STUDY OF TRACE GASES AND AEROSOLS IN MIXED USE AREA OF DELHI

Thesis Submitted for the Award of Degree of
Doctor of Philosophy
in
Civil Engineering

By
Ms. PAPIYA MANDAL
(11/Ph.D/CE/2010)

Under the esteemed guidance of

Dr. Anubha Mandal
Prof and UGC Scientist
&
Dr. Raju Sarkar
Asst Prof. DTU

DEPARTMENT OF CIVIL ENGINEERING
DELHI TECHNOLOGICAL UNIVERSITY
(formerly Delhi College of Engineering)
Shahbad Daulatpur, Bhawana Road, Delhi-110042

2016

Declaration

I, hereby declare that the thesis entitled, **“Study Of Trace Gases And Aerosols In Mixed Use Area Of Delhi”**, is being submitted to Civil Engineering Department of Delhi Technological University, Bhawana Road, Delhi-11007842 (India), in the fulfillment of the requirements for the award of the degree of **Doctor of Philosophy in Civil Engineering** is the original research work of mine and has not formed previously the basis for the award of any degree, diploma or any other similar title or recognition.

Place: Delhi **Papiya Mandal**
Date:

Certificate

This is to certify that the present thesis entitled, **“Study Of Trace Gases And Aerosols In Mixed Use Area Of Delhi”**, is being submitted to Civil Engineering Department of Delhi Technological University, Bhawana Road, Delhi-110042 (India), in the fulfillment of the requirements for the award of the degree of **Doctor of Philosophy in Civil Engineering** is the original research work carried out by **Mrs. Papiya Mandal.** The work embodied in this thesis has been carried out in Civil Engineering Department of Delhi Technological University and CSIR-National Environmental Engineering Research Institute, New Delhi, India. To the best of our knowledge, she has not submitted this work previously in part or full for any other degree or diploma of Delhi Technological University or any other University.

Dr. Anubha Mandal
(Supervisor)
Department of Civil Engineering
Delhi Technological University
Bhawana, Delhi-110042

Dr. Raju Sarkar Mandal
(Co-Supervisor)
Department of Civil Engineering
Delhi Technological University
Bhawana, Delhi-110042

Chairman D.R.C
Civil Engineering Department
Delhi Technological University

ACKNOWLEDGEMENT

This thesis is an account of six years dedicated work in the field of ambient air quality in mixed use area of Delhi, India with Civil Engineering Department of Delhi Technological University in collaboration with CSIR – National Environmental Engineering Research Institute (NEERI), Delhi Zonal Laboratory.

First and foremost I would like to express my sincere gratitude, respect, honor and appreciation to my advisors Dr. Anubha Mandal (Supervisor) and Dr. Raju Sarkar (Co-Supervisor) for their kindness, help, patience, guidance, enthusiastic support, expert feedback and providing me this opportunity to complete my PhD thesis. I am also thankful to Dean of Civil Engineering Department, Delhi Technological University for encouragements and suggestions. I am also thankful to the Director, CSIR-NEERI for allowing using the facilities at National Environmental Engineering Research Institute.

I am grateful to Dr. T.K. Mandal, Dr. S. Sharma, Dr. S. Kumar, Er. J.K. Bassin, Ms Rashmi Mishra, Mr. Sanjay Kumar for their valuable suggestions, supports and encouragements. I am thankful to Dr. Trilokya Saud, who helped me to publish the research works. I am thankful to Dr. Neel Kamal and Er. Prashant Patel for providing me excellent technical support to analyze the samples.

Finally, but by no means least, thanks goes to my parents, *Lt (Mr). B.R. Bardhan,* and *Mrs. Ila Bardhan,* brother *Biswendu Bardhan,* husband *Mr. Bholanath Mandal* and special thanks to my dearest daughters, *Ms. Meenakshi Mandal* and *Ms. Shreyashi Mandal* for almost unbelievable support.

(Ms. Papiya Mandal)

ABSTRACT

ABSTRACT

The study of trace gases and aerosol concentrations were carried out in urban area (Naraina Industrial Area) of Delhi, India. This location represents the mixed use area (combination of residential, commercial, institutional and industrial uses) of Delhi India. The samples were collected from January to December, 2011. The study revealed the poor ambient air quality in the selected hotspot location was mostly anthropogenic. The particulate matter (PM_{10} and $PM_{2.5}$) both were beyond the permissible limit of National Ambient Air Quality Standards (NAAQS) notification published by Central Pollution Control Board (CPCB), Government of India, New Delhi on 18th November, 2009. The average contribution of total carbonaceous aerosol in PM_{10} and $PM_{2.5}$ were 62% and 50% respectively and contribution of secondary organic aerosol in $PM_{2.5}$ was 27% of $PM_{2.5}$ mass. The concentrations of PM_{10} and the concentrations of trace gases like SO_2 NO_2 and NH_3 are interlinked to a large extent due to atmospheric reactions. The contribution of atmospheric inorganic secondary particles (sulfates, nitrates and ammonium) in PM_{10} during the study period was 20%. Heavy metal and particulate polycyclic aromatic hydrocarbon contributions in PM_{10} were 3%, and 1%, respectively. 14% of total aerosol mass of PM_{10} was not identified in this study. The unknown mass may be contributed by bioaerosols, heavy metals, inorganic salts and PAHs which are not included in the proposed study objectives. PCA-MLR explained the eight major sources which had contribution to increase the concentrations of particulate matter at Naraina mixed use area of Delhi. The contribution of sources are like Industrial emission was (30%), vehicular emission (25%), road dust (16%), iron and steel foundries (14%), pigment industry (6%), biomass burning (5%), smoke (4%) and miscellaneous sources (2%). The mass concentrations of particulate matter (PM_{10} and $PM_{2.5}$) were followed the order of post-monsoon> winter> pre-monsoon > monsoon. Mass closure analysis (MCA) was also carried out for both PM_{10} and $PM_{2.5}$.The chemicals compositions of PM_{10} were grouped into nine classes. The annual distributions of chemical compositions in percentage are of: organic matter (41%), elemental carbon (8%), non-sea salt sulphate (6%), nitrate (5%), ammonium (3%), sea-salt (0%), mineral dust (19%), non-dust elements (1%) and unaccounted mass (17%). The chemical components of $PM_{2.5}$ were grouped into two classes. Only organic matter and elemental carbon were measured for $PM_{2.5}$. The other chemical components like non-sea salt sulphate, nitrate, ammonium, sea-salt, mineral dust are considered in unaccounted mass of $PM_{2.5}$. The annual distributions of chemical compositions in percentage are of: organic matter (39%), elemental carbon (9%) and unaccounted mass (52%). Biomass

combustion is also a significant source of fine particle emissions and their characterization and reduction is an important issue. The emission control of effluent gases, proper maintenance of roads and plantation of dust capturing plants may reduce the emission at urbanized industrial area. More attention is required to control emission of air pollutants at source itself.

LIST OF FIGURES

LIST OF TABLES

CONTENTS

ANNEXURES

ABBREVIATIONS

AIIMS	All India Institutes of Medical Sciences
CPCB	Central Pollution Control Board
IARC	International Agency For Research on Cancer
USEPA	United States Environmental Protection Agency
NAAQS	National Ambient Air Quality Standards
ITO	Income Tax Office
OC	Organic Carbon
EC	Elemental Carbon
OP	Pyrolysis
TC	Total carbon
TCA	Total Carbonaceous Aerosols
POC	Primary Organic Carbon
SOC	Secondary Organic Carbon
SOA	Secondary Organic Aerosols
HM	Heavy Metal
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate Matter
PCA	Principle Component Analysis
PCA-MLR	Principle Component Analysis-Multiple Linear Regression
GC	Gas Chromatograph
WS	Wind Speed
WD	Wind Direction
RH	Relative Humidity
PHE	Phenanthrene
ANT	Anthracene
FLR	Fluoranthene
PYR	Pyrene
BaA	Benzo(a)anthracene
CHR	Chrysene
BbF	Benzo(b)fluoranthene
BkF	Benzo(k)fluoranthene
BaP	Benzo(a)pyrene
DahA	Dibenz(a,h)anthracene
BghiP	Benzo(ghi)pyrelene
IcdP	Indeno(123-cd)pyrene
NP	Naphthalene
ACY	Acenaphthylene
ACE	Acenaphthene
FL	Fluorene
BaP-TEQ	BaP-carcinogenic equivalents
MEQ	BaP-mutagenic equivalents

Chapter-I

INTRODUCTION

Chapter-I

INTRODUCTION

Urban air pollution with respect to emissions of trace gases and aerosols are the major concern in India.The rapid population growth, unplanned development, industrialization, increasing demand of efficient transportation facilities, processing of municipal and other waste materials such as composting of organic waste, etc. has resulted in deterioration of air quality in Indian cities. The speed of urban air pollution has increased in most of the urban cities in India. Delhi is no exception as it boasts of all the right mix of sources and created an unacceptable urban air pollution scenario. With a view to looking at interlinkages of air pollution, climate change and health, World Health Organization (WHO) once ranked Delhi city as the fourth-most polluted mega city of the world. The concentrations of ambient particulate matter in most of the mega cities in India are drastically high as compared to the concentrations of ambient gaseous pollutants.In most of the cities in India, the concentration of particulate matter is alarmingly high as compared to National Ambient Air Quality Standards (NAAQS) of Central Pollution Control Board (CPCB), Government of India. The industrial revolution has expanded point source of large emissions from various processes. The traffic source has expanded very rapidly over the last three decades. The ambient air pollution of Delhi city is directly linked with increasing trend of the density of population, industry and traffic.

The resident of Delhi is directly or indirectly exposed to particulate and gaseous pollutants from many different localand regional sources. The examples of local sources are traffic, biomass burning anddust of particulate matter, while regional sources are dominated by combustion processes from indoor and outdoor several activities, traffic and industrial emission.In response to the emerging scientific information, the small particles are especially responsible for damaging to public health and environment. The monitoring and evaluation of smaller particles, with acut-point of 10 μm aerodynamic diameter (PM_{10}) and more recently with a 2.5 μm aerodynamic diameter ($PM_{2.5}$) are essential to evaluate the health effect and climate change. Recently, in most of the mega cities in India have begun the monitoring of PM_{10} and insome cases monitoring of $PM_{2.5}$ has also started. However till date very limited data is available about the ambient concentration of $PM_{2.5}$ at various sectors. Several epidemiological studies suggested that there is a cordial association between increase in morbidity and mortality due to increase in particulate matter (PM) specially the finer fraction (Schwartz et al. 1996, Pop and Dockery, 2006). The toxicity level of contaminated particulate matter depends on several factors like dose, route of exposure, chemical species, age, gender, genetics and nutritional status of exposed individuals (Tchounwou et al. 2014). The smaller ($PM_{2.5}$) and ultra-smaller particles ($PM_{1.0}$) penetrate deep into the lung and can reach the alveolar region. The fine particles has the major importance as they are large in numbers as compared to coarse particles and having large surface area which has the tendency to absorb/adsorb toxic compounds such as heavy metals, carbonaceous compounds, cation, anion and polycyclic aromatic hydrocarbon (PAHs).

The accurate measurements of ambient air pollutants identify the major sources causing the air pollution, and take stringent action in controlling air pollution at source are the key issues in the global environment.The lack of key air pollution measurement instruments and procedures, scientists and policy makers are facing difficulty in improving the status of existing air quality. CPCB, Government of India is making continuous effort for documentation of various criteria pollutants monitoring protocol and its analysis proceduresto maintain quality assurance (QA) and quality control (QC) of air quality data. As an enforcing agency, CPCB is also encouraging national, international and private organizations to monitor and analyze the criteria pollutants mentioned in the NAAQS by adopting the standard protocol of CPCB and shared with them for national interest. The generation of air quality data base is essential for further development of policy decisions. Accordingly, over the years CPCB, have implemented a number of policy measures and prepared urban air pollution prevention act.

Present urban land use pattern of Delhi city, industrial emissions, motor vehicle emissions, as well as other indoor and outdoor anthropogenic sources providesstrip rise to gaseous pollutants as well as smaller fractions of particulate matter.Though several monitoring and assessment projects are being carried out in residential, commercial, industrial, traffic intersection area of Delhi city, but still there is a need to evaluate air quality assessment in urbanized mixed land use area of Delhi city. People spend approximately 30% to 100% of their total time in the mixed use area. So they are more susceptible to both indoor and outdoor air pollution. In general, mixed use areas areunder natural ventilation, which is ‘uncontrolled’ and ‘unpredictable’ in different climatic conditions.Thus poor air quality may influence, the working efficiency of the people and may result in to potential health hazards.

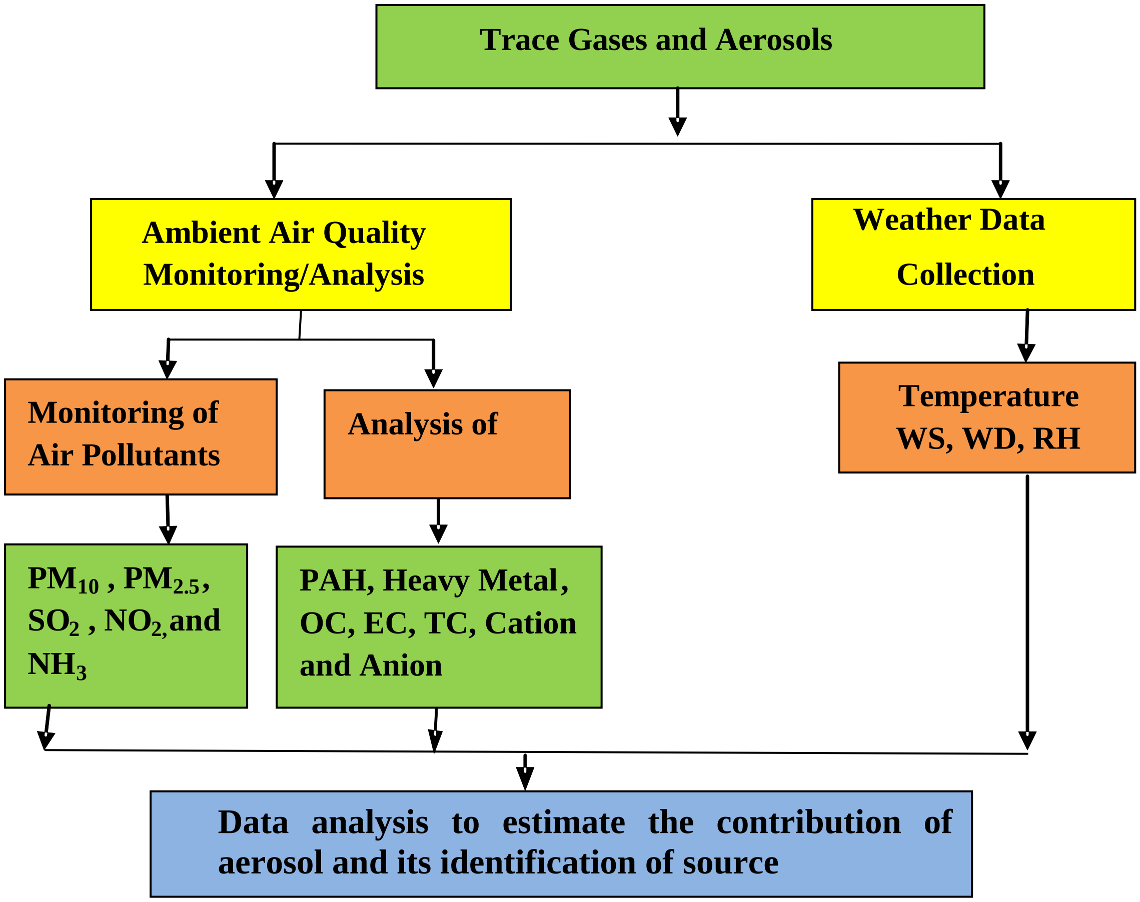
The urbanized mixed use area of Delhi city comprises of residential colonies, small and medium scale industries and commercial activities.The actual concentration of pollutants in the ambient air due to multiple emission sources in a particular areawill remain undetermined until detailed sampling and measurements of air pollutantsare carried out. In view of above, a study was conducted based on a common methodology delineated by CPCB at Naraina mixed use area of Delhi city to understand the concentrations of trace gases and aerosol formation in the ambient air. Naraina (latitude $28^0 38'27''$N and longitude 77^0 $8'38''$E) is one of the hotspot locations in South West Delhi. This location is the hub of industrial, residential, and commercial activities. It is adjacent to the western segment of the ring road, Delhi between Dhaula Kuan and Rajouri Garden. Other adjacent landmark locations are Inderpuri, Delhi Cantt, Patel Nagar, Pusa Colony, Satyam Park, Mayapuri and Ranjitnagar.

Aim of the study:

- To find monthly and seasonal variation of PM_{10} and $PM_{2.5}$ concentration.
- To find monthly and seasonal variation in concentrations of SO_2, NO_2 and NH_3.
- To estimate the concentrations of carbonaceous aerosol (OC, EC and TC) in PM_{10} and $PM_{2.5}$
- To estimate the concentrations of particulate PAHs, heavy metals, and cation and anion in PM_{10}
- To study the meteorological parameters such as temperature, relative humidity, wind speed and wind direction etc.
- Identification of the emission sources by applying appropriate receptor modeling.

The aim of this study was to find various parameters of air pollutants in Delhi as mentioned above in the bullatized form. However, since it is not possible to comprehensively monitor and study a large metro-polish like Delhi, It is decided to focus the attention in an area which is most polluted, the mixed used area of Delhi. The mixed use area designates the residential, commercial and industrial hub which are all playing a major role in creating air pollution

Proposed Study Approach



Structure of the thesis

Thesis categorized in five chapters. The detailed of each chapter is summarizing below.

Chapter 1: Introduction

This chapter deals with the definition of the urban air pollution, types, sources and effect on human health and climate change. This chapter also deals with the importance of the study and its study approach.

Chapter 2: Literature Review

This chapter deals with the reported information about chemical aerosols in National and International level and the gap still existing to evaluate the total quantification of aerosols in the atmosphere.

Chapter 3 Methodology

This chapter deals with the description of sampling site, monitoring, collection, preservation and analysis protocol of particulate matter and trace gases in the ambient air. The analysis protocol ofchemical aerosols of particulate matter eg. carbonaceous species, water-soluble ionic species, heavy metals, polycyclic aromatic hydrocarbon are also described in this chapter. The metrological parameters were collected and accordingly wind roses were prepared season wise. The methodology adopted for source identification and quantification of each type of aerosols are also included in this chapter.

Chapter 4 Result and Discussion

This chapter deals with the monthly/ seasonal variation of trace gases and aerosols of urbanised mixed use area of Delhi during the study period (January–December 2011). The concentrations of primary and secondary aerosols are compared with National and International Standard if any. Aerosols quantification and source identification were carried out by using appropriate suitable model.

Chapter 5 Conclusion

This chapter deals with the overall estimation of aerosols in PM_{10} in urbanized mixed use area of Delhi and the environmental management plan to control the air pollution.

Chapter-II

LITERATURE REVIEW

Chapter-II

LITERATURE REVIEW

This chapter deals with the reported information about trace gases and aerosols in National and International level and the gap still existing to evaluate the total quantification of aerosols in the atmosphere. The literature review was carried out for trace gases (SO_2, NO_2 and NH_3) and particulate natter (PM_{10} and $PM_{2.5}$) and for secondary air pollutants (OC, EC, HM, inorganic salts, and particulate PAHs).

2.1 Trace Gases

Trace gases are defined as gases whose concentrations are less than in the atmosphere. Trace gases indicates an extremely small portion of a mixture of gases. Except nitrogen and oxygen all other gases (oxides of nitrogen, oxides of sulphur, ammonia, carbon dioxide, methane, ozone, water vapour etc.) of the earth’s atmosphere are considered a trace gases. Though trace gases contribution is small (<1%), but it has several importance effects on both the earth's weather and climate change. The Earth's climate is sensitive to changes in trace gas concentrations and temperature in between upper troposphere and lower stratosphere zone (6 to 25 km above the sea level) of the atmosphere. Some of the trace gases eg., SO_2, NO_2, NH_3, CO, O_3 etc. are anthropogenic and chemically reactive in the atmosphere. SO_2, NO_2, and NH_3 are the trace gases which are directly linked with atmospheric reaction in the ambient air and form secondary aerosols. The atmospheric lifetime of trace gases are variable, depends on location, season and mixing time of its emission. Trace gases are produced by physical, biological and chemical processes on land and in the oceans. The natural cycles include emissions of a large variety of chemical species, which have been perturbed over the past decades by human activities, such as agriculture and deforestation. Fossil fuel extraction and burning, biomass burning, energy production and consumption, industrial activities, transportation and landfills have also led to the emissions of large quantities of pollutants into the atmosphere. Air pollutants in terms of either particulate matters ($PM_{2.5}$, PM_{10} etc.) or gases (NH_3, SO_2, NO_2, etc.), not only have a serious impact on health, but also have significant role in global climate change. The study reported to air quality in Delhi is described below.

Rapid industrialization, transportation and extensive use of fossil fuel consumption, escalating air pollution problem in worldwide. The diverse meteorological factors also influence our environment to a great extent. Population explosion has led to remarkable increase in vehicular population and solely depends upon the lifestyle of the citizen. A study was carried out during the period of 2006 to 2010 at identified hotspot locations in Delhi. Both locations were categorized as traffic intersection and a non-traffic area in Delhi. The trace gases (SO_2 and NO_2) sampling and analysis were carried out in week days and weekends. It was observed that pollutant concentration levels on weekend and public holidays were lower (SO_2 1.27 times and NO_2 5.76 times) as compared to weekdays (including Sunday) were (Gaur et al. 2015). This clearly indicated that pollutions level increased during week days periods due to vehicular emissions on roads, rails, air or water etc reported by **Gaur et al. 2015**.

The temporal changes different seasons were carried out from November 2005 to February 2008. The average NO_2 and SO_2 concentration during the study period was 33±15 and 15±7 μgm^{-3} (excluding the dust storm events) respectively. The maximum concentration of NO_2 was 77 (18 August 2006) and minimum concentration was 9 (23 December 2005). Similarly maximum concentration of SO_2 was 52 μgm^{-3} (9 January 2008) and minimum concentration was 2 μgm^{-3} (18 March 2006) reported by **Singh et al. 2014**.

The ambient trace gases (SO_2 and NO_2) concentrations were also carried out during pre-Diwali month (DM), Diwali day (DD), and post-Diwali month during the period 2006 to 2008 in the residential areas of Delhi, India. There was a significant increase in sulphur dioxide (SO_2) concentration but the concentration of nitrogen dioxide (NO_2) did not show any considerable variation. The study showed a strong correlation between SO_2 and NO_2 ($R^2 \geq 0.9$) on DD reported by **Mandal et al. 2011**. The average concentration of the pollutants during DD was found higher in 2007 which could be due to adverse meteorological conditions. The statistical interpretation of data indicated that the celebration of Diwali festival in Delhi affects the ambient air quality. The ambient air quality with respect to SO_2, and NO_2 were also carried out for pre-Diwali, Diwali festival, post-Diwali, and foggy day (October, November, and December) in Delhi during the period of 2002 to 2007. The extensive use of fireworks was found to be related to short-term variation in air quality. During the celebration of Diwali festival the concentrations of SO_2, and NO_2 were increased two to six times during the Diwali period when compared to the data reported for an industrial site. Similar trend was observed when the concentrations of pollutants were compared with values obtained for a typical foggy day each year in December reported by Singh et al. 2010. The levels of selected pollutants were found higher during Diwali period due to adverse meteorological conditions, i.e., decrease in 24 h average mixing height, temperature, and wind speed. On Diwali day, 24-h values for NO_2 in 2004 and 2007 were found to be higher than prescribed limits (80 μgm^{-3}) of National Ambient Air Quality Standards. The impact of fireworks on air quality was also reported for the Hisar city (adjacent to Delhi) in the year 1999 by **Ravindra et al. 2003**. It was observed that during the festival the concentration of SO_2 was observed to be increased ∼10-fold at few sites, whereas the concentrations of NO_2 increased 2–3 times, compared to the data collected on a typical winter day in December 1999. The maximum NO_2 concentration was observed a day after the festival. The diurnal pattern of the above pollutants showed a slight increase in the night. The levels of these pollutants observed during Diwali were found to be moderately high, which could be associated with serious health impacts.

The mixing ratios of ambient NH_3 and NO_2 over three different environmental locations viz Delhi, Dibrugarh and Thiruvananthapuram were compared in the year 2009. The objective of the study was to observe the diurnal variations, concentration and source strength. The average mixing ratio of NH_3 over Delhi, Dibrugarh and Thiruvananthapuram were recorded as 13.24 ± 0.39, 13.46 ± 2.52 and 12.65 ± 1.51 ppb respectively. The average mixing ratio of NO_2 was recorded as 12.69 ± 0.39 with maxima of 20.22 ppb and minima of 0.75 ppb over Delhi whereas, the mixing ratio of ambient NO_2 ranges from 0.65 to 3.65 ppb and 0.83 to 3.02 over Dibrugarh and Thiruvananthapuram respectively. **Sharma et al. 2010** also reported that the mixing ratio of NO_2 was varying significantly at all the three locations except NH_3 might be due to source strength and meteorological conditions of the locations. Result revealed that the mixing ratio of ambient NH_3 is positively correlated with ambient temperature ($r^2 = 0.872$) and NO_2 ($r^2 = 0.975$) over Delhi whereas non-significant at other locations. The diurnal and seasonal variation of ambient NH_3, NO_2 and SO_2 over Delhi were measured continuously during winter, summer and autumn seasons also using NH_3 and NOx-analyzer, which operates by chemiluminescence method with a higher estimation efficiency (>90%) than the chemical trap method (reproducibility 4.7%) in the year 2009. Prominent diurnal, day-to-day and seasonal variations of ambient mixing ratio of NH_3, NO_2 and SO_2 were observed during the study period. Seasonal variation with higher mixing ratio in winter was observed for all measured trace gases. Day-night variation of all measured trace gases observed was higher in winter in comparison with summer. Late morning increase in NO_2 mixing ratio might be attributed to conversion of NO to NO_2 with the interaction of O_3. Ambient NH_3 concentration reaches its maxima (46.17 ppb) at night and minimum during midday. The result revealed that the ambient NH_3 concentration was positively correlated with ambient NO_2 ($r^2 = 0.91$) and mixing ratio, whereas negatively correlated with ambient temperature ($r^2 = -0.32$). Wind direction and wind speed indicated that the nearby (~500 m NW) agricultural fields might be the major source of ambient NH_3 at the observational site.

The ambient trace gases (SO_2 and NO_2) were also carried out in both indoor and outdoor environment in an office of multistory mechanically ventilated building. The objective of the study was to evaluate the diversity of SO_2 and NO_2 inside building and penetration of pollutants, mostly found outside, from outside to inside in an airtight building. Ground floor of the building was selected for study. Horizontal measurement of SO_2 and NO_2 were done inside the building at four sampling stations. Simultaneously outdoor measurement too was carried out at two sampling stations to analyze the ratio of indoor to outdoor pollution**. Katiyar et al. 2007** observed that penetration of outside pollutants to inside the building. Activities of building users, occupants and visitors, play vital role manipulating the concentration of pollutants inside. No predominant sources of these pollutants were found inside.

The implementation of Compressed Natural Gas (CNG) in the replacement of diesel in transportation sector in Delhi was initiated from April 2001. Several initiatives were taken to reduce extremely high levels of pollutants present in the ambient air of urban city. One of the initiatives was to move public transport to CNG. Delhi boasted CNG in nearly 2200 buses, 25,000 three wheelers, 6000 taxis and 10,000 cars. However, more than half of the vehicles were still remaining to be converted to CNG. A relative comparison of ambient air concentration of pollutants, e.g. SO_2 and NO_x were carried out carried out by **Goyal et al. 2003** during the years 1995-2000 (without CNG) and the year 2001 (with CNG) has been made in order to assess the impact of CNG vehicles on ambient air quality in Delhi. It was observed that the concentration contribution of above mentioned pollutants were reduced considerably. The concentration of annual averages of SO_2 and NO_X decreased to 14 from 18μg/$m^3$and 34 from 36μg/m^3, respectively, and are well within the permissible limits of National Ambient Air Quality

Standards of Central Pollution Control Board (2009). An analysis of SO_2/NO_X whose correlation coefficient r^2 has the values 0.7613 respectively, indicated that point sources were contributing to SO_2 and mobile sources are contributing to NO_X concentrations in the ambient air.

The increasing trend of air pollution was also linkaged with acute and chronic illnesses amongst all age groups. Therefore, monitoring of ambient concentrations of various air pollutants as well as quantification of the dose inhaled becomes quite important, especially in view of the fact that in many countries, policy decisions for reducing pollutant concentrations are mainly taken on the basis of their health impacts. The dose when gets combined with the likely responses, indicates the ultimate health risk (HR). Thus, as an extension of our earlier studies, HR has been estimated for three pollutants, namely, NO_2 and SO_2 for Delhi City in India. For estimation and analyses, three zones have been considered, namely, residential, industrial and commercial. The total population has been divided into three age classes (infants, children and adults) with different body weights and breathing rates. The exercise takes into account age-specific breathing rates, body weights for different age categories and occupancy factors for different zones. **Pandey et al. 2005** indicated that a health risk due to air pollution in Delhi was highest for children. For all age categories, health risks due to SO_2 (HR_ SO_2) was the lowest. Hence, HR_ SO_2 has been taken as the reference with respect to which HR values of NO_2 had been compared. All age categories and their occupancy in different zones, average HR values for NO_2 was 16.13 times more than HR_ SO_2.

The annual average concentration of $SO_{2,}$ NO_2 and NH_3 were within the permissible limit of NAAQS, of CPCB (2009). Air quality has been categorized into four broad categories based on an exceedence factor (the ratio of annual mean concentration of a pollutant with that of a respective standard). **CPCB, 2012** reported that among the four categories are low (0 to 50µg/m^3), moderate (51 to 100µg/m^3), high (101 to 150µg/m^3), and critical (> 150µg/m^3). Low levels were observed in Nagpur, Kolkata and residential areas of Mumbai in India. Moderate levels were observed in Hyderabad, Delhi, Chennai and industrial areas of Mumbai in India. The annual mean concentration of $SO_{2,}$ and NH_3 in Delhi city has decreased over the years whereas concentration of NO_2 has increased steadily in line with the increase in number of diesel vehicles.The decreasing trend was observed might be due to various air pollution control strategies were carried out in recent years. The reduction in sulphur content in diesel, use of cleaner fuel such as CNG in Delhi, change in domestic fuel from coal to LPG etc. were initiated. The control of magnitude of traffic flow on roads is another alternative solution to reduce the ambient trace gases concentrations. The enjoyment of firecrackers during Diwali festivals is badly deteriorating the ambient air quality. So, public awareness about the health risks associated with the celebrations of Diwali festival so as to take proper precautions.

2.2 Particulate Matter

Particulate air pollution is defined as an air-suspended mixture of both solid and liquid particles. They are often classified to coarse, fine and ultrafine particles. Coarse particles having aerodynamic diameter ≤ 10 microns can be termed as PM_{10}. Inhalable particles less than 10 micrometer (µm) in diameter used as a nominal surrogate for particles between 2.5 and 10µm in diameter; found near roadways and dusty industries. Particles having aerodynamic diameter ≤ 2.5 microns can be termed as $PM_{2.5}$. $PM_{2.5}$ are the inhalable particles having diameter less than 2.5µm; generally found in smoke and haze, emitted from natural sources like forest fires and industrial combustion sources, or formed when gases react in the air. $PM_{1.0}$ is the subset of inhalable $PM_{2.5}$ particles, diameter less than 1µm. The fine (0.1 to 2.5µm in diameter) and ultra-fine (<0.1µm in diameter) particles remain in suspension for longer. To put things into perspective, human hair has a diameter of 50-70µm and a grain of sand has a diameter of 90µm.The smaller particles include combustion particles, organic compounds, polycyclic aromatic hydrocarbons, ions and trace metals. The sizes of PM_{10} and $PM_{2.5}$ are largely associated with the potential damaging effects on human health. The World Health Organisation (WHO) believes particles are affecting more people worldwide than any other pollutant. Primary health effects include damage to the respiratory and cardiovascular systems. Due to the small size of PM_{10} and $PM_{2.5}$ particles, they can penetrate the deepest parts of the lungs as well as access the gas exchange regions of the lung via diffusion.

Air Pollution is an escalating worldwide problem due to urbanization, industrialization and rapid growth of population which increased the demand of transportation as a result the consumption of fossil fuel is also increased in global scale. The ambient air quality has been deteriorated with respect to trace gases and particulate matter. In the present urban land use pattern, industrial emission, motor vehicle emissions, as well as other anthropogenic sources gives rise to gaseous pollutants and smaller fractions of particulate matter due to chemical compositions like carbonaceous and polycyclic aromatic hydrocarbon compounds (PAHs), heavy metals inorganic salts etc. Several epidemiological studies suggested that there is a cordial association between increase in morbidity and mortality due to increase in particulate matter (PM) specially the finer fraction. The smaller ($PM_{2.5}$) and ultra-smaller particles ($PM_{1.0}$) penetrate deep into the lung and can reach the alveolar region. The fine particles has the major importance as they are large in numbers as compared to coarse particles and having large surface area which has the tendency to absorb/adsorb toxic compounds such as heavy metals and PAHs. Several monitoring and assessment projects are being carried out in residential, commercial, industrial, traffic intersection area of Delhi. **Gaur et al. 2015** informed that a study was carried out a study during the period of 2006 to 2010 at two identified hotspot locations in Delhi. Both locations were categorized as traffic intersection and a non-traffic area of Delhi. It was observed that the concentration of $PM_{2.5}$ was 1.18 times higher in week days as compared to weekends and public holidays indicating that vehicular emissions on roads, rails, air or water are the major sources of pollution.

It was reported by **Ravindra et al. 2003** that fireworks during the celebrations of Diwali festival for the Hisar city (adjacent to Delhi) in the year 1999 increased the concentrations of air pollutants. The concentrations of PM_{10} increased 2–3 times, compared to the data collected on a typical winter day in December 1999. The diurnal pattern of the above pollutants showed a slight increase in the night. Similarly, **Singh et al. 2010**, assessed the variation of ambient air quality of PM_{10} for pre-Diwali, Diwali festival, post-Diwali, and foggy day (October, November, and December), Delhi (India), from 2002 to 2007. The extensive use of fireworks was found to be related to short-term variation in ambient air quality. The concentrations of PM_{10}, increased two to six times during the Diwali period when compared to the data reported for an industrial site. Similar trend was observed when the concentrations of pollutants were compared with values obtained for a typical foggy day each year in December. The levels of these pollutants observed during Diwali were found to be higher due to adverse meteorological conditions, i.e., decrease in 24 h average mixing height, temperature, and wind speed. The trend analysis shows that PM_{10} concentration increased just before Diwali and reached to a maximum concentration on the day of the festival. The values gradually decreased after the festival. On Diwali day, 24-h values for PM_{10} in all the years from 2002 to 2007 were found to be higher than prescribed limits of National Ambient Air Quality Standards and exceptionally high (3.6 times) for PM_{10} in 2007.

These results indicate that fireworks during the Diwali festival affected the ambient air quality adversely due to emission and accumulation of $PM_{10.}$ **Mandal et al. 2011**, investigated variation PM_{10} during pre-Diwali month (DM), Diwali day (DD), and post-Diwali month during the period 2006 to 2008 in the residential areas of Delhi. The use of fireworks during DD showed 1.3 to 4.0 times increase in concentration of PM_{10} than the concentration during DM. The average concentration of PM_{10} during DD was found higher in 2007 which could be due to adverse meteorological conditions.

Aerosols are fine, airborne mixture of liquid and/or solid particles, range from manometer to micrometer in size influence the global climate balance, hydrological cycles, atmospheric circulation and the abundance of greenhouse and reactive trace gases. They force the climate in both a direct and indirect ways. They directly scatter and absorb the solar and infrared radiation in the atmosphere whereas indirectly decrease the precipitation efficiency of warm clouds, changes in cloud properties. The sources of aerosol are industrial pollution, biomass combustion, windblown dust from arid and semi-arid regions and natural. The ocean is the major source of natural aerosol as the solid sea salt particles are present in the atmosphere as aerosol. The dominant species of pollutant from industrial emissions are water-soluble inorganic (sulphate, nitrate, ammonium), poly cycle aromatic hydrocarbon, organic carbon and elemental carbon. The major contributions of biomass combustion are organic carbon and elemental carbon. Windblown atmospheric dust deposits of mineral-rich dust and silt is also known as loess.

The annual mean of PM_{10} concentration has the increasing trend. The reasons being emission from generator sets, small scale industries, biomass incineration, suspension of traffic dust, natural dust, commercial and domestic fuel and vehicular emission etc. The increasing trend PM_{10} concentrations were observed during the period of 2001 to 2010 (**CPCB report, 2012**). The monitoring and analysis of $PM_{2.5}$ (aerodynamic size <2.5) were measured in few (total six) hotspot locations namely Pitampura, Sirifort, Janakpuri, Nizamuddin, Shahzada Bagh and Shahdara in in Delhi by using continuous air monitoring analyzer (CAMS) in the year 2010 (January to December) by the agency of CPCB. It was noted that minimum and maximum concentrations of $PM_{2.5}$ were varied from 22 to 261µg/m^3 respectively in selected hotspot locations of Delhi, India. The average concentrations of $PM_{2.5}$ were varied from 75 to 114µg/m^3 respectively. The most of the time the concentrations of $PM_{2.5}$ exceeded the NAAQS, 2009 (annual mean 40 µg/m^3) In general the trend of $PM_{2.5}$ followed the pattern of winter > summer > rainy due to variation of climatic condition.

An aerosol can be defined as a system of solid or liquid particles remain suspended in air or other gaseous environment. Aerosols vary in size and composition. The formation of aerosol can be either naturally or manmade generated. There is a wide range of aerosol present in the ambient air. The small size (<100 nm) to airborne particulate matter emitted from the industrial emission , vehicular emission, viruses etc. have an adverse effect in visibility and human health, known as bad aerosols. Aerosols are classified into two classes, namely primary aerosols and secondary aerosols according to the mechanisms of their origination. They are characterized by the concentration, mass, size, shape, chemical composition and aerodynamic and optical properties. Particle size distributions play a crucial role in the physics and chemistry of aerosols. The shape of the particles normally assumes as spheres and sometimes aerosols may comprise irregularly shaped particles also. The non-spherical of particles creates many problems as some cases reveal fractal properties. The emission of particles directly from source due to incomplete combustion of fossil fuels, biomass burning, natural dust, windblown dust, biological materials as plant fragments, airborne microbes pollen etc. are represented as primary particles. The secondary particles formed by the chemical interaction of trace gases with primary particles of crustal or marine origin. Volatile organic compounds and condensation of gaseous precursors act as a source for secondary organic aerosol. It is expected to exert a cooling of the atmosphere. Gas to particle conversion is linked with debates about atmospheric pollution, reduction of visibility, effects on public health, climate change and the oxidative capacity of the atmosphere. One or two imported international papers described for chemical analysis of particulate matter are described.

Airborne particulate matter in the PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ size ranges has been sampled at three sites (Bristol Road site, Birmingham City Centre site and Churchill Pumping Station site) within 20 km of one another, from University of Birmingham campus representing urban background, urban roadside and rural locations. The samples have been subject to chemical analysis for major constituents and the gravimetrically measured mass reconstructed using the pragmatic mass closure model of Harrison et al. 2003. Despite the separation in both time and space and the inclusion of a rural site, the coefficients determined in the earlier mass closure study provide an equally good mass closure on the current dataset. This extends also to the $PM_{1.0}$ fraction when the coefficients determined for $PM_{2.5}$ are applied. The mass and composition data for $PM_{2.5}$ and $PM_{1.0}$ are inter compared and perhaps surprisingly the differences are accounted for more by components typical of fine fraction particles such as ammonium sulphate and ammonium nitrate than those residing primarily in the coarse fraction such as sea salt, calcium- and iron-rich dusts. A comparison of the composition of 24-h samples collected on days when average PM_{10} exceeded 50 mg/m^3 with data for all days demonstrates the immense importance of nitrates, which together with their strongly bound water, account for on average 39% of PM_{10} and 46% of $PM_{2.5}$ during episode conditions, which is more than double their contribution to the overall dataset reported by **Harrison et al. 2008**.

In atmospheric research purpose the term particulate matter is usually restricted to particles with ultra-fine particulate matter ($PM_{1.0}$), (aerodynamic diameters $\leq$ 1 μm), fine particulate matter ($PM_{2.5}$) (aerodynamic diameters $\leq$ 2.5 μm), and coarse particulate matter (PM_{10}) (aerodynamic diameters $\leq$ 10 μm). Ultra-fine particles are characterized by highest number density while coarse particles are characterized by high mass density. The accumulation of size of particles is in the range of 0.1 -1 µm, formed by coagulation of particles due to nucleation mode and/or by condensation of gaseous species on the surface of pre-existing particles (**Perrino et al. 2010**). The particle size ($\geq$ 1 μm) includes particles formed by mechanical processes, such as erosion of the earth surface (mineral dust) and other materials, including the ocean surface (sea spray). Coarse particles are dominated by emission of primary particles, formation of secondary particles and windblown crustal dust, sea spray etc. The particle residence time in the atmosphere depends on size of the particle and their specific gravity. Coarse particles are rapidly removed from the air by sedimentation (residence time vary from minutes to hours). However, ultra / fine particles are transformed into coarser particles by coagulation processes. They have highest residence time in the atmosphere may be up to some weeks and mostly transported in the prevailing wind direction up to thousands of kilometres from the area of their formation.

Particulate matter (PM) is a very complex matrix and composed of many chemical species such as carbonaceous aérosols, sea-salt, mineral dust, and polycyclic aromatic hydrocarbons etc. which are great concern as it can be more easily inhaled. In general, the smaller the particle, the stronger its potential impact on climate change and human health. The past and present information about the chemical compositions of PM_{10} are described below.

2.2.1 Organic Carbon, Elemental Carbon and Total Carbon

Atmospheric Total Carbon is the combination of two components: Organic Carbon (OC) and Elemental Carbon (EC). The several studies had been carried out regarding the OC and EC components in the atmospheric air. The literature reviews of OC and EC are as follows:

The fractions of carbonaceous aerosols in PM_{10} were carried out on monthly basis in the urbanized industrial area of Delhi in the year 2011. The concentrations of PM_{10} ranged from 95.9-453.5 µg/m^3 with an annual average concentration of 280±126.10 µg/m^3 exceeding the limit of 60µg/m^3 of NAAQS, CPCB (2009). OC ranged from 28.8-159.4 µg/m^3 with an annual average of 93.03±44.72 µg/m^3. EC ranged from 75.5-44 µg/m^3 with an annual average of 27.30±13.35 µg/m^3. Strong correlation between total carbon (TC) and PM_{10} (R^2=0.99) and between OC and EC during pre-monsoon and winter seasons (R^2=0.79, 0.72) was observed indicating similar sources for both OC and EC. The concentrations of PM_{10}, OC, and EC during the study period were in the following order: Post monsoon>winter >Pre -monsoon>Monsoon. Annual average % of total carbonaceous aerosols (TCA), OC and EC in PM_{10} were estimated as 61.87, 32.75, 9.47 respectively reported by **P. Mandal et al. 2013**.

Monthly average (OC/EC) ratio was obtained in the range 3.02-3.96 indicating the formation of secondary OC. Analysis of carbon fractions indicated multiple emission sources e.g. motor vehicle exhaust, industrial emission and biomass burning. Variation of OC and EC in PM_{10} were studied over Delhi, an urban site of the Indo Gangetic Plain (IGP), India in 2010. Strong seasonal variation was noticed in the mass concentration of PM_{10} and its chemical composition. During winter season the concentrations of PM_{10}, OC and EC were maximum (PM_{10}: 213.17±14.9 µg/m^3; OC: 36.05±11.60 µg/m^3; EC: 9.64±2.56 µg/m^3) and minimum was observed during monsoon season (PM_{10}: 134.7±39.9 µg/m^3; OC: 14.72±6.95 µg/m^3; EC: 3.35±1.45 µg/m^3) respectively reported by **Sharma et al. 2014**. Biomass burning had the major contribution to increase the concentrations of OC and EC. The contribution of biomass burning was 14.3% to PM_{10} mass concentration at the observational site of Delhi. In the same location the fractions of carbonaceous aerosols in $PM_{2.5}$ were carried out on monthly basis in the year 2011. Results showed annual average concentration of $PM_{2.5}$ of 145µg/m^3 (NAAQS) in which OC was 41.12µg/m^3 and EC was founded 13.25µg/m^3. The correlations between OC and EC in pre-monsoon and winter season were found 0.83 and 0.79 respectively. The ratio of OC/EC in $PM_{2.5}$ ranged from 2.71 to 5.29 with an annual average of 5.28. The Annual average concentration of OC was 75% of total carbon (TC). The annual average concentration of OC was 60.34% of TC. OC and EC were higher in post-monsoon and winter season indicating that meteorological condition were a main governing faster. The emission sources were vehicle exhaust, coal combustion, biomass combustion etc. The chemical characterization of $PM_{2.5}$ with respect to OC and EC were also carried out at an urban site of Delhi, India from January, 2013, to December, 2014 in Delhi. The annual average mass concentration of $PM_{2.5}$ was 122±94.1 µg m^{-3} Sharma et al. 2016. Strong seasonal variation was observed in $PM_{2.5}$ mass concentration and its chemical composition with maximum during winter season and minimum during monsoon season. A receptor model, positive matrix factorization (PMF) was applied for source apportionment of $PM_{2.5}$ mass concentration. It was observed that biomass burning contribution also 14.3%. It was observed that present-day scenario of growing anthropogenic activities, carbonaceous aerosols contribute significantly (~20-70%) to the total atmospheric particulate matter mass and, thus, have immense potential to influence the Earth's radiation budget and climate on a regional to global scale. In addition, formation of secondary organic aerosols is being increasingly recognized as an important process in contributing to the air-pollution and poor visibility over urban regions. It is, thus, essential to study atmospheric concentrations of carbonaceous species (EC, OC and WSOC), their mixing state and absorption properties on a regional scale.

The comprehensive data on emission sources, chemical characteristics and optical properties of carbonaceous aerosols from selected urban sites in the Indo-Gangetic Plain (IGP) and from a high-altitude location in the central Himalaya was reported by **Ram and Sarin 2015**. The mass concentrations of OC, EC and WSOC exhibit large spatio-temporal variability in the IGP. This is attributed to seasonally varying emissions from post-harvest agricultural-waste burning, their source strength, boundary layer dynamics and secondary aerosol formation. The high concentrations of OC and SO_4^{2-}, and their characteristic were shown high mass scattering efficiency, contribute significantly to the aerosol optical depth and scattering coefficient. This has the major implications during the assessment of single scattering albedo and aerosol radiative forcing on a regional scale. The variations of carbonaceous aerosols (OC, EC and TC) in particulate matter (PM_{10} and $PM_{2.5}$) were reviewed in South and East Asia during the period of 2007 to 2014. TC (total carbon) is the combination of OC and EC (TC= OC+ EC). The selected countries in South and East Asia were Bangladesh, China, India and Nepal. The selected countries in South and East Asia are Bangladesh, China, India and Nepal. The major sources of carbonaceous aerosols are anthropogenic or biogenic sources, atmospheric oxidation of volatile organic compounds and subsequent gas-to-particle conversion processes.

Gupta et al. 2014, reported the review of the numerous studies, which were carried out in various hotspot locations (namely residential, industrial, traffic intersections, rural, indoor environment etc) of selected countries in Asian continent. OC/EC ratio in Bangladesh (Dhaka) varied from 0.78 to 1.3. OC/EC ratio in China (Chongqing, Xi'an, Xink-en, Pearl River Delta regions) varied from 1.13 to 6.92. OC/EC ratio in India (Delhi, Agra, and Mumbai) varied from 0.15 to 16.2. OC/EC ratio in Nepal (Kathmandu, Kathmandu valley) varied from 2.7 to 2.86. OC/EC ratio is generally varies with seasons. Most of the country OC/EC ratio exceeded 2, indicating the formation of secondary organic carbon (SOC). SOC is one of the major contributors of OC and its contribution varied from 18 to 61% in the selected locations. In Dhaka city, Bangladesh, EC concentrations were alarmingly high due to operation of diesel based power plants. The concentrations of OC in PM_{10} and $PM_{2.5}$ varied from 15 to 33% and 26 to 46% respectively. Similarly the concentrations of EC in PM_{10} and $PM_{2.5}$ varied from 3 to 10% and 9 to 10% respectively. The morphology study of particulate matter suggested that the origin of carbonaceous aerosols were mostly from combustion processes only.

The chemical speciation of atmospheric concentrations of $PM_{2.5}$ mass in the foothills of NE–Himalaya (NE–H) at Barapani (25.7 °N; 91.9 °E; 1064 above msl) among which EC, OC and water–soluble organic carbon (WSOC) were studied for three winter months (January–March). Except the winter months, during which aerosols from the Indo–Gangetic Plain get transported to this region, the rest of the year is relatively clean due to SW and NE–monsoon. The concentration of $PM_{2.5}$ widely varied from 39–348 $\mu g\ m^{-3}$, with average contribution of OC and EC as 36±8% and 6±3%, respectively reported by **Rajput et al. 2013**. The region is influenced by the winds bringing in residues from biomass burning in the Indo Gangetic plain, evident from high OC/EC ratio (10–15) (relatively high compared to fossil–fuel source). WSOC/OC ratio exceeded 0.5 suggesting formation of Secondary organic aerosols. Also, compared to upwind regions situated in the Indo–Gangetic Plain the OC/$PM_{2.5}$ ratio in NE–H is found to be higher.

$PM_{2.5}$ samples at traffic, rural and campus sites in Agra during November 2010 to February 2011and characterized for carbonaceous aerosols (OC and EC). $PM_{2.5}$ concentration ranged from 210.8 to 381.7µg/m^3 with an average of 308.3± 51.8µg/m^3 at traffic site, 72.9 to 118.2µg/m^3 with an average of 91.8±17.3µg/m^3 at rural site and 101.3 to 163.9µg/m^3 with an average of 140.8±22.3 µg/m^3. All the selected locations the concentrations of $PM_{2.5}$ were exceeding the limit of 40 µg/m^3 (NAAQS, 2009). The average concentration of OC was 86.1±5.2, 30.3±12.9, 44.5±18.5 µg/m^3 at traffic, rural and campus site respectively while that of EC concentration were found to be 19.4±2.4, 4±1.5, 5±1.4 µg/m^3 at same. OC/EC ratios were found to be 8.1 at campus site, 7.4 at rural and 4.4 at traffic site indicating the presence of secondary organic carbon (SOC) at all the sites reported by **Pachauri et al. 2013**. SOC concentration were found to be 15.3±6.3, 8.2±5.8 and 28.8±15.8 µg/m^3, accounting for 18, 24 and 60.7 % of total OC at traffic, rural and campus sites, respectively. A good OC-EC correlation with correlation coefficient (R) of 0.87, 0.94, and 0.79 at traffic, rural and campus site suggested presence of common dominant sources for OC and EC. Also a significant correlation was observed between soluble K^+ and OC at rural (R^2=0.63) and campus (R^2=0.53) sites as compared to traffic site (R^2=0.35).This might be attributed to increased biomass burning emission at rural and campus site. Surface morphology of the particles was analyzed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDX). Result indicated chain like aggregates of carbon bearing spheres at traffic and rural sites while at the campus site carbon rich and mineral dust particles were dominant ones.

A synthesis of the chemical and optical properties of ambient aerosols studied from selected sites (high altitude and urban) in Northern India was presented by **Ram and Sarin 2012.** Atmospheric carbonaceous (OC and EC) and water-soluble inorganic species (WSOC) account for nearly two-third of the total aerosol mass during the winter time, whereas their contribution is only 35 % during summer. The mass concentrations of carbonaceous species (EC, OC and WSOC) at urban sites are an order of magnitude higher than those at a high altitude site. Several factors, namely source variability, emission strength, secondary aerosol formation and boundary layer dynamics, contribute to the atmospheric concentrations of carbonaceous species and their temporal variability. Based on diagnostic ratios, K^+/OC and OC/EC, biomass burning emission (wood-fuel and post-harvest agricultural-waste burning) can be identified as major sources of carbonaceous aerosols. The large variability in the WSOC/OC ratio suggests significant contribution from secondary organic aerosols (SOC). The formation of SOC and their hygroscopic growth has implications to the scattering properties of aerosols, a process that could be invoked for the fog-haze formation during the wintertime over Northern India.

The variation of day- and night-time of EC, OC and WSOC in ambient aerosols ($PM_{2.5}$ and PM_{10}) sampled from an urban site (Kanpur) in the Indo-Gangetic Plain during the period of October 2008 to April 2009 (except January). The chemical data also provide evidence for the secondary aerosol formation and variability in the composition of particulate matter. The aerosol mass is dominated by fine-mode particles and $PM_{2.5}$/ PM_{10} mass ratio exhibit significant temporal variability (range: 0.46 to 0.86) reported by **Ram and Sarin 2011**. The chemical composition suggests that total carbonaceous aerosols (TCA=1.6 OC +EC). The mass concentrations of $PM_{2.5}$, EC and OC show about 30% increase during night-time. A significant linear relation between EC-OC (R^2=0.66) suggest biomass burning emission as a dominant source. The average WSOC/OC ratio is relatively high in the day-time samples (0.66± 0.11) compared to that in the night-time (0.47± 0.07); suggesting increased contribution of secondary organic aerosols. The concentrations of OC and EC show 2 to 4 fold increase during the haze events.

24 hourly basis integrated samples of PM_{10} and $PM_{2.5}$ in a kerb site of major Indian Urban community impacted by diesel automobile exhaust emissions during May 2005 to January 2006. EC concentrations were found to be 14.4-48.8μg/m^3 with minimum during the month of June and maximum observed during the month of October whereas OC concentrations were found to be 1.7-9.2μg/m^3 with maximum during September and minimum during June. OC/EC was found to be 0.09 to 0.31 with an average of 0.15 overall correlation coefficient between OC and EC as monthly average found to be R^2=0.86, between $PM_{2.5}$ and EC R^2=0.24, between $PM_{2.5}$ and OC was R^2=(- 0.17) i.e. negative reported by **Kumar et al. 2010**. Overall EC and OC concentration accounted for 20% to 48% and 3.6%-9.2% of $PM_{2.5}$ respectively.

Similarly another project was carried out inside rural households, ambient air and vehicular emissions from highway in a rural area in the Indo-Gangetic-Plains region of India to establish the role of both solid biomass based cooking in traditional stoves and diesel vehicles in contributing to high BC, EC, OC and solar adsorption in the month of October 2009 by **Rehman I.H et al 2011**. Indoor BC (also known as EC) sampling was conducted in two periods, initially during the period of 27 September to 29 November 2009 in randomly selected 35 households. Next samples were carried out during the period of 1-9 September 2010 in 18 of 35 households. In addition, 24hr indoor BC samples were collected using cell-phone based monitoring system (BC_CBM). Miniaturized Aerosol filter Sampler (MAS) in BC CBM system draws air at flow rate of 0.57L/min and deposit particulate matter on quartz filter. Some of these filters collected were analyzed for EC and organic carbon (OC) concentrations using thermal-optical EC/OC analyzer (Sunset Laboratory Inc., Forest Grove, OR) employing NIOSH TOT protocol. Real time outdoor BC concentration was measured continuously from November 2009 using Aethalometer Model AE42. Indoor BC concentrations during morning cooking hours (05:00 to 08:00) varied from ~3 - 1970µg/m^3 with a mean value of 54±7µg/m^3. During evening cooking hours (17:00 to 19:00) BC concentration varied from ~3 – 1070µg/m^3 with a mean value of 62±61µg/m^3. Outdoor BC concentrations during morning cooking hours varied from 3 - 390µg/m^3 with a mean value of 24 ± 39µg/m^3. During evening cooking hours BC concentration varied from 3 - 180µg/m^3 with a mean value of 26±18µg/m^3. Similar diurnal variation in outdoor and indoor BC concentration suggests strong influence of indoor cooking on outdoor BC concentration. BC measurements were recorded from 19 – 27 November 2009 at a traffic junction intersected by highway. Diesel driven transport trucks and passenger buses dominated the traffic. The BC concentration at the highway location during the non-cooking hours is a factor of 3 to 5 larger than the village center BC. The BC concentrations ranged from 20-50µg/m^3 on the highway crossing whereas BC ranged from 3-15µgm^{-3} in the village. OC/EC ratio was considered as a function of EC concentration in indoor and outdoor samples. The OC/EC ratio of indoor samples varied from 2.9-8.4 (mean value of 5.3±1.6); the corresponding EC concentration varied from 14-200µg/m^3.

The characteristic feature of their abundance pattern of aerosols was also investigated during wintertime (December–March) from selected sites (urban, rural and high-altitude) in northern India in the year 2007. A characteristic feature of their abundance pattern, at urban sites, is reflected in the OC/EC ratios (range: 2.4–14.5, Av=7.8±2.4, n =77) indicating dominant contribution from biomass burning sources (wood-fuel and agriculture waste). This is in sharp contrast to the OC/EC ratios at a rural site (range: 2.1–4.0, Av=3.1±0.6, n=7) influenced by emissions from coal-fired industries. The long-term measurements made from a high-altitude site (~2000 m from msl) reveal significantly lower abundances of EC and OC; suggesting that boundary layer dynamics (during wintertime) play an important role in efficient trapping of pollutants within the Indo-Gangetic Plain (northern India). The WSOC/OC ratios are fairly uniform (~0.35) in aerosols over urban sites but relatively enhanced contribution of WSOC and higher ratios (~0.5) at a high-altitude site emphasizes the significance of secondary organic aerosols. The comprehensive data set on EC, OC and WSOC/OC ratios from northern India is crucial to improve model parameterization of carbonaceous aerosols for atmospheric scattering and absorption of solar radiation on a regional scale reported by **Ram and Sarin 2010.** Similarly, OC/EC ratio of outdoor samples varied from 2.8-8.7 (mean value of 4.9±1.5); the corresponding EC concentration varied from 6.3-25μg/m^3.

Another comparison of Indoor and outdoor concentration of $PM_{2.5}$ were measured simultaneously at two sites ie., residential (Khar) and industrial (Mahul) in Mumbai city, India during summer, post monsoon and winter season for a week during the period of 2007-2008. The measured $PM_{2.5}$ was monitored using the metrics Minivol and DRI thermal optical analyzer was used for measuring OC, EC and TC. The average $PM_{2.5}$ concentrations at residential sites were found to be 88.89±39.12 μg/m^3 and 69.75±27.02 μg/m^3 exceeding the limit of 40μg/m^3 as per Indian NAAQS, 2009. OC concentration was 32.76±15.09 μg/m^3 and 24.5±8.58 μg/m^3 and EC concentration was 7.76±5.17 μg/m^3 and 6.6±5.38 μg/m^3. At industrial sites average $PM_{2.5}$ concentrations were 96.84±24.53μg/m^3 and76.58±28.05 μg/m^3 exceeding the limit of 40μg/m^3 as per Indian NAAQS, 2009. Average OC concentrations were 29.09±16.32 μg/m^3 and 19.25±9.5 μg/m^3 while average EC concentrations were 7.61±3.79 μg/m^3 and 3.61±2.95 μg/m^3 reported by **Elizabeth et al. 2009**. At industrial site excellent correlation among $PM_{2.5}$ with OC and EC ($r=0.67$, $r=0.85$, $p<0.01$) is due to common combustion sources like vehicles. At residential site good correlation between $PM_{2.5}$ and EC indoors with EC outdoors ($r=0.52$ and $r=0.53$, $p<0.05$) indicates penetration of outdoor air affecting inside air quality as site is close to freeway. OC/EC ratio outdoors at R and I site were greater than two (>2) with an average ratio of 5.31 and 3.9 implying presence of Secondary organic carbon (SOC).

The carbonaceous aerosols at sub urban site, Dayal Bagh Agra (a state of Northern India) were also carried out from January to October 2009. Average Total suspended particulate (TSP) concentration ranged from 79-658 µg/m^3 with a mean of 273±174.9 µg/m^3 exceeding Indian NAAQS of 40µg/m^3. Highest TSP was recorded in months of March, April and lowest in monsoon. Concentration of OC ranges 20.4-147.4 µg/m^3 while EC ranged from 1.4-20.3 µg/m^3. Average concentration of OC and EC were 60.9±40.5 µg/m^3 and 7.5±4.6 µg/m^3 respectively. OC and BC contribute 22 and 3% of TSP respectively reported by **Satsangi et al 2010**. Correlation coefficient (R) b/w OC and BC is 0.79 (P>0.001). Daily average OC/EC ratio varies b/w 5.2 and 16.2 with an average of 8.1. OC concentration is always greater than BC as OC is obtained from primary origin as well as secondary sources while EC has only primary origin. High concentrations of OC and BC are contributed by increasing heating sources such as fuel wood burning, coal burning and other biomass burning and meteorological conditions (calm condition and lower temperature) that cause stagnation of pollutants. The highest OC concentration was recorded in April as133.9 µg/m^3 and lowest in July as 19.6µg/m^3.

Several studies were carried out regarding the concentrations of OCEC in the ambient air in other countries. A few reported studies are described below.

The hourly measurements of OC and EC in $PM_{2.5}$ in Beijing, China, for a whole year 2013, with annual mean concentrations reported as 14.0 ± 11.7 and 4.1 ± 3.2 µg/m-^{3}, respectively reported by **Ji et al. 2016**. The OC and EC concentrations were reported to have high values in the autumn and winter with low peaks in the spring and summer. Also, the diurnal OC and EC pattern found high values at night and in the morning because of low boundary-layer heights at these hours. OC peak was observed to be high at noon due to photochemical activity. More than 75% of the OC samples had concentrations with a minimum of 0.9 µg/m^3 and maximum of 18.0 µg/m^3 and 75% of the EC samples had concentrations with a minimum of 0.4 µg/m^3 and maximum of 5.6 µg/m^3.In this study, autumn and winter concentrations of secondary organic carbon (SOC) were found high due to low temperatures, which favor the absorption and condensation of semi-volatile organic compounds on existing particles. High correlations were found between the estimated SOC and $PM_{2.5.}$ The annual average contribution of OC from Biomass burning to the total OC concentration was also estimated and found to be 18.4%, suggesting its dominant contribution. Compared to reports over the past ten years, the study found lower concentrations but higher than those reported from North America and Europe.

Air particulate matter ($PM_{2.5}$) samples using Air Metrics samplers from 11-17 January and 19-27 January, 2012 at Amin bazaar and Farm gate sites of Bangladesh respectively. The sampling time was from 8 a.m-4 p.m. The samples were analyzed for OC and EC. At Amin bazaar site concentration of EC varied from 28.5 $^-$ 55.2 µg/m^3 while that of total carbon (TC) varied from 55.9 - 95.1 µg/m^3. The average EC/TC ratio was found to be 0.56 during 11-17 January, 2012. At Farm gate sites EC concentration varied from 16.1- 32.1 µg/m^3. TC concentration from 40.1 to 70.6 µg/m^3 and average EC/TC ratio was found to be 0.43 reported by **Begum et al. 2012**. The concentrations of carbonaceous material and their sourced were also explored in the airborne particulate matter (PM), comprehensive PM sampling was performed (3 to 14 January 2010) at a traffic hot spot site (HS), Farm Gate, Dhaka using several samplers: Air Metrics Mini Vol (for PM_{10} and $PM_{2.5}$) and MOUDI (for size fractionated submicron PM). Long-term PM data (April 2000 to March 2006 and April 2000 to March 2010 in two size fractions ($PM_{2.2}$ and $PM_{2.2\text{-}10}$) obtained from two air quality-monitoring stations, one at Farm Gate (HS) and another at a semi-residential (SR) area (Atomic Energy Centre, Dhaka Campus, (AECD)), respectively were also analyzed. The long-term PM trend shows that fine particulate matter concentrations have decreased over time as a result of government policy interventions even with increasing vehicles on the road. The ratio of $PM_{2.5}/PM_{10}$ showed that the average $PM_{2.5}$ mass was about 78% of the PM_{10} mass. It was also found that about 63% of $PM_{2.5}$ mass is PM_1 established by **Hopke et al. 2011**. The total contribution of BC to $PM_{2.5}$ is about 16% and showed a decreasing trend over the years. It was observed that PM_1 fractions contained the major amount of carbonaceous materials, which mainly originated from high temperature combustion process in the $PM_{2.5}$. From the IMPROVE TOR protocol carbon fraction analysis, it was observed that emissions from gasoline vehicles contributed to PM_1 given the high abundance of EC1 and OC2 and the contribution of diesel to PM_1 is minimal as indicated by the low abundance of OC1 and EC2. Source apportionment results also show that vehicular exhaust is the largest contributors to PM in Dhaka. There is also transported $PM_{2.2}$ from regional sources. With the increasing economic activities and recent GDP growth, the number of vehicles and brick kilns has significantly increased in and around Dhaka. Further action will be required to further reduce PM-related air pollution in Dhaka. It was estimated that diesel, gasoline, coal/wood combustions were the major sources for air quality deterioration at Amin bazaar and Farm gate sites of Bangladesh. The indoor and outdoor PM_{10} concentration and its chemical composition in six monitoring stations and selected residential dwellings were studied in May 2010 in Kathmandu Valley. Six stations were strategically located viz-urban roadside, urban hospital, urban residential, urban background and valley background. PM_{10} concentration was observed for 12 hours duration from 8 a.m. to 8 p.m. IMPROVE TOR protocol was used for carbon analysis. Eight carbon fractions were studied namely OC1, OC2, OC3, OC4, OCP, EC1, EC2, EC3. Indoor and Outdoor PM_{10} concentration was also determined. Air sampling locations, both indoor and outdoor were at respiratory level i.e. 1.5 m above ground. Indoor PM_{10} concentration varies as: urban roadside <urban background-TU <urban hospital<urban residential<urban background-bhaktpur <valley background ranging from103.6±29.1 μg/m3 to 373.1±330.8 μg/m^3. The major reason being carbonaceous aerosol was biomass burning used for cooking purposes. The average outdoor PM_{10} concentrations vary from 60.6±36.1 μg/m^3 to 199.2±38.5 μg/m^3 in following order: valley background>urban background-TU> urban background-Bhaktpur>urban hospital>urban residential>urban roadside. The major sources were the vehicle exhaust and re-suspension dust. The average indoor/outdoor (I/O) ratio ranged from 0.05±0.5 to 4.2±0.04 in following order: urban roadside<urban residence<urban background-TU<urban hospital<valley background< urban background-Bhaktpur. Indoor and outdoor ratio (I/O) less than one (≤1), indicated the sources of PM_{10} was from outdoors only. The major source of outdoor PM_{10} concentration sources was from diesel motor vehicle exhaust. The average OC indoor concentration was found to be 51.5±37.2 μg/m^3 and varies as follows: urban background-TU<urban hospital<urban residential<urban roadside<urban background-Bhaktpur<valley background. Indoor OC ranged from 18.7±3.5 μg/m^3 to 103.7±118.3 μg/m^3. Outdoor OC concentration varied from 20.3±1.2 μg/m3 to 54.6±4.6 μg/m^3 with an average of 30.1±3.4 μg/m^3 with: urban background-TU<urban hospital<urban background-Bhaktpur<valley background< urban residential<urban roadside. The average indoor EC concentration was 21.4±18.9 μg/m^3 and ranged from 1.87±0.48 μg/m^3 to 3.6±0.69 μg/m^3 with highest at valley background and lowest at urban background-Bhaktpur. The average outdoor EC concentration was 2.7±0.91 μg/m^3 with highest at valley background (4.25±0.22 μg/m^3) to lowest at urban roadside (1.81±0.04 μg/m^3). The average value of OC/EC was estimated as 3.01 indicating importance of secondary organic carbon. The strong correlation

between OC and EC (R2=0.88) in outdoor environment and (R2=0.89) in indoor environment was found.

The investigation of OC, EC and WSOC were measured in a total of 1510 daily aerosol samples of $PM_{2.5}$ samples collected from May 2008 to April 2013 in Athens, Greece. OC and EC concentrations were 2.1±1.3 µg m^{-3} and 0.54±0.39 µg m^{-3}, accounting for 11±3 % and 3±1 % of $PM_{2.5}$ mass, respectively, with an average OC/EC ratio of 4.7±3.1 reported by **Paraskevopoulou et al. 2014**. Significant correlation was found between OC and EC during the whole period, indicating emissions by common primary sources on a regional scale. WSOC concentration ranged from 0.03 to 10.6 µg m^{-3}, with an average of 1.5±0.9 µg m^{-3}. By considering the Finokalia (Crete) station as a reference, it was estimated that, during the warm season in Athens, 67±7 % of emitted OC and 53±12 % of emitted EC is regional, while, during cold months, the regional contribution of OC is only 33±7 % and of EC 29±8 %. Furthermore, secondary organic carbon (SOC) was calculated for the warm period of the year (April to October). The estimated SOC constituted about 75±6 % of $PM_{2.5}$ organic carbon in Athens, highlighting significant aging processes on a regional scale. In the period 2011–2013 and during wintertime, an increase in OC and EC levels was observed, attributed to an increase in wood burning for domestic heating due to the economic crisis.

The concentrations of fine particulate matter ($PM_{2.5}$) and OC and EC were measured 6 years (2002-2007) in which continuously in capital of Chile. The contributions of carbonaceous aerosols to the primary and secondary fractions were estimated at three different sampling sites and in both warm and cool seasons. The concentrations of OC, EC and $PM_{2.5}$ exhibited minima in spring-summer (Sep-Feb) i.e. warm seasons (44±18%) and maxima in winter-autumn (March-Aug) i.e. cool seasons (53±41%) reported by **Toro Araya et al. 2014**. The greater contribution of total carbonaceous aerosols (TCA) to $PM_{2.5}$ was greater for cool seasons might be attributed to more significant emission sources of carbonaceous aerosols and meteorological factors (low temperatures, low wind speed and low mixing height). The mean OC and EC concentration in $PM_{2.5}$ were highest in urban industrial area and lowest in urban-suburban areas. It was observed that the minimum values of OC/EC ranged from 1.2±0.02 to 1.92±0.05 in cool season and from 1.15±0.03 to 1.43±0.04 in warm seasons. The annual average concentration of secondary organic carbon (SOC) and its contribution to ambient OC were estimated as 1.6 µg/m^3 (25.2%), 1.3

$\mu g/m^3$ (23.7%), 1.6 $\mu g/m^3$ (28.8%) in warm seasons and 3.2 $\mu g/m^3$ (29.6%), 4.2 $\mu g/m^3$ (26.8%) and 6.8 $\mu g/m^3$ (37.6%) in cool seasons at all the three numbers of selected sites. Also the impact of $PM_{2.5}$ and carbonaceous fraction on human health was studied and it was found to be related with premature death and adverse cardiovascular effects.

The concentration of PM_{10} and $PM_{2.5}$ and its chemical speciation in 4 sites (industrial, commercial and residential zones) were studied in a metropolitan area in Costa Rica. The concentrations of OC and EC were evaluated for the four sites. The annual mean PM levels were found to be higher in traffic–commercial (55 $\mu g/m^3$ for PM_{10} and 37$\mu g/m^3$ for $PM_{2.5}$) and industrial sites (52$\mu g/m^3$ for PM_{10} and 36$\mu g/m^3$ for $PM_{2.5}$) compared to residential areas (25 μgm^{-3} for PM_{10} and 18 $\mu g\ m^3$ for $PM_{2.5}$). $PM_{2.5}$ was majorly constituted by organic matter (OM) and EC (44.5–69.9%). On the other hand, PM_{10} majorly consisted OM+EC (32.7–59.4%) reported by **Murillo et al. 2013**. Wind patterns greatly influences concentrations of PM_{10} and $PM_{2.5}$ due to which rainy seasons seem to have high concentration than dry seasons in this region.

The concentrations of OC and EC were evaluated at a suburban site in Madrid for two years with mean values of OC and EC as 3.7 $\mu g\ m^{-3}$ and 1.3$\mu g\ m^{-3}$ respectively reported by **Plaza et al. 2011.** The highest individual concentrations were recorded during winters. Throughout the year, OC concentrations were fairly uniform. High EC concentrations were attributed to daily traffic rush hour patterns, with a delay in the OC peak suggesting formation of SOC's. The mean value of the OC/EC was reported as 4.9 with OC/EC ratios reaching the maximum during summers suggesting the formation of SOC's due to higher photochemical activity during summers. By following the primary OC/EC ratio approach method, a mean primary ratio of OC/EC (0.59) was used for measurement of hourly SOC concentrations throughout the study period. In summer the daily SOC production ranged from 80 to 92%, whereas in the winter months it varied from 70 to 84%.

The concentrations of OC and EC in indoor fine particles ($PM_{2.5}$) were conducted at nine residences located in Guangzhou. Nine residences were classified into 5 types, Urban without smoker, Urban with smoker, newly remodeled urban, roadside and sub Urban. Average indoor $PM_{2.5}$ concentration was 47.4 $\mu g/m^3$ exceeding limit consisting 12.5 $\mu g/m^3$ of OC and 4.4 $\mu g/m^3$ of EC i.e. 24.6% and 9.9% of indoor $PM_{2.5}$ respectively. Higher $PM_{2.5}$, OC and EC concentrations were observed in urban residences with smokers as 48.9-95.2 μg/m^3, 10.5±2.6 to 34.5±6.1 μg/m^3, 5.3±1.4 to 3.1±1.6 μg/m^3 respectively indicating poor condition of ventilation in kitchen. Roadside concentrations were 45.3-55.4 μg/m^3, 11.4±2.1 μg/m^3, 7.6±3.7 μg/m^3 respectively reported by **Lai et al. 2010**. The analysis report suggested the importance of indoor sources and outdoor penetration. Urban residences without smokers and recently remodeled residences had similar $PM_{2.5}$, OC and EC concentrations. Suburban residences had lowest $PM_{2.5}$, OC concentrations (32.1 μg/m^3 and 6.9±1 μg/m^3) while EC concentrations was lower than roadside residences (4.5±1 μg/m^3). OC/EC has maximum value of 1.1 at urban residence with smoker and minimum at suburban and roadside residence site. Average OC/EC at outdoor was found to be 2.5. Eight carbonaceous fractions by thermal optical reflectance (TOR) method were determined namely OC1, OC2, OC3, OC4, OP, EC1, EC2, EC3. Among these fractions OC2, OC3 and EC1 were most abundant fractions found. The author also reported the characteristics of carbonaceous aerosols (Carbonate Carbon (CC), EC, and OC) in Xi'an, China near Asian dust source regions in spring 2002. The Samples were collected during both DS (dust storms) and NDS (non-dust storms) periods over 28 days. Lowest value of CC recorded was 0.1μg/m^3 and highest value was 15.8μg/m^3. It was noticed that CC concentrations were high during dust storms periods. Average value of CC during DS events was 7.8μg/m^3 and 1.8μg/m^3 during NDS events. OC concentration ranges from 8.2-63.7 μg/m^3 while EC concentration ranges from 2.4-17.2 μg/m^3. Average EC concentrations during DS events (9.8 μg/m^3) are nearly same as those in NDS (9.8 μg/m^3) while average OC concentrations in DS events was 40.9 μg/m^3 and 31.8 μg/m^3 in NDS. OC-EC correlation (R^2=0.76, n=6) was good in DS periods while stronger in NDS period (R^2=0.90, n=25). Average % of total carbon (CC=OC=EC) in $PM_{2.5}$ during NDS events was 22.6% higher than 13.6% during DS periods. EC, CC and OC accounted for 16.4%, 12.9% and 70.7% of TC in DS events respectively. Average ratio of OC/EC was 5.0 in DS events and 3.3 in NDS periods. % of water soluble OC (WSOC) in TC accounted for 15.7% and ranges from 13.3%-22.3% during DS events. Distribution of eight carbon fractions implies that local emissions such as motor vehicle exhaust were dominant contributors to carbonaceous particles.

