




Research Article



Polycyclic aromatic hydrocarbons in urban and rural residential soils, levels, composition profiles, source identification and health risk & hazard

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Abstract

The presence of PAHs in soil and the close proximity of soils to humans may lead to human exposure through various pathways. Therefore, levels of priority sixteen PAHs in soils were measured for human and environmental health risk assessments. No recent study on human and environmental health effects due to PAHs in soils is available for Delhi. The levels of total PAHs in soils ranged between 213–851 $\mu\text{g kg}^{-1}$ with the mean of $550 \pm 55 \mu\text{g kg}^{-1}$, which was comparatively lower in rural area. Seven carcinogenic PAHs (7CPAHs) accounted for 28.6% of $\Sigma 16\text{PAHs}$. However, benzo(a)pyrene toxicity equivalency (BaP_{TE}) of 7CPAHs accounted for 98.2% to $\Sigma \text{BaP}_{\text{TE}}$. Lifetime average daily dose (LADD) of PAHs through soil for human adults and children was $9.43 \times 10^{-8} \text{ mg kg}^{-1} \text{ d}^{-1}$ and $3.53 \times 10^{-7} \text{ mg kg}^{-1} \text{ d}^{-1}$, respectively. The estimated incremental lifetime cancer risk (ILCR) for children (4.80×10^{-5}) was comparatively higher than adults (1.29×10^{-5}). The index of additive cancer risk (IACR), potential threat to potable groundwater water quality from leaching of carcinogenic PAHs from soil were also estimated and presented. The observed levels of PAHs in soils and their human health risk and environmental health hazard at different locations were assessed using recommended guidelines.

Keywords PAHs · Soil · Cancer risk · IACR

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of organic compounds containing 2 or more benzene rings are released to the environment from petroleum products (petrogenic sources) and from various anthropogenic activities. Anthropogenic sources of PAHs include incomplete combustion of coal, petroleum products and biomass (pyrogenic sources). PAHs exert genotoxic effects with induced mutations through formation of

DNA-PAH adducts and cause to developing carcinogenesis [1]. Among several PAHs, 16 compounds namely naphthalene (NPT), acenaphthylene (ACY), acenaphthene (ANE), fluorine (FLE), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DBA), benzo(g,h,i)perylene (BghiP) and indeno (1,2,3-cd)pyrene (IndP) are classified and listed as the priority pollutants by

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USEPA [2] and European Community [3]. Based on the carcinogenicity, USEPA's carcinogenicity risk assessment verification endeavor work group [1] and WHO's the International Agency for Research on Cancer (IARC) [4] classified 16 PAHs into different groups. BaP has sufficient evidence of carcinogenicity in human, and classified as human carcinogen (group I). DBA with limited evidence of carcinogenicity in human and sufficient evidence of carcinogenicity in experimental animals, classified as probable carcinogens (group 2A). BaA, NPT, CHR, BbF, BkF, and IndP classified as possible carcinogens (group 2B), since inadequate evidence of carcinogenicity in human and limited evidence of carcinogenicity in experimental animals [1, 4].

PAHs are often transported over long distances through the atmosphere and partitioned into particulate and gaseous phase. They are ubiquitously distributed in various environmental compartments including air, water bodies, soil and vegetation [1]. Soils might be act as the source and sink for many organic pollutants including PAHs, and could play important role in the fate and distribution of PAHs in the environment. Industrial activities and vehicles are main sources of PAHs in urban soils [1, 5]. Worldwide, several researchers reported health risk to humans through PAHs with in the soil [6–13].

In India, some studies have been carried out on PAHs associated risk for humans. Among them, few were on health impact due to PAHs through soils [14–19]. But, no recent report on humans and environmental health effects due to PAHs in soils is available for Delhi. However, PAHs were measured and reported for various soils including agricultural soils (range, 830–3880 $\mu\text{g kg}^{-1}$) [20], industrial soil ($11,460 \pm 8390 \mu\text{g kg}^{-1}$), roadside soil ($6960 \pm 4820 \mu\text{g kg}^{-1}$), residential soil ($2120 \pm 1120 \mu\text{g kg}^{-1}$) [21], and mixed landuse soils ($511\text{--}2241 \mu\text{g kg}^{-1}$) [22] from Delhi. This study was focused on the amount and composition profiles of priority sixteen PAHs in soils, their possible sources, toxicity and health risk in urban and rural areas of Delhi.

2 Materials and methods

2.1 Solvents, chemicals and standards

Solvents & chemicals, HPLC grade and analytical grade, respectively (Fisher Scientific, India), were utilized in sample processing and analysis. Activated silica (100–200 mesh) (Sigma-Aldrich, USA) was utilized in column chromatography for extract clean-up. Working

standard solutions with suitable concentrations of PAH compounds were prepared with serial dilutions of stock solutions of individual standard solutions of sixteen PAHs including NPT (naphthalene), ANY (acenaphthylene), ANE (acenaphthene), PHE (phenanthrene), ANT (anthracene), FLT (fluoranthene), PYR (pyrene), BaP (benzo(a)pyrene), BghiP (benzo(g,h,i)perylene), FLE (fluorene), BaA (benzo(a) anthracene), CHR (chrysene), BbF (benzo(b)fluoranthene), BkF (benzo(k)fluoranthene), DBA (dibenzo(a,h)anthracene) and IndP (indeno(1,2,3-cd)pyrene) (Supelco, Sigma-Aldrich, USA). Mixture of 16PAH compounds was used for calibration and internal quality control analysis.

