Environ Monit Assess (2008) 147:317–326
DOI 10.1007/s10661-007-0123-3

Distributions, sources and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in topsoil at Ji'nan city, China

Jiulan Dai · Shujing Li · Yongli Zhang · Renqing Wang · Yue Yu

Received: 29 May 2007 / Accepted: 19 December 2007 / Published online: 26 January 2008

Abstract Surface soil (0–5 cm) samples from 17 sampling sites including different functional areas at Ji'nan city in Shandong Province of China were collected and analyzed for 16 EPA priority polycyclic aromatic hydrocarbons (PAHs). The total PAH concentrations were in the range from 1.31 mg kg^{-1} to 254.08 mg kg^{-1} (dry weight), and the average level of total PAHs was 23.25 mg kg^{-1}. The highest total PAHs concentrations were found in steel and iron plant at industrial areas. The total PAHs concentrations in industrial areas were markedly higher than those in other different functional areas. According to comparing total PAHs concentration in Ji'nan city to that of other urban areas, it was found that total PAHs concentrations were 6 to 137 times higher than other areas because of some specific sampling sites such as steel and iron plant and one main roadside. The results showed that PAHs in topsoil of Ji'nan city were suffered from strong pyrogenic influence, especially in industrial areas. However about 52.9% soil samples were mainly originated from both pyrogenic and petrogenic mixed sources based on Flu/Pyr ratios and Phe/Ant ratios. Furthermore, It was found that all individual PAHs except Fle were significantly correlated ($P<0.01$) with LMW, HMW, total PAHs and SOM, and individual PAHs except Fle in soils were significantly correlated ($P<0.01$) with each other. The nemerow composite index to assess the environmental quality showed that the soil sample of steel and iron plant in industrial areas and one main roadside were heavy pollution of PAHs, and about 47% soil sampling sites were safety, about 53% soil sampling sites were got different grades of PAHs pollution.

Keywords PAHs · Urban topsoil · Distribution · Risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of stable chemical compounds including two or more rings, are ubiquitous organic contaminants in environments and belong to a class of POPs, and 16 of them have been identified as priority pollutants by the US Environmental Protection Agency (US EPA) and European Union (EU). Six individual PAHs including

J. Dai · S. Li · Y. Zhang · R. Wang (✉)
Environment Research Institute, Shandong University,
Ji'nan 250100, China
e-mail: wrq@sdu.edu.cn

J. Dai · Y. Zhang · R. Wang · Y. Yu
College of Life Science, Shandong University,
Ji'nan 250100, China

S. Li
College of Environmental Science and Engineering,
Nankai University,
Tianjin 300071, China

benzo(a)pyrene, fluoranthene, indeno(1,2,3-c,d)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and benzo(g,h,i)perylene are substitutes of total PAHs in environment by World Health Organization (WHO), and four individual PAHs including benzo(a)pyrene, chrysene, indeno(1,2,3-c,d)pyrene, and benzo(b)fluoranthene have produced carcinogenic, mutagenic, and genotoxic effects in animal experiments (Thyssen et al. 1981; Deutsch-Wenzel et al. 1983). PAHs are mostly originated from anthropogenic processes, such as incomplete burning of fossil fuels and other organic substances (Simoneit 1977; Kim et al. 2003). Other sources of PAHs include oil spill accidents and wastewater discharge from domestic and industrial activities (Tam et al. 2001). PAHs in the environment have a long-term threat to human health and have received more and more environmental concern.

Because of the high hydrophobicity and stable chemical structure, PAHs are not very soluble and can be adsorbed rapidly onto soil particles, particularly on soil organic matter (Means et al. 1980). PAHs in soils can be dispersed by surface runoff and dust production, soils can therefore be considered as one of the pollution sources for PAHs contamination in air and sediments (Mai et al. 2003), especially in urban topsoil. It was reported that PAHs concentrations in soil were associated significantly with the corresponding levels in air (Vogt et al. 1987), house dust (Chuang et al. 1995), urban street dust (Takada et al. 1990; Essumang et al. 2006) and plants (Wang et al. 1982). Furthermore, outdoors hand-to-mouth activities, the exposure to skins and the inhalation of polluted dust are the main routes of PAHs in urban soils ingested by people, especially for children. Therefore, PAHs concentrations in soil may provide important information on the environmental pollution and urban atmosphere environmental quality (Trapido 1999), which will be helpful to the future development of study areas and human health.

Soil contamination with polycyclic aromatic hydrocarbons (PAHs) is an increasing problem in many countries, including China, especially in urban regions, with the consumption of the large amount of energy sources. The Ji'nan urban is highly polluted due to rapid industry development and urbanization, especially coal combustion for warming in winter at north China. Main industries such as the market of build material, steel plant, the plant of electric power, the refinery of petroleum and many other small industrial mills were at the dominant wind orientations (Hao 2005), this is enhanced by the location of the city with hill-around in three orientations and contaminations are difficult to diffuse quickly from urban district to suburb. Coal is the main energy source in Ji'nan city and annual coal consumption was about 15 million tons in 3257 km^2 urban area, therefore, there is a typical pollution city of coal combustion in north china. Annual petroleum consumption was about 10 million tons (Hao 2005). The pollution of vehicle exhaust is another PAHs source and has an increasing trend. Previous studies have been conducted on the sources of PAHs in atmospherical particles in Ji'nan city (Cheng et al. 2004). However, little is known about concentrations and distributions of polycyclic aromatic hydrocarbons (PAHs) in topsoil of Ji'nan urban district. The main objectives of this study are to determine the concentrations and distributions of the 16 total PAHs in Ji'nan topsoils, and to identify the possible sources of pollutants. We also evaluate environment quality of urban topsoil through nemerow composite index.

