Occurrence of nitro- and oxy-PAHs in agricultural soils in eastern China and excess lifetime cancer risks from human exposure through soil ingestion

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ABSTRACT

The quality of agricultural soil is vital to human health, however soil contamination is a severe problem in China. Polycyclic aromatic hydrocarbons (PAHs) have been found to be among the major soil contaminants in China. PAH derivatives could be more toxic but their measurements in soils are extremely limited. This study reports levels, spatial distributions and compositions of 11 nitrated (nPAHs) and 4 oxygenated PAHs (oPAHs) in agricultural soils covering 26 provinces in eastern China to fill the data gap. The excess lifetime cancer risk (ELCR) from the exposure to them in addition to 21 parent PAHs (pPAHs) via soil ingestion has been estimated. The mean concentration of ΣnPAHs and ΣoPAHs in agricultural soils is $50 \pm 45\,\mu g/kg$ and $9 \pm 8\,\mu g/kg$ respectively. Both ΣnPAHs and ΣoPAHs follow a similar spatial distribution pattern with elevated concentrations found in Liaoning, Shanxi, Henan and Guizhou. However if taking account of pPAHs, the high ELCR by soil ingestion is estimated for Shanxi, Zhejiang, Liaoning, Jiangsu and Hubei. The maximum ELCR is estimated at ca.10^{-5} by both deterministic and probabilistic studies with moderate toxic equivalent factors (TEFs). If maximum TEFs available are applied, there is a 0.2% probability that the ELCR will exceed 10^{-4} in the areas covered. There is a great chance to underestimate the ELCR via soil ingestion for some regions if only the 16 priority PAHs in agricultural soils are considered. The early life exposure and burden are considered extremely important to ELCR. Emission sources are qualitatively predicted and for areas with higher ELCR such as Shanxi and Liaoning, new loadings of PAHs and derivatives are identified. This is the first large scale study on nPAHs and oPAHs contamination levels in agricultural soils in China. The risk assessment based on this underpins the policy making and is valuable for both scientists and policy makers.

1. Introduction

The agricultural land in Eastern China produces 64% of grains and 80% of vegetables, which serves 70% of Chinese population (China Ministry of Agriculture, 2014). The 'Report on national soil pollution survey (2014)' reveals that ca. 20% of farmland in China has pollutant levels exceeding guideline values and polycyclic aromatic hydrocarbons (PAHs) are one of the major pollutant categories (MEP and MLR, 2014). PAHs are a class of carcinogens from the incomplete combustion of organic fuels. Their derivatives such as nitrated (nPAHs) and oxygenated PAHs (oPAHs) could derive primarily from the incomplete combustion or the photochemical reaction of parent PAHs (pPAHs) and

oxidants as secondary sources (Cochran et al., 2016; Kielhorn et al., 2003). About 21–34% of 16 USEPA priority PAHs (listed in Table S1 in the Supporting information (SI)) emissions (106 Gg in 2007) in China are produced in rural areas (Shen et al., 2013a; Xu et al., 2006; Zhang et al., 2008). Human health may be highly sensitive to the contamination level of PAHs and derivatives in agricultural soils, as PAH species could be easily exposed to farmers via soil ingestion during cultivation activities, or bio-accumulated by crops and expose a wider population of potential consumers into health risks (Davis and Mirick, 2006; Man et al., 2013; Yu et al., 2011). Most rural areas in China have relatively lower economic level, incomplete infrastructures and poorer social services compared to urban areas in the same region, which

result in higher amount of dusts and wastes around the living environment. Children in rural areas in China possibly receive less education on hygiene habits such as washing hands frequently, especially before meals. These all probably lead to higher intake levels of pPAHs and derivatives for the rural population due to greater soil ingestion rates.

Epidemiologic surveys prove that higher incidences of different cancers are associated with the occupational exposure to PAHs and the quantitative monitoring data of PAHs are primary to the investigation of the exposure and risks (ATSDR, 2009). Parental exposure to PAHs may lead to behaviour problems for children such as attention-deficit hyperactivity disorder (Mortamais et al., 2017; Perera et al., 2012; Perera et al., 2011). nPAHs and oPAHs could be potentially more threatening to human health than their pPAHs, as they are found to directly react with DNA without metabolic activation and exhibit mutagenic properties, unlike pPAHs (Lundstedt, 2003; Pedersen et al., 2004; Pitts et al., 1978). nPAHs could strongly adhere to organic contents of soils and therefore be more persistent in top soils than corresponding pPAHs due to generally higher sorption coefficients (Koc) and lower water solubility compared to the corresponding pPAHs (Kielhorn et al., 2003).

To evaluate human health risks of soil PAHs and derivatives, measurements in soils are needed. Additionally, it is essential to investigate the composition, emission sources and contributions of different PAHs species to the risk. Reports on pPAHs in soils are relatively abundant but only the 16 priority PAHs are considered in the national soil survey mentioned above or widely studied in most relevant scientific researches (Sun et al., 2017; Tao et al., 2011; Zuo et al., 2007; MEP and MLR, 2014). Measurements of soil nPAHs and oPAHs are extremely limited especially for China (Bandowe and Meusel, 2017), and the few existing gauging campaigns in China are on city/regional scales (Cai et al., 2017; Wei et al., 2015; Zhang et al., 2013). In addition, many publications focus on excess lifetime cancer risks from the inhalation exposure to PAHs for the Chinese population (Shen et al., 2014; Zhang et al., 2016; Zhang et al., 2009) but much fewer are on the exposure via soil ingestion.

In the present study, a large scale gauging campaign for nPAHs and oPAHs in agricultural soils has been conducted in 26 provinces in eastern China to fill the data gap. This study reports the occurrence, spatial distribution and composition of these species in agricultural soils and diagnoses their potential emission sources. In terms of this work and previously reported pPAHs concentrations in agricultural soil for the same sampling sites (Sun et al., 2017), average daily doses (ADD) of PAHs and derivatives and an excess lifetime cancer risk (ELCR) via soil ingestion are estimated. This could supplement the knowledge on human health risks from exposure to PAHs and derivatives through multiple exposure pathways. The burden of PAHs species during childhood stage is specifically discussed. As far as the author knows, this is the first large scale study on nPAHs and oPAHs in agricultural soils in China. Such investigation reduces the systematic uncertainty for spatial analysis caused by gauging campaigns accomplished by different research groups and also provides valuable first-hand data for risk assessments. Severe soil pollution is easily neglected by the public in China, because, unlike smog for instance, it is not directly visible. However there are growing awareness and concerns among politicians and scientists (Economist, 2017). Outputs from this study will support the management of the agricultural soil quality in China.

2. Methods and materials

2.1. Sample collection and target chemicals

82 soil samples were collected during April–May 2013 from agricultural land in 26 provinces in eastern China (SI Fig. S3) by a team in Zhejiang University (Niu et al., 2014). The analysis of PAH derivatives was completed in Peking University. In short, the overlying vegetation

was removed before sample collection. Five top soil samples (0–20 cm) were taken by a pre-cleaned scoop for each sampling site and then mixed into one composition sample and packed in a pre-cleaned aluminium foil bag. Soil samples were air-dried, ground, sieved (2 mm) and stored at − 20 °C until analysis. More detailed sampling methods can be found in previous studies (Niu et al., 2014; Sun et al., 2017).

