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RESEARCH ARTICLE

Occurrence and geographic distribution of polycyclic aromatic hydrocarbons in agricultural soils in eastern China

Zhe Sun[1] · Jing Liu[1] · Shaojie Zhuo[1] · Yuanchen Chen[1] · Yanyan Zhang[1] ·
Huizhong Shen[1] · Xiao Yun[1] · Guofeng Shen[1] · Weiping Liu[2] · Eddy Y. Zeng[3] · Shu Tao[1]

Abstract Polycyclic aromatic hydrocarbons (PAHs) in agricultural soils, eastern China, were studied through a collection of surface samples at 109 sites. The study covered US EPA priority pollutants but also several non-priority isomers including some dibenzopyrenes which are expected to have higher toxic potentials. The total PAH concentrations varied extensively from 8.8 to 3880 μg/kg, with a geometric mean of 158 μg/kg. There were significant differences in both the concentrations and composition profiles between the south and the north regions. The overall geographical distribution pattern was strongly influenced by both the per capita gross domestic product and soil organic carbon (SOC) content. The former is an indicator of anthropogenic emissions while soil SOC content is associated with the accumulative capacities of the soils. The sequestration mechanism is an important process controlling fates of PAHs in agricultural soil.

Keywords Polycyclic aromatic hydrocarbons · Agricultural soil · Soil organic carbon · Eastern China

Highlights
- Characterization of priority and some non-priority PAHs in agricultural soil in eastern China
- Emission strength and soil accumulation potential dominate geospatial distribution.
- Sequestration mechanism is an important process controlling soil organics.
- Severely contaminated surface agricultural soils act as a secondary emission source of ambient PAHs.

✉ Guofeng Shen
gfshen12@gmail.com

✉ Shu Tao
taos@pku.edu.cn

[1] College of Urban and Environmental Sciences, Peking University, Beijing 100871, China

[2] College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China

[3] School of Environment, Jinan University, Guangzhou 510632, China

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants that are mainly produced from incomplete combustion processes. The total emission of 16 US EPA priority PAHs in China was 106 Gg in 2007, contributing to about 21% of the global total emission (Shen et al. 2013). Because of favorable topographical and meteorological conditions, over 70% of the Chinese population live in eastern China, and most agricultural products, including 64% of grains and 80% of vegetables, are produced from this region (Ministry of Agriculture 2014). The spatial overlap of agricultural production and soil contamination would pose a direct risk of food contamination. In fact, soils, especially the agricultural soils in eastern China, are severely contaminated by a variety of pollutants including PAHs (Tao et al. 2011; Wang et al. 2012; Niu et al. 2014). Consequently, relatively high health risks due to PAH exposure might be expected in this region (Zhang et al. 2009; Xia et al. 2010; Yu et al. 2011).

Concentrations of soil PAHs are directly affected by a number of factors like emissions from multiple combustion sources in surrounding areas, irrigation water, usage of sewage sludge as fertilizer, and removal mechanism(s) due to microbial degradation, uptake by vegetables, and soil erosion, as well as air-to-soil exchange (Enell et al. 2016; Li and Ma 2016; Tao et al. 2006a; Wang et al. 2011a, b, c). Soil organic

matter, often measured and reported as soil organic carbon (SOC), is an important factor governing the fate and spatial distribution of PAHs in soil. A positive correlation between soil SOC content and PAH concentration is often reported (Wilcke 2000; Mackay 2001).

Over the past three decades, a series of localized studies have been conducted to investigate the occurrences of organic pollutants, including PAHs, in soil (Cao et al. 2003; Tao et al. 2004; Ping et al. 2007; Zuo et al. 2007; Wang et al. 2010, 2012). However, due to the differences in sampling methods, study periods, analytical procedures, and also data reporting, it is often difficult, if not impossible, to pool the data and draw an overall picture of the PAH contamination in agricultural soils of the entire eastern China region. Recently, a campaign was conducted to collect surface soil samples from agricultural land throughout eastern China to investigate organochlorine pesticides and other organic contaminants in this region (Niu et al. 2013a, b). A portion of the samples was analyzed in this study to address PAH contamination issues including their concentration, spatial variation, composition profile, and potential risk, in this region. The samples were analyzed for a total of 20 parent PAHs, including 15 US EPA priority pollutants and several highly toxic dibenzopyrenes (Tilton et al. 2015).