Materials and methods

Area description and sampling procedure

Topsoils (at the depth of 0–5 cm) used in this study were collected from the main different functional sections in urban areas of Ji'nan, Shandong Province (Fig. 1). These sampling areas could be categorized into campuses of university, school and kindergarten, main roadsides, industrial areas, suburb farmland, residential area and travel sites where many people always play and rest on and have important effect on urban environment quantity. In total 17 soil samples were collected, and each sample consisted of 5–7 subsamples collected randomly from the surrounding of each site and bulked together to form one composite sample. Among the 17 soil samples, 5 were form main roadsides, 3 were from school, 5 were from industrial areas, 2 were from suburb farmland, 1 was from residential area and 2 from travel sites. All the samples were immediately freeze-dried about 48 h and after transported to the laboratory. Dried soil samples were sieved to pass 2-mm mesh after removing stones and residual roots,

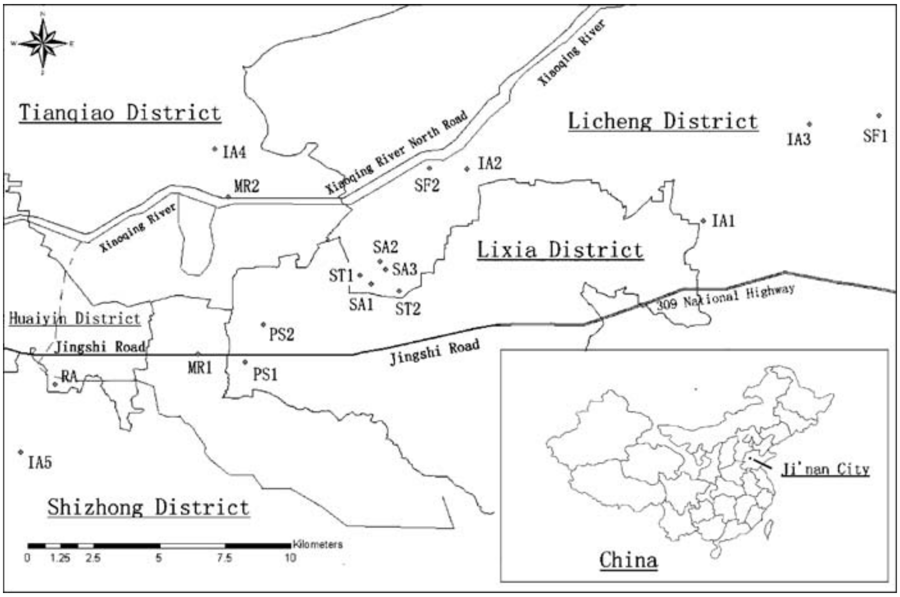

Fig. 1 Schematic map showing the soil sampling sites in the urban areas at Ji'nan City. *PS1*, Public squares-arboretum; *PS2*, public squares/Roadsides-Quancheng square; *MR1*, main roadsides-Jingshi road; *MR2*, main roadsides-Xiaoqing river north road; *RA* residential area near one machine-tool factory; *ST1* one filling station at Shanda road; ST2: Ji'nan east bus station; *SF1*, suburb farmland; *SF2* suburb farmland; *SA1*, school area-Shandong University; *SA2*, School area-Hongjialou elementary school; *SA3*, School area-one kindergarten at Honglou south road; *IA1*, one refinery plant; *IA2*, industrial areas-one power plant; IA3: Ji'nan steel and iron group company*;* *IA4*, roadsides of Luokou industrial area at Tianqiao district; IA5: Industrial areas-one cement plant

then sealed in Kraft paper envelopes and stored at −20°C prior to analysis of PAHs.

Sample analysis

Dichloromethane, dichloroethane, hexane, pentane and cyclohexane solvents were of chromatographic grade and purchased from Tianjin Kemi'ou Chemical Centre (Tianjin, China) and acetone purchased from Tianjin Guangcheng Chemical Factory (Tianjin, China) were of analytical grade and redistilled in all glass system before use. Silica gel (80–100 mesh) purchased from Qingdao Haiyang Chemical Co. (Shangdong, China) was activated at 130°C for 12 h, then kept in a desiccator for sample purification. The stock reference standard mixture of 16 PAHs (Supelco Co., USA) includes naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ane), fluorene (Fle), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (Bbf), benzo(a)pyrene (Bap), indeno(1,2,3-c,d)pyrene (Icdp), benzo(k)fluoranthene (Bkf), dibenz(ah)anthracene (DaA), and benzo(ghi)perylene (Bgp) respectively.

Soil samples (about 10 g dry weight) were weighed precisely and placed into Soxhlet apparatus prior to cleanup using 250 ml acetone-dichloroethane solvent (1:1 *v*/*v*) for 4 h at 60°C. The samples were Soxhlet extracted for 16 h at 60°C with 250 ml acetone/dichloromethane solvent (1:1 *v*/*v*; Cui et al. 2002). The solvents were removed by rotary evaporation, the eluent was further concentrated to about 3–5 ml (at 55°C) and finally evaporated to drying under a gentle steam of pure nitrogen, then dissolved to 1 ml with hexane.

