

Uncertainty Calculation in Aerosol Measurements

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For the Award of the Degree of

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in Environmental Engineering

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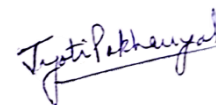
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This is to certify that the research work embodied in the thesis entitled “*Uncertainty Calculation in Aerosol Measurements*” being submitted for the award of degree of **Doctor of Philosophy** to Delhi Technological University, India, represents the original and authentic research work carried out by me under the supervision of **Dr. Anubha Mandal**, Department of Environmental Engineering, Delhi Technological University and **Dr. Shankar. G. Aggarwal**, CSIR-National Physical Laboratory, New Delhi.

The results obtained in this thesis have not been submitted in a part or fully to any other University or Institute for the award of any degree or diploma.

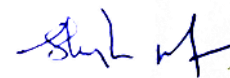
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CERTIFICATE

This is to certify that the research work embodied in the thesis entitled “*Uncertainty Calculation in Aerosol Measurements*” submitted by **Ms. Jyoti Pokhariyal** with registration number **2K12/Ph.D./ENV/07** is the result of his original research carried out in the Department of Environmental Engineering, Delhi Technological University, and CSIR-National Physical Laboratory, New Delhi for the award of **Doctor of Philosophy** under the supervision of **Dr. Anubha Mandal & Dr. Shankar.G.Aggarwal**.

It is further certified that this work is original and has not been submitted in part or fully to any other University or Institute for the award of any degree or diploma.

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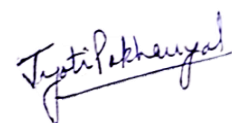
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Jyoti Pokhariyal

ABSTRACT

Mass measurements of particles in the atmosphere are important for regulatory and scientific purposes. In nearly all of the countries, particulates $\leq 10 \mu\text{m}$ in aerodynamic size (PM_{10}) is one of the most significant parameters of National Ambient Air Quality Standards (NAAQS). In India, as given in NAAQS, the PM_{10} regulatory limit is $60 \mu\text{g m}^{-3}$ which is based on the annual mean weight of samples (minimum 104) annually at a specific site taken for two/three days in a week for 24-hour. In this study, the components of uncertainty involved in the filter-based sampling of PM_{10} along with the gravimetric determination of mass have been calculated. As per the EPA guidelines, PM_{10} mass was monitored for a year at NPL (National Physical Laboratory), New Delhi from January 2014 to January 2015. Monitoring of PM_{10} was done using the gravimetric method.

Polyaromatic hydrocarbons (PAHs) are the compound which consists of multiple benzene rings bonded in straight, groups or angular forms. They are also found in atmospheric aerosols. In the atmosphere, they can be emitted primarily as a result of incomplete combustion of natural sources (fossil fuels, forest fires, smoke etc.) or anthropogenic sources (coal burning, vehicular emissions, smoke, etc.) or secondarily by atmospheric processes. Depending on the anthropogenic sources, PAHs may occur in significant concentration in urban and industrial ambient air, i.e., bounded with particulate matter (PM). Benzo(a)pyrene (BaP) is among the most toxic and carcinogenic PAHs. Both PM_{10} and BaP are among the 12 criteria pollutants listed in Indian National Ambient Air Quality Standards (NAAQS). BaP concentration in PM_{10} collected in a representative site of New Delhi was studied during the year 2014–2015. The uncertainty components in measurements were also estimated along with statistical analysis.

In this study, the concentration of metals/element of air quality importance in PM₁₀ were also determined. There are three metal pollutants which are listed as the criteria pollutant in the National Ambient Air Quality Standards (NAAQS) i.e., Arsenic (As), Nickel (Ni) and Lead (Pb). PM₁₀ was collected on quartz filter from January 2014 to January 2015 for the determination of metal concentration in it. 104 PM₁₀ sample was digested in the microwave digestion system and the metals were analyzed on Inductively Coupled Plasma-Optical Emission Spectrometer instrument (ICP-OES) and the metal/element concentration of As, Ni and Pb were calculated. The regulated limits in NAAQS of these metals/elements are Pb -1 $\mu\text{g m}^{-3}$, Ni - 20 ng m^{-3} , As - 6 ng m^{-3} respectively. The studies were carried out to monitor the compliance of metal concentration with reference to the regulatory limits.

The thesis is categorized into five chapters. The short description of each chapter is given as follows:

Chapter 1: Introduction

This chapter includes the definition of aerosols, their sources of emission, effects, properties and their chemical composition. This chapter also deals with the objectives of the study in detail.

Chapter 2: Review of literature

This chapter describes the PM₁₀ studies at the national and international level. Also, the chemical analysis of various parameters was discussed according to different research studies all over the world.

Chapter 3: Materials and Methods

The chapter deals with the description of sampling site, monitoring, collection and instrumental analysis of PM₁₀ samples collected in New Delhi. The method used in the study of polyaromatic

compounds viz., BaP and heavy metals are also described along with the description of instruments used for the analysis of the same.

Chapter 4: Result and Discussion

The chapter deals with a detailed evaluation of mass concentration of PM₁₀ samples in various seasons collected from a representative site of New Delhi from January 2014 to January 2015. The results of the different parameters studied were discussed. Polyaromatic hydrocarbons viz., benzo(a)pyrene is also determined in all the PM₁₀ samples and correlated with mass concentration and season variation. Metals/element which are the criteria pollutants of NAAQS, i.e. Arsenic, Nickel and Lead, are also determined in PM₁₀ samples. Uncertainty in measurement was estimated, and uncertainty budget was calculated for all the PM data.

Chapter 5: Conclusion

This chapter deals with the use of the study and the information provided through various objectives. It also describes the various solutions to control the ongoing issues of air pollution in New Delhi. The future scope of the study was also discussed.

List of Publication

1. **Jyoti Pokhariyal**, A. Mandal and S. G. Aggarwal, Uncertainty Estimation in PM₁₀ Mass Measurements, MAPAN-Journal of Metrology Society of India 34(1) (2019)129–133 (Impact Factor-1.25).
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3. S. G. Aggarwal, S. Kumar, P. Mandal, B. Sarangi, K. Singh, **Jyoti Pokhariyal**, S. K. Mishra, S. Agarwal, D. Sinha, S. Singh, C. Sharma and P. K. Gupta. Traceability Issue in PM_{2.5} and PM₁₀ Measurements, MAPAN-Journal of Metrology Society of India 28(3) (2013)153–166 (Impact Factor-1.25).
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Abbreviations

AAQS	Ambient Air Quality Standards
AQI	Air Quality Index
CCN	Cloud Condensation Nuclei
NAAQS	National Ambient Air Quality Standards
USEPA	United States Environmental Protection Agency
PM	Particulate Matter
PAHs	Polyaromatic Hydrocarbons
OC	Organic Carbon
RM	Reference Method
SI	International System of Units
VIM	International Vocabulary of Metrology
CPCB	Central Pollution Control Board
BaP	Benzo(a) Pyrene
BIPM	Bureau of Weights and Measures
NMI	National Measurement Institutes
TSP	Total Suspended Particle
PCA	Principal Component Analysis
HVS	High Volume Sampler
LVS	Low Volume Sampler
NPL	National Physical Laboratory
TEOM	Tapered Element Oscillating Microbalance
GC/MS	Gas Chromatography/Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
CRM	Certified Reference Material
HPLC	High Performance Liquid Chromatography
EU	European Union
ICP-MS	Inductively Coupled Plasma-Mass Spectrometer
AAS	Atomic Absorption Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometer
NCR	National Capital Region

ISO	International Organization for Standardization
SMPS	Scanning Mobility Particle Sizer
APS	Aerodynamic Particle Sizer
R^2	Correlation coefficients
SD	Standard deviation
SPM	Suspended Particulate Matter
T	Temperature
RH	Relative Humidity

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INTRODUCTION

The term “aerosol” was coined almost 100 years ago (Hinds et al., 1999). It is used to describe solid particles or liquid droplets which form a suspension in air. It is formed by various processes like dust, smog fume, haze, mist, fog and smoke (Seinfeld et al., 1998). Thus, the aerosol is a suspension of particles in air that vary in diameter size of a few nanometers (nm) to 100 micrometres (μm).

Particles can be categorized into two types according to their source of emission. The particles which are directly released into the atmosphere are known as primary particles. Whereas, secondary particles are formed by the gaseous emissions that are transformed to aerosol particles by chemical reactions in the atmosphere and the process is called as gas-to-particle conversion. Secondary aerosols are formed by two simple processes: an existing particle may condense from the gas phase process, or new particle develops by homogeneous nucleation. For example, cloud condensation nuclei (CCN), particles formed by the oxidation of precursor gases of aerosol such as nitrogen oxides, volatile organic compounds (VOCs) and sulphur dioxide (Finlayson-Pitts et al., 1997; Seinfeld et al., 1998). CCN is water-soluble, and it reacts with various substances to form a new particle when the water evaporates (Seinfeld et al., 1998).

Based on the process of formation, different types of sources are identified. Drylands and oceans are the two major natural sources of aerosols in the atmosphere. Seaspray and air bubbles are formed when sea salts and water droplets are emitted into the atmosphere from the surface of the sea. Evaporation of water droplet leaves behind the salt which remains suspended in the air giving rise to sea-salt aerosols (e.g. sodium chloride, magnesium sulphate). Wind laden mineral dust from the dry land regions, like semi-arid and deserts areas is also a major source of primary particles. Other natural

sources are volcanic ash, biological matter (plant remains, pollen, etc.) and clay particles from soil erosion.

Furthermore, anthropogenic activities, like combustion of fossil fuel, burning of biomass and industrial processes are also responsible for the formation of numerous particles. The nature of particles released through industrial activities lead to the formation of secondary particles but vary upon the type of industrial process. Particles coming from the combustion processes have black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs) as dense organic material (Bond et al. 2007). **Figure 1.1**, given below, shows the different sources of aerosols.

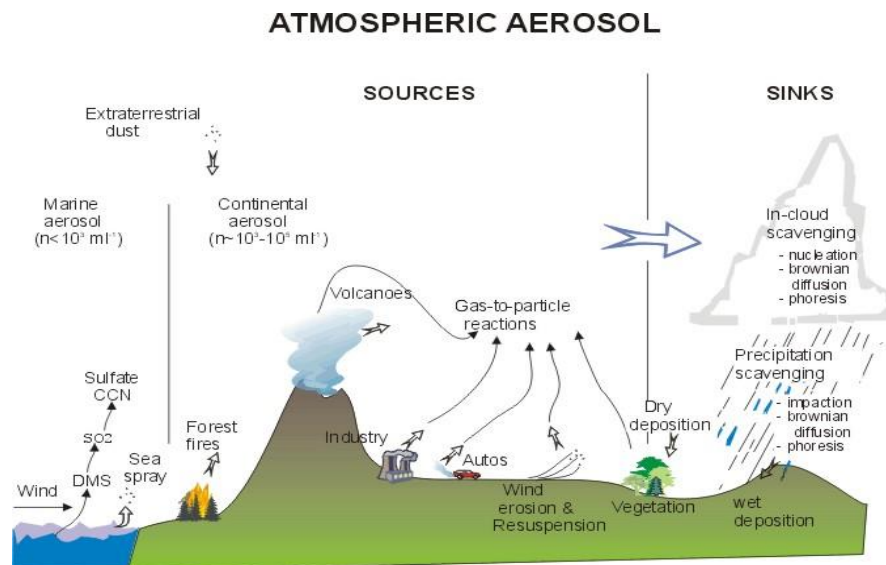


Figure 1.1: Sources and sinks of atmospheric aerosol particles (Source: National Oceanic and Atmospheric Administration NOAA)

1.1 Effects of Aerosols

1.1.1 Climatic Effects

Aerosols have direct or indirect effects on the climate. The direct effect on climate occurs from scattering and absorptive properties of particles which produce changes in the overall radiation balance of the world (Charlson et al., 1992). A light colour aerosol mostly reflects solar radiation and causes

cooling by decreasing the incoming energy. A dark colour aerosol absorbs solar radiation and warming of the climate. Few Aerosols are responsible for cloud formation. When relative humidity is high, particles absorb enough water vapour to grow into a stable cloud droplet, and when they acquire approximate size, they behave as (CCN) (DeMott et al. 2010). As the number of CCN increases, size of cloud droplets become small, increasing cloud reflectivity and lifetime. Thus, the longer lifespan and increased reflectivity of solar radiation cause increased cooling of the atmosphere (as shown in **Figure 1.2**). Absorption of solar radiation by greenhouse gases causes global warming and reduces the cooling effect of aerosols.

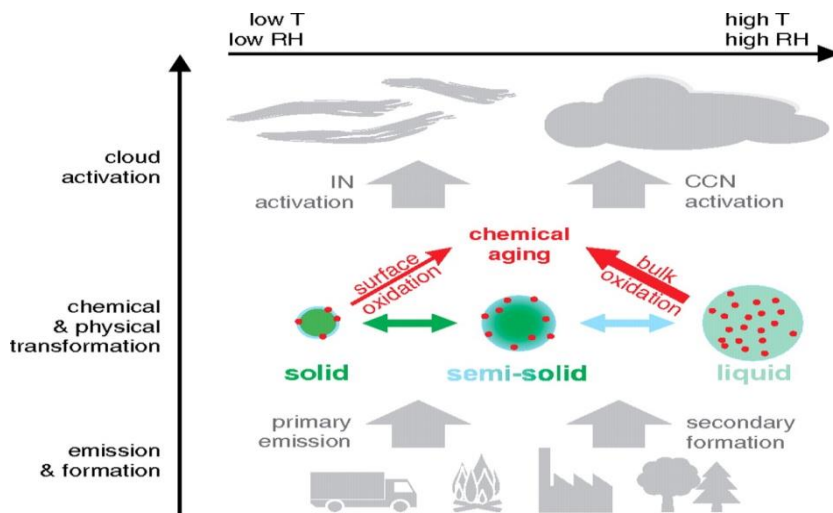


Figure 1.2: Gas uptake and chemical ageing of aerosols (Shiraiwa et al., 2011)

1.1.2 Health Effects

Particulate matter has major contribution in numerous human health issues. Particulate matter is the major health hazard worldwide as compared to any other pollutant. World Health Organization (WHO) evaluates approximately 7 million premature deaths every year from PM pollution (<http://www.who.int/mediacentre/news/releases/2014/air-pollution/en/>). The health effects of the particles depend on their size. Particulate matter greater than 100 μm in size are mostly too large to be

inhaled. Particulate matter having size between 10-100 μm are inhalable but are generally trapped in the mucus linings present in our respiratory system. Particles having size $< 10 \mu\text{m}$ in size are coarse, inhalable and settle deeper in the lungs. These particles size are between 2.5 - 10 μm in diameter (PM_{10}) and are generally deposited in the nose, larynx and pharynx. Particles size less than 2.5 μm in diameter ($\text{PM}_{2.5}$) are fine and travel deeper into the lungs and settle in the trachea, bronchioles, and alveoli.

Studies related to particle pollution show health issues like asthma, reduced lung function, coughing, and difficulty in breathing, premature death and Irregular heartbeat in people with respiratory and cardiovascular disease (Wilson et al., 1996). Due to their health risks, aerosols are significant part of ambient air quality standards (AAQS). United States Environmental Protection Agency (USEPA) has developed National Ambient Air Quality Standards (NAAQS) to regulate the concentration of air pollutants like $\text{PM}_{2.5}$ and PM_{10} particles, in ambient air (www.epa.gov/air/criteria.html). The EPA uses Air Quality Index, which is related to reporting of diurnal air quality and is indicated by a digit between 0-500. The AQI is based on the measurement of five major pollutants present in air using the continuous methods viz., $\text{PM}_{2.5}$ and PM_{10} , ozone, sulfur dioxide, carbon monoxide and nitrogen dioxide. The concentration of each pollutant is converted to a number on the AQI index. (AirNow.gov - Home of the U.S. Air Quality Index).

Annexure 1 given in the annexure section shows the effect of air quality with the concentration of PM_{10} which affect human health (www.airnow.gov).

1.2 Aerosol Properties

1.2.1 Size Distribution

Aerosols present in the atmosphere have various shapes which can be characterized by a particle diameter, which ranges from a few nanometers to about 100 μm . Particle size is used to define the behaviour of aerosols, affecting both their physical and chemical properties. Aerosol distribution is

mostly described in terms of their volume, number or surface. Atmospheric particles can be distributed into different modes based on the particle distributions:

- (i) Nucleation (Aitken) mode** – These particles have size range of less than $0.1\ \mu\text{m}$ in diameter. They are formed during condensation of natural gas into particle or by condensation of vapours in combustion activities. They are small and constitute the majority of particles in the atmosphere.
- (ii) Accumulation mode** – These particles have a size that ranges between $0.1\ \mu\text{m} > d > 1\ \mu\text{m}$ in diameter. They are formed mainly when smaller particles agglomerate to form larger particles or condensation of vapours onto the existing particles, and thus they grow in size. Sometimes, they can also be released into the atmosphere from incomplete combustion. These particles can be replaced from the atmosphere mostly by wet deposition. They also have the highest surface area.
- (iii) Coarse mode** – These particles have size $> 1\ \mu\text{m}$ in diameter. These particles are mostly released into the atmosphere by natural and anthropogenic activities (e.g. sea-salt from sea, mineral dust and soil, biological matter). They have large mass, and due to their rapid sedimentation, they have short lifespan in the atmosphere.

The concentration of mass or volume is measured for the particles in accumulation and coarse modes. The aerosols show characteristic pattern for size, area and volume distributions at various sites (e.g. rural, urban, remote continental or marine areas) (Lagzi et al., 2013).

1.2.2 Chemical Composition

The chemical composition of atmospheric aerosols is very variable and complex. Due to the transformations and different emission sources, every single particle has its composition. Atmospheric particles generally consist of different amounts of nitrate, crustal elements, ammonium, sulphate, sea salt, elemental and organic carbon and other organic matter. Fine particles mostly consist of ammonium, sulphate, nitrate, elemental and organic carbon and few trace metals like nickel, arsenic, mercury,

copper etc. Coarse particles are made up of crustal elements, dust, nitrate, sodium chloride and biological material (e.g. pollen, spores, plant fragments etc.) (Kumar et al., 2017; Kanakido et al., 2018).

Sulphate is present in the atmosphere as sulphur dioxide and is emitted from volcanoes and anthropogenic sources. Nitrate is produced mainly from the oxidation of nitrogen dioxide present in the atmosphere. Ammonium salts present in the ambient aerosols are formed by reactions between ammonia and acids, like nitric and sulphuric acid, which forms sulphate and nitrate salts of ammonia. The chemical reaction between ammonia and hydrochloric acid forms ammonium chloride and sea-salt which are the major sources of chloride in the environment. Carbonaceous compounds constitute a large fraction of the ambient aerosol. Aerosols consist of carbonaceous compounds in the form of BC or elemental carbon (EC) and organic carbon (OC). The major sources of EC are fossil fuel combustion and biomass burning. The main source of OC is a secondary organic aerosol, combustion activities and biomass burning (Lagzi et al., 2013). Trace metals present in the atmosphere are anthropogenically emitted in the atmosphere from industrial production activities. Other major anthropogenic sources that cause metal pollution in the atmosphere include vehicle exhaust which emits lead; smelting emits arsenic, zinc and copper; insecticides which emit arsenic and combustion of fossil fuels emits nickel, selenium, vanadium, mercury and tin (He et al., 2005). Major sources of PAH emissions are of four types: stationary sources (industrial and domestic sources), natural sources, agriculture activities, and mobile emissions. Domestic sources have an important contribution to the total PAHs emissions of the atmosphere. The major domestic sources of PAHs are cooking and heating. The combustion and pyrolysis of gas, garbage, oil, coal, organic materials in industries and wood are all domestic sources. The mobile sources are main sources of PAH emissions in urban regions which relates to the use of lubricant oil, diesel, coal and gasoline. These include exhaust fumes of automobiles, vehicles, railways, aircraft, ships and other vehicles. Natural sources of PAH are unintended burning of forests, moorland

and woodland due to lightning bolt. Volcanic episodes and decaying organic material are also major natural sources which increase the concentrations of PAHs in the environment (Lee et al., 2010).

1.3 Importance of Metrology in Aerosol Measurement

Aerosols are an integral part of atmospheric chemistry and physics. Therefore, they affect the regional as well as global climate. They also have adverse effect on human health, and thus are an important component of ambient air quality standards (AAQS). In most of the AAQS of the countries, particulate matter (PM) whose cutoff sizes are $\leq 10 \mu\text{m}$ are called PM_{10} while $\leq 2.5 \mu\text{m}$ are called $\text{PM}_{2.5}$. They have been included as regulatory parameters with the statement of their reference methods, i.e. RMs (Hauck et al., 2004). Instruments used for these measurements must be calibrated with traceable standards for precise and accurate results. The traceable calibration in PM measurements is not so simple as the measurement depends on numerous parameters, e.g., mass, size, time, flow, etc. Parameters like optical, temperature, wavelength, frequency, pressure also need traceable standards (Aggarwal et al., 2013).

SI traceability in the measurements is all about linking of measurement results with the reference value, i.e., measurement performed by an instrument which is calibrated with traceable standard can be linked with the international system of units (SI) (Aggarwal et al., 2013). The SI is based on seven units: mass in kilogram, length in metre, time in second, temperature in kelvin, electrical current in ampere, luminous intensity in candela and amount of substance in mole. All the terms related to traceability are well defined in International Vocabulary of Metrology (VIM). Thus, measurement traceability is defined as the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty (VIM, JSGM, 2012). Further, every measurement results involve uncertainty. Uncertainty of measurement is the distribution of measurement result that may fairly attribute to value of the measurand. Thus to produce a traceable result from measurement, it is important to use calibrated (SI traceable) instruments,

use certified reference material and also use the standard procedures of the measurements. Secondly, measurement results should be given with the uncertainty considering all the uncertainty sources that can arise in the measurement (ISO/IEC Guide 98, 2008).

The first environmental law laid by the U.S. Congress was the clean air act in 1963. The act creates the relationship between the federal-state that allows the U.S. EPA, to establish (NAAQS) and authorizes the states to implement the regulations to achieve them (USEPA,1997). Almost all countries have their air quality standards named as national or ambient air quality standards. Recent epidemiological studies focused on health risks caused by particulate matter. The regulatory limit of criteria pollutants in the standards varies for different countries. In India, as per the powers conferred Air Prevention and Control of Pollution Act, 1981 and notifications on NAAQS published by the central pollution control board (CPCB), New Delhi values for different pollutants was set up, i.e., the maximum concentrations levels of air pollutants to reduce the harmful effects on human health and atmosphere as given in **Annexure 2**. Apart from the limit values, the data quality objectives and the RMs were also defined. As given in Annexure 2, other criteria pollutants associated with PM mass and size are benzo (a) pyrene (BaP), lead (Pb), arsenic (As) and nickel (Ni). These parameters are generally determined following the method recommended in the NAAQS and standard procedures. The air quality standards describe the measurement procedures of a criteria pollutant, but it gives no information about regulation of measurement traceability and uncertainty of the data or calibration procedures for the instruments. This issue was discussed in BIPM (Bureau of Poids and Measures), France, and 25% expanded uncertainty ($k = 2$) was indicated for $PM_{2.5}$ and PM_{10} mass measurements.

1.4 Motivation for Work

1. This work was taken up as there have been few studies regarding the uncertainty in the PM measurement. Therefore, the metrology of aerosols is very important for the quality of life.
2. Variations in the concentration between PM₁₀ or PM_{2.5} recorded at one place from the same monitoring instruments is due to the limited standards/calibration facilities available.
3. Air quality data is precise and accurate, only if the measurement data is accompanied by uncertainty values.
4. These aerosol measurements whenever and wherever are measured, the results must be acceptable everywhere. These data are comparable and can be used for the betterment of life and also improves the quality of air.

1.5 Objectives

1. **Uncertainty in mass determination:** Particle sampling size depends on the cut size of inlet device (cyclone or impactor) used in the samplers. Further, the cut size of a sampler depends on the flow rate of sampling. However, flow rate may vary depending on the particle loading on the filter and environmental conditions (humidity and temperature). It was observed that because of this flow issue PM₁₀ mass may not truly be mass of PM₁₀. Hence this variable sampling flow generates a significant PM mass bias in the measurement.
2. **Uncertainty determination in benzo(a)pyrene (BaP) measurement:** Polyaromatic hydrocarbons (PAHs) are the persistent chemical in the atmosphere and impact on health adversely. As per NAAQS, the regulated limit of one of the particulate bound PAHs, i.e. benzo(a)pyrene is 1 ng m⁻³ (annual mean). Therefore, to better understand the air quality in context of BaP concentration level, a comprehensive measurement result (traceable and with extended uncertainty) is needed.

3. Uncertainty estimations in the determination of metal pollutants in PM₁₀: As discussed in NAAQS, three metals, viz., lead (Pb), arsenic (As) and nickel (Ni) are given as criteria pollutants, which is associated with their concentration level determined in PM₁₀. Lead is generally present in dominant concentration as compared to that of As and Ni. The regulated limits in NAAQS of these elements are Pb - 1 µg m⁻³, Ni - 20 ng m⁻³, As - 6 ng m⁻³ respectively. As stated above, concentration with uncertainty needs to determine as per NAAQS guideline to present an example for future studies.

REVIEW OF LITERATURE

This chapter includes PM₁₀ studies at the national and international level. Also, the chemical analysis of various parameters was discussed with reference to different studies all over the world.

2.1 Mass Concentration and Seasonal Variation of PM₁₀ Samples

PM₁₀ are small particles with an aerodynamic diameter of $\leq 10 \mu\text{m}$. Due to their small size (it includes PM₁, PM_{2.5}), they can reach deep within the lungs where they get deposited and cause harmful health effects. PM₁₀ is also responsible for reduction in visibility due to their small size they remain in gaseous state. Measurements of PM mass concentrations are important for regulatory and scientific reasons. Few years back, most of the NAAQS for aerosols was based on the mass concentrations for PM₁₀. Later, United States established similar standards for particles smaller than 2.5 μm in aerodynamic diameter (PM_{2.5}) (USEPA, 1997). Therefore, PM mass concentrations are consistently measured in monitoring stations in various parts of the world. The most common technique used for measuring PM mass concentration is gravimetric using filter substrate (Chow et al. 1995; McMurry et al. 2000). Filters are weighed under controlled meteorological conditions before and after sampling, and mass concentrations are determined from the increase in filter mass and the volume of air sampled. The samplers used for monitoring consists of inlets that eliminate particles above a specified cut off size.

Chow et al., 1995, critically reviewed that methods used in measurement and their affectivity to the compliance are the key matter of NAAQS. The samples taken for measurement are also used for source identification and to estimate the efficiency of controls and to regulate the relationships between air pollution and human health. Topics related to measurement procedures used to determine compliance with standards, present and future measurement procedures and their limitations were also identified.

Keary et al., 1998, studied the PM₁₀ mass concentration for various areas in Dublin City during 1st January 1996 to 30th June 1996. Gravimetric measurements of PM₁₀ mass concentration were made using low - volume Partisol 2000 samplers with an impaction type PM₁₀ inlet. The collection was done on the glass fibre filters of 47 mm in diameter. A tapered element oscillating microbalance (TEOM) PM₁₀ mass monitor was also used for finer time resolution measurements. A comparative analysis was performed between the procedures of mass concentrations of PM₁₀ and mass concentration obtained from the standard black smoke method and showed that the relationship is site-specific. The PM₁₀ mass concentration was analyzed with reference to meteorological factors and traffic density. During the first six months of 1996, the mean PM₁₀ concentration ranged from 49 $\mu\text{g m}^{-3}$ at the urban site of Dublin city centre to 14 $\mu\text{g m}^{-3}$ at the suburban site. Statistical analysis shows a good correlation among PM₁₀ levels and traffic density and bad correlation between PM₁₀ levels and amount of rainfall, air temperature and wind speed.

McMurry et al., 2000, reviewed the developments in aerosol measurements. This review focused on the determination of aerosol integral, physical-chemical properties, size distribution and size-resolved composition of aerosols. These measurements help in the study of secondary aerosols which are formed by the atmospheric chemical transformation. In 1970s, the development of instrumentation led to the formation of calibration aerosols of known size, concentration, and composition. But the uncertainties measurements of calibrated aerosols generated in the laboratory were lacking even if the instruments used for atmospheric measurements were calibrated. This was due to the variation in the aerosol properties like density, composition, and shape, etc. For accuracy in measurements, more efforts are required which can be achieved by real-time atmospheric sampling. Only 10% of the organic species in the atmosphere can be identified by analytical methods. Therefore, there has to be significant development in the aerosol measurements. The development of various modern instruments

significantly expands the range of aerosol in the atmosphere that can be measured experimentally. They claimed that the instruments represent the most important advances in aerosol analysis in recent years.

Mönkkönen et al., 2004, studied mass concentration and number concentration of PM_{10} of urban areas in various seasons in New Delhi during 2002 along with the measurement of SO_2 , NO_2 and CO concentration. It was observed that the number concentration of aerosols increases upto $300 \mu g m^{-3}$ of the mass concentration and then decreases thereafter although the mass concentration keeps increasing. The nonlinear trend is explained by means of a dynamic model using the concept of coagulation sink. When the mass concentration is relatively low, the linear relationship between number concentration and mass in the ambient air is valid. A high sink indicates high number concentration causing decrease in the number against the mass graph. Strong diurnal, weekly and seasonal deviations in concentration were studied. They observed that aerosols number concentrations were high in the morning and the evening. The number concentration of aerosols was high in March and lowest in June while mass concentration was highest in November and lowest in the month of June. The number concentration of aerosols was high in weekdays while mass concentration was high at weekends. The number concentration of aerosols relates with concentration of NO_2 , which shows that the main source of aerosols in New Delhi is vehicular emission and fossil fuels and biofuels were minor sources.

Karar et al., 2006, studied seasonal and spatial variations of TSP (total suspended particle) and PM_{10} from November 2003-2004 of an Indian city, Kolkata, having high pollution and population density. The ambient mass concentration of PM_{10} and TSP was measured at two sampling sites (one residential and one industrial) of Kolkata. Sampling sites were identified according to the activities prevailing in the region. Meteorological data of factors like wind speed, rainfall, wind direction, temperature and relative humidity were also taken from Meteorological Division of Kolkata, India for the period of study. The 24h mean concentrations of PM_{10} and TSP was measured and varied in the range of 68.2–280.6 $\mu g m^{-3}$ and 139.3–580.3 $\mu g m^{-3}$ for residential area, while for industrial area it was 62.4–401.2 μg

m^{-3} and $125.7\text{--}732.1 \mu\text{g m}^{-3}$ respectively. In winters, the concentration of both PM_{10} and TSP is highest as the particulates stay in the atmosphere for longer time due to low mixing height and low winds. Analysis of particle size shows that PM_{10} is almost 52% of TSP from residential area and 54% of TSP from industrial area. The high concentration in industrial area may be due to road dust, industrial emissions, soil dust and automobile exhausts. Non-uniform mixing conditions and emission of air pollution sources in an urban area causes spatial variation of concentration of pollutants.