Materials and methods

Sample collection

One hundred surface soil samples were collected by a team from Zhejiang University. Detailed methods of the sampling design, collection, and pretreatment can be found in a previous paper (Niu et al. 2014). Briefly, the sampling sites were selected according to the distribution of arable soils in China (National Bureau of Statistics of China 2013). Before collection, overlying vegetation was removed thoroughly. A composite sample was obtained by mixing five individual surface soil samples (0–20 cm) suing a precleaned scoop and sealed in a precleaned aluminum foil bag at each site (Niu et al. 2014). The soil samples were air-dried, grounded, and sieved (2 mm). A portion of soil samples (~20 g) was shipped to Peking University for PAH analysis. The samples were stored at −20 °C until analysis.

Extraction and cleanup

The procedure for sample extraction followed the method used in previous studies (Wang et al. 2010; Li et al. 2014) with a slight modification. In brief, ~8 g soil sample was extracted with 25 mL of *n*-hexane/acetone (1:1, *v/v*) using a microwave accelerated reaction system (CEM MARSXpress, NC, USA). The procedure temperature was set to reach 110 °C in 10 min and held at 110 °C for another 10 min. The extract was then concentrated to 1 mL using a rotary evaporator (N-1100;

EYELA, Japan). The extract was added to the silica/alumina gel column (1 cm of anhydrous sodium sulfate, 12 cm of silica gel, and 12 cm of alumina from the top to the bottom) and pre-eluted with 20 mL of *n*-hexane. A dichloromethane/*n*-hexane mixture (50 mL, 1:1, *v/v*) was used to elute the PAHs. The eluent was concentrated to 1 mL and transferred to a hexane solution. Finally, 200 ng of internal standards (naphthalene-d8, acenaphthene-d10, anthracene-d10, chrysene-d12, and perylene-d12; J&K Chemical, Newark, DE, USA) was added.

Analysis

A gas chromatograph coupled with a mass spectrometer (GC-MS, Agilent 6890/5973, CA, USA) with a DB-5MS capillary column (0.25 mm i.d. × 30 m, 0.25 μm film thickness) in electron ionization (EI) mode was used for PAH analysis. Helium was used as the carrier gas. The oven temperature program was set as follows: held at 50 °C for 1 min, increased to 150 °C in 10 min, to 240 °C at a rate of 3 °C/min, and finally increased to 280 °C in 20 min. The following 20 parent PAHs were identified and quantified according to the individual retention times and qualitative ions of the internal standards in selected ion mode (SIM): acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), pyrene (PYR), fluoranthene (FLA), retene (RET), benzo[a]anthracene (BaA), chrysene (CHR), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (PER), benzo[k]fluoranthene (BkF), benzo[b]fluoranthene (BbF), indeno[1,2,3-cd]pyrene (IcdP), benzo[g,h,i]perylene (BghiP), di-benzo[a,h]anthracene (DahA), di-benzo[a,l]pyrene (DalP), and di-benzo[a,e]pyrene (DaeP). Naphthalene was not included due to its low recovery rate. The SOC contents were measured using a total organic carbon analyzer (SSM-5000A, Shimadzu, Japan).

Quality control and assurance

Procedural and reagent blanks were analyzed for each batch of sample analysis. All samples were measured in duplicate. The reagents, acetone, *n*-hexane, and dichloromethane, were all of chromatographic purity (Tianjin Siyou, Tianjin, China). The recoveries of the spiked standards of individual PAHs were 76.1–110%, with an arithmetic mean of 93.7%. The recoveries of two surrogates (2-fluoro-1,1′-biphenyl and *p*-terphenyl-d14) that were added in 20% randomly selected samples were 85 ± 4 and 103 ± 7%, respectively. Results reported here are blank-corrected, but not corrected with recoveries.

Data analysis

SPSS 22.0 (SPSS Inc., USA) was used for most of the statistical analyses. The data were log-transformed and standardized for autocorrelation and principle component analysis. Varimax rotation was applied for principal component analysis (PCA). The

global and local Moran's I values were calculated using an inverse Euclidean squared distance method in ArcGIS (ESRI). A significance level of 0.05 was applied for all significance tests.