The target PAH derivatives included 11 nPAHs and 4 oPAHs. The nPAHs were 1-nitro-naphthalene (1N–NAP), 2-nitro-naphthalene (2N–NAP), 5-nitro-acenaphthene (5N–ACE), 2-nitro-fluorene (2N–FLO), 3-nitro-phenanthrene (3N–PHE), 9-nitro-phenanthrene (9N–PHE), 9-nitro-anthracene (9N–ANT), 3-nitro-fluoranthene (3N–FLA), 1-nitro-pyrene (1N–PYR), 7-nitro-benzo[*a*]anthracene (7N–BaA) and 6-nitro-chrysene (6N–CHR). Additionally the oPAHs were 9-fluorenone (9FO), anthracene-9,10-dione (ATQ), benzo[*a*]anthracene-7,12-dione (BaAQ) and benzanthrone (BZO). The 21 pPAHs (Sun et al., 2017) included in the risk assessment and their abbreviations are in SI Table S1.

2.2. Sample extraction, analysis and quality control

The extraction and the cleanup methods reported by previous studies (Li et al., 2016) were adopted for analysis of nPAHs and oPAHs in soils. Briefly, ca. 8 g soil packed in a glass fibre filter (GFF) were extracted by 25 mL hexane/acetone (1:1, *v/v*) solution using a microwave accelerated reaction system (CEM MARSXpress, NC, USA) for 20 min. The procedure temperature was raised to 110 °C in the first 10 min and held afterwards. The extract was concentrated to 1 mL before being purified by a silica gel/alumina column (12 cm alumina, 12 cm silica gel and 1 cm anhydrous sodium sulfate were added into the column in sequence). 20 mL hexane was added into the column for pre-elution (discarded) followed by 50 mL hexane/dichloromethane mixed solution (1:1, *v/v*) for eluting nPAHs and oPAHs, which was collected. The eluate was evaporated to 1 mL and solvent-exchange to hexane, which was ultimately concentrated to 1 mL. 1-nitroanthracene-d_9 and 1-nitropyrene-d_9 were spiked as internal standard (J & W Chemicals, USA).

nPAHs and oPAHs were analysed by GC–MS (Agilent 5973 GC, Agilent 5975 MS) with a HP-5 MS capillary column in negative chemical ionization mode using the selected ion monitoring. The carrier gas and the reagent gas were high-purity helium and methane respectively. The oven temperature of the gas chromatograph was set to rise from 60 to 150 °C at a rate of 15 °C/min and then to 300 °C at a rate of 5 °C/min, and remain for 15 min. The individual PAH derivatives were quantified based on the retention time. Procedural and reagent blanks were analysed with the samples concomitantly. All reagents and solutions used in the purification above were of chromatographic purity. Duplicate samples were measured. The recoveries of the spiked standards of individual PAH derivatives ranged 80–133% (SI Table S3). All concentrations reported here were blank- but not recovery-corrected and are given on a dry weight basis.

2.3. Estimates of excess lifetime cancer risk by soil ingestion

A chemical-specific approach was adopted officially by US EPA and Health Canada, and also widely used in scientific researches to probabilistically estimate the ELCR from exposure to PAHs via soil ingestion (Health Canada, 2010; Lemieux et al., 2015; USEPA, 2017; Williams et al., 2013). This method employed concentrations of contaminants, body weights, exposure factors, soil ingestion rates and the oral slope factor. Concentrations of individual PAHs and derivatives were converted to BaPeq (BaP equivalent concentration) by the toxicity equivalency factor (TEF) for the calculation. As a result of the uncertainty of TEF, a comprehensive review into TEF values for these chemicals was conducted with the aim to include the possible range of TEFs (Table S1). Because of the lack of TEF values for most PAH derivatives, only those with available TEFs (see SI Table S1, 27 PAHs and derivatives in total) were included in the risk estimation. The Average Daily Dose

(ADD, mg/kg bw/day, bw indicates body weight) and ELCR were calculated by Eq. 1 and Eq. 2.

$$\text{ADD}_i = \frac{C_{eq,i} \times IR_i \times CF \times EF_i \times ED_i}{BW \times AT} \tag{1}$$

$$\text{ELCR}_i = ADD_i \times SF \times ADAF_i \tag{2}$$

where $C_{eq,i}$ (mg/kg) is the BaPeq concentration of the ith pPAHs or derivatives. IR_i (mg/day) is the soil ingestion rate. CF is the unit conversion factor (10^{-6} kg/mg). EF_i (days/year) is the exposure frequency and ED_i (years) is the exposure duration. BW (kg) and AT (days) indicate the body weight and the average time respectively. SF ((mg/kg·day)$^{-1}$) and $ADAF_i$ ($-$) refer to the oral slope factor and Age-Dependent Adjustment Factors. 70 years old was assumed to be the average life expectancy for the Chinese population in this study. The calculated ELCR reflects the probability of cancer developed by age 70 attributed to the exposure to pPAHs and derivatives included in current estimates by soil ingestion.

Two exposure scenarios were investigated in this study in terms of different age intervals and soil ingestion rates. Deterministic values were used in the scenario studies. Scenario 1 (Sc1) applied moderate ingestion rates of 200 mg/day for age 0– < 6 and 100 mg/day for age 6–70. This was recommended by USEPA for resident children and adult outdoor workers for the screening level assessment (USEPA, 2017). Scenario 2 (Sc2) considered possibly higher soil ingestion rates of 400 mg/day for age 0– < 13 and 100 mg/day for age 13–70, which was adopted for the 'reasonable maximum estimate' in a previous study for a conservative risk assessment (Williams et al., 2013). Taking account of living conditions in most rural areas in China, it is reasonable to assume a higher soil ingestion rate for children, which is still within the range of ingestion rates compiled in the 'Child-specific exposure factors handbook' (Diaz et al., 2008). AT was 25,550 days for estimations of 70-year ELCR and ADD, and was 365 for estimations of annual ADD to study the burden for different life stages. For TEF, values suggested in the 'Technical guidance of national soil pollution assessment' by Ministry of Environmental Pollution China (MEP, 2008) were used for the 16 USEPA priority PAHs (marked in Table S1), which were also widely adopted in many other studies and government documents. For other PAHs and derivatives, mean TEF was used in the deterministic study in both scenarios, if more than one TEF value were found. These TEFs were referred to as 'moderate' values in Table S1 (the 'Moderate' column). Other values for inputs to the two exposure scenarios are shown in Tables S4–S5 (USEPA, 2017; Williams et al., 2013).

