advanced RMs like PCA (17%) and CMB (8%) were in use [184]. Unavailability of regional source profile may possibly restrict the use of advanced RM. It was only during the second half of the 20th century that source profiling of airborne particulates has been initiated [187-188] before which USEPA speciate database was only available to explore. Since 2010–14, a total of 81 publications were found involving many advanced RMs likewise PCA (36%), PMF (15%), UNMIX (3%) and CMB (10%) [184]. Fig. 2.2, shows how the number of SA studies are increased over the years, indicating their reliability and effectiveness in source identification.

For the entire SA study, most preferred particulate metrics were PM_{10} (41%) followed by $PM_{2.5}$ (26%) and SPM (22%). In India, considerable amount of particulate SA was carried out from 2010 and 5 years of research resulted to staggering 44 publications (49% of total) [184]. Besides these RMs, some authors have used HYSPLIT [189,190] and CPF [191, 192] for the verification of receptor model results. Table 2.1 summarizes the various SA studies that are carried out in the recent past using different receptor model techniques in India.

Table 2.1. Source apportionment studies that are carried out in India

Receptor model	SA Studies
PCA	[185,193, 194]
UNMIX	[132, 195]
PMF	[153, 131, 194]
CMB	[186, 196-200]

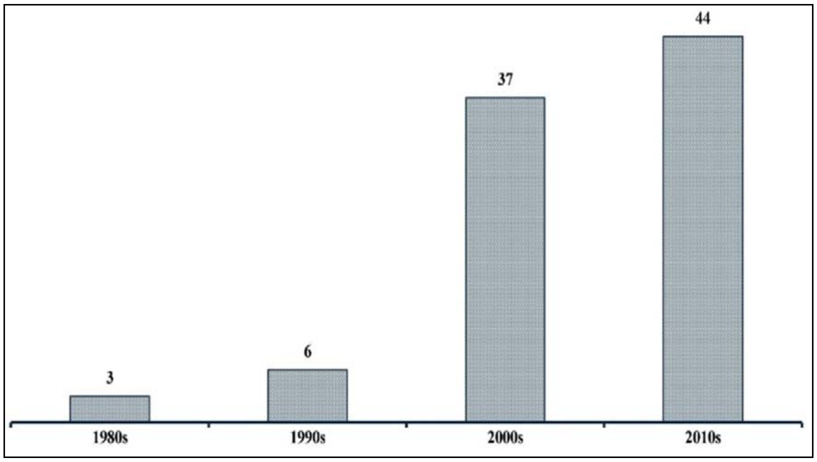


Fig.2.2. Decadal variation of SA studies in India Fig. adopted from [195]

Fig.2.3. shows the geographical distribution of SA studies that have been conducted in India. It is evident that most of SA studies have been performed in and around Delhi, Mumbai, Chennai and Kolkata with some contributions from Hyderabad, Tirupati, Durg, Kanpur, Agra and Chandigarh.

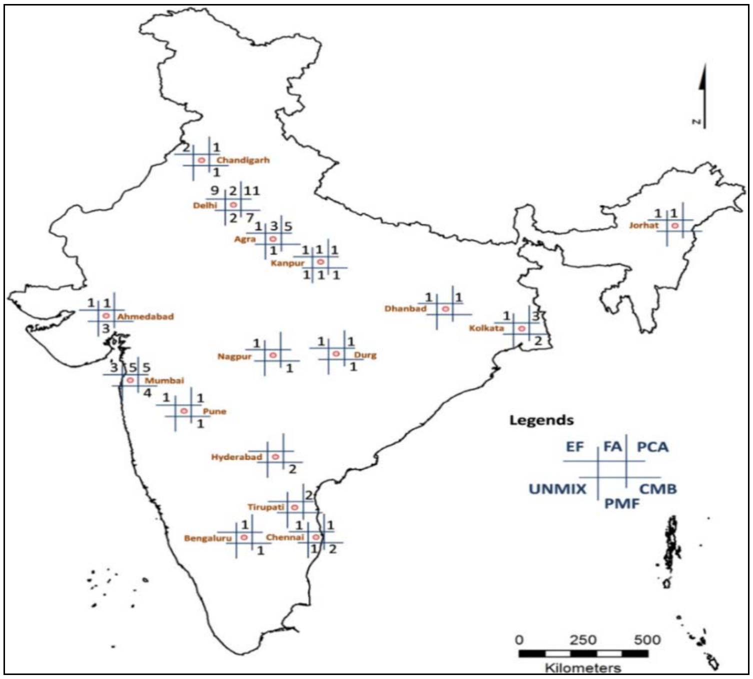


Fig.2.3. Geographic distribution of RMs for SA studies in India [184]

Region wise source apportionment studies in India

Large heterogeneities have been recognized in terms of regional SA studies within India. Characteristically, 40% of SA studies have been originated in Northern India (N: 43, 40%) with 22% of apportionments from Delhi itself. Western India (W: 31, 29%) has also been studied extensively representing 29% of the total publications. Both Southern (S: 12, 11%), and East and Central India (E & C: 21, 20%) have been briefly studied in terms of particulate SA, predominately in Kolkata (6%) and Chennai (5%). Such meta-analysis clearly identifies four definite circles (viz. Delhi, Mumbai, Kolkata and Chennai) which share 47% of the total SA studies in aggregate [184].

Table 2.2 to 2.5 gives the list of different SA studies that are carried out in India using different receptor model along with identified source and their percentage contributions.

Table 2.2 Summary of topical CMB applications for particulate source apportionment

Location and time frame	**Targeted metric**	**Tracer species used**	**Sources identified**	**Reference**
Hyderabad (Nov 2005–Dec2006) (summer, winter and monsoon)	PM_{10}	Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Na, Mg, Ca, Al, Si, K, Fe, OC, EC	Vehicular emissions (30%), vehicular with resuspension dust (30–45%), coal combustion (7–20%) Road dust resuspension (15%), coal combustion (11–36%), open waste burning (10%).	[126]
Bengaluru, Chennai, Delhi, Kanpur, Mumbai and Pune	PM_{10}	39 elements, 12 ions, EC, OC	Unpaved road dust, electric arc furnace, wood combustion chulha, wood fired boilers.	[186]
Chennai (November 2008–April 2009)	PM_{10}	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Se, Sr, Te, Tl, V, Zn, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_2^-, SO_4^{2-}, NO_3^-	Diesel exhaust (43–52%), gasoline exhaust (6–16%), paved road dust (0–2.3%), brake lining dust (0.1%), brake pad wear dust (0.1%), marine aerosol (0.1%), cooking (0.8%)	[156, 193]

Table 2.3 Summary of topical PCA applications for particulate source apportionment

Location and time frame	**Targeted metric**	**Tracer species used**	**Sources identified**	**Reference**
Agra (Jan 2008–May 2009)	PM_{10}	Fe, Zn, Cu, Cd, Cr, Mn, Ni, Pb	Automobile (37.06%), chalk dust and soil (36.07%), metal processing (15.17%), vehicular emission and soil dust (47.56%), vehicular wear and tear (33.79%), garbage burning and other activities (17.98%).	[201]
Agra (March 2007–Feb. 2008)	PM_{10}	Na, Mg, Al, Si, S, Ca, Sc, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Cd, Ba, Pb, NH_4^+, K^+, SO_4^{2-}, $NO_3^{-\cdot}$, F^-, Cl-	Wind blown dust, re-suspended dust, dust from paved and unpaved roads, and undisturbed soil, agricultural, and construction activities (55.47%), emission associated different process of vehicular movement (16.90%), industrial process (9.04%), biomass burning (7.34%), and secondary inorganic origin (4.55%)	[202]
Pune Urban site (June 2011 and May 2012)	PM_{10}	Cu, Zn, Mn, Fe, Ba, Ca, Co, Cr, K, Na, Ni, Pb, Sr, Cd, Al, Mg	Tire and brake drum abrasion, biomass burning, waste incineration (52.5%), traffic emission, geogenic origin (14.4%)	[203]

Table 2.4 Summary of topical PMF applications for particulate source apportionment

Location and time frame	**Targeted metric**	**Tracer species used**	**Sources identified**	**Reference**
Delhi (2010)	PM_{10}	Na, Mg, Al, Si, P, S, Cl, K, Ca, Cr, Ti, Fe, Zn, Mn, NH_3, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-	Soil dust (20.7%), vehicular emissions (17.0%), secondary inorganic aerosol (21.7%), sea salt (4.4%), fossil fuel combustion (17.4%), biomass burning (14.3%), and industrial emission (4.5%)	[153]
Chennai (November 2008–April 2009)	PM_{10}	Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, NO_2^-, NO_3^-, and SO_4^{2-}, Cl^-, Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Se, Sr, Te, Tl, V, Zn	Marine aerosol (40.4%), secondary inorganic aerosol (22.9%), vehicular emissions (16%), biomass burning (0.7%), tire and brake wear (4.1%), soil (3.4%), other sources (12.7%)	[156,196]
Ahmedabad (December 2006–January 2007)	PM_{10}	Cd, Pb, Fe, Al, Ca, Mg, Ba, Sr, Cr, Cu, Mo, Zn, Ni, Co, Mn, Na, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, K, OC, EC, SO_4^{2-}	Mineral dust (34%), biomass burning (33%), Industrial or/and incineration emissions (11%), coal-based power stations/industrial/vehicular emissions (31%)	[197]

Table 2.5 Summary of topical UNMIX applications for particulate source apportionment

Location and time frame	**Targeted metric**	**Tracer species used**	**Sources identified**	**Reference**
Kanpur (July, 2008–May, 2009)	PM_{10}	F^-, Cl^-, NO_3^-, PO_4^3, SO_4^{2-}, As, Ca, Co, Cr, Cd, Mg, Fe, Ni, Pb, Cu, Zn, V, Se.	Secondary sources (39%), vehicular emissions (24%), road dust (14%), un-apportioned (12%), coal combustion (11%)	[195]
Delhi 2008	PM_{10}	Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb, Cd, Sn and Sb, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}	Vehicular emissions (60%) followed by crustal elements as a major source	[132]

From literature study it was understood that there are many studies reported at an urban residential as well as urban industrial locations. But, very less PM related studies are reported in and around the existing and new DAE sites. This is the main motivation to conduct the present study at Jogannapalem, Parawada and Trombay sites. The Jogannapalem is a new site selected for establishing DAE facilities. This site is surrounded by various industries that can cause PM air pollution. Similarly, Trombay is also a DAE site that is surrounded by major and minor industries. There is a need to assess the PM pollution levels and the sources contributing to PM at Jogannapalem before establishing DAE facilities to have a baseline data on air pollution status. The present study data at Trombay will be helpful in assessing the changes in PM sources over the years. Parawada site was chosen for the present study since it is close to Jogannapalem site and surrounded by various industries which can also contribute to air pollution. The present study results will be helpful as a baseline survey for the new DAE site and in knowing the impact of surrounding industries on DAE sites.

CHAPTER 3

Materials and Methods

This chapter mainly discusses about the sampling sites and the various industries that are present near the sampling sites. The working principles of PM samplers used in the present study are discussed in detail. Chemical processing procedures adopted for the extraction of particle bound chemical species from collected filter papers were also explained. Details on different analytical techniques used for the analyses of various chemical species are provided along with optimization procedures to get good sensitivity and selectivlity. This chapter ends with the discussion on the receptor models used for source apportionment study.

3.1. Sampling sites description

Topography of Visakhapatnam is surrounded by hill ranges on three sides and sea on the other side and is often called as bowl area for assessment of environmental related issues [204]. Visakhapatnam is presently witnessing a boom in industrialization and a consequent explosion in population (Growth over the decade 2001-2011 was 11.89%). Fig. 3.1a and 3.1b illustrates the PM sampling locations along with list of industries present near the sampling sites.

Site 1: Jogannapalem is a rural area in Atchuthapuram Mandal with a Bay of Bengal on one side and residential area with paddy fields on the other side. Many industries such as alloy industry, equipment manufacturing industry, metal manufacturing industry, granite industry, power plant, metal extraction plant, textile industry etc., are present just few kilometers away from this sampling site as shown in Fig 3.1a. At this site, people were mostly dependent on wood and wood coal burnings for cooking and other purposes.

Site 2: Parawada is a suburb Mandal in Visakhapatnam district and surrounded by many industries such as steel plant, thermal power plant (TPP), fertilizer industries, petroleum industries, chemical, pharma industries, etc. This site is far away from Bay of Bengal as compared to Jogannapalem site. Visakhapatnam port is also near to this site as compared to Jogannapalem site. Being suburban location, vehicular emissions are also higher at this site.

Site 3: Trombay is a northeastern part of Mumbai represents an area of about 25 sq. km. The sampling site is located about 20 km from the Mumbai main center with the Arabian Sea on one side and an industrial area on the other side. As shown in Fig. 3.1b, thermal power plant operating on coal/oil, oil refineries, fertilizer complex, chemical, paint industries and small scale metal industries are situated near the sampling site. Several other industrial areas such as MIDC-Taloja, Turbhe, TTC, etc. are also present near the sampling site. Mumbai port and Jawaharlal Nehru (NhavaSheva) port are the largest ports in India and handle liquid chemicals, crude petroleum products, etc. Both these port areas are few kilometers away from the sampling site as shown in Fig. 3.1b. Mumbai is a densely populated city and affected by worst traffic in India.

Soil samples were collected from all major industries such as thermal power plant, steel plant, alloy industry, oil refineries, iron ore industry and metal industries. Soil samples are also collected from road side where vehicular movement is high near Parawada and Trombay sites. Soil sampling locations are also shown in Fig. 3.1a, b. Multiple numbers of soil samples (10 to 15) are collected from each industry of interest. The collected soil samples from each location are mixed to get one representative sample for that industry. These samples are analyzed for metals content using EDXRF and elemental profiles obtained are used to compare with receptor model factor profiles to confirm the model results.

Fig.3.1a. Figure showing Jogannapalem, Parawada PM sampling locations (shown with red color) and nearby industries

Fig.3.1b. Figure representing the Trombay PM sampling location along with nearby industries

3.2 Meteorological conditions at sampling sites

At Visakhapatnam, predominantly three seasons are experienced i.e. summer (March to June), monsoon (July to October) and winter (November to February). The average high temperatures (33-35^{0}C) were observed during March to June, whereas average minimum temperatures were found in the range of 18-19^{0}C during December and January. The wet season at Visakhapatnam persists mainly during the south-west monsoon with a total annual precipitation of 955 mm (38 inches). The maximum rainfall was observed in the range of 133 to 179 mm, during July to October months. Relative humidity was in the range of 68-78% with least value during May month. Wind speed was observed in the range of 4.3 to 6.4 m/s with annual average of 5.4 m/s. The highest wind speed is observed in July (6.4 m/s) and August (6.3 m/s) months followed by June (6.1 m/s) and April (5.8 m/s). The predominant wind directions at Visakhapatnam are SW and NE with 37.9% and 17.6% respectively.

At Mumbai, the mean maximum temperature is about 32 °C (90 °F) in summer and 30 °C (86 °F) in winter, while the average minimum temperatures are 25 °C (77 °F) and 20.5 °C (68.9 °F) in summer and winter respectively. Mumbai receives heavy rainfall during the monsoon season from July to September (300 to 800 mm) with an annual rainfall of 2240 mm. During winter the winds are generally calm and come from the north and northeast direction and during monsoon season the winds come from the southwest direction which are stronger, moist and from marine areas. The wind speed at the study site varies from 0.5 to 7.5 m/s during summer and winter, whereas the wind speed increased to as high as 17 m/s during monsoon season.

3.3. PM$_{10}$ samplers

The objective of the study includes chemical characterization of PM using different (both destructive and non-destructive) analytical techniques. Accordingly two types of PM samplers are used in the present study. Two different samplers includes high volume sampler (Envirotech make model 460NL) and low volume sampler (Gent's sampler) were used for PM$_{10}$ samples collection. In high volume sampler, PM samples were collected on Whatman EPM 2000 glass fiber filter paper (8'' X 10"), whereas in Gent's sampler, PM was collected on nuclepore polycarbonate filter of diameter 47mm. Sampling was carried out at about 15 m from ground level at all the sites. The filter papers used for the collection of PM samples were preconditioned (48 h in desiccators under the conditions of temperature of 25 ± 2^0C and relative humidity $50 \pm 5\%$) before and after sampling. After sampling, all the loaded filters are transported to lab by keeping them in a clean polyethylene covers with a proper coding on it. The working principal and the other technical details of the PM samplers used in the present study are discussed below.

3.3.1. High Volume Sampler (HVS)

In the present study, Envirotech make high volume sampler, model APM-460 NL (illustrated in Fig.3.2) was used for PM sample collection. The sampler contains a cyclone body to separate the particles of size less than 10 µm. A standard regenerative suction pump is used for sucking the ambient air. Sucked air when enters into a cone body, the air makes rotating motion at high speed leading to separation of large particles (>10 µm). These separated particles fall through the cyclone conical hopper and are collected in the **dust cup** placed at the bottom of cone body. The air containing the particles with diameter < 10 µm (PM$_{10}$) exit through the cylindrical outlet, and get collected on the glass fiber filter paper. In the current study, samples are collected at an average flow rate of 1.1 m^3/min. The instrument is provided with a time totalizer to record the duration of sampling. Time readings were noted before and after each sampling occasion to determine the duration of the sampling. This sampling time is again converted into volume using average flow rate.

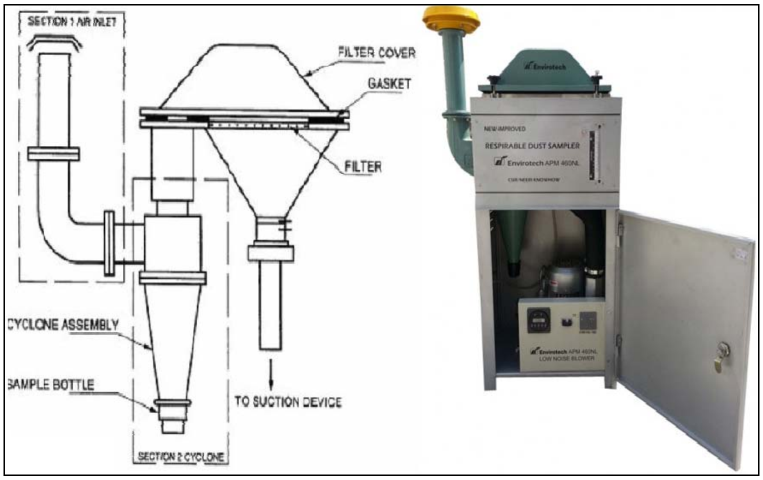


Fig.3.2. Picture of High volume sampler (Envirotech make, model APM 460NL)

3.3.2. Gent's sampler

In Gent's 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 schematic diagram of sampling head with the pre-impaction stage is depicted in Fig.3.3. The sampler was operated at an average flow rate of about 16 Lpm. At this flow rate the pre-impaction stage inside the container has 50% collection efficiency for particles having 10 μm equivalent aerodynamic Diameter (AD, Acts as a PM_{10} inlet). Dry gas meter is provided to measure the total volume of air sampled in 24 hrs time period. Mass of the loaded polycarbonate filters were then measured by gravimetry and subsequently analyzed for the chemical components using EDXRF.

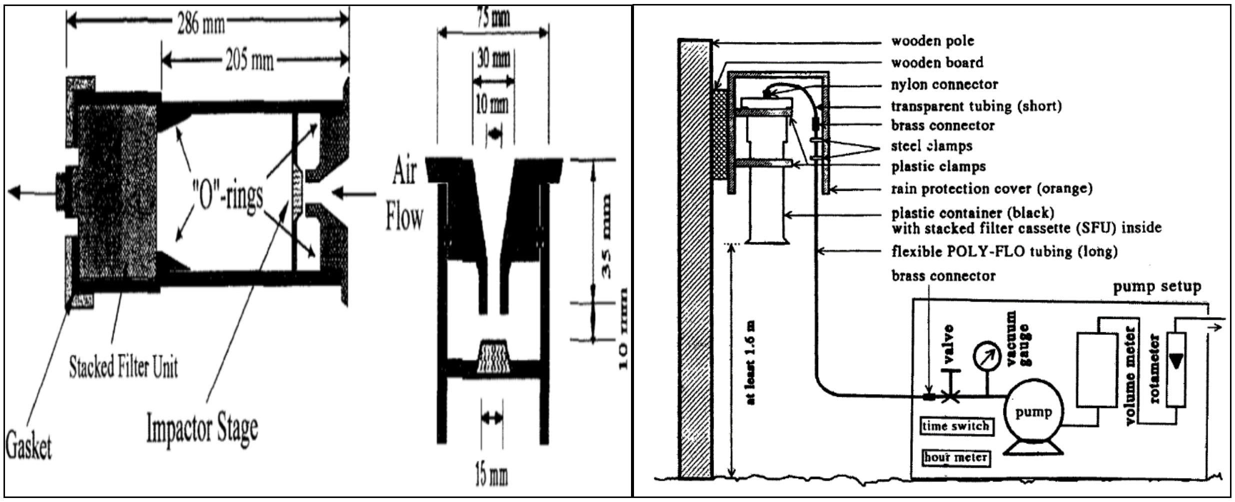


Fig.3.3. Schematic diagram of Gent sampler's [SFU (left) and Gent sampling unit (right)]

The samplers are calibrated once in a year by the instrument supplier. For good sampling efficiency, SFU of Gent's sampler and cyclone part of high volume sampler were cleaned. Also the impactor of SUF is greased once in a month. The sampling was carried out twice in a week covering all the days in a given month. A total of 153, 158 and 160 samples were collected at Jogannapalem, Parawada and Trombay sites respectively.

In the present study, weighing of all the filter samples was carried out using Mettler (Model AE240) weighing balance that has sensitivity of 10 µg. All the loaded conditioned filters were weighed thrice and the readings are averaged to get the accurate mass. Final PM_{10} concentrations were determined by subtracting the pre-sampling filter weight from post sampling filter weight and obtained net mass was divided with total air volume to get PM_{10} concentration in $\mu g/m^3$.

3.4. Chemical processing procedures

One portion of the sample filters were soaked in mixed acid (HNO_3 and $HClO_4$) and kept on a hot plate at high temperature until the mix solution was boiled and clarified [118, 154]. After complete digestion, sample solution was slowly reduced to near dryness at low temperature to remove excess acid. Then, 0.25% HNO_3 was added to the above sample and resulting solution was filtered into 25 ml volumetric flask. A separate digestion procedure was used for Arsenic extraction using high purity concentrated HCl and HNO_3 as discussed by Guor-Cheng [205]. Metals (Al, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Pb and Cd) analyses was carried out using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Jobin Yvon, Model ULTIMA 2), flame atomic absorption spectrometer (AAS, GBC-Avanta) system and a voltammetry instrument (Metrohm make Autolab Model 693VA Processor equipped with a 663 VA stand). ICP-AES was used for the analyses of Al, Mn, Cr, V, Fe, Ni, and Zn, whereas an analysis of Pb, Cu and Cd was carried out using voltammetry system and As was analyzed using AAS by hydride generation technique.

Another portion of the glass fiber filters were treated with deionized water (resistivity 18.2 MΩ.cm) for the extraction [206] of water soluble ions bound to PM_{10} viz. chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and Magnesium (Mg^{2+}). Ion Chromatography (Metrohm make, Model IC 733) was used for the analysis of these ions under optimized conditions. In the present study, anion analysis was carried out using metro SepA Supp5 column, whereas for cation analysis Metrosep cation 1-2 columns was used.

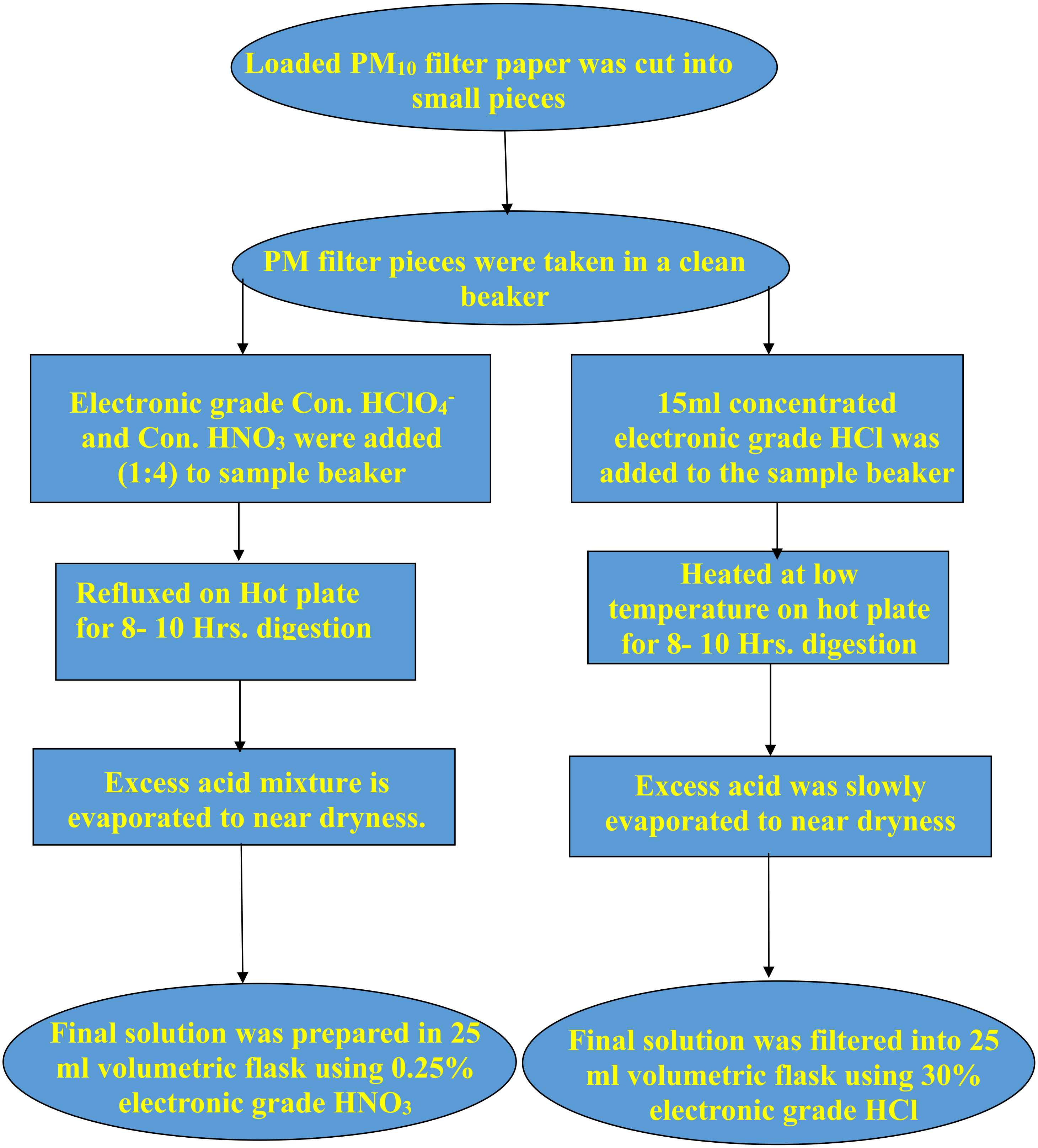


Fig.3.4a. Flow chart of steps involved in acid digestion of PM for metals extraction

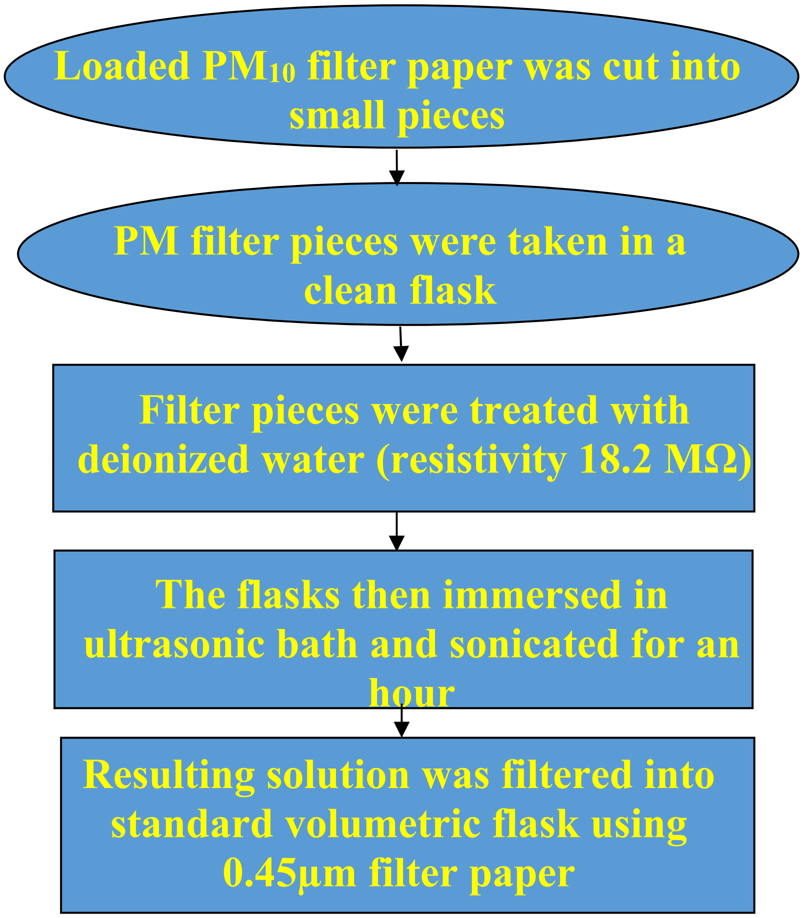


Fig.3.4b. Flow chart of steps involved in water digestion of PM for ions extraction

No chemical processing steps were followed for the elemental analyses of PM collected on polycarbonate filter papers using EDXRF technique. Intense care was taken in the sample preservation and analysis. Similarly, no sample preparation was followed for BC analysis using smoke stain reflectometer.

In the present study, field blank filters are digested in same way as discussed above to quantify the metals and ions present in the blank filters. The resulting filter blank solutions are analyzed for metals and ions using diferent analytical technique. These blank filter concentrations are substracted from the concentrations obtained in the sample filter to get the actual chemical species concentrations. The metals and ionic content of blank filter papers are presented in the results and discussion section.

3.5. Analytical instruments for chemical analyses

As discussed earlier various analytical techniques are available in the market for the chemical characterization of PM. Each and every instrument has its own advantages and disadvantages. Considering the instrumental parameters such as capability to analyze multiple elements in short period of time, sensitivity, selectivity, detection limits, repeatability for a set of elements one has to carefully select the proper instrument for the sample analyses. In the present study, chemical analyses were carried out to quantify the metals, inorganic ions and black carbon concentrations associated with PM at all the sampling sites.

All the chemical species cannot be measured using single analytical instrument. Hence, in the present study, multiple numbers of instruments (destructive and non-destructive) were used for the wide range of chemical species analysis. The selected instruments have different sensitivity and detection limits for a given elements of interest. For eg. ICP-AES has good sensitivity and low detection limits for Al, V, Ni, Cr, etc, hence ICP-AES was chosen for their analysis. Similarly, DPASV has good sensitivity and very low detection capability for Pb, Cu and Cd. Hence, in the present study, samples which contain very low Pb, Cd and Cu concentrations are analyzed by using DPASV method. AAS was used for Arsenic analysis that has very good selectivity and sensitivity for As. Some other elements are also analyzed using AAS because of its high selectivity. Ions are analyzed using IC because of its high sensitivity and low detection limits. Details on method optimization procedures followed to achieve good sensitivity for the analysis of chemical species of interest are discussed in the following section.

3.5.1. Atomic absorption spectrometry (AAS)

AAS is an analytical technique that was used to quantify the trace and major metals in various environmental matrices such as soil, water, biological samples, sediment and particulate matter [118, 207-208]. This analytical technique has good selectivity leading lower elemental interferences during metal analysis. Following section gives the details of the instrumental parameters that were optimized for metal analyses.

In the present study, GBC make AAS system (model Avanta-∑) was used for the metal analysis in PM_{10}. The AAS picture in our laboratory is shown in Fig.3.5.

Fig.3.5. Picture of a flame atomic absorption spectrometer (GBC make, model Avanta-∑)

FAAS is a suitable technique for determining metals at lower part per million (ppm) concentration levels with good precision [209]. FAAS technique fecilitate fast samples analysis (2-5s per sample) with very good precision (repeatability) [210]. Using this system, elements such as Fe, Mn, Cu, Pb, Ni, Zn and As were analyzed. Arsenic (As) was analyzed using hydride generation atomic absorption spectrometry technique. In hydride generation technique, the analyte element (As, Se, Sb, Bi, Pb) from the sample solution is converted into its volatile hydride (as shown in Fig.3.6) in acidic medium using $NaBH_4$ as reduing agent [211]. The hydride generation procedure can also be used for differential determination of As^{+3} and As^{+5}, based on the fact that As^{+3} reacts with tetrahydroborate at higher pH as compared to As^{+5}.

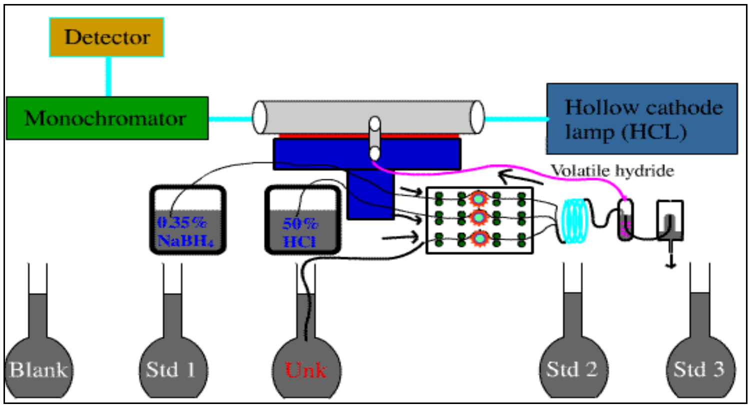


Fig.3.6. Schematic diagram of Hydride generation atomic absorption spectrometer setup

Before proceeding for analysis in AAS, general instrumental parameters such as work head height, burner angle and work head centre are adjusted in such a way that the hallow cathode lamp light must pass parallel to the centre of the burner and reach the entrance slit without any cut–off of light beam. The fuel flow rate and oxidant flow rates are varied in different proportions and absorbance of Cu (324.7 nm) was recorded. The flow rates of gases are fixed at which, Cu (324.7 nm) line has the highest absorbance signal. Similarly for Arsenic also these parameters were fixed by analyzing As standard. In the case of As analysis, the flow rate of

Argon carrier gas was also optimized using As (193.7 nm) characteristic absorption line. The optimized parameters of AAS are given in Table 3.1.

Each element has multiple characteristic absorption lines that can be used for different concentration ranges. In the current study, all the characteristic lines of element of interest are tested using know concentration. The absorbance of each characteristic line of an element was recorded at a given concentration. Based on absorbance data the best sensitive line was chosen for sample analysis. The lists of lines chosen for chemical quantification of elements are given in Table 3.2. AAS was calibrated using a set of three known single element standards and elemental quantification was done using calibration curves for each element.

Table 3.1 Instrumental parameters that are optimized in AAS for elemental analysis

	Fuel flow	Oxidant flow	Ar flow rate	Work head height	Burner angle	Work head center
For other metals	2 L/min.	10 L/min.	NA	8.8 mm	0.3	-0.6 mm
For As	2 L/min.	10 L/min.	1.2 L/min.	16.2 mm	0.3	-0.6 mm

Table 3.2 Element specific parameters that are used in AAS system during quantitative analysis

Element	**Mn**	**Fe**	**Cu**	**Ni**	**Zn**	**As**
Wave length (nm)	279.8	248.3	324.7	232	213.9	193.7
Slit width (nm)	0.2	0.2	0.5	0.2	0.5	1
Sensitivity (µg/ml)	0.022	0.05	0.025	0.04	0.008	0.01ng/ml
Lamp current (mA)	5	7	3	4	5	8

3.5.2. Inductively coupled atomic emission spectrometer (ICP-AES)

ICP-AES is widely used for the chemical analysis of wide range of elements viz. alkali, alkaline metals, transition metals, rare earths as well as some non-metals [212-214] in ppb level. The instrument was proved to have multiple advantages such as multi element analysis over wide concentration ranges, low chemical and matrix interferences. Especially, the instrument was widely used for the elemental analyses in PM_{10} all over the world [43, 48, 87, 154, 156, 170].

