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Polycyclic aromatic hydrocarbons (PAHs) in rural soils of Dongjiang River Basin: occurrence, source apportionment, and potential human health risk

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Abstract

Purpose A comprehensive study was conducted to investigate the presence of polycyclic aromatic hydrocarbons (PAHs) in Dongjiang River Basin (DRB) soils and to evaluate their sources and ecological and health risk. In addition, factors affecting the distribution and fate of PAHs in the soils such as emission density, soil organic matter, degradation, etc. were studied.

Materials and methods Surface soil (0–20 cm) samples from 30 sampling sites in the rural areas of DRB were collected and analyzed for 17 polycyclic aromatic hydrocarbons (16 EPA priority PAHs and perylene). Positive matrix factorization model was used to investigate the source apportionment of these PAHs, and an incremental lifetime cancer risk (ILCR) was used to estimate the integrated lifetime risks of exposure to soil-borne PAHs through direct ingestion, dermal contact, and inhalation collectively.

Results and discussion The total PAH concentrations in the rural soils in DRB range from 23.5 to 231 μg/kg with a mean concentration of 116 μg/kg. The predominant PAHs in the rural soils were naphthalene, fluoranthene, phenanthrene, and benzo(*b*)fluoranthene. Cluster analysis was performed to classify the soil PAHs into three clusters, which could be indicative of the soil PAHs with different origins and different properties. Source apportionment results showed that coal, biomass, oil, commercial creosotes, and vehicle contributed 24 %, 24 %, 17 %, 17 %, and 18 % of the total soil PAH burden, respectively. The ILCR results indicated that exposure to these soil-borne PAHs through direct ingestion, dermal contact, and inhalation collectively produces some risk.

Conclusions PAHs in the soils of the DRB will produce long-term influences on rivers and oceans via soil erosion and river transport. Therefore, PAHs in rural soils of DRB have potential impacts on the water supply and human health risk.

Keywords Human health risk · Occurrence · PAHs · Soil organic matter · Source apportionment

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) include several hundred individual compounds possessing at least two benzene rings, and 16 of them have been identified as “priority pollutants” by the United States Environmental Protection Agency (US EPA) (Zhang et al. 2006). Many PAHs have mutagenic, carcinogenic, and teratogenic properties and are ubiquitously present in environmental media, such as soils, waters, sediments, and air. Soil is one of the major reservoirs for organic pollutants. For example, it was estimated that at least 90 % of PAHs burden in Great Britain was stored in soils (Wild and Jones 1995). PAHs are primarily emitted from incomplete combustion of organic matter, such as coal, liquid fossil fuel, and biomass (Neff 1979).

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It is important to identify the source apportionment of PAHs in the soils, which makes it conducive to propose effective pollution abatement strategies (Chen et al. 2012). PAH isomer ratios such as BaA/(BaA+Chry), Flu/(Flu+Pyr), and InP/(InP+BgP) were commonly used to identify the source of PAHs in the soils. However, using this method can only find out what are the major contributions to the soil PAH burden rather than provide a quantitative analysis. Thus, several receptor models have been developed in the past decades to quantitatively analyze the contributions of the diverse PAH sources (Gordon 1988), including chemical mass balance mode (Li et al. 2003; Gu et al. 2003), principal component analysis (PCA) (Larsen and Baker 2003; Zuo et al. 2007), etc. Receptor models include the application of multivariate statistical methods to the identification and quantitative apportionment of pollutants to their sources (Wang et al. 2009). These models are based on the idea that the time dependence of a chemical species at the receptor site will be the same for the species from the same source. Species of similar variability are grouped together in a minimum number of factors, which explains the variability of the data set (Liu et al. 2003). It is assumed that each factor is associated with a source or source type.

Positive matrix factorization (PMF) model is one of such models (Paatero and Tapper 1994; Paatero 1997; US EPA 2008). PMF is a multivariate factor analysis tool developed by Paatero and Tapper (1994) in the early 1990s. It has been employed in different research efforts as an alternative to factor analysis (FA, such as the principal component analysis), including bulk wet deposition in Finland (Anttila et al. 1995), airborne fine particles (Kim and Hopke 2007; Xie et al. 2012), organic aerosol (Ulbrich et al. 2009), PAHs in the soils in Dalian and Shanghai, China (Wang et al. 2009; Wang et al. 2013), and PCBs in the sediments in USA (Soonthornnonda et al. 2011). The factor loadings and factor scores may be negative in the traditional factor analysis model (e.g., PCA). In this case, it is very difficult to identify the sources (Wang et al. 2009). However, PMF rotates the matrices of factor loadings and scores with positive constraints, which makes the factor axes less orthogonal and the factor loadings and factor scores more interpretable (Paatero and Tapper 1994).

PAHs accumulated in soils cause a health risk to humans (Phillips 1999). Human exposure to PAHs is mainly by inhalation of particulates carrying PAHs, dietary intake of contaminated food products, and direct contact with polluted soils. Peng et al. (2011) used an incremental lifetime cancer risk (ILCR) to estimate the integrated lifetime risks of exposure to soil-borne PAHs through direct ingestion, dermal contacts, and inhalation collectively. Therefore, the objectives of our study were to (1) investigate the levels and source of 17 PAHs (16 EPA priority pollutants and perylene) in soils, (2) investigate the profiles and source apportionment of the PAHs in the soils, and (3) evaluate the potential ecological and health risk of PAHs in the soils.

