

**CHARACTERISTICS OF POLYCYCLIC AROMATIC  
HYDROCARBONS WITH RESPECT TO THEIR  
SOURCES IN THE AMBIENT  
ATMOSPHERE OF DELHI**

*Dissertation submitted to Jawaharlal Nehru University in partial  
fulfilment of the requirement for the award of the Degree of*

**MASTER OF PHILOSOPHY**

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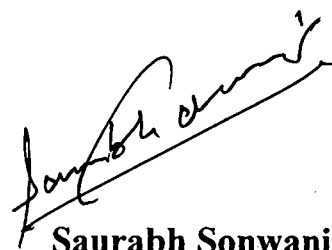
**2014**



जवाहरलाल नेहरू विश्वविद्यालय  
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**CERTIFICATE**

The research work embodied in this entitled “**Characteristics of polycyclic aromatic hydrocarbons with respect to their sources in the ambient atmosphere of Delhi**” has been carried out at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India. This work is original and has not been submitted in part or full for any degree/diploma of any other University.



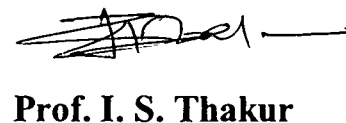
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To my parents

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## *Acknowledgement*

*It would not have been possible to write my M. Phil, dissertation without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here.*

*First and foremost, I wish to acknowledge with gratitude for the inspiring guidance provided to me by my supervisor Prof. P. S. Khillare. He provided me a wonderful environment to work. His valuable motivation and moral support have enabled me to pursue this research work smoothly.*

*I extended my thanks to Prof. A .K Attri ex-Dean and Prof. I. S Thakur, present Dean, School of Environmental Science, for providing me with the necessary facility to carry out my research work. I would also like to thanks all faculty and staff members of the school for their kind support during the study period.*

*I am thankful to UGC for providing me with fellowship during this work.*

*I am thankful to Mr. Hoshiyar Singh for his kind assistance during lab activities.*

*I would like to express heartfelt thanks to my lab mates- Amreen Mam, Sapna Mam, and Reema and especially Darpa Sir - for their support in every possible way. They helped me immensely during my sampling, analysis and dissertation compilation.*

*I owe thanks to my friends- specially Sughosh, Sushil, Arif, Amit, Chandrashekhhar, Sashishekhhar, Vineet and many more for their constant help and support.*

*I want to thank my parents for their kind support, the confidence and the love they have shown to me. You are my greatest strength and I am blessed to be your son. . I also would like to thank my beloved sisters and brother Vandana, Neelam and Gaurav for being a good friend and understanding me well in various situations.*

*And at last but very necessarily to all the readers going through even the last line of my acknowledgement.*

*Saurabh Sonwani*

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## Introduction

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Air quality in Asian cities has been widely reported to be deteriorating and the attributed reasons are unprecedented population growth, ever increasing vehicular numbers, rapid industrialization, and increased energy use. Motor vehicles are the major sources of urban air pollution. Environmental contamination of natural resources with persistent organic pollutants (POPs) is of great world-wide concern.

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous persistent organic pollutants (POPs). Among POPs, PAHs are compounds consisting of 2 to 7 aromatic rings (Sharma and Tripathi 2009; Stanley et al. 2003). They are known as critically hazardous pollutant. Some of the PAHs have been designated to be carcinogenic by various international agencies (US Environmental Protection Agency (EPA), US Department of Health and Human Services (DHHS) and the International Agency for Research on Cancer (IARC). Because of persistence nature, bio accumulative properties, carcinogenicity, and mutagenicity nature of PAHs make them very popular in the research community. (Costantiono et al., 1995; Kalina et al., 1998; Oanh et al., 1999). Polycyclic aromatic hydrocarbons (PAHs) mainly originate from combustion related sources (pyrogenic sources) and petroleum products (petrogenic sources). Combustion processes are mostly related to anthropogenic activities, such as incomplete combustion of coal, petroleum products, and biomass (ATSDR, 1995, Takasuga et al. 2007). Incomplete combustion of organic materials such as crude oil, coal, and natural gas leads to formation of many of PAHs compounds and consequent release in to the atmosphere (Netto et al. 2007; Shibamoto 1998; Slezakova et al. 2010; WHO, 1998).

Traffic emission sources are known as the main PAHs contributors among various PAHs emission sources in urban areas. (Pyysalo et al., 1987; Tuominen et al., 1988).

The risk due to PAHs exposure to human being is very high in the urban environment, as it has high population density, increasing traffic numbers and insufficient dispersion of the atmospheric pollutants (Caricchia et al., 1999).

## 1.1 URBAN AIR QUALITY

It is estimated that more than 1 billion people are exposed to outdoor air pollution annually. According to UNEP (2014), urban air pollution is responsible for 1 million immature deaths and 1 million pre-natal deaths per year. Rapid urbanisation causes intense pollution scenarios in most of the cities located in developing countries. The environmental impacts are very severe in Asian countries where they have a combination of intense industrial activity, large populations, and increased motor vehicle usage. In most of the developing countries poor maintenance of vehicle and low fuel quality are the root cause for creating over 90% of air pollution in the cities. (UNEP, 2014).

## 1.2 PARTICULATE MATTER (PM)

PM includes small solid particles and liquid droplets suspended in the Earth's atmosphere. It is very difficult to see most of the particulate matter from naked eyes except some large size particle like dust, dirt, soot or smoke. For the detection of the small size particles scientist generally use electron microscope. Particulate matter includes respirable particulates with aerodynamic diameters less than 10 micrometers.

The particulates emitted directly from their sources (construction sites, unpaved roads, fields, smokestacks or fires) known as primary particulates like sulfur dioxides and nitrogen oxides that are emitted from power plants, industries and automobiles. While secondary particulates form by chemical reactions in the atmosphere.

### 1.3 PARTICULATE MATTER CLASSIFICATION (ON THE BASIS OF EMISSION)

1.3.1 **Primary PM:** Primary particulate matter present in the atmosphere in the same chemical composition as they emitted from their source. It commonly includes windblown dust such as road dust, fly ash, soot etc.

1.3.2 **Secondary PM:** Secondary particulate matters are formed by photochemical or only chemical reactions in the atmosphere. It includes sulphates, nitrates etc.

### 1.4 PARTICULATE MATTER CLASSIFICATION (ON THE BASIS OF SIZE)

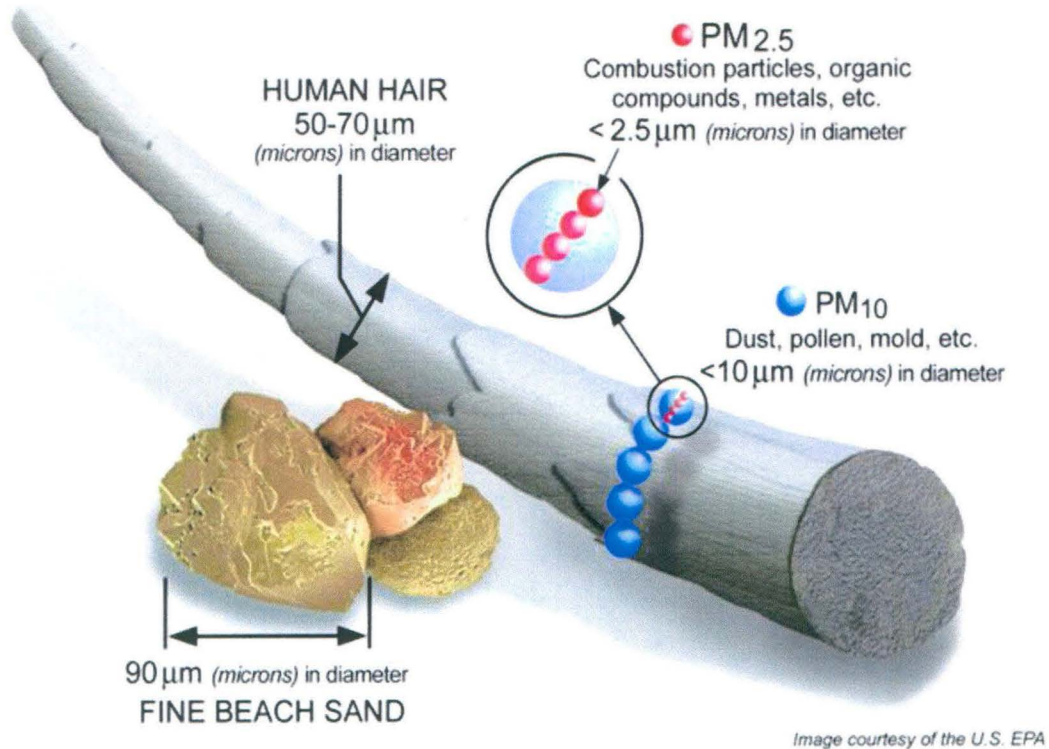
Table 1.1 and Figure 1.1 shows the classification and size of particulate matter.

**Table 1.1 Classification of particulate matter**

| Fraction   | Size range   |
|--|--|
| Respirable suspended particulate matter<br><br>(RSPM) or PM10      | $\leq 10 \mu\text{m}$ diameter<br><br>Known as the thoracic fraction.  |
| Accumulation mode or Fine particles or PM2.5 (respirable fraction) | $\leq 2.5 \mu\text{m}$ in diameter<br><br>These particles can penetrate into the deeper lungs and consequently may initiate host of respiratory problems and even premature death. They are generally made up of carbon (organic and elemental), inorganic compounds |

|                           |   |
|---------------------------|---|
|                           | (sulfate, nitrate, and ammonium), and trace metal compounds   |
| Ultrafine particles (UFP) | <p>≤0.1 μm with high surface area per unit mass. They act as carriers of harmful gaseous compounds. They have ability to penetrate tissue and may be absorbed directly into the bloodstream and can't be easily remove from the body. It may cause pulmonary inflammation and hemorrhage, interstitial oedema, disruption of epithelial and endothelial cell layers and even death.</p> |

Figure: 1.1 Different size fractions of particulate matter



PM<sub>10</sub> (RSPM) are the particles with upper size limited by a 50% cut at 10  $\mu\text{m}$  aerodynamic diameter (USEPA, 1996). Organic carbon (OC), elemental carbon (EC), metals/elements (silicon, iron, magnesium, ions like sulphates, nitrates, ammonium) are the major components of PM<sub>10</sub>.

Particulates may contain hazardous substances which in turn creates adverse health effects when they are deposited into the lungs. PM in diesel exhaust has been cited as a probable human carcinogen by several agencies. Increase in PM<sub>10</sub> and PM<sub>2.5</sub> levels is associated with increased daily mortality and increased rates of hospital admissions due to respiratory diseases (WHO, 2005).

## 1.5 POLYCYCLIC AROMATIC HYDROCARBONS (PAHS)

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. PAHs vary in volatility; the larger molecules ( $\geq 4$  ring) have lower vapour pressures and are generally adsorbed onto particulate matter, while the smaller, lighter molecules are generally present in gaseous phase in the ambient atmosphere (Park et al, 2002). PAHs are hydrophobic in nature and have high fat solubility. PAH undergoes photo degradation/decomposition in the presence of UV light, when they present in the water or on the surface of particulate.

In the atmosphere, PAHs shows many reactions with some pollutants such as  $O_3$ ,  $NO_x$ ,  $SO_x$  and yields diones, nitro- and dinitro-PAHs, and sulfonic acids, respectively. PAHs may also be degraded by some microorganisms in the soil (WHO, 1987; ATSDR, 1994). Combustion-generated PAHs are initially generated at source in the gaseous state, a proportion of which then adsorbs onto particles upon cooling of the emission. At higher combustion temperatures larger proportions of PAHs are present as gaseous PAHs. Furthermore, their semi-volatility and high environmental half-lives result in global planetary distribution (Martinez et al., 2004).

In the pure form PAHs are colourless, white, or pale yellow-green solids. These pure PAHs are generally found in coal tar, crude oil, creosote, and roofing tar. Some pure PAHs are used form manufacturing of medicines, dyes, plastic etc. (ATSDR, 1995). Some of the key attributes of PAHs are:

- High molecular weight PAHs are mostly found in the particulate phase.
- As they are semi volatile compounds they can readily volatilise into the air.



- In the presence of the sun light PAHs easily break down in the air, over a period a period of days to weeks.
- The presence of PAHs in water indicates their discharges from industrial and wastewater treatment plants in to that water body.
- As PAHs are hydrophobic in nature, they usually stick to solid particles in water body and settle to the bottoms of lakes or rivers.
- Due to bioaccumulation, PAH contents of plants and animals may be higher than PAH contents of soil or water in which they live.

### **1.6 PHYSICAL AND CHEMICAL PROPERTIES OF PAHS**

Physico-chemical properties of PAHs are represented in Table 1.2. PAHs are non-polar organic substances made up of carbon and hydrogen atoms grouped with at least two condensed or fused aromatic ring structures (CCME, 2010). Pure PAHs are usually coloured, crystalline solids at ambient temperature. The physical properties of PAHs depend on their molecular weight and structure. PAHs are highly lipophilic and therefore miscible in organic solvents. In addition, aqueous solubility decreases for each additional ring added to the PAH. Aqueous solubility can be explained by using octanol-water partitioning coefficient ( $K_{ow}$ ). Low molecular weight with less than four rings are water-soluble than high molecular weight with four and more than four rings. The vapor pressure of PAHs decreases with increasing molecular weight (Akyuz and Cabuk, 2010). Once released into the atmosphere, PAHs are partitioned between the particulate matter (PM) and gas phases depending on their molecular weight (Chen et al. 2005; Furuuchi et al. 2007). Comparatively low molecular-weight (LMW) PAHs are partitioned more in the vapour phase, whereas high molecular-weight (HMW) PAHs are associated with suspended solid particles (Ravindra et al.

2006; Wang et al. 2007). LMW PAHs produce fewer toxic impacts compared with the HMW PAHs, which contain five to six aromatic rings (ATSDR 1990).

Table 1.2 Physico-chemical properties of PAHs

| Compounds              | Abbr. | Mol. Wt. | Mol. Formula                    | No. of rings | Melting Point<br>(°C) | Boiling Point<br>(°C) | Vap.Press.<br>Pa (25°C) | Log K <sub>ow</sub> * | Water solubility<br>µg l <sup>-1</sup> (25°C) | Henry's constant<br>Kpa m <sup>3</sup> /mol<br>(25°C) |
|------------------------|-------|----------|---------------------------------|--------------|-----------------------|-----------------------|-------------------------|-----------------------|---|---|
| Naphthalene            | Naph  | 128      | C <sub>10</sub> H <sub>8</sub>  | 2            | 81                    | 217.9                 | 1.4                     | 3.4                   | 3.17 x 10 <sup>4</sup>                        | 4.89 x 10 <sup>-2</sup>                               |
| Acenaphthylene         | Acy   | 152      | C <sub>10</sub> H <sub>8</sub>  | 3            | 92-93                 | 265-275               | 8.8 x 10 <sup>-1</sup>  | 4.07                  | -   | 1.14 x 10 <sup>-3</sup>                               |
| Acenaphthene           | Acen  | 154      | C <sub>12</sub> H <sub>10</sub> | 3            | 85                    | 279                   | 2.9 x 10 <sup>-1</sup>  | 3.92                  | 3.93 x 10 <sup>3</sup>                        | 1.48 x 10 <sup>-2</sup>                               |
| Fluorene               | Flu   | 166      | C <sub>13</sub> H <sub>10</sub> | 3            | 115-116               | 293-295               | 8 x 10 <sup>-2</sup>    | 4.18                  | 1.98 x 10 <sup>3</sup>                        | 1.01 x 10 <sup>-2</sup>                               |
| Phenanthrene           | Phen  | 178      | C <sub>13</sub> H <sub>10</sub> | 3            | 216.4                 | 342                   | 1.6 x 10 <sup>-2</sup>  | 4.6                   | 1.29 x 10 <sup>3</sup>                        | 3.98 x 10 <sup>-3</sup>                               |
| Anthracene             | Anth  | 178      | C <sub>14</sub> H <sub>10</sub> | 3            | 100.5                 | 340                   | 8 x 10 <sup>-4</sup>    | 4.5                   | 73  | 7.3 x 10 <sup>-2</sup>                                |
| Fluoranthene           | Flan  | 202      | C <sub>16</sub> H <sub>10</sub> | 4            | 108.8                 | 375                   | 1.2 x 10 <sup>-3</sup>  | 5.22                  | 260   | 6.5 x 10 <sup>-4</sup>                                |
| Pyrene                 | Pyr   | 202      | C <sub>16</sub> H <sub>10</sub> | 4            | 150.4                 | 393                   | 6 x 10 <sup>-4</sup>    | 5.18                  | 135   | 1.1 x 10 <sup>-3</sup>                                |
| Benzo[a]Anthracene     | BaA   | 228      | C <sub>18</sub> H <sub>12</sub> | 4            | 160.7                 | 400                   | 2.8 x 10 <sup>-5</sup>  | 5.16                  | 14  | -   |
| Chrysene               | Chry  | 228      | C <sub>18</sub> H <sub>12</sub> | 4            | 253.8                 | 448                   | 8.4 x 10 <sup>-5</sup>  | 5.91                  | 2   | -   |
| Benzo[b]Fluoranthene   | BbF   | 252      | C <sub>20</sub> H <sub>12</sub> | 5            | 168.3                 | 481                   | 6.7 x 10 <sup>-5</sup>  | 6.12                  | 1.2   | 5.1 x 10 <sup>-5</sup>                                |
| Benzo[k]Fluoranthene   | BkF   | 252      | C <sub>20</sub> H <sub>12</sub> | 5            | 215.7                 | 480                   | 1.3 x 10 <sup>-8</sup>  | 6.84                  | 2.5   | 4.4 x 10 <sup>-5</sup>                                |
| Benzo[a]Pyrene         | BaP   | 252      | C <sub>20</sub> H <sub>12</sub> | 5            | 178.1                 | 496                   | 7.3 x 10 <sup>-7</sup>  | 6.5                   | 3.8   | 3.4 x 10 <sup>-5</sup>                                |
| Dibenzo[a,h]Anthracene | DBA   | 278      | C <sub>22</sub> H <sub>12</sub> | 5            | 278.3                 | 545                   | 1.3 x 10 <sup>-8</sup>  | 6.5                   | 0.5 (27°C)                                    | 7 x 10 <sup>-6</sup>                                  |
| Benzo[ghi]Perylene     | BghiP | 276      | C <sub>22</sub> H <sub>12</sub> | 6            | 163.6                 | 536                   | 1.4 x 10 <sup>-8</sup>  | 7.1                   | 0.26  | 2.7 x 10 <sup>-5</sup>                                |
| Indeno[1,2,3-cd]Pyrene | IP    | 276      | C <sub>22</sub> H <sub>12</sub> | 6            | 266.6                 | 524                   | 1.3 x 10 <sup>-8</sup>  | 6.58                  | 62  | 2.9 x 10 <sup>-5</sup>                                |

### **1.7 EXPOSURE OF POLYCYCLIC AROMATIC HYDROCARBONS**

The following are the routes of PAHs exposure:

- Significant work place exposure containing PAHs, like coal-tar and asphalt production plants.
- Significant personal exposure such as during cigarette smoking, domestic biomass burning etc.
- Eating grilled food like meat, bread and processed foods.
- Drinking polluted/contaminated water or milk. (ATSDR, 1995)

### **1.8 PM10 BOUND POLYCYCLIC AROMATIC HYDROCARBONS**

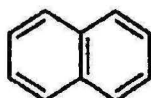
In the atmosphere, PAHs are present in both, particulate and gaseous phase. However, HMW PAHs, the ones that are carcinogenic are predominantly associated with particulate phase. From the health perspective, monitoring the levels of particulate phase PAHs in urban environment is very important (Chetwittachan et al., 2002). The highest concentrations of particulate phase PAHs are usually found in urban environment due to the increasing vehicle numbers and the insufficient dispersions of atmospheric pollutants.

Amongst p-PAHs, PAHs associated to ambient PM10 are known as PM10 bound PAHs. Like other PAHs compounds these are also formed during the incomplete combustion and pyrolysis of organic material. In many urban areas motor vehicles have been identified as the most significant source of airborne PAHs (Kavouras et al., 1999; Dunbar et al., 2001)

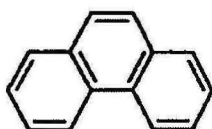
Figure 1.2 Structures of USEPA reported 16 PAHs

PAH components

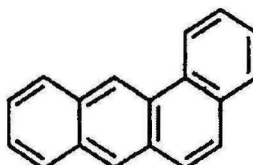
1. Naphthalene (Naph)



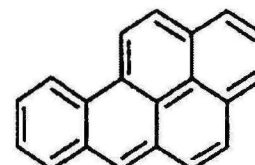
5. Phenanthrene (Phe)



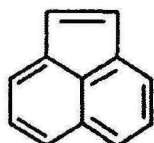
9. Benzo(a)anthracene (BaA)



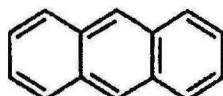
13. Benzo(a)pyrene (BaP)



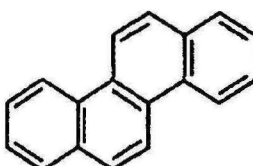
2. Acenaphthylene



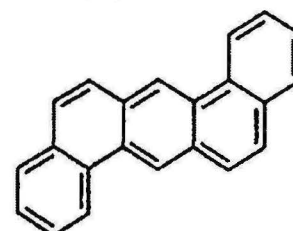
6. Anthracene (Ant)



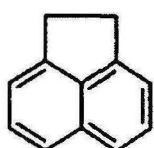
10. Chrysene (Chr)



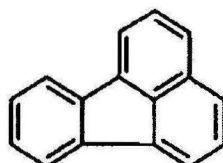
14. Dibenzo(a,h)anthracene (DBA)



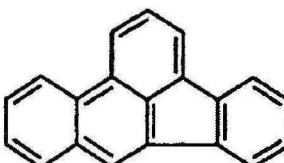
3. Acenaphthene (Ace)



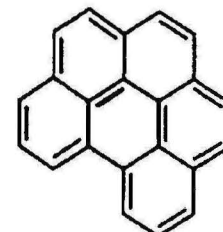
7. Fluoranthene (Flu)



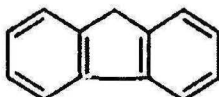
11. Benzo(b)fluoranthene (BbF)



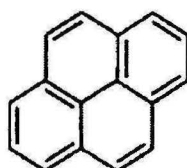
15. Benzo(g,h,i)perylene (BghP or BP)



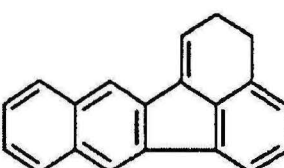
4. Fluorene (Fl)



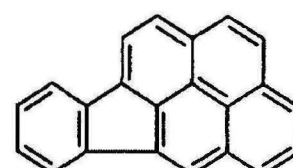
8. Pyrene (Pyr)



12. Benzo(k)fluoranthene (BkF)



16. Indeno(1,2,3-c,d)pyrene (InP)



## 1.9 BACKGROUND AND SIGNIFICANCE OF STUDY

Delhi is a megacity and the capital of India. Delhi has population of 16.7 million spread over an area of 1483 km<sup>2</sup> (Census, 2011). The atmospheric pollution level in Delhi is a matter of concern now-a-days. Rapid urbanization and industrialization in Delhi are the primary causes of increasing level of atmospheric pollution. The central pollution control board (CPCB) declared that the city of Delhi was “India’s Asthma capital” (Today News, 1999). By virtue of being a growing city, sectors such transport, energy, infrastructure and industry have contributed to the rising air pollution levels in the city and consequently health and respiratory impacts.