Due to the possible uncertainty of soil ingestion rates and body weights at different age stages, the probabilistic evaluation of ELCR was conducted by Monte Carlo simulation with 10,000 runs. Random body weights and soil ingestion rates were generated for each run based on respectively normal and lognormal distributions. The mean and standard deviation (STD) for generating the random values that align the corresponding distribution for each age stage were from the compilation of a previous study (SI Table S6) (Williams et al., 2013). For each run the concentration of ΣBaPeq chosen from a random site out of the 82 sampling sites was used. The probabilistic study was conducted three times with respective moderate, maximum and minimum TEF values taking account of the possible range of TEFs. To investigate the contribution to the ELCR from the 16 priority PAHs out of the 27 PAHs and derivatives, the probabilistic estimation was additionally conducted on the 16 priority PAHs with moderate TEFs. The probabilistic estimation could exhibit the probabilistic ELCR for agricultural soil in eastern China.

3. Results and discussion

3.1. nPAHs and oPAHs concentrations

Table 1 shows that four out of the eleven nPAHs (1N–NAP, 2N–NAP,

Table 1
Statistics of nPAHs and oPAHs in agricultural soil (µg/kg d.w.)

Chemical		Detection frequency	Mean ± STD (µg/kg)	Median (µg/kg)	Range (µg/kg)
nPAHs	1N–NAP	100%	27.0 ± 33.4	19.4	0.2–267
	2N–NAP	100%	15.2 ± 12.8	10.3	0.3–66
	5N–ACE	6%	2.2 ± 2.7	0.9	0.7–7.7
	2N–FLO	2%	8.3 ± 0.9	8.3	7.5–9.2
	3N–PHE	6%	5.5 ± 6.8	0.5	0.4–17
	9N–PHE	70%	3.5 ± 4.9	1.9	0.4–29
	9N–ANT	6%	1.9 ± 3.3	0.2	0.2–8.5
	3N–FLA	18%	2.1 ± 2.2	1.3	0.7–9.1
	1N–PYR	1%	8.8	8.8	8.8
	7N–BaA	40%	10.7 ± 8.9	6.7	2–41
	6N–CHR	0%	n.d.	n.d	n.d.
	ΣnPAH$_{11}$	100%	50 ± 45	37.4	0.5–314
oPAHs	9FO	4%	3.7 ± 4.8	0.3	0.3–10
	ATQ	57%	7.1 ± 6	5.1	0.9–26
	BaAQ	4%	2.9 ± 3.8	0.3	0.2–8.4
	BZO	41%	6.1 ± 4.8	4.1	1.7–23
	ΣoPAH$_4$	100%	9 ± 8	6.7	1–42

Notes: n.d. indicates not detected; mean indicates arithmetic mean; the statistics do not consider the n.d. values.

9N–PHE and 7N–BaA) have detection rates over 40%. 1N–NAP and 2N–NAP are identified in all samples. Five nPAHs have detection rates below 10%. 6N–CHR is not detected in any of the samples. ATQ and BZO have detection rates of 57% and 41% respectively. The other two oPAHs only have detection rates of 4%. The range, arithmetic mean, median and STD in Table 1 only reflect the statistics for the chemicals detected. The mean and STD of ΣnPAH$_{11}$ and ΣoPAH$_4$ are respectively 50 ± 45 µg/kg (range, 0.5–314 µg/kg) and 9 ± 8 µg/kg (1–42 µg/kg). The STD is relatively high, which indicates a high spatial variation. The coefficient of variance (CV) of concentrations ranges 10–130% for individual chemicals. Except for chemicals with low detection rates, the remaining individual PAH derivatives, such as 1N–NAP, 2N–NAP, 9N–PHE and ATQ, and ΣnPAH$_{11}$, ΣoPAH$_4$ are lognormally distributed (Fig. S1). The statistic distribution of individual PAH derivatives is shown in Fig. 1.

Existing researches on measurements of nPAHs and oPAHs in soils are scarce. Most studies to date focus on urban or industrial soils and only a few on agricultural soils globally as shown in Table 2. The mean concentration of individual PAH derivatives in eastern China in this study is higher than that in agricultural soil samples by another study in Spain (García-Alonso et al., 2012). The mean concentration of individual nPAH species in this study (1.9–27 µg/kg) is mostly higher than that in urban soils by other studies (Cai et al., 2017; De Guidi et al., 2016; Niederer, 1998; Wei et al., 2015; Zhang et al., 2013) except for 3N–FLA and 1N–PYR in Spain, which have reached 33 and 18 µg/kg respectively in roadside soils (García-Alonso et al., 2012). Up to date, the authors have not found any other studies on oPAH concentrations especially in agricultural soils. The mean concentration of individual oPAHs (3–7 µg/kg) in this study is generally lower than that in urban soils by other studies, except for BZO in surface soils in the Yangtze River Delta, China, which is 4.6 µg/kg (Cai et al., 2017; Wei et al., 2015; Boll et al., 2015). Other studies find that gasworks sites and some other industrial soils (i.e. wood tar production, coke oven plant, metallurgy and wood preservation) are seriously contaminated by nPAHs and oPAHs, with concentrations dramatically higher than those in agricultural soils in eastern China by this study (García-Alonso et al., 2012; Lundstedt, 2003; Arp et al., 2014).

By comparison, the level of individual oPAHs is in the same order of magnitude as or one order of magnitude lower than that of individual nPAHs in agricultural soils in this study. Contrarily, much higher concentrations of individual oPAHs than those of individual nPAHs in urban and gasworks soils are found in other studies which have covered the same species of PAH derivatives as our study. For the PAH
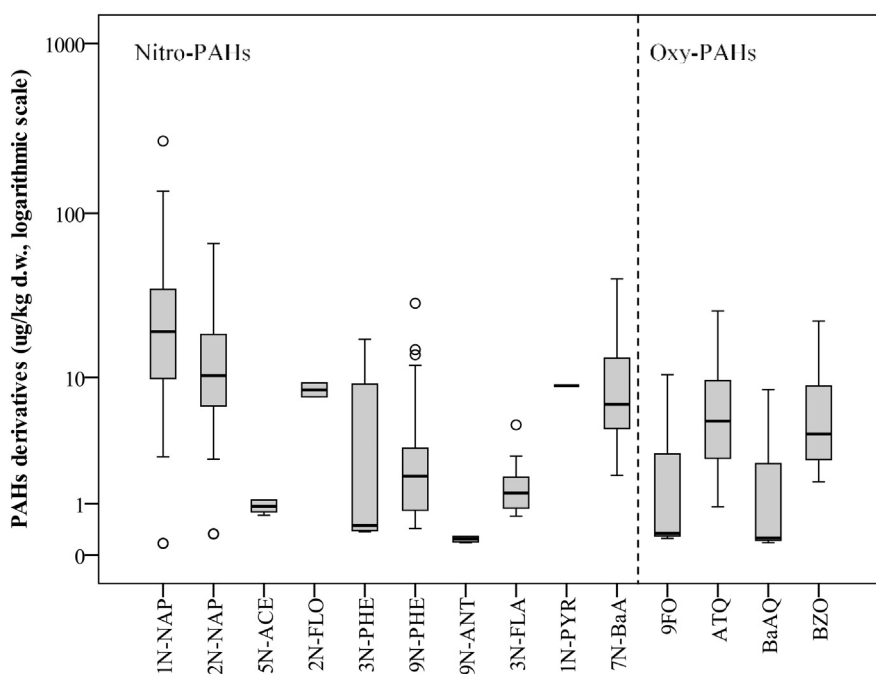
Fig. 1. Statistical distribution of 10 nPAHs and 4 oPAHs by boxplot in logarithmic scale; the horizontal solid line in the box is the median; the top and bottom of each box are 75th and 25th percentiles; the top and bottom of the whisker are the highest and lowest cases within 1.5 times of the interquartile range; circles indicate the outliers out of the range of whiskers.

