Distribution, Composition Profiles and Source Identification of Polycyclic Aromatic Hydrocarbons in Roadside Soil of Delhi,

India

Kumar Bhupander^{*}, Goel Gargi, Gaur Richa, Prakash Dev, Kumar Sanjay, and Sharma Chandra Shekhar National Reference Trace Organics Laboratory, Central Pollution Control Board, East Arjun Nagar, Delhi, India-110032

*Corresponding author: bhupander_kumar@yahoo.com

Abstract

Distribution, composition profiles and sources of polycyclic aromatic hydrocarbons (PAHs) were evaluated in roadside soils from Delhi, India. PAH determination was made by Sonication extraction and chromatographic clean-up with final analysis by high performance liquid chromatography with ultraviolet-diode array detector (HPLC-UV-DAD). The average concentration of Σ PAHs was 6838.6±3528.4 µg kg⁻¹ and ranged between 81.6 to 45017.4 µg kg⁻¹. Seven possible carcinogenic PAHs (Σ 7c-PAHs) accounted 67.4% to the total PAHs. Diagnostic ratios of individual PAHs and LMW_{PAHs} to HMW_{PAHs} ratio were calculated and applied to assess the possible sources of PAHs which, indicates the mixed pyrogenic activities such as petroleum, biomass and coal combustion are the main contributors. Although, concentrations of individual PAHs were lower than the guideline values but, the concentrations of some high molecular weight PAHs were higher at the locations in the vicinity of industrial areas and there is probable some risk to human health.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), HPLC-UV, roadside soil, diagnostic ratio, India

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of persistent, bio-accumulative and toxic organic compounds (Blumer, 1976; Hites et al., 1977). They consists at least two benzene rings and hydrophobic in nature. They are of environmental concern, because they have harmful effects on invertebrates and mammals including humans (Gupta et al., 1993; Szezeklik et al., 1994; Ravindra et al., 2001). Some PAHs have endocrine disrupting properties and some have shown to affect the immune system (IARC, 1983). The carcinogenicity classifications verified by EPA Carcinogenicity Risk Assessment Work Group (USEPA, 1994) shows that Benzo(a)athracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Chrycene, Dibenzo(a,h)anthracene and Indeno(1,2,3,cd)pyrene are considered to be probable human carcinogens. Therefore, US EPA has designated sixteen PAHs as priority environmental pollutants (USEPA, 2002).

They are released to the environment through two sources, the anthropogenic and natural processes (Lee *et al.*, 1995). Anthropogenic input was regarded as the main source for the elevated concentration of PAHs in the environmental matrix. There are two types of anthropogenic sources of PAHs: petrogenic and pyrogenic. Petrogenic sources include crude oil and petroleum products. Pyrogenic sources from by the incomplete combustion of organic matter in industrial operation, garbage incinerators, power plants, vehicle engines and forest fires (Baek *et al.*, 1991).

Due to their hydrophobicity, low water solubility, and vapor pressures, PAHs tend to accumulate and persist

for longer period in soil (Wilcke, 2000). Owing to their toxicity and widespread distribution around the globe, identification of the sources of PAHs is important. The identification of PAH sources is requisite to regulation of the input of PAHs to environment. The initial step in source identification is differentiation between petrogenic and pyrogenic sources, which is relevant to the impacts of PAH accumulation on aquatic and benthic ecosystems. Petrogenic PAHs may be more available for biological uptake than pyrogenic PAHs, since it tends to bind more strongly to particulate particles (Gustafsson *et al.*, 1997). Soils are a major reservoir and sink for urban pollutants because of its quantity and holding capacity for organic pollutants (Wild and Jones, 1995).

The amount of PAHs in urban soil and the close proximity of these soils to humans lead to human exposure via ingestion, inhalation or dermal contact (Mielke *et al.*, 2001; Abrahams, 2002). Hence, the PAHs contamination of soils and identification of PAHs sources is essential for their fate and transport in the environment. Therefore, this study was carried out to determine the distribution of PAHs in roadside soils in Delhi, India

2. Material and Methods

2.1 Study Area

The study area, National Capital Territory (NCT) Delhi $(28^0 \ 36' \ 36'' \ N \ to \ 77^0 \ 13' \ 48''E)$, is the administrative capital city of India with 16.6 million populations (Figure 1). Delhi lies in northern India with a total area of 1,483 km². There was single mode of transport in Delhi till 2002 when first Delhi metro was started. The number of in use vehicle population growth increased from 3.05 million in 2000 to 6.5 million on 30,985 km road length during 2010 (DoEF Delhi, 2010). There are five power plants (two coal based and three gas based) for electricity generation and a number of medium to small-scale industries in Delhi, which contribute total suspended particulate mass concentrations (>500 µg m⁻³) to the environment in Delhi (Aneja *et al.*, 2001).



