

Concentrations, source identification and health risk of selected priority polycyclic aromatic hydrocarbons in residential street soils

Bhupander Kumar¹, Jyoti Tyagi², V. K. Verma¹, Richa Gaur¹ and C. S. Sharma¹

¹National Reference Trace Organics Laboratory, Central Pollution Control Board, East Arjun Nagar Delhi, India
²Amity Institute of Environmental Science, Amity University, Noida, India

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) released to the environment are petrogenic sources and pyrogenic sources. Sixteen PAHs have been listed as priority pollutant by the US Environmental Protection Agency. This study deals with the distribution of concentration, possible sources identification and health risk of selected priority PAHs in residential street soils from an industrial city. The concentrations of Σ PAHs ranged 36 – 898 $\mu\text{g kg}^{-1}$ with an average value of $315 \pm 67 \mu\text{g kg}^{-1}$. The concentration of studied, probable human carcinogenic PAHs accounted for 60% of Σ PAHs. Benzo(a)pyrene Toxicity Equivalency (BaP_{TEQ}) for studied PAHs was estimated and ranged 0.61 – 197 $\mu\text{g BaP}_{\text{TEQ}} \text{kg}^{-1}$ with the mean value of $46.78 \pm 15.97 \mu\text{g BaP}_{\text{TEQ}} \text{kg}^{-1}$. The composition profile analysis and diagnostic molecular ratios of PAHs suggested mixed pyrogenic sources of PAHs from combustion of coal and diesel combustions in vehicles and industrial activities. Potential risk to contaminated ground water from leaching of carcinogenic PAHs and from soil was assessed by estimating the Index of Additive Cancer Risk (IACR) and found to be less than safe limit. Study concluded that concentrations of selected PAHs were within acceptable limits of soil quality guidelines and the study area got classified as weakly contaminated.

Keywords: Residential Soil, Polycyclic aromatic hydrocarbons, BaP Toxicity Equivalency, Diagnostic molecular ratio, Index of Additive Cancer Risk,

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) also called polyaromatic hydrocarbons or polynuclear aromatic hydrocarbons refer to a group of organic arene compounds composed of two or more fused aromatic benzene rings. There are hundreds of PAH compounds occurring in an extremely complex mixture in the environment. Sixteen parent PAH compounds listed by the US Environmental Protection Agency on its priority pollutant list. These compounds are among those which have been frequently used for the purposes of environmental quality assessments. The base structures of the sixteen parent compounds are composed of 2-6 aromatic rings with molecular weight ranging from 128 Dalton to 278 Dalton. These include Naphthalene (Npt), Acenaphthylene (Any), Fluorene (Fle), Phenanthrene (Phe), Anthracene (Ant), Acenaphthene (Ane), Chrysene (Chr), Fluoranthene (Flt), Pyrene (Pyr), Benzo(a)anthracene (BaA), Benzo(a)pyrene (BaP), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Dibenzo(a,h)anthracene (DBA), Benzo(ghi)perylene (BghiP) and Indeno(1,2,3,cd)pyrene (Ind) as priority environmental pollutants.

PAHs are organic compounds with two or more aromatic benzene rings, released to the environment predominantly from petroleum products (petrogenic sources) and anthropogenic activities of incomplete combustion processes

involving coal, petroleum products and biomass (pyrogenic sources) [1]. Polycyclic aromatic hydrocarbons (PAHs) is a matter of concern because of their toxicity and tendency to accumulate in sediments and soils through bioaccumulation, biomagnifications in the food chain [2,3].

Polycyclic aromatic hydrocarbons (PAHs) have long been recognized for potential to cause health effects including carcinogenic and mutagenic effects in wide variety of organisms, animal species, including humans [4]. High molecular weight (HMW) PAHs tend to be more carcinogenic, but less acutely toxic than low molecular weight (LMW) PAHs. The carcinogenicity classifications verified by US EPA carcinogenicity risk assessment work group shows that benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene and indeno(1,2,3,cd)pyrene are considered to be probable human carcinogens [5]. The International Agency for Research on Cancer of World Health Organization (IARC/WHO) concluded that BaP in particular is carcinogenic in experimental animals and most probable carcinogenic in humans (Group 1 of IARC) and is often used as a hazard index for PAH exposure [4]. Metabolites of BaP in human and animals may elicit toxicity through binding with DNA (deoxyribonucleic acid) which can interfere with or alter DNA replication, and may be associated with induced risk of cancer [1]. The effects of PAHs exposure include alteration of development and function of immune system; and reduced fertility in offspring during adulthood due to BaP exposure during pregnancy [6,7]. Human exposure to PAHs can occur through inhalation, dermal contact, and ingestion. Inhalation and skin contact have been proven to be important pathways for atmospheric PAH to enter the biota.

Due to their characteristic properties of hydrophobicity, strong affinity to soil colloids, resistance to physicochemical degradation and biodegradation, PAHs may persist for longer period in soils [8]. Due to its quantity and holding capacity, soils can act as the sink as well as source for these pollutants. Depositions via atmospheric transport and local anthropogenic sources are important sources of PAHs in urban soils [9].

