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Polycyclic Aromatic Hydrocarbons in $PM_{2.5}$ and $PM_{2.5–10}$ in Urumqi, China: Temporal Variations, Health Risk, and Sources

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Abstract: $PM_{2.5}$ and $PM_{2.5–10}$ samples were simultaneously collected in Urumqi from January to December 2011, and 14 priority polycyclic aromatic hydrocarbons (PAHs) were determined. The mean concentrations of total PAHs in $PM_{2.5}$ and $PM_{2.5–10}$ were 20.90~844.22 ng m^{-3} and 19.65~176.5 ng m^{-3} respectively, with the highest in winter and the lowest in summer. Above 80% of PAHs were enriched in $PM_{2.5}$, which showed remarkable seasonal variations compared to coarse particles. High molecular weight (HMW) PAHs were predominant in $PM_{2.5}$ (46.61~85.13%), whereas the proportions of lower molecular weight (LMW) and HMW PAHs in $PM_{2.5–10}$ showed a decreasing and an increasing trend, respectively, from spring to winter. The estimated concentrations of benzo[a]pyrene equivalent carcinogenic potency (BaP_{eq}) in $PM_{2.5}$ (10.49~84.52 ng m^{-3}) were higher than that of in $PM_{2.5–10}$ (1.15~13.33 ng m^{-3}) except in summer. The estimated value of inhalation cancer risk in $PM_{2.5}$ and $PM_{2.5–10}$ were 1.63×10^{-4}~7.35×10^{-3} and 9.94×10^{-5}~1.16×10^{-3}, respectively, far exceeding the health-based guideline level of 10^{-4}. Diagnostic ratios and positive matrix factorization results demonstrated that PAHs in $PM_{2.5}$ and $PM_{2.5–10}$ were from similar sources, such as coal combustion, biomass burning, coking, and petroleum combustion, respectively. Coal combustion was the most important source for PAHs both in $PM_{2.5}$ and $PM_{2.5–10}$, accounting for 54.20% and 50.29%, respectively.

Keywords: PAHs; particulate matter; particle size distribution; sources

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous constituents of particulate matter in the atmosphere and well-known to be carcinogenic and/or mutagenic [1,2], and are emitted into the atmosphere from natural as well as anthropogenic sources. Natural sources include forest fires and volcanic eruptions, while anthropogenic sources include meat cooking, motor vehicles, road dust (including particles generated by tire wear and brake lining erosion), natural gas home appliances, tobacco smoke, asphalt, boilers, coal combustion, wood burning [3,4], solid waste incineration, and petroleum spills and discharge [5].

Urumqi, the capital of Xinjiang Uygur Autonomous Region of China, is in central Xinjiang, which is on the north foot of Tianshan Mountain and the south edge of Jungger Basin. It is located in the center of Asia, north of the Taklimakan desert and south of the Gurbantunggut desert (Figure 1). Three sides of it are surrounded by the Tianshan Mountain, of which the highest elevation is 5000 m. The particles are brought into the urban area from the Quasigeer basin through the north–south route [6,7]. Rapid economic development has caused more and more serious air pollution problems in Urumqi, which is one of the most polluted cities during winter in China [8]. During the six months of heating, the city was covered by the haze for at least one third of the time. Li et al. (2008) reported that the mean concentrations of PM_{10} in the winter of 2006 in Urumqi was 305.6 $\mu g\ m^{-3}$ with a maximum of 1048.5 $\mu g\ m^{-3}$, and the mean concentrations of $PM_{2.5}$ (particle diameter $\leq$2.5 µm) and TSP (Total Suspended Particulate, particle diameter $\leq$100 µm) in the winter of 2007 were 187 and 385 $\mu g\ m^{-3}$ with a maximum of 487 and 1313 $\mu g\ m^{-3}$, respectively, far higher than the National Ambient Air Quality Standard of China [6].

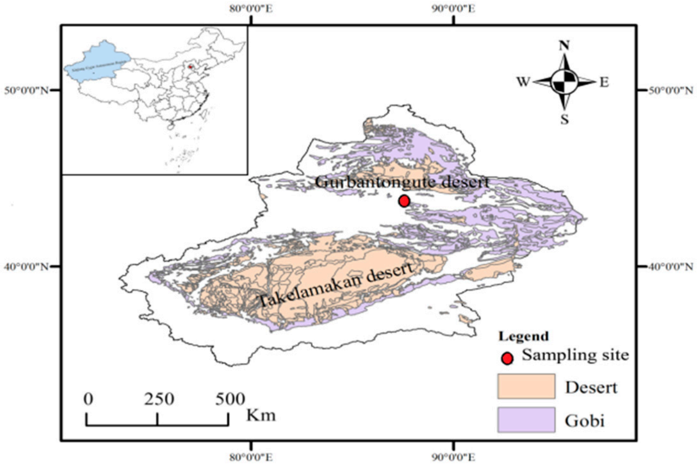

Figure 1. Location of sampling site.