Figure 1: Map showing the study site

2.2 Sample collection

Soil sample was collected from fourteen roadside urban locations in Delhi during June 2011. At each sampling location, approximately 1/2 kg of soil sample was collected, and after removing pebbles, wood sticks and leaves the sample was mixed thoroughly to homogenized, then a part was transferred to clean and

labelled wide mouth amber glass containers. After collection, samples were transported to the laboratory and kept at 4 0 C until further analysis.

2.3 Chemicals and Solvents

Solvents used included n-hexane, acetone and dichloromethane (DCM) (analytical grade, procured from E-Merck India. Silica gel (100–200 mesh) was obtained from Sigma-Aldrich (USA) and was activated at 130 ⁰C for 16 h immediately prior to use. Granular anhydrous sodium sulfate were cleaned with solvents and stored in the sealed desiccator. A mixture of 16 PAHs standards and individual PAHs were purchased from Supelco (Sigma-Aldrich, USA).

2.4 Sample Extraction

The soil samples were extracted following EPA Method 3550C-ultrasonic extraction. In brief, 20 g portion of soil was extracted with 50 ml mixture of acetone-hexane (1:1 v/v) for 30 min in ultrasonic bath. After Sonication the sample was 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 1-2 ml under reduced pressure in a 40 $^{\circ}$ C water bath using a rotary evaporator (Eyela, Tokyo, Japan).

2.5 Chromatographic Column Clean-up

The concentrated extracts and two 2-ml portions of n-hexane from rinsing the sample flask were transferred to top of a chromatography column (30 cm \times 10 mm i.d.) packed with 10 g activated silica gel (100–200 mesh) and 1 cm layer of sodium sulphate to separate the PAHs fraction from other interfering matters. The silica gel was loaded in n -hexane and capped with a thin layer of absorbent cotton (extracted with DCM as samples) to prevent the gel from spilling, and approximately 2 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 DCM to produce fractions enriched in aliphatic hydrocarbons and PAHs at the flow rate of ~2 ml min⁻¹. The elute of the PAHs fraction was concentrated to near 1 ml and solvent exchanged to acetonitrile. Then the sample was transferred to 2.0 ml vial for HPLC analysis.

2.6 Quantification of PAH in sample extracts

Sixteen priority PAHs were selected and they are abbreviated as naphthalene (Npt), acenapthylene (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). The analytical methods were based on EPA Method 8310. Briefly, PAHs were quantitatively analysed by HPLC system (Agilent 1100 Series) equipped with UV Diode Array Detector (DAD, λ =254 nm), quaternary pump and degasser. Extract injection 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) was used as guard column. Acetonitrile and HPLC grade water was used as mobile phase with gradient mode as below:

Time	Acetonitrile	Water	Flow
	(%)	(%)	(ml min^{-1})
0.00	60	40	1.0
15.00	65	35	1.0
20.00	85	15	1.2
25.00	95	5	1.2

30.00	100	0	1.2
40.00	100	0	1.2
42.00	60	40	1.0

	No of	RT	Recovery	DL
Compound	Ring	(min.)	(%)	(µg kg ⁻¹)
Naphthalene (Npt)	2	8.189	81	0.15
Acenaphthylene (ANy)	3	9.485	55	0.32
Acenaphthene (ANe)	3	11.980	79	0.20
Fluorene (Fle)	3	12.584	82	0.32
Phenanthrene (Phe)	3	14.865	86	0.19
Anthracene (Ant)	3	17.525	90	0.18
Fluoranthene (Flt)	4	19.742	89	0.32
Pyrene (Pyr)	4	21.100	80	0.16
Benzo(a)Anthracene (BaA)	4	24.389	88	0.40
Chrysene (Chr)	4	25.266	81	0.16
Benzo(b)Fluoranthene (BbF)	5	27.743	86	0.33
Benzo(k)Fluoranthene (BKF)	5	29.133	94	0.29
Benzo(a)Pyrene (BaP)	5	30.581	92	0.89
Benzo(g,h,i)Perylene (Bpe)	6	32.484	95	0.40
Dibenzo(a,h)Anthracene (DBA)	5	34.087	85	0.35
Indeno(1,2,3-Cd)Pyrene (Ipy)	6	35.241	87	0.18

