



Characteristics of polycyclic aromatic hydrocarbons in indoor and outdoor atmosphere in the North central part of India

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ABSTRACT

Twenty-three polycyclic aromatic hydrocarbons (PAHs) were measured simultaneously in indoor and outdoor environment of ten homes at urban and roadside sites in the north central part of India during winter season (November 2006 to February 2007). The average concentration of total PAH (TPAH) was 1946.84 ng/m³ in kitchen, 1666.78 ng/m³ in living room and 1212.57 ng/m³ in outdoors at urban site, whereas at roadside site it was 2824.87 ng/m³, 2161.26 ng/m³, and 3294.28 ng/m³ in kitchen, living room and outdoors respectively. The two, three and four ring PAHs were predominant in vapour phase, while the five, six ring PAHs were primarily associated with the particulate phase. The concentration trends of the PAHs in present study were naphthalene > 2-methylnaphthalene > 1-methylnaphthalene > biphenyl > acenaphthylene in indoor and outdoor environment of both the sites. The spatial trend of total PAHs concentrations in the house located at urban sites, was kitchen > living room > outdoors whereas at roadside site, the trend was outdoors > kitchen > living room. Correlation analysis has been used to identify the sources of PAHs. The correlation between CO₂ and ratio of living room/outdoors (L/O) and kitchen/outdoor (K/O) of total PAHs concentration for two sites was found to be significant.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are among the pollutants of concern for human health due to carcinogenic and mutagenic properties of certain compounds from the PAH class. PAHs arise from variety of combustion processes and are therefore ubiquitous in the environment. The largest PAH sources to the atmosphere are motor vehicles, [1,2] power generation via combustion of coal and oil, incineration [3,4,5] and wood burning [6,7]. In India as well as in other countries of the world the sources of indoor PAHs are cooking [8], smoking, burning of natural gas, liquid petroleum gas, kerosene [9,10,11], wood, dung, coal [11,12], candles and incense [13,14] as well as transport from the outdoor [8,15].

PAHs concentration in indoor air and their attribution to indoor and outdoor sources have been characterized in a number of studies [5,8,14,15] but the quality, quantity, scale and extent of monitoring for PAH levels is to date almost inversely related to where the

chances of exposure seems greatest. We are fairly certain about levels experienced by those in cleaner environments of North America [16] and European Cities [17] and are least certain about levels in the dirtiest environments such as the cities and households of the developing world. Therefore a comprehensive assessment of indoor PAH concentrations in urban areas with different microenvironments and their relationship to different types of outdoor emission sources would significantly contribute to the present understanding of people exposure to pollutants of indoor and outdoor origin [18].

Agra (India) has experienced rapid urbanization and industrial expansion resulting in increased utilization of fossil fuels in automobiles, trucks and public transportation. It has an arid climate that may further aggravates pollution levels resulting in enormous levels of respirable suspended particulate matter (RSPM), which have been reported to vary between 167 µg/m³ and 274 µg/m³ [19]. Studies on characterization of wet deposition, dry deposition, aerosols, fog and dew have been carried out at Agra particularly with reference to their inorganic constituents [20–24]. However, no data on PAHs and other organic compounds are available except for a recent study on PAH in ambient air at industrial site [25]. Thus the specific objective of the present study is: (i) to determine the indoor and outdoor concentrations of PAHs in gaseous as well as in particulate phase in two different microenvironments; (ii) to compare

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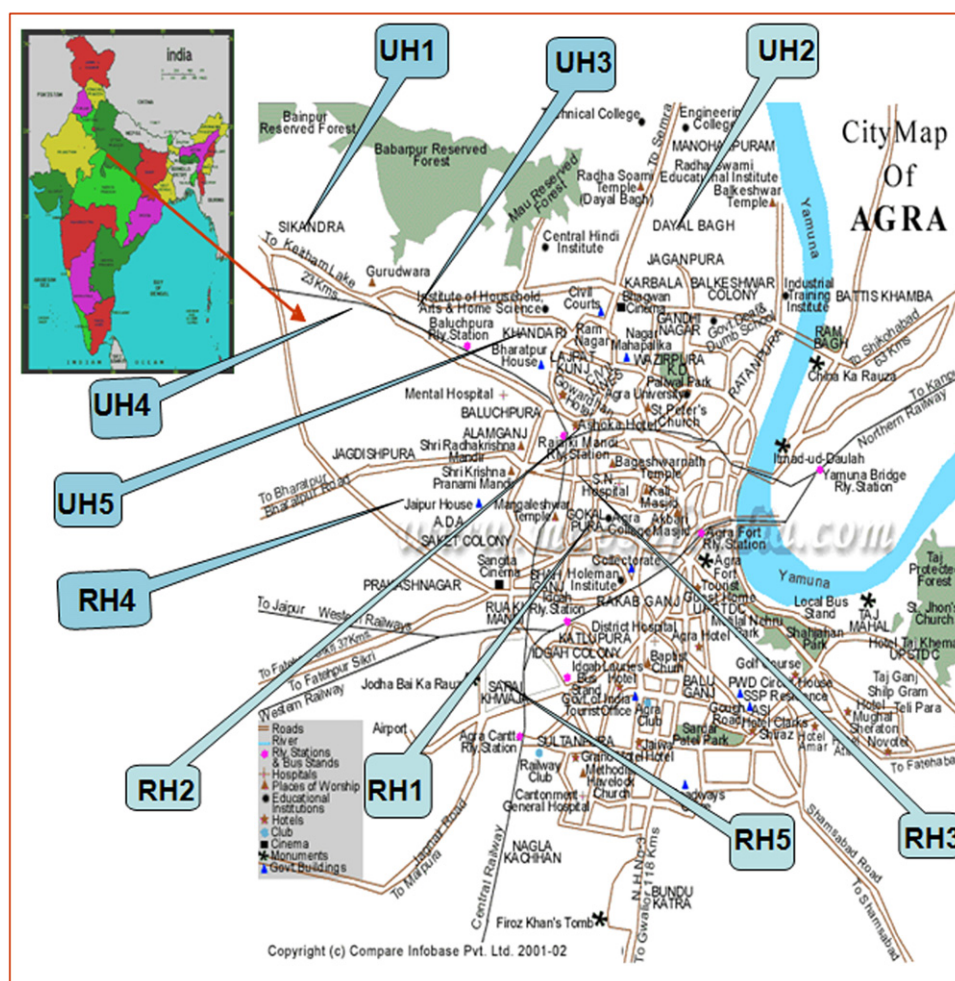


