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Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) Pollution in Soil of Suburban Areas in Tianjin, China

Jungang Lv · Rongguang Shi · Yanming Cai · Yong Liu

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Abstract Soil contamination with polycyclic aromatic hydrocarbons is an increasing problem and has aroused more and more concern in many countries, including China. In this study, representative soil samples (n = 87) of suburban areas in Tianjin (Xiqing, Dongli, Jinnan, Beichen) were evaluated for 16 polycyclic aromatic hydrocarbons. Surface soil samples were air-dried and sieved. Microwave assisted extraction was used for polycyclic aromatic hydrocarbons preparation prior to analysis with gas chromatography–mass spectrometry. The total concentrations of tested polycyclic aromatic hydrocarbons in Xiqing, Dongli, Jinnan, Beichen ranged in 58.5–2,748.3, 36.1–6,734.7, 58.5–4,502.5, 29.7–852.5 ng/g and the averages of total concentration of polycyclic aromatic hydrocarbons were 600.5, 933.6, 640.8, 257.3 ng/g, respectively. Spatial variation of polycyclic aromatic hydrocarbons in soil was illustrated; Pollution status and comparison to other cities were also investigated. Serious polycyclic aromatic hydrocarbons soil pollution was found in Dongli district, on the contrary, Bap in most sites in Beichen did not exceed relative standards and most sites in Beichen should be classified as non-contaminated soil. Principal component analysis was used to identify the possible sources of different districts. It turned out that coal combustion still was the most important sources in three districts except Beichen. Coking, traffic, cooking, biomass combustion also accounted for polycyclic aromatic hydrocarbons pollution to certain extent in different districts. These data can be further used to assess the health risk associated with soils polluted with polycyclic aromatic hydrocarbons and help local government find proper way to reduce polycyclic aromatic hydrocarbons pollution in soils.

Keywords Polycyclic aromatic hydrocarbons · Soil · Suburban · Tianjin

J. Lv (✉) · Y. Liu
Institute of Forensic Science, Supreme People's Procuratorate, People's Republic of China, Lugu East Street 5, Beijing 100040, China
e-mail: sdtaljg@163.com

R. Shi · Y. Cai
Agro-Environmental Protection Institute of Ministry of Agriculture, Tianjin 300191, China

Soil is the most important reservoir and reemission source of PAHs. Polycyclic aromatic hydrocarbons pollution in soil will impact bad influence on human health (Menzie et al. 1992). Polycyclic aromatic hydrocarbons are resistant to degradation and can bio-accumulate through the food chain, so PAHs also may pose threat to human health over a long period. Considering the high toxicities of these PAHs, it is necessary to study the concentrations, profiles and sources of PAHs in the soil. Polycyclic aromatic hydrocarbons come from two main sources. Natural PAHs are mainly from volcanic eruptions, plant emissions and natural fires. It is reported that typical concentrations of PAHs in soil without anthropogenic pollution were $1 \sim 10\ ng \cdot g^{-1}$ (Edwards 1983). Anthropogenic PAHs are mostly generated during the combustion of carbonaceous materials such as coals, gasoline, and diesel (Kavouras et al. 2001). Previous study suggested that PAH concentrations decreased significantly along the urban–suburban–rural transect (Wang et al. 2007). Soils in suburban areas of cities, most of which are used as agricultural fields and impact great influence to food chain and therefore human health, are liable to be polluted by PAHs generated and transferred from cities, so PAHs pollution in soils of suburban areas has really aroused many concerns. Many researches on the PAHs pollution in Tianjin, the third

biggest city of China were undertaken before 2004 and most of these studies mainly focused on the PAHs in Tianjin urban area. Polycyclic aromatic hydrocarbons pollution in the soil of suburban areas was not investigated since then to our best of knowledge. In this study an extensive and systematic survey has been undertaken to evaluate the spatial variation, contamination status, sources of PAHs in suburban soils in Tianjin.

