Identification of Polycyclic Aromatic Hydrocarbons in Atmospheric Particles of PM_{10} at Agra, India.

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Abstract— **Polycyclic aromatic hydrocarbons (PAHs) have been widely accepted as a class of ubiquitous and mutagenic environmental pollutants and attracted much attention in previous studies on air pollution recently. PAHs are products of incomplete combustion and pyrolysis of fossil fuels such as petroleum and coal and other organic materials from natural and anthropogenic sources the urban atmosphere. Sixteen polycyclic aromatic hydrocarbons were determined in PM_{10} (particulate matter with aerodynamic diameter $\leq$ 10 µm) collected at Agra from July 2010-December 2012 using Fine Particulate Sampler (Envirotech APM 550) on 47mm glass micro fibre filters The filters were extracted in ultrasonic bath with dichloromethane and analyzed by gas chromatography (Shimadzu 17A). Results show that the total PAHs concentrations varied between 20.2 ng/m^3 to 3214.1 ng/m^3 while the concentration of individual compounds ranged from 55.2 ng/m^3 to163.8 ng/m^3. PAH concentrations exhibited seasonal variation with maximum values in winter (1978.25 ng/m^3) followed by monsoon (1467.3 ng/m^3), post monsoon (1367.9 ng/m^3) and summer (1240.8 ng/m^3), respectively. Meteorological conditions such as wind speed and temperature, solar intensity, relative humidity had a strong influence on the seasonal variation. 3& 4 ring PAHs were the abundant compounds and accounted for 59.19–83.7% of TPAHs. Carcinogenic PAHs contributed 31.49% to total PAHs while the contribution of combustion derived PAHs was 49.87% to total PAHs**

Index Terms— **Polycyclic aromatic hydrocarbons (PAHs), PM_{10}, Envirotech APM 550.**

I. INTRODUCTION

Particulate matter (PM) is a ubiquitous component of the atmosphere and has become a persistent and pervasive environmental problem that imposes significant health risk attributable to the complexity in particle size and chemical composition. Exposure to particulate matter has recently received considerable attention as a result of epidemiological findings showing association between ambient their concentrations and mortality (Pope, 2000; Van *et al.,* 2004). Recent epidemiological studies have suggested that an increase in the concentration of inhaled particles of 10 mg/ m^3 is associated with a 1% increase in premature mortality (Schwartz *et al.,* 1996). Fine and ultrafine aerosol particles can be transported long distances, penetrate deep into the lungs and can elicit mutagenic and carcinogenic effects. Thus, due to its potential health impact, PM_{10} (particulate matter $\leq$10 µm in diameter) has been widely studied to assess and

regulate air quality. Particles with an aerodynamic diameter <10 µm (PM_{10}) can deposit and accumulate in the respiratory system representing a significant threat to human health (WHO, 2000; Hauser *et al.,* 2001). Polycyclic aromatic hydrocarbons [PAHs] have received serious attention owing to their potential toxic, carcinogenic and mutagenic effects. Particulate-phase PAHs in particular are considered to be a significant hazard to human health through breathing (Spurny, 1996). In view of this health concern, monitoring the level of PAHs in urban areas has become more important. Thus, it is important to understand abundance, distribution and potential sources of PAHs in PM_{10} so that the diverse effects caused by particulate matter can be efficiently controlled. Many of these PAH compounds have been classified as possible or probable carcinogens (IARC, 1983), for example benzo(a)pyrene [B(a)P] has been directly linked to lung cancer through its selective adducts along a tumor suppressor gene (Denissenko *et al.,* 1996). PAHs are mainly emitted from incomplete combustion processes associated with anthropogenic and natural sources such as volcanic eruptions and forest fires (Jenkins *et al.,*1996; Finlayson-Pitts and Pitts, 2000). Approximately 90% of PAHs emissions are estimated to be emitted from anthropogenic sources typically including the combustion of fossil fuels, industrial processes and domestic heating systems (Benner and Wise, 1989; Rogge *et al.,* 1993a, b). Vehicular traffic is considered to be the major contributor to the urban atmosphere (Schauer *et al.,* 1996; Fang *et al.,* 2004; Yang and Chen, 2004).