Results and discussion

PAH concentrations

PAH concentrations in soils were log-normally distributed, which is similar to many other trace pollutants (Wang et al. 2010). The calculated coefficients of skewness and kurtosis of the 20 PAHs were between 2.10–9.05 and 5.98–87.9, respectively, and the values became −1.28–3.39 and −0.77–12.3, respectively, after log transformation. The frequency distributions of three representative compounds (PHE, PYR, and BaP) with different molecular weights (MWts), before and after log transformation, are shown in Fig. S1 as typical examples. Accordingly, geometric means, rather than arithmetic average, should be applied as descriptive statistics. However, since arithmetic statistics are widely reported in literature, both the geometric means and arithmetic means with standard deviations are listed in Table 1. The measured SOC contents are also summarized in Table 1.

As observed, the standard deviations are rather high in all cases. In fact, the coefficients of variance (CVs) for each individual ranged from 86 to 392%. Results from the duplicated sample measurements indicated that the error from the analytical procedure was in 17.2%. Given the limited seasonal variation in the soil PAH concentrations (Lang et al. 2007), high overall variation from the present study can be primarily attributed to the spatial variation. In fact, high spatial variations of PAH concentrations in surface soils have been reported in some previous studies (Tao et al. 2011; Wang et al. 2012), and it is expected to be due to differences in emissions, discharges, transport patterns associated with meteorological conditions, and soil properties (Wang et al. 2011c; Aichner et al. 2015). A discussion on geographic distribution of PAHs in agricultural soils is provided in the next section.

In general, the measured concentrations fell in the reported range in past studies at the same studied region (Tao et al. 2004; Wang et al. 2011c, 2012). The concentrations in the agricultural soils in this study were significantly higher than those in forest soils (Xiao et al. 2014) and lower than those from urban (Jiang et al. 2009) and industrial areas (Duan et al. 2015). The levels were much higher than most data reported for western China, for example, the average concentration of total PAHs was 51.8 ± 38.5 μg/kg in the Qinghai-Tibetan Plateau (Tao et al. 2011).

Geographical distribution

Because of the large spatial variations in the emissions, meteorological conditions, and soil properties, the PAH concentrations in the surface soils varied extensively. Figure 1 shows the geographical distributions of the measured PAHs, using PHE, PYR, and BaP as typical examples. The concentrations in the north were generally higher than those in the south. A similar pattern was observed for the PAH emission density (Shen et al. 2013). Other than emissions, atmospheric transport and air-to-soil deposition are key processes governing the input of PAHs to surface soils (Li et al. 2010; Tao et al. 2011). Another important factor governing the distribution is the soil property, which affects the accumulation of PAHs in soil. Of these factors, the emissions are dependent on population and industrial and transportation activities (Shen et al. 2013).

The spatial variations of most factors discussed above including anthropogenic activities, meteorological conditions, and soil properties are not randomly distributed. As a result, spatial autocorrelation can often be found for many pollutants in surface soil (Liu et al. 2013). The spatial autocorrelation was tested in this study by calculating Global Moran's I (Table S1). It was found that 15 PAH individuals, as well as the total concentrations of all 20 PAHs, were significantly clustered in the study region ($p < 0.05$). Cluster and outlier analyses were also conducted using Anselin Local Moran's I as an index, which showed the same tendency that high values were clustered in Northern Plain, while low values were clustered in south coastal areas (Fig. S2).

In surface soil, the concentrations of many hydrophobic pollutants including PAHs are often reported to be correlated with soil SOC (Agarwal et al. 2009; Wilcke 2000; Mackay 2001). In some past localized studies in China, such a correlation was also reported. For example, a significant correlation between PAHs and SOC was found for surface soils collected from Beijing, Tianjin, and surrounding areas in northern China (Wang et al. 2010). In the present study, a significantly positive correlation was also observed between the log-transformed total PAHs and the arcsine-transformed SOC ($r = 0.466$, $p < 0.0001$), as shown in Fig. 2 (left panel). In fact, besides the total concentration, the concentrations of most individual PAH compounds are correlated with SOC (Table S2).

