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PAPER

# Polycyclic aromatic hydrocarbons with molecular weight 302 in PM<sub>2.5</sub> at two industrial sites in South China†

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Daytime and nighttime PM<sub>2.5</sub> samples were collected between August 5 and 16, 2009 and between January 24 and February 4, 2010 in an industrial complex site (site A) and an electronic waste recycling site (site B) to determine the seasonal and diurnal variations of 19 individual polycyclic aromatic hydrocarbons (PAHs) with molecular weight 302 (MW302) including four highly carcinogenic dibenzopyrene (DBP) isomers dibenzo[*a,l*]pyrene (DB*al*P), dibenzo[*a,e*]pyrene (DB*ae*P), dibenzo[*a,i*]pyrene (DB*ai*P), and dibenzo[*a,h*]pyrene (DB*ah*P). This is the first report on DBP isomers in air particles from South China. The total concentration of PAH MW302 isomers ranged from 1.65 to 3.60 ng m<sup>-3</sup> in summer and 3.82 to 9.81 ng m<sup>-3</sup> in winter. The strongest peaks in the chromatograms of the MW302 isomers were naphtha[2,1-*a*]pyrene (N21*a*P), dibenzo[*j,l*]fluoranthene (DB*jl*F), naphtha[1,2-*b*]fluoranthene (N12*b*F), naphtha[1,2-*k*]fluoranthene (N12*k*F) and dibenzo[*a,e*]fluoranthene (DB*ae*F), constituting 52.0 to 55.4% of the total MW302 isomers. All the MW302 isomers showed notable seasonal variations. Most of the MW302 isomers in site B showed distinctive diurnal variations with higher concentrations occurring in the night. Taking into account both concentration and potency equivalence factors (PEFs), the strongest carcinogen in the analyzed samples was DB*ai*P, and the ratios of sum carcinogenic potency of four highly carcinogenic DBP isomers to benzo[*a*]pyrene (BaP) was about 0.94 in winter to 1.89 in summer, indicating the importance of DBP isomers for the risk assessment. Health risk assessment indicated that on average, 1 in 100 000 residents in the two industrial sites may have an increased risk of cancer due to PAH exposure.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a worldwide concern due to their known carcinogenic and mutagenic properties.<sup>1–3</sup> They can be emitted from the incomplete combustion of carbon-containing materials, and from nearly all anthropogenic sources in urban environments.<sup>4</sup> The composition and sources of PAHs in the atmosphere has been extensively studied.<sup>5–7</sup> Due to the ubiquitous occurrence and the extreme eco-toxicological relevance of PAHs, the U.S. Environmental Protection Agency (U.S EPA) and the European Community selected 16 PAHs with molecular weights (MW) from 128 to 278 for their “Priority Pollutant List”. The most well-known priority PAH is benzo[*a*]

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### Environmental impact

Priority PAHs have been extensively studied due to their known carcinogenic and mutagenic properties. However, some studies show that priority PAHs may constitute only a portion of the mutagenic and carcinogenic PAH-related activities, and PAHs with high molecular weight (HMW) exhibit a large contribution. Therefore, accurate measurements should be made to quantify the HMW PAHs to evaluate the potential health risks related to PAH pollution in the atmosphere. This study characterized the seasonal and diurnal variations of 19 individual PAHs with molecular weight (MW) 302 including four highly carcinogenic dibenzopyrene isomers. The results would expand the current knowledge of the carcinogenic risk of PAHs in the atmosphere of South China.

pyrene (BaP), which is classified by the International Agency for Research on Cancer (IARC) as carcinogen to human beings. However, some studies have shown that priority PAHs may constitute only a portion of the mutagenic and carcinogenic PAH-related activities in complex environmental samples.<sup>8,9</sup>

In recent years, PAHs with MW greater than 300, so-called high molecular weight (HMW) PAHs have been studied more and more widely. HMW PAHs extracted from environmental and combustion samples showed a positive mutagenic response.<sup>9–11</sup> Marvin *et al.*<sup>10</sup> observed that the PAHs with MW 302 to 352 in coal-tar-contaminated sediment exhibited ~25% of the total PAHs mutagenic activity. PAHs with MW 302 (12 species) in urban airborne particles contributed ~33% to the total mutagenicity of the PAHs fraction, and observed that naphtha[2,1-*a*]pyrene (N21aP), dibenzo[*a,l*]pyrene (DBaIP), dibenzo[*a,e*]pyrene (DBaeP), naphtha[2,3-*a*]pyrene (N23aP), naphtha[2,3-*e*]pyrene (N23eP), and dibenzo[*b,k*]fluoranthene (DBbkF) were the most active mutagens.<sup>12</sup> Wornat *et al.*<sup>11</sup> found strong mutagens of DBaeP and N21aP in soot extract from domestic coal-burning stoves.