Table 1: Retention times, recovery and detection limits for 16 PAHs

2.7 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 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 quality control (QA/QC) analysis was performed, including analysis of procedural blanks (analyte concentrations were <MDL 'method detection limit'), random duplicate samples (Standard deviation <10), calibration curves with the r^2 value of 0.999. Each sample was analyzed in duplicate and the average was used in calculations. The limit of detection (LOD) was calculated by multiplying standard deviation of each PAH congener by Student's *t* value (at 99% confidence level). The detection limits were in range of 0.15-0.89 µg kg⁻¹).

Recovery study was undertaken by analysis of fortified sample. Separate replicates of sample were spiked with known standard solutions of PAHs, then extracted and analyzed in the same way as the real samples. The percent recoveries were in range of 79% - 94% except for acenapthylene for which a value of 55% was obtained. The mean retention times, recoveries and detection limits for 16 PAHs achieved in this study are shown in Table 1.

3. Results and Discussions

3.1 Distribution of PAHs

The concentrations of 16 individual PAHs, sum of 16 PAHs (\sum 16PAHs) and seven carcinogenic PAHs (\sum 7c-PAHs) in soil samples from different locations in Delhi, India are shown in Table 2 and Table 3. The concentrations of \sum PAHs, categorized as priority pollutants by US EPA, were in range of 81.9-45017.4 µg kg⁻¹, with a mean of 6838.6 µg kg⁻¹. Earlier studies reported lower concentration of PAHs in soils of Delhi (4694±3028 µg kg⁻¹; Agarwal, 2009; 4430 µg kg⁻¹ Roy *et al.*, 2008). However, higher concentrations have been reported for other Indian cities. The observed levels in roadside soils were lower than Agra, India (12980 µg kg⁻¹; Masih and Taneja, 2006) and Jalandhar, India (16380 µg kg⁻¹; Kumar and Kothiyal, 2011). In this study the higher concentrations of \sum PAHs (>10,000 µg kg⁻¹) were detected in soil samples at DS13 and DS14 (Figure 2). These locations were located near the vicinity of industrial estates.



Figure 2: SPAHs concentrations in roadside soil at different locations in Delhi

	Ra	nge	Mean	Std Err	% of
PAHs	min	max	_	(±)	∑PAHs
Naphthalene			< 0.15		
Acenaphthylene			< 0.32		
Acenaphthene	267.1	504.8	386.0	44.9	0.8
Fluorene	585.0	772.5	678.8	35.4	1.4
Phenanthrene	51.1	1099.3	283.0	93.8	4.1
Anthracene	41.1	231.6	98.4	21.7	0.5
Fluoranthene	187.9	5166.3	1110.0	389.8	13.9
Pyrene	170.5	3216.7	938.4	303.2	11.8
Benzo(a)Anthracene*	60.2	3700.0	625.2	296.9	7.8

Table 2: Concentration of PAHs in roadside soils from Delhi (µg kg⁻¹)

Chrysene *	47.6	6466.0	1036.3	553.7	13.0
Benzo(b)Fluoranthene*	52.5	3824.2	646.9	314.0	7.4
Benzo(k)Fluoranthene*	117.0	8761.2	2598.4	925.7	16.3
Benzo(a)Pyrene *	107.7	5547.2	1657.8	650.7	10.4
Benzo(g,h,i)Perylene			< 0.40		
Dibenzo(a,h)Anthracene*	399.7	9145.2	2711.5	1147.8	11.3
Indeno(1,2,3-Cd)Pyrene*	107.4	1031.5	569.5	174.7	1.2
∑PAHs	81.9	45017.4	6838.6	3528.4	100
∑7c-PAHs*	<2.6	34514.8	4612.5	2723.8	67.4
LMW-PAHs	81.6	2479.9	470.3	190.0	6.9
HMW-PAHs	<3.5	42537.5	6368.3	3340.8	93.1

