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Association of soil polycyclic aromatic hydrocarbon levels and anthropogenic impacts in a rapidly urbanizing region: Spatial distribution, soil–air exchange and ecological risk

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HIGHLIGHTS

- Land use types are less relevant in defining the spatial distribution of soil PAHs.
- Anthropogenic impacts play a major role in the spatial pattern of soil PAHs.
- Soil has become a secondary source of individual PAHs to the atmosphere.
- Contaminated soil is concentrated in populated areas, subjecting more residents to higher risk.

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ABSTRACT

The occurrence of polycyclic aromatic hydrocarbons (PAHs) in soil of the Pearl River Delta (PRD) and surrounding areas was examined on a basis of six land-use types and four geographic regions, from which the impacts of anthropogenic events on the terrestrial environment were evaluated. No significant difference in the concentrations of Σ_{28}PAH and Σ_{15}PAH (sums of 28 and 15 PAHs, respectively) was found among the land-use types of industry, landfill and residency. On the other hand, higher soil PAH concentrations occurred in the central PRD characterized by dense population and high urbanization level, compared to other geographic regions. Source diagnostics implicated the combustions of coal and refined petroleum as the major input sources of anthropogenic PAHs. Furthermore, low molecular weight PAHs tended to volatilize from soil to air while the opposite was prevailing for high molecular weight PAHs. The mean annual diffusive flux of Σ_{15}PAH (852 μg m^{-2} yr^{-1}) from the soil to the atmosphere in the central PRD was greater than those in the PRD's periphery (195 μg m^{-2} yr^{-1}), West region (322 μg m^{-2} yr^{-1}) and East region (84.9 μg m^{-2} yr^{-1}), suggesting that the central PRD may have become a secondary source of PAHs to the surrounding areas. Finally, ecological risk assessment based on the classification from Maliszewska-Kordybach showed that 3.5% of soil within the central PRD was heavily contaminated by PAHs and 5.2 million residents may be subjected to high health risk.

1. Introduction

Urbanization, an inevitable consequence of rapid economic development, is a multi-dimensional process with complicated outcomes (Zhu et al., 2011), such as increased domestic waste discharge (Wang et al., 2007), and water and air pollution (Cheung et al., 2003; Wang et al., 2007, 2011a; Pan et al., 2012; Zhang et al., 2012). As an important matrix in urban terrestrial environment, soil has been a major sink of contaminates (Jones, 1994; Hippelein and Mclachlan, 1998; Manzetti, 2013) and well interacts with other environmental compartments. On the other hand, contaminated soil may also be a secondary emission source for some contaminates in the atmosphere (Jones, 1994; Hippelein and Mclachlan, 1998; Li et al., 2010; Wang et al., 2011b; Zhang et al., 2011b). Thus, investigations into the occurrence and soil–air exchange of contaminates in soil can help to understand the fate of contaminates and impacts of anthropogenic activities on the environment under the backdrop of rapid urbanization.

Polycyclic aromatic hydrocarbons (PAHs) are environmentally significant due to their widespread occurrence and potentially toxic to wildlife and humans (Bjøseth et al., 1978; Lioy and Daisey, 1986; Petry et al., 1996; Cousins and Jones, 1998; Weinstein et al., 2010). They mainly originate from anthropogenic activities, such as incomplete combustion of organic materials (e.g., wood, coal oil, gas, tobacco and straw), as well as from automobile exhausts and industrial processes (Yunker et al., 2002a, 2002b). As a result, PAHs have been used to assess the magnitude of anthropogenic impacts on the environment (Jones et al., 1989; Page et al., 1999; Liu et al., 2012b, 2012c; Yang et al., 2012).

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The Pearl River Delta (PRD), located in South China (Fig. S1 of the Supplementary data; "S" indicates lists of PAHs, tables, and figures in the Supplementary data afterwards), has been one of the most economically prosperous regions in China. Aside from the extensive accumulation of contaminants in the environment of the PRD throughout the years due to intensive agricultural and industrial activities (Cai et al., 2007; Wang et al., 2007; Pan et al., 2012), increasing urbanization since the early 1980s has further worsened the situation. The large urban centers within the PRD, such as Guangzhou, Foshan, Jiangmen, Zhongshan, Zhuhai, Dongguan, Shenzhen and Huizhou (Fig. S1a) with urbanization levels of more than 60% in 2010 (Statistical Bureau of Guangdong Province, 2011), have constituted an economically fast growing urban agglomeration. In contrast, administrative districts surrounding the PRD, such as Shanwei, Heyuan, Shaoguan, Qingyuan, Yangjiang, Zhaoqing and Yunfu, have remained less economically prosperous and lower urbanized than those within the PRD (Fig. S1a). Therefore, the PRD, faced with the urgent task of balancing between sustainable socioeconomic development and environmental protection, is an ideal site for assessing anthropogenically derived contamination (Cai et al., 2007; Yang et al., 2010; Wang et al., 2011a). Previous studies have examined the occurrence of PAHs in soil of the PRD (Yu et al., 2007; Ma et al., 2008; Wang et al., 2012), but existing data are insufficient for an integrated assessment of urbanization-induced anthropogenic impacts on the environment.

To achieve the above-mentioned objectives, soil samples were collected from a large number of locations grouped into six land-use types or four geographic regions (Fig. S1) and analyzed for PAHs. Possible impacts of anthropogenic activities on the environment were examined through detailed analyses of the occurrence and spatial distribution of PAHs. Soil–air exchange was also examined to identify the main soil–air transfer modes of PAHs. Finally, soil guidelines (Maliszewska-Kordybach, 1996) were used to assess the magnitude of contamination by PAHs on a regional scale.

2. Materials and methods

2.1. Sampling design and collection

The sampling campaign was conducted from December 2009 to March 2010 within a region of approximately 72 000 km^2 with six land-use types, i.e., industry, agriculture, drinking water source, landfill, residency, and forestry (Fig. S1b). Furthermore, to elucidate the spatial patterns of soil contamination by PAHs and its correlation with socioeconomic development, the administrative districts within the sampling region are divided into four groups based on the geographic locality and urbanization level (Statistical Bureau of Guangdong Province, 2011), i.e., the collection of Shenzhen, Dongguan, Zhuhai, Zhongshan, Guangzhou and Foshan is defined as the central PRD, and the combinations of three eastern districts (Shaoguan, Heyuan and Shanwei) and two western districts (Yangjiang and Yunfu) are defined as the East and West regions, respectively. Moreover, the remaining districts, i.e., Zhaoqing, Qingyuan, Jiangmen and Huizhou are combined and defined as the PRD's periphery (Fig. S1a). The urbanization levels of the districts within four regions (the central PRD, the PRD's periphery, the East and West regions) were in the ranges of 84%–100%, 42%–62%, 40%–54% and 37%–47%, respectively (Statistical Bureau of Guangdong Province, 2011). One hundred and sixty soil samples were collected from the centers of hexagonal grid (12.9 km in grid length) based equilateral triangles (United States Environmental Protection Agency, 1986, 2002). Additional 69 soil samples were randomly collected from selected industrial, landfill and residential areas to increase the sampling density. At each sampling site, more than three sub-samples were taken within an approximate area of 100 m^2 and composited into one sample in a 250 or 500 mL brown glass bottle. All samples were transported to the laboratory where they were stored in a freezer at −20 °C until extraction.