Fig. 1. Map of Agra showing sampling locations.

the correlation of the indoor levels with the corresponding outdoor measurements in winter season; (iii) to see the spatial trends in domestic homes. Moreover no standards have been formulated for PAHs in ambient as well as indoor air till date in India but according to WHO a target was set up for PAHs with benzo(a)pyrene [B(a)P] as an indicator substance at 1 ng/m^3 as the long term average. This level corresponds to theoretical lifetime cancer risk of 1×10^{-5} according to WHO risk estimate [26]. Even for ambient air in India the standard for [B(a)P] has been set as 1 ng/m^3 up to the year 2010, though the limit for PAHs is not legally binding but it is common consensus that it require maximum emission reduction or 'zero levels'. This data can be a step towards focusing intervention in the domestic homes of cities in the developing countries where the problems of urbanization and fuel usage are almost similar.

2. Materials and methods (site description)

Agra, the city of Taj ($27^{\circ}10'N$ $78^{\circ}02'E$) is located in the North Central Part of India about 200 km South of Delhi in the Indian state of Uttar Pradesh. Agra is one of the most famous tourist spots of the country. The city situated on the West bank of river Yamuna, is known throughout the world as the home to a wonder of the world, Taj Mahal. A part of the great northern Indian plains, Agra is considered as a semi-arid zone as two-third of its boundaries are surrounded by the Thar desert of Rajasthan. Three national highways cross through the city. In winter the temperature ranges from

5.5°C to 30.5°C . The dominant downward wind is north, northeast and west in this season.

2.1. Sampling sites

Ten houses in two locations, representing urban site and roadside site were selected for indoor and outdoor sampling. The urban houses were selected in general urban area without impacts of heavy vehicle traffic and industrial production. The roadside homes were selected to adjacent road which have heavy motor vehicle traffic throughout the day. The urban houses are labeled with UH1, UH2, UH3, UH4, UH5 and roadside houses with RH1, RH2, RH3, RH4 and RH5 as shown in Fig. 1. Questionnaires describing the site characteristics and the ongoing activities in the homes were completed with the assistance of the occupants. Information relating to the building type, building age, dimensions of the homes, indoor furnishing materials, frequency of opening windows, smoking activities, meals cooked per day, burning of incense, candles, mosquito coils, and use of air cleaners were included. The nearest distance between two sampling sites was about 1 km, and the farthest distance between two sites was over 12 km. The purpose of considering the distance was to eliminate the possibility of interactions between two sites. In each of the monitored homes handy samplers were placed in the living room, kitchen and for outdoor sampling they were kept on the rooftops. Table 1 shows the mean temperature, humidity, ventilation rate, sample duration, sample number and fuel/material used for prayer in indoor and outdoor environment of ten selected homes.

Table 1
Average levels of temperature, humidity and air change rate in indoor and outdoor environment of ten selected houses.

Home no.	Mean temp.(°C)		RH* (%)		Average ACH (h ⁻¹)	Samplig duration (h)	No. of samples	Fuel used for cooking/prayer material
	IN	OUT	IN	OUT				
RH1	18.6	19.9	68.7	53.2	3.1	24	16	LPG/Incense
RH2	16.9	17.9	69.4	56.7	1.5	24	16	LPG/nil
RH3	15.4	17.2	70.0	55.2	3.2	24	16	LPG/Electric
RH4	19.3	20.3	61.8	58.1	2.6	24	16	LPG/incense/ghee
RH5	14.9	16.5	56.4	60.2	5.1	24	16	LPG/incense, ghee diya
UH1	12.9	15.6	72.1	65.3	1.9	24	16	LPG/incense
UH2	14.6	16.8	45.7	48.2	4.7	24	16	LPG/incense
UH3	18.7	20.3	55.9	59.1	3.8	24	16	LPG/nil
UH4	16.5	18.4	58.4	62.4	8.4	24	16	LPG/incense/dhoop
UH5	15.9	16.7	78.1	65.3	3.7	24	16	LPG/nil

RH* = relative humidity, ACH = air change rate, LPG = liquefied petroleum gas, RH = Roadside home, UH = urban side home.

