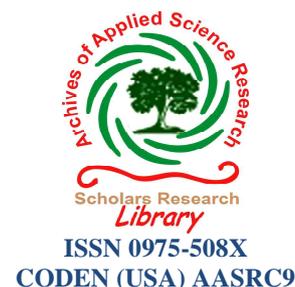




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Distribution of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls and their Source Identification in Urban Roadside Soils

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ABSTRACT

This study deals with distribution and identification of possible sources of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in urban roadside soils of Kurukshetra, a developing city in Haryana, India. The concentration of $\Sigma 16\text{PAHs}$ and $\Sigma 28\text{PCBs}$ was ranged between $16.1\text{-}2538.0 \mu\text{g kg}^{-1}$ and $3.33\text{-}34.81 \mu\text{g kg}^{-1}$. The average concentration of total PAHs, total possible carcinogenic PAHs, total PCBs and dioxin-like PCBs was $631.6\pm 44.5 \mu\text{g kg}^{-1}$, $568.8\pm 38.8 \mu\text{g kg}^{-1}$, $11.57\pm 2.00 \mu\text{g kg}^{-1}$ and $2.85\pm 0.34 \mu\text{g kg}^{-1}$, respectively. Carcinogenic fractions of PAHs and PCBs accounted for 90.1% and 34.6% to the total PAHs and PCBs, respectively. Diagnostic ratios of individual PAHs and higher fraction of high molecular weight PAHs indicate the pyrogenic activities such as motor vehicles, biomass and coal combustion as major sources of PAHs. Group homolog pattern shows that lower chlorinated PCBs were higher in concentrations than high chlorinated PCBs. Combustion of mixtures of waste, containing paper, cartons, plastics and painted wood, may be the possible sources of dioxin like-PCBs. Concentrations of PAHs and PCBs observed in this study were compared with available soil quality guidelines, which were lower than the guideline values, and analysed soils may be categorised in non contaminated soils.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Urban Soil, Soil Quality Guidelines

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are two groups of toxic organic compounds [1], ubiquitously present in every compartment of the environment including soils, sediments, plants, animals, and human beings [2]. These groups of compounds are environmental and human health concern, because of their harmful effects on invertebrates and mammals including humans through toxicological health risks such as carcinogenic, neurological and hormone disruption to exposed population [3]. Therefore, PAHs and PCBs have been designated as priority pollutant [4-5].

PAHs get released to the environment through, natural processes and anthropogenic activities (pyrogenic and petrogenic). Anthropogenic sources includes, petroleum products and sources of the incomplete combustion of organic matter in industrial operations, garbage incinerators, power plants, vehicle engines, household wood fires and forest fires [6]. PCBs were primary used in transformers and capacitors (dielectric and coolant fluids), lubricants,

flame retardants, paint additives, in carbonless copy paper and in plastics etc. [7]. Though the production or usage of PCBs has either been banned or restricted in many countries; still these are continuously found in environmental samples from around the world [8].

PAHs and PCBs are characterized by low vapour pressures, low water solubility, hydrophobicity, and lipophilicity. These compounds have the ability to accumulate in soil, sediments, biota, humans and food webs, posing significant health threats to humans, animals and the environment [9]. PAHs and PCBs tend to accumulate and remain for longer period in soil [10]. Because these compounds have tendency to bind more strongly to those particles which settle in soil and sediments [11], and serve as a major sink and re-emission sources for urban pollution [12]. In urban environment, cumulative effects of atmospheric depositions and local sources are the important sources of PAHs and PCBs [13]. Therefore, comparatively higher concentrations of these pollutants have been reported in urban soils compared with sub-urban or rural soils [14-15].

The amount of PAHs and PCBs in urban soil and the close proximity of these soils to humans lead to human exposure through ingestion, inhalation and dermal contact. Assessment of contamination levels of PAHs and PCBs in urban soils could be useful to planners, policy makers, and environmentalists to determine the risk exposure to residential inhabitants and terrestrial life [16]. Therefore, assessment of contamination levels of PAHs and PCBs in soils and identification of their sources is essential for their fate and transport in the environment. This study was undertaken to determine the distribution of PAHs and PCBs in roadside soils in a developing town of Haryana, India. This study may provide a baseline data during comparison of concentration of organic pollutants in future in the environment of developed metropolitan cities.