derivatives studied, measured concentrations of individual oPAHs are normally much higher than those of individual nPAHs in the outdoor atmosphere or the indoor air close to household emission sources (Ding et al., 2012; Li et al., 2015; Zhuo et al., 2017a), which could generally be the primary sources of PAH derivatives in soils (Wang et al., 2012; Agarwal et al., 2009). This aligns the relationship of measured emission factors (EFs) between oPAHs and nPAHs for the same group of PAH derivatives targeted in this study. Measured EFs of these oPAHs are generally two orders of magnitude higher than those of nPAHs in residential sectors (Shen et al., 2013b; Shen et al., 2012). The lower levels of individual oPAHs than those of individual nPAHs in present study might be a result of the more frequent leaching conditions due to irrigation of agricultural soils compared to other landuse types and a higher water solubility of oPAHs than corresponding pPAHs. Therefore oPAHs transfer more easily from top soils to deeper layers or ground water. Meanwhile, nPAHs are possibly immobile and retained more

persistently than corresponding pPAHs in soils because they adhere to soil solids more strongly as mentioned above. Additionally, the higher Kp allows for higher deposition fluxes of nPAHs from the atmosphere to soils as a result of stronger absorption to atmospheric particles than corresponding pPAHs (Li et al., 2016), which potentially leads to higher inputs of nPAHs to soils. This also explains the comparable concentrations of nPAHs and related pPAHs shown in Fig. S2 with, however, much lower nPAH EFs. The comparison of water solubility, LogKoc and logK_P between pPAHs and corresponding PAH derivatives is shown in Table S2. It should be noticed that this study only targets limited types of PAH derivatives, therefore further studies are needed to test whether our findings for agricultural soil also apply to other species of oPAHs and nPAHs.

Table 2
Comparison of occurrence levels of nPAHs and oPAHs in soils in this study with those in other studies (mean concentrations µg/kg d.w.)

Chemical		This study	Other studies	Reference
nPAHs	1N–NAP	27	0.4, 0.9, < 0.03, 6.99 (urban)	Cai et al. (2017); Wei et al. (2015); Niederer (1998); Zhang et al. (2013)
	2N–NAP	15.2	1.2, < 0.03, 7.47 (urban)	Cai et al. (2017); Niederer (1998); Zhang et al. (2013)
	5N–ACE	2.2	1.3, 0.03 (urban)	Wei et al. (2015); Niederer (1998)
	2N–FLO	8.3	0.4, 0.07, 1.3 (urban)	Wei et al. (2015); Niederer (1998); Zhang et al. (2013)
	3N–PHE	5.5	0.1, 0.024 (agricultural); 1.9, 8.71 (urban); 277 (gasworks)	De Guidi et al. (2016); García-Alonso et al. (2012); Zhang et al. (2013)
	9N–PHE	3.5	1.2, 6.7 (urban); 0.016 (agricultural); 291 (gasworks)	Wei et al. (2015); García-Alonso et al. (2012)
	9N–ANT	1.9	0.4, 3.44, 0.011 (urban)	Wei et al. (2015); Zhang et al. (2013); Pham (2015);
	3N–FLA	2.1	1.5, 11.2, 0.03, 33 (urban); 0.018 (agricultural); 3361 (gasworks)	Cai et al. (2017); Wei et al. (2015); Niederer (1998); García-Alonso et al. (2012)
	1N–PYR	8.8	1.6, 4, 0.15, 3.11, 0.04, 18 (urban); 0.1; 0.072 (agricultural); 1360 (gasworks)	Cai et al. (2017); Wei et al. (2015); De Guidi et al. (2016); Niederer (1998); Zhang et al. (2013); Pham (2015); García-Alonso et al. (2012)
	7N–BaA	10.7	0.02 (urban)	Pham (2015)
oPAHs	9FO	3.7	16.4, 603.8, 174 (urban); 26,000, 1263, (gasworks), 8992 (other industry*)	Cai et al. (2017); Wei et al. (2015); Lundstedt (2003); Boll et al. (2015); Arp et al. (2014)
	ATQ	7.1	13.3, 56.8, 35.6, 477 (urban); 24,000, 2232 (gasworks); 4802 (other industry*)	Cai et al. (2017); Wei et al. (2015); Niederer (1998); Lundstedt (2003); Boll et al. (2015); Arp et al. (2014)
	BaAQ	2.9	3.3, 22, 30.3, 197 (urban); 4300, 1003 (gasworks); 3354 (other industry*)	Cai et al. (2017); Wei et al. (2015); Niederer (1998); Lundstedt (2003); Boll et al. (2015); Arp et al. (2014)
	BZO	6.1	4.6, 18.6, 743 (urban); 2680 (gasworks); 7753 (other industry*)	Cai et al. (2017); Niederer (1998); Boll et al. (2015); Arp et al. (2014)

Notes: *other industry includes wood tar production, coke oven plant, coke oven and metallurgy and wood preservation in the study by Arp et al. (2014).
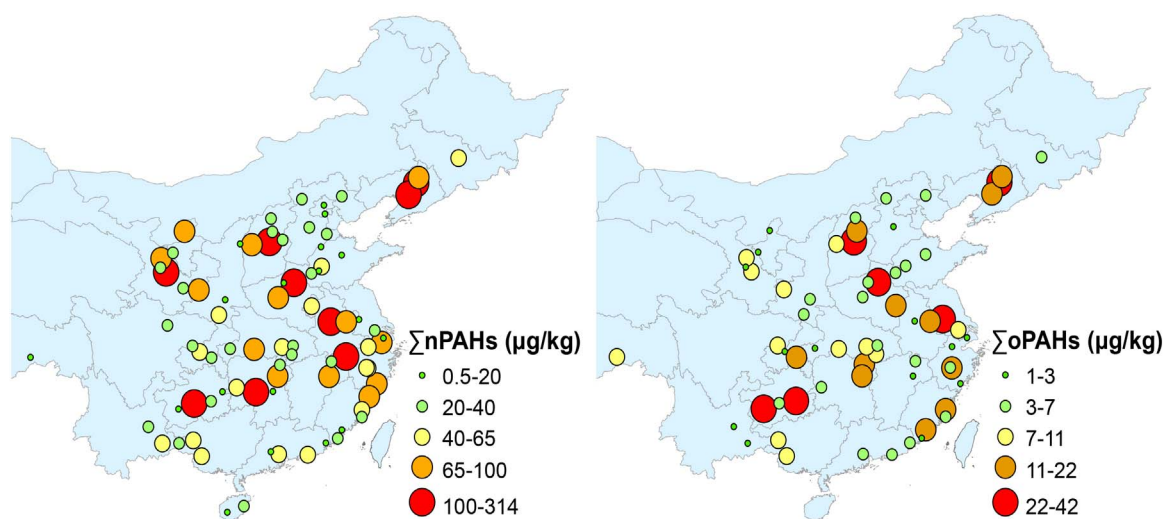
Fig. 2. Spatial distribution of ΣnPAHs and ΣoPAHs in agricultural soil in eastern China.

