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Spatial distribution, emission source and health risk of parent PAHs and derivatives in surface soils from the Yangtze River Delta, eastern China

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ABSTRACT

243 surface soil samples were collected from the Yangtze River Delta (YRD) region, and the concentration distributions and compositional profiles of 27 parent PAHs (PPAHs), nitro- and oxy-derivatives (NPAHs and OPAHs), respectively, and health risk of 16 PPAHs were determined. Atmospheric samples were collected at two sites with high topsoil concentrations of PAHs to assist in identifying the emission sources of PPAHs. The total concentrations of PPAHs, NPAHs and OPAHs fell in the ranges of 21.0 –3563.2 ng/g, 0.4–4.6 ng/g and 2.1–834.1 ng/g, respectively. PPAHs in topsoil were dominated by low and medium molecular weight species. The main components of OPAHs were 9FO and ANQ. For NPAHs, only 1N-NAP was frequently detected. Overall, the northern parts of the YRD region were more heavily contaminated by PPAHs and their corresponding derivatives. The soil TOC fraction and GDP per capita were significantly correlated with the spatial distribution of PPAHs. Specific ratios of isomeric species and principal component analysis (PCA) designated combustion of industrial coal and biomass, and traffic exhaust as the main mixed emission sources of PPAHs in surface soils in this region. The detected NPAHs and OPAHs were significantly associated with the corresponding PPAHs. The estimated incremental lifetime cancer risk attributed to 16 PPAHs in surface soil was greater than 10^{-6}, indicating a potential risk of contracting cancer by exposure to topsoil from the YRD region. The cumulative probability of cancer risk for both adults and children via three exposure pathways followed the sequence of dermal contact > ingestion > inhalation.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a typical group of persistent organic pollutants (POPs) prevalent in the environment and some of the individuals have been identified as a kind of carcinogenic substance (IARC, 2010). Many studies have shown that in recent years, increasing incidences of lung cancer, bronchitis, asthma and heart diseases are associated with exposure to PAHs (Haritash and Kaushik, 2009; Fu et al., 2012). Nitro-PAHs (NPAHs) and oxy-PAHs (OPAHs) are important derivatives of parent PAHs (PPAHs). Some NPAHs and OPAHs have been confirmed to show comparable or greater toxicity and carcinogenicity than their parent components, thus their corresponding concentrations and distributions are of great concern to the government and the public (Bandowe and Wilcke, 2010).

PPAHs mainly originate from anthropogenic sources, i.e., incomplete combustion or pyrolysis of fossil fuels and biomass, as well as the leakage of petroleum (Wang et al., 2011). In addition to the primary emission sources, including vehicle exhaust and the burning of biomass (Bamford and Baker, 2003), NPAHs and OPAHs may generate from the secondary transformation of PPAHs by photochemical oxidation and (bio)degradation (Walgraeve et al., 2010; Keyte et al., 2013). PPAHs emitted into the atmosphere can enter surface soil by wet and dry deposition (Kaya et al., 2012), and are readily adsorbed by soil solid particles and soil organic matter. As environmental conditions change, soil may become a re- emission source with release of various organic pollutants into the air (Tao et al., 2008). PPAHs in soil can be bio-accumulated in crops via the food chain (Li et al., 2008) and ultimately affect human health. Therefore, deep insight into concentration and distribution of PPAHs in soil may facilitate pollution control, decrease in crop damage, and reduction of human exposure. Numerous studies have involved almost all the aspects of PPAHs mentioned above. How- ever, considering that a variety of NPAH and OPAH components have similar or stronger cellular and immune toxicity and carcinogenicity compared to their parental precursors (IARC, 2013), a corresponding study on derivatives is insufficient, especially distribution characteristics and relationships with their parental precursors.

The Yangtze River Delta (YRD) is one of the most densely populated and economically prosperous regions in the world. Intensive anthropogenic activities, large ownership of vehicles and high consumption of fossil fuels lead to massive emissions and accumulation of PPAHs and their derivatives, directly threatening the local environment quality and human health (Zhang et al., 2009). Therefore, it is of critical significance to determine the concentration range and geographical distribution of PPAHs, NPAHs and OPAHs in surface soils in this region, to provide fundamental data for monitoring and controlling contamination from POPs, and to create a reliable basis for risk management and decision-making by the local government.

To date, many studies have been performed on topsoil PPAHs in the YRD region (Jiang et al., 2011; Wang et al., 2015); yet these studies mainly focused on historical occurrence and concentration range of PPAHs and only covered some small-scale areas. Few recent studies characterize, on the entire region-scale of surface soils, geographic distribution and source apportionment of PPAHs, being essential for policy-makers to take effective measures to control and abate the pollution. Similarly, only a minority of reports have addressed NPAHs and OPAHs in atmosphere, partly due to time-consuming and laborious measurements, so the filling of data gap is urgently needed. In this study, we collected surface soil (0–10 cm) samples (sample size n = 243) from 11 cities in the re- gion to: (1) investigate the concentration ranges, compositional profiles and geographical distributions of 27 PPAHs, 12 OPAHs and 4 OPAHs; (2) preliminarily identify the local emission sources of PPAHs and their derivatives; (3) reveal the associations of NPAHs and OPAHs with the corresponding PPAHs in surface soils; and (4) initially assess the potential health risk of PPAHs for local adults and children exposed to surface soils via different pathways. Moreover, based on some previous results (Ping et al., 2007; Jiang et al., 2011), ambient air samples, including active and passive sampling with a total of 32 samples and a sampling period of 60 days, were gathered at 2 sites with high topsoil PPAHs concentrations to assist in diagnosing the local emission sources of PPAHs in surface soils.

MATERIALS AND METHODS

Background of the sampling region

As a highly developed agricultural and industrial region in China, the YRD region concentrated various large-scale industrial bases, and 4.6 million vehicles accounted for 16% of the national total (NBSC, 2015), leading to a large quantity of traffic exhaust. Fossil fuels, e.g., coal, liquefied petroleum gas (LPG) and natural gas gradually displaced traditional domestic fuels (crop straw and firewood); whereas crop straws were directly open burned after harvest.

Sample collection

Surface soil samples

An evenly distributed sampling network composed of 243 sites was created to cover 11 cities, including Shanghai (n = 30), Nanjing (n = 12), Zhenjiang (n = 14), Changzhou (n = 24), Wuxi (n = 18), Suzhou (n = 22), Huzhou (n = 26), Jiaxing (n = 24), Hangzhou (n = 25), Shaoxing (n = 18) and Ningbo (n = 30). The detailed information was shown in Fig. S1 and in the relevant statements in S- 1 (Supplementary Materials).

Ambient air samples

Based on our preliminary investigation and related data from previous studies (Ping et al., 2007; Jiang et al., 2011), air samples, including simultaneous active sampling and passive sampling, at two sites in Kunshan City (affiliated to Suzhou) with reported high topsoil PPAHs concentrations were collected. PPAHs and their derivatives in the particulate phase and gaseous phase were gathered using a glass fiber filter (GFF) and polyurethane foams (PUFs), respectively. The full descriptions on atmospheric sampling were given in S-1. A total of 32 air samples, i.e., 16 paired samples (gaseous phase plus particulate phase), were obtained.