Atmospheric PAHs are partitioned between the particulate and the gaseous phase. PAHs emitted in gaseous form may be condensed into the particulate phase mostly with $PM_{2.5}$ (Sicre *et al.,*1987) and may later accumulate on larger particle sizes (Miguel *et al.,* 2004) and thus could be present in both particulate (p-PAHs) and gaseous form (g-PAHs). However, the carcinogenic 5, 6- ring PAHs are predominantly associated with particles. The composition of PAHs in any phase changes significantly according to their emission sources, this feature can be used to identify possible emission sources (Barale *et al.,*1991; Venkataraman *et al.,*1994) which in turn serves as the basis for exposure regulations through emission control and for public health measures. The total number of PAHs and their individual mass concentration play important roles in exposure and risk assessment, while the PAHs size distribution has an impact on the site and type of patho-physiological lesions in the exposed personnel. Since the carcinogenic PAH concentrations may be taken as an 'index' for the biologically active (mutagenic, genotoxic, embryo toxic) components in air particulate samples, their high-quality monitoring data may be useful for related epidemiological studies. At Agra, urban and suburban areas are likely to be highly polluted due to industrial activities, traffic density and firewood combustion. The current study was implemented with the major objective of assessing the

exposure levels of 16 US EPA prioritized PAHs of respirable PM$_{10}$ in ambient air. The PAH compounds under study were: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorine (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chy), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenz(a,h)anthracene (DbA), Benzo(g,h,i) perylene (BghiP) and Indeno (1,2,3-c,d) pyrene (IP).

II. METHODOLOGY

Description of Sampling Site

Agra is situated in the extreme southwest corner of Uttar Pradesh. It stretches across 26º 44'N to 27º 25'N and 77º 26'E to 78º 32'E. Its borders touch Rajasthan to its west and south, the district of Firozabad to its East and the districts of Mathura and Etah to its North. It is situated on the banks of river Yamuna; it has a limited forest area supporting mainly deciduous trees. According to census 2001, the area of Agra district is 4027 km^2 with a total population of about 1,316,177 and density about 21,148 of km^2 with 386,635 vehicles registered and 32,030 generator sets. In Agra, 60% pollution is due to vehicles [RTO, 2008]. Three National Highways (NH-2, NH-11 and NH-3) pass through the city. Like most cities of north India, the weather and climate of Agra is extreme and tropical. Agra suffers from extremities of climate with scorching hot summers and chilly winters. It is about 169 m above the mean sea level and has a semiarid climate with atmospheric temperature ranging from 11-48°C (maximum) and 0.7-30°C (minimum), relative humidity 25-95%, light intensity 0.7-5.6 oktas (cloudiness) and rainfall 650 mm per year. The climate of Agra has been broadly divided into four seasons: winter (December to February), summer (March to June), monsoon (July to September) and post-monsoon (October to November). During monsoon period the temperature ranges between 26 and 39°C and relative humidity varies between 70 and 100% respectively. The winter months are cool, temperature ranges between 2 to 15°C while relative humidity is 60 to 90%. Summers are characterized by high temperature ranging between 23 to 45°C and low relative humidity 25 to 40%.

Sampling was conducted on the roof of the faculty building in the Institute at Dayalbagh. The site is dominated primarily by agricultural areas towards its north but about 2 km south of the site lies a busy roadway intersection situated on the National Highway No.2 (NH-2). NH-2 connects Delhi to Kolkata via Agra and is one of the busiest Highways. On an average six to seven thousand vehicles ply on this highway and comprise about 3500 light motor vehicles (LMV), 500 light commercial vehicles (LCV's) and 2500 heavy commercial vehicles (HCV) [NHAI, 2007]. PM$_{10}$ 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 Whatman glass microfiber filters (47 mm diameter) at a flow rate of 16.6 liter 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 and stored at 4ºC until analysis. From the difference of the initial and final weights and volume of air sampled, the mass concentration of fine particulate matter was calculated by dividing mass deposited by volume of air.

Monitoring of Meteorological Parameters

Meteorological data such as ambient temperature, rainfall, relative humidity, wind speed and wind direction were recorded through an automatic weather monitoring system (Envirotech's Wind Monitor WM271) mounted on the roof 8m above the ground level at the sampling site. It was programmed to collect data at 1 minute interval and store them in memory to be downloaded to a computer and software.