Considering their toxic potential, it is essential to understand the health risks from PAHs in soil with proximity to humans for effective environmental management. There have been several studies worldwide on assessment of health risks of human population from PAHs in soils [10-16]. Few studies have been reported on PAHs in soils from India [17-25]. Consequently, in this study, distribution and source identification of selected priority PAHs in residential street soils from industrial belt of Ghaziabad in Uttar Pradesh was carried out.

MATERIALS AND METHODS

Sampling Area and Sampling

Sampling locations were in residential areas of Ghaziabad, India, a part of National Capital Region (NCR) located near National Capital Territory (NCT), Delhi in western Uttar Pradesh province of India. This is a growing industrial city with small scale (~14000 units) to medium and heavy industries (145 units). Majority of operational industries includes electric machinery, chemicals, rubber, plastic & petroleum, metal products, paper & textiles, manufacturing of transport parts, food products, pharmaceuticals and beverages (<http://ghaziabad.nic.in/industry.htm>).

Region experiences a typical hot and humid climate during summers (April to October) and the monsoon season in between. Winter season starts in November, peaks in January and heavy fog often occur. Ambient temperature ranges varies as low as 3 °C (winters) and up to 45 °C (summers). The average annual rainfall in the area is ~730 mm.

Street soil samples were collected from fifteen locations in residential areas of Ghaziabad. From each sampling location, approximately 500 grams of soil was collected in duplicates, materials such as pebbles, plant leaves and wood sticks were removed manually and collected soils were mixed thoroughly to ensure the representative sample from each location. Then a part of the samples were transferred to clean wide mouth amber glass containers. Sample containers with samples were labelled and transported ice preserved to the laboratory and kept at 4 °C until processing, extraction and analysis.

Solvents, Chemicals and Standards

All solvents (hexane, acetone, dichloromethane, water, and acetonitrile) used in sample processing and analysis were HPLC grade and procured from Merck India. Silica gel (100–200 mesh) used as absorbent during chromatographic column clean-up procured from Sigma-Aldrich (USA) and activated at 130 °C for 16 h. Anhydrous sodium sulphate (Merck, India) was cleaned with solvents and stored in the sealed desiccator. Individual standard

solutions of PAHs compounds [phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), chrysene (Chr), benzo[k]fluoranthene (BkF), Benzo(a)pyrene (BaP), benzo[ghi]perylene (BghiP), and indeno[1,2,3-cd]pyrene (Ind)] were purchased from Supelco (Sigma-Aldrich, USA). Standard solutions with suitable concentrations were used for instrument calibration and quality control analysis.

Sample Extraction and Clean-up

Collected soil samples were air dried in clean environment, grinded and passed through 1 mm sieve and stored in air tight glass bottle in refrigerator. For extraction of PAHs, ~20 g of sample was thoroughly mixed with anhydrous sodium sulphate and extracted three times with acetone-hexane (1:1 v/v) mixture in ultrasonic bath. After extraction the sample was allowed to settle and solvent layer was filtered through Whatman 41 filter paper and concentrated to 2 ml under reduced pressure in a water bath 40 °C using a rotary evaporator (Eyela, Tokyo, Japan).

Cleanup of sample extracts for the separation of analytes from interfering compounds, methods after Wang *et al.* [26] were followed. Cleanup was carried out using a glass chromatography column (25 cm × 10 mm) packed with 10 g activated silica gel (100–200 mesh) and 1 cm layer of anhydrous sodium sulphate. The concentrated extracts and two 2-ml portions of hexane from rinsing the sample flask were transferred on top of the column. The column was first eluted with 30 ml of hexane containing aliphatic hydrocarbons and discarded. Finally, elution was made with 35 ml of dichloromethane at the flow rate of ~2 ml min⁻¹; this fraction was retained and concentrated to near 1 ml with rotary evaporator. An additional 20 ml hexane was added to the concentrated extracts and evaporated to remove traces of dichloromethane. Final volume was solvent exchanged to acetonitrile for PAH analysis by HPLC.

PAHs Analysis and Analytical Quality Control

PAH compounds were analyzed using HPLC (Agilent 1100 Series) equipped with autosampler and diode array detector (DAD, λ=254 nm), quaternary pump and degasser. 20 µl sample extract was injected for separation of compounds by LC-PAH SupelcosilTM (25cm x 4.6 mm, 5 µm film) analytical column and Eclipse XDB-C8 (4.6 x 12.5 mm, 5 µm) as guard column. Mixture of Acetonitrile and water was used as mobile phase with linear flow of 60% acetonitrile and 40% water @ 1.0 ml/min to 100% acetonitrile in 42 min. Details of mobile phase program has been given elsewhere [22].

