Pattern, sources and toxic potential of PAHs in the agricultural soils of Delhi, India

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ABSTRACT

Surface soil (0–5 cm) from various agricultural sites in Delhi was analyzed to discern the contents of 16 priority polycyclic aromatic hydrocarbons (PAHs). Reference and deuterated standards were used for identification and quantification of PAHs by high performance liquid chromatography (HPLC) with UV detection. $\sum_{16}$PAHs ranged from 830 to 3880 $\mu g\,kg^{-1}$ (dry wt.) with an arithmetic mean of $1910 \pm 1020\,\mu g\,kg^{-1}$ $\sum_{16}$PAHs values at the urban sites were 2–5 times higher as compared to the rural sites. In general, low molecular weight PAHs were predominant. Total organic carbon (TOC) was found to be significantly correlated with $\sum_{16}$PAHs. Isomer pair ratios and Principal component analysis (PCA) suggested biomass and fossil fuel combustion as the main sources of PAHs. The toxic equivalency factors (TEFs) were used to estimate benzo[a]pyrene-equivalent concentration (B[a]P$_{eq}$). Therewith, PAH content of urban agricultural soil was found to have more carcinogenic potential.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) belong to a class of organic contaminants of great environmental concern. They are composed of two or more fused aromatic rings of carbon and hydrogen atoms. PAHs have grasped much attention due to their carcinogenic potential and ubiquitous presence in the environment [1]. The US Environmental Protection Agency (EPA) has listed 16 unsubstituted PAHs as priority pollutants. Several PAH species have been classified into probable (2A) or possible (2B) human carcinogens by the International Agency for Research on Cancer [2]. The most prominent and ubiquitous source of PAHs in the environment is incomplete combustion of modern biomass (such as wood) and fossil fuels (petroleum, coal) [3].

Soil ecosystem seems to be the ultimate repository for most of the hydrophobic organic contaminants such as PAHs. Atmospheric deposition is the most common source of pollution in soil, [4,5] so it is expected that most combustion derived PAHs will be restricted to the top layer of the soil. Many hydrophobic contaminants (such as PAHs) retain in the soil matrix for a long time after adsorption to the soil organic matter. PAHs present in soil not only create a risk to humans (through food contamination and accidental ingestion), but they may also exhibit a toxic activity towards different biological elements of the soil environment such as plants and microorganisms [6].

Arable soils are the most "sensitive" part of the soil environment with respect to human health risk [7]. Contamination of agricultural soil with PAHs creates a serious risk of introduction of these xenobiotics into the human food chain. Human exposure to PAHs is mainly by inhalation of particulates carrying PAHs, dietary intake of contaminated food products and direct contact with polluted soils [8]. Identification and apportionment of PAHs sources in the agricultural soil are important in terms of pollution control and to minimize the risk of human exposure.

There are some studies on the concentrations of PAHs in the air-borne particulates and sediments reported from India. Information about the distribution of PAHs in soils is rare. Moreover, the concentration of PAHs in soils is not yet regulated in India and only a few guidelines – Dutch standards (20–50 $\mu g\,kg^{-1}$), Mexican standards (0–6000 $\mu g\,kg^{-1}$) and Polish standards (200–10000 $\mu g\,kg^{-1}$) – exist worldwide. PAH contamination status of Delhi soils is of immense importance because soils in the urban and sub-urban areas of the city are being extensively used for agricultural purposes especially vegetable production posing threat to human health.

2. Study area

Delhi, the National Capital Territory of India, has a geographic area of 1483 sq km, with a population of 13.79 million. It is stretched in the east–west width approximately 51.9 km and in the north–west width approximately 48.48 km. Delhi is situated at the

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latitude of 28°24′17″ to 28°53 and the longitude of 76°20′37″ to 77°20′37″ with an altitude of 216 m above mean sea level in the semi-arid zone of India. To the north the Himalayas are at a distance of just 160 km and to the south are the central hot plains. To the west of Delhi is the Great Indian Desert (The Thar) of Rajasthan and cooler hilly regions to the northeast. Soils of Delhi have developed mainly on alluvium of river Yamuna and its tributaries. In the flood plains and recent alluvial plains they are mostly less developed whereas in the old alluvial plains they are comparatively less developed.