HMW PAHs have been identified in combustion-related samples such as coal tar,<sup>13–15</sup> fuel combustion exhaust,<sup>16–18</sup> and in the environmental air particulate matter.<sup>19–21</sup> The U.S. Department of Health and Human Services (HHS) has listed four MW302 isomers including dibenzo[*a,l*]pyrene (DBaIP), DBaeP, DBaIP, and dibenzo[*a,h*]pyrene (DBahP) as potential carcinogens to humans.<sup>22</sup> DBaIP was probably the most potent chemical carcinogen ever tested based on the study by Platt *et al.*<sup>23</sup> Therefore, accurate measurements should be taken to quantify the HMW PAHs to evaluate the potential health risks related to PAH pollution in the atmosphere.

Qingyuan is located in South China, adjacent to the Pearl River Delta (PRD), with a total area of 19 000 km<sup>2</sup> and a population of 4 000 000. Rapid urbanization and industrialization in the last few decades have caused serious atmospheric pollution problems. The atmospheric conditions are under the strong influence of the Asian monsoon system, with the southwesterly monsoons bringing in relatively clean air from the ocean in the summer, and northeasterly winds bringing in air masses moving across northern cities in winter. In previous papers, we reported the detailed studies on phase partitioning, size distribution and seasonal variation of priority PAHs in the atmosphere of the PRD region.<sup>24,25</sup> The purpose of this study was to (1) analyze the seasonal and diurnal variation of the PAH isomers with MW302 associated with PM<sub>2.5</sub>; (2) identify the emission sources of the MW302 isomers; and (3) assess the carcinogenic risk of the MW302 isomers. The results would expand the current knowledge of the carcinogenic risk of PAHs in the atmosphere of South China.

## 2. Materials and methods

### 2.1 Sites description

Two sampling sites were chosen in the Qingcheng district and Longtang town of Qingyuan. Site A was located in an industrial complex area that included numerous factories for clothing, photocopier, automobile services, *etc.* The samples were collected on the rooftop of a five-story building approximately

15 m above ground. Site B was located in a primary school surrounded by electronic waste (e-waste) lots and workshops, with electrical cables and wires being the major e-waste materials. Burning wires for copper recovery was an occasional event in this area as well. Site A was situated approximately 10 km northwest of site B.

Sampling was conducted between August 5 and 16, 2009, and between January 24 and February 4, 2010. During these periods, the diurnal PM<sub>2.5</sub> samples were collected from 07:30 to 19:30 (local time) for the daytime samples, and from 19:30 to 07:30 the following day for the nighttime samples. The air samples were drawn at about 1.13 m<sup>3</sup> min<sup>-1</sup> through the quartz fiber filters (QFFs, 20.3 cm × 25.4 cm, Whatman) using a high-volume sampler (GUV-15HBL1, Thermo, USA) equipped with a PM<sub>2.5</sub> size-selective inlet. Other special devices such as diffusion denuders and foam plugs were not used due to the difficulties in applying these devices. Consequently, volatilization losses or decomposition artifacts may occur on the filter for semi-volatile organic compounds (Grosjean, 1983), but for the high molecular weight compounds, these artifacts should be negligible. Before and after sampling, the filters were put under constant temperature (25 °C) and relative humidity (50%) for 24 h before weighing. The sampled filters were wrapped with annealed aluminum foil and stored in a refrigerator at -40 °C until analysis. The weather parameters during the sampling periods are presented in Table S1, ESI†.

### 2.2 Extraction and instrumental analyses

The extraction and instrumental analyses have been published elsewhere.<sup>25–27</sup> Briefly, surrogate standard dibenzo[*a,l*]pyrene-d14 was spiked onto the filters prior to extraction. The ultrasonic extraction with dichloromethane was applied, although Sun and Weavers (2006) observed that the ultrasonic bath used for extraction may lead to partial semi-volatile PAH degradation. Then the extracts were filtered, concentrated and separated by a silica-alumina column. Fraction I (40 mL of hexane) was discarded, while fraction II (100 mL of DCM–hexane (1 : 1)) which contained the HMW PAHs was collected and reduced almost to dryness, then dissolved with *n*-hexane. Internal standard corone-d12 was added before instrumental analyses.

