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ORIGINAL PAPER

Polycyclic aromatic hydrocarbons in farmland soils around main reservoirs of Jilin Province, China: occurrence, sources and potential human health risk

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Abstract Study on the occurrence, sources and potential human health risk of polycyclic aromatic hydrocarbons in farmland soils around reservoirs is of great significance for the people drinking water security. In the present study, representative farmland soil samples around main reservoirs of Jilin Province, China, were investigated for 16 PAHs. The total concentrations of 16 priority PAHs in 32 farmland soil samples ranged from 602.12 to 1271.87 ng/g, with an arithmetic average of 877.23 ng/g, and the sum of seven carcinogenic PAH concentrations ranged from 30.07 to 710.02 ng/g, with a mean value of 229.04 ng/g. The 3-ring and 4-ring PAHs were major exist and account for 45.78 and 32.03%, respectively. Non-cancer and cancer risk of pollutants were calculated, and the results indicate that the complex PAHs in farmland soils were not considered to pose significant health effects. The isomer ratios Fla/(Fla + Pyr) and BaA/(BaA + Chr) show that the PAHs in soils were generally derived from biomass and coal combustion.

Keywords Polycyclic aromatic hydrocarbons (PAHs) · Reservoirs · Farmland soils · Human health risk

Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of two or more fused aromatic carbon rings, are bioaccumulative and hardly degradable in the environment. They enter the environment through natural and anthropogenic processes (Zhang et al. 2016; Bragato et al. 2012; Bouloubassi et al. 2012). They are ubiquitous environmental pollutions that caught much attention in recent years due to their persistence, bioaccumulation and high toxicity (carcinogenic, teratogenic and mutagenic) in the environment (Al-shaarawy et al. 2016; White et al. 2016; Kaur et al. 2013; Sarkar and Khillare 2013; Gu et al. 2016). They are widespread in atmosphere, water sediment and soil environment on account of their persistence and long-range transport capabilities (Yu et al. 2016; Liu et al. 2012). In 1979, 16 PAHs were included in the list of priority pollutants from 129 kinds of priority pollutants by the US Environmental Protection Agency (USEPA) (Kusmierz et al. 2016; Liu et al. 2016). Among these 16 PAHs, seven of them were carcinogenic. The seven carcinogenic PAHs were included into the blacklist of priority controlled pollutants in China.

Soil is the primary environmental reservoir and sink for semi-volatile organic compounds. PAHs can be absorbed by soil organic matter (Yin et al. 2008), and PAHs in soil can enter water and atmosphere through evaporation and surface runoff and then cause

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secondary pollution (Sarria-Villa et al. 2016). PAHs in soil are mainly from atmospheric deposition, waste water irrigation and sludge for agricultural. PAHs are fat-soluble, and they can enter the food chain via root uptake, accumulate in human body through food chain and become a potential carcinogen (Yan et al. 2016). PAHs can also be dispersed by surface soil emissions and dust production, which is another way of exposure to PAHs (Mai et al. 2003).

Xinlicheng reservoir, Shitoukoumen reservoir, Shuangyang reservoir and Xingxingshao reservoir are the main source of water in Jilin Province, China. Pollutants in the surrounding soil may contaminate the surface drinking water source through rainfall and surface runoff. It is of great significance to research the soil contamination of the region. The objectives of the present study were to investigate the contamination level of PAHs, to evaluate the potential human health risk in the study area and to identify the possible source of PAHs to the farmland soil. The result of this research may be useful for the local government in controlling and alleviating PAH contamination.

Materials and methods

Study area and soil sampling

The study area is located in the middle of Jilin Province, China, around the Xinlicheng reservoir, Shitoukoumen reservoir, Shuangyang reservoir and Xingxingshao reservoir (Fig. 1). Those reservoirs are utilized in the irrigation of farmlands as well as in fish farming. Xinlicheng reservoir and Shitoukoumen reservoir are the primary water source for local residents of Changchun City, the capital of Jilin Province. Those reservoirs are surrounded by abundant farmland which may influence the environmental quantity of reservoir. To evaluate the PAH pollution levels, 32 farmland soil samples (0–20 cm) were collected with a stainless steel shovel in April 2016 from 32 villages around those reservoirs. All the sample sites were recorded using a handheld Global Positioning System (GPS). For each sampling site, five subsamples within an area of 100 m^2 were mixed to one composite sample. After being sent to the laboratory, plant tissue and stones were removed and air-dried at room temperature, sieved through 2-mm mesh and stored at −20 °C for further analyses. All the soil samples were extracted and analyzed in quintuplicates (Wang et al. 2013).

