



Characterization, Sources and Excessive Cancer Risk of PM_{2.5}-Bound Polycyclic Aromatic Hydrocarbons in Different Green Spaces in Lin'an, Hangzhou, China

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Abstract

PM_{2.5} samples were collected from residential, commercial, plaza and public green spaces in Lin'an, Hangzhou, in spring (March and April) and winter (February and December) in 2017. PAHs were detected by gas chromatography-mass spectrometry (GC-MS), and their sources were identified using the diagnostic ratio (DR) and principal component analysis-multiple linear regression (PCA-MLR). The average PAH concentration in winter was 1.3 times that in spring ($p < 0.01$). The PAH concentrations in the green spaces decreased as commercial > residential > plaza > public green space ($p < 0.05$). The sources of PAHs were vehicle emissions and coal combustion pollution transported by northern Chinese air masses. Slightly higher excessive cancer risks were determined in the commercial and residential green spaces than in the plaza and public green spaces. Green coverage, pedestrian volume, traffic flow and building density greatly influenced the decrease in the PAH concentration in the green spaces. Among the 4 types of green spaces, public green space had the most ecological benefits and should be fully utilized in urban green space planning to improve public health in urban spaces.

Keywords Urban green spaces · PM_{2.5} · PAHs · Concentration dynamics · Sources

Good air quality is the most basic prerequisite for cities to provide a living space for humans. In recent years, the accelerated urbanization in China, rapid development of chemical companies in cities and continuous increase in private car ownership have released high pollutant emissions into the urban atmosphere, which has decreased the air quality and has seriously affected the living environment (Butt et al.

2017). PAHs were discovered as the first and most numerous carcinogens and are mutagenic in nature (Longoria-Rodríguez et al. 2020). Studies have shown that high-ring and low-ring PAHs achieve free migration and mobility by adsorption on the surface of fine particles (e.g., PM_{2.5}) and coarse particles, respectively (Wu et al. 2006). They can be present anywhere in a city, such as the atmosphere,

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water bodies and soil. PAHs enter the human body through the respiratory tract, skin and other organs with particulate matter and endanger human health (Ma et al. 2020; Mihan-khah et al. 2020). At present, the common risk assessments include the exposure model, toxic model and risk model. BaP has the highest carcinogenicity among the 16 priority PAHs and usually serves as the indicator of the relative toxicity and carcinogenic risk of PAHs (Jamhari et al. 2014). They also precipitate to the soil through wet and dry deposition, affecting plant carbon allocation and root growth and polluting natural water bodies (Desalme et al. 2013), which can cause serious environmental problems if not addressed. Therefore, analyzing the pollution characteristics of PAHs in the atmosphere is an essential step in assessing urban ambient air quality and maintaining the health of a population.

Due to the rapid development of cities, the urban population has increased rapidly, and urban green spaces of all kinds have become essential spaces for human production, leisure and recreation. Numerous human activities continuously generate pollution emissions and have become the main sources of atmospheric PAHs in urban green spaces, seriously affecting the air quality of these spaces. Lodovici et al. (2003) analyzed the BaP concentration in the atmosphere of Florence and found that the PAH concentration in the mountains was lower than that at the other sites, and sometimes the concentration in urban parks was higher than that in the urban residential areas. He also found that vehicle exhaust was the main source of PAHs at all the sites. Dias et al. (2016) investigated the sources of PAHs on leaves in 4 types of forests, including a semi-deciduous forest and broad-leaved forest near the Atlantic Ocean, and found that all 4 communities were polluted by local vehicle exhaust. PAHs from biomass burning and chemical emissions were also detected in some communities. Indeed, urban green spaces play an important role in reducing PAH concentrations in the air. A plant canopy can impede airflow and thus reduce the diffusion of pollutants (Xing et al. 2020). The morphological characteristics of plant leaves can greatly influence PAHs at the micromolar scale, and leaf wax has a strong ability to retain PAHs with intermediate molecular weight and multiple rings (Tian et al. 2019). Therefore, airborne PAHs in urban green spaces should receive more attention.

The atmosphere of Hangzhou, the capital city of Zhejiang Province, is heavily polluted due to economic development, which has attracted the attention of many scholars. Zhu et al. (2009) analyzed PAH contents in indoor and outdoor air in Hangzhou's residential areas and found that the outdoor environment was the main source of indoor PAHs and that PAH contents were highest in the kitchen. In summer and winter, the permanent lung cancer risk reached 1.9×10^{-3} and 0.9×10^{-3} , respectively, which was higher than the average lung cancer risk for the general public. Bai et al.

