

# Characteristics of PAHs in farmland soil and rainfall runoff in Tianjin, China

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Received: 20 July 2017 / Accepted: 5 October 2017 / Published online: 14 October 2017  
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**Abstract** Rainfall runoff can remove certain amounts of pollutants from contaminated farmland soil and result in a decline in water quality. However, the leaching behaviors of polycyclic aromatic hydrocarbons (PAHs) with rainfall have been rarely reported due to wide variations in the soil compositions, rainfall conditions, and sources of soil PAHs in complex farmland ecosystems. In this paper, the levels, spatial distributions, and composition profiles of PAHs in 30 farmland soil samples and 49 rainfall-runoff samples from the Tianjin region in 2012 were studied to investigate their leaching behaviors caused by rainfall runoff. The contents of the  $\Sigma_{16}$ PAHs ranged from 58.53 to 3137.90  $\mu\text{g}/\text{kg}$  in the soil and 146.58 to 3636.59  $\mu\text{g}/\text{L}$  in the runoff. In total, most of the soil sampling sites (23 of 30) were contaminated, and biomass and petroleum combustion were proposed as the main sources of the soil PAHs. Both the spatial distributions of the soil and the runoff PAHs show a decreasing trend moving away from the downtown, which suggested that the leaching behaviors of

PAHs in a larger region during rainfall may be mainly affected by the compounds themselves. In addition, 4- and 5-ring PAHs are the dominant components in farmland soil and 3- and 4-ring PAHs dominate the runoff. Comparisons of the PAH pairs and enrichment ratios showed that acenaphthylene, acenaphthene, benzo[a]anthracene, chrysene, and fluoranthene were more easily transferred into water systems from soil than benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, and indeno[123-cd]pyrene, which indicated that PAHs with low molecular weight are preferentially dissolved due to their higher solubility compared to those with high molecular weight.

**Keywords** Polycyclic aromatic hydrocarbons (PAHs) · Rainfall runoff · Farmland · Leaching

## Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of persistent organic pollutants (POPs), have been a global concern for many years. Due to their mutagenic, carcinogenic, and teratogenic properties (Gan et al. 2009; Rianawati and Balasubramanian 2009), a total of 16 PAHs have been listed as priority pollutants by the United States Environmental Protection Agency (US EPA) (Kwon and Choi 2014; Ma et al. 2015). Anthropogenic activities, including the incomplete combustion of fossil fuels, traffic emissions, and petroleum spills in industrials and urban areas, are the major sources of

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**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10661-017-6290-y>) contains supplementary material, which is available to authorized users.

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environmental PAHs (Baek et al. 1991; Gubler et al. 2015).

After a transportation period in the atmosphere, particulate and gaseous PAHs settle on terrestrial surfaces through dry and/or wet deposition (Lee and Lee 2004; Esen et al. 2008). Soil is one of the most important sinks for PAHs in terrestrial systems (Zheng et al. 2012), and farmland soil plays a key role in ensuring the safety of food and human health. In recent years, the farmland soil in some developed regions of China has been reported to be suffering from severe pollution (Cao et al. 2013). Therefore, monitoring and removing contaminants from farmland soil has become an urgent issue.

In terrestrial systems, the techniques for removing PAHs from soil can be divided into the solid-gas exchange (Zhong and Zhu 2013), microbial degradation (Hwang and Cutright 2003; Zhang et al. 2006; Crampon et al. 2014), Fenton and electrochemical remediation (Pazos et al. 2010; Yap et al. 2011), soil washing technology (Lau et al. 2014), and rainfall-runoff process (Lang et al. 2008; Zheng et al. 2012). These techniques, excluding the rainfall-runoff process, have been systematically studied (Haritash and Kaushik 2009). While rainfall-runoff processes are a critical mechanism for PAH transfer from soils to aquatic environments (Chen et al. 2004; DiBlasi et al. 2009), few studies have been reported. The enrichment behaviors and transport mechanisms of soil-bound PAHs during rainfall runoff have been systematically studied through simulated rainfall experiments (Zheng et al. 2012; Luo et al. 2013; Luo et al. 2015). Soil organic matter (SOM) may be the main carrier of PAHs from soil, and the leaching behaviors are highly dependent on the rainfall conditions and the PAH species (Zheng et al. 2012). The model for estimating the enrichment ratio (ER) of PAHs also indicated that PAH leaching is dependent on their physiochemical properties, the sediment composition, and the composition evolution during a rainfall event (Luo et al. 2015). However, evaluating the effectiveness of rainfall on the leaching of PAHs from soils is still very difficult because there are large differences in the soil compositions, rainfall conditions, and soil PAHs in complex farmland ecosystems. In addition, to our knowledge, a field investigation on the leaching behaviors of PAHs has never been reported.

In this paper, the level, spatial distribution, and composition of 16 priority PAHs were determined in farmland soils and runoffs in the Tianjin Region. By comparing the characteristics of PAHs in soils and runoffs,

the sources of the soil PAHs and their leaching behaviors caused by rainfall events were studied.