Aggarwal et al., 2010, reviewed the data published from the laboratories and aerosol field operations showing the importance of aerosol metrology. A study of atmospheric aerosols is very complex due to the restricted number of certified reference materials, traceability data and standard procedures for aerosols. It is difficult to study aerosol properties with minimum uncertainty. The recent advances in aerosol analytical methods have enhanced the knowledge about the chemical characterization of aerosols, sources, concentration and their possible climate impacts. The various analytical techniques used are gas chromatography/flame ionization detector, mass spectrometry, isotope ratio mass spectrometry, ion chromatography, organic or elemental carbon and organic carbon analyzers, and for physical parameters using hygroscopicity tandem differential mobility analyzer (HTDMA) and scanning mobility particle sizer (SMPS), cloud condensation nuclei-counter.

Bathmanabhan et al., 2010, conducted the analysis and explained the daily, weekly and seasonal variation of 1h average concentrations levels for PM_1 , $\text{PM}_{2.5}$ and PM_{10} in Chennai, India from November 2007 to May 2008. The PM concentration was highest during daytime in diurnal cycle and lowest concentration of PM was found in the afternoon and night. The seasonal variation of PM indicated increased levels in post monsoon season (PM_{10} - $189 \mu\text{g m}^{-3}$, $\text{PM}_{2.5}$ - $84 \mu\text{g m}^{-3}$, PM_1 - $66 \mu\text{g m}^{-3}$) than in the winter season (PM_{10} - $135 \mu\text{g m}^{-3}$, $\text{PM}_{2.5}$ - $73 \mu\text{g m}^{-3}$, PM_1 - $59 \mu\text{g m}^{-3}$) and summer season (PM_{10} - $102 \mu\text{g m}^{-3}$, $\text{PM}_{2.5}$ - $50 \mu\text{g m}^{-3}$, PM_1 - $34 \mu\text{g m}^{-3}$). The size distribution of particle showed two modes viz., accumulation and coarse during summer, winter and post-monsoon seasons. The

frequency distribution showed PM_{10} concentration values under moderate to poor categories. More than 50% of 24-h mean PM_{10} concentrations showed noncompliance with NAAQS, India ($100 \mu\text{g m}^{-3}$) and WHO standard ($50 \mu\text{g m}^{-3}$) in post-monsoon and winter seasons. In case of average $PM_{2.5}$ concentrations, 75% of it showed noncompliance with NAAQS and WHO irrespective of seasons.

Singh et al., 2010, studied the ambient levels of different pollutants like TSP, PM_{10} , NO_2 , and SO_2 during the period of pre Diwali, Diwali day, post Diwali along with foggy days in months of October, November, December in Delhi during 2002 - 2007. Widespread usage of firework during Diwali was responsible for the changes in the air quality during Diwali. As compared with the data of industrial sites in Delhi in all the years, TSP concentration during Diwali festival is almost of the same order while the levels of PM_{10} , NO_2 and SO_2 increased from twice to six times. Similar observation was found when the levels of all the pollutants studied were compared with foggy days in December. The concentration of pollutants was higher throughout Diwali festival due to unfavorable meteorological conditions, like reduction of 24 hour mean mixing height, wind speed and temperature. The trend analysis displays that the concentration of pollutants was highest on Diwali day. The levels decreased gradually after the festival. Thus, the 24-h values for TSP and PM_{10} during 2002 to 2007 and for NO_2 during 2004 and 2007 were found to exceed the regulatory limits of NAAQS. It was concluded that use of fireworks during Diwali festival caused emission and accumulation of TSP, PM_{10} , NO_2 and SO_2 and affected the ambient air quality significantly.

Sharma et al., 2012, studied mass concentrations for PM_1 , $PM_{2.5}$ and PM_{10} at Delhi within the period of August to December 2007. The mean mass concentration for PM_{10} , $PM_{2.5}$ and PM_1 showed huge variations. It ranged from 20-180 $\mu\text{g m}^{-3}$ in monsoon and from 100-500 $\mu\text{g m}^{-3}$ in the winter season. High levels of mass concentrations in PM_1 , $PM_{2.5}$ and PM_{10} , can be related with high relative humidity and decrease in concentration can be related to high ambient temperature. The PM_1 , $PM_{2.5}$ and PM_{10} levels after the elapsed times are simulated with average mass scavenging coefficients. The study of the

area with HYSPLIT model is useful in predicting the PM_1 , $PM_{2.5}$, PM_{10} concentration in winter season along with monsoon season in air-mass movements over Delhi.

Triantafyllou et al., 2012, conducted study on the temporal variation of PM_{10} concentrations for two main urban regions (Athens and Thessaloniki) of Greece during 2001 to 2010. Literature survey has shown that PM concentration in the atmosphere in main cities of Greece was more than other cities in Europe with same geographical area. These data were based on studies that were performed over a short duration. In Athens, yearly average concentrations of PM_{10} at the urban sampling sites varied between 32.3 to 62.5 $\mu\text{g m}^{-3}$ and in suburban sites between 21.5 to 62.9 $\mu\text{g m}^{-3}$. While in Thessaloniki, PM_{10} concentrations varied between 41.7 to 70.8 $\mu\text{g m}^{-3}$ in urban sites and between 23.4 to 51.5 $\mu\text{g m}^{-3}$ in suburban sites. At urban stations in Athens, the highest and the lowest monthly mean concentrations of PM_{10} are studied in the winter or autumn season and in summer season, respectively. For suburban sites, the highest levels were found in spring season and lowest in the winter season. In Thessaloniki, highest PM_{10} values were in the autumn season while in summer season the lowest levels were observed for both the urban and the suburban sites.

Aggarwal et al., 2013, reviewed the measurement traceability of PM. In many countries, particle size and measurements of mass concentration are the key parameters to study their AAQS. The regulatory limits of mass concentration of PM is measured on annually and the hourly time-weighted-mean basis for particles having size of $\leq 2.5 \mu\text{m}$ in diameter known as $PM_{2.5}$ and for $\leq 10 \mu\text{m}$ are known as PM_{10} . These regulatory limits are different in various countries. There has been very less work done globally on traceability and calibration of PM measurements. The review discusses the air quality regulation in different countries, standard methods used for the measurement of particle size and mass concentration, uncertainty in PM measurements, calibration facility status of size and mass of PM, National Measurement Institutes (NMI) working on PM measurements, limitations in the studies of PM

measurement etc. The traceability related to SI in PM measurements is acceptable everywhere wherever and whenever it is measured and data should be used to improve the quality of air.

Singh et al., 2013, studied the PM₁₀ size distribution and its ionic characteristics during January 2006 to December 2007 in Delhi. The sampling of PM₁₀ was carried out by 8-stage Andersen Cascade impactor sampler. The mass for fine particles (PM_{2.5}) along with coarse particles (PM_{10 to 2.5}) was calculated from mass of particle measured in different stages. Mean mass measurement of PM_{2.5} and PM_{10-2.5} were found as $306 \pm 182 \mu\text{g m}^{-3}$ and $136 \pm 84 \mu\text{g m}^{-3}$ that exceeded the prescribed limit of NAAQS ($60 \mu\text{g m}^{-3}$ for PM₁₀ and PM_{2.5} is $40 \mu\text{g m}^{-3}$). The maximum concentrations of PM₁₀ and PM_{2.5} was found as 505 ± 44 and $368 \pm 61 \mu\text{g m}^{-3}$ in the summer season in the month of June 2006. This is due to repeated dust storms in summer season where the coarse particles are present more than the fine particles. Thus, the lowest concentration for PM_{10-2.5} and PM_{2.5} was found as $35 \pm 9 \mu\text{g m}^{-3}$ and $29 \pm 13 \mu\text{g m}^{-3}$ in the summer in the month of September 2007. PM_{2.5} concentration was high in winter season than in summer season as there is an increased emission from human activities, anthropogenic sources and biomass burning. The PM_{2.5}/PM₁₀ ratio (0.58) was high in winter and low (0.24) in monsoon. Apart from mass concentration, main cations, e.g. Mg²⁺, NH₄⁺, Na⁺, K⁺ and Ca²⁺ and anions F⁻, Cl⁻, NO₃⁻ and SO₄²⁻ were also determined.

Gupta et al., 2013, used a Weather Research and Forecasting model combined with chemistry module during June, 2010. This model used simulated PM₁₀ mass concentration to observe effect of transportation of long range pollutants in air above Delhi along with diverse geographical regions covering the whole of Asia and respective emissions. In Delhi, PM₁₀ concentrations are often high which exceeded the standard limits of ambient air quality standards. It was observed that Delhi contributed alone to 11% – 41% to emissions. Rest of the contribution was from outside Delhi. Thus, regional chemical transport model used in the study performs well and it can be used to study the transport of long range pollutants and effectively address the effect of the remote sources away from the

airshed in urban area. This model can thus be used as a tool for development and implementation of the regulatory policies for the control of air pollution.

Zhao et al., 2013, studied the visibility data at Shenyang in Northeast China during 2010 to 2012. Mass measurements of PM along with meteorological parameters were also statistically analyzed. These measurements showed that monthly mean values of visibility in Shenyang were high in the month of March and September (19.0 ± 4.3 km and 17.1 ± 4.3 km, respectively). Visibility was low in January (11.0 ± 4.7 km). Wind speed was the major meteorological parameter that affected mass concentrations of PM and visibility. The presence of fine particles in urban regions is the main factor for the decrease in visibility in Northeast China. The weekly and diurnal variation of visibility and PM is mostly due to human activities. It was concluded that fine particles were responsible for pollution in air and visibility in the studied urban region of Northeast China.

Achilleos et al., 2014, studied the PM₁₀ concentration in Nicosia (urban site) from 1 April 1993 to 11 December 2008 and in Ayia Marina (rural sites) from 1 January 1999 to 31 December 2008 in Cyprus. Air quality is affected by transported and local pollution and dust storms in Cyprus. The measurement was performed using TEOM. Mass concentration of PM₁₀, satellite records and meteorological data was used in the study of days of dust-storm. A Generalized Additive Model (GAM) was used for studying long-term trends over a week, a month, relative humidity, ambient temperature and wind speed. In Nicosia, yearly PM₁₀ mass concentration varied within $50.4 - 63.8 \mu\text{g m}^{-3}$ which exceeded the annual standard limit of EU ($40 \mu\text{g m}^{-3}$). A significant impact of urban sources was observed in Nicosia during 2000-2008, and it was observed to be high in weekday, colder months, traffic hours and low-wind conditions. The annual PM₁₀ concentration in Nicosia decreased from $59.4 \mu\text{g m}^{-3}$ in 1993 to $49.0 \mu\text{g m}^{-3}$ in 2008 due to the implementation of regulation policies for strict traffic emission norms in Cyprus. Yearly concentration in Ayia Marina varied from 27.3 to $35.6 \mu\text{g m}^{-3}$. The concentrations at Cyprus are similar to concentrations reported in other countries in Eastern Mediterranean. During dust storms, mean

diurnal PM₁₀ concentration was 100 µg m⁻³ since 2000 which was higher than in previous years. Frequent dust storm episodes were responsible for diurnal PM₁₀ limit exceedances. Other natural sources like sea salt and resuspended soil may be the reason for limit exceedances of PM₁₀.

Krasnov et al., 2014, studied the PM₁₀ concentrations to monitor the impact of dust storms in Beer - Sheva, Negev, Israel, from 2001-2012. During the study, it was observed that diurnal PM₁₀ concentration ranged between 6-2000 µg m⁻³. Every year, almost 10% of the diurnal concentration values exceeded the calculated permissible values (71 µg m⁻³). Mean daily total contribution of dust to PM₁₀ of 122 µg m⁻³ was determined for the entire duration of study. Also, the parameter of dust storm intensity was used in the study to analyze various storms having high PM₁₀ concentration (hourly mean of 1000 - 5197 µg m⁻³). The study indicated that major storms occurred in the past three years of the study. It was observed that the arid urban areas have high PM₁₀ levels. It was concluded that there is little information about the impact of dust storms to atmospheric PM₁₀ for urban areas near to dust sources.

Mishra et al., 2015, collected the real time PM records from construction sites of metro to study the pollution caused by construction activities of metro train. EPAM HAZ 5000 dust sampler was used for sampling and collect the data for the PM₁₀ mass concentration at construction sites of metro at Najafgarh, Badli and Mayapuri areas of Delhi, India. It was observed that PM levels were very high during rush hours at Najafgarh (245 ppm) and Mayapuri(222 ppm) construction sites of metro. However, hourly weighted mean of PM₁₀ mass concentration exceeded the NAAQS limits of 100 µg m⁻³.

Deng et al., 2015, conducted study on concentration levels of ambient PM₁₀ in urban areas of Changsha, China. Meteorological factors and PM₁₀ concentrations were observed hourly during 2008. The variation in PM₁₀ concentration and the meteorological factors associated were statistically analyzed. The PM₁₀ concentration was high in cold seasons and weekdays than in hot seasons and weekends.

Bimodal distribution was observed in the diurnal PM₁₀ variations in the morning and evening hours. The temporal variation is affected by both meteorological factors and anthropogenic activities. High concentration in daytime is due to human activities and at nighttime is mainly due to unfavourable meteorological factors. High concentrations in night were the main reason for the existence of exceedance periods. It was concluded that the best way to decrease pollution in China was by regulating the concentration of PM₁₀ at night-time. The study conducted provided data to implement control strategies in China.

Singh et al., 2015, studied the levels of mass concentration of PM_{2.5} and PM₁₀ from industrial site for two seasons in Delhi by portable aerosol spectrometer. It was observed that mean concentration varied from 57 to 457 $\mu\text{g m}^{-3}$ for PM₁₀ in pre-monsoon season and 78 to 900 $\mu\text{g m}^{-3}$ in post monsoon. The concentration PM_{2.5} varied between 15 to 65 $\mu\text{g m}^{-3}$ for pre monsoon season and 16 to 772 $\mu\text{g m}^{-3}$ for post monsoon. The average concentration showed increased values on weekdays as compared to weekends during pre-monsoon while the concentration during weekends was higher than weekdays during post monsoon. The mass fraction of PM_{10-2.5} showed high concentration in post monsoon (105 $\mu\text{g m}^{-3}$) and pre-monsoon season (81 $\mu\text{g m}^{-3}$). It was concluded that the people residing in adjoining areas of industries are at a high risk of developing respiratory issues.

Watson et al., 2015, studied the commonly used method to determine the concentration of PM_{2.5} and PM₁₀ through sampling on the filter medium and weighing before and after the air is drawn through the filter. The weight gain of the filter from the PM deposition is also affected by retention of water by the filter, adsorption of gases onto the filter, electrostatic charges between the filter and the surface, contamination in handling of filter, evaporation loss, and losses or additions to filter material. Filters must be weighed and equilibrated in an environment having constant temperature and humidity with clean air. Balances used for weighing of filters must be calibrated with primary standards and must have sensitivities of $\leq 1 \mu\text{g}$. Electrostatic charges are neutralize by ionizing sources. Filters must be checked

for any faults before and after sampling, replicate filter weights, periodic balance zero and periodic checks, independent system and performance audits are part of quality control and assurance.

Lacey et al., 2015, estimated the uncertainty of measurement for three different TSP sampler along with uncertainty budget. The objectives of this study was estimation, development and measurement of total uncertainty of atmospheric factors. Three different TSP samplers used was TMU HVS with flow rate- $1.42 \text{ m}^3 \text{ min}^{-1}$, TMU LVS Sampler with flow rate- 17 L min^{-1} and EPA TSP with flow rate- 1.1 and $1.7 \text{ m}^3 \text{ min}^{-1}$. The total measurement uncertainty was in the range of $6.1 \times 10^{-6} \text{ g m}^{-3}$ to $18 \times 10^{-6} \text{ g m}^{-3}$, which signified the uncertainty measurement of 1.7% to 5.2%. Uncertainty parameters that had major contribution in total uncertainty were uncertainty in the measurement of pressure drop over orifice meter and uncertainty of airflow standard. Five uncertainty parameters for environmental conditions were taken into consideration for the measurement of viz., volumetric airflow rate, ambient TSP concentration, ambient relative humidity, ambient temperature, and ambient pressure. Volumetric airflow rate and ambient TSP concentration have major contribution to the overall uncertainty. The procedure used in the study can be used for other studies where there are no methods available to measure the data empirically.

Song et al., 2016, studied the ambient PM_{10} in Pingdingshan, industrial city in North China. PM_{10} samples collection was performed using three different sampling sites (roadside, mining area, and power plant) in Pingdingshan City. Overall 44 PM_{10} samples were collected in the winter season of 2013 and were gravimetrically measured and chemically analyzed. It was found that the PM_{10} emission sources in Pingdingshan were, industrial metal smelting, coal burning and disintegration of waste dumps.

Filonchyk et al., 2016, studied the concentration of pollutants in the Gansu State of China in the month of June and August of 2015. The mean PM concentrations in Gansu State exceeded the prescribed limits of WHO guideline which indicated a severe effect on humans and the atmosphere. The PM pollution is much more severe in China than in USA and Europe. $\text{PM}_{2.5}$ concentration exceeded the NAAQS

standards in 20% of all summer days while for PM_{10} concentration; it exceeded the NAAQS standards in 33% of all summer days. PM_{10} concentrations was found in the range of $60\text{--}70 \mu\text{g m}^{-3}$ which was similar for all other studied cities of China. Thus, it was concluded that PM pollution was a regional problem in China.

Sehgal et al., 2016, conducted study on the air quality for two locations in Delhi in 2013. It was observed that the concentration of PM_{10} , benzene and oxides of nitrogen was found to exceed the standard limits of NAAQS. The concentration of PM_{10} exceeded the standard limits for 24 h mean measurements given by NAAQS in almost on all sampling days. The study conducted also showed seasonal variation in the concentration of pollutants, very high in winter season due to comparatively stable meteorological conditions and the low concentration in monsoon due to, strong winds, turbulence and rains. The correlation between PM_{10} , benzene and NO_x levels shows that the vehicular emissions have major contribution in increasing the levels of these pollutants. Policies have to be made by regulatory authorities for improving the quality of air in Delhi.

Chlebowska-Styś et al., 2017, analyzed the concentrations of PM_{10} at urban sites and traffic stations in the selected 17 European cities. The data was analyzed from report of Chief Inspectorate of Environment Protection and European Environment Agency. The annual and diurnal mean concentrations of PM_{10} in 2014 showed that in the European cities there is a problem with high PM_{10} concentrations, mainly in Poland and some eastern countries. For diurnal mean concentrations of PM_{10} , the highest concentrations were found in the winter season This is due to the low-stack-emissions from the municipal sector which lowers the air quality in these cities.

Rovelli et al., 2017, investigated the mass concentration, temporal variability and size-distribution of ambient PM in an urban site of Como in Northern Italy during May 2015 to March 2016. For the collection of particulates of $0.028 - 10 \mu\text{m}$ of size range, a 13-stage Low Pressure Impactor was used. The PM mean mass concentration was higher during the heating season. Concentration levels were 3.5

times more in heating season than non-heating season. Temporal variability was due to PM urban emission sources like traffic, household heating which mostly influenced the submicrometer and fine particles. The average concentrations for PM_{2.5} (22.4 $\mu\text{g m}^{-3}$) and PM₁₀ (27.7 $\mu\text{g m}^{-3}$) exceeded the annual Air Quality Guideline limits (10 $\mu\text{g m}^{-3}$ and 20 $\mu\text{g m}^{-3}$) regulated by WHO.

Zhang et al., 2017, collected data for dust deposition and ambient PM₁₀ concentration from 14 monitoring sites in Xinjiang State of China from 2000 to 2013. It was found that yearly mean dust deposition varied from 255.7 to 421.4 t km⁻². Yearly mean PM₁₀ concentration ranged from 100 to 196 $\mu\text{g m}^{-3}$. The highest dust deposition of 1394.1 t km⁻² and highest PM₁₀ levels of 352 $\mu\text{g m}^{-3}$ was found in Hotan which exceeded the maximum limits of WHO standard for long-term exposure (WHO, 2016b).

Hamid et al., 2018, studied the data received as per Environment Department and determined 24h mean concentrations of PM₁₀ during 2010 to 2014. The relationship between concentration of PM₁₀ and monsoon season in Larkin and Pasir Gudang (Northeast Monsoon and Southwest Monsoon) was also studied. It was estimated that PM₁₀ concentration was high in the Southwest Monsoon because of the dry season. The results indicated that highest PM₁₀ concentration was reported during 2010 -2014 in the monsoon season. During the Southwest Monsoon, the yearly mean of PM₁₀ concentration exceeded the permissible limit of Ambient Air Quality Standard of Malaysia (50 $\mu\text{g m}^{-3}$) while during the Northeast Monsoon, the PM₁₀ concentration remained below the standard limit. The study concluded with the observation that the PM₁₀ concentration during 2013 was higher for every monsoon season at both the sites.

Pokhariyal et al., 2018, evaluated the uncertainty parameters involved in the determination of mass concentration of PM₁₀ gravimetrically. The sampling of PM₁₀ was performed as per the EPA guidelines, from January 2014 to January 2015 at NPL, New Delhi. The 24-h average mass concentration for 104 samples of PM₁₀ ranged from 32.5 to 480.2 $\mu\text{g m}^{-3}$ during the period of one year. Mass loading was high during the month of December to February. Major uncertainty component was the flow rate of the

size-segregated PM sampling. The maximum contribution in the total uncertainty budget came from the flow rate during the sampling (90.4%) and charge effect of filter (6.7%). Other uncertainty components, e.g., balances (0.39%) and conditioning of filter (2.39%) had the minimum contribution.

Jain et al., 2019, conducted study of spatial and temporal variations for chemical characterization of PM₁₀ in the Indo Gangetic Plain (IGP) India. The study also focused on source apportionment of PM₁₀ on the same chemical species with the help of various receptor model like Positive Matrix Factorization (PMF) and Principal Component Analysis (PCA). The study focused mainly on the comparison of the models used and produced robust results. The mean PM₁₀ concentration was studied at Delhi, Varanasi, and Kolkata and was found as 202.3 ± 74.3 , 206.2 ± 77.4 and $171.5 \pm 38.5 \mu\text{g m}^{-3}$, respectively from January, 2011 to December, 2011. Study of all the three models showed almost same source profile in all the monitoring areas apart from few sources. The PMF analysis showed secondary aerosols, soil dust, automobile emissions, biomass and fossil fuel combustion, salts of sodium and magnesium and industrial activities as major sources in Delhi. While in Varanasi, similar sources were reported along with coal combustion instead of fossil. In Kolkata, the emission sources were recognized as secondary sulfate, soil dust, secondary nitrate, biomass combustion, vehicular emission, sodium and magnesium salt and industrial emission. Secondary aerosols, vehicular emission, biomass burning, and soil dust were the main source of PM₁₀ mass concentration in the IGP of India as per the studies by the three models used.

Pant et al., 2019, reviewed the measurement methods and data on air pollution in India. Air quality is health risk to the environment. In India, major part of the population resides in regions having poor air quality. PM₁₀ mass measurement data from the national regulatory monitoring network were analyzed during 2004–2015. Only less than 1% of PM₁₀ measurements results complied with the air quality guideline given by WHO ($20 \mu\text{g m}^{-3}$), while 19% remained within the Indian air quality standard limit for PM₁₀ ($60 \mu\text{g m}^{-3}$) Efforts should be taken for better measurement reportage and quality through the

use of better monitoring systems, consistent methods for data analysis and sampling and easier data accessibility.

2.2 Study of Polycyclic Aromatic Hydrocarbons (PAHs) as Benzo (a) pyrene

Polyaromatic hydrocarbons were known to be among the most toxic air pollutants in urban air. They are mostly formed through incomplete combustion of organic material. Seventeen PAHs, including BaP, have been identified for environmental monitoring and compliance purposes. Benzo (a) pyrene is a type of PAH that is formed as a by-product of incomplete combustion of carbon. Apart from ambient aerosols, it is also found in wastewater, surface water, drinking water and in charbroiled foods. It has a chemical formula of $C_{20}H_{12}$. It has a structure formed by a benzene ring fused to pyrene, as shown in **Figure 2.2**. It is mostly emitted in air and exists in PM phase. BaP is among the most toxic and carcinogenic PAHs. Both PM_{10} and BaP in it are among the 12 criteria pollutants listed in NAAQS, India.

The study conducted included determination of BaP in PM_{10} samples.

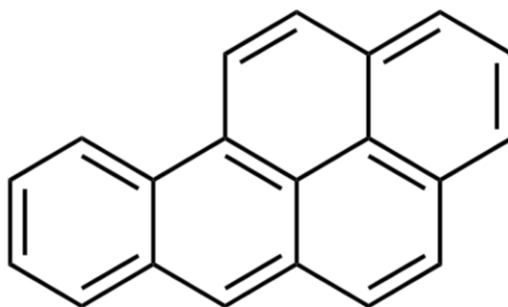


Figure 2.2: Structure of BaP

Latimer et al., 2003, discussed the important fate processes, sources and transport of PAHs in anthropogenic sources, marine environment, global mass balances, major transport routes and processes, spatial source trends, spatial distributions in seawater, and ocean sediments. PAHs as aromatic compounds can possibly affect a variety of marine organisms. They are formed by high pressure

reactions of natural organic matter and naturally by low temperature; and thus form a significant part of petroleum hydrocarbons. They are also formed from partial combustion of wood and petroleum products. PAHs are present in all environmental matrix, i.e., water, sediment, air and biota etc. Some PAHs, like perylene, are formed from the breakdown of natural organic matter, such as peat, in the aquatic environment.

Zhang et al., 2009, estimated 16 PAHs (registered as criteria pollutants in the US EPA) for atmospheric emissions of 37 countries by using data of emission factor and emission activity during 2004. A data report was compiled for geometric means, emission factors and frequency distributions used for emission calculation and also for uncertainty measurements, respectively. The data for 37 countries were compared with data of other PAH emission. The major sources of the world's total atmospheric emission for 16 PAHs in 2004 came from 56.7 % of biofuel, 17 % of wildfire and 6.9 % of consumer product usage. The topmost three countries with the highest PAH emissions are China, India and US. The emission sources of PAH in the various countries showed considerable variation. For example, the burning of biofuel was the major source of PAH in India. In Brazil wildfire emissions were the main source of PAH while in United States consumer products was a significant source of PAH emission. In China, biomass combustion was the major emission source along with the coke ovens. BaP contributed for 0.05 % to 2.08 % of total PAH emission. Thus, developing countries contributed to much higher percentages of BaP.

Shi et al., 2010, collected PM₁₀ samples from six monitoring sites in Tianjin, China during April 2008 to January 2009. Seventeen PAHs were determined in PM₁₀ for their concentration. Characterization of PAHs for spatial and seasonal variations was also performed. The most important PAHs found in the samples of PM₁₀ were phenanthrene, chrysene, benz[a]anthracene, fluoranthene, pyrene, benzo[b]fluoranthene, anthracene, indeno[1,2,3-cd], pyrene, and BaP constituting to almost 85% of total PAHs. The concentration of total PAHs in six monitoring sites varied from 23.4 to 513 ng m⁻³.

Spatial variations were observed due to various types of sources of emission. In heating period, the concentration of total PAHs at two monitoring sites viz., Dogli Monitoring Station (DL) site and Bechen Science and Technology Park (BC) site was higher than at other four sites. Total PAHs concentrations in two other sites viz., Meijang community (MJ) site and BC site were found to be higher during no-heating period. It was concluded that in six sampling sites, the PAHs concentration was high in the heating period. This was due to high emissions from stationary combustion sources, faster dispersion of air, photo degradation and washout effects. PCA was done to estimate main sources of PM₁₀ assisted PAHs. It was concluded that coal combustion was the main source of PM₁₀ assisted PAHs, followed by vehicular exhaust and wood burning.

Milena et al., 2010, collected and analyzed TSP samples during 2005 and 2008. Concentration of BaP was studied for ambient TSP in Belgrade metropolitan region for ten years, for the local air pollution monitoring program. TSP bound BaP samples were collected for 24 h at once every month at particular sampling sites. Initially, all the samples were considered as TSP. But the methods of sampling changed in the mid of 2008 due to EU guidelines and then PM₁₀ fraction was collected and analysed by GC/MS. The BaP concentrations were high during winter season at almost all monitoring sites.

Callén et al., 2011, conducted study of four urban and rural monitoring sites in Spain during summer and winter season from 2008 to 2009. Nineteen PAHs bound with PM₁₀ were analysed by using gas chromatography-mass spectrometry-mass spectrometry detection (GC-MS-MS) using internal standard procedure. The PAH concentration was 5-10 times more in urban and industrial monitoring sites than rural sites. The PAH concentrations were highest during the winter season because of the added influence of household heating emission sources and meteorological factors like solar irradiation and low temperature. As per the studies of molecular diagnostic ratios, the carbon combustion (vehicle exhausts and crude oil combustion) were the major sources of PAH. BaP levels which have carcinogenic property present in some samples were also due to the petroleum combustion sources.

Wickramasinghe, et al., 2011, studied the ambient PM₁₀ bound PAHs 8h average concentrations at 20 monitoring sites in urban, suburban and rural areas of Kandy, SriLanka. PM₁₀ samples were collected by HVS on the glass microfibre filters during July 2008 to March 2009. PM₁₀ bound PAHs were extracted using the standard method and analysis was performed using HPLC with UV detector. The study of firewood mass combustion and 24-hour traffic volume counts was used at each sampling site to identify the category and strength of potential anthropogenic sources of emission that cause major changes in the environment. These studies can work as a dataset to evaluate the pollution levels, PAH sources and human exposure. The average PM₁₀ concentration values ranged from 55 - 221 $\mu\text{g m}^{-3}$ that exceeded the air quality permissible limits of WHO. Total mean concentration for 16 priority PAHs (ΣPAHs) varied between 57.43 to 1246.12 ng m^{-3} . Further, 695.94 ng m^{-3} was found at urban site with dense traffic, 105.55 ng m^{-3} in urban locations with light traffic, 337.45 ng m^{-3} in suburban site with dense traffic-flow, 154.36 ng m^{-3} at suburban station with light traffic-flow, 192.48 ng m^{-3} at rural site with increased firewood combustion region and 100.31 ng m^{-3} at rural site with decreased firewood combustion regions.

Salam et al., 2011, collected suspended particulate matter at two monitoring sites of urban and suburban areas of residential site in Yokohama, Japan during 1999 to 2005. Ten compounds of PAHs were analyzed by GC-MS. The net concentrations in urban residential area were higher than suburban residential area. The concentration varied from 0.31- 6.16 ng m^{-3} with a mean of 2.07 ng m^{-3} in the urban areas and 0.33-2.87 ng m^{-3} with a mean of 1.02 ng m^{-3} in suburban areas. The major compounds present in both the sampling sites were benzo[b]fluoranthene, benzo[e]pyrene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. The PAHs concentration having 5 and 6-ring structure were dominant in the urban areas as compared to the suburban areas. Source apportionment was determined by principal component analysis. The study concluded that emission from vehicles and stationary source was the key sources of PAHs.