The climate of Delhi is mainly influenced by its inland position and the prevalence of continental air during the major part of the year. The summer and winter are extreme with mean maximum and minimum temperatures 40.5 °C and 27.6 °C in summer and 22.2 °C and 25 °C in winter respectively. The average annual temperature ranges between 22 °C to 25 °C. The mean annual rainfall is 612 mm, of which 80% is received during monsoon months (July–September). The air in Delhi is dry for most of the year, with very low relative humidity from April to June and markedly higher humidity in July and August, when weather conditions are oppressive. Except during the monsoon months (July to mid-September), winds are predominantly from a westerly or northwesterly direction. In the monsoon months, easterly and southeasterly winds are more common.

Industries, vehicular traffic and domestic burning are major contributors of pollution in Delhi. Vehicular emissions account for nearly 65% of the total air pollution load in Delhi. It out ranks other sources of air pollution like thermal power plants, industries and domestic coal burning. Thermal power plants rank second with 16%, followed by industries (12%) and domestic sector (7%) [9].

Land use in Delhi has undergone significant changes during the last 25 years due to ever increasing population, rapid industrialisation and urbanisation. The potential agricultural lands have been reduced by 60% within 25 years and have been used for non-agricultural purposes. This is creating ecological imbalance and pollution hazards in the state. The main urban agricultural area in the core of the city of Delhi is the floodplain along the Yamuna River that flows through the city North–South way. The area beyond the urban conglomeration of "Greater Delhi" is still predominantly agricultural.

2.1. Description of sampling sites

Samples were collected from seven different agricultural sites in Delhi during January 2006. Location of sampling sites in Delhi is shown in Fig. 1. Agricultural fields, AF02 and AF03, were selected in North-Delhi (upwind to the city) in Kushak and Kadipur village respectively. Agriculture is the main activity in these villages. Selected fields were ~5 km away from each other. Kushak and Kadipur villages are far away from the main city and source of pollution in the area is mainly household and agricultural activities. Three sites, AF01, AF04 and AF05, were taken along the Yamuna floodplain (west-side) where agricultural activities take place during non-monsoon period. AF01 was located in Palla village, which is surrounded by agricultural fields and is far away from any traffic and industrial activity. Other two sites AF04 and AF05 selected on the floodplain were located in the middle of the city. Site AF04 was selected near a heavy traffic flyover (ITO bridge). Site AF05 was located near IndraPrastha power plant, which might receive pollution from the power plant and the adjacent heavy traffic roads. Agricultural fields: AF06 and AF07 were taken in the southwest Delhi in Palam and Najafgarh village respectively. Palam, a heavily populated village is not much away from the main city. Since, Palam is located in the downwind direction; it is prone to receive the pollution load from different sources in the city. Najafgarh village is far away from the main city with no major pollution source in vicinity.
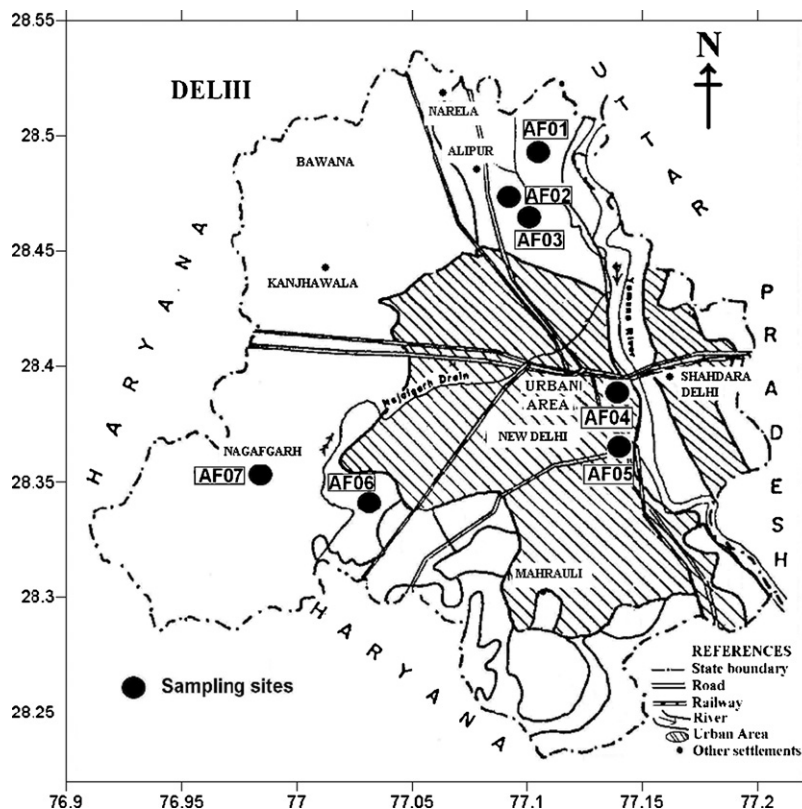

Fig. 1. Map of Delhi showing location of sampling sites.