3.2. nPAHs and oPAHs geographic distribution

Fig. 2 shows that both nPAHs and oPAHs have elevated total concentrations in agricultural soils in Liaoning, Shanxi, Henan and Guizhou with a range of 65 (Liaoning) – 314 (Guizhou) μg/kg for ΣnPAHs and 15 (Guizhou) – 42 (Liaoning) μg/kg for ΣoPAHs. They both have generally lower total concentrations in Beijing, Hebei, Shandong and Guangdong than in other areas, which range 15–40 μg/kg for ΣnPAHs and 2–5 μg/kg for ΣoPAHs (sites without detected ΣoPAHs exist in these areas but are not included in discussion). The lowest detected agricultural soil concentration is in Hunan for ΣnPAHs and in Yunnan for ΣoPAHs. The significant correlation between soil concentrations of pPAHs and derivatives (Fig. 3A–B) indicates a significant spatial distribution correlation between pPAHs and derivatives. Because the emission of pPAHs is normally accompanied by nPAHs and oPAHs, and the EFs of pPAHs are found to be positively correlated with those of nPAHs and oPAHs for various combustion sources (Shen et al., 2011; Shen et al., 2013b; Shen et al., 2012). The location of provinces is in Fig. S3. A list of cities covered in this study is also enclosed in the Appendix.

However, the correlation between concentrations of ΣoPAHs and ΣpPAHs was weaker than that between concentrations of ΣnPAHs and ΣpPAHs. This reveals that the extent of potential effect from the secondary formation or human activities (e.g. irrigation and plough) to nPAHs and oPAHs concentrations varies in different regions. Meanwhile, different physicochemical properties may also play a role. This may explain why the correlation between soil concentrations of ΣoPAHs and ΣnPAHs is not significant until excluding the four contrasting points (in the two black circles) in Fig. 3C (p and p' are the statistical significance values before and after removing the four

contrasting points), meanwhile the air concentrations of ΣoPAHs and ΣnPAHs for the same chemical species are found to be usually significantly correlated in other studies (Ding et al., 2012; Li et al., 2015). The contrasting points which have lowest ΣnPAHs but relatively high ΣoPAHs in agricultural soils are in Jiangsu and Tibet and those that have highest ΣnPAHs but relatively low ΣoPAHs are in Anhui and Guizhou. Significant contrasts can also be observed in Fig. 2. For example, generally the soil concentration is elevated in Ningxia, Gansu and Anhui for ΣnPAHs but lower in these areas than in other regions for ΣoPAHs. Meanwhile the level of ΣoPAHs is higher in Jiangsu, where lower ΣnPAHs concentrations have been found compared to other areas.

Pearson test finds significantly spatial correlation only between contents of soil organic carbon (SOC) and concentrations of ΣnPAHs ($p = 0.01$) but not between SOC and ΣoPAHs, nor between per capita gross domestic product (GDPcap) and either of ΣnPAHs and ΣoPAHs ($p > 0.05$, Fig. S4). In contrast, a previous study on the same group of samples finds that levels of both GDPcap and SOC significantly correlate to total concentrations of ΣpPAHs in agricultural soils (Sun et al., 2017), which is also found by other studies on surface soils for other regions (Cai et al., 2017; Wang et al., 2010). This probably reveals that soil levels of ΣpPAHs in presently studied areas mainly originate from atmospheric sources, which are related to socioeconomic levels (GDPcap), and are at steady state without significant new loadings or dramatic reductions (Nam et al., 2008; Wang et al., 2010). PAH derivatives will be initially released together with pPAHs but are probably affected more by secondary formation and human activities on agricultural land than on other land use types, especially for oPAHs with higher water solubility as discussed above (Nam et al., 2008). Besides, low contamination levels of oPAHs may also lead to the insignificant
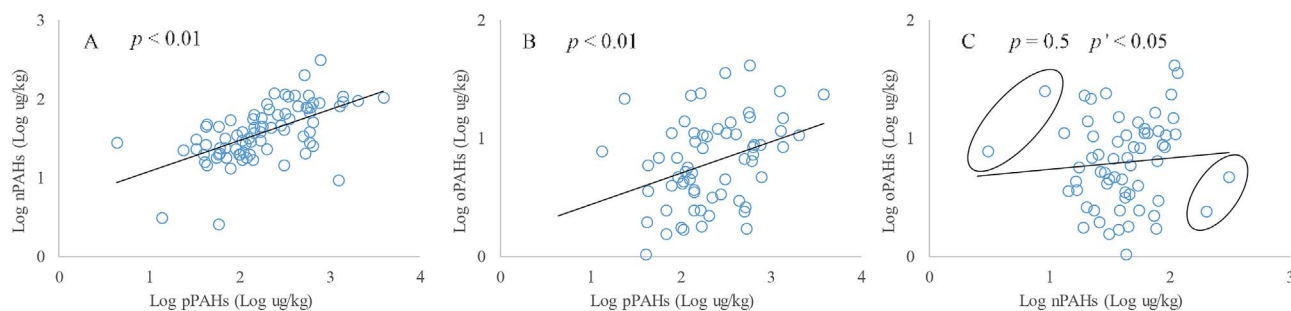

Fig. 3. Correlation of ΣpPAHs, ΣnPAHs and ΣoPAHs concentrations (log-transformed) in agricultural soils in China; p′ in (C) is the statistical significance value after excluding the contrasting points in the two black circles. Pearson test has been used in the correlation test.
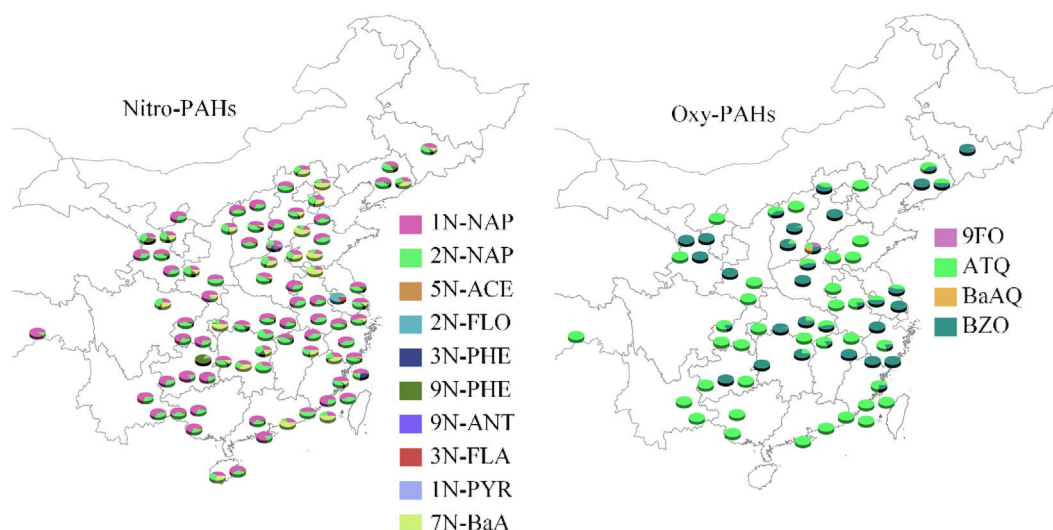
Fig. 4. Spatial variation of the composition of nitro-PAHs and oxy-PAHs in agricultural soil in eastern China.

correlation with SOC levels (Zhang et al., 2006).