(2016) studied the distribution, sources and cytotoxicity of PM_{2.5}-bound PAHs on city roads in Hangzhou and discovered that roadside PAHs mainly came from fuel combustion, houses and industrial emissions. The toxicity of micromolar PAHs is low, but they can enhance the toxicity of cytotoxic compounds and thus potentially pose a public health risk. Chen et al. (2017a) conducted experiments on the cytotoxicity of PAHs in fine particulates in Hangzhou's residential and commercial areas and found that the PAHs in fine particulates mainly originated from combustion and vehicle exhaust. The smaller the particulate size was, the greater the cytotoxicity. Most researchers have based their studies on large-scale urban districts or functional zones to analyze PAH concentration changes and sources, while few have probed the PAH pollution in urban green space microenvironments. Urban green spaces have many ecological benefits and can reduce the PAH concentration in the air effectively. Therefore, this study narrowed the research range (from the urban environment to urban green spaces) and compared the characteristics of PM_{2.5}-bound PAH pollution in different urban green spaces at the level of an individual's exposure. This study also evaluated carcinogenic risk and explored the influence of various green space factors on PAH concentrations to inform efforts to reduce the potential for direct contact with pollution sources in daily life, decrease the effects of pollution on the human body and improve the quality of human life.

Methods and Materials

The Lin'an District (118°51' ~ 119°52'E, 29°56' ~ 30°23'N) is located in northwest Hangzhou, Zhejiang Province, China, with a monsoonal climate and subtropical broad-leaved evergreen forests. According to the *Standard for Classification of Urban Green Spaces*, urban green spaces can be classified into 5 major categories, 13 sub-categories and 11 minor categories (MOHURD 2017). According to the proximity of a type of urban green space to daily life activities, residential green space, commercial green space, plaza green space and public green space were selected for the study. To minimize and eliminate interference from other factors that could lead to errors in the test results, the test design required consistency and comparability of test conditions as much as possible. The selection of the research objects was determined on the basis of thorough research and evaluation, with the main considerations including human activities and natural environmental conditions. With the distribution of green spaces in Lin'an District fully considered, 4 places were selected for research: the "Spring" Community, "Yijin" Commercial Street, "Wuzhou" Plaza and the East Lake Campus of Zhejiang A&F University as they were less disturbed by the surrounding environment and other factors (Fig. 1).

The 4 study sites are surrounded by similar physical conditions, with good accessibility, flat topography, adequate sunlight, no other heat sources and no high-emission pollution sources within a 5 km diameter. Each site is enclosed by roads to ensure its independence and integrity, and the interior mainly consists of buildings and vegetation. The characteristic indicators of plant landscape configuration, plant species, planting density, depression and maturity were generally consistent.

The “Spring” Community, which is located at the foot of Mount Linglong, has a green area ratio of 42.5%. The sampling site was chosen between buildings 3 and 4 of the plot, with an area of approximately 1500 m². “Yijin” Commercial Street is located in the center of Lin’an, with an area of 1800 m² consisting of approximately 40% green space. “Wuzhou” Plaza is located in the northeast of Lin’an, with an area of 4500 m² mainly consisting of hard pavement and a green space of 35%. The selected public green area is located on the south side of building 4 at the Zhejiang A&F University East Lake Campus, which has a sample area of 1600 m².

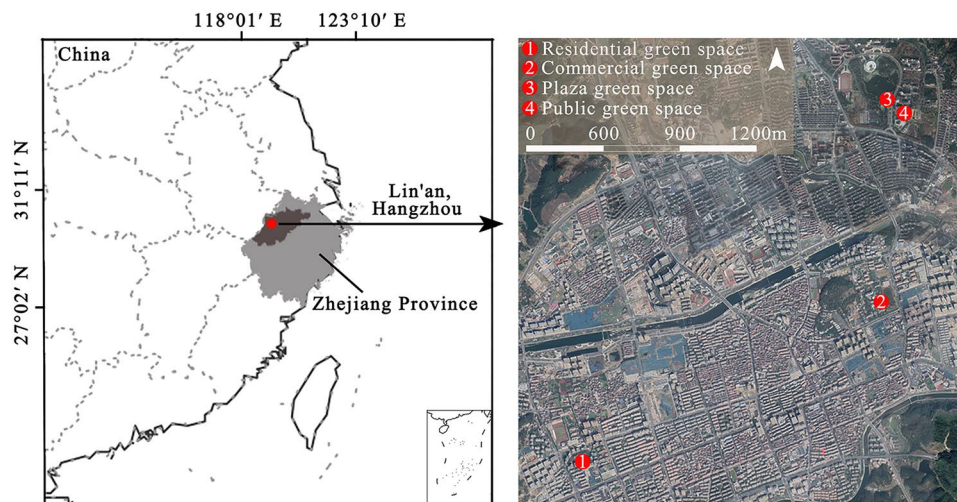
In this study, PM_{2.5} sampling was performed in strict accordance with the Chinese National Standard HJ 194-2017 (MOEP 2017). Before sampling, the filter papers were burned in a muffle furnace covered with silver paper (temperature of 450°C) for 4 h to remove impurities. Then, they were placed in a constant-temperature and consistent-humidity chamber (Premium ICH) (temperature of 25°C; relative humidity of 50%) for 48 h. The mass of the filter papers was weighed and immediately recorded after removal using a 10000th electronic balance (SI-234). The weighing was repeated 3 times, and an average value was taken as the mass of the filter papers before sampling. Then, the filter papers were stored at room temperature in filter boxes for later use. A previous study showed that the PM_{2.5} pollution of Hangzhou is higher in spring and winter than that in other seasons (Bao et al. 2010), which indicated that spring and winter