The concentrated extracts were cleanup using a column consisting of 10 g activated silica gel and capped with anhydrous sodium sulfate. The chromatographic column was pre-washed with 40 ml pentane at 2 ml min^{-1} and discarded the washed solution, and transfered using 4 ml cyclohexane, then cleaned using 25 ml pentane and discarded above pentane and finally eluted with 25 ml mixture of dichloromethane and pentane (2:3 *v*/*v*). Afterward, this extract was evaporated to drying under a gentle steam of pure nitrogen, and then dissolved to 1 ml with hexane for analysis of PAHs.

The final concentrated extracts from the soil samples were analyzed using GC-MS (Shimadzu Corporation, QP2010, Japan) equipped with DB-5 capillary column (30 m, 0.25 mm I.D× 0.25 μm film thickness) and a mass spectrometer detector. The carrier gas was helium (high purity, 99.99%). The oven temperature was initially set at 60°C and held for 2 min, ramped at 16°C min^{-1} to 290°C and held for 10 min, and then 5°C min^{-1} from 290°C to 300°C and held for 2 min. Total rate was 23.1 ml min^{-1} and column rate was 1.10 ml min^{-1}. The ionization was performed in the electron impact mode at 70 eV, the temperature of ionization source was 200°C and interface temperature was 290°C; The time of solvent retention was 8 min and the time of data collection was 57 min. Prepared sample was injected by an auto-injector.

Identification and quantification of 16 PAHs were based on matching their retention time with a mixture of PAHs standards. The average recovery of the internal standards ranged from 86% to 112%. Solvent blanks and duplicate samples were also analyzed and the variation of PAHs concentrations of replicated samples was less than 10%. The limit of detection (LOD) defined as the standard deviation from the mean blank (n=3) ranged from 8 to 12 μg kg^{-1}. For identification, selected ion monitoring (SIM) mode was carried out using the molecular ions selective for individual PAHs. Chromatographic data were collected and processed using Chemstation software.

Soil pH was determined with a pH meter (PHS-3C, Leici, China) in a 1:2.5 suspension in H_2O. Soil organic matter (SOM) was determined by oxidation with of potassium dichromate-titration of $FeSO_4$, which is standard methods recommended by the Chinese Society of Soil Science (Lu 2000). Soil particle size distribution was measured by a micro-pipette method (Miller and Miller 1987). The basic properties of soils used in this study are shown in Table 1.

Data analysis

We used the method of nemerow composite index (P value) to assess the soil environmental quality based on 10 PAHs of environmental standards of the soil target value by Netherlands. Risk assessment indexes are Nap, Ant, BaA, Bkf, Bap, Chr, Phe, Flu, Icdp, Bgp.

Nemerow composite index (P value) is calculated as follows:

$$P = \left\{ \left[(Pi_{\text{av}})^2 + (Pi_{\max})^2 \right] \Big/ 2 \right\}^{1/2}$$

Table 1 Basic properties of soils used in this study

Sampling sites		pH (H_2O)	SOM (%)	Particle size distribution (%)[a]			Textural classification
				Sand	Silt	Clay	
PS1	Public squares	7.57	2.86	27.3	68.7	4.0	Silt loam
PS2	Public squares/Roadsides	7.47	5.54	42.5	49.8	7.7	Silt loam
MR1	Main roadsides	7.77	1.83	37.6	59.4	2.9	Silt loam
MR2	Main roadsides	7.91	2.72	27.2	54.4	18.4	Silt loam
RA	Residential areas	7.47	4.85	56.0	41.8	2.3	Sandy loam
ST1	Station/Roadsides	7.77	2.23	26.9	65.2	7.9	Silt loam
ST2	Station/Roadsides	8.02	2.26	51.5	44.1	4.5	Sandy loam
SF1	Suburb farmland	7.95	4.93	41.0	54.6	4.4	Silt loam
SF2	Suburb farmland	7.86	2.52	25.9	66.5	7.6	Silt loam
SA1	University	7.63	3.68	31.6	56.5	12.0	Silt loam
SA2	School	7.92	3.83	46.4	43.5	10.1	Loam
SA3	Kindergarten	7.73	1.58	30.4	66.4	3.2	Silt loam
IA1	Industrial areas/Roadsides	7.93	2.71	55.2	37.8	7.0	Sandy loam
IA2	Industrial areas	7.56	5.02	42.3	57.0	0.7	Silt loam
IA3	Industrial areas	8.02	13.29	51.5	47.0	1.5	Sandy loam
IA4	Industrial areas/Roadsides	8.53	11.12	66.3	31.2	2.5	Sandy loam
IA5	Industrial areas	7.9	1.1	19.6	77.7	2.6	Silt loam

IA Industrial areas, *SA* School area, *SF* Suburb farmland, *ST* Station areas, *RA* Residential areas, *PS* Public squares, *MR*, Main roadsides

[a] Sand (0.05–2 mm), Silt (0.002–0.05 mm), Clay(<0.002 mm)

Table 2 Total polycyclic aromatic hydrocarbons, selected PAHs ratios and nemerow composite index in topsoil