The positive correlations between SOC and organic concentrations are generally interpreted by a strong affinity of organic pollutants to soil organic matter (Mackay 2001). However, the result of a multimedia fugacity modeling demonstrated that the mechanism for such a correlation could be due to the sequestration of PAHs by natural organic matter during the aging process and subsequent reduction of the bioavailability of PAHs to bacteria (Tao et al. 2003). It is interesting to find that the PAH-SOC correlations were dependent on the PAH molecular weight (MW), as shown in Fig. 2 (right panel), which illustrated a significant and positive correlation between the p values and PAH MW ($p < 0.01$). Since the affinities of low MW PAHs to soil organic matter were relatively lower than those of high MW PAHs, the positive correlation found here did not support an affinity-controlled

Table 1 The measured PAH concentrations (µg/kg) and SOC contents (%) in the surface soils from agricultural land in eastern China

| PAH | Arithmetic | | Geomean | Percentile | | | | | Raw data | | Log-transformed | |
	Mean	Std. dev.		P_5	P_{25}	P_{50}	P_{75}	P_{95}	Skewness	Kurtosis	Skewness	Kurtosis
ACY	2.17	3.56	0.89	0.17	0.25	0.83	2.47	10.1	3.15	10.7	0.33	−0.77
ACE	1.07	4.22	0.45	0.33	0.33	0.33	0.33	5.02	9.05	87.9	3.39	12.3
FLO	13.7	11.8	9.74	2.13	6.05	9.50	17.9	36.2	2.10	5.98	−0.74	1.74
PHE	33.8	33.3	22.6	3.85	13.9	26.7	42.9	88.8	3.20	15.0	−1.28	4.47
ANT	1.94	5.02	0.46	0.17	0.17	0.17	1.56	8.20	5.96	44.5	1.14	−0.10
FLA	30.7	61.5	10.4	0.64	4.52	10.6	33.1	158	4.74	28.1	−0.40	0.74
PYR	32.7	56.1	13.3	0.98	6.43	13.1	34.1	50.2	3.94	19.7	−0.50	1.18
BaA	17.3	40.4	5.49	0.89	1.95	3.84	13.5	94.1	5.41	36.7	0.69	0.05
CHR	30.6	57.9	12.7	1.14	6.07	11.2	32.0	129	5.32	37.3	0.07	0.15
RET	26.6	81.6	9.82	1.08	4.59	9.16	21.3	71.3	8.29	76.5	0.40	0.90
PER	2.85	6.17	1.00	0.33	0.33	0.63	2.47	13.9	4.53	24.6	0.99	0.00
BbF	37.0	75.7	12.9	0.80	6.15	12.1	34.9	197	4.97	31.7	−0.07	0.32
BkF	26.9	55.0	9.50	0.58	4.46	8.77	25.3	143	4.96	31.7	0.01	0.16
BeP	12.6	24.0	4.85	0.33	2.21	4.40	10.7	60.4	4.57	27.1	0.16	−0.08
BaP	12.1	25.1	4.03	0.33	1.42	3.37	10.6	68.4	4.31	22.7	0.47	−0.19
IcdP	7.91	18.7	2.30	0.33	0.76	2.00	5.94	40.5	4.83	27.1	0.61	−0.25
BghiP	8.17	18.6	2.54	0.33	0.86	2.36	6.25	36.8	4.83	26.3	0.50	−0.33
DahA	1.87	4.35	0.77	0.33	0.33	0.42	1.28	8.26	5.46	35.5	1.33	1.06
DaeP	1.49	1.66	1.13	0.67	0.67	0.86	1.70	4.19	4.60	28.7	1.31	1.44
DalP	1.71	2.63	1.10	0.67	0.67	0.67	1.65	7.14	4.16	18.8	1.75	2.80
Total	303	490	158	32.9	77.9	134	304	1290	4.52	26.8	0.34	0.37
SOC (%)	1.62	0.93	1.36	0.31	1.00	1.56	2.11	3.28	1.68	5.85	0.28[a]	1.38[a]

The results are presented as the arithmetic means and standard deviations; geometric means; 5th, 25th, 50th, 75th, and 95th percentiles; coefficients of skewness and kurtosis before and after log transformation for PAHs; and arcsine transformation for SOC

[a] Arcsine-transformed

interpretation. On the other hand, low MW PAHs with relatively small sizes are more ready to be embedded into the complex structure of natural organic matter during the aging process. Therefore, though both sequestration and sorption could be important processes controlling fates of organics in soils, and these two processes may co-occur (Arp et al. 2011), the positive correlation between the p values and MW in this study may indicate that in the east China region, the sequestration mechanism is an important process controlling levels of PAHs in agricultural soil.

