

# Polycyclic Aromatic Hydrocarbons in Atmospheric Particles of PM<sub>10</sub> at Yamuna Nagar, Haryana, India.

Jitendra Dubey, Vyoma Singla, K. Maharaj Kumari, Anita Lakhani

**Abstract**— PM<sub>10</sub> samples were collected at Yamuna Nagar in the month of October, 2011 using fine particulate sampler and then extracted with dichloromethane (DCM) using a sonicator. 16 priority PAHs compounds were analyzed by using gas chromatography (Shimadzu 17A). PM<sub>10</sub> concentrations ranged between 246.2 to 622.3 µg/m<sup>3</sup>, which were well above the NAAQS standard. Mean concentrations of individual PAHs varied between 44.5 to 149.1 ng/m<sup>3</sup> while the average value of ΣPAHs was 1006.8 ng/m<sup>3</sup>. The dominant compounds were low and middle molecular weight PAHs including naphthalene, acenaphthene, phenanthrene, anthracene, pyrene, and fluoranthene which are associated with low temperature pyrolytic processes. Carcinogenic and combustion derived PAHs contributed 18 and 41.3 % respectively to ΣPAHs

**Index Terms**— PM<sub>10</sub>, dichloromethane, gas chromatography

## I. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants, which mainly originate from incomplete combustion of fossil fuels and wood (Terzi and Samara, 2004). Polycyclic aromatic hydrocarbons [PAHs] have received serious attention owing to their potential toxic, carcinogenic and mutagenic effects (Ames et al., 1975), and particulate-phase PAHs are considered to be a significant hazard to human health through breathing (Spurny, 1996). In view of this health concern, monitoring the level of priority PAHs in urban areas has become more important (Chetwittachan et al., 2002). Due to the rapid growth of industrial activities, city populations and traffic density, the PAHs in urban atmospheres are almost dominated by anthropogenic origin, while the contribution from natural sources (forest burning, volcanic emissions, etc.) is limited. Thus, it is important to understand abundance, distribution and potential sources of PAHs in PM<sub>10</sub> (particles having aerodynamic diameter, ≤10 µm) so that the diverse effects caused by particulate matter can be efficiently controlled. Atmospheric PAHs concentrations especially in developed

countries has become a major concern for environmental scientists and policy makers (Liu et al., 2007).

The aim of this study was to investigate the distribution of atmospheric PAHs in the urban air of Yamuna Nagar (Haryana), estimate the percent abundance of 2, 3, 4 and 5 ring compounds, identification of carcinogenic and combustion derived PAHs.

## II. METHODOLOGY

For the present study, sampling was conducted on the roof of double storied building in residential area of Yamuna Nagar, Haryana. PM<sub>2.5</sub> aerosols were collected using fine particulate sampler with Wins-Anderson Impactor (APM 550) with sharp cut points of 10 µm and 2.5 µm. Samples were collected on desiccated and pre-weighed Whatmann glass micro fibre filters (47 mm diameter) at a flow rate of 16.6 LPM (litres per minute) for 24 hours. After sampling all filters were again desiccated and weighed till constant weight. The filters were then sealed in polyethylene zip-lock bags wrapped in aluminium foils and stored at 4°C until analysis. From the difference of the initial and final weights the mass concentration of fine particulate matter was calculated. Sampling was performed every third day in the month of October, 2011 collecting a total of 10 samples. To monitor the background contamination, un-exposed filters (operational blanks) were processed simultaneously with field samples.

The filters were cut into small pieces and extracted ultrasonically thrice with 150 ml of Dichloromethane (DCM). Each extraction lasted for 45 minutes. The organic extract was filtered and concentrated on Buchi Rotavapour at a bath temperature of ≤ 40°C. The extract was cleaned employing a silica gel column of 15cm length and 1.5cm diameter. To remove the interference of aliphatic hydrocarbons the column was first eluted by 50 ml of hexane followed by a second elution by DCM : hexane (1:1). This fraction containing the PAHs was again concentrated by rotary evaporation, reduced to dryness under a gentle stream of N<sub>2</sub> and re-dissolved in DCM to 1.5ml. The samples were stored in glass vials wrapped in aluminum foil and stored at low temperature until analysis.

**Jitendra Dubey**, Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra (UP)

**Vyoma Singla**, Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra (UP)

**K. Maharaj Kumari**, Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra (UP)

**Anita Lakhani**, Department of Chemistry, Dayalbagh Educational Institute, Dayalbagh, Agra (UP)

PAHs were analyzed in the splitless mode using a temperature gradient program by Gas Chromatograph (Shimadzu 17AATF, version 3.0) equipped with a Flame Ionization Detector (FID) and capillary column (25 m length, 0.3 mm internal diameter: BP) with dimethyl polysiloxane as stationary phase. Nitrogen was the carrier gas at a flow rate of 12.7 ml /min. The oven temperature was held at 40°C for 5 minutes and programmed to rise to 179°C at 10°C / min, held for 2 minutes and then elevated to 300°C at 9°C/min. The temperature of injector and detector was maintained at 210°C and 310°C respectively. The GC was calibrated with a standard solution of 16 PAH compounds (Supelco EPA 610 PAH mixture). The procured PAH mixture contained the following 16 EPA priority PAHs in mixed solvent (methanol: dichloromethane; vol/vol, 1:1); naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phen), anthracene (Anth), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chy), benzo(b)fluoranthrene (BbF), benzo(k)fluoranthrene (BkF), benzo (a) pyrene (BaP), dibenzo (a,h) anthracene (DbA), benzo (ghi) perylene (BghiP) and indeno (1,2,3-cd) pyrene (IP). Five point calibration curves for all the target analytes were obtained by analysis of serial dilution of PAH standard. Calibration curves were plotted by regression analysis. 1 µl of the extracted sample was injected into GC and the program was set to run for 40 minutes. Individual PAH was identified by comparing its retention time with the standard chromatogram. Each PAH compound was quantified by plotting its peak area on the regression curve of standard. The compounds phenanthrene and anthracene, chrysene and benzo(A) anthracene, benzo(b)fluranthrene (BbF) and benzo(k)fluranthrene (BkF), co-elute, hence these pair of compounds have been reported as their sums. IP, DbA and BghiP were below detection limits in all the samples.