Extraction

The filters were cut into small pieces and extracted in Dichloromethane (DCM) by ultra-sonication for about two hours with an interval of 5 minutes at every 15 minutes. The extract was filtered through Whatman filter paper and cleaned through column chromatography employing silica gel column of 15 cm length and 1.5 cm diameter. These extracts were concentrated by rotary evaporator and finally reduced to 2 ml under the stream of nitrogen gas and stored in a Teflon vial at a low temperature until analysis of PAHs.

III. ANALYSIS

PAHs were analyzed in the split less mode using a temperature gradient program by Gas Chromatograph (GC, Shimadzu 17AATF, version 3.0) equipped with a FID detector 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^{-1}. The oven temperature was held at 40°C for 5 minutes and programmed to rise to 179°C at 10°C min^{-1}, held for 2 minutes and then elevated to 300°C at 9°C min^{-1}. The temperature of injector and detector was maintained at 210 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), Acenapthylene (Acy), Acenapthene (Ace), Fluorene (Flu), Phenanthrene (Phen), Anthracene (Anth), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chy), Benzo(b)fluranthrene (BbF), Benzo(k)fluranthene (BkF), Benzo(a)pyrene (BaP), Dibenzo(a,h) anthracene (DbA), Benzo(ghi)perylene (BghiP), Indeno (1,2,3-c,d)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. 1µl of the extracted sample was injected into GC and the program was run for 40 minutes. Individual PAH were identified by comparing their 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), Benzo(k)fluranthene (BkF), co-elute. Therefpre in the present study these pair of compounds have been reported as their sums.

Quality Control and Assurance

The limits of detection (LOD) for PAHs were determined through repeated runs (n=6) of respective standard of lowest concentration. The LOD was based as three times the observed standard deviation of six replicate analyses of the lowest standard (Notar and Leskovsek, 2000). PAH concentrations only above their corresponding LOD are reported here.

IV. RESULTS AND DISCUSSION

Mass Concentration of PM_{10}

PM_{10} were collected from July 2010-December 2012. PM_{10} mass concentration ranged from 24.1 to 124.0 $\mu g/m^3$ in monsoon (geometric mean (GM), 49.8 ± 0.9 $\mu g/m^3$), 35.8 to 420.9 $\mu g/m^3$ in post monsoon (GM, 197.3 ± 1.3 $\mu g/m^3$), 18.2 to 599.5 $\mu g/m^3$ in summer (GM, 148.0 ± 1.3 $\mu g/m^3$) and 110.9 to 593.3 $\mu g/m^3$ in winter (GM, 281.8 ± 2.1 $\mu g/m^3$) with an annual average of 126.5 ± 1.1 $\mu g/m^3$. A comparison of the mass concentrations of PM_{10} in different seasons is displayed in Fig. 1. 86% of PM_{10} samples were found above the NAAQS standards of 40 $\mu g/m^3$. The observations are found to be consistent with earlier studies reported in India (Sharma et al., 2007; Mohanraj et al., 2010).
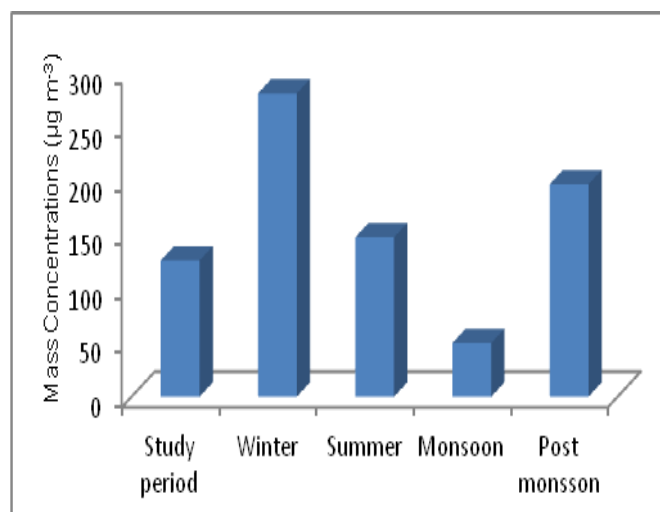

Fig. 1- Seasonal variation in mass concentration of PM_{10}

PAH concentrations in PM_{10}

16 PAH compounds [Napthalene (Nap), Acenapthalene (Ace), Acynapthalene (Acy), Anthracene (Anth), Phenanthrene (Phen), Fluorene (Flu), Fluoranthene (Fla), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chy), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Benzo(ghi)pyrelene (BghiP), Dibenzoanthracec (DbA), Indeno(123-c,d)pyrene (IP)] were determined in the samples by gas chromatography. Among these 16 compounds BghiP, DbA and IP were below detection limit in most of the samples, hence they have been excluded from further analysis. The geometric mean concentrations are presented in Table 1. The concentration of individual compounds varied between 55.2 ng/m^3 to 191.4 ng/m^3, while summed PAH mass concentration (ΣPAHs) in

