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Contamination characteristics and source apportionment of methylated PAHs in agricultural soils from Yangtze River Delta, China*

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ABSTRACT

Alkylated PAHs (APAHs) have been shown to be more toxic and persistent than their non-alkylated parent compounds. However, little is known about the extent of soil contamination by these pollutants. To help understand agricultural soil pollution by these compounds at a regional scale, a total of 18 methylated PAHs (MPAHs, a major class of APAHs) in 243 soil samples were analyzed. These soil samples were collected from 11 sites in the Yangtze River Delta (YRD) region, a representative fast developing area in China. The total concentration of MPAHs ($\sum 18\text{MPAHs}$) ranged from 5.5 to 696.2 ng/g dry soil, with methylnaphthalenes (M-NAPs) and methylphenanthrenes (M-PHEs) accounting for more than 70% of the compositional profile. Relatively high concentrations of $\sum 18\text{MPAHs}$ were found in Jiaxing and Huzhou areas of Zhejiang province, as well as on the border between the cities of Wuxi and Suzhou. Different MPAH groups showed dissimilar spatial distribution patterns. The spatial distribution of lower molecular weight MPAHs was related to agricultural straw burning and emissions/depositions from industrial activities, whereas that of higher molecular weight MPAHs was much more a function of the total organic carbon (TOC) content of soil. Although coal, biomass (crop straw and wood), and petroleum combustion were identified to be the major emission sources for most of the sampling sites, the areas with relatively severe pollution with $\sum 18\text{MPAHs}$ resulted from the localized hotspots of petroleum leakage. Isomeric MPAHs with methyl group substituted at 2- (β) position exhibited significantly higher concentrations than those substituted at 1- (α) position. Results of this work help to understand soil pollution by MPAHs, and are useful for designing effective strategies for pollution control so as to ensure food safety in areas with fast economic growth.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), defined as a group of organic compounds containing two or more fused benzene rings, have been widely investigated in various environmental matrices, largely due to their potentially mutagenic and carcinogenic properties. They are ubiquitous in the environment. As a similar persistent pollutant group, alkylated PAHs (APAHs) have been shown to be more toxic and persistent than their non-alkylated parent compounds (Casal et al., 2014). Most parent PAHs are considered to be carcinogenically inactive, whereas their alkylated derivatives exhibit greater overall non-carcinogenic toxicity. For example, LaVoie et al. (1985) demonstrated that for various methylated anthracenes tested, those with higher mutagenic potency and tumor-initiating activity were associated with the presence of a methyl substituent at 9- and 10- position of anthracene. The production instruction of 9-methylanthracene shows that this compound is very toxic to aquatic life with chronic effects, and it can cause serious irreversible damage to skin/eyes/lungs (Alfa Aesar Chemical Co. Ltd). However, anthracene was proposed to be carcinogenically inactive with a relatively low benzo[a]pyrene- equivalent factor (Nisbet and LaGoy, 1992). Researchers have tried to elucidate the carcinogenic activity of methylated PAHs (MPAHs, a typical class of APAHs), using topologically simple Hückel theory. The authors found that some mono-, di-, and tri-methylated benz [a]anthracenes and benzo[a]pyrenes had extremely high carcinogenic activity, but the methylbenzo[c]phenanthrenes with a substituent at 3-, 4-, or 5-position were moderately and weakly active (Braga et al., 1999). Some APAHs could induce dioxin-like response via activation of aryl hydrocarbon receptor (AhR); Lee et al. (2015) reported that the dioxin-like potency of 1-methylchrysene was generally higher than chrysene with the aid of theoretical computation and molecular docking method. The authors concluded that dioxin-like potency of PAHs was significantly affected by alkylation, in addition to the benzene ring numbers.

Furthermore, exposure to water polluted by weathered crude oil in which APAHs were identified to be the major constituents ac- counting for 98% of the total PAH fraction (Lian et al., 2009a; Malmquist et al., 2015; Requejo et al., 1996) led to malformations, genetic damage and mortality in early life stages of fish even at a low dose (Carls et al., 1999; Heintz et al., 2000).

The distribution of APAHs in surface sediments (Miki et al., 2014; Planas et al., 2006; Yuan et al., 2015), sediment porewater (Hawthorne et al., 2005), dustfall and surface soils (Lian et al., 2009b; Wei et al., 2015), as well as mobile exhaust (Casal et al., 2014) have been investigated in previous studies. However, agri- cultural soil at a regional scale is a significant sink for persistent organic pollutants and present food safety-related concerns; a comprehensive assessment of APAHs in this environment is lacking.

The Yangtze River Delta (YRD), the sampling region of this study, is one of the most rapidly developing areas in Eastern China, where intensive farming activities are performed and a great number of chemical and industrial plants exist near the provincial boarders (Sun et al., 2016). Automatic exhaust, gas stations, waste discharge from towns and village enterprises, as well as crop straw burning, were considered as potential sources of PAHs and their derivatives in this region (Ping et al., 2007; Zhang et al., 2012). Parent PAHs, as well as representative endocrine disrupting chemicals including phthalate esters, organochlorine pesticides and polybrominated diphenyl ethers, have been investigated previously in soils of the YRD region (Ping et al., 2007; Sun et al., 2016; Li et al., 2016). Aside from soil, concentrations and source apportionment of the parent PAHs in surface water (Zhang et al., 2012), sludge (Shen et al., 2007) and street dust (Zhao et al., 2009) in this area have also been studied. However, to date no information is available on APAHs in agricultural soils in the YRD area. To address this knowledge gap, the pollution status of APAHs in surface soils in this area was determined, with the goal of establishing effective strategies for pollution control and ensuring food safety.