MATERIALS AND METHODS

Study Area

Kurukshetra town is situated in the Thanesar sub-division of the Kurukshetra district in Haryana state of India. It covers approximately 120 km² area in the district Kurukshetra and lies between geographical coordinates of 29° 57' 57" N longitude and 76° 50' 13" E latitude, about 160 km north of New Delhi, the capital of India. Kurukshetra is a land of historical and religious importance. The average texture of the soil is generally alluvial. Climate is very hot in summer (up to 47 °C) and cold in winter (down to 1 °C) with rains during July to August. Designated area has been developed for promotion of small scale industrial units. Agriculture is the main source of livelihood for majority of its population and Kurukshetra is called as "Rice bowl of India" where Basmati rice is the major cultivar, and other cultivated crops are wheat, rice, sugarcane and vegetables especially potato.

Sample collection

Thirteen sampling locations were selected near school, hospital, residential, tourist place, university campus and busy traffic intersection areas in Kurukshetra. Sampling was conducted during July 2012. Approximately 1/2 kg of soil sample was collected in triplicate from each location, unwanted materials such as pebbles, plant leaves and wood sticks were removed manually and all three parts of soils were mixed thoroughly to ensure representative sample of each location. An aliquot was transferred to clean and labelled aluminum foil lined bags. After collection, samples were transported to the laboratory and kept at 4 °C until further extraction and cleanup.

Chemicals and Solvents

HPLC grade solvents (hexane, acetone and dichloromethane) and anhydrous sodium sulphate were procured from E-Merck India. Silica gel (100–200 mesh) was obtained from Sigma-Aldrich (USA) and was activated at 130 °C for 16 h prior to use. Anhydrous sodium sulfate was cleaned with solvents and stored in the sealed desiccator. Solutions 16 PAHs standards mixture and individual PAHs were purchased from Supelco (Sigma-Aldrich, USA). Individual PCB congener standards were purchased from Dr. Ehrenstorfer (GmbH, Germany). After serial dilutions of the standards; and mixing at appropriate proportions, working standards mixture solution was used for instrument calibration and other quality control exercises.

Sample Extraction and Clean-up

The soil samples were extracted following USEPA Methods (ultrasonic extraction). In brief, 20 g portion of soil was mixed with anhydrous sodium sulphate to get free flowing mixture and extracted with 50 ml mixture of acetone-hexane (1:1 v/v) for 30 min in ultrasonic bath. Copper powder was added during extraction to remove elemental sulfur. After extraction samples were allowed to settle and solvent layer was filtered through a Whatman 41 filter

paper. The process was repeated for two more times. The solvent extracts were concentrated to 2 ml under reduced pressure in a 40 °C water bath using a rotary vacuum evaporator (Eyela, Japan). An additional 20 ml hexane was added to the concentrated extracts and evaporated to a volume of 1ml.

Chromatographic column clean up of the sample extracts was carried out using the methods [17] meant for the separation of PAHs and organochlorines from interfering compounds. The concentrated extracts and two 2-ml portions of n-hexane were transferred by rinsing the sample flask to top of the chromatography glass column (30 cm × 10 mm) packed with 10 g activated silica gel (100–200 mesh) and 1 cm layer of anhydrous sodium sulphate to separate the PAHs from other interfering compounds. The silica gel was loaded in hexane and capped with a thin layer of cotton (extracted with DCM as samples) to prevent the gel from spilling, and approximately 1 cm length of anhydrous sodium sulfate was added in the top. The column was sequentially eluted with 30 ml of n -hexane and 35 ml of dichloromethane at the flow rate of ~2 ml min⁻¹. Hexane fraction containing aliphatic hydrocarbons was discarded and dichloromethane fraction containing PAHs and PCBs was retained and concentrated to near 1 ml. Final volume was adjusted to 2 ml and divided into two fractions of 1 ml each. One fraction was solvent exchanged to acetonitrile for PAH analysis by HPLC and another fraction was exchanged to hexane for PCB analysis by gas chromatograph with electron capture detector (GC-ECD).