Chemicals and reference materials

Copper power, dichloromethane (DCM), acetone and n-hexane were supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Mix standard solution of 16 priority PAHs (100 ug/mL in dichloromethane for each) was obtained from the National Standard Material Center (Beijing, China). The standard solutions included naphthalene (Nap) (2-ring), acenaphthylene (Acy) c, acenaphthene (Ace) (3-ring), fluorene (Flo) (3-ring), phenanthrene (Phe) (3-ring), anthracene (Ant) (3-ring), fluoranthene (Fla) (4-ring), pyrene (Pyr) (4-ring), benz[a]anthracene (BaA) (4-ring), chrysene (Chr) (4-ring), benzo[b]fluoranthene (BbF) (5-ring), benzo[k]fluoranthene (BkF) (5-ring), benzo[a]pyrene (BaP) (5-ring), dibenz[a,h]anthracene (DahA) (5-ring), indeno[1,2,3-cd]pyrene (IcdP) (6-ring) and benzo[g,h,i]perylene (BghiP) (6-ring). They are dominantly lipophilic in nature and have been classified into two subgroups which are the low molecular weight (LMW) (two or three fused rings) and high molecular weight (HMW) (four or more fused rings) (Ogbonnaya et al. 2017). The total concentrations of the 7 carcinogenic PAHs include BaA, Chr, BbF, BkF, BaP, IcdP and DahA) (Wang et al. 2012). All solvents used were of chromatographic grade.

Determination of PAH content

Detailed procedures for determination of PAH are described in our previous study (Chen et al. 2016). 5 g of soil samples mixed with 5 g of copper power was extracted in ultrasonic bath with dichloromethane (DCM)/acetone (1:1/v:v). The extracts were cleaned up by the silica chromatography columns (Cleanert Florisil 1000 mg/6-mL cartridge, Agela Technologies Inc., USA), respectively. After that, the columns were eluted with *n*-hexane/DCM (7:3/v:v), then concentrated to near dryness with a rotary vacuum evaporation apparatus and re-dissolved in 10 ml of n-hexane. The elutes were reduced to 1 ml with a rotary evaporator (RE-52AA, Shanghai Yarong Inc., Shanghai, China) and transferred to 2-ml capped Teflon-lined vials for gas chromatograph (GC) analysis.