Most previous APAHs studies focused on constiutents with 2 - 4 rings, since no APAHs with higher molecular weight (5 - 7 rings) were detected from dustfall, sediment porewater and crude oil (Hawthorne et al., 2005; Lian et al., 2009b; Requejo et al., 1996). PAHs-34 required by the United States Environmental Protection Agency (US EPA) narcosis model for benthic organisms risk assessment aimed at the prominent C1 to C4 alkyl derivatives of 2 - 4 ring parent PAHs as well. Here, C1, C2, C3, and C4 referred to methyl, dimethyl, trimethyl, and tetramethyl, respectively. Furthermore, a recent study on 29 priority parent PAHs in the same 243 soil samples from the YRD region reported that the predominant species were chemicals with 2 - 4 rings (Li et al., 2016). Therefore, 2 - 4 ring APAHs were taken as the target compounds in the present work. In addition, it is well known that different classes of substituted moieties on PAHs can dramatically affect carcino- genic activity (Jones and Matthews, 1974). Methyl substitution has been attracting increasing research concerns and low-molecular- weight APAHs with one to a few methyl groups are predominant species in the areas polluted by APAHs (Jiang et al., 2009; Miki et al., 2014). Few studies focused on the difference between isometric APAHs, which are generally classified into groups instead of being analyzed individually. It is therefore important to shed light on specific difference in isomers with a same substituent (methyl in this study) at different positions. Therefore, a number of 2 - 4 ring methylated PAHs (MPAHs), including several isomers along with their parent PAHs, were investigated in this work.

Overall, the key objectives of the current study were to: 1) clarify the pollution status and compositional profile of 18 MPAHs in agricultural soils in the Yangtze River Delta region of China; 2) understand the spatial distribution pattern and identify the possible source of MPAHs in the relatively heavily polluted areas and; 3) compare and interpret the difference in pollution status of the target isomeric MPAHs with methyl at different positions in agricultural soils.

MATERIALS AND METHODS

Sample collection and target compounds

In June 2014, two hundred and forty three surface soil samples were collected from the YRD region using uniform gird method. The study area covers the core part of the YRD region (including 11 cities with variable land-use types) and contributes 21% of China's GDP with a 2012 population of more than 150 million (Yearbook of Yangtze River Delta Development, 2013). GPS was used to delineate the sampling sites, and related information such as geographical coordinates, geomorphic features and the status of agricultural production was recorded for further analysis. Field blanks were also collected from several sites in the forest areas of Zhejiang Province, where soils are largely unaffected by human activities. For each sampling site, an area of 100 m x 100 m was set and five topsoil samples (0 - 10 cm in depth, four from corners and one from center of the area) were collected and composited into one sample of approximately 500 - 1000 g. All samples were stored in plastic automatic sealing bags, delivered to laboratory, air-dried and stored in a freezer (-4°C) for further analysis.

Eighteen individual MPAHs (all mono-methylated PAHs), associated with the corresponding seven parent PAHs (2 - 4 rings), were examined. They included Naphthalene (NAP), 1-Methylnaphthalene (1-M-NAP), 2-Methylnaphthalene (2-M-NAP); Fluorene (FLU), 1-Methylfluorene (1-M-FLU), 2-Methylfluorene (2-M-FLU); Phenanthrene (PHE), 1-Methylphenanthrene (1-M-PHE), 2-Methylphenanthrene (2-M-PHE), 3-Methylphenanthrene (3-

M- PHE), 9-Methylphenanthrene (9-M-PHE); Anthracene (ANT), 2-Methylanthracene (2-M-ANT), 9-Methylanthracene (9-M-ANT); Fluoranthene (FLT), 1-Methylfluoranthene (1-M-FLT), 2-Methylfluoranthene (2-M-FLT); Pyrene (PYR), 1-Methylpyrene (1- M-PYR); Benzo[c]phenanthrene (BcP), 1-Methylbenzo[c]phenanthrene (1-M-BcP), 2-Methylbenzo[c]phenanthrene (2-M-BcP), 3-Methylbenzo[c]phenanthrene (3-M-BcP), 4-Methylbenzo[c]phenanthrene (4-M-BcP), 5-Methylbenzo[c]phenanthrene (5-M-BcP).

Chemicals and reagents

Standard solutions of the target compounds were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The internal standard solutions (Naphthalene-d_8, Phenanthrene-d_{10} and Chrysene-d_{12}) and surrogate recovery standard solutions (2- Fluorobiphenyl, Pyrene-d_{10}) for GC-MS analysis were purchased from o2si smart solutions (Charleston, SC, USA). Silica gel and neutral aluminum oxide (for column chromatography, 100 - 200 mesh) were obtained from Sinopharm Chemical Reagent Co., Ltd., China. All organic solvents used (hexane, acetone and dichloro- methane; ACS/HPLC certified) were obtained from J&K Scientific, USA. Silica gel and neutral aluminum oxide, as well as all glassware, were heated at 450°C for 6 h prior to use to remove the possible organic residues. The silica gel and neutral aluminum oxide were further activated at 130°C for 13 h, reactivated with Milli-Q water (3%, w/w) for 2 h and were then soaked in hexane for 12 h before packing in the chromatographic column.

Sample pretreatment

All soil samples were air-dried, ground and sieved through a stainless steel 70-mesh sieve during which a quartering method was applied to ensure homogeneity. To extract the chemicals under study, 200 ng surrogate standards (2-Fluorobiphenyl, Pyrene-d10) were added to 8 g soil samples, followed by extraction with 20 mL hexane/acetone (1:1; v/v) in a microwave digestion system (MARS Xpress, USA). The temperature for digestion was started from the room temperature, increased to 110°C at a rate of 10°C/min, held for 10 min and then cooled down. The extract was filtered with a sand core funnel (aperture 2 - 5 μm), concentrated with a rotary evaporator at 30°C, and cleaned up with a glass chromatographic column containing: from bottom to top: 12 g soaked neutral aluminum oxide, 12 g soaked silica gel, 1 g anhydrous sodium sulfate (after baked for 6 h at 600°C). The extract was eluted with 50 mL of hexane/dichloromethane (1:1; v/v). The eluent containing the target compounds was condensed to 1 - 2 mL with a rotary evaporator, then solvent-exchanged to hexane and re-evaporated to 1 mL. Internal standards were added to each concentrated sample prior to storage in 2 mL glass vials at 4°C in preparation for GC-MS analysis. The total organic carbon (TOC) content of soils was measured with a SHIMADZU TOC-5000A Analyzer (SSM-5000).

