Assessment of PAHs in soil around the International Airport in Delhi, India

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Abstract

Present study was undertaken to determine the level of PAH contamination due to jet turbine exhaust in the peripheral soil of the International Airport in Delhi, India. Densely populated residential areas surrounding the airport come directly under both the landing and take-off flight paths. Twelve priority polycyclic aromatic hydrocarbons (PAHs) were analyzed in the <2 mm surface soil fraction. Identification and quantification of PAHs was done by high performance liquid chromatography (HPLC). The sum of 12 PAHs ranged from 2.39 $\mu g\,g^{-1}$ to 7.53 $\mu g\,g^{-1}$ with a mean concentration of 4.43 ± 1.45 $\mu g\,g^{-1}$. PAH levels observed in the present study were found to be higher as compared to most of the literature values. Among the three sampling sites selected around the International Airport, the site near landing point revealed maximum concentration of PAHs, while minimum concentration was observed at the site near take-off point. Predominance of pyrene was observed in the airport soil. Factor analysis and isomer pair ratios suggest pyrogenic origin of PAHs in the study area.
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1. Introduction

Little is known about the possible exposure of people living near airports to polycyclic aromatic hydrocarbons (PAHs). It has been conjectured that jet turbine exhaust near airplane flight paths may result in significant human exposure to PAHs. At major airports, aircrafts are routed through corridors or discrete pathways significantly localizing the distribution of any fallout, subject to meteorological effects. The plume could move directly to the ground as a cohesive unit due to electrostatic charge or saturation effects and get deposited on soil or pass into residential areas. Thus, posing risk of PAH exposure [1].

The primary aviation fuels are kerosene-range distillates [2]. The combustion of these fuels produces non-methane hydrocarbons (NMHCs) [3]. PAHs, a group of ubiquitous organic contaminants are included in the list of NMHCs. PAHs mainly originate from anthropogenic sources. They are a subject of public concern due to their demonstrated carcinogenic and mutagenic potential [4]. The United States Environmental Protection Agency (USEPA) has listed 14 hazardous air pollutants (HAPs), believed to be present in the aircraft exhaust. The list includes a group of 16 PAHs, as polycyclic organic matter (POM) [5].

Aircraft engines (piston and turbine) have been demonstrated to emit considerable amounts of benzo(*a*)pyrene (2–10 mg min^{-1}), a known carcinogenic hydrocarbon associated with particulates [6]. So, particulate associated PAHs emitted from aircrafts [7], represent a source of carcinogenic pollution in the vicinity of airports [8]. Particulate associated PAH flux to soil is mainly influenced by their concentration in the atmosphere and by the effectiveness of wet and dry deposition fluxes [9]. PAH flux to soil correlates significantly with the corresponding levels in air [10] and urban street dust [11]. Therefore, PAH determination in soil may provide important information on the environmental pollution state [12]. Impact of aviation exhaust on carcinogenic environmental pollution is important because of its spread and distribution over a very wide area [13].

Few studies have reported PAH levels in ambient air at different locations in India, for example, Delhi [14], Mumbai [15], Kolkata [16] and Ahmedabad [17]. Some scattered information is available on PAH concentration in sediments [18–20], biodegradation of PAHs [21], in the field of PAH biomarkers

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[22] and seasonal biomonitoring of PAHs [23]. But, information on the PAH levels in Indian soils is very scarce [24].

The principal objective of the present study was to determine the concentration levels of PAHs in the surface soil around the Indira Gandhi International (IGI) airport, Delhi. The database generated from this study will be of immense importance in characterizing airport soils with respect to PAHs in India. The study may also be helpful in land-use planning of urban regions.

2. Materials and methods

2.1. Sampling sites

Delhi, the capital of India is situated at a latitude of 28°24′17″N to 28°53′N and the longitude of 76°20′37″E to 77°20′37″E with an altitude of 216 m above mean sea level. To the north the Himalayas are situated at a distance of 160 km and to the south are the central hot plains. To the west of Delhi is the Great Indian Desert (Thar Desert) of Rajasthan and the Gangetic plains lie in the east. North-west wind usually prevails, except during monsoon when south-east winds are pre-dominant [25].