3.3. Composition of nPAHs and oPAHs

On average, ΣpPAHs accounted for the highest proportion (85%) of the sum of all pPAHs and derivatives detected in this study, and ΣnPAHs and ΣoPAHs contribute 13% and 2% respectively (Fig. S5A). For only nPAHs, NAP derivatives are the most abundant (1N–NAP, 54%; 2N–NAP, 30%), followed by 7N–BaA (9%) and 9N–PHE (5%) (Fig. S5B). ATQ and BZO are the most abundant oPAHs, which contribute respectively 59% and 37% of ΣoPAHs (Fig. S5C). The composition of PAH derivatives in samples from Yangtze River Delta (YRD) in this study is different with that reported by Cai et al. (2017) for the same region, probably due to different sampling locations and land use types. However both studies find relatively high proportion of ATQ in Wuxi, where the largest ATQ synthetizing manufacturer is located. Components of nPAHs and oPAHs both vary regionally (Fig. 4). Most sites have the highest proportion of 1N–NAP (18–89%) and 2N–NAP (9–66%) among all nPAHs, and the sum of the two chemicals could range 35–100% for those sites with detected nPAHs. The few sampling sites that have different composition are in Kaifeng, Henan with almost equal proportions of the 7 detected nPAHs besides 1N–NAP and 2N–NAP; in Yangzhou, Jiangsu with highest proportion of 2N–FLO (82%); in Shandong with a high proportion of 7N–BaA (33–62%) and in Tongren, Guizhou with a high proportion of 9N–PHE (> 98%). For oPAHs, ATQ and BZO clearly dominated (94%) at most sampling sites (75%). About 73% of sites only have one of the two chemicals detected. The sample from Kaifeng, Henan shows a different pattern with an equal contribution from the four oPAHs.

3.4. ADD and ELCR estimations

With the moderate TEF, the deterministic study finds that the estimated 70-year ADD of BaP$_{eq27}$ through agricultural soil ingestion ranges 10^{-6}–~2×10^{-3} μg/kg bw/day in Sc1 and 1.6×10^{-6}–3.2×10^{-3} μg/kg bw/day in Sc2. The 70-year ADD in Sc2 is about twice of that in Sc1. The estimated ELCR ranges about 10^{-8}–10^{-5} in the two scenarios and ELCR in Sc2 is about twice of that in Sc1. The population with the highest estimated ELCR (4.9×10^{-5} in Sc1 and 9.9×10^{-5} in Sc2) are estimated in Yichang, Hubei (Fig. 5B). The estimated ELCR of sites in Zhejiang, Liaoning, Jiangsu and Shanxi is also relatively higher than that in other areas. USEPA generally considers that the excess cancer risk over 10^{-4} will desire remediation and that below 10^{-6} is negligible (USEPA, 2016). An acceptable risk is

between 10^{-6}–10^{-4}, however investigations on a case-by-case basis is necessary (Williams et al., 2013). In the deterministic study, about 55% sites in Sc1 and 63% sites in Sc2 have the ELCR between 10^{-6}–10^{-4}. No site has an estimated ELCR over 10^{-4} in either scenarios apart from the site in Yichang, Hubei, which, as mentioned above, has an ELCR extremely close to 10^{-4}. The 16 priority PAHs contribute ca. 2%–~100% (Fig. S6) with an average of 54% to the ELCR from all 27 PAHs and derivatives regardless of different scenarios. The ELCR attributed to the 16 priority PAHs ranges about 10^{-9}–10^{-5} in the two scenarios. If applying the maximum TEF to Sc2 for a conservative estimate, ELCRs above 10^{-4} are obtained for 6 out of the 82 sites (in Zhejiang, Tibet, Hebei, Henan, Guizhou and Guangdong, see Fig. S7). Due to the vulnerability of children, the susceptibility of early-life exposure to carcinogens such as pPAHs and derivatives should be assessed. About 50% and 60% of the 70-year cumulative burden of BaP$_{eq}$ is attributed to the exposure before the age of 6 and 16 in Sc1 and ca. 55% and 80% in Sc2. A significantly higher cumulative burden of BaP$_{eq}$ is achieved by age 16 in Sc2 than Sc1. About 80% and 90% ELCR has accumulated by age 6 and 16 in Sc1 and about 79% and 94% in Sc2, according to estimations. The annual ADD has also been calculated by Eq. 1 to investigate the annual burden of BaP$_{eq}$. It is found in both scenarios that the annual burden of BaP$_{eq}$ is dramatically higher in early life than during adulthood (Fig. 5A). The annual ADD in Sc2 could be twice and four times of that in Sc1 between age 0–5 and age 6–13 respectively. The annual BaP$_{eq}$ intake stabilises after age 14 in both scenarios. Comparing the difference of the annual ADD between the two scenarios, ages with the most distinct annual burden of BaP$_{eq}$ are estimated to be 6–13 years old.

The probabilistic study estimates that the 70-year ELCR ranges 3×10^{-9}–9×10^{-5}, 2×10^{-9}–2×10^{-5} and 1×10^{-8}–2×10^{-4} (median: 6×10^{-7}, 2×10^{-7} and 2×10^{-6}) respectively when using moderate, minimum and maximum TEFs by the exposure to the 27 pPAHs and derivatives included in the estimation through agricultural soil ingestion in eastern China (Fig. 6). The probability of estimated ELCR exceeding 10^{-6} is ca. 40%, 13% and 60% when using moderate, minimum and maximum TEFs respectively (Fig. 6B). There is a 0.2% probability that the ELCR will exceed 10^{-4} if the maximum TEFs are used. Fig. 6B provides an extent of probability of ELCRs with the area between the two dashed lines with minimum and maximum TEFs. The probabilistic ELCR attributed to the 16 priority PAHs ranges 5.5×10^{-10}–2.5×10^{-5} with a median of 2×10^{-7}. The probability of ELCR exceeding 10^{-5} is ca. 17% if only the 16 priority PAHs are taken into account. The composition of BaP$_{eq}$ indicates that pPAHs in this study contribute major human health risks by soil ingestion, with
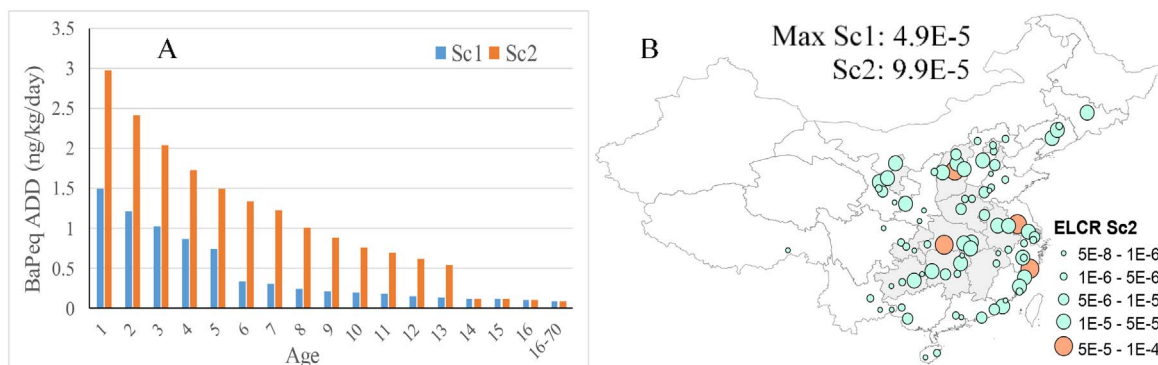
Fig. 5. Annual BaP$_{eq}$ ADD (ng/kg bw/day) for different life stages (A) and distribution of estimated 70-year ELCR (B) by deterministic estimation. Moderate TEFs was used.