Chemical analysis

Compound quantification was performed using an Agilent 6890 gas chromatograph (GC) coupled with a 5973 mass spectrometer (MS) detector. The MS detector was initially operated in scanning mode (SCAN) to obtain the retention time of each compound (qualitative analysis), and then was operated in electron impact (EI: 70 eV) selected ion monitoring (SIM) mode (quantitative analysis). The GC was equipped with a DB-5MS column (30 m long x 0.25 mm internal diameter x 0.25 μm film thickness). Helium was used as the carrier gas with a constant flow rate of 1.0 mL/ min and a constant head pressure of 30 kPa. The injection mode was splitless and the injection volume was 1 µL. The oven temperature was started at 60°C for 1 min, increased to 270°C at a rate of 5°C/min, held for 2 min, increased to 290°C at a rate of 3°C/min, held for 1 min, and increased to the final temperature of 305°C at a rate of 10°C/min and held for 12 min. The injector, ion source and quadrupole temperatures were 290, 230 and 150°C, respectively. For quantification, an eight-point calibration curve of MAPHs standard solutions was established (1 - 500 mg/L; $R^2 > 0.99$).

Quality control

Four levels of quality control were implemented to ensure the accurate quantification of MPAHs: (1) A representative soil sample with a relatively low MPAHs concentration was spiked with approximately 120 ng 18 MPAHs, 7 parent PAHs, and two surrogates; the recoveries of these compounds in the spiked soil sample ranged from 68.4 to 100.4% with RSD below 10% (n = 3). The recoveries of two surrogates were comparable to those of 18 MAPHs and 7 PAHs (Tables SIe1 in the Supplementary Data). (2) Duplicate method blanks were routinely included in each batch (20 - 30 samples) of experiments and all final concentrations of the MPAHs were blank-corrected (Sun et al., 2016). Contaminants in the blanks were mainly low molecular weight MPAHs/PAHs and details are displayed in Tables S1 - 2. Also, one duplicate sample was included in each batch (20 - 30 samples) to test the experimental reproducibility; the RSD was lower than 15% (n = 3). (3) 2- Fluorobiphenyl was used as a surrogate of low molecular weight MPAHs (2 - 3 rings), with recovery ranging from 61.2% to 108.7% (mean 81.5% ± 10.5%); Pyrene-d_{10} was employed to represent the medium molecular weight MPAHs (3 - 4 rings), with recovery ranging from 61.2% to 125.0% (mean 101.2% ± 11.2%). The reported data in this study were not corrected with surrogate recoveries since these could not adequately represent all tested compounds. (4)

Method detection limits (MDLs) were calculated by quantifying a replicate (n = 7, after instrumental stability) standard solution (2.5 µg/L) following the US EPA approach (Ma et al., 2010), and a concentration range within 0.03 - 0.28 ng/g dry soil sample was obtained for all 25 chemicals tested including the parent and methylated PAHs (with details in Table 1).

Data analysis

The Kolmogorov-Smirnov test was applied to test the data's distribution pattern, and Paired Samples T-test was employed to examine significance of the difference in the concerned comparisons after concentrations of the target compounds were log- transformed to fit normal distribution (concentrations below MDLs were assumed as 10^{-5}). The statistical analysis mentioned above was performed using IBM SPSS Statistics 20.0 (IBM Analytics), and statistical significance was considered as $p < 0.05$. The ordinary Kriging interpolation method (spherical model) was used to map the concentrations of individuals, groups and the sum of MPAHs for spatial distribution analysis (ArcGIS 10.2).

RESULTS AND DISCUSSION

Concentration levels

Twenty five compounds of interest (7 parent PAHs þ 18 monomethylated PAHs derived from these 7 parent PAHs) were analyzed. The majority of these compounds were detected in the 243 soil samples; the detection rate of most compounds was over 90%. This indicates that MPAHs are ubiquitous in agricultural soils of the YRD region. Details of the measurements such as mean, median, minimum and maximum values are summarized in Table 1. The K-S test showed that concentrations of the tested compounds followed a logarithmic normal distribution pattern. Their mean concentrations are described as geometric mean if not specifically indicated.

The detected MPAHs were divided into three groups in terms of their carbo-atomic ring numbers (including benzene rings and heterocyclic rings), namely $\sum \mathrm{MPAHs} - 2\mathrm{R}$ (2 rings, M-NAPs), $\sum \mathrm{MPAHs} - 3\mathrm{R}$ (3 rings, M-FLUs + M-PHEs + M-ANTs), $\sum \mathrm{MPAHs} - 4\mathrm{R}$ (4 rings, M-FLTs + M-PYR + M-BcPs). Overall, the total concentration of $\sum 18\mathrm{MPAHs}$ ranged from 5.5 to 696.2 ng/g dry soil, with a mean value of 51.0 ng/g dry soil. Across the three categories, $\sum \mathrm{MPAHs} - 2\mathrm{R}$ (i.e., M-NAPs) was the dominant group, with a mean value of 21.2 ng/g (range: 2.6 - 467.0 ng/g), followed by $\sum \mathrm{MPAHs} - 3\mathrm{R}$ (mean: 21.1 ng/g; range: 1.7e218.7 ng/g). The $\sum \mathrm{MPAHs} - 4\mathrm{R}$ exhibited the lowest concentration (mean: 5.0 ng/g; range: 0.4e - 0.6 ng/g). This indicated that 2 - 3 ring MPAHs dominated the study area, and that the concentration percentage contributed from individual groups to P18MPAHs decreased with increasing carboatomic ring numbers.

Several investigations on alkylated PAHs (APAHs) from the literature are summarized in Tables SIe3. Because APAHs consist of a large number of homologs due to their diverse fused benzene ring structures and different alkyl substituents, the tested APAHs in different studies did not include the same species. This confounds the comparison of our results with current literature reports. However, it is interesting to note that the concentration range of 18MPAHs detected in this study was comparable to a recent study focusing on the surface soils from Xi'an, China (232 - 819 ng/ g), in which only 6 alkylated PAHs were studied (Wei et al., 2015).