2.2. Sample extraction and instrument analysis

The detailed procedures for sample extraction and purification of PAHs were described previously (Liu et al., 2012c). Briefly, each freeze-dried sample (approximately 20 g) was added with surrogate standards (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12} and benzo[*g*,*h*,*i*]perylene-d_{12}) and Soxhlet-extracted with 170 mL of hexane:acetone:dichloromethane mixed solvent (2:1:2 in volume) for 48 h at 57 °C. The extract was concentrated, solvent-exchanged, and purified/fractionated by a glass chromatography column filled with 6 cm alumina and 12 cm silica gel. The fraction containing PAHs was eluted with 80 mL of hexane: dichloromethane mixed solvent (7:3 in volume), concentrated and solvent-exchanged to hexane, then transferred to a GC vial after evaporating to 0.5 mL. Known amounts of the internal standards (2-fluoro-1,1-biphenyl, *p*-terphenyl-d_{14}, and dibenzo[*a*,*h*]anthracene-d_{14}) were added to the extract prior to quantitative analysis. Twenty-nine PAHs (List S1; acronyms for individual PAHs are defined in Table S1) were quantified with a Shimadzu GC/MS-QP2010 Plus equipped with an AOC-20i auto injector (Shimadzu, Kyoto, Japan). Chromatographic separation of individual PAH components was achieved with a 60 m × 0.25 mm-i.d. (0.25 μm film thickness) DB-5MS column. All the samples were analyzed in the full-scan mode, with the detailed procedures described previously by Liu et al. (2012c).

2.3. Quality assurance and quality control (QA/QC)

For every 18 field samples, a set of quality control samples including a procedural blank, spiked blank (standards spiked into solvent), matrix blank, matrix spiked sample, and three sample replicates were also processed. Soil samples used as matrix blank and matrix spiked samples were randomly selected from those extracted. The recoveries (mean ± standard deviation) of all target analytes were from 55 ± 8% to 92 ± 23% in spiked blank and matrix spiked samples. Recoveries of the surrogate standards, i.e.,naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}, and benzo[*g*,*h*,*i*]perylene-d_{12}, for quality control samples were 50 ± 9%, 61 ± 10%, 79 ± 12%, 101 ± 12%, 87 ± 18%, and 94 ± 12%, while those recoveries for field samples were 45 ± 10%, 68 ± 15%, 90 ± 11% for, 104 ± 12%, 96 ± 15%, and 94 ± 10%, respectively. The lowest calibration concentrations were 100 ng/mL for DPA, IcdP, DahA, and BghiP, and 50 ng/mL for other target PAH compounds, which divided by the average sample weight (18.6 g), were used as their reporting limits (RL), i.e. 2.69 ng/g for DPA, IcdP, DahA, BghiP and 1.34 ng/g for other target PAH compounds.

2.4. Data analysis

Concentrations of PAHs were normalized to dry sample weight and blank corrected, but not corrected by the surrogate standard recovery data. Naphthalene was found to be unusually high in several blank and matrix blank samples, but not in field samples; therefore it was excluded from the target analyte list. Σ_{28}PAH is defined as the sum of remaining 28 PAHs (List S2) and Σ_{15}PAH (List S3) stands for the sum of the 16 priority PAH compounds designated by the United States Environmental Protection Agency (List S4) minus naphthalene. Zero was used for any measured concentration below the RL in concentration calculation and half of the RL was used in compositional analysis. Principal component analysis was used in source diagnostics in the present study.

Flux of soil–air diffusive exchange for an analyte (D_{flux}; μg m^{-2} yr^{-1}) can be calculated as:

$$D_{flux} = D_{SA}(f_S - f_A) \quad (1)$$

where f_S (Pa) and f_A (Pa) are the fugacity values of an analyte in soil and air, respectively; and D_{SA} (mol Pa^{-1} m^{-2} h^{-1}) is the diffusive coefficient

of the analyte across the soil–air interface. Available atmospheric gas-phase concentrations of individual PAHs in nine districts (Guangzhou, Jiangmen, Foshan, Shenzhen, Zhuhai, Zhongshan, Zhaoqing, Huizhou and Dongguan) for calculating f_A were acquired from Wang (2007) and are listed in Table S2. The Monte Carlo simulation (Gardner et al., 1981) was used to estimate the uncertainty range of each parameter in multi-parameter calculation. Detailed procedures to estimate all parameters are presented in the Supplementary data.

In addition, the Ordinary Kriging interpolation method (Isaaks and Srivastava, 1990) was employed to analyze the spatial distributions of Σ_{28}PAH and Σ_{15}PAH concentrations using ArcGIS Version 9.3 (ESRI, Redlands, CA, USA). A one-way analysis of variance and nonparametric Kruskal–Wallis H tests with statistical significance defined at $p < 0.05$ were used to evaluate the differences in PAH concentrations and compositions between/among six land-use types or four geographical regions. Statistical analysis was performed with SPSS Version 13.0 (SPSS, Chicago, IL, USA).

3. Results and discussion

3.1. Occurrence and spatial distribution of soil PAHs

Concentrations of Σ_{28}PAH and Σ_{15}PAH varied in the ranges of 8.2–21000 and 5.1–12000 ng/g, with the arithmetic mean (median) values at 399 (145) and 268 (97) ng/g, respectively (Table 1). Extremely high concentrations of Σ_{28}PAH and Σ_{15}PAH were observed in three samples from a landfill site in Zhongshan (5500 and 4400 ng/g), a residential area in Guangzhou (8800 and 7500 ng/g), and an industrial district in Dongguan (21000 and 12000 ng/g), which were taken near traffic-congested road, sewage-polluted river and petroleum company and possibly impacted by point sources. Excluding these three samples, the concentrations of Σ_{28}PAH and Σ_{15}PAH were in the ranges of 8.2–3300 ng/g (mean: 248 ng/g; median: 144 ng/g) and 5.1–2380 ng/g (mean: 166 ng/g; median: 96 ng/g) (Table 1).

A comparison of the data in the present study with those previously acquired in the PRD indicated that soil PAH concentrations increased moderately from 1999 to 2010 (Table S3). In addition, the soil PAH concentrations in the present study were in the midpoint of the global range (Table S3). It is interesting to note that the Σ_{15}PAH concentrations in the present study were lower than those in Urumqi (range: 263–14100 ng/g; mean: 4430 ng/g) of Northwest China (Chen et al., 2013), but energy consumption (29 million tons/yr), a main source of PAHs, in Urumqi was much lower than that (220 million tons/yr) in the PRD in 2010 (Statistical Bureau of Guangdong Province, 2011; Statistical Bureau of Urumqi, 2011). The disparity in PAH levels and energy consumptions between the two regions may be attributed to a higher forest coverage (57%) in the PRD (Statistical Bureau of Guangdong Province, 2011) than that (4.9%) in Urumqi (Statistical Bureau of Urumqi, 2011). As plant leaves were believed to have the ability of capturing particulates in the air (Terzaghi et al., 2013), higher forest coverage would lower the deposition of particulate-bound PAHs from the atmosphere to soil. Moreover, Manzetti (2013) pointed out that PAHs tend to deposit on vegetation and then in soil. Vegetation plays an important role in the transport of PAHs during its lifecycle and may transfer adsorbed PAHs to soil in Autumn and Winter. However, heavy rainfalls during the wet weather season (e.g., 1870 mm/yr in 2010) may have pushed PAHs in plants towards aquatic environments and into sediments in the PRD (Statistical Bureau of Guangdong Province, 2011), which would further reduce the levels of soil PAHs in the PRD.

Spatially, there were no significant differences ($p > 0.05$) for Σ_{28}PAH concentrations between industry and drinking water source, industry and landfill, industry and residency, drinking water source and residency, and landfill and residency, while other land-use types had significances differences ($p < 0.05$) between each other (Table S4). Similar results were observed for $\sum_{15}$PAH concentrations except that drinking water source was significantly different from forestry. Overall, there was no apparent disparity of PAH concentrations among the land-use types of industry, landfill and residency.

Table 1
Concentrations (ng/g dry weight) of soil PAHs in different districts and geographic regions from the Pearl River Delta and surrounding areas, South China (Fig. S1).