2.2. Sampling and analysis

Envirotech Handy Sampler APM-821, Okhla New Delhi, India was used to collect PAH samples. Temperature, CO₂, humidity and ventilation rate in indoor and outdoor were measured by using Young Environment System (YES-206, 205 Canada) which are IAQ monitors and use non-dispersive infrared (NDIR) method of CO₂ gas detection. For PAH the pump was set at a flow rate of 2 L/min 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 at a height of 1.5–1.8 m above the ground to simulate the humans breathing zone. 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 min. These vials were allowed to settle for 30 min. 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 96% to 120% and 97% to 126% respectively and its relative percent difference (RPD) ranged from 0% to 12%. The limit of quantification for various PAHs ranged from 13.7 ng/m³ to 125 ng/m³ and 76% 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 [27]. 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 [28]. The concentration of twenty-three identified analytes was calculated by relating the MS response of the quantitation ion produced by the

Table 2
The average concentrations in (ng/m³) with standard deviation and indoor/outdoor ratio of individual indoor and outdoor PAHs at urban and roadside sites.

PAHs	Roadside			Urban						
	K	L	O	K/O	L/O	K	L	O	K/O	L/O
NAP	1483.33 ± 210.79	1088.73 ± 117.30	1314.66 ± 240.99	1.12	0.82	991.66 ± 211.79	951.66 ± 94.11	562.00 ± 103.68	1.76	1.69
2MNAP	311.00 ± 58.84	221.00 ± 53.11	488.10 ± 24.10	0.63	0.45	257.00 ± 63.23	208.00 ± 49.86	217.00 ± 43.23	1.18	0.95
1MNAP	205.00 ± 51.46	140.00 ± 5.56	337.70 ± 12.62	0.60	0.41	163.66 ± 41.18	184.00 ± 24.75	143.96 ± 54.78	1.13	1.27
BPHY	176.00 ± 9.74	67.00 ± 6.56	221.16 ± 5.48	0.79	0.30	85.33 ± 3.48	74.06 ± 22.98	64.43 ± 21.14	1.32	1.14
2,6-DMNAP	137.83 ± 14.58	87.80 ± 6.80	115.83 ± 6.75	1.18	0.75	53.26 ± 17.00	51.36 ± 18.40	41.90 ± 6.16	1.27	1.22
ACY	148.13 ± 9.45	152.50 ± 4.94	174.33 ± 15.37	0.84	0.87	89.96 ± 6.16	73.45 ± 5.22	25.53 ± 11.09	3.52	2.87
ACE	26.15 ± 1.34	ND	25.56 ± 3.33	1.02	–	12.76 ± 0.55	ND	ND	–	–
DBF	72.03 ± 4.02	54.65 ± 1.20	80.93 ± 6.92	0.89	0.67	48.40 ± 3.80	21.05 ± 2.23	33.05 ± 11.66	1.46	0.63
FLU	59.85 ± 12.51	32.70 ± 0.42	71.16 ± 6.24	0.84	0.45	44.70 ± 0.55	16.30 ± 0.98	24.95 ± 13.36	1.79	0.65
PHE	67.05 ± 7.42	31.30 ± 2.40	110.63 ± 3.19	0.60	0.28	72.90 ± 0.7	26.90 ± 3.39	29.93 ± 2.07	2.43	0.89
ANT	ND	43.80 ± 2.96	17.93 ± 1.20	–	2.44	ND	29.75 ± 6.57	43.69 ± 13.90	–	0.68
CAR	ND	ND	70.76 ± 1.16	–	–	10.00 ± 1.03	ND	ND	–	–
FLT	16.00 ± 1.41	ND	33.06 ± 8.41	0.48	–	14.00 ± 1.14	ND	10.95 ± 0.35	1.27	–
PRY	13.16 ± 0.85	ND	29.16 ± 10.36	0.45	–	10.85 ± 0.91	ND	14.98 ± 1.36	0.72	–
B(a)A	21.80 ± 7.21	54.00 ± 3.67	31.30 ± 0.56	0.69	1.72	13.80 ± 2.26	17.40 ± 0.98	ND	–	–
CHR	17.40 ± 0.75	48.13 ± 1.38	33.25 ± 5.30	0.52	1.44	13.70 ± 1.97	–	ND	–	–
B(b)F	23.85 ± 4.31	71.40 ± 1.83	35.65 ± 5.72	0.66	2.00	17.70 ± 1.13	12.85 ± 0.07	ND	–	–
B(k)F	ND	ND	18.35 ± 0.21	–	–	10.68 ± 2.00	ND	ND	–	–
B(e)P	20.06 ± 1.10	30.50 ± 2.54	19.75 ± 1.76	1.01	1.54	10.13 ± 1.23	ND	ND	–	–
B(a)P	13.10 ± 0.95	37.75 ± 3.74	27.95 ± 1.62	0.46	1.35	13.60 ± 1.13	ND	ND	–	–
I(123-CD)P	ND	ND	15.50 ± 1.15	–	–	ND	ND	ND	–	–
DBA	ND	ND	ND	–	–	ND	ND	ND	–	–
B(ghi)P	13.13 ± 0.56	ND	21.56 ± 1.00	–	–	12.75 ± 0.63	ND	ND	–	–
Total PAH	2824.87	2161.26	3294.28			1946.84	1666.78	1212.37		