Instrumental Quantification in sample extracts

Sixteen priority PAHs were analysed following the USEPA Methods. Briefly, PAHs were quantitatively analysed by HPLC system (Agilent 1100 Series) equipped with Diode Array Detector (DAD, λ=254 nm), quaternary pump and degasser. Extract injections with 20 µl sample loop were chromatographed on a 25cm x 4.6 mm, 5 µm (SupelcosilTM LC-PAH) analytical column and Eclipse XDB-C8 (4.6 x 12.5 mm, 5 µm) used as guard column. Gradient grade acetonitrile and HPLC water were used as mobile phase with initial ratio of acetonitrile (60%) and water (40%) to finally acetonitrile (100%) at linear flow @1.0 ml/min in 42 min.

Polychlorinated biphenyls (PCBs) congeners were separated and quantified using gas chromatograph (Shimadzu SPD 2010, Japan) equipped with autosampler and an Electron Capture Detector (ECD, ⁶³Ni), on fused silica capillary column (HP-5MS, Agilent) 60 m x 0.25 mm x 0.25 µm film. The column oven temperature was maintained at 170 °C for 1 min, and increased @ 3 °C min⁻¹ to 270 °C and held for 1 min; the temperature was again increased @ 10 °C min⁻¹ to 290 °C and finally holds for 3 min. The injector and detector temperatures were maintained at 225 °C and 300 °C, respectively. Purified analytical grade nitrogen gas was used as carrier at the flow rate of 1.0 ml. min⁻¹.

Analytical Quality Control

The concentrations of target compounds were determined by external standard method using the peak area of the samples and the five level calibration curves of the standards. The peak identification was conducted by comparison with the accurate retention time of each standard. A procedural blank consisting of all chemicals and solvents was run to check for interferences and cross contamination. Appropriate quality assurance and quality control (QA/QC) exercises were performed, with procedural blanks, random duplicate samples (Standard deviation <10), calibration curves with the *r*² value of 0.999.

The instrument detection limits were calculated by using signal to noise ratio 3:1 for a valid quantifiable peak. Each sample was analysed in duplicate and the average was used in calculations. Method detection limits were established by processing eight aliquots of a spiked sample to produce a detectable response (s/n >3) and multiplying the standard deviation by 3 (*t*_{students} approximate value for eight replicates). The limit of detection (LOD) was calculated by multiplying standard deviation of each PAH and PCB congener by Student's *t* value (at 99% confidence level). Statistically calculated value (MDL) for all PCB congeners (0.01ng g⁻¹) and PAHs (1.0 µg kg⁻¹) was used during data interpretation. Recovery of analytes was established by matrix spiked analysis and recovery was ±20%. Further, it may be noted that our laboratory had been participating in proficiency testing (PT) exercises conducted by UNEP and other international agencies and scores of performance were satisfactory for PAHs and PCBs compounds.

RESULTS AND DISCUSSION

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs Concentration in Soils

In this study 16 individual PAHs namely naphthalene (Npt), acenaphthylene (ANy), acenaphthene (ANe), fluorene (Fle), anthracene (Ant), phenanthrene (Phe), 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 (Bpe) and indeno (1,2,3-c,d) pyrene (Ipy), were analysed and quantified.

Table 1: Concentration of PAHs in urban roadside soils ($\mu\text{g kg}^{-1}$)

Name of PAHs	PAH Concentration				
	Range	Mean	Median	Std Err	%
Naphthalene	43.0-71.1	57.0	57.0	5.3	1.8
Acenaphthylene	BDL				
Acenaphthene	BDL				
Fluorene	BDL				
Phenanthrene	5.6-26.1	14.7	11.3	2.3	8.8
Anthracene	BDL				
Fluoranthene	60.4-62.3	61.4	61.4	0.4	1.9
Pyrene	48.3-219.7	106.1	50.2	26.3	5.0
Benzo(a)Anthracene	6.5-133.1	35.9	19.0	12.2	4.0
Chrysene	6.9-163.5	36.9	17.7	5.0	4.1
Benzo(b)Fluoranthene	8.3-195.0	44.9	25.8	7.9	5.0
Benzo(k)Fluoranthene	17.8-100.2	46.9	34.8	10.2	3.0
Benzo(a)Pyrene	6.8-167.4	43.3	14.1	6.3	4.8
Benzo(g,h,i)Perylene	112.1-1960.4	850.5	479.0	61.6	40.4
Dibenzo(a,h)Anthracene	175.0-755.8	499.2	566.6	79.2	23.7
Indeno(1,2,3-Cd)Pyrene	24.3-161.7	108.1	138.3	19.6	5.1
Σ PAHs	16.1-2538.0	631.6	93.0	44.5	100
Σ c-PAHs	6.8-2538.0	568.8	79.2	38.8	90.1
LMW-PAHs	5.6-71.1	31.2	16.5	8.2	3.0
HMW-PAHs	6.8-2538.0	612.9	79.2	46.3	97.0