2 Materials and methods

2.1 Study area

The Dongjiang River Basin (DRB) locates in the northeast of the Pearl River Delta, which is adjacent to Hong Kong and Guangzhou. The climate of the Pearl River Delta belongs to a subtropical monsoon and is humid, with an annual average temperature of about 28–31 °C. The period from April to September is the wet season. The main land use patterns in DRB are agriculture, forest, pasture, range, urban area, and water surface (Wu and Chen 2009). The Dongjiang River is quite important to not only the local region but also Hong Kong because approximately 80 % of Hong Kong's water supply is originated from the Dongjiang River through cross-basin water transport.

2.2 Sampling

The soil collection method is described elsewhere (Ma et al. 2008). Thirty surface (0–20 cm) soil samples were collected from the rural area of Guangzhou, Dongguan, and Huizhou (with a total area of 6,990 km^2), and the samplings sites were plotted in Table S1 ("Electronic supplementary material"). In order to mitigate the effects of human activities, the soil samples were taken from remote sites (i.e., away from towns, roads, or other human activity). In addition, the sampling sites covered all land use types in the study region (Table S1, "Electronic supplementary material"). The soils covering a relatively large area (0.5 ha) in each site were collected, which thus can be regarded as a representative site. A composite of ten cores from 0 to 20 cm in depth for each surface sample was scooped using a pre-cleaned stainless steel. Three cores, taken over an area of several square meters, were bulked together to form one sample. Plant residues in each sample were discarded with a clean tweezer. The samples were wrapped in aluminum foil twice and sealed in plastic bags. The soil samples were brought back and kept at −18 °C until further analysis. Details of the sampling sites are shown in Fig. 1. The sampling sites labeled in green color were sampled in this study, while those labeled in blue and red color were cited in previous papers of our research team such as Chen et al. (2005) and Ma et al. (2008), respectively.

2.3 PAHs analysis and quality control/assurance

The analytical procedure, including extraction, separation, and analysis, of PAHs for the samples were described in detail in previous investigations (Mai et al. 2002; Zhang et al. 2002).

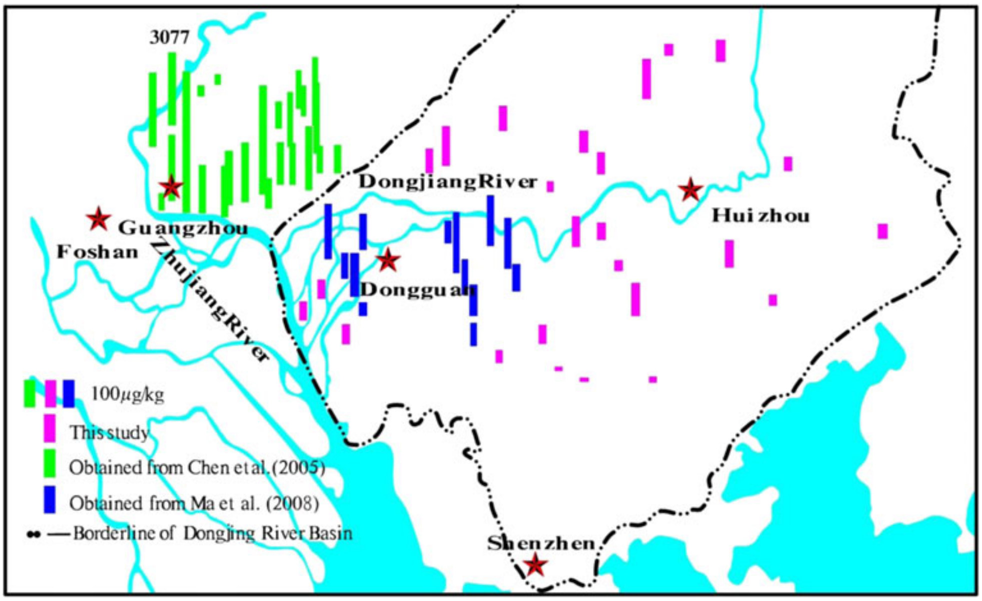

Fig. 1 Map of total PAH concentrations in the soils from Dongjiang River Basin

In brief, before extraction, every sample (about 10 g) was spiked with a given quantity of deuterated PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}) in order to monitor the efficiency of the extraction and cleanup procedure. After extraction, the extract was concentrated to about 1 mL, with the solvent changed to hexane, and then purified using 1:2 aluminum/silica column chromatography. The first fraction containing aliphatic hydrocarbons was eluted with 15 mL hexane, which was discarded. The second fraction containing PAHs was eluted with a 70-mL mixture of DCM and hexane (*v*/*v* 30:70).

Then, the PAHs fraction's solvent was changed to hexane and vacuum-evaporated to 1 ml and concentrated to 500 μl under a gentle nitrogen stream. In order to quantify the PAH concentrations, a given mass (2,500 ng) of hexamethylbenzene was spiked into the vial as internal standard prior to GC/MS analysis. PAHs were analyzed using Hewlett-Packard HP-6890 equipped with a 30-m DB-5 MS capillary column coupled with a HP-5975 mass spectrometer operated in the electron impact mode (70 eV). The chromatographic conditions were as follows: injector temperature 280 °C, and temperature program 60 °C for 5 min, 60–290 °C at 3 °C /min, and 290 °C for 40 min. The carrier gas was helium at a constant flow rate of 1.5 ml/min. A sample at 1 μl was injected in the splitless model.

