



Soil Polycyclic Aromatic Hydrocarbons Across Urban Density Zones in Shenzhen, China: Occurrences, Source Apportionments, and Spatial Risk Assessment

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ABSTRACT

Urbanization may cause increased exposure levels to polycyclic aromatic hydrocarbons (PAHs) and associated health risks for over half of the world's population living in cities, but little evidence has shown a direct spatial relationship between urbanization and soil PAH pollution. Based on the monitored PAH concentrations in 188 topsoil (0–5 cm) samples in Shenzhen, the most rapidly developing city in China, in recent decades, we applied geographical demarcation to determine the occurrences, source apportionments, and spatial ecological risks of soil PAHs across five zones of varying urban densities. Mean concentrations of the 16 US Environmental Protection Agency (EPA) priority PAHs ($\Sigma_{16}\text{PAHs}$) and the 7 carcinogenic PAHs ($\Sigma_7\text{CarPAHs}$) both followed the order: Zone D (60%–80% constructive land density (CLD)) > Zone E (80%–100% CLD) > Zone C (40%–60% CLD) > Zone B (20%–40% CLD) > Zone A (0%–20% CLD), suggesting that the highest PAH levels occurred in the suburban-urban center transitional zone (Zone D) rather than the urban center zone (Zone E) in Shenzhen. There were significant correlations of $\Sigma_{16}\text{PAHs}$ to TOC and sampling altitude across all samples but not within highly-urbanized regions (Zones D and E), implying a considerable disturbance of urbanization to the soil PAH pool. Source apportionments suggested that soil PAHs of all zones were mainly derived from fossil fuel combustion, with Zone E showing the highest contribution from oil sources among different zones. Spatial ecological risk analysis showed that the contaminated area (467 km²; 23.9% of total area; toxic equivalency quotients > 33 ng g⁻¹) had a higher contribution from the highly-urbanized regions (Zones D and E) than the uncontaminated area (42.3% vs. 18.1%). Overall, our study highlighted a strong spatial relationship between urbanization and soil PAH pollution.

Key Words: altitude, carcinogenic PAHs, soil PAH pollution, total organic C, toxic equivalency quotient, urbanization, US EPA priority PAH

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INTRODUCTION

Sprawling cities around the world support over half of the earth's population (UN DESA, 2010). Understanding how urbanization potentially influences the occurrence and environmental behavior of the potentially toxic polycyclic aromatic hydrocarbons (PAHs) is one critical issue linking urban development and environmental public health (Jiang *et al.*, 2009; Peng *et al.*, 2012). Polycyclic aromatic hydrocarbons, especially the 16 US Environmental Protection Agency (EPA) priority PAHs ($\Sigma_{16}\text{PAHs}$), are ubiquitous in the environment with well-documented carcinogenic, mutagenic, and teratogenic properties (Lehr and Jerina, 1977; Wang *et al.*, 2013). They originate mainly from incomplete anthropogenic organic matter combustion and oil volatilization or leakage (Von Lau *et al.*, 2012),

though some are related to natural processes such as volcanic eruptions and forest fires (Zhang *et al.*, 2004; Choi, 2014). Among various environmental matrices, surface soil is a common focus for its role as a large PAH reservoir in the terrestrial system (> 90%) (Wild and Jones, 1995) and its sensitivity to anthropogenic activities (Zheng *et al.*, 2012). Due to their lipophilicity and persistence, PAHs tend to persist in the soil (Wang *et al.*, 2013), which to varying degrees jeopardizes human health through dermal contact and/or ingestion of contaminated food (Zhang *et al.*, 2012; Bortey-Sam *et al.*, 2014). Further, as the most crucial carrier of pollutants from high-intensity anthropogenic activities, urban soil can also be a source of atmospheric PAHs through volatilization and water PAHs through surface runoff (Diblasi *et al.*, 2009), thereby increasing PAH exposure to urban residents.

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PAH contamination in urban soils has been widely reported worldwide. For example, Peng *et al.* (2012) found relatively high levels of soil Σ_{16} PAH concentrations under covers of tree-shrub-herb (1782 ng g⁻¹), greenbelt (1117 ng g⁻¹), woodland (1101 ng g⁻¹), and grassland (455 ng g⁻¹) in urban green spaces. Morillo *et al.* (2007) compared soil PAH concentrations from three European cities and identified climatic conditions, soil organic carbon, and pollution source as significant factors affecting soil PAH accumulation. Soil PAHs in Ulsan, Korea were investigated by Kwon and Choi (2014) and found to have mainly originated from vehicles and industrial complexes. In addition, environmental samples collected along main transportation routes show similar PAH sources, suggesting that traffic exhaust is a major cause (Zhang and Wang, 2011). However, few studies focus on the mass inventory and source apportionment of PAHs from different urban density zones, and there is limited understanding of the quantitative differentiation of soil PAH occurrence, sources, and ecological risks across the urbanization gradient. Although some studies refer to the concept of “urbanization levels”, most adopted a cursory or empirical definition for urban density zoning (Zuo *et al.*, 2007; Cai *et al.*, 2012; Xie *et al.*, 2012), making it difficult to explore the in-depth correlation between urbanization levels and soil PAH occurrence.