2.2 Study area and sampling

Delhi (28.38 N and 77.13°E) is the capital of India with 1483 km² area and 16.78 million of total population. The climate of Delhi is tropical semi-arid. The atmospheric temperature varied between 4 and 5 °C and 40–45 °C during winter and summer season, respectively. Generally, winds are north–western and south–eastern during monsoon season. The region received ~714 mm annual average rainfall mostly in monsoon season. The transportation is predominantly road based and therefore the total numbers of registered vehicles in Delhi are 9.7 million [23]. In terms of particulate, Delhi was listed among the foremost polluted cities. The amount of particulate in Delhi air varied seasonally and greatly influenced by environmental conditions [24]. The main sources of air pollution in Delhi are reported because of local sources, including long range atmospheric transport (LRAT) of pollutants [25].

The selected sampling locations, Sirifort (S-1), Dilshad Garden (S-2), Janakpuri (S-3) and Pitampura (S-5) were in urban residential districts, while the location of Bakhtawarpur (S-4) is in rural residential area of Delhi. Sampling locations S-1, S-2, S-3 and S-5 are located in South Delhi, West Delhi, East Delhi and North Delhi respectively. While, the location S-4 is in rural district of North Delhi in. In 2016, during summer season, total forty soil samples were collected from different points of selected sampling locations (Fig. 1, Table S1). 3–5 sampling points were within a 100–200 m radius of every sampling location that was selected for soil sampling. Three ~500 g of sub-surface (0–20 cm depth) soil sample was collected from each selected point from different locations. After manual removal of unwanted materials, the collected subsample at each points of every location are combined and mixed thoroughly to make sure a representative sample of that point of an equivalent location. An

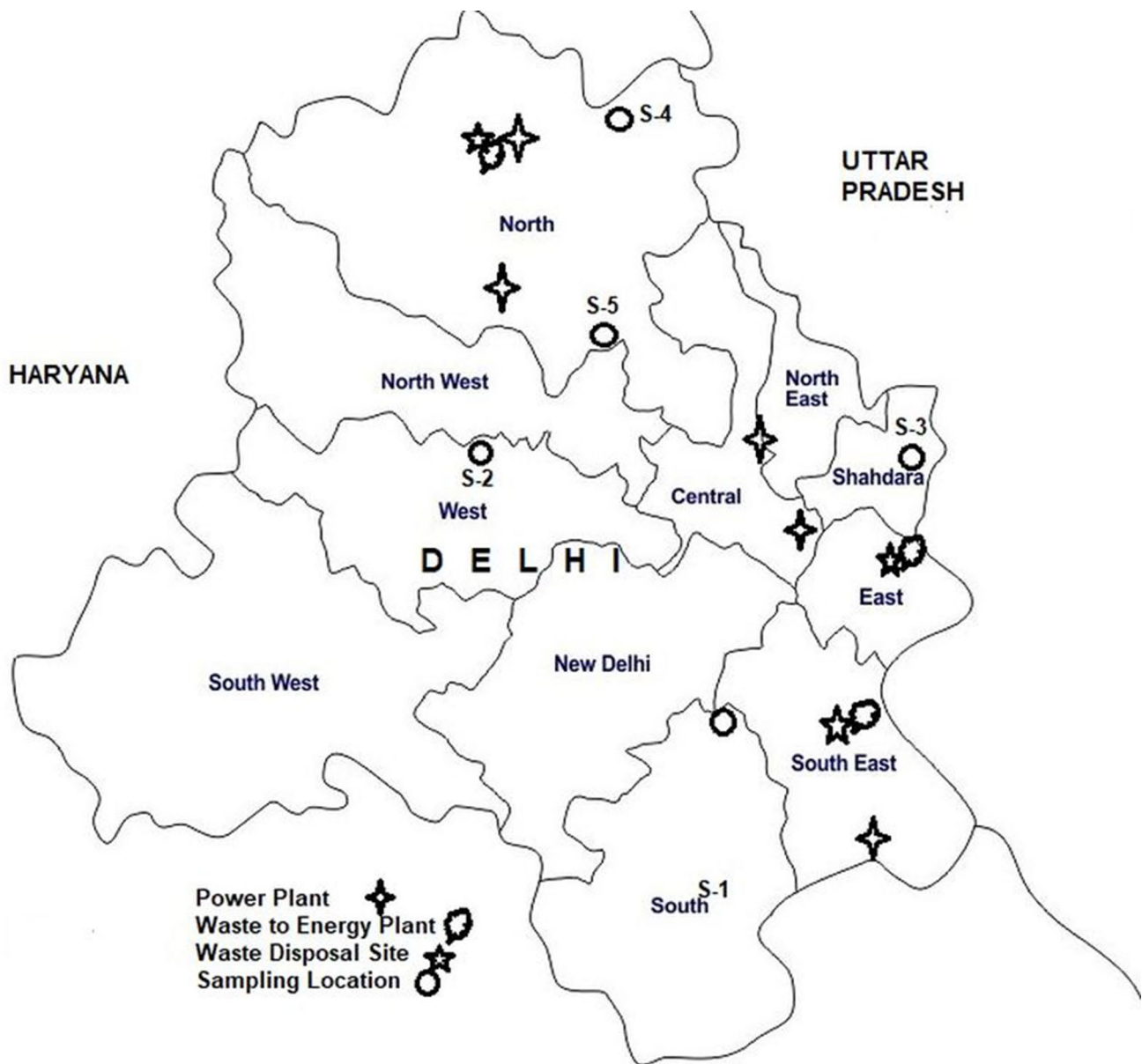


Fig. 1 Map showing sampling locations in study area in Delhi, India

aliquot of mixed soil (~200 g) in duplicates was collected in wide mouth amber glass containers, and transported to the laboratory.