Method blanks (solvent), duplicate samples, and spiked blanks (standards spiked into solvent) were analyzed. In addition, surrogate standards were added to each of the samples to monitor procedural performance and matrix effects. One laboratory blank and one duplicate were run with every five samples. The recoveries of 17 PAHs in spiked blanks ($n=5$) varied from 48.6 % (Nap) to 114.3 % (BgP). Limit of detection (LOD) was calculated as five times the noise level of the chromatogram in the blank sample with a sample size of 10 g and a final volume of 500 μl. The range of the LODs of PAHs was calculated to be 0.0040–0.56 μg/kg. The average recoveries for the surrogates naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12} in the samples were 49.86, 67.82, 76.77, 89.25, and 80.76 %, respectively. The recovery ratios for the surrogates in the samples conform to the ranges reported by the United States Environmental Protection Agency. The concentrations of PAHs were not corrected for the recovery ratios for the surrogates. The deviation between the duplications of PAH concentrations was < 5 %.

2.4 Measurement of total organic carbon

The analytical procedure to measure total organic carbon (TOC) in the soil samples was similar to previous investigations (Mai et al. 2002; Ran et al. 2002; Ran et al. 2003). Briefly, about one gram of an air-dried soil sample was treated with 10 % HCl to eliminate inorganic carbon. The residue was washed by distilled water until the solution pH reached neutral and dried overnight at 60 °C. Elemental composition (e.g., C, H, N) of the treated soil was quantified on an elemental analyzer (Vario EL III Elementar, Germany). Acetanilide was used as external standard.

2.5 Human health risk

Several PAHs such as benzo[*a*]pyrene (BaP) and benz[*a*]-anthracene (BaA) are carcinogenic; moreover, some are the precursors to carcinogenic daughter compounds such as benzo[b]fluoranthene (BbF) (Larsen and Baker 2003; Dickhut et al. 2000). Kameda et al. (2005) and Yu et al. (2008) have pointed out that exposures to PAHs were potentially harmful to ordinary residents (Peng et al. 2011). For example, the potential mutagenic and carcinogenic effects of PAHs may lead the residents to suffer from cancer (Colombo et al. 2006; Szabová et al. 2008). People are exposed to PAHs in the environment through three main channels such as direct ingestion, dermal contacts, and inhalation (Rajput et al. 2008). In this study, an ILCR was used to estimate the integrated lifetime risks of exposure to soil-borne PAHs through direct ingestion, dermal contacts, and inhalation collectively (Peng et al. 2011).

2.6 PMF model

Positive matrix factorization (PMF) is a receptor modeling tool, which has been developed by Paatero and Tapper (1994) and described in detail elsewhere (Paatero and Tapper 1994; Paatero 1997; US EPA 2008). Thus, it will be explained briefly here. A special data set (matrix *X* of *i* by *j* dimensions) which can be factored into two matrices—factor contributions and factor profiles—has been defined in PMF, where *i* and *j* mean the number of samples and chemical species measured, respectively. The PMF can be described according to the following equation:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where x_{ij} is the *j*th species concentration measured in the *i*th sample, *p* is the number of factors, *f* is the species profile of each source, *g* is source contribution, and e_{ij} is the residual for each sample/species.

The objective function (*Q*) related to the residual and uncertainty is used to minimize using weighted least squares by PMF, which can be defined as:

$$Q = \sum_{i=1}^{n=1} \sum_{j=1}^{m} \left(e_{ij} \big/ u_{ij} \right)^2 = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \tag{2}$$

where *n* and *m* are the number of samples and species, respectively, e_{ij} is the deviation between the observations and the model, and u_{ij} is the uncertainty of each observation.

If the concentration is less than or equal to the method detection limit (MDL) provided, the uncertainty can be calculated with the following equation:

$$\mathrm{Unc} = \frac{5}{6}\mathrm{MDL} \tag{3}$$

But when the concentration is greater than the MDL, it can be calculated as:

$$\mathrm{Unc} = \sqrt{(\mathrm{MU} \times \mathrm{concentration})^2 + (\mathrm{MDL})^2} \tag{4}$$

PMF analysis has been conducted with the help of US EPA PMF 3.0 model (US EPA 2008).

3 Results and discussion

3.1 Spatial variation of PAHs in the soils

Contents of individual PAHs vary considerably within the soil samples. Figure 1 shows the map for total PAH concentrations investigated in the soils from Dongjiang River Basin. The total PAH concentrations in the rural soils in DRB range from 23.5 to 231 μg/kg, with a mean concentration of 116 μg/kg, but the total PAH concentrations in the urban soils of Dongguan City in DRB range from 128 to 357 μg/kg, with a mean concentration for 226 μg/kg (Ma et al. 2008). When compared with the target value set by the Dutch government for uncontaminated soils (20–50 μg/kg) (Aannokkee 1990), PAHs in most of the rural soils are higher than this value. However, the PAH concentrations in most of the urban soils are much higher (> 200 μg/kg). In comparison with previous investigation (Chen et al. 2005) in the urban area of Guangzhou City, the PAH concentrations in both of the rural and urban soils (Dongguan City) from the DRB are much lower than those of the urban soils in Guangzhou City. Moreover, naphthalene (Nap), fluoranthene (Flu), phenanthrene (Phe), and Benzo(b)fluoranthene (B(b)F) are the major PAH congeners in the rural soils, respectively, accounting for 16.48, 17.54, 9.59, and 12.55 % of the 17 PAHs, while Phe, Flu, Chrysene (Chry), and B(b)F dominated in the urban soils in DRB, Guangzhou, and Dongguan, respectively, accounting for 17.8, 15.5, 17.7, and 15.8 % of the 16 PAHs.

In addition, a comprehensive comparison was conducted between the PAH concentrations in this study and those in urban and rural soils from other global regions such as Hong Kong, South Korea, Norway, and UK (Nam et al. 2003; Zhang et al. 2006; Nam et al. 2008) (Table 1). PAH concentrations (23.5–231 μg/kg) in the rural soils from the Dongjiang River basin are much higher than those in Hong Kong (7–200 μg/kg) but much lower than those in Norway (8.6–1,100 μg/kg). When compared to PAH concentrations in urban soils in Hong Kong (50–410 μg/kg) and Norway (42–11,200 μg/kg), PAH concentrations in this region are much lower.