China has undergone rapid urbanization (Lin *et al.*, 2015), with urbanization levels increasing from 19% in 1980 to 47% in 2010 (UN, 2010). It took developed countries such as UK and USA much longer to accomplish this (Ni *et al.*, 2011). As a representative city with the most rapid urbanization rate in China over the last three decades, Shenzhen developed from a rural fishing village in the 1980s (population = 0.33 million, GDP = 0.27 billion RMB) to a modern metropolis in 2010 (population = 10.37 million, GDP = 958.15 billion RMB) (Shenzhen Municipal Bureau of Statistics, 2014). However, the accompanying densely populated aggregation and constructive land sprawl, such as increasing industry and transportation, have delivered a negative impact on urban environmental quality and human health (Wang *et al.*, 2011; Sun *et al.*, 2012; Sun *et al.*, 2013). Studying the soil PAH occurrence in Shenzhen, our previous research estimated the overall potential fate of and human non-dietary exposure to soil PAHs (Cao *et al.*, 2010; Ni *et al.*, 2011). Yet little is known about the dependence of PAH occurrence, composition, and spatial ecological risks on the spatial pattern of urbanization. This study adopted geographical demarcation to separate zones with different urban densities and focused on the variations in mass inven-

tory, sources, and ecological risk of exposure to surface soil PAHs across the urbanization gradient. The correlations of soil PAH levels with soil total organic carbon (TOC) and sampling altitude were also evaluated in different urbanization regions. The results of this study will be instrumental in coupling the change of spatial environmental quality with urban expansion.

MATERIALS AND METHODS

Study area and soil sampling

Located on the southern coast of Guangdong Province, Shenzhen is the “experimental field” of China’s reform and opening-up. It has a subtropical monsoon climate. Its average annual temperature, rainfall, and hours of sunshine are 22.4 °C, 1933.3 mm, and 2120.5 h, respectively. A total of 188 surface soil samples (0–5 cm) were collected in winter 2007 from different types of land use according to principles of even distribution and random sampling. Specifically, a five-point sampling method was adopted, and five samples (about 500 g each) from four 10 m × 10 m square corner points and the center point were fully mixed as the local sample (Cao *et al.*, 2010). Soil samples were placed in a cool, dark room and air-dried. Then soil samples were stored in amber glass bottles at –4 °C in a refrigerator after being crushed and sieved (100 mesh) until further analysis. The spatial distribution of sampling sites is shown in Fig. 1. Soil TOC content and sampling altitude of the 188 topsoil samples are shown in Table I.

Urban density zoning

Shenzhen land-use data was obtained from the Urban Planning & Design Institute of Shenzhen, China. We chose constructive land density (CLD) as the urbanization level indicator which is closely connected with the corresponding intensity of human activities and urban population (Zeng *et al.*, 2007; Zhao *et al.*, 2013). An ArcGIS 10.0 neighborhood statistics analysis was used to divide the entire study area into five urban gradients based on CLD (including industrial, commercial, transportation, and residential land-use types) with a 20% interval (Fig. 1). Then the zones with CLD levels of 0%–20%, 20%–40%, 40%–60%, 60%–80%, and 80%–100% were defined as a rural zone (Zone A), rural-suburban transitional zone (Zone B), suburban zone (Zone C), suburban-urban center transitional zone (Zone D), and urban center zone (Zone E), respectively. These five zones, from Zone A to Zone E, covered 33.9%, 22.5%, 20.4%, 16.9%, and 6.3% of the city’s gross area, respectively. Number of topsoil samples in the each zone ranged from 27 to 61.

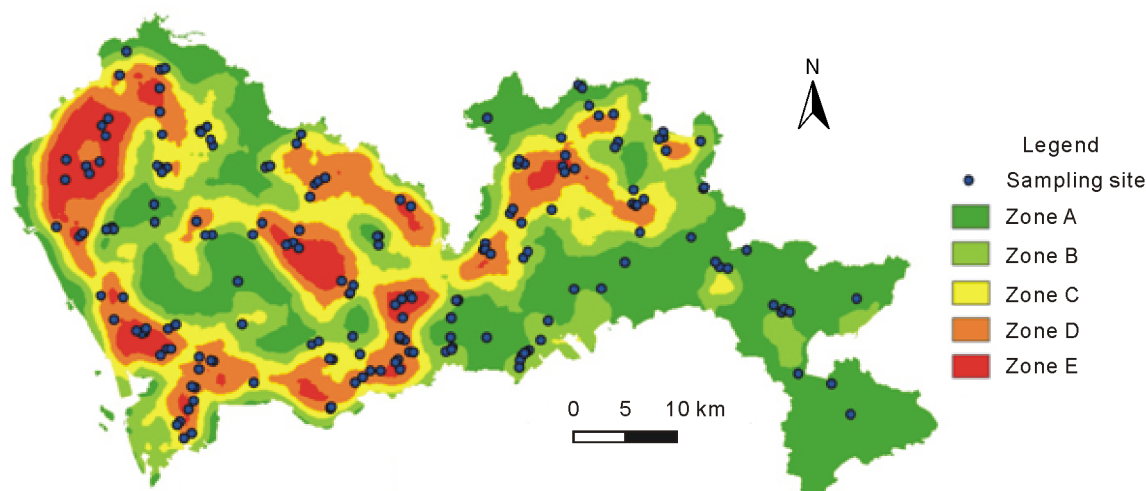


Fig. 1 Sampling sites and urbanized density zoning based on constructive land density (CLD) of Shenzhen, China. Zone A, Zone B, Zone C, Zone D, and Zone E represent rural zone (0%–20% CLD), rural-suburban transitional zone (20%–40% CLD), suburban zone (40%–60% CLD), suburban-urban center transitional zone (60%–80% CLD), and urban center zone (80%–100% CLD), respectively.

TABLE I

Statistics of total organic carbon (TOC) concentration and sampling altitude of the 188 topsoil samples in Shenzhen, China

Item	Minimum	Maximum	Mean	Median	SD ^{a)}
TOC concentration (mg g ⁻¹)	15	505	120	96	89
Altitude (m)	2.0	557.0	55.0	40.0	62.6

^{a)}Standard deviation.

Chemicals

Standards of the 16 US EPA priority PAHs were purchased from the Accustandard Company (New Haven, USA). The names and abbreviations of PAHs are listed in Table II. Five deuterated surrogate PAH standards (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂) and two internal standards (2-fluorobiphenyl and p-terphenyl-d₁₄) were purchased from Cambridge Isotope Laboratories (Andover, USA). Both silica gel (80–100 mesh) and alumina (100–200 mesh) were Soxhlet-extracted with methanol and dichloromethane for 24 h, respectively. Hexane, dichloromethane, methanol, and acetone were all redistilled through a glass apparatus before use.