The increasing number of new vehicles on the road is one of the possible reasons for increasing urban atmospheric pollution. In 2000-01, approximately 580 vehicles were registered every day; this has almost doubled in 5 years to approximately 1000 in 2005-06 (Roychoudhury A., 2007).

According to Delhi government’s transport department the total vehicle registered up to the date of 30 April 2014 are 7,952,978 and 335,815 (private vehicles and commercial vehicles respectively) (Transport department, 2014). The number of registered vehicle in city has grown with rate 85.53% between 1997-98 and 2007-08. Owing the relative influence of the city’s population, private car penetration in Delhi (85 cars per 1000 population) is more than 10 times national average (8 cars per 1000 population) (Planning Department, 2009).

In the present study two sites were selected. One was Jawaharlal Nehru University campus (JNU), New Delhi. JNU is an institutional area in south Delhi situated on the ridge of the Aravalli Hills in the midst of a 4 km<sup>2</sup> forested area,

surrounded by major roads carrying heavy volume of vehicular traffic. It also had some particulate matter generating construction activities inside the university campus during sampling period. The second site was Gomti Guest House, Mandi House, New Delhi, characterized by dense traffic dominated area and surrounded by some government buildings. Unlike the first site, second sampling site was very near to the traffic area. JNU is considered as urban background site because it acts as receptor site for all the air pollutants due to prevailing wind direction (form North-West to South-East) from most part of the year in Delhi.

#### **1.10 OBJECTIVES OF STUDY**

1. To determine the ambient concentration of respirable suspended particulate matter (RSPM) at two different sites in Delhi.
2. To determine the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in RSPM at selected sites in Delhi.
3. To find out the correlation between PAHs and meteorological parameters.
4. To carry out source apportionment of PAHs at the study sites.
5. To carry out health risk assessment due to inhalation exposure of PAHs

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## Literature Review

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This section includes detailed literature review of particulate matter, polycyclic aromatic hydrocarbons, different sample pre-treatment, chromatographic method for PAHs analysis, source apportionment methodologies and health risk assessment of PAHs.

## 2.1 PARTICULATE MATTER (PM)

Particulate matter (PM) refers to a suspension of solid, liquid or a combination of solid and liquid particles in the air (Hinds, 1999). Particulate matters produced from man-made and natural sources both, can be categorised in to primary and secondary pollutants on the basis of their origin. Primary particulate matters are emitted directly from emission sources and they often associated with combustion sources. Secondary particulate matters are formed in the atmosphere by various photo-chemical reactions from primary pollutants like NO<sub>x</sub>, SO<sub>x</sub>, and VOCs (Blanchard et al., 1999; Ito et al., 2004).

US EPA focuses on better understanding of particulates such as; processes of emission, conversion of particulates from gaseous compounds, transportation, and exposure to human being through various routes (inhalation, dermal and ingestion) and adverse health effects due to PM exposure to mankind. Due to their ubiquitous nature and adverse effect, PM come under the category of pollutants of critical investigations. As compare to PM (PM<sub>10</sub> and PM<sub>2.5</sub>) the Total suspended particulates (TSP) are larger in size (>30 mm) remain suspended for only a relatively short period of time as compared to the smaller size fractions PM<sub>10</sub> and PM<sub>2.5</sub>, which are PM fractions with an aerodynamic diameter of less than 10 and 2.5 mm, respectively.

Anthropogenic airborne particulate matter comes from a variety of sources, which include, but are not restricted to traffic, industries, commerce and domestic heating and cooking. Among them, traffic-related particulates have been under intensive scrutiny for at

least two reasons. One is due to the evidence that particulates generated from combustion processes, especially diesel exhaust particulates (DEP), are more potent in posing adverse health effects than those from non-combustion process (Laden et al., 2000; Janssen et al., 2002). In London, UK, more than 80% of particulate matter is from road traffic (Department for Transport, 2002).

### **2.1.1 Sampling methodologies of Particulate matter**

There are two basic methods to collect particulate matter – samplers with fixed and mobile inlet. There are varieties of the filters that are used for the collection of particulate matters. It can be a membrane, granular bed and nucleopore filter. Pre and post-treatment of the filter is required under controlled temperature and relative humidity conditions for sampling. Air flow rate through filter sampling system may be high (1.2-1.5 m<sup>3</sup>/min, the so called “high volume samplers”) or low (20-30 L/min, the so called “low volume samplers”) depending of the analyte of interest and other important requirements. Size dependent aerosol sampling with sharp cut points can be done by Cascade impactors. Some time the heavy loading of aerosol causes bouncing of particle inside the impactors. It can be overcome by coating of some substances (oil or grease). Cyclones, on the other hand, are not affected by particle bounce; however the performance must be determined empirically since in cyclone no theory provides reliable design criteria.

### **2.1.2 Levels of PM10**

According to the World Bank PM10; country level (micrograms per cubic meter) in India was last measured at 57.13 in 2009. Particulate matter concentrations refer to fine suspended particulates matters <10 microns in diameter (PM10). They are capable to penetrate deep into the respiratory tract and cause significant health damage.

TSP refers to particles ranging in size from the smallest to a generally accepted upper limit of 50-100 microns in diameter (1 micron = 1 millionth of a metre). TSP is dominated by the larger sized particles commonly referred to as “dust” and is associated with aesthetic and environmental impacts. (Air Quality Monitoring Network, 2008).

The levels of TSP and PM10 in India cities routinely exceed the national ambient air quality standard (NAAQS). PM10 levels in the “residential area” class in 2008 indicated 2 cities in the “low” category, 21 cities in the “moderate category”, 40 in “high level” category and 41 (including Delhi) in the critical level of category (CPCB, 2009a).

Many authors observed considerably higher concentration of PM10 in many urban areas across the India such as Ahmedabad (118  $\mu\text{g}/\text{m}^3$ ; Sunder Raman et al., 2001), Agra (154  $\mu\text{g}/\text{m}^3$ ; Kulshreshtha et al., 2009), Chennai (157  $\mu\text{g}/\text{m}^3$ ; Oanh et al., 2006), Kanpur (80-281  $\mu\text{g}/\text{m}^3$ ; Sharma and Maloo, 2005), Mumbai (1032-1176  $\mu\text{g}/\text{m}^3$ ; SPM; Kumar et al., 2001).

### **2.1.3 Health effects of PM10**

Detrimental effects of PM10 have been reported worldwide. Inhalation of PM causes risk of mortality. Long-term exposures to PM have been linked with decline in life span, due to cardiopulmonary mortality and lung cancer, among other diseases.

Children with asthma are also more susceptible to ambient PM10 (Pope & Dockery, 1992). Indian cities today are among the most polluted in the world and it is estimated that outdoor air pollution leads to approximately 670,000 deaths annually (Lim et al., 2013).

## 2.2 POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons (PAHs) are a group of toxic pollutants formed during incomplete combustion of organic materials such as wood, fossil fuels, meat, and tobacco. They are released from automobile exhaust, wood smoke, cigarette smoke, and also found at high concentrations in certain food such as barbequed food (ATSDR, 1995). These are typically more concentrated near urban areas (Hyytiäinen and Oikari 2004).

### 2.2.1 Sources

The United Nations estimated that over 600 million people in urban areas worldwide were exposed to dangerous levels of traffic-generated air pollutants (Cacciola et al., 2002). Urban atmosphere include automobiles, re-suspended soils, refineries and power plants as PAHs emission sources. (Omar et al. 2002; Yang et al. 2002; Dyke et al. 2003). Vehicular emissions are important mobile source of PAHs, Other possible sources are tire wear debris, asphalt particles (Binet et al. 2002) and stationary combustion sources or crematoria (Santasiere et al. 2005). Additional contributions to ambient air levels arise from tobacco smoking (Sakai et al. 2002), while the use of heating sources also can increase PAH concentrations in indoor air (WHO 1987). While in the rural areas of the country India biomass burning is the major of PAHs emission source for indoor air pollution. (Bhargava et al. 2004).

Apart from anthropogenic sources, Natural sources of pyrogenic PAH such as volcanic activity and forest fires do not significantly contribute - for the present - to overall PAH emission (Wild et al., 1995, Sims et al., 1983).

## **2.2.2 Sample pre-treatment before PAHs Analysis**

### **2.2.2.1 Extraction of PAHs**

The extraction is the first main step in the determination of polycyclic aromatic hydrocarbons (PAHs) collected on filter paper with particulate matter. And it is generally achieved by any of the variety of methods such as soxhlet extraction, ultrasonic extraction, superficial fluid extraction etc.

#### **Soxhlet extraction**

It is the process of transferring the partially soluble components of a solid to the liquid phase using a Soxhlet extractor. The solid is placed in a filter paper thimble which is then placed into the main chamber of the Soxhlet extractor. The solvent (heated to reflux) travels into the main chamber and the partially soluble components are slowly transferred to the solvent. The choice of the solvent or solvent mixture is a crucial factor. Typical time for extraction is 20 hours at a rate of 4 cycles per hour. (Agrawal, 2008). It is considered a comparably slow technique. Soxhlate extraction is the widely reported in the literature, for dichloromethane (DCM) (Harrison et al., 1996), DCM/acetone (1:1) (Liu et al., 2007), DCM/acetone (1:3) (Cecinato et al., 2003), acetone/hexane (1:1) (Wang et al., 2008), DCM/hexane (1:1) (Tsai et al., 2002), hexane (Tsapakis and Stephanou, 2005), benzene (Pandit et al., 2011) etc.

#### **Ultrasonic extraction**

In ultrasonic extraction or sonication, passive acoustic vibrations with frequencies > 20 kHz are applied to the sample, resulting in agitation. Sound waves propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles or voids in the

liquid, which then collapse violently (cavitation) during compression, creating very high local temperatures. Chemical compounds and particles are removed mechanically from the matrix surface and adsorption sites by the shock waves generated when the cavitation bubbles collapse. This is considered as a fast extraction technique and is widely used for the PAH extraction from collected filter samples. Earlier, ultrasonic extraction of PAHs from filter samples with acetonitrile was used by Manoli and Samara, 1995; Papageorgopoulou et al., 1999; Manoli et al., 2002), DCM (Lakhani, A. 2012, Hu et al., 2007), toluene (Khillare et al., 2008), hexane/acetone (1:1) (Akyüz and Çabuk, 2008), methanol (Saarnio et al., 2008), acetone (Tian et al., 2009), acetonitrile (Trezi and Samara, 2005) etc.

#### **Accelerated solvent extraction (ASE)**

It is also referred to as pressurized fluid extraction (PFE) technique. Briefly, using ASE a solid sample is enclosed in a sample cell that is filled with an extraction solvent; after the cell is sealed, the sample is permeated by the extracting solvent under elevated temperature and pressure for short periods (5 to 10 min). (Agrawal, 2008). Typically, the samples are extracted under static conditions, where the fluid is held in the cell for controlled time periods to allow sufficient contact between the solvent and the solid for efficient extraction. ASE/PSE has been used by various authors with solvents such as DCM/acetone (1:1) (Tao et al., 2004), DCM (Jia et al., 2011), toluene (Burkart et al., 2011), hexane/acetone (2:1) (Wilcke et al., 2002), acetone/toluene (Chen et al., 2005) etc. in various environmental matrices.

#### **2.2.2.2 Clean-up**

Purification of extracted samples is very important before analysis, as it removes other classes of interfering substances from samples. Most commonly used clean up method is adsorption column chromatography. (Agrawal, 2008). Solvent/ Sorbent commonly used for

clean-up and separation process include silica gel (Bhargawa et al., 2004; Tsapakis and Stephanou, 2005), Silicagel/ Na<sub>2</sub>SO<sub>4</sub> (Akyüz and Çabuk, 2004), alumina (Cecinato et al., 2000, 2003), Silica-alumina (Lohmann et al., 2001). Solid phase extraction (SPE) is another technique which is recently being used for clean-up in addition to the conventional methods. SPE has been performed by using Florosil cartridges (Mielke et al., 2004), Sephadex LH-20 (Khillare et al., 2008), and silica gel-aluminum oxide columns (Wilcke et al., 2002) etc.

### **2.2.3 Analysis of PAHs**

#### **2.2.3.1 HPLC**

High performance liquid chromatography is one of the most powerful technique in analytical chemistry. It has the ability to separate, identify, and quantify the compounds that are present in any sample that can be dissolved in a liquid.

Reverse-phase high performance liquid chromatography (RP-HPLC) is a tool used for the separation of individual PAHs from complex mixtures. Silica particles chemically bonded to linear C<sub>18</sub> hydrocarbon chains are considered as the packing material most suitable for PAH separation. For the separation of the compounds present in the samples, gradient mode is useful as it separates the compounds on the basis of their chromatographic polarity with variable eluent composition. It shows good selectivity in separating individual PAHs and their isomers, sensitivity when coupled with fluorescence or UV detectors. Typically, octadecylsilane (C<sub>18</sub>) columns are used for PAHs adsorption; however other stationary phase like dinitro-aryl silica column is also used. Various detection techniques generally used for quantification of PAHs using HPLC include the fluorescence (FL) detection (Ravindra et al., 2006; Akyüz and Çabuk, 2008, 2009), ultraviolet (UV) detection (Pandit et al., 2001, Ray et al., 2008), UV coupled with FL (UV-FL) detection (Harrison et al., 1996), diode array (DA) detection (Fetzer et al., 1986), DA coupled with FL (DA-FL) detection (Burkart et al., 2011).

Sometimes liquid chromatography may include high performance liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (HPLC-APCI-MS). (Titato and Lanças, 2006), particle beam LC-MS (Bonfanti et al., 1996), capillary liquid chromatography coupled with selective fluorescence quenching (Howerton et al., 2002) etc.

#### **2.2.3.2 Gas chromatography**

The Gas Chromatography is an excellent separation technique ( $\geq 3000$  plates per meter) is obtained by fused silica capillary columns. It is used to analyse very complex mixtures containing over one hundred PAHs. The most widely used stationary phases are the methylpolysiloxanes: especially SE-54 (5% Phenyl, 1 % vinyl- substituted) and SE-52 (5% phenyl-), but also SE- 30 and OV-IOI (unsubstituted), OV-17 (50% phenyl-), Dexsil 300 (carborane-), as well as their equivalent phases (Agrawal, 2008). Splitless or on-column injections are necessary to gain sensitivity in trace analysis, the latter being preferred as it allows better reproducibility. Flame ionisation detector (FID) is provides excellent response linearity, sensitivity and reliability, therefore it is widely referred by various authors (Karar and Gupta, 2006, Khillare et al., 2008, Wang et al., 2008). GC-MS coupled with mass spectroscopy (GC-MS) is more accurate than conventional universal detection methods such as GC-FID for quantification of PAHs (Poster et al., 2006). GC-MS, especially electron impact (EI) MS operated in the selective ion monitoring (SIM) mode, is widely used for the detection and quantification of PAHs in airborne samples, for eg., Lohmann et al., (2001), Tsai et al., (2002), Liu et al., (2007), Jia et al., (2011) etc.

#### **2.2.4 Ambient PAHs level in India**

Karar and Gupta (2006) observed five PAHs associated with PM<sub>10</sub> at a residential and industrial site in Kolkata during 2003-2004. Twenty three PAHs species were quantified in



both particle and gaseous phase in outdoor air at an urban and roadside site in Agra by Masih et al., (2010). PAHs associated with atmospheric TSP were observed by Rajut and Lakhani (2009) in an industrial location in Agra. Gas + particle phase PAHs concentrations (4.1-30.4 ng/m<sup>3</sup>) were observed by Pandit et al., (2006) at five different locations at the creek adjoining the Mumbai Harbur. Sharma et al., (2003) reported PAHs concentration levels at a residential site in Delhi in winter season from December 2001 to March 2002.

### **2.2.5 Source apportionment methodology**

Source apportionment of PAHs is a step toward their risk assessment. Various methods are mentioned in the literature for the sources apportionment of PAHs present in the environment.

#### **2.2.5.1 Diagnostic ratios**

It is the primary method for source identification. it is the method for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions. (Ravindra et al. 2008). Parent PAH ratios widely used as tracers of PAH emission sources include LMW/HMW (Mastral and Callén, 2010), Anth/Anth+Phen (Budzinski et al. (1997), B[a]A/B[a]P+Chry (Yunker et al. 2002), Flan/Flan+Pyr (Yunker et al, 2002), (Simicik et al. 1999), IP/(IP+B[ghi]P) (Yassaa et al. 2001), B[a]P/B[ghi]P (Simicik et al. 1999), Flu/(Flu+Pyr) (Rogge et al.1993a,b); Fang et al. (2004); Ravindra et al. (2006a,b) and Pyr/B[a]P (Ravindra et al.(2008).

#### **2.2.5.2 PCA**

It is the reliable model and often used to identify the major source of air pollutant emissions. (Guo et al. 2003); (Li et al. 2006). It is the most widely used multivariate statistical technique

in atmospheric sciences. The primary function of this analysis is the reduction of the number of variables while retaining the original information as such. In this model the variables with similar characteristics are grouped in to factors. These factors can be interpreted as emission source. The principal components with maximum percentage of total variance of data set are used as the factors. In most of the applications, mathematical and statistical software are used for source grouping by using PCA with varimax rotation and retention of principal components having eigenvalue >1 of complete data set of PAH concentrations. (Ravindra et al. 2008). High factor loading of B[a]P, B[b]F, B[ghi]P and IP has been suggested for gasoline emission (Guo et al., 2003). Whereas gasoline powered vehicle has a high factor loading for Fluoranthene, pyrene, and especially B[ghi]P + coronene and fluoranthene, pyrene with high factor loading of B[b]F and B[k]F indicates diesel-powered vehicle. (Duval and Friendlander, 1981; Khalili et al., 1995). High factor loading for IP and all forms of benzo derivatives of fluorine, fluoranthene, anthracene, pyrene and perylene indicates towards vehicular emission source (gas+diesel). (Randolph et al., 2003). Elevated levels of B[k]F relative to other PAHs have been suggested to indicates diesel vehicles. (Venkataraman et al., 1994). The high factor loading of IP indicates towards emission from diesel and gasoline both. (may et al., 1984; Randolph et al., 2003). According to sum authors high loading of fluoranthene, pyrene, phenanthrene and anthracene are the markers of coal combustion. (Harrison et al., 1996; Simcik et al et al., 1999 and Masklet et al., 1986).

#### **2.2.6 Health risk assessment**

US EPA reported 16 priority PAHs, in which BaP is the reference compound for which there are sufficient toxicological data available for derivation of a carcinogenic factor. Therefore, the carcinogenic risk of a PAHs mixture is expressed by its BaP equivalent concentration (BaP<sub>eq</sub>). Based on the carcinogenic potency of each other individual PAH relative to that of

BaP (Toxic Equivalent Factors, TEFs), the carcinogenic potency of each PAH in the mixture is expressed by its BaP<sub>eq</sub>. There are different TEFs developed by different agencies and scientists, the TEFs, developed by Nisbet and LaGoy (1992), were proved to be a better set of TEFs values (Petry et al., 1996). These are most commonly reported TEFs to calculate carcinogenic potency of PAHs mixtures (Tsai et al., 2001).

To get a quantitative idea about the health risks associated with airborne PAHs, various calculation were done by many authors with different method to calculated ICR for exposed inhabitants. One of the most popular method used by many scientist is to calculate ICR by calculating BaP<sub>eq</sub> and ambient concentration of different species of PAHs. Sarkar and Khillare (2011), calculated the incremental lifetime cancer risk values for three different location (traffic, industrial and urban residential area) in Delhi, India. Xia et al. in 2013 calculated incremental lifetime cancer risk at three different locations(background, rural and urban areas) Taiyuan, China. While Cheng et al. (2007) introduced BaP-equivalent carcinogenic potency index (BaPE) to calculate the lifetime cancer risk in th industrial area of Shanghai, China. In the other important study Chen and Liao, 2006 calculated Occupancy probability, daily exposure level and incremental lifetime cancer risk in the local population of China. They worked on the secondary data of different studies (Fang et al., 2004; Tsai et al., 2004). They calculate ILCR for different age groups (adult, children and adult) with sensitivity analysis.

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## Materials and Methods

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This chapter provides the information about the study area (physiography, demography, land-use pattern and climate) and the sampling sites. It also provides the information about sampling and analytical protocols.

### 3.1 Study area: Delhi

#### 3.1.1 Physiography, demography, land-use pattern

Delhi, the capital of India is geographically located in the northern part of India (28°-24'-17" and 28°-53'-00" North and longitudes of 76°-50'-24" and 77°-20'-37" East) and present in between the Thar Desert of Rajasthan to the west, the central hot plains to the south and the cooler hilly region to the north and east. Soil deposits are mixed type. The Aravalli hill extends from south part to west bank of the Yamuna River, a stretch of up to 35 km is composed of Quartz rock. The Aravali hill ranges are also called as the lungs of the city as they covered with forest and help to maintain its environment. This Ridge also acts as a barrier between the Rajasthan Desert and the plains to slow down the dust and wind movement from the desert. The terrain of Delhi is flat in general except for a low NNE-SSW trending ridge (extensions of the Aravalli hills).

Uttar Pradesh and Haryana are the states adjacent to the Delhi. Delhi has an area of 1,483 sq km. of which 783 sq. km is rural, and 700 sq. km. urban. Its maximum length is 51.90 km and greatest width is 48.48 km. Thus the shape of the city is almost circular with radial patterns. The area can be broadly classified in to two main physiographic domains: i) northern and central adulatory terrain (197 to 260 m amsl) and ii) southern upland rocky region (20 to 340 m amsl) (Kaul and Pandit, 2004).