BDL=Below Detection Limit, Σ PAHs=Sum of 16 PAHs, Σ c-PAHs=Sum of probable human carcinogenic PAHs, LMW-PAHs= Σ <4 ring PAHs, HMW-PAHs= Σ \geq 4 ring PAHs

Table 2: Diagnostic ratios of individual PAH concentration

PAHs ratios	Value of ratios and indicate for	Reference	This study
Flt/(Flt+Pyr)	<0.4	Petrogenic [20]	0.56
	\geq 0.4-0.5	Pyrogenic [20]	
	>0.5	Biomass, Coal [21]	
BaA/(BaA+Chr)	<0.2	Petrogenic [22]	0.56
	0.2-0.35	Petroleum comb. [20]	
	>0.35	Biomass, Coal [20]	
BaP/(BaP+Chr)	0.07-0.24	Biomass, Coal [24]	0.56
	0.49	Gasoline [19]	
	0.73	Diesel [19]	
BaP/Bpe	<0.6	Non-traffic sources	0.80
	>0.6	Traffic sources [21]	
Ipy/(Ipy+Bpe)	<0.2	Petrogenic	0.25
	\geq 0.2-0.5	Pyrogenic [20]	

The concentrations of total PAHs and individual PAHs in soil samples from different locations in Kurukshetra, India are presented in Table 1. The concentrations of Σ PAHs, were in range of 19.1-2538.0 $\mu\text{g kg}^{-1}$, with the mean and median values of 631.6 $\mu\text{g kg}^{-1}$ and 93.0 $\mu\text{g kg}^{-1}$ ($\pm 44.5 \mu\text{g kg}^{-1}$), respectively. Concentration of benzo(g,h,i)perylene and dibenzo(a,h)anthracene was comparatively higher among all 16 individual PAHs at all the locations and accounted for 40% and 24%, respectively. Concentration of total probable human carcinogenic PAHs was ranged between 6.8-2538.0 $\mu\text{g kg}^{-1}$ with the mean and median concentration of 568.8 $\mu\text{g kg}^{-1}$ and 79.2 $\mu\text{g kg}^{-1}$ ($\pm 38.8 \mu\text{g kg}^{-1}$), respectively. The abundance of carcinogenic PAHs was more than 90% of the total PAHs. The concentration of BaP, the most potent carcinogenic PAH was between 6.8 to 167.4 $\mu\text{g kg}^{-1}$ with mean and median of 43.3 $\mu\text{g kg}^{-1}$ and 14.1 $\mu\text{g kg}^{-1}$, respectively. In this study the highest concentration of Σ PAHs ($>800 \mu\text{g kg}^{-1}$) was detected in soil

samples at location 6 followed by location 2 and 8 (Figure 1), these locations were in the busy traffic intersection of the study area.