Sampling sites		Total PAHs (mg kg^{-1})	6 PAHs carcinogen (mg kg^{-1})/Ratios		Phe/Ant index	Flu/Pyr index	Dominant origin	P^{a}
PS1	Public squares	1.89	0.76	39.91	9.69	0.81	Pyro[b] and Petro[c]	0.18
PS2	Public squares/Roadsides	1.91	0.71	37.42	13.27	0.90	Pyro and Petro	0.16
MR1	Main roadsides	53.97	30.96	57.37	5.79	1.39	Pyro	7.67
MR2	Main roadsides	7.24	3.93	54.27	14.96	0.99	Pyro and Petro	0.90
RA	Residential areas	2.70	1.25	46.46	7.71	1.23	Pyro	0.26
ST1	Station/Roadsides	1.31	0.45	34.58	10.93	0.77	Pyro and Petro	0.12
ST2	Station/Roadsides	5.36	2.31	43.07	10.11	1.34	Pyro and Petro	0.87
SF1	Suburb farmland	7.61	4.53	59.45	6.33	1.26	Pyro	0.74
SF2	Suburb farmland	1.63	0.95	58.31	24.85	0.72	Petro	0.16
SA1	University	1.76	0.77	43.60	11.35	1.02	Pyro and Petro	0.16
SA2	School	15.12	8.22	54.40	17.88	1.40	Pyro and Petro	1.87
SA3	Kindergarten	4.85	2.48	51.16	13.36	0.85	Pyro and Petro	0.76
IA1	Industrial areas/Roadsides	8.51	3.67	43.08	0.99	1.06	Pyro	0.79
IA2	Industrial areas	4.23	1.85	43.73	9.67	1.23	Pyro	0.60
IA3	Industrial areas	254.08	161.11	63.41	4.95	1.25	Pyro	28.73
IA4	Industrial areas/Roadsides	21.31	13.34	62.59	8.84	1.19	Pyro	2.19
IA5	Industrial areas	1.77	0.87	49.43	5.79	0.88	Pyro and Petro	0.26

IA industrial areas, *SA* school area, *SF* suburb farmland, *ST* station areas, *RA* residential areas, *PS* public squares, *MR* main roadsides

[a] Nemerow composite index based on 10 PAHs for environmental standards of the soil target value by Netherlands

[b] Pyrogenic source

[c] Petrogenic source

Where Pi_{av} is the average value of individual pollutants indexes and $Pi_{\max}$ is the maximum value of individual pollutants indexes (State Environmental Protection Administration of China 2004; Ge et al. 2005).

Statistical analyses including correlation among variables were calculated with SPSS 13 for Windows. ArcGis 9.0 and photoshop was used to draw the sampling sites map.

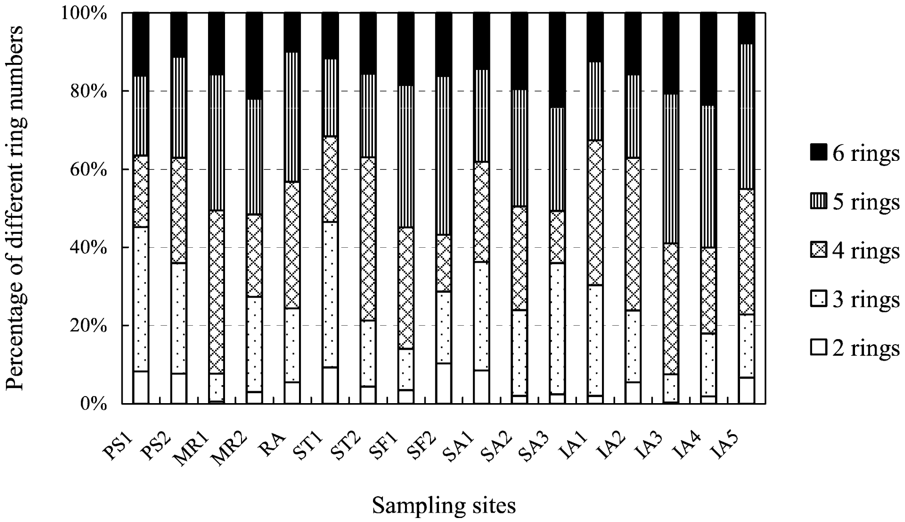

Fig. 2 The distribution of PAHs with different ring numbers in different soil samples

Table 3 Correlation coefficient matrix for PAHs and soil basic properties in soil samples at different locations in urban areas of Ji'nan city (*n*=17)

	Nap	Any	Ane	Fle	Phe	Ant	Flu	Pyr	BaA	Chr	Bbf	Bkf
Nap	1											
Any	0.933**	1										
Ane	0.907**	0.954**	1									
Fle	0.370	0.262	0.334	1								
Phe	0.973**	0.944**	0.966**	0.359	1							
Ant	0.886**	0.888**	0.945**	0.274	0.945**	1						
Flu	0.939**	0.924**	0.961**	0.319	0.986**	0.941**	1					
Pyr	0.941**	0.933**	0.968**	0.318	0.988**	0.947**	0.999**	1				
BaA	0.938**	0.931**	0.964**	0.312	0.985**	0.934**	0.999**	0.999**	1			
Chr	0.935**	0.942**	0.974**	0.325	0.981**	0.939**	0.991**	0.993**	0.992**	1		
Bbf	0.947**	0.954**	0.979**	0.325	0.991**	0.939**	0.992**	0.995**	0.995**	0.995**	1	
Bkf	0.948**	0.957**	0.976**	0.407	0.985**	0.923**	0.976**	0.981**	0.979**	0.984**	0.992**	1
BaP	0.946**	0.943**	0.971**	0.311	0.990**	0.941**	0.997**	0.999**	0.999**	0.993**	0.998**	0.985**
Icdp	0.952**	0.952**	0.978**	0.362	0.992**	0.936**	0.992**	0.994**	0.994**	0.994**	0.999**	0.995**
DaA	0.948**	0.941**	0.965**	0.316	0.991**	0.930**	0.996**	0.997**	0.998**	0.989**	0.996**	0.985**
Bgp	0.952**	0.964**	0.981**	0.313	0.991**	0.942**	0.982**	0.987**	0.986**	0.988**	0.997**	0.993**
LMW PAHs	0.965**	0.937**	0.969**	0.438	0.995**	0.949**	0.978**	0.981**	0.976**	0.976**	0.984**	0.987**
HMW PAHs	0.947**	0.948**	0.975**	0.328	0.991**	0.941**	0.996**	0.998**	0.997**	0.996**	0.999**	0.990**
Carcinogenic PAHs	0.950**	0.952**	0.977**	0.333	0.992**	0.940**	0.994**	0.996**	0.996**	0.995**	1.00**	0.992**
Total PAHs	0.950**	0.948**	0.976**	0.336	0.992**	0.942**	0.995**	0.998**	0.997**	0.995**	0.999**	0.991**
SOM	0.823**	0.762**	0.697**	0.144	0.763**	0.667**	0.672**	0.682**	0.678**	0.666**	0.711**	0.724**
Sand	0.439	0.266	0.239	0.059	0.356	0.380	0.269	0.271	0.249	0.254	0.262	0.258
Silt	−0.369	−0.183	−0.181	−0.172	−0.273	−0.307	−0.180	−0.183	−0.160	−0.170	−0.179	−0.186
Clay	−0.266	−0.270	−0.201	0.297	−0.287	−0.265	−0.292	−0.287	−0.290	−0.275	−0.275	−0.242
pH	0.444	0.293	0.192	0.227	0.337	0.294	0.234	0.238	0.228	0.202	0.244	0.267