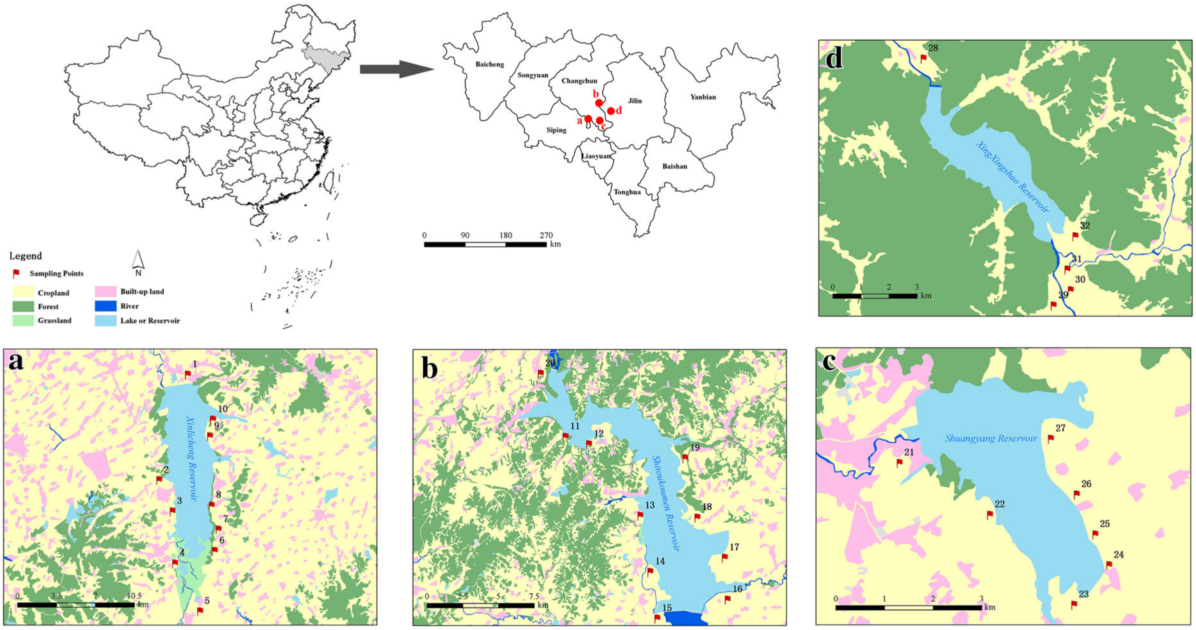


Fig. 1 Location of the sampling sites

Sixteen PAHs were analyzed on a GC equipped with a flame ionization detector (Clarus 680, PerkinElmer Inc., USA). The HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent, USA) was used to separate target compounds. Helium (99.999%) was used as the carrier gas, with a constant flow of 1 ml/min. The GC oven temperature was initially set at 50 °C (2 min), then increased at 19 °C/min to 200 °C (2 min), then to increase at 4.5 °C/min to 240 °C (2 min) and finally increased at 2.5 °C/min to 300 °C (5 min).

Quality control

All analytical data were monitored with strict quality control. The external standard method was used with a 16 PAH reference material mixture, and the correlation coefficients for calibration curves were all higher than 0.99. Recoveries of 16 PAHs ranged from 79 to 111%, whereas the respective relative standard deviations ranged from 6.9 to 14.1%. The results of recoveries and RSDs are acceptable according to USEPA methods (USEPA 1984). Detection limits for 16 PAHs were 0.364–1.087 ng/g for soil samples. Method blanks operation of laboratory showed no detectable amounts of PAHs. All results are expressed on a dry weight basis.

Risk assessment

In order to estimate the human health risk of soil PAHs, the non-cancer and carcinogenic risk of pollutants was calculated according to the methods recommended by the USEPA. In this study, the exposure of the local population was assumed by two major pathways: incidental ingestion and dermal contact. The average daily intake (ADI) (mg/kg/day) of a pollutant via soil ingestion and dermal contact as exposure pathways can be calculated by using Eqs. (1) and (2):

$$\mathrm{ADI}_i = (\mathrm{CS} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{CF})/(\mathrm{BW} \times \mathrm{AT}) \tag{1}$$

$$\mathrm{ADI}_d = (\mathrm{CS} \times \mathrm{SA} \times \mathrm{AF} \times \mathrm{EF} \times \mathrm{ED} \times \mathrm{DAF} \times \mathrm{CF})/(\mathrm{BW} \times \mathrm{AT}) \tag{2}$$

where CS is the chemical concentration (mg/kg); IR is the ingestion rate (mg/day); EF is the exposure frequency (day/year); CF is a conversion factor (10^{-6} kg/mg); SA is the exposed skin surface area (4200 cm^2); AF is the adherence factor (0.1 mg/cm^2day); DAF is the dermal absorption factor (0.13 unitless). BW is the body weight of the exposed individual (64.9 kg); and AT is the time period over which the dose is averaged (day).

Non-cancer risk is typically characterized by the hazard index (HI) which are summed the ingestion and dermal adsorption pathway for PAHs. Because no dermal reference dose has been established yet for some of the pollutants studied here, this value was assumed to be equal to the oral reference dose (RfD). If HI values are smaller than 1, no risk of non-carcinogenic effects is believed to occur, whereas HI values are higher than 1 indicated a probability of adverse health effects, and probability increases with the increase in HI values. A hazard index (HI) approach has been applied (Pongpiachan et al. 2017). HI can be estimated using Eq. (3):

$$\mathrm{HI} = \sum (\mathrm{DI}/\mathrm{RfD}) \tag{3}$$

where RfD is the chronic reference dose for the PAHs (mg/kg day) (Table 1).

Cancer risks (CRs) were assessed by multiplying the predicted slope factor. The slope factor (SF) is composed of the oral SF for ingestion and dermal contact. If the CR values are higher than 1×10^{-4}, it means unacceptable. CR values below 1×10^{-6} are not considered to pose significant health effects. CR values between 1×10^{-4} and 1×10^{-6} are generally considered an acceptable range. Cancer risk (CR) can be estimated using Eq. (4):

$$\mathrm{CR} = \mathrm{SF} \times \mathrm{ADI} = \mathrm{SF} \times (\mathrm{ADI}_i + \mathrm{ADI}_d) \tag{4}$$

where SF is slope factor (kg day/mg) (Table 1).

Source apportionment

Isomer pair ratios were used to explain the possible sources of PAHs in the soil of the study area. PAHs produced from different sources would exhibit different molecular compositions. Usually, the petrogenic sources are richer in low molecular weight (LMW) PAHs and the pyrogenic sources contain greater percentage of high molecular weight (HMW) PAHs (Boll et al. 2008). It is often used to identify whether the combustion or petroleum source is dominant (Tobiszewski and Namiesnik 2012).