As per Census 2011, India's population is 1.2 billion, of which the urban population is 377 million. By the presence of large number of industries and migration from neighbouring states, a large number of vehicles ply on the roads of Delhi. The level of urbanization rose from 27.8% to 31.2% from year 2001 to 2011. Out of 42.6% urban population in India, 15.4% of the total urban population live only in four major cities (Delhi, Kolkata, Mumbai, and Chennai) of India.

The current population of the Delhi is 16.7 million (Census, 2011) and has increased by 21% between 2001 and 2011. The population density has increased from 9340 person per sq km in 2001 to 11,297 persons per sq km in 2011. There are 9 districts in Delhi, namely: North West (area: 442.84 sq km, population: 3,651,261), North (area: 58.92 sq km, population: 883,418), North East (area: 56.32 sq km, population: 2,240,749), East (area: 48.9 sq km, population 1,707,725), New Delhi (area: 34.95 sq km, population: 133,713), Central (area: 23.36 sq km, population: 578,671), West (area: 130.56 sq km, population: 2,531,583), South west (area: 420.8 sq km, 2,292,363) and South (area: 249.44 sq km, population: 2,733,752). Out of a total area of 1483 sq km, an area of 924.68 km<sup>2</sup> is designated urban while the remaining 558.32 sq km is designated rural. As per 2001 estimates, 93.18% of Delhi's population was urban while the remaining 6.82% was rural. Population urbanization in Delhi has mentioned an annual exponential growth rate of 4.2% between 1991 and 2001 (Planning Department, 2009).

### **3.1.2 Climate:**

Delhi has a semi-arid climate with long and extremely hot summers (from early April to mid-October with average temperature of 45<sup>0</sup>C), average rainfall (714 mm) and very cold winter (November and January with average temperature of 4<sup>0</sup>C). The average temperature ranges

from 40 to 45°C in the summer months, while during winters it ranges from 4 to 5°C in Delhi. Delhi area is under the influence of monsoon winds (ranging from North East to North West in winter and South East to South West in the summer) with average annual rainfall in Delhi is 714 mm, 75% of which falls in July, August and September (CPCB, 2010).

The forest cover in Delhi has increased from 0.76 percent to 5.96 percent since 1980 to 2001. Sand and stone are the basic mineral resources in Delhi used for construction activities. However, the stone quarries in the Ridge area have been shut down since 1984 on account of environmental considerations.

### 3.2 Sampling Sites

Map of the sampling sites is shown in the Table 3.1, while nature of the sampling sites has been shown in Table 3.1. Meteorological data of sampling period was procured from [http://www.wunderground.com/history/airport/VIDP/2014/1/1/MonthlyHistory.html?req\\_city=NA&req\\_state=NA&req\\_statename=NA](http://www.wunderground.com/history/airport/VIDP/2014/1/1/MonthlyHistory.html?req_city=NA&req_state=NA&req_statename=NA), and is presented in Table 1 (Appendix 2).

The first sampling site was located in Jawaharlal Nehru University campus, New Delhi. The sampler was located on the roof of a school building at about 15 m from the ground. JNU is an institutional area in south Delhi situated on a ridge of the Aravalli Hills in the midst of a 4 km<sup>2</sup> forested area. It is widely regarded as a clean and sensitive area of Delhi (Srivastava and Jain, 2008). Hence it is considered as the urban receptor site for Delhi.

While second site was Gomti guest house, Mandi House, New Delhi. The Gomti Guest House area is dominated by dense traffic area and Government buildings. It is also very near (2.6 km) to the commercial area (Connaught place, Delhi). The sampler was

located on the roof of a Guest house building at about 15 m from the ground. The location of the sampling site is indicated in Fig. 3.1.

**Table 3.1 Information of sampling stations**

| S. No. | Stations                                       | Code  | Nature of sampling sites  |
|--------|--|-------|---|
| 1      | Jawaharlal Nehru University campus, New Delhi. | JNU   | Very less traffic inside the campus.<br><br>Acts as Urban receptor site of Delhi.                                 |
| 2      | Gomti guest house, Mandi House, New Delhi      | Gomti | Traffic dominated area and Government buildings.<br><br>Near to the commercial area (Connaught Place, New Delhi). |



Figure: 3.1 Map of the study area showing sampling sites



### 3.3 Sampling Protocol

PM<sub>10</sub> sample were collected simultaneously at the two sites during study period (July 2013- January 2014). The sampling frequency was once a week and sampling duration for each sample was 24 hour (10 AM to 10 AM the following day). Seasonal distribution of sample was as follows: winter- 16 and 17 for JNU and Gomti site respectively, while Monsoon- 12 and 10 for JNU and Gomti site, respectively. Some of the samples were lost due to genuine reasons like electricity problems, malfunctioning of sampler, and excess rain etc. A total of 55 samples (28 from JNU and 27 from Gomti) were collected during study period. PM<sub>10</sub> was collected on Whatman GF/A (8"x10") glass fibre filters (pre-combusted at 450<sup>0</sup>C for 12 hour) using High-Volume sampler (Respirable Dust Sampler, Model MLRDS-002, Mars Bio-analytical Pvt. Ltd.) having a constant flow rate of 1.1 m<sup>3</sup>/ min. The combination of High Volume sampler with glass fibre filter is widely used for the determination of atmospheric PAHs (Hong et al., 2007; Ravindra et al., 2006; Sharma et al., 2007, 2008; Rajput and Lakhani, 2009 etc.).

### 3.4 Chemicals and reagents

All solvents (toluene, n-Hexane and Acetonitrile) were purchased from Merck India Ltd. of HPLC grade. All glassware used were purchased from Borosil. Highly pure deionised water taken form water Millpore system at 18.2MΩ.

### 3.5 Determination of PAHs

#### 3.5.1 Extraction, concentration and clean-up

Circular portions (ø 8 cm) cut from each filter using a metallic punch and extracted in toluene (50 ml) for 15 min in the pulse mode by ultrasonic agitation (Sonicator 3000, Misonix Inc,

USA) with a frequency of 50 kHz in a water bath (10-15<sup>0</sup>C). After 30 min, the extract was decanted followed by fresh addition of 50 ml of toluene and subsequent ultrasonic agitation for another 15 min. The two extracts were combining and then filtered through Whatman No. 1 filter. The extracts were then concentrated to 0.5 to 1.0 ml in a Rotary evaporator (Büchi Rotavapor, Switzerland). PAHs in a concentrated extract were fractioned by silica gel column. Three gram of silica gel (silica gel 60, particle size 0.0630-0.2 nm, 70-230 mesh ASTM, procured from Merck KgaA, Darmstadt, Germany) was activated at 180 <sup>0</sup>C for 24 hours and then deactivated with 1% Milli-Q water. Then 40 ml of n- hexane was added to prepare the slurry, and kept overnight for degassing. After proper degassing, the slurry was packed in a column while taking precautions to avoid cracking of the column. Hexane was subsequently eluted and previously concentrated extract was transferred to the column. Further elution was done by 10 ml of Hexane and then 50 ml of 1:1 hexane: toluene mixture to obtain PAH fractions. The fraction containing PAHs was again concentrated to 0.5 ml in a rotary evaporator followed by solvent exchange with acetonitrile for further chromatographic analysis. Finally, the sample was filtered by 0.2 nylon syringe filter and transferred to a clean vial and stored at 4<sup>0</sup>C till further analysis.

### 3.5.2 Analysis

PAH analysis of sample was carried out using a high performance liquid chromatography (HPLC) system (Waters, USA). The HPLC system consisted of following:

- i. Waters 510 HPLC pump
- ii. Waters 484 tunable absorbance detector
- iii. Waters 746 data module
- iv. Injection valve (20 µl)

PAH residues were separated using a waters PAH C<sub>18</sub> column and individual PAHs were quantified using reference PAH standards. Gradient elution was executed using a mixture of acetonitrile and degassed water. PAHs detections were carried out on a UV detector at a wavelength of 254 nm.

The operating conditions for HPLC were as follows:

|                   |   |
|-------------------|---|
| Column:           | Water PAH C <sub>18</sub> (4.6x 250 mm, particle size 5 μm)   |
| Temperature :     | 25 ± 3 °C   |
| Mobile phase:     | 50% acetonitrile held for 5 min; linear gradient to 100 % acetonitrile in 5-20 min; 100 % acetonitrile held till 28 min and linear gradient to 50% acetonitrile from 28-32 min. |
| Flow rate:        | 1.5 ml min <sup>-1</sup>  |
| Detector:         | UV detector at 254 nm   |
| Injection Volume: | 20 μL   |

Filters were spiked with internal standard solution prior to extraction in order to monitor procedural performance and matrix effects. Surrogate compounds were represented for the analysis as follows: Naphthalene- d<sub>8</sub> for Naph; Acenaphthene-d<sub>10</sub> for Acy, Acen and Flu; Phenanthrene-d<sub>10</sub> for Phen, Anth, Flan and Pyr; Chrysene-d<sub>12</sub> for B[a]A and Chry; Perylene-d<sub>12</sub> for B[b]F, B[k], B[a]P, DB[ah]A, B[ghi]P and IP.

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## Results and Discussion

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The present study was framed to find the particulate phase polycyclic aromatic hydrocarbons (PAHs) concentrations in Delhi. Two sampling sites were selected to characterize the PAHs concentrations in ambient air of Delhi. The first site, i.e. Gomti guest house, Mandi House lies in the vicinity of traffic areas and the second sampling site, i.e. Jawaharlal Nehru University (JNU) campus can be considered as urban background site. Weekly 24 h PM<sub>10</sub> sampling was carried out simultaneously at two sites for a period of 7 months from July 2013 to January 2014. The collected samples were analysed for 16 US EPA priority PAHs concentrations and the results are presented in this section.

Concentration levels, spatial and seasonal variation of PM<sub>10</sub> are presented in section 4.1. PAH levels, their spatial and seasonal variations and profile are included in section 4.2. Correlation between meteorological parameter and total PAHs are summarized in the section 4.3. Source apportionment of PAHs (molecular diagnostic ratio of PAHs and principal component analysis of PAHs) are included in the section 4.4. Health risk assessment due to inhalation exposure of PAHs is summarized in the section 4.5.

#### **4.1 AMBIENT RESPIRABLE PARTICULATE MATTER AT SAMPLING SITES (RSPM / PM<sub>10</sub>)**

##### **4.1.1 Levels of concentration and spatial variations**

A total of 55 samples (28 from JNU and 27 from Gomti) of PM<sub>10</sub> aerosols were collected within the period of July 2013 to January 2014 at two different locations in Delhi, India. Table 4.1 and 4.2 (Appendix 1) presents the mean concentrations of PM<sub>10</sub> observed during the study period at JNU and Gomti respectively. Sample wise and monthly PM<sub>10</sub> concentration at JNU and Gomti are mentioned in Table 4.3 and 4.4 (Appendix 1) respectively. The concentration of PM<sub>10</sub> aerosols ranged from 88.61 to 434.35  $\mu\text{g}/\text{m}^3$ , with

an average of  $211.20 \pm 84.67 \mu\text{g}/\text{m}^3$  in JNU, while in the case of Gomti it ranged from 50.35 to  $328.03 \mu\text{g}/\text{m}^3$  with an average of  $158.39 \pm 86.80 \mu\text{g}/\text{m}^3$ . The difference between the two sites was found to be significant (ANOVA,  $F=5.218$ ,  $p=0.026$ ). The mean PM10 concentration at the two sites during study period was  $185.28 \pm 89 \mu\text{g}/\text{m}^3$ . 96% samples in JNU and 69% samples in Gomti had high PM10 concentration compare to prescribed limit for  $100 \mu\text{g}/\text{m}^3$  (24h standard as set by the National Ambient Air quality Standards of India) (NAAQS, 2009).

JNU site had high level of PM10 concentrations than Gomti site as it is the receptor site due to prevailing wind direction (form North-West to South-East) from most part of the year in Delhi and receives particulate matter from all over the city. The sampling site was only 100 m away from a construction site inside the university campus. This might be the other possible reason of high PM10 concentration at JNU site.

#### 4.1.2 Seasonal variation in PM10 concentration

For the investigation of the seasonal variation, the sampling period was divided into two seasons: Monsoon (July to September) and winter (October to January). The seasonal concentration variation of PM10 at both the sites is present in Table 4.1 and 4.2 (Appendix1), while Fig. 4.1 shows monthly concentrations variation of PM10 at both the sites.

The monitored data from the above study period at Delhi reveals a general trend of PM10 as it had high concentration during winter in comparison to monsoon at both the location in Delhi.

During monsoon and winter, the PM10 concentration was found to be in the range of 124.97 to  $237 \mu\text{g}/\text{m}^3$  and 88.61 to 434.34 with an average of  $168.63 \pm 37.15$  and  $243.13 \pm 96.72 \mu\text{g}/\text{m}^3$  for monsoon and winter season respectively at JNU while in case of Gomti it was in

the range of 51.38 to 214.03  $\mu\text{g}/\text{m}^3$  and 50.35 to 328.03  $\mu\text{g}/\text{m}^3$  with an average of  $84.88 \pm 48.93$  and  $201.63 \pm 74.38$   $\mu\text{g}/\text{m}^3$  for monsoon and winter season respectively at Gomti site (Table 4.1 and 4.2) (Appendix 1). The difference between the season was found to be highly significant (ANOVA,  $F=18.291$ ,  $p<0.001$ ). The overall mean concentration of PM10 was high ( $221.75 \pm 87.15$ ) in winter season than monsoon season ( $130.57 \pm 59.76$ ) in Delhi.

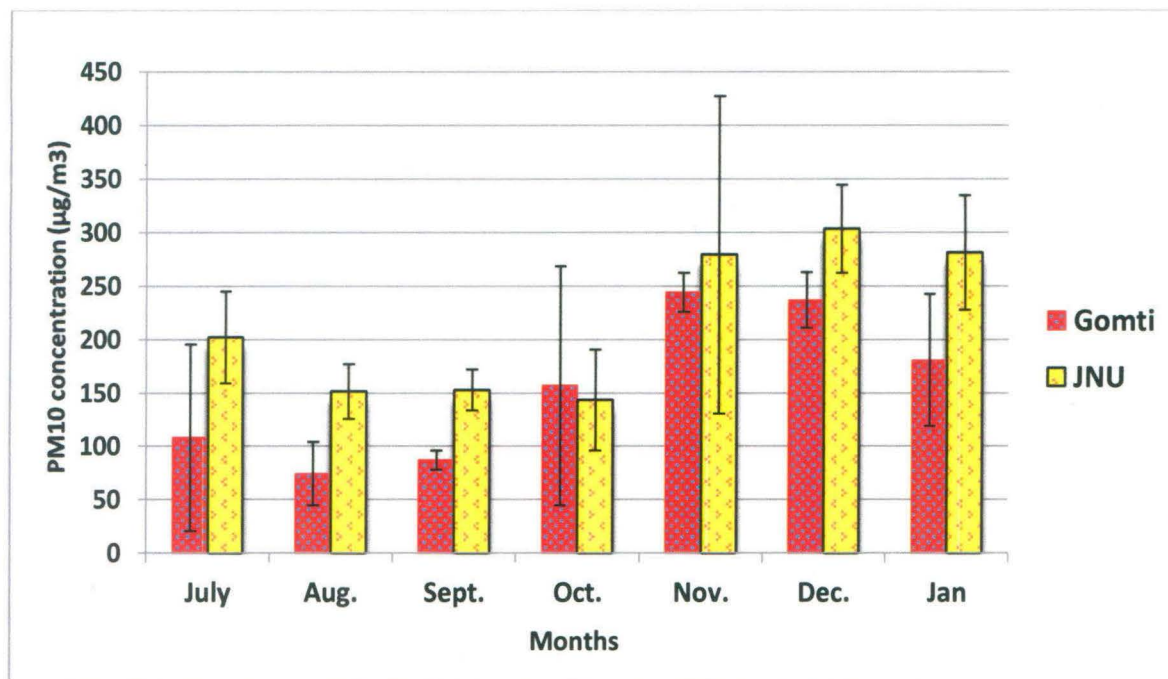
Monsoon season had low PM10 concentration at both sites due to wash out effect along with high humidity which led to the reduced resuspension of crustal dust. Precipitation and humidity had a significant negative correlation with PM10 at both the sites as shown in the table 4.6 and 4.7 (Appendix 1).

The variation in PM10 concentration is also influenced by some anthropogenic activities during the study period. The reason behind higher PM10 concentration in winter is due to the massive biomass burning especially during night time in winter days. People use wood and cow dung, in open fires for heat generation in winter, resulting in the release of significant quantities of airborne smoke particles.

The high concentration of PM10 observed during winter season can be attributed to low wind speed and low temperature, which led to lower mixing height and poor dispersion conditions coupled with increase in anthropogenic activities such as biomass burning, vehicular emission and space heating etc. Therefore, the meteorological conditions that prevailed in winter resulted in higher PM10 levels at Delhi.



Figure: 4.1 Monthly variation of PM 10 ( $\pm$  standard deviation) in  $\mu\text{g}/\text{m}^3$  at study site



During the monsoon season, high PM10 concentration was observed in the month of July at both the sampling sites in Delhi as long range pollutant transport are dominant in the months of May-July from nearby sub-tropical arid (desert) areas (Gupta and Mohan, 2013, Rajput and Lakhani, 2010). During winter months, the highest concentrations of PM10 observed in the month of November and December for Gomti and JNU respectively. High level of PM10 at both the sites can be attributed to strong temperature inversion and calm conditions in the start of winter season. Temperature and wind speed both had a significant negative correlation with PM10 as shown in the Table 4.6 and 4.7 (Appendix 1).

#### 4.2 POLYCYCLIC AROMATIC HYDROCARBON IN PM10 AT SAMPLING SITES

16 PAH compounds [Naphthalene (Naph), Acenaphthalene (Acen), Acynaphthalene (Acy), Anthracene (Anth), Phenanthrene (Phen), Fluorene (Flu), Fluoranthene (Flan), Pyrene (Pyr),

Benzo(a)anthracene (B[a]A), Chrysene (Chry), Benzo(b)fluoranthene (B[b]F), Benzo(k)fluoranthene (B[k]F), Benzo(a)pyrene (B[a]P), Benzo(ghi)pyrene (B[ghi]P), Dibenzanthracene (DBA), Indeno(123-c,d)pyrene (IP)] were determined in the samples by High Performance Liquid Chromatography (HPLC). The sum of 16 US EPA priority PAHs analysed in the study is denoted by  $\sum_{16}$  PAHs. Naph is the sole 2-ring PAH, 3 ring PAHs includes Acy, Acen, Flu, Phen and Anth, 4-ring PAHs include Flan, Pyr, B[a]A and Chry, 5-ring PAHs includes B[b]F, B[k]F, B[a]P, DBA, and 6-ring PAHs include B[ghi]P and IP. Low Molecular weight (LMW) PAHs includes 2- and 3-ring species while high molecular weight (HMW) PAHs includes 4-, 5-, and 6-ring species. The seven carcinogenic PAHs listed by US EPA include B[a]A, Chry, B[b]F, B[k]F, B[a]P, DBA and IP and are denoted by  $\sum_7$ PAHs.

#### 4.2.1 Levels and Comparisons with other studies

Sample wise concentrations of  $\sum_{16}$  PAHs are mentioned in the Table 4.3 and 4.4 (Appendix 1) for JNU and Gomti respectively. Seasonal and overall mean value of  $\sum_{16}$  PAHs concentrations along with overall maximum and minimum values at JNU and Gomti sites are presented in Table 4.1 and 4.2 respectively (Appendix 1). Seasonal distribution of  $\sum_{16}$  PAHs also can be explained on the basis of figure 4.3. Monthly distribution of  $\sum_{16}$  PAHs at both the sites is shown in figure 4.2. The mean  $\sum_{16}$  PAHs concentration at JNU and Gomti during the study period was found to be  $55.12 \pm 29.87$  and  $67.81 \pm 40.2$  ng/m<sup>3</sup>, respectively, which gives an overall mean of  $61.47 \pm 8.97$  ng/m<sup>3</sup> for Delhi. The  $\sum_{16}$  PAHs concentrations ranged from 23.03 to 136.78 at JNU and 26.07 to 172.47 at Gomti. The difference across both the sites was found to be not significant (ANOVA, F=1.772, p=0.189).

In the present study relatively lower concentration of PAHs were found in JNU than Gomti ( $55.12 \pm 29.87$  and  $67.81 \pm 40.2$  respectively). In contrast to PAHs relatively higher concentration of PM<sub>10</sub> were found in JNU than Gomti ( $211.20 \pm 84.67$  and  $158.39 \pm 86.8$ ).

It can be observed that the highest PAH concentrations are not always associated with samples with the highest PM<sub>10</sub> concentrations. Nevertheless, positive correlations ( $r=0.44$  and  $r=0.62$  at JNU and Gomti respectively) at 95% confidence level (Pearson correlation) between PM<sub>10</sub> and total PAH concentrations were observed. Similar trend were observed by Call n et al. (2010) in Spain and Wiriya et al. (2013) in Chiang Mai, Thailand and Mantis et al. (2005) in Athens, Greece. Table 4.5 (Appendix 1) shows a comparison of total analysed PAHs concentration observed in present study (mean of two sites) with those reported by various authors in India and the world. Location, site type, type of particulate matter sampled, numbers of PAHs analysed in various studies are also mentioned in the Table 4.5 (Appendix 1). Most of the listed studies were performed in urban residential areas and preferred type of particulate matter collected was PM<sub>10</sub>. The PAHs analyzed varied from 6 to 28; however, a majority of study included the 16 US EPA priority PAHs.

It is clear from Table 4.5 (Appendix 1) that atmospheric PAHs concentration in European and US cities are far lower as compare to their Asian (especially Chinese and Indian) counterparts. PAHs emission densities in Asia, most of the European cities have PAHs levels of 3 – 55 ng/m<sup>3</sup>. The present comparison shows that atmospheric particulate PAHs level in US cities are low as  $\sim 3$  ng/m<sup>3</sup>. European city S o Paulo and Zagreb showed very low PAHs level of 3.1 and 7.5 ng/ m<sup>3</sup> respectively. High level of ambient PAHs ( $\sim 94$  ng/ m<sup>3</sup>) in Turkey, a Eurasian country, could be attributed to vehicular emission and residential heating. (especially in winters) (Esen et al. 2008). Most of the Asian countries had high average PAHs concentration in the ambient air, ranges from 24 to 244 ng/ m<sup>3</sup>. In contrary to Asian countries

Japan had a low PAHs concentration  $2.37 \text{ ng/ m}^3$  (Tham et al. 2008). China had highest PAHs concentration  $244 \text{ ng/ m}^3$  in comparison of all countries (Wang et al., 2008). While in the case of Hong Kong and Korea they had a value of  $34.20 \pm 14.62$  and  $26.3 \pm 29.4$  respectively (Guo et al., 2003, Park et al., 2002).