LMW PAHs, low molecular weight PAHs (2–3-ring PAHs); *HMW PAHs*, high molecular weight PAHs (4–6-ring PAHs); *SOM*, soil organic matter

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

*Correlation is significant at the 0.05 level (2-tailed)

Results and discussion

Concentrations and distributions of PAHs

The total PAHs in topsoil of Ji'nan city were from 1.31 mg kg^{-1} to 254.08 mg kg^{-1} (dry weight) (Table 2), and the mean concentration of total PAHs was 23.25 mg kg^{-1} of the 16 PAHs. High molecular weight PAHs with 4–6-rings were the major fractions of the total soil PAHs in topsoil of Ji'nan city, and was above 90% proportion in the soil samplings of IA3 and MR1 (Fig. 2). The highest concentration level was found for soil samples at steel and iron plant (IA3) in industrial areas (254.08 mg kg^{-1}), and higher level was observed at one main roadside (MR1, 53.97 mg kg^{-1}). Many processes such as sintering, coking process and steel-making may produce a lot of PAHs, and were main reasons of highest PAHs concentration in steel and rion plant. Wu (2002) studied the PAHs concentration in dust of steel-making and found 90.84 mg kg^{-1} in dust with <10 μm particle sizes and 38.99 mg kg^{-1} with <100 μm particle sizes at one steel and iron plant, such dust with high PAHs concentration were transferred to soil wia dry/wet deposition and brought high concentration in soil with long time. To know about the level of total PAHs in topsoil at Ji'nan city, we compared with the concentrations of PAHs in other areas of the world. The results showed that the concentrations of total PAHs in topsoil of Ji'nan city (23.25 mg kg^{-1}) are 6 to 137 times higher than those of Beijing urban soil (3.92 mg kg^{-1}, Tang et al. 2005), Tianjin urban soil (1.84 mg kg^{-1}, Duan et al. 2005), Hongkong urban

BaP	Icdp	DaA	Bgp	LMW PAHs	HMW PAHs	Carcinogenic PAHs	Total PAHs	SOM	Sand	Silt	Clay	pH
1												
0.997**	1											
0.999**	0.996**	1										
0.993**	0.996**	0.991**	1									
0.982**	0.989**	0.981**	0.984**	1								
0.999**	0.999**	0.998**	0.995**	0.985**	1							
0.999**	0.999**	0.997**	0.997**	0.986**	1.00**	1						
0.999**	0.999**	0.998**	0.995**	0.987**	1.00**	1.00**	1					
0.704**	0.711**	0.715**	0.747**	0.739**	0.703**	0.712**	0.706**	1				
0.265	0.265	0.277	0.288	0.346	0.264	0.267	0.271	0.634**	1			
−0.177	−0.185	−0.186	−0.205	−0.282	−0.179	−0.184	−0.187	−0.564*	−0.939**	1		
−0.288	−0.264	−0.299	−0.277	−0.235	−0.279	−0.276	−0.276	−0.297	−0.331	−0.013	1	
0.248	0.256	0.253	0.277	0.337	0.244	0.252	0.251	0.425	0.400	−0.411	−0.038	1

soil (0.17 mg kg^{-1}, Zhang et al. 2006), Pearl River Delta (0.24 mg kg^{-1}, Yu et al. 2004), Yangtze River Delta region (0.397 mg kg^{-1}, Ping et al. 2007), Tarragona in Spain (1.00 mg kg^{-1}, Nadal et al. 2004), New Orleans in America (2.93 mg kg^{-1}, Howard et al. 2004), National urban soil controlled sites in Switzerland (0.45 mg kg^{-1}, Thomas et al. 2004) and urban soil in Belgrade, the capital of Serbia (0.375 mg kg^{-1}, Dragan et al. 2007). This results should be caused caution by people for environmental quality of study area.