Chemical reagents

The objective species of 27 PPAHs included NAP, ACE, ACY, FLO, PHE, ANT, FLA, RET, 7H-BCF, PYR, BaA, CHR, BbF, BkF, BcPh, CcdP,

BaP, DahA, IcdP, BghiP, BeP, PER, DaeF, DacP, DBalP, COR and DBaeP. Moreover, the target components of NPAHs were 1N-NAP, 2N-NAP, 5N-ACE, 2N-FLO, 3N-PHE, 9N-PHE, 9N-ANT, 3N-FLA, 1N-PYR, 7N-

BaA, 6N-CHR and 6N-BaP. Additionally, the studied OPAHs com- pounds included 9FO, BZO, ANQ and BaAQ. The full names of the abbreviation for each target compound was listed in Table S1 of S-2 (Supplementary Materials).

A mixture of 2-fluorobiphenyl and 4-terphenyl-d14 was used as the surrogate standard for PPAHs. 1-Br-2-nitrobenzene was employed as the surrogate standard for NPAHs and OPAHs. More- over, NAP-d_8, ACE-d_{10}, ANT-d_{10}, CHR-d_{12} and Perelyne-d_{12} were utilized as the internal standards for 27 PPAHs, and 9-nitroANT-d9 and 1-nitroPYR-d9 were used as the internal standards for NPAHs and OPAHs, respectively. The stock standards mentioned above were purchased from AccuStandard (New Haven, USA), and all of the chemical reagents were GC grade or better.

Sample pretreatment, determination, quality assurance (QA) and quality control (QC)

The extraction and cleanup procedures for PPAHs, NPAHs and OPAHs in surface soils were adapted from the reported methods (Li et al., 2014, 2015), and the corresponding details were described in S-3 (Supplementary Materials). As for the ambient air samples, the GFFs used for collecting the particulate phase PPAHs were cut into pieces and then transferred into PTEF microwave tubes. The sub- sequent extraction and purification procedures were identical to those for the soil samples mentioned above. For simplicity, the related details could be seen in S-3 similarly.

PPAHs and their derivatives were quantified using GC/MS (Agilent GC6890/5973 MSD). As for PPAHs, a DB-5 MS capillary column (30 m x 0.25 mm x 0.25 mm) was employed. PPAH species were qualitatively identified based on the retention times and ionic mass-charge ratios of standard PPAHs and determined quantitatively using the external standard method. As for NPAHs and OPAHs, a HP-5 MS capillary column (30 m x 0.25 mm x 0.25 mm) was utilized. The analytical conditions selected for qualitative and quantitative determinations of PPAHs, NPAHs and OPAHs were summarized in S-3 as well.

All of the concentrations in the soil samples were shown on a dry weight (d.w.) basis. The initial concentrations of PPAHs and derivatives in the air samples were calibrated using active sampling results based on the related regression models. The total organic carbon (TOC) fraction in the topsoil was measured by a TOC analyzer (TOC-V CPH, Shimadzu 5000-A, Japan).

All of the data were subject to quality control procedures to ensure the correct identification and accurate quantification of the target compounds. The acquired results are summarized in Table S2. The corresponding recoveries for 27 PPAHs fell in the range of 62%–120%, and for the 16 PPAH derivatives, except for 6N-BaP, they were 61%–104%, all of which satisfies the accuracy requirements of real samples. The surrogate recoveries of 2- fluorobiphenyl and 4-terphenyl-d14 for PPAHs were 73 ± 13% and 76 ± 12%, respectively, and that of 1-Br-2-nitrobenzene for NPAHs and OPAHs ranged from 50% to 103%, all of which were acceptable. Other corresponding details on QA/QC could be found in S-3 also.

Source apportionment of PPAHs

The commonly-used methods for source apportionment of PPAHs included chemical mass balance model (CMB, Li et al., 2003); specific ratios of paired isomeric species (Yunker et al., 2002; Tobiszewski and Namie'snik, 2012); multivariate statistics (Golobo canin et al., 2004); isotopic ratios of $\delta^{13}C$, $\Delta^{14}C$, and $\delta^{2}H$ (Bosch et al., 2015); and multimedia fugacity model calibration (Zhang et al., 2005). Among these methods, the specific ratios of paired isomeric species were simple and easy to use. On the other hand, it should be noted that some limitations existed in this method; for example, in the real multimedia environments, the paired isomers were (bio)degraded and transformed to different extents during the transport process, and therefore, the isomeric ratios changed from emission sources to receiving media, leading to a misjudgment in source apportionment. Zhang et al. (2005) proposed an application of the multimedia fugacity model to calibrate the deviations of isomeric ratios. Due to the extremely high cost of multimedia sampling in a large area, such as the YRD region, and some restrictions on the pretreatment and analytical conditions, we simply adopted the specific ratios of paired isomeric species to preliminarily diagnose the local emission sources of PPAHs in this study. In addition, principal component analysis (PCA) combined with multivariate linear regression (MLR) was also employed to assist in source appointment, and the identification results were verified by the local emission inventory of PPAHs.

Health risk assessment on PPAHs

In this study, the incremental lifetime cancer risk (ILCR) was estimated to evaluate the potential health risk associated with exposure to soil PPAHs in the YRD region for both adults and children using the USEPA standard models (USEPA, 1991). Gener- ally, humans are exposed to soil pollutants through three routes: ingestion, inhalation and dermal uptake. The calculation of ILCR of the three pathways was shown in the Supplementary Materials (see S-4 and the complementary explanations).

Individual BaP_{eq}s for 16 PPAH species were calculated by multiplying the measured component concentrations with the corresponding toxicity equivalence factors (TEFs, see Table S3). The parameters referred to the Risk Assessment Guidance of the Beijing Municipal Environmental Protection Bureau and to other studies (the detailed information summarized in Table S4). The total risk was the sum of individual risks associated with each exposure route. The health risks of NPAHs and OPAHs were not considered in the present study due to the lack of relevant TEF data.

Statistical analysis and spatial mapping

The statistics used in this study included principal component analysis (PCA), multivariate linear regression (MLR) and Pearson correlation analysis. Prior to Pearson correlation analysis, all of the measured data were checked for a normal distribution. In the cases in which the distribution was non-normal, a log-transformation was applied to approximate the normal distribution. The statistical significance was assigned at $p < 0.05$. The statistical software used was SPSS 21.0 (IBM Co., USA). The geographical distributions of PPAHs, NPAHs, and OPAHs in surface soils from the YRD region were illustrated using the data interpolation method based on or- dinary Kriging in ArcGIS 10.2 (ESRI, Redlands, CA, USA).

RESULTS AND DISCUSSION

Concentration range and spatial distribution of PPAHs and their derivatives in topsoiLl

Concentration range

The statistical results of the concentration ranges of PPAHs and their derivatives in surface soils are summarized in Table 1. Most of the 16 PPAHs with US EPA priority were detected, while other nonpriority PPAHs showed relatively low detection rates. The concentration of 27 PPAHs at all sites in the YRD region demonstrated a great degree of variability, with a range of 21.0–3563.2 ng/g and a arithmetic average of 310.6 ng/g. The concentrations of the 16 PPAHs with US EPA priority fell in a range of 10.1–3058.6 ng/g, with an arithmetic mean of 266.6 ng/g, which was much higher than those of the non-priority PPAHs.