Research on atmospheric PAHs in China is mainly focused on the Yangtze River Delta and the Pearl River Delta region [9–14]. In contrast, much fewer studies (most published in Chinese) have been carried out in Urumqi [7,8,15–20]. Early, Peng et al. (2006) analyzed the sources of PAHs in TSP and in PM_{10} in Urumqi with the composition of carbon isotope [20]. Diao et al. (2005) analyzed PAHs using a GC/MS technique in Urumqi Xinshi district from December 2004 to January 2005 (winter) and reported that the major source of PAHs in Urumqi Xinshi district was coal combustion and vehicle exhaust [15]. Lately, Limu et al. (2013) analyzed the PAHs in $PM_{2.5}$ and $PM_{2.5\text{–}10}$ in Urumqi's southern urban area from 26 September 2010 to 3 March 2011 (autumn and wintertime) [7]. The results showed that the ΣPAHs (sum of 15 PAHs) ranged from 0.11 to 1058.08 $ng\ m^{-3}$ in $PM_{2.5}$ and 0.01 to 90.89 $ng\ m^{-3}$ in $PM_{2.5\text{–}10}$, respectively, and 90% of the ΣPAHs existed in $PM_{2.5}$. The above studies were based on the winter or autumn seasons, and the source analysis of PAHs in Urumqi was limited to the ratio and the principal component analysis methods. Although Ren et al. (2017) reported particle size distribution of PAHs in the atmosphere of Urumqi and analyzed their source using the Positive Matrix Factorization (PMF) model, it was also limited to the heating season [8]. Urumqi belongs to typical temperate semiarid continental climate, with a large temperature difference between winter and summer. Winter is long and cold, and the temperature is stable. It is windy in spring and autumn, and the precipitation is concentrated in summer, which has the effect of washing and purifying pollutants in the atmosphere. The pollution characteristics of PAHs in different seasons may vary greatly. However, to date, there are few detailed studies about the pollution levels, particle size distributions, temporal variations, health risk, identification, and apportionment of the specific pollution sources of PAHs using PMF model in $PM_{2.5}$ and $PM_{2.5–10}$ in Urumqi throughout the year. Our study sought to fill this knowledge gap.

2. Materials and Methods

2.1. Sampling

Samples were collected at the rooftop (9 m above the ground) of the Xinjiang branch of Chinese academy of sciences (N43°51′51″, E87°34′9″) in Xinshi district in Urumqi. This point is 500 m away from the main road (Beijing road). Xinshi district, located in the northwest of Urumqi city with a total area of 143 km^2 and a total population of 730,307 (2010), is the National Technology Industry Development Zone. It is also the transportation center to the north Xinjiang, representing an area of mixed residential, commercial, and industrial activities.

On five rainless days each month from January to December 2011, a middle-volume sampler (NL20; Tokyo Dylec Co, Tokyo, Japan) equipped with quartz fiber filter (Whatman, Mainstone, UK) was used to collect 24-h $PM_{2.5}$ and $PM_{2.5–10}$ particles simultaneously at a flow rate of 20 L/min. The filters were wrapped within aluminum foil and baked for 4 h at 450 °C before sampling. After sampling, samples were also wrapped in prebaked aluminum foil, sealed with clean Teflon bags and stored at −20 °C until analysis [7].

2.2. Pretreatment and Analysis of Samples

Extraction and analysis of PAHs was performed according to a previously published protocol [10]. Before solvent extraction, deuterium PAH standards (Naphthalene-d_8, Acenaphthene-d_{10}, Phenanthrene-d_{10}, Chrysene-d_{12}, and Perylene-d_{12}), were added to the samples as surrogates. Each sample was ultrasonically extracted three times with 30 mL dichloromethane for 30 min each time. Then, the extracts were combined and concentrated to 1~2 mL by a rotary evaporator. Solvent was exchanged to *n*-hexane purified using a 1:2 alumina/silica column chromatography. Two fractions were eluted. The first fraction containing nonpolar compounds was eluted by 30 mL of hexane. The second fraction was eluted by 70 mL of DCM/hexane (3:7 *v/v*). The two fractions were combined, concentrated to ~1.0 mL by a rotary evaporator, and blown down to 0.3 mL under a gentle nitrogen stream.

2.3. GC/MS Analysis

All samples were analyzed by a gas chromatography-mass spectrometer (GC-MS) (Agilent 6890-5973N, Santa Clara, CA, USA) equipped with a HP-5MS elastic quartz capillary column (30 m × 0.25 mm × 0.25 mm). Injection of 1 μL samples was conducted with an automatic sampler in the splitless mode.

The chromatographic condition was as follows: carrier gas was helium with a purity of 99.9%; Inlet and transfer line temperatures were 290 °C; the oven temperature program was initiated at 65 °C (held for 2 min) and increased to 290 °C at 5 °C/min (held for 20 min). Mass spectrometric conditions were: electron impact (EI) selective ion monitoring mode, electron impact energy 70 ev [21]; multiplier voltage, 1624 V; scanning range (M/Z), 50~500 amu (unit of molecular mass).