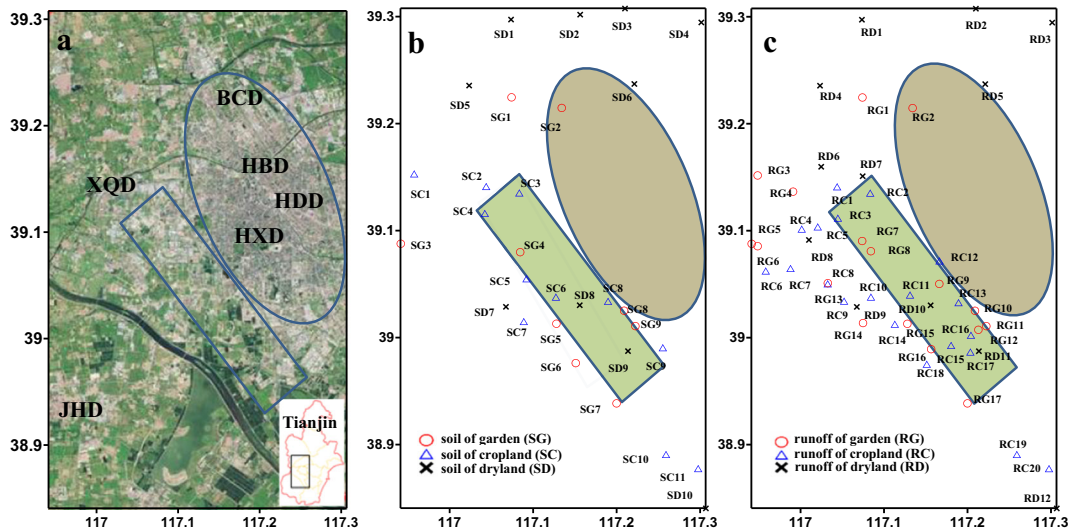
## Materials and methods

### Sampling and classification

Tianjin, China's third largest industrial center, is located in northern China, is adjacent to the Bohai Sea, has an area of ca. 12,000 km<sup>2</sup>, and has a population of more than 15,000,000 (Chen et al. 2015b). The annual precipitation has been between 300 and 800 mm over the past few decades with a decreasing trend (Duan et al. 2012). As a highly industrialized area with low rainfall, most of the regions in Tianjin have suffered from severe pollution as a result of the rapid industrialization and urbanization. The PAH pollution in this region is mainly from local industry and automobiles (Shi et al. 2005). In addition to atmospheric deposition, wastewater irrigation is another important input pathway for contaminants to enter the farmland soils (Wang et al. 2002).

The satellite imagery of the sampling area was captured from the Baidu satellite map (Fig. 1a), and the maps of the sampling sites are shown in Fig. 1, including 30 soil sites (Fig. 1b) and 49 surface runoff sites (Fig. 1c). The soil agro-types were classified as garden, cropland, and dryland, according to the vegetation types. Surface soils were collected at depths of 0–20 cm using systematic random sampling in June of 2008. The samples were air-dried at room temperature, ground, sieved with a stainless-steel griddle (100 meshes), and stored at –20 °C until the analysis.

The runoff samples were collected in July and September of 2008. The annual rainfall in Tianjin was 552.1 mm in 2008, and the monthly rainfalls were 131.9, 143.4, 71.3, and 68.2 mm from June to September, respectively. At each site, 2000 mL runoff samples were collected in polyethylene bottles, and the bottles were covered with aluminum foil. After the runoff samples were transferred to the lab, the samples were well blended, centrifuged, and filtered through a glass fiber membrane. The suspended particles were freeze-dried, ground, sieved, and stored at –20 °C. In addition, the water samples were kept in a refrigerator until the analysis. The concentration of the PAHs in the runoff samples was the sum of the PAHs dissolved in the water and the PAHs adsorbed on the suspended particles.



**Fig. 1** The satellite map of the sampling region (a) and maps of the sampling sites in Tianjin soil (b) and surface runoff (c). A total of 9 garden soil, 11 cropland soil, 10 dryland soil, 17 garden runoff, 20 cropland runoff, and 12 dryland runoff samples were

collected. BCD, HBD, HDD, HXD, XQD, and JHD are 6 districts in Tianjin, that is, Beichen, Hebei, Hedong, Hexi, Xiqing, and Jihai, respectively. The gray ellipse and olive diamond areas separately represent urban and industry areas

Chemicals and reagents

The 16 US EPA-priority PAH-mixed standard solution (each at 100, 200, 1000, or 2000 µg/mL) and internal standard mixture (naphthalene-d<sub>8</sub>, acenaphthylene-d<sub>10</sub>, chrysene-d<sub>12</sub>, perylene-d<sub>12</sub>, and phenanthrene-d<sub>10</sub>) were purchased from Supelco (Bellefonte, USA). The 16 PAHs and their elution orders were as follows: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Acp), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]anthracene (DbA), benzo[ghi]perylene (BghiP), and indeno[123-cd]pyrene (InP). Acetone, petroleum ether, ethyl acetate, methanol, dichloromethane, and n-hexane were supplied by J.T. Baker (Phillipsburg, NJ, USA). Anhydrous sodium sulfate was supplied by Kanto Chemical Co., Inc. (Tokyo, Japan). Silica gel (70–230 mesh) was supplied by Merck (Darmstadt, Germany). Deionized water was obtained from a Milli-Q system (Millipore, Watford).