The segregated particle samples were collected in October 2007 at Xinken site, China on the mouth of Pearl River. A total of eight daytime and night time size segregated samples classified into continental and coastal trajectories were analyzed for mass concentration, OC and EC. Comparisons of day and night time as well as continental and coastal samples were carried out for every component in all considered particle size classes. PM_{18} was found to range from 58.9 to 127.4µg/m^3. Total carbon (TC) fraction of PM mass was found to be between 12% and 18%. Mean size distribution of OC and EC was found to be in the range Dp_{aer}=0.056 -18 µm. Mean size of OC, EC and TC over 15 runs were calculated as 7.3, 6.2, 13.5 µgC/m^3 respectively reported by **Gnauk et al. 2008.** OC/EC in different size classes was found to be mostly greater than one (>1) with maximum of 2.7 in coarse mode while measurement at sites being strongly dominated by traffic resulted in an OC/EC ratio near 0.3 in fine particle size other than technological processes, soot producing processes, fossil fuel burning, private burning of electric cable. EC fraction in fine particle size ranges about 80%. OC from biogenic sources are major source of primary coarse particle.EC in PM_{10} showed higher daytime concentration due to higher soot emissions from traffic, industry, etc. Similarly higher daytime OC concentration in different size ranges from, mainly in coastal samples may be due to new particle formation, volatilization of sea spray. Ultrafine particles account for 2.4% of total OC and 1.4% of total EC accumulation mode particles for 71.2 % OC and 85.6% EC and coarse particles for 26.4% OC and 13% EC.

The measurement of PM_{10} and $PM_{2.5}$ in an urban area in Huelva, which is influenced by industrial emissions and a rural site near Huelva close to an ecologically interesting area were reported by **Campa et al. 2009**. The measurement of OC and EC were taken for a year from June 2005 and June 2006. For the rural site, mean concentrations for PM_{10} was reported as 29 µgm^{-3} with maximum of 62 µg m^{-3} and minimum of 9 µgm^{-3}; for $PM_{2.5}$ mean concentration was reported as 21 µgm^{-3} with maximum of 36 µgm^{-3} and minimum of 10 µgm^{-3}.At the rural site, for OC concentrations in PM_{10} mean was 2.8 µgm^{-3} with a maximum of 8.9 µg m^{-3} and minimum of 1 µg m^{-3}; for EC concentrations in PM_{10} mean was 0.6 µg m^{-3} with a maximum of 1.7 µgm^{-3} and minimum of 0.2 µgm^{-3}.Similarly, at the rural site, for OC concentrations in $PM_{2.5}$ mean was 3 µgm^{-3} with a maximum of 7.2 µgm^{-3} and minimum of 0.6µg m^{-3}; for EC concentrations in $PM_{2.5}$ mean was 0.6 µgm^{-3} with a maximum of 1.6 µgm^{-3} and minimum of 0.1 µgm^{-3}. For the urban site, mean concentrations for PM_{10} was reported as 30 µgm^{-3} with maximum of 76 µgm^{-3} and minimum of 10 µgm^{-3};for $PM_{2.5}$ mean concentration was reported as 21 µgm^{-3} with maximum of 49 µgm^{-3} and minimum of 6 µgm^{-3}.At the urban site, for OC concentrations in PM_{10} mean was 3.5 µgm^{-3} with a maximum of 9 µgm^{-3} and minimum of 0.9 µgm^{-3}; for EC concentrations in PM_{10} mean was 1.5 µgm^{-3} with a maximum of 3.8 µgm^{-3} and minimum of 0.3 µgm^{-3}.Similarly, at the rural site, for OC concentrations in $PM_{2.5}$ mean was 2.9 µgm^{-3} with a maximum of 8.2 μgm^{-3} and minimum of 0.8μgm^{-3}; for EC concentrations in $PM_{2.5}$ mean was 1.1 $\mu g\ m^{-3}$ with a maximum of 3.9 μgm^{-3} and minimum of 0.2 $\mu g\ m^{-3}$.

The measurement of OC and EC in PM_{10} loadings were investigated at two sites in Prague: a suburb and a downtown site. At the suburb site, mean PM_{10}, OC and EC concentrations were 33$\mu g/m^3$, 5.5$\mu g/m^3$ and 0.74$\mu g/m^3$ respectively. In the downtown site mean PM_{10}, OC and EC concentrations were 37$\mu g/m^3$, 4.8$\mu g/m^3$ and 0.80 $\mu g/m^3$ respectively reported by **Schwarz et al. 2008**. OC and EC concentrations were found to be 3 times and 2 times high respectively, in winter's relative summer concentrations at the suburban site. EC concentrations were found to be 1.5 times high in autumn and winter relative summer concentrations at the downtown site. Minimum OC/EC ratios were 3.4 and 1.3 at the suburban site and downtown site respectively. This study also investigated that air masses re-circulating over central Europe and arriving from southeastern Europe in winter had a major impact in PM_{10} concentrations. Air masses transported from west and northwest originating above the Atlantic Ocean and the Artic brought the cleanest air masses to the sites. During the non-heating season the northwesterly winds affected the EC concentrations greatly at the suburban site situated upwind of Prague.

The concentration of OC and EC in PM_{10} were carried out at nine urban sites and one urban background using an elemental analyzer in China. The correlation between OC and EC were investigated in detail. Annual average concentration of PM_{10} at urban sites found to be 268.7±97.5 $\mu g/m^3$ while at urban background site it was found to be 130.6±55.6 $\mu g/m^{3,}$ much less as compare to urban site. Similarly average OC and EC concentration at nine urban sites was found to be 57.5±20.8 $\mu g/m^3$ and 8.3±3.9 $\mu g/m^3$ respectively, while at urban background site it was recorded 21.7±9.7 $\mu g/m^3$ and 3.1±1.8 $\mu g/m^3$ respectively reported by **Di Yeet et al. 2007**. Also seasonal variation was noticed in which OC concentrations in autumn were higher than those in spring while EC showed very little distinction between seasons. On an average, total carbonaceous aerosol (TCA) accounted for 33.2% in spring and 35% in autumn of PM_{10} mass. Correlation between EC and PM_{10} was moderate ($r = 0.45$, $p< 0.05$) and between OC and PM_{10} was good($r =0.82$, $p<0.01$). OC/EC ratio exceeding 2.0 indicates the presence of secondary organic carbon (SOC). Estimated SOC concentrations were 26.7 and 39.4 $\mu g/m^3$ and accounted for 48.9% and 61.7% of TCA in spring and autumn respectively.

The aerosol samples from urban, rural and coastal areas in Europe for carbonaceous content by measured by thermal optical transmission method. Total eight sites were selected for monitoring in which four sites were in urban area, three in rural background and one site in remote area. It has been found that carbonaceous matter (total carbon) concentrations are highest in urban areas and minimum in remote areas. Enrichment in OC was observed for remote and rural locations in comparison to urban locations. Result suggest that in summer there is increased formation of secondary organic carbon (SOC) because of more favorable conditions for gas-particle conversion of VOCs as a result of photochemical activity. SOC can reach significant levels in summer periods as a consequence of semi volatile primary organic carbon (POC) evaporation at higher temperatures. OC /BC ratio obtained at urban sites (Birmingham, Oporto, Coimbra, Aveiro) ranges from 1.1-1.3 during a year while at rural sites it was found to be 1.5 observed by **Castro et al. 1999**. In Averio (Portugal), at coastal and rural sites OC/BC was 1.5. However in winter it is found to be 2.6 while in other seasons as 1.5.

The estimation of primary organic aerosol (POA) and secondary organic aerosol (SOA) fractions from total mass of $PM_{2.5}$ particulates was recorded in urban atmosphere of Santiago City during 2002-2005. To accomplish this EC and OC determinations developed by automatic monitoring stations were installed at three sites. Seasonal fluctuations of EC and OC were observed showing that autumn-winter concentrations (April-September) are higher than spring-summer (October-March). Reason being the presence of permanent subsidence and thermal inversion layer and mixing height are around 400m in winter time and around 1000m in summer. OC and EC represent significant component in $PM_{2.5}$ which reaches from 19% to 26% in mass. However OC is dominant component accounting at least 80% of total carbon Observed by **Segual et al. 2009**. The result showed the highest mean OC and EC concentration occurred at urban site influenced by local primary emissions from nearby industrial, international airport. Lowest OC and EC concentrations occur at the site which was exclusively residential area. OC/BC ratio at all 3 sites were recorded >2 indicating presence of Secondary Organic Carbon (SOC). SOC concentrations were determined by EC tracer method and they were reaching up to 20% of total organic aerosol matter.

The effects of carbonaceous aerosols on environment and health were also reported by **Hamilton et al. 1992**. OC constituting generally 60-90% of the total carbon mass is linked with possible mutagenic and carcinogenic effects. Black carbon (BC) also known as EC has been associated to various detrimental environmental effects including global warming. These submicron particles can penetrate deeply into the lungs and get deposited in the pulmonary regions according to their different sizes slowing down the clearance mechanisms. In addition these could provide adsorption sites for toxic pollutants. Its radioactive properties are such that it absorbs light contributing to global warming by absorbing different wavelengths of solar radiation and reducing the atmospheric visibility. Also, it can lead to soiling of buildings by getting deposited on their facades**,** discussed

Traffic related emissions at a heavy-traffic roadside in Xi'an at the end of April 2008 to survey exposure of chemical composition (OC, EC, PAHs) of PM_{10} during daily heavy traffic periods (morning, noon and evening traffic rush hours) were carried out by **Shen et al. 2010.** The concentrations of OC and EC in PM_{10} samples were analyzed with IMPROVE (Interagency Monitoring of Protected Visual Environment) thermal optical protocol (TOR) as well as eight carbonaceous fractions were determined (OC1, OC2, OC3, OC4, OCP, EC1, EC2, EC3). PM_{10} concentration ranged from 337.9 to 718µg/m^3 with an average value of 569.2µg/m^3 exceeding limit as per Chinese NAAQS. This would have been enhanced due to slow decrease in mixing layer height towards sunset. The average OC and EC levels were 53 and 17µg/m^3. The ratio of OC/EC during three rush periods were in the range of 2.8-3.3, with mean value of 3.2. The average concentrations of OC2, OC3, OC4 and EC1 were relatively abundant in study, while OC1, OP, EC2 and EC3 were at lower level. This indicates predominant contribution from gasoline exhaust.

The concentrations of Indoor and outdoor $PM_{2.5}$, and its composition with respect to OC and EC were investigated at three rural sites during the winter of 2007 and the summer of 2008 in Shaanxi, China. The average indoor concentrations of $PM_{2.5}$, OC and EC were found to be higher in winter (237.2µg/m^3, 61.1µg/m^3, and 6.2µg/m^3 respectively) than in summer (99.0 µg/m^3, 18 µg/m^3, and 2.8 µg/m^3, respectively). The average indoor/outdoor (I/O) ratios for $PM_{2.5}$ and EC were close to or less than 1.0. The average OC/EC ratios ranged from 4.6 to 23.6 with an average of 9.1 during winter and from 4.2 to 12.0 with an average of 6.3 during summer reported by **Cao et al. 2010**. The high levels of OC and EC, and higher OC/EC ratios than in urban areas were the distinct characteristics of carbonaceous aerosols in rural areas of Shaanxi. These observations may be due to more biomass fuel burning and fewer emissions from motor vehicles. Owing to the large population living in rural areas, the agricultural fuel burning-activity in rural areas could significantly contribute to emissions inventories. Clean energy resources, such as wind and solar energy, are currently underutilized. Strategies and technology for improving energy efficiency and structure will be very important in reducing emissions in rural areas of Shaanxi, China

A few studies were carried out in India, even outside India also regarding the concentrations of carbonaceous aerosols (OC and EC) in both size of particulate matter (PM_{10} and $PM_{2.5}$) in the ambient air. The detailed analysis of formation of secondary organic aerosols (SOC) was further less. No studies were carried out at urbanized mixed use area of Delhi. So there was the basis need to develop the data about the concentrations of carbonaceous aerosols in mixed use area of Delhi. Accordingly this study will fulfill the research gap in Delhi and India also. So, the concentrations of carbonaceous aerosols in PM_{10} and $PM_{2.5}$ were carried out at urbanized mixed use area of Delhi.

2.2.2 Heavy Metals

In general, people living in urban areas are exposed to complex mixture of environmental pollutants due to heterogeneous and spatial distribution of emission sources and micro-meteorological conditions. The several studies suggested that increased levels of fine particles in the ambient air are associated with health hazards such as heart diseases, altered lung function and lung cancer. India is facing progressive deterioration in air quality attributable to growing trends of particulate matter (PM), particulate associated heavy metal (HM), and other toxic air pollutants in ambient air. Thus, characterization of toxic air pollutants and their impacts on climate and human health's has become a major concern among the researchers. The several studies have revealed that HM and their compounds are associated with PM_{10} are respirable and can persist in the atmosphere for longer duration. HM are indestructible and most of them have toxic effects on living organisms; although some of the metals are essential to human in order to remain healthy, at high level they can also pose toxicological risk to environment and humans health.Though HMs are originating from both natural and anthropogenic sources, but anthropogenic origin are of the major concern due to their toxic and potential carcinogenic characteristics. The natural sources of HM include terrestrial dust, bioorganic emanations emission from forest fires etc.The literature reviews of ambient HMs are as follows:

A study was conducted to understand the concentration of total suspended particulate matter (TSPM) in the occurrence of dust storm, and some trace metals in TSPM in the Delhi city during the time period March 20 - 22, 2012. A severe dust-storm was originated from Middle-East and crossed across the Delhi. Dust-storm (DS) aerosol samples, after dust-storm (ADS) and winter (WS) samples were collected and analyzed for metals As Cd, Cr, Cu, Fe, Ni, Pb, Sb, Se, Sn, Sr, V and Zn. The high aerosol mass concentrations of 1097-1965 µg/m-^{3} were recorded in DS samples. Ni and V are abundantly found in crude oils of Middle-East and their transport to the study region was evident by their high concentrations in the DS samples than that of ADS and WS samples. It can be suggested that these two metals can be used for tracers of dust storm from Middle East. Fe and Sr concentrations were reportedly 3-5 fold higher in DS samples than ADS and WS. The concentrations of metals As Cd, Cr, Cu, Fe, Ni, Pb, Sb, Se, Sn, Sr, V and Zn were 0.025±0.007, 0.005±0.007, 0.351±0.169, 0.135±0.045, 79.06±25.0, 0.137±0.049, 0.467±0.092, 0.006±0.001, 0.003±0.001, 0.021±0.006, 0.556±0.22, 0.161±0.059, 0.703±0.221 respectively reported by **Kumar et al. 2016**.

The concentration of PM_{10} and metal fraction of it at three residential sites in Delhi, India during December 2008–November 2009 reported by **Khillare et al. 2012**. The mean annual as well as 24–h PM_{10} concentrations exceeded the WHO limit by 8-10 times. It ranged from 166.5–192.3 μgm^{-3} .The mean concentrations of Fe, Mn, Cd, Cu, Ni, Pb, Zn and Cr were varied from 8-11.2, 0.25-0.02, 0.01-0.02, 0.18-0.27, 0.28-0.37, 0.27-0.46, 4.1-4.7, 0.13-0.23 μgm^{-3} respectively at the three sites. The concentrations of crustal metals mostly peaked in summer while metals from various anthropogenic sources peaked in winter. The concentrations of metals distributed spatially were influenced by closeness to traffic and industrial areas. Receptor modeling was carried out through principal component analysis–multiple linear regressions (PCA–MLR) suggested 3 major sources: crustal (49–65%), vehicular (27–31%) and industrial (4–21%). Theoretical health risk assessment calculated estimated blood lead levels in children ranging from 10.2–13.3 μgdL^{-1}, suggesting lead toxicity. Incremental lifetime cancer risk (ILCR) calculated for Cd, Cr (VI) and Ni showed that excess cancer cases could be 102, 2559 and 247 μgdL^{-1} respectively due to ambient metals concentrations in Delhi.

The concentrations of 12 heavy metals and 16 polycyclic aromatic hydrocarbons (PAHs) in $PM \leq 2.5$ μm and $PM \leq 10$ μm was carried out in the year 2007–2008 at urban site in Delhi

(India) during the winter and summer periods. The higher concentrations were observed during winters than summers with annual mean concentrations for PM_{10} and $PM_{2.5}$ recorded as 138.5±40.4 μgm^{-3} and 50.6±20.4 μgm^{-3}, during winters and summers respectively. The concentration of metals Al, Ca, Cd, Cu, Fe, Ni, Zn , V , Pb,Cr and Mn were detected in the PM_{10} during the summer season were 5251, 9452, 1.8, 22.3, 2021, 31.02, 431.5, 2.2, 210.5, 144.7, 19.1ngm^{-3} respectively. The concentration of metals Al, Ca, Cd, Cu, Fe, Ni, Zn , V , Pb, Cr and Mn detected in the PM_{10} during winters were recorded as 3690, 4152, 9.2, 36.2, 2884, 15.3, 612.3, 60.4, 420.7,128.5, 44.7 ngm^{-3} respectively. The concentration of metals Al, Ca, Cd, Cu, Fe, Ni, Zn , V , Pb,Cr and Mn detected in the $PM_{2.5}$ during summer were 2454, 917.2, 2.4, 65.2, 612.7, 29.5, 477.2, 1.8, 500.2, 74.1,33.7ngm^{-3} respectively. The concentration of metals Al, Ca, Cd, Cu, Fe, Ni, Zn ,V, Pb,Cr and Mn detected in the $PM_{2.5}$ during winters were 2880, 424.1, 12.6, 125.3, 2446, 15.3, 825.1, 5.6, 630.8, 80.5, 25.6 ngm^{-3} respectively reported by **Singh et al. 2011**. The concentrations of total PAH at both sizes of particulate matter (PM_{10} and $PM_{2.5}$) were reportedly higher in winter season (81.5 and 96 ngm^{-3}, respectively) than summer season (33.1 and 45.8 ngm^{-3}, respectively) with PAHs having 4-6 rings accounting for 80–95.8% of total PAHs. In general, the PAH concentrations was higher in finer mode than in the coarse mode. The transportation of dust from kerb-side areas of roads, combustion from vehicles and biomass burning, industrial processes as well as natural sources seem to contribute to the loadings of selected pollutants in both sizes of particulate matter.

The elemental composition, EC and OC of ambient PM_{10} particles in Delhi, India during the festival of “Diwali” The concentrations of PM_{10} were exceeded the WHO standard by 6–12 times, recording levels of 317.2–616.8 $\mu g/m^3$. The event also recorded high concentrations of Ba (16.8 $\mu g/m^3$), K (46.88 $\mu g/m^3$), Mg (21.38 $\mu g/m^3$), Al (8 $\mu g/m^3$) and EC (40.58 $\mu g/m^3$) respectively reported by **Sarkar et al. 2010**. On the day of Diwali, concentrations of Ba, K, Sr, Mg, Na, S, Al, Cl, Mn, Ca and EC exceeded their background levels by a factor of 264, 18, 15, 5.8, 5, 4, 3.2, 3, 2.7, 1.6 and 4.3 respectively. Secondary organic carbon (SOC) formation could be suggested by the peaking of OC concentrations in the post-Diwali days. In this study, Ba, K and Sr could be best represented as tracers of firework pollution. All in all aerosol contribution from firework resulted varied from 23 to 33% contributions to ambient PM_{10} loadings on the day of Diwali. A 2% increase in non-carcinogenic hazard index (HI) was also estimated due to Diwali celebrations.

Total 14 metallic species (six crustal and eight trace metals) in TSPM at a rural and urban location of Delhi, India were quantized for a period of one year (from September 2003 to August 2004. Particulate matter was collected on glass fiber filters. Rank sum test revealed that the TSPM concentration at the urban site was significantly (P=0.47) higher as compared to the rural site reported by **Sridhar et al. 2010**. Urban site showed highest TSPM concentration during winter while rural site during summer. Enrichment factor (EF) and coefficient of variation (CV) were calculated to assess the variability of elemental concentration data. Trace metals viz. Pb, Cd, Cu and Zn were observed to be highly enriched at both the sites, but EF for Zn and Cu was 2–3 times higher at the urban site as compared to the rural site. Trace and crustal metal concentration displayed less variability at the urban site. In the urban area, metals were mainly found to come from construction and industrial activities in surrounding. At the rural site, re-suspended and wind-blown dust appeared to be the source of observed elemental concentration.

A study of the atmospheric particulate size distribution of TSPM and associated heavy metal concentrations has been carried out for the city of Delhi. Urban particles were collected using a five-stage impactor at six sites in three different seasons, viz. winter, summer and monsoon in the year 2001. Five samples from each site in each season were collected. Each sample (filter paper) was extracted with a mixture of nitric acid, hydrochloric acid and hydrofluoric acid. The acid solutions of the samples were analyzed in five-particle fractions by atomic absorption spectrometry (AAS). The impactor stage fractionation of particles shows that a major portion of TSPM concentration is in the form of PM0.7 (i.e. <0.7 μm). Similarly, the most of the metal mass viz. Mn, Cr, Cd, Pb, Ni, and Fe are also concentrated in the PM0.7 mode. The only exceptions are size distributions pertaining to Cu and Ca. Though, Cu is more in PM0.7 mode, its presence in size intervals 5.4–1.6 μm and 1.6–0.7 μm is also significant, whilst in case of Ca there is no definite pattern in its distribution with size of particles. The average PM10.9 (i.e. <10.9 μm) concentrations are approximately 90.2% ± 4.5%, 81.4% ± 1.4% and 86.4% ± 9.6% of TSPM for winter, summer and monsoon seasons, respectively reported by **Srivastava et al. 2009** . Source apportionment reveals that there are two sources of TSPM and PM10.9, while three and four sources were observed for PM1.6 (i.e. <1.6 μm) and PM0.7, respectively.

Results of regression analyses show definite correlations between PM10.9 and other fine size fractions, suggesting PM10.9 may adequately act as a surrogate for both PM1.6 and PM0.7, while PM1.6 may adequately act as a surrogate for PM0.7.

24-hourly basis samples of airborne aerosols (PM_{10} and $PM_{2.5}$) were collected at an urban and a rural site of the North central, semi-arid part of India during May 2006 to March 2008. Seven trace metals (Pb, Zn, Ni, Fe, Mn, Cr and Cu) were determined for both sizes. The annual mean concentration for PM_{10} was 154.2μg/m^3 and 148.4μg/m^3 at urban and rural sites whereas $PM_{2.5}$mean concentration was 104.9μg/m^3 and 91.1μg/m^3 at urban and rural sites, respectively reported by **Kulshrestra et al. 2009**. Concentrations of PM_{10} and $PM_{2.5}$ have been compared with prescribed WHO standards and NAAQS given by CPCB India and were found to be higher. Weekday/weekend variations of PM_{10} and $PM_{2.5}$ have been studied at both monitoring sites. Lower particulate pollutant levels were found during weekends, which suggested that anthropogenic activities are major contributor of higher ambient particulate concentration during weekdays. Significant seasonal variations of particulate pollutants were obtained using the daily average concentration of PM_{10} and $PM_{2.5}$ during the study period. $PM_{2.5}$/ PM_{10} ratios at urban and rural sites were also determined during the study period, which also showed variation between the seasons. Three factors have been identified using Principal Component Analysis at the sampling sites comprising re-suspension of road dust due to vehicular activities, solid waste incineration, and industrial emission at urban site whereas re-suspension of soil dust due to vehicular emission, construction activities and windblown dust carrying industrial emission, were common sources at rural site.

Source apportionment of TSPM and associated heavy metals has been carried out for the city of Delhi using the Chemical Mass Balance Model, Version 8 (CMB 8), as well as principle component analysis (PCA) of SPSS (Varimax Rotated Factor Matrix method) in coarse- and fine-size mode. Urban particles were collected using a five-stage impactor at six sites in the winter of 2005-06. The impactor segregates the TSPM into five different size ranges (viz. > 10.9, 10.9– 5.4, 5.4–1.6, 1.6–0.7 and < 0.7 μm). Four samples were collected from six different sites every 24 hours. Samples were analyzed in five size ranges gravimetrically and chemically for the estimation of SPM and metals. The five different size ranges were divided into two broad categories: coarse (1.6 to > 10.9 μm) and fine (< 1.6 μm). The CMB8 and PCA were executed separately for both coarse and fine size ranges. Results obtained by CMB8 indicate the dominance of vehicular pollutants (62%), followed by crustal dust (35%) in the fine size range; while in the coarse size range crustal dust dominated (64%) over vehicular pollution (29%). Little contribution from paved-road dust and industrial sources was observed. Results of PCA (or factor analysis) reveal two major sources (vehicular and crustal re-suspension) in both coarse and fine size ranges. The correlations of factors (sources) with the metals show that in the coarse size range the dominant source is crustal re-suspension (68%) followed by vehicular pollution (23%). However, this is reversed in the case of the fine size range factor analysis where vehicular pollution (86%) dominated over crustal re-suspension (10%) reported by **Srivastava et al. 2007.**

The concentrations of 14 metals were carried out during Diwali week which were reportedly higher than background concentrations of industrial sites. On the day of Diwali, concentration of metals in the order K>Al>Ba>Mg>Fe>Sr>Na>Ca>Cu>Mn>As>V>Ni>Bi were reported. Ba, K, Al and Sr could be suggested as tracers of Diwali pollution reported by **Kulshrestha et al. 2004.** Their concentrations on the day of Diwali went up to 1091, 25, 18 and 15 times respectively than the previous Diwali day. The concentration of K was recorded as 58ug/m^3 which was highest among all the selected metals on the day of the Diwali festival. This study suggested that that burning of fireworks during the celebrations of Diwali could be a strong source of high metals pollution in the ambient air.

Ambient air concentration of PM$_{10}$ and heavy metals at six different sites (including three sub-urban and three rural) was assessed in Roorkee (adjacent to Delhi), India. Monthly measurements were carried out continuously between January and March 2007 at all the sites. PM$_{10}$ concentrations at the rural sites ranged from 37-959 µg/m³ as compared to 151-422 µg/m³ at sub-urban sites reported by **Gurjar et al. 2012**. These concentrations were well above NAAQS, 2009 of CPCB (Central Pollution Control Board, Delhi) standards during all sampling months, except February. In case of heavy metals, highest concentrations were 2.04, 30, 0.80, 7.13 and 15.6ng/m³ for Cr, Fe, Mn, Zn and Al respectively at rural sites as compared to 0.28, 0.37 and 0.02 ng/m³ for Ni, Cu and Cd, respectively at an industrial site. Main sources of PM$_{10}$ and heavy metals at sub-urban sites were road dust, traffic exhaust, tire abrasion, industrial emissions and oil lubricants use at vehicle-servicing centre. Heavy metals and PM$_{10}$ at the rural sites came from coal and wood burning, sugar mill and brick furnace emissions, fertilizers use in farming, agricultural activity, road construction activity and the dust from long range transport along with naturally occurring re-suspended dust. Among all, wood burning was identified as the most significant source of elevated PM_{10} concentrations at rural sites. As opposed to the PM_{10} that remains a concern, concentrations of all heavy metals were found to be far below the standard limits prescribed by WHO and EPA.

An investigation was carried out about the metal loadings in the urban soil in the industrial city of Ghaziabad (adjacent to Delhi), India. The concentrations of different metals like Cu, Cr, Pb, Cd, Zn, Mn, Fe and Ni concentrations in the top soil samples were 122, 288, 147, 0.4, 187, 386, 21,433 and 147 mg/kg respectively. The concentrations of Cu, Cr, Pb, Zn and Ni were reportedly higher than other cities in the world, when compared to other studies reported by **Chabukdhara et al. 2013**. The study classified the sampling sites into three groups: Group 1- commercial, industrial or dumpsite, group 2 and 3: commercial or residential sites. Group 1 had relatively higher concentrations than the other two groups. Receptor modeling done through principal component analysis (PCA) indicated group 1 sites had a common industrial source for Cu, Pb and Zn metals. Cr could originate from point anthropogenic sources. For group 2 sites except Zn and Ni all metals suggested natural sources while. For group 3, PCA pointed to metals having lithogenic source. The health risk assessment carried out (ingestion, dermal and inhalation) indicated that hazard index (HI) for children exceeded the safe level (HI=1) for Cr =2.21. For non-cancer risks, HI's for adults and children decreased in the order of Cr> Pb> Mn> Ni> Cu> Cd. The theoretical excess cancer risk due to Cr, Pb, Cd and Ni were all within acceptable values. ($1E^{-06}$ to $1E^{-04}$).

A study was conducted to investigate the concentration of zinc (ZN) and chromium (Cr) concentration in street dust in TSPM in Anand city, the milk capital of India. This state is a developing city with increasing vehicles and developmental activities going on at a fast pace. This study attempts to investigate the Ten sampling locations were selected based on the traffic density on the roads and different anthropogenic activity. Sampling was carried out in the dry months of January to March 2011. The range of Zn and Cr was 16.82 - 108.29 ppm and 118 - 151.5 ppm in the street dust respectively reported by **Bhattacharya et al. 2013**. Zn concentration in Suspended particulate matter lies in the range of 12.41 to 86 ppm and Cr concentration between 75 to 130 ppm. The range of Cr in foliar deposited dust varied from 79.54 ppm to 31 ppm. Whereas, for Zn maximum concentration was in S10 which is 42.34 ppm and minimum was in site S9, 23.73 ppm. ANOVA single factor showed that at 0.05 level of significance site wise variation of Zn and Cr concentration in TSPM, Street dust and foliar deposited dust was not significant signifying similar source of contamination. Which was further strengthened by the good positive correlation found between the Zn and Cr concentration of street dust, leaf deposited dust and TSPM. The Contamination Factor (CF) in the sites where metal concentration was high was 1.24 in S10 and 1.06 in S5 for Zn. For Cr the value of CF was 1.77 in S10 and 1.67 in S5. These values indicate that street dust is moderately contaminated with respect to Zn and Cr.

The concentration of some heavy metals in suspended and respirable particulate matter (TSPM and PM_{10}) collected from five different zones situated in Kota city during both summer (March, April, May and October) and winter (January, February, November and December) seasons of 2011–2012. The mean concentrations of anthropogenic origin metals (Pb, Zn, Cu and Cd) were higher in winter and lower in summer with their relative abundance in order: Zn > Pb > Cu > Cd while reverse trend was observed for crustal origin metals (Ca, Mg and Fe) at all zones reported by **Rani et al. 2016**. Meteorological conditions such as temperature, relative humidity, wind velocity and wind direction during winter and summer were found affecting the metals concentration trends in different seasons. Wind roses indicate that the zones lying in predominant North-east wind direction from point source (KSTPS) in winter (25.74%) and summer (15.31%) faced higher metal burden following zone 1, which is suffering most owing to its closest location to the source. Statistical analysis by Pearson’s correlations, enrichment factor and principal component analysis indicates that coal based Thermal Power Plant is the major source of heavy metals besides other industrial activities in the study area. It was noticed that because of higher residence time, significant concentration of Pb was found at all the zones in the city which, probably, had its origin in earlier vehicular exhaust as well.

The concentrations of OC and EC and some selected heavy metals were investigated during the winter season at two residential sites of Bhilai, India during the Indian Diwali festival in November 2012. Total 38 chemical species including eight speciated carbonaceous fractions (SCFs) of elemental (EC) and organic carbon (OC), twenty one metallic elements, and nine water soluble ionic species. Our objectives were to investigate: 1) relative abundances of SCFs contained in $PM_{2.5}$ during the Diwali festival period compared to normal days, and 2) enrichment pattern of potential inorganic markers of firework emission in ambient $PM_{2.5}$ during the festival days. Eight-fold increase in$PM_{2.5}$mass concentrations were measured during the Diwali festival days compared to concentrations occurring in normal days. Bursting of firecrackers in the residential streets have shown significant contribution to the emission markers (K, Mg, Zn, S, EC and OC) along with crustal markers (Ca, Fe, Al) in ambient $PM_{2.5}$ aerosol samples. Concentrations of water soluble ionic species were found to be 10 times greater than those found in normal days. Further, the anion/cation ratios were found to reach a factor of 2; indicating the acidic character of emissions resulting from fireworks reported by **Pervez et al. 2015**. The relative abundance of SCFs and higher ratios of OC to EC during the Diwali episode suggested the significant formation of secondary organic carbon (SOC) aerosols. We estimate that aerosols emitted from firework bursting contribute up to 32% of total ambient $PM_{2.5}$ during the Diwali festival.

The ambient concentrations of PM_{10} and associated heavy metals measured at 3 sites in the mining areas of Jharia coal field during October 2012-February 2013. Among the selected 5 types of metals (Mn, Ni, Co, Cd, Pb) studied two metals (Ni and Pb) are considered as criteria pollutants as per NAAQS (2009) of Central Pollution Control Board (CPCB). According to the magnitude of the mean concentrations of metals, they can be ranked in the following order Mn > Ni > Co > Cd > Pb. PM_{10} and heavy metals loading in coal mining area was found to be almost 2 times higher than that of control site reported by **Mishra et al. 2013**. The selected heavy metal concentrations in coal mining areas were found to be higher as compared to most of the cities in India. The correlation analysis showed strong relationships between Cd–Ni, Ni–Mn, and Cd–Mn in the coal field in India.

Ambient air quality monitoring was carried out to understand the temporal and special variation of PM_{10} and its associated heavy metal content in the atmosphere of Nagpur, Maharashtra State, India during 2001 as well as in 2006. Heavy metals released from different sources in urban environment get adsorbed on PM_{10} and are important from public health point of view causing morbidity and mortality. PM_{10} fraction was observed to exceed the stipulated standards of NAAQS, 2009 in both years. It was also observed that minimum range of PM_{10} was observed to be increased in 2006 indicating increase in human activity during nighttime also. Six heavy metals were analyzed and were observed to occur in the order Zn > Fe > Pb > Ni >Cd > Cr in 2006, similar to the trend in other metro cities in India. Pb and Ni were observed to be within the stipulated standards reported by **Chaudhari et al. 2012**. Poor correlation coefficient (R^2) between Pb and PM_{10} indicated that automobile exhaust was not the source of metals to air pollution. Commercial and industrial activity as well as geological composition might be the potential sources of ambient heavy metal pollution. Total load of heavy metals was found to be increased in 2006 with prominent increase in Zn, Pb, and Ni in the environment. Public health impacts of heavy metals as well as certain preventive measures to mitigate the impact of heavy metals on public health are also summarized.

Eight types of selected heavy metals like Cr, Ni, Cu, Cd, Pb, Zn, Mn and Co in the airborne $PM_{2.5}$ component fraction were collected in four different seasons in a coal burning city of Taiyuan, China in the study period November, 2014. The concentrations of Zn and Pb in the air were high due to coal burning in the ambient air with greater concentrations in spring and winter. Experimental assays to assess the myocardial toxicity were conducted. It showed that the heavy metal component of $PM_{2.5}$ fraction was the reason for season-dependent apoptosis in rat H9C2 cells through a oxygen reactive species mediating inflammatory response reported by **Zhang et al. 2016**. Myocardial toxicity in this area could be as a result of greater $PM_{2.5}$ loadings in the air due to coal burning. This study indicated that coal burning also emitted Zn and Pb in the ambient air. City like Delhi coal and biomass burning are most common activities which are also involved to increase the concentrations of PM_{10} and $PM_{2.5}$. In India, Pb free fuels are used in the transportation sector. Pb has phase out in India, in the year 1999, but still Pb present in any type of collected dust samples. Coal burning may be the major cause to present Pb in the dust samples.

In India several studies were carried out in evaluate the airborne HMs concentrations in various sectors of rural and urban areas in TSP (Total suspended particulate matter). A few studies were carried out to evaluate the HMs concentrations in $PM_{10,}$ $PM_{2.5}$ and PM_1 size fractions of particulate matter.The reported value for As, Cd and Co were low as compared to common HMs. In India NAAQS, 2009 Standards has been formulated only for As, Ni and Pb. Most of the Ni concentrations were exceeded the annual mean concentrations (0.2 µg/m^3) of NAAQS, 2009 (**Kulshrestha et al. 2009, Vijayan et al. 2008, Shridhar et al. 2010, Khillare and Sarkar,**

2012). Pb and As concentrations were within the permissible limit of NAAQS, 2009. The anthropogenic sources includes emissions from power plants, non-ferrous metal smelters, incinerators, steel, cement plants, fossil fuel burning, electroplating, surface coating, transportation, domestic combustions and re-entrained road or paved/ unpaved surface dust. The ambient PM, its associated HM concentrations and greenhouse gases are generally higher in mega cities and industrial areas in comparison with the rural environments (**Gurjar et al. 2008**). The rapid increase of city's population with a derivative increase in the number of vehicles (6 million approx) without a coextensive increase in road length, and industrial emission are the major governing factors to increase airborne PM in urbanized area of Delhi. The several studies were carried out about the airborne inhalable HM concentrations at different sites (mines, residential area, commercial area etc.) of Indo- Gangetic plain but most of them were in total suspended particles (TSP). HMs concentrations were carried out in PM_{10} at the urban mixed use area of Delhi, India which will provide adequate information about the HM concentration, sources and their effects at different sites of Indo- Gangetic plain. No HMs, study was carried out at urbanized mixed use area of Delhi, so concentrations of HMs in PM_{10} were carried out in mixed use area of Delhi.

2.2.3 Cation and Anion

Atmospheric particulate matter originates from both natural and anthropogenic sources and has a wide range of physical, chemical, and thermodynamic properties. Particles from primary sources emitted directly into the atmosphere. They are in general, wind-blown dust, sea salt, road dust, mechanically generated particles and combustion-generated particles, e.g., fly ash and soot etc. Crustal species including sodium, potassium, calcium, magnesium, manganese, aluminum, silicon, and iron are mostly present in the coarse particles. The secondary particles are formed in the atmosphere through atmospheric reactions. They are formed by two major particle formationsprocesses. The chemical coupling between the atmospheric trace gases, particles and drop phases in shown in **Figure 2.1.**

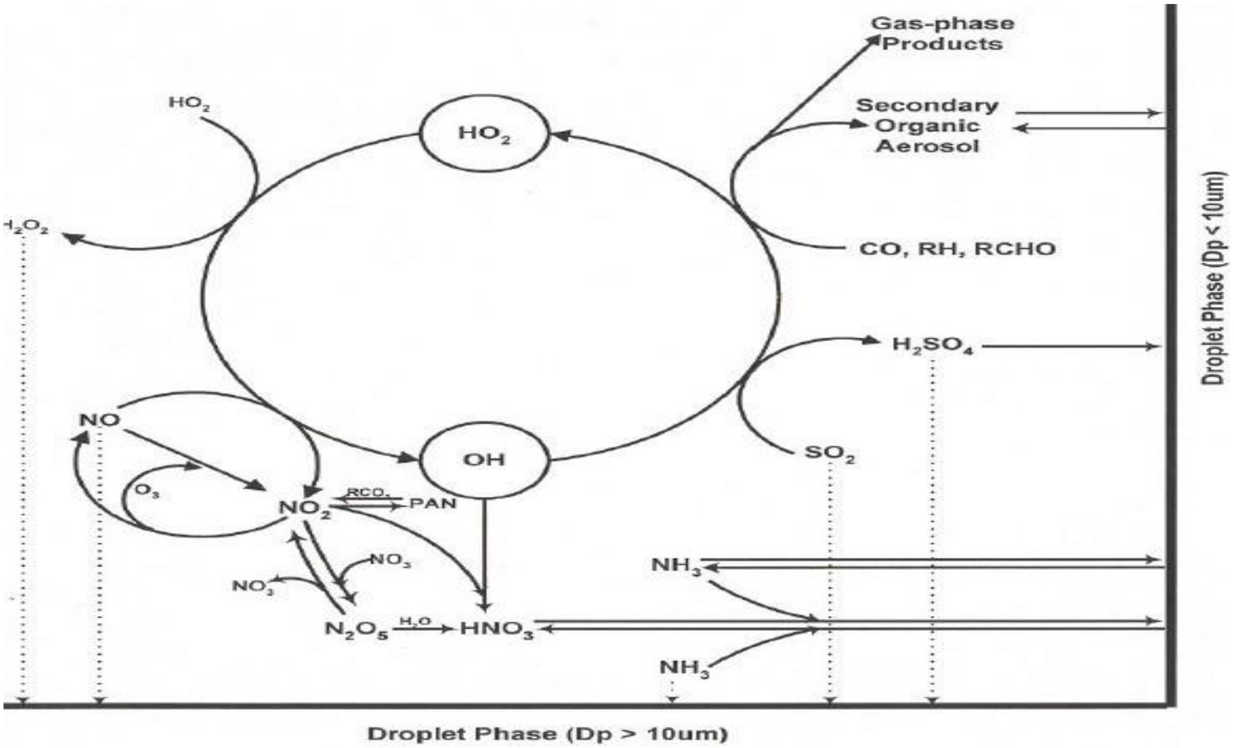


Figure 2.1 *The chemical coupling between the atmospheric trace gases, particles & drop phases* ***(Source:*** *Meng et al., 1995****)***

One process is the nucleation process by low vapor pressure gases, in which either directly emitted or formed by chemical reactions in the atmosphere.The second process is the condensation of low vapor pressure gases on the surface of existing particles. Fine particles ($PM_{2.5}$) include both the accumulation. Nucleation processes in the atmosphere, may involve organic compound, NH_3, water, and sulfuric acid (H_2SO_4) generated by the homogenous hetero molecular nucleation of H_2SO_4 vapor from the gas phase oxidation of SO_2 and OH radicals in the atmosphere.The particles in the nuclei mode may be transferred into the accumulation mode due tocoagulation.The accumulation mode of the particles is not converted ordinarily into the coarse mode, because concentrations of the particles are too low for coagulation and to be effective.Nucleation process leads to an increase in particle numbers as well as increase in particle mass, while condensation leads only to an increase of particle mass and surface area, not affect the total number of particles (Menget et al.1997).A route of incorporation of chemical species into atmospheric particulate matter is shown in **Figure 2.2.**

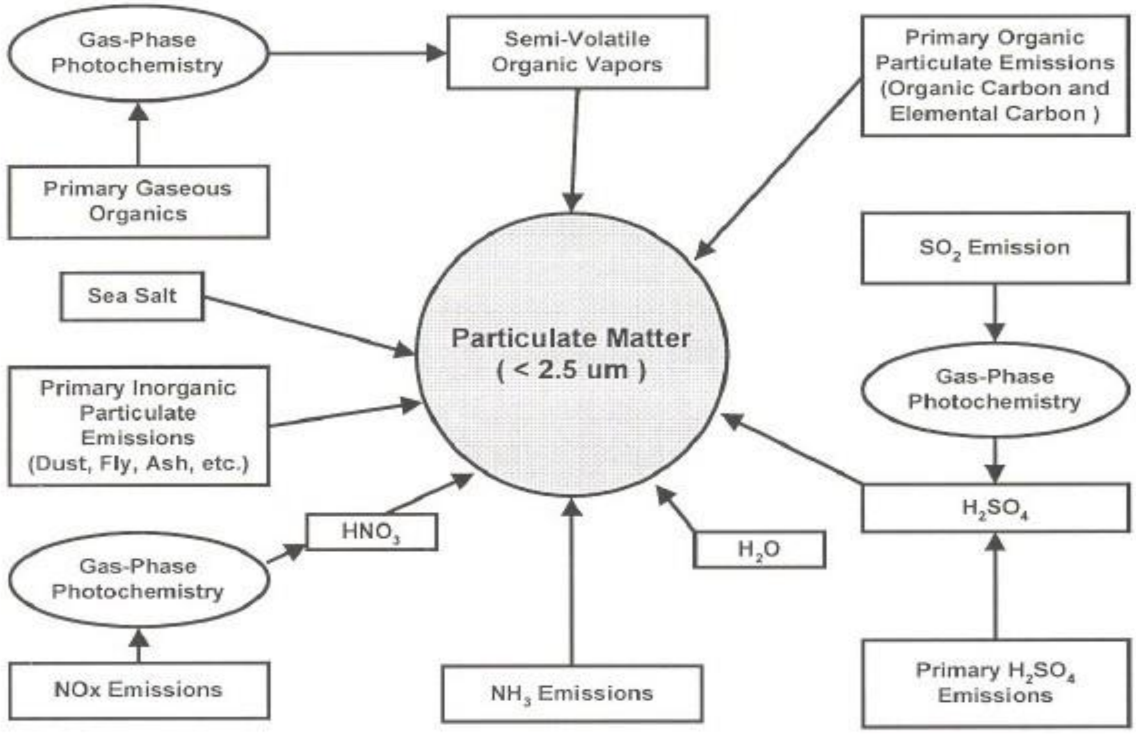


Figure 2.2 A r*outes of incorporation of chemical species into atmospheric particulate matter* ***(Source:*** *Meng et al., 1995****)***

The secondary particulate matter undergoes thermodynamic equilibrium chemical reaction is known as gas-to-particle conversion process. This process tends to reside in the accumulation mode PM range (typically 0.1 to 2.5 µm). This fine PM range is the most critical with respect to human health, visibility, and detrimental ecosystem effects caused by acid dry/wet deposition. Due to complicated chemical reactions in the atmosphere, secondary particulate matter formation rate could depend on numerous factors like precursor concentrations; reactive gaseous concentrations, such as ozone, hydroxyl radical, nitrate radical, peroxy radicals and hydrogen peroxide, organic carbon; and atmospheric conditions, such as temperature and relative humidity. The common formations of atmospheric inorganic aerosol are such as sulfate, nitrate, and ammonium, insoluble materials, organics, and crustal material by several different pathways.

There are a few studies have reported the concentrations of measured trace gases like SO_2, NO_2, NH_3, HNO_3, and PM_{10}concentrations in the ambient air at urban locations of Indo- Gangetic plain. Till now no studies has reported the gas to particle formation in urbanized industrial area in Indo-Gangetic plain. Most of the studies have reported that gas to particle conversion ration depends on seasonal and diurnal variation in NOx, NH_3, HNO_3 and $PM_{2.5}$ and PM_{10}

concentrations. Micrometeorology (WS, WD, RH and Temp) plays an important role for formation of aerosol in the ambient air. So, it is necessary to study monthly/seasonal variation of ambient trace gases and its contributions to chemical aerosol in the urbanized area of Indo-Gangetic plain. The information about seasonal variation the trace gases and its conversion is summarized below. The literature reviews of gas to particle conversion in the atmosphere are as follows:

The abundance and distribution of gaseous NH_3 and particulate NH_4^+ at Delhi was carried out during the period of 2010 and 2011. Gaseous NH_3 and particulate NH_4^+ concentrations were measured during pre-monsoon, monsoon and post-monsoon seasons of the years 2010 and 2011. Average concentrations of gaseous NH_3 during pre-monsoon, monsoon and post-monsoon seasons were recorded as 26.4, 33.2 and 32.5 $\mu g/m^3$, respectively. Gaseous NH_3 concentrations were the highest during monsoon, thought to be due to decay and decomposition of plants and other biogenic material under wet conditions, leading to increased NH_3 emission. The results showed that particulate NH_4^+ was always lower than the gaseous NH_3 during all the seasons. The concentrations of particulate NH_4^+ were recorded as 11.6, 22.9 and 8.5 $\mu g/m^3$ during pre-monsoon, monsoon and post-monsoon seasons, respectively reported by **S. Singh and U. C. Kulshrestha 2012**. The percent fraction of particulate NH_4^+ was noticed to be highest during the monsoon season, which is attributed to increased humidity levels favoring partitioning into the aerosol phase. On an average, 33.3 % of total N-NHx was present as particulate NH_4^+. Higher concentrations of NH_3 noticed during night time may be due to stable atmospheric conditions. The study highlighted that, as compared with rural sites, urban sites showed higher concentrations of gaseous NH_3 in India, which may be due to higher population density, human activities and poor sanitation arrangements.

The chemical composition of TSPM and secondary aerosol formation were investigated during wintertime fog and haze events from urban sites (Allahabad and Hisar) in the Indo-Gangetic Plain. The atmospheric abundances of EC, OC and WSOC suggested that organic matter (OM) was a major component of TSPM, followed by concentrations of sulphate and nitrate under varying meteorological conditions. The concentrations of EC, OC, and WSOC show a nearly 30% increase during fog and haze events at Allahabad and a marginal increase at Hisar; whereas inorganic constituents (NH_4^+, NO_3^- and SO_4^{2-}) are 2–3 times higher than those during clear days at both the locations reported by **Ram et al. 2012**. The sulphur and nitrogen oxidation ratios

(SOR and NOR) also exhibit significant increases suggesting possible enhancement of secondary formation of $SO_4^{2-}$and $NO_3^{\ -}$ during fog and haze events. The significant correlation between NH_4^+ and SO_4^{2-} ($R^2 = 0.66$, n = 61) and an NH_4^+/SO_4^{2-}equivalent ratio ≥ 1 during fog-haze conditions suggest near complete neutralization of sulphuric acid by ammonia. In contrast, NH_4^+/SO_4^{2-}equivalent ratios are less than 1 during normal days suggesting an NH_3-deficient environment and the possible association of $SO_4^{2-}$with mineral dust for neutralization. Secondary inorganic aerosol formation and their hygroscopic growth can have significant impact on atmospheric chemistry, air-quality and visibility impairment during fog-haze events over northern India.

A comprehensive set of 2 years of data (January 2009–December 2010) on the chemical composition of ambient aerosols were collected at a university campus in Agra (Near by state of Delhi), which lies on the Indo-Gangetic Plain (IGP). The average concentration of TSPM was 213.2±91.4 μg/m^3. The most abundant ions in TSPM were Ca^{2+}, NO_3^- and SO_4^{2-}, which contributed about 3.2%, 3.1% and 2.7%, respectively. TSPM and most of the ions, such as F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+ and K^+, had the highest mass concentrations in winter, while higher mass concentrations of Ca^{2+} and Mg^{2+} were found in summer. Higher ionic concentrations during the winter season may be attributed to a combined effect of biomass burning and meteorological conditions (low temperature, wind speed and mixing height). The $[NO_3^-]/[SO_4^{2-}]$ ratio at the present sampling site was 1.1±0.4, which indicates that there were equal contributions from both stationary sources and vehicles. In winter, high $[NO_3^-]/[SO_4^{2-}]$ ratios (1.7±0.4) could be due to the extensive use of fuel wood and cow-dung cakes to combat the cold. The acidity in aerosols is neutralized by the alkaline species, as indicated by the correlation between NO_3^- and SO_4^{2-} and sum of (Ca^{2+}, Mg^{2+} and NH_4^+) reported by **Kumari et al. 2013**. Ca^{2+} is the major acid neutralizing cation in the aerosols, followed by Mg^{2+} and NH_4^+. The crustal source contribution was observed based on the ratios of various ions with respect to Ca in soil and aerosol. On the basis of backward trajectories and the associated concentrations of the ions, the aerosol samples were classified into sectors in relation to their origin to determine the related sources. The major sources of water soluble ions identified at Agra are biomass combustion and local soil.

It was investigated that levels of fine particulate matter, SO_2 and NOx are interlinked through atmospheric reactions to a large extent. NOx, NH_3, SO_2, temperature and humidity are the important atmospheric constituents/conditions governing formation of fine particulate sulfates and nitrates. To understand the formation of inorganic secondary particles (nitrates and sulfates) in the atmosphere, a study was undertaken in Kanpur, India during the period of December 2004 to January 2005. Specifically, the study was designed to measure the atmospheric levels of NH_4^+; Ca^{2+}; Mg^{2+}; Na^+; K^+; NO_3^-, SO_4^{2-} ; Cl^-; NH_3 (gas); HNO_3 (gas); NO_2 and PM_{10} ($PM_{2.5}$:PM_{10} ratio = 0:74) covering winter and summer seasons and day and night samplings to capture the diurnal variations. Results showed NO_3^- ; SO_4^{2-} ; NH_4^+ ; K^+ are found to be significantly high in winter season compared to the summer season reported by **Sharma et al. 2007**. In winter, the molar ratio of NH_4^+ to SO_4^{2-} was found to be greater than 2:1. This higher molar ratio suggests that in addition to $(NH_4)_2SO_4$, NH_4NO_3 will be formed because of excess quantity of NH_4^+ present. In summer, the molar ratio was less than 2:1 indicating deficit of NH_4^+ to produce NH_4NO_3. The nitrogen conversion ratio (NO_2 to NO_3) was found to be nearly 50% in the study area that suggested quick conversion of NO_2 into nitric acid.

The atmospheric concentrations of $PM_{2.5}$ and PM_1 mass, water soluble inorganic components and their seasonal variations measured between the period of July 2009 and June 2010 were carried out in Durg city (20°23' to 22°02'N and 80°46' to 81°58'E), Chhattisgarh, India. A cascade impactor sampler with Whatman 41 glass filters was used to collect aerosol samples in $PM_{2.5}$ and PM_1 size fractions. The results showed that the annual mean concentration of $PM_{2.5}$ and PM_1 were 135µg/m^3 and 64.7µg/m^3, respectively. Annual cycle shows highest concentration of $PM_{2.5}$ and PM_1 mass and water soluble ions in winter season and the lowest during rainy season. This is attributed to the enhanced production of aerosols and prevailing meteorological conditions. The higher PM_1/$PM_{2.5}$ ratio (0.48) during the whole campaign clearly indicates larger PM_1 particle fractions were in $PM_{2.5}$ at this location. Out of the total aerosol mass, water soluble constituents contributed an average of 11.57% (7.48% anions, 4.09% cations) in $PM_{2.5}$ and 16.98% (11.14% anions, 5.85% cations) in PM_1. The concentrations of SO_4^{2-} and NO_3^- were highest in all size fractions and accounted for 32.76% and 13.38% of the total mass of the water soluble ions in $PM_{2.5}$ and 32.78% and 12.21% in PM_1 size fractions. Na^+, Mg^{2+} and Ca^{2+}, derived from the soil dust particles, were higher in spring and summer, as the dry weather in this season was favorable for the re-suspension of soil particles reported by **Deb et al. 2011**. The seasonal variation of Cl^-, K^+ and secondary components (NH_4^+, NO_3^- and SO_4^{2-}) were similar with high concentrations in winter and low concentrations in fall. Two principal components explaining 76.6% and 65.9% of the variance for $PM_{2.5}$ and PM_1 data set respectively were identified. Factor

1 has significant loading of species of anthropogenic origins and factor 2 showed partial associations with species of natural origins.

The sulphate size distributions was investigated at the coastal station of Mumbai city (formerly Bombay) through 1998, during the Indian ocean experiment (INDOEX) first "field phase (FFP), to fill current gaps in size-resolved aerosol chemical composition data. The paper examines meteorological, seasonal and source-contribution effects on sulphate aerosol and discusses potential effects of sulphate on regional climate. Sulphate size-distributions were largely involved with a condensation mode (mass median aerodynamic diameter or MMAD 0.6 µm), a droplet mode (MMAD 1.9-2.4 µm) and a coarse mode (MMAD 5 µm). Condensation mode sulphate mass-fractions were highest in winter, consistent with the high meteorological potential for gas-to-particle conversion along with low relative humidity (RH) reported by **Venkataraman et al. 2001**. The droplet mode concentrations and MMADs were larger in the pre-monsoon and winter than in monsoon, implying sulphate predominance in larger sized particles within this mode. In these seasons the high RH, and consequently greater aerosol water in the droplet mode, would favor aerosol-phase partitioning and reactions of SO_2. Coarse mode sulphate concentrations were lowest in the monsoon, when continental contribution to sulphate was low and washout was efficient. In winter and pre-monsoon, coarse mode sulphate concentrations were somewhat higher, likely from SO_2 gas-to-particle conversion. Low daytime sulphate concentrations with a large coarse fraction, along with largely onshore winds, indicated marine aerosol predominance. High nighttime sulphate concentrations and a coincident large fine fraction indicated contributions from anthropogenic/industrial sources or from gas-to-particle conversion. Monthly mean sulphate concentrations increased with increasing SO_2 concentrations, RH and easterly wind direction, indicating the importance of gas-to particle conversion and industrial sources located to the east. Atmospheric chemistry effects on sulphate size distributions in Mumbai, indicated by this data, must be further examined.

Several studies were carried out regarding the formation of fine particulate matter due to conversion of gas to particle in other countries also. A few reported studies were carried out in Asian countries are described below.

The linkage between $PM_{2.5}$ and gaseous pollutants (SO_2, HNO_2, HNO_3, HCl, and NH_3) were investigated for the city like Beijing, China. The samples were collected simultaneously by

Partisol ® Model 2300 Sequential Speciation Sampler with denuder-filter pack system in the spring of 2013 in Beijing. Water-soluble inorganic ions and gaseous pollutants were measured by Ion Chromatography. Results showed that the concentrations of NH_3, NH_4^+ and $PM_{2.5}$ had similar diurnal variation trends and their concentrations were higher at night than in daytime. The results of gas-to-particle conversion revealed that $[NH_3]:[NH_4^+]$ ratio was usually higher than 1; however, it was less than 1 and the concentration of NH_4^+ increased significantly during the haze episode, indicating that NH_3 played an important role in the formation of fine particle reported by **Tan et al. 2015**. Research on the sampling artifacts suggested that the volatilization loss of NH_4^+ was prevalent in the traditional single filter-based sampling. The excess loss of HNO_3 and HCl resulted from ammonium-poor aerosols and semi-volatile inorganic species had severe losses in the clean day, whereas the mass of NH_4^+ was usually overestimated during the single filter-based sampling due to the positive artifacts. Correlation analysis was used to evaluate the influence of meteorological conditions on the volatilization loss of NH_4^+. It was found that the average relative humidity and temperature had great effects on the loss of NH_4^+. The loss of NH_4^+ was significantly under high temperature and low humidity, and tended to increase with the increasing of absorption of gaseous pollutants by denuder. The total mass of volatile loss of NH_4^+, NO_3^- and Cl^- could not be ignored and its maximum value was 12.17 μgm^{-3}. Therefore it is important to compensate sampling artifacts for semi-volatile inorganic species.

Another study was also carried out in Beijing city during the period of June 2012 to April 2013. Daily basis $PM_{2.5}$ samples were collected across four consecutive seasons from June 2012 to April 2013. Major water-soluble inorganic ions, carbonaceous species and elements were analyzed to investigate their temporal variations and evaluate their contributions to visibility impairment over different seasons and under different pollution levels. The mass concentrations of $PM_{2.5}$ ranged from 4.3 to 592.4$\mu g/m^3$ with an annual average of 112.4±94.4$\mu g/m^3$. The predominant components of $PM_{2.5}$ were secondary inorganic ions (NH_4^+, NO_3^- and SO_4^{2-}) and carbonaceous compounds, which accounted for 45.9% and 24.1% of the total $PM_{2.5}$ mass, respectively reported by **Li et al. 2015**. Distinct seasonal variation was observed in the mass concentrations and chemical components of $PM_{2.5}$. The average mass concentrations of $PM_{2.5}$ were the highest in winter, followed by spring, and lowest in autumn. Light extinction coefficients (b_{ext}) were discussed over four seasons. $(NH_4)_2SO_4$ was the largest contributor

(28.8%) to b_{ext}, followed by NH_4NO_3 (24.4%), OM (19.5%), EC (7.4%), and coarse mass (7.2%), while fine soil, sea salt, NO_2 and Rayleigh made minor contributions, together accounting for 12.7% of b_{ext}. During the polluted periods, the contributions of $(NH_4)_2SO_4$ and NH_4NO_3 to b_{ext} increased dramatically. Therefore, in addition to control primary particulate emissions, the reduction of their precursors like SO_2, NOx and NH_3 could effectively improve air quality and visibility in Beijing, China.

An examination was carried out about the transportation and oxidation states of sulfur compounds from China to Japan, SO_2 concentration in the atmosphere and the non-sea salt sulphate (nss SO_4^{2-}) concentration and selenium (Se) concentration in aerosols were observed at four sites in western Japan. High SO_2 concentrations in the atmosphere and the nss SO_4^{2-} concentration and Se concentration in aerosols were found when the air mass passed through the planetary boundary layer (PBL) over large cities or industrial areas in China during winter with winds from the northwest. A bibliographic survey of Se and sulphur (S) concentrations in aerosols over eastern Asia during 1991–2004 revealed that the average Se and S concentrations in aerosols at seven sites of urban or industrial areas in China were, respectively, 15.7ng/m^3 and 7.4μg/m^3. The S concentration and Se concentration in aerosols in China were, respectively, about 3 times and 10–20 times higher than those of Korea and Japan. The Se/S ratios of aerosols in China were higher (avg. 2.5×10^{-3}) than that of Korea (avg. 0.6×10^{-3}) or Japan (avg. 0.7×10^{-3}) reported by **Kagawa et al. 2014**. SO_2 conversion rate was ascertained as 0.1% h^{-1} to 1.5% per hour using the Se (sum)/S ratio technique, when the air mass passed over large combustion sources in China and later reached Japan. The Se/S (or its reverse) technique provides useful information to ascertain the SO_2 to SO_4^{2-} conversion rate.

A study was carried out to determine the size distribution of atmospheric particulate ions at a coastal site in Portugal. A Berner impactor was used to collect size-differentiated aerosol samples from March to August 2003 in the city of Aveiro, on the Portuguese west coast. The samples were analyzed for the main water-soluble ion species. The average concentration of sulphate, nitrate, chloride and ammonium was 6.38, 3.09, 1.67 and 1.27 μg m^{-3}, respectively. The results show that SO_4^{2-} and NH_4^+ were consistently present in the fine fraction <1 μm, which represents, on average, 72 and 89% of their total atmospheric concentrations, respectively reported by **Alves et al. 2007** . The NO_3^- particles were concentrated in the coarse size. Chloride presented the characteristic coarse mode for marine aerosols. During some spring/summer events, an ammonium surplus was observed (NH_4^+/ SO_4^{2-} molar ratios >2), possibly due to greater availability of ammonia coming from agricultural activities or from the neighboring chemical industrial complex. During the remaining periods, the aerosol was found to be somewhat acidic and predominantly in the form of ammonium bisulphate (NH_4^+/ SO_4^{2-} molar ratios = 0.5-1.25). Samples collected under a major or exclusive influence of maritime air masses were essentially constituted by coarse particles with enrichment in sea salt, while for air masses of continental origin the contribution of water-soluble ionic species in the fine mode was more pronounced.

Atmospheric aerosol particles comprise a complex mixture of organic and inorganic compounds like sulfates, nitrates, ammonium, sea salt, mineral dust, organic carbon and elemental carbon etc. The emission of trace gases (SO_2, NO_2 and NH_3) are transfer to secondary air pollutants due to photochemical reactions in the atmosphere. In the monsoon season the acid rain can cause health problems, kill animals and their habitats and also have negative impact on nature. These pollutants are directly linked with increase the concentrations of particulate matter (PM). The primary precursors are converted to ammonium; nitrate and sulfate due to NH_3, SO_2 and NO_2 trace gases in the ambient air. The formation of trace gases (NH_3, SO_2 and NO_2) to secondary aerosol particles mostly depends on micro-metrological parameter (temperature, humidity solar insulation) and presence of other constituents in the atmosphere. The night time gas to particle conversion is more as compared to day time. PM_{10} consist of heavy metals, soil dust, earth crust material etc., while $PM_{2.5}$ comprise of secondary organic aerosols which are formed due to gas to particle conversion like sulphate, nitrate, ammonium and other organic compounds like organic carbon, elemental carbon, polycyclic aromatic hydrocarbons etc. The composition of coarse and fine particles and their contribution in percentage depends on industrial emission, biomass burning; windblown dust and re-suspension of road dust. The present study was carried out into the urban cum industrial area of Delhi, India which will provide adequate information about the seasonal wise variation of gas to particle conversion at Indo- Gangetic plain, India.

A few studies were carried out in India to determine the linkage between the trace gases (SO_2, NO_2 and NH_3) and particulate matter (PM_{10} and $PM_{2.5}$). The formation of fine inorganic secondary particles depends on seasonal meteorological variations. Three states of Indo-

Gangetic Plain (Delhi, Kanpur and Agra) were suggested that trace gases played an important role in the formation of fine inorganic secondary particles during winter months. This present study was carried out to understand the linkage between the trace gases and PM_{10} in urbanized mixed use area of Delhi.

2.2.4 Polycyclic Aromatic Hydrocarbons

Polycyclic (Polynuclear) aromatic hydrocarbon compounds (PAHs) are a class of complex organic chemicals, which include carbon and hydrogen with a fused ring structure containing at least two benzene rings. Atmospheric PAHs are formed as a result of incomplete combustion (pyrolysis) or high temperature pyrolytic process during anthropogenic activities like combustion of fossil fuels/ combustion of natural gas/ processing of coal and crude oil/ combustion of refuse material /cooking and tobacco smoking/ biomass burning etc. It may also produce due to natural processes such as carbonization (pyro-synthesis). The two main mechanisms like pyrolysis and pyro-synthesis are involved for formation of PAHs in the atmosphere. Low hydrocarbons form PAHs by pyro-synthesis process. When temperature increased 500^0C or greater than 500^0C, carbon-hydrogen and carbon-carbon bonds are broken and free radicals are released in the atmosphere. These free radicals are combined with acetylene, which further condenses with aromatic ring structures. PAHs on reaction with other atmospheric pollutants viz., NOx, SO_2, O_2 etc. may form hetero-PAHs and nitro-PAHs. The best known PAHs is benzo[a]pyrene (BaP) due to first chemical carcinogen to be discovered. **Figure.2.3** illustrates the formation of PAHs starting with ethane.

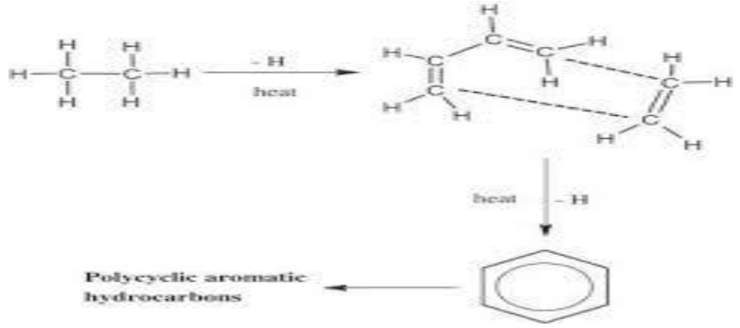
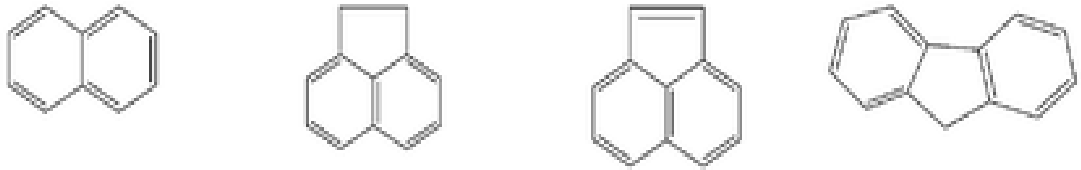
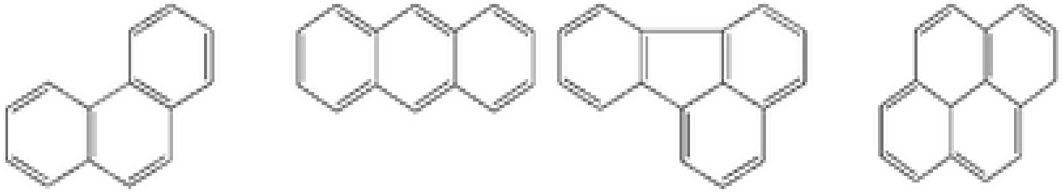


Figure 2.3 Pyro-synthesis of PAHs starting with ethane

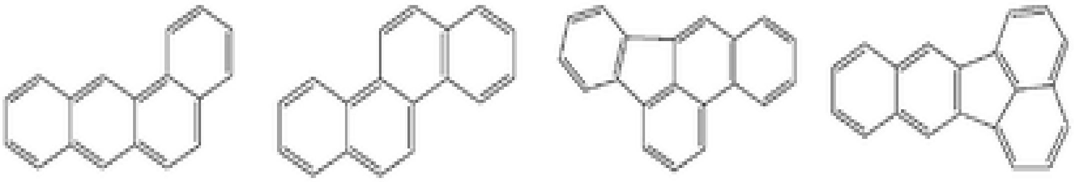
United States Environmental Protection Agency (USEPA) has identified the sixteen PAHs as carcinogen. The molecular structure of PAHs is shown in **Figure 2.4**.



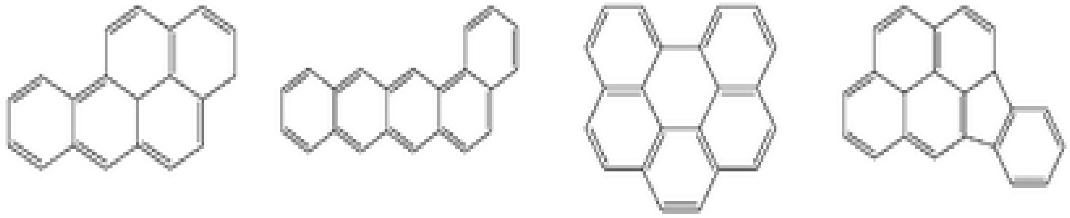
1. Naphthalene 2. Acenaphthene 3. Acenaphthylene 4. Fluorene



5. Phenanthrene 6. Anthracene 7. Fluoranthene 8. Pyrene



9. Benzo(*a*)anthracene 10. Crysene 11. Benzo(*b*)fluoranthene 12. Benzo(*k*)fluoranthene



13. Benzo(*a*)pyrene 14. Dibenzo(*a,h*)anthracene 15. Benzo(*g,h,i*)perylene 16. Indeno(*1,2,3-c,d*)pyrene

Figure 2.4 USEPA identified PAHs and their molecular structure

The physical and chemical characteristics of individual PAHs vary with molecular weight.The most common atmospheric PAHs and their molecular weight, presence of benzene rings, water solubility, classification as per International Agency for Research on Cancer (IARC) and their phase distribution in the ambient air is shown in **Table 2.1**.

Table 2.1: Common atmospheric PAHs and their characteristics

Particulate PAHs	Molecular Formula	Molecular Wt(g)	Benzene Rings	Water Solubility mg/l 25^0C	Classification as per IARC*	Particle/ Gas Phase Distribution
Naphthalene	$C_{10}H_8$	128	2	31	NE	Gas Phase
Acenaphthylene	$C_{10}H_8$	128	2	16	NE	Gas Phase
Acenaphthene	$C_{10}H_8$	128	2	3.8	NE	Gas Phase
Phenanthrene	$C_{14}H_{10}$	178	3	1.1	Group 3	Particle Gas Phase
Anthracene	$C_{14}H_{10}$	178	3	0.04	Group3	Particle Gas Phase
Fluoranthene	$C_{16}H_{10}$	202	4	0.2	Group3	Particle Gas Phase
Pyrene	$C_{16}H_{10}$	202	4	0.13	Group3	Particle Gas Phase
Benzo(a)anthracene	$C_{18}H_{12}$	228	4	0.011	Group2B	Particle Phase
Chrysene	$C_{18}H_{12}$	228	4	0.0019	Group2B	Particle Phase
Benzo(b)fluoranthene	$C_{20}H_{12}$	252	5	0.0015	Group2B	Particle Phase
Benzo(k)fluoranthene	$C_{20}H_{12}$	252	5	0.0008	Group2B	Particle Phase
Benzo(j)fluoranthene	$C_{20}H_{12}$	252	5	0.0008	Group2B	Particle Phase
Benzo(e)pyrene	$C_{20}H_{12}$	252	5	0.0015	Group1	Particle Phase
Benzo(a)pyrene	$C_{20}H_{12}$	252	5	0.0015	Group1	Particle Phase
Benzo(ghi)pyrelene	$C_{22}H_{12}$	276	6	0.00015	Group3	Particle Phase
Dibenz(ah)anthracene	$C_{22}H_{14}$	278	5	0.0005	Group2A	Particle Phase
Indo(123-cd)pyrene	$C_{22}H_{12}$	276	6	0.00019	Group2B	Particle Phase
Coronene	$C_{24}H_{12}$	300	7	0.00014	Group3	Particle Phase

Group 1	Carcinogenic to humans
Group 2A	Probably carcinogenic to humans
Group 2B	Possibly carcinogenic to humans
Group 3	Not classifiable as its carcinogenicity to humans
Group 4	Probably not carcinogenic to humans
NE	Not Evaluated

IARC*International Agency for Research on Cancer

Emission of atmospheric polycyclic aromatic hydrocarbons is gaining considerable importance in present-day scenario, as they are ubiquitous and some of them are having carcinogenic and mutagenic potency to human's health. Though PAH have few natural sources like forest fires, volcanic eruption etc. but major emission of PAHs are directly linked with urbanization, industrialization and vehicular emission. Both rural and urban environment, PAHs has significant contribution to contaminate the ambient air. Recent interest has centered to identify and quantify of PAHs in soil, water and air environment, identify their emission sources through various approaches and to evaluate their carcinogenicity and mutagenicity to human's health. The approaches distinguish anthropogenic multiple emission sources of PAHs like from petroleum combustion, diesel combustion, coal combustion industrial emission and biomass burning. This paper deals with concentrations of ambient PAHs, their emission sources and total carcinogenic and mutagenic potential risk to human's health.

In general, PAHs have high melting and boiling points for solid, low vapor pressure, and very low aqueous solubility.The solubility of PAHs decreases with increasing molecular weight, but resistance to oxidation and reduction increases. So, PAHs has different behavior, distribution in the environment, and their effects on biological systems. Low-molecular-weight PAHs (two and three rings) are weaker carcinogenic and mutagenic as compared to multi-ringed PAHs (four rings or more) and potential to health risk. Naphthalene ($C_{10}H_8$; MW=128 g), formed from two benzene rings fused together, has the lowest molecular weight of all PAHs. The environmentally significant PAHs have molecules ranged between two (e.g., naphthalene) to six benzene rings (e.g., coronene with a chemical formula $C_{24}H_{12}$; MW=300 g).A few studies were carried out in India, regarding characterization of particulate PAHs in PM_{10} in the ambient air till date and to assess its carcinogenicity and mutagenicity. PAHs are widely distributed in the atmosphere. The emission factors of atmospheric PAHs and their carcinogenic and mutagenic effects were also reviewed. The emission of PAHs are either from pyro-genic source (natural) or petro-genic source (anthropogenic).Though there are many petro-genic sources, but in global air environment, maximum emission of PAHs is from bio-fuels (57.6%) only. India is the major contributor of PAHs from bio-fuels (92.5%) followed by China (66.4%) and USA (9.1%). PAHs are one of the major contributors of airborne inhalable particles. Hence it is necessary to understand the importance to measure the individual PAHs and their emission sources, so that management control plan to reduce emission of PAHs at source only may be prepared. The reported ambient PAHs concentrations are described below.

The concentrations in both particulate and gas phase PAHs was investigated to the urban site of Delhi. Sampling was done by using modified Respirable Dust (PM ≤10**μ**m) sampler attached with polyurethane foam (PUF) plugs and compared with conventional Respirable Dust (PM ≤10 **μ**m) sampler. Total 16 EPA PAHs (gaseous + particulate) were determined by Gas Chromatograph-Mass Spectrophotometer (GC-MS). The 3-ring PAH constitutes approximately 90% of the gaseous PAHs with phenanthrene, fluoranthene, acenapthylene, and acenaphthene being the most abundant gaseous PAHs. PAHs with 4- to 6- rings accounted for 92%, 87% and 78% in samples collected during winter, summer and monsoon season respectively reported by **Singh et al. 2012**. Gaseous PAHs, particulate PAHs and total PAHs were higher during winter as compared to summer and monsoon seasons. The contribution of particulate PAHs were 1.4, 2.1, and 2.5 times higher in winter, summer and monsoon, respectively than of gaseous PAHs. Indeno[123-cd]pyrene, benzo[ghi]perylene, dibenzo[ah]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and chrysene were found to be the most abundant PAH compounds in the particulate PAHs during all the sea-sons. The result from application of diagnostic ratio suggests that the higher particulate PAHs emissions were predominantly associated with vehicular emissions along with emissions from biomass burning during winter season

The status of ambient PAHs concentrations at the six hotspot National Ambient Air Quality Monitoring sampling sites (ITO, Janakpuri, Nizamuddin, PitamPura, ShahzadaBagh, Siri Fort, Shahdra) in Delhi were carried out for three months (January, February, March) in the year 2012. The samples were analyzed for their toxicity using the GC (Gas Chromatography) method for the parameter like Benzo(a)Pyrene [BaP] and Total PAH [TPAH]. The Principal Component Analysis (PCA) was conducted using the Principal Component Extraction method. The average concentration of Benzo(a)pyrene (BaP) ranged from 0.27 to 17.86 whereas, total PAH (TPAH) ranged from 4.61 to 52.96 ng/m^3 reported by **Sharma et al. 2014**.