2.4. Quality Control and Quality Assurance (QA/QC)

All samples were subjected to strict quality control and assurance, according to U.S. EPA-610 method [7]. Limits of detection (LOD) for each compound were calculated as three times the signal-to-noise ratio, which was taken as the standard deviation of the lowest level standard [22]. In this work, the LOD of PAHs was in the range of 0.02~0.12 ng m^{-3}. The recovery experiment was done by spiking the standard solution onto blank filters ($n = 3$). Amounts of target compounds in the standard solution are similar to those in real samples. After being evaporated to dryness, the spiked filters were analyzed in a manner the same as the real samples [22]. The recoveries of deuterium polycyclic aromatic hydrocarbons in the samples were Naphthalene-d_8 32% ± 9%, Phenanthrene-d_{10}

38% ± 10%, Acenaphthene-d_{10} 42% ± 8%, Chrysene-d_{12} 88% ± 11%, and Perylene-d_{12} 69% ± 9%. Field and laboratory blanks were also extracted and analyzed in the same way as the field samples. Target compounds were very low (0~0.05 ng m^{-3}) and in most cases not detectable in the blanks. Data reported here are all corrected for the blanks, but not corrected for the recoveries.

In this study, 14 PAHs were analyzed including phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), benzo[g,h,i]perylene (BghiP), dibenz[a,h]anthracene (DahA), and Coronene (Cor). Because Naphthalene (Nap), Acenaphthene (Ace), Acenaphthylene (Acy), and Fluorene (Fl) are low molecular weight compounds with highly volatile characteristics which lead to low recovery rates, we did not discuss these compounds.

2.5. Source Apportionment with Positive Matrix Factorization (PMF)

Positive Matrix Factorization (PMF), a receptor-based source apportionment model, is based on a least squares method. In this study, the USEPA PMF 5.0 model was applied to identify the sources of observed ambient PAHs. The principles, detailed concepts, and applications of the PMF model for source apportionment can be found in previous studies [23,24]. In our study, we have tested 3~7 factors and discovered that three-factor solution produced a good fit to the data and was the most stable and interpretable. Additional factors made negligible contributions to PAHs and caused factor splitting for tracers. Therefore, more than three factors did not produce meaningful results compared with that of three factors. After the initial run, the Q values were stable, and the Q values in the robust mode were approximately equal to the degrees of freedom [25]. All of the scaled residuals were between −3 and 3. There was a good correlation between measured and predicted PAH concentrations, indicating that most of the species were simulated well.

3. Results and Discussion

3.1. Size Distributions of PAHs in Aerosols

The mean concentrations and particle size distributions of individual and total PAHs in $PM_{2.5}$ and $PM_{2.5–10}$ were shown in Table 1. The mean concentrations of individual PAHs in $PM_{2.5}$ and $PM_{2.5–10}$ were in the range of 0.24 ng m^{-3} (Cor)~148.68 ng m^{-3} (BbF) and 0.09 ng m^{-3} (Cor)~44.50 ng m^{-3} (Phe), respectively. The mean concentration of total PAHs (Σ_{14}PAHs) varied 20.90~844.22 ng m^{-3} (mean: 303.37 ng m^{-3}) in $PM_{2.5}$ and 19.65~176.50 ng m^{-3} (mean: 72.06 ng m^{-3}) in $PM_{2.5–10}$, respectively. We found that the mean concentrations of $PM_{2.5}$- and $PM_{2.5–10}$-bound PAHs in this study were much lower than those reported that Liaoning ($PM_{2.5}$: 75.32~1900.89 ng m^{-3} and $PM_{2.5–10}$: 16.74~303.24 ng m^{-3}) [26], north of Portugal ($PM_{2.5}$: 29 ± 10 μg m^{-3} and $PM_{2.5–10}$: 14 ± 8 μg m^{-3}) [27], whereas they were higher than Beijing ($PM_{2.5}$: 199.23 ng m^{-3} and $PM_{2.5–10}$: 64.06 ng m^{-3}) [28]. The result of correlation analysis of the annual mean concentration of each individual PAHs in $PM_{2.5}$ and $PM_{2.5–10}$ indicated that, except for BaP ($R^2 = 0.35$, $p < 0.05$) and BghiP ($R^2 = 0.05$, $p < 0.05$), all the other individuals' correlation coefficients (R^2) in $PM_{2.5}$ and $PM_{2.5–10}$ were higher than 0.57, and the highest level reached 0.89 (BaA). The proportions ($\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$) of the annual mean concentrations of $PM_{2.5}$-bound individual PAHs in total ($PM_{2.5}$ + $PM_{2.5–10}$) were Phe 57.99%, Ant 45.40%, Flu 69.85%, Pyr 70.21%, BaA 77.63%, Chr 76.71%, BbF 78.96%, BkF 77.33%, BeP 76.54%, BaP 80.16%, IcdP 81.04%, Bghi P 79.36%, DahA 79.21%, and Cor 78.45%, respectively. The results indicated that, except for Ant, all the other PAHs were mainly distributed in fine particles and agreed with other studies [26,29,30], reflecting the influence of physicochemical properties and sources of particles.