In the present study, Horiba make Jobin-Yvon (model ULTIMA 2) ICP-AES system was used for the major and trace metal analysis. Fig.3.7 illustrates the ICP-AES system in our lab and its block diagram. Different elements such as Al, Fe, V, Cr, Mn, Cu, Ni, Zn and Pb were analyzed using ICP-AES.

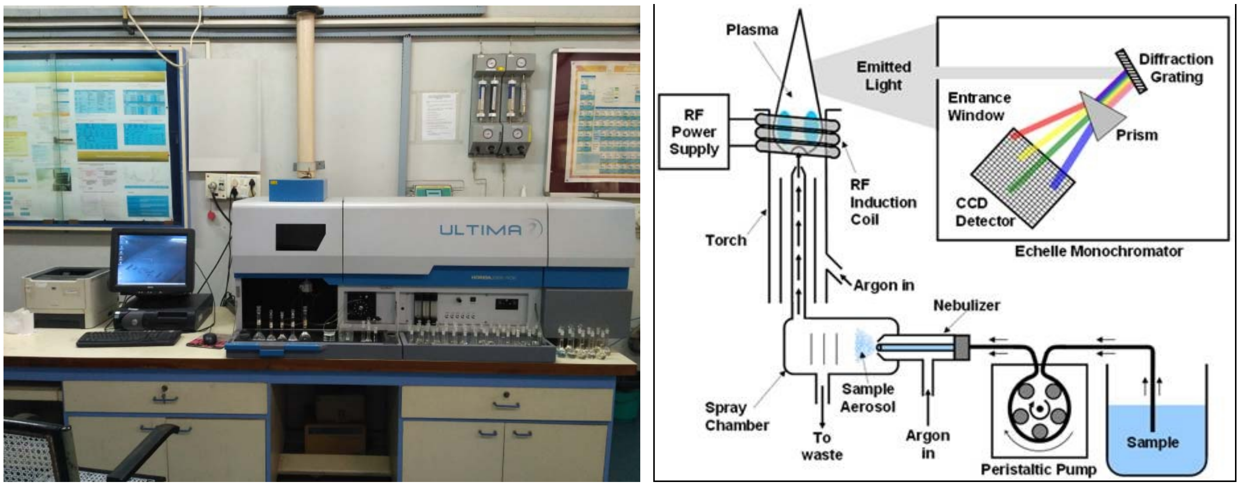


Fig.3.7. Picture of Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Before quantification of elemental concentrations, a method was developed by choosing proper line that has best sensitivity. For this purpose, peak profiling and peak search was carried out with a known standard for all the characteristic emission lines of set of elements of interest

(Fe, V, Cr, Mn, Cu, Ni, Zn and Pb). The emission intensity was noted down for each characteristic emission line. Out of many emission lines of a given element, the one which has highest net emission intensity and that doesn't have interference from other element was chosen for quantitative analysis. Each emission line was corrected for background for accurate results. Table 3.3 and 3.4 gives the details of instrumental parameters and sensitive emission lines that are selected for elemental analysis.

Table 3.3. Different parameters of ICP-AES that are set for elemental analysis of PM samples

S.No	Parameter	value		Parameter	value
1	Nebulizer type	Concentric	5	Scanning mode Sweeps/reading Readings/replicate Replicates Measuring points Integration time Gain of PMT Increments of grating	Peak hopping 20 1 3 9 0.5 sec. 100 0.002 nm
2	Plasma gas	High purity Argon	6	**Sampling parameters** Sample flush time Sample flush pump speed Read delay Read delay pump speed Wash time Wash pump speed Mixing coil length(cm)	 35s 24rpm 65s 20rpm 30s 20rpm 100
3	Spray chamber	Teflon	7	Gas flow rates Plasma Nebulizer Auxiliary	 12 $Lmin^{-1}$ $1Lmin^{-1}$ $1Lmin^{-1}$
4	Torch injector	Quartz	8	RF power	1000W

Table 3.4. Sensitive characteristic emission lines selected for the chemical analysis

Element	Al	V	Cr	Mn	Fe	Cu	Ni	Zn	Pb
Wave length (nm)	237.3	290.8	205.5	257.6	217.8	223.0	231.6	213.8	220.3

In the present study, ICP-AES was calibrated for each metal using a set of five multi element standards (VHG labs make). The calibration curve was checked frequently by injecting the known standard solution. The results are corrected using a correction factor, if any deviation was observed in known concentration value. During analysis, field blanks were analysed for all metals of interest and the data were subsequently blank corrected to determine accurate results of chemical species. Fig.3.8 shows the peaks of few metals of interest along with their calibration curves.

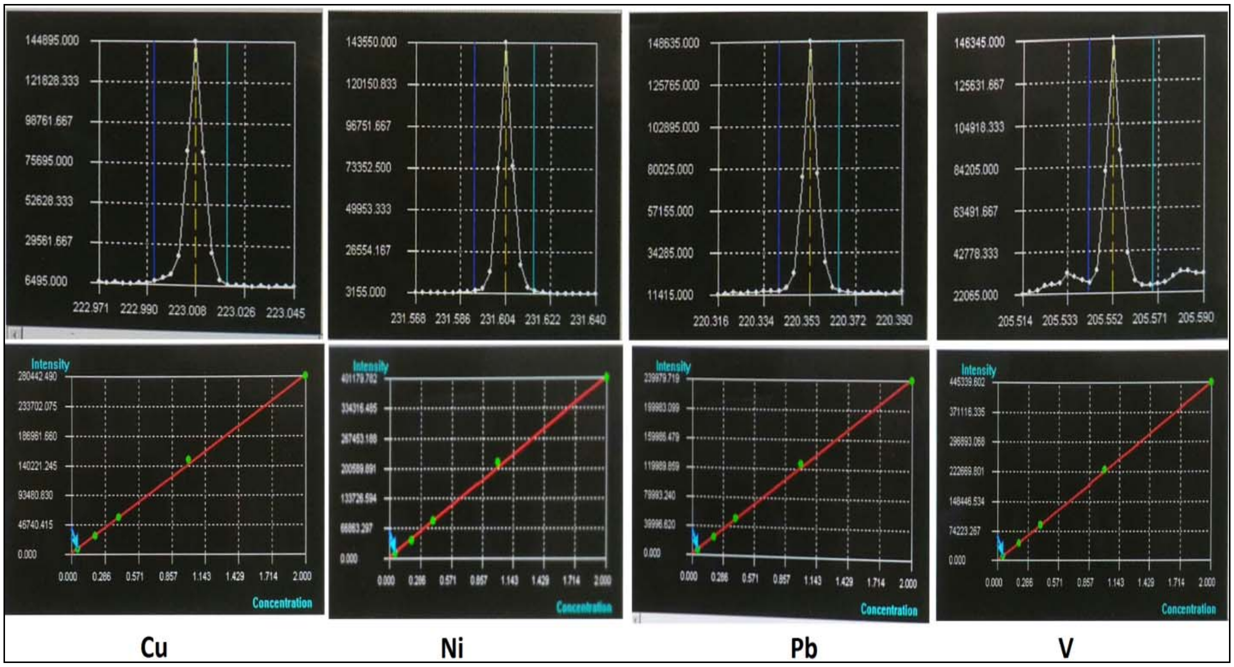


Fig.3.8. Emission intensities of characteristic lines and calibration curves of metals obtained using ICP-AES

3.5.3. Differential Pulse Anodic Stripping Voltammetry technique

Voltammetric methods are applicable to the determination of a wide variety of both organic and inorganic species [215-216]. Among different voltammetry techniques Differential pulse voltammetry is a widely employed technique for quantitative analysis. It provides superior detection limits as compared to linear sweep and cyclic voltammetry, and allows resolution of more closely spaced electrode processes. In this technique, the potential vs. time program which is applied to the electrode consists of a linearly increasing ramp upon which a series of small amplitude (5 to 100 mV) pulses are superimposed, as indicated in Fig. 3.9. The duration of the pulses is approximately 50 ms. the current is sampled just prior to the application of each pulse (at t_1), and again very near the end of the pulse (t_2). The difference between these two values, $\Delta i = i(t_2) - i(t_1)$, is then plotted against the ramp potential as indicated in Fig. 3.9. The area under the curve is calibrated with know standard concentration for qualification of unknown samples.

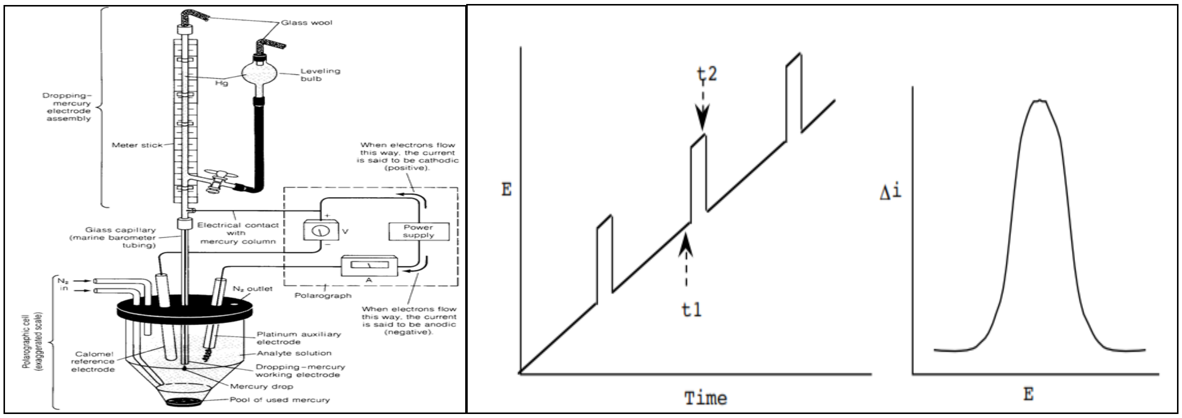


Fig.3.9. Figure presenting the differential pulse that applied to working electrode in voltammetry

In the present study, Metrohm make Autolab Potentiostat instrument (Model 693 VA Processor equipped with a 663 VA stand) was used for the Pb, Cd and Cu analysis. Before calibration of the instrument, different parameters such as purging time, deposition time, equilibrium time and pulse parameters were optimized to achieve best sensitivity and good peak shape. Purging time was varied from 30 sec to 180 sec and analysis was carried out keeping all other parameters constant. Results show that, after 60 sec of purging time no significant change in current was observed. Hence, 60 sec purging time was fixed for further analysis in the current study. Similarly, deposition time was also varied from 20 to 120 sec and current was recorded in each case. It was found that, as deposition time increases the current was increased sharply till 60 sec deposition times. On further increase in deposition times, the current was also increased but to a less extent. Hence, 60 sec deposition time was chosen as an optimized deposition times for Pb, Cd, and Cu analysis in PM. The details of optimized analytical parameters in voltammetry technique are given in table 3.5. The calibration of the instrument was carried out using mixed standard containing Pb, Cd and Cu at optimized parameters. Fig. 3.10 shows the instrumental setup in our laboratory along with analytical peaks of Pb, Cd and Cu obtained using optimized parameters in DPASV mode.

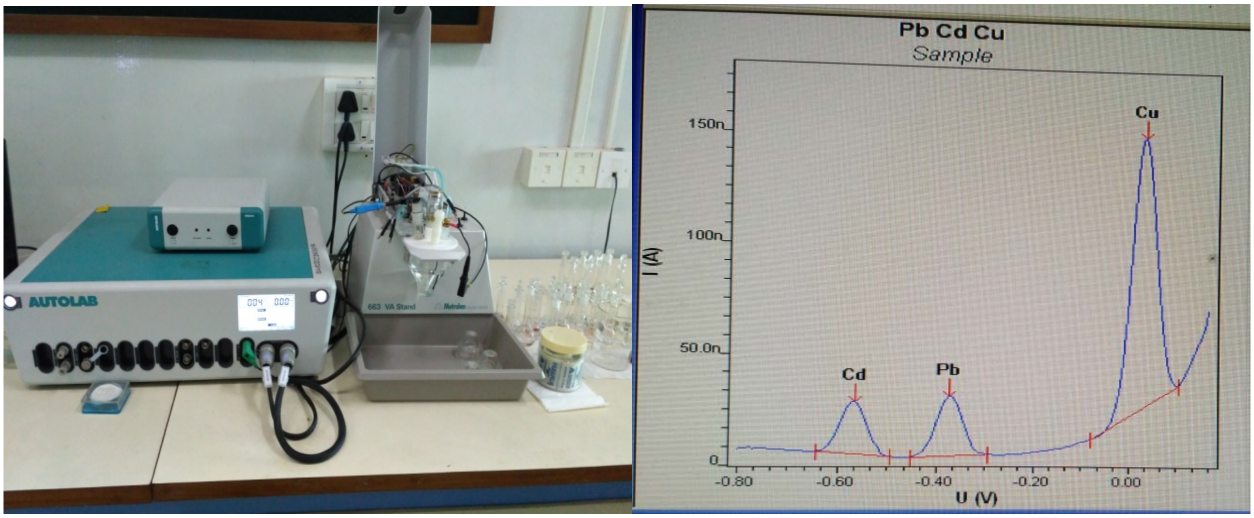


Fig.3.10. Metrohm make voltammetry system and voltammogram of selected metals

Table 3.5 Different analytical parameters that are set for the analyses of Pb, Cd, and Cu using DPASV

Parameters	**Value chosen**	**Parameters**	**Value chosen**
Initial N_2 purge time	60 sec.	End potential	0.17 V
Deposition time	60 sec.	Pulse amplitude	0.05 V
Equilibration time	10 sec.	Pulse time	0.04 Sec
Deposition potential	-0.8V	Voltage step	0.005951V
Starting potential	-0.8 V	Voltage step time	0.1 Sec.

3.5.4. Ion chromatography

Determination of the ionic composition of PM is important as their mass contribution to PM is significant. In the present study, quantification of ions was carried out using IC (Metrohm make, 733 IC Separation Centre) with conductivity detector. Fig. 3.11 shows the picture of IC setup along with its basic block diagram. Ion chromatography (IC) is a well-established technique for the analyses of anionic and cationic components of environmental samples like water, soil, sediment and particulate matter samples [217-218].

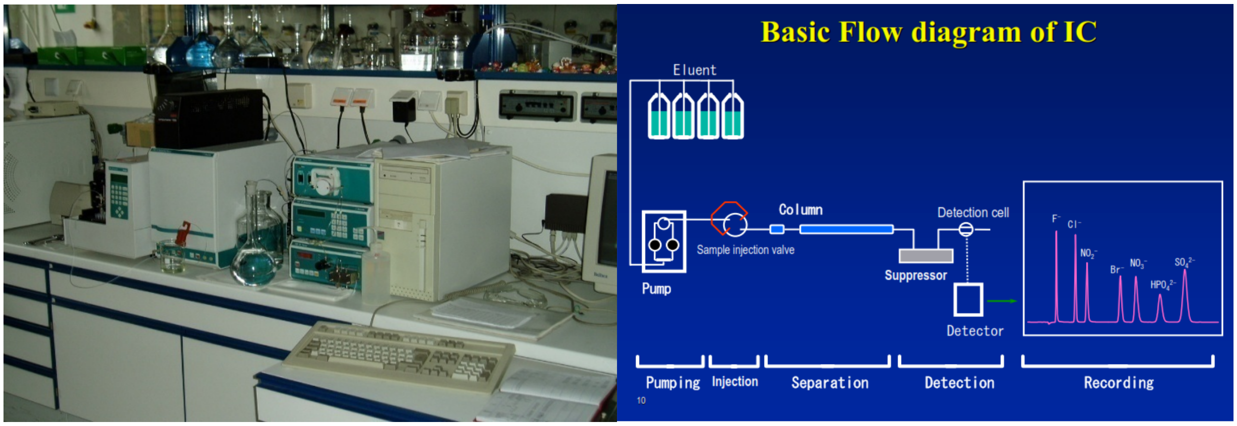


Fig.3.11. Ion chromatography system and its basic block diagram

Anion analysis was carried out by analytical column (Metrosep A Supp 4 – 250) of 25 cm length and 0.40 cm diameter packed with polyvinyl alcohol with quaternary ammonium groups with a guard column preceeding the analytical column. The concentrations of Cl^-, NO_3^-, and SO_4^{2-} are determined in the water digested air particulate samples using sodium carbonate/sodium bicarbonate mixture as an eluent (having strength 3.2 mmolar/1 mmolar) with a flow rate of 1 ml/min. The analytical column (Metrosep Cation 1-2 having 12.5 cm length and 0.4 cm diameter) packed with Silica gel with carboxyl groups with a guard column preceding the analytical column was used for cation analyses. A mixture of Tartaric acid/ dipicolinic acid eluent 4.0 mmol/L and 0.75 mmol/L was used as the mobile phase. Direct chromatographic detection with electronic background suppression was used for the analysis of sodium, potassium, calcium, and magnesium.

3.5.5. Energy Dispersive X-Ray Fluorescence (EDXRF)

EDXRF is one of the most important and simple non-destructive analytical techniques that was used for the qualitative and quantitative analysis of metals and non-metals in solid and liquid matrices such as PM, water, soil, sediment, medicine, etc. [48, 219-220]. The advantage of EDXRF analytical technique is that it is capable of doing multi element analyses with minimal or no sample preparation.

In the present study, Xenemetrix make EDXRF instrument (model EX-6600) was used for the quantitative analysis. This consists of an X-ray tube with Rh anode as the source of X-rays with a 60 kV, 5 mA power supply. The system consists of a Si (Li) detector with a resolution of 150 eV at 5.9 keV Mn X-ray. Secondary targets (Si, Ti, Ge and Mo) were used to modify primary X-ray beam spectrum from the X-ray tube and was finally used to excite the elements in the sample. The concentrations of 18 elements, Viz. Na, Mg, Al, S, Si, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb associated with PM are analyzed using EDXRF. Fig. 3.12 shows the Xenematrix make EDXRF system along with spectrum of trace metals analyzed using Ge secondary target. Elements with atomic number less than or equal to 20 were analyzed using Si and Ti secondary targets in vacuum environment and rest of the metals are analyzed using Ge and Mo secondary targets in air atmosphere. To achieve the best sensitivity for elements of interest, different parameters viz. voltage, analysis time and current are varied. For a given set of elements of interest and secondary target the voltage was varied from V_{min} to 55 kV and the counts are noted down corresponding to each voltage. Similarly, the filament current was also varied from 500 µA to 5500 µA for a known standard and the corresponding peak intensities are recorded. After analyzing the peak intensities, the optimum values of voltage and current are fixed for further analyses. Table 3.6, shows the optimized EDXRF parameters that are used for the analyses of wide range of elements of interest. These parameters are chosen to have minimum counting error and the dead time was maintained within 20% throughout the analysis. The calibration of the instrument was carried out using micro matter thin film standards and quantitative analysis was performed using the built-in nEXT software.

Table 3.6. Optimized EDXRF parameters used for the elemental analysis of PM

Secondary Target	**Elements**	**Voltage**	**Current**	**Analysis Time**	**Atmosphere**
		(kV)	**(µA)**	**(Sec.)**	
Si and Ti	Na, Mg, Al, S, Si, Cl, K, Ca	25	4800	600	Vacuum
Ge	Ti, V, Cr, Mn, Fe, Ni, Cu, Zn	40	800	600	Air
Mo	As, Pb	40	1000	600	Air

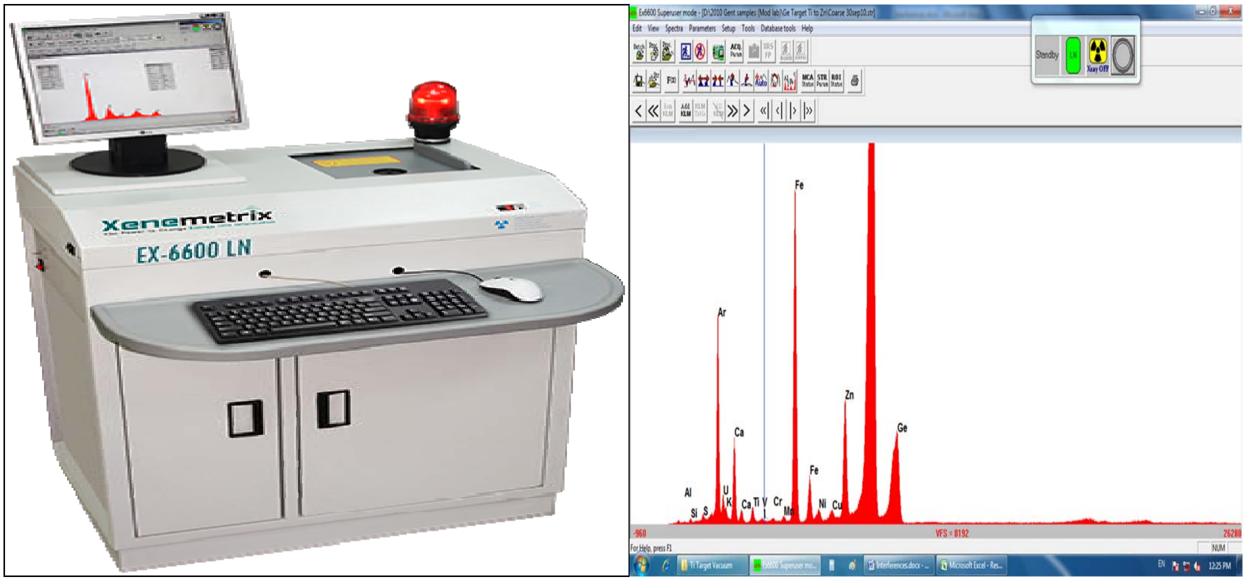


Fig.3.12. Xenematrix make EDXRF (model EX-6600) system along with spectrum for trace metals analyzed using Ge secondary target

3.5.6. Smoke Stain Reflectometer

BC is a non-volatile fraction known as black carbon or elemental carbon (EC) [44]. BC is formed through incomplete combustion of fossil fuels, biofuels, and residues from biomass burning, etc. [221-222]. Black carbon (BC), the optically absorbing part of carbonaceous aerosols, is the major anthropogenic component of atmospheric aerosol system, which has significantly different optical and radiative properties, as compared to the other normal constituents. In global scale, BC aerosol is considered to be the second largest radiative forcing agent after carbon dioxide [223].

In the present study, BC quantification was carried out using an EEL 43D Smoke Stain Reflectometer (Diffusion Systems Ltd., London, UK, as shown in fig. 3.13). In this method, the light from the tungsten lamp passes through an orifice of an annular photocell to project a well defined spot on the sample, and the reflected light is measured by photocells located in the black housing. Each filter was examined five times to check homogeneity of the deposited air filters and the average value was used in the calculations.

Fig.3.13. EEL Smoke stain reflectometer (Model 43D) for quantification of BC in PM

Prior to the analysis of BC, the instrument was calibrated using the white or gray standard marked with their reflectance values. The mask and measuring head are placed on the white standard and the sensitivity control adjusted to produce a reading of 100 as per the standard procedure. They are then transferred to grey standard and the new reading is taken. The BC levels in air particulate matter collected on filters are estimated using the formula given below. For this purpose a mass absorption coefficient of 9.7 m^2/g was used. 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 coefficient (m^2/g); R_o = unloaded filter reflectance; R = loaded filter reflectance; 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 analyses.

3.6. Source apportionment of PM using receptor models

Receptor-oriented or receptor models can be used to identify the sources and the apportion the observed pollutant concentrations to those sources [224-225]. These models search for correlation between the different (groups of) components in time and use these to find an optimal solution to explain all observed concentrations by decomposing a matrix of speciated sample data. The data are interpreted on a pure statistical basis without pre-formulated assumptions providing an independent source of information.

Initially CMB was used by many researchers [197-199] to identify and quantify the PM sources at study location. CMB model is based on the balance of chemical species masses among sources and receptors [200]. However, this balance might be disturbed [97]. Firstly, besides the major sources (such as soil, coal and vehicles), there are thousands of insignificant sources that contribute to the ambient receptor measured. The contribution of each insignificant source to the ambient receptor is very small and usually ignored by the CMB model. However, the sum of them cannot be ignored and does disturb the balance. Secondly, uncertainties in the sampling and chemical analysis can disturb the balance. Hence, in the present study, PMF and PCFA are used for the source apportionment study.

3.6.1. Positive Matrix Factorization (PMF)

The PMF method was developed by the US Environmental Protection Agency [106]. The objective of PMF receptor model was to identify p independent factors representing different PM sources, their elemental profiles, their contribution to the total determined PM, and their contribution to the total concentration of specific species. The PMF method is based on the principle of mass conservation [106].

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

Where x_{ij} is the measured concentration of the j^{th} species in the i^{th} sample, f_{kj} is the concentration of the j^{th} species in material emitted by source k, g_{ik} is the contribution of the k^{th} source to the i^{th} sample, and e_{ij} is the residual associated with the j^{th} component concentration determined in the i^{th} sample. The task of PMF is to minimize the object function (*Q*), based upon the uncertainties.

$$Q = \sum \sum \left(\frac{e_{ij}}{s_{ij}}\right)^2$$

Where, s_{ij} is the uncertainties in x_{ij}. The results are constrained so that all species profiles (matrix F) are non–negative and each sample has a non–negative source contribution (matrix *G*). Solution of above equation and the model are described in detail elsewhere [106, 109].

Measured uncertainty is one input parameter for the PMF analysis. An equation-based method to calculate the measurement uncertainty [226] is given below. Two parameters including the method detection limit (MDL) and error fraction are involved in the equation-based method [227].

$$U = \sqrt{(F * C)^2 + (0.5 * MDL)^2} \qquad C > MDL$$

Where U is the uncertainty; C is the component concentration; MDL is the method detection limit; and F is an error fraction. Error fractions for particle chemical species pollutants were estimated as 10 and 15% according to the error sources of the measurements. If the chemical species are less than or equal to the MDL provided, the uncertainty (Unc) is calculated by the following equation:

$$Unc = \frac{5}{6} MDL$$

The advantage of PMF is the ability of the model to handle the incomplete data such as missing data, below detection limit data and negative value data [228-229]. For the particle chemical species, missing concentration values in the original data set were estimated by linear interpolation of the measured concentration value. Uncertainties for the missing data were assumed as 3 times of the mean [230]. F_{peak} is a parameter used to explore the rotational ambiguity of a PMF solution a posteriori. F_{peak} was changed from -2 to 2. The results from Q examinations suggested that the solution at $F_{peak} = 0$ had to be retained.

3.6.2. Principal Component Factor Analysis (PCFA)

In the present study, source apportionment of collected PM was also carried out using another receptor model called PCFA for comparison purpose. The main objective of PCFA was to reduce a large number of variables to a smaller set of factors that retain most of the information (variability) in the original dataset [231]. In PCFA, principal components explains the observed variance of the concentration of analyzed chemical species; the outcome of PCFA model was interpreted for the possible sources of the PM based on the presence of signature elements [232].

PCAF model requires the normalazation of the data set to minimize the biasness due to wide variation in the concentration levels of chemical species in PM. Variables are normalized as follows:

$$z_{ij} = \frac{c_{ij} - c_j}{\sigma_j}$$

Where, $i = 1,\ldots, n$ samples, $j = 1,\ldots\ m$ elements, z_{ij} is the reduced concentration of the j^{th} element in i^{th} sample. c_{ij} is the elemental concentration of j^{th} element measured in i^{th} sample. c_j and σ_j are the mean concentration and the standard deviation for j^{th} element respectively [106, 161]. The model assumes that the concentration of each element is made up of the linear sum of the elemental contributions from each k^{th} pollution source component at the receptor site. A mass balance equation can be written as shown below.

$$X_{ij} = \sum_{k=1}^{p} a_{ik} f_{kj}$$

Where X_{ij} is the j^{th} species concentration measured in i^{th} sample, a_{ik} is the particulate mass concentration from the k^{th} source contributing to the i^{th} sample, f_{kj} is the j^{th} species concentration contributed from k^{th} source and p is the total number of independent sources. This equation is solved by eigen vector decomposition. Later, the varimax rotation was used to redistribute the variance and provide a more interpretable structure to the factors. The varimax rotations maximize the principal components in the factor loading matrix without changing the total variance as well as the variance of the single element in the model. After the rotation, elements of common origin are grouped in the same factor. Thus, elements with high loadings were used to identify a particular emission source.

In the next step, the absolute principal component scores (APCS) were calculated according to the method described in detail by Thurston and Spengler (1985) [233]. The source contributions to the total PM_{10} mass can be described as follows [234].

$$\text{Total mass} = a_0 + \sum_{p=1}^{n} APSC_p * a_p$$

Where the average of $APCS_p * a_p$ for all samples represents the average contribution of the p^{th} source to the total mass of the receptor.

3.6.3. HYSPLIT

In the present study, NOAA HYSPLIT [235, 236] model was used to identify the pollutants contribution from long range transport. This trajectory model calculates the position of air being sampled backward in time from the receptor site from various starting times throughout the sampling interval. The model input paramets are discussed in details in results and discussion chapter.

Some of the bases of limitations of HYSPLIT are discussed as follows; The HYSPLIT does not incorporate the effects of chemical reactions, dense gases and complex terrain. HYSPLIT's minimum time step is 1 minute, so the model cannot be used for transport less than the distance it takes for the pollutant to move in 1 minute.

Chapter 4

Physico-chemical characterization of PM and chemical speciation of Arsenic at study sites

This chapter mainly elaborates the PM_{10} and particulate bound chemical species concentrations at all the study sites; the temporal and seasonal variations of PM and particle bound chemical species during study period are discussed. Performance evaluation results of the samplers used for PM_{10} collection in the present study are elaborated. Inter comparison of elemental concentrations at study sites and also inter comparison of analytical instruments for the chemical analyses of selected elements are discussed in detail. Steps involved in the method optimization for the chemical speciation of Arsenic were provided at the end of the chapter along with As chemical speciation results for all the sampling locations.

4.1. Physico-chemical characterization of PM at study sites

4.1.1. PM_{10} concentration levels at study locations

The PM_{10} concentration levels observed during the entire study period are summarized in Table 4.1. It can be observed from table 4.1 that the Trombay has the highest average (of two years) PM_{10} concentration followed by Parawada and Jogannapalem. The annual average values observed in 2010 and 2011 are exceeded the National Ambient Air Quality (NAAQ) standard (60 μg/m^3). Similarly, the present study reported annual average values were also exceeded the annual limits given by World Health Organization (20 μg/m^3), United States Environmental Protection Agency (50 μg/m^3) and European Union (40 μg/m^3).

The daily PM_{10} NAAQ standard (100 μg/m^3) was observed to be violated about 6.8%, 21.3% and 35.0% of the sampling days at Jogannapalem, Parawada and Trombay sites respectively. Throughout the study period, the PM_{10} concentrations were observed to be highest at Trombay sites as compared to Parawada and Jogannapalem sites.

Table 4.1 Statistical summary of PM_{10} (μg/m^3) concentration at Jogannapalem, Parawada and Trombay sites during the study period

	Jogannapalem (n=153)	**Parawada** (n=158)	**Trombay** (n=160)
	PM_{10}	PM_{10}	PM_{10}
Minimum	34.8	32.3	38.6
Maximum	109.7	137.3	182.3
Average of two years data	65.4	74.7	90.1
Standard deviation	17.9	26.2	37.9
Annual average in 2010	63.6	71.4	99.7
Annual average in 2011	67.2	76.9	80.7

Comparison of PM_{10} concentration between two study years (i.e., 2010 and 2011) indicates that, at Jogannapalem and Parawada sites the higher PM_{10} concentrations were observed in 2011 as compared to 2010, whereas, at Trombay site, reversed trend was observed as shown in Table 4.1. The observed variation could be due to the variations in emission sources and meteorological parameters (wind direction, temperature and wind speed) in a given year. From Table 4.1, it was found that the standard deviation of PM_{10} concentration was observed to be slightly higher for Trombay site as compared to other study sites. Emissions from large varieties of PM sources (viz. major and minor industries, traffic emissions, biomass burning etc.)

present near the Trombay site could have resulted in the observed highest concentrations which in turn leads to observed wider concentration range (i.e., higher SD) at this site.

Table 4.2 provides the PM_{10} concentration levels observed at various locations all over the world. Comparison of PM concentration reported at other countries with the present study indicates that their PM_{10} concentrations are significantly lesser than that observed at Jogannapalem, Parawada and Trombay sites. In contrary, present study PM_{10} concentrations are lesser than, some of locations of India (Delhi, Agra) and China.

Table 4.2 PM_{10} concentration levels reported at different locations all over the world

Location	**Type of location**	**PM_{10} concentration ($\mu g/m^3$)**	**Reference**
Agra	Rural	148.4±64.4	[118]
Agra	Urban	154.2±68.0	
Agra	suburban	234.54±128.27	[237]
Delhi	Rural industrial	102.1 ± 41.1	[120]
	Urban	177.9±49.5	[153]
Spain	rural	22	[136]
Spain	Suburban	29±10	[143]
	Urban	49.5	
Allahabad	rural	25.08 ± 14.60	[135]
China	rural	45.7	[146]
	suburban	58.7	
	Urban	135.4	
Australia	rural	21.1	[137]
Roorkee	rural	37–959	[119]
	suburban	151–422	
Turkey	suburban	46.8	[138]
	Urban	79.8	
Hong Kong	suburban	46.8	[150]
	Urban	81.3	
Athens, Greece	suburban	34.8	[140]
Malaysia	suburban	75±24	[151]
Taiwan	Rural	52.4±27.2	[149]
USA	Rural	10.9	[147]

4.1.2. Temporal variation of PM_{10} at study locations

Fig. 4.1 illustrates the PM_{10} concentration distribution during entire study period. From Figs.4.1a, b, c, it can be observed that the PM_{10} concentration has its minimum during August month and the highest daily concentrations were observed during November, January and December with monthly average concentration values of 109.7, 137.3 and 182.2 µg/m^3, respectively at Jogannapalem, Parawada and Trombay sites. Observed highest and lowest concentrations in different months during study period could be due to the changes in meteorological parameters (like wet precipitation, wind speed, humidity) and variation in PM source activities with respect to month.