Std Err=SD/ \sqrt{n} , \sum PAHs=Sum of EPA's 16 PAHs, \sum^{T_c} -PAHs=Sum of 7 possible carcinogenic PAHs, LMW-PAHs= \sum of 2-3 ring PAHs, HMW-PAHs= \sum of >4 ring PAHs

The lower concentrations (<500 µg kg⁻¹) were observed in soil samples at DS2, DS6, DS7, DS8, DS11 and DS12 (Table 3). DS5 location was least contaminated with PAHs, where only Phenanthrene was present with the concentration of 43.5 µg kg⁻¹. The concentration of \sum 7c-PAHs accounted for 67.4% of \sum PAHs in soils from Delhi. Moreover, BaP, one of the most potent carcinogenic PAHs varied from 107.7 to 5547.2 µg kg⁻¹ with a mean of 1657.8 µg kg⁻¹. Concentration of BaP in Delhi urban soil was higher than those in urban soil of Beijing, China (5-270 µg kg⁻¹; Ma *et al.*, 2005) but, lower than roadside soils of Shanghai, China (7050 µg kg⁻¹; Jiang *et al.*, 2009).

The obtained data for PAHs concentrations in soil samples compared with data from literature and found remarkably varied. The concentration of \sum PAHs in this study was lower than those in soil from USA (58680 µg kg⁻¹, Rogge *et al.*, 1993), Tilahuac and Milpa Alta, Maxico (9130-11220 µg kg⁻¹, and 11430-35770 µg kg⁻¹, Rutilio *et al.*, 2011). But PAHs concentration level in Delhi urban soil was higher than those in urban soil of Tokushima, Japan (611 µg kg⁻¹, Yang *et al.*, 2002), Hong Kong, China (21-554 µg kg⁻¹, Chung *et al.*, 2007), Kota Bharu, Malaysia (1450 µg kg⁻¹, Fadzil *et al.*, 2008), Sanghai, China (3780 µg kg⁻¹, Jiang *et al.*, 2009), Valasske, Czeck Republic (860-10840 µg kg⁻¹, Placha *et al.*, 2009), Miami, Florida (1869 µg kg⁻¹, Banger *et al.*, 2010).

3.2 Source Identification by Diagnostic Ratios of PAHs

It is essential to identify the origin and potential sources of PAHs in the environment to assess the environmental risk. The anthropogenic release of PAHs can be attributed to petrogenic and pyrogenic origins. The PAHs of petrogenic (petroleum derived residues) origins are characterized by the predominance of 2- and 3-ring or low molecular weight, while PAHs from pyrogenic (combustion derived) origins are characterized with high proportion 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 (Mastral and Callen, 2000); this gives different ratio of LMW_{PAHs} to HMW_{PAHs} in soil depending upon the sources. The soil in Delhi contained a considerable amount of high molecular weight PAHs (81-96%) (Table 3) and low LMW_{PAHs} to HMW_{PAHs} ratio (<1.0) which indicated the major input of PAHs are from vehicle emissions (Figure 3).



Figure 3: Ratio of LMW and HMW PAHs in roadside soil at different locations in Delhi

Further, diagnostic ratios of selected PAH concentrations are the most widely used technique to identify and characterize the sources (Yunker *et al.*, 2002; Pies *et al.*, 2008). In order to identify sources of PAHs in Delhi soil, the isomer ratio of Ant/(Ant+Phe), Flt/(Flt+Pyr), BaA/(BaA+Chr), Flt/Pyr and BaP/(BaP+Chr) were used to distinguish between petrogenic and pyrogenic sources (Table 4).

The concentrations of specific PAH compounds, or a group of PAHs, have been used to indicate towards 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 (Duval and Friedlander, 1981; Khalili *et al.*, 1995). These markers indicate some degree of similarity and overlap between the profiles from different source categories.