Cavanagh, et al., 2012, discussed the ambient BaP and As levels in New Zealand. Annual mean BaP concentrations in some cities of New Zealand exceeded the national ambient air standard limits of 0.3 ng m^{-3} by 20 times and the European Union target limit of 1 ng m^{-3} by 6 times. Mean concentrations of As at urban sites in New Zealand exceeded the standard limits of national ambient air quality (5.5 ng m^{-3}) and the European Union target limit of 6 ng m^{-3} by 2 times. Residential wood combustion is supposed to be responsible for the high BaP and As emissions, with arsenic emissions arising from the burning of treated timber. Reliable sampling and analytical methods are required to study the amount of elevated concentrations of BaP and As across New Zealand. Proper management options should be implemented to reduce the emission sources of BaP and As.

Lakhani et al., 2012, collected ambient TSPM from an industrial sampling area of Agra, India. The TSPM samples were analyzed for 16 polycyclic aromatic hydrocarbons recommended by US EPA using gas chromatography technique. The main industries in Agra are foundries which consume coke and coal in the form of fuel which has now been replaced by natural gas. Similarly rise in the number of motor vehicles has also increased the use of compressed natural gas. The sum of 16 priority PAHs has an average value of $72.7 \pm 4.7 \text{ ng m}^{-3}$. The change of fuel causes changes in the study on source apportionment of ambient PAH. The major TSPM bound PAHs have high molecular weight e.g. BaP, DbA, BghiP and IP. PCA and diagnostic ratios were performed to detect the main sources of PAHs in aerosols. It was concluded that combined emissions from natural gas and diesel were the important sources of PAHs in the city.

Nagarajappa et al., 2012, studied concentration of PM_{10} associated BaP in ambient air at selected 8 monitoring sites in the industrial region (Peenya) of Bangalore city of India. BaP samples collected in ambient air for once in a month for 24 h at selected sampling sites located within the Peenya industrial site during February 2011 to April 2011. The concentrations of BaP collected from 8 monitoring sites varied from $0- 0.049 \text{ ng m}^{-3}$. Spatial variations were observed due to various types of source emission.

The total BaP concentrations were higher in one monitoring site (Kongovi monitoring station) than rest of the seven sites. It is concluded that BaP concentrations were highest in the winter season at all the monitoring sites.

Kim et al., 2013, reviewed about polycyclic aromatic hydrocarbons (PAHs) properties, human exposure, health effects (acute and chronic), transformations and fates associated with their emission to the atmosphere. They further define that PAHs are type of organic compounds with two or more benzene rings fused together and arranged in different patterns. PAHs are present as atmospheric pollutants and are created by the incomplete combustion of organic materials. PAHs present in ambient air has carcinogenicity and mutagenicity properties due to which they are potential health hazard. Permissible concentrations and emissions of ambient PAHs are regulated as their exposure requires control through the air quality management.

Guimarães et al., 2013, developed a reliable and practical analytical technique for the method validation and uncertainty evaluation for PAHs in dust samples from urban areas. GC/MS method was used for the determination of better accuracy in the results. Five PAHs viz., benzo[*a*]anthracene, benzo[*ghi*]perylene, fluoranthene, phenanthrene and BaP were analysed. This technique was applied in the CCQM-K50b key comparison for PAHs in particulate matter. The Certified Reference Material (CRM) or reference standard used was NIST SRM 1649a urban dust for the measurement of accuracy and precision. The LOD and LOQ were measured as 0.075 and 0.250 µg/g, respectively. The linear correlation coefficient (R^2) was found as 0.99. Accuracy and reliability of analyzed PAH have major contribution in the uncertainty measurement.

Gianelle et al., 2013, conducted measurement of BaP air concentration for three years at 13 sampling sites in Lombardy (Italy). Complete emission data was maintained for the entire region to study the contribution of various sources to BaP ambient levels. The ambient BaP concentrations was analyzed weekly and monthly along with the cluster analysis and BaP/PM₁₀ ratios. The emissions from wood

combustion in few residential areas were identified as the major emission source in all sampling sites, except for sites in Milan. The cluster analysis of BaP/PM₁₀ ratios is based on location of the site, i.e. plain area, valley zones or mountain sites. Among all the emission sources, wood combustion dominated in all the residential areas in the city of Milan.

Wiriya et al., 2013, collected 94 PM₁₀ samples in dry and wet seasons during 2010 and in the dry season during 2011 at Chiang Mai, Thailand. The PM₁₀ bound 16 PAHs were analysed using GC-MS. The mean concentrations of PM₁₀ were $104.91 \pm 32.70 \mu\text{g m}^{-3}$ in dry season of 2010, $13.28 \pm 11.34 \mu\text{g m}^{-3}$ in the wet season of 2010 and $36.24 \pm 19.16 \mu\text{g m}^{-3}$ in the dry season of 2011. On the other hand, the mean concentrations of 16-PAHs were 25.87 ± 10.13 , 3.12 ± 2.18 and $4.58 \pm 2.18 \text{ ng m}^{-3}$, respectively. During the dry season of 2010, high correlation was found between PM₁₀ concentrations and carcinogenic PAHs ($r = 0.927$). This was due to the presence of the particulate PAHs generated from open burning.

Suvarapu et al., 2013, reviewed the BaP concentrations in Indian scenario from 1983. Sixty research papers published in International journals on the determination of ambient BaP in India were reviewed. The literature review indicated that the major research on the BaP concentration in India has been performed in recent years. The review discussed all the analytical methods, like extraction process, analytical apparatus, monitoring procedures and detection limit in measurement of BaP in the ambient air. Apart from this, comparison of the BaP concentration reported in India with respect to other Western and Asian countries was also discussed. It was concluded that the concentrations of ambient BaP observed in India was much higher as compared to western countries like Italy, Germany, UK USA, and Greece. In case of Asian countries, the BaP concentrations observed in India were higher than the concentrations observed in the countries, like Japan, Taiwan, Hong Kong and Korea but similar to China.

Kaur et al., 2013, analyzed 16 priority PAH compounds in PM₁₀ samples collected from various geographical sites using high-volume sampler. Total PAHs concentrations range from 37-274 ng m⁻³, and this data was compared with data of other Indian cities as well as many cities around the globe. The carcinogenic property of PAHs was measured as BaP toxic equivalency (BaPTEQ). It was concluded that dibenzo(a,h)anthracene is the main contributor of PAHs (88.7%) followed by BaP (6.67%).

Jamhari et al., 2014, studied the concentration of PM₁₀ bound PAHs and the source apportion by using PCA and diagnostic ratio analysis. The health effects due to exposure to ambient BaP_{eq} were also studied. The sampling was done on two urban sites in Klang Valley, Kuala Lumpur (KL) and one industrial site in Petaling Jaya (PJ), one semi-urban site at Bangi (BG). Collection of PM₁₀ samples was performed by High Volume Sampler (HVS) for 24h on glass fiber filters during September 2010 to April 2011. PM₁₀ samples were extracted in dichloromethane-methanol (3:1). 16 priority PAHs recommended by USEPA were analysed through GC-MS. It was found that concentrations of total PAHs in monsoon season for KL, PJ and BG sites varied between 1.33 ng m⁻³ to 2.97 ng m⁻³, 2.24 ng m⁻³ to 4.84 ng m⁻³ and 1.64 ng m⁻³ to 3.45 ng m⁻³. PAHs with 5-ring and 6-ring such as, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene and benzo[k]fluoranthene constituted more than 80% of total PAHs. Benzo[g,h,i]perylene concentration was high in all the monitoring sites due to vehicular exhausts. Diagnostic ratio analysis and PCA also show vehicular emissions. Total BaP_{eq} was responsible for more than 50% of the major health issues.

Csanádi, et al., 2015, studied the yearly concentration and seasonal variation of PM₁₀ associated BaP in urban and a rural monitoring site of Northwestern Hungary during 2008–2012. A total of 280 PM₁₀ samples were collected from each monitoring site, and BaP was analyzed using gas chromatography technique. The BaP concentrations varied from ND (not detected) to 8 ng m⁻³ with the mean value of 1.01 ng m⁻³ in the urban monitoring site and from ND to 4.07 ng m⁻³ with the mean value of 0.52 ng m⁻³ in the rural monitoring site. Concentrations of BaP were found high in samples collected from both the

monitoring sites during heating seasons as compared with non-heating seasons. The yearly average BaP concentrations can be compared with the reported data of other sites of Hungary.

Morales M et al., 2015, studied the concentration of PM₁₀ bound BaP in samples by microwave-assisted extraction and analysis by HPLC using a fluorescence detector. The LOD was calculated as 1×10^{-3} ng m⁻³ and BaP recovery from certified reference material (CRM) PAH in Fine Dust quantified as 86%. A total of 115 PM₁₀ samples were collected from various monitoring sites in Southwest Spain during 2011-2012, and were analysed for BaP using the validated method. Various parameters like spatial variations, seasonal variability meteorological factors and concentrations of different air pollutants were investigated. Thus, a standardized method for assessment of health issues was used for evaluation of cancer risk caused by BaP in the areas of the study.

Nagy et al., 2015, studied concentration of PM₁₀ bound PAHs in ambient air in an urban monitoring site of Győr, Hungary during 2011. The total PAHs and each of its compounds show high variation during the study. The total PAH concentration varied from 0.88 ng m⁻³ to 95.80 ng m⁻³ with average value of 20.06 ng m⁻³. It was observed that four and five-ring compounds of PAHs viz., benz[a]anthracene, benzo[a]pyrene, sum of the three benzofluoranthene isomers, indeno[1,2,3-c,d]pyrene and dibenz[a,h]anthracene were the main components in the samples. The carcinogenic property of PAH studied as compared with published reports of other cities in Hungary.

Guerreiro et al., 2016, studied the concentration, population exposure and major health effects due to exposure to ambient BaP in Europe. The studies were conducted by using the data from various studies and chemical transport models. It was observed that the BaP levels exceed the European permissible values in 2012, particularly in central-eastern Europe. High uncertainty was found in the BaP concentrations in areas with few sampling sites. It was estimated that 60% of the population of Europe had BaP exposure and thus had health effects which covered areas limited to the requirements of modelling of BaP concentrations. About 20% of Europe's population is exposed to concentration of BaP

exceeding the permissible limits of EU and only 7% of the population lives in areas having BaP concentrations within the permissible limits. Importantly, 370 lung cancer cases were reported in 60% of the population having BaP exposure per year. BaP concentrations have increased in the last few years due to rise in emissions from biomass burning. It was concluded that BaP measurements should be done at areas with high concentrations, e.g. in Bulgaria, Romania and other Balkan states. The relationship between climate regulation policies in Europe and air quality can reduce the risk posed by PAH exposure.

Styszko et al., 2016, conducted study on PAHs and NPAHs levels in the PM₁₀ collected from Kraków during January and February month of 2014. 13 PAHs and 4 NPAHs: anthracene, phenanthrene, fluorene, pyrene, fluoranthene, benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, chrysene, indeno[1,2,3-c,d]pyrene, benzo[k]fluoranthene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, 9-nitroanthracene, 2-nitrofluorene, 1-nitropyrene and 3-nitrofluoranthene were extracted from PM₁₀ and analysed using GC-MS method. The calculated relative recoveries varied between 72 to 94%. The PM₁₀ concentrations ranged from 23.5 - 153.8 $\mu\text{g m}^{-3}$ throughout the sampling period. The values of average concentrations of PAHs varied between 26.6 to 276.4 ng m^{-3} and for NPAHs varied between 0.6 to 9.1 ng m^{-3} . The maximum concentration was reported for fluoranthene benzo[a]anthracene, BaP and pyrene. BaP is marker for particle-assisted ambient PAHs. The mean concentration of BaP was reported as 9.5 ng m^{-3} .

Sun et al., 2016, studied the level of pollution, sources of emission, and risk of lung cancer in the PM₁₀ assisted PAHs during summer season of the year 2015 in Nanjing, China. PM₁₀ bound 16 priority PAHs were extracted after sampling and then analyzed. The average concentrations of PAHs were $7.49 \pm 2.60 \text{ ng m}^{-3}$, and for BaP_{eq} was $1.21 \pm 0.24 \text{ ng m}^{-3}$. Study of diagnostic ratios showed that PAHs were mainly emitted from vehicular emissions, particularly from diesel vehicles. To study the BaP exposure, the incremental lung cancer risk (ILCR) were determined which showed reduced lung cancer risk.

P. Di Vaio et al., 2016, studied PM_{10} assisted PAHs and identified their potential sources using PCA and diagnostic ratio methods in Naples at the urban background site (NA01) and urban traffic site (NA02). The PM_{10} samples were collected for 15 days in a month for 24 h by Low Volume Sampler (LVS) on quartz filters during October 2012 and July 2013 in summer, spring, autumn and winter season. The mass concentration of PM_{10} was determined gravimetrically. The filters of PM_{10} samples were extracted in dichloromethane and determined by GC-MS analysis for 12 priority PAHs recommended by USEPA. The PM_{10} levels were considerably higher in urban-traffic site (NA02) than in urban-background site (NA01) in all seasons. The concentration of BaP ranges between 0.065 ng m^{-3} in autumn season to 0.872 ng m^{-3} in spring season in the urban-background site (NA01) and between 0.120 ng m^{-3} in autumn season to 1.48 ng m^{-3} of winter season in the urban-traffic site (NA02). The EU permitted limits for PM_{10} was 1 ng m^{-3} . It was found that average concentration of 12 PAHs in urban-traffic site was more than twice the concentration of that in the urban-background site. PAHs with 5 and 6 rings, having carcinogenic property i.e, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene and benzo[k]fluoranthene were found to contribute approximately 50 – 55% of total PAHs present in PM_{10} at two monitoring sites. Diagnostic ratio analysis and PCA show that vehicular emission was one of the major sources of PAHs in the monitoring sites.

Widziewicz et al., 2017, studied the PM_{10} assisted BaP emission from household combustion which caused lung cancer in Poland and nearby areas. It was found that 31% of the total lung cancer cases were due to BaP exposure. Therefore health risk analysis was made to check the effect of BaP. The data for the concentration of BaP was acquired from database of Polish Chief Inspectorate of Environmental Protection (CIEP). The study was done from 2010 to 2015 in rural sites, urban sites and the rest of the areas. It was found that the average BaP concentration ranged from 1.39 ng m^{-3} at rural sites to 4.86 ng m^{-3} at rest of the areas. BaP concentration was above the permissible limits causing the lung cancer risk.

It was concluded that the results obtained from the study can be used for implementing long-term policies to decrease the ambient BaP concentrations.

2.3 Metal / Element Concentration in PM₁₀

India is facing deterioration in air quality for last few years due to the increase in the ambient PM, PM bound trace metals and gaseous pollutants. Several studies have indicated that PM bound metals are respirable and can persist in the atmosphere for longer duration. These metals are indestructible and have toxic effects on living organisms. Some metals are essential to humans but they have toxic effect if their concentration exceeds the desired limit. They are emitted in the atmosphere through natural as well as anthropogenic sources. The anthropogenic source is of major concern as it is responsible for the increase of toxic metals in the atmosphere. The natural sources of metals in the atmosphere are dust, bioorganic emissions, forest fires etc. The anthropogenic sources are emissions from power plants, metal smelters, incinerators, steel and cement plants, fossil fuel combustion etc. The PM bound trace metal concentrations are higher in urban industrial areas as compared to rural areas. The objectives of the study were to quantify the PM₁₀ bound metals viz., As, Ni and Pb which are listed as the criteria pollutant in the NAAQS, India.

Álvarez et al., 2004, conducted studies on the size distribution of metals in ambient particles in 24 monitoring sites of Seville, Spain. Collection of particles was carried out using a high-volume sampler with PM₁₀ inlet and cascade impactor. Samples collected were extracted by acid digestion mixture of HNO₃: HClO₄ (3:1, v/v) using a microwave digestion system. As was analysed by AAS using hydride generation assembly, mercury by cold vapour AAS and Pb, Ni and Cd were analysed using inductively coupled plasma atomic emission spectrometry (ICP-AES). PM₁₀ analysis indicated that highest average concentrations were determined for Pb (14.04 ng m⁻³). Arsenic and Ni concentration values were 3.42 and 2.88 ng m⁻³, respectively. The lowest concentrations were measured for Cd (0.49 ng m⁻³) and Hg

(0.07 ng m⁻³). The study of size segregated analysis showed that As and Pb were present in PM_{0.6} along with Cd and Ni at high percentage of 74.8, 69.0, 61.3 and 57.5%, respectively. Mercury was present in low percentage of 40.4 %. The study of mass concentrations showed that Pb and Cd were mostly present in the particles size range between 1.3 and 0.6 µm in diameter. Mercury was present mostly in PM_{0.6} particles. Ni was present in particle of all size ranges. As was dominant in PM_{0.6} which shows that As is most toxic in relation to its size distribution.

Karar et al., 2006, studied the ambient PM₁₀ at industrial (Cossipore) and residential (Kasba) urban monitoring sites of Kolkata in India during November 2003 to 2004. The selection of monitoring sites was based on the major anthropogenic sources. Metal components of ambient PM₁₀ were collected over glass fibre filters and analyzed using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Seven trace metals viz., Cr, Zn, Ni, Cd, Pb, Mn and Fe were quantified from the PM₁₀ samples. Ninety samples of PM₁₀ were collected and 24 h mean concentration of Cr, Zn, Pb, Cd, Ni, Mn and Fe was determined. The concentration values were found to be 6.9, 506.1, 79.1, 3.3, 7.4, 2.4 and 103.6 ng m⁻³, respectively. The mean PM₁₀ concentration for 24 h at both industrial (Cossipore) and residential (Kasba) monitoring sites were 140.1 and 196.6 µg m⁻³, respectively which exceeded NAAQS permissible limits. Meteorological studies indicated the effect of air masses by rainfall, relative humidity, temperature, wind speed and wind direction. It was observed that the toxic trace metals were indirectly related to temperature, relative humidity and wind speed. The emission sources were identified through factor analysis which is a receptor modelling technique. It was observed that four potential sources of studied trace metals were vehicular traffic, road dust, soil dust and solid waste dumping at residential site (Kasba), while tanning industry, galvanizing, road dust, electroplating industry and vehicular traffic were the potential sources at industrial site (Cossipore).

Lee et al., 2007, analyzed PM bound heavy metals viz., Zn, Cu, Fe, Pb, Mn, Cd, Ni and Cr. It was observed that all the metals content studied in the samples of PM_{2.5} and PM₁₀ had higher concentration

in spring season than in summer season, except Cr which had similar concentrations between these two seasons. Seasonal variations observed in the concentrations of metal may be due to winds movement through industry or traffic areas and change in wind directions. Enrichment factors analysis of metals indicated highly enriched Zn, Cd, Cu and Pb.

Pallarés et al., 2007, conducted studies on the concentration of nickel, arsenic and cadmium in Alcora, Vila-real and Castellón areas of Spain in 2002. Arsenic, Cd and Ni were determined to check whether they are within the guidelines of the future directive limits. Three sampling sites were selected (Alcora, Vila-real and Castellón), that is part of the ceramic cluster of the state of Castellón (Spain). The study was conducted to measure temporal variation of As, Cd, Ni and PM₁₀ levels in the atmosphere during 2002. PM₁₀ concentration was decreased during summer due to reduction in industrial activities. Thus, industrial activities were responsible for high PM₁₀ levels. As levels exceeded the prescribed limits of the Directives. This was attributed due to colemanite and the hydroboracite, used in the ceramic industries located in the area of study. Ni and Pb followed the limits of the Directives.

Vassilakos et al., 2007, collected PM₁₀ during summer and winter season in 2003 at two different monitoring sites in Athens, to determine the heavy metals concentration in PM₁₀ and their relationship with gaseous pollutants and meteorological factors. The heavy metals studied were As, Ni, Cd and Hg. The mean concentrations of heavy metal in the first monitoring site (Spata) ranged from 0.66 - 14.7 ng m⁻³ in the summer season and 0.14 - 19.5 ng m⁻³ in the winter season. At the second monitoring site (Koropi), the concentration varied from 0.89 - 13.3 ng m⁻³ and 0.16 - 24.7 ng m⁻³, respectively. PM₁₀ bound Ni, Cd and Hg concentration showed high mass concentration and daily variations in the summer season. Whereas, PM₁₀ bound Pb showed high mass concentration in the winter. Studies of relationship between meteorological parameters and heavy metals showed a higher correlation with relative humidity and temperature. All the heavy metals except Hg, show correlation with nitrate oxides, ozone

and PM₁₀. Correlations with gaseous pollutants and meteorological parameters were very high in the winter season.

Karakas et al., 2009, optimized a method for multi-elemental analysis. 35 metals were analyzed in 274 PM samples of coarse and fine type using HR-ICP-MS. The methods were validated. Measurement uncertainties were calculated for all the elements as well as for sampling. The mean recoveries obtained using NIST SRM 1648 for urban dust for each element and were found to range between 79% and 129%. For the analytical methods, the uncertainties calculated varied from 2.9% and 18% for both types of samples. The major contribution to the uncertainty budget was from the repeatability, calibration curves and volume of air.

Cozzi et al., 2010, collected PM₁₀ samples in winter and summer seasons in two selected sampling sites of Trieste (Italy). The PM₁₀ bound Cd, As, Cr, Pb, Ni, V and Mn content was analysed by means of inductively coupled plasma-mass spectrometry (ICP-MS). It was observed that concentration of the elements in ambient air was below the standard limits in both the monitoring sites and season. Correlation analysis was conducted to identify the relationship between metals and their origin. For example, the Ni-V couple showed the effect of combustion of heavy oils in PM₁₀ sample for both seasons and sites. The seasonal variability in concentrations of PM₁₀ and metal was studied in both the sites. Vehicular traffic had a strong impact on the concentration of PM₁₀ and metal in both the sites and seasons. "Bora" wind affected the local climate and thus affected the concentration of PM₁₀ and toxic elements for the urban site during both seasons due to the dispersion of the pollutants by wind.

Gerboles et al., 2011, presented the data of an inter comparison exercise of thirteen laboratories for the study of Pb, As, Ni and Cd in PM₁₀ which followed the European Directives guidelines for ambient air quality. European reference methods were used for determination of metals. The samples PM₁₀ was extracted by microwave acid digestion and analysis of metal content was performed by ICP-MS or GFAAS. Every participating laboratory analysed five samples viz., a CRM, two samples of NIST dust

SRM (digested and non-digested) and two mass laden filters (digested and non-digested). It was observed that 93% of the samples tested by all the participating laboratories complied with the Data Quality Objectives of European Directive (expanded uncertainty of 40% for As, Cd and Ni and 25% for Pb). Only 76% of DQOs were met in case of loaded filter digested by the participants. Rest of the samples were difficult to analyse due to contamination by the digestion processes. Other methods were also used for digestion like high pressure techniques and Soxhlet extraction. Analytical techniques used were ICP-OES for Pb, Cd and Ni, EXRF for Pb and Ni, Voltammetry for As, Pb and Ni. The uncertainties confirmed for 77% of results were 10% for Pb and 15-20% for As, Cd and Ni. The reproducibility of the methods used was 41-54% while repeatability ranged between 5-12% except for the analysis of As on filters which was up to 20%.

Gajghate et al., 2011, collected the different size fractions of PM₁₀ viz., (0.4–0.7) μm, (0.7–1.1) μm, (1.1–2.1) μm, (2.1–3.3) μm, (3.3–4.7) μm, (4.7–5.8) μm, (5.8–9.0) μm and (9.0–10.0) μm by 8-stage Andersen cascade impactor sampler on glass fiber filter. The samples of PM₁₀ were extracted by microwave assisted acid digestion, and mercury analysis was performed by Direct Mercury Analyzer, DMA - 80. Uncertainty calculations were done for the sampling and analytical procedure. Major uncertainty sources were identified and an uncertainty budget was prepared. Uncertainty parameter of repeatability showed highest contribution in the uncertainty followed by calibration curve and volume of air sampled. The relative expanded uncertainties at 95% confidence interval were between 15 and 26% for mercury content in different PM₁₀ size range.

Popescu et al., 2011, studied the relationship between heavy metals, e.g. Pb and Cd in TSP and vehicle traffic source. The study was performed for one year in a street gorge area considered as hot spot due to high traffic flow (Pitesti), as compared to a blank area, without any traffic flow (Calinesti, Arges). Sampling of heavy metals was done for 24 hours during 2008. Pb concentration is high in working days

while cadmium concentration remains constant in urban area. Furthermore, correlations between PM_{10} , Pb and carbon monoxide are much better in urban area than in rural area.

Singh et al., 2011, determined SPM bound arsenic and investigated major sources of uncertainty involved in the measurement with uncertainty budget. Seven Different monitoring sites were selected in Delhi for the collection of SPM during 31st Jan. 2008 to 7th Feb. 2008. SPM samples were collected using HVS and arsenic content was analyzed by hydride generation in Atomic Absorption Spectrometer (AAS-HG) and uncertainty budget was estimated. Various sources of uncertainties were considered during the study of arsenic in SPM samples. The uncertainty measurement was estimated by EURACHEM guide. The uncertainty budget included major parameters like the uncertainty in sampling by HVS, weighing balance, final volume prepared. The concentration of arsenic varies between 1.44 ± 0.25 to $5.58 \pm 0.55 \text{ ng m}^{-3}$ using confidence level of 95% ($k = 2$). The measurement of arsenic content in SPM should be accurate and precise as it indicates its toxicity levels in the atmosphere and thus, control measures can be taken in the affected regions. Assessment of quality assurance was also significant in study of arsenic content in SPM samples.

Foley et al., 2012, studied the concentrations of ambient PM_{10} and metals (Ni, Mg, Cd, Be, Co, Cr, Pb and As) and eight metalloids in the southern area of Tucson metropolitan and also estimated the potential mobile and stationary sources. Almost 200 samples of PM_{10} were collected and analyzed from six schools located in the Sunnyside Unified School District. The study was undertaken to measure the concentration of metals especially ambient beryllium in the ceramics-processing area. It was observed that the area under study has good air quality and PM_{10} and metals concentration were within the US EPA and WHO standards limits.

Prasad et al., 2013, conducted study of the three toxic trace carcinogenic metals (As, Ni and Pb) concentration levels in AAQ in Tirupati during February 2011-2012. For this study, 5 sampling sites were identified in Tirupati. PM_{10} sampling was performed for 24 - hour and twice a week. For this

study, 15 PM₁₀ samples were collected, digested and analysed for As, Pb and Ni using ICP-MS. The concentration levels of Pb, Ni and As in various areas of Tirupati was found less than that of standard limits of NAAQS.

Aleix et al., 2014, studied concentrations of PM₁₀ and PM_{2.5} and its As content during 2005-2010. Analysis was performed on ICP-MS. Concentrations of PM₁₀ and As range between 27- 46 µg m⁻³ and 0.7- 6 ng m⁻³ in the industrial area, and 25 - 40 µg m⁻³ and 0.7 - 2.8 ng m⁻³ in the urban area, respectively.

Kim et al., 2014, conducted studies on the concentration of Ni in seven most important cities in Korea for 13 years from 1998–2010. The average concentrations of Ni observed during the entire period of the study varied between 3.71 (Gwangju) to 12.6 ng m⁻³ (Incheon). Six cities out of seven showed reduction in the concentration of Ni over the entire study period. Studies were done on the relationship between the concentrations of Ni and the potential sources. Also, the effect of transport of dust particles from Asia in regulating Ni concentration was estimated. The study concluded with the observation that Ni concentrations decrease during the entire study period regardless of changes in localized non-road source activities. The concentration of Ni at all the sampling sites remained within the standard limits (20 ng m⁻³).

García-Aleix et al., 2014, studied the concentration of PM₁₀ and PM_{2.5} and analyzed the arsenic content by ICP-MS in Spain during 2005-2010. PM₁₀ concentrations and its arsenic content varied from 27- 46 µg m⁻³ and 0.7-6 ng m⁻³ in the industrial region, respectively, and from 25- 40 µgm⁻³ and from 0.7-2.8 ng m⁻³ in urban area, respectively. Similarly, PM_{2.5} concentration and arsenic levels varied between 12- 14 µg m⁻³ and from 0.5 -1.4 ng m⁻³ in urban area, respectively. The arsenic levels in PM₁₀ and PM_{2.5} have decreased in last few years due to reduction in the production of the ceramic material in the area of study. This is due to technological improvements and replacement of boron due to As impurities.

Epidemiological studies on cancer show the area under study in Spain points as one with the high risk of cancer.

Proorocu et al., 2014, conducted the assessment of PM₁₀ levels and Cd, Pb and Ni content in the densely populated town of Bucharest in Romania during 2004 – 2013. Data were collected from 8 monitoring sites of Bucharest. The raw data were acquired from the Romanian National Agency of Environmental Protection. For the data processing IBM SPSS software, v. 6.0 was used. It was observed that industries were the major source of PM₁₀ but by the implementation of directive, air quality issues can be solved.

Pal et al., 2014, collected PM₁₀ samples from three monitoring sites in Moradabad city of India. The sampling was performed simultaneously two days a week from April 2011-March 2012. The concentration of metal content bound with PM₁₀ was analyzed through an ICP-OES. Monthly average PM₁₀ concentration was found between 63-226 $\mu\text{g m}^{-3}$ which exceeded the standard limit of 100 $\mu\text{g m}^{-3}$ of NAAQS. The concentration of Zn, Fe, Cu, Cr and Ni was 21.24, 18.43, 15.23, 0.41, 0.03 $\mu\text{g m}^{-3}$, respectively and was found to be mostly high in the industrial area of the city. The concentration of Pb (2.72 $\mu\text{g m}^{-3}$) and Cd (0.20 $\mu\text{g m}^{-3}$) was high in commercial area with heavy traffic flow. The study concluded that the brassware industries and large number of vehicles are the reason for high concentration of heavy metals in the city.

Palomo-Marín et al., 2015, presented the results of program on quality assurance evaluation used in the estimation of trace metals in samples of PM₁₀ using the air quality surveillance network of Extramadura, Spain. Various analytical techniques were used like limits of detection, long-term blank values evaluation, CRM recoveries, comparison studies for multi-elemental and gravimetric analysis and method uncertainty. The uncertainty measurement for PM₁₀ bound As, Ni, Pb, and Cd was also estimated. The uncertainty was evaluated according to UNE-EN 14902:2006. Sampling was performed only for 15 days. The relative uncertainty was calculated as 15.3 % for As, 9.5 % for Cd, 13.8 % for

Pb and 13.7 % for Ni. The uncertainty sources of analytical methods, reference material and sampling volume were considered. The expanded uncertainty was estimated with a coverage factor $k = 2$ as 42 % for As, 40 % for Cd, 36 % for Pb and 32 % for Ni. The uncertainty value for As and Pb exceeds the legal limit. For the quality assurance studies, laboratory took part in the inter laboratory quality control program (IQCP) developed by National Institute for Occupational Safety and Hygiene in Spain. Target metals were Pb, Cr, Cd and Ni. The sample in IQCP was analysed using the methods as used for real samples.

