Seasonal Variation and Sources of Polycyclic Aromatic Hydrocarbons (PAHs) in Indoor and Outdoor Air in a Semi Arid Tract of Northern India

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ABSTRACT

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

Keywords: Indoor and outdoor air; Gas/Particulate; PAHs; Seasonality; Toxic assessment; Source apportionment.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), formed mainly during carbonization and incomplete combustion of organic materials (Lin *et al*., 2009), and have been widely investigated due to their potentially carcinogenic and mutagenic nature (Kawai *et al*., 1967; NRC, 1983). They are also generated by combustion sources inside house and workplaces (Lin *et al*, 2009), such as burning of candles and incense, cigrate smoking, cooking, fuel burning, domestic heating, and so on. In addition, people spend more than 80% of their time indoors (NRC, 1981), thus is important to evaluate indoor and outdoor PAH characteristics for assessing total human exposure to PAH.

In the past, great number studies were conducted to characterize ambient PAHs in the particulate phase in different parts of the world (Harkow *et al*., 1985; Menichine *et al*., 1992; Li and Ro, 2000). In addition the influences, meteorological factors on the distributions of gaseous and particulate phase as well as size distributions of particulate PAHs were also evaluated (Kamens *et al*., 1986). However, there have only been few field investigations undertaken to investigate composition characteristics of indoor PAHs (Offerman *et al*., 1983; Mumford *et al*., 1989; Daisey *et al*., 1989; Chuang *et al*., 1992; Mitra and Wilson, 1992; Li and Ro, 2000), and their relationship with the corresponding outdoor PAHs. The studies indicated that indoor PAH concentrations always exceed outdoor PAH concentrations with certain combustion sources (Mumford *et al*., 1989; Wilson *et al*., 1989; Chuang *et al*., 1991). Moreover, PAH levels in winter were observed to be higher than the summer season concentrations in Europe, North America, Australia and Japan (Li and Ro, 2000).

Recently, attention has been paid to the deterioration of air quality in metropolitan areas from the global standpoint as the cities are steadily increasing in both number and size (Gurjar and Lelieveld, 2005; Gurjar *et al*., 2010). The situation is even more severe in Asia with the economic development of the most densely-populated area in the world. India has experienced rapid urbanization and industrial expansion resulting in increased utilization of fossil fuels

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in automobiles, trucks and public transportation. Agra is no exception to it, moreover it has an arid climate that may further aggravate pollution levels resulting in enormous levels of respirable suspended particulate matter (RSPM), which have been reported to vary between 167 µg/m^3 and 274 µg/m^3 (Parivesh, 2009).

Few studies (Lawrence *et al.*, 2005; Taneja *et al.*, 2008; Massey *et al.*, 2009) have explored gaseous and particulate pollutants in indoor and outdoor microenvironment of this region along with the characterization of PM$_{10}$, PM$_{5.0}$, and PM$_{2.5}$ with respect to its water soluble constituents, ions and metals (Kulshrestha *et al.*, 2009a, b). Less attention has been paid on monitoring of Persistent organic pollutants (POPs), especially PAHs that requires more elaborate sampling and analytical protocols. Short term studies in ambient air related to PAHs in particulate phase only have been conducted in this area ignoring the gaseous phase (Rajput *et al.*, 2009; Masih *et al.*, 2010a). Although gas phase PAHs have weaker carcinogenic/mutagenic properties, they are the most abundant in the urban atmosphere and react with other pollutants to form more toxic derivatives (Akyuz *et al.*, 2010). Through this study seasonal variation of PAHs is being explored for gaseous as well as particulate phase PAHs for the first time in indoor and outdoor air of the homes in this region. The results of the present study can be useful for assessing health risk and for environmental policy making regarding indoor/outdoor PAHs pollution caused by both vehicular as well as domestic combustion sources in different microenvironments.

MATERIALS AND METHODS

Site Description

Agra, the city of Taj (27°10'N, 78°02'E) is located in the north central part of India about 204 km South of Delhi in the Indian State of Uttar Pradesh. It is one of the most famous tourist spots because of the presence of Taj Mahal and situated on the west bank of river the Yamuna. It is bounded by the Thar Desert of Rajasthan on its South East, West and North West peripheries and is therefore, a semiarid area (Kulshrestha *et al.*, 2009b). During summer the climate is hot and dry with temperature ranging from 32°C to 48°C. In winter the temperature ranges from 3.5°C to 30.5°C. The downwind is South–South–East i.e. SSE 29% and North–East i.e. NE 6% in summers and it is West–North–West i.e. WNW 9.4% and North–North–West i.e. NNW 11.8% in winters. The average concentration of meteorological parameters is shown in Table 1. The atmospheric pollution load is high because of downwind sources. Agra has around 13, 11,000 inhabitants and population density is about 21,148 persons per sq. Km. It has 386,635 registered

vehicles and 32,030 diesel power generator sets. In Agra, 60% pollution is due to vehicular emission. Three national highways cross the city with high vehicular traffic of about 105 vehicles per day (Kulshrestha *et al.*, 2009a).