seasons were more conducive to the detection of accurate PAH concentrations; thus, our study was conducted in spring (March and April) and winter (February and December) of 2017. The experiment could not be implemented in January and May 2017 due to persistent low temperatures, snowfall, and continuous rainfall during the rainy season. There was no rain or strong wind for 5~7 days before the experiment. On the experiment day, the weather should be clear, and the wind speed should be less than 2 m/s to avoid errors in the test results caused by external factors. The sampling was simultaneously conducted at each green space. One intelligent medium-flow TSP sampler (KC-120H) was installed at the center of each green space, 1.5 m above the ground, with a quartz fiber filter membrane (CAT No. 1851-090) and a sampling head of ϕ 2.5 μ m. We reset the sampler value to zero and continuously sampled for 24 h (8:00~8:00 the next day). In total, 96 PM_{2.5} samples were obtained during the sampling period. After sampling, the filter papers were weighed under constant temperature and humidity again, and the mass was recorded. The difference in mass between the 2 measured times was the concentration of PM_{2.5}.

Gas chromatography analysis conditions: the chromatographic column was a DB-5MS capillary column (30 m \times 0.25 mm \times 0.25 μ m). The carrier gas was highly purified helium with a flow rate of 1.0 ml/min and temperature of 240°C. Splitless injection was used. In the temperature program, the temperature was initially held at 70°C for 2 min, increased to 300°C at a rate of 10°C/min and held for 5 min. Mass spectrometry analysis conditions: the ion source temperature was set at 230°C, the quadrupole temperature was set at 150°C, and the connector temperature was set at 280°C. The ionization energy was 70 eV. Ion scanning mode was applied for qualitative analysis. The mass range was 35~500 amu.

The processed filters were cut into pieces of 0.5 cm², wrapped with filter paper, and placed into a Soxhlet extractor

Fig. 1 Location of the sampling sites



with ether: hexane (1:9). Then, the samples were extracted for 16 h. The extract was transferred to a round-bottom flask, and n-hexane was added to the Soxhlet extractor for further extraction. The 2 extracts were combined, and the solvent was evaporated to near dryness on a rotary evaporator (R-210). Then, the extract was redissolved in 1 ml of n-hexane for analysis. Next, the PAHs were quantitatively and qualitatively analyzed using the total ion scanning mode of the gas chromatograph-mass spectrometer (7890A/5975C) based on the relative retention time of the analytes and the peak area variations of target ions (MOEP 2013). Mixed solutions of 16 PAH standards (200 mg/ml, 1 ml) were added to hexane and prepared into different concentration gradients of 0.5 mg/ml, 1 mg/ml and 2 mg/ml to generate standard curves. A blank sample was analyzed every 8 samples for blank analysis and recovery analysis. In the blank experiment, the target compounds were not detected and thus did not affect the results. Naphthalene- d_8 (0.5 mg/l; representative of 2-3 ring PAHs) and perylene- d_{12} (0.5 mg/l; representative of PAHs with more than 4 rings) were added to all the quality-assured samples before Soxhlet extraction to serve determine the method recoveries. The recovery of naphthalene- d_8 was 45% ~ 52% with a standard deviation of 4.2% ~ 5.6%. The recovery of perylene- d_{12} was 70% ~ 120% with a standard deviation of 4.8% ~ 7.9%, which met the requirements for standard methods.

The diagnostic ratio (DR) has been widely used in source analysis studies. Here, Flu/(Flu + Pyr), BaA/(BaA + Chr), IcdP/(IcdP + BghiP) and BaP/BghiP were chosen to qualitatively analyze the sources of $PM_{2.5}$ -bound PAHs (Tobiszewski et al. 2012). The principal component analysis-multiple linear regression (PCA-MLR) model was run in SPSS 23.0 to identify pollution sources quantitatively (Mehmood et al. 2020). The Kaiser-Meyer-Olkin (KMO) test of the variables in PCA returned a value > 0.78, and the determination

coefficient R^2 of MLR was > 0.90; these values are suitable for the running conditions. The total equivalent concentration (TEQ) and excessive cancer risk (ECR) of PAHs were calculated using the PAH total equivalence factors (TEFs) and unit risk (UR_{BaP}), which can be used to estimate the risk of developing lung cancer from exposure to atmospheric PAHs (Fan et al. 2018). The equations are as follows:

$$TEQ = \sum_{i=1}^n C_i \times TEF_i$$

$$ECR = \sum (TEQ) \times UR_{BaP}$$

TEQ is the total carcinogenic equivalent concentration of PAHs (ng/m^3); C_i is the concentration of the i^{th} individual PAH in $PM_{2.5}$; TEF_i is the i^{th} toxic equivalence factor of PAH; ECR is the excessive cancer risk; and UR_{BaP} is 8.7×10^{-5} per ng/m^3 according to the World Health Organization (WHO) data.