Kundu et al., 2015, conducted systematic air quality assessment as per standard guideline at Jharia in Rajapur, India at the opencast mine. The SPM mean concentration, PM_{10} and $PM_{2.5}$ varied in range of 294 -965 $\mu\text{g m}^{-3}$, 100-498 $\mu\text{g m}^{-3}$ and 85-296 $\mu\text{g m}^{-3}$ respectively. The concentration of SO_2 and NO_x varied from 48.2 - 98.2 $\mu\text{g m}^{-3}$ and 32.8 - 149.39 $\mu\text{g m}^{-3}$, respectively. The trace metals, e.g. Pb, Ni, As associated with PM_{10} were determined by AAS technique. The trace metals concentration were found as Pb $0.380 \pm 0.009 \mu\text{g m}^{-3}$, Ni $0.06 \pm 0.02 \mu\text{g m}^{-3}$, and As $0.00432 \pm 0.028 \mu\text{g m}^{-3}$. These concentrations exceeded the regulatory limits of air quality standard.

Tirez et al., 2015, determined inorganic arsenic content in PM_{10} and $PM_{2.5}$ in metallurgical industrial plant located in an urban area. Arsenic (III) and As (V) species were analysed through high performance liquid chromatography – inductively coupled plasma mass spectrometry (HPLC-ICP-MS). Limit of quantification was calculated as 0.34 ng m^{-3} for As (III) and 0.23 ng m^{-3} for As(V). The mean concentration of As in PM_{10} during a 40-day sampling period was found as 30 ng m^{-3} which exceeded the European standard limit of 6 ng m^{-3} . Concentration of As(III) ranged between 19 - 61% in PM_{10} .

Kushwaha et al., 2016, studied concentration of heavy metal in ambient PM_{10} in industrial area of Thiruvottiyur in Chennai, India. Monitoring was performed for 24 hours and twice in a week for NAMP. Gravimetric method was used for PM_{10} monitoring. The PM_{10} filter were collected during April 2015 - November 2015 for heavy metals analysis. Acid digestion of aliquot of glass fibre filters (EPM

2000) is done followed by heavy metal analysis using ICP-OES. PM₁₀ concentration was found between 13 - 93 $\mu\text{g m}^{-3}$ during the entire sampling period which complied with the standard limits of NAAQS. Highest concentrations observed as 0.449 , BDL , 0.209 , 1.58 , 0.019 , 0.82 , 0.192 , 16.3 , 0.829 and 0.011 $\mu\text{g m}^{-3}$ for Cu, Cd, total Cd, Fe⁺³, Mn, Ni, Pb, Zn, Co and As respectively. Lead concentration was within the regulatory limits of NAAQS (2009). Concentration of Ni 18.8% and Arsenic 12.5% did not comply with other metals and standard regulatory limits.

Busan et al., 2016, collected samples of PM₁₀ in Zagreb, Croatia during 2006-2015 at three monitoring sites: densely populated area of city centre, industrial area in western part of the city and least populated region with few industries in the eastern part of the city. Samples were collected on 90 mm diameter membrane filters with flow rate of $\sim 100 \text{ m}^3$ of air per day, and of 47 mm diameter quartz filters with flow rate $\sim 50 \text{ m}^3$ of air per day. Metals in PM₁₀ samples were extracted using microwave acid digestion system. Metal samples were analysed by-AAS and ICP-MS. Yearly average mass concentration varied from 0.07- 0.9 ng m^{-3} for Cd, 0.5 - 1.5 ng m^{-3} for As, 0.6 - 4.4 ng m^{-3} for Ni and 6.0 - 20.0 ng m^{-3} for Pb at all the three monitoring sites in Zagreb. Statistical analysis showed no major variation in the concentrations of metal studied between all the monitoring sites. A slight reduction in yearly average concentration of Cd, Ni, As and Pb showed a strong decreasing trend due to high consumption of lead-free gasoline in Croatia.

Police et al., 2016, collected PM₁₀ samples at two monitoring sites of Jogannapalem and Parawada areas in Visakhapatnam. PM₁₀ concentrations varied from 34.8 - 109.7 $\mu\text{g m}^{-3}$ and 32.3 - 37.3 $\mu\text{g m}^{-3}$ at the two monitoring sites respectively. Chemical analysis of PM₁₀ bound metals viz., V, Al, Mn, Cr, Fe, Cu, Ni, As, Zn, Cd, Pb, Cl⁻, F⁻, SO₄²⁻, NO⁻³, K⁺, Na⁺, Ca²⁺ and Mg²⁺ was performed to measure the concentration. The average concentration of Al was highest at both the monitoring sites (4.1 $\mu\text{g m}^{-3}$ at Jogannapalem and 3.8 $\mu\text{g m}^{-3}$ at Parawada) followed by K at Jogannapalem site and Ca at Parawada site. Concentration of all trace metals except Mn and Fe and PM₁₀ concentration was high at Parawada site

than at Jogannapalem site, indicating high pollution levels at Parawada. Source apportionment studies indicated six key sources in Jogannapalem and seven sources in Parawada. The five common sources at the two monitoring sites were sea-salt spray, crustal, oil combustion, metal industry and coal combustion. The other sources are biomass combustion at Jogannapalem; secondary aerosols and road traffic at Parawada. At Jogannapalem, biomass combustion (35%) is the major source, whereas coal burning (22.6%) is major source at Parawada. Analysis of PMF factor indicated comparable metal profiles at various industrial areas of Visakhapatnam.

Gangwar et al., 2016, evaluated PM₁₀ and heavy metal content in e-waste burning and industrial area during April 2015- September 2015 at five monitoring sites during summer and monsoon seasons in Moradabad city of India. Metals concentration was analyzed in PM₁₀ samples using ICP-OES. Highest concentrations of PM₁₀ were reported in summer and lowest in monsoon at all the monitoring sites. Average concentration of PM₁₀ and heavy metals was found highest at industrial sites and e-waste burning site as compared to that in the residential sites. The mean concentrations of heavy metals followed the sequence of Cr < Ni < Cd < Pb < Cu < Zn. PCA was also conducted to investigate the main emission sources of various air pollutants in the monitoring sites. The major emission sources were e-waste processes, industrial processes, vehicular emissions and wind-blown dust was the minor one. PM₁₀ and heavy metal concentration exceeded the standard limits which caused adverse effects to the environment and also imposed heavy metal exposure to the local residents.

Arora et al., 2017, conducted study on the concentrations for heavy metals viz., As, Ni and Pb in PM₁₀ at seven sites of National Capital Region (NCR) of India. The 24 hours average PM₁₀ concentrations varied from 126 to 237.67 $\mu\text{g m}^{-3}$, which exceeded the standard limit (100 $\mu\text{g m}^{-3}$) of NAAQS and also standard yearly daily limit of US EPA (50 $\mu\text{g m}^{-3}$). The metal analysis showed that Ni dominated the ambient air as compared to As. Ghazipur, which is a waste dumping site with heavy traffic flow is found to be the most polluted area and Mayur Vihar phase-I, Delhi being the least polluted area of NCR

region. High concentration of Ni was observed in Ghazipur due to waste dumping and mobile sources. Indrapuram area in Ghaziabad is a residential area with high industrial influence and high concentration of Pb but within the permissible limit, due to point emission sources. The ambient concentration of Ni was very high at three locations viz., Ghazipur, Vasundhra (Ghaziabad) and Noida- Sec26, and exceeds the WHO limits (10 ng m^{-3}). The concentration of As was found to be within the permissible limit at all locations. The conclusion of the study was that the ambient level of heavy metals in NCR region is due to presence of heavy traffic flow and industrial emission, which is extremely hazardous due to their carcinogenic and toxic effect on humans.

Suvarapu et al., 2017, discussed the importance of heavy metal in ambient air because of their toxicity to humans. Heavy metals viz., As, Ni, Cd and hexavalent chromium have been identified as carcinogens. Heavy metals can accumulate in different animals and plants and enter human body through the food chain. Most of the toxicity studies were done on metals e.g. As, Ni, Cd, Cr and Pb. In few studies, plants are used as bio-monitors for studying the concentration of heavy metals. In some studies, heavy metals had high concentrations in the industrial areas as compared to residential areas. In most of the studies, main sources of the PM and heavy metals in ambient air are secondary aerosols, vehicular exhausts and industrial emissions.

Cheng et al., 2018, studied the trace metal content in PM_{10} in Chengdu, a megacity of China, and also estimate the health risks in human caused by PM_{10} exposure. PM_{10} samples were collected from an urban sampling site in Chengdu during November 2014– October 2015. The yearly average PM_{10} concentration was $173.6 \pm 77.9 \text{ } \mu\text{g m}^{-3}$, which is 2.5 times higher than national permissible limit ($70 \text{ } \mu\text{g m}^{-3}$). Arsenic level in PM_{10} was 2.9 times higher than standard limits regulated by NAAQS of China. The concentrations of rest of the metals were within the standard limit. Study of enrichment factor showed that metals e.g. As, Pb, Zn, Cu, Cd, and Sb mostly came from anthropogenic activities. The emission sources found were road dust (19.4%), soil dust (48.4%), metallurgy industry (3.5%)

electroplating industry (13.8%) and fossil fuel combustion (14.9%). The assessment of health risk showed that Cr can be carcinogenic to both adults and children while other elements were measured to be within the regulatory limits. However, As was observed to be above the threshold.

Vaio et al., 2018, conducted studies for estimation of seasonal variation for compositions and mass concentrations of heavy metals in PM₁₀ collected in urban-industrial site of Acerra, Italy. The seasonal variation observed in concentration of PM₁₀ exceeded the daily concentration of 50 µg m⁻³ in all the seasons except autumn. PM₁₀ samples were determined for heavy metals viz., Cd, Al, As, Cr, Co, Cu, Mn, Ni, Fe, Pb, V, Zn, and Sb, which constituted approximately 8% of total PM₁₀ concentration. Concentration of carcinogenic metals remained within the mean yearly limit of EU and Italy. PCA was performed to investigate major emission sources of the heavy metals in PM₁₀, and these are industrial emissions, oil combustion and vehicle emissions. The health effects due to ambient PM₁₀ metals were the Cancer Risk (CR) which was similar for all age types.

Kori et al., 2019, studied the ambient PM₁₀ associated heavy metals nearby Mandideep industrial area, Madhya Pradesh, India. The heavy metals under study were As, Ni, Pb, Cr, Cu, Co, Mn, Zn, Fe and Cd. Only three heavy metals, i.e. Pb, Ni, As were reported as priority pollutants in NAAQS 2009. Among all heavy metals mainly the Pb average concentration was measured as 0.5 µg m⁻³ and As was measured within standard limit as per NAAQS 2009. While Ni exceeded the standard limit at one monitoring location (101 ng m⁻³) but remained within standard limit at all other monitoring locations around Mandideep. While Ni exceeded the standard limit at one monitoring location (101 ng m⁻³) but remained within standard limit at all other monitoring locations around Mandideep.

2.4 Uncertainty Calculations in PM Measurements

In most of the AAQS, the method for the determination of a criteria pollutant is given. Still, there is nothing mentioned about the regulation of measurement uncertainty and traceability of the data or calibration of the instruments. Precise and accurate traceable measurement of ambient PM concentration

is currently a difficult task because only limited standards for ambient PM are available. This study was conducted for the measurement of uncertainty in the PM data for quality assurance.

VIM, JCGM 200. 2000, This Guide describes the common rules required for calculating and expressing uncertainty in measurement results that can be used for different type of measurements. The Guide was developed by CIPM (International Committee for Weights and Measures) and Working Group on uncertainty. This Working Group was developed by Bureau International Weights and Measures (BIPM) on recommendation of CIPM. The CIPM recommendation is regarding the expression of uncertainty in measurement results approved by an intergovernmental organization. This Guide was developed in collaboration of experts nominated by BIPM, the International Electrotechnical Commission (IEC), the International Organization for Standardization (ISO) and International Organization of Legal Metrology (OIML).

Heal et al., 2000 conducted 24 h sampling of ambient PM₁₀ for determination of mass concentration. The sampling was performed for 33 days using five different samplers at an undisturbed indoor location. The five different samplers used were- PQ100 gravimetric sampler with Gaseby Andersen PM₁₀ inlet; an Airmetrics Minivol static gravimetric sampler; a Casela cyclone personal gravimetric sampler and two DustTrak, TSI Inc. real-time optical scattering samplers. The uncertainty for two gravimetric samplers was higher (20%) and comparable with that for PQ100 gravimetric sampler (5%). Uncertainty measurements for the DustTrak sampler was comparatively low (15%). Estimation of measurement uncertainty for the concentration of PM₁₀ with Minivol was 5%. This data can be compared with PQ100 sampler data ($r \sim 0.97$, $n \sim 8$) but was 23% greater on average. Intercomparison assessments are important for revealing systematic bias and measurement error. A sampling of PM₁₀ by two DustTraks samplers indicated the temporal and spatial variation of PM₁₀ in the city of Edinburgh, UK. The variation observed emphasizes the need to determine truly personal exposure profiles of PM₁₀ for quantifying exposure and response relationships for epidemiological studies.

Price et al., 2004, discussed the importance of uncertainty evaluation in a gravimetric measurement of PM concentration. The Federal Clean Air Act regulates both PM_{10} and $PM_{2.5}$ for gravimetric measurement of PM concentration in ambient air. While the measurement is accurate and precise, various uncertainty factors interfere with the analysis causing high uncertainty altogether in the determination of concentration. First order Taylor Series approximation and analytical derivatives were used to calculate the overall system uncertainty. The study uses a sensitivity analysis for determination of the uncertainty sources which would help to identify the most difficult measurements and their effects on the design of PM samplers, calibration and operation.

Brown et al., 2005, compiled the results of various studies undertaken to improve the gravimetric methods for filter and increase the validity of UK-wide series of equivalence trials for particulate monitors. The purpose of the study was to make an optimized weighing procedure and define the properties of the balances used, thus identifying the main sources of error in the gravimetric method. An uncertainty budget was also prepared for the method. Once proven, the weighing procedure can be used to determine the most appropriate material for filter used in the measurement of PM in ambient air. The effects of humidity, temperature, transport, storage, and inter-laboratory mass weighing of various filter materials were studied. It was concluded that the filter material must be selected considering various factors like change in mass of filter with relative humidity and temperature, flow resistance, structural integrity, particle sampling efficiency, chemical effects and static charge effects. Thus, the selection of Emfab (PTFE-bonded glass fibre) was done considering the above factors.

Bounanno et al., 2009 proposed a model on the uncertainty budget for measurement of ambient particle mass size distributions, particle number and surface area. Numerous studies have been done on the health effect of PM on humans. But there is less information regarding the particle size and origin with reference to its health effects. Air quality standards focus mostly on smaller particles. The latest air quality standards only regulate $PM_{2.5}$ and PM_{10} . The most reliable method for measuring PM is the

gravimetric method which has traceability to the SI unit. But this method neglects short period intra-day variations of various atmospheric factors i.e., temperature, emission sources, wind direction, relative humidity and speed. Tandem system established by Scanning Mobility Particle Sizer (SMPS) and Aerodynamic Particle Sizer (APS) was used to measure number size distribution and total number concentration in the range of 0.014 – 20 μm of particle size.

Buonanno et al., 2011, reviewed the metrological characterization of the gravimetric method used in measuring PM concentrations. The review focused on the critical aspects of the technical standard in evaluating the uncertainty budget of PM measurement and effect of single uncertainty contributions to the combined uncertainty. The comparative analysis between US and European standards limits in PM measurement was also discussed. The studies of the PM exposure led to the updating of the new air quality standards by air quality management community and regulatory authorities. Measurement of variations in periodic PM concentration should be taken to characterize the exposure by humans. To achieve this, continuous or semi-continuous measurement procedures were developed.

Ohenoja., 2015. discussed the methods used in the estimation of measurement uncertainty and sampling error. The uncertainties evaluated in processing of virtual measurements , digital signal and other methods were also discussed. All measurements have some level of uncertainty. The uncertainty calculated during any measurement helps in decision making. There are different methods of estimating the measurement uncertainty at instrument and system levels. There are some statistical methods for uncertainty evaluation and some practical guides are published for analytical measurements. Though, sometimes the sampling process does not consider the uncertainty evaluation and errors as well.

Zhang et al., 2015, quantified uncertainties related with emission modeled $\text{PM}_{2.5}$ concentrations and sensitivities using a reduced form. The models used in the regional air quality are applied to study the control strategy effectiveness. Therefore, it is essential to study the accuracy of model simulations to create confidence in its performance and to help in the development of other model. This method is

computationally efficient than conventional Monte Carlo method. The reduced-form model represents the concentration-emission response and is constructed using sensitivities of the first and second order obtained from a single CMAQ / HDDM-PM simulation. The study was conducted in the Houston-Galveston-Brazoria (HGB) area. The uncertainty of modelled, daily average $PM_{2.5}$ concentrations due to uncertain emissions ranged between 42% to 52% for different simulated concentration levels, and the uncertainty is evenly distributed in the modelling domain. Emission-associated uncertainty can account for much of the difference between simulation and ground measurements as 60% of observed $PM_{2.5}$ concentrations fall within the range of one standard deviation of corresponding simulated $PM_{2.5}$ concentrations. Uncertainties in meteorological areas and model representation for secondary organic aerosol formation are the major contributors to the uncertainty of modelled $PM_{2.5}$. The uncertainties of the simulated first-order sensitivities were also investigated, and it was found that the larger the first-order sensitivity, the lower its uncertainty associated with emissions. Sensitivity of $PM_{2.5}$ to primary PM has the lowest uncertainty while sensitivity of $PM_{2.5}$ to VOC has the highest uncertainty associated with emission inputs.

Woollatt et al., 2017, developed a suitable method to evaluate the uncertainty related with measurement of PM from the stationary source of emissions in South Africa. The estimation of measurement uncertainty for emissions from stationary sources is the most important parameter related to PM emission records in South Africa. A sequence of In-Stack measurements was taken following the international methodology of ISO 9096:1992 and 2003 at two selected industrial sites, signifying a compliant and non-compliant setup. Comparison of the two setups revealed that the sampling methods have the highest error. The study conducted focused on the effect of total uncertainty (analytical, field sampling and process) on the final emission values obtained. This will give rise to the overall error associated with quantification of the emission values of stationary source of PM. The combined expanded uncertainty calculated for both sets of data was between 62 - 72%. It was observed that the

uncertainty obtained from compliant and non-compliant sampling campaigns indicated that the variation in data was too high for both the setups to make any valid statistically observations. Therefore, a sampling suitability matrix was developed as an alternative tool for evaluating the reliability and quality of reported emission data. It will add significant value to the final emission data. The tool can be used as supplementary information for all emission data reports in future. It will help the plant regulator and operator to evaluate the quality of reported data and results of final emission establishing the compatibility with their Air Emission License (AEL) requirements.

Owczarek et al., 2018, discussed the importance of the equivalence of results obtained by using the standard method. One of the equivalence issues is the estimation of measurement uncertainty of other methods in relation to the standard method. This uncertainty can be defined as the probability of obtaining the measurement results which differs from the result obtained by standard method by a fixed value. Uncertainty can occur by many factors: inadequate application of the definition of the measurand, insufficient information about the effect of other factors, heterogeneity of the analyzed process, errors involved in assessing device and others. Discussion was done on the procedures involved in estimating the uncertainty of measurements used in the equivalence study and also applying the test methods with equivalence model.

MATERIALS AND METHODS

Aerosol measurements require a combination of techniques. A single instrument cannot measure particle sizes over the range of 1 nm - 100 μm . Each measurement provides different information about the particle. Therefore, different instruments are used for characterization of aerosols.

The common methods used for sampling of atmospheric aerosol are cascade impactors and filters, which collect the aerosol particles onto a surface. The sample collected is estimated for size and composition. Collection method should be simple despite its other problems. The development of inexpensive acquisition systems and modern electronics has provided complex and automatic monitoring methods. Methods used for collection are being replaced with both chemical and physical analysis, digital electronic devices and automatic methods (Papastefanou et al., 2008).

For regulatory purposes, PM_{10} and $\text{PM}_{2.5}$ sampling is recommended. Further, for particulate mass and its chemical characterization, filter based sampling is recommended. Widely used sampling to air is size separator inlet (PM_{10} or $\text{PM}_{2.5}$) followed by filter holder, temperature and differential pressure sensor, flow controller and air pump system. PM_{10} sampler with their specifications and with flow rate 16.7 lpm was used in this work throughout PM mass and chemical measurements.

Apart from the various techniques available for chemical analysis, extraction or microwave digestion, HPLC or ICP-OES are the major techniques used throughout the thesis work. Therefore only these techniques were discussed in the succeeding sections in detail.

3.1 Description of Sampling Site

New Delhi is situated between latitudes 28° 24' 17" N to 28° 53' 00" N and longitude 76° 50' 24" to 77°20'37" E at 216 meters above the mean sea level. The monitoring and measurement were performed at National Physical Laboratory (NPL) CSIR, New Delhi, during January 2014 to January 2015 (**Figure 3.1**). This measurement site is a good representation of aerosols in urban areas of New Delhi with the mixed effect of vehicular, residential, industrial and agricultural emissions.

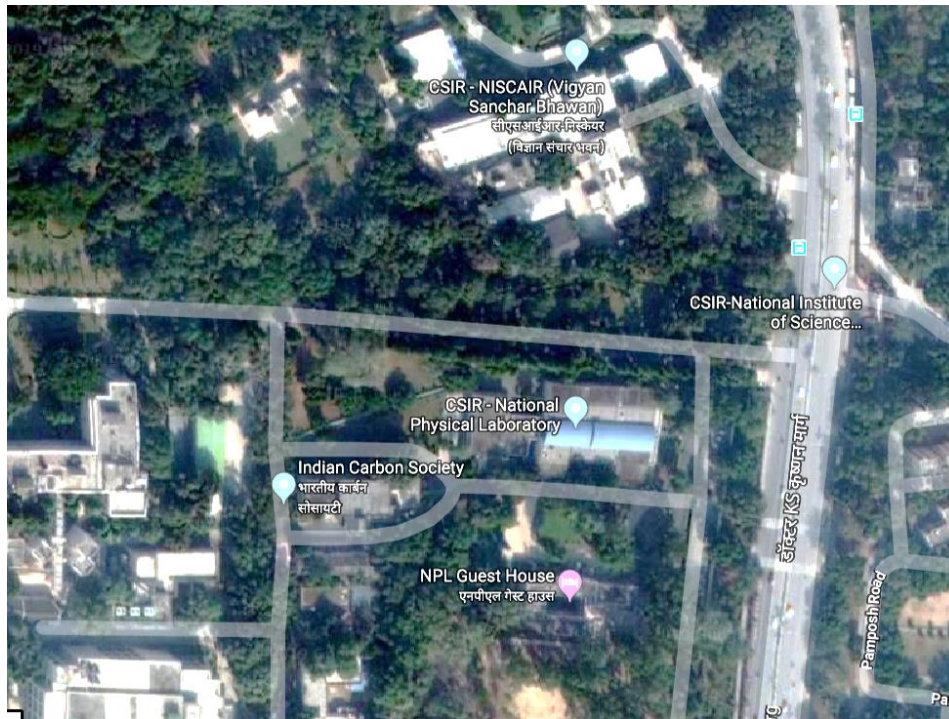


Figure 3.1: The surrounding location of National Physical Laboratory, New Delhi.

3.2 Monitoring Method for Collection of PM₁₀

A year-round sampling of PM₁₀ was done, throughout the year using a low-volume [16.7 lpm (litres per minute)] particulate sampler (Envirotech APM 550), as shown in **Figure 3.2** as per the guidelines given in NAAQS. Collection of PM₁₀ samples was done at the laboratory rooftop at approximately 15 m above the ground. The filter collection done in the thesis work is used for

gravimetric measurement and regulatory chemical analyses. The samples were collected for 24 hours for thrice a week every month for one year (January 2014 to January 2015). 104 samples of PM₁₀ were collected as given in the NAAQS. The EPA guidelines were followed during sampling of PM₁₀. The methods for sample collections are given below.

3.2.1 Filter Collection

Filter collection is done for many analysis viz., gravimetric analysis (for mass determination), microscopic analysis (for shape, number, morphology, and elemental contents), microchemical analysis (for organic and inorganic analysis, elements and compounds), and radioactivity analysis. The filter used can be open-faced, in line or cassette types. Selection of the filters must be done before sampling according to the application. Testing of filter should be performed for various parameters like stability at high temperature, efficiency of filter for the aerosol size distribution, pressure drop across filter, compatibility of filter with the environmental conditions (temperature, pressure, humidity, etc.), cost constraints relating to the number of filters required. Filters are of different types according to the filtration mechanism.

1. Fibrous filter work on the principle of diffusion.
2. Porous filter work on the mechanism of inertial impaction.
3. Pore membrane filters work on the process of inception, and
4. Granular bed filters work on gravitational settling.

In this thesis work, the fibrous filter was used due to following reasons:

- It consists of mat of fine fibers arranged perpendicular to the path of the airflow.
- Porosity is very high ranging from 70% - 90%.
- Size of fibers range from few micrometers to 100nm and is made up of cellulose, wood fibers, glass fibers and polymer fibers.
- It collects particles through the mechanism of interception, impaction, and diffusion.

- The air velocity for fibrous filter is very low (10cm/s) which refer to high collection.
- Pressure drops are the lowest in case of fibrous filters.

3.2.2 Inertial Collection Techniques

Inertial collection techniques are highly suitable for large size particles. It is used for the measurement of mass size distribution of aerosols. Inertial collectors are based on the theory that particles present in a gaseous medium are denser than air surrounding them. A particle travelling in air stream has the same velocity as the air and it has greater momentum (inertia) as compared to the volume of air, it displaces due to its high mass. When there is sudden change in direction of the air stream, the momentum possessed by the particle will cause it to be deflected less than the air surrounding it. Such a deflection is observed if there is an object placed in the path of an air stream. If particle has sufficient inertia (bigger size particle), it will hit the object and collect on it. Particles with low inertia (smaller size) will follow air stream and collect on following stages. The momentum of particles in the air stream will increase with the high incident velocities thereby increasing their elimination by collecting on object. Air stream should be passed through an orifice in order to increase its velocity. An impactor works on this principle.

3.2.3 Centrifugal Separation Devices

Centrifugal separation is a process of the inertial collection where centrifugal force causes removal of the particles from an air stream by moving the particle swiftly along a circular path. Many sampling apparatus work on the principle of centrifugal separation. A cyclone uses centrifugal and inertial forces to separate PM from the polluted air stream while moving along the cyclone. The collection efficiency of a cyclone for a PM is directly associated to size distribution of particles in polluted air stream. Generally, cyclones collect PM having size greater than 10 μm in diameter (PM_{10}). Cyclones are also called as "pre-cleaners" as they decrease the inlet particulate loading of collection devices to downstream by removing coarse particles. For the collection of fine particles, a high efficiency cyclone

is required with high pressure drop and energy saving. A cyclone consists of an inlet having cylindrical section and conical section while the outlet has gas duct, collection hopper and dust tube. It uses an induced draft fan which produces centrifugal force on the air stream within its conical region. Formation of a double vortex take place inside the cyclone and the incoming air moves in a spiral path along the cyclone. When the air reaches the bottom of the cyclone, it goes up to the center of the cyclone and then exit from the top of the cyclone. The centrifugal force produced by the spinning of the air stream move large particles towards the walls of the cyclone. Gravitational force pulls the large particles to down the cyclone. Various small diameter tubes arranged in parallel to form a cyclone are termed as multicyclone or multiclones. This arrangement has high efficiency due to small size ability to handle large volumes of air. But has some common operational problems like plugging of the dust or gas inlet, erosion of part of cyclone in contact with particles of high velocity and air in leakage that affects the collection efficiency and inlet velocity of the cyclone.



Figure 3.2: Envirotech APM 550 installed at NPL, New Delhi used for sampling of PM₁₀

3.3 Mass Measurement for PM₁₀

The determination of the mass concentrations of the particles in the ambient air is essential for scientific and regulatory purposes. All over the world, PM $\leq 10 \mu\text{m}$ in aerodynamic size known as PM₁₀ is a component of regulatory parameters of NAAQS. According to NAAQS guidelines, regulatory limit of PM₁₀ is $60 \mu\text{g m}^{-3}$ in India. This regulatory limit is based on yearly average weight of sample (minimum samples collected -104) collected for 24 h at a specific monitoring site for two or three days in a week. In addition to this mass measurement, measurement uncertainty was also estimated.

The PM₁₀ particles were collected on prebaked, conditioned, and weighed quartz filters of 47 mm diameter size. After sampling, filter was conditioned in a similar manner and weighed for particulate mass determination. Weighing was performed on a 5 digit balance, as shown in **Figure 3.3a**. Sampling flow rate was tested every month once, before and after sampling to see the flow variation (one of the important uncertainty components). Other factors, such as humidity, temperature were also studied for the influence on the particulate collection and weighing uncertainty. Meteorological data were also recorded for the year-round period of sampling. The air of measured volume is passed through a filter for a set period of time (24 hour). Data of hourly meteorological parameters e.g. temperature and relative humidity for the measurement period were obtained from the weather station of NPL, New Delhi.

(a)



(b)



Figure 3.3: (a) Mettler-Toledo AX105 (range 0.1-100 mg) balance used for weighing PM₁₀ filters and metal standards and (b) Mettler AT20 (range 0-22g) balance used for the standard preparation of BaP

3.4 Instrumentation

3.4.1 Working Principle of High Performance Liquid Chromatography (HPLC)

It is a type of column chromatography where an analyte or sample is mixed with a solvent (mobile phase) at high pressure which passes through a column (stationary phase) packed with solid adsorbent material. HPLC can be used for the separation, quantification and identification of the compounds present in any sample and that can be dissolved in a liquid or solvent at a minimum concentrations levels of parts per trillion. Due to its versatility, HPLC has multiple applications in the industries and research laboratories such as chemicals, forensics, pharmaceutical and environmental. The retention time of the sample may vary due to the interaction between the stationary phase, mobile phase and the

molecules being analyzed. When the analyte passes through the column, there is an interaction between the stationary phase and mobile phase and the compounds are separated according to the difference in their polarity. Compounds that have the least polarity will exit the column first. **Figure 3.4.1(a)** shows the schematic diagram of HPLC, and **Figure 3.4.1(b)** shows the HPLC system in NPL used for the analysis of BaP during the study.