Indira Gandhi International (IGI) Airport is located (Fig. 1) 23 km south of New Delhi and is a vital link between India and rest of the globe. It is one of the busiest airports in South Asia. The International Terminal has 35 airlines flying to the major cities across the world. It has a terminal capacity of 1150

aircrafts, while it operates about 250 flights per day [26]. The airport on an average currently handles cargo operations of all major international airlines, besides transporting 9500 international passengers daily. The runway is oriented in the east-west direction. The capital has a single 40 km long commercial air traffic corridor, which is oriented in the east to west direction for both incoming and outgoing flights [27].

The major residential areas surrounding the International Airport are Palam, Dwarka, Mahipalpur, Pappan Kalan and Pahladpur. There are no industries and heavy traffic roads in the vicinity of the airport. The IGI airport is served by subsidiary thin traffic road emerging from National highway (NH-8). National highway (NH-8) having heavy traffic is at a distance of ∼4–5 km from the airport. So, the direct impact of vehicular emission from the highway is minimal on the sampling sites.

Location of sampling sites is depicted in Fig. 1. Three sampling sites were selected in the area surrounding the airport and one background site was chosen in a remote area. Site-I (LP) was selected near the landing point of the airport, while site-II (T/I) was located near the taxi/idle point (south of the runway). Site-III (T-O) was situated near the take-off point of the airport. The background (BG) sampling site was sited at a remote area at a distance of ∼10 km from the airport and there was no direct source of emission in the surroundings, i.e. no residential, industrial or vehicular emissions in the close vicinity.

2.2. Sample collection

Samples were taken on monthly basis, i.e. one sample in each month for a total period of 6 months (from November, 2005 to May, 2006). Samples were taken with the help of a stainless steel auger up to a depth of 5 cm. The samples were transferred into polythene bags, transported to the laboratory and were preserved at 4 °C till further processing. At each sampling site 8–10 samples were collected by grab sampling, within a distance of 50 m. In the laboratory the samples were dried in dark, twigs and stones were removed. Those grab samples were mixed thoroughly to make a composite sample. After homogenization, the soil samples were sieved through 2 mm sieve. Representative samples were obtained after quartering and coning.

2.3. Chemicals

Standard mixture containing 16 PAHs (16 compounds specified in USEPA method 610) and deuterated PAHs internal standard (IS) mixture (naphthalene-d_8; acenaphthene-d_{10}; phenanthrene-d_{10} and chrysene-d_{12}) were procured from Supelco (Bellefonte, PA, USA). All solvents (toluene, n-hexane, acetonitrile, etc.) used for sample processing and analysis, were of HPLC grade. High purity deionised water from Milli-Q system was used as the mobile phase during the HPLC analysis.

2.4. Sample extraction and clean-up

Soil samples were extracted by ultra-sonication, a method developed and recommended by various authors [28,29]. Details of extraction and clean-up method are described elsewhere [20].
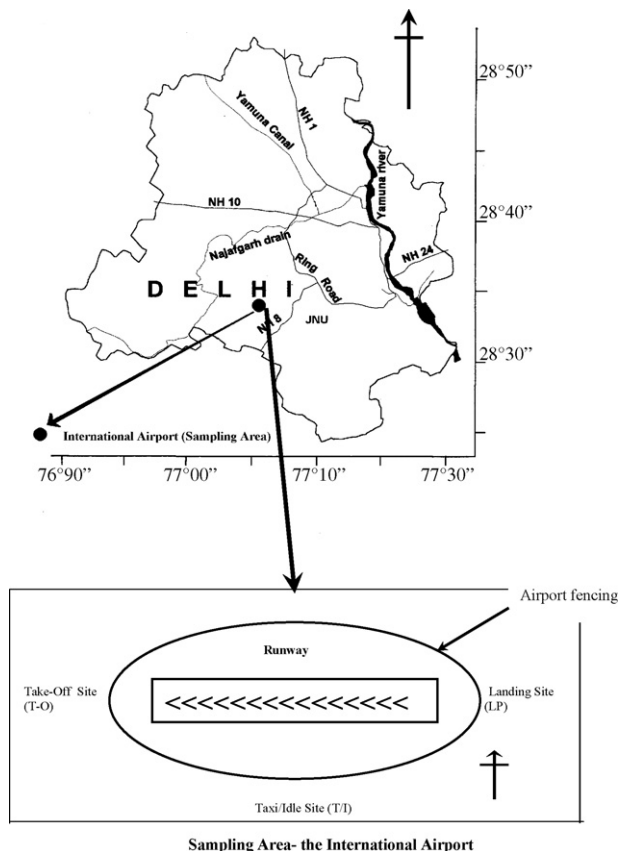

Fig. 1. Map of Delhi showing location of sampling area—the International Airport.