Sample extraction and cleanup

The soil samples were extracted using a Soxhlet extractor (Soxtherm Gerhardt Variostat; Soxtherm V7.5, Germany). Briefly, a 5-g soil sample was extracted thrice in

5 mL of acetone and 3 mL of petroleum ether with 30 min of vibration. The extracts were transferred into a separatory funnel. Then, 30 mL of deionized water was thrice added into the separatory funnel to remove any water-soluble interferences. The extracts were dehydrated using anhydrous sodium sulfate (Kanto Chemical Co., Inc., Tokyo, Japan). The dehydrated extracts were collected in a round-bottomed flask and concentrated to 1 mL using a rotary evaporator. The solvent was exchanged with methanol. The PAHs in the extracts were fractionated using a silica gel column (4 mm i.d.). The column was first eluted with 10 mL of n-hexane, and the eluate was discarded. The PAH fraction was then eluted with 25 mL of a dichloromethane/hexane mixture (1:1; v/v). The eluate was concentrated to 0.1 mL using a gentle nitrogen gas stream for a gas chromatography-mass spectrometer (GC-MS) analysis.

The runoff samples (1 L) were filtered through glass fiber membranes to collect any suspended particles. After being freeze-dried, the suspended particle samples were extracted using the same pretreatment procedure used for the soil samples and the eluates were combined with the water extracts.

The runoff water samples (1 L) were extracted using a solid phase extraction (SPE) system from Supelco following the previous literature (Zhou et al. 2000). The SPE column was preconditioned with 5 mL of ethyl acetate, 5 mL of methanol, and 2 × 5 mL of deionized

water. The runoff water samples were passed through an SPE column at a flow rate of 4–5 mL/min. Then, 5 mL of deionized water was added to the SPE column to remove the water-soluble interferences, and the SPE column was drained under vacuum conditions for 30 min. Finally, 3 mL of dichloromethane and 5 mL of ethyl acetate were separately added into the column pipe to elute the analytes. The eluates of the suspended particles and water from the same runoff samples were combined and further concentrated by  $N_2$  to 0.1 mL for the GC-MS analysis.

#### GC-MS analysis of the PAHs

The 16 PAHs were quantified by an Agilent 5890 gas chromatography-mass spectrometer equipped with an electron impact ion source and HP-5MS capillary column (30 m  $\times$  0.25 mm i.d., 0.25- $\mu$ m film thickness), according to previous literature (Zhang et al. 2004). Briefly, 2  $\mu$ L of the extract was injected in the splitless mode by an autosampler with a 1.0 mL/min helium gas flow. The electron emission energy was 70 eV, and the interface, ion source, and quadrupole temperatures were 280, 280, and 250  $^{\circ}$ C, respectively. The oven temperature program was as follows: the initial temperature was 60  $^{\circ}$ C for 3 min, the temperature increased to 120  $^{\circ}$ C at a rate of 10  $^{\circ}$ C/min, and then increased to 280  $^{\circ}$ C at 5  $^{\circ}$ C/min and was held for 10 min. The identification of the PAHs was based on the selected ions and a comparison of the retention times between the sample peaks and the standard solution peaks containing the individual PAHs.

#### Quality assurance/quality control

The detection limits (LODs) ranged from 0.03 to 0.37  $\mu$ g/kg for the soil PAHs and 0.22 to 2.37 ng/L for the runoff PAHs ( $S/N = 3$ ). The recoveries of the 16 PAHs in the spiking experiment were 75.2–99.5% and 66.3–108.6% with relative standard deviations of 6.2–25.9% and 5.9–20.5% ( $n = 3$ ) for the solid and aqueous samples, respectively. The labeled PAHs were spiked in all of the samples as surrogates to monitor the recoveries. The recoveries of the surrogates in all the samples ranged from  $63.5 \pm 6.3\%$  to  $104.7 \pm 9.2\%$  for the soil and sediment samples and  $65.4 \pm 8.3\%$  to  $123.2 \pm 8.1\%$  for the water samples.