2.3 Analysis and internal quality control

The air dried homogenized samples of 1 mm size (~20 g) were extracted with acetone-hexane (1:1 v/v) on ultrasonic bath (USEPA Method 3550C). After sonication, solvent extracted layer was passed through anhydrous sodium

sulphate on Whatman 41 paper, and the process was repeated for 2 more times. The pooled extract was concentrated to close 2 mL under reduced pressure at 40 °C using vacuum rotary evaporator (Eyela, Tokyo, Japan). Column chromatography with activated silica was followed for clean-up following the USEPA Method 3630C. Individual PAH compounds were quantified following method detailed elsewhere [26].

Strict analytical quality control analysis was followed with inclusion of multi-level calibration, calibration

verification, method blanks analysis and analysis in duplicates. Five level calibration curves with required linearity (r^2 , 0.999) and accurate retention time of each standard PAHs were used for identification of the individual PAH compounds in samples. Measurement of every sample extract was taken in duplicate and therefore the average of duplicate analyses was utilized in calculations. Accuracy of method performance was checked by recovery study. Recovery was carried out by analysis of fortified samples with the addition of known quantity of 1-fluoronaphthalene (surrogate standard) and individual 16PAH standards. The recoveries of added 16 PAHs were between 82%–109% (± 2 –12%), while recovery of surrogate standard was 94%. Method detection limits (DLs) were estimated at signal to noise ratio $>3:1$ ($s/n > 3$) by processing and analysis of eight replicates of a sample. Estimated DLs for sixteen PAH compounds were between 0.09–0.21 (± 0.03) $\mu\text{g kg}^{-1}$ on dry weight basis.

2.4 Toxicity potential and health risk assessment

Previously defined toxicity equivalency factors (TEFs) [27] were used to estimate the BaP_{TE} of the remaining PAHs relative to BaP (Table S4). The toxicity equivalent (based on carcinogenicity) of every individual PAH was obtained by multiplying its concentration with the acceptable TEF.

As recommended by Canadian soil quality guidelines, BaP Total Potency Equivalents (BaP TPE) and IACR were estimated [28]. BaP TPE is the sum of the estimated cancer potency relative to BaP for all potentially carcinogenic PAHs (BaA, BaP, BbF, BkF, BghiP, CHR, DBA, IndP) [28].

Human exposure to PAHs may occur through inhalation, ingestion and dermal contact. During this study, human health risk estimation was based on consideration of ingestion pathway of PAHs through soil. The LADD and ILCR were estimated using input parameters (Table S2) with following equations [5, 29]:

$$\text{LADD} (\text{mg kg}^{-1} \text{d}^{-1}) = (\text{C} \times \text{IR} \times \text{F} \times \text{EF} \times \text{ED}) / (\text{BW} \times \text{AT}) \quad (1)$$

$$\text{Cancer Risk} = \text{LADD} \times \text{CSF} \quad (2)$$

Non-carcinogenic effects of PAHs as environmental hazard were assessed by comparison of observed concentrations with recommended soil quality guidelines for mammals and residential/park land use [28, 31].

2.5 Statistical analyses

Microsoft Excel was used for the data processing, graphics and Pearson's correlation analysis. The Pearson correlation analysis was used to identify the sources of PAHs in soils. This statistical approach is predicted on the coefficient of correlation between the concentrations of the individual PAHs can give a thought, whether or not they originate from an equivalent source or not. Results were considered statistically significant if the p -value was <0.01 . Each PAH was evaluated for values below detection limit before inclusion within the processing. Missing data points resulting from limit of detection weren't considered in calculations. Nemerow composite index (P value) was calculated for the assessment of environmental quality of soil due to PAHs [32].

3 Results and discussions

3.1 Levels of PAHs

The average concentration of total PAHs was comparatively higher in urban soils ($550 \pm 55 \mu\text{g kg}^{-1}$) than rural soils location ($224 \pm 7.1 \mu\text{g kg}^{-1}$) (Fig. 2). The spatial distribution of total PAHs at different locations was with increasing order at $S-3 > S-5 > S-2 > S-1 > S-4$. Levels of PAHs in soils from rural location (S-4) were comparatively less than the opposite locations (urban). Urban soils show dominance of FLT, PYR, NPT, PHE, and BghiP, followed by ANY, ANE, ANT, BaP and DBA. Their contribution was accounted for 15.1%, 12.6%, 8.5%, 7.5%, 7.1%, 6.1%, 5.6%, 5.1%, 5.1% and 5.0%, respectively to ΣPAHs .