Compositional profile

Nearly half of $\sum 18\text{MPAHs}$ were M-NAPs (46%), resulting in the spatial distribution pattern of P18MPAHs being highly consistent with that of $\sum \text{MPAHs} - 2\text{R}$ (i.e., M-NAPs) (Fig. 1). The concentration contribution percentages of $\sum \text{MPAHs} - 3\text{R}$followed an order of MPHEs (29%) > M-FLUs (13%) > M-ANTs (2%). In comparison, three compounds of PMPAHs-4R (i.e., M-FLTs, M-PYR and M-BcPs) contributed small fractions to $\sum 18\text{MPAHs}$, with values being 6%, 2%, and 2%, respectively (Fig. SI-1 in the Supplementary Data). Such a compositional profilewas consistent with that of a previous study on MPAHs in dustfall from Shanghai, China, where it was demonstrated that alkyl-NAPs and alkyl-PHEs were two dominant contributors, comprising over 50% to the total (Lian et al., 2009b). This indicated that deposition of airborne particles was an important source for MPAHs in soils in the YRD region (Lian et al., 2009b).

Importantly, no considerable differences in compositional profile was observed between the studied 11 cities; M-NAPs and M-PHEs generally accounted for more than 70% of the total MPAHs (Fig. SI- 2). Although the total concentration of MAPHs varied significantly across the cities, their compositional profile was similar. Overall, lower molecular weight MPAHs dominated in the YRD region.

Spatial distribution

The total concentration of $\sum 18\text{MPAHs}$ in the surface soils ranged from 5.5 to 696.5 ng/g dry soil, indicating significant spatial variation in the surface soil MPAHs in the study area. To help visualize this phenomenon, the spatial distribution pattern of $\sum 18\text{MPAHs}$ along with those of three MPAHs categories were derived using the ordinary Kriging interpolation approach (Fig. 1).

The spatial distribution patterns of specific MPAHs groups are shown in Fig. SI-3 as well. It is evident that $\sum 18\mathrm{MPAHs}$, $\sum \mathrm{MPAHs}-2\mathrm{R}$, $\sum \mathrm{MPAHs}-3\mathrm{R}$, and $\sum \mathrm{MPAHs}-4\mathrm{R}$ exhibited dissimilar spatial distribution patterns. As for $\sum 18\mathrm{MPAHs}$, the most severely contaminated region was in Jiaxing, followed by relatively heavily polluted areas in Wuxi, Suzhou, Huzhou, and Shanghai. The northwest and southeast parts of the study area exhibited less overall contamination (Fig. 1a). Relatively high concentrations of $\sum \mathrm{MPAHs}-2\mathrm{R}$ (i.e., MNAPs) were observed in the east area of Jiaxing city and on the border between Jiaxing and Shanghai. Significantly higher concentrations were detected at the sites Z41, Z42, Z43, Z61, and Z63 in Jiaxing city, with concentrations being 251.0, 252.3, 434.6, 529.0,131.1 ng/g dry soil, respectively (Fig.1b). For $\sum \mathrm{MPAHs}-3\mathrm{R}$ (Fig. 1c), areas with higher concentrations covered a large portion of the study region, namely Jiaxing, Huzhou, and the border between Wuxi and Suzhou cities, displaying a more even distribution pattern compared to $\sum \mathrm{MPAHs}-2\mathrm{R}$ (Fig.1b) and $\sum \mathrm{MPAHs}-4\mathrm{R}$ (Fig. 1d). As for $\sum \mathrm{MPAHs}-4\mathrm{R}$ (Fig. 1d), higher concentrations were detected at isolated sites in Wuxi (J61, J68, J73), Suzhou (J82, J90) and Jiaxing (Z41), which is quite different from the homogeneous distribution patterns of $\sum \mathrm{MPAHs}-2\mathrm{R}$ and $\sum \mathrm{MPAHs}-3\mathrm{R}$.

Soil organic matter (SOM) has been shown to play a dominant role in retaining persistent hydrophobic organic contaminants (HOCs) in soil. As reported, if the soil organic carbon content is over 0.1%, it will act as a dominant partitioning medium for HOCs (Chiou et al., 1998; Morillo et al., 2007; Schwarzenbach and Westall, 1981). In a recent study, PAH concentrations in soils were normalized to total organic carbon (TOC) content to analyze their spatial distribution characteristics, ruling out the effects from geochemical variance (Wang et al., 2013). In the present study, TOC content of the soil samples ranged from 0.2% to 3.4%, indicating that the impact of this parameter on compound concentration must be considered when discussing the difference in spatial distribution of MPAHs. No significant difference in spatial distribution pattern was observed for lower molecular weight compounds (including $\sum \mathrm{MPAHs} - 2\mathrm{R}$ and $\sum \mathrm{MPAHs} - 3\mathrm{R}$) before and after TOC normalization; conversely, a very different distribution pattern was found for $\sum \mathrm{MPAHs} - 4\mathrm{R}$ (Fig. SI-4). After TOC normalization, higher concentration areas of $\sum \mathrm{MPAHs} - 4\mathrm{R}$ centered in Wuxi and Suzhou cities, especially on their borders (Fig. SI-4d). This is quite different from the case showing that they were located at isolated sites prior to TOC normalization (Fig. 1d). Significant positive correlations between $\sum \mathrm{MPAHs} - 2\mathrm{R}$ (R = 0.226, $p < 0.001$, n = 243; R: correlation coefficient, p: significance level, n: sample size), $\sum \mathrm{MPAHs} - 3\mathrm{R}$ (R = 0.257, $p < 0.001$, n = 243), $\sum \mathrm{MPAHs} - 4\mathrm{R}$ (R = 0.412, $p < 0.001$, n = 243) and the TOC content of soils were observed based upon Spearman correlation analysis. Notably, the correlation coefficient tended to be higher with increasing MPAHs ring numbers. This is because the sorption affinity of HOCs with similar chemical composition to SOM increases with increasing hydrophobicity (Yang et al., 2014). Furthermore, after normalization with TOC, the distribution pattern of $\sum \mathrm{MPAHs} - 4\mathrm{R}$ still exhibited significant heterogeneity; the areas with higher concentrations were located in the cities of Suzhou and Wuxi (Fig. SI- 4d). This is most likely because physicochemical properties such as SOM hydrophobicity in these two cities differ considerably from those in other areas; previous findings have shown that SOM hydrophobicity strongly affected sorption of HOCs by SOM on unit carbon basis and greatly influenced retention in soil (Wang et al., 2005).