The environmental fate and transport capability are dependent on the molecular weight profile of PAHs. The isomer ratios Fla/(Fla + Pyr) and BaA/(BaA + Chr) can discriminate petroleum combustion from other kinds of combustion. A Fla/(Fla + Pyr) < 0.4 indicates a petroleum derivation. Fla/(Fla + Pyr) > 0.5 indicates biomass and coal combustion sources, and the ratio in the range of 0.4 and 0.5 indicates liquid fossil fuel combustion. In addition, an Ant/(Ant + Phe) < 0.1 indicates a petroleum derivation, while an Ant/(Ant + Phe) > 0.1 implies biomass and coal combustion sources. BaA/(BaA + CHR) and IcdP/(IcdP + BghiP) were also used to identify the sources of PAHs. An IcdP/(IcdP + BghiP) < 0.20 indicates a petroleum source; IcdP/(IcdP + BghiP) > 0.50 indicates combustion of biomass and coal sources, and ratios between 0.20 and 0.50 indicate petroleum combustion. Moreover, a BaA/(BaA + CHR) below 0.2 indicates a petroleum source, while ratios between 0.2 and 0.35 indicate the

Table 1 RfD of the non-carcinogenic PAHs and SF of the carcinogenic PAHs (Nisbet and LaGoy 1992)

Non-carcinogenic PAHs	Incidental ingestion (mg/kg day)	Dermal contact (mg/kg day)	Carcinogenic PAHs	Incidental ingestion (kg day/mg)	Dermal contact (kg day/mg)
Nap	0.02	0.02	BaA	0.73	3.747
Acy	0.06	0.06	Chr	0.073	0.3747
Ace	0.06	0.06	BbF	0.73	3.747
Flo	0.04	0.04	BkF	0.73	3.747
Phe	0.03	0.03	BaP	7.3	37.47
Ant	0.3	0.3	IcdP	0.73	3.747
Fla	0.04	0.04	DahA	7.3	37.47
Pyr	0.03	0.03			
BghiP	0.03	0.03			

liquid fossil fuel combustion, and values > 0.35 indicate the combustion of coal and biomass (Yunker et al. 2002).

Results and discussion

Contamination level

In this study, 16 USEPA priority PAHs (16 PAHs) in farmland soils around main reservoirs are presented in Table 2. The total concentrations of 16 PAHs ranged from 602.12 to 1271.87 ng/g (dry weight) with a mean concentration of 877.23 ng/g. The concentrations of 7 carcinogenic PAHs (7 PAHs) ranged from 30.07 to 710.02 ng/g with a mean concentration of 229.04 ng/g. The measured total concentration for the 7 carcinogenic PAHs in soil was lower than the target value set by Dutch Government for unpolluted soil (475 ng/g dry weight for 7 carcinogenic PAHs) (Sun et al. 2013). Seven PAH levels accounted for 10–52% of 16 PAHs, indicating the different proportions of 7 PAHs present in 16 PAHs. Among these PAHs, the percentages of 2-, 3-, 4-, 5- and 6-ring PAHs to the 16 PAHs were 4.17, 45.78, 32.03, 10.04 and 7.99%, respectively. The mean concentration of lower molecular weight 2–3-ring PAHs (L-PAHs) was 438.14 ng/g, which accounting for 49.95% of the total PAHs. The concentration of higher molecular weight 4–6-ring PAHs (H-PAHs) was 439.09 ng/g, accounting for 50.05% of the total PAHs. Significant levels of 3-ring Phe and 4–5-ring PAHs in soil have been previously reported (Zhang et al. 2011). To compare with other agricultural soils of China, the contribution of L-PAHs of this research was similar to that of Dalian (50%, Wang et al. 2007) and Xinzhou (59.7%, Zhao et al. 2014), lower than that of Guangzhou and Shenzhen (76%, Cai et al. 2008), and higher than that of Nanjing (15%, Wang et al. 2015a, b) and Beijing (30–34%, Ma et al. 2015). In this study, the proportion of 3-ring and 4-ring PAHs is the highest while the proportion of 5-ring and 6-ring PAHs is low. Since 5-ring and 6-ring PAHs have lower saturated vapor pressure values, they are ready to bind to particles and can be transported only a short distance. In contrast, 3-ring and 4-ring PAHs in the vapor phase can undertake long-range transport resulting from their higher saturated vapor pressure (Zhang and Chen 2017). Coefficients of variation (CV) values range from 37 to 124% for individual PAHs in soil samples, and the

Table 2 PAH concentrations in farmland soils around main reservoirs of Jilin (ng/g)