	No.[a]	$\sum_{28}$PAH[b]			$\sum_{15}$PAH[c]		
		Range	Mean	Median	Range	Mean	Median
Dongguan	20	50.6–21000	1530 ± 4630	313	25.4–12000	930 ± 2660	210
Guangzhou	26	44.5–8790	714 ± 1670	207	27.4–7510	548 ± 1450	137
Zhongshan	10	33.9–5460	814 ± 1650	280	24.7–4410	590 ± 1350	136
Zhuhai	7	89.3–2100	484 ± 724	151	54.9–1770	331 ± 634	96.6
Foshan	11	16.1–1690	304 ± 480	177	9.15–1370	210 ± 394	66.3
Shenzhen	9	37.1–411	162 ± 121	152	22.7–224	110 ± 74.3	103
Zhaoqing	29	15.6–1600	294 ± 377	164	8.36–1390	202 ± 303	105
Jiangmen	25	29.1–411	179 ± 106	169	14.4–258	116 ± 65.9	120
Qingyuan	17	22.0–802	197 ± 180	150	14.8–557	126 ± 122	109
Huizhou	37	16.5–480	120 ± 109	90.7	12.0–404	75.3 ± 73.2	54.6
Yangjiang	4	21.2–500	187 ± 224	113	12.7–267	101 ± 119	62.7
Yunfu	8	28.4–376	151 ± 108	134	12.7–240	96.9 ± 68.1	96.7
Shanwei	4	56.2–174	121 ± 58.3	126	33.8–144	94.6 ± 56.1	100
Shaoguan	3	39.8–177	112 ± 68.9	120	18.4–120	80.8 ± 54.7	104
Heyuan	19	8.2–424	115 ± 132	50.7	5.1–329	77.2 ± 92.9	41
The PRD[d]	83	16.1–21000	790 ± 2540	192	9.15–12000	535 ± 1610	121
The PRD's periphery[e]	108	15.6–1600	192 ± 230	134	8.36–1390	127 ± 178	92.1
The West region[f]	12	21.2–500	163 ± 146	134	12.7–267	98.4 ± 82.7	96.6
The East region[g]	26	8.2–424	115 ± 116	74.7	5.1–329	80.3 ± 82.9	56.9
Total[h]	229	8.2–21000	399 ± 1560	145	5.1–12000	268 ± 997	97
Total[i]	226	8.2–3300	248 ± 362	144	5.1–2380	166 ± 273	96

[a] Number of samples.
[b] Sum of 28 PAH compounds (List S2).
[c] Sum of 15 PAH compounds (List S3).
[d] Including Dongguan, Guangzhou, Zhongshan, Zhuhai, Foshan, and Shenzhen (Fig. S1a).
[e] Including Zhaoqing, Jiangmen, Qingyuan, and Huizhou (Fig. S1a).
[f] Including Yangjiang and Yunfu (Fig. S1a).
[g] Including Shanwei, Shaoguan, and Heyuan (Fig. S1a).
[h] All soil samples.
[i] Three extremely high $\sum_{28}$PAH and $\sum_{15}$PAH concentrations were excluded, i.e., a landfill area in Zhongshan (5500 and 4400 ng/g), an industrial site in Dongguan (21000 and 12000 ng/g) and a residential district in Guangzhou (8800 and 7500 ng/g), respectively.

On the other hand, higher concentrations of both $\sum_{28}$PAH and $\sum_{15}$PAH occurred in the central PRD as compared to other geographic regions (Table 1, Figs. 1 and S2), which was consistent with the fact that the central PRD is home to a larger number of petrochemical processing facilities and is more traffic-congested (Ma et al., 2008; Statistical Bureau of Guangdong Province, 2011). Compared to the insignificant difference of PAH concentrations among the land-use types of industry, landfill and residency, the spatial distribution of soil PAHs in the geographic regions was characterized by higher concentrations within the central PRD. The result suggested that land-use type may have become less relevant in defining the spatial distribution of soil PAHs, because the land-use types in the present study are quite overlapped and the boundaries between different land-use types are becoming murky as a result of accelerating urbanization in the region.

3.2. Source diagnostics

Three methods, i.e., proportion analysis, principal component analysis and isomeric ratio, were used to diagnose the potential sources of soil PAHs in the PRD and surrounding areas. First, the proportions of 2-, 3-, 4-, and 5-ring PAHs constituted 18%, 32%, 23%, and 22% of total PAHs, while 6- and 7-ring PAHs only contributed 3.6% and 1.5% to the total (Fig. S3). The relative abundances of 15 unalkylated PAH compounds exhibited no significant differences ($p > 0.05$) among different land-use types or four geographical regions. They were similar to those in typical emission sources dominated by 3- and 4-ring PAHs (Fig. S4) (Xu et al., 2006), suggesting that soil PAHs in the present study were mainly derived from residues of combustion of coal, refined petroleum and biomass (Sporstol et al., 1983; Levendis and Atal, 1998; Larsen and Baker, 2003; Robinson et al., 2006).

Second, principal component analysis obtained four factors, accounting for 84% of the total variance in the PAH data (Table S5). The first factor, accounting for 53% of the total variance, predominantly contained 3-, 4-, 5-, 6- and 7-ring PAHs except for Flo, Ace, Per and DPA, and is related to PAHs from combustion of coal and refined petroleum products (Sporstol et al., 1983; Levendis and Atal, 1998; Larsen and Baker, 2003; Robinson et al., 2006). This is consistent with the fact that coal has remained the most important energy source in the PRD and surrounding areas, accounting for 48% of all energy consumption in 2010 (Statistical Bureau of Guangdong Province, 2011). The second factor, responsible for 18% of the total variance, was enriched with 1-mNa, 2-mNa, Bp, 2,6-dimNa and Flo from petroleum spill (Sporstol et al., 1983). In addition, the third and fourth factors, contributing to 9% and 4% of the total variance, were related to Ace, Per and DPA from diagenesis and diesel combustion (Table S5), respectively (Hites et al., 1980; Concord Scientific Corporation and Beak Consultants, 1992; Larsen and Baker, 2003). These results further implicated oil spill and combustions of coal and refined petroleum as the primary sources of PAHs, consistent with the conclusions reached by proportion analysis.

Finally, BaA / (BaA + Chr), a source diagnostic index, varied in the range of 0–0.9, further confirming that soil PAHs were originated mainly from petroleum residues, as well as combustion of coal, soot, diesel, petroleum and wood (Fig. 2) (Yunker et al., 2002a, 2002b). In addition, Flu/(Flu + Pyr) values were higher than 0.5, while IcdP/(IcdP + BghiP) varied between 0.2 and 0.5, suggesting that combustions of coal, grass, wood and liquid fossil fuel were the main sources of PAHs (Yunker et al., 2002a, 2002b). This inconsistent notion was also observed in Dongjiang sediment of the PRD (Zhang et al., 2011a) and continental shelf sediment off China (Liu et al., 2012a), and it indicates that simple PAHs diagnostic indices may not be able to derive definite conclusions about input sources. Nevertheless, all these methods collectively suggested that soil PAHs in the present study were mainly sourced from combustion of coal and refined petroleum.