Sampling and Analysis

For sampling five urban residential homes situated in those areas which have little traffic and lots of greenery in the vicinity, five roadside homes with heavy traffic density was selected as shown in Fig. 1. Handy Sampler HS-7A (K.D.M Instruments), New Delhi, India was used to collect PAH samples. Sampling was done once in a week for a period of eight months. For PAH the pump was set at a flow rate of 2 L/min for 24 hrs (6 am to 24 hrs) aspirating air through two stage XAD-2 resin tubes (600 mg, SKC, Inc. Catalog No. 226-30-06) to retain PAHs in gaseous phase. It is also then followed by a PTFE filter paper (37 µm dia, from SKC) for collecting particulate phase simultaneously. Samples flow was measured before and after sampling using calibrated rotameter with an accuracy of ± 1%. After sampling XAD-2 resin and PTFE filters were placed separately in 4 mL screw-top vials. In each vials 2 mL methylene chloride was added and they were shaken for 2 minutes. These vials were allowed to settle for 30 minutes. From each vials containing XAD resin or filter 1 mL extract was transfer to autosampler vial for further analysis on GC/MS. For Quality Assurance and Quality Control (QA/QC) three sets of XAD-2 tubes and three sets of Filter Blank spike and Blank Spike duplicate (BS/BSDs) were spiked with PAH spiking solution mixture of 23 PAHs (Supelco 4-8902, U.S.A) custom made. The recoveries of each PAH from the XAD-2 tubes and filters ranged between 95 to 120% and 98 to 123% respectively and its relative percent difference (RPD) ranged from 0 to 12%. The limit of quantification for various PAHs ranged from 11.7 ng/m^3 to 115 ng/m^3 and 79% samples of total PAHs exceeded the limit of quantification. All PAH concentration efficiencies and method detection limits were corrected for the 23 PAHs recoveries. No detectable amounts of PAHs were found in any of the blank samples which were extracted in the same way as the regular samples.

The analysis was carried out by gas chromatography/ mass spectrometry (GC/MS) [Hewlett Packard (HP), 6890 GC/5972 MS] controlled by HP enviroquant software operating in selective ion monitoring (SIM) mode as described in detail in our earlier study (Masih *et al.*, 2010b). The detailed procedure of analysis was followed from Response Engineering and analytical Contract (REAC), USEPA. The REAC method is based on modified National Institute for Occupational Safety and Health (NIOSH) method 5515 for the analysis of PAHs in air samples REAC (2002).

Table 1. Average levels of meteorological parameter of summer and winter season.

Parameter	Indoor		Outdoor	
	Summer	Winter	Summer	Winter
Air Temp (°C)	28.5	19.25	32.7	19.2809
Humidity (%)	38.75	64.45	48.34583	61.10696
Wind speed (m/s)	NA	NA	4.690407	1.936048
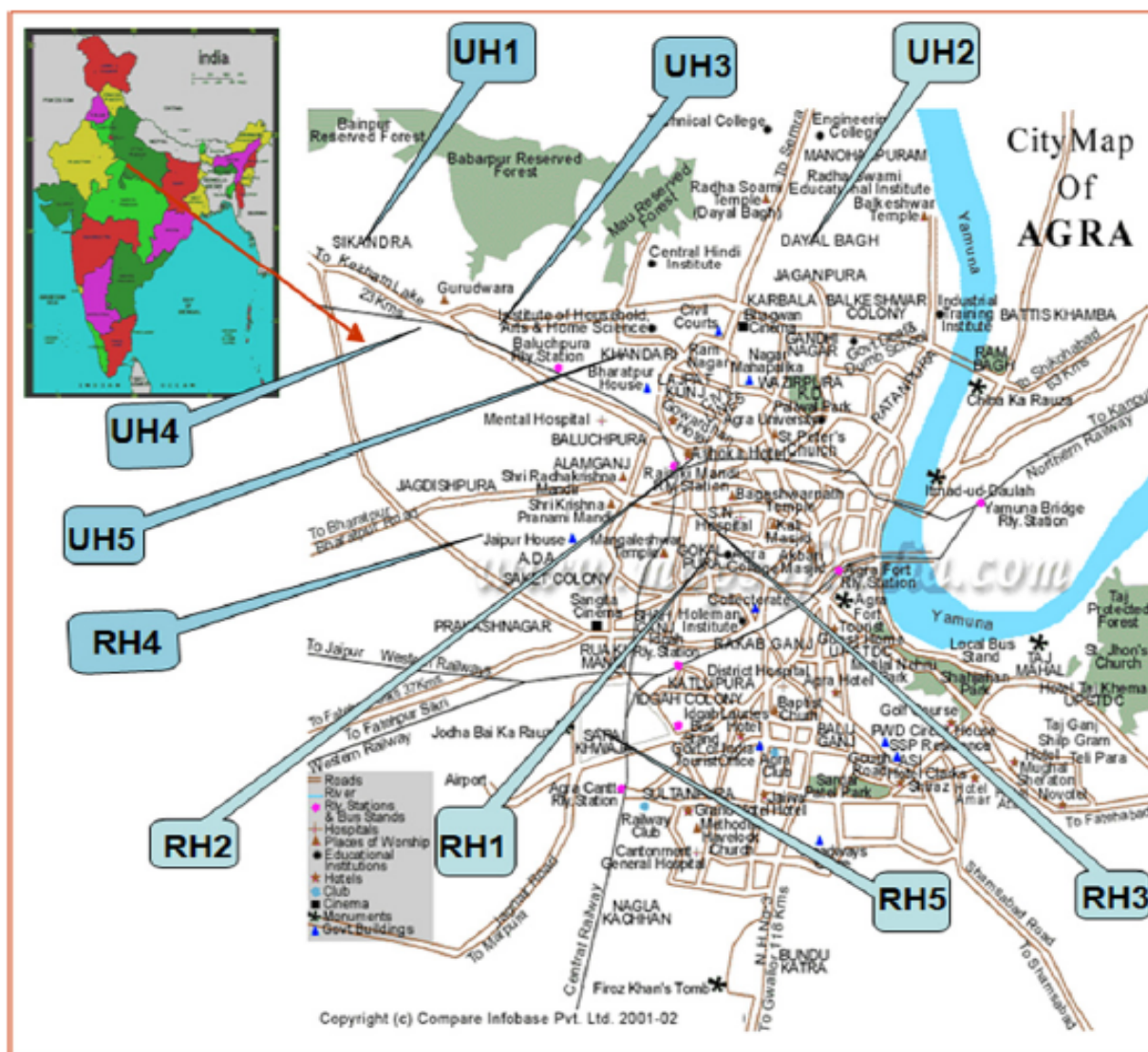
UH-Urban Residential House; RH-Roadside House.