Materials and Methods

The sampling sites in four suburban districts of Tianjin: Dongli, Xiqing, Jinnan, Beichen, are illustrated in Fig. 1. All samples were sampled in August 2008. A total of 87 soil samples (0–10 cm soil layer, 1 kg each) were collected with a stainless steel scoop and stored in PE bags. Each sample was composed of 20 sub samples collected within the 10 × 10 m^2 of sampling site. Between sampling the scoop was rinsed by acetone. All soil samples were placed in dark and transported to the laboratory as soon as possible. Soil samples were air dried and then ground and sieved through a 50 mesh sieve. All samples were stored in −20°C before analysis.

All organic solvents from Fisher (Fair Lawn, NJ, USA) were pesticide grade. PAHs standard solution (EPA M-610, 1 mL 0.1 mg/mL) and ^{2}D-labeled surrogate standards (EPA M-525-IS, 1 mL 2.0 mg/mL in acetone) were purchased from Accustandard Inc. (CT, USA). 40 mg/L ^{2}D-chrysene was spiked 25 μL before extraction as surrogate in all samples. The extraction of PAHs from soil was modified from Chee's method (Chee et al. 1996). Microwave-assisted extraction was carried out with a MarsXpress (maximum power: 1,200 W) laboratory microwave extraction system (CEM, Matthews, NC, USA). Briefly, 5.0 g of soil sample was extracted for half an hour with 15 mL of acetone:hexane (v:v/1:1) twice. Then the mixture each time was centrifuged for 5 min at 4,000 rpm. The supernatant was poured into a new vial together and 45 mL of ultra pure water was added to keep the polarity, then LC-18 SPE columns were employed to retain PAHs and remove polar impurities (Sun et al. 1998). Dichloromethane was used to elute the PAHs for three times (3 mL each time). The elution was collected and then concentrated to 0.5 mL with gentle nitrogen flow for GC–MS injection.

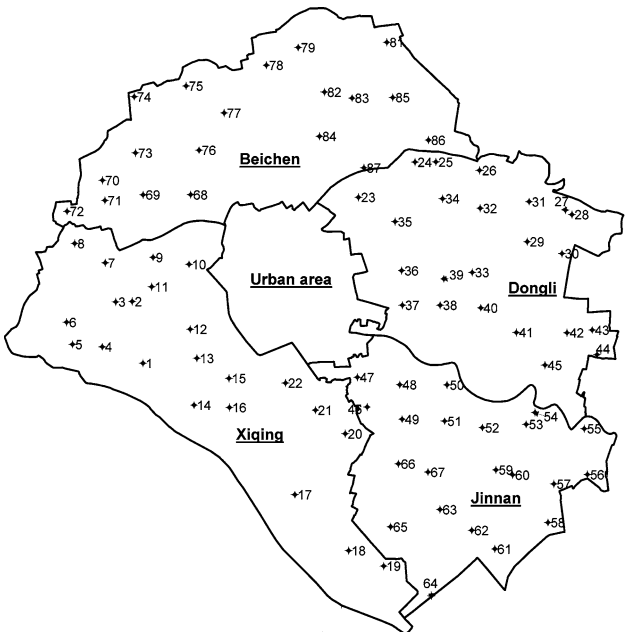

Fig. 1 Sampling sites

Polycyclic aromatic hydrocarbons were quantified on Agilent 6890 gas chromatography with Agilent 5973 N mass spectrometer with electron impact ion source. Helium was the carrier gas at a constant flow of 1.0 mL min^{-1}. Two micro liters of the extract were injected with 7673 auto sampler in splitless mode. A DB-5MS fused silica capillary column (30 m × 0.25 μm × 0.25 mm) was used to separate the PAHs. The electron emission energy was set at 70 eV. The ion source and the quadrupole temperature were set at 230 and 150°C, respectively. The oven temperature program were as follow: began at 60°C, held for 2 min, increased to 200°C at 19°C min^{-1}, held for 2 min, then increased to 240°C at 4.5°C min^{-1}, held for 2 min, finally increased to 290°C at 2.5°C min^{-1}, held for 2 min. SIM mode was used, the parameters in SIM according to US EPA Compendium Method TO-13A. Spiked tests indicated that recoveries of 16 native PAHs were between 62.2% (naphthalene) to 116.7% (benzo(a)-pyrene) with RSD (n = 3) from 0.7% (fluorene) to 16.3% (naphthalene). All of the recoveries were higher than 70% except naphthalene. The detection limits of this method ranged from 0.08 to 4.68 ng/g depending on the analyte. The recoveries of surrogate in all samples ranged from 70.6% to 119.1%.