Apart from the impact of TOC content, direct and indirect inputs may affect the residual HOC concentration in soil. Significant positive correlations were found between $\sum \mathrm{MPAHs} - 2\mathrm{R}$ and $\sum \mathrm{PAHs} - 2\mathrm{R}$ (R = 0.689, $p < 0.001$, n = 243), $\sum \mathrm{MPAHs} - 3\mathrm{R}$ and $\sum \mathrm{PAHs} - 3\mathrm{R}$ (R = 0.465, p <

0.001, n = 243), as well as between $\sum \mathrm{MPAHs}-4\mathrm{R}$ and $\sum \mathrm{PAHs}-4\mathrm{R}$ (R = 0.919, p < 0.001, n = 243); these were derived from the partial correlation analysis taking TOC content of soils as a controlling factor. This suggests similar sources of MPAHs and their corresponding parent PAHs (Here, $\sum \mathrm{PAHs}-2\mathrm{R}$ = naphthalene, $\sum \mathrm{PAHs}-3\mathrm{R}$ = Fluorene + Phenanthrene + Anthracene, $\sum \mathrm{PAHs}-4\mathrm{R}$ = Fluorene + Phenanthrene + Anthracene). The areas with relatively high $\sum 18\mathrm{MPAHs}$ were in Jiaxing, the border between Suzhou and Wuxi, Huzhou, and the north part of Hangzhou. As a region that plays a major role in providing food (mostly rice) for Zhejiang Province, grain cultivation is the most important land-use pattern in Jiaxing city (Zhejiang Province Statistical Yearbook, 2014). Moreover, published studies have concluded that PAHs originating from biomass combustion processes mainly consist of low molecular weight and alkylated PAHs (Jiang et al., 2009). Therefore, higher concentrations of MPAHs in Jiaxing city could result from the intensive biomass burning activities given that rice straw burned by local farmers were found at the sites Z61 and Z63 at sampling. Meanwhile, sites Z41 and Z42 were close to a highway, suggesting traffic exhaust as another possible source. Statistical reports showed that Suzhou and Wuxi were ranked as the top two in gross heavy industrial production of Jiangsu Province in 2014 (Jiangsu Province Statistical Yearbook, 2014), indicating that intensive heavy industrial activities in these two areas may produce a large number of pollutants, including PAHs and their derivatives. Separately, a previous study focusing on topsoil contamination by

15 priority parent PAHs ($\sum 15\mathrm{PAHs}$) in the YRD region suggested that the two most heavily polluted areas were the northwest part of Suzhou and east part of Wuxi (Ping et al., 2007); this is consistent with the present study. The relatively higher concentrations of $\sum 15\mathrm{PAHs}$ in Suzhou and Wuxi were ascribed to emissions from small coal-combustion plants and crop straw burning, as well as exhaust from heavy traffic (Ping et al., 2007). Moreover, the rapid growth of advanced

materials manufacturing, the biopharmaceutical industry and new energy development and utilization in the Huzhou economic and technological development zone may explain the higher concentrations of MPAHs observed in Huzhou city. Additionally, it was interesting to notice that $\sum 18\mathrm{MPAHs}$ on the borders between Shanghai and Jiangsu, Shanghai and Zhejiang, and that between Huzhou and Hangzhou were slightly higher than the surrounding areas (Fig. 1a). This was likely due to a large number of chemical plants that were built along the city borders in the YRD region, with the goal of reducing cost and mitigating administrative management pressures (Sun et al., 2016). In conclusion, the spatial distribution of $\sum \mathrm{MPAHs} - 2\mathrm{R}$ and $\sum \mathrm{MPAHs} - 3\mathrm{R}$ was mainly influenced by the agricultural straw burning and emissions from heavy industrial activities; that of $\sum \mathrm{MPAHs} - 4\mathrm{R}$ was significantly affected by soil TOC content.

Source apportionment

In general, a number of diagnostic ratios of selected parent and alkylated PAHs (e.g., HWM/LWM, MPHEs/PHE, Alkylated-PAHs/ Parent-PAHs, FLT/(FLT + PYR), ANT/(ANT + PHE), BaA/ (BaA + CHR)) have been developed to identify the possible sources of the contaminants and their derivatives (Barakat et al., 2011; Luo et al., 2006; Miki et al., 2014; Prahl and Carpenter, 1983; Yan et al.,m 2009; Yunker et al., 2002). Previous investigators analyzed as large a number of suitable diagnostic ratios as possible to identify possible sources of the alkyl- and parent PAHs; reliance on a single ratio could give misleading information. Given that the present study focused mainly on several 2 - 4 ring mono-methylated PAHs and their parent PAHs, some commonly used ratios such as BaA/ (BaA + CHR), and the ratio of four-to six-ring parent PAHs to the sum of two- and three-ring parent PAHs (HMW/LMW) could not be used since some of the compounds were not examined. For our case, significant positive correlation between MPAHs and the corresponding parent PAHs indicated similar emission sources, making it reasonable to employ such ratios for their source apportionment. Normally, combustion sources include those from coal, grass, wood and/or petroleum; petroleum sources refer to the release of un-combusted petroleum products (Yan et al., 2009). Prahl and Carpenter (1983) reported that the MPHEs/PHE ratio could be used to distinguish petroleum sources from those that are combustion dominated. Yunker et al. (2002) proposed that FLT/ (FLT + PYR) ratio was suitable for discriminating petroleum combustion from other types of combustion. Based on the data availability, the ratios of MPHEs/PHE and FLT/(FLT + PYR) were used to achieve the source apportionment in the current work.