	ID	Ra	ange	- Mean	Std			
Location	ID	min	max	Mean	Err	LMW (%)	HMW (%)	
IP Extension	DS1	51.1	1206.9	386.6	138.3	282.7 (18.3)	1263.6 (81.7)	
Gokulpuri	DS2	86.6	449.3	209.7	40.0	162.9 (12.9)	1095.1 (87.1)	
Chilla	DS3	41.1	2283.4	851.0	182.5	273.7 (4.0)	6534.2 (96.0)	
Bhajanpura	DS4	53.4	639.1	226.0	45.5	388.4 (19.1)	1645.3 (80.9)	
Rohini-I	DS5	<4.8	81.9	43.5	5.0	81.9 (100.0)	<3.5	
Rohini-II	DS6	70.3	404.0	213.3	37.7	92.3 (6.2)	1400.8 (93.8)	
Mayur Vihar Ph-I	DS7	45.2	399.7	159.8	27.8	122.7 (8.5)	1315.3 (91.5)	
Mayur Vihar Ph-II	DS8	47.6	187.9	109.5	14.9	116.1 (17.7)	540.8 (82.3)	
Mayur Vihar Ph-III	DS9	60.2	1070.6	342.7	80.4	486.3 (17.7)	2255.1 (82.3)	
Nand Nagri	DS10	62.1	634.0	238.1	50.6	190.9 (11.5)	1475.5 (88.5)	
Bhalswa	DS11	63.0	372.4	198.1	32.8	139.1 (11.7)	1049.3 (88.3)	
Jahangirpuri	DS12	82.8	417.0	196.9	32.5	82.8 (7.0)	1098.4 (93.0)	
Badli	DS13	120.7	9145.2	3462.9	755.0	2479.9 (5.5)	42537.5 (94.5)	
Gazipur	DS14	585.0	6466.0	2863.0	476.4	1684.3 (5.9)	26945.3 (94.1)	

Table 3: Concentration of PAHs (µg kg⁻¹ dw) in roadside soils from different locations in Delhi

Std Err=SD/ \sqrt{n} , LMW-PAHs= \sum of 2-3 ring PAHs, HMW-PAHs= \sum of >4 ring PAHs

The value of Ant/(Ant+Phe) (<0.1) and Flt/(Flt+Pyr) (<0.4) ratio has been used for petrogenic sources and value of >0.1 and \geq 0.4-0.5, respectively used for pyrogenic sources (Hwang *et al.*, 2003). The higher ratio (>0.5) of Flt/(Flt+Pyr) has been used for grass, wood and coal combustion sources (Fadzil *et al.*, 2008). The ratio of BaA/(BaA+Chr) <0.2 indicates petrogenic, 0.2-0.35 implies petroleum combustion, and >0.35 value shows grass, wood and coal combustion (Yunker *et al.*, 2002; Hwang *et al.*, 2003). Lee *et al.* (1982) reported Flt/Pyr ratio for diesel and gasoline (<1.0) and wood and coal combustion (1.0-1.4). Khalili *et al.*, (1995) and Guo *et al.*, (2003) indicated that the ratio of BaP/(BaP+Chr) was 0.49 and 0.73 for gasoline and diesel engines, respectively, while 0.07-0.24 value (Chen *et al.*, 2005) indicative of grass, wood and coal combustion (Table 4).

The PAHs ratio values in our study indicate that mixed pyrogenic activities such as petroleum, biomass and coal combustion (Table 4) are the main sources of PAHs to Delhi soils. This contamination will be an ongoing issue 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.

PAHs ratios	Value of ratios and indicative of		Reference	Present study	
Ant/(Ant+Phe)	< 0.1	petrogenic	Hwang <i>et al.</i> , 2003	0.11	
	>0.1	pyrogenic	-		
	< 0.4	petrogenic	Hwang et al., 2003		
Flt/(Flt+Pyr)	≥0.4-0.5	pyrogenic	Hwang et al., 2003	0.54	
	>0.5	biomass, coal comb.	Fadzil et al., 2008		
	< 0.2	petrogenic	Yunker et al., 2002		
BaA/(BaA+Chr)	0.2-0.35	Petroleum comb.	oleum comb.		
	>0.35	biomass, coal comb.	Hwang <i>et al.</i> , 2003		
Elt/Dur	<1.0	gasoline, diesel	Loo et al. 1082	1 27	
Flt/Pyr	1.0-1.4	biomass, coal comb.	Lee <i>et al.</i> , 1982	1.37	
	0.49	gasoline	Khalili et al., 1995		
BaP/(BaP+Chr)	0.73	diesel	Khalili et al., 1995	0.23	
	0.07-0.24	biomass, coal comb.	Chen et al., 2005		

Table 4: Diagnostic ratios of indi	vidual PAH concentration	for source diagnosis
------------------------------------	--------------------------	----------------------

3.3 Ecotoxicological Risk Assessments of PAHs

Effects on the organisms are usually considered to be an early warning indicator of potential human health impacts. In India, no environmental standards have been established for PAHs in soil and sediments. Therefore, ecotoxicological effects of these pollutants in this study area were roughly evaluated by applying published guidelines from National Oceanography and Atmospheric Administration (NOAA) (NOAA, 1999) and from Canada (CCME, 2002).