3. Materials and methods

3.1. Sample collection

Surface soils (0–5 cm depth) were taken with a stainless steel soil auger after removal of the uppermost plant cover. Twelve samples were collected over an area of several hundred square meters, pooled and homogenized to provide a composite sample. Samples were preserved at 4 °C till further processing. In the laboratory the samples were dried in dark, twigs and stones were removed. Soil samples were sieved through 2 mm sieve and representative samples were obtained after coning and quartering.

3.2. Chemicals

Standard mixture containing 16 PAHs (16 compounds specified in EPA method 610) and deuterated PAHs internal standard (IS) mixture (Naphthalene-D8; Acenaphthene-D10; Phenanthrene-D10; Chrysene-D12 and Perylene-D12) were procured from Supelco (Bellefonte, PA, USA). All solvents (toluene, *n*-hexane, acetonitrile etc.), used for sample processing and analysis, were of HPLC grade. Water used for the analysis was high purity deionized water taken from the Mili-Q system.

3.3. Sample extraction and clean-up

Soil samples were extracted by ultra-sonication, a method developed and recommended by various authors [10–12]. Soil samples (10 g) were extracted twice in 50 ml of toluene for 15 min by ultrasonic agitation (Misonix Ultrasonic Processor-XL) with a frequency of 20 kHz in a water bath (10–15 °C). Both the extracts were subsequently mixed and centrifuged at 894×*g* for 20 min. The extracts were concentrated to 0.5–1.0 ml by rotary evaporator.

PAHs in the extracts were fractionated by a silica gel column (4 mm i.d.). Three grams of silica gel (Silica gel 60, particle size 0.0630–0.200 mm, 70–230 mesh ASTM purchased from Merck KGaA, Darmstadt, Germany) was activated at 180 °C for 24 h and kept overnight in exsiccator. Before use, silica gel was deactivated with 1% water. Then 40 ml of *n*-hexane was added to make slurry, and was kept overnight for degassing. Concentrated sample extract was poured over the packed column. The column was first eluted with 10 ml of *n*-hexane and the eluate was discarded. The PAH fraction was eluted with 20 ml hexane/toluene [13]. The PAHs containing fraction was concentrated to 0.5–1.0 ml using a rotary evaporator and solvent was exchanged with acetonitrile for further chromatographic analysis.

3.4. Analysis

All the samples were analyzed on high performance liquid chromatography system (Waters), equipped with tunable absorbance UV detector (254 nm) and Waters PAH C18 column (4.6 mm × 250 mm, particle size 5 μm). The mobile phase was a gradient of acetonitrile and degassed water (50% acetonitrile held for 5 min; linear gradient to 100% acetonitrile in 5–20 min; 100% acetonitrile held till 28 min and linear gradient to 50% acetonitrile from 28 min to 32 min; flow rate: 1.5 ml/min).

The quantitative analysis was done by the internal calibration method and PAHs identification was performed by comparison of their retention time with those of authentic standards. Mixture of internal standards was added to the sample just before the injection. Internal standard Naphthalene-D8 was used for naphthlene (Naph); Acenaphthene-D10 was used for acynaphthylene (Acy), acenaphthene (Acen), flourene (Flu), benz[*b*]fluoranthene (B[*b*]F), dibenz[*a*,*h*]anthracene (DB[*ah*]A),

benz[*ghi*]perylene (B[*ghi*]P) and indeno[1,2,3-*cd*]pyrene (IP); Phenanthrene-D10 was used for phenanthrene (Phen), anthracene (Anth), fluoranthene (Flan); Chrysene-D12 was used for pyrene (Pyr), benz[*a*]anthracene (B[*a*]A), chrysene (Chry) and Perylene-D12 was used for benz[*k*]fluoranthene (B[*k*]F), benz[*a*]pyrene (B[*a*]P). Response factors for different PAHs were measured by injecting a standard reference solution of the 16 PAHs spiked with the internal standards. Peak area responses and response factors were used to calculate the concentration of each compound [14].

3.5. Determination of total organic carbon (TOC)

Total organic carbon content of soil samples was determined by potassium dichromate oxidation method.

3.6. Quality control

Analytical methods were checked for the precision and accuracy. All the samples were analyzed in triplicate. Replicate analyses gave an error between ±10% and ±15%. The recovery efficiency was checked by analyzing soil samples spiked with known amount of PAH standard. Recoveries ranged from 79% to 95% for the reported PAHs in soil samples. Procedural blanks were performed periodically to prevent contamination.