3.3. Anthropogenic impacts on the distribution of soil PAHs

Higher concentrations of both $\sum_{28}$PAH and $\sum_{15}$PAH occurred in the central PRD with more urbanization level, whereas low concentrations were found in the other three regions (Figs. 1 and S2). The relationship between the population density and $\sum_{28}$PAH or $\sum_{15}$PAH concentrations on the basis of administrative districts was poor ($r^2 = 0.20$, $p > 0.05$ for both regressions; Fig. S5a), but the correlation was substantially improved ($r^2 = 0.84$, $p < 0.0001$ for both regressions) after the data from Shenzhen were excluded (Fig. S5b). Because of the rapid urban development of Shenzhen, no pristine surface soil was available for collection in central Shenzhen; hence, samples were

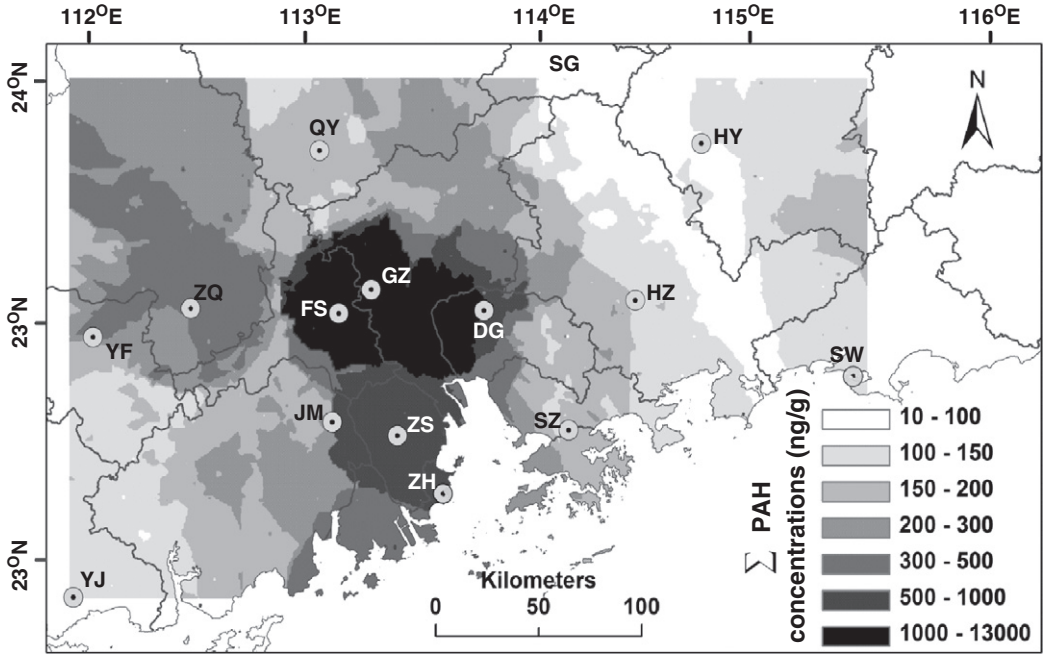

Fig. 1. Map of the spatial distributions of $\sum_{28}$PAH concentrations (ng/g dry weight) in soil of the Pearl River Delta and surrounding areas, South China (Fig. S1). $\sum_{28}$PAH is described in the Supplementary data (List S2). SG, QY, YF, ZQ, YJ, GZ, FS, JM, ZS, ZH, DG, SZ, HY, HZ and SW are acronyms of district names, i.e., Shaoguan, Qingyuan, Yunfu, Zhaoqing, Yangjiang, Guangzhou, Foshan, Jianmen, Zhongshan, Zhuhai, Dongguan, Shenzhen, Heyuan, Huizhou and Shanwei.

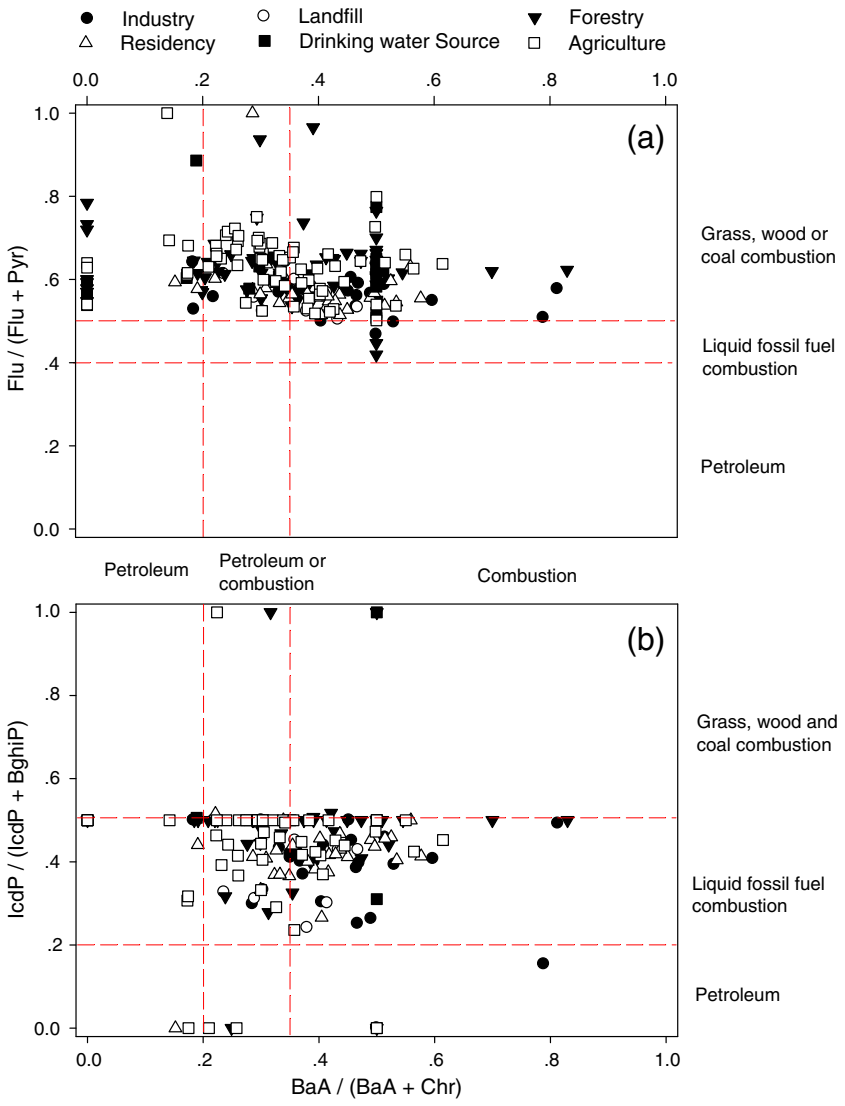

Fig. 2. Cross plots for PAH isomeric ratios in the Pearl River Delta and surrounding areas, South China (Fig. S1) in soil samples of different land-use types: (a) BaA / (BaA + Chr) versus Flu / (Flu + Pyr) and (b) BaA / (BaA + Chr) versus IcdP/(IcdP + BghiP). Flu, Pyr, BaA, Chr, IcdP and BghiP are acronyms of fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, indeno[1,2,3-*cd*]pyrene and benzo[*g*,*h*,*i*]perylene, respectively.

collected from the peripheral of Shenzhen with less urbanization and lower population density. Furthermore, new technologies used to improve the efficacy of energy consumption have been introduced by the city, resulting in reduced emissions of PAHs and consequently lightened soil contamination by PAHs in Shenzhen. With respect to the geographic regions, a good relationship was observed between the urbanization levels and $\sum_{28}$PAH or $\sum_{15}$PAH ($r^2 = 0.95$ or $r^2 = 0.96$; Fig. 3a). Correlation between soil PAH concentrations and gross domestic production was another indicator of anthropogenic impacts. A highly significant correlation between gross domestic production and $\sum_{28}$PAH or $\sum_{15}$PAH among the four geographic regions ($r^2 = 0.99$, $p < 0.05$ for both regressions; Fig. 3b) suggested a strong anthropogenic impact on the distribution of soil PAHs. This finding implicates soil PAHs in the central PRD as a source of urban health concern, e.g., hormonal interferences, as PAHs were shown to potentially correlate with infertility and the mutagenicities of PAHs increase exponentially with increasing structural resemblance to estrogens (Manzetti, 2012).