Compound	Min	Max	Mean	Median	SD	CV
Nap	4.11	117.60	36.58	25.55	30.37	0.83
Acy	6.76	244.05	60.51	45.54	59.93	0.99
Ace	7.15	292.44	84.71	70.71	74.07	0.87
Flo	6.78	324.80	60.97	53.37	55.10	0.90
Phe	8.75	427.42	148.48	133.69	110.49	0.74
Ant	4.43	159.31	46.89	41.04	26.43	0.56
Fla	1.16	323.60	78.69	21.56	89.51	1.14
Pyr	31.95	191.15	88.13	87.73	32.79	0.37
BaA	17.63	145.90	64.60	54.76	35.01	0.54
Chr	2.35	156.73	49.53	47.66	44.76	0.90
BbF	1.21	98.17	20.90	13.20	20.57	0.98
BkF	1.09	33.45	12.84	12.35	7.09	0.55
BaP	1.07	99.10	14.67	10.42	18.22	1.24
DahA	5.67	109.96	39.63	31.64	31.32	0.79
IcdP	1.05	66.71	26.87	24.38	19.00	0.71
BghiP	7.54	165.70	43.23	28.42	38.77	0.90
16 PAHs	602.12	1271.87	877.23	833.37	187.01	0.21
L-PAHs	37.98	1565.62	438.14	369.89	356.41	0.81
H-PAHs	70.72	1390.47	439.09	332.10	337.03	0.77
7 PAHs	30.07	710.02	229.04	194.38	175.97	0.77

SD denotes standard deviation, *CV* denotes coefficients of variation high data indicate that PAH concentrations are greatly connected with the presence of localized sources of PAHs. Overall, L-PAHs are more volatile and mainly exist in the gas phase and may be easy to get photochemical degradation during transport, while H-PAHs are largely in the particle phase and easy to be accumulated in soil through dry and wet deposition of ambient particles, and will stay in the soil under the processes of absorption, adsorption and sequestration (Zhang et al. 2013).

Compared with the other studies all over the world (Table 3), the mean concentration of 16 PAHs in this study was lower than the concentrations reported in soils of the coal stockpile sites in South Kalimantan (11,720 ng/g, Mizwar et al. 2016), agricultural soil of Changzhi (917 ng/g, Liu et al. 2016), urban soil of Beijing (1228.1 ng/g, Peng et al. 2011) and agricultural soil of Delhi (1906 ng/g, Agarwal et al. 2009). However, the mean concentration of 16 PAHs in this study was higher than concentrations reported in agricultural soil of Jiangsu (438.4 ng/g, Wang et al. 2017), agricultural soil of Zhejiang (508.6 ng/g, Wang et al. 2017), agricultural soil of Shanghai (363.4 ng/g, Wang et al. 2017), rural soil of Jiangsu (640.6 ng/g, Cao et al. 2017), suburban soil of Beijing (321.8 ng/g, Peng et al. 2016), rural soil of Beijing (219.2 ng/g, Peng et al. 2016), urban and suburban soil of Shanghai (807 ng/g, Wang et al. 2015a, b), agricultural soil of Xinzhou (202 ng/g, Zhao et al. 2014), agricultural soil of Poland (423 ng/g, Maliszewska-Kordybach et al. 2009). Compared with other agricultural areas, the concentrations of PAHs in our study were higher. This may be because anthropogenic activities of agricultural mechanization and straw burning as the pollution source (Sun et al. 2015). At present, there are no guidelines in China about PAH classification in soil, and there are few existing recommendations or guidelines worldwide (Duan et al. 2015, Wang et al. 2010). A soil contamination classification system developed by (Maliszewska-Kordybach 1996) has been widely used to estimate PAH pollution in soil. The system based on 16 PAHs as follows: non-contamination (< 200 ng/g), weakly contaminated

Table 4 Correlation coefficients among the concentrations of ΣPAHs and TOC in farmland soils around main reservoirs of Jilin

	TOC	L-PAHs	H-PAHs
L-PAHs	0.191	–	–
H-PAHs	−0.285	−0.65**	–
16 PAHs	−0.034	0.657**	0.146

**$p < 0.01$; * $p < 0.05$

Table 3 Concentration of PAHs in soils from other cities (ng/g)