L, living room; K, kitchen; O, outdoor; ND, not detected; K/O, kitchen/outdoor ratio; L/O, living room/outdoor ratio.

compound that was used as an internal standard. The identified analytes are: naphthalene (NAP), 2-methylnaphthalene (2MNAP), 1-methylnaphthalene (1MNAP), biphenyl (BPHY), 2,6-dimethylnaphthalene (2,6-DMNAP), acenaphthylene (ACY), acenaphthene (ACE), dibenzofuran (DBF), flourene (FLU), phenanthrene (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], indeno(1,2,3-cd)pyrene [I(123-cd)P], dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene [B(ghi)P].

3. Results and discussions

3.1. Description of PAHs in air

Table 2 represents the average concentration and indoor/outdoor ratios of individual PAHs found in the homes at two different sites. The total PAH (TPAH) concentrations were 1946.84 ng/m³, 1666.78 ng/m³ and 1212.37 ng/m³ in kitchen, living room and outdoor in urban site homes, whereas in roadside it was 2824.87 ng/m³ in kitchen, 2161.26 ng/m³ in living room and 3292.28 ng/m³ in outdoors. At urban site, the mean concentrations of detectable PAHs were found to be 97.34 ng/m³, 138.89 ng/m³ and 101.03 ng/m³ in kitchen, living room and outdoor and it ranged from 10.00 ± 1.03 ng/m³ to 991.66 ± 211.79 ng/m³, 12.85 ± 0.07 ng/m³ to 951.66 ± 94.11 ng/m³ and 10.95 ± 0.35 ng/m³ to 562.00 ± 103.68 ng/m³ in kitchen, living room and outdoors respectively. In case of roadside site, the mean concentration of detectable PAHs were 156.94 ng/m³, 144.08 ng/m³ and 149.74 ng/m³ in kitchen, living room and outdoor and ranged from 13.10 ± 0.95 ng/m³ to 1483.33 ± 210.79 ng/m³, 30.50 ± 2.54 ng/m³ to 1088.73 ± 117.30 ng/m³ and 15.50 ± 1.15 ng/m³ to 1314.66 ± 240.99 ng/m³ respectively. In roadside homes, average concentration of TPAH in kitchen, living room and outdoors were 1.45, 1.29 and 2.71 times that of concentration found in kitchen, living room and outdoor of urban homes. Regarding indoor and outdoor PAH relationship, the indoor levels of most of the evaluated PAHs were significantly higher than the corresponding outdoor ones at urban site homes as found in earlier studies [14,29]. The higher concentration of PAHs in roadside site may be because of the intense automobile traffic about 10⁵ vehicles per day [30] besides household's indoor activities like cooking, incense burning, and cigarette smoking [29]. The kitchen/outdoor, living room/outdoor ratios were higher than one for all PAHs compound at urban site homes indicating the additional indoor sources, whereas at roadside homes I/O ratio were found to be less than 1, which suggested that indoor concentrations of these PAHs may also be attributed to outdoors sources.

The implications of human exposure to mixtures of PAHs, rather than to individual substances, are very important. Occupationally or environmentally, people are generally exposed to a mixture of PAHs and very rarely to a single PAH compound. In India no such studies have been published to date in which PAHs are measured in both indoor and outdoor air in different microenvironments. Thus we have compared our results with studies done in different parts of the world as shown in Table 3. The results of the study were comparable with concentrations recorded during incense burning in Taiwan and the study done in Columbus (Ohio) in smoker and nonsmoker homes. Besides this, our results are also comparable with the concentrations found in other studies reported in table except naphthalene and its derivatives which were found higher in the present study. These higher values of naphthalene and its derivatives made the sum of the total PAHs considerable higher.

Table 3

Comparison of total PAHs in (ng m⁻³) with other studies done in other parts of the world.

Site location	Indoor	Outdoor	References
Agra (India)			
Roadside	4986.13	3294.28	Present study
Urbanside	3813.62	1212.37	Present study
Kanpur ^a (India)	56.87	NA	[52]
Columbus ^b (Ohio)	8880.86	259.57	[9]
Taipei (Taiwan)	267.00	209.00	[14]
Losangel	220.00	64.00	[16]
Houstan	310.00	160.00	[16]
Elizabeth	350.00	110.00	[16]
Taiwan ^c	6258.00	231.00	[53]

NA, not available.