Experimental pretreatment

The 16 priority PAHs in topsoil were analyzed following the method described in a previous study (Cao *et al.*, 2010). Specifically, 20.0 g freeze-dried soil sample was mixed with 2.0 g copper and recovery standards, and was Soxhlet-extracted using a 200-mL mixture of hexane and acetone (1:1, volume:volume) for 48 h. The extracts were concentrated to about 1 mL using rotary evaporation, then separated and purified by silica gel

and alumina column with the ratio of 2:1 by volume. The column was eluted with 20 mL hexane, then with 70 mL mixture of hexane and dichloromethane (7:3, volume:volume). The latter fraction was collected, concentrated to about 1 mL, transferred to a clean vial, and further reduced to 0.5 mL with a gentle N₂ steam. Then internal standards were added into the bottle prior to instrumental analysis. We also used an element analyzer (multi N/C 3100, Analytik Jena AG, Jena, Germany) to determine total organic carbon (TOC) of each sample after removing the inorganic carbon with 10% hydrochloric acid. All glassware in this study was cleaned with sulfuric acid, rinsed with both tap water and Milli-Q water at least three times, and baked at 450 °C for > 24 h.

Instrumental analysis

Target PAH concentrations were determined using Shimadzu GC-MS equipped with a 30 m DB-5MS GC capillary column (0.25-mm inner diameter and 0.25-μm film thickness; J & W Scientific, Folsom, USA) under splitless mode. Helium was used as carrier gas. Injection volume was 1 μL. The column oven temperature programming was as follows: increased from 60 to 200 °C at a rate of 5 °C min⁻¹, to 250 °C at a rate of 2 °C min⁻¹, and then to 290 °C at a rate of 20 °C min⁻¹

TABLE II

Concentrations of the 16 US Environmental Protection Agency (EPA) priority polycyclic aromatic hydrocarbons (PAHs) in surface soils from different urbanized density zones^{a)} of Shenzhen, China

PAH	Abbreviation	Rings	Zone A (n = 27)	Zone B (n = 34)	Zone C (n = 38)	Zone D (n = 61)	Zone E (n = 28)
ng g ⁻¹							
Naphthalene	NAP	2	8.1 ± 7.6 ^{b)}	11.7 ± 11.6	12.3 ± 18.4	10.7 ± 16.2	5.0 ± 4.8
Acenaphthylene	AC	2	1.4 ± 1.5	2.1 ± 2.7	2.6 ± 4.4	2.5 ± 4.8	1.0 ± 1.2
Acenaphthene	ACE	2	0.9 ± 0.7	1.3 ± 1.4	1.2 ± 1.6	1.4 ± 2.0	0.8 ± 0.9
Fluorine	FL	2	5.1 ± 5.3	5.9 ± 7.4	8.1 ± 10.9	7.5 ± 13.9	3.6 ± 4.5
Phenanthrene	PHE	3	18.3 ± 25.4	18.9 ± 23.7	23.5 ± 45.1	40.9 ± 99.9	20.2 ± 22.8
Anthracene	ANT	3	3.4 ± 4.1	3.3 ± 3.9	3.0 ± 5.1	7.1 ± 14.9	3.9 ± 5.5
Fluoranthene	FLU	3	18.4 ± 37.8	22.4 ± 41.7	20.7 ± 50.0	59.5 ± 166.1	24.0 ± 30.9
Pyrene	PYR	4	13.5 ± 28.5	19.0 ± 37.9	15.7 ± 36.6	47.2 ± 123.3	19.6 ± 26.7
Benzo(a)anthracene	BaA ^{c)}	4	5.3 ± 15.1	7.2 ± 17.1	8.1 ± 20.7	28.5 ± 84.9	10.8 ± 17.1
Chrysene	CHR ^{c)}	4	10.9 ± 23.8	18.4 ± 42.0	19.8 ± 44.2	52.4 ± 120.2	33.4 ± 52.4
Benzo(b)fluoranthene	BbF ^{c)}	4	15.3 ± 38.0	27.2 ± 69.4	28.5 ± 65.5	66.6 ± 179.9	34.4 ± 51.7
Benzo(k)fluoranthene	BkF ^{c)}	4	4.5 ± 10.6	8.6 ± 22.0	8.4 ± 18.8	20.5 ± 58.5	10.5 ± 16.6
Benzo(a)pyrene	BaP ^{c)}	5	6.9 ± 18.8	8.9 ± 19.1	10.7 ± 26.0	26.1 ± 72.9	11.9 ± 17.7
Indeno(1,2,3-cd)pyrene	IcdP ^{c)}	5	9.8 ± 24.4	15.0 ± 32.4	18.1 ± 44.1	40.0 ± 100.3	21.0 ± 33.3
Dibenzo(a,h)anthracene	DahA ^{c)}	5	2.1 ± 6.8	3.7 ± 10.0	4.2 ± 10.3	13.6 ± 38.8	6.1 ± 12.1
Benzo(g,h,i)perylene	BghiP	6	15.2 ± 36.3	23.3 ± 45.2	27.3 ± 65.1	54.9 ± 121.4	35.2 ± 59.3
Σ ₁₆ PAHs ^{d)}			139.3 ± 267.7	196.9 ± 358.0	212.2 ± 442.5	479.4 ± 1147.8	241.3 ± 324.6
Σ ₇ CarPAHs ^{e)}			54.8 ± 136.8	89.0 ± 210.9	97.7 ± 227.7	247.7 ± 626.4	128.0 ± 186.4

^{a)} See Fig. 1 for details of Zones A–E.

^{b)} Means ± standard deviations.