Here, MPHEs/PHE referred to the concentration ratio of the sum of 3-M-PHE, 2-M-PHE, 9-M-PHE, and 1-M-PHE to PHE. A MPHEs/ PHE ratio below 1 suggests emissions from coal, crop straw, and/or petroleum combustion; values of 1 - 2 indicate both combustion of the abovementioned materials and petroleum leakage; a ratio of 2 - 6 corresponds to petroleum leakage sources (Luo et al., 2006; Prahl and Carpenter, 1983). A FLT/(FLT þ PYR) ratio < 0.4 was taken as indicative of petroleum leakage and a ratio > 0.4 indicated combustion sources (Yunker et al., 2002). For the present work, 22 sampling sites (9.1%) were ascribed to petroleum origin according to the MPHEs/PHE ratio, while according to the FLT/(FLT þ PYR) ratio only 6 sampling sites (2.5%) were attributable to this source; 3 sites were found to overlap between these two groups. Importantly, 221 sampling sites (91.0%) were mostly contaminated by combustion processes (including the sites polluted by mixed sources) as indicated by the MPEHs/PHEs ratio; conversely, 237 sites (97.5%) were attributed to this origin based on the FLT/(FLT + PYR) ratio. A total of 218 sites overlapped with the 221 sampling sites identified by the MPEHs/PHEs ratio. Although the classification criteria for source apportionment of these two ratios were somewhat different, their results matched well; both suggested that combustion processes (including petroleum and biomass/coal combustion) were the major source of PAHs and 2 - 4 ring MAPHs in the YRD region.

When the 22 sampling sites with MPHEs/PHE ratio over 2 were plotted on the interpolated spatial distribution map of $\sum$ 18MPAHs, it was interesting to observe that these sites well matched with the most heavily polluted areas. Since M-PHEs only accounted for 29% of $\sum$ 18MPAHs, this was not a sufficient explanation. To better understand this phenomenon, the 22 most heavily polluted sites were also plotted on the map. It was found that 6 sites with MPHEs/PHE ratio over 2 overlapped exactly with 6 out of 22 most heavily polluted sites (27.3%) (Fig. 2). This indicated the areas with heavier pollution of 18MPAHs were contaminated by petroleum leakage, although combustion emission was the major source for most sampling sites in the study area (more than 90%). Such a phe- nomenon can be supported by a previous investigation on parent PAHs in agricultural soils from Jiaxing city, where it was shown that petroleum leakage was an important source of PAHs and their methylated derivatives (Liu et al., 2010).

Isomer differences

As reported, different MPAH isomers posed dissimilar health risks to exposed organisms (Braga et al., 1999). Thus, it is important to identify and quantify individual isometric MPAH compounds. The Paired Samples T-test (after log-transformation) showed that the homologs with methyl group substituted at 2- (β) position (2-M-NAP, 2-M-PHE, 2-M-FLU, 2-M-FLT) generally exhibited significantly higher concentrations than those substituted at 1- (α) position (1-M-NAP, 1-M-PHE, 1-M-FLU, 1-M-FLT). This is consistent with a previous study which reported that the concentrations of 2- M-NAP in the sediment samples from Dalian coastal area were significantly higher than those of 1-M-NAP (Hong et al., 2016). Moreover, among each MAPH group, concentration of 2-M-PAH was generally the highest, with exceptions of 2-M-PYR (not determined) and 2-M-BcP. Furthermore, concentrations of M-PHEs decreased in an order of 2-M-PHE > 3-M-PHE > 9-M-PHE > 1-M- PHE, agreeing well with a previous study on alkylated PAHs emitted from diesel/biodiesel exhaust (Casal et al., 2014), suggesting that traffic exhaust was an important input. Also, in the present study the 3-M-BcP concentration was higher than the other four isomers, which is similar to that detected in the River Elbe sediment, although its contamination level was much severe (Skoczynska et al., 2013).

To date, no clear mechanism explains why concentrations of some MPAH isomers with substituted methyl group at a specific position were much higher than others; little research has focused on isometric analysis to date. A few possible causes were proposed as follows. First, a larger amount of specific isomers such as 2-M- PHE or 3-M-BcP were released into the environment from sources such as diesel/biodiesel exhaust (Casal et al., 2014). Second, the stability and bioavailability of isometric MPAHs in soils were different, and this was dependent on the substituted positions. This is supported by the previous findings showing that methyl sub- stitution at certain positions accelerated the microbial oxidation of MPAHs while those at other positions inhibited transformation (Budzinski et al., 1998; Malmquist et al., 2015). It is thus plausible that the isomers with higher concentrations are relatively more persistent. Third, rearrangement of the substituted groups on PAHs could occur during long-term exposure to the complex soil envi- ronment; this may be induced by some environmental factors such as microbes or through photocatalytic reactions. Additional research is needed to clarify the precise mechanisms responsible for the existing contaminant distribution.

Future perspectives

In this study, 2-,4-,5-,6-Methylchrysene, 1-,2-,3-,4-,5-,6-,7-,9-,10-Methylbenz[a]anthracene and 7-,8-,9-,10-Methylbenzo[a]pyrene were included at the beginning of the study. However, because they could not be clearly separated by GC-MS even though various oven temperature programs were tested, the data for these chemicals were not included. It seems that accurate separation of various isomers of specific compound groups by GC-MS at a high resolution remains a challenge likely only solved by GC-MS/MS capability.

Although toxic or carcinogenic characteristics of MPAHs have been investigated and partial success has been achieved (Braga et al., 1999; Lee et al., 2015), systematic toxicity data such as dose-response curves and toxicity equivalency factors of MPAHs are scarce and this prevents accurate risk assessment. For instance, direct comparison between different hazardous MPAH groups or between isomers within the same MPAH group, as well as the estimation of the exposure health risks of these chemicals, are rather limited. Additional work to elucidate these key processes and behaviors is clearly warranted.