Quality assurance/ quality control (QA/QC) analysis were done with procedural blanks, duplicate samples, five - level calibration curves (r^2 , 0.999) and matrix spiked recovery. The instrument was calibrated, before every batch of sample analysis. Calibration verification was <10%. Analysis of samples was carried out in duplicate and the average of two analyses was used in calculations. Detection limits (DL) were estimated by processing the eight aliquots of a spiked sample to produce a detectable response ($s/n > 3$) and multiplying the standard deviation by 3 (t_{students} value for eight replicates at 99% confidence level). Statistically calculated detection limits for all PAHs were ranged between 0.02-0.51 ng. The matrix spiked recoveries for target PAHs were in range of 85% - 92%.

Health Risk Assessment

Ingestion, inhalation and dermal contact are the main pathways of life-long exposure to contaminants for humans. In this study, soil ingestion pathway was considered as exposure route of PAHs for human health risk assessment. The Benzo(a)pyrene (BaP) toxicity equivalent (TEQ) concentration was estimated using BaP toxic equivalent factors (TEFs) of individual PAHs [27]. The BaP_{TEQ} is calculated by multiplying the concentration of each PAH in the soil by its BaP toxic equivalent factor (TEFs) using the following equation:

$$\text{BaP}_{\text{TEQ}} = C \times \text{TEF}$$

Where, C is the concentration of individual PAH (µg kg⁻¹) and TEF is the corresponding toxic equivalency factor.

Similar to BaP_{TEQ}, Benzo(a)pyrene total potency equivalents (B[a]P TPE) was calculated for assessment of human health risk from direct contact with PAHs contaminated soil [28]. Index of Additive Cancer Risk (IACR), the potential threat to potable groundwater quality from leaching of carcinogenic PAH from soil was also assessed [28-29].

Further, observed PAHs concentrations were compared with soil quality guidelines for the protection of environment and human health [29-30].

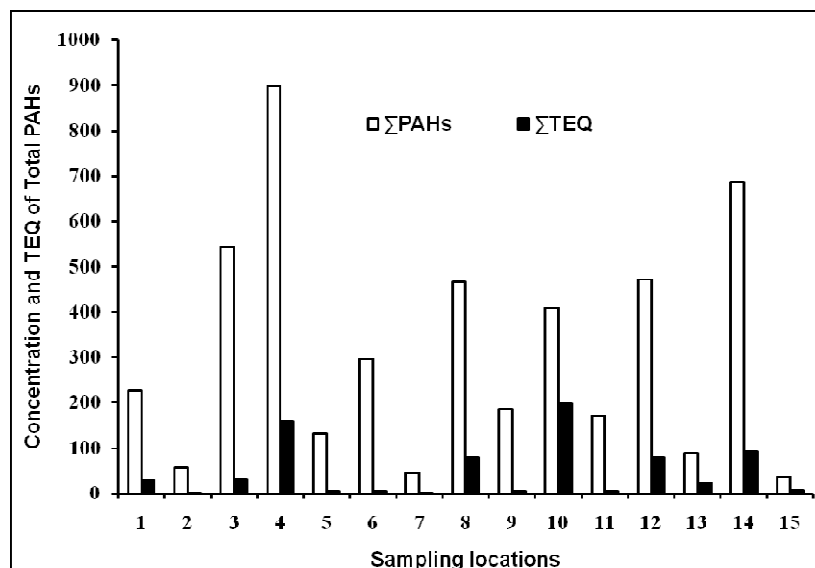
RESULTS AND DISCUSSION

Concentration of PAHs in Soils

The obtained concentration of PAHs in soils was presented in Table 1 and Figure 1 & 2. Total PAHs concentration ranged between 36 - 898 $\mu\text{g kg}^{-1}$ with the mean value of $315 \pm 67 \mu\text{g kg}^{-1}$. The average concentration of individual PAHs, Phe, Ant, Flt, Pyr, Chr, BkF, BaP, BghiP, and Ind was $74 \pm 16 \mu\text{g kg}^{-1}$, $110 \pm 13 \mu\text{g kg}^{-1}$, $144 \pm 18 \mu\text{g kg}^{-1}$, $83 \pm 10 \mu\text{g kg}^{-1}$, $70 \pm 16 \mu\text{g kg}^{-1}$, $58 \pm 8 \mu\text{g kg}^{-1}$, $67 \pm 15 \mu\text{g kg}^{-1}$, $157 \pm 22 \mu\text{g kg}^{-1}$, and $69 \pm 8 \mu\text{g kg}^{-1}$, respectively. The dominant PAHs were Ant, Flt, and BghiP, and accounted for 13%, 17% and 19% to total PAHs concentration.