City	Soil type	Minimum	Maximum	Mean	References
Jiangsu	Agricultural	189.6	491.0	438.4	Wang et al. (2017)
Zhejiang	Agricultural	205.5	1070.4	508.6	Wang et al. (2017)
Shanghai	Agricultural	285.2	503.8	363.4	Wang et al. (2017)
Jiangsu	Rural	1820.8	126.8	640.6	Cao et al. (2017)
Changzhi	Agricultural	250.49	9387.26	2780.42	Liu et al. (2016)
Beijing	Suburban	28.6	2571.9	321.8	Peng et al. (2016)
Beijing	Rural	37.5	1245.9	219.2	(Peng et al. 2016)
South Kalimantan	Coal stockpile	4690	22,670	11,720	Mizwar et al. (2016)
Changzhi	Agricultural	9	10,514	917	Liu et al. (2017)
Shanghai	Urban and suburban	18.8	6320	807	Wang et al. (2015a, b)
Xinzhou	Agricultural	N.D.	782	202	Zhao et al. (2014)
Beijing	Urban	93.3	13,141.5	1228.1	Peng et al. (2011)
Delhi	Agricultural	827	3884	1906	Agarwal et al. (2009)
Poland	Agricultural	73	7356	423	Maliszewska-Kordybach et al. (2009)
Jilin	Agricultural	602.12	1271.87	877.23	Our study

Table 5 Hazard index (HI) risk of PAHs in soils

	Nap	Acy	Ace	Flo	Phe	Ant	Fla	Pyr	BghiP	HI
Ingestion										
Min	1.09E−07	1.19E−07	1.26E−07	1.80E−07	3.09E−07	1.56E−08	3.06E−08	1.13E−06	2.66E−07	2.29E−06
Max	3.12E−06	4.31E−06	5.17E−06	8.61E−06	8.61E−06	8.61E−06	8.61E−06	8.61E−06	8.61E−06	6.42E−05
Mean	9.69E−07	1.07E−06	1.50E−06	1.62E−06	5.25E−06	1.66E−07	2.09E−06	3.11E−06	1.53E−06	1.73E−05
Dermal										
Min	5.67E−08	6.22E−08	6.58E−08	9.36E−08	1.61E−07	8.15E−09	1.60E−08	5.88E−07	1.39E−07	1.19E−06
Max	1.62E−06	2.25E−06	2.69E−06	4.48E−06	7.86E−06	2.93E−07	4.47E−06	3.52E−06	3.05E−06	3.02E−05
Mean	5.05E−07	5.57E−07	7.79E−07	8.41E−07	2.73E−06	8.63E−08	1.09E−06	1.62E−06	7.95E−07	9.00E−06

(200–600 ng/g), contaminated (600–1000 ng/g) and heavily contaminated soils (> 1000 ng/g). In this study, 72% samples were contaminated and 28% samples were heavily contaminated, with a total concentration of the 16 PAHs all higher than 600 ng/g. However, much high levels of PAHs strongly indicated that the agricultural soils in our study region are extensively and severely contaminated. The risk assessment and pollution control strategies are urgently needed to improve soil quality and protect human health.

Correlation between PAHs and total organic carbon (TOC)

Soil TOC is an important character influencing the PAH concentration in urban and contaminated soils (Nam et al. 2008; Wilcke 2000; Wang et al. 2015a, b). Several studies reported a linear relationship between PAHs and TOC in highly contaminated soil (Agarwal et al. 2009; Wang et al. 2010; Wilcke 2000). It was suggested that some factors such as organic matter composition and temperature could affect yields and distribution of PAHs formed during incomplete combustion of organic matter or during its thermal maturation (Baumard et al. 1999).

In this study, the TOC concentrations in soil samples ranged from 4.8 to 20.6%, with a mean value of 11.56%. The Pearson's correlation coefficients between the soil TOC contents and the 16 PAH, L-PAH and H-PAH concentrations in agricultural soils around main reservoirs of Jilin are listed in Table 4. Concentrations of 16 PAHs, L-PAHs and H-PAHs were not significantly correlated with soil TOC ($p > 0.05$); therefore, TOC does not appear to influence the PAH distribution in the area, which may be due to the result of non-equilibrium adsorption between TOC and PAHs and that the sampling sites in this study are located mainly in agricultural areas where the artificial introduction of organic fertilizers is expected (Nam et al. 2008; Zhao et al. 2014).

Risk assessment of PAHs in soils

The non-cancer health risk was evaluated by HI (Luo et al. 2012). The results of non-cancer health risks via different pathways are shown in Table 5. The HI values in farmland soils are all smaller than 1, which indicates that the public may not likely to face a health risk according to the guidance issued by USEPA (2004). It can be judged that the concentration levels of PAHs in our study area are relatively safe to the local residents.