Fig. 1 Geographical distributions of the PHE, PYR, and BaP concentrations in surface agricultural soils in eastern China. The areas of the *symbols* are proportional to the concentrations
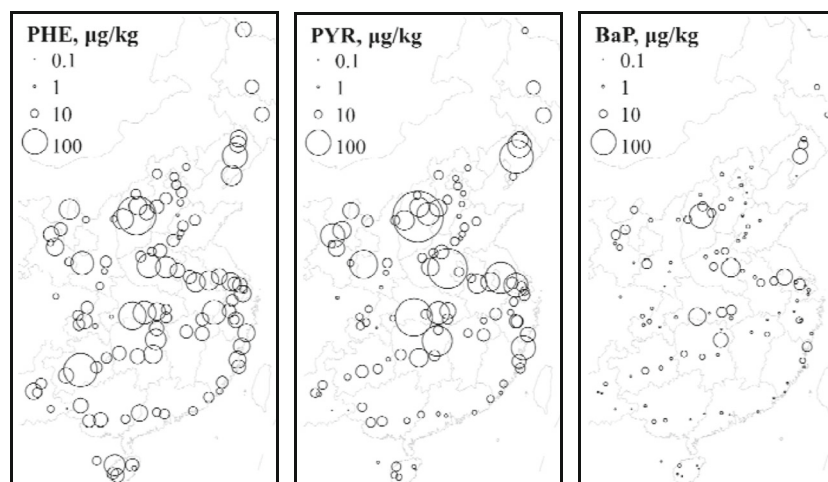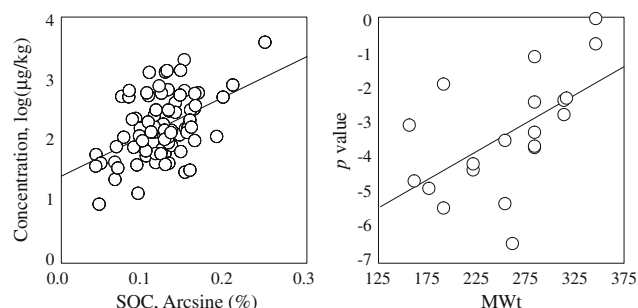
Fig. 2 Relationship between the log-transformed total concentrations of 20 parent PAHs and the arcsine-transformed SOC of the surface soil samples from eastern China (*left panel*) and the dependence of the correlation significance level (*p* value, log-transformed) on the PAH MW (*right panel*)

Li et al. (2010) calculated the air-to-surface deposition of PAHs in Tianjin, China, and found that the surface soil PAH concentrations are dependent on both the deposition rate and SOC content. Because the deposition rate could not be derived in this study, a series of parameters that was believed to be associated with inputs was evaluated for their relationship with the PAH concentrations. Among the parameters tested, the gross domestic product per capita (GDP_{cap}) and SOC were found to be significant in a stepwise multiple regression analysis based on standardized data:

$$\log PAHs = 0.566 \, \text{arcsin} SOC + 0.288 \log GDP_{cap}, \quad R^2_{adj} = 0.325.$$

Here, GDP_{cap} represents the status of development associated with emission (Chen et al. 2015), and SOC can be regarded as the accumulation capacity of the surface soil for PAHs. The two variables contributed approximately one third of the overall variation. It should be noted that the purpose of such a standardized regression analysis was not to develop a prediction tool. Instead, the main factors affecting the spatial variation were addressed. For this reason, intercept was not included in the regression, and all variables were normalized.

Composition profile

Generally, three- and four-ring, median-sized compounds from FLO (MW 166) to BkF (MW 252) were dominated (Fig. S3, top panel), which was similar to the composition profiles reported in past studies (Tao et al. 2004; Wang et al. 2011b; Duan et al. 2015). As discussed above, the PAH concentrations in the surface soils are partially governed by emissions. A comparison of the composition profile of 15 US EPA priority PAHs (emission data for other compounds were not available) in emission and soil is illustrated in Fig. S3. Though both profiles were dominated by median-sized PAHs, the concentration profile in soil is not exactly identical to the emission profile, due to the different behaviors including gas-particle partitioning, degradation under the influence of OH radicals and radiation, dry and wet deposition, sequestration in the soil

matrix, and mineralization by soil microorganisms, of individual PAHs in a multimedia environment (Lang et al. 2007).

Although there was a general composition profile pattern with median-sized PAHs dominated, differences can still be observed among the 109 sites, as shown in Fig. 3. In general, relative contributions of high MW PAHs (MW ≥252) were relatively high in northern China, which agreed with high autocorrelations of these compounds in the north, as discussed above. Because northern China has a larger population density and is colder, requiring more heating in the winter time, more PAH contamination can be expected. The very different profiles of several extreme cases shown in the figure are likely due to specific local emissions. For example, the high fraction of low MW PAHs at the Heihe site (the most northern site) is believed to be associated with forest fires that often occur in this taiga forest area (Liu et al. 2009).