^a Measurements were taken at cooking site for selected three fuels.

^b Measurements were taken inside the temple.

^c Measurements were taken in smoker and nonsmoker homes.

According to World Health Organization (WHO), and agencies like National Institute for Occupation Safety and Health (NIOSH), the threshold limit for CO₂ is 1000 ppm (8 h average) for indoor air [26,31]. On comparing our results with these limits, CO₂ is found to be within the limit, but PAH concentrations were higher. Fig. 2 shows the correlation coefficients between CO₂ and ratios of K/O, L/O of total PAHs concentrations for urban and roadside homes. One use of correlation analysis can be to establish relationship to predict the concentration of PAH by knowing CO₂ concentration. This is immensely useful, as the determination of PAH is complex and CO₂ can easily be monitored online. The results of correlation indicate that CO₂ and PAH concentration were significantly correlated with the R² values 0.676, 0.836 (urban site) and 0.842, 0.767 (roadside) respectively. This observation can be useful in planning of interventions in these types of domestic homes located in this part of the world.

3.2. Spatial trends of PAHs in homes

Fig. 3 shows the concentration trends of PAHs at urban and roadside sites. At urban site, the trends of PAHs concentration in the houses were kitchen > living room > outdoors, whereas at roadside site, the trends of PAHs concentration in the houses were outdoors > kitchen > living room. In indoor air the concentration of PAHs was found to be higher in kitchens at both site homes due to

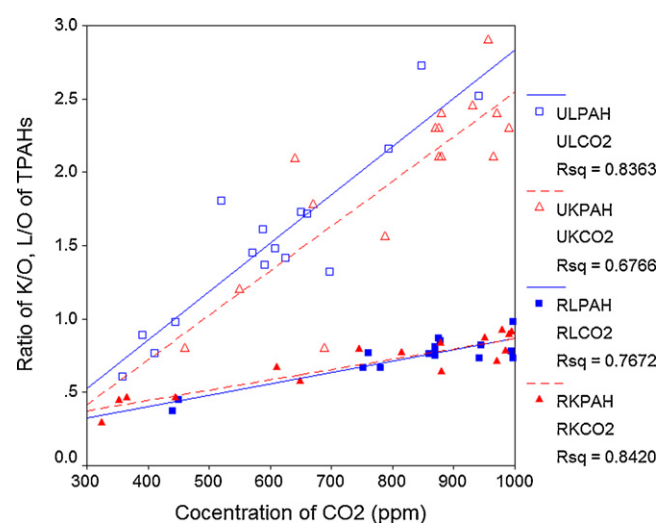


Fig. 2. Correlation between the concentration of CO₂ and K/O, L/O PAHs concentration at urban and roadside sites. L/O, living room/outdoors, UK, urban kitchen, UL, urban living room, RK, road kitchen, RL, road living room, and Rsq-R².

Table 4a

Correlation matrix between the PAHs in indoor at Urban Site home.

	NAP	2MNAP	1MNAP	BHPY	2,6-DMNAP	ACY	ACE	DBF	FLU	PHE	ANT	CAR	FLT	PRY	B(a)A	CHR	B(b)F	B(K)F	B(e)P	B(a)P	B(ghi)P	
NAP	1.000																					
2MNAP	0.997	1.000																				
1MNAP	0.952	0.973	1.000																			
BHPY	1.000	0.995	0.946	1.000																		
2,6-DMNAP	0.921	0.887	0.757	0.928	1.000																	
ACY						1.000																
ACE	–	–	–	–	–	0.975	1.000															
DBF	–	–	–	–	–	0.041	–	1.000														
FLU						0.776	0.617	0.662	1.000													
PHE	–	–	–	–	–	0.567	0.736	–		1.000												
ANT						0.543	0.343	0.861	0.951	–	1.000											
CAR				0.180	0.533	–	–	0.969	0.456	–	0.709	1.000										
FLT	–	–	0.027	–	–	0.326	0.528	–	–	0.963	–	–	1.000									
PRY	0.894	0.855	0.713	0.902	0.998	–	–	0.368	–	–	–	0.587	–	1.000								
B(a)A	–	–	–	–	–	0.992	0.995	–	0.692	0.665	0.434	–	0.441	–	1.000							
CHR	–	–	–	–	–	0.375	0.571	–	0.976	–	–	–	0.999	–	0.487	1.000						
B(b)F						0.797	0.911	–	0.238	0.949	–	–	0.831	–	0.866	0.858	1.000					
B(K)F	–	–	–	–	–	0.422	0.612	–	–	0.986	–	–	0.995	–	0.531	0.999	0.884	1.000				
B(e)P						0.349	0.548	–	0.970	–	–	–	1.000	–	0.463	1.000	0.844	0.997	1.000			
B(a)P						0.649	0.464	0.787	0.983	–	0.991	0.610	–	–	0.549	–	–	–	–	1.000		
B(ghi)P	–	–	0.089	–	–	0.267	0.474	–	–	0.945	–	–	0.998	–	0.384	0.993	0.794	0.986	0.996	–	–	1.000

Correlation is significant ($p < 0.01$) with few exception.**Table 4b**

Correlation matrix between the PAHs in outdoor at Urban Site home.