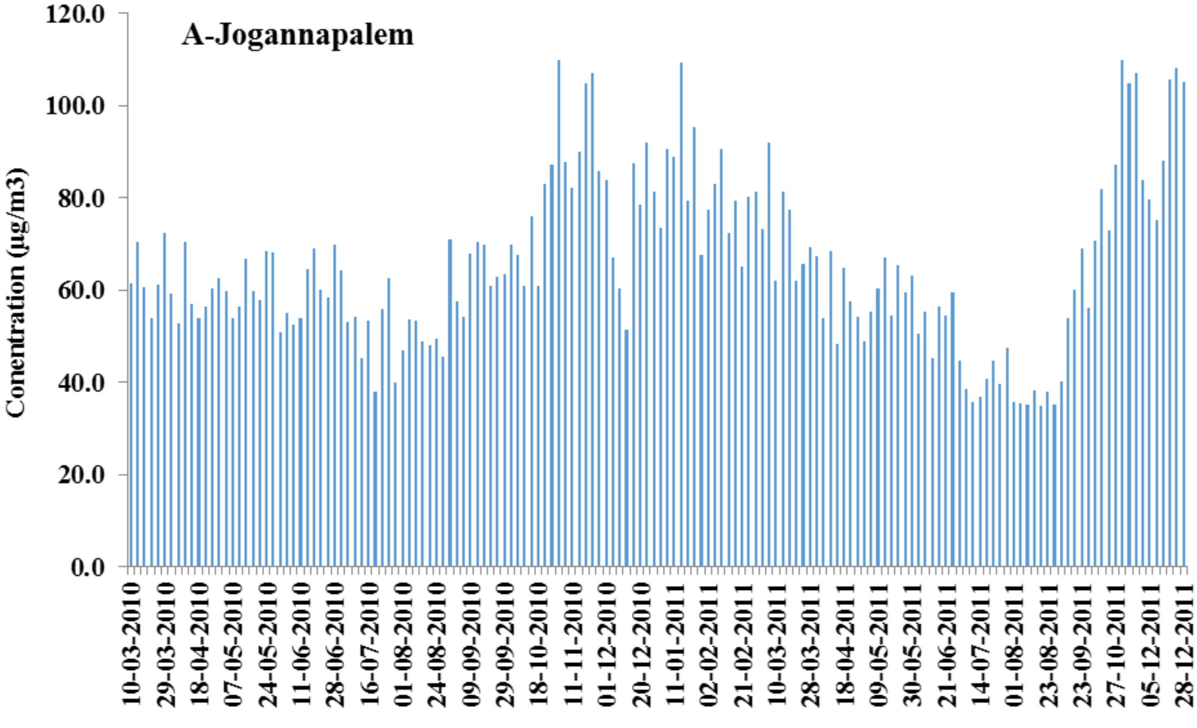


Fig.4.1a. Temporal variation of PM_{10} concentrations at Jogannapalem site during study period

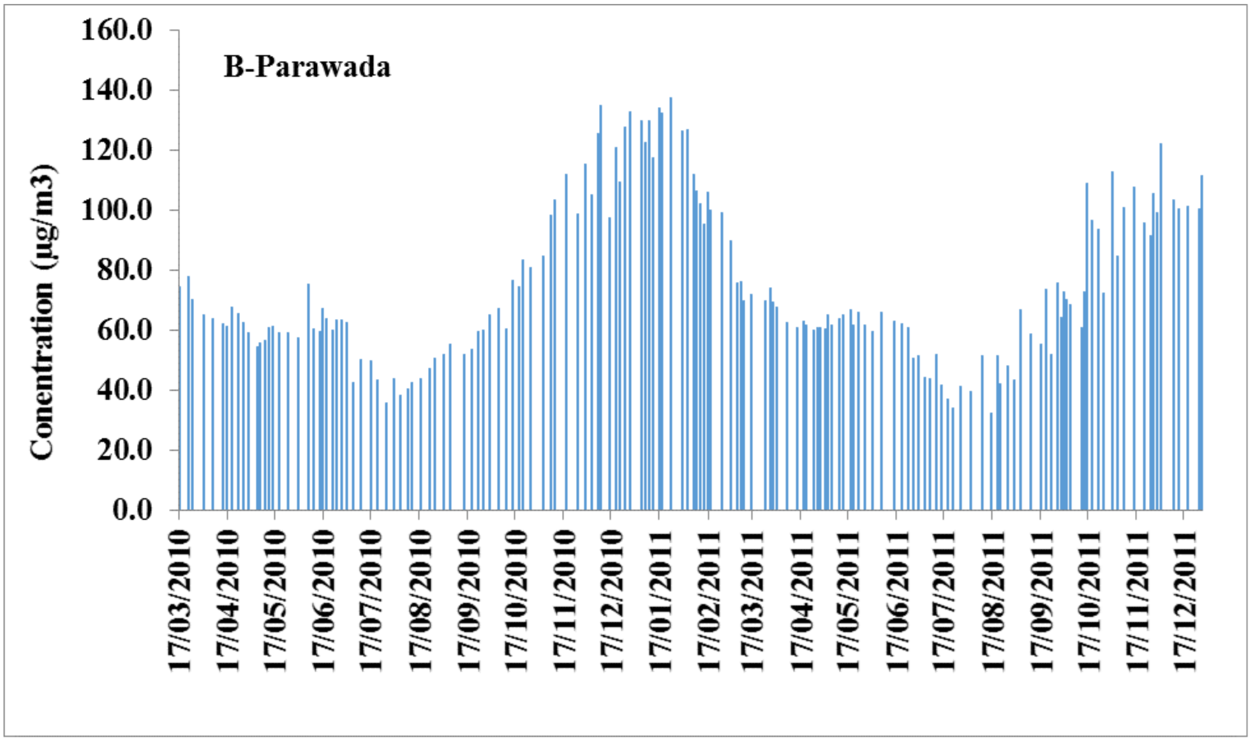


Fig.4.1b. Temporal variation of PM_{10} concentrations at Parawada site during study period

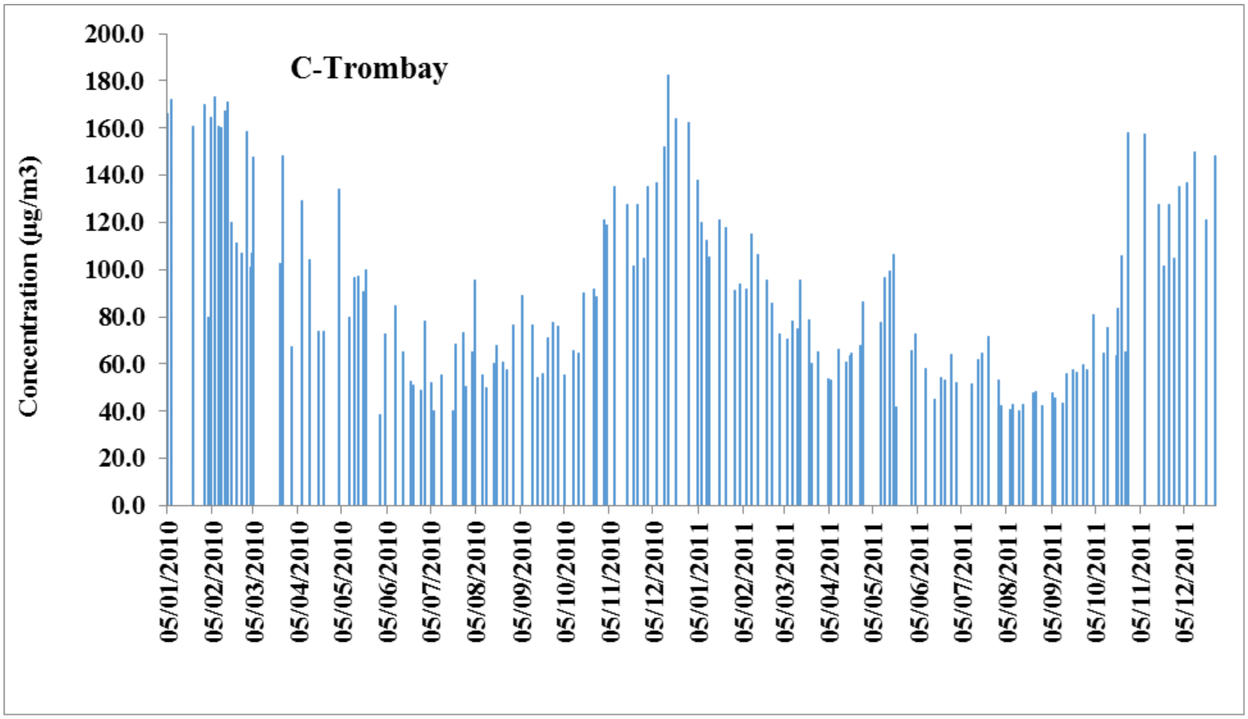


Fig.4.1c. Temporal variation of PM_{10} concentrations at Trombay site during study period

4.1.3. Comparison of PM_{10} concentrations collected using High Volume Sampler (HVS) and Gent's Sampler

In the present study two different samplers viz. HVS and Gent's samplers were used for the PM_{10} collection. Both the samplers work on the impaction principle but HVS has a flow rate of 1.1 m^3/min, whereas Gent's sampler works at a flow rate of 0.96 m^3/hr (16 L/min.). Hence, a short term study was conducted to analyze the PM_{10} concentration estimated using HVS and Gent's samplers. In this experiment both the samplers were kept at the same height on the terrace of the building and sampling was carried out for 24 hrs time period. The sampler filters were preconditioned in same way and weighed for PM_{10} mass load. The measured PM mass load was normalized by air volume to get the final PM_{10} concentration in µg/m^3. Comparison study results are shown in Fig.4.2.

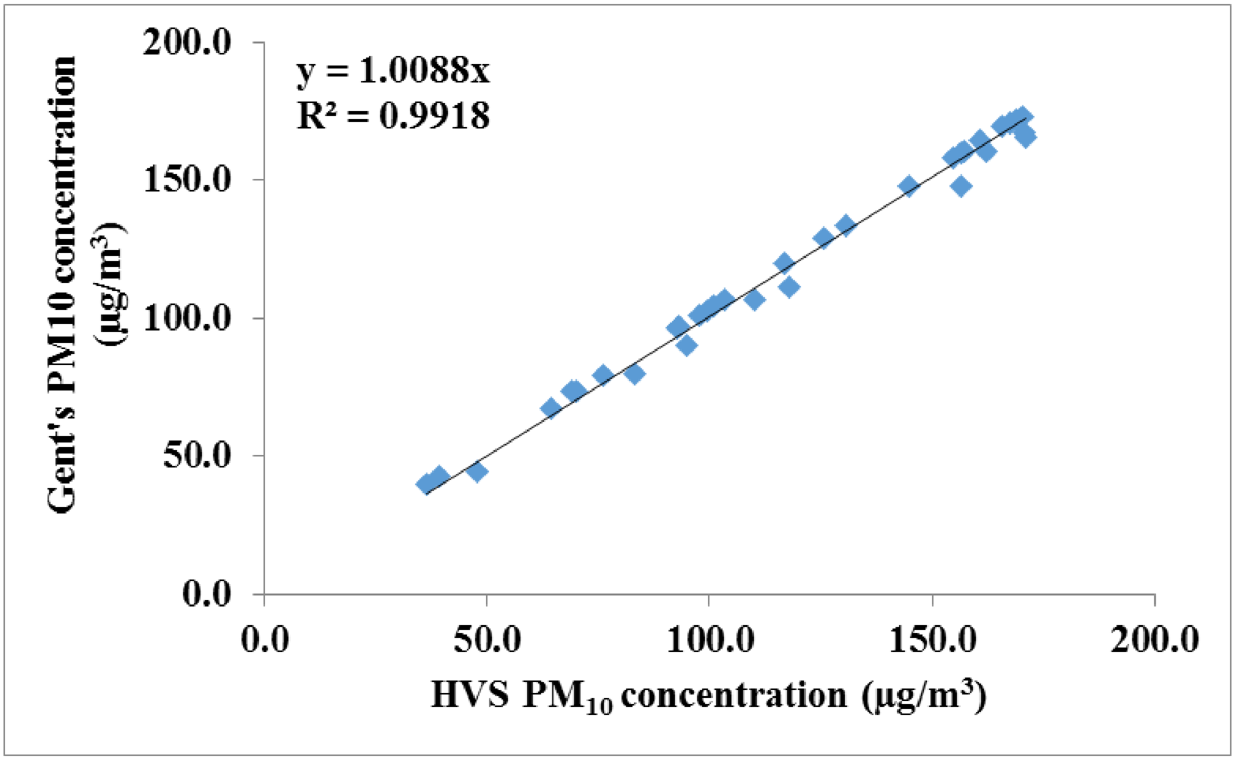


Fig.4.2. Scattered plot of PM_{10} concentrations observed using HVS and Gent's sampler

It can be observed from results that, there was no much difference in the PM concentration levels observed in both the samplers especially in the higher concentration range. Whereas, the concentration difference between samplers was observed in the lower PM concentration range. A maximum of 8.9% difference in PM mass concentration was observed between both the samplers in the present study. From Fig.4.2 it can also be observed that there exists a good correlation between PM concentrations observed from both the samplers.

Hopke et al., 1997 [239], evaluated the Gent's sampler performance by inter comparing it with other commercially available PM_{10} sampler. He reported that the results obtained using Gent's sampler is in quite reasonable agreement with other samplers.

4.1.4. Chemical characterization of PM samples collected at study sites

Various chemical species such as Si, Al, Na^+, Mg^{2+}, Ca^{2+}, K^+, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, Pb, As, Cl^-, NO_3^-, SO_4^{2-} and BC were analyzed in blank filters as well as in sample filters using different analytical techniques. Final concentrations are estimated after blank correction. The concentrations of different metals in blank filters are presented in Table 4.3.

Table 4.3 Concentration of metals in blank filters

	EPM2000 Glass fiber filter		**Polycarbonate filter**
	(µg/g)		(ng/cm^2)
Na	45.23	Na	55.41
Mg	25.35	Mg	27.32
Ca	38.21	Ca	8.38
Fe	30.52	Fe	21.20
K	35.21	K	17.41
Cr	0.32	Cr	3.37
Pb	0.37	Pb	2.76

Cu	0.31	Cu	4.34
Ni	0.18	Ni	5.42
V	0.10	V	0.37
Mn	1.50	Mn	0.63
Zn	2.84	Zn	0.43
SO_4^{2-}	10.50	S	8.88
Cl^-	54.63	Cl	72.32
NO_3^-	6.73	Al	108.80
F^-	0.50	Si	67.10
As	0.07	Ti	0.68

The detailed statistical summary on concentration of chemical species analyzed in PM is given in Table 4.3, 4.4 and 4.5. It was observed that, the standard deviation for few chemical species was higher than their mean value. It suggests that, those metals follow a lognormal distribution, Hence, geomentric mean and geometric standard deviation is given for those metals.

Among different chemical species analyzed, the highest mass concentration was observed for Al at Jogannapalem and Parawada sites, whereas BC has the highest contribution to PM_{10} at Trombay. Contribution from multiple numbers of emission sources such as biomass burning, vehicular emissions, and ship emissions could be the reason for observed higher BC concentrations at Trombay site [35, 240].

The decreasing order of concentration of analyzed chemical species was found to be as follows; Al> K^+> SO_4^{2-}> Fe> Ca^{2+}> Cl^-> Na+> BC> NO_3^-> Zn> Mg^{2+}> Mn> F^-> Pb> Cr> Ni> Cu> V> As at Jogannapalem, whereas at Parawada, the observed order was found to be Al> SO_4^{2-}> Ca^{2+}> K^+> Fe> NO_3^-> Cl^-> Zn> BC> Na^+> Mg^{2+}> F^-> Pb> Mn> Cu> Cr> Ni> As> V> Cd. The decreasing order of chemical species at Trombay sites was found to be BC> Si> Al> Cl> Fe> Ca^{2+}> Na^+> S> Mg^{2+}> K^+> Pb> Ti> Zn> V> Mn> Ni> Cu> Cr> As. From this concentration order one can quickly know which kind of (toxic or non-toxic) chemical species are dominanting the PM_{10} at a given study site. This can also be helpful in getting crude idea about the most dominant source at study site if one has the emission inventory data.

Table 4.4. Chemical constituent's concentration (ng/m^3) at Jogannapalem site

Element	**Min.**	**Max.**	**Mean**	**Stdev.**
Al	1109.7	8873.2	4079.5	1980.9
Ca^{2+}	223.1	6399.9	2361.1	1371.1
Cr	0.8	31.1	7.4	6.7
Cu	0.6	20.8	3.5	3.2
Ni	0.7	34.8	*4.1	**2.4
Pb	1.6	27.6	9.1	4.7
Mn	7.1	797.6	*86.9	**3.0
Zn	79.9	1909.2	676.8	407.4
Fe	63.9	7538.5	2741.0	1406.5
As	0.2	7.3	2.5	1.6
F^-	0.5	177.0	54.3	31.1
Cl^-	105.7	4951.5	1803.5	1394.5
NO_3^-	386.0	1669.0	840.3	291.9
SO_4^{2-}	1199.0	5336.0	2854.6	1056.0
K^+	398.4	11716.5	3156.2	2323.5
Na^+	88.3	2971.9	1229.7	672.6
Mg^{2+}	85.1	963.6	351.1	201.6
V	0.3	16.2	3.5	3.1
BC	192.4	3292.0	1172.7	728.6

Table 4.5. Chemical species concentration (ng/m^3) at Parawada site

Element	Min	Max	Mean	Stdev.
Al	729.1	9877.9	3828.0	1923.5
Ca^{2+}	300.0	6880.0	2501.5	1137.5
Cr	0.9	53.9	*6.2	**2.6
Cu	0.2	53.4	*6.0	**2.9
Ni	0.8	28.3	7.3	4.8
Pb	1.1	83.2	23.0	15.7
Mn	0.3	62.8	18.2	13.2
Zn	60.4	3686.8	927.5	692.2
Fe	287.6	5646.9	2350.8	1270.9
As	0.2	24.3	*2.9	**2.7
F^-	4.8	1260.0	* 96.4	**2.2
Cl^-	306.9	2584.3	948.4	384.8
NO_3^-	400.3	4256.0	1833.3	840.5
SO_4^{2-}	717.2	7336.0	3194.8	1432.0
K^+	240.0	5874.0	2361.2	1061.1
Na^+	226.8	1980.1	710.1	291.5
Mg^{2+}	55.0	760.0	287.9	151.7
Cd	0.04	8.0	1.9	1.6
V	0.6	18.3	5.2	3.4
BC	123.7	2116.2	772.7	471.5

Table 4.6. Chemical species concentration (ng/m^3) at Trombay site

Element	Min.	Max.	Mean	Stdev.
Na	362.0	6508.6	1749.4	1207.5
Mg	34.2	3844.8	1026.2	777.6
Al	157.0	11085.7	2933.2	2022.0
Si	298.7	14175.2	3889.7	2751.0
S	195.0	7471.2	1624.2	1219.3

Cl	504.9	8426.6	2461.0	1688.4
K	113.9	4855.2	939.8	836.9
NO_3^-	410.0	5710.2	2305.5	1085.0
SO_4^{2-}	506.1	12800.5	5210.6	2210.0
Ca^2	136.2	6797.6	1966.1	1410.5
Ti	15.5	842.2	210.4	151.2
V	5.0	388.7	58.8	49.5
Cr	2.0	149.6	*11.8	**2.5
Mn	5.6	368.7	53.8	46.8
Fe	250.3	8707.5	2121.0	1421.6
Ni	3.3	246.3	*24.3	**2.1
Cu	2.0	283.0	*15.7	**2.7
Zn	5.7	1429.4	*92.3	**3.9
Pb	11.6	1219.8	229.7	213.1
As	0.7	10.9	3.4	2.1
BC	681.3	9650.0	3942.1	2393.9

*** indicates Geometric mean and ** indicates geometric standard deviation**

Inter comparison of chemical species concentrations indicates that Al, Ca^{2+}, K^+ and Fe have higher concentrations at Jogannapalem followed by Parawada and Trombay. Among these metals, K^+ and Ca^{2+} have their highest concentrations at Jogannapalem and Parawada sites respectively. The K concentration at Jogannapalem (3156.2 ng/m^3) and Parawada sites (2361.2 ng/m^3) are found to be 3.4 times and 2.5 times the concentration observed at Trombay site (939.8 ng/m^3) site. Potassium (K^+) was considered as an important marker element for biomass burning activity by many researchers all over the world. Biomass burning was the most common activity being carried out at Jogannapalem (rural area). That could be the reason for observed high K concentration at Jogannapalem as compared to other study sites. As suggested by Chan et al. (1997) [241], "K-smoke" was estimated to indicate the presence of K^+ contributed by biomass burning and is taken equal to (K^+-0.6*Fe). As expected, an excess K_{smoke} value was observed at Jogannapalem (1511.6 ng/m^3) as compared to Parawada site (950.7 ng/m^3).

The observed highest concentration of Ca^{2+} at Parawada could be due to the excess contribution of Ca from construction activities that are being carried out near the sampling site during study period. In contrary, the highest concentrations of Na^+, Mg^{2+} and Cl^- were found at Trombay site as compared to Jogannapalem and Parawada sites. The Trombay average concentrations of Na^+ and Cl^- are about 1.4 times and 2.5 times the concentrations observed at Jogannapalem and Parawada sites respectively. In the case of Mg^{2+}, the Trombay average concentration was found to be 2.9 and 3.6 times that observed at Jogannapalem and Parawada sites respectively. In the present study, Cl^-/Na^+ ratio was found to be 1.5, 1.4 and 1.4 at Jogannapalem, Parawada and Trombay sites respectively, which is close to the actual value of 1.8 in seawater [242] indicating that these ions could be originated from sea salt spray. Slightly lower Cl^-/Na^+ ratio at the sampling sites could be due to the loss of Cl^- through reactions between the marine aerosol and atmospheric nitric acid, sulfuric acid and SO_2. Observed highest concentration of these ions at Trombay could be due to the close proximity of Arabian Sea to Trombay sampling site as compared to the distance between Bay of Bengal to Jogannapalem and Parawada sampling sites.

In the present study, BC concentration was measured in only few samples (selected from both the years covering all the seasons) that are collected at Jogannapalem and Parawada sites. The BC concentration was observed in the range from 192.4 - 3292.0 ng/m^3 and from 123.7 - 2116.2 ng/m^3 at Jogannapalem and Parawada site respectively. The average of measured BC concentration was found to be 1172.7 ng/m^3 and 772.7 ng/m^3 at Jogannapalem and Parawada sites respectively. Similarly, the concentrations of SO_4^{2-} and NO_3^- were estimated in few samples of Trombay site. The concentrations of SO_4^{2-} and NO_3^- were found in the range of 0.5 - 12.8 μg/m^3 and 0.4 – 5.7 μg/m^3 with a mean values of 5.2 μg/m^3 and 2.3 μg/m^3 respectively.

Sulfate is one of the most important ionic species that can be contributed from both natural and anthropogenic sources. As sea water contains significant concentration of sulfate, there is a possibility of sulfate contribution from sea salt. In the present study, non-sea salt sulfate ($nssSO_4^{2-}$) was calculated to know the percentage contribution of sulfate from other sources by using $nssSO_4^{2-} = SO_4^{2-}-0.25* Na^+$ equation. Where, 0.25 is the typical ratio of SO_4^{2-} to Na^+ in seawater. It was found that, about 89% and 94% of observed sulfate was contributed from non-sea-salt sources at Jogannapalem and Parawada respectively. Most probable anthropogenic sources of sulfate at Jogannapalem and Parawada sites could be the biomass burning and gaseous precursur (SO_2) emitted from thermal power plants near the study sites [156].

In the case of trace metals (such as V, Cr, Mn, Pb, As, Ni, Zn, etc.), the highest concentration was observed for Zn at Jogannapalem and Parawada sites, whereas Pb was observed to have the highest concentration at Trombay site. In the present study, the Parawada average Zn concentration was found to be 4.7 times that observed at Trombay site. Interestingly, Mn has the highest concentration at Jogannapalem followed by Trombay and Parawada sites. Large numbers of metal industries present near Jogannapalem and Parawada sites (as shown in Fig. 3.1a) might be responsible for observed high concentrations of Zn and Mn. The Pb concentration at Trombay site was observed to be 25 times and 10 times the Pb concentration found at Jogannapalem and Parawada sites respectively. Contribution from road dust that was accumulated with Pb (emitted from leaded petrol over the years) [243-245], non-exhaust vehicular emissions (Pb is also contributed by vehicular brake wear emissions [143]) and other industrial emissions (viz. chemical industries and refineries) could be the reason for observed high Pb in PM at Trombay; Throughout the study period, the concentrations of trace metals viz. Cr, V, Ni and Cu were observed to be significantly higher at Trombay site as compared to

Parawada and the least concentrations of these metals were observed at Jogannapalem sites. Fuel oil combustion sources such as oil fired power plants, oil refineries and ship emissions are the major sources of Ni and V [48,139]. Close proximity of these industries to Trombay sites (as shown in Fig. 3.1b) could be the reason for observed higher concentrations of Ni and V. Among all chemical species analyzed, Arsenic (As) has the least concentration at Trombay and Jogannapalem sites, whereas at Parawada site, Cd was observed to have the least concentration. Limited number of emission sources and low emissions from limited sources could be responsible for observed lowest concentrations of As and Cd at stuyd sites.

CPCB [246] has given annual safety standards for some toxic elements such as As (6 ng/m^3), Ni (20 ng/m^3), Pb (500 ng/m^3) and Cd (5 ng/m^3). In the present study, none of these elements mean concentration was observed to exceed the NAAQ safety limit at Jogannapalem and Parawada site. Whereas, the Ni mean concentration at Trombay site was exceeded the NAAQ annual safety limit value.

In the current study, high BC levels were observed on few sampling days at Trombay site. These high concentrations could be either contributed from local sources or from distant sources through long range transport of pollutants. As the life time of BC particles is 7–10 days [247] and they are present in the fine fraction of the air PM causing them to migrate long distances in the atmosphere. In the present study, Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to determine the possibility of BC contribution from long range transport at the sampling site. In the HYSPLIT model meteorological data, coordinates of the receptor site, altitude, initial time and end time are given as input parameters. The meteorological data was obtained from CDC1 to run HYSPLIT. The data with a spatial resolution of 1^0X 1^0 in longitude and latitude was used in the present study [248]. Analysis was carried out at different heights as shown in Fig. 4.3.

To study the contribution of long range transport of BC, only those days were considered which has highest BC concentration. There were 3 days (01/07/10, 02/22/10 and 12/20/10) during which the highest levels of BC were observed at Trombay site. Back trajectories were calculated to obtain the place where the air mass was located 72 h before arriving to the measurement site. Then, trajectories were grouped depending on its position in a grid.

Fig. 4.3 presents the backward trajectories during high BC levels. As shown in Fig. 4.3, all the 3 days (72 hrs.) backward trajectories were originated from the northern and central part of India. In this region of India, higher BC levels are reported by several researchers during winter seasons due to high biomass burning, low mixing heights and a stable atmospheric boundary layer [249-250]. Such clouds of smoke generally spread southward as it is unable to move northward over the Himalayas. Air trajectories then move towards the southwest which could have resulted observed high BC concentrations at Trombay study site. An earlier study carried out also observed similar patterns during the winter period [251].

Concentrations of different chemical species associated with PM_{10} at various locations of India and other parts on the world are given in Table 4.6. From Table 4.6, it can be observe that the concentrations of Al, Ca, and Fe were found to be higher at present study locations as compared to location of other countries. These metals are believed to be mostly originated from crustal material which is one of the dominant PM contributors in the world [152]. The concentrations of other chemical species observed in the present study are within the range reported by other studies.

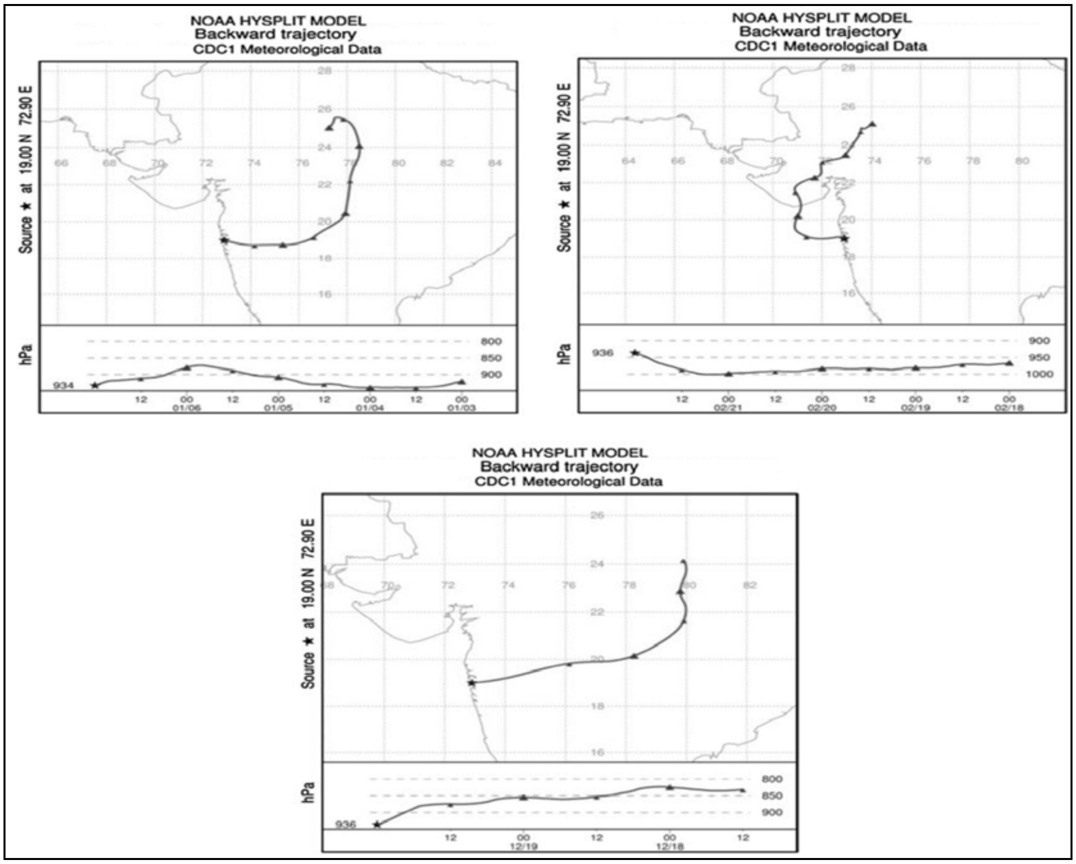


Fig.4.3. Backward trajectories at Trombay, Mumbai during days of high BC levels

Table 4.7. Particle (PM_{10}) bound chemical species concentrations (ng/m^3) reported at various locations of India and other countries

	Agra	**Mexico**	**Italy**	**Spain**	**Spain**	**China**	**China**	**Roorkee**	**Malaysia**	**Taiwan**	**Delhi**	**Turkey**
Na	-	900	1700	294	1700	-	6380	-	5210	-	3010	672.9
Mg	-	300	300	117	400	-	3470	-	713	509	1800	3.6
Al	-	1400	83.0	400.6	370.4	-	14180	15.6	3840	1490	2950	531.8
Fe	3200	800	277.0	222	101.4	-	12600	30	901	571	1000	268.8
Cl	-	400	1300.0	349	1100	-	-	-	-	-	3240	-
K	-	1200	477.0	203	300	-	9010	-	1460	-	1440	195.9
Ca	-	1200	668.0	930	1300	-	22430	-	3980	1070	4970	902.0
Mn	900	18.4	9.0	5	4.3	-	670	0.80	-	20.1	20	9.7
Zn	1600	29.8	40.0	30	45	102-356	12900	7.13	4400	131	510	113.3
V		36.5	3.0	2	6.2	5.3-14.8	50		9.83	10.7	-	7.1

Cr	1300	1.4	3.0	<1	5.2		50	2.04	395	30.7	280	9.6
Cu	200	25.7	12.0	3	37	25.3-78.7	220	-	24.7	15.7	-	15.5
S	-	-	-	-	-		-	-	-	-	4400	-
Ni	1700	7.1	4.0	5	3.2	5.5-14.5	60	-	107	9.8	-	7.8
Pb	2200	4.2	12.0	10	6.6	68.3-111	1960	-	10.7	21.2	-	32.9
As	-	1.1	-	-	0.38	-	10-560	-	2.36	3.4	-	-
SO_4^{2-}	-	9200	3400	3877	4100	-	27040	-	5490	-	8270	-
	Rural	Rural	Sub-urban	Rural	Sub-urban	Rural	Urban	Rural	Sub-urban	Rural	Urban	Sub-urban
	[161]	[252]	[135]	[136]	[143]	[144]	[144]	[119]	[151]	[238]	[161]	[139]

4.1.5. Analytical quality control

To validate the metal extraction procedure used in the current work, NIST SRM 1649a (urban dust) was processed in the same way as the PM samples. After chemical processing, reference material sample solutions were analyzed for various trace and toxic metals using different analytical techniques. Percentage recoveries of ions and other metals which are not certified in the reference material were estimated by spiking known amounts of chemical components on glass fiber filter. The spiked samples were dried and processes in the same way as that of PM samples. The percentage recoveries of different chemical components are given in Table 4.7. The high recovery values are observed in the case of spiked species (e.g. Cl^-, Mg^{2+}, SO_4^{2-}, etc). This is due to the small error in the spiked concentrations and also due to the fluctuation in the concentrations of these species in black filters.

During metal analysis ICP-AES and AAS were calibrated for each metal using a set of three to five standards. The calibration curve was checked frequently by injecting the known standard solution. The results were corrected using a correction factor obtained by injecting a known standard. Field blanks were analyzed and the data was subsequently blank corrected to determine accurate results of chemical species.

Table 4.8. Percentage recovery of different metals from NIST SRM 1649a and from spiked filter paper

Elements	**Percentage recovery**	**Chemical species spiked on filter paper**	**Percentage recovery**
As	96.0 ± 1.4	Zn	94.9 ± 2.3
Cu	99.5 ± 2.1	Cl^-	98.5 ± 5.1
Cd	88.5 ± 3.5	SO_4^{2-}	97.3 ± 4.1
Cr	93.7 ± 2.0	NO_3^-	98.2 ± 4.3
Fe	87.3 ± 2.8	Na^+	97.8 ± 3.3
Mn	95.5 ± 2.1	Ca^{2+}	98.3 ± 5.1
Ni	99.6 ± 2.0	K^+	97.1 ± 2.5
Pb	97.0 ± 1.4	Mg^{2+}	98.1 ± 3.2
V	99.5 ± 2.1	Al	99.1 ± 4.1

4.1.6. Percentage contribution of chemical species associated with PM_{10} at study sites

Fig.4.4 illustrates the percentage mass contribution of chemical species to PM_{10} at all the three sites. Since some chemical species can have very less (<0.1%) mass contribution to PM_{10}, the analyzed species are divided into two categories viz. major (Al, Ca^{2+}, Fe, K^+, Mg^{2+}, BC, SO_4^{2-}, NO_3^-, Na^+, Cl^-, Zn and Mn) and minor (Cr, Cu, Ni, V, F^-, Pb and As) to clearly illustrate their percentage contributions to PM_{10} mass. From Fig.4.4. it can be observed that, Al (6.2% and

5.1%) has the highest contribution to PM_{10} at Jogannapalem and Parawada sites followed by K^+ (4.8%) at Jogannapalem, whereas at Parawada second highest percentage mass contribution was observed from SO_4^{2-} (4.3%) followed by Ca^{2+} (3.3%). At Trombay site, BC has the highest percentage mass contribution (4.4%) which was followed by Si (4.3%) and Al (3.3%).

The percentage mass contribution of Al, Ca^{2+}, K^+ and Fe at Trombay site was observed to be much lesser as compared to Jogannapalem and Parawada sites. On contrary, the percentage mass contributions of Cl^-(2.7%), Na^+(1.9%) and Mg^{2+}(1.1%) observed at Trombay was found to be higher than the Parawada. Although the concentrations of Cl^- and Na^+ are higher at Trombay site, but the percentage mass contribution of these ions was observed to be same at Trombay and Jogannapalem. The SO_4^{2-} percentage mass contribution was found to be similar at Jogannapalem and Parawada sites. Whereas, the percentage mass contribution of NO_3^- at Parawada was about two times that observed at Jogannapalem site. The observed high NO_3^- could be contribution from gases released from coal power plant near Parawada site [156].