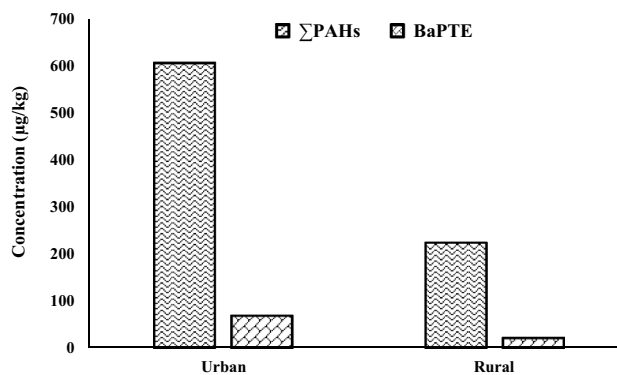


Fig. 2 Concentrations of ΣPAHs and $\Sigma\text{BaP}_{\text{TE}}$ ($\mu\text{g/kg}$) in soil

However, ANE, PHE, NPT, and ANT were the dominant PAHs in rural soils, followed by ANY, BaA, BbF, CHR, PYR and FLE. The contribution of ANE, PHE, NPT, ANT, ANY, and BaA in rural soils accounted for 9.8%, 8.6%, 8.3%, 7.5%, 6.9%, and 6.6%, respectively to Σ PAHs (Table S3). The observed composition profiles of PAHs suggested diesel-powered vehicles emission and biomass combustions as major sources of PAHs [33]. Similar sources of PAHs are reported for different environmental matrices in Delhi [22, 24, 25]. However, with the limitations of sampling during summer season, these observations may be varied with different seasons.

The observed concentration of PAHs was compared with similar recent studies round the world including India. It was found that the concentrations are comparable with concentrations reported for Dibrugarh (45.6–1653 $\mu\text{g}/\text{kg}$), Tezpur (75.9–1099 $\mu\text{g}/\text{kg}$) [17], Ghaziabad (574 \pm 304 $\mu\text{g}/\text{kg}$) [18], and Gwalior (481 \pm 92 $\mu\text{g}/\text{kg}$) [19] in India. But, lower concentration was reported for Itanagar (15.8–98.9 $\mu\text{g}/\text{kg}$) [17]. However, elevated concentrations are reported for a few Indian cities, including Dhanbad (3488 $\mu\text{g}/\text{kg}$) [14], Guwahati (50.5–4686 $\mu\text{g}/\text{kg}$) [15], and north-eastern region (10,945 $\mu\text{g}/\text{kg}$) [16]. Recently, elevated concentrations of seven PAHs (Σ of NPT, FLE, PHE, ANT, FLT, PYR & BaP) (956–2714 $\mu\text{g}/\text{kg}$) were reported in soils from power station area, interstate bus terminals and heavy traffic intersections in Delhi [34]. On comparison with similar studies from other countries, the observed concentrations were much less than concentrations reported for Beijing (736 \pm 894 $\mu\text{g}/\text{kg}$) [35], Orlando (3227 \pm 4676 $\mu\text{g}/\text{kg}$) and Thampa (4562 \pm 10,031 $\mu\text{g}/\text{kg}$) Florida in USA [36], Shengli (2160 $\mu\text{g}/\text{kg}$) [37], Xian (2053 $\mu\text{g}/\text{kg}$) [38], Shandong (3016 $\mu\text{g}/\text{kg}$) [39], Nanjing (980 $\mu\text{g}/\text{kg}$) [40], Ulsan (810 $\mu\text{g}/\text{kg}$) and Pohang (2384 $\mu\text{g}/\text{kg}$) [41], Kathmandu (1172 $\mu\text{g}/\text{kg}$) [42], Cape Town (4080 \pm 2640 $\mu\text{g}/\text{kg}$) [43], and San Mateo Ixtatán (1401 $\mu\text{g}/\text{kg}$) [13]. But, PAHs concentrations in our study were above than those reported from Gwangju (51.2 $\mu\text{g}/\text{kg}$) [10] and Gyeonggi (253 $\mu\text{g}/\text{kg}$) [41].

3.2 Toxicity of PAHs

On the basis of cancer risk to humans, the Canadian Government established safe level of BaP_{TE} (600 $\mu\text{g}/\text{kg}$) for soils [28]. Observed Σ BaP_{TE} for urban soils was comparatively above than rural soil. For urban soil, it had been ranged between 17.8–153.8 $\mu\text{g}/\text{kg}$ (mean, 68.35 $\mu\text{g}/\text{kg}$). While, for rural soils it ranged between 21.2–21.5 $\mu\text{g}/\text{kg}$ (Fig. 2). The typical mean