India has second highest PAHs concentration in all Asian countries after China. According to some studies, ambient air PAHs concentration in India ranges between 39 to  $105 \text{ ng/ m}^3$ , (Sarkar and Khillare, 2013, Kulkarni and Venkatraman, 2000), which is similar to that found in the present study, having mean PAHs concentration of two different location in Delhi i.e.  $61.47 \pm 8.97 \text{ ng/ m}^3$ .

#### 4.2.2 Spatial and seasonal variation

Seasonal distribution of  $\Sigma_{16}$  PAHs at JNU and Gomti are mentioned in Table 4.1, 4.2 (Appendix 1) and Fig. 4.3. Table 4.3, 4.4 (Appendix 1) and Figure 4.2 shows monthly variation of  $\Sigma_{16}$  PAHs at the study sites. The mean concentration of  $\Sigma_{16}$  PAHs at JNU and Gomti sites were  $55.12 \pm 29.87$  and  $67.81 \pm 40.2 \text{ ng/ m}^3$  respectively. The observed high concentration of  $\Sigma_{16}$  PAHs at Gomti can be attributed to the nearby traffic dominated area. Similar results were also discussed by Call en et al. (2011) and Srogi (2007). The other possible reason of low PAHs in JNU could be the relative absence of PAHs emission source in immediate proximity. In the present study JNU acts as a receptor site for city emissions in Delhi due to prevailing wind direction (form North-West to South-East) for most part of the year.

The seasonal distribution of particle associated PAHs is controlled by combination of various factors like emission factors, dispersion conditions and chemical mechanisms. (Carricchia et al., 1999; Menichini et al., 1999). This balance depends on the relative

importance of degradation process and emission sources (Guo et al., 2003a). Table 4.6 and 4.7 includes the correlation coefficient between PAHs and meteorological parameters, it can be observed that  $\Sigma_{16}$  PAHs concentrations are negatively correlated with temperature ( $r = -0.646$ ,  $p < 0.01$  for JNU and  $r = -0.599$ ,  $p < 0.01$  for Gomti), wind speed ( $r = -0.544$ ,  $p < 0.01$  for JNU and  $r = -0.483$ ,  $p < 0.05$  for Gomti), precipitation ( $r = -0.607$ ,  $p < 0.01$  for JNU and  $r = -0.488$ ,  $p < 0.01$  for Gomti) and relative humidity ( $r = -0.094$ ,  $p < 0.05$  for JNU and  $r = -0.195$ ,  $p < 0.05$  for Gomti). According to the present study, the mean  $\Sigma_{16}$  PAHs concentrations in monsoon season were  $33.38 \pm 8.21$  and  $38.8 \pm 15.25$   $\text{ng/m}^3$  for JNU and Gomti site respectively, while in the winter season  $71.43 \pm 29.91$  and  $84.87 \pm 40.75$   $\text{ng/m}^3$  for JNU and Gomti site respectively. The difference across the seasons was found to be highly significant (ANOVA,  $F = 28.431$ ,  $p < 0.001$ ). The high concentration of particulate PAHs during winter time at both the sites can be attributed to: (a) increased emissions from heating sources; (b) shift of gas/particle partitioning toward the particulate phase induced by low atmospheric temperature; (c) Lower atmospheric mixing heights (d) reduced photochemical degradation of some PAHs by solar radiation in winter. Traffic congestion during winter due to poor visibility, fog, mist and haze might also increase the PAHs levels (Rajput and Lakhani, 2010). In contrast, low concentrations in monsoon season were attributable to absence of seasonal sources (i.e. residential heating, cold start of vehicles), higher percentage in vapour phase, wash out effect, and photochemical degradation (Li et al., 2011; Lobscheid, 2007; Dube et al., 2014; Akyuz et al., 2008). The highest  $\Sigma_{16}$  PAHs concentration in winter season was observed in the month of January ( $85.96 \pm 17.48$   $\text{ng/m}^3$ ) and November ( $128.20 \pm 30.58$   $\text{ng/m}^3$ ) in JNU and Gomti respectively. While the lowest  $\Sigma_{16}$  PAHs concentration in the monsoon season was observed in the month of July ( $27.41 \pm 3.37$   $\text{ng/m}^3$ ) and September ( $30.86 \pm 2.91$   $\text{ng/m}^3$ ) in JNU and Gomti respectively as shown in the figure 4.2.

Fig: 4.2 Monthly mean concentration ( $\pm$  standard deviation) of  $\Sigma_{16}$  PAHs at study site

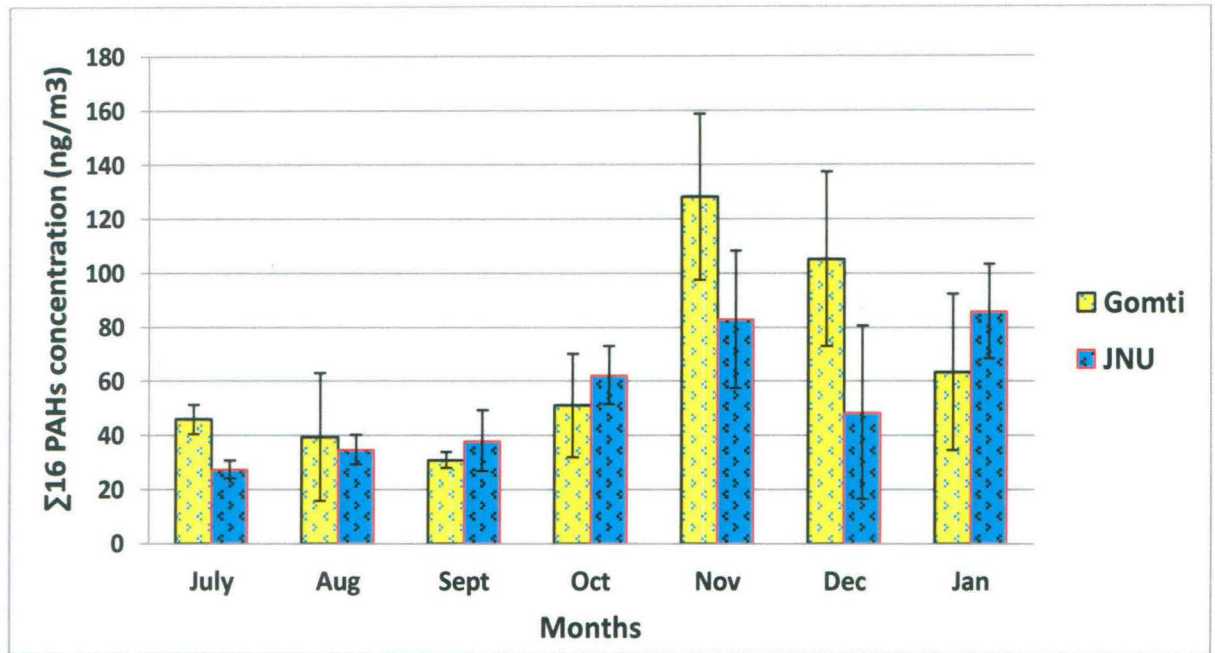
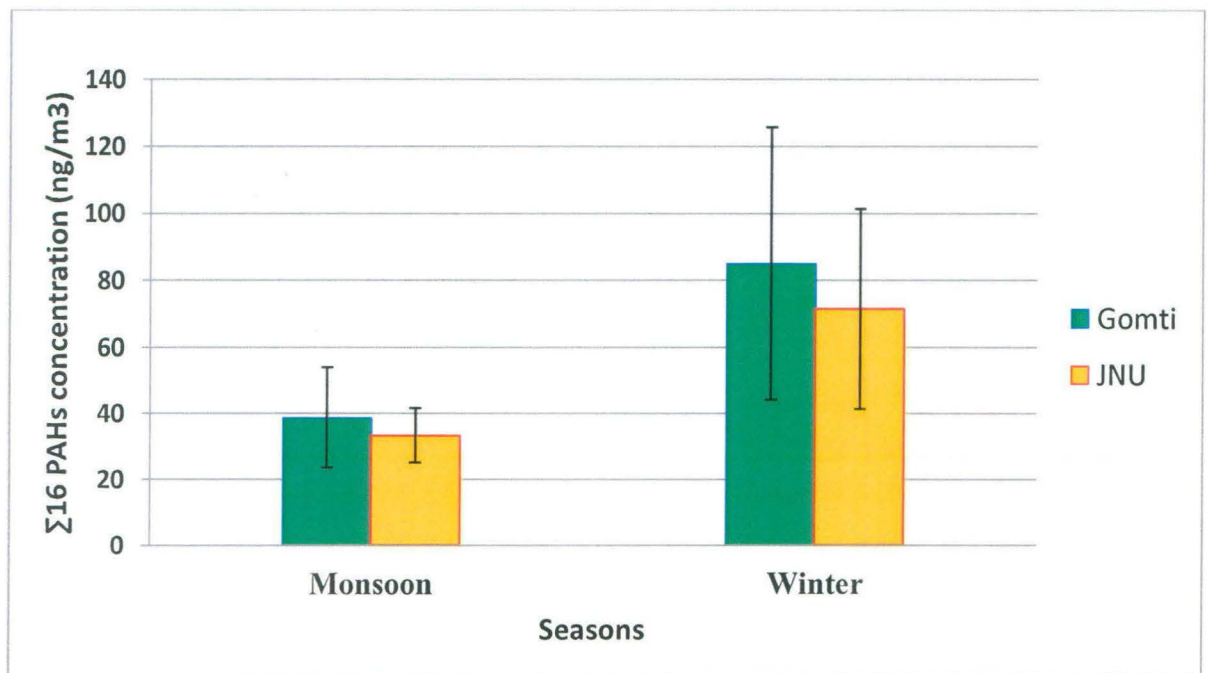


Fig: 4.3 Seasonal distribution (mean value  $\pm$  standard deviation) of  $\Sigma_{16}$  PAHs at study site



### 4.2.3 Individual and ring-wise distribution profile

Sum of sixteen US EPA priority PAHs analysed in the present study is denoted by  $\sum_{16}$  PAHs. According to their number of aromatic rings: Naph is sole 2-ring PAH, 3 ring PAHs includes Acy, Acen, Flu, Phen and Anth, 4-ring PAHs include Flan, Pyr, B[a]A and Chry, 5-ring PAHs includes B[b]F, B[K]F, B[a]P, DBA, and 6-ring PAHs include B[ghi]P and IP. Low Molecular weight (LMW) PAHs includes 2- and 3-ring species while high molecular weight (HMW) PAHs includes 4-, 5-, and 6-ring species.

The average individual PAH concentration is mentioned in the Table 4.1 and 4.2 (Appendix 1). The percentage ring wise distribution of the individual sample in Delhi is mentioned in the Fig: 4.4 and Fig: 4.5 for JNU and Gomti respectively. The average concentration of two to six- ring PAHs is mentioned in the Table 4.8 (Appendix 1) for both the sites, which was (1.54±1.41), (10.38±4.09), (11.09±8.62), (22.07±16.28) and (9.37±9.66) ng/m<sup>3</sup> at JNU, while in the case of Gomti, it was (1.60±1.72), (12.11±3.92), (12±7.24), (30.20±26.81) and (11.82± 10.64) ng/m<sup>3</sup> for two – six ring PAHs respectively. The percentage ring-wise contribution of two, three, four, five and six- ring PAHs for both the sampling sites were mentioned in Figure 4.6, and according to this figure, three and five ring PAHs are contributing more (~ 60 % of total PAHs) at both the sites. This indicates towards mixed sources.

Ring wise distribution of PAHs showed the following order- 5-ring (40.53 %) followed by 4-ring (20.36 %), 3-ring (19.06 %), 6-ring (17.21 %) and 2-ring (2.83 %) in case of JNU, while in case of Gomti it was 5-ring (44.58 %) followed by 3-ring (17.89%), 4-ring (17.72 %), 6-ring (17.45 %), and 2-ring (2.36 %). PAHs can also be classified on the basis of their molecular weight, i.e., LMW PAHs with two and three aromatic rings (Naph, Acy,

Acen, Flu, Phen, Anth, Fla and Pyr) and HMW PAHs with four, five and six aromatic rings (BaA, Chry, BbF, BkF, BaP, DBA and BghiP) (Kaur et al., 2013). The characteristic mass distribution pattern of PAH shows in figure 4.7 and 4.8 and it indicates that the mass distribution in ambient air of Delhi was dominated by HMW PAHs (4, 5, and 6 rings) with 70 to 75 % of  $\sum_{16}$  PAHs than LMW (2, and 3 rings) with ~ 25 % of  $\sum_{16}$  PAHs. As PAHs are semi-volatile organic compounds, they occur in gaseous and particulate phases in the atmosphere. The HMW PAHs are mainly derived from the vehicular emissions and are known to exist as adsorbed on particulate matter owing to their low vapour pressure. According to Table 4.1 and 4.2 (Appendix 1), the high concentration of HMW was observed in Gomti than JNU, because Gomti site is very close to PAHs emission sources. Same pattern were also observed by Lakhani in 2012 and CPCB, 2003.



Fig: 4.4 Percentage contribution of ring wise PAHs to  $\Sigma$ 16 PAHs at JNU site

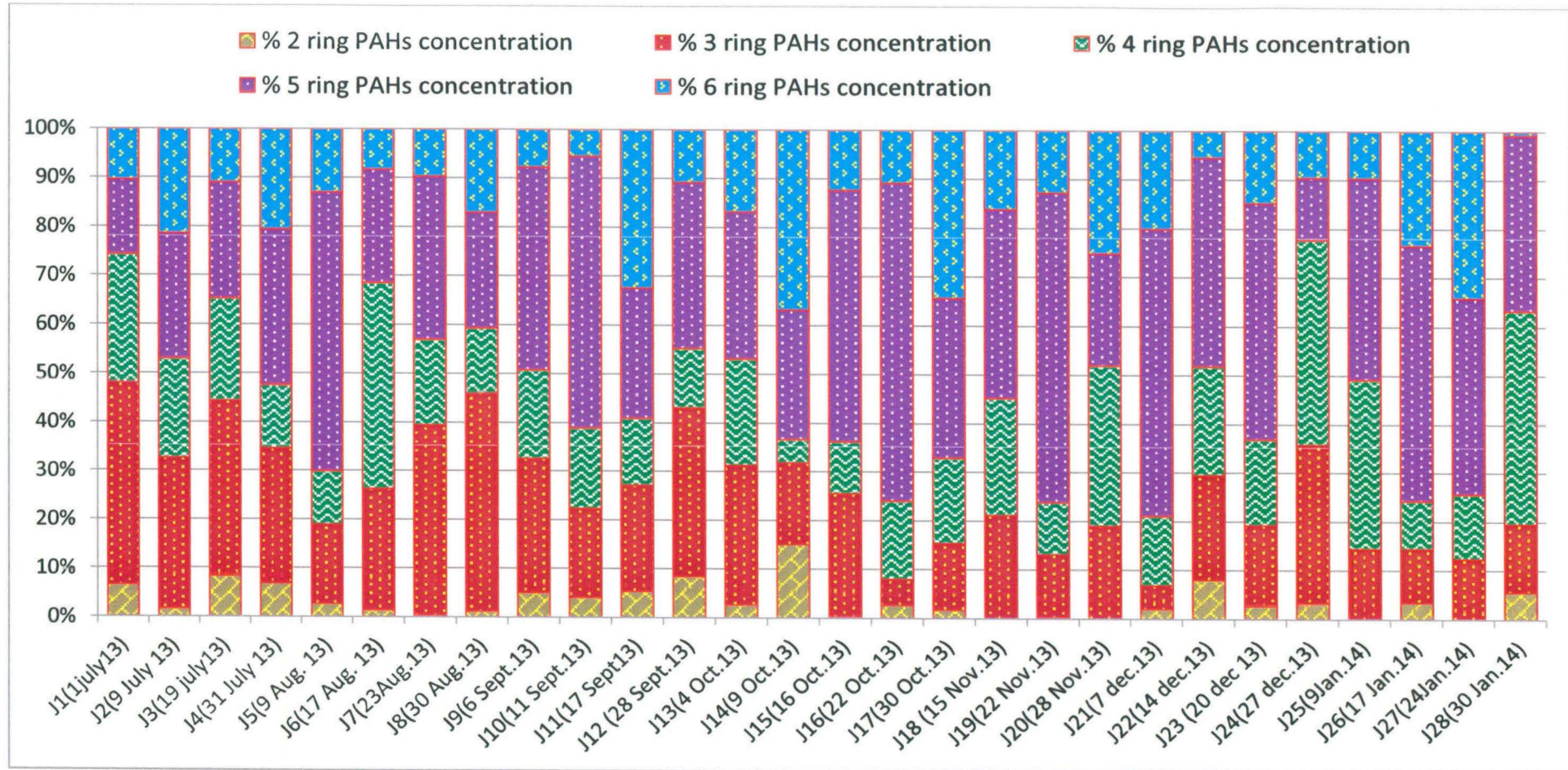


Fig: 4.5 Percentage contribution of ring wise PAHs to  $\Sigma$ 16 PAHs at Gomti

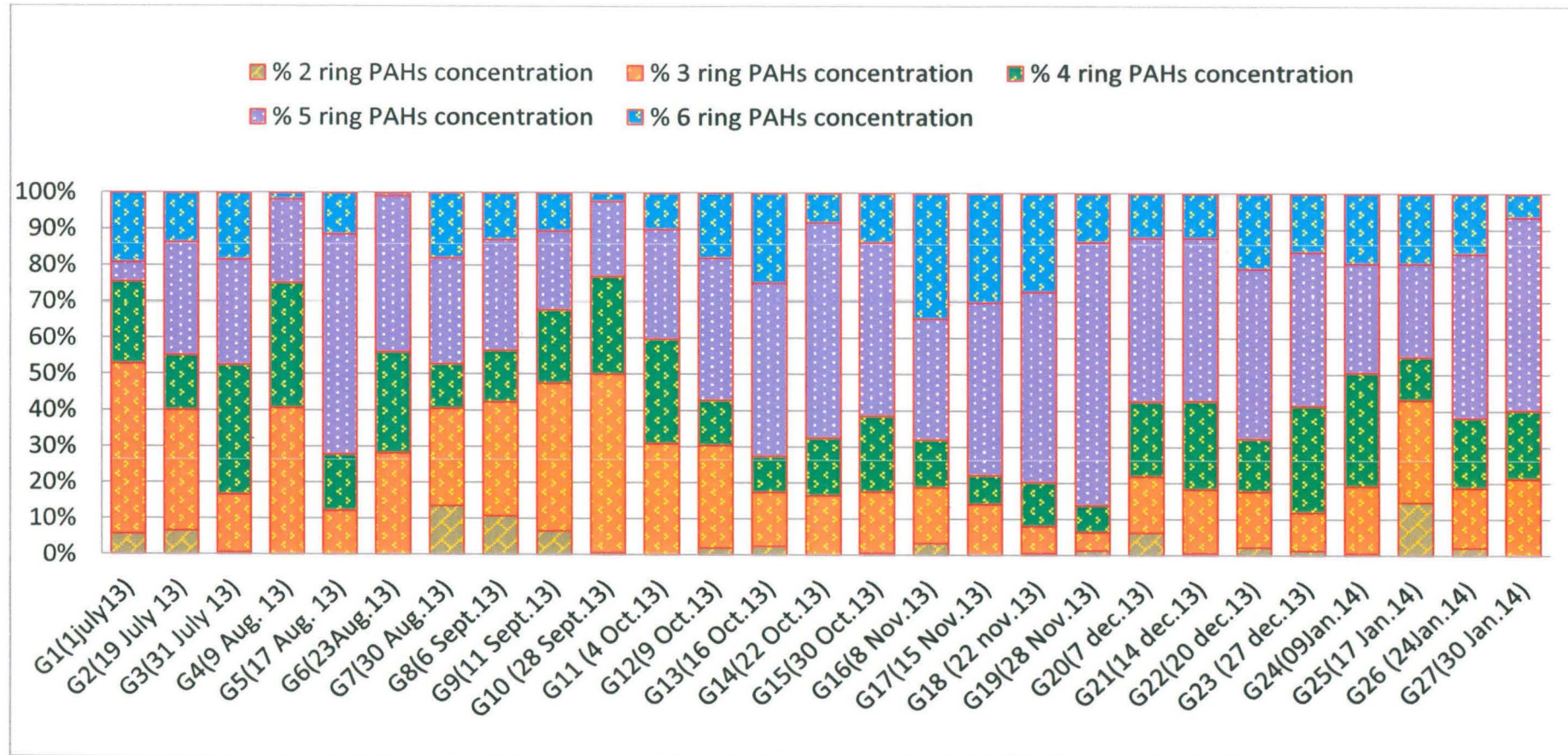
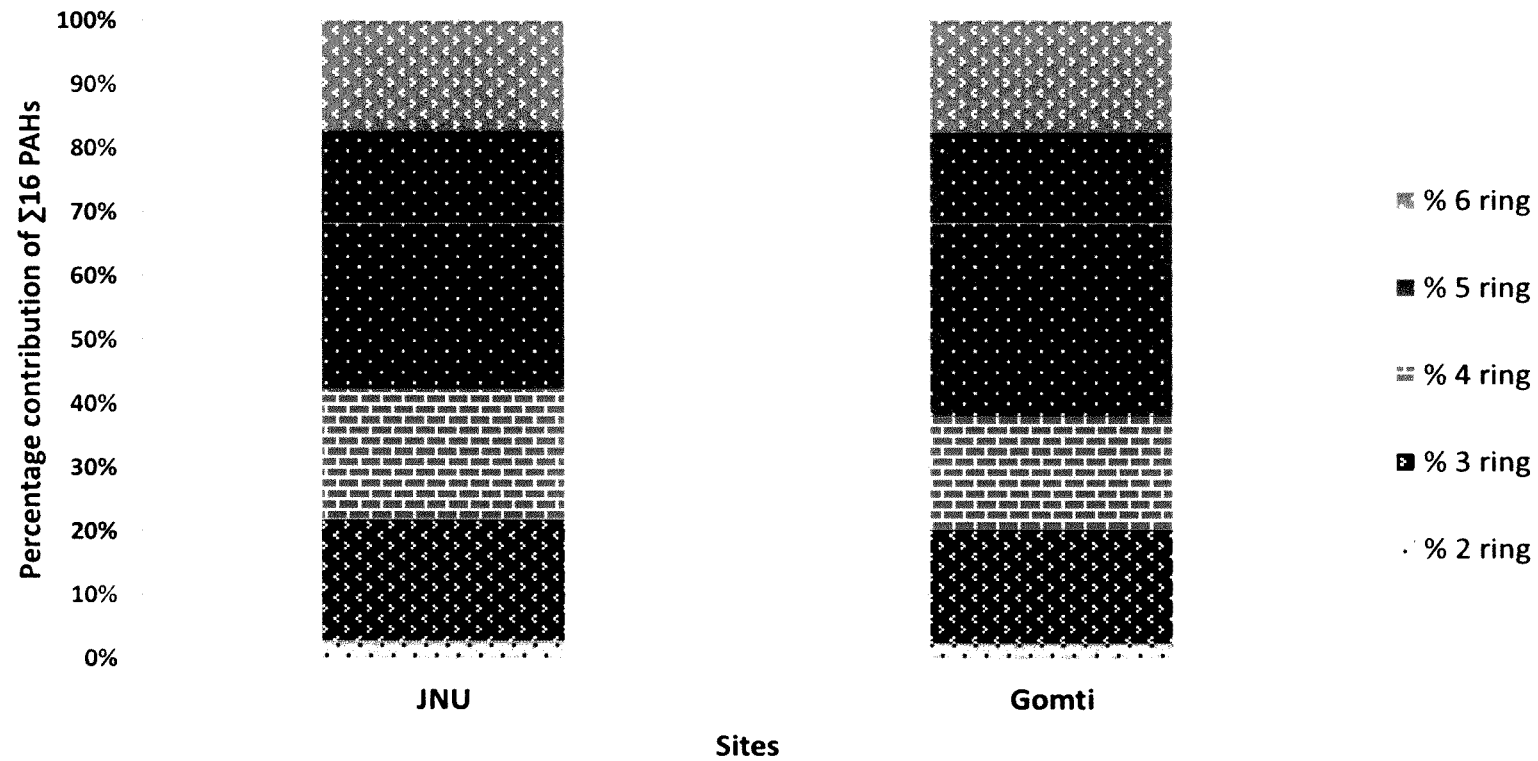