BaPeq concentration and spatial distribution

Based on the data measured in this study and the BaP carcinogenic equivalent factors of individual compounds (Nisbet and LaGoy 1992), the BaP equivalent carcinogenicities of the agricultural soils were derived for each of the 109 sites. The calculated values varied from 8.23 to 486 μg/kg, with a mean and a standard deviation of 47.5 ± 75.5 μg/kg, and the results are mapped in Fig. 4. The spatial distribution pattern was
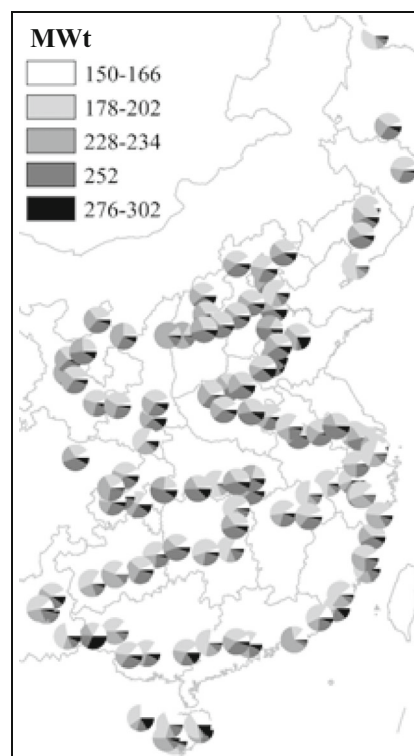

Fig. 3 Spatial distribution of the composition profiles of the measured PAHs in the surface agricultural soils from eastern China. The 20 parent PAHs are grouped into five categories with different MWs of 150–166, 178–202, 228–234, 252, and 276–302
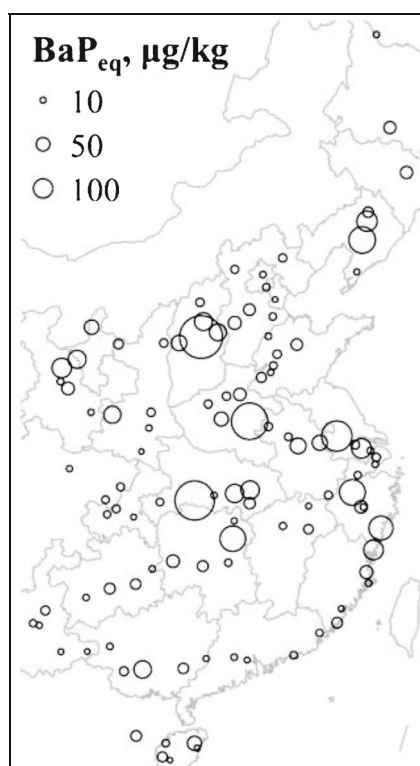
Fig. 4 Geographical distribution of the calculated BaP equivalent carcinogenicity of surface agricultural soils in eastern China based on the measured parent PAHs

basically the same as those of the high MW PAHs, which contributed largely to the BaP equivalent concentration.

Insights on soil-air exchange

Previous studies from the multimedia fate modeling under a steady-state assumption reported that soils and sediments are

major sinks of PAHs in the North China Plain (Wang et al. 2011b). In addition to being a sink, PAH-contaminated soil may become a secondary emission source, releasing PAHs into ambient air (Zhang et al. 2011). The air-to-surface exchange of PAHs was roughly quantified using the fugacity calculation (Mackay 2001) to provide the direction and strength of the exchange. Based on the data collected in this study and ambient PAH concentrations from the previous study (Zhang et al. 2009; Shen et al. 2014), the annual mean fugacities of both surface soils and ambient air were calculated. The ratios (soil fugacity divided by mean fugacity of soil and air) are mapped in Fig. 5 for the three typical examples of PHE, PYR, and BaP. The results indicate that the calculated air-to-soil fugacity ratios of BaP at most sites were below 0.3, suggesting that soils are long-term sink of BaP. On the other hand, the fugacity ratios of PHE, as well as other small MW PAHs, tended to be greater than 0.7, indicating a net emission tendency on an annual basis. Although air-to-surface exchange is the dominant source of PAHs entering the surface soil, the input is in both the gaseous (diffusion) and particulate (dry and wet depositions) phases. Net evaporation from soil to air can still occur, even though the total exchange of both phases should be in the direction from air to soil because the predominant pathway of removing PAHs from the soil is through degradation by microorganisms (Tao et al. 2003). For the median-sized PAHs such as PYR, the exchanges are more or less balanced.