PAHs concentrations in industrial areas were relatively higher (from 4.23 mg kg^{-1} to 254.08 mg kg^{-1}, and the average concentration was 72.03 mg kg^{-1} except the sampling site of cement plant) than those of other functional areas. Coal combustion by generating station, oil refining by refinery and steel production by steel plant were the main reasons for PAHs emission in those industrial areas and high PAHs concentrations. The lowest concentration of 16 PAHs was two public areas (Arboretum and Quancheng square) only about 1.90 mg kg^{-1}. Other different functional areas such as schools (7.24 mg kg^{-1}), suburb farmlands in industrial areas (4.62 mg kg^{-1}) and residential areas near one machine building factory (2.7 mg kg^{-1}) should be paid particular attention by people because people denseness in those areas was comparatively high. In fact, PAHs concentration in main roadsides (30.6 mg kg^{-1}) was rather high and there is the potential for exposure to high levels of PAHs for road users and those living in those areas (Essumang et al. 2006). Therefore, people should seldom walk to those areas. In addition, PAHs concentrations near bus stations/petrol stations (3.33 mg kg^{-1}) were a little high. Main roadsides and stations are always jammed with motor vehicles which brought PAHs emission and PAHs pollution.

The concentrations of 6 PAHs considered as carcinogens including Flu, Bbf, Bkf, Bap, Icdp and Bgp by the US EPA and WHO were from 0.45 mg kg^{-1} to

161.11 mg kg^{-1} and the percentage was from 34.58% to 63.41%. The percentages of 6 carcinogenic PAHs were highest at industrial areas and relatively low at public squares. About 88% of collected soils in Ji'nan city were associated with 10 PAHs concentrations including Nap, Ant, BaA, Bkf, Bap, Chr, Phe, Flu, Icdp, Bgp over 1 mg kg^{-1} set to be the soil target value by Netherlands, and average value of topsoil in Ji'nan city was 16.1 mg kg^{-1}, indicating their potential risk to human health. However, such environmental standards for PAHs in soil are not established yet in many countries and areas, including China (Tang et al. 2005).

Sources of the PAHs

It is essential to identify the origin and potential sources of soil PAHs in order to assess the environmental risk and control environmental pollution by PAHs. PAHs compositions and their ratios as a way to distinguish different anthropogenic PAHs sources (Yunker et al. 1999; Sanders et al. 2002). The usefulness of these indices relies on the fact that during low temperature processes the PAHs distribution is governed by thermodynamic properties. For high temperature processes, such as pyrolysis of organic matter, their distribution is governed by kinetic characteristics. Therefore, PAHs distribution is dependent on temperature (Alberty and Reif 1988). Phenanthrene is more thermochemically stable than anthracene, so at low temperature molar fraction of phenanthrene produced is much higher than that of anthracene. High temperature courses, such as the incomplete combustion of organic materials, are characterized by low Phe/Ant ratio values. The discrimination of the origins of PAHs was also performed according to the value of Flu/Pyr. The ratios of phenanthrene/anthracene (Phe/Ant) within the 3-ring PAHs group and fluoranthene/pyrene (Flu/Pyr) within the 4-ring PAHs group were used to form molecular indices (Baumard et al. 1998). Usually, Phe/Ant ratio$<$10 and Flu/Pyr ratio$>$1 indicate that PAHs come from pyrogenic source and Phe/Ant$>$15 and Flu/Pyr$<$1 indicate petrogenic origins of PAHs (Baumard et al. 1998). The ratios of Phe/Ant and Flu/Pyr are listed in Table 2.

The Flu/Pyr ratios in all samples ranged from 0.72 to 1.40 and Phe/Ant ratios ranged from 0.99 to 24.85. Data from each sample were grouped according to the origins of these PAHs in soils. It can be seen that there was a strong pyrogenic influence on soil PAHs except one suburb farmland, especially in industrial areas, PAHs of sampled soil were mainly originated from pyrogenic source. However, other sampled areas were mainly suffered from mixed source of both pyrogenic source and petrogenic inputs. About 52.9% in all of sampled areas were mainly from mixed sources of both pyrogenic source and petrogenic inputs.

Risk assessment of PAHs in topsoil at Ji'nan city

Nemerow composite index (P value) may indicate the role of pollutants to soil, especially effect of high concentration pollutants on soil environmental quality, and is widely used to assess PAHs environmental pollution in soil (Ge et al. 2005; Cheng 2006). Based on indexes, soil environmental quality is divided into five environmental pollution grades which are cleanness (safety) ($P\leq0.7$), warning value ($0.7<P\leq1.0$), light pollution ($1.0<P\leq2.0$), middle high pollution ($2.0<P\leq3.0$) and heavy pollution ($P>3.0$) (State Environmental Protection Administration of China 2004). In this study the data analysis used nemerow composite index to assess soil environmental quality with 10 PAHs including Nap, Ant, BaA, Bkf, Bap, Chr, Phe, Flu, Icdp, Bgp based on environmental standards of the soil target value by Netherlands. The results showed that nemerow composite indexes in topsoil were from 0.12 to 28.73 (Table 2). The nemerow composite index of the soil sample at steel and iron plant (IA3) in industrial areas was highest and heavy pollution, another heavy pollution sampling site was the main roadsides (MR1). The P values in industrial areas and main roadsides were relatively higher than other sampling sites, and should be paid attention to one school (SA2) and kindergarten (SA3) which the soil samplings were light pollution and alertness, respectively. Other soil sampling sites were mainly safety. In a word, about 53% of all soil sampling sites were got different grades pollution and about 47% were safety (cleanness).