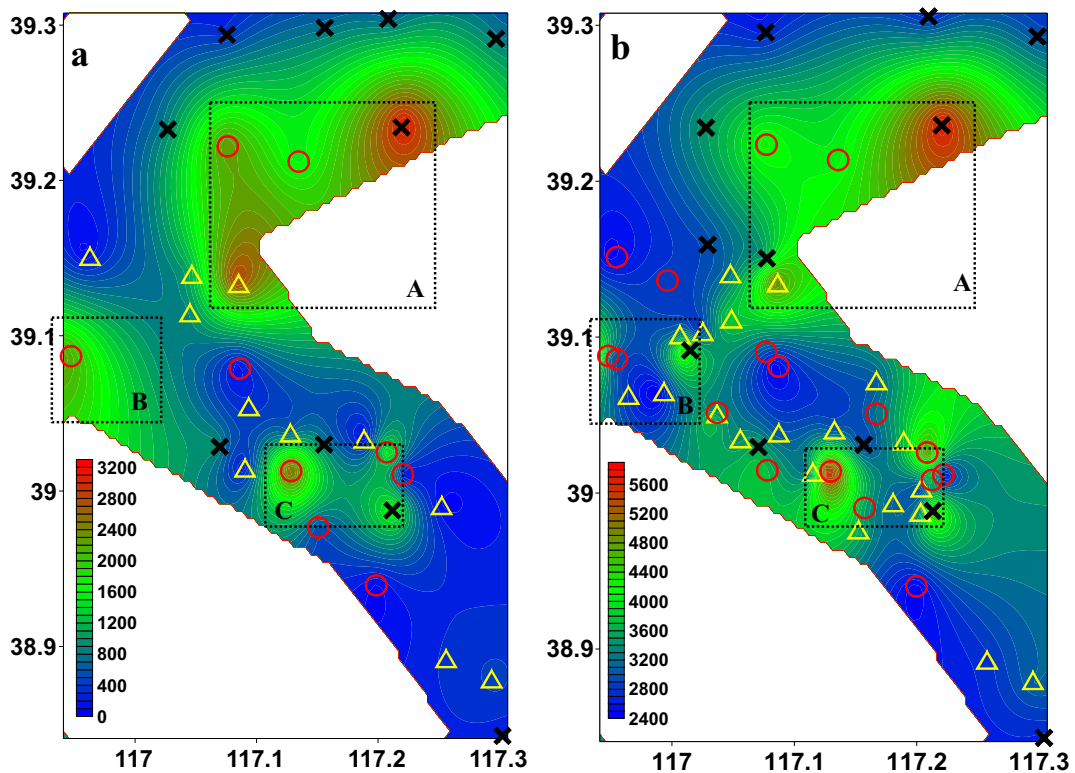
## Results and discussion

### Characterization of the PAHs in farmland soils

The 16 PAHs were detected in all 30 farmland soil samples, and the total PAH contents ( $\Sigma_{16}$ PAHs) (Table S1) ranged from 58.53  $\mu$ g/kg to 3137.90  $\mu$ g/kg dry weight (dw) with a mean value of 941.27  $\mu$ g/kg dw. The content of the  $\Sigma_{16}$ PAHs in this study is comparable to the contents in the regions near Beijing (16–3884  $\mu$ g/kg) (Ma et al. 2005), Delhi (830–3880  $\mu$ g/kg) (Agarwal et al. 2009), and Tehran (130–3920  $\mu$ g/kg) (Bayat et al. 2015), and the content is slightly higher than the content in the southern pluvial regions in China (Shantou Special Economic Zone, 22.1–1256.9  $\mu$ g/kg (Hao et al. 2007)). According to the PAH contamination classification by Maliszewska-Kordybach (Maliszewska-Kordybach 1996), 23 of the 30 sites contained contaminated soil ( $\geq 200$   $\mu$ g/kg). Among these, 9 sites were heavily contaminated ( $> 1000$   $\mu$ g/kg), 7 sites were contaminated (600–1000  $\mu$ g/kg), and 7 sites were weakly contaminated (200–600  $\mu$ g/kg).

The spatial distributions of the  $\Sigma_{16}$ PAHs in the farmland soils are shown in Fig. 2a. Clearly, the PAH contents have a decreasing trend away from the city downtown, which was similar to previous reports (Wang et al. 2007; Chen et al. 2015b). The high values of the heavily contaminated areas were mainly located in the regions adjacent to the downtown (region A, 1519.40–3137.90  $\mu$ g/kg), the intersections of highways (region B, 2290.90  $\mu$ g/kg), and the industrial district (region C, 1656.65–2748.26  $\mu$ g/kg). Usually, these regions are often consistent with combustion, industry, and traffic emissions (Marusenko et al. 2011; Kwon and Choi 2014). In the regions farther from the downtown and industrial areas, the PAH contents ranged from 58.53 to 442.77  $\mu$ g/kg, which indicated non-contaminated or weakly contaminated soils (Maliszewska-Kordybach 1996). The spatial pattern indicated that the human activities of combustion, industry manufacturing, and traffic emissions are likely the main emission sources of soil PAHs in the Tianjin regions. Naturally, atmospheric deposition and a small amount of biomass combustion are major paths for PAHs to reach soils in remote rural areas because the rainfall and runoff in this region are low.