It was commonly accepted that the levels of persistent organic pollutants in surface soils depended positively on SOM (Karickhoff 1984; Voutsa and Samara 1998; Kipopoulou et al. 1999; Meijer et al. 2003; Tao et al. 2004; Cornelissen et al. 2005; Schwarzenbach et al. 2006; Yang et al. 2010). For instance, a global survey on polychlorinated biphenyls (PCBs) in surface soil presented a positive correlation between soil PCBs and SOM, and a tenfold increase in SOM led to a sixfold increase in total PCB concentrations in soils (Meijer et al. 2003). In our studies, the results are similar. With the total organic carbon concentration decreasing from 20.09 to 2.5 mg/g soil, the total PAH concentrations

Table 1 Comparison of averages of PAHs (μg/kg dry weight) in soils

Location	Hong Kong[a]		UK	Norway	South Korea	DRB		
References	Zhang et al. 2006		Nam et al. 2008		Nam et al. 2003	This study	Chen et al. 2005	Ma et al. 2008
No. of samples	45R	8U	27U	26R	226R	30R	29U	12U
Nap	5.49	6.24	13 (2.5–300)	11 (2.2–45)	24.0 (4.8–157)	16.4 (3–32.6)	19.2 (1–64)	26.6 (15–46)
Ace	nd	0.53	3.7 (0.7–74)	3.2 (1.0–11)	1.5 (<0.35–33.7)	0.83 (0.3–1.8)	1.50 (nd–9)	0.63 (0–1)
Acy	1.82	2.73	nd	nd	2.1 (<0.3–41.5)	0.88 (0.1–2.7)	nd	0
Flo	4.67	28.0	5.1 (1.3–20)	6.8 (1.4–22)	3.6 (<0.53–39.4)	4.90 (1.0–17)	6.10 (1–40)	5.09 (3–7)
Phe	2.06	16.7	54 (4.6–350)	40 (6.7–110)	20.5 (0.70–141)	18.1 (3–68.4)	56.9 (4–281)	58.6 (35–114)
Ant	0.73	3.57	6.8 (0.7–65)	3.4 (1.8–7.4)	7.5 (<0.30–43.1)	2.78 (0.2–7.6)	4.20 (nd–34)	3.91 (3–6)
Flu	1.97	4.56	110 (6.8–1,770)	14 (1.0–110)	33.7 (2.6–353)	13.0 (1.4–28)	67.7 (3–583)	35.9 (13–64)
Pyr	5.44	27.1	87 (4.4–1,420)	13 (0.7–120)	26 (1.6–317)	7.90 (0.9–20)	49.0 (2–492)	24.4 (9–38)
Chry	0.90	16.2	68 (4.3–1,100)	14 (0.8–120)	14.6 (<0.44–267)	6.36 (0–15)	91.5 (1–693)	19.1 (6–34)
BaA	1.52	8.97	44 (2.2–1,160)	4.5 (0.4–77)	18.6 (<1.58–284)	6.47 (0.2–26.2)	25.1 (0–232)	8 (2–19)
B(b+k)F	0.99	26.7	108 (7.5–2,120)	19.1 (1.5–253)	39.5 (<1.31–569)	20.9 (0.6–46)	55.6 (1–368)	20.8 (7–46)
BaP	2.26	9.90	46 (1.8–1,600)	5.3 (0.5–86)	16.3 (<0.42–294)	4.89 (0.2–6.0)	14.8 (nd–136)	5.27 (2–16)
Per	nd	nd	nd	nd	nd	3.77 (0–10.1)	nd	nd
InP	0.75	8.26	nd	nd	12.2 (<0.32–248)	6.98 (0–13.4)	(nd–47)	7.36 (3–18)
BghiP	2.46	9.82	51 (2.8–1,200)	9.3 (0.9–110)	12.4 (<0.25–120)	6.35 (0–12.2)	12.8 (nd–70)	7.91 (3–20)
DbA	Nd	nd	6.0 (0.4–42)	1.2 (0.1–16)	3.2 (<0.43–221)	0.75 (0–3.3)	8.10 (nd–42)	2.36 (1–6)
$\sum_{17}$PAHs	31.1 (7–200)	172 (50–410)	603 (42–11,200)	145 (8.6–1,100)	236 (23.3–2,834)	116 (23.5–231)	422 (42–3,077)	226 (128–357)
$\sum_{7}$carcinogenic PAHs[b]	6.42	70.0	272	44.1	104	46.4	205	62.9

nd no data, *R* rural area, *U* urban area

[a] There are no data about the range of individual PAH concentrations in Hong Kong soils

[b] Chrysene, benzo[*a*]anthracene, benzo[*k*]fluoranthene, benzo[*b*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, and dibenzo[*ah*]anthracene

in the rural soils from Dongjiang River Basin decrease from 231 to 23.5 μg/kg. It suggests that a sevenfold increase in SOM leads to a ninefold increase in total PAH concentrations in the surface soils (Fig. S2, "Electronic supplementary material").