4. Results and discussion

4.1. Concentrations and distribution of PAHs

The PAH concentrations at different sites are given in Table 1. Results are given as mean value of triplicate analysis of each composite sample. The $\sum_{16}$PAHs refers to the sum of 16 PAHs analyzed. $\sum_{16}$PAHs at different agricultural sites of Delhi varied from 830 μg kg^{-1} (AF03) to 3880 μg kg^{-1} (AF05) (dry wt.) with an arithmetic mean of 1910 ± 1020 μg kg^{-1} (Table 1). Observed PAHs concentrations were much higher than the typical concentration (200 μg kg^{-1}) reported for the sum of 16 EPA PAHs in arable soils [15]. Seven PAHs – B[*a*]A, Chry, B[*b*]F, B[*k*]F, B[*a*]P, DB[*ah*]A and IP – have been classified as probable human carcinogens by the IARC. The total concentrations of seven probably carcinogenic PAHs ranged from 180 μg kg^{-1} (AF07) to 1120 μg kg^{-1} (AF05) with an arithmetic mean of 580 ± 350 μg kg^{-1}. $\sum_{16}$PAHs concentrations varied distinctly at different sites. In general, observed $\sum_{16}$PAHs values were 2–5 times higher at the urban agricultural sites – AF04 and AF05 – as compared to the rural agricultural sites – AF01, AF03, AF06 and AF07. Levels of PAHs in soils in urban areas have been reported to be approximately 2–10 times higher than those in rural areas [16,17]. Highest $\sum_{16}$PAHs concentration (3880 μg kg^{-1}) was observed at site AF05 (Fig. 2) that could be due to the combined effect of vehicular traffic and power plant present in the immediate vicinity. Remote site AF03, located in the upwind direction of the main city revealed lowest $\sum_{16}$PAHs concentration (830 μg kg^{-1}). This could be because of less anthropogenic activities in the rural area located in the outskirt of the city. Consequently less PAHs in the ambient air available for deposition.

The $\sum_{16}$PAHs concentrations (830–3880 μg kg^{-1}) observed in this study were found in the same range as reported in the soils of vegetable fields of Pearl River Delta, South China ($\sum_{16}$PAHs 160–3700 μg kg^{-1}) [18]. In the agricultural soils of Poland and South Korea [19] lower $\sum_{16}$PAHs concentrations, 264 μg kg^{-1} and 236 μg kg^{-1} respectively have been reported. Higher PAHs values have been reported in the agricultural soils of Agra, India ($\sum_{14}$PAHs 6730 μg kg^{-1}) [20]. As high as 11.2–153,000 μg kg^{-1} ($\sum_{11}$PAHs) and 366–27,825 μg kg^{-1} ($\sum_{16}$PAHs) have been reported in the urban soils of Estonia [10] and China [21] respectively.

Table 1
PAH concentrations ($\mu g\,kg^{-1}$) at different sites in Delhi

Compound	Abbreviation	AF01	AF03	AF02	AF04	AF05	AF06	AF07	Average	S.D.
Naphthlene	Naph	136	99	252	110	706	234	187	246	211
Acynaphthylene	Acy	119	106	297	80	324	150	202	183	96
Acenaphthene	Acen	197	56	412	185	430	317	380	282	140
Flourene	Flu	78	65	74	56	154	63	50	77	35
Phenanthrene	Phen	42	38	77	79	191	49	52	76	54
Anthracene	Anth	13	22	46	59	109	43	48	48	31
Fluoranthene	Flan	119	70	231	105	520	146	148	191	153
Pyrene	Pyr	51	69	108	225	267	90	57	124	87
Benz[a]anthracene[a]	B[a]A	83	76	75	64	472	29	46	121	156
Chrysene[a]	Chry	36	18	85	50	143	45	28	58	43
Benz[b]fluoranthene[a]	B[b]F	54	33	69	137	187	83	46	87	56
Benz[k]fluoranthene[a]	B[k]F	71	23	65	62	68	57	25	53	21
Benz[a]pyrene[a]	B[a]P	52	18	63	68	38	71	36	49	19
Dibenz[a,h]anthracene[a]	DB[ah]A	n.d.	85	69	276	n.d.	106	n.d.	134	96
Benz[ghi]perylene	B[ghi]P	n.d.	45	166	214	60	84	12	97	77
Indeno[1,2,3-cd]pyrene[a]	IP	n.d.	3	7	226	214	22	4	79	109
$\sum_{16}$PAH		1049	827	2095	1997	3884	1590	1320	1906	1021
$\sum_{7}$PAH		295	255	433	884	1123	413	184	581	353
OC%		0.88	0.88	1.02	0.87	1.31	0.82	0.88	0.95	0.17

[a] Probable human carcinogen.