In this study, 4 of 12 studied NPAHs, including 1N-NAP, 2N-NAP, 1N-PYR and 3N-FLA, were detected, and only 1N-NAP exhibited a high detection rate (90%), while the concentrations of other components were very low; for example, 2N-NAP was only detected at 2 sites. In the whole

YRD region, 4 NPAH components manifested an average concentration of 0.6 ± 0.6 ng/g, 3 orders of magnitude lower than the corresponding 4 PPAH species (206.8 ± 282.0 ng/g). Niederer (1998) also found that the concentrations of NPAHs in the soil were 3e4 orders of magnitude less than those of PPAHs. As for OPAHs in the topsoil, all of the detection rates were comparatively high, and the concentrations of 4 OPAHs revealed a mean value of 36.3 ± 57.0 ng/g. Compared with other similar studies, the concentrations of NPAHs and OPAHs in surface soils from the YRD region were relatively low (Niederer, 1998; Hasei et al., 2009).

Spatial distribution

The spatial distributions of PPAHs, NPAHs, and OPAHs and the $\sum BaP_{eq}$ concentrations in topsoil, based on data interpolation using ordinary Kriging, are plotted in Fig. 1. To a certain extent, $\sum BaP_{eq}$ may reflect the potential exposure risk to PPAHs of local residents (Duan et al., 2015). The sum of the total of 27 PPAHs in surface soils had a similar pattern of spatial distribution to that of $\sum BaP_{eq}$, where the sampling sites with high concentrations were mainly located in the northern part of the YRD region, such as Suzhou, Wuxi, and Shanghai, as well as northwest Nanjing. In contrast, both the total PPAHs and $\sum BaP_{eq}$ concentrations were low in most areas in the southern part of the region, except for Hangzhou and southeast Ningbo. As for NPAHs in surface soils, the areas with high concentrations shift to the northwest part of the region, primarily including Nanjing and Zhenjiang, while the southeast part of the studied region revealed relatively low concentrations. According to the field records, sites with higher concentrations of PPAHs and NPAHs were mostly situated in the vicinity of urban zones or near main roads and factories. Similar to the distribution characteristics of PPAHs, the areas with higher concentrations of

OPAHs generally occurred in the northern part of the region. A significant cluster phenomenon of relevant industries appeared in the YRD region (Wei, 2008), which was closely associated with the trend of the concentration distribution. For instance, many small manufactures (clothing, textile and hardware) are aggregated in the southern part of the region, with relatively low emission of PPAHs and their derivatives, whereas metallurgy and the petrochemical industry, as the principal emission sources of PPAHs and their derivatives (Rachwał et al., 2015), are mainly assembled in the northern part. Furthermore, the northern part possessed a larger population and more vehicles with respect to the southern part (NBSC, 2015), leading to greater emissions from traffic exhaust. The distribution pattern of PPAHs was consistent with that of polychlorinated biphenyls (PCBs) in this region (Sun et al., 2016a), while it was quite different from recently reported patterns of organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and phthalate esters (PAEs) (Sun et al., 2016b), which implied complex sources and fate behaviors of different POPs in the soil system. It should be noted that the sampling interval in the present study is relatively large (see Fig. S1), the resulted interpolations by ordinary Kriging may have more or less deviations, and additional sampling with high density is needed in the near future.

The soil TOC fraction usually plays a significant role in the soil adsorption and sequestration of PAHs (Duan et al., 2015). In the current study, the soil TOC fraction in the YRD region ranged from 0.2% to 3.4%, with a mean of 1.4%, and significant correlations with the concentrations of total PPAHs, low molecular weight (LMW, 2–3 rings), median molecular weight (MMW, 4 rings) and high molecular weight (HMW, 5–6 rings) components are shown in Fig. S2. However, insignificant associations between the concentrations of NPAHs and TOC ($r = -0.067$, $p = 0.297$) and between the concentrations of OPAHs and TOC ($r = -0.042$, $p = 0.519$) were found. A possible explanation is ascribed to the lower octanol-water partitioning coefficients (l_gK_{ow}s) of the studied

NPAHs and OPAHs relative to those of the corresponding PPAHs, suggested stronger polarity and water solubility of the nitro- and oxyderivatives (Schlanges et al., 2008), which is responsible for the easier migration and weaker influence from the TOC fraction in soil (Lundstedt et al., 2007).

Based on a global emissions inventory in 2008 (Shen et al., 2013), the emission densities of the 16 PPAHs with USEPA priority in the 11 cities of the YRD region were extracted. The relationships of the measured PPAHs concentrations with emission density, local GDP per capita and population density (NBSC, 2015) are listed in Table S5. It is not surprising that the PPAHs concentrations are positively correlated with the GDP per capita, indicating the influ- ence of local socioeconomic development. Generally, the emission density would impose a direct influence on the spatial distribution of PPAHs. However, no significant correlation was observed in our statistical results. One possible reason for this observation is due to some deviations in calculating the emission inventory based on the corresponding emission factors (EFs). For example, the EFs reported in some previous studies showed variations in orders of magnitude (Zhang and Tao, 2009). In addition, other factors that were not considered in this study, such as unknown emission sources, long- range transboundary transport (Zheng et al., 2003), and degradation and transformation of PPAHs (Mao and Guan, 2016), may also affect the spatial distributions of PPAHs in soil.

Compositional profiles of PPAHs and their derivatives in surface soils

The compositional profiles of PPAHs in surface soils from the YRD region are depicted in Fig. S3A. Obviously, LMW components with 2–3 rings and MMW components with 4 rings were dominant, and on the whole, a decreasing trend of the LMW contribution to the total amount of PPAHs from the northwest to the southeast can be seen in the region, while the fraction of HMW species showed the opposite trend. It should be demonstrated that the compositional profiles of individual components emitted from different sources into ambient air may change, to different extents, when the parental compounds enter the receiving media (e.g., topsoil) after transportation with different distances via dry and wet depositions from air, so the inconsistence of compositional profiles of the individual components between emission sources and receiving media may be often found, due to various reactions or processes, such as (bio)degradation and transformation.

The major components of OPAHs detected in surface soils from most areas in the YRD region were 9FO and ANQ, which contributed 44% and 35% (see Fig. S3B) to the total amount, respectively. Ban- dowe et al. reported that 9FO and ANQ each accounted for 40% of the total amount in the soil samples collected from the Angren industrial area in Uzbekistan (Bandowe and Wilcke, 2010), which agrees with our results. Here, an exception occurred in Wuxi, which is characterized by a prevailing fraction of ANQ and may be related to the fact that the largest ANQ synthetizing enterprise in the world (Changjiang Chemical Plant) was located in Wuxi. Combined with the molecular weights of the studied OPAHs (9FO: 180.2, ANQ: 208.2, BZO: 230.3 and BaAQ: 258.3, unit: g/mol), components with low molecular weight tended to have a higher contribution to the total amount of OPAHs, which is in agreement with the compositional profiles of PPAHs. Since NPAHs were rarely detected in this study, their overall compositional profiles could not be obtained.

Concentrations of PPAHs and their derivatives in ambient air at two sites

The calibration result of passive sampling data by active air sampling is shown in the Supplementary Materials (see Fig. S4 and the complementary explanations in S-8). The calculated concentrations of PPAHs after calibration matched well with the measured concentrations. The total concentrations of PPAHs, NPAHs and OPAHs in the ambient air at the two sampling sites are tabulated in Table S6, and the results of different components are summarized in Table S7. The total concentrations of 27 PPAHs in the gaseous phase were obviously higher than those in the particulate phase at both sites, and LMW components mainly existed in the gaseous phase, while MMW species (no detection of HMW ones) chiefly presented in the solid phase. A minority of studied NPAHs (1N-NAP and 2N-NAP) were only detected in the particulate phase. 9FO and ANQ were identified in the particulate phase at both sites, while in the gaseous phase, 4 objective OPAHs were found with dominant 9FO and ANQ. In contrast to the situation of PPAHs, higher concentrations of NPAHs and OPAHs occurred in the particulate phase than in the gaseous phase, possibly due to their lower saturated vapor pressure and resultant weaker volatility (Schlanges et al., 2008) or due to the physicochemical processes (e.g., photolysis), thus the exact reasons should be further explored in future.