The seasonal distribution and the possible sources of PAHs in the atmospheric environment were carried out in Tamil Nadu, India. Passive air sampling was performed at 32 locations during the period from April 2009 to January 2010, and PAHs were quantified using a gas chromatograph-mass spectrometer. Analysis showed that the concentrations of PAHs were in the range of 5–47.5 ng/m^3 with uniform distribution in urban areas in all seasons. Pre-monsoon season showed the highest cumulative concentration of PAHs in both agricultural and coastal areas. Among PAHs, phenanthrene, fluoranthene, and pyrene levels were found to be predominant in all the samples, contributing up to 36%, 35.5%, and 24.5% of total PAHs, respectively reported by **Ramaswamy et al. 2015**. The signature of the PAHs obtained through diagnostic ratio and principal component analysis revealed that a diesel emission was the probable source of PAHs in all locations. Based on World Health Organization guidelines, the human lung cancer risk due to observed level of PAH concentration (i.e., PAHs exposure) is meager. However, the risk is predicted to be more in the coastal area during summer (18 individuals among 0.1 million people). To the knowledge of these authors, this report is the first on the seasonal analysis of PAHs using passive air sampling in India.

There is an increasing concern about the occurrence of PAHs in the environment as they are ubiquitous in ambient air and some of them are among the strongest known carcinogens. PAHs and their derivatives are produced by the incomplete combustion of organic material arising, partly, from natural combustion such as forest and volcanic eruption, but with the majority due to anthropogenic emissions. The PAH concentration varies significantly in various rural and urban environments and is mainly influenced by vehicular and domestic emissions. The review serves as a database to identify and characterize the emission sources of PAHs and hence various approaches including diagnostic ratio (DR) and principal component analysis (PCA) are discussed in detail. These approaches allow individual PAHs to be associated with their origin sources. Although the levels of low molecular weight PAHs are high in vapor phase, most of the probable human carcinogenic PAHs are found to be associated with particulate matter, especially in fine mode particles in ambient air reported by **Ravindra et al. 2008**. Many countries have proposed a non-mandatory concentration limit for PAHs, whereas the health risk studies conducted in relation to PAH exposure, urge that these pollutants should be given a high priority when considering air quality management and reduction of impacts.

The global atmospheric emissions of the 16 PAHs listed as the US EPA priority pollutants were estimated using reported emission activity and emission factor data for the reference year 2004. A database for emission factors was compiled, and their geometric means and frequency distributions applied for emission calculation and uncertainty analysis, respectively. The results for 37 countries were compared with other PAH emission inventories. It was estimated that the total global atmospheric emission of these 16 PAHs in 2004 was 520 giga grams per year (Gg/y) with bio-fuel (56.7%), wildfire (17.0%) and consumer product usage (6.9%) as the major sources, and China (114 Gg/y), India (90 Gg/y) and United States (32 Gg/y) were the top three countries with the highest PAH emissions reported by **Tao et al. 2009**. The PAH sources in the individual countries varied remarkably. For example, bio-fuel burning was the dominant PAH source in India, wildfire emissions were the dominant PAH source in Brazil, while consumer products were the major PAH emission source in the United States. In China, in addition to biomass combustion, coke ovens were a significant source of PAHs. Globally, benzo (a) pyrene accounted for 0.05% to 2.08% of the total PAH emission, with developing countries accounting for the higher percentages. The PAH emission density varied dramatically from 0.0013 kg/km^2/year in the Falkland Islands to 360 kg/km^2/year in Singapore with a global mean value of 3.98 kg/km^2/year. The major emission sources of USEPA identified PAHs in global, China, India and USA is shown in **Table 2.2.**

Table 2.2.Major emission sources of USEPA identified PAHs in China, India and USA

Source	Global	China	India	USA
Biofuel	56.70%	66.4%	92.5%	9.1%
Wild fire	17.00%	0.0%	0.0%	3.3%
Consumer product use	6.90%	0.9%	0.6%	35.1%
Traffic oil	4.80%	2.0%	Insignificant	23.0%
Domestic coal	3.70%	10.7%	1.30%	Insignificant
Coke production	3.60%	14.4%	Insignificant	Insignificant
Petroleum refining	2.40%	1.0%	Insignificant	8.70%
Waste incineration	1.90%	Insignificant	Insignificant	9.50%
Aluminum electrolysis	1.40%	Insignificant	Insignificant	1.90%
Open straw burning	Insignificant	2.0%	3.20%	Insignificant
Gasoline distribution	Insignificant	Insignificant	Insignificant	3.00%
Aerospace industry	Insignificant	Insignificant	Insignificant	2.50%
Other	1.50%	-	2.70%	3.90%
Tonnes in thousands	**530**	**114**	**90**	**32**

(Source: *Tao et al.2009****)***

The atmospheric emission of PAHs was positively correlated to the country’s gross domestic product and negatively correlated with average income.

The preliminary analysis was to assess human health risks of exposure to 16 PAHs by way of inhalation by children and adults living in urban area of Amritsar, Punjab, India. In particular, the United States Environmental Protection Agency's (USEPA's) 16 priority PAH compounds were analyzed in PM_{10} from different geographical locations by high-volume air sampler. Sum concentrations of PAHs (37–274 ng m^{-3}) were comparable with those of other cities in India as well many cities on a global scale. Pyrene, naphthalene, acenaphthene, acenaphthylene, fluoranthene, fluorene, and dibenzo(a,h)anthracene accounted for >80 % of ∑16PAH concentrations. Furthermore, the contribution of seven carcinogenic PAHs accounted for 12 % of ∑16PAHs. The estimated carcinogenicity of PAHs in terms of benzo(a)pyrene toxic equivalency (BaPTEQ) was assessed and confirmed that dibenzo(a,h)anthracene was the dominant PAH contributor (88.7 %) followed by benzo(a)pyrene (6.67 %). Homolog pattern and diagnostic ratios of PAHs suggested that mixed pyrogenic sources—including biomass burning, coal combustion, and petrogenic sources, such as vehicular emissions—are dominant PAH sources in Amritsar. Health risk of adults and children by way of PAHs was assessed by estimating the lifetime average daily dose (LADD) and corresponding incremental lifetime cancer risk (ILCR) using USEPA guidelines. The assessed cancer risk (ILCR) was found to be within the acceptable range (10^{-6}–10^{-4}) reported by **Senthil Kumar et al. 2012.**

The atmospheric particulate PAH concentrations were measured at two locations in Mumbai (formerly Bombay), India. Total PAH concentrations (seven compounds) at Saki Naka and Indian Institute of Technology (IIT) were 38.8 and 24.5 ng $m^{\sim 3}$ reported by **Venkataraman et al. 2000**. Pyrene and benz(a)anthracene + chrysene were abundant at both sites while benzo(b)fluoranthene and benzo(k)fluoranthene were abundant, in addition, at the IIT site. The large amount of pyrene in the ambient samples in Mumbai is likely from cooking-fuel combustion (animal manure, kerosene and liquefied petroleum gas) in addition to vehicular emissions. Pyrene and chrysene are also emitted from industrial oil burning while the low concentrations of benzo(a)pyrene indicate that wood burning is not a significant source. At the IIT site, primarily vehicular emissions along with cooking fuel emissions are the likely contributors while industrial oil burning is an additional contributor at Saki Naka, accounting for the higher concentrations of pyrene and chrysene/benz(a)anthracene. In urban areas vehicular emissions are likely to be the primary contributor to PAH concentrations with additional local contributors like cooking fuel or industrial emissions.

The status of ambient PAHs of Nagpur city in India was investigated in PM_{10} and $PM_{2.5}$. PAHs are by product of petroleum processing or combustion. The both forms (gaseous PAHs and particulate PAHs) can be inhaled into the lungs. Out of total sixteen PAH's Benzo(a) Anthracene [BaA], Benzo (b) Flouranthene [BbF] and Benzo (a) Pyrene [BaP] are known to be potentially weak, and moderate carcinogenic selected for this study. This report presents the profile of PAH, monitored in the particle bound ambient air of Nagpur City in Maharashtra. The study revealed that ambient B(a)A concentration ranged from 0.0 to 1.56 ng/m^3, B(b)F concentration ranged from 0.0 to 1.28 ng/m^3 and B(a)P concentration ranged from 0.0 to 1,01 ng/m^3 reported by **Battalwar et al. 2012**. The concentration of PAH's recorded were higher as compare to monsoon & summer seasons. This might be due to foggy conditions in winter season.

PAHs concentration in both particulate and gas phase at indoor and outdoor environment of urban residential and roadside homes in a semiarid region of India. The samples were collected during winter and summer season (Nov 2006–Jun 2007). In particulate phase at roadside homes the annual mean concentration of PAHs in indoor was 5.53 to 952.28 ng/m^3, in outdoor it ranged 15.47 to 1036.79 ng/m^3 whereas at urban residential homes the particulate PAHs concentration range was 4.10 to 826.73 ng/m^3 (indoor) and 8.32 to 826.73 ng/m^3 (outdoor). The annual mean concentration of gaseous phase PAHs ranged from 2.75 to 90.34 ng/m^3indoors, 2.29 to 113.56 ng/m^3 outdoors at roadside homes. In urban residential homes it ranged 2.64 to 87.58 ng/m^3 in indoor, 4.79 to 51.83 ng/m^3 in outdoor respectively. Significant seasonal variations of total PAHs concentrations were observed with higher levels during winter season period. The average BaP equivalent exposure, calculated by using toxic equivalent factors was approximately 8.99 ng/m^3 (indoors) and 14.03 ng/m^3 (outdoors) reported by **Masih et al. 2012**. Principal component analysis (PCA) revealed that in indoor the most common sources of PAHs were cooking, smoking, incense burning whereas in outdoor PAHs mainly generated from petrol and diesel combusted fuel and diesel exhaust from generator sets.

Several studies were carried out regarding the concentrations of gaseous and particulate PAHs in the ambient air in other countries. A few reported studies are described below.

Source apportionment (SA) were carried out using Positive Matrix Factorization (PMF) with a dataset of 29 individual PAH (sum of vapor and particulate forms) collected by the UK National

Network between 2002 and 2006. PAH are currently generating a great deal of interest because of their recognized toxicity, including carcinogenicity. The data were analyzed for 14 urban sites revealed four major source categories corresponding to unburned petroleum, diesel combustion, wood combustion and coal combustion. When a separate set of sites known to be influenced by local industrial sources was analyzed, three source categories were identified corresponding to the unburned petroleum, diesel combustion and coal combustion seen in the full data analysis. When SA data were applied to the individual sites, the estimated apportionment could be explained in terms of local emission characteristics. It was observed that unburned petroleum showed the highest contribution to the sum of PAH, averaging 51.9% across the network, but benzo(a)pyrene (BaP) was more influenced by the coal combustion source which contributed 59.5% across the entire network reported by **Horrison et al. 2013**. At the subset of sites with local industrial influence, industry was both the main contributor to the sum of PAH (accounting for 48.4% of PAH mass) and of BaP (67.9% of mass). A spatial analysis was also conducted in which the traffic source was evaluated by the difference between a roadside and a nearby urban background site, the urban source by difference between urban background and a rural site, and the industrial source by difference between a site close to a major steelworks subtracting data from a local urban background site. This showed considerable similarity between the net urban contribution and the road traffic factor, and between the net industrial contribution and the PMF coal factor profile. In both cases the congener profiles corresponded fairly well to UK national emissions inventory data. When PMF was applied separately to a more recent dataset for particle-bound PAH (2008-10) in three site groupings, it was able to distinguish the domestic coal burning source from the industry-related coal combustion source. For the urban sites, vehicle exhausts contributed the largest amount of particulate PAH and BaP across the whole year, with significant attribution to domestic coal combustion seen in the cold season.

Global atmospheric emissions of 16 PAHs from 69 major sources were estimated for a period from 1960 to 2030. Regression models and a technology split method were used to estimate country and time specific emission factors, resulting in a new estimate of PAH emission factor variation among different countries (like China, India, Indonesia, Brazil, Angola and united states) and over time. PAH emissions in 2007 were spatially resolved to 0.1° × 0.1° grids based on a newly developed global high-resolution fuel combustion inventory (PKU-FUEL-2007). The global total annual atmospheric emission of 16 PAHs in 2007 was 504 Gg (331-818 Gg, as inter quartile range), with residential/commercial biomass burning (60.5%), open-field biomass burning (agricultural waste burning, deforestation, and wildfire, 13.6%), and petroleum consumption by on-road motor vehicles (12.8%) as the major sources. South (87 Gg), East (111 Gg), and Southeast Asia (52 Gg) were the regions with the highest PAH emission densities, contributing half of the global total PAH emissions reported by **Shen et al. 2013**. Among the global total PAH emissions, 6.19% of the emissions were in the form of high molecular weight carcinogenic compounds and the percentage of the carcinogenic PAHs was higher in developing countries (6.22%) than in developed countries (5.73%), due to the differences in energy structures and the disparities of technology. The potential health impact of the PAH emissions was greatest in the parts of the world with high anthropogenic PAH emissions, because of the overlap of the high emissions and high population densities. Global total PAH emissions peaked at 592 Gg in 1995 and declined gradually to 499 Gg in 2008. Total PAH emissions from developed countries peaked at 122 Gg in the early 1970s and decreased to 38 Gg in 2008. Simulation of PAH emissions from 2009 to 2030 revealed that PAH emissions in developed and developing countries would decrease by 46-71% and 48-64%, respectively, based on the six IPCC SRES scenarios.

The information about conventional risk assessment of total carcinogenic and mutagenic potencies of PAH mixtures on humans health. The main emission sources of 11 particle-phase PAHs listed as carcinogenic and mutagenic agents by the IARC were collected in $PM_{2.5}$ and analyzed for risk assessment by a risk apportionment method. The contribution of sources of total PAHs of Venice-Mestre, Northern Italy was also quantified. A receptor model based on factor and multiple linear regression analyses was applied to estimate the source-specific risk associated to PAH inhalation in an urban background area of a large city. The proposed approach has discriminated the sources of mutagenic and carcinogenic congeners and their role in determining a serious hazard for human health. Results, interpreted on the basis of seasonal variations and atmospheric conditions, have shown that even though domestic heating is the main source of total PAHs in winter, a background pollution including traffic mainly accounts for the carcinogenic and mutagenic risk during the whole year reported by **Masiol et al. 2012.**

The association of ten PAH in total suspended particulate matter (TSPM) in the ambient air was carried out at two sampling sites: urban and suburban residential areas of Yokohama, Japan from

1999 to 2005. The concentrations of target compounds were determined using gas chromatography-mass spectrometry. The total concentrations were higher in urban residential area than suburban residential area. They ranged from 0.31 to 6.16 ng/m^3 with a mean of 2.07 ng/m^3 and 0.33 to 2.87 ng/m^3 with a mean of 1.02 ng/m^3 in the urban and suburban residential areas, respectively reported by **Salam et al. 2011**. The predominant compounds determined both in the urban and suburban residential areas were benzo[b]fluoranthene, benzo[ghi]perylene, indeno[1,2,3-cd]pyrene and benzo[e]pyrene. The concentrations of 5- and 6-ring polycyclic aromatic hydrocarbons were higher in the urban than the suburban residential area, accounting for 77.3 % and 72.1 % of total polycyclic aromatic hydrocarbons, respectively. Source identification was performed by principal component analysis. Two principal components were identified for each study area and these accounted for 95.9 % and 83.3 % of total variance, respectively. The results revealed that stationary source and vehicle emissions were the major pollution sources in the studied areas. The impact of emission regulations for automobiles in large Japanese cities, which were enacted during 2002 and 2003, was also studied. Based on the average total concentration, emission reduction was 47.8 % and 18.6 % in urban residential and suburban residential areas, respectively.

The understanding sources, concentrations, and transformations of PAHs in the atmosphere is important because of their potential threat for mutagenic and carcinogenic risk. The measurement of particle-bound PAHs by three different methods in the Mexico City Metropolitan Area field campaign in April 2003 presents a unique opportunity for characterization of these compounds and inters comparison of the methods. The three methods are (1) collection and analysis of bulk samples for time-integrated gas- and particle-phase speciation by gas chromatography/mass spectrometry; (2) aerosol photoionization for fast detection of PAHs on particles' surfaces; and (3) aerosol mass spectrometry for fast analysis of size and chemical composition. This research represents the first time aerosol mass spectrometry has been used to measure ambient PAH concentrations and the first time that fast, real-time methods have been used to quantify PAHs alongside traditional filter-based measurements in an extended field campaign. Spatial variation of PAH measurements suggest that motor vehicles and garbage and wood burning are important sources in Mexico City. The diurnal concentration patterns captured by aerosol photoionization and aerosol mass spectrometry are generally consistent. Ambient concentrations of particle phase PAHs typically peak at ∼110 ng m^{-3} during the morning rush hour and rapidly decay due to changes in source activity patterns and dilution as the boundary layer rises, although surface-bound PAH concentrations decay faster reported by **Marr et al. 2006**. The more rapid decrease in surface versus bulk PAH concentrations during the late morning suggests that freshly emitted combustion-related particles are quickly coated by secondary aerosol material in Mexico City's atmosphere and may also be transformed by heterogeneous reactions.

The movement of traffic has long been recognized as the major contributor to PAH emissions to the urban atmosphere stationary combustion sources in the city of Damascus, Syria. Stationary combustion sources, including residential space heating systems, are also a major contributor to PAH emissions. This study revealed the profile and concentration of PAHs in stack flue gas emissions from different kinds of space heaters in order to increase the understanding of the scale of the PAH pollution problem caused different kinds of space heaters. The characteristics of PAHs and their corresponding benzo[a]pyrene equivalent emissions were determined from a few types of domestic heaters and central heating systems to the urban atmosphere. Nine different types of heating systems were selected with respect to age, design, and type of fuel burned. The concentrations of 15 individual PAH compounds in the stack flue gas were determined in the extracts of the collected samples using high-performance liquid chromatography system (HPLC) equipped with ultraviolet–visible and fluorescence detectors. In general, older domestic wood stoves caused considerably higher PAH emissions than modern domestic heaters burning diesel oil. The average concentration of ΣPAH (sum of 15 compounds) in emissions from all types of studied heating systems ranged between 43 ± 0.4 and $316 \pm 1.4 \mu g/m^3$. The values of total benzo[a]pyrene equivalent ranged between 0.61 and 15.41 $\mu g/m^3$ reported by **Alkurdi et al. 2014**.

The hazard posed by PAHs contained in the dusts emitted from motor vehicle braking systems have been analyzed. PAHs constitute a group of chemical compounds that pose a serious danger to the human health, chiefly because of their carcinogenic properties. Investigations into the issue of environmental pollution with PAHs generated by motor vehicle traffic were carried out in connection with the work being done at PIMOT on systems to reduce dust emission from motor vehicle braking systems. The investigations included determination of PAH contents of the dust emitted from vehicle braking systems as well as the PAH concentrations in the indoor air in a room with the stand for testing dust emissions from braking systems and in the duct to carry away gases from that room. Moreover, the PAH contents of soil were measured in the context of location of the soil sampling points in relation to traffic routes. The PAH contents were measured in Warsaw and in Zabrze. The investigation results confirmed that PAHs considered as being most harmful to the human health due to their carcinogenic properties were actually present in the dusts emitted from braking systems. The PAH contents of soil were found to be very sensitive to the location of the soil sampling points in relation to traffic routes and this is a confirmation of the thesis that motor traffic is an important source of environmental pollution with polycyclic aromatic hydrocarbons reported by **Suchocka et al. 2016.**

PAH diagnostic ratios have recently come into common use as a tool for identifying and assessing pollution emission sources. Some diagnostic ratios are based on parent PAHs, others on the proportions of alkyl-substituted to non-substituted molecules. The ratios are applicable to PAHs determined in different environmental media: air (gas + particle phase), water, sediment, soil, as well as bio-monitor organisms such as leaves or coniferous needles, and mussels. These ratios distinguish PAH pollution originating from petroleum products, petroleum combustion and biomass or coal burning. The compounds involved in each ratio have the same molar mass, so it is assumed they have similar physicochemical properties. Numerous studies show that diagnostic ratios change in value to different extents during phase transfers and environmental degradation. It was reported that fluoranthene/ (fluoranthene + pyrene) value ranged between 0.4-0.5 indicated fossil fuel combustion. Fluoranthene/ (fluorene + pyrene) value less than 0.5 (<0.5) indicating petrol emission. Fluorene/ (fluorene + pyrene) value greater than 0.5 (>0.5) indicating diesel emission reported by **Tobiszewski et al. 2012.**

The application of benzo(a)pyrene (BaP)-toxic equivalent factor to polycyclic aromatic hydrocarbons (PAH) concentrations can provide a more accurate risk assessment from environmental exposure to PAH was reported by **Miller et al. 2010**. It was hypothesized that BaP-equivalent toxicity determined following residential air monitoring among young urban children may vary by season. Residential indoor and outdoor air levels of PAH measured over two-weeks in a cohort of 5–6 year old children (n = 260) in New York City were normalized to the cancer and mutagen potency equivalent factor of BaP (BaP =1). Data are presented as carcinogenic equivalents (BaP-TEQ) and mutagenic equivalents (BaP-MEQ) for the sum of 8

PAH (∑8PAH; MW ≥ 228) and individual PAH and compared across heating versus nonheating seasons. Results show that heating compared to non-heating season was associated significantly with higher (BaP-TEQ)∑8PAH and (BaP-MEQ)∑8PAH both indoors and outdoors ($p< 0.001$). Outdoor (BaP-TEQ)∑8PAH and (BaP-MEQ)∑8PAH were significantly higher than the corresponding indoor measures during the heating season ($p < 0.01$). These findings suggest that at levels encountered in New York City air, especially during the heating season, residential exposure to PAH may pose an increased risk of cancer and mutation.

This review identifies the vehicular, biofuels (wood, coal etc.) burning and industrial emissions are the significant sources of PAHs in the atmosphere. It is observed from several studies that carcinogenicity and mutagenicity of PAHs depends on benzene rings and their molecular weights. The lighter molecular weight (MW ≤ 228) PAHs are remain in the atmosphere in the gaseous phase and less carcinogen as compared to heavier molecular weight (MW ≥ 228) PAHs,which remain in the atmosphere in particulate phase and more carcinogen. Benzo(a)pyrene B(a)P, is well recognizedas most carcinogenic PAHs due to its carcinogenic and mutagenic properties.

A few studies were carried out in India regarding the PAHs concentrations in the ambient air and their source apportionment. In India till date no studies has reported the contribution of TPAHs in the urbanized mixed use area. Even outside India also contribution of TPAHs were not reported. So this study has great importance in both India and aboard. National Ambient Air Quality Standards (NAAQS) formulated by Central Pollution Control Board (CPCB) in the year 2009 prescribed the standard of BaP only. In the standard, it is mentioned that BaP concentration should not exceed 1 ng/m^3 (annual average). From the literature review it was observed that in India BaP concentration exceed 1 ng/m^3 (annual average) in multiplication of 6 to 10 times. Moreover carcinogenic and mutagenic risk of ambient particulate PAH in India till date not reported. In this thesis, the concentrations of particulate PAHs in PM_{10}, source profile and their carcinogenic and mutagenic risk study was carried out at urbanized mixed use area of Delhi.

Several studies were carried out separately in residential, commercial, industrial and traffic intersection area respectively of Delhi to measure the concentrations of particulate matter and gaseous pollutants. Not a single study was carried out in urbanized mixed use area of Delhi. The urbanized mixed use area comprises of residential, commercial and hub of industrial activities. As such mixed use areas are under natural ventilation system, which is always ‘uncontrolled’ and ‘unpredictable’ in the different climatic conditions of the season. People living or working in the mixed use area of Delhi, India may have the potential health hazards. This is the research gap in literature review for Delhi. Thus the study will fulfill the research gap.

Chapter-III

METHODOLOGY

Chapter-III

METHODOLOGY

This chapter deals with the description of sampling site, monitoring, collection, preservation and analysis protocol of particulate matter and trace gases in the ambient air in mixed use area of Delhi. The analysis protocol of chemical compounds of particulate matter eg. carbonaceous species, water-soluble ionic species, heavy metals, polycyclic aromatic hydrocarbon are also described in this chapter. The metrological parameters were collected during the study period and accordingly wind rose diagramwere prepared. The methodology adopted for source identification is also included in this chapter.

3.1 Description of sampling site

Delhi, the Capital of India is situated between latitudes 28°24' 17" and 28°53'00 N andlongitudes 76°50'24" and 77°20'37" E at 216 meters above the mean sea level (MSL). It is spread over an area of approximately 1500 sq. km. The Delhi Development Authority (DDA) is responsible for planning and implementation of various development plans for the city. The city surrounded by other major growth centers of adjoining states such as Haryana and Uttar Pradesh.

Ambient Air Quality Monitoring (AAQM) location is selected at CSIR R&D Building, Naraina Industrial Area, Phase-I (latitude $28^0$38´3.1´´N and longitude $77^0$8´0.1´´E), New Delhi-110028. The location has been selected based on land use terrain of the study area and representation of valid cross sectional distribution of downwind direction. The distance of the sampler from any flow obstacle i.e., buildings were kept more than two times the height of the obstacle above the sampler. The unrestricted air flow was maintained in the four quadrants. Certain trees may also be sources of particulate matter in the form of detritus, pollen or insect plants. Thus the selected location was kept away from more than 20 meter from the adjacent trees.

Figure 3.1 describes the location of Naraina IndustrialArea (NIA) in Delhi. The study zone has an estimated population of about 75,000 spread in the areas like Loha Mandi, Budh Nagar, NarainaVihar, Rajaouri Garden, Ramesh Nagar etc.The ring road from DhaulaKuan passes through the study zone and is about 800m (aerially) away from the monitoring location. The other main road is Naraina road connecting Loha Mandi to ring road. The several industries are located in Mayapuri industrial area in N-E and S-E direction within 3 km of selected study area. A railway line passes through the study zone. The common industries located in Naraina industrial area are small scale units like electrical, electronics, hospital equipment's, plastics, garments, printing press, engineering machinery etc. Naraina industrial area itself covers approximately 2000 industries in two phases. NIA Phase I has approximately 700 industries which includes garment, footwear, packaging, printing, dye, pan masala, electroplating, service stations etc. The major industries are located in NIA Phase-II are minerals, metal alloys, textiles, yarn and fabrics, paper and paper products, electronic goods manufacturing, grinding, cutting, forging, foundries, automobile tires, construction machinery and materials, rolling mill and machinery, batteries, extruding casting and moulding, acrylics and plastics, surface coating and finishing, printing machinery services, car service station etc. Both NIA Phases I and II are located in the same direction and close to each other. However NIA Phase-I is located in the downward direction of NIA Phase-II and approximately 0.5 km away industries of NIA Phase-II. The sampling location at NIA Phase-I was chosen as the monitoring of air pollutants as NIA Phase-I act as the receptor point of air pollutants of both NIA Phase-I and II in the industrial area of Delhi.

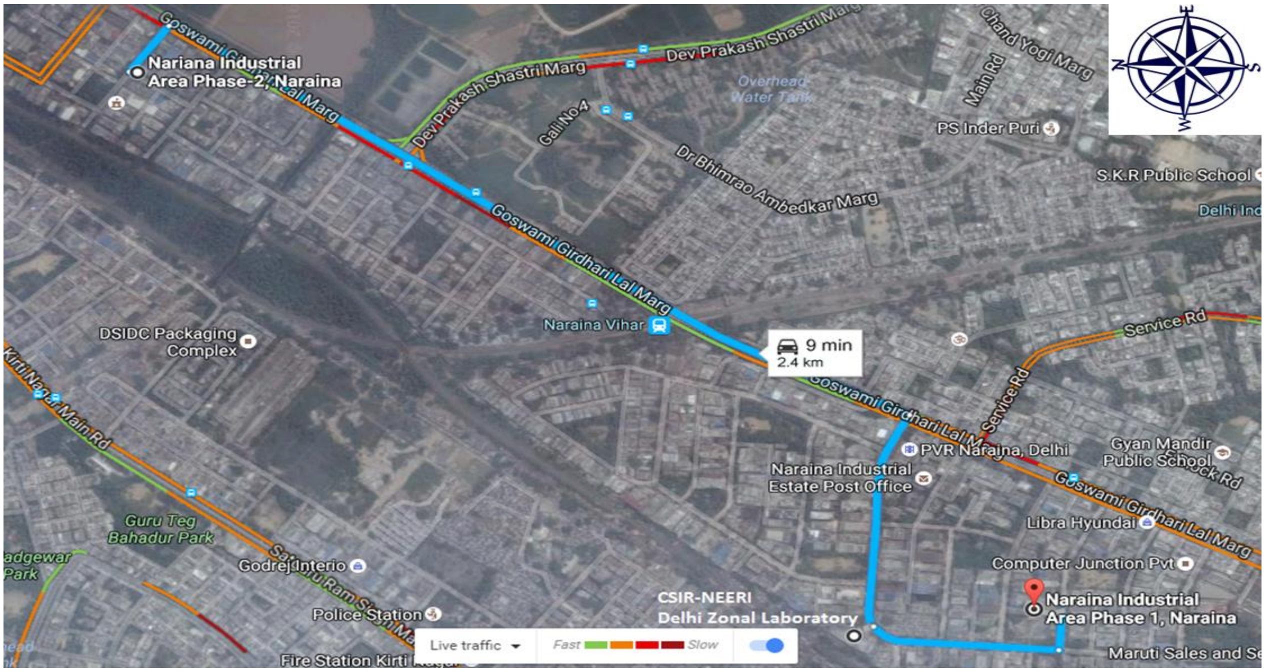


Figure 3.1 The surroundings location of Naraina Industrial area in Delhi
(Source: Google Map)

The study zone can be characterized as urbanized mixed use area (combination of residential, commercial, institutional and industrial activities) of Delhi city.

The uses of diesel generator sets are most common in household, industrial as well as for commercial purposes due to perennial power shortage, mostly pronounced in pre-monsoon season (April to June). Economically weaker section use wood, kerosene, biomass, refuse material burning for cooking activities. Biomass and refuse material burning for heating purposes is common phenomena during winterseason. The movement of private and commercial vehicles are frequent due to the importance of the location. Construction activities and poor maintenance of roads are the common problems in NIA of Delhi city.

The sampling was carried out at the roof of CSIR-National Environmental Engineering Research Institute (latitude 28 038´´3.1´and longitude 770 8´´0.1´) at a height of approximately 6 m above ground level. The samples were collected for 8 to 10 days per month for one year i.e., January 2011 to December, 2011. The sampling location in Naraina Industrial area city is shown in **Figure- 3.2.**

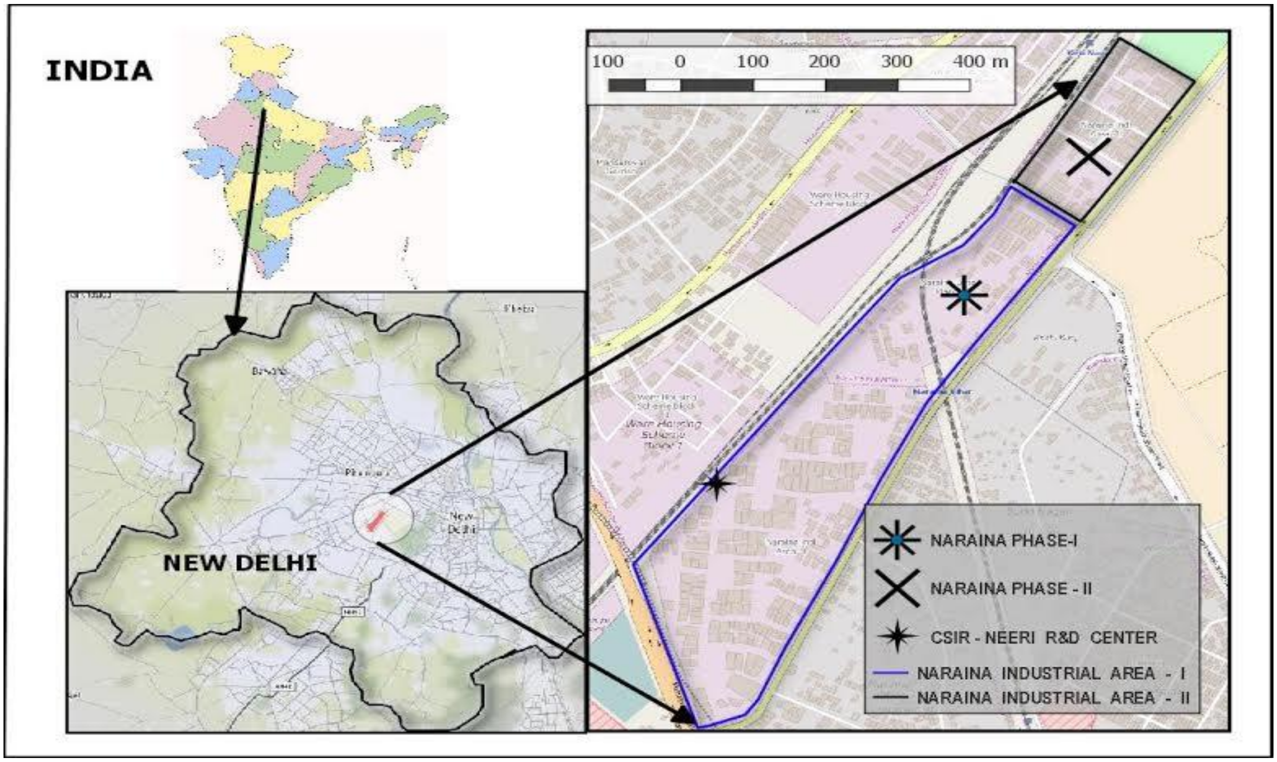


Figure 3.2 Sampling Location in Naraina, Urbanized Mixed Use Area of Delhi City

3. 2 Monitoring protocol for collection of air samples

Ambient particulate (PM_{10} and $PM_{2.5}$) and gaseous samples were collected as per the standard methods of CPCB. The samples were collected by using gravimetric methods. Two instruments were used simultaneously for collection of each size of particulate matter. The gaseous samples were collected by attaching separate gas collection system i.e. Envirotech APM 433 with RDS-Envirotech, APM 460 NL. The samples were collected 8 to 10 days in a month for one year (January 2011 to December 2011). The samples were collected at four distinct seasons: winter (December–March), pre-monsoon (April–June), monsoon (July–September) and post-monsoon (October–November). The filter paper were pre-baked in a muffle furnace at 550^0C for 6 h to remove the organic impurities and kept in desiccators for 24 h before and after sampling. The quality in monitoring and analyses of these pollutants is controlled by adopting standard procedures and calibration of the samplers /instruments. The list of samples collected during the study period at the Naraina mixed use area of Delhi is shown in **Annexure-I.**

3. 2.1 Monitoring and analysis of particulate matter (PM_{10})

The air samples of PM_{10} (particles less than or equal to 10 micrometers in diameter) were collected by respirable dust sampler (RDS- Envirotech, APM 460 NL) and Fine Dust Sampler (Envirotech APM 550). Whatman glass fibre filterpaper (size 8” x 10”) was used for RDS-Envirotech, APM 460 NL instrument whereas quartz filter paper (size 47 mm) was used for Envirotech APM 550 instrument. PM_{10} samples were carried out simultaneously 24 hourly bases at a flow rate of 1 to 1.5 m^3/min. The size of PM_{10} are generally vary from 2.5 to 10 micrometers in diameter. The instruments technique incorporates air to be drawn through cyclone which captures particles greater than 10 micron and the particles equal or less than 10 micron are retained on the filter papers.

Figure 3.3 Envirotech, APM 460 NL and APM 550New Delhi (Air Samples of PM_{10})

The initial flow rate as well as time of starting of the instruments was recorded before starting the air sampling. Flow rates were checked after every hour and recorded to the field data sheet. The filter papers were kept in desiccators for 24 hour before and after sampling to de-moisturize them. Whatman glass fibre filters were used to measure the concentrations of PM_{10} in the ambient air and other secondary analysis of chemical aerosols like heavy metals, cation, anion, particulate polycyclic aromatic hydrocarbons etc. Quartz filter papers were only used for measurement of particulate carbonaceous aerosols.

The conditioned and weighed filter papers were transported to the sampling location in closed envelopes to avoid contamination of the filter papers. The weights of Whatman glass fibre filterpapers were measured by Mettler –Toledo AG balance (Greifensee, Switzerland, Europe) with a resolution of ±0.1mg. The concentrations of PM_{10} ($\mu g/m^3$) were calculated by difference between initial and final weight of filter paper divided by the total volume of air passed during the sampling period.

PM_{10} (µg/m^3) = ((W$_f$-W$_i$) x 10^6)/ V

Where:

PM_{10} = Mass concentration of particulate matter less than 10 micron in µg/m^3
W_i = Initial weight of filter paper in gm
W_f = Final weight of filter paper in gm
V= Volume of air samples in m^3
10^6= Conversion to gm to µg

3. 2.2 Monitoring and analysis of particulate matter ($PM_{2.5}$)

The air samples of $PM_{2.5}$ (particulate matter 2.5 micrometers or less in diameter) were measured using Fine Dust Sampler (Envirotech APM 550). The instrument maintained the constant flow rate by mass flow controller coupled to a microprocessor into specially designed inertial particle-size separator (cyclones or impactors). $PM_{2.5}$ was collected in two types of filter papers namely quartz filter papers and teflon filter paper on 24 hourly bases at a constant volumetric flow rate of 16.7 lpm (1 m^3/h). The initial flow rate as well as time of starting of the instruments was recoded before starting of the air sampling. Flow rates were checked after every hour and recorded to the field data sheet. Teflon filters were used to measure the concentrations of $PM_{2.5}$ in the ambient air. Whereas quartz filter paper were used for measurement of particulate carbonaceous aerosols concentrations in the ambient air. The filter paper were pre-baked in a muffle furnace at 550^0 C for 6 h to remove the organic impurities and kept in desiccators for 24 h before sampling. The filter paper were equilibrated (pre and post sampling) in a controlled environment at 45±5% humidity and 25±2^{0}C temperature for a minimum period of 24 hours prior to weighing. The balance room was also maintained at the same condition.

Figure 3.4 Envirotech, APM 550, New Delhi (Air Samples of $PM_{2.5}$*)*

Whatman Teflon filter papers were measured by six digit microbalance – Sartorious Micro Balance.

Figure 3.5 Sartorius microbalance used for weighing PM10 and PM2.5 Filter Paper

The concentrations of $PM_{2.5}$ ($\mu g/m^3$) were measured by difference between initial and final weight of filter papers divided by an amount of total volume of air passed during the sampling period.

$PM_{2.5}$ ($\mu g/m^3$) = ((W_f -W_i) x 10^6) / V

Where:

$PM_{2.5}$= Mass concentration of particulate matter less than 2.5 micron in $\mu g/m^3$
W_i = Initial weight of filter paper in gm
W_f = Final weight of filter paper in gm
V= Volume of air samples in m^3
10^6= Conversion to gm to µg

To maintain QA/QC of the analysis, one tenth of the samples were re-weighed by adopting the same procedure to calculate particulate matter (PM_{10} and $PM_{2.5}$) concentrations. The both the sizes of the filter papers were reweighed to cross check the variation of the concentrations were within the range of 5% of the calculated value of the observed concentrations.The filter papers were stored in a (4^0C) refrigerator until secondary analyses were carried out.

3.3 Monitoring protocol for collection of gaseous pollutants

A set of three impinges in series (having 20 ml of absorbing solution in each impinges) are kept in an ice bath for each of selected gases during ambient air sampling of trace gases.

Figure 3.6 Envirotech, APM 460 NL &APM 330, New Delhi (Air Samples of Gaseous)

The measurements of (SO_2 NO_2 and NH_3) were done by standard wet chemical methods of CPCB. Gaseous samples of SO_2, $NO_2$and NH_3 were collected simultaneously with a separate attachment i.e. Envirotech APM 433 attached with respirable dust sampler RDS-Envirotech, APM 460 NL on 24 hourly bases.

3.3.1 Monitoring and Analysis of SO_2

The method for determination of SO_2in air is Improved West and Gaeke Method. SO_2 from air is absorbed in a solution of potassium tetra chloromercurate. Total 20 ml of absorbing media were taken in a clean small (35 ml capacity) impinger and air was allowed to pass through it by using suction source. The flow rate of 1.0 L/min was maintained with the help of manifold and flow rate of air was continuously measured after every hour throughout the sampling period with the help of rotameter. The top of the impinger was removed and samples were kept open for 20 min to allow any ozone to decompose. One impinger was kept blank filled with 20 ml of AM as blank. 1 ml of salfamic acid, 2 ml of para-rosaniline and 2 ml of formaldehyde solutions were added in each samples including blank samples. Mix the reagents thoroughly after addition of each reagent. Make up the volume of each upto 25 ml with distilled water including blank tube. The final solution was thoroughly checked to maintain the pH of 1.6±0.1. Otherwise phosphoric acid solution is continuously added on the mixed samples. The solutions were kept for 30 minutes for developing the colour. A dichlorosulphitomercurate complex was formed. Once formed, this complex is generally stable to strong oxidants such as ozone and oxides of nitrogen. The complex is made to react with pararosaniline and formaldehyde to form the intensely colored pararosanilinemethylsulphonic acid. The absorbance of the solution is measured by means of a suitable spectrophotometer.In the meantime spectrophotometer was warm up. A UV spectrophotometer was used for measurement of absorbance at 560 nm. The zero reading was adjusted with cuvette (made of quartz only) with blank solution. The blank solution was checked for 100% transmission. The samples were placed to cuvette and noted the % of transmission. The concentrations of SO_2were computed using the standard calibration curves. Precision, accuracy, and detection limit of the method are 4.6%, ±10.4%, and 0.75 μg SO_2 per sample, respectively. The minimum detection limit of the concentration of SO_2 is 2 $\mu g/m^3$. The concentration of SO_2 ($\mu g/m^3$) in the sample was calculated as follows:

C (SO_2 µg/m^3) = ((A-A_0) x10^3 x B)/V

Where:
A = Sample absorbance
A_0= Reagent blank absorbance
10^3= Conversion litres to cubic meters
B= Calibration factor, µg/absorbance
V= Volume of air samples in liters

3.3.2 Monitoring and Analysis of NO_2

The method for determination of NO_2in air is Jacob–Hochheiser modified method. Ambient NO_2 was collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. Absorbing Media used for NO_x contained 0.4% sodium hydroxide and 0.1% sodium arsenite in distilled water. Total 20 ml of absorbing media were taken in a clean small (35 ml capacity) impinger and air was allowed to pass through it by using suction source. The flow rate of 0.5 L/min was maintained with the help of manifold and flow rate of air was continuously measured after every hour throughout the sampling period with the help of rotameter.

One impinger was kept blank filled with 20 ml of absorbing media. One ml of hydrogen peroxide, 5 ml of sulfanilamide and 1 ml of N-(1-naphthyl)-ethylenediamine di-hydrochloride (NEDA) solutions were added in each samples including blank. Mix the reagents thoroughly after addition of each reagent. Make up the volume of each upto 30 ml with distilled water. The solutions were kept for 10 minutes for developing the colour. The concentration of nitrite ion produced during sampling was determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulfanilamide and NEDA. Nitric oxide (NO) has a positive interferant and carbon dioxide (CO_2) has a negative interferant. The average error is resulting from normal ambient concentrations on NO and CO_2 are small for most monitoring situations and does not necessitate applying a correction to measurements obtained with the method. However the potential interference from SO_2 was eliminated by converting any SO_2 to sulphate with hydrogen peroxide. Precision, accuracy, and detection limit of the method are 2.6%, ±14.6%, and 1 µg NO_2 per sample, respectively.The minimum detection limit of the concentration of NO_2 is 9µg/m^3. In the meantime spectrophotometer was warm up. UV spectrophotometer was suitable for measurement of absorbance at 540 nm. The zero reading was adjusted with cuvette (made of quartz only) with blank solution. The blank solution was checked for 100% transmission. The samples were placed to cuvette and noted the % of transmission. The concentrations of NO_2 were computed using the standard calibration curves. The concentration of NO_2 ($\mu g/m^3$) in the sample was calculated as follows:

$$\mathbf{NO_2 = (C\ NO_2 \times V_s \times D)/\ (V_a \times 0.82 \times V_t)}$$

Where:
NO_2 = Concentrations in $\mu g/m^3$
CNO_2 = NO_2Concentration in analyzed sample in µg
V_a= Volume of air sample in m^3
V_s = Final volume of sampling solution
V_t= Aliquot taken for analysis
D= Dilution factor (D= 1 for no dilution; D= 2 for 1:1 dilution)
0.82 = sampling efficiency of the standard method

3.3.3 Monitoring and Analysis of NH_3

The method for determination of NH_3in air is Indophenol Blue method. Ammonia in the atmosphere is collected by bubbling a measured volume of air through a diluted solution of sulfuric acidto form ammonium sulfate. The ammonium sulfate formed in the sample was analyzed colorimetrically by reaction with phenol and alkaline sodium-hypochlorite to produce indophenol, a blue dye. The reaction is accelerated by the addition of sodium nitro-prusside as a catalyst. Total 20 ml of absorbing media were taken in a clean small (35 ml capacity) impinger and air was allowed to pass through it by using suction source. The flow rate of 0.5 L/min was maintained with the help of manifold and flow rate of air was continuously measured after every hour throughout the sampling period with the help of rotameter.

2 ml of buffer, 5 ml of working phenol solution were added in each samples including blank. 2.5 ml of working hypo-chloride solutions were added and rapidly mix. After mixing all the reagents thoroughly, the samples were kept in the dark place for 30 min to develop colour. The minimum detection limit of the concentration of NH_3 is $2\mu g/m^3$. The absorbance was measured at 630 nm wavelength by spectrophotometer.

$\mathbf{C_{NH3} = ((A_s - A_b) \times C_f)/V_a}$

Where:

$\mathbf{C_{NH3}}$ =Concentration of Ammonia inµg/m^3

As = Sample absorbance

A_b= Reagent blank absorbance

V_a= Volume of air sampled in m^3

$\mathbf{C_f}$= Calibration factor

To maintain the QA and QC of the collection and analysis of particulate and gaseous pollutants preventive maintenance of equipment, calibration of the equipment and analysis of blanks are required as per the standard method of CPCB.

3. 4 Determination of aerosols

The chemical properties of aerosols are essentially to be assessed as they have adverse effects on various issues on human health, air quality and global climate change. However, the identities and concentrations of many atmospheric species, particularly organic carbon, and polycyclic aromatic hydrocarbon are still unknown. To characterize the chemical composition of the complex mixture of air, the characterization of particulate matter and its source apportionment with respect to organic carbon, polycyclic aromatic hydrocarbon, heavy metals and conversion of gas to particle are necessary to understand the contribution of each aerosol compounds in percentages in a particulate mass.

3.4.1 Determination of carbonaceous aerosols (OC, EC and TC)

Carbonaceous species like organic carbon (OC) and elemental carbon (EC) have significant influence on climate change and having adverse effects on human health. EC is the dominant anthropogenic absorber of solar radiation in the atmosphere. It also absorbs thermal infrared radiations from the ground and within clouds. EC (also known as Black Carbon) directly heats the surface on which it is deposited. In case of snow and ice, this leads to fast melting of ice. Moreover, EC or Black Carbon (BC) changes albedo (surface reflectivity) of ice and snow, leading to additional warming of surface and melting. It is the second most important component of global warming after CO_2 and exerts positive radioactive force. OC is mainly a scattering medium and exerts a negative climate forcing influence; as a result it produces a cooling effect on atmosphere. The combination of OC and EC is termed as total carbon (TC).

The samples were analyzed for OC and EC using Desert Research Institute (DRI), Model 2001A Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). DRI thermal/optical carbon analyzer is based on preferential oxidation of OC and EC compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in a helium atmosphere at low temperature, while EC is not oxidized and removed.

A 0.5 cm^2 punch from the exposed filter was analyzed using IMPROVE_A analysis protocol (Chow et al., 2007), in which the sample was heated to four temperature plateaus (120^0C, 250^0C, 450^0C and 550^0C) in pure helium and three temperature plateaus (550^0C, 700^0C and 800^0C) in 98% helium and 2% oxygen. This produced four OC fractions (OC1, OC2, OC3, and OC4 at 120 ^{0}C, 250^0C, 450 ^{0}C and 550^0C) respectively, in a helium atmosphere. A pyrolyzed carbon fraction (OP), was determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere. Three EC fractions (EC1, EC2, and EC3 at 550^0C, 700^0C, and 800^0C) respectively were determined in a 2% oxygen and 98% helium atmosphere.

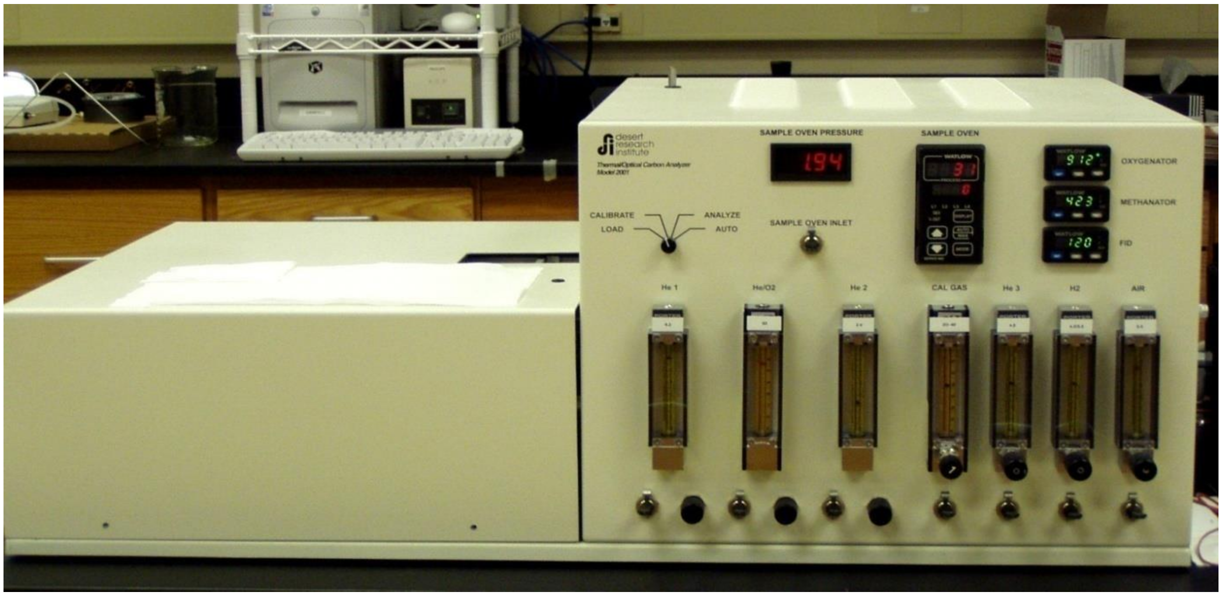


Figure 3.7 DRI Model 2001A Thermal/Optical Carbon Analyzer

The carbon fractions evolved during the continuous heating process were oxidized to carbon dioxide (CO_2), then converted to methane (CH_4) and finally subsequently quantified by Flame Ionization Detector (FID). The end of each analysis, a fixed volume of 5% CH_4 in helium (as an internal standard) was injected to monitor the efficiency of FID. Sucrose solution was used as an external standard to ascertain the conversion efficiency of CO_2 to CH_4 in this adopted thermo-optical method. The overall analytical uncertainty in the measurement was calculated by summing up the absolute and relative uncertainties.

Standardization of OCEC instrument was carried out by sucrose solution (3.2 $\mu g\ \mu l^{-1}$). 10 µl of sucrose solution gives 32.0±1.8 µg OC. To maintained QA/QC, the analyzer was initially calibrated using a blank punch of pre-heated quartz filter paper and standard sucrose solution was freshly prepared at every time. Sampled quartz filter papers were also analyzed similarly for blank corrections. The overall blank concentrations from the quartz filters for OC and EC were 0.5±0.2 and 0.0±0.02 $\mu g\ cm^{-2}$, respectively. These were subtracted from the measured OC and EC concentrations of the aerosol samples.The minimum detection limits of DRI carbon analyzer are 0.82$\mu g/cm^2$ for TC and 0.18$\mu g/cm^2$ for EC respectively.The calculation of OC, EC and TC are given below.

OC= OC1+ OC2+OC3+OC4+OP

EC =EC1+ EC2+EC3 - OP.

TC = OC+ EC

3.4.2 Determination of water-soluble ionic species

Major anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) and major cations (NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}) in aerosol samples were determined by using by Ion Chromatograph (DIONEX-ICS-5000, USA). The collected filters were extracted for 90 min in ultrasonic extractor for the determination of water-soluble ions. The extract was filtered through Whatman glass fibre filter paper and transferred to polypropylene sample bottles (these bottles were dipped in 2% HNO_3 overnight before storage and then again dipped in de-ionized distilled water overnight to remove any impurities in these bottles. The concentrations of F^-, Cl^-, NO_3^- and SO_4^{2-} were determined by using an Ion Pac-AS11-HC analytical column (4x250mm, Dionex, USA) with a guard column (IonPac AG11-HC, 4 x 50mm, Dionex, USA), ASRS-300 4 mm anion micro-membrane suppressor, 20 mM of NaOH (50%w/w) as eluent and triple-distilled water as regenerator were used for sample preparation. After each analytical run, the calibration curves were displayed on the screen, and a visual check was made for linearity and replication.Na^{+}, K$^{+,}$ Ca^{2+}, Ba^{2+} and Mg^{2+} were determined by using a separation column (IonPac CS17-HC, 4x250 mm, Dionex, USA) with a guard column (IonPac CG17-HC, 4x50 mm, Dionex, USA),suppressor CSRS-300 (4mm, Dionex, USA) and 5mM of MSA as eluent.

The IC system was fitted with a 25µL of sample loop that was used to introduce the sample manually. Chromatographic data were collected at 5Hz and chromatograms were processed using the Chromeleon (R) software. The working standards were prepared from stock standard solutions procured from M/S Dionex. All the standard solutions were filtered using 0.45µm nylon membrane filters (Millipore) and degassed by ultra-sonication.

Figure 3.8 DIONEX-ICS-5000, USA (Cation and Anion Analyzer)

For quality control, unexposed filter paper was extracted as the procedure described above and analyzed for blank corrections. The blankvalues were subtracted from the measured ionic concentrations of the aerosol samples.

3.4.3 Determination of heavy metals (HMs)

All analytical grade reagents were used for analysis of airborne heavy metals (HM). The standard metal stock solutions (1000 ppm) were used to prepare working standards. MilliQ type I water was used for dilution and other preparatory work for HM analysis. Metal analysis was carried out by inductively coupled plasma optical emission spectrophotometry (model iCAP 6300 Duo, Thermo Fisher Scientific, Cambridge, England).

Figure 3.9 Thermo Fisher iCAP 6300Duo, England (Heavy Metal Analyzer)

The composited papers (in equal weight) were digested and analyzed for airborne HM concentrations in PM_{10} size of particulate matter. Initially, a known weight of filter paper was digested with concentrated acid solution (10 ml of HNO_3 + 3 ml of HF) in a microwave digester. The final extraction volume was 20 ml. The excess acid was boiled off after digestion. The dry residue was re-dissolved in 2.5 ml of HNO_3 and 10 ml of double distilled water by gentle heating. The solution obtained was cooled and diluted to 100 ml in a graduated flask by triple washing with MilliQ water and then filtered (Killare et al. 2004: Gaghate and Hasan 1999). The reagent blank was also prepared by digesting blank/ unexposed filter paper by adopting the same protocol. The concentrations of HM were calculated by comparing the absorbance of the samples with standard metal solutions. The standard solution was repeatedly aspirated to ensure the calibration was within the limits of a control chart. To achieve QA/QC, one tenth of the samples were analyzed in duplicates. The level of agreement for duplicate analyses was fixed to ±5%. A reproducibility test indicated the stability/precision of the instrument was within the range of 5% of the calculated value. Otherwise standard calibration process was repeatedly performed. Blank samples were also repeated after 10 samples of each analysis.

Shewart's analytical quality control chart was also maintained for good quality data. The detection limit and working range for each metal were followed in the working instrument. To produce good quality data, quality control checks were performed and independent audits of the measurement process; documentation of the data and use materials, instruments and measurement procedures were kept in record by adopting the appropriate standard of reference.

Accuracy, pretreated Certified Reference Material (CRM) was analyzed repeatedly to understand the stability/precision of the instrument. The mean and standard deviation were calculated. If the calculated value given for the CRM was within the interval of mean ± standard deviation, indicated that the instrument was ready for sample analysis. Otherwise the whole process was rechecked again. The procedure followed to determine the metal concentrations is given below.

$$\mathbf{C = ((M_s - M_b) \times V_s \times F_a) / (V \times F_t) \quad and \quad V = Q \times t}$$

Where:

C =Concentration, µg metal/m^3

M_s = Metal concentration, µg/ mL

M_b= Blank concentrationµg/ mL

F_a= Total area of exposed filter in cm^2

V= Volume of air sampled in m^3

F_t= Area of filter taken for digestion in cm^2

Q = Average sampling rate, m^3/ min

t= Time in minutes

3.4.4. Determination of polycyclic aromatic hydrocarbons (PAHs)

PAH was measured by adopting United State Environmental Protection Agency (USEPA) method of TO-13. This method is designed to collect particulate phase PAHs from ambient air, fugitive emissions and to determine individual PAH compound by using capillary gas chromatograph equipped with flame ionization detector (FID). It is a high volume (1.2 m^3/ min) sampling method capable of detecting sub.ng/m^3 concentration of PAH in 24 hours sample (480 m^3sampling volume of air).

After sampling, filter papers were kept in the controlled laboratory conditions (20-25^{0}C) in an envelope marked with necessary identification information. Filters were wrapped in aluminum foil and kept it in refrigerator at 4^{0}Cin dark environment to avoid photo oxidation of PAHs.

A piece of each filter paper containing particulates-phase PAHs was cut into strips using scissors and transfer to 250 ml beaker. Add 30ml of HPLC-grade dichloromethane (DCM) and then extracted ultrasonically for 30 min in an ultrasonic bath, followed by mechanical shaking for 30 min. This process was repeated for twice for complete extraction of particulate PAHs. When the extract procedure was completed, and the samples were then filtered through a 0.45 µm PVDF (Polyvinylidene fluoride) syringe filters (make: Millipore). The filtrate was evaporated to dryness with an evaporator (Zymark, Turbovap 500). The filtered samples were stored in 2 µl capacity of amber vial having gas tight syringe. The samples were analyzed through GC (make: Perkin Elmer, model no. Clarus500).

Stock Standard Solution of sixteen PAHs mix (EPA 610 PAHs), were purchased from Supelco (Bellefonte, PA, USA) was usedfor analysis of PAHs. The selected PAHs included are naphthalene, acenapthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[123-cd]pyrene, dibenzo[ah]anthracene, and benzo[ghi]perylene. The working standard solutions (5, 10, 15, 20, 25 ng/µl concentrations) were prepared from stock solution. Each µl of working standard solutions (5, 10, 15, 20, 25ng/µl) were injected in triplicate and the area ratio were plotted to analyze PAHs compounds. The instrument was internally calibrated as per its manual/ software instructions. Laboratory blank samples were routinely analyzed to evaluate analytical bias and precision of the PAHs data. If replicate analysis provides an error within the range of ±10% to ±15%, indicating the analyzer was ready for sample analysis. Individual PAHs of the blank samples were normally very low and in most cases the GC-MS integrated area was less than the detection limit.

3.4.4.1. GC based analysis for particulate PAHs

The final step of PAH analysis consisted of the GC separation, identification and quantification of individual PAHs. To fulfill the above mentioned purpose, a GC-5890B Gas Chromatograph and MSD-5971A Mass Selective detector were normally used. The both the required materials were supplied by Hewlett-Packard (Paolo Alto, CA, USA).

Figure 3.10 GC Perkin Elmer, Clarus 500 (Polycyclic Aromatic Hydrocarbon Analyzer)

Injection of the samples was operated in split-less mode, with portioning valve closed for 60sec. The separation capillary column was DB-5MS type (L=30m, i.d= 250µm). The samples were analyzed in the helium (0.5 ml/min) carrier gas environment. PAH elution was repeatedly run under the controlled temperature program, as described below:

$T_0 = 90^oC$, $t_0 = 1min$, $rate_1 = + 20^oC/min$ up to $T_1 = 170^oC$,

$T_1 = 170^oC$, $t_1 = 2min$, $rate_2 = + 4^oC/min$ up to $T_2 = 280^oC$,

$T_2 = 280^oC$, $t_2 = 20min$, $rate_3 = + 5^oC/min$ up to $T_3 = 290^oC$, $t_3 = 5min$

Five point calibrations were carried out for quantification of PAHs. The analytical method was repeatedly checked for the precision and accuracy of the calculated data. For recovery, efficiency of PAHs surrogate standards were also added to the samples prior to the extraction and analysisof PAHs. The recoveries should fall within the range of 75-125%. The retention time of each sample PAH component was compared with the standard solution of individual 16 PAHs. The fragmentation pattern and masses of molecular ions of PAHs were compared with the standard 16 PAHs solutions. The concentrations of each individual PAHs (ng/m^3) were calculated by using the following formula.

C = (Cs x Ve)/(Vi x Vs) and V= Q x t

Where:

C =Concentration of PAHs in ng/µl in the sample extract recorded by GC

Ve = Final volume of extract in µl (i,e 1000)

Vi= Injection Volume (ie., 1µl)

V= Volume of air sampled in m^3

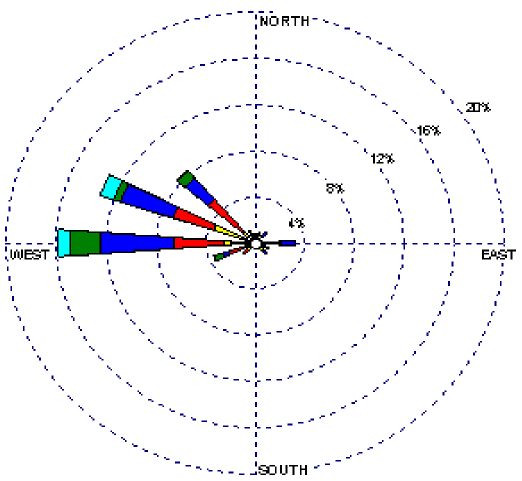
Q = Average sampling rate, m^3/ min

t= Time in minutes

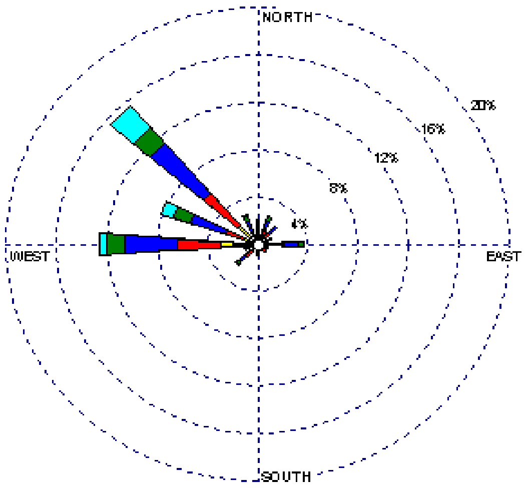
3. 5 Meteorology for the year 2011

The meteorological parameters are contributing significant concentrations of particulate and gaseous pollutants in the ambient air. The four meteorological parameters like relative humidity, temperature, wind speed and wind direction are generally measured simultaneously with ambient air pollutants sampling at the site. In the present study the status of the meteorological conditions with respect to above mentioned four selected parameters were collected from India Metrological Department (IMD), Govt of India. The temperature was measured by the temperature sensor. Relative humidity was measured by the hygrometer sensors. Hygrometer sensors are normally placed in a well-ventilated hood which are protecting sensor from direct sun rays.

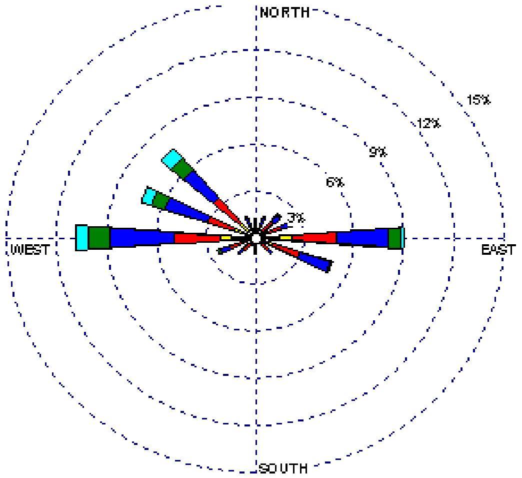
Wind direction is directed by wind vane. The wind vane is aligning to north direction accurately. The head of the arrow indicates the direction of wind is blowing. The wind direction can either record in degree (0-360) or on 16 point of compass (N, NNE, NE, ENE, E, ESE, SE, SSE, S, SSW, SW, WSW, W, WNW, NW. NNW). The wind velocity/ speed is normally measured by cup anemometer. The unit of the measurement may be km/h or m/s. The meteorological parameter during the Year 2011 is shown in **Figure 3.11**.



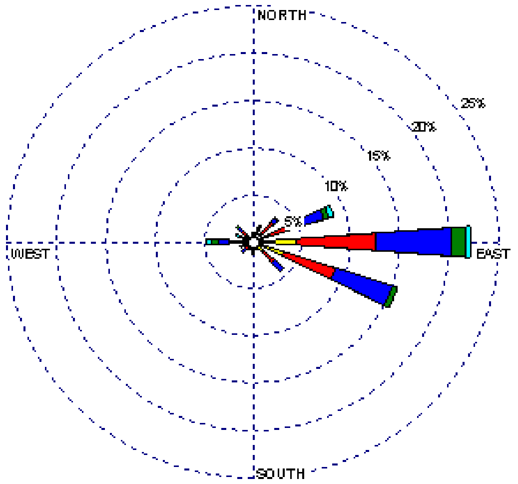
Winter



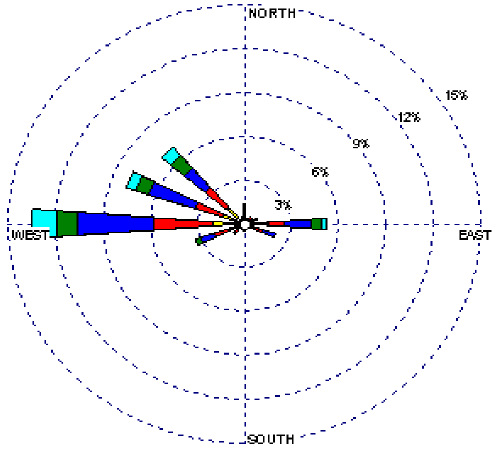
Pre-monsoon



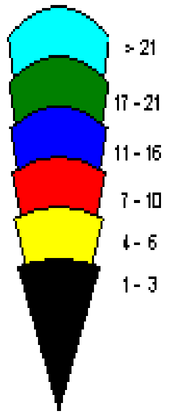
Monsoon



Post-Monsoon



Annual



Legend of Wind Speed (Knots)

Season wise Calm (%)	
Winter	51
Pre monsoon	40
Monsoon	26
Post monsoon	54
Annual	43

Figure 3.11 (Wind Roses for the Year 2011)

Some manufacturer supply wind vane and cup anemometer for mounting on single root/ mast, other may supply separate root/ mast. The anemometer is generally preferred to install in the middle of the flat roofs rather than in the edge of the roof in order to avoid a possible bias to one direction or the other in the open level terrain.Open level terrain is defined as an area where the distance between the anemometer and an obstruction object is to be at least 10 times the height of the obstruction object. The climate of Delhi varies from arid to semi-arid. Winter season was moderately cold whereas pre-monsoon was extremely hot with frequent dust storms. The annual rainfall in Delhi varies from 600 to 800 mm and maximum rainfall occurs during monsoon season only. The predominant wind direction was west (W), northwest (NW), west-northwest (WNW) directions during winter, pre-monsoon and post-monsoon seasons respectively during the study period. The wind direction was east (E) and east-southeast (ESE) directions during monsoon season of the study period. The annual average calm condition in the year 2011 was 43%. The percentage of maximum calm condition was in post-monsoon (54%) followed by winter (51%), pre-monsoon (40%) and monsoon (26%).

The season wise variations of temperature (^{0}C) and relative humidity (%) during the study period is shown in **Figure 3.12**

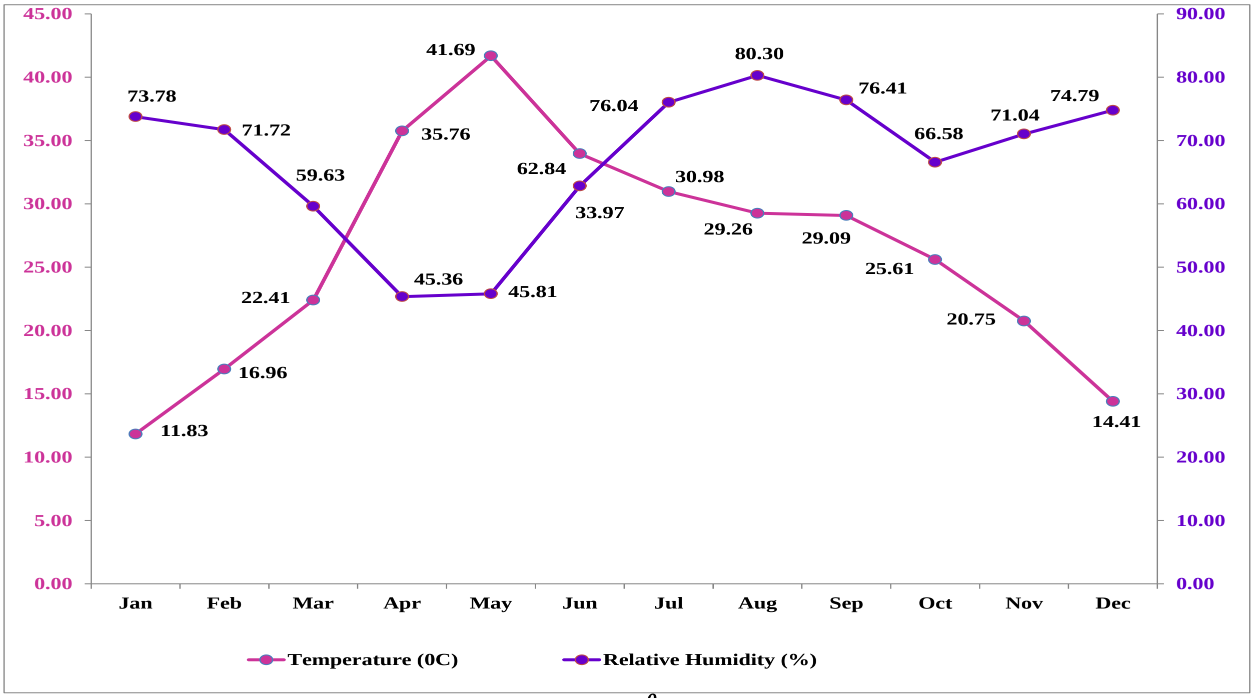


Figure 3.12 Monthly variation of Temperature (^{0}C) and relative humidity (%) in the year 2011

The minimum temperature and relative humidity were 11.83±1.38 and 45.36±5.65 respectively. The maximum temperature and relative humidity were 41.69±4.94 and 80.30±12.17 respectively.

3.6 Source apportionment analysis for air polluants

Ambient air quality data analyses with the help of receptor modeling are receiving increased interest among the policy makers for effective air quality management. Identifying the types of emission sources like anthropogenic or natural and their relative contributions to measured air pollution helps to identify and quantify the emission sources that would be most effective to take the decision of control measures.

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

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

When sources are known, a regression technique is used to match chemical profiles or "fingerprints" in the measured ambient particulate matter to those in the emissions from potential sources. Chemical Mass Balance (CMB) requires a prior knowledge of major sources and their emission characteristics in the study area. It provides a means by which to estimate the percentage contribution of each source to the measured pollutant concentration. These statistical techniques are used for identifying and quantifying the contribution of important emission sources. The majority of the analytical procedures were exactly as described by Harrison et al. (2003) (http://www.sciencedirect. com/science/article/Pii/S1352231007008989? Via %3 Dihub).

Factor Analysis and Positive Matrix Factorizationtechnique are used in general; when sources are unknown for the measured air quality data to perform source apportionment. These models are based on the internal variability of the data to determine the factor profiles and their each contribution to every sample. These factor profiles are related back to specific sources, like burning or diesel emissions. Over a long time period air quality data are required for this technique. Receptor models have limited capability to distinguish the sources of secondary particulate matter compounds except when combined with elements of source-oriented models and/or other supporting analysis.

Source apportionment (receptor modeling) studies involve the ambient sampling and measurement of atmospheric particles or gases, followed by laboratory analyses to separate and identify the constituents of the samples collected, by their chemical composition. Chemical speciation monitoring helps the scientists to understand the properties of the airborne pollutants at the receptor site(s) and to identify the emissions sources, including potential sources. Additionally, the analyses help quantify the contribution of known emissions sources and can help validate and improve the emissions inventory itself.

The advantages of source apportionment studies of particular local and regional level are given below.

- Identification and quantification of selected aerosols at a particular receptor site.
- Evaluation of effectiveness of control strategies and management over time.
- Preparation of emission inventories by identifying the major emission sources of air pollutants like particulate matter and gaseous pollutants.
- Strengthening environmental managementcontrol strategy, particularly at local and regional levels.
- Enhance of linkages between identified specific emissions sources and the status of ambient air quality.
- Evaluating the continuous improvement of the source model outcome.
- Generation of air quality data to support, after implementing control strategy to control the emissions sources.

Source apportionment studies are widely used due to relatively accurate, rapid, and cost-effective solution to identify the selected pollution emission sources and their relative contributions to the total pollution load in the ambient air. The outcomes of the source apportionment studies provide information to the scientists as well as policy decision-makers to adopt most efficient airpollution control strategy.

Source apportionment studies is the tool to identify and quantify the different emission sources of air pollution, preparedness of cost effective policy, regulatory measures and to prepare air pollution control strategies to bring down the air pollutant concentrations within the permissible standards of CPCB. Additionally, this type of study identifies the specific air pollutants, whichmay also be further evaluated to assess climatic impacts, identify clean energy measures and greenhouse gas emission reduction strategies.

In the present source apportionment study, Principal component analysis (PCA) followed by multiple linear regression (MLR) was carried out by using Statistical Package for Social Sciences (SPSS 20.0) (make IBM, California, USA)software for the selected air particular and gaseous pollutants. MLR was performed stepwise through SPSS software. The purpose is to represent the total variability of the original air pollutantsanalytical data into a minimum numbers of factors to identify thepollution sources and their contributions in percentage of different air pollutant sources. PCA factor scores serve as independent variables (Xi). The total air pollutants concentration serves as dependent variable (y).

$$y = \sum m_i x_i + b \ldots\ldots\ldots. (1)$$

The influence of each independent variable and the dependent variable are compared by the regression coefficients. The variables of equation (1) are normalized, the regression coefficients are represented as B, and the intercept (b) is zero.

$$z = \sum B_i X_i \ldots\ldots\ldots. (2)$$

Where z is the standardized normal deviate of the total air pollutants concentration (dependent variable), B_i is the partial regression coefficient and X_i is the PCA factor scores for source i (independent variable). By expanding z and rearranging terms, the multiple linear regression equation is given below:

$$T = \sum B_i \sigma_T FS_i + TM^* \ldots\ldots\ldots. (3)$$

where TM is the total air pollutants, TM* is the mean total air pollutants concentration, σTM is the corresponding standard deviation and FS_i is the factor score for source i. The mean contribution of source i can then be calculated as:

$$mean\ contribution\ of\ source\ i\ (\%) = 100\,\frac{B_i}{\sum B_i} \text{ ....} \quad (4)$$

The contributions of source i can be calculated as:

$$Dailycontributionofsource'i'\left(\frac{\mu g}{m^3}\right) = TM^*\frac{B_i}{\sum B_i} + B_i\sigma_T FS_i \text{ ....} \quad (5)$$

Where Bi /ΣBi is the ratio of the regression coefficient for factor i to the sum of all the regression coefficients. PCA factors were segregated using by varimax rotation with Kaiser Normalization. Eigen value>1 was considered for selecting of factors. The level of significance of 0.5 was considered as the factor score. PCA was applied to identify the source and contribution of each source in percentage for chemical characterization of particulate matter eg., heavy metals (HMs), cation and anion, polycyclic aromatic hydrocarbons (PAHs), organic carbon (OC), elemental carbon (EC) and total carbon (TC) for urbanized mixed use area of Delhi.