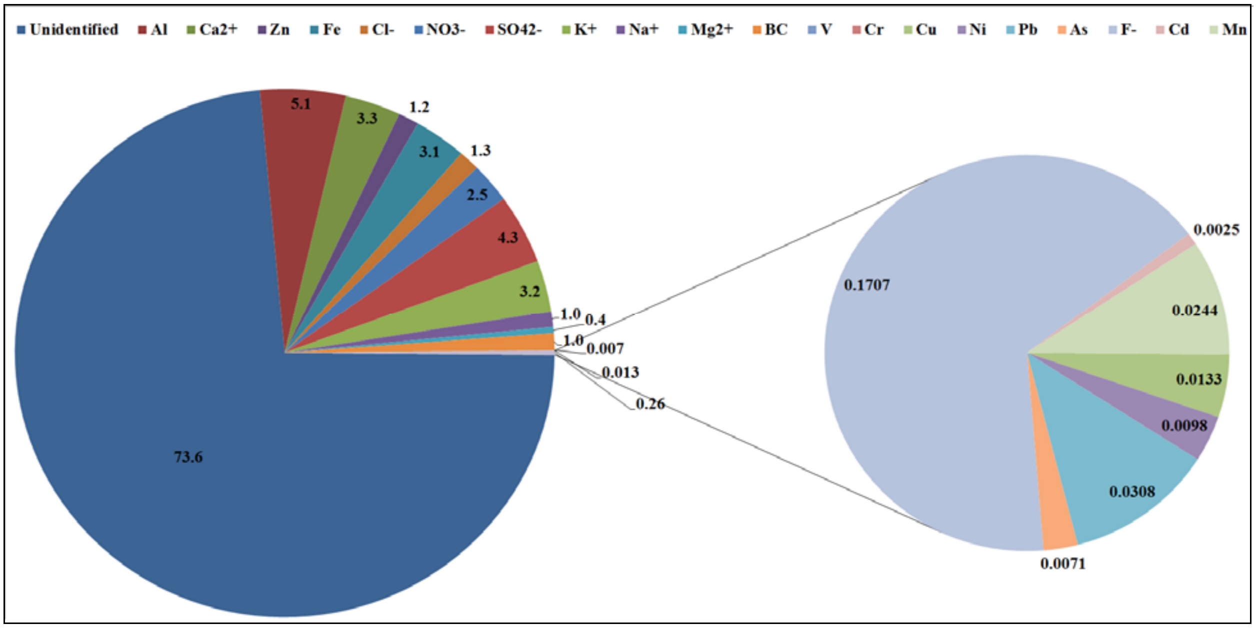


Fig. 4.4a Percentage mass contribution of chemical components to PM_{10} mass at Jogannapalem

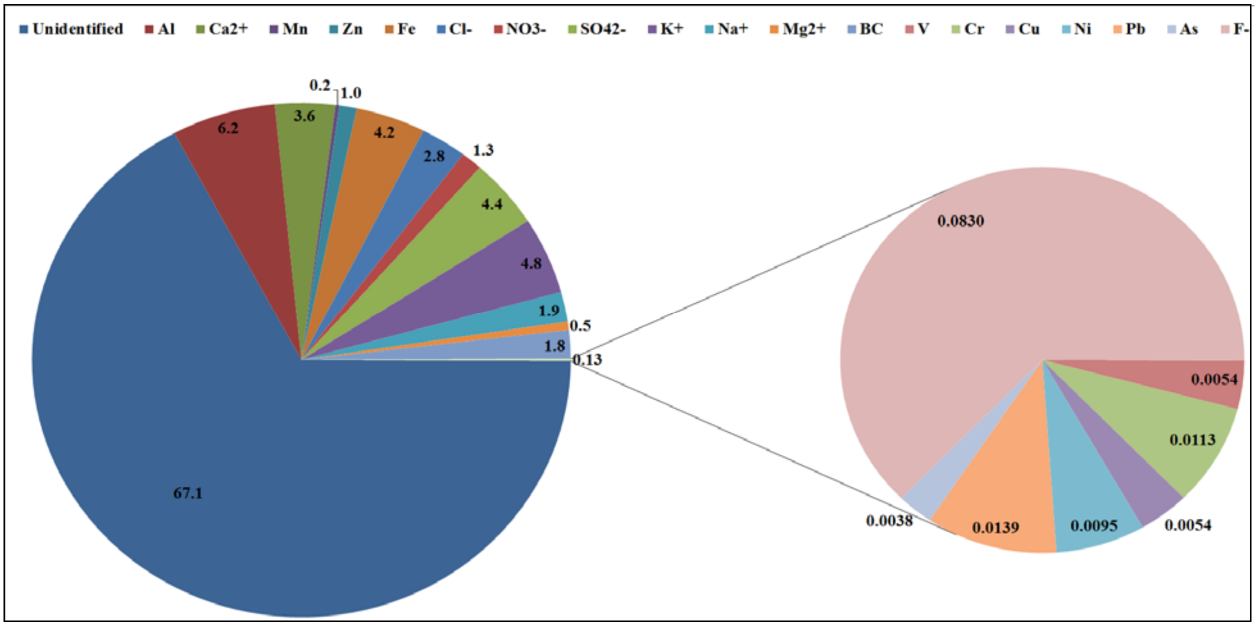


Fig. 4.4b Percentage mass contribution of chemical components to PM_{10} mass at Parawada

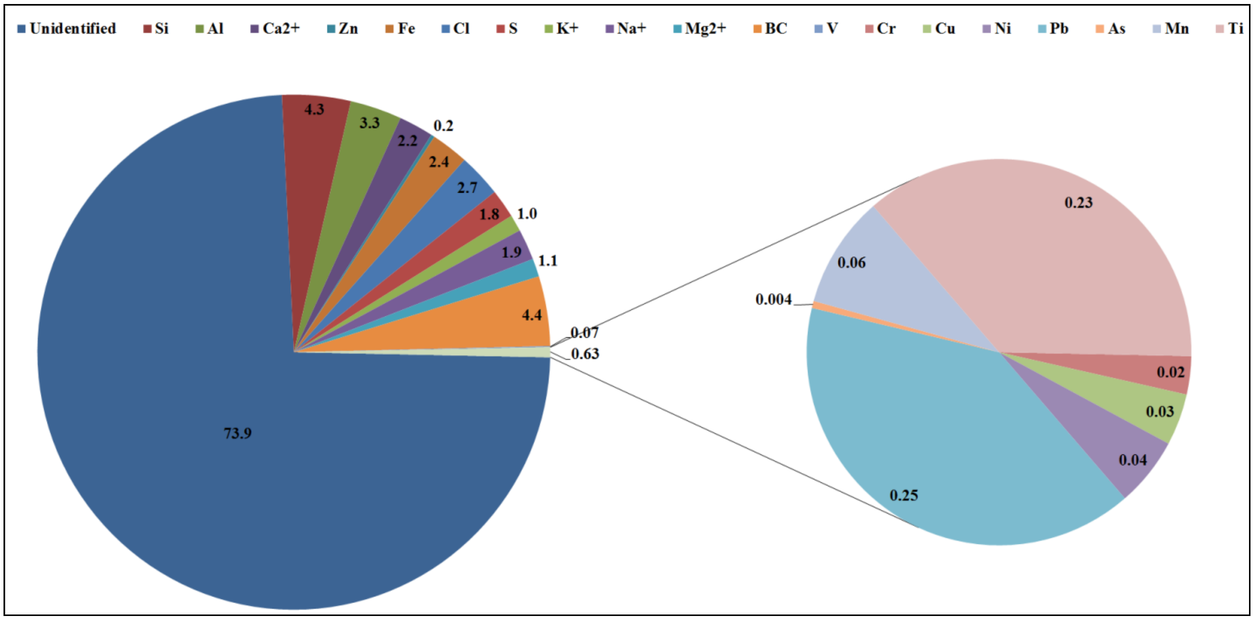


Fig. 4.4c. Percentage mass contribution of chemical components to PM_{10} mass at Trombay

Among trace metals, Zn has the highest percentage mass contribution to PM_{10} at Parawada (1.2%) followed by Jogannapalem (1%) and Trombay site (0.2%). Whereas, Pb was found to have the highest percentage mass contribution to PM_{10} at Trombay site (0.25%).

Percentage mass contribution of Cr, Cu, V, As and Ni was observed to be very less, but their contribution was higher at Trombay site as compared to other study sites.

PM mass reconstruction

An aerosol mass reconstruction (AMR) analysis was conducted to explore the relative contributions of the measured chemical species and their relationship to the total measured gravimetric mass. For the purpose of chemical mass reconstruction, chemical components were grouped into six categories: crustal materials (CM), trace metal oxides (TMO), sea salt (SS), BC and secondaryions (SI). CM represents the sum of typical crustal materials, including Al, K, Fe, Ca, Mg and Si. Each of these species was multiplied by the appropriate factors to account for their common oxides based on the following equation [144, 253, 254]. In the absence of NH_4^+ measurement, SO_4^{2-} and NO_3^- are assumed to be neutralized to ammonium sulfate ($(NH4)_2SO_4$) and ammonium nitrate (NH_4NO_3), with the NH_4^+ fraction accounted for by stoichiometric multipliers: 1.375 SO_4^{2-} and 1.29NO_3^-, respectively.

Trace elements were also converted to their common oxides. Trace elements only represent a small percentage of the total PM mass; however, they were also added to the analysis because they have a great environmental importance due to their toxicity and anthropogenic origin. TMO contribution was calculated using the following equation [255].

$$\text{Crustal matetail (CM)} = 2.20\ Al + 2.49\ Si + 1.63\ Ca + 2.42\ Fe + 1.21\ K + 1.66\ Mg$$

$$\text{Sea salt (SS)} = Cl^- + ssNa^+ + ssMg^{2+} + ssK^+ + ssCa^{2+} + ssSO_4^{2-}$$

$$\text{Carbonates } (CO_3^{2-}) = 1.5Ca^{2+} + 2.5\ Mg^{2+}$$

$$\text{Trace metal oxide (TMO)} = 1.47\,V + 1.29\,Mn + 1.27\,Ni + 1.25\,Cu + 1.08\,Pb + 1.31\,Cr$$

$$\text{Secondary Ions (SI)} = 1.375\,SO_4^{2-} + 1.29NO_3^{-}$$

The results are presented in Table 4.9. From results, it can be observed that, PM_{10} at all sites has the highest contribution from crustal matter followed by secondary ions. Least contribution was observed from TMO. Sea salt contribution to PM_{10} was also found to be high. The unknown mass includes the organic matter and water content in PM.

Table 4.9. Percentage mass contribution of different sources to PM_{10}

	Jogannapalem	**Parawada**	**Trombay**
Crustal matter (CM)	36.5	28.8	30.3
Sea salt (SS)	7.7	3.7	7.7
Trace metal oxides (TMO)	0.4	0.1	0.6
Secondary ions (SI)	7.2	9.0	10.7
Black carbon (BC)	1.8	1.0	4.4
Carbonates	6.8	6.0	6.1
Recovered PM mass	60.4	48.6	59.8

4.1.7. Seasonal variation of PM$_{10}$ and particle bound chemical species at study site

Indian atmosphere can be affected by mainly three kinds of seasons viz. winter, summer and monsoon. Previous studies suggest that the seasonal variation exhibits a significant influence on the PM$_{10}$ and particulate bound chemical species concentrations. In the present study, season wise PM and their chemical species concentrations were calculated to observe the influence of seasonal variations. Fig. 4.5 and 4.6, illustrates the season wise concentration variation of PM$_{10}$ and its associated chemical species during study period at all the three sampling sites.

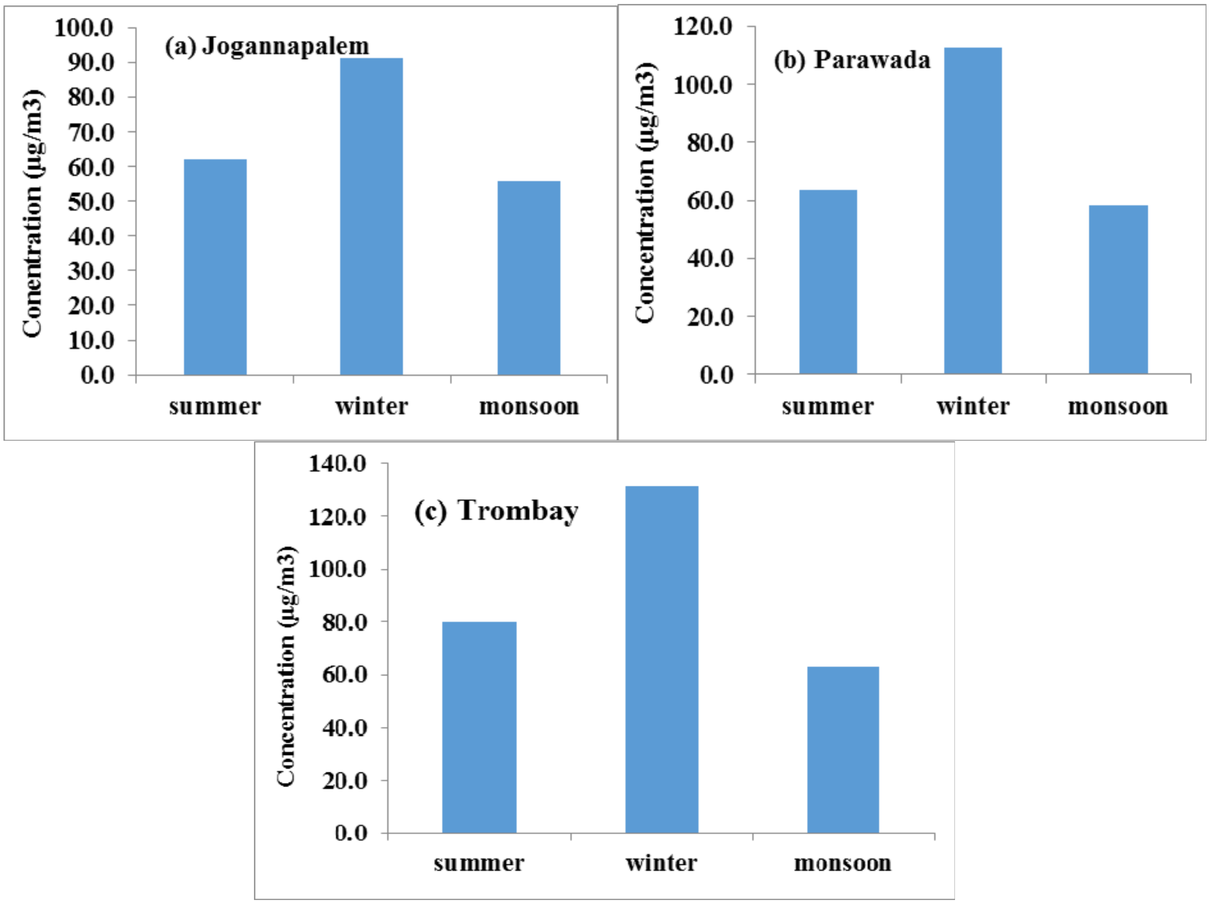


Fig.4.5. Seasonal variation of PM$_{10}$ at (a) Jogannapalem, (b) Parawada and (c) Trombay sites

From Fig. 4.5, it can be observed that the winter season has the highest PM$_{10}$ concentration and the least PM concentration was observed during monsoon season at all the study sites. The highest winter concentration was found to be 91.4 µg/m^3, 112.5 µg/m^3 and 131.6 µg/m^3 and the least concentration was observed to be 55.8 µg/m^3, 58.3 µg/m^3 and 62.8 µg/m^3 in monsoon at Jogannapalem, Parawada and Trombay sites respectively. In the present study, winter PM concentration was 1.6 to 2.1 times the concentration observed during monsoon season. Intermediate concentrations were observed in summer season at all the sites. Similar seasonal trends were reported by most of the studies carried out in India [118, 256-257] and also by researches from other countries [141, 258].

As shown in Fig. 4.6, clear seasonal trends were observed for particle bound chemical species during the study period. The trends are similar to that observed for PM_{10} concentration (i.e., highest concentrations during winter followed by summer and monsoon season) with few exceptions. For example, the concentrations of F^-, V, Ni and K at Jogannapalem site and for F^-, V, Ni and Cu at Parawada site were observed to have high concentrations during monsoon as compared to summer season.

Observed least concentrations during monsoon season could be due to the washout of PM and its associated (especially with coarse PM) chemical species along with rain water [67]. Also, relatively higher humidity in this season resists the PM to suspend in ambient air, leading to lowest concentrations [259]. In contrary, some metals which are associated with very fine particles cannot be scavenged by the rain water droplets [260] resulting in a higher concentrations of these metals (like Ni, V, Cu, K, S, and F^- in present study) in monsoon. Also, the predominant winds from sea to earth's surface [52, 261] during monsson could be the reason for observing high concentrations of Cl^-, Na^+, Mg^{2+} and K in monsoon season [242]. In the present study, the daily concentrations of PM_{10} and metals (As, Cd, Pb and Ni) were not exceeded the daily NAAQ standards in this season, suggesting least pollution among all season.

Meteorological conditions such as Low wind speed, low temperature and low mixing height might be the cause of observed high concentrations of pollutants during winter [185, 262]. Also, the increased anthropogenic activities such as biomass burning, space heating etc. during winter season contribute to the pollution load leading to obsereved high winter concentration [263-265]. The winter average concentrations of Cr (15.2 ng/m^3) and As (4.5 ng/m^3) were observed to be 3.7 times and 3 times that found during monsoon season at Jogannapalem site. Whereas, Zn (1.7 µg/m^3) and As (10.3 ng/m^3) were observed to have 2.6 times and 3.6 times the concentration observed during monsoon at Parawada site.

At Trombay site, the average winter concentrations of Cr (31.5 ng/m^3), Cu (39.9 ng/m^3), Ni (54.8 ng/m^3), Zn (370.3 ng/m^3), Pb (404.7 ng/m^3) and V (94.4 ng/m^3) were found to be 3 to 4 times that observed in monsoon season. As (4 ng/m^3) and BC (6.4 µg/m^3) winter concentrations were almost two times that found during monsoon. K has the highest concentration in winter season followed by monsoon and summer at Jogannapalem and Trombay sites. Nitrate was also reported to have higher concentration in winter and generally attributed to the low thermal stability of nitrate in summer season [242]. Winter season can be considered as the most contaminated season as PM_{10} daily concentrations were found to be exceeding the daily NAAQ standards at all the study locations. The Pb daily concentration limit was also exceeded at Trombay site indicating highest pollution among all seasons.

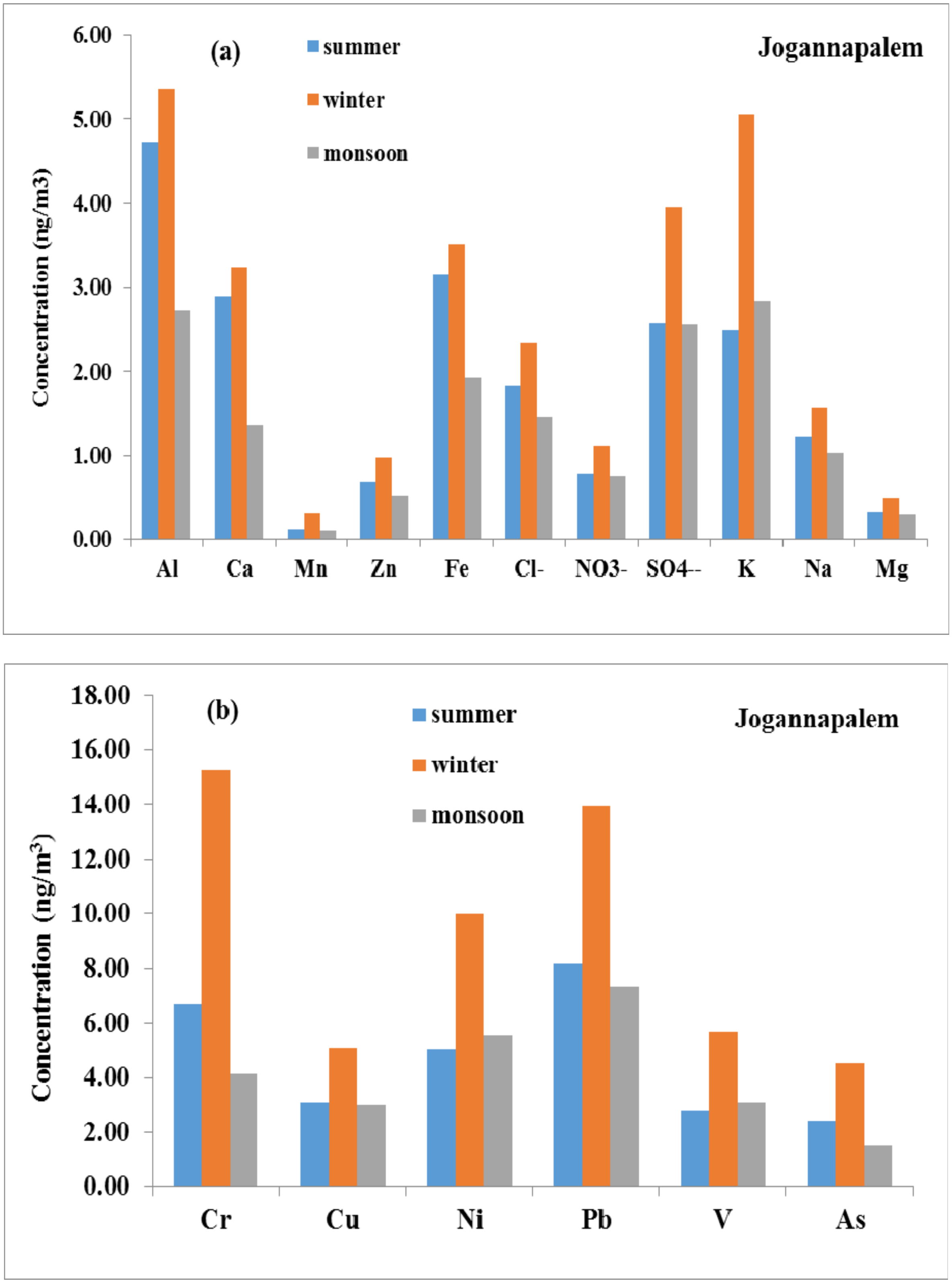


Fig.4.6a. Seasonal variation of (a) major and (b) trace chemical constituents at Jogannapalem

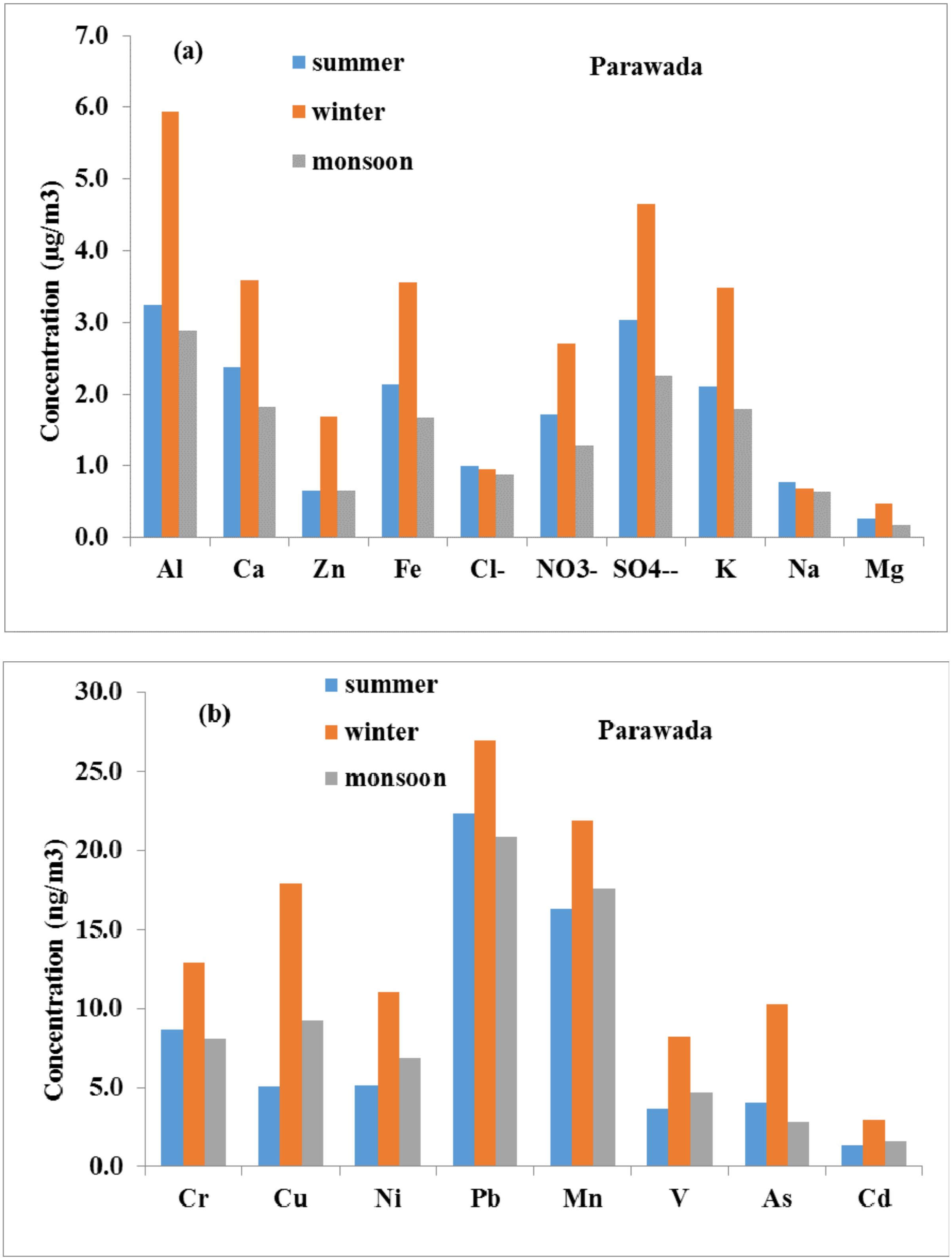


Fig.4.6b. Seasonal variation of (a) major and (b) trace chemical constituents at Parawada site

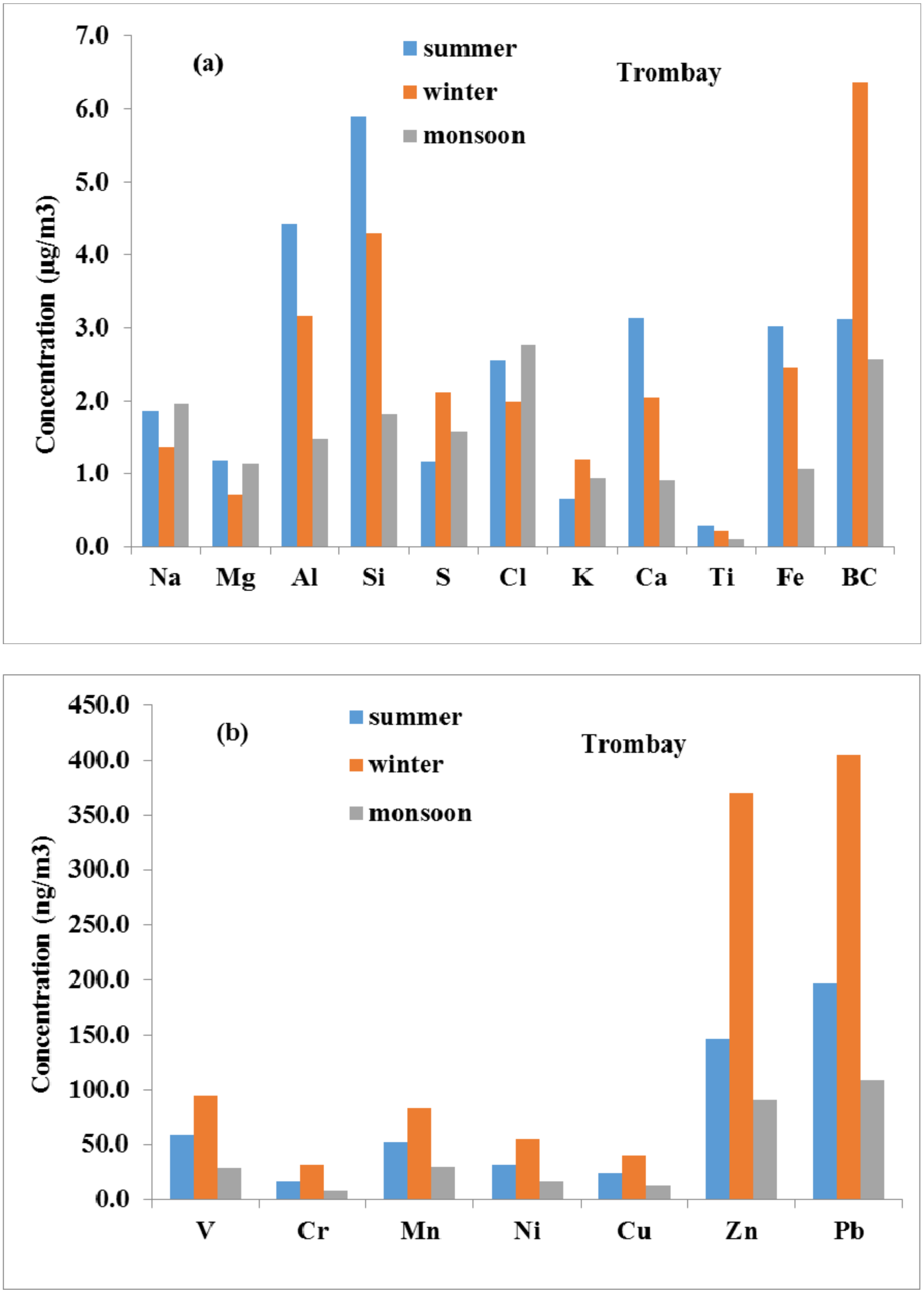


Fig.4.6c. Seasonal variation of (a) major and (b) trace chemical constituents at Trombay site

Intermediate concentrations were observed during the summer season (March to June), which could be due to decrease in wet precipitation. This causes a reduction in the cleaning effect on the atmosphere and consequently a greater concentration in the ambient air. Also high temperatures during this season lead to increased dryness of the air, which favors the re-suspension of soil substrate leading to higher pollution levels as compared to monsson season [185].

4.1.8. Inter comparison of different analytical techniques for elemental analysis

In the present study, many analytical techniques were used for metal analysis. Some metals can be quantified using AAS, ICP-AES and DPASV. Hence, an inter comparison of different analytical technique for selected metal analysis was also carried out. As a part of this work, chemical analysis of elements such as Fe, Zn, Mn and Cr was done both using ICP-AES and Flame-AAS. Similarly Pb, Cd and Cu analysis was carried out in few samples using ICP-AES and DPASV technique. Samples were selected from each season to cover wide range of concentration variation for inter comparison test. The results of the study are elaborated in the following section.

Inter comparison results (shown in Table 4.9 and 4.10) indicates that there is no much difference in concentration measured by AAS and ICP-AES for Fe, Mn and Zn. The maximum difference in measured concentration was observed in samples that are collected during monsoon (i.e. low metal concentration). The highest percentage difference in concentration of Fe, Zn, Mn and Cr (measured using ICP-AES and AAS) was found to be 6.4%, 8.2%, 9.1% and 11.3% respectively.

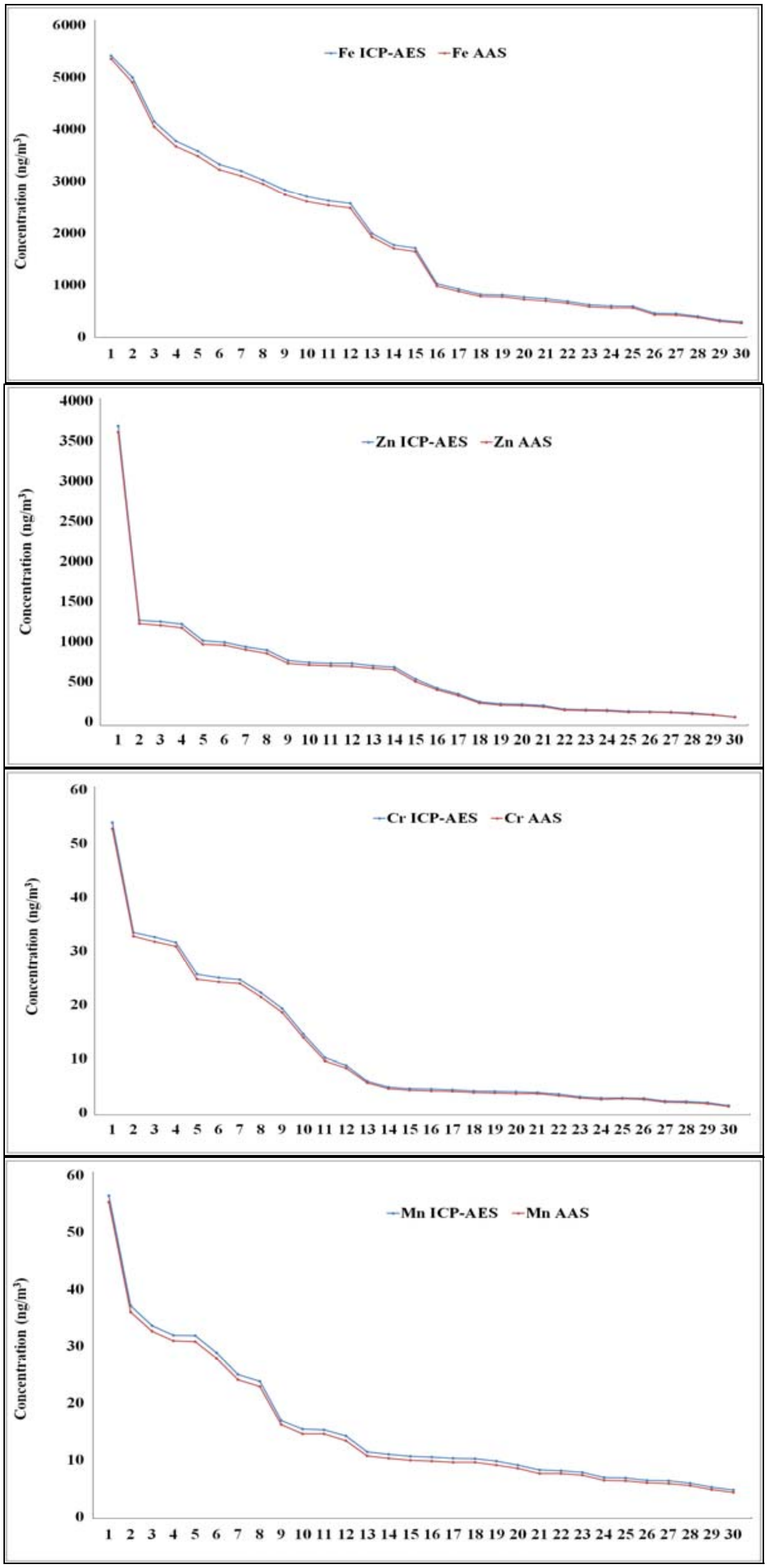


Fig.4.7. Inter comparison of elemental concentrations (ng/m^3) quantified using ICP-AES and AAS

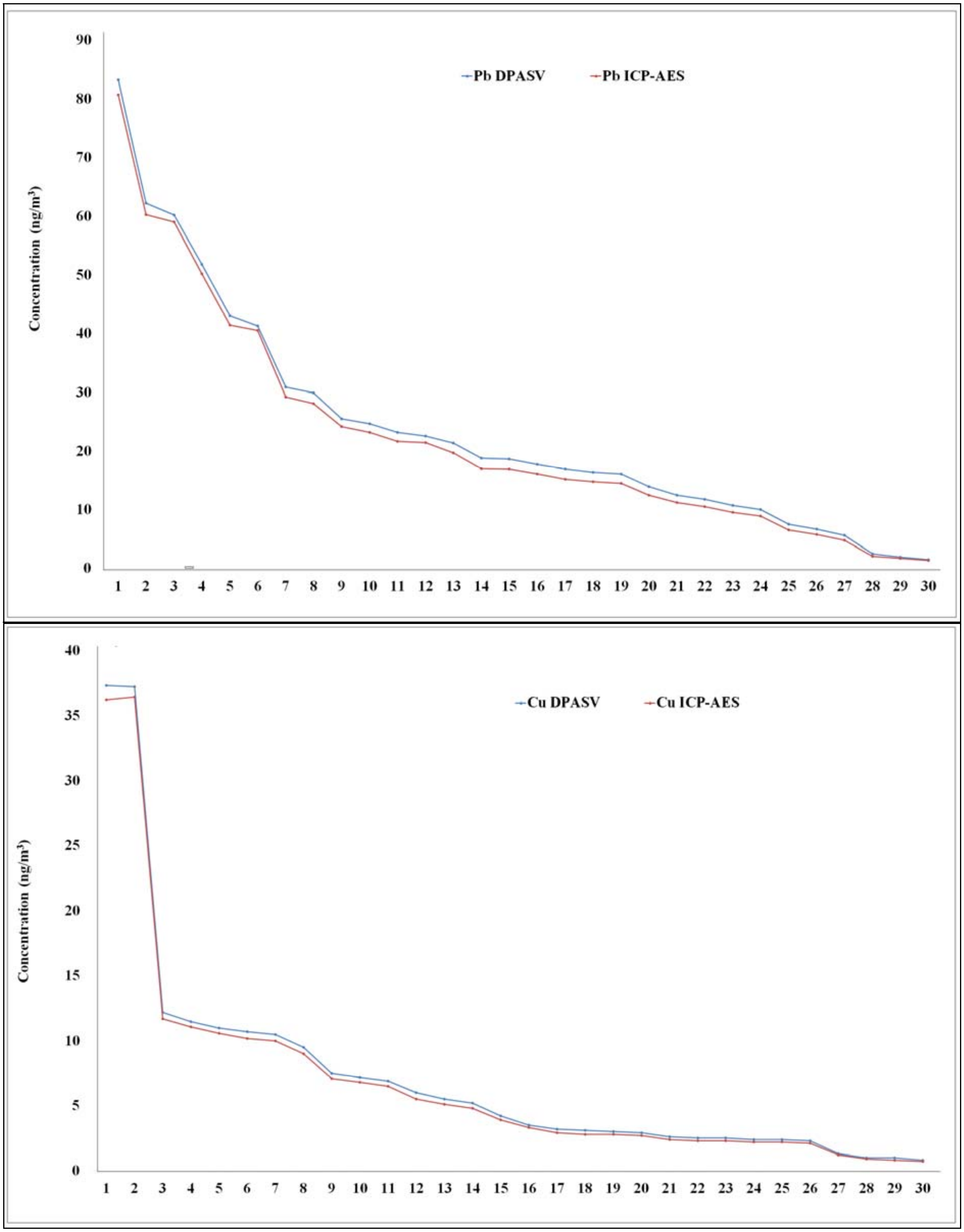


Fig. 4.8. Inter comparison of elemental concentrations (ng/m^3) quantified using ICP-AES and DPASV

In the case of Pb analysis, higher percentage difference was observed between ICP-AES and AAS analysis results especially in monsoon season samples. This is due to very low Pb concentration during monsoon in collected PM samples which limits the use of AAS for Pb analysis, as AAS has higher detection limit value. Whereas, Pb analysis using DPASV indicates that there is no much difference in measured concentrations (especially with high Pb concentrations) using ICP-AES and DPASV. Cd in the present study was observed to have very low concentrations due to which DPASV was opted as it has very good sensitivity and low detection limit. Similarly, for Cu analysis, DPASV provided better results as compared to ICP-AES. Higher concetration differences are observed in measured Cu concentration values using DPASV and ICP-AES. Hence, for the Cu and Pb analysis DPASV was opted in the present study in preference to the ICP-AES.