PAHs	Soil	guidelines*	Present
РАП	NOAA	CCME	study
Naphthalene (Npt)	5000	$600-22x10^3$	<0.15
Acenaphthylene (ANy)	-	-	<0.32
Acenaphthene (ANe)	-	-	386
Fluorene (Fle)	-	-	679
Phenanthrene (Phe)	5000	$5 \text{x}10^3 \text{-} 50 \text{x}10^3$	283
Anthracene (Ant)	-	-	98
Fluoranthene (Flt)	-	-	1110
Pyrene (Pyr)	$10 \text{ x} 10^3$	$10x10^3 - 100x10^3$	938
Benzo(a)anthracene (BaA)*	1000	-	625
Chrysene (Chr)*	-	$1000-10 \text{ x} 10^3$	1036
Benzo(b)fluoranthene (BbF)*	1000	$1000-10 \text{ x}10^3$	647
Benzo(k)fluoranthene (BkF)*	1000	$1000-10 \text{ x}10^3$	2598
Benzo(a)pyrene (BaP)*	1000	700	1658
Benzo(ghi)perylene (Bpe)	-	-	<0.40
Dibenzo(a,h) anthracene (DBA)*	1000	$1000-10 \text{ x}10^3$	2712
Indene(1,2,3-cd)pyrene (Ipy)*	1000	$1000-10 \text{ x}10^3$	570

Table 5: Guidelines for individual PAHs in soil ($\mu g kg^{-1} dw$): comparison with this study

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

Table 5 shows the recommended guideline concentration of these pollutants in soils from environmental agencies. Concentrations of individual PAHs were comparable with guideline values. Low molecular weight PAHs were lower than the guideline values and assumed no adverse effects to the biota. On the other hand, on comparing the individual PAHs concentrations with recommended guideline values, the concentrations of some high molecular weight PAHs were higher, specially Benzo(a)pyrene (BaP) was higher than guidelines proposed by NOAA and CCME.

4. Conclusions

The study shows moderate to high pollution with PAHs in soils. The concentrations of \sum PAHs were in the range of 81.6 - 45017.4 µg kg⁻¹ with a mean of 6838.6±3528.4 µg kg⁻¹. Out of 16 EPA priority PAHs, 13 PAHs were detected in surface soils of Delhi. High molecular weight PAHs accounted 93% (including 67.4% of \sum 7c-PAHs) of the total PAHs. Diagnostic ratio of individual PAHs indicates the mixed pyrogenic activities such as petroleum, biomass and coal combustion sources of PAHs. Concentrations of individual PAHs were lower than guideline values except some high molecular weight PAHs, which exceeded the guidelines at some locations.

5. Acknowledgements

The authors are grateful to Chairman and Member Secretary of Central Pollution Control Board for

providing the necessary facilities and infrastructure in National Reference Trace Organics Laboratory to conduct the present work.

References

Agarwal, T. (2009). Concentration level, pattern and toxic potential of PAHs in traffic soil of Delhi, India. *Journal of Hazardous Materials*,171 (1-3): 894-900.

Aneja, V.P., Agarwal, A., Roelle, P.A., Phillips, S.B., Tong, Q., Watkins, N., Yablonsky, R. (2001). Measurements and analysis of criteria pollutants in New Delhi, India. *Environment International*, 27: 35–42.

Baek, S., Field, R.A., and Goldstone, M.E. (1991). A review of atmospheric polycyclic aromatic hydrocarbons: Sources, fate and behaviour. *Water Air Soil Poll*, 60, 279–300.

Blumer, M. (1976). Polycyclic aromatic compounds in nature. Scientific America, 234: 34–45.

Caricchia, A.M., Chiavarini, S., Pezza, M. (1999). Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmospheric Environment*, 33: 3731–3738.

