Vegetative cover and PAHs accumulation in soils of urban green space

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ARTICLE INFO

Article history:

Received 4 July 2011

Received in revised form

19 September 2011

Accepted 27 September 2011

Keywords:

Polycyclic aromatic hydrocarbons

Urban soil

Land use

Vegetation

Soil organic matter

Beijing

ABSTRACT

We investigated how urban land uses influence soil accumulation of polycyclic aromatic hydrocarbons (PAHs) in the urban green spaces composed of different vegetative cover. How did soil properties, urbanization history, and population density affect the outcomes were also considered. Soils examined were obtained at 97 green spaces inside the Beijing metropolis. PAH contents of the soils were influenced most significantly by their proximity to point source of industries such as the coal combustion installations. Beyond the influence circle of industrial emissions, land use classifications had no significant effect on the extent of PAH accumulation in soils. Instead, the nature of vegetative covers affected PAH contents of the soils. Tree–shrub–herb and woodland settings trapped more airborne PAH and soils under these vegetative patterns accumulated more PAHs than those of the grassland. Urbanization history, population density and soil properties had no apparent impact on PAHs accumulations in soils of urban green space.

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1. Introduction

Green spaces are vital elements of modern cities. They enhance the quality of urban residents' life by refreshing them from mental fatigue, reducing their stress levels, and providing them open space for physical and recreational activities (Grahn and Stigsdotter, 2010; Schipperijn et al., 2010). About 70% dwellers of Beijing utilize the open green spaces at least once a week (Lo and Jim, 2010). Besides the aesthetic enhancements, urban green spaces also have ecological and environmental benefits. They produce food, harbor biodiversity, alter urban microclimate, generate oxygen, break up strong winds, reduce noise, and improve air quality (Escobedo and Nowak, 2009; Kong et al., 2010; Rafiee et al., 2009; Shan et al., 2007; Yang et al., 2005). Meanwhile, urban areas are geographical regions of intense resource inputs, energy consumptions and waste emissions. In urban settings, harmful contaminants may be inadvertently released into the atmosphere and then deposited in the soil that has a large capacity for retaining persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) (Cai et al., 2007; Wong et al., 2004).

PAHs are ubiquitous environment contaminants produced by incomplete combustion of organic substances (Agarwal, 2009; Aichner et al., 2007; Mantis et al., 2005) and some are human carcinogens prevalent in the modern cities (Szabová et al., 2008).

PAHs accumulated in urban soils may have a direct impact on public health as they are readily transferable into human body via ingestion, inhalation, and dermal contact (Jiang et al., 2009). Furthermore, they may exhibit toxic effects toward plants and soil biota (Andreoni et al., 2004). The United States Environmental Protection Agency (USEPA) identified 16 priority PAHs as targets of regulatory attention that have become focuses of environmental investigations worldwide (Hao et al., 2007; Nam et al., 2008; Wang et al., 2007; Wong et al., 2004).

Once released, the distribution and fate of PAHs in the environment are affected by factors including ambient temperature, intensity and direction of prevailing wind, precipitation pattern, vegetation, and physicochemical properties and microbial activities of soils (Diamond and Hodge, 2007; Heywood et al., 2006). PAH concentrations are substantially lower in the less populated rural than the densely populated urban areas (Jensen et al., 2007). Soils of higher PAH concentrations are found in the proximity of emission sources that are susceptible to high rates of airborne depositions (Nam et al., 2008). Therefore, the urban land uses that determine locations of emission sources, patterns of transport and deposition, and characteristics of receptors are crucial factors influencing PAHs accumulation in the soils. Moreover, PAHs are adsorbed by soil organic matter (SOM) and volatilization, degradation and leaching of adsorbed PAHs are inhibited (Yu et al., 2006). The chemical properties of PAH congeners would eventually determine the extent of its fate in the soils (Nam et al., 2008; Wang et al., 2007; Zhang et al., 2006a). In all, 90% of the PAHs in the terrestrial environment accumulate in the soils (He et al., 2009).