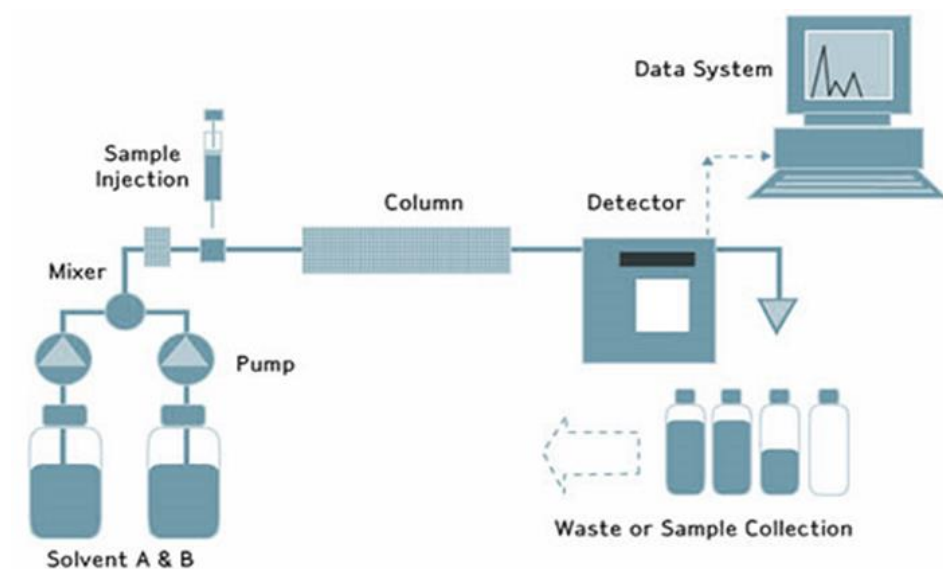


Figure 3.4.1: (a) Schematic diagram of HPLC (Source: Merck website)



Figure 3.4.1: (b) Shimadzu Prominence Model LC-20AD HPLC for BaP determination

3.4.2 Working Principle of Microwave Digestion System

Microwave digestion is a process used to extract metals present in a sample before analysis by analytical techniques like AAS or AES and ICP measurements. The process of digestion involves treating the sample with a strong concentrated acid in a closed vessel having high pressure and temperature through microwave radiation. The high temperature and high pressure causes the thermolysis of sample and the extraction of metals in solution form. After the metals come in solution form, they can be quantified through analytical techniques. (Kingston et al., 1988). **Figure 3.4.2** shows the Microwave digestion system used during the extraction of metals from PM₁₀ samples.



Figure 3.4.2: Speedwave Bergohf Microwave digestion system used for acid digestion for analysis of As, Ni and Pb in PM₁₀ samples

3.4.3 Working Principle of Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

It is one of the most efficient and common analytical equipment for determination of trace elements in different types of samples. The process involves excitation of atoms and ions by RF discharge followed by the spontaneous emission of photons. Solid samples have to go through extraction or acid digestion to make the analyte in a solution form while liquid and gas samples may be directly injected into the instrument. The sample is then converted to an aerosol and enters the central part of the plasma (as shown in **Figure 3.4.3 (a)**). At its centre, the ICP maintains a temperature of ~ 10000 K, due to which the aerosol is easily vaporized. The elements present in the sample are released in the form of free atoms in the gaseous state. These atoms now collide with plasma and gain energy, promoting them to excited states. Now the atoms are changed into ions by gaining energy and promoting them to excited state. Atoms and ions emit a photon and come to the ground state. The wavelength of emitted photons can be used to identify the elements from which they originated. The total number of photons emitted is directly related with the concentration of the element in sample. The instrumentation related with an ICP-OES system is comparatively simple. A part of the photon emitted is captured on a concave mirror or a lens. This focusing lens or mirror produces an image of the ICP on the aperture of a monochromator (wavelength selection device). The wavelength exits from the monochromator and is converted to an electrical signal by a photodetector. The signal is then amplified, processed and displayed on a computer (Hou et al., 2000). **Figure 3.4.3 (b)** shows the ICP-OES used in the study for analysis of metals from PM₁₀ samples.

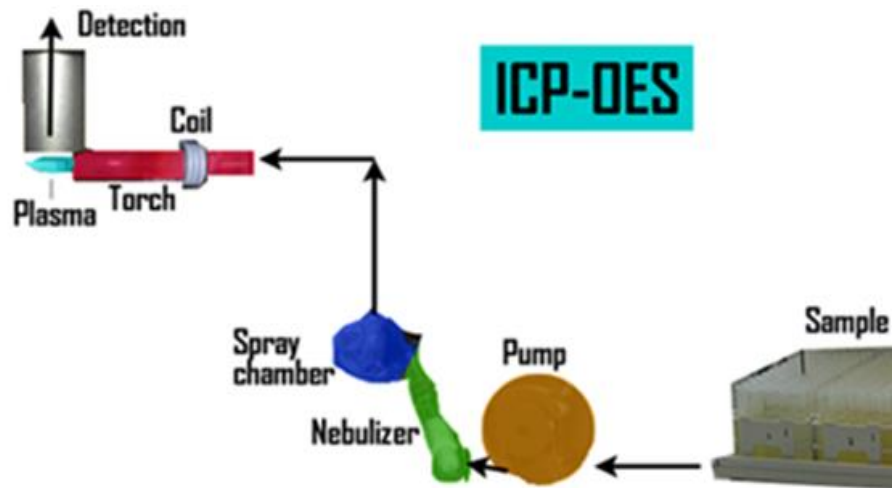


Figure 3.4.3: (a) Schematic diagram of ICP-OES (Dhuri et al., 2018)



Figure 3.4.3: (b) SpectroCiros ICP-OES used for the analysis of As, Ni and Pb

3.5 Determination of PAHs

PAHs are the compound which consists of multiple benzene rings bonded in straight, groups or angular forms. They are also found in atmospheric aerosols. In the atmosphere, they can be emitted mostly due to incomplete combustion of natural sources (fossil fuels, forest fires, smoke, etc.) or anthropogenic sources (coal burning, vehicular emissions, smoke, etc.) or secondarily by atmospheric processes. Depending on the anthropogenic sources, PAHs may occur in significant concentration in urban and industrial ambient air i.e., bounded with PM. A particle whose aerodynamic diameter is $\leq 10 \mu\text{m}$ is called PM_{10} . BaP is among the most carcinogenic and toxic PAHs. Both PM_{10} and BaP are among the 12 criteria pollutants listed in NAAQS. BaP concentration was calculated in PM_{10} collected in a representative site of New Delhi was studied during the year 2014–2015.

BaP was extracted from the exposed PM_{10} sample. The sample filter (quartz) was cut into 14 mm diameter disk. The filter papers were then extracted with toluene using ultrasonic bath. The extract was then passed through silica gel column for the cleanup process using cyclohexane (high performance liquid chromatography, HPLC grade) (ISO16362, 2005). Finally, before analysis, the extract was evaporated on a rotatory evaporator till dryness and was redissolved in 1 ml acetonitrile (HPLC grade). The extracts were analyzed by a HPLC system (Shimadzu Prominence Model LC-20AD) with programmed fluorescence detection (Shimadzu RX-10AXL) for BaP. BaP is determined in year-round PM_{10} samples. These samples were transferred to a 1.5 ml vial and stored in -20°C . The uncertainty components in the measurement, such as sampling, extraction and instrumental biases will be considered.

The method was tested with quality assurance (verification of instrument calibration and repeatability test of the instrument). Two replicates of blank samples were used as real samples to check any contaminations of the analytes. The stock solution of standard was prepared gravimetrically by using BaP standard (Sigma-Aldrich, B1760). The gravimetric measurement was performed on balance

shown in **Figure 3.3 b**. For calibration, BaP standard solution was prepared by serial dilution of stock solutions in acetonitrile (by weight). Standard solutions used for the calibration were stored at 4 °C in the dark. In India, the regulatory limit of BaP in NAAQS is 1 ng m^{-3} (annual). PM₁₀ sample filters were analyzed for BaP according to the ISO 16362: 2005.

3.5.1 Determination of BaP in PM₁₀ Samples using HPLC

The extract obtained was then analyzed for BaP through a HPLC system with programmed fluorescence detection (Shimadzu RX-10AXL). Analysis of the BaP was determined using a HPLC reversed phase C18 column (dimension 250 mm x 4.6 mm, make Shim-pack), with a elution of binary gradient from 50% acetonitrile (HPLC grade) and water mixture to 100 % acetonitrile in 45 min . BaP was detected in PM₁₀ samples by means of a fluorescence detector with respect to its retention time. The detection was done by fluorescence detector with excitation wavelength of 361 nm and emission wavelength of 405 nm. Calibration of the instrument was done by injecting three different concentrations of BaP standards as a function of peak area using a linear curve. The peak identification of BaP in PM₁₀ samples was done by comparing retention time of sample with that of the standard. The instrument was calibrated after every 10 analysis of the sample. Other statistical data for instrument calibration, i.e., correlation coefficients (R^2), standard deviation (SD) etc., along with a limit of detection (LOD) and limit of quantification (LOQ) was also calculated.

3.6 Sample Preparation of Metals /Element in PM₁₀ Samples

There are three metals/element which are listed as the criteria pollutant in the NAAQS viz., As, Ni and Pb. Monitoring of PM₁₀ was done using the gravimetric method. PM₁₀ was collected on quartz filter from January 2014 to January 2015 for metals analysis. The PM₁₀ quartz filter was digested in the microwave digestion system, and the heavy metal was analyzed on ICP-OES. The concentration of metal was calculated for the entire sampling period and compared with NAAQS regulatory limits.

The PM₁₀ filters were cut into 14 mm diameter and put into the digestion vessel. All reagents used were of high purity grade. MilliQ water was used to prepare the sample and standard solutions. High purity grade of concentrated nitric acid and hydrogen peroxide was used during digestion. The blank samples were also prepared and analyzed in the same way as the sample filters to avoid the interferences. The standard used for the calibration in ICP-OES was CRM of As, Ni, Pb solution (Traceable to KRISS, Korea). All the PM₁₀ samples were acid digested using microwave digestion system (Speedwave Bergohf). The PM₁₀ samples were digested using 5 ml concentrated HNO₃ (high purity) and 1 ml H₂O₂ (high purity). After digestion, the sample is washed with DI water and transferred to a preweighed 50 ml polypropylene bottle and volume made up to 20-30 ml approximately. The solution was then filtered with microfilter disc (0.5 µm). The bottle was again weighed with the final solution. The acid digested samples were then analyzed for As, Ni and Pb on ICP-OES (SpectroCiros, CCD). Thus, ICP-OES is used for determination of the metal content in particulate matter in the concentration of ppm. The primary standard is used to determine the metal concentration in a single aspiration.

3.6.1 Analysis of Arsenic, Nickel and Lead using ICP-OES

There are many heavy metals studied but regulatory limits are notified for only three metals (As, Ni and Pb). Therefore, only these three metals have been analyzed. Standard of these metals (traceable to KRISS, Korea) is further diluted using ultrapure water by mixing both the standard and water gravimetrically using a calibrated balance. The calibration standards were prepared in a series of concentration from 0.1 to 1.0 mg kg⁻¹ by weighing the calculated amount of standard from the standard solution.

The concentration of As, Ni and Pb was expressed in ng m⁻³ which is calculated as the volume of air sampled and the total area of filter on which PM₁₀ were collected. The quartz filters were of 47mm diameter in size and the total volume of air sampled was ~ 24 m³ for 24 hour sampling period (at 16.7

L/min). Each concentration was multiplied by 5.71, and divided by 24, to convert to $\mu\text{g m}^{-3}$. These values were compared with data of PM bound metal concentrations from other studies and with permitted limits. The concentration of As, Ni and Pb in PM_{10} (measurand) can be obtained from the ICP-OES software, and/or calculated from the calibration plot versus concentration.

RESULTS & DISCUSSION

The aerosol study is an important part of atmospheric chemistry and physics; hence, it has a huge impact on regional as well as global climate. Aerosols affect human health adversely and therefore, are major parameters of National Ambient Air Quality Standards (NAAQS). In nearly all of the countries, PM with size measurements as $\leq 2.5 \mu\text{m}$ in diameter are known as $\text{PM}_{2.5}$, and $\leq 10 \mu\text{m}$ in diameter are known as PM_{10} . These are included in NAAQS as regulatory parameters on account of their measurement techniques, i.e., reference or equivariance procedures. (Hauck et al., 2004, Aggarwal et al., 2013). For accurate and precise data of NAAQS, the instruments used in the measurement laboratory and measurement must be as per the NAAQS and ISO standard. For such measurements, instruments must be calibrated with the standards with traceability and should be as per the recommendation of NAAQS. For SI units, measurement traceability is defined as linking of the measurement results with the reference value, i.e., linkage of the results of measurement (results obtained by instrumental analysis, which is calibrated with the standard) with the SI. The calibration that is traceable is not so straightforward in aerosol measurements as it involves different parameters, e.g., time, size, flow, mass, and if the equipment working is dependent upon various parameters related to frequency, optical, temperature, wavelength, absorbance, pressure, then all these parameters require traceable standards (Aggarwal et al., 2013). Thus, SI is defined as a system of seven base units, viz. measurement of length (meter), mass (kilogram), time (second), temperature (kelvin), electrical current (ampere), luminous intensity (candela) and amount of substance (mole). For traceability to SI units, it is significant that the standards used must have a calibration hierarchy of its set measured values to SI units (VIM, 2012).

Further, measurement results should involve uncertainty. The measurement uncertainty is defined as the distribution of measurement results that is fairly assigned to the value of the measurand.

Thus, to produce a traceable result from a measurement exercise, as a first step, it is important to use traceable standards. Most of the NAAQS for PM was initially developed for the mass concentrations of particulates $\leq 10 \mu\text{m}$ in aerodynamic diameter (PM_{10}). In 1997, USEPA introduced standards for particles $\leq 2.5 \mu\text{m}$ in aerodynamic diameter. Thereafter, mass measurements of atmospheric particles are consistently determined at monitoring sites in different regions around the world. The most common method used for measuring the mass concentrations of particulates is the gravimetric filter-based method. An accurately controlled environment, with stable humidity and temperature and clean air, is required for processing and weighing of filter that satisfies these conditions. Balances with sensitivities of $\sim 1 \mu\text{g}$ or equivalent are calibrated with traceable standards and be regularly serviced.

In this study, identification and also evaluation of uncertainty components associated with the filter-assisted sampling of PM_{10} and its gravimetric measurement of mass in New Delhi has been conducted. Air pollution in Delhi is caused by various factors like meteorological conditions, sources of pollution and geographical location of Delhi. PM_{10} concentrations largely vary and are reported to have violated standards at most places in Delhi. Various uncertainty components like conditioning of filters, weighing of filters, the flow rate of low-volume sampler have been taken into account.

4.1 Uncertainty Estimation in PM_{10} Measurements

Measurement of uncertainty in the mass concentration of PM_{10} is dependent on two factors:

- (1) the volume of the air sampled and
- (2) particle mass measurement

Figure 4.1 shows the uncertainty components involved in these measurements in the form of cause effective diagram. The uncertainty in the measurement of various components that belong to the

mass of particle and volume measurement by means of the low-volume sampler is considered in the measurement of the mass of PM₁₀.

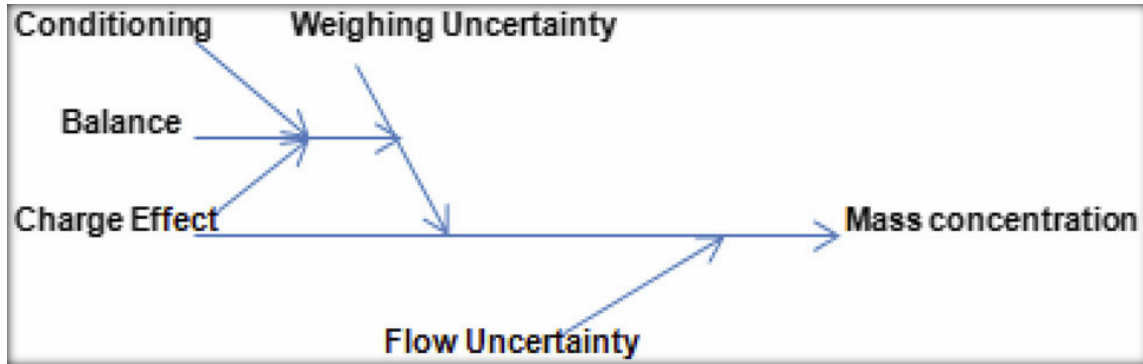


Figure 4.1: Cause-effect diagram showing uncertainty components

The uncertainties parameters involved in the determination of mass concentration are calculated for PM₁₀ samples. The combined standard uncertainty (u_c) is defined as:

$$u_c = \sqrt{\sum_i (u_i)^2} \quad (1)$$

$$U_e = k \times u_c \quad (2)$$

where u_i is the standard uncertainty of i , and U_e is the combine expanded uncertainty at k (coverage factor). In this work, $k = 2$ at 95% confidence level.

The uncertainty involved in the measurement of the mass of the particle has a significant contribution of these parameters which are given as follows:

4.1.1 Uncertainty in Conditioning

While doing the conditioning of filters, there may be two possibilities:

- (a) Aerosol water content/moisture may add up to the mass (positive effect).
- (b) There may be some losses in particulate mass due to the evaporation of volatile material from the surface of particles (negative effect).

To study their common effect and estimate the uncertainty due to these two factors, measurement of mass has to be considered.

Therefore, five PM₁₀ filters were prebaked and conditioned before sampling. Uncertainty was calculated for the change in mass of the same loaded filter at different conditioning times, i.e., 12, 24, 36 and 72 hours after sampling. The standard uncertainty is calculated by the equation given below:

$$u_1(m) = \frac{\sqrt{\frac{\sum_{i=1}^n (m_i - \bar{m})^2}{n-1}}}{\sqrt{n}} \quad (3)$$

where m_i is the mass of particles before conditioning, \bar{m} is the average mass above m_i , and n is the number of samples. Uncertainty was calculated for different hours of conditioning for five different mass loaded filters of PM₁₀ and then the average of the mass was taken. The combined standard uncertainty was calculated as 36.713 µg. The relative standard uncertainty was calculated as 0.005.

4.1.2 Uncertainty Due to Balance Used for Weighing of Filters

The entire filter weighing was done on Mettler Toledo AX105 balance with a maximum capacity of 100 mg. The uncertainty of the balance is estimated using the above Equation 3. Type A uncertainty is determined as the standard deviations of repeated measurement results having a normal distribution. Type B uncertainty is based on values given in the calibration certificate of the balance with rectangular distribution. Combining both type A and type B, we get standard uncertainty as 3.759 µg. Relative standard uncertainty is calculated as 0.031.

4.1.3 Uncertainty Due to the Charge Effect

Aerosol mass drop from the filter, contaminations, electrostatic charging of filters and variations in relative humidity may result in the deviations from the actual mass value (Almeida et al., 2003). An electrostatic charge eliminator (Haug Mettler Toledo) was used to eliminate the static charge collected on the filters before each weighing. The PM₁₀ filter masses were determined by taking the weight of the filters with and without using the electrostatic charge eliminator as given in Equation 3. The standard

uncertainty calculated for the difference in mass before and after the use of a static charge eliminator was found to be as 1.204 μg .

4.1.4 Uncertainty Due to PM_{10} Sampler Inlet Flow Rate

Rotameters are the most widely used as flow meter to determine flow rate in PM_{10} samplers. It consists of a rotating float in a tapered tube that keeps falling and rising and thus measures the flow rate. They are gravity-type flow meters because they are based on the resistance between the downward force of gravity and the upward force of the incoming air. The flow rate is indicated on a graduated scale. Air is drawn by means of a blower into the sampler through a quartz filter so that PM collects on the surface of the filter. Due to the size-select-type inlet, particles $\leq 10 \mu\text{m}$ in diameter are collected on the quartz filter. A flow-rate indicator records the volume of air sampled. A reference orifice meter is used to calibrate the flow-rate indicator (Melymuk et al., 2014). PM_{10} low-volume sampler flow rate [16.7 lpm (litres/minute)] is measured by rotameter. This rotameter is calibrated with the reference flow meter in NPL traceable to the SI unit. The flow rate was measured at the start of sampling and then at the completion of the sampling. The mass of filter on loading in a sampler and removing from the sampler (after sampling) was also recorded (as shown in **Figure. 4.2**, given below). The sampling was performed for 24, 48, 96 and 120 hours to observe any change in the flow rate of sampling (if any).



Figure 4.2: Schematic representation of the measurement of the flow rate during the sampling of PM₁₀

The relative uncertainty in flow measurement is calculated as given in Equation 3. The uncertainty in flow rate was calculated using the mass, volume with the corresponding sampling time. The type A uncertainty is calculated by five repeatable measurements and the normal distribution is calculated as 0.03 lpm. Type B uncertainty as given in the calibration certificate of reference flow meter is 0.54 lpm. Standard uncertainty of flow rate $u(q_2)$ at the low-volume sampler inlet for the entire duration of sampling is estimated using Equation 4. as given below:

$$q_1 = \frac{u(q)}{\bar{q}}\%$$

$$u_{(q_2)} = \frac{\sqrt{\frac{\sum_{i=1}^n \left(\frac{\Delta m}{\Delta V} \times q_1\% - \frac{\Delta \bar{m}}{\Delta V} \times q_1\% \right)^2}{n-1}}}{\sqrt{n}} \quad (4)$$

Where, Δm is the difference in mass of filters, ΔV is the difference in volume of the air sucked during the start and end of sampling, q_1 is the % flow rate during sampling and q_2 is the average flow rate calculated throughout the entire sampling period (for n number of samples). The total standard uncertainty (Type A & B) was calculated as $0.318 \mu\text{g m}^{-3}$.

Mass concentration is calculated from measured mass and volume using Equation 5. The combined standard uncertainty for the determination of mass concentration $u(x)$ can be calculated as:

$$u_{(x)} = \sqrt{(u_{(m)})^2 + (u_{(v)})^2} \quad (5)$$

The uncertainty budget for the PM_{10} mass measurements in all the four uncertainty components is listed in **Table 4.1** as follows:

Table 4.1: Uncertainty budget for PM_{10} mass measurements

Uncertainty Components	Uncertainty Type	Standard Uncertainty	Distribution	Relative Standard Uncertainty	Relative contribution to standard Uncertainty (%)
Conditioning	Type A	36.713 μg	Normal	0.005	0.4
Balance	Type A	3.759 μg	Normal	0.031	2.4
	Type B		Rectangular		
Charge Effect	Type A	1.204 μg	Normal	0.089	6.8
Flow Uncertainty	Type A	0.318 $\mu\text{g m}^{-3}$	Normal	1.180	90.4
	Type B		Rectangular		

Only two uncertainty parameters had a major contribution: uncertainty in flow rate and uncertainty in charge effect. Of these, the uncertainty in flow rate had the greatest impact. The flow rate is affected by various factors like the inconsistent movement of the fan used to draw ambient air through the filter, decrease in porosity of filter due to particulate mass accumulation causes an increase in resistance to air (Lacey et al., 2015).

The combined uncertainty for mass measurement of PM₁₀ samples was calculated as 1.18 µg m⁻³. Using the combined U, the expanded U is estimated as 2.36. Lacey et al., 2015 also reported similar findings as shown in this study.

4.2 Monthly / Seasonal Variation of PM₁₀ in the Ambient Air

During the study, the entire year was categorized into four seasons viz., winter, summer, monsoon and post-monsoon. The winter months are from December to February. March to May are summer months. Monsoon starts from June to last in the month of August. Post-monsoon months are from September to November. **Figure 4.3** shows the monthly variation of mass concentration (µg m⁻³) versus the months of sampling for PM₁₀ samples. The 24-h time-weighted mass concentration for a year-round determination of PM₁₀ samples (n=104) varied from 32.5 to 480.2 µg m⁻³. The monthly mean mass

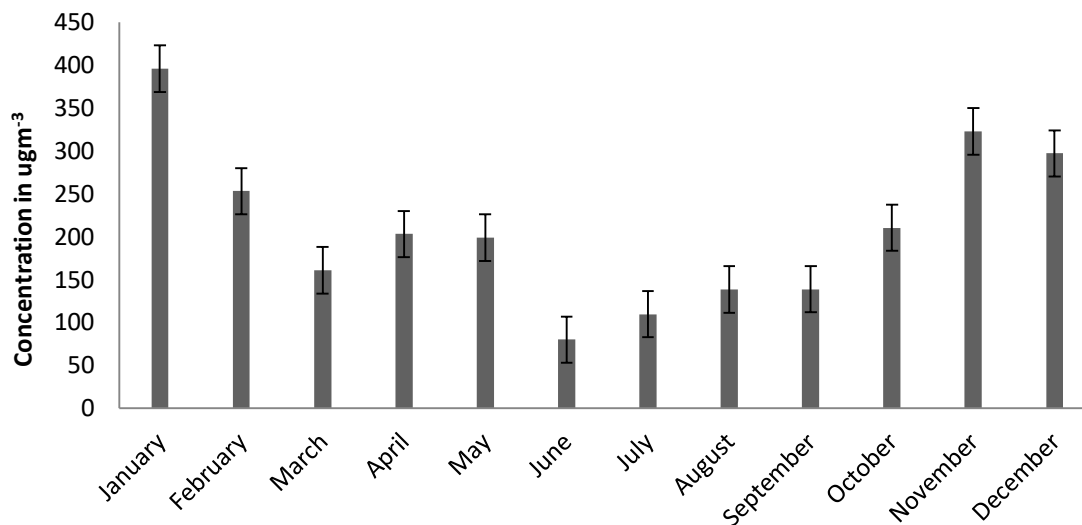


Figure 4.3: Monthly variation of mass concentration of PM₁₀ samples for the year 2014–2015

concentration of PM₁₀ ranged from 80.09 ± 27.1 µg m⁻³ to 395.63 ± 88.81 µg m⁻³ which did not comply with the permissible limit (60 µg m⁻³) as prescribed by NAAQS. Mass loading on filters was high during the months of December to February. The concentration of PM₁₀ was highest in the month of January as 395.63 µg m⁻³ and lowest concentration was observed in the June month as 80.09 µg m⁻³. The mean

concentration of PM₁₀ during summer, monsoon, post monsoon and winter were 187.61±63.11, 109.46±69.80, 223.99 ± 55.89 and 315.21± 98.33 μg m⁻³.

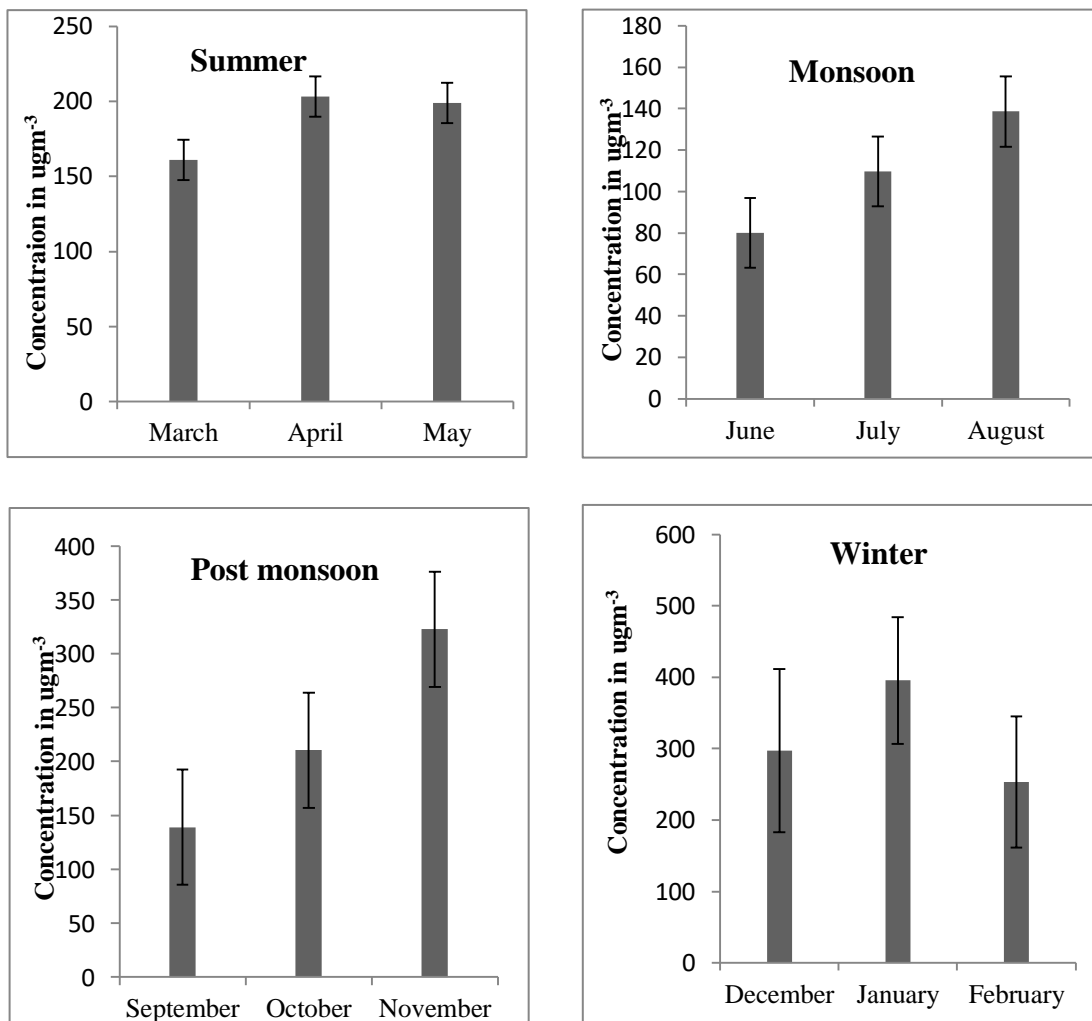


Figure 4.4: Monthly/Seasonal variation of mass concentration of PM₁₀

There was a sharp rise in PM₁₀ concentrations as observed during post monsoon season in the year 2014, as seen in **Figure 4.4**. This can be attributed to the burning of crackers during Diwali celebration, which increases concentrations of PM₁, PM_{2.5} and PM₁₀ by 300,350 and 400 μg m⁻³ (Tiwari et al., 2012). The PM₁₀ concentration was very high during Diwali when compared with the normal days and the day before Diwali. The concentration of PM₁₀ is high as the aerosol released in the atmosphere remains suspended in the ambient air (Verma et al., 2014). An important study reported that the concentration of

PM₁₀ remained high in ambient air for even about one month after the Diwali festival. The higher value of PM₁₀ as compared to the NAAQS is a serious indication of air pollution which affects the health of people. (Ravindra et al., 2003). The levels of PM₁₀ are high in summer due to higher wind speed that makes the soil dust airborne, which is very dry and loose. Also, the PM₁₀ levels in daytime are slightly higher than nighttime levels in summer (Sharma et al., 2007). The high concentration of PM₁₀ during the winter season and post-monsoon season was due to the reduced precipitation, low wind speed and lower boundary layer height and temperature (Hama et al., 2020).

4.2.1 Effect of Relative Humidity (RH) on the Mass Concentration of PM₁₀

Relative humidity affects the mass concentration of PM samples. In the atmosphere, the particle can retain water if RH is around 80% or more. However, below 80% RH, though particle retains water, it is not so significant. Therefore, in high RH conditions, this aerosol water content may have a major contribution toward PM₁₀ mass concentration. In winter, especially on foggy days, nighttime RH is recorded to be more than 90% which influences the mass concentration. The particle mass determined only after conditioning of filters (Aggarwal et al., 2007). Relative humidity (RH), as shown in **Figure 4.5** shows high values during the month of December, January and February.