PM_{10} varied between 20.1 to 3214 ng/m^3. On an average, PAHs accounted for 0.51% of the PM_{10} mass. The annual as well as the seasonal mean values of Total PAHs (sum of all measured PAHs) in this area are much higher than those reported for Amritsar (154 ng/m^3, Kaur et al., 2013), Agra (120 ng/m^3, Rajput et al., 2010), Delhi (668-672 ng/m^3, Sharma et al., 2007), London (17.23 ng/m^3, Baek et al.,1992; Brown et al.,1996), Hong Kong (5.30 ng/m^3, Chang et al., 2012) and moderately higher than Giza (1430 ng/m^3, Hassan and Khoder, 2012).

The major PAH compounds in PM_{10} at the monitoring site were Benzo(b)fluoranthene, Fluoranthene, Acenaphthylene, Benzo(a)anthracene, Anthracene, Phenanthrene, Chrysene, Pyrene and Naphthalene. These are strongly related to emissions from motor vehicles, coal, wood, bio-mass and refuse combustion. The composition of PAHs depends on the combustion temperature. At low to moderate temperature, as in the wood stove or as from the combustion of coal, low molecular weight PAH compounds are abundant, whereas, at higher temperature, such as in the vehicle emissions, the higher molecular weight PAH compounds are dominant (Zhang et al.,2004). The sixteen PAHs can be classified according to their number of aromatic rings: two (Nap), three (Acy, Ace, Flu, Phen, Anth), four (Pyr, Fla, BaA, Chy), five (BbF, BkF, BaP) and six (BghiP, DbA and IP). In this study, on an annual basis three and four ring compounds were dominant (almost >59%) in all seasons, indicating mixed sources (Fig. 2). The two ring compounds were predominant in summer while in winter the three ring compounds were dominant. 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. Moreover, the low molecular weight (2–3 ring) PAHs are dominantly present in gaseous phase in the atmosphere and during interactions with aerosols in the atmosphere, considerable fraction of these may get adsorbed/ absorbed on the particulate matter thus, resulting in to building up of their higher concentrations. Flu, Pyr, Chy, BbF, BkF, BaA, BaP, IP and BghiP are the main combustion derived PAH (COMPAH) (Bourotte et al., 2005). The sum of these combustion derived PAHs comprised 49.87% of the total PAHs.
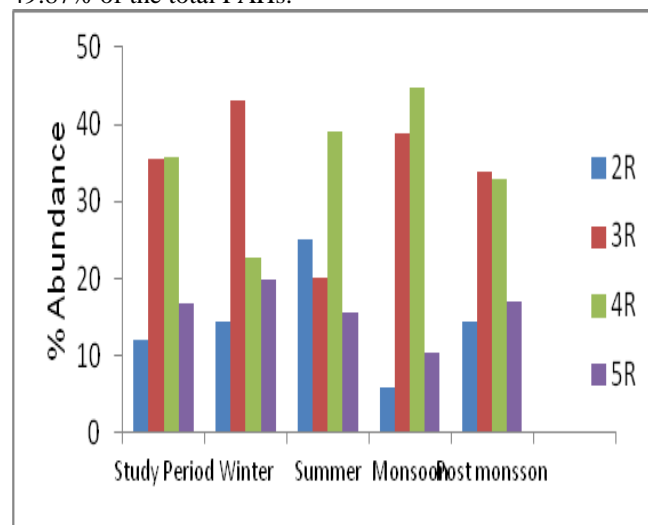

Fig. 2- Abundance of PAH in PM_{10} on the basis of aromatic rings

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Table 1- Seasonal variation of PAHs concentrations
(Geometric Mean in ng/m³)