Fig. 1. Map of Agra showing sampling locations.

The concentration of twenty-three identified analytes was calculated by relating the MS response of the quantitation ion produced by the compound that was used as an internal standard. The identified analytes are: Naphthalene (NAP), 2-methylnaphthalene (2MNAP), 1-methylnapthalene (1MNAP), biphenyl (BPHY), 2,6dimethylnapthalene (2,6DMNAP), acenaphthylene (ACY), acenapthene (ACE), dibenzofuran (DBF), flourene (FLU), phenantharene (PHE), anthracene (ANT), carbazole (CAR), fluoranthene (FLT), pyrene (PRY), benzo(a)anthracene [B(a)A], chrysene (CHR), benzo(b)fluoranthene [B(b)F], benzo(k)fluoranthene [B(k)F], benzo(e)pyrene [B(e)P], benzo(a)pyrene [B(a)P], indenol(1,2,3-cd)pyrene [I(123-cd)P], dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene [B(ghi)P].

RESULTS AND DISCUSSION

Seasonal Concentration of PAHs in Gaseous and Particulate Phase

The concentration of PAHs in gaseous and particulate phase in indoors and outdoors of roadside and urban residential homes was determined in Agra India between Nov-2006 to Jun 2007. To investigate the seasonal variation of PAHs concentration in gas and particle phase the year was divided into two periods viz November to February (winter season) and March to June (summer season). The arithmetic mean with standard deviation of individual PAHs in gaseous and particle phase in indoor and outdoor environment in two different seasons at roadside and urban residential site are given in Table 2 and Table 3. Throughout the discussion, the term "Total PAHs" refers to the sum of all detected PAHs in gaseous and particulate phase among selected analytes in the study.

In winter season, the sum of total PAHs (TPAHs) concentration in particulate phase in indoor and outdoor environment at roadside homes was 486.63 ng/m^3, 603.70 ng/m^3 and in summer season it was 159.55 ng/m^3, 149.34 ng/m^3. At urban residential homes the TPAHs concentration

Table 2. Average seasonal concentration of particulate phase PAHs in indoor and outdoor air of roadside and urban residential homes (ng/m³).

PAHs	Raodside				Residential site			
	Winter		Summer		Winter		Summer	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
NAP	114.96 ± 14.11	140.03 ± 27.64	65.72 ± 11.95	87.09 ± 18.41	99.82 ± 17.64	55.77 ± 13.18	75.33 ± 14.56	47.89 ± 5.75
ACY	39.76 ± 9.49	54.56 ± 12.05	10.96 ± 4.90	ND	31.79 ± 7.76	9.93 ± 4.37	15.42 ± 2.88	3.50 ± 1.03
ACE	4.95 ± 1.29	9.37 ± 2.37	ND	ND	2.42 ± 0.59	ND	10.79 ± 2.80	5.07 ± 0.98
DBF	21.91 ± 6.03	26.22 ± 4.30	6.06 ± 3.29	5.74 ± 2.13	11.11 ± 3.17	10.28 ± 3.43	12.45 ± 4.43	7.01 ± 1.31
FLU	17.36 ± 2.71	30.48 ± 20.29	6.32 ± 5.28	8.37 ± 2.39	13.04 ± 3.08	10.00 ± 4.98	12.55 ± 5.30	9.92 ± 1.97
PHE	20.91 ± 6.71	47.91 ± 3.09	20.15 ± 7.02	14.21 ± 4.17	18.50 ± 5.58	11.89 ± 6.07	21.71 ± 7.25	14.51 ± 2.13
ANT	5.26 ± 1.31	2.29 ± 0.53	0.23 ± 0.11	ND	4.47 ± 1.54	13.13 ± 4.89	ND	ND
CAR	ND	70.41 ± 4.29	11.45 ± 2.31	ND	ND	ND	34.46 ± 5.26	ND
FLT	2.57 ± 0.67	10.48 ± 4.75	3.58 ± 1.25	4.18 ± 0.93	2.21 ± 0.79	3.52 ± 0.89	5.88 ± 0.90	4.39 ± 1.05
PRY	2.29 ± 0.64	9.98 ± 5.29	3.62 ± 1.86	ND	1.48 ± 0.96	5.21 ± 2.78	3.79 ± 1.36	4.37 ± 1.55
B(a)A	39.75 ± 11.46	31.34 ± 4.86	4.56 ± 2.88	2.68 ± 1.39	14.02 ± 4.56	ND	2.68 ± 0.45	ND
CHR	32.96 ± 3.24	32.92 ± 6.15	5.57 ± 0.42	2.43 ± 1.37	5.08 ± 1.54	ND	1.25 ± 0.14	ND
B(b)F	53.30 ± 20.43	34.95 ± 7.17	5.73 ± 0.36	ND	11.43 ± 4.80	ND	1.90 ± 0.09	ND
B(K)F	72.13 ± 4.30	18.68 ± 3.87	4.67 ± 2.23	5.52 ± 1.19	3.97 ± 0.89	ND	4.00 ± 1.89	ND
B(e)P	22.51 ± 6.02	18.75 ± 6.78	4.10 ± 1.63	5.10 ± 0.94	3.69 ± 0.50	ND	3.69 ± 1.13	ND
B(a)P	22.35 ± 6.69	28.02 ± 4.12	2.76 ± 1.04	3.55 ± 1.13	5.74 ± 1.07	ND	4.42 ± 1.02	ND
I(123-CD)P	ND	15.74 ± 3.60	ND	6.20 ± 1.57	ND	ND	ND	ND
B(ghi)P	13.66 ± 3.77	21.57 ± 3.63	4.07 ± 1.57	4.27 ± 2.66	4.95 ± 1.79	ND	6.30 ± 1.89	ND
SUM	486.63	603.7	159.55	149.34	233.72	119.73	216.62	96.66