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). PAHs in the extracts were fractionated by a silica gel (Silica gel 60, particle size 0.0630–0.200 mm, 70–230 mesh ASTM purchased from Merck KgaA, Darmstadt, Germany) column (4 mm i.d.). The PAH containing fraction was concentrated to 0.5–1.0 ml by using a rotary evaporator and solvent was exchanged with acetonitrile for further chromatographic analysis.

2.5. Analysis

All the samples were analyzed on HPLC (Waters), equipped with tunable absorbance UV detector (254 nm) and Waters PAH C18 column (4.6 × 250 mm, 5 μm-particle size). 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 (five-point calibration) and PAH identification was performed by comparison of their retention time with those of authentic standards. 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 were used against concentration of each compound and internal standard to calculate the response factors [30].

2.6. Analytical 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.

3. Results and discussion

3.1. Spatial profile

Soil samples from the sampling area: the International Airport, Delhi were analyzed for 12 USEPA priority parent PAHs. ΣPAH values ranged from 2.39 μg g^{-1} to 7.53 μg g^{-1} (Table 1) with a mean concentration of 4.43 ± 1.13 μg g^{-1} (Table 2). ΣPAH referred to the sum of 12 identified PAH components in the investigated samples. Results of PAH concentrations were given as arithmetic mean of 6 months. The average concentrations of ΣPAHs in soil samples at different sampling sites were shown in Fig. 2.

Average ΣPAH concentration was found to be maximum (5.68 ± 1.66 μg g^{-1}) at the sampling site (LP) near landing point (Fig. 2), while it was minimum (3.49 ± 0.73 μg g^{-1}) at the sampling site (T-O) near take-off point of the airport. At other sampling sites viz. taxi/idle (T/I) and background (BG), average ΣPAH concentrations were found to be 4.12 ± 0.90 μg g^{-1} and 1.71 ± 0.33 μg g^{-1}, respectively (Table 1).

The ΣPAH concentration in the soils of the sampling area was ~2.58 times higher than that of the background (BG) site. Atmospheric deposition is the most common source of soil contamination. So the deposition of particulate associated PAHs emitted from the aircraft could be responsible for spatial variability and enhanced values in the study area. Studies conducted inside and in the vicinity of airports of Russia [5,31], Japan [32], France [33] and Poland [34] have also reported PAH contamination in soils through deposition of aircraft emissions.

Exhaust emissions, especially PAH emissions are strongly dependent on the power settings of the engine [35,36]. According to a study, overall mass of PAH emitted during the take-off conditions was around 18% less than during the landing operations [39]. During landing operations, engine is set at low power settings [37] at which engine emit maximum hydrocarbons due to incomplete combustion [38]. So, highest concentration at LP-site could be due to its location near the landing point. PAH emissions tend to decrease as power setting increases, i.e. during take-off [36], which supported the minimum ΣPAH concentra-

Table 1
PAH concentrations (μg g^{-1}) at different sampling sites

Compounds	LP	T/I	T-O	BG
Phen	0.376 ± 0.171	0.199 ± 0.103	0.244 ± 0.113	0.172 ± 0.052
Anth	0.319 ± 0.070	0.235 ± 0.075	0.221 ± 0.098	0.144 ± 0.017
Flan	0.848 ± 0.161	0.654 ± 0.242	0.629 ± 0.201	0.194 ± 0.087
Pyr	1.045 ± 0.269	0.668 ± 0.186	0.655 ± 0.163	0.345 ± 0.059
B(a)A	0.212 ± 0.089	0.156 ± 0.068	0.163 ± 0.040	0.095 ± 0.012
Chry	0.188 ± 0.062	0.117 ± 0.028	0.142 ± 0.077	0.044 ± 0.017
B(b)F	0.421 ± 0.160	0.223 ± 0.067	0.214 ± 0.070	0.110 ± 0.017
B(k)F	0.437 ± 0.327	0.275 ± 0.077	0.237 ± 0.135	0.123 ± 0.019
B(a)P	0.260 ± 0.126	0.229 ± 0.095	0.182 ± 0.067	0.112 ± 0.022
DB(ah)A	0.951 ± 0.699	0.734 ± 0.379	0.390 ± 0.167	0.191 ± 0.082
B(ghi)P	0.405 ± 0.120	0.394 ± 0.145	0.290 ± 0.105	0.100 ± 0.014
IP	0.213 ± 0.111	0.239 ± 0.135	0.119 ± 0.068	0.084 ± 0.038
Sum	5.676 ± 1.655	4.122 ± 0.901	3.487 ± 0.726	1.714 ± 0.330
Range	3.131–7.529	2.394–4.893	2.517–4.661	1.205–2.127