BaP and DalP accounting for the highest proportions (Fig. S8A). This composition is different with that of original concentrations of pPAHs and derivatives (Fig. S8B). The estimate of ADD and ELCR in this study may have uncertainties in that TEFs for many PAH derivatives and spatially varied values of parameters for the deterministically spatial risk assessment are lacked; and the PAHs species covered in present study are limited. However this is the best approach and assessment the author could achieve with the available data.

3.5. Potential emission sources

The identification of primary emission sources of PAHs and derivatives is essential for the soil quality and risk management. As mentioned above, PAHs and derivatives in agricultural soils are commonly from the atmospheric deposition, which initially derive from the combustion. However, regionally or locally wastewater irrigation or fuel spills from tractors or other farm vehicles may also contribute. Occasional fuel spills may cause severe contamination to some sites but will not deliver PAHs and derivatives to large area of agricultural soils. The delivery of PAHs and derivatives by wastewater irrigation could be a type of secondary contamination to agricultural soils, as PAHs and derivatives in the wastewater could be from the ground surface, where these chemicals are initially from the atmospheric deposition or fuel spills and are then flushed into wastewater systems (Wild and Jones, 1993). 7% of irrigated areas in China currently receive wastewater irrigation, of which ca. 85% are in Liaohe, Haihe, Huaihe and Yellow River basins (Zhang et al., 2015a). For some farmlands in these regions, wastewater irrigation might potentially be an additional source of PAHs and derivatives and possibly lead to higher concentrations of PAHs than those in agricultural soils receiving reclaimed water or groundwater irrigation (Tao et al., 2004; Jin et al., 2014). The composition of PAH

species delivered by wastewater irrigation may be complicated, nonetheless some studies find the low molecular PAHs to be dominant (Tao et al., 2004; Jin et al., 2014). References on the composition of PAH derivatives in wastewater are limited. Raw sewage sludge could also contain abundant PAHs and derivatives but is forbidden to be directly applied to agricultural soils in China and, therefore, could be neglected (Zhang et al., 2015b). Furthermore, some studies find that sewage sludge increases the removal of soil PAHs under certain proper conditions (Fernández-Luqueño and Ceballos-Ramírez, 2016). In this study, the direct deposition from atmosphere as a result of combustions is assumed to be the only contamination source, as the information on wastewater irrigation has not been available for the present sampling sites. Further survey on historical irrigation is needed next step to accomplish a more complete source investigation.

Associations and ratios of individual pPAHs isomers or derivatives are applied rather than models such as Positive Matrix Factorization (PMF) and Principal Component Analysis-Multiple Linear Regression (PCA-MLR) to identify the contribution of potential combustion emission sources to soil PAH derivatives in this study. These models are frequently used in quantitative source diagnose for PAHs (Kamiya et al., 2016; Mai et al., 2003; Zhuo et al., 2017a) but are probably inappropriate to identify the dominant sources on a large scale area as in this study, as the main regional sources of pPAHs and derivatives would vary remarkably (Shen et al., 2013a; Zhu et al., 2015). Diagnostic ratios may have limitations for the source identification, as the residue of individual PAH species would change with different extent during the long-range transport in air, deposition to soil or retention in soils due to a function of different physicochemical properties and effects by environmental processes, the secondary contamination from wastewater irrigation or the secondary formation for pPAHs and derivatives (Zhang et al., 2005; Zhu et al., 2014). However, they could still provide useful
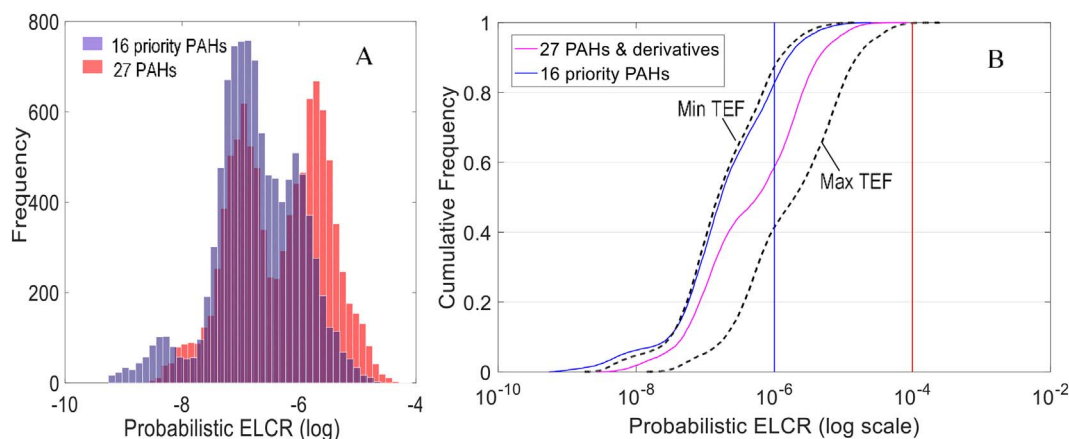

Fig. 6. Histograms (A) and cumulative frequency (B) of probabilistic ELCR. (A) The 27 PAHs include pPAHs and derivatives. (B) The minimum TEFs and maximum TEFs for individual PAHs and derivatives were applied for the two dash curves respectively; the moderate TEFs were used for the solid curves.

quanlitive information (Huang et al., 2014).