In the present study the ambient air quality data has been analyzed by using two appropriate models (Principal component analysis and Mass closure analysis).

Chapter-IV
RESULT & DISCUSSION

Chapter-IV

RESULT AND DISCUSSION

This chapter deals with the result and discussion of trace gases and aerosols of urbanised mixed use area of Delhi. The study was carried out for one year, January–December, 2011. Air pollutants are broadly classified into two categories as particulate matter and trace gases like nitrogen dioxide (NO_2), sulphur dioxide (SO_2), Ozone (O_3), carbon monoxide (CO) etc. Both particulate matter and trace gas pollutants have potential health hazard and can harm the present as well as future generation of our society and environment. Delhi is the most polluted city in India and the above mentioned pollutants are usually released to the atmosphere due to internal combustion engines exhaust and fossil fuel burning (Katsouyanni, 2003; Poschl, 2005). It was estimated that hundreds of thousands of cases of respiratory illness are associated with atmospheric pollution each year in Delhi (Faiz and Sturm 2000) and out of every ten school children in Delhi; one suffers from asthma (Cropper et al. 1997).The most common complaint of Delhi residents were eye irritation (44%), cough (28.8%), pharyngitis (16.5%), nausea (10%) and respiratory problems (5.9%) reported by CPCB during health campaigning during 1997–1998.Nervous system problems like headaches and depression were common and widespread to residents of Delhi. Even the lung functioning test like forced expiratory volume (FEV1), forced vital capacity (FVC), and peak expiratory flow (PEF) were found to be much lower than the Clement Clarks standard, probably due to high exposure of air pollution and traffic annoyance. It was also observed that non-smoking people in Delhi have more risk to acute and chronic illness among all age groups as compared to smokers in Delhi due to urban pollution (Mandal et al. 2011).The smaller size of particulate matter ($PM_{2.5}$) may enter the alveolar epithelium and cause lung inflammation (Ghio and Huang, 2004). NO_2 increase the risk of respiratory infections (Panday et al. 2005). Chen et al. 2015, reported that a study of Southern California children showed that long term exposure of higher concentration of NO_2 in children having lower lung function as compared to other children.

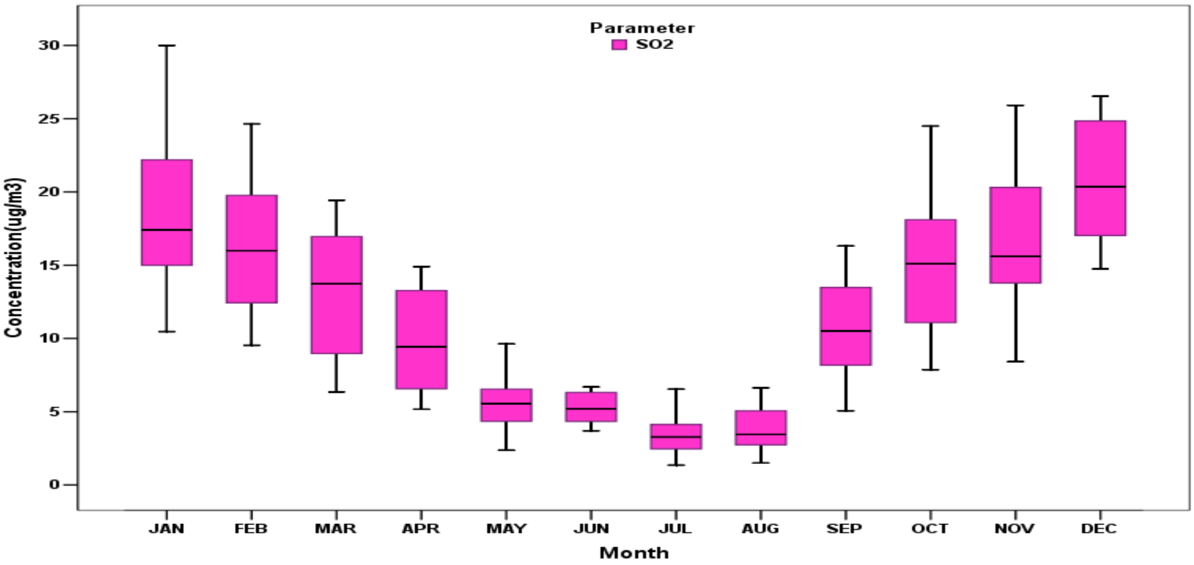
The selected trace gases such as SO_2, NO_2 and NH_3, those have potential to increase the concentrations of particulate matter. The secondary analysis like carbonaceous aerosols, particulate PAHs, cation and anion and heavy metals in PM_{10}were estimated. The source profiles of each secondary components of PM_{10} were also estimated by using Principal Component Analysis and Multiple Linear Regression (PCA-MLR) of Receptor Modelling.

4.1 Monthly/ Seasonal variation of trace gases in Delhi

Trace gasses play a vital role for changes the atmospheric chemistry, adverse effect to human health and visibility. The acidic trace gases like SO_2, NO_2 and NH_3 through different chemical reactions in the atmosphere are converted to acid and subsequently deposited to land and water environment.The acidic gas NOx, NH_3, SO_2, metrological parameter like temperature and humidity are the important atmospheric constituents/conditions governing the formation of fine particulate sulfates and nitrates (Sharma et al. 2007). The temperature and humidity are the most important atmospheric constituents/conditions for formation of atmospheric fine particulate matter. So it is the deemed necessary to understand the monthly/ seasonal variation of trace gases, metrological parameters like temperature and humidityand their conversion in the form of inorganic secondary particulate matter in the atmosphere. The monthly/seasonal variation of trace gases SO_2, $NO_2$and NH_3in the urbanized mixed use area of Delhi in the year 2011 is described below.

4.1.1 Monthly/ Seasonal variation of SO_2

The monthly/ seasonal variation of SO_2, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.1.** The figure revealed that the concentrations of SO_2, varied from 3 to 21μg/m^3 respectively with an average value of 12±6 μg/m^3. The highest concentration was observed in the month of December, 2011 whereas a lowest concentration was observed in the month of July, 2011. During the peak winter season, SO_2 concentration was high due to additional source of biomass burning associated with day to day common activities like combustion of fossil fuel, oxidation of organic materials in soils, vehicular emissions etc. The lifetime of SO_2 molecules in the troposphere and stratosphere are varied from few days to several weeks, during which sulphate aerosols are produced. SO_2 is removed in the troposphere by dry or wet deposition. Monsoon season acidified the rain and deposited by wet precipitations whereas during the winter season inorganic sulphate aerosols were formed and increased the concentrations of particulate matter. SO_2 is formed due to burning of fossil fuel especially coal and oils (George et al. 2013).The highest concentration of SO_2 in the month of December, 2011 was much below the permissible limit of revised National Ambient Air Quality Standards (NAAQS) of Central Pollution Control Board (CPCB).



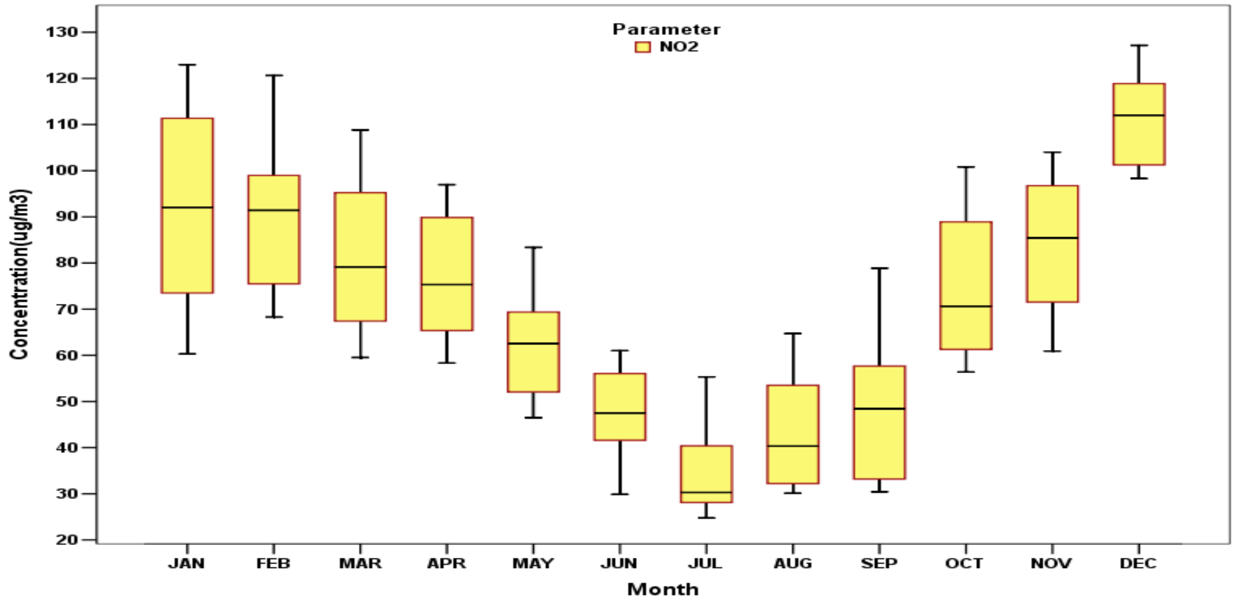
Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	30	25	19	15	10	9	7	7	16	24	26	27
Min	10	10	6	5	2	4	1	1	5	8	8	15
75 percentile	16	12	9	7	4	4	3	3	8	11	14	17
50 percentile	17	16	14	9	6	5	3	3	11	15	16	20
25 percentile	21	20	17	13	6	6	4	5	13	18	20	25
Average	19	16	13	10	6	5	3	4	11	15	17	21

Figure 4.1 Monthly/Seasonal variation of SO_2 in Naraina Industrial Area of Delhi

The average concentrations of SO_2 during winter, pre-monsoon, monsoon and post-monsoon seasons were 17±3, 7±2, 6±4 and 16±1µg/m^3, respectively. The average of daily average value observed in winter, summer and monsoon at R.K. Puram location of Delhi were 21.9, 14.8 and 10.3 µg/m^3 respectively. The average of daily average value observed in winter, summer and monsoon at Mandir Marg location of Delhi was 23.1, 18.6 and 9.1µg/m^3 respectively (George et al. 2013).The concentrations of SO_2 observed in Naraina industrial area was comparable with the reported value at R.K. Puram and Mandir Marg location of Delhi. Mandal et al. 2011 reported that although, SO_2 concentration during Diwali day was within the permissible limit of NAAQS, but it was two to eighteen times higher as compared to Diwali month in the residential areas during 2006 to 2008. High levels of SO_2 are particularly dangerous in the presence of particulate matter because it slowly adsorbs on fine atmospheric particles and can be transported very deep into the lungs and can stay for long duration of time (Singh et al. 2009). 4 hour averages for the period of 2006 - 2010, SO_2 concentration were found within the permissible limits of revised NAAQS (annual mean 50 µg/m^3) in Delhi and annual 24 hourly average was 16.19 µg/m^3 (Gaur et al. 2015).

4.1.2Monthly/ Seasonal variation of NO_2

NO_2 is an important constituent of oxides of nitrogen ($NOx = NO + NO_2$). NO_2 is not emitted directly into the ambient air as it is the by-product of the combustion process. NO_2 in the atmosphere is formed due to atmospheric reaction of nitrogen oxide (NO) with ozone (O_3).The major source of $NO_2$was combustion of fossil fuels like coal, gas and oil, especially fuel used in cars. Other major sources are welding and using explosives, refining of petrol and metals, cooking activities, agricultural fertilization etc. The residence time of NO_2 are varied from half day to maximum two days. NO_2 is removed from the atmosphere by both dry and wet deposition. Monsoon season acidified the rain and deposited by wet precipitations whereas during the winter season inorganic nitrate aerosols were formed and increased the concentrations of particulate matter (Sharma et al. 2007). The monthly/ seasonal variation of NO_2, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.2.**



Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	123	121	109	97	83	61	55	65	79	88	97	127
Min	60	68	60	58	46	30	25	30	30	56	61	98
75 percentile	74	76	68	66	53	42	28	32	34	61	72	101
50 percentile	92	91	79	75	63	48	30	40	48	71	85	112
25 percentile	111	98	95	90	69	56	39	53	58	88	97	118
Average	93	89	82	77	63	48	34	43	48	75	84	112

Figure 4.2 Monthly/ Seasonal variation of NO_2 in Naraina Industrial Area of Delhi

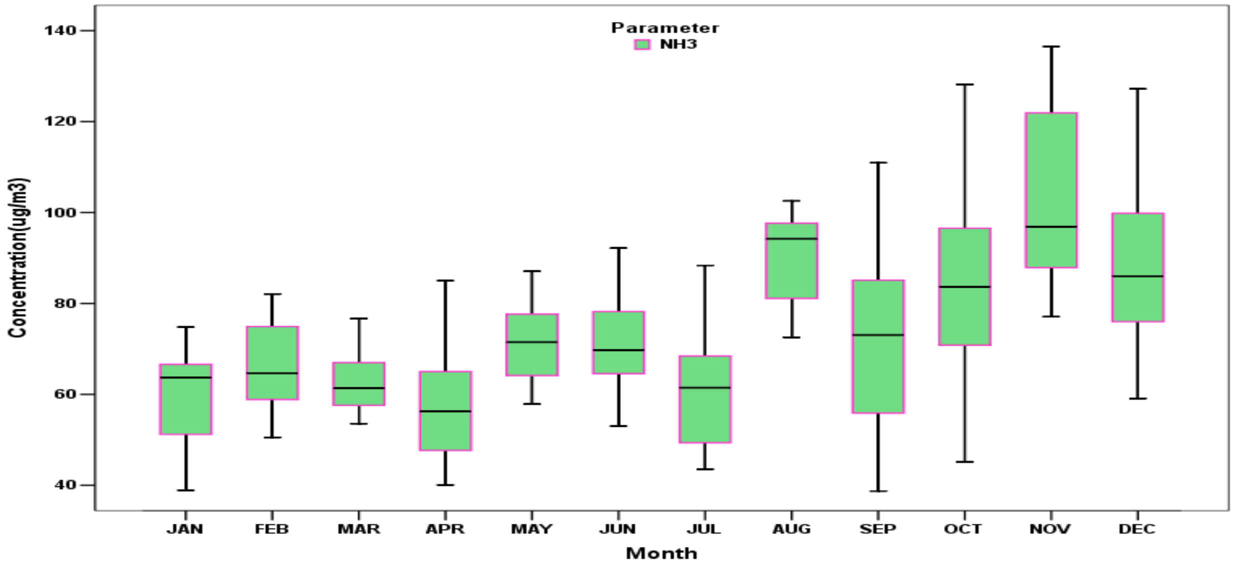
The concentration of NO_2 was highest (112 µg/m^3) in the month of December, 2011, whereas a lowest (34 µg/m^3) concentration was in the month of July, 2011. Naraina Industrial Area, the concentration of NO_2 varied from 34 to 112µg/m^3, with an average value of 71±23 µg/m^3. The average concentration of NO_2 was frequently exceeded the revised National Ambient Air Quality Standards (NAAQS) of Central Pollution Control Board (CPCB).The average concentrations of NO_2during winter, pre-monsoon, monsoon and post-monsoon seasons were 94±13, 63±13, 42±7 and 80±7 µg/m^3,respectively. The average of daily average value observed in winter, summer and monsoon at R.K. Puram location at Delhi was 119.5, 87.5 and 39.6µg/m^3 respectively. The average of daily average value observed in winter, summer and monsoon at another hotspot location Mandir Marg of Delhi was 92.5, 55.5 and 50.6 µg/m^3 respectively (George et al. 2013).4 hour averages for the period of 2006-2010, NO_2 persistently violating the permissible limits of revised NAAQS (annual mean 40 µg/m^3) in Delhi and annual 24 hourly average was 97.62 at traffic intersection area of Delhi (Gaur et al 2015).

4.1.3 Monthly/ Seasonal variation of NH_3

The highest concentration of NH_3 (102 µg/m^3) was observed in the month of November, 2011, whereas a lowest (58 µg/m^3) concentration was in the month of April, 2011. Naraina Industrial Area, the concentration of NH_3 varied from 58 to 102µg/m^3, with an average value of 74±14µg/m^3. The monthly/ seasonal variation of NH_3, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.3.** NH_3 is a colorless, but have a very distinctive pungent odor trace gas. NH_3 essentially neutralizes the major atmospheric acidic species (nitric and sulfuric acid) in the troposphere and form solid in the form of ammonium (NH_4^+) salt. It reduces the atmospheric emissions of NO_2 and SO_2 trace gases from industrial and vehicle combustion processes. NH_4^+ salt is also known as secondary particulate matter which increases the fine particulate matter in the ambient air. The gaseous NH_3, has a short atmospheric lifetime of only a few hours and mostly deposits to its source or far away (depending on climatic conditions) through wet or dry deposition to surrounding plant and soil surfaces. The wet deposition to surface water contributed to eutrophication and changes the aquatic ecosystems. The average concentrations of NH_3 during winter, pre-monsoon, monsoon and post-monsoon seasons were 70±14, 67±8, 75±15 and 93±13µg/m^3, respectively. NH_3 showed highest concentration in post-monsoon season followed by monsoon, winter andpre-monsoon. Srivastava et al. 2009 reported that concentrations of NH_3

at Agra showed highest values during the monsoon season and lowest during the winter season. This might be possible due to more emission of NH_3 from vegetation and favorable metrological condition for microbial activity in Agra city. Rice-wheat cropping system of subtropical agricultural soil of Delhi are also contributing ambient NH_3 approximately 9% due to lost as NH_3 after application of nitrogen to soil. (Sharma et al. 2015) NH_3 did not follow any season trend like SO_2 and $NO_{2.}$ Pre-monsoon and post monsoon season NH_4 may be transformed to NH_3 due to high temperature and low relative humidity. Thus increase the concentrations of NH_3 during the pre-monsoon and post monsoon season.

The highest concentration of NH_3 was much below the permissible limit of revised NAAQS of CPCB.



Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	75	82	88	85	98	92	88	103	111	128	137	127
Min	39	51	54	40	58	53	44	97	39	45	77	59
75 percentile	53	59	58	48	64	65	50	81	56	72	88	76
50 percentile	64	65	61	56	71	70	61	94	73	84	97	86
25 percentile	66	75	66	65	77	77	67	97	84	95	122	97
Average	59	66	64	58	72	71	61	90	72	84	102	90

Figure 4.3Monthly/Seasonal variation of* NH_3 *in Naraina Industrial Area of Delhi

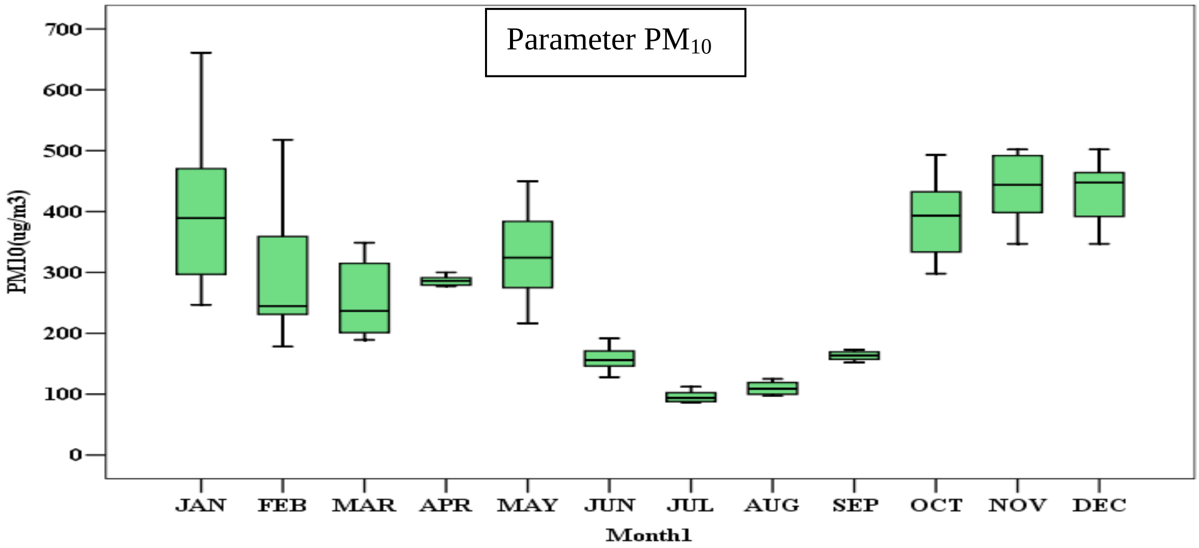
The average concentrations of ambient NH_3 were recorded as 21.2±5.4 ppb and 20.8±4.7 ppb respectively, during winter and summer at Delhi. The results emphasized that the traffic movement could be one of the significant sources of ambient NH_3 at the urbanised location of Delhi as illustrated by positive correlations of NH_3 with traffic related air pollutants (NO, NO_2 and CO) (Sharma et al. 2015). NH_3 was monitored and analyzed at selected continuous air monitoring locations (six Nos) i.e., R.K.Puram, Punjabi Bagh, Mandir Marg, Anand Vihar, Civil Lines and IGI Airport in Delhi during the period of December 2014 to February 2015 by CPCB. 24 hourly average concentrations of NH_3 in Delhi ranged between 31 to 72µg/m³ which was within the NAAQS 2009 of 400µg/m³ (CPCB, 2015).

4.2Monthly/Seasonal variation of particulate matter

Air-suspended mixture of both solid and liquid particles is defined by the United States Environmental Protection Agency (USEPA) as particulate matter. A few particles are visible and dark enough is known as soot or smoke, whereas small or tiny particles that individually cannot be detected without electronic microscope are mostly aerosols. The size segregated particulate matter (PM_{10} and $PM_{2.5}$) in the urbanized industrial area were studied.

4.2.1 Concentrations of PM_{10} in the ambient air

The concentrations of PM_{10} in the Naraina Industrial Area of Delhi ranged between 95.9–453.5 µg/m^3. The annual mean concentrations of PM_{10} were 280.72±126.10 µg/m^3 which was alarmingly high as compared to NAAQS (***annual mean 60 µg/m^3***) of CPCB, 2009. The lowest and highest concentrations of PM_{10} were observed 95.93±9.29 and 453.45±62.92 µg/m^3 respectively in the month of July and December 2011.The average concentrations of PM_{10} during winter, pre-monsoon, monsoon and post-monsoon seasons were 351.17±92.79, 258.0±88.77, 122.92±35.58 and 410.62±30.87 µg/m^3, respectively. A strip rise of PM_{10} concentrations during post-monsoon season in the year 2011 might be impacted due to burning of crackers during Diwali celebration. PM_{10} concentration during Diwali day was 1.3 to 4 times higher than Diwali month during the period (2006-2008) (Mandal et al. 2011). Fireworks during Diwali festival led to a short-term variation of air quality and two to three times increase in PM_{10} and total suspended particulate matter concentration in Hissar City, India (Ravindra et al. 2003). The concentrations of PM_{10} were comparatively low during pre-monsoon seasons but moderately higher than monsoon season might be due to maximum mixing ratio and wind speed during pre-monsoon season. Industrial emission, mobile and stationary combustion, suspended road dust, inverse metrological condition, slow dispersion, low-average mixing height and calm condition during post-monsoon (54.41%) and winter (51.25%) season were attributed the maximum concentrations of PM_{10} as compared to pre-monsoon and monsoon seasons. The increasing trend of concentrations of PM_{10} is dangerous as, hospital emergency admissions for asthma, bronchitis and pneumonia in older people are associated with increase in PM_{10} (Ye et al. 2001). The monthly/ seasonal variation of PM_{10}, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.4.**



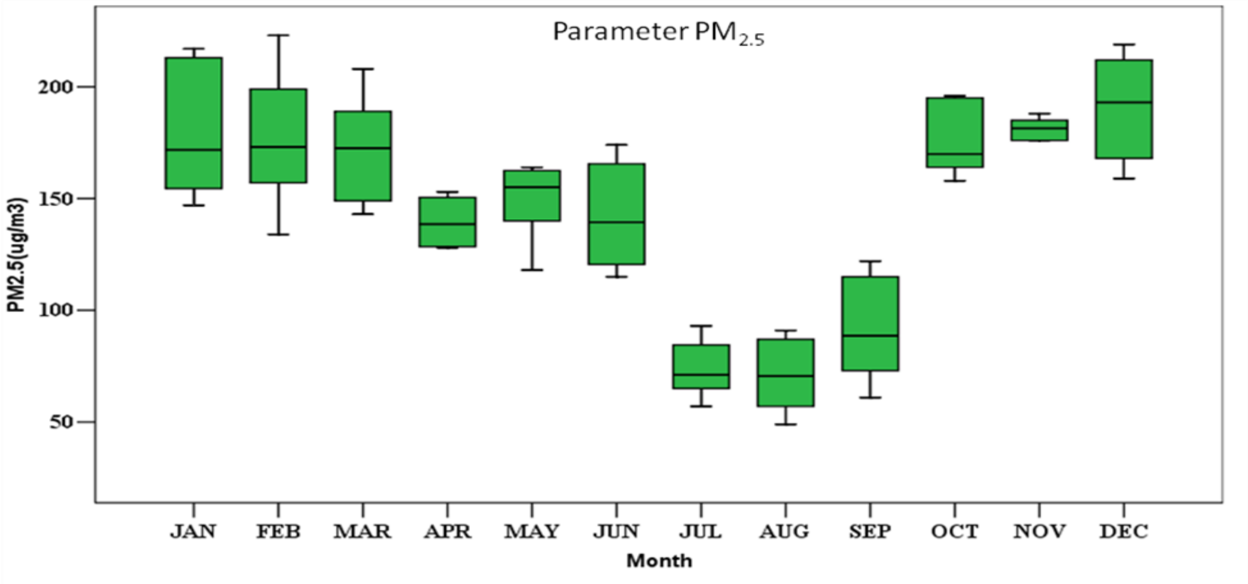
Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	661	518	349	300	450	192	112	125	173	493	502	502
Min	247	178	189	277	216	128	87	97	152	298	347	347
25 percentile	311	234	202	280	285	146	88	101	158	347	402	395
50 percentile	389	245	236	286	324	156	94	109	164	394	443	447
75 percentile	437	333	307	291	383	171	100	119	168	429	488	463
Average	403	295	253	286	329	159	96	110	163	389	411	453

Figure 4.4 Monthly/Seasonal variation of PM_{10} in Naraina Industrial Area of Delhi

The emission from fireworks during Diwali in the post-monsoon season increased PM_{10} concentrations (in the year 2007-2008) upto 400 μg/m^3 (Tiwari et al. 2012). In the present study the impacts of fireworks during Diwali celebration in mixed use area of Delhi was in the post-monsoon season increased of PM_{10} concentrations upto 432 μg/m^3. The present data is comparable with the reported value in Delhi. During the winter and monsoon season in the year 2010, the concentrations of PM_{10} were 213.10±14.9 and 134.70±39.9 μg/m^3 respectively in the urban location of Delhi (adjacent to selected sampling location) was reported by Sharma et al. 2014. Winter season reported below was less but higher during the monsoon season might be due to metrological condition. As such mixed use area consists of small and medium scale industries also could be the reason to increase the higher concentration of PM_{10} mass in the ambient air. In India three types of fuels are used in the transportation sector. The contributions of different fueled vehicles (diesel, petrol and CNG) in PM_{10} are 81%, 13%, 6% respectively was reported by Goyal et al. 2014. The percentage of PM_{10} from diesel vehicles is more in comparison to petrol and CNG. Diesel fuel is sulfur contained which is favorable to increase the particulate emission.

4.2.2 Concentrations of $PM_{2.5}$ in the ambient air

The lowest and highest concentrations of $PM_{2.5}$ were observed 73.88±12.55 and 190.56±32 µg/m^3 respectively in the month of July and December 2011. The concentrations of $PM_{2.5}$ in the Naraina Industrial Area of Delhi ranged between 70.88-190.56 µg/m^3. The annual mean concentration of $PM_{2.5}$ was 145.59±25.22 µg/m^3, which was alarmingly high as compared to NAAQS (***annual mean 40 µg/m^3***) of CPCB, 2009. The alarming news about the ambient quality of air in Delhi, was $PM_{2.5}$ concentrations in the national capital of India was 10 times higher than the safety limit prescribed by the World Health Organization (10 µg/m^3) and four times higher than even the Indian safety limit (40 µg/m^3) ***(PTI, New Delhi: February 16, 2015).***The annual average concentration of $PM_{2.5}$ from 2006-2010, had been found to be 3.34 times more than the NAAQS Standard (Gaur et al. 2015). The monthly/ seasonal variation of $PM_{2.5}$, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.5.**



Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	217	223	208	153	203	174	93	91	122	196	188	219
Min	147	134	143	128	118	115	57	49	61	158	158	159
25 percentile	155	157	152	129	140	121	65	59	75	165	177	168
50 percentile	172	173	173	139	155	140	71	71	89	170	182	193
75 percentile	211	189	188	149	162	164	83	84	111	190	185	212
Average	180	177	173	139	156	143	74	71	91	176	178	191

Figure 4.5 Monthly/Seasonal variation of $PM_{2.5}$ in Naraina Industrial Area

In India the reported value of ambient $PM_{2.5}$ concentrations were less as a few studies were undertaken. Tyagi et al. 2016 reported that during the celebration of republic day in Delhi during the period of January 22 to 27 (winter season), 2014 and 2015, the concentrations of $PM_{2.5}$ was varied from 125 to 480.7 µg/m^3 respectively which was approximately 100 times more than the standard value. In the January month (year 2011), the average concentrations of PM_{10} in the study area was 403 µg/m^3. The present data is comparable with the reported value. The impacts of fireworks during the celebration of Diwali in the post-monsoon season, $PM_{2.5}$ concentration was 350µg/m^3 (Tiwari et al. 2012). In the present study the concentration of $PM_{2.5}$ during the celebration of Diwali was 432µg/m^3 which was comparable with the reported value. Vehicle exhaust, construction activity and road side dust are important sources of $PM_{2.5}$ reported by Biswas et al. 2011. Zhang et al. 2011 reported that the annual average $PM_{2.5}$ at Xiamen in China varied from 63.88-74.80 µg/m^3 respectively. In city like Delhi the annual mean concentration of $PM_{2.5}$ was 2 times higher than rapid urbanization and industrialization location of Xiamenin China. Implementation of the Compressed Natural Gas (CNG) in replacement of diesel fuel in the year 2004 was the last major intervention to deal with poor air quality in Delhi was undertaken by the Govt. However, till date, the regulatory and enforcement agency in Delhi are unable to prevent the strip rise of vehicular growth and construction activity in the city. The odd-even movement of private vehicle was implemented by the Delhi Government twice for fifteen days duration in the year 2016. In the first phase (January 1, 2016 to January 15, 2016) of odd-even movement of vehicle, the analysis data suggested the reduction of car on road was 21% and 18% increase in speed. The second phase (15 April 2016 to 29April 2016), there was a 17% decrease in car numbers and 13% increase in vehicle speed. The reduction of the concentration of $PM_{2.5}$ in both the phases varied from only 4-7% as in general private car make limited contribution to the fine particles in the ambient air. As compared to phase one, Delhi's air pollution rises 23% during second odd-even phase (Business Standard, April 30, 2016). Odd-even studies revealed that this system cannot sustain in the long term without additional actions like improvement of bus services, curbing factory and emission from heavily loaded commercial diesel vehicles. The construction dust and dust from adjacent Rajasthan state, India desert are the major contributors of particulate matter in Delhi and National Capital Region. The metrological parameter like wind speed, wind direction, temperature, humidity and solar radiation also affect the air quality. These are the primary causes of poor ambient air quality, in addition to industrial emissions, biomass burning and re-suspended of road dust.

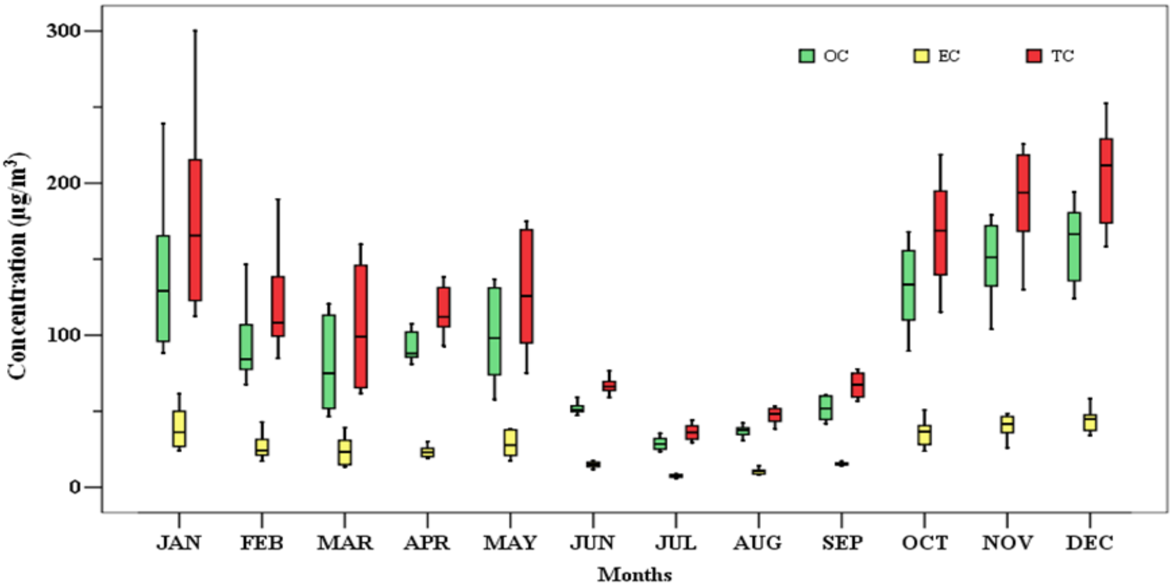
4.3 Carbonaceous aerosols

Carbonaceous aerosols are the single largest absorber of solar radiation, and their heterogeneous reactions change the dynamics of atmospheric boundary layer which reduces visibility and also create health hazard (Yang et al. 2011). They are broadly classified into two categories, organic carbon (OC) and elemental carbon (EC), which are the important constituents of both PM_{10} and $PM_{2.5}$ sizes of particulate matter. The major sources of carbonaceous aerosols are, from fossil fuel combustion biomass burning. Carbon-containing components like OC and EC have the negative impact on climate change as it reduces the visibility. Kwangsam et al. 2004, reported that the OC and EC were responsible for 27% and 44% of the incident light extinction at Lennox and Duarte, respectively, in the Los Angeles air basin.

The rapid industrialization and urbanization in most of the mega cities in India require more energy consumption that leads to high emissions of atmospheric carbonaceous aerosols. They lead to poor air quality which directly or indirectly impact on climate and human health. The chemical composition of carbonaceous aerosols has rarely been studied in India especially in industrial areas and urbanised mixed use area of India. In the present study, monthly/seasonal variation of carbonaceous aerosols in both size segregated particulate matter were studied in urbanised industrial area of Delhi from January, 2011 to December, 2011. They are the major dominant contributors to aerosol components especially in highly industrialized and urbanized areas. The combination of OC and EC is known as total carbon (TC) which is mostly dominated by OC only. The emission of EC occurs directly from the primary sources, whereas the emission of OC occurs either directly or formed into the atmosphere due to atmospheric oxidation of biogenic and the condensation of volatile organic compounds (VOCs) (Mandal et al. 2013).

4.3.1 Monthly/Seasonal variation of carbonaceous aerosols (OC, EC and TC) in PM_{10}

The monthly/ seasonal variation of OC, EC and TC in PM_{10}, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.6.** The higher concentrations of OC, EC and TC in the month of December 2011 were found to be 159.40±25.93, 47.14±11.42 and 206.55±33.88 µg/m^3, respectively, whereas lower concentrations observed in the month of July were 28.82±4.38, 7.34±0.93and 95.93±9.29 µg/m^3, respectively.



Concentrations of OC in PM_{10}

Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	239	147	121	107	137	59	35	42	61	168	179	194
Min	88	68	47	81	58	47	24	31	42	90	104	124
25 percentile	96	78	52	86	76	50	26	35	45	117	132	136
50 percentile	129	84	75	88	98	51	29	38	52	133	139	166
75 percentile	162	100	111	101	131	53	32	39	60	152	172	180
Average	139	94	81	92	100	52	29	37	52	132	149	159

Concentrations of EC in PM_{10}

Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	61	43	39	30	39	17	9	14	17	51	48	58
Min	24	17	14	19	17	12	6	8	14	24	26	34
25 percentile	28	22	15	20	21	14	7	9	15	29	36	38
50 percentile	36	24	23	23	28	15	8	11	15	37	42	45
75 percentile	49	29	31	25	38	16	8	11	16	41	47	47
Average	39	27	24	23	29	15	7	10	15	36	40	44

Concentrations of TC in PM_{10}

Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	300	189	160	138	175	77	44	53	78	219	226	252
Min	113	85	62	93	75	59	29	39	57	115	130	158
25 percentile	123	100	66	107	97	64	32	43	60	149	170	174
50 percentile	165	108	99	112	126	66	36	48	67	169	194	212
75 percentile	210	129	143	130	169	69	40	51	75	191	217	229
Average	178	121	105	116	129	67	36	47	67	168	190	203

Figure 4.6 Monthly/Seasonal variations of OC, EC and TC in PM_{10} in Naraina Industrial Area of Delhi

The trends of OC, EC and TC concentrations were decreasing from January to March 2011, while sharp increasing trends were observed during the months of April and May 2011. The concentrations of OC, EC and TC during winter, pre-monsoon, monsoon and post-monsoon seasons were (118.22±36.90, 36.86±11.18 and 155.08±47.91µg/m^3), (81.51±25.92, 22.89±7.75 and 104.40±33.36 µg/m^3), (39.25±11.73, 11.47±3.99 and 50.71±15.64 µg/m^3) and (140.58±12.31, 38.53±2.52 and 179.11±14.83 µg/m^3), respectively. The results showed a clear seasonal variability of OC, EC and TC. The season wise OC, EC and TC concentrations during the study period were followed the same season wise pattern of the particulate matter. (**Figure 4.6**). The concentrations of OC ranged 28.8–159.4, EC ranged 7.5–44.0 and TC 36.29–203.39 µg/m^3; those values were higher than reported values in India till date and other Asian countries. OC and EC reported to Ahmedabad (12.8 and 2.1µg/m^3), (Rastogi and Sarin 2009), Mumbai (25.3 and 12.6 µg/m^3) (Venkataraman et al. 2002), Dhaka (46 and 22 µg/m^3) (Salam et al. 2003).

4.3.1.1 The correlation and regression of OC, EC and TC in PM_{10}

OC and EC were correlated with each other, implying the existence of similar emission sources such as coal combustion, biomass burning and vehicular exhaust. The correlation and regression of OC, EC, TC and PM_{10} in Delhi is shown in **Figure 4.7 (i) to Figure 4.7 (iv)**

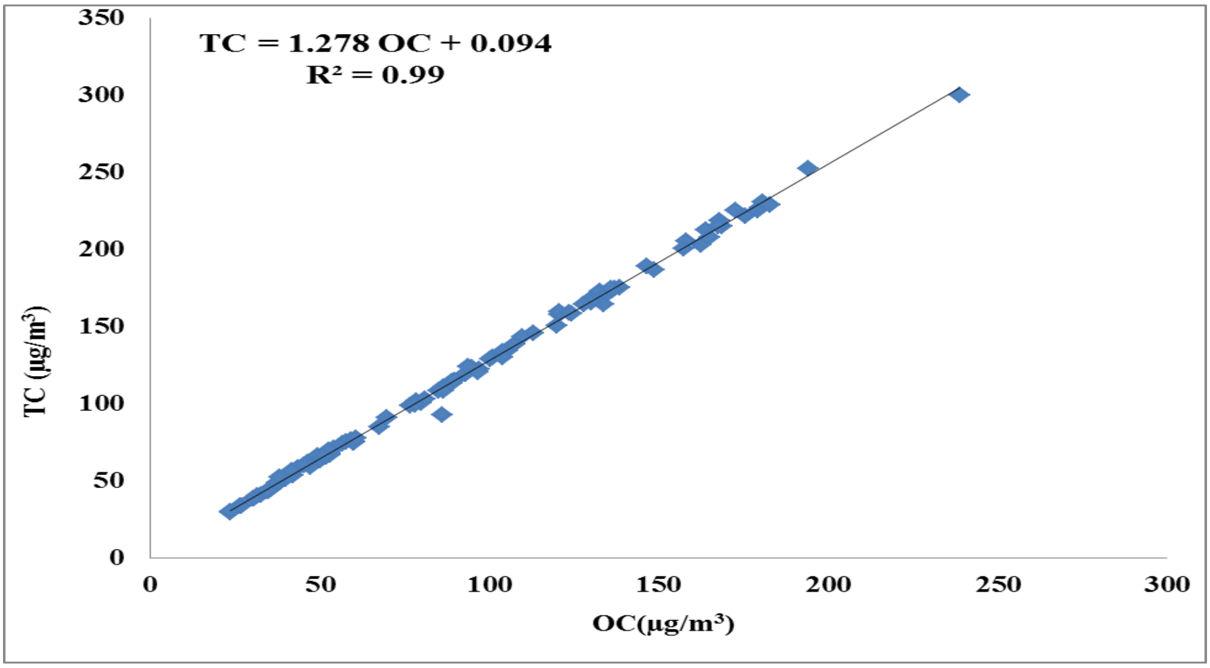


Figure 4.7 (i) Correlations between OC and TC in PM_{10} (2011)

The strong correlation and regression of OC and TC ($R^2 = 0.99$) of PM_{10} in Naraina Industrial Area of Delhi implied that OC was the significant contributor to TC during the study period.

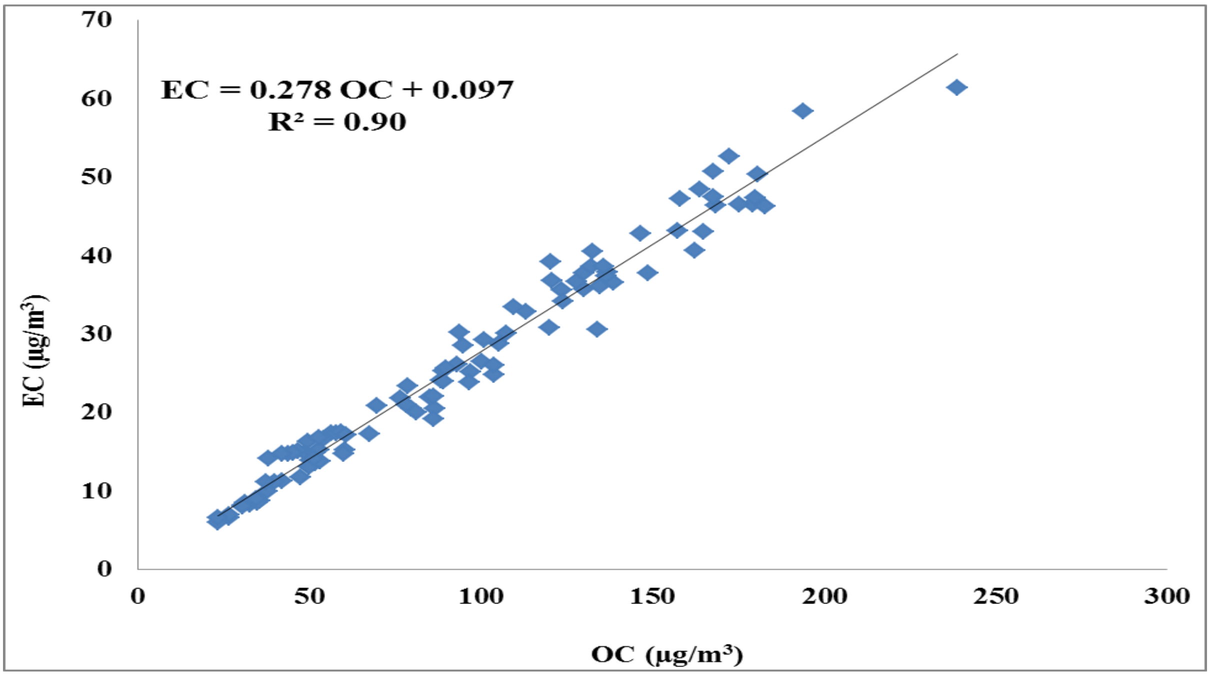


Figure 4.7 (ii) Correlations between OC and EC in PM_{10} (2011)

OC and EC were correlated with each other ($R^2 = 0.90$), implying the existence of similar emission sources such as coal combustion, biomass burning and vehicular exhaust. Dayal Bagh, the urban location of Agra city the reported OC and EC ratio ($R^2 = 0.85$) which was similar to the present study (Pachauri et al. 2013).

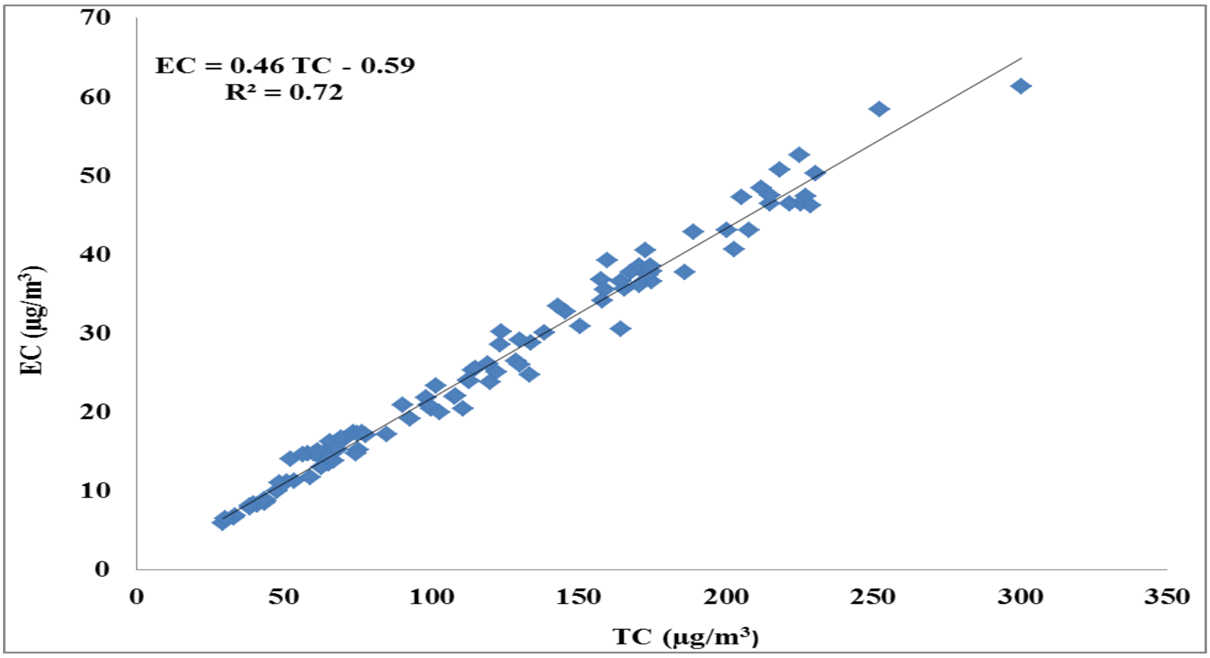


Figure 4.7 (iii) Correlations between EC and TC in PM_{10} (2011)

EC and TC were correlated with each other ($R^2 = 0.72$). The emission sources of OC and EC were same indicated the similar emission sources.

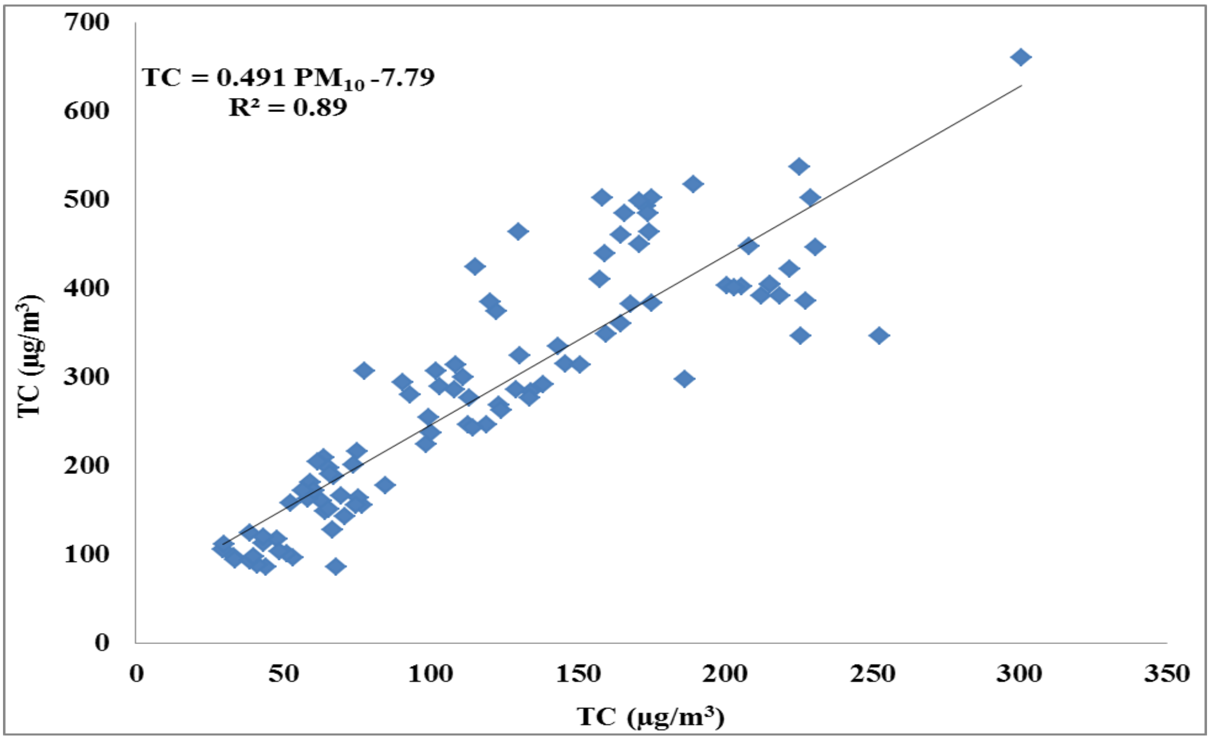


Figure 4.7 (iv) Correlations between TC and PM_{10} (2011)

The strong correlation between TC and PM_{10} ($R^2 = 0.89$) implied that TC was the significant contributor to PM_{10} during the study period (2011) and released from the single, dominant primary source (Mandal et al. 2013).

4.3.1.2 Estimation of OC and EC ratios in PM_{10}

The ratio of monthly average organic carbon (OC) with elemental carbon (EC) was obtained in the range of 3.02–3.96 (**Table 4.1)**. The monthly average ratio of OC with EC was exceeded 2.0 in the present study.

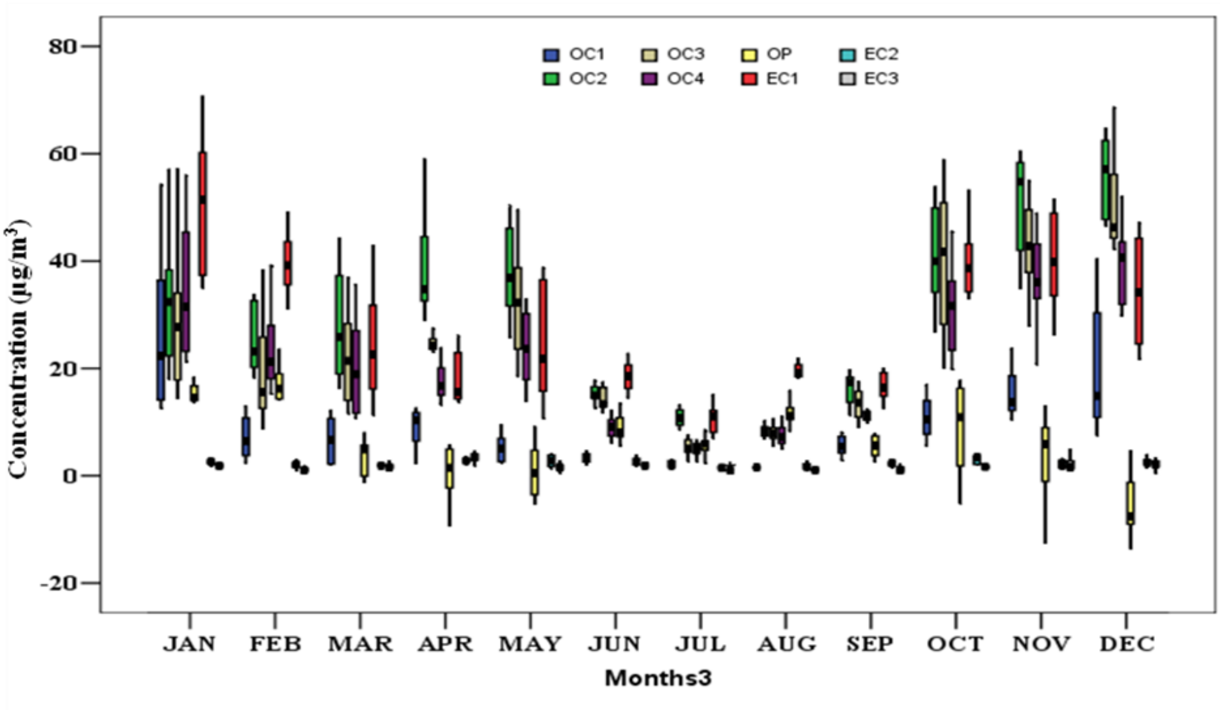
Table 4.1: **Monthly/Seasonal variation of OC and EC ratios in PM_{10} (2011)**

Winter Season					**Pre-monsoon Season**				**Monsoon Season**				**Post-monsoon Season**		
Dec	Jan	Feb	Mar	**Avg**	Apr	May	Jun	**Avg**	Jul	Aug	Sep	**Avg**	Oct	Nov	**Avg**
3.38	3.07	3.02	3.38	**3.21**	3.96	3.3	3.48	**3.58**	3.93	3.14	3.39	**3.49**	3.59	3.7	**3.65**

The ratio of OC with EC was greater than 2.0 indicated the formation of secondary organic aerosols (SOC) (Chow et al. 1996). The formation of SOC is in general controlled by ambient temperature and solar radiation of the sun light. During the premonsoon season, temperature increases up to 47^0C, and hence, the formation of SOC could not be ignored. Low temperature with dense haze fog during winter season indicated low SOC formation in the atmosphere. The higher ratio of OC with EC in PM_{10} indicated the influence of biomass burning, while lower ratios attribute to fossil fuel combustion (Ram et al. 2010). Watson et al. (2001) reported ratio of OC with EC for coal combustion, vehicle emission, and biomass burning were 2.7, 1.1 and 9.0, respectively. Saarikoski et al. 2008, reported ratio of OC with EC of 6.6 for biomass burning and 0.71 for vehicular emissions. The ratios of OC with EC were affected by emission sources, e.g., formation of atmospheric secondary organic aerosol (Cao et al. 2005). The study revealed that the major sources of OC and EC were due to coal combustion and vehicular emission. The coal combustion occurred at tandoor cooking activities, open biomass burning and contribution from industrial emissions. Vehicular emission occurred due to continuous movement of heavy diesel based commercial vehicles and private vehicles (two wheelers and four wheelers).

4.3.1.3 Estimation of OC and EC fractions in PM_{10}

The fractions of OC (OC1, OC2, OC3 and OC4), pyrolysis (OP) and fractions of EC (EC1, EC2 and EC3) in $PM_{10,}$ had analysed seasonally is presented by whistle plot in **Figure 4.8.**



Fractions of Carbons		**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**
OC1	**Max**	54	13	12	13	9	5	3	2	8	17	24	40
	Min	13	2	2	2	3	2	1	1	3	6	11	8
	25 percentile	14	4	2	8	3	3	2	1	4	8	12	11
	50 percentile	22	7	7	10	5	3	2	2	5	11	14	15
	75 percentile	36	10	11	11	6	4	3	2	7	14	17	30
	Average	27	7	7	9	5	3	2	2	6	11	15	20
OC2	**Max**	57	52	44	59	50	18	13	10	20	54	60	65
	Min	18	18	16	29	26	13	9	7	11	27	35	47
	25 percentile	23	21	19	33	32	14	10	8	14	36	42	49
	50 percentile	32	23	26	35	37	15	11	8	17	40	55	57
	75 percentile	38	32	37	42	45	17	12	9	18	49	58	62
	Average	33	28	28	39	38	15	11	8	16	41	51	56
OC3	**Max**	57	38	37	27	49	17	7	11	17	59	55	69
	Min	14	9	12	23	19	12	3	6	9	20	28	42
	25 percentile	18	13	14	24	24	13	5	7	11	30	38	44
	50 percentile	28	16	21	24	32	13	5	8	14	42	43	46
	75 percentile	34	25	28	25	38	16	7	9	16	50	49	55
	Average	29	19	22	25	32	14	5	8	13	40	43	50
OC4	**Max**	56	39	36	24	33	12	7	11	12	45	49	52
	Min	21	15	11	13	14	6	3	5	10	20	21	30
	25 percentile	24	19	12	15	18	7	4	6	10	24	33	32
	50 percentile	32	21	19	17	24	9	5	7	11	32	36	41
	75 percentile	44	25	27	20	29	10	6	9	12	36	43	44
	Average	35	24	20	18	24	9	5	8	11	31	37	39

OP	**Max**	22	24	17	15	14	16	8	8	8	23	23	18
	Min	14	5	1	9	5	6	2	16	3	5	12	13
	25 percentile	14	14	0	2	3	7	5	11	4	2	2	9
	50 percentile	15	16	5	1	0	8	6	11	6	11	6	8
	75 percentile	16	19	6	5	4	11	6	12	7	16	9	2
	Average	16	16	5	4	4	9	6	12	5	10	8	7
EC1	**Max**	71	49	43	26	39	23	15	22	20	53	51	47
	Min	35	31	11	14	11	15	7	14	13	33	26	22
	25 percentile	38	36	16	14	17	16	8	19	15	35	35	25
	50 percentile	51	39	23	16	22	19	11	19	16	39	40	34
	75 percentile	59	43	31	22	36	21	12	21	19	42	49	43
	Average	50	40	25	18	25	19	11	19	17	40	40	34
EC2	**Max**	3	2	2	4	8	4	2	3	3	4	3	4
	Min	2	1	2	2	1	2	1	1	2	2	1	1
	25 percentile	2	2	2	3	2	2	1	1	2	2	2	2
	50 percentile	3	2	2	3	3	3	1	2	2	3	2	2
	75 percentile	3	2	2	3	4	3	2	2	3	4	3	3
	Average	3	2	2	3	3	3	1	2	2	3	2	3
EC3	**Max**	2	2	3	4	3	3	2	1	2	2	5	3
	Min	0	1	1	2	1	1	1	1	1	1	1	1
	25 percentile	2	1	1	3	1	2	1	1	1	1	1	2
	50 percentile	2	1	1	3	2	2	1	1	1	2	2	2
	75 percentile	2	1	2	4	2	2	1	1	2	2	2	3
	Average	2	1	2	3	2	2	1	1	1	2	2	2

Figure 4.8 Seasonal variation of carbon fractions of *PM_{10}*

The high concentrations of OC1, OC2, OC3, OC4, OP and EC1 during winter season may be represented the source of coal combustion, motor vehicle exhaust and biomass burning and the result is justified by Cao et al. 2005. The study reported that the carbon fractions OC2, OC3, OC4, OP and EC1 represent gasoline motor vehicle exhaust or coal combustion (Cao et al. 2005). The high concentrations of EC2 and EC3 during pre-monsoon and monsoon seasons were indicated diesel vehicle exhaust justified by (Watson et al. 1994). This study revealed that the high concentrations of EC2 and EC3 represent diesel vehicle exhaust as it contains lots of high temperature component of elemental carbon particles (Watson et al. 1994).The high OC1 concentration during post-monsoon season was observed and it might be due to biomass burning (Watson et al. 1994). Approximately the annual percentage variation of OC and EC fractions in TC is shown in **Table 4.2.** Table represented that the most dominated fractions of TC was OC2, OC3, OC4 and EC1. Other fraction contributed less than 15% in TC.

Table 4.2: **Percentage variation of OC and EC fractions in TC (2011)**

Organic Carbon (OC)				Elemental Carbon (EC)		
OC1	**OC2**	**OC3**	**OC4**	**EC1**	**EC2**	**EC3**
4 –13%	23 -27%	15 -24%	25 -29%	14 -19%	2 -4%	2 -3%

Thus the high concentrations of EC2 and EC3 during pre-monsoon and monsoon seasons were indicated diesel vehicle exhaust (Mandal et al. 2013).

4.3.1.4 Determination of total carbonaceous aerosols in PM_{10}

The total carbonaceous aerosols (TCA) are one of the major constituents of $PM_{10.}$ The major two components of TCA are OC and EC which contributed large fraction of atmospheric particulate matter by exhibiting a wide range of molecular structure. They have a strong influence on climate and health related issues. TCA is calculated from the formula given below **(**Turpin and Huntzicker 1995**)**. Ambient TCA concentration was highest in the post-monsoon season followed by winter, pre-monsoon and monsoon. The annual average percentage of TCA, OC and EC in PM_{10} were estimated as 61.87, 32.75 and 9.47%, respectively. The percentage contribution of TCA in PM_{10} was estimated during post-monsoon season (63.75±0.56%), winter season (63.62±3.62%), pre-monsoon season (59.92±2.91%) and monsoon season (60.20±4.52%), respectively.

TCA= OM+ + EC

Where **OM= Organic Matter = 1.6 x OC (For urban aerosol)**

OM= Organic Matter = 2.1 x OC (For non-urban aerosol)

OC= Organic Carbon

EC= Elemental Carbon

The Naraina urbanized mixed use area fall under urban category, TCA was measured by using the empirical formula **(TCA= 1.6 x OC + EC).** The monthly/ seasonal variation of TCA and percentage contribution of OC, EC and TCA in PM_{10} at Naraina, the urbanized mixed use area of Delhi is shown in **Table 4.3.**

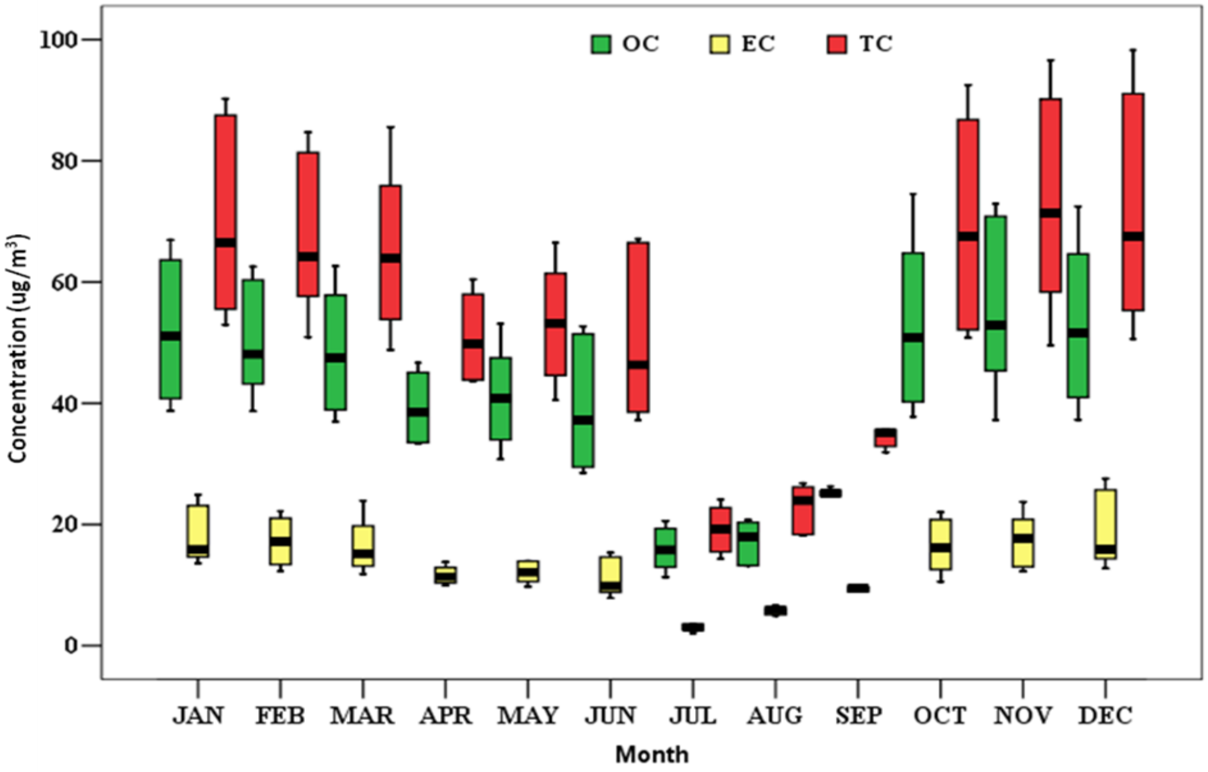
Table 4.3: **Monthly/Seasonal variation of TCA and percentage contribution of OC, EC and TCA in PM_{10} (2011)**

Season	Month	TCA	%TCA in PM_{10}	% of OC in PM_{10}	% of EC in PM_{10}
Winter	December (n=10)	302.19±49.02	66.47±2.17	35.06±1.48	10.37±1.64
	January (n=8)	266.88±71.87	66.25±8.11	34.32±4.47	11.34±1.72
	February (n=8)	181.53±55.14	63.01±6.94	32.90±4.65	10.36±1.10
	March (n=10)	153.48±60.58	58.74±10.38	30.96±5.87	9.19±3.12
	Average (n=36)	**226.02±70.03**	**63.62±3.62**	**33.31±1.80**	**10.32±0.88**
Pre-monsoon	April (n=8)	171.36±30.30	59.77±9.85	32.26±4.85	8.15±2.20
	May (n=8)	190.59±58.86	57.09±6.82	30.03±4.01	9.04±1.48
	June (n=8)	97.96±10.26	62.90±10.89	33.33±5.25	9.57±2.96
	Average (n=24)	**153.30±48.88**	**59.92±2.91**	**31.87±1.68**	**8.92±0.72**
Monsoon	July (n=8)	53.46±7.81	55.75±6.53	30.06±3.77	7.65±0.61
	August (n=8)	70.90±6.63	64.78±3.31	33.78±2.16	10.73±1.32
	September (n=8)	98.43±14.80	60.07±5.45	31.65±3.97	9.43±1.05
	Average (n=24)	**74.26±22.67**	**60.20±4.52**	**31.83±1.87**	**9.27±1.54**
Post-monsoon	October (n=8)	247.75±51.34	63.36±3.25	33.69±2.27	9.45±1.32
	November (n=8)	279.17±53.27	64.15±4.09	34.27±2.51	9.32±1.53
	Average (n=16)	**263.46±22.22**	**63.75±0.56**	**33.98±0.41**	**9.39±0.09**
Annual	**(n=100)**	**176.14±84.70**	**61.87±2.10**	**32.75±1.07**	**9.47±0.60**

The analytical data showed that TCA formation in the ambient air was highest in the post-monsoon season followed by winter, monsoon and pre-monsoon. The percentage variation of TCA in PM_{10} was more or less same (59.92 to 63.75) in the ambient year during the study period (January 2011 to December 2011). The annual average of TCA in PM_{10} was 61.87 ≈ 62% during the study period in Delhi. The city like Delhi is greatly influences by anthropogenic carbonaceous aerosols due to large movement of traffic movement and small and medium scale industrial emission. Bisht et al. 2015 reported that TCA accounted for an averaged 45% of PM_{10} mass at a rural station in southern peninsular India. Pachauri et al. 2013 reported that average TCA concentration was 47.6% of PM_{10} mass at urban location of Agra city, India. The present study was carried out in urbanized mixed use area, thus the contribution of TCA were high as compared to reported value.

4.3.2 Monthly/Seasonal variation of OC, EC and TC in $PM_{2.5}$

A few studies were carried out in India to evaluate the OC, EC and TC concentrations in $PM_{2.5}$ especially in Delhi. In the present study, carbonaceous aerosols were found a major part, of around 50% of $PM_{2.5}$ (Mandal et. al 2014). Carbonaceous aerosol in $PM_{2.5}$ fraction were investigated in Naraina, urbanised mixed use of Delhi in the 2011. The annual average concentrations of OC, EC and TC were 41.12±9.17, 13.25±3.11 and 54.37±11.96 µg/m^3 respectively. The highest concentrations of OC, EC and TC, in the month of December 2011 were 52.91±13.81, 18.92±5.88 and 71.83±19.33 µg/m^3, respectively, whereas lower concentrations observed in the month of July were16.01±3.64, 3.16±0.83 and 19.17±3.98 µg/m^3, respectively.The monthly/seasonal variation of OC, EC and TC in $PM_{2.5}$, in Naraina, the urbanized mixed use area of Delhi is shown by whistle plot in **Figure 4.9.**



Concentrations of OC in $PM_{2.5}$

Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	67	63	63	47	53	53	21	21	26	75	73	72
Min	39	39	37	33	31	29	11	13	23	38	37	37
25 percentile	41	43	39	34	34	29	13	14	25	41	46	41
50 percentile	51	48	48	39	41	37	16	18	25	51	53	52
75 percentile	63	59	57	44	47	51	19	20	25	63	68	64
Average	52	51	49	40	41	40	16	18	26	53	55	53

Concentrations of EC in $PM_{2.5}$

Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	25	22	24	14	14	15	5	7	11	22	24	28
Min	14	12	12	10	10	8	2	5	8	11	12	13
25 percentile	15	13	13	11	11	9	3	5	9	13	14	15
50 percentile	16	17	15	11	12	10	3	6	9	16	18	15
75 percentile	23	21	20	12	14	15	3	6	10	20	20	26
Average	18	17	17	12	12	11	3	6	10	16	18	19

Concentrations of TC in $PM_{2.5}$

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	90	85	86	60	66	67	24	27	36	93	97	93
Min	53	51	49	44	40	37	14	18	32	51	50	51
25 percentile	56	58	54	44	45	39	15	20	33	53	60	56
50 percentile	66	64	64	50	53	46	19	24	35	67	71	57
75 percentile	87	80	75	57	60	66	22	26	36	85	88	91
Average	70	68	66	51	54	51	19	24	35	70	73	72

Figure 4.9 Monthly/Seasonal variations of OC, EC and TC in $PM_{2.5}$ in Naraina Industrial Area of Delhi (2011)

The trends of OC, EC and TC concentrations were decreasing from January 2011 to March 2011, while sharp increasing trends were observed during the months of April 2011 and May 2011. The concentrations of OC, EC and TC during winter, pre-monsoon, monsoon and post-monsoon seasons were (51.07±11.42, 17.77±4.72 and 68.84±15.79 µg/m^3), (40.20±8.71 11.71±2.23 51.91±10.81 µg/m^3), (19.99±2.93, 6.30±0.85, 26.29±3.46 µg/m^3) and (54.26±14.75, 16.96±4.57, 71.22±18.76 µg/m^3), respectively. The results showed a clear seasonal variability of OC, EC and TC in $PM_{2.5}$ size of particulate matter. The season wise OC, EC and TC concentrations during the study period were followed the same season wise pattern of the particulate matter of $PM_{2.5}$. The concentrations of OC ranged 16.01–55.36, EC ranged 3.16–18.92 and TC 19.17–71.83µg/m^3 respectively. The annual mean of OC and EC concentration were 41.12±9.17 and 13.25±3.11 µg/m^3, respectively. Zhang et al. 2011, reported that the annual average OC and EC concentrations at three rapid urbanization and industrialization locations at Xiamen city in China ranged between 15.81-19.73 and 2.74-3.49 µg/m^3 respectively in the year 2011. The observed values of OC and EC in this study in Delhi were comparatively higher than Xiamen city in China. The values of OC and EC in Delhi as compared to other city of Asian countries are quite high due to traffic emission, industrial emission and biomass burning. The contribution of OC, EC and TC were attributed to high emissions from bursting of fire crackers during Diwali festival (post-monsoon), biomass burning and unfavourable metrological conditions (stability of atmospheric boundary layer, low-average mixing height and slow dispersion) during winter season as compared to pre-monsoon and monsoon seasons in urbanised mixed use area of Delhi (Mandal et al. 2014).

4.3.2.1 The correlation and regression of OC, EC TC of $PM_{2.5}$

The correlation and regression of OC, EC, TC and $PM_{2.5}$ in Delhi is shown in **Figure 4.10 (i), to Figure 4.10 (iv)**.The annual average strong correlation between OC and EC was (R^2= 0.74). The strong correlation between OC and EC was observed in pre-monsoon (R^2=0.83), followed by winter (R^2 =0.79) and post-monsoon (R^2=0.71) seasons. The weak correlation was in monsoon (R^2 =0.57) season. OC and EC were correlated with each other, implying the existence of similar emission sources such as coal combustion, biomass burning and vehicular exhaust. Chen et al. 2013, reported that correlations between OC and EC in $PM_{2.5}$ were found to be strong in Pingtan (R^2=0.70) and Jin'an (R^2=0.66) in the location of Fuzhou in China, suggesting that there were similar primary pollutants of OC and EC. The correlations between OC and EC was found in spring (R^2=0.50) and autumn (R^2=0.73) at Xiamen (rapid urbanized and industrialized) in China suggesting the similar emission and transport processes for carbonaceous aerosols (Zhang et al. 2011). The measurements of OC and EC provide an idea to identify the possible sources of carbon emissions. EC is a good marker for the diesel–fuel engine exhaust emissions (Gray and Cass 1998; Funasaka et al.1998).

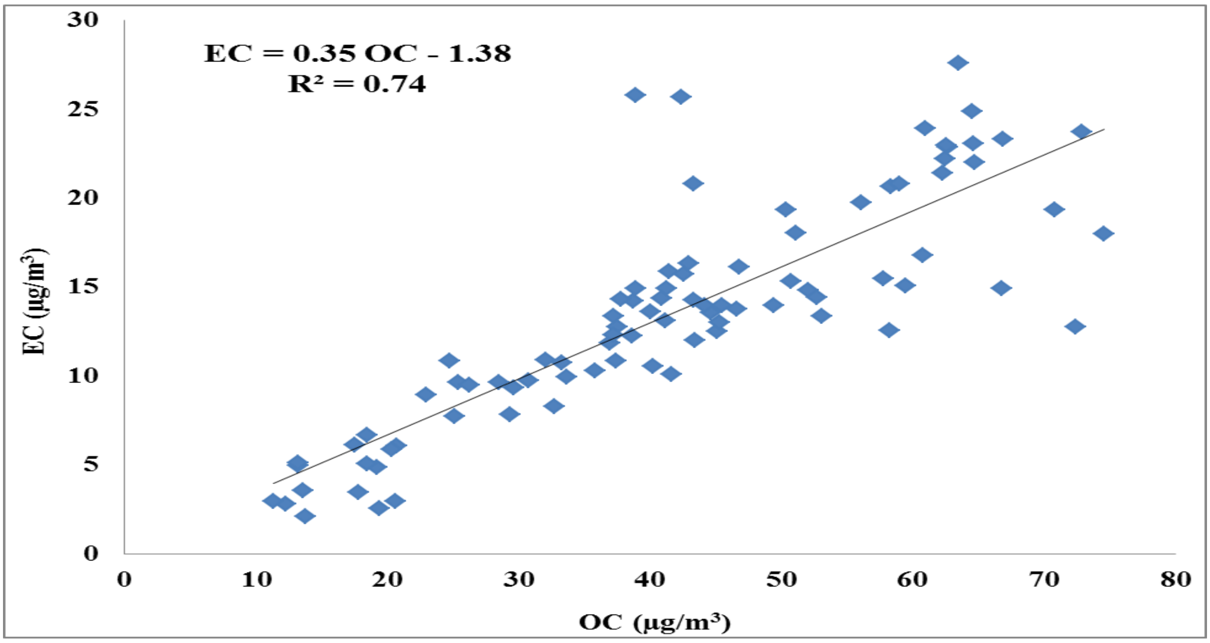


Figure 4.10 (i) Correlations between OC and EC in $PM_{2.5}$ (2011)

Annual EC and TC in $PM_{2.5}$ were correlated with each other (R^2=0.85).The emission sources of EC and TC were also indicated the similar emission sources. Annual average variation of EC in TC varied from 16 to 27% with an average mean of 24% during the study period (2011).