### III. RESULTS AND DISCUSSION

The mass concentration of PM<sub>10</sub> ranged from 246.2 to 622.3 µg/m<sup>3</sup> with an average of 360.85 µg/m<sup>3</sup>. All samples were found above the 24 h average NAAQ standard of 40 µg/m<sup>3</sup>. The observations are found to be consistent with earlier studies reported in India (Sharma et al., 2007; Mohanraj et al., 2011).

There was a significant variation in the PAH concentrations over the sampling period. The concentrations of the PAHs in PM<sub>10</sub> are given in Table1. The average concentration of individual compounds varied between 44.5 to 149.1 ng/m<sup>3</sup>. The average values of total PAHs was 1006.8 ng/ m<sup>3</sup> (sum of all measured PAHs). This is comparatively higher than those reported from Amritsar (154 ng/ m<sup>3</sup>, Kaur et al., 2013), Agra (120 ng/m<sup>3</sup>, Rajput et al., 2010), Delhi (668-672 ng/ m<sup>3</sup>, Sharma et al., 2007), Hong Kong (5.30 ng /m<sup>3</sup>, Chang et al.,

2012) and lower than Giza (1430 ng/ m<sup>3</sup>, Hassan and Khoder, 2012) and Agra (1455.5 ng/m<sup>3</sup>, Singla et al, 2012). The major PAH compounds in PM<sub>10</sub> at the monitoring site were Ace, Fla, Nap, Anth+Phen and Pyrene. These are mainly reported to originate from motor vehicles, coal, wood, bio-mass and refuse combustion. The PAH concentration was dominated by 3 and 4 ring compounds (almost >75%) followed by 2 ring and 5 ring compounds. The dominance of the 2 and 3 ring compounds suggests that low temperature pyrolysis (combustion) is the main source of PAHs in the study area. Flu, Pyr, Chy, BbF, BkF, BaA, BaP, IP and BghiP are the main combustion derived PAHs (COMPAHs) (Bourotte et al., 2005). They accounted for 41.3% of the total PAHs. The seven PAHs (BaA, BaP, BbF, BkF, Chy, DbA, and IP) are suggested to be probable human carcinogens (CANPAHs) (IARC 2006), they comprised 18% of ΣPAHs (Table 1). PAHs are reported to have carcinogenic, mutagenic, teratogenic, and endocrine-disruptive effects on human health (Jia et al., 2011, Hawliczek et al., 2012, Vu et al., 2012). The mean concentration and the range of BaP in ambient air was 44.5 and 32.9-67.3 ng/m<sup>3</sup>, respectively. According to The World Health Organization the acceptable unit risk for lung cancer is 87×10<sup>-6</sup> ng (BaP)/m<sup>3</sup> for a life time of cumulative exposure. The acceptable level represents the increase of cancer by one in the group of million of people (USEPA, 1993). Exposure to PAHs is strongly suspected to increase lung cancer risk (Jia et al. 2011; Vu et al. 2012).

Table1- Concentrations (ng /m<sup>3</sup>) of PAHs in PM<sub>10</sub>.

PAHs	No. of Rings	Study Period			
		Mean	Min	Max	Percentage of ΣPAHs
Nap	2	127.1	34.4	276.5	12.6
Acy	3	82.5	69.6	113.6	8.2
Ace	3	115.6	84.3	175.1	11.5
Flu	3	67.3	21.2	89.7	6.6
Anth+Phen	3	149.1	74.7	238.1	14.8
Pyr	4	167.7	97.2	22.3	16.6
Fla	4	116.0	76.9	184.5	11.5
Chy+BaA	4	66.6	11.2	217.0	6.6
BbF+BkF	5	70.4	30.0	147.1	7.0
BaP	5	44.5	32.9	67.3	4.4
ΣPAHs		1006.8	11.2	276.5	100
ΣCANPAHs		181.5	11.2	217.0	18.0
ΣCOMPAHs		416.5	11.2	217.0	14.4

#### IV. CONCLUSION

In this study, concentrations of ambient air polycyclic aromatic hydrocarbons bound to PM<sub>10</sub> were monitored during the month of October, 2011 in Yamuna Nagar (Haryana, India). Results showed that the average concentrations of Σ16 PAHs was 1006.8 ng/m<sup>3</sup> which is higher than those reported from several sites in India. The PAH concentration was dominated by three and four ring compounds (almost >75%) followed by 2 ring and 5 ring compounds, indicating mixed sources i.e. from gasoline and diesel vehicle exhausts, with some contribution from coal, wood and biomass combustion. Carcinogenic and combustion derived PAHs contributed 18 and 41.3 % to ΣPAHs.

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