	NAP	2MNAP	1MNAP	BHPY	2,6-DMNAP	ACY	DBF	FLU	PHE	ANT	FLT	PRY
NAP	1.000											
2MNAP	0.937	1.000										
1MNAP	0.940	1.000	1.000									
BHPY	0.966	0.996	0.997	1.000								
2,6-DMNAP	0.932	1.000	1.000	0.994	1.000							
ACY	0.940	1.000	1.000	0.996	1.000	1.000						
DBF	–	–	–	–	–	–	1.000					
FLU	–	–	–	–	–	–	0.985	1.000				
PHE	0.992	0.885	0.890	0.925	0.878	0.889	–	–	1.000			
ANT	0.980	0.988	0.990	0.998	0.986	0.989	–	–	0.946	1.000		
FLT	–	–	–	–	–	–	0.901	0.814	–	–	1.000	
PRY	–	–	–	–	–	–	0.488	0.331	–	–	0.817	1.000

Correlation is significant ($p < 0.01$) with few exception.

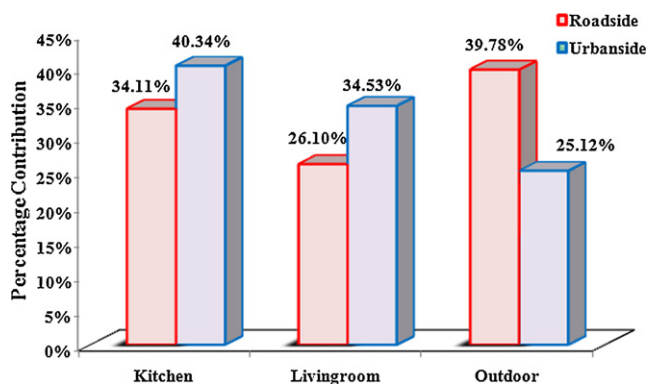


Fig. 3. Percentage contribution of TPAHs in kitchen, living room and outdoors at urban and roadside sites.

the combustion of liquefied petroleum gas for cooking purposes for long hours and the activities such as frying, stir frying, deep frying, boiling, steaming and stewing food are quite often which may be responsible for generating PAHs [32]. Though most of the kitchens had ventilating fans installed, but even than the PAHs could not be diluted in time while cooking food probably because of the small space of kitchen. Thus the concentration levels of PAHs were found higher in kitchens in comparison to living room, whereas at urban site it was found lowest at outdoors. The main factor responsible for lower concentration was less traffic, greener surrounding, better ventilation and thus lack of PAHs sources. The other reason of this can be mixing of PAHs with the ambient atmosphere and the consequence diluting of concentrations which do not happen in the case of indoor concentrations. The concentration trends of major PAH found in present study are Nap > 2-methylnaphthalene > 1-methylnaphthalene > biphenyl > acenaphthylene in indoor and outdoor at urban as well as roadside sites.

3.3. The indoor PAH correlation pattern

Tables 4 and 5 present the correlation coefficient values of PAHs at urban and roadside sites. Correlation analysis was performed by using univariate Pearson correlation coefficient for all pairs of compounds to determine relationships between individual PAH and to hypothesize probable sources on the assumption that two or more components may correlate either due to a common origin or atmospheric behavior.

From the results of Table 4 at urban site indoors NAP and its derivatives (2MNAP, 1MNAP, 2,6-DMNAP), BHPY showed strong correlation with each other ($R^2 = 0.997-0.952$) and good correlation ($R^2 = 0.713-0.894$) with PRY, which might be generated from oil fumes during frying activities on gas while cooking food [33–38]. Frying and use of oil in large quantities is very common in Indian style of cooking. ACY showed strong correlation with ACE ($R^2 = 0.975$), ACY and ACE showed good correlation with FLU ($R^2 = 0.776, 0.617$) and ACE showed good correlation with PHE ($R^2 = 0.736$) while ACY showed significant correlation with PHE and ANT. All these are three-ring PAHs emitted in vapor phase from cooking activities [35,39]. PHE, ACE and ACY showed strong correlation with high molecular weight PAHs [B(a)A, CHR, B(b)F, B(k)F, B(e)P, B(ghi)P]. PHE, ACE are generated from low temperature cooking [40], whereas high molecular weight PAHs in indoors are emitted from meat cooking and incomplete combustion which takes place at low temperature for longer duration [10]. DBF and ANT correlated well with each other and also with CAR and B(a)P whereas CAR correlated with PRY and B(a)P, this correlation might be inferred from cooking activities and tobacco smoke [9,27,41]. The correlation of FLT and B(a)A, CHR, B(b)F, B(k)F, B(e)P with five

Table 5a
Correlation matrix between the PAHs in indoor at roadside home.