4.1.9. Element to element correlation analysis at Jogannapalem, Parawada and Trombay sites

Correlation study provides insights into source characterization of atmospheric particles. Hence, it is important to study the correlation for analyzed chemical species. Pearson product moment correlation coefficient was calculated (presented in Table 4.11a, b, c) to know the correlations between the chemical species.

In the present study, a strong correlation between V-Ni and Na-Cl^- was observed with a correlation coefficient of 0.9 at all the sampling sites. High correlation between these pair of metals indicates that these metals could have contributed from same or similar sources. As shown in Fig. 3.1a and 3.1b the oil refineries present near the Trombay and Parawada sampling sites might be the common source of observed Ni and V in PM. A strong correlation was also observed between NO_3^--SO_4^{2-} at Jogannapalem and Parawada sites. Thermal power plant flue gases contain SO_2 and NO_x which can be transformed to particles by chemical reactions [136, 193]. A coal based power plant near the sampling sites (as shown in Fig. 3.1a, b) could be a source of NO_3^--SO_4^{2-} in PM.

A very good correlation was observed between Al-Ca^{2+}-Fe and Al-Si-Ca^{2+}-Fe-Ti at Jogannapalem and Trombay sites respectively with a correlation coefficient >0.8. At Parawada site, these metals are well correlated but to a less extent as compared to other sampling sites. K and Mg^{2+} were also observed to have good correlation with Al-Fe-Ca^{2+} at Parawada site. One of the most common sources of these metals is assumed to be the soil/road dust [152]. Some of the metals such as Fe, K^+ and Ca^{2+} can also be contributed from industrial activities such as themal power plant (fly ash is enriched with Ca^{2+}, Fe and K^+) [266] and metals industries near Parawada. Interestingly, K^+ at Jogannapalem site was not correlated with any other chemical species suggesting that it could have emitted from a separate source. Whereas, Potassium (K^+) at Trombay site was found to have a good correlation with elementas such as As-S-Pb-Cu-V-Ni-BC.

Trace metals such as Cu-Mn-Pb-Zn were observed to have a good correlation at Jogannapalem and Trombay sites. Similarly, Cr-As-Zn metals were also moderately correlated at Jogannapalem and Parawada sites. These set of metals could be contributed from wide range of anthropogenic source such as metal industries, non-exhaust vehicular emissions and from coal based combustion sources [52-53, 267-268]. A number of metal industries (alloy industry, steel plant, and iron ore industry) present near the Jogannapalem and Parawada sites (as shown in Fig. 3.1a.) could be the most probable source of these metals.

Table 4.10a. Element to element correlations observed at Jogannapalem site

J	**Al**	**Ca^{2+}**	**Cr**	**Cu**	**Ni**	**Pb**	**Mn**	**Zn**	**V**	**Fe**	**As**	**F^-**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**	**K^+**	**Na^+**	**Mg^{2+}**
Al	1.0																	
Ca^{2+}	**0.8**	1.0																
Cr	0.3	0.3	1.0															
Cu	0.2	0.2	0.4	1.0														
Ni	0.2	0.3	**0.5**	0.3	1.0													
Pb	0.4	0.4	0.4	0.3	0.5	1.0												
Mn	0.3	0.3	0.4	**0.5**	0.4	**0.6**	1.0											
Zn	0.3	0.5	0.5	0.3	0.5	**0.8**	**0.5**	1.0										
V	0.2	0.3	0.5	0.3	**0.9**	0.4	0.4	0.4	1.0									
Fe	**0.8**	**0.8**	0.3	0.2	0.2	0.4	0.3	0.4	0.2	1.0								
As	0.4	0.4	**0.7**	0.3	0.2	0.4	0.4	0.4	0.2	0.3	1.0							
F^-	0.0	0.1	0.3	0.3	0.4	0.3	0.2	0.4	0.3	0.1	0.1	1.0						
Cl^-	0.2	0.3	**0.5**	0.3	0.2	0.3	0.4	0.3	0.2	0.2	0.5	0.3	1.0					
NO_3^-	0.3	0.4	0.5	0.4	**0.6**	**0.6**	**0.6**	**0.5**	0.5	0.4	0.5	0.3	0.4	1.0				
SO_4^{2-}	0.3	0.4	0.5	0.4	**0.6**	**0.5**	**0.6**	0.5	**0.5**	0.3	0.5	0.3	0.4	**1.0**	1.0			
K^+	0.2	0.2	0.3	-0.1	0.2	0.3	0.2	0.2	0.1	0.1	0.4	0.0	0.2	0.4	0.5	1.0		
Na^{2+}	0.1	0.3	0.5	0.3	0.2	0.3	0.3	0.3	0.2	0.2	0.4	0.3	**1.0**	0.4	0.4	0.2	1.0	
Mg^{2+}	0.2	0.3	0.4	0.3	0.2	0.4	0.3	0.3	0.2	0.2	0.4	0.3	**0.8**	0.4	**0.5**	0.3	**0.9**	1.0

Table 4.10b. Element to element correlations observed at Parawada site

P	**Al**	**Ca^{2+}**	**Cr**	**Cu**	**Ni**	**Pb**	**Mn**	**Zn**	**V**	**Fe**	**As**	**F^-**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**	**K^+**	**Na^+**	**Mg^{2+}**	**Cd**
Al	1.0																		
Ca^{2+}	**0.7**	1.0																	
Cr	0.1	0.1	1.0																
Cu	0.4	0.3	0.1	1.0															
Ni	0.3	0.3	0.4	0.2	1.0														
Pb	0.0	-0.1	0.4	0.2	0.2	1.0													
Mn	-0.1	-0.1	0.4	0.2	0.3	**0.6**	1.0												
Zn	**0.6**	**0.6**	**0.6**	0.4	0.5	0.2	0.2	1.0											
V	0.3	0.4	0.3	0.2	**0.9**	0.2	0.2	0.4	1.0										
Fe	**0.6**	**0.6**	-0.1	0.2	0.3	-0.2	-0.2	0.3	0.4	1.0									
As	**0.6**	**0.5**	0.2	0.3	0.4	-0.1	-0.1	**0.7**	0.4	**0.5**	1.0								
F^-	0.3	0.2	0.1	-0.1	0.2	-0.1	-0.3	0.0	0.1	0.3	0.2	1.0							
Cl^-	-0.2	0.0	0.4	-0.1	0.2	0.2	0.2	-0.1	0.2	-0.1	-0.3	0.0	1.0						
NO_3^-	0.4	0.4	**0.5**	0.4	0.4	0.1	0.1	**0.6**	0.4	0.3	0.4	0.3	0.0	1.0					
SO_4^{2-}	0.4	0.4	**0.5**	0.4	0.5	0.1	0.01	**0.6**	0.4	0.3	0.5	0.3	0.0	**0.9**	1.0				
K^+	**0.8**	**0.7**	0.3	0.3	0.4	0.0	0.0	**0.7**	0.4	**0.6**	**0.5**	0.2	0.0	**0.6**	**0.6**	1.0			
Na^{2+}	-0.2	-0.0	0.3	-0.2	0.1	0.2	0.1	-0.2	0.1	0.0	-0.3	0.0	**0.9**	-0.1	0.0	0.0	1.0		
Mg^{2+}	**0.7**	**0.6**	0.3	0.4	0.4	0.0	0.0	**0.7**	0.3	0.5	**0.6**	0.2	0.0	**0.6**	**0.6**	**0.8**	0.0	1.0	
Cd	**0.5**	**0.5**	0.1	**0.5**	0.3	0.0	0.0	**0.5**	0.3	0.4	0.4	0.1	-0.2	0.4	0.4	**0.5**	-0.0	**0.5**	1.0

Table 4.10c. Element to element correlations observed at Trombay site

T	Na^+	Mg^{2+}	Al	Si	S	Cl	K^+	Ca^{2+}	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb	As	BC
Na^+	1.0																		
Mg^{2+}	**0.8**	1.0																	
Al	0.2	0.3	1.0																
Si	0.2	0.3	**1.0**	1.0															
S	-0.2	0.0	0.3	0.4	1.0														
Cl^-	**1.0**	**0.8**	0.2	0.2	-0.2	1.0													
K^+	-0.2	0.1	0.3	0.3	**0.9**	-0.1	1.0												
Ca^{2+}	0.2	0.3	**0.9**	**0.9**	0.3	0.2	0.3	1.0											
Ti	0.2	0.3	**0.9**	**0.9**	0.4	0.2	0.4	**0.8**	1.0										
V	-0.1	0.1	0.2	0.3	**0.6**	-0.1	**0.7**	0.3	0.3	1.0									
Cr	-0.2	-0.2	0.2	0.3	**0.5**	-0.2	0.4	0.3	0.2	0.4	1.0								
Mn	-0.2	-0.1	0.2	0.3	**0.5**	-0.2	**0.5**	0.3	0.2	**0.5**	**0.9**	1.0							
Fe	0.2	0.3	**0.9**	**0.9**	0.3	0.2	0.4	**0.9**	**0.8**	0.3	0.3	0.3	1.0						
Ni	0.0	0.2	0.2	0.3	**0.6**	0.0	**0.7**	0.3	0.3	**0.9**	0.4	0.5	0.3	1.0					
Cu	-0.1	0.0	0.3	0.3	**0.6**	-0.1	**0.7**	0.3	0.3	**0.7**	**0.6**	**0.6**	0.3	**0.7**	1.0				
Zn	-0.1	0.0	0.1	0.2	0.5	-0.1	**0.6**	0.2	0.1	**0.6**	0.3	0.4	0.2	**0.6**	**0.8**	1.0			
Pb	0.0	0.1	0.2	0.3	**0.6**	0.0	**0.7**	0.3	0.3	**0.6**	0.5	**0.6**	0.3	**0.7**	**0.9**	**0.8**	1.0		
As	-0.2	-0.1	0.3	0.3	**0.8**	-0.1	**0.7**	0.2	0.3	0.5	0.5	0.5	0.3	0.5	**0.5**	0.4	0.5	1.0	
BC	-0.2	-0.1	0.3	0.3	**0.6**	-0.2	**0.6**	0.2	0.3	**0.5**	0.4	**0.5**	0.2	0.5	**0.6**	**0.5**	**0.5**	**0.8**	1.0

4.2. Chemical speciation of Arsenic in PM_{10} at study sites

The present PM sampling locations are near to thermal power plant as shown in Fig. 3.1. Coal fly ash released from coal combustion sources are reported to be the major source of As in PM [266]. The As observed in collected PM couldo be contributed from coal combustion sources. Arsenic is one of the most toxic elements that has a wide range of concentration in PM and can exist in different oxidation states. The toxicity of As is entirely dependent on the oxidation state of As. Hence, it is important to know the oxidation state of Arsenic in PM. Many analytical techniques such as ion chromatography, voltammetry and some hyphenated techniques viz. HPCL-AAS/AAF, IC-AAS, etc. were used by many authors for the chemical speciation of As in PM. Despite the variety of sensitive analytical techniques for trace element determination, atomic absorption spectrometry is still the method of choice for routine determination of large number of elements. Atomic absorption spectrometry with hydride generation allows easy and sensitive determination of arsenic in different forms. The key concept behind the chemical speciation of As was that, As^{+5} converts to its volatile hydride at low pH range (pH <2) only, whereas As^{+3} can be converted to its volatile form even at high pH value (about pH 4-5) also. In the present study, this key concept was used for the As chemical speciation. For this purpose, the reducing agent ($NaBH_4$) concentration and the acidic solution strength needed to carry out the Arsenic speciation were optimized.

The reducing agent concentration was prepared by weighing known amount of $NaBH_4$ into double distilled water and small quantity of NaOH was also added to above mixture. In this way, different $NaBH_4$ solutions with concentration in the range from 0.05 to 2% (W/V) were prepared. A known amount of As^{+5} standard was added to the blank solution of filter paper and analysis was carried out using high concentration of citric acid (400 mM). The corresponding absorbance was measured at each $NaBH_4$ concentration. The results of this study are presented in Fig. 4.7, which indicate that at 0.6% of $NaBH_4$ concentration maximum absorbance was observed. Hence, in the present study 0.6% of $NaBH_4$ was chosen as an optimum concentration for As^{+3} reduction.

In the next step, As^{+3} analysis (that was spiked in filter blank sample) was carried out by varying the concentration of citric acid from 5 to 400 millimolar and fixing the $NaBH_4$ concentration at 0.6% (W/V). The results of the study are given in Fig. 4.8. It can be observed from Fig. 4.8. that, as the citric acid concentration increases the absorbance increases and reaches maximum at 50 millimolar citric acid concentration.

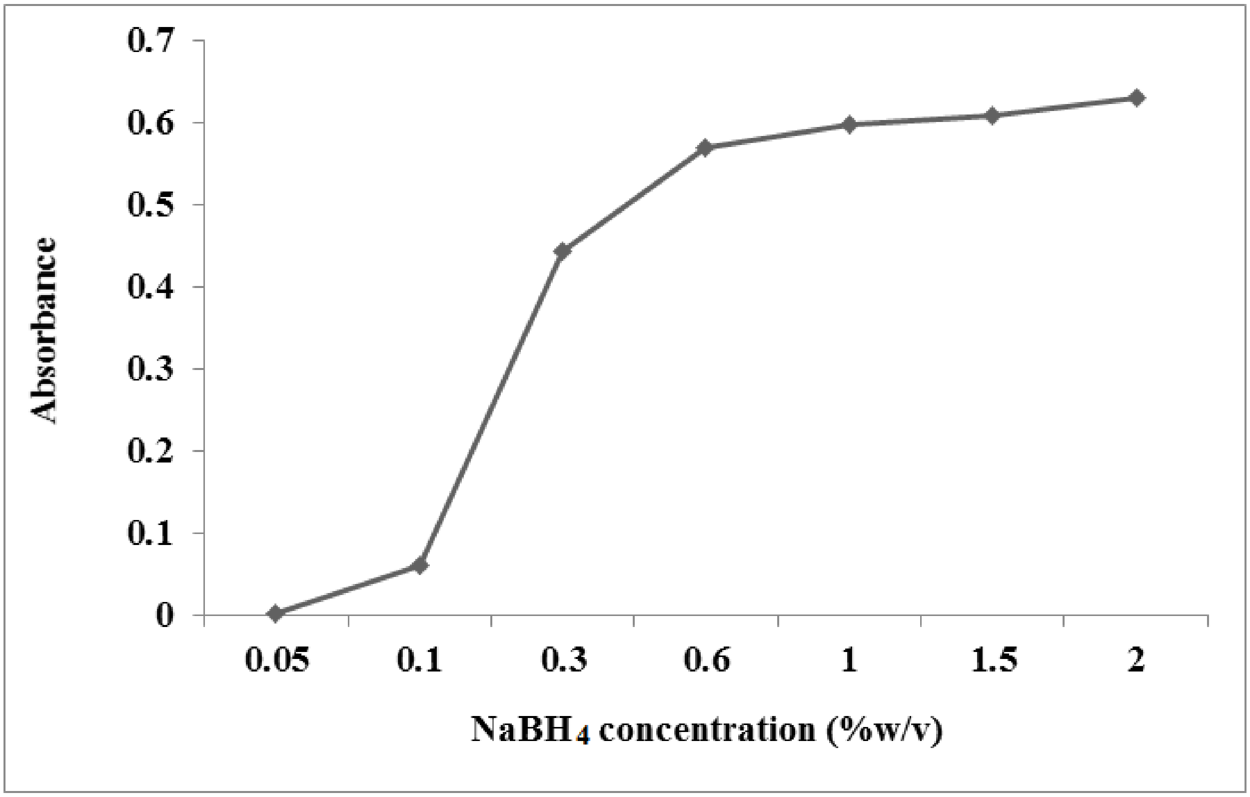


Fig.4.9. Variation of absorbance with respect to the reducing agent concentration

Using optimized parameters, recovery test was carried out by spiking the filter blank solutions with different concentrations of As^{+3} and As^{+5}. These spiked solutions were analyzed for As species. The results of recovery study are presented in Table 4.12. A minimum of 92% recovery was observed for both the species at optimized conditions. After recovery test, some field samples collected from Jogannapalem, Parawada and Trombay sites were analyzed for As^{+3} and As^{+5} concentration levels using optimized parameters. The results of the speciation study are summerized in Table 4.13. From results, it can be observed that As is majorly present in As^{+5} form in PM at all the study sites.

Presence of As predominantly in As^{+5} form indicates that, it might be contributed from some combustion sources, where As^{+3} also gets converted to As^{+5}. The As^{+5} species is less toxic, it is about 20 times less toxic than As^{+3} [269, 270]. Since, As concentration is lower than NAAQ standard, we can say air quality is good with respect to Arsenic air pollution.

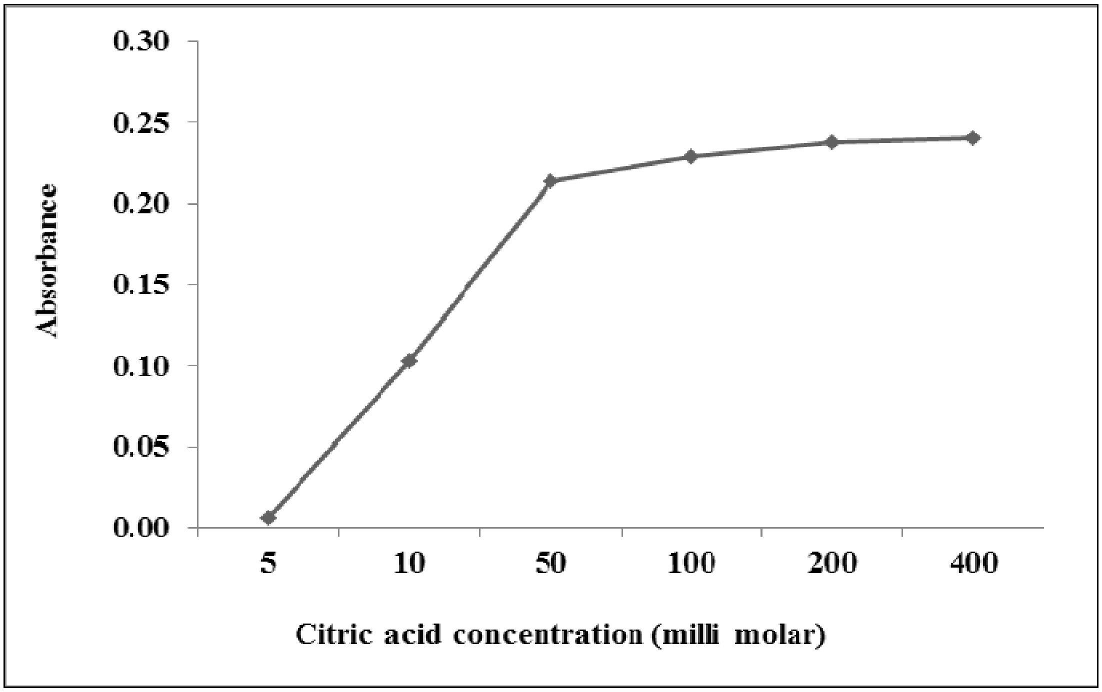


Fig.4.10 Variation of absorbance with respect to the citric acid concentration

Table 4.11. As^{+3} and As^{+5} recovery test using optimized parameters

S.No.	Spiked concentration	Species	Reaction medium	Observed concentration	% recovery
1	10 ppb	As^{+3}	Citric cid	9.8	98.0
2	20 ppb	As^{+3}	Citric cid	20.48	102.4
3	30 ppb	As^{+3}	Citric cid	29.48	98.3
4	10ppb each	As^{+3}&As^{+5}	Citric cid	9.7	97.0
5	10ppb each	As^{+3}&As^{+5}	HCl	18.46	92.3

Table 4.12. As^{+3} and As^{+5} concentrations observed at study sites during entire study period

	Jogannapalem			**Parawada**			**Trombay**		
	As^{+3}	As^{+5}	As total	As^{+3}	As^{+5}	As total	As^{+3}	As^{+5}	As total
Min.	0.3	1.5	1.8	0.2	2.4	2.6	0.2	1.6	1.9
Max.	1.0	4.9	5.9	2.4	9.7	12.1	1.1	4.6	5.2
Avg.	0.6	3.1	3.7	1.3	6.0	7.3	0.5	2.9	3.4

4.3. Conclusions

It can be concluded from this chapter that, mean PM_{10} concentrations at all study sites were exceeded the CPCB annual standards. The highest PM_{10} concentrations were observed during November, January and December months with mean monthly concentration values of 109.7 μg/m^3, 137.3 μg/m^3 and 182.2 μg/m^3 at Jogannapalem, Parawada and Trombay sites respectively. Least concentrations were observed during August at all sampling sites. Chemical characterization of collected PM indicates that Al has the highest mass concentration at Jogannapalem and Parawada sites, whereas BC has the highest contribution to PM_{10} at Trombay. Among different chemical species Al (6.2% and 5.1%) has the highest percentage mass contribution to PM_{10} at Jogannapalem and Parawada sites. At Trombay site, BC has the highest percentage mass contribution (4.4%) which was followed by Si (4.3%) and Al (3.3%).

Seasonal variation observed to have strong influence on elemental concentrations. Most of the chemical species observed to have highest concentration during winter season and least concentration during monsoon season. Highest concentration observed during winter season could be due to the temperature inversion effect and low wind speed which leads to the accumulation of emitted pollutants. A good correlation with a correlation coefficient > 0.8 was observed between few set of chemical species indicating their emission from similar or same source. This chapter also discussed the chemical speciation results of As in PM at study sites. It was observed that As majorly exists in As^{+5} form at all study sites.

Chapter 5

Source Identification and apportionment using different receptor models

As a preliminary step to source identification, crustal enrichment factor analysis was carried out for the analyzed chemical species. For the, source apportionment of collected PM_{10} samples, receptor models such as PMF and PCFA are used in the present study. Some experimental results were provided at the end of this chapter for the verification of receptor model results.

5.1. Enrichment factor

The crustal enrichment factor method gives an idea about the relative contributions of anthropogenic vs. crustal sources to trace elements bound to PM. The crustal enrichment factors (EFs) were evaluated for different elements in PM_{10} using an average re-suspended background soil composition determined in the studied areas. Silicon, Al, or Fe is generally used as the reference elements because they are abundant in soils; other elements such as Sr, Ti or Mn have also been used [271, 272]. In the present study, EF was calculated using Al as reference element for all the study sites using equation given below.

$$EF_{crustal} = \frac{\left(\frac{X}{Al}\right) in\ PM}{\left(\frac{X}{Al}\right) in\ soil}$$

Where, X and Al are respectively the element and the reference element concentrations in the air particulate matter and soil.

The calculated EFs of different chemical species observed at Jogannapalem, Parawada and Trombay sites are given in Fig.5.1. In the present study, elements with EF values near unity are assumed to have originated from crustal erosion. Since the trace element's concentrations can have some degree of uncertainty due to the natural variations of the earth crust, EF values lower than 5 are assumed as crustal contribution [273]. Whereas, chemical species having EF greater than 5 can be regarded as the contribution from both natural as well as from anthropogenic sources [274]. EF values ranging from 10-100 are considered to be purely contributed from anthropogenic sources and elements with EF values greater than 100 indicates intense contribution from anthopogenic sources at study area.

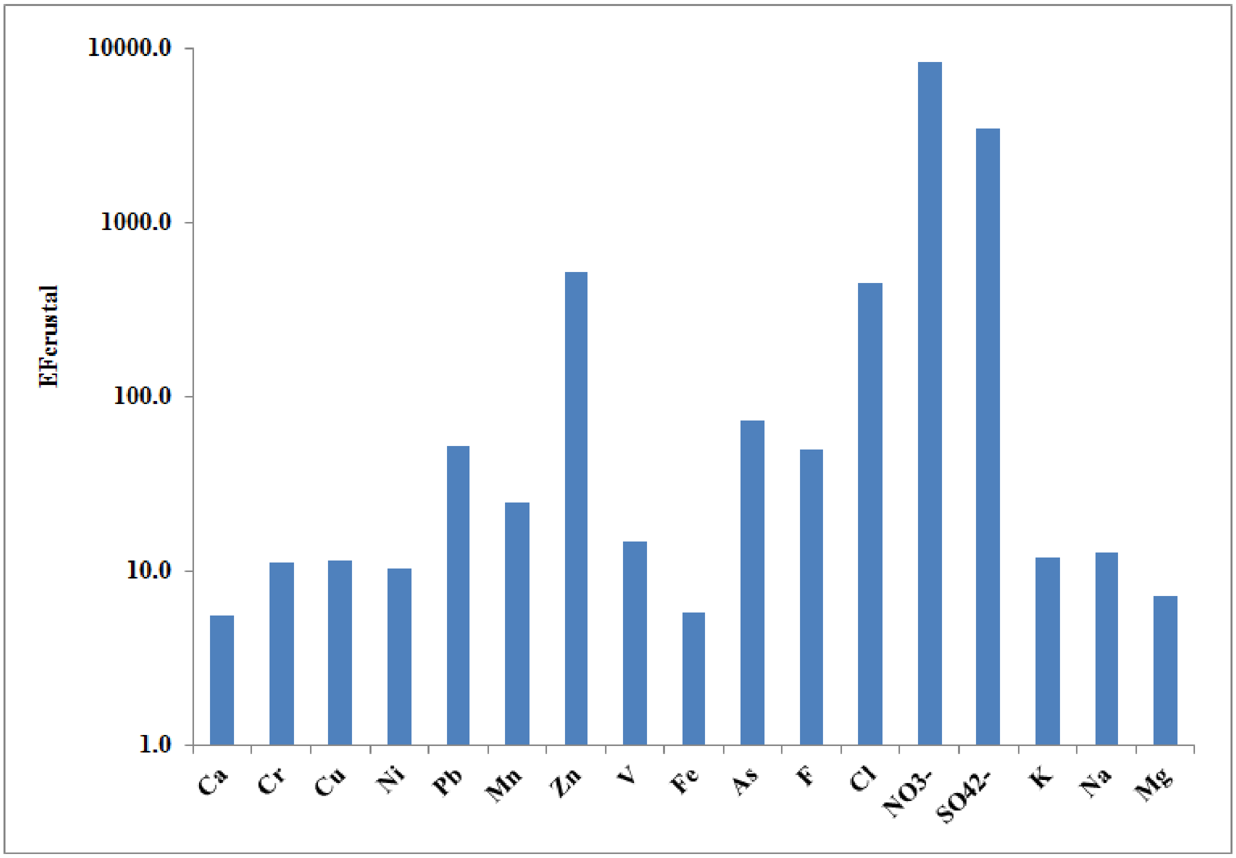


Fig.5.1a. Crustal enrichment factor of different chemical species at Jogannapalem

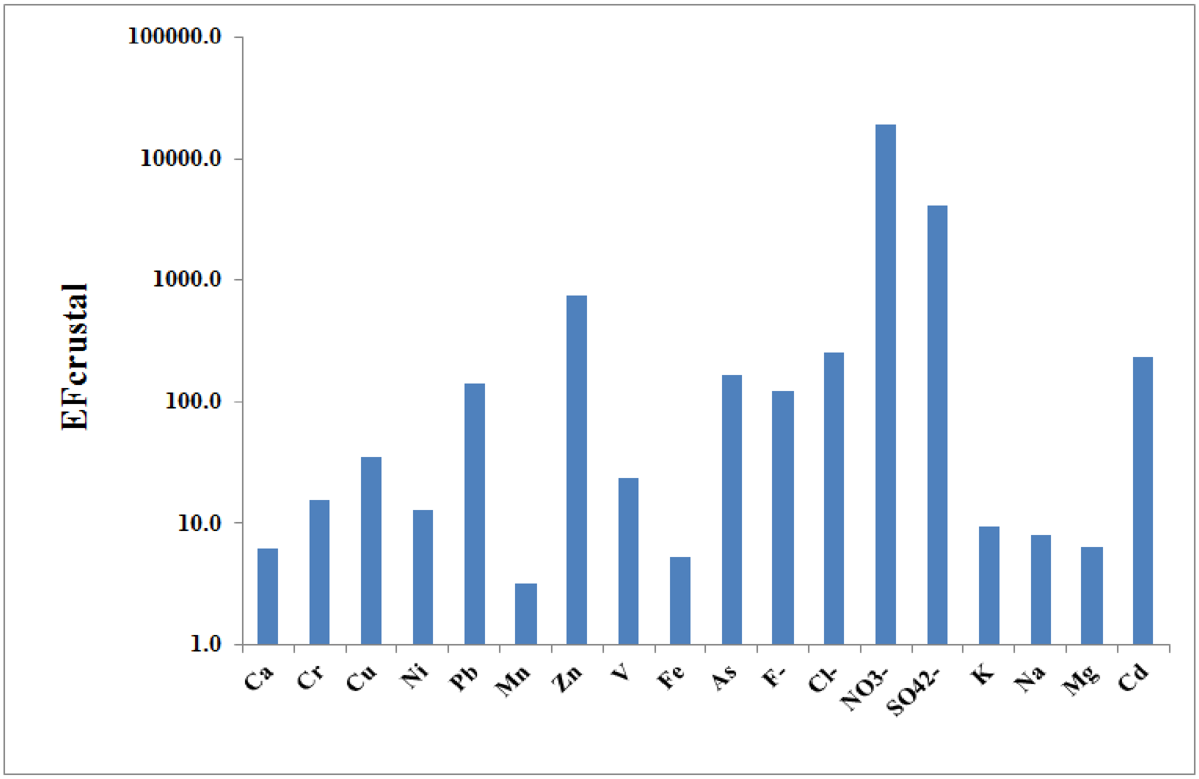


Fig.5.1b. Crustal enrichment factor of different elemental species at Parawada

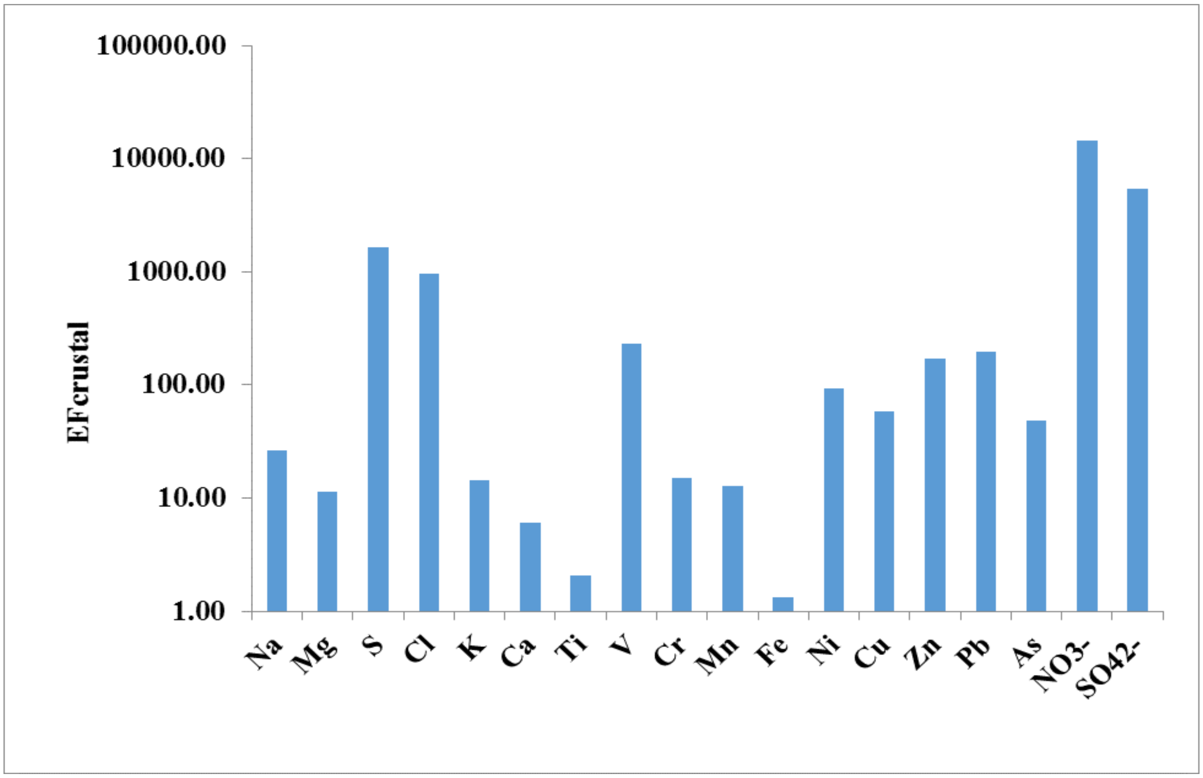


Fig.5.1c. Crustal enrichment factor of different elemental species at Trombay

In the present study, EF values lower than 6 was observed for Ca and Fe at Jogannapalem and for Mn and Fe at Parawada site, whereas at Trombay site, Ti and Fe were found to have EF <6 in PM_{10}. This indicates that these elements are originated from crustal material (e.g., soil and re-suspended dust). Mg^{2+} at Jogannapalem, K^+ and Ca^{2+} at Parawada and Ca^{2+} at Trombay site were found to have EF between 6 and 10, indicating that these could be contributed from both natural and anthropogenic sources. Moderate enrichment (with EF>10) was observed for Ni, Cr, Cu, K, Na^+, V, Mn, F^-, Pb and As at Jogannapalem (as shown in Fig. 5.1a), and for Na^+, Ni, Cr, V and Cu at Parawada site. A moderate enrichment was observed for Mg^{2+}, Mn, K^+, Cr, Na^+, As, Cu and Ni at the Trombay site. Most of the metals have higher EF values at Trombay site as compared to other sampling sites except for Cr at Parawada and Mn at Jogannapalem.

Chemical species such as Zn, Cl^-, NO_3^- and SO_4^{2-} at Jogannapalem site and F^-, Pb, As, Cd, Zn, Cl^-, NO_3^- and SO_4^{2-} at Parawada site and Zn, Pb, V, Cl^- and S at Trombay were found to be highly enriched (with EF > 100) in PM_{10}, indicating that they are immensely originating from anthropogenic sources. Mobile sources (such as vehicular emissions) and industrial activities could be the major anthropogenic sources of the enriched elements in PM [149, 275-276].