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Forests are effective of scavenging airborne lipophilic organic compounds and depositing them in the soils (Staci and Simonich, 1994). Trees remove gaseous air pollution via leaf stomata uptake and absorption at the cuticles (Wania and McLachlan, 2001). Meanwhile the foliar canopy will intercept airborne particulate pollutants (Nowak et al., 2006). The intercepted PAHs are directly deposited on the ground, washed off the trees by rains, and dropped along with falling leaves and twigs. The stagnant atmosphere underneath the tree canopy likely will slow down the volatilization of PAHs from soils (Cousins et al., 1999). Furthermore, once volatilized from the soil in which the vegetation is growing, PAHs may subsequently be reabsorbed by plants and start the cycling over (Collins and Finnegan, 2010). Urban tree stands may therefore play a significant role in deciding the environmental fate of PAHs, decreasing their airborne half-life and transferring the chemical from the atmosphere to the soils (McLachlan and Horstmann, 1998). The deposition fluxes of PAHs are much greater in forests than adjacent grasslands (Hassanin et al., 2003; Meijer et al., 2002).

The vegetated open spaces in urban settings were expected to modulate PAH accumulations in surface soils (Tam and Wong, 2008). Plants might take up soil borne PAHs thus reducing their contents of the soils (Gao and Zhu, 2004; Lin et al., 2007; Watts et al., 2006). More importantly, plants might attenuate the PAH contaminated soils by providing a conducive environment for growth and metabolism of soil microorganisms through releases of nutrients and enzymes and transport of oxygen to the rhizosphere (Macek et al., 2000). Although PAH could undergo photochemical degradation and chemical oxidation, microbial degradation was by far the most significant process of PAH elimination in the soil (Haritash and Kaushik, 2009).

We hypothesized that the deposition and accumulation of PAHs in soils are affected interactively by the way urban land was used, nature of vegetative covers constituted the open spaces, and characteristics of soil in reacting with PAHs. This study identified the PAHs accumulation in the primary land use categories of urban environment, described how the vegetation patterns influencing PAH contents of soils, and delineated effects of soil properties, urbanization history and population density on PAHs accumulation in urban green spaces of Beijing.

2. Material and methods

2.1. Study area

Beijing is the largest yet typical metropolis of northern China with rapid urban development, dense population, heavy pedestrian and automobile traffic, rapid industrialization, and in the winter large-scale coal-fired heating installations throughout the City. The 650 km² city proper is anchored by the Forbidden City at the center and surrounded by five concentric squares of developments and circular traffic thoroughways (i.e. the ring roads). The city is interspersed with green and open spaces characterized by woods, parks, greenbelts, school grounds, roadside trees, and grassy open fields covering 44.4% of the surface areas. The population has exceeded 16 million and growing. The intense human activities and supporting services bringing in food, water, and energy may strongly influence the ecological integrity of the metropolitan area. The PAHs are found in Beijing's air and soils (Jiao et al., 2009; Li et al., 2006; Ma et al., 2005; Tang et al., 2005; Yu et al., 2008). The emissions from automobile traffic, coal combustion for domestic heating, and industrial activities are primary sources of PAHs in Beijing (Peng et al., 2011).

2.2. Sampling description

Ninety seven sites where the soil profile had not been recently disturbed were selected for soil sampling. They spread out across the City (Fig. 1) representing the green/open spaces of different vegetation compositions and were located in neighborhoods of different land uses (Table S1). Each collected sample was the composite of five 0–10 cm depth soil cores obtained within a 10 m × 10 m area using a stainless steel hand auger. The sampling areas were at least 10 m away from the edge of the prescribed green space. After removing the vegetative debris, samples were air-dried at room temperature and then ground to pass a sieve of 2 mm openings. The finished soil samples were stored in amber color glass container at –25 °C until time for chemical analyses.