Table 2
Mean concentration, toxic equivalent factors (TEFs) and B(a)P equivalent concentration [B(a)P$_{eq}$] at the Airport site in Delhi (µg/g)

| PAHs	Airport (Mean) ($\mu g\,g^{-1}$)	BG ($\mu g\,g^{-1}$)	TEFs	B(a)P$_{eq}$	
				Airport	BG
Phen	0.273	0.172	0.001	0.000273	0.000172
Anth	0.259	0.144	0.01	0.00259	0.00144
Flan	0.71	0.194	0.001	0.00071	0.000194
Pyr	0.789	0.345	0.001	0.000789	0.000345
B(a)A	0.177	0.095	0.1	0.0177	0.009519
Chry	0.149	0.044	0.01	0.00149	0.000439
B(b)F	0.286	0.11	0.1	0.0286	0.010957
B(k)F	0.316	0.123	0.1	0.0316	0.012254
B(a)P	0.223	0.112	1	0.223	0.111505
DB(ah)A	0.692	0.191	1	0.692	0.191193
B(ghi)P	0.363	0.1	0.01	0.00363	0.001004
IP	0.191	0.084	0.1	0.0191	0.008415
Total	4.428	1.714	2.433	1.021	0.347
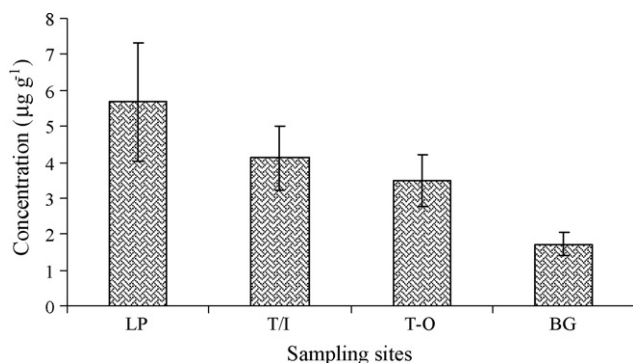
Fig. 2. Total concentrations ($\mu g\,g^{-1}$) of ΣPAHs at different sampling sites.

tion at the sampling site near take-off point. Moreover, since the same runway was used for both, landing and take-off operations, landing site received deposition fluxes from both landing and taking-off planes whereas the take-off site was only under the effect of taking-off planes.

PAH concentration at T/I site was observed to be higher than T-O, probably because T/I was located downwind of the runway, closer to the landing site (LP). Hence, T/I was under the

influence of emissions both from landing operations and from numerous aircrafts awaiting maintenance operations. While T-O site only handled aircrafts during take-off operations. So lesser PAH concentration at T-O site could be justified.

Loads of individual PAHs followed the trend—Pyr (19%) > Flan~DB(ah)A (16%) > B(ghi)P (8%) > B(k)F (7%) > B(b)F~Phen~Anth (6%) > B(a)P (5%) > IP~B(a)A (4%) > Chry (3%) (Table 3, Fig. 3). Abundance of Flan and Pyr has also been observed in the airport soil in France [33]. This is also in agreement with the study reported by Moses [40]. According to literature Flan and Pyr are considered as typical pyrogenic products. They are associated with incineration and oil combustion and are generated from high temperature condensation of low molecular weight compounds [41]. DB[ah]A is considered as an ubiquitous product of incomplete combustion. Duval and Friedlander [42], as cited by Harrison et al. [43], noted that B(b)F, in addition to B(ghi)P, Cor, Flan and Pyr, are indicators of diesel powered vehicles.

PAH profiles, with regard to the aromatic-ring number of individual PAHs, at different sites are plotted in Fig. 4. Profiles showed that the 4-ring PAHs (41%) dominated the PAHs composition. Ring-wise PAH composition was found to be similar as reported by Ducoulombier and Rychen [33].