The geographical distribution pattern of PAHs concentration in soils should be controlled by the spatial distribution of PAHs emission sources and deposition processes. Wang et al. (2012) investigated the relationship between the concentrations of PAHs in surface soils and their emissions and found a significantly positive correlation between them ($p<0.05$). In order to examine the correlation between the PAHs in the surface soils of DRB and the PAH emissions in the areas studied, high-resolution emission data (Zhang et al. 2007) were used in this study. PAH emission density and $\sum_{17}$PAH concentrations in the soils were both log-transformed. After that, the correlation between log-transformed PAH$_{17}$ concentrations in the soils and log-transformed PAH emission density was analyzed. It was found that there was a positive linear correlation between log-transformed PAH$_{17}$ concentrations in the soils and log-transformed PAH emission density ($n=26$; $r=0.52$; $p<0.01$; Fig. 2). Therefore, it is concluded that the PAH emission density in the areas studied in this study played a great influence on the spatial distribution of PAH concentrations in the surface soils of these regions (Fig. 2).

3.2 Compositional profiles of PAHs

As mentioned above, Nap (two-ring PAH), Phe (three-ring PAH), Flu (four-ring PAH) and B(b)F (five-ring PAH) dominated in the rural soils of DRB (Table 1), respectively, accounting for 16.48 %, 17.54 %, 9.59 %, 12.55 % of the 17 PAHs. But Phe, Flu, Chry and B(b)F are the major PAHs in the urban soils in DRB, Guangzhou, and Dongguan, respectively, accounting for 17.8 %, 15.5 %, 17.7 % and 15.8 % of the 17 PAHs. Figure 3 further shows that in the rural soils of DRB average concentrations of 2-3 rings PAHs were higher or equal to those of 4 and 5-6 rings PAH. In contrast, 4 rings PAH dominated the PAH profile of the urban soils in DRB, Guangzhou, and Dongguan. The reason for the differences between the PAH sources of the rural and urban soils of DRB is that several 4-rings PAH such as Chry and Flu are typical markers for fossil fuel combustion (Wilcke 2000). Cluster analysis was performed to identify the groups of individual PAHs in DRB soils. The results in the hierarchical dendrogram (Fig. 4) revealed that the 15 PAHs (Per and DbA were not included in the analysis due to their low detectable frequency) are divided into two major

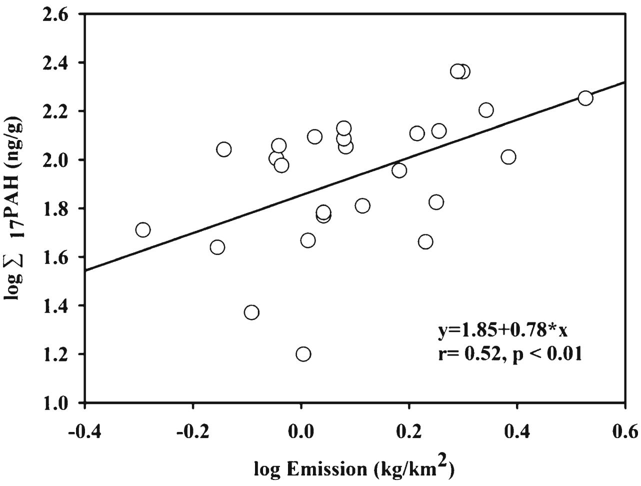

Fig. 2 The correlation between the PAH concentrations in the soils and the emission density of PAHs

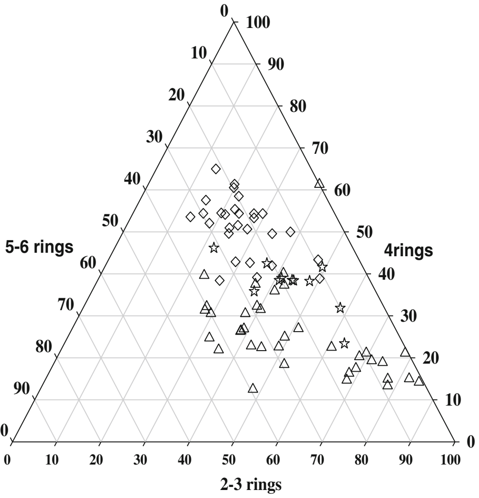

Fig. 3 Triangular diagram of percentage concentration for the 17 PAHs in soil samples from Guangzhou City (*open diamond*) (Chen et al. 2005), Dongguan city (*open star*) (Ma et al. 2008), and this study (*open triangle*)

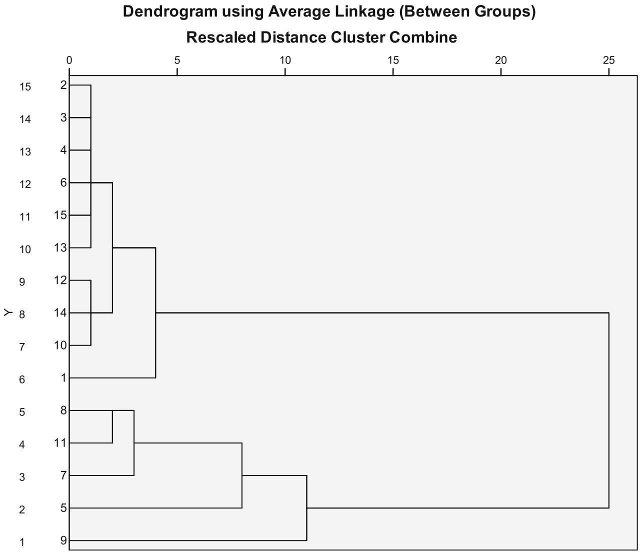

Fig. 4 Hierarchical dendrogram for 16 individual PAHs in soils from Dongjiang River Basin using average linkage between groups and Pearson correlation as measuring interval

groups. The first major group can be further subdivided into two subgroups. The first subgroup consists of Flo, Phe, Pyr, B(b+k)Fla, Chry, BaA, BaP, InP, and BgP, which are low in rural soils but high in urban soils, in particular for Pyr and Chry. The second subgroup consists of Nap, which is derived from anthropogenic and pedogenic origins (Azuma et al. 1996; Atanassova et al. 2004). It was reported that Nap is one of the major PAHs produced in vegetation fire (Freeman and Cattell 1990). At the same time, as Nap possesses high vapor pressure, mainly existing in gaseous phase, and can be transported for a long distance (long-range transportation, LRT), its properties may explain why Nap concentrations in both rural and urban soils in this investigation are within the same range. The second major group is Ant as its concentration levels vary considerably in both urban areas and rural areas. This phenomenon may be related to the fact that Ant undergoes severe photochemical degradation in the environmental mediums.