^{c)} Individual carcinogenic PAH.

^{d)} The 16 US EPA priority PAHs.

^{e)} The 7 carcinogenic PAHs.

and held for 20 min. The injector temperature was programmed from 100 to 280 °C at a rate of 180 °C min⁻¹ and then held for 40 min.

Quality assurance and quality control

Spiked blanks, procedural blanks, matrix-spiked blanks, and field blanks were processed with every batch of 20 samples. The surrogate standard recoveries of all samples were 40% ± 16%, 55% ± 18%, 73% ± 22%, 73% ± 16%, and 96% ± 25% for naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, and perylene-d₁₂, respectively. Since most of the low-molecular-weight PAHs were detected in procedural and field blanks, the lowest levels of calibration standards were chosen as reporting limits if the concentrations of individual PAHs in blanks were lower than the lowest concentrations of the calibration standards. For the other PAHs, a mean concentration plus one standard deviation in the blanks was calculated for each of these congeners, and used as the reporting limit. The PAH recoveries tested from spiked and matrix-spiked blanks ranged from 56% to 131% and 61% to 127%, respectively (Cao *et al.*, 2010). The reporting PAHs values were not corrected with the recoveries.

Data analysis

Calculation of mass inventories (MI). Mass inventories of topsoil Σ₁₆PAHs and 7 carcinogenic PAHs (Σ₇CarPAHs) in five zones were calculated as follows:

$$MI_i = f \times C_i \times A_i \times d \times \rho \quad (1)$$

where MI_{*i*} (Mg) represents the mass inventory of topsoil PAHs from zone *i*; *f* is the corresponding unit conversion factor, which is 1.0 × 10⁻⁵ (cm² × Mg) (km² × ng)⁻¹; *C_i* is the average PAH concentration (ng g⁻¹) from zone *i*; *A_i* is the area of zone *i* (km²); *d* represents the depth of soil sampling (cm), and *ρ* represents the average bulk density of dry samples (g cm⁻³). In this study, *d* was 5 cm and *ρ* was 1.7 g cm⁻³. The areas of the five zones were obtained from the GIS spatial analysis.

Calculation of toxic equivalency quotients (TEQs). We conducted a risk assessment for all soil samples by calculating the TEQs of 10 PAHs, including naphthalene (NAP), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLU), benzo(a)anthracene (BaA), chrysene (CHR), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (IcdP),

and benzo(g,h,i)perylene (BghiP) (TEQ₁₀):

$$\text{TEQ}_{10} = \sum C_i \times \text{TEF}_i \quad (2)$$

where C_i represents the concentration of target PAH i ($i = 1, 2, 3, \dots, 10$) (ng g^{-1}) and TEF_i (dimensionless number) is the corresponding TEQ factor of individual PAH relative to BaP (Ma *et al.*, 2009).

Statistical and geostatistical analyses. Using SPSS 16.0, a principal component analysis (PCA) and multiple linear regression (MLR) were conducted to identify PAH sources (Zuo *et al.*, 2007). The PCA was conducted after varimax rotation with Kaiser Normalization converging in three iterations, with the extraction eigenvalue set as > 1.0 . According to Lilliefors test for normality, all data sets were typical log-normal distribution, and were log-transformed prior to MLR analysis. Standardized scores of principal components and Σ_{16} PAHs concentrations were defined as independent variables and dependent variables, respectively. Then MLR coefficients were regarded as relative contributions of different PAH sources. We applied the function of ArcGIS ordinary Kriging interpolation with spherical model to predict the spatial PAH pollution in the entire city, before which interpolation data had been log-transformed. Values of range, sill, and nugget in this model were 0.05, 1.13, and 3.17, respectively.

RESULTS AND DISCUSSION

Concentrations and mass inventories of soil PAHs

Soil PAH concentrations in the five zones are listed in Table II. The average concentrations of both Σ_{16} PAHs and Σ_7 CarPAHs follows: Zone A (Σ_{16} PAHs,

139.3 ng g^{-1} ; Σ_7 CarPAHs, 54.8 ng g^{-1}) $<$ Zone B (Σ_{16} PAHs, 196.9 ng g^{-1} ; Σ_7 CarPAHs, 89.0 ng g^{-1}) $<$ Zone C (Σ_{16} PAHs, 212.2 ng g^{-1} ; Σ_7 CarPAHs, 97.7 ng g^{-1}) $<$ Zone E (Σ_{16} PAHs, 241.3 ng g^{-1} ; Σ_7 CarPAHs, 128.0 ng g^{-1}) $<$ Zone D (Σ_{16} PAHs, 479.4 ng g^{-1} ; Σ_7 CarPAHs, 247.7 ng g^{-1}). Composition of Σ_{16} PAHs in soil from each zone is shown in Fig. 2. The percentages of PAHs with higher molecular weights (HMW, 4–6 rings) in Σ_{16} PAHs increased with increasing urban density levels from Zone A to Zone E.

Both Σ_{16} PAHs and Σ_7 CarPAHs demonstrated the maximum values in the suburban-urban center transitional zone (Zone D). Such observation was inconsistent with the common hypothesis that the most polluted places are located in urban center areas (Nagy *et al.*, 2013). This result could be due to existing heavier traffic and municipal engineering in Zone D than those in other zones. The average soil Σ_{16} PAHs level of highly-urbanized region (Zones D and E) was about 360 ng g^{-1} , which was relatively low compared to those of other urbanized regions around the world (Table III). Yet this value was higher than those of the surrounding urbanized areas such as Hong Kong (169 ng g^{-1} ; Zhang *et al.*, 2006), Shantou City (317 ng g^{-1} ; Hao *et al.*, 2004), and the Pearl River Delta (315 ng g^{-1} ; Ma *et al.*, 2008). As the soil PAH concentrations in highly-urbanized region have reached a considerable level, particular public health concern should be placed on such highly-urbanized regions.