PAHs	Study Period			Winter			Summer			Monsoon			Post Monsoon			Winter/ Summer Ratio
	Mean	Min	Max	**Mean**	Min	Max	**Mean**	Min	Max	**Mean**	Min	Max	**Mean**	Min	Max	
Nap	**156.5±1.8**	30.5	315.4	**284.0±1.0**	254.6	315.4	**299.5±1.5**	90.9	415.5	**85.0±1.6**	30.5	147.6	**225.3±1.1**	197.5	254.3	0.94
Acy	**111.0±2.1**	19.1	275.5	**234.8±1.1**	215.7	275.5	**101.9±2.3**	43.1	240.7	**112.1±1.7**	55.7	236.9	**82.1±2.1**	19.1	173.4	2.30
Ace	**80.7±3.7**	2.2	310.9	**224.1±9.7**	85.6	310.9	**18.5±4.1**	2.2	119.5	**145.3±1.3**	112.5	271.6	**86.8±2.9**	4.7	215.4	12.12
Flu	**97.9±2.5**	6.3	296.5	**145.8±2.2**	22.4	296.5	**27.8±4.0**	6.3	183.5	**82.2±1.8**	45.4	271.7	**119.5±1.9**	21.9	222.6	5.24
Anth+Phen	**173.4±2.4**	18.2	706.1	**247.1±1.4**	118.6	366.8	**91.9±2.2**	22.1	296.7	**230.5±2.5**	18.2	706.1	**173.8±2.1**	37.6	413.1	2.68
Pyr	**142.1±2.0**	11.9	516.5	**102.3±1.5**	50.5	199.7	**108.2±3.3**	11.9	287.7	**234.5±1.4**	133.4	516.5	**141.5±1.7**	61.7	328.8	0.94
Fla	**133.0±2.8**	4.9	902.4	**225.4±1.4**	137.8	573.9	**72.5±3.7**	4.9	315.4	**159.1±2.3**	56.2	902.4	**134.2±2.5**	23.5	485.1	3.11
Chy+ BaA	**191.4±3.1**	5.1	584.7	**122.4±4.8**	5.1	520.4	**284.0±1.2**	231.7	348.2	**264.4±1.4**	130.8	569.5	**172.7±3.6**	5.2	584.7	0.43
BbF+Bkf	**164.7±1.1**	54.3	555.1	**303.0±1.4**	206.9	555.1	**146.8±1.6**	79.9	305.1	**110.4±1.5**	54.3	183.3	**179.2±1.5**	98.7	346.9	2.06
BaP	**55.2±1.8**	15.9	162.6	**88.8±1.4**	60.6	162.6	**39.4±1.1**	89.4	89.4	**43.3±1.8**	15.9	133.3	**52.5±1.5**	28.9	101.5	0.99
Σ PAHs	**1306.3**			**1978.2**			**1240.8**			**1467.3**			**1367.9**			
ΣCAN PAHs	**411.4**			**514.3**			**520.3**			**418.2**			**404.5**			
Σ COMPAHs	**651.4**			**762.5**			**606.4**			**735.0**			**665.6**			

Seasonal Variation of PAH

Relatively higher concentrations of PAHs were found in winter as compared with other seasons as shown in Table 1. Source emissions and meteorological conditions as well as gas particle partitioning may result in winter and summer difference of PAHs concentrations (Harrison, 2004). Emissions increased obviously owing to the fossil fuel usage for space heating which was one reason for the higher concentrations in winter. The cold start conditions for the vehicles in winter may also contribute to the higher PAHs concentrations. Lower temperatures and atmospheric mixing heights as well as decreased photochemical oxidation intensity can also explain the higher PAHs concentrations in winter (Lobscheid, 2007). PAHs belong to the semi-volatile organic contaminants and occur in both gaseous and particulate phases in the atmosphere. 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 (Zonguldak *et al.,* 2007, Akyuz *et al.,* 2008). Conversely, a higher ambient temperature in summer could change the distribution of PAHs between the gaseous and particulate phases by increasing the vapor pressure of pollutants that adhered to atmospheric aerosols, favoring the volatilization of PAHs from the particulate to gaseous phase, but it could also increase the mixing height of the atmosphere resulting in excellent dilution and dispersion of PAHs and hence reduce them. Ambient air concentrations of PAHs were temperature-dependent. In this study, high molecular weight PAHs had a higher contribution in the summer while low molecular weight PAHs had a higher contribution in the winter. For instance, (BbF +BkF) and BaP occupied about 19.8 and 19.0 % of the ΣPAHs in winter and summer respectively, whereas in monsoon their contribution reduced to 10.47%. Lower concentrations in the monsoon are probably due to wash out effects. Higher PAHs concentrations in winter and lower concentrations in summer were also widely observed in a previous study on PAH content in TSPM in Agra (Rajput *et al.,* 2010), Lucknow (Pandey *et al.,* 2013) and some Asian cities like Guangzhou (Harrison *et al.,* 2004), Taichung (Zonguldak *et al.,* 2007).