All samples were analyzed using gas chromatography with mass selective detection (GC/MS). The mass spectrometer was operated in electron impact ion (EI) mode and selected ion monitoring (SIM). Chromatographic peaks of samples were identified based on the molecular mass ion and the retention times, and *m/z* 302 were used for quantification of individual PAH isomers. The quantification of each compound was based on the reference standards or the relative response factors.<sup>27</sup> The instrumental conditions for MW302 PAH isomers as well as priority PAHs, and quality assurance/quality control (QA/QC) are provided in the ESI†.

### 2.3 Elemental carbon (EC) analysis

A Thermal–Optical Carbon Aerosol Analyzer (Sunset Laboratory) operating with a modified NIOSH (National Institute of Occupational Safety and Health) thermal–optical transmission (TOT) protocol was used for the EC analysis. A punch

( $1.5 \times 1.0 \text{ cm}^2$ ) of each filter was heated stepwise at temperatures of 310, 475, 615, and 840 °C in a pure He atmosphere for detecting the organic carbon (OC) fraction, and at temperatures of 550, 625, 700, 775 and 850 °C in an oxidizing atmosphere of 2% oxygen in a balance of He for detecting the EC fraction. Replicate analyses were performed to eliminate the non-uniformity of filter samples. The difference determined from replicate analyses was smaller than 15% for EC. The detection limits for EC were below  $0.1 \mu\text{g cm}^{-2}$ . The concentrations of EC are presented in Table S1, ESI†.

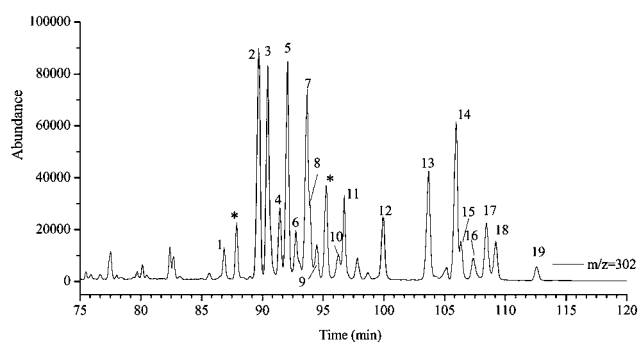
## 2.4 Statistical analysis

Correlations between individual compounds and meteorological parameters were tested using the *Pearson* coefficients. The non-parametric Mann–Whitney *U*-test was employed to detect the differences between sites, diurnal and seasonal variations. A *p* value of  $< 0.05$  was considered to indicate statistical significance. The levels of all compounds were  $\log_{10}$  transformed to obtain a normal distribution, and data were analyzed using the SPSS software package.

## 3. Results and discussion

### 3.1 Occurrence of the PAH MW302 isomers

The average concentrations of 19 individual PAH MW302 isomers are given in Table 1 and a representative chromatogram is depicted in Fig. 1. The average  $\sum$ MW302 isomers were measured with concentrations ranging from 1.65 to  $3.60 \text{ ng m}^{-3}$  in summer and 3.82 to  $9.81 \text{ ng m}^{-3}$  in winter. Although the non-parametric Mann–Whitney *U*-test confirmed the significant higher concentrations in site A than in site B for most of the MW302 isomers (Table S2, ESI†), the distribution pattern of



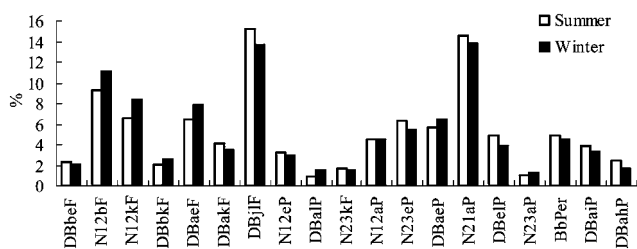
**Fig. 1** GC/MS chromatogram obtained in selected ion monitoring mode (extracted ion *m/z* 302) in this study. Peaks marked with asterisks correspond to the unknown compounds. For peak numbering refer to Table 1.

MW302 PAHs was quite similar, indicating a similar emission source for these PAH species. The most abundant MW302 isomers were N21aP, DBj/F, N12bF, N12kF and dibenzo[*a,e*]fluoranthene (DBaeF), which constituted 52.0% to 55.4% of the total MW302 isomers in sites A and B (Fig. 2). A similar profile was also found in other studies.<sup>12,15</sup> The abundance order for the highly carcinogenic DBP isomers in this study was identified as the following: DBaeP ( $0.08\text{--}0.67 \text{ ng m}^{-3}$ ) > DBaiP ( $0.07\text{--}0.34 \text{ ng m}^{-3}$ ) > DBahP ( $0.05\text{--}0.14 \text{ ng m}^{-3}$ )  $\approx$  DBalP ( $0.01\text{--}0.23 \text{ ng m}^{-3}$ ), which was nearly identical with the air particulates of SRM 1648, SRM 1649a and atmosphere particulate matters in Stockholm.<sup>20,27</sup>