Table 3. Average seasonal concentration of gas phase PAHs in indoor and outdoor air of roadside and urban residential homes (ng/m³).

PAHs	Raodside				Residential site			
	Winter		Summer		Winter		Summer	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
NAP	1159.90 ± 158.17	1251.46 ± 232.12	744.66 ± 129.90	822.11 ± 173.85	942.30 ± 166.53	526.48 ± 124.46	711.15 ± 137.46	452.11 ± 54.32
2MNAP	293.33 ± 39.03	488.38 ± 138.32	143.50 ± 15.04	158.20 ± 44.73	282.50 ± 57.24	217.00 ± 231.96	121.49 ± 7.47	106.00 ± 8.64
1 MNAP	223.31 ± 75.72	336.91 ± 138.59	110.17 ± 48.48	97.42 ± 30.45	173.83 ± 55.28	143.97 ± 34.30	106.99 ± 5.21	78.03 ± 13.68
BPHY	164.49 ± 44.73	221.53 ± 106.36	54.29 ± 23.06	45.99 ± 11.37	79.69 ± 17.16	64.43 ± 8.23	53.27 ± 4.32	52.43 ± 9.00
2,6 DMNAP	127.52 ± 24.67	115.98 ± 14.93	60.90 ± 6.13	70.59 ± 28.01	52.32 ± 17.48	41.90 ± 3.69	61.15 ± 11.24	49.85 ± 12.23
ACY	85.50 ± 20.42	117.31 ± 25.90	23.56 ± 10.55	ND	49.91 ± 12.19	15.60 ± 6.87	24.21 ± 4.53	5.50 ± 2.19
ACE	8.12 ± 2.12	15.37 ± 3.89	ND	ND	3.96 ± 0.97	ND	17.70 ± 4.59	8.32 ± 1.62
DBF	41.42 ± 11.40	49.56 ± 8.13	11.45 ± 1.66	10.85 ± 4.03	20.99 ± 5.99	19.43 ± 6.48	23.54 ± 8.38	13.26 ± 2.48
FLU	20.13 ± 3.15	35.35 ± 23.54	7.33 ± 1.82	9.71 ± 2.77	15.13 ± 3.57	11.61 ± 3.78	14.56 ± 6.15	11.51 ± 2.29
PHE	26.14 ± 8.43	59.89 ± 28.71	25.19 ± 8.77	18.67 ± 5.21	28.03 ± 8.45	18.03 ± 7.20	32.90 ± 10.98	21.99 ± 3.23
ANT	35.10 ± 8.79	15.29 ± 3.54	1.50 ± 0.43	ND	10.40 ± 3.60	30.55 ± 11.37	ND	ND
FLT	5.42 ± 1.42	22.12 ± 10.02	7.55 ± 0.97	8.82 ± 1.96	4.66 ± 1.67	7.43 ± 1.89	12.42 ± 1.91	9.27 ± 2.23
PRY	4.28 ± 1.19	18.66 ± 9.90	6.77 ± 1.38	ND	2.76 ± 1.80	9.76 ± 2.20	5.44 ± 1.36	8.18 ± 2.90
SUM	2194.66	2747.81	1196.87	1242.36	1666.48	1106.19	1184.82	816.45

was 233.72 ng/m^3, 119.73 ng/m^3 in indoors and outdoors in winter season, and in summer season it was 216.62 ng/m^3, 96.66 ng/m^3. In gaseous phase the concentration of TPAHs was 2194.66 ng/m^3 (indoors) 2747.81 ng/m^3 (outdoors) in winter season and 1196.87 g/m^3 (indoors), 1242.36 ng/m^3 (outdoors) in summer season at roadside homes. At urban residential homes the TPAHs concentration in indoor in gas phase was 1666.48 ng/m^3 (winter season) and in outdoor it was 1106.19 ng/m^3 (winters), whereas in summer season it was 1184.82 ng/m^3 (indoors), 816.45 ng/m^3 (outdoors). In particulate phase, the predominant PAHs in indoor and outdoor environment at both sites were found to be BaA (15.84 ng/m^3), CHR (13.37 ng/m^3), BbF (23.71 ng/m^3), BkF (18.16 ng/m^3), BeP (9.64 ng/m^3) BaP (11.14 ng/m^3), I (123cd), P (10.97 ng/m^3) and BghiP (9.14 ng/m^3). In gaseous phase the predominant PAHs compounds were NAP (826.27 ng/m^3), Methyl Naphthaline (321.73 ng/m^3), BPHY (92.02 ng/m^3), ACY (54.86 ng/m^3), ACE (10.66 ng/m^3), DBF (23.81 ng/m^3), FLU (15.67 ng/m^3), PHE (28.86 ng/m^3), ANT (18.64 ng/m^3), FLT (9.71 ng/m^3) and PRY (9.31 ng/m^3) in both winter and summer season at urban residential and roadside sites. Their concentrations were found to be more in winter season and the results was in agreement with the earlier published studies (Vardar *et al.*, 2002; Cincinelli *et al.*, 2007; Akyuz *et al.*, 2010). The gas particulate distribution of PAHs revealed a general tendency that the lower molecular mass PAHs were mostly found in gaseous phase and higher mass PAHs predominated in the particulate phase which was in agreement with our previous study (Masih *et al.*, 2010b), as well as it also in consistent with the other studies done in different parts of the world (Li *et al.*, 2006; Cincinelli *et al.*, 2007).