Moreover, there was a good linear correlation between energy consumption and $\sum_{28}$PAH or $\sum_{15}$PAH concentrations ($r^2 = 0.98$, $p < 0.05$ for both regressions) on the basis of geographic regions (Fig. 4a). Published data (Statistical Bureau of Guangdong Province, 2011) suggested that coal and petroleum have remained the dominant energy types used in Guangdong Province, with the amounts of coal and petroleum consumed increasing by 2.4 times from 2002 to 2010 (Fig. S6). By comparison, the mean concentration (304 ng/g) of soil $\sum_{15}$PAH in the central PRD and PRD's periphery in 2010 was twice as that in 2000 (158 ng/g) (Yu et al., 2007). Furthermore, coronene concentrations were correlated well with traffics intensities (Gordon and Bryan, 1973). The same pattern was also observed in the present study, i.e., a strong linear correlation between the coronene concentrations and number of civil vehicles based on geographic regions ($r^2 = 0.99$, $p < 0.05$; Fig. 4b).

Overall, these findings indicated that social and economic factors, e.g., urbanization level, gross domestic production, energy consumption, and number of motored vehicles, have driven the regional distribution of soil PAHs in the PRD and surrounding areas. In particular, coal and petroleum combustions were confirmed as the dominant emission source of soil PAHs. In fact, coal and petroleum accounted for 48% and 29% of total energy consumption in Guangdong Province in 2010 (Statistical Bureau of Guangdong Province, 2011). Xu et al. (2006) demonstrated that the emission factors of PAHs for domestic and coking coal combustions (111 and 102 mg/ton) were much greater than those

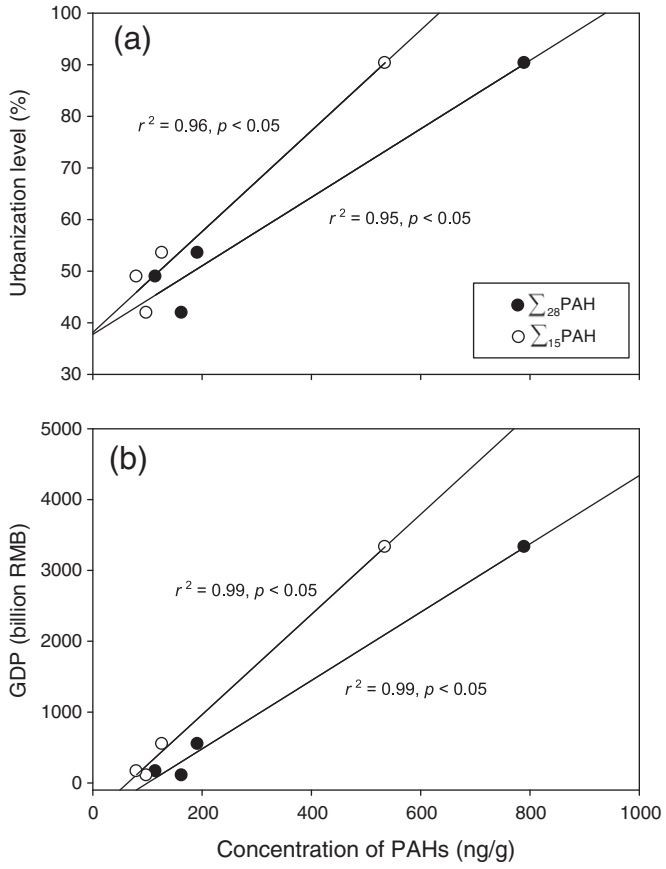

Fig. 3. Correlation between the mean concentrations of $\sum_{28}$PAH (ng/g dry weight; black dots) or $\sum_{15}$PAH (ng/g dry weight; white dots) and (a) proportion of urban population to total population in district (urbanization level; %) and (b) gross domestic production (GDP; in billion yuan (RMB)) (Statistical Bureau of Guangdong Province, 2011) among the central PRD, PRD's periphery, West region and East region (Fig. S1). $\sum_{28}$PAH and $\sum_{15}$PAH are described in Lists S2 and S3 of the Supplementary data.

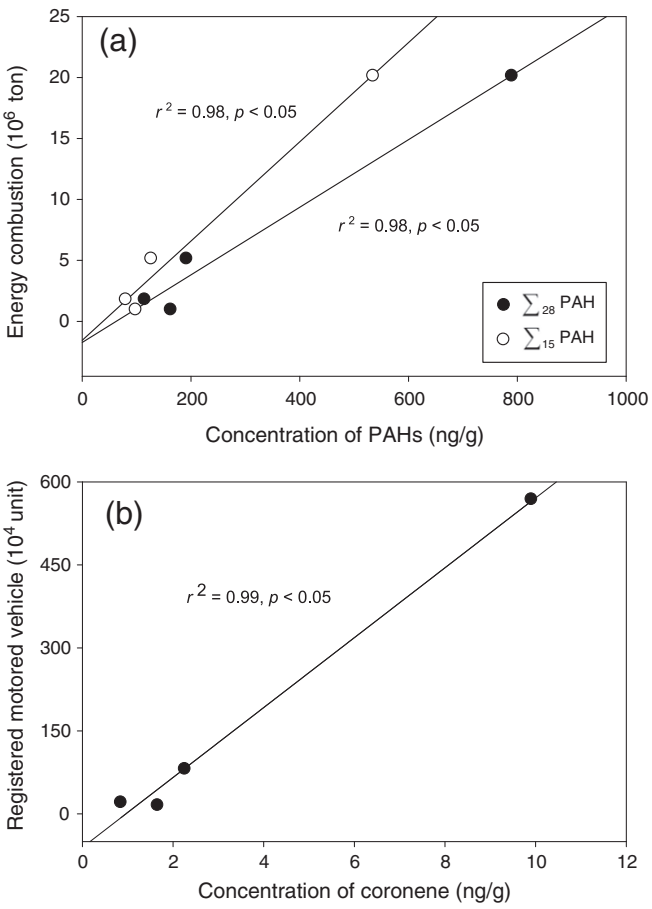

Fig. 4. (a) Correlation between energy combustion (10^6 tons standard coal) and mean concentrations of $\sum_{28}$PAH (ng/g dry weight; black dots) or $\sum_{15}$PAH (ng/g dry weight; white dots) and (b) correlations between the number of registered motored vehicles in 2010 (10^4 unit) and mean concentrations of coronene (ng/g dry weight) among the central PRD, PRD's periphery, West region, and East region (Fig. S1). $\sum_{28}$PAH and $\sum_{15}$PAH are described in Lists S2 and S3 of the Supplementary data.

(54 and 22 mg/ton) for petroleum used in the purposes of transportation and non-transportation (e.g., lubricant, pitch, and petroleum coke). In addition, combustion of industrial coal under high temperature and pressure releases only naphthalene, Phe, and Flu (Xu et al., 2006). Use of natural gas also generates almost no PAHs (Rom and Markowitz, 2007), which, however, has accounted for less than 5% of total energy consumption in Guangdong Province in 2010 (Statistical Bureau of Guangdong Province, 2011). Therefore, increasing use of natural gas and liquefied petroleum gas in automobiles, industrial production, domestic cooking and heating, among others, should be encouraged (Zhang et al., 2011a).

3.4. Regional implications for soil–air exchange of PAHs

Polycyclic aromatic hydrocarbons released from various sources can diffuse and deposit into soil through atmospheric transport, or contaminated soil may become a source of PAHs in the atmosphere. Our fugacity-based modeling shows that 3-ring PAHs (Acy, Ace, Flo, Phe and Ant) tend to evaporate from soil to air with escaping diffusive fluxes ranging from 0.79 to 713 μg m^{-2} yr^{-1}, whereas 5- and 6-ring PAHs (BaP, DahA, IcdP and BghiP) are likely to deposit from air to soil with deposition fluxes varying between 0.99 and 10.2 μg m^{-2} yr^{-1} (Table 2). These results were consistent with the findings of several previous studies, conducted in Beijing (Zhang et al., 2011b), Tibetan Plateau (Wang et al., 2014), Dalian (Wang et al., 2008) and Zhejiang Province (Zhong and Zhu, 2013) of China, and in Turkey (Bozlaker et al., 2008), that soil is a secondary source of low molecular weight PAHs, but a sink of high molecular weight PAHs. It is interesting to note that the mean escaping or deposition fluxes of Flu and Pyr ranged from 1.3 to 1.41 or from 0.17 to 1.7 μg m^{-2} yr^{-1} (Table 2), and the soil–air fugacity fractions of Flu and Pyr ranged from 0.27 to 0.67 (Table S6), approximately within the range of 0.30–0.70 used to suggest the soil–air equilibrium state of a target compound in a region (Harner et al., 2001; Meijer et al., 2003). As a result, soil–air equilibrium may have been reached for these two compounds.