Results and Discussion

The total concentrations of tested PAH in Xiqing, Dongli, Jinnan, Beichen ranged in 58.5–2,748.3, 36.1–6,734.7, 58.5–4,502.5, 29.7–852.5 ng/g and the averages of total concentration of PAHs(T-PAHs) were 600.5, 933.6, 640.8, 257.3 ng/g, respectively. As clearly shown in Fig. 2, sampling sites with high T-PAHs in Dongli, Jinnan, Xiqing were much more than those in Beichen. Soil in Dongli, which located between the urban area and TEDA (Tianjin Economic Development Area), affected by these two highly developed industrial areas, its own industry and busy traffic, were seriously polluted. As the best index of

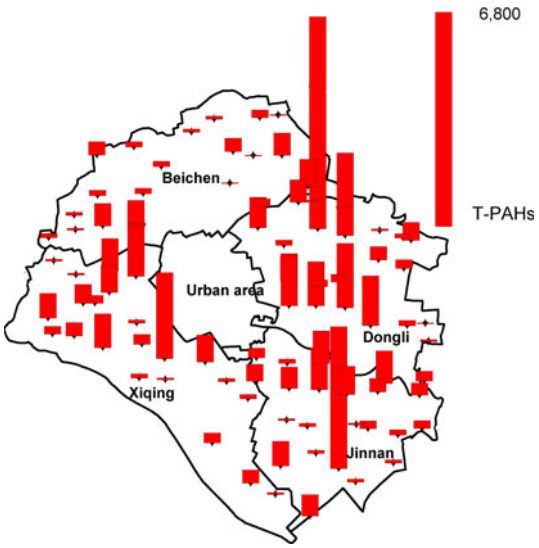

Fig. 2 T-PAHs concentrations

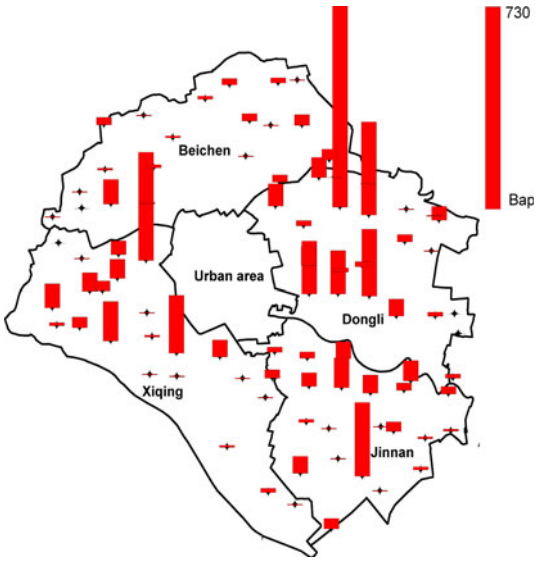

Fig. 3 Bap Concentrations

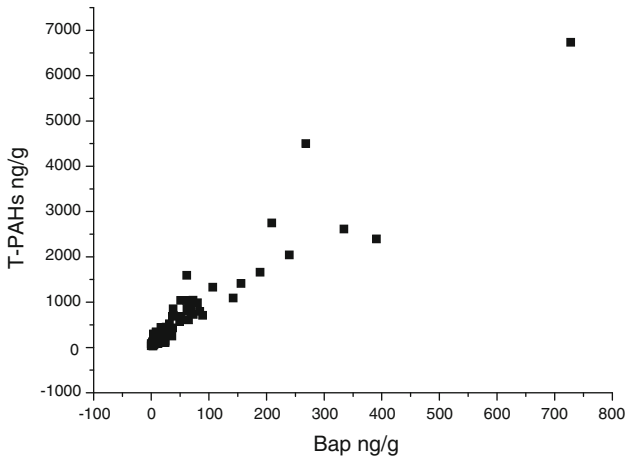

Fig. 4 Relationship between T-PAHs and Bap

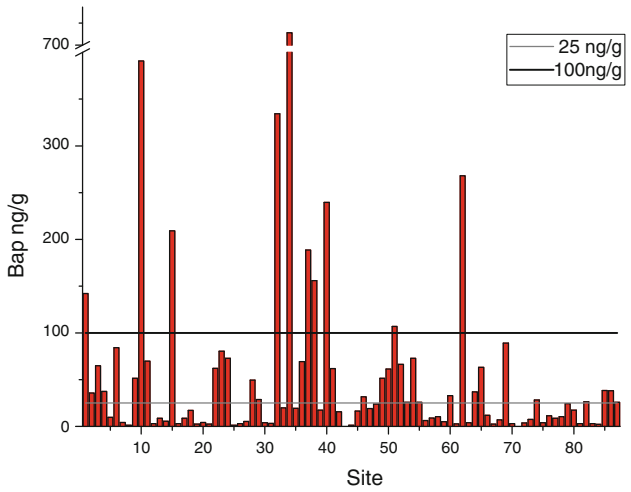

Fig. 5 Bap concentrations in different sites

PAHs toxicity, Benzo(a)pyrene(Bap) showed the same trend in spatial distribution (Figs. 3 and 4). R = 0.946 in the linear Regression between T-PAHs and Bap, $p < 0.0001$, It indicated that Bap levels could represent the PAHs pollution well in soil in this area. There is few recommendation or guideline of T-PAHs in soil even worldwide, so Bap concentrations were used to evaluate the T-PAHs pollution status. Figure 5 revealed soil pollution in this area referring to Canadian Soil Quality Control Standard(the black line, 100 ng/g), the target of polluted soil treatment in Netherlands(the grey line 25 ng/g). 