The concentration levels of four highly carcinogenic DBP isomers were compared with the other studies (Table S3, ESI†). For instance, the average concentration of DBaeP in this study was  $314 \text{ pg m}^{-3}$ , which was higher than that in Boston ( $133 \text{ pg m}^{-3}$ ),<sup>19</sup> Riverside, USA ( $2.7 \text{ pg m}^{-3}$ )<sup>28</sup> and Stockholm, Sweden

**Table 1** Average concentrations of PM<sub>2.5</sub>-bound PAH isomers with MW302 (unit:  $\text{ng m}^{-3}$ )

Peak No.	Peak identity	Abbreviate	Summer				winter			
			Site A		Site B		Site A		Site B	
			Day ( <i>n</i> = 11)	Night ( <i>n</i> = 11)	Day ( <i>n</i> = 11)	Night ( <i>n</i> = 11)	Day ( <i>n</i> = 10)	Night ( <i>n</i> = 11)	Day ( <i>n</i> = 10)	Night ( <i>n</i> = 11)
1	dibenzo[ <i>b,e</i> ]fluoranthene	DBbeF	0.07	0.07	0.04	0.07	0.17	0.18	0.09	0.11
2	naphtho[1,2- <i>b</i> ]fluoranthene	N12bF	0.37	0.29	0.13	0.35	1.01	1.14	0.41	0.61
3	naphtho[1,2- <i>k</i> ]fluoranthene	N12kF	0.28	0.21	0.09	0.24	0.79	0.92	0.29	0.45
4	dibenzo[ <i>a,e</i> ]fluoranthene	DBaeF	0.26	0.20	0.09	0.26	0.72	0.82	0.29	0.44
5	dibenzo[ <i>b,k</i> ]fluoranthene	DBbkF	0.08	0.07	0.03	0.09	0.24	0.28	0.09	0.15
6	dibenzo[ <i>a,k</i> ]fluoranthene	DBakF	0.14	0.12	0.07	0.12	0.26	0.31	0.13	0.16
7	dibenzo[ <i>i,l</i> ]fluoranthene	DBj/F	0.49	0.42	0.28	0.46	1.10	1.20	0.59	0.69
8	naphtho[1,2- <i>e</i> ]pyrene	N12eP	0.11	0.08	0.06	0.09	0.25	0.25	0.13	0.15
9	dibenzo[ <i>a,l</i> ]pyrene	DBalP	0.04	0.04	0.01	0.05	0.15	0.23	0.03	0.10
10	naphtho[2,3- <i>k</i> ]fluoranthene	N23kF	0.06	0.06	0.03	0.05	0.14	0.18	0.05	0.08
11	naphtho[1,2- <i>a</i> ]pyrene	N12aP	0.16	0.13	0.08	0.13	0.39	0.47	0.16	0.23
12	naphtho[2,3- <i>e</i> ]pyrene	N23eP	0.22	0.18	0.11	0.20	0.46	0.44	0.23	0.27
13	dibenzo[ <i>a,e</i> ]pyrene	DBaeP	0.22	0.18	0.08	0.23	0.58	0.67	0.23	0.37
14	naphtho[2,1- <i>a</i> ]pyrene	N21aP	0.51	0.42	0.26	0.44	1.14	1.30	0.55	0.67
15	dibenzo[ <i>e,l</i> ]pyrene	DBelP	0.14	0.12	0.10	0.15	0.25	0.26	0.18	0.19
16	naphtho[2,3- <i>a</i> ]pyrene	N23aP	0.06	0.04	0.01	0.04	0.13	0.19	0.03	0.07
17	benzo[ <i>b</i> ]perylene	BbPer	0.17	0.15	0.08	0.17	0.38	0.49	0.15	0.23
18	dibenzo[ <i>a,l</i> ]pyrene	DBalP	0.13	0.11	0.07	0.12	0.28	0.34	0.12	0.16
19	dibenzo[ <i>a,h</i> ]pyrene	DBahP	0.07	0.06	0.05	0.06	0.11	0.14	0.07	0.07
	$\sum$ MW302 isomers		3.60	2.95	1.65	3.33	8.53	9.81	3.82	5.20



**Fig. 2** The average distribution of individual PAH isomers with MW302 in sites A and B.

(23.7  $\text{pg m}^{-3}$ ).<sup>20</sup> Layshock *et al.*<sup>21</sup> observed the extremely high concentrations of these four MW302 isomers (total  $\sim 24 \text{ ng m}^{-3}$ ) in Beijing, China, which were much higher than those in this study. The highest concentration of up to  $2.75 \text{ ng m}^{-3}$  for the four isomers was measured in this study in site A on the night of January 28, 2010.