The sampling locations were divided according to eight land use categories namely industries, school grounds, residential communities, roadsides of heavy traffic and light traffic, plantations, and vacant lots and four vegetative cover classes namely greenbelt, tree–shrub–herb composite, woodland, and grassland. The selections were intended to cover all potential PAH emission and receptor sources and all vegetation compositions that might influence its distribution and accumulation in soils of Beijing proper. The locations were categorized as follows. Greenbelts, 15 locations, represented narrow green space along major thoroughfares and promenades that were well landscaped and routinely maintained. Tree–shrub–herb settings, 37 locations, were urban ornamental garden with multilayer composition consisting of trees, shrubs and herbaceous plants that organize as a parterre in residential communities, public parks, and other institutions accessible to the public. Woodlands, 27 locations, consisted of tree stands with little shrub and grass understory. Grasslands, 18 locations, were open space with ornamental lawn or nature grass covers. Industrial facilities, 7 locations, consisted of soils underneath varieties of vegetative covers at 5 just-closed large industrial complexes and two

Fig. 1. Location of sample collection sites by land use and vegetative cover.

municipal wastewater treatment plants. Roadsides were sections of roads lined with closely cropped trees and were further divided according to designation of the municipality into roads of heavy traffic, 16 locations and roads of light traffic, 11 locations. Other land use categories such as park, 13 locations; vacant lot, 6 locations; residential settings, 26 locations; plantation, 9 locations, and school, 9 locations were selected for their omnipresence throughout the cities.

2.3. PAH analysis

The soil samples in 5 g aliquot along with 5 g anhydrous sodium sulfate were extracted in an Automated Soxhlet apparatus (BUCHI B-811, Inc., Switzerland) with 120 ml 1:1 (v/v) acetone-dichloromethane solvent mixture for 2 h. The newly developed apparatus allowed soil samples be extracted in continuous solvent flow under warm or hot temperature therefore significantly reduced the time for extraction. The extracts was concentrated under a gentle nitrogen stream and then purified by passing through a solid-phase silica-gel extraction column (Supelco Inc., USA). The PAHs in the purified extract were analyzed by an Agilent 6890 gas chromatography equipped with a 5975C mass selective detector (GC-MSD). Oven temperature was programmed as follows: 50 °C held for 1 min, increased to 150 °C at 25 °C/min held for 1 min and then increased to 300 °C at 4 °C/min held for 4.5 min. The mass scan mode was selective ion monitoring (SIM).

The external standard method was used to determine the following 16 EPA priority PAHs: Naphthalene (NAP), Acenaphthylene (ACPY), Acenaphthene (ACP), Fluorene (FL), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLT), Pyrene (PYR), Chrysene (CHR), Benzo(a)anthracene (BaA), Benzo(k)fluoranthene (BkF), Benzo(b)fluoranthene (BbF), Benzo(a)pyrene (BaP), Dibenzo(a, h)anthracene (DBA), Indeno(1, 2, 3-cd)pyrene (IND), and Benzo(g, h, i)perylene (BghiP). The standard solutions of PAHs were obtained from Supelco Inc., USA. The total 16 PAH concentrations in method blanks were less than 20 ng/g. The PAH recovery ratios of matrix-spiked samples were 64% for NAP, and 86%–119% for the remaining PAHs. Replicated analyses showed a replicated percentage deviation between –20% and +20% for PAHs in soils.

2.4. SOM and pH analysis

Total organic carbon contents of soils were determined by combustion method using an elemental analyzer (Elementar, Germany). Prior to the analysis, carbonates were eliminated by treating the soil with 10% HCl and then air drying the vacuum filter recovered soil overnight. The soil organic matter (SOM) was obtained by multiplying measured organic carbon content of the soil by 1.724 (Nascimento et al., 2004). Soil pH was determined in distilled water at a soil-to-solution ratio of 1: 2.5.