Table 1. Concentrations of 9 priority PAHs in soils from Ghaziabad, India

Name of PAHs	Concentration ($\mu\text{g kg}^{-1}$)				%
	Range	Mean	SD	SE	
Phenanthrene (Phe)	BDL - 196	74	62	16	9
Anthracene (Ant)	BDL - 156	110	51	13	13
Fluoranthene (Flt)	BDL - 220	144	72	18	17
Pyrene (Pyr)	BDL - 112	83	40	10	10
Chrysene (Chr)	8.2 - 198	70	62	16	8
Benzo(k)Fluoranthene (BkF)	BDL - 78	58	32	8	7
Benzo(a)Pyrene (BaP)	BDL - 192	67	58	15	8
Benzo(g,h,i)Perylene (BghiP)	BDL - 318	157	84	22	19
Indeno(1,2,3-Cd)Pyrene (Ind)	BDL - 90	69	30	8	8
Σ PAHs	36 - 898	315	258	67	100
Σ PAH _{carcinogen}	20 - 694	188	208	54	60
PAH _{LMW}	20 - 472	104	136	35	33
PAH _{HMW}	BDL - 248	238	87	23	76

**Figure 1: Concentration of Σ PAHs ($\mu\text{g kg}^{-1}$) and Σ TEQ ($\mu\text{g kg}^{-1}$) in soils at different locations**

The observed concentrations of PAHs in the present study were compared with the recent measurements at other soils around the world including India (Table 2). The average concentration of PAHs observed in Ghaziabad street soils is comparable with the other cities including Korba ($385 \pm 118 \mu\text{g kg}^{-1}$) [24] and Gwalior ($481 \pm 92 \mu\text{g kg}^{-1}$) [25] in India, Bincheng, China ($360 \mu\text{g kg}^{-1}$) [16]. However, higher concentration of PAHs in soils have been reported for major cities such as Agra ($6440-12500 \mu\text{g kg}^{-1}$) [20], Delhi ($1551-11460 \mu\text{g kg}^{-1}$) [21] & ($6839 \pm 3528 \mu\text{g kg}^{-1}$) [22], Jalandhar ($4040 \mu\text{g kg}^{-1}$) [19] and Kurukshetra ($632 \pm 45 \mu\text{g kg}^{-1}$) [23] in India. The observed concentrations of PAHs in soils from Ghaziabad were much lower than those reported from Shenyang, China ($1510 \pm 1640 \mu\text{g kg}^{-1}$) [15], Anhui, China ($840 \mu\text{g kg}^{-1}$) [12], Liaoning, China ($1118 \mu\text{g kg}^{-1}$) [31], NE China ($675 \mu\text{g kg}^{-1}$) [14], Northern China ($1041 \mu\text{g kg}^{-1}$) [32], Zhanjiang, China ($553 \mu\text{g kg}^{-1}$) [33], Florida, USA ($771 \mu\text{g kg}^{-1}$) [34], Arizona, USA ($523 \pm 1886 \mu\text{g kg}^{-1}$) [35], Esbjerg, Denmark ($2500 \mu\text{g kg}^{-1}$) [36], Gipuzkoa, Spain ($18450 \mu\text{g kg}^{-1}$) [37], Addis Ababa, Ethiopia ($800 \mu\text{g kg}^{-1}$) [38] and South Africa ($9730-61240 \mu\text{g kg}^{-1}$) [39]. Saba et al. [40]

reported very high concentration of PAHs in urban soils from Rawalpindi, Pakistan ($3672 \pm 592 \text{ mg kg}^{-1}$). Compared with these areas, Ghaziabad has a tropical climate under strong influence of sunshine and rainfall every year, which made soil PAHs decrease by evaporation and runoff.