To better understand the soil PAH pool in different urbanized zones and provide reference to pollution management, we estimated mass inventories of PAHs in each urban density zone (Table IV). Both the

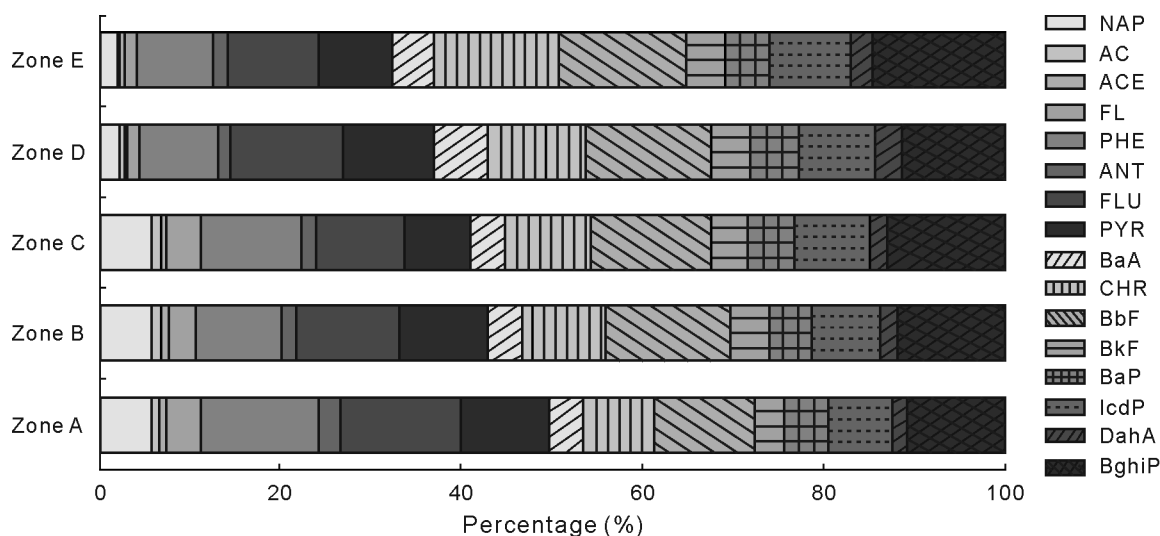


Fig. 2 Composition of the 16 US Environmental Protection Agency priority polycyclic aromatic hydrocarbons (PAHs) in topsoil of each urbanized density zone of Shenzhen, China. See Fig. 1 and Table II for details of Zones A–E and PAHs, respectively.

TABLE III

Concentrations of the 16 US Environmental Protection Agency priority polycyclic aromatic hydrocarbons (Σ_{16} PAHs) in topsoil of the highly-urbanized zone of Shenzhen, China in this study and other cities in previous studies

Region	Country	Mean	Range		Reference
			ng g ⁻¹		
Shenzhen	China	360	2–6 745		This study
Hong Kong	China	169	NA ^{a)}		Zhang <i>et al.</i> (2006)
Shantou City	China	317	22–1 257		Hao <i>et al.</i> (2004)
Pearl River Delta	China	315	58–3 077		Ma <i>et al.</i> (2008)
Beijing	China	1 228	93–13 141		Peng <i>et al.</i> (2011)
Nanjing	China	3 330	59–18 000		Wang <i>et al.</i> (2015)
Naples	Italy	890	90–7 700		De Nicola <i>et al.</i> (2014)
Ulsan	South Korea	960	65–12 000		Kwon and Choi (2014)
Addis Ababa	Ethiopia	NA	177–1 640		Prasse <i>et al.</i> (2012)
Bratislava	Slovakia	2 065	45–12 151		Hiller <i>et al.</i> (2015)
Isfahan	Iran	2 001	58–11 730		Moore <i>et al.</i> (2015)
Miami	USA	1 869	1 508–2 364		Banger <i>et al.</i> (2010)
Greater London	UK	18 000	4 000–66 000		Vane <i>et al.</i> (2014)

^{a)}Not available.

TABLE IV

Estimated mass inventories of polycyclic aromatic hydrocarbons (PAHs)^{a)} in topsoil of different urbanized density zones^{b)} of Shenzhen, China

Zone	Areas	Mass inventory		
		Σ_{16} PAHs	Σ_7 CarPAHs	BaP
	km ²	Mg		
Zone A	662	7.84	3.08	0.39
Zone B	440	7.37	3.33	0.33
Zone C	399	7.20	3.31	0.36
Zone D	329	13.40	6.93	0.73
Zone E	123	2.52	1.34	0.12
Total	1 953	38.33	17.99	1.94

^{a)} Σ_{16} PAHs = 16 US Environmental Protection Agency priority PAHs; Σ_7 CarPAHs = 7 carcinogenic PAHs; BaP = benzo(a)pyrene.

^{b)}See Fig. 1 for details of Zones A–E.

maximum mass inventories of Σ_{16} PAHs (38.33 Mg) and Σ_7 CarPAHs (17.99 Mg) were present in Zone D, and the mass inventory value of Σ_{16} PAHs from Zone A was high because of the large area of this zone (34% of total area). The total mass inventory of Σ_7 CarPAHs was near 50% of that of Σ_{16} PAHs.

TABLE V

Pearson correlation coefficients of the topsoil polycyclic aromatic hydrocarbon (PAH) concentration^{a)} with total organic carbon (TOC) concentration and sampling altitude after logarithmic transformation

Item	Total region ($n = 188$)			Less-urbanized region ($n = 99$)			Highly-urbanized region ($n = 89$)		
	Σ_{16} PAHs	LMW PAHs	HMW PAHs	Σ_{16} PAHs	LMW PAHs	HMW PAHs	Σ_{16} PAHs	LMW PAHs	HMW PAHs
TOC	0.157*	0.118	0.180*	0.201*	0.161	0.235*	0.110	0.074	0.118
Altitude	-0.238**	-0.139	-0.304**	-0.306**	-0.147	-0.411**	-0.108	-0.116	-0.101

*, **Significant at $P < 0.05$ and $P < 0.01$, respectively.