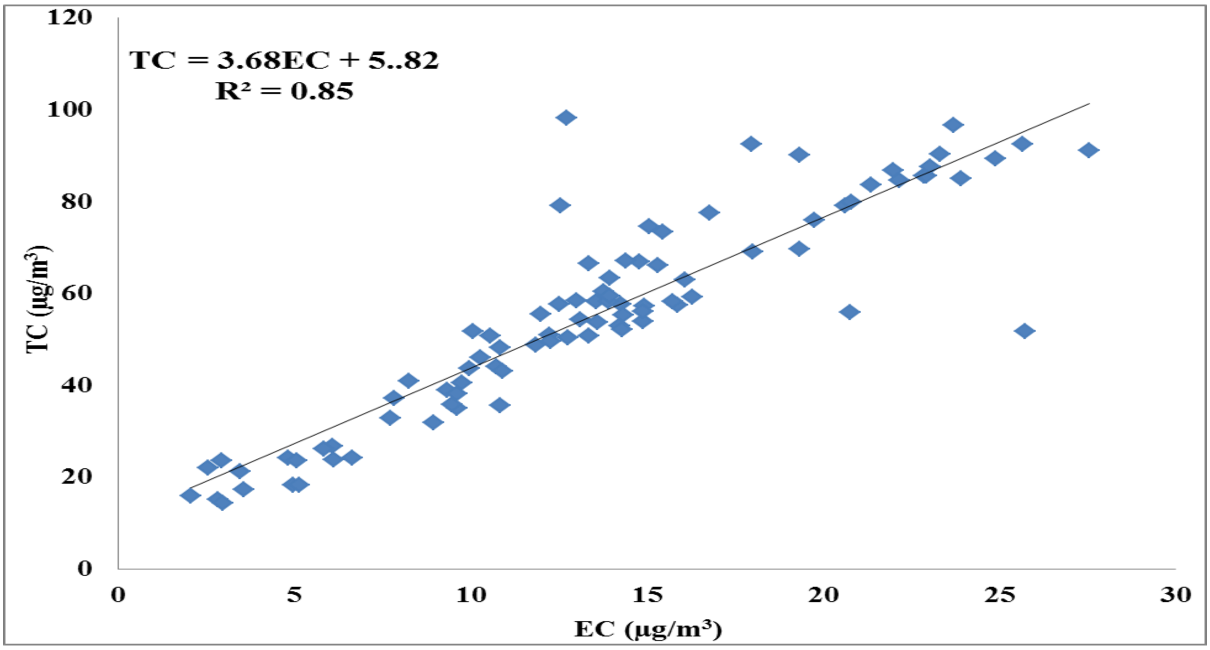


Figure 4.10 (ii) Correlations between EC and TC in $PM_{2.5}$ (2011)

In general EC contribution to TC is governed by traffic and industrial emissions in and around the sampling location.

OC and TC was strongly correlated with each other (R^2 = 0.98) during the study period indicating the similar source emission.

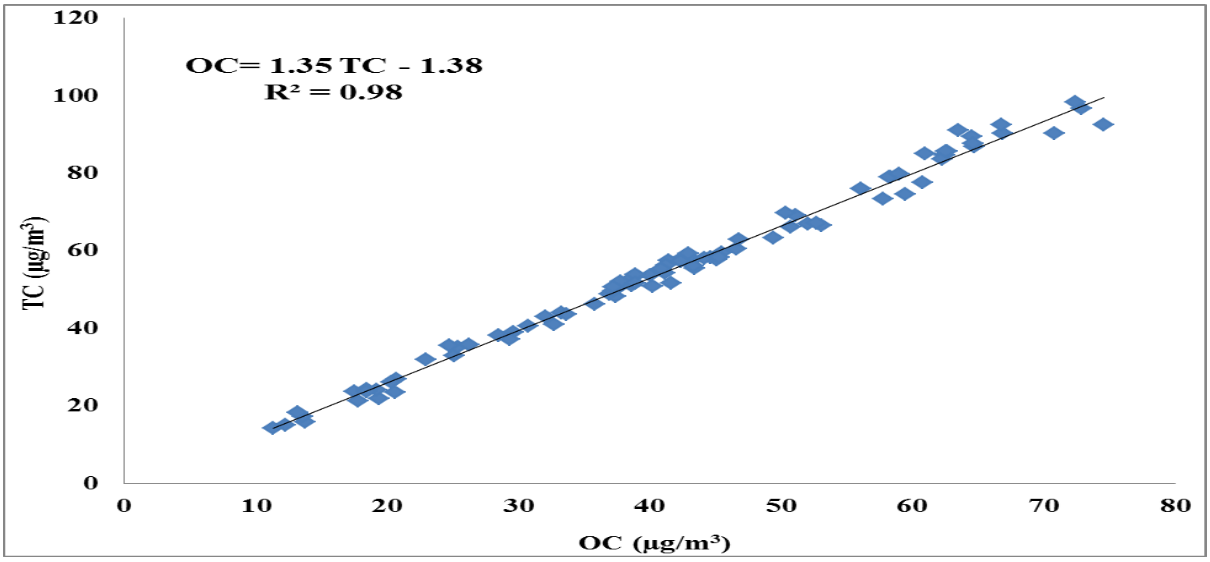


Figure 4.10 (iii) Correlations between OC and TC in $PM_{2.5}$ (2011)

The contribution of OC in TC was varied from 74% to 86% with an average variation of 76%. OC was the predominant contributor to TC with an average percentage of more than 70% (Yang et al. 2011).

Annual TC and $PM_{2.5}$ were correlated with each other ($R^2 = 0.97$) which indicated that TC had significant contribution to increase the concentration of $PM_{2.5}$.

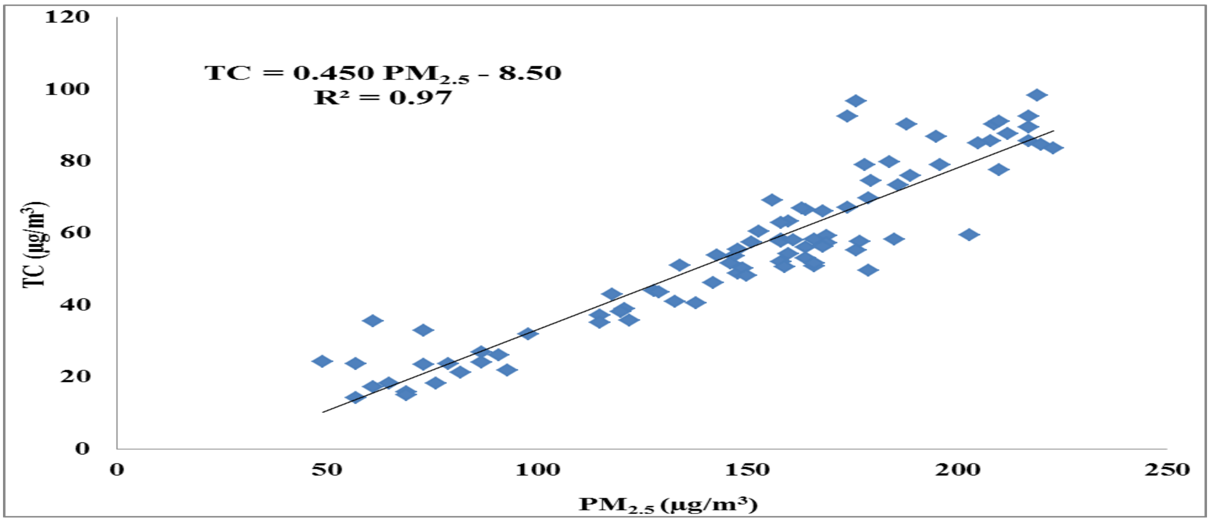


Figure 4.10 (iv) Correlations between TC and $PM_{2.5}$ (2011)

TC contribution in $PM_{2.5}$ varied from 26 to 41% with an average contribution of 37% during the study period in urbanized industrial area of Delhi in the year 2011.

4.3.2.2 Estimation of OC and EC ratios in $PM_{2.5}$

The ratio of monthly average organic carbon (OC) with elemental carbon (EC) in $PM_{2.5}$ was obtained in the range 2.71–5.29 with an annual average of 3.28 indicated multiple emission sources such as vehicular exhaust, coal smoke, biomass burning (**Table 4.4)**. The monthly average ratio of OC with EC was exceeded 2.0 in the present study. The ratio of OC and EC ratios could be used to distinguish different origin and transformation characteristics (Chu 2005). The OC/EC ratios vary for vehicular exhaust (2.5–5.0) (Schauer et al. 2002), coal smoke (2.5–10.5) (Chen et al. 2006), kitchen emissions (4.3–7.7) (See and Balasubramanian 2008) and biomass burning (3.8–13.2) (Zhang et al. 2007) etc. respectively.

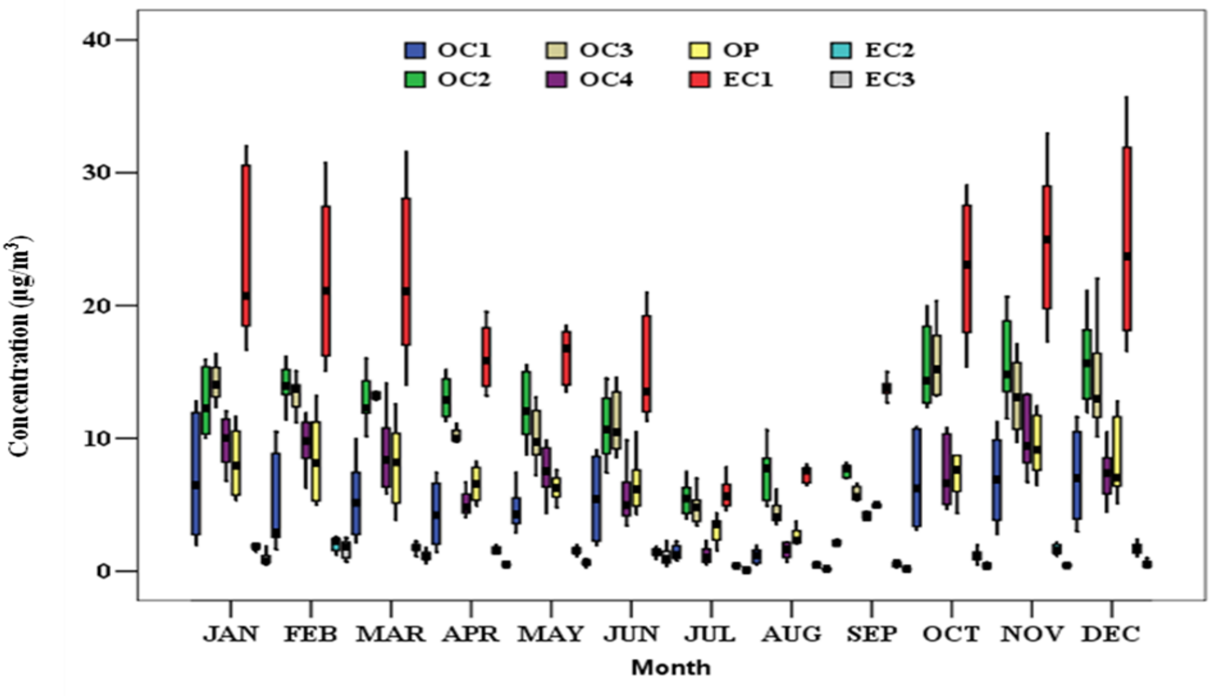
Table 4.4: **Monthly/Seasonal variation of OC and EC ratios in $PM_{2.5}$ (2011)**

Winter Season					**Pre-monsoon Season**				**Monsoon Season**				**Post-monsoon Season**		
Dec	Jan	Feb	Mar	**Avg**	Apr	May	Jun	**Avg**	Jul	Aug	Sep	**Avg**	Oct	Nov	**Avg**
2.85	2.89	2.98	2.96	**2.92**	3.36	3.39	3.56	**3.43**	5.29	2.94	2.71	**3.65**	3.30	3.16	**3.23**

In the present study, ratio of OC with EC was high in the month of April, October and November (3.96, 3.70 and 3.65) may be due to formation of atmospheric SOC. The OC/EC ratios varied from 2.1 to 8.7 with an annual average of 5.7, indicating that vehicle exhaust, coal smoke and biomass burning was main source apportionments of carbonaceous fractions in Xiamen (Zhang et al. 2011).

4.3.3 Characterization of carbon fractions in $PM_{2.5}$

Season wise fractions of OC (OC1, OC2, OC3 and OC4), pyrolysis (OP) and fractions of EC (EC1, EC2 and EC3) in $PM_{2.5}$, during the study period in urbanised mixed use area of Delhi in the year 2011 is showed by whistle plot in **Figure 4.11.**The concentrations of OC1, OC2, OC3, OC4, OP and EC1 during winter season represented the mixture of coal combustion, motor vehicle exhaust and biomass burning. The concentrations of EC2 and EC3 during pre-monsoon and monsoon seasons were indicated the emission from diesel vehicle exhaust as it contains lots of high temperature component of EC (Watson et al. 1994). A sharp increase in levels of OC1 and EC1 (ie., EC-OP) during winter at two residential sites of Kanpur city, India revealed that biomass burning could be a significant contributor to carbonaceous aerosols (Behera et al. 2015). Carbon fraction (OC1) represents biomass burning, whereas carbon fractions OC2, OC3, OC4, OP and EC1 represent gasoline motor vehicle exhaust or coal combustion (Cao et al. 2005).



OC FRACTIONS		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
OC1	**Max**	13	11	10	7	7	9	2	2	2	11	11	12
	Min	2	2	2	1	3	2	1	1	2	3	3	3
	25 percentile	3	3	3	2	4	2	1	1	2	4	4	4
	50 percentile	6	3	5	4	4	5	1	1	2	6	7	4
	75 percentile	12	9	7	6	6	9	2	2	2	10	10	10
	Average	7	5	5	4	5	5	1	1	2	6	7	7
OC2	**Max**	16	16	16	15	16	15	7	11	8	20	21	18
	Min	10	11	10	11	9	7	4	5	7	12	11	13
	25 percentile	10	13	12	12	10	9	4	6	7	13	14	13
	50 percentile	12	14	12	13	12	11	5	8	8	14	15	14
	75 percentile	15	15	14	14	15	13	6	8	8	18	18	17
	Average	13	14	13	13	12	11	5	7	8	15	16	16
OC3	**Max**	16	15	15	11	13	15	7	6	7	20	17	22
	Min	12	11	12	10	7	9	3	4	5	13	10	10
	25 percentile	14	12	13	10	9	9	4	4	5	13	11	12
	50 percentile	14	14	13	10	10	10	5	4	6	15	13	13
	75 percentile	15	14	13	10	12	13	5	5	6	18	15	16
	Average	14	13	13	10	10	11	5	4	6	15	13	14
OC4	**Max**	12	12	14	7	10	10	2	2	4	11	13	9
	Min	7	6	6	4	4	3	1	1	4	5	7	5
	25 percentile	8	9	7	5	6	4	1	1	4	5	8	6
	50 percentile	10	10	8	5	8	5	1	2	4	7	9	7
	75 percentile	11	11	11	5	9	7	2	2	4	10	12	8
	Average	10	10	9	5	8	6	1	2	4	7	10	7
OP	**Max**	12	13	13	8	8	10	4	3	7	13	12	13
	Min	5	5	4	5	5	4	2	2	4	4	6	5
	25 percentile	6	5	6	6	6	5	2	2	5	6	8	7
	50 percentile	8	8	8	7	6	6	4	2	5	8	9	7
	75 percentile	10	11	10	8	7	7	4	3	5	9	11	7
	Average	8	8	8	7	6	7	3	3	5	8	9	9
EC1	**Max**	32	31	32	20	19	21	8	8	15	29	33	36
	Min	17	15	14	13	14	11	5	6	13	15	17	17
	25 percentile	18	16	17	14	14	12	5	7	13	18	20	20
	50 percentile	21	21	21	16	17	14	6	8	14	23	25	20
	75 percentile	30	27	27	18	18	19	6	8	14	28	29	32
	Average	24	22	22	16	16	15	6	7	14	22	25	25
EC2	**Max**	3	3	2	2	2	2	1	1	1	1	2	2
	Min	1	1	1	1	1	1	0	0	0	0	1	1
	25 percentile	2	2	2	1	1	1	0	0	0	0	1	1
	50 percentile	2	2	2	2	2	1	0	0	1	1	2	2

	75 percentile	2	2	2	2	2	2	0	1	1	1	2	2
	Average	2	2	2	2	2	1	0	0	1	1	2	2
EC3	**Max**	2	3	2	1	1	2	0	0	1	0	1	1
	Min	0	1	1	0	0	0	0	0	0	0	0	0
	25 percentile	1	1	1	0	1	1	0	0	0	0	0	0
	50 percentile	1	2	1	1	1	1	0	0	0	0	0	0
	75 percentile	1	2	1	1	1	1	0	0	1	0	1	1
	Average	1	2	1	0	1	1	0	0	0	0	1	1

Figure 4.11 Season wise fractions of OC (OC1, OC2, OC3 and OC4), pyrolysis (OP) and fractions of EC (EC1, EC2 and EC3) in PM$_{2.5}$ (2011)

The annual percentage variation of fractions of OC and EC is shown in **Table 4.6**

Table 4.4 a: **Percentage variation of OC and EC fractions in TC of PM$_{2.5}$ (2011)**

Organic Carbon (OC)				**Elemental Carbon (EC)**		
OC1	**OC2**	**OC3**	**OC4**	**EC1**	**EC2**	**EC3**
0.4–13%	22 -28%	23 -24%	4 -14%	32 -36%	2 -3%	0.4 -3%

In the present study OC2, OC3, OC4, OP and EC1 concentrations were higher as compared to OC1, EC2 and EC3. Behera et al. 2015, reported that the average abundances of OC1, OC2, OC3, OC4, OP, EC1, EC2, and EC3 in total carbon (TC) at all the urban sites for three seasons were 10.03, 19.04, 20.03, 12.32, 10.53, 33.39, 3.21, and 1.99%, respectively which justified the present study (Mandal et al. 2014).

4.3.4 Estimation of primary organic carbon and secondary organic carbon

Secondary organic carbon **(**SOC) is formed from reactive organic gases through different processes like oxidation and reduction followed by nucleation and condensation (Kwangsam et al. 2004). The separation and quantification of primary organic carbon **(**POC) and formation of SOC are difficult as no simple direct analytical technique is not available (Yu et al. 2007, 2004), although there are many methods are available for quantification of total organic carbon (TOC) ie OC. The ratio of OC and EC (direct measurement) received wide spread application. The method is suggested that lowest ratio of OC and EC of each samples contain almost exclusively primary carbonaceous organic carbon (POC). The formation of SOC in the atmosphere is depended on metrological favourable conditions like higher temperature and more intense solar radiation for photochemical activity. The formation of SOC is low when photochemical activity is low, indicates low OC/EC ratios. The contribution of SOC in OC concentration was significantly high in the study area (Naraina, mixed use area of Delhi) during pre-monsoon season due to favourable climatic condition (higher temperature and more intense solar radiation). The minimum ratio of OC/EC was obtained to estimate the formation of SOC (Castro et al. 1999) in the atmosphere. The equations to estimate SOC are given below.

$$\mathbf{SOC = TOC - POC}$$

$$\mathbf{POC = EC * (OC/EC)_{minimum}}$$

The minimum ratio of OC/EC during the study period (2011) at urbanized industrial area of Delhi was 1.25. It was observed that SOC concentrations varied significantly from season to season. The seasonal fluctuation of POC and SOC and EC in $PM_{2.5}$ is illustrated in **Fig. 4.12**. The distribution of SOC during the study period (2011) in pre-monsoon, monsoon, post-monsoon and winter seasons were 49.36, 47.09, 46.42 and 41.87 % of TC, respectively.

The atmospheric formation of SOC was followed the decreasing trend in pre-monsoon, post-monsoon, winter and monsoon, whereas POC followed the decreasing trend in monsoon, winter, post-monsoon, pre-monsoon may be due to variation of photochemical activity in different seasons. There was no significant variation of EC with the seasons. Wang-Li et al. 2013 reported that ambient SOC formation ranged from 68% to 87% at an animal agricultural intensive area in North Carolina, USA during the one year study period (December, 2008 to December, 2009). However in the present study the variation of SOC varied from 42% to 60%. The reported SOC concentration at North Carolina, USA is high as compared to the study in Delhi, India. This might be due to the favourable meteorological conditions which could cause more particle agglomeration and hygroscopic growth.

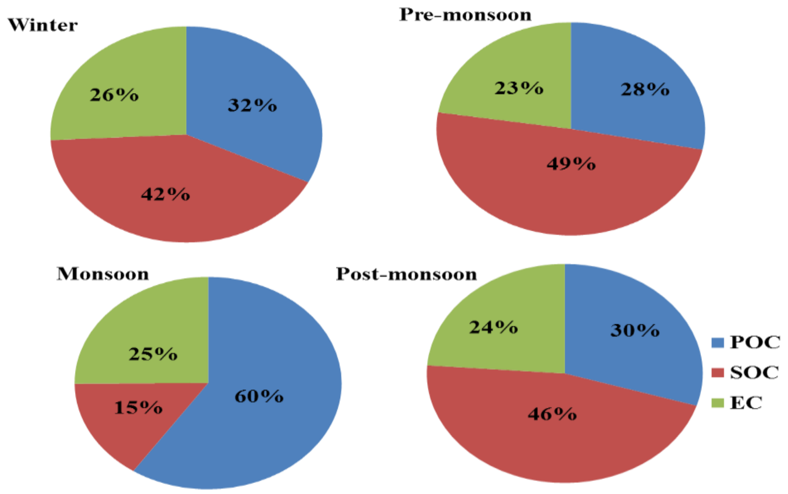


Figure 4.12 The seasonal fluctuation of POC and SOC and EC in $PM_{2.5}$ (2011)

Secondary Organic Aerosols (SOAs) are the air pollutants emitted either from natural sources or from anthropogenic sources. They are mostly formed in the air through a complex interaction of sunlight, volatile organic compounds from natural air pollution sources like trees, plants, or from anthropogenic sources like vehicular or industrial emissions, biomass burning, and cooking activities etc. SOA plays an important role on physical and chemical properties of atmosphere, relating to haze, visibility, climate and health. SOA cannot be directly measured through any sophisticated instruments or analyser. However the empirical formula to measure the concentration of SOA (Turpin and Huntzicker 1995) in the urban aerosol and non-urban aerosol (Cao et al. 2005) are given below.

Secondary organic aerosol = SOA = 1.6 x SOC (for urban aerosol)
Secondary organic aerosol = SOA = 2.1 x SOC (for non-urban aerosol)
Where
SOC = Secondary organic carbon

The annual average concentration of SOA during the study period (January, 2011- December, 2011) was 39.93µg/m$^{3.}$ The annual average concentration of SOC was 60.34% of OC (Mandal et al. 2014). The annual average contribution of SOA was 27.42% of $PM_{2.5}$ mass, which indicated that SOA contributed a major fraction of $PM_{2.5}$ mass in Delhi.

4.3.4.1 Determination of total carbonaceous aerosols in $PM_{2.5}$

The lower concentrations of TCA occurred in monsoon, whereas higher concentrations occurred in post-monsoon and winter seasons respectively. The higher EC concentration was due to increased soot particles from vehicles and industrial emissions. The determination of TCA in $PM_{2.5}$ was carried out by using the empirical formula (Cao et al.2005).

TCA= OM+ + EC

Where **OM= Organic Matter = 1.6 x OC (For urban aerosol) (1)**

OM= Organic Matter = 2.1 x OC (For non-urban aerosol) (2)
OC= Organic Carbon
EC= Elemental Carbon

The Naraina urbanized mixed use area fall under urban category, TCA was measured by using the empirical formula (2).The monthly/ seasonal variation of TCA and percentage contribution of OC, EC and TCA in $PM_{2.5}$ is shown in **Table 4.5.**

Table 4.5: **Monthly/Seasonal variation of TCA and percentage contribution of TCA in $PM_{2.5}$**

Season	Month	TCA	% of TCA in $PM_{2.5}$
Winter	December (n=10)	103.58±27.57	51.81±5.93
	January (n=8)	101.52±23.84	55.83±5.24
	February (n=8)	98.10±18.88	55.54±5.81
	March (n=10)	94.74±20.13	54.19±4.50
	Average (n=36)	**99.48±22.61**	**54.34±5.37**
Pre-monsoon	April (n=8)	75.03±11.11	53.74±2.85
	May (n=8)	78.37±16.60	50.93±7.19
	June (n=8)	74.68±20.37	51.63±5.87
	Average (n=24)	**76.03±16.03**	**52.10±5.30**
Monsoon	July (n=8)	28.77±6.14	38.92±5.13
	August (n=8)	35.14±8.64	41.46±4.74
	September (n=8)	50.95±0.80	43.02±1.12
	Average (n=24)	**38.29±5.19**	**41.14±3.66**
Post-monsoon	October (n=8)	101.44±27.62	54.39±7.96
	November (n=8)	106.12±27.50	51.31±7.71
	Average (n=16)	**103.78±27.56**	**52.85±7.83**
Annual	**(n=100)**	**79.04±17.43**	**50.23±5.34**

The seasonal variation of annual average concentrations of TCA in $PM_{2.5}$ in the urbanized industrial area of Delhi, was in the descending order of winter (54.34±5.37)%, post-monsoon (52.85±7.83)%, pre-monsoon (52.10±5.30)% , monsoon (41.14±3.66)%. Winter season leads to frequent particle agglomeration and hygroscopic growth in lower atmospheric layer. Yang et al. 2015 reported, that the annual average concentrations of TCA accounted for 32.6% of the total $PM_{2.5}$ mass in the year 2013, at Wanzhou, (commercial area), China, which was lower than annual average concentrations of TCA accounted for 50% of the total $PM_{2.5}$ mass in the year 2011 at Naraina, urbanised area of Delhi. This could be less emission of primary pollutants and formation of secondary organic aerosol (SOC) in Wanzhou, China than Delhi city. Satsangi et al.2012, reported TCA accounted for an averaged 49.5% of $PM_{2.5}$ mass in suburban location of Agra in the year 2012, Pachauri et al. 2013 reported that TCA contribute 52%, 54% and 58% to total $PM_{2.5}$ mass at traffic, campus and rural sites of Agra city.

4.4 Heavy Metals

India is facing progressive deterioration in air quality attributable to growing trends of particulate matter (PM), particulate associated heavy metals (HMs), and other air pollutants in ambient atmosphere (Agarwal et al. 2003). Thus, air pollution and its impacts on health have become a major concern at all levels in India. It was estimated urban air pollution causes approximately 3, 60,000 premature deaths each year in Asia (Stone et al. 2010) and the city like Delhi, the estimated 10,500 premature deaths per year for the same reason (Gurjar et al. 2012). Air borne PM is a unique class of air contaminants because of its potential complexity both in terms of chemical composition and physical properties. The effects of PM on the atmosphere, climate and public health are among the central topics in recent environmental research. They are solid and liquid particles varying in size within the nanometer to micrometer range. They are also responsible for climate change by disturbing the energy balance of the earth, hydrological cycles, atmospheric circulation and the abundance of greenhouse and reactive trace gases (Poschl et al. 2005).

Several studies reported that HMs and their compounds that are associated with PM_{10} are respirable and can persist in the atmosphere for longer duration. Heavy metals are indestructible and most of them have toxic effects on living organisms. Although some of the metals are essential to human in order to remain healthy, at high levels they can also pose toxicological risks (Shinggu et al. 2010). The multiple applications of heavy metals in various sectors like industrial, domestic, agricultural, medical and technological applications, have led to wide range of distribution to the environment. Over the past decade, several epidemiological studies have established a definite link between air borne particles and human mortality and morbidity (Schwartz et al. 1996, Pop and Dockery, 2006). The toxicity level of HMs depends on several factors like dose, route of exposure, chemical species, age, gender, genetics and nutritional status of exposed individuals (Tchounwou et al. 2014). They may originate from both natural and anthropogenic sources but anthropogenic origin is of major concern (Mafuyai et al. 2014). The natural sources of HMs include terrestrial dust, bioorganic emanations, emission from forest fires etc. The anthropogenic sources includes emissions from power plants, non-ferrous metal smelters, incinerators, steel and cement plants, fossil fuel burning, electroplating, surface coating, transportation, domestic combustions and re-entrained road or paved/ unpaved surface dust. The ambient particulate matter (PM), its associated HM concentrations and greenhouse gases are generally higher in megacities and industrial areas in comparison with the rural environment (Gurjar et al. 2008).

In the present study, PM_{10} samples were collected in four seasons ie., winter (January to March, December), pre-monsoon (April to June), monsoon (July to September) and post-monsoon (October to November) in the year 2011. Total 50 numbers of samples were analyzed to evaluate seasonal variation of heavy metals (HMs) in PM_{10} samples. The samples were analyzed through inductively coupled plasma optical emission spectrophotometry (model iCAP 6300Duo, Thermo Fisher Scientific, Cambridge, England).

4.4.1 Seasonal variation of HMs in mixed use area of Delhi

Airborne inhalable HMs concentrations in PM_{10} in an industrialized urban area of Delhi were determined for proper identification and quantification of their emission sources. Total ten (10 No's) of heavy metals (HMs) like arsenic (As), cadmium (Cd), cobolt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) concentrations were determined in PM_{10} size of particulate matter. The seasonal variation of HMs concentration is presented **Table 4.6.**

Table 4.6: Seasonal variation of HMs (2011)

Species	**Annual**	**Seasons**			
		Winter	**Pre-monsoon**	**Monsoon**	**Post-monsoon**
As	0.002±0.002	0.003±0.001	0.003±0.001	0.001±0.001	0.003±0.002
Cd	0.030±0.020	0.029±0.022	0.025±0.015	0.021±0.010	0.038±0.008
Co	0.003±0.002	0.003±0.002	0.002±0.002	0.002±0.001	0.004±0.003
Cr	0.170±0.081	0.192±0.084	0.180±0.054	0.092±0.037	0.227±0.093
Cu	0.183±0.120	0.243±0.065	0.176±0.110	0.035±0.013	0.292±0.104
Fe	4.774±1.889	4.857±2.106	4.591±1.640	4.083±1.153	5.919±2.745
Mn	0.258±0.145	0.314±0.150	0.271±0.088	0.096±0.036	0.369±0.129
Ni	0.170±0.146	0.217±0.144	0.165±0.129	0.021±0.006	0.307±0.110
Pb	0.345±0.207	0.442±0.198	0.348±0.143	0.091±0.020	0.527±0.069
Zn	1.806±1.042	2.370±0.889	1.859±0.679	0.457±0.165	2.621±0.531

Concentration values are reported in µg/m^3

The annual mean concentrations of ten major HMs were As (0.002±0.002), Cd (0.030±0.020), Co (0.003±0.002), Cr (0.170±0.081), Cu (0.183±0.120), Fe (4.774±1.889), Mn (0.258±0.145), Ni (0.170 ± 0.146), Pb (0.345±0.207) and Zn (1.806±1.042) µg/m^3 respectively. HMs concentrations in PM$_{10}$ followed the decreasing trend of post-monsoon, winter, pre-monsoon and monsoon season respectively in the year 2011. The annual mean concentrations of As and Pb were within the permissible limit of the National Ambient Air Quality Standards (NAAQS) of CPCB, 2009. The concentrations of Pb varied from 0.071 to 0.731µg/m^3. The mean Pb concentration during the post-monsoon season exceeded the annual standard of 0.50µg/m^3. After implementation of lead free petrol in India in the year 1999, though ambient Pb concentration has decreased, but still Pb was present in the study area could be due to road dust and multiple industrial applications. Nickel was present at concentrations ranging from 0.014 to 0.528µg/m^3. The mean seasonal concentrations of Ni exceeded the NAAQS (both the 24-hour and annual are 0.020µg/m^3) in all four seasons. Stainless steel, Ni alloys, mining, grinding, smelting, cutting, forging, foundries, casting and moulding industries of Naraina phase II were possible major contributors of Ni emissions in the ambient air. Oil-fired combustion, incineration of municipal garbage and sewage sludge, Cd-Ni battery production, production of electronic goods, electroplating of metal, dye and fabric, printing and paper industries may also have contributed to the concentrations of Ni in ambient air. Cigarette smoking and windblown dust also contributed small fractions of Ni emission in the ambient air. Ni is widely used for multiple purposes at Naraina Industrial Area and this might be vital reason for ambient Ni concentrations regularly exceeded the revised NAAQS of CPCB, 2009. Only three heavy metals like (As, Ni and Pb) were included in revised NAAQS of CPCB. However the emissions of HMs at urbanized mixed use area of Delhi was quite high but comparable with residential and commercial area of Delhi. Few studies were reported ambient cobolt (Co) concentrations in India especially in Delhi. Co concentrations varied from 0.002±0.001 to 0.004±0.003 µg/m^3 with an annual average value of 0.003±0.002 µg/m^3. Co might be present in the selected location due to vehicular exhaust and cigarette smoke (Report of toxicological summary for Co dust 2002) and wide application of Co in the industrial application.

4.4.2 Pearson Correlation Matrix of airborne HMs

The degree of association among the ambient inhalable heavy metals was measured by a correlation coefficient. Pearson Correlation Coefficients among the HMs is presented in **Table 4.7**.

Table 4.7: Pearson Correlation Coefficients among HMs

	As	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
As	1.00									
Cd	0.29*	1.00								
Co	0.46*	0.14	1.00							
Cr	0.34	0.19	0.36	1.00						
Cu	0.36	0.18	0.20	0.35	1.00					
Fe	-0.24	-0.07	0.12	-0.11	0.45*	1.00				
Mn	0.19	0.06	0.24	0.59**	0.60**	0.52**	1.00			
Ni	0.47*	0.10	0.37	0.56**	0.51*	0.02	0.56**	1.00		
Pb	0.22	0.46*	0.23	0.31	0.49*	0.48*	0.54**	0.40	1.00	
Zn	0.36	0.07	0.37	0.46*	0.84**	0.53**	0.73**	0.62**	0.59**	1.00

*Correlation is significant at the 0.05 level (2- tailed)

** Correlation is significant at the 0.01 level (2- tailed)

The positive correlations were obtained among most of the HMs, during the study period at mixed use area of Delhi, indicating the relationship between the two variables, in which both variables move in tandem. The only negative correlations were obtained between Fe-As, Fe-Cd and Fe-Cr, indicating that the source of Fe was different from the emission sources of As, Cd and Cr. As-Cd, As-Co, As-Ni, Cd-Pb, Cr-Zn, Cu-Ni, Cu-Pb, Cu-Fe, Fe-Pb were correlated at the 0.05 level (2-tailed) of significance. Cr-Mn, Cr-Ni, Cu-Mn, Cu-Zn, Fe-Mn, Fe-Zn, Mn-Ni, Mn-Pb and Mn-Zn Ni-Zn, are Pb-Zn were correlated at the 0.01 level (2-tailed) of significance.

4.4.3 Principle Component Analysis of Heavy Metals

Principle component analysis (PCA), described in methodology (3.5.1) was performed to concentrate the variability of HMs data and to characterize the sources that are responsible for ambient HM emission in urbanized mixed use area of Delhi. The lowest eigen value for extracted factors was restricted to more than 1.0 of the total variance. Three factors (PC1, PC2 and PC3) were obtained through PCA analysis. PCA factors were identified using Varimax rotation with Kaiser Normalization. Three factors explained total 76.45% of the variance of HM data. Factor greater or equal to 0.5 was selected for lowest level of significance within a factor. The PCA factor scores for airborne HMs is shown in **Table 4.8**.

Table 4.8 PCA factor scores for airborne HMs (2011)

Heavy Metals	**PC1**	**PC2**	**PC3**
As	-0.07	**0.70**	0.31
Cd	0.10	0.09	**0.94**
Co	0.07	**0.70**	0.09
Cr	0.21	**0.77**	0.03
Cu	**0.77**	0.36	0.18
Fe	**0.86**	-0.32	-0.03
Mn	**0.82**	0.38	-0.01
Ni	0.38	**0.77**	0.05
Pb	**0.67**	0.16	**0.57**
Zn	**0.80**	0.48	0.34
Eigen Value	**4.68**	**1.81**	**1.15**
% Variance	**32.96**	**28.17**	**15.32**
Cumulative %	**32.96**	**61.13**	**76.45**

The factor PC1 represents total 32.96% of variance. This factor is weighted by Cu, Fe, Mn, Pb and Zn, representing a major contribution of HMs from industrial emissions. Fe is the major contributor of airborne HM due to various small and medium scale industries like metal alloys, forging, foundries, casting, moulding etc. in the selected sampling location. Mn, Pb and Zn had significant contributions in the ambient air due to multiple application of such metals like electroplating, dye, fabric, textile, printing and paper products industries located in Naraina Industrial Area in both the phases I and II respectively in Delhi. Khillare et al. 2012 reported that Cd, Ni, Pb, Zn and Cr positively indicated industrial emission sources but European Commission (2000) also reported that other major sources for emission of Cd were from road transport, and from stationary combustion sources. Pakade et al. 2014 reported that agricultural soils are mostly contaminated with heavy metals like Pb, Cu and Mn.

The factor PC2 comprised 28.17% of the total variance. This factor is weighted by As, Co, Cr and Ni, representing the impacts of mobile and stationary combustion sources. Pollution as Zn is considered as the marker of vehicular pollution as Zn is emitted from lubricant oil, brake lining and tires (Zhou et al. 2004). The ratio of Cu and Zn varied from 0.051 to 0.172 respectively during the study period also strongly suggesting vehicular sources (Cadle et al. 1999). The stationary combustion sources likely included small and medium scale roadside dhabas as well as commercial and household kitchen activities. Road side dhaba's use various types of fuels for cooking purposes, including LPG gas, coal, kerosene and sometimes wood and dry leaves. Arsenic and its compounds are extensively used for wood preservations, manufacturing of glass, electronic items and medical application. Various report suggested that As emissions were derived from stationary combustion sources also. Cobalt powder is widely used for formulation of brass and steel alloys in Naraina Industrial Area, phase II. Other major sources of atmospheric Co emissions are from vehicular exhaust and cigarette smoke (Report of toxicological summary for Co dust 2002).

The factor PC3 is consists of 15.32% of the total variance. This factor was weighted by Cd and Pb representing the impacts of suspended/re-suspended of dust. Windblown dust and crustal origin contribute HMs to ambient air. The high concentrations of Co, Cr, Cu, Mn and Ni may derive in part from industrial road dust in Delhi (Rajaram et al. 2014).The emissions of effluent gases from industries and vehicular exhaust contain trace metals which are either deposited to paved or unpaved locations or suspended with vehicular movement on roads. Though Pb was phased out in India in 1999, it is still Pb is present in the road dust. The European Commission (2000) reported that 18% of airborne Cd emissions were from road transport, and 30 to 70 % were from stationary combustion sources. The residues of stationary combustion at the site may have been suspended/ re-suspended with windblown dust during the study period. Gurjar et al. 2004 reported that the presence of Cd varied from 0.004 to 0.01 ng/m^3 might be due to wood and coal combustion at the rural atmospheric environments of Northern India.

4.4.3.1 Time Series Analysis for Airborne Heavy Metals in Delhi

A time series analysis for airborne heavy metals (HMs) concentrations at Naraina mixed use area of Delhi was carried out through Principle Component Analysis-Multiple Linear Regression (PCR-MLR) described in methodology (3.5.1). PCA-MLR is the receptor model and widely used for source identification and quantification from unknown source of emissions of air pollutants. The contribution of airborne HMs was lowest in monsoon season as particulate bound HMs settle down with rain precipitation. The contribution of airborne HMs was maximum in post-monsoon season only. Metrological parameters like wind speed, wind direction, temperature, relative humidity and rainfall played an important role for contributions of air borne HM concentrations at Naraina urban cum Industrial area of Delhi. A strip rise of HM concentrations from October to November in the year 2011 might be impacted due to burning of firecrackers and fireworks during the Diwali celebration. Industrial emission, mobile and stationary combustion, suspended road dust, inverse metrological condition, slow dispersion, low-average mixing height and calm condition during post-monsoon (54%) and winter (51%) seasons were factors that likely contributed to the high concentrations of airborne HMs as compared to pre-monsoon and monsoon seasons. Monthly source contributions of airborne HMs based on PCA-MLR is presented in **Figure 4.13**.

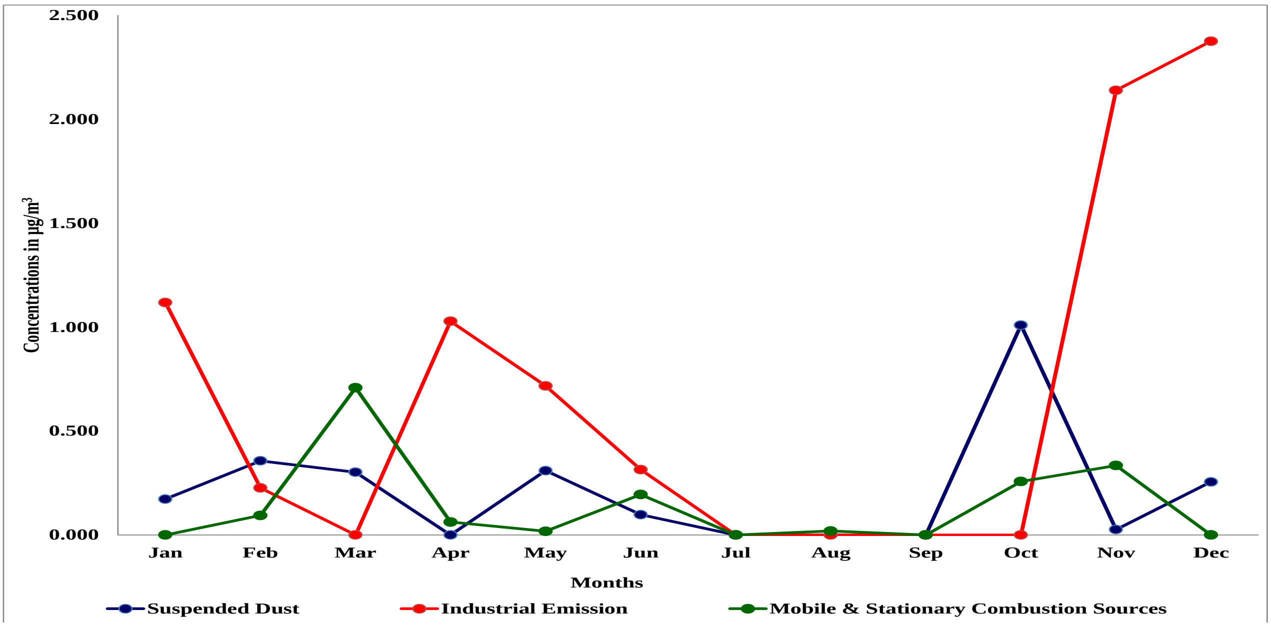


Figure 4.13 Monthly source contributions of airborne HMs in Delhi (2011)

The contributions of airborne HMs were lowest in the monsoon season, as particulate bound HMs settle down with rain precipitation. In general, the source contributions of HMs at this industrialized urban area followed the pattern: industrial emissions (70%) > mobile and stationary combustion (16%) > and suspended dust (14%) at this industrialized urban area. The contributions of HMs were more than 50% from the various types of emissions in industrialized urban area of Delhi. The months of high HM levels attributable to industrial emissions would appear to result in the high overall percentage value of 70% for the industrial contribution.

A steep rise of HM concentrations from October to November in the year 2011 may have been due to burning of firecrackers and fireworks change the relative level of importance of industrial emissions at this time. Industrial emissions, mobile, stationary combustion, suspended road dust, inverse metrological condition, slow dispersion, low-average mixing height and calm conditions during post-monsoon (54%) and winter (51%) seasons were factors that likely contributed to the high concentrations of airborne HMs as compared to premonsoon and monsoon seasons. The concentrations of airborne HMs during the premonsoon season were higher as compared to the monsoon season. The reason might be due to a higher mixing ratio with increased wind velocity during premonsoon season as compared to other seasons.

The common airborne HMs associated with PM_{10} was characterized at an industrialized urban area of Delhi, India for identification and quantification of the anthropogenic emission sources. The analysis based on PCA-MLR suggested the major contribution of HMs were from industrial emissions (70%), mobile and stationary combustion sources (16%), and suspended and crustal dust (14%). It is very difficult to identify the most polluting industries in the industrial area. The proper maintenance of roads and the planting of dust capturing plants within the industrial boundary may reduce the suspension of road dust. Construction activities with preventive measures may reduce the suspended road dust in the ambient air. The proper ventilation of stationary combustion sources will reduce the airborne HM contaminations. The collaboration of industrial associations, researchers, academicians and enforcement agencies is needed to design and implement effective mitigation measures to abate industrial airborne emissions.

4.5 Polycyclic aromatic hydrocarbon

Polycyclic aromatic hydrocarbon (PAHs) are the ubiquitous pollutants containing two or more fused aromatic (benzene) rings with different arrangements and present in various environmental media such as soils, waters, sediments and air. The term "PAH" refers to compounds consisting only carbon and hydrogen atoms. In general PAHs are formed through pyrolysis process and subsequently recombined with other organic molecules. Both physical and chemical characteristics of PAHs vary with molecular weight. The general PAHs have high melting and boiling points (solid), low vapor pressure, and very low aqueous solubility. They have the tendency to decrease its solubility with increasing molecular weight but resistance to oxidation and reduction increases. So, PAHs has different behavior, distribution in the environment, and their effects on biological systems. Low-molecular-weight PAHs (two and three rings) are weaker carcinogenic and mutagenic as compared to multi-ringed PAHs (four rings or more) and potential to health risk. Naphthalene ($C_{10}H_8$; MW = 128.16 g), formed from two benzene rings fused together, has the lowest molecular weight of all PAHs. The environmentally significant PAHs have molecules ranged between two (e.g., naphthalene) to seven benzene rings (e.g., coronene with a chemical formula $C_{24}H_{12}$; MW = 300.36 g). PAHs emissions in the atmosphere are in the form of either gaseous or particulate phases. PAHs are highly lipophilic and mostly soluble in organic solvents. PAHs also manifest various functions in the environment such as light sensitivity, heat resistance, conductivity, emittability, corrosion resistance, and physiological action.

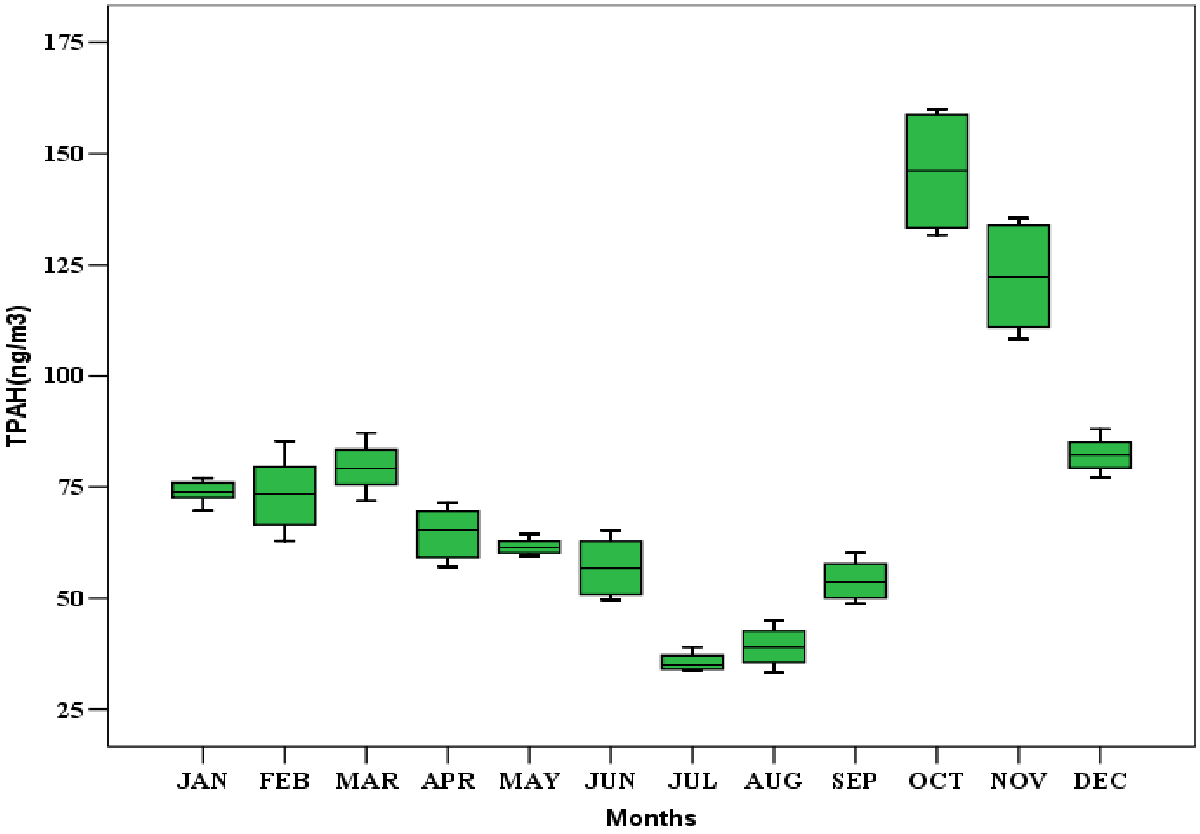
United States of Environmental Protection Agency (USEPA) has classified sixteen PAHs as carcinogenic. Incomplete combustion and pyrolysis of organic material influences the emission of PAHs in the gaseous form and settles on either in particulates or in soils or sediments after condensation (Marr et al. 2006, Douben et al. 2003). Though PAH has natural and anthropogenic sources but emission of PAHs are almost anthropogenic in origin (Park et al. 2002). PAHs reacts with atmospheric pollutants eg., ozone, hydroxyl radicals, nitrogen dioxide and sulfur dioxide, yielding diones, nitro- and dinitro-PAHs, and sulfonic acids (WHO report, 2000). The emission sources of individual PAHs are mostly from motor vehicles or wood smoke. PAHs has multiple emission sources, broadly categorized into five major emission sources eg., natural, domestic, mobile, industrial and agricultural sources.

The occurrence of PAHs in the atmosphere and their carcinogenicity and mutagenicity potential are of great interest in the urban atmosphere as individual are exposed to it. Mostly people are exposed to PAHs in both ways either inhalation of contaminated air or consumption of contaminated food and water. The contaminated foods have more route of exposure of PAHs as compared to inhalation of contaminated air. Several epidemiological studies reported that complex mixture of PAHs with different molecular weights is associated with adverse health risks and potential carcinogens and mutagens (Miller et al. 2010). WHO, 2002) reported that approximately 75% people in China, India and South East Asia, and 50–75% people in various parts of South America and Africa use solid fuels (wood, dried animal-dung-cake and crop waste) for daily cooking. Air quality guidelines for Europe country estimated that the unit risk is $9x10^{-5}$ would theoretically lead to one extra cancer case in 1 lakh exposed individuals (Bostrom et al. 2002). It was estimated that in India, Indo-Gangetic Plains alone contributes 30.21% PAHs emissions of total PAH emissions from India (Singh et al. 2013). The annual PAHs emissions of India are estimated to be 90 Gg per year (Zang and Tao 2009).The congested traffic movement at urban areas promotes the emissions of PAHs. Other major sources of PAH emission are from vehicle tyre abrasion, asphalted surfaces and brake lining (Rogge et al. 1993).

In the present study, PM_{10} samples were collected in four seasons ie., winter (January to March, December), pre-monsoon (April to June), monsoon (July to September) and post-monsoon (October to November) in the year 2011. Total 50 numbers of samples were analyzed for 12 types of particulate PAHs in PM_{10} samples through Gas Chromatograph. PAHs was identified and quantified to estimate carcinogenicity and mutagenicity of human health.

4.5.1 Seasonal variation of total polycyclic aromatic hydrocarbon (TPAHs)

The identification and quantification of 12 compounds of particulate PAHs in PM_{10} were determined. The monthly variation of the total particulate PAHs at Naraina mixed use area of Delhi is shown in **figure** by whistle plot **4.14.** The figure revealed that the concentrations of total PAHs, varied from 30 to139 ng/m^3 respectively with an average value of 69±31 ng/m^3 for 12 Nos of identified particulate PAHs in Delhi. The highest concentration (130.85±17.19) was observed in the month of October, 2011 whereas a lowest concentration (30.32±4.29) was observed in the month of July, 2011.The annual average total PAHs concentration was 74.04±32.02 ng/m^3 respectively. Singh et al. 2012 reported that annual average value of total particulate PAHs concentration was 70.80 ng/m^3 in Guru Gobind Singh Indraprastha University Campus (Kashmere Gate), Central Delhi in the period (November 2007 to September 2008) which was comparable with the present study at Naraina mixed use area of Delhi in the year 2011.



Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	77	85	87	71	64	65	39	45	60	160	135	88
Min	70	63	72	57	55	50	34	33	49	132	108	77
25 percentile	73	67	76	59	60	51	34	36	50	133	111	79
50 percentile	74	73	79	65	61	57	35	39	54	146	122	82
75 percentile	76	79	83	69	63	62	37	42	57	159	134	85
Average	74	73	80	65	61	57	36	39	54	146	124	82

Figure 4.14 Monthly variations of total PAHs in Naraina Industrial Area of Delhi (2011)

The concentration of ambient total particulate PAHs in Mumbai was 26.30ng/m^{3}, which was approximately three times lesser than ambient PAHs concentrations in Delhi city (Kulkarni et al. 2000). Few studies like Delhi (Kannan and Kapoor et al. 2004), Mumbai (Sahu et al. 2008), and Ahmedabad (Raiyani et al.1993) were reported the total PAHs concentrations were 24, 28, and 90 ng/m^{3}, respectively in the ambient air. CPCB reported total PAH concentrations at seven major traffic intersection areas of Delhi during winter season in the year 2012. PAH concentrations at the selected locations like ITO (19.61–52.96), Janakpuri (23.01-35.91), Nizamuddin (4.61- 23.27), PitamPura (14.23 -48.63), Shahzada Bagh (12.44 - 38.45), Siri Fort (13.79 -30.72) and Shahdara (12.10-34.11) ng/m^{3} respectively. The highest concentration of total PAH (52.96 ng/m^{3}) was reported at ITO, in the month of January, 2012 and lowest concentration of total PAH (4.61 ng/m^{3}) was reported in Nizamuddin location in the month of March, 2012 (Tyagi et al. 2013). The reported PAH concentration indicated the predominant traffic source only. The PAH concentrations at Naraina, urbanized mixed use area of Delhi indicated the multiple predominant sources like industrial emission, vehicular emission and re-suspended of road dust.

Singh et al. 2008, reported that in few locations, ambient PAHs concentrations at rural region were higher as compared to urban region in India may be due to incomplete combustion of biomass burning of agricultural wastes. The report also revealed that A group of rural Indian children had significantly higher blood PAH concentrations (125.55±26.99 ppb) than those from an urban region (23.96±13.46 ppb), consistent with higher home exposure to the burning of wood, coal, cow dung and kerosene.

The total 12 types of PAHs are: Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLR), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHR), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenz(a,h)anthracene (DahA), Benzo(ghi)pyrelene (BghiP) and Indeno(123-cd)pyrene (IcdP) respectively were analyzed through Gas Chromatograph (GC). Naphthalene (NP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FL) were not detected in the collected PM_{10} samples as selected PAHs are mostly remain in the gaseous form in the ambient air. The characterization of each PAH like molecular weight, benzene rings, water solubility, classification of each PAHs as per IARC is shown in **Table 4.9.** This Table also provides information about the season wise variation of 12 types of particulate PAHs at Naraina urbanized mixed use area of Delhi in the year 2011.

The emission of PHE, ANT, FLR and PYR were in the gaseous and particulate form, where as other identified PAHs emissions were in the particulate form in the ambient air. Season wise average PHE concentrations varied from 3.94±0.74 ng/m^3 (winter) 2.75±0.55 (pre-monsoon), 1.76±0.52 ng/m^3 (monsoon), and 3.35±1.43 (post-monsoon) with an annual average concentration of 3.00±1.14 ng/m^3. Singh et al. 2012 reported that PHE concentrations varied from 0.8 ng/m^3 (winter), 0.5 ng/m^3 (summer) and 1.9 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. The present study PHE data was comparatively higher than reported value as the selected location is the hub of urbanized industrial location of Delhi. As per International Agency for Research on Cancer (IARC, 1983; 1987), PHE falls under the category of 3 indicated not classifiable as its carcinogenicity to humans. The predominant source of PHE emission was from motor vehicle wood smoke and incineration of waste (Ravindra et al. 2006, 2008).

Table 4.9 Seasonal variation of selected PAHs in PM$_{10}$ in Delhi (2011)

Particulate PAHs	Abbreviation	Molecular Weight	Benzene Rings	Water Solubility mg/l at 25^0C	Classification as per IARC	Winter (N=16) (ng/m^3)	Premonsoon (N=12) (ng/m^3)	Monsoon (N=12) (ng/m^3)	Postmonsoon (N=10) (ng/m^3)	Annual (N=50) (ng/m^3)
Phenanthrene	PHE	$C_{14}H_{10}$	3	1.1	Group 3	3.94±0.74	2.75±0.55	1.76±0.52	3.35±1.43	3.00±1.14
Anthracene	ANT	$C_{14}H_{10}$	3	0.04	Group3	5.24±1.42	3.23±0.68	2.11±0.75	4.30±0.96	3.80±1.59
Fluoranthene	FLA	$C_{16}H_{10}$	4	0.2	Group3	5.68±2.02	4.45±1.77	4.27±0.81	9.92±2.34	5.72±2.61
Pyrene	PYR	$C_{16}H_{10}$	4	0.13	Group3	9.07±1.20	6.94±1.06	6.15±0.61	15.56±2.43	8.89±3.50
Benzo(a)anthracene	BaA	$C_{18}H_{12}$	4	0.011	Group2B	6.81±3.02	5.60±1.21	5.10±4.15	13.14±2.76	7.14±3.98
Chrysene	CHR	$C_{18}H_{12}$	4	0.0019	Group2B	2.24±1.33	1.92±0.75	0.81±0.40	3.68±0.96	2.04±1.30
Benzo(b)fluoranthene	BbF	$C_{20}H_{12}$	5	0.0015	Group2B	4.51±1.13	3.75±0.67	2.02±0.96	9.92±1.11	4.60±2.77
Benzo(k)fluoranthene	BkF	$C_{20}H_{12}$	5	0.0008	Group2B	5.93±0.92	2.73±0.62	1.76±0.73	8.44±1.34	4.17±3.10
Benzo(a)pyrene	BaP	$C_{20}H_{12}$	5	0.0015	Group1	6.92±1.25	5.94±0.94	2.82±1.47	13.72±2.50	6.78±3.82
Dibenz(ah)anthracene	DahA	$C_{22}H_{14}$	5	0.0005	Group2A	7.95±1.13	5.94±0.80	4.54±0.98	16.41±1.16	8.01±4.18
Benzo(ghi)pyrelene	BghiP	$C_{22}H_{12}$	6	0.00015	Group3	10.59±1.53	8.77±1.67	5.50±0.77	17.48±1.86	10.01±4.17
Indo(123-cd)pyrene	IcdP	$C_{22}H_{12}$	6	0.00019	Group2B	10.35±1.88	8.79±1.24	6.06±0.67	16.33±3.72	9.89±3.84

Group 1	Carcinogenic to humans
Group 2A	Probably carcinogenic to humans
Group 2B	Possibly carcinogenic to humans
Group 3	Not classifiable as its carcinogenicity to humans
Group 4	Probably not carcinogenic to humans

The emission of PHE, ANT, FLA and PYR were in the gaseous and particulate form, where as other identified PAHs emissions were in the particulate form in the ambient air. Season wise average PHE concentrations varied from 3.94±0.74 ng/m^3 (winter) 2.75±0.55 (pre-monsoon), 1.76±0.52ng/m^3 (monsoon), and 3.35±1.43 (post-monsoon) with an annual average concentration of 3.00±1.14 ng/m^3. Singh et al. 2012 reported that PHE concentrations varied from 0.8 ng/m^3 (winter), 0.5 ng/m^3 (summer) and 1.9 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. The present study PHE data was comparatively higher than reported value as the selected location is the hub of urbanized industrial location of Delhi. As per International Agency for Research on Cancer (IARC, 1983; 1987), PHE falls under the category of 3 indicated not classifiable as its carcinogenicity to humans. The predominant source of PHE emission was from motor vehicle wood smoke and incineration of waste (Ravindra et al. 2006, 2008).

Season wise average ANT concentrations were 5.24±1.42 ng/m^3 (winter) 3.23±0.68 (pre-monsoon), 2.11±0.75 ng/m^3 (monsoon), and 4.30±0.96 ng/m^3 (post-monsoon) with an annual average concentration of 3.80±1.59 ng/m^3. Singh et al. 2012 reported that ANT concentrations varied from 2.4 ng/m^3 (winter), 0.8 ng/m^3 (summer) and 1.5 ng/m^3 (monsoon) in the year 2007-2008 at Kashmere Gate, urban road side location in Delhi. In the present study, ANT concentration was comparatively high due to industrial emission and stationary and mobile combustion sources at mixed use area of Delhi. As per IARC report (1983; 1987), particulate PAHs ANT falls under the category of 3. The ratio of ANT/ (ANT+ PHE) was varied from 0.3 to 0.6 during the study period at Naraina Industrial was indicated predominant source of PAHs from pyrogenic source ie., combustion of wood, coal, coal tar etc. (Pies et al. 2008).

Season wise average FLA concentrations were 5.68±2.02 ng/m^3 (winter) 4.45±1.77 (pre-monsoon), 4.27±0.81 ng/m^3 (monsoon), and 9.92±2.34 ng/m^3 (post-monsoon) with an annual average concentration of 5.72±2.61 ng/m^3. Singh et al. 2012 reported that FLA concentrations varied from 1.7 ng/m^3 (winter), 1.6 ng/m^3 (summer) and 0.8 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. The reported study FLA data was quite less as compared to the present study might be due to industrial emission and stationary and mobile sources at mixed use area of Delhi. According to IARC report (1983; 1987), FLR falls under the category of 3 and its predominant source of emission in the ambient air are mostly from motor vehicles and biomass burning (Ravindra et al. 2008).

Season wise average PYR concentrations were 9.07±1.20 ng/m^3 (winter) 6.94±1.06 (pre-monsoon), 6.15±0.61 ng/m^3 (monsoon), and 15.56±2.43 ng/m^3 (post-monsoon) with an annual average concentration of 8.89±3.50 ng/m^3. Singh et al. 2012 reported that PYR concentrations varied from 4.1ng/m^3 (winter), 2.5 ng/m^3 (summer) and 1.2 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. The present study PYR concentration was high as compared to reported data might be due to industrial emission and stationary and mobile sources at mixed use area of Delhi. (Ravindra et al. 2008) reported that source of emission of pyrene in the ambient air were from motor vehicle and biomass burning. IARC (1983; 1987), classified PYR under the category 3. Ravindra et al. 2008 reported that if the ratio of FLA/ (FLR+PYR) within the range of 0.4-0.5 indicating the fossil fuel combustion and if the ratio greater than 0.5 indicating grass, wood and coal combustion. The above study also reported that if the ratio less than 0.5 indicating petrol emission and the ratio greater than 0.5 indicating diesel emission sources. (Torre-Roche et al. 2009) In the present study, at Naraina, mixed use area of Delhi, the ratio of FLR/ (FLR+PYR) was varied from 0.23 to 0.55 which indicating the multiple emission sources like petrol, diesel, grass, wood and coal combustion. Incineration of waste also indicates the high concentrations of PHE, FLR and PYR in PAHs reported by Smith and Harrison, 1998 and Ravindra et al. 2006.

Season wise average BaA concentrations were 6.81±3.02 ng/m^3 (winter) 5.60±1.21 (pre-monsoon), 5.10±4.15 ng/m^3 (monsoon) and 13.14±2.76 ng/m^3 (post-monsoon) with an annual average concentration of 7.14±3.98 ng/m^3. Singh et al. 2012 reported that BaA concentrations varied from 3.2 ng/m^3 (winter), 2.1 ng/m^3 (summer) and 1.4 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location (Kashmere Gate) in Delhi. The present study BaA concentration was comparatively higher than the reported BaA concentration, might be due to emission are mostly from motor vehicle and wood smoke (Ravindra et al. 2008). IARC (1983; 1987) recommended that BaA falls under the category of 2B, indicated positively carcinogenic to human.

Season wise average CHR concentrations were 2.24±1.33 ng/m^3 (winter) 1.92±0.75 (pre-monsoon), 0.81±0.40 ng/m^3 (monsoon), and 3.68±0.96 ng/m^3 (post-monsoon) with an annual average concentration of 2.04±1.30 ng/m^3. Singh et al. 2012 reported that concentrations of CHR varied from 4.4ng/m^3 (winter), 2.2ng/m^3 (summer) and 1.7ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location (Kashmere Gate) in Delhi. The reported value of CHR concentration was higher as compared to present study. As per IARC report (1983;

1987), CHR falls under the category of 2B, indicated positively carcinogenic to human. Tobiszewski et al. 2012 reported that the ratio of BaA/ (BaA+CHR) greater than 0.35, indicating vehicular emission. The ratio of BaA/(BaA+CHR)in the study area varied from 0.6 to 0.94, indicating the vehicular emission.

Season wise average BbF concentrations were 4.51±1.13 ng/m^3 (winter) 3.75±0.67 (pre-monsoon), 2.02±0.96 ng/m^3 (monsoon), and 9.92±1.11 ng/m^3 (post-monsoon) with an annual average concentration of 4.60±2.77 ng/m^3. Singh et al. 2012 reported that BbF concentrations varied from 8.8 ng/m^3 (winter), 4.4 ng/m^3 (summer) and 2.3 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location (Kashmere Gate) in Delhi. The present study BbF data was less as compared to reported data might be due to existence of less BbF emission source. IARC (1983; 1987) report informed that BbF falls under category of 2B indicated positively carcinogenic to human. Ravindra et al. 2008 reported that the sources of BbF emission are from motor vehicle and wood smoke.

Season wise average BKF concentrations were 5.93±0.92 ng/m^3 (winter) 2.73±0.62 (pre-monsoon), 1.76±0.73 ng/m^3 (monsoon), and 8.44±1.34 ng/m^3 (post-monsoon) with an annual average concentration of 4.17±3.10 ng/m^3. Singh et al. 2012 reported that BkF concentrations varied from 9.6 ng/m^3 (winter), 5.9 ng/m^3 (summer) and 2.9 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location (Kashmere Gate) in Delhi. The reported BkF concentrations was approximately 1.5 times higher than present determined concentrations at Naraina mixed use area of Delhi. As per IARC (1983; 1987) report BkF falls under category of 2B indicated positively carcinogenic to human. Ravindra et al. 2008 reported that the sources of BkF emission are from motor vehicle and wood smoke. Pandey et al. 1999 and Park et al. 2002 reported that the ratio of BbF/BkF greater than 0.5, indicating diesel emission. The ratio of BbF/BkF in the present study varied from 0.53 to 2.2 indicating the emission of particulate PAHs from commercial diesel vehicle emission.

PAHs are mostly formed during the incomplete combustion and pyrolysis of fossil fuels or wood, and from the release of petroleum products (Manahan, 1994; Ravindra 2008). Season wise average BaP concentrations in PM_{10} varied from 6.92±1.25 ng/m^3 (winter) 5.94±0.94 (pre-monsoon), 2.82±1.47 ng/m^3 (monsoon), and 13.72±2.50 ng/m^3 (post-monsoon) with an annual average concentration of 6.78±3.82 ng/m^3. There is no standard available till date in India for various carcinogenic and mutagenic PAHs accept BaP. BaP is used as an indicator of PAHs for exposure in epidemiological studies in national and international standards. The annual average concentration of BaP in PM_{10} was alarmingly high as compared to NAAQS, 2009 Standards (annual mean: 1.0 ng/m^3) of CPCB. The particulate BaP in PM_{10} concentration has been incorporated as regulatory parameters in NAAQS with the statement of their measurement methods, ie. reference methods due to their carcinogenic health impact.

Singh et al. 2012 reported that BaP concentrations were 6.9 ng/m^3 (winter), 3.1 ng/m^3 (summer) and 1.8 ng/m^3 (monsoon) in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. The present study BaP concentration in the winter seasons were comparable with reported concentration of BaP of Singh et al. 2012. However during pre-monsoon BaP concentration was almost two times higher than the reported value by Singh et al. 2012 might be due to movement of more vehicles as compared to winter season and other local emission sources. As per IARC (1983; 1987) report BaP, falls under the category of 1(one) indicated carcinogenic to human. CPCB was evaluated BaP concentrations at seven hotspot locations during winter season in Delhi in the year 2012. BaP concentrations at the selected locations e.g., ITO (1.98–17.85), Janakpuri (1.98 -10.40), Nizamuddin (0.27-6.57), Pitam Pura (6.71-11.43), ShahzadaBagh (1.07-13.53), Siri Fort (1.86-11.55) and Shahdara (5.54-10.62) ng/m^3 respectively. The variation of BaP concentration in the month of January, 2012 was from 6.57 (Nizammudin) to 17.85 (ITO), February, 2012 month, varied from 1.07 (Shahzada Bagh) to 12.36 (ITO) and in the month of March,2012 it ranged from 0.27 (Nizamuddin) to 8.40 (Janakpuri) respectively in the winter season, 2012 (Tyagi et al.2013). The reported concentrations of BaP at seven locations of Delhi were comparatively higher than the presently reported concentration, as most of the locations were adjoin to the major traffic intersection and major source of emission of BaP is from vehicular emission. It was scientifically proved by Stenberg et al.1979, that the emission from mobile source combustion from petrol and diesel use, emitted high BaP and BghiP at the atmosphere.

Season wise average DahA concentrations were 7.95±1.13 ng/m^3 (winter) 5.94±0.80 (pre-monsoon), 4.54±0.98 ng/m^3 (monsoon), and 16.41±1.16 ng/m^3 (post-monsoon) with an annual average concentration of 8.01±4.18 ng/m^3. Singh et al. 2012 reported that seasonal variation of DahA concentrations during winter season 9.8ng/m^3, summer 4.7ng/m^3, and monsoon 2.3 ng/m^3 respectively in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. In the present study, DahA concentration during winter season was comparatively less than the reported value at Kashmere Gate, might be due to more mixing ratio of air pollutants in the atmosphere in the year 2011, than winter months in the year 2007-2008. Other season

PAHs concentrations were high might be due to multiple sources like industrial emission, traffic emission, biomass burning and re-suspension of road dust. As per IARC (1983; 1987) report, DahA falls under the category of 2A, indicated probably carcinogenic to human.

Season wise average BghiP concentrations varied from 10.59±1.53 ng/m^3 (winter) 8.77±1.67 (pre-monsoon), 5.50±0.77 ng/m^3 (monsoon), and 17.48±1.86 ng/m^3 (post-monsoon) with an annual average concentration of 10.01±4.17 ng/m^3 respectively. Singh et al. 2012 reported that BghiP concentrations during winter season 12.5 ng/m^3, summer 6.4 ng/m^3, and monsoon 3.3 ng/m^3 respectively in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. In the present study at Naraina mixed use area of Delhi, the emission of BghiP concentration during winter season was comparatively less than the reported value at Kashmere Gate, might be due to more mixing ratio of air pollutants in the atmosphere in the year 2011. As per IARC (1983; 1987) report BghiP falls under the category of 3, indicated not classified as carcinogenic to human. Katsoyiannis et al. 2007 reported that the ratio of BaP/Bghi greater than 0.6, indicating the traffic emission and ratio of BaP/Bghi less than 0.6, indicating the non-traffic emission. The ratio of BaP/Bghi in the present study varied from 0.24 to 0.86 indicating the emission of particulate PAHs from both traffic and non-traffic emission at Naraina mixed use area of Delhi.

Season wise average IcdP concentrations were 10.35±1.88 ng/m^3 (winter) 8.79±1.24 (pre-monsoon), 6.06±0.67 ng/m^3 (monsoon), and 16.33±3.72 ng/m^3 (post-monsoon) with an annual average concentration of 9.89±3.84 ng/m^3. Singh et al. 2012 reported, that IcdP concentrations during winter season 13 ng/m^3, summer 4.6 ng/m^3, and monsoon 2.9ng/m^3 respectively in the year 2007-2008 at the urban road side location, Kashmere Gate in Delhi. Except winter season, other season IcdP concentrations at Naraina mixed use area of Delhi were high due to multiple emission sources like industrial emission, vehicular emission and re-suspended of road dust. As per IARC (1983; 1987) report IcdP falls under the category of 2B, indicated positively carcinogenic to human.

4.5.2 Principle Component Analysis of Polycyclic Aromatic Hydrocarbon

Principle component analysis (PCA) described in methodology (3.5.1) was performed to determine the variability of Polycyclic Aromatic Hydrocarbon(PAH) concentration and to characterize the prominent sources that are responsible for ambient particulate PAH emission in urbanized mixed use area of Delhi. The lowest eigen value for extracted factors was restricted to more than 1.0 of the total variance. Two factors (PC1and PC2) were obtained through PCA analysis. A varimax rotation with Kaiser Normalization factor analysis was performed to identify the major dominant sources that influence the concentration of particulate PAHs in the urban mixed use area of Delhi. Two factors explained total 85.63% of the variance of total particulate PAH. Factor greater or equal to 0.5 was selected for lowest level of significance within a factor. The PCA factor scores for airborne particulate PAH is shown in **Table 4.10**.

Table 4.10: PCA factor scores for airborne particulate PAHs (2011)

Particulate PAHs	**PC1**	**PC2**
PHE	0.208	**0.924**
ANT	0.187	**0.929**
FLR	**0.862**	0.129
PYR	**0.927**	0.296
BaA	**0.839**	0.046
CHR	**0.789**	0.163
BbF	**0.870**	0.304
BkF	**0.959**	0.141
BaP	**0.863**	0.423
DahA	**0.917**	0.242
BghiP	**0.857**	0.411
IcdP	**0.900**	0.306
Eigen Value	**8.82**	**1.45**
% Variance	**73.52**	**12.11**
Cumulative %	**73.52**	**85.63**

The factor PC1 represents total 73.52% of variance. This factor is weighted by FLR, PYR, BaA, CHR, Mn, BbF, BKF, BaP, DahA, BghiP and IcdP representing the major contribution of PAHs from industrial, vehicular emission and use of diesel generators during interruption of power supply (Smith and Harrison, 1998; Ravindra et al. 2006, Jiang et al. 2009). ANT, FLT, PRY, BaA, CHR, BbF, BkF, BaP and IcdP particulate PAHs were present in the atmosphere might be due to the petrol and natural gas combustion engine vehicles on road (Khalili et al. 1995; Yunker et al. 2002; Jiang et al. 2009).

The factor PC2 represents total 12.11% of variance. This factor is weighted by PHE and ANT representing the biomass burning. The presence of PHE, ANT and FLR in the ambient air was due to burning of wood for heating purposes (Khalili et al. 1995).