Table 1. Mean particulate PAH mass concentrations in $PM_{2.5}$ and $PM_{2.5–10}$ (ng m^{-3}) and the proportion of $\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$. (n = sample number).

	Spring (n = 30)			**Summer (n = 24)**			**Autumn (n = 26)**			**Winter (n = 17)**		
T (°C)	**−4~20 (8.5)** [a]			**16~30 (22)**			**3~24 (12)**			**−20~−8 (−14)**		
RH (%)	**37~72 (53)**			**22~83 (50)**			**30~77 (52)**			**77~84 (80)**		
Name	**Fine**	**Coarse**	**$\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ (%)**	**Fine**	**Coarse**	**$\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ (%)**	**Fine**	**Coarse**	**$\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ (%)**	**Fine**	**Coarse**	**$\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ (%)**
Phe	30.47	44.50	40.64	7.58	4.68	61.72	8.05	5.59	59.04	47.07	19.66	70.54
Ant	2.07	3.33	38.27	0.83	1.10	42.96	2.76	1.44	65.66	7.87	14.81	34.69
Flu	10.99	6.13	64.19	1.11	1.10	50.08	4.89	1.42	77.49	92.71	13.07	87.65
Pyr	7.93	4.09	65.98	0.82	0.97	45.79	3.19	0.84	79.24	58.37	6.60	89.84
BaA	5.76	1.02	84.92	0.55	0.62	46.82	4.71	0.71	86.83	48.73	4.28	91.93
Chr	8.88	1.74	83.64	0.75	0.89	45.82	8.27	1.14	87.90	59.25	6.96	89.49
BbF	21.52	1.93	91.76	1.88	1.87	50.12	50.18	3.84	92.90	148.68	34.77	81.04
BkF	12.45	1.27	90.76	1.17	1.30	47.36	33.70	2.76	92.43	90.29	24.33	78.77
BeP	12.38	1.53	88.98	1.40	1.70	45.05	31.31	2.80	91.80	82.73	20.27	80.32
BaP	3.58	0.33	91.55	0.77	0.96	44.37	3.12	0.28	91.73	31.04	2.34	92.99
IcdP	9.57	0.82	92.13	2.33	2.16	51.88	33.25	1.74	95.03	93.50	16.34	85.13
BghiP	6.03	0.61	90.80	1.51	1.82	45.31	22.61	1.26	94.72	55.88	8.63	86.62
DahA	1.76	0.20	89.99	0.47	0.41	53.09	4.30	0.48	89.90	13.93	2.68	83.85
Cor	0.66	0.09	87.56	0.24	0.33	41.80	3.99	0.19	95.54	14.17	1.77	88.90
Σ_{14}PAHs	134.05	67.59	66.48	20.90	19.65	51.57	214.30	24.48	89.75	844.22	176.50	82.71

[a] Range (mean); Note: Spring includes the samples of March, April, and May; Summer includes the samples of June, July, and August; Autumn includes the samples of September, October, and November; Winter includes the samples of January, February, and December.

3.2. Seasonal Variations of PAHs in Aerosols

Table 1 presents seasonal variation of mean concentrations of Σ_{14}PAHs in $PM_{2.5}$ and $PM_{2.5–10}$, whose values were 134.05 ng m^{-3} and 67.59 ng m^{-3} in spring, 20.90 ng m^{-3} and 19.65 ng m^{-3} in summer, 214.30 ng m^{-3} and 24.48 ng m^{-3} in autumn, and 844.2 ng m^{-3} and 176.5 ng m^{-3} in winter, respectively. The result suggested that the distribution of PAHs in particulate matter was significantly associated with seasonal variation. Namely, whether in $PM_{2.5}$ or in $PM_{2.5–10}$, the mean concentration of total PAHs was the lowest in summer and the highest in winter. This could be explained by adverse weather conditions for pollutant dispersion in cold season [31]. In $PM_{2.5}$, the concentrations of total PAHs in autumn were higher than in spring, while an opposite trend was found in $PM_{2.5–10}$. In addition, the $\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ value of total PAHs decreased from 80% over in autumn and winter with colder temperature to 51.57% in summer. This behavior may be explained by higher incidence of resuspension and abrasion processes in summer [32]. The result was in agreement with Manoli et al. (2002), showing that the $\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ value of total PAHs during cold periods was 96.1~98.4%, and in relatively warm periods slightly decreased to 92.2~97.8% in Thessaloniki [33]. However, Guo et al. (2003) observed that the proportion of $PM_{2.5}$-bound total PAHs in PM_{10} was 72% in winter, and it was increased to 79% in summer in Hong Kong [34].