As discussed above, EF gives information about the nature and strength of contributing source to PM. More reliable source identification and apportionment can be carried out using receptor models. The following section elaborated the use of receptor models such as PMF and PCFA for source identification and apportionment of collected PM.

5.2. Source apportionment of PM collected at Jogannapalem, Parawada and Trombay sites using PMF model

In the present study, source apportionment was performed using EPA PMF v5 software. Version 5 provides a flexible modeling approach that permits the imposition of constraints and utilizing data from multiple sites. A total of 19 chemical species viz. F^-, Cl^-, NO_3^-, SO_4^{2-}, Na, Mg^{2+}, K^+, Al, Ca^{2+},V, Cr, Mn, Fe, Cu, Ni, Zn, As, Cd and Pb were considered for the PMF study at Jogannapalem and Parawada sites. Whereas at Trombay site, 18 species viz. Na^+, Mg^{2+}, K^+, Cl^-, Al, Ca^{2+}, V, S, Cr, Mn, Fe, Ti, Cu, Ni, Zn, As, BC and Pb were considered for the PMF analyses. All the species included in the matrix are qualified as “strong” (signal to noise: $S/N > 2$).

In the current study, a range of PMF solutions were examined with different number of factors (varied from 3 to 9) and base runs (varied from 20 to 100). In each case, the model was run in the robust mode with number of repeat runs to insure the model least-squares solution representing a global rather than local minimum. In PMF analysis, the rotational FPEAK variable was held at the default value of 0.0. The number of base runs equal to 35 was selected (based on number of trails) for PMF analysis and the run with the minimum Q value was chosen as the base run solution. The number of factor solutions was varied from 3 to 9 as discussed above (with 35 base runs) and PMF factor profiles were examined for each pre-selected factor numbers. In the case of 3 and 4 factor solutions, no meaningful sources were identified as there was a mixing of most of the trace/marker elements. But, 6 factors solution (at Jogannapalem and Trombay) and 7 factors solution (at Parawada) was observed to have factor profiles that are interpretable in terms of the nature of the sources in the study area and for their known physical meaning. Again, beyond 7 factors solution, the sources were observed to split further leading to no meaningful conclusions. Hence, the 6 and 7 factors solution was taken as the meaningful PMF result for the present study. The sources were identified and named based on the appearance and percentage contribution of marker elements in particular factor profile.

Jogannapalem and Parawada locations commonly contributed by five PM sources viz. crustal material, sea salt spray, coal combustion, fuel oil combustion and metal industry. The other sources include biomass burning at Jogannapalem; road traffic and secondary aerosols at Parawada. At Trombay site six sources were identified which includes crustal material, sea salt spray, coal/biomass combustion, fuel oil combustion, road traffic and metal industry. Figs. 5.2a, b, c shows the factor profiles observed in the PMF model at Jogannapalem, Parawada and Trombay sampling sites respectively. In figures, the red dot indicates the percentage contribution and the bar indicates the concentration of a species. PMF factor profile observed at each study sites are discussed in detail in the following section.

Elemental profiles of factor 1 at Jogannapalem site and factor 3 at Parawada site were predominantly contributed by As, Cr and Zn. The percentage explained variations (EV) of As, Cr and Zn was found to be 75%, 52%, 23% and 69%, 40%, 51% at Jogannapalem and Parawada site respectively. At Trombay site, factor 1 was dominantly contributed from As (69.8%), S (72.7%), K (71%), and BC (59.2%) with a minor contribution from Pb (18%). Literature study indicate that arsenic (As) is one of the important tracer of coal fired power plant emissions [286] and S, Cr, Zn are also typical for combustion of coal sources [52-53, 298]. Hence these factors were named as coal combustion source. Coal combustion sources near Parawada and Trombay site might have contributed to these metals observed in PM. Additionally, the contribution of K and BC was observed in the factor profiles of Trombay site. These are considered to be the important marker elements for biomass burning activities [39, 278]. There are many slum areas near the Trombay sampling site where the biomass burning is a common activity for heating and cooking purpose. Hence, the factor 1 at Trombay site was named as coal/biomass combustion source in the present study.

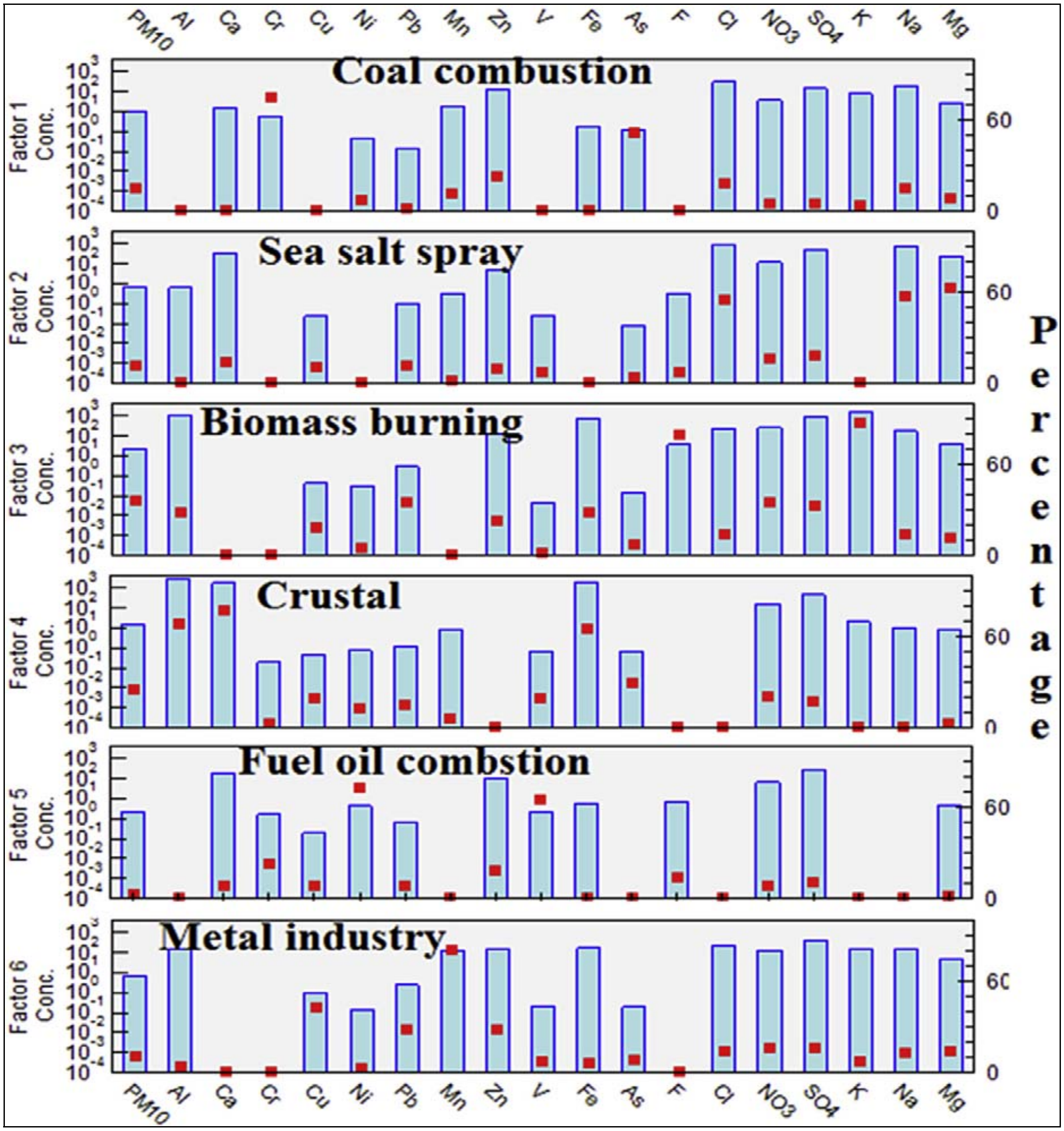


Fig.5.2a. PMF factor profiles observed at Jogannapalem site

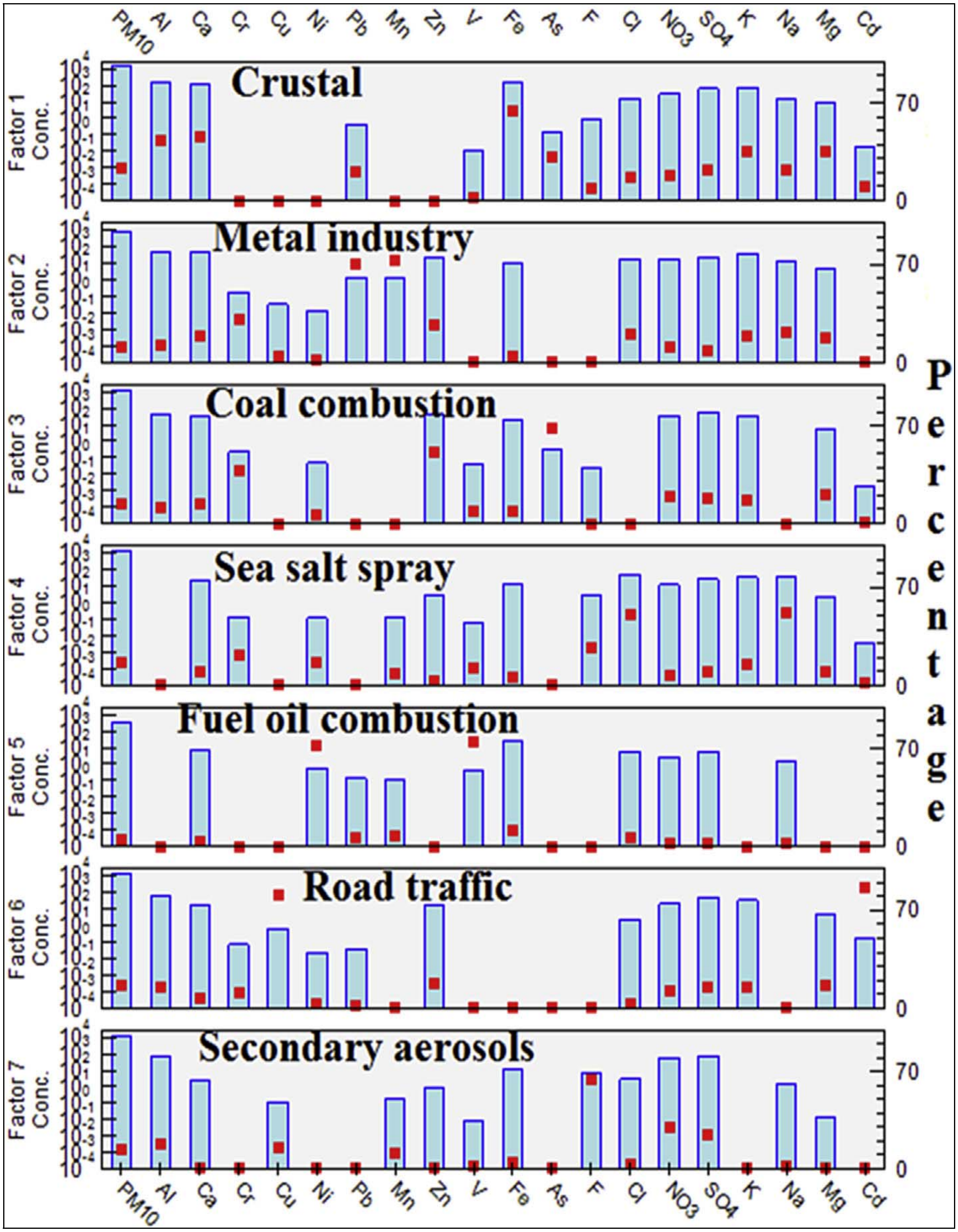


Fig.5.2b. PMF factor profiles observed at Parawada site

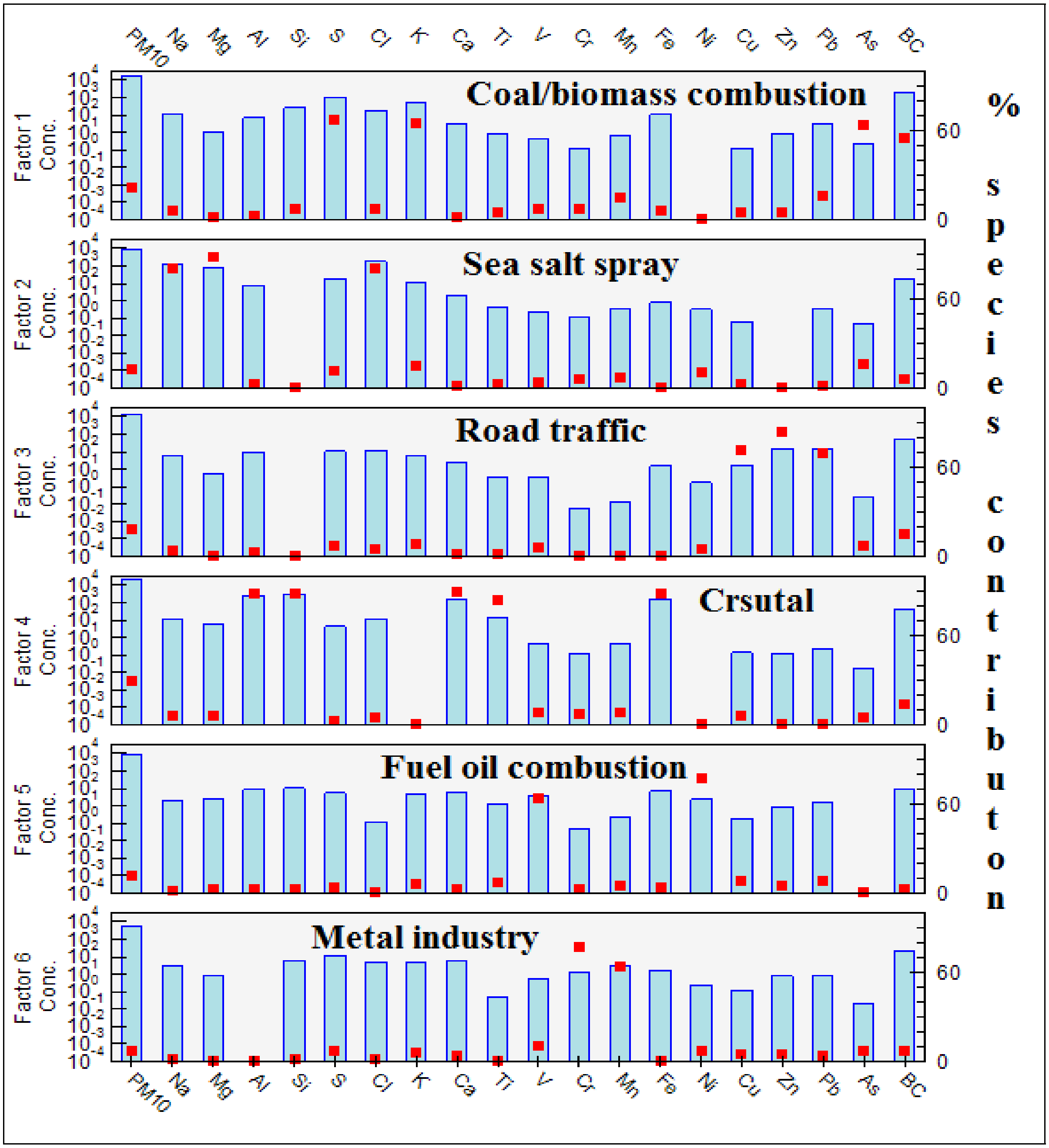


Fig.5.2c. PMF factor profiles observed at Trombay site

Enhanced percentage EV of Cl^-, Na^+ and Mg^{2+} was observed in factor 2 at Jogannapalem and Trombay sites and factor 4 at Parawada was dominantly contributed by Na^+ and Cl^-. In the present study, the percentage EV of Cl^- was observed in the range of 52 to 79.7% and that of Na^+

in the range of 49 to 79.3%. Similarly, the EV of Mg was found in the range of 62.6 to 88.5% at Jogannapalem and Trombay sites respectively. Many studies from all over the world have identified the particle bound Na^+, Cl^- and Mg^{2+} as the contribution of sea salt spray [152, 157]. Hence, these factors were named as "sea salt spray". Bay of Bengal and Arabian Sea present near the sampling sites could have contributed to these species in PM_{10}. A good correlation (R^2>0.85) observed between Na^+ and Cl^- at all the sites with Cl^- to Na^+ ratio close to the actual sea salt ratio, further supports the PMF model results. At Jogannapalem site, low percentage contribution of SO_4^{2-} and NO^-_3 was also observed in sea salt spray source; similar observation was made by Aldabe et al. (2011) [152]. This could be due to higher ss-SO_4^{2-} contribution to PM_{10} at Jogannapalem site as compared to other study site as discussed above.

Factor 3 at Jogannapalem site was dominated by K, F^- and a minor contribution of SO_4^{2-}, NO_3^-, was also observed. Various authors [50, 51] indicated the contribution of K from biomass burnings. Observed contribution of SO_4^{2-} and NO_3^- in this factor could be due to the wood combustion been carried out for heating and cooking purposes at the sampling site [279]. Metals observed in this factor might be contributed from the miscellaneous sources, which may include the industrial emission and coal combustion sources. Similar observation was made by Hang and Oanh [51].

Factor 4 at Jogannapalem and Trombay sites and factor 1 at Parawada were characterized by high EV values for the major metals such as Al, Ca and Fe. The observed EV values for Al, Ca and Fe are 68%, 77.7% and 65.4% at Jogannapalem, 48%, 68.2% and 45.2% at Parawada sites, and 88.7%, 89.4% and 88.8% at Trombay site. In addition to Al, Ca and Fe, the factors at Jogannapalem and Parawada sites were also contributed by other metals; this could be due to the presence of these chemical components in soil dust due to the contamination from nearby industrial activities. Aldabe et al. (2011) [152] also reported the presence of other metals in crustal material. At Trombay site, Si and Ti were also present in factor 4 with EV values 88.7% and 84.2% of Trombay site. Observed good correlation between these set of elements indicates that, these metals could be emitted from identical or same source. The major source of these metals at the sampling sites could be re-suspension of regional dust and hence named this factor as crustal source.

In the present study, Ca to Al ratio was found to be 0.58, 0.73 and 0.70 at Jogannapalem, Parawada and Trombay sites respectively. Slightly higher ratios (than the reference ratio value of 0.44 in soils) observed at study sites could be due to the additional contribution of Ca from anthropogenic sources such as construction activities near these sampling sites or thermal power plants fly ash which is highly enriched with Ca [280]. Many researchers [45, 115,156, 278, 281] have also identified these clusters of metals as the contribution from the crustal material. The crustal material particles make up the largest fraction of global aerosol mass in the atmosphere and can be suspended in the air medium by wind, mechanical disturbance of soil [44, 45].

At all the sampling sites, the elemental profile of factor 5 was dominantly contributed by the V and Ni. The EV values were found in the range of 65.2% to 75% and 71% to 76.5% for V and Ni respectively. Typical emission of these metals could be from fuel oil combustion sources such as shipping emissions, emissions from crude oil refineries and industrial power plants that use heavy oil [48, 139, 143]. Hence these factors are named as fuel oil combustion sources. A characteristic value of V/Ni ratio between 2.5 and 3.5–4.0 is considered typical for ships emissions [282]. Lower ratios (approaching 0.5) are typically found in diesel combustion particles [283]. In the present study, V/Ni ratio was observed in the range from 0.11 to 2.98, 0.11 to 3.44 and from 0.34 to 5.67 with a mean value of 0.71, 0.76 and 2.05 at Jogannapalem, Parawada and Trombay sites respectively. These metals might be contributed from petroleum industries present near the study sites. Ship emission is also one of the major sources of V and Ni [284]. Since all the sampling sites are near to one of the leading ports in India, the possibility of ship emissions to PM can't be neglected.

Highest concentrations of Mn, Zn and Pb were observed in the factor profiles of factor 6 at Jogannapalem and factor 2 at Parawada. Additionally, Cu and Cr were observed in factor profiles of Jogannapalem and Parawada sites respectively. Factor 6 at Trombay site was predominantly contributed from Cr and Mn with 80% and 65.6% of EV values. Many previous studies [48-49, 285] identified the presence of these metals as the contribution from metal manufacturing and metal processing industries. Hence, in the present study these factors were named as "metal industries". The soil samples collected around various metal processing/production industries at Visakhapatnam were also observed to have enriched concentrations of Mn, Zn, Pb, Cr and Cu [286], which further supports the model results.

Predominant concentrations of Cu, Cd and Zn were observed in factor 6 at Parawada site. Similarly, factor 3 at Trombay site has the highest concentrations of Cu, Zn and Pb with a minor contribution from BC. This factor was identified as road/vehicular traffic, as the dust originated from combustion of lubricating oil, tire wear and motor brake abrasion contains Pb, Cd and Zn [48, 158, 287]. In other studies, it was concluded that Cu was derived especially from brake linings [85, 288] and Zn from lubrication oil/tyre, whereas metal wear particles from Cd bearing alloys are also emitted. Liu et al., (2015) [158] indicated that BC was the main constituent in soot released from gasoline and diesel powered vehicles. Mumbai being metropolitan city has the highest usage of personal vehicles for transportation and witness heavy traffic jams every day. Similarly, Parawada site was also affected by vehicular moment but very less as compared to the

Trombay site. Thus, this source was named as road traffic. This source was not observed at Jogannapalem site as it is rural residential area with negligible vehicular movement. Vehicular emissions are a major source of PM and research indicates that they contribute 10 to 80% to PM in cities across India [115].

Factor 7 at Parawada was found to have the highest loadings of F^-, SO_4^{2-} and NO_3^-. These marker species were identified as the secondary aerosol component in many source apportionments studies performed [156]. The origin of SO_4^{2-} and NO_3^- could be from the oxidation of SO_2 and NO_2 emitted by combustion processes [51]. Airborne Fluoride (F^-) mostly emitted in gaseous form from anthropogenic sources, but at sampling site, we observed F^- in particulate form; this could be due to the gas to particle conversion phenomena.

The percentage contribution of observed sources to PM_{10} at Jogannapalem, Parawada and Trombay sites are presented in Fig. 5.3. At Jogannapalem site, the highest contribution to PM_{10} was observed from biomass burning (35%) and the least contribution was observed from fuel oil combustion (1.5%). At Parawada, the highest contribution to PM_{10} was observed from coal combustion (22.6%) followed by crustal source (22.5%) and the least contribution was observed from fuel oil combustion source (3.5%). Similar to Parawada site, Trombay site was observed to have the highest contribution from coal/biomass combustion (21.7%) followed by crustal material (20.7%) and the least contribution was observed from metal industry source.

Among all the identified sources, crustal material source contribution was observed to be highest at Jogannapalem and the least contribution of this source was observed at Trombay site. The higher contribution of crustal material at Jogannapalem could be due to the usage of unpaved roads for transportation. Similarly, biomass burning was also found to have the highest contribution at Jogannapalem site. As mentioned earlier, the public in and around Jogannapalem site are mostly dependent on wood/wood char coal/cow dung burnings for cooking and heating purposes. Also, the agricultural waste burning events are quite common at Jogannapalem leading to the highest contribution of biomass burning source. In contrary, sea salt spray contribution was observed to be higher at Trombay site as compared to Jogannapalem and Parawada sites. Coal combustion and metal industry sources have their highest contribution at Parawada site followed by Trombay and Jogannapalem. The close proximity of thermal power plant and various major, minor metal industries to Parawada sampling site might be the reason for observed highest contribution these sources at Parawada.

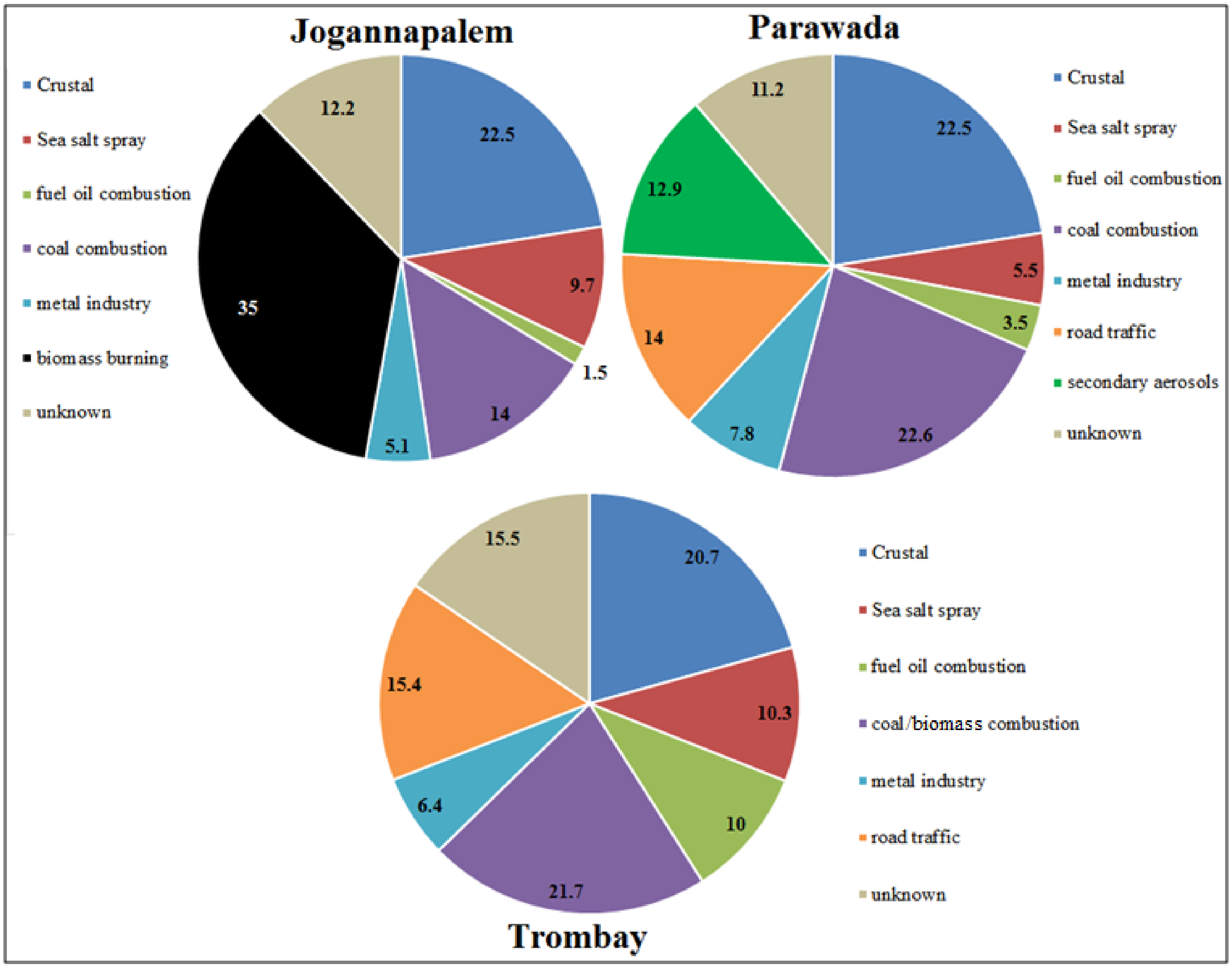


Fig.5.3. Percentage contribution of sources observed at Jogannapalem, Parawada and Trombay sites.

The other anthropogenic sources such as fuel oil combustion and road transport were having their highest contribution at Trombay site followed by Parawada and the least contribution of these sources was observed at Jogannapalem site. Oil combustion sources such as ship emissions, oil refineries and oil fired power plants are close to the Trombay sampling site as shown in Fig. 3.1b. The Trombay sampling site is close to many high traffic jam areas which might be the reason for observed highest road traffic source contribution.

Table 5.1 gives the percentage mass contribution of various sources to PM_{10} reported in different countries. From table 5.1 it can be said that the source contributions observed in the present study are in comparable range with those reported from all over the world.

Table 5.1. Percentage contribution of various sources to PM_{10} reported in different countries

Sources	**Spain**	**Mexico**	**Taiwan**	**Saudi Arabia**	**Turkey**	**Delhi**	**China**	**Greece**
Crustal	35	-	44	64	12	20.7	10	33
SSS	17	-	-	9	3	4.4	-	8
CC	-	-	25	-	30	-	-	13
FOC	-	18	23	18		17.4	16	-
BB		-	-	-	-	14.3	11	19
Road traffic	-	17	8	-	16	17.0	-	12
Metal industry	-	6	-	-	-	4.5	6	-
Secondary aerosols	-	10	-	-	-	21.7	-	-
Location type	Rural	Rural	Rural	Suburban	Suburban	urban	urban	urban
	[152]	[252]	[149]	[253]	[139]	[153]	[163]	[289]

*crustal+sulfate contribution; SSS= sea salt spray; cc=coal combustion; BB=biomass burning; FOC= fuel oil combustion

5.3. Experimental verification of PMF source profile

In the present study, multiple numbers of soil samples were collected around major industries (viz. steel plant (SP), TPP (thermal power plant), PR (petroleum refineries), Ore industry (AO), Alloy industry (AI), southern biotech industry (SB), Granite industry (GI) and road dust (CR)), around Jogannapalem, Parawada and Trombay sampling sites to verify the PMF source profiles experimentally. The soil samples are collected from locations as close as possible to industry with an assumption that the surrounding soil at a given industry is majorly contains signature elements of that particular industry. Collected multiple numbers of samples at a given industry were mixed properly to get a representative sample of the industry. The soil samples were dried and sieved to collect particles of size < 75 µm in size. The representative samples of each industry were then made a thin pellet and analyzed in EDXRF for major and trace metals such as Mg^{2+}, Al, K^+, Ca^{2+}, V, Ti, Cr, Mn, Fe, Cu, Ni, Zn, As, Br, and Pb. The elemental profiles of each soil samples collected at different industrial location of Visakhapatnam and Trombay site are presented in Fig. 5.4 and 5.5.

Chemical profiles of soil collected at PR site show that Fe, Al, Ca^{2+} and K^+ were predominant species among major elements. As far as the trace metals are concerned, PR site soil was highly enriched with V and Ni as compared to other industrial sites. Usually, V and Ni are considered to be the marker species for fuel oil combustion [290-291] and can be present in high concentrations. Similar observations have also been reported by Yatkin and Bayram (2008) [139]. A high correlation between V and Ni was observed in PM collected at Jogannapalem and Parawada site, suggests that these metals might be contributed from similar or identical sources. In PMF factor profiles also these metals are grouped in same factor and named as "fuel oil combustion" source. Observed high concentrations of V and Ni at PR site supports the PMF factor profile results found for Fuel oil combustion source at study sites.

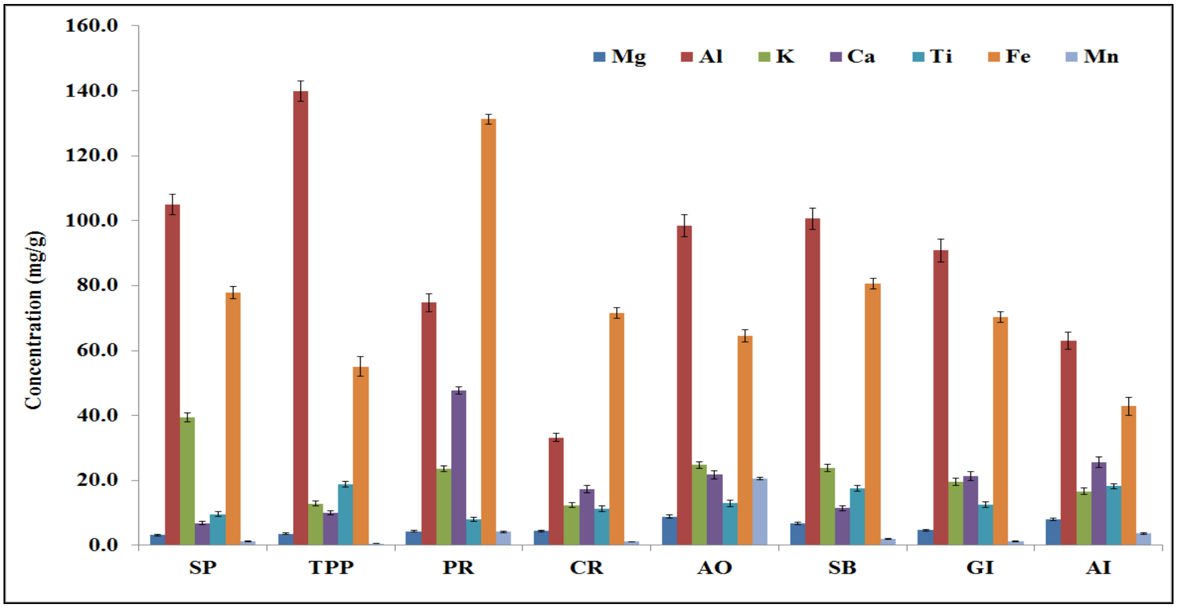


Fig.5.4a. Major metals concentration distribution in soil samples collected at different industries of Visakhapatnam

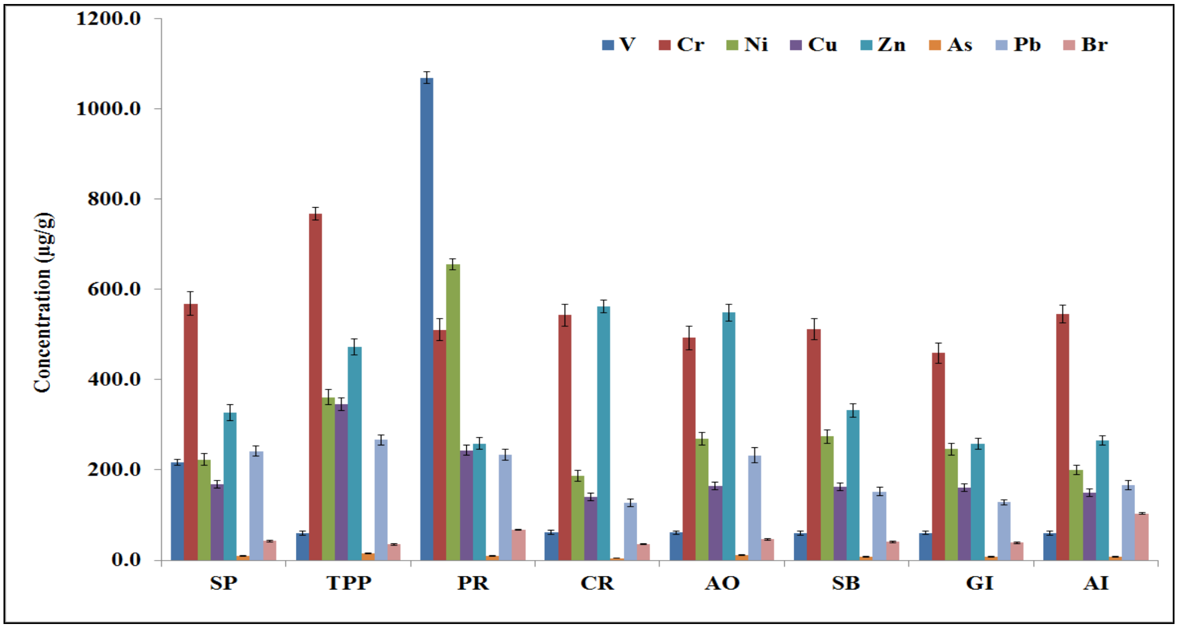


Fig 5.4b. Trace metals concentration distribution in soil samples collected at different industries of Visakhapatnam

In the present study, chemical profiles were developed for soil samples collected from TPP (2,000 MW). Prominent species in these profiles were also found to be crustal elements viz. Al, Fe, K^+, Ca^{2+}, Ti and Mg^{2+}. Similar trend was reported by US EPA in SPECIATE for coal fired power plant [292]. Geological component (Al) is the potential marker of soil dust and coal combustion fly ash [293]. Trace elements such as Cr, Zn, Ni, Cu and Pb were found to be highly enriched in samples collected at TPP. Also Arsenic, which is often used as a marker element for coal-fired power plant emissions [294] was also present in higher concentrations in this soil as compared to other samples collected. Similarly, the soil sample collected around thermal power plant near Trombay site was observed to have high concentration As, S and K. Similar elemental profiles were observed in the source apportionment studies of particulate matter (PM) collected at Jogannapalem, Parawada and Trombay sites, which confirms the contribution of coal combustion source to collected PM.