Fig: 4.6 Percentage contributions (mean) of ring wise PAHs to  $\Sigma 16$  PAHs at study site



**Fig: 4.7 Distribution of High Molecular Weight and Low Molecular Weight PAHs during sampling period at JNU**

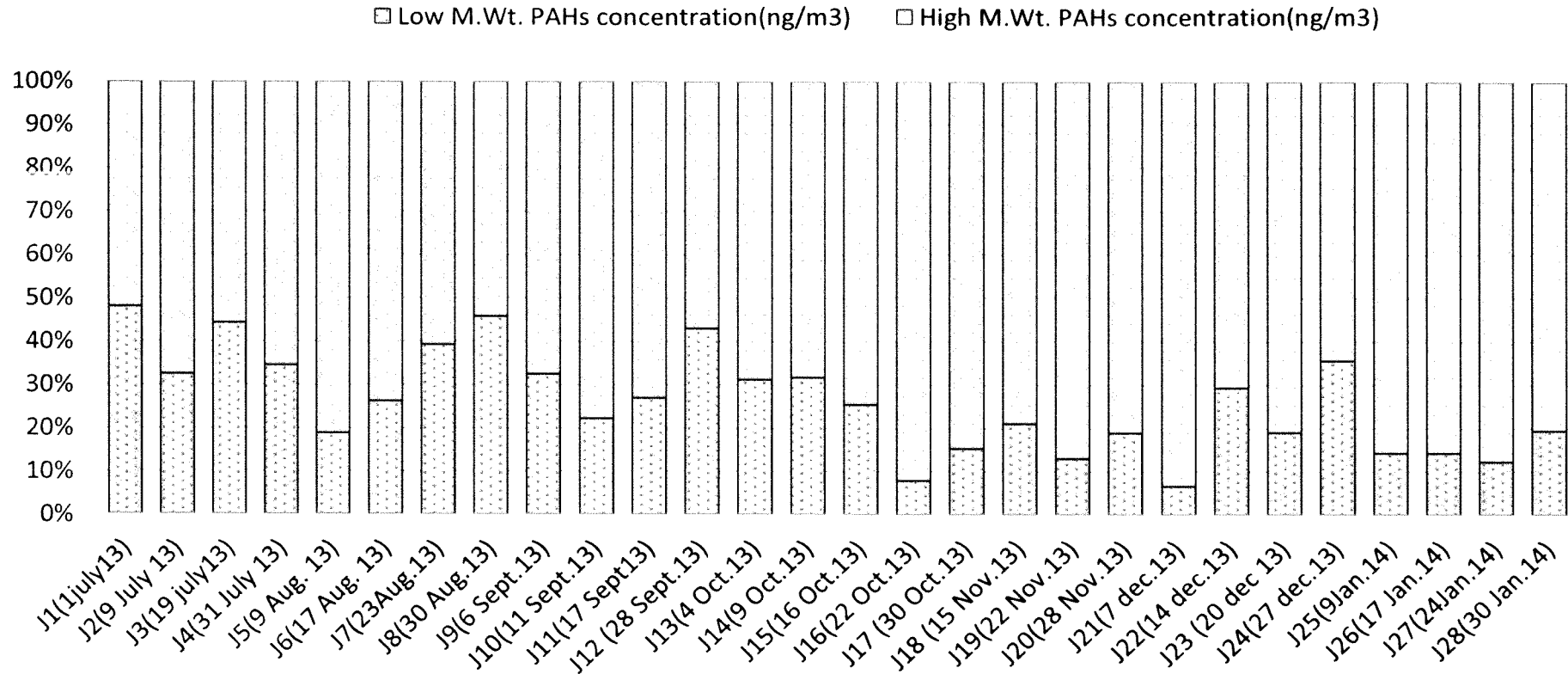
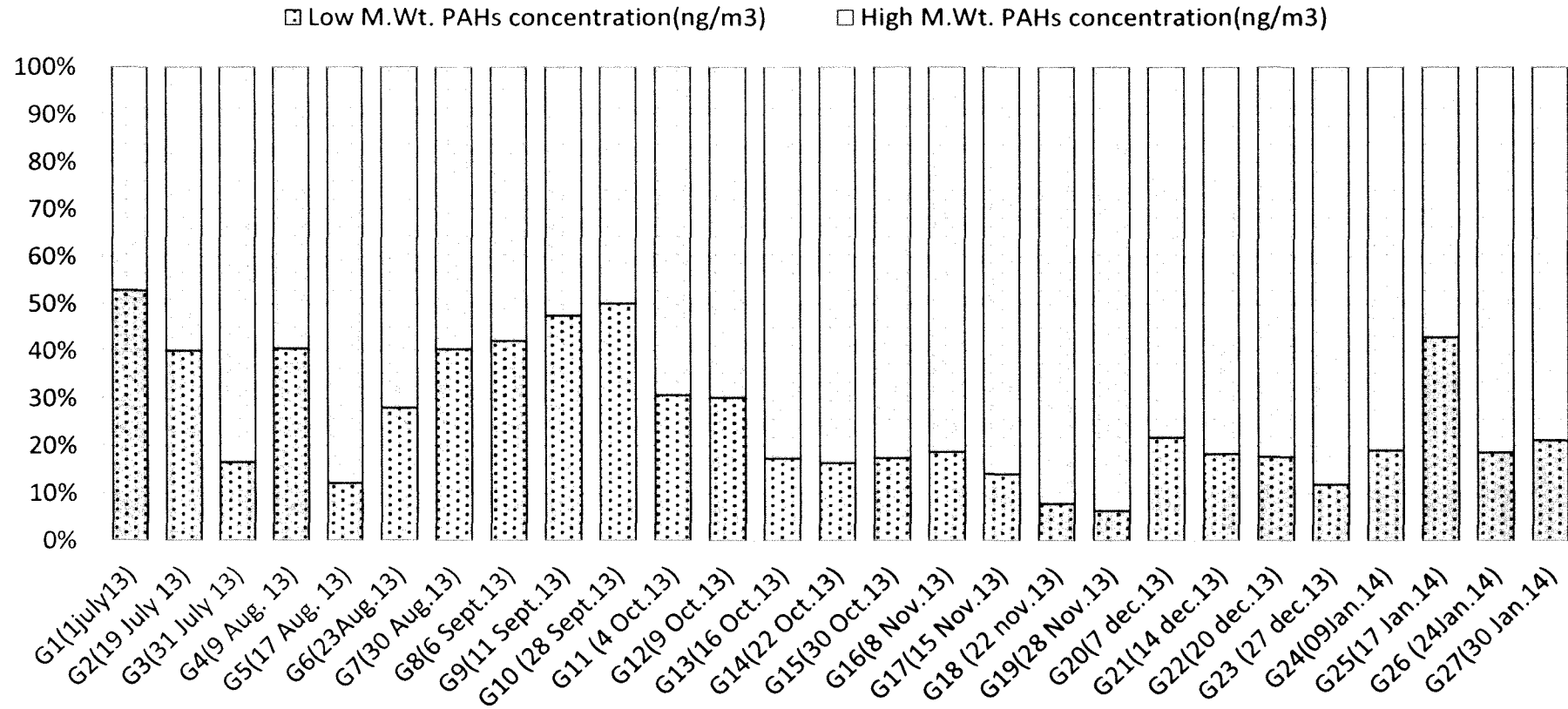


Fig: 4.8 Distribution of High Molecular Weight and Low Molecular Weight PAHs during sampling Period at Gomti site



#### 4.2.4 Carcinogenic PAHs

The United States Environmental Protection Agency has included 7 PAHs (B[a]P, Chry, B[b]F, B[k]F, B[a]P, DB[ah]A and IP) in the list of possible and probable carcinogens (US EPA, 2002). Out of these parent PAHs, B[a]P is considered to be most carcinogenic (Mastral et al., 2003; Hien et al., 2007) and therefore, is generally accepted as a surrogate for the carcinogenicity of the whole PAH fraction.

In the present study the mean  $\sum_7$  PAHs concentrations was found to be  $30.63 \pm 20.14$   $\text{ng/m}^3$  at JNU and  $40.40 \pm 32.85$   $\text{ng/m}^3$  at Gomti respectively. The observed percentage contribution was 55.57% and 59.58% for JNU and Gomti site, respectively, as shown in the Figure 4.9a and 4.9b. However, it should be noted that the carcinogenic potential of particulate matter does not necessarily follow the decay of known carcinogenic PAHs, as aromatic ketones and quinones are produced by atmospheric photooxidation and photolysis of PAHs which are more carcinogenic than parent PAHs. (Saarnio et al. 2008).

Figure 4.9a Percentage contribution of  $\Sigma 7$  carcinogenic PAHs to  $\Sigma 16$  PAHs in JNU site, Delhi

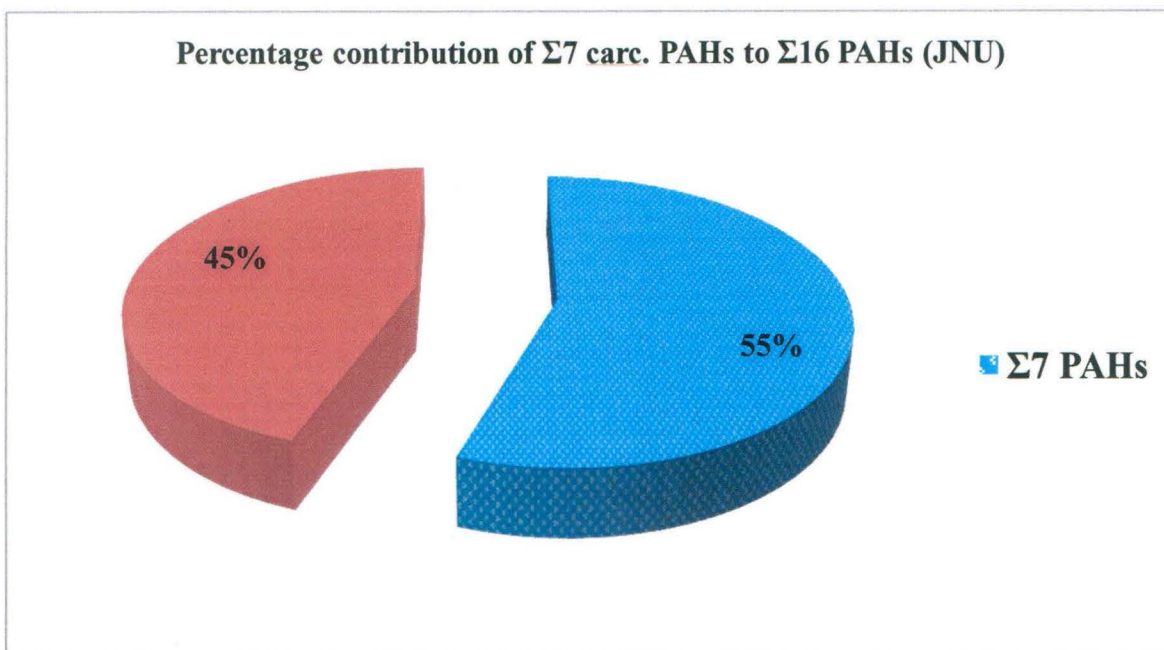
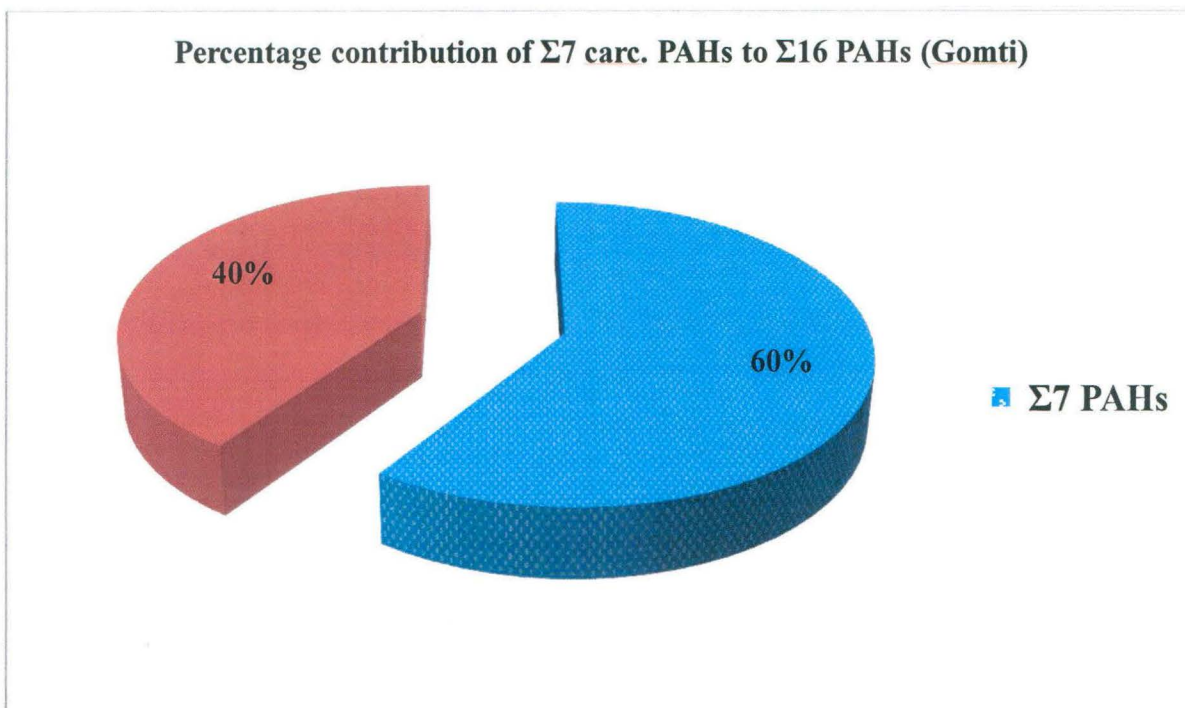


Figure 4.9b Percentage contribution of  $\Sigma 7$  carcinogenic PAHs to  $\Sigma 16$  PAHs in Gomti site, Delhi



### 4.3 CORRELATION OF PAHS WITH METEOROLOGICAL PARAMETERS

Apart from source emissions and gas particle partitioning, meteorological conditions may also result in variations of PAHs concentrations (Tan et al., 2006). The relationship of  $\sum$  16 PAHs concentrations with meteorological parameters, such as precipitation (PPT), wind speed (WS), temperature (Temp) and relative humidity (RH) are explained by Pearson correlation matrix and mentioned in the Table 4.6 and 4.7 (Appendix 1). The correlation between PAHs concentration and meteorological parameters also can be explained on the basis of scatter plot mentioned in Fig 4.10a, 4.10b, 4.10c and 4.10d. PAH concentrations varied inversely with temperature ( $R^2=0.4168$  for JNU and  $R^2=0.3588$  for Gomti) that is, higher concentrations in the cold months and lower ones in the warm months. The increase in particulate PAH concentration during the winter and the dependence of PAH concentration on atmospheric temperature have been reported in a number of studies (Taspkis et al., 2005, Sanderson et al., 2004).

Lower mixing height in winter could reduce atmospheric dispersion, which caused higher pollutant concentrations in ambient air during winter. Low atmospheric temperature can affect the distribution of PAHs between the gas and particle phases and result in a relatively larger portion of PAHs partitioning to the particle phase in winter. In contrast during the monsoon a higher ambient temperature could change the distribution of PAHs between the gaseous and particulate phases by increasing the vapour pressure of pollutants that adhered to atmospheric aerosols and favouring the volatilization of PAHs from the particulate to gaseous phase.

Precipitation is another factor having negative associations with ambient PAHs concentration ( $R^2= 0.3689$  for JNU and  $R^2= 0.2385$  for Gomti). Temperature also had a



negative association with PAHs at both the sampling sites. Association of wind speed and PAHs ( $R^2= 0.2956$  for JNU and  $R^2= 0.2328$  for Gomti) was observed to be negative at both the sites in Delhi. The negative association between PAHs and wind speed indicates the expected dilution effect of atmospheric turbulence on pollutant concentrations (Tan et al., 2006). Table 4.6 and 4.7 (Appendix 1) also explained that there was a less significant negative association with relative humidity ( $R^2= 0.0088$  for JNU and  $R^2= 0.038$ ) was observed in Delhi.

**Figure 4.10a Association of PAHs with meteorological parameters (PPT and WS) at JNU (A and B)**

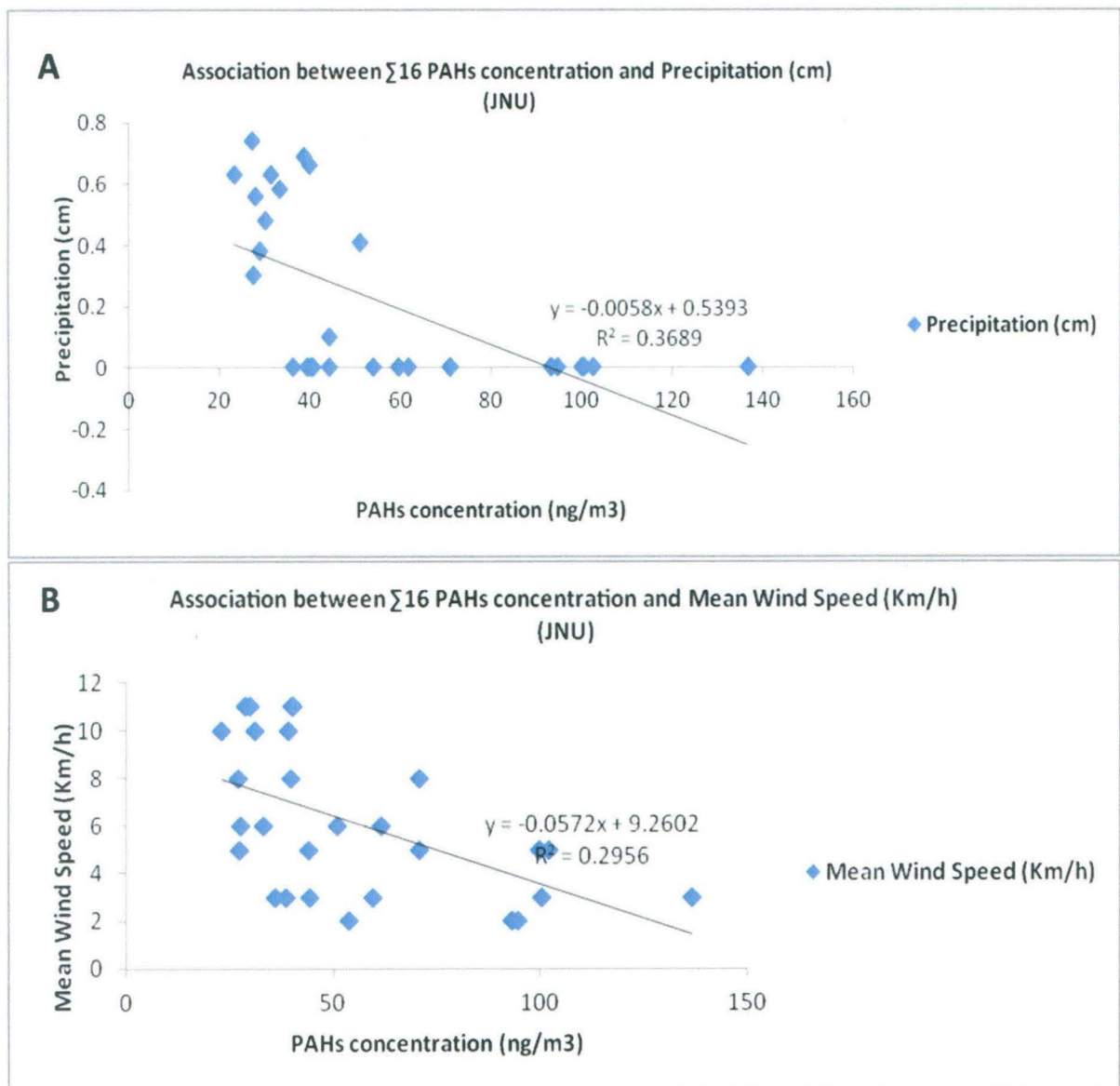


Figure 4.10b Association of PAHs with meteorological parameters (Temp and RH) at JNU (C and D).