In this paper, the contents of the PAHs with different numbers of aromatic rings were compared in the three studied soils to determine the difference

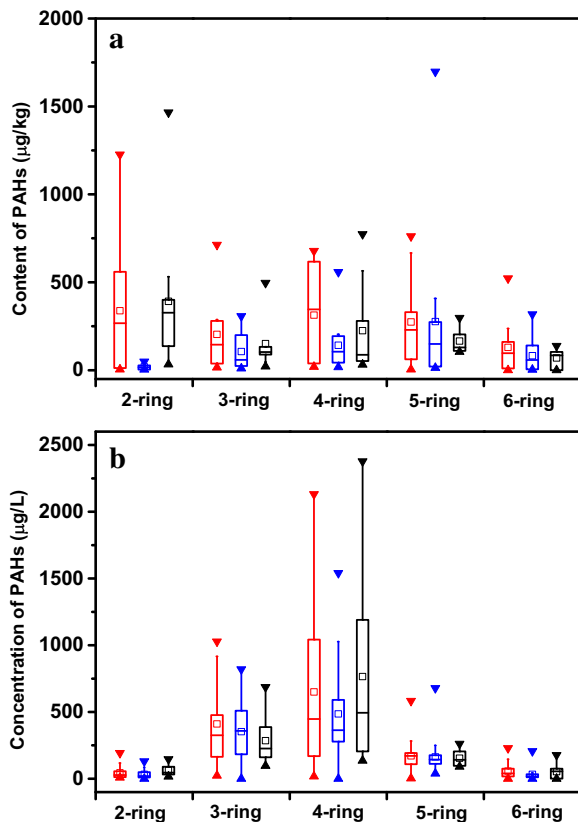


**Fig. 2** Spatial patterns of  $\Sigma_{16}$ PAH in **a** soil ( $\mu\text{g}/\text{kg}$ ) and **b** runoff samples ( $\mu\text{g}/\text{L}$ ) (made by Surfer software 8.0)

in the soil PAH characteristics in the classified vegetation types. The  $\Sigma_{16}$ PAHs in soil are  $1258.57 \pm 1069.36 \mu\text{g}/\text{kg}$ ,  $624.70 \pm 819.71 \mu\text{g}/\text{kg}$  and  $1003.93 \pm 853.04 \mu\text{g}/\text{kg}$  for garden, cropland, and dryland soils, respectively. In total, the proportions of PAHs with 2 to 6 rings were  $21 \pm 20\%$ ,  $19 \pm 8\%$ ,  $24 \pm 10\%$ ,  $27 \pm 13\%$ , and  $9 \pm 7\%$ , respectively. The PAH contents in garden soil were much higher than those in the cropland and dryland soils (Fig. 3a), which indicated that the former is more polluted with PAHs. In the past several decades, large amounts of wastewater have been used to irrigate agriculture soils in the Tianjin region (TEPB 1996; Wang et al. 2002). Compared with the cropland and dryland soils, the wastewater irrigation frequency for garden soils is much higher because of the need for greening. The contents of individual PAHs were shown in Table S2 and Fig. S1a. For individual PAHs, the most abundant compound was Nap ( $21 \pm 20\%$ ) and it was followed by BbF ( $10 \pm 6\%$ ), Phe ( $9 \pm 4\%$ ), Fla ( $9 \pm 8\%$ ), and BkF ( $7 \pm 5\%$ ).

#### Source identification and risk assessment of the PAHs in soil

The PAH diagnostic ratios of Fla/(Fla + Pyr) and BaA/(BaA + Chr) have been proposed as useful tools to determine the possible contamination sources, e.g., petroleum and combustion origins (Ping et al. 2007; Agarwal et al. 2009). A ratio of Fla/(Fla + Pyr) < 0.4 indicates a petroleum input, a ratio between 0.4 and 0.5 represents fossil fuel (vehicle and crude oil) combustion, and a ratio > 0.5 indicates coal, wood, and grass combustions (Yunker et al. 2002). In this study, approximately 80% of the Fla/(Fla + Pyr) ratios (0.06–0.91) were > 0.5 (Fig. 4), which indicated the dominant contribution of biomass combustion to the soil PAH contamination in the Tianjin region. For garden and dryland soil, all of the Fla/(Fla+Pyr) ratios were > 0.5, indicating the entire source of biomass combustion for PAHs. Over 60% of the Fla/(Fla+Pyr) ratios for the cropland was < 0.4, which indicated the dominant contribution to the cropland soil PAH contamination is petroleum input.



**Fig. 3** The level of PAHs with different rings in **a** soil samples and **b** runoff samples. The content/concentration of 25th and 75th percentiles is represented by boxes and the median content/concentration is represented by middle lines. In the figure, “□” represents mean content/concentration value. The whiskers extending from the box are the lowest and highest non-outlier values. “▲” and “▼” represent the lowest and highest values, respectively. The columns remarked red, green, and blue represent values of PAHs in garden, cropland, and dryland, respectively

For BaA/(BaA + Chr), a ratio < 0.2 represents a petroleum origin, a ratio > 0.35 indicates a combustion origin, and a ratio from 0.2 to 0.35 denotes a mixed origin. Here, 50% of the BaA/(BaA + Chr) ratios (0.09–0.73) were higher than 0.35, and 40% of the ratios were between 0.2 and 0.35 (Fig. 4), which suggested that the soil PAHs were mainly from biomass combustion and petroleum combustion (Agarwal et al. 2009). With respect to the vegetation types, the garden soil PAHs mainly originated from combustion sources, while the cropland and dryland soil PAHs were from mixed sources of petroleum and combustion. Straw burning (Chen et al. 2015a) and the energy composition in the Tianjin region contributed to the dominance of biomass combustion as the source of soil PAHs.