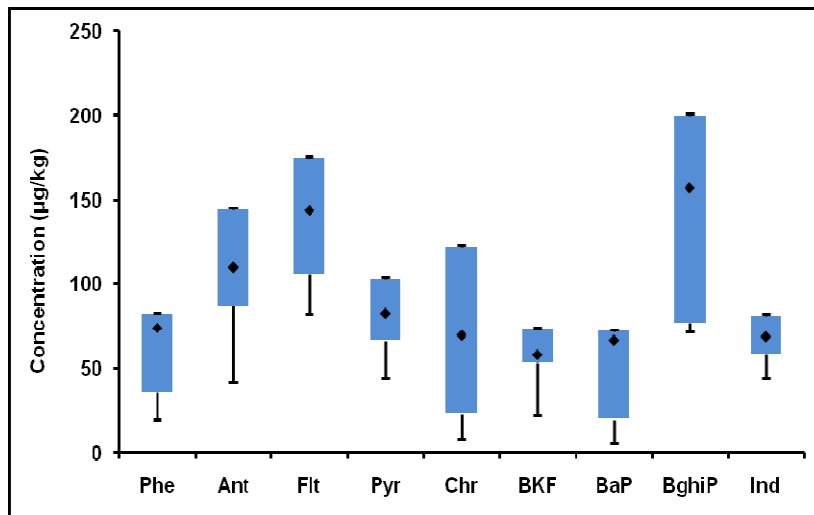


Figure 2: Box and Whisker Plot for concentration of selected PAHs

Table 2. A global comparison of PAHs in soils with this study

Country/City	No of PAHs	Σ PAHs ($\mu\text{g kg}^{-1}$)		Reference
		Range	Average	
India				
Agra	16	-	6440 - 12500	[20]
Delhi	16	-	1551 - 11460	[21]
Delhi	16	82 - 45017	6839 ± 3528	[22]
Ghaziabad	9	36 - 898	315 ± 67	Present study
Gwalior	16	76 - 1391	481 ± 92	[24]
Jalandhar	16	8 - 28400	4040	[51]
Kurukshetra	16	19 - 2538	632 ± 45	[23]
Korba	16	7.3 - 2151	385 ± 118	[25]
Other countries				
Anhui, China	16	130 - 3540	840	[12]
Florida, USA	14	83 - 2371	731	[34]
Northern China	16	323 - 23245	1041	[32]
Arizona, USA	16	67 - 10117	523 ± 1886	[35]
Esbjerg, Denmark	6	240 - 7600	2500	[36]
Gipuzkoa, Spain	10	200 - 136260	18450	[37]
NE China	16	293 - 1736	675	[14]
Zhanjiang, China	16	9.5 - 6618	553	[33]
Rawalpindi, Pakistan	16	2700 - 4443*	$3672 \pm 592^*$	[40]
Ethiopia	20	186 - 3150	800	[38]
Bincheng, China	16	181 - 2176	360	[16]
Shenyang, China	16	90 - 8350	1510 ± 1640	[15]
Liaoning, China	16	5 - 5642	1118	[31]
South Africa	16	9730 - 61240	-	[39]

*concentration in mg/kg

Toxic Fraction of PAHs and BaP Toxic Equivalency (BaP_{TEO})

The concentration of probable human carcinogenic PAHs ($\Sigma PAH_{\text{carcinogen}}$) in studied soils ranged between 20-472 $\mu\text{g kg}^{-1}$ with an average of $104 \pm 35 \mu\text{g kg}^{-1}$ and accounted for 33% of total PAHs (Table 1). Among the priority PAHs, BaP has been considered as the potential reference by World Health Organization (WHO) for other PAH toxicity. Therefore, BaP often used as a general indicator of PAHs contamination. The average concentration of BaP in this study was $67 \pm 15 \mu\text{g kg}^{-1}$ (range, BDL - 192 $\mu\text{g kg}^{-1}$) and accounted for 8% to total PAHs.

Table 3. BaP Toxicity Equivalency (BaP_{TEQ}) of 9 priority PAHs in studied soils

Name of PAHs	BaP Toxicity Equivalency ($\mu\text{g kg}^{-1}$)				%
	Range	Mean	SD	SE	
Phenanthrene	BDL – 0.10	0.04	0.03	0.01	0.04
Anthracene	BDL – 0.08	0.06	0.03	0.01	0.06
Fluoranthene	BDL – 11	7.20	3.58	0.92	7.46
Pyrene	BDL – 0.11	0.08	0.04	0.01	0.09
Chrysene	0.25 – 5.94	2.09	1.86	0.48	2.16
Benzo(k)fluoranthene	BDL – 3.90	2.90	1.59	0.41	3.00
Benzo(a)pyrene	BDL – 192	74.15	57.8	14.9	76.82
Benzo(g,h,i)perylene	BDL – 6.36	3.15	1.67	0.43	3.26
Indeno(1,2,3-Cd)pyrene	BDL – 9.00	6.87	2.98	0.77	7.11
Σ PAHs	0.61 - 197	46.78	61.81	15.97	100.00
Σ PAH _{carcinogen}	0.60 - 193	44.80	59.66	15.42	95.77
PAH _{LMW}	BDL – 0.12	0.05	0.04	0.01	0.11
PAH _{HMW}	0.60 - 197	46.74	61.80	15.97	99.92

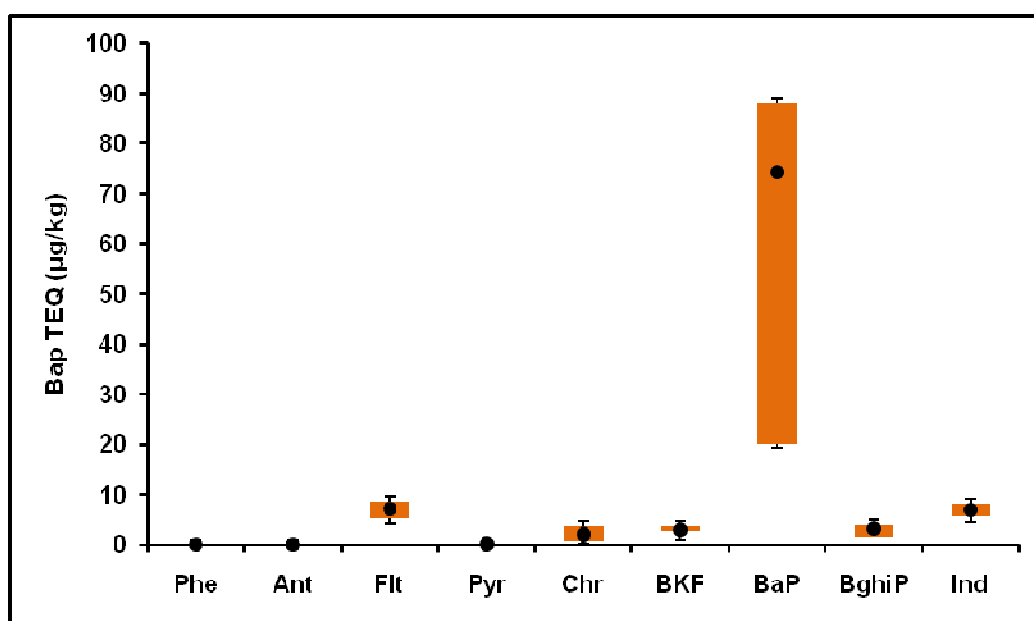


Figure 3: Box and Whisker Plot for BaP Toxicity Equivalent (BaP_{TEQ}) of selected PAHs