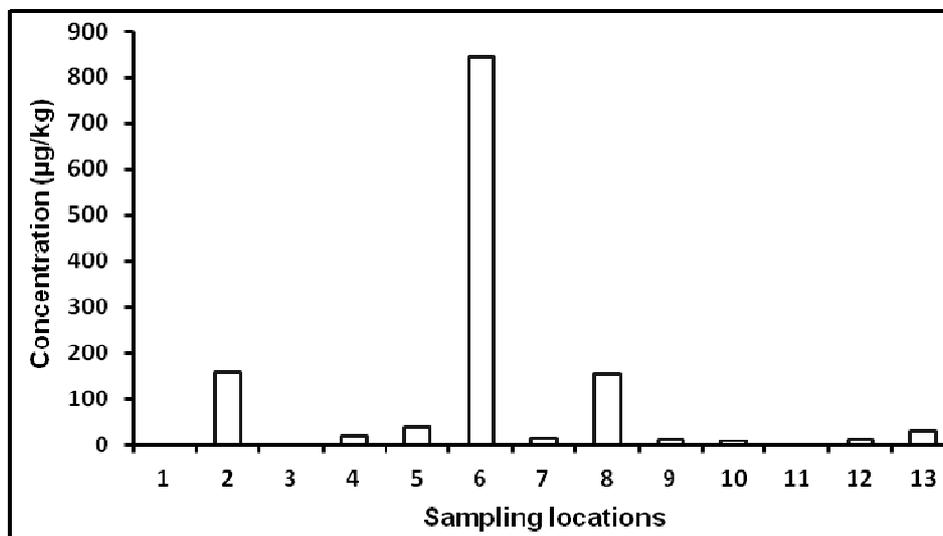


Figure 1: Average concentration of total 16 PAHs in soils at different locations

Possible Sources of PAHs

Identification of the PAHs origin sources is essential in the environment to assess the environmental risk. PAHs are released to the environment through anthropogenic activities of petrogenic and pyrogenic origins. Petrogenic (petroleum derived residues) origin PAHs are characterized by the predominance of 2 and 3 ring or low molecular weight, while pyrogenic (combustion derived) origin PAHs are characterized with higher abundance of above 4-ring or high molecular weight PAHs. LMW_{PAHs} are generated at low to moderate temperatures such as during biomass combustion; the HMW_{PAHs} are generated at high temperature combustion such as vehicle emissions [18]; which gives different ratio of LMW_{PAHs} to HMW_{PAHs} in soil depending upon the sources. The LMW_{PAHs} to HMW_{PAHs} ratio of <1 suggests the pyrolytic source of PAHs, while the ratio of >1 indicates petrogenic origin. The studied soil in Kurukshetra contained a comparatively very high concentration of high molecular weight PAHs (97%) (Table 1) and consequently lower ratio of LMW_{PAHs} to HMW_{PAHs} (<1.0) suggesting pyrolytic origin of PAHs. The concentrations of specific PAH compounds, or a group of PAHs, have been used to identify the corresponding emission sources, such as Ant, Phe, Flt, Pyr, BaA and Chr for coal combustion; Ant, Phe, BaP and Bpe for coke production; Phe, Flt and, especially, Pyr for incinerators. Ant, Phe, Flt and Pyr are indicators for combustion of wood; Flt and Pyr for oil burning; Flt, Pyr and, especially, Bpe for petrol powered vehicles; Flt, Pyr with higher ratio of BbF and BkF for diesel-fueled vehicles [19]. Further, diagnostic ratios of selected PAH concentrations are the most widely used technique to identify and characterize the sources. The ratio of Flt/(Flt+Pyr) (<0.4) has been attributed to petrogenic sources and ratio of ≥0.4-0.5 to pyrogenic sources [20]. The higher ratio (>0.5) of Flt/(Flt+Pyr) has been attributed to biomass combustion sources [21]. BaA/(BaA+Chr) ratio of <0.2 indicates petrogenic, 0.2-0.35 petroleum combustion, and >0.35 shows biomass combustion [19,20,22]. Khalili *et al.*, [19] and Guo *et al.*, [23] suggested that the ratio of BaP/(BaP+Chr) was 0.49 and 0.73 for gasoline and diesel engines, respectively, while the ratio between 0.07-0.24 indicates the biomass combustion [24]. Ratio of Ipe/(Ipe+Bpe) was also suggested by Hwang *et al.* [20] for petrogenic (<0.2) and pyrogenic (≥ 0.2-0.5) sources. Fadzil *et al.* [21] used BaP/Bpe ratios to distinguish traffic (>0.6) and non-traffic sources (<0.6) (Table 2). In this study the compounds ratio of Flt/(Flt+Pyr), BaA/(BaA+Chr), BaP/Bpe, Ipy/(Ipy+Bpe) and BaP/(BaP+Chr) were used to identify the possible sources of PAHs in soil.

On the basis of Table 2, the isomeric ratios indicated that pyrogenic sources such as combustion of petroleum products, grasses, woods and coal are the major sources of PAHs to the Kurukshetra soils. Furthermore, ratio of BaP/Bpe (0.80) shows that fuels combustions used by the vehicles is the major source of PAHs. Source analysis in various studies [17, 25] indicate that urban soil PAHs are mainly of pyrolytic origin with both mobile (e.g. motor vehicle exhausts) and stationary (e.g. power generation by coal or oil combustion and use of heating oil) emissions as

the primary sources of PAHs. This contamination will be an ongoing process as PAHs are persistent and human exposure by inhalation of particles, dietary intake of contaminated food products such as vegetables, and direct contact with polluted water, soil, sludge and sediment will continue.