The winter/summer (W/S) ratios of total PAHs in indoors and outdoors were 3.05, 4.04 (Roadside) and at urban residential site 1.08, 1.24 for particle phase. In gas phase W/S ratio in indoor was 1.83 and 2.21 in outdoor at roadside homes. At urban residential homes it was 1.41 (indoors), 1.35 outdoors for gas phase PAHs. In particulate phase the W/S ratios in indoor ranged from 0.63 (PRY) to 15.45 (BkF), whereas for outdoor 1.61 (NAP) to 13.55 (CHR) at roadside site. For urban residential site the W/S ratio for indoors ranged from 0.22 (ACE) to 6.02 (BbF) and in outdoors it ranged 0.80 (FLT) to 2.84 (ACY). In gas phase the winter to summer ratios range was 0.63 (PRY) to 23.40 (ANT) in indoor and in outdoor it ranged 1.52 (NAP) to 4.57 (DBF) at roadside site. At urban residential site it was 0.38 (FLT) to 2.33 (2MNAP) in indoor and at outdoor it ranged from 0.80 (FLT) to 2.84 (ACY) which also indicated significant seasonal variations of individual PAHs on comparing other urban pollution studies (Guo *et al.*, 2003; Esen *et al.*, 2008; Akyuz *et al.*, 2010). The higher W/S ratios can be explained on the basis of poor mixing height due to inversion condition and additional emissions from the residential sector due to heating in the winter season. Further the photo dissociation of PAHs in the summer season by the impact of high temperature in comparison to winter season could lead to lower concentration during the summer season (Marchand *et al.*, 2004). The average monthly (Nov 2006 to Jun 2007) concentration of PAHs in both gas

and particulate phase are shown in Fig. 2, which also exhibit apparently the extent of the seasonal variation. The figure depicts that the monthly concentrations of PAHs in indoor and outdoor environment at both site homes in gas and particle phase was found in excess during winter months. This may be attributed to the general practice of more residential fuel combustion for heating and other household purposes during winter season. Fig. 3 demonstrated the seasonal variation in different ring TPAHs concentration. By using ANOVA test in between two to six ring PAHs compound concentration significant differences was found for both indoors and outdoors at roadside homes (*p > 0.005*). At urban residential homes significant differences in winter PAHs concentration were found for two, three, four and five ring PAHs concentrations in indoor environment. In outdoors, significant difference was observed for two ring PAHs compound only. For both urban residential and roadside PAHs concentration, the calculated *F* value was much higher than the *F* critical value which illustrated that PAHs concentration in winter season was also influenced by some other factors.

Toxic Assessment of PAHs

PAHs in the environment exhibit high toxicity. Thus the investigation of PAHs concentrations will be incomplete without assessing individual PAHs carcinogenic potency in the indoor and outdoor environment of the homes. Although the lighter PAHs are the most abundant in the atmosphere, it is their heavier counterparts that have been associated with adverse health effects and in this study have higher emission factors in particulate phase. To assess the human health risk associated with exposure to PAHs emitted in indoor and outdoor environment, the relative carcinogenic contribution of each individual PAH was calculated for indoor and outdoor PAHs concentration using Toxic Equivalence Factor (TEFs) proposed by Nisbet and LaGoy (1992).

The relative carcinogenic contribution of each individual PAH and their considerable differences in the PAH profile for indoor and outdoor are shown in Fig. 4. The mean concentration of PAH concentrations in indoor and outdoor air samples of urban residential and roadside homes, were reduced when their contribution to carcinogenicity were taken into account. Based on the proposed TEF values, we can calculate that among the PAHs detected and considered in the analysis, BaP account for 58–61% of the total carcinogenic activity.