Table 4. Diagnostic ratios and possible sources of PAHs in this study

PAHs ratios	This study*	Diagnostic ratio & indicative of possible sources		
		Ratio	Possible Sources	Reference
PAH _{LMW} /PAH _{HMW}	0.13 – 1.90 (0.56)	<1	Pyrolytic	[8]
		>1	Petrogenic	[8]
Phe/Ant	0.55 – 1.33 (0.88)	<10	Pyrogenic	[49]
		>10	Petrogenic	[49]
		2-8	Vehicle emission	[43]
BaP/BghiP	0.21 - 1.89 (0.78)	<0.6	Non-traffic sources	[26]
		>0.6	Vehicle emission	[26]
Flt/(Flt+Pyr)	0.61 – 0.66 (0.63)	<1.0	Gasoline, diesel engine	[45]
		<0.4	Petrogenic	[46]
		>0.4	Gasoline, diesel engine	[48]
		1.0-1.4	Coal combustion	[45]
		0.3-0.7	Diesel engine	[44]
BaP/(BaP+Chr)	0.27 – 0.89 (0.59)	0.07-0.24	Coal combustion	[42]
		0.49	Gasoline	[43]
		0.73	Diesel engine	[43]
		0.3-0.7	Diesel engine	[44]

*Average in parenthesis

BaP has sufficient toxicological data for the representation of relative carcinogenic potential to the rest of the priority PAHs. Therefore, for conservative purpose, BaP toxic equivalent factors (TEFs) for other priority PAHs were derived and used for quantification of the cancer risk in terms of benzo(a)pyrene toxicity equivalency (BaP_{TEQ}). BaP_{TEQ} for this study was estimated and presented in Table 3 and Figure 3. Estimated $\sum BaP_{TEQ}$ for 9 PAHs ranged between $0.61-197 \mu g BaP_{TEQ} kg^{-1}$, with the mean value of $46.78 \pm 15.97 \mu g BaP_{TEQ} kg^{-1}$. BaP_{TEQ} for $\sum PAH_{carcinogen}$ ranged between $0.60 - 193 \mu g BaP_{TEQ} kg^{-1}$ with the mean of $44.80 \pm 15.42 \mu g BaP_{TEQ} kg^{-1}$ and accounted for 95.77% to $\sum BaP_{TEQ}$. In this study, HMW PAHs were the major contributors and LMW PAH compounds contributed negligible towards total carcinogenic potency of PAHs. BaP was the dominant contributors and accounted for 76.82% to total BaP_{TEQ} .

Possible Source Identification of PAHs

Compositional Analysis of PAHs

The studied priority PAHs can be classified in four homolog groups, according to their number of aromatic rings as 3- rings (Phe and Ant), 4- rings (Flt, Pyr, and Chr), 5- rings (BkF and BaP) and 6- rings (BghiP and Ind). The average concentration of PAHs homolog group was $104 \mu g kg^{-1}$, $130 \mu g kg^{-1}$, $105 \mu g kg^{-1}$ and $69 \mu g kg^{-1}$, respectively for 3-ring, 4-ring, 5-ring and 6-ring PAHs. Their contribution was accounted for 25.5%, 31.9%, 25.8% and 16.8%, respectively to total PAHs. The distribution pattern of group homolog of PAHs with different aromatic rings at different sampling locations is shown in Figure 4. The homolog distribution pattern in the area was in order of 4-ring > 5-ring > 3-ring > 6-ring PAHs. The observed pattern at different sampling locations was due to contamination with different group of PAHs. This variation in distribution pattern may have been due to mixed sources of PAHs from various sources.