Preliminary source apportionment of PPAHs

Some commonly used specific ratios of paired isomers included FLA/(FLA + PYR), ANT/(ANT + PHE), BaA/(BaA + CHR) and IcdP/(IcdP + BghiP). The paired MMW or HMW isomers were generally presumed to manifest similar (bio)degradation rates, and their ratios may be slightly influenced by environmental changes (Yunker et al., 2002; Zhang et al., 2005; Tobiszewski and Namiesnik, 2012). Therefore, the relatively stable FLA/(FLA + PYR) and IcdP/(IcdP + BghiP) were selected to preliminarily identify the local emission sources of soil PPAHs in this study. A ratio of FLA/ (FLA + PYR) < 0.4 indicated a petrogenic source, while ratios of 0.4—0.5 and >

0.5 suggested sources from fossil fuel burning and coal/biomass combustion, respectively. A ratio of IcdP/ (IcdP ＋ BghiP) < 0.2 also indicated a petrogenic source, and ratios of 0.2—0.5 and > 0.5 designated traffic exhaust and coal/biomass combustion sources, respectively (Yunker et al., 2002). As for air samples, a ratio of IcdP/(IcdP ＋ BghiP) was replaced by BaA/ (BaA ＋ CHR) since IcdP and BghiP were rarely detected in the local ambient air. The BaA/(BaA ＋ CHR) values of <0.2, 0.2—0.35 and > 0.35 corresponded to petrogenic sources, coal combustion and traffic exhaust, respectively (Tobiszewski and Namiesnik, 2012). Fig. S5 in S-10 demonstrated the ratios of FLA/(FLA ＋ PYR), which ranged from 0.32 to 0.70, with an average of 0.50, and the ratios of IcdP/(IcdP ＋ BghiP), which ranged from 0.32 to 0.61, with a mean of 0.52. Consequently, the PPAHs in most soil samples in the YRD region were largely derived from a mix of coal/biomass combustion and traffic exhaust sources. A minor amount could be attributed to petrogenic sources, such as petroleum leakage. As for atmospheric PPAHs, the ratios of FLA/(FLA ＋ PYR) fell between 0.49 and 0.61, which designated coal/biomass burning and automobile exhaust as the major sources. The ratios of BaA/(BaA ＋ CHR) exceeded 0.35 for all air samples, which indicated a dominant emission source of vehicle exhaust (i.e., traffic tailing gas) at the two sampling sites. On the whole, such source appointment results of PPAHs by the paired isomeric ratios in topsoil samples coincided well with those in air samples.

In considering the limitations of specific isomeric ratios, PCA combined with a MLR model was further applied as a supplement to diagnose the local emission sources. Detailed information is given in the Supplementary Materials (see Table S8 and the complementary explanations in S-10). The PCA results showed that PPAHs in local surface soils predominantly originated from the combustion of coal and biomass and the tailing gas of motor vehicles. A small amount of coking production contributed to PPAHs in topsoil as well. Regarding the standardized scores of the total concentrations of the 16 PPAHs with USEPA priority as the dependent variable, the following regression equation was obtained through the MLR model.

$$\sum 16\mathrm{PAHs}_{\mathrm{soil}} = 0.287 \times F_1 + 0.031 \times F_2 \quad r = 0.997,\ p < 0.05$$

Based on the regression coefficients, the combustion of coal and biomass and vehicle exhaust contributed 90% of the total amount of PPAHs, and PPAHs released from coking production accounted for approximately 10%. The source identification results by the PCA combined with the MLR were consistent with those from the aforementioned paired isomeric ratios.

The PCA results of air samples showed that the combustion of biomass and industrial coal, vehicle exhaust and coking production contributed to the majority of PPAHs in ambient air. The corresponding regression equation is given below:

$$\sum 16\mathrm{PAHs}_{\mathrm{air}} = 0.356 \times F_1 - 0.068 \times F_2 \quad r = 0.987,\ p < 0.01$$

The regression coefficients noted that the combustion of fossil fuels (like household coal) and biomass (including straw and fire- wood) contributed 84% of the total amount of PPAHs, and the emissions from coking production and traffic tailing gas accounted for the remaining 16%. This situation was, on the whole, in agree- ment with the results of soil samples. It should be noted that the source apportionment of PPAHs in ambient air was utilized only as a reference due to the extremely limited number of air samples.

On the basis of a global emission inventory of the 16 priority PPAHs in 2008 (Shen et al., 2013), the relevant source profiles in the YRD region were extracted (see Fig. S6). The source composition revealed that motor vehicle exhaust served as a chief source of PPAHs in this region, with a contribution of approximately 37.9% of the total local emissions, and together with biomass (straw and firewood) burning and industrial coal combustion, these sources accounted for up to 88.7% of the total. Coking production contrib- uted the remainder of the local emissions. The compositional fractions of individual emission sources, on the whole, also confirmed the preliminary results of source appointment mentioned previously.

The ratio of 2N-FLO/1N-PYR was frequently applied to identify the sources of NPAHs, and ratios of <0.5 or >0.5 may indicate a primary source or formation from a secondary reaction (Dimashki et al., 2000). However, since the detection rates of 1N-PYR and 2N-FLO were low in this study, the sources of NPAHs could not be identified by ratio calculation. Additionally, since a well-developed method of source appointment for OPAHs has not been established in the current literatures, we did not discuss it in this study.

Associations of NPAHs and OPAHs with corresponding PPAHs

Associations of NPAHs and OPAHs with their corresponding PPAHs may assist in the determination of the sources of NPAHs and OPAHs (Lundstedt et al., 2007). Since only 1N-NAP in soil NPAHs was frequently detected in the current study, the association with the corresponding PPAH component was implemented. The results showed that 1N-NAP was significantly correlated with its corresponding PPAH at the 0.01 level of statistical significance ($r = 0.187$, $p = 0.006$). Moreover, significant correlations of the summed OPAHs with the corresponding PPAHs and $\sum \mathrm{COMB} - \mathrm{PAHs}$, as well as close associations of individual OPAH species with PPAHs and SCOMB-PAHs, are summarized in Table S9 of Supplementary Materials (S-11). COMB-PAHs were defined as the PPAHs generated from various combustion sources, including BaA, BbkF, BaP, BeP, BghiP, IcdP, DahA and CHR (Wilcke et al., 2014). The correlations of $\sum \mathrm{COMB}-\mathrm{PAHs}$ with the different OPAH components studied (9FO, ANQ, BZO and BaAQ) appeared to become closer, which to some extent indicated that HMW species were more readily released together with $\sum \mathrm{COMB}-\mathrm{PAHs}$ with respect to the LMW components. Similarly, Bandowe et al. (2011) also found that HMW OPAHs were significantly correlated with $\sum \mathrm{COMB}-\mathrm{PAHs}$, while the associations between LMW OPAHs and $\sum \mathrm{COMB}-\mathrm{PAHs}$ were relatively weak.