45.5%, 50%, 52.2%, 30.0% sites in Xiqing, Dongli, Jinnan, Beichen exceeded the grey line, 13.6%, 27.3%, 8.7% sites in Xiqing, Dongli, Jinnan exceeded the black line, no sites in Beichen exceeded the black line. This revealed serious soil pollution in suburban Tianjin, especially in Dongli district. Maliszewska (1996) proposed a classification method based on the T-PAHs concentrations: non-contaminated soil (<200 ng/g), weakly contaminated soil (200–600 ng/g), contaminated soil (600–1,000 ng/g), and heavily contaminated soil (1,000–10,000 ng/g). According to this classification, more than 36.3%, 40.9%, 34.8% and 15.0% sites in Xiqing, Dongli, Jinnan, Beichen should be classified at least as contaminated soil, especially in Dongli district, where 27.2% sites should be classified as heavily contaminated soil. Higher molecular weight (HMW) PAHs with higher toxicity were more prominent in the soil samples than lower molecular weight (LMW) PAHs. PAHs with 4–6 rings accounted for more than 60% in all four

Table 1 Comparison of PAHs concentration in suburban soil in different cities

Region	Species	Min	Max	Mean	Reference
Tianjin	16	29.7	6,734.7	619.9	This study
Tianjin	16	199	5,190	839	Duan et al. 2005
Beijing	16	16	3,884	464	Ma et al. 2005
Hongkong	15			34.20	Zhang et al. 2005a
Dongguan	16	29	4,079	413	Zhang et al. 2005b
New Orleans	16	527	3,753	731	Mielke et al. 2004
In Poland	13	28	2,450	264	Maliszewska 1996
In South Korea	16	23.3	2,834	236	Nam et al. 2003