V. HEALTH RISK ASSESSMENT

Low molecular weight PAHs with two, three and four aromatic rings produce fewer toxic impacts compared with the high molecular weight PAHs, which contain five to six aromatic rings (ATSDR, 1990). The PAHs BaA, BaP, BbF, BkF, Chy, DbA, and IP have been identified as probable human carcinogens (USEPA, 1994; IARC, 2006). These carcinogenic species ranged between 5.1 to 584.7 ng/m³ (GM 101.6 ng/m³) and accounted for 31.49 % of ΣPAHs. The carcinogenic PAHs also showed seasonal variation with contributions being 26.0, 41.9, 28.5 and 29.5 % in winter, summer, monsoon and post monsoon, respectively (Fig. 3). The concentrations of benzo[a] pyrene, which is often used as an indicator of PAH and regarded by the World Health Organisation (WHO) as a good index for PAH carcinogenicity, were in the range of 15.9 to 162.6 ng/m³. In principle, the health risk assessment of PAHs can be assessed based on its BaP equivalent concentration (BaPeq). The carcinogenic potency of total PAHs can be assessed by the sum of the BaPeq concentrations of each PAHs. BaPeq concentration for each PAHs was calculated by multiplying its concentration with the corresponding toxic equivalent factor (TEF) which represents the relative carcinogenic potency of the corresponding PAH suggested by Nisbet and Lagoy (Hong *et al.,* 2007, Akyuz *et al.,* 2008). The total BaPeq concentrations were found to be 88.8 ng /m³. The annual mean BaPeq concentrations at Agra (88.85 ng/m³) are higher when compared to particulate samples from other urban atmospheres, Liaoning (40.05 ng/m³, Kong *et al.,* 2010), Florence (0.916 ng/m³, Lodovici *et al.,* 2003), Zonguldak (14.1 ng/m³, Akyuz *et al.,* 2009) and Nanjing (7.1 ng/m³, Wang *et al.,*2006). The observed BaPeq

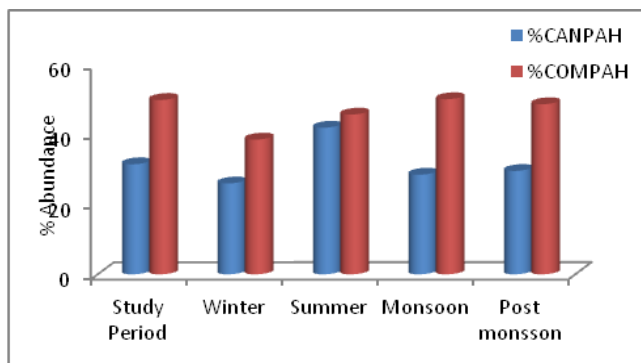concentrations are an alarming signal for pollution risks in relation to human health.

Fig. 3- Comparative study of Carcinogenic and combustion derived PAHs

VI. CONCLUSIONS

Sixteen polycyclic aromatic hydrocarbons were identified and quantified in the PM10 during the period from July 2010 to December 2012. It was observed that ambient air particle (PM10)-bound PAHs were higher or comparable with those of other cities of India and a few overseas countries. Levels of PM_{10} and PM_{10}-associated PAHs also showed distinct seasonal variations with peak levels in winter and post monsoon, respectively. The concentration of individual compounds varied between 55.2 to 163.8 ng/m^3, while summed PAH mass concentration (ΣPAHs) in PM_{10} varied between 20.1 to 3214 ng /m^3. The dominance of three- to four-aromatic–ring PAHs in the majority of samples indicates that biomass combustion and vehicle emissions were the predominant sources. The concentration of total combustion derived and carcinogenic PAHs bound to ambient air particles (PM_{10}) of Agra accounted for 52.2% and 35.7% of ΣPAHs, which comes from combustion sources.

Estimation of health risk associated with exposure to these compounds was made by using BaPeq than using the simple concentrations of BaP. The potential BaPeq, based on total concentration is 88.8 ng/m3 is larger than the limits of 1 ng/m3 set by various legislations.

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