Among individual PAHs, Acen was the most abundant species at four out of seven sampling sites (namely AF01, AF02, AF06 and AF07) with an average concentration ranging from 60 (AF03) to 430 $\mu g\,kg^{-1}$ (AF05) and an arithmetic mean of $280 \pm 140\,\mu g\,kg^{-1}$. At sites AF03 and AF04 also low molecular weight (LMW) species Acy and Naph respectively were abundant. Only at site AF04, predominance of a high molecular weight (HMW) species DB[ah]A was observed. Cai et al. [18] also observed the predominance of 3-ring PAH-Acy. Predominance of 3-ring PAH-Acen is not expected in soil because of the high volatility nature of low molecular weight PAHs. Low molecular weight PAHs mainly originate from low temperature combustion and indicate recent inputs. In rural areas biomass burning is a common practice, which is a low temperature combustion process.

4.2. PAH pattern

PAH profiles with regard to the aromatic-ring number of PAHs at different sites are plotted in Fig. 3. PAH profiles revealed the influence of the extent of urbanisation at individual sites. In general at all the sites, 2,3-ring PAHs contributed ~50% to the total PAHs except at site AF04. Remote site AF07, remotely located in the downwind direction of the city was characterized by the 2,3-ring PAHs accounting for 70% of total PAHs. This could be due to the long-range atmospheric transport of PAHs from point sources of pollution to remote rural sites [22,23]. The traveling distance of PAHs decreases with increasing molecular weight [24,25], and therefore gaseous PAHs (2,3-ring PAHs) may be distributed over longer distances [26,15]. In spite of the urban location, site AF05 showed ~50% contribution of 2,3-ring PAHs, however 4-ring PAHs (36%) were highest at this site. Highest percentage of 4-ring PAHs at this site could be due to the presence of a coal-fired power plant in the immediate vicinity [27]. Site AF04 revealed fingerprints of typical urban soil. This site showed lowest contribution of 2,3-ring PAHs, ~30% of the total PAHs. Contribution of 5,6-ring PAHs to the total PAHs was ~50% which could be because of the deposition of high molecular weight PAHs from vehicular emission. There were heavy traffic roads and flyovers in the immediate vicinity of this site.

The predominance of low molecular weight PAHs in the agricultural soils of Delhi reflects the presence of significant combustion products from low temperature pyrolytic processes such as biomass burning [28,29] and/or petrogenic sources [8]. Furthermore, it indicates recent pollution, since the lighter PAHs are more biodegradable and less lipophilic and are not expected to persist
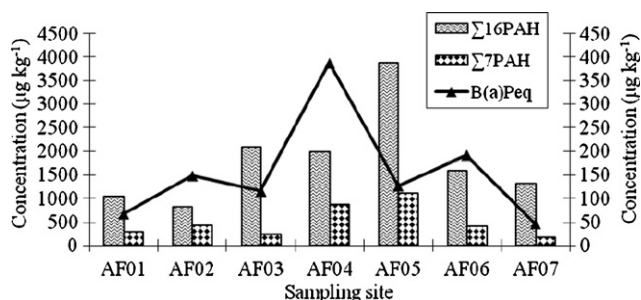

Fig. 2. Graph showing $\sum_{16}$PAH, $\sum_{7}$PAH concentrations ($\mu g\,kg^{-1}$) on primary Y-axis and total B[a]P$_{eq}$ concentrations ($\mu g\,kg^{-1}$) associated with seven probable carcinogenic PAH on the secondary Y-axis.
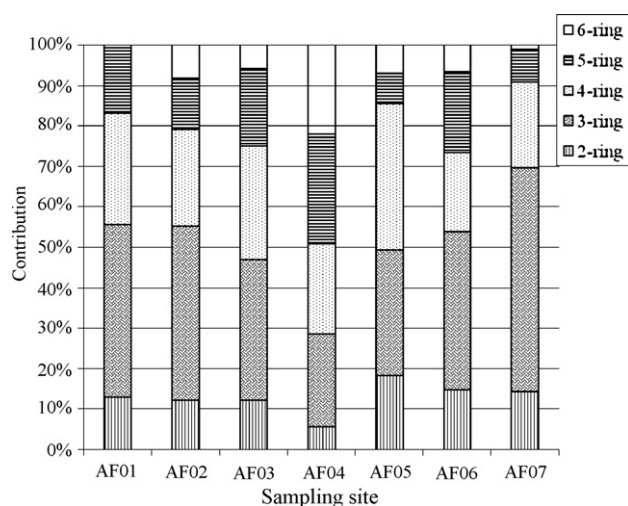