Total PAH and B(a)P concentrations observed in the present study were found to be higher as compared to most of the literature values reporting PAH concentrations in the airport soils (Table 4). Higher PAH values observed in the present study could be explained as the Indian Government imports aircrafts having an average age of 15 years [44], while the commercial Indian fleet has an average age of 22.8 years [45]. It has been observed that with newer aircrafts, the hydrocarbon emission decreased by 10% [46]. Thus it seems that the high PAH emissions at the IGI Airport could be due to the usage of older aircraft models.

There are no PAH limiting values in soil in India. So the present data was compared with Dutch standards (0.02–0.05 $\mu g\,g^{-1}$), Mexican standards (0–6 $\mu g\,g^{-1}$) and Polish standards (0.02–10 $\mu g\,g^{-1}$) [47]. The comparison showed that the PAH concentration in IGI airport soils exceeded the Dutch standard by ~100 times, while it slightly exceeded the Mexican standard. It is observed that according to the Polish standards, the IGI airport soil can be classified under the pollution class of

Table 3
Properties and average percentage distribution of PAHs measured around the IGI airport

| Compounds	Abbreviations	Mol. wt.	No. of rings	Vapour Pressure (Pa) at 25 °C	Average percentage (%)
Phenanthrene	Phen	178	3	1.6×10^{-2}	6
Anthracene	Anth	178	3	8.0×10^{-2}	6
Fluoranthene	Flan	202	4	1.2×10^{-3}	16
Pyrene	Pyr	202	4	6.0×10^{-4}	19
Benzo[a]anthracene	B(a)A	228	4	2.8×10^{-5}	4
Chrysene	Chry	228	4	8.4×10^{-5}	3
Benzo[b]fluoranthene	B(b)F	252	5	6.7×10^{-5}	6
Benzo[k]fluoranthene	B(k)F	252	5	1.3×10^{-8}	7
Benzo[a]pyrene	B(a)P	252	5	7.3×10^{-7}	5
Dibenzo[a,h]anthracene	DB(ah)A	278	5	1.3×10^{-8}	16
Benzo[g,h,i]perylene	B(ghi)P	276	6	1.4×10^{-8}	8
Indeno[1,2,3-cd]pyrene	IP	276	6	1.3×10^{-8}	4
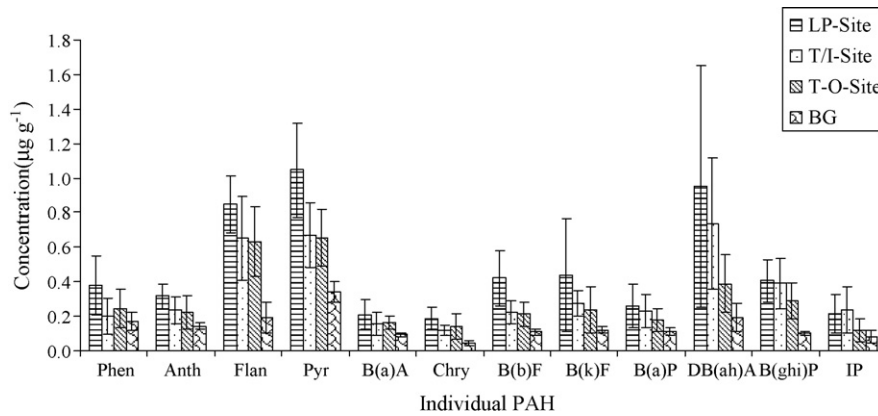
Fig. 3. Average concentrations ($\mu g\,g^{-1}$) of individual PAH species at different sampling sites.

IV, and can be assessed as "heavily polluted" soil with respect to PAH contamination.