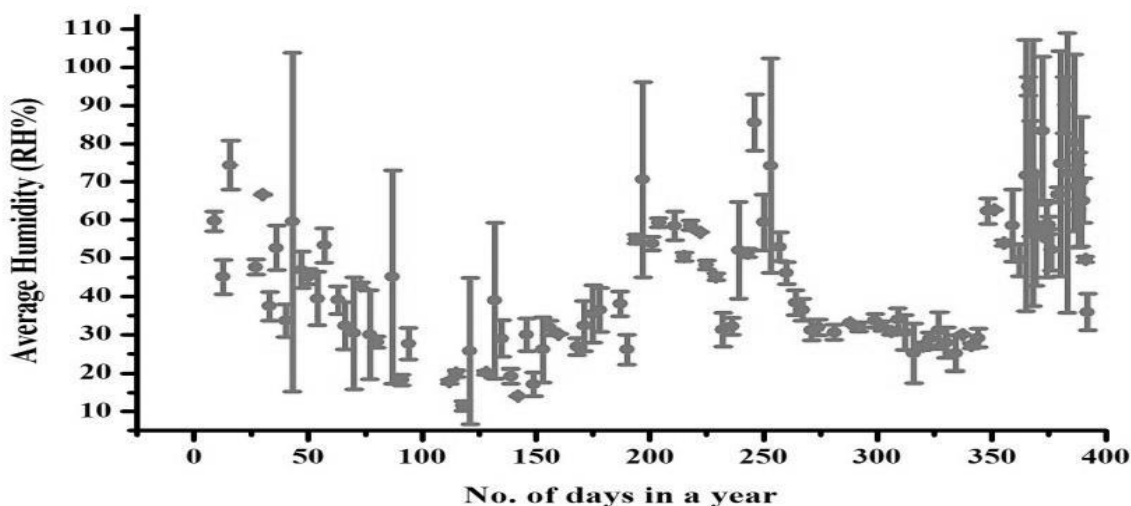


Figure 4.5: Mean relative humidity (RH) during the sampling of PM₁₀ samples

4.2.2 Effect of Temperature (T) on the Mass Concentration of PM₁₀

The mass concentration also depends on the temperature. In **Figure 4.6**, the mean temperature was found to be high in the month of May and June, and subsequently, the mass concentration was low in these months. When the mean temperature was low in the months of November, December, January and February, mass loading was more. In winters, there are many sources which affect the aerosol mass loading. One of the major sources is the secondary aerosol formation, i.e., the uptake of gases into aerosols (Varotsos et al., 2010). OC, EC, WSOC and total inorganic ion concentrations were approximately 3–4 times high in winter season than in summer season. The reason behind heavy mass loading in winters is as follows:

- (1) increased anthropogenic activities in the winter season,
- (2) prominent oxidative exhaustion of particles,
- (3) reduced mixing height
- (4) low wind speed and geographical location of Delhi.

The presence of high humidity and temperature in the tropics, there is wet removal of particulates in the summer season (Aggarwal et al., 2013).

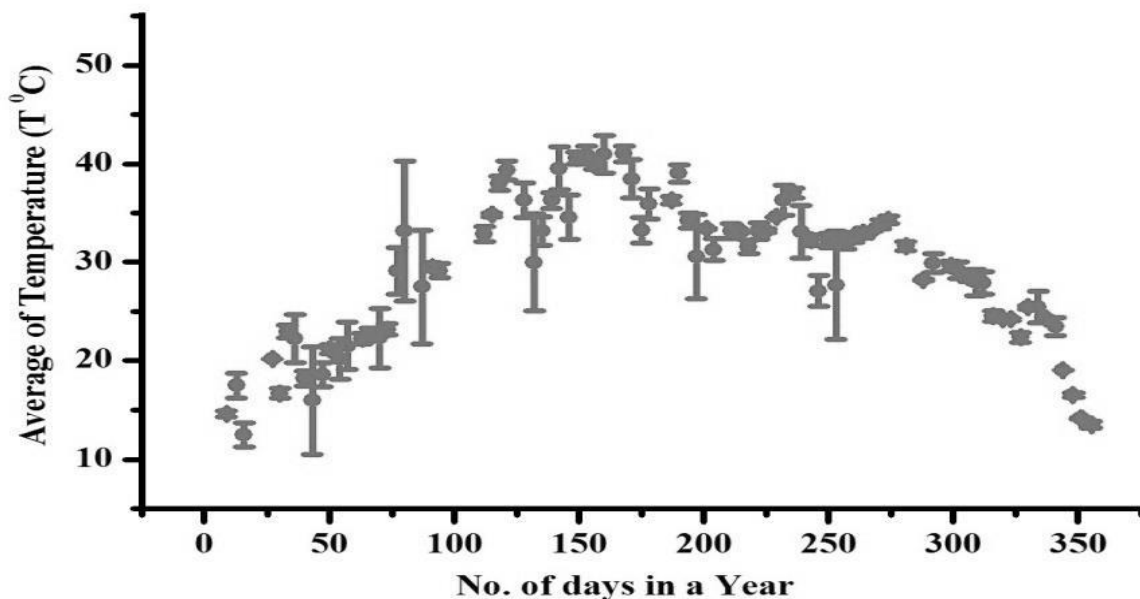


Figure 4.6: Mean Temperature during the sampling of PM₁₀ samples

4.3 Measurement of BaP in PM₁₀ Collected in New Delhi

Chemically the term “PAH” is used for compounds having carbon and hydrogen atoms. Their structure consists of multiple benzene rings bonded in straight, groups, or angular forms (Arey et al., 2003, Di-Toro et al., 2000). The primary source of PAHs in the atmosphere is mainly due to incomplete combustion of fossil fuels emitted from suburban, natural, industrialized and vehicular sources. **Annexure 3** in the annexure section describes the sources of emissions of PAHs all over the world (Zhang et al., 2009). Polyaromatic hydrocarbons having small molecular weight exists both in a gaseous phase in the atmosphere and also in particulate phase by the condensation after emission. Polyaromatic hydrocarbons having high-molecular weight are mainly found as particulate in the atmosphere (Kim et al., 2013). Thus, PAHs are ubiquitous as they are present in the air, soil, and water in our environment (Kim et al., 2013; Latimer et al., 2003). There is an urgent need for monitoring the toxic compounds present in the atmosphere as they are hazardous for human health and atmosphere (Brown et al., 2013). International Agency for Research on Cancer (IARC) has selected few PAHs (e.g., benzo [a] anthracene

(BaA) and BaP as distinguished carcinogens for humans (Jones et al. 1989). Among them, BaP is referred to as a “carcinogenic substance- level 1” (IARC 1984, IARC 1987 and IARC 1989). Different studies have been done regarding the increasing concentrations of BaP in the atmosphere all over the globe. The highest concentration of BaP ($> 0.4 \text{ ng m}^{-3}$) was found in the central and eastern part of Europe (Guerreiro et al., 2016). Exposure to BaP concentration beyond the permissible value was major and extensive in the eastern and central part of Europe. From 2009 to 2011, 22% - 31% of the urban residents were exposed to BaP concentrations beyond the permissible limit of 1 ng m^{-3} (Guerreiro et al., 2014). In the latest report, it was observed that in summer, average concentrations of BaP in the atmosphere in urban areas were $3.6 \pm 4.11 \text{ ng m}^{-3}$. In the winter season, concentrations are higher (average $7.1 \pm 5.1 \text{ ng m}^{-3}$) mainly because of the emission from domestic and industrial heating sources using fossil fuels. (Kasimov et al., 2017). PM_{10} -bound BaP emitted from domestic heating sources was responsible for the lung cancer cases in various parts of the cities of Poland (Widziewicz et al., 2017).

4.3.1 HPLC Analysis of BaP in PM_{10} Samples

Analysis of the BaP was performed using an HPLC reversed - phase C18 column (dimension 250 mm x 4.6 mm, make Shim-pack), with elution of binary gradient between 50% acetonitrile (HPLC grade) and water mixture to 100% acetonitrile in 45 min. BaP was detected in PM_{10} samples by means of a fluorescence detector with respect to its retention time. The fluorescence detection was done at 361 nm (excitation wavelength) and at 405 nm (emission wavelength). The method was tested with quality assurance (verification of instrument calibration and repeatability test of the instrument). Two replicates of blank samples were used as real samples to check any contaminations of the analytes. The stock solution of the standard was prepared by diluting aliquots of the BaP standard (Sigma-Aldrich, B1760). For calibration, BaP standard solution was prepared by successive dilution of stock solutions in acetonitrile (by weight). Calibration standard solutions were stored at $4 \text{ }^\circ\text{C}$ in the dark. In India, the

regulatory limit of BaP in NAAQS is 1 ng m^{-3} (annual). PM_{10} sample filters were analyzed for BaP according to the ISO 16362: 2005. The data was calculated as follows:

The BaP concentration in PM_{10} samples (in ng m^{-3}) is calculated from Equation 6 given as:

$$\text{Concentration of BaP (ng m}^{-3} \text{)} = \frac{C \text{ (ng m}^{-2}\text{)} \times A_{\text{sample}} \text{ (m}^2\text{)}}{V_{\text{air}} \text{ (m}^3\text{)}} \quad (6)$$

where C is the BaP concentration calculated from the analytical data and area of filter taken (ng m^{-2}), A_{sample} is the total area of the PM_{10} filter exposed (m^2), V_{air} is the volume of the sampled air (m^3).

Calibration of the instrument was done by injecting three different concentrations of BaP standards as a function of peak area using a linear curve. The peak identification of BaP in PM_{10} samples was made by comparing the retention time of the sample with the standard. **(Figures. 4.7 and 4.8).**

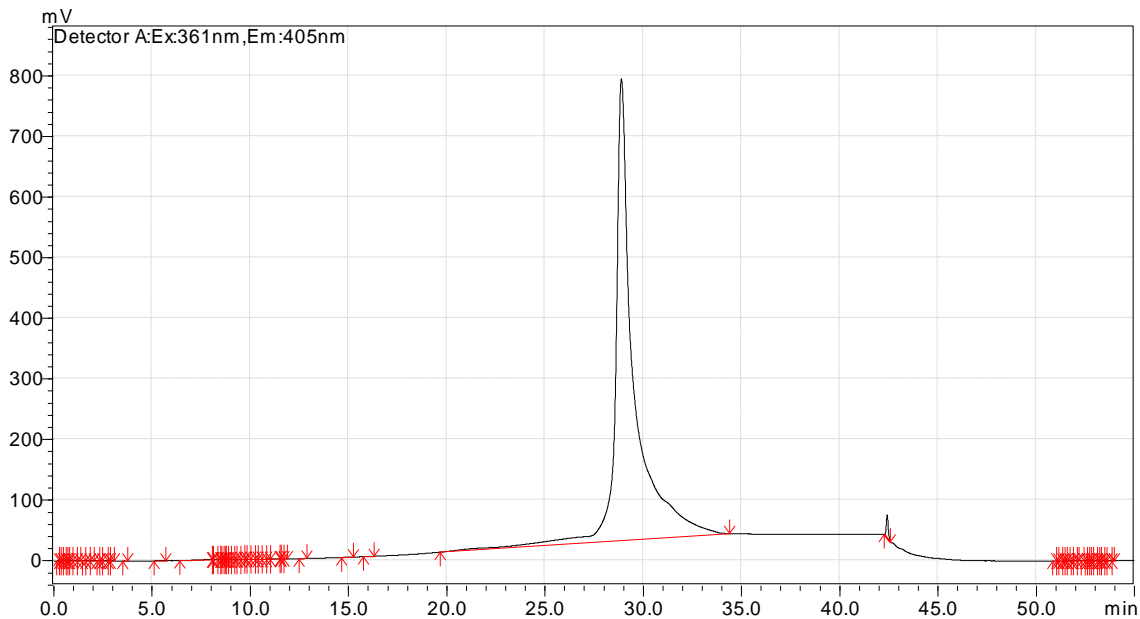


Figure 4.7: HPLC chromatogram of BaP standard

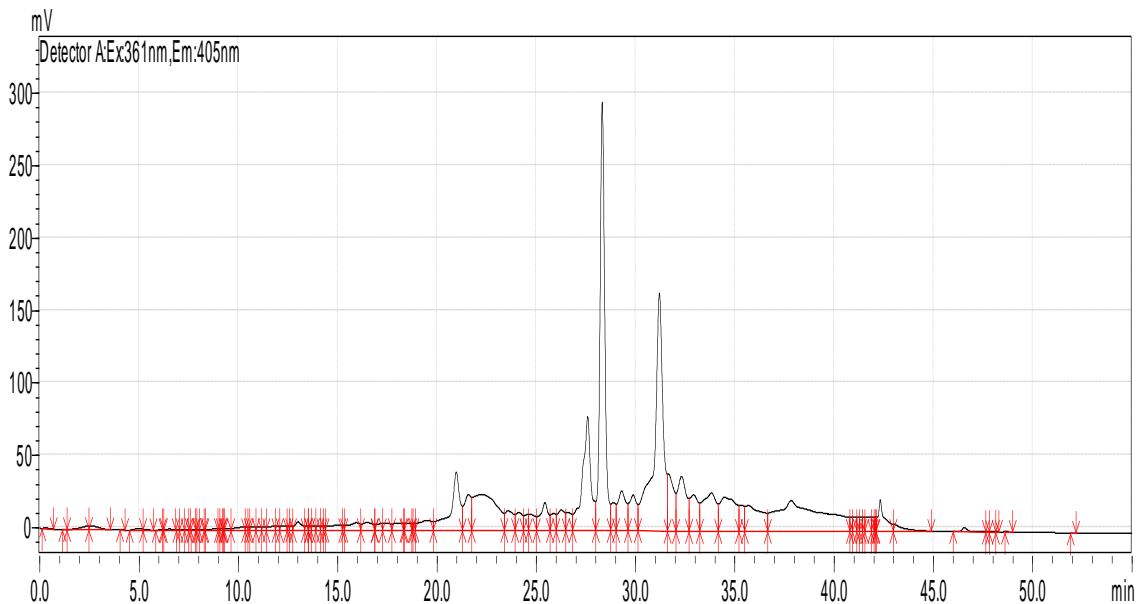


Figure 4.8: HPLC chromatogram of BaP for PM₁₀ sample

The instrument was calibrated after every ten analysis of the sample. Other statistical data for instrument calibration, i.e. correlation coefficients (R^2), standard deviation (SD) etc., along with a limit of detection (LOD) and limit of quantification (LOQ) were also calculated and are listed in **Table 4.2**.

Table 4.2: Statistical data for HPLC calibration

Compound Name	Retention time (min)	Calibration range (ppm)	Precision (%)	Correlation coefficients (R^2)	LOD (ppm)	LOQ (ppm)
BaP	28.8	0.025-1.00	0.89	0.9928	0.011	0.021

4.3.2 Uncertainty Estimation for BaP Measurement in PM₁₀ Samples

Any type of small error in the measurement of aerosols can have a substantial impact on its understanding. Therefore, to understand the physical and chemical properties of aerosols, their measurements should be accurate (Aggarwal et al., 2010). PAH levels in the atmosphere are very low.

Therefore the measurement methods for their recording, collection and analysis study are very sophisticated and have high uncertainties values due to low recovery despite large sampling volume (USEPA, 1999). The study was conducted for the determination of the concentration of BaP in the PM₁₀ samples of New Delhi collected in the year 2014-15. The uncertainty components during sampling extraction and analysis of BaP are also taken into consideration.

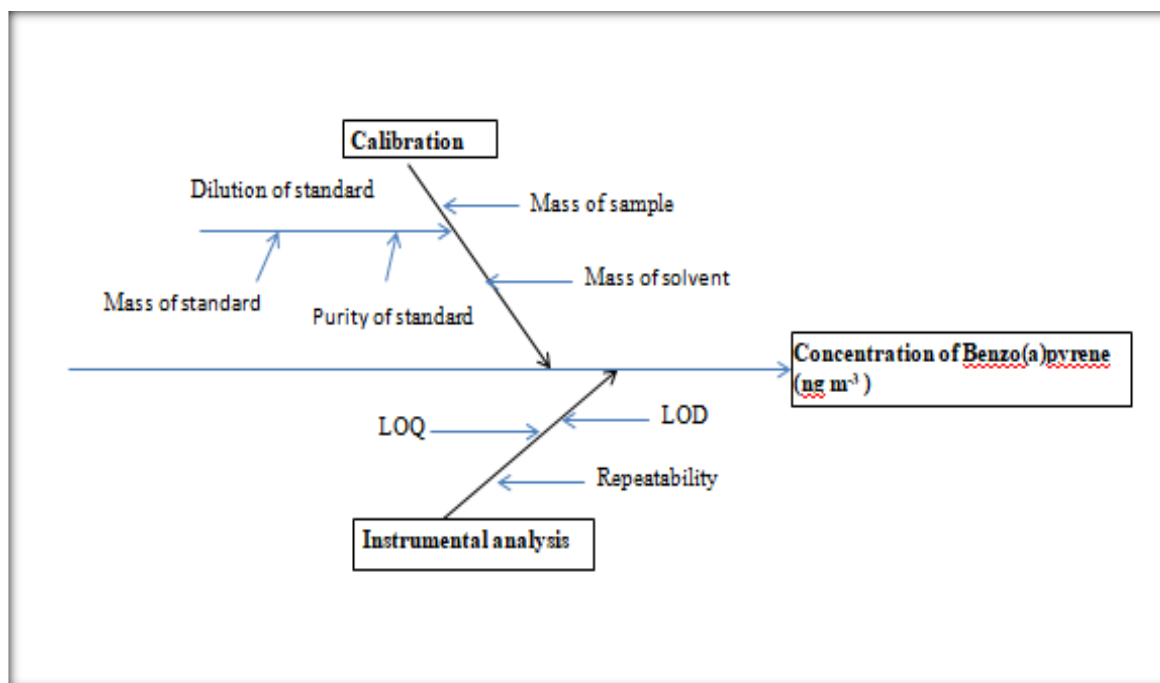


Figure 4.9: Uncertainty associated with standard and sample preparation

The main sources of uncertainty in the preparations of standard stock solutions in the HPLC method are shown in the form of the cause and effect diagram in **Figure 4.9** as shown above:

- Mass of standard (M_{st}) and
- Purity of the standard (P)

4.3.2.1 Uncertainty in Measurement of Mass of the BaP Standard and Sample

Uncertainty in mass weighing was calculated for standard and sample according to Equation 7:

$$u(M_{st}) = \frac{S}{\sqrt{n}} \quad (7)$$

where s represents the standard deviation (as per the balance certificate), and n is the number of measurements of mass weighing of 20g weight (in case of standard)and 1g weight in case of the sample) respectively.

4.3.2.2 Uncertainty in Measurement of Purity of BaP Standard

The purity of is given in the form $\geq y$ % and the range $(100-y)$ % is described as the rectangular distribution. The standard uncertainty is therefore calculated as:

$$u_p = \frac{100-y}{2\sqrt{3}} \quad (8)$$

The uncertainty components involved in the measurement of the concentration of BaP, as discussed are calculated as in **Table 4.3**.

Table 4.3: Uncertainty components and their standard and relative uncertainties associated with the preparation of standard and sample of BaP by HPLC

Symbol	u Component	x	u(x)	u(x)/x
M_{st}	Standard Mass	20g/g	$4/\sqrt{10}$ g/g = 1.26	0.06
u_p	Standard Purity	2 g L ⁻¹	$2/\sqrt{3}$ g L ⁻¹ = 1.15	0.57
M_{sample}	Sample Mass	1g/g	$0.2/\sqrt{4}$ g/g = 0.10	0.10

The major contribution from uncertainty components was from the purity of the standard (77.9%). The other parameters, like the mass of standard and sample, contributed to 8.5% and 13.5%.

The combined uncertainty is calculated by summing up the square of all the uncertainty components calculated as shown in Equation 9. The input quantities are those that are responsible for the uncertainty of the analytical method.

$$u_c = \sqrt{(M_{st})^2 + (u_p)^2 + (uM_{sample})^2} \quad (9)$$

The combined uncertainty (U_c) is calculated as 0.58 ngm^{-3} .

Calculation of the expanded uncertainty (U) is done by multiplying the combined standard uncertainty (U_c) of the input quantity with k (coverage factor). The value of $k = 2$.

$$U = U_c \times k \quad (10)$$

The expanded U is calculated as 1.16.

4.4 Seasonal Variation of BaP in PM₁₀ Samples

Delhi has a subtropical climate, and due to emission of trace gases from various sources, the ambient air quality is considerably affected (Sharma et al., 2017). The average rainfall during monsoon season in Delhi is generally of the order of ~800 mm. During the study, the entire year was categorized into four seasons viz., winter, summer, monsoon and post-monsoon. The winter months are from December to February. March to May are summer months. Monsoon starts from June to last in the month of August. Post-monsoon months are from September to November. The temperature of Delhi varies from lowest in winter to highest in summer.

Figure 4.10 shows the monthly concentration (ng m^{-3}) of BaP calculated for the year 2014-15 in NPL, New Delhi. The seasonal variation in concentrations of BaP was found to be 0.04 ng m^{-3} to 25.7 ng m^{-3} in PM₁₀ samples collected at the sampling site from January 2014 - January 2015. A general trend in the monthly distribution of BaP is observed.

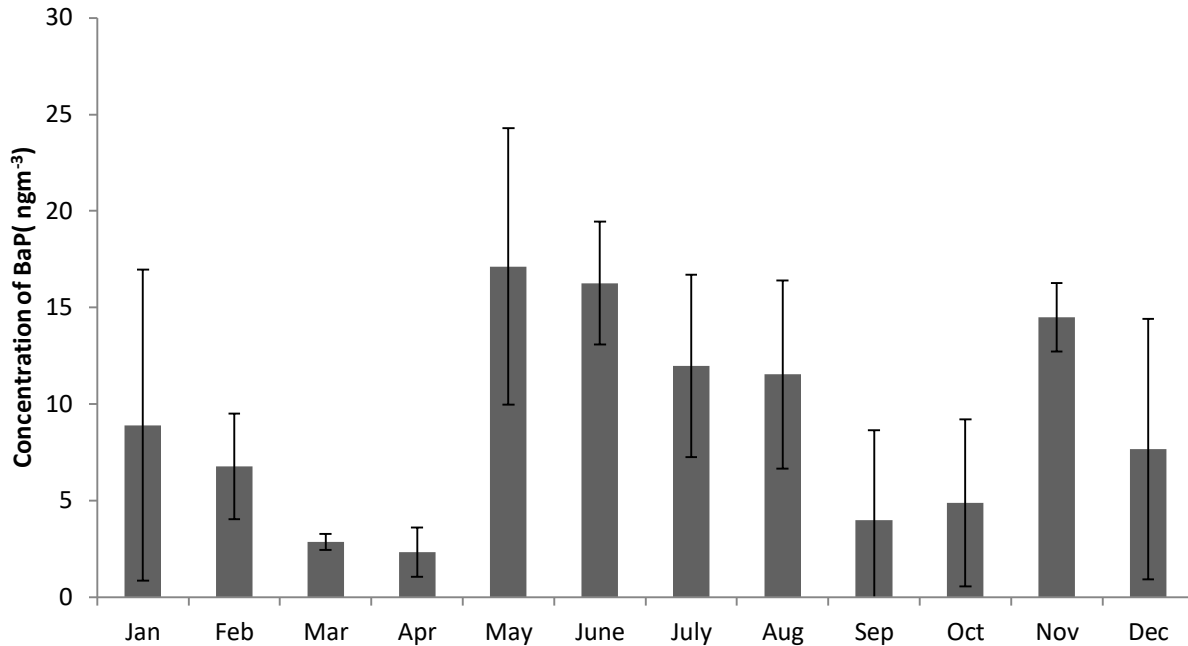


Figure 4.10: Monthly BaP concentration in PM₁₀ samples in the year 2014-15

In Delhi, there has been a rise in the number of motor vehicles over the years, which affects the entire consumption of fuel. This also increases the idling time of vehicles leading to traffic congestion which finally results in increased emission of hydrocarbons, CO and NO_x (Gurjar et al., 2004). The major sources observed for the increase in levels of BaP were from the traffic emission (Vaio et al., 2016). As shown in **Figure 4.11**, it was observed that BaP concentrations decrease during the monsoon and post-monsoon season, i.e. between July to September. This happens due to the scrubbing effect of precipitation. During the rains, the suspended particulates in the air settle down and therefore, the concentration of pollutants in the ambient air is reduced (Guo et al., 2016). Winter months experience increase in BaP levels (November to January) possibly because of the additional fuel combustion, biomass burning, increase in vehicular traffic etc., (Kumar et al., 2015; Li et al., 2014). Major vehicular emission includes diesel and natural gas combustion while the emissions from vehicles using coal, gasoline and coke as fuels have a minor contribution (Lakhani et al. 2012).

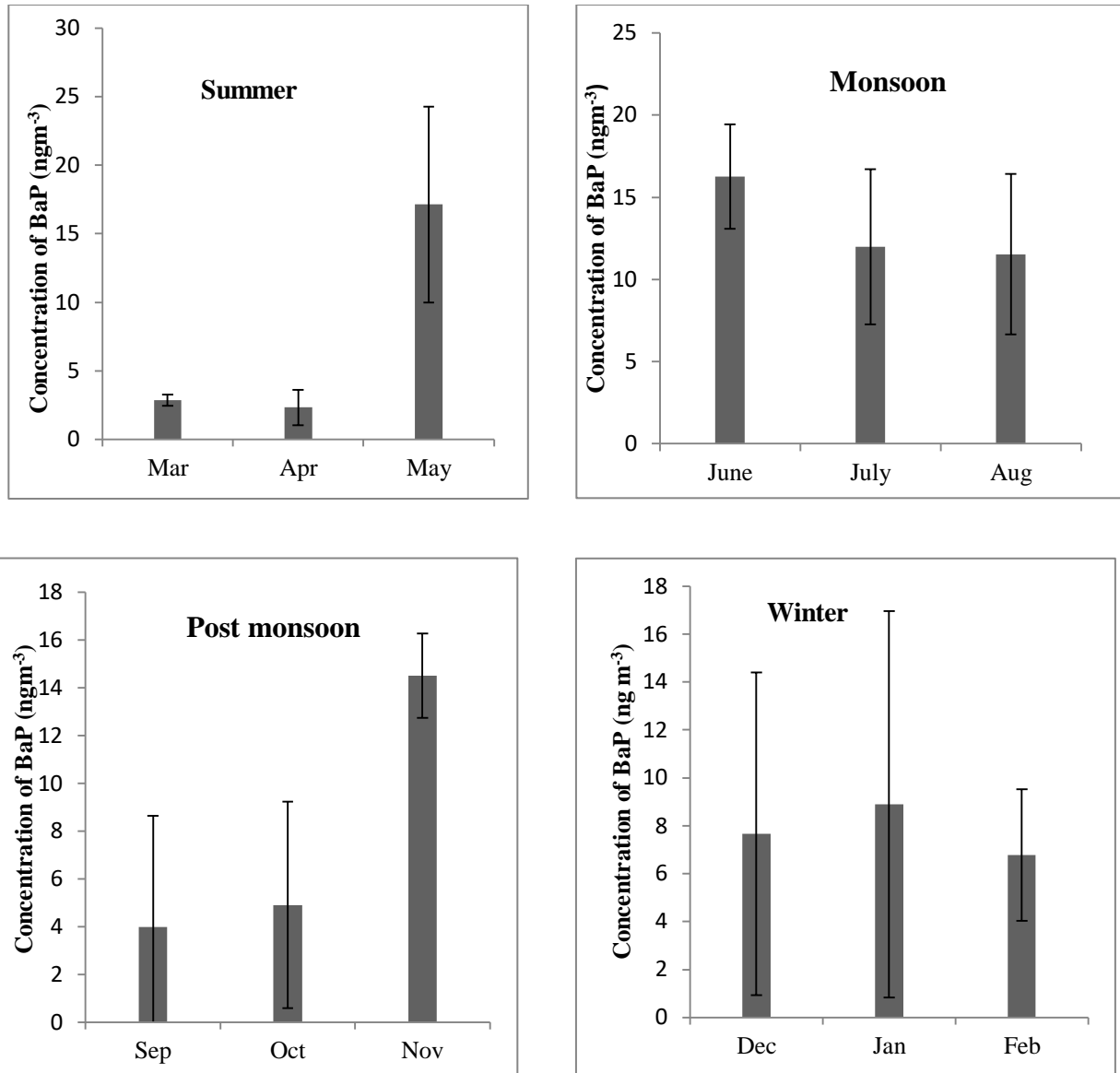


Figure 4.11: Monthly/Seasonal variation of concentration of BaP in PM_{10}

The high concentration of BaP in the winter months was due to the stable inversion layer in which the pollutants remain suspended in the air for long and have greatly increased residence times. This makes winter months particularly harmful for asthmatics and people suffering from other respiratory disorders. As the inversion layer starts to break in the summer months, the pollution level also starts decreasing. As recommended by CPCB (Central Pollution Control Board), average mass concentration for PM_1 , $\text{PM}_{2.5}$ and PM_{10} was 3-4 times higher than the permitted values given in

NAAQS due to emission from the crop residue burning (Saggu et al., 2018). In North India, there is a high variation in local weather in all the seasons as compared to South India. In the western part of India, there are deserts and western disturbances. Apart from the natural influences, an increase in the urbanization also results in the changes in the atmospheric conditions (Prasad et al., 2013). Therefore, in recent years, the concentration of ambient BaP reported in India is much higher than developed countries like Italy, Greece, USA, UK and Germany. The concentration of BaP in India was also reported higher than Asian countries like Japan, Taiwan, Korea and Hong Kong but was similar to China (Suvarapu et al., 2017).

4.5 Study of Metal Concentration in PM₁₀ Samples

Ambient air quality is the most important environmental issue in the cities of developing countries around the world. For the last twenty years, due to an increase in the population of Delhi, there is remarkable growth in terms of vehicular growth, urban infrastructure and industrial activities. The main sources of air pollutants are due to the vehicular traffic, domestic, industrial and thermal power plants, etc. All these activities emit toxic chemical compounds in the ambient air of Delhi (Mishra et al., 2015).

PM₁₀ present in the SPM collected from the polluted air can reach into lung tissues of humans while inhalation resulting in respiratory and cardiovascular diseases. The heavy metals content in the particulates matter comes from the time of exposure to toxic trace metals such as Ni, As, Cr and Cd. Even at low concentrations, these metals can cause cancer (Akoto et al., 2008). Heavy metals are released into atmosphere by natural and anthropogenic activities. Most important anthropogenic sources consist of combustion of coal and oil, construction activities, industrial activities, vehicular movement, incineration, road dust and crustal materials (Shah et al., 2010). There are different methods for the chemical analysis and preparation of the samples. The most common method used is the destructive analytical techniques which consist of microwave-assisted digestion of filter-based samples followed by ICP-MS. The choice of reagents for acid digestion depends on the determination and characterization of

multiple elements in aerosols present in ambient air (Allen et al., 2001). The study of heavy metal in the ambient air is the most important topic of research for the environmentalists owing to their toxicity. Some significant metals e.g. As, Ni, Cd and Cr are listed as carcinogens. These metals through the organic process find their way in the plant cells and human organs. Major studies have been done on cytotoxic metals like As, Ni, Pb, Cd and Cr, Plants can also be used as biomarkers to study the toxic metal levels in the atmosphere. It was found that the high concentration of the significant metals was found in the industrial areas as compared to residential areas. The major sources of significant metals and PM in the atmosphere is found to be as primary aerosols including industrial emissions and transport emissions (Suvarapu et al., 2017).