^{a)} Σ_{16} PAHs = 16 US Environmental Protection Agency priority PAHs; LMW PAHs = low-molecular-weight PAHs; HMW PAHs = high-molecular-weight PAHs.

Correlations of PAH concentrations with TOC and sampling altitude

According to Pearson correlation analysis, a positive correlation ($P < 0.05$) was found between the Σ_{16} PAH concentration and TOC concentration across the total 188 samples as well as the 99 samples in less-urbanized region (Zones A, B, and C), but no significant correlation across the 89 samples in highly-urbanized region (Zones D and E) (Table V). This indicated that for topsoil samples in the entire city, PAHs adsorbed by corresponding TOC were in a general equilibrium state (Wang *et al.*, 2010). In the highly-urbanized region, however, such a correlation tended to be disturbed by high-intensity human activities (Zhang *et al.*, 2006), the mechanism of which could be related to vast anthropogenic carbon input and soil stirring coerced by municipal engineering and similar problems.

The sampling altitude was negatively correlated with the Σ_{16} PAH concentration after logarithmic transformation for the whole region ($n = 188$; $P < 0.01$), as well as for those from the less-urbanized region ($P < 0.01$) (Table V). However, no relationship

was found for the samples collected in the highly-urbanized region. The main reason could be that the PAHs in the highly-urbanized region are generally distributed on the flat and lower terrain and could also be linked to surface runoff and atmospheric sedimentation which tended to carry PAHs to relatively lower altitudes. Interestingly, there were similar correlations for HMW PAHs compared to the Σ_{16} PAHs but not for low-molecular-weight (LMW) PAHs, which may be due to the relatively high volatility and complex sources of the LMW PAHs within this rapidly urbanized city.

PAH sources in different urban density zones

As different sources of PAHs can have distinct composition of PAH species, analyses of the quantitative relations among PAH species can suggest the source apportionment of PAHs (Yunker *et al.*, 2002; Tobiaszewski and Namiesnik, 2012). The composition of Σ_{16} PAHs also varied among five zones (Fig. 2), suggesting that the PAH source apportionments could be different among the zones. To quantitatively determine source apportionment of PAHs in each urban density zone, PAH data were analyzed by PCA with MLR. Two principal components (PC 1 and PC 2) were extracted for all city zone data except rural zone samples, which had three components (Table VI). Previous studies elucidated that incomplete gasoline combustion releases benzo(b)fluoranthene (BbF), BkF, CHR, and BghiP (Simcik *et al.*, 1999); IcdP is

an important indicator of the diesel combustion process (Li and Kamens, 1993); and BaA, BaP, and BkF are thought to be typical indicators of natural gas combustion and home cooking (Rogge *et al.*, 1993). Therefore, PC 1 can be identified as a fossil fuel combustion source (gasoline, diesel, natural gas, coal, *etc.*) and PC 2 that mainly contained LMW PAHs can be defined as an oil source (Soclo *et al.*, 2000; Mai *et al.*, 2002; Liao *et al.*, 2011). Research by Zhang *et al.* (2011) showed that more NAP was produced by crop (including rice, wheat, and corn) residue burning than other LMW PAHs such as acenaphthylene (AC), acenaphthene (ACE), or fluorine (FL). In fact, considerable straw burning occurred in the city's agricultural area. We suspected that NAP may be associated with the crop residue burning which is represented by PC 3.

Multiple linear regression was applied to investigate standardized regression coefficient and relative contribution of each principle component. A recent study suggested that topsoil Σ_{16} PAHs in Shenzhen were derived mainly from burning fossil fuels, while a small amount was related to oil pollution (Zhang *et al.*, 2014). This study suggests that although fossil fuel burning was a dominant source for all zones, different urban density zones did not demonstrate the same PAH source apportionment.

As shown in Table VII, urban center zone samples were most significantly polluted by oil with a contamination rate of 40.1%, which could be caused by cate-

TABLE VI

Factor loadings for the 16 US Environmental Protection Agency priority polycyclic aromatic hydrocarbons (PAHs)^{a)} in topsoil of different urbanized density zones^{b)} of Shenzhen, China

PAH	Zone A			Zone B		Zone C		Zone D		Zone E	
	PC ^{c)} 1	PC 2	PC 3	PC 1	PC 2	PC 1	PC 2	PC 1	PC 2	PC 1	PC 2
NAP	-0.014	0.135	0.953	0.499	0.742	0.246	0.920	-0.114	0.816	-0.339	0.824
AC	0.220	0.936	0.219	0.097	0.957	0.413	0.891	0.552	0.787	0.355	0.921
ACE	0.277	0.689	0.601	0.366	0.899	0.340	0.928	0.313	0.811	0.356	0.894
FL	0.255	0.959	-0.024	0.042	0.825	0.339	0.902	0.546	0.773	0.286	0.776
PHE	0.893	0.267	0.313	0.754	0.580	0.870	0.363	0.935	0.311	0.577	0.786
ANT	0.831	0.134	0.363	0.781	0.478	0.823	0.319	0.808	0.451	0.520	0.643
FLU	0.941	0.192	0.246	0.869	0.371	0.946	0.229	0.962	0.244	0.554	0.804
PYR	0.897	0.165	0.359	0.692	0.455	0.954	0.269	0.841	0.398	0.593	0.774
BaA	0.973	0.200	-0.052	0.974	0.170	0.962	0.263	0.851	0.369	0.394	0.833
CHR	0.973	0.210	0.083	0.960	0.204	0.878	0.445	0.846	0.444	0.609	0.656
BbF	0.972	0.213	-0.048	0.969	0.170	0.897	0.407	0.960	0.166	0.950	0.291
BkF	0.975	0.206	0.024	0.968	0.160	0.841	0.466	0.960	0.174	0.951	0.286
BaP	0.953	0.237	-0.116	0.969	0.211	0.935	0.316	0.973	0.125	0.939	0.300
IcdP	0.976	0.204	0.026	0.959	0.225	0.902	0.370	0.949	0.173	0.954	0.269
DahA	0.936	0.198	-0.045	0.957	0.148	0.923	0.363	0.880	0.241	0.945	0.287
BghiP	0.961	0.184	0.093	0.920	0.331	0.893	0.400	0.930	0.211	0.950	0.290
Variance (%)	67.624	17.409	11.083	63.579	26.349	64.037	30.320	66.523	22.485	47.698	42.660

^{a)} See Table II for details of PAHs.