Results and Discussion

Figure 2a shows the average PAH concentrations and ring counts in spring and winter in Lin'an. The PAH concentrations were $23.56 \pm 4.79 ng/m^3$ in spring and $31.43 \pm 5.22 ng/m^3$ in winter ($p < 0.01$), which showed a trend of high values in winter and low values in spring. This finding has been confirmed in studies by other scholars (Albuquerque et al. 2016; Chang et al. 2019). According to the statistics from the Lin'an meteorological station, the total rainfall in spring was 305.2 mm (178.4 mm in March and 126.8 mm in April), and that in winter was 67.2 mm (22.3 mm in February and 44.9 mm in December). Frequent rainfall in spring

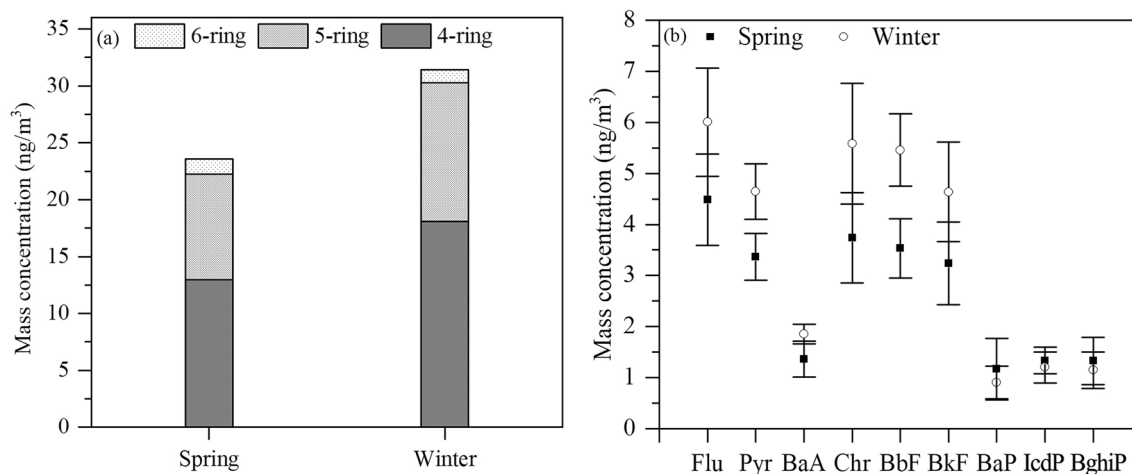


Fig. 2 Seasonal changes in PAH mean concentrations and ring numbers (a) and PAH monomer concentrations (b) in Lin'an

accelerates the wet deposition of PAHs, resulting in lower concentrations than those in winter (Gao et al. 2012; Wang et al. 2013). In both seasons, the PAH concentrations followed a pattern of 4-ring > 5-ring > 6-ring PAHs. This may be a result of PAHs with different molecular weights having different settling rates in the atmosphere (Liu et al. 2006). Figure 2b shows the seasonal variations in the PAH monomer concentrations. The concentrations of PAH monomers with lower molecular weights, such as Flu and Pyr, were higher in winter, while the concentrations of monomers with higher molecular weights, such as BaP and IcdP, were lower in winter. The high molecular weight PAHs (6-ring) mainly originated from the exhaust of large construction vehicles or heavy trucks (diesel vehicles) in the vicinity of urban green spaces. Due to the low winter temperatures, construction activity in urban areas was significantly lower in winter than that in spring, resulting in a lower intensity of polymeric PAH emissions in winter. Chen et al. (2016) found similar results, with higher concentrations of PM_{2.5}-bound PAHs in winter than that in spring but lower concentrations of individual PAH monomers, such as Ant, Pny, BbF and Ind, in winter than that in spring and summer. The concentrations of BaP in Hangzhou were 1.17 ± 0.60 ng/m³ in spring and 0.91 ± 0.32 ng/m³ in winter, which were lower than those in large cities, such as Beijing (13.3 ng/m³) and Shenzhen (2.0 ng/m³), China (Liu et al. 2010; Chen et al. 2017b), and met the Chinese environmental standard (2.5 ng/m³) (MOEE 2012). Compared with European urban atmospheric BaP (1.0–10.0 ng/m³), it was at a low level (Sosa et al. 2017).

The changes in the PAH monomer concentrations in each urban green space are shown in Fig. 3. The mean concentrations in spring were 16.98 ± 4.73 ~ 27.26 ± 6.21 ng/m³ in the green spaces with the following descending order: commercial green space (27.26 ± 6.21 ng/m³) > residential

green space (26.94 ± 5.51 ng/m³) > plaza green space (23.08 ± 2.66 ng/m³) > public green space (16.98 ± 4.74 ng/m³). In winter, the PAH concentrations in each green space were 26.32 ± 4.26 ~ 37.23 ± 5.28 ng/m³, exhibiting the same trend as that in spring. However, all values were higher than those in spring, suggesting that the meteorological factors had a small impact on PAHs in the microcosm. The difference in the PAH contamination level in the commercial green space and public green space was large in both seasons, similar to the findings of Wang et al. (2017). The commercial green space is located in the business areas of Lin'an District with abundant commercial activities and heavy vehicle traffic, which led to increase PAH concentrations, while the public green space was mainly for teaching with a single type of activity and a good environment, which was conducive to low PAH levels, and the overall pollution was lower than that of the commercial green space. The BaP concentrations in the residential (1.96 ± 0.99 ng/m³) and commercial (1.19 ± 0.50 ng/m³) green spaces were higher than those in the public (0.60 ± 0.16 ng/m³) and plaza (0.61 ± 0.25 ng/m³) green spaces. During the sampling period, there was high traffic flow in the residential and commercial green spaces: 40–80 vehicles/h and 150–250 vehicles/h, respectively. The flow in plaza green space was 50–100 vehicles/h, and the traffic flow was lowest in the public green space. BaP supposedly originates from vehicle exhaust, and its concentration variation might be related to the traffic flow in the green spaces.