3.3 Source comparison of PAHs using PAH isomer ratios

Identifying the origin and potential source of PAHs in the soil is conducive to assess the environmental risk caused by them. The combustion and petroleum sources of PAHs in the soil can be distinguished using the concentration ratios of diversity PAHs. For a molecular mass of 228, benz[*a*]anthracene to benz[*a*]anthracene plus chrysene (BaA/228) ratio lower than 0.20 implies petroleum source, whereas a ratio from 0.20 to 0.35 is for either petroleum or combustion, and any ratio higher than 0.35 for combustion origin (Yunker et al. 2002). According to Yunker et al. (2002), Flu/(Flu+Pyr) ratio lower than 0.4 suggests petroleum origin, while a ratio between 0.4 and 0.5 liquid indicates fossil fuel combustion origin, such as vehicle and crude oil combustion, and a ratio higher than 0.5 indicates grass, wood, or coal combustion. As shown in Fig. 5, BaA/(BaA+Chry) ratios in all of the soil samples in Guangzhou are lower than 0.35 (Chen et al. 2005), some of which are lower than 0.20. Hence, it reveals that combustion or petroleum is the major source for PAH inputs in Guangzhou, which is consistent with another investigation conducted by Zakaria et al. (2002) on Malaysia urban river sediments. In their study, used crankcase oil is indicated to be one of the major inputs into the sedimentary PAHs. For some soil samples from Dongguan, BaA/(BaA+Chry) ratios are between 0.20 and 0.35, and the others are higher than 0.35 (see Fig. 5), which reveals that combustion in addition to petroleum are the major PAH sources. While BaA/(BaA+Chry) ratios for most of the rural soil samples are > 0.35, only a few rural soil sample from sites close to Dongguan are between 0.20 and 0.35, indicating that combustion is the major PAH source for the rural area in this study.

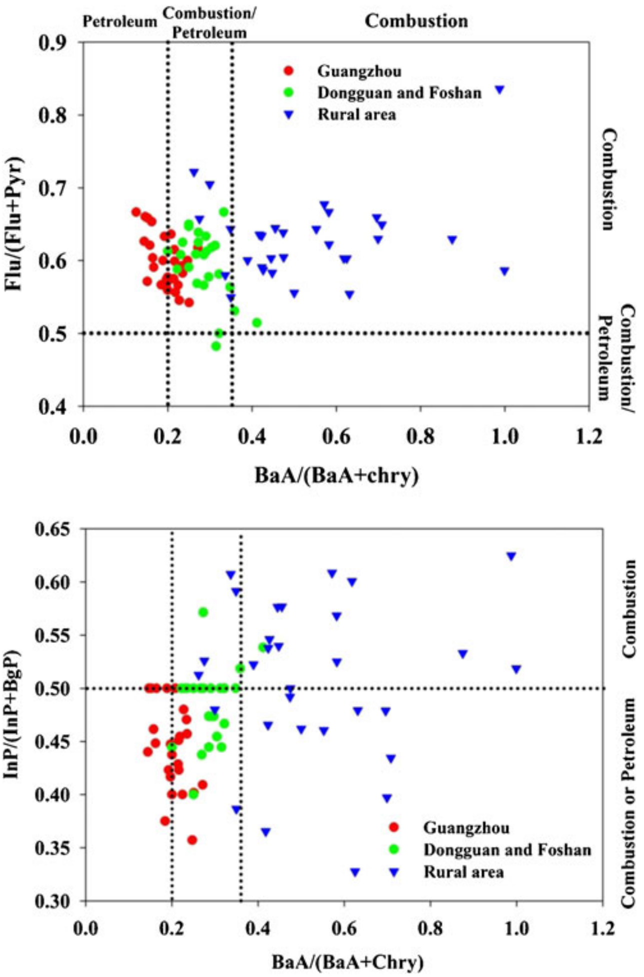

Fig. 5 Plots of PAH isomer ratios for the identification of PAH sources: BaA/(BaA+Chry) vs. InP(InP+BgP)

Moreover, Flu/(Flu+Pyr) ratios in almost all of the soils in Guangzhou, Dongguan, and this study are higher than 0.5. Therefore, Flu/(Flu+Pyr) ratios are not that suitable for the indication of PAH sources in the soils from these areas. InP/(InP+BgP) ratios lower than 0.20 indicate PAHs in the soils which probably originated from petroleum, while the ratios between 0.20 and 0.50 indicate liquid fossil fuel (vehicle and crude oil) combustion, and the ratios higher than 0.50 suggest grass, wood, and coal combustion (Yunker et al. 2002). InP/(InP+BgP) ratios in the soils from Guangzhou and from major sites in Dongguan are lower than 0.5, indicating a petroleum input in addition to liquid fossil fuel (vehicle and crude oil) combustion. InP/(InP+BgP) ratios>0.5 only occur in three sites, located in the outskirts of Dongguan.