3.2. Source apportionment: principal component analysis (PCA) and isomer pair ratios

Principal component analysis (PCA) was used to confirm that the primary source of PAH contamination in the study area was jet turbine exhaust. PCA is the oldest and most widely used multivariate statistical technique. The principle of PCA is to transform the original set of variables into a smaller set of linear combinations that account for most of the variance of the original
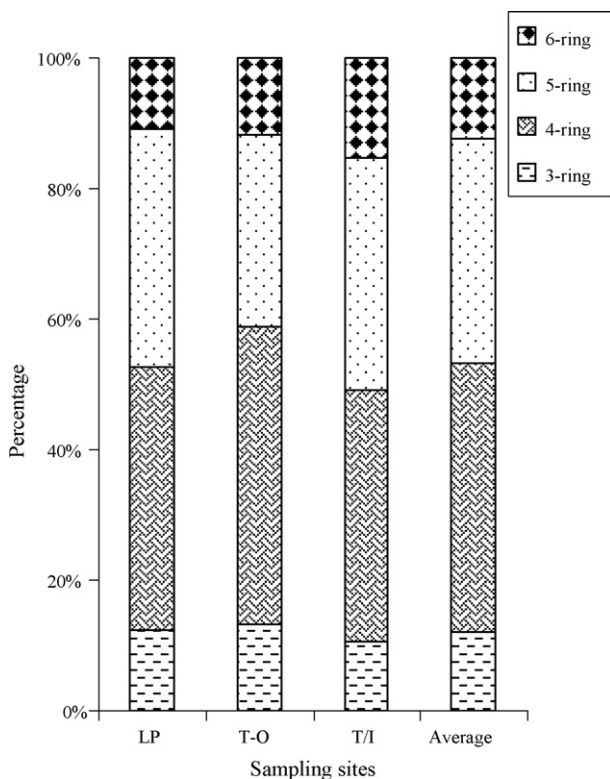

Fig. 4. Percentage composition of 3-, 4-, 5- and 6-ring PAHs in the soils of different sampling sites (3-ring PAHs include Phen and Anth; 4-ring PAHs include Flan, Pyr, B[a]A and Chry; 5-ring PAHs include B[b]F, B[k]F, B[a]P and DB[a,h]A; 6-ring PAHs include IP and B[g,h,i]P).

set. The primary function of this analysis is the reduction of the number of variables while retaining the original information as much as possible, and thus variables with similar characteristics can be grouped into factors [48]. 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 5, the majority of the variance (79.28%) of the scaled data was explained by four Eigen vectors. The first factor responsible for 46.97% of the total variance was heavily weighted by Pyr (0.643), B(a)A (0.847), Chry (0.660), DB(ah)A (0.676) and B(ghi)P (0.682), all of which were indicators of diesel combustion [48–50]. Thus factor 1 reflected the effects of diesel combustion.

The second factor responsible for 13.25% of the total variance predominately weighed in Flan (0.671), B(k)F (0.782) and IP (0.854). Thus, representing mixed sources from both diesel and coal combustion. The third factor responsible for 10.34% of the total variance had high loading factor for Anth (0.903), Pyr (0.530), B(b)F (0.619) and DB(ah)A (0.619). The compounds Anth and Pyr represented sources of wood combustion [48], while B(b)F and DB(ah)A are products of diesel combustion [48,50]. Thus compounds representing factor 3, were all indicators of mixed sources comprising of wood and diesel combustion.

The fourth factor responsible for 8.72% of the total variance is weighted in Phen (0.678), Chry (0.615) and B(a)P (0.884). B(a)P can be attributed to diesel combustion [50,51], while Phen is a product of wood combustion and Chry is a product of coal combustion [48]. This factor in all probability represented products of mixed sources from diesel, wood and coal combustion.

The products of diesel combustion were found to be similar to those from aircraft fuel combustion [39] and no significant differences were observed for the PAH spectra of diesel engines and aircraft turbine engines [52]. So it could be concluded that factor 1, factor 2 and factor 3 represented the sources of aviation fuel combustion.

To corroborate the above conclusions, the ratios Anth/178 and Flan/Flan + Pyr were calculated. These ratios have been used to distinguish between petrogenic and pyrogenic sources of PAHs. Anth/178 ratio of >0.10 suggested strong pyrogenic ori-

Table 4
Concentration ranges of total polycyclic aromatic hydrocarbons (PAHs) and B(a)P in airport soils from different countries

Location	No. of PAH	Range of PAHs (ng/g)	Reference
Indira Gandhi International Airport, India	12	2394–7529	Present study
Military Airfield, Poland	16	349–5657	[34]
Greater Cincinnati and Northern Kentucky Airport, U.S.A.	19	130–880	[1]
French Airport, France	16	1.7–43.17	[33]
Indira Gandhi International Airport, India	1 [B(a)P]	69–395	Present study
Greater Cincinnati and Northern Kentucky Airport, U.S.A	1 [B(a)P]	1.0–530	[1]
Military airfield, Poland	1 [B(a)P]	9.9–464	[34]
Nagoya Airport, Japan	1 [B(a)P]	225	[32]
Kola Peninsula, Russia	1 [B(a)P]	30–200	[31]
Moscow Airport, U.S.S.R	1 [B(a)P]	15.4–64.3	[6]
French Airport, France	1 [B(a)P]	18.42	[33]
Pavlodar Airport, Northern Kazakhstan	1 [B(a)P]	5.5	[6]