4.5.2.1 Time Series Analysis for Airborne particulate PAHs in Delhi

A time series analysis for airborne polycyclic aromatic hydrocarbon (PAHs) concentrations at Naraina, urbanized mixed use area of Delhi was carried out through Principle Component Analysis-Multiple Linear Regression (PCR-MLR), described in the methodology (3.5.1). PCA-MLR is one of the important receptor model and widely used for air pollutants source identification and quantification. Monthly source contributions of airborne PAHs based on PCA-MLR is presented in **Figure 4.15**.

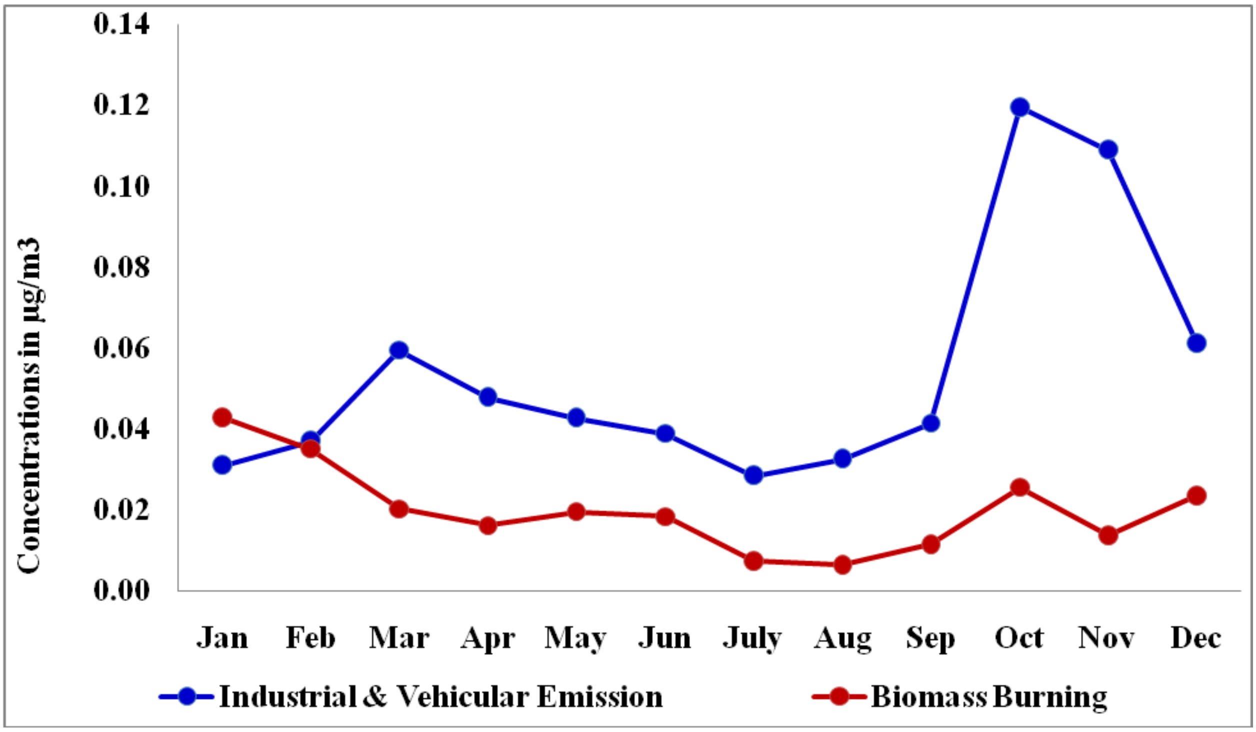


Figure 4.15 Monthly source contributions of airborne particulate PAHs in Delhi (2011)

Figure 4.15 revealed the contribution of particulate PAHs lowest in monsoon season (July 2011 - September, 2011) may be due to rainfall precipitation. The contribution of PAHs was maximum in post-monsoon season followed by winter season, pre-monsoon season and monsoon season. Metrological parameters like wind speed, wind direction, temperature, relative humidity and periodical rainfall played an important role for contributions of PM_{10} bound PAHs in Delhi. Additional burning of firecrackers and fireworks during the Diwali celebration was the culprit for maximum concentrations of PAHs during post-monsoon season in the mixed use area of Delhi in association with industrial emission, mobile and stationary combustion and suspended road dust. Inverse metrological condition, slow dispersion, low-average mixing height and calm condition were the natural factors that likely to contribute high concentrations of air pollutants in post-monsoon and winter season as compared to pre-monsoon and monsoon seasons. The concentrations of particulate PAHs were low in pre-monsoon season due to higher mixing ratio and increased wind velocity as compared to other seasons. It was scientifically proved that in the ambient air, emission of PAHs were mostly from industrial and vehicular emission (Ravindra et al. 2006, Khalili et al. 1995). Biomass burning is the major source of emission in the Northern India, which contributes significant concentrations of air pollutants in the ambient air (WHO, 2002). The present study of PCA-MLR explained the two major sources which were contributing particulate PAHs at Naraina mixed use area of Delhi. The contribution of industrial and vehicular emission was 73% of total particulate PAH emissions whereas biomass burning contributing 27% of total particulate PAH.

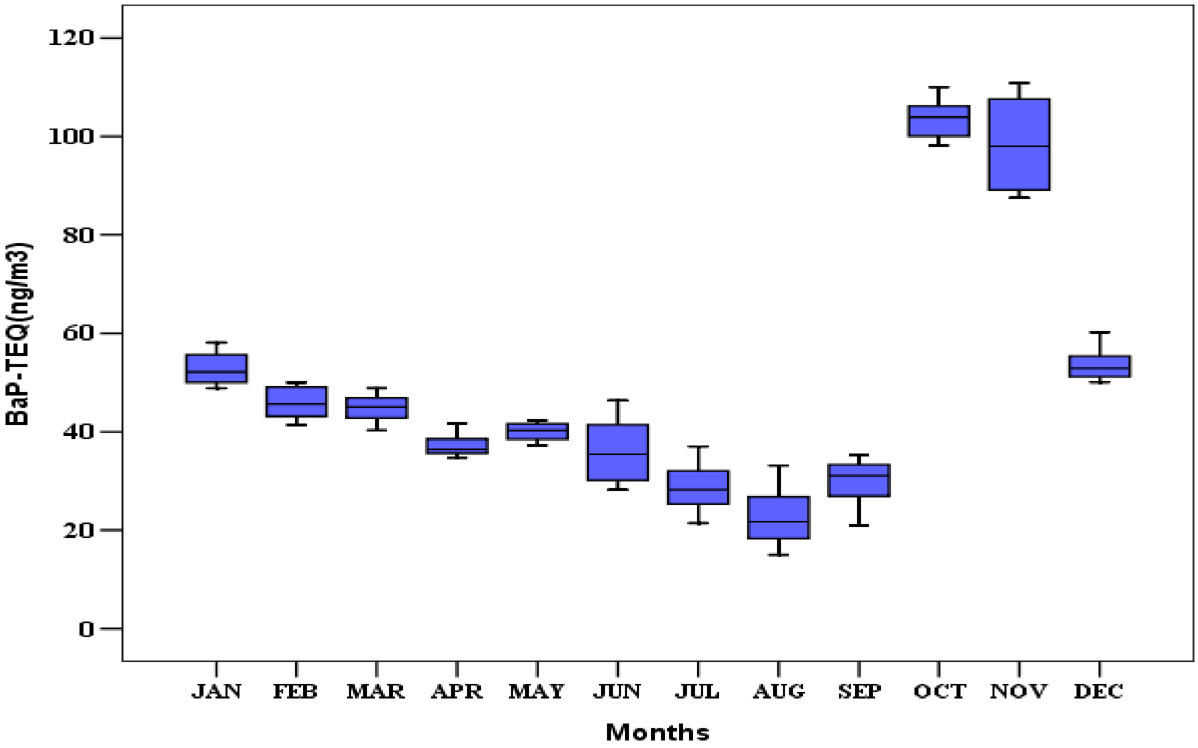
4.5.3 Carcinogenicity and mutagenicity risk of airborne particulate PAHs

A substance that has the ability or tendency to cause cancer is known as carcinogen. It may damage the genome material (mostly DNA) of an organism or can disrupt the cellular metabolic processes. IARC classified few substances (60 in number) which are probably or positively carcinogenic to humans. These substances are classified according to agents and groups of agents, mixtures and exposure circumstances. Few PAHs are probably or positively carcinogens to human. Among them, benzo(a)pyrene (BaP) is the indicator for measurement of carcinogenicity. Thus BaP-equivalent toxicity of other carcinogenic PAHs was evaluated for cancer risk assessment analysis. This approach might provide over estimation of cancer and mutagen potency of individual particulate PAH as every PAH are comparatively less carcinogen than BaP. BaP-TEQ (carcinogenic equivalents, ng/m^3) and BaP-MEQ (mutagenic equivalents, ng/m^3) were calculated to estimate ambient air PAH carcinogenic and mutagenic hazards in Naraina, urbanized mixed use area of Delhi, which may lead to the greater risk for adverse health consequences due to emission of particulate PAH in the ambient air.

BaP-TEQ was estimated by multiplying the concentrations of each PAH compound with its toxic equivalency factor (TEF) for cancer potency, equivalent to BaP. BaP-TEQ is the sum of particulate PAH and was estimated for selected eight particulate PAHs. The selected particulate PAHs are benzo(a)anthracene(BaA), chrysene(CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene, (BkF),benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), benzo(ghi)pyrelene (BghiP) and indeno (123-cd)pyrene (IcdP) respectively. The formula for estimation of BaP-TEQ (Miller et al. 2010) is given below.

$$(\mathrm{BaP\text{-}TEQ})_{\Sigma 8PAH} = [\mathrm{BaA}]\times 0.1 + [\mathrm{CHR}]\times 0.01 + [\mathrm{BbF}]\times 0.1 + [\mathrm{BkF}]\times 0.1 + [\mathrm{BaP}]\times 1 + [\mathrm{IP}]\times 0.1 + [\mathrm{DahA}]\times 5 + [\mathrm{BghiP}]\times 0.01 \text{ --------} \qquad (1)$$

The monthly/ seasonal variation of BaP-TEQ is shown by whistle plot in **Figure 4.16**



Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	58	50	49	42	42	46	37	33	35	110	111	60
Min	49	41	40	35	37	28	21	15	21	98	88	50
25 percentile	50	43	43	36	39	31	25	19	27	100	90	51
50 percentile	52	46	45	36	40	36	28	22	31	104	98	53
75 percentile	55	49	47	39	41	41	32	26	33	106	107	55
Average	53	46	45	37	40	36	29	23	30	103	98	54

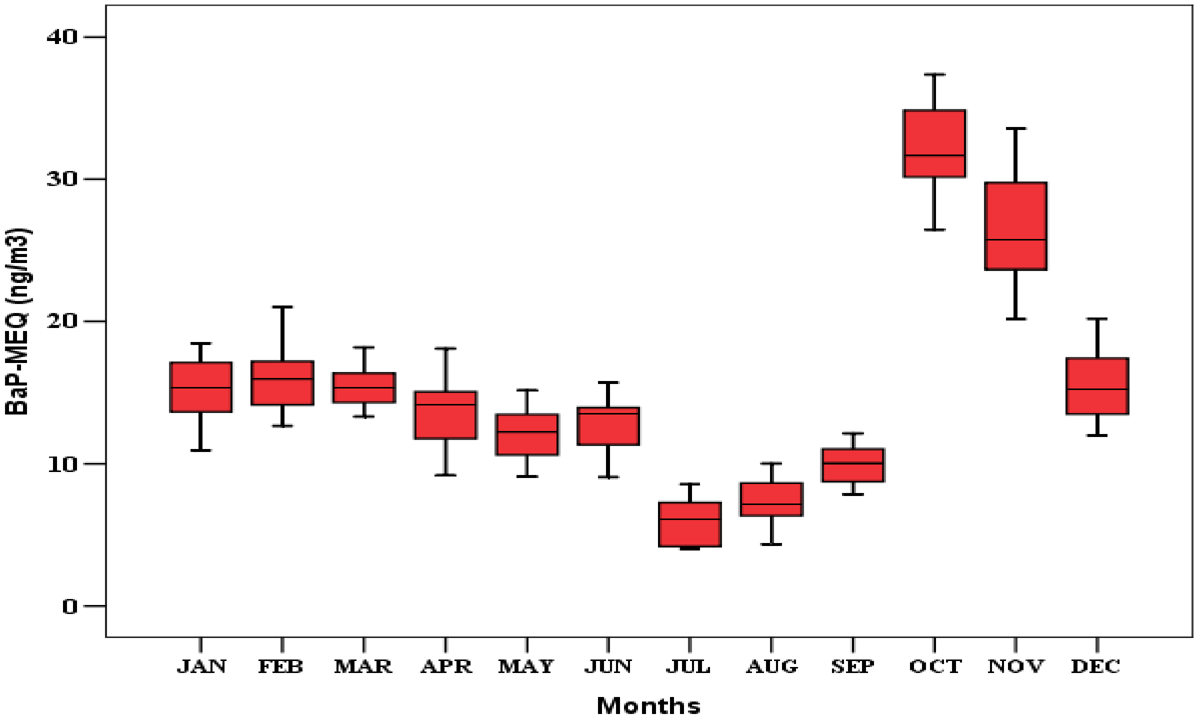
Figure 4.16 Monthly variations of BaP-TEQ of particulate PAHs in Delhi (2011)

BaP-TEQ concentration was varied from 0.023 to 0.103ng/m^3 with an average value of 0.050±0.005 ng/m^3. The maximum was in the month of October, 2011 at Naraina mixed use area of Delhi whereas minimum value was observed in the month of August, 2011. The cancer potency is prominent in the month of Diwali festival (ie., October, 2011) due to inverse metrological condition and burning of fire crackers due to Diwali celebrations.

BaP-MEQ was similarly estimated by multiplying the concentrations of each PAH type with its mutagenic potency equivalent factors (MEF) relative to BaP. BaP-MEQ is the sum of particulate PAH and was estimated for selected eight particulate PAHs. The selected particulate PAHs are benzo(a)anthracene(BaA),chrysene(CHR),benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF),benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DahA), benzo(ghi)pyrelene (BghiP) and indeno(123-cd)pyrene (IcdP) respectively. The formula for estimation of BaP-MEQ (Miller et al. 2010) is given below.

$$\mathbf{(BaP\text{-}MEQ)_{\Sigma 8PAH} = [BaA]\times 0.082 + [CHR]\times 0.017 + [BbF]\times 0.25 + [BkF]\times 0.11 + [BaP]\times 1 + [IP]\times 0.31 + [DahA]\times 0.29 + [BghiP]\times 0.19} \text{ --------} \qquad \mathbf{(2)}$$

Both BaP-TEQ and BaP-MEQ may provide accurate information to assess the potential health risk to human. The monthly/seasonal variation of BaP-MEQ is shown by whistle plot in **Figure 4.17.**



Item	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Max	18	21	18	18	15	16	9	10	12	37	34	20
Min	11	13	13	9	9	9	4	4	8	26	20	12
25 percentile	14	14	14	12	11	12	4	7	9	30	24	14
50 percentile	15	16	15	14	12	14	6	7	10	32	26	15
75 percentile	17	17	16	15	13	14	7	8	11	35	30	17
Average	15	16	15	14	12	13	6	7	10	32	27	16

Figure 4.17 Monthly variations of BaP-MEQ of particulate PAHs in Delhi (2011)

BaP-MEQ concentration was varied from 0.006 to 0.034ng/m^3 with an average value of 0.016±0.002 ng/m^3. The maximum was in the month of October, 2011 at Naraina mixed use area of Delhi whereas minimum value was observed in the month of July, 2011. The cancer potency is prominent in the month of Diwali festival (ie., October, 2011) due to calm condition (54.40%) and burning of crackers.

The qualitative and quantitative analysis of particulate PAHs and their diagnostic ratios indicated that anthropogenic emission of PAH derived from industrial, vehicular and biomass burning. PAHs concentrations were high in post-monsoon season followed by winter, pre-monsoon and monsoon season. The strip rise of vehicular registrations within the year of 2007-2010 was might also be the reason to increase the PYR concentrations in the ambient air.

4.6 Cation and Anion

Cation and anion are having the significant contribution to increase the concentrations atmospheric particulate matter. Airborne, inhalable particulate matter is the major concern in worldwide due to their potential complexity in terms of both chemical composition and physical properties (Balasubramanian et al. 2003). Several researches are being conducted to understand the aerosol particulate formation, physical and chemical properties and their adverse effect to climate change and human health. It is the complex mixture of cation and anion like sulfates, nitrates, ammonium, sea salt, mineral dust, organic carbon, elemental carbon, heavy metals etc. (Menon et al. 2002). Aerosol have the capability to affect the atmospheric radiation, which can disturb the balancing of climate force, nuclei cloud formation and photochemical reactions (Charlson et al.1992). The light extinction effects are also influencing the global climate change and visibility (Seinfeld and Pandis, 1998; Tsai et al. 2003).Cation and anion are the water-soluble ions constitute and major fraction of particulate matter especially in PM_{10}. The concentrations of cation and anion in PM_{10} are influenced by industrial emission, vehicular emission, agricultural activities, biomass burning, geographic conditions and natural dust. The origin of the water soluble aerosols are mostly influenced by wide range of sources through a series of complex mechanisms. The emission of trace gases (SO_2, NO_2 and NH_3) are converted to secondary air pollutants due to atmospheric photochemical reactions and directly linked with increase the concentrations of particulate matter (PM). The primary precursors are converted to ammonium (NH_4^+); nitrate

(NH_3^-) and sulfate (SO_4^{2-}) due to NH_3, NO_2 and SO_2 trace gases in the ambient air. In the monsoon season, the acid rain can cause health problems, kill animals and their habitats and also have negative impact on nature due to conversion of trace gases to acids (Tiwari et al. 2006). The formation of trace gases (NH_3, SO_2 and NO_2) to secondary aerosol particles mostly depends on meteorological parameter like temperature, humidity, low wind speed and presence of other gaseous pollutants in the atmosphere (Utsunomiya and Wakamatsu 1996; Kumar et al. 2004 and Gupta et al. 2003).

The composition of coarse and fine particles and their contribution in percentage depends on industrial emission, biomass burning; windblown dust and re-suspension of road dust. There are a few studies have reported the concentrations of measured SO_2, NO_2, NH_3 and their contribution in PM_{10} in the ambient air. Till date no studies has reported the gas to particle formation in urbanized industrial area in Indo- Gangetic plain. The present study was carried out into the urban cum industrial area of Delhi, India which will provide adequate information about the seasonal wise variation of gas to particle conversion.

In the present study, PM_{10} samples were collected in four seasons ie., winter (January to March, 2011 and December 2011), pre-monsoon (April to June), monsoon (July to September) and post-monsoon (October to November) in the year 2011. Total 50 numbers of samples were analyzed to evaluate of cation and anion concentrations in $PM_{10.}$ The seasonal variation of cation and anion were also identified. The samples were analyzed through Ion Chromatograph (DIONEX-ICS-5000, USA). Although it is well known that OH radical plays a vital role for formation of SO_4 and NO_3, in the ambient air, but no method is available till date for direct measurement of secondary aerosols. Therefore, role of SO_2, NO_2, NH_3, temperature and humidity were measured during the study period to understand the formation of particulate sulfate, nitrate and ammonium in the ambient air.

4.6.1 Seasonal variation of Cation and Anion in mixed use area of Delhi

Airborne inhalable cation and anion concentrations in PM_{10} in an industrialized urban area of Delhi were determined for proper identification and quantification of their emission sources. Total five cations like sodium (Na), potassium (K), ammonium (NH_4), magnesium (Mg) and calcium (Ca) concentrations were detected in PM_{10}.The seasonal variation of cation in PM_{10}samples during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.18.**

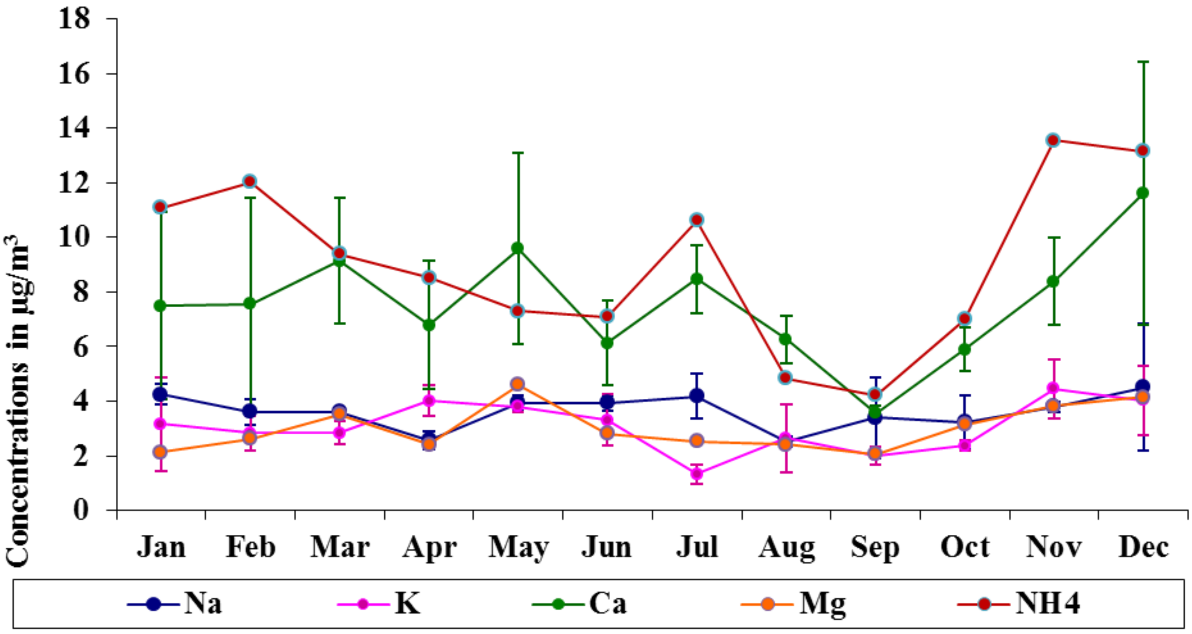


Figure 4.18 Monthly variation of cation in PM_{10} in mixed use area of Delhi (2011)

Monthly variation of cation in PM_{10}represented that the most abundant ions were Ca^{2+} and NH_4^+as compared to other cations like Na, K and Mg respectively in the Naraina mixed use area of Delhi in the year 2011.

The average concentrations of Na varied from 2.52 to 6.16µg/m^3 with an annual average concentration of 3.63±0.62 µg/m^3. The origin of Na in the ambient air was from re-suspended of crustal dust. The variation of Na in the Naraina mixed use area of Delhi was not significant.

The average concentrations of K varied from 1.34 to 4.46µg/m^3 with an annual average concentration of 3.07±0.92µg/m^3. The highest average concentration (3.78±0.34 µg/m^3) of K was observed in the winter (January to March, December) season and a lowest average concentration (2.0±0.65 µg/m^3) was observed in the monsoon (July to September) season. The origin of K in the ambient air was from re-suspended of crustal dust and biomass burning. The maximum concentration of K in winter season might be occurred due to from vegetation (Kleinman et al. 1979) and biomass burning (Penner et al. 1995). In northern India, it is a common practice to burn agriculture residue to clear the field of unwanted vegetation in the winter season that will enhance emission of K (Sharma et al.2007).

The average concentrations of Ca varied from 3.57 to 11.63µg/m^3 with an annual average concentration of 7.58±2.08 µg/m^3. The highest average concentration (8.90±1.83 µg/m^3) of

Ca was observed in the pre-monsoon (April to June) season and a lowest average concentration (6.1±2.96 µg/m^3) was observed in the monsoon season. The origin of the Ca in the ambient air was from re-suspended of crustal dust and due to construction activities and soil airborne dust, which may lead to the formation of $Ca(NO_3)_2$ and $CaSO_4$ (Kumari et al. 2013).

The average concentrations of Mg varied from 2.06 to 4.59µg/m^3 with an annual average concentration of 3.02±0.83 µg/m^3. The highest average concentration (3.61±1.10 µg/m^3) of Mg was observed in the pre-monsoon (April to June) season and a lowest average concentration (2.34±0.25 µg/m^3) was observed in the monsoon season. Mg was expected to be derived from dust (Gota et al. 2014) and wide application in the industrial activities especially dyes textile and paint industry. In the present study, season wise ambient concentrations of Ca and Mg in PM_{10} are comparable with the concentration reported for urban area of Kanpur city by Sharma et al.2007. The concentrations of Ca and Mg were high in the pre-monsoon season due to wind speed which makes soil dust airborne.

The average concentrations of NH_4 varied from 4.22 to 13.57µg/m^3 with an annual average concentration of 9.07±3.10 µg/m^3. The highest average concentration (11.42±1.59 µg/m^3) of NH_4 was observed in the winter (January to March, December) season and a lowest average concentration (6.55±3.53 µg/m^3) was observed in the monsoon season. NH_4 was the major fraction of cation in PM_{10} which is formed as secondary inorganic aerosol due to oxidation of NOx and subsequent neutralization with ambient gaseous pollutant ammonia (NH_3) or scavenging by existing particles (Seinfeld and Pandis, 1998). NH_3 has short life (3-10 days) and in general influenced by meteorological factors like temperature, humidity, low wind speed etc. The ratios of ammonia (NH_3) trace gas and ammonium (NH_4^+) salt varied from 5.32 to 18.76 respectively during the study period, indicating the formation of the fine particles. Tan et al. 2015 and Kulshrestha et al.1995 reported that gas-to-particle conversion revealed that [NH_3]: [NH_4^+] ratio was usually higher than one, indicating that NH_3 played an important role in the formation of fine particle. During the present study period in the year 2011, the highest temperature was in the month of May (41.69 ^{0}C) and lowest humidity was in the month of April (45.36%). The formation of secondary inorganic NH_4^+ salt in the atmosphere varied from 7.30 to 8.52µg/m^3, during the pre-monsoon season and 9.4 to 13.16 µg/m^3 during the winter season in the year 2011. In the present study, the concentration of NH_4^+ salt during the pre-monsoon season might be less as compared to winter season due to loss of NH_4^+ at Naraina mixed use area of Delhi. Tan et al. 2015 was also observed that during spring season in Beijing, loss of NH_4^+ was significant under high temperature and low humidity.

Total four anions like fluoride (Fl), chloride (Cl), sulphate (SO_4) and nitrate (NO_3) concentrations were determined in PM_{10}. The seasonal variation of anion concentration in PM_{10} during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.19.**

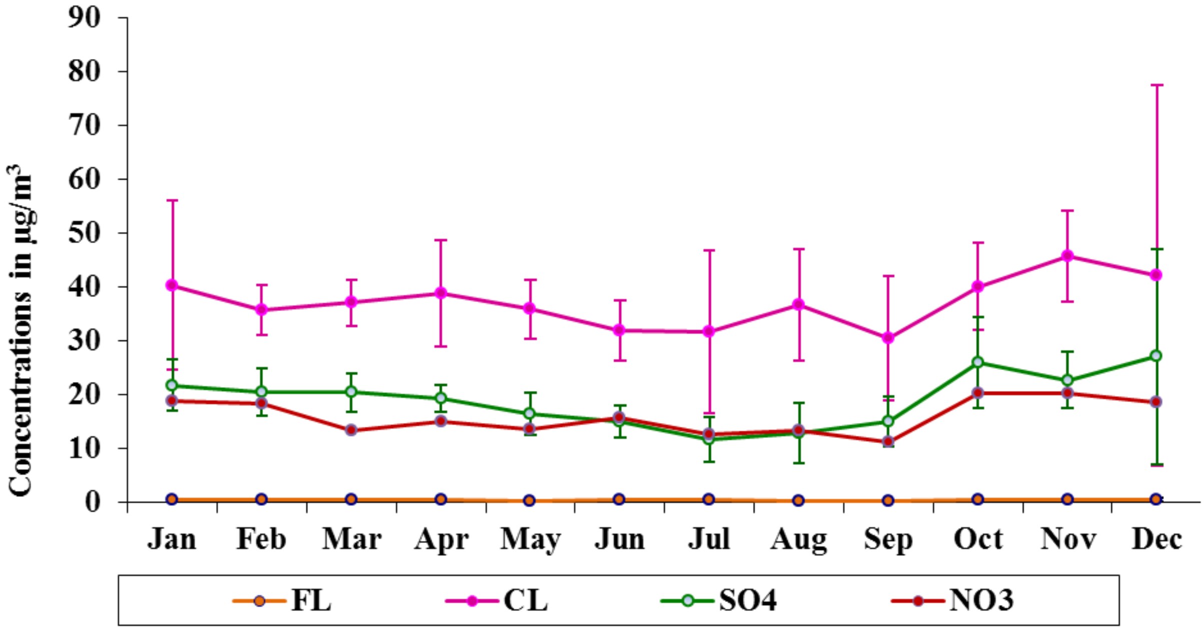


Figure 4.19 Monthly variation of anion in PM_{10} in mixed use area of Delhi (2011)

Fluoride (Fl) concentration in Naraina mixed use area of Delhi in the study period (2011) varied from 0.38 to 0.51µg/m³ with an annual average concentration of 0.43±0.10 µg/m³. There was no significant variation of Fl in the atmosphere. Fl is mostly present in the soil dust. The other emission sources of Fl might be from coal combustion and industrial processes like steel manufacture, aluminum, copper and nickel production etc.

Chloride (Cl) concentration varied from 30.42 to 45.61µg/m³ with an annual average of 37.20±4.52 µg/m³. The average concentration of Cl was the highest in the post-monsoon season (42.83±3.92 µg/m³), followed by winter season (38.81±2.94 µg/m³), pre-monsoon season (35.52±3.46 µg/m³)) and monsoon season (32.87±3.23 µg/m³) respectively. Cl is mostly present in the soil dust. It is the indicator of burning of municipal solid waste and has a relatively higher contribution to PM_{10} (DPCC report, 2016).

Sulphate (SO_4) concentration varied from 11.70 to 25.94µg/m³ with an annual average of 18.76±4.47µg/m³. The average SO_4concentration was the highest in the winter season

(22.09±1.30 µg/m^3), followed by post-monsoon season (20.51±7.68 µg/m^3), pre-monsoon season (18.68±2.04 µg/m^3) and monsoon season (13.24±1.69 µg/m^3) respectively. SO_4^- concentrations is expected to be high during pre-monsoon season due to high rate of photochemical activity and more formation of OH^- concentration, which ultimately increases the oxidation of SO_2 and accelerate its conversion of SO_2 to SO_4^{2-} (Stockwell and Calvert 1983; Khoder 2002; Utsunomiya and Wakamatsu 1996; Cadle 1985; Gupta et al. 2003). In the aqueous phase, H_2O_2 and O_3 are responsible for oxidation of SO_2 to SO_4^{2-}. However, in the present study at Naraina mixed use area of Delhi, it was observed that higher concentration of SO_4^{2-} was in winter season (**Fig. 4.20**) might be due to maximum biomass burning during the winter season. Kadowaki et al. 1986 was reported that high oxidant concentration (i.e. OH· and sunlight) and relative humidity are the important factors for conversion of SO_2 to SO_4^{2-}. SO_4^{2-} formation rate in the atmosphere is in general high with the maximum relative humidity (70±7%) and low temperature will enhance sulfate formation in winter season. The low relative humidity (51±10%) during pre-monsoon season may be the reason of low concentration of sulfate in summer as compared to winter. Awang et al. 2014, reported that the ambient concentration of SO_4 was high due to gaseous emission from motor vehicles in the heavy traffic movement. Emission of anthropogenic pollutants such as sulphur dioxide, vehicular exhaust, and natural emission from decaying plants and animals may increase the concentration of SO_4^{2-} in the air. Generally, anions like SO_4^{2-} and NO_3^- are the secondary particulates, formed into the atmosphere due to conversion of trace gases (SO_2 and NO_2) into the particulate matter. Air pollution is usually dominated by secondary particulate matter by increasing the concentration of fine particulate matter (Tsitouridou et al. 2003).

Nitrate (NO_3^-) concentration varied from 11.28 to 20.33µg/m^3 with an annual average of 15.80±3.13µg/m^3. NO_3 concentration was the highest in the winter season (18.77±1.21 µg/m^3), followed by post-monsoon season (15.70±6.25 µg/m^3), pre-monsoon season (14.67±1.11 µg/m^3) and monsoon season (13.83±1.60 µg/m^3) respectively. It was scientifically proved by several researchers that during the winter season NO_3^- concentrations were higher as compared to pre-monsoon season because high temperatures and low relative humidity, particulate ammonium nitrate (NH_4NO_3) is the gaseous pollutants as a result NH_4NO_3 will be in the gaseous phase. (Kaneyasu et al. 1995; Utsunomiya and Wakamatsu 1996; Mészáros et al. 1984; Willison et al. 1985).

4.6.2 Correlation coefficient and regression of selected cation and anion

The correlation coefficient (r) and regression among the selected cations (Na, K, NH_4, Mg, Ca) and anion (Fl, Cl, SO_4, NO_3) were determined to understand formation of secondary inorganic aerosols in the atmosphere. The correlation coefficient and linear regression equation of Fl with all selected cations during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.20 (a), 4.20 (b), 4.20(c), 4.20(d) and 4.20 (e).**

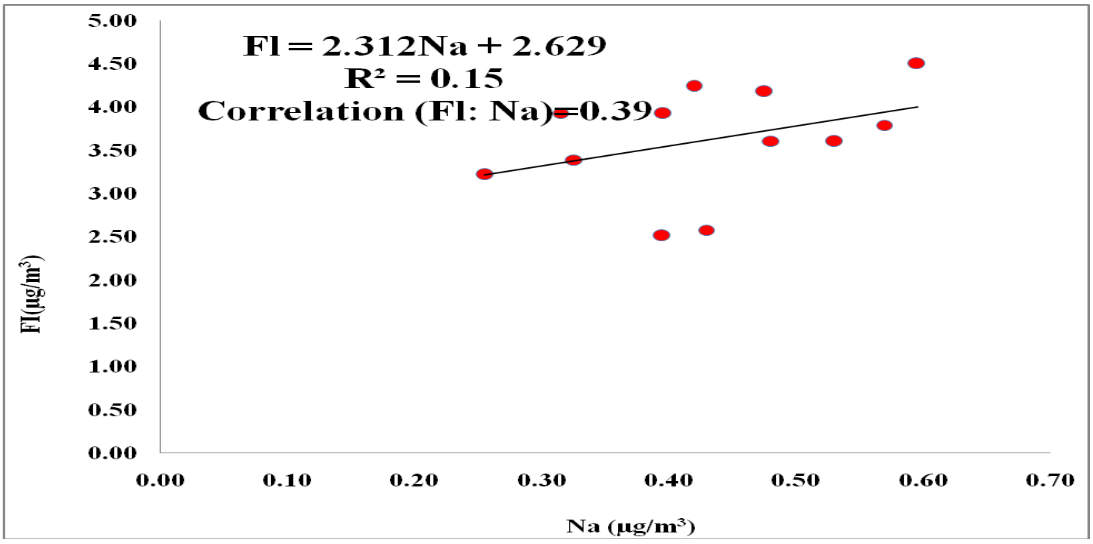


Figure 4.20 (a) Correlation and Regression of fluoride with sodium

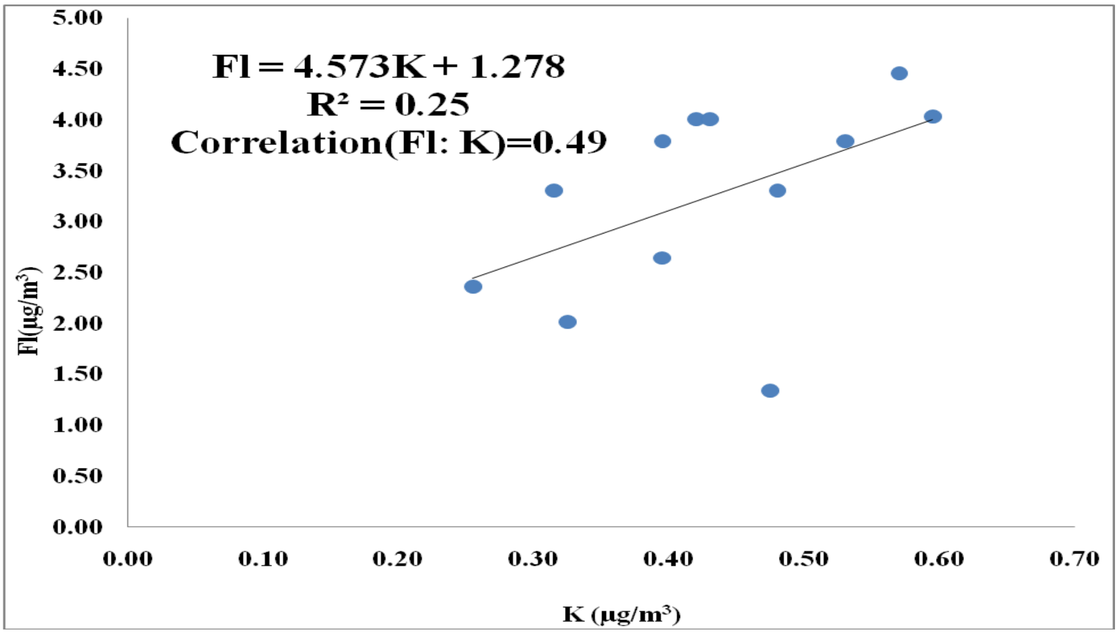


Figure 4.20 (b) Correlation and Regression of fluoride with potassium

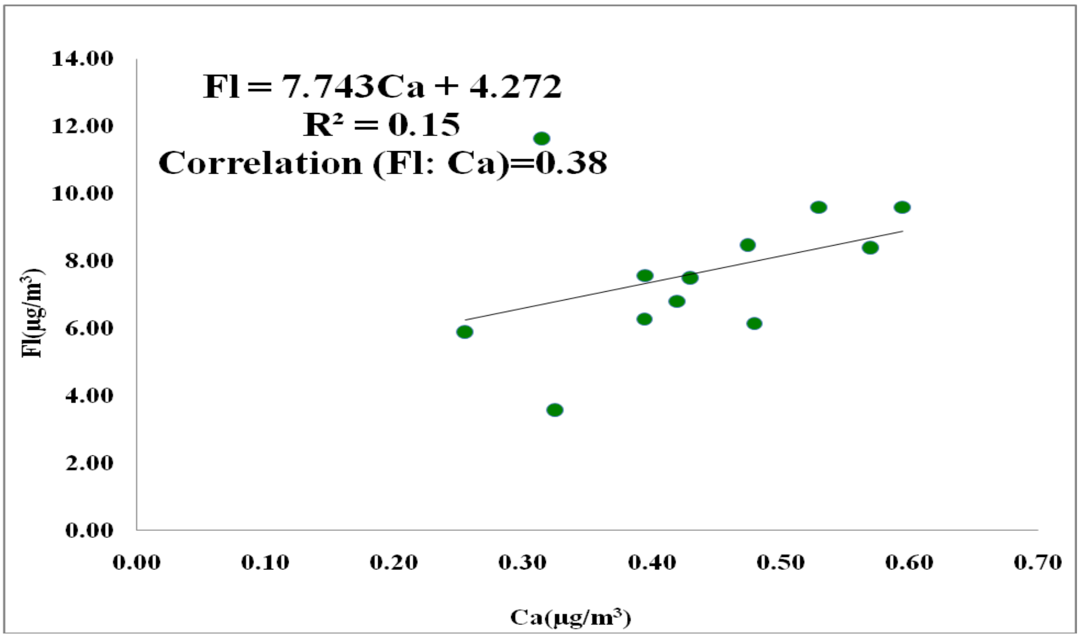


Figure 4.20 (c) Correlation and Regression of fluoride with calcium

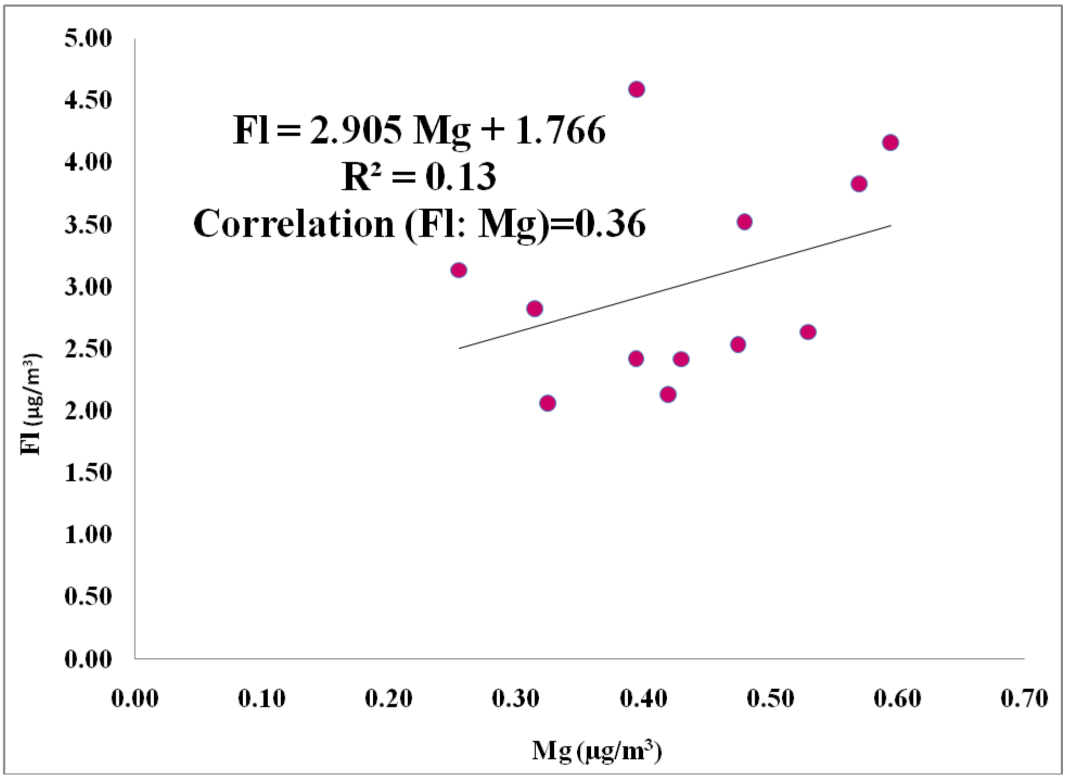


Figure 4.20 (d) Correlation and Regression of fluoride with magnesium

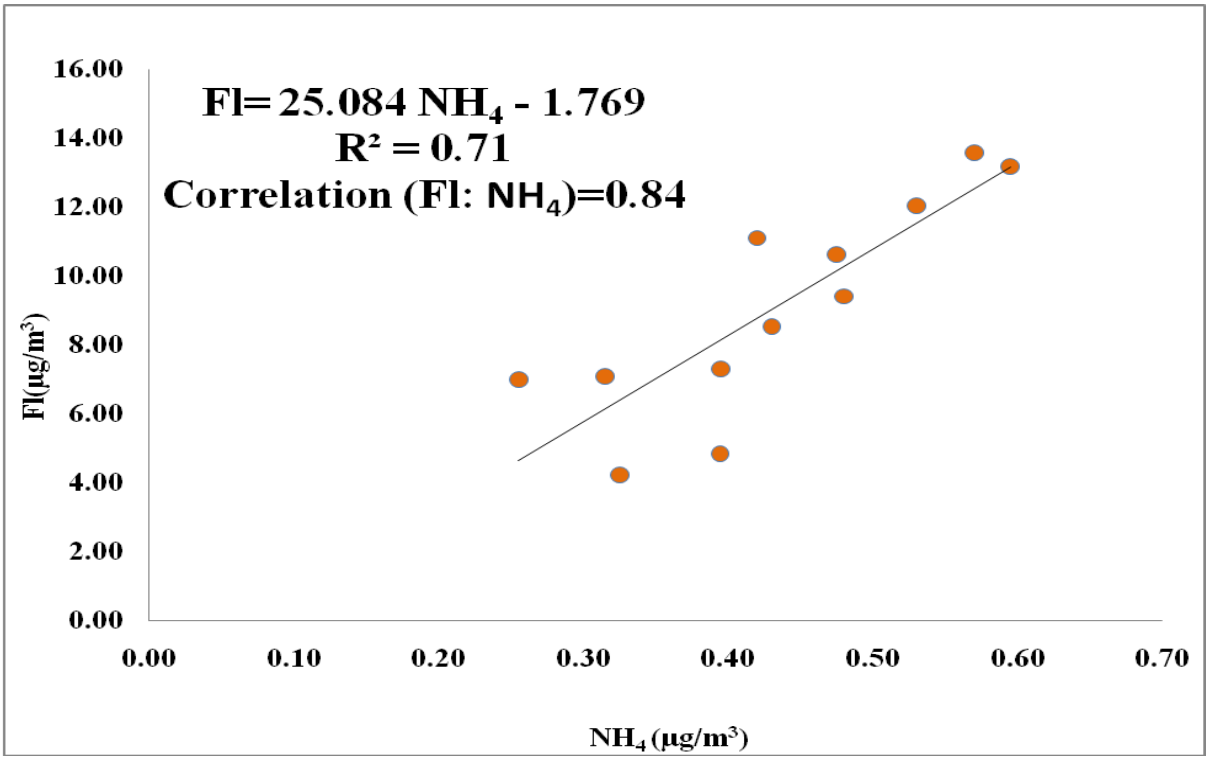


Figure 4.20 (e) Correlation and Regression of fluoride with ammonium

The correlation and regression of fluoride with cations (Na, K, Ca, Mg and NH_4) in urbanized mixed use area of Delhi is shown in **Figure 4.20 (a), 4.20(b), 4.20(c), 4.20(d) and 4.21(e)**. Fluoride (Fl) had strong correlation coefficient (r = 0.84) among with ammonium (NH_4) salt suggested that NH_4F was formed into the atmosphere. Moderate correlation coefficient (r = 0.49) was observed with K, indicated that KF was also formed in the atmosphere. Weak correlation coefficient was observed with Fl other cations like Na, Ca and Mg indicated the formation of NaF, CaF_2 and MgF_2 were less during the study period at Naraina mixed use area of Delhi in the year 2011. Fl is mostly present in the natural soil dust, metal processing and production of electronic components.

The correlation coefficient and linear regression equation of Cl with all selected cations during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.21 (a), 4.21(b), 4.21(c), 4.21(d) and 4.21(e).**

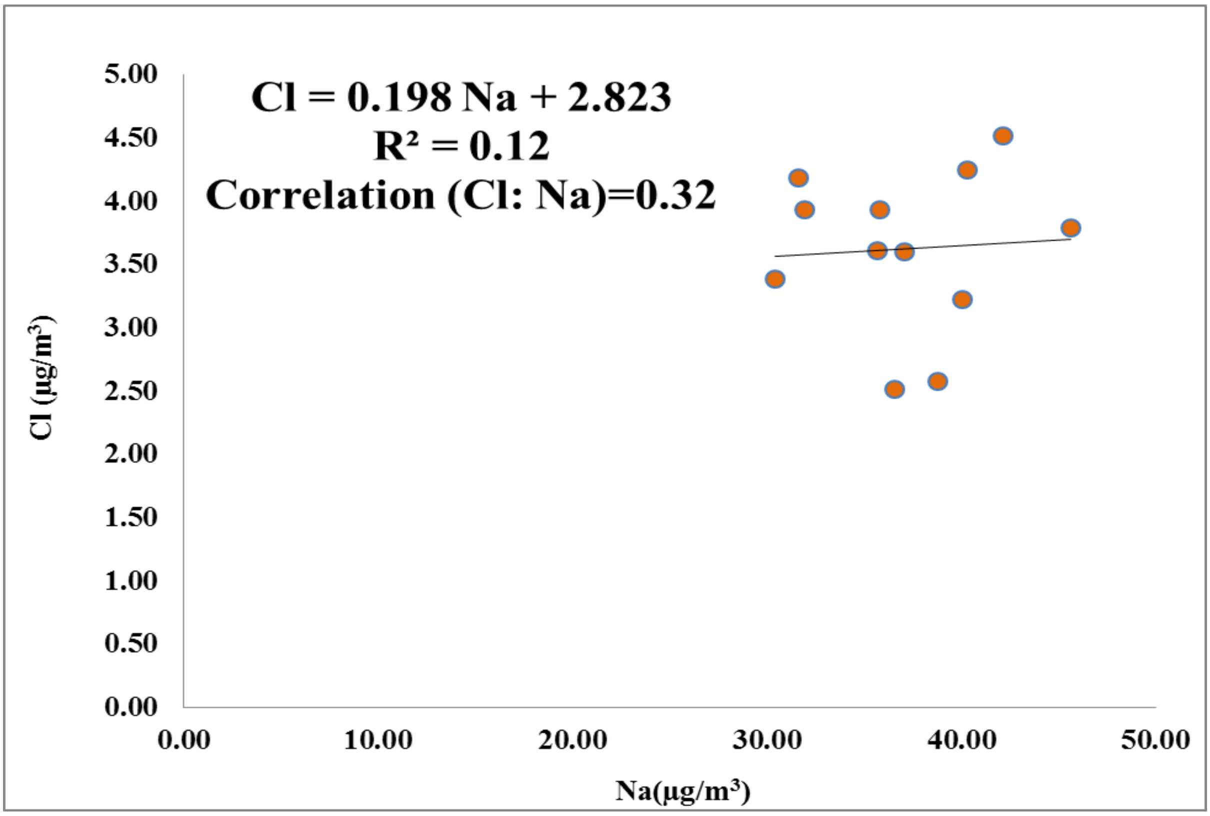


Figure 4.21 (a) Correlation and Regression of chloride with sodium

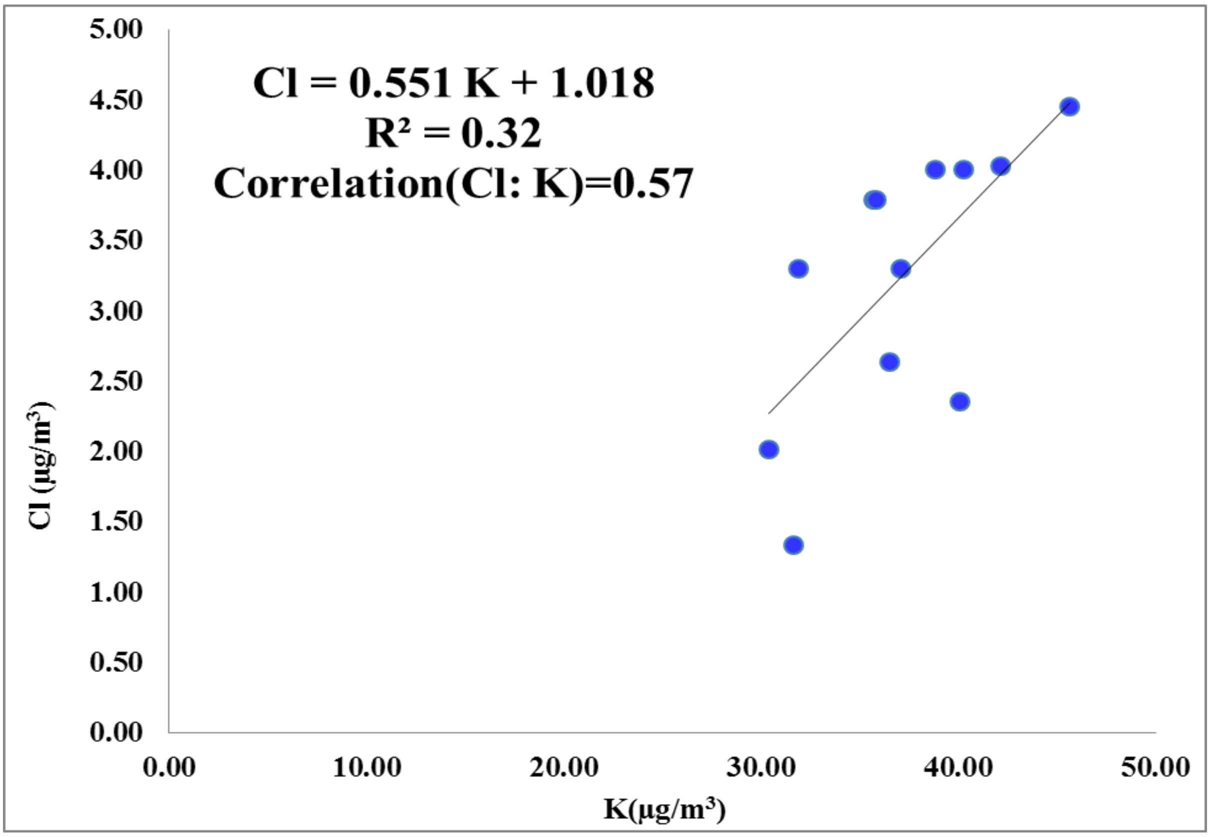


Figure 4.21 (b) Correlation and Regression of chloride with potasium

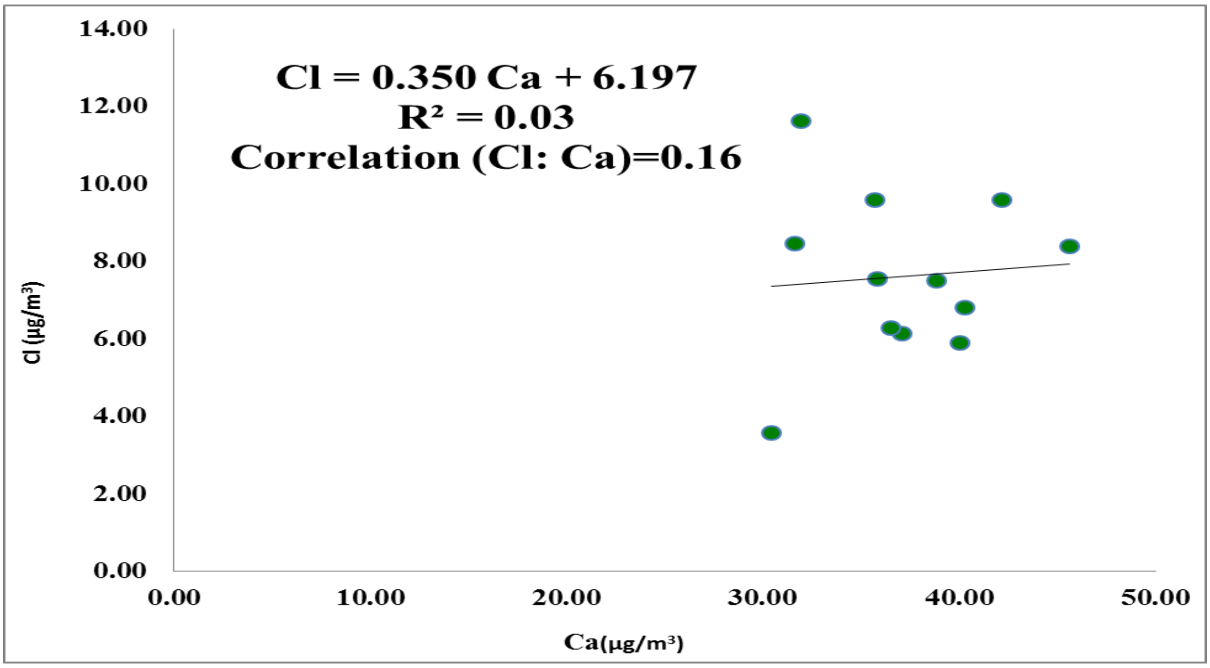


Figure 4.21 (c) Correlation and Regression of chloride with caicium

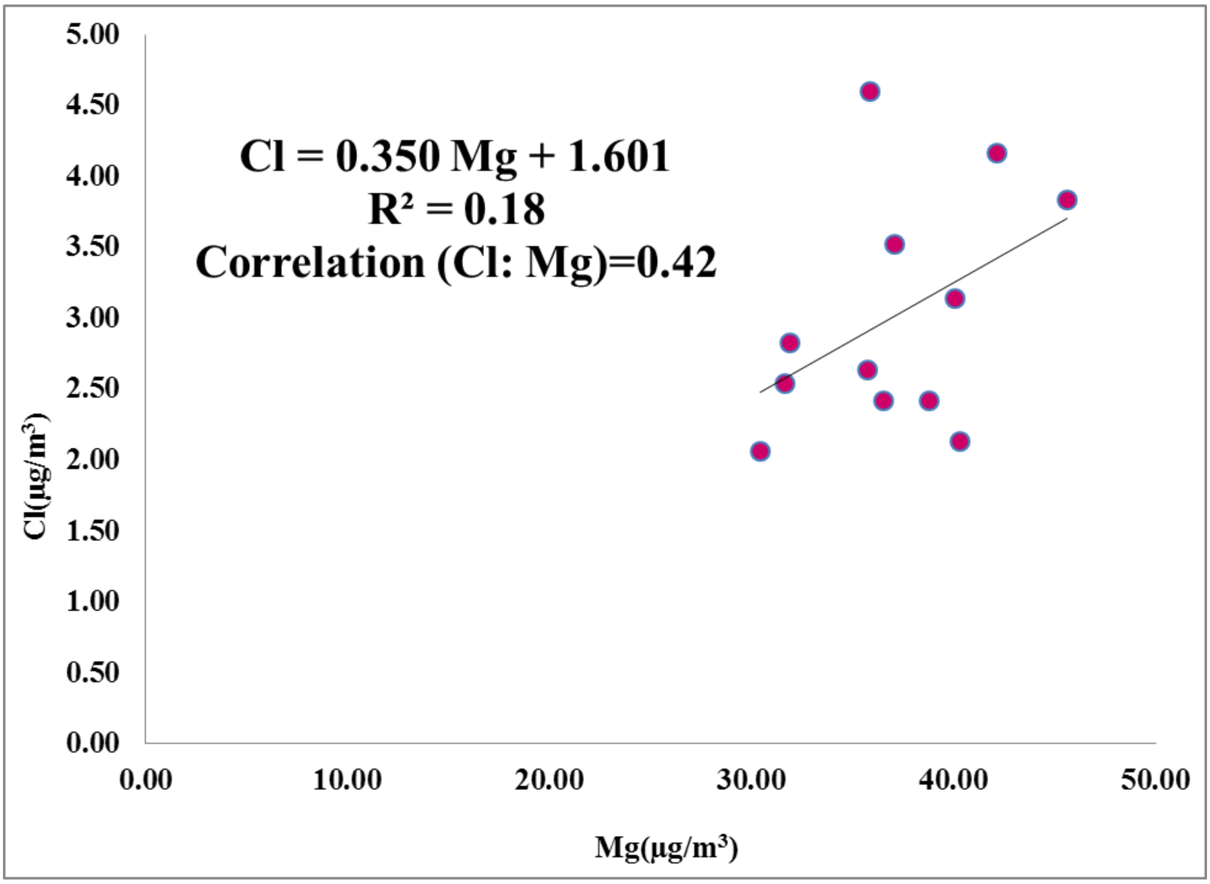


Figure 4.21 (d) Correlation and Regression of chloride with magnesium

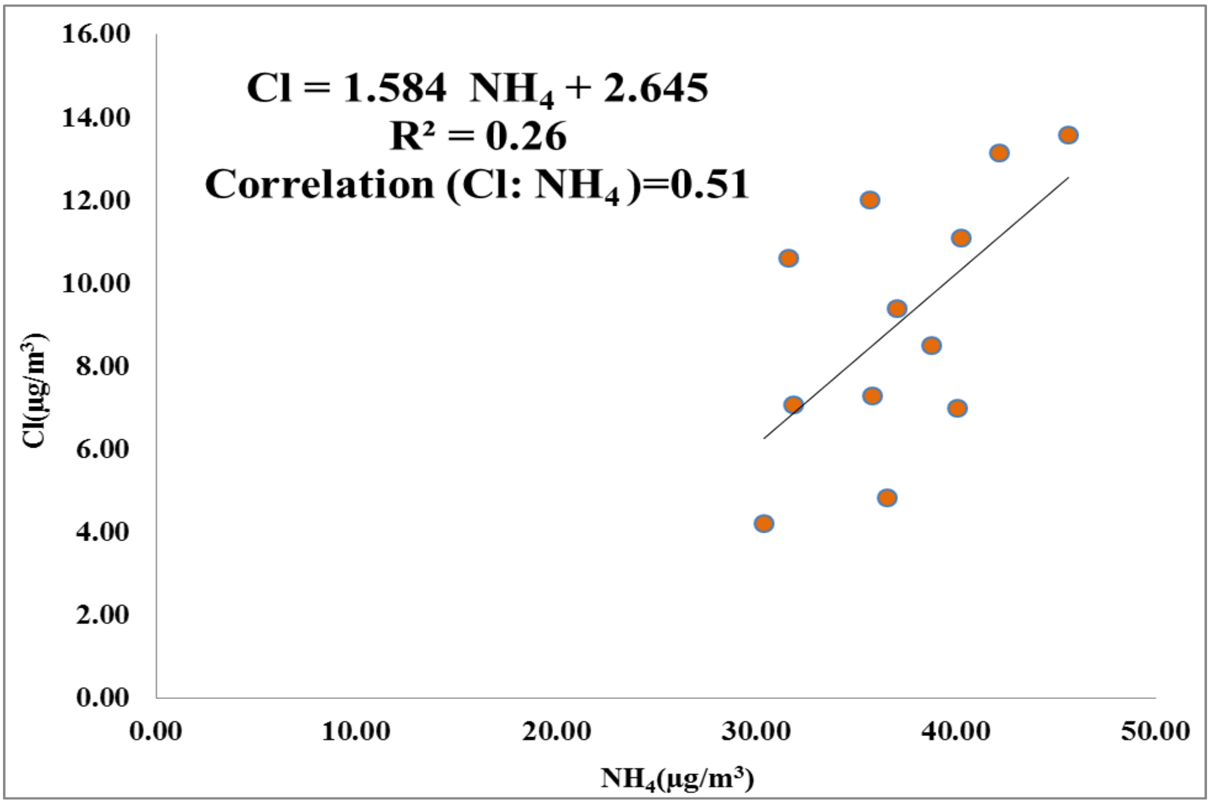


Figure 4.21 (e) Correlation and Regression of chloride with ammonium

The correlation coefficient and linear regression equation of Cl with selected cations (Na, K, NH_4, Mg and Ca) during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.21(a), 4.21(b), 4.21(c), 4.21(d) and 4.21(e).** No significant correlation coefficient (r) observed of chloride (Cl) with cation like Na, Ca and Mg, suggested that the formation of chloride salt like NaCl, $CaCl_2$ and $MgCl_2$ were meager in the atmosphere. However moderate correlation coefficient (r = 0.57) was observed with K and NH_4 (r =0.51) might have indicated that small fraction of KCl and NH_4Cl were formed into the atmosphere. The sources of K and NH_4 were from the biomass burning and conversion of trace gas ammonia (NH_3) into inorganic salt.

The correlation coefficient and linear regression equation of SO_4 with selected cations (Na, K, NH_4, Mg and Ca) during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.22(a), 4.22(b), 4.22(c), 4.22(d) and 4.22(e).**

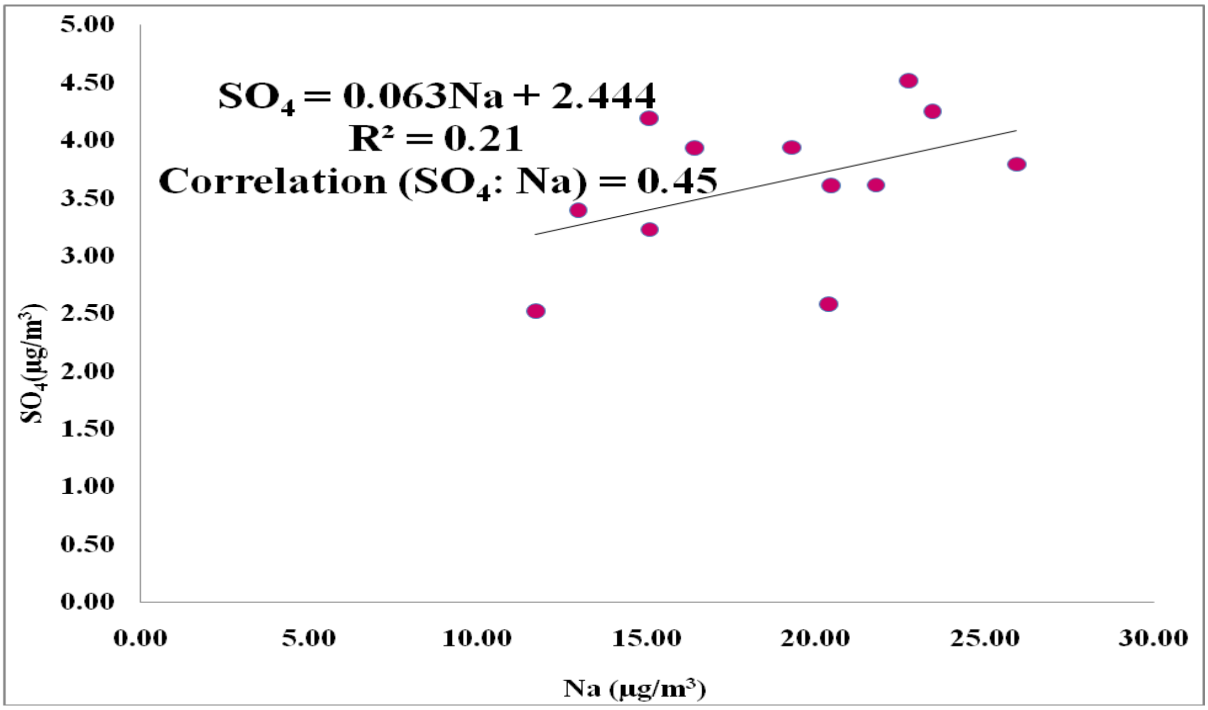


Figure 4.22 (a) Correlation and Regression of sulphate with sodium

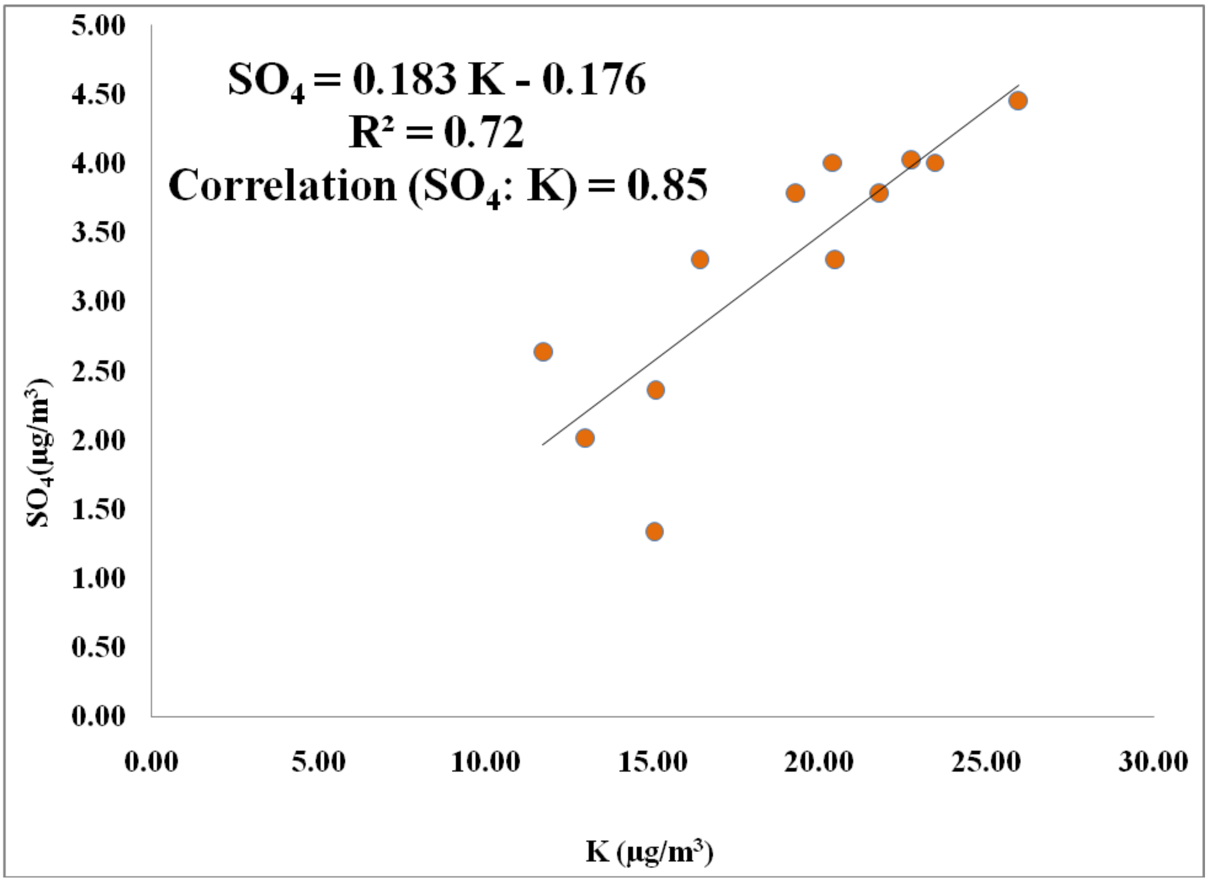


Figure 4.22 (b) Correlation and Regression of sulphate with potasium

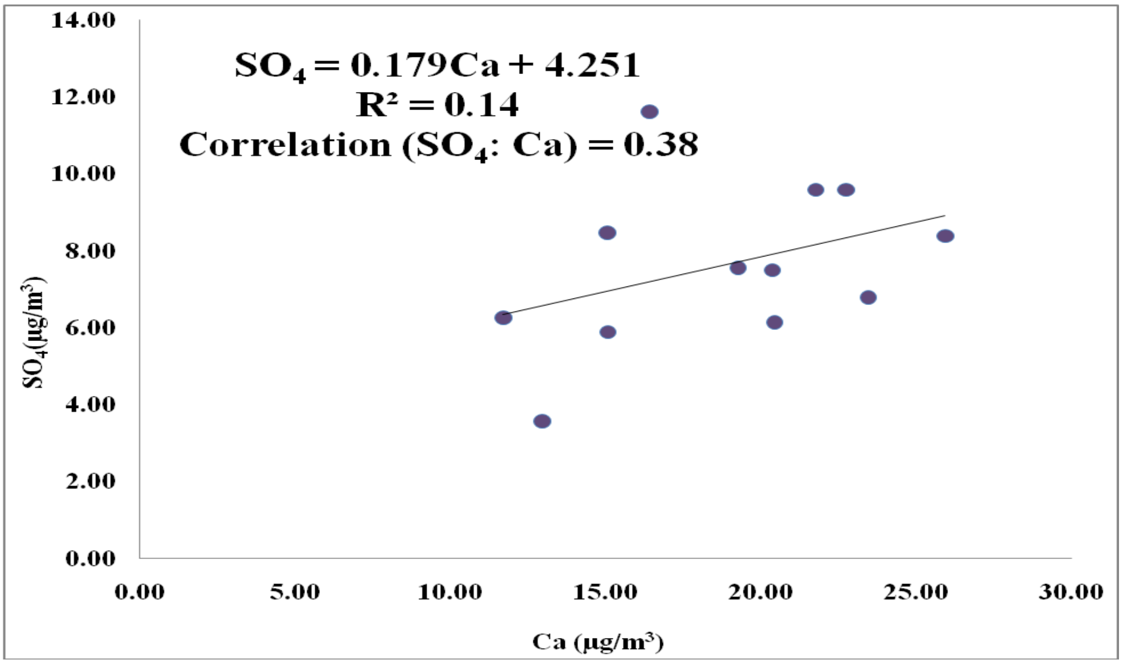


Figure 4.22 (c) Correlation and Regression of sulphate with calcium

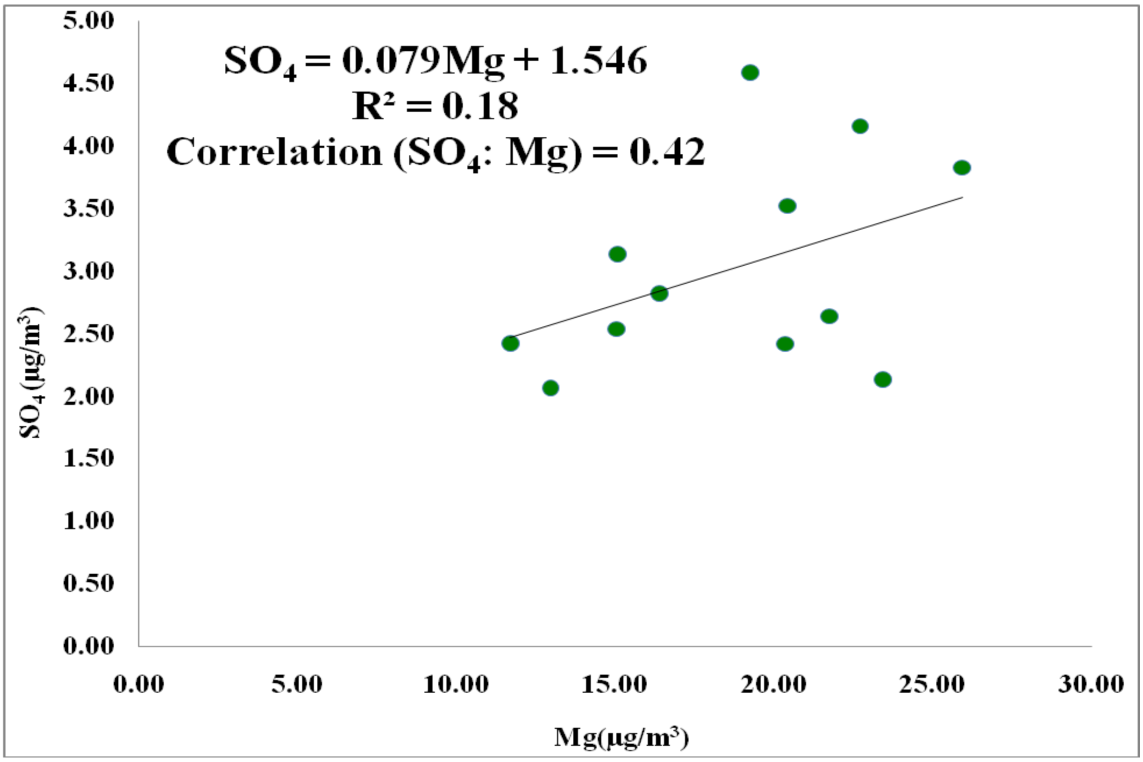


Figure 4.22 (d) Correlation and Regression of sulphate with magnesium

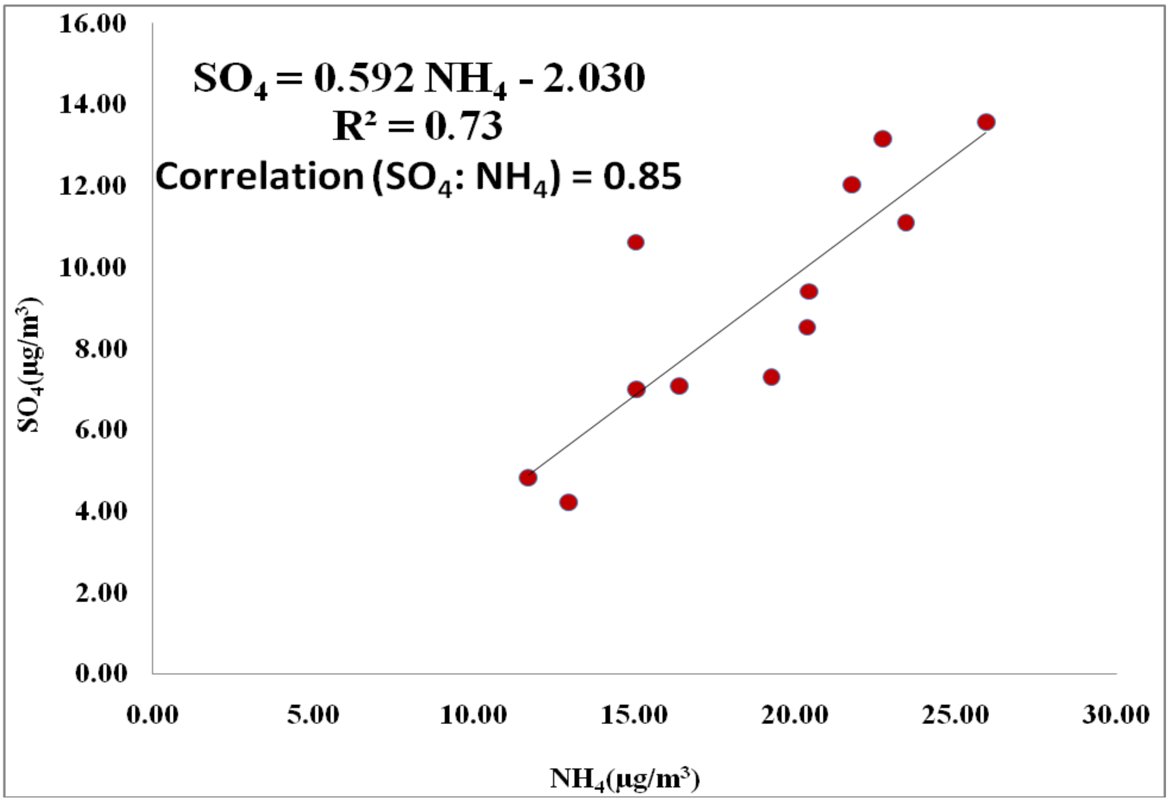


Figure 4.22 (e) Correlation and Regression of sulphate with ammonium

The correlation coefficient and linear regression equation of SO_4 with selected cations (Na, K, NH_4, Mg and Ca) during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.22(a), 4.22(b), 4.22(c), 4.22(d) and 4.22(e).** The strong correlation coefficient (r = 0.85) of SO_4 was observed with potassium (K) and with ammonium (NH_4) salt might have suggested that K_2SO_4 and $(NH_4)_2SO_4$ were formed into the atmosphere during the study period in the year 2011 at Naraina mixed use area of Delhi. Weak correlation was observed of SO_4 with other cations like Na, Ca and Mg might be indicated the formation of Na_2SO_4, $CaSO_4$, and $MgSO_4$ were less in the atmosphere. The strong correlation of SO_4 with NH_4 during the study period indicated that ammonium sulfate $(NH_4)_2SO_4$ was formed in the atmosphere (Wall et al. 1988).