Relationship between soil basic properties and PAHs

Once deposited into soil, most PAHs will be absorbed by soil organic matter (Wilcke 2000) and the strong sorption will inhibit PAH degradation and leaching (Beck et al. 1996). The total concentration of PAHs was often strongly correlated with SOM or TOC (Total organic carbon) (Wilcke et al. 1999; Tang et al. 2005, 2006; Chung and Alexander 2002). Therefore, the organic matter content is considered to be a very important factor related to PAHs pollution of soils (Boehm et al. 2002). Soil organic matter varied greatly between soil samples ranging from 1.1 to 13.29% with a mean of 4.24%. The relationship among individual, total concentrations of PAHs in soils and soil basic properties has been extensively investigated (Table 3). The result of the correlation test showed that all individual PAHs except Fle were significantly correlated with LMW, HMW, total PAHs and SOM ($P<0.01$), and individual PAHs except Fle in soils were significantly correlated with each other ($P<0.01$). This relationship illustrates that the level of soil contamination with PAHs may be pre-determined by soil organic matter contents, despite the fact that the input of PAHs to each site is rather different. While the weak correlation among Fle, other individual PAHs, LMW, HMW and SOM with each other. Furthermore, there were no correlation between soil different particle sizes or pH and individual PAHs, total PAHs. This results was agreement with Chen's study (2005) that there was no correlation between soil PAHs and clay.

Conclusion

Data from the this study revealed that urban soils from Ji'nan city, China were contaminated with PAHs ranging from 1.31 mg kg^{-1} to 254.08 mg kg^{-1} (dry weight), and high molecular weight PAHs were the major fractions of the total soil PAHs. Based on themolecular indices (Phe/Ant and Flu/Pyr)) of PAHs in soils, it was suggested that PAHs in soil samples were suffered from strong pyrogenic influence. Individual PAHs (except Fle), LMW, HMW, total PAHs in soils were strongly correlated with soil organic matter (SOM), and showed that SOM was the key factor determining the retention of PAHs in topsoils. The risk assessment of PAHs environmental quality demonstrated that about 53% soil sampling sites were got different grades pollution through nemerow composite indexes, especially one school (SA2) and kindergarten (SA3) should be paid more attention.

Acknowledgements This project is supported by China Postdoctoral Science Foundation (No. 20060400981), Shandong Postdoctoral Science Foundation (No. 200601005) and Environmental Protection Program of Shandong Environmental Protection Bureau (No. 2004132).

References

Alberty, R. A., & Reif, A. K. (1988). Standard chemical thermodynamic properties of polycyclic aromatic hydrocarbons and their isomer groups I Benzene series. *Journal of Physical and Chemical Reference Data*, *17*, 241–253.

Baumard, P., Budzinski, H., Michon, Q., Garrigues, P., Burgeot, T., & Bellocq, J. (1998). Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment. *Estuarine Coastal and Shelf Science*, *47*, 77–90.

Beck, A. J., Johnson, D. L., & Jones, K. C. (1996). The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils. *Science of the Total Environment*, *185*, 125–149.

Boehm, P. D., Burns, W. A., Page, D. S., Bence, A. E., Mankiewicz, P. J., Brown, J. S., et al. (2002). Total organic carbon, an important tool in an holistic approach to hydrocarbon source fingerprinting. *Environmental Forensics*, *3*, 243–250.

Chen, J., Wang, X. J., & Tao, S. (2005). The influence s of soil total organic carbon and clay contents on PAHs vertical distributions in soils in Tianjin area. *Research of Environmental Sciences*, *18*(4), 79–83.

Cheng, S. B. (2006). Accumulation, transformation and ecological risk assessment of PAHs in surface dust in Shanghai city. *East China Normal University master's thesis, China*, 79–80.

Cheng, P. Q., Yan, H. Z., et al. (2004). Investigation of contamination of PAHs in atmospherical particles in Ji'nan city in 2000. *Literature and Information on Preventive Medicine*, *10*(2), 140–141.

Chuang, J. C., Callahan, P. J., et al. (1995). Monitoring methods for polycyclic aromatic hydrocarbons and their distribution in house dust and track in soil. *Environmental Science Technology*, *29*, 494–500.

Chung, N., & Alexander, M. (2002). Effect of soil properties on bioavailability and extractability of phenanthrene and atrazine sequestered in soil. *Chemosphere*, *48*, 109–115.

Cui, Y. H., Zhu, X. M., et al. (2002). Measurement of PAHs in soil samples from wastewater irrigated soil from Tianjin. *Environmental Chemistry*, *21*(4), 392–396.

Deutsch-Wenzel, R. P., Brune, H., Grimmer, G., Dettbarn, G., & Misfeld, J. (1983). Experimental studies in rat lungs on the carcinogenicity and doseresponse relationships of eight frequently occurring environmental polycyclic aromatic hydrocarbons. *Journal of the National Cancer Institute*, *71*, 539–544.

Dragan, C., Mirjana, R., Anka, J., & Dušan, A. (2007). Levels of PAHs in the soils of Belgrade and its environs. *Environmental Monitoring Assessment*, *125*, 75–83.

Duan, Y. H., Tao, S., & Wang, X. J. (2005). Spatial distribution and sources of PAHs in Tianjin's topsoil. *Acta Pedologica Sinica*, *42*(6), 942–947.

Essumang, D. K., Dodoo, D. K., Obiri, S., & Oduro, A. K. (2006). Analysis of Polycyclic aromatic hydrocarbons in street soil dust in Kumasi metropolis of Ghana. *Environmental Monitoring Assessment*, *121*, 401–408.