Figure 4a shows the DR of PM_{2.5}-bound PAHs in the 4 types of urban green spaces in spring. Flu/(Flu + Pyr) in all the green spaces was higher than 0.50, and BaP/BghiP was all higher than 0.60, which indicated that the ubiquity of biomass burning, coal combustion and vehicle exhaust existed in the 4 types of green spaces. Biomass burning

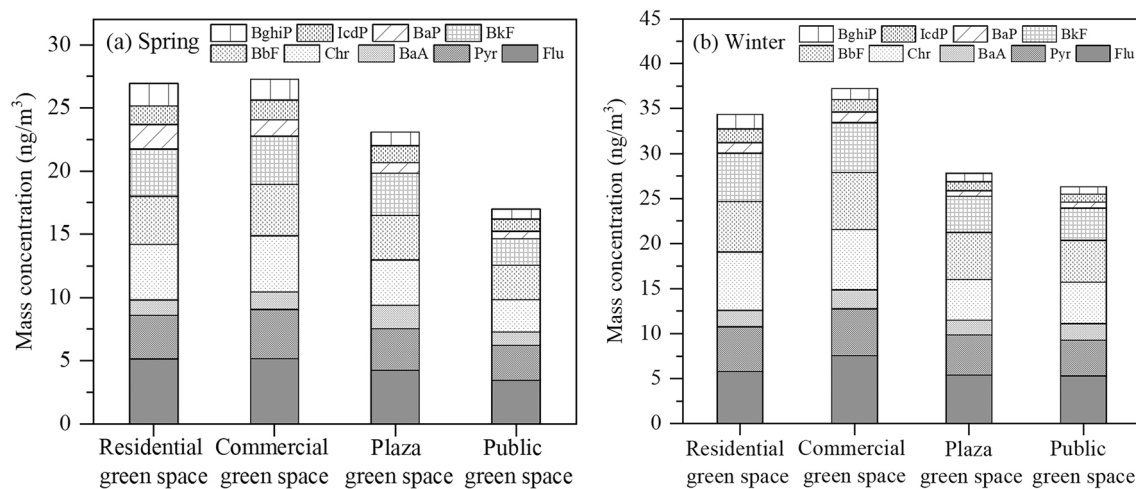


Fig. 3 Changes in the PAH monomer concentrations in the 4 types of green spaces in spring (a) and winter (b)