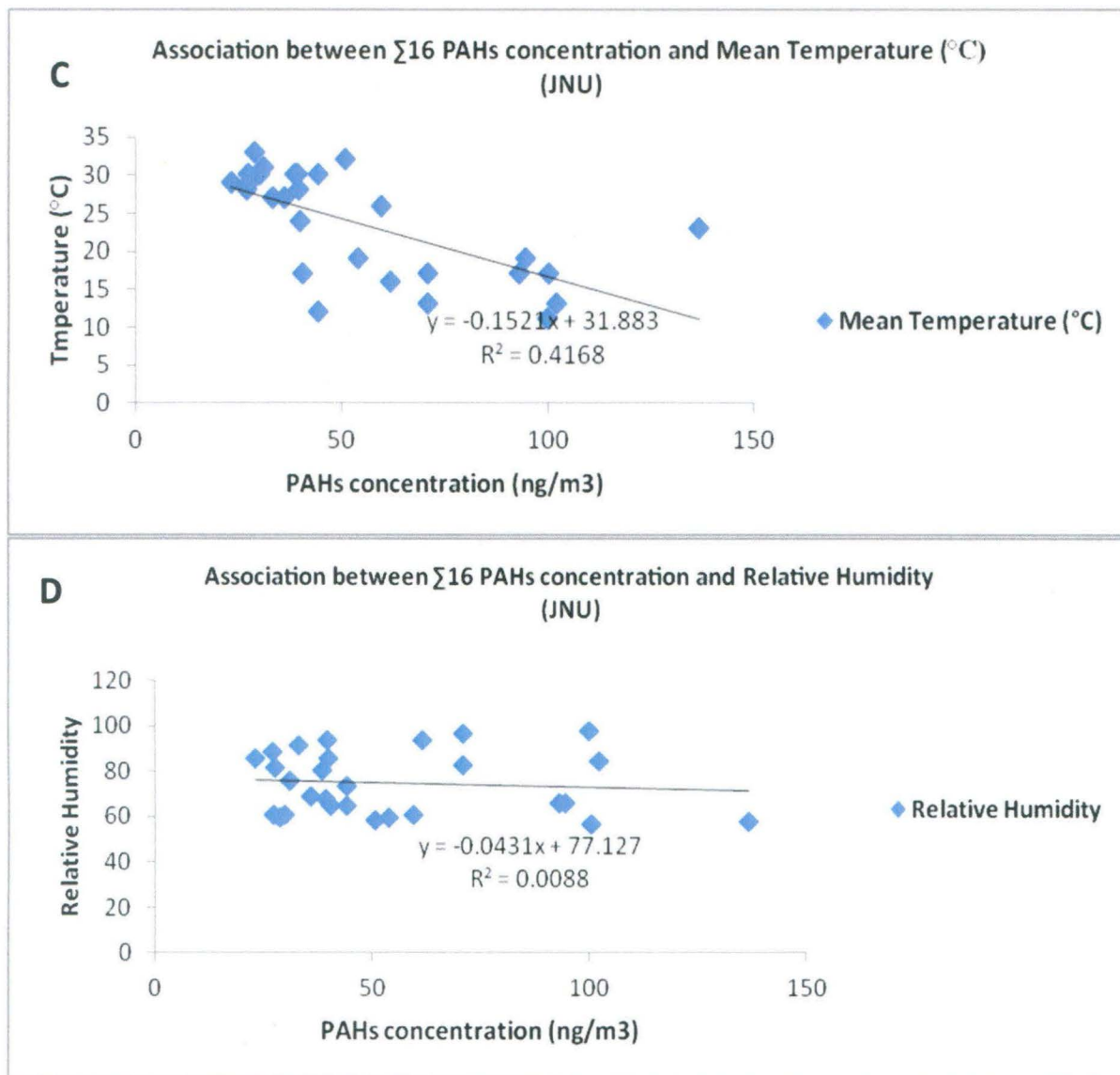


Figure 4.10c Association of PAHs with meteorological parameters (PPT and WS) at Gomti (E and F).

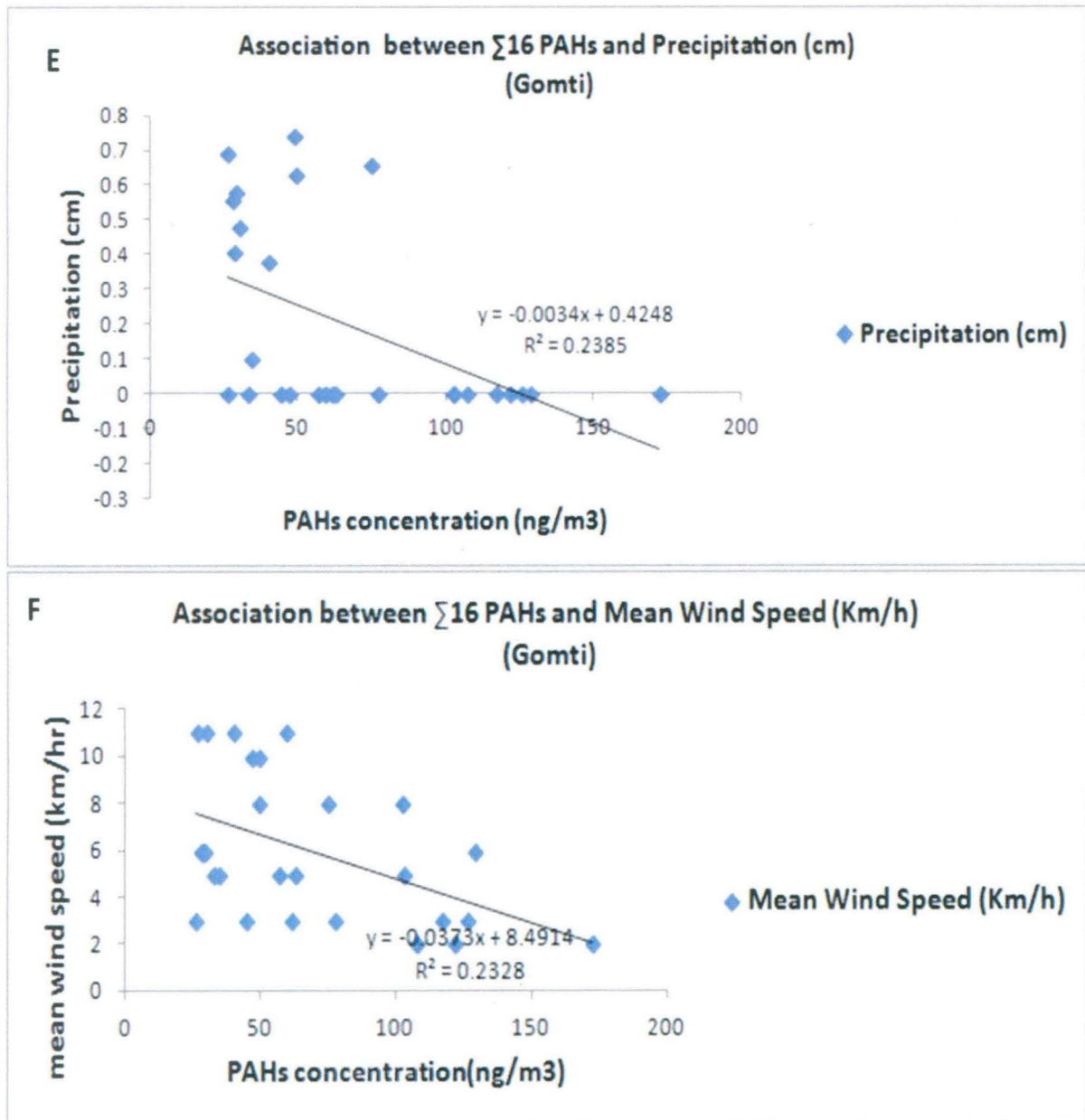
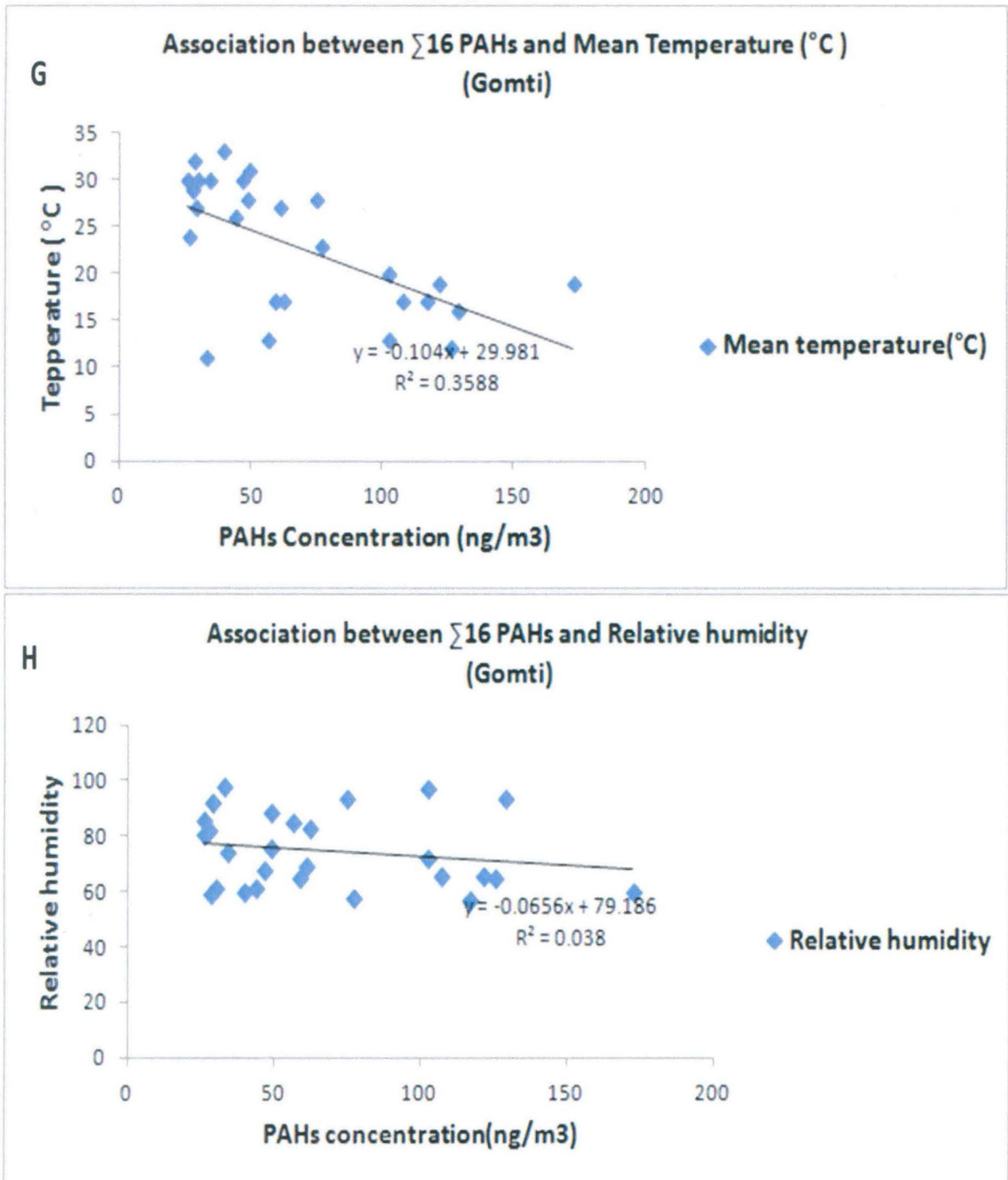


Figure 4.10d Association of PAHs with meteorological parameters (Temp and RH) at Gomti (G and H)



#### 4.4 SOURCE APPORTIONMENT

Molecular diagnostic ratios of PAHs were used for preliminary identification of sources. Final identification of sources has been performed by using principal component analysis (PCA).

##### 4.4.1 Diagnostic Molecular Ratios

It is the ratios of individual PAH isomers in ambient samples. Specific ratios are characteristics of particular emissions sources and are used as diagnostic tools to identify the origin of PAHs in ambient atmosphere (Bi et al. 2003; Guo et al. 2003a,b; Sienna et al. 2005; Fang et al. 2006; Ravindra et al. 2006; Kannan et al. 2005). The ratio of isomer pairs of PAHs can be used to distinguish between traffic dominated PAH profiles and other sources (Hooper et al., 1993). The diagnostic ratios, such as LMW/HMW, Anth/Anth+Phen, B[a]A/B[a]A+Chry, Flan/Flan+Pyr, IP/(IP+B[ghi]P), B[a]P/B[ghi]P, Flu/(Flu+Pyr) and Pyr/B[a]P could be used to identify the origin or as an indication of the aging of air samples. The diagnostic ratios calculated in this study were compared with those reported in literature (Table 4.9) (Appendix 1). The ratio LMW/HMW was found to be  $>1$  for petroleum emission (petrogenic) and  $<1$  for combustion emission (pyrogenic) source (Mastral and Callén, 2000). The value in JNU and Gomti were indicating towards their combustion (pyrogenic) sources. The ratio Anth/Anth+Phen was found to be  $<0.1$  for petroleum emissions and  $>0.1$  for combustion emission source (Budzinski et al. (1997). The value in JNU ( $0.35\pm 0.14$ ) and Gomti ( $0.43\pm 0.2$ ) both indicates their emission from combustion source. According to Yunker et al. (2002), the ratio B[a]A/B[a]A+Chry tells about Petroleum ( $<0.2$ ), Petroleum/combustion ( $0.2-0.35$ ) and combustion ( $>0.35$ ) source. The value of JNU ( $0.62\pm 0.2$ ) indicates combustion source while value at Gomti ( $0.51\pm 0.25$ ) indicates towards both combustion and petroleum/combustion source. The ratio Flan/Flan+Pyr was found to be ( $<0.4$ ) for Petroleum emission,

(0.4) for gasoline source and ( $>0.5$ ) for coal/wood related emission source (Yunker et al., 2002, Simcik et al; 1999). In the present study value of Flan/Flan+Pyr ratio was  $0.48\pm 0.23$  for JNU and  $0.54\pm 0.24$  for Gomti. It indicates that coal/wood combustion was the emission source in the ambient sample of both the sampling area. Yassaa et al., (2001) found that ratio  $IP/(IP+B[ghi]P)$  indicates towards gasoline, diesel and petroleum emission source for value 0.22, 0.5 and 1.3 respectively (Yassaa et al., 2001). The value of  $IP/(IP+B[ghi]P)$  ratio was  $0.39\pm 0.21$  for JNU and  $0.39\pm 0.24$  for Gomti. It indicates that both had common gasoline and diesel emission source. The ratio  $B[a]P/B[ghi]P$  was found to be (0.3-0.78) for vehicular emission source and (0.9-6.6) for coal emission source (Simcik et al in 1999). The value of  $B[a]P/B[ghi]P$  for JNU was ( $1.61\pm 3.62$ ), it indicates their emission from coal combustion and ratio for Gomti was ( $2.74\pm 6.86$ ) indicating towards vehicle and coal emission source. The ratio  $Flu/(Flu+Pyr)$  was found to be  $>0.5$  for diesel and  $<0.5$  for gasoline emission source (Rogge et al. (1993a ,b); Fang et al. (2004); Ravindra et al.(2006a, b). In the present study the value of  $Flu/(Flu+Pyr)$  ratio was  $0.46\pm 0.18$  for JNU, indicating towards gasoline emission source and value  $0.52\pm 0.26$  for Gomti indicates their emission from diesel powered emission source. The ratio  $Pyr/B[a]P$  was found to be  $\sim 10$  for diesel emission and  $\sim 1$  for gasoline emission source (Ravindra et al., 2008). In the present study this ratio had a value of  $1.27\pm 1.04$  for JNU indicating their emission from gasoline source and the value  $2.44\pm 4.03$  for Gomti indicates gasoline and diesel both as their ambient air emission source.

#### 4.4.2 Principal Component Analysis:

In addition to the diagnostic ratios between PAH, Principal Component Analysis (PCA) was used as it is a powerful tool to increase the accuracy of emission source identification by selecting statistically independent source tracers (Guo et al., 2003).

The primary function of PCA is to reduce the number of variables while retaining the original information as much as possible. Variables with similar characteristics are grouped into factors. Each factor from PCA is associated with some sources characterized by its most representative chemical marker, PAH compound(s) in this case.

The first factor represents the weighted (factor loadings) linear combination of the original variables (i.e., individual PAHs) that account for the greatest variability. Each subsequent factor accounts for less variability than the previous (Table 4.10 and 4.11) (Appendix 1). By critically evaluating the factor loadings, an estimate of the chemical source responsible for each factor can be made.

Some PAH compounds and their combinations are frequently used as source markers such as Flu, Pyr, BbF, and BkF for heavy duty diesel vehicles (Ravindra et al., 2008, Sienna et al., 2005) Ant, Phe, Flu, Pyr, BaA, and Chr for coal combustion (Ravindra et al., 2008, Wang et al. 2008, Khalili et al. 1995, Tian et al. 2009), Ant, Phe, BaP, BghiP, and Chr (Ravindra et al., 2008) for steel industry emissions, Flu and Pyr (Ravindra et al., 2008, Wang et al. 2006] for oil burning, BaA, BaP, BbF, BghiP and IP (Guo et al. 2003) BghiP for gasoline-powered vehicles (Ravindra et al., 2008, Hien et al. 2007, Tian et al. 2009) and Flu and BaP (Bourotte et al. 2005) or Ant, Phe, Flu, and Pyr (Ravindra et al., 2008, Wang et al. 2008, Bourotte et al. 2005, Khalili et al. 1995) or NaP and Ant (Khalili et al. 1995) for wood combustion. BaA, Chr, and BaP are associated with combustion of natural gas (Kulkarni et al. 2000, Rogge et al.

1993, Simcik et al. 1997) and BaA has been considered as a tracer for this source (Simcik et al. 1997). The presence of Chr with BaA, Fla, and Pyr in natural gas combustion has also been reported by Daisey et al. (Daisey et al. 1986). Gasoline vehicles emissions are known to have higher loadings of BghiP and DbA + IP. Elevated levels of benzo[*k*]fluoranthene relative to other PAHs have been suggested to indicate diesel vehicles (Venkataraman et al. 1994). Indeno[1,2,3-cd]-pyrene was also found in both diesel and gas engine emissions (May et al. 1986). Several authors report fluoranthene, pyrene, phenanthrene, and anthracene as predominant coal combustion profiles (Harison et al. 1996, Simcik et al. 1999, Masclet et al. 1986, Mastral et al. 1996).

The results from application of PCA to the data at JNU and Gomti are presented in Tables 4.10 and 4.11 (Appendix 1).

#### **JNU:**

**PC 1:** The first factor is responsible for 16.57 % of the total variance. This factor is heavily loaded by BaA, Flu, Anth, Flan and Chry with low loading of Pyr. The presence of Flu, Phen, Anth, Flan, Chry and Pyr in the factor indicates towards coal combustion. (Khalili et al., 1995, Duval and Friendlander, 1981., Ravindra et al., 2008, Wang et al., 2008, and Tian et al., 2009). The second possible emission source in the JNU through factor 1 was natural gas, confirmed by the presence of BaA + Chry and Flan. This factor can also be attributed to natural gas by the presence of BaA + Chry and Flan. (Kulkarni and Venkataraman, 2000; Rogge et al., 1993, Simcik et al, 1997). Daisey et al also reported the presence of Chry with BaA, Flan and Pyr in natural gas combustion. (Daisey et al, 1986).

**PC2:** The second factor is responsible for 11.97 % of the total variance. This factor is heavily loaded by BbF, BaP and Flan. Presence of BbF and Flan was indicating towards oil



combustion emission sources, also reported by various authors. (Ravindra et al. 2006a and Harrison et al, 1996). Presence of BbF and BaP in gasoline emission has been reported by Guo et al, 2003. (Guo et al, 2003).

**PC3:** The third factor is responsible for 10.20 % of the total variance. This factor is heavily loaded by DBA and BkF, which indicates toward wood combustion (Khalili et al, 1995) and vehicular emission source (gas +Diesel) (Larsen and Baker, 2003).

**PC4:** The fourth factor is responsible for 9.95 % of total variance. This factor is has high loading of BghiP and low loading of Anth, according to some author the presence of BghiP indicates towards its emission from gasoline power vehicle. (Lakhani, 2012, Khalili et al, 1995). BghiP and Anth are the indicators of steel industry emissions (Ravindra et al, 2008).

**PC5:** The fifth and last factor for JNU site is responsible for 9.07 % of variance. This factor has high loading of IP and BkF with low loading of Naph. Elevated level fo BkF relative to other PAHs indicates towards diesel Vehicle. (Venkataraman et al, 1994). Low loading of Naph with BkF also indicates toward diesel vehicle emission. (Khalili et al, 1995, Duval and Friedlander, 1981) According to May et al, (1984) IP is also an indicator of both diesel and gas engine emissions (May et al, 1984).

#### **GOMTI:**

**PC 1:** The first factor is responsible for 22.12% of the total variance. This factor is heavily weighted by indeno[1,2,3-*cd*]pyrene and benzo derivatives of fluoranthene, anthracene and pyrene. According to the literature, this source appears vehicular (gasoline and diesel) in nature. (Larsen and Baker, 2003), BbF and BkF with low loading of Fluorene are indicators of

diesel power vehicle (Venkataraman et al.; 1994 and Khalili et al., 1995) or heavy duty diesel power vehicle (Ravindra et al.; 2008 and N. G. Sienna, et al.; 2005).

**PC2:** The second factor is responsible for 17.68 % of the total variance. This factor is heavily weighted by BghiP, BbF and Pyr. BghiP, BbF indicating towards gasoline powered vehicle (Guo et al., 2003; Lakhani, 2012), high factor loading of Pyr with low loading of Flan and Anth represents coal combustion (Ravindra et al., 2008, Wang et al., 2008, Khalili et al., 1995 and Tian et al., 2009). According to some other authors fluoranthene, pyrene and anthracene are indicating towards coal combustion profiles (1) Harrison et al., 1996, Simcik, et al., 1999, Masclet et al., 1986, Mastral et al., 1996

**PC3:** The third factor is responsible for 10.03 % of the total variance. This factor is heavily weighted by DBA and BaP with low loading of BghiP. These are indicators of wood combustion (Khalili et al., 1995, Freeman and Cattel 1990).

### 4.3 HEALTH RISK ASSESMENT

In the present study health risk is explained on the basis of BaP, BaP<sub>eq</sub>, % BaP<sub>eq</sub> contribution, ILCR and Expected cancer cases w.r.t. both the sites in Delhi and mentioned in the Table 4.12 (Appendix 1).