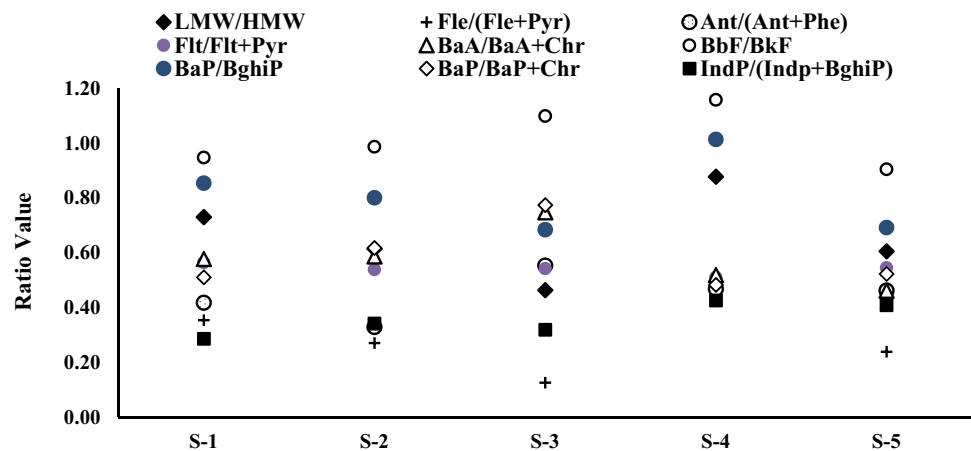
value of Σ BaP_{TE} at S-1, S-2, S-3, S-4 and S-5 locations was 21.21 $\mu\text{g}/\text{kg}$, 88.12 $\mu\text{g}/\text{kg}$, 97.64 $\mu\text{g}/\text{kg}$, 21.32 $\mu\text{g}/\text{kg}$ and 80.59 $\mu\text{g}/\text{kg}$, respectively (Table S4). However, BaP_{TE} for Σ 7CPAHs at S-1, S-2, S-3, S-4 and S-5 locations was 20.7 $\mu\text{g}/\text{kg}$, 87.0 $\mu\text{g}/\text{kg}$, 95.7 $\mu\text{g}/\text{kg}$, 20.9 $\mu\text{g}/\text{kg}$ and 79.4 $\mu\text{g}/\text{kg}$, respectively. The mean value of 7CPAHs in urban and rural soils was 171 \pm 16 $\mu\text{g}/\text{kg}$ and 80 \pm 2.89 $\mu\text{g}/\text{kg}$, respectively, which accounted for 28.6% and 35.8%, respectively to Σ 16PAHs. Whereas, their percent contribution to Σ 16CPAHs at S-1, S-2, S-3, S-4 and S-5 was 26.5, 31.6, 28.6, 35.8 and 25.6, respectively (Table S3). The 2–3-ring PAHs show a negligible contribution (0.7–1.2%) to BaP_{TE}. However, 5-ring PAHs and 6-ring PAHs were the main contributors to total BaP_{TE}, followed by 4-ring PAHs. The contribution of 5-ring and 6-ring PAHs accounted for 94.7% and 91.2% to Σ BaP_{TE} for urban soils and rural soils, respectively. Results of BaP_{TE}, indicated that DBA and BaP including with other PAHs (BaA, BbF and BkF) play a substantial role in the toxicity potential of PAHs. However, observed BaP_{TE} were lower than safe level [28], suggested low carcinogenic potential in soils. The observed values of BaP_{TE} were less than those reported for soils from Orlando & Tampa in USA (452 & 802 $\mu\text{g}/\text{kg}$) [36], Kolkata (1129 $\mu\text{g}/\text{kg}$) [14], Dhanbad (120–720 $\mu\text{g}/\text{kg}$) [44], and Delhi region (154–671 $\mu\text{g}/\text{kg}$) [20–22] in India. However, lower concentrations of BaP_{TE} are reported for Wuhan (34.55 $\mu\text{g}/\text{kg}$) [9], Tajikistan (0.21–31.19 $\mu\text{g}/\text{kg}$) [45], and Rawalpindi (12.88 $\mu\text{g}/\text{kg}$) [46].

3.3 Possible source identification of PAHs

3.3.1 PAHs with different rings

The 16 PAHs are often grouped according to the presence of aromatic rings as 2–3 rings, 4-rings, 5-rings and 6-rings PAHs. Occurrence of these groups of PAHs within the environment are indicative of their possible origin sources. The 2–3-rings PAHs were the dominant homolog, followed by 4-ring PAHs, and 5-ring to 6-ring PAHs at different locations (Table S3). The dominance of 2–3 ring and 4-ring PAHs indicated mixed pyrogenic sources. Local vehicular emissions may be the sources of 3- to 4-rings PAHs in rural area. These homologs can exist both within the vapor and particulate phase [22], and settle down in nearby areas. The concentration of 5-ring (107 \pm 2.4 $\mu\text{g}/\text{kg}$) and 6-ring (157 \pm 14 $\mu\text{g}/\text{kg}$) PAHs was comparatively higher at location S-3. Comparatively higher contribution of 2–3 ring PAHs to Σ PAHs was

Fig. 3 Molecular ratio of selected PAHs



observed at rural site (46.7%) than all urban sites (36.5%). 4-ring PAHs were dominant at urban sites than rural sites, and their contribution was accounted for 35.2% 24.4% to Σ PAHs, respectively. The contribution of 5-ring and 6-ring PAHs was between 12.9–17.6% and 11.3–15.0% to Σ PAHs, respectively.

Further, different PAHs with their molecular weights are often related to various emission sources. For instance, high molecular weight PAHs ($_{\text{HMW}}$ -PAHs) are usually released from pyrogenic sources including coal combustion and vehicular emissions. While, low molecular weight PAHs ($_{\text{LMW}}$ -PAHs) are related to petrogenic sources and combustion of woods, grass and industrial oil [33, 47, 48]. The typical concentration of Σ_{LMW} -PAHs & Σ_{HMW} -PAHs in urban and rural soils accounted for 35% & 64%, and 47% & 53%, respectively to Σ 16PAHs. Comparatively higher fraction of $_{\text{HMW}}$ -PAHs and low ratio between $_{\text{LMW}}$ -PAHs and $_{\text{HMW}}$ -PAHs (<1.0) (Fig. 3, Table S5), indicating pyrogenic processes as major sources of PAHs [41]. Various pyrogenic sources for air particles in Delhi are reported from vehicular emissions, construction activities, diesel engines, power plants, industries and biomass burning [24, 25].