According to Figs. 3 and 5, four-ring PAHs are dominant in the soils from Guangzhou City and Dongguan City, while two- to three-ring PAHs are dominant in the rural soils in this study. From the above results, it is concluded that PAHs in the rural area are mainly derived from grass, wood, or coal combustion, and LRT from the urban area such as Guangzhou and

Dongguan. In comparison, PAHs in the urban soils from Guangzhou and Dongguan are mainly derived from petroleum input and liquid fossil fuel (vehicle and crude) combustion.

3.4 Source apportionment of PAHs in rural soils of Dongjiang River Basin using PMF model

PMF model was used to identify and quantitatively analyze the contribution of the diverse PAH sources in rural soils of DRB. In the PMF analysis, the data of PAH concentrations and observation uncertainty were inputted and run in robust mode. The random seed mode with 100 random starting points was chosen and three to seven factors were investigated. In a further discussion, five factors were found to be best by using PCA. Coal combustion, biomass combustion, oil, creosote, and vehicle (Wang et al. 2013) were adopted as the candidate sources. Among the 17 PAH studied in this study, Phe, Ant, Flu, Pyr, B(k)F, BaA, and Chry were identified as emissions from coal combustion. In addition, Acy is often used to indicate biomass combustion; Nap also could be designated for incomplete combustion-related sources. The predominant components of PAHs in commercial creosotes are identified to be Ace, Flo, Phe, Ant, Flu, and Pyr. InP, B(b)F, BkF, and Chr are suggested to be tunnel traffic markers.

Source profiles of PAH obtained from PMF model have been listed in Fig. 6. In addition, the loading percentages of individual PAH compounds in these five factors from the PMF model output have been listed in Fig. S3 ("Electronic supplementary material"). From this figure, we can find that Flu, Pyr, Chr, B(b)F, and B(k)F are dominated and BaA is also moderately dominated in the source 1 profile. Therefore, source 1 can be identified as coal combustion. Source 2 is highly weighted by Acy and moderately weighted by Nap, and thus it can be identified as biomass combustion. In addition, in source 3, Nap and Ace are dominated and Acy is moderately dominated. Therefore, source 3 reflected oil contribution (unburned petroleum). In the source 4 profile, BaP, InP, and BgP are mostly dominated, indicating that it reflected motor vehicle emissions. As source 5 is highly weighted by DbA and is moderately weighted by BaP, Per, BaA, and BbF, it can be identified as commercial creosotes. The mass apportionment method was described (Wang et al. 2013). In brief, mass apportionment was carried out by multiple linear regressions (MLR) of the elements in the G matrix (source contribution) against the corresponding Σ17PAHs for each soil sample. A minimum 95 % confidence level was stipulated for the MLR. The regression was performed by SPSS 15.0 using a forward stepwise method. The average contributions of each source to Σ_{17}PAHs in rural soils of DRB have been listed in Fig. 7. The mean contributions of five factors are 24 % for coal combustion, 24 % for biomass contribution, 17 % for oil (unburned petroleum), 18 % for vehicle, and 17 % for commercial creosotes. Therefore, we can figure out that the major sources of PAHs in the rural soils of DRB are coal/biomass combustion, accounting for 48 % of total PAH sources. As mentioned in "Section 3.3", combustion is indicated to be the major PAH source for the rural soils of DRB using PAH isomer ratios. Therefore, there is a good consistency between the results obtained from the PAH isomer ratios cited earlier and the results from the PMF model.

3.5 Health risk assessment of PAHs in soils and the influences of TOC

Benzo[*a*]pyrene is the only PAH congener for which toxicological data are sufficient for derivation of a carcinogenic potency factor among all of the known potentially carcinogenic PAHs (Peters et al. 1999). The toxic equivalency factors (TEFs) are available to quantify the carcinogenicity of other PAHs relative to B[*a*]P. According to US EPA, the relative toxic potencies for B[*a*]A, B[*a*]P, B[b]F, B[k]F, InP, DB[ah]A, and Chry are 0.1, 1, 0.1, 0.01, 0.1, 1, and 0.001, respectively. These values are used to estimate benzo[*a*]pyrene equivalent doses (B[*a*]P_{eq} dose) by using the following equation:

$$\text{Total B[a]P}_{\text{eq}}\ \text{dose} = \sum \text{dose}_i \times \text{TEF}_i \tag{5}$$

where dose_i is the concentration of special PAH, and TEF_i is the corresponding toxic equivalency factor.

Total B[*a*]P_{eq} dose estimated for the soil samples ranges from 0.10 to 21.52 μg/kg dry weight, with an average of 8.36 μg/kg dry weight. Among different PAHs, the contribution to the B[*a*]P_{eq} dose decreases in the order: BaP (58.49 %)>B(b)F (14.71 %)>DaA (8.97 %)>InP (8.36 %)>BaA (7.74 %)>B(k)F (0.99 %)>Chry (7.60 %).