Ge, C. J., An, Q., & Dong, Y. H. (2005). Residue and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils around a steel mill. *Rural Eco-Environment*, *21*(2), 66 – 69, 73.

Hao, M. T. (2005). Study on source analysis of atmospheric particulate matter in city. *Shandong University master's thesis, China*, 45.

Howard, W. M., Wang, G. D., et al. (2004). PAHs and metals in the soils of inner-city and suburban New Orleans, Louisiana, USA. *Environmental Toxicology and Pharmacology*, *18*, 243–247.

Kim, E. J., Oh, J. E., & Chang, Y. S. (2003). Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil. *Science of the Total Environment*, *311*, 177–189.

Lu, R. K. (2000). The analysis method of soil agricultural chemistry. *The Chinese Society of Soil Science edited*. China agricultural science and technology publishing company published.

Mai, B., Qi, S., Zeng, E. Y., Yang, Q., Zhang, G., Fu, J., et al. (2003). Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: Assessment of input sources and transport pathways using compositional analysis. *Environmental Science Technology*, *37*, 4855–4863.

Means, J. C., Wood, S. G., Hassett, J. J., & Banwart, W. L. (1980). Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science Technology*, *14*, 1524–1528.

Miller, W. P., & Miller, D. M. (1987). A micro-pipetts method for mechanical analysis. *Communications in Soil Science and Plant Analysis*, *18*, 1–15.

Nadal, M., Schuhmacher, M., & Domingo, J. L. (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environmental Pollution*, *132*, 1–11.

Ping, L. F., Luo, Y. M., Zhang, H. B., et al. (2007). Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. *Environmental Pollution*, *147*, 358–365.

Sanders, M., Sivertsen, S., & Scott, G. (2002). Origin and distribution of polycyclic aromatic hydrocarbons in surficial sediments from the Savannah River. *Archives of Environmental Contamination and Toxicology*, *43*, 438–448.

Simoneit, B. R. T. (1977). Diterpenoid compounds and other lipids in deep-sea sediment and their geochemical significance. *Geochimica et Cosmochimica Acta*, *41*, 463–476.

State Environmental Protection Administration of China (SEPA) (2004). The technical specification for soil environmental monitoring. *The trade criterions of environmental protection in P R China, HJ/T 166*, 25.

Takada, H., Onda, T., & Ogura, N. (1990). Determination of polycyclic aromatic by capillary gas chromatography. *Environmental Science Technology*, *24*, 1179–1186.

Tam, N. F. Y., Ke, L., Wang, X. H., & Wong, Y. S. (2001). Contamination of polycyclic aromatic hydrocarbons in surface sediments of mangrove swamps. *Environmental Pollution*, *114*, 255–263.

Tang, L. L., Tang, X. Y., Zhu, Y. G., et al. (2005). Contamination of polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China. *Environment International*, *31*, 822–828.

Tang, X. Y., Tang, L. L., Zhu, Y. G., et al. (2006). Assessment of the bioaccessibility of polycyclic aromatic hydrocarbons in soils from Beijing using an in vitro test. *Environmental Pollution*, *140*, 279–285.

Thomas, D., Bucheli, F. B., André, D., et al. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere*, *56*, 1061–1076.

Thyssen, J., Althoff, J., Kimmerle, G., & Mohr, U. (1981). Inhalation studies with benzo[a]pyrene in Syrian golden hamsters. *Journal of the National Cancer Institute*, *66*, 575–577.

Trapido, M. (1999). Polycyclic aromatic hydrocarbons in Estonian soil: Contamination and profiles. *Environmental Pollution*, *105*, 67–74.

Vogt, N. B., Brakstad, F., et al. (1987). Polycyclic aromatic hydrocarbons in soils and air: Statistical analysis and classification by the SIMCA method. *Environmental Science Technology*, *21*, 35–44.

Wang, D., & Meresz, O. (1982). Occurrence and potential uptake of polynuclear aromatic hydrocarbons of highway trafic origin by proximal gown food crops. In M. Cooke, & A. J. Dennis (Eds.) *Polynuclear aromatic hydrocarbons: physical and biological chemistry* (pp. 885–896). Columbus, NY: Batelle Press.

Wilcke, W. (2000). Polycyclic aromatic hydrocarbons (PAHs) in soil-a review. *Journal of Plant Nutrition and Soil Science*, *163*, 229–248.

Wilcke, W., Muller, S., Kanchanakool, N., Niamskul, C., & Zech, W. (1999). Polycyclic aromatic hydrocarbons (PAHs) in hydromorphic soils of the tropical metropolis Bangkok. *Geoderma*, *91*, 297–309.

Wu, J. H. (2002). Study on source profiles of polycyclic aromatic hydrocarbons (PAHs) on urban airborne particulate. *Nankai University master's thesis, China*, 26.

Yu, L. L., Zou, S. C., & Zhang, G. (2004). Distribution and spatial trends of polycyclic aromatic hydrocarbons in surface soils of the Pearl River Delta, China. *The report of fifth innovative chemistry at the school of chemistry and chemical engineering of Sun Yat-Sen University*, 161–167.

Yunker, M. B., Macdonald, R. W., Gpyette, D., Paton, D. W., Fowler, B. R., Sullivan, D., et al. (1999). Natural and anthropogenic inputs of hydrocarbons to the Strait of Georgia. *Science of the Total Environment*, *225*, 181–209.

Zhang, H. B., Luo, Y. M., Wong, M. H., et al. (2006). Distributions and concentrations of PAHs in Hong Kong soils. *Environmental Pollution*, *141*, 107–114.