In addition, Liu et al. (2011) estimated that the net deposition fluxes of Phe and Flu from air to soil were 5.1–285 μg m^{-2} yr^{-1} in ten cities and districts of Guangdong Province (Guangzhou, Dongguan, Zhuhai, Zhaoqing, Qingyuan, Panyu, Nanhai, Shunde, Zhongshan and Jiangmen) in 2001. By comparison, the present study obtained mean escaping fluxes of Phe from soil to the atmosphere at 13.9–51.5 μg m^{-2} yr^{-1} (Table 2). Clearly, soil has transformed from a sink to a source of Phe from 2001 to 2010, which may be ascribed to the ever changing energy consumption pattern in the region and accumulation of soil contamination. On one hand, the use of clean energy (natural gas and electricity) in Guangdong Province has been growing fast, at an annual rate of approximately 50% during the last decade. In 2010, clean energy types consisted 23% of total energy consumption. Previous studies found that atmospheric concentrations of $\sum_{12}$PAH ($\sum_{15}$PAH subtracting Ace, Acy and IcdP) in Guangzhou decreased from 300 ng/m^3 in 2001 to 71 ng/m^3 in 2010 (Li et al., 2009; Guo et al., 2014). On the other hand, coal and petroleum have remained the main fossil fuel in Guangdong Province, accounting for 77% of total energy consumption in 2010

Table 2
Soil–air diffusive exchange fluxes (μg m^{-2} yr^{-1}) of PAHs in different regions of the Pearl River Delta (PRD) and surrounding areas, South China (Fig. S1).

Target[a]	The central PRD[b]	The PRD's periphery[c]	The West region[d]	The East region[e]
Acy	713 ± 1120	152 ± 162	238 ± 230	76.8 ± 53.6
Ace	47.8 ± 124	19.5 ± 14.3	38.7 ± 42.0	10.2 ± 12.9
Flo	36.6 ± 64.8	23.2 ± 17.8	48.5 ± 56.5	14.7 ± 23.5
Phe	51.5 ± 146	15.7 ± 16.6	28.0 ± 26.8	13.9 ± 14.1
Ant	7.50 ± 28.6	1.31 ± 2.45	1.16 ± 1.63	0.79 ± 1.15
Flu	1.41 ± 8.21	−1.69 ± 2.86	−0.37 ± 1.30	−1.05 ± 1.05
Pyr	1.28 ± 9.62	−0.74 ± 1.40	−0.17 ± 0.59	−0.48 ± 0.47
BaA	−0.53 ± 1.26	−0.84 ± 0.99	−1.41 ± 1.24	−1.43 ± 0.95
Chr	−0.09 ± 3.92	−2.24 ± 2.45	−2.28 ± 2.24	−1.96 ± 1.13
BbF	0.01 ± 0.63	−0.40 ± 0.39	−0.66 ± 0.57	−0.58 ± 0.35
BkF	−0.02 ± 0.32	−0.13 ± 0.15	−0.09 ± 0.10	−0.10 ± 0.07
BaP	−0.99 ± 1.09	−1.48 ± 1.63	−2.53 ± 2.52	−2.29 ± 1.87
DahA	−2.48 ± 2.53	−2.76 ± 1.92	−8.42 ± 10.0	−7.40 ± 6.51
IcdP	−0.38 ± 0.38	−3.56 ± 3.79	−6.44 ± 2.81	−9.55 ± 4.32
BghiP	−2.14 ± 2.23	−2.51 ± 1.73	−10.2 ± 12.8	−6.71 ± 5.40
$\sum_{15}$PAH[f]	852 ± 1140	195 ± 165	322 ± 243	84.9 ± 62.5

[a] Acronyms of individual 15 PAH compounds (Table S1).
[b] Including Guangzhou, Foshan, Dongguan, Zhongshan, Zhuhai and Shenzhen (Fig. S1a).
[c] Including Zhaoqing, Qingyuan, Jiangmen and Huizhou (Fig. S1a).
[d] Including Yangjiang and Yunfu (Fig. S1a).
[e] Including Heyuan, Shanwei and Shaoguan (Fig. S1a).
[f] Sum of 15 PAHs (List S3).

(Statistical Bureau of Guangdong Province, 2011). In addition to the diffusive process discussed above, dry and wet depositions are two other transport mechanisms for PAHs released from consumption of coal and petroleum to deposit into soil from air. From 2001 to 2010, the dry and wet deposition fluxes of PAHs increased from 460 to 600 μg m^{-2} yr^{-1} (Li et al., 2009; Guo et al., 2014). Therefore, continuous emissions of PAHs from energy consumption and evolving energy consumption pattern have consolidated soil as a secondary source of individual PAHs.

The average D_{flux} of $\sum_{15}$PAH (852 ± 1140 μg m^{-2} yr^{-1}) in the central PRD was greater than those in the PRD's periphery (195 ± 165 μg m^{-2} yr^{-1}), West (322 ± 243 μg m^{-2} yr^{-1}) and East (84.9 ± 62.5 μg m^{-2} yr^{-1}) regions (Table 2). In particular, the net escaping fluxes of individual 3-ring PAH compounds in the central PRD were also 1.2–9.5 times of those in other three regions except for Flo, which was similar to the spatial pattern of soil PAH concentrations. In addition, the net deposition fluxes of high molecular weight PAHs (4-, 5- and 6-ring PAHs except for Flu and Pyr) in the central PRD were smaller than those in other geographic regions (Table 2). Therefore, the central PRD may serve as a secondary source of PAHs, and further dissipates PAHs to other areas through atmospheric transport.

3.5. Ecological risk assessment

Soil PAHs are not regulated in China, and only a few soil quality guidelines, e.g., Canadian Soil Quality Guidelines (Canadian Council of Ministers of the Environment, 2008), the Netherlands maximum permissible concentrations (Kalf et al., 1997) and Danish soil quality criteria (Grøn and Andersen, 2003) are available around the world. The concentrations of individual PAH compounds in the present study were well below Environment Canada's acceptable thresholds (1320, 1320, 1980,4950 and 33 000 μg/g for Flo, Flu, Ace, BaA and Ant, respectively), while the maximum concentrations of Ant (415 ng/g), BaP (631 ng/g), BaA (1040 ng/g), and Phe (2350 ng/g) in the present study (Table S1) exceeded the Netherlands maximum permissible concentrations (120, 260, 250, and 510 ng/g). Similarly, the maximum concentrations of BaP and DahA (631 and 269 ng/g) in the present study (Table S1) were much higher than the Danish soil quality criteria (both 100 ng/g).