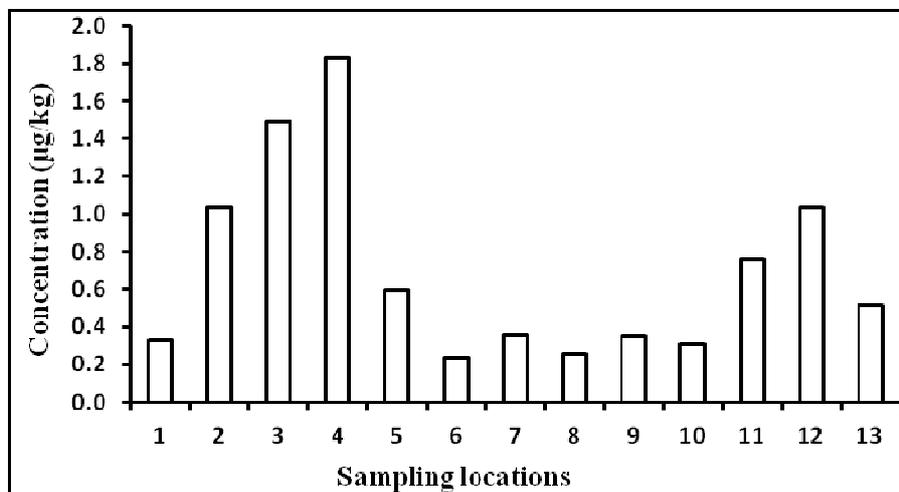


Figure 2: Average concentration of total 28 PCBs in soils at different sampling locations

Polychlorinated Biphenyls

PCBs Concentrations in Soil

PCB congeners are known by the numbers denoted to them by the International Union of Pure and Applied Chemistry (IUPAC). In the present study 16 PCB congeners (CB -18, -37, -44, -49, -52, -70, -74, -119, -128, -138, -151, -168, -170, -177, -187, and -207) and 12 dl-PCB congeners (CB-77, -81, -105, -114, -118, -123, -126, -156, -157, -167, -169 and CB-189) were analyzed. The concentrations of 28 individual congeners and their sum in urban roadside soils from Kurukshetra, India are presented in Table 3. The observed mean and median levels of total PCBs including dl-PCBs were 11.57 ng g^{-1} and 8.23 ng g^{-1} ($\pm 2.00 \text{ ng g}^{-1}$), respectively and their range were between $3.33\text{-}34.81 \text{ ng g}^{-1}$. The concentration of 12 dl-PCBs was ranged between $0.36\text{-}5.78 \text{ ng g}^{-1}$ with the mean and median values of 2.85 ng g^{-1} and 2.16 ng g^{-1} ($\pm 0.34 \text{ ng g}^{-1}$), respectively. Dioxin like-PCBs accounted for approximately 25 percent to total PCBs. IUPAC congener number CB-18 (39%), CB-169 (19%) and CB-52 (11%) were the dominant congeners among all twenty eight PCBs. Levels of total PCBs in soils at location number 4 and 3 were comparatively higher than other locations (Figure 2).

Table 4: PCB Homologs (3-7CB) in urban roadside Soils ($\mu\text{g kg}^{-1}$)

Statistics	Group homolog of PCBs				
	Tri-CBs	Tetra-CBs	Penta-CBs	Hexa-CBs	Hepta-CBs
Mean	4.81	2.59	1.07	2.62	0.51
Median	0.39	2.37	0.58	2.00	0.45
Range	<0.01-22.41	0.91-5.26	0.22-2.73	0.20-5.47	0.08-1.17
% of Σ PCBs	41.61	22.40	9.24	22.60	4.45

Group Homolog of PCBs

Group homolog of PCBs was presented in Table 4 and their profile at different sampling locations was depicted in Figure 3. Homolog of PCBs was dominated by tri-chlorinated (41.61%), tetra-chlorinated (22.40%) and hexa-chlorinated biphenyls (22.60%). Average concentration of 3-CBs, 4-CBs, 5-CBs, 6-CBs and 7-CBs was 4.81 ng g^{-1} , 2.59 ng g^{-1} , 1.07 ng g^{-1} , 2.62 ng g^{-1} and 0.51 ng g^{-1} , respectively. The PCB homolog distribution patterns show that the low molecular weighted PCBs (LMW-PCB) were the major contributors accounting for more than 60%, than high molecular weight PCBs (HMW-CBs), with approximately 35%. Researchers have reported that low molecular weight PCBs were primarily used in electrical equipments while high molecular weights were mainly used as additives in various applications [26]. The PCB sources in the study area may be due to off gassing from closed electrical system such as transformers that contain large quantities of PCB fluids, recycling of used capacitors, condensers etc. The other sources of PCBs may be from electric and electronic waste recycling, industrial emission