### 3.2 Seasonal variation of PAH MW302 isomers

Seasonal variation of MW302 isomers was noted during this study, which may be governed by meteorological conditions such as atmospheric stability and variations in the strength of potential emission sources. The non-parametric Mann–Whitney *U*-test confirmed that the individual MW302 isomers were significantly different between the two seasons ( $p < 0.01$ ) (Table S2, ESI<sup>†</sup>). In site A, the mean concentrations of individual MW302 isomers were higher in winter than in summer, and increased by a factor of 0.6–4.8. While in site B, it increased by a factor of 0.2–2.2. The ratio between winter and summer MW302 isomer concentrations was approximately one-third of those for priority PAHs (0–10.1 in site A, and 0–10.6 in site B) (Table S4, ESI<sup>†</sup>), showing a small influence of season. This could be explained by their non-volatility and association mainly with fine particles. Qingyuan is known to have no significant increase of domestic home heating sources of coal and wood burning in winter, which have been suggested to account mainly for the increase of ambient concentrations of PAHs in winter in the northern cities of China.<sup>29</sup> The seasonal variation of MW302 isomers might correlate with the Asian monsoon climate of Qingyuan. When the southwesterly monsoon prevails in warm seasons, relatively clean air ventilates from the ocean, and when northeasterly winds prevail in cold seasons, “dirty” air masses are brought in from northern cities. Moreover, the accumulation of inverse layers frequently occurring in cold seasons also play a role in the higher concentrations of MW302 isomers.

In order to investigate the influence of meteorological conditions on the seasonal variation of MW302 isomers, correlations between the individual MW302 isomers and the meteorological parameters were calculated (Table 2). MW302 isomers showed statistically significant negative correlations with ambient temperature and wind speed. The negative correlation between MW302 PAHs and wind speed can be interpreted as pollutant dilution caused by higher atmospheric turbulence and vertical mixing as wind speed increases.<sup>30</sup> A significant positive correlation between individual MW302 PAHs and relative humidity was also observed in site B. Additionally, it can be seen that the meteorological parameters exhibited greater influence on the monitored variable in site B than in site A, which suggested that

the emission sources in the e-waste recycling site were more localized and stable.

### 3.3 Diurnal variation of PAH MW302 isomers

In this study, the average concentrations of MW302 isomers were generally higher after the boundary layer collapsed at night, but the opposite trend was observed during summer at site A, with higher concentrations found in the day samples, when the mixing layer depth was relatively high and primary emissions were intense (Table 1). The non-parametric Mann–Whitney *U*-test indicated that there was no significant diurnal variation for all the individual MW302 PAHs at site A, but significant diurnal variations were observed at site B for most of the individual MW302 isomers (Table S2, ESI<sup>†</sup>). The diurnal variation of four representative MW302 isomers including DBakF, N23kF, N23aP and DBaIP in site B are present in Fig. S1, ESI<sup>†</sup>.

The diurnal variation of organic pollutants in the atmosphere was possibly governed by source characterization, temperature, OH radical concentration, atmospheric mixing layer height and stability.<sup>31</sup> In this study, mixing layer height and temperature caused by the day-to-night transition did not equally affect the concentrations of all MW302 isomers in sites A and B. Meanwhile, the effects from OH reaction and photolysis were not significant for the HMW PAHs either, since they are almost exclusively in the particles. Thus, source characterization and atmospheric stability might be the significant factors controlling the short-term variability of MW302 isomers in this study. Since site A was characterized by complex industries, the production and motor transportation activities in this area would generate much more MW302 PAH emission in the daytime, while the low mixing layer at night would have a concentrating effect on the PAH isomers, thus offsetting the less anthropogenic emission.<sup>32,33</sup> This may explain the lack of diurnal variations in site A. Whereas, the diurnal behavior in site B is characteristic for air pollutants from local emissions.<sup>31</sup>

### 3.4 Emission sources of PAH MW302 isomers

The PAH MW302 isomers have been identified in combustion-related samples indicating a direct emission characteristic in the atmosphere.<sup>34–36</sup> Black carbon, also known as elemental carbon (EC), is essentially a primary pollutant, emitted directly during the incomplete combustion of fossil and biomass carbonaceous fuels.<sup>37</sup> We performed a correlation analysis between the individual MW302 isomers and EC (Table 2). The strong relationships ( $p < 0.01$ ) were observed for all the species in both sites confirming the similar sources between MW302 isomers and EC.