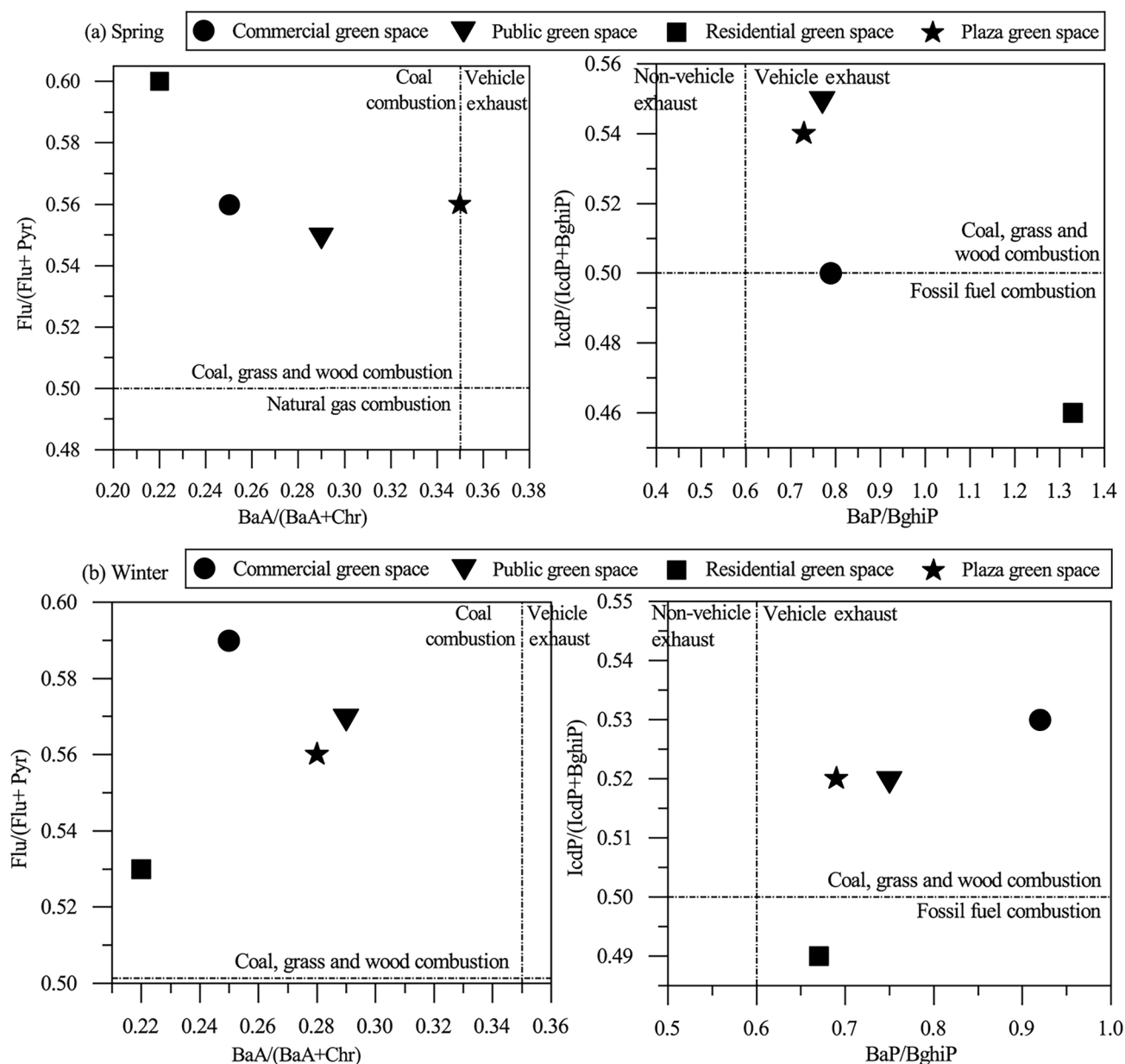


Fig. 4 DR of PM_{2.5}-bound PAHs in the 4 types of urban green space in spring (a) and winter (b)

pollution might result from the biomass materials in the coal. BaA/(BaA + Chr) was 0.35 in the plaza green space but lower than 0.35 in the residential, commercial and public green spaces, which again indicated that there was coal combustion pollution in the 4 types of green spaces. IcdP/(IcdP + BghiP) was lower than 0.50 in the residential green space, which might originate from the combustion of fossil fuels (natural gas). However, it was higher than 0.50 in the plaza and public green spaces, which were impacted by sources of coal, grass and wood combustion. The ratio was 0.50 in the commercial green space, where the sources were

complex and might have included the combustion of fossil fuels, coal, grasses and woods.

Figure 4b shows the analysis result for winter. In all types of green spaces, Flu/(Flu + Pyr) was higher than 0.50, BaA/(BaA + Chr) was lower than 0.35, and BaP/BghiP was higher than 0.60. These data indicated that the main pollution sources in all the green spaces were similar, namely, coal combustion and vehicle exhaust. IcdP/(IcdP + BghiP) was lower than 0.50 only in the residential green space, showing that the pollution source here was more likely to be fossil fuel combustion (natural gas). The pollution in the other

types of green space might have originated from coal, grass and wood combustion.

Tables 1 and 2 show the results of the PCA. BkF, BbF, IcdP and BghiP originate from diesel and gasoline engines, and diesel exhaust contains higher levels of polymeric PAHs than gasoline exhaust (Callén et al. 2013). Flu and Pyr are byproducts of coal combustion (Tian et al. 2009), and BaA and Chr are markers of natural gas (Lee et al. 2007). Table 1 shows the principal components of PAHs in the 4 types of green spaces in spring. The PC 1 values of the residential, commercial and public green spaces were closely associated with multiple PAH monomers and were presumed to come from mixed sources. The monomers in PC 2 of the commercial green space were mainly Flu (0.738) and Pyr (0.484), and the outdoor eateries at this green space use coal as the main energy source, which might be the source. PC 1 of the plaza green space was associated with characteristic monomers, such as BbF (0.864), Chr (0.857) and IcdP (0.809). PC 3 was mainly related to BaP and BghiP. Combined with the actual situation of the plaza green space, it could be seen that vehicles around the green space moved frequently; thus, the pollution sources were mainly vehicle emissions and diesel engines. Moreover, PC 2 is mainly related to Pyr, BaA and BkF, which might originate from coal combustion. PC 2 of the public green space had a high proportion of macromolar PAHs, which came from diesel engines. The winter results are presented in Table 2. The high scores for each of the individual components in both PC1 of the residential green space and PC1 of the public green space might be due to the small spacing of buildings within the green spaces, which was not conducive to the dispersion of PAHs, and the aggregation formed a mixed source. PC 2 of the residential green space was associated with BaP (0.790), BghiP (0.633) and

IcdP (0.434). BaP originated from vehicle exhaust (Bortey-Sam et al. 2015). The majority of residents in the settlements own only petrol-based private cars. The diesel exhaust might come from the emissions of medium-weight and heavy trucks (diesel vehicles) outside the green space. PC 1 of the commercial green space was highly correlated with Chr (0.919), Pyr (0.873) and BaA (0.861), which represented coal and natural gas. PC 2 was associated with polymeric monomers, possibly from diesel engines. PC 3 contained Pyr (0.337) and BaP (0.728), which originated from natural gas combustion. Low-ring PAHs in PC 1 of the plaza green space possibly originated from coal and petrol engines. PC 2 was opposite and was likely from diesel engines. PC 3 was associated with Chr (0.895) and Flu (0.247) and represented a coal combustion source. PC 2 of the public green space had distinct characteristic monomers of Chr (0.659), BkF (0.549) and Pyr (0.465) from coal and petrol engines. The public green space had low anthropogenic disturbances and tailpipe emissions, and the sources of pollution were not obvious and probably affected by atmospheric circulations.