According to different molecular weight, 14 kinds of PAHs were classified into lower molecular weight PAHs (LMW, 2- and 3-rings PAHs) including Phe and Ant, middle molecular weight PAHs (MMW, 4-rings PAHs) including Flu, Pyr, BaA, Chr, and higher molecular weight PAHs (HMW, $\geq$5 rings of PAHs) including BbF, BkF, BeP, BaP, IcdP, BghiP, DahA, and Cor [32]. Figure 2 shows that in $PM_{2.5}$, the proportion of HMW PAHs was dominant in all season, accounting for 46.61~85.13%. Especially in the autumn, the proportion reached 85.13%, while the MMW PAHs and LMW PAHs proportions reached the minimum value, 9.82% and 5.04%, respectively. The highest proportion of MMW PAHs and LMW PAHs were found in winter and summer, 30.69% and 38.02%, respectively. In $PM_{2.5–10}$, the proportions of middle molecular weight PAHs did not exhibit distinct seasonality, whereas the proportions of lower molecular weight and HMW PAHs showed decreasing and increased trends, respectively, from spring to winter.

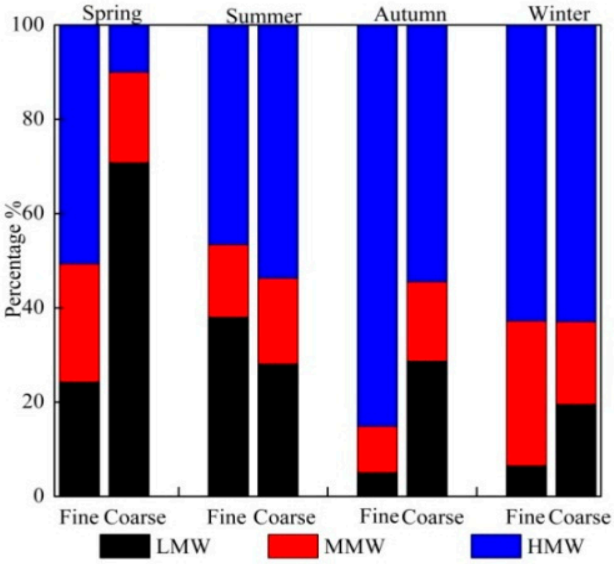

Figure 2. Distributions of different PAHs in fine and coarse particles.

Figure 3 illustrates that the ratios of individual PAH concentrations in winter to summer (w/s) in fine particles had a wider range (from 6.61 (Phe) to 89.48 (BaA)) than that in the coarse particles (from 4.45 (Phe) to 18.75 (BkF)). This result was similar to that in Liaoning (6.5~125.8 and 1.7~37.6, respectively) and Turkish Zonguldak (7.0~70.7 and 1.5~12.0, respectively) [26]. In $PM_{2.5}$ and $PM_{2.5–10}$, the w/s values of BbF and BkF, which mainly existed in the particle phase, were higher than those of Phe and Ant with higher volatility, indicating different source contributions to PAHs between summer and winter. Except Ant, the w/s values of PAHs in fine particles were higher than in coarse particles, suggesting that PAHs might be transported from coarse particles to fine particles in winter [26]. In addition, the $\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ values of Flu~Cor in summer were lower than in other season, and the $\varrho_{2.5}/(\varrho_{2.5} + \varrho_{2.5–10})$ value of 4-ring PAHs in winter were greater than in other season (Table 1).

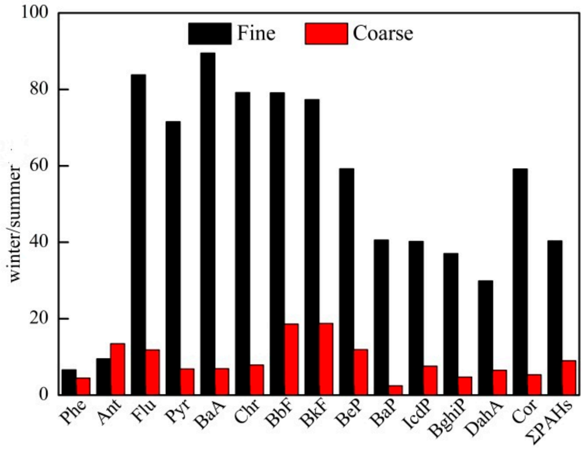

Figure 3. Winter to summer ratios of atmospheric PAHs for fine and coarse particles. The w/s was calculated by the concentration of PAHs in winter divided by concentration of PAHs in summer.

3.3. Risk Assessment of PAHs Exposure

BaP has been widely used as an indicator of total PAHs in the inhalation risk assessment due to its high carcinogenicity. The mean concentration of BaP in $PM_{2.5}$ was 6.82 ng m^{-3}, far exceeding the standard (NAAQSS GB 3095-2012, 1.0 ng m^{-3}), and its concentration in $PM_{2.5–10}$ was 0.78 ng m^{-3}. In order to further explain the effects of PAHs exposure on human during sampling, the toxicity of PAHs was evaluated by BaP toxicity equivalent concentration (BaP_{eq}) [23,35]:

$$BaP_{eq} = \sum PAH_i \times TEF_i \quad (1)$$

The toxic equivalent factor (TEF_i) values were taken from Nisbet and LaGoy (1992) [36] and are shown in Table 2.