2.5. Data analysis

The statistical inferences of data were determined using the analyses of variance (ANOVA) with least significant difference test, Kolmogorov–Smirnov goodness of fit test, regression analysis, and Pearson correlation analysis software packages in the SPSS (version 18.0). When applicable, the data were log-transformed into the normal distribution for statistical analyses.

3. Results and discussions

3.1. Effects of land use types on PAHs accumulation

PAHs are ubiquitous in the Beijing metropolitan area. All 16 PAHs were detected in every soil sample we collected. Based on the total mass concentration of USEAP 16 priority PAH (Σ PAHs), the soils in the vicinity of industrial establishments accumulated the highest amounts of PAHs at mean of 4768 ng/g with a standard deviation of 5548 ng/g, reflecting the significance of point source emissions and wide dispersion of PAH emissions of the sources. The relative proportion of PAH congeners in the soil followed essentially the same pattern regardless of the land use categories (Table 1). Judging the means and respective standard of deviations, the data representing each land use category exhibited considerable degree of dispersion reflecting the variability of PAH concentrations within a category. The variability was caused by the differences in time periods, vegetative covers, soil organic matter and soil microbial activities.

The PAH concentrations of soils near Gaobeidian and Weijia Water Purification Plants, two major industrial complexes, recorded Σ PAHs = 406 and 378 ng/g, respectively that were the lowest among the industrial land use category. Apparently, no substantive combustion installation was on sites. Had these two locations been excluded, the mean Σ PAHs of the industrial areas would be 3 times higher than that of school grounds (the next highest category), and more than 5–12 times higher than that in park, roadsides of heavy traffic, residential area, plantation, wasteland, roadsides of light traffic and vacant lots ($p < 0.05$). The soils at two industrial locations associating with coal combustions recorded the highest Σ PAHs concentrations in Beijing, 13 141 ng/g for Beijing Coking Plant and 11 650 ng/g for Beijing Carbonization Plant. The coal combustion processes though relocated left lasting legacies inside the city and contributed heavily to the accumulation of PAHs in soils of the surrounding green spaces. For future development of land parcels, the PAH tainted soils would have to be remediated.

The automobile exhausts were also significant sources of PAHs in Beijing (Li et al., 2006; Tang et al., 2005). Consequently, the PAH concentrations of soils at roadsides of heavy traffic were significant higher than those at roadsides of light traffic ($p < 0.05$). The automobile exhausts were emitted close to the ground and the road

Table 1
Mean and standard deviation of PAH concentrations in urban soils of Beijing.