The results of the DR analysis were similar to those of the PCA. The 4 urban green spaces had a complicated variety of sources of PAH pollution, most of which were associated with human activities and mainly affected by vehicle exhaust and coal combustion. There were differences in the sources of PAHs in spring and winter, indicating that seasonal changes impact pollution sources. The Lin'an District is dominated by tourism and high-tech equipment manufacturing industries, and there are no large heavy industrial enterprises that use coal as their main fuel; therefore, much of the pollution from coal combustion in the green spaces comes from the transport of air masses from northern China to a great extent.

Table 1 Principal component analysis of PAHs in each green space in spring

PAHs	Residential green space		Plaza green space			Public green space		
	PC1	PC1	PC2	PC1	PC2	PC3	PC1	PC2
Flu	0.958	0.541	0.738	- 0.530	- 0.593	- 0.432	0.963	- 0.052
Pyr	0.893	0.815	0.484	0.705	0.532	- 0.086	0.727	0.375
BaA	0.975	0.813	0.415	- 0.550	0.634	0.412	0.821	0.189
Chr	0.962	0.917	- 0.129	0.857	- 0.056	- 0.313	0.923	0.080
BbF	0.963	0.905	- 0.141	0.864	- 0.251	0.084	0.839	- 0.114
BkF	0.979	0.783	- 0.456	0.329	0.864	0.056	0.956	0.048
BaP	- 0.233	0.789	- 0.348	- 0.396	- 0.211	0.860	0.107	0.851
IcdP	0.848	0.792	- 0.272	0.809	- 0.163	0.321	- 0.320	0.861
BghiP	0.661	0.901	- 0.041	0.592	- 0.528	0.535	- 0.243	0.891
Cumulative (%)	74.34	66.16	81.64	42.58	67.03	84.82	53.03	80.36
Sources	Mixed sources	Mixed sources	Coal combustion	Vehicle emissions	Coal combustion	Diesel engines	Mixed sources	Diesel engines

Table 2 Principal component analysis of PAHs in each green space in winter

PAHs	Residential green space		Commercial green space		Plaza green space		Public green space		
	PC1	PC2	PC1	PC2	PC1	PC2	PC1	PC2	
Flu	0.931	-0.244	0.661	0.445	0.836	0.462	0.778	-0.469	
Pyr	0.891	-0.272	0.873	-0.292	0.913	0.224	0.764	0.465	
BaA	0.691	-0.374	0.861	-0.060	0.772	0.448	0.709	0.188	
Chr	0.939	-0.246	0.919	-0.070	0.327	0.243	0.702	0.659	
BbF	0.938	-0.120	0.760	-0.264	0.830	0.284	0.901	0.285	
BkF	0.948	-0.248	0.808	-0.387	0.788	-0.041	0.763	0.549	
BaP	0.572	0.790	-0.025	0.637	-0.452	0.773	0.842	-0.462	
IcdP	0.858	0.434	0.283	0.888	-0.548	0.725	0.847	-0.505	
BghiP	0.760	0.633	0.389	0.911	-0.700	0.676	0.815	-0.547	
Cumulative (%)	71.55	18.04	47.19	28.16	50.44	24.29	62.99	22.83	
Sources	Mixed sources	Vehicle exhaust	Coal and gas combustion	Diesel engines	Coal and petrol engines	Diesel engines	Coal combustion	Mixed sources	Coal and petrol engines

Table 3 shows the MLR results of the PAH pollution sources in the 4 types of urban green space. The mixed sources in the residential (74.34%) and commercial green space (78.41%) had a high rate of contribution in spring. As there were frequent human activities in these 2 green spaces and the sources of PAHs were diverse, PAHs were easily mixed under the influence of the atmospheric environment. The high contribution of vehicle emissions in the plaza green space, 53.04% and 84.62% in spring and winter, respectively, might be due to the absence of tall buildings and trees separating the road from the plaza green space. Mixed sources accounted for a high proportion of the total pollution sources in the public green space, amounting to 65.20% in spring and 52.43% in winter. This might have resulted from the poor diffusion conditions due to dense plant coverage in the green spaces.