CCME (Canadian Council of Ministers of the Environment), (2002). Summary of Existing Canadian Environmental Quality Guidelines, Summary Table- Updated 2002: Winnipeg.

Chen, Y.G., Sheng, G.Y. and Bi, X.H. (2005). Emission Factors for Carbonaceous Particles and Polycyclic Aromatic Hydrocarbons from Residential Coal Combustion in China. *Environ. Sci. Technol.* 39: 1861–1867.

Chung, M.K., Hu, R., Cheung, K.C., Wong, M.H. (2007). Pollutants in Hong Kong soils: polycyclic aromatic hydrocarbons. *Chemosphere*, 67: 464–473.

Plachá, D., Raclavská, H., Matýsek, D. and Rümmeli, M. H. (2009). The polycyclic aromatic hydrocarbon concentrations in soils in the Region of Valasske Mezirici, the Czech Republic. *Geochemical Transactions*,10:12. doi:10.1186/1467-4866-10-12.

DoEF (Department of Environment & Forest), Delhi, (2010). State of Environment Report of Delhi. www.environment.delhigovt.nic.in.

Duval, M.M., Friedlander, S.K. (1981). Source resolution of polycyclic aromatic hydrocarbons in Los Angeles atmosphere. *US EPA* Report No EPA-600/2-81-161.

Fang, G.C., Wu, Y.S., Chen, M.H., Ho, T.T., Huang, S.H., Rau, J.Y. (2004). Polycyclic aromatic hydrocarbons study in Taichung, Taiwan, during 2002-2003. *Atmospheric Environment*, 38: 3385-3391.

Fadzil, M. F., Norhayati, M. T., Wan , M. K. and Wan, M. Z. (2008). Concentration and distribution of polycyclic aromatic hydrocarbons (PAHs) in the town of Kota Bharu, Kelantan Darul Naim. Malaysian J. Anal. Sci., 12 (3): 609 - 618

Gupta, P., Banerjee, D.K., Bhargava ,S.K., Kaur, R., and Shankar, R.V. (1993). Prevalence of impared lung function in rubber manufacturing factory workers exposed to benzo(a)pyrene and Respirable particulate matter. *Indoor Built Environ*, 2: 26–31.

Gustafsson, O., Haghseta, F., Chan, C., Macfarlane, J., Gschwend, P.M. (1997). Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environmental Science and Technology*, 31: 203–209.

Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., Zou, S.C. (2003). Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmospheric Environment* 37, 5307-5317.

Hites, R.A., Laflamme, R. E., Farrington, J. W. (1977). Polycyclic aromatic hydrocarbons in recent sediments. *Science*, 198: 829-831.

Hwang, H. M., Wade, T. L. & Sericano, J. L.,(2003). Concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico and United States. *At. Env*, 37, 2259-2267.

International Agency for Research on Cancer (IARC), (1983). Polynuclear Aromatic Compounds, Part 1, Chemical, Environmental and Experimental Data. In: Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, vol. 32. IARC, Lyone, France, pp. 1–447.

Jiang Yu-Feng , Wang Xue-Tong , Wang Fei , Jia Ying , Wu Ming-Hong , Sheng Guo-Ying , Fu, Jia-Mo. (2009). Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. *Chemosphere* 75: 1112–1118.

Khalili, N. R., Scheff, P. A., Holsen, T. M. (1995). PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment* 29, 533-542.

Kumar, V. and Kothiyal, N. C. (2011). Distribution behavior of polycyclic aromatic hydrocarbons in roadside soil at traffic intercepts within developing cities. *Int. J. Environ. Sci. Tech*, 8 (1): 63-72.

Lee, W.J., Wang, Y.F., Lin, T.C., Chen, Y.Y., Lin, W.C., Ku, C.C., Cheng, J.T. (1995). PAH characteristics in the ambient air of traffic-source. *Science of the Total Environment* 159, 185-200.

Ma, L.L., Chu, S.G., Wang, X.T., Cheng, H.X., Liu, X.F., Xu, X.B. (2005). Polycyclic aromatic hydrocarbons in the surface soils from outskirts of Beijing, China. *Chemosphere* 58, 1355–1363.

Masih, A., Taneja, A. (2006). Polycyclic aromatic hydrocarbons concentrations and related carcinogenic potencies in soil at a semi-arid region of India. *Chemosphere* 65, 449–456.