Fig. 3. Percentage composition of 2,3,4,5,6-ring PAHs in the agricultural soils of Delhi (2-ring PAHs include Naph; 3-ring PAHs include Acy, Acen, Flu, Phen and Anth; 4-ring PAHs include Flan, Pyr, B[a]A and Chry; 5-ring PAHs include B[b]F, B[k]F, B[a]P and DB[ah]A; 6-ring PAHs include IP and B[ghi]P).

or be sorbed as strongly as the heavier PAHs. Open burning of agricultural residue is a common practice in rural areas. Low temperature conditions during open burning of agricultural residue lead to incomplete combustion and prevalence of low molecular weight PAHs. Open burning of agricultural waste is characterized by low molecular PAHs (Naph, Acen, Acy, Phen and Flan) [30]. Moreover, agricultural soils are susceptible for the accidental inputs of fossil fuel such as diesel, which is commonly used in the vehicles used for various farm practices. Source of combustion derived HMW PAHs could be the use of generators, tractors etc. for agricultural purposes.

4.3. Correlation among individual PAHs and with total organic carbon (TOC)

Correlation exercise (Table 2) among the individual PAHs revealed that most of the 2,3,4-ring PAHs were significantly correlated with one another. However, they did not show significant positive correlation with high molecular weight 5,6-ring PAHs. This symbolizes different sources of these two groups of PAHs at the studied sites. Low molecular weight PAHs with high atmospheric mobility might have been transported from remote sites by medium or long-range atmospheric transport [26].

In this study, TOC was found to be significantly correlated with $\sum_{16}$PAHs and 2,3- (except Acen), 4-ring (except Pyr) PAHs. Poor correlation of TOC with 5,6-ring species in contrast to the low molecular weight (LMW) species is generally not observed. A key property for soil–air partitioning of semi-volatile organic compounds such as PAH is their vapor pressure [31]. This parameter determines a compounds vapor–particle partitioning and thus the fraction that is available for long-range atmospheric transport and phase transfer into soil OM. Baek et al. [32] proposed that 2,3-ring PAHs are mainly in the gas phase, 4-ring PAHs are in both gas phase and particle phase, and 5,6-ring PAHs are mainly attached to particles. Strong association of LMW PAHs with organic carbon could be interpreted as preferential adsorption of gas phase PAHs to soil organic matter. Lack of correlation between TOC and 5,6-ring PAHs may be interpreted as non-equilibrium situation because these compounds are deposited in association with particles and therefore are not readily available for partitioning to soil organic matter [25]. Wilcke and Amelung [33] and Bucheli et al. [34] also observed strong correlation between soil organic matter and LMW PAHs.

4.4. Possible sources of PAHs

Isomer pair ratios and principal component analysis were used to elucidate the possible sources of PAHs in the soil of the study area.

4.4.1. Isomer pair ratios

PAH isomer pair ratios have widely been used to elucidate the possible sources. The ratio of fluoranthene to fluoranthene plus pyrene (Flan/Flan + Pyr) and benz[a]anthracene to benz[a]anthracene plus chrysene (B[a]A/B[a]A + Chry) have been frequently used in published studies [16,8]. A plot of ratios between B[a]A/B[a]A + Chry and Flan/Flan + Pyr is given in Fig. 4. In this study, the values of B[a]A/B[a]A + Chry ratio varied between 0.35 and 0.91. Yunker et al. [35] suggested that values <0.2 and >0.35 were indicative of petroleum and combustion origin respectively whereas values between these two critical values implied mixed origin e.g. petroleum combustion. Therefore, PAHs in the soil of agricultural sites in Delhi might be mainly of combustion origin.

Moreover, another ratio has been used to identify biomass and petroleum combustion [8]. Yunker suggested that a Flan/Flan + Pyr ratio <0.4 indicates petroleum input, ratio between 0.4 and 0.5

Table 2
Correlation coefficient matrix for PAHs and TOC concentrations in the agricultural soils