^{b)} See Fig. 1 for details of Zones A–E.

^{c)} Principal component.

TABLE VII

Multiple linear regression of principle component scores^{a)} against the 16 US Environmental Protection Agency priority polycyclic aromatic hydrocarbons (Σ_{16} PAHs) in topsoil of different urbanized density zones^{b)} of Shenzhen, China

Parameter	Zone A			Zone B		Zone C		Zone D		Zone E	
	S1	S2	S3	S1	S2	S1	S2	S1	S2	S1	S2
Regression coefficient	0.961	0.236	0.142	0.940	0.339	0.907	0.421	0.953	0.299	0.828	0.554
Contribution (%)	71.8	17.6	10.6	73.5	26.5	68.3	31.7	76.1	23.9	59.9	40.1

^{a)}S1 = fossil fuel combustion; S2 = oil; S3 = crop residue burning.

^{b)}See Fig. 1 for details of Zones A–E.

ring and household waste in the highly dense commercial district and residential area; three principle components occupied the rural zone samples, indicating the combined effect of anthropogenic and natural PAH sources. Agricultural biomass burning in this zone could not be ignored as a PAH source. The highest contribution rate defined as combustion source of fossil fuels was 76.1% in the suburban-urban center transitional zone, which partly explained why the value of Σ_{16} PAHs from this zone was higher than those in other zones. Such a high proportion (76.1%) of fossil fuel combustion source reflects the high intensity transportation and industrial activities in this region that consumed massive quantities of gasoline, diesel, and coal.

Risk assessment of surface soil PAHs

Maliszewska-Kordybach (1996) proposed that soil contaminated by PAHs can be classified to four levels: non-contaminated (Σ_{16} PAHs concentration < 200 ng g⁻¹), weakly contaminated (200 ng g⁻¹ concentration $< \Sigma_{16}$ PAHs concentration ≤ 600 ng g⁻¹), contaminated (600 ng g⁻¹ $< \Sigma_{16}$ PAHs concentration ≤ 1000 ng g⁻¹), and heavily contaminated (Σ_{16} PAHs concentration > 1000 ng g⁻¹). From Table VIII, soil samples classified as non-contaminated accounted for $> 70\%$ for Zone A, Zone B, and Zone C, as well as all 188 soil samples (72%). However, the contamination rates of soil samples (Σ_{16} PAHs concentration > 200 ng g⁻¹) from Zones E and D were 40% and 36%, re-

spectively, and the heavily contaminated rate of Zone D samples (Σ_{16} PAHs concentration > 1000 ng g⁻¹) was as high as 13%.

Our previous study showed that, for all 188 samples, the TEQ₁₀ values ranged from 3.58×10^{-3} to 598 ng g⁻¹, with an average of 21 ng g⁻¹. This average value was lower than 33 ng g⁻¹, the PAH contamination threshold of Dutch agricultural soil (Dutch Standard), and thus about 86.2% samples can be regarded as not contaminated (Zhang *et al.*, 2014). In this study, we further explored the spatial distribution of soil TEQ₁₀ which belongs to a significant environmental geography issue.

Ordinary Kriging interpolation was used to evaluate soil ecological risk with all samples symmetrically scattered in the entire city and log-transformed TEQ₁₀ data passing the normal distribution test. Compared to the Dutch standard, 76.1% of Shenzhen was still uncontaminated (TEQ₁₀ ≤ 33 ng g⁻¹) (Fig. 3). The polluted regions (TEQ₁₀ > 33 ng g⁻¹) were mainly distributed in high-level urbanized areas of north Bao'an and Longgang Districts probably because of heavy transportation, industry, and commerce activities in those areas. In addition, some contaminated regions near Shenzhen's city boundary in the south should also draw attention from the government and local environment protection department.

Although the background for PAH level in topsoil before urbanization was unavailable, the differences in PAH occurrences, sources, and ecological risks sugges-

TABLE VIII

Contamination levels of the 16 US Environmental Protection Agency priority polycyclic aromatic hydrocarbons (Σ_{16} PAHs) in topsoil from different urbanized density zones^{a)} of Shenzhen, China

Contamination level	Σ_{16} PAHs concentration	Total		Zone A		Zone B		Zone C		Zone D		Zone E	
		n	Percentage	n	Percentage	n	Percentage	n	Percentage	n	Percentage	n	Percentage
	ng g ⁻¹		%		%		%		%		%		%
Non-contaminated	≤ 200	135	72	23	85	24	71	32	84	39	64	17	60
Weakly contaminated	200–600	34	18	2	7	8	23	3	8	12	20	9	32
Contaminated	600–1000	5	3	1	4	1	3	0	0	2	3	1	4
Heavily contaminated	> 1000	14	7	1	4	1	3	3	8	8	13	1	4

^{a)}See Fig. 1 for details of Zones A–E.