Total PAHs in indoor and outdoor air at both sites homes contributed mostly by light molecular weight NAP, ACE, ACY, FLU, PHE, however, total BaPeq was contributed mainly by the carcinogenic compounds BaA and BaP. The sum of these compounds accounted for 69.89% indoors, 66.12% outdoors at roadside homes whereas for urban residential site homes it was 71.13% in indoors of total BaPeq in indoor environment. The results underline and confirm the importance of BaP as a surrogate compound for PAH mixture for indoor and outdoor air in the different microenvironment. Other PAHs like BghiP, BkF, BbF, BaA, FLT and CHR that dominated in indoor and outdoor of the homes obviously played only a minor role in the
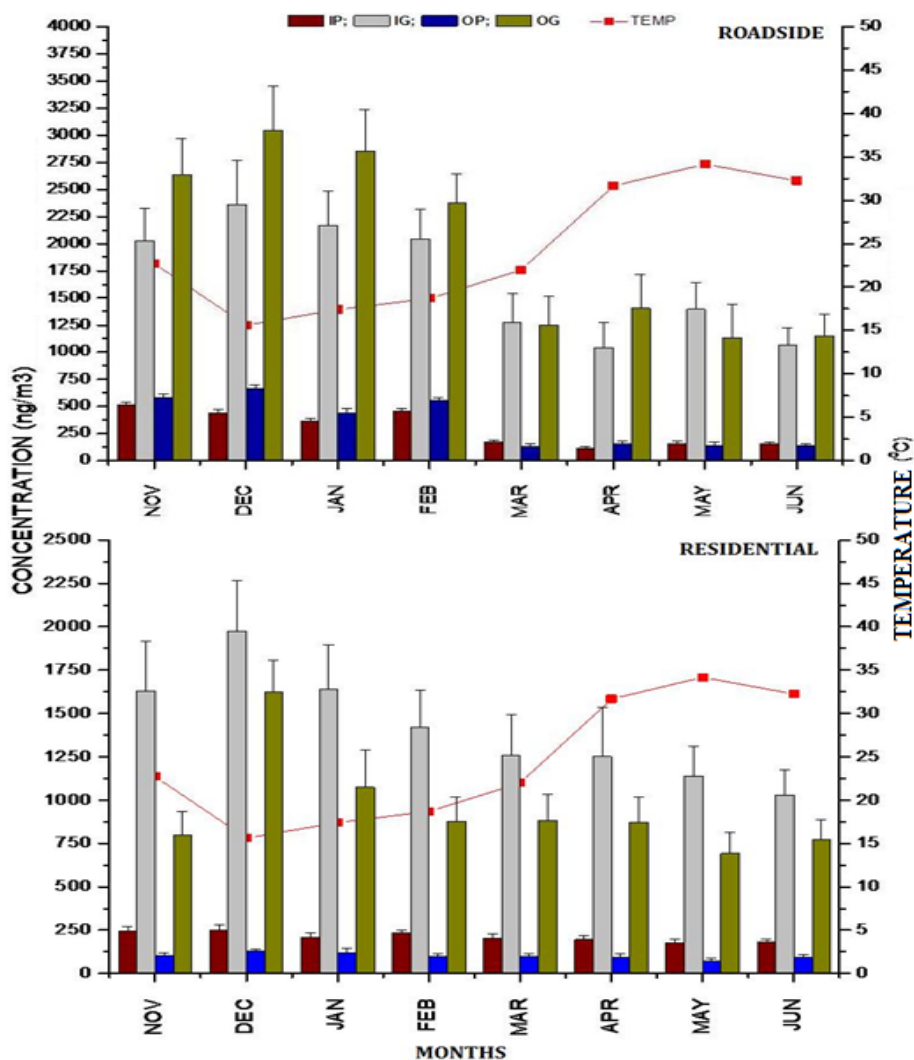
IP-indoor particulate; IG-Indoor gaseous; OP-Outdoor particulate; OG-Outdoor gaseous; Temp- Temperature.

Fig. 2. Monthly mean concentration of PAHs in particulate and gas phase and temperature variation over the sampling period.

carcinogenicity of the PAH mixture. Thus, BaP in both indoors and outdoors of the homes is clearly an important indicator of health risk in different microenvironment where people mostly invest their time.

Source Apportionment

Principal Component Analysis (PCA) is a well-established tool for analyzing structure in multivariate data sets (Derwent *et al*., 1995). Beginning with a large number of correlated variables, it seeks to identify a smaller number of independent factors (principal factors) that can be used to explain the variance in the data. The number of extracted principal components corresponds to the number and the nature of the variables included. For the purpose of this study, the factors are the sources of combinations of PAHs, while the variables are the PAH concentrations in air. A varimax rotated factor analysis was performed to identify the main sources influencing the concentration of studied pollutants in the air of urban residential and roadside sites homes. In this statistical method a set of multiple inter-correlated variables is replaced by small number of

independent variables (factors) by orthogonal transformations (rotations). This is achieved by diagnosing the correlation matrix of the variable, i.e. by computing their Eigen values and Eigen vectors. "Factor loadings" obtained after the varimax rotation give the correlation between the variables and the factors. Data are included in the matrix only if the Eigen value for the factor is greater than 1. The varimax procedure was adopted for rotation of the factor matrix to transfer the initial matrix into one that was easier to interpret. In the present study, the Statistical Package for Social Scientist (SPSS version 10.0) computer software was used to perform factor analysis.