	Naph	Acy	Acen	Flu	Phen	Anth	Flan	Pyr	B[a]A	Chry	B[b]F	B[k]F	B[a]P	DB[ah]A	B[ghi]P	IP	$\sum_{16}$PAH	$\sum_{7}$PAH	OC%
Naph	1.00																		
Acy	0.80*	1.00																	
Acen	0.67	0.86*	1.00																
Flu	0.93**	0.67	0.42	1.00															
Phen	0.94**	0.70	0.56	0.91**	1.00														
Anth	0.87**	0.65	0.63	0.74	0.94**	1.00													
Flan	0.99**	0.85*	0.70	0.93**	0.95*	0.87*	1.00												
Pyr	0.66	0.34	0.28	0.65	0.86*	0.87*	0.68	1.00											
B[a]A	0.94**	0.64	0.42	0.98**	0.95*	0.82*	0.93*	0.72	1.00										
Chry	0.93**	0.82*	0.67	0.89**	0.95*	0.86*	0.96*	0.77*	0.87*	1.00									
B[b]F	0.75	0.39	0.40	0.73	0.89*	0.89**	0.76*	0.97**	0.77*	0.82*	1.00								
B[k]F	0.38	0.26	0.33	0.46	0.43	0.30	0.43	0.47	0.34	0.59	0.58	1.00							
B[a]P	-0.13	-0.07	0.27	-0.22	-0.07	0.01	-0.10	0.16	-0.30	0.11	0.24	0.68	1.00						
DB[ah]A	-0.53	-0.62	-0.27	-0.85	0.51	0.71	-0.38	0.94	-0.06	-0.07	0.89	0.34	0.38	1.00					
B[ghi]P	-0.23	-0.17	-0.08	-0.16	0.02	0.02	-0.14	0.42	-0.20	0.15	0.32	0.66	0.73	0.68	1.00				
IP	0.47	0.04	0.05	0.54	0.72	0.77	0.49	0.97**	0.61	0.58	0.92**	0.59	0.20	0.99**	0.43	1.00			
$\sum_{16}$PAH	0.92**	0.73	0.65	0.85*	0.98**	0.95**	0.94**	0.87*	0.87*	0.97**	0.91**	0.52	0.11	0.38	0.15	0.71	1.00		
$\sum_{7}$PAH	0.70	0.34	0.29	0.71	0.87*	0.86*	0.71	0.99**	0.76*	0.80*	0.99**	0.57	0.20	0.94	-0.09	0.95**	0.89**	1.00	
OC%	0.93**	0.82*	0.57	0.94**	0.95*	0.82*	0.97**	0.69	0.95**	0.94*	0.71	0.37	-0.23	-0.36	0.40	0.50	0.90**	0.71	1.00

* Correlation is significant at the 0.05 level (2-tailed).
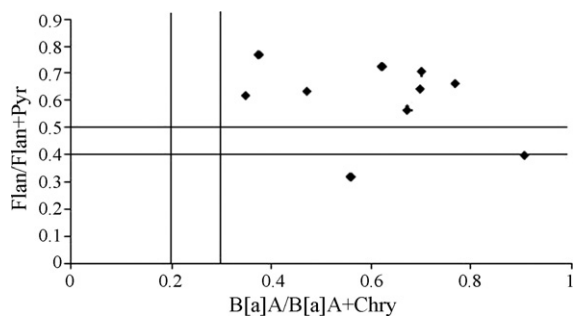** Correlation is significant at the 0.01 level (2-tailed).

Fig. 4. Cross plot of the values of Flan/Flan + Pyr ratio against the values of the B[*a*]A/B[*a*]A + Chry ratio.

liquid fossil fuel (vehicle and crude oil) combustion and ratio >0.5 grass, wood or coal combustion. In this study, the values of Flan/Flan + Pyr ratio varied between 0.32 and 0.77. The lowest value was found at site AF04, indicating that the input of PAHs was derived from petroleum. Site AF04 was located at the river flood-plain and the irrigation with the polluted river water containing petroleum could be the source of PAHs at this site. At other sites ratio was found to be >0.5, indicating biomass combustion as the main PAH source at the studied sites.

4.4.2. Principal component analysis (PCA)

The purpose of a factor analysis is to determine the number of common factors and their factor loading. The factor scores, which are obtained for each component within the factors generated by the PCA, are a type of correlation coefficient, and higher values are therefore associated with greater significance. A factor score of 0.5 was selected as the lowest level of significance within a factor. The Statistical Package for the Social Sciences (SPSS), version 10.0 was used to perform PCA. Factors were identified using Varimax rotation and eigenvalue >1.