The concentration ratios of the studied OPAHs to their parental PAHs (OPAH/PPAH) in topsoil indicated that the percentages of 243 surface soil samples with ratios of 9FO/FLO and ANQ/ANT greater than 1.0 reached up to 52% and 91%, respectively (see Table S10). The extensive occurrence and higher concentrations of the studied OPAHs in surface soils, along with the stronger toxicity relative to their parental species, made it urgent to regularly monitor OPAHs in the future (Lundstedt et al., 2007).

Health risk assessment

According to the total concentration of the 16 priority PPAHs, the European soil quality standards categorized the soil pollution conditions into four grades (Barbara, 1996): uncontaminated (<200 ng/g), weakly contaminated (200–600 ng/g), moderately contaminated (600–1000 ng/g), and heavily contaminated (>1000 ng/g). Hence, approximately half of all of the sampling sites in the YRD region were contaminated to different degrees by PPAHs in surface soils (>200 ng/g), and the sample numbers corresponding to weakly, moderately and heavily contaminated were 94, 14 and 10, respectively. The three sampling sites with the most severe contamination of PPAHs in topsoil were situated in northern part of the region, with concentrations of 3579 ng/g, 3421 ng/g, and 2895 ng/g.

Based on the guidelines recommended by the US EPA, ILCR values of <10^{-6}, $^{10-6}$ – 10^{-4}, and >10^{-4} denoted a negligible risk, potential risk and high risk of cancer, respectively (USEPA, 1991). The estimated ILCR values responsible for the average concentra- tions of 16 priority PPAHs in surface soils from the YRD region are listed in Table 2.

The listed results exhibited that the 90th percentile cumulative probabilities of ILCR for local adults and children exposed to the

average concentration of PPAHs in topsoil were estimated at 3.77 x 10^{-5} and 1.02 x 10^{-5}, respectively. The mean ILCR data fell in the range from 10^{-6} to 10^{-4}, which meant that exposure of local adults and children to PPAHs in topsoil may cause a potential risk of cancer, especially for local adults. The cancer risks for both local adults and children via the three exposure pathways manifested in the following sequence: dermal contact > ingestion > inhalation. The 90th percentiles of the ILCR by respiratory inhalation and dermal contact for local adults were obviously higher than those for the local children, while they were approximately the same by soil ingestion. In addition, the 90th percentile cumulative probability of cancer risk by inhalation of PPAHs in surface soil particles was 4–5 orders of magnitude lower than that via the other two routes, and could be neglected.

Finally, the contribution of NPAHs and OPAHs in surface soils to human health risk (e.g., ILCR in this study) could not be quantified due to the lack of available toxicity equivalence factors. However, these compounds are crucial to the local soil system and humans because of their known stronger toxicity than the corresponding parent PAHs (IARC, 2013), and in addition to PPAHs, more attention should be paid to the effective control and abatement of their derivatives.

CONCLUSIONS

Based on field sampling, the total concentrations of 27 PPAHs in surface soils from the YRD region ranged from 21.0 ng/g to 3563.2 ng/g, with a mean of 310.6 ng/g. The concentrations of the 16 PPAHs that are USEPA priorities were much higher than those of the non-priority PPAHs. The summed concentrations of 4 NPAH components varied from 0.4 ng/g to 4.6 ng/g, with an average of 0.6 ± 0.6 ng/g, which was 3 orders of magnitude lower than that of the corresponding parental PAH species (206.8 ± 282.0 ng/g). In addition, the total concentrations of 4 OPAHs showed a range of 2.1–834.1 ng/g, with a mean value of 36.3 ± 57.0 ng/g. The compositional profiles of different PPAH components indicated a prevailing role of species with 2–4 rings, while OPAHs were dominated by 9FO and ANQ. NPAHs were detected at lower rates, except for 1N-PAH.

On the whole, surface soils in the northern areas of the YRD region were more heavily contaminated by PPAHs and OPAHs, and higher topsoil concentrations of NPAHs occurred in the northwest part of the YRD region. The local GDP per capita and topsoil TOC fractions were significantly correlated with the geographic distribution of PPAHs in surface soils. PPAHs in local surface soils from the YRD region may be mainly emitted from the combustion of coal and biomass and motor vehicle exhaust.

There were close associations of NPAHs and OPAHs with their corresponding parental PAHs in surface soils. About half of the total topsoil samples were considered to be contaminated by PPAHs to different degrees. The ILCR values of PPAHs were estimated at a magnitude of 10^{-5} in this study and showed that the exposure of the local adults and children to topsoil PPAHs in the YRD region may come with the potential risk of cancer. Moreover, the exposure risk primarily originated from the ingestion of and dermal contact with PPAHs in surface soils.

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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.chemosphere.2017.03.057