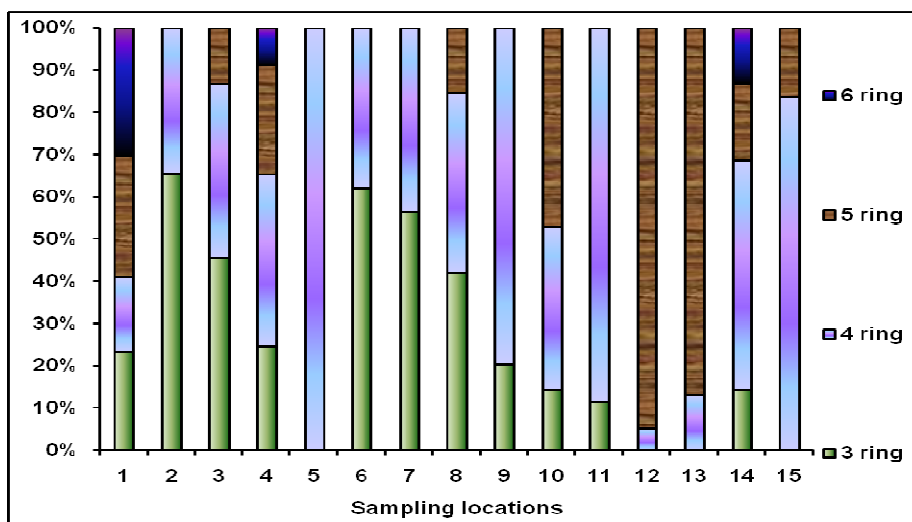


Figure 4: Percent contribution of different PAHs homolog (3- to 6-ring) in soils at different locations

PAHs have been classified with respect to molecular weights as low molecular weight PAHs (PAH_{LMW}) with <4 aromatic rings and high molecular weight PAHs (PAH_{HMW}) with ≥ 4 aromatic rings. Different PAHs sources release to the environment such as petrogenic or pyrogenic origins of PAHs widely used to identify through the levels of PAH_{LMW} and PAH_{HMW} in the environment. Petrogenic sources are dominated by PAH_{LMW} , while pyrogenic sources are characterized with HMW_{PAHs} . Thus, the ratios of PAH_{LMW} to PAH_{HMW} in the environment can be used as tool to identify the origin of PAH sources. Pyrolytic sources indicates the ratio of <1, while the petrogenic origins show ratio of >1 [8,41]. In this study, PAH_{LMW} / PAH_{HMW} ratio ranged between 0.13 – 1.90 and average was 0.56. In this study, the average concentration of PAH_{LMW} and PAH_{HMW} was $104 \pm 35 \mu g kg^{-1}$ and $238 \pm 23 \mu g kg^{-1}$, respectively. So, low fraction of PAH_{LMW} (33%) and high fraction of PAH_{HMW} (76%), and consequently low ratio of PAH_{LMW} to PAH_{HMW} (<1.0), indicating pyrogenic origin of PAHs in Ghaziabad city. The PAH_{HMW} are usually associated with coal fired industries, heavy oil combustion, coke oven and heavy-duty motor vehicle engines [42,43]. Such activities are dominant in the study area.

Diagnostic molecular Ratios of PAHs

Furthermore, the characteristic diagnostic molecular ratios of selected PAHs have been widely used to identify the sources of PAHs in the environment [44]. We have calculated the diagnostic ratios of the selected PAHs for this study and presented in Table 4. The molecular ratios of PAHs used to identify the possible sources of PAHs in this study area were Phe/Ant, BaP/(BaP+BghiP), Flt/(Flt+Pyr) and BaP/(BaP+Chr). These, selected ratios have been used for characterization of various possible sources of PAHs from petrogenic and pyrogenic origin (diesel combustion, gasoline, vehicle emission, non-vehicle and coal combustion emissions) [42-49].

The calculated ratios of Phe/Ant, BaP/(BaP+BghiP), Flt/(Flt+Pyr) and BaP/(BaP+Chr) ranged 0.55 – 1.33, 0.21-1.89, 0.61-0.66 and 0.27-0.89, respectively. As shown in Table 4, the Phe/Ant ratio (0.88) indicates pyrogenic source through anthropogenic activities. BaP/(BaP+BghiP) ratios (0.78) suggested vehicular emissions. The ratios of Flt/(Flt+Pyr) (0.63) indicating different combustion sources of PAHs, particularly from coal combustion, diesel combustion and gasoline. Ratios of BaP/(BaP+Chr) (0.59) shows sources of PAHs from gasoline and diesel combustion. Therefore, these observed ratios suggest pyrogenic sources of PAHs from combustion of coal, vehicular emissions and diesel combustions in vehicles and industrial activities.

Health Risk of PAHs

The benzo(a)pyrene total potency equivalent (BaP TPE) is the sum of estimated cancer potency relative to BaP for all carcinogenic PAHs [28]. The Canadian government has stipulated human health-based soil quality guidelines (SQG_{DH}) for PAHs based on incremental lifetime cancer risk (ILCR) through direct soil exposure as 1 in 1,000,000 (10^{-6}) and ILCR of 1 in 100,000 (10^{-5}) as 0.6 mg kg^{-1} and 5.3 mg kg^{-1} , respectively [29]. The estimated BaP TPE in this study ranged between 2.0×10^{-4} - $2.3 \times 10^{-1} \text{ mg kg}^{-1}$ with the mean value of $6.7 \times 10^{-2} \text{ mg kg}^{-1}$, which was lower than guideline values.