	PAH concentration of soil according to land use (ng/g, mean $\pm$ S.D.)							
	Industrial	School	Park	Roadside (heavy traffic)	Residential	Plantation	Roadside (light traffic)	Vacant lots
NAP	54 $\pm$ 48	20 $\pm$ 11	28 $\pm$ 43	24 $\pm$ 17	21 $\pm$ 12	14 $\pm$ 8	10 $\pm$ 7	8 $\pm$ 2
ACPY	51 $\pm$ 69	17 $\pm$ 17	15 $\pm$ 25	12 $\pm$ 7	9 $\pm$ 8	7 $\pm$ 5	8 $\pm$ 6	5 $\pm$ 3
ACP	48 $\pm$ 65	7 $\pm$ 8	6 $\pm$ 8	4 $\pm$ 3	3 $\pm$ 4	3 $\pm$ 1	2 $\pm$ 1	2 $\pm$ 1
FL	52 $\pm$ 63	16 $\pm$ 12	12 $\pm$ 9	12 $\pm$ 7	12 $\pm$ 12	8 $\pm$ 2	8 $\pm$ 3	8 $\pm$ 3
PHE	404 $\pm$ 447	156 $\pm$ 154	110 $\pm$ 128	93 $\pm$ 65	91 $\pm$ 101	61 $\pm$ 23	50 $\pm$ 29	54 $\pm$ 33
ANT	142 $\pm$ 199	31 $\pm$ 37	23 $\pm$ 36	19 $\pm$ 18	14 $\pm$ 13	10 $\pm$ 5	11 $\pm$ 7	11 $\pm$ 9
FLT	634 $\pm$ 758	260 $\pm$ 307	167 $\pm$ 232	124 $\pm$ 112	105 $\pm$ 108	85 $\pm$ 53	64 $\pm$ 42	71 $\pm$ 45
PYR	515 $\pm$ 625	204 $\pm$ 238	132 $\pm$ 185	99 $\pm$ 85	80 $\pm$ 78	66 $\pm$ 43	51 $\pm$ 35	56 $\pm$ 35
BaA	349 $\pm$ 411	138 $\pm$ 164	85 $\pm$ 135	65 $\pm$ 53	51 $\pm$ 49	42 $\pm$ 31	35 $\pm$ 26	35 $\pm$ 20
CHR	443 $\pm$ 511	174 $\pm$ 185	116 $\pm$ 160	91 $\pm$ 62	74 $\pm$ 62	64 $\pm$ 41	49 $\pm$ 30	45 $\pm$ 20
BbF	461 $\pm$ 516	212 $\pm$ 229	133 $\pm$ 191	107 $\pm$ 72	83 $\pm$ 70	74 $\pm$ 55	57 $\pm$ 36	51 $\pm$ 20
BkF	452 $\pm$ 508	195 $\pm$ 215	127 $\pm$ 187	100 $\pm$ 69	77 $\pm$ 64	72 $\pm$ 53	54 $\pm$ 34	49 $\pm$ 19
BaP	376 $\pm$ 447	173 $\pm$ 207	100 $\pm$ 154	80 $\pm$ 67	58 $\pm$ 58	49 $\pm$ 40	40 $\pm$ 28	39 $\pm$ 20
IND	341 $\pm$ 395	177 $\pm$ 214	102 $\pm$ 157	85 $\pm$ 59	58 $\pm$ 54	50 $\pm$ 38	41 $\pm$ 27	38 $\pm$ 17
DBA	92 $\pm$ 110	37 $\pm$ 46	23 $\pm$ 40	17 $\pm$ 13	12 $\pm$ 10	11 $\pm$ 9	9 $\pm$ 6	8 $\pm$ 3
BghiP	347 $\pm$ 405	164 $\pm$ 199	100 $\pm$ 160	85 $\pm$ 57	56 $\pm$ 50	50 $\pm$ 37	41 $\pm$ 28	37 $\pm$ 15
LMW PAHs	753 $\pm$ 878	250 $\pm$ 227	196 $\pm$ 247	166 $\pm$ 102	153 $\pm$ 146	105 $\pm$ 43	91 $\pm$ 51	90 $\pm$ 51
HMW PAHs	4014 $\pm$ 4678	1738 $\pm$ 1996	1089 $\pm$ 1603	860 $\pm$ 634	657 $\pm$ 605	568 $\pm$ 401	446 $\pm$ 293	432 $\pm$ 214
Σ PAHs	4768 $\pm$ 5548	1989 $\pm$ 2217	1285 $\pm$ 1848	1026 $\pm$ 726	811 $\pm$ 748	673 $\pm$ 442	538 $\pm$ 340	523 $\pm$ 259

lined with greenbelt formed a barrier that prevented much of the fugitive pollutants such as PAHs from spreading. The mobile source PAHs emitted by moving motor vehicles nevertheless was diffused and tended to be deposited along direction of the traffic. Meanwhile, the stationary source PAHs emissions of the industrial establishments were more concentrated and tended to be deposited near the vicinity of emission sources following the direction of prevailing wind. The patterns were reflected in the distinctively different soil PAH concentrations of these two land use categories. The soils at school grounds also exhibited high PAH concentrations that might be due to the long history of burning coal for onsite space heating during winter months. The plantations and vacant lots were found in the less populated and more remote outskirt locations that were outside of the 4th ring road far away from point emission sources and heavily traveled roads thus exhibited the lowest soil PAH concentrations. However, the outcomes of ANOVA test showed that PAH concentrations of soils in Beijing were not significantly different between the land use categories if the industrial land use category was excluded. It appeared that the variance caused by the point source emissions at industrial complexes was more significant than the variances associated with other factors of land use classifications such as mobile source, population density and the distance to urban center.