depositions and from biomass burning including PVC (polyvinylchloride). The higher concentrations of PCBs have been reported in soils in many studies from the areas those have fugitive emissions from conventional heating for cooking and heating in residential areas, especially during the winter season. Mixtures of waste containing paper, cartons, plastics and painted wood, may release relatively large amounts of dioxin like-PCBs [27-29].

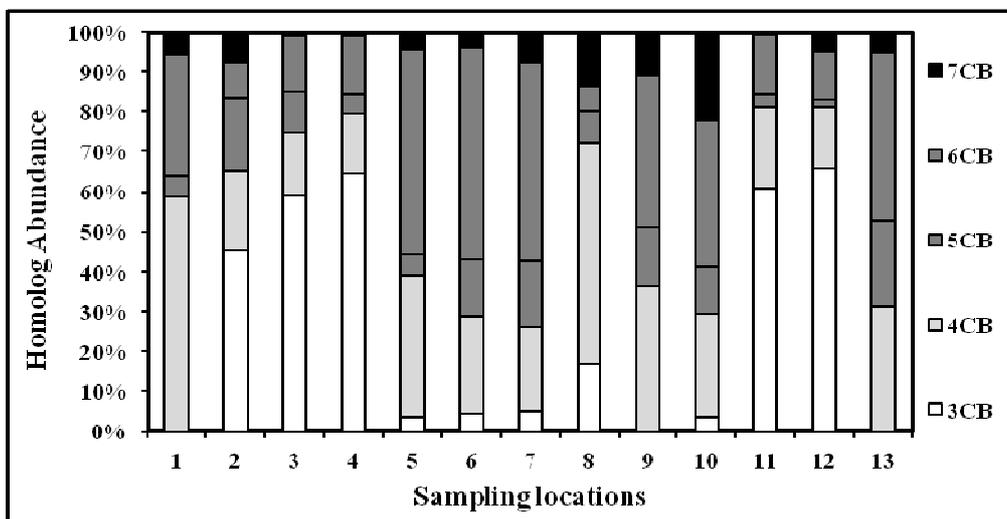


Figure 3: Distribution of PCBs homolog in soils at different sampling locations

Table 3: PCBs congener concentrations ($\mu\text{g kg}^{-1}\text{dw}$) in urban roadside soils

PCB Congeners	PCB Concentration				%
	Range	Mean	Median	Std Err*	
<i>Polychlorinated Biphenyls (PCBs)</i>					
PCB - 18	6.54-20.82	11.78	9.78	1.69	39
PCB - 37	0.17-1.59	0.53	0.39	0.14	2
PCB - 44	0.73-1.26	1.06	1.13	0.06	3
PCB - 49	0.17-1.25	0.48	0.26	0.14	1
PCB - 52	0.17-2.75	1.43	1.35	0.29	11
PCB - 70	0.04-0.98	0.55	0.49	0.08	3
PCB - 74	0.13-1.15	0.37	0.27	0.10	3
PCB - 119	0.13-2.62	0.84	0.42	0.24	7
PCB - 128	<0.01				
PCB - 138	0.03-0.62	0.17	0.16	0.05	1
PCB - 151	0.01-0.46	0.26	0.30	0.06	1
PCB - 168	0.02-0.77	0.13	0.05	0.06	1
PCB - 170	0.01-0.42	0.10	0.04	0.03	<1
PCB - 177	0.13-0.16	0.27	0.24	0.03	1
PCB - 187	0.02-0.59	0.21	0.12	0.06	1
PCB - 207	0.01-0.59	0.12	0.05	0.04	1
ΣPCBs	1.64-29.77	8.72	4.46	1.85	75
<i>Dioxin like-polychlorinated biphenyls (dl-PCBs)</i>					
dl-PCB - 77	<0.01				
dl-PCB - 81	0.01-0.02	0.02	0.02	<0.01	<1
dl-PCB - 126	0.02-0.08	0.05	0.05	0.01	<1
dl-PCB - 169	0.13-5.31	2.20	1.90	0.42	19
dl-PCB - 105	0.01-0.27	0.06	0.05	0.03	<1
dl-PCB - 114	0.03-0.34	0.15	0.14	0.03	1
dl-PCB - 118	0.01-0.07	0.03	0.02	0.01	<1
dl-PCB - 123	0.05-0.40	0.17	0.07	0.04	1
dl-PCB - 156	0.01-0.07	0.04	0.04	0.01	<1
dl-PCB - 157	0.01-0.29	0.07	0.04	0.03	<1
dl-PCB - 167	0.01-0.24	0.06	0.04	0.02	<1
dl-PCB - 189	0.04-0.95	0.23	0.18	0.06	2
$\Sigma\text{dl-PCBs}$	0.36-5.78	2.85	2.16	0.34	25
Total (PCBs+dl-PCBs)	3.33-34.81	11.57	8.23	2.00	100