The correlation coefficient and linear regression equation of NO_3 with selected cations (Na, K, NH_4, Mg and Ca) during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.23(a), 4.23 (b), 4.23 (c), 4.23 (d) and 4.23 (e).**

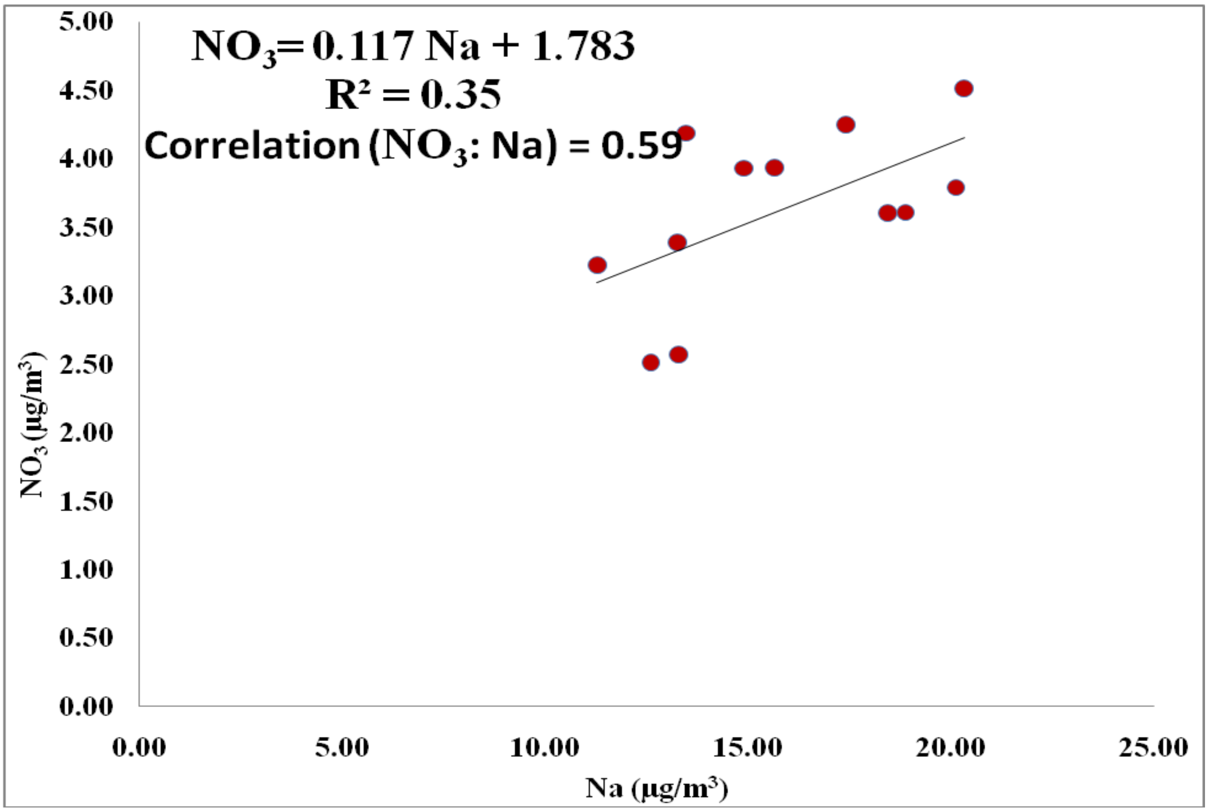


Figure 4.23 (a) Correlation and Regression of nitrate with sodium

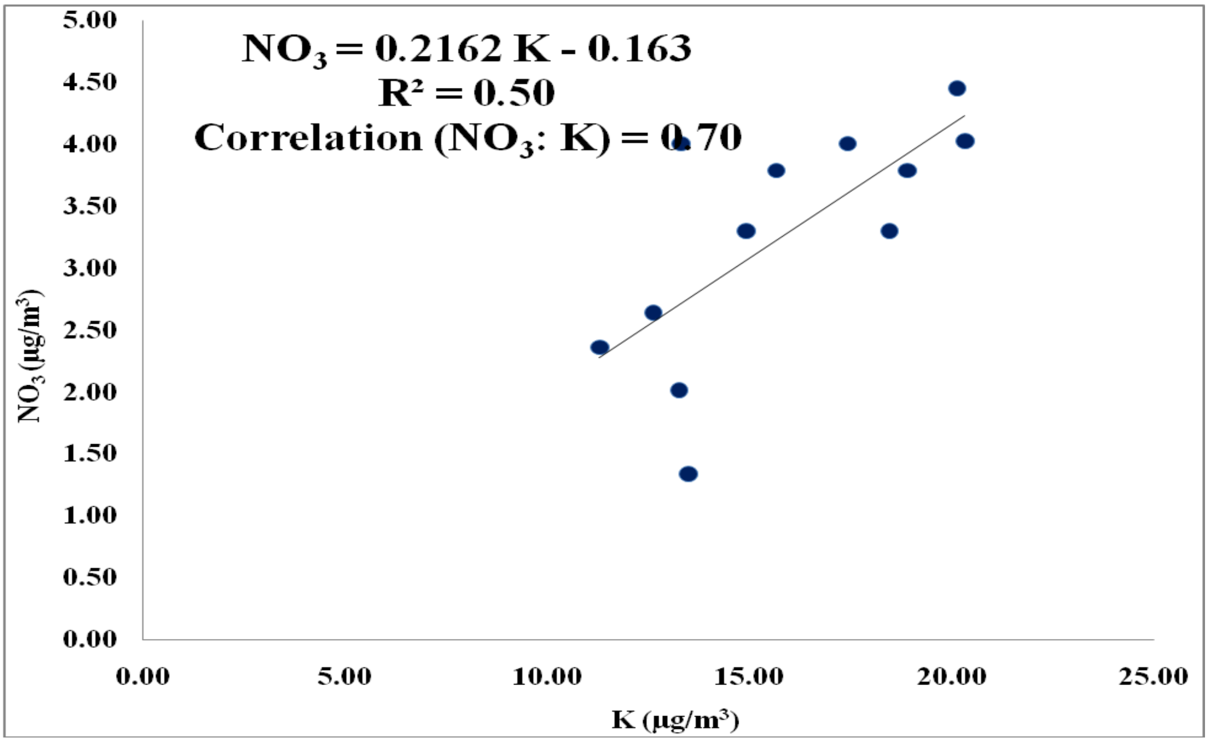


Figure 4.23 (b) Correlation and Regression of nitrate with potassium

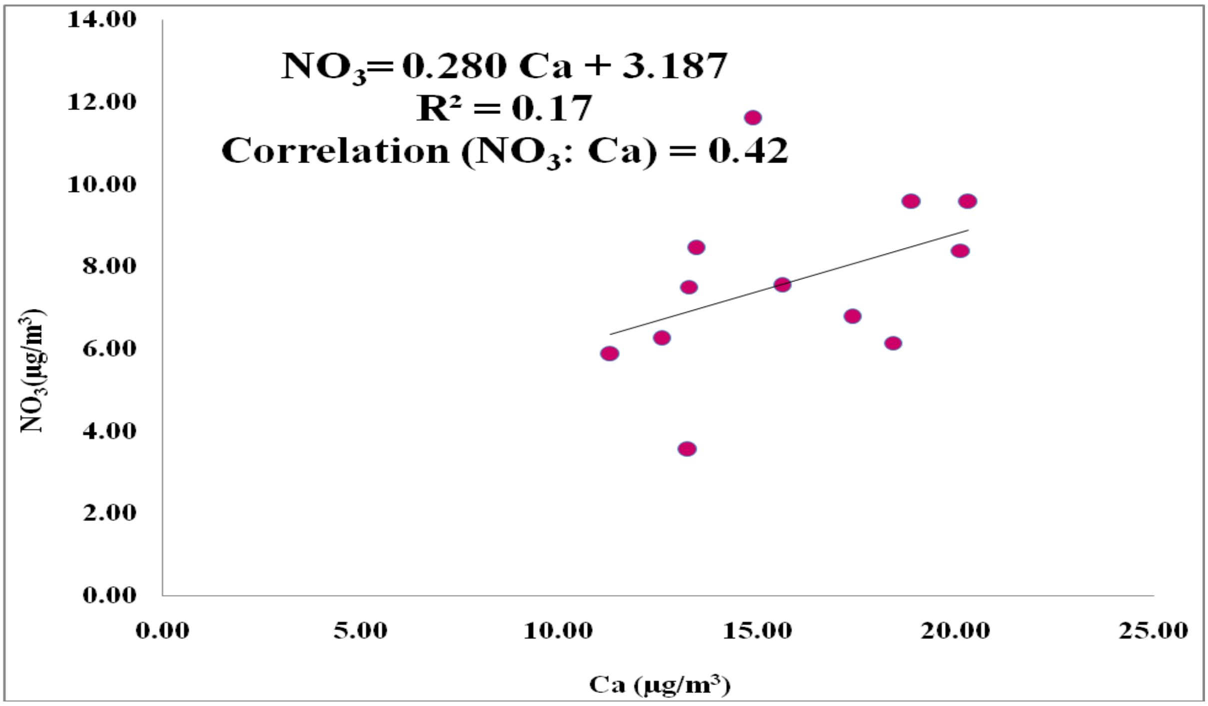


Figure 4.23 (c) Correlation and Regression of nitrate with calcium

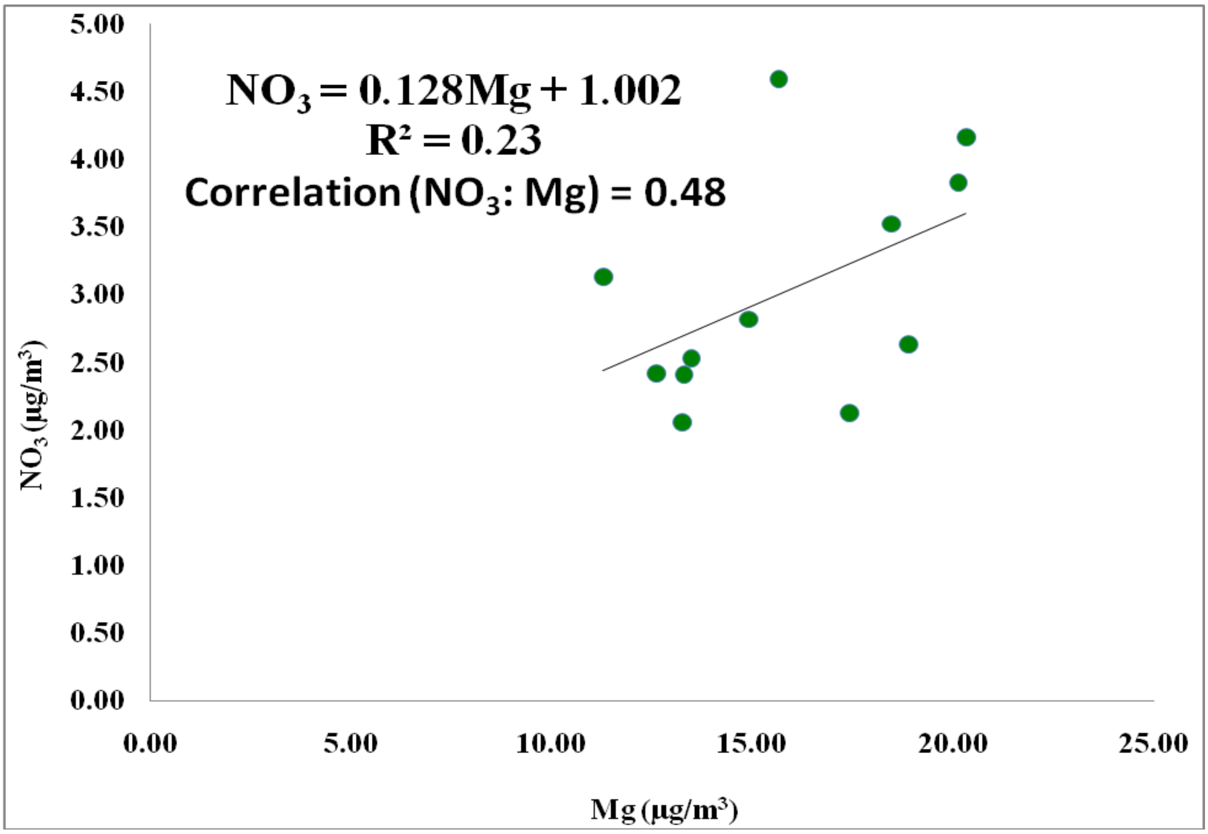


Figure 4.23 (d) Correlation and Regression of nitrate with magnesium

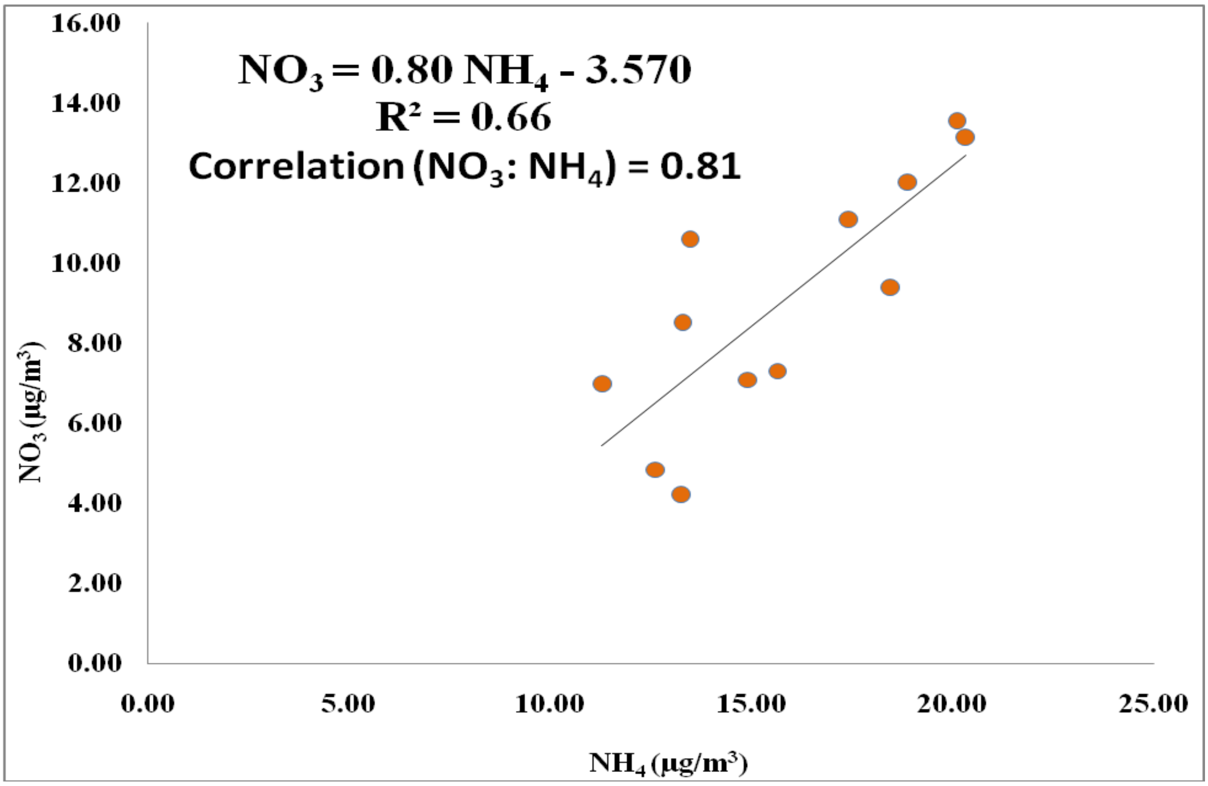


Figure 4.23 (e) Correlation and Regression of nitrate with ammonium

The correlation coefficient and linear regression equation of NO_3 with selected cations (Na, K, NH_4, Mg and Ca) during the study period in the year 2011 at urbanized Naraina mixed use area of Delhi is shown in **Figure 4.23 (ai), (aii), (aiii), (aiv) and (av).** NO_3 had strong correlation coefficient (r = 0.81) with ammonium (NH_4) salt and with potassium (K) salt (r = 0.70) might have suggested that NH_4NO_3 and KNO_3 were formed into the atmosphere. The moderate correlation was observed with other cations like Na, and Mg indicated that few percentage of $NaNO_3$ and $Mg(NO_3)_2$ were formed into the atmosphere. The poor correlation was observed with Ca might be indicated the formation of $Ca(NO_3)_2$, was less in the atmosphere.

In the present study, the higher concentration of SO_4 concentration could be represent the transport of aerosols over a long distance or precursors from a continental air mass (Sharma et al., 2010). Sharma et al. 2007 reported that NH_3 is a precursor pollutant for formation of NH_4NO_3 and $(NH_4)_2SO_4$. NH_3 is present in the ambient air with sufficient quantities to neutralize a significant fraction of sulfate, nitrate and chloride particles (Sharma et al. 2007). It was reported by Adams et al. 1999 that the temperature more than 25°C prevents the significant formation of particulate NH_4NO_3. In the present study, the average pre-monsoon temperature and relative humidity were 37±2°C and 51±10% respectively, preventing the formation of particulate NH_4NO_3 in the Naraina mixed use area of Delhi in the year 2011. NH_4 generally combines with NO_3 and SO_4 in the atmosphere and form ammonium nitrate and ammonium sulphates (**Sharma et al. 2007**). However during the pre-monsoon season NH_4 will be transformed to NH_3 due to high temperature and low relative humidity. Thus increase the concentrations of NH_3 during the pre-monsoon season.

4.7 Correlation coefficient of various selected fractions of PM_{10}

The fractions of PM_{10} are divided into four categories:

- Carbonaceous aerosols (OC, EC)
- Heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn)
- Inorganic aerosols (Na, K, Ca, Mg, NH_4, F, Cl, SO_4 and NO_3)
- Particulate polycyclic aromatic hydrocarbons (PAHs)

The correlation coefficient among the selected parameters during the study period (2011) at urbanized Naraina mixed use area of Delhi is shown in **Table 4.11.**

Positive correlations were obtained among the selected variables, during the study period at mixed use area of Delhi, indicating the relationship between the two variables, in which both variables move in tandem. The only negative correlations were obtained in cation and anions selected parameters indicating that the sources of the individual emission sources are different. OC-EC, SO_4-NO_3, SO_4-NH_4 As-Co, As-Ni, Cd-Pb, Cr-Zn, Cu-Ni, Cu-Pb, Cu-Fe, Fe-Pb were correlated at the 0.05 level (2-tailed) of significance. Cr-Mn, Cr-Ni, Cu-Mn, Cu-Zn, Fe-Mn, Fe-Zn, Mn-Ni, Mn-Pb and Mn-Zn, Ni-Zn, are Pb-Zn were correlated at the 0.01 level (2-tailed) of significance.

Table 4.11 Correlation coefficient of selected parameters in PM_{10} size of airborne particulate matter (2011)

Components	EC	OC	SO_4	NO_3	NH_4	K	Na	Mg	Ca	Cl	Fl	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	PHE	ANT	FLR	PYR	BaA	CHR	BbF	BkF	BaP	DahA	BghiP	IcdP
EC	1.00																																
OC	0.9**	1.00																															
SO_4	0.30	0.30	1.00																														
NO_3	0.13	0.14	0.83*	1.00																													
NH_4	0.19	0.18	0.87**	0.84**	1.00																												
K	0.45	0.45	0.45	0.29	0.26	1.00																											
Na	0.06	0.08	0.48	0.54	0.52	-0.04	1.00																										
Mg	0.20	0.20	0.52	0.46	0.48	0.27	0.48	1.00																									
Ca	0.05	0.05	0.68*	0.69*	0.76*	0.24	0.53	0.79	1.00																								
Cl	0.05	0.05	0.69*	0.85**	0.76*	0.22	0.35	0.40	0.72	1.00																							
Fl	0.02	0.02	0.78*	0.76*	0.71*	0.31	0.49	0.55	0.65	0.53	1.00																						
As	0.39	0.38	0.45	0.33	0.38	0.57	-0.08	0.48	0.48	0.42	0.35	1.00																					
Cd	0.26	0.26	0.07	0.06	0.05	0.17	-0.21	0.09	-0.11	-0.13	0.01	0.25	1.00																				
Co	0.31	0.31	0.44	0.53	0.37	0.15	0.45	0.55	0.52	0.50	0.34	0.47	0.14	1.00																			
Cr	0.44	0.43	0.61	0.42	0.55	0.27	0.39	0.36	0.28	0.30	0.46	0.30	0.19	0.36	1.00																		
Cu	0.69*	0.69*	0.30	0.20	0.23	0.26	0.13	0.30	0.21	0.06	0.12	0.31	0.18	0.20	0.35	1.00																	
Fe	0.12	0.12	-0.17	-0.10	-0.16	-0.26	0.16	0.26	0.07	-0.14	-0.30	-0.24	-0.07	0.12	-0.11	0.45	1.00																
Mn	0.48	0.47	0.45	0.21	0.32	0.04	0.37	0.55	0.36	0.03	0.35	0.09	0.06	0.24	0.59	0.60	0.52	1.00															
Ni	0.56	0.53	0.61	0.28	0.52	0.32	0.24	0.41	0.46	0.32	0.32	0.43	0.09	0.37	0.56	0.51	0.02	0.56	1.00														
Pb	0.43	0.44	0.34	0.17	0.23	0.33	0.18	0.43	0.22	0.00	0.01	0.17	0.46	0.23	0.31	0.49	0.48	0.54	0.40	1.00													
Zn	0.68*	0.67*	0.43	0.33	0.34	0.35	0.32	0.47	0.39	0.25	0.22	0.31	0.07	0.37	0.46	0.84	0.53	0.73*	0.62	0.59	1.00												
PHE	0.58	0.58	0.26	0.19	0.18	0.07	0.21	0.00	0.03	-0.05	0.01	0.02	0.17	0.12	0.33	0.74	0.44	0.56	0.38	0.55	0.62	1.00											
ANT	0.70*	0.71*	0.39	0.22	0.23	0.22	0.20	0.00	0.05	0.05	0.14	0.03	-0.04	0.06	0.39	0.72	0.21	0.55	0.45	0.37	0.60	0.81**	1.00										
FLR	0.57	0.56	0.02	-0.15	0.04	0.10	-0.01	0.18	-0.03	-0.19	-0.25	0.08	0.28	0.13	-0.01	0.54	0.35	0.28	0.51	0.55	0.46	0.34	0.29	1.00									
PYR	0.66*	0.64*	0.15	0.01	0.11	0.18	-0.06	0.15	-0.05	-0.08	-0.16	0.11	0.35	0.20	0.23	0.67	0.40	0.41	0.53	0.59	0.58	0.49	0.43	0.89**	1.00								
BaA	0.44	0.42	-0.09	-0.19	-0.17	0.06	-0.27	0.14	-0.24	-0.24	-0.21	0.05	0.37	0.04	0.09	0.45	0.34	0.30	0.30	0.57	0.38	0.26	0.22	0.75*	0.79**	1.00							
CHR	0.79**	0.78*	0.11	0.01	0.01	0.51	0.00	0.32	0.03	-0.04	-0.10	0.33	0.29	0.22	0.19	0.54	0.20	0.33	0.42	0.54	0.57	0.31	0.34	0.70*	0.72*	0.62	1.00						
BbF	0.65*	0.62	0.31	0.12	0.26	0.34	0.05	0.26	0.03	0.04	0.04	0.23	0.22	0.20	0.58	0.62	0.25	0.52	0.61	0.52	0.60	0.41	0.45	0.65	0.86**	0.68*	0.69*	1.00					
BkF	0.60	0.58	0.23	0.11	0.20	0.32	-0.02	0.35	0.07	0.01	0.01	0.24	0.40	0.29	0.36	0.60	0.30	0.43	0.53	0.59	0.54	0.33	0.30	0.79*	0.93**	0.78*	0.74*	0.92**	1.00				
BaP	0.65*	0.63	0.17	-0.03	0.06	0.29	-0.07	0.11	-0.15	-0.15	-0.14	0.09	0.32	0.10	0.39	0.71*	0.41	0.50	0.50	0.65	0.61	0.57	0.53	0.74*	0.93**	0.77*	0.68*	0.91**	0.90**	1.00			
DahA	0.69*	0.66*	0.28	0.10	0.26	0.24	0.07	0.30	0.08	0.02	-0.01	0.19	0.26	0.28	0.45	0.61	0.28	0.51	0.57	0.52	0.55	0.37	0.41	0.78*	0.92**	0.67*	0.73*	0.93**	0.95**	0.88**	1.00		
BghiP	0.69*	0.67*	0.30	0.09	0.23	0.38	0.01	0.15	0.00	0.00	-0.09	0.13	0.30	0.19	0.46	0.65*	0.33	0.49	0.62	0.68	0.65	0.54	0.51	0.75*	0.92**	0.67*	0.70*	0.91**	0.88**	0.95**	0.90**	1.00	
IcdP	0.71*	0.69*	0.15	-0.05	0.14	0.24	-0.03	0.31	0.07	-0.10	-0.06	0.20	0.29	0.10	0.31	0.73*	0.39	0.57	0.63	0.60	0.69	0.47	0.46	0.84*	0.90**	0.76*	0.80*	0.85*	0.88**	0.87**	0.88**	0.86**	1.00

*Correlation is significant at the 0.05 level (2- tailed)

** Correlation is significant at the 0.01 level (2- tailed)

4.8 Principle Component Analysis of selected fractions of PM_{10}

Principle component analysis (PCA), described in methodology (3.5.1) was performed to concentrate the variability of various fractions of PM_{10} is shown in **Table 4.12**.

Table 4.12 PCA factor scores for fractions of PM_{10}

Components	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8
EC	**.550**	.011	**.658**	.303	-.184	.071	.300	.053
OC	**.523**	.006	**.673**	.314	-.175	.072	.304	.037
SO_4	.104	**.862**	.211	.192	-.056	.087	-.018	.237
NO_3	-.032	**.942**	.135	.059	.022	-.027	.146	.029
NH_4	.103	**.919**	.090	.004	-.064	.024	-.009	.128
K	.188	.256	.106	**.906**	-.084	.022	-.024	.066
Na	-.086	**.480**	.142	-.094	.127	.213	.210	.124
Mg	.188	**.479**	-.096	.157	.255	**.711**	.268	.046
Ca	-.069	**.781**	-.018	.086	.198	.404	.192	-.084
Cl	-.068	**.872**	-.037	.068	.036	-.124	.285	-.036
Fl	-.136	**.777**	.067	.061	-.224	.433	-.111	.202
As	.078	.357	.070	**.532**	-.135	.254	.409	.025
Cd	.271	-.018	.014	.052	-.064	.008	.090	.044
Co	.130	.426	.028	-.006	.101	.109	**.811**	.098
Cr	.238	.377	.241	.076	-.091	.090	.132	**.800**
Cu	**.507**	.154	**.697**	.032	.221	.210	.038	-.007
Fe	.282	-.162	.219	-.236	**.826**	.167	.086	-.094
Mn	.331	.176	.461	-.113	.315	**.517**	-.045	.417
Ni	**.487**	.386	.282	.054	-.072	.159	.086	.216
Pb	**.486**	.133	.220	.266	**.542**	.082	-.041	.049
Zn	**.450**	.261	**.567**	.172	.379	.268	.158	.107
PHE	.240	.078	**.836**	-.074	.303	-.120	-.045	.091
ANT	.253	.141	**.891**	.045	.001	-.061	-.118	.114
FLR	**.854**	-.101	.153	-.036	.040	.063	.054	-.324
PYR	**.944**	.005	.244	-.034	.103	-.058	.052	-.055
BaA	**.820**	-.207	.051	-.048	.113	.122	-.051	-.062
CHR	**.723**	-.091	.244	.470	-.030	.186	.222	-.140
BbF	**.889**	.117	.182	.113	.035	.009	.021	.342
BkF	**.952**	.109	.058	.080	.070	.083	.085	.088
BaP	**.877**	-.052	.309	.092	.195	-.078	-.067	.205
DahA	**.935**	.107	.161	.020	-.009	.045	.116	.160
BghiP	**.869**	.080	.275	.176	.172	-.159	-.012	.203
IcdP	**.886**	-.025	.304	.066	.084	.222	-.025	-.003
Eigen Value	**13.63**	**6.57**	**2.44**	**1.981**	**1.44**	**1.16**	**1.01**	**0.90**
% Variance	**29.68**	**17.81**	**12.80**	**5.35**	**5.35**	**4.93**	**4.38**	**4.34**
Cumulative %	**29.68**	**47.49**	**60.29**	**65.64**	**70.99**	**75.92**	**80.30**	**84.64**

The lowest eigen value for extracted factors was restricted to more than 1.0 of the total variance. Eight factors (PC1, PC2, PC3, PC4, PC5, PC6, PC7 and PC8) were obtained through PCA analysis. PCA factors were identified using varimax rotation with Kaiser Normalization. Eight factors explained total 84.64% of the variance of PM_{10}. The factors greater or equal to 0.5 was selected for lowest level of significance within a factor.

The factor PC1 represents total 29.68% of variance. This factor is weighted by EC, OC, Cu, Ni, Pb, Zn, FLR, PYR, BaA, CHR, BbF, BkF, BaP, BghiP and IcdP representing a major contribution from industrial emissions. Emission from small and medium scale industries like metal alloys, forging, foundries, casting, molding etc. in the Naraina Industrial Area of Delhi. Coke oven, aluminium production, iron and steel foundries, coal gasification and coke production are the main industrial sources of PAHs in the ambient air. Petroleum refining, thermal power plant, occupations where coaltars, pitch, asphalt (bitumen), shell-oil and creosotes are used, emit much of PAH to make air polluted (CPCB, 2003, Sharma et al. 2014, Smith and Harrison, 1998; Ravindra et al. 2006, Jiang et al. 2009).

The factor PC2 comprised 17.81% of the total variance. This factor is weighted by SO_4, NO_3, NH_4, Na, Mg, Ca, Cl and Fl representing the impacts of road dust. The secondary particles (SO_4+ NO_3 + NH_4), fractions of secondary particles have potential sources of crustal component, secondary particles and combustion contribution (DPCC Report, 2016, Sharma et al. 2014). Na, Mg, Ca, Cl and Fl are the most common trace elements readily available in the road dust. Gases to particle conversation substances are mostly present in the industrial road dust.

The factor PC3 comprised 12.80% of the total variance. This factor is weighted by EC, OC, Cu, Zn, PHE and ANT representing the impacts of vehicular emission due to traffic movement. Pollution as Zn is considered as the marker of vehicular pollution as Zn is emitted from lubricant oil, brake lining and tyres (Zhou et al. 2004). The ratio of Cu and Zn varied from 0.051 to 0.172 respectively during the study period also strongly suggesting vehicular sources (Cadle et al. 1999).

The factor PC4 comprised 5.35% of the total variance. This factor is weighted by K and As representing the impacts of biomass burning. Average values of K/EC (0.28) suggest the influences of biomass burning (Sharma et al. 2014). In the present study the ratio of K/EC varied from 0.2-0.39 indicating biomass burning. Davy et al. 2012 reported that As is present in the fine particulate matter and associated with biomass burning. The stationary combustion sources included small and medium scale roadside dhabas as well as commercial and household kitchen activities. Road side dhaba's use various types of fuels for cooking purposes, including LPG gas, coal, kerosene and sometimes wood and dry leaves also. As and its compounds are extensively used for wood preservations, manufacturing of glass, electronic items and medical application. Various report suggested that As emissions were derived from stationary biomass combustion sources also.

The factor PC5 comprised 5.35% of the total variance. This factor is weighted by Fe and Pb representing the impacts of Iron and steel foundries. Though Pb was phased out in India in 1999, it is still Pb is present in the road dust and widely used for multiple industrial applications like electroplating, surface coating, dye, paint etc. Airborne metals found in concentrations greater than 1 ug/m^3 include Fe, Pb, Zn, and Mg are present in sizeable quantities in emission particulates from coal-fired power plants, iron and steel foundries, brass/ bronze refineries etc (Robert E. Lee Jr. & Darryl J. von Lehmden et al 2012).

The factor PC6 comprised 4.93% of the total variance. This factor is weighted by Mg and Mn representing the impacts of pigment/ dye/ painting industry. Metals like Mn, Cu, Pb, Mg, etc. are having maximum uses in textile, tannery, pigment, painting and dye industries. These metals are directly polluting the ground water and soil. However, re-suspension of dust is the major cause to present the metals in the airborne particles (Gurjar et al. 2004).

The factor PC7 comprised 4.38% of the total variance. This factor is weighted by Cd and Co representing the impacts of smoke of vehicular exhaust and cigarette. Co powder is widely used for formulation of brass and steel alloys in Naraina Industrial Area, phase II. Smokes are directly/indirectly transferred to humans. Cd is generally deposited into waters or soils during monsoon season, then eventually transferred to plants and animals and finally enter the human body through the food chain. Gurjar et al. 2004 reported that the presence of Cd varied from 0.004 to 0.01ng/m^3 at the rural atmospheric environments of Northern India might be due to smoke emissions from wood and coal combustion.

The factor PC8 comprised 4.34% of the total variance. This factor is weighted by Cr representing the impacts of miscellaneous sources. Cr is widely used for multiple purposes like electroplating, dye, paint etc. The European Commission (2000) reported that 18% of airborne Cd emissions were from road transport, and 30 to 70 % were from stationary combustion sources. The residues of stationary combustion at the site may have been suspended/ re-suspended with windblown dust during the study period. The high concentrations of Co, Cr, Cu, Mn and Ni may derive in part from industrial road dust in Delhi (Rajaram et al. 2014).

4.8.1 Time Series Analysis for airborne selected parameters in Delhi

A time series analysis for airborne selected parameters like carbonaceous aerosols (OC, EC), heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn), cation and anion (Na, K, Ca, Mg, NH_4, F, Cl, SO_4 and NO_3) and particulate polycyclic aromatic hydrocarbon (PHE, ANT, FLR, PYR, BaA, CHR, BbF, BkF, BaP, DahA, BghiP and IcdP) concentrations at Naraina, urbanized mixed use area of Delhi was carried out through Principle Component Analysis-Multiple Linear Regression (PCR-MLR), described in the methodology (3.5.1). PCA-MLR is one of the important receptor model and widely used for air pollutants source identification and quantification. Monthly source contributions of airborne above mentioned selected parameters is presented in **Figure 4.24**.

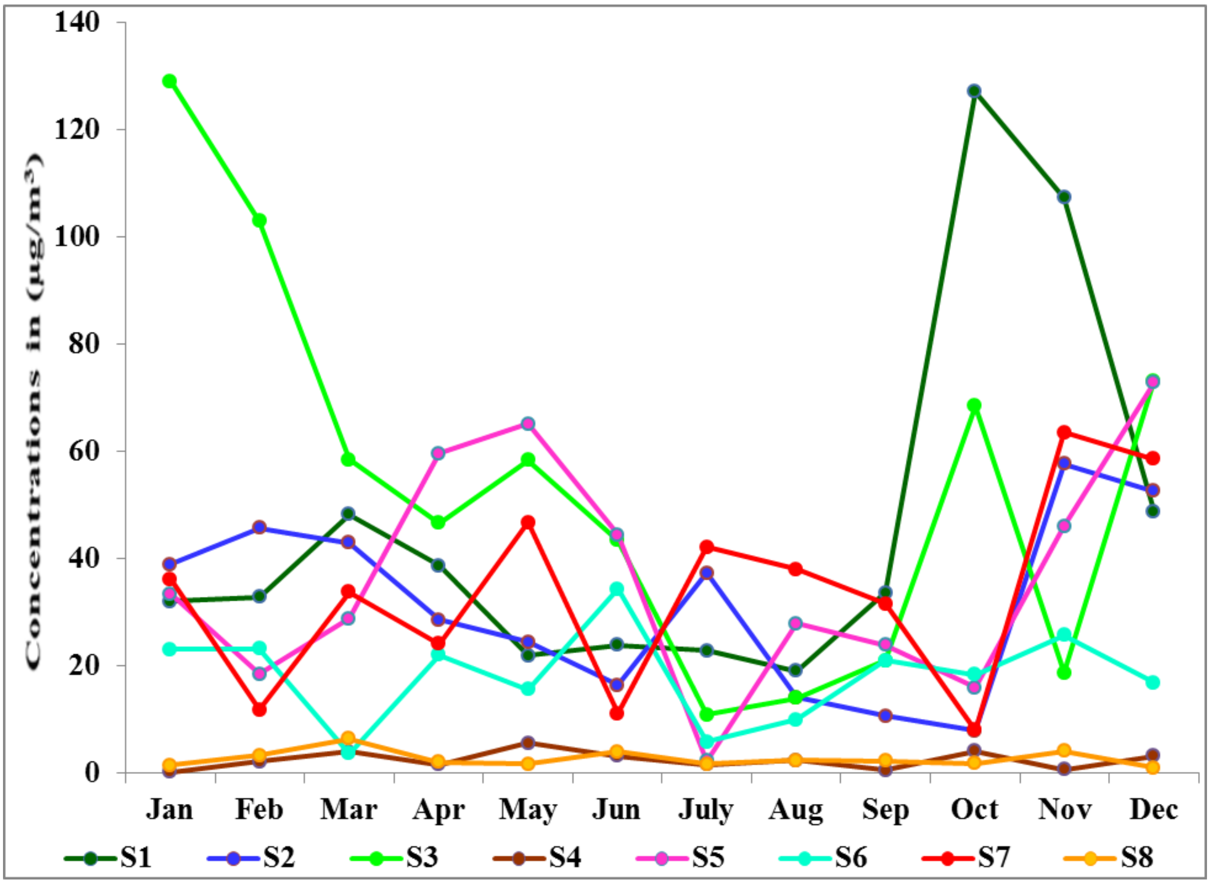


Figure 4.24 Monthly source contributions of selected airborne parameters in Delhi (2011)

PCA-MLR explained the eight major sources which has contribution to increase the concentrations of particulate matter at Naraina mixed use area of Delhi. The contribution of sources are like Industrial emission was (30%), vehicular emission (25%), road dust (16%), iron and steel foundries (14%), pigment industry (6%), biomass burning (5%), smoke (4%) and miscellaneous sources (2%).

Positive matrix factorization (PMF) was carried out at urban location in Delhi to analysis the contribution of particular mass (PM_{10}) composition for the year 2010. Sharma et al. 2014 reported that the contribution of soil dust (20.7%), vehicle emissions (17%), secondary aerosols (21.7%), fossil fuel combustion (17.4%) and biomass burning (14.3%) to PM_{10} mass concentration. The contribution of road dust at both the location is same. Biomass contribution was high at the urban location as compared to mixed use area of Delhi. The emission from vehicular though comparable but still higher side at urbanized mixed use area of Delhi. Industrial emissions were not included in the PMF factorization of urban location of Delhi.

The overall baseline emission inventory for the Delhi city is developed for the period November 2013 to June 2014 was reported by Sharma et al 2016 at residential/industrial/commercial location of Delhi. During the winter season the composition of particulate matter (PM_{10}) were include: secondary particles (25-30%), vehicles (20-25%), biomass burning (17–26%), MSW burning (9-8%) and to a lesser extent soil and road dust. During the summer season the composition of particulate matter (PM_{10}) were include: coal and fly-ash (37-26%), soil and road dust (26–27%), secondary particles (10-15%), biomass burning (7-12%), vehicles (6–9%) and MSW burning (8–7%). It was also informed that the compositions of particulate matter (PM_{10} and $PM_{2.5}$) are generally the same and average vehicle contribution to $PM_{2.5}$ at about 28%. The emission inventory for the Delhi city varies from year to year and even from season to season also. The selection of the sampling location has also great importance to understand the particular mass composition, source apportionment in Delhi. It is difficult to make compare the concentrations among the sites, as these were not measured simultaneously, or even sometimes not in the same seasons.

4.9 Mass Closure Analysis of particulate matter

Mass closure model has been adopted here to characterize the measured particle mass of PM_{10} and $PM_{2.5}$ using the conversion factors reported by Harrison et al. 2003 and 2008.

4.9.1 Mass Closure Analysis of PM_{10}

Mass closure analysis (MCA) was carried out for particulate matter (PM_{10}). The summary statistics of measured components of particulate matter (PM_{10}) is summarized in **Table 4.13**.

Table 4.13 The summary statistics measured components of particulate matter (PM_{10})

Parameters	N	AM	GM	Median	Min	Max	SD
PM_{10}	48	280.72	247.21	286.38	88.96	502.49	129.73
OM	48	130.24	112.03	123.49	35.20	254.50	67.47
EC	48	25.83	22.11	24.37	6.53	51.13	13.36
SO_4^{-2}	48	18.76	17.92	18.35	8.73	31.89	5.48
NO_3^-	48	15.80	15.26	16.38	8.89	23.50	3.99
Cl^-	48	36.89	36.0	37.21	20.98	51.61	7.85
F^-	48	0.43	0.41	0.45	0.21	0.67	0.13
∑anions	49	71.88	69.96	71.59	41.08	101.81	16.18
NH_4^+	48	9.07	8.21	9.03	2.78	17.39	3.89
K^+	48	3.07	2.86	3.14	1.09	5.22	1.08
Na^+	48	3.63	3.52	3.71	2.34	6.16	0.88
Mg^{++}	48	3.02	2.88	2.75	1.64	5.53	0.97
Ca^{++}	48	7.58	7.12	7.25	3.37	15.04	2.71
∑Cations	49	26.36	25.24	25.20	13.74	45.66	7.74
As	48	0.00	0.00	0.00	0.00	0.01	0.001
Cd	48	0.03	0.02	0.02	0.01	0.08	0.02
Co	48	0.00	0.002	0.00	0.00	0.01	0.002
Cr	48	0.17	0.15	0.15	0.06	0.33	0.08
Cu	48	0.18	0.13	0.18	0.02	0.41	0.12
Fe	48	4.77	4.42	4.52	1.90	9.07	1.85
Mn	48	0.26	0.22	0.26	0.07	0.54	0.14
Ni	48	0.17	0.11	0.13	0.01	0.53	0.14
Pb	48	0.35	0.27	0.35	0.07	0.73	0.20
Zn	48	1.81	1.43	1.90	0.24	3.90	1.02

The reported values were obtained after subtracting blank values from the measured values. The concentrations show log-normal distributions. Therefore, median or geometric mean concentrations reflect more exactly the composition of aerosol since they are not affected by the highest concentrations of components. However, arithmetic means were used for both the comparison of data and all calculations. The results indicate that all species in aerosols varied in two orders of magnitude. The highest degree of variation was observed for EC and OC as both have pre-defined air pollution sources. It was observed from **Table 4.13** that sulphate was the basic component and the mass of sulphate on average was approximately 10% of water soluble inorganic aerosol mass. Therefore, sulphate makes up the largest portion of the analyzed aerosol mass. The anion and cation average concentrations followed the pattern of $Cl^- > SO_4^{-2} > NO_3^- > F^-$ and $NH_4^+ > Ca^{++} > Na^+ > Mg^{2+} > K^+$. The maximum concentrations of SO_4^{-2} and NO_3^- were observed in the month of November and December, 2011.

In general, significant differences are observed from one month to another month. Ions of Ca^{++}, Na^+, K^+, Mg^{++} had highest concentrations during the post-monsoon season due to the wind-blown dust. On a regional scale, Ca^{++}, and K^+ originate from crustal material; only in very remote oceanic sites, a marine contribution to the atmospheric concentrations of these ions were not considered due to far distance from sea for Delhi state, the capital of India. During the winter season, the selected sampling location was covered most of the time with fog. That leaded also to high crustal contribution during winter season (December, January, February and March) in the year 2011. NH_4^+, Ca^{++}, Na^+, Mg^{++}, K^+ were the major source for crustal elements. The observed ions concentrations in aerosols are in general affected by both dust and sea salt particles in the atmosphere. The contributions of the selected halide ions concentration increases from vehicular activities during the winter season. The monthly variation of NH_4^+ ion was in phase with the fertilizing activities which was highest in post-monsoon and pre-monsoon seasons. The highest concentrations of SO_4^{-2} and NO_3^- were observed during November and December and March and April in the year 2011. Other than the elemental concentrations, particulate matter (PM) loading showed episodic behavior, throughout the whole sampling period of twelve months in the year 2011. Episodic increases on dust loading were more frequent in pre-monsoon and post-monsoon months. Initially it was difficult to express the observation with the existing sources as episode concentrations were much higher than the average concentrations. Considering the sampling area which is a clearing of 1 km 2 within a pine forest, it is reasonable to have substantial amounts of organic acids. Also contributions of organic anions for up to 35% of anions in the aerosols have been reported elsewhere (Keene and Galloway, 1984; Guiang *et al.,* 1984; Keene *et al.,* 1983).

The concentration of species in aerosols depends on various factors such as chemical and physical transformations, the source strengths and various meteorological factors. Because of this, many species measured in aerosols show significant changes from one season to another season. **Table 4.14** lists the equivalent concentration ratios for cation to anion on a monthly basis.

Table 4.14 Monthly average concentration ratio of ∑(cation)/(anion)

Month	**∑(cation)/(anion)**
Jan	0.346
Feb	0.351
Mar	0.379
Apr	0.342
May	0.398
Jun	0.352
Jul	0.426
Aug	0.338
Sep	0.251
Oct	0.385
Nov	0.396
Dec	0.415

In general, the ratio was higher than the total average in post-monsoon indicating strong anion deficiency in these months as compared to others. These missing cations can be explained by organic base or salt. The equivalent ratios of total cations to anions were calculated to observe the major ionic species were accounted or not. If they are all accounted for the ratio would be equal to 1. The range of equivalent ratio of total cations to anions varied from 0.25 to 0.45 indicating that a few major cation species had been excluded.

A multiple linear regression was applied to SO_4^{-2} and NO_3^- separately using $[Ca^{2+}]$, $[Mg^{2+}]$, $[NH_4^+]$, $[K^+]$ and $[Na^+]$ as independent variables in order to understand the main chemical forms of SO_4^{-2} and NO_3^- in aerosols. The r^2 values, % of r^2 values and partial correlation coefficients is shown in **Table 4.15**.

Table 4.15 Multiple linear regressions

Sulphate ion $[SO_4^-] = a + a1\,[Ca^{2+}] + a2\,[Mg^{2+}] + a3\,[NH_4^+] + a4\,[K^+] + a5\,[Na^+]$

a	2.40	r^2	0.829
a 1	-0.295	% of r^2 explained by Ca^{2+}	28.90
a 2	0.829	% of r^2 explained by Mg^{2+}	22.10
a 3	1.121	% of r^2 explained by NH_4^+	36.98
a 4	1.267	% of r^2 explained by K^+	19.12
a 5	0.538	% of r^2 explained by Na^+	20.40

Nitrate ion $[NO_3^-] = b + b1\,[Ca^{2+}] + b2\,[Mg^{2+}] + b3\,[NH_4^+] + b4\,[K^+] + a5\,[Na^+]$

b	5.031	r^2	0.734
b1	0.213	% of r^2 explained by Ca^{2+}	33.12
b 2	0.351	% of r^2 explained by Mg^{2+}	21.60
b 3	0.668	% of r^2 explained by NH_4^+	40.27
b 4	0.431	% of r^2 explained by K^+	13.92
b 5	0.789	% of r^2 explained by Na^+	25.92

Relatively high residuals (a and b are positive values) and high correlation coefficients (r values) suggest that the observed concentrations of SO_4^{-2} and NO_3^- in the aerosols still match with the presence of neutralizing cations and also low r^2 values give the explained part of the dependent variables with the independent variables. Partial correlation coefficients were used to calculate % of the explained part with cation.

All the statistical parameters are calculated by using SPSS (Version: 13). Here the standard deviation of cation, the correlation coefficient between cation and anion, the partial correlation coefficient of cation, and the standard deviation of anion are calculated as per literature available. This is an indication of the presence of SO_4^{-2} and NO_3^- in the form of H_2SO_4 and HNO_3. The results also suggested that approximately 20% of SO_4^{-2} and 30% of NO_3^- concentrations were associated with H^+ ion, i,e. on the other side only 80% of the SO_4^{-2} and 70% of the NO_3^- could be explained by these cations approximately. Out of these explained parts, approximately 37% of SO_4^{-2} and 40% of NO_3^- were neutralized by airborne NH_4^+, major source was concentrations of atmospheric ammonia gas. Approximately 29% of SO_4^{-2} and 33% of NO_3^- are neutralized by airborne Ca^{2+}, major source was mineral dust. Approximately 22% of SO_4^{-2} and 21% of NO_3^- are neutralized by airborne Mg^{2+}, major source was mineral dust. Approximately 40% of SO_4^{-2} and 40% of NO_3^- are neutralized by airborne K^{2+} and Na^+, major source was also mineral dust. However, the total explained part is not significant. This is probably because of the biogenic emissions from the forest and dense agriculture area in and around the Delhi city. A little bit organics combine the aerosol particles in form of a thin film and avoid neutralization of H_2SO_4 and HNO_3.

MCA Part-2 (Chemical Mass Closure for PM_{10})

After chemical analysis through all possible standard method, these chemical components of particulate matter (PM_{10}) were grouped into nine classes as follows:

1) Organic matter (OM)
2) Elemental carbon (EC)
3) Non-seasalt sulphate (nss-SO_4^{2-})
4) Nitrate (NO_3^-)
5) Ammonium (NH_4^+)
6) Sea-salt
7) Mineral dust
8) Non-dust elements
9) Unaccounted mass

To account for associated oxygen and hydrogen mass, OM was obtained by multiplying the measured concentration of organic carbon (OC) by a conversion factor, which is the ratio of the average molecular mass to the carbon mass for the organic aerosol. In order to be consistent in our comparative study, a single 1.4 conversion factor was applied.

The non-sea salt sulphate (nss SO_4^{2-}) was calculated from the measured SO_4^{2-} minus the sea-salt fraction of SO_4^{2-} (ss $SO_4^{2-} = 0.252 \times Na^+$). Sea-salt concentrations were calculated from soluble sodium concentrations, assuming that sea-salt mass is equal to $3.252 \times Na^+$. Mineral dust was considered as the sum of Al_2O_3, SiO_2, CO_3^{2-}, Ca, Fe, K, Mg, Mn, Ti and P, where Al_2O_3, SiO_2, CO_3^{2-}, were indirectly determined by using empirical equations ($Al_2O_3 = 1.89 \times Al$; $SiO_2 = 3 \times Al_2O_3$; $CO_3^{2-} = 1.5 \times Ca$). Non-dust elements correspond to the sum of the common measured trace elements (i.e., Cu, Ni, Pb, V, Zn) other than geological ones. However, only Fe concentrations were determined it has been considered equivalently to aluminum.

The unaccounted mass was obtained by calculating the difference between measured PM mass concentration and the reconstructed mass (i.e., the sum of aerosol component concentrations). This fraction could be attributed to analytical errors, as well as to the estimation of mineral dust. Moreover, a part of the unaccounted PM mass was likely to be described to particle bound water, especially if mass concentrations were determined at relative humidity (RH).The water content in particulate matter (PM) samples will vary for different samples and measurement sites, depending on the particle composition, ambient relative humidity (RH) and temperature. It was estimated that unaccounted PM mass varied from 20% to 35% of PM mass. Indeed, some of the inorganic species (e.g. ammonium nitrate and ammonium sulphate) present in the ambient aerosol are mostly hygroscopic by nature and exhibit the property of deliquescence in humid air. They could also retain water if RH was increased which thus affects the physical and chemical properties of aerosol particles.

4.9.1.1 Chemical composition of PM_{10} and its mass balance

During the study period (January to December 2011), filter papers were used to collect and analyze the concentrations of particulate matter (PM). The gravimetric method was carried out to determine (PM) concentrations. Secondary analysis of PM was carried out for carbonaceous fractions (organic matter and elemental carbon), inorganic aerosol, sea salt, mineral dust etc. The description of each selected measuring components is given below.

4.9.1.1.1 Carbonaceous fraction

On an annual basis, organic matter ((OM= 1.4*Organic Carbon OC)) mean concentration accounted for 130 μgm^{-3} (41% of PM_{10} mass) in the year 2011 as a whole. OM constituted the most important fraction of particulate matter (PM) in Delhi and this contribution was comparable to the highest values reported for urban sites in Delhi, India. EC mean concentration ranged between 6.53 to 51.13$\mu g/m^3$ respectively. The results of EC were also comparable with reported value of other Indian urban sites. However, EC presented homogeneous concentration compared to OC. This could be due to the existence of various sources of OC, including direct particle emissions and atmospheric oxidation of reactive organic gases; whereas EC is emitted from primary combustion sources. Significant seasonal variations were observed for both the carbonaceous fractions (OC and EC).

4.9.1.1.2 Seasonal variation OC-to-EC ratios

OC-to-EC ratio has been used in several studies as a useful tool that provides information on the origins of the carbonaceous fraction and formation of secondary organic carbon. The OC-to-EC ratios are strongly source dependent and quite variable for the different sources. Hence, the variations of OC-to-EC ratio may be used to determine changes in emission sources, aging evolution and the presence of secondary organic aerosol. But in the present study OC-to-EC ratio was almost remained constant in the year 2011.

4.9.1.1.3 Inorganic aerosol (nss-SO_4^{2-}, NO_3^- and NH_4^+)

On an annual basis, the secondary inorganic fraction accounted annually for 43.63 μg m^{-3} which is the 15% of PM_{10}. These are the prevailing anion, contributing of the PM_{10} mass. These results were consistent with the high levels of SO_4^{2-} measured. Therefore the relative contribution of the nss-SO_4^{2-} to PM_{10} mass was accounting for 7.24% on mainly during the pre-monsoon period while in winter it was only 6.29% of PM_{10}. The analysis of the seasonal variation of the secondary inorganic fraction revealed that the nss-SO_4^{2-}, relative contribution to the PM_{10} mass was, as expected, higher during pre-monsoon at urbanized mixed use area of Delhi, India. The annual as well as season wise contributions of inorganic aerosols are shown in **Figures 4.25 to 4.29** respectively.

The maximum concentrations of sulphate during pre-monsoon season might be due to several possibilities.
(a) An enhanced photochemical activity, which increase the oxidation of SO_4^{2-} and its conversion rate to sulphate,
(b) The stagnation of air masses over the geological basin.

Conversely, nitrate aerosols are more sensitive to temperature and the shift in equilibrium from gas-phase ammonia and nitric acid to particulate phase ammonium nitrate is favored at lower temperatures. In the present study, the relative contribution of nitrate to total PM_{10} mass was peaked mainly during the winter period. Monsoon season the contribution of nitrate to total PM_{10} mass was 5.7% whereas during winter season, the contribution of nitrate to total PM_{10} mass was 11.25%. The larger availability of NOx gaseous precursor released from combustion during the winter season could play an important role for contribution of maximum nitrate during winter season.

4.9.1.1.4 Sea-salt

Sea-salt contribution to aerosol mass is highly dependent on the distance of the sampling site from the sea location. But in the present case, sea is far away from the location of sea. Therefore sea-salt was not the contributor to the coarse fraction. In the present study, it was contributed marginally to PM_{10} mass. Annual relative contribution was relatively much lower in Delhi city (ie. 0.01%).

4.9.1.1.5. Mineral dust

Mineral dust present mostly in the coarse mode of particulate matter but it also influences the concentrations of particulate matter (PM). On an annual basis, the relative contribution of dust to PM_{10} mass ranged from 10 to 36%. The contribution of mineral dust to PM_{10} followed the following order: winter (10%), post-monsoon (18%), pre-monsoon (25%), monsoon (36%), and which was one of the major predominant constituent of PM_{10}. Moreover, mineral dust concentration exhibited a marginal seasonal variability at the selected sampling location of Delhi. The annual and season wise contributions of mineral dust in PM_{10} are shown in **Figures 4.25 to 4.29** respectively. Crustal PM contributions might derive from both external and local sources (e.g. road dust re-suspension, construction activities). This means that most of mineral matter was mainly related to nearby sources, e.g. civil construction activities. Likewise, the abundance of dust particles in the city like Delhi was mostly due to mineral matter released from the large renovation and development activities implemented during the long monitoring campaign. These observations highlight the singularity of the study year and the impact of construction activities on the concentrations of ambient particulate matter (PM) over the Delhi city.

Table-4.16 The concentrations of chemical components of PM_{10}

S.No	Chemical Component	Annual	Winter	Pre-monsoon	Monson	Post-monsoon
1	Organic Matter	130.24	165.51	114.11	54.94	196.81
2	Elemental Carbon	9.21	33.34	22.81	10.62	38.16
3	Non-sea salt sulphate	6.35	21.08	17.80	12.39	19.62
4	Nitrate	5.62	18.77	13.89	13.83	15.70
5	Ammonium	3.23	11.42	7.64	6.55	10.28
6	Sea-salt	0.32	1.01	0.88	0.85	0.89
7	Mineral dust	22.22	31.96	65.29	54.62	75.78
8	Non-dust element	0.96	3.51	2.75	0.72	4.02
9	Unaccounted mass	19.64	78.78	50.27	13.03	121.88

The selected chemical components were measured in $\mu g/m^3$

The annual distribution of chemical composition of PM_{10} in Delhi is shown in **Figure 4.25**. The season-wise (winter, pre-monsoon, monsoon and post-monsoon) distribution of chemical composition of PM_{10} in Delhi are shown in **Figures 4.26 to 4.29** respectively.

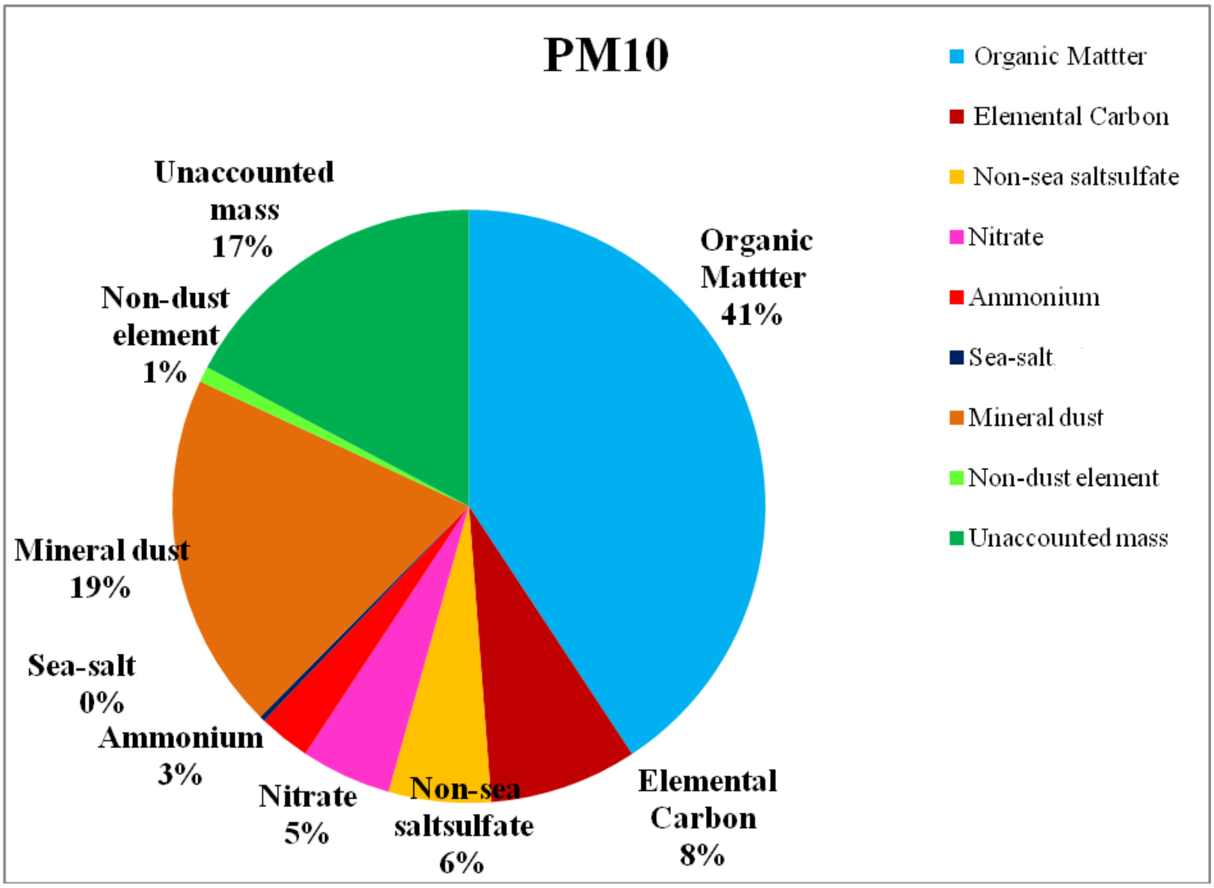


Figure 4.25 The annual distribution of chemical composition of PM_{10} in Delhi

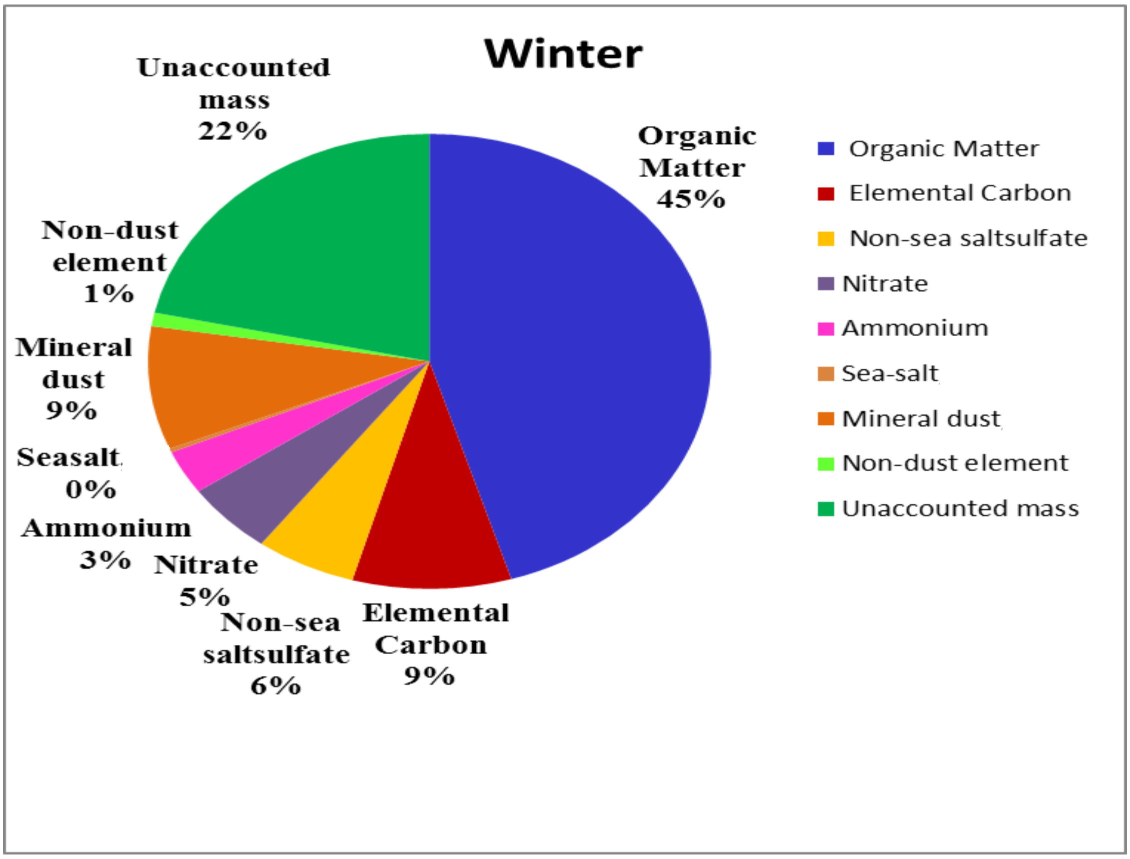


Figure 4.26 The winter season distribution of chemical composition of PM$_{10}$ in Delhi

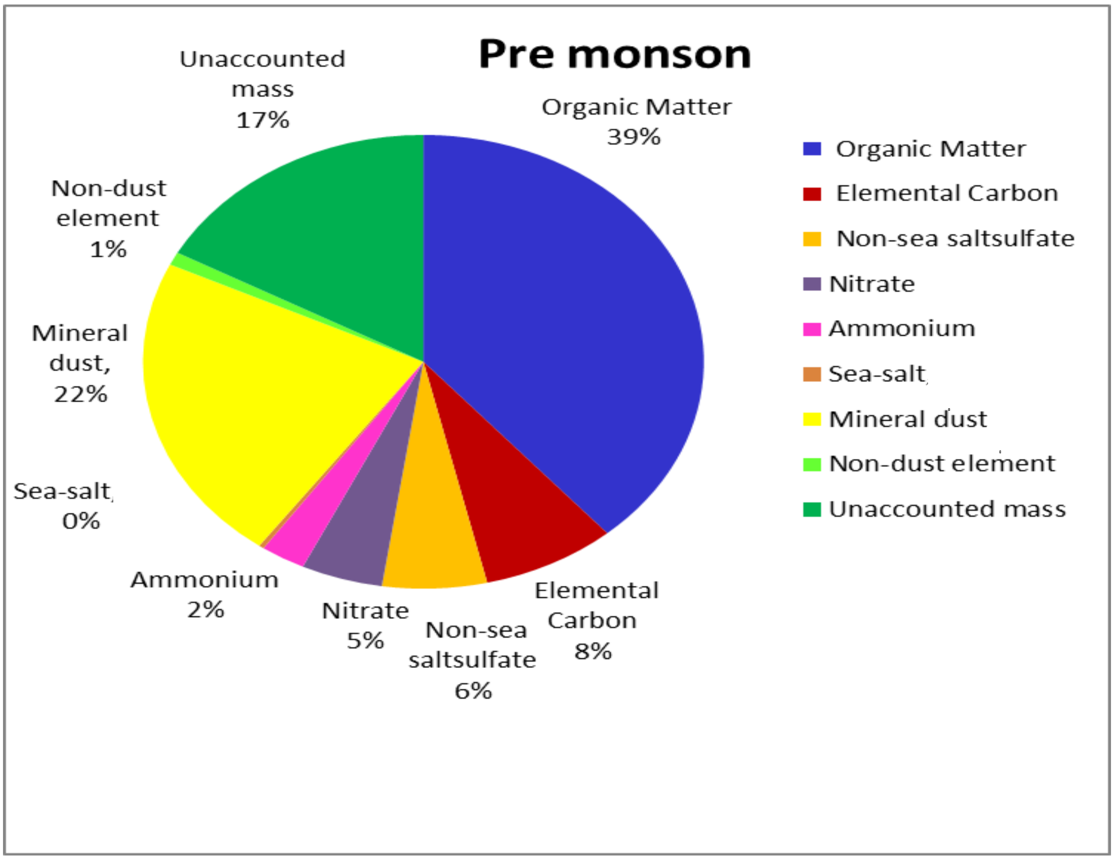


Figure 4.27 The pre-monsoon distribution of chemical composition of PM$_{10}$ in Delhi

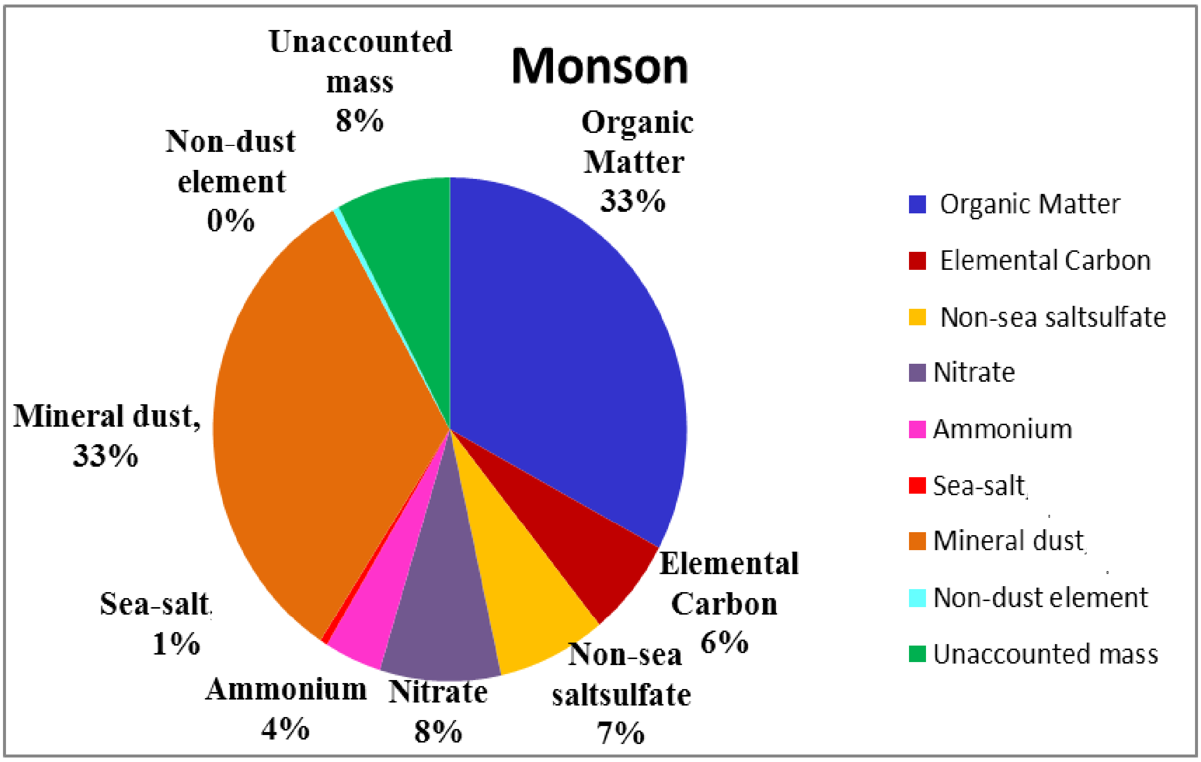


Figure 4.28 The monsoon distribution of chemical composition of PM_{10} in Delhi

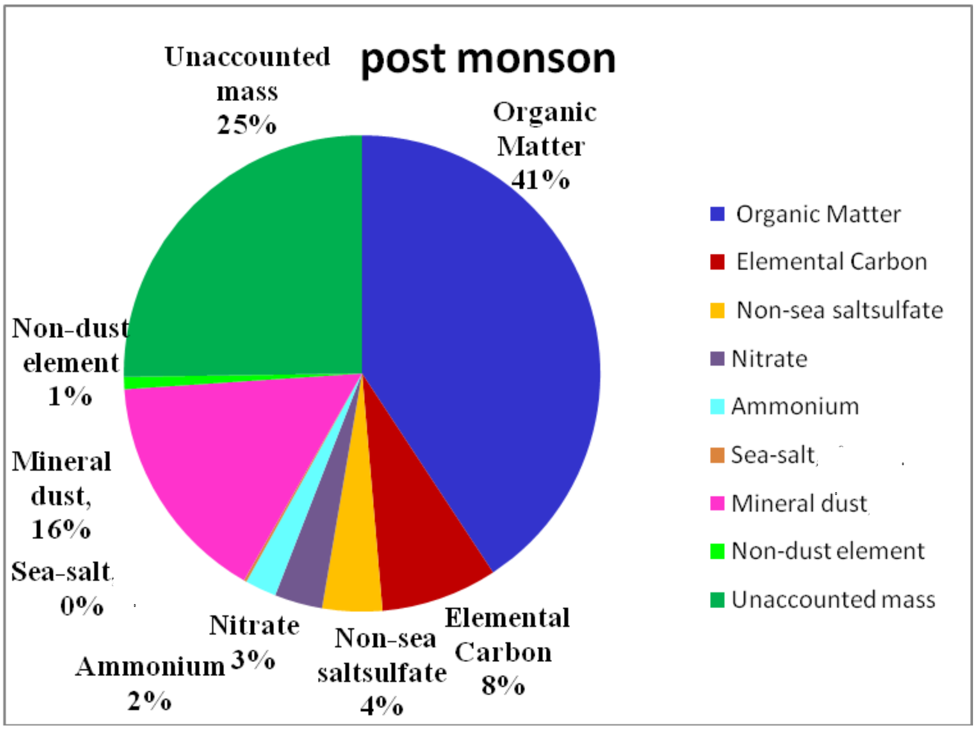


Figure 4.29 The post-monsoon distribution of chemical composition of PM_{10} in Delhi

4.9.2 Mass Closure Analysis of $PM_{2.5}$

The chemical components of $PM_{2.5}$ were grouped into two classes. The annual and season-wise concentrations of organic matter and elemental carbon were presented in **Table 4.16.** Only organic matter and elemental carbon were measured for $PM_{2.5.}$ The other chemical components like non-sea salt sulphate, nitrate, ammonium, sea-salt, mineral dust are considered in unaccounted mass of $PM_{2.5.}$

Table-4.17 Annual and season-wise concentrations of organic matter and elemental carbon in $PM_{2.5}$

Particulate Matter	Annual	Winter	Pre-Monsoon	Monson	Post-Monsoon
$PM_{2.5}$	149	181	147	78	177
Organic Matter	58	72	56	26	76
Elemental Carbon	14	18	12	6	17
Unaccounted Mass	77	90	79	46	84

The selected chemical components were measured in µg/m^3

The annual distribution of chemical composition of $PM_{2.5}$ in Delhi is shown in **Figure 4.30**. The season-wise (winter, pre-monsoon, monsoon and post-monsoon) distribution of chemical composition (organic matter, elemental carbon and unaccounted mass) of $PM_{2.5}$ in Delhi are shown in **Figures 4.31 to 4.34** respectively.