As presented in Table 3, 94.75% variance of the scaled data was explained by three factors. Factor 1 explained 56.89% of the total variance of the data and had high loadings for Phen (0.88), Anth (0.70), Pyr (0.98), B[*b*]F (0.73), DB[*ah*]A (0.84), B[*ghi*]P (0.96) and IP

Table 3
Factor analysis scores following Varimax rotation for all PAHs (factor loadings >0.5 are shown in bold)

Variable	Component		
	1	2	3
Naph	−0.09	**0.84**	0.47
Acy	−0.02	**0.87**	0.39
Acen	0.02	**0.88**	0.32
Flu	0.33	**0.64**	**0.66**
Phen	**0.88**	0.36	0.25
Anth	**0.70**	**0.71**	0.09
Flan	0.21	**0.97**	−0.02
Pyr	**0.98**	0.20	0.06
B[*a*]A	0.19	−0.27	−0.77
Chry	0.46	0.26	**0.84**
B[*b*]F	**0.73**	0.02	**0.67**
B[*k*]F	0.44	0.13	**0.86**
B[*a*]P	0.35	0.40	**0.82**
DB[*ah*]A	**0.84**	−0.36	0.39
B[*ghi*]P	**0.96**	0.28	0.07
IP	**0.89**	−0.39	0.23
Eigenvalues	9.10	4.11	1.95
% of variance	56.89	25.69	12.17
Cumulative %	56.89	82.58	94.75
Probable sources	Diesel and coal combustion	Biomass combustion	Wood burning

(0.89). Duval and Friedlander [36], as cited by Harrison et al. [37], noted that B[*b*]F, in addition to B[*ghi*]P, Cor, Flan and Pyr, are indicators of diesel powered vehicles. Khalili et al. [38] identified that Phen, Anth, Flan, Pyr, B[*a*]A and Chry were markers of coal combustion. Both B[*ghi*]P and IP have been identified as typical tracers of vehicular source of PAHs [37,39,40]. This factor seems to represent a combination of petroleum and coal combustion sources.

The second factor responsible for 25.69% of the total variance predominantly weighed in low molecular weight PAHs Naph (0.84), Acy (0.87), Acen (0.88), Flu (0.64), Anth (0.71) and Flan (0.97). This factor represents biomass (especially agricultural residue waste) burning as the source of this group of PAHs [28].

The third factor accounted 12.17% of the total variance and had high loadings of Flu (0.66), Chry (0.84), B[*b*]F (0.67), B[*k*]F (0.86) and B[*a*]P (0.82). Wood burning has been suggested as the source of Flu, B[*b*]F, B[*k*]F and B[*a*]P [41,42].

Inferences drawn from the principal component analysis are similar to that of isomer pair ratios identifying combustion of biomass and fossil fuel as the main sources of PAHs contamination in the agricultural sites of Delhi.

4.5. Assessment of soil toxicity based on the total concentration of seven probable carcinogenic PAHs

The toxic equivalency factors (TEFs) were used to quantify the carcinogenicity of other PAHs relative to B[*a*]P and to estimate benzo[*a*]pyrene-equivalent concentration (B[*a*]P$_{eq}$) [43,44]. Benzo[*a*]pyrene is the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor among all known potentially carcinogenic PAHs [45]. According to the USEPA, Calculated TEFs for B[*a*]A, B[*a*]P, B[*b*]F, B[*k*]F, IP, DB[*ah*]A and Chry are 0.1, 1, 0.1, 0.01, 0.1, 1 and 0.001 respectively [46]. The total benzo[*a*]pyrene-equivalent concentration (B[*a*]P$_{eq}$) was calculated as

$$\text{Total } B[a]P_{eq} = \sum_i C_i \times TEF_i$$

where C_i is the concentration of individual PAH and TEF_i is the corresponding toxic equivalency factor.

Calculated total B[*a*]P$_{eq}$ concentrations at different sampling sites varied from 45.64 μg kg^{-1} to 387.13 μg kg^{-1} (dry wt.), with an average value of 154.12 ± 113.61 μg kg^{-1}. Total B[*a*]P$_{eq}$ concentration was highest at site AF04 (Fig. 2) and it was 2–8 times higher as compared to other sites. Though the total concentration of carcinogenic PAHs ($\sum_7$PAH) was highest at AF05 but $\sum_7$PAH content at site AF04 were found to have highest carcinogenic potential. This is due to the higher concentration of PAH species having higher carcinogenic potency at site AF04.

5. Conclusion

Urban sites showed 2–5 times more PAH contamination as compared to the rural agricultural sites. However, highest B[*a*]P$_{eq}$ concentration at an urban site was 2–8 times higher as compared to other sites. Effect of proximity to the source reflected in the PAH patterns at different sites. Contribution of high molecular weight PAHs to the total PAH content was highest at one of the urban sites. Low molecular weight PAHs were strongly correlated with organic carbon content implying the preferential adsorption of gas phase PAHs to the soil organic matter.

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