Table 2 Primarily classification of the sources in different districts

District	PC1	PC2
Xiqing	Coal combustion	Coking plant
Dongli	Coal combustion	Traffic, diesel combustion
Jinnan	Coal combustion	Coking plant, traffic
Beichen	Cooking, biomass combustion	Traffic, coking plant

districts. Table 1 showed the comparison of PAHs concentration in suburban soil in different cities. PAHs concentration in this study was much higher than those in most previous studies, but was lower than the values in New Orleans and Tianjin reported by Duan in 2005, Duan's study involved not only suburban areas, but also urban area and TEDA. According to Wang (Wang et al. 2007), PAHs in urban area and TEDA should be higher than those in suburban areas, and finally contribute to the higher mean value in Duan's study.

Principal component analysis (PCA) is a powerful tool to identify the sources of PAHs in many studies (Li et al. 2006; Cincinelli et al. 2007). The PCA results of 16 PAHs in soil were listed in Table 2. Pa, Flu, Pyr, Ant and HMW PAHs are typical representation of coal combustion (Harrison et al. 1996), while combustion of gasoline will mainly generate Bbf, Bkf, Chr and Bghip (Simcik et al. 1999), diesel will generate Ind (Li and Kamens 1993). High contents of Flu and Ant represent coking sources (Simcik et al. 1999). Rogge also suggested that household cooking and gas combustion mainly release Baa, Bap and Bap (Rogge et al. 1993). Although sources of PAHs are very complex, we can primarily classify the sources of different districts according to the findings of former researches.

Table 2 indicated the different sources according to Table 3 in combination with local real status. It indicated that coal combustion still was the most important sources in three districts except Beichen. Coking, traffic, cooking, biomass combustion also accounted for PAHs pollution to certain extent in different districts. These results obtained above will be helpful to local government take proper steps to reduce the PAHs generation and pollution in soil.

Table 3 PCA of PAHs in different districts in Tianjin suburban areas

PAHs species	Abbr.	Xiqing		Dongli		Jinnan		Beichen	
		73.65%	15.36%	74.83%	10.41%	60.72%	13.54%	55.19%	14.87%
Naphthalene	Nap	0.73	0.42	0.26	0.49	0.15	0.53	0.35	−0.11
Acenaphthylene	Acpy	0.63	0.04	0.56	0.79	0.48	0.22	0.55	0.81
Acenaphthene	Acp	0.68	0.41	0.25	−0.21	0.25	−0.67	0.24	−0.09
Fluorene	Flu	0.71	0.66	0.90	0.26	0.34	−0.73	0.65	0.70
Phenanthrene	Pa	0.88	0.45	0.91	−0.28	0.89	0.34	0.69	0.70
Anthracene	Ant	0.85	0.43	0.86	−0.45	0.59	0.20	0.61	0.66
Fluoranthene	Fl	0.95	−0.23	0.95	−0.26	0.96	−0.19	0.95	0.25
Pyrene	Pyr	0.94	−0.29	0.95	−0.25	0.96	−0.19	0.96	0.05
Benz(a)anthracene	Baa	0.96	0.08	0.98	−0.13	0.95	−0.22	0.84	−0.35
Chrysene	Chr	0.89	−0.45	0.99	−0.06	0.99	−0.07	0.93	−0.21
Benzo(b)fluoranthene	Bbf	0.91	−0.35	0.98	0.34	0.98	0.02	0.91	−0.37
Benzo(k)fluoranthene	Bkf	0.88	−0.42	0.98	0.23	0.93	0.02	0.87	0.02
Benzo(a)pyrene	Bap	0.85	−0.44	0.99	−0.01	0.99	0.03	0.84	−0.27
Indeno(1,2,3-cd)pyrene	Ind	0.93	−0.08	0.93	0.26	0.33	0.71	0.73	−0.35
Dibenz(a,h)anthracene	Dba	0.82	−0.41	0.82	0.42	0.76	0.32	0.41	−0.19
Benzo(ghi)perylene	Bghip	0.96	0.15	0.98	0.05	0.96	0.21	0.85	−0.31

Note Two percentages in each districts mean the percent of first two principal components PC1, PC2

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