CONCLUSIONS

Both the general public and government agencies have expressed increasing concern over soil pollution in the Yangtze River Delta given that it is one of the most developed areas in Eastern China, with extensive agricultural and industrial activities. The agricultural soil pollution status of 18 MPAHs, including their concentration levels, compositional profile and spatial distribution patterns was obtained and characterized. Contaminant emission source apportionment and isomeric difference analysis were also performed. The results provide significant information for a systematic understanding of the agricultural soil contamination status by MPAHs; this is significant given that these derivatives have been shown to be more persistent and toxic than their parent PAHs. The ubiquitous presence of the hazardous MPAHs in the YRD region may pose potential risks to human health via direct exposure or through food chain. Addition research and regulatory efforts should be focused on the control and management of agricultural soil contamination in this area so as to ensure food safety and public health.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2017.07.035.

LIST OF TABLES AND FIGURES

Table 1

Concentrations (ng/g, dry soil) of the concerned parent and methylated PAHs in the agricultural soils from the YRD region.

Analyte	Abbreviation	Ring number[a]	MDL[b] (ng/g)	Detection rate (%)	Mean[c] (ng/g)	Median (ng/g)	Min (ng/g)	Max (ng/g)
Naphthalene	NAP	2	0.14	100	8.5	9.5	0.5	73.1
1-Methylnaphthalene	1-M-NAP	2	0.27	100	7.4	6.7	1.0	126.1
2-Methylnaphthalene	2-M-NAP	2	0.26	100	13.8	13.3	1.6	340.9
	M-NAPs[e]				21.2	20.7	2.6	467.0
	∑MPAHs-2R[f]				21.2	20.7	2.6	467.0
Fluorene	FLU	3	0.07	100	7.5	9.6	0.4	62.8
1-Methylfluorene	1-M-FLU	3	0.28	99.2	2.2	2.2	0.2	31.0
2-Methylfluorene	2-M-FLU	3	0.15	99.6	2.9	2.9	0.1	58.1
	M-FLUs				5.2	5.2	0.5	89.1
Phenanthrene	PHE	3	0.07	100	20.5	24.6	ND[d]	192.6
1-Methylphenanthrene	1-M-PHE	3	0.11	100	1.5	1.6	0.1	16.5
2-Methylphenanthrene	2-M-PHE	3	0.08	100	5.8	6.3	0.4	56.1
3-Methylphenanthrene	3-M-PHE	3	0.09	100	4.2	4.4	0.3	42.2
9-Methylphenanthrene	9-M-PHE	3	0.08	100	2.9	3.0	0.2	32.0
	M-PHEs				14.5	15.2	1.0	146.8
Anthracene	ANT	3	0.07	100	2.0	2.1	ND	36.6
2-Methylanthracene	2-M-ANT	3	0.08	99.2	0.6	0.6	0.0	9.3
9-Methylanthracene	9-M-ANT	3	0.10	67.1	0.1	0.2	ND	3.6
	M-ANTs	3			0.7	0.8	0.0	11.8
	∑MPAHs-3R[g]				21.1	22.4	1.7	218.7
Fluoranthene	FLT	4	0.09	100	23.5	24.0	ND	588.4
1-Methylfluoranthene	1-M-FLT	4	0.06	99.6	1.0	1.0	1.0	17.3
2-Methylfluoranthene	2-M-FLT	4	0.08	100	1.9	1.9	0.1	33.9
	M-FLTs				2.9	2.9	0.2	46.8
Pyrene	PYR	4	0.07	100	21.3	19.5	1.3	449.0
1-Methylpyrene	1-M-PYR	4	0.06	100	1.0	1.0	0.1	21.5
Benzo[c]phenanthrene	BcP	4	0.07	100	1.3	1.4	ND	22.6
1-Methylbenzo[c]phenanthrene	1-M- BcP	4	0.08	33.3	0.0	0.0	ND	1.4
2-Methylbenzo[c]phenanthrene	2-M- BcP	4	0.03	87.2	0.1	1.0	ND	1.3
3-Methylbenzo[c]phenanthrene	3-M- BcP	4	0.08	100	0.6	0.6	0.1	6.8
4-Methylbenzo[c]phenanthrene	4-M- BcP	4	0.07	90.1	0.1	0.2	ND	2.2
5-Methylbenzo[c]phenanthrene	5-M- BcP	4	0.05	93.0	0.1	0.1	ND	3.5
	M-BcPs				1.0	1.0	0.1	13.1
	∑MPAHs-4R[h]				5.0	4.8	0.4	80.6
	∑18MPAHs[i]				51.0	51.8	5.5	696.2

[a] Ring number, including benzene rings and heterocyclic rings.

[b] MDL, method detection limit.

[c] Geometric mean; since K-S test showed the concentration data followed the logarithmic normal distribution pattern, geometric mean would be more appropriate to describe the pollution situation in the study area.

[d] ND, not detected.

[e] M-NAPs indicates a sum of mono-methylnaphthalenes; M-FLUs, M-PHEs, M-ANTs, M-FLTs, M-PYRs and M-BcPs indicate the corresponding ones.

[f] ∑MPAHs-2R means a sum of MPAHs containing 2 carboatomic rings, including M-NAPs only in this study.

[g] ∑MPAHs-3R = M-FLUs + M-PHEs + M-ANTs.

[h] ∑MPAHs-4R = M-FLTs + M-PYR + M-BcPs.

[i] ∑18MPAHs indicates a sum of 18 methylated PAHs.