	NAP	2MNAP	1MNAP	BHPY	2,6-DMNAP	ACY	ACE	DBF	FLU	PHE	ANT	FLT	PRY	B(a)A	CHR	B(b)F	B(e)P	B(a)P	B(ghi)P
NAP	1.000																		
2MNAP		1.000																	
1MNAP			1.000																
BHPY				1.000															
2,6-DMNAP					1.000														
ACY						1.000													
ACE							1.000												
DBF								1.000											
FLU									1.000										
PHE										1.000									
ANT											1.000								
FLT												1.000							
PRY													1.000						
B(a)A														1.000					
CHR															1.000				
B(b)F																1.000			
B(e)P																	1.000		
B(a)P																		1.000	
B(ghi)P																			1.000

Correlation is significant ($p < 0.01$) with few exceptions.

Table 5b
Correlation matrix between the PAHs in outdoor at roadside home.

	NAP	2MNAP	1MNAP	BHPY	2,6-DMNAP	ACY	ACE	DBF	FLU	PHE	ANT	CAR	FLT	PRY	B(a)A	CHR	B(b)F	B(k)F	B(e)P	B(a)P	B(ghi)P		
NAP	1.000																						
2MNAP	0.867	1.000																					
1MNAP	0.452	0.837	1.000																				
BPHY	-	-	0.098	1.000																			
2,6-DMNAP	-	-	-	0.207	1.000																		
ACY	0.363	0.780	0.995	0.195	-	1.000																	
ACE	-	-	-	0.757	0.796	-	1.000																
DBF	0.649	0.942	0.972	-	-	0.945	1.000																
FLU	0.407	0.808	0.999	0.148	-	0.999	0.959	1.000															
PHE	-	-	0.481	0.920	-	0.564	0.440	0.262	0.524	1.000													
ANT	-	-	-	0.970	0.439	-	0.893	-	-	0.797	1.000												
CAR	-	0.099	0.627	0.837	-	0.700	0.275	0.427	0.666	0.984	0.678	1.000											
FLT	-	0.216	0.715	0.766	-	0.780	0.159	0.532	0.750	0.957	0.586	0.993	1.000										
PRY	-	0.218	0.717	0.764	-	0.781	0.157	0.533	0.751	0.956	0.585	0.993	1.000										
B(a)A	0.963	0.969	0.675	-	-	0.600	-	0.829	0.637	-	-	0.019	0.138	0.140	0.985	1.000							
B(b)F	0.904	0.997	0.791	-	-	0.727	-	0.912	0.759	-	-	0.020	0.139	0.141	0.985	0.984	1.000						
B(k)F	0.965	0.967	0.669	-	-	0.728	-	0.913	0.760	-	-	-	-	-	1.000	0.984	0.984	1.000					
B(e)P	0.990	0.928	0.573	-	-	0.594	-	0.825	0.631	-	-	-	-	-	0.991	0.955	0.954	0.992	1.000				
B(a)P	0.949	0.980	0.710	-	-	0.490	-	0.749	0.530	-	-	-	0.016	0.018	0.999	0.993	0.992	0.998	0.998	1.000			
B(ghi)P	-	-	-	0.816	0.734	-	0.638	-	0.856	0.674	-	-	0.253	0.251	-	-	-	-	-	-	-	1.000	

Correlation is significant ($p < 0.01$) with few exceptions.

and six ring PAHs was attributed to incense burning and gas utilities [14,42]. At this site in outdoor air NAP and its derivatives (2MNAP, 1MNAP, 2,6-DMNAP) BPHY, ACY and PHE ($R^2 = 0.885$ – 1.000) inter-correlated with each other and was imputed to petrol powered vehicles [37,43,44]. Further strong correlation of DBF with FLU and FLT; FLU with FLT; PHE with ANT and FLT with PRY was attributed from diesel exhaust (generator use) [45,46].

Table 5 presents the correlation in indoor and outdoor air in roadside homes. From this Table 1 MNAP, 2MNAP, ACY and ACE showed strong correlation with each other and was attributed to deep frying and oil cooking activities [33–35]. NAP showed strong correlation with PHE, ANT and CHR ($R^2 = 0.973, 0.996, 0.971$) which was ascribed from diesel powered vehicles and transportation from outdoors to indoors [45]. NAP also showed strong correlation with B(a)A and B(ghi)P and was accredited to the use of heavy generators [27]. 2MNAP, 1MNAP, 2,6-DMNAP, BPHY, ACY, ACE, DBF, FLU, FLT, B(b)F, B(e)P and B(a)P showed correlation among each other and was traced to cooking activities indoors and also from outdoor vehicular emission [27,34,35,38,41,43,46]. While at outdoor environment of this site NAP, 2MNAP, 1MNAP, BPHY, ACY, FLU, B(a)A, CHR, B(b)F, B(k)F, B(e)P and B(a)P correlated to each other. The common source of origin for these PAHs was gasoline combustion engines on road [39,47,48]. The other correlation of PHE, ANT, CAR and PRY among each other and DBF correlation with four and five ring PAHs was assigned to diesel exhausts vehicles [1,45,46,49].