Moreover, Maliszewska-Kordybach (1996) created a classification of soil $\sum_{16}$PAH contamination in 1996, i.e., a soil is characterized as being non-contaminated, weakly contaminated, contaminated, or heavily contaminated if its $\sum_{16}$PAH concentration is lower than 200, within 200–600, between 600 and 1000, or higher than 1000 ng/g. If naphthalene is assumed not to contribute significantly to the overall ecological impact of $\sum_{16}$PAH, the $\sum_{15}$PAH data acquired in the present study can still be used to characterize soil contamination (Motelay-Massei et al., 2004; Maliszewska-Kordybach et al., 2008; Lin et al., 2013). Based on this classification, 80.3% of the soils investigated in the present study can be considered being non-contaminated, 13.1% weakly contaminated, 3.1% contaminated, and 3.5% as heavily contaminated by PAHs. Although only 3.5% of the soil samples were heavily contaminated with PAHs, the polluted area (2.5% of total area in the study region) represented by these soil samples is concentrated in the central PRD, with 5.2 million residents subjecting to high health risk (Statistical Bureau of Guangdong Province, 2011). If the soil PAH concentrations would double every ten years based on the increase rate of 1.9 from 2000 to 2010 and the energy consumption pattern remains the same in the next few decades, 50% of the soil in the PRD and surrounding areas will become heavily contaminated by 2060. As a result, the heavily contaminated area will occupy approximately 60% of the total soil area within the PRD and surrounding areas, and 83% of the total population will be subject to high health risk.

4. Conclusions

Anthropogenic impacts have played a major role in shaping the spatial pattern of soil PAH concentrations in the study region, mainly through combustion of coal and petroleum. Continuous emissions of PAHs and evolving energy consumption pattern have consolidated soil as a significant secondary source of individual PAHs to the atmosphere. Atmospheric transport of PAHs in the central PRD to other distant regions would substantially increase the proportion of contaminated soil areas, if emissions of PAHs continue. Ecological risk assessments show that the heavily contaminated soil by PAHs is concentrated in the densely populated central PRD, with a large number of residents subjecting to high health risk.

Conflict of interest declaration

On behalf of my co-authors and myself, we declare no conflict of interest to this work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.12.106.

References

Bjøseth A, Bjørseth O, Fjeldstad PE. Polycyclic aromatic hydrocarbons in the work atmosphere. II. Determination in a coke plant. Scand J Work Environ Health 1978;4(3):224–36.
Bozlaker A, Muezzinoglu A, Odabasi M. Atmospheric concentrations, dry deposition and air–soil exchange of polycyclic aromatic hydrocarbons (PAHs) in an industrial region in Turkey. J Hazard Mater 2008;153(3):1093–102.
Cai Q-Y, Mo C-H, Li Y-H, Zeng Q-Y, Katsoyiannis A, Wu Q-T, et al. Occurrence and assessment of polycyclic aromatic hydrocarbons in soils from vegetable fields of the Pearl River Delta, South China. Chemosphere 2007;68(1):159–68.
Canadian Council of Ministers of the Environment. Canadian soil quality guidelines carcinogenic and other polycyclic aromatic hydrocarbons (PAHs) (environmental and human health effects). Scientific supporting document: Canadian Council of Ministers of the Environment; 2008.
Chen M, Huang P, Chen L. Polycyclic aromatic hydrocarbons in soils from Urumqi, China: distribution, source contributions, and potential health risks. Environ Monit Assess 2013;185(7):5639–51.
Cheung KC, Poon BHT, Lan CY, Wong MH. Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China. Chemosphere 2003;52(9):1431–40.
Concord Scientific Corporation and Beak Consultants. Polycyclic aromatic hydrocarbons: source, fate and levels in air, water, soil, sediment and food in Ontario. Ontario: Queen's Printer for Ontario; 1992.
Cousins IT, Jones KC. Air–soil exchange of semi-volatile organic compounds (SOCs) in the UK. Environ Pollut 1998;102(1):105–18.
Gardner RH, O'Neill RV, Mankin JB, Garney JH. A comparison of sensitivity analysis and error analysis based on a stream ecosystem model. Ecol Model 1981;12(3):173–90.
Gordon RJ, Bryan RJ. Patterns in airborne polynuclear hydrocarbons concentrations at four Los Angeles sites. Environ Sci Technol 1973;7(11):1050–3.
Grøn C, Andersen L. Human bioaccessibility of heavy metals and PAH from soil. Danish Environmental Protection Agency; 2003.
Guo L-C, Bao L-J, She J-W, Zeng EY. Significance of wet deposition to removal of atmospheric particulate matter and polycyclic aromatic hydrocarbons: a case study in Guangzhou, China. Atmos Environ 2014;83:136–44.
Harner T, Bidleman TF, Jantunen LMM, Mackay D. Soil–air exchange model of persistent pesticides in the United States cotton belt. Environ Toxicol Chem 2001;20(7):1612–21.
Hippelein M, Mclachlan MS. Soil/air partitioning of semivolatile organic compounds. 1. Method development and influence of physical–chemical properties. Environ Sci Technol 1998;32(2):310–6.
Hites RA, Laflamme RE, Windsor Jr JG, Farrington JW, Deuser WG. Polycyclic aromatic hydrocarbons in an anoxic sediment core from the Pettaquamscutt River (Rhode Island, U.S.A.). Geochim Cosmochim Acta 1980;44(6):873–8.
Isaaks EH, Srivastava RM. An introduction to applied geostatistics. USA: Oxford University Press; 1990.
Jones KC. Observations on long-term air–soil exchange of organic contaminants. Environ Sci Pollut Res 1994;1(3):172–7.
Jones KC, Stratford JA, Waterhouse KS, Vogt NB. Organic contaminants in Welsh soils: polynuclear aromatic hydrocarbons. Environ Sci Technol 1989;23(5):540–50.
Kalf DF, Crommentuijn T, van de Plassche EJ. Environmental quality objectives for 10 polycyclic aromatic hydrocarbons (PAHs). Ecotoxicol Environ Saf 1997;36(1):89–97.
Larsen RK, Baker JE. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environ Sci Technol 2003;37(9):1873–81.
Levendis Y, Atal A. On the correlation of CO and PAH emissions from the combustion of pulverized coal and waste tires. Environ Sci Technol 1998;32(23):3767–77.
Li J, Cheng H, Zhang G, Qi S, Li X. Polycyclic aromatic hydrocarbon (PAH) deposition to and exchange at the air–water interface of Luhu, an urban lake in Guangzhou, China. Environ Pollut 2009;157(1):273–9.
Li Y-F, Harner T, Liu L, Zhang Z, Ren N-Q, Jia H, et al. Polychlorinated biphenyls in global air and surface soil: distributions, air–soil exchange, and fractionation effect. Environ Sci Technol 2010;44(8):2784–90.
Lin C, Liu J, Wang R, Wang Y, Huang B, Pan X. Polycyclic aromatic hydrocarbons in surface soils of Kunming, China: concentrations, distribution, sources, and potential risk. Soil Sediment Contam 2013;22(7):753–66.
Lioy PJ, Daisey JM. Airborne toxic elements and organic substances. Environ Sci Technol 1986;20(1):8–14.
Liu G, Yu L, Liu X, Zhang G. PAHs in soils and estimated air–soil exchange in the Pearl River Delta, South China. Environ Monit Assess 2011;173(1–4):861–70.
Liu L-Y, Wang J-Z, Qiu J-W, Liang Y, Zeng EY. Persistent organic pollutants in coastal sediment off South China in relation to the importance of anthropogenic inputs. Environ Toxicol Chem 2012a;31(6):1194–201.
Liu L-Y, Wang J-Z, Wei G-L, Guan Y-F, Wong CS, Zeng EY. Sediment records of polycyclic aromatic hydrocarbons (PAHs) in the continental shelf of China: implications for evolving anthropogenic impacts. Environ Sci Technol 2012b;46(12):6497–504.
Liu L-Y, Wang J-Z, Wei G-L, Guang Y-F, Zeng EY. Polycyclic aromatic hydrocarbons (PAHs) in continental shelf sediment of China: implications for anthropogenic influences on coastal marine environment. Environ Pollut 2012c;167:155–62.
Ma XX, Ran Y, Gong J, Zou MY. Concentrations and inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in watershed soils in the Pearl River Delta, China. Environ Monit Assess 2008;145(1–3):453–64.
Maliszewska-Kordybach B. Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. Appl Geochem 1996;11(1–2):121–7.
Maliszewska-Kordybach B, Smreczek B, Klimkowicz-Pawlas A, Terelak H. Monitoring of the total content of polycyclic aromatic hydrocarbons (PAHs) in arable soils in Poland. Chemosphere 2008;73(8):1284–91.
Manzetti S. Are polycyclic aromatic hydrocarbons from fossil emissions potential hormone-analogue sources for modern man? Pathophysiology 2012;19(1):65–7.
Manzetti S. Polycyclic aromatic hydrocarbons in the environment: environment fate and transformation. Polycycl Aromat Comp 2013;33(4):311–30.
Meijer SN, Shoeib M, Jantunen LMM, Jones KC, Harner T. Air–soil exchange of organochlorine pesticides in agricultural soils. 1. Field measurements using a novel in situ sampling device. Environ Sci Technol 2003;37(7):1292–9.
Motelay-Massei A, Ollivon D, Garban B, Teil MJ, Blanchard M, Chevreuil M. Distribution and spatial trends of PAHs and PCBs in soils in the Seine River Basin, France. Chemosphere 2004;55(4):555–65.
Page DS, Boehm PD, Douglas GS, Bence AE, Burns WA, Mankiewicz PJ. Pyrogenic polycyclic aromatic hydrocarbons in sediments record past human activity: a case study in Prince William Sound, Alaska. Mar Pollut Bull 1999;38(4):247–60.
Pan S-H, Li J, Lin T, Zhang G, Li X-D, Yin H. Polycyclic aromatic hydrocarbons on indoor/outdoor glass window surface in Guangzhou and Hong Kong, South China. Environ Pollut 2012;169:190–5.
Petry T, Schmid P, Schlatter C. The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs). Chemosphere 1996;32(4):639–48.
Robinson AL, Subramanian R, Donahue NM, Bernardo-Bricker A, Rogge WF. Source apportionment of molecular markers and organic aerosol-1. Polycyclic aromatic hydrocarbons and methodology for data visualization. Environ Sci Technol 2006;40(24):7803–10.
Rom WN, Markowitz SB. Environmental and occupational medicine, vol. 81. Philadelphia: Lippincott Williams & Wilkins; 2007.
Sporstol S, Gjos N, Lichtenthaler RG, Gustavsen KO, Urdal K, Oreld F, et al. Source identification of aromatic hydrocarbons in sediments using GC/MS. Environ Sci Technol 1983;17(5):282–6.
Statistical Bureau of Guangdong Province. Guangdong Statistical Yearbook 2011. http://www.gdstats.gov.cn/tjnj/2011/table/21/e21-02-0.htm2011, 2011. [(Accessed on October 25, 2013) (in Chinese)].
Statistical Bureau of Urumqi. Urumqi Statistical Yearbook 2011. http://www.wlmqtj.gov.cn/tjnj/2011/index.htm2011, 2011. [(Accessed on October 25, 2013) (in Chinese)].
Terzaghi E, Wild E, Zacchello G, Cerabolini BEL, Jones KC, Guardo AD. Forest filter effect: role of leaves in capturing/releasing air particulate matter and its associated PAHs. Atmos Environ 2013;74:378–84.
United States Environmental Protection Agency. Field manual for grid sampling of PCB spill sites to verify cleanup. http://www.epa.gov/osw/hazard/tsd/pcbs/pubs/gridsampling.pdf, 1986. [(Accessed on September 12, 2013)].
United States Environmental Protection Agency. Guidance on choosing a sampling design for environmental data collection. http://www.epa.gov/quality/qs-docs/g5s-final.pdf, 2002. [(Accessed on September 12, 2013)].
Wang C, Wang X, Gong P, Yao T. Polycyclic aromatic hydrocarbons in surface soil across the Tibetan Plateau: spatial distribution, source and air–soil exchange. Environ Pollut 2014;184:138–44.
Wang D, Yang M, Jia H, Zhou L, Li Y. Seasonal variation of polycyclic aromatic hydrocarbons in soil and air of Dalian areas, China: an assessment of soil–air exchange. J Environ Monit 2008;10(9):1076–83.
Wang J-Z, Guan Y-F, Ni H-G, Luo X-L, Zeng EY. Polycyclic aromatic hydrocarbons in riverine runoff of the Pearl River Delta (China): concentrations, fluxes, and fate. Environ Sci Technol 2007;41(16):5614–9.
Wang J. Passive air sampling survey of polycyclic aromatic hydrocarbons (PAHs), organic chlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the Pearl River Delta. Ph. D; 2007 [in Chinese].
Wang W, Huang M-J, Kang Y, Wang H-S, Leung AOW, Cheung KC, et al. Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: status, sources and human health risk assessment. Sci Total Environ 2011a;409(21):4519–27.
Wang W, Simonich S, Giri B, Chang Y, Zhang Y, Jia Y, et al. 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 2011b;409(15):2942–50.
Wang Y, Tian Z, Zhu H, Cheng Z, Kang M, Luo C, et al. Polycyclic aromatic hydrocarbons (PAHs) in soils and vegetation near an e-waste recycling site in South China: concentration, distribution, source, and risk assessment. Sci Total Environ 2012;439(21):187–93.