3.3.2 Diagnostic ratios of selected PAHs

Molecular diagnostic ratios of selected PAHs including ANT/(ANT + PHE), FLT/(FLT + PYR), BaA/(BaA + CHR), BbF/BkF, BaP/BghiP, BaP/(BaP + Chr), and IndP/(Indp + BghiP) were used for identification of possible sources of PAHs [33, 47–53]. The estimated values of selected ratio for this study was presented in Fig. 3, Table S5, which suggested mixed pyrogenic sources of PAHs. The ratio of BaA/Chr in the present study was ranged between 0.44–0.78

indicating recent deposition, also as transportation of fresh and older masses onto Delhi soils. It was reported that BaA/Chr ratio <0.40 indicates the movement of older sources of PAHs, while >0.04 ratio value indicates recent emissions and comparatively low photochemical degradation of PAHs [54]. Supported with these results, study suggested mixed pyrolytic sources. PAHs emissions from vehicles, diesel engines, coal, wood & biomass combustions and gasoline have been reported in Delhi [22, 55]. However, petrogenic sources could also be from accidental spills of petroleum products and automobile workshops.

3.3.3 Pearson's coefficient of correlation

Correlation analysis was performed for the idea that two or more PAHs could also be correlated to common source of origin. Relationships between individual PAH as Pearson's moment correlation coefficients were determined and presented in Table S6. Significant correlation (*two tailed*, $p < 0.01$, $p < 0.001$) between the $_{\text{LMW}}$ -PAHs as well as $_{\text{HMW}}$ -PAHs was obtained during this study. A significantly strong correlation between $_{\text{LMW}}$ -PAHs like ANY, ANE, FLE, PHE, and ANT are often associated to biomass combustions at low temperature. Strong correlation between FLE, PHE, ANT, CHR and PYR suggested biomass combustions sources. A significant correlation among FLT, BbF, PYR, BaA, CHR, BkF, BaP, BghiP, DBA and IndP suggested emissions sources from high temperature combustion process like in vehicles, industries and coal combustion [33, 49, 50]. Stationary source emissions are related to correlations between BaA with BaP, BghiP and IndP [55]. The presence of industrial and coal combustion emissions within the vicinity of the inhibited area has been attributed to stationary sources. These results demonstrated

the mixed sources of PAHs in soils. The study concluded that pyrogenic sources like biomass and coal combustion and vehicular emissions could be the foremost significant sources of PAHs in the soils from Delhi. Various combustion processes are reported as the primary sources of PAHs in Delhi region [20, 55, 56].

3.4 Human health risk and environmental health hazard assessment

3.4.1 Human health risk

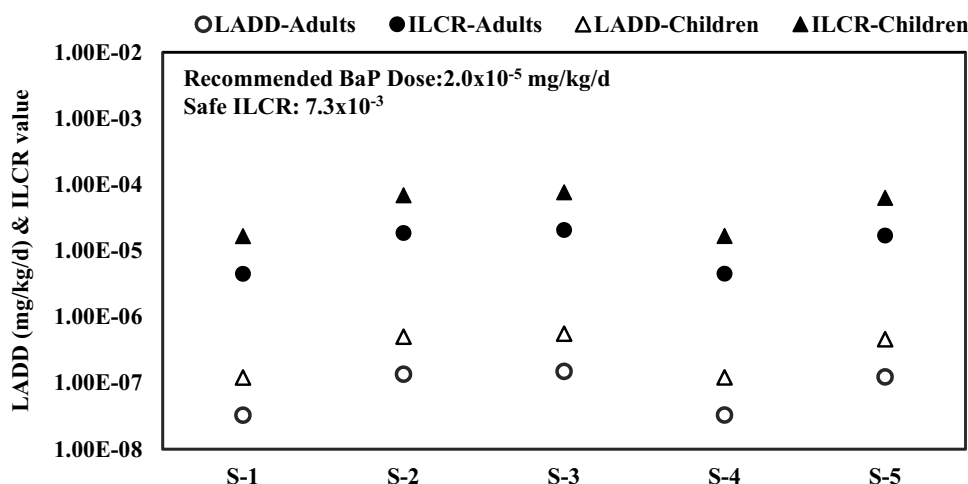
Human health risk assessment was supported on assumption that humans could be exposed directly or indirectly to PAHs contaminated soil. Health risk to Humans as ILCR was based on the calculated daily intake of PAHs as LADD for human adults and youngsters. The recommended daily intake of BaP for human adult is $0.02 \mu\text{g kg}^{-1} \text{d}^{-1}$ [57]. Various agencies have recommended acceptable ILCR of 10^{-6} [28] and 7.3×10^{-3} [29]. Soil quality guidelines for direct contact (SQG_{DH}) based on ILCR of 10^{-6} due to carcinogenic PAHs (BaA, BaP, BbF, BkF, BghiP, Chr, and IndP) were stipulated as $600 \mu\text{g kg}^{-1}$. Further, IACR of ≤ 1 has been recommended as safe level for the protection of potable water (SQG_{PW}) [28].