Estimated ratios of individual PAH derivatives to corresponding pPAHs for agricultural soils are shown in Table S7. For all sampling sites, ratios of most nPAHs/pPAHs pairs range 0.01–38.8 except for 3N–PHE/PHE and 3N–FLA/FLA at some sites. This is generally higher than the ratio of measured EFs (Shen et al., 2013b; Shen et al., 2012; Tang et al., 2005). The secondary formation and the higher persistence of nPAHs in soil than related pPAHs could both explain the higher ratios. Secondary formation is considered to make the major contributon to the higher ratios, as the difference of chemical properties would not be large enough. 60% of sites ($N = 5$, N is the total number of sites with the detected pairs of pPAHs and derivatives) have a 3N–PHE/PHE ratio of $\sim 10^{-3}$ (in Pingdingshan, Henan Province and Taiyuan, Lyuliang, Shanxi Province) and the remaining sites have a ratio > 0.3. About 15% of sites ($N = 13$) have a 3N–FLA/FLA ratio of $\sim 10^{-3}$ (in Taiyuan, Shanxi Province and Anshan, Liaoning Province) and the remaining sites have a ratio > 0.01. These indicate that the primary sources mainly contribute to the occurrence of 3N–PHE and 3N–FLA in soil samples taken in the counties in Henan, Shanxi Provinces and in Shanxi, Liaoning Provinces. Pingdingshan, Taiyuan and Lyuliang are all well-known counties with abundant storage and active mining of coal in China. Anshan is a city famous for steelmaking, which is an energy intensive industry and demands high amount of fossil fuels (Almaula, 2005). The low ratio of the two pairs of species is a marker of new loadings of pPAHs and derivatives to agricultural soils from these industries in the vicinity. This corresponds with the higher estimated ELCR for Shanxi and Liaoning than for many other areas. The 1N–PYR/PYR ratio is considered to be an indicator of diesel engine exhaust (Tang et al., 2005). However, 1N–PYR is detected only at one site (Kaifeng, Henan) with an 1N–PYR/PYR ratio of 0.27, which is comparable to the ratio for diesel engine exhaust (Tang et al., 2005). Ratios of 9FO/FLO and BaAQ/BaA ($N = 3$) in this study are generally lower than the measured ratios of EFs for wood, crop residue and coal combustions (Shen et al., 2012), except for Kaifeng in Henan, which may have higher a rate of secondary formation than loss for oPAHs.

The study on ratios of PAH derivatives to pPAHs is limited and additionally the detection rate of nPAHs and oPAHs in soils is low in this study. Ratios such as ANT/(ANT + PYR), FLA/(FLA + PYR), IcdP/(IcdP + BghiP) and BaA/(BaA + CHR) are more widely used (Alves et al., 2016; Yunker et al., 2002) and could possibly reflect an overall insight of primary sources for pPAHs and derivatives as a result of the accompanied emission (Shen et al., 2011; Shen et al., 2013b; Shen et al., 2012). Ratios of FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) are found to be more stable than other species for soils (Peng et al., 2016) and therefore are applied here. The specific ratios for possible sources are shown in Fig. 7 (Yunker et al., 2002). At a high proportion of sites

(44%, $N = 82$), petroleum combustion and traffic exhaust are possibly the main sources. 23%, 12%, 11% and 9% of the sites are possibly primarily affected respectively by (1) traffic exhaust and petrogenic sources, (2) traffic exhaust and grass, wood and coal combustion, (3) grass, wood and coal combustion and (4) petroleum combustion and grass, wood and coal combustion. Only at one site (Zhangzhou, Fujian) petrogenic sources and grass, wood and coal combustion possibly appear to be the main sources. The distribution of these sites with differentiated main emission sources are shown in Fig. S9. This method may have uncertainties, however taking Beijing and Shanghai as an example, where the traffic vehicle emission is believed to be main source of PAHs, petroleum combustion and traffic exhaust are identified as the main sources by this method. Further more intensive gauging campaigns or source dioganosis studies by other methods may be needed to identify regional emission sources more accurately.

4. Conclusions and implications for soil management

As a first study to report levels of nPAHs and oPAHs in agricultural soils covering such a large area in eastern China, this paper fills a data gap and provides a valuable basis for human health risk assessment from the exposure to pPAHs and derivatives in soils for both scientists and policy makers. This study finds that the average concentration of ΣnPAHs and ΣoPAHs in agricultural soils are 50 and 9 μg/kg respectively. Both deterministic and probabilistic estimations conclude the maximum ELCR at a level of 10^{-5} from the exposure to PAHs and derivatives through soil ingestion with moderate TEFs applied. The ELCR estimation is sensitive to TEF values, and if maximum TEFs are used, sites with ELCR exceeding 10^{-4} could be identified. However, only a very low probability of exceedance is estimated by the probabilistic study that has considered the uncertainty of parameters and the maximum TEFs. The ELCR could be largely underestimated for some regions if only taking account of the 16 priority PAHs. Further monitoring and assessment are needed in areas with higher ELCR compared to other regions such as Shanxi, Zhejiang, Liaoning, Jiangsu and Hubei. More intensive regional surveys should be conducted, especially for regions identified to receive possible new inputs of PAHs such as in Shanxi and Liaoning. Life-stage estimations conclude that an extremely high proportion of the pPAHs and derivatives burden and ELCR (60–80%) by soil ingestion is accumulated during childhood.

The quality and the sustainable management of soils are vital for human health and sustainable development. However, soil contamination is a severe problem with little public awareness. The Chinese government has released the 'Action Plan for Soil Pollution Prevention' in May 2016 (SCC, 2016). The risk-based approach is believed to be important to underpin the soil management although limits
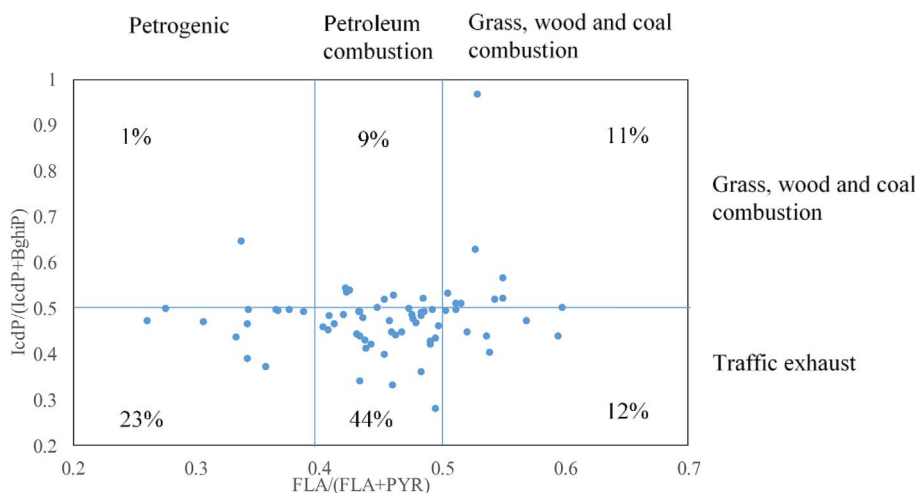

Fig. 7. Ratios of FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) for identifying the primary sources of PAHs.

exist (Umeh et al., 2017). More intensive monitoring data and seasonal gauging are required in the future. The emission diagnosis can support the emission management especially for areas with higher estimated risks, which will help the soil quality management.

Acknowledgement

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.envint.2017.09.001.

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