PAH emitted from different emission sources would have different congener compositions. In a large metropolis such as Beijing, PAH emission sources were numerous and diverse. There were point sources and diffused non-point sources and there were stationary sources and mobile sources. They scattered throughout the city. Hypothetically, the compositions of PAH congeners in receiving soils would change according to PAH emitted from sources of land use categories. However, the relative contributions of PAH congeners toward the Σ PAHs of the eight land use categories were essential the same (Fig. S1) when the congener distributions were tested according to Kolmogorov–Smirnov goodness of fit. The outcomes of Pearson correlation matrix (Table 2) showed that the concentrations of PAH congeners in soils were significant correlated ($p < 0.01$) indicating PAH deposited in soils of different land use categories encountered comparable environmental fate and transport processes. The low molecular weight PAHs were more volatile and had considerably higher Henry's Law constant and shorter degradation half-life. Once emitted, they would less likely be adsorbed by airborne particulates. The molecules in gaseous forms would be susceptible to rapid photolysis. The high molecular weight PAHs were associated with airborne particulates and were prone to deposition according to particle sizes. Consequently, the larger PAH containing particles deposited and accumulated in soils close to the emission source (Nam et al., 2008; Wang et al., 2007) and smaller PAH containing particles would be airborne and suspended for longer period of time. The fact that the relative compositions of PAH congeners of soils were comparable across the land use categories appeared to indicate that this class of suspended PAH containing particulates from different sources were intermingle throughout the air-shed. In this manner, the PAH profiles influenced by the industrial emissions were compensated by the emissions from other sources such as home heating and domestic cooking. The PAH compositions of soils in Beijing were thus equalized through degradation of low molecular weights PAHs upon emission coupled with the mixing and transport of PAH containing particulates prior to the deposition.

3.2. Effects of vegetative covers

The USEPA 16 priority PAHs concentrations of soils under the vegetative covers of tree–shrub–herb, greenbelt, woodland, and grassland were 1782, 1117, 1101, and 455 ng/g, respectively (Fig. 2).

Table 2
Correlations between population density, pH and PAH congeners.

	Population density ^a	pH	NAP	ACPY	ACP	FL	PHE	ANT	FLT	PYR	BaA	CHR	BbF	BkF	BaP	IND	DBA	BghiP
NAP	0.135	-0.047	1															
ACPY	-0.072	-0.052	0.765**	1														
ACP	-0.125	0.027	0.649**	0.917**	1													
FL	-0.043	0.017	0.634**	0.926**	0.940**	1												
PHE	-0.031	-0.012	0.693**	0.942**	0.924**	0.968**	1											
ANT	-0.111	0.015	0.638**	0.956**	0.959**	0.971**	0.948**	1										
FLT	-0.082	-0.021	0.645**	0.945**	0.908**	0.938**	0.980**	0.955**	1									
PYR	-0.085	-0.018	0.643**	0.948**	0.914**	0.941**	0.976**	0.963**	0.994**	1								
BaA	-0.101	-0.018	0.671**	0.949**	0.918**	0.919**	0.969**	0.948**	0.996**	0.994**	1							
CHR	-0.079	-0.027	0.675**	0.954**	0.920**	0.935**	0.974**	0.959**	0.995**	0.996**	0.996**	1						
BbF	-0.07	-0.034	0.700**	0.948**	0.900**	0.904**	0.966**	0.929**	0.988**	0.986**	0.996**	0.993**	1					
BkF	-0.08	-0.037	0.698**	0.950**	0.907**	0.907**	0.967**	0.935**	0.989**	0.988**	0.997**	0.994**	0.999**	1				
BaP	-0.079	-0.021	0.683**	0.942**	0.900**	0.901**	0.959**	0.928**	0.984**	0.983**	0.994**	0.988**	0.997**	0.996**	1			
IND	-0.062	-0.024	0.703**	0.936**	0.871**	0.878**	0.948**	0.906**	0.974**	0.972**	0.984**	0.978**	0.994**	0.991**	0.996**	1		
DBA	-0.097	-0.02	0.718**	0.956**	0.914**	0.899**	0.955**	0.937**	0.979**	0.979**	0.993**	0.987**	0.995**	0.995**	0.995**	0.992**	1	
BghiP	-0.07	-0.029	0.713**	0.946**	0.892**	0.890**	0.957**	0.921**	0.979**	0.978**	0.990**	0.984**	0.996**	0.995**	0.996**	0.998**	0.996**	1