Risk assessment of soil PAHs was performed using the total contents of 7 potential carcinogenic PAHs, BaA, Chr, BbF, BkF, BaP, DbA, and InP (Hopkins 1991; Chen and Chen 2011). The total contents of the 7 CPAHs ( $\Sigma_7$ CPAHs) varied from 3.35 to 2398.54  $\mu\text{g}/\text{kg}$  (a mean value of 366.10  $\mu\text{g}/\text{kg}$ ) (Table S1) and accounted for 8–76% of  $\Sigma_{16}$ PAH. The fractions of  $\Sigma_7$ CPAHs were  $35 \pm 17\%$ ,  $48 \pm 14\%$ , and  $32 \pm 14\%$  in the garden, cropland, and dryland soils, respectively. The spatial pattern of the  $\Sigma_7$ CPAHs (Fig. S2a) was consistent with that of the  $\Sigma_{16}$ PAHs, which indicated that the high-risk areas were consistent with the areas suffering from heavy PAH contamination. To further evaluate the ecological risk, the total toxic BaP equivalent ( $\text{TEQ}^{\text{carc}}$ ) for the  $\Sigma_7$ CPAHs was also calculated and discussed (Peters et al. 1999). The equation (Eq. 1) for  $\text{TEQ}^{\text{carc}}$  can be expressed as the following (Savinov et al. 2003; Chen and Chen 2011).

$$\text{Total TEQ}^{\text{carc}} = \sum_i C_i \times \text{TEF}_i^{\text{carc}} \quad (1)$$

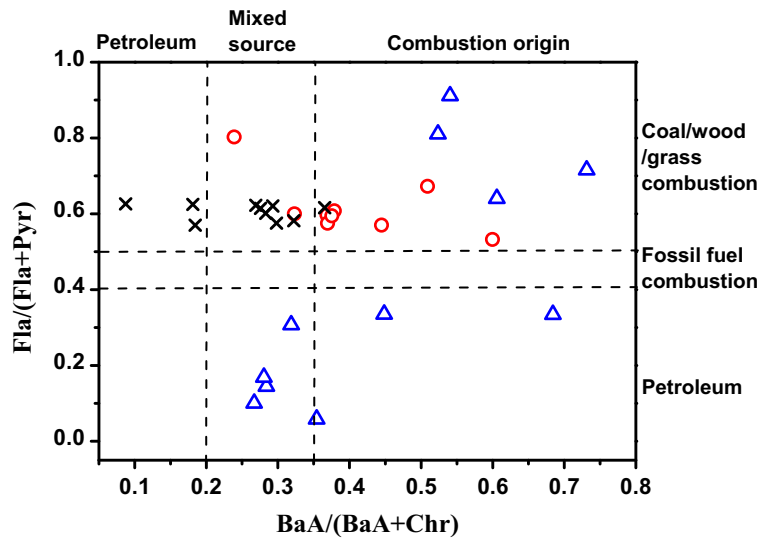
where  $C_i$  is the content of each CPAH ( $\mu\text{g}/\text{kg}$ ) and  $\text{TEF}_i^{\text{carc}}$  is the toxic factor of a CPAH versus BaP, which was abbreviated by the toxic equivalency factor. Here, the  $\text{TEFs}^{\text{carc}}$  values used for BaA, Chr, BbF, BkF, BaP, DbA, and InP were 0.1, 0.001, 0.1, 0.01, 1, 1, and 0.1, respectively (USEPA 1993; Li et al. 2015).

The total  $\text{TEQ}^{\text{carc}}$  in the farmland soil varied from 3.00 to 571.57  $\mu\text{g}/\text{kg}$ -BaP<sub>eq</sub> with a mean value of 99.06  $\mu\text{g}/\text{kg}$ -BaP<sub>eq</sub> (Table S1 and Fig. S2b), which was lower than that of Shanghai in China (186–892  $\mu\text{g}/\text{kg}$ -BaP<sub>eq</sub>) (Jiang et al. 2009) and comparable to that of Delhi in India (45.64–387.13  $\mu\text{g}/\text{kg}$ -BaP<sub>eq</sub>) (Agarwal et al. 2009). The result suggests that the carcinogenic potency of PAHs should be given more attention due to the potential environmental risk in the study area. For the individual CPAH, their contributions to the total  $\text{TEQ}^{\text{carc}}$  were in the following order: BaP ( $56.3 \pm 25.7\%$ ), DbA ( $26.2 \pm 25.7\%$ ), BbF ( $10.0 \pm 5.8\%$ ), BaA ( $3.8 \pm 4.1\%$ ), InP ( $3.0 \pm 3.0\%$ ), BkF ( $0.6 \pm 0.3\%$ ), and Chr ( $0.05 \pm 0.03\%$ ).