Observed LADD for adults and children are varied with respect to concentrations of PAHs at different sampling locations (Table 1). The daily intake of PAHs as LADD for human adults was ranged between 3.28×10^{-8} – $1.07 \times 10^{-7} \text{ mg kg}^{-1} \text{d}^{-1}$, and for children it had been ranged between 1.22×10^{-7} – $5.04 \times 10^{-7} \text{ mg kg}^{-1} \text{d}^{-1}$ (Fig. 4). Average LADD for human adults and children (1.05×10^{-7} and $3.91 \times 10^{-7} \text{ mg kg}^{-1} \text{d}^{-1}$) were higher at urban sites than rural site (3.28×10^{-8} and $1.22 \times 10^{-7} \text{ mg kg}^{-1} \text{d}^{-1}$), but were less than the recommended guidelines. Daily intake of Σ_{LMW} -PAHs ($2.64 \times 10^{-9} \text{ mg kg}^{-1} \text{d}^{-1}$) was less than the Σ_{HMW} -PAHs ($3.48 \times 10^{-7} \text{ mg kg}^{-1} \text{d}^{-1}$). Among HMW -PAHs, the BaP (5-ring PAH) and the DBA (6-ring PAHs) were the main contributor to BaP_{TE} , thus increasing the LADD (Table S7). The estimated ILCR at different locations was comparatively higher for youngsters than adults (Table 2). ILCR for adults varied between 4.47×10^{-6} – 4.49×10^{-6} , and for children it had been ranged between 1.66×10^{-5} – 7.64×10^{-5} . ILCR for human adults (1.44×10^{-5}) and children (5.35×10^{-5}) at urban locations was comparatively higher, than rural location (adult, 4.49×10^{-6} , and children, 1.67×10^{-5}), but within the acceptable guidelines. Among urban locations, ILCR for human adults and children lower at location S-1 (4.47×10^{-6} & 1.66×10^{-5}) than other locations (Fig. 4). Almost like LADD, majority of ILCR was

Table 1 Average LADD ($\text{mg kg}^{-1} \text{d}^{-1}$) for humans due to PAHs through soil from different locations in Delhi

PAHs	Urban location						Rural location					
	S-1		S-2		S-3		S-5		All urban		S-4	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Σ_{2-3} -ring	4.46×10^{-10}	1.66×10^{-9}	8.22×10^{-10}	3.05×10^{-9}	1.11×10^{-9}	4.12×10^{-9}	8.37×10^{-10}	3.11×10^{-9}	7.66×10^{-10}	2.84×10^{-9}	3.92×10^{-10}	1.46×10^{-9}
Σ_{4} -ring	3.10×10^{-9}	1.15×10^{-8}	4.64×10^{-9}	1.7×10^{-8}	8.94×10^{-9}	3.32×10^{-8}	3.72×10^{-9}	1.38×10^{-8}	4.73×10^{-9}	1.76×10^{-8}	2.51×10^{-9}	9.32×10^{-9}
Σ_{5} -ring	2.50×10^{-8}	9.29×10^{-8}	6.03×10^{-8}	2.24×10^{-7}	1.04×10^{-7}	3.85×10^{-7}	4.96×10^{-8}	1.84×10^{-7}	5.50×10^{-8}	2.04×10^{-7}	2.37×10^{-8}	8.79×10^{-8}
Σ_{6} -ring	4.07×10^{-9}	1.51×10^{-8}	6.98×10^{-8}	2.59×10^{-7}	3.66×10^{-7}	1.36×10^{-7}	6.99×10^{-8}	2.60×10^{-7}	4.46×10^{-8}	1.66×10^{-7}	6.22×10^{-9}	2.31×10^{-8}

Fig. 4 Average LADD (mg kg⁻¹ day⁻¹) and ILCR to humans due to exposure to Σ16PAHs through soil



contributed by Σ_{HMW}-PAHs (4.76×10^{-5}) compared with Σ_{LMW}-PAHs (3.61×10^{-7}). Higher TEF for BaP and DBA [27] has increased the ΣBaP_{TE} (>93%) and ILCR.

The observed ILCR for humans due to PAHs during this study were comparable with ILCR reported for various Indian locations like Dhanbad (adults, 6.93×10^{-5} , children, 6.22×10^{-5} ; adults, 1.82×10^{-5} , children, 1.85×10^{-5} ; adults, 3.36×10^{-6} – 7.53×10^{-6} , children 2.65×10^{-6} – 8.19×10^{-6}) [14–16], Ghaziabad (adults 7.7×10^{-5} , children 4.5×10^{-5}) [18], Gwalior (adults, 6.4×10^{-5} , children, 2.4×10^{-4}) [19], Korba (adults, 6.7×10^{-5} , children, 3.5×10^{-5}) [58] and Kurukshetra (adults, 8.1×10^{-6} , children, 4.2×10^{-5}) [59]. ILCR was also comparable with reported for cities of other countries including Beijing, China (adults, 2.48×10^{-6} – 3.08×10^{-6} , children, 1.56×10^{-6} – 2.69×10^{-6}) [35], and USA (6×10^{-5}) [60]. But was less than Mashad, Iran (adults, 6.2×10^{-4} , children, 7×10^{-4}) [8], Kutahya, Turkey (adults, 5.71×10^{-6} to 3.19×10^{-4}) [12], Guatemala (adults, 1.61×10^{-4}) [13], and higher than Yinma (children, 1.00×10^{-6} to 1.18×10^{-6} , adults, 1.10×10^{-6} to 4.22×10^{-6}) [6], Liaohe (children, 4.03×10^{-8} , adults, 1.14×10^{-7}) [7], Wuhan (adults 1.13×10^{-8} to 3.54×10^{-8} , children 9.23×10^{-7} to 9.51×10^{-6}) [9], Gwangju in South Korea (adults, 8.41×10^{-6} , children,

3.61×10^{-7}) [10], and North-West China (adults, 1.19×10^{-9} Children, 1.79×10^{-9}) [11].