**Correlation is significant at the 0.01 level (2-tailed).

^a The data of population density on street scale were obtained from Beijing 2000 population census data (BMBS, 2002).

Fig. 2. Mean and standard deviation of PAH concentrations in soils having different vegetative covers, A: All relevant data (97 observations); B: Excluding data representing industrial areas (90 observations).

The PAHs accumulations of the tree–shrub–herb and woodland settings were respectively 3 and 2 times higher than that in grassland ($p < 0.05$). When the green space was in the proximity of a strong emission source such as an industrial complex, effects of vegetative covers were shadowed by the heavy depositions. Meanwhile, the land uses in terms of PAH accumulation in the soils could be divided into two categories based on results of ANOVA, namely industrial area and other land uses. When the data representing locations subjected to direct influences of industrial emissions were excluded, the soil PAH concentrations of the tree–shrub–herb, roadside, and woodland vegetative classes became comparable (Fig. 2B) and were two times higher than that of the grassland ($p < 0.05$). The grassland type of open space in urban area on the other hand has a low vertical profile to capture PAHs suspended in the air stream and would rely entirely on direct deposition for PAHs to accumulate in the soils. Besides, a significant part of the grassland is lawns that are mowed and whose clippings are removed regularly. They were the urban green spaces least impacted by the PAHs.

The forests were more efficient than grassland or non-vegetated in capturing PAH particulates suspended in the atmosphere. Larger canopy and diversified species composition would enhance interception of airborne pollutants (Jim and Chen, 2008; Yang et al., 2005). For example, the tree–shrub–herb and woodland settings had multiple layers of vegetation including understory and groundcover plants that were effective in trapping airborne PAHs. Consequently, soil PAHs accumulations in tree–shrub–herb and woodland settings were not significantly different.

The urban vegetation captured the airborne pollutants and helped to improve the urban air quality (Jim and Chen, 2008; Nowak et al., 2006) yet soils of the urban green spaces would accumulate PAHs. The high PAH concentrations in urban soils might inevitably expose residents to potential carcinogens and subject soil ecosystems to potentially harmful substances.

3.3. Effects of urbanization history and population density

Urbanization history, length of time the location had been urbanized, and population density would influence might influence the pollutants concentrations of urban soils (Chen et al., 2005; Liu et al., 2008; Xia et al., 2011). Beijing in the past several decades had expanded from the ancient inner city outward through sustained urban renewal and development. We divided urban Beijing into

four parts according to the progression of urban development as represented by the concentric ring roads and organized the data accordingly. The PAH concentration of soils in these four progressively newer urban sectors bordered by the ring roads were not significantly different, $p > 0.05$ (Fig. 3). It appeared that soil PAH contents of the inner city were primarily due to legacies of long human inhabitation yet soil PAH contents of the new development were influenced by a new sets of emission sources such as automobile traffics and industrial production activities. In concentric form, the surface areas of outer city are considerably larger than those of the inner city. As a result, the new developments in Beijing accumulated far greater amounts of PAH in the soils.