#### Characterization of the PAHs in the surface runoff

The concentrations of the  $\Sigma_{16}$ PAH in the surface runoff varied between 146.58 and 3636.59  $\mu\text{g}/\text{L}$  with an average value of 1222.69  $\mu\text{g}/\text{L}$ . The values were several orders of magnitude higher than those found in river and marine water columns, i.e., the Tonghui River

**Fig. 4** Diagnostic ratios of Fla/(Fla + Pyr) against BaA/(BaA + Chr). Horizontal and vertical lines are the thresholds for each emission source. Symbols  $\circ$ ,  $\Delta$ , and  $\times$  represent garden, cropland, and dryland soils, respectively.

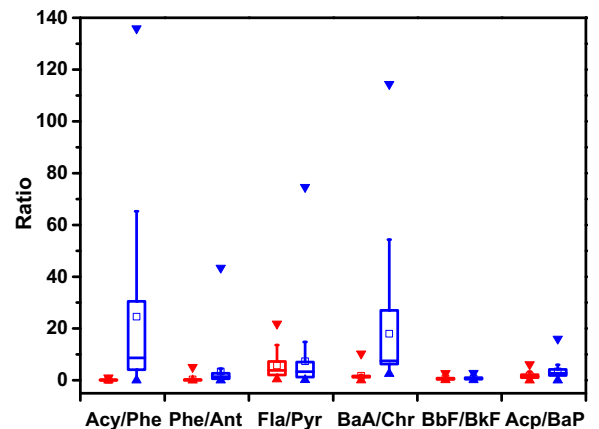


(192.5–2651 ng/L) (Zhang et al. 2004); Daliao River (946.1–13,448.5 ng/L) (Guo et al. 2007); Pearl River (987.1–2878.5 ng/L); Macao harbor, China (944.0–6654.6 ng/L) (Luo et al. 2004); Kisumu City Bay of Winam Gulf, Lake Victoria-Kenya (3.32–55.8  $\mu\text{g/L}$ ) (Kwach et al. 2009); and Ligurian Sea, Western Mediterranean (1–60  $\mu\text{g/L}$ ) (Pane et al. 2005). The much higher concentrations indicated that runoff caused by rainfall is a critical mechanism by which PAHs transfer from soil to aquatic systems (Chen et al. 2004; DiBlasi et al. 2009).

Similar to the spatial patterns of the soil PAHs, the  $\Sigma_{16}$ PAHs in the runoff also had a decreasing trend moving away from the downtown (Fig. 2b). The higher  $\Sigma_{16}$ PAH values were located in the industrial and urban areas (RG15, 3636.59  $\mu\text{g/L}$ ; RD5, 3542.30  $\mu\text{g/L}$ ; RC2, 2850.42  $\mu\text{g/L}$ ), and the lower values were adjacent to villages or residential areas (WC7, 147.58  $\mu\text{g/L}$ ; WG8, 216.43  $\mu\text{g/L}$ ; WG17, 217.13  $\mu\text{g/L}$ ; WG3, 247.80  $\mu\text{g/L}$ ). These results indicated that rainfall runoff is an effective pathway for soil PAHs to move into aqueous systems (Chen et al. 2004; DiBlasi et al. 2009). Meanwhile, the consistency of PAHs in soils and runoffs also suggested that the leaching behaviors of PAHs in a larger region mainly depend on the contents of the soil PAHs, but soil organic matter has also been speculated to be one of the most important factors affecting PAH leaching in simulation experiments (Zheng et al. 2012).

For the individual PAH components, Acy, Chr, Fla, and BaA were the dominant species in the runoff water samples (Fig. S1b), and their contributions were  $17.25 \pm 14.64\%$ ,  $16.51 \pm 10.12\%$ ,  $15.69 \pm 5.97\%$ , and

$10.19 \pm 6.35\%$ , respectively. According to the number of aromatic rings, the concentrations of the 2–4-ring PAHs (nd-981.11  $\mu\text{g/L}$ ) were higher than those of the 5–6-ring PAHs (nd-366.02  $\mu\text{g/L}$ ) (Fig. 3b). The results can be attributed to the lower levels of the 5–6-ring PAHs in soil (Fig. 3a), the stronger adsorption between 5- and 6-ring PAHs and soil organic matter (Yan et al. 2012), and the higher solubility of 2–4-ring PAHs (Gan et al. 2009; Clément et al. 2015).



**Fig. 5** Ratios of contents/concentrations of several individual PAHs in soil and runoff samples. Acy/Phe means the ratio of concentration of Acy and Phe, and the colors of red and blue columns present soil and runoff, respectively. The ratio of 25th and 75th percentiles is represented by boxes and the median ratio is represented by middle lines. In the figure, “ $\square$ ” represents mean ratio value. The whiskers extending from the box are the lowest and highest non-outlier values. “ $\blacktriangle$ ” and “ $\blacktriangledown$ ” represent the lowest and highest values. The columns with red and blue represent ratios of PAHs in soil and runoff samples, respectively

## Leaching behaviors of the individual PAHs

Laboratory experiments have noted that the leaching behaviors of soil PAHs are closely related to the solubility and adsorption of the individual PAHs onto soil organic matter (Jonker and Koelmans 2002; Zheng et al. 2012; Luo et al. 2015). Here, the leaching behaviors of the individual PAHs caused by rainfall were also studied using the ratios of some of the PAH pairs in the soil and runoff samples (Fig. 5) and the enrichment factors of individual PAHs at the same sampling sites (Table S3).