The patterns of MW302 isomers in the coal tar (SRM 1597),<sup>27</sup> diesel particles (SRM 1650, SRM 2975)<sup>16, 38</sup> and in the air particles have been reported.<sup>20,21</sup> In order to further identify the sources, their patterns were compared with this study. Due to the limited data, the four highly carcinogenic MW302 PAHs (DBaIP, DBaeP, DBaIP and DBahP) were chosen as examples. The distributions in sites A and B were quite similar and the DBaeP and DBaIP contribution (74.7–76.2%) to the total four DBP isomers was much higher than that of DBaIP and DBahP (23.8–25.3%) (Fig. 3). The distribution pattern from street canyons from Stockholm, Sweden<sup>20</sup> was in accordance with the

**Table 2** Pearson correlation analyses of individual MW302 isomers with ambient parameters

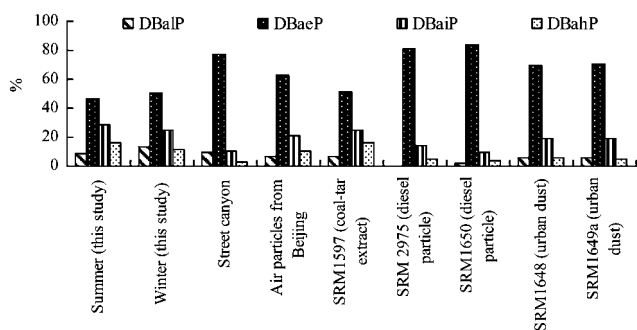
MW302 isomers	Site A				Site B			
	Temperature	Relative humidity	Wind speed	EC	Temperature	Relative humidity	Wind speed	EC
DBbeF	-0.475 <sup>a</sup>	0.279	-0.337 <sup>b</sup>	0.929 <sup>a</sup>	-0.434 <sup>a</sup>	0.443 <sup>a</sup>	-0.476 <sup>a</sup>	0.860 <sup>a</sup>
N12bF	-0.480 <sup>a</sup>	0.234	-0.327 <sup>b</sup>	0.936 <sup>a</sup>	-0.496 <sup>a</sup>	0.554 <sup>a</sup>	-0.523 <sup>a</sup>	0.851 <sup>a</sup>
N12kF	-0.485 <sup>a</sup>	0.232	-0.324 <sup>b</sup>	0.931 <sup>a</sup>	-0.477 <sup>a</sup>	0.429 <sup>a</sup>	-0.508 <sup>a</sup>	0.790 <sup>a</sup>
DBaeF	-0.477 <sup>a</sup>	0.234	-0.338 <sup>b</sup>	0.932 <sup>a</sup>	-0.502 <sup>a</sup>	0.569 <sup>a</sup>	-0.530 <sup>a</sup>	0.850 <sup>a</sup>
DBbkF	-0.465 <sup>a</sup>	0.245	-0.358 <sup>b</sup>	0.939 <sup>a</sup>	-0.486 <sup>a</sup>	0.583 <sup>a</sup>	-0.534 <sup>a</sup>	0.842 <sup>a</sup>
DBakF	-0.446 <sup>a</sup>	0.255	-0.331 <sup>b</sup>	0.887 <sup>a</sup>	-0.468 <sup>a</sup>	0.479 <sup>a</sup>	-0.489 <sup>a</sup>	0.843 <sup>a</sup>
DBj/F	-0.473 <sup>a</sup>	0.267	-0.341 <sup>b</sup>	0.933 <sup>a</sup>	-0.370 <sup>b</sup>	0.359 <sup>b</sup>	-0.359 <sup>b</sup>	0.686 <sup>a</sup>
N12eP	-0.474 <sup>a</sup>	0.242	-0.300 <sup>b</sup>	0.921 <sup>a</sup>	-0.430 <sup>a</sup>	0.436 <sup>a</sup>	-0.457 <sup>a</sup>	0.849 <sup>a</sup>
DBalP	-0.478 <sup>a</sup>	0.227	-0.357 <sup>b</sup>	0.897 <sup>a</sup>	-0.430 <sup>a</sup>	0.538 <sup>a</sup>	-0.450 <sup>a</sup>	0.684 <sup>a</sup>
N23kF	-0.465 <sup>a</sup>	0.260	-0.372 <sup>b</sup>	0.889 <sup>a</sup>	-0.448 <sup>a</sup>	0.547 <sup>a</sup>	-0.502 <sup>a</sup>	0.800 <sup>a</sup>
N12aP	-0.504 <sup>a</sup>	0.253	-0.306 <sup>b</sup>	0.916 <sup>a</sup>	-0.470 <sup>a</sup>	0.423 <sup>a</sup>	-0.352 <sup>b</sup>	0.699 <sup>a</sup>
N23eP	-0.418 <sup>a</sup>	0.217	-0.264	0.813 <sup>a</sup>	-0.476 <sup>a</sup>	0.525 <sup>a</sup>	-0.491 <sup>a</sup>	0.864 <sup>a</sup>
DBaeP	-0.482 <sup>a</sup>	0.245	-0.338 <sup>b</sup>	0.929 <sup>a</sup>	-0.464 <sup>a</sup>	0.576 <sup>a</sup>	-0.552 <sup>a</sup>	0.849 <sup>a</sup>
N21aP	-0.488 <sup>a</sup>	0.254	-0.323 <sup>b</sup>	0.920 <sup>a</sup>	-0.499 <sup>a</sup>	0.528 <sup>a</sup>	-0.511 <sup>a</sup>	0.880 <sup>a</sup>
DBelP	-0.503 <sup>a</sup>	0.278	-0.265	0.875 <sup>a</sup>	-0.470 <sup>a</sup>	0.419 <sup>a</sup>	-0.380 <sup>b</sup>	0.757 <sup>a</sup>
N23aP	-0.435 <sup>a</sup>	0.151	-0.324 <sup>b</sup>	0.846 <sup>a</sup>	-0.333 <sup>b</sup>	0.424 <sup>a</sup>	-0.456 <sup>a</sup>	0.604 <sup>a</sup>
BbPer	-0.468 <sup>a</sup>	0.270	-0.345 <sup>b</sup>	0.885 <sup>a</sup>	-0.449 <sup>a</sup>	0.594 <sup>a</sup>	-0.509 <sup>a</sup>	0.820 <sup>a</sup>
DBaiP	-0.482 <sup>a</sup>	0.238	-0.329 <sup>b</sup>	0.894 <sup>a</sup>	-0.433 <sup>a</sup>	0.524 <sup>a</sup>	-0.539 <sup>a</sup>	0.833 <sup>a</sup>
DBahP	-0.463 <sup>a</sup>	0.244	-0.284	0.833 <sup>a</sup>	-0.413 <sup>a</sup>	0.374 <sup>b</sup>	-0.382 <sup>b</sup>	0.732 <sup>a</sup>