PAHs can be absorbed by humans through the skin and respiratory tract, and they may cause skin cancer, lung cancer, liver cancer, stomach cancer and other diseases. Exposure to PAHs in the environment for a long time may cause chronic poisoning. In order to evaluate the potential carcinogenic risk caused by integrated effects of PAHs through ingestion and dermal adsorption, CR values of soils were calculated and are listed in Table 6. The CR values for both ingestion and dermal adsorption were smaller than 1×10^{-6}, which indicated that the complex PAHs in farmland soils were not considered to pose significant health effects according to the guidance issued by USEPA (2004).

Table 6 Cancer risk (CR) of PAHs in soils

	BaA	Chr	BbF	BkF	BaP	DahA	IcdP	CR
Ingestion								
Min	4.66E−09	6.20E−12	3.20E−10	2.88E−11	2.83E−09	1.50E−08	2.77E−10	2.31E−08
Max	3.86E−08	4.14E−10	2.59E−08	8.84E−10	2.62E−07	2.91E−07	1.76E−08	6.36E−07
Mean	1.71E−08	1.31E−10	5.52E−09	3.39E−10	3.88E−08	1.05E−07	7.10E−09	1.74E−07
Dermal								
Min	2.44E−09	3.25E−12	1.67E−10	1.51E−11	1.48E−09	7.85E−09	1.45E−10	1.21E−08
Max	2.02E−08	2.17E−10	1.36E−08	4.63E−10	1.37E−07	1.52E−07	9.23E−09	3.33E−07
Mean	8.94E−09	6.86E−11	2.89E−09	1.78E−10	2.03E−08	5.48E−08	3.72E−09	9.09E−08

Possible sources of PAHs

Isomer pair ratios

In this study (Fig. 2), the ratios Fla/(Fla + Pyr) were about 59% lower than 0.4, and about 41% greater than 0.5, the ratios Ant/(Ant + Phe) were about 91% greater than 0.1, the ratios IcdP/(IcdP + BghiP) were about 91% greater than 0.35 and the ratios BaA/(BaA + Chr) were about 72% greater than 0.35. The ratios FlA/(FlA + Pyr) show that a part of PAHs originate from petroleum. However, the ratios Ant/(Ant + Phe) show that a large part of PAHs originate from grass, wood, coal and petroleum combustion. The ratios IcdP/(IcdP + BghiP) and BaA/(BaA + Chr) indicate that biomass and coal combustion were the main source of PAHs.

In summary, these ratios indicated that the PAHs in soils from the mid-southern part of the YRD were mainly derived from the petroleum sources; while in the remainder of YRD area, mixed sources of petroleum combustion including coal and biomass combustion were predominant.