Whether in fine particles or coarse particles, BaP_{eq} values in all season were greater than 1 ng m^{-3}. The BaP_{eq} values in $PM_{2.5}$ and $PM_{2.5–10}$ (1.87 ng m^{-3} and 2.01 ng m^{-3}, respectively) were similar in summer. The BaP_{eq} values in $PM_{2.5}$ (10.49~84.52 ng m^{-3}) were much higher than that in $PM_{2.5–10}$ (1.15~13.33 ng m^{-3}) in the other seasons; In winter, the BaP_{eq} values in $PM_{2.5}$ and $PM_{2.5–10}$ (84.51 ng m^{-3} and 13.33 ng m^{-3}, respectively) were the highest (1.87~19.97 ng m^{-3} and 1.16~1.72 ng m^{-3}, respectively). During September 2010 to March 2011 in Urumqi, the mean concentration of BaP_{eq} in $PM_{2.5}$ was 5.96 ng m^{-3} and the higher values mostly occurred in winter [7]. The annual mean BaP_{eq} concentration in $PM_{2.5}$ (29.22 ng m^{-3}) was higher when compared to particulate samples from other urban atmospheres, such as Guangzhou (1.93 ng m^{-3}) [10], Nanjing (0.84 ng m^{-3}) [13], Beijing (3~26 ng m^{-3}) [37], and was lower than that in five cities in Liaoning province in China (40.05 ng m^{-3}) [26]. The BaP_{eq} value in $PM_{2.5–10}$ (4.55 ng m^{-3}) was higher than that of Lhasa (TSP + Gas, 0.1~1.6 ng m^{-3} (0.75 ± 0.36)) [38], Zaragoza, and Spain (0.08~4.42 ng m^{-3}, PM) [39]. The higher BaPeq concentrations ($PM_{2.5}$: 29.22 ng m^{-3}; $PM_{2.5–10}$: 4.55 ng m^{-3}) were an alarming signal for pollution risks in relation to human health [26]. In $PM_{2.5}$ and $PM_{2.5–10}$, proportion ranges of BaP in the total BaP_{eq} were 15.63~41.18% and 16.37~47.76%, respectively. Other PAHs, such as BaA, BbF, BkF, DahA, and IcdP, are also considered to be potential carcinogens [40]. The proportion ranges of several carcinogenic polycyclic aromatic hydrocarbons (CANPAHs) in total BaP_{eq} in $PM_{2.5}$

and $PM_{2.5–10}$ were 56.97~82.58%, 50.17~80.81%, respectively. The results implied that HMW PAHs are also harmful to human health.

Table 2. BaP_{eq} concentrations (ng m^{-3}) for fine and coarse particles in different seasons.

PAH	TEF	Spring		Summer		Autumn		Winter	
		Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Phe	0.001	0.031	0.045	0.008	0.005	0.008	0.006	0.047	0.020
Ant	0.01	0.021	0.033	0.008	0.011	0.028	0.015	0.079	0.148
Flu	0.001	0.011	0.006	0.001	0.001	0.005	0.002	0.093	0.013
Pyr	0.001	0.008	0.004	0.0008	0.001	0.004	0.001	0.058	0.007
BaA	0.10	0.58	0.10	0.055	0.062	0.47	0.071	4.87	0.43
Chr	0.01	0.089	0.017	0.0075	0.009	0.083	0.011	0.59	0.07
BbF	0.10	2.15	0.19	0.19	0.19	5.02	0.38	14.87	3.48
BkF	0.10	1.25	0.13	0.12	0.13	3.37	0.28	9.03	2.43
BaP	1.00	3.58	0.33	0.77	0.96	3.12	0.28	31.04	2.34
IcdP	0.10	0.96	0.082	0.23	0.22	3.33	0.17	9.35	1.63
BghiP	0.01	0.060	0.006	0.015	0.018	0.23	0.013	0.56	0.086
DahA	1.00	1.76	0.20	0.47	0.41	4.30	0.48	13.93	2.68
BaP_{eq}		10.50	1.14	1.88	2.02	19.97	1.71	84.52	13.33
BaP/BaP_{eq} (%)		34.10	28.87	41.06	47.60	15.63	16.38	36.73	17.55
$CANPAHs/BaP_{eq}$ (%) *		63.81	61.42	56.79	50.17	82.58	80.81	61.59	79.87

* $CANPAHs/BaP_{eq}$ (%) refers to the proportion of several carcinogenic polycyclic aromatic hydrocarbons (CANPAHs, such as BaA, BbF, BkF, DahA, and IcdP) in total BaP_{eq}.

Inhalation cancer risk (*ICR*) was used to estimate the cancer risk from PAH exposure and calculated by multiplying BaP_{eq} by the inhalation unit risk (*IURBaP*) [39]:

$$ICR = BaP_{eq} \times IURBaP \tag{2}$$

IURBaP was defined as the maximum theoretical increased probability of lung cancer that was caused by continuing exposure to atmospheric BaP (1 ng m^{-3}) in the life cycle (70-year) [40]. WHO (1987) has used 8.7×10^{-5} in every ng m^{-3} Bap as *IURBaP* [41].