Weinstein JE, Crawford KD, Garner TR, Flemming AJ. Screening-level ecological and human health risk assessment of polycyclic aromatic hydrocarbons in stormwater detention pond sediments of Coastal South Carolina, USA. J Hazard Mater 2010;178(1–3):906–16.
Xu S, Liu W, Tao S. Emission of polycyclic aromatic hydrocarbons in China. Environ Sci Technol 2006;40(3):702–8.
Yang B, Xue N, Zhou L, Li F, Cong X, Han B, et al. Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. Ecotoxicol Environ Saf 2012;84:304–10.
Yang Y, Guo P, Zhang Q, Li D, Zhao L, Mu D. Seasonal variation, sources and gas/particle partitioning of polycyclic aromatic hydrocarbons in Guangzhou, China. Sci Total Environ 2010;408(12):2492–500.
Yu L, Li J, Liu G, Liu X, Qi S, Zhang G. Polycyclic aromatic hydrocarbons in surface soils of the Pearl River Delta, South China. Ecol Environ 2007;16(6):1683–7. [(in Chinese)].
Yunker MB, Backus SM, Graf Pannatier E, Jeffries DS, Macdonald RW. Sources and significance of alkane and PAH hydrocarbons in Canadian Arctic rivers. Estua Coastal Shelf Sci 2002a;55(1):1–31.
Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Geoyette D, Sylvestre S. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 2002b;33(4):489–515.
Zhang K, Wang J-Z, Liang B, Zeng EY. Occurrence of polycyclic aromatic hydrocarbons in surface sediments of a highly urbanized river system with special reference to energy consumption patterns. Environ Pollut 2011a;159(6):1510–5.
Zhang K, Liang B, Wang J-Z, Guan Y-F, Zeng EY. Polycyclic aromatic hydrocarbons in upstream riverine runoff of the Pearl River Delta, China: an assessment of regional input sources. Environ Pollut 2012;167:78–84.
Zhang Y, Deng S, Liu Y, Shen G, Li X, Cao J, et al. A passive air sampler for characterizing the vertical concentration profile of gaseous phase polycyclic aromatic hydrocarbons in near soil surface air. Environ Pollut 2011b;159(3):694–9.
Zhong Y, Zhu L. Distribution, input pathway and soil–air exchange of polycyclic aromatic hydrocarbons in Banshan Industry Park, China. Sci Total Environ 2013;444:177–82.
Zhu Y-G, Ioannidis JPA, Li H, Jones KC, Martin FL. Understanding and harnessing the health effects of rapid urbanization in China. Environ Sci Technol 2011;45(12):5099–104.