<sup>a</sup>  $p < 0.01$ . <sup>b</sup>  $p < 0.05$ .

diesel particles (SRM 2975, SRM 1650),<sup>38</sup> and this may demonstrate the major vehicle emission source in street canyons. The distribution in the air particles in Beijing, China during winter<sup>21</sup> was also identical to that from St. Louis, USA (SRM1648) and Washington D.C., USA (SRM 1649a).<sup>27</sup> The distribution in this study was closer to that of coal-tar extract (SRM 1597) and air particles from urban Beijing, and distinct from that of diesel particles (SRM 2975, SRM 1650).<sup>38</sup> These results suggested that coal combustion may contribute significantly to the MW302 isomers in this study. Additionally, a relatively high contribution of DBalP was found, which was also observed in street canyons in Stockholm, Sweden,<sup>20</sup> suggesting vehicle emission being a significant contributor as well.

### 3.5 Health risk assessment

Since each PAH is different in carcinogenic activity, their aggregate concentration is not a good measure for assessing



**Fig. 3** Average distribution patterns of the four highly carcinogenic MW302 PAHs from sites A and B, street canyons from Stockholm, Sweden,<sup>20</sup> air particles from Beijing,<sup>21</sup> SRM 1648, 1649a,<sup>27</sup> and SRM 1597, 2975, 1650.<sup>38</sup>

health risks. A better way is to multiply their respective concentrations and potency equivalency factors (PEFs), that is, total BaP carcinogenic equivalence concentrations (BaP-CEC), which are often used for risk assessment of PAHs.<sup>39</sup> In order to assess the risk of PAHs, seven priority PAHs including benz[a]anthracene (BaA), chrysene (Chry), benzo[b]fluorethene (BbF), benzo[k]fluorethene (BkF), BaP, indeno[1,2,3-cd]pyrene (IcdP), and dibenzo[ah]anthracene (DBahA) and four highly carcinogenic DBPs were included. The concentrations of the priority PAHs are listed in Table S4, ESI†. The PEFs developed by the Office of Environmental Health Hazard Assessment (OEHTA) by comparing the cancer activity of the chemicals relative to BaP,<sup>40</sup> were applied in the present study (Table 3). BaP-CEC in site A were higher (5.31–20.3 ng m<sup>-3</sup>, average 12.8 ng m<sup>-3</sup>) than in site B (3.27–9.49 ng m<sup>-3</sup>, average 6.38 ng m<sup>-3</sup>).