#### 4.3.1 Benz[a]Pyrene and Benz[a]Pyrene equivalents

As Benz[a]Pyrene is only PAHs for which toxicological data are sufficient for derivation of carcinogenic potency factor among all known potentially carcinogenic PAHs. Exposure to B[a]P is regulated by NAAQS criteria is 1 ng/m<sup>3</sup> (NAAQS, 2009) and in European Law, the maximum concentration of BaP is set to 0.7 to 1.3 ng/m<sup>3</sup>, (Menichini, 1999). In the present study, BaP concentration was found with the mean value of 6.39 ng /m<sup>3</sup> in Gomti, which was

much higher than that in 2.73 ng /m<sup>3</sup> at JNU, Delhi (present study), Los Angeles (0.29 ng /m<sup>3</sup>, Fraser et al. 1998), London (2.0 ng/m<sup>3</sup>, Baek et al. 1992 and 3.67ng/m<sup>3</sup>, Cheng et al, 2007). The BaP equivalent concentration (B[a]P eq) is oftenly used to express carcinogenic risk of a PAHs mixture. B[a]Peq were calculated using toxic equivalency factors (TEFs) listed in Nisbet and LaGoy (1992). There are some TEFs developed by different agencies and scientists are listed in Table 3 (Appendix 2). BaPeq is used to estimate the effect from all the PAHs species, the factor TEF is used to convert the effect of PAH species *i* to the equivalent values measured based on BaP (Yang et al., 2007):

$$\text{Total B[a]P eq} = \sum_i (C_i \times \text{TEF}_i)$$

*C<sub>i</sub>*: concentration of a PAHs species *i*, *TEF<sub>i</sub>*: toxic equivalency factor for a PAHs species *i*

According to present study, the B[a]P eq concentration ranges between 3.19 to 37.48 in JNU and 1.53 to 94.47 ng/m<sup>3</sup> in Gomti. The observed overall mean of study period was (12.96±9.28) and (17.73±19.26) ng/m<sup>3</sup> at JNU and Gomti, respectively, as mentioned in the Table 4.1 and 4.2. B[a]P value (mean of both sites) recorded in the present study (15.30±15.08 ng/m<sup>3</sup>) is more than 15 times the annual NAAQS.

In the present study, BaP is the major contributor of BaPeq with 21.06 % and 36.04 % at JNU and Gomti respectively. The observed high value of BaPeq and BaP both in the case of Gomti indicates potential health risk at Gomti. Similarly, Y.Hu et al. (2007) reported high concentration of BaPeq concentration in traffic police man than workers in carbon black manufacturing industries and coke plants and booth attendant at highway toll stations in Tianjin, China. In other study, high concentration of BaPeq was observed in traffic area as compare to indoor and outdoor locations.

The total mean BaP<sub>eq</sub> concentrations at Delhi ( $15.30 \pm 15.08 \text{ ng/m}^3$ ) was found to be higher than Florence, Italy ( $0.916 \text{ ng/m}^3$ , Lodovici *et al.*, 2003), and Nanjing, China ( $7.1 \text{ ng/m}^3$ , Wang *et al.*, 2006). Hong Kong ( $0.64 \text{ ng/m}^3$ , Zheng and Fang 2000), Los Angeles ( $0.27 \text{ ng/m}^3$ , Fraser *et al.* 1998) and London ( $1.83 \text{ ng/m}^3$ , Baek *et al.* 1992). The observed BaP<sub>eq</sub> concentrations are an alarming signal for pollution risks in relation to human health.

#### 4.3.2 Incremental Lifetime Cancer Risk (ILCR) assessment

The total excess incremental lifetime cancer risk (ILCR) for a combination of pollutant is obtained by summing of cancer risk from individual pollutants. ILCR assessment to get a quantitative idea about the health risks associated with airborne PAHs we calculated ILCR for exposed inhabitants. The mean benz[a]pyrene equivalent of two sites ( $15.30 \pm 15.08 \text{ ng/m}^3$ ), “Carcinogenic PAHs and B[a]P-equivalents”) was used as a surrogate for the carcinogenicity of  $\Sigma 16$ PAHs. The following equation was used (Lau *et al.*, 2003; Yu *et al.*, 2008):

$$\text{ILCR} = \sum_i (\text{EC}_i \times \text{IUR}_i)$$

where  $\text{EC}_i$  is the ambient concentration of chemical  $i$  (in nanograms per cubic meter) and  $\text{IUR}_i$  is the inhalation unit risk defined as the risk of cancer from lifetime (70 years) inhalation of unit mass of chemical  $i$  (in nanograms per cubic meter).

In the present study the ILCR was calculated for inhalation exposure to PAHs. As IUR values are not available for each individual PAH species, their respective concentrations were converted in to B[a]P<sub>eq</sub> values (section 4.3.1). In this model, the exposure-carcinogenic effect is considered to be linear (US EPA, 2005).

World Health Organization (1987) has suggested an IUR of  $8.7 \times 10^{-5} \text{ ng/m}^3$  for B[a]P while California Environmental Protection Agency (2004) recommended value of  $1.1 \times 10^{-3} \mu\text{g/m}^3$

for the same time. Despite the large difference between them, both these values are widely accepted. Both the values are used by different authors for calculation of PAHs health risk (Yu et al. 2008; Pengchai et al. 2009). In this study, B[a]P IUR value recommended by WHO (1987), has been used. Mean concentrations of B[a]Peq were  $(12.96 \pm 9.28)$  and  $(17.73 \pm 19.26)$   $\text{ng/m}^3$ , while the estimated ILCRs for PAHs, were  $1.13 \times 10^{-3}$  and  $1.54 \times 10^{-3}$ , for JNU and Gomti, respectively.

Most of the regulatory bodies cites an ILCR between  $10^{-6}$  and  $10^{-4}$  for potential risk, means ILCR more than  $10^{-4}$  indicates towards high potential health risk (Liao and Chiang, 2006). An value of ILCR  $10^{-6}$  represents a lower bound zero risk value. In the present study, high potential risk was observed at both the sampling location in Delhi, but some high risk was observed at JNU in comparison to Gomti. The ILCR at both the sites fall in the range of  $10^{-2}$  to  $10^{-4}$ , higher than acceptable risk level ( $10^{-6}$ ) and in the range of lower than the priority risk level ( $10^{-3}$ ). These values are higher than the value reported by the Bai et al. (2009), Chen and Liao (2006), Xia et al. (2013), Froehner et al. (2011). The calculated societal risk with respect to the computed risk at the sites were 19167 for JNU and 26220 for Gomti. These excess cancer cases may occur in Delhi due to lifetime inhalation exposure to PAHs at their respective concentrations observed in sites of the study. The calculation of total societal ILCR was done by multiplying individual ILCRs by Delhi's population i.e. 17 million. (Census 2011). These number of cancer cases in Delhi are higher than the possible cases observed (1293) in Beijing, China in year 1997 due to PAHs exposure through inhalation. (Yajuan et al. 2008).

In the present study, it was found by PCA method that vehicular sources are one of the predominant factor explaining the observed variance of  $\Sigma 16$  PAHs at the Gomti. Therefore it can be concluded that vehicular source are associated with observed high risk at Gomti.

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## Conclusions

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The aim of the present study was to define the characteristics of 16 USEPA priority PAHs with respect to their sources, which are associated with airborne inhalable particulate matter (PM10) and collected from two different locations in Delhi, India. The sampling locations that were chosen are as follows: JNU (urban receptor site); Gomti (dominated by traffic area and Government buildings). Spatial and seasonal distribution of PM10 and PAHs were investigated. Identification of sources contributing to the analysed chemical species was carried out at each sampling site. The health risk assessments for inhalation exposure with respect to observed pollutants were also performed to compare the health risk at both the sites.

On the basis of results obtained, the following major conclusions are drawn. The conclusions are categorised in to three categories PM10, PAHs, Risk assessment.

#### **PM10**

1. Mean 24-h PM10 concentration of sampling period (July 13 to January 14) at JNU and Gomti were  $211.20 \pm 84.67 \mu\text{g}/\text{m}^3$  and  $158.39 \pm 86.80 \mu\text{g}/\text{m}^3$ , respectively with the overall mean  $185.28 \pm 89 \mu\text{g}/\text{m}^3$  for Delhi.
2. Out of 55 samples of PM10 (28 in JNU and 27 in Gomti) 96 % samples in JNU and 69% samples in Gomti had high PM10 concentrations compare to 24 h NAAQS.
3. The higher mean PM10 concentration was observed in winter season ( $221.75 \pm 87.15 \mu\text{g}/\text{m}^3$ ) than monsoon season ( $130.57 \pm 59.76 \mu\text{g}/\text{m}^3$ ) in Delhi.

#### **PAHs**

4. Mean  $\sum_{16}$  PAHs concentration during sampling period (July 13 to January 14) at JNU and Gomti were  $55.12 \pm 29.87 \text{ ng}/\text{m}^3$  and  $67.81 \pm 40.2 \text{ ng}/\text{m}^3$ ; respectively, with overall mean of  $61.47 \pm 8.97 \text{ ng}/\text{m}^3$  for Delhi.

5. PAHs level observed in this study were more than an order of magnitude greater than values reported from similar locations in European countries.
6. The observed overall mean  $\sum_{16}$  PAHs concentration in Gomti was high than JNU.
7. Mean  $\sum_{16}$  PAHs concentrations during sampling period (July 13 to January 14) were found high in winter as compare to monsoon at both the sites (JNU:  $71.43 \pm 29.91$  ng/m<sup>3</sup> and  $33.38 \pm 8.21$  ng/m<sup>3</sup>, respectively, Gomti:  $84.87 \pm 40.75$  ng/m<sup>3</sup> and  $38.80 \pm 15.25$  ng/m<sup>3</sup>, respectively) in Delhi.
8. Ring wise distribution of PAHs was dominated by 5-ring (40.53 %) followed by 4-ring (20.36 %), 3-ring (19.06 %), 6-ring (17.21 %) and 2-ring (2.83 %) in case of JNU, while in case of Gomti it was 5-ring (44.58 %) followed by 3-ring (17.89%), 4-ring (17.72 %), 6-ring (17.45 %), and 2-ring (2.36 %).
9. High molecular weight PAHs (HMW) contributed more (70-75%) of  $\sum_{16}$  PAHs than Low molecular weight PAHs (LMW) (  $\square$  25 %) in Delhi.
10. Overall mean of  $\sum_7$  PAHs (sum of seven carcinogenic PAHs concentration) were  $30.63 \pm 20.14$  ng/m<sup>3</sup> at JNU and  $40.40 \pm 32.85$  ng/m<sup>3</sup> at Gomti, respectively and contributed 55.57% and 59.58%, respectively in Delhi.
11. Molecular diagnostic ratios of PAHs suggested vehicular emissions in the form of diesel and gasoline exhaust are the major emission sources in Gomti, while coal combustion is the major source in case of JNU.
12. Principal Component Analysis (PCA) identified the following sources – JNU: coal combustion, oil combustion, wood combustion, Gasoline powered vehicle, Diesel vehicle emission; Gomti: vehicular (gas + diesel), Gasoline powered vehicle and wood combustion.



**Health risk assessment**

13. The mean B[a]P<sub>eq</sub> concentration (during sampling period from July 13 to January 14) were  $12.96 \pm 9.28 \text{ ng/m}^3$  and  $17.73 \pm 19.26 \text{ ng/m}^3$  at JNU and Gomti, respectively; with overall mean of  $15.30 \pm 15.08 \text{ ng/m}^3$  in Delhi.
14. The calculated incremental life time cancer risk by inhalation exposure was  $1.13 \times 10^{-3}$  and  $1.54 \times 10^{-3}$  for JNU and Gomti, respectively.
15. With respect to the risk, 26220 and 19167 excess cancer cases are calculated at Gomti and JNU, respectively.
16. Overall, it can be concluded that Gomti had higher concentration of  $\sum_{16} \text{PAHs}$  than JNU which indicates towards traffic emission sources near Gomti site; due to which higher health risk was observed at Gomti.

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## Appendices

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**Table: 4.1 Descriptive statistic of analyzed species concentrations at JNU, PM10 in  $\mu\text{g}/\text{m}^3$  whereas PAHs concentrations are in  $\text{ng}/\text{m}^3$ .**

| SN | Species                           | Monsoon              | Winter               | Min   | Max.   | Mean $\pm$ SD        |
|----|-----------------------------------|----------------------|----------------------|-------|--------|----------------------|
|    |                                   | (N=12)               | (N=16)               |       |        | (N=28)               |
| 1  | <b>PM10</b>                       | (168.63 $\pm$ 37.15) | (243.13 $\pm$ 96.72) | 88.61 | 434.35 | (211.20 $\pm$ 84.67) |
| 2  | <b>Naph</b>                       | (1.4 $\pm$ 1.01)     | (1.65 $\pm$ 1.68)    | 0.06  | 5.87   | (1.54 $\pm$ 1.41)    |
| 3  | <b>Acy</b>                        | (2.19 $\pm$ 1.11)    | (2.214 $\pm$ 1.34)   | 0.35  | 5.49   | (2.2 $\pm$ 1.22)     |
| 4  | <b>Acen</b>                       | (4.99 $\pm$ 2.93)    | (4.66 $\pm$ 1.86)    | 0.92  | 12.17  | (4.8 $\pm$ 2.34)     |
| 5  | <b>Flu</b>                        | (1.67 $\pm$ 0.84)    | (2.12 $\pm$ 1.78)    | 0.31  | 5.87   | (1.93 $\pm$ 1.45)    |
| 6  | <b>Phen</b>                       | (0.65 $\pm$ 0.42)    | (1.07 $\pm$ 0.96)    | 0.17  | 3.28   | (0.89 $\pm$ 0.79)    |
| 7  | <b>Anth</b>                       | (0.32 $\pm$ 0.16)    | (0.73 $\pm$ 0.78)    | 0.05  | 2.62   | (0.56 $\pm$ 0.63)    |
| 8  | <b>Flan</b>                       | (1.72 $\pm$ 0.84)    | (4.05 $\pm$ 5.45)    | 0.2   | 18.93  | (3.05 $\pm$ 4.26)    |
| 9  | <b>Pyr</b>                        | (1.95 $\pm$ 1.16)    | (3.42 $\pm$ 2.97)    | 0.23  | 9.11   | (2.79 $\pm$ 2.45)    |
| 10 | <b>B[a]A</b>                      | (1.96 $\pm$ 3.03)    | (4.34 $\pm$ 3.77)    | 0.09  | 13.24  | (3.32 $\pm$ 3.62)    |
| 11 | <b>Chry</b>                       | (0.68 $\pm$ 0.87)    | (2.86 $\pm$ 2.08)    | 0.07  | 6.72   | (1.92 $\pm$ 1.98)    |
| 12 | <b>B[b]F</b>                      | (1.94 $\pm$ 1.54)    | (9.73 $\pm$ 6.49)    | 0.45  | 26.2   | (6.39 $\pm$ 6.3)     |
| 13 | <b>B[k]F</b>                      | (1.88 $\pm$ 1.8)     | (6.61 $\pm$ 5.56)    | 0.13  | 17.81  | (4.58 $\pm$ 4.92)    |
| 14 | <b>B[a]P</b>                      | (2.09 $\pm$ 1.47)    | (3.21 $\pm$ 1.93)    | 0.71  | 7.08   | (2.73 $\pm$ 1.81)    |
| 15 | <b>DBA</b>                        | (5.36 $\pm$ 4.38)    | (10.61 $\pm$ 8.96)   | 0.44  | 31.57  | (8.36 $\pm$ 7.71)    |
| 16 | <b>B[ghi]P</b>                    | (2.7 $\pm$ 1.67)     | (8.58 $\pm$ 8.64)    | 0.3   | 22.71  | (6.06 $\pm$ 7.17)    |
| 17 | <b>IP</b>                         | (1.59 $\pm$ 0.66)    | (4.6 $\pm$ 5.03)     | 0.27  | 17.33  | (3.31 $\pm$ 4.06)    |
| 18 | <b><math>\Sigma</math>16 PAHs</b> | (33.38 $\pm$ 8.21)   | (71.43 $\pm$ 29.91)  | 23.03 | 136.78 | (55.12 $\pm$ 29.87)  |
| 19 | <b>LMW</b>                        | (11.23 $\pm$ 3.44)   | (12.44 $\pm$ 4.55)   | 6.27  | 20.96  | (11.84 $\pm$ 0.86)   |
| 20 | <b>HMW</b>                        | (21.87 $\pm$ 7.24)   | (58.03 $\pm$ 27.59)  | 14.88 | 115.72 | (39.95 $\pm$ 25.57)  |
| 21 | <b>B[a]P<sub>eq</sub></b>         | (8.24 $\pm$ 4.92)    | (16.50 $\pm$ 10.30)  | 3.19  | 37.48  | (12.96 $\pm$ 9.28)   |

**Table: 4.2. Descriptive statistic of analyzed species concentrations at GOMTI, PM10 in  $\mu\text{g}/\text{m}^3$  whereas PAHs concentrations are in  $\text{ng}/\text{m}^3$ .**

| S.No. | Species                           | Monsoon             | Winter               | Min    | Max.   | Mean $\pm$ SD       |
|-------|-----------------------------------|---------------------|----------------------|--------|--------|---------------------|
|       |                                   | (N=10)              | (N=17)               |        |        | (N=27)              |
| 1     | <b>PM10</b>                       | (84.88 $\pm$ 48.93) | (201.63 $\pm$ 74.38) | 50.353 | 328.03 | (158.39 $\pm$ 86.8) |
| 2     | <b>Naph</b>                       | (1.49 $\pm$ 1.5)    | (1.67 $\pm$ 1.88)    | 0.05   | 6.66   | (1.6 $\pm$ 1.72)    |
| 3     | <b>Acy</b>                        | (2.9 $\pm$ 2.06)    | (2.31 $\pm$ 1.63)    | 0.31   | 5.58   | (2.53 $\pm$ 1.78)   |
| 4     | <b>Acen</b>                       | (4.59 $\pm$ 3.05)   | (4.05 $\pm$ 1.93)    | 0.17   | 10.58  | (4.25 $\pm$ 2.36)   |
| 5     | <b>Flu</b>                        | (1.6 $\pm$ 1.13)    | (3.57 $\pm$ 2.63)    | 0.14   | 10.47  | (2.84 $\pm$ 2.37)   |
| 6     | <b>Phen</b>                       | (1.7 $\pm$ 2.65)    | (1.32 $\pm$ 1.04)    | 0.1    | 9.18   | (1.46 $\pm$ 1.77)   |
| 7     | <b>Anth</b>                       | (0.8 $\pm$ 0.54)    | (1.17 $\pm$ 1)       | 0.04   | 3.12   | (1.03 $\pm$ 0.86)   |
| 8     | <b>Flan</b>                       | (3.47 $\pm$ 3.25)   | (3.54 $\pm$ 3.65)    | 0.59   | 13.5   | (3.51 $\pm$ 3.45)   |
| 9     | <b>Pyr</b>                        | (1.41 $\pm$ 1.02)   | (3.82 $\pm$ 4.35)    | 0.06   | 18.01  | (2.93 $\pm$ 3.66)   |
| 10    | <b>B[a]A</b>                      | (2.8 $\pm$ 2.68)    | (2.58 $\pm$ 2.04)    | 0.06   | 9.31   | (2.66 $\pm$ 2.25)   |
| 11    | <b>Chry</b>                       | (0.83 $\pm$ 0.94)   | (4.12 $\pm$ 2.92)    | 0.11   | 9.43   | (2.9 $\pm$ 2.86)    |
| 12    | <b>B[b]F</b>                      | (4.49 $\pm$ 6.83)   | (11.27 $\pm$ 6.66)   | 24.96  | 0.87   | (8.76 $\pm$ 7.39)   |
| 13    | <b>B[k]F</b>                      | (1.99 $\pm$ 2.27)   | (8.44 $\pm$ 5.31)    | 0.11   | 16.43  | (6.05 $\pm$ 5.4)    |
| 14    | <b>B[a]P</b>                      | (2.17 $\pm$ 2.59)   | (8.87 $\pm$ 8.88)    | 0.07   | 28.27  | (6.39 $\pm$ 7.85)   |
| 15    | <b>DBA</b>                        | (3.82 $\pm$ 3.89)   | (12.05 $\pm$ 14.13)  | 0.16   | 21.92  | (9 $\pm$ 12.02)     |
| 16    | <b>B[ghi]P</b>                    | (3 $\pm$ 2.46)      | (9.64 $\pm$ 8.73)    | 0.21   | 29.9   | (7.18 $\pm$ 7.73)   |
| 17    | <b>IP</b>                         | (1.54 $\pm$ 1.36)   | (6.46 $\pm$ 6.14)    | 0.04   | 23.97  | (4.64 $\pm$ 5.45)   |
| 18    | <b><math>\Sigma</math>16 PAHs</b> | (38.8 $\pm$ 15.25)  | (84.87 $\pm$ 40.75)  | 26.07  | 172.47 | (67.81 $\pm$ 40.2)  |
| 19    | <b>LMW</b>                        | (13.08 $\pm$ 4.75)  | (14.09 $\pm$ 4.79)   | 7.29   | 23.45  | (13.58 $\pm$ 0.71)  |
| 20    | <b>HMW</b>                        | (25.52 $\pm$ 16.18) | (70.78 $\pm$ 38.90)  | 14.83  | 161.47 | (48.15 $\pm$ 32.00) |
| 21    | <b>B[a]P eq</b>                   | (7.14 $\pm$ 5.94)   | (23.96 $\pm$ 21.72)  | 1.53   | 94.47  | (17.73 $\pm$ 19.26) |