Table 4 shows the ECR of PAHs in each green space. The average TEQ in winter ($1.15 \pm 0.08 \text{ ng/m}^3$) was higher than that in spring ($1.09 \pm 0.17 \text{ ng/m}^3$). The ECR was $(10.10 \pm 1.00) \times 10^{-6} \text{ ng/m}^3$ in winter and $(9.47 \pm 0.83) \times 10^{-6} \text{ ng/m}^3$ in spring, which is 9~10 times higher than the US standard, whose risk exceeds human tolerable levels (1×10^{-6}). Lu et al. (2017) revealed that the ECR of PAHs in Hangzhou is high, with risk values of $5.8 \times 10^{-6} \sim 2.5 \times 10^{-4}$, which is similar to the results of this study. The risk was highest in spring in the residential green space, at $(13.30 \pm 1.06) \times 10^{-6} \text{ ng/m}^3$, and lowest in the public green space, at $(5.73 \pm 0.55) \times 10^{-6} \text{ ng/m}^3$. In winter, the risk was lowest in the public green space and highest in the commercial green space. In the commercial green space, the intensity and frequency of anthropogenic activities were high, and there were more potential sources of pollution, especially in low temperature conditions when PAH concentrations rise more rapidly, which can lead to increased risk. In the public green space, there was less human interference and relatively low risk. The risk in the residential green space was higher in spring than that in winter for 2 reasons. On the one hand, the macromolar PAH concentrations (such as BaP, IcdP and BghiP) in this zone was higher in spring than that in winter. These macromolar PAHs have high toxicity equivalence factors (TEFs)(Fan et al. 2018), which indicates high toxicity. Thus, higher concentrations of these PAHs led to a high ECR. On the other hand, the increase in the number of leaves and leaf density in spring enhanced the canopy density inside the community and impeded the transport of PAHs. Studies have revealed that the absorptivity of PAHs on plants can be influenced by leaves (leaf surface number and leaf density), canopy morphology and specific species behavior (new leaf growth and flower bud burst) (Terzaghi et al. 2015). Different types of plants have different influences on the air pollution in cities. In narrow streets, tall trees aggravate air pollution, while short hedges reduce it (Abhijith et al. 2017).

Table 3 Source contributions for PAHs in the 4 types of urban green space in spring and winter

Types of green space	Spring			Winter		
	Source	Contribution (%)	Regression coefficient	Source	Contribution (%)	Regression coefficient
Residential green space	Mixed sources	74.34	$\sum_{PAHs} = 0.630PC1$	Mixed sources	67.48	$\sum_{PAHs} = 0.166PC1 + 0.080PC2$
Commercial green space	Mixed sources	78.41	$\sum_{PAHs} = 0.697PC1 + 0.187PC2$	Coal and gas combustion	48.39	$\sum_{PAHs} = 0.951PC1 + 0.898PC2 + 0.116PC3$
	Coal combustion	21.59		Diesel engines	45.70	
Plaza green space	Gas combustion			Gas combustion	5.91	
	Vehicle emissions	53.04	$\sum_{PAHs} = 0.279PC1 + 0.140PC2 + 0.107PC3$	Coal and petrol engines	84.62	$\sum_{PAHs} = 0.908PC1 + 0.165PC2 + 0.160PC2$
	Coal combustion	26.62		Diesel engines	15.37	
Public green space	Diesel engines	20.34		Coal combustion	14.91	
	Mixed sources	65.20	$\sum_{PAHs} = 0.770PC1 + 0.411PC2$	Mixed sources	52.43	$\sum_{PAHs} = 0.464PC1 + 0.421PC2$
	Diesel engines	34.80		Coal and petrol engines	47.57	

Table 4 ECR assessment of PAHs in each green space

	Risk parameter		Residential green space	Commercial green space	Plaza green space	Public green space
Spring (ng/m ³)	TEQ		1.53 ± 0.05	1.23 ± 0.05	0.94 ± 0.07	0.66 ± 0.03
	ECR	× 10 ⁻⁶	13.30 ± 1.06	10.70 ± 0.96	8.11 ± 0.76	5.73 ± 0.55
Winter (ng/m ³)	TEQ		1.35 ± 0.11	1.41 ± 0.09	0.93 ± 0.05	0.91 ± 0.08
	ECR	× 10 ⁻⁶	11.70 ± 0.97	12.30 ± 1.90	8.18 ± 0.65	7.95 ± 0.44

In general, the pollution by PM_{2.5}-bound PAHs was mild in Lin’an, Hangzhou. The average PAH concentration was 23.56 ± 4.79 ng/m³ in spring and 31.43 ± 5.22 ng/m³ in winter. The concentration in winter was 1.3 times that in spring (*p* < 0.01). The abundances of PAHs with different numbers of rings in the 2 seasons followed a trend of 4-ring > 5-ring > 6-ring. The differences in distribution characteristics were distinct in all the green spaces (*p* < 0.05). The average PAH concentration across all the green spaces was 16.98 ± 4.73 ~ 27.26 ± 6.21 ng/m³ in spring and 26.32 ± 4.26 ~ 37.23 ± 5.28 ng/m³ in winter, and the average PAH concentration in each green space decreased as commercial green space > residential green space > plaza green space > public green space. The major sources of PAHs in the green spaces were vehicle exhaust and coal combustion transported by northern Chinese air masses. The ECR in the plaza and public green spaces was lower than that in the commercial and residential green spaces. The total PAH concentration was mainly influenced by pedestrian volume, traffic flow, green coverage and building density. Among the 4 types of green spaces, public green space had the most ecological benefits and should be fully utilized in urban green space planning to improve the quality of public health in urban spaces.

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