Note: <0.01=below detection limit, Std Err (standard Error)=standard deviation/ \sqrt{n}

Ecotoxicological health Risk of PAHs and PCBs

Environmental standards have not yet been set in India for PAHs and PCBs in soil and sediments. Therefore, ecotoxicological effect of PAHs and PCBs in this study area was assessed by applying established soil quality guidelines those from National Oceanography and Atmospheric Administration (NOAA) [30] and Canada [31, 32]. Table 5 shows the recommended guideline concentration of individual PAHs and total PCBs in soils from environmental agencies and their comparison with the average concentrations observed in this study. Concentrations of individual PAHs and PCBs were comparable with guideline values and indicated no such environmental health risk and adverse effects to the biota.

Table 5: Soil quality guidelines for PAHs and PCBs ($\mu\text{g kg}^{-1}$) and comparison with this study

Name of Pollutants	Soil guidelines*		Present study
	NOAA	CCME	
Polycyclic Aromatic Hydrocarbons (PAHs)			
Naphthalene	5000	6000	57.0
Acenaphthylene	-	-	BDL
Acenaphthene	-	-	BDL
Fluorene	-	-	BDL
Phenanthrene	5000	5000	14.7
Anthracene	-	-	BDL
Fluoranthene	-	-	61.4
Pyrene	10×10^3	10×10^3	106.1
Benzo(a)anthracene	1000	1000	35.9
Chrysene	-	-	36.9
Benzo(b)fluoranthene	1000	1000	44.9
Benzo(k)fluoranthene	1000	1000	46.9
Benzo(a)pyrene	1000	700	43.3
Benzo(ghi)perylene	-	-	850.5
Dibenzo(a,h) anthracene	1000	1000	499.2
Indene(1,2,3-cd)pyrene	1000	1000	108.1
Polychlorinated Biphenyls (PCBs)			
Polychlorinated Biphenyls	5000	1300	11.57

*guidelines for residential and parkland soil, NOAA-National Oceanic and Atmospheric Administration, CCME-Canadian Council of Ministers of the Environment

Furthermore, contamination of soils by PAHs can be categorised through a documented classification [33]. This classification's threshold values were derived from the PAHs contents in European soils as well as from an estimation of risk of human exposure to PAHs through food. According to this classification, the soils are divided into four categories depending upon the concentration of total 16 PAHs in soils: 1-not contaminated: $<200 \mu\text{g kg}^{-1}$; 2-medium contaminated: $200\text{--}600 \mu\text{g kg}^{-1}$; 3-contaminated: $600\text{--}1000 \mu\text{g kg}^{-1}$; and 4-heavily contaminated: $>1000 \mu\text{g kg}^{-1}$. Our study had shown concentration of total PAHs below $200 \mu\text{g kg}^{-1}$ in the study area, which may be classified as not contaminated.

CONCLUSION

The study shows that PAHs and PCBs contamination of Kurukshetra roadside soils is lower than soil quality guidelines. The concentration of high molecular weight PAHs including possible human carcinogenic PAHs was higher than low molecular weight PAHs. PCB contaminations are mainly from low molecular weight PCBs including tri-chlorinated and tetra-chlorinated biphenyls. Further, it is recommended to conduct more intensive studies in small developing towns for persistent organic pollutants, due to human health and environment concerns and to aid better environmental management in future.

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