The BaP TPE and IACR was ranged between 0.017–0.153 mg kg⁻¹ (mean, 0.061 mg kg⁻¹) and 0.26–0.99 (mean, 0.55), respectively, and less than specified guidelines for SQG_{DH} and SQG_{PW}. PAHs associated human health hazard in terms of BaP TPE and IACR was relatively low at S-1 and S-2 than other locations (Fig. 5).

3.4.2 Environmental and human health hazard

PAHs levels observed during this study were compared with specified SQGs for the protection of environmental and human health for the assessment of health hazard from non-carcinogenic effects of PAHs [28, 31]. It was found that the observed levels of Σ16PAHs, _{LMW}-PAHs, _{HMW}-PAHs, and individual compounds were less than recommended SQGs (Table S8), suggested low environmental and human health hazard. Further, NCI values (range, 0.02–0.19, mean 0.06) revealed that the pollution level due to PAHs was in safe category. Furthermore, as per classification of pollution level of PAHs in soils [61], soils in Delhi were found to be weakly polluted at S-1 and S-2 locations,

Table 2 Average ILCR for humans due to PAHs through soil from different locations in Delhi

PAHs	Urban location						Rural location					
	S-1		S-2		S-3		S-5		All urban		S-4	
	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children	Adult	Children
Σ2-3-ring	6.11×10^{-8}	2.27×10^{-7}	1.13×10^{-7}	4.18×10^{-7}	1.52×10^{-7}	5.64×10^{-7}	1.15×10^{-7}	4.26×10^{-7}	1.05×10^{-7}	3.90×10^{-7}	5.37×10^{-8}	2.00×10^{-7}
Σ4-ring	4.24×10^{-7}	1.58×10^{-6}	6.35×10^{-7}	2.36×10^{-6}	1.22×10^{-6}	4.55×10^{-6}	5.10×10^{-7}	1.89×10^{-6}	6.48×10^{-7}	2.41×10^{-6}	3.44×10^{-7}	1.28×10^{-6}
Σ5-ring	3.43×10^{-6}	1.27×10^{-5}	8.26×10^{-6}	3.07×10^{-5}	1.42×10^{-5}	5.27×10^{-5}	6.79×10^{-6}	2.52×10^{-5}	7.54×10^{-6}	2.80×10^{-5}	3.24×10^{-6}	1.20×10^{-5}
Σ6-ring	5.57×10^{-7}	2.07×10^{-6}	9.57×10^{-6}	3.55×10^{-5}	5.02×10^{-6}	1.86×10^{-5}	9.57×10^{-6}	3.56×10^{-5}	6.11×10^{-6}	2.27×10^{-5}	8.52×10^{-7}	3.17×10^{-6}

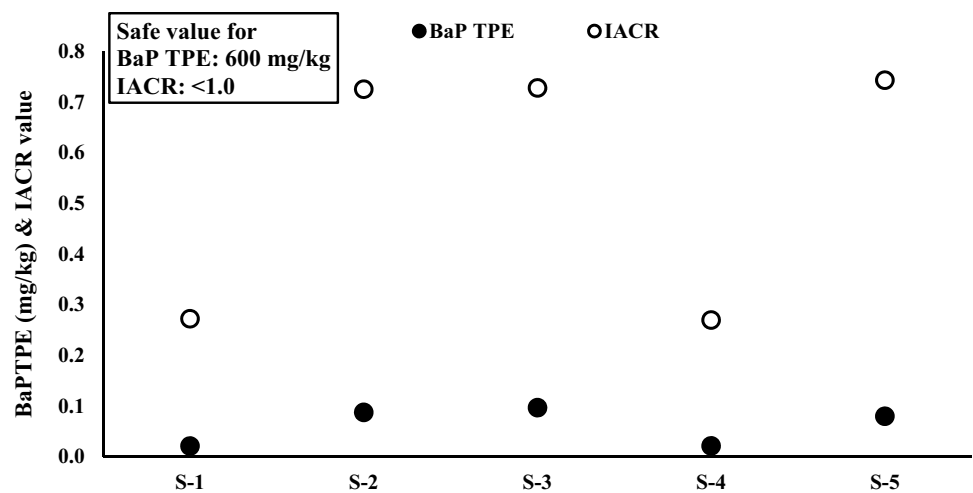
while S-3, S-4 and S-5 locations as moderately polluted soils with PAHs.

4 Conclusions

This study revealed that the levels of PAHs in soils from rural location were comparatively lower than the urban locations, and those were less than SQGs suggested low environmental health hazard. NCI and soil classification, suggested weekly polluted soils with PAHs, but, categorized in safe category. The dominant PAH compounds in soils were FLT, PYR, NPT, PHE, ANY, ANE, ANT, BaP and BghiP, and their combined contribution accounted for 72% to Σ16PAHs. Study indicated mixed pyrolytic sources from vehicular emissions from diesel engines; coal, wood & biomass combustions, and gasoline are the significant contributor of PAHs to soils in Delhi.

Daily intake of PAHs as LADD and subsequent ILCR for adults and children, varied location-wise with variable concentrations and the PAHs sources. Σ_{HMW}-PAHs were the major contributor to total LADD and ILCR. However, LADD and ILCR were less than the guidelines. Observed values of BaP_{TE}, BaP TPE and IACR were also lower than guidelines indicated low health hazard due to carcinogenic effects of PAHs.

Fig. 5 BaP TPE (mg kg^{-1}) and IACR in urban and rural soils



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Compliance with ethical standards

Conflict of interest All authors declare that they have no conflict of interest.

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