For the Acy/Phe, Acp/BaP, and Fla/Pyr pairs, their ratios in the runoff (24.57, 3.40, and 17.95) were much higher than those in the soil (0.16, 0.32, and 1.74), which indicated Acy, Acp, and Fla more easily release into solutions than Phe, BaP, and Pyr. For the BaA/Chr pairs, the ratios in the soil and runoff were 0.73 and 0.76, respectively, which suggested both have similar leaching behaviors during the rainfall process. For the Phe/Ant and BbF/BkF pairs, their ratios in the runoff (7.35 and 3.37, respectively) were slightly higher than those in the soil (5.71 and 1.85, respectively), which suggested that the solubilities of Ant and BkF are better than those of Phe and BbF. Overall, Acy, Acp, and Fla prefer to transfer into water systems.

The enrichment ratio (ER) representing the leaching capacity of the PAHs was calculated using Eq. 2 (Zheng et al. 2012).

$$ER = \frac{C_r}{C_s} \quad (2)$$

where ER,  $C_r$ , and  $C_s$  are the enrichment ratio of the PAHs in the runoff and soil and the concentrations of the specified PAHs in the runoff and soil, respectively. The water-soil distribution coefficient ( $K_d$ ) is a key parameter in adsorption characteristics and migration simulations of substances. In this study, the ER values of the  $\Sigma_{16}$ PAH ranged from 0.77 to 3.64 (except SC8), and these values were lower than the  $K_d$  value in estuarine water and suspended particular matter ( $0 < \log K_d < 6$ ) (Wang et al. 2016). The lower ER values corresponded well with the unbalanced state of the PAHs due to the transitory rainfall scour.

For the individual PAHs, most of the low molecular weight (LMW) PAHs (2–4 rings), excluding Nap ( $1.16 \pm 1.19$ ), Phe ( $0.46 \pm 0.70$ ), and Ant ( $0.74 \pm 0.44$ ), showed high ER values, e.g., Acy ( $55.24 \pm 177.29$ ), Acp ( $34.50 \pm 78.35$ ), BaA

( $7.44 \pm 3.91$ ), Chr ( $7.06 \pm 3.00$ ), and Fla ( $6.79 \pm 8.78$ ) (Table S3). The results indicated these LMW PAHs are prone to transfer into runoff during rainfall processes (Zheng et al. 2012), which was consistent with the results shown in Fig. 5. The poor leaching behaviors of the high molecular weight (HMW) PAHs (5–6 rings) may be due to the strong hydrophobicity of the HMW PAHs combined with absorption on SOM (Readman et al. 1984).

For the different vegetation types, there were also some differences in the PAH profiles with higher ER values (Table S3). They were Acy ( $27.17 \pm 27.65$ ), Acp ( $24.51 \pm 46.61$ ), BaA ( $7.74 \pm 4.64$ ), Chr ( $7.51 \pm 2.77$ ), and Flu ( $3.37 \pm 3.77$ ) in the garden soil; Acy ( $139.27 \pm 328.95$ ), Acp ( $91.66 \pm 134.81$ ), Fla ( $17.14 \pm 10.51$ ), BaA ( $6.58 \pm 5.35$ ), and BaP ( $6.56 \pm 15.58$ ) in the cropland soil; and Acy ( $17.95 \pm 0.00$ ), BaA ( $7.80 \pm 0.00$ ), Chr ( $7.26 \pm 1.25$ ), Acp ( $6.38 \pm 0.00$ ), and Flu ( $3.31 \pm 0.00$ ) in the dryland soil. Both the use of wastewater and different sources of PAHs can lead to variations in the ER values.

## Conclusions

In this paper, the levels, spatial distributions, and composition profiles of PAHs in soil and rainfall runoff were determined to study their pollution characteristics and leaching behaviors from soil into runoff. The farmland soils in the Tianjin region had moderate levels of PAHs. Biomass and petroleum combustion pollution were the likely major sources. The leaching behaviors of the PAHs mainly depend on their chemical properties. LMW PAHs with higher solubilities are more prone to be released from soil during rainfall events than HMW PAHs are. In summary, this study provides field data for reference and comparison with simulated experiments. However, due to the difficulty of sampling soils and runoffs in a larger area during rainfall events, more studies are needed to further identify the factors affecting the leaching behaviors of soil PAHs.

**Acknowledgements** This study was supported by the National Natural Science Foundation of China (21477138), the State Key Laboratory Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (KF2016-12), and the China Postdoctoral Science Foundation (2016 M602210).



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