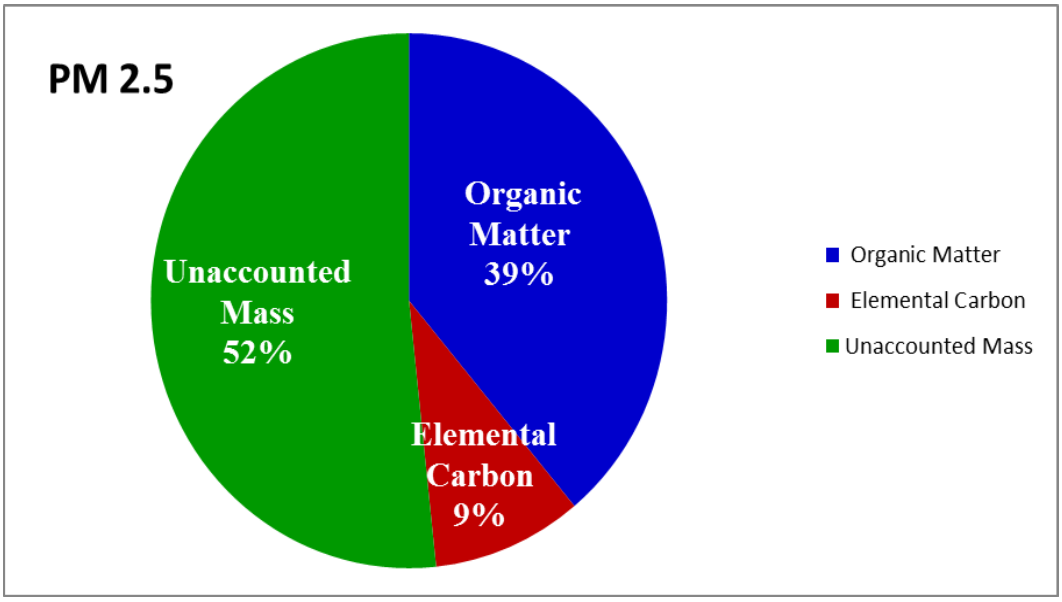


Figure 4.30 The annual distribution of chemical composition of $PM_{2.5}$ in Delhi

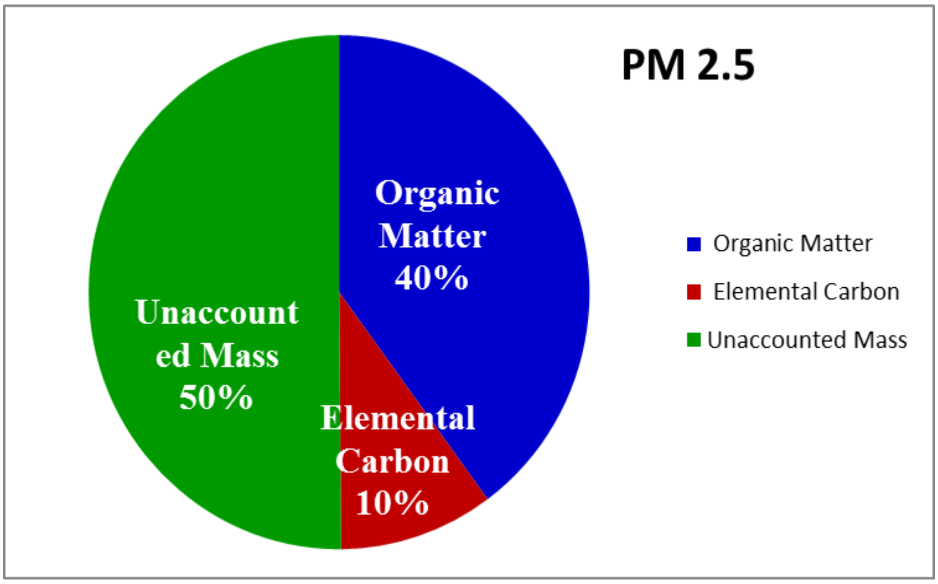


Figure 4.31 The winter season distribution of chemical composition of $PM_{2.5}$ in Delhi

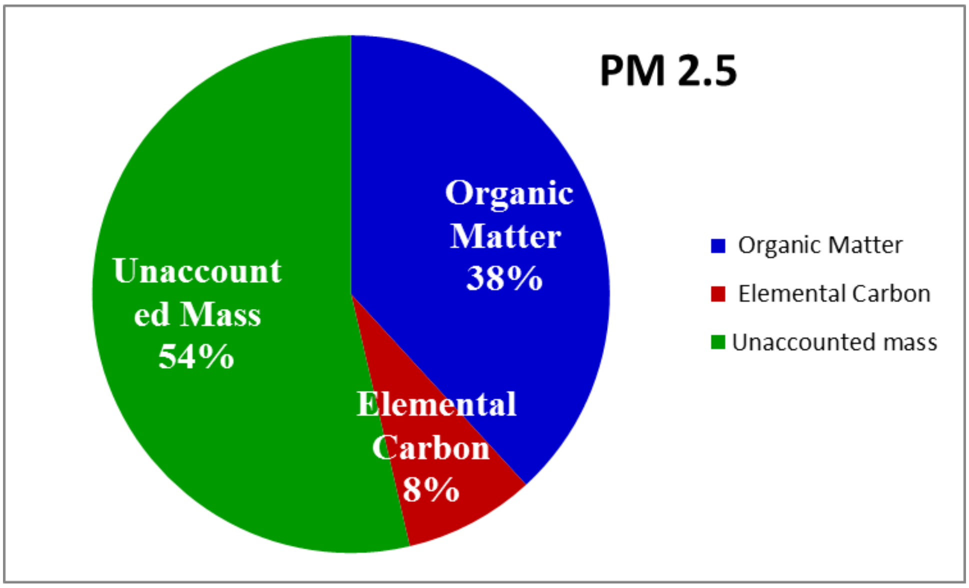


Figure 4.32 The pre-monsoon season distribution of chemical composition of $PM_{2.5}$ in Delhi

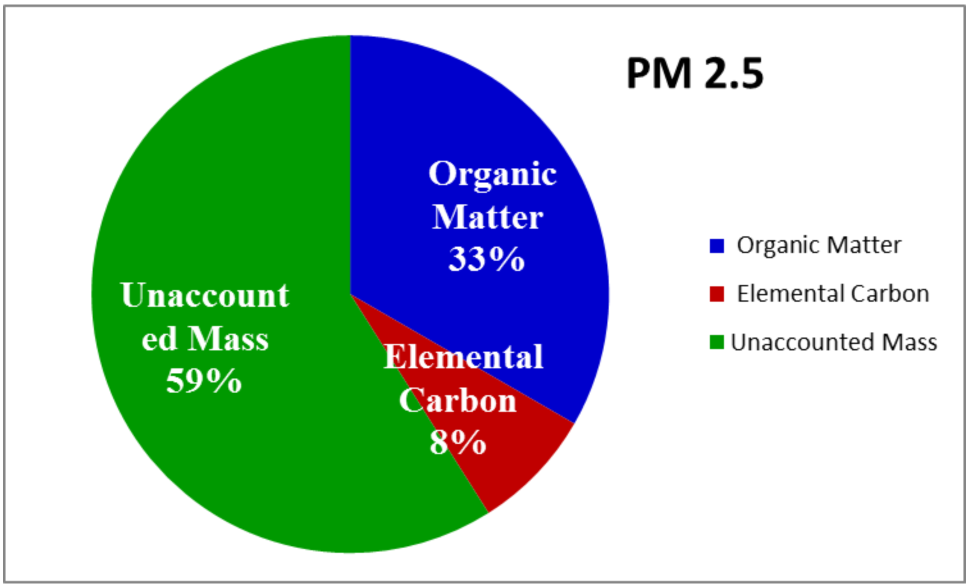


Figure 4.33 The monsoon season distribution of chemical composition of PM$_{2.5}$ in Delhi

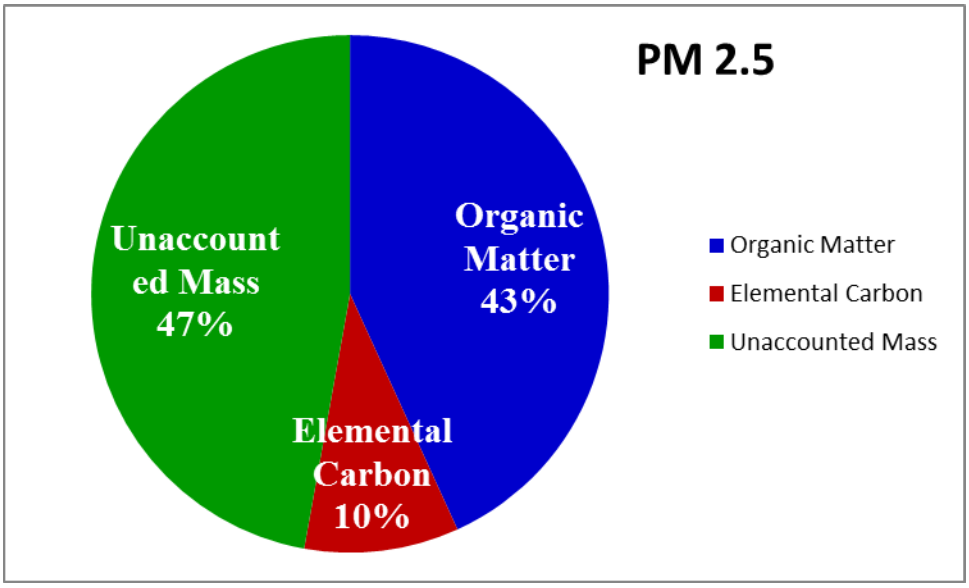


Figure 4.34 The post-monsoon season distribution of chemical composition of PM$_{2.5}$ in Delhi

Chapter-V

CONCLUSION& FUTURE PLAN

Chapter-V

CONCLUSIONAND FUTURE PLAN

The study of trace gases and aerosol in urbanized mixed use area of Delhi indicated that the poor ambient air quality was mostly anthropogenic. The trace gases like SO_2 and NH_3 were within the permissible limit of National Ambient Air Quality Standards (NAAQS) of CPCB (2009). The trace gases like NO_2 sometimes during the post-monsoon and winter season exceeded the permissible limit of NAAQS of CPCB (2009). The concentrations of trace gases (SO_2 and NO_2) in the year 2011 were highest in the month of December, 2011 and lowest in the month of July, 2011. NH_3 did not follow any trend; however the concentration of NH_3 was highest in the month of November, 2011 and lowest in the month of April, 2011. Trace gases ($SO_{2,}$ NO_2 and NH_3) are mostly removed from the ambient air due to wet precipitations. In the monsoon season, the rain is acidified due to trace gases and deposited in land and water environment by wet precipitations. Non-monsoon season inorganic aerosols were formed in the ambient air which increases the concentrations of particulate matter.

The concentrations of particulate matter (PM_{10} and $PM_{2.5}$) both were beyond the permissible limit of National Ambient Air Quality Standards (NAAQS) of CPCB (2009) even during the monsoon season also. During the festive season of Diwali, the concentrations of selected air pollutants were around 8 to 10% higher than the regular ambient pollution concentrations level. The average contribution of total carbonaceous aerosol in PM_{10} and $PM_{2.5}$ were 62% and 50% respectively. The contribution of secondary organic aerosol (SOC) in $PM_{2.5}$ was 27% of $PM_{2.5}$ mass during the study period (2011) at Naraina mixed use area of Delhi. The contribution of cation and anion in PM_{10} concentrations was approximately 20%. Airborne heavy metals and particulate polycyclic aromatic hydrocarbons contribution in PM_{10} were 3%, and 1% respectively. 14% of total aerosol mass of PM_{10} was not identified in this study. This might be due to bioaerosols contamination and other metal which were not included in the proposed study objectives. Meteorological parameters (wind speed, wind direction, temperature and relative humidity) played the vital role to increase the ambient concentrations of PM_{10} and $PM_{2.5}$. The meteorological calm condition in the post-monsoon season (54%) was more as compared to winter season (51%), this could be the one of the reason to receive higher concentrations of air pollutants in the post-monsoon season as compared to winter season. In the monsoon season, calm condition was lowest i.e., only 26% indicated the dispersion of air pollutants was maximum. So, the receptor end (study area) concentration of air pollutants was lowest. Moreover the pollutants are removed during the monsoon season from atmospheric environment due to wet deposition also. The high emissions of PM_{10} and $PM_{2.5}$ in the ambient air were attributed due to celebration of holy festival Diwali with burning of fire crackers and lightning and stubble burning during post-monsoon season and inverse meteorological condition.

The seasonal/monthly concentrations of trace gases ($SO_{2,}$ NO_2 and NH_3) and particulate matter (PM_{10} and $PM_{2.5}$) were followed the seasonal trend. The seasonal trend of trace gases and particulate matter were followed the order of post-monsoon> winter> pre-monsoon > monsoon. The selected chemical components of particulate matter like carbonaceous aerosols (OC, EC), heavy metals (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn), inorganic aerosols (Na, K, Ca, Mg, NH_4, F, Cl, SO_4 and NO_3) and particulate PAHs (PHE, ANT, FLA, PYR, BaA, BbF, BkF, BaP, DahA, BghiP, IcdP) were also followed mostly the same pattern. PCA-MLR explained the eight major sources which has contribution to increase the concentrations of particulate matter at Naraina mixed use area of Delhi in the year 2011. The contribution of sources are like Industrial emission was (30%), vehicular emission (25%), road dust (16%), iron and steel foundries (14%), pigment industry (6%), biomass burning (5%), smoke (4%) and miscellaneous sources (2%).

Mass closure analysis (MCA) was carried out for both PM_{10} and $PM_{2.5}$. The chemical components of PM_{10} were grouped into nine classes. The annual distributions of chemical compositions in percentage are of organic matter (41%), elemental carbon (8%), non-sea salt sulphate (6%), nitrate (5%), ammonium (3%), sea-salt (0%), mineral dust (19%), non-dust elements (1%) and unaccounted mass (17%). The chemical components of $PM_{2.5}$ were grouped into two classes. Only organic matter and elemental carbon were measured for $PM_{2.5}$. The other chemical components like non-sea salt, sulphate, nitrate, ammonium, sea-salt, mineral dust are considered in unaccounted mass of $PM_{2.5}$. The annual distributions of chemical compositions in percentage are of: organic matter (39%), elemental carbon (9%) and unaccounted mass (52%).

Biomass combustion had the significant contribution to increase the concentrations of particle matter in the study period (2011), especially during the post-monsoon and winter season. The regular basis biomass burning (wood, coal, dry leaves, kerosene, LPG, waste papers) at road side area during winter season were contributed significant amount of organic matter in the ambient air. A detailed inventory is required to understand the emission of trace gases and particulate matter due to biomass burning. Accordingly, technology may be adopted for reduction of emission of air pollutants due to biomass burning. The celebrations of Diwali during post monsoon season had significant impact to increase the concentrations of particulate matter and toxic trace gases in the ambient air. Public awareness is necessary to understand that lighting through firecrackers, release the toxic trace gases and particulate matters which are harmful to all living beings. The proper maintenance of roads and plantations of dust capturing plants will minimize the contribution of air borne re-suspension of road dust. Plants besides producing aesthetic sense, they also help in maintenance of cleaner air in the surrounding environments.

The major contribution of particulate matter was from industrial emission, vehicular emission and re-suspension of road dust. The emission control of air pollutants from each industry will reduce drastically the contribution of trace gases, particulate matter and its associated chemical compounds in the ambient air. Therefore it is necessary to pay more attention to emission control at the source itself.

FUTURE PLAN

Based on the investigations carried out on trace gases (SO_2, NO_2 and NH_3) and particulate matter (PM_{10} and $PM_{2.5}$), the following are the areas recommended for further study.

1. Investigations of trace gases (SO_2, NO_2 and NH_3) and particulate matter (PM_{10} and $PM_{2.5}$) in the indoor environment and its comparison with outdoor environment.
2. Continuous monitoring the other trace gases like gaseous PAHs, carbonyls and ultrafine particular matter (PM_1) in both indoor and outdoor environment and its comparison.
3. Study on various emission reduction technology for trace gases and particulate matter.
4. Source profile identification of the pollutants.
5. Study on emission reduction capacity of dust capturing plant, so accordingly the dust capturing plant may be selected to control the air pollution at source.

REFERENCES

References

Adams P.J., Seinfeld J. H., Koch D. M. "Global concentration of tropospheric sulfate, nitrate and ammonium aerosol simulated in a general circulation model." Journal of Geophysical Research, 104 (1999), 13791–13823.

Agrawal M., Singh B., Rajput M., Marshall F., Bell J. "Effect of air pollution on peri-urban agriculture: a case study." Environmental Pollution 126(2003),323-329.

Alkurdi F., Karabet F., Dimashki M. "Characterization and concentrations of polycyclic aromatic hydrocarbons in emissions from different heating systems in Damascus, Syria." Environmental Science and Pollution Research, 21(2014), 5747-5759.

Araya R.T., Flocchini R., Segura M. R. GE., Guzmán M. A. L. "Carbonaceous Aerosols in Fine Particulate Matter of Santiago Metropolitan Area, Chile." The Scientific World Journal 2014(2014), Article ID 794590, http://dx.doi.org/10.1155/2014/794590.

Battalwar D.G., Yenkie M.K.N., Meshram S.U., Puri P.J. "Studies on presence of PAHs in ambient air of Nagpur City (India)." Rasayan Journal of Chemistry 5(2012), 343-350.

Begum B.A., Hossain A., Nahar N., Markwitz A., Hopke P.K. "Organic and Black Carbon in $PM_{2.5}$ at an Urban Site at Dhaka, Bangladesh." Aerosol and Air Quality Research, 12 (2012), 1062–1072.

Begum B.A., Hossain A., Saroar G., Biswas S.K., Nasiruddin Md., Nahar N., Chowdury Z., Hopke P.K. "Sources of carbonaceous materials in the airborne particulate matter of Dhaka." Asian Journal of Atmospheric Environment, 5-4 (2011), 237-246.

Behera S. N. and Sharma M. "Spatial and seasonal variations of atmospheric particulate carbon fractions and identification of secondary sources at urban sites in North India." Environmental Science and Pollution Research, 22(2015), 13464–13476.

Bhattacharya T., Chakraborty S., Tuteja D., Patel M. "Zinc and chromium load in road dust, suspended particulate matter and foliar dust deposits of Anand City, Gujarat." Open Journal of Metal, 3 (2013), 42-50.

Bisht D.S., Dumka U.C., Kaskaoutis D.G., Pipal A.S., Srivastava A.K., Soni V.K., Attri S.D., Sateesh M., Tiwari S. "Carbonaceous aerosols over Delhi urban environment: temporal evolution, source apportionment and radiative forcing." Science of the Total Environment, 521–522: (2015), 431– 445.

Biswas J., Upadhyay E., Nayak M., Yadav A.K. "An Analysis of Ambient Air Quality Conditions over Delhi, India from 2004 to 2009." Atmospheric and Climate Sciences, 1 (2011), 214-224.

Bostrom C.E., Gerde P., Hanberg A., Jerntrom B., Johansson C., Kyrklund T., Rannug A., Tornqvist M., Victorin K., & Westerholm R. “Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air.” Environment Health Perspectous 110 (2002), 451-488.

Alves C., Pio C., Campos E., Barbedo P. “Size distribution of atmospheric particulate ionic species at a coastal site in Portugal.” Quim. Nova, 30(8), (2007), 1938-1944.

Cadle S.H., Mulawa P., Hunsanger E. C., Nelson K., Ragazzi R.A., Barrett R., Gallagher G.L., Lawson D. R., Knapp K. T., Snow R. “Light-duty motor vehicle exhaust particulate matter measurement in the Denver, Colorado, area.” Journal of Air Waste Management Association, 49 (1999), 164-174.

Campa M., Sa´nchezdela., Pio C., DelaRosa J. D., Querol X., Alastuey A., Gonza´lez-Castanedo Y. “Characterization and origin of EC and OC particulate matter near the Don˜ana National Park (SW Spain). ” Environmental Research, 109 (2009), 671–681.

Cao J.J., Chow J.C., Lee S.C., Li Y., Chen S.W., An Z.S., Fung K., Watson J.G., Zhu C.S., Liu S.X. “Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi’an, China.” Atmospheric Chemistry and Physics Discuss 5(2005), 3561–3593.

Castro L.M., Pio C.A., Harrison R. M., Smith D. J. T. “Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon Concentrations.” Atmospheric Environment, 33 (1999), 2771–2781.

Chabukdhara M., and Nema A. K. “Heavy metals assessment in urban soil around industrial clusters in Ghaziabad, India: Probabilistic health risk approach.” Ecotoxicology and Environmental Safety 87 (2013), 57–64.

Chaudhury P., Gupta R., Gajghate D. G., Wate S. R. “Heavy metal pollution of ambient air in Nagpur City.” Environmental Monitoring and Assessment, 184 (2011), 2487–2496.

Chen Z., Salam M.T., Eckel S.P., Breton C.V., Gilliland F.D. “Chronic effects of air pollution on respiratory health in Southern California children: findings from the Southern California Children's Health Study.” Journal of Thoracic Disease, 7(2015), 46-58.

Chow J.C., Watson J.G., Lu Z. “Descriptive analysis of $PM_{2.5}$ and PM_{10} at regionally representative locations during SJVAQS/AUSPEX.” Atmospheric Environment 30(1996), 2079–2112.

Chu S.H. “Stable estimate of primary OC/EC ratios in the EC tracer method.” Atmospheric Environment 39(2005), 1383-1392.

Central Pollution Control Board (CPCB) (2001). September, Newsletter, Air Pollution and human Health. Parivesh Bhavan, Delhi. http://cpcb.nic.in/.

Central Pollution Control Board (CPCB) (2003). November, Newsletter, Polycyclic Aromatic Hydrocarbons (PAHs) in Air and Their Effects on Human Health. Parivesh Bhavan, Delhi. http://cpcb.nic.in/.

Central Pollution Control Board CPCB (2009). National ambient air quality standards in India.http://cpcb.nic.in/uplo /Publication/ Publication_514_air quality status 2009.pdf

Central Pollution Control Board CPCB (2012). www.cpcb.nic.in/WQ_Status_Report.pdf.

Central Pollution Control Board CPCB(2015). Report_AQStatus_in_ NCR _250 22015 . pdf.

Delhi Pollution Control Committee (2016).
http://delhi.gov.in/DoIT/Environment/PDFs/Final_Report.pdf

Davy P.K., Ancelet T., Trompetter W.J., Markwitz A., Weatherburn D.C. “Composition and Source Contributions of Air Particulate Matter Pollution in a New Zealand Suburban town.” Atmospheric Pollution Research, 3(2012), 143–147.

Deshmukh D.K., Deb M.K., Tsai Y. I., Mkoma S.L. “Water Soluble Ions in $PM_{2.5}$ and PM_1 Aerosols in Durg City, Chhattisgarh, India.” Aerosol and Air Quality Research, 11(2011), 696–708.

Douben., and Peter ET. “PAHs: an ecotoxicological perspective.” John Wiley & Sons (Ecological and Environmental Toxicology Series), 2003.

European Comission (2000) Ambient air pollution by As, Cd and Ni compounds; Position Paper
Funasaka K., Miyazaki T., Kawaraya T., Tsuruho K., Mizuno T. Characteristics of particulates and gaseous pollutants in a highway tunnel.” Environmental Pollution, 102 (1998),171–176.

Gaghate D., and Hasan M. “Ambient lead levels in urban areas.” Bulletin of Environmental Contamination and Toxicology, 62(1999), 403-408.

Gaur A., Singh S.K., Tyagi S.K., Mandal A. “Variation in Parameters of Ambient Air Quality in National Capital Territory (NCT) of Delhi (India).” Atmospheric and Climate Sciences, 5(01) (2015), 13-22. DOI: 10.4236/acs.2015.51002.

George M.P., Kaur J., Sharma A., Mishra S. “Delhi smog 2012: cause and concerns.” Journal of Pollution Effects & Control 1(2013),1-6. http://dx.doi. org/ 10.4172 /jpe. 1000103.

Kannan G. K., and Kapoor S.C. “Analysis of particles size fraction (PM_{10} and $PM_{2.5}$) and PAH of urban ambient air.” Delhi: DRDO, Ministry of Defence, (2004).

Gnauk T., Muller K., Pinxteren D.V., He L-Y., Niu Y., Hu M., Herrmann H. “Size-segregated particulate chemical composition in Xinken, Pearl River Delta, China: OC/EC and organic compounds.” Atmospheric Environment, 42 (2008), 6296–6309.

Gota S. "Improving Fuel Efficiency and Reducing Carbon Emissions from Buses in India." Journal of Public Transportation, 17(2014), 39-50.

Goyal P., and Sidhartha. "Present scenario of air quality in Delhi: A case study of CNG implementation." Atmospheric Environment, 37 (2003), 5423-5431.

Goyal P., and Kumar A. "Air Quality Prediction of PM_{10} through an Analytical Dispersion Model for Delhi." Aerosol and Air Quality Research, 14(2014), 1487–1499.

Gray H., and Cass G. "Source Contributions to Atmospheric Fine Carbon Particle Concentrations." Atmospheric Environment. 32 (1998), 3805– 3825.

Guiang S. F., Krupa S. V., Pratt G. C. "Measurement of S (IV) and organic anions in Minnesota Rain." Atmospheric Environment 18, (1984), 1677-1682.

Gupta S., Mandal P., Dohare D. "Characterizations of Carbonaceous Aerosol in South and East Asia: A review from 2007 to 2014." International Journal of Engineering Sciences & Research Technology, 3 (2014), ISSN: 2277- 9655.

Gurjar B.R., Butler T., Lawrence M., Lelieveld J. "Evaluation of emissions and air quality in megacities." Atmospheric Environment,42(2008), 1593-1606.

Gurjar B.R., Aardenne J.A.V., Lelieveld J., Mohan M. "Emission Estimates and Trends (1990–2000) for Megacity Delhi and Implications." Atmospheric Environment 38 (2004), 5663–5681.

Gurjar B.R., V. Tyagi., N. Joshi., P. Kumar. "PM_{10} and heavy metals in sub-urban and rural atmospheric environments of Northern India." Journal of Hazardous Toxics and Radioactive Waste 16(2012), 175-182.

Hamilton T.A., and Mansfield. "Airborne particulate elemental carbon: its sources, transport and contribution to dark smoke and soiling." Atmospheric Environment, 25A (1992), 715-723.

Harrison R.M., E. Jang., M.S.Alam. "Source apportionment of polycyclic aromatic hydrocarbons in urban air using positive matrix factorizations and spatial distribution analysis." Atmospheric Environment, 79 (2013), 271-285.

Harrison R.M., and Yin Jianxin. "Pragmatic mass closure study for $PM_{1.0}$, $PM_{2.5}$, and PM_{10} at roadside, urban background and rural sites." Atmospheric Environment, 42 (2008), 980-988.

Harrison, R.M., Jones, A.M., Lawrence, R.G. "A pragmatic mass closure model for airborne particulate matter at urban background and roadside sites.", 2003. Atmospheric Environment 37 (2003), 4927–4933.

IARC (1983). Polynuclear aromatic compounds, Part 1, chemical, environmental and experimental data. IARC Monographs on the Evaluation of the Carcinogenic Risks to Chemicals to Humans, 32, 1–453.

IARC (1987). Polynuclear aromatic compounds, Part 1, chemical, environmental and experimental data. IARC Monographs on the Evaluation of the Carcinogenic Risks to Humans, vol 1-42, Supplement-7, 1–403.

Ji D., Hang J., He J., Wang X., Pang B., Liu Z., Wang L., Wang Y. “Characteristics of atmospheric organic and elemental carbon aerosols in urban Beijing, China.” Atmospheric Environment, 125 (2016), 293-306.

Jiang Y.F., Wang X.T., Wang F., Jia Y., Wu M.H., Sheng G.Y., Fu J.M. “Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China.” Chemosphere 75(2009), 1112-1118.

Joseph A.E. Unnikrishnan S., Kumar R. “Indoor and outdoor carbon composition of $PM_{2.5}$ aerosol in Mumbai, India.” (2009), European Aerosol Conference, Karlsruhe (2009).

Kadowaki S. “On the nature of the atmospheric oxidation processes of SO_2 to sulfate and of NO_2 to nitrate on the basis of diurnal variations of sulfate, nitrate, and other pollutants in an urban Area.” Environmental Science and Technology, 20 (1986), 1249–1253.

Kagawa M., and Ishizaka Y. “Conversion of SO_2 to Particulate Sulfate during Transport from China to Japan–Assessment by Selenium in Aerosols.” Aerosol and Air Quality Research, 14 (2014), 269–279.

Kaneyasu N., Ohta S., Murao N. “Seasonal variation in the chemical composition of atmospheric aerosols and gaseous species in Sapporo, Japan.” Atmospheric Environment, 29 (1995), 1559–1568.

Katiyar V., and Khare M. Horizontal Measurements of SO_2, NO_2 and SPM in Indoor Air and relationship to Outdoor concentration. Proceedings of Clima 2007, Well Being Indoors.

Katsoyiannis A., Terzi E., Cai Q.Y. “On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources.” Is this use appropriate? Chemosphere 69(2007), 1337-1339.

Kaur S., Senthilkumar K., Verma V.K., Kumar B., Kumar S., Katnonia J.K., C.S.Sharma, “Preliminary Analysis of Polycyclic Aromatic Hydrocarbons in Air Particles (PM_{10}) in Amritsar, India: Sources, Apportionment, and Possible Risk Implications to Humans.” Archives of Environmental Contamination Toxicology 65 (2013),382-395.

Keene W., C., Galloway J.N. “Organic acidity in precipitation of North America.” Atmospheric Environment, 18 (2012), 2491-2497.

Keene W., C., Galloway J.N., Holden J.D. “Measurement of weak organic acidity in precipitation from remote areas of the world.” Journal of 9eophysical Research 88, (1983) 5122-5130.

Khalili N.R., Scheff P.A., Holsen T.M. “PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions.” Atmospheric Environment, 29(1995), 533–542

Khillare P, Balachandran S., Meena B.R. “Spatial and temporal variation of heavy metals in atmospheric aerosol of Delhi.” Environmental Monitoring & Assessment, 90(2004),1-21.

Khillare P.S., and Sarkar S. “Airborne inhalable metals in residential areas of Delhi, India: distribution, source apportionment and health risks.” Atmospheric Pollution Research, 3 (2012), 46-54.

Khoder M.I. “Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area.” Chemosphere, 49(2002), 675–684.

Kim K. H., Sekiguchi K., Kudo S., Sakamoto K. “Characteristics of atmospheric elemental carbon (Char and Soot) in ultrafine and fine particles in a roadside environment, Japan.” Aerosol and Air Quality Research, 11(2011), 1–12.

Kleinman M.T., Tomezyk C., Leaderer B.P., Tanner R.L. “Inorganic nitrogen compounds in New York City.” Annals of the New York Academy of Sciences, 322(1979), 115-123.

Kulkarni P., and Venkataraman C. “Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India.” Atmospheric Environment 34 (2000), 2785-2790.

Kulshrestha C., Nageswara T., Kulshrestha A. S. “Emissions and accumulation of metals in the atmosphere due to crackers and sparkles during Diwali festival in India.” Atmospheric Environment 38 (2004), 4421–4425.

Kumar S., Aggarwal S.G., Malherbe J., Barre J.P.G., Berail S., Gupta P.K., Donard O.F.X. “Tracing dust transport from Middle-East over Delhi in March 2012 using metal and lead isotope composition.” Atmospheric Environment, 132 (2016), 179-187.

Kumari K.M., Satsangi A., Pachauri T., Singla V., Lakhani A. “Water Soluble Ionic Species in Atmospheric Aerosols: Concentrations and Sources at Agra in the Indo-Gangetic Plain (IGP).” Aerosol and Air Quality Research, 13 (2013), 1877–1889.

Kwangsam N., Aniket A., Sawant., Chen S., Cocker D.R. “Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California.” Atmospheric Environment 38 (2004) 1345–1355.

Lai S.C., Ho K. F., Zhang Y. Y., Lee S. C., Huang Yu, Zou S.C. “Characteristics of Residential Indoor Carbonaceous Aerosols: A Case Study in Guangzhou, Pearl River Delta Region.” Aerosol and Air Quality Research, 10 (2010), 472 – 478.

Li X., Wang H., Tian M., Chang Q., Cao J., Yang F., Ma Y., He K. “Chemical Composition and Light Extinction Contribution of $PM_{2.5}$ in Urban Beijing for a 1-Year Period.” Aerosol and Air Quality Research, 15 (2015), 2200–2211.
Li X., Cao J., Chow J., Han Y., Lee S., Watson J. “Chemical characteristics of carbonaceous aerosols during dust storms over Xi'an in China.” Advances in Atmospheric Sciences, 25(5) (2008), 847–855.

Manandharb A., Leea S.C., Hoa K.F., Hunga W.T., Joshib G.R., P.K.C. “Identification of indoor and outdoor particulate concentration and its chemical composition in Kathmandu Valley.” http://cleanairasia.org/portal/sites/default/files/AP_Study_Final_0.pdf.

Mandal P., Sarkar R., Mandal A., Saud T. “Seasonal variation and sources of aerosol pollution in Delhi, India.” Environmental Chemistry Letters 12(4) (2014), 529-534.

Mandal P., Saud T., Sarkar R., Mandal A., Sharma S. K., Mandal T. K., Bassin J. K. “High seasonal variation of atmospheric C and particle concentrations in Delhi, India.” Environmental Chemistry Letters, 12 (2013), 225-230.

Mandal P., Prakash M., Bassin J. K. “Impact of Diwali celebrations on urban air and noise quality in Delhi City, India.” Environmental Monitoring and Assessment, 184 (1) (2012), 209-215.

Mandal P., Sarkar R., Mandal A., Patel P., Kamal N. “Study on Airborne Heavy Metals in Industrialized Urban Area of Delhi, India.” Bulletin of Environmental Contamination and Toxicology, **DOI:** 10.1007/s00128-016-1944-y.

Mandal P., Sarkar R., Mandal A. “Ambient Polycyclic Aromatic Hydrocarbons and its Carcinogenic and Mutagenic Risk – A Review.” International Advanced Research Journal in Science, Engineering and Technology, 3(9), (2016), 189-197.

Manahan, S.E. “Environmental Chemistry”, sixth ed. Lewis Publisher, New York (1994).

Marr L.C., Dzepina K., Jimenez J. L., Reisen F., Bethel H. L., Arey J., Gaffney J. S., Marley N. A., Molina M.J. “Sources and transformation of particle–bound polycyclic aromatic hydrocarbons.” Atmospheric Chemistry and Physics 6(2006),1733-174.

Masih J., Singhvi R., Kumar K., Jain V.K., Taneja A. “Seasonal variation and sources of polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air in a semi-arid tract of Northern India.” Aerosol and Air Quality Research, 12 (2012), 515–525.

Masiol M., Hofer A., Squizzato S., Piazza R., Rampazzo G., Pavoni B. “Carcinogenic and mutagenic risk associated to airborne particle-phase polycyclic aromatic hydrocarbons: A source apportionment.” Atmospheric Environment 60 (2012), 375-382.

Meng Z., Seinfeld J.H., Saxena P., Kim Y.P. “Atmospheric gas-aerosol equilibrium, IV: thermodynamics of carbonates.” Aerosol Science and Technology, 23 (1995), 131–154.

Mészáros E., and Horváth L. “Concentration and dry deposition of atmospheric sulfur and nitrogen compounds in Hungary.” Atmospheric Environment 18 (1984), 1725–1730.

Miller R.L., Jung K.H., Yan B., Chillrud S.N., Perera F.P., Whyatt R., Camann D. “Assessment of benzo(a)pyrene-equivalent carcinogenicity and mutagenicity of residential indoor versus outdoor polycyclic aromatic hydrocarbons exposing young children in New York City.” International Journal of Environmental Research and Public Health, 7(2010), 1889–1900.

Mishra A. K., Maiti S. K., Pal A. K. “Status of PM_{10} bound heavy metals in ambient air in certain parts of Jharia coal field, Jharkhand, India.” International Journal of Environmental Sciences 4 (2013), 141-150.

Murillo J.H., Roman S.R., Marin J. F. R., Ramos A. C., Jimenez S. B., Gonzalez B. C., Baumgardner D. G. “Chemical characterization and source apportionment of PM_{10} and $PM_{2.5}$ in the metropolitan area of Costa Rica, Central America.” Atmospheric Pollution Research 4(2013), 181-190.

Pachauri T., Satsangi A., Singla V., Lakhani A., Kumari K. M. “Characteristics and sources of carbonaceous aerosols in $PM_{2.5}$ during Winter time in Agra, India.” Aerosol and Air Quality Research, 13(2013), 977–991.

Pakade Y., Vanita C., Piar C., Avinash N., Kaur K.J. “Evaluation of heavy metals contamination and its genotoxicity in agricultural soil of Amritsar, Punjab, India.” International Journal of Research in Chemistry and Environment, 4(2014), 20-28.

Pandey J.S., Kumar R., Devotta S. “Health risks of NO_2, SPM and SO_2 in Delhi (India).” Atmospheric Environment, 39 (2005), 6868–6874.

Pant P., Guttikundab S. K., Peltier R. E. “Exposure to particulate matter in India: A synthesis of findings and future directions.” Environmental Research, 147 (2016), 480–496.

Paraskevopoulou D., Liakakou1 E., Gerasopoulos1 E., Theodosi C., Mihalopoulos N. “Long-term characterization of organic and elemental carbon in the $PM_{2.5}$ fraction: the case of Athens, Greece.” Atmospheric Chemistry and Physics, 14 (2014), 13313–13325.

Park S.S., Kim Y.J., Kang C.H. “Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea.” Atmospheric Environment, 36 (2002), 2917–2924.

Penner J.E., Charlson R.J., Heintzenberg J. “Carbonaceous aerosol influencing atmospheric radiation: black carbon and organic carbon.” Aerosol Forcing of Climate (1995), 91–108.

Pervez S., Chakrabarty K., Dewangan S. “Chemical speciation of aerosols and air quality degradation during the festival of lights (Diwali).”Atmospheric Pollution Research 7(2015), 92-99.

Plaza J., Artíñano B., Salvador P., Francisco J., Gómez-Moreno., Pujadas M., Pio C.A. “Short-term secondary organic carbon estimations with a modified OC/EC primary ratio method at a suburban site in Madrid (Spain).” Atmospheric Environment, 45 (2011), 2496-2506.

Pies C., Hoffmann B., Petrowsky J., Yang Y., Ternes T.A., Hofmann T. “Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils.” Chemosphere 72 (2008), 1594-1601.

Pope C.A., and Dockery D.W. “Health effects of fine particulate air pollution: lines that connect.” Journal of Air Waste Management Association, 56 (2006),709-742

Rajaram B.S., Suryawansh P.V.I., Bhanarkar A.D., Rao C.V.C. “Heavy metals contamination in road dust in Delhi City,India.” Environmental Earth Sciences,11(2014),3929-3938. DOI:10.1007/s12665-014-3281-y

Rajput P., Sarin M., Kundu S.S. “Atmospheric particulate matter ($PM_{2.5}$), EC, OC, WSOC and PAHs from NE–Himalaya: abundances and chemical characteristics.” Atmospheric Pollution Research, 4 (2013), 214–221.

Raiyani C.V., Jani J.P., Desai N.M., Shah P.G., Parikh D.J., Kashyap S.K. “Assessment of indoor exposure to polycyclic aromatic hydrocarbons from urban poor using various types of cooking fuels.” Environmental Contamination and Toxicology, 50 (1993), 757–763.

Ram K. and M.M. Sarin. “Atmospheric carbonaceous aerosols from Indo-Gangetic Plain and Central Himalaya: impact of anthropogenic sources.” Journal of Environmental Management, 148 (2015), 153-163.

Ram K., Sarin M.M., Sudheer A.K., Rengarajan R. “Carbonaceous and Secondary Inorganic Aerosols during Wintertime Fog and Haze over Urban Sites in the Indo-Gangetic Plain.” Aerosol and Air Quality Research, 12(2012), 359–370.

Ram K., and Sarin M.M. “Carbonaceous Aerosols Over Northern India: Sources and Spatio-temporal Variability.” Proceedings of the National Academy of Sciences, India Section B: Biological Sciences, 78 (2012), 523-533.

Ram K., and Sarin M.M. “Day-night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic Plain: Implications to secondary aerosol formation.” Atmospheric Environment, 45 (2011), 460-468.

Ram K., and Sarin M.M. “Spatio-temporal variability in atmospheric abundances of EC, OC and WSOC over Northern India.” Journal of Aerosol Science, 41 (2010), 88–98.

Ramaswamy B.R., Sampath S., Shanmugam G., Selvaraj K. K. “Spatio-Temporal Distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in Atmospheric Air of Tamil Nadu, India, and Human Health Risk Assessment.” Journal of Environmental Forensics, 16 (2015), 76-87.

Rani A., Meena M., Meena B. S., Chandrawat U. “Seasonal Variation of Selected Metals in Particulate Matter at an Industrial City Kota, India.” Aerosol and Air Quality Research, 16 (2016), 990–999.

Rastogi N., and Sarin M.M. “Quantitative chemical composition and characteristics of aerosols over western India: one-year record of temporal variability.” Atmospheric Environment 43(2009), 3481–3488.

Ravindra K., Wauters E., Grieken R. V. “Variation in particulate PAHs levels and their relation with the transboundary movement of the air masses.” Science of the Total Environment, 396 (2008), 100-110.

Ravindra K., Bencs L., Wauters E., Hoog J. D., Deutsch F., Roekens E., Bleux N., Bergmans P., Grieken R. V. “Seasonal and site specific variation in vapor and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities.” Atmospheric Environment 40 (2006), 771–785.

Ravindra K., Suman M., Kaushik C.P. “Short-term variation in air quality associated with firework events: A case study.” Journal of Environmental Monitoring, 5(2) (2003), 260-264.

Rehman I. H., Ahmed T., Praveen P. S., Kar A., Ramanathan V. “Black carbon emissions from biomass and fossil fuels in rural India.” Atmospheric Chemistry and Physics, 11 (2011), 7289–7299.

Report of toxicolological Cobolt dust (7440-48-4), february 2002, https:// ntp.niehs.nih.gov/ntp/ (Final Verson)

Report of Business Standard “Delhi's air pollution rises 23% during second odd-even phase
Data indicate that the scheme cannot work in the long term without additional actions, such as improving bus services, curbing factory and truck emissions.” www.business-standard.com › Current Affairs › News › National April 30, 2016.

Robert E. Lee Jr., and Darryl J. von Lehmden. “Trace Metal Pollution in the Environment.” Journal of the Air Pollution Control Association, 23(10), 2012, 853-857.

Rogge W.F., Hildemann L.M., Mazurek M.A., Cass G.R., Simoneit B.R.T. “Sources of fine organic aerosol: 2. Non-catalyst and catalyst-equipped automobiles and heavy-duty diesel trucks.” Environmental Science and Technology, 27(1993),636–651.

Saarikoski S., Timonen H., Saarnio K., Aurela M., Jarvi L. “Sources of organic carbon in fine particulate matter in northern European urban air.” Atmosperic Chemistry and Physics 8 (2008),6281–6295.

Salam M. A., Shirasuna Y., Hirano K., Masunaga S. “Particle associated polycyclic aromatic hydrocarbons in the atmospheric environment of urban and suburban residential area.” International Journal of Environmental Science and Technology 8(2011), 255-266.

Sarkar S., Khillare P. S., Jyethi D. S., Parween M. “Chemical speciation of respirable suspended particulate matter during a major firework festival in India.” Journal of Hazardous Materials 184(2010), 321-330.

Sahu S. K., Pandit G. G., Puranik V. D. “Dry Deposition of Polycyclic Aromatic Hydrocarbons Associated with Atmospheric Particulate Matters in an Urban Site, Mumbai, India.” Aerosol and Air Quality Research, 8 (2008), 437-446.

Satsangi A., Pachauri T., Singla V., Lakhani A., Maharaj K. K. “Organic and Elemental Carbon Aerosols at a Suburban Site.”Atmospheric Research, 113(2012), 13–21.

Satsangi A., Pachauri T., Singla V., Lakhani A., Kumari K. M. “Carbonaceous aerosols at a suburban site in Indo-Gangetic plain.” Indian journal of Radio and Space physics. 39 (2010), 218 – 222.

Schauer J.J., Kleeman M.J., Cass G.R., Simoneit B.R.T. “Measurement of emissions from air pollution sources 5. C1–C32 organic compounds from gasoline-powered motor vehicles.” Environment Science & Technology 36(2002),1169–1180.

Schwarz J., Chi X., Maenhaut W., Civiš M., Hovorka J., Smolík J. “Elemental and organic carbon in atmospheric aerosols at downtown and suburban sites in Prague.” Atmospheric Research, 90 (2008), 287–302.

See S.W., and Balasubramanian R. “Chemical characteristics of fine particles emitted from different gas cooking methods.” Atmospheric Environment 42 (2008), 8852-8862.

Seguel R.A., Morales R.G. E. S., Guzman M. A. L. “Estimations of primary and secondary organic carbon formation in $PM_{2.5}$ aerosols of Santiago City, Chile.” Atmospheric Environment, 43 (2009), 2125–2131.

Seinfeld J.H., and Pandis S.N. “Atmospheric Chemistry and Physics.” Wiley-Interscience, New York (1998).

Sharma A., Tyagi S.K., Kulshrestha D., Masih Jamson. “Source apportionment study of polycyclic aromatic hydrocarbons (PAHs) in New Delhi, India.” International Journal of Environmental Sciences 4(2014), 1141-1149.

Sharma M., Kishore S., Tripathi S. N., Behera S. N. “Role of atmospheric ammonia in the formation of inorganic secondary particulate matter: A study at Kanpur, India.” Journal of Atmospheric Chemistry 58 (2007), 1–17.

Sharma S.K., Datta A., Saud T., Mandal T.K., Ahammed Y.N., Arya B.C., Tiwari M.K. “Study on concentration of ambient NH_3 and interactions with some other ambient trace gases.” Journal of Environmental Monitoring and Assessment, 162 (2010), 225-235.

Sharma S.K., Mandal T.K., Jain S., Saraswati, Sharma A., Saxena M. “Source Apportionment of $PM_{2.5}$ in Delhi, India Using PMF Model.” Bulletin of Environmental Contamination and Toxicology, 97 (2) (2016), 286-293.

Sharma S.K., Saxena M., Mandal T. K., Ahammed Y.N., Pathak H., Datta A., Saud T., Arya B.C. “Variations in mixing ratios of ambient ammonia, nitric oxide and nitrogen dioxide in different environments of India.” Journal of Earth Science & Climatic Change, 1 (2010), ISSN: 2157-7617.

Sharma S.K., Mandal T.K., Saxena M., Rashmi., Sharma A., Datta A., Saud T. “Variation of OC, EC, WSIC and trace metals of PM_{10} in Delhi, India.” Journal of Atmospheric and Solar-Terrestrial Physics, 113 (2014), 10–22.

Sharma S.K., Datta A., Saud T., Saxena M., Mandal T.K., Ahammed Y.N., Arya B.C. “Seasonal variability of ambient NH_3, NO, NO_2 and SO_2 over Delhi.” Journal of Environmental Sciences, 22 (2010), 1023-1028.

Shen H., Huang. R. Wang Y., Zhu D., Li W., Shen G., Wang B., Zhang Y., Chen Y., Lu Y., Chen H., Li T., Sun K., Li B., Liu W., Liu J., Tao S. “Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions.” Environmental Science and Technology 47(2013), 6415-6424.

Shen Z., Han Y., Cao J., Tian J., Zhu C., Liu S., Liu P., Wang Y. “Characteristics of Traffic-related Emissions: A Case Study in Roadside Ambient Air over Xi’an, China.” Aerosol and Air Quality Research, 10(2010), 292–300.

Shi J., Peng Y., Li W., Qiu W., Bai Z., Kong S., Jin T. “Characterization and Source Identification of PM_{10}-bound Polycyclic Aromatic Hydrocarbons in Urban Air of Tianjin, China.” Aerosol and Air Quality Research, 10(2010), 507–518.

Shinggu D.Y., Ogugbuaja V., Toma O., Barminas J.T. “Determination of Heavy Metals in Street Dust in Yola, Nigeria.” African Journal of Pure and Applied Chemistry 4 (2010), 17-20.

Shridhar V., Khillare P. S., Agarwal T., Ray S. “Metallic species in ambient particulate matter at rural and urban location of Delhi.” Journal of Hazardous Materials 175 (2010), 600-607.

Singh D.P., Gadi R., Mandal T.K. “Characterization of gaseous and particulate polycyclic aromatic hydrocarbons in Ambient Air of Delhi, India.” Journal of Polycyclic Aromatic Compounds 32(2014), 556-579.

Singh D.P., Gadi R., Mandal T.K., Dixit C.K., Singh K., Saud T., Singh N., P. K. “Study of temporal variation in ambient air quality during Diwali festival in India.” Environmental Monitoring and Assessment, 169 (2009), 1-4.

Singh D.P., Gadi R., Mandal T.K. “Characterization of particulate-bound polycyclic aromatic hydrocarbons and trace metals composition of urban air in Delhi, India.” Atmospheric Environment 45 (2011), 7653-7663.

Singh K., Singh D. P., Dixit C. K., Singh N., Sharma C., Sahai S., Jha A. K., Khan Z. H., Gupta P.K. “Chemical characteristics of aerosols and trace gas distribution over North and Central India.” Environmental Monitoring and Assessment 184 (2012), 4553–4564.

Singh K., Khan Z. H., Gupta P. K. “Temporal changes in particulate matter and trace gases concentrations: A case study of Delhi.” Open Journal of Atmospheric and Climate Change, 1(2) (2014), 51-59.

Singh S., and Kulshrestha U. C. “Abundance and distribution of gaseous ammonia and particulate ammonium at Delhi, India.” Biogeosciences, 9(2012), 5023–5029.

Smith D.J.T., Harrison R.M. “Polycyclic aromatic hydrocarbons in atmospheric particles.” In: Harrison, R.M., Van Grieken, R. (Eds.), Atmospheric Particles. Wiley (1998).

Srivastava A., Gupta S., Jain V.K. “Source apportionment of total suspended particulate matter in coarse and fine size ranges over Delhi.” Aerosol and Air Quality Research, 8 (2008), 188-200.

Srivastava A., and Jain V.K. “Size distribution and source identification of total suspended particulate matter and associated heavy metals in the urban atmosphere of Delhi.” Chemosphere 68 (2007), 579–589.

Stenberg U., Alsberg T., Blomberg L., Wannman T. “Gas chromatographic separation of high-molecular ploy-nuclear aromatic hydrocarbons in samples from different sources, using temperature stable glass capillary columns.” P.W., Leber, P. (Eds.), Polynuclear Aromatic Hydro-carbons, 3rd International Symposium, Ann Arbor Science, Ann Arbor, MI, (1979), 313–326.

Stockwell W.R., and Calvert J.G. “The mechanism of the HO–SO2 reaction.” Atmospheric Environment, 17(1983), 2231–2235.

Stone A. A., Schwartz J. E., Broderick J. E., Deaton A. “A snapshot of the age distribution of psychological well-being in the United States.” Proceedings of the National Academy of Science U S A, 107(22), (2010), 9985-9990. doi: 10.1073/pnas.1003744107.

Stockwell W.R., and Calvert J.G. “The mechanism of the HO–SO_2 reaction.” Atmospheric Environment, 17(1983), 2231-2235.

Suchocka K., Chłopek Z., Dudek M., Jakubowski A. “Hazards posed by polycyclic aromatic hydrocarbons contained in the dusts emitted from motor vehicle braking systems.” Archives of Environmental Protection 42(2016), 3–10.

Tchounwou P.B., Clement G. Y., Patlolla A.K., Sutton D.J. “Heavy Metals Toxicity and the Environment.” Molecular Clinical and Environmental Toxicology, 101(2014), 133-164.

Tiwari S., Chate D.M., Srivastava A.K., Bisht D.S., Padmanabhamurty B. “Assessments of PM_1, $PM_{2.5}$ and PM_{10} concentrations in Delhi at different mean cycles.” GEOFIZIKA, (Original scientific paper UDC 551.510.41) 29 (2012), 125-141

Tyagi S., Tiwari S., Mishra A. “Impact of air pollution on visibility over New Delhi, India: A case study of winter fog.” International Journal of Advances in Science Engineering and Technology, 2016 (4), issue 4, ISSN: 2321-9009.

Tobiszewski M., and Namiesnik J. “PAH diagnostic ratios for the identification of pollution emission sources.” Journal of Environmental Pollution 162 (2012), 110-119.

Tsai Y.I., Sopajaree K., Kuo S., Hsin T.Y. “Chemical Composition and Size-Fractionated Origins of Aerosols over a Remote Coastal Site in Southern Taiwan.” Aerosol and Air Quality Research, 15 (2015), 2549–2570.

Turpin B.J., and Huntzicker J.J. “Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS.” Atmospheric Environment, 29(1995), 3527–3544.

Utsunomiya, A., and Wakamatsu S. “Temperature and humidity dependence on aerosol composition in the northern Kyushu, Japan.” Atmospheric Environment, 30 (1996), 2379–2386.

Venkataraman C., Negi G., Sardar S.B., Rastogi R., “Size distributions of polycyclic aromatic hydrocarbons in aerosol emissions from biofuel combustion.” Aerosol Science 33(2002), 503–518.

Venkataraman C., Sinha P., Bammi S. “Sulphate aerosol size distributions at Mumbai, India, during the INDOEX-FFP (1998).” Atmospheric Environment 35 (2001), 2647-2655.

Vijayanand C., Rajaguru R., Kalaiselvi K., Selvam K.P., Palanivel M. “Assessment of heavy metal contents in the ambient air of the Coimbatore city,Tamilnadu, India.” Journal of Hazard Material, 160(2008),548-553.

Wall S.M., John W., J. L. “Measurement of aerosol size distribution for nitrate and major ionic species.” Atmospheric Environment 22 (1988), 1649–1656.

Wang-Li Lingjuan, Li Q.F., Jayanty R. K. M., Sanjay., Shah B. “Organic and Elemental Carbon in Atmospheric Fine Particulate Matter in an Animal Agriculture Intensive Area in North Carolina: Estimation of Secondary Organic Carbon Concentrations.” Open Journal of Air Pollution 2 (2013), 7-18.

Watson J.G., Chow J.C., Lowenthal D.H., Pritchett L.C., Frazier C.A., Neuroth G.R., Robbins R. “Differences in the Carbon Composition of Source Profiles for Diesel-and Gasoline-Powered Vehicles.” Atmospheric Environment 28(1994), 2493–2505.

Watson J.G., Chow J.C., James E.H. “$PM_{2.5}$ chemical source profiles for vehicle exhaust, vegetative burning, geological materials and coal burning in Northwestern Colorado during 1995.” Chemosphere 43(2001), 1141–1151.

Willison M.J., Clarke A.G., Zeki E.M. “Seasonal variation in atmospheric aerosol concentration and composition at urban and rural sites in northern England.” Atmospheric Environment, 19(1985), 1081–1089.

World Health Organization (2000), report “Regional publication, European Series 91 (2nd Edn)”, 2000.

World Health Organization (WHO), 2000, report (Chapter5.9 Polycyclic aromatic hydrocarbons (PAHs) WHO/ Europe www. euro. who. int/__.../ AQG 2ndEd _5_9 PAH.pdf.

World Health Organization (WHO), 2002,“Reducing Risks, Promoting Life”./ http:// www.who. int/whr/en/S.

Yang F., Zhang L., Huang Y., Liu Y., Lan G., Fu C., Wang J. “Characteristics of Carbonaceous Species in $PM_{2.5}$ in Wanzhou in the Hinterland of the Three Gorges Reservior of Northeast Chongqing, China.” Atmosphere 6 (2015), 534-546.

Yang F., Huang L., Duan F., Zhang W., He K., Ma Y., Brook J.R., Tan J., Zhao Q., Cheng Y. “Carbonaceous species in $PM_{2.5}$ at a pair of rural/urban sites in Beijing, 2005–2008.” Atmospheric Chemistry and Physics 11(2011), 7893–7903.

Yang F., He K., Ma Y., Zhang Q., Cadle S.H., Chan T., Mulawa P.A. “Characterization of Carbonaceous Species of Ambient $PM_{2.5}$ in Beijing, China.” Journal of the Air & Waste Management Association, 55(2005), 984-992.

Ye D., Zhao Q., Jiang C., Chen J., Meng X. “Characteristics of elemental carbon and organic carbon in PM_{10} during spring and autumn in Chongqing, China.” China Particuology, 5 (2007), 255–260.

Yu S., Bhave P.V., Dennis R. L., Mathur R. “Seasonal and regional variations of primary and secondary organic aerosols over the continental United States: observation-based estimates and model evaluation.” (2007) Environmental Science & Technology 41(2007), 4690–4697.

Yu S., Dennis R. L., Bhave P.V., Eder B. “Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios.” Atmospheric Environment 38 (2004), 5257–5268.

Yunker M.B, Macdonald R.W., Vingarzan R., Mitchell R.H., Goyette D., Sylvestre S. “PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition.” Organic Geochemistry 33 (2002), 489-515.

Zhang Y., and S. Tau. “Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs).” Atmospheric Environment 43(2009), 812-819.

Zhang Y., Ji X., Ku T., Li G., Sang N. “Heavy metals bound to fine particulate matter from northern China induce season-dependent health risks: A study based on myocardial toxicity.” Environmental Pollution 216 (2016), 380-390.

Zhang Y.X., Shao M., Zhang Y.H., Zeng L.M., He L.Y., Zhu B. “Source profiles of particulate organic matters emitted from cereal straw burnings.” Journal of Environmental Science 19 (2007), 167–175.

Zhou L. , Hopke P.K., Paatero., Ondov J.K., Pancras J.P., Penkey N.J. “Advanced factor analysis for multiple time resolution aerosol composition data.” Atmospheric Environment, 38(2004),4909-4920.

Zhu C.S., Ji J., Cao., Tsai C.J., Shen Z.X., Ho K.F., Liu S.X. “The Indoor and Outdoor Carbonaceous Pollution during winter and summer in rural areas of Shaanxi, China.” Aerosol and Air Quality Research, 10 (2010) 550–558.

ANNEXTURES

Annexure – I

List of Samples Collected at Naraina Mixed Use Area of Delhi

Month	Date	Trace Gases			Particulate Matter	
		SO_2 (μg/m3)	NO_2 (μg/m3)	NH_3 (μg/m3)	PM_{10} (μg/m3)	$PM_{2.5}$ (μg/m3)
January	4/1/2011	18	68	39	-	-
	5/1/2011	29	101	66	-	-
	6/1/2011	17	75	39	-	-
	7/1/2011	30	111	66	-	-
	11/1/2011	13	67	48	269	147
	12/1/2011	19	112	61	-	-
	13/1/2011	10	60	46	538	209
	15/1/2011	17	76	54	247	151
	17/1/2011	14	88	67	-	-
	18/1/2011	16	121	68	403	179
	20/1/2011	11	72	62	-	-
	22/1/2011	19	123	68	325	158
	23/1/2011	16	96	57	403	217
	25/1/2011	25	111	65	375	164
	28/1/2011	18	88	66	661	217
	31/1/2011	28	123	75	-	-
February	1/2/2011	12	82	62	307	158
	2/2/2011	18	104	75	-	-
	3/2/2011	13	77	72	-	-
	5/2/2011	25	96	82	411	220
	7/2/2011	13	74	58	-	-
	8/2/2011	22	89	67	225	169
	10/2/2011	11	73	70	-	-
	12/2/2011	22	97	77	247	178
	14/2/2011	13	68	57	-	-
	15/2/2011	18	101	62	178	134
	16/2/2011	10	70	51	-	-
	19/2/2011	19	97	53	237	156
	22/2/2011	12	79	61	243	177

	23/2/2011	20	121	79	-	-
	24/2/2011	16	94	60	-	-
	25/2/2011	16	110	75	518	223
March	4/3/2011	10	66	57	-	-
	5/3/2011	16	84	61	201	148
	8/3/2011	9	71	54	263	189
	9/3/2011	18	95	68	-	-
	10/3/2011	9	63	55	-	-
	12/3/2011	17	105	62	209	143
	15/3/2011	13	64	58	315	179
	16/3/2011	19	93	66	-	-
	18/3/2011	6	60	63	-	-
	19/3/2011	16	109	88	198	166
	21/3/2011	7	69	58	-	-
	22/3/2011	14	89	64	349	208
	24/3/2011	8	75	57	205	160
	26/3/2011	18	95	70	285	205
	29/3/2011	14	71	61	189	149
	31/3/2011	17	100	77	315	186
April	5/4/2011	5	72	46	300	126
	6/4/2011	12	90	59	-	-
	7/4/2011	7	66	45	-	-
	8/4/2011	10	90	68	278	141
	12/4/2011	6	61	50	286	146
	13/4/2011	15	97	65	-	-
	14/4/2011	8	65	46	-	-
	15/4/2011	13	91	85	290	142
	18/4/2011	5	61	62	-	-
	19/4/2011	14	78	75	277	128
	20/4/2011	7	58	53	-	-
	22/4/2011	13	78	65	292	148
	25/4/2011	10	69	53	-	-
	26/4/2011	15	86	62	-	-
	27/4/2012	8	72	40	281	129
	30/4/2012	9	96	49	286	153

May	2/5/2011	2	58	77	-	-
	3/5/2011	6	81	80	-	-
	4/5/2011	3	50	71	255	142
	6/5/2011	5	83	98	-	-
	8/5/2011	6	50	64	383	161
	11/5/2011	10	68	74	-	-
	12/5/2011	5	47	62	295	138
	13/5/2011	6	65	73	-	-
	16/5/2011	5	46	68	385	160
	18/5/2011	6	67	87	216	118
	19/5/2011	4	54	58	-	-
	23/5/2011	7	68	66	450	203
	24/5/2011	5	57	64	-	-
	26/5/2011	7	80	78	-	-
	27/5/2011	4	60	61	314	150
	30/5/2011	8	71	72	335	164
June	1/6/2011	4	33	65	181	168
	2/6/2011	5	55	80	-	-
	6/6/2011	4	30	73	-	-
	8/6/2011	5	59	83	143	121
	9/6/2011	6	41	66	-	-
	10/6/2011	7	57	76	178	163
	14/6/2011	5	40	53	-	-
	15/6/2011	6	55	60	128	115
	17/6/2011	5	42	57	-	-
	19/6/2011	6	51	74	149	120
	22/6/2011	4	43	64	147	133
	23/6/2011	7	61	71	-	-
	24/6/2011	5	42	65	-	-
	26/6/2011	6	54	92	156	146
	29/6/2011	4	44	68	-	-
	30/6/2011	9	57	91	192	174
July	4/7/2011	2	25	62	-	-
	5/7/2011	3	38	74	87	69
	6/7/2011	1	25	48	-	-

	7/7/2011	4	29	64	98	93
	11/7/2011	2	30	61	-	-
	12/7/2011	4	55	74	87	69
	14/7/2011	3	30	72	95	82
	15/7/2011	3	37	88	-	-
	19/7/2011	2	28	50	89	57
	20/7/2011	3	34	59	-	-
	22/7/2011	3	30	47	106	87
	25/7/2011	5	45	65	-	-
	26/7/2011	4	28	60	94	61
	27/7/2011	5	44	65	-	-
	28/7/2011	3	28	44	112	73
	29/7/2011	7	42	47	-	-
August	4/8/2011	2	30	85	-	-
	5/8/2011	5	52	101	98	64
	7/8/2011	3	34	73	125	76
	9/8/2011	4	57	94	-	-
	10/8/2011	1	32	81	-	-
	11/8/2011	3	55	97	97	65
	14/8/2011	3	30	81	113	87
	16/8/2011	3	33	98	-	-
	17/8/2011	2	47	84	-	-
	18/8/2011	5	65	102	102	76
	21/8/2012	3	35	97	118	91
	23/8/2012	6	64	103	-	-
	25/8/2011	4	32	80	104	57
	26/8/2011	5	43	94	-	-
	30/8/2011	4	38	74	120	49
	31/8/2011	7	49	96	-	-
September	1/9/2011	5	30	73	159	79
	2/9/2011	13	58	81	-	-
	5/9/2011	8	32	56	167	98
	6/9/2011	14	56	73	-	-
	7/9/2011	10	35	87	-	-
	8/9/2011	14	58	100	165	73

	12/9/2011	9	31	90	163	110
	13/9/2011	16	55	111	-	-
	14/9/2011	6	36	60	-	-
	15/9/2011	13	79	82	152	61
	19/9/2011	10	32	59	172	122
	20/9/2011	15	55	84	-	-
	21/9/2011	8	34	39	-	-
	22/9/2011	11	63	54	156	75
	28/9/2011	7	42	47	-	-
	29/9/2011	11	67	56	173	106
October	4/10/2011	8	66	68	307	174
	5/10/2011	15	83	86	-	-
	6/10/2011	12	61	75	-	-
	7/10/2011	17	90	85	425	180
	11/10/2011	8	59	47	298	166
	12/10/2011	14	88	84	-	-
	13/10/2011	13	56	80	-	-
	14/10/2011	17	98	99	385	196
	17/10/2011	10	63	65	360	164
	18/10/2011	23	76	115	-	-
	19/10/2011	17	59	83	-	-
	20/10/2011	24	97	120	440	174
	24/10/2011	15	63	73	-	-
	25/10/2011	19	77	94	402	158
	27/10/2011	10	61	45	493	195
	31/10/2011	22	101	128	-	-
November	3/11/2011	8	73	90	392	170
	4/11/2011	14	97	95	-	-
	7/11/2011	9	77	97	485	184
	8/11/2011	13	102	137	-	-
	11/11/2011	10	61	81	347	158
	14/11/2011	23	104	125	374	176
	15/11/2011	15	73	89	-	-
	16/11/2011	20	94	122	-	-
	17/11/2011	14	70	77	405	180

	18/11/2011	21	96	111	-	-
	21/11/2011	17	68	87	502	188
	23/11/2011	25	93	124	-	-
	24/11/2011	15	74	97	-	-
	25/11/2011	26	94	122	423	185
	28/11/2011	16	70	82	-	-
	29/11/2011	19	102	101	359	182
December	1/12/2011	15	113	59	402	159
	2/12/2011	21	118	79	-	-
	7/12/2011	17	101	71	-	-
	8/12/2011	25	122	85	485	217
	12/12/2011	16	101	72	427	169
	13/12/2011	22	118	95	-	-
	14/12/2011	16	100	77	-	-
	15/12/2011	25	111	113	464	210
	19/12/2011	18	98	87	425	168
	20/12/2011	21	120	105	-	-
	21/12/2011	20	102	94	-	-
	22/12/2011	26	126	127	502	210
	24/12/2011	18	108	81	437	166
	26/12/2011	24	115	119	460	219
	29/12/2011	17	106	75	447	176
	31/12/2011	27	127	94	478	212

Note: For the study, the monitoring protocol for PM_{10} and $PM_{2.5}$ was decided twice in a week for one year (January 2011 to December 2011).

Annexure – II

National Ambient Air Quality Standards, India (Revised, 2009)
Central Pollution Control Board's National Standards, India

Pollutants	Time	Concentration in Ambient Air		Methods of Measurement
		Industrial, Residential, Rural and other Areas	**Ecologically Sensitive Area (Notified by Central Government)**	
Sulphur Dioxide (SO_2), µg/m^3	Annual *	50	20	-Improved West and Gaeke Method -Ultraviolet Fluorescence
	24 Hours **	80	80	
Nitrogen Dioxide (NO_2), µg/m^3	Annual *	40	30	-Jacob &Hochheiser modified, ($NaOH$-$NaAsO_2$) Method, Gas Phase Chemiluminescence
	24 Hours **	80	80	
Particulate Matter	Annual *	60	60	-Gravimetric
(Size less than 10µm)	24 Hours **	100	100	-TEOM
or PM_{10}, µg/m^3				-Beta attenuation
Particulate Matter (Size less than 2.5µm)or $PM_{2.5}$, µg/m^3	Annual *	40	40	-Gravimetric
	24 Hours **	60	60	-TEOM
				-Beta attenuation
Ozone (O_3), µg/m^3	8 Hours *	100	100	-UV Photometric
	1 Hour **	180	180	-Chemiluminescence
				-Chemical Method
Lead (Pb), µg/m^3	Annual *	0.5	0.5	-AAS/ICP Method after sampling on EPM 2000 or equivalent filter paper
	24 Hours **	1	1	-ED-XRF using Teflon filter
Carbon Monoxide(CO),	8 Hours *	2	2	-Non dispersive Infrared (NDIR)

mg/m^3	1 Hour **	4	4	Spectroscopy
Ammonia (NH_3), µg/m^3	Annual *	100	100	-Chemiluminescence
	24 Hours **	400	400	-Indophenol blue method
Benzene (C_6H_6), µg/m^3	Annual *	5	5	-Gas Chromatography (GC) based continuous analyzer
				-Adsorption and desorption followed by GC analysis
Benzo(a)Pyrene (BaP)Particulate phase, ng/m^3	Annual *	1	1	-Solvent extraction followed by HPLC/GC analysis
Arsenic (As),ng/m^3	Annual *	6	6	-AAS/ICP Method after sampling on EPM 2000 or equivalent filter paper
Nickel (Ni),ng/m^3	Annual *	20	20	-AAS/ICP Method after sampling on EPM 2000 or equivalent filter paper

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

** 24 hourly or 8 hourly or 1 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.

Annexure – III

National Ambient Air Quality Standards of Environmental Protection Agency's, 1990

Pollutant	**Primary/ Secondary**	**Averaging Time**	**Level**	**Form**
Carbon Monoxide	Primary	8-hour	9 ppm	Not to be exceeded more than once per year
		1-hour	35 ppm	
Lead	Primary and secondary	Rolling 3 month average	0.15 µg/m^3	Not to be exceeded
Nitrogen Dioxide	Primary	1-hour	100 ppb	98th percentile, averaged over 3 years
	Primary and secondary	Annual	53 ppb	Annual Mean
Ozone	Primary and secondary	8-hour	0.075 ppm	Annual fourth-highest daily maximum 8-hr concentration, averaged over 3 years
PM$_{2.5}$	Primary and secondary	Annual	15 µg/m^3	Annual mean, averaged over 3 years
		24-hour	35 µg/m^3	98th percentile, averaged over 3 years
PM$_{10}$	Primary and secondary	24-hour	150 µg/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide	Primary	1-hour	75 ppb	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
	Secondary	3-hour	0.5 ppm	Not to be exceeded more than once per year

Annexure – IV

Health Issues due to Air Pollution in Delhi

Name of Medical Issue	Male N = 788	Female N = 533	Total N = 1321	%
Irritation of eye	354	233	587	44.4
Cough	224	157	381	28.8
Pharyngitis	138	81	219	16.5
Dyspnea	117	97	214	16.2
Headache	78	114	192	14.5
Nausea	50	82	132	10
Vomiting	44	79	123	9.3
Conjunctivitis	59	47	106	8
Abdominal pain	36	50	86	6.5
Respiratory problems	51	27	78	5.9
Rhinitis	23	21	44	3.3
Bronchitis	17	13	30	2.3
Burning of mouth and throat	8	3	11	0.8
Epistaxis	2	4	6	0.5
Depression	2	–	2	0.2
Non-smokers	–	–	–	87
Smokers	–	–	–	13

Mandal et al.2011

Annexure – V

List of proposed moderate and high dust capturing Plants

Type	Plant Species		
Moderate	**Herbs**	**Shrubs**	**Trees**
	1. Lilium species (Lily)	1. Bambusa species (Bamboo)	1. Luecenaleucophloea (Shoe Babool)
	2. Draceana species	2. Lagerstomiaindica (Crape Myrtle)	2. Pinusgerardiana (chilgoja)
	3. Halianthusannuus (Sunflower)	3.Nerium indicum (Kaner Pink)	3. Ficuselestica (Indian Rubber)
	4. Tegetespatula (Genda)	4. Codiumvarigatum (Croton)	4. annonasquamosa (Sugar Apple)
	5. Pothusaureus (Money Plant)	5. Thevetiaperuviana (Kaner Yellow)	5. Mangiferaindica (Mango)
		6. Wrightiaarborea (Dudhi)	6. Argyreiaroxburghira (Wolly Morning Glorry)
		7. Rosa indica (Rose)	7. Ficusreligiosa (Peepal)
		8. Ipomea nil (Beshrum)	8. Acacia famesoana (VilayatiKikkar)
		9. Tabermaemontanadivaricata (Chandani)	9. Psidiumguyava (Amrood)
		10 Acalyphahispida (Copper leaf)	10. Prunuscommiunis (Plums)
		11. Plumeria acuminate (temple Tree)	11. Syzygiumcuminii (Jemun)
			12. Tectonagrandis (Teak)
			13. Citrus lamina (Lemon)
			14. Morus alba (Mulberry)
			15. Archissapota (Chikoo)
			16. Anthosephaluscadamba (Kadam)
			17. Shorearobusta (Sal)

Table (Contd...): List of proposed moderate and high dust capturing Plants

Type	**Plant Species**		
Moderate	**Herbs**	**Shrubs**	**Trees**
			18. Delbergiasissoo (Sheasm) 19. Delonixregiosa (Gulmohar) 20. Albizzialebbek (Siris) 21. Artocarpusintegrifolia (Jack Fruit) 22. Lxoraparviflora (Torch Tree) 23. Bauhinia varigata (Kanchnar) 24. Moringaolieifera (Drum Stick) 25. Aeglefamesiana (Beal) 26. Pithocolobiumdule (Jangalijalebi)
High	1. Colocasiaantiquorum (Elephants Ear) 2. Celosia argentea (cock'scomb)	1. Hibiscus rosasinensis (Gurhal) 2. Bougainvillea glavara (Bougainvillea)	1. Cassia fistula (Amaltas) 2. Pinuscontora (Pine) 3. Bombaxceiba (Samal) 4. Buteamonosperma (Palas) 5. Alstoniascholaris (Satani) 6.Azadirachta indica (Neem) 7. Polyalthialongifokia (Ashoka) 8. Callistemon citrinus (Bottle Brush) 9. Terminaliacatappa (Jangal) 10 Terminaliaarjuna (Arjun)

Table (Contd...): List of proposed moderate and high dust capturing Plants

Type	**Plant Species**		
High	**Herbs**	**Shrubs**	**Trees**
			11. Meliaazadirachta (Melia) 12. Phoenix dactylifera (Khajoor) 13. Ficusinfectoria (Pilkan) 14. Holipteliaintegrifolia (Papadi) 15. Eucalyptus globules (Blue Gum) 16. Madhucaindica (Mahua) 17. Citrus maxima (Chaktora)

LIST OF PUBLICATIONS

LIST OF PUBLICATIONS

1. **Papiya Mandal,**T. Saud, R. Sarkar, A. Mandal, S. K. Sharma, T. K. Mandal , J. K. Bassin; High seasonal variation of atmospheric C and particle concentrations in Delhi, India. (2013) Environ Chem Lett. DOI 10.1007/s10311-013-0438-y.
2. **Papiya Mandal**, R. Sarkar, A. Mandal, T. Saud; Seasonal variation and sources of aerosol pollution in Delhi, India (2014) Environ Chem Lett. DOI 10.1007/s10311-014-0479-x.
3. **Papiya Mandal,** R. Sarkar, A. Mandal; Ambient Polycyclic Aromatic Hydrocarbons and its Carcinogenic and Mutagenic Risk – A Review. (2016) International Advanced Research Journal in Science, Engineering and Technology. Vol. 3, Issue 9.
4. **Papiya Mandal**, R. Sarkar, A. Mandal, P. Patel, N. Kamal; Study on Airborne Heavy Metals in Industrialized Urban Area of Delhi, India (2016) Bull Environ Contam Toxicol. DOI 10.1007/s00128-016-1944-y.

AUTHOR BIBLIOGRAPHY

AUTHOR BIOGRAPHY

Ms. PAPIYA MANDAL
Scientist
Council of Scientific and Industrial Research (CSIR)-
National Environmental Engineering Research Institute
Delhi Zonal Laboratory, Delhi
Email: p_mandal@neeri.res.in,
papiya.mandal1942@gmail.com

Ms. Papiya Mandal received the Bachelor of Engineering (B.E) in Civil Engineering from Malaviya National Institute of Technology Jaipur, Rajasthan University in the year 1995. She completed her Master of Engineering (M.E) in Civil Engineering from Delhi Technological University, (formerly Delhi College of Engineering), Delhi in the year 2000. Presently she is working as scientist in CSIR-National Environmental Engineering Research Institute, Delhi Zonal Laboratory, Delhi. She has published several papers and book chapters in national and international journals. Her research interest includes environmental monitoring and assessment in air, water and soil environment.