Elemental profiles of soil samples collected around different metal industries (Steel plant, Iron ore industry, Alloy Industry) near Jogannapalem and Parawada sites were observed to have high concentration of major elements such as Fe, Al, K, Ca, Mn. Whereas, among trace metals Zn, Cr and Pb were dominating followed by Ni, Cu and Br. Interestingly, Mn has the highest concentration at these metal industries as compared to other industrial sites such as PR, TPP, GI and biotech industry. The observed elemental profiles of soil samples collected at metal industrial sites are similar to the PMF profiles of factor 6 at Jogannapalem, and Trombay; and factor 2 Parawada sites. This supports the observed PMF model results for metal industrial sources at study sites. The soil samples collected at Traffic junctions near Trombay site are enriched with Zn, Cr, Pb, Ni and V. Elevated concentration of Ti in road dust samples (as shown in Fig. 5.5a) might be linked to the emission of alkali metal titanates from disk brake pads, brake drumlinings and other friction applications [295]. Similar elemental profiles are observed in factor 3 for Trombay site which supports the PMF result.

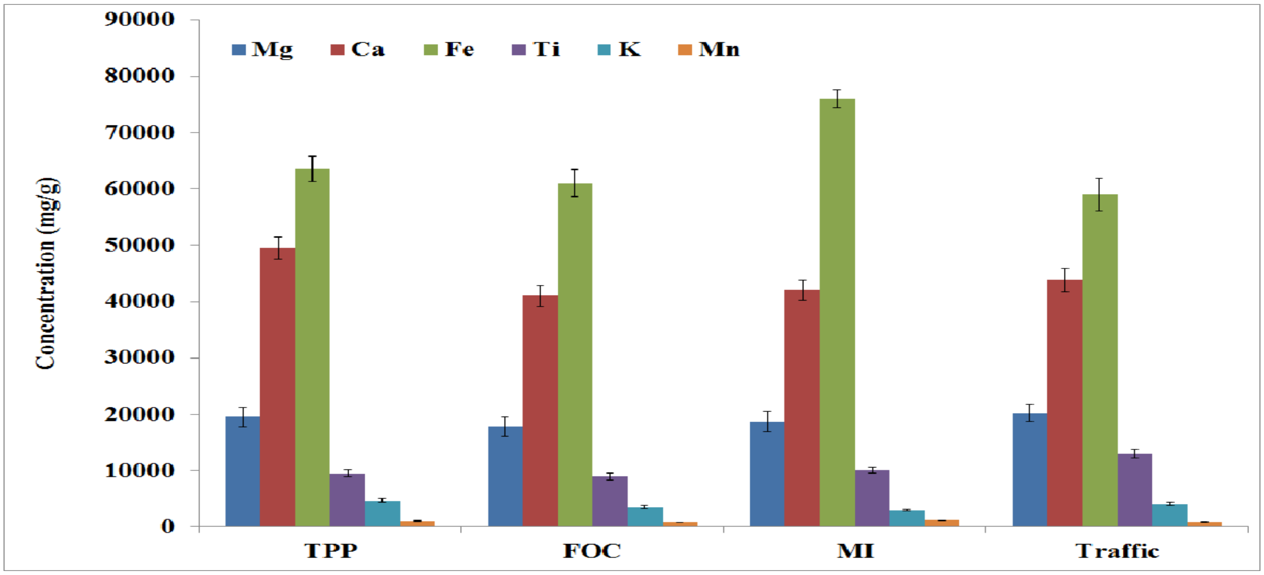


Fig.5.5a. Major metals concentration distribution in soil samples collected at different industries at Trombay

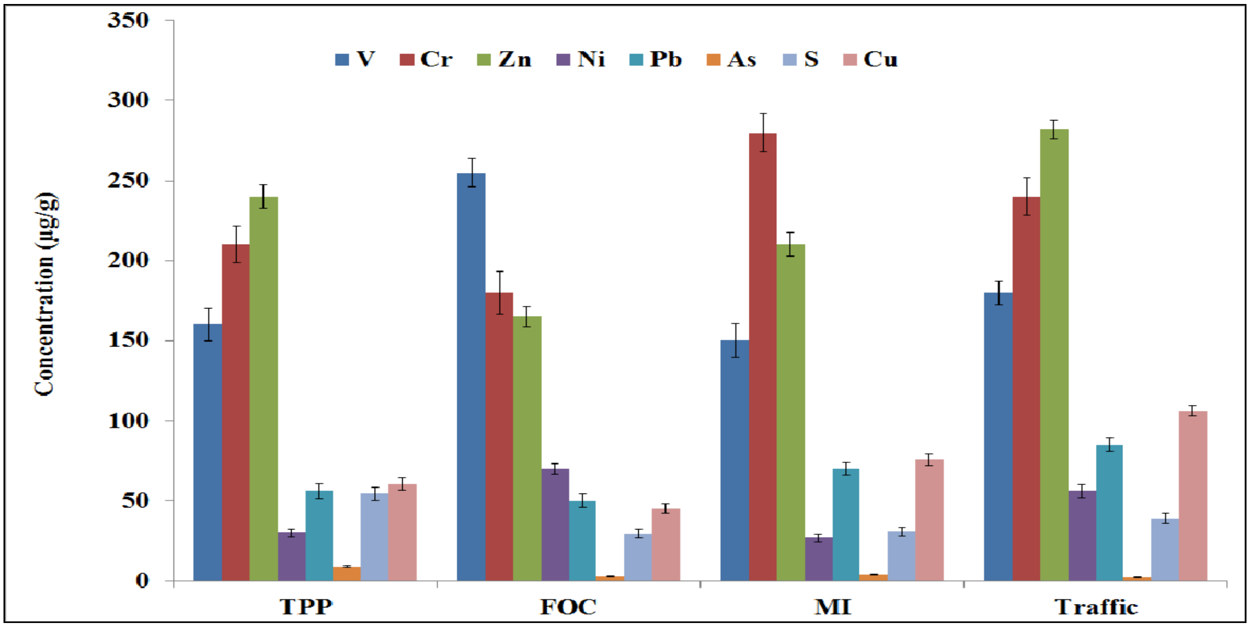


Fig.5.5b. Trace metals concentration distribution in soil samples collected at different industries in Trombay

5.4. Source apportionment of PM using another receptor model – A comparative analysis study

Source apportionment of PM_{10} collected at Jogannapalem and Parawada sites was also carried out using another receptor model viz. PCFA (Principal Component Factor Analysis) for comparison purpose.

In the present study, source identification was carried out by taking into account the concentrations of 19 chemical species analyzed in the PM samples. The number of factors having Eigen values greater than 0.5 [161] was chosen for explaining the maximum variance. The sources are identified and named based on the presence of marker elements with high loadings in a given factor. The factor loading matrix after varimax rotation for both the sites is shown in Table 5.2 and 5.3. Predominantly, six and seven number of sources contributions was identified, explaining 86% and 89% of total variance at Jogannapalem and Parawada sites respectively.

As shown in Table 5.2 and 5.3, Factor 1 at Jogannapalem and factor 3 at Parawada site was observed to have high loadings of Pb, Mn and Zn. Additionally, Cu has high loading on Factor 1 at Jogannapalem. These set of elements could have originated from metal manufacturing industries present around the sampling sites as shown in Fig. 3.1. Many authors [48, 296] identified these cluster of metals as industries contribution, hence named the factors as industrial source. This factor explained 43.1 % and 11.0 % of total variance at Jogannapalem and Parawada sites respectively.

Highest loadings of Na^{+}, Cl^{-} and Mg^{2+} were observed in factor 2 of Jogannapalem and Parawada sites. One of the major sources of these species at study location could be sea salt spray. This factor explained about 11.4 % and 19.1 % of variance in PM_{10} at Jogannapalem and Parawada sites respectively.

Table 5.2. Factor loading matrix for PM_{10} at Jogannapalem

	F1	**F2**	**F3**	**F4**	**F5**	**F6**
Al	0.11	0.02	**0.92**	0.15	0.04	0.10
Ca	0.14	0.15	**0.89**	0.13	0.14	0.10
Cr	0.25	0.29	0.12	0.22	0.29	**0.79**
Cu	**0.82**	0.17	0.05	0.02	0.23	0.03
Ni	0.19	0.07	0.08	0.11	**0.92**	0.25
Pb	**0.87**	0.13	0.13	0.16	0.09	0.19
Mn	**0.89**	0.14	0.15	0.10	0.17	0.09
Zn	**0.83**	0.15	0.18	0.11	0.03	0.23
V	0.22	0.10	0.18	0.13	**0.91**	0.17
Fe	0.16	0.12	**0.90**	0.05	0.10	0.05
As	0.28	0.21	0.18	0.21	0.26	**0.79**
F	0.00	0.19	0.05	**0.74**	0.00	0.35
Cl	0.17	**0.92**	0.11	0.11	0.08	0.17
NO_3^-	0.46	0.16	0.24	**0.68**	0.32	-0.09
SO_4^{2-}	0.44	0.22	0.20	**0.71**	0.32	-0.09
K	0.02	0.07	0.08	**0.86**	0.02	0.17
Na	0.18	**0.95**	0.09	0.12	0.05	0.13
Mg	0.18	**0.88**	0.11	0.19	0.09	0.11
Eigenvalue	7.8	2.1	1.9	1.7	1.4	0.9
Probable source	Industrial	Sea salt spray	Soil dust	Biomass burning	Fuel oil combustion	Coal combustion

Table 5.3. Factor loading matrix for PM_{10} at Parawada

	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**
Al	**0.88**	-0.06	0.14	0.15	0.05	0.22	0.11
Ca^{2+}	**0.86**	0.06	0.13	0.18	0.04	0.12	0.14
Cr	0.08	0.22	0.31	0.12	**0.86**	0.08	0.22
Cu	0.25	-0.04	0.18	0.19	0.07	**0.90**	0.09
Ni	0.21	0.17	0.25	0.10	0.17	0.11	**0.87**
Pb	0.09	0.17	**0.88**	0.02	0.27	0.11	0.17
Mn	0.00	0.19	**0.82**	-0.07	0.31	0.20	0.19
Zn	0.10	0.02	**0.92**	0.03	0.04	0.12	0.10
V	0.33	0.11	0.19	0.10	0.13	0.09	**0.87**
Fe	**0.82**	0.03	-0.07	0.21	-0.13	0.06	0.20
As	0.08	0.13	0.25	0.17	**0.90**	0.04	0.09
F^-	0.10	0.00	0.03	**0.89**	-0.04	0.15	0.00
Cl^-	-0.02	**0.92**	0.09	-0.05	0.17	0.01	0.15
NO_3^-	0.42	-0.12	-0.02	**0.75**	0.29	0.13	0.15
SO_4^{2-}	0.43	-0.02	-0.03	**0.76**	0.30	0.15	0.15
K^+	**0.84**	0.06	0.07	0.13	0.25	0.17	0.11
Na^+	0.01	**0.95**	0.10	-0.09	0.13	-0.05	0.05
Mg^{2+}	0.07	**0.91**	0.11	0.06	0.01	-0.01	0.06
Cd	0.24	-0.02	0.20	0.18	0.04	**0.91**	0.10
Eigenvalue	6.8	3.6	2.1	1.5	1.2	1.0	0.8
Probable source	Soil dust	Sea salt spray	Industrial	Secondary aerosols	Coal combustion	Road traffic	Fuel oil combustion

Factor 3 at Jogannapalem and factor 1 at Parawada site was observed to have the highest loadings of Al, Fe and Ca explaining 10.7 % and 35.9% of total variance. These elements could be contributed from the generic 'soil dust' source which is a very common source in India. These particles can be lofted into the air by winds on unpaved roads, agricultural tilling and by vehicles on roadways. Usage of unpaved roads for transportation and agricultural tilling activity in and around the sampling locations might be contributing to these metals.

The highest loadings of K, F^-, SO_4^{2-} and NO_3^- were observed in Factor 4 of Jogannapalem site. Potassium is believed to be an important marker element for biomass burning activity [297]. SO_4^{2-} and NO_3^- observed in this factor could also be contributed from biomass burning activities [279, 298] near the sampling site. These species could have contributed from biomass burning activity at Jogannapalem. This factor explains 9.2% of observed variance in PM_{10} at Jogannapalem site.

Factor 4 at Parawada site was predominantly contributed from SO_4^{2-}, NO_3^- and F^- explaining second largest fraction (20.3 %) of total variance. This set of species are identified as secondary particles by many authors [45, 164], hence named this factor as secondary aerosol source. The precise allocation of possible sources of these secondary particles is difficult; hence, complementary information on the meteorological conditions as well as spatio temporal analysis of the pollutants is required for this purpose [299].

Ni and V were having the highest loadings in Factor 5 and Factor 7 of Jogannapalem and Parawada sites respectively. These metals are considered to be the major marker elements for the residual fuel oil combustion by many researchers globally [45, 90]. This source explains about 7.7 % and 4.2 % of total variance at Jogannapalem and Parawada sites respectively.

Factor 6 at Jogannapalem site and factor 5 at Parawada were dominated by As and Cr explaining 5.2 % and 6.6 % of the total variance. These metals are assumed to be the important marker elements for the coal combustion sources [52, 296]. Coal combustion sources near Parawada might have contributed to these metals observed in PM.

The highest loadings of Cu and Cd were observed in factor 6 explaining 4.2 % of total variance at Parawada site. These set of elements are often associated with traffic emissions, either vehicular exhaust emissions or non-engine combustion sources, such as tyres and clutch wear [48, 300]. Hence, Factor 6 was named as road traffic source. This source is not observed at Jogannapalem site, as there was no much vehicular moment near this sampling site.

PCFA-MLR

Since, the PCFA results are based on normalized data, the true zero for each factor score should be calculated as follows.

$$(z_{0_j}) = \frac{0 - c_j}{\sigma_j}$$

Absolute Principal Component Scores (APCS) were derived based on the PCFA factor scores according to the method described in detail by Thurston and Spengler, 1985 [233]. Finally, regression was used to derive the source contributions.

In the present study, the above discussed procedure was **adopted** to derive the PM sources contribution to PM_{10} at Jogannapalem and Parawada sites. The PCFA-MLR results are presented in Table 5.4 along with PMF source contribution results for comparision purpose.

It was observed that the contribution of most of the sources estimated using PCFA-MLR is less as compared to the corresponding percentage contribution estimated in PMF receptor model. Also, the unexplained portion estimated using PCFA-MLR was found to be higher than that observed using PMF model.

Table 5.4 Percentage contributions of identified sources to PM calculated using PMF and PCFA-MLR

Sources	**Jogannapalem**		**Sources**	**Parawada**	
	PMF	**PCFA**		**PMF**	**PCFA**
crustal material	22.5%	17.5%	crustal material	22.5%	23.4%
sea salt	9.7%	10.0%	sea salt	5.5%	2.8%
coal combustion	14.0%	7.8%	coal combustion	22.6%	12.9%
Fuel oil combustion	1.5%	3.1%	Fuel oil combustion	3.5%	3.3%
Industrial	5.1%	6.5%	Industrial	7.8%	7.0%
biomass burning	35.0%	26.7%	secondary aerosol	12.9%	7.3%
Unknown	12.2%	28.4%	road traffic	14.0%	13.1%
			Unknown	11.2%	30.2%

5.5. Conclusions

This chapter majorly focuses on the source identification and apportionment of collected PM. As a preliminary step crustal EF of all chemical species associated with PM was estimated. Results indicate that Al, Fe Ca, Si and Ti were originated from natural source and rest of all chemical species was originated from anthropogenic sources. In the next step, PMF model was used for the source identification and apportionment. PMF identified the contribution of six sources at Jogannapalem and Trombay site, whereas Parawada site was observed to be contributed from seven sources. Among identified sources, biomass burning activity has the highest contribution at Jogannapalem and coal combustion source has the highest contribution at Parawada and Trombay sites. Least PM contribution was observed from fuel oil combustion source at Jogannapalem and Parawada sites; metal industrial emissions observed to have least contribution to PM at Trombay site. PM sources identified using PMF model were confirmed using source profiling technique. Source apportionment was also carried out using PCFA-MLR along with PMF for comparison purpose.

Chapter 6

Summery and Conclusions

This chapter summarizes the results and conclusion of the present study. The summery and few major conclusions drawn from the study are given below.

Summary

Particulate matter air pollution is one of the major problems causing adverse effects on environment as well as on human health. There are large numbers of PM studies in India that are carried out majorly at urban residential and industrial locations. Very limited information is available on PM pollution at existing and new DAE sites. This is the main motivation to carry out the present study at Jogannapalem, Parawada and Trombay sites, India. A long term study needs to be carried out to estimate representative PM pollution levels for the study sites. Hence, the current study was carried out for two consecutive years (2010 and 2011). The summary of the important findings of the present work described in chapters 4 and 5 are discussed here.

In chapter 4, PM_{10} daily concentrations as well as temporal and seasonal variations were summarized for each study location. The highest PM_{10} concentrations were observed during winter season and least concentrations during monsoon season at all sites. Similar seasonal trends are reported by many authors [260, 262]. Observed daily and annual mean concentrations are higher than the daily and annual Indian National Ambient Air Quality standards [246]. Different analytical techniques viz. AAS, ICP-AES, IC, smoke stain reflectormeter and EDXRF were used for the chemical analysis of PM. This chapter also summarizes the chemical species (Si, Al, Na^+, Mg^{2+}, Ca^{2+}, K^+, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, Pb, As, Cl^-, NO_3^-, SO_4^{2-} and BC) concentrations associated with collected PM at Jogannapalem, Parawada and Trombay sites.

Summary of inter comparison of chemical species concentrations observed at study sites indicates that the concentration of Al, Fe and Ca^{2+} are highest at Jogannapalem site, whereas the concentration of Cl^-, Na^+ and Mg^{2+} are highest at Trombay site. The highest concentration of BC was found at Trombay site and the least at Parawada site. Very high BC concentrations are observed at Trombay site on few sampling days of winter season. HYSPLIT model was used to determine the possibility of contribution from long range transport of BC at the sampling site. Model results indicate the contribution of long range transport to BC concentration in addition to the local sources.

The annual mean concentrations of elements such as Pb, As and Cd were found to be well within the NAAQS [246], whereas the concentration of Ni at Trombay site was exceeded the annual limit. Seasonal variation of chemical species concentration was studied for all the study sites. Element to element correlation study indicates that chemical species such as Cl^--Na, Al-Si-Fe-Ca, V-Ni, etc. found to have good correlation with a correlation coefficient >0.8, suggesting that these set of species could have contributed from same or similar sources. This chapter also provided the chemical speciation analysis results of As associated with PM. Results indicate that Parawada site has the highest As concentration and Jogannapalem site has the least As concentration. This speciation study indicates that As in PM majorly exists in As^{+5} form.

Chapter 5 majorly discusses the different approaches followed for the source identification and apportionment of collected PM. As a preliminary step for the source identification, crustal enrichment factor analysis was carried out for all elements analyzed in PM. EF value greater than 5 was chosen to distinguish the contribution of natural and anthropogenic source contributions [274]. Calculated crustal EF values indicate that Fe, Al, Si and Ca could be contributed from natural sources, whereas all the other chemical specie's EF values indicate their anthropogenic source contribution. EF results gave limited information about the PM sources. Hence, in the next step, PMF receptor model technique was applied to concentration data matrix obtained at all locations and apportioned the PM mass to different observed sources. PMF model identified the contribution of six major sources at Jogannapalem and Trombay, whereas seven major sources contribution to PM was observed at Parawada site. The present study sites are contributed commonly by five PM sources viz. crustal material, sea salt spray, fuel coil combustion, coal combustion and metal industry source. Biomass burning contribution was majorly observed at Jogannapalem site and at Trombay site this source contribution was identified in combination with coal combustion source. Road traffic source was not observed at Jogannapalem as the site is far away from vehicular movement area; whereas contribution of this source was identified majorly at Trombay site and Parawada site. Secondary aerosol source contribution was observed only at Parawada site.

An attempt was made to confirm the PM sources identified using receptor model technique. For this purpose, multiple numbers of soil samples were collected from each industry and at heavy traffic areas near the sampling sites. Collected soil samples were analyzed for the concentration levels of different elements of interest. Later the developed soil elemental profiles were compared with the elemental profiles observed in the PMF receptor model. It was found that the soil elemental profiles observed at coal combustion source, fuel oil combustion source, metal industry and traffic emission source are matched with the elemental profiles observed through receptor model. Source apportionment of PM_{10} using another receptor model (PCFA) was also carried out for comparison purpose.

Conclusions

From results it can be concluded that the study sites are polluted with respect to PM with an annual mean PM_{10} concentrations exceeding the Indian annual NAAQS. Trombay being urban area had comparatively higher PM pollution as compared to other study sites. Among different seasons, winter was highly polluted with PM and monsoon has low pollution levels. Chemical characterization of PM_{10} suggests that trace metals (such as Cr, As, Ni, V, Pb, Zn, etc.) are majorly contributed from industries nearby the sampling locations. Crustal EF values of these metla support this observation. Annul mean concentrations of toxic metals (As, Cd, Pb and Ni) were found be well within the CPCB limits at study sites (except Ni at Trombay) indicating a good air quality with respect to toxic metals. Arsenic chemical speciation analysis results conclude that As exists mostly in As^{+5} form.

The present study reported that biomass burning is the predominant source contributing to PM at Jogannapalem. Whereas, the PM collected at Parawada and Trombay sites has predominant contribution from coal combustion source. Road traffic emission source has the highest contribution to PM at Trombay followed by Parawada site. In the present study, the contribution of anthropogenic sources was found to be higher than the natural sources at all the study sites. The present study results can be useful in creating awareness in the public in and around Jogannapalem about the disadvantages of using traditional cooking methods. The present study results also indicate that PMF is more efficient technique for the source identification and apportionment as compared to PCFA receptor model.

Limitations of the present study

The present study discussed about the seasonal variations of PM_{10} and associated chemical species concentration levels at all study sites. The study does not take into account the effect of meteorological conditions on the PM and associated chemical species. Also, the organic matter content of PM was also not studied in the present study.

Future perspectives

The PM and associated chemical species concentrations can vary depending upon season. The meteorological parameters such as temperature, wind speed, wind direction and humidity have a wide range of values depending upon season. These parameters strongly influence the PM and associated chemical species concentrations. Also, having metal's chemical speciation data is important as it will be helpful in the risk calculations. Hence, the study on effect of meteorological parameters on PM and chemical speciation of metals was chosen as an extension to the present work.

References

1. R. Mohanraj, and P.A. Azeez, Current sci., 2004, **87(6)**, 741-748.
2. K. Amrit, K.M. Rajeev and S.K. Singh, Suan Sunandha Sci. Tech. J., 2015, **2(1),** 25-37.
3. World Health Organization, Reducing risks, promoting health. Report, Geneva, 2002.
4. WHO Air quality guidelines, global update 2005.
5. B. Sportisse, Fundamentals in Air pollution: from Processes to Modelling. Ed. Springer, 2010.
6. A.J. Cohen, H. Ross Anderson, B. Ostro, K.D. Pandey, M. Krzyzanowski, N. Künzli, K. Gutschmidt, A. Pope, I. Romieu, J.M. Samet, and K. Smith, 2005, J. Toxicol. Environ. Health. Part A, **68**, 1301-1307.
7. *R.M. Harrison, 2001, 4th Edn. Pollution; Cause, Effect, and Control. The Royal Society of Chemistry, United Kingdom, pp.169-351.*

8. Seinfeld, J.H. and Pandis, S.N. (2006) Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. 2nd Edition, John Wiley & Sons, New York.
9. C.A. Pope, R.T. Burnett, M.J. Thun, E.E. Calle, D. Krewski, K. Ito, and G.D. Thurston, JAMA 2002, **287**, 1132–1141.
10. T. Götchi, J. Heinrich, J. Sunyer, and N. Künzli, Epidemiology, 2008, **19**, 690–701.
11. S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, and M.A. Trancoso. Atmos. Environ., 2005, **39,** 3127–3138.
12. B. Huang, M. Liu, Z. Ren, X. Bi, G. Zhang, G. Sheng, and J. Fu, Atmos. Pollut. Res., 2013, **4,** 298–305.
13. R. Prasannavenkatesh, R. Andimuthu, P. Kandasamy, G. Rajadurai, D.S. Kumar, P. Radhapriya, and M. Ponnusamy, The Scientific World J., 2015, Article ID 643714, 11 pages.
14. T. Ancelet, P.K. Davy, W.J. Trompetter, and A. Markwitz, Atmos. Pollut. Res., 2014, **5**, 572-580.
15. S.S. Lim, T. Vos, A.D. Flaxman, G. Danaei, K. Shibuya, H. Adair- Rohani, et al (2010). Lancet, 2012,**380**, 222460.
16. H.I. Abdel-Shafy and M.S.M. Mansour, Egyptian J. Petroleum, 2016, **25**, 107–123
17. P. Danihelka, Z. Volna, J.M. Jones and A. Williams Int. J. Energy Res., 2003; **27**, 1181–1203
18. F.C. Lockwood and S. Yousif, Fuel Process. Technol., 2000, **65–66**,439–457.
19. WHO. (2015, May 21). Global Health Observatory Data Repository. Geneva, Switzerland.
20. B. Chen and H. Kan, Environ. Health Preventive Med., 2008, **13(2)**, 94–101.

21. T. Eötvös, Acta Climatologica ET Chorologica, Universitatis Szegediensis, Tomus, 2007, **40-41**, 179-185.
22. From air pollution to climate change. New Jersey: John Wiley and Sons, Inc. Climate change in Asia, 2013.
23. B. Pratik, V. Priyam, and B. Girish, I. J. Inn. Res. Sci. Eng. Tech., 2017, 6(4), 6639-6644.
24. K.V.S. Badarinath, S. K. Kharol, and A.R. Sharma, J. Atmos. Solar-Terrestrial Phy., 2009,**71(1)**, 112-120.
25. K.P. Amee, H.C. Hardik, S.P. Khushbu and J.S. Dhrubo, World J. Pharm. Sci., 2014, **2(8)**, 729-744.
26. WHO and UNEP, "Indoor air pollution and household energy". 2011.
27. C.A. Pope III, and D.W. Dockery, J. Air & Waste Manage. Assoc., 2006, **56**, 709–742.
28. D.V. Martello, N.J. Pekney, R.R. Anderson, C.I. Davidson, P.K. Hopke, E. Kim, W.F. Christensen, N.F. Mangelson and D.J. Eatough, J. Air & Waste Manage. Assoc., 2008, **58**, 357–368.
29. W.C. Hinds, 1999, Aerosol technology: properties, behavior and measurement of airborne particles. Wiley-Blackwell, 2nd Edition.
30. R.C. Easter, and L.K. Peter, J. appl. Meteorol., 1994, **33**, 775-784.
31. M.J. Cubison, M.R. Alfarra, J. Allan, K.N. Bower,H. Coe, G.B. McFiggans, J.D. Whitehead, P.I. Williams, Q. Zhang, J.L. Jimenez,J. Hopkins, and J. Lee, Atmos. Chem. Phys., 2006, **6,** 5573-5588.
32. X. Wang, G. Chancellor, J. Evenstad, J.E. Farnsworth, A. Hase, G.M. Olson, A. Sreenath, and J.K. Agarwal, Aerosol Sci. Technol., 2009,**43(9)**, 939-950.
33. EPA, 2004. Air quality criteria for particulate matter. U.S. Environmental Protection Agency. Research Triangle Park, NC. EPA/600/P-99/002aF-bF.

34. S. Pipal and P. G. Satsangi, Atmos. Res., 2015, **154**, 103–115.
35. M. Rashid, S. Yunus, R. Mat, S. Baharun, and P. Lestari, Atmos. Pollut. Res., 2014, **5,** 610-615.
36. S. Manzoor and U. Kulshrestha, Current World Environ., 2015, **10(3)**, 738-746.
37. P. Pant, A. Shukla, S.D. Kohl, J.C. Chow, J.G. Watson, and R.M. Harrison, Atmos. Environ., 2015, **109**, 178–189.
38. C.–H. Jeong, M.L. McGuire, D. Herod, T. Dann, E. Dabek–Zlotorzynska, D. Wang, L. Ding, V. Celo, D. Mathieu and Greg Evans, Atmos. Pollut. Res., 2011, **2**, 158-171.
39. Zs. Kertész, Z. Szoboszlai, A. Angyal, E. Dobos, I. Borbély-Kiss, Nucl. Instr. Meth. Phys. Res. B., 2010, **268**, 1924–1928
40. S. Tiwari, P.K. Hopke, A.S. Pipal, A.K. Srivastava, D.S. Bisht, S. Tiwari, A.K. Singh, V.K. Soni, and S.D. Attri, Atmos. Res., 2015, **166**, 223–232.
41. A.S. Pipal, R. Jan, P.G. Satsangi1,S. Tiwari, and A. Taneja, Aerosol Air Qual. Res.,2014, **14**, 1685–1700.
42. S. Gummeneni, Y.B. Yusup, M. Chavali, and S.Z. Samadi, Atmos. Res., 2011, **101(3)**, 752-764.
43. J. Wang, Z. HU, Y. Chen, Z. Chen, and S. Xu, Atmos. Environ., 2013, **68**, 221-229.
44. B.A. Begum, S.K. Biswas, A. Markwitz, and P.K. Hopke, Aerosol Air Qual. Res., 2010, **10**, 345–353.
45. Y. Cheng, S. Lee, Z. Gu, K. Ho, Y. Zhang, Y. Huangc,J.C. Chow, J.G. Watson, J. Cao, and R. Zhang, Particuology, 2015, **18**, 96–104.

46. T. Moreno, X. Querol, A. Alastuey, J. de la Rosa, A.M. Sánchez de la Campa, M. Minguillón, M. Pandolfi, Y. González-Castanedo, E. Monfort, and W. Gibbons, Sci. Total Environ., 2010,**408(20)**, 4569-4579.
47. S. Becagli, D.M. Sferlazzo, G. Pace, A.D. Sarra, C. Bommarito, G. Calzolai, C. Ghedini, F. Lucarelli, D. Meloni, F. Monteleone, M. Severi, R. Traversi, and R. Udisti, Atmos. Chem. Phys., 2012, **12(7)**, 3479-3492.
48. M.C. Minguillón, M. Cirach, G. Hoek, B. Brunekreef, T. Ming, H. Keesd, J. Aleksandra, M.K. Ingeborg, M. Nieuwenhuijsen, and Q. Xavier, Atmos. Environ., 2014, **89**, 268-281.
49. D. Mooibroek, M. Schaap, E.P. Weijers, and R. Hoogerbrugge, Atmos. Environ., 2011, **45**, 4180-4191.
50. G. Indrani, S. Abhaysinh, and K. Rakesh, Sci. World J., 2012, **13**, 585791.
51. N. Hang, and N.T.K. Oanh, Atmos. Res., 2014, **145-146**, 214-225.
52. X. Song, L. Shao, S. Yang, R. Song, L. Sun, S. Cen, Atmos. Pollut. Res., 2015, **6**, 469-475.
53. E. Hedberg, L. Gidhagen, and C. Johansson, Atmos. Environ., 2005, **39**, 549-561.
54. J.H. Seinfeld, and S.N. Pandis (1998) Atmospheric chemistry and physics: from air pollution to climate change. Wiley-Interscience publications.
55. K. Ravindra, R. Sokhi, and R. Van Grieken, Atmos. Environ., 2008, **42**, 2895-2921.
56. M. Kanakidou, J.H. Seinfeld, S.N. Pandis, I. Barnes, F.J. Dentener, M.C. Facchini, R. Van Dingenen, B. Ervens, A. Nenes, C.J. Nielsen, E. Swietlicki, J.P. Putaud,
57. R. Guaita, M. Pichiule, T. Mate, C. Linares, J. Diaz, Int. J. Environ. Health. Res., 2011, **21**, 260–74.

58. I. Halonen, T. Lanki, T.Y. Tuomi, P. Tiittanen, M. Kulmala, and J. Pekkanen., Epidemiology, 2009, **20**,143–53.

59. E. Samoli, R. Peng, T. Ramsay, M. Pipikou, G. Touloumi, F. Dominici, R. Burnett, A. Cohen, D. Krewski, J. Samet, and K. Katsouyanni,Environ. Health Perspect, 2008, **116(11)**, 1480–1486.

60. M. Brauer, M. Amann, R.T. Burnett, A. Cohen, F. Dentener, M. Ezzati, S.B. Henderson , M. Krzyzanowski,R.V. Martin, R. Van Dingenen, A. van Donkelaar, and G.D. Thurston, Environ. Sci. Technol., 2012, **46,** 652–60.

61. U. Pöschl, Angew. Chem., 2005, **44**, 7520-7540.

62. J.M. Samet, S.L Zeger, F. Dominici, F. Curriero, I. Coursac, D.W Dockery, J. Schwartz, and A. Zanobetti, Res. Reports Health Effects Institute, 2000, **94(pt 2),** 5–79.

63. B. Brunekreef, and B. Forsberg, Eur. Respir. J., 2005, **26**, 309-318.

64. P.E. Schwarze, J. Øvrevik, M. Låg, M. Refsnes, P. Nafstad, R.B. Hetland, and E. Dybing, Hum. Exp. Toxicol., 2006, **25**, 559-579.

65. C.-J. Tsai and Y.-H. Cheng, Air & Waste Manage. Assoc., 2017, **46**, 142-147.

66. A. Soutar, M Watt, J. W. Cherrie and A. Seaton, Atmos. Environ., 1999, **33**, 4373-4377.

67. J. Burkart, G. Steiner, G. Reischl, H. Moshammer, M. Neuberger, and R. Hitzenberger,J. Aerosol Sci., 2010, **41(10)**, 953–962.

68. F.A. Vargas, N.Y. Rojas , J.E. Pachon, and A.G. Russell, Atmos. Pollut. Res., 2012, **3,** 72-80.

69. B. Vijay Bhaskar, R. V. Jeba Rajasekhar, P. Muthusubramanian,and A.P. Kesarkar, Air Qua.l Atmos. Health, 2008, **1**, 45–55

70. D.K. Deshmukh, M.K. Deb, and S.L. Mkoma, Air Qual. Atmos. Health, 2013, **6**, 259–276

71. P.C.B. Pabroa , F.L. Santos, R.P. Morco, J.M.D. Racho, A.T. Bautista VII, and C.G.D. Bucal, Atmos. Pollut. Res.,2011, 2(2), 213–218

72. K.O. Owoade, P.K. Hopke, F.S. Olise, O.O. Adewole, L.T. Ogundele, O.G. Fawole,Atmos. Pollut. Res., 2016, **7(5)**, 843-857.

73. M. Santoso, D.D. Lestiani, and P.K. Hopke, J. Air & Waste Manage. Assoc., 2013, **63,** 1022–1025

74. B.A. Begum, A. Hossain , N.Nahar, A. Markwitz, and P.K. Hopke, Aerosol and Air Qual. Res., 2012, **12**, 1062–1072.

75. S.K. Biswas, S.A. Tarafdar, A. Islam, M. Khaliquzzaman, H. Tervahattu, and K. Kupiainen, J. Air Waste MA., 2003, **53**, 1355–1362

76. Park, S.S., Hansen, A.D.A., Cho, S.Y., Atmos. Environ., 2010, **44 (11)**, 1449-1455.

77. Y.-H. Cheng and L.-S. Yang, Atmos. Meas. Tech. Discuss., 2015, 8, 2851–2879.

78. S.A. Rahman, M.S. Hamzah, M.S. Elias, N. Ashifa A. Salim, A. Hashim, S. Shukor, W.B. Siong, and A.K. Wood. Aerosol and Air Qual. Res., 2015, **15**, 2291–2304.

79. K.O. Owoade, P.K. Hopke, F.S. Olise, O.O. Adewole, L.T. Ogundele, O.G. Fawole,Atmos. Pollut. Res., 2016, **7(5)**, 843-857.

80. T.M. Sturtz, S.D. Adar, T. Gould, and T.V. Larson, Atmos. Environ., 2014, **84**, 65-77

81. S.A. Orogade1, K.O. Owoade, P.K. Hopke, D.B. Adie, A.Ismail, C.A. Okuofu, Aerosol and Air Qual. Res., 2016, **16**, 1179–1190.