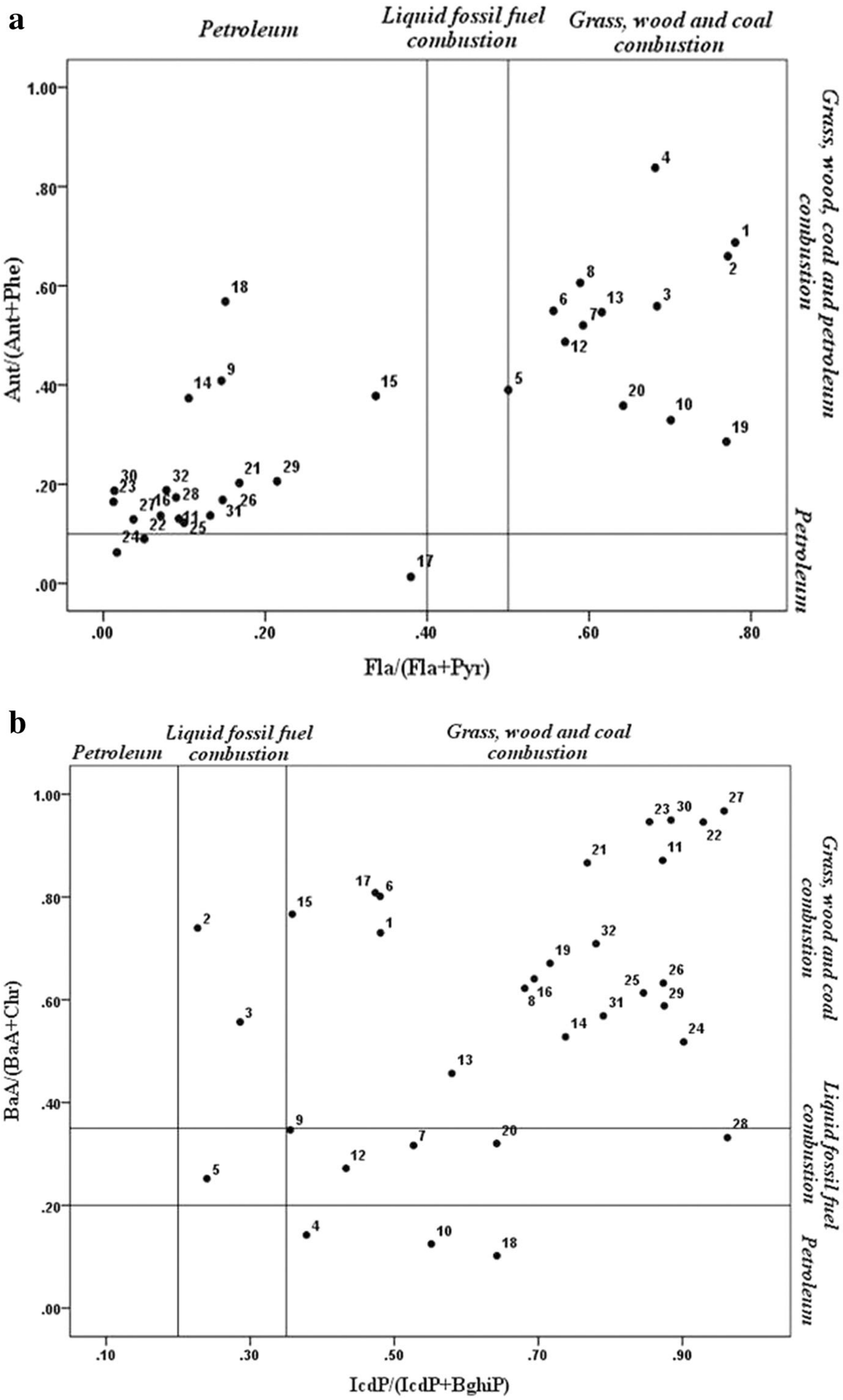
Conclusions

Sixteen priority PAHs were detected in 32 farmland soil samples around main reservoirs of Jilin Province, and they were analyzed to investigate the contamination level, potential health risks to the residents and possible sources. The total concentrations of 16 PAHs in soil were 602.12 to 1271.87 ng/g, with a mean value of 877.23 ng/g. The compounds of 3 rings and 4 rings were the major components of PAHs in our study area. There were no significances correlation between the 16 PAHs, L-PAHs, H-PAHs and TOC, and the results are possibly due to soil microbial mineralized or degraded PAHs and the semi-continuous inputs from anthropogenic sources, such as the use of farmland machinery.

In our study, the total HI values ranged from 10^{-6}–10^{-5} and the CR values ranged from 10^{-8}–10^{-7}, which indicated that the non-cancer risk and cancer risk for local people of PAH concentrations wouldn't pose significant health effects. Source identification indicated that the biomass and coal combustion were the main source of PAHs in this area. Local government could take some targeted measures in soil pollution governance according to the contamination levels and contamination source of PAHs in the studied area.

From these conclusions, we could find that the agricultural soils around main reservoirs of Jilin Province were extensively and severely contaminated, but the non-cancer risk and cancer risk for local people wouldn't pose significant health effects. The reasons for this ostensible contradiction are various. Firstly, contamination level of PAHs represents the sum concentration values of 16 PAHs, while risk values are based on both the concentration and the human exposure parameters (see Table 1). Sometimes, a kind of PAH has a high concentration value, but its exposure parameter is very low, so the comprehensive risk value maybe very low, which means that to the less dangerous PAH for people, even the concentration is high; maybe, it has less risk to people. In our study, the contamination values of BaA and Chr were high

Fig. 2 Isomeric ratios from plotting Ant/(Ant + Phe) versus Fla/(Fla + Pyr)(a) and BaA/(BaA + Chr) versus IcdP/(IcdP + BghiP)



among the 7 carcinogenic PAHs, and the SF of them is low. So their risk values were not very high. Secondly, the different thresholds make different results. The low thresholds of acceptable cancer and non-cancer risk defined by USEPA are 1 × 10^{-6} and 1, respectively. The widely used PAH contamination classification in soil was developed by Maliszewska-Kordybach (1996). The conclusions were drawn by these thresholds, respectively. Thirdly, even when the soils were contaminated, the risk might not be beyond the acceptable threshold. Health risk for people depends on many factors. Except contaminated soil, environmental self-purification capacity, transmission mode, exposure degree can also impact the risk level. Therefore, more factors need to be considered and their mechanism to risk needs to be researched in the future.

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Compliance with ethical standards

Conflict of interest All the authors declare that they have no conflict of interest.

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