Mastral, A., and Callen, M.S.(2000). A review on PAH emissions from energy generation. *Environ. Sci. Technol.* 34, 3051–3057.

Mielke, H.W., Wang, G., Gonzales, C.R., Le, B., Quach, V.N., Mielke, P.W. (2001). PAH and metal mixtures in New Orleans soils and sediments. *Sci. Total Environ.* 281, 217–227.

National Oceanic and Atmospheric Administration (NOAA), (1999). NOAA screening quick reference tables (SQuiRTs), HAZMAT REPORT 99-1, and Updated Feb 2004. Coastal Protection and Restoration Division, Seattle, Washington.

Pandey, P.K., Patel, K.S., Lenicek, J. (1999). Polycyclic aromatic hydrocarbons: Need for assessment of health risks in India? -Study of an urban industrial location in India. *Environmental Monitoring and Assessment* 59, 287-319.

Park, S.S., Kim, Y.J., Kang, C.H. (2002). Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. *Atmospheric Environment* 36, 2917-2924.

Pies, C., Hoffmann, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T. (2008). Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. *Chemosphere* 72, 1594–1601.

Ravindra, K., Mittal, A.K., Van Grieken, R. (2001). Health risk assessment of urban suspended particulate matter with special reference to polycyclic aromatic hydrocarbons: A review. *Reviews on Environmental Health* 16, 169-189.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T. (1993). Sources of fine organic aerosol: 2. Non-catalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. *Environ. Sci. Technol.*, 27, 636-651.

Ray, S., Khillare, P.S., Agarwal, T., Shridhar, V. (2008). Assessment of PAHs in soil around the International Airport in Delhi, India. *J. Hazard. Mater.* 156, 9–16.

Rutilio O., Salvador V., Rey G., Richard G., Beatriz S., Marı´a de Lourdes R. (2011). Presence of Polycyclic Aromatic Hydrocarbons (PAHs) in Top Soils from Rural Terrains in Mexico City. Bull. *Environ. Cont. Toxicol.*, DOI 10.1007/s00128-011-0434-5

Szczeklik, A., Szczeklik, J., Galuszka, Z., Musial, J., Kolarzyk, E., and Targosz, D. (1994). Humoral im-mune suppression in men exposed to polycyclic aromatic hydrocarbons and related carcinogens in polluted environments. *Environ. Health Pers.* 102, 302–304.

USEPA, (1994). Peer Review and Peer Involvement at the U.S. Environmental Protection Agency, Science Policy Council, Office of the Science Advisor, Environmental Protection Agency. ID 2872. http://epa.gov/osa/spc/htm/perevmem.htm

USEPA. (2009). Information on the Toxic Effects of Various Chemicals and Groups of Chemicals. http://www.epa.gov/R5Super/ecology/html/toxprofiles.htm.

Wang, Z., Chen, J., Qiao, X., Yang, P., Tian, F. & Huang, L. (2007). Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: A case study in Dalian, China. *Chemosphere* 68. 965-971.

Wild, S.R., Jones, K.C. (1995). Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environ. Pollut.* 88, 91–108.

Wilcke, W. (2000). Polycyclic aromatic hydrocarbons (PAHs) in soil-a review. J. Plant Nut. Soil Sci. 163, 229–243.

Yang, Y., Zhang, X.X., Korenaga, T. (2002). Distribution of polynuclear aromatic hydrocarbons in the soil of Tokushima, Japan. *Water Air Soil Pollut*. 138,51–60.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S. (2002). PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33, 489–515.

This academic article was published by The International Institute for Science, Technology and Education (IISTE). The IISTE is a pioneer in the Open Access Publishing service based in the U.S. and Europe. The aim of the institute is Accelerating Global Knowledge Sharing.

More information about the publisher can be found in the IISTE's homepage: <u>http://www.iiste.org</u>

The IISTE is currently hosting more than 30 peer-reviewed academic journals and collaborating with academic institutions around the world. **Prospective authors of IISTE journals can find the submission instruction on the following page:** <u>http://www.iiste.org/Journals/</u>

The IISTE editorial team promises to the review and publish all the qualified submissions in a fast manner. All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Printed version of the journals is also available upon request of readers and authors.

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library, NewJour, Google Scholar