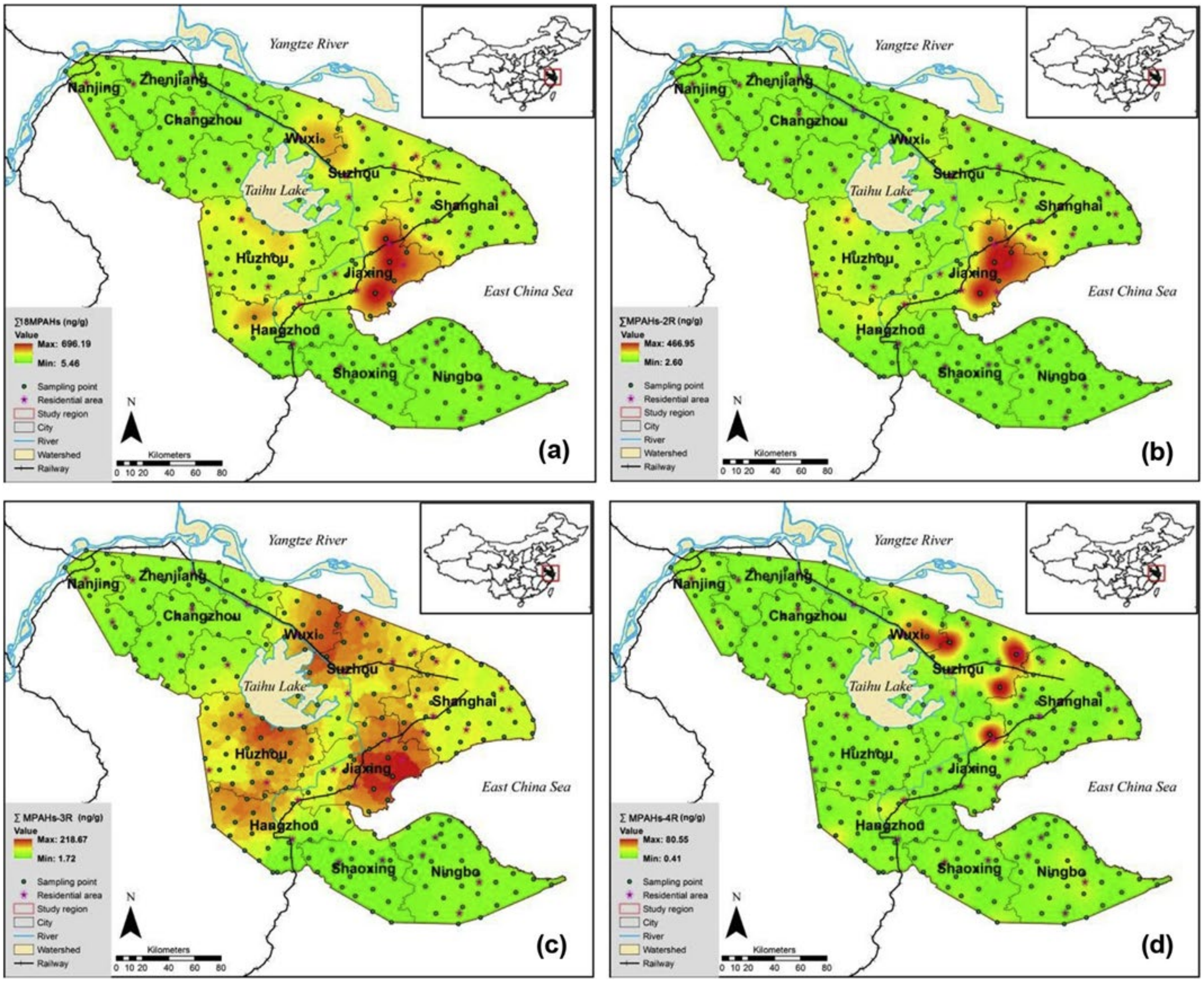

Fig. 1. Spatial distribution of (a) $\sum 18\mathrm{MPAHs}$, (b) $\sum \mathrm{MPAHs}-2\mathrm{R}$, (c) $\sum \mathrm{MPAHs}-3\mathrm{R}$, and (d) $\sum \mathrm{MPAHs}-4\mathrm{R}$ in agricultural soil samples from the YRD region.

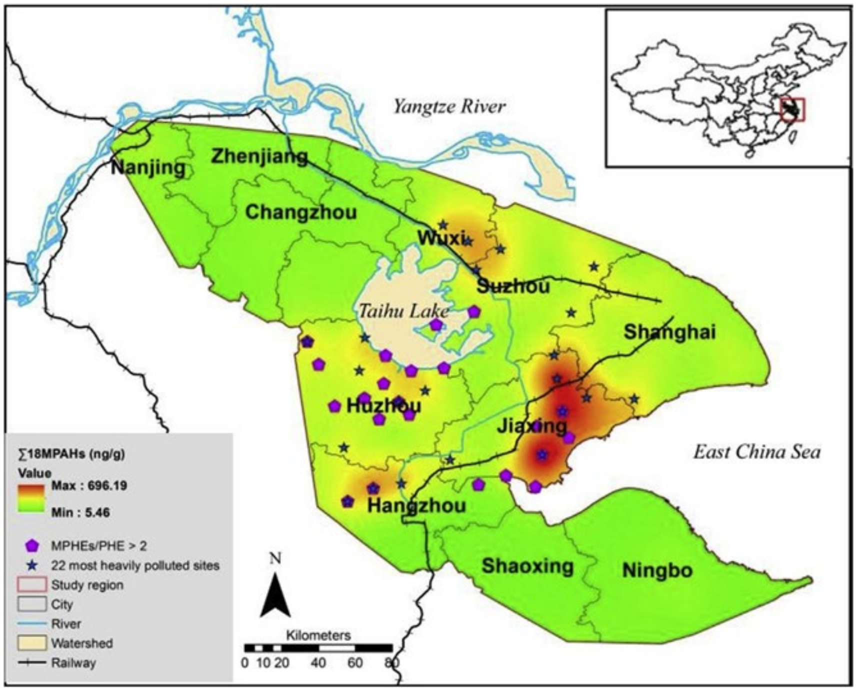

Fig. 2. Geographical locations of the 22 most heavily polluted sites and the 22 sites with MPHEs/PHE ratio over 2.

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