LIST OF TABLES AND FIGURES

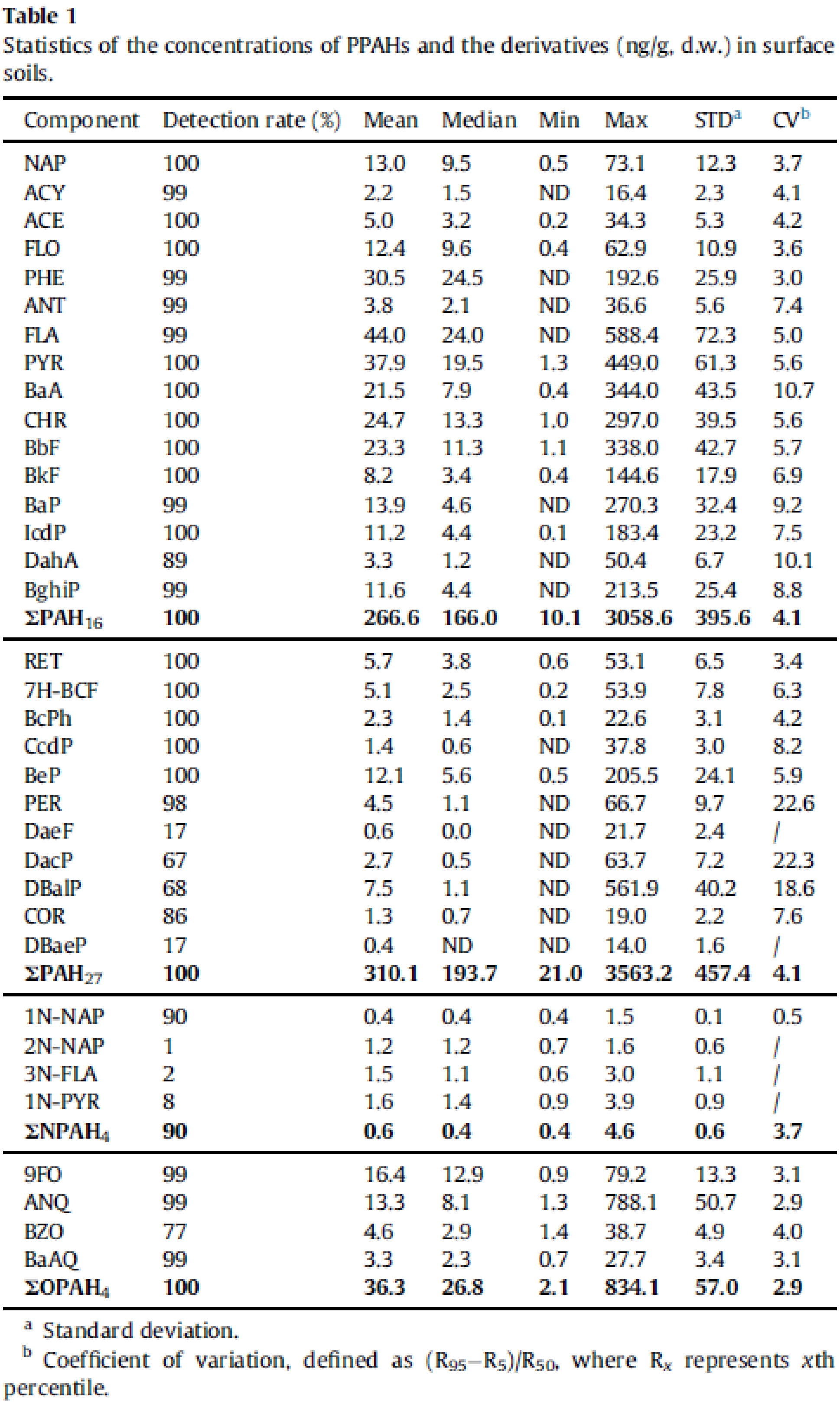


Table 1

Statistics of the concentrations of PPAHs and the derivatives (ng/g, d.w.) in surface soils.

Component	Detection rate (%)	Mean	Median	Min	Max	STD[a]	CV[b]
NAP	100	13.0	9.5	0.5	73.1	12.3	3.7
ACY	99	2.2	1.5	ND	16.4	2.3	4.1
ACE	100	5.0	3.2	0.2	34.3	5.3	4.2
FLO	100	12.4	9.6	0.4	62.9	10.9	3.6
PHE	99	30.5	24.5	ND	192.6	25.9	3.0
ANT	99	3.8	2.1	ND	36.6	5.6	7.4
FLA	99	44.0	24.0	ND	588.4	72.3	5.0
PYR	100	37.9	19.5	1.3	449.0	61.3	5.6
BaA	100	21.5	7.9	0.4	344.0	43.5	10.7
CHR	100	24.7	13.3	1.0	297.0	39.5	5.6
BbF	100	23.3	11.3	1.1	338.0	42.7	5.7
BkF	100	8.2	3.4	0.4	144.6	17.9	6.9
BaP	99	13.9	4.6	ND	270.3	32.4	9.2
IcdP	100	11.2	4.4	0.1	183.4	23.2	7.5
DahA	89	3.3	1.2	ND	50.4	6.7	10.1
BghiP	99	11.6	4.4	ND	213.5	25.4	8.8
ΣPAH_{16}	**100**	**266.6**	**166.0**	**10.1**	**3058.6**	**395.6**	**4.1**
RET	100	5.7	3.8	0.6	53.1	6.5	3.4
7H-BCF	100	5.1	2.5	0.2	53.9	7.8	6.3
BcPh	100	2.3	1.4	0.1	22.6	3.1	4.2
CcdP	100	1.4	0.6	ND	37.8	3.0	8.2
BeP	100	12.1	5.6	0.5	205.5	24.1	5.9
PER	98	4.5	1.1	ND	66.7	9.7	22.6
DaeF	17	0.6	0.0	ND	21.7	2.4	/
DacP	67	2.7	0.5	ND	63.7	7.2	22.3
DBalP	68	7.5	1.1	ND	561.9	40.2	18.6
COR	86	1.3	0.7	ND	19.0	2.2	7.6
DBaeP	17	0.4	ND	ND	14.0	1.6	/
ΣPAH_{27}	**100**	**310.1**	**193.7**	**21.0**	**3563.2**	**457.4**	**4.1**
1N-NAP	90	0.4	0.4	0.4	1.5	0.1	0.5
2N-NAP	1	1.2	1.2	0.7	1.6	0.6	/
3N-FLA	2	1.5	1.1	0.6	3.0	1.1	/
1N-PYR	8	1.6	1.4	0.9	3.9	0.9	/
$\Sigma NPAH_4$	**90**	**0.6**	**0.4**	**0.4**	**4.6**	**0.6**	**3.7**
9FO	99	16.4	12.9	0.9	79.2	13.3	3.1
ANQ	99	13.3	8.1	1.3	788.1	50.7	2.9
BZO	77	4.6	2.9	1.4	38.7	4.9	4.0
BaAQ	99	3.3	2.3	0.7	27.7	3.4	3.1
$\Sigma OPAH_4$	**100**	**36.3**	**26.8**	**2.1**	**834.1**	**57.0**	**2.9**

[a] Standard deviation.

[b] Coefficient of variation, defined as $(R_{95}-R_5)/R_{50}$, where R_x represents xth percentile.