In $PM_{2.5}$ and $PM_{2.5–10}$, the *ICR* values ranged 1.63×10^{-4}~7.35×10^{-3} (mean: 2.5×10^{-3}) and 9.94×10^{-5}~1.16×10^{-3} (mean: 3.96×10^{-4}), respectively. The *ICR* values reached 7.35×10^{-3}, 1.16×10^{-3} in winter, and which were higher than that in Guangzhou (3.94×10^{-4}) [42]. According to the US-EPA (2001), it is believed that one in a million (10^{-6}) over an average lifetime of 70 years is the risk level acceptable or inconsequential, between 10^{-6} and 10^{-4} is defined as a potential risk, whereas a one in ten thousand level (10^{-4}) is considered serious based on the resultant BaP (1 ng m^{-3}) [13,23,43]. However, all these values far exceeded the high level of 10^{-4}, and indicated that Urumqi has higher inhalation cancer risk.

3.4. Sources of Particulate PAHs

3.4.1. Diagnostic Ratios (DR) Analysis

Some of the identified components and ratios in PAHs can reflect part of the characteristics of the emission sources in the study area. The DR method was commonly utilized for identifying PAH sources by comparing ratio of pairs of frequently found PAH emissions [44]. The Flu/Pyr and IcdP/BghiP were isomer pairs. Therefore, they were photolytically degraded at comparable rates [45,46]. Thus, their ratios preserved the original compositional information during atmospheric transport. Yunker et al. (2002) summarized the results of different sources and proposed that for Flu/(Pyr + Flu), the petroleum boundary ratio appears close to 0.40, and the ratio between 0.40 and 0.50 was characteristic of petroleum combustion (liquid fossil fuel combustion), whereas a ratio >0.50 was characteristic of grass, wood, or coal combustion; for IcdP/(BghiP + IcdP), a ratio <0.20 indicates unburned petroleum (petrogenic source), 0.20~0.50 implies petroleum combustion (liquid fossil fuel combustion), and >0.50 was implies grass, wood, or coal combustion [47].

Figure 4 shows that the variation ranges of Flu/(Flu + Pyr) in $PM_{2.5}$ and $PM_{2.5–10}$ were 0.49~0.76 and 0.43~0.81, respectively. The variation ranges of IcdP/(IcdP + BghiP) in $PM_{2.5}$ and $PM_{2.5–10}$ were 0.51~0.68 and 0.46~0.66, respectively. A large number of data were mainly distributed in the grass/wood/coal combustion area, and only some of the data were distributed in petroleum combustion, which accounted for a total of 12.77%. The result indicated that the main source of PAHs in Urumqi was grass/wood/coal combustion, and the minor source was petroleum combustion. The information about the specific source was obtained by the ratio method, but it was unable to estimate the contribution from the specific source categories. However, such information can be obtained by PMF easily. Therefore, the combination of these two methods could make the analysis results more reliable.

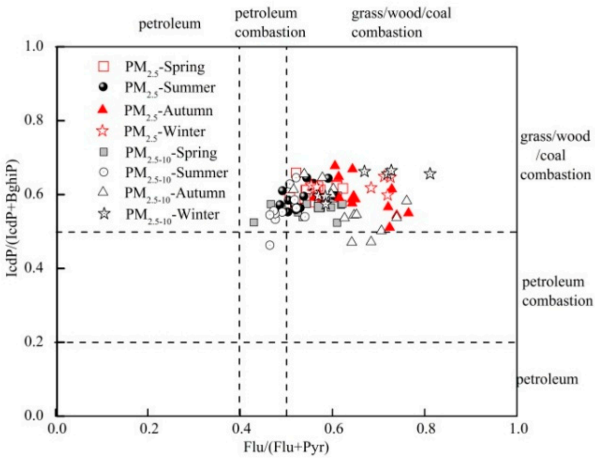

Figure 4. Ratios of IcdP/(BghiP + IcdP) vs. Flu/(Pyr + Flu) for $PM_{2.5}$ and $PM_{2.5–10}$.

3.4.2. Sources of PAHs with Positive Matrix Factorization (PMF)

To further identify and evaluate the major sources of PAH contaminants in $PM_{2.5}$ and $PM_{2.5–10}$ in Urumqi, the PMF model (EPA PMF 5.0) was used. We selected 3 factors which were most stable and interpretable, as shown in Figure 5. During the process of analyzing the generated results, there were some differences in the source contribution rates of PAHs in $PM_{2.5}$ and $PM_{2.5–10}$, but two profiles are identified as the same sources, which have similar composition and present the same tracer species.