Earlier reports had noted that PAH concentrations of urban soils differed according to population density of the cities (Hafner et al., 2005; Liu et al., 2008; Wang et al., 2011b; Zhang et al., 2006b). The population density in these cases denoted in essence characteristics of between cities and did not account for distribution of populations within the city. When the samples we collected were cataloged according to the population density of their respective sampling locations, it distinguished the population density within a city and showed that it did not significantly affect the PAH concentration of the soils (Table 2). Clearly, residential communities were not significant contributors of PAH emissions in Beijing. Natural gas has replaced coal as the primary fuel for domestic energy needs (Wang et al., 2011a; Xu et al., 2005). The improvements in combustion efficiency significant reduced amounts of PAH emitted from the domestic sources (Ravindra et al., 2008). The intensity and duration of PAH emissions due to community wide home heating installations were lower than that of the industrial combustion installations. Space heating needs were seasonal and heat generating facilities spread throughout the city. As emissions, their behavior mimicked those of non-point sources and acted merely to enhance the background levels.

3.4. Effects of soil properties

The organic matter contents of the soils in Beijing varied from 0.42% to 5.96% with a mean of 2.36%. The linear regression between amounts of PAHs accumulated in and the organic matter contents of soils was significant at $p < 0.01$ (Fig. 4A). According to the determination coefficient of regression equation, however, the soil organic matter accounted for less than 10% of the observed variations in soil PAHs. Eleven data points were above the horizontal line of $\Sigma\text{PAHs} = 2000 \mu\text{g/kg}$ and deviated from the remainder data

Fig. 3. Mean and standard deviation of PAH concentrations in the areas separated by the concentric ring roads of Beijing.

Fig. 4. Linear regression of SOM and total PAH content of soils (A) with all sampling data (97 observations), (B) with outliers of total PAH > 2000 ng/g excluded (86 observations).

points that were much closely cropped (Fig. 4A). Their concentrations apparently influenced by factors other than the adsorptive characteristics of SOM. The outliers including three industrial sites, one roadside (heavy traffic), two parks, and wooded areas at one residential and four school sites. Fig. 4B showed the linear regression between PAHs and SOM of the soils when the outliers were excluded. The determination coefficient increased slightly from 9.4% to 14.6%. The soil organic matter content though significantly related to soil PAHs was not the primary factor in determining PAH accumulation in urban soils.

The pH value of the soil ranged from 7.19 to 8.31, with a mean of 7.88. The Pearson correlation analysis showed there were no significant correlation between the soil pH and the PAH concentrations in soils (Table 2). Being non-polar organic compounds, the PAHs' mobility and accumulation in soils were not affected by the soil pH that ranged from 7.19 to 8.31.

4. Conclusions

In all, emissions of fuel combustions in industrial complexes were by far the most significant factor in determining PAH accumulation in the soils of urban green spaces in metropolitan Beijing. Once outside of the area of immediately influenced by industrial emissions, the land use categories, nature of emission sources,

population density, and length of time it had been urbanized had little effect of amount of PAHs in soils. Instead the vegetative cover was a significant factor. The tree–shrub–herb and woodland settings captured and accumulated more fugitive PAHs than that of the grassland setting in which the lawns were mowed and clippings were collected and removed regularly. The soil organic matter content though significantly related to soil PAHs was not the deciding factor on PAH accumulation in urban soils.

Acknowledgments

We gratefully acknowledged financial supports provided by the National Natural Science Foundation of China (Grant No. 41030744), the Technical Supporting Programs of China (Grant No. 2007BAC28B01) and the Special Foundation of State Key Lab of Urban and Regional Ecology.

Appendix. Supplementary material

Supplementary material associated with this article can be found, in the online version, at www.sciencedirect.com, doi:10.1016/j.envpol.2011.09.027.

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