Table 5: Health hazard in terms of B(a)P TPE (mg/kg) and IACR

Parameters*	Range		Mean	SD	SE
	Minimum	Maximum			
B(a)P TPE	2.0×10^{-4}	2.3×10^{-1}	6.7×10^{-2}	8.3×10^{-2}	2.2×10^{-2}
IACR	0.01	1.27	0.39	0.44	0.11

*B(a)P TPE-Benzo(a)pyrene total potency equivalent, IACR-Index of additive cancer risk

Potential risk to contaminated ground water from leaching of carcinogenic PAHs was assessed by estimating the Index of Additive Cancer Risk (IACR) [28]. The Index of Additive Cancer Risk (IACR) is potential threat to potable groundwater water quality from leaching of carcinogenic PAH mixtures from soil. The IACR is calculated following the Canadian soil quality guidelines for the protection of environmental and human health. The recommended safe guideline level of IACR is ≤ 1 , for the protection of potable water (SQG_{PW}) [28]. The estimated IACR ranged from 0.01-1.27 with the mean of 0.39, and was much lower than safe guideline level. The estimated BaP TPE and IACR were presented in Table 5 and shown in Figure 5.

Furthermore, environmental health risk assessment was carried out with consideration of non-carcinogenic effects of PAHs on human and ecological functioning of soil microorganisms. For this purpose, established soil quality guidelines from National Oceanography and Atmospheric Administration (NOAA) of USA [30] and Canadian government [28] were applied for the assessment of ecotoxicological health effect of PAHs (Table 6). NOAA and Canada recommended environmental soil quality guidelines (SQGs) for individual PAHs in the ranges of 700 - 10,000 $\mu\text{g kg}^{-1}$. The levels of PAHs concentrations observed from this study were much lower than the recommended guidelines and indicated no environmental health risk and adverse effects on the soil biota. Maliszewska-Kordibach [50] classified the soils on the basis of contamination with PAHs. On the basis of concentration of \sum PAHs, soils were divided into four categories; not contaminated (with PAHs $< 200 \mu\text{g kg}^{-1}$), weakly contaminated (with PAHs 200 – 600 $\mu\text{g kg}^{-1}$), contaminated (with PAHs 600 – 1000 $\mu\text{g kg}^{-1}$) and heavily contaminated (with PAHs $> 1000 \mu\text{g kg}^{-1}$). Therefore, soils from Ghaziabad streets can be categorised as weakly contaminated with PAHs ($315 \mu\text{g kg}^{-1}$).

Therefore, this study may be concluded that concentrations of selected PAHs and their health risk were within acceptable limits, those stipulated by regulatory agencies [28, 30].

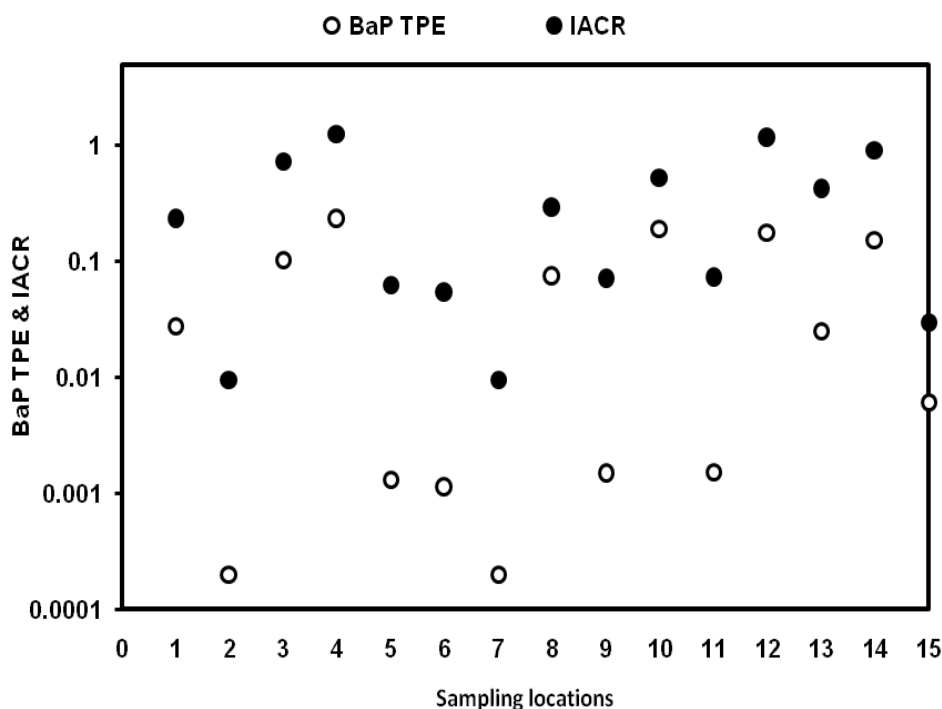


Figure 5: BaP TPE (mg kg⁻¹) and IACR in soils at different locations

CONCLUSION

This study concluded that Korba soils are weakly contaminated with selected priority PAHs. Contamination is dominated by high molecular weight PAHs (≥ 4 -ring PAHs). Analysis of composition profiles and molecular ratios of PAHs suggested the possible sources of PAHs originated from mixed pyrogenic activities such as coal combustion, vehicular emissions from diesel combustions. Estimated human and environmental health risk was lower than acceptable levels for human health and environmental quality.

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