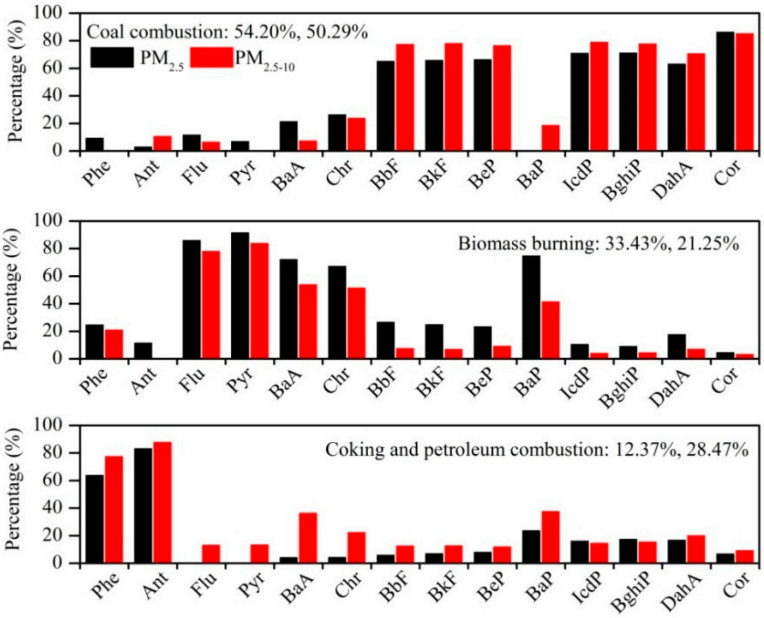

Figure 5. Factor profiles (% of total) of $PM_{2.5}$, $PM_{2.5–10}$ obtained from the EPA PMF model.

Factor 1 explained 54.20% and 50.29% of the total PAHs in $PM_{2.5}$ and $PM_{2.5–10}$, respectively, and was mainly loaded by HMW: Cor (87.10%, 85.94%), BghiP (71.88%, 78.54%), IcdP (71.72%, 79.75%), BeP (67.10%, 77.26%), BkF (66.60%, 78.82%), BbF (65.95%, 78.20%), and DahA (63.98%, 71.41%). Therefore, this factor was identified as coal combustion according to previous studies which showed similar PAH loadings [42,48,49].

Factor 2 accounted for 33.43% and 21.25% of total PAHs in $PM_{2.5}$ and $PM_{2.5–10}$, respectively. It was mainly loaded with Pyr (92.35%, 84.69%), Flu (86.74%, 78.84%), BaP (75.51%, 42.18), BaA (72.90%, 54.71%), and Chr (67.95%, 52.21%). Flu and Pyr are fingerprints of biomass burning [24,48,50,51]. Thus, factor 2 was classed as biomass burning.

Factor 3 was predominantly loaded with Ant (96% 88.59%) and Phe (64.56% 78.32%). In the results of Khalili et al. (1995), predominant PAHs in coke oven emissions were Nap, Acy, Phe, Fl, Ant, and Flu [50]. Ant, Phe were also used as indicative species of coking and petroleum combustion [24,52]. So factor 3 was considered as composite source of coking and petroleum combustion sources, explaining 12.37% and 28.47% of total PAHs in $PM_{2.5}$ and $PM_{2.5–10}$, respectively.

In the sampling period, emissions from coal combustion (54.20%, 50.29%), biomass burning (33.43%, 21.25%), and coking and petroleum combustion (12.37%, 28.47%) contributed to PAHs bound PM in Urumqi, with coal combustion being the most important source. This result was consistent with the previous results obtained before changing coal to natural gas in Urumqi [8], and we found that the contribution of coal combustion was apparently smaller than that in 2002 (84%) [20].

4. Conclusions

The concentrations of PAHs in $PM_{2.5}$ and $PM_{2.5–10}$ in Urumqi were measured from January to December 2011, and the mean concentration ranges of total PAHs were 20.90~844.22 ng m^{-3} and 19.65~176.50 ng m^{-3}, respectively. PAHs existed predominantly in fine particles. Total PAHs had significant seasonal variation, with the highest in winter and the lowest in summer. The w/s values of the individual PAHs were 6.61~89.48 and 4.45~18.75 for $PM_{2.5}$ and $PM_{2.5–10}$, respectively. HMW PAHs dominated in $PM_{2.5}$. In $PM_{2.5–10}$, a decreasing trend of LMW PAHs was found from spring to winter. In contrast, HMW PAHs showed an increasing trend. In $PM_{2.5}$ and $PM_{2.5–10}$, the annual mean BaP_{eq} concentration 29.22 and 4.55 ng m^{-3}, and BaP accounted for 31.88% and 27.60% of the total BaP_{eq}, respectively. The CANPAHs accounted for 66.19% and 68.07% of total BaP_{eq}. The *ICR* averaged 2.5×10^{-3} and 3.96×10^{-4}, respectively, exceeded the USEPA guideline levels. Three potential sources of PAHs were identified by combining DR and PMF, including: coal combustion, biomass burning, and coking and petroleum combustion. Coal combustion had the largest contribution to PAHs of 54.20% and 50.28%, respectively. Our results may help the environmental agency, government, and stakeholders recognize the characteristics of PAHs in $PM_{2.5}$ and $PM_{2.5–10}$, while providing research data on carbon aerosols in northwest China.

Author Contributions: The study was completed with cooperation between all authors. D.T., X.W., B.G. have conceived and designed the experiments; X.W. provided the laboratory apparatus and accommodation; Y.T., M.M., A.A. have provided valuable comments and suggestions for the modification of the manuscript. B.G., S.R., Y.T. have performed graphic processing and data analysis; S.R., D.T., B.G., wrote the paper and D.T., B.G. contributed grammar correcting of all text.

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