It is necessary to note that the fugacity calculation here is a simple rough estimation. Though the PAH concentrations in soil remain relatively constant all year long, the air concentrations of PAHs vary widely across different seasons (Lang et al. 2007). The ambient air PAH concentrations in summer can be at least one order of magnitude lower than those in winter (Li et al. 2014), indicating that the fugacity ratios, and

Fig. 5 The calculated air-to-soil fugacity ratios of the three representative PAHs of PHE, PYR, and BaP at all sampling sites
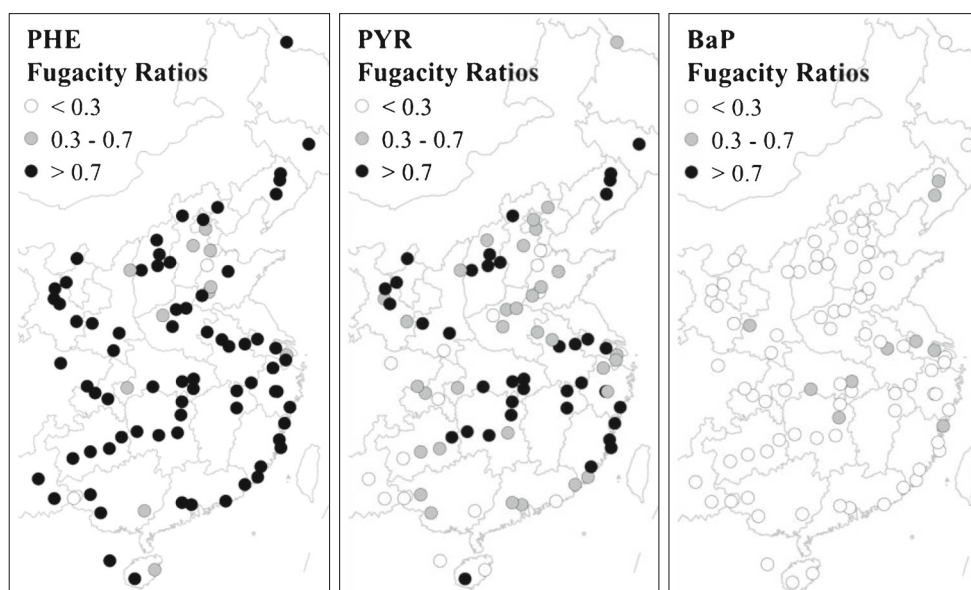
subsequently the direction of air-to-surface exchange, can vary dramatically within a year. It is very likely that greater re-emission of PAHs from soil to air may occur in summer. In addition to seasonal variations, long-term changes in the overall emissions from anthropogenic sources to the environment may lead to changes in the exchange direction of PAHs between soil and air. A typical example was the process of banning beehive coke ovens in China, which usually contributed more than 20% of the overall PAH emissions. Since the early 1990s, the phasing out of these coke ovens has led to a substantial reduction in PAH emissions (Shen et al. 2013). In recent years, a campaign to replace coal with clean energy for industry and power generation is underway (Ziková et al. 2016), and a significant reduction in PAH emissions is thus expected, which may promote the re-emission of previously accumulated PAHs in soil. If the input flow is reduced by a certain extent during a short period of time, the steady-state condition will be disrupted, and the contaminated soil may become a secondary source to the air (Tao et al. 2008).

Conclusion

Concentrations of PAHs in surface soils from agricultural land in eastern China varied extensively and log-normally distributed. The concentrations are spatially auto-correlated, affected by both input and accumulative potential. Per capita gross domestic product can serve as an indicator to the input, while the accumulative potential is associated with SOC. Currently, there are no soil standards for PAHs in China. A set of generalized soil quality standards for representative PAH compounds could help to reduce management costs. Fortunately, BaP will be a new addition to the amendment of the "Soil Environmental Quality Standards for Agricultural Land (GB-15618-1995)," which will be in force in the near future (Ministry of Environmental Protection 2016).

Compliance with ethical standards

Conflict of interest   The authors declare that they have no conflicts of interests.

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