At urban residential site in indoor and outdoor air three factors with Eigene value > 1 (Table 4) were identified, accounting 91% and 89% of the variance respectively. For indoor air the first factor, which contributed 36.23% of the total variance and contains NAP, B(a)A, CHR, B(b)F, B(K)F, B(e)p and B(ghi)P suggests cooking as the main source of PAHs (Kabouras *et al*., 1999; See *et al*., 2006; Masih *et al*., 2010a). The second factor, which contributed 31.38% of the total variance explaining the PAH loads of 2
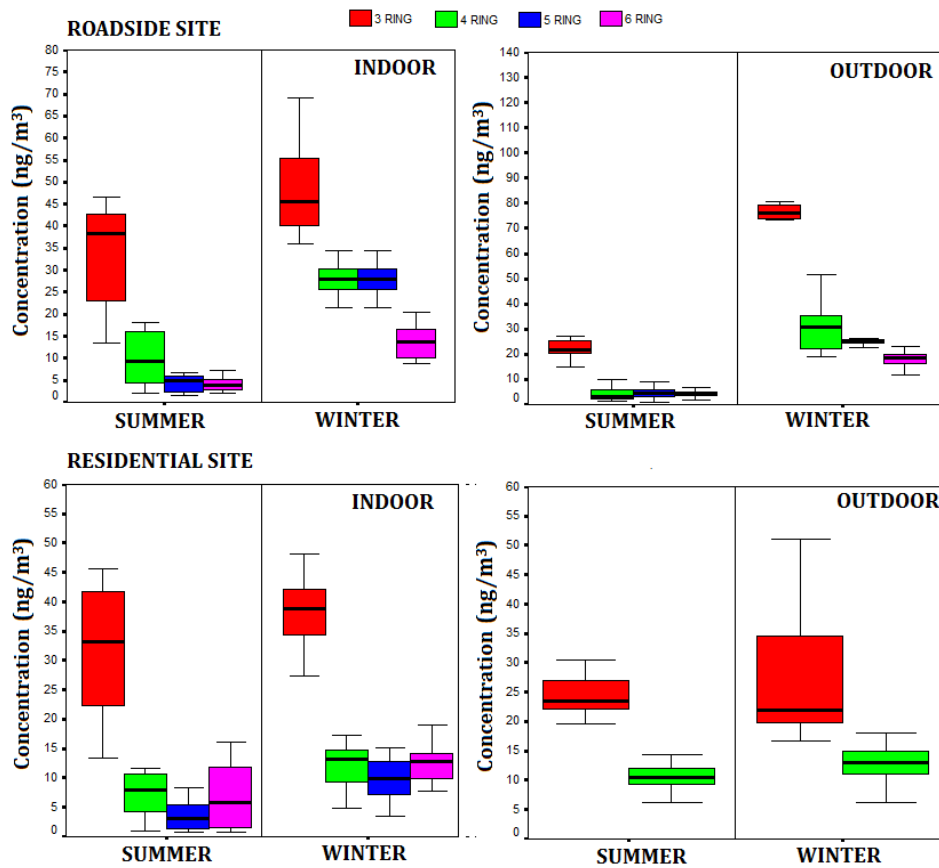
Fig. 3. Seasonal distribution of PAHs in different ring arrangements in Indoor/Outdoor environment. The upper box represents 75th percentile while the lower box represents 25th percentile. Line in between the boxes represents median concentration.
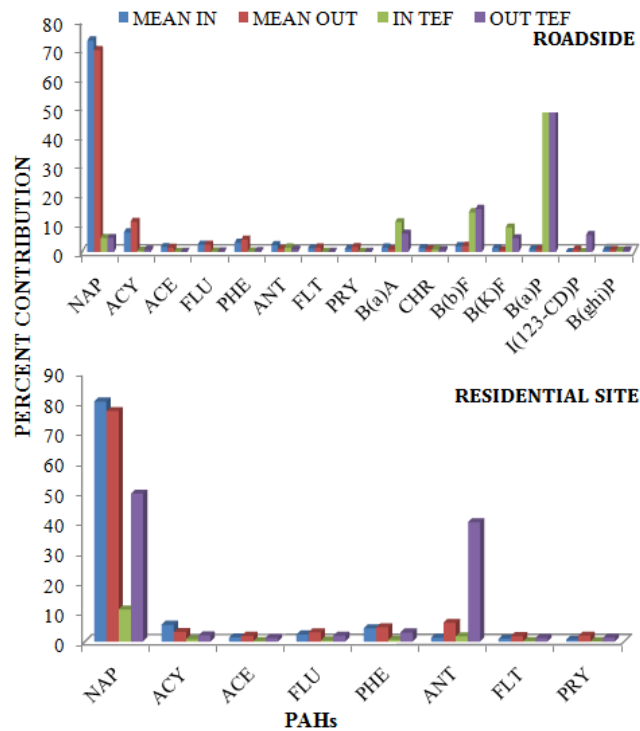
Fig. 4. Percentage contribution of individual PAHs to total PAHs and their relative carcinogenicity in indoor and outdoor air of the homes.

Table 4. Factor analysis of total PAH concentration in indoor and outdoor at urban residential homes.

PAHs	Indoor			Outdoor		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
NAP	0.534	0.715	–0.451	–0.156	0.203	–0.967
2MNAP	0.142	0.99		0.678	0.592	0.436
1MNAP	0.258	0.958	0.127	0.73	0.342	0.592
2,6 DMNAP	0.278	0.956		0.651	0.504	0.568
BPHY	0.175	0.892	0.416	0.677	0.611	0.409
ACY	0.279		0.96	0.473	0.869	0.145
ACE	–0.822	–0.508	–0.256	0.834	–0.342	0.434
DBF		0.661	0.745	0.52	0.607	0.6
FLU	–0.318	–0.145	0.937	0.766	0.255	0.591
PHE		–0.176	0.983	0.333	0.48	0.812
ANT	0.15	0.637	0.756	0.216	0.976	
CAR	–0.814	0.564	0.141	–	–	–
FLT	–	–	–	0.4	–0.915	
PRY	–0.815	–0.564	–0.133	0.99	0.122	
B(a)A	0.847	0.449	–0.283	–	–	–
CHR	0.986	0.103	0.129	–	–	–
B(b)F	0.916	0.374	–0.147	–	–	–
B(k)F	0.974		0.208	–	–	–
B(e)P	0.967	0.205	0.149	–	–	–
B(a)P		–0.956	0.285	–	–	–
B(ghi)P	0.967	0.229	–0.110	–	–	–
Total	8.047	7.278	4.675	4.971	4.479	3.55
% Variance	36.234	31.389	23.377	32.241	30.453	26.306
Cumulative %	36.234	76.623	91	32.241	70.694	89
Predicted source	Cooking	Oil Fumes	Tobacco smoking	Petrogenic source	Diesel emission	Wood burning