In the present study, PM₁₀ samples were collected for a year i.e. from January 2014- January 2015. The metal concentration was studied for four seasons *i.e.*, summer, monsoon, post monsoon and winters. Total of 104 samples were analyzed to evaluate seasonal variation of metals in PM₁₀ samples. The samples were analyzed through inductively coupled plasma-optical emission spectrophotometry. There are many heavy metals studied for PM but standard limits are notified for only three metals (As, Ni and Pb). Therefore, only these three metals are reported here. The study conducted on these three metals is presented below:

Anthropogenic sources of emission like metal smelting, fuel burning of gas and carbon coal are contributing to about two-thirds of the total arsenic emissions in the atmosphere. Semiconductor industries are one of the important sources of As in air (Chein et al., 2006). The natural sources of arsenic are forest fires, volcanoes and sea spray (Matschullat et al., 2000). Arsenic concentration varies inversely with temperature. Oxides of arsenic from various sources are emitted into the atmosphere where they condense. Thus, arsenic oxides form an equilibrium between aerosol and vapour phase depending on the temperature. The concentration of arsenic is high at low temperature as it remains in

the aerosol phase at low temperature and in the vapour phase at high temperatures (Pallare's et al., 2007).

Figure 4.12 explains the arsenic concentration in the PM₁₀ samples collected in New Delhi from 2014-15. The mean concentration ranged from $0.30 \pm 0.08 \text{ ng m}^{-3}$ to $6.24 \pm 2.39 \text{ ng m}^{-3}$. The maximum concentration of Arsenic was observed during November to January and the minimum concentration of As was observed from June to August. Arsenic concentration was thus many times found to be more than the prescribed limit of 6 ng m^{-3} as described in NAAQS.

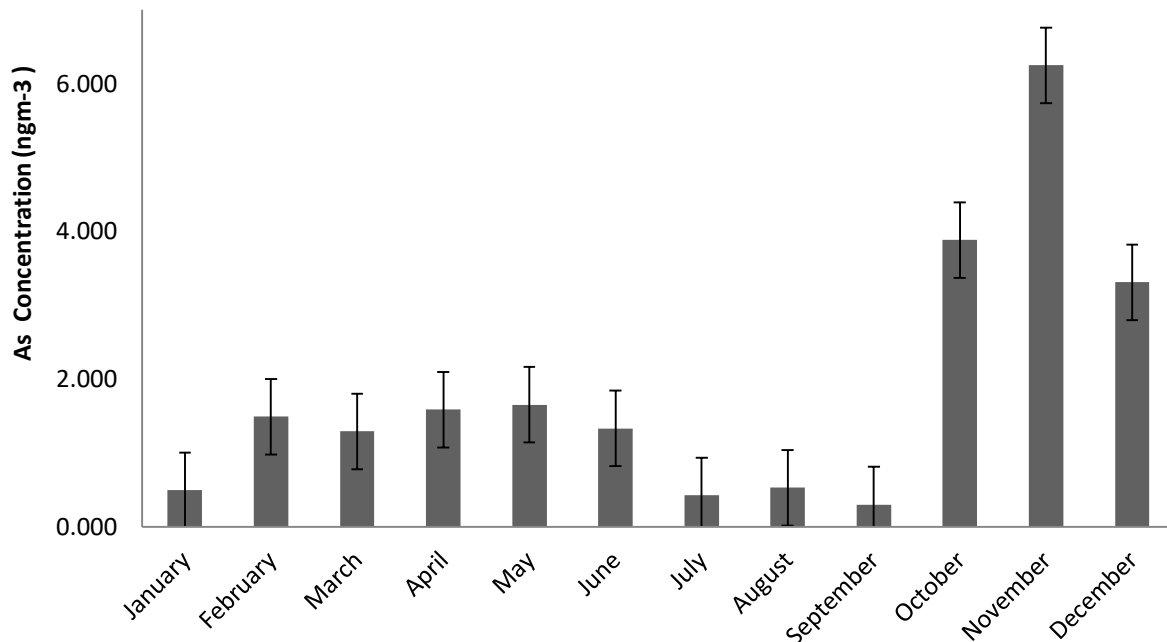


Figure 4.12: Arsenic concentration in PM₁₀ samples

Arsenic is emitted in the atmosphere from arsenic trioxide which is a formed by metal smelting operations. About 70% of arsenic produced in the world is used in timber preservation, 22% in agricultural chemicals and the rest in metallic alloys, pharmaceuticals and glass industries. Thus, mining, coal-using power plants, metal smelting and combustion of fossil fuels are the major industrial processes that contribute to As contamination of air (Kushwaha et al., 2016). As shown in **Figure 4.13**, Arsenic concentration in the PM₁₀ samples was very high in winters between $0.49 \pm 0.23 \text{ ng m}^{-3}$ to 3.30

$\pm 1.42 \text{ ng m}^{-3}$. This is because As is a very volatile element and only during the winter season, it condenses onto the surface of the atmospheric particulate matter. There is an increase in the wood/biomass burning activities season which also contribute to As emission (Gargava et al., 2014). As concentration in summers was very low $1.29 \pm 0.36 \text{ ng m}^{-3}$ to $1.64 \pm 0.25 \text{ ng m}^{-3}$ as arsenic remains in the vapour phase at high temperature.

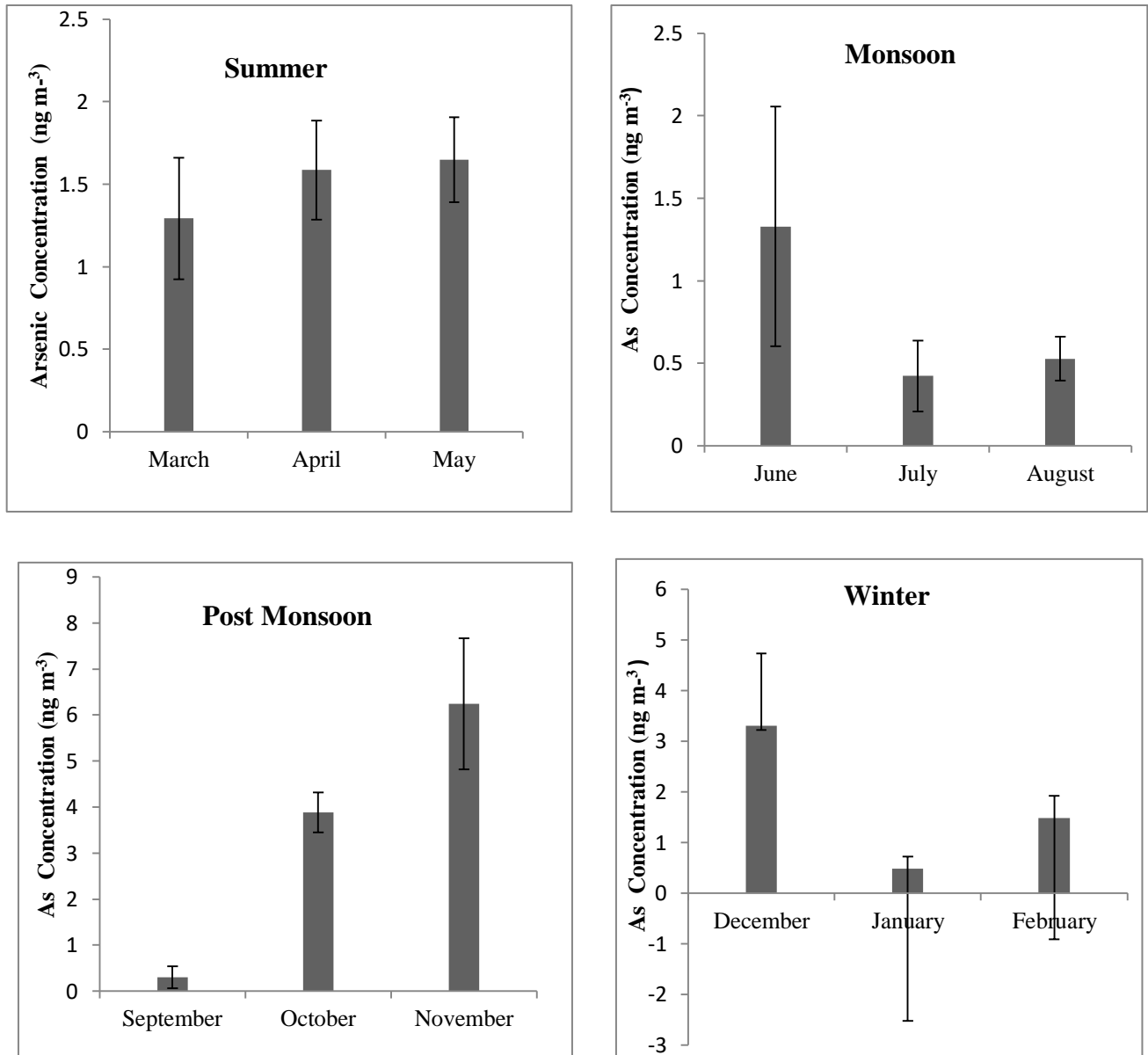


Figure 4.13: Monthly/Seasonal variation of concentration of Arsenic in PM₁₀

Nickel is one of the most prevalent trace metals in atmospheric environment (Kim et al., 2014). It is present in the atmosphere from emission of natural and anthropogenic sources with both mobile and stationary emissions (Cempel et al., 2006). The natural sources of PM assisted Ni are forest fire, soil dust, vegetation, meteoric dust, volcanic emission and sea salt. The anthropogenic sources of Ni are metallurgical processes, combustion of fuel oil, diesel and coal and other activities (Nriagu et al., 1979).

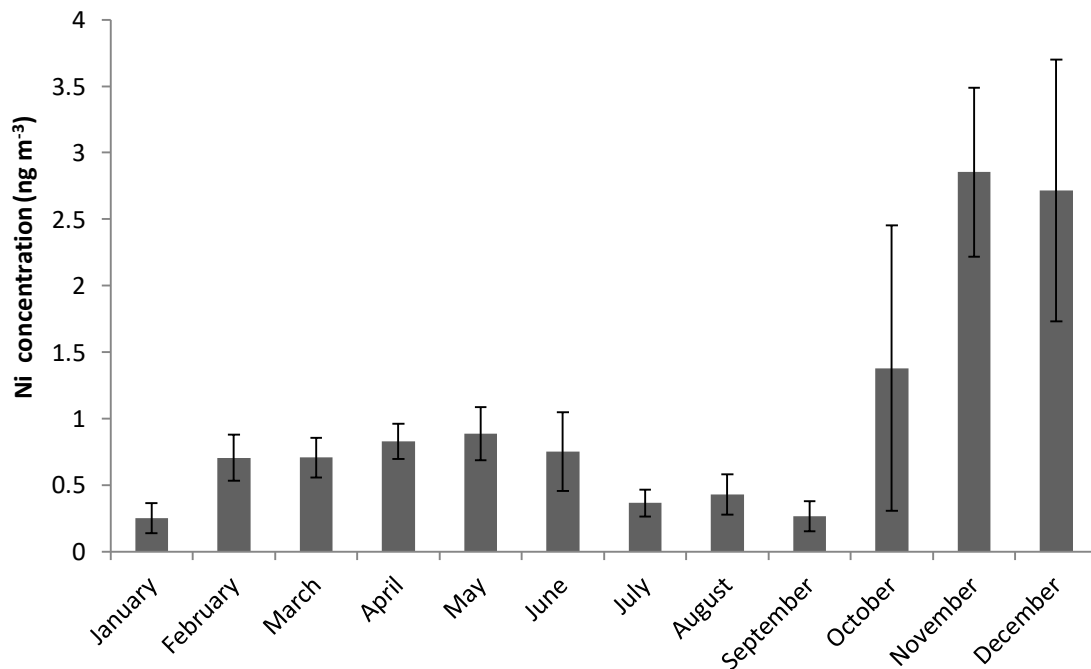


Figure 4.14: Nickel concentration in PM₁₀ samples

Figure 4.14 shows the highest Ni concentration during the month of November 2014, whereas low concentration was found during the month of May to August 2014. Mean concentration of nickel was found to be $0.25 \pm 0.11 \text{ ng m}^{-3}$ to $2.85 \pm 0.63 \text{ ng m}^{-3}$. Thus, the concentration of Ni studied was found to be within the National Standard limit ($0.02 \mu\text{g m}^{-3}$). Ni concentration varies with temperature. Ni is emitted in the form of airborne ashes from the emission sources (Boix et al., 2001). At high temperature, atmospheric turbulence as well as dispersion of particles is very high (Wark et al., 2000) which causes the airborne ashes to travel great distances and thus increase the levels of nickel. Also, after spring

season in April and May months, Delhi received dust episodes originated from the Middle East, and it was observed that Ni concentrations in these dust particles are dominated (Kumar et al., 2016). The RH is one more parameter that directly affect the levels of nickel. High RH causes faster condensation (McGregor et al.,1999) and thus increases the levels of Ni. The Ni levels decreased in China after 2008 due to reduction in coal consumption, reconstruction of energy structure, strict emission guidelines and improved waste control techniques for industrial and vehicular emissions (Xu et al., 2017). **Figure 4.15** shows the seasonal variation of Ni in PM₁₀ samples. In summer, the Ni concentration ranged from $0.70 \pm 0.14 \text{ ng m}^{-3}$ to $0.88 \pm 0.19 \text{ ng m}^{-3}$ while in winters, it varied from $0.25 \pm 0.11 \text{ ng m}^{-3}$ to $2.71 \pm 0.98 \text{ ng m}^{-3}$.

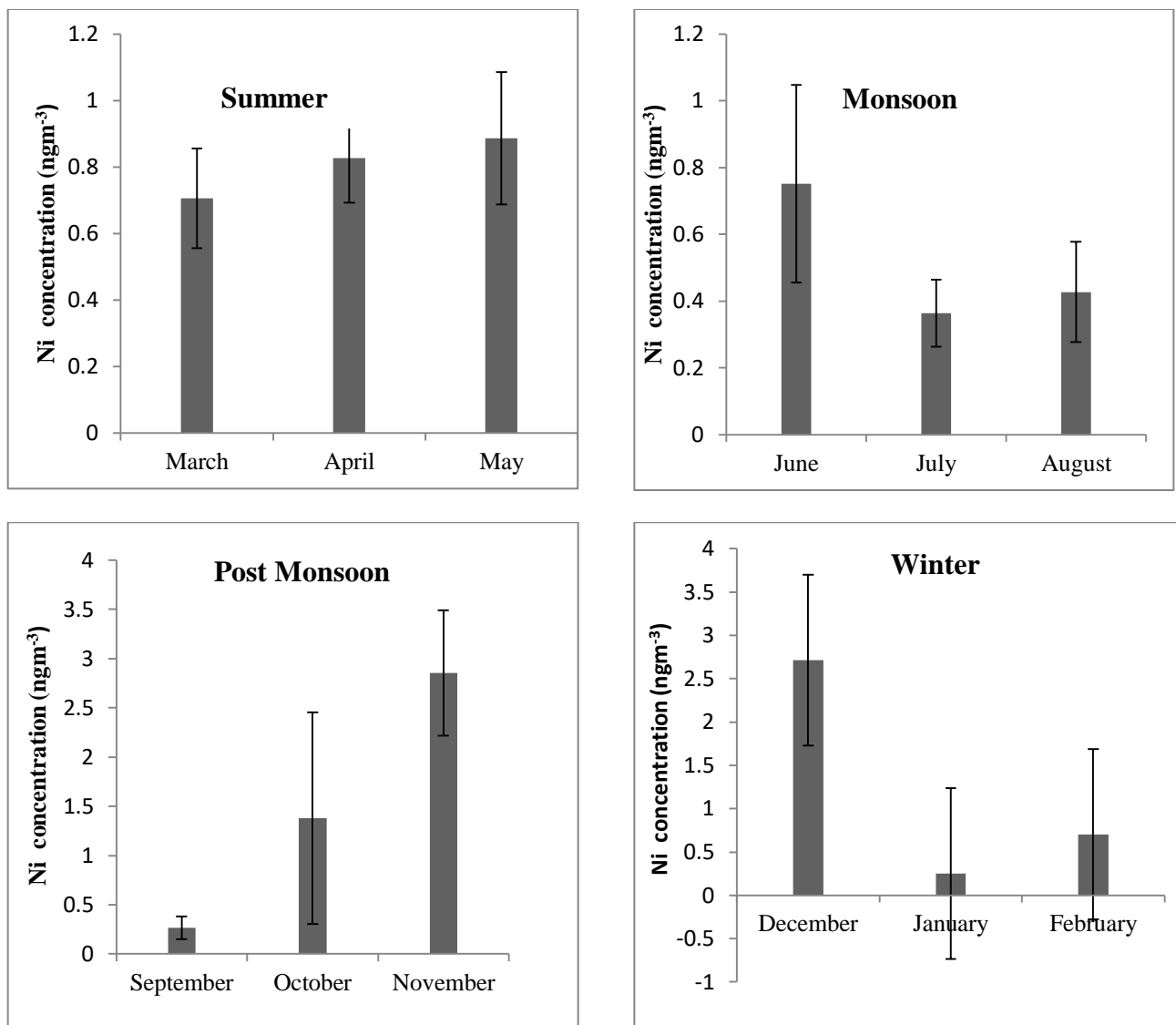


Figure 4.15: Monthly/Seasonal variation of concentration of Ni in PM_{10}

Lead is emitted in the atmosphere in the gaseous form mainly due to anthropogenic activities including processes activities involving high temperatures like waste incineration, fuel combustion, and production of nonferrous metal production or metal processing (EPA, 1998). Lead condenses in the atmosphere to form smaller particles (Blando et al., 2000). Lead concentration inversely related to the wind direction and is directly related to the wind velocity. It is heavier than As and Ni and has high concentration in particles. The emission source of Pb are quite similar is closer than that to the previous

elements, strong wind velocities are required to displace it. The concentration of Pb is directly related to atmospheric pressure and relative humidity. An increase in relative humidity causes condensation and thus increases the concentration of Pb (McGregor et al., 1999). Similarly, an increase in atmospheric pressure decreases the expansion of the lower layers of the atmosphere and reduces the dispersion of the pollutants and thus causes increase in the concentration of Pb (Wark et al., 2000).

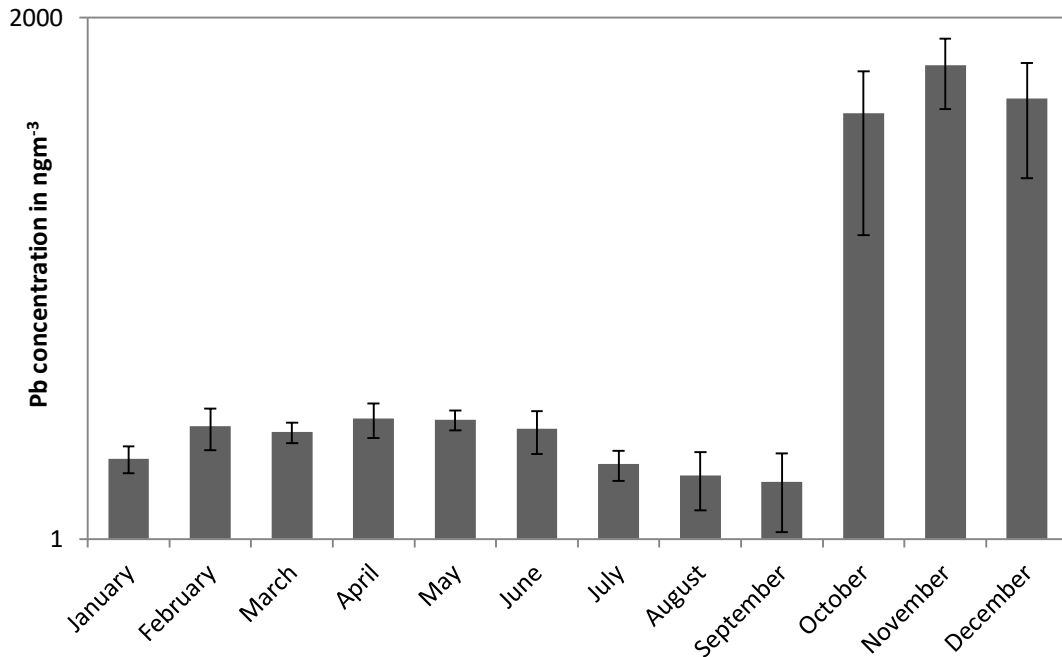


Figure 4.16: Lead concentration in PM₁₀ samples

(The above graph have been drawn using logarithmic scales as few points are much larger than the bulk of the data)

The concentration of Pb from January to September shows a little variation. **Figure.4.16** shows that the highest Pb concentration during the months of October-December. Although it is found that Pb concentration was more than the prescribed limit of NAAQS (1 ug m⁻³). Mean concentration of Pb varied from $2.29 \pm 1.18 \text{ ng m}^{-3}$ to $1003.03 \pm 473.10 \text{ ng m}^{-3}$.

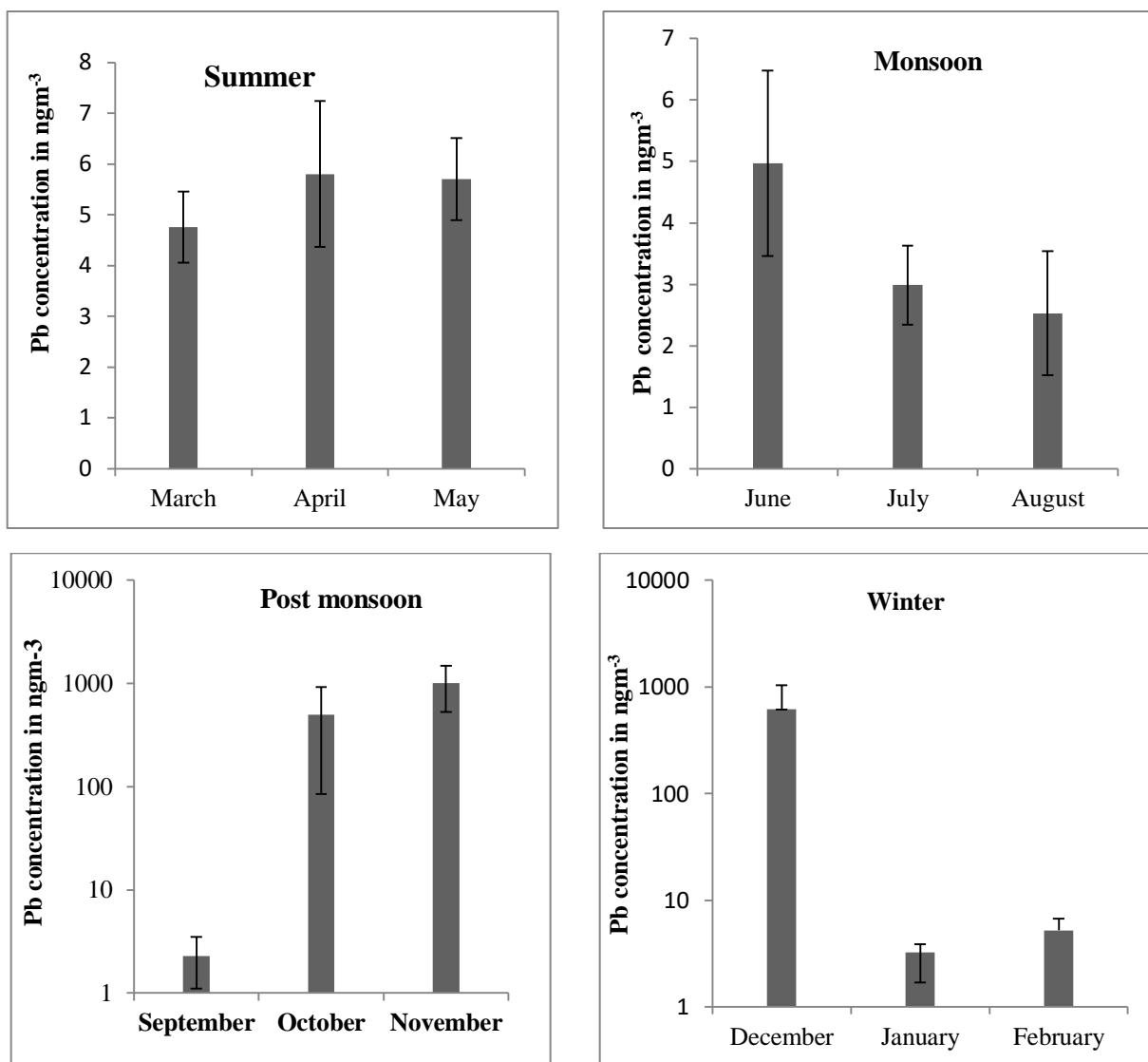


Figure 4.17: Monthly/Seasonal variation of concentration of Pb in PM_{10}

(Post monsoon and winter graphs have been drawn using logarithmic scales as one or a few points are much larger than the bulk of the data)

Figure 4.17 shows the seasonal variation in the concentration of Pb. In summer season, Pb concentration is low due to its high dispersion in the atmosphere. An increase in the Pb levels in post-monsoon season can be related to the shifting of boundary layer, local nonpoint sources and excessive biomass and coal burning. Although, the high concentrations of Pb were found in the night time in all

the seasons of the year as compared to those of the day time. The high concentration of Pb in winter season may be due to lower inversion layer and atmospheric stability prevailing in this season. As the atmospheric boundary layer shifts towards the earth surface, it causes decrease in the dispersion of Pb particles, resulting in its increased concentration. During the summer season, there is increased dispersion of pollutants in the atmosphere due to vertical mixing. Therefore, the ambient Pb levels have been found as considerably low in summer season than winter season (Chandra et al., 2014). After the implementation of Pb free petrol in India in the year 1999, though ambient Pb concentration has decreased, still Pb was present in the study area could be due to road dust and multiple industrial applications.

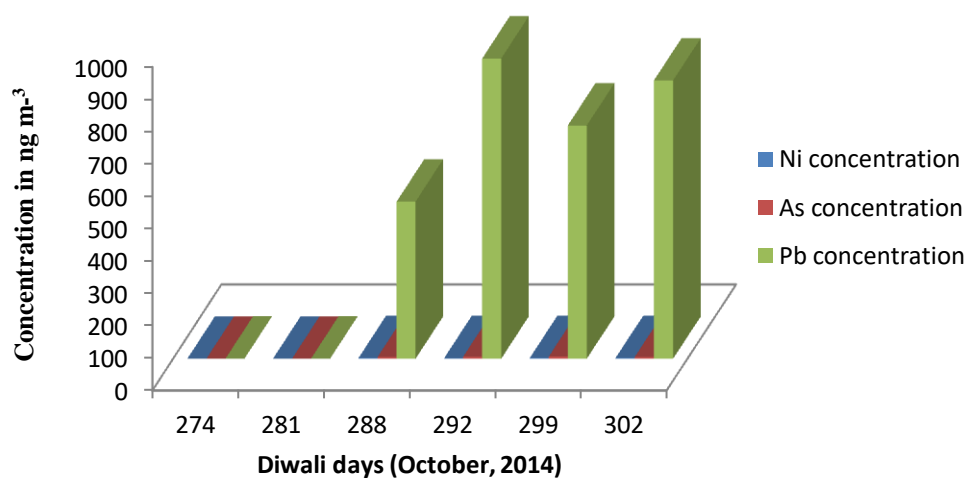


Figure 4.18: As, Ni and Pb concentration during Diwali days in October 2014

During the Diwali week, (as shown in **Figure 4.18**), the concentration of Ni was found to be in the range of 0.03 to 2.30 ng m⁻³. Concentration of As ranged from 0.04 to 6.53 ng m⁻³ and Pb concentration ranged from 0.26 to 928.20 ng m⁻³. Out of the three metal concentrations studied, Arsenic concentration was found to be above the prescribed limit of 6 ng m⁻³.

Fireworks contributed 21–27% to ambient PM₁₀ on Diwali. The correlation between trace gases, PM₁₀ and metals indicate the fireworks emissions are responsible for the fluctuations in the air quality during Diwali due to emission and accumulation of PM₁₀, SO₂, NO₂, O₃, and trace metals. (Ambade et al., 2018). The concentration of these pollutants was high during Diwali due to adverse meteorological conditions as well, like, wind speed, temperature and decrease in 24 h average mixing height (Singh et al., 2010).

4.5.1 Uncertainty Parameters in the Measurement of As, Ni and Pb Concentration

Arsenic, Pb and Ni are among the list of the criteria pollutants of NAAQS. The concentration of As, Ni & Pb in PM₁₀ (measurand) can be obtained from the ICP-OES software, and/or calculated from the calibration plot versus concentration. **Figure 4.19** shows the cause and effect diagram which explains the uncertainty sources used in the determination of the concentration of metal. The most important parameters are those involved in the instrumental analysis and calibration of the instrument.

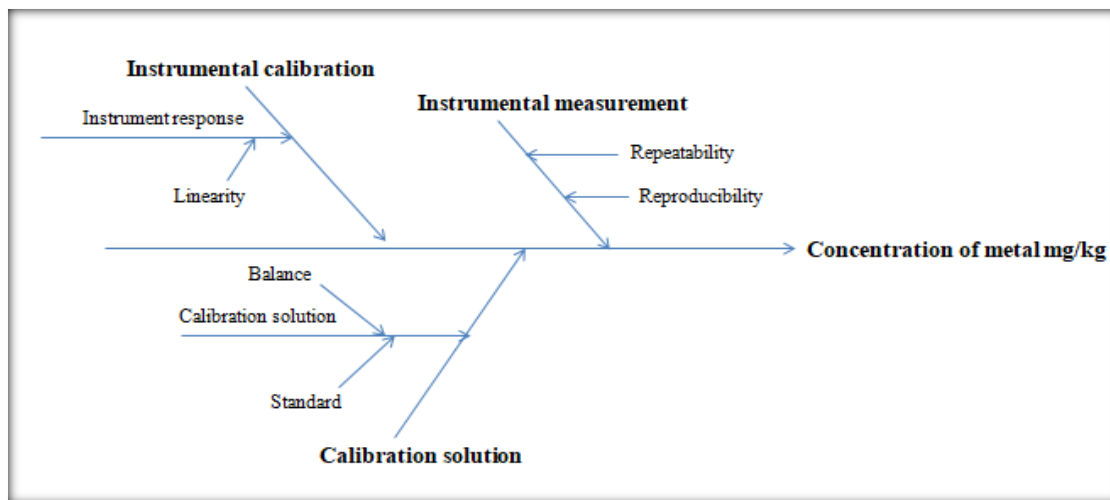


Figure 4.19: Cause and effect diagram for analysis of As, Ni and Pb in PM₁₀ by ICP-OES

The uncertainty contribution due to each component can be calculated as under:

4.5.1.1 Uncertainty due to CRM (calibration solution)

As per the calibration certificate, concentration of a multielement standard solution prepared from individual elements i.e. As, Ni and Pb are given in the **Table 4.4** given below. Uncertainty given in the certificate of the CRM can be taken for the calculation of standard uncertainty of the CRM used, $u(CRM)$. Here the uncertainty is given as expanded uncertainty at 95 % confidence level, $k=2$. So the standard uncertainty is calculated as follows:

Table 4.4: Uncertainty calculation for As, Pb and Ni CRM

Metal CRM	Uncertainty value as on certificate (at $k=2$)	Distribution, Type A & B, Divisor	Standard uncertainty $u(CRM)$
As 1001.5mg/kg	± 2.4 mg/kg	Normal, Type B, 2	$2.2/2 = 1.1$ mg/kg
Ni 1000.3 mg/kg	± 2.4 mg/kg	Normal, Type B, 2	$2.1/2 = 1.05$ mg/kg
Pb 1000.8 mg/kg	± 1.5 mg/kg	Normal, Type B, 2	$1.5/2 = 0.75$ mg/kg

Concentration of stock calibration standard can be calculated as:

$$C_{\text{Stock}} = (C_{\text{CRM}} \times W_{\text{CRM}}) / W_{\text{Stock}} \quad \text{where,}$$

C_{Stock} = Concentration of stock calibration standard

C_{CRM} = Concentration of CRM solution

W_{CRM} = Weight of CRM solution taken

W_{Stock} = Weight of stock calibration solution

4.5.1.2 Uncertainty due to Balance used for the Preparation of Calibration Standard

Standard uncertainty can be obtained from the uncertainty associated with the balance (**Figure 3.3b**) given in calibration certificate of the balance, $u(\text{Balance})$.