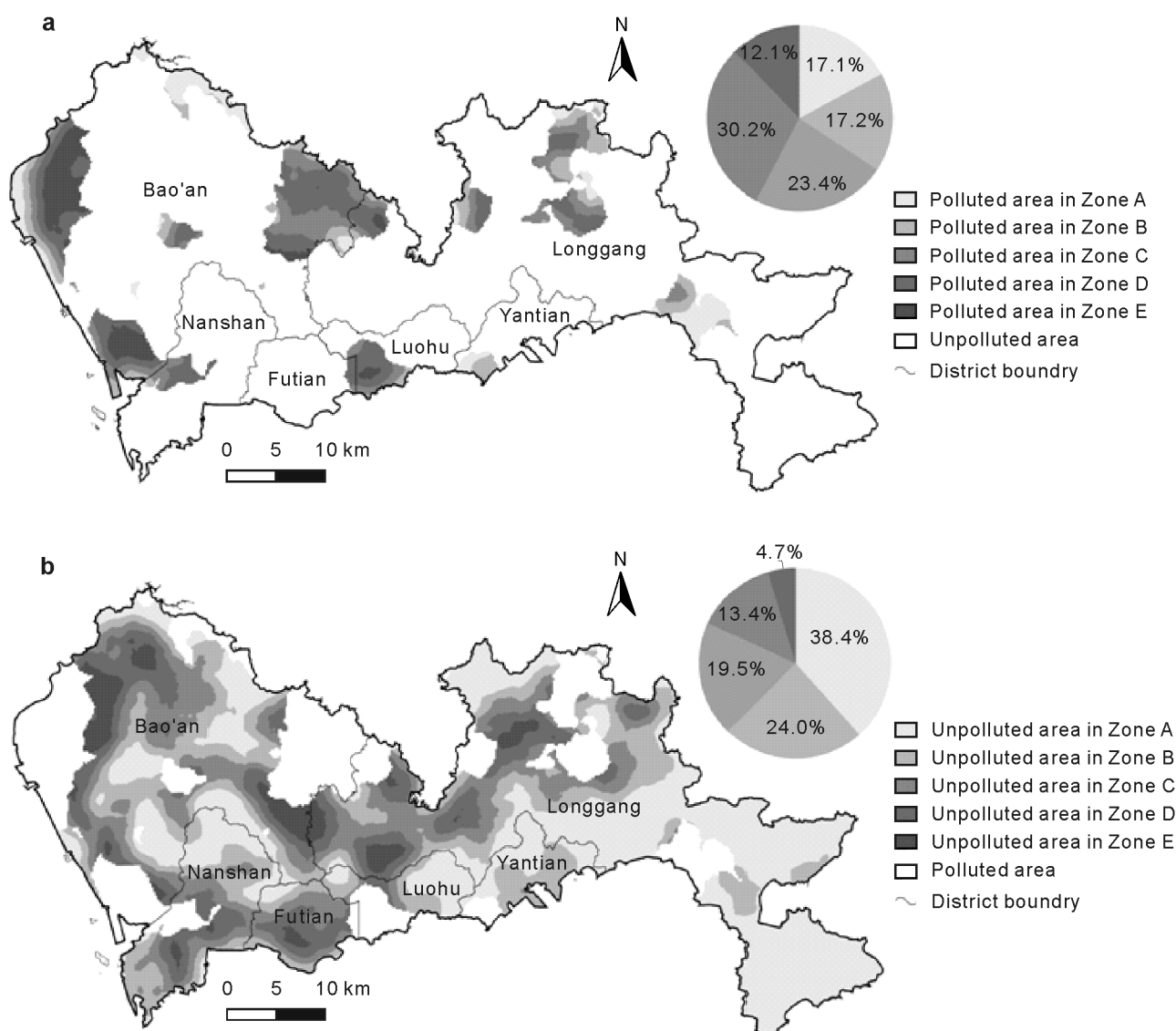


Fig. 3 Spatial urban density zoning for polycyclic aromatic hydrocarbon (PAH)-contaminated (466.8 km²) (a) and uncontaminated (1486.2 km²) (b) areas in different urbanized density zones of Shenzhen, China. See Fig. 1 for details of Zones A–E.

ted that the spatial PAH distribution was likely coupled with the urbanization level. Our results indicated that 466.8 km² in Shenzhen (23.9% of total area) was contaminated by PAHs, and 42.3% of the contaminated area was located in the highly-urbanized region (Zones D and E) (Fig. 3a). In contrast, the 1486.2 km² of unpolluted area (76.1% of total area) realized only an 18.1% contribution by the highly-urbanized region (Zones D and E) (Fig. 3b). Such high dependence of the spatial ecological risks of PAHs on the spatial urbanization pattern implies that the rapid urbanization of Shenzhen caused substantial environmental quality deterioration. In fact, the size and spatial distribution of soil PAH-polluted area in Shenzhen, closely related with the city's energy utilization, can provide a scientific basis for decisions regarding optimization of ener-

gy and industrial structure.

CONCLUSIONS

Average values of the Σ_{16} PAHs concentration in topsoil ranged from 139.3 to 479.4 ng g⁻¹, increasing in the order of Zone A < Zone B < Zone C < Zone E < Zone D. The mass inventories of Σ_{16} PAHs, Σ_7 CarPAHs, and BaP in topsoil were about 38.33, 17.99, and 1.94 Mg, respectively. High intensity urbanization accompanied by anthropogenic carbon input and soil stirring was a noticeable factor disrupting the equilibrium between PAHs and TOC. Fossil fuel combustion was the main source of PAHs for the five zones, with its maximum contribution observed in Zone D. The highest oil source contribution was in Zone E,

and the source apportionment of crop residue burning was only found in Zone A. About 42.3% of Shenzhen's PAH contaminated area was distributed in the highly-urbanized region, although only 23.9% of the entire city's area was polluted. Our study indicated that rapid urbanization of Shenzhen caused substantial environmental quality deterioration and PAH occurrences in highly-urbanized region which should cause concern.

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