MNAP, 1MNAP, BPHY and CAR which is due to the oil fumes (Yunker *et al*., 2002; Li *et al*., 2009; Masih *et al*., 2010a). The third factor contributes 23.37% of the total variance, and was probably related to tobacco smoking (BUA *et al*., 1994; Gundel *et al*., 1995; NLM, 2000). For outdoor air at this site the first factor contributed 32.24% with the loading of 2MNAP, 1MNAP, BPHY, ACE, DBF, FLU and PRY; this was due to the petrogenic sources (Daisey *et al*., 1986; BUA *et al*., 1994; Dallolarosa *et al*., 2005). The second factor accounts 30.45% of the total variance, and contains 2MNAP, 2,6 DMAP, BPHY, ACY, DBF and ANT. Diesel emissions from generator are the main source of these PAHs (NLM, 2000; Yunker *et al*., 2002; Tavares *et al*., 2004). The third factor contributes 26.30% of the total variance, contains 1 MNAP, DBF, FLU and ANT and may be explained by the burning of wood for heating purpose which contains mainly PHE, FLU and DBF (Khalili *et al*., 1995; NLM, 2000).

Table 5 shows the factor analysis of the measured PAHs at roadside homes. It reveals three factors for indoor environment with Eigen value > 1 accounting for 94% of the variance. The first factor, which accounts for 32.21% of the total variance contains NAP, 2MNAP, ACE, FLU, CHR, and may be attributed from oil fumes during combustion activities (cooking) (Yunker *et al*., 2002; Zhu *et al*., 2009; Masih *et al*., 2010a). The second factor, contributing 29.58% of the variance, contains ACE, B(a)A, B(b)F, B(e)P, B(a)P and B(ghi)P with smoking and incense burning as combined

probable source (Huynn *et al*., 1991; Gundel *et al*., 1995; Li and Ro, 2000). The third factor contributes 25.20% of the total variance and may be explained by the use of diesel generators used for power supply and also transported from outdoor diesel engine vehicular emissions (Smith and Harrison, 1996; Ravindra *et al*., 2006). In outdoor environment two factors were accounted with Eigen value > 1 accounting for 90% of the variance. The first factor was accounted for 48.65% with the high loading of NAP, 2MNAP, 1MNAP, ACY, ACE, DBF, FLU, PHE, ANT, CAR, CHR, B(b)F and B(e)P. The probable source of these PAHs might be from diesel powered vehicles (Harrison *et al*., 1996; Tavares *et al*., 2004; Jiang *et al*., 2009; Rajput *et al*., 2009). The second factor had loading of 1MNAP, 2MNAP, ACY, ANT, CAR, FLT, PRY, B(a)A, CHR, B(b)F, B(k)F, B(a)P and I(123cd)P which account for 41.34% of the total variance and was probably due to the petrol and natural gas combustion engine vehicles on road (Khalili *et al*., 1995; Yunker *et al*., 2002; Dallarosa *et al*., 2005; Jiang *et al*., 2009; Zhu *et al*., 2009).

CONCLUSION

PAHs concentrations in indoor and outdoor air samples of urban residential and roadside locations were collected between November 2006–June 2007 in the semi arid region of India. Their seasonal variation, their concentration between particle and gas phase were characterized. Significant seasonal variations of PAHs concentration were observed

Table 5. Factor analysis of total PAH concentration in indoor and outdoor at roadside homes.

PAHs	Indoor			Outdoor	
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2
NAP	0.998			1.000	
2MNAP	0.791		–0.612	0.932	0.362
1MNAP	–0.914	–0.293	0.280	0.732	0.681
2,6 DMNAP		–0.472	0.880	–0.113	0.994
BPHY	0.138		0.986	–0.811	–0.585
ACY	–0.454	–0.262	0.851	0.829	0.560
ACE	0.752	0.622	0.219	0.999	
DBF	–0.201	–0.150	0.968	0.996	
FLU	0.990		–0.125	1.000	
PHE	0.803	0.596	0.596	0.997	
ANT		–0.984	0.176	0.839	0.544
CAR	–0.716	–0.628	–0.304	0.813	0.582
FLT	–0.931	–0.328	–0.160	0.460	0.888
PRY	–0.283	–0.164	–0.945	0.454	0.891
B(a)A	0.100	0.971	–0.218	0.199	0.980
CHR	0.919	0.296	–0.261	0.501	0.866
B(b)F	0.140	0.801	–0.583	0.614	0.789
B(k)F	–0.695	–0.653	–0.302	–0.810	0.586
B(e)P	0.298	0.952		0.543	–0.840
B(a)P	0.443	0.739	–0.507	0.268	0.963
I(123cd)P				–0.379	0.925
B(ghi)P		0.997			–0.999
Eigen Value	8.024	6.843	6.133	11.364	10.636
% Variance	32.210	29.584	25.206	48.653	41.347
Cumulative %	32.210	61.794	94.004	48.653	90.000
Predicted source	Oil Fumes for cooking	Smoking & incense burning	Diesel exhaust	Diesel Vehicular emission	Petrol & CNG power Vehicles

with higher levels during winter seasons due to residential fuel combustion for heating and other household purposes. The higher total BaPeq concentrations in urban residential/ roadside sites were alarming signal for pollution risks. Results obtained from principal component analysis revealed that in indoor environment PAHs was attributable mainly from gas utilities, cooking (frying and oil combustion), smoking and incense burning at urban residential and roadside homes whereas at outdoor point the most common sources of PAHs was both from petrol and diesel combusted fuel vehicles and diesel fumes from generator sets used for electrical supply during power failure.

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