82. P. Avino, G. Capannesi, A. Rosada, Microchemical Journal, 2008, **88(2)**, 97-106.

83. E. Alemóna, L. Herreraa, E. Ortizb, and L.C. Longoria, Appl. Radiat. Isot., 2004, **60**, 815–823

84. P. Lestari, and Y.D. Mauliadi, Atmos. Environ., 2009, **43**, 1760–1770.

85. M.L.D.P. Godoy, J.M. Godoy, L.A. Roldáo, D.S. Soluri, and R.A Donagemma, Atmos. Environ., 2009, **43,** 2366–2374.

86. K. Cheung, N. Daher, W. Kama, M.M. Shafer, Z. Ning, J.J. Schauer, C. Sioutas, Atmos. Environ., 2011, **45**, 2651-2662

87. P. Pipalatkar, V.V. Khaparde, D.G. Gajghate, M.A. Bawase, Aerosol Air Qual. Res., 2014, **14**, 1089–1099, 2014

88. S. Tiwari, D.M. Chate, P. Pragya, K. Ali, and D.S. Bisht, Aerosol Air Qual. Res., 2012, **12**, 20–29.

89. A.B. Chelani, D.G. Gajghate, and S. Devotta, Bull. Environ. Contam. Toxicol., 2008, **81(2)**, 190-195.

90. H. Lee, Y. Honda, Y.-H. Lim, Y. L. Guo, M. Hashizume, and H. Kim, Atmos. Environ., 2014, **89**, 309–317.

91. P. Li, J. Xin, Y. Wang, S. Wang, K. Shang, Z. Liu, G. Li,X.Pan, L, Wei, M. Wang, Atmos. Environ., 2013, **81**, 253–262.

92. J.D. Schwartz, Occup. Environ. Med., 2004, **61**, 956 – 961.

93. M.L. Bell, J. Samet, and F. Dominici, (2003, November). Time series studies of particulate matter. Johns Hopkins University, Department of Biostatistics Working Paper 10, Johns Hopkins, Bloomberg School of Public Health.

94. USEPA. (1970). The Clean Air Act (CAA); 42 U.S.C.s/s 7401 et seq. (1970), Clean Air Act and Amendments of 1970 (PL 91-604; 42 USC 1857h-7 et seq.; amended

1970).United States Environmental Protection Agency. Retrieved fromhttp://www2.epa.gov/laws-regulations/summary-clean-air-act

95. K. Balakrishnan, B. Ganguli, S. Ghosh, S. Sankar, V. Thanasekaran, V.N. Rayadu, and H. Caussy, Health Effects Inst., 2011, **157**, 7-44.
96. WHO. (2006). Air Quality Guidelines Global Update. Copenhagen: WHO Regional Office for Europe.
97. P. Zannetti, A.D. Daly, F.R. Freedman, J Air Waste Manag. Assoc., 2015, **65(2)**, 171-185.
98. G.A. Abril, S.C. Diez, M.L. Pignata, J. Britch, Atmos. Pollut. Res., 2016, **7**, 180-189
99. P.K. Hopke, K. Ito, T. Mar, W.F. Christensen, D.J. Eatough, R.C. Henry, E. Kim,F. Laden,R. Lall, T.V. Larson, H. Liu, L. Neas, J. Pinto, M. Stolzel, H. Suh, P. Paatero, and G.D. Thurston, J. Expo. Sci. Env. Epid., 2006, **16**, 275–286.
100. C.A. Belis, F. Karagulian, B.R. Larsen, and P.K. Hopke, Atmos. Environ., 2013, **69**, 94–108.
101. J.G. Watson, L.-W. Antony Chen, J.C. Chow, P. Doraiswamy, and D.H. Lowenthal, Air Waste Manage. Assoc., 2008, **58**, 265–288.
102. N.B.A. Wahid, M.T. Latif, L.S. Suan, D. Dominick, M. Sahani, S.A. Jaafar, N.M. Tahir, Bull. Environ. Contam. Toxicol.2014, **92**, 317–322
103. J. Xu, Y.Z. Tian, Y. Zhang, C.S. Guo, G.L. Shi, C.Y. Zhang, Y.C. Feng, J. Hazard. Mat.,2013, **260**, 483– 488
104. Y. Song, S. Xie, Y. Zhang, L. Zeng, L.G. Salmon, M. Zheng, Sci. Total Environ., 2006, **372**, 278–286.
105. D.A. Olson, and G.A. Norris, Atmos. Environ., 2008, **42**, 7310–7315.

106. P. Paatero, U. Tappert, Environmetrics, 1994, **5**, 111–126.

107. R.C. Henry, Chemometr. Intell. Lab., 2003, **65**, 189–197.

108. J. Chow, and J. Watson, Energy Fuels, 2002, **16**, 222–260.

109. P. Paatero, Intell. Lab., 1997, **37**, 23–35.

110. P. Paatero, J. Comput. Graph. Stat., 1999, **8**, 854–888.

111. A.E. Gildemeister, P.K. Hopke, and E. Kim, Chemosphere, 2007, **69**, 1064–1074.

112. R. Vedantham, G. Norris, and R. Duvall, 2013, Receptor and Hybrid Modeling Tools. Encyclopedia of Environmetrics. Wiley.

113. M.-S. Bae, J.J. Schwab, W.-N. Chen, C.-Y. Lin, O.V. Rattigan, and K.L. Demerjian, 2011. Atmos. Environ., **45 (15)**, 2531-2540

114. F. Wang, D.S. Chen, S.Y. Cheng, J.B. Li, M.J. Li, and Z.H. Ren, 2010, Environ. Model. & Softw., **25**, 927-934

115. S.K. Sharma, T.K. Mandal, Mohit Saxena, Rashmi, Rohtash, A. Sharma, R. Gautam, Urban Climate, 2014, **10 (4)**, 656-670

116. R. Das, K. Bahareh, S. Bijayen, D. Subhajit, K.S. Pradip, D. Richard, and X.W. Webster, Atmos. Pollut. Res., 2015, **6**, 742-750.

117. T.V. Lakshmi Kumar, P. Ajay, K. Aruna and J.S. Sudarsan, Int. J. ChemTech Res., 2015, **7(3)**, 1414-1420.

118. A. Kulshrestha, P. G. Satsangi, J. Masih, and A. Taneja, Sci. **Total** Environ., 2009, **407,** 6196–6204.

119. V. Tyagi, B. R. Gurjar, N. Joshi, and P. Kumar, J. Hazard. Toxic Radioact. Waste, 2012, **16**, 175-182.

120. K. K. Shandilya, M. Khare, and A. B. Gupta, Environ. Monit. Assess., 2007, **128**, 431–445.

121. K.Ram and M.M. Sarin, Atmos. Environ.,2011,**45**, 460–468.

122. S.K. Guttikunda, R.V. Kopakka, P. Dasari, and A.W. Gertler, Environ. Monit. Assess., 2013, **185**, 5585–5593.

123. M. Pandey, A.K. Pandey, A. Mishra, B.D. Tripathi, Urban Clim., 19 (2017) 141–154

124. P.K. Khillare, S. Balachandran and B.R. Meena, Environ. Monitor. Assess., 2004, **90**, 1–21.

125. C. Venkataraman and G.U.M. Rao, Sci. of Total Environ., 2002, **35**, 2100–2107.

126. S. Basha, J. Jhala, R. Thorat, S. Goel, R. Trivedi, K. Shah, G. Menon, P. Gaur, K.H. Mody and B. Jha, Atmos. Res., 2010, **97**, 257–265.

127. S.Yadav and P.G. Satsangi, Environ. Monit. Assess., 2013, **185**, 7365–7379.

128. V. Shridhar, P.S. Khillare, T. Agarwal and S. Ray, J. Hazard. Mater., 2010, **175**, 600–607.

129. S. Sarkar and P.S. Khillare, Environ. Monit. Assess., 2013, **185**, 1199–1213.

130. E.J. Abba, S. Unnikrishnan, R. Kumar, B. Yeole, and Z. Chowdhury, Int. J. Environ. Health Res., 2012, **22**, 134–149.

131. A.K. Sudheer and R. Rengarajan, Aerosol Air Qual. Res., 2012, **12**, 923–933.

132. S. Tiwari, S. Pervez, P. Cinzia, D.S. Bisht, A.K. Srivastava, and D. Chate, Sustain. Environ. Res., 2013, **23 (5)**, 295–306.

133. M. Sharma and S. Maloo, Atmos. Environ., 2005, **39**, 6015–6026.

134. B. Dubey, A. Kumar Pal and G. Singh, Atmos. Pollut. Res., 2012, 3, 238-246

135. R. Kushwaha, N. Hazarika, and A. Srivastava,Int. J. Adv. Res., 2013, **1(5)**, 248-255.

136. S. Rodríguez, X. Querola, A. Alastueya, M.-M. Vianaa, M. Alarcónb, E. Mantillac, and C. R. Ruiz, Sci. **Total**Environ., 2004, **328,** 95–113.

137. B. Gomiščček, H. Hauck, S. Stopper, and O. Preining, Atmos. Environ., 2004, **38,** 3917–3934.

138. F. Karaca, O. Alagha, and F. Ertürk, 2005, Chemosphere, **59**, 1183–1190.

139. S. Yatkin, and A. Bayram, Chemosphere, 2008a, **71**, 685–696.

140. St. Pateraki, D.N. Asimakopoulos, Th. Maggos, and Ch. Vasilakos, J. Hazard.Mater., 2010, **182,** 801–811.

141. M. Masiol, G. Formenton, A. Pasqualetto, and B. Pavoni, Atmos. Environ., 2013, **79,** 811-821.

142. A. Kahnt, S. Behrouzi, R. Vermeylen, M. S. Shalamzari, J. Vercauteren, E. Roekens, M. Claeys, and W. Maenhaut, Atmos. Environ., 2013, **81**, 561-568.

143. J. Pey, A. Alastuey, and X. Querol,Sci.**Total**Environ., 2013, **456–457,** 267–277

144. X.S. Luo, C.C. M. Ip, W. Li, S. Tao, and X.D. Li, Atmos. Chem. Phys. Discuss., 2014, **14**, 13133–13165.

145. A.A. Jamhari, M. Sahani, M.T. Latif, K.M. Chan, H.S. Tan, M.F. Khan, and N. Mohd Tahir, Atmos. Environ., 2014,**86**, 16-27.

146. Y.Q. Wang, X.Y. Zhang, J.Y. Sun, X.C. Zhang, H.Z. Che, and Y. Li, Atmos. Chem. Phys., 2015, **15**, 13585–13598.

147. J.P. Engelbrecht, I.G. Kavouras, D.S. Shafer, D. Campbell, S. Campbell, G. McCurdy, S. D. Kohl, G. Nikolich, L. Sheetz, and A.W. Gertler, Water Air Soil Pollut., 2015, **226**, 217-226.

148. W. Li, C. Wang, H. Wang, J. Chen, C. Yuan, T. Li, W. Wang, H. Shen, Y. Huang, R. Wang, B. Wang, Y. Zhang, H. Chen, Y. Chen, J. Tang, X. Wang, J. Liu, R. M. Coveney Jr., and S. Tao. Environ. Pollut. 2014, **185,** 134-140.
149. S.C.Hsu, S.C.Liu, F.Tsai, G.Engling, I.I.Lin, C.K.C.Chou, S.J.Kao, S.C.C.Lung, C.Y.Chan, S.C. Lin, J.C.Huang, K.H.Chi,W.N. Chen, F.J.Lin, C.H.Huang, C.L.Kuo, T.C.Wu, and Y.T. Huang, J. Geophys. Res., 2010**, 115**, D17309.
150. Y. Gao, S.-C. Lee, Y. Huang, J.C. Chow, and J. G. Watson, Atmos. Res.,2016, **170**, 112–122.
151. N. Mohamad, M. T. Latif, and M. F. Khan. Ecotoxicol. Environ. Saf., 2016, **124**, 351–362.
152. J. Aldabe, D. Elustondo, C. Santamaría, E. Lasheras, M. Pandolfi, X. Querol, J. M. Santamaría, A. Alastuey, Atmos. Res., 2011, **102,** 191-205.
153. S.K. Sharma, T.K. Mandal, M. Saxena, Rashmi, A. Sharma, A. Datta, and T. Saud, 2014, J. Atmos. Solar-Terres. Phys., **13**,10–22.
154. P.G. Satsangi, S. Yadav, A.S. Pipal, and N. Kumbhar, Atmos. Environ., 2014, **92,** 384-393.
155. S. Yatkin, and A. Bayram, Sci. **Total**Environ.,2008b, **390**, 109 – 123.
156. B. Srimuruganandam, and S.M. Shiva Nagendra, Atmos. Environ., 2012a, **433**, 8–19.
157. D. Cesari, A. Genga, P. Ielpo, M. Siciliano, G. Mascolo, F.M. Grasso, D. Contini, Sci. Total Environ., 2014, **497–498,** 392–400.
158. G.Liu, J.Li, D.Wu, and H.Xu, Particuology, 2015, **18**, 135–143.
159. W. Hailin, Z. Yahui, W. Ying, S. Yele, Y. Hui, Z. Guoshun, and H. Zhengping, J. Environ. Sci., 2008, **20**, 1323–1327.

160. X. Querola, A. Alastueya, S. Rodrigueza, F. Planaa, C.R. Ruiza, N. Cotsb, G. Massaguéb, and O. Puig, Atmos. Environ., 2001, **35**, 6407–6419.

161. G.M. Marcazzan, M. Ceriani, G. Valli, and R. Vecchi,*Sci. Total Environ.,*2003, ***317***, 137–147.

162. S.M. Almeida, C.A. Pio, M.C. Freitas, M.A. Reis, and M.A. Trancoso, Sci. Total Environ., 2006, **368**, 663–674.

163. L. Yu, G. Wang, R. Zhang, L. Zhang, Y. Song, B. Wu, X. Li, K. An, and J. Chu, Aerosol Air Qual. Res., 2013, **13**, 574–583.

164. H. Jorquera, and F. Barraza, Sci. Total Environ., 2013, **444**, 327–335.

165. T. Byrd, M. Stack, and A. Furey, Atmos. Environ., 2010, **44**, 75–87.

166. T. Schilirò, S. Bonetta, L. Alessandria, V. Gianotti, E. Carraro, and G. Gilli, Environ. Toxicol. Pharmacol., 2015, **39,** 833–844.

167. L. Frazer, Environ. Health Perspect., 2002, **110**, A471–A473.

168. M.Z. Jacobson, Nature, 2001, **409**, 695–697.

169. G.-L. Shi, Y.-Z. Tian, S. Ye, X. Peng, J. Xu, W. Wang, B. Han, Y.-C. Feng, Sci. Total Environ., 2015, **505**, 1182–1190.

170. R. Rengarajan, M.M. Sarin, A.K. Sudheer, Atmos. Res., 2011, **102**, 420–431.

171. X H Bi, G.Y. Sheng, P.A. Peng, Y.J Chen, and J.M Fu, Atmos. Environ., 2005, **39(3)**, 477–487.

172. G.H. Wang, L.M. Huang, X. Zhao, H.Y. Niu, and Z.X Dai, Atmos. Res., 2006, **81(1)**, 54–66.

173. S.P Wu, S. Tao, Z.H. Zhang, T. Lan, and Q. Zuo, Atmos. Environ., 2005, **39(38)**, 7420–7432.

174. H. Sharma, V.K. Jain, and Z.H. Khan, Chemosphere, 2007, **66(2)**, 302–310.
175. M.C. Pietrogrande, G. Abbaszade, J. Schnelle-Kreis, D. Bacco, M. Mercuriali, and R. Zimmermann, Environ. Pollut., 2011, **159(7),** 1861–1868.
176. O. Pindado, R.M. Pérez, S García, M. Sánchez, P. Galán, and M. Fernández, Atmos. Environ., 2009, **43(7)**, 2796–2803.
177. P.K. Gayathree Devi, C.H. Sujatha, Atmos. Pollut. Res., 2016, **7**, 1053-1064.
178. S. Kumar and R.S. Raman, Atmos. Environ., 2016, **143**, 152–163.
179. K.V.S. Badarinath, Shailesh Kumar Kharol, R.R. Reddy, K. Rama Gopal, K. Narasimhulu, L. Siva Sankara Reddy and K. Raghavendra Kumar, Atmos. Sci. Let.,2009, 10, 29–33.
180. S.K. Sahu, G. G. Pandit, V. D. Puranik, Aerosol and Air Qual. Res., 2008, 8(4), 437-446.
181. M. Tiwari, S.K. Sahu, R.C. Bhangare, P.Y. Ajmal, G.G. Pandit, 2013, Microchemical Journal 106, 79-86.
182. D.N. Sharma, A.A. Sawant, R. Uma and D.R. Cocker III, Atmos. Environ., 2003, 37, 4317–4323
183. P. Khare**,** B.P. Baruah and P.G. Rao, Tellus, **2011, 63(5), 990–**1000DOI: 10.1111/j.1600-0889.2011.00564.x
184. T. Banerjee, V. Murari, M. Kumar, and M.P. Raju, Atmos. Res., 2015, **164–165**, 167–187.
185. P.S. Khillare, and S. Sarkar, Atmos. Pollut. Res., 2012, **3**, 46–54.
186. R.S. Patil, R. Kumar, R. Menon, M. Kumar, and V. Sethi, Atmos. Res., 2013, **132-133**, 1–11.
187. N.M. Gadkari, S. Pervez, Atmos. Environ., 2007, **41**, 7951–7963.

188. A.K. Gupta, K. Karar and A.Srivastava, J. Hazard. Mater., 2007, **142**, 279–287.

189. S. Achilleos, J.S. Evans, P.K. Yiallouros, S. Kleanthous, J. Schwartz, and P. Koutrakis, J. Air & Waste Manage. Associat., 2014, **64**, 1352–1360

190. Z. Zong, X. Wang, C. Tian, Y. Chen, L. Qu, L. Ji, G. Zhi, J. Li, and G. Zhang, Atmos. Chem. Phys., 2016, 16, 11249–11265.

191. N.J. Pekney, C.I. Davidson, A. Robinson, L. Zhou, P.K. Hopke, D. Eatough and W.F. Rogge, Aerosol Sci. Technol., 2006, **40**, 910–924

192. M.-S. Bae, J.J. Schwab, W.-N. Chen, C.-Y. Lin, O.V. Rattigan, and K.L. Demerjian, Atmos. Environ., 2011, **45**, 2531-2540

193. Yadav, S., Satsangi, P.G., Environ. Monit. Assess., 2013, **185,** 7365–7379.

194. Massey, D., Kulshrestha, A., Masih, J., Taneja, A., Build. Environ., 2012, **47**, 223–231.

195. A. Chakraborty, and T. Gupta, Aerosol Air Qual. Res., 2010, **10**, 433–445.

196. B. Srimuruganandam, and S.M.S. Nagendra, Chemosphere, 2012b, **88**, 120–130.

197. A.K. Sudheer, and R. Rengarajan, Aerosol Air Qual. Res., 2012, **12**, 923–933.

198. J.C. Chow, J.G. Watson, D.H. Lowenthal, L.W.A. Chen, B. Zielinska, L.R. Mazzoleni, and K.L. Magliano,Atmos. Chem. Phys., 2007, **7**, 1741–1754.

199. G.L. Shi, X. Li, Y.C. Feng, Y.Q. Wang, J.H. Wu, J. Li and T. Zhu, Atmos. Environ., 2009, **43**, 2929–2937.

200. US Environmental Protection Agency, 2004. EPA CMB8 2 User's Manual. Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711.

201. M. Habil, D.D. Massey, and A. Taneja, Air Qual. Atmos. Health, 2013, **6**, 575–587.

202. R. Singh, and B.S. Sharma, Environ. Monit. Assess., 2012, **184**, 5945–5956.

203. Yadav, S., Satsangi, P.G., Environ. Monit. Assess., 2013, **185,** 7365–7379.

204. J. Srinivas, and A.V. Purushotham, Res. J. Eng. Sci., 2013, **2(6)**, 13-24.
205. F. Guor-Cheng, L. Chia-Ching, H. Jun-Han, and H. Yi-Liang, Aerosol Air Qual. Res., 2011, **11**, 218-229.
206. B. Alharbi, M.M. Shareef, T. Husain, Atmos. Pollut. Res.,2015, **6**, 88-98.
207. B. Buszewski, A. Jastrzębska, T. Kowalkowski and A. Górna-Binkul, Polish J. Environ. Stud., 2000, **9(6)**, 511-515.
208. M.Á. Álvarez, G. Carrillo,Talanta, 2012, **97**, 505–512.
209. A.B.M. Helaluddin, R.S. Khalid, M. Alaama, and S.A. Abbas, Tropical J. Pharmaceutical Res., 2016, **15(2)**, 427-434.
210. H. Lajunen, and P. Perämäki, Cambridge UK, Royal Society of Chemistry, 2004, 6-8.
211. A.M. Abdel-Lateef, R.A. Mohamed and H.H. Mahmoud, Adv. Chem. Sci., 2013, 2(4), 110-113
212. Limbeck, C. Wagner, B. Lendl, A. Mukhtar. Analytica. Chimica. Acta.,2012, **750**, 111–119.
213. G. Klaver, M. Verheul, I. Bakker, E. Petelet-Giraud, P. Négrel, Appl. Geochem.,2014, **47,**186-197.
214. R. Shynu, V. Purnachandra Rao, G. Parthiban, S. Balakrishnan, T. Narvekar, P.M. Kessarkar, Marine Geol., 2013, **346**, 326-342.
215. K. Tyszczuk, and M. Korolczuk, Comb. Chem. High Throughput Screen, 2010, **13(8)**, 753-7.
216. J. Buffle, and M.-L. Tercier-Waeber,Trends Anal. Chem., 2005, **24(3)**.
217. R.J.C. Brown, and P.R. Edwards, Talanta, 2009, **80**, 1020-1024.
218. T. Fosco, andM. Schmeling, Environ. Monit. Assess., 2007, **30(1-3)**, 187-199.

219. S.R.G. Barreto, J. Nozaki, E. De Oliveira, V.F. Do Nascimento Filho, P.H.A. Aragão, I.S. Scarminio, and W. J. Barreto. Talanta**,** 2004,**64(2)**, 345–354.

220. E. Mantas, E. Remoundaki, I. Halari, P. Kassomenos, C. Theodosi, A. Hatzikioseyian, and N.Mihalopoulos. Atmos. Environ.,2014, **94**, 154-163.

221. C.A. Masiello, Marine Chem., 2004, **92**, 201–213.

222. K. Hammes, R.J. Smernik, J.O. Skjemstad, M.W.I. Schmidt, Appl. Geochem., 2008, **23**, 2113–2122

223. V. Ramanathan and G. Carmichael, Nat. Geosci., 2008, **1**, 221–227.

224. Hopke, P.K., 1991. In: Hopke, P.K. (Ed.), Receptor Modeling for Air Quality Management. Elsevier, Amsterdam, The Netherlands.

225. P.K. Hopke, K. Ito, T. Mar, W.F. Christensen, D.J. Eatough, R.C. Henry, E. Kim, F. Laden, R. Lall, T.V. Larson, H. Liu, L. Neas, J. Pinto, M. Stolzel, H. Suh, P. Paatero, and G.D. Thurston, J. Expo. Sci. Environ. Epidemiol., 2006, **16(3)**, 275–286.

226. A.V.Polissar, P.K.Hopke, P.Paatero, W.C.Malm, and J.F.Sisler, J. Geophys. Res., 1998, **103(D15)**, 19045–19057.

227. Z.R. Liu, B. Hu, Q. Liu, Y. Sun, and Y.S. Wang, Atmos. Environ., 2014, **96,** 359-369.

228. W. Chueinta, P.K. Hopke, and P.Paatero, Atmos. Environ., 2000, **34**, 3319–3329.

229. X.H. Song, A.V. Polissar and P.K.Hopke, Atmos. Environ., 2001, **35,** 5277-5286.

230. J.W.Gu, M.Pitz, J.Schnelle-Kreis, J.Diemer, A.Reller, R.Zimmermann, J.Soentgen, M. Stoelzel, H.E.Wichmann, A.Peters, and J. Cyrys, Atmos. Environ., 2011, **45**, 1849-1857.

231. J.H. Murillo, S.R. Roman, J.F.R. Marin, A.C. Ramos, S.B. Jimenez, B.C. Gonazalez, and D.B. Baumgardner, *Atmos. Pollut. Res.*, 2013, *4*, 181–190.

232. T.W. Chan, and M. Mozurkewich, *Atmos. Chem. Phys.*, 2007, **7**, 875–886.

233. G.D. Thurston, and J.D. Spengler, Atmos. Environ., 1985, **19,** 9–25.

234. H. Guo, T. Wang, and P. K. K. Louie, Environ. Pollut., 2004, **129**, 489– 498.

235. Draxler RR, Hess GD (1997) Description of the HYSPLIT_4 modeling system, NOAA Tech. Memo. ERL ARL_224, NOAA Air Resource Laboratory, Silver Spring, MD

236. Escudero, M., A. Stein, R. R. Draxler, X. Querol, A. Alastuey, S. Castillo, and A. Avila, J. Geophys. Res., 2006: 111, D06210, doi: 10.1029/2005JD006395.

237. A.S. Pipal, A. Kulshrestha, and A. Taneja, Atmos. Environ., 2011, **45**, 3621-3630.

238. C.-Y. Hsu, H.-C. Chiang, S.-L. Lin, M.-J. Chen, T.-Y. Lin, and Y.-C. Chen, Sci **Total** Environ., 2016, **541**, 1139–1150.

239. L P.K. Hopke, Y. Xie, T. Raunemaa, S. Biegalski, S. Landsberger, W. Maenhaut, P. Artaxo and D. Cohen, Aerosol Sci. Technol., 1997, **27(6)**, 726-735.

240. B. Shubhankar and B. Ambade, SpringerPlus, 2016, **5**, 837

241. Y.C. Chan, R.W. Simpson, G.H. McTainsh, P.D. Vowles, D.D. Cohen, G.M. Bailey, Atmos. Environ., 1997, **31**, 3773-3785.

242. D. Contini, D.Cesari,A. Genga, M. Siciliano, P. Ielpo, M.R.Guascito, and M.Conte, Sci. Total Environ., 2014, **472,**248-261.

243. S.S. Andra, D. Sarkar, S.K.M. Saminathan and R. Dutta, Environ. Sci. Poll. Res., **75**, 2011, 661-67.

244. S.K. Prajapati, B.D. Tripathi, and V. Pathak, Environ. Monit. Assess, **148**, 2009, 176-172.

245. P.V. Suryawanshi, B.S. Rajaram, A.D. Bhanarkar and C.V. Chalapati Rao, Atmósfera, 2016, **29(3)**, 221-234.

246. MoEF Ministry of Environment and Forests, 2009. Environment (Protection) Seventh Amendment Rules. Government of India Press, New Delhi.

247. S.S. Babu, and K.K. Moorthy, Curr. Sci. India, 2001, **81(9)**, 1208–1214

248. Hafner, W.D., Solorzano, N.N., Jaffe, D.A., 2007, Atmos. Environ., **41**, 3071-3081.

249. K. Rai, A.K. Sarkar, and A.P. Mitra, IASTA Bulletin Spl. Issue, 2002, **14/1**,155–158.

250. S.N. Tripathi, S. Dey, V. Tare, and S.K. Satheesh, Geophys. Res. Lett., 2005, **32**, L08802 1–L08802 4.

251. A.B. Bilkis, S.K. Biswas, G.G. Pandit, I.V. Saradhi, W. Shahida, S. Naila, S.M.C. Shirani, D.D. Cohen, A. Markwitz, and P.K. Hopke,Atmos. Poll. Res.,2011, **2**,151–157.

252. A.A. Campos–Ramos, A. Aragon–Pina, A. Alastuey, I. Galindo–Estrada, X. Querol. Levels, Atmos. Pollut. Res., 2011, **2**, 409-417.

253. M. Khodeir, M. Shamy, M. Alghamdi, M. Zhong, H. Sun, M. Costa, L.C. Chen and P. Maciejczyk. Atmos. Pollut. Res., 2012, **3,** 331-340

254. E. Terzi, G. Argyropoulos, A. Bougatioti, N. Mihalopoulos, K. Nikolaou, and C. Samara, Atmos. Environ., 2010. **44**, 2231-2239.

255. Marcazzan, G.M., Vaccaro, S., Valli, G., Vecchi, R., Atmos. Environ., 2001, **35**, 4639-4650.

256. K. Karar, A. K. Gupta, A. Kumar, and A. K. Biswas, Environ. Monit. Assess., 2006, **118(1)**, 369–381

257. K.M. Latha, K.V.S. Badarinath,and K.K. Moorthy,Curr. Sci.,2004. **86**, 451–453.

258. G.-C. Fang, and S.-C. Chang, Atmos. Res., 2010, **98**, 368–377.

259. P.D. Hien, V.T. Bac, H.C. Tham, D.D. Nhan and L.D. Vinh, 2002, Atmos. Environ., **36**, 3473–3484.

260. G. Balakrishnaiah, K. Raghavendra Kumar, B.S.K. Reddy, K.R. Gopal, R.R. Reddy, L.S.S. Reddy, K. Nareasimhulu, Y.N. Ahammed, C. Balanarayana, K.K. Moorthy and S.S. Babu, Indian J Radio and Space Phy., 2011, **40**, 95-104.
261. K. Puja, B.P. Baruah and P.G. Rao, Tellus, 2011, **63B**, 990–1000
262. J. Li, G. Zhuang, K. Huang, Y. Lin, C. Xu, and S. Yu, Atmos. Environ., 2007, **42**, 776 787.
263. S. Chandra, M.J. Kulshrestha, and R. Singh, Int. J. Atmos. Sci., 2014, **Article ID 323040**, 8 pages, http://dx.doi.org/10.1155/2014/323040
264. K. Sagar and R.K. Srivastava, Int. J. Curr. Res. Biosci. Plant Biol., 2015, **2(7)**, 158-167.
265. H. Yongming, D. Peixuan, C. Junji, and E.S. Posmentier, Sci. Total Environ., 2006, **355**, 176.
266. F. Kabadayi, and H. Cesur, Environ. Monit. Assess.,**2010, 168**, 241.
267. F. Amato, M. Pandolfi, T. Moreno, M. Furger, J. Pey, A. Alastuey, N. Bukowiecki, A. S.H. Prevot, U. Baltensperger, and X. Querol, Atmos. Environ., 2011, **45**, 6777.
268. R.A.Goyer, McGraw-Hill Publisher, 2001, 811-867.
269. P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla and D.J. Sutton, EXS., 2012, **101**, 133–164. doi:10.1007/978-3-7643-8340-4_6.
270. G. Dongarrà, E.Manno, D.Varrica, M.Voltaggio,. Atmos. Environ., 2007, **41**, 7977–7986.
271. M.Sakata, and K.Asakura, Atmos. Environ., 2011, **45**, 1075–1083.
272. P.D. Hien, N.T.Binh, Y.Truong, N.T. Ngo, and L.N.Sieu, Atmos. Environ., 2001**, 35**, 2669.
273. Y. Hao, Z.Guo, Z.Yang,M. Fang, and J.Feng, Atmos. Res., 2007**, 85**, 27.
274. W.Birmili, A.Allen, F.Bary, and R.Harrison, Environ. Sci. Technol., 2006**, 14(4)**, 1144.

275. J.J.Cao, Z.X.Shen, J.C.Chow, G.W.Qi, and J.G. Watson, Particuology, 2009**,** **7**, 161.

276. S.F. Dai, X.B. Wang, V.V. Seredin, J.C. Hower, C.R. Ward, J.M.K. O'Keefee, W.H. Huang, X. Li, H.D. Liu, W.F. Xue, and L.X. Zhao, Int. J. Coal Geol., 2012, **90**, 72-99.

277. S. Abdul Rahman, M. Suhaimi Hamzah, A. Khalik Wood, M. Suhaimi Elias, N. A. Adullah Salim and E. Sanuri, Atmos. Pollut. Res., 2011, **2**, 197-206.

278. H. Zhang, J. Hu, M. Kleeman, and Q. Ying, Sci. Total Environ., 2014, **490**, 71-181

279. D. D. Cohen, J. Crawford, E. Stelcer, and V.T. Bac, Atmos. Environ., 2010, **44,** 320-328.

280. M. Pandolfi, Y. Gonzalez-Castanedo, A. Alastuey, J. de la Rosa, E. Mantilla, A. Sanchez de la Campa, et al.Environ. Sci. Pollut. Res., 2011,**28**, 260–9.

281. B. Horemans, C. Cardell, L. Bencs, V. Kontozova-Deutsch, K. De Wael, and R. Van Grieken, Microchem. J., 2011,**99**, 429–38.

282. T. Moreno, N. Perez, X. Querol, F. Amato, A. Alastuey, R. Bhatia, B. Spiro, M. Hanvey, and W. Gibbons, Atmos. Environ., 2010, **44**, 2563-2576.

283. V.Shridhar, P.S.Khillare, T.Agarwal, and S.Ray, J. Hazard. Mat., 2010, **175**, 600–607.

284. P. Sandeep, P. Kothi, C. B. Dusane, S. K. Sahu, and G. G. Pandit, J. Radioanalytical Nucl. Chem., 2014, **302(3)**, 1371-1376.

285. S.Basha,J. Jhala, R.Thorat, S.Goel, R.Trivedi, K. Shah, G.Menon, P.Gaur, K.H. Mody, and B.Jha, Atmos. Res., 2010, **97**, 257–265.

286. M. Khodeir, M. Shamy, M. Alghamdi, M. Zhong, H. Sun, M. Costa, L-C. Chen, and P. Maciejczyk. Atmos. Pollut. Res., 2012, **3(3)**, 331–340.

287. M.Manousakas, E.Diapouli, H.Papaefthymiou, A.Migliori, A.G.Karydas, R.Padilla-Alvarez, M.Bogovac, R.B.Kaiser, M.Jaksic, I.Bogdanovic-Radovic, and K.Eleftheriadis, Nucl. Instr. Meth. Phys. Res. B, 2015, **349**, 114–124.

288. G.D. Thuraton, K. Ito, R. Lall, Atmos. Environ., 2011, **45**, 3924–3936

289. H. Agrawal, Q. Malloy, W.A. Welch, J.W. Miller, and D. R. Cocker, Atmos. Environ., 2008, **42**, 5504– 5510.

290. USEPA (2002) The United States environmental protection agency. (Website Available from: http://www.epa.gov/ttn/chief/software/speciate)

291. Y.C. Feng, Y.H. Xue, X.H. Chen, J.H. Wu, T. Zhu, Z.P. Bai, S.T. Fu, and C.J. Gu, J. Air Waste Manage. Assoc., 2007, **57**, 561–575.

292. L. Senlin, S. Longyi, W. Minghong, J. Zheng, and C. Xiaohui, Environ Monit Assess 2007, **133(1)**, 79–85.

293. E. Adamiec, E. Jarosz-Krzemińska and R. Wieszała, Environ. Monit. Assess., 2016, **188**, 369-379.

294. Q.L. Dai, X.H. Bi, J.H. Wu, Y.F. Zhang, J. Wang, H. Xu, L. Yao, L. Jiao, and Y.C. Feng, Aerosol Air Qual. Res., 2015, **15**, 875–887.

295. O. Ee-Ling, N.I.H. Mustaffa, N. Amil, M.F. Khan, and M.T. Latif, Bull. Environ. Contam. Toxicol., 2015, **94**, 537–542.

296. S.N. Behera, and R. Balasubramanian, Adv. Meteorol., 2014 Article ID 828491, 13 pages http://dx.doi.org/10.1155/2014/828491

297. M.H Sowlat, K. Naddafi, M. Yunesian, P.L Jackson, and A. Shahsavani, Bull. Environ. Contam. Toxicol., 2012, **88**, 735–740.

298. J. Srinivas, and A.V. Purushotham, Res. J. Eng. Sci., 2013, **2(6)**, 13-24.

299. O. Ee-Ling, N.I.H. Mustaffa, N. Amil, M.F. Khan, and M.T. Latif, Bull. Environ. Contam. Toxicol., 2015, **94**, 537–542.