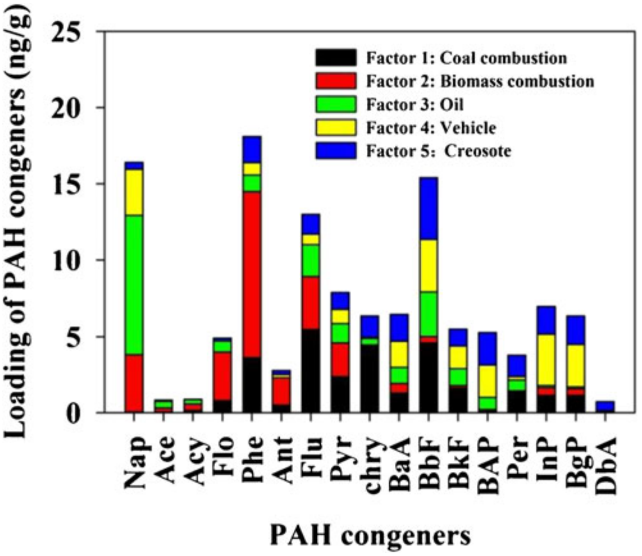

Fig. 6 Source profiles of PAH obtained from PMF model

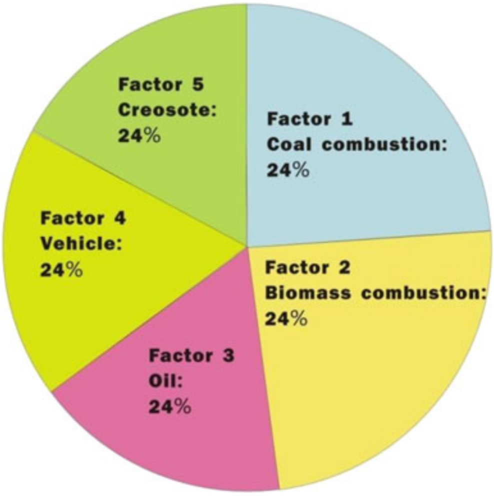

Fig. 7 Source average mass contribution (%) of each factor to bulk PAH burden in the rural soils of DRB

Figure 8 presents a regression analysis between total B[*a*]P$_{eq}$ dose and TOC concentrations in the soil samples. It is obvious in Fig. 8 that total B[*a*]P$_{eq}$ dose is positively related to the TOC concentrations (r=0.84, p<0.0001). Besides enhancing the accumulation of hydrophobic organic pollutants in soils, SOM is also an important factor in governing the toxic effects of PAHs in soils. Hence, the health risk for human exposure to PAHs in the soils increases with increasing SOM contents.

An ILCR was used to estimate the integrated lifetime risks of exposing to soil-borne PAHs through direct ingestion, dermal contacts, and inhalation collectively (Peng et al. 2011). In addition, the normal and extreme exposures can be used to evaluate the durations of PAH exposure, which are 7–24 years for adults and 2–6 years for children, respectively. Virtual safety is indicated when ILCR≤10^{-4}, while a potentially high risk is indicated when ILCR≥10^{-4} (Liao and Chiang 2006). The ILCR is suggested to be described as (Peng et al. 2011):

$$\sum \mathrm{ILCRs(normal)} = \sum \mathrm{PAHs} \times \left(6.94 \times 10^{-10}\right) - 3.42 \times 10^{-08} \tag{6}$$

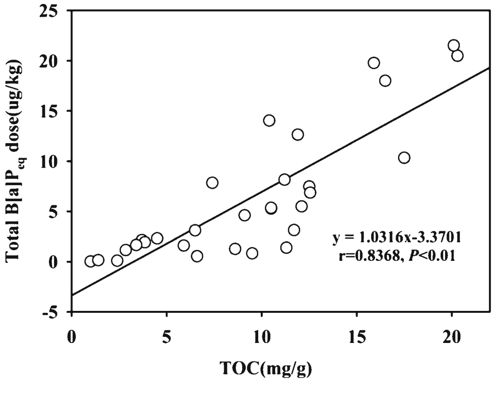

Fig. 8 Correlation between TOC concentrations and total B[*a*]P$_{eq}$ dose

$$\sum \mathrm{ILCRs(extreme)} = \sum \mathrm{PAHs} \times \left(9.75 \times 10^{-09}\right) - 4.81 \times 10^{-07} \tag{7}$$

With a given ILCR level, the corresponding PAH concentrations can be calculated with Eqs. (5) and (6). The estimated ∑PAHs for ILCR of 10^{-6} are 489 and 152 μg/kg for normal and extreme exposures, respectively, but those for ILCR of 10^{-4} are 144,059 and 10,304 μg/kg. There are nine out of 30 rural soil samples with PAH concentrations above the virtually safe concentration for ILCR (152 μg/kg). These results indicate that although PAHs in the rural soils of DRB are relatively low because of the low soil organic matter concentration, they still can produce some threats to the health of human, especially those of children.

4 Conclusions

The concentrations of total PAHs in the surface rural soils range from 23.5 to 231 μg/kg, with higher concentrations in urban soils than those in rural soils. SOM played a key role in the accumulation levels of PAHs. A sevenfold increase in SOM led to a 14-fold increase in total PAH concentrations in the surface soils. The four dominant PAHs were Nap, Flu, and Phe in the rural soils, while Phe, Flu, Chry, and B(b+k)F were dominant in the urban soils. Petroleum and liquid fossil fuel (vehicle and crude oil) combustion is the major source for PAHs in the soils of Guangzhou and Dongguan, while grass, wood, or coal combustion and LRT from the urban area such as Guangzhou and Dongguan are the major sources for PAHs in rural soils. Coal, biomass, oil, commercial creosotes, and vehicle contributed 24, 24, 17, 17, and 18 % of the total soil PAH burden, respectively. In addition, seven carcinogenic PAHs made up 40 % of 17 PAHs. Thus, we can figure out that although the concentrations of 17 PAHs in the rural soil of DRB are relatively lower than those in the urban soil, its carcinogenic potency is not that low. In addition, there are nine out of 26 rural soil samples with PAH concentrations above the virtually safe concentration for ILCR. It indicates that these urban soil PAHs may pose a potential threat to potable groundwater water quality due to leaching of carcinogenic PAH mixtures from the soil. Therefore, it should be pointed out that there is certain risk for human to directly contact these soils. Moreover, the health risk for human exposure to PAHs in the soils also increases with the increasing SOM concentrations.

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