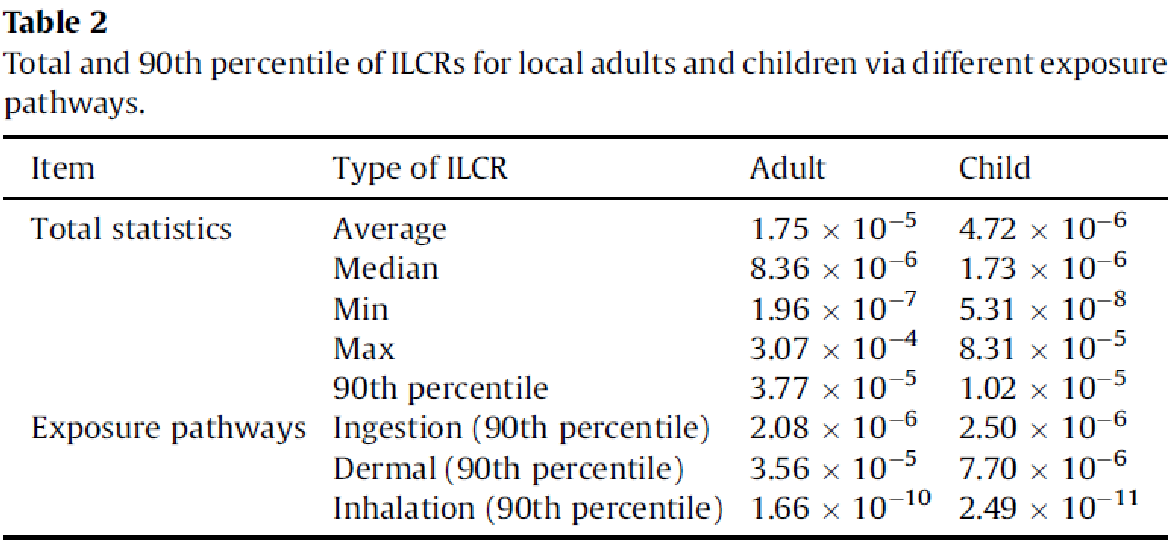
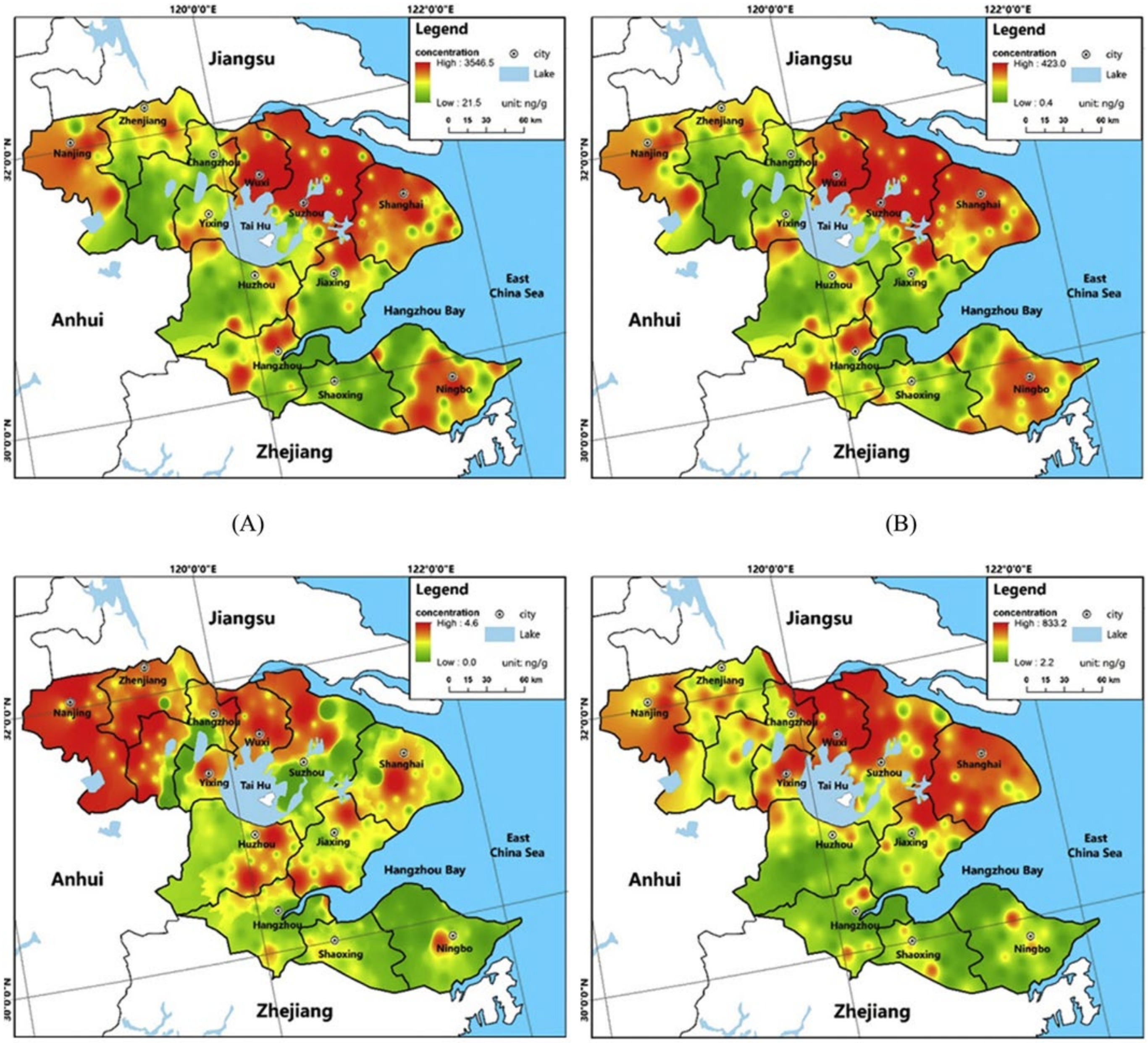


Table 2

Total and 90th percentile of ILCRs for local adults and children via different exposure pathways.

Item	Type of ILCR	Adult	Child
Total statistics	Average	1.75×10^{-5}	4.72×10^{-6}
	Median	8.36×10^{-6}	1.73×10^{-6}
	Min	1.96×10^{-7}	5.31×10^{-8}
	Max	3.07×10^{-4}	8.31×10^{-5}
	90th percentile	3.77×10^{-5}	1.02×10^{-5}
Exposure pathways	Ingestion (90th percentile)	2.08×10^{-6}	2.50×10^{-6}
	Dermal (90th percentile)	3.56×10^{-5}	7.70×10^{-6}
	Inhalation (90th percentile)	1.66×10^{-10}	2.49×10^{-11}



(A) (B)

(C) (D)

Fig. 1. Contour map of the spatial distribution of the total concentrations of PPAHs (A), PPAH-SBaP$_{eq}$ (B), NPAHs (C), and OPAHs (D) in surface soils in the YRD.

REFERENCES

Bamford, H.A., Baker, J.E., 2003. Nitro-polycyclic aromatic hydrocarbon concentra- tions and sources in urban and suburban atmospheres of the Mid-Atlantic re- gion. Atmos. Environ. 37 (15), 2077–2091.

Bandowe, B.A.M., Wilcke, W., 2010. Analysis of polycyclic aromatic hydrocarbons and their oxygen-containing derivatives and metabolites in soils. J. Environ. Qual. 39 (4), 1349–1358.

Bandowe, B.A.M., Sobocka, J., Wilcke, W., 2011. Oxygen-containing polycyclic aro- matic hydrocarbons (OPAHs) in urban soils of Bratislava, Slovakia: patterns, relation to PAHs and vertical distribution. Environ. Pollut. 159 (2), 539–549.

Barbara, M., 1996. Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. Appl. Geochem. 11 (1e2), 121–127.

Bosch, C., Andersson, A., Krusa, M., Bandh, C., Hovorkova, I., Klanova, J., Knowles, T., Pancost, R., Evershed, R., Gustafsson, O., 2015. Source apportionment of poly- cyclic aromatic hydrocarbons in Central European soils with compound-specific triple isotopes (d13C, D14C, and d2H). Environ. Sci. Technol. 49 (13), 7657–7665.

Dimashki, M., Harrad, S., Harrison, R.M., 2000. Measurements of nitro-PAH in the atmospheres of two cities. Atmos. Environ. 34 (15), 2459–2469.

Duan, Y., Shen, G., Tao, S., Hong, J., Chen, Y., Miao, X., Li, T., Su, S., Shen, H., Fu, X., Meng, Q., Zhang, J., Zhang, B., Han, X., Song, K., 2015. Characteristics of poly- cyclic aromatic hydrocarbons in agricultural soils at a typical coke production base in Shanxi, China. Chemosphere 127, 64–69.

Fu, P.P., Xia, Q., Sun, X., Yu, H., 2012. Phototoxicity and environmental trans- formation of polycyclic aromatic hydrocarbons (PAHs)-light-induced reactive oxygen species, lipid peroxidation, and DNA damage. J. Environ. Sci. Health Part C Environ. Carcinog. Ecotoxicol. Rev. 30 (1), 1–41.

Golobo canin, D.D., Akrbi'c, B.D., Miljevi'c, N.R., 2004. Principal component analysis

for soil contamination with PAHs. Chemom. Intell. Lab. Syst. 72 (2), 219–223.

Haritash, A.K., Kaushik, C.P., 2009. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): a review. J. Hazard. Mater. 169 (1e3), 1–15.

Hasei, T., Watanabe, T., Endo, O., Sugita, K., Asanoma, M., Goto, S., Hirayama, T., 2009. Determination of 3, 6-dinitrobenzo[e]pyrene in surface soil and airborne particles, and its possible sources, diesel particles and incinerator dusts. J. Health Sci. 55 (4), 567–577.

IARC, International Agency for Research on Cancer, 2010. Monographs on the evaluation of carcinogenic risk of chemicals to humans. In: Some Non- heterocyclic Polycyclic Aromatic Hydrocarbons and Some Related Exposures, vol. 92. IARC, Lyon.