**Table: 4.3.  $\Sigma$ 16 PAHs concentration and monthly Avg.  $\Sigma$ 16 PAHs conc. ( $\text{ng}/\text{m}^3$ ) and ( $\pm$  standard deviation) and PM10 at JNU site ( $\mu\text{g}/\text{m}^3$ ) and monthly avg. PM10 at JNU site ( $\mu\text{g}/\text{m}^3$ ).**

|  | $\Sigma$ 16<br>Concentration<br>( $\text{ng}/\text{m}^3$ ) | PAHs<br>Monthly Avg. $\Sigma$ 16<br>PAHs Conc. And<br>STDV | PM10 at JNU site<br>( $\mu\text{g}/\text{m}^3$ ) | Monthly<br>PM10 at JNU site<br>( $\mu\text{g}/\text{m}^3$ ) | Avg. |
|--|--|--|--|---|------|
| J1(1july13)  | 28.66216   |  | 237  |   |      |
| J2(9 July 13)  | 23.03077   | 27.41638   | 194.3515   |   |      |
| J3(19 july13)  | 31.0422  | 3.374825*  | 143.8285   | 201.6532  |      |
| J4(31 July 13)   | 26.93038   |  | 231.4327   |   |      |
| J5(9 Aug. 13)  | 33.14049   |  | 171.7361   |   |      |
| J6(17 Aug. 13)   | 39.61169   |  | 124.9658   | 151.4994  |      |
| J7(23Aug.13)   | 38.37913   | 34.69585*  | 175.2033   |   |      |
| J8(30 Aug.13)  | 27.65209   | 5.470091   | 134.0925   |   |      |
| J9(6 Sept.13)  | 29.99134   |  | 142.0054   |   |      |
| J10(11 Sept.13)  | 50.8046  |  | 164.8639   | 152.7494  |      |
| J11(17 Sept13)   | 27.19265   | 38.01618   | 172.8452   |   |      |
| J12 (28 Sept.13)   | 44.07614   | 11.28145*  | 131.2831   |   |      |
| J13(4 Oct.13)  | 39.91981   |  | 106.3701   |   |      |
| J14(9 Oct.13)  | 39.16739   |  | 88.61111   |   |      |
| J15(16 Oct.13)   | 35.9524  | 62.2384  | 139.8866   | 143.3718  |      |
| J16(22 Oct.13)   | 59.47008   | 10.701*  | 191.0088   |   |      |
| J17(30 Oct.13)   | 136.6823   |  | 190.9823   |   |      |
| J18(15 Nov.13)   | 100.4105   |  | 138.7164   |   |      |
| J19(22 Nov.13)   | 94.54686   | 82.90167   | 434.3478   | 278.9677  |      |
| J20(28 Nov.13)   | 53.74759   | 25.41782*  | 263.8388   |   |      |
| J21(7 dec.13)  | 93.14901   |  | 348.538  |   |      |
| J22(14 dec.13)   | 40.33123   |  | 326.991  |   |      |
| J23 (20 dec 13)  | 61.57951   | 59.79927   | 265  | 303.0297  |      |
| J24(27 dec.13)   | 44.13734   | 24.08094*  | 271.5897   |   |      |
| J25(9Jan.14)   | 102.2614   |  | 326.9389   |   |      |
| J26(17 Jan.13)   | 99.90263   | 85.96499   | 233.8211   | 281.0581  |      |
| J27(24Jan.14)  | 70.83928   | 17.48216*  | 235.6944   |   |      |
| J28(30 Jan.14)   | 70.85668   |  | 327.7778   |   |      |
| Average<br>PAHs<br>Concentration<br>( $\text{ng}/\text{m}^3$ ) | $\Sigma$ 16 (55.12 $\pm$ 29.87)                            |  | Average<br>PM10<br>( $\mu/\text{m}^3$ )          | (211.20 $\pm$ 84.67)  |      |

\*standard deviation in monthly Avg.  $\Sigma$ 16 PAHs Concentration

**Table: 4.4  $\Sigma$ 16 PAHs concentration and monthly Avg.  $\Sigma$ 16 PAHs conc. (ng/m<sup>3</sup>) with  $\pm$  standard deviation, PM10 and monthly avg. PM10 at Gomti ( $\mu$ g/m<sup>3</sup>).**

|  | $\Sigma$ 16 PAHs    | Monthly $\Sigma$ 16 PAHs and STDV                    | Avg. PM10            | Monthly Avg. PM10 |
|--|---------------------|--|----------------------|-------------------|
| G1(1July13)  | 39.80724            |  | 214.0351             |                   |
| G2(19 July 13)   | 49.03272            | 45.90286   | 68.08224             | 113.4548          |
| G3(31 July 13)   | 48.86863            | 5.279604*  | 58.24707             |                   |
| G4(9 Aug. 13)  | 28.78227            |  | 69.16996             |                   |
| G5(17 Aug. 13)   | 74.8764             |  | 58.71212             |                   |
| G6(23Aug.13)   | 26.07238            | 39.42671   | 117.3913             | 74.1642           |
| G7(30 Aug.13)  | 27.97578            | 23.66042*  | 51.3834              |                   |
| G8(6 Sept.13)  | 29.84597            |  | 80.55275             |                   |
| G9(11 Sept.13)   | 28.59863            | 30.86891   | 67.32543             | 70.6096           |
| G10 (28 Sept.13)   | 34.16213            | 2.919407*  | 63.95062             |                   |
| G11 (4 Oct.13)   | 26.28346            |  | 50.35389             |                   |
| G12(9 Oct.13)  | 46.74198            |  | 69.9894              |                   |
| G13(16 Oct.13)   | 61.19011            | 51.07145   | 138.9474             | 156.5933          |
| G14(22 Oct.13)   | 44.14809            | 19.07529*  | 195.6456             |                   |
| G15(30 Oct.13)   | 76.9936             |  | 328.0303             |                   |
| G16(8 Nov.13)  | 102.4198            |  | 259.9003             |                   |
| G17(15 Nov.13)   | 116.6306            |  | 256.5217             | 243.9255          |
| G18 (22 nov.13)  | 121.2887            | 128.2025   | 239.693              |                   |
| G19(28 Nov.13)   | 172.4709            | 30.58401*  | 219.5869             |                   |
| G20(7 dec.13)  | 107.3386            |  | 207.7327             |                   |
| G21(14 dec.13)   | 59.04399            | 105.1817   | 267.964              | 236.8014          |
| G22(20 dec.13)   | 128.6449            | 32.17054*  | 225.5556             |                   |
| G23(27 dec.13)   | 125.6993            |  | 245.9535             |                   |
| G24(09Jan.14)  | 56.58045            |  | 216.6667             |                   |
| G25(17 Jan.14)   | 32.7271             | 63.47112   | 120.9402             | 180.4535          |
| G26 (24Jan.13)   | 102.2445            | 28.85217*  | 136.0593             |                   |
| G27(30 Jan.13)   | 62.33246            |  | 248.1481             |                   |
| (Average $\Sigma$ 16 PAHs $\pm$ STDDEV) (ng/m <sup>3</sup> ) | (67.81 $\pm$ 40.20) | (Average PM10 $\pm$ STDEV) ( $\mu$ /m <sup>3</sup> ) | (158.39 $\pm$ 86.80) |                   |

\*standard deviation in monthly Avg.  $\Sigma$ 16 PAHs Concentration

**Table: 4.5 Comparison of ambient PAHs concentration (in nanogram per cubic meter)**

| Location                 | Site type                    | PM type   | Total PAHs       | Value (ng/m <sup>3</sup> ) | Reference                       |
|--------------------------|------------------------------|-----------|------------------|----------------------------|---------------------------------|
| Delhi, India             | Residential<br>(2 sites)     | PM10      | $\sum_{16}$ PAHs | 61.47±8.97                 | Present study                   |
| Delhi, India             | Residential                  | PM10      | $\sum_{16}$ PAHs | 105.3±84.9                 | Sarkar and Khillare, 2013       |
| Mumbai, India            | Residential                  | PM10      | $\sum_{16}$ PAHs | 38.8                       | Kulkarni and Venkatraman, 2000a |
| Seoul, Korea             | Urban                        | PM2.5     | $\sum_{16}$ PAHs | 26.3±29.4                  | Park et al., 2002               |
| São Paulo, Brazil        | Urban                        | TSP       | $\sum_{13}$ PAHs | 3.1                        | Vasconcellos et al. (2003)b     |
| Thessaloniki, Greece     | Residential                  | PM10      | $\sum_{13}$ PAHs | 25.6                       | Manoli et al., 2004             |
| Zagreb, Croatia          | Residential                  | PM10      | $\sum_6$ PAHs    | 7.51±10.01                 | Šišović et al. (2008)c          |
| Higashi Hiroshima, Japan | Urban                        | PM10      | $\sum_{13}$ PAHs | 2.37                       | Tham et al. (2008)              |
| Beijing, China           | 20 sites                     | PM 2.5-10 | $\sum_{16}$ PAHs | 244±208                    | Wang et al. (2008)d             |
| Zonguldak, Turkey        | Urban                        | PM10      | $\sum_{14}$ PAHs | 93.7±121.6                 | Akyüz and Çabuk (2009)          |
| Atlanta, USA             | Residential                  | PM2.5     | $\sum_{28}$ PAHs | 2.92                       | Li et al., 2009                 |
| Hong Kong                | Traffic and Industrial sites | PM10      | $\sum_{16}$ PAHs | 34.20±14.62                | Guo et al., 2003                |
| Naples, Italy            | Traffic                      | PM10      | $\sum_{15}$ PAHs | 54.8                       | Caricchia et al., 1999          |
| Naples, Italy            | Residential                  | PM10      | $\sum_{15}$ PAHs | 22.7                       | Caricchia et al., 1999          |

a Sampling from 19 to 22 and 27 to 30 November 1996

b Sampling from 18th August to 3rd September 2000

c Sampling from 2001–2004

d Sampling from 20th December 2005 to 19th January 2006

## Appendix 1 | 2014

**Table: 4.6. Correlation coefficient between PAHs, PM10 and meteorological parameters along with associated significant levels (\*p<0.05; \*\*p<0.01) at JNU (N=28).**

|                                 | $\Sigma$ 16 PAHs | Precipitation<br>(cm) | WS(km/hr) | Temp(°C) | RH     | PM10( $\mu$ g/m <sup>3</sup> ) |
|---------------------------------|------------------|-----------------------|-----------|----------|--------|--------------------------------|
| $\Sigma$ 16 PAHs                | 1                |                       |           |          |        |                                |
| Precipitation (cm)              | -.607**          | 1                     |           |          |        |                                |
| WS (km/hr)                      | -.544**          | 0.373                 | 1         |          |        |                                |
| Temp (°C)                       | -.646**          | .682**                | 0.371     | 1        |        |                                |
| RH                              | -0.094           | 0.253                 | 0.236     | -0.213   | 1      |                                |
| PM10 ( $\mu$ g/m <sup>3</sup> ) | .443*            | -.381*                | -0.332    | -.636**  | -0.021 | 1                              |

## Appendix 1 | 2014

Table: 4.7. Correlation coefficient between PAHs, PM10 and meteorological parameters along with associated significant levels (\*p<0.05; \*\*p<0.01) at Gomti (N=27).

|                                | $\Sigma$ 16 PAHs | Precipitation(cm) | WS(km/hr) | Temp(°C) | RH     | PM10( $\mu$ g/m <sup>3</sup> ) |
|--------------------------------|------------------|-------------------|-----------|----------|--------|--------------------------------|
| $\Sigma$ 16 PAHs               | 1                |                   |           |          |        |                                |
| Precipitation (cm)             | -.488**          | 1                 |           |          |        |                                |
| WS (km/hr)                     | -.483*           | 0.337             | 1         |          |        |                                |
| Temp (°C)                      | -.599**          | .677**            | 0.37      | 1        |        |                                |
| RH                             | -0.195           | 0.24              | 0.199     | -0.211   | 1      |                                |
| PM10( $\mu$ g/m <sup>3</sup> ) | .620**           | -.631**           | -.448*    | -.601**  | -.421* | 1                              |



**Table: 4.8 Ring wise distribution (mean  $\pm$  standard deviation) of  $\Sigma$ 16 PAHs concentration (ng/m<sup>3</sup>) at JNU and Gomti.**

| PAHs<br>Concentration | JNU   |       | Gomti |       |
|-----------------------|-------|-------|-------|-------|
|                       | Mean  | STDEV | Mean  | STDEV |
| 2 ring                | 1.54  | 1.41  | 1.60  | 1.72  |
| 3 ring                | 10.38 | 4.09  | 12.11 | 3.92  |
| 4 ring                | 11.09 | 8.62  | 12.00 | 7.24  |
| 5 ring                | 22.07 | 16.28 | 30.20 | 26.81 |
| 6 ring                | 9.37  | 9.66  | 11.82 | 10.64 |

**Table: 4.9 Molecular diagnostic ratios of PAHs at the study sites along with corresponding source signatures obtain from existing literature.**

| Diagnostic Ratio        | JNU         | Gomti       | Literature Values  |
|-------------------------|-------------|-------------|--|
| <b>LMW/HMW</b>          | 0.296       | 0.282       | Petroleum (Petrogenic) (>1) and combustion (Pyrogenic) (<1), Ref: Mastral and Call n, 2000)  |
| <b>Anth/Anth+Phen</b>   | (0.35±0.14) | (0.43±0.2)  | Petroleum (petrogenic) (<0.1) and Combustion (pyrogenic) (>0.1) Ref: Budzinski et al. (1997)   |
| <b>B[a]A/B[a]A+Chry</b> | (0.62±0.2)  | (0.51±0.25) | Petroleum (<0.2), Petroleum/combustion (0.2–0.35) and combustion (>0.35) , Ref: Yunker et al. (2002)   |
| <b>Flan/Flan+Pyr</b>    | (0.48±0.23) | (0.54±0.24) | Petroleum (<0.4) <sup>b</sup> and Gasoline (0.4) <sup>c</sup> and Coal/wood (>0.5) <sup>b</sup> Ref: b: Yunker et al. (2002) c: Simcik et al. (1999) |
| <b>IP/(IP+B[ghi]P)</b>  | (0.39±0.21) | (0.39±0.24) | Gasoline (0.22), Diesel (0.5) and Petroleum (1.3) Ref: Yassaa et al. (2001)  |
| <b>B[a]P/B[ghi]P</b>    | (1.61±3.62) | (2.74±6.86) | Vehicles (0.3–0.78) and Coal (0.9–6.6); Ref: Simcik et al. (1999)  |
| <b>Flu/(Flu+Pyr)</b>    | (0.46±0.18) | (0.52±0.26) | Diesel (>0.5) and Gasoline(<0.5); Ref: Rogge et al. (1993a ,b); Fang et al. (2004); Ravindra et al.(2006a, b)  |
| <b>Pyr/B[a]P</b>        | (1.27±1.04) | (2.44±4.03) | Diesel engine (~10) and Gasoline engine( ~1); Ref: Ravindra et al.(2008)   |

**Table: 4.10 Results of principal component analysis (varimax rotation with Kaiser Normalization) at JNU. Only factor loadings  $\geq 0.4$  are shown. Loading  $\geq 0.5$  are in bold.**

| <b>Principal Component Analysis (PCA)</b> |              |              |              |              |              |
|---|--------------|--------------|--------------|--------------|--------------|
| <b>Rotated component matrix</b>           |              |              |              |              |              |
| <b>Species</b>                            | <b>PC1</b>   | <b>PC2</b>   | <b>PC3</b>   | <b>PC4</b>   | <b>PC5</b>   |
| Naph                                      |              |              |              |              | 0.404        |
| Acy                                       |              |              |              |              |              |
| Acen                                      |              |              |              |              |              |
| Flu                                       | <b>0.655</b> |              |              |              |              |
| Phen                                      |              |              |              |              |              |
| Anth                                      | <b>0.546</b> |              |              | 0.421        |              |
| Flan                                      | <b>0.647</b> | <b>0.603</b> |              |              |              |
| Pyr                                       | 0.422        |              |              |              |              |
| B[a]A                                     | <b>0.74</b>  |              |              |              |              |
| Chry                                      | <b>0.602</b> |              |              |              |              |
| B[b]F                                     |              | <b>0.94</b>  |              |              |              |
| B[k]F                                     |              |              | <b>0.682</b> |              | <b>0.505</b> |
| B[a]P                                     |              | <b>0.609</b> |              |              |              |
| DBA                                       |              |              | <b>0.931</b> |              |              |
| B[ghi]P                                   |              |              |              | <b>0.934</b> |              |
| IP  |              |              |              |              | <b>0.869</b> |
| <b>Eigenvalues</b>                        | 2.651        | 1.915        | 1.632        | 1.591        | 1.451        |
| <b>% of Variance</b>                      | 16.571       | 11.968       | 10.202       | 9.946        | 9.066        |
| <b>Cumulative %</b>                       | 16.571       | 28.539       | 38.742       | 48.687       | 57.753       |

Table: 4.11. Results of principal component analysis (varimax rotation with Kaiser Normalization) at Gomti. Only factor loadings  $\geq 0.4$  are shown. Loading  $\geq 0.5$  are in bold.

| Principal Component Analysis (PCA) |              |              |              |
|------------------------------------|--------------|--------------|--------------|
| Rotated component matrix           |              |              |              |
|                                    | PC1          | PC2          | PC3          |
| Naph                               |              |              |              |
| Acy                                |              |              |              |
| Acen                               |              |              |              |
| Flu                                | 0.441        |              |              |
| Phen                               |              |              |              |
| Anth                               |              | 0.418        |              |
| Flan                               |              | 0.481        |              |
| Pyr                                |              | <b>0.762</b> |              |
| B[a]A                              | <b>0.517</b> |              |              |
| Chry                               | <b>0.775</b> |              |              |
| B[b]F                              | <b>0.513</b> | <b>0.74</b>  |              |
| B[k]F                              | <b>0.794</b> |              |              |
| B[a]P                              | <b>0.829</b> |              | <b>0.511</b> |
| DBA                                |              |              | <b>0.938</b> |
| B[ghi]P                            |              | <b>0.791</b> | 0.403        |
| IP                                 | <b>0.818</b> |              |              |
| Eigenvalues                        | 3.539        | 2.829        | 1.604        |
| % of Variance                      | 22.121       | 17.681       | 10.028       |
| Cumulative %                       | 22.121       | 39.801       | 49.829       |

**Table 4.12. BaP, BaP<sub>eq</sub>, % BaP contribution, ILCR and Expected cancer cases at study site, JNU and Gomti in Delhi.**

|                                       | JNU         | Gomti        |
|---------------------------------------|-------------|--------------|
| <b>BaP</b>                            | 2.73*       | 6.39*        |
| <b>BaP<sub>eq</sub></b>               | 12.96±9.28* | 17.73±19.26* |
| <b>% BaP contribution</b>             | 21.06       | 36.04        |
| <b>ILCRs</b>                          | 0.00113     | 0.00154      |
| <b>Expected cancer cases in Delhi</b> | 19167**     | 26220**      |

\* Unit in ng/m<sup>3</sup>

\*\*Total cases in 17 million population in Delhi/year.

**Table 1 Meteorological data record in Delhi during the study Period (July 2013- January 2014).**

| Date of Sampling | Temperature (°C) | Relative Humidity (%) | Wind Speed (Km/h) | Precipitation (cm) |
|------------------|------------------|-----------------------|-------------------|--------------------|
| 1 July 13        | 33               | 60                    | 11                | 0.38               |
| 9 July 13        | 29               | 86                    | 10                | 0.63               |
| 19 July 13       | 31               | 76                    | 10                | 0.63               |
| 31 July 13       | 28               | 89                    | 8                 | 0.74               |
| 9 Aug. 13        | 27               | 92                    | 6                 | 0.58               |
| 17 Aug. 13       | 28               | 94                    | 8                 | 0.66               |
| 23 Aug. 13       | 30               | 81                    | 3                 | 0.69               |
| 30 Aug. 13       | 29               | 82                    | 6                 | 0.56               |
| 6 Sept. 13       | 30               | 61                    | 11                | 0.48               |
| 11 Sept. 13      | 32               | 59                    | 6                 | 0.41               |
| 17 Sept 13       | 30               | 61                    | 5                 | 0.3                |
| 28 Sept. 13      | 30               | 74                    | 5                 | 0.1                |
| 4 Oct. 13        | 24               | 86                    | 11                | 0                  |
| 9 Oct. 13        | 30               | 68                    | 10                | 0                  |
| 16 Oct. 13       | 27               | 69                    | 3                 | 0                  |
| 22 Oct. 13       | 26               | 61                    | 3                 | 0                  |
| 30 Oct. 13       | 23               | 58                    | 3                 | 0                  |
| 8 Nov 13         | 26               | 61                    | 3                 | 0                  |
| 15 Nov. 13       | 17               | 57                    | 3                 | 0                  |
| 22 Nov. 13       | 19               | 66                    | 2                 | 0                  |
| 28 Nov. 13       | 19               | 60                    | 2                 | 0                  |
| 7 Dec. 13        | 17               | 66                    | 2                 | 0                  |
| 14 Dec. 13       | 17               | 65                    | 11                | 0                  |
| 20 Dec 13        | 16               | 94                    | 6                 | 0                  |
| 27 Dec. 13       | 12               | 65                    | 3                 | 0                  |
| 9 Jan. 14        | 13               | 85                    | 5                 | 0                  |
| 17 Jan. 14       | 11               | 98                    | 5                 | 0                  |
| 24 Jan. 14       | 13               | 97                    | 8                 | 0                  |
| 30 Jan. 14       | 17               | 83                    | 5                 | 0                  |

Source:

[http://www.wunderground.com/history/airport/VIDP/2014/1/1/MonthlyHistory.html?req\\_city=NA&req\\_state=NA&req\\_statename=NA](http://www.wunderground.com/history/airport/VIDP/2014/1/1/MonthlyHistory.html?req_city=NA&req_state=NA&req_statename=NA)

Table: 2. Toxic Equivalent factor (TEFs) suggested by different authors.

| <b>Compounds</b>       | <b>Nisbet and LaGoy (1992)</b> | <b>Malcolm and Dobson (1994)</b> | <b>Kalberlah et al. (1995)</b> | <b>Larsen and Larsen (1998)</b> | <b>Tsai et al. (2004)</b> |
|------------------------|--------------------------------|----------------------------------|--------------------------------|---------------------------------|---------------------------|
| Naphthalene            | 0.001                          | 0.001                            | -                              | -                               | 0.001                     |
| Acenaphthylene         | 0.001                          | 0.001                            | 0.001                          | -                               | 0.001                     |
| Acenaphthene           | 0.001                          | 0.001                            | 0.001                          | -                               | 0.001                     |
| Fluorene               | 0.001                          | 0.001                            | 0                              | 0.0005                          | 0.001                     |
| Phenanthrene           | 0.001                          | 0.001                            | 0                              | 0.0005                          | 0.001                     |
| Anthracene             | 0.01                           | 0.01                             | 0.01                           | 0.0005                          | 0.01                      |
| Fluoranthene           | 0.001                          | 0.001                            | 0.001                          | 0.05                            | 0.001                     |
| Pyrene                 | 0.001                          | 0.001                            | -                              | 0.001                           | 0.001                     |
| Benzo[a]Anthracene     | 0.1                            | 0.1                              | 0.1                            | 0.005                           | 0.1                       |
| Chrysene               | 0.01                           | 0.01                             | -                              | 0.03                            | 0.01                      |
| Benzo[b]Fluoranthene   | 0.1                            | 0.1                              | 0.1                            | 0.1                             | 0.1                       |
| Benzo[k]Fluoranthene   | 0.1                            | 0.1                              | 0.1                            | 0.05                            | 0.1                       |
| Benzo[a]Pyrene         | 1                              | 1                                | 1                              | 1                               | 1                         |
| Dibenzo[a,h]Anthracene | 1                              | 1                                | 1                              | 1.1                             | 1                         |
| Benzo[ghi]Perylene     | 0.01                           | 0.01                             | 0.01                           | 0.02                            | 0.01                      |
| Indeno[1,2,3-cd]Pyrene | 0.1                            | 0.1                              | 0.1                            | 0.1                             | 0.1                       |

# HPLC Chromatogram of an external standard