Thus, standard uncertainty for the mass measurement is given as follows:

(i) Make and model of balance used = Mettler Toledo AX105

(ii) Maximum capacity = 110 g

(iii) Uncertainty reported in certificate = $\pm 0.00003\text{g}$ ($k = 2$, at 95 % confidence level)

During preparation of stock solution, approximate 10 g of standard is diluted to approximately 100 g. Uncertainty due to balance is taken for once as for weighing of 100 g the relative uncertainty contribution is negligible.

4.5.1.3 Uncertainty due to Instrumental Calibration

Instrument software provides the concentration of a metal/element. It calculates concentration based on the calibration of standard solutions performed before the analysis. The regression a versus the concentration ($\mu\text{g kg}^{-1}$) of that metal (x) present in the injected standard solution. Here, using three numbers ($n = 3$) of calibration standards, the standard deviation (SD_{Reg}) is determined using regression statistic of the linear fit shown below in the **Figure 4.20, 4.21 and 4.22** SD_{Reg} which is taken as the standard uncertainty due to instrument response and is calculated according to Equation 11 given in the EURACHEM Guide:

$$SD_{\text{Reg}} = \sqrt{\frac{(s_{yy} - (b_1^2 \times s_{xx}))}{(N - 2)}} \quad (11)$$

where, $s_{yy} = \sum(y - y_{\text{avg}})^2$, $s_{xx} = \sum(x - x_{\text{avg}})^2$, b_1 = slope of the linear fit.

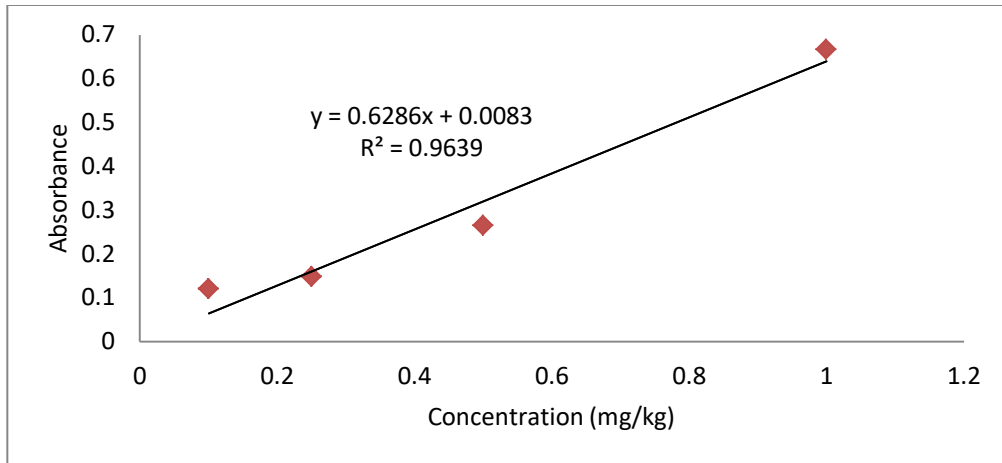


Figure 4.20: Calibration curve for determination of Arsenic by ICP-OES

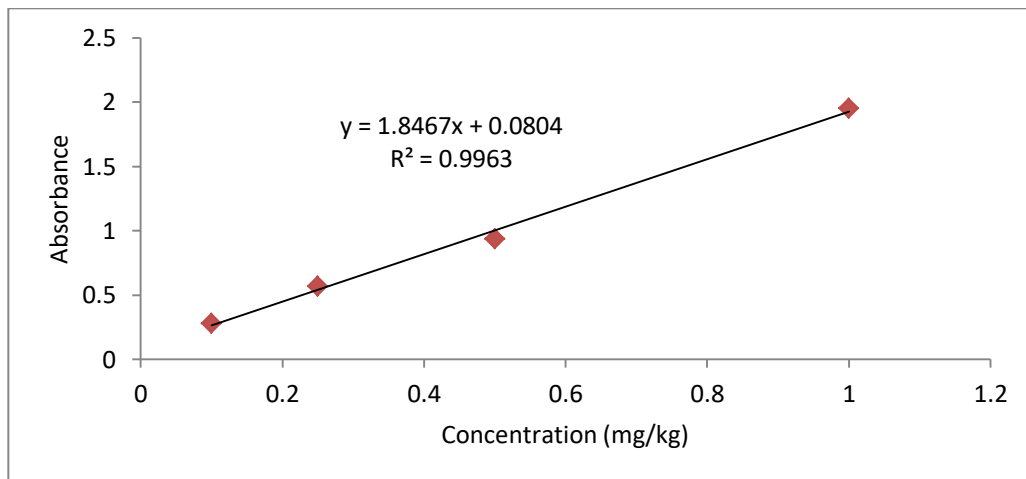


Figure 4.21: Calibration curve for determination of Nickel by ICP-OES

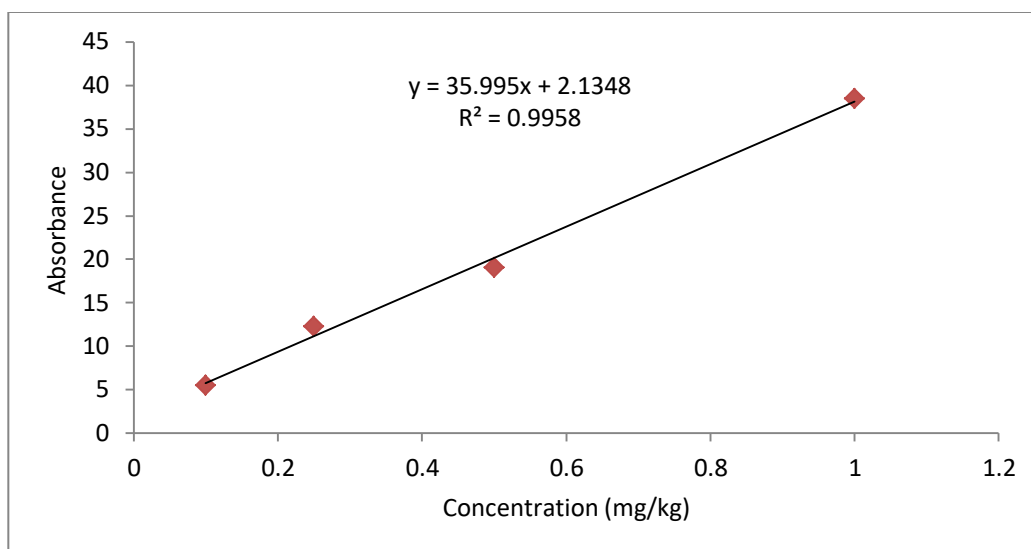


Figure 4.22: Calibration curve for determination of Pb by ICP-OES

The range of the concentration of Arsenic, Nickel and Lead in the calibration standard solutions was determined as per their expected values of concentration in the digested samples. Calibration was done in the range 0.1–1 mg/kg to check the performance of the instrument.

Uncertainty budget is a tabulated form of components that contribute to the uncertainty in the measurement results (JCGM 200_2008. VIM), i.e. a summary of the uncertainty calculations.

Table 4.5: Uncertainty budget for determination of As

Sources of Uncertainty	Estimated value, x_i	Limits, Dx_i	Distribution/ Type A & B/ Divisor	Standard Uncertainty $u(x_i)$	Relative Standard Uncertainty $u(x_i)/x_i$		
Instrument response	0.645	mg/kg	0.005	Normal, type A	0.0057	mg/kg	0.008
Concentration of As standard	1001.5	mg/kg	2.4	Normal, Type B, 2.2	1.2	mg/kg	0.001
Balance	10	g	0.00003	Normal, type B, 2	0.000015	g	0.00000030
Combined standard Uncertainty U_c	0.008						
Expanded Uncertainty, U	0.018	mg/kg	at $k=2$				

Table 4.6: Uncertainty budget for determination of Ni

Sources of Uncertainty	Estimated value, x_i		Limits, Dx_i	Distribution/ Type A & B/ Divisor	Standard Uncertainty $u(x_i)$		Relative Standard Uncertainty $u(x_i)/x_i$
Instrument response	0.560	mg/kg	1.49012×10^{-8}	Normal, type A	1.49012×10^{-8}	mg/kg	0.000000027
Concentration of Ni Standard	1000.3	mg/kg	2.4	Normal, Type B, 2.1	1.2	mg/kg	0.001
Balance	10	g	0.00003	Normal, type B,2	0.000015	g	0.00000030
Combined standard uncertainty U_c	0.001						
Expanded Uncertainty, U	0.002	mg/kg				g at k=2	

Table 4.7: Uncertainty budget for determination of Pb

Sources of Uncertainty	Estimated value, x_i		Limits, Dx_i	Distribution/ Type A & B/ Divisor	Standard Uncertainty $u(x_i)$		Relative Standard Uncertainty, $u(x_i)/x_i$
Instrument response	0.550	mg/kg	4.76837×10^{-7}	Normal, type A	4.76837×10^{-7}	mg/kg	0.000000867
Concentration of Pb Standard	1002.7	mg/kg	2.2	Normal, Type B, 2.2	1.1	mg/kg	0.001
Balance	10	g	0.00003	Normal, type B,2	0.000015	g	0.00000030
Combined standard uncertainty U_c	0.001						
Expanded Uncertainty, U	0.002	mg/kg				at k=2	

The uncertainty budget for As, Ni and Pb in ambient PM₁₀ is shown in **Table 4.5, 4.6, and 4.7.**

Source of relative combined uncertainty of each element viz., As, Ni and Pb with its percent

contribution are shown in **Figure 4.23, 4.24 and 4.25**. Arsenic major contribution was from ICP-OES i.e. instrument response (88%) followed by Standard concentration (11.9%), and finally balance (8.3%). For Ni, major contribution was from Standard concentration (99.9%), balance (0.025%) and ICP-OES i.e. instrument response (0.002%). For Pb, major contribution was from Standard concentration (99.8%), ICP-OES i.e. instrument response (0.078%) and balance (0.027%), The expanded uncertainty, U, of the measurement result was calculated using level of confidence of approximate 95 % and a coverage factor of 2 ($k=2$).

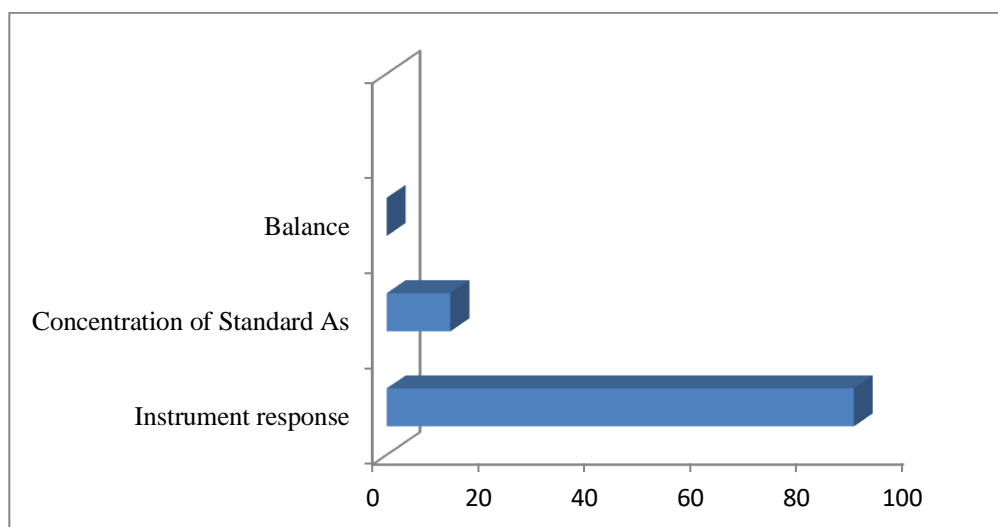


Figure 4.23: The % contribution of Uncertainty Sources for Arsenic in PM₁₀

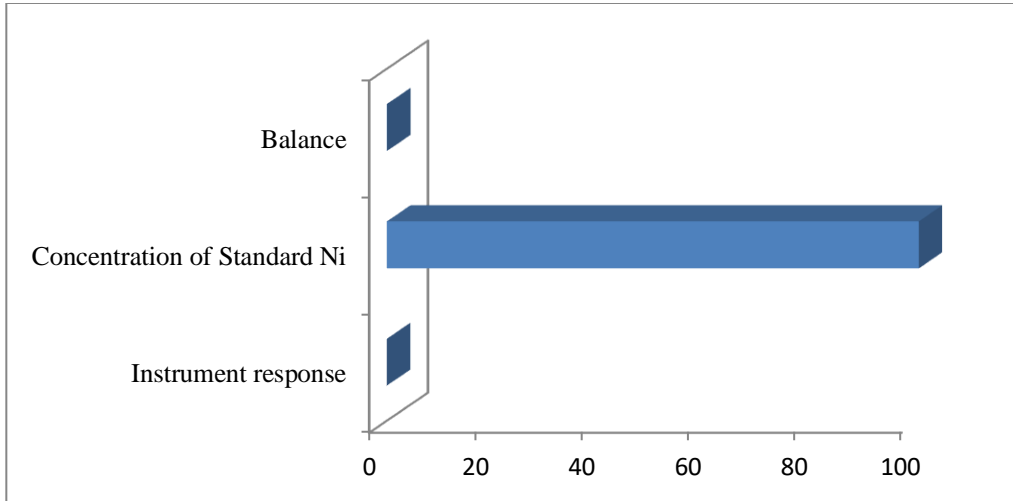


Figure 4.24: The % contribution of Uncertainty Sources for Nickel in PM₁₀

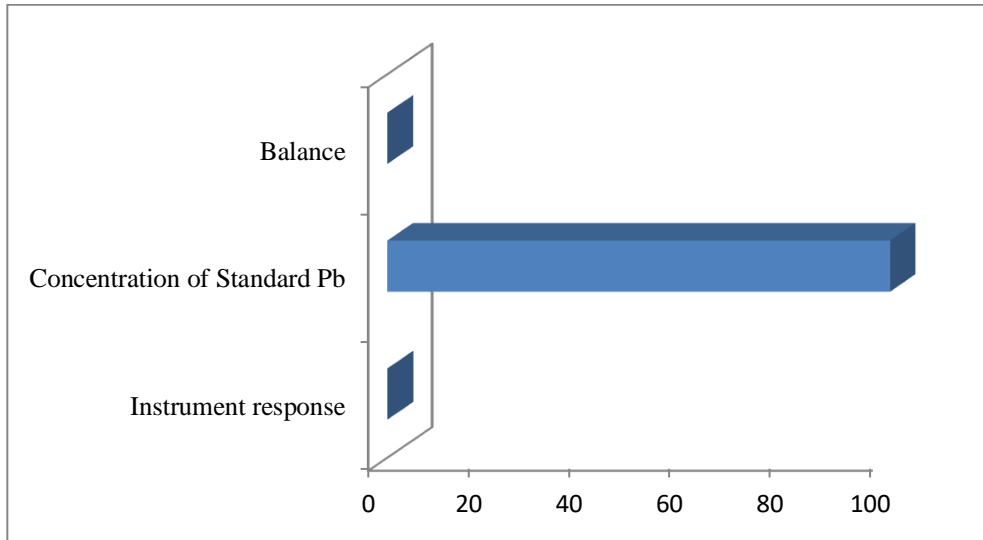


Fig 4.25: The % contribution of Uncertainty Sources for Lead in PM₁₀

Chapter V

CONCLUSIONS

The metrology of aerosols is very important for the quality of life. Variation in PM concentration recorded at one place from the same monitoring instrument is due to the limited number of standards/calibration facilities are available to calibrate the samplers. Therefore, for precise and accurate air quality data, the measurement data must have uncertainty.

In this study, PM₁₀ mass concentration, BaP concentration and PM₁₀ bound As, Ni and Pb level was measured in New Delhi as per NAAQS guidelines for the year-round period from January 2014 to January 2015. Also, the uncertainty sources present in the PM₁₀ characterization were identified. The important conclusions and findings are summarized below:

- Year-round monthly average mass concentration of PM₁₀ was calculated ($88 \pm 27 \mu\text{g m}^{-3}$ to $396 \pm 89 \mu\text{g m}^{-3}$). It is observed that PM₁₀ mass loading peaked in winters (January $396 \pm 89 \mu\text{g m}^{-3}$) and minimized in the summer (June $88 \pm 27 \mu\text{g m}^{-3}$). The increased concentration of mass can be due to the low planetary boundary layer and increased biomass burning in the winter season.
- In addition to this mass measurement, the measurement uncertainty was also estimated. Each primary measurement has its own contribution to the total calculated uncertainty. It was found that uncertainty contribution due to flow measurement in PM₁₀ mass measurement could be up to 90.4%, followed by charge effect 6.8%, conditioning 2.4%, and microbalance also as 0.39%. Combined uncertainty is also calculated to increase the level of confidence in the measurement.
- The measure should be taken to minimize PM₁₀ concentration in the atmosphere. The proper maintenance of roads and plantation of dust capturing plants will minimize the contribution of air borne re-suspension of road-dust.

- The uncertainty calculations in PM₁₀ measurements should be such that whenever and wherever it is measured, it should be acceptable universally. This data should be comparable for improving the air quality and thus quality of life.
- BaP is one of the criteria pollutant in the NAAQS guidelines. It was analysed in PM₁₀ samples through HPLC. BaP level decrease during monsoon and postmonsoon (July-September) and then increase in winters (November-January) The main reason behind the high PAHs concentration in New Delhi is the vehicular exhaust due to increase in number of vehicles over the years. From the study, it can be concluded that risk associated with high PAHs concentrations still persists in New Delhi. The average annual levels are 10–20 times higher than permitted value of 1 ng m⁻³.
- The measurement of uncertainty of various parameters involved in the measurement of BaP is also calculated which is an important aspect for quality assurance and quality control studies.
- Measures should be taken to control the vehicular exhausts especially diesel exhaust by implementing strict emission norms. Also the use of solid fuels should be reduced which will help to lower the BaP concentrations in the atmosphere.
- Arsenic, Ni and Pb concentration was studied in PM₁₀ samples as they are the criteria metal pollutants according to NAAQS guidelines. The metals were extracted by microwave digestion and analyzed on ICP-OES.
- The arsenic concentration varies from 0.300 ± 0.08 ng m⁻³ to 6.244 ± 2.3 ng m⁻³. Nickel concentration varied from 0.250 ± 0.11 ng m⁻³ to 2.853 ± 0.63 ng m⁻³. Lead concentration varied from 2.294 ± 1.18 ng m⁻³ to 1003.031 ± 473.1 ng m⁻³. Concentrations of As and Pb were observed to have exceeded the regulatory limits as prescribed by NAAQS. The major sources for the contamination of these metals in the environment are due to heavy traffic site and industrial activities.

- The possible uncertainty sources during measurement of As, Ni & Pb concentration in PM₁₀ were also evaluated. The results show that instrument response showed maximum uncertainty in case of As, as the metal concentration was very low. In case of Pb and Ni the calibration standard has the highest contribution in uncertainty. This may be due to other factors that are not as significant in case of Pb and Ni as they are in case of As.
- The emission control of air pollutants from each industry will reduce drastically the contribution of particulate matter and its metal contents in the ambient air. Therefore, it is necessary to focus on the emission control at source itself.

FUTURE SCOPE

Based on the investigation carried out on PM₁₀ mass concentration, PM₁₀ bound BaP and metal content, the following are the areas recommended for further study.

1. Uncertainty measurements for PM_{2.5}.
2. Investigation of mass concentration, BaP and metals for PM_{2.5}.
3. Study of other metals which are toxic to the environment.
4. Study of the source apportionment to derive information about the pollution sources.
5. Study on various emission reduction technology for PM.
6. In NAAQS, uncertainty should also be mentioned, which will help to take compliance decision more confidently.

Chapter VI

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Annexure 1. Effect of air quality with the concentration of PM₁₀ (www.airnow.gov).

Level of Health Concern	AQI (Air Quality Index)	PM₁₀ Concentrations (µg/m³)
Good	0-50	0-54
Moderate	51-100	55-154
Unhealthy for Sensitive Groups	101-150	155-254
Unhealthy	151-200	255-354
Very Unhealthy	201-300	355-424
Hazardous	301-500	425-604

Annexure 2. National Ambient Air Quality Standards, Central Pollution Control Board Notification, 2009

NATIONAL AMBIENT AIR QUALITY STANDARDS

S. No.	Pollutant	Time Weighted average	Concentration in Ambient Air		Methods of Measurement
			Industrial, Residential, Rural and Other Area	Ecologically sensitive area (notified by Central Govt.)	
(1)	(2)	(3)	(4)	(5)	(6)
1	Sulphur Dioxide (SO ₂), µg/m ³	Annual*	50	20	<ul style="list-style-type: none"> • Improved West and Geake • Ultraviolet fluorescence
		24 hours**	80	80	
2	Nitrogen Dioxide (NO ₂), µg/m ³	Annual*	40	30	<ul style="list-style-type: none"> • Modified Jacob & Hochheiser (Na-Arsenite) • Chemiluminescence
		24 hours**	80	80	
3	Particulate Matter (size less than 10 µm) or PM ₁₀ µg/m ³	Annual*	60	60	<ul style="list-style-type: none"> • Gravimetric • TOEM • Beta attenuation
		24 hours**	100	100	
4	Particulate Matter (size less than 2.5 microns) or PM _{2.5} µg/m ³	Annual*	40	40	<ul style="list-style-type: none"> • Gravimetric • TOEM • Beta attenuation
		24 hours**	60	60	
5	Ozone (O ₃) µg/m ³	8 hours **	100	100	<ul style="list-style-type: none"> • UV photometric • Chemiluminescence • Chemical method
		1 hour **	180	180	
6	Lead (Pb) µg/m ³	Annual*	0.5	0.5	<ul style="list-style-type: none"> • ASS / ICP method after sampling on EPM 2000 or equivalent filter paper • ED – XRF using Teflon filter
		24 hours**	1.0	1.0	

(1)	(2)	(3)	(4)	(5)	(6)
7	Carbon Monoxide (CO) mg/m ³	8 hours**	2	2	Non Dispersive Infra RED (NDIR) Spectroscopy
		1 hour**	4	4	
8	Ammonia (NH ₃) µg/m ³	Annual*	100	100	<ul style="list-style-type: none"> • Chemiluminescence • Indophenol blue method
		24 hours**	400	400	
9	Benzene (C ₆ H ₆) µg/m ³	Annual*	5	5	<ul style="list-style-type: none"> • Gas chromatography based continuous analyser • Adsorption and desorption followed by GC analysis
10	Benzo (a) Pyrene (BaP) – particulate phase only ng/m ³	Annual*	1	1	Solvent extraction followed by HPLC / GC analysis
11	Arsenic (As) ng/m ³	Annual*	6	6	AAS / ICP method after sampling on EPM 2000 or equivalent filter paper
12	Nickel (Ni) ng/m ³	Annual*	20	20	AAS / ICP method after sampling on EPM 2000 or equivalent filter paper

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

** 24 hourly or 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 3. Main sources of emission in China, India and the USA for the USEPA (Zhang et al, 2009)

Sources of emission	Global (%)	China(%)	India(%)	USA(%)
Biofuel	56.7	66.4	92.5	9.1
Wildfir	17.0	0	0	3.3
Consumer productwise	6.9	0.9	0.6	35.1
Traffic oil	4.8	2.0	IS	23.0
Coke production	3.7	10.7	1.3	IS
Domestic coal	3.6	14.4	IS	IS
Petroleum refining	2.4	1.0	IS	8.7
Waste incineration	1.9	IS	IS	9.5
Aluminium electrolysis	1.4	IS	IS	1.9
Open straw burning	IS	2.0	3.2	IS
Gasoline distribution	IS	IS	IS	3.0
Aerospace industry	IS	IS	IS	2.5
Other	1.5	0	2.7	3.9
Tonnes in thousand	530	114	90	32

IS- Insignificant

Annexure 4.

Queries from the external examiner (India)

Minor revision / queries for incorporation by the candidate in the Ph.D Thesis.

(Please use extra sheet, if required)

7. The most significant contributing uncertainty component identified is the purity of the BaP standard which has the highest uncertainty contribution as 77%. Major uncertainty contribution for Arsenic was from instrument response (88%) followed by standard concentration (11.9%) and balance (8.3%). For Nickel, major contribution was from standard concentration (99.9%), balance Page 3 of 3 (0.025%) and instrument response (0.002%). For Lead, major contribution was from standard concentration (99.8%), instrument response (0.078%) and balance (0.027%). Whereas in case of PM₁₀ in the same study, the flow rate of the sampling (90.4%) and charge effect of the filter (6.7%) had the major contribution in the total uncertainty budget of PM₁₀ mass measurement. Rest of the uncertainty components, e.g., balances (0.39%) and conditioning of filter (2.39%), had the least contribution.

The research scholar should have considered the sampling component particularly flow component into consideration while estimating the uncertainty budget for the BaP & three metal (As, Ni & Pb) may decrease the contribution of other contribution factors & uncertainty factors and will be more rationalized.

(This queries may be addressed during the viva-voce examination).

Answer:

As suggested by the examiner, the uncertainty of sampling component (flow component) has been added with the combined u_c of various parameters in the table given below. The difference in the values and their % difference is also given.

Parameter	Combined uncertainty u_c	Combined uncertainty u_c + Flow uncertainty	Difference	% Difference
BaP (ng m ⁻³)	0.588980475	0.588980476	6.75725E-10	6.75725E-12
Arsenic (mg/kg)	0.008918069	0.008918114	4.46271E-08	4.46271E-10
Nickel (mg/kg)	0.001199641	0.001199973	3.31711E-07	3.31711E-09
Lead (mg/kg)	0.001097039	0.001097402	3.62725E-07	3.62725E-09

The mass measurement of PM₁₀ and BaP concentration in PM₁₀ has been published as:

Jyoti Pokhariyal, A. Mandal and S. G. Aggarwal, Uncertainty Estimation in PM₁₀ Mass Measurements, MAPAN-Journal of Metrology Society of India 34(1) (2019)129–133 (Impact Factor-1.25).

Jyoti Pokhariyal, A. Mandal and S. G. Aggarwal, Measurement of Benzo(a)pyrene in PM₁₀ Collected in New Delhi. MAPAN-Journal of Metrology Society of India 34(2019) 465–471 (Impact Factor-1.25).

The above two papers have received the DTU-Research Excellence Award -2019 with prize money of Rs. 1.0 lakhs.

10. The research scholar should make a presentation considering the sampling component particularly flow component into consideration while estimating the uncertainty budget in excel for the BaP & three metal (As, Ni & Pb) As Raised at Point no 7.

Answer :

The table given above was shown and discussed in the viva-voce presentation.

Annexure 5.

Queries from the external examiner (Abroad)

6. Please provide below your detailed evaluation report on the Thesis.

(Please use extra sheet, if required)

1. The work mentioned in the thesis is a good attempt and of global significance in terms of air quality measurements and interpretation. A comparison with another location at distinct geographical condition would have added more value.

2. Thesis has excellent analysis, would have suggested some novelty on sample collection, cause of uncertainty and better equipment utilization.

3. Candidate has published three publications but all in one journal - MAPAN. Not clear why other journals were not approached. 4. Overall, satisfactory attempt on PM10 determinations that can be used by the authorities to understand the variations in data production as well as further study PM2.5.

Answer1:

The thesis work undertaken has been compared with the following work:

Variation of carbonaceous species and trace elements in PM10 at a mountain site in the central Himalayan region of India S. K. Sharma, Nikki Choudhary , Priyanka Srivastava , Manish Naja , N. Vijayan & Garima Kotnala , T. K. Mandal. Journal of Atmospheric Chemistry (2020) 77:49–62.

PM10 samples were collected at a high altitude site ARIES, Nainital,, situated 1958 m above mean sea level in the Shivalik ranges of the central Himalayas from October 2018 to February 2019. The following observation were done during the study:

Species	Average	Range	Autumn	Winter
PM ₁₀ (µg m ⁻³)	44 ± 13	23 – 71	54 ± 12	39 ± 10
Arsenic (µg m ⁻³)	0.022 ± 0.003	0.018–0.026	0.024 ± 0.002	0.020 ± 0.002
Nickel (µg m ⁻³)	0.036 ± 0.005	0.028–0.044	0.038 ± 0.005	0.035 ± 0.004
Lead (µg m ⁻³)	0.056 ± 0.007	0.046–0.069	0.050 ± 0.003	0.061 ± 0.006

The following table shown below shows the data of same species observed in the thesis work:

Species	Average	Range	Post monsoon	Winter
PM ₁₀ ($\mu\text{g m}^{-3}$)	222.24 \pm 11.38	32.5- 480.2	223.9 \pm 55.8	315.2 \pm 98.3
Arsenic (ng m^{-3})	0.002 \pm 0.003	0.30-6.24	3.47 \pm 1.83	2.05 \pm 0.83
Nickel (ng m^{-3})	0.001 \pm 0.005	0.25–2.85	1.49 \pm 0.60	1.15 \pm 0.35
Lead (ng m^{-3})	0.247 \pm 0.007	2.29–1003.03	501.55 \pm 296.4	213.87 \pm 127.4

Answer 3.

The thesis work undertaken was based on aerosol metrology. Few journals are available on metrology. MAPAN is an SCI E index journal based on metrology. It has an impact factor of 1.25. That is why the thesis work was considered for publication in MAPAN.

Brief Curriculum-Vitae

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Educational Qualification

Exam. Passed	Year	Board/ University
PhD (Pursuing)	2012 to present	DTU, Delhi
M.Sc (Ecology & Environment)	2003	Sikkim Manipal University, Gangtok
B.Sc. (Chemistry, Biology, Zoology)	1999	Lucknow University, Lucknow

Areas of Interest

Metrology in Chemistry

Experience

15 years (In the field of chemical metrology)

Publication:

15 publications

(JYOTI POKHARIYAL)