IARC, 2013. Diesel and Gasoline Engine Exhaust and Some Nitroarenes, Lyon (France). Online available from: http://monographs.iarc.fr/ENG/Monographs/ vol105/index.php.

Jiang, Y.F., Wang, X.T., Wu, M.H., Sheng, G.Y., Fu, J.M., 2011. Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in agricultural soil of Shanghai, China. Environ. Monit. Assess. 183 (1–4), 139–150. Kaya, E., Dumanoglu, Y., Kara, M., Altiok, H., Bayram, A., Elbir, T., Odabasi, M., 2012. Spatial and temporal variation and air-soil exchange of atmospheric PAHs and

PCBs in an industrial region. Atmos. Pollut. Res. 3 (4), 435–449.

Keyte, I.J., Harrison, R.M., Lammel, G., 2013. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons-a review. Chem. Soc. Rev. 42, 9333–9391.

Li, A., Jang, J., Scheff, P.A., 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in lake calumet, chicago. Environ. Sci. Tech- nol. 37 (13), 2958–2965.

Li, W., Wang, C., Wang, H., Chen, J., Shen, H., Shen, G., Huang, Y., Wang, R., Wang, B., Zhang, Y., Chen, H., Chen, Y., Su, S., Lin, N., Tang, J., Li, Q., Wang, X., Liu, J., Tao, S.,2014. Atmospheric polycyclic aromatic hydrocarbons in rural and urban areas of northern China. Environ. Pollut. 192, 83–90.

Li, W., Shen, G., Yuan, C., Wang, C., Shen, H., Jiang, H., Zhang, Y.Y., Chen, Y.C., Su, S., Lin, N., Tao, S., 2015. The gas/particle partitioning of nitro- and oxy-polycyclic aromatic hydrocarbons in the atmosphere of northern China. Atmos. Res. 172 (1), 18–22.

Li, Y.T., Li, F.B., Chen, J.J., Yang, G.Y., Wan, H.F., Zhang, T.B., Zeng, X.D., Liu, J.M., 2008.

The concentrations, distribution and sources of PAHs in agricultural soils and vegetables from Shunde, Guangdong, China. Environ. Monit. Assess. 139, 61e76. Lundstedt, S., White, P.A., Lemieux, C.L., Lynes, K.D., Lambert, I.B., Oberg, L., Haglund, P., Tysklind, M., 2007. Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. AMBIO A J. Hum. Environ. 36 (6), 475–485.

Mao, J., Guan, W., 2016. Fungal degradation of polycyclic aromatic hydrocarbons (PAHs) by and its application in bioremediation of PAH-contaminated soil. Acta Agric. Scand. Sect. B - Soil & Plant Sci. 1–7.

National Bureau of Statistics of China (NBSC), 2015. China Statistical Yearbook for Regional Economy 2014. China Statistics Press, Beijing.

Niederer, M., 1998. Determination of polycyclic aromatic hydrocarbons and sub- stitutes (nitro-, oxy-PAHs) in urban soil and airborne particulate by GC-MS and NCI-MS/MS. Environ. Sci. Pollut. Res. 5, 209–216.

Ping, L.F., Luo, Y.M., Zhang, H.B., Li, Q.B., Wu, L.H., 2007. Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, East China. Environ. Pollut. 147 (2), 358e365.

Rachwał, M., Magiera, T., Wawer, M., 2015. Coke industry and steel metallurgy as the source of soil contamination by technogenic magnetic particles, heavy metals and polycyclic aromatic hydrocarbons. Chemosphere 138, 863–873.

Schlanges, I., Meyer, D., Palm, W.U., Ruck, W., 2008. Identification, quantification and distribution of PAC-metabolites, heterocyclic PAC and substituted PAC in groundwater samples of tar-contaminated sites from Germany. Polycycl. Aro- mat. Compd. 28, 320–328.

Shen, H., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G., Wang, B., Zhang, Y., Chen, Y., Lu, Y., 2013. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environ. Sci. Technol. 47 (12), 6415–6524.

Sun, J.T., Pan, L.L., Zhan, Y., Lu, H.N., Tsang, D.C.W., Liu, W.X., Wang, X.L., Li, X.D., Zhu, L.Z., 2016a. Contamination of phthalate esters, organochlorine pesticides and polybrominated diphenyl ethers in agricultural soils from the Yangtze River Delta of China. Sci. Total Environ. 544, 670–676.

Sun, J.T., Pan, L.L., Tsang, D.C.W., Zhan, Y., Liu, W.X., Wang, X.L., Zhu, L.Z., Li, X.D., 2016b. Polychlorinated biphenyls in agricultural soils from the Yangtze River Delta of China: regional contamination characteristics, combined ecological effects and human health risks. Chemosphere 163, 422–428.

Tao, S., Liu, W., Li, Y., Yang, Y., Zuo, Q., Li, B., Cao, J., 2008. Organochlorine pesticides contaminated surface soil as reemission source in the Haihe Plain, China. En- viron. Sci. Technol. 42 (22), 8395–8400.

Tobiszewski, M., Namie'snik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

USEPA, 1991. Risk assessment guidance for superfund. In: Human Health Evaluation Manual (Part B, Development of Risk-based Preliminary Remediation Goals), vol. 1. EPA/540/R-92/003 Publication 9285.7–01B.

Walgraeve, C., Demeestere, K., Dewulf, J., Zimmermann, R., Van Langenhove, H., 2010. Oxygenated polycyclic aromatic hydrocarbons in atmospheric particulate matter: molecular characterization and occurrence. Atmos. Environ. 44, 1831–1846.

Wang, C., Wu, S., Zhou, S., Wang, H., Li, B., Chen, H., Yu, Y., Shi, Y., 2015. Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: concen- tration, source, spatial distribution, and potential human health risk. Sci. Total Environ. 527–528, 375–383.

Wang, W., Simonich, S., Giri, B., Chang, Y., Zhang, Y., Jia, Y., Tao, S., Wang, R., Wang, B., Li, W., 2011. Atmospheric concentrations and air-soil gas exchange of polycyclic aromatic hydrocarbons (PAHs) in remote, rural village and urban areas of Beijing-Tianjin region, North China. Sci. Total Environ. 409, 2942–2950.

Wei, L.X., 2008. The Study on the Structure and Distribution of Population and Industry in Yangtze River Delta. East China Normal University (in Chinese).

Wilcke, W., Bandowe, B.A.M., Lueso, M.G., 2014. Polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives (oxygenated PAHs, Azarenes) in soils along a climosequence in Argentina. Sci. Total Environ. 473, 317–325.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33 (4), 489–515.

Zhang, X., Tao, S., Liu, W., Yang, Y., Zuo, Q., Liu, S., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ. Sci. Technol. 39 (23), 9109–9114.

Zhang, Y., Tao, S., Shen, H., Ma, J., 2009. Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. Proc. Natl. Acad. Sci. 106 (50), 21063–21067.

Zhang, Y., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aro- matic hydrocarbons (PAHs) for 2004. Atmos. Environ. 43 (4), 812–819.

Zheng, Y., Wang, X.J., Liu, R.M., Tao, S., 2003. Kriging analysis and pollution assessment for the polycyclic aromatic hydrocarbons (PAHs) in the soil of Tianjin. China Environ. Sci. 23 (2), 113–116 (in Chinese).