The concentration of ΣMW302 isomers (1.65–9.81 ng m<sup>-3</sup>, average 4.86 ng m<sup>-3</sup>) was approximately one tenth of Σpriority PAHs (10.5–98.9 ng m<sup>-3</sup>, average 46.4 ng m<sup>-3</sup>) in this study (Table S4, ESI†). However, the contribution of the MW302 isomers (32.1–60.0%, average 43.0%) to BaP-CEC was equally important as that of the priority PAHs (40.0–67.9%, average 57.0%). The average contribution of the individual PAHs to the BaP-CEC in sites A and B is demonstrated in Table 3. Although BaP represented the biggest contribution to the total carcinogenic potency, the contributions of the four MW302 PAHs were comparably higher than or equal to the other priority PAHs. The mean contribution of the four MW302 isomers in this study in winter (average 33.3%) was quite similar to the recent study that reported ~30% contribution to the total carcinogenic PAHs in Beijing, China.<sup>21</sup> The MW302 isomers represented a larger contribution to the BaP-CEC during summer (average 51.4%). The strongest carcinogen in the analyzed samples was DBaiP (Table 3), and the ratios of sum carcinogenic potency of four highly carcinogenic DBP isomers to BaP was about 0.94 in winter to 1.89 in summer, indicating the importance of the DBP

**Table 3** Potency equivalency factors (PEFs) (OEHHA, 2005) and average relative contribution (%) of individual PAHs to BaP-CEC from sites A and B

Compounds	PEFs	Summer	Winter
BaA	0.1	0.71	0.95
Chry	0.01	0.14	0.21
BbF	0.1	3.30	6.15
BkF	0.1	1.45	2.50
BaP	1	27.1	35.4
IcdP	0.1	9.48	11.8
DBaH <sub>A</sub>	0.4	6.42	9.74
DBaP	10	8.17	8.54
DBaE <sub>P</sub>	1	4.14	3.10
DBaI <sub>P</sub>	10	25.1	15.1
DBaH <sub>P</sub>	10	14.0	6.53

isomers for the risk assessment. Therefore, the assessment of carcinogenic risks of PAHs species would be grossly underestimated without considering PAH MW302 isomers.

Further human health risk assessment was conducted based on the inhalation unit risk (UR). The UR<sub>BaP</sub> of  $1.1 \times 10^{-3}$  ( $\mu\text{g m}^{-3}$ )<sup>-1</sup>, obtained from an animal study, has been used for inhalation risk calculation.<sup>40</sup> The lifetime cancer risk were then estimated using the following equation:<sup>21</sup>

$$\text{Cancer risk} = \text{BaP-CEC} \times \text{UR}_{\text{BaP}} \quad (1)$$

The average BaP-CEC in summer and winter were used. The calculated excess cancer risk was  $5.8 \times 10^{-6}$  for site A and  $3.6 \times 10^{-6}$  for site B during the summer, and  $2.2 \times 10^{-5}$  for site A and  $1.0 \times 10^{-5}$  for site B during the winter. Based on the calculations, there is approximately three times as great a risk as based on BaP alone in this study. Similarly, Layshock *et al.*<sup>21</sup> reported a ten times increase when the same 11 PAHs were included in the risk assessment of the particles from Beijing, China, compared with the risk based on BaP alone. Sauvain *et al.*<sup>41</sup> also observed a five times increase in risk when 15 PAHs were included in the risk assessment for the diesel exhaust-exposed worker in Switzerland. To some extent, the importance of including other PAHs in risk assessments was addressed. Previous investigations have reported the annual excess cancer risk of Chinese people at  $6.5 \times 10^{-6}$  for population-weighted PAHs concentrations,<sup>42</sup> lower than the average lifetime cancer risk of this study ( $1.0 \times 10^{-5}$ ). Therefore, effective management policies and remediation techniques are urgently needed to prevent the deterioration of environmental quality in the industrial sites. Additionally, it should be recognized that gas phase PAHs and the other particulate matter components were not taken into account and only IARC classified carcinogens were included, which implies an underestimation of the risk.

#### 4. Conclusion

This study reports 19 MW302 isomers in air particles from two industrial sites of Qingyuan, South China. All the WM302 PAHs showed notable seasonal variation with higher concentrations in winter, and MW302 isomers showed significant contribution in assessing the cancer risk. The findings suggest that including DBP isomers along with BaP may improve the determination of the carcinogenic potency of PAHs in ambient air.

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