3.4. Distribution of PAH compounds in gaseous and particulate phase

In the atmosphere PAHs distribute between particulate and vapour phase, which predominantly depends on the physical characteristics of the compounds themselves and the environmental situations such as temperature and humidity. Concentrations of vapour PAHs correlate well with their sub cooled liquid vapour pressures [50,51]. The vapour pressure of PAHs strongly correlates with their molecular weights. With the increase in molecular weight, the estimated sublimation pressure is brought down correspondingly and thus the vapour phase concentration of PAHs in the atmosphere. In present study, the distribution of TPAHs in vapour and particulate phase were found to be 95.25% and 4.75% in kitchen, 98.18% and 1.81% living room, 93.66% and 6.34% in outdoors at urban site, whereas at roadside site they were found to be 94.23% and 5.77%, 87.58% and 12.42%, 93.55% and 6.45% in kitchen, living room and outdoors respectively. Fig. 4 illustrates the distribution of PAHs based on the number of benzene rings in gaseous and particulate phase at urban and roadside locations. From the figure it is clear that two and three-rings (MW = 142–154) PAHs existed in gaseous phase but the four-ring PAHs (MW = 202–228) such as ANT, FLT and PRY distributed themselves between gaseous as well as particulate phase. The five and six-ring (High MW, 228–276) PAHs were primarily associated with particulate phase only Fig. 4a and b. The individual PAH percentage contribution in kitchen, living room and outdoor environments at urban site homes was found to be 0.51–50.93%, 0.77–57.09% and 0.90–46.35% respectively, whereas at roadside it was found to be 0.16–52.50%, 1.41–50.37%, and 0.47–39.90% in kitchen, living room and outdoors. For each determined PAH, it was observed that NAP and its derivatives have highest concentrations followed by FLU, PHE and PRY concentrations in indoors and outdoors respectively. The observed high levels of naphthalene, i.e. 40–57% in domestic environments might be released due to the popular use of camphor balls and other chemicals for household activities. Furthermore incense and mosquito coil burning may be related to emission of other PAHs such as FLU, PRY, B(a)P, and, B(ghi)P [38].

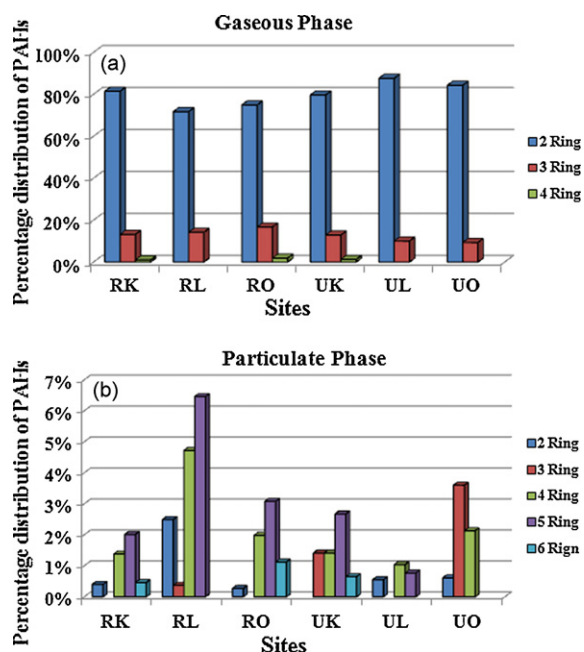


Fig. 4. Distribution of PAHs based on number of benzene rings in gaseous and particulate phase at urban and roadside. RK, road kitchen, RL, road living room, RO, road outdoor, UK, urban kitchen, UL, urban living room, UO, urban outdoor.

4. Conclusion

The indoor and outdoor PAH characteristics are evaluated at roadside and urban site homes of Agra in India. Our observation agreed with the reports in other parts of the world which demonstrated that indoor PAH concentrations generally exceed outdoor PAH concentration except roadside homes where PAH concentration were higher at outdoors in this study. The concentrations of TPAHs at roadside homes ranged from 2161.26 ng/m³ to 3294.28 ng/m³ and at urban site it ranged from 1212.37 ng/m³ to 1946.84 ng/m³. Naphthalene was found dominating at both sites homes in indoor and outdoor environment and it ranged from 562.00 ng/m³ to 1483.33 ng/m³. The spatial trends of PAHs showed that concentration of TPAHs were higher in kitchens than in living rooms at both the sites. Comparison between the two sites showed higher concentrations at roadside both indoors and outdoors due to affect of vehicular emissions. The concentrations of PAH in present study were found to be significantly higher in the vapour fraction of samples at both the sites than in the particulate fraction. The correlation analysis of PAHs suggested that PAHs in indoor environment was attributable mainly from gas utilities, cooking (frying and oil combustion), smoking and incense burning whereas at outdoor point the most common sources of PAHs was both combustion from petrol and diesel fuel vehicles. Thus this study provides significant scientific base for the research of PAHs in indoor air, and so contributes to the present understanding of people's exposure of pollutants of indoor origin.

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