gin, while Flan/Flan + Pyr ratio between 0.4 and 0.5 represented petroleum combustion [53]. Cross-plot analysis (Fig. 5.) showed that according to Anth/178 ratio, 100% of the samples fell in the combustion zone. Subsequently, according to Flan/Flan + Pyr on an average 66% of the samples were in petroleum combustion zone. Thus, it could be inferred that the primary source of PAHs in the study area was petroleum combustion.

3.2.1. Estimation of carcinogenic potencies

Densely populated residential areas surrounding the airport come directly under both the landing and take-off flight paths. So the knowledge of soil contamination with PAHs is needed to know the extent of carcinogenic exposure on the residents around the airport site. Several PAH species including B(a)P, the most carcinogenic have been classified into probable (2A) or possible (2B) human carcinogens by IARC [54].

Carcinogenic potency associated with exposure of a given PAH compound can be obtained by calculating its B(a)P equivalent concentration [B(a)P$_{eq}$]. To calculate the B(a)P$_{eq}$ of
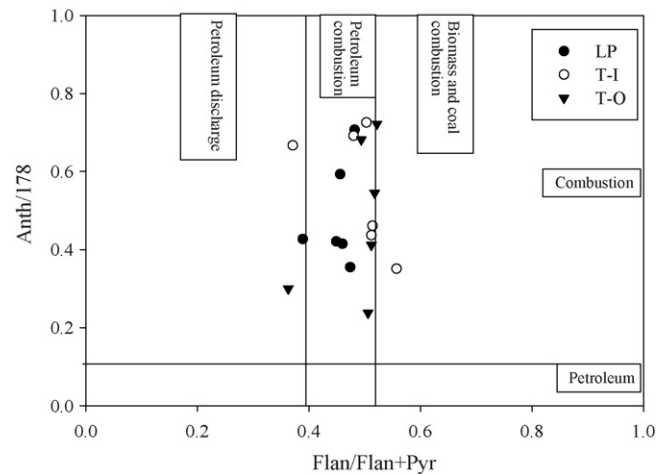
Fig. 5. Cross-plots of the values of Anth/178 ratio against the values of the Flan/Flan + Pyr ratio for the sampling area—the International Airport.

Table 5
Factor analysis scores following varimax rotation for all PAHs (only values exceeding 0.5 are shown for clarity)

Variable	Component			
	1	2	3	4
Phen				0.678
Anth			0.903	
Flan		0.671		
Pyr	0.643		0.53	
B(a)A	0.847			
Chry	0.66			0.615
B(b)F			0.619	
B(k)F		0.782		
B(a)P				0.884
DB(ah)A	0.676		0.6	
B(ghi)P	0.682			
IP		0.854		
Eigen values	5.64	1.59	1.24	1.05
% of variance	46.97	13.25	10.34	8.72
Cumulative (%)	46.97	60.22	70.56	79.28
Probable sources	Diesel combustion	Diesel and coal combustion	Wood and diesel combustion	Wood, coal diesel combustion

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization loading >0.5 is considered statistically significant.

individual species, toxic equivalent factor (TEF) of the given species relative to B(a)P was used. The list of TEFs compiled by Tsai et al. [55] was adopted in this study. B(a)P has been assigned a TEF of one, which is highest among all PAHs. To compare the carcinogenic potencies associated with the total PAH concentrations in the background and airport soil, sum of each individual BaP$_{eq}$ (i.e., total BaPeq) was used. According to the TEFs or carcinogenic activity factors calculated (Table 2), the carcinogenic potency of the airport site was 2.94 times higher than the background site. This suggests higher carcinogenic burden at the IGI airport site through aircraft emission.

4. Conclusions

PCA and isomer pair ratios revealed aircraft exhaust as an important source of PAHs in the soil around the IGI airport. The study concluded that the airport soil was 2.58 times more contaminated with PAHs, than background soil. Thus, the increased PAH load at the IGI airport area requires appropriate remedial measures